Supplementary Information for

Mechanistic study on the side arm effect in a palladium/Xu-Phos-catalyzed enantioselective alkoxyalkenylation of γ-hydroxyalkenes

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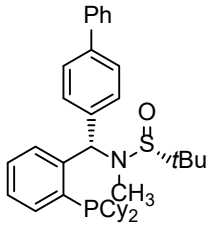
1. General Information

Unless otherwise noted, all reactions were carried out under an argon atmosphere; materials obtained from commercial suppliers were used directly without further purification. The [±] D was recorded using PolAAr 3005 High Accuracy Polarimeter (λ = 589 nm, T = 20 °C). ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{31}P NMR spectra were recorded on a Bruker 400 MHz and 500 MHz spectrometer in $CDCl_3$ NMR. Experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 pp m) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Tetrahydrofuran (THF), toluene, hexane and ether were dried with sodium benzophenone and distilled before use; Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

2. General Procedure for the Synthesis of Xu-Phos

2.1 Synthesis of Xu3, Xu11

2.1.1 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(2-(dicyclohexylphosphanyl)-phenyl)-methyl)-N,2-dimethyl-propane-2-sulfinamide (Xu3)

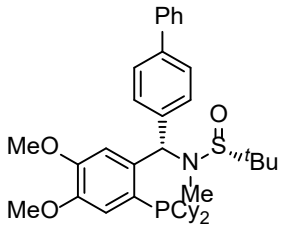


Xu3

To a solution of dicyclohexylphosphine borane (5 mmol) in dry PhMe/THF (2:1, 10 mL) was added *n*-BuLi (5 mmol, 2.4 M in hexane) dropwise under argon at -78 °C. The resulting solution at this temperature during 1 hour and 1,2-dibromobenzene (5 mmol) was added dropwise followed by *n*-BuLi (5 mmol, 2.4 M in hexane). After 10 minutes at -78 °C, (Rs)-sulfinyl imine (6 mmol) was added and the reaction mixture was warmed to room temperature overnight. The reaction mixture was cooled to 0 °C and added Methyl trifluoromethanesulfonate (7.5 mmol). The resulting solution was stirred at this temperature during 1 hour. Then, the reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was dealed with Et_2NH (20 mL) and the resulting solution was stirred under argon at 50 °C. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (Petroleum ether: Acetone = 30:1) to afford the product **Xu3** as a white solid (1.3 g, 45% yield). Mp: 68.4-70.2 °C. $[\alpha]_D^{20}$ = 52.8 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.74 (m, 1 H), 7.59 – 7.53 (m, 2 H), 7.54 – 7.45 (m, 3 H), 7.47 – 7.38 (m, 3 H), 7.35 – 7.29 (m, 2 H), 7.29 – 7.23 (m, 2 H), 6.94 (d, *J* = 10.0 Hz, 1 H), 2.64 (s, 3 H), 2.01 – 1.82 (m, 2 H), 1.83 – 1.72 (m, 1 H), 1.72 – 1.62 (m, 2 H), 1.62 – 1.57 (m, 1 H), 1.57 – 1.51 (m, 1 H), 1.51 – 1.39 (m, 4 H), 1.36 – 1.17 (m, 6 H), 1.15 – 1.06 (m, 10 H), 0.94 – 0.86 (m, 3 H), 0.65 – 0.51 (m, 1 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 147.1 (d, *J* = 22.2 Hz), 140.7, 139.9, 139.1, 134.9 (d, *J* = 21.2 Hz), 133.1 (d, *J* = 3.2 Hz), 131.0, 128.7, 128.6, 128.0 (d, *J* = 4.9 Hz), 127.1, 126.9, 126.6, 69.8 (d, *J* = 31.8 Hz), 58.6, 34.7 (dd, *J* = 12.9, 10.8 Hz), 30.6 (d, *J* = 17.8

Hz), 30.3 – 29.8 (m), 29.5 (d, J = 10.0 Hz), 29.3 (d, J = 10.0 Hz), 27.0 (dd, J = 12.0, 9.7 Hz), 26.3, 26.1, 24.0. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -16.85. HRMS (ESI) calculated for [$C_{36}H_{49}NOPS$] [M+H]$^+$: 574.3267 found: 574.3269.

2.1.2 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(2-(dicyclohexylphosphanyl)-4,5-dimethoxy-phenyl)-methyl)-N,2-dimethylpropane-2-sulfinamide (Xu11)

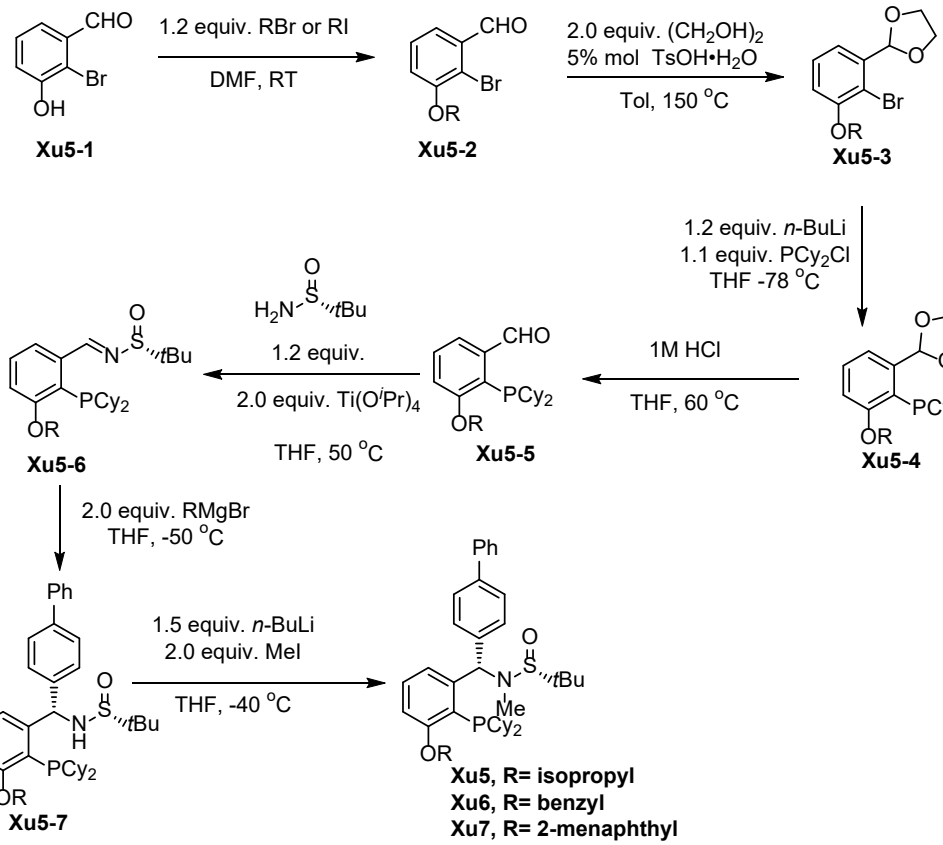


Xu11

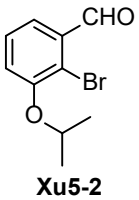
To a solution of dicyclohexylphosphine borane (5 mmol) in dry PhMe/THF (2:1, 10 mL) was added *n*-BuLi (5 mmol, 2.4 M in hexane) dropwise under argon at -78 °C. The resulting solution at this temperature during 1 hour and 1,2-dibromo-4,5-dimethoxybenzene (5 mmol) was added dropwise followed by *n*-BuLi (5 mmol, 2.4 M in hexane). After 10 minutes at -78 °C, (Rs)-sulfinyl imine (6 mmol) was added and the reaction mixture was warmed to room temperature overnight. The reaction mixture was cooled to 0 °C and added Methyl trifluoromethanesulfonate (7.5 mmol). The resulting solution was stirred at this temperature during 1 hour. Then, the reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was dealed with Et_2NH (20 mL) and the resulting solution was stirred under argon at 50 °C. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (Petroleum ether : Acetone = 30:1) to afford the product **Xu11** as a white solid (1.4 g, 44% yield). Mp: 75.6-78 ℃. $[\alpha]_D^{20}$ = 112.7 (*c* = 0.4, Chloroform-*d*). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.53 (d, J = 3.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 2.6 Hz, 2H), 6.98 (d, J = 2.2 Hz, 1H), 6.83 (d, J = 10.3 Hz, 1H), 4.00 (s, 3H), 3.93 (s, 3H), 2.67 (s, 3H), 1.96 – 1.79 (m, 4H), 1.73 – 1.65 (m, 2H), 1.58 – 1.47 (m, 4H), 1.47 – 1.38 (m, 3H), 1.35 – 1.16 (m, 7H), 1.12 (s, 9H), 0.92 – 0.87 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 149.8, 147.2, 140.7, 140.1 (d, J

= 23.0 Hz), 139.9, 139.4, 131.3, 128.6, 127.1, 126.9, 126.4, 125.8 (d, J = 20.1 Hz), 115.1 (d, J = 2.9 Hz), 111.1 (d, J = 5.6 Hz), 69.9 (d, J = 33.1 Hz), 58.7, 56.0, 55.9, 35.0 (dd, J = 12.6, 8.3 Hz), 31.0 – 30.4 (m), 30.1 (d, J = 15.6 Hz), 229.4 (dd, J = 11.4, 9.4 Hz), 27.3-26.7 (m), 26.3, 26.1, 24.3. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -17.3. HRMS (ESI) calculated for $[C_{38}H_{53}NO_3PS]$ $[M+H]^+$: 634.3478 found: 634.3483.

2.2 Synthesis of Xu5, Xu6 and Xu7 [1]



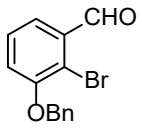
2.2.1 2-bromo-3-isopropoxybenzaldehyde (Xu5-2)



Prepared from 2-bromo-3-hydroxybenzaldehyde **Xu5-1** (30 mmol) in DMF (50 mL) was added 2-iodopropane (36mmol, 1.2 equiv.) and K_2CO_3 (45 mmol, 1.5 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O

and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. the crude product was then purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 40: 1) to afford the product **Xu5-2** as a white liquid (5.5 g, 75% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.42 (s, 1 H), 7.49 (d, *J* = 7.7 Hz, 1 H), 7.32 (t, *J* = 7.9 Hz, 1 H), 7.13 (d, *J* = 8.1 Hz, 1 H), 4.65 – 4.53 (m, 1 H), 1.40 (d, *J* = 6.1 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.4, 154.9, 134.9, 128.0, 121.4, 120.4, 118.9, 72.6, 21.9. HRMS (ESI) calculated for [$C_{10}H_{12}BrO_2$] $[M+H]^+$: 243.0015 found: 243.0017.

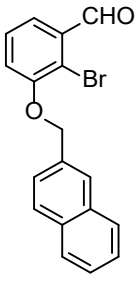
2.2.2 3-(benzyloxy)-2-bromobenzaldehyde (Xu6-2)



Xu6-2

To a solution of 2-bromo-3-hydroxybenzaldehyde **Xu5-1** (30 mmol) in DMF (50 mL) was added benzyl bromide (36mmol, 1.2 equiv.) and K_2CO_3 (45 mmol, 1.5 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu6-2** as a white solid (6.7 g, 77% yield). Mp: 64.0 – 64.5 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.43 (d, J = 0.8 Hz, 1H), 7.49 (ddd, J = 15.1, 7.9, 1.3 Hz, 3H), 7.43 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.14 (dd, J = 8.1, 1.5 Hz, 1H), 5.19 (s, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.24, 155.39, 135.94, 134.92, 128.72, 128.28, 128.23, 127.06, 121.79, 118.79, 117.90, 71.29. HRMS (ESI) calculated for [$C_{14}H_{12}BrO_2$] $[M+H]^+$: 291.0015 found: 291.0013.

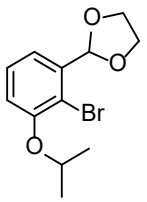
2.2.3 2-bromo-3-(naphthalen-2-ylmethoxy)-benzaldehyde (Xu7-2)



Xu7-2

Prepared from 2-bromo-3-hydroxybenzaldehyde **Xu5-1** (30 mmol) in DMF (50 mL) was added 2-(bromomethyl) naphthalene (36mmol, 1.2 equiv.) and K_2CO_3 (45 mmol, 1.5 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and washing by petroleum ether with a little ethyl acetate to afford the product **Xu7-2** as a white solid (8.7 g, 85% yield). Mp: 130.3 – 131.2 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.47 (s, 1 H), 8.00 – 7.80 (m, 4 H), 7.59 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.56 – 7.47 (m, 3 H), 7.33 (t, *J* = 7.9 Hz, 1 H), 7.20 (dd, *J* = 8.1, 1.5 Hz, 1 H), 5.36 (s, 2 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.2, 155.3, 134.8, 133.3, 133.2, 133.1, 128.5, 128.2, 127.9, 127.7, 126.3, 126.2, 126.0, 124.7, 121.8, 118.8, 117.8, 71.4. HRMS (ESI) calculated for $[C_{18}H_{14}BrO_2]$ $[M+H]^+$: 341.0172 found: 341.0175.

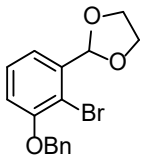
2.2.4 2-(2-bromo-3-isopropoxyphenyl)-1,3-dioxolane (Xu5-3)



Xu5-3

Prepared from 2-bromo-3-isopropoxybenzaldehyde **Xu5-2** (20 mmol) in 50 mL toluene, was added ethylene glycol (40 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (1 mmol, 5% mol). The resulting solution was stirred 18 hours at 150 ℃. The reaction mixture was washed by the addition of H_2O and the combined organic layers were dried over Na_2SO_4, filtered, concentrated, the crude product was then purified by flash column chromatography on silica gel (Petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu5-3** as a white liquid (4.9 g, 85% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.9 Hz, 1 H), 7.20 (dd, *J* = 7.8, 1.7 Hz, 1 H), 6.92 (dd, *J* = 8.0, 1.7 Hz, 1 H), 6.16 (s, 1 H), 4.62 – 4.49 (m, 1 H), 4.17 – 4.10 (m, 2 H), 4.10 – 4.03 (m, 2 H), 1.38 (d, *J* = 6.1 Hz, 6 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.6, 138.3, 127.7, 119.5, 116.2, 114.7, 102.7, 72.3, 65.3, 21.9. HRMS (ESI) calculated for $[C_{12}H_{16}BrO_3]$ $[M+H]^+$: 287.0277 found: 287.0279.

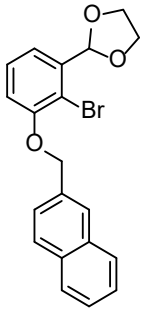
2.2.5 2-(3-(benzyloxy)-2-bromophenyl)-1,3-dioxolane (Xu6-3)



Xu6-3

To a solution of 3-(benzyloxy)-2-bromobenzaldehyde **Xu6-2** (20 mmol) in 50 mL toluene, was added ethylene glycol (40 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (1 mmol, 5% mol). The resulting solution was stirred 18 hours at 150 ℃. The reaction mixture was washed by the addition of H_2O and the combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu6-3** as a white solid (5.7 g, 85% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 6.9 Hz, 2 H), 7.45 – 7.39 (m, 2 H), 7.38 – 7.32 (m, 1 H), 7.32 – 7.24 (m, 2 H), 6.97 (dd, *J* = 7.2, 2.4 Hz, 1 H), 6.22 (s, 1 H), 5.19 (s, 1 H), 4.21 – 4.06 (m, 4 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.9, 138.3, 136.3, 128.4, 127.8, 127.8, 126.9, 119.7, 114.3, 113.4, 102.6, 70.9, 65.3. HRMS (ESI) calculated for $[C_{16}H_{16}BrO_3]$ $[M+H]^+$: 335.0277 found: 325.0279. Mp: 82.7 – 83.4 ℃.

2.2.6 2-(2-bromo-3-(naphthalen-2-ylmethoxy)-phenyl)-1,3-dioxolane (Xu7-3)

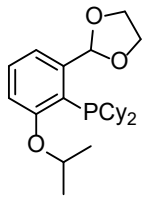


Xu7-3

Prepared from 2-bromo-3-(naphthalen-2-ylmethoxy)-benzaldehyde **Xu7-2** (20 mmol) in 50 mL toluene, was added ethylene glycol (40 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (1 mmol, 5% mol). The resulting solution was stirred 18 hours at 150 ℃. The reaction mixture was washed by the addition of H_2O and the combined organic layers were dried over Na_2SO_4, filtered, concentrated, after washing by petroleum ether with a little ethyl acetate to afford the product **Xu7-3** as a white solid (6.9 g, 90% yield). Mp: 96.8 – 97.6 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (s, 1 H), 7.92 – 7.84 (m, 3 H), 7.60 (dd, *J* = 8.4, 1.7 Hz, 1 H), 7.55 – 7.48 (m, 2 H), 7.32 – 7.22 (m, 2 H), 7.03 – 6.97 (m, 1 H), 6.24 (s, 1 H), 5.33 (s, 2 H), 4.22 – 4.14 (m, 2 H), 4.14 – 4.06 (m, 2 H). ^{13}C

NMR (125 MHz, Chloroform-*d*) δ 155.0, 138.4, 133.8, 133.1, 133.0, 128.3, 127.9, 127.6, 126.1, 126.0, 125.8, 124.7, 119.8, 114.4, 113.5, 102.6, 71.2, 65.4. HRMS (ESI) calculated for [$C_{20}H_{18}BrO_3$] $[M+H]^+$: 385.0434 found: 385.0438.

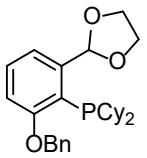
2.2.7 (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane (Xu5-4)



Xu5-4

Prepared from 2-(2-bromo-3-isopropoxyphenyl)-1,3-dioxolane **Xu5-3** (15 mmol) in 20 mL anhydrous THF, was added *n*-BuLi (18 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (17 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated, after washing by petroleum ether with a little ethyl acetate to afford the product **Xu5-4** as a white solid (4.5 g, 74% yield). Mp: 41.0-42.5 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 8.0 Hz, 1 H), 7.23 (dd, *J* = 7.8, 3.1 Hz, 1 H), 6.83 (d, *J* = 7.9 Hz, 1 H), 6.76 (d, *J* = 8.1 Hz, 1 H), 4.73 – 4.55 (m, 1 H), 4.16 – 4.08 (m, 2 H), 4.08 – 4.00 (m, 2 H), 2.54 – 2.38 (m, 2 H), 1.99 – 1.87 (m, 2 H), 1.86 – 1.72 (m, 2 H), 1.69 – 1.53 (m, 4 H), 1.3 8 (s, 3 H), 1.37 (s, 3 H), 1.33 – 1.23 (m, 6 H), 1.21 – 1.07 (m, 4 H), 1.02 – 0.91 (m, 2 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.4 (d, *J* = 4.0 Hz), 146.5 (d, *J* = 21.5 Hz), 130.3, 123.6 (d, *J* = 30.3 Hz), 117.5 (d, *J* = 6.9 Hz), 110.7, 101.5 (d, *J* = 39.5 Hz), 68.3, 65.3, 34.7 (d, *J* = 9.7 H z), 32.8 (d, *J* = 24.3 Hz), 30.5 (d, *J* = 9.1 Hz), 27.3 (d, *J* = 8.7 Hz), 27.1 (d, *J* = 14.3 Hz), 26.3, 26.3, 21.7. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.97. HRMS (ESI) calculated for [$C_{24}H_{38}O_3P$] $[M+H]^+$: 405.2553 found: 405.2556.

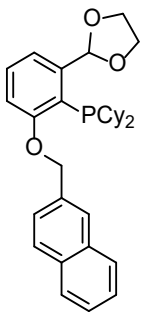
2.2.8 (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane (Xu6-4)



Xu6-4

To a solution of 2-(3-(benzyloxy)-2-bromophenyl)-1,3-dioxolane **Xu6-3** (15 mmol) in 20 mL anhydrous THF, was added *n*-BuLi (18 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (17 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu6-4** as a white solid (6.0 g, 88% yield). Mp: 101.2-103.0 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 4 H), 7.40 – 7.29 (m, 3 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 6.83 (d, *J* = 7.9 Hz, 1 H), 5.06 (s, 2 H), 4.19 – 4.08 (m, 2 H), 4.10 – 4.01 (m, 2 H), 2.41 – 2.28 (m, 2 H), 1.85 – 1.74 (m, 2 H), 1.73 – 1.65 (m, 2 H), 1.63 – 1.51 (m, 4 H), 1.35 – 1.18 (m, 4 H), 1.1 9 – 1.104 (m, 6 H), 1.03 – 0.92 (m, 2 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.8 (d, *J* = 3.9 Hz), 146.3 (d, *J* = 21.3 Hz), 136.6, 130.5 (d, *J* = 1.5 Hz), 128.4, 128.0, 127.9, 123.9 (d, *J* = 31.3 Hz), 118.5 (d, *J* = 6.7 Hz), 111.1, 101.5 (d, *J* = 38.7 Hz), 70.4, 65.3, 34.1 (d, *J* = 9.7 H z), 32.6 (d, *J* = 23.6 Hz), 30.6 (d, *J* = 9.4 Hz), 27.1 (d, *J* = 8.9 Hz), 26.9 (d, *J* = 14.1 Hz), 26.2. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.61. HRMS (ESI) calculated for $[C_{28}H_{38}O_3P]$ $[M+H]^+$: 453.2553 found: 453.2556.

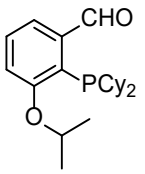
2.2.9 (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane (Xu7-4)



Xu7-4

Prepared from 2-(2-bromo-3-(naphthalen-2-ylmethoxy)phenyl)-1,3-dioxolane **Xu7-3** (15 mmol), in 20 mL anhydrous THF, was added *n*-BuLi (18 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (17 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu7-4** as a white solid (5.3 g, 70% yield). Mp: 108.1-112.0 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.86 (m, 3 H), 7.86 – 7.82 (m, 1 H), 7.60 – 7.49 (m, 3 H), 7.41 – 7.31 (m, 2 H), 6.93 (dd, *J* = 7.6, 1.7 Hz, 1 H), 6.85 (d, *J* = 7.9 Hz, 1 H), 5.25 (s, 2 H), 4.18 – 4.11 (m, 2 H), 4.10 – 4.03 (m, 2 H), 2.47 – 2.35 (m, 2 H), 1.86 – 1.75 (m, 2 H), 1.71 – 1.55 (m, 6 H), 1.40 – 1.30 (m, 2 H), 1.29 – 1.18 (m, 2 H), 1.19 – 1.07 (m, 6 H), 1.07 – 0.95 (m, 2 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.9 (d, *J* = 3.8 Hz), 146.4 (d, *J* = 21.3 Hz), 134.2, 133.2, 133.0, 130.6, 128.3, 127.8, 127.7, 126.5, 126.3, 126.1, 125.5, 124.0 (d, *J* = 31.3 Hz), 118.7 (d, *J* = 6.7 Hz), 111.3, 101.5 (d, *J* = 38.9 Hz), 70.5, 65.4 , 34.2 (d, *J* = 9.9 Hz), 32.6 (d, *J* = 23.7 Hz), 30.6 (d, *J* = 9.3 Hz), 27.2 (d, *J* = 8.8 Hz), 26.9 (d, *J* = 14.0 Hz), 26.3. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.44. HRMS (ESI) calculated for $[C_{32}H_{40}O_3P]$ $[M+H]^+$: 503.2710 found: 503.2715.

2.2.10 2-(dicyclohexylphosphanyl)-3-isopropoxybenzaldehyde (Xu5-5)

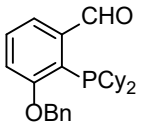


Xu5-5

Prepared from (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane **Xu5-4** (2 mmol) in 2 mL THF, was added 3 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and

purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu5-5** as a yellow solid. Mp: 91.0-92.8 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.25 (dd, J = 9.1, 3.7 Hz, 1H), 7.48 (dt, J = 7.3, 3.4 Hz, 1H), 7.40 (td, J = 8.0, 3.6 Hz, 1H), 6.99 (dd, J = 8.3, 3.5 Hz, 1H), 4.68 (m, J = 5.8 Hz, 1H), 2.49 (dt, J = 11.5, 3.9 Hz, 2H), 1.93 (dt, J = 10.1, 4.5 Hz, 2H), 1.80 (d, J = 10.2 Hz, 2H), 1.65 – 1.57 (m, 4H), 1.42 (t, J = 4.9 Hz, 6H), 1.36 (dd, J = 9.6, 4.6 Hz, 1H), 1.29 (tt, J = 14.0, 6.5 Hz, 6H), 1.21 – 1.13 (m, 3H), 0.98 – 0.90 (m, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.8 (d, *J* =45.0 Hz), 160.1(d, *J* =3.6 Hz), 145.3 (d, *J* =17.3 Hz), 130.5, 127.7 (d, *J* =35.6 Hz), 119.0 (d, *J* =6.7 Hz), 115.1, 69.0, 34.4 (d, *J* =10.3 Hz), 32.5 (d, *J* =23.3 Hz) 30.7 (d, *J* =8.5 Hz), 27.2 (d, *J* =8.3 Hz), 27.0 (d, *J* =14.4Hz), 26.3, 21.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.79. HRMS (ESI) calculated for $[C_{22}H_{34}O_2P]$ $[M+H]^+$: 361.2291 found: 361.2287.

2.2.11 3-(benzyloxy)-2-(dicyclohexylphosphanyl)-benzaldehyde (Xu6-5)

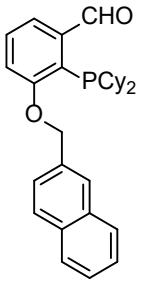


Xu6-5

To a solution of (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane **Xu6-4** (2 mmol) in 2 mL THF, was added 3 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and then was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu6-5** as a yellow solid. Mp: 85.2-87.2 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.27 (d, J = 8.9 Hz, 1H), 7.57 (dt, J = 7.4, 3.4 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.14 (t, J = 6.1 Hz, 1H), 5.13 (d, J = 3.6 Hz, 2H), 2.39 (dp, J = 11.5, 3.9 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.73 (dd, J = 9.1, 4.8 Hz, 2H), 1.66 – 1.57 (m, 4H), 1.37 – 1.31 (m, 2H), 1.26 – 1.05 (m, 8H), 0.98 (ddt, J = 12.1, 5.9, 3.3 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.6 (d, J = 44.6 Hz), 161.6 (d, J = 3.6 Hz), 145.0 (d, J = 17.1 Hz), 136.2, 130.7, 128.7, 128.4, 128.1, 127.8, 119.9 (d, J = 6.6 Hz), 115.5, 70.9, 34.0 (d, J = 10.5 Hz), 32.3 (d, J = 22.8 Hz), 30.7 (d, J = 8.7 Hz), 27.0 (d, J =

8.7 Hz), 26.8 (d, J = 14.2 Hz), 26.3.^{31}P NMR (202 MHz, Chloroform-*d*) δ -16.41. HRMS (ESI) calculated for [$C_{26}H_{34}O_2P$] $[M+H]^+$: 409.2291 found: 409.2302.

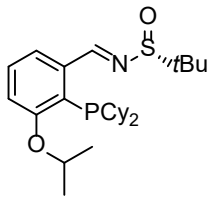
2.2.12 2-(dicyclohexylphosphanyl)-3-(naphthalen-2-ylmethoxy)-benzaldehyde (Xu7-5)



Xu7-5

Prepared from (2-(benzyloxy)-6-(1,3-dioxolan-2-yl)-phenyl)-dicyclohexylphosphane **Xu7-4** (2 mmol) in 2 mL THF, was added 3 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu7-5** as a yellow solid. Mp: 107.1-110.2 ℃. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.27 (d, *J* = 8.7 Hz, 1H), 7.95 – 7.75 (m, 4H), 7.54 (ddd, *J* = 15.2, 6.9, 2.8 Hz, 4H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 5.27 (s, 2H), 2.42 (dtd, *J* = 11.6, 7.8, 3.6 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.71 – 1.65 (m, 2H), 1.59 (t, *J* = 12.8 Hz, 4H), 1.39 – 1.32 (m, 2H), 1.24 – 1.06 (m, 8H), 1.01 – 0.92 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.6 (d, *J* = 44.8 Hz), 161.5 (d, *J* = 3.4 Hz), 145.0, 144.9, 133.7, 133.2, 133.1, 130.7, 128.5, 127.8, 127.7, 126.8, 126. 5, 126.3, 125.5, 119.9 (d, *J* = 6.5 Hz), 115.5, 70.9, 34.0 (d, *J* = 10.5 Hz), 32.3 (d, *J* = 23.0 Hz), 30.7 (d, *J* = 8.7 Hz), 27.0 (d, *J* = 8.6 Hz), 26.7 (d, *J* = 14.3 Hz), 26.2. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -16.35. HRMS (ESI) calculated for [$C_{30}H_{36}O_2P$] $[M+H]^+$: 459.2447 found: 459.2455.

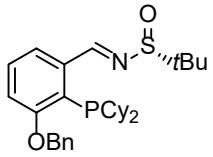
2.2.13 (*R*,*E*)-N-(2-(dicyclohexylphosphanyl)-3-isopropoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu5-6)



Xu5-6

Prepared from 2-(dicyclohexylphosphanyl)-3-isopropoxybenzaldehyde the crude product **Xu5-5** in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (2.4 mmol, 1.2 equiv.) and titanium tetraisopropanolate (4 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentratedand purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu5-6** as a yellow solid. Mp: 102.1-104.2 ℃. $[\alpha]_D^{20}$= -108.9 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.86 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.55 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.35 (td, *J* = 8.0, 1.9 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.66 (pd, *J* = 6.1, 2.0 Hz, 1H), 2.52 – 2.38 (m, 2H), 1.93 – 1.82 (m, 2H), 1.78 – 1.75 (m, 2H), 1.59 (q, *J* = 10.7, 8.8 Hz, 4H), 1.40 (td, *J* = 4.9, 3.7, 2.0 Hz, 6H), 1.28 (dd, *J* = 9.3, 2.1 Hz, 15H), 1.19 – 1.08 (m, 4H), 0.97 – 0.89 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.0 (d, *J* = 41.2 Hz), 160.1 (d, *J* = 3.5 Hz), 143.8 (d, *J* = 21.8 Hz), 130.3,127.1 (d, *J* = 33.9 Hz), 119.6 (d, *J* = 6.3 Hz), 113.1, 68.8, 57.7, 34.6 (d, *J* = 11.5 Hz), 32.3 (dd, *J* = 23.5, 4.8 Hz), 30.5 (dd, *J* = 17.4, 8.7 Hz), 27.2 (dd, *J* = 8.4, 4.5 Hz), 27.0 (dd, *J* = 14.3, 7.8 Hz), 26.3, 22.7, 21.8 (d, *J* = 5.6 Hz). ^{31}P NMR (202 MHz, Chloroform-*d*) δ -12.13. HRMS (ESI) calculated for $[C_{26}H_{43}NO_2PS]$ $[M+H]^+$: 464.2747 found: 464.2753.

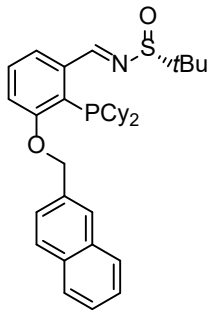
2.2.14 (*R*, *E*)-N-(3-(benzyloxy)-2-(dicyclohexylphosphanyl)benzylidene)-2-methylpropane-2-sulfinamide (Xu6-6)



Xu6-6

To a solution of 3-(benzyloxy)-2-(dicyclohexylphosphanyl)-benzaldehyde the crude product **Xu6-5** in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (2.4 mmol, 1.2 equiv.) and titanium tetraisopropanolate (4 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and then was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu6-6** as a yellow solid. Mp: 48.1-52.0 ℃. $[\alpha]_D^{20}$ = -110.0 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (d, J = 7.2 Hz, 1H), 7.63 (ddd, J = 7.8, 3.1, 1.0 Hz, 1H), 7.48 – 7.33 (m, 6H), 7.05 – 6.96 (m, 1H), 5.08 (s, 2H), 2.32 (tt, J = 7.7, 3.4 Hz, 2H), 1.78 – 1.66 (m, 4H), 1.56 (d, J = 8.6 Hz, 4H), 1.27 (s, 9H), 1.20 – 1.04 (m, 8H), 0.97 – 0.81 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.8 (d, *J* = 40.5 Hz), 161.6 (d, *J* = 3.4 Hz), 143.5 (d, *J* = 21.2 Hz), 136.4, 130.4, 128.6, 128.3,127.3 (d, *J* = 35.0 Hz), 120.5 (d, *J* = 6.2 Hz), 113.5, 70.7, 57.8, 34.1 (dd, *J* = 11.6, 5.3 Hz), 32.2, 32.0 (d, *J* = 1.9 Hz), 30.5 (dd, *J* = 13.1, 8.9 Hz), 29.7, 27.2 – 26.6 (m) 26.3, 22.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -11.79. HRMS (ESI) calculated for $[C_{30}H_{43}NO_2PS]$ $[M+H]^+$: 512.2747 found: 512.2757.

2.2.15 (*R*, *E*)-N-(2-(dicyclohexylphosphanyl)-3-(naphthalen-2-ylmethoxy)-benzylidenee)-2-methylpropane-2-sulfinamide (Xu7-6)

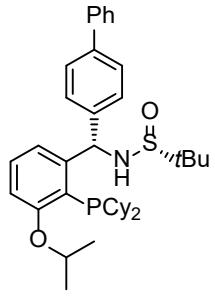


Xu7-6

Prepared from 2-(dicyclohexylphosphanyl)-3-(naphthalen-2-ylmethoxy)-benzaldehyde the crude product **Xu7-5** in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (2.4 mmol, 1.2 equiv.) and titanium tetraisopropanolate (4 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted

with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentratedand purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu7-6** as a yellow solid. Mp: 80-82.1 °C. $[\alpha]_D^{20}$= -77.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (d, *J* = 7.2 Hz, 1H), 7.92 – 7.87 (m, 3H), 7.84 (dt, *J* = 6.2, 3.5 Hz, 1H), 7.64 (ddd, *J* = 7.8, 3.1, 1.0 Hz, 1H), 7.53 (ddd, *J* = 10.8, 7.4, 2.5 Hz, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.02 (m, 1H), 5.26 (s, 2H), 2.46 – 2.32 (m, 2H), 1.78 – 1.70 (m, 2H), 1.69 – 1.63 (m, 2H), 1.62 – 1.53 (m, 4H), 1.38 – 1.29 (m, 3H), 1.27 (s, 10H), 1.11 (q, *J* = 8.3, 7.4 Hz, 6H), 1.02 – 0.90 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7 (d, *J* = 40.3 Hz), 161.6 (d, *J* = 3.3 Hz), 143.6, 143.4, 133.9, 133.3, 133.1, 130.5, 128.4, 127.8, 127.8, 126.7, 126.4, 126.2, 125.5, 120.6 (d, *J* = 6.1 Hz), 113.7, 70.7, 57.8, 34.2 (dd, *J* = 11.4, 5.0 Hz), 32.0 (d, *J* = 2.2 Hz), 30.6 (dd, *J* = 12.9, 8.9 Hz), 27.1 (dd, *J* = 8.6, 2.7 Hz), 26.8 (dd, *J* = 14.1, 4.4 Hz), 26.3, 22.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -11.66. HRMS (ESI) calculated for $[C_{34}H_{45}NO_2PS]$ $[M+H]^+$: 562.2903 found: 562.2908.

2.2.16 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-phenyl)-methyl)-2-methylpropane-2-sulfinamide (Xu5-7)

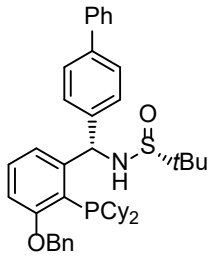


Xu5-7

Prepared from (*R*,*E*)-N-(2-(dicyclohexylphosphanyl)-3-isopropoxybenzylidene)-2- methylpropane-2-sulfinamide the crude product **Xu5-6** in 2 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (4 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered,

concentrated.and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu5-7** as a white solid (507 mg, 41% yield). Mp: 182.3-185.0 ℃. $[\alpha]_D^{20}$ = -99.7 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2 H), 7.51 – 7.47 (m, 4 H), 7.46 – 7.39 (m, 2 H), 7.38 – 7.29 (m, 2 H), 7.28 – 7.21 (m, 1 H), 7.01 (s, 1 H), 6.72 (d, *J* = 8.1 Hz, 1 H), 4.69 – 4.53 (m, 1 H), 4.08 (s, 1 H), 2.45 – 2.27 (m, 2 H), 1.94 – 1.83 (m, 2 H), 1.81 – 1.73 (m, 1 H), 1.72 – 1.66 (m, 1 H), 1.65 – 1.56 (m, 2 H), 1.55 – 1.47 (m, 1 H), 1.40 – 1.34 (m, 7 H), 1.30 – 1.22 (m, 13 H), 1.21 – 1.09 (m, 4 H)，1.03 – 0.89 (m, 4 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0 (d, *J* = 3.4 Hz), 151.3 (d, *J* = 23.7 Hz), 142.3, 141.0, 139.9, 130.1, 129.1, 129.1, 128.6, 127.1, 127.0, 126.9, 123.0 (d, *J* = 29.2 Hz), 119.8 (d, *J* = 6.7 Hz), 109.1, 68.4, 60.4 (d, *J* = 35.8 Hz), 55.8, 35.6 (d, *J* = 10.4 Hz), 34.8 (d, *J* = 11.2 Hz), 33.4 (d, *J* = 26.9 Hz), 32.5 (d, *J* = 23.8 Hz), 30.3 (d, *J* = 9.6 Hz), 30.0 (d, *J* = 6.9 Hz), 27.4 (dd, *J* = 8.2, 3.3 Hz), 27.1 (dd, *J* = 14.7, 9.9 Hz), 26.2 (d, *J* = 3.6 Hz), 22.7, 21.9, 21.8. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.70. HRMS (ESI) calculated for $[C_{38}H_{53}NO_2PS]$ $[M+H]^+$: 618.3529 found: 618.3526.

2.2.17 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-phenyl)-methyl)-2-methylpropane-2-sulfinamide (Xu6-7)

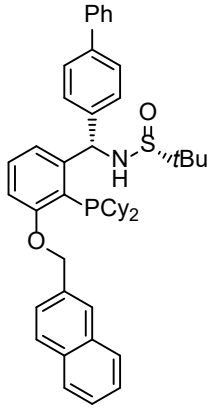


Xu6-7

To a solution of (*R*, *E*)-N-(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-benzylidene)-2-methyl-propane-2-sulfinamide the crude product **Xu6-6** in 2 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (4 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was purified by flash column chromatography on silica gel

(petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu6-7** as a white solid (573 mg, 43% yield). Mp: 94.1-96.0 °C. $[\alpha]_D^{20}$ = -101.7 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.5 8 – 7.51 (m, 2 H), 7.49 (s, 4 H), 7.46 – 7.35 (m, 8 H), 7.36 – 7.29 (m, 2 H), 7.02 (s, 1 H), 6.84 (d, *J* = 8.1 Hz, 1 H), 5.10 – 4.99 (m, 2 H), 4.04 (s, 1 H), 2.36 – 2.11 (m, 2 H), 1.74 – 1.65 (m, 3 H), 1.64 – 1.53 (m, 3 H), 1.52 – 1.42 (m, 1 H), 1.38 – 1.31 (m, 1 H), 1.31 – 1.22 (m, 11 H), 1.21 – 1.88 (m, 10 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 3.6 Hz), 151.2 (d, *J* = 23.5 H z), 142.2, 141.0, 140.1, 136.7, 130.3, 129.19, 129.17, 128.7, 128.5, 128.1, 128.0, 127.18, 127.11, 127.0, 123.5 (d, *J* = 30.3 Hz), 120.9 (d, *J* = 6.5 Hz), 109.6, 70.5, 60.4 (d, *J* = 35.5 Hz), 55.9, 35.1 (d, *J* = 10.4 Hz), 34.2 (d, *J* = 11.2 Hz), 33.2 (d, *J* = 26.4 Hz), 32.3 (d, *J* = 22.9 Hz), 30.5 (d, *J* = 10.0 Hz), 30.2 (d, *J* = 7.4 Hz), 27.3 (t, *J* = 8.5 Hz), 27.0 (dd, *J* = 14.2, 11.7 H z), 26.3, 22.8. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.35. HRMS (ESI) calculated for $[C_{42}H_{53}NO_2PS]$ $[M+H]^+$: 666.3529 found: 666.3526.

2.2.18 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-phenyl)-methyl)-2-methylpropane-2-sulfinamide (Xu7-7)

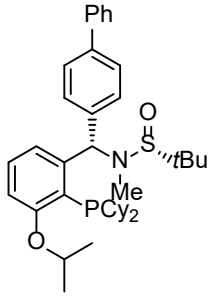


Xu7-7

Prepared from (*R*,*E*)-N-(2-(dicyclohexylphosphanyl)-3-(naphthalen-2-ylmethoxy)benzylidene)-2-methylpropane-2-sulfinamide the crude product **Xu7-6** in 2 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (4 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered,

concentrated and purified by flash silica gel column chromatography (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu7-7** as a white solid (659 mg, 46% yield). Mp: 95.2-98.3 ℃. $[\alpha]_D^{20}$ = -80.2 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.87 (m, 3 H), 7.86 – 7.82 (m, 1 H), 7.57 – 7.56 (m, 1 H), 7.56 – 7.54 (m, 2 H), 7.54 – 7.53 (m, 1 H), 7.53 – 7.50 (m, 5 H), 7.46 – 7.37 (m, 3 H), 7.37 – 7.31 (m, 2 H), 7.06 (s, 1 H), 6.89 (d, *J* = 7.9 Hz, 1 H), 5.33 – 5.18 (m, 2 H), 4.06 (s, 1 H), 2.44 – 2.21 (m, 2 H), 1.81 – 1.63 (m, 4 H), 1.63 – 1.53 (m, 2 H), 1.53 – 1.44 (m, 1 H), 1.43 – 1.31 (m, 3 H), 1.31 – 1.25 (m, 10 H), 1.22 – 1.14 (m, 2 H), 1.12 – 0.95 (m, 6 H), 0.94 – 0.87 (m, 1 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 3.3 Hz), 151.1 (d, *J* = 23.4 Hz), 142.1, 140.9, 140.0, 134.2, 133.2, 133.0, 130.3, 129.1, 129.1, 128.6, 128.3, 127.8, 127.7, 127.1, 127.03, 127.00, 126.5, 126.3, 126.1, 125.5, 123.5 (d, *J* = 30.2 Hz), 120.9 (d, *J* = 5.2 H z), 109.7, 70.5, 60.3 (d, *J* = 40.4 Hz), 55.9, 35.1 (d, *J* = 10.4 Hz), 34.2 (d, *J* = 11.1 Hz), 33.2 (d, *J* = 26.4 Hz), 32.3 (d, *J* = 22.9 Hz), 30.4 (d, *J* = 10.0 Hz), 30.2 (d, *J* = 7.4 Hz), 27.3 (t, *J* = 8.3 Hz), 26.9 (dd, *J* = 14.5, 12.3 Hz), 26.2, 22.8. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.19. HR MS (ESI) calculated for $[C_{46}H_{55}NO_2PS]$ $[M+H]^+$: 716.3686 found: 716.3689.

2.2.19 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(2-(dicyclohexylphosphanyl)-3-isopropoxyphenyl)-methyl)-N,2-dimethylpropane-2-sulfinamide (Xu5)

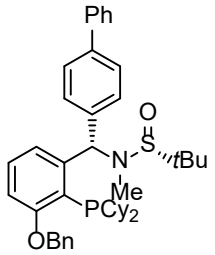


Xu5

Prepared from (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)phenyl)-methyl)-2-methylpropane-2-sulfinamide **Xu5-7** (0.5 mmol) in 2 mL anhydrous THF, was added *n*-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl

(aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu6** as a white solid (234 mg, 74% yield). Mp: 85.7-87.2 ℃. $[\alpha]_D^{20}$ = -1.2 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2 H), 7.50 – 7.44 (m, 2 H), 7.43 – 7.36 (m, 4 H), 7.33 – 7.29 (m, 1 H), 7.29 – 7.23 (m, 2 H),7.15 (d, *J* = 11.7 Hz, 1 H), 6.72 (dd, *J* = 7.0, 2.4 Hz, 1 H), 4.69 – 4.55 (m, 1 H), 2.64 (s, 3 H), 2.55 – 2.41 (m, 1 H), 2.22 – 2.09 (m, 1 H), 1.90 – 1.71 (m, 3 H), 1.70 – 1.54 (m, 3 H), 1.43 – 1.33 (m, 7 H), 1.31 – 1.21 (m, 5 H), 1.20 – 0.99 (m, 13 H), 0.99 – 0.72 (m, 4 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.0 (d, *J* = 3.6 Hz), 150.0 (d, *J* = 22.8 Hz), 140.9, 139.8, 139.2, 131.7, 130.2, 128.6, 127.0, 126.9, 126.3, 122.8 (d, *J* = 28.5 Hz), 119.5 (d, *J* = 5.4 Hz), 109.1, 70.5 (d, *J* = 40.5 Hz), 68.3, 58.6, 35.4 (d, *J* = 10.0 Hz), 34.4 (d, *J* = 11.2 Hz), 33.5 (d, *J* = 27.1 Hz), 32.3 (d, *J* = 23.1 Hz), 30.7 (d, *J* = 10.7 Hz), 30.3, 29.6 (d, *J* = 6.7 Hz), 27.3 (dd, *J* = 8.4, 3.4 Hz), 27.0 (dd, *J* = 14.5, 9.3 Hz), 26.4, 26.1, 24.1, 21.87, 21.83. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.40. HRMS (ESI) calculated for $[C_{39}H_{55}NO_2PS]$ $[M+H]^+$: 632.3686 found: 632.3684.

2.2.20 ((*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-phenyl)-methyl)-N,2-dimethylpropane-2-sulfinamide (Xu6)

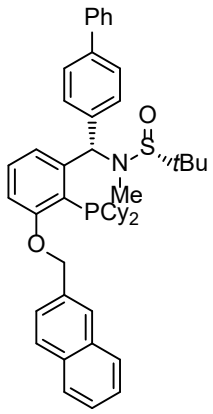


Xu6

To a solution of (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)phenyl) methyl)-2-methylpropane-2-sulfinamide **Xu6-7** (0.5 mmol) in 2 mL anhydrous THF, was added *n*-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl

(aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu6** as a white solid (245 mg, 72% yield). Mp: 79.1-81.3 °C$[\alpha]_D^{20}$ = -26.1 (*c* = 0.4, Chloroform).. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2 H), 7.51 – 7.44 (m, 3 H), 7.43 (s, 1 H), 7.42 – 7.39 (m, 5 H), 7.39 – 7.34 (m, 1 H), 7.34-7.30 (m, 1 H), 7.29 – 7.23 (m, 3 H), 7.14 (d, *J* = 11.6 Hz, 1 H), 6.85 (d, *J* = 8.2, 1.0 Hz, 1 H), 5.03 (d, *J* = 2.3 Hz, 2 H), 2.64 (s, 3 H), 2.40 – 2.29 (m, 1 H), 2.07 – 1.95 (m, 1 H), 1.74 – 1.65 (m, 2 H), 1.64 – 1.56 (m, 3 H), 1.54 – 1.46 (m, 1 H), 1.41 – 1.34 (m, 1 H), 1.32 – 1.15 (m, 5 H), 1.14 – 1.10 (m, 12 H), 0.99 – 0.80 (m, 4 H), 0.79 – 0.70 (m, 1 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 3.6 Hz), 149.9 (d, *J* = 22.5 Hz), 140.9, 139.9, 139.1, 136.7, 131.7, 130.4, 128.6, 128.4, 128.1, 128.0, 127.1, 127.0, 126.4, 123.3 (d, *J* = 29.6 Hz), 120.6 (d, *J* = 5.3 Hz), 109.6, 70.6 (d, *J* = 39.6 Hz), 70.4, 58.6, 34.9 (d, *J* = 10.0 Hz), 33.9 (d, *J* = 11.3 Hz), 33.2 (d, *J* = 26.4 Hz), 32.1 (d, *J* = 22.5 Hz), 30.8 (d, *J* = 11.3 Hz), 30.4, 29.8 (d, *J* = 7.5 Hz), 27.2 (dd, *J* = 8.5, 6.5 Hz), 26.9 (d, *J* = 2.9 Hz), 26.8 (d, *J* = 4.9 Hz), 26.4, 26.1, 24.1. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -9.99. HRMS (ESI) calculated for $[C_{43}H_{55}NO_2PS]$ $[M+H]^+$: 680.3686 found: 680.3689.

2.2.21 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(2-(dicyclohexylphosphanyl)-3-(naphthalen-2-ylmethoxy)-phenyl)-methyl)-N,2-dimethylpropane-2-sulfinamide (Xu7)

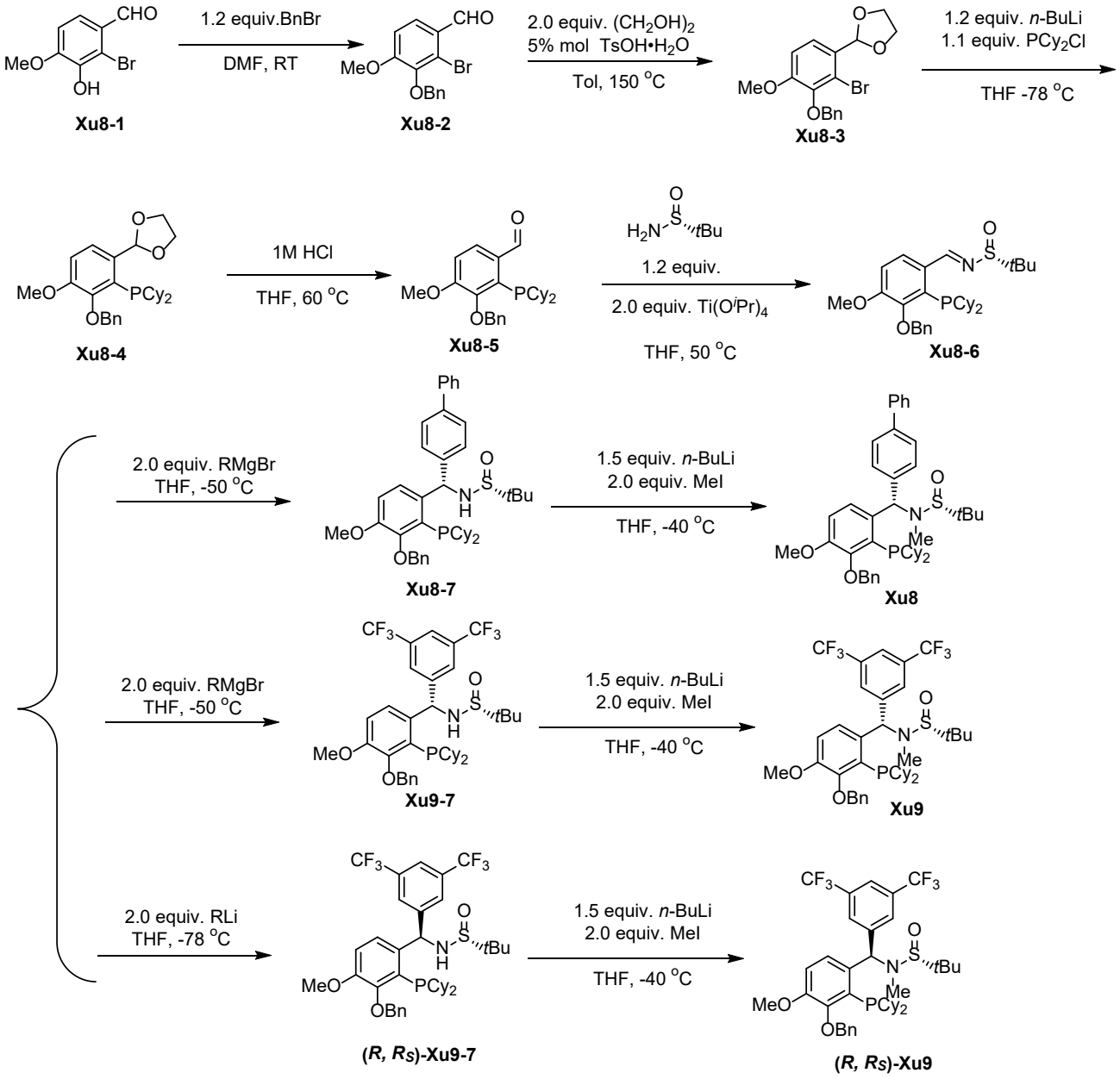


Xu7

Prepared from (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)phenyl)-methyl)-2-methylpropane-2-sulfinamide **Xu7-7** (0.5 mmol) in 2 mL anhydrous THF, was added

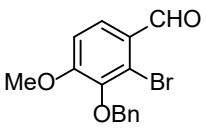
n-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu7** as a white solid (277 mg, 76% yield). Mp: 89.1-91.3 ℃. $[\alpha]_D^{20}$ = -44.34 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.85 (m, 3 H), 7.85 – 7.80 (m, 1 H), 7.61 – 7.52 (m, 3 H), 7.52 – 7.46 (m, 5 H), 7.46 – 7.39 (m, 3 H), 7.36 – 7.29 (m, 1 H), 7.30 – 7.24 (m, 2 H), 7.16 (d, *J* = 11.6 Hz, 1 H), 6.90 (d, *J* = 8.1, 1 H), 5.21 (d, *J* = 2.1 Hz, 2 H), 2.66 (s, 3 H), 2.51 – 2.33 (m, 1 H), 2.17 – 2.02 (m, 1 H), 1.74 – 1.54 (m, 5 H), 1.53 – 1.42 (m, 1 H), 1.41 – 1.32 (m, 2 H), 1.29 – 1.04 (m, 16 H), 0.97 – 0.84 (m, 4 H), 0.81 – 0.70 (m, 1 H). ^{13}C NMR (125MHz, Chloroform-*d*) δ 161.6 (d, *J* = 3.6 Hz), 149.9 (d, *J* = 22.7 Hz), 140.9, 139.9, 139.1, 134.2, 133.2, 133.0, 131.7, 130.5, 128.6, 128.2, 127.7, 127.7, 127.1, 127.0, 126.6, 126.4, 126.3, 126.1, 125.6, 123.3 (d, *J* = 29.5 Hz), 120.6 (d, *J* = 5.4 Hz), 109.7, 70.6 (d, *J* = 39.9 Hz), 70.5, 58.6, 35.0 (d, *J* = 10.0 Hz), 33.9 (d, *J* = 11.3 Hz), 33.2 (d, *J* = 26.5 Hz), 32.1 (d, *J* = 22.6 Hz), 30.8 (d, *J* = 11.2 Hz), 30.4, 29.8 (d, *J* = 7.3 Hz), 27.2 (dd, *J* = 8.6, 5.5 Hz), 26.8 (dd, *J* = 14.5, 3.2 Hz), 26.3, 26.1, 24.1. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -10.19. HRMS (ESI) calculated for $[C_{47}H_{57}NO_2PS]$ $[M+H]^+$: 730.3842 found: 730.3847.

2.3 Synthesis of Xu8, Xu9, (*R*, *R*$_S$)-Xu9



Prepared from 2-bromo-3-hydroxy-4-methoxybenzaldehyde, according to the preparation of **Xu5**

2.3.1 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde (Xu8-2)

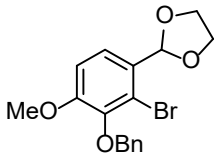


Xu8-2

Prepared from 2-bromo-3-hydroxy-4-methoxybenzaldehyde (30 mmol) in DMF (50 mL) was added benzyl bromide (36mmol, 1.2 equiv.) and K_2CO_3 (45 mmol, 1.5 equiv.). The resulting

solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu8-2** as a white solid (8.4 g, 87% yield). Mp: 72.2-74.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.25 (d, *J* = 0.9 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.43 – 7.28 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 1H), 5.04 (s, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.9, 158. 7, 145.0, 136.5, 128.4, 128.3, 128.2, 127.3, 126.5, 123.4, 110.9, 74.7, 56.2. HRMS (ESI) calculated for [$C_{15}H_{13}BrNaO_3$] [M+Na]$^+$: 342.9940 found: 342.9930.

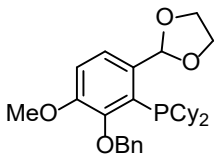
2.3.2 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde (Xu8-3)



Xu8-3

Prepared from 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **(Xu8-2)** (20 mmol) in 50 mL toluene, was added ethylene glycol (40 mmol, 2.0 equiv.) and *p*-toluenesulfonic acid (1 mmol, 5% mol). The resulting solution was stirred 18 hours at 150 °C. The reaction mixture was washed by the addition of H_2O and the combined organic layers were dried over Na_2SO_4, filtered, concentrated, The crude product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu8-3** as a white liquid (3.9 g, 53% yield). Mp: 106.2-108.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.51 (m, 2 H), 7.44 – 7.28 (m, 4 H), 6.89 (d, *J* = 8.6 Hz, 1 H), 6.07 (s, 1 H), 5.00 (s, 1 H), 4.16 – 4.09 (m, 2 H), 4.09 – 4.01 (m, 2 H), 3.86 (s, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.3, 145.1, 137.0, 129.4, 128.3, 128.2, 127.9, 123.0, 119.1, 111.0, 102.6, 74.5, 65.3, 56.0. HRMS (ESI) calculated for [$C_{17}H_{17}BrNaO_4$] [M+Na]$^+$: 387.0202 found: 387.0205.

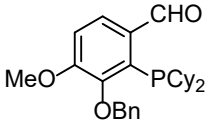
2.3.3 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde (Xu8-4)



Xu8-4

Prepared from 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **(Xu8-3)** (5 mmol) in 20 mL anhydrous THF, was added *n*-BuLi (18 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (17 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu8-4** as a white liquid. Mp: 96.2-98.8 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 7.5 Hz, 2H), 7.37 (td, J = 6.9, 6.5, 3.8 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.26 (d, J = 3.1 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.59 (d, J = 7.3 Hz, 1H), 5.14 (s, 2H), 4.11 (q, J = 3.5, 2.6 Hz, 2H), 4.01 (dd, J = 4.6, 2.7 Hz, 2H), 3.88 (s, 3H), 1.94 – 1.84 (m, 4H), 1.78 (d, J = 12.9 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.58 – 1.50 (m, 2H), 1.34 – 1.14 (m, 8H), 1.06 (td, J = 12.1, 11.6, 4.0 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.3, 149.2, 137.2 (d, *J* = 21.7 Hz), 136.8, 128.4, 127.9, 127.6, 126.5 (d, *J* = 23.1 Hz), 115.1, 110.8 (d, *J* = 6.7 Hz), 101.0 (d, *J* = 33.0 Hz), 70.7, 65.3, 56.2, 34.2 (d, *J* = 12.1 Hz), 30.5 (d, *J* = 17.7 Hz), 29.1 (d, *J* = 8.0 Hz), 27.1 (d, *J* = 9.0 Hz), 27.0 (d, *J* = 4.3 Hz), 26.3. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -17.48. HRMS (ESI) calculated for $[C_{29}H_{40}O_4P]$ $[M+Na]^+$: 483.2659 found: 483.2672.

2.3.4 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde (Xu8-5)

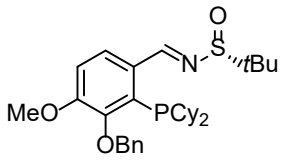


Xu8-5

Prepared from 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde the crude product **(Xu8-4)** in 2 mL THF, was added 3 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours.

The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu8-5** as a yellow solid. Mp: 95.5-97.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.07 (d, *J* = 8.7 Hz, 1H), 7.78 (dd, *J* = 8.6, 3.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 5.20 (s, 2H), 3.92 (s, 3H), 2.36 (tdt, *J* = 11.4, 7.4, 3.3 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.75 – 1.66 (m, 2H), 1.64 – 1.52 (m, 4H), 1.39 – 1.32 (m, 2H), 1.26 – 1.09 (m, 8H), 1.04 – 0.91 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.4 (d, *J* = 42.1 Hz), 156.0, 150.6, 138.0, 136.7, 133.4 (d, *J* = 37.7 Hz), 128.3, 127.7, 127.3, 124.4 (d, *J* = 6.2 Hz), 113.3, 73.9, 55.7, 34.5 (d, *J* = 11.6 Hz), 32.4 (d, *J* = 23.2 Hz), 30.8 (d, *J* = 9.7 Hz), 26.8 (d, *J* = 8.9 Hz), 26.6 (d, *J* = 14.0 Hz), 26.2 (d, *J* = 1.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ -13.94. HRMS (ESI) calculated for $[C_{27}H_{36}O_3P]$ $[M+H]^+$: 439.2397 found: 439.2407.

2.3.5 (*R*, *E*)-N-(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu8-6)

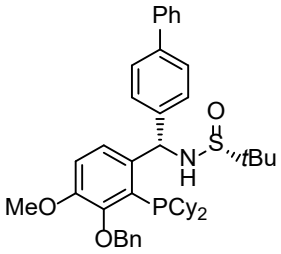


Xu8-6

Prepared from 3-(benzyloxy)-2-bromo-4-methoxybenzaldehyde the crude product **Xu8-5** in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (2.4 mmol, 1.2 equiv.) and titanium tetraisopropanolate (4 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu8-6** as a yellow solid. Mp: 111.2-114.1 ℃. $[\alpha]_D^{20}$ = -90.7 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.65 (s, 1H), 7.87 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.47 – 7.39 (m,

2H), 7.38 – 7.30 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 3.90 (s, 3H), 2.33 (dddp, *J* = 14.9, 11.3, 7.7, 3.5, 3.0 Hz, 2H), 1.79 (d, *J* = 11.9 Hz, 2H), 1.69 (d, *J* = 7.6 Hz, 2H), 1.57 (d, *J* = 7.5 Hz, 4H), 1.38 – 1.31 (m, 2H), 1.26 (s, 9H), 1.25 – 1.06 (m, 8H), 1.03 – 0.90 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 163.7, 154.5, 151.0, 138.0, 128.3, 127.6, 127.4, 124.3, 124.3, 113.5, 74.0, 57.5, 55.6, 34.8, 32.3 (d, *J* = 24.1 Hz), 30.7 (dd, *J* = 9.7, 7.1 Hz), 26.8 (d, *J* = 8.9 Hz), 26.6 (dd, *J* = 13.9, 4.4 Hz), 26.2, 22.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -9.32. HRMS (ESI) calculated for [$C_{31}H_{45}NO_3PS$] [M+H]$^+$: 542.2852 found: 542.2865.

2.3.6 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxy-phenyl)-methyl)-2-methylpropane-2-sulfinamide (Xu8-7)

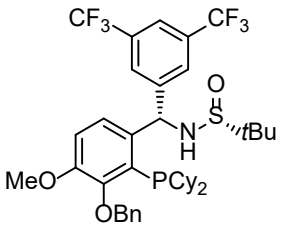


Xu8-7

Prepared from (*R*, *E*)-N-(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxybenzylidene)-2-methylpropane-2-sulfinamide the crude product **Xu8-6** in 2 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (4 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu8-7** as a white solid (626 mg, 18% yield). Mp: 87.8-89.0 ℃. $[\alpha]_D^{20}$ = -109.2 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2 H), 7.52 – 7.45 (m, 6 H), 7.45 – 7.36 (m, 5 H), 7.35 – 7.28 (m, 2 H), 7.06 (d, *J* = 8.6 Hz, 1 H), 6.93 (s, 1 H), 5.28 (d, *J* = 11.7 Hz, 1 H), 5.17 (d, *J* = 11.7 Hz, 1 H), 4.00 (s, 1 H), 3.86 (s, 3 H), 2.34 – 2.16 (m, 2 H), 1.79 – 1.53 (m, 6 H), 1.51 – 1.41 (m, 1 H), 1.38 – 0.87 (m, 22 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 150.8 (d, *J* = 3.7 H z), 150.5, 142.4, 141.9 (d, *J* = 23.9 Hz), 140.9, 140.0, 138.5, 129.18, 129.17, 128.7 (d, *J* = 29.4 Hz), 128.6, 128.1, 127.3, 127.1, 127.03, 127.00, 126.9, 123.2 (d,

J = 6.5 Hz), 113.8, 73.3, 60.0 (d, *J* = 35.5 Hz), 55.8, 55.5, 35.2 (d, *J* = 10.7 Hz), 34.3 (d, *J* = 11.3 Hz), 33.1 (d, *J* = 25.9 Hz), 32.3 (d, *J* = 22.8 Hz), 30.4 (dd, *J* = 21.4, 9.2 Hz), 27.0 (dd, *J* = 8.6, 6.2 Hz), 26.8 (dd, *J* = 14.2, 8.0 Hz), 26.2, 22.7. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -6.74. HRMS (ESI) calculated for [$C_{43}H_{54}NNaO_3PS$] $[M+Na]^+$: 718.3454 found: 718.3457.

2.3.7 (*R*)-N-((*S*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5-bis(trifle-oromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide (Xu9-7)

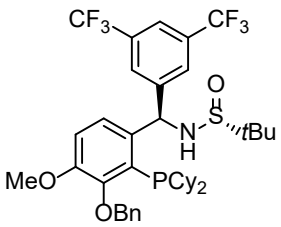


Xu9-7

Prepared from (*R*, *E*)-N-(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxybenzylidene)-2-methylpropane-2-sulfinamide the crude product **Xu8-6** in 2 mL anhydrous THF, was added (3,5-bis(trifluoromethyl)phenyl)magnesium bromide (10 mmol, 5.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu9-7** as a white solid (800 mg, 53% yield). Mp: 68.1-71.3 ℃. $[\alpha]_D^{20}$ = -67.8 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 2H), 7.71 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 2H), 7.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.86 (s, 1H), 5.28 (dd, *J* = 11.7, 1.7 Hz, 1H), 5.15 (d, *J* = 11.6 Hz, 1H), 3.87 (d, *J* = 1.8 Hz, 3H), 2.23 (d, *J* = 14.7 Hz, 2H), 1.80 – 1.47 (m, 10H), 1.40 – 1.33 (m, 1H), 1.27 (d, *J* = 1.9 Hz, 9H), 1.16 – 0.91 (m, 9H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 151.2, 151.0, 146.4,140.5 (d, *J* = 24.7 Hz), 138.3, 131.3 (q, *J* = 33.0 Hz), 128.9, 128.2, 127.5, 127.1, 124.4, 123.1, 122.2, 120.9, 114.2, 73.5, 56.2, 55.5, 35.3 (d, *J* = 10.0 Hz), 34.3 (d, *J* = 10.4 Hz), 33.1 (d, *J* = 25.9 Hz), 32.3 (d, *J* = 22.5 Hz), 30.6 (d, *J* = 9.3 Hz), 30.5 (d, *J* = 10.5 Hz), 27.0, 26.9, 26.9, 26.8 (d, *J* = 3.6 Hz), 26.7 (d, *J* = 4.5 Hz), 26.1 (d, *J* = 5.1 Hz) , 22.7. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -5.95.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.72. HRMS (ESI) calculated for [$C_{39}H_{49}F_6NO_3PS$] $[M+H]^+$: 756.3069 found: 756.3083.

2.3.8 (*R*)-N-((*R*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5bis(trifle-oromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide

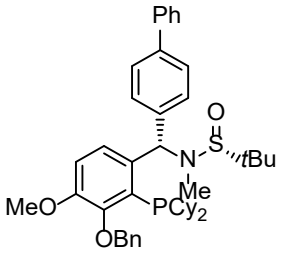


(*R, R*$_S$)-Xu9-7

To a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (4 mmol) in dry THF (4 mL) was added *n*-BuLi (4 mmol, 2.4 M in hexane) dropwise under argon at -78 °C. The resulting solution at this temperature during 1 hour and the **Xu8-6** (2 mmol) in 2 mL anhydrous THF was added dropwise. Then the reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **(*R*, *R*$_S$)-Xu9-7** as a white solid (720 mg, 48% yield). Mp: 79.2-81.1 °C. $[\alpha]_D^{20}$ = -3.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.89 (m, 2H), 7.70 (s, 1H), 7.47 – 7.42 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.27 – 7.23 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.87 (dd, *J* = 9.1, 4.5 Hz, 1H), 5.25 (d, *J* = 11.6 Hz, 1H), 5.16 (d, *J* = 11.6 Hz, 1H), 4.24 (s, 1H), 3.84 (s, 3H), 2.32 – 2.16 (m, 2H), 1.75 – 1.49 (m, 8H), 1.42 (q, *J* = 3.5, 2.5 Hz, 1H), 1.27 (d, *J* = 8.3 Hz, 11H), 1.06 (ddd, *J* = 31.2, 15.6, 7.6 Hz, 9H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 151.3 (d, *J* = 3.5 Hz), 151.2, 146.1, 141.5 (d, *J* = 24.3 Hz), 138.3,131.2 (q, *J* = 33.2 Hz), 128.9, 128.3, 127.5, 127.1, 124.5,122.6 (d, *J* = 7.2 Hz), 122.3, 120.8, 114.7, 73.6, 59.7 (d, *J* = 31.4 Hz), 56.3, 55.6, 35.3 (d, *J* = 10.2 Hz), 34.7 (d, *J* = 10.0 Hz), 33.1 (d, *J* = 25.4 Hz), 32.4 (d, *J* = 22.5 Hz), 30.7 (d, *J* = 9.7 Hz), 30.6 (d, *J* = 7.2 Hz), 27.1, 27.0, 26.9 (d, *J* = 4.6 Hz), 26.8 (d, *J* = 3.4 Hz), 26.6, 26.1, 22.8. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -6.70. ^{19}F NMR (376

MHz, Chloroform-*d*) δ -62.79. HRMS (ESI) calculated for [$C_{39}H_{49}F_6NO_3PS$] $[M+H]^+$: 756.3069 found: 756.3072.

2.3.9 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxyphenyl)-methyl)-N,2-dimethylpropane-2-sulfinamide (Xu8)

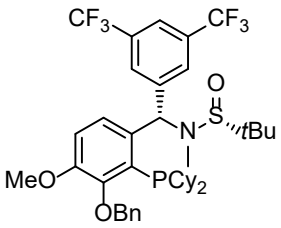


Xu8

Prepared from (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphanyl)-4-methoxyphenyl)methyl)-2-methylpropane-2-sulfinamide **Xu8-7** (0.5 mmol) in 2 mL anhydrous THF, was added *n*-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu8** as a white solid (245 mg, 69% yield). Mp: 86.0-87.2 °C. $[\alpha]_D^{20}$ = 11.3 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 3 H), 7.50 – 7.44 (m, 4 H), 7.45 – 7.35 (m, 4 H), 7.35 – 7.28 (m, 2 H), 7.28 – 7.21 (m, 2 H), 7.09 (d, *J* = 8.6 Hz, 1 H), 7.03 (d, *J* = 11.4 Hz, 1 H), 5.21 (s, 2 H), 3.87 (s, 3 H), 2.64 (s, 3 H), 2.45 – 2.30 (m, 1 H), 2.13 – 1.97 (m, 1 H), 1.75 – 1.54 (m, 5 H), 1.54 – 1.44 (m, 1 H), 1.41 – 1.35 (m, 2 H), 1.24 – 1.14 (m, 4 H), 1.14 – 1.02 (m, 11 H), 0.99 – 0.69 (m, 6 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 150.9 (d, *J* = 3.8 Hz), 150.4, 140.9, 140.4 (d, *J* = 22.9 Hz), 139.8, 139.4, 138.6, 131.7, 128.6, 128.6 (d, *J* = 30.9 Hz), 128.1, 127.3, 127.1, 127.02, 127.01, 126.3, 122.9 (d, *J* = 5.7 Hz), 113.9, 73.3, 70.5 (d, *J* = 39.9 Hz), 58.6, 55.5, 35.2 (d, *J* = 10.4 Hz), 34.0 (d, *J* = 11.6 Hz), 33.2 (d, *J* = 26.1 Hz), 32.2 (d, *J* = 22.3 Hz), 30.9 (d, *J* = 11.5 Hz), 30.5 , 29.9 (d, *J* = 8.0 Hz), 27.0 (t, *J* = 9.4 Hz), 26.8 (d, *J* = 2.9

Hz), 26.7 (d, *J* = 4.8 Hz), 26.3, 26.0, 24.1. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -6.11. HRMS (ESI) calculated for [$C_{44}H_{56}NNaO_3PS$] $[M+Na]^+$: 732.3611 found: 732.3614.

2.3.10 (*R*)-N-((*S*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5-bis(trifleoromethyl)phenyl)methyl)-N,2-dimethylpropane-2-sulfinamide (Xu9)

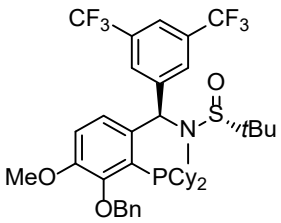


Xu9

Prepared from (*R*)-N-((*S*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5-bis-(trifle-oromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide **Xu9-7** (0.5 mmol) in 2 mL anhydrous THF, was added *n*-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu9** as a white solid (230 mg, 60% yield). Mp: 146-148.5 ℃. $[\alpha]_D^{20}$ = 45.9 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.65 (s, 2H), 7.57 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 10.1 Hz, 2H), 5.22 (s, 2H), 3.88 (s, 3H), 2.65 (s, 3H), 2.32 (q, *J* = 10.8 Hz, 1H), 2.08 (q, *J* = 11.3 Hz, 1H), 1.68 (d, *J* = 9.1 Hz, 3H), 1.61 (d, *J* = 9.8 Hz, 3H), 1.52 – 1.39 (m, 3H), 1.36 (d, *J* = 12.5 Hz, 1H), 1.25 – 1.14 (m, 4H), 1.07 (s, 10H), 0.96 – 0.73 (m, 5H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 151.3 (d, *J* = 3.8 Hz), 151.1, 143.6, 138.4, 138.0 (d, *J* = 22.8 Hz), 131.6, 131.0 (q, *J* = 33.1 Hz), 128.5 (d, *J* = 30.7 Hz), 128.3, 127.5, 127.1, 124.4, 122.8 (d, *J* = 5.5 Hz), 122.2, 120.9, 114.3, 73.6, 70.2 (d, *J* = 41.2 Hz), 59.2, 55.5, 35.3 (d, *J* = 10.0 Hz), 33.8 (d, *J* = 10.8 Hz), 33.2 (d, *J* = 26.2 Hz), 32.2 (d, *J* = 21.8 Hz), 31.0, 30.9, 30.2 (d, *J* = 7.5 Hz), 27.0 (d, *J* = 9.5 Hz), 26.8 – 26.6 (m), 26.6, 26.3, 26.0, 24.1. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -5.88.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.83. HRMS (ESI) calculated for [$C_{40}H_{51}F_6NO_3PS$] [M+H]$^+$: 770.3226 found: 770.3246.

2.3.11 (*R*)-N-((*R*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5-bis(trifluoromethyl)phenyl)methyl)-N,2-dimethylpropane-2-sulfinamide ((*R*, *R*$_S$)-Xu9)

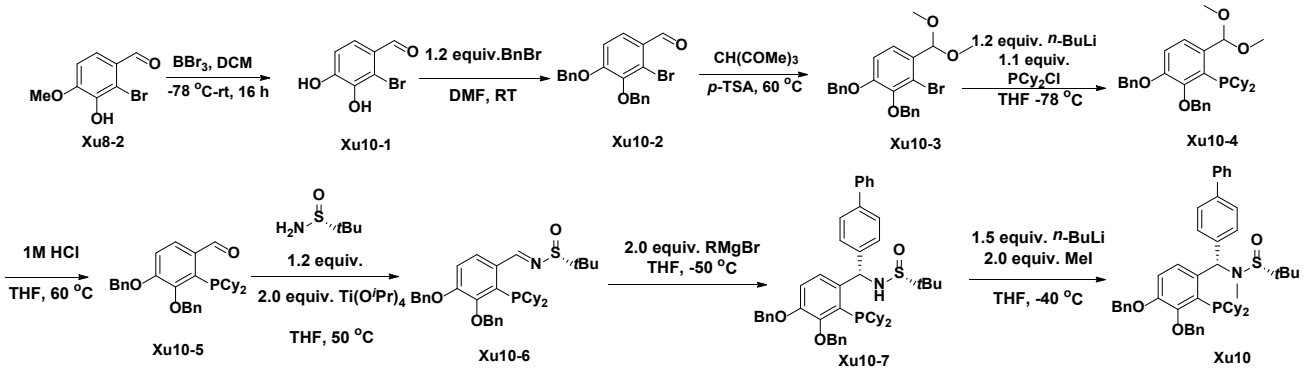


(*R*, *R*$_S$)-Xu9

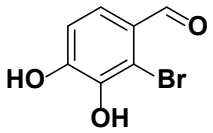
Prepared from (*R*)-N-((*R*)-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-methoxyphenyl)(3,5-bis-(trifle-oromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide **(*R*, *R*$_S$)-Xu9-7** (0.5 mmol) in 2 mL anhydrous THF, was added *n*-BuLi (0.75 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (1 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **(*R*, *R*$_S$)-Xu9** as a white solid (238 mg, 62% yield). Mp: 67.5-70.1 ℃. $[\alpha]_D^{20}$ = -23.4 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 2H), 7.70 (s, 1H), 7.48 – 7.27 (m, 6H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 9.9 Hz, 1H), 5.29 – 5.09 (m, 2H), 3.87 (s, 3H), 2.60 (s, 3H), 2.31 (dtt, *J* = 11.7, 8.5, 3.4 Hz, 1H), 2.11 – 1.95 (m, 1H), 1.71 – 1.57 (m, 5H), 1.52 (ddd, *J* = 12.1, 4.8, 2.4 Hz, 2H), 1.39 – 1.30 (m, 2H), 1.30 – 1.21 (m, 3H), 1.18 (s, 9H), 1.11 – 1.02 (m, 2H), 0.93 – 0.83 (m, 4H), 0.82 – 0.72 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.3 (d, *J* = 3.6 Hz), 150.9, 143.9, 138.4, 140.1 (d, *J* = 23.1 Hz), 131.3,131.7 – 130.6 (m), 128.7 (d, *J* = 32.3 Hz), 128.2, 127.5, 127.0, 124.7,121.9 (d, *J* = 6.2 Hz), 121.1 – 120.5 (m). 114.2,73.5, 58.9, 55.5, 35.6 (d, *J* = 10.6 Hz), 34.2 (d, *J* = 11.5 Hz), 33.1 (d, *J* = 26.7 Hz), 32.2 (d, *J* = 22.3 Hz), 31.0 (d, *J* = 11.0 Hz), 29.9 (d, *J* = 7.1 Hz), 26.9 (ddd, *J* = 21.0, 17.3,

8.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ -6.86. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.76. HRMS (ESI) calculated for $[C_{40}H_{51}F_6NO_3PS]$ $[M+H]^+$: 770.3226 found: 770.3241.

2.4 Synthesis of Xu10



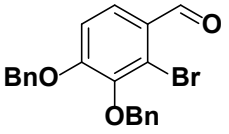
2.4.1 2-bromo-3,4-dihydroxybenzaldehyde (Xu10-1)



Xu10-1

To a solution of 2-bromo-3-hydroxy-4-methoxybenzaldehyde **Xu8-2** (3.45g, 15 mmol) in anhydrous CH_2Cl_2 (60 mL) at -78 °C was added BBr_3 (1M in CH_2Cl_2, 60 mL, 60 mmol). The mixture was warmed up to 25 °C and stirred for 16 h. Then the solution was cooled down to -78 °C and MeOH (35 mL) was added. The mixture was poured into water (100 mL) and extracted with EtOAc (3 x 100 mL). Combined organic fractions were washed with brine (100 mL), dried over MgSO4, filtered, and the solvent was evaporated. The residue was added to next step.

2.4.2 3,4-bis(benzyloxy)-2-bromobenzaldehyde (Xu10-2)

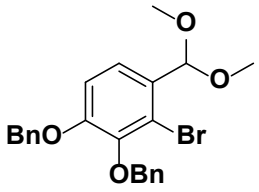


Xu10-2

Prepared from 2-bromo-3,4-dihydroxybenzaldehyde **Xu10-1** (10 mmol) in DMF (20 mL) was added benzyl bromide (30 mmol, 3 equiv.) and K_2CO_3 (30 mmol, 3 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of

H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu10-2** as a white solid (1.5 g, 38% yield). Mp: 136.5-137.4 ℃.^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.24 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.28 (m, 10H), 7.01 (d, *J* = 8.6 Hz, 1H), 5.18 (s, 2H), 5.04 (d, *J* = 1.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.8, 157.7, 145.4, 136. 5, 135.4, 128.7, 128.6, 128.4, 128.3, 128.2, 127.5, 127.4, 126.4, 123.6, 112.3, 74.8, 71.1. HRMS (ESI) calculated for [$C_{21}H_{17}BrNaO_3$] [M+Na]$^+$: 419.0253 found: 419.0242.

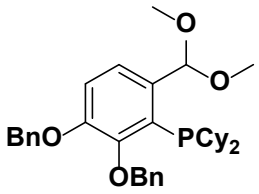
2.4.3 (((3-bromo-4-(dimethoxymethyl)-1,2-phenylene)bis(oxy))bis(methylene))dibenzene (Xu10-3)



Xu10-3

Prepared from 3,4-bis(benzyloxy)-2-bromobenzaldehyde **(Xu10-2)** (3 mmol) in trimethoxymethane (30 mmol, 10 equiv.) and *p*-toluenesulfonic acid (0.15 mmol, 5% mol). The resulting solution was stirred 5 hours at 60 ℃. The reaction mixture was washed by the addition of $NaHCO_3$ (aq.) and the combined organic layers concentrated. The crude product was purified by flash column chromatography on aluminum oxide (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu10-3** as a white liquid (1.1 g, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.21 (m, 7H), 6.88 (d, *J* = 8.6 Hz, 1H), 5.46 (s, 1H), 5.05 (s, 2H), 4.96 (s, 2H), 3.29 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.0, 145.7, 137.1, 136.5, 130.5, 129.9, 128.6, 128.6, 128.3, 128.2, 128.1, 127.5, 123.5, 119.4, 112.8, 103.1, 74.7, 71.2, 54.0. HRMS (ESI) calculated for [$C_{23}H_{23}BrNaO_4$] [M+Na]$^+$: 465.0672 found: 465.0682.

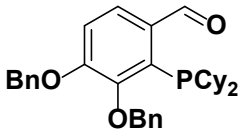
2.4.4 (2,3-bis(benzyloxy)-6-(dimethoxymethyl)phenyl)dicyclohexylphosphane (Xu10-4)



Xu10-4

Prepared from (((3-bromo-4-(dimethoxymethyl)-1,2-phenylene)bis(oxy))bis(methylene))dibenzene (**Xu10-3**) (2 mmol) in 4 mL anhydrous THF, was added *n*-BuLi (2.4 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (2.6 mmol, 1.3 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were concentrated. The crude product was purified by flash column chromatography on aluminum oxide (petroleum ether: ethyl acetate = 20: 1) to afford the crude product **Xu10-4** as a yellow liquid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.27 (m, 12H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 5.25 (s, 2H), 5.09 (s, 2H), 3.36 (s, 6H), 2.35 (dtt, *J* = 11.7, 7.9, 3.7 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 2H), 1.68 (d, *J* = 11.1 Hz, 2H), 1.62 – 1.57 (m, 4H), 1.35 (d, *J* = 15.3 Hz, 3H), 1.29 (s, 1H), 1.25 (s, 1H), 1.13 (d, *J* = 10.1 Hz, 5H), 1.03 – 0.91 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.6, 138.5, 136.6, 128.5, 128.2, 128.0, 127.6, 127.4, 127.2, 121.4 (d, *J* = 7.1 Hz), 115.8, 102.5, 102.1, 73.5, 71.2, 53.9, 34.6 (d, *J* = 10.8 Hz), 32.8 (d, *J* = 23.7 Hz), 30.9 (d, *J* = 10.3 Hz), 27.0 (d, *J* = 8.9 Hz), 26.8 (d, *J* = 13.8 Hz), 26.3. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -6.73. HRMS (ESI) calculated for [$C_{35}H_{46}O_4P$] $[M+H]^+$: 561.3128 found: 561.3128.

2.4.5 3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)benzaldehyde (Xu10-5)

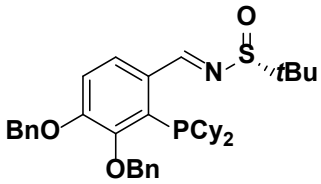


Xu10-5

Prepared from (2,3-bis(benzyloxy)-6-(dimethoxymethyl)phenyl)dicyclohexylphosphane **(Xu10-4)** in 2 mL THF, was added 1 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted

with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu10-5** as a yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.06 (d, *J* = 8.7 Hz, 1H), 7.76 (dd, *J* = 8.6, 3.1 Hz, 1H), 7.46 – 7.28 (m, 10H), 7.15 (d, *J* = 8.6 Hz, 1H), 5.22 (s, 2H), 5.17 (s, 2H), 2.36 (tdt, *J* = 11.4, 7.4, 3.4 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.71 (t, *J* = 5.2 Hz, 2H), 1.59 (d, *J* = 8.1 Hz, 4H), 1.34 (d, *J* = 3.4 Hz, 2H), 1.26 (s, 2H), 1.16 (d, *J* = 8.2 Hz, 6H), 1.04 – 0.92 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.41 (d, J = 41.3 Hz), 155.1, 151.0, 137.9, 135.8, 128.7, 128.4, 128.3, 127.7, 127.5, 124.3 (d, *J* = 6.0 Hz), 115.0, 73.9, 71.0, 34.6 (d, *J* = 11.0 Hz), 32.6, 32.4, 31.5, 31.0, 30.9, 30.2, 29.7, 26.9, 26.8, 26.8, 26.6, 26.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -13.80. HRMS (ESI) calculated for $[C_{33}H_{40}O_3P]$ $[M+H]^+$: 515.2710 found: 515.2724.

2.4.6 (*R, E*)-N-(3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)benzylidene)-2-methylpropan-e-2-sulfinamide (Xu10-6)

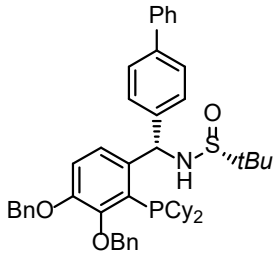


Xu10-6

Prepared from 3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)benzaldehyde **(Xu10-5)** in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (2.4 mmol, 1.2 equiv.) and titanium tetraisopropanolate (4 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu10-6** as a yellow solid. Mp: 63.7-65.2 ℃. $[\alpha]_D^{20}$ = -66.1 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.66 (s, 1H), 7.86 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.53 – 7.30 (m, 10H), 7.14 (dd, *J* = 8.7, 1.9 Hz, 1H), 5.31 – 5.09 (m, 4H), 2.42 – 2.24 (m, 2H), 1.83 (d, *J* = 12.8 Hz, 2H), 1.72 (s, 2H), 1.60 (d, *J* = 6.8 Hz, 4H), 1.38 (dd, *J* = 16.8, 7.0 Hz, 2H), 1.29 (d, *J* = 2.0 Hz, 11H), 1.18 (d, *J* = 7.9 Hz, 6H), 1.07 – 0.96 (m, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 163.94 (d, *J* = 34.5 Hz), 153.76, 151.56, 138.00, 136.11, 134.97, 133.35 (d, *J* = 36.4 Hz), 128.67, 128.35, 128.28, 128.25, 127.68, 127.65,

124.30, 115.32, 74.08, 71.02, 57.64, 34.97 (d, J = 12.1 Hz), 32.45 (d, J = 23.4 Hz), 31.55, 30.77 (t, J = 10.2 Hz), 30.19, 29.73, 26.94 (d, J = 8.6 Hz), 26.79 (d, J = 6.4 Hz), 26.68 (d, J = 5.8 Hz), 26.28, 22.72. ^{31}P NMR (203 MHz, $CDCl_3$) δ -9.13. HRMS (ESI) calculated for [$C_{37}H_{49}NO_3PS$] [M+H]$^+$: 618.3165 found: 618.3179.

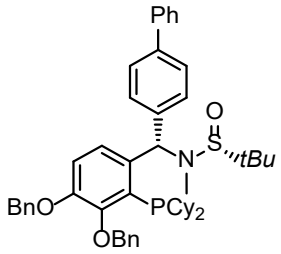
2.4.7 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)phenyl) methyl)-2-methylpropane-2-sulfinamide (Xu10-7)



Xu10-7

Prepared from (R, E)-N-(3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)benzylidene)-2-Methyl-propane-2-sulfinamide **(Xu10-6)** in 1 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (1 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu10-7** as a white solid (262 mg, 68% yield). Mp: 85-86.5 ℃. $[\alpha]_D^{20}$ = -64.6 (c = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.44 (m, 6H), 7.44 – 7.26 (m, 14H), 7.13 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 9.4 Hz, 1H), 5.31 (d, J = 11.6 Hz, 1H), 5.20 (d, J = 11.6 Hz, 1H), 5.09 (s, 2H), 3.98 (s, 1H), 2.36 – 2.12 (m, 2H), 1.75 – 1.51 (m, 6H), 1.50 – 1.41 (m, 1H), 1.26 (s, 22H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.4, 149.7, 142.4, 141.0, 140.1, 138.4, 136.6, 129.2 (d, J = 2.2 Hz), 128.7, 128.5, 128.1, 128.0, 127.7, 127.3, 127.1, 127.1, 127.0, 123.2 (d, J = 4.2 Hz), 115.9, 73.4, 71.1, 55.9, 35.3 (d, J = 10.8 Hz), 34.4 (d, J = 11.6 Hz), 33.2 (d, J = 25.9 Hz), 32.3 (d, J = 22.7 Hz), 30.4 (dd, J = 18.4, 8.9 Hz), 27.7 – 26.4 (m), 26.2, 22.8.^{31}P NMR (162 MHz, Chloroform-*d*) δ -6.59. HRMS (ESI) calculated for [$C_{49}H_{59}NO_3PS$] [M+H]$^+$: 772.3948 found: 772.3967.

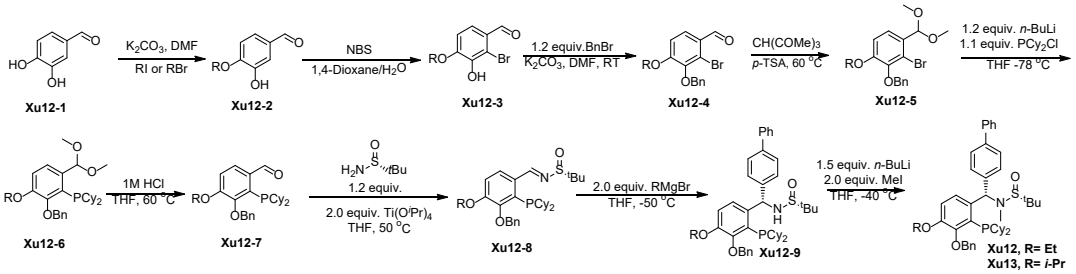
2.4.8 (*R*)-N-((*S*)-[1,1'-biphenyl]-4-yl(3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneyl)phenyl)methyl)-N,2-dimethylpropane-2-sulfinamide (Xu10)



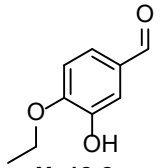
Xu10

Prepared from (R)-N-((S)-[1,1'-biphenyl]-4-yl(3,4-bis(benzyloxy)-2-(dicyclohexylphosphaneylphenyl)methyl)-2-methylpropane-2-sulfinamide (Xu10-7) in 1 mL anhydrous THF, was added *n*-BuLi (0.5 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (0.6 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu10** as a white solid (170 mg, 72% yield). Mp: 72-74.7 ℃. $[\alpha]_D^{20}$ = 14.7 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (ddd, *J* = 8.2, 5.3, 2.9 Hz, 3H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.28 (m, 12H), 7.25 (dd, *J* = 8.4, 4.1 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.03 (d, *J* = 11.4 Hz, 1H), 5.25 (s, 2H), 5.10 (s, 2H), 2.64 (s, 3H), 2.35 (dqd, *J* = 11.3, 7.2, 4.8, 3.1 Hz, 1H), 2.06 (dtt, *J* = 11.7, 8.4, 3.4 Hz, 1H), 1.71 – 1.57 (m, 5H), 1.50 (dd, *J* = 10.8, 6.4 Hz, 1H), 1.41 – 1.34 (m, 2H), 1.21 (td, *J* = 15.5, 14.6, 5.7 Hz, 5H), 1.09 (s, 9H), 0.98 – 0.82 (m, 6H), 0.77 (tt, *J* = 12.3, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.6 (d, *J* = 3.7 Hz), 149.6, 141.2 (d, *J* = 23.0 Hz), 141.1, 139.9, 139.5, 138.5, 136.7, 131.8, 129.1, 128.8, 128.7, 128.5, 128.2, 128.0, 127.8, 127.4, 127.2, 127.1, 127.0, 126.5, 122.9 (d, *J* = 5.7 Hz), 116.2, 73.5, 71.3, 70.6 (d, *J* = 39.9 Hz), 58.7, 35.3 (d, *J* = 10.4 Hz), 34.7, 34.1(d, *J* = 11.7 Hz), 33.3(d, *J* = 26.3 Hz), 32.3 (d, *J* = 22.4 Hz), 31.0 (d, *J* = 11.6 Hz), 30.6, 30.0 (d, *J* = 8.0 Hz), 27.2 – 26.6 (m), 26.2, 25.3, 24.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -5.94. HRMS (ESI) calculated for $[C_{50}H_{61}NO_3PS]$ $[M+H]^+$: 786.4104 found: 786.4118.

2.5 Synthesis of Xu12, Xu13



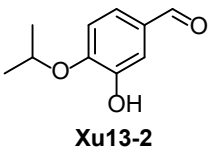
2.5.1 4-ethoxy-3-hydroxybenzaldehyde (Xu12-2)



Xu12-2

Prepared from 3,4-dihydroxybenzaldehyde **Xu12-1** (30 mmol) in DMF (50 mL) was added iodoethane (33mmol, 1.1 equiv.) and K_2CO_3 (33 mmol, 1.1 equiv.). The resulting solution was stirred at 0 °C 48 h. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. the crude product was then purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to afford the product **Xu12-2** as a white liquid (2.7 g, 55% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.86 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.0, 151.1, 146.2, 130.5, 124.5, 114.1, 110.8, 64.9, 14.6. HRMS (ESI) calculated for $[C_9H_{11}O_3]$ $[M+H]^+$: 167.0704 found: 167.0703.

2.5.2 3-hydroxy-4-isopropoxybenzaldehyde (Xu13-2)

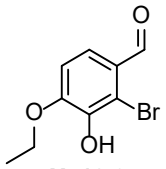


Xu13-2

Prepared from a stirred suspension of 3,4-dihydrobenzaldehyde **Xu12-1** (30 mmol), KI (3 mmol) and anhydrous potassium carbonate(30 mmol) in dry DMF (60 ml) was heated to 40℃ and 2-bromopropane (39 mmol) added dropwise under nitrogen during 1.0 h. The mixture was stirred for a further 12 h and cooled to room temperature. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered,

concentrated. the crude product was then purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the product **Xu13-2** as a white liquid (2.8 g, 52% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 7.95 – 7.27 (m, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.06 (s, 1H), 4.74 (h, *J* = 6.1 Hz, 1H), 1.42 (d, *J* = 6.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 150.1, 146.7, 130.1, 124.3, 114.2, 111.9, 71.9, 21.9.HRMS (ESI) calculated for [$C_{10}H_{12}NaO_3$] $[M+Na]^+$: 203.0679 found: 203.0678.

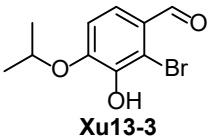
2.5.3 2-bromo-4-ethoxy-3-hydroxybenzaldehyde (Xu12-3)



Xu12-3

Prepared from 4-ethoxy-3-hydroxybenzaldehyde (Xu12-2) (15 mmol) in 1,4-Dioxane/H_2O (v:v=1:1, 20 mL) was added NBS slowly (15.75 mmol, 1.05 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. the crude product was then purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the product **Xu12-3** as a white liquid (2.4 g, 75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.26 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.28 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.0, 151.0, 143.3, 127.0, 122.6, 112.8, 109.8, 65.4, 14.6. HRMS (ESI) calculated for [$C_9H_9BrNaO_3$] $[M+H]^+$: 266.9634 found: 266.9627.

2.5.4 2-bromo-3-hydroxy-4-isopropoxybenzaldehyde (Xu13-3)

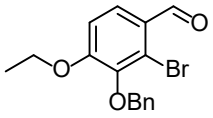


Xu13-3

Prepared from 3-hydroxy-4-isopropoxybenzaldehyde (Xu13-2) (15 mmol) in 1,4-Dioxane/H_2O (v:v=1:1, 20 mL) was added NBS slowly (15.75 mmol, 1.05 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. the crude product was then purified by flash

column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the product **Xu13-3** as a white liquid (3 g, 80% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.26 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.17 (s, 1H), 4.74 (p, *J* = 6.0 Hz, 1H), 1.43 (d, *J* = 6.0 Hz, 8H).^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 150.0, 143.9, 126.9, 122.4, 112.9, 110.9, 72.7, 22.0.

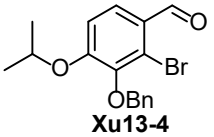
2.5.5 3-(benzyloxy)-2-bromo-4-ethoxybenzaldehyde (Xu12-4)



Xu12-4

To a solution of 2-bromo-4-ethoxy-3-hydroxybenzaldehyde (Xu12-3) (10 mmol) in DMF (20 mL) was added benzyl bromide (12mmol, 1.2 equiv.) and K_2CO_3 (15 mmol, 1.5 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu12-4** as a white solid (2 g, 60% yield). Mp: 59.7 – 60.5 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.28 (s, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.51 (m, 2H), 7.50 – 7.31 (m, 4H), 6.97 (d, *J* = 8.7 Hz, 1H), 5.09 (s, 2H), 4.20 (q, *J* = 7.0 Hz, 2H), 1.53 (t, *J* = 7.0 Hz, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 158.1, 145.1, 136.7, 128.5, 128.4, 128.3, 127.2, 126.5, 123.5, 111.6, 74.7, 64.9, 14.6. HRMS (ESI) calculated for [$C_{16}H_{15}BrNaO_3$] $[M+Na]^+$: 357.0097 found: 357.0096.

2.5.6 3-(benzyloxy)-2-bromo-4-isopropoxybenzaldehyde (Xu13-4)

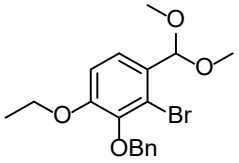


Xu13-4

To a solution of 2-bromo-3-hydroxy-4-isopropoxybenzaldehyde (Xu13-3) (10 mmol) in DMF (20 mL) was added benzyl bromide (12 mmol, 1.2 equiv.) and K_2CO_3 (15 mmol, 1.5 equiv.). The resulting solution was stirred at room temperature overnight. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4,

filtered, concentrated. The crude product was then washed by petroleum ether with a little ethyl acetate to afford the product **Xu13-4** as a white solid (2.6 g, 76% yield). Mp: 72.8 – 73.5 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.28 (s, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.41 (dt, *J* = 12.1, 6.8 Hz, 3H), 6.98 (d, *J* = 8.7 Hz, 1H), 5.06 (s, 2H), 4.75 (p, *J* = 6.1 Hz, 1H), 1.45 (d, *J* = 6.0 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 157.2, 145.8, 136.8, 128.6, 128.4, 128.3, 127.0, 126.4, 123.8, 112.8, 74.7, 71.7, 21.9. HRMS (ESI) calculated for [$C_{17}H_{17}BrNaO_3$] $[M+Na]^+$: 371.0253 found: 371.0249.

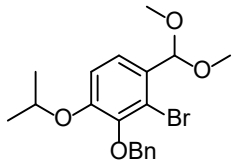
2.5.7 2-(benzyloxy)-3-bromo-4-(dimethoxymethyl)-1-ethoxybenzene (Xu12-5)



Xu12-5

Prepared from 3-(benzyloxy)-2-bromo-4-ethoxybenzaldehyde (Xu12-4) (3 mmol) in trimethoxymethane (30 mmol, 10 equiv.) and *p*-toluenesulfonic acid (0.15 mmol, 5% mol). The resulting solution was stirred 5 hours at 60 ℃. The reaction mixture was washed by the addition of $NaHCO_3$ (aq.) and the combined organic layers concentrated. The crude product was purified by flash column chromatography on aluminum oxide (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu12-5** as a white liquid (1.0 g, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.31 (m, 2H), 6.93 (d, *J* = 8.6 Hz, 0H), 5.33 (d, *J* = 204.6 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 1H), 3.41 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 145.2, 137.1, 129.7, 129.6, 128.3, 128.1, 127.9, 123.3, 119.0, 111.7, 102.9, 74.4, 64.4, 53.7, 14.7.HRMS (ESI) calculated for [$C_{18}H_{21}BrNaO_4$] $[M+Na]^+$: 403.0515 found: 403.0518.

2.5.8 2-(benzyloxy)-3-bromo-4-(dimethoxymethyl)-1-isopropoxybenzene (Xu13-5)

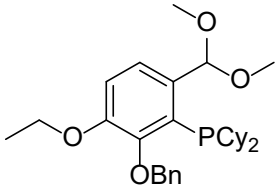


Xu13-5

Prepared from 3-(benzyloxy)-2-bromo-4-isopropoxybenzaldehyde (Xu13-4) (3 mmol) in trimethoxymethane (30 mmol, 10 equiv.) and *p*-toluenesulfonic acid (0.15 mmol, 5% mol). The resulting solution was stirred 5 hours at 60 ℃. The reaction mixture was washed by the addition of

$NaHCO_3$ (aq.) and the combined organic layers concentrated. The crude product was purified by flash column chromatography on aluminum oxide (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu13-5** as a white liquid (1.0 g, 90% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 5.53 (s, 1H), 5.01 (s, 2H), 4.57 (p, *J* = 6.1 Hz, 1H), 3.36 (s, 6H), 1.33 (d, *J* = 6.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 146.1, 137.2, 129.8, 128.4, 128.3, 128.2, 128.1, 127.8, 123.1, 119.2, 113.9, 103.0, 74.3, 71.3, 53.7, 21.9. HRMS (ESI) calculated for [$C_{19}H_{24}O_4Br$] $[M+H]^+$: 394.0780 found: 394.0781.

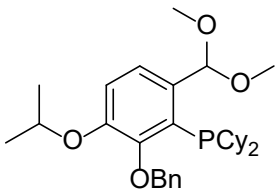
2.5.9(2-(benzyloxy)-6-(dimethoxymethyl)-3-ethoxyphenyl)dicyclohexylphosphane (Xu12-6)



Xu12-6

Prepared from (((3-bromo-4-(dimethoxymethyl)-1,2-phenylene)bis(oxy))bis(methylene))dibenzene (**Xu12-5**) (2 mmol) in 4 mL anhydrous THF, was added *n*-BuLi (2.4 mmol, 1.6 M in hexane) dropwise under argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (2.6 mmol, 1.3 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were concentrated. The crude product was added to next step.

2.5.10(2-(benzyloxy)-6-(dimethoxymethyl)-3-isopropoxyphenyl)dicyclohexylphosphane(Xu13-6)

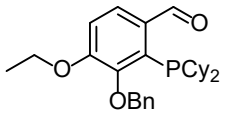


Xu13-6

Prepared from 2-(benzyloxy)-3-bromo-4-(dimethoxymethyl)-1-isopropoxybenzene (Xu13-5) (2 mmol) in 4 mL anhydrous THF, was added *n*-BuLi (2.4 mmol, 1.6 M in hexane) dropwise under

argon at -78 °C, The resulting solution at this temperature during 1 hour, and dicyclohexylchlorophosphine (2.6 mmol, 1.3 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight. The re action mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were concentrated. The crude product was added to next step.

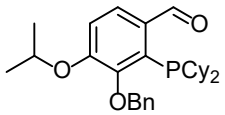
2.5.11 3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxybenzaldehyde (Xu12-7)



Xu12-7

Prepared from (2-(benzyloxy)-6-(dimethoxymethyl)-3-ethoxyphenyl)dicyclohexylphosphane (Xu12-6) in 2 mL THF, was added 1 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu12-7** as a yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.07 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.6, 3.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 5.24 (s, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 2.37 (tdt, *J* = 11.5, 7.5, 3.4 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.75 – 1.65 (m, 2H), 1.59 (d, *J* = 6.9 Hz, 4H), 1.40 (t, *J* = 7.0 Hz, 4H), 1.29 – 1.13 (m, 8H), 0.99 (tdd, *J* = 13.1, 6.0, 2.8 Hz, 2H), 0.86 (tt, *J* = 9.9, 5.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 193.1, 155.3, 150.6, 138.2, 136.4, 136.3, 133.5, 133.1, 128.2, 127.5, 127.2, 124.3, 124.2, 114.0, 73.7, 64.3, 34.5 (d, *J* = 11.6 Hz), 32.4 (d, *J* = 23.3 Hz), 30.8 (d, *J* = 9.7 Hz), 26.8 (d, *J* = 8.8 Hz), 26.6 (d, *J* = 14.1 Hz) 26.1, 14.5.^{31}P NMR (162 MHz, $CDCl_3$) δ -13.99. HRMS (ESI) calculated for $[C_{28}H_{38}O_3P]$ $[M+H]^+$: 453.2553 found: 453.2556.

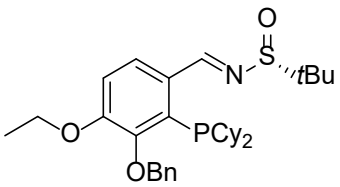
2.5.12 3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxybenzaldehyde (Xu13-7)



Xu13-7

Prepared from (2-(benzyloxy)-6-(dimethoxymethyl)-3-isopropoxyphenyl)dicyclohexylphosphane(Xu13-6) in 2 mL THF, was added 1 mL HCl (1.0 M) under argon at 60 °C. The resulting solution was stirred 5 hours. The reaction mixture was quenched by the addition of $NaHCO_3$ (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to afford the product **Xu13-7** as a yellow liquid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.08 (d, *J* = 8.8 Hz, 1H), 7.77 (dt, *J* = 8.7, 2.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 5.23 (s, 2H), 4.69 (hept, *J* = 6.3 Hz, 1H), 2.49 – 2.28 (m, 2H), 1.90 – 1.79 (m, 2H), 1.77 – 1.69 (m, 2H), 1.65 – 1.55 (m, 4H), 1.36 (dd, *J* = 6.2, 1.5 Hz, 7H), 1.32 – 1.10 (m, 9H), 1.07 – 0.95 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.18 (d, *J* = 42.2 Hz), 154.22, 151.42, 138.23, 136.22 (d, *J* = 15.3 Hz), 133.58 (d, *J* = 37.5 Hz), 128.15, 127.46, 127.07, 124.05 (d, *J* = 6.1 Hz), 115.49, 73.62, 71.08, 34.47 (d, *J* = 11.6 Hz), 32.38 (d, *J* = 23.5 Hz), 30.75 (d, *J* = 10.0 Hz), 26.74 (d, *J* = 9.0 Hz), 26.54 (d, *J* = 13.9 Hz), 26.11, 21.81. ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.95. HRMS (ESI) calculated for $[C_{29}H_{40}O_3P]$ $[M+H]^+$: 467.2710 found: 467.2715.

2.5.13(*R*,*E*)-*N*-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu12-8)

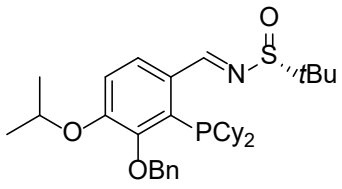


Xu12-8

Prepared from 3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxybenzaldehyde (Xu12-7) in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (1.2 mmol, 1.2 equiv.) and titanium tetraisopropanolate (2 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu12-8** as a yellow

solid. Mp: 56.6-57.5 ℃. $[\alpha]_D^{20}$=-58.9(*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 7.86 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 5.23 (s, 2H), 4.20 – 4.07 (m, 2H), 2.40 – 2.26 (m, 2H), 1.87 – 1.77 (m, 2H), 1.71 (d, *J* = 7.4 Hz, 2H), 1.59 (d, *J* = 6.9 Hz, 4H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.36 (d, *J* = 3.5 Hz, 2H), 1.28 (s, 9H), 1.17 (d, *J* = 7.1 Hz, 7H), 1.08 – 0.93 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 163.7, 153.9, 151.1, 138.2, 134.2, 133.1, 132.7, 128.2, 127.5, 127.4, 124.2, 114.3, 73.8, 64.2, 57.5, 34.8 (t, *J* = 13.3 Hz), 32.3 (d, *J* = 23.7 Hz), 30.6 (dd, *J* = 9.7, 7.4 Hz), 27.1 – 26.3(m). 26.2, 22.6, 14.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ -9.32. HRMS (ESI) calculated for $[C_{32}H_{46}NNaO_3PS]$ $[M+Na]^+$: 578.2828 found: 578.2829.

2.5.14(*R*,*E*)-*N*-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu13-8)

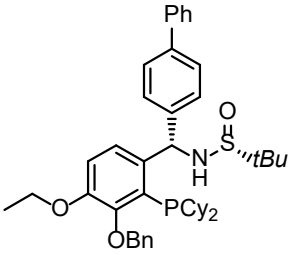


Xu13-8

Prepared from 3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxybenzaldehyde (Xu13-7) in 2 mL THF, was added (*R*)-2-methylpropane-2-sulfinamide (1.2 mmol, 1.2 equiv.) and titanium tetraisopropanolate (2 mmol, 2.0 equiv.) under argon at 50 °C. The resulting solution was stirred 8 hours. The reaction mixture was quenched by the addition of H_2O (aq.) and diluted with EtOAc. The solution was filtered and the residue was washed twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to afford the crude product **Xu13-8** as a yellow solid. Mp: 73.8-74.5 ℃. $[\alpha]_D^{20}$ = -79.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 7.82 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 5.18 (s, 2H), 4.63 (hept, *J* = 6.1 Hz, 1H), 2.31 (ddt, *J* = 14.8, 11.2, 8.3 Hz, 2H), 1.86 – 1.75 (m, 2H), 1.70 (d, *J* = 7.0 Hz, 2H), 1.57 (d, *J* = 7.1 Hz, 4H), 1.33 (d, *J* = 6.0 Hz, 8H), 1.26 (s, 9H), 1.25 – 1.05 (m, 8H), 1.05 – 0.91 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.83 (d, *J* = 34.9 Hz), 152.7, 152.0, 138.3, 134.3, 133.1 (d, *J* = 36.1 Hz), 128.1, 127.4, 127.2, 124.0, 116.1, 73.7, 71.1, 57.4, 35.1 – 34.4 (m), 32.3 (d, *J* = 23.8 Hz), 30.6 (dd, *J* = 9.8, 7.5 Hz),

26.8 (d, J = 8.6 Hz), 26.6 (dd, J = 13.9, 4.5 Hz), 26.1, 22.6, 21.9, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -9.37. HRMS (ESI) calculated for $[C_{33}H_{49}NO_3PS]$ $[M+H]^+$: 570.3165 found: 570.3161.

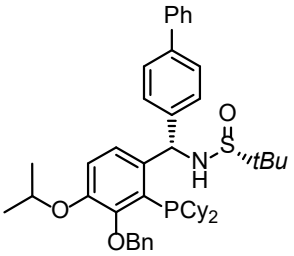
2.5.15(*R*)-*N*-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (Xu12-9)



Xu12-9

Prepared from (*R*,*E*)-*N*-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu12-8) in 1 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (1 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu12-9** as a white solid (230 mg, 65% yield). Mp: 81.2-82.1 ℃. $[\alpha]_D^{20}$ = -87.5 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.49 (m, 8H), 7.43 (p, J = 6.3, 5.5 Hz, 5H), 7.39 – 7.32 (m, 2H), 7.09 (d, J = 8.6 Hz, 1H), 7.02 – 6.90 (m, 1H), 5.37 (d, J = 11.8 Hz, 1H), 5.26 (d, J = 11.8 Hz, 1H), 4.10 (q, J = 7.0 Hz, 3H), 2.38 – 2.22 (m, 2H), 1.81 – 1.58 (m, 6H), 1.52 (d, J = 12.3 Hz, 1H), 1.39 (q, J = 6.7 Hz, 5H), 1.31 (s, 9H), 1.11 (dddd, J = 34.0, 23.7, 15.1, 5.0 Hz, 9H), 0.91 (dq, J = 8.8, 3.8 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 149.8, 142.5, 142.0, 141.8, 141.0, 140.0, 138.8, 129.2, 129.1, 128.7, 128.6, 128.4, 128.1, 127.2, 127.1, 127.0, 126.9, 126.9, 123.1, 123.1, 114.9, 73.2, 64.1, 60.1 (d, J = 34.3 Hz), 55.8, 35.3 (d, J = 10.8 Hz), 34.4 (d, J = 11.3 Hz), 33.1 (d, J = 25.7 Hz), 32.3 (d, J = 23.1 Hz), 30.5 (d, J = 10.6 Hz), 30.3 (d, J = 8.1 Hz),27.1, 27.0, 26.9 (d, J = 5.8 Hz), 26.8 (d, J = 6.2 Hz), 26.7 (d, J = 7.4 Hz), 26.2, 22.7, 14.8.^{31}P NMR (162 MHz, $CDCl_3$) δ -6.67. HRMS (ESI) calculated for $[C_{44}H_{57}NO_3PS]$ $[M+H]^+$: 710.3791 found: 710.3795.

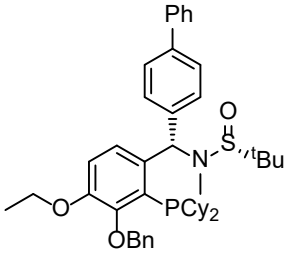
2.5.16(*R*)-*N*-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (Xu13-9)



Xu13-9

Prepared from (*R*,*E*)-*N*-(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxybenzylidene)-2-methylpropane-2-sulfinamide (Xu13-8) in 1 mL anhydrous THF, was added [1,1'-biphenyl]-4-ylmagnesium bromide (1 mmol, 2.0 equiv.) dropwise under argon at -50 °C. The reaction mixture was warmed to room temperature overnight and was quenched by the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu13-9** as a white solid (198 mg, 55% yield). Mp: 73.8-74.5 ℃. $[\alpha]_D^{20}$ = -72.5 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 8H), 7.48 – 7.32 (m, 7H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.02 – 6.85 (m, 1H), 5.35 (d, *J* = 11.8 Hz, 1H), 5.24 (d, *J* = 11.9 Hz, 1H), 4.58 (h, *J* = 6.1 Hz, 1H), 4.06 (s, 1H), 2.29 (p, *J* = 11.6 Hz, 2H), 1.81 – 1.58 (m, 6H), 1.39 (q, *J* = 6.5, 4.6 Hz, 2H), 1.32 (d, *J* = 6.1 Hz, 15H), 1.25 – 0.88 (m, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 148.6, 142.5, 142.2 (d, *J* = 23.7 Hz), 141.0, 140.0, 138.9, 129.2, 129.1, 128.6, 128.1, 127.2, 127.1, 127.0, 126.9, 126.8, 123.1, 123.1, 117.3, 73.2, 71.3, 60.2 (d, *J* = 35.4 Hz), 55.8, 35.3 (d, *J* = 10.6 Hz), 34.5 (d, *J* = 11.3 Hz), 33.1 (d, *J* = 25.9 Hz), 32.3 (d, *J* = 23.0 Hz), 30.5 (d, *J* = 10.3 Hz), 30.4 (d, *J* = 7.9 Hz), 27.1, 27.0 (d, *J* = 2.8 Hz) , 27.0, 26.9 (d, *J* = 5.9 Hz), 26.7 (d, *J* = 7.1 Hz), 26.2, 22.7, 22.1, 22.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.78. HRMS (ESI) calculated for $[C_{45}H_{59}NO_3PS]$ $[M+H]^+$: 724.3948 found: 724.3945.

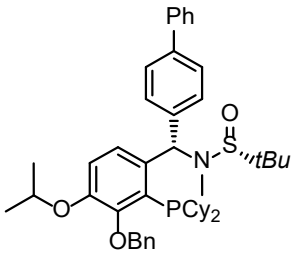
2.5.17(*R*)-*N*-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxyphenyl)methyl)-N,2-dimethylpropane-2-sulfinamide (Xu12)



Xu12

Prepared from (*R*)-*N*-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-ethoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (Xu12-9) in 1 mL anhydrous THF, was added *n*-BuLi (0.5 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (0.6 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu12** as a white solid (113 mg, 52% yield). Mp: 80.1-80.9 ℃. $[\alpha]_D^{20}$ = 13.6 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.3 Hz, 3H), 7.51 (d, *J* = 7.9 Hz, 4H), 7.43 (q, *J* = 8.0 Hz, 4H), 7.37 – 7.28 (m, 4H), 7.10 (t, *J* = 10.6 Hz, 2H), 5.31 (s, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.48 – 2.35 (m, 1H), 2.18 – 2.07 (m, 1H), 1.76 – 1.64 (m, 4H), 1.57 – 1.51 (m, 1H), 1.48 – 1.42 (m, 2H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.26 (dt, *J* = 22.5, 8.5 Hz, 4H), 1.14 (s, 9H), 1.02 – 0.86 (m, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 151.0, 149.7, 140.9, 140.5, 140.2, 139.8, 139.5, 138.8, 131.7, 128.7, 128.6, 128.4, 128.1, 127.2, 127.0, 126.9, 126.9, 126.3, 122.8, 122.8, 114.9, 73.3, 70.5 (d, *J* = 40.0 Hz), 64.1, 58.6, 35.2 (d, *J* = 10.5 Hz), 34.1 (d, *J* = 11.6 Hz), 33.2 (d, *J* = 26.2 Hz), 32.2 (d, *J* = 22.5 Hz), 30.9 (d, *J* = 11.6 Hz),30.5 , 29.9 (d, *J* = 7.9 Hz), 27.0 (d, *J* = 8.9 Hz), 26.8 (d, *J* = 10.8 Hz), 26.6 (d, *J* = 3.0 Hz), 26.3, 26.1, 24.1, 14.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.10. HRMS (ESI) calculated for $[C_{45}H_{59}NO_3PS]$ $[M+H]^+$: 724.3948 found: 724.3946.

2.5.8(*R*)-*N*-((*S*)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxyphenyl)methyl)-N,2-dimethylpropane-2-sulfinamide(Xu13)

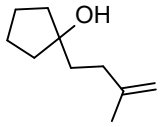


Xu13

Prepared from (R)-N-((S)-[1,1'-biphenyl]-4-yl(3-(benzyloxy)-2-(dicyclohexylphosphaneyl)-4-isopropoxyphenyl)methyl)-2-methylpropane-2-sulfinamide (Xu13-9) (Xu13-9) in 1 mL anhydrous THF, was added *n*-BuLi (0.5 mmol, 1.6 M in hexane) dropwise under argon at -40 °C. The resulting solution at this temperature during 1 hour and iodomethane (0.6 mmol, 2 equiv.) was added. After 1 hour, the reaction mixture moved to 0 °C and stirred 1 hour. The reaction mixture was the addition of NH_4Cl (aq.) and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 5: 1) to the product **Xu13** as a white solid (118 mg, 60% yield). Mp: 82-82.7 °C. $[\alpha]_D^{20}$ = 10.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.54 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.45 – 7.40 (m, 3H), 7.39 (s, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 11.5 Hz, 1H), 5.26 (s, 2H), 4.57 (p, *J* = 6.0 Hz, 1H), 2.67 (s, 3H), 2.38 (dtd, *J* = 11.5, 8.5, 3.8 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.77 – 1.61 (m, 6H), 1.42 – 1.28 (m, 15H), 1.12 (s, 9H), 0.93 (ddt, *J* = 15.8, 10.1, 6.3 Hz, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ152.4 (d, *J* = 3.7 Hz),148.5, 141.0, 140.7 (d, *J* = 23.1 Hz), 139.8, 139.6, 138.9, 131.8, 128.7, 128.1, 127.2, 127.1, 127.1, 127.0, 126.9, 126.4, 122.9 (d, *J* = 5.8 Hz), 117.7, 73.3, 71.4, 70.5 (d, *J* = 40.2 Hz), 58.7, 35.3 (d, *J* = 10.3 Hz), 34.2 (d, *J* = 11.6 Hz), 33.2 (d, *J* = 26.2 Hz), 32.3 (d, *J* = 22.5 Hz), 31.5 (d, *J* = 7.2 Hz), 31.0 (d, *J* = 11.6 Hz), 30.6, 30.2 (d, *J* = 5.8 Hz), 23.0 (d, *J* = 8.0 Hz), 29.6 (d, *J* = 21.7 Hz), 27.0 (t, *J* = 9.1 Hz), 26.9 – 26.6 (m), 26.3 (d, *J* = 26.3 Hz), 24.2, 22.1, 22.0.^{31}P NMR (162 MHz, Chloroform-*d*) δ -6.25. HRMS (ESI) calculated for $[C_{46}H_{61}NO_3PS]$ $[M+H]^+$: 738.4104 found: 738.4107.

3. General procedure for preparation of substrates

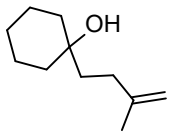
3.1 Synthesis of 1-(3-methylbut-3-en-1-yl)-cyclopentan-1-ol (1c)[2]



1c

To a solution of (3-methylbut-3-en-1-yl)-magnesium bromide (55 mmol, 1.1 equiv.) in dry Et_2O (30 mL), was added cyclopentanone (50 mmol, 1.0 equiv.) dropwise under argon at -30 °C. The reaction mixture was warmed to room temperature overnight. The reaction mixture was quenched by the addition of HCl (1 M) and diluted with EtOAc. The organic layer was separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to the product **1c** as a white liquid (3.5 g, 45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.69 (s, 2 H), 2.21 – 2.07 (m, 2 H), 1.83 – 1.76 (m, 2 H), 1.75 – 1.72 (m, 4 H), 1.70 (t, *J* = 3. 2 Hz, 1 H), 1.67 – 1.53 (m, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.5, 109.6, 82.4, 39.6, 39.3, 33.0, 23.7, 22.5. HRMS (ESI) calculated for [$C_{10}H_{18}ONa$] [M+Na]$^+$: 177.1250 found: 177.1252.

3.2 Synthesis of 1-(3-methylbut-3-en-1-yl)-cyclohexan-1-ol (1d)[2]



1d

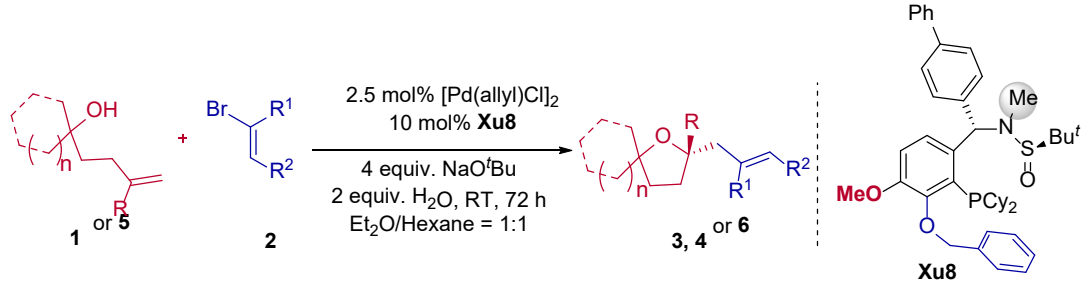
To a solution of (3-methylbut-3-en-1-yl)-magnesium bromide (55 mmol, 1.1 equiv.) in dry Et_2O (30 mL), was added cyclohexanone (50 mmol, 1.0 equiv.) dropwise under argon at -30 °C. The reaction mixture was warmed to room temperature overnight. The reaction mixture was quenched by the addition of HCl (1 M) and diluted with EtOAc. The organic layer was separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to the product **1d** as a white liquid (4.0 g, 48% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.69 (s, 2 H), 2.17 – 2.00 (m, 2 H), 1.73 (s, 3 H), 1.61 – 1.46 (m, 8 H), 1.46 – 1.37 (m, 3 H), 1.32 – 1.21 (m, 1 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.5,

109.5, 71.3, 40.1, 37.3, 31.1, 25.8, 22.5, 22.1. HRMS (ESI) calculated for [$C_{11}H_{20}ONa$] $[M+Na]^+$: 191.1406 found: 191.1409.

Substrate **9a-9i**[3], **9j-9n**[4-5], **9o, 9p, 9r**[6], **9q**[7] were synthesized from reported procedure and the analytical data was consistent with the literature.

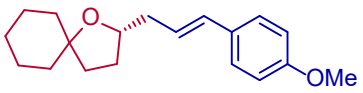
4. General Procedure and HPLC spectra

4.1 General Procedure for reactions of tertiary γ-hydroxyalkenes with alkenyl bromides



To a sealed tube was added $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%). The flask was evacuated and refilled with argon. Then tertiary γ-hydroxyalkenes (0.2 mmol), alkenyl halides (0.4 mmol), NaO^tBu (4.0 equiv.), H_2O (2.0 equiv.) and a mixed solution of Et_2O/Hexane (1: 1, 2 mL) was added to the tube, and stirred at room temperature for 72 hours. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product.

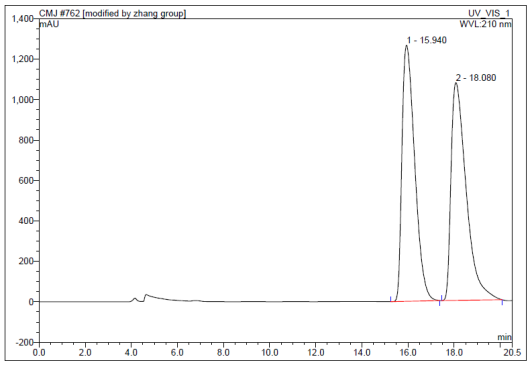
4.1.1 (*S*, *E*)-2-(3-(4-methoxyphenyl)allyl)-1-oxaspiro[4.5]decane (3a)



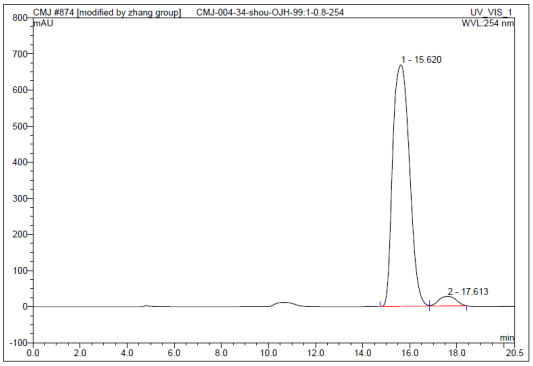
3a

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 40: 1) give the product **3a** as a white liquid (42 mg, 74% yield) with 92% *ee*. $[\alpha]_D^{20}$ = -11.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2 H), 6.96 – 6.69 (m, 2 H), 6.38 (d, *J* = 15.6 Hz, 1 H), 6.17 – 5.99 (m, 1 H), 4.16 – 4.01 (m, 1 H), 3.8 0 (s, 3 H), 2.60 – 2.43 (m, 1 H), 2.43 – 2.20 (m, 1 H), 2.04 – 1.91 (m, 1 H), 1.82 – 1.61 (m, 5 H), 1.60 – 1.46 (m, 4 H), 1.45 – 1.31 (m, 4 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.1, 130.5, 127.0, 124.7, 113.8, 82.6, 77.5, 55.2, 39.8, 38.5,

37.6, 35.7, 30.6, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{19}H_{26}NaO_2]$ $[M+Na]^+$: 309.1825 found: 309.1828. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.8 mL/min, 254 nm); major enantiomer tr = 15.62 min, minor enantiomer tr = 17.61 min.

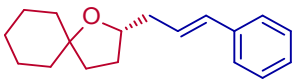


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.94	n.a.	1265.297	807.186	49.60	n.a.	BMB*
2	18.08	n.a.	1076.631	820.219	50.40	n.a.	BMB*
Total:			2341.928	1627.406	100.00	0.000	



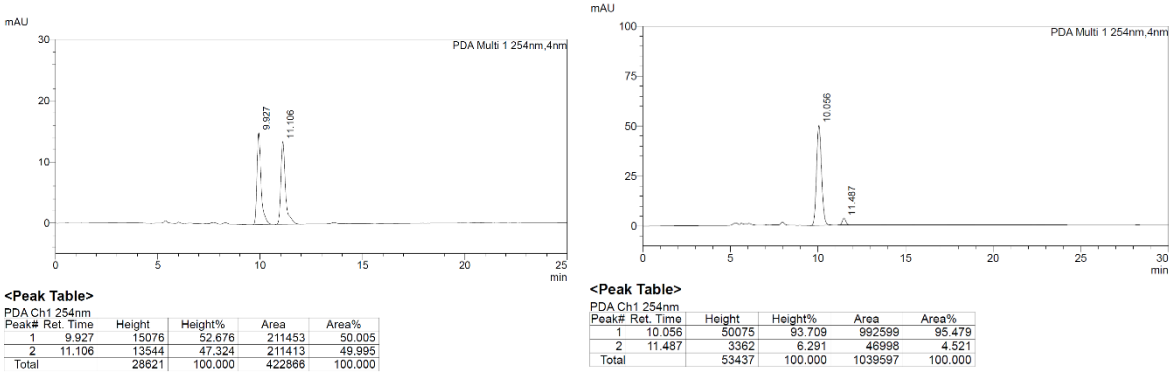
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.62	n.a.	668.591	552.155	96.02	n.a.	BM *
2	17.61	n.a.	26.449	22.896	3.98	n.a.	MB*
Total:			695.040	575.051	100.00	0.000	

4.1.2 (*S*)-2-cinnamyl-1-oxaspiro[4.5]decane (3b)



3b

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3b** as a white liquid (31 mg, 61% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -5.5 (*c* = 0.4, Chloroform).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.28 – 6.21 (m, 1H), 4.11 – 4.06 (m, 1H), 2.55 – 2.48 (m, 1H), 2.41 – 2.35 (m, 1H), 2.05 – 1.95 (m, 1H), 1.80 – 1.63 (m, 5H), 1.60 – 1.47 (m, 4H), 1.41 – 1.35 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.7, 131.8, 128.4, 126.9, 126.9, 126.0, 82.8, 77.4, 39.9, 38.5, 37.6, 35.7, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{18}H_{24}NaO]$ $[M+Na]^+$: 279.1719 found: 279.1710. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 10.056 min, minor enantiomer tr = 11.487 min.



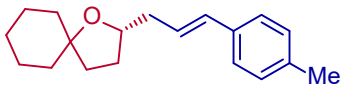
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.927	15076	52.676	211453	50.005
2	11.106	13544	47.324	211413	49.995
Total		28621	100.000	422866	100.000

<Peak Table>
PDA Ch1 254nm

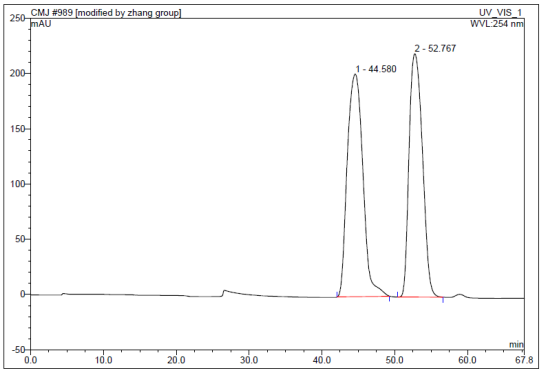
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.056	50075	93.709	992599	95.479
2	11.487	3362	6.291	46998	4.521
Total		53437	100.000	1039597	100.000

4.1.3 (*S*, *E*)-2-(3-(p-tolyl)-allyl)-1-oxaspiro[4.5]decane (3c)

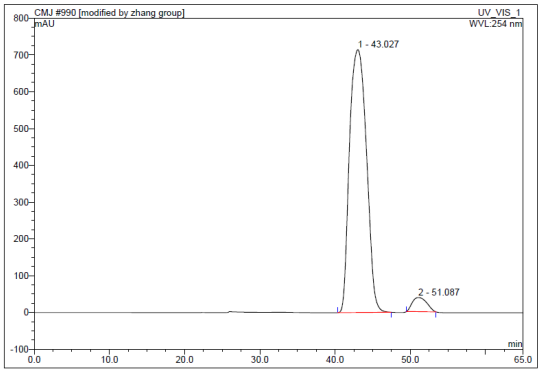


3c

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3c** as a white liquid (26 mg, 51% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -1.3 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 9.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.23 – 6.17 (m, 1H), 4.10 – 4.08 (m, 1H), 2.58 – 2.48 (m, 1H), 2.43 – 2.35 (m, 1H), 2.35 (s, 3H), 2.04 – 1.97 (m, 1H), 1.81 – 1.63 (m, 5H), 1.63 – 1.48 (m, 4H), 1.49 – 1.41 (m, 1H), 1.43 – 1.32 (m, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.6, 134.9, 131.6, 129.1, 125.9, 125.8, 82.8, 77.5, 39.9, 38.5, 37.6, 35.7, 30.6, 25.7, 24.1, 23.8, 21.1. HRMS (ESI) calculated for $[C_{19}H_{26}NaO]$ $[M+Na]^+$: 293.1876 found: 293.1866. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.3 mL/min, 254 nm); major enantiomer tr = 43.03 min, minor enantiomer tr = 51.09 min.

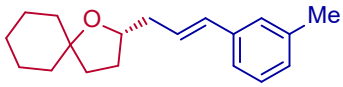


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.58	n.a.	201.460	501.693	51.77	n.a.	BM *
2	52.77	n.a.	220.085	467.392	48.23	n.a.	BMB*
Total:			421.545	969.085	100.00	0.000	



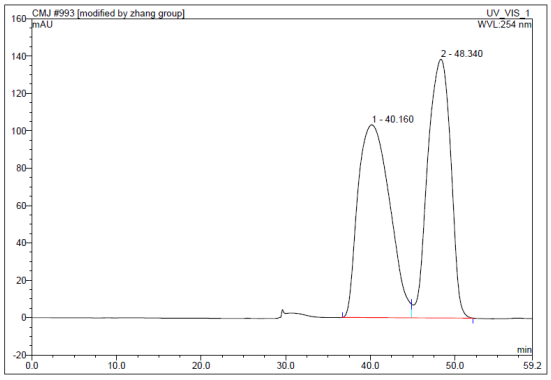
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	43.03	n.a.	714.243	1868.921	95.62	n.a.	BMB*
2	51.09	n.a.	38.309	85.587	4.38	n.a.	BMB*
Total:			752.552	1954.508	100.00	0.000	

4.1.4 (*S*, *E*)-2-(3-(m-tolyl)-allyl)-1-oxaspiro[4.5]decane (3d)

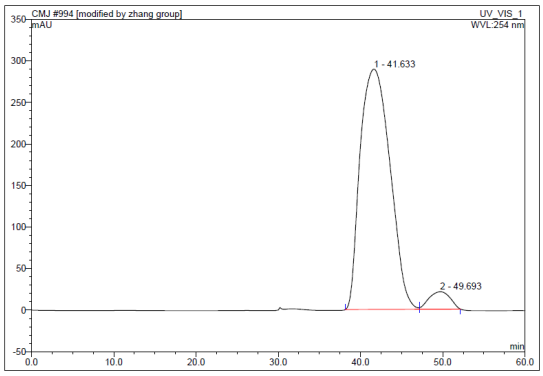


3d

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3d** as a white liquid (40 mg, 78% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -1.2 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 – 7.12 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 16 Hz, 1H), 6.28 – 6.18 (m, 1H), 4.12 – 4.03 (m, 1H), 2.57 – 2.48 (m, 1H), 2.42 – 2.34 (m, 1H), 2.34 (s, 3H), 2.04 – 1.95 (m, 1H), 1.80 – 1.61 (m, 5H), 1.62 – 1.46 (m, 4H), 1.48 – 1.31 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.9, 137.6, 131.8, 128.3, 127.6, 126.7, 126.6, 123.1, 82.7, 77.4, 39.9, 38.4, 37.6, 35.7, 30.6, 25.7, 24.1, 23.8, 21.3. HRMS (ESI) calculated for $[C_{19}H_{26}NaO]$ $[M+Na]^+$: 293.1876 found: 293.1873. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.3 mL/min, 254 nm); major enantiomer tr = 41.63 min, minor enantiomer tr = 49.69 min.

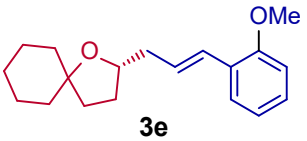


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	40.16	n.a.	103.156	448.941	50.82	n.a.	BM *
2	48.34	n.a.	138.496	434.444	49.18	n.a.	MB*
Total:			241.653	883.385	100.00	0.000	



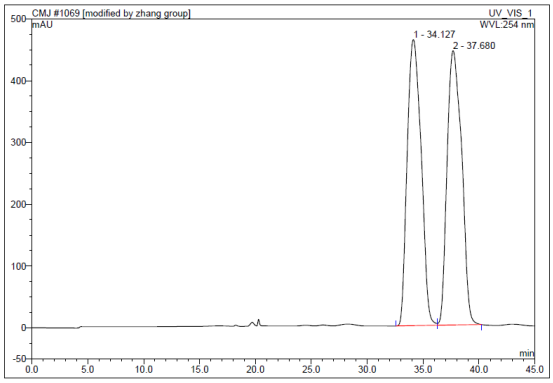
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	41.63	n.a.	289.180	1219.669	95.12	n.a.	BM *
2	49.69	n.a.	21.004	62.514	4.88	n.a.	MB*
Total:			310.184	1282.183	100.00	0.000	

4.1.5 (*S*, *E*)-2-(3-(2-methoxyphenyl)-allyl)-1-oxaspiro[4.5]decane (3e)

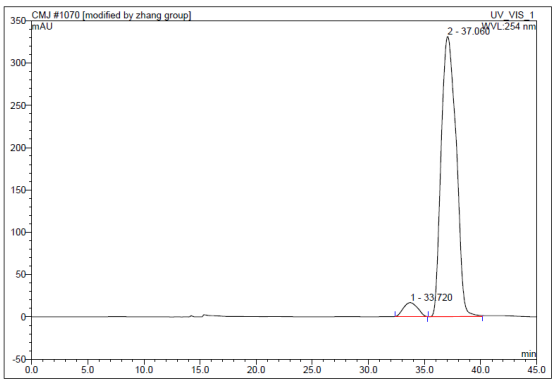


3e

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **3e** as a white liquid (44 mg, 77% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -13.1 (*c* = 0.4, Chloroform) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.26 – 6.18 (m, 1H), 4.11 – 4.05 (m, 1H), 3.84 (s, 3H), 2.58 – 2.52 (m, 1H), 2.43 – 2.36 (m, 1H), 2.05 – 1.95 (m, 1H), 1.77 – 1.63 (m, 5H), 1.60 – 1.47 (m, 4H), 1.45 – 1.31 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 127.9, 127.6, 126.8, 126.4, 126.4, 120.6, 110.8, 82.7, 77.6, 55.5, 40.3, 38.5, 37.6, 35.8, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{19}H_{26}NaO_2]$ $[M+Na]^+$: 309.1825 found: 309.1816. Enantiomeric excess was determined by HPLC with a Chiralpak ODH+OD3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 37.06 min, minor enantiomer tr = 33.72 min..

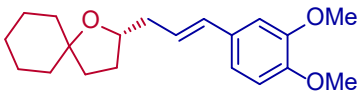


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	34.13	n.a.	462.964	669.110	50.00	n.a.	BM *
2	37.68	n.a.	443.814	669.042	50.00	n.a.	MB*
Total:			906.778	1338.152	100.00	0.000	



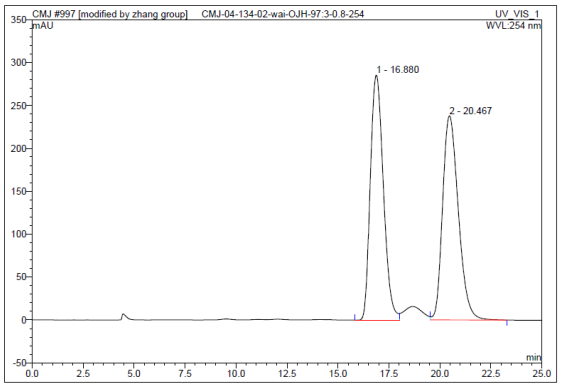
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.72	n.a.	16.415	24.126	4.50	n.a.	BMB*
2	37.06	n.a.	330.940	512.265	95.50	n.a.	BM *
Total:			347.355	536.390	100.00	0.000	

4.1.6 (*S*, *E*)-2-(3-(3,4-dimethoxyphenyl)-allyl)-1-oxaspiro[4.5]decane (3f)

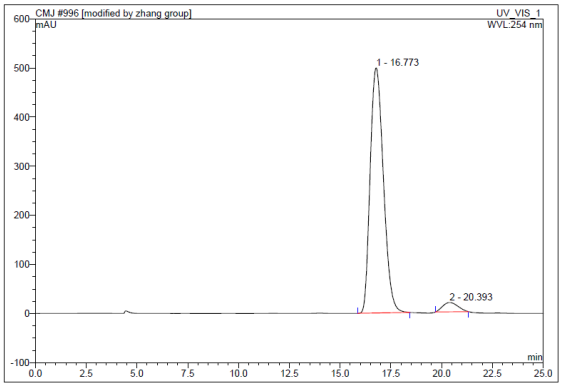


3f

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20: 1) give the product **3f** as a white liquid (40 mg, 66% yield) with 92% *ee*. $[\alpha]_D^{20}$ = -3.2 (*c* = 0.4, Chloroform).^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.91 (d, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 15.5 Hz, 1H), 6.12 – 6.06 (m, 1H), 4.09 – 4.03 (m, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.52 – 2.47 (m, 1H), 2.38 – 2.32 (m, 1H), 2.02 – 1.94 (m, 1H), 1.77 – 1.70 (m, 2H), 1.69 – 1.62 (m, 3H), 1.59 – 1.46 (m, 4H), 1.44 – 1.29 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 148.9, 148.3, 131.4, 130.9, 125.0, 118.9, 111.1, 108.5, 82.8, 77.5, 55.9, 55.7, 39.8, 38.5, 37.6, 35.7, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{20}H_{28}NaO_3]$ $[M+Na]^+$: 339.1931 found: 339.1934. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 97: 3, 0.8 mL/min, 254 nm); major enantiomer tr = 16.77 min, minor enantiomer tr = 20.39 min.

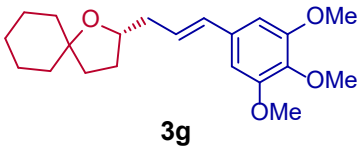


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.88	n.a.	285.677	211.606	49.83	n.a.	BM *
2	20.47	n.a.	237.953	213.029	50.17	n.a.	MB*
Total:			523.629	424.635	100.00	0.000	



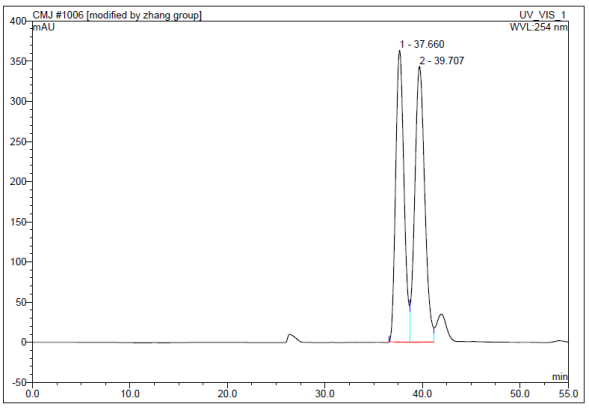
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.77	n.a.	499.175	376.740	95.85	n.a.	BMB*
2	20.39	n.a.	18.929	16.332	4.15	n.a.	BMB*
Total:			518.104	393.071	100.00	0.000	

4.1.7 (*S*, *E*)-2-(3-(3,4,5-trimethoxyphenyl)-allyl)-1-oxaspiro[4.5]decane (3g)

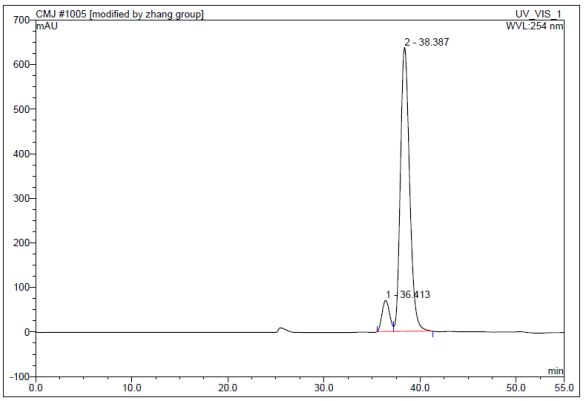


3g

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10: 1) give the product **3g** as a white liquid (28 mg, 42% yield) with 84% *ee*. $[\alpha]_D^{20}$ = -3.5 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.57 (s, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.17 – 6.11 (m, 1H), 4.10 – 4.05 (m, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 2.52 – 2.46 (m, 1H), 2.39 – 2.33 (m, 1H), 2.02 – 1.96 (m, 1H), 1.77 – 1.71 (m, 2H), 1.69 – 1.64 (m, 3H), 1.60 – 1.45 (m, 4H), 1.44 – 1.29 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.2, 137.3, 133.5, 131.6, 126.5, 103.0, 82.9, 77.4, 60.9, 56.0, 39.8, 38.5, 37.6, 35.7, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{21}H_{30}NaO_4]$ $[M+Na]^+$: 369.2036 found: 369.2031. Enantiomeric excess was determined by HPLC with a Chiralpak ASH+ASH column (hexanes: 2-propanol = 90: 10, 0.3 mL/min, 254 nm); major enantiomer tr = 38.39 min, minor enantiomer tr = 36.41 min.

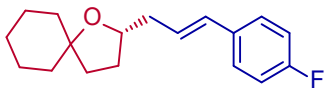


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	37.66	n.a.	363.371	358.189	46.97	n.a.	BM *
2	39.71	n.a.	343.531	404.409	53.03	n.a.	M *
Total:			706.902	762.598	100.00	0.000	



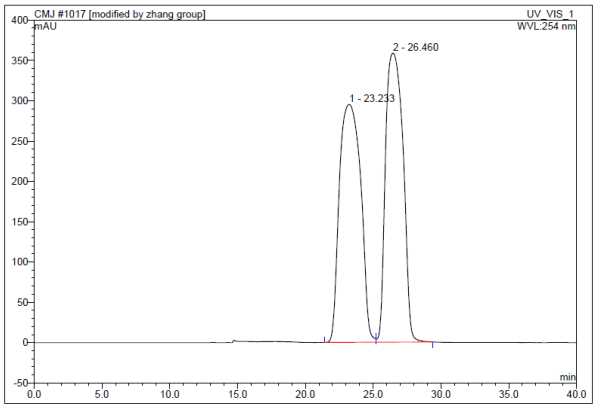
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	36.41	n.a.	70.018	63.364	8.26	n.a.	BM *
2	38.39	n.a.	636.766	704.101	91.74	n.a.	MB*
Total:			706.784	767.465	100.00	0.000	

4.1.8 (*S*, *E*)-2-(3-(4-fluorophenyl)-allyl)-1-oxaspiro[4.5]decane (3h)

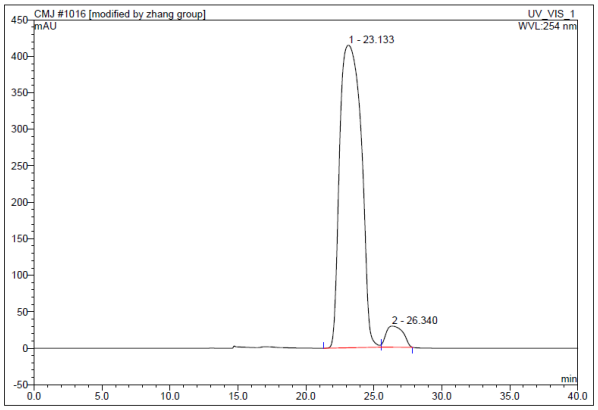


3h

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3h** as a white liquid (35 mg, 64% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -6.4 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 2H), 6.99 – 6.96 (m, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.18 – 6.12 (m, 1H), 4.10 – 4.04 (m, 1H), 2.52 – 2.46 (m, 1H), 2.40 – 2.33 (m, 1H), 2.01 – 1.95 (m, 1H), 1.77 – 1.61 (m, 5H), 1.58 – 1.52 (m, 4H), 1.46 – 1.30 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 245.7 Hz), 133.8 (d, *J* = 3.2 Hz), 130.6, 127.4, 127.4, 126.7 (d, *J* = 2.1 Hz), 115.3, 115.2, 82.8, 77.4, 39.8, 38.5, 37.6, 35.7, 30.7, 25.7, 24.1, 23.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.6. HRMS (ESI) calculated for $[C_{18}H_{23}NaFO]$ $[M+Na]^+$: 297.1625 found: 297.1617. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 23.13 min, minor enantiomer tr = 26.34 min.

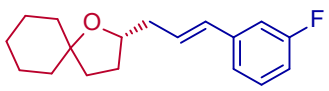


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.23	n.a.	295.112	538.078	50.01	n.a.	BM *
2	26.46	n.a.	358.484	537.810	49.99	n.a.	MB*
Total:			653.596	1075.888	100.00	0.000	



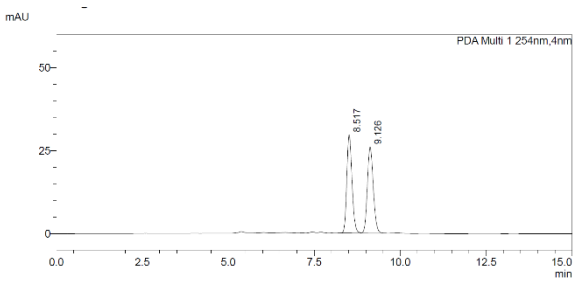
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.13	n.a.	414.757	761.724	94.75	n.a.	BM *
2	26.34	n.a.	28.895	42.212	5.25	n.a.	MB*
Total:			443.652	803.936	100.00	0.000	

4.1.9 (*S*, *E*)-2-(3-(3-fluorophenyl)-allyl)-1-oxaspiro[4.5]decane (3i)



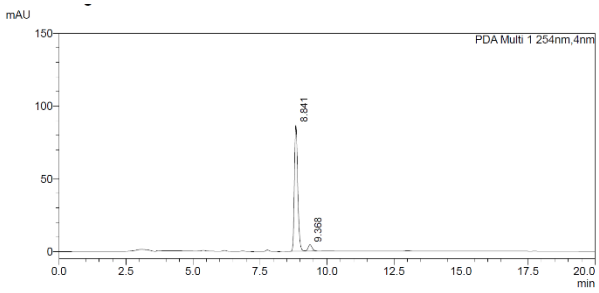
3i

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3i** as a white liquid (26 mg, 48% yield) with 88% *ee*. $[\alpha]_D^{20}$ = -1.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.91 – 6.86 (m, 1H), 6.40 (d, *J* = 16 Hz, 1H), 6.29 – 6.21 (m, 1H), 4.11 – 3.03 (m, 1H), 2.54 – 2.47 (m, 1H), 2.42 – 2.35 (m, 1H), 2.04 – 1.94 (m, 1H), 1.80 – 1.59 (m, 5H), 1.62 – 1.44 (m, 4H), 1.46 – 1.29 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 244.7 Hz), 140.1 (d, *J* = 7.7 Hz), 130.8 (d, *J* = 2.6 Hz), 129.8 (d, *J* = 8.5 Hz), 128.5, 121.9 (d, *J* = 2.6 Hz), 113.7 (d, *J* = 21.4 Hz), 112.4 (d, *J* = 21.7 Hz), 82.9, 77.2, 39.8, 38.5, 37.6, 35.8, 30.7, 25.7, 24.1, 23.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.9. HRMS (ESI) calculated for $[C_{18}H_{23}NaFO]$ $[M+Na]^+$: 297.1625 found: 297.1615. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 8.841 min, minor enantiomer tr = 9.368 min.



<Peak Table>
PDA Ch1 254nm

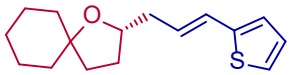
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.517	29605	53.258	312115	50.098
2	9.126	25984	46.742	310895	49.902
Total		55589	100.000	623010	100.000



<Peak Table>
PDA Ch1 254nm

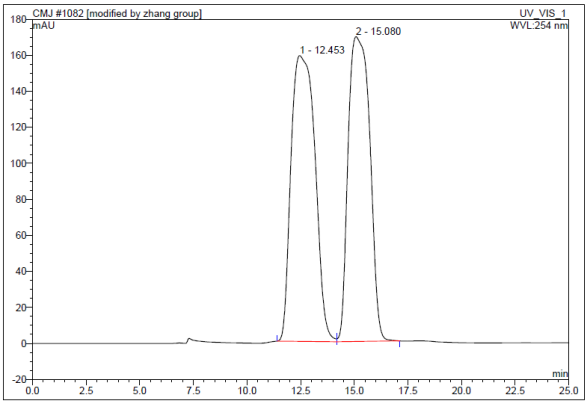
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.841	86923	95.144	747094	94.178
2	9.368	4436	4.856	46185	5.822
Total		91359	100.000	793279	100.000

4.1.10 (*S*, *E*)-2-(3-(thiophen-2-yl)-allyl)-1-oxaspiro[4.5]decane (3j)

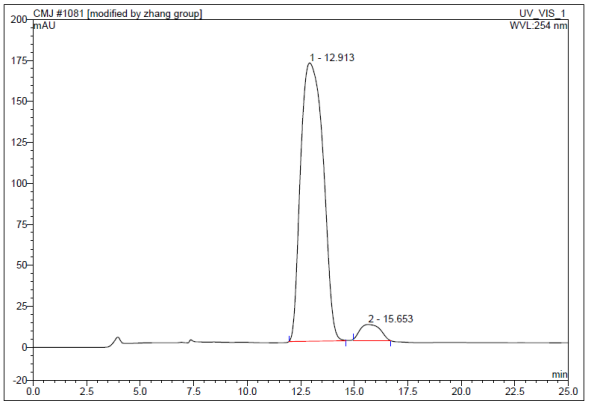


3j

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3j** as a white liquid (21 mg, 41% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -1.3 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 5.2 Hz, 1H), 6.93 (dd, *J* = 4.8, 3.2 Hz, 1H), 6.87 (d, *J* = 3.6 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.10 – 6.03 (m, 1H), 4.10 – 4.03 (m, 1H), 2.51 – 2.44 (m, 1H), 2.38 – 2.30 (m, 1H), 2.02 – 1.94 (m, 1H), 1.78 – 1.60 (m, 5H), 1.61 – 1.43 (m, 4H), 1.46 – 1.28 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.9, 127.1, 126.9, 125.0, 124.4, 123.2, 82.8, 77.3, 39.7, 38.5, 37.6, 35.8, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{16}H_{22}NaSO]$ $[M+Na]^+$: 285.1284 found: 285.1279. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 12.91 min, minor enantiomer tr = 15.65 min.

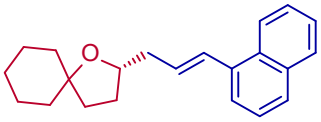


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.45	n.a.	158.759	205.988	50.96	n.a.	BM *
2	15.08	n.a.	169.302	198.194	49.04	n.a.	MB*
Total:			328.061	404.181	100.00	0.000	



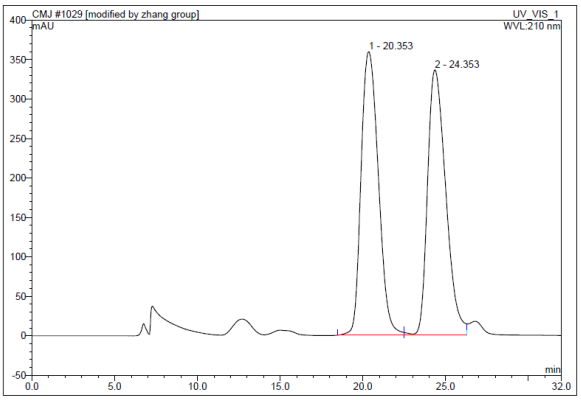
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.91	n.a.	169.709	207.284	94.98	n.a.	BM *
2	15.65	n.a.	9.869	10.965	5.02	n.a.	MB*
Total:			179.578	218.249	100.00	0.000	

4.1.11 (*S*, *E*)-2-(3-(naphthalen-1-yl)-allyl)-1-oxaspiro[4.5]decane (3k)

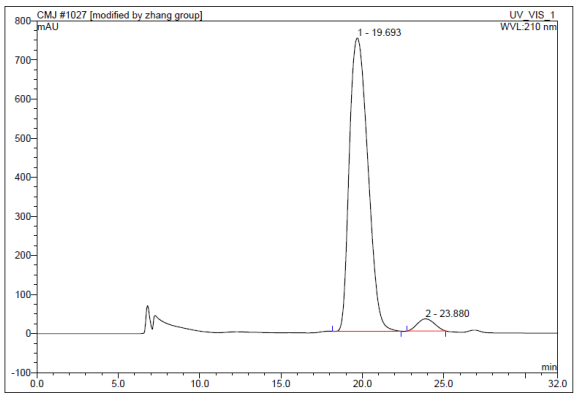


3k

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3k** as a white liquid (40 mg, 65% yield) with 93% *ee*. $[\alpha]_D^{20}$ = -8.3 (*c* = 0.4, Chloroform).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 15.5 Hz, 1H), 6.30 – 6.24 (m, 1H), 4.19 – 4.14 (m, 1H), 2.70 – 2.64 (m, 1H), 2.55 – 2.49 (m, 1H), 2.08 – 2.01 (m, 1H), 1.82 – 1.68 (m, 5H), 1.66 – 1.50 (m, 4H), 1.49 – 1.34 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.5, 133.6, 131.1, 130.2, 129.0, 128.4, 127.3, 125.8, 125.6, 125.6, 123.9, 123.6, 82.8, 77.4, 40.2, 38.5, 37.6, 35.8, 30.7, 25.7, 24.1, 23.8. HRMS (ESI) calculated for $[C_{22}H_{26}NaO]$ $[M+Na]^+$: 329.1876 found: 329.1875. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 210 nm); major enantiomer tr = 19.69 min, minor enantiomer tr = 23.88 min.

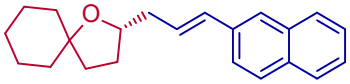


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.35	n.a.	359.090	434.804	50.33	n.a.	BM *
2	24.35	n.a.	336.199	429.149	49.67	n.a.	M *
Total:			695.289	863.954	100.00	0.000	



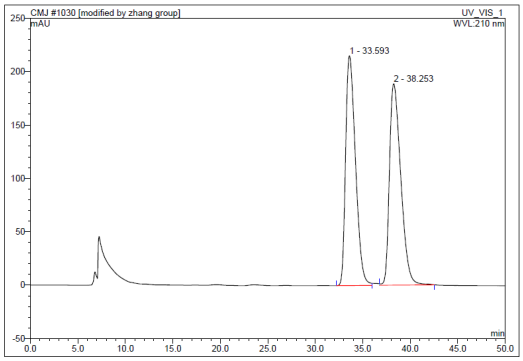
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.69	n.a.	750.029	987.366	96.30	n.a.	BMB*
2	23.88	n.a.	31.042	37.950	3.70	n.a.	BMB*
Total:			781.071	1025.316	100.00	0.000	

4.1.12 (*S*, *E*)-2-(3-(naphthalen-2-yl)-allyl)-1-oxaspiro[4.5]decane (3l)

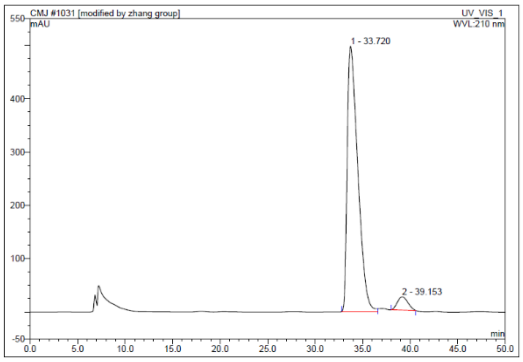


3l

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3l** as a white liquid (34 mg, 56% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -5.4 (*c* = 0.4, Chloroform).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.63 (m, 3H), 7.69 (s, 1H), 7.60 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.41 – 6.35 (m, 1H), 4.15 – 4.10 (m, 1H), 2.62 – 2.56 (m, 1H), 2.48 – 2.42 (m, 1H), 2.06 – 1.98 (m, 1H), 1.82 – 1.65 (m, 5H), 1.65 – 1.49 (m, 4H), 1.49 – 1.31 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.1, 133.6, 132.7, 131.9, 128.0, 127.8, 127.6, 127.4, 126.1, 125.5, 125.5, 123.5, 82.8, 77.4, 40.0, 38.5, 37.6, 35.7, 30.8, 25.7, 24.2, 23.8. HRMS (ESI) calculated for $[C_{22}H_{26}NaO]$ $[M+Na]^+$: 329.1876 found: 329.1869. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 210 nm); major enantiomer tr = 33.72 min, minor enantiomer tr = 39.15 min.

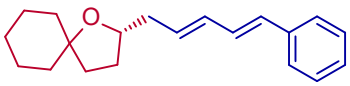


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.59	n.a.	215.210	258.937	49.82	n.a.	BM *
2	38.25	n.a.	188.558	260.833	50.18	n.a.	MB*
Total:			403.768	519.770	100.00	0.000	



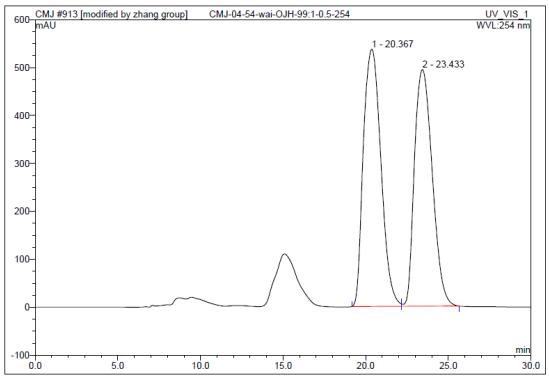
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.72	n.a.	496.638	640.731	95.31	n.a.	BM *
2	39.15	n.a.	24.851	31.534	4.69	n.a.	BMB*
Total:			521.489	672.264	100.00	0.000	

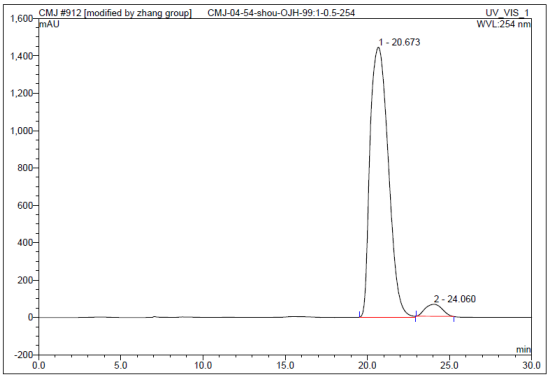
4.1.13 (*S*)-2-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)-1-oxaspiro[4.5]decane (3m)



3m

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3m** as a white liquid (47 mg, 83% yield) with 92% *ee*. $[\alpha]_D^{20}$ = 10.4 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.3 Hz, 1 H), 7.33 – 7.27 (m, 2 H), 7.20 (t, *J* = 7.3 Hz, 1 H), 6.77 (dd, *J* = 15.6, 10.4 Hz, 1 H), 6.46 (d, *J* = 15.6 Hz, 1 H), 6.26 (dd, *J* = 15.2, 10.4 Hz, 1 H), 5.90 – 5.77 (m, 1 H), 4.10 – 3.98 (m, 1 H), 2.54 – 2.41 (m, 1 H), 2.38 – 2.23 (m, 1 H), 2.07 – 1.90 (m, 1 H), 1.77 – 1.65 (m, 4 H), 1.64 – 1.47 (m, 5 H), 1.48 – 1.31 (m, 4 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.5, 132.4, 131.5, 130.4, 129.2, 128.5, 127.1, 126.1, 82.7, 77.3, 39.8, 38.5, 37.5, 35.6, 30.7, 25.6, 24.1, 23.8. HRMS (ESI) calculated for $[C_{20}H_{26}NaO]$ $[M+Na]^+$: 305.1876 found: 305.1878. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 20.67 min, minor enantiomer tr = 24.06 min.

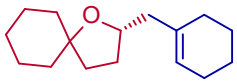




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.37	n.a.	536.876	661.609	51.68	n.a.	BM *
2	23.43	n.a.	493.854	618.488	48.32	n.a.	MB*
Total:			1030.730	1280.097	100.00	0.000	

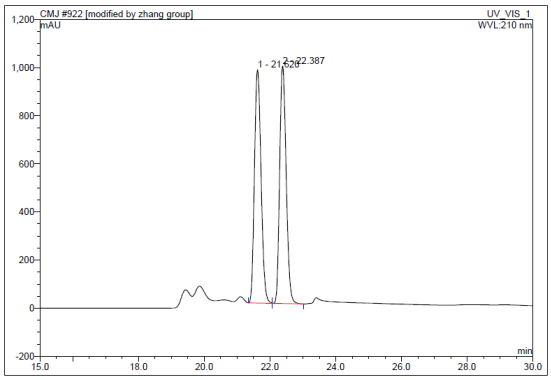
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.67	n.a.	1444.133	1854.477	96.00	n.a.	BM *
2	24.06	n.a.	63.956	77.235	4.00	n.a.	BMB*
Total:			1508.089	1931.712	100.00	0.000	

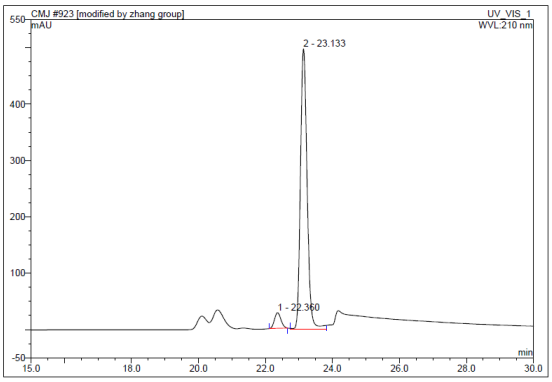
4.1.14 (*S*)-2-(cyclohex-1-en-1-ylmethyl)-1-oxaspiro[4.5]decane (3n)



3n

Prepared according to typical procedure at RT for 96 hours by using $[Pd(allyl)Cl]_2$ (5 mol%), **Xu8** (20 mol%) from γ-hydroxyalkenes **1b** (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **3n** as a white liquid (28 mg, 60% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -5.8 (*c* = 0.4, Chloroform). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.42 (t, *J* = 3.5 Hz, 1 H), 4.10 – 3.91 (m, 1 H), 2.30 (dd, *J* = 13.4, 5.5 Hz, 1 H), 2.03 – 1.87 (m, 6 H), 1.74 – 1.61 (m, 4 H), 1.61 – 1.43 (m, 9 H), 1.42 – 1.28 (m, 4 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.2, 122.7, 82.4, 76.7, 45.1, 38.6, 37.6, 35.6, 31.1, 29.0, 25.7, 25.2, 24.1, 23.8, 22.9, 22.4. HRMS (ESI) calculated for $[C_{16}H_{26}NaO]$ $[M+Na]^+$: 257.1876 found: 257.1878. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 210 nm); major enantiomer tr = 23.13 min, minor enantiomer tr = 22.36 min.

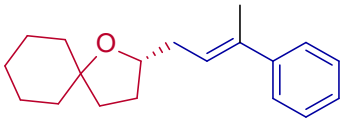




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.62	n.a.	970.096	226.119	50.00	n.a.	BM *
2	22.39	n.a.	987.383	226.124	50.00	n.a.	MB*
Total:			1957.479	452.243	100.00	0.000	

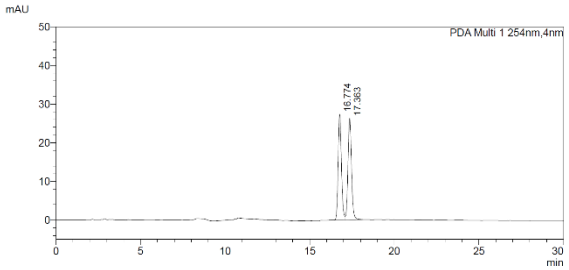
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.36	n.a.	27.638	6.157	5.09	n.a.	BMB*
2	23.13	n.a.	496.817	114.717	94.91	n.a.	M *
Total:			524.455	120.874	100.00	0.000	

4.1.15 Synthesis of (*S*, *E*)-2-(3-phenylbut-2-en-1-yl)-1-oxaspiro[4.5]decane (3o)



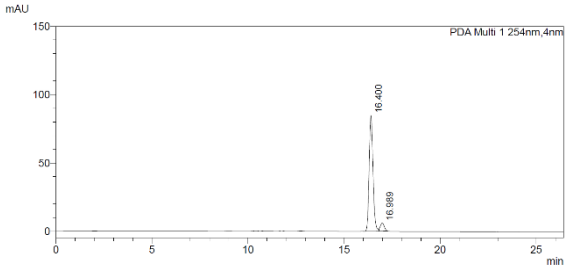
3o

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **3o** as a white liquid (34 mg, 63% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -2.5 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 5.80 (tq, *J* = 7.3, 1.4 Hz, 1H), 4.07 (tt, *J* = 7.5, 5.4 Hz, 1H), 2.56 (dddd, *J* = 14.5, 7.2, 5.2, 1.0 Hz, 1H), 2.35 (dtd, *J* = 14.6, 7.4, 1.0 Hz, 1H), 2.08 – 2.01 (m, 3H), 2.02 – 1.93 (m, 1H), 1.79 – 1.61 (m, 5H), 1.53 (tq, *J* = 6.3, 3.7 Hz, 4H), 1.45 – 1.28 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9, 136.3, 128.1, 126.6, 125.7, 124.3, 82.7, 77.6, 38.6, 37.7, 35.9, 35.7, 30.9, 25.7, 24.2, 23.9, 16.1. HRMS (ESI) calculated for $[C_{19}H_{26}NaO]$ $[M+Na]^+$: 293.1876 found: 293.1868. Enantiomeric excess was determined by HPLC with a Chiralpak OJH-OJH column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 16.400 min, minor enantiomer tr = 16.989.



<Peak Table>
PDA Ch1 254nm

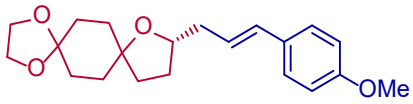
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.774	27340	51.036	370033	49.417
2	17.363	26230	48.964	378770	50.583
Total		53570	100.000	748803	100.000



<Peak Table>
PDA Ch1 254nm

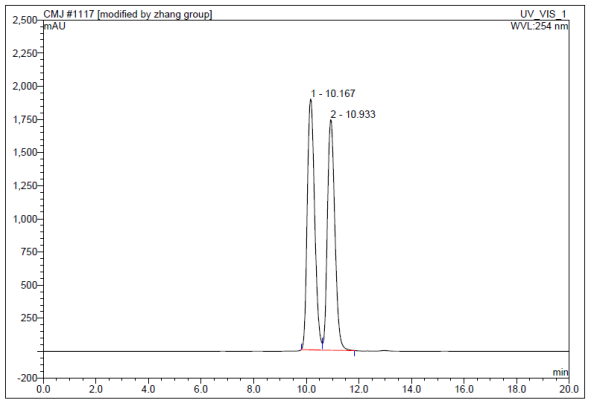
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.400	84703	93.596	1185985	93.439
2	16.989	5796	6.404	83276	6.561
Total		90499	100.000	1269261	100.000

4.1.16 (*S*, *E*)-10-(3-(4-methoxyphenyl)-allyl)-1,4,9-trioxadispiro[4.2.48.25]tetradecane (4a)

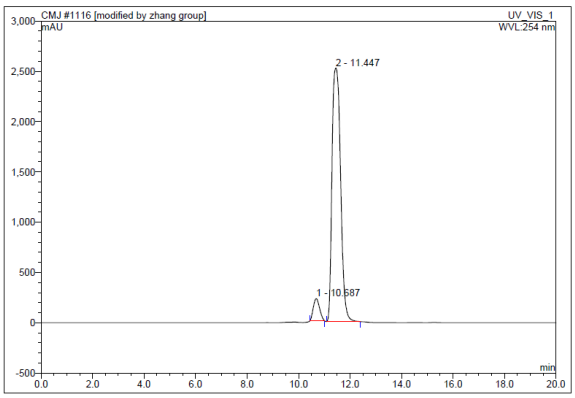


4a

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10: 1) give the product **4a** as a white liquid (43 mg, 63% yield) with 88% *ee*. $[\alpha]_D^{20}$ = -9.6 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 6.85 – 6.81 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.12 – 6.04 (m, 1H), 4.08 – 4.01 (m, 1H), 3.97 – 3.90 (m, 4H), 3.79 (s, 3H), 2.50 – 2.43 (m, 1H), 2.38 – 2.31 (m, 1H), 2.01 – 1.96 (m, 1H), 1.93 – 1.84 (m, 2H), 1.80 – 1.70 (m, 4H), 1.70 – 1.64 (m, 2H), 1.61 – 1.52 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.2, 130.5, 127.0, 124.6, 113.9, 108.7, 81.0, 77.9, 64.2, 64.1, 55.2, 39.8, 36.2, 35.5, 34.3, 31.8, 31.8, 30.5. HRMS (ESI) calculated for $[C_{21}H_{28}NaO_4]$ $[M+Na]^+$: 367.1880 found: 367.1873. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 60: 40, 0.5 mL/min, 254 nm); major enantiomer tr = 11.45 min, minor enantiomer tr = 10.69 min.

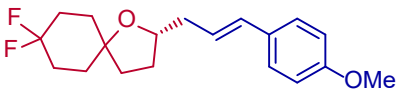


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.17	n.a.	1892.219	615.732	51.87	n.a.	BM *
2	10.93	n.a.	1739.297	571.296	48.13	n.a.	MB*
Total:			3631.517	1187.028	100.00	0.000	



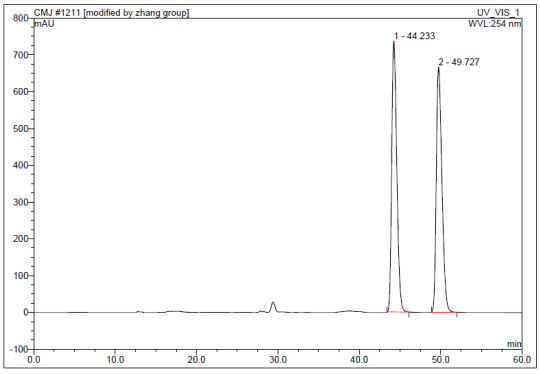
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.69	n.a.	222.057	62.811	6.09	n.a.	BMB*
2	11.45	n.a.	2521.153	968.983	93.91	n.a.	BMB*
Total:			2743.210	1031.794	100.00	0.000	

4.1.17 (*S*, *E*)-8,8-difluoro-2-(3-(4-methoxyphenyl)-allyl)-1-oxaspiro[4.5]decane (4b)

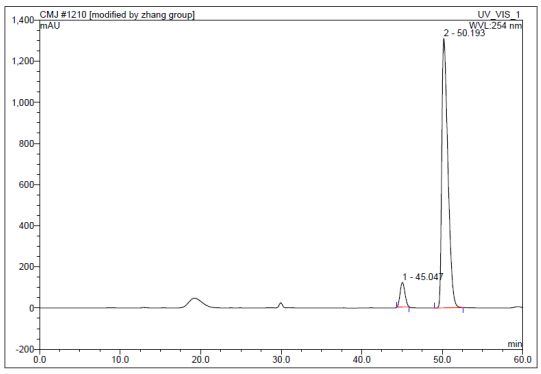


4b

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4b** as a white liquid (38 mg, 60% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -5.4 (*c* = 0.4, Chloroform).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 15.5 Hz, 1H), 6.10 – 6.04 (m, 1H), 4.09 – 4.04 (m, 1H), 3.80 (s, 3H), 2.50 – 2.45 (m, 1H), 2.39 – 2.33 (m, 1H), 2.23 – 2.05 (m, 2H), 2.04 – 1.99 (m, 1H), 1.96 – 1.86 (m, 2H), 1.82 – 1.59 (m, 7H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.8, 131.4, 130.4, 127.1, 124.3, 123.6 (t, *J* = 240.1 Hz), 113.9, 80.0, 78.2, 55.2, 39.6, 36.4 (d, *J* = 2.1 Hz), 34.3 (dd, *J* = 7.8, 2.0 Hz), 33.0 (dd, *J* = 8.0, 2.0 Hz), 30.9 (d, *J* = 24.5 Hz), 30.7 (d, *J* = 24.1 Hz), 30.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -93.8 (d, *J* = 235.0 Hz), -102.5 (d, *J* = 234.9 Hz). HRMS (ESI) calculated for $[C_{19}H_{24}NaF_2O_2]$ $[M+Na]^+$: 345.1637 found: 345.1627. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 90: 10, 0.5 mL/min, 254 nm); major enantiomer tr = 50.19 min, minor enantiomer tr = 45.05 min.

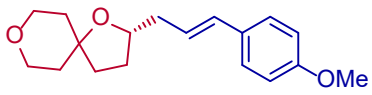


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.23	n.a.	736.491	531.933	49.87	n.a.	BMB*
2	49.73	n.a.	666.416	534.668	50.13	n.a.	BMB*
Total:			1402.907	1066.601	100.00	0.000	



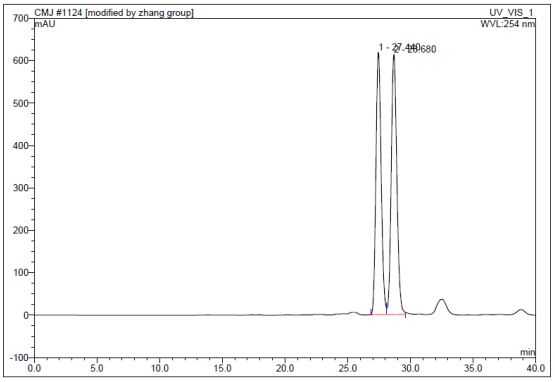
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	45.05	n.a.	119.288	82.333	6.68	n.a.	BMB*
2	50.19	n.a.	1309.592	1150.666	93.32	n.a.	BMB*
Total:			1428.880	1232.999	100.00	0.000	

4.1.18 (*S*, *E*)-2-(3-(4-methoxyphenyl)-allyl)-1,8-dioxaspiro[4.5]decane (4c)

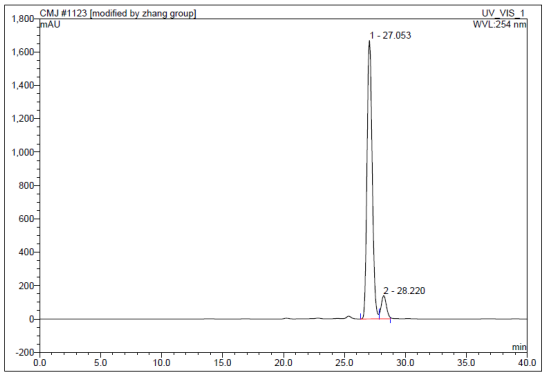


4c

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^tBu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10: 1) give the product **4c** as a white liquid (42 mg, 75% yield) with 85% *ee*. $[\alpha]_D^{20}$ = -7.8 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.11 – 6.03 (m, 1H), 4.11 – 4.04 (m, 1H), 3.87 – 3.81 (m, 2H), 3.79 (s, 3H), 3.66 – 3.59 (m, 2H), 2.53 – 2.46 (m, 1H), 2.39 – 2.32 (m, 1H), 2.06 – 1.98 (m, 1H), 1.85 – 1.76 (m, 1H), 1.75 – 1.69 (m, 2H), 1.68 – 1.59 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 131.4, 130.4, 127.1, 124.3, 113.9, 79.4, 77.9, 65.5, 65.4, 55.2, 39.7, 38.7, 37.6, 36.5, 30.3. HRMS (ESI) calculated for $[C_{18}H_{24}NaO_3]$ $[M+Na]^+$: 311.1618 found: 311.1611. Enantiomeric excess was determined by HPLC with a Chiralpak IC+IC column (hexanes: 2-propanol = 60: 40, 0.5 mL/min, 254 nm); major enantiomer tr = 27.05 min, minor enantiomer tr = 28.22 min.

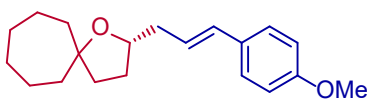


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.44	n.a.	618.687	299.629	48.57	n.a.	BM *
2	28.68	n.a.	613.191	317.211	51.43	n.a.	M *
Total:			1231.878	616.840	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.05	n.a.	1668.984	824.067	92.25	n.a.	BM *
2	28.22	n.a.	138.669	69.224	7.75	n.a.	M *
Total:			1807.654	893.291	100.00	0.000	

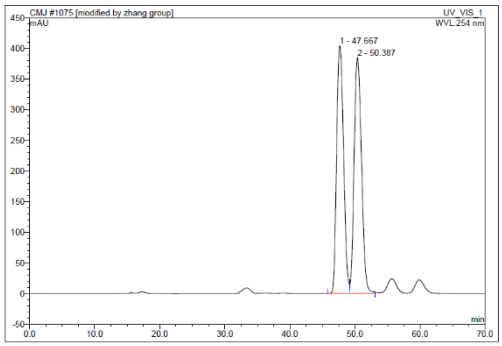
4.1.19 (*S*, *E*)-2-(3-(4-methoxyphenyl)-allyl)-1-oxaspiro[4.6]undecane (4d)



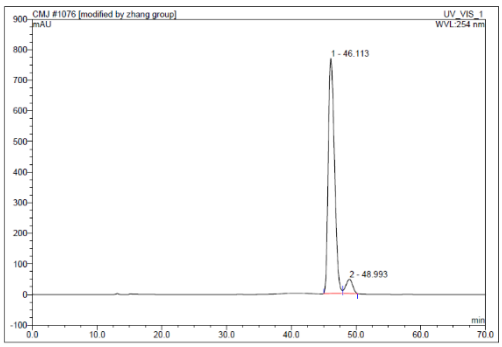
4d

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4d** as a white liquid (32 mg, 54% yield) with 88% *ee*. $[\alpha]_D^{20}$ = -5.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400

MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 16 Hz, 1H), 6.11 – 6.03 (m, 1H), 4.03 – 3.97 (m, 1H), 3.79 (s, 3H), 2.53 – 2.46 (m, 1H), 2.37 – 2.29 (m, 1H), 1.99 – 1.92 (m, 1H), 1.82 – 1.50 (m, 13H), 1.49 – 1.35 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.1, 130.6, 127.1, 124.7, 113.9, 86.4, 77.7, 55.2, 41.6, 40.6, 39.7, 37.9, 30.5, 29.5, 29.4, 23.2, 22.9. HRMS (ESI) calculated for [$C_{20}H_{28}NaO_2$] [M+Na]$^+$: 323.1982 found: 323.1978. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 46.11 min, minor enantiomer tr = 48.99 min.

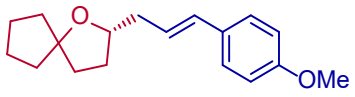


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	47.67	n.a.	404.595	499.529	49.54	n.a.	BM *
2	50.39	n.a.	385.167	508.828	50.46	n.a.	M *
Total:			789.763	1008.357	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	46.11	n.a.	769.025	867.489	93.96	n.a.	BM *
2	48.99	n.a.	46.420	55.798	6.04	n.a.	MB*
Total:			815.445	923.287	100.00	0.000	

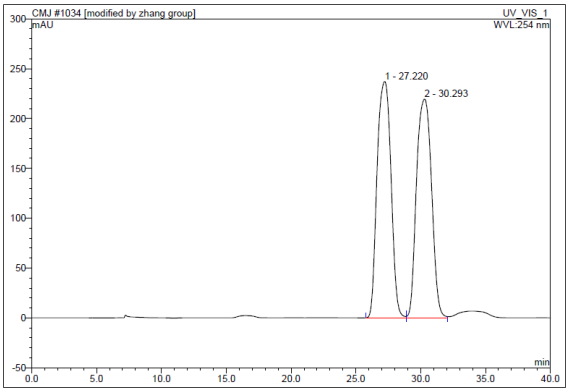
4.1.20 (*S*, *E*)-2-(3-(4-methoxyphenyl)-allyl)-1-oxaspiro[4.4]nonane (4e)



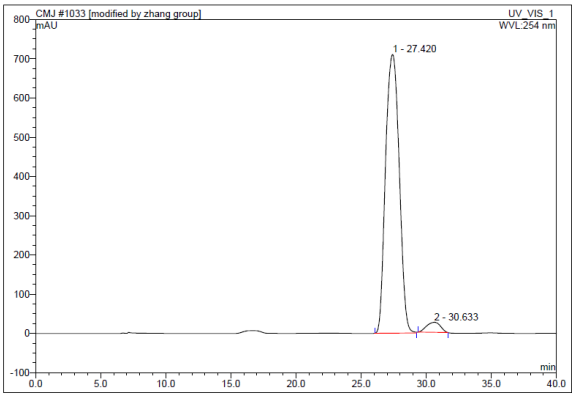
4e

Prepared according to typical procedure at RT for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4e** as a white liquid (43 mg, 79% yield) with 93% *ee*. $[\alpha]_D^{20}$ = -11.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.10 – 6.03 (m, 1H), 4.06 – 3.99 (m, 1H), 3.78 (s, 3H), 2.52 – 2.46 (m, 1H), 2.37 – 2.30 (m, 1H), 2.03 – 1.95 (m, 1H), 1.89 – 1.73 (m, 6H), 1.56 – 1.64 (m, 1H), 1.63 – 1.45 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.2, 130.5, 127.1, 124.6, 113.9, 91.2, 77.9, 55.2, 39.9, 39.1, 38.3, 36.5, 31.1, 24.0. HRMS (ESI) calculated for [$C_{18}H_{24}NaO_2$] [M+Na]$^+$: 295.1669 found: 295.1668.

Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 27.22 min, minor enantiomer tr = 30.29 min.

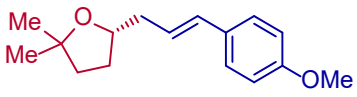


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.22	n.a.	237.244	294.787	49.94	n.a.	BM *
2	30.29	n.a.	219.533	295.518	50.06	n.a.	M *
Total:			456.777	590.305	100.00	0.000	



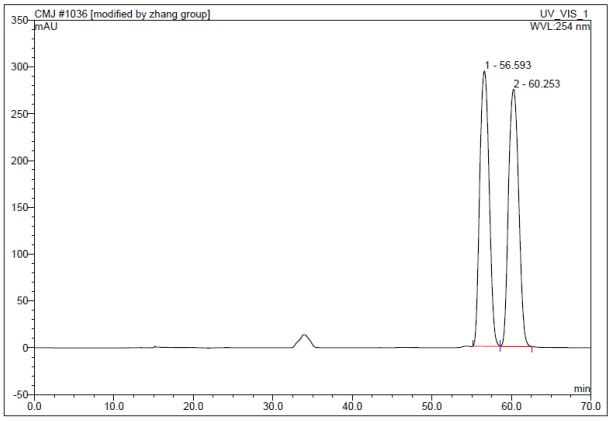
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.42	n.a.	710.108	864.106	96.49	n.a.	BM *
2	30.63	n.a.	25.582	31.478	3.51	n.a.	BMB*
Total:			735.689	895.584	100.00	0.000	

4.1.21 (*S*, *E*)-5-(3-(4-methoxyphenyl)-allyl)-2,2-dimethyltetrahydrofuran (4f)

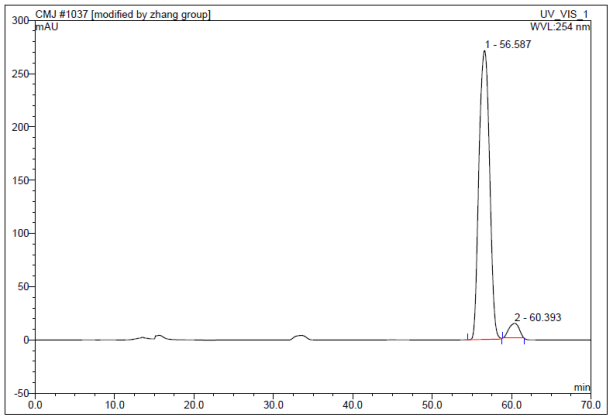


4f

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^tBu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4f** as a white liquid (43 mg, 87% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -12.7 (*c* = 0.4, Chloroform). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.12 – 6.04 (m, 1H), 4.11 – 4.05 (m, 1H), 3.80 (s, 3H), 2.53 – 2.46 (m, 1H), 2.39 – 2.31 (m, 1H), 2.04 – 1.98 (m, 1H), 1.72 – 1.69 (m, 1H), 1.67 – 1.65 (m, 2H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 131.3, 130.6, 127.1, 124.5, 113.9, 80.7, 78.2, 55.3, 39.9, 38.5, 31.2, 29.2, 28.1. HRMS (ESI) calculated for $[C_{16}H_{22}NaO_2]$ $[M+Na]^+$: 269.1512 found: 269.1507. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 56.59 min, minor enantiomer tr = 60.39 min.

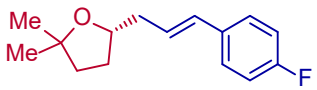


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	56.59	n.a.	294.033	403.581	49.78	n.a.	BM *
2	60.25	n.a.	274.703	407.222	50.22	n.a.	MB*
Total:			568.736	810.803	100.00	0.000	



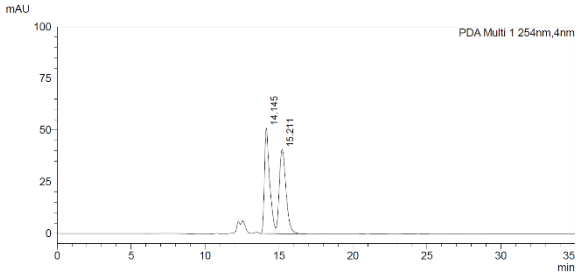
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	56.59	n.a.	271.243	420.597	95.29	n.a.	BM *
2	60.39	n.a.	13.821	20.796	4.71	n.a.	BMB*
Total:			285.065	441.393	100.00	0.000	

4.1.22 (*S*, *E*)-5-(3-(4-fluorophenyl)-allyl)-2,2-dimethyltetrahydrofuran (4g)



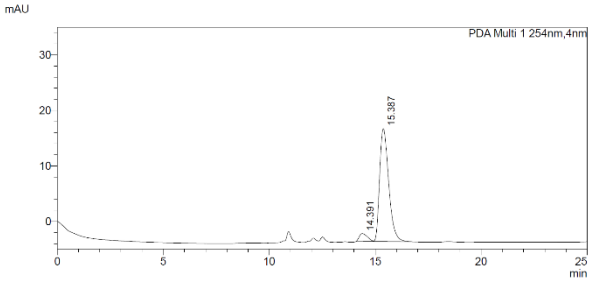
4g

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^{t}Bu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4g** as a white liquid (20 mg, 43% yield) with 89% *ee*. $[\alpha]_D^{20}$ = -8.4 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 6.99 – 6.95 (m, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.18 – 6.10 (m, 1H), 4.11 – 4.05 (m, 1H), 2.53 – 2.46 (m, 1H), 2.40 – 2.33 (m, 1H), 2.06 – 1.98 (m, 1H), 1.78 – 1.63 (m, 3H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 244.3 Hz), 133.8 (d, *J* = 3.3 Hz), 130.7, 127.4 (d, *J* = 7.8 Hz), 126.5 (d, *J* = 2.3 Hz), 115.3 (d, *J* = 21.2 Hz), 80.8, 78.0, 39.8, 38.4, 31.2, 29.2, 28.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.6. HRMS (ESI) calculated for $[C_{15}H_{19}NaFO]$ $[M+Na]^+$: 257.1312 found: 257.1303. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 99.5: 0.5, 0.6 mL/min, 254 nm); major enantiomer tr = 15.387 min, minor enantiomer tr = 14.391 min.



<Peak Table>
PDA Ch1 254nm

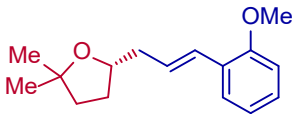
Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.145	51006	55.673	1240202	49.025
2	15.211	40611	44.327	1289554	50.975
Total		91617	100.000	2529756	100.000



<Peak Table>
PDA Ch1 254nm

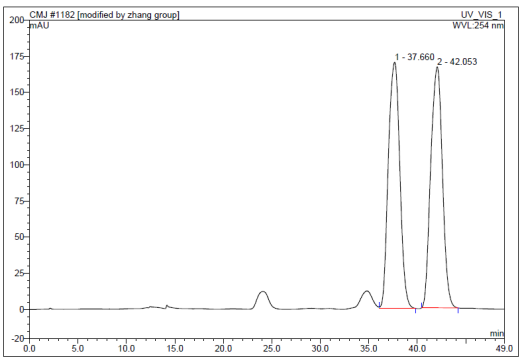
Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.391	1390	6.403	36183	5.642
2	15.387	20325	93.597	605183	94.358
Total		21716	100.000	641367	100.000

4.1.23 (*S*, *E*)-5-(3-(2-methoxyphenyl)-allyl)-2,2-dimethyltetrahydrofuran (4h)

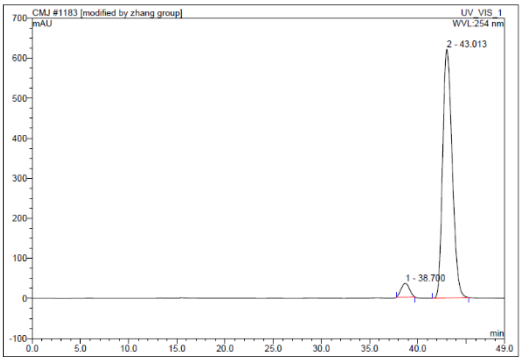


4h

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^tBu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4h** as a white liquid (34 mg, 68% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -16.3 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.26 – 6.18 (m, 1H), 4.14 – 4.07 (m, 1H), 3.84 (s, 3H), 2.59 – 2.52 (m, 1H), 2.44 – 2.37 (m, 1H), 2.05 – 1.99 (m, 1H), 1.77 – 1.69 (m, 3H), 1.28 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 127.9, 127.3, 126.7, 126.5, 126.4, 120.6, 110.8, 80.6, 78.2, 55.4, 40.2, 38.4, 31.1, 29.1, 28.1. HRMS (ESI) calculated for $[C_{16}H_{22}NaO_2]$ $[M+Na]^+$: 269.1512 found: 269.1508. Enantiomeric excess was determined by HPLC with a Chiralpak ODH+OD3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 43.01 min, minor enantiomer tr = 38.70 min.

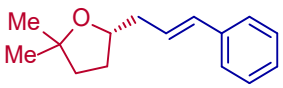


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	37.66	n.a.	170.118	233.404	50.16	n.a.	MB*
2	42.05	n.a.	166.414	231.920	49.84	n.a.	BMB*
Total:			336.532	465.323	100.00	0.000	



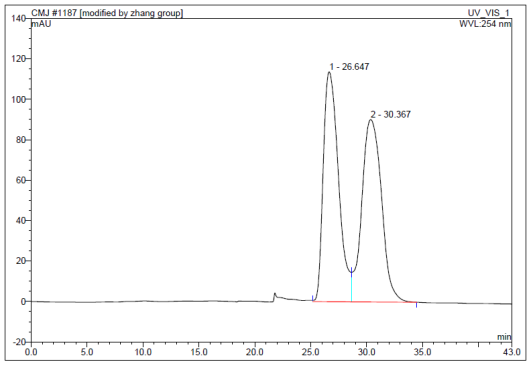
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	38.70	n.a.	34.788	34.652	4.65	n.a.	BMB*
2	43.01	n.a.	621.030	710.111	95.35	n.a.	BMB*
Total:			655.819	744.763	100.00	0.000	

4.1.24 (*S*)-5-cinnamyl-2,2-dimethyltetrahydrofuran (4i)

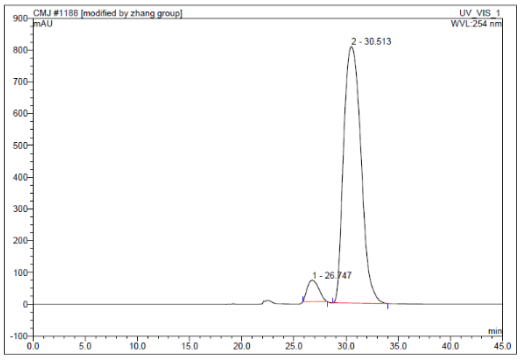


4i

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^{t}Bu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4i** as a white liquid (21 mg, 47% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -14.3 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.35 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.27 – 6.20 (m, 1H), 4.13 – 4.07 (m, 1H), 2.56 – 2.49 (m, 1H), 2.42 – 2.35 (m, 1H), 2.06 – 1.98 (m, 1H), 1.77 – 1.73 (m, 2H), 1.72 – 1.68 (m, 1H), 1.28 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.9, 128.4, 126.9, 126.7, 126.0, 80.7, 78.1, 39.8, 38.4, 31.2, 29.2, 28.1. HRMS (ESI) calculated for $[C_{15}H_{20}NaO]$ $[M+Na]^+$: 239.1406 found: 239.1398. Enantiomeric excess was determined by HPLC with a Chiralpak ODH+ODH+OD3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 30.51 min, minor enantiomer tr = 26.75 min.

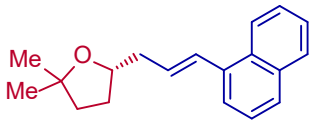


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.65	n.a.	113.645	179.576	49.33	n.a.	M *
2	30.37	n.a.	90.180	184.443	50.67	n.a.	MB*
Total:			203.825	364.019	100.00	0.000	



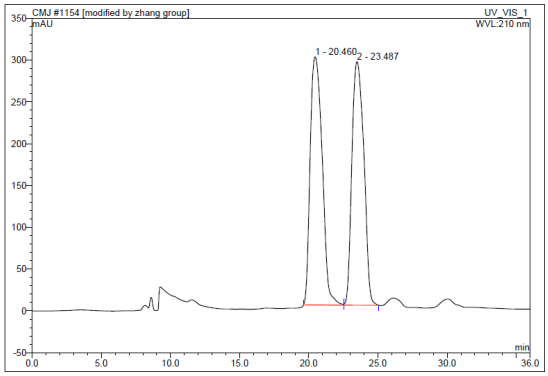
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.75	n.a.	67.322	86.004	5.25	n.a.	BMB*
2	30.51	n.a.	807.107	1551.586	94.75	n.a.	BMB*
Total:			874.430	1637.590	100.00	0.000	

4.1.25 (*S*, *E*)-2,2-dimethyl-5-(3-(naphthalen-1-yl)-allyl)tetrahydrofuran (4j)

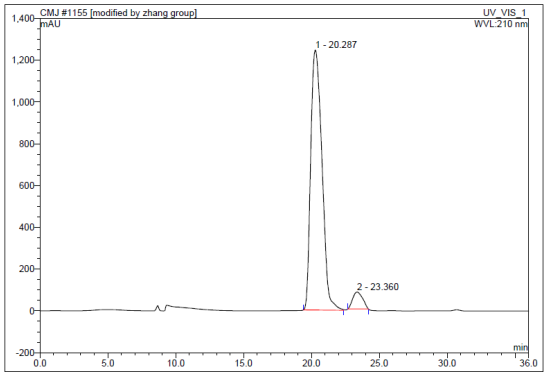


4j

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^{t}Bu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4j** as a white liquid (39 mg, 73% yield) with 89% *ee*. $[\alpha]_D^{20}$ = -15.7 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.21 (d, *J* = 15.6 Hz, 1H), 6.35 – 6.20 (m, 1H), 4.27 – 4.12 (m, 1H), 2.74 – 2.62 (m, 1H), 2.60 – 2.47 (m, 1H), 2.15 – 2.05 (m, 1H), 1.86 – 1.74 (m, 4H), 1.33 (s, 4H), 1.29 (s, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.4, 133.6, 131.1, 129.9, 129.2, 128.4, 127.3, 125.8, 125.6, 123.9, 123.6, 80.7, 78.0, 40.1, 38.5, 31.2, 29.2, 28.1. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.9, 128.4, 126.9, 126.7, 126.0, 80.7, 78.1, 39.8, 38.4, 31.2, 29.2, 28.1. HRMS (ESI) calculated for $[C_{19}H_{22}NaO]$ $[M+Na]^+$: 289.1563 found: 289.1559. Enantiomeric excess was determined by HPLC with a Chiralpak ODH+ODH column (hexanes: 2-propanol = 99: 1, 0.8 mL/min, 210 nm); major enantiomer tr = 20.29 min, minor enantiomer tr = 23.36 min.

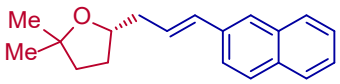


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.46	n.a.	296.784	299.000	50.72	n.a.	BM *
2	23.49	n.a.	291.250	290.503	49.28	n.a.	MB*
Total:			588.034	589.503	100.00	0.000	



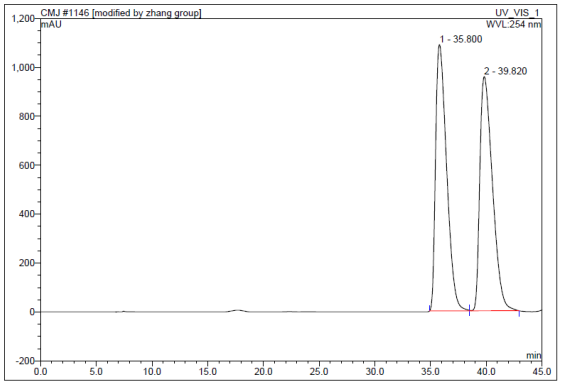
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.29	n.a.	1244.059	1194.477	94.56	n.a.	BM *
2	23.36	n.a.	80.944	68.668	5.44	n.a.	BMB*
Total:			1325.003	1263.145	100.00	0.000	

4.1.26 (*S*, *E*)-2,2-dimethyl-5-(3-(naphthalen-2-yl)-allyl)tetrahydrofuran (4k)

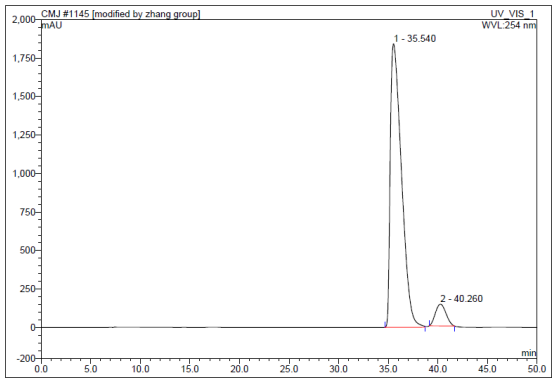


4k

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^{t}Bu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4k** as a white liquid (38 mg, 71% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -13.7 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.781 – 7.768 (m, 3H), 7.71 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.43 – 6.36 (m, 1H), 4.19 – 4.13 (m, 1H), 2.64 – 2.57 (m, 1H), 2.50 – 2.43 (m, 1H), 2.13 – 2.03 (m, 1H), 1.80 – 1.72 (m, 3H), 1.32 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.1, 133.6, 132.7, 132.0, 128.0, 127.8, 127.6, 127.2, 126.1, 125.5, 125.5, 123.6, 80.7, 78.1, 40.0, 38.4, 31.2, 29.2, 28.1. HRMS (ESI) calculated for $[C_{19}H_{22}NaO]$ $[M+Na]^+$: 289.1563 found: 289.1556. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 35.54 min, minor enantiomer tr = 40.26 min.

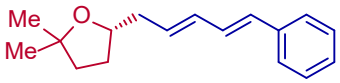


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.80	n.a.	1088.639	1245.067	49.79	n.a.	BM *
2	39.82	n.a.	957.640	1255.733	50.21	n.a.	MB*
Total:			2046.279	2500.800	100.00	0.000	



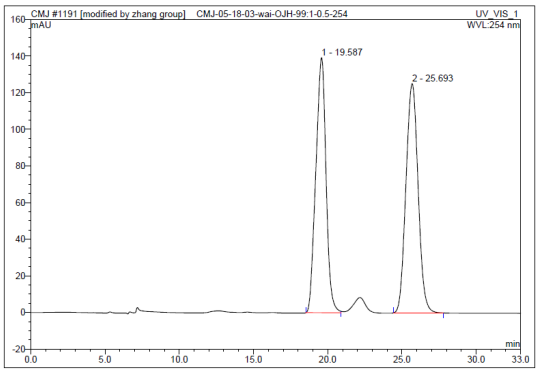
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.54	n.a.	1840.915	2403.351	93.25	n.a.	BM *
2	40.26	n.a.	140.914	173.832	6.75	n.a.	BMB*
Total:			1981.829	2577.183	100.00	0.000	

4.1.27 (*S*)-2,2-dimethyl-5-((2*E*, 4*E*)-5-phenylpenta-2,4-dien-1-yl)tetrahydrofuran (4l)

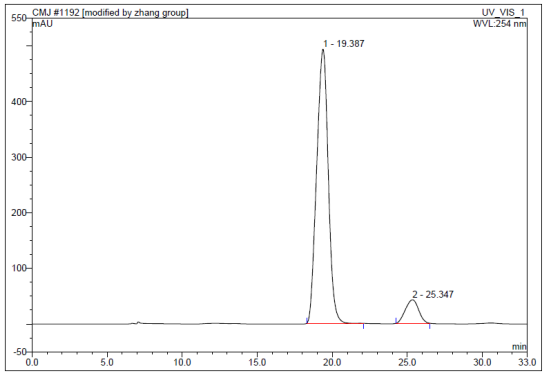


4l

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol), NaO^{t}Bu (0.4 mmol), alkenyl bromide (0.4 mmol) and no additive H_2O, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **4l** as a white liquid (27 mg, 56% yield) with 83% *ee*. $[\alpha]_D^{20}$ = -8.9 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.37 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.76 (dd, *J* = 16.0, 10.0 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.26 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.87 – 5.79 (m, 1H), 4.09 – 4.02 (m, 1H), 2.49 – 2.43 (m, 1H), 2.35 – 2.28 (m, 1H), 2.06 – 1.98 (m, 1H), 1.76 – 1.64 (m, 3H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.5, 132.6, 131.4, 130.5, 129.3, 128.5, 127.1, 126.1, 80.7, 78.0, 39.8, 38.4, 31.3, 29.2, 28.1. HRMS (ESI) calculated for $[C_{17}H_{22}NaO]$ $[M+Na]^+$: 265.1563 found: 265.1558. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 19.39 min, minor enantiomer tr = 25.35 min.

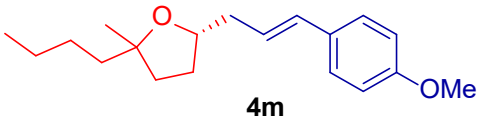


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.59	n.a.	139.275	111.190	48.31	n.a.	BM *
2	25.69	n.a.	125.180	118.970	51.69	n.a.	BMB*
Total:			264.455	230.160	100.00	0.000	



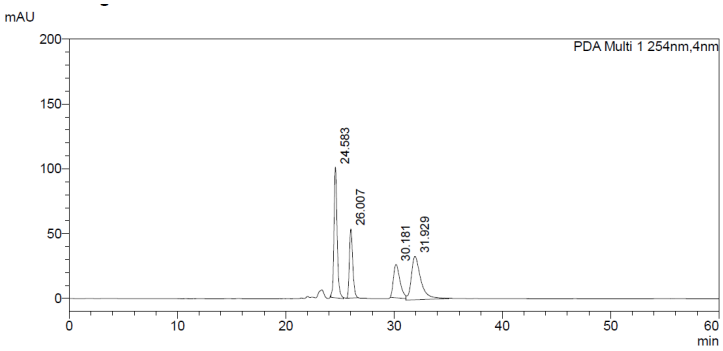
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.39	n.a.	492.752	440.381	91.06	n.a.	BMB*
2	25.35	n.a.	42.328	43.261	8.94	n.a.	BMB*
Total:			535.080	483.643	100.00	0.000	

4.1.29 Synthesis of (5*S*)-2-butyl-5-((*E*)-3-(4-methoxyphenyl)allyl)-2-methyltetrahydrofuran (4m)



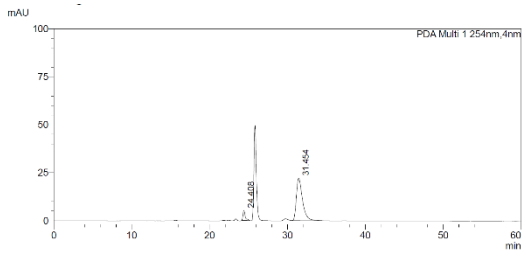
4m

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **4m** as a white liquid (32 mg, 56% yield, dr : 1.1:1) with 84% *ee* (major)，93% *ee* (minor). $[\alpha]_D^{20}$ = -11.2 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.37 (ddt, *J* = 15.8, 2.8, 1.4 Hz, 1H), 6.08 (dt, *J* = 15.9, 7.2 Hz, 1H), 4.05 (dqd, *J* = 22.6, 6.9, 5.3 Hz, 1H), 3.79 (s, 3H), 2.50 (ddddd, *J* = 13.9, 12.5, 6.9, 5.2, 1.5 Hz, 1H), 2.34 (dtdd, *J* = 14.0, 7.1, 4.3, 1.4 Hz, 1H), 2.06 – 1.90 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 – 1.61 (m, 2H), 1.50 (qd, *J* = 5.8, 2.1 Hz, 1H), 1.36 – 1.29 (m, 5H), 1.19 (d, *J* = 7.8 Hz, 3H), 0.91 – 0.87 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 131.2, 130.6, 127.1, 124.6, 113.9, 83.1, 78.5, 55.3, 41.5, 39.8, 36.9, 31.2, 27.1, 24.4, 22.7, 14.1. HRMS (ESI) calculated for $[C_{19}H_{26}NaO_2]$ $[M+Na]^+$: 309.1825 found: 309.1820. Enantiomeric excess was determined by HPLC with a Chiralpak ADH-ADH-ADH column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); Minor [tr (minor) = 24.408 min, tr (major) = 31.454 min; 84% ee] major [tr (minor) = 29.766 min, tr (major) = 25.831 min; 90% ee].



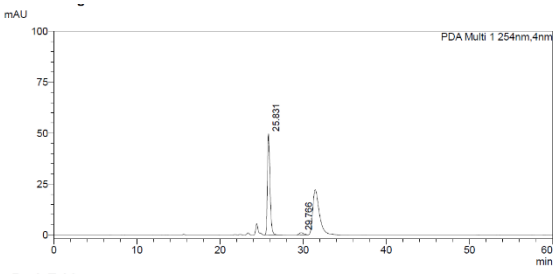
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.583	100810	47.256	2031825	32.232
2	26.007	53356	25.011	1149676	18.238
3	30.181	25737	12.065	1080062	17.134
4	31.929	33425	15.668	2042199	32.397
Total		213329	100.000	6303763	100.000



<Peak Table>
PDA Ch1 254nm

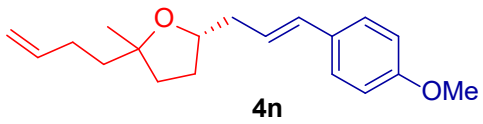
Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.408	5288	19.274	105439	8.001
2	31.454	22147	80.726	1212358	91.999
Total		27434	100.000	1317797	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	25.831	49645	98.000	1073331	96.584
2	29.766	1013	2.000	37964	3.416
Total		50658	100.000	1111295	100.000

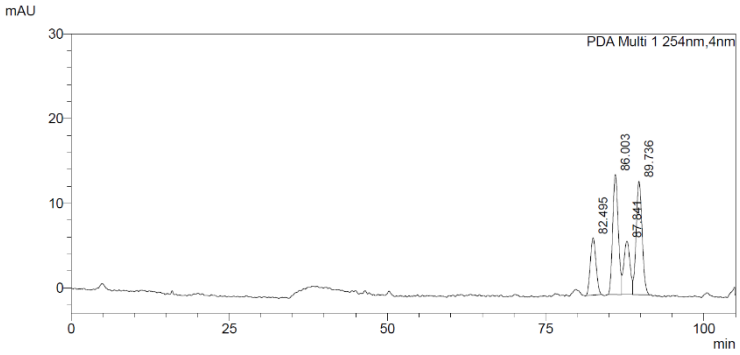
4.1.30 Synthesis of (5*S*)-2-(but-3-en-1-yl)-5-((*E*)-3-(4-methoxyphenyl)allyl)-2-methyltetrahydrofuran (4n)



4n

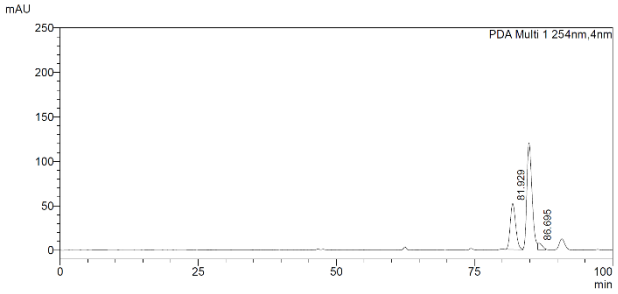
Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu6** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **4n** as a white liquid (27 mg, 52% yield, dr : 2:1) with 82% *ee* (major)，80% *ee* (minor). $[\alpha]_D^{20}$ = -7.1 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.5 Hz, 2H), 6.83 (dd, *J* = 8.6, 1.5 Hz, 2H), 6.38 (dd, *J* = 15.9, 2.8 Hz, 1H), 6.17 – 6.00 (m, 1H), 5.85 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.09 – 4.79 (m, 2H), 4.17 – 3.93 (m, 1H), 3.80 (s, 3H), 2.56 – 2.44 (m, 1H), 2.36 (dtd, *J* = 14.1, 7.1, 1.3 Hz, 1H), 2.23 – 2.06 (m, 2H), 2.06 – 1.94 (m, 1H), 1.86 – 1.73 (m, 1H), 1.67 (dddd, *J* = 20.1, 10.1, 7.4, 5.4 Hz, 4H), 1.26 – 1.20 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 139.1, 131.3, 130.5, 127.1, 124.5, 114.0, 113.9, 82.8, 78.6, 55.3, 40.4, 39.8, 37.0, 31.2, 29.0,

27.1.RMS (ESI) calculated for [$C_{19}H_{26}NaO_2$] [M+Na]$^+$: 309.1825 found: 309.1820. Enantiomeric excess was determined by HPLC with a Chiralpak OJH-OJH-OJ3 column (hexanes: 2-propanol = 99.5: 0.5, 0.6 mL/min, 254 nm); Minor [tr (minor) = 86.695 min, tr (major) = 81.929 min; 80% ee] major [tr (minor) = 90.829 min, tr (major) = 84.875 min; 92% ee]



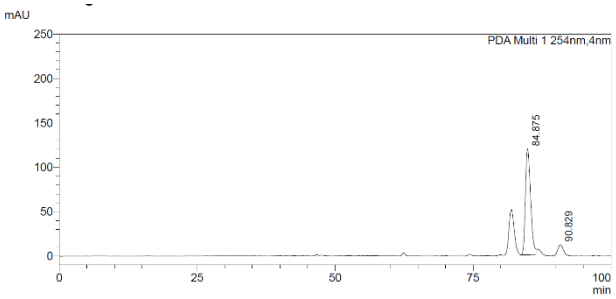
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	82.495	6753	16.614	421079	16.146
2	86.003	14167	34.854	874184	33.520
3	87.841	6320	15.550	429223	16.458
4	89.736	13406	32.982	883432	33.875
Total		40646	100.000	2607918	100.000



<Peak Table>
PDA Ch1 254nm

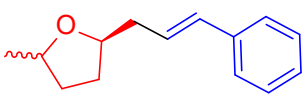
Peak#	Ret. Time	Height	Height%	Area	Area%
1	81.929	51645	87.926	3507763	90.103
2	86.695	7092	12.074	385309	9.897
Total		58737	100.000	3893072	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	84.875	119152	90.954	7727271	90.951
2	90.829	11850	9.046	768775	9.049
Total		131003	100.000	8496045	100.000

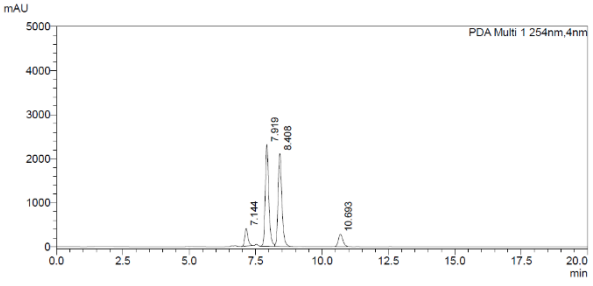
4.1.31 Synthesis of (2*R*)-2-cinnamyl-5-methyltetrahydrofuran (4o)



4o

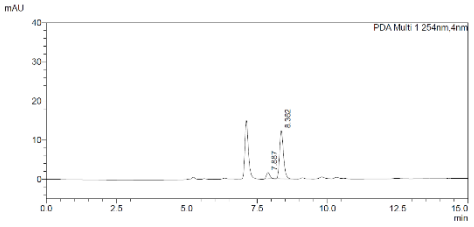
Prepared according to typical procedure at -20 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **(*R*, *R*$_S$)-Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **4o** as a white liquid (21 mg, 21% yield, dr = 1.1:1, 94% ee(major), 80% ee (minor). $[\alpha]_D^{20}$ = 4.3 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.23 – 7.16 (m, 1H), 6.48 – 6.40 (m, 1H), 6.23 (dtd, *J* = 15.8, 7.1, 5.4 Hz, 1H),

4.14 (ddt, *J* = 8.1, 5.8, 3.4 Hz, 1H), 3.97 (dqd, *J* = 12.5, 6.3, 2.7 Hz, 1H), 2.52 (ddddd, *J* = 14.2, 10.2, 7.2, 5.8, 1.4 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.05 (dddd, *J* = 12.7, 11.3, 5.6, 2.6 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.68 – 1.61 (m, 1H), 1.46 (ddddd, *J* = 11.8, 9.8, 8.4, 4.9, 3.5 Hz, 1H), 1.24 (dd, *J* = 13.0, 6.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 132.0, 128.5, 127.0, 126.8, 126.1, 78.9, 75.5, 39.7, 33.9, 31.8, 21.4. HRMS (ESI) calculated for [$C_{14}H_{19}O$] [M+H]$^+$: 203.1430 found: 203.1435. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); Minor [tr (minor) = 7.887 min, tr (major) = 8.362 min; 80% ee] major [tr (minor) = 10.327 min, tr (major) = 7.119 min; 94% ee]



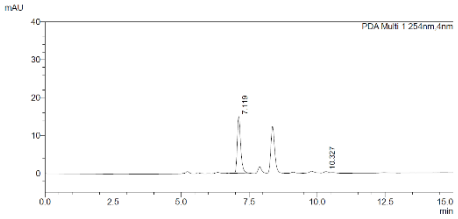
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.144	398617	7.818	3318975	6.840
2	7.919	2310089	45.308	21087685	43.460
3	8.408	2114753	41.477	20906902	43.088
4	10.693	275171	5.397	3208193	6.612
Total		5098630	100.000	48521755	100.000



<Peak Table>
PDA Ch1 254nm

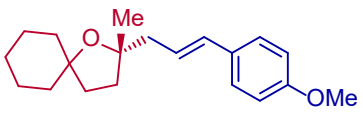
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.887	1587	11.408	13350	10.134
2	8.362	12321	88.592	118386	89.866
Total		13908	100.000	131736	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.119	14973	97.453	132553	96.947
2	10.327	391	2.547	4174	3.053
Total		15364	100.000	136727	100.000

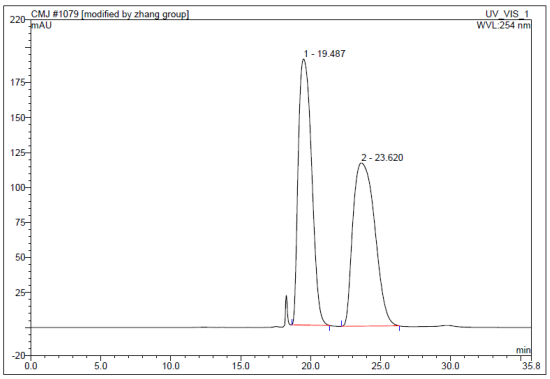
4.1.32 (*S*, *E*)-2-(3-(4-methoxyphenyl)-allyl)-2-methyl-1-oxaspiro[4.5]decane (6a)



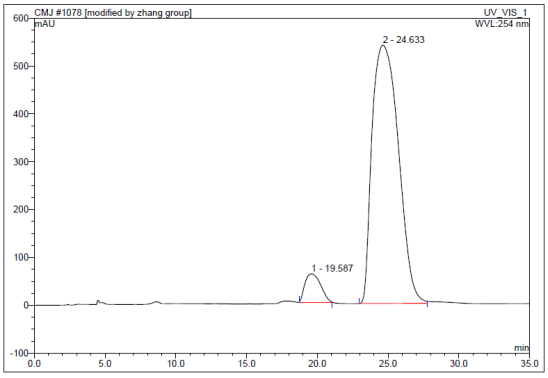
6a

Prepared according to typical procedure at RT for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6a** as a white liquid (38 mg, 63% yield) with 88% *ee*. $[\alpha]_D^{20}$ = -6.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 15.6 Hz, 1H),

6.15 – 6.08 (m, 1H), 3.80 (s, 3H), 2.38 – 2.35 (m, 2H), 1.97 – 1.92 (m, 1H), 1.85 – 1.76 (m, 2H), 1.72 – 1.64 (m, 5H), 1.56 – 1.51 (m, 4H), 1.34 – 1.28 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.6, 130.7, 127.1, 125.1, 113.9, 83.4, 82.4, 55.3, 46.0, 39.4, 38.8, 35.7, 28.4, 25.7, 24.2. HRMS (ESI) calculated for [$C_{20}H_{28}NaO_2$] [M+Na]$^+$: 323.1982 found: 323.1972. Enantiomeric excess was determined by HPLC with a Chiralpak ADH+ADH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 24.63 min, minor enantiomer tr = 19.59 min.

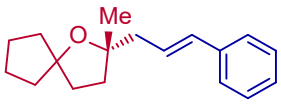


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.49	n.a.	190.105	209.880	49.81	n.a.	BMB*
2	23.62	n.a.	116.605	211.479	50.19	n.a.	BMB*
Total:			306.709	421.359	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.59	n.a.	59.535	76.526	6.16	n.a.	MB*
2	24.63	n.a.	539.830	1166.426	93.84	n.a.	BM *
Total:			599.365	1242.952	100.00	0.000	

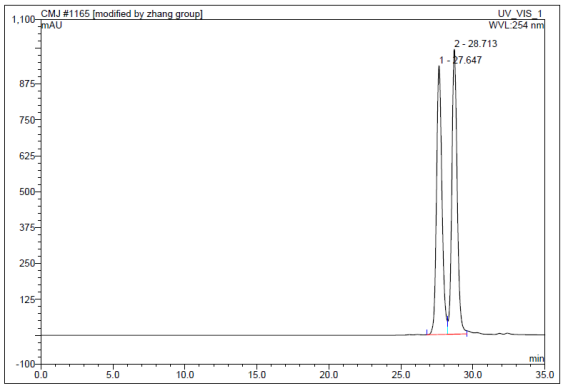
4.1.33 (*S*)-2-cinnamyl-2-methyl-1-oxaspiro[4.4]nonane (6b)



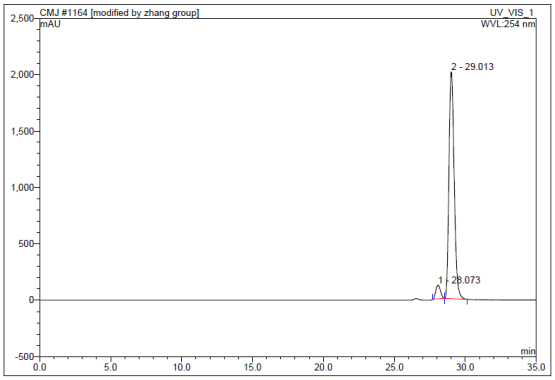
6b

Prepared according to typical procedure at RT for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6b** as a white liquid (47 mg, 91% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -4.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.30 – 6.22 (m, 1H), 2.42 – 2.39 (m, 2H), 1.97 – 1.87 (m, 3H), 1.84 – 1.72 (m, 5H), 1.64 – 1.53 (m, 4H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 132.3, 128.4, 127.2, 126.9, 126.0, 91.5, 82.6, 45.9, 39.8, 39.4, 37.2, 36.6, 28.0, 23.9, 23.8. HRMS (ESI) calculated for [$C_{18}H_{24}NaO$] [M+Na]$^+$: 279.1719 found: 279.1717. Enantiomeric excess was determined by HPLC

with a Chiralpak IA+IA column (hexanes: 2-propanol = 99: 1, 0.3 mL/min, 254 nm); major enantiomer tr = 29.01 min, minor enantiomer tr = 28.07 min.

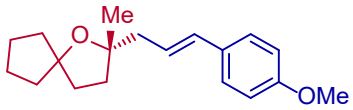


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.65	n.a.	935.553	410.474	49.22	n.a.	BM *
2	28.71	n.a.	992.006	423.508	50.78	n.a.	M *
Total:			1927.559	833.982	100.00	0.000	



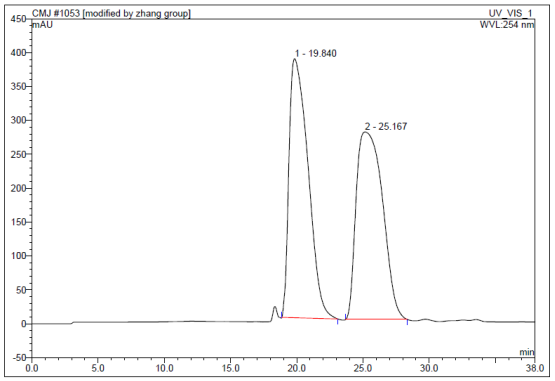
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.07	n.a.	121.916	46.445	5.14	n.a.	BMb*
2	29.01	n.a.	2010.599	857.131	94.86	n.a.	BMB*
Total:			2132.515	903.576	100.00	0.000	

4.1.34 (*S*, *E*)-2-(3-(4-methoxyphenyl)-allyl)-2-methyl-1-oxaspiro[4.4]nonane (6c)

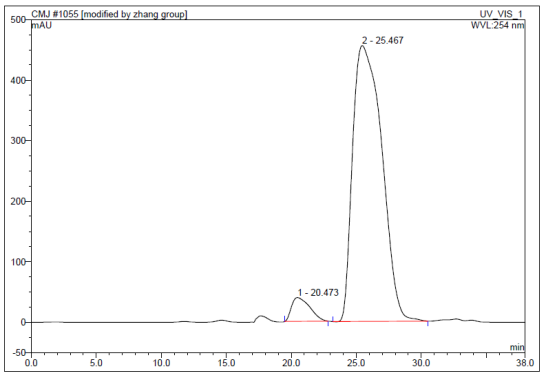


6c

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6c** as a white liquid (51 mg, 90% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -5.2 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.14 – 6.07 (m, 1H), 3.79 (s, 3H), 2.40 – 2.37 (m, 2H), 1.98 – 1.86 (m, 3H), 1.83 – 1.70 (m, 5H), 1.63 – 1.54 (m, 4H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.6, 130.6, 127.0, 124.9, 113.9, 91.4, 82.7, 55.2, 45.8, 39.7, 39.4, 37.2, 36.5, 27.9, 23.8, 23.8. HRMS (ESI) calculated for $[C_{19}H_{26}NaO_2]$ $[M+Na]^+$: 309.1825 found: 309.1832. Enantiomeric excess was determined by HPLC with a Chiralpak IC+IC column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 20.47 min, minor enantiomer tr = 25.47 min.

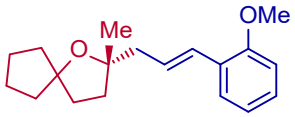


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.84	n.a.	382.411	636.893	49.85	n.a.	BMB*
2	25.17	n.a.	276.698	640.812	50.15	n.a.	BMB*
Total:			659.109	1277.704	100.00	0.000	



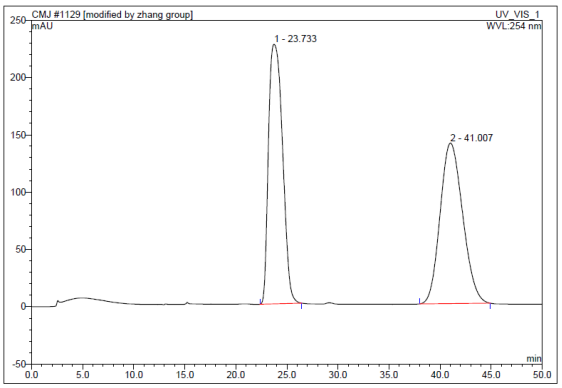
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.47	n.a.	39.276	63.688	5.10	n.a.	BMB*
2	25.47	n.a.	455.705	1186.216	94.90	n.a.	BMB*
Total:			494.981	1249.904	100.00	0.000	

4.1.35 (*S*, *E*)-2-(3-(2-methoxyphenyl)-allyl)-2-methyl-1-oxaspiro[4.4]nonane (6d)

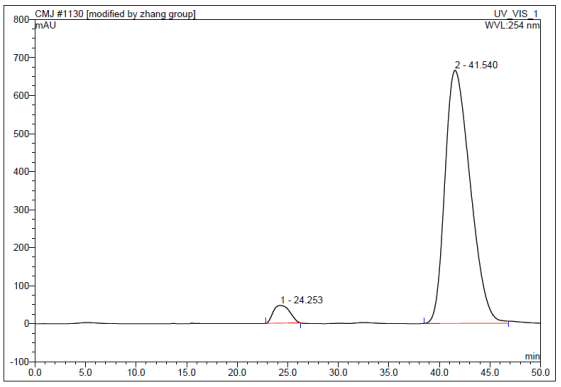


6d

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6d** as a white liquid (59 mg, 91% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -9.7 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.22 (m, 1H), 3.84 (s, 3H), 2.49 – 2.38 (m, 2H), 2.01 – 1.94 (m, 1H), 1.92 – 1.88 (m, 2H), 1.84 – 1.69 (m, 5H), 1.64 – 1.53 (m, 4H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 127.8, 127.7, 126.8, 126.8, 126.4, 120.6, 110.8, 91.4, 82.7, 55.4, 46.3, 39.8, 39.4, 37.2, 36.4, 28.0, 23.9, 23.8. HRMS (ESI) calculated for $[C_{19}H_{26}NaO_2]$ $[M+Na]^+$: 309.1825 found: 309.1817. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 41.54 min, minor enantiomer tr = 24.25 min.

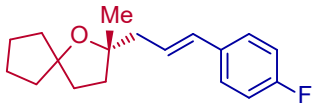


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.73	n.a.	226.529	360.978	50.17	n.a.	BMB*
2	41.01	n.a.	140.060	358.594	49.83	n.a.	BMB*
Total:			366.589	719.573	100.00	0.000	



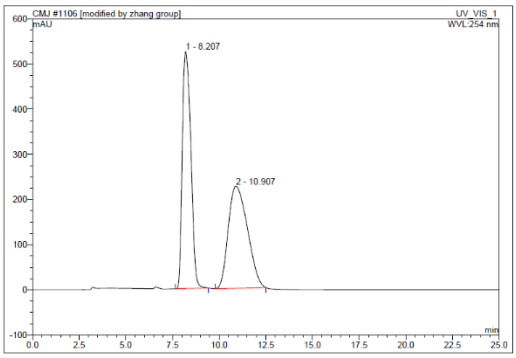
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.25	n.a.	46.364	88.746	4.40	n.a.	BMB*
2	41.54	n.a.	665.365	1929.304	95.60	n.a.	BM *
Total:			711.729	2018.050	100.00	0.000	

4.1.36 (*S*, *E*)-2-(3-(4-fluorophenyl)-allyl)-2-methyl-1-oxaspiro[4.4]nonane (6e)

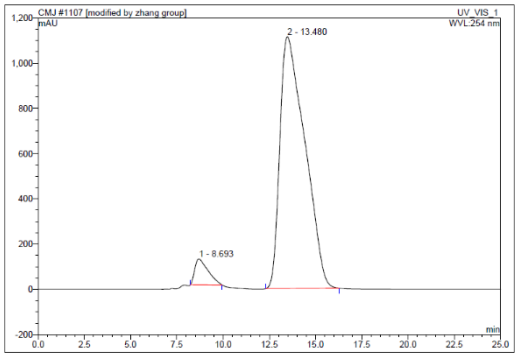


6e

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6e** as a white liquid (54 mg, 93% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -1.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.29 (m, 2H), 7.00 – 6.95 (m, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.20 – 6.12 (m, 1H), 2.38 (d, *J* = 7.2 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.87 – 1.85 (m, 1H), 1.83 – 1.71 (m, 5H), 1.63 – 1.54 (m, 4H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 244.2 Hz), 133.9 (d, *J* = 3.3 Hz), 131.1, 127.4 (d, *J* = 7.8 Hz), 126.9 (d, *J* = 2.2 Hz), 115.3 (d, *J* = 21.4 Hz), 91.5, 82.5, 45.8, 39.7, 39.4, 37.2, 36.6, 27.9, 23.8, 23.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.6. HRMS (ESI) calculated for $[C_{18}H_{23}NaFO]$ $[M+Na]^+$: 297.1625 found: 297.1613. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 13.48 min, minor enantiomer tr = 8.69 min.

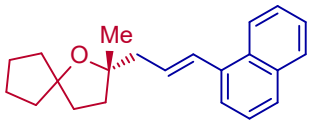


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.21	n.a.	524.517	278.913	50.91	n.a.	BMB*
2	10.91	n.a.	226.044	268.966	49.09	n.a.	BMB*
Total:			750.560	547.879	100.00	0.000	



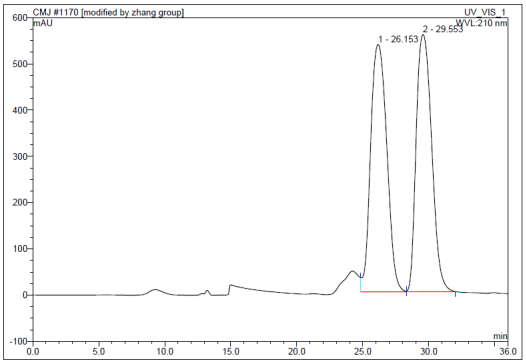
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.69	n.a.	113.657	93.937	5.11	n.a.	BMB*
2	13.48	n.a.	1113.249	1744.306	94.89	n.a.	BMB*
Total:			1226.907	1838.243	100.00	0.000	

4.1.37 (*S*, *E*)-2-methyl-2-(3-(naphthalen-1-yl)-allyl)-1-oxaspiro[4.4]nonane (6f)

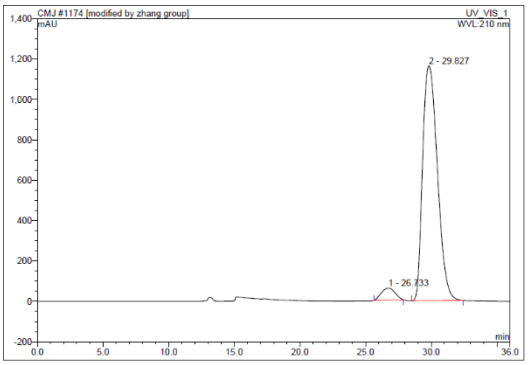


6f

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6f** as a white liquid (59 mg, 95% yield) with 91% *ee*. $[\alpha]_D^{20}$ = -12.2 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.86 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.18 (d, *J* = 15.6 Hz, 1H), 6.33 – 6.26 (m, 1H), 2.56 (d, *J* = 7.2 Hz, 2H), 2.08 – 1.99 (m, 1H), 1.96 – 1.92 (m, 2H), 1.87 – 1.76 (m, 5H), 1.67 – 1.55 (m, 4H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.5, 133.6, 131.1, 130.4, 129.5, 128.4, 127.3, 125.8, 125.6, 125.6, 123.9, 123.5, 91.5, 82.6, 46.3, 39.8, 39.5, 37.3, 36.6, 28.0, 23.9, 23.8. HRMS (ESI) calculated for $[C_{22}H_{26}NaO]$ $[M+Na]^+$: 329.1876 found: 329.1878. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 210 nm); major enantiomer tr = 29.83 min, minor enantiomer tr = 26.73 min.

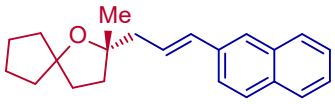


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.15	n.a.	534.916	761.249	50.16	n.a.	M *
2	29.55	n.a.	556.323	756.381	49.84	n.a.	MB*
Total:			1091.240	1517.631	100.00	0.000	



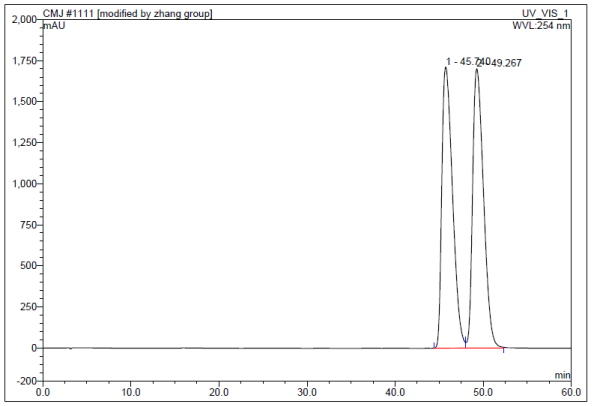
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.73	n.a.	59.608	72.137	4.54	n.a.	BMB*
2	29.83	n.a.	1163.639	1516.278	95.46	n.a.	BMB*
Total:			1223.247	1588.416	100.00	0.000	

4.1.38 (*S*, *E*)-2-methyl-2-(3-(naphthalen-2-yl)-allyl)-1-oxaspiro[4.4]nonane (6g)

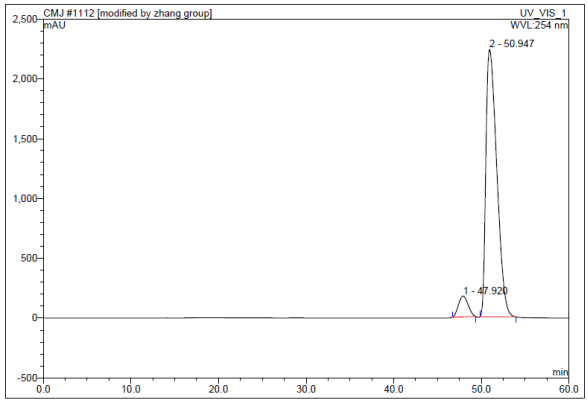


6g

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6g** as a white liquid (58 mg, 95% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -7.8 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 3H), 7.71 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.44 – 6.37 (m, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.07 – 1.98 (m, 1H), 1.94 – 1.90 (m, 2H), 1.87 – 1.76 (m, 5H), 1.66 – 1.55 (m, 4H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.2, 133.6, 132.7, 132.4, 128.0, 127.8, 127.6, 127.6, 126.1, 125.5, 125.4, 123.6, 91.5, 82.7, 46.0, 39.7, 39.4, 37.2, 36.6, 28.0, 23.9, 23.8. HRMS (ESI) calculated for $[C_{22}H_{26}NaO]$ $[M+Na]^+$: 329.1876 found: 329.1872. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJH column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 50.95 min, minor enantiomer tr = 47.92 min.

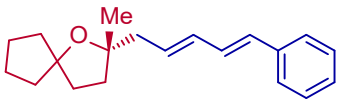


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	45.74	n.a.	1711.146	2405.939	49.63	n.a.	BM *
2	49.27	n.a.	1700.048	2441.483	50.37	n.a.	M *
Total:			3411.194	4847.422	100.00	0.000	



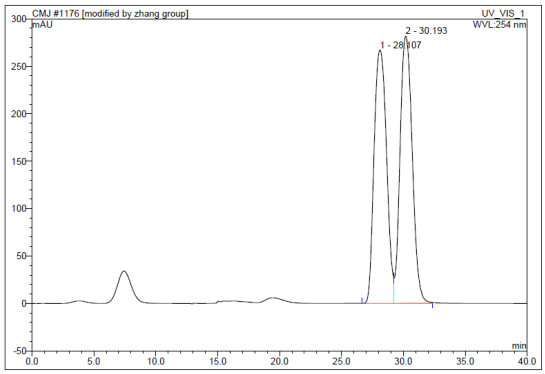
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	47.92	n.a.	175.122	223.399	6.49	n.a.	BMB*
2	50.95	n.a.	2235.016	3219.556	93.51	n.a.	BMB*
Total:			2410.137	3442.955	100.00	0.000	

4.1.39 (*S*)-2-methyl-2-((2*E*, 4*E*)-5-phenylpenta-2,4-dien-1-yl)-1-oxaspiro[4.4]nonane (6h)

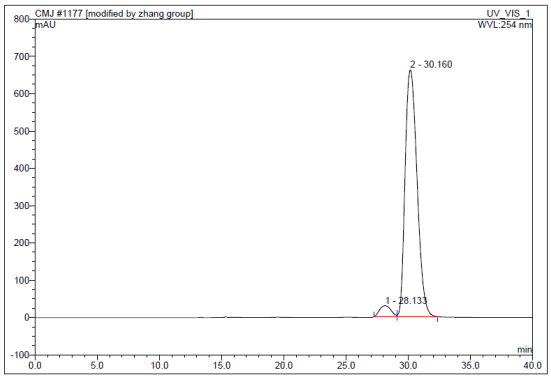


6h

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu8** (10 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product **6h** as a white liquid (57 mg, 96% yield) with 92% *ee*. $[\alpha]_D^{20}$ = -13.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 6.79 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.90 – 5.82 (m, 1H), 2.35 (d, *J* = 7.6 Hz, 2H), 1.93 – 1.87 (m, 3H), 1.81 – 1.71 (m, 5H), 1.64 – 1.50 (m, 4H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.5, 133.0, 131.8, 130.4, 129.3, 128.5, 127.1, 126.1, 91.4, 82.6, 45.8, 39.7, 39.4, 37.2, 36.7, 27.8, 23.9, 23.8. HRMS (ESI) calculated for $[C_{20}H_{26}NaO]$ $[M+Na]^+$: 305.1876 found: 305.1874. Enantiomeric excess was determined by HPLC with a Chiralpak OJH+OJ3 column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 30.16 min, minor enantiomer tr = 28.13 min.

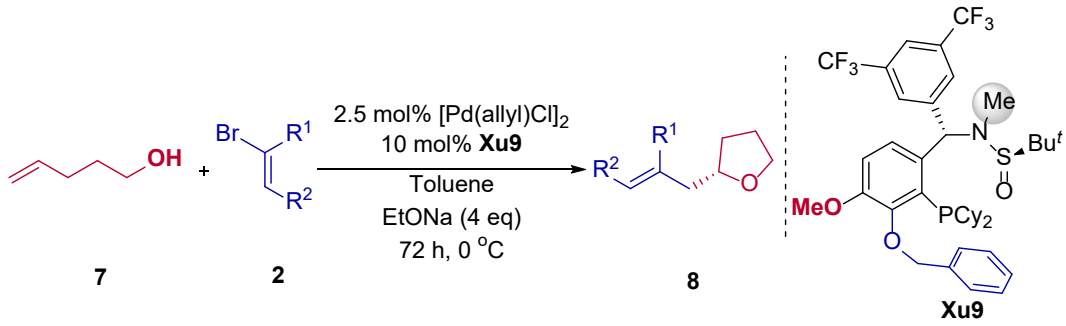


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.11	n.a.	267.061	312.245	49.30	n.a.	BM *
2	30.19	n.a.	281.624	321.071	50.70	n.a.	M *
Total:			548.684	633.316	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.13	n.a.	29.427	31.134	4.07	n.a.	BM *
2	30.16	n.a.	661.171	733.290	95.93	n.a.	MB*
Total:			690.599	764.424	100.00	0.000	

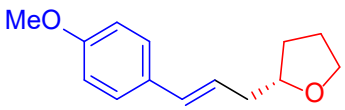
4.2 General Procedure for reactions of 4-penten-1-ol with alkenyl bromides



7 2 8 Xu9

To a sealed tube was added $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%). The flask was evacuated and refilled with argon. Then γ-hydroxyalkenes (0.5 mmol), alkenyl halides (1 mmol), EtONa (4.0 equiv.), and solution of toluene (3.5 mL) was added to the tube, and stirred at 0 °C for 72 hours. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product.

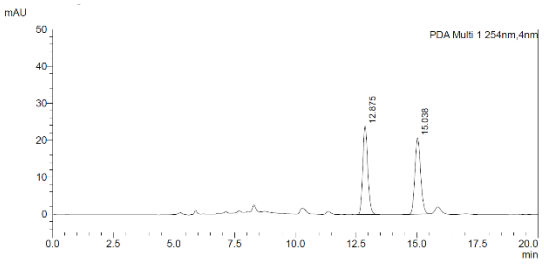
4.2.1 Synthesis of (*S*, *E*)-2-(3-(4-methoxyphenyl)allyl)tetrahydrofuran (8a)



8a

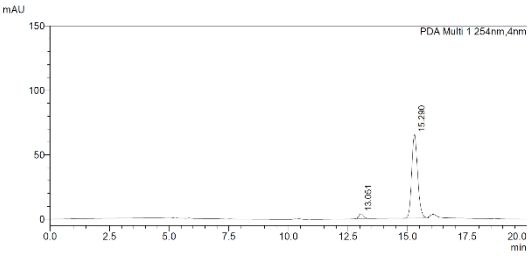
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8a** as a white liquid (74 mg, 68% yield) with 92% ee. $[\alpha]_D^{20}$ = -2.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.23 (m, 2H), 6.87 – 6.79 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.09 (dt,

J = 15.7, 7.1 Hz, 1H), 4.02 – 3.84 (m, 2H), 3.79 (s, 3H), 3.74 (q, *J* = 7.4 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.43 – 2.31 (m, 1H), 1.99 (tdd, *J* = 11.4, 7.0, 4.8 Hz, 1H), 1.89 (ddd, *J* = 12.3, 7.8, 6.2 Hz, 2H), 1.56 (dq, *J* = 11.7, 7.8 Hz, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 131.3, 130.4, 127.2, 124. 6, 113.9, 78.9, 68.0, 55.3, 39.3, 30.9, 25.8. HRMS (ESI) calculated for [$C_{14}H_{18}NaO_2$] [M+Na]$^+$: 241.1199 found: 241.1199. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 97: 3, 0.6 mL/min, 254 nm); major enantiomer tr = 15.290 min, minor enantiomer tr = 13.051 min.



<Peak Table>
PDA Ch1 254nm

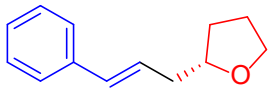
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.875	23959	53.696	341864	50.130
2	15.038	20660	46.304	340093	49.870
Total		44619	100.000	681957	100.000



<Peak Table>
PDA Ch1 254nm

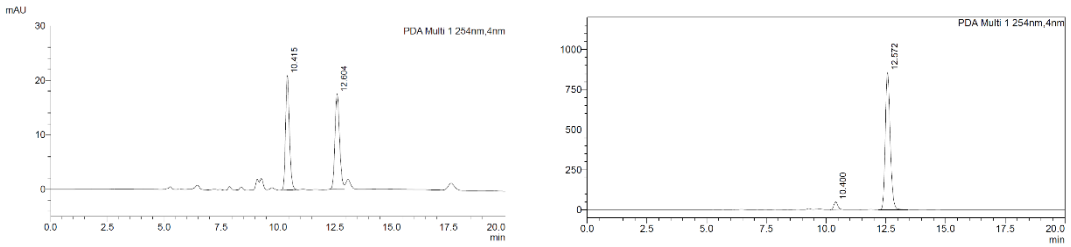
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.051	3559	5.198	48367	4.113
2	15.290	64906	94.802	1127608	95.887
Total		68465	100.000	1175975	100.000

4.2.2 Synthesis of (*S*)-2-cinnamyltetrahydrofuran (8b)



8b

Prepared according to typical procedure at 0 °C for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8b** as a white liquid (69 mg, 73% yield) with 92% ee. $[\alpha]_D^{20}$ = 1.3 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.05 – 3.85 (m, 2H), 3.82 – 3.68 (m, 1H), 2.57 – 2.44 (m, 1H), 2.45 – 2.32 (m, 1H), 1.98 (tdd, *J* = 9.3, 7.7, 4.3 Hz, 1H), 1.89 (ddd, *J* = 12.1, 7.9, 6.2 Hz, 2H), 1.63 – 1.46 (m, 1H).^{13}C NMR (101 MHz, Chloroform-*d*)δ 137.5, 131.9, 128.4, 127.0, 126.7, 126.0, 78.7, 67.9, 39.2, 30.8, 25.7. HRMS (ESI) calculated for [$C_{13}H_{17}O$] [M+H]$^+$: 189.1274 found: 189.1278. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 12.572 min, minor enantiomer tr = 10.400 min.



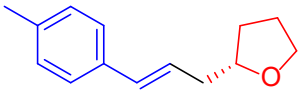
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.415	20994	54.535	247505	50.055
2	12.604	17503	45.465	246962	49.945
Total		38497	100.000	494466	100.000

<Peak Table>
PDA Ch1 254nm

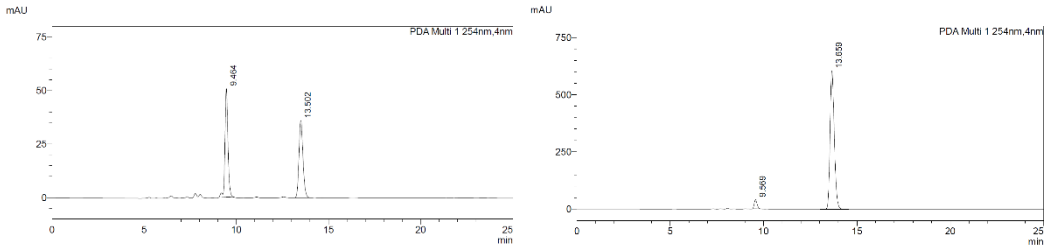
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.400	47743	5.284	529798	4.163
2	12.572	855751	94.716	12195728	95.837
Total		903495	100.000	12725526	100.000

4.2.3 Synthesis of (*S*, *E*)-2-(3-(p-tolyl)allyl)tetrahydrofuran (8c)



8c

Prepared according to typical procedure at 0 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8c** as a white liquid (65 mg, 64% yield) with 92% ee. $[\alpha]_D^{20}$ = -3.8 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.24 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.00 – 3.84 (m, 2H), 3.79 – 3.69 (m, 1H), 2.54 – 2.43 (m, 1H), 2.45 – 2.33 (m, 1H), 2.31 (s, 3H), 2.06 – 1.93 (m, 1H), 1.93 – 1.79 (m, 2H), 1.55 (dq, *J* = 11.7, 7.8 Hz, 1H).^{13}C NMR (100 MHz, Chloroform-*d*)δ 136.6, 134.7, 131.7, 129.1, 125.9, 125.6, 78.8, 67.9, 39.2, 30.7, 25.7, 21.0. HRMS (ESI) calculated for $[C_{22}H_{26}NaO]$ $[M+Na]^+$: 225.1250 found: 225.1245. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 13.659 min, minor enantiomer tr = 9.569 min.



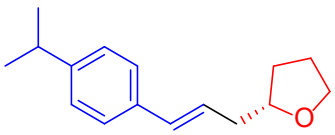
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.464	50684	58.462	550763	50.195
2	13.502	36011	41.538	546479	49.805
Total		86695	100.000	1097242	100.000

<Peak Table>
PDA Ch1 254nm

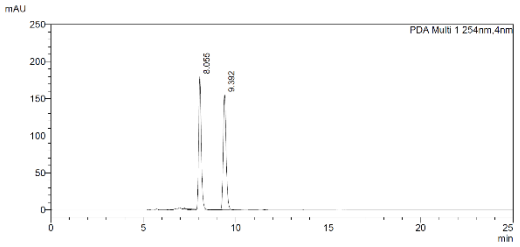
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.569	39713	6.153	410947	4.106
2	13.659	605713	93.847	9598708	95.894
Total		645425	100.000	10009655	100.000

4.2.4 Synthesis of (*S*, *E*)-2-(3-(4-isopropylphenyl)allyl)tetrahydrofuran (8d)



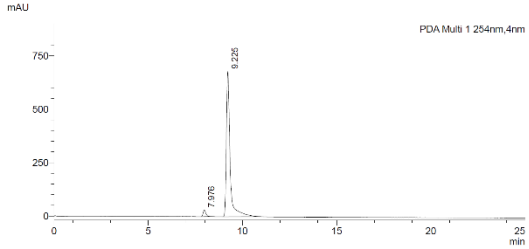
8d

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8d** as a white liquid (62 mg, 54% yield) with 94% ee. $[\alpha]_D^{20}$ = -5.9 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.01 – 3.82 (m, 2H), 3.82 – 3.67 (m, 1H), 2.87 (p, *J* = 6.9 Hz, 1H), 2.58 – 2.42 (m, 1H), 2.43 – 2.32 (m, 1H), 2.02 – 1.77 (m, 3H), 1.61 – 1.47 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 135.2, 131.8, 126.6, 126.1, 125.8, 78.9, 68.0, 39.3, 33.9, 30.8, 25.8, 24.0. HRMS (ESI) calculated for $[C_{16}H_{22}NaO]$ $[M+Na]^+$: 253.1563 found: 253.1565. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 9.225 min, minor enantiomer tr = 7.976 min.



<Peak Table>
PDA Ch1 254nm

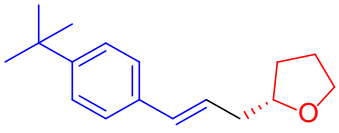
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.055	179306	53.561	1665650	49.220
2	9.392	155465	46.439	1718466	50.780
Total		334771	100.000	3384116	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.976	30472	4.290	307962	3.214
2	9.225	679861	95.710	9274605	96.786
Total		710333	100.000	9582567	100.000

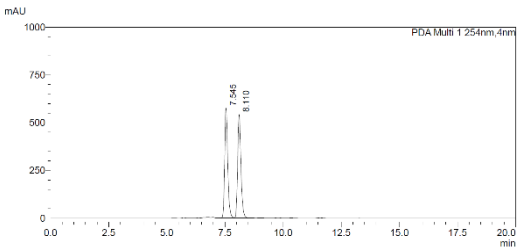
4.2.5 Synthesis of (*S*, *E*)-2-(3-(4-(tert-butyl)phenyl)allyl)tetrahydrofuran (8e)



8e

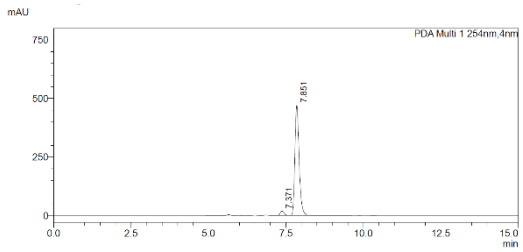
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8e** as a white liquid (82 mg, 67% yield) with 93% ee. $[\alpha]_D^{20}$ = -7.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 4H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.7, 7.1 Hz,

1H), 4.03 – 3.82 (m, 2H), 3.73 (td, *J* = 7.9, 6.6 Hz, 1H), 2.56 – 2.31 (m, 2H), 2.02 – 1.77 (m, 3H), 1.62 – 1.48 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.1, 134.8, 131.7, 125.9, 125.8, 125.4, 78.9, 68.0, 39.3, 34. 6, 31.4, 30.8, 25.8. HRMS (ESI) calculated for [$C_{17}H_{24}NaO$] [M+Na]$^+$: 267.1719 found: 267.1726. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 7.851 min, minor enantiomer tr = 7.371 min..



<Peak Table>
PDA Ch1 254nm

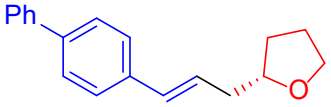
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.545	575694	51.498	5301871	50.000
2	8.110	542194	48.502	5301814	50.000
Total		1117888	100.000	10603685	100.000



<Peak Table>
PDA Ch1 254nm

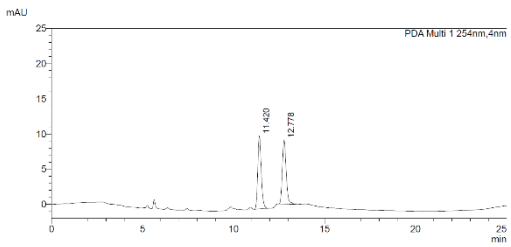
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.371	18870	3.851	165540	3.567
2	7.851	471087	96.149	4475553	96.433
Total		489957	100.000	4641092	100.000

4.2.6 Synthesis of (*S*, *E*)-2-(3-([1,1'-biphenyl]-4-yl)allyl)tetrahydrofuran (8f)



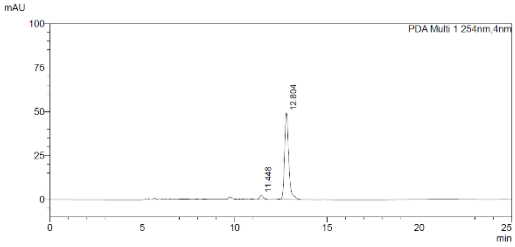
8f

Prepared according to typical procedure at 0 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8f** as a white solid (70 mg, 53% yield) with 92% ee. Mp: 79.5 – 83.1 ℃. $[\alpha]_D^{20}$ = 0.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.55 – 7.49 (m, 2H), 7.41 (dt, *J* = 7.8, 3.6 Hz, 4H), 7.36 – 7.26 (m, 1H), 6.54 – 6.43 (m, 1H), 6.28 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.04 – 3.84 (m, 2H), 3.74 (td, *J* = 7.8, 6.3 Hz, 1H), 2.51 (dtd, *J* = 14.8, 6.6, 1.4 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.98 (dddd, *J* = 11.3, 8.3, 6.3, 4.8 Hz, 1H), 1.92 – 1.81 (m, 2H), 1.56 (ddt, *J* = 11.5, 8.4, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.8, 139.8, 136.7, 131.5, 128.8, 127.2, 127.2, 127.0, 126.9, 126.6, 78.8, 68.1, 39.4, 30.9, 25.8. HRMS (ESI) calculated for [$C_{19}H_{20}NaO$] [M+Na]$^+$: 287.1406 found: 287.1401. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 12.804 min, minor enantiomer tr = 11.448 min.



<Peak Table>
PDA Ch1 254nm

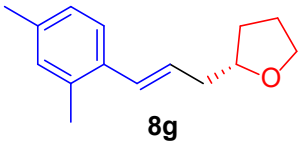
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.420	10350	53.281	137788	50.737
2	12.778	9076	46.719	133784	49.263
Total		19426	100.000	271573	100.000



<Peak Table>
PDA Ch1 254nm

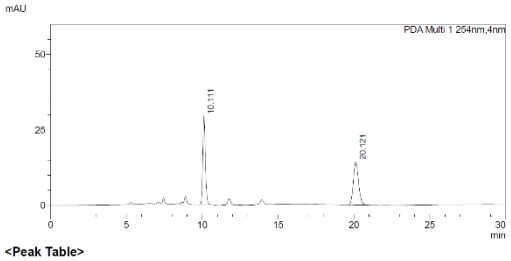
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.448	2358	4.573	30827	3.872
2	12.804	49212	95.427	765287	96.128
Total		51570	100.000	796114	100.000

4.2.7 Synthesis of (*S*, *E*)-2-(3-(2,4-dimethylphenyl)allyl)tetrahydrofuran (8g)



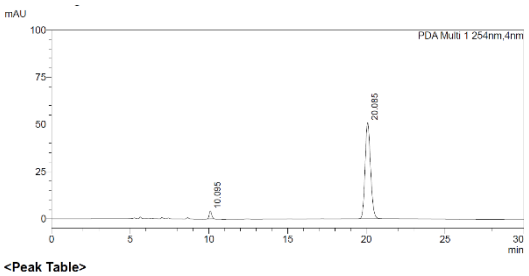
8g

Prepared according to typical procedure at 0 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8g** as a white liquid (62 mg, 57% yield) with 93% ee. $[\alpha]_D^{20}$ = -7.6 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.61 (d, *J* = 15.7 Hz, 1H), 6.05 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.02 – 3.83 (m, 2H), 3.74 (td, *J* = 7.9, 6.5 Hz, 1H), 2.52 (dddd, *J* = 13.2, 7.2, 5.9, 1.4 Hz, 1H), 2.46 – 2.35 (m, 1H), 2.29 (d, *J* = 5.1 Hz, 6H), 2.08 – 1.82 (m, 3H), 1.63 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.5, 134.7, 133.7, 130.8, 129.5, 127.0, 126.6, 125.3, 78.8, 67.9, 39.4, 30.7, 25.7, 21.0, 19.7. HRMS (ESI) calculated for $[C_{15}H_{20}NaO]$ $[M+Na]^+$: 239.1406 found: 239.1409. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 20.085 min, minor enantiomer tr = 10.095 min.



<Peak Table>
PDA Ch1 254nm

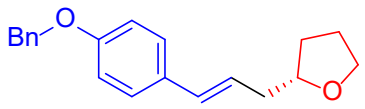
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.111	29278	67.233	340671	49.942
2	20.121	14269	32.767	341459	50.058
Total		43547	100.000	682129	100.000



<Peak Table>
PDA Ch1 254nm

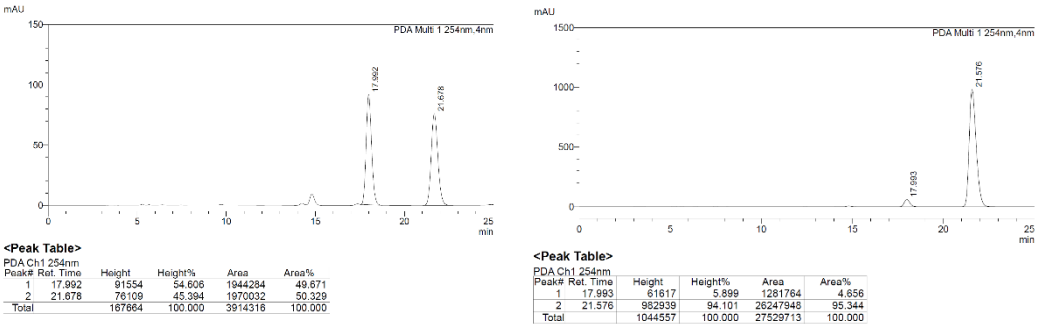
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.095	4190	7.603	45663	3.610
2	20.085	50923	92.397	1219312	96.390
Total		55113	100.000	1264975	100.000

4.2.8 Synthesis of (*S*, *E*)-2-(3-(4-(benzyloxy)phenyl)allyl)tetrahydrofuran (8h)

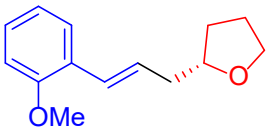


8h

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8h** as a white solid (83 mg, 56% yield) with 91% ee. Mp: 40.0 – 41.5 °C. $[\alpha]_D^{20}$ = -2.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.24 (m, 7H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.6, 7.1 Hz, 1H), 5.03 (s, 2H), 3.99 – 3.83 (m, 2H), 3.81 – 3.67 (m, 1H), 2.52 – 2.42 (m, 1H), 2.42 – 2.31 (m, 1H), 2.04 – 1.80 (m, 3H), 1.54 (dq, *J* = 11.7, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0, 137.0, 131.3, 130.7, 128.6, 128.0, 127.5, 127.2, 124.7, 114.9, 79.0, 70.0, 68.0, 39.3, 30.9, 25.8. HRMS (ESI) calculated for $[C_{20}H_{22}NaO_2]$ $[M+Na]^+$: 317.1512 found: 317.1509. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 21.576 min, minor enantiomer tr = 17.993 min.



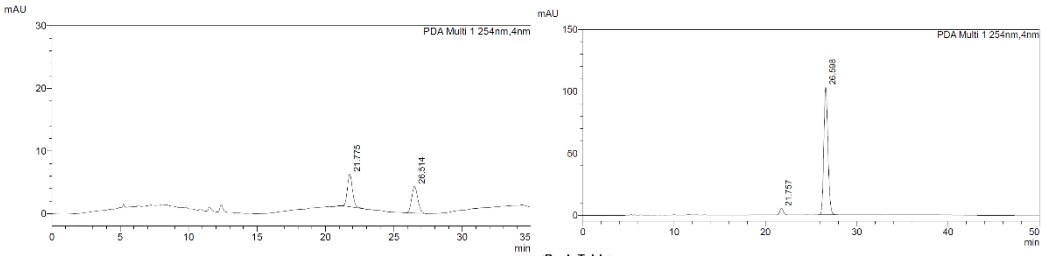
4.2.9 Synthesis of (*S*, *E*)-2-(3-(2-methoxyphenyl)allyl)tetrahydrofuran (8i)



8i

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8i** as a white liquid (70 mg, 64% yield) with 92% ee. $[\alpha]_D^{20}$ = -4.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 6.90 (td,

J = 7.5, 1.0 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.78 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.22 (dt, *J* = 15.9, 7.2 Hz, 1H), 4.01 – 3.86 (m, 2H), 3.83 (s, 3H), 3.74 (td, J = 7.9, 6.4 Hz, 1H), 2.53 (dddd, *J* = 14.6, 7.3, 6.1, 1.5 Hz, 1H), 2.41 (dddd, *J* = 13.9, 7.5, 6.5, 1.5 Hz, 1H), 2.07 – 1.79 (m, 3H), 1.63 – 1.54 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 128.1, 127.4, 126.6, 126.5, 120.6, 110.7, 79.0, 68.0, 55.5, 39.7, 30.8, 25.8. HRMS (ESI) calculated for [$C_{14}H_{18}NaO_2$] [M+Na]$^+$: 241.1199 found: 241.1205. Enantiomeric excess was determined by HPLC with a Chiralpak ODH column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 26.598 min, minor enantiomer tr = 21.757 min.



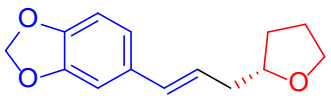
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.775	5229	55.025	137274	51.007
2	26.514	4274	44.975	131852	48.993
Total		9503	100.000	269126	100.000

<Peak Table>
PDA Ch1 254nm

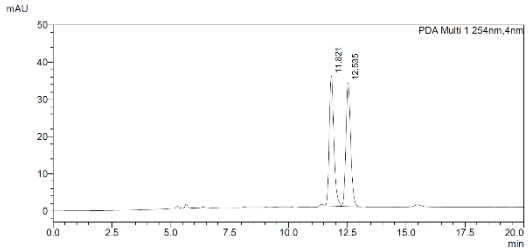
Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.757	5427	5.005	137850	4.092
2	26.598	103014	94.995	3231245	95.908
Total		108441	100.000	3369094	100.000

4.2.10 Synthesis of (*S*,*E*)-5-(3-(tetrahydrofuran-2-yl)prop-1-en-1-yl)benzo[d][1,3]dioxole (8j)



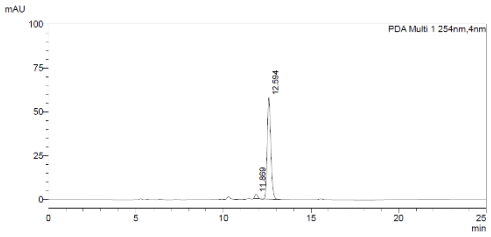
8j

Prepared according to typical procedure at 0 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8j** as a white liquid (54 mg, 56% yield) with 94% ee. $[\alpha]_D^{20}$ = 0.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 1.7 Hz, 1H), 6.82 – 6.67 (m, 2H), 6.35 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.13 – 5.99 (m, 1H), 5.92 (s, 2H), 4.00 – 3.83 (m, 2H), 3.74 (td, *J* = 7.9, 6.5 Hz, 1H), 2.53 – 2.30 (m, 2H), 2.04 – 1.78 (m, 3H), 1.54 (ddt, *J* = 11.7, 8.4, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 146.6, 132.0, 131.4, 124.9, 120.4, 108.1, 105.4, 100.9, 78.8, 67.9, 39.0, 30.8, 25.7. HRMS (ESI) calculated for [$C_{14}H_{16}NaO_3$] [M+Na]$^+$: 255.0992 found: 255.0989. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 12.594 min, minor enantiomer tr = 11.869 min.



<Peak Table>
PDA Ch1 254nm

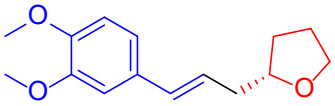
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.821	35024	51.244	473897	50.156
2	12.535	33324	48.756	470946	49.844
Total		68348	100.000	944843	100.000



<Peak Table>
PDA Ch1 254nm

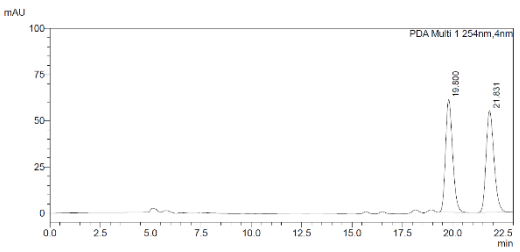
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.869	2512	4.152	27651	3.247
2	12.594	57995	95.848	823913	96.753
Total		60508	100.000	851564	100.000

4.2.11 Synthesis of (*S*, *E*)-2-(3-(3,4-dimethoxyphenyl)allyl)tetrahydrofuran (8k)



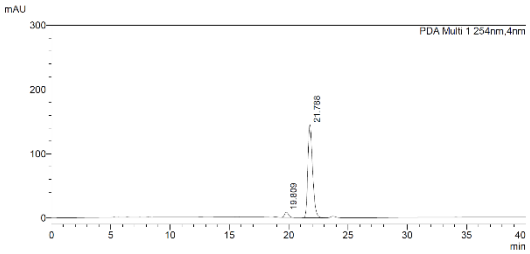
8k

Prepared according to typical procedure at 0 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8k** as a white liquid (54 mg, 44% yield) with 91% ee. $[\alpha]_D^{20}$ = 1.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 2.0 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.39 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.11 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.99 – 3.90 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.75 (td, *J* = 7.9, 6.4 Hz, 1H), 2.55 – 2.30 (m, 2H), 2.00 (dddd, *J* = 11.3, 8.4, 6.3, 4.9 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.57 (ddt, *J* = 11.6, 8.4, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.9, 148.4, 131.5, 130.7, 124.9, 119.1, 111.1, 108.5, 78.9, 68.0, 55.9, 55.8, 39.21, 30.9, 25.7. HRMS (ESI) calculated for $[C_{15}H_{20}NaO_3]$ $[M+Na]^+$: 271.1305 found: 271.1313. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 21.788 min, minor enantiomer tr = 19.809 min.



<Peak Table>
PDA Ch1 254nm

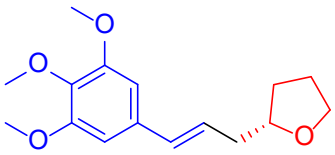
Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.800	61010	52.511	1490991	49.757
2	21.831	55174	47.489	1505550	50.243
Total		116184	100.000	2996542	100.000



<Peak Table>
PDA Ch1 254nm

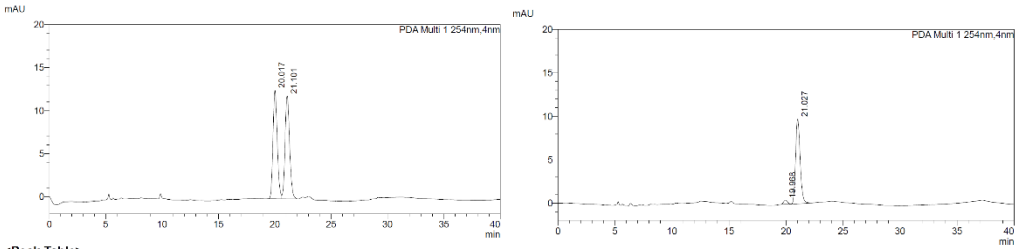
Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.809	8113	5.302	191973	4.536
2	21.788	144910	94.698	4040662	95.464
Total		153023	100.000	4232635	100.000

4.2.12 Synthesis of (*S*, *E*)-2-(3-(3,4,5-trimethoxyphenyl)allyl)tetrahydrofuran (8l)



8l

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8l** as a white liquid (52 mg, 37% yield) with 92% ee. $[\alpha]_D^{20}$ = 3.6 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.59 (s, 2H), 6.38 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.17 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.87 (s, 6H), 3.83 (s, 3H), 3.76 (td, *J* = 7.9, 6.4 Hz, 1H), 2.56 – 2.31 (m, 2H), 2.07 – 1.82 (m, 3H), 1.57 (ddt, *J* = 11.7, 8.5, 7.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.2, 137.4, 133.4, 131.8, 126.4, 103.1, 78.8, 68.0, 60.9, 56.0, 39.2, 30.9, 25.7. HRMS (ESI) calculated for $[C_{16}H_{22}NaO_4]$ $[M+Na]^+$: 301.1410 found: 301.1415. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr =21.027 min, minor enantiomer tr = 19.968 min.



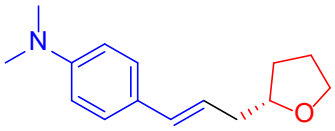
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.017	12630	51.358	330939	49.807
2	21.101	11963	48.642	333501	50.193
Total		24593	100.000	664439	100.000

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.968	477	4.672	11163	3.966
2	21.027	9732	95.328	270334	96.034
Total		10209	100.000	281497	100.000

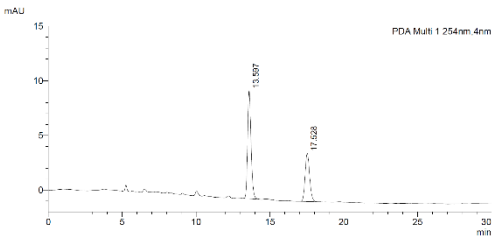
4.2.13 Synthesis of (*S*, *E*)-N,N-dimethyl-4-(3-(tetrahydrofuran-2-yl)prop-1-en-1-yl)aniline (8m)



8m

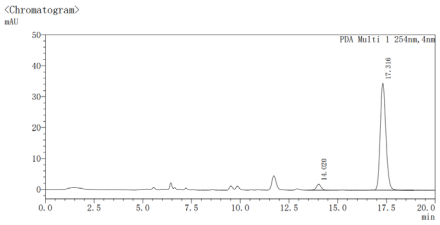
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8m** as a white liquid (60 mg, 52% yield) with 91% ee. $[\alpha]_D^{20}$ = -6.7 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.16 (m, 2H), 6.76 – 6.60 (m, 2H), 6.42 – 6.29 (m, 1H), 6.01 (dt,

J = 15.8, 7.2 Hz, 1H), 4.07 – 3.80 (m, 2H), 3.73 (td, J = 7.9, 6.4 Hz, 1H), 2.92 (s, 6H), 2.47 (dddd, J = 14.5, 7.3, 6.0, 1.5 Hz, 1H), 2.35 (dddd, J = 13.9, 7.6, 6.5, 1.4 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.93 – 1.78 (m, 2H), 1.55 (ddt, J = 11.7, 8.6, 7.5 Hz, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.8, 131.8, 127.0, 126.4, 122.4, 112.6, 79.2, 68.0, 40.6, 39.3, 30.8, 25.8. HRMS (ESI) calculated for [$C_{15}H_{22}NO$] [M+Na]$^+$: 232.1696 found: 232.1698. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 17.316 min, minor enantiomer tr = 14.020 min. (Note: The mixture of 8m and ent-8m with different concentration to gain the HPLC time, all HPLC time difference are less than one minute.)



<Peak Table>
PDA Ch1 254nm

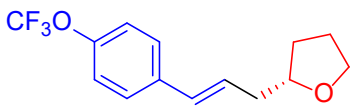
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.597	9889	69.079	161482	63.476
2	17.528	4427	30.921	92918	36.524
Total		14316	100.000	254399	100.000



<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	14.020	1939	5.315	32398	4.456
2	17.316	34550	94.685	694591	95.544
Total		36489	100.000	726988	100.000

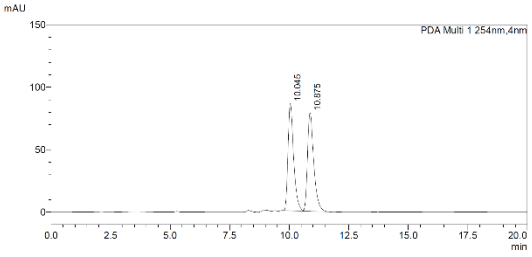
4.2.14 Synthesis of (*S*, *E*)-2-(3-(4-(trifluoromethoxy)phenyl)allyl)tetrahydrofuran (8n)



8n

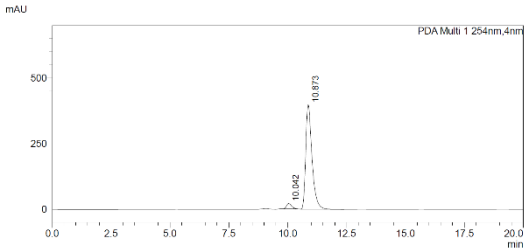
Prepared according to typical procedure at 0 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8n** as a white liquid (67 mg, 49% yield) with 92% ee. $[\alpha]_D^{20}$ = 4.1 (c = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.44 (d, J = 15.9 Hz, 1H), 6.23 (dt, J = 15.8, 7.1 Hz, 1H), 4.02 – 3.83 (m, 2H), 3.82 – 3.68 (m, 1H), 2.53 – 2.32 (m, 2H), 1.95 (dddd, J = 36.0, 14.7, 7.2, 4.4 Hz, 3H), 1.55 (dq, J = 11.6, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.1 (d, J = 1.9 Hz), 136.4, 130.5, 128.1, 127.2, 121.0, 120.5 (d, J = 256.8 Hz). 78.6, 68.0, 39.2, 30.9, 25.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.91. HRMS (ESI) calculated for [$C_{14}H_{15}F_3NaO_2$] [M+Na]$^+$: 295.0916 found: 295.0909. Enantiomeric excess was determined by

HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254nm); major enantiomer tr = 10.873 min, minor enantiomer tr = 10.042 min.



<Peak Table>
PDA Ch1 254nm

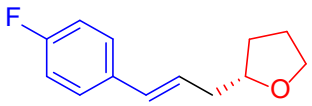
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.045	85789	52.098	1418330	49.535
2	10.875	78879	47.902	1444936	50.465
Total		164669	100.000	2863266	100.000



<Peak Table>
PDA Ch1 254nm

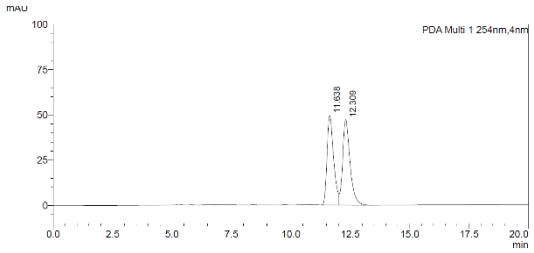
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.042	20344	4.868	311600	4.056
2	10.873	397567	95.132	7371144	95.944
Total		417911	100.000	7682745	100.000

4.2.15 Synthesis of (*S*, *E*)-2-(3-(4-fluorophenyl)allyl)tetrahydrofuran (8o)



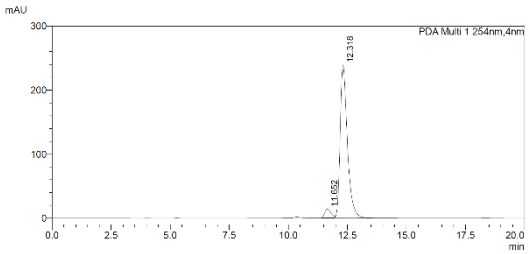
8o

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8o** as a white liquid (52 mg, 50% yield) with 91% ee. $[\alpha]_D^{20} = 3.3$ (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.07 – 6.91 (m, 2H), 6.48 – 6.35 (m, 1H), 6.15 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.06 – 3.84 (m, 2H), 3.75 (td, *J* = 7.9, 6.4 Hz, 1H), 2.55 – 2.24 (m, 2H), 2.00 (dddd, *J* = 11.3, 8.4, 6.3, 4.9 Hz, 1H), 1.96 – 1.80 (m, 2H), 1.56 (ddt, *J* = 11.6, 8.4, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.8 Hz), 133.7 (d, *J* = 3.3 Hz), 130.7, 127.5 (d, *J* = 7.8 Hz), 126.6 (d, *J* = 2.3 Hz), 115.3 (d, *J* = 21.5 Hz), 78.8, 68.0, 39.2, 30.9, 25.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.44. HRMS (ESI) calculated for $[C_{13}H_{15}FNaO]$ $[M+Na]^+$: 229.0999 found: 229.0999. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 12.318 min, minor enantiomer tr = 11.652 min.



<Peak Table>
PDA Ch1 254nm

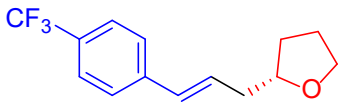
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.638	49440	51.142	952266	48.197
2	12.309	47232	48.858	1023516	51.803
Total		96672	100.000	1975782	100.000



<Peak Table>
PDA Ch1 254nm

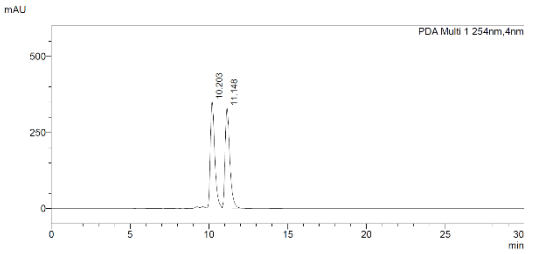
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.652	13674	5.412	249482	4.684
2	12.318	238961	94.588	5076296	95.316
Total		252635	100.000	5325758	100.000

4.2.16 Synthesis of (*S*, *E*)-2-(3-(4-(trifluoromethyl)phenyl)allyl)tetrahydrofuran (8p)



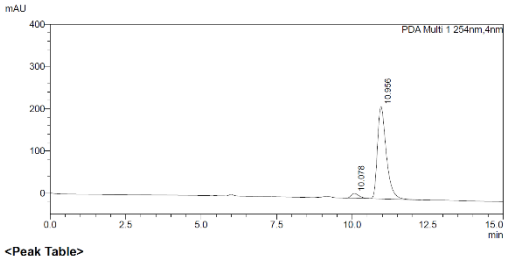
8p

Prepared according to typical procedure at 0 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8p** as a white liquid (74 mg, 58% yield) with 91% ee. $[\alpha]_D^{20}$=3.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.19 – 7.07 (m, 2H), 6.44 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.23 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.05 – 3.85 (m, 2H), 3.75 (td, *J* = 7.8, 6.4 Hz, 1H), 2.54 – 2.34 (m, 2H), 2.07 – 1.80 (m, 3H), 1.62 – 1.44 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.13, 148.11, 136.38, 130.47, 128.06, 127.22, 121.77, 120.97, 119.21, 78.64, 67.98, 39.14, 30.91, 25.70. ^{19}F NMR (376 MHz, CDCl3) δ -57.92. HRMS (ESI) calculated for $[C_{14}H_{16}F_3O]$ $[M+H]^+$: 257.1148 found: 257.1145. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 10.956 min, minor enantiomer tr = 10.078 min.



<Peak Table>
PDA Ch1 254nm

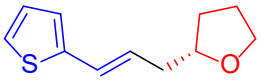
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.203	349182	51.530	6748061	49.813
2	11.148	328451	48.470	6798604	50.187
Total		677633	100.000	13546665	100.000



<Peak Table>
PDA Ch1 254nm

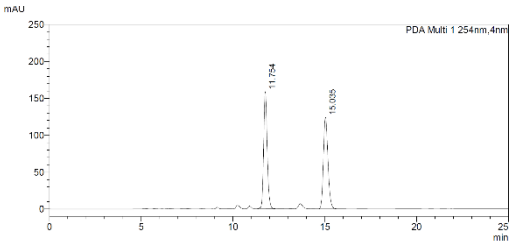
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.078	11204	4.867	206445	4.424
2	10.956	218974	95.133	4459941	95.576
Total		230178	100.000	4666385	100.000

4.2.17 Synthesis of (*S*, *E*)-2-(3-(thiophen-2-yl)allyl)tetrahydrofuran (8q)



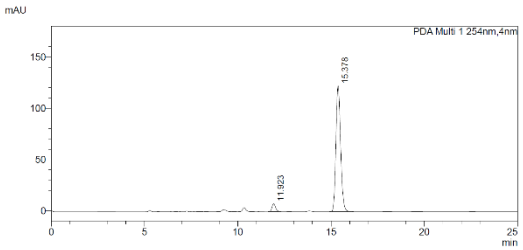
8q

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8q** as a white liquid (64 mg, 65% yield) with 91% ee. $[\alpha]_D^{20}$ = 5.3 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (dt, *J* = 5.1, 0.8 Hz, 1H), 6.97 – 6.84 (m, 2H), 6.58 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.07 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.01 – 3.84 (m, 2H), 3.74 (td, *J* = 7.8, 6.4 Hz, 1H), 2.54 – 2.26 (m, 2H), 2.00 (dddd, *J* = 11.4, 8.4, 6.4, 4.9 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.55 (ddt, *J* = 11.7, 8.4, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 127.2, 126.7, 125.2, 124.7, 123.4, 78.6, 68.0, 39.1, 30.9, 25.8. HRMS (ESI) calculated for $[C_{11}H_{15}OS]$ $[M+H]^+$:195.0838 found: 195.837. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 15.378 min, minor enantiomer tr = 11.923 min.



<Peak Table>
PDA Ch1 254nm

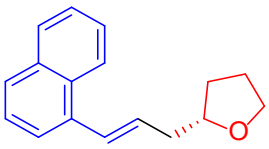
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.754	158840	56.135	2136142	50.154
2	15.035	124119	43.865	2122985	49.846
Total		282959	100.000	4259127	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.923	7758	5.955	102316	4.570
2	15.378	122514	94.045	2136413	95.430
Total		130271	100.000	2238729	100.000

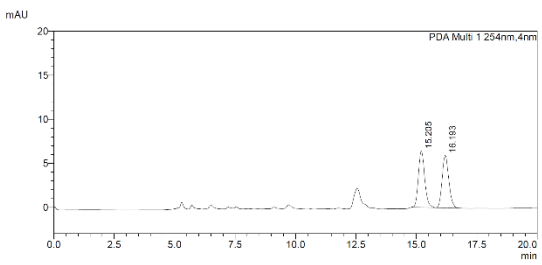
4.2.18 Synthesis of (*S*, *E*)-2-(3-(naphthalen-1-yl)allyl)tetrahydrofuran (8r)



8r

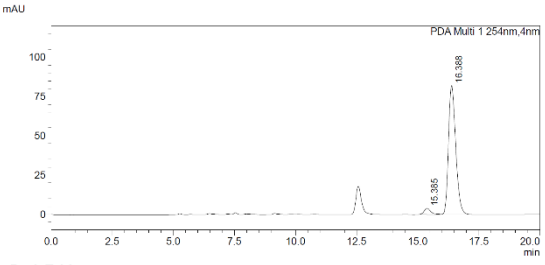
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8r** as a white liquid (79 mg, 66% yield) with 92% ee. $[\alpha]_D^{20}$ = -4.0 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.06 (m, 1H), 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H),

7.57 (dt, *J* = 7.1, 0.9 Hz, 1H), 7.53 – 7.39 (m, 3H), 7.19 (d, *J* = 15.6 Hz, 1H), 6.25 (dt, *J* = 15.5, 7.1 Hz, 1H), 4.03 (dq, *J* = 7.7, 6.3 Hz, 1H), 3.93 (ddd, *J* = 8.3, 7.2, 6.2 Hz, 1H), 3.77 (td, *J* = 7.9, 6.4 Hz, 1H), 2.58 (ddddd, *J* = 44.9, 14.0, 7.6, 6.3, 1.5 Hz, 2H), 2.04 (dddd, *J* = 11.6, 8.5, 6.5, 4.9 Hz, 1H), 1.99 – 1.81 (m, 2H), 1.69 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.4, 133.6, 131.1, 130.1, 129.2, 128.5, 127.5, 125.9, 125.7, 123.9, 123.7, 78.8, 68.1, 39.6, 30.9, 25.8. HRMS (ESI) calculated for [$C_{17}H_{18}NaO$] [M+Na]$^+$: 261.1250 found: 261.1256. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 16.388 min, minor enantiomer tr = 15.385 min.



<Peak Table>
PDA Ch1 254nm

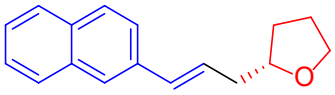
Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.205	6399	51.745	115888	50.176
2	16.193	5967	48.255	115076	49.824
Total		12366	100.000	230964	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.385	3810	4.439	72662	4.124
2	16.388	82021	95.561	1689255	95.876
Total		85831	100.000	1761918	100.000

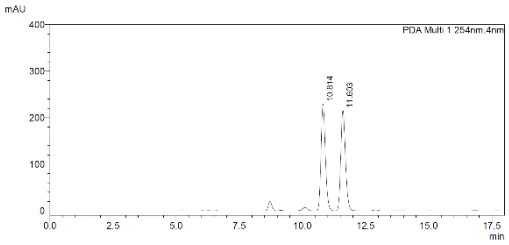
4.2.19 Synthesis of (*S*, *E*)-2-(3-(naphthalen-2-yl)allyl)tetrahydrofuran (8s)



8s

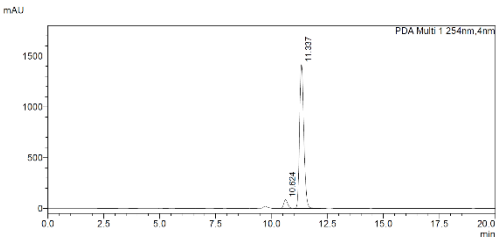
Prepared according to typical procedure at 0 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8s** as a yellow solid (69 mg, 58% yield) with 90% ee. Mp: 31.2– 34.3 ℃. $[\alpha]_D^{20}$ = 0.9 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.75 (t, *J* = 8.3 Hz, 3H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.40 (pd, *J* = 7.0, 1.4 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.07 – 3.85 (m, 2H), 3.81 – 3.69 (m, 1H), 2.48 (dq, *J* = 30.7, 7.2 Hz, 2H), 2.05 – 1.93 (m, 1H), 1.93 – 1.79 (m, 2H), 1.56 (dq, *J* = 11.7, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 134.9, 133.5, 132.6, 131.9, 127.9, 127.8, 127.5, 127.2, 126.0, 125.6, 125.5, 123.5, 78.7, 67.9, 39.3, 30.8, 25.6. HRMS (ESI) calculated for [$C_{17}H_{18}NaO$] [M+Na]$^+$: 261.1250 found: 261.1255. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes:

2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 11.337 min, minor enantiomer tr = 10.624 min.



<Peak Table>
PDA Ch1 254nm

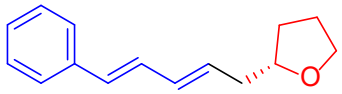
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.814	229931	51.566	2769786	49.873
2	11.603	215963	48.434	2783912	50.127
Total		445894	100.000	5553697	100.000



<Peak Table>
PDA Ch1 254nm

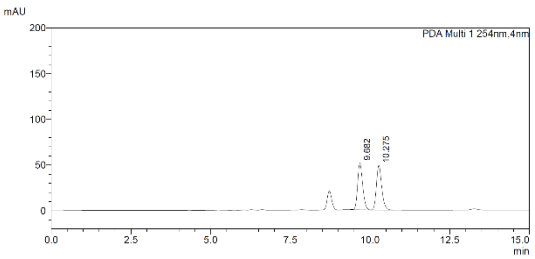
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.624	86975	5.776	1036500	5.191
2	11.337	1418805	94.224	18932652	94.809
Total		1505781	100.000	19969152	100.000

4.2.20 Synthesis of (*S*)-2-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)tetrahydrofuran (8t)



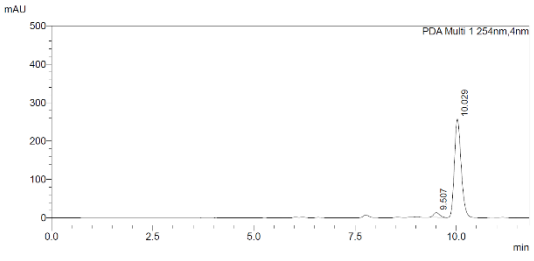
8t

Prepared according to typical procedure at 0 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8t** as a white liquid (78 mg, 73% yield) with 91% ee. $[\alpha]_D^{20}$ = 4.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.29 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.23 – 7.15 (m, 1H), 6.76 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.36 – 6.19 (m, 1H), 5.83 (dt, *J* = 14.9, 7.3 Hz, 1H), 4.01 – 3.83 (m, 2H), 3.74 (td, *J* = 7.9, 6.5 Hz, 1H), 2.51 – 2.27 (m, 2H), 2.06 – 1.77 (m, 3H), 1.53 (ddt, *J* = 11.8, 8.5, 7.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 132.6, 131.4, 130.7, 129.2, 128.6, 127.2, 126.2, 78.8, 68.0, 39.1, 30.9, 25.7. HRMS (ESI) calculated for $[C_{15}H_{18}NaO]$ $[M+Na]^+$: 237.1250 found: 237.1249. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr =9.507 min, minor enantiomer tr = 10.029 min.



<Peak Table>
PDA Ch1 254nm

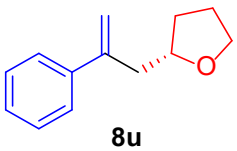
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.682	51207	51.164	568802	49.875
2	10.275	48877	48.836	571648	50.125
Total		100085	100.000	1140450	100.000



<Peak Table>
PDA Ch1 254nm

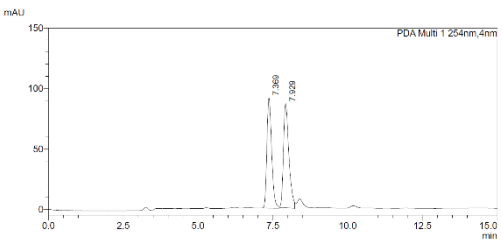
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.507	12468	4.628	133356	4.277
2	10.029	256942	95.372	2984693	95.723
Total		269410	100.000	3118049	100.000

4.2.21 Synthesis of (*S*)-2-(2-phenylallyl)tetrahydrofuran (8u)



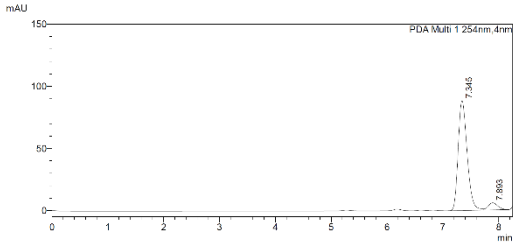
8u

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8u** as a white liquid (32 mg, 34% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -1.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.32 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 2H), 7.29 – 7.26 (m, 1H), 5.34 (d, *J* = 1.5 Hz, 1H), 5.15 (q, *J* = 1.3 Hz, 1H), 4.00 – 3.84 (m, 2H), 3.69 (td, *J* = 8.2, 6.2 Hz, 1H), 2.88 (ddd, *J* = 14.3, 6.5, 1.3 Hz, 1H), 2.60 (ddd, *J* = 14.3, 7.0, 1.2 Hz, 1H), 1.97 – 1.73 (m, 3H), 1.58 – 1.43 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.7, 141.1, 128.5, 128.3, 127.4, 126.2, 126.1, 114.2, 77.6, 67.8, 41.6, 31.1, 25.6. HRMS (ESI) calculated for $[C_{13}H_{17}O]$ $[M+H]^+$: 189.1274 found: 189.1278. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 7.345 min, minor enantiomer tr = 7.893 min.



<Peak Table>
PDA Ch1 254nm

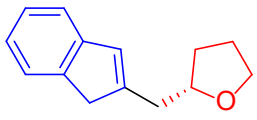
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.389	91287	51.415	1010353	48.224
2	7.929	86261	48.585	1084779	51.776
Total		177548	100.000	2095132	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.345	88434	93.855	989897	93.596
2	7.893	5790	6.145	67731	6.404
Total		94224	100.000	1057628	100.000

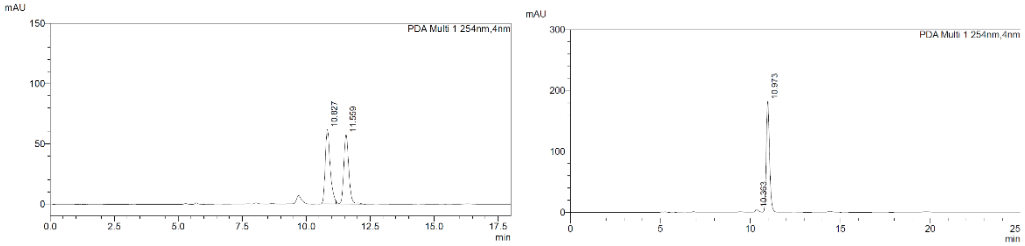
4.2.22 Synthesis of (*S*)-2-((1H-inden-2-yl)methyl)tetrahydrofuran (8v)



8v

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8v** as a white liquid (82 mg, 82% yield) with 95% *ee*. $[\alpha]_D^{20}$ = -3.7 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.38 (dq, *J* = 7.4, 0.9 Hz, 1H), 7.28 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.21 (td, *J*

= 7.4, 1.0 Hz, 1H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 6.61 – 6.57 (m, 1H), 4.11 (dq, *J* = 7.6, 6.4 Hz, 1H), 3.91 (ddd, *J* = 8.3, 7.1, 6.2 Hz, 1H), 3.75 (td, *J* = 7.9, 6.5 Hz, 1H), 3.42 – 3.34 (m, 2H), 2.78 (ddd, *J* = 14.8, 6.6, 1.3 Hz, 1H), 2.66 (ddd, *J* = 14.8, 6.2, 1.1 Hz, 1H), 2.02 (dddd, *J* = 11.6, 8.4, 6.4, 5.0 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.59 – 1.51 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.1, 145.4, 143.3, 128.0, 126.2, 123.8, 123.4, 120.1, 78.6, 67.9, 41.7, 37.4, 31.3, 25.7. HRMS (ESI) calculated for [$C_{14}H_{17}O$] [M+H]$^+$: 201.1274 found: 201.1278. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 10.973 min, minor enantiomer tr = 10.363 min.



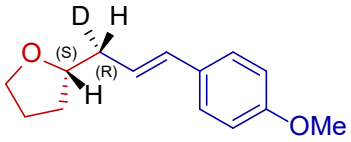
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.827	61939	51.817	833252	51.710
2	11.559	57596	48.183	778144	48.290
Total		119535	100.000	1611396	100.000

<Peak Table>
PDA Ch1 254nm

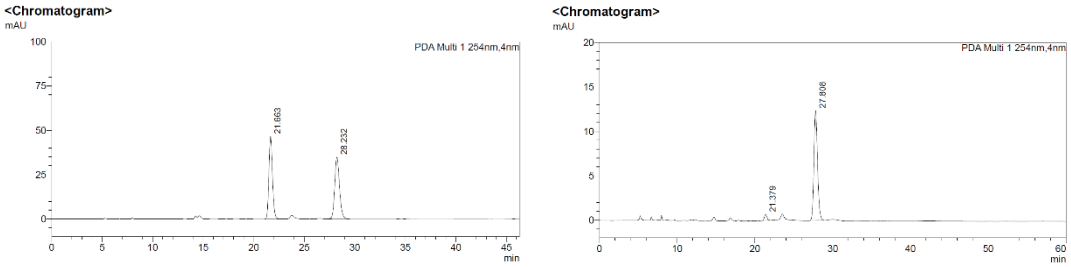
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.363	4796	2.567	57272	2.428
2	10.973	182044	97.433	2301977	97.572
Total		186840	100.000	2359248	100.000

4.2.23 Synthesis of (*S*)-2-((*R*, *E*)-3-(4-methoxyphenyl)allyl-1-d)tetrahydrofuran (8-D)



8-D

Prepared according to typical procedure at 0 ºC for 36 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from D-γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **8-D** as a white liquid (68 mg, 62% yield) with 92% *ee*, >20:1 dr. $[\alpha]_D^{20}$ = -2.5 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.89 – 6.77 (m, 2H), 6.39 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.0 Hz, 1H), 3.98 – 3.85 (m, 2H), 3.78 (s, 3H), 3.74 (td, *J* = 7.9, 6.4 Hz, 1H), 2.45 (td, *J* = 6.7, 1.7 Hz, 1H), 1.98 (dddd, *J* = 11.4, 8.6, 6.4, 4.9 Hz, 1H), 1.92 – 1.79 (m, 2H), 1.55 (ddt, *J* = 11.7, 8.5, 7.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 131.2, 130.3, 127.1, 124.4, 113.8, 78.8, 67.9, 55.2, 39.1-38.4 (m), 30.7, 25.7.RMS (ESI) calculated for [$C_{14}H_{17}DNaO_2$] [M+Na]$^+$: 242.1262 found: 242.1258. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 27.808 min, minor enantiomer tr = 21.379 min.



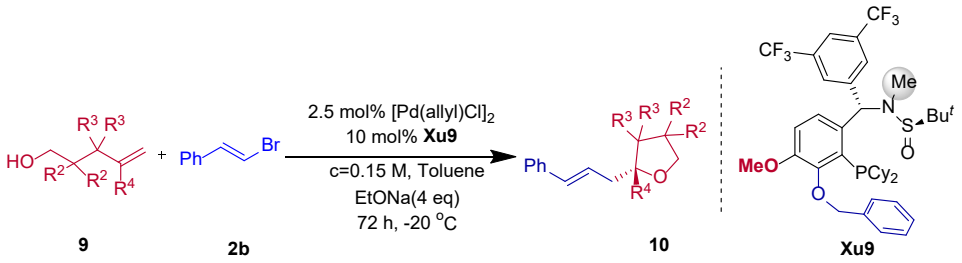
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.663	46657	57.187	1151447	49.928
2	28.232	34929	42.813	1154755	50.072
Total		81586	100.000	2306202	100.000

<Peak Table>
PDA Ch1 254nm

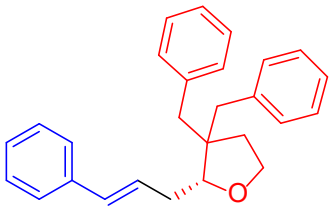
Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.379	681	5.216	15769	3.804
2	27.808	12371	94.784	398785	96.196
Total		13051	100.000	414554	100.000

4.3 General procedure for reactions of primary /secondary γ-hydroxy alkenes with 2b



To a sealed tube was added $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%). The flask was evacuated and refilled with argon. Then γ-hydroxyalkenes (0.5 mmol), alkenyl halides (1 mmol), EtONa (4.0 equiv.), and solution of toluene (3.5 mL) was added to the tube, and stirred at -20 ºC for 72 hours. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product.

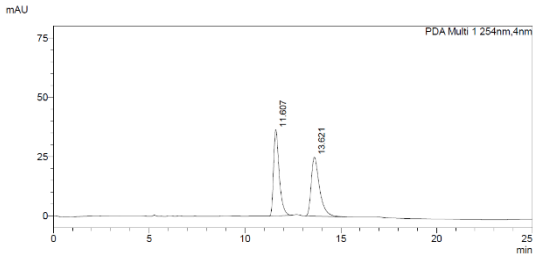
4.3.1 Synthesis of (*R*)-3,3-dibenzyl-2-cinnamyltetrahydrofuran (10a)



10a

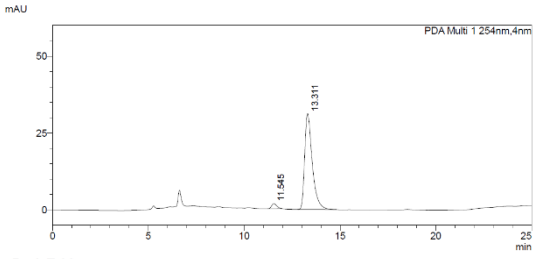
Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes **9a** (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10a** as a white liquid (116 mg, 63% yield) with 93% *ee*. $[\alpha]_D^{20}$ = 59.5 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 4H), 7.30 – 7.16 (m, 9H), 7.05 – 7.00 (m, 2H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.00 – 3.89 (m, 1H), 3.67 (ddt, *J* = 9.7, 6.7, 3.2

Hz, 2H), 2.88 – 2.73 (m, 3H), 2.68 – 2.60 (m, 1H), 2.56 – 2.42 (m, 2H), 1.83 (ddd, *J* = 12.8, 7.4, 3.2 Hz, 1H), 1.67 – 1.57 (m, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.7, 137.6, 137.4, 131.6, 131.0, 130.9, 128.5, 128.2, 128.1, 128.0, 127.1, 126.4, 126.2, 82.8, 65.1, 48.0, 39.9, 38.7, 33.1, 31.7. HRMS (ESI) calculated for [$C_{27}H_{28}NaO$] [M+Na]$^+$: 391.2032 found: 391.2022. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 13.311 min, minor enantiomer tr = 11.545 min.



<Peak Table>
PDA Ch1 254nm

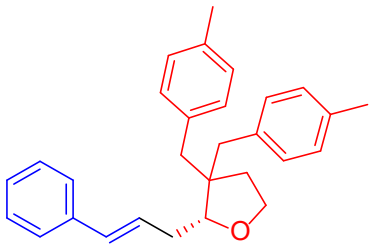
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.607	36318	59.387	741970	49.824
2	13.621	24837	40.613	747222	50.176
Total		61155	100.000	1489192	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.545	1679	5.105	31366	3.526
2	13.311	31207	94.895	858270	96.474
Total		32885	100.000	889636	100.000

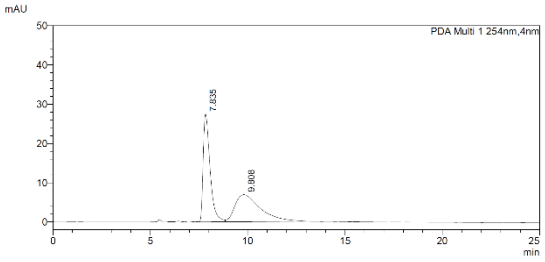
4.3.2 Synthesis of (*R*)-2-cinnamyl-3,3-bis(4-methylbenzyl)tetrahydrofuran (10b)



10b

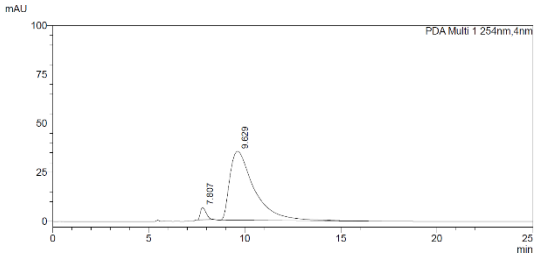
Prepared according to typical procedure at -20 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10b** as a white liquid (116 mg, 63% yield) with 92% *ee*. $[\alpha]_D^{20}$ = 41.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.28 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.21 – 7.09 (m, 5H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.86 (m, 2H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.99 – 3.87 (m, 1H), 3.66 (ddd, *J* = 9.4, 8.3, 3.1 Hz, 2H), 2.84 – 2.68 (m, 3H), 2.63 – 2.56 (m, 1H), 2.48 (dddt, *J* = 13.2, 6.7, 3.0, 1.4 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.82 (ddd, *J* = 12.7, 7.4, 3.1 Hz, 1H), 1.66 – 1.57 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 135.8, 135.5, 134.3, 131.4, 130.8, 130.8, 128.9, 128.8, 128.5, 128.1, 127.0, 126.2, 82.8, 65.1, 48.0, 39.4, 38.2, 33.1, 31.6, 21.1, 21.1, 21.0. HRMS (ESI) calculated for [$C_{29}H_{32}NaO$] [M+Na]$^+$: 419.2345 found: 419.2354. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexanes:

2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 9.629 min, minor enantiomer tr = 7.807 min.



<Peak Table>
PDA Ch1 254nm

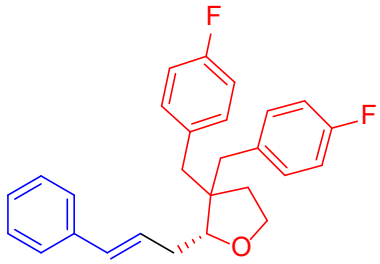
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.835	27493	79.952	679075	51.772
2	9.808	6894	20.048	632587	48.228
Total		34386	100.000	1311661	100.000



<Peak Table>
PDA Ch1 254nm

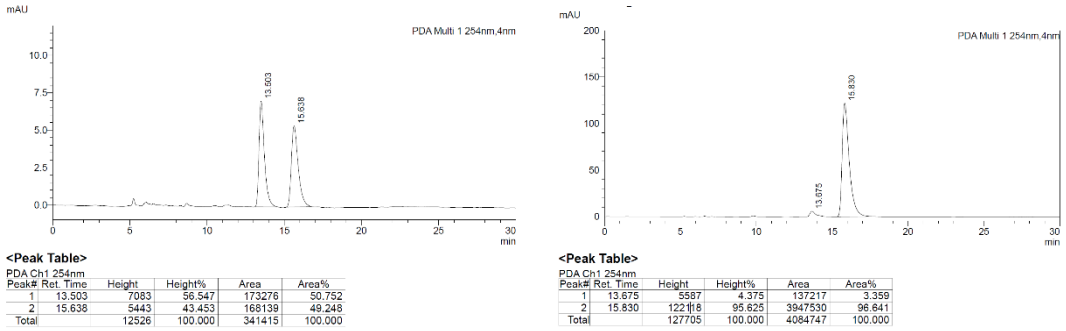
Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.807	6290	15.199	130915	4.035
2	9.629	35092	84.801	3113322	95.965
Total		41381	100.000	3244237	100.000

4.3.3 Synthesis of (*R*)-2-cinnamyl-3,3-bis(4-fluorobenzyl)tetrahydrofuran (10c)



10c

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10c** as a white liquid (140 mg, 69% yield) with 93% *ee*. $[\alpha]_D^{20}$ = 57.1 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.24 – 7.12 (m, 3H), 7.08 – 6.89 (m, 6H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.92 (td, *J* = 8.7, 7.5 Hz, 1H), 3.73 – 3.59 (m, 2H), 2.82 (d, *J* = 13.7 Hz, 1H), 2.79 – 2.67 (m, 2H), 2.59 (d, *J* = 13.7 Hz, 1H), 2.54 – 2.44 (m, 2H), 1.79 (ddd, *J* = 12.8, 7.5, 3.3 Hz, 1H), 1.65 – 1.53 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.72 (d, *J* = 244.9 Hz), 161.64 (d, *J* = 245.1 Hz), 137.4, 134.1 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 3.4 Hz), 132.8, 132.8, 132.2, 132.1, 131.7, 128.5, 127.6, 127.2, 126.2, 115.1 (d, J = 10.5 Hz), 114.9 (d, J = 10.4 Hz), 82.7, 65.0, 47.9, 39.0, 37.9, 33.1, 31.5. ^{19}F NMR (376 MHz, CDCl3) δ -116.37, -116.57. HRMS (ESI) calculated for $[C_{27}H_{26}F_2NaO]$ $[M+Na]^+$: 427.1844 found: 427.1848. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 15.830 min, minor enantiomer tr = 13.675 min.



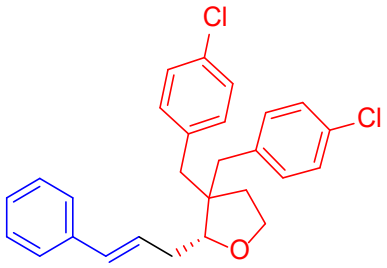
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.503	7083	56.547	173276	50.752
2	15.638	5443	43.453	168139	49.248
Total		12526	100.000	341415	100.000

<Peak Table>
PDA Ch1 254nm

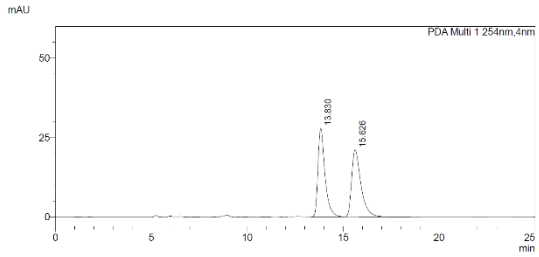
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.675	5587	4.375	137217	3.359
2	15.830	122118	95.625	3947530	96.641
Total		127705	100.000	4084747	100.000

4.3.4 Synthesis of (*R*)-3,3-bis(4-chlorobenzyl)-2-cinnamyltetrahydrofuran (10d)



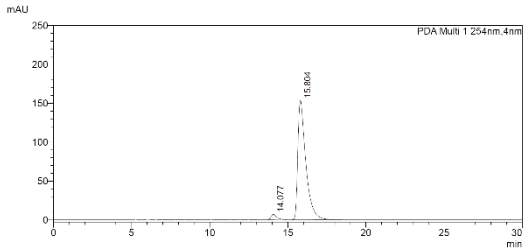
10d

Prepared according to typical procedure at -20 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10d** as a yellow solid (170 mg, 78% yield) with 94% *ee*. Mp: 86.0-89.1 °C. $[\alpha]_D^{20}$ = 41.0 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.16 – 7.09 (m, 2H), 6.97 – 6.91 (m, 2H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.91 (td, *J* = 8.7, 7.5 Hz, 1H), 3.71 – 3.57 (m, 2H), 2.82 (d, *J* = 13.5 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.63 – 2.55 (m, 1H), 2.54 – 2.39 (m, 2H), 1.78 (ddd, *J* = 12.9, 7.5, 3.3 Hz, 1H), 1.64 – 1.56 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.4, 136.8, 135.5, 132.4, 132.1, 132.1, 131.7, 128.5, 128.4, 128.3, 127.4, 127.2, 126.2, 82.6, 64.9, 47.9, 39.2, 38.1, 33.0, 31.5. HRMS (ESI) calculated for $[C_{27}H_{26}Cl_2NaO]$ $[M+Na]^+$: 459.1253 found: 459.1263. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 15.804 min, minor enantiomer tr = 14.077 min.



<Peak Table>
PDA Ch1 254nm

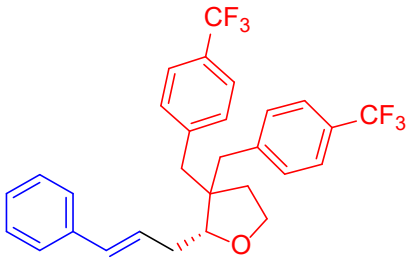
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.830	27864	56.930	706017	49.857
2	15.626	21080	43.070	710054	50.143
Total		48943	100.000	1416071	100.000



<Peak Table>
PDA Ch1 254nm

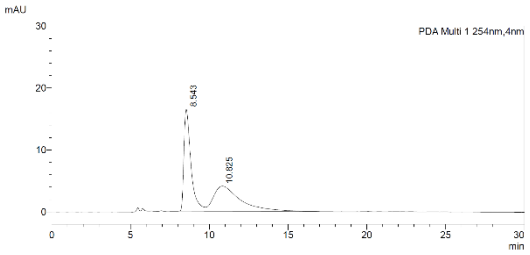
Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.077	6560	4.099	154553	2.763
2	15.804	153468	95.901	5440036	97.237
Total		160028	100.000	5594589	100.000

4.3.5 Synthesis of (*R*)-2-cinnamyl-3,3-bis(4-(trifluoromethyl)benzyl)tetrahydrofuran (10e)



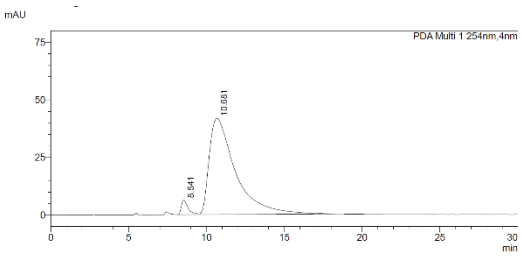
10e

Prepared according to typical procedure at -20 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10e** as a white liquid (192 mg, 76% yield) with 93% *ee*. $[\alpha]_D^{20}$ = 41.5 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.31 (td, *J* = 8.0, 6.2 Hz, 4H), 7.24 – 7.19 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.61 – 6.43 (m, 1H), 6.32 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.95 (td, *J* = 8.6, 7.5 Hz, 1H), 3.77 – 3.56 (m, 2H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.84 (s, 2H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.61 – 2.46 (m, 2H), 1.82 (ddd, *J* = 12.9, 7.5, 3.3 Hz, 1H), 1.70 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6 (d, *J* = 1.5 Hz), 141.3 (d, *J* = 1.4 Hz), 137.4, 131.9, 131.2, 131.2, 128.9 (q, *J* = 32.3 Hz), 128.6, 127.3, 126.2,125.2 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 3.8 Hz), 82.7, 64.9, 48.1, 39.7, 38.7, 33.1, 31.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.27, -62.32. HRMS (ESI) calculated for $[C_{29}H_{26}F_6NaO]$ $[M+Na]^+$: 527.1780 found: 527.1783. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 10.681 min, minor enantiomer tr = 8.541 min.



<Peak Table>
PDA Ch1 254nm

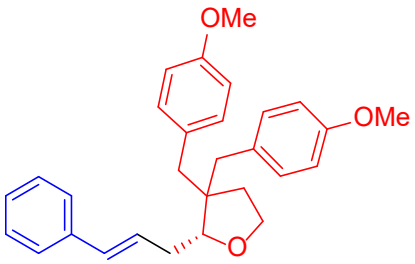
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.543	16420	80.220	503635	50.737
2	10.825	4049	19.780	488996	49.263
Total		20469	100.000	992631	100.000



<Peak Table>
PDA Ch1 254nm

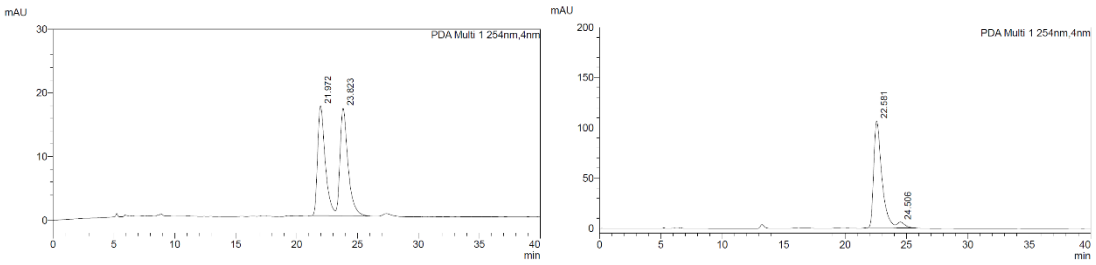
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.541	6211	12.964	185678	3.652
2	10.681	41698	87.036	4898546	96.348
Total		47908	100.000	5084224	100.000

4.3.6 Synthesis of (*R*)-2-cinnamyl-3,3-bis(4-methoxybenzyl)tetrahydrofuran (10f)



10f

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10f** as a white liquid (136 mg, 63% yield) with 90% *ee*. $[\alpha]_D^{20}$ = 45.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.07 (m, 1H), 7.05 – 7.00 (m, 2H), 6.87 – 6.81 (m, 2H), 6.79 – 6.75 (m, 2H), 6.69 (dq, *J* = 9.6, 3.1, 2.7 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.60 – 3.52 (m, 2H), 2.72 – 2.55 (m, 3H), 2.46 (d, *J* = 13.6 Hz, 1H), 2.42 – 2.31 (m, 2H), 1.70 (ddt, *J* = 14.8, 7.4, 3.7 Hz, 1H), 1.50 (dt, *J* = 11.9, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.3, 158.2, 137.7, 131.9, 131.8, 131.5, 130.6, 129.4, 128.5, 128.1, 127.1, 126.2, 113.7, 113.5, 82.8, 65.1, 55.3, 55.2, 55.2, 48.1, 39.0, 37.7, 33.1, 31.7. HRMS (ESI) calculated for $[C_{29}H_{32}NaO_3]$ $[M+Na]^+$: 451.2244 found: 451.2256. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 22.581 min, minor enantiomer tr = 24.506 min.



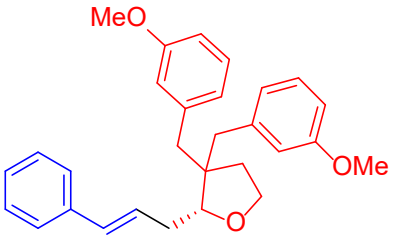
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.972	17214	50.456	746236	49.101
2	23.823	16903	49.544	773568	50.899
Total		34117	100.000	1519804	100.000

<Peak Table>
PDA Ch1 254nm

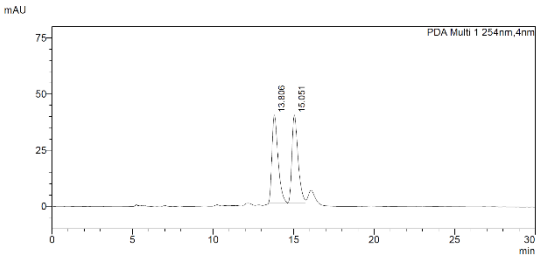
Peak#	Ret. Time	Height	Height%	Area	Area%
1	22.581	106664	94.602	4941485	94.967
2	24.506	6086	5.398	261889	5.033
Total		112750	100.000	5203374	100.000

4.3.7 Synthesis of (*R*)-2-cinnamyl-3,3-bis(3-methoxybenzyl)tetrahydrofuran (10g)



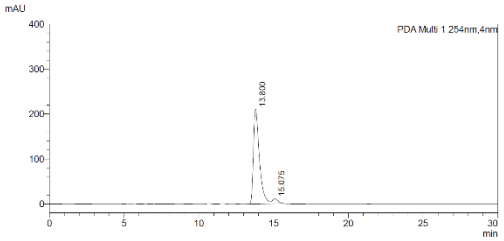
10g

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10g** as a white liquid (137 mg, 64% yield) with 90% *ee*. $[\alpha]_D^{20}$ = 56.4 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 2H), 7.25 (dt, *J* = 9.0, 7.6 Hz, 3H), 7.20 – 7.09 (m, 2H), 6.84 – 6.76 (m, 3H), 6.73 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.63 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.58 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.94 (td, *J* = 8.7, 7.4 Hz, 1H), 3.78 (s, 3H), 3.72 – 3.63 (m, 5H), 2.86 – 2.71 (m, 3H), 2.60 (d, *J* = 13.4 Hz, 1H), 2.54 – 2.37 (m, 2H), 1.85 (ddd, *J* = 12.7, 7.4, 3.2 Hz, 1H), 1.73 – 1.59 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.5, 159.4, 140.3, 139.0, 137.6, 131.6, 129.2, 129.0, 128.5, 128.0, 127.1, 126.2, 123.5, 123.4, 117.2, 116.8, 111.8, 111.3, 83.0, 65.1, 55.2, 55.2, 48.0, 40.1, 38.8, 33.2, 32.0. HRMS (ESI) calculated for $[C_{29}H_{32}NaO_3]$ $[M+Na]^+$: 451.2244 found: 451.2254. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90: 10, 0.6 mL/min, 254 nm); major enantiomer tr = 13.800 min, minor enantiomer tr = 15.075 min..



<Peak Table>
PDA Ch1 254nm

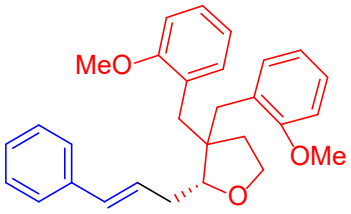
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.806	39336	49.966	1040769	50.028
2	15.051	39390	50.034	1039590	49.972
Total		78726	100.000	2080359	100.000



<Peak Table>
PDA Ch1 254nm

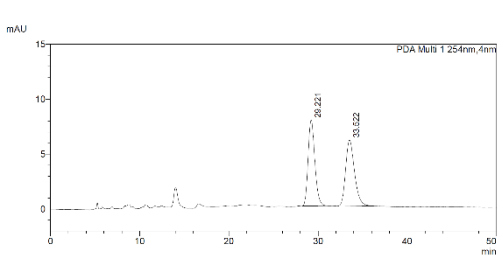
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.800	210524	94.878	5817507	95.059
2	15.075	11366	5.122	302387	4.941
Total		221890	100.000	6119893	100.000

4.3.8 Synthesis of (*R*)-2-cinnamyl-3,3-bis(2-methoxybenzyl)tetrahydrofuran (10h)



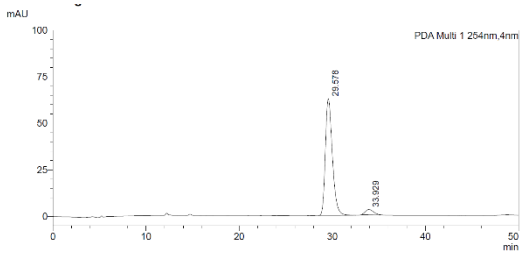
10h

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10h** as a white liquid (133 mg, 62% yield) with 90% *ee*. $[\alpha]_D^{20}$ =61.6 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.31 – 7.22 (m, 3H), 7.22 – 7.14 (m, 3H), 6.96 – 6.86 (m, 3H), 6.81 (ddd, *J* = 8.3, 4.3, 1.1 Hz, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.04 (dt, *J* = 9.4, 7.4 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.64 (ddd, *J* = 10.0, 7.7, 2.4 Hz, 1H), 3.52 (dd, *J* = 10.2, 1.6 Hz, 1H), 2.98 (dd, *J* = 15.0, 13.4 Hz, 2H), 2.80 (ddt, *J* = 14.8, 6.6, 1.7 Hz, 1H), 2.74 – 2.59 (m, 2H), 2.47 (dddd, *J* = 15.0, 10.2, 6.8, 1.4 Hz, 1H), 1.76 (ddd, *J* = 12.6, 7.2, 2.4 Hz, 1H), 1.67 – 1.60 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.4, 158.2, 137.9, 133.2, 133.0, 130.9, 129.2, 128.4, 127.6, 127.5, 127.5, 126.8, 126.2, 126.1, 120.1, 119.9, 110.5, 110.1, 82.9, 65.5, 55.1, 49.0, 33.4, 32.9, 32.2, 31.3. HRMS (ESI) calculated for $[C_{29}H_{32}NaO_3]$ $[M+Na]^+$: 451.2244 found: 451.2255. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 97: 3, 0.6 mL/min, 254 nm); major enantiomer tr = 29.578 min, minor enantiomer tr = 33.929 min.



<Peak Table>
PDA Ch1 254nm

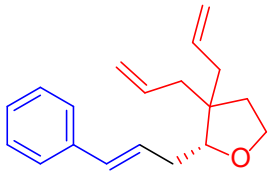
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.221	7816	56.628	408769	49.825
2	33.522	5987	43.372	411633	50.175
Total		13803	100.000	820402	100.000



<Peak Table>
PDA Ch1 254nm

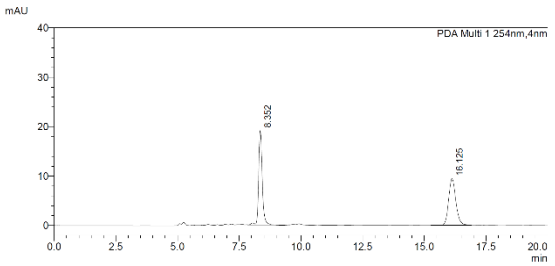
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.578	62662	95.659	3272914	94.933
2	33.929	2843	4.341	174688	5.067
Total		65506	100.000	3447603	100.000

4.3.9 Synthesis of (*R*)-3,3-diallyl-2-cinnamyltetrahydrofuran (10i)



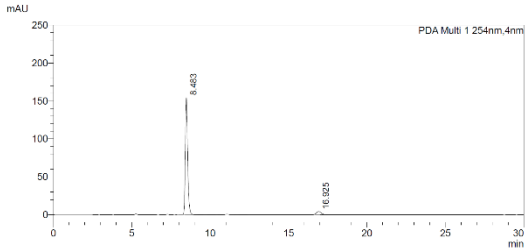
10i

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10i** as a white liquid (95 mg, 71% yield) with 90% *ee*. $[\alpha]_D^{20}$ = 15.4 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.11 (m, 1H), 6.52 – 6.38 (m, 1H), 6.29 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.84 (tddd, *J* = 17.6, 14.4, 9.3, 7.2 Hz, 2H), 5.16 – 5.04 (m, 4H), 3.89 (td, *J* = 8.3, 6.5 Hz, 1H), 3.81 – 3.70 (m, 1H), 3.65 (dd, *J* = 8.1, 4.9 Hz, 1H), 2.44 – 2.32 (m, 2H), 2.24 – 2.12 (m, 4H), 1.93 – 1.82 (m, 1H), 1.81 – 1.72 (m, 1H). ^{13}C NMR (100MHz, Chloroform-*d*) δ 137.6, 135.1, 134.5, 131.4, 128.4, 128.0, 127.0, 126.1, 126.1, 118.0, 117.7, 85.2, 65.5, 46.7, 40.9, 37.7, 35.5, 34.1. HRMS (ESI) calculated for $[C_{19}H_{24}NaO]$ $[M+Na]^+$: 291.1719 found: 291.1717. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 8.483 min, minor enantiomer tr = 16.925 min.



<Peak Table>
PDA Ch1 254nm

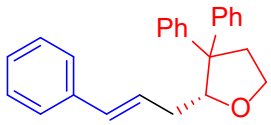
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.352	19102	66.971	189661	50.072
2	16.125	9421	33.029	189118	49.928
Total		28523	100.000	378779	100.000



<Peak Table>
PDA Ch1 254nm

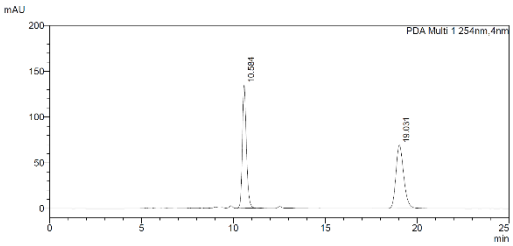
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.483	153914	97.435	1616107	95.094
2	16.925	4051	2.565	83379	4.906
Total		157966	100.000	1699486	100.000

4.3.10 Synthesis of (*R*)-2-cinnamyl-3,3-diphenyltetrahydrofuran (10j)



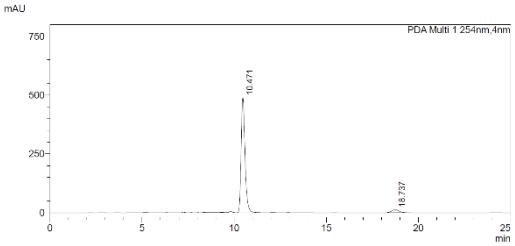
10j

Prepared according to typical procedure at -20 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10j** as a white liquid (119 mg, 71% yield) with 91% *ee*. $[\alpha]_D^{20}$ = 110.4 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 9H), 7.23 – 7.13 (m, 4H), 7.11 – 7.06 (m, 2H), 6.28 – 6.18 (m, 2H), 4.68 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.19 (td, *J* = 8.7, 3.3 Hz, 1H), 3.82 (q, *J* = 8.4 Hz, 1H), 2.94 (dt, *J* = 12.4, 8.8 Hz, 1H), 2.30 (ddd, *J* = 12.3, 7.9, 3.4 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.85 (ddd, *J* = 14.2, 9.6, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.5, 145.0, 137.7, 131.5, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.0, 126.5, 126.3, 126.1, 84.1, 66.0, 58.2, 39.2, 37.1. HRMS (ESI) calculated for $[C_{25}H_{24}NaO]$ $[M+Na]^+$: 363.1719 found: 363.1712. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 10.471 min, minor enantiomer tr = 18.737 min.



<Peak Table>
PDA Ch1 254nm

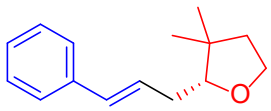
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.584	134501	65.990	2072740	50.559
2	19.031	69318	34.010	2026878	49.441
Total		203819	100.000	4099618	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.471	489109	97.569	7129223	95.618
2	18.737	12189	2.431	326737	4.382
Total		501298	100.000	7455960	100.000

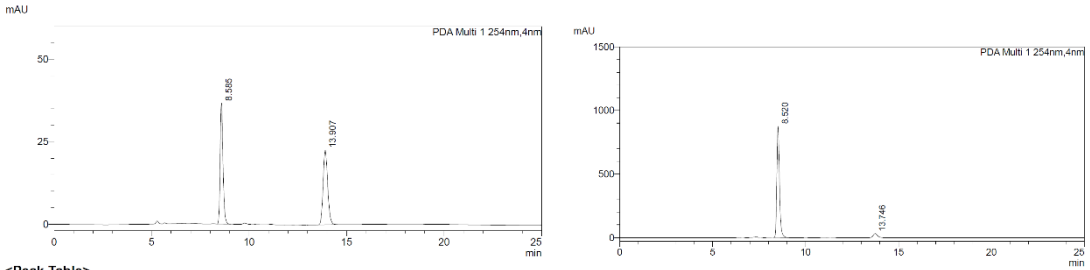
4.3.11 Synthesis of (*R*)-2-cinnamyl-3,3-dimethyltetrahydrofuran (10k)



10k

Prepared according to typical procedure at -20 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10k**

as a white liquid (72 mg, 67% yield) with 90% *ee*. $[\alpha]_D^{20}$ = 23.8 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.23 (m, 2H), 7.21 – 7.14 (m, 1H), 6.47 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.29 (dt, *J* = 15.8, 7.0 Hz, 1H), 3.90 (q, *J* = 8.1 Hz, 1H), 3.80 (td, *J* = 8.7, 4.6 Hz, 1H), 3.46 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.32 (tt, *J* = 7.0, 1.3 Hz, 2H), 1.84 – 1.68 (m, 2H), 1.07 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.3, 128.4, 128.1, 126.9, 126.1, 86.6, 65.4, 41.4, 40.5, 34.0, 25.5, 21.7. HRMS (ESI) calculated for [$C_{15}H_{20}NaO$] [M+Na]$^+$: 239.1406 found: 239.1409. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 8.520 min, minor enantiomer tr = 13.746 min.



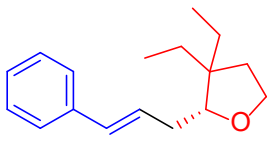
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.585	36606	61.864	368848	49.963
2	13.907	22566	38.136	369388	50.037
Total		59171	100.000	738236	100.000

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.520	874754	96.683	8651106	95.126
2	13.746	30012	3.317	443225	4.874
Total		904765	100.000	9094331	100.000

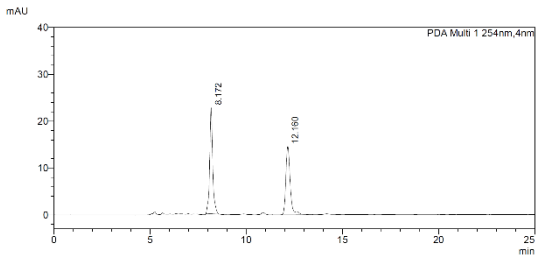
4.3.12 Synthesis of (*R*)-2-cinnamyl-3,3-diethyltetrahydrofuran (10l)



10l

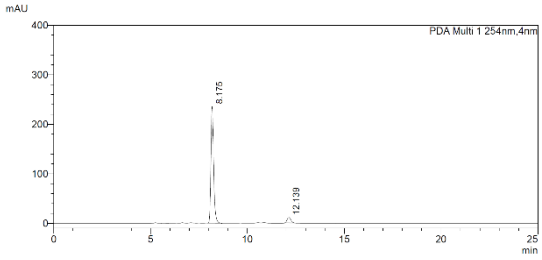
Prepared according to typical procedure at -20 ºC for 72 hours by using [Pd(allyl)Cl]$_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10l** as a white liquid (84 mg, 69% yield) with 88% *ee*. $[\alpha]_D^{20}$ = 34.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.12 (m, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.87 (td, *J* = 8.3, 5.8 Hz, 1H), 3.73 (td, *J* = 8.4, 6.6 Hz, 1H), 3.62 (dd, *J* = 7.7, 5.3 Hz, 1H), 2.33 (td, *J* = 7.1, 6.6, 1.5 Hz, 2H), 1.73 (dddd, *J* = 33.5, 12.4, 8.4, 6.1 Hz, 2H), 1.50 – 1.34 (m, 4H), 0.88 (dt, *J* = 9.2, 7.5 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.2, 128.5, 128.4, 126.9, 126.1, 85.7, 65.6, 47.1, 36.1, 34.7, 28.3, 24.5, 9.1, 9.0. HRMS (ESI) calculated for [$C_{17}H_{24}NaO$] [M+Na]$^+$: 267.1719 found: 267.1721.

Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 8.175 min, minor enantiomer tr = 12.139 min..



<Peak Table>
PDA Ch1 254nm

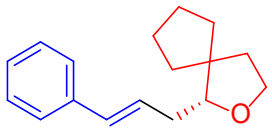
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.172	22706	60.773	248963	51.955
2	12.160	14656	39.227	230231	48.045
Total		37361	100.000	479194	100.000



<Peak Table>
PDA Ch1 254nm

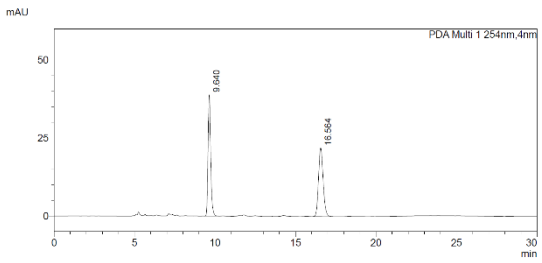
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.175	236057	95.566	2319162	94.136
2	12.139	10953	4.434	144471	5.864
Total		247011	100.000	2463633	100.000

4.3.13 Synthesis of (*R*)-1-cinnamyl-2-oxaspiro[4.4]nonane (10m)



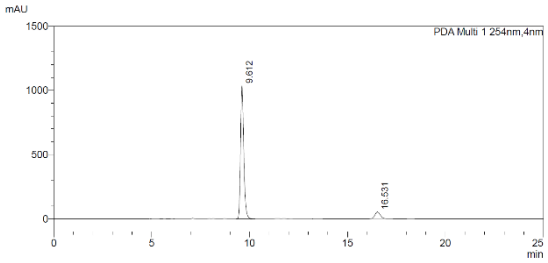
10m

Prepared according to typical procedure at -20 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10m** as a white liquid (79 mg, 65% yield) with 85% *ee*. $[\alpha]_D^{20}$ = 31.3 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.26 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.20 – 7.12 (m, 1H), 6.55 – 6.39 (m, 1H), 6.30 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.84 (dtd, *J* = 27.5, 8.2, 6.4 Hz, 2H), 3.70 (dd, *J* = 7.3, 5.5 Hz, 1H), 2.33 (td, *J* = 6.3, 5.6, 1.5 Hz, 2H), 1.79 (qdd, *J* = 12.0, 7.8, 6.4 Hz, 2H), 1.64 (ddddd, *J* = 8.5, 7.2, 4.9, 3.7, 2.0 Hz, 5H), 1.59 – 1.52 (m, 2H), 1.38 (tq, *J* = 5.5, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.4, 128.4, 128.1, 126.9, 126.1, 84.9, 66.0, 52.6, 39.8, 36.5, 35.2, 32.2, 24.9, 24.0. HRMS (ESI) calculated for $[C_{17}H_{22}NaO]$ $[M+Na]^+$: 265.1563 found: 265.1566. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 9.612 min, minor enantiomer tr = 16.531 min.



<Peak Table>
PDA Ch1 254nm

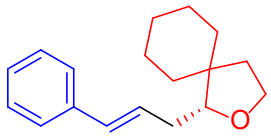
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.640	38913	63.852	444762	50.178
2	16.564	22030	36.148	441605	49.822
Total		60943	100.000	886367	100.000



<Peak Table>
PDA Ch1 254nm

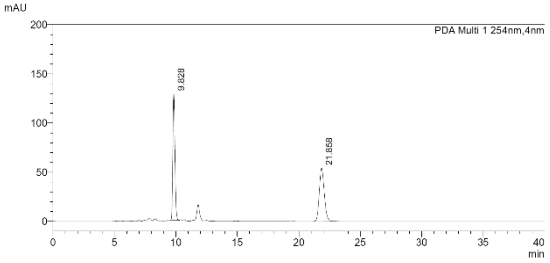
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.612	1034020	95.316	11820743	92.597
2	16.531	50814	4.684	945084	7.403
Total		1084834	100.000	12765827	100.000

4.3.14 Synthesis of (*R*)-1-cinnamyl-2-oxaspiro[4.5]decane (10n)



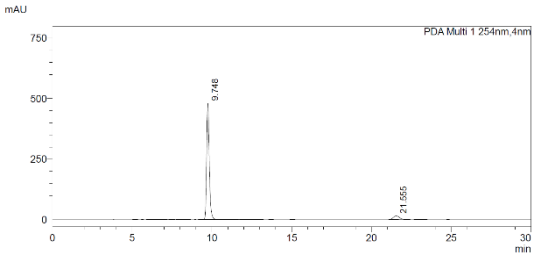
10n

Prepared according to typical procedure at -20 ºC for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10n** as a white liquid (86 mg, 67% yield) with 87% *ee*. $[\alpha]_D^{20}$ = 33.7 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 2H), 7.26 (dd, J = 8.5, 6.8 Hz, 2H), 7.21 – 7.11 (m, 1H), 6.51 – 6.41 (m, 1H), 6.31 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.90 (td, *J* = 8.3, 6.5 Hz, 1H), 3.76 (td, *J* = 8.7, 5.9 Hz, 1H), 3.44 (dd, *J* = 7.2, 5.8 Hz, 1H), 2.32 (td, *J* = 6.3, 5.7, 1.4 Hz, 2H), 1.95 (ddd, *J* = 12.4, 8.2, 5.9 Hz, 1H), 1.70 – 1.57 (m, 4H), 1.50 – 1.41 (m, 1H), 1.40 – 1.32 (m, 4H), 1.31 – 1.13 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 131.3, 128.4, 126.9, 126.1, 87.3, 65.7, 44.8, 35.7, 35.4, 33.9, 30.3, 26.5, 24.0, 23.0. HRMS (ESI) calculated for $[C_{18}H_{24}NaO]$ $[M+Na]^+$: 279.1719 found: 279.1720. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 9.748 min, minor enantiomer tr = 21.555 min.



<Peak Table>
PDA Ch1 254nm

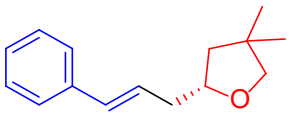
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.828	129058	70.296	1524000	49.767
2	21.858	54535	29.704	1538260	50.233
Total		183593	100.000	3062260	100.000



<Peak Table>
PDA Ch1 254nm

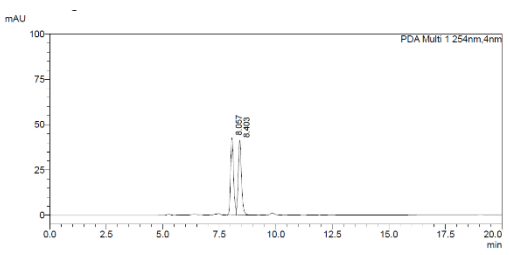
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.748	480932	96.987	5579582	93.556
2	21.555	14943	3.013	384333	6.444
Total		495875	100.000	5963916	100.000

4.3.15 Synthesis of (*R*)-2-cinnamyl-4,4-dimethyltetrahydrofuran (10o)



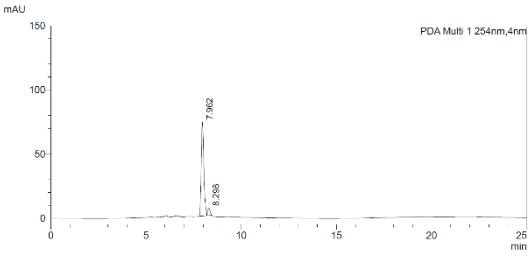
10o

Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10o** as a white liquid (78 mg, 72% yield) with 87% *ee*. $[\alpha]_D^{20}$ = -4.3 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.28 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.22 – 7.16 (m, 1H), 6.45 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.13 (dq, *J* = 9.0, 6.4 Hz, 1H), 3.55 (d, *J* = 8.1 Hz, 1H), 3.47 (d, *J* = 8.1 Hz, 1H), 2.53 (dtd, *J* = 13.6, 6.7, 1.4 Hz, 1H), 2.41 (dddd, *J* = 14.0, 7.4, 6.2, 1.4 Hz, 1H), 1.80 (dd, J = 12.2, 6.5 Hz, 1H), 1.44 (dd, *J* = 12.3, 9.0 Hz, 1H), 1.10 (d, *J* = 3.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 132.0, 128.5, 127.0, 126.7, 126.1, 80.2, 78.9, 46.4, 39.8, 39.7, 26.9, 26.6. HRMS (ESI) calculated for $[C_{15}H_{20}NaO]$ $[M+Na]^+$: 239.1406 found: 239.1412. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 7.962 min, minor enantiomer tr = 8.298 min.



<Peak Table>
PDA Ch1 254nm

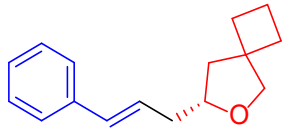
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.057	42410	50.693	383037	48.545
2	8.403	41249	49.307	406000	51.455
Total		83659	100.000	789036	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.962	73064	92.824	692291	93.452
2	8.298	5648	7.176	48511	6.548
Total		78712	100.000	740802	100.000

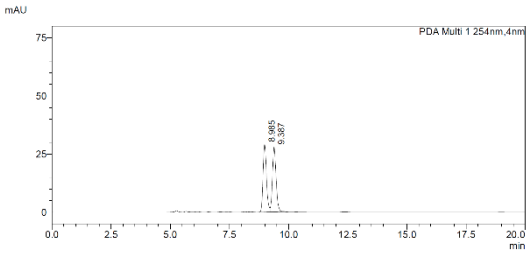
4.3.16 Synthesis of (*R*)-7-cinnamyl-6-oxaspiro[3.4]octane (10p)



10p

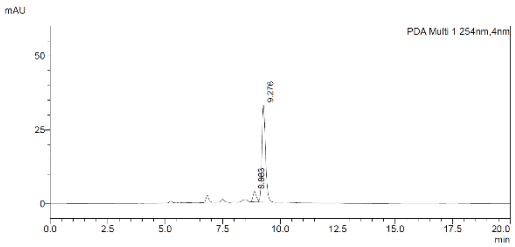
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10p**

as a white liquid (84 mg, 74% yield) with 82% *ee*. $[\alpha]_D^{20}$ = -7.9 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.28 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.22 – 7.16 (m, 1H), 6.44 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.21 (dt, *J* = 15.9, 7.2 Hz, 1H), 4.01 (dq, *J* = 8.4, 6.2 Hz, 1H), 3.80 (d, *J* = 8.4 Hz, 1H), 3.73 (d, *J* = 8.4 Hz, 1H), 2.49 (dddd, *J* = 13.5, 7.3, 6.3, 1.4 Hz, 1H), 2.39 (dddd, *J* = 14.0, 7.4, 6.2, 1.4 Hz, 1H), 2.12 – 1.95 (m, 5H), 1.91 – 1.79 (m, 2H), 1.69 – 1.60 (m, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 132.0, 128.5, 127.0, 126.7, 126.1, 79.1, 78.4, 46.2, 44.8, 39.5, 33.1, 31.5, 16.5. HRMS (ESI) calculated for $[C_{16}H_{20}NaO]$ $[M+Na]^+$: 251.1406 found: 251.1412. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 95: 5, 0.6 mL/min, 254 nm); major enantiomer tr = 9.276 min, minor enantiomer tr = 8.883 min.



<Peak Table>
PDA Ch1 254nm

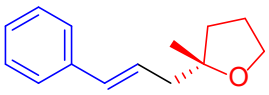
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.985	29084	50.994	295513	49.421
2	9.387	27950	49.006	302442	50.579
Total		57034	100.000	597955	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.883	3582	9.832	36586	9.100
2	9.276	32851	90.168	365454	90.900
Total		36433	100.000	402040	100.000

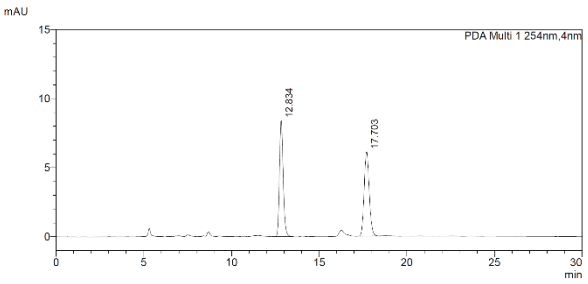
4.3.17 Synthesis of (*S*)-2-cinnamyl-2-methyltetrahydrofuran (10q)



10q

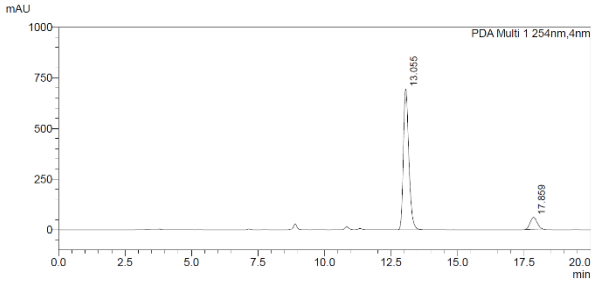
Prepared according to typical procedure at 0 °C for 72 hours by using $[Pd(allyl)Cl]_2$ (2.5 mol%), **Xu9** (10 mol%) from γ-hydroxyalkenes (0.5 mmol) and alkenyl bromide (1 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 50: 1) give the product **10q** as a white liquid (70 mg, 69% yield) with 81% *ee*. $[\alpha]_D^{20}$ = 7.0 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.22 – 7.16 (m, 1H), 6.51 – 6.37 (m, 1H), 6.25 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.93 – 3.76 (m, 2H), 2.41 (dd, *J* = 7.4, 1.2 Hz, 2H), 1.99 – 1.79 (m, 3H), 1.65 (ddd, *J* = 11.6, 5.6, 2.6 Hz, 1H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.7, 132.5, 128.5, 127.0, 126.8, 126.1, 82.6, 67.5, 44.9, 36.3, 26.3, 26.2. HRMS (ESI) calculated for [C14H18NaO] $[M+Na]^+$: 225.1250 found: 225.1255. Enantiomeric excess was

determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 99: 1, 0.5 mL/min, 254 nm); major enantiomer tr = 13.055 min, minor enantiomer tr = 17.859 min.



<Peak Table>
PDA Ch1 254nm

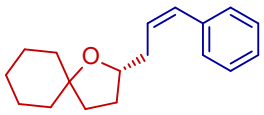
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.834	8430	57.949	124878	50.497
2	17.703	6117	42.051	122418	49.503
Total		14547	100.000	247297	100.000



<Peak Table>
PDA Ch1 254nm

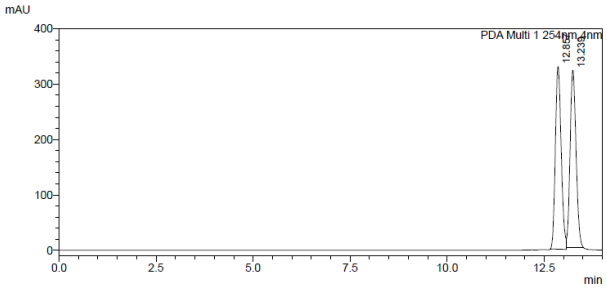
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.055	694608	92.226	9920559	90.364
2	17.859	58553	7.774	1057932	9.636
Total		753162	100.000	10978491	100.000

4.4 (*S*, *Z*)-2-(3-phenylallyl)-1-oxaspiro[4.5]decane (*Z*-3b)



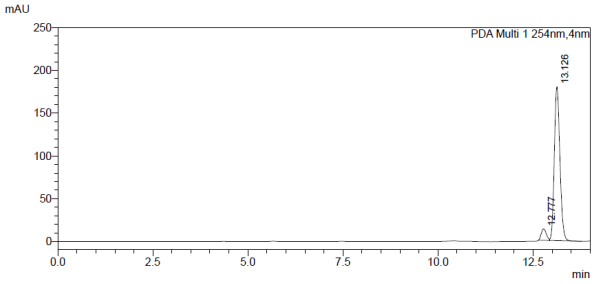
Z-3b

Prepared according to typical procedure at RT for 72 hours by using $[Pd(allyl)Cl]_2$ (5 mol%), **Xu2** (20 mol%) from γ-hydroxyalkenes (0.2 mmol) and alkenyl bromide (0.4 mmol), after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 80: 1) give the product ***Z*-3b** as a white liquid (29 mg, 57% yield) with 88% *ee*. $[\alpha]_D^{20}$ = -34.9 (*c* = 0.4, Chloroform).^{1}H NMR (400 MHz, Chloroform-*d*)δ 7.34 – 7.28 (m, 4H), 7.21 (ddd, J = 6.7, 5.7, 2.6 Hz, 1H), 6.50 (dt, J = 11.7, 1.7 Hz, 1H), 5.73 (dt, J = 11.8, 7.2 Hz, 1H), 4.05 (dq, J = 12.4, 6.2 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.49 (dtd, J = 8.6, 6.9, 1.8 Hz, 1H), 2.04 – 1.92 (m, 1H), 1.75 – 1.62 (m, 4H), 1.57 – 1.42 (m, 5H), 1.42 – 1.23 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 130.3, 128.8, 128.7, 128.1, 126.5, 100.0, 82.8, 38.5, 37.6, 35.8, 35.3, 31.0, 25.7, 24.2, 23.8. HRMS (ESI) calculated for $[C_{18}H_{24}NaO]$ $[M+Na]^+$: 279.1720 found: 279.1719. Enantiomeric excess was determined by HPLC with a Chiralpak ADH+ADH column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 13.126. min, minor enantiomer tr = 12.777 min.



<Peak Table>
PDA Ch1 254nm

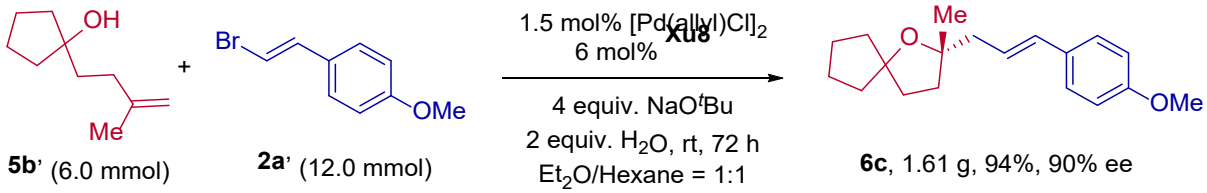
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.857	330006	50.706	3461776	50.357
2	13.239	320813	49.294	3412760	49.643
Total		650819	100.000	6874536	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.777	13371	6.919	123072	6.266
2	13.126	179866	93.081	1841196	93.734
Total		193237	100.000	1964269	100.000

4.5 Gram-scale synthesis of 6c:

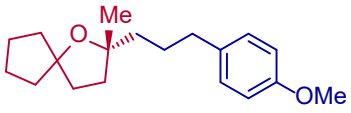


5b' (6.0 mmol) **2a**' (12.0 mmol) **6c**, 1.61 g, 94%, 90% ee

To a 100 mL tube was added $[Pd(allyl)Cl]_2$ (0.09 mmol, 32.9 mg, 1.5 mol%), **Xu8** (0.36 mmol, 234.8 mg, 6 mol%). The flask was evacuated and refilled with argon. Then tertiary γ-hydroxyalkenes **5b** (6 mmol), alkenyl halides **2a** (12 mmol), NaO^{t}Bu (24 mmol, 2.3g, 4.0 equiv.), H_2O (12 mmol, 324 mg, 2.0 equiv.) and a mixed solution of Et_2O/Hexane (1: 1, 60 mL) was added to the tube, and stirred at room temperature for 72 hours. After the reaction was complete (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product **6c** (1.61g, 94%, 90% ee).

4.6 Procedure for synthetic applications

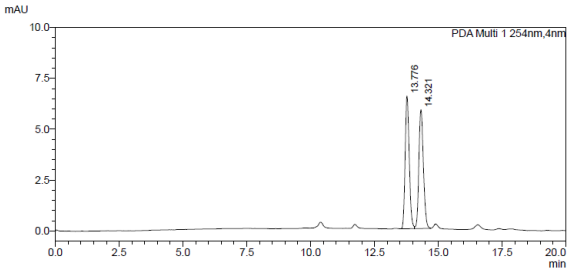
4.6.1 (*R*)-2-(3-(4-methoxyphenyl)propyl)-2-methyl-1-oxaspiro[4.4]nonane (11)



11

To a solution of **(*S*)-5c** (0.1 mmol, 52.2 mg) in MeOH (1 mL) was added 10% Pd/C (1 mol%, 1 mg) at room temperature. The reaction flask was evacuated twice under reduced pressure, and a H_2

balloon was placed on the top. After stirring at room temperature for 3.5 h, the mixture was concentrated and the residue was purified by column chromatography on a silica gel column(hexanes/EtOAc=80/1) to afford the desired product **11** (25.5mg, 89% yield) with 90% *ee*. $[\alpha]_D^{20}$ = -9.3 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, J = 8.6 Hz, 2H), 6.84 – 6.75 (m, 2H), 3.78 (s, 3H), 2.54 (t, J = 7.4 Hz, 2H), 1.88 – 1.56 (m, 12H), 1.50 (ddd, J = 13.5, 8.1, 3.9 Hz, 4H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.7, 134.8, 129.3, 113.7, 91.0, 82.6, 55.3, 42.1, 39.8, 39.6, 37.4, 37.0, 35.6, 27.5, 27.0, 24.0, 23.9. HRMS (ESI) calculated for [$C_{19}H_{28}NaO_2$] [M+Na]$^+$: 311.1982 found: 311.1977. Enantiomeric excess was determined by HPLC with a Chiralpak ADH+ ADH column (hexanes: 2-propanol = 99: 1, 0.6 mL/min, 254 nm); major enantiomer tr = 14.356 min, minor enantiomer tr = 13.818 min.



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
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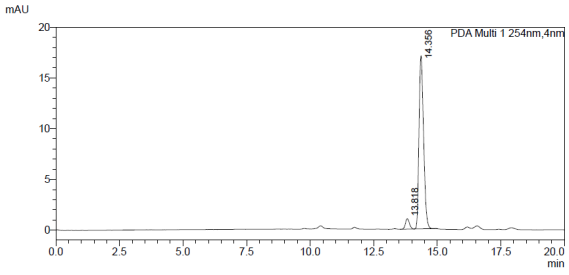
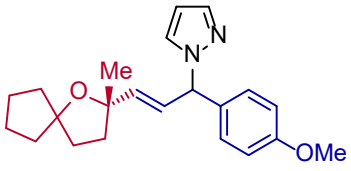
2	14.321	5836	47.227	72053	49.788
Total		12357	100.000	144720	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.818	1023	5.654	11318	5.038
2	14.356	17068	94.346	213343	94.962
Total		18090	100.000	224661	100.000

4.6.2 1-((*S, E*)-3-(4-methoxyphenyl)-1-((*S*)-2-methyl-1-oxaspiro[4.4]nonan-2-yl)allyl)-1H-pyrazole (12)

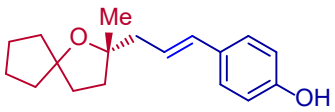


12

To a solution of 1, 4-dioxane (1.0 mL) was added **(*R*)-5c** (0.2 mmol), (0.24 mmol) and DDQ (0.28 mmol). The reaction mixture was stirred at room temperature for 8 h and then the solvent was removed under vacuum. The residue was purified by column chromatography on a silica gel column(hexanes/EtOAc=80/1) to afford the desired product **12** as a white liquid (62 mg, 88% yield) with 1.2:1 dr. $[\alpha]_D^{20}$ = -12.6 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.47 (m, 1H), 7.38 (dd, J = 4.3, 2.3 Hz, 1H), 7.09 (dt, J = 4.5, 2.2 Hz, 2H), 6.85 (dd, J = 8.7, 1.0 Hz, 2H),

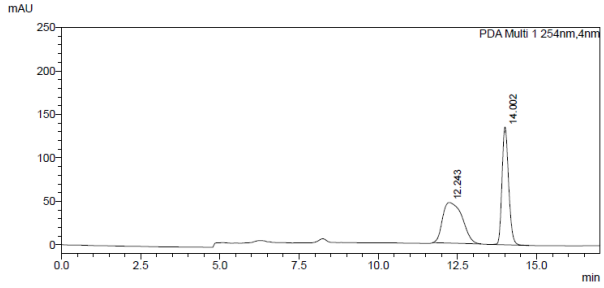
6.25 (dd, J = 4.1, 2.1 Hz, 1H), 6.17 (ddd, J = 15.3, 6.7, 1.2 Hz, 1H), 5.99 (d, J = 6.6 Hz, 1H), 5.56 (ddd, J = 15.3, 4.8, 1.3 Hz, 1H), 3.78 (d, J = 0.7 Hz, 3H), 1.96 – 1.67 (m, 8H), 1.66 – 1.48 (m, 4H), 1.31 (d, J = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.2, 141.3, 141.3, 139.2, 132.0, 131.9, 128.7, 128.6, 128.1, 128.0, 125.4, 125.3, 114.0, 105.4, 105.3, 92.2, 92.1, 81.9, 81.9, 66.5, 66.4, 55.3, 39.6, 39.0, 38.9, 38.5, 38.4, 36.7, 28. 4, 28.1, 23.9. HRMS (ESI) calculated for [$C_{22}H_{28}N_2NaO_2$] [M+Na]$^+$: 375.2043 found: 375.2038.

4.6.3 (*S, E*)-4-(3-(2-methyl-1-oxaspiro[4.4]nonan-2-yl)prop-1-en-1-yl)phenol (13) [8-9]



13

$C_{12}H_{25}SH$ (204 mg, 1 mmol) was added to a stirred suspension of sodium hydride (60% dispersion in mineral oil) (44 mg, 1.1 mmol) in dry diethyl ether (2 mL) over 10 min at a temperature around 5 °C. The solvent was removed in a vacuum, and the obtained residue was added NMP (1 mL). Then **(*R*)-5c** (143 mg, 0.5 mmol) was added with vigorous stirring at room temperature. The mixture was allowed to heat to 130 °C and kept at that temperature for 18 h. The solvent was neutralized to pH < 7 by using a diluted hydrochloric acid solution and extracted with ethyl acetate (3 × 15 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated, after flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 5: 1) give the product **13** as a yellow solid (108.4 mg, 80% yield, 90% ee). m.p. 137-147 ºC. $[\alpha]_D^{20}$ = 0.57 (*c* = 0.4, Chloroform). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (s, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.78 (t, J = 5.6 Hz, 2H), 6.30 (d, J = 15.8 Hz, 1H), 6.11 – 5.97 (m, 1H), 2.44 – 2.31 (m, 2H), 1.97 – 1.81 (m, 5H), 1.79 – 1.67 (m, 3H), 1.58 (dddd, J = 14.4, 10.4, 9.8, 5.4 Hz, 4H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.43, 132.12, 129.92, 127.23, 123.88, 115.52, 92.21, 83.58, 45.67, 39.54, 39.36, 37.16, 36.79, 27.48, 23.69.RMS (ESI) calculated for [$C_{18}H_{24}NaO_2$] [M+Na]$^+$: 295.1662 found: 295.1669. $[\alpha]_D^{20}$ = 0.57 (*c* = 0.4, Chloroform). Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 99: 10, 0.5 mL/min, 254 nm); major enantiomer tr = 12.151 min, minor enantiomer tr = 14.004 min.



<Peak Table>
PDA Ch1 254nm

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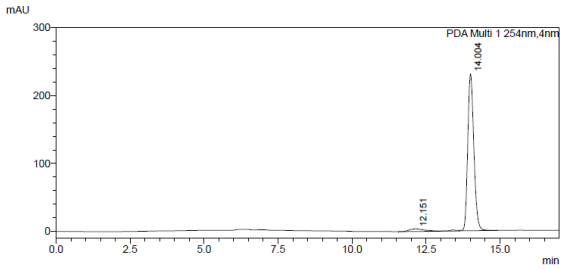
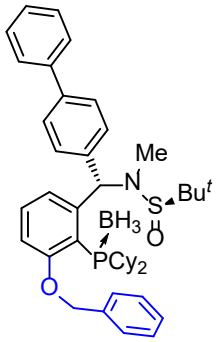
1	12.243	46705	25.629	2009709	50.680
2	14.002	135528	74.371	1955797	49.320
Total		182233	100.000	3965507	100.000



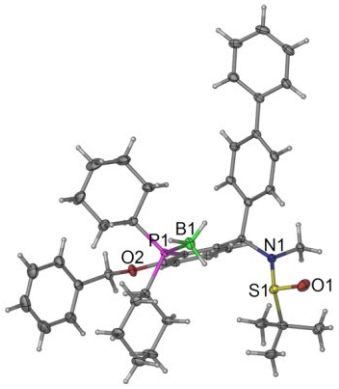
<Peak Table>
PDA Ch1 254nm

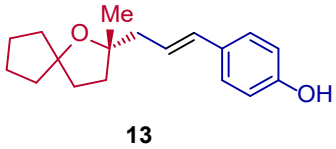
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.151	3746	1.595	169043	4.853
2	14.004	231146	98.405	3314183	95.147
Total		234893	100.000	3483227	100.000

5. X-ray structure of Xu6 and 13.

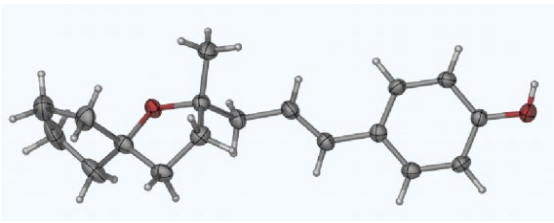


Xu**6**





13



6. Procedure of vibrational circular dichroism (VCD) experiment

VCD and IR measurements of **8-D** were performed on a BioTools ChiralIR-2X FT-VCD spectrometer, equipped with a single photoelastic modulation and a mercury cadmium tellurium detector. 15 mg of sample was dissolved in 300μL $CDCl_3$ and placed in a BaF_2 cell with a pathlength of 75μm. Data were acquired at a resolution of 4 cm-1 for 15 h.

7. Computational details

General calculation procedure

Density functional theory (DFT) calculations were carried out using Gaussian 09 E.01 software package.[10] All structure optimizations and frequency calculations were performed using the PBE0 functional[11] with D3BJ dispersion correction (PBE0-D3BJ) and combined basis set.[12-13] That is SDD basis set[14] for Palladium and 6-31G* basis set for all other elements.[15-16] Intrinsic reaction coordinate calculations were performed to ensure every TS is connected with corresponding equilibrium structure[17-18]. Single point energies were further calculated using PBE0-D3BJ functional and def2-TZVP basis set[19] for higher accuracy. Truhlar and coworkers' SMD solvation model[20] was employed to consider the solvent effect of the mixed solvent of Et_2O and Hexane. The solvent is defined by 7 parameters. As it is not on the solvent list of Gaussian 09 software, the parameters used in calculation are the average value of Et_2O and Hexane: eps (3.06095), epsinf (1.36375), HBondAcidity(0.00), HBondBasicity(0.205), SurfaceTensionAtInterface(24.855), CarbonAromaticity(0.000), ElectronegativeHalogenicity(0.000). 3D structures and isosurfaces are visualized by VMD 1.9.3[21] and CYLview v0.1b[22].

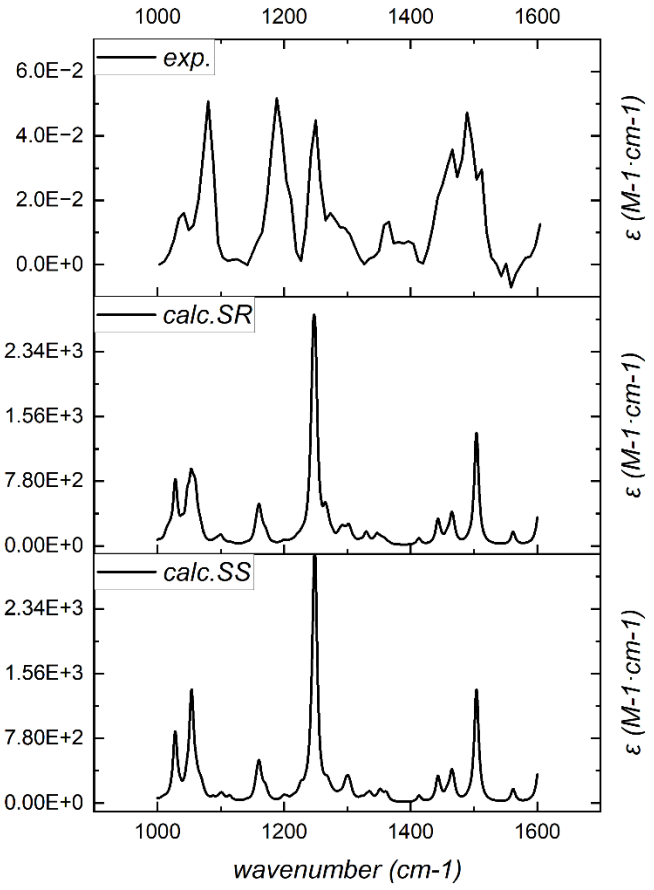
VCD calculation procedure

VCD spectra of different conformers may differ considerably. In order to compare with the experimental spectrum, conformation search and Boltzmann weighted spectrums are essential. First, systematic conformation search of both configuration (*S* and *R*) of **8-D** (**8-D-*S*** and **8-D-*R***) was performed with **CREST** program developed by Prof. Grimme.[23] (detailed input: "crest xtbopt.xyz --T 4 --v3 --ewin 6 --rthr 0.35 --ethr 0.2 --chrg 0 --noreftopo --temp 298.15 --gfn 2 --shake 1 --hmass 1") Then, **isostat** component of **Molclus** program developed by Tian Lu et al.[24] is used to remove the duplicated conformers (detailed input: "isostat crest_conformers.xyz -nt 4 -Nout 60 -Eout 5 -Edis 0.3 -Gdis 0.3 -T 298.15"). 23 and 28 low-energy conformations of **8-D-*S*** and **8-D-*R*** were achieved, respectively.

Then, optimization and free energy calculations of the structures were carried out using the Gaussian 09 E.01 software package.[10] All structure optimizations, frequency and VCD spectrum calculations (invoked by "freq=vcd" keyword) were performed using B3LYP functional[25-27] with D3BJ dispersion correction developed by Grimme et al. And 6-31G* basis set was chosen to match the frequency correction factor (0.9614) provided by Multiwfn.[28] The solvent was changed to chloroform (specified by "scrf=(smd,solvent=chloroform)" in the command line of Gaussian input file) to match the solvent ($CDCl_3$) used in the VCD experiment. Single point energies were further calculated at B3LYP-D3BJ/def2-TZVP level for higher accuracy.

After obtaining the free energy of all conformations, their VCD spectrum were calculated according to Boltzmann distribution with Multiwfn.[28] FWHM was set as 8.0 cm^{-1}, while frequency correction factor is 0.9614.

Experimental and simulated (with the same procedure stated above) IR spectrum of **8-D-*SR*** and **8-D-*SS*** are provided is **Supplementary Figure1**.



Supplementary Figure1. Experimental and simulated IR spectrum of 8-D-*SR and 8-D-SS*

Considering that free energy profile of conformations may be sensitive to the computational parameters, which will influence the Boltzmann distribution result and consequently result in differences in simulated spectrums, we slightly altered the calculation parameters and reperformed the calculation. The Boltzmann distribution profile are provided in **Supplementary Table1** and spectrums are provided in **Supplementary Figure2**. We observed that while there are variations in the Boltzmann distribution of different conformers and the spectra, the overall trend remains consistent across various calculation levels. Therefore, we believe that this result lends support to our initial conclusion.

Supplementary Table1. Boltzmann distribution profile of 8-D-*S* conformers under different computational parameters

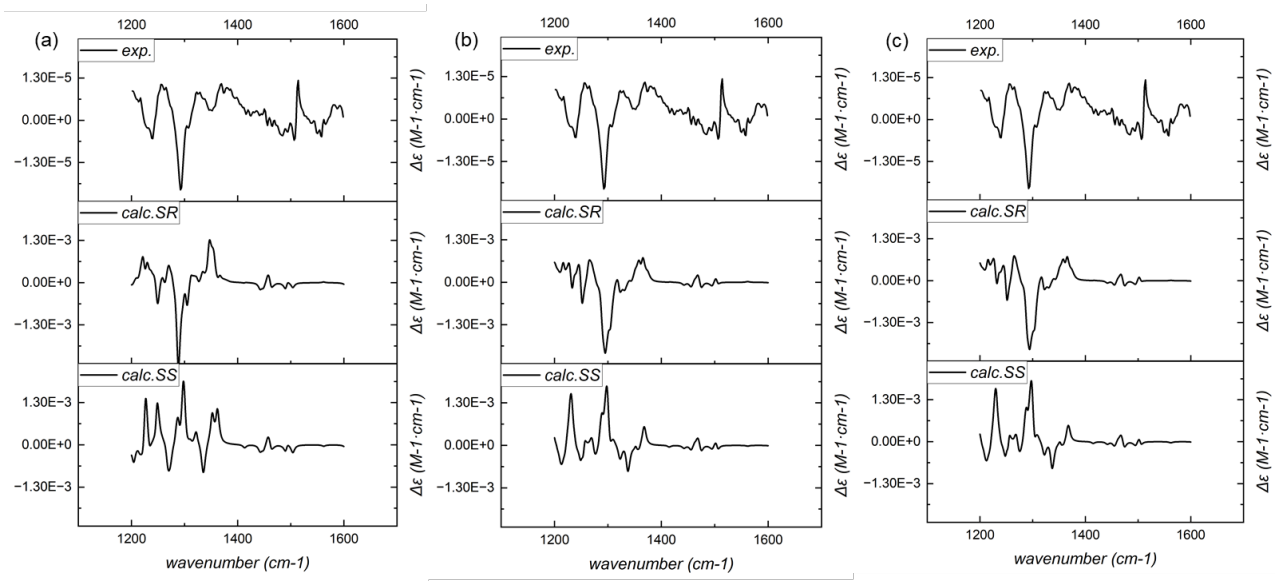
structure index	standard*	no-disp-scrf**	no-disp-scrf-dp***
0	4.80%	2.40%	2.51%
1	4.62%	4.93%	4.89%
2	6.96%	6.78%	6.90%

3	14.23%	14.60%	10.50%
4	11.03%	4.25%	4.69%
5	10.99%	4.25%	4.69%
6	4.74%	1.90%	1.96%
7	5.39%	6.17%	6.26%
8	0.77%	0.35%	0.26%
9	2.83%	3.99%	4.04%
10	0.44%	0.22%	0.20%
11	7.11%	12.98%	13.46%
12	8.69%	0.38%	0.43%
13	3.83%	7.70%	8.19%
14	3.63%	4.01%	4.23%
15	1.42%	3.90%	4.18%
16	1.55%	4.65%	4.73%
17	3.58%	10.66%	11.87%
18	0.52%	0.18%	0.18%
19	1.55%	4.69%	4.74%
20	0.71%	0.33%	0.33%
21	0.31%	0.34%	0.38%
22	0.31%	0.34%	0.38%

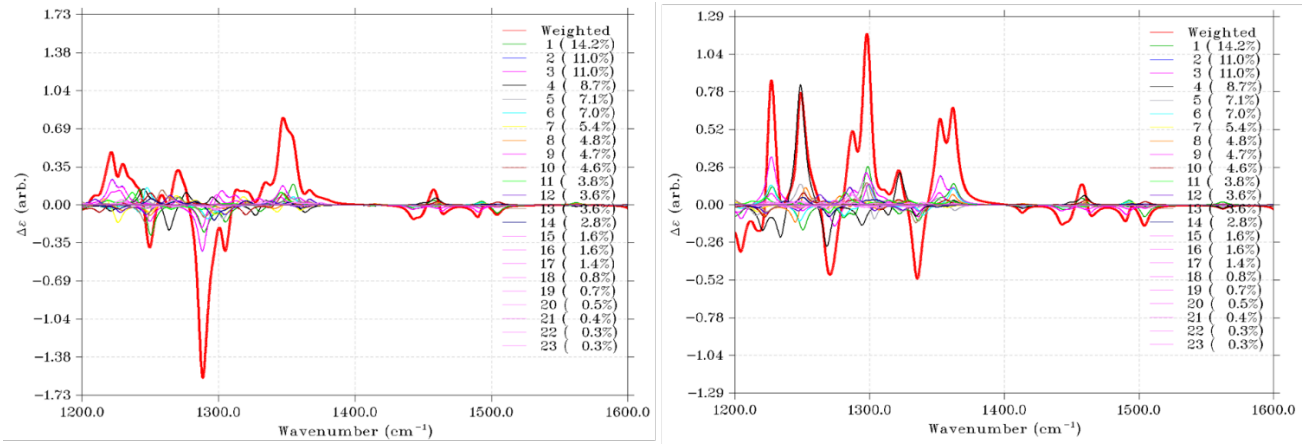
* standard parameter

** standard parameter without dispersion correction and solvent model

*** standard parameter without dispersion correction and solvent model and change basis from 6-31G* to 6-31G** in optimization process

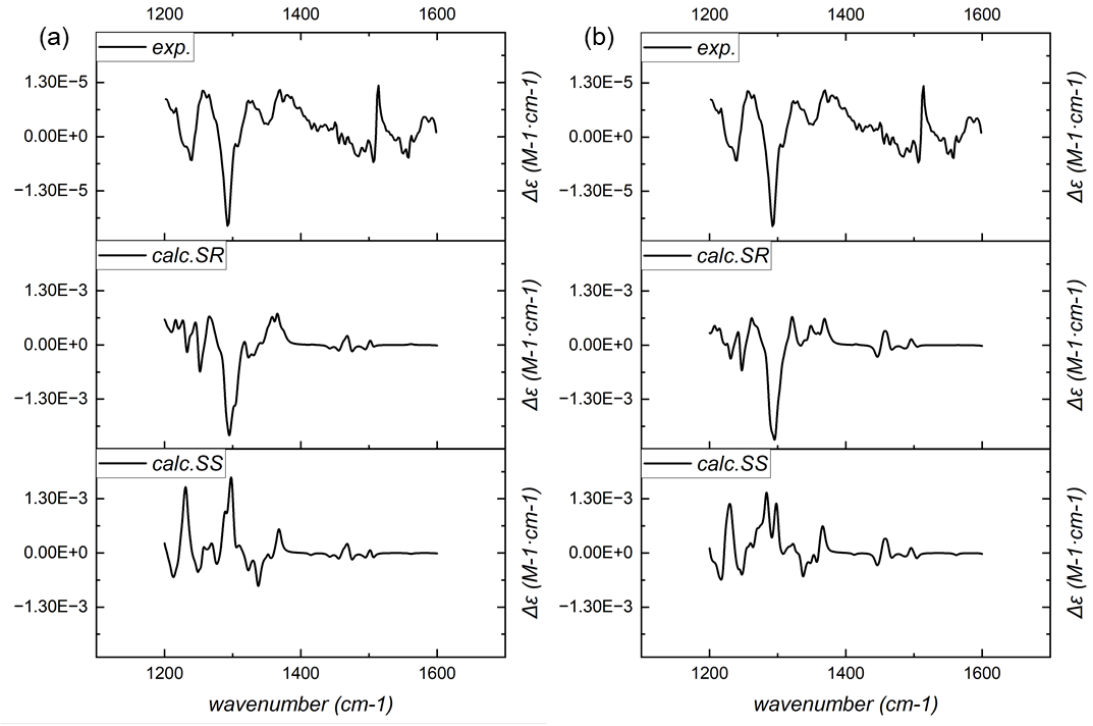


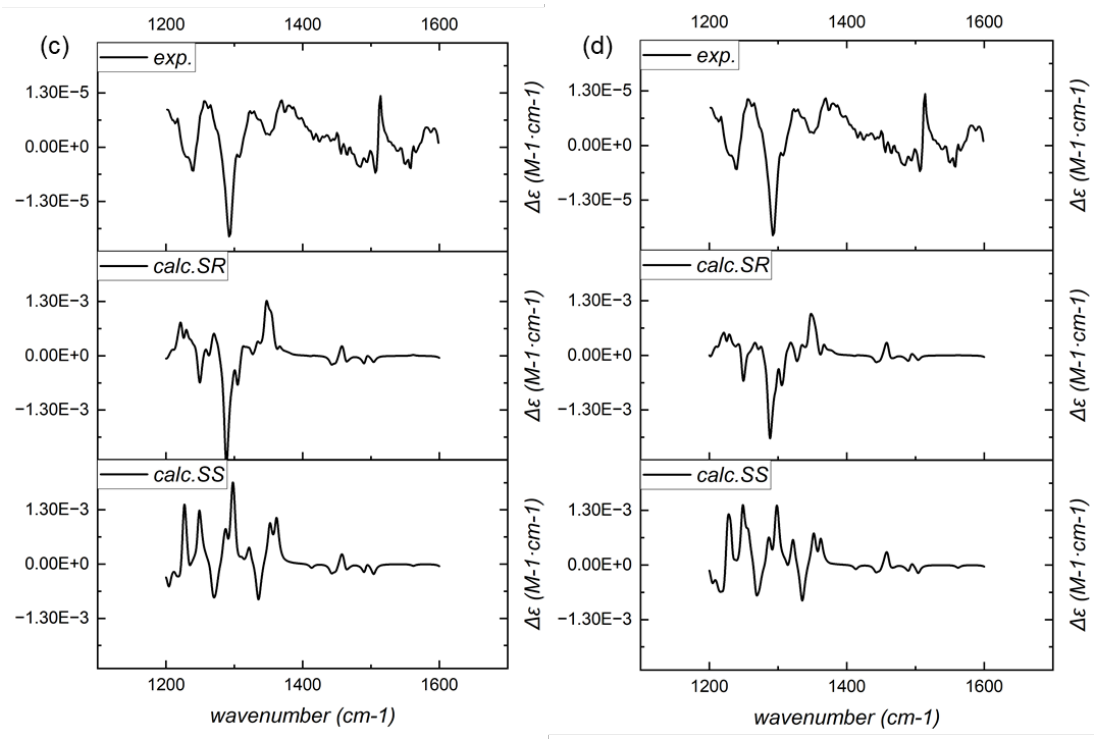
Supplementary Figure2. VCD spectrum of 8-D-*SR* and 8-D-*SS* under different computational parameters. (a) standard parameter; (b) standard parameter without dispersion correction and solvent model; (c) standard parameter without dispersion correction and solvent model and change basis from 6-31G* to 6-31G** in optimization process.



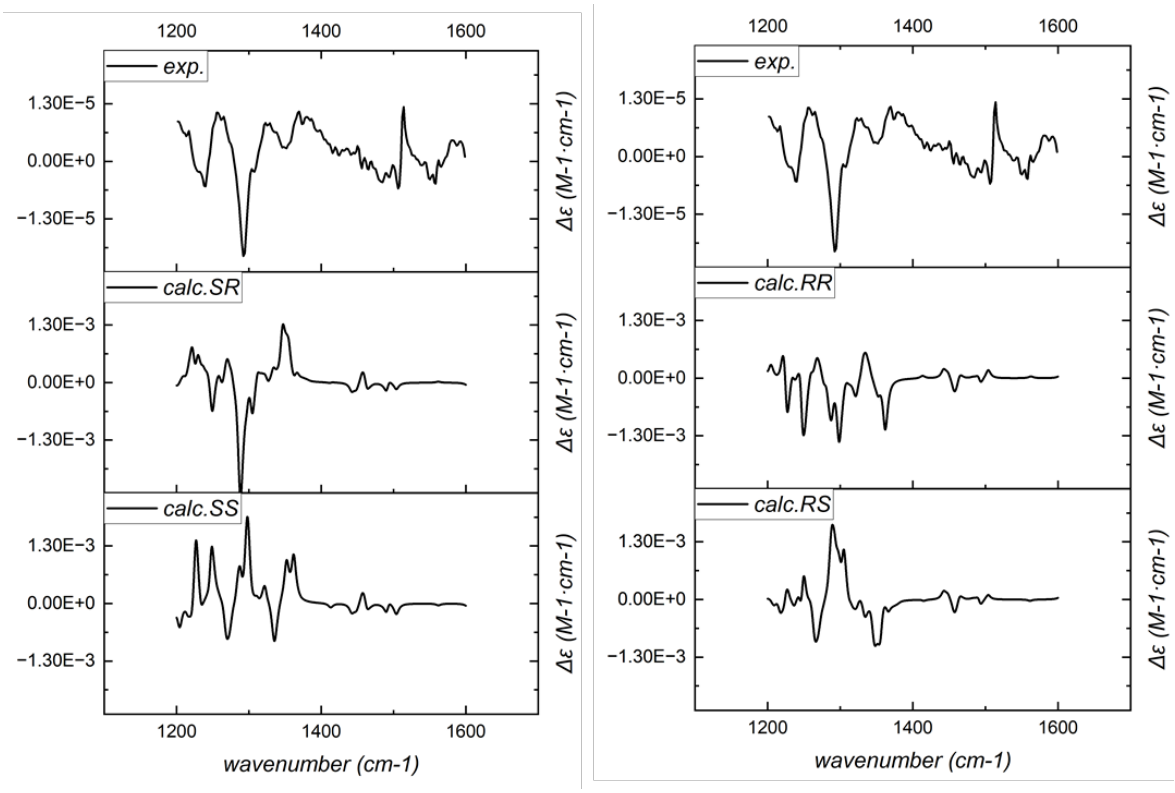
Supplementary Figure3. Overlayed and weighted 8-D-*SR* (left) and 8-D-*SS* (right) VCD spectra of all conformers under standard calculation parameters

In order to be certain that we have considered enough conformers, clustering threshold was tightened in **isostat** (modified input: "isostat crest_conformers.xyz -nt 4 -Nout 60 -Eout 5 -Edis 0.2 -Gdis 0.2 -T 298.15"), and 38 and 42 low-energy conformations of 8-D-S and 8-D-R were achieved. VCD calculation procedure were applied to these conformers and the comparison between the 8-D-SS and 8-D-SR VCD spectra of different number of conformers are provided in **Supplementary Figure4**. From which we may conclude that the conformers we have taken into consideration is basically sufficient and the spectra is reliable.





Supplementary Figure4. Comparison between VCD spectrum calculated with different number of conformers. (a) standard parameter without dispersion correction and solvent model, 23 conformers; (b) standard parameter without dispersion correction and solvent model, 38 conformers; (c) standard parameter, 23 conformers; (d) standard parameter, 38 conformers.



Supplementary Figure5. Comparison between 8-D-S (left) and 8-D-R (right) VCD spectrum.

Transition state calculations

Since the conformations of the TSs are quite complicated, in order to prove that the TS core structures found in **Xu8** are representative in this reaction other than a result by chance, **Xu1, Xu2, Xu3, Xu6, Xu8, Xu9** were taken as templates to calculate the free energy difference between major and minor TSs based on the core TS conformation found in **Xu8**. The calculated *ee*% are in good accordance with the experimental results (**Supplementary Table2**). TS structures are provided in related .xlsx file along with the SI, named as **Xu1-1a-2a-major** and **Xu1-1a-2a-minor** etc.

Supplementary Table2. Calculated and experimental *ee*%

Entry	Ligand and reactants	Calc. ΔΔG (kcal/mol)	Calc. *ee*%	Exp. *ee*%
1	**Xu1** + **1a** + **2a**	-0.02	-2	2
2	**Xu2** + **1a** + **2a**	0.87	63	85
3	**Xu3** + **1a** + **2a**	1.42	83	86
4	**Xu6** + **1a** + **2a**	0.98	68	82
5	**Xu8** + **1a** + **2a**	2.23	95	92
6	**Xu9** + **1a** + **2a**	1.81	91	92

Energy difference decomposition calculations

In order to analysis the key stereo-controlling factors and investigate the CH-π interaction quantitively, energy difference decomposition calculations were carried out. Firstly, from **Supplementary Table3**, we can tell that metal-involved interactions are quite similar between TSs of **Xu6** and **Xu8**. In other words, these interactions do not contribute much to the ΔΔE between them. Therefore, Pd atoms are removed from the TS structures in the later analysis, to eliminate the interaction difference involving metal centers. And weak interactions between **Xu-Phos** and substrates are focused.

Supplementary Table3. Calculated ΔΔG and ΔE of structure without Pd (kcal/mol)

Entry	Ligand and reactants	Calc. ΔΔG	no Pd ΔE	Metal-involved interaction
1	**Xu6** + **1a** + **2a**	0.98	7.86	6.88
2	**Xu8** + **1a** + **2a**	2.23	9.35	7.12

Secondly, to investigate interaction between **Xu-Phos** and substrates, no Pd TS structures were split into two dimers: (a) **Xu-Phos**-alcohol dimer (referenced as dimer1 later) and (b) **Xu-Phos**-vinyl substrate dimer (referenced as dimer2 later). ΔE_{dimer1} and ΔE_{dimer2} are provided in **Supplementary Table4**.

Supplementary Table4. Calculated ΔE_{dimer1} and ΔE_{dimer2} (kcal/mol)

Entry	Ligand and reactants	ΔE_{dimer1}	ΔE_{dimer2}
1	**Xu6** + **1a** + **2a**	2.53	3.80
2	**Xu8** + **1a** + **2a**	1.84	8.20

From **Supplementary Table4**, it is clear that the energy difference of dimer2 is the main contributor of the total energy gap. So, we further separate the dimer into (a) **Xu-Phos** and (b) vinyl substrate. More analysis results (**Fig 7b**) are provided in the manuscript.

Analysis of different conformation of Xu6 and Xu8 TSs

We proposed that the side-arm conformation of **Xu6** and **Xu8** are critical to the enantioselectivity. To certify that current conformations are not a result by chance, we replaced H adjacent to the side-arm in **Xu6** TSs to OMe to generate new conformation of **Xu8** TSs and also generated new conformation of **Xu6** TSs with similar procedure. The energy difference profile of the TSs is provided in **Supplementary Table5**, the structures are shown in **Supplementary Figure6**, and coordinates are provided in related .xlsx file along with the SI.

Supplementary Table5. Energy difference between conformations of Xu6 and Xu8 TSs (kcal/mol)

Entry	TS name	$\Delta E_{Xu\text{-}phos}$	ΔE_{other}	$\Delta E_{int\text{-}sidearm}$	$\Delta E_{int\text{-}all}$	ΔE_{all}	ΔG_{all}
1	**Xu6-major**	2.51	1.55	-0.04	-3.08	0.98	0.66
2	**Xu6-minor**	-1.50	0.06	3.67	3.83	2.39	4.07
3	**Xu8-major**	0.36	-0.08	0.02	-0.39	-0.10	1.42
4	**Xu8-minor**	1.90	-0.28	-3.03	-0.50	1.12	2.08

1) All energy differences are calculated as the new TSs' energy subtract the original TSs' energy

2) $E_{Xu\text{-}phos}$ refers to the single point energy of **Xu-phos** segment in the TS structures

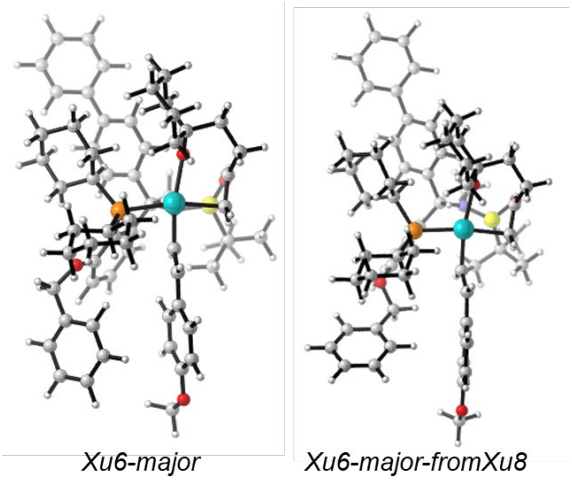
3) E_{other} refers to the sum of single point energy of all segments except for **Xu-phos** (i.e. vinyl substrate and alcohol substrate) in the TS structures

4) $E_{int\text{-}sidearm}$ refers to the interaction energy between side-arm and vinyl substrate in the TS structures

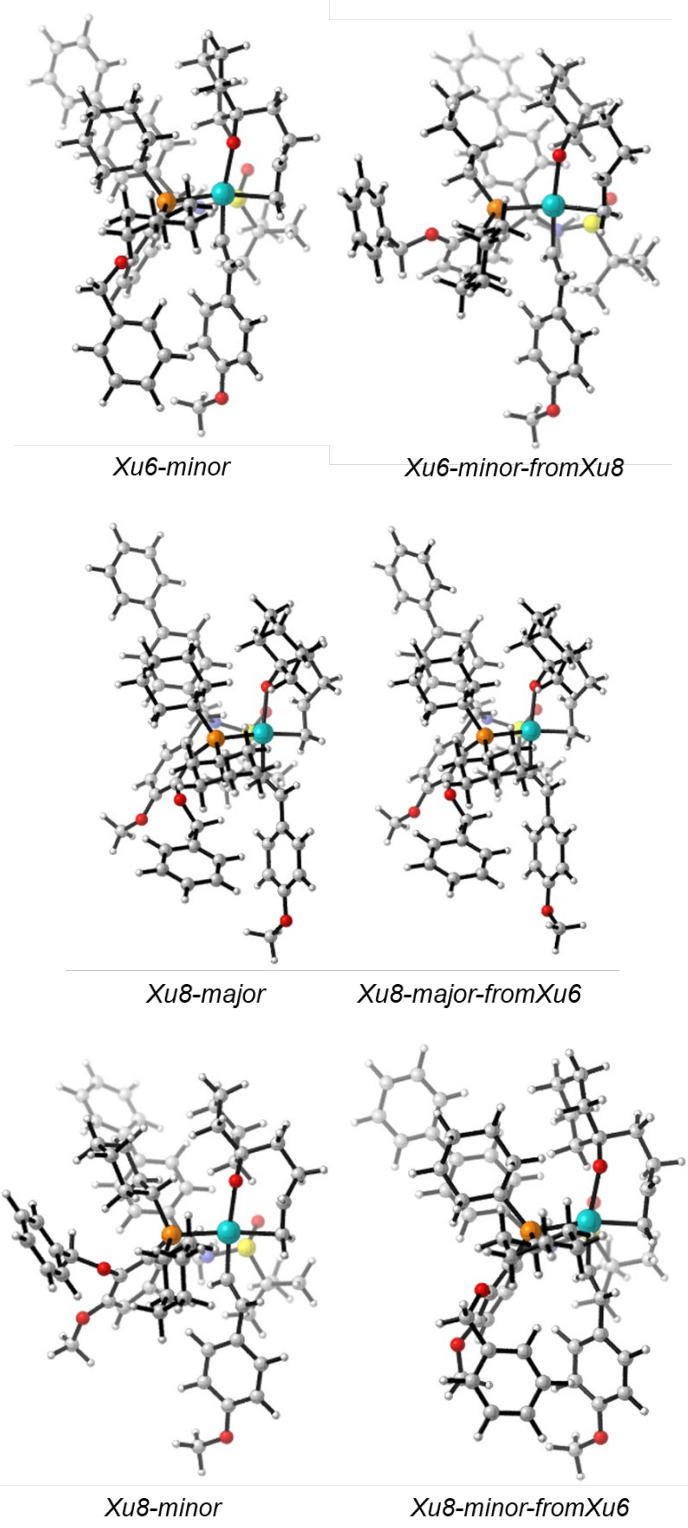
5) $E_{int\text{-}all}$ refers to the sum of interaction energy between all segments in the TS structures

6) E_{all} refers to the single point energy of the TS structures

7) G_{all} refers to the free energy of the TS structures



Xu6-major *Xu6-major-fromXu8*



Supplementary Figure6. Structures of different structures of Xu6 and Xu8 TSs.

Referring to **Supplementary Table5**, we can make the following observations: 1) None of the new TS structures exhibit lower free energy compared to their corresponding original TS structures. This reinforces our analysis, which is primarily based on the original TS structures; 2) Focusing on the **Xu6**-major TSs, a noteworthy increase in energy, denoted by $\Delta E_{Xu\text{-}phos}$, suggests that the introduction of the OMe group does indeed compel the side-arm to adopt a different position (even though both positions are downward), resulting in an overall higher energy for the entire ligand (+2.51 kcal/mol); 3) Concerning the **Xu6**-minor TSs, it is notable that the primary contributor to

the increase in energy (+3.67 kcal/mol) is the loss of interaction between the side-arm and the vinyl substrate. This underscores the significance of this interaction in the overall energetics of the system; 4) In the case of **Xu8**-major TSs, after the H was substituted with OMe, side-arm was optimized spontaneously to a conformation similar to the original **Xu8**-major TS. As a result, the single-point energies of these structures turned out to be very similar.; 5) Concerning **Xu8**-minor TSs, forcing the side-arm to take the downward conformation indeed make the ligand energy higher (+1.90 kcal/mol), which is the main contributor of the overall energy rise, and although interaction between the side-arm and vinyl substrate is stronger, it is masked by the loss of other interactions.

Analysis of the effect of OR groups ortho to the side-arm

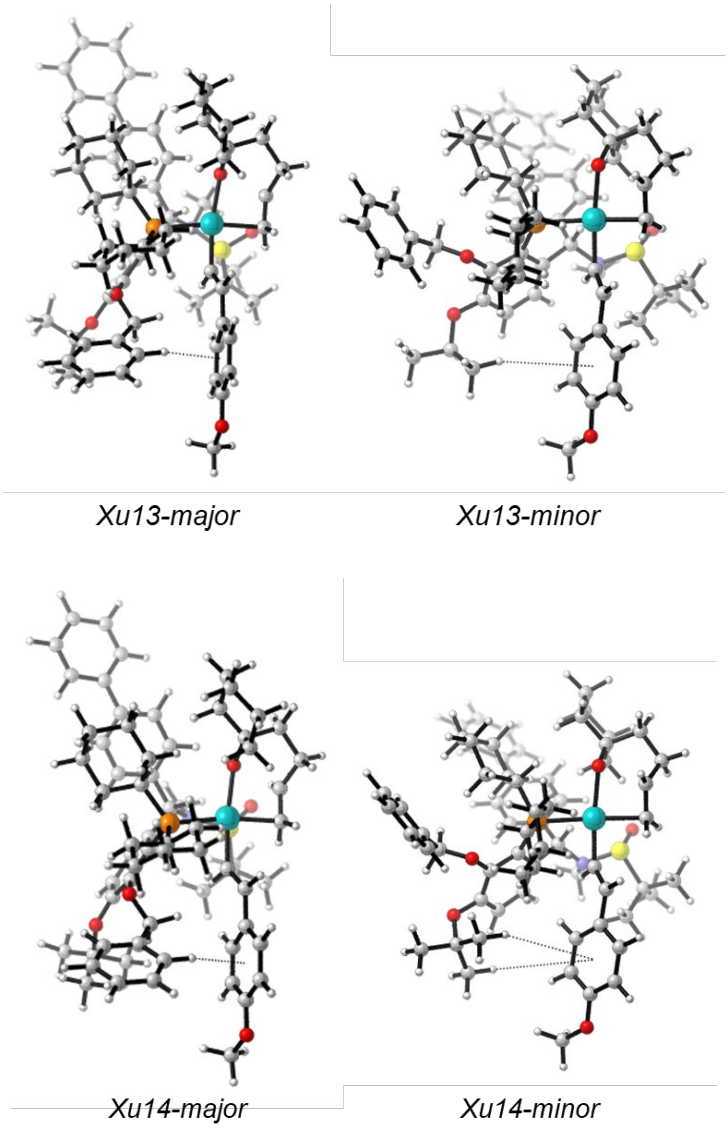
We originally proposed that the main reason of OMe promoting the side-arm effect is its steric influence. To verify this proposal, OMe group was replaced with OEt, OiPr and OtBu groups respectively to generate new ligands **Xu12**, **Xu13** and **Xu14**. Difference of free energies and *ee*% values were calculated according to the standard procedure and provided in **Supplementary Table6**.

Supplementary Table6. Calculated and experimental *ee*% of ligands with different OR groups

Entry	Ligand and reactants	Calc. ΔΔG (kcal/mol)	Calc. *ee*%	Exp. *ee%*
1	**Xu12** + **1a** + **2a**	2.16	94	90
2	**Xu13** + **1a** + **2a**	0.99	68	85
3	**Xu14** + **1a** + **2a**	1.08	72	/*

***** Multiple attempts to synthesize **Xu14** all failed, so experimental *ee%* value of **Xu14** is not available.

The high calc. and exp. *ee%* value of **Xu12** supports that the steric effect of OR groups are beneficial to improvement of *ee%*. However, we also found that when the OR group gets bulkier, the *ee%* value starts to drop. From visual inspection of the TSs of **Xu13** and **Xu14**, we suspect that as the OR groups might have weak interaction with vinyl substrate (**Supplementary Figure7**). To verify this, interaction energy between OR groups and vinyl substrates are calculated and provided in **Supplementary Table7**.



Supplementary Figure7. Structure of Xu13 and Xu14 TSs

Supplementary Table7. Weak interaction energy between different OR groups and vinyl substrate (kcal/mol)

Entry	Ligand and reactants	Eint	ΔEint	Calc. ΔΔG
1	**Xu8-major**	-0.01	/	/
2	**Xu8-minor**	-0.13	-0.12	2.23
3	**Xu12-major**	-0.03	/	/
4	**Xu12-minor**	-0.17	-0.14	2.16
5	**Xu13-major**	-0.07	/	/
6	**Xu13-minor**	-0.77	-0.70	0.99
7	**Xu14-major**	-0.56	/	/
8	**Xu14-minor**	-1.48	-0.91	1.08

From **Supplementary Table7**, it is clear that when the OR group is OMe or OEt, the interaction between OR group and vinyl substrate is quite weak and negligible, but when it comes to OiPr and OtBu, the interaction become significant. More importantly, the interactions in the minor TSs are

stronger than those in the major TSs due to the conformation difference. And ΔEint accounts for the major part of the decrease of the ΔΔG and thus the decrease of *ee%*.

In conclusion, we posit that the enhancement in ee% achieved by introducing the OMe group into the ortho position of the side-arm is primarily attributed to its steric effect. Nonetheless, the introduction of bulkier substitution groups is likely to lead to weak interactions with the vinyl substrate, particularly in the minor transition state, consequently resulting in a decrease in ee%.

Visualization of weak interaction

We calculated weak interactions between two fragments: 1. Side-arm (OBn group, atom index 77-91 in **Xu8-ts**) 2. Vinyl substrate (atom index 108-126 in **Xu8-ts**). Weak interaction is calculated with IGM method by Multiwfn.[28] Isovalue of the isosurface shown in **Fig 7** is 0.01.

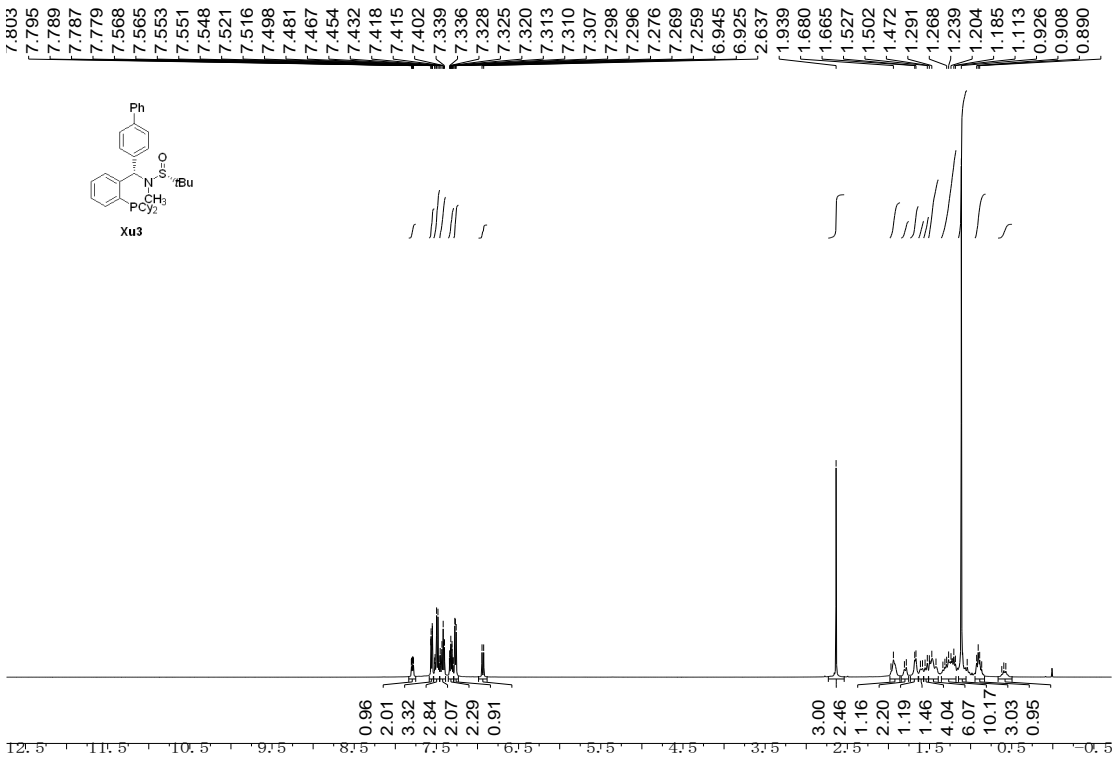
Quantitative calculation of weak interaction

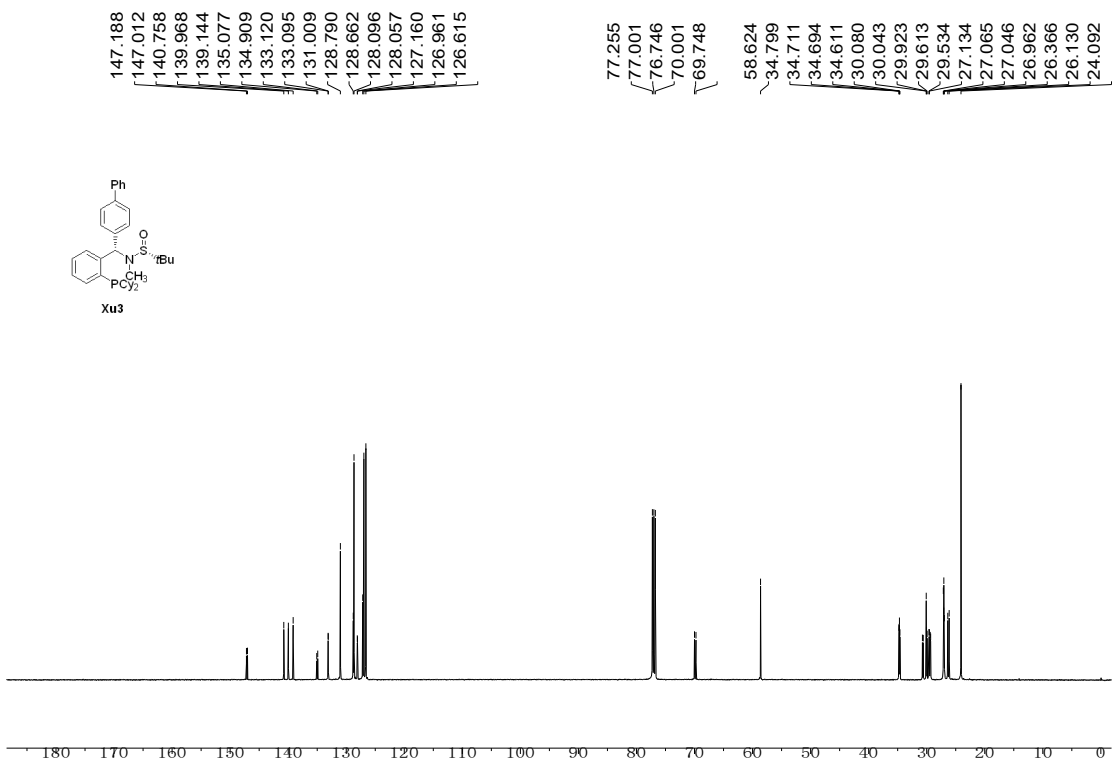
The interaction energy values are defined as the single point energy gap between the complex and components of the complex (**Eq 1**).[29]

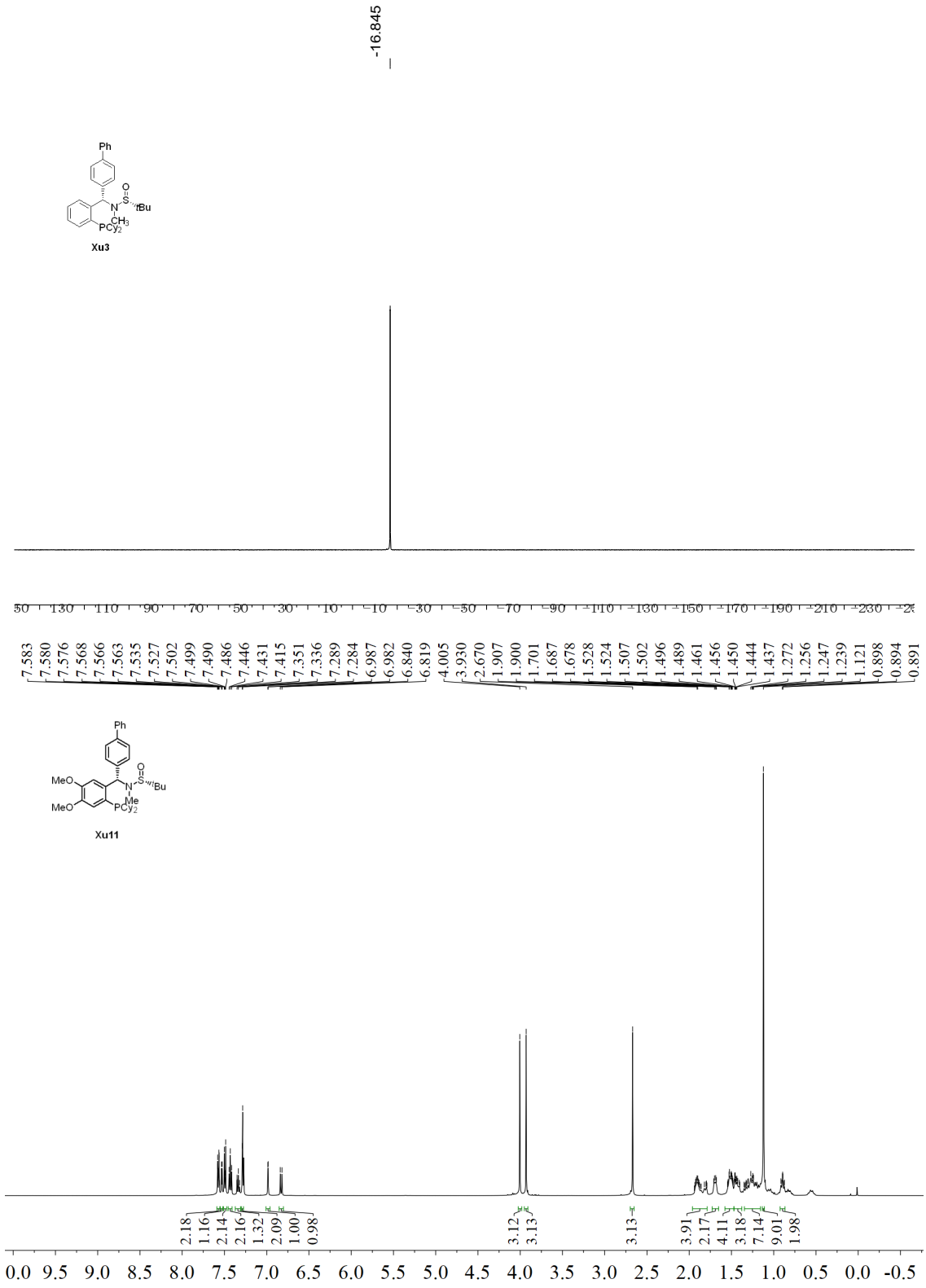
$$E_{int} = E_{complex} - E_{component1} - E_{component2} \quad \textbf{(Eq 1)}$$

To illustrate the calculation procedure, we will use the example of calculating the interaction energy between the side-arm and the vinyl substrate in Xu8-ts. Firstly, we isolate the side-arm (OBn group, atom index 77-91) and the vinyl substrate (atom index 108-126) from the TS structure. Next, we introduce a hydrogen atom at each break point of the covalent bonds within these isolated molecules. The positions of these added hydrogen atoms are then optimized using standard optimization parameters (as outlined in the General Calculation Procedure), with all other atoms held strictly constrained. Finally, we perform a single-point energy calculation using standard parameters (as specified in the **General Calculation Procedure**). This calculation yields the energy of the complex as well as the individual energies of its constituent parts.

9. ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectra



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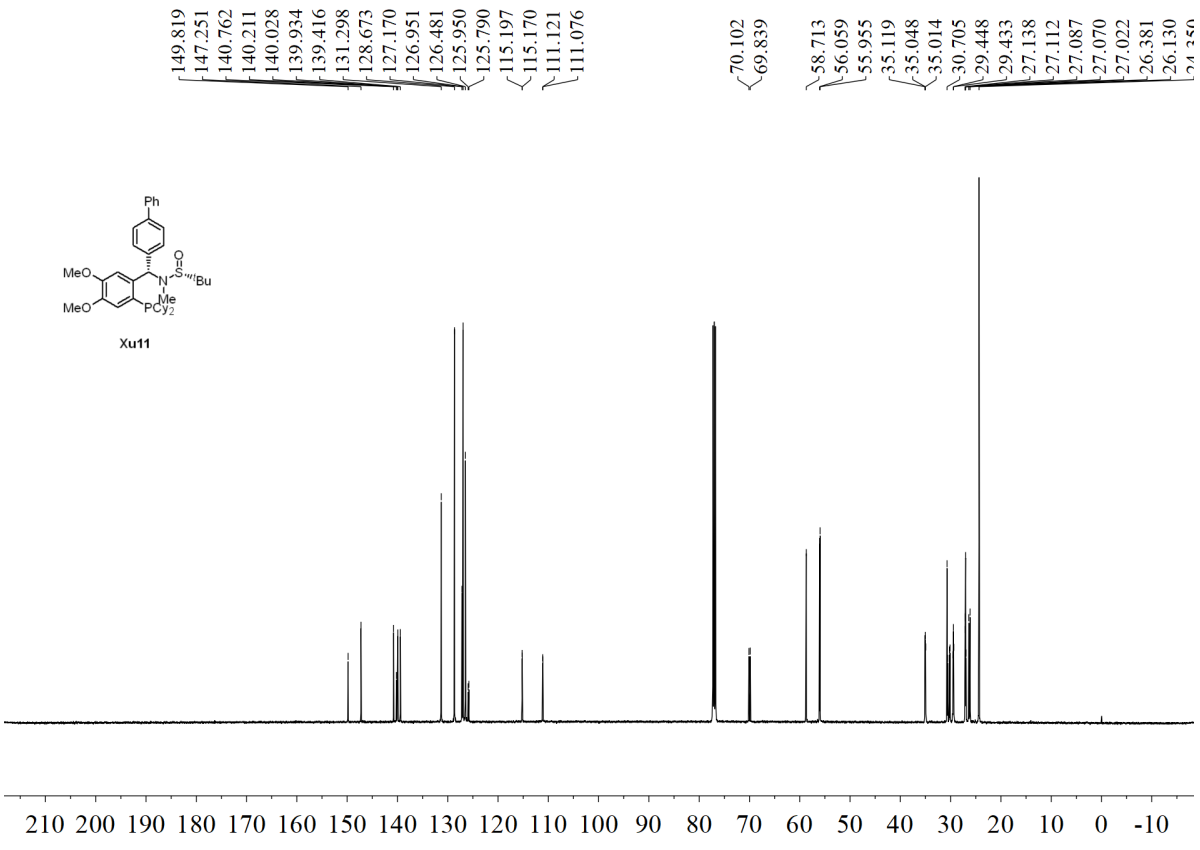
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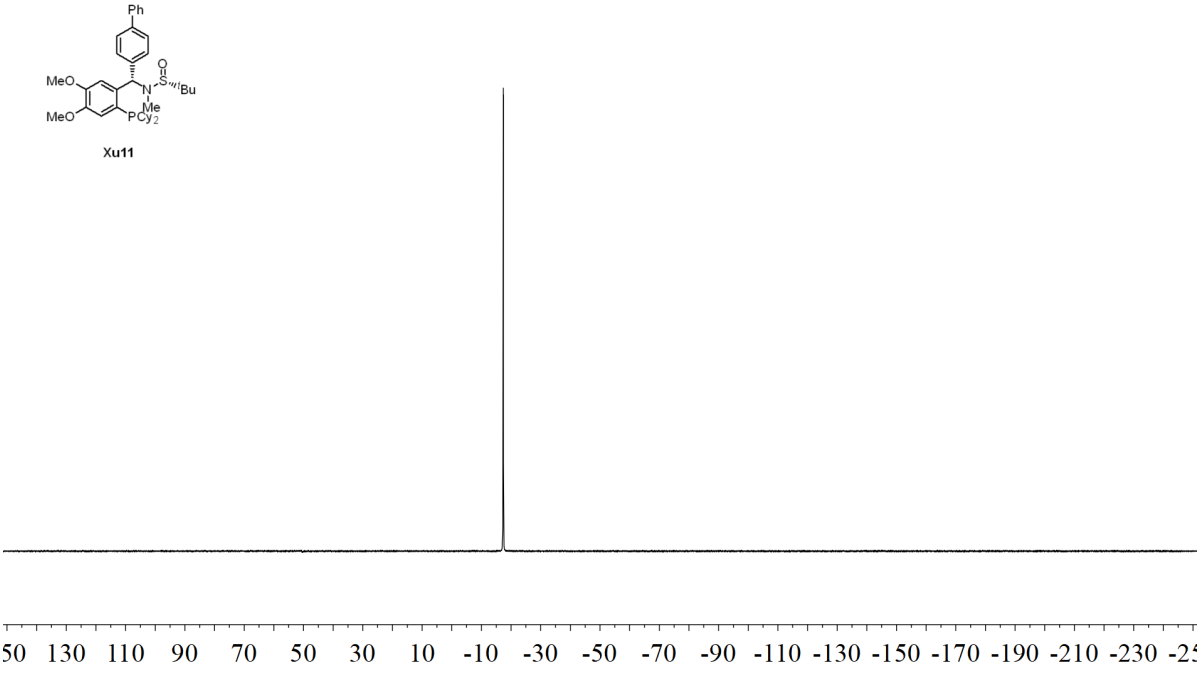
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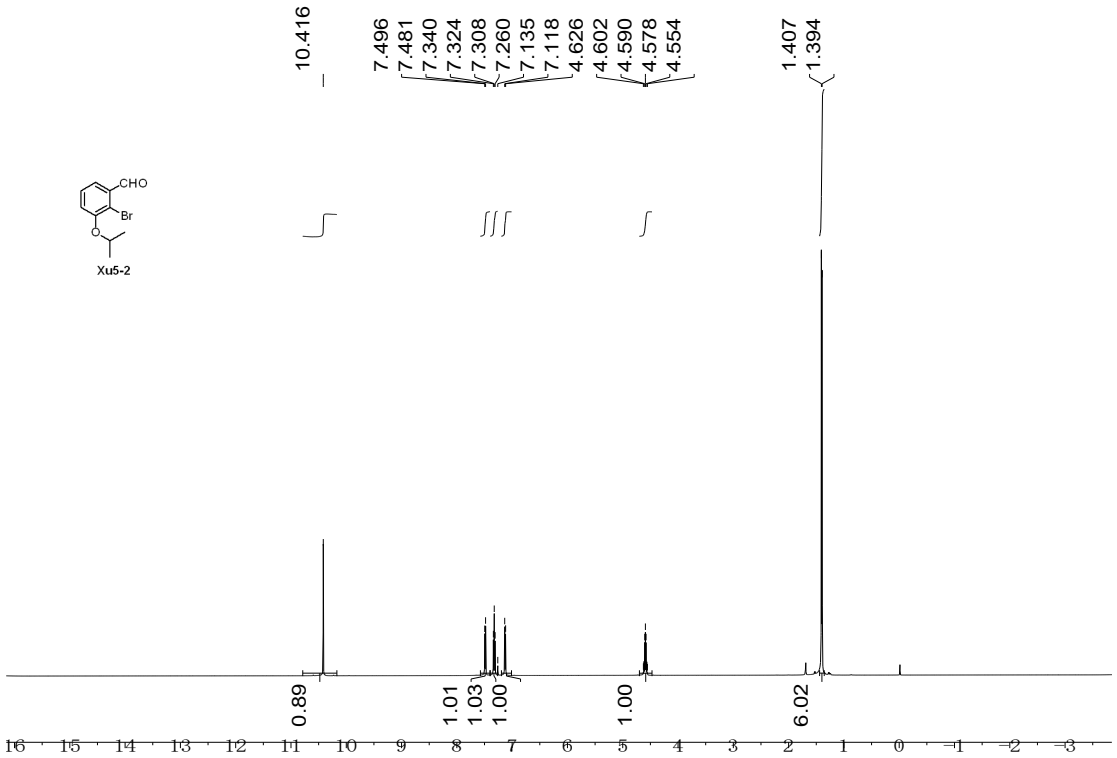
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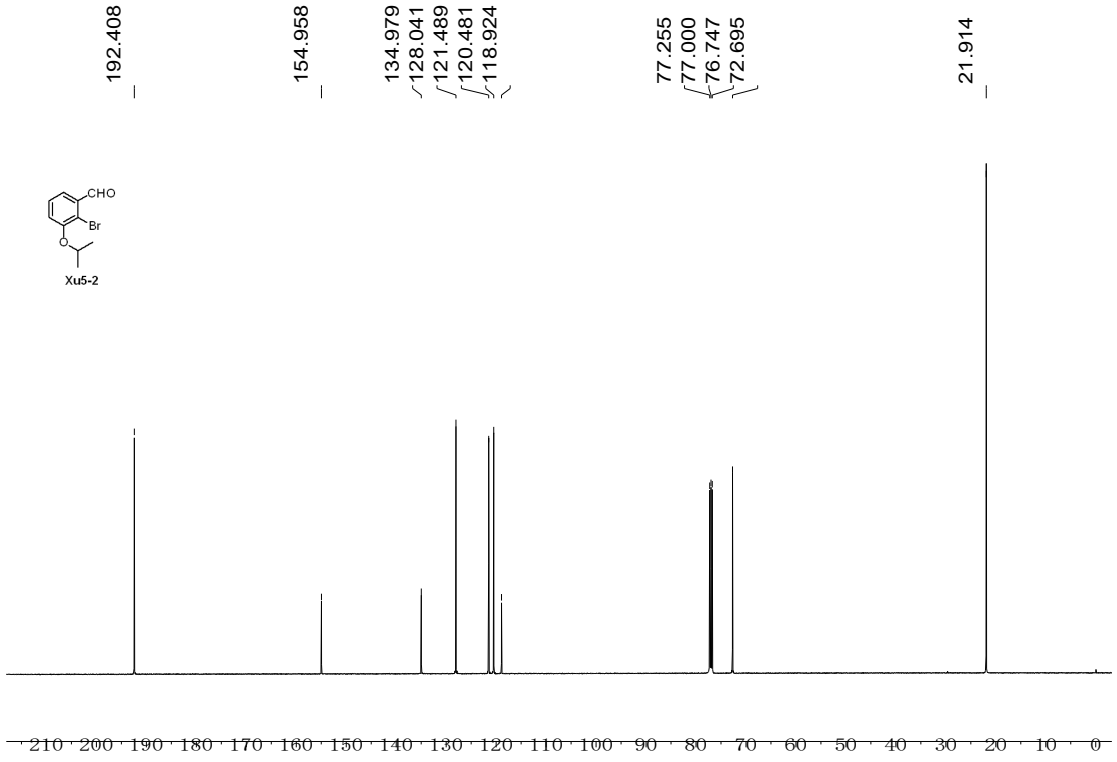
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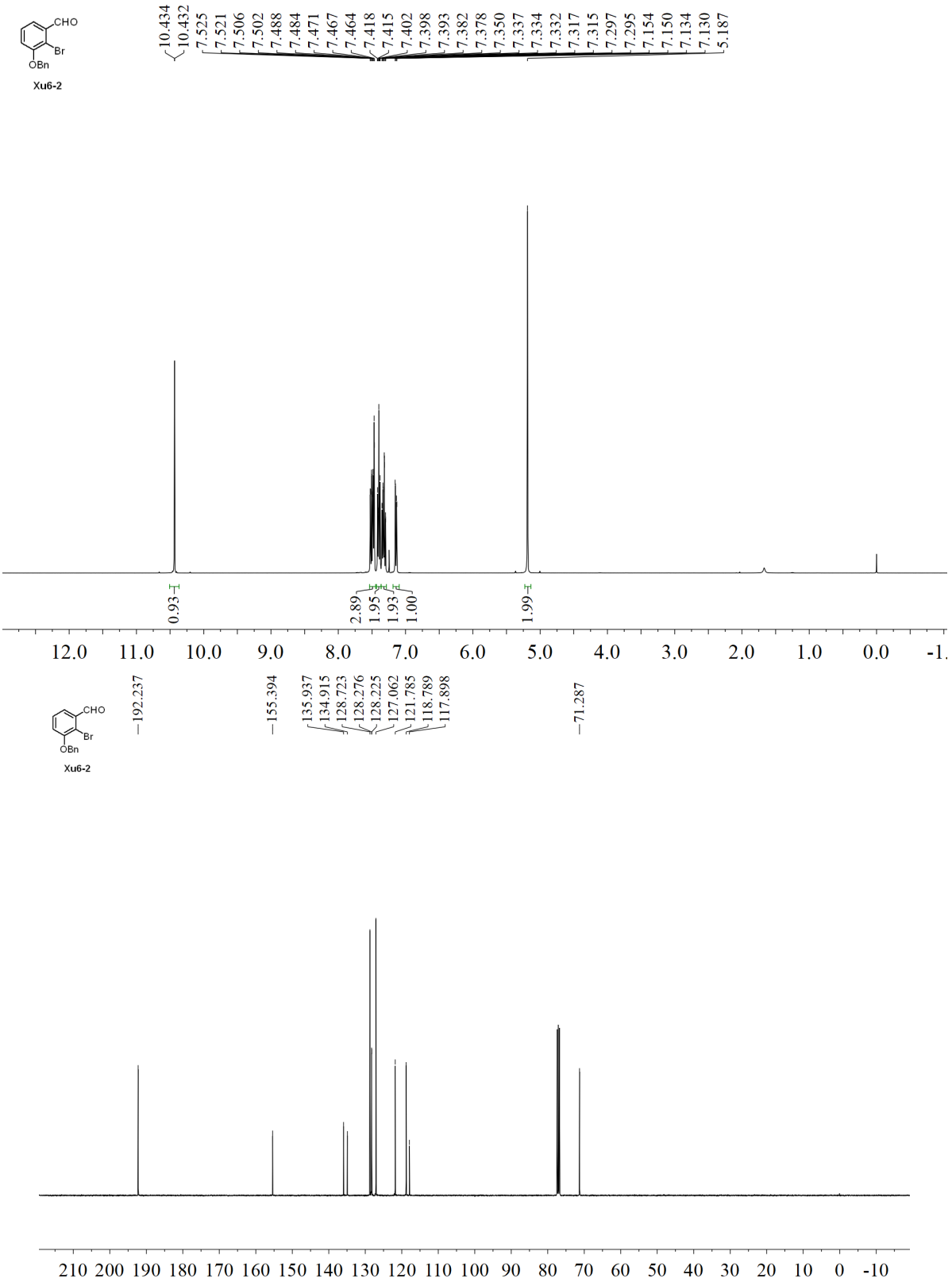
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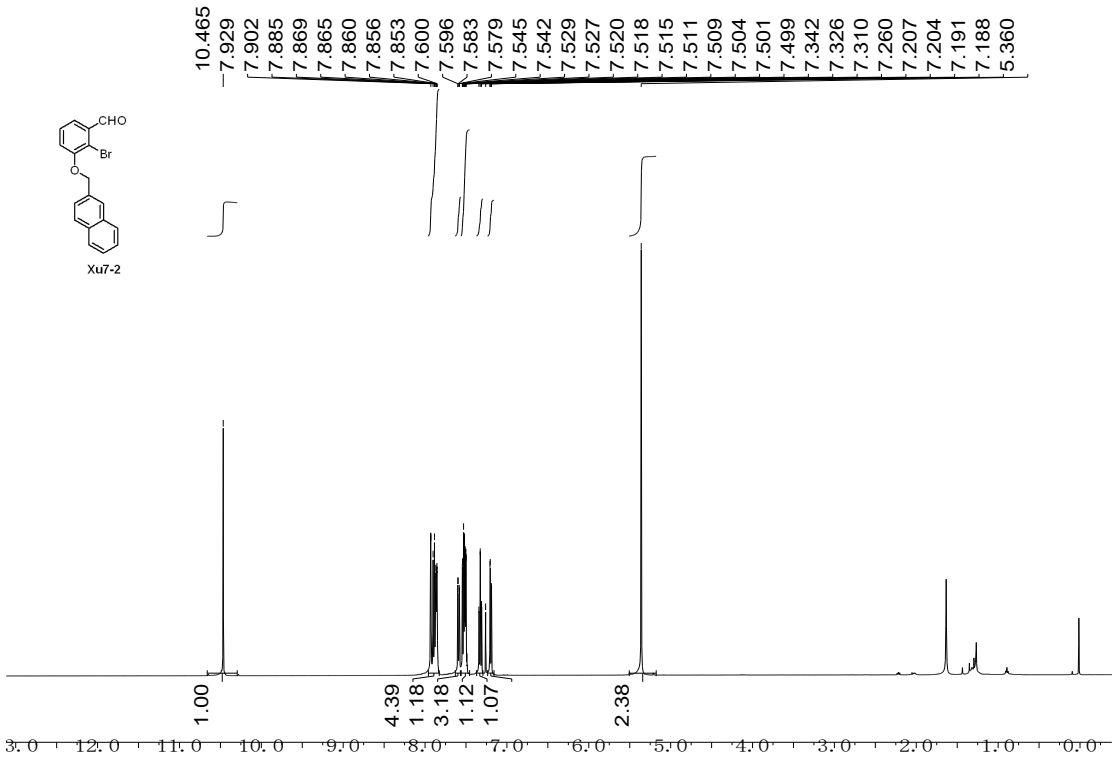
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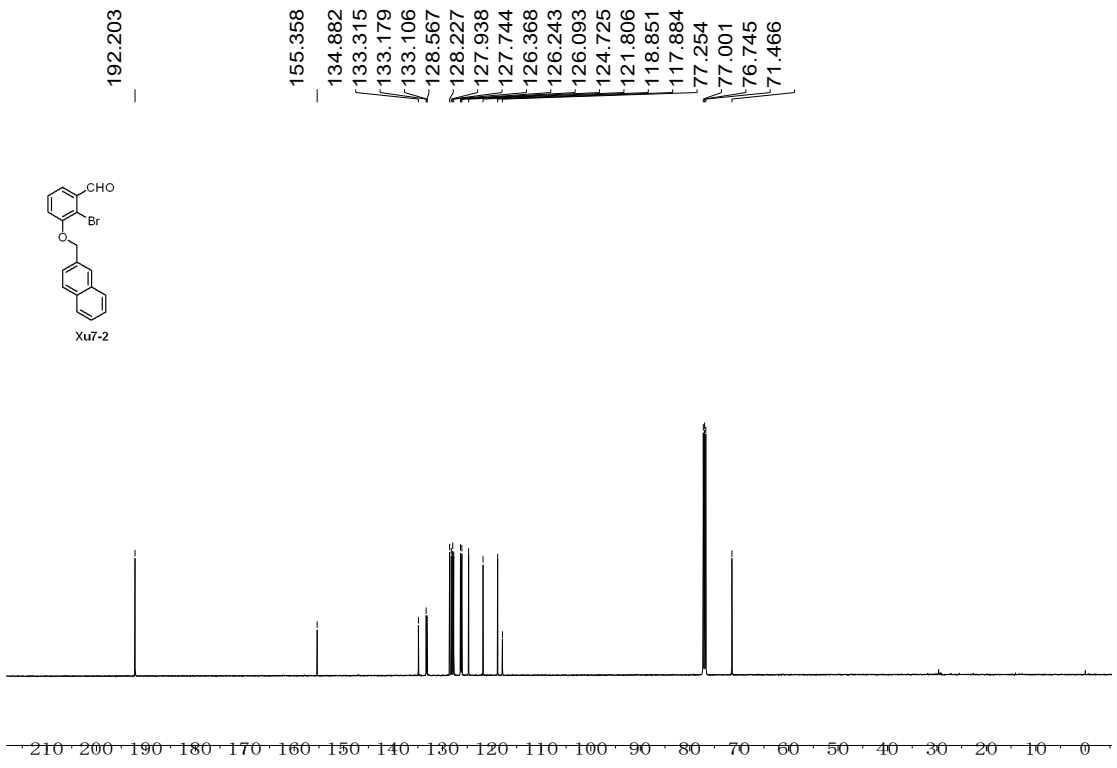
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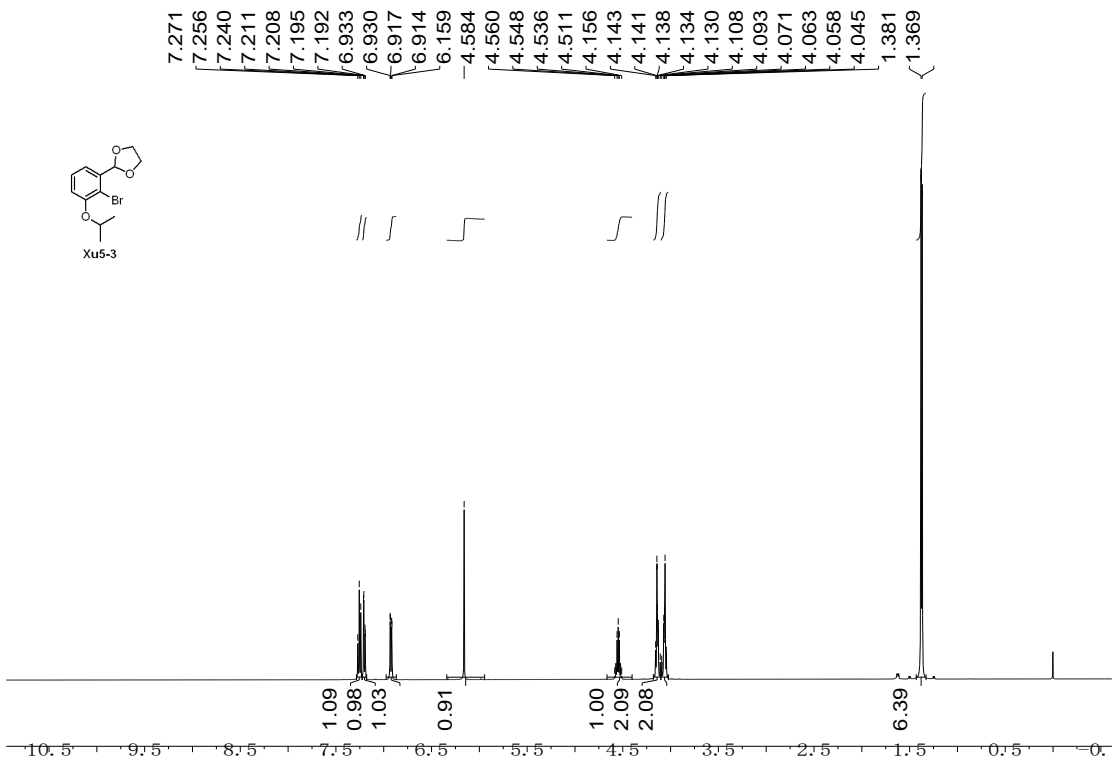
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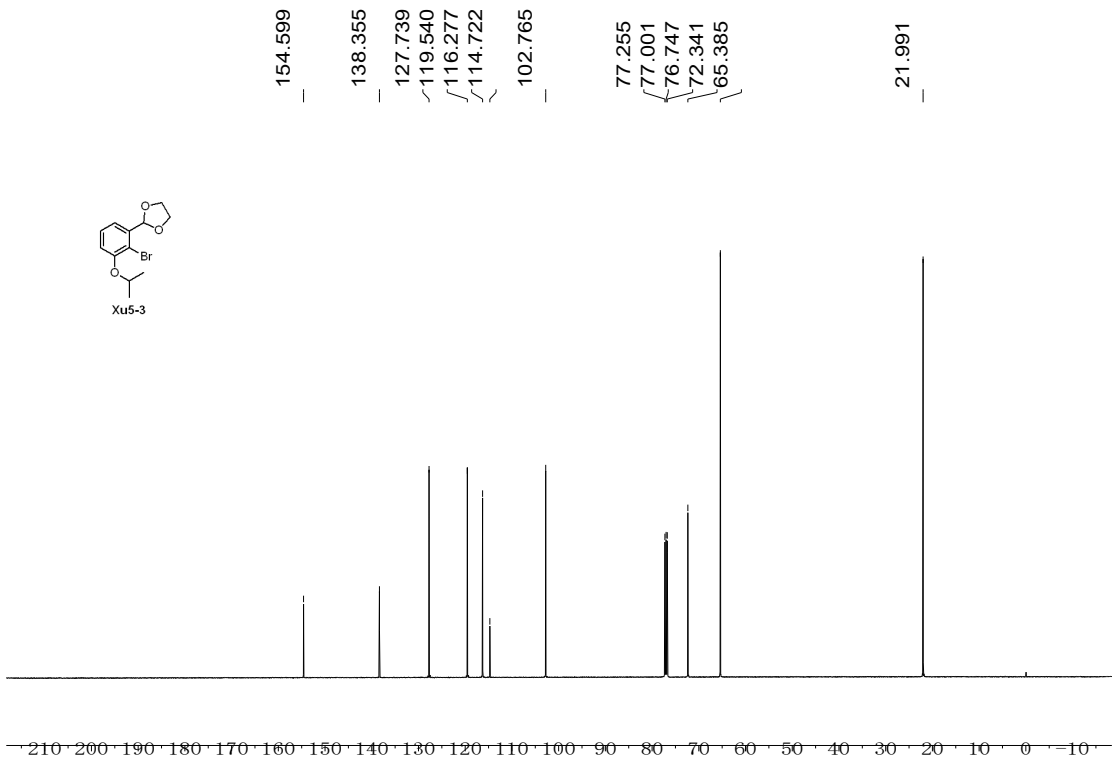
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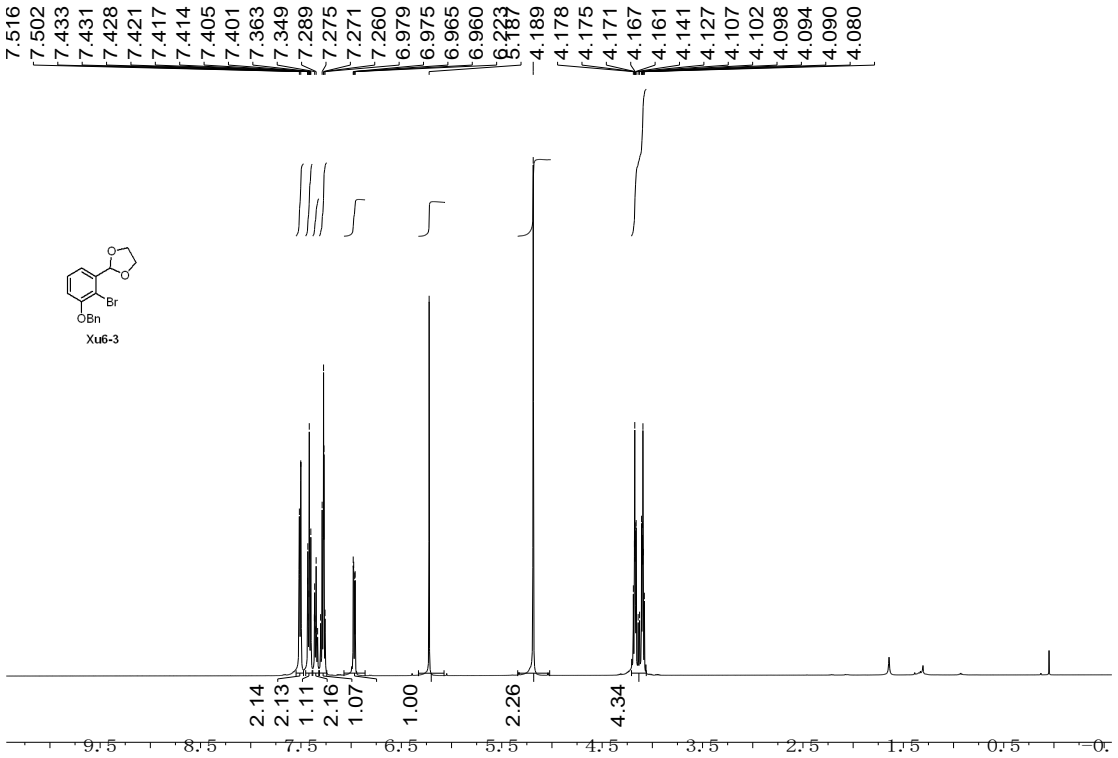
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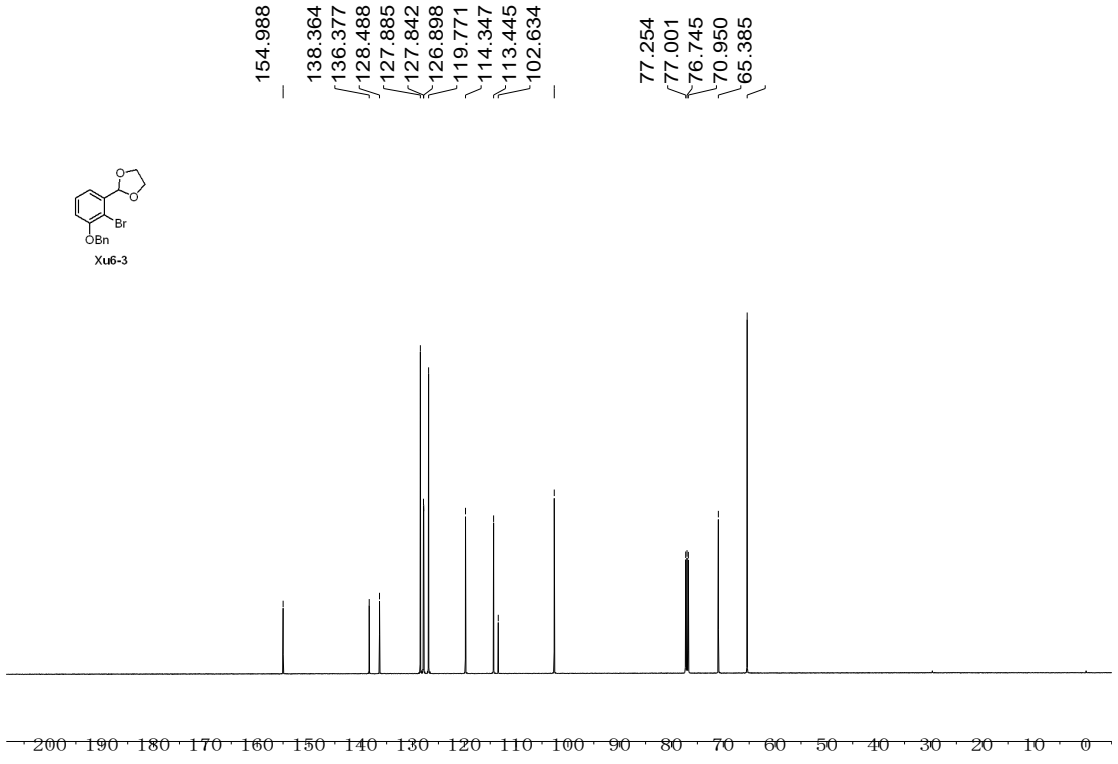
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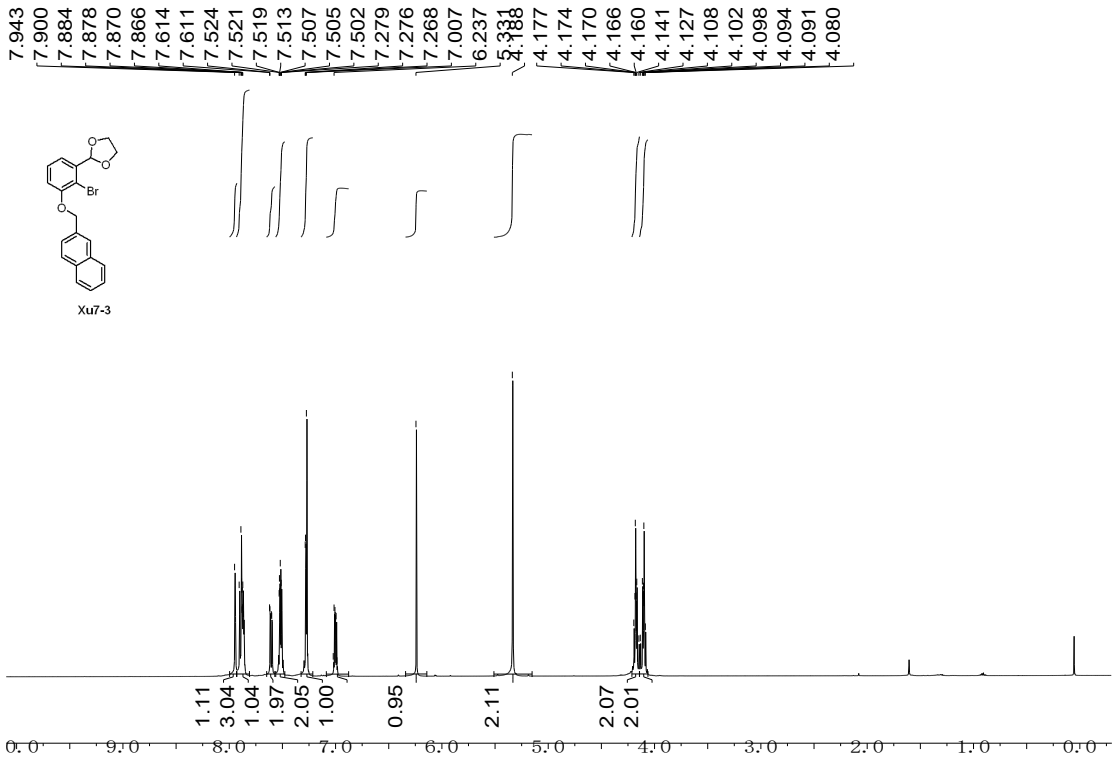
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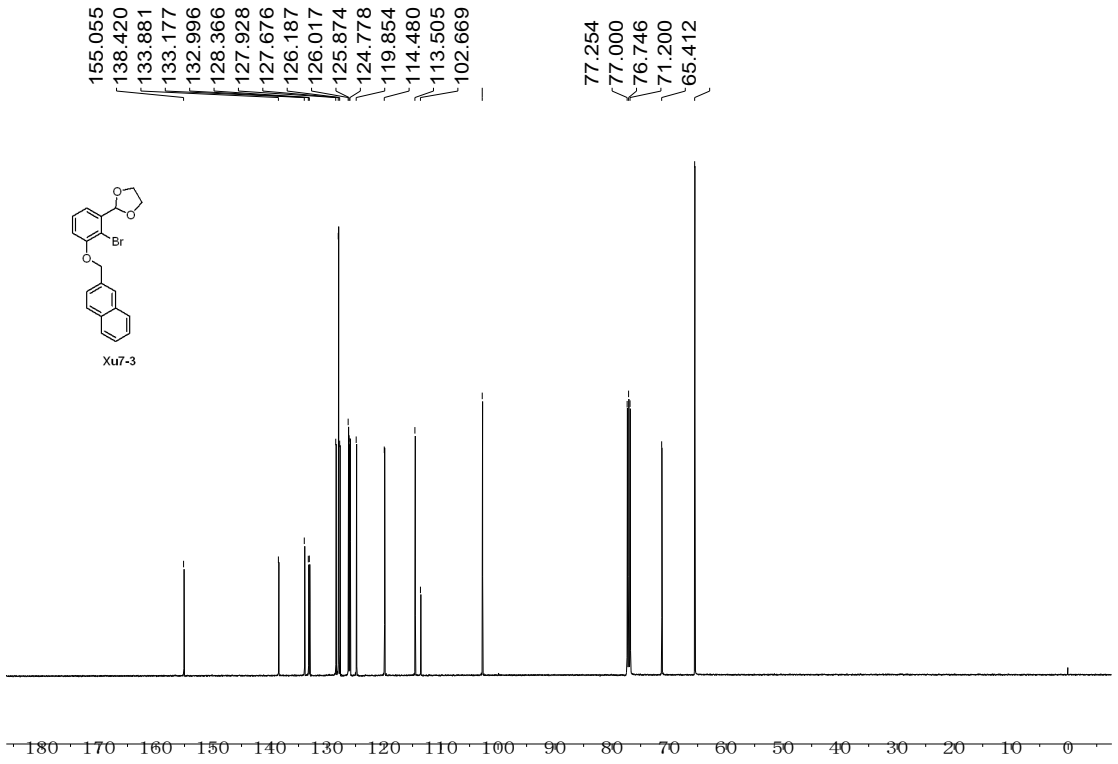
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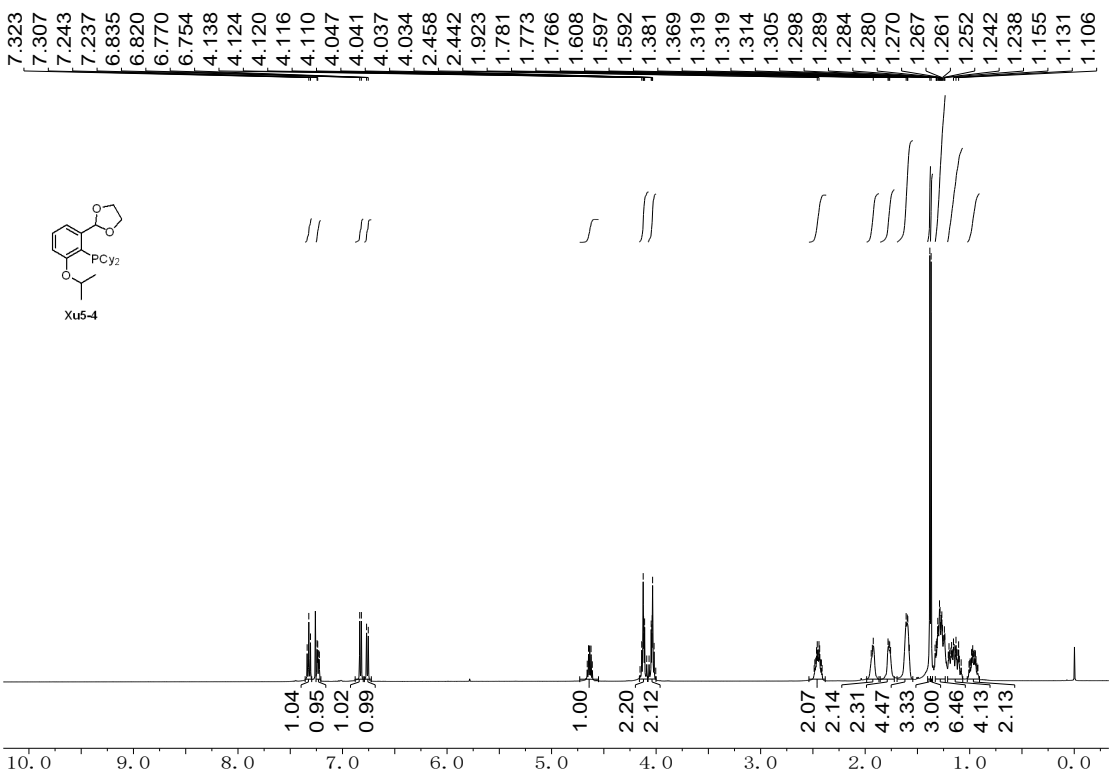
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4.037
4.034
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2.442
1.923
1.781
1.773
1.766
1.608
1.597
1.592
1.381
1.369
1.319
1.319
1.314
1.305
1.298
1.289
1.284
1.280
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1.242
1.238
1.155
1.131
1.106
PCy2
Xu5-4
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1.02
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2.20
2.12
2.07
2.14
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4.47
3.33
3.00
6.46
4.13
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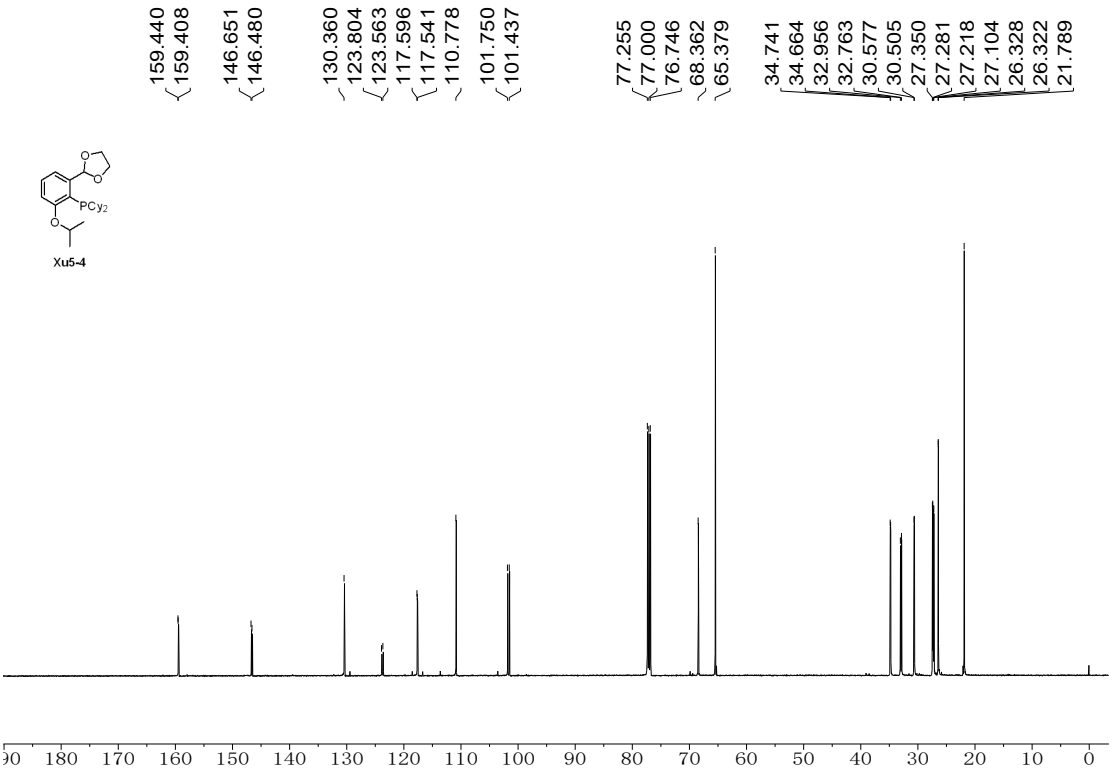
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27.218
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26.322
21.789
PCy2
Xu5-4
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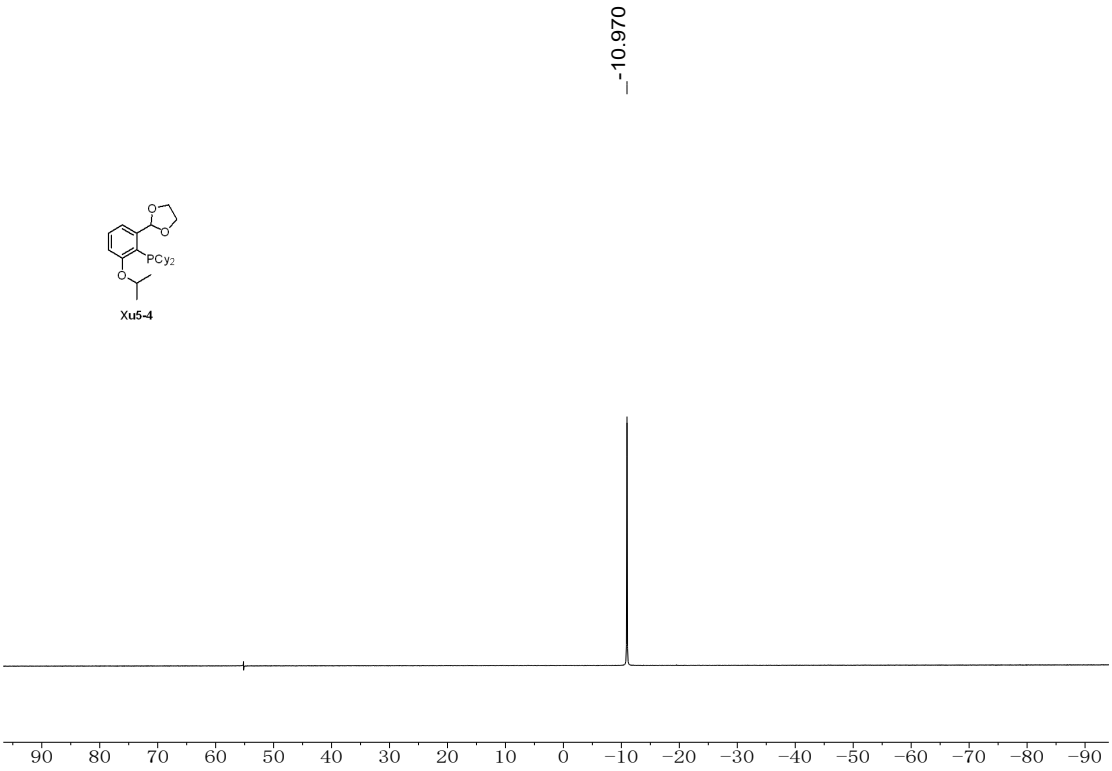
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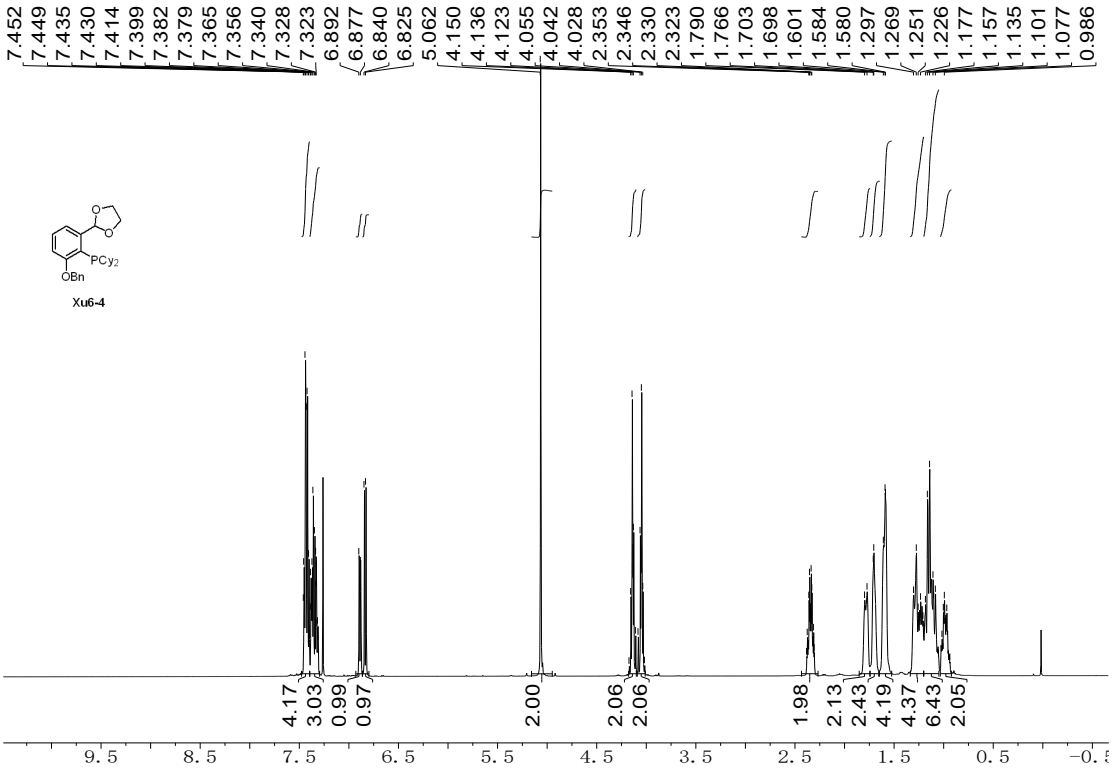
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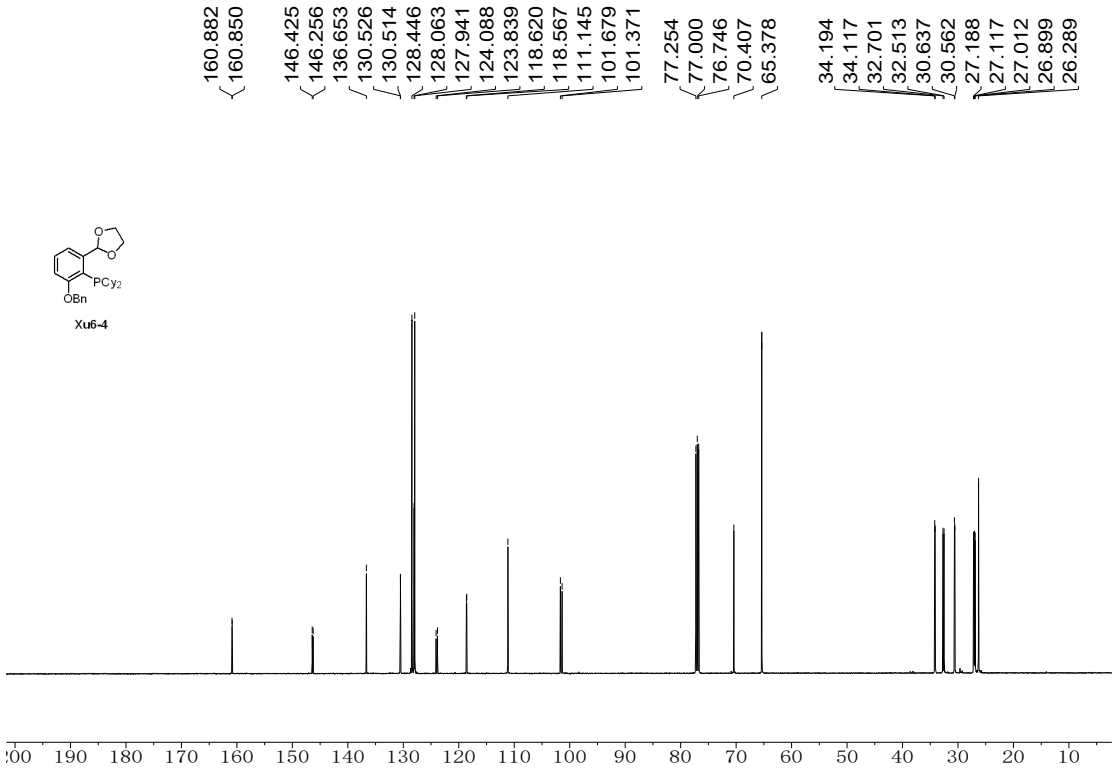
PCy2
OBn
Xu6-4
4.17 3.03 0.99 0.97 2.00 2.06 2.06 1.98 2.13 2.43 4.19 4.37 6.43 2.05
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5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118.567
111.145
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101.371
77.254
77.000
76.746
70.407
65.378
34.194
34.117
32.701
32.513
30.637
30.562
27.188
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26.289
PCy2
OBn
Xu6-4
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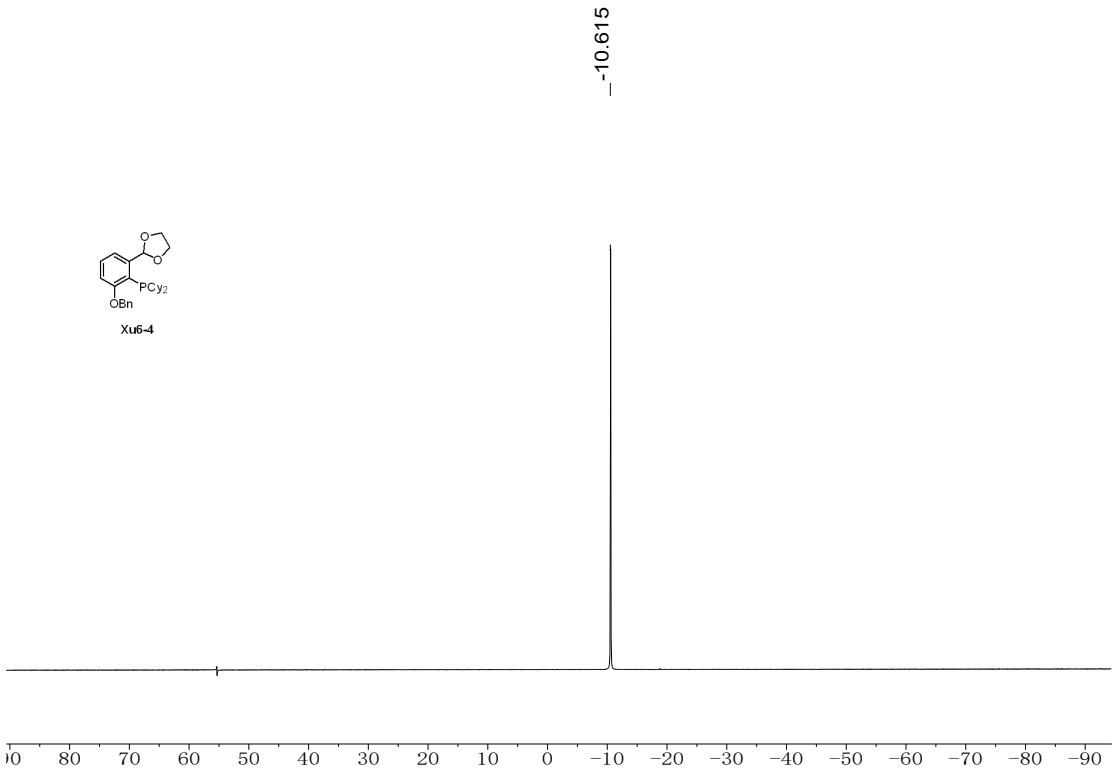
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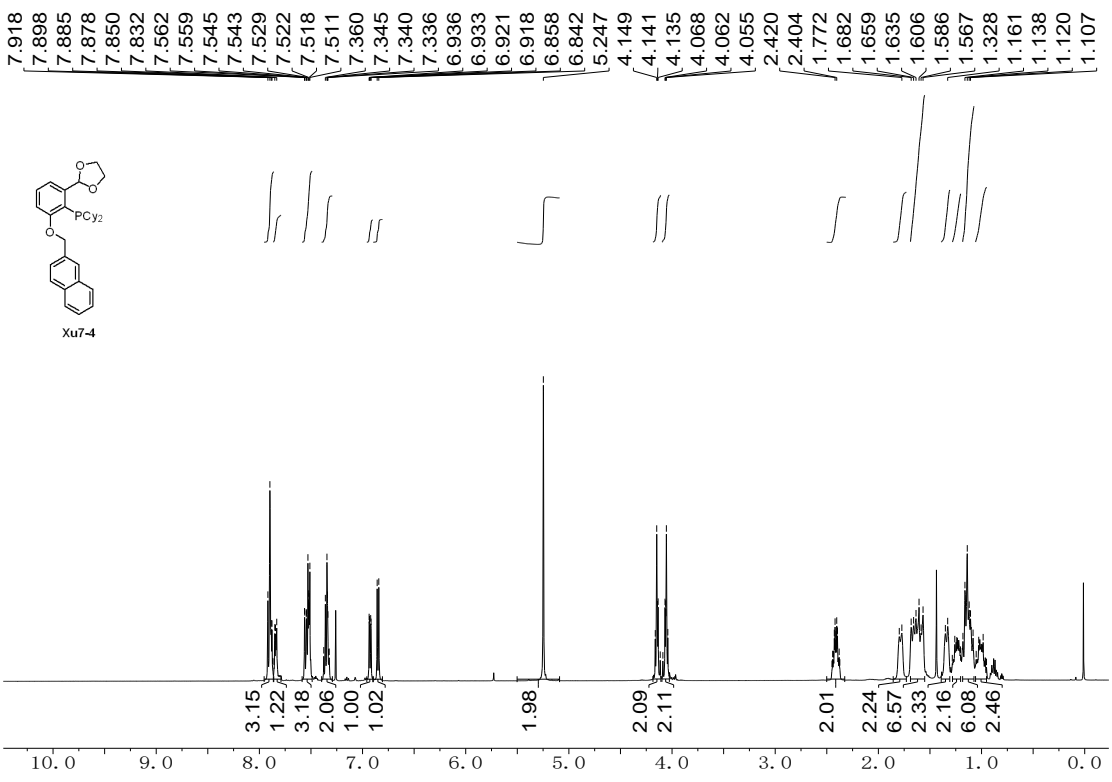
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7.518
7.511
7.360
7.345
7.340
7.336
6.936
6.933
6.921
6.918
6.858
6.842
5.247
4.149
4.141
4.135
4.068
4.062
4.055
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2.404
1.772
1.682
1.659
1.635
1.606
1.586
1.567
1.328
1.161
1.138
1.120
1.107
PCy2
Xu7-4
3.15
1.22
3.18
2.06
1.00
1.02
1.98
2.09
2.11
2.01
2.24
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6.08
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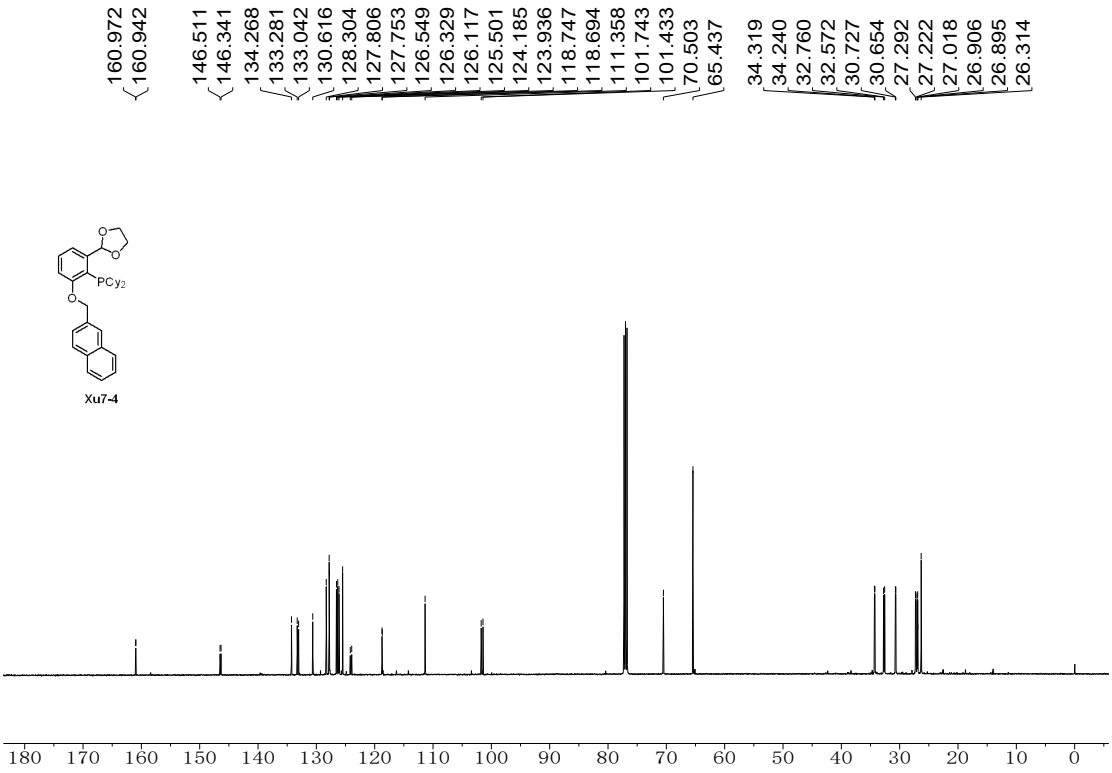
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125.501
124.185
123.936
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111.358
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101.433
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65.437
34.319
34.240
32.760
32.572
30.727
30.654
27.292
27.222
27.018
26.906
26.895
26.314
PCy2
Xu7-4
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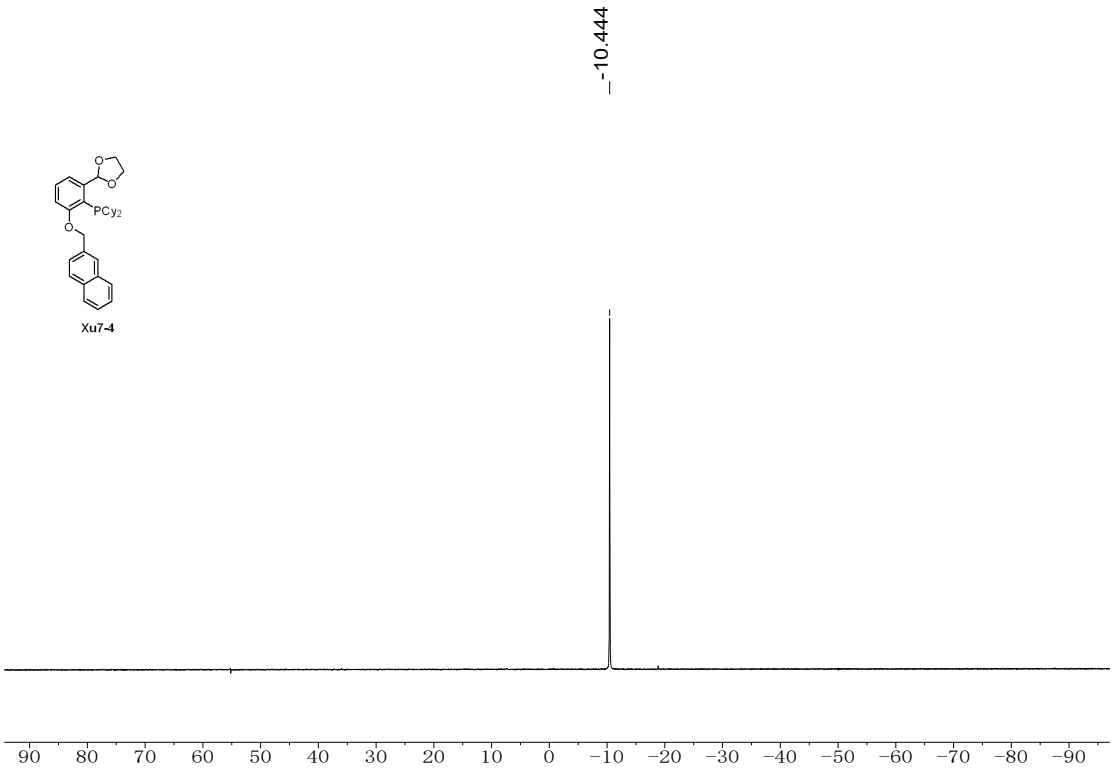
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−50
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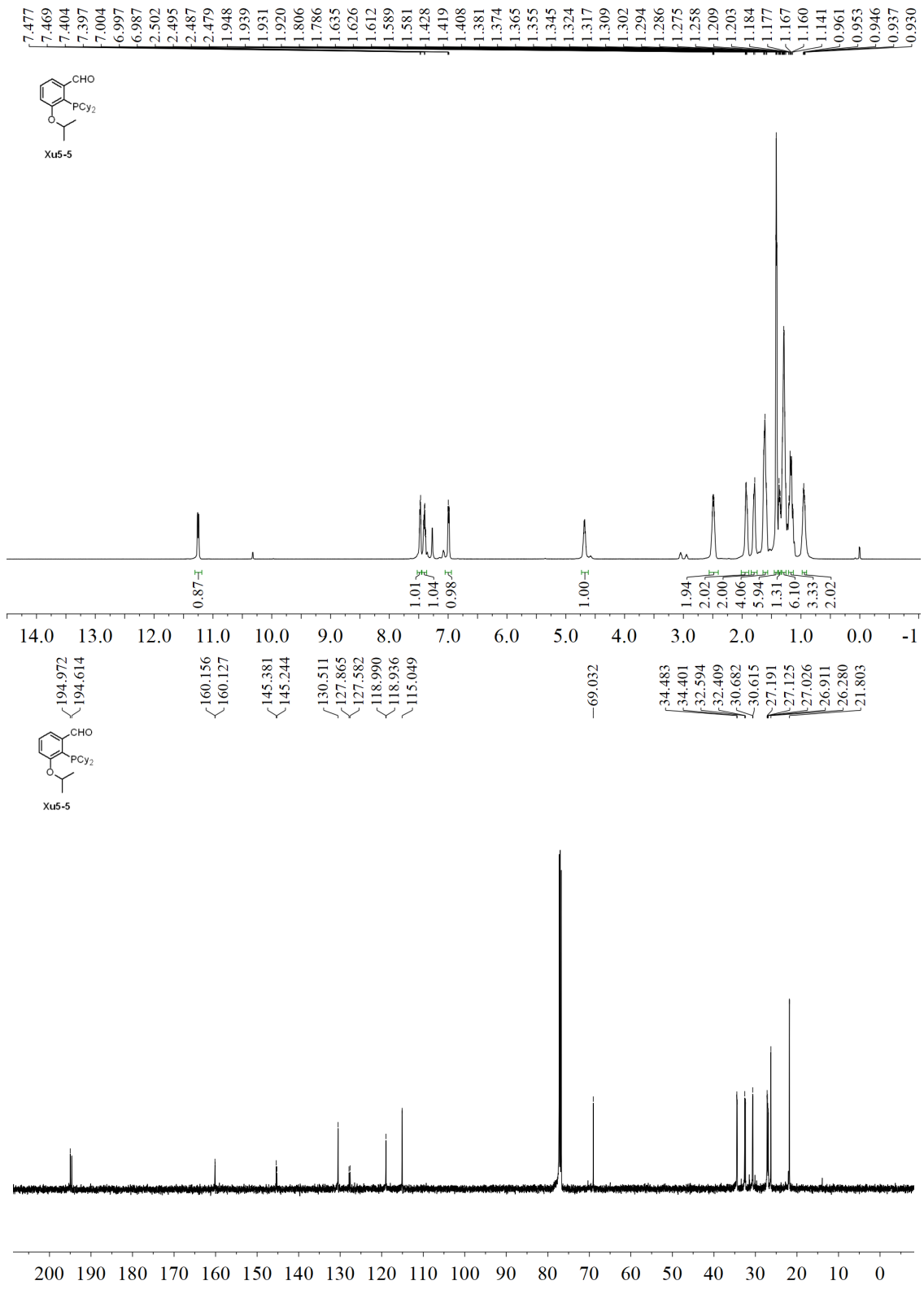
−70
−80
−90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1.939
1.931
1.920
1.806
1.786
1.635
1.626
1.612
1.589
1.581
1.428
1.419
1.408
1.381
1.374
1.365
1.355
1.345
1.324
1.317
1.309
1.302
1.294
1.286
1.275
1.258
1.209
1.203
1.184
1.177
1.167
1.160
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0.953
0.946
0.937
0.930
CHO
PCy2
O
Xu5-5
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1.04
0.98
1.00
1.94
2.02
2.00
4.06
5.94
1.31
6.10
3.33
2.02
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
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194.614
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160.127
145.381
145.244
130.511
127.865
127.582
118.990
118.936
115.049
69.032
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34.401
32.594
32.409
30.682
30.615
27.191
27.125
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Xu5-5
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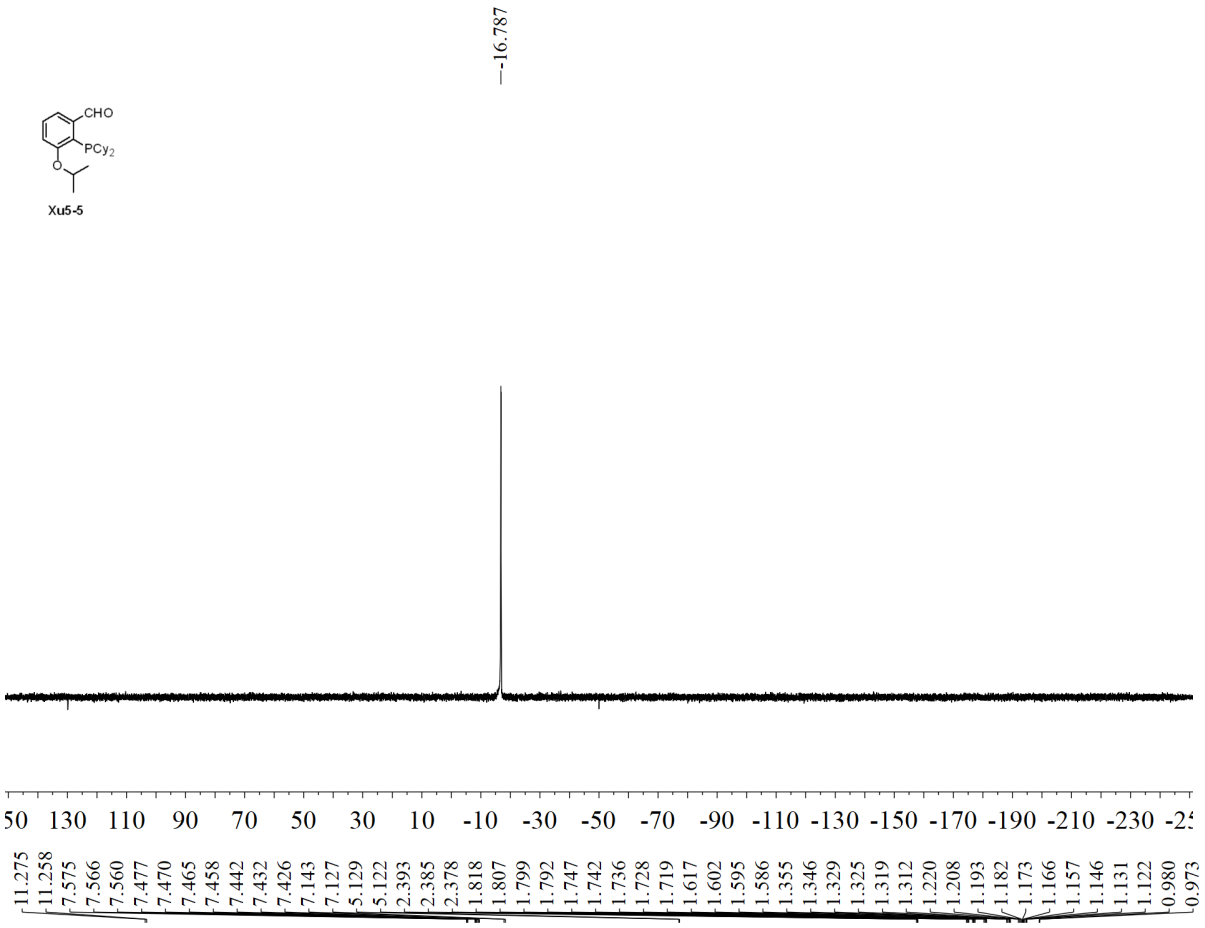
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7.566
7.560
7.477
7.470
7.465
7.458
7.442
7.432
7.426
7.143
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1.747
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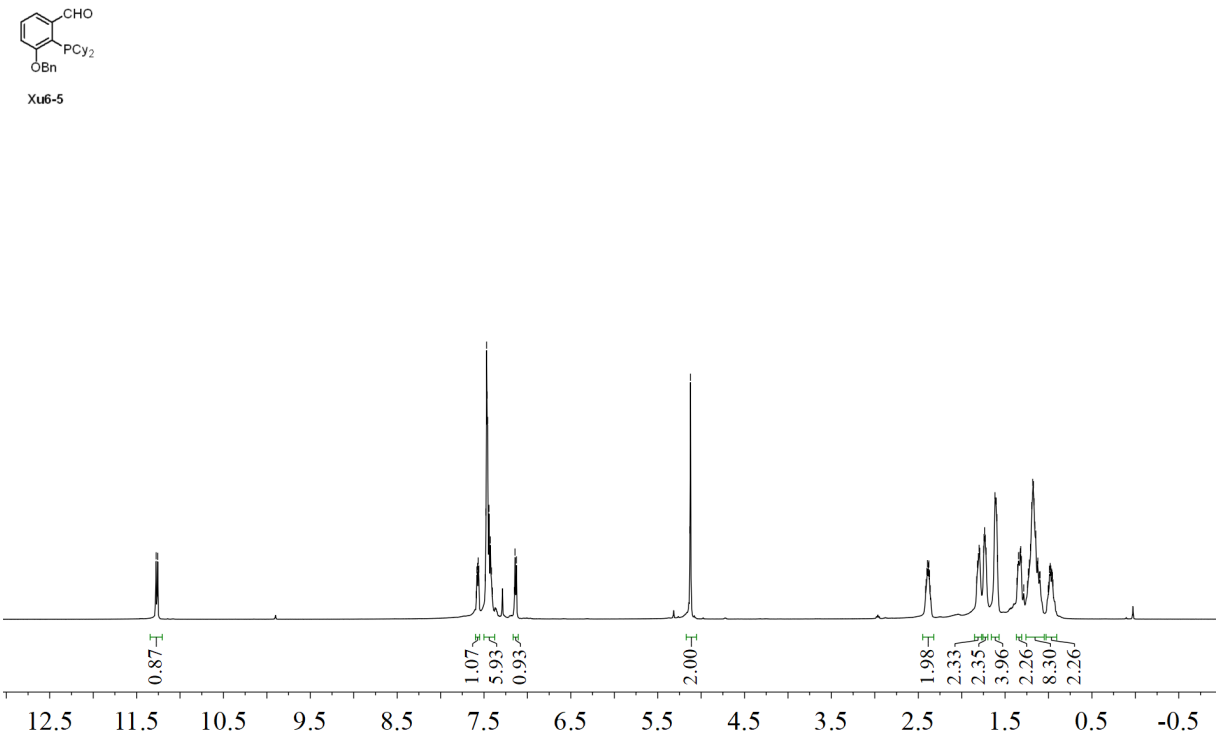
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PCy2
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Xu6-5
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3.96
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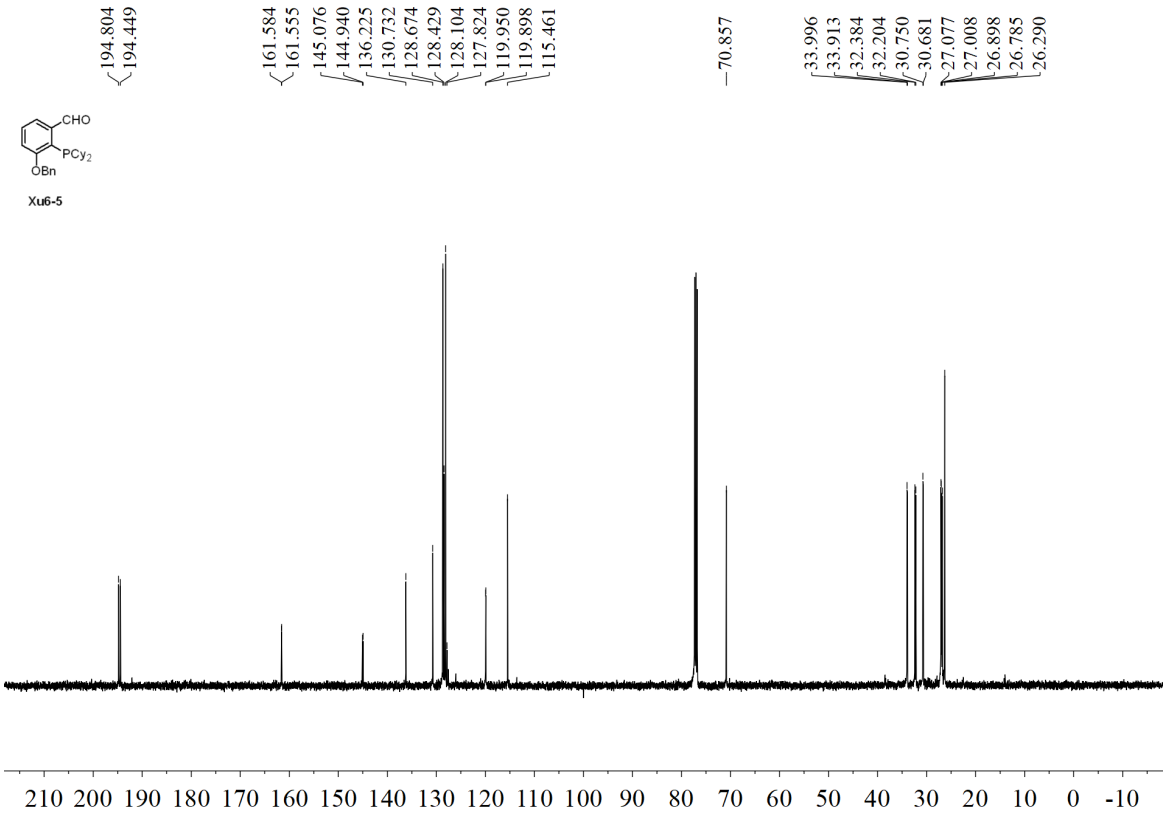
2.26
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5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70.857
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33.913
32.384
32.204
30.750
30.681
27.077
27.008
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26.290
CHO
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OBn
Xu6-5
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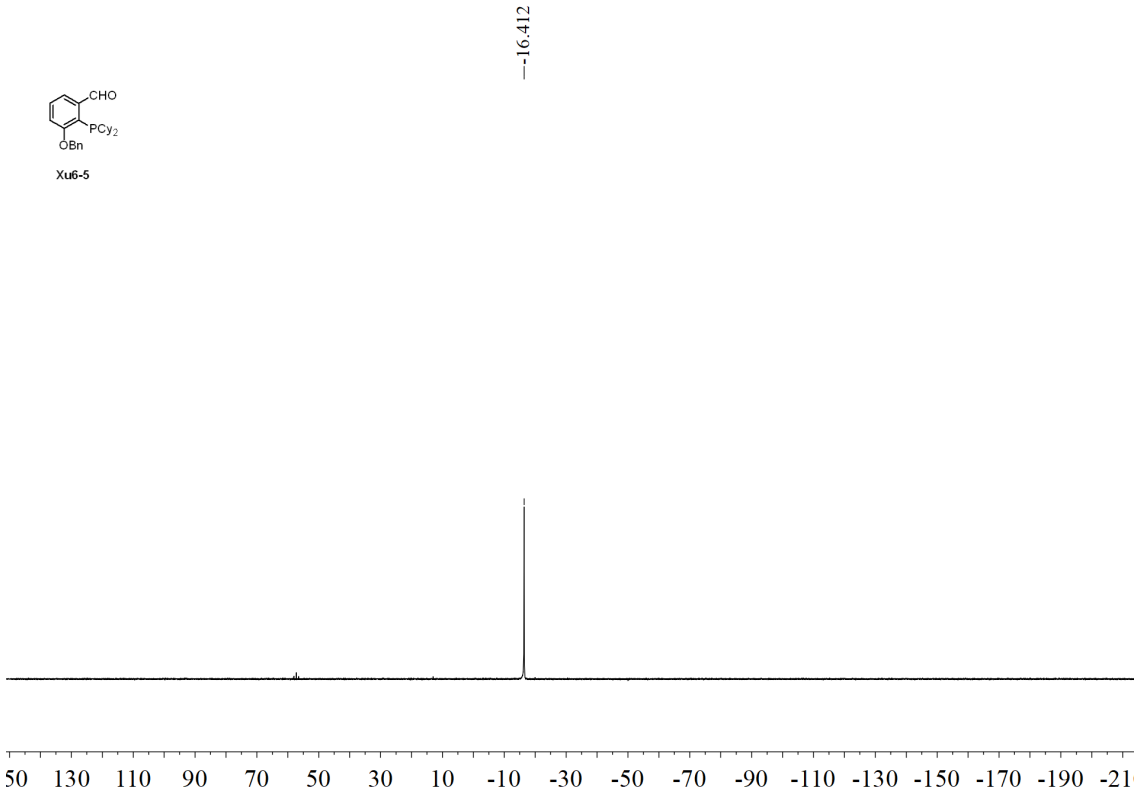
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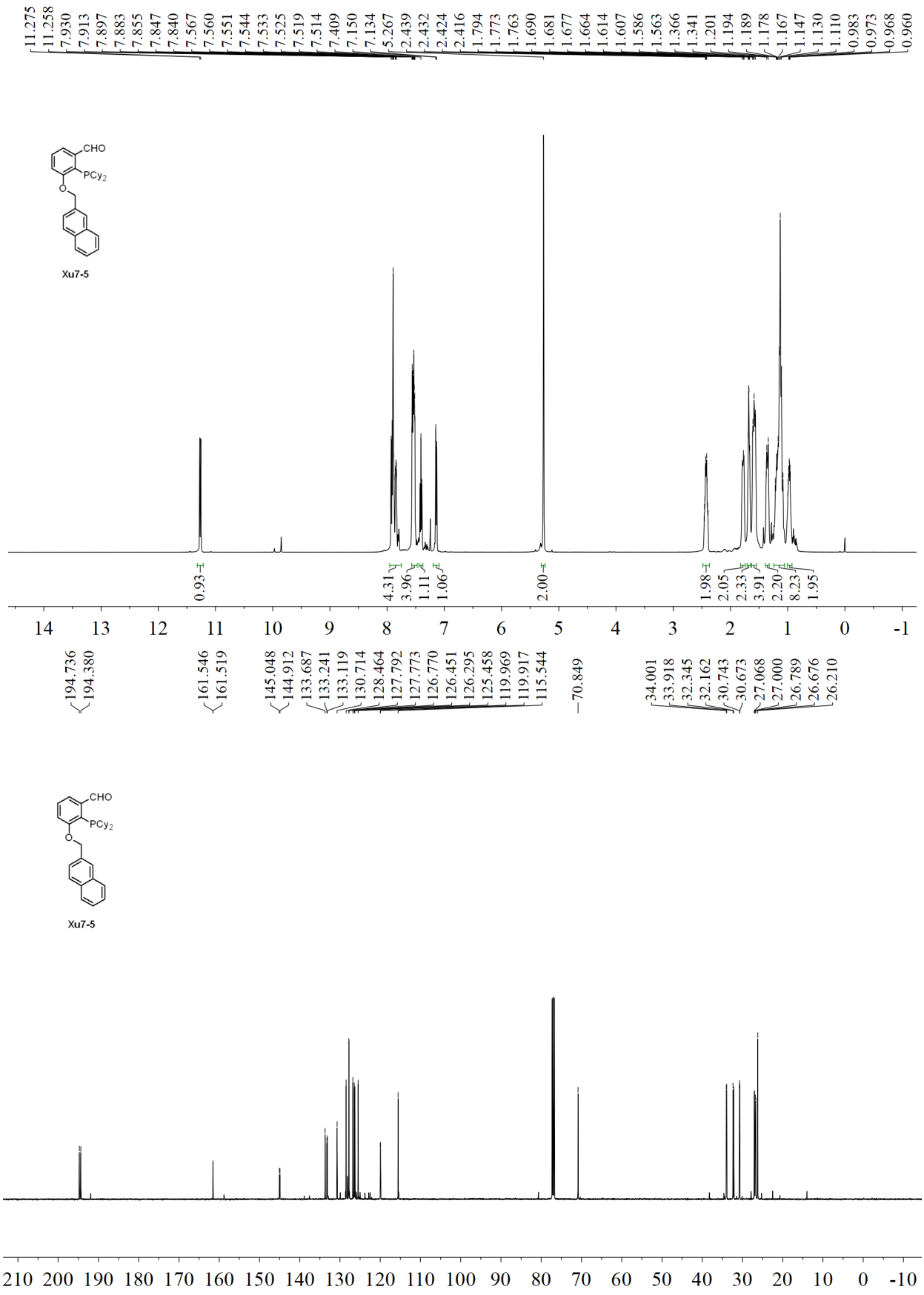
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7.519
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2.416
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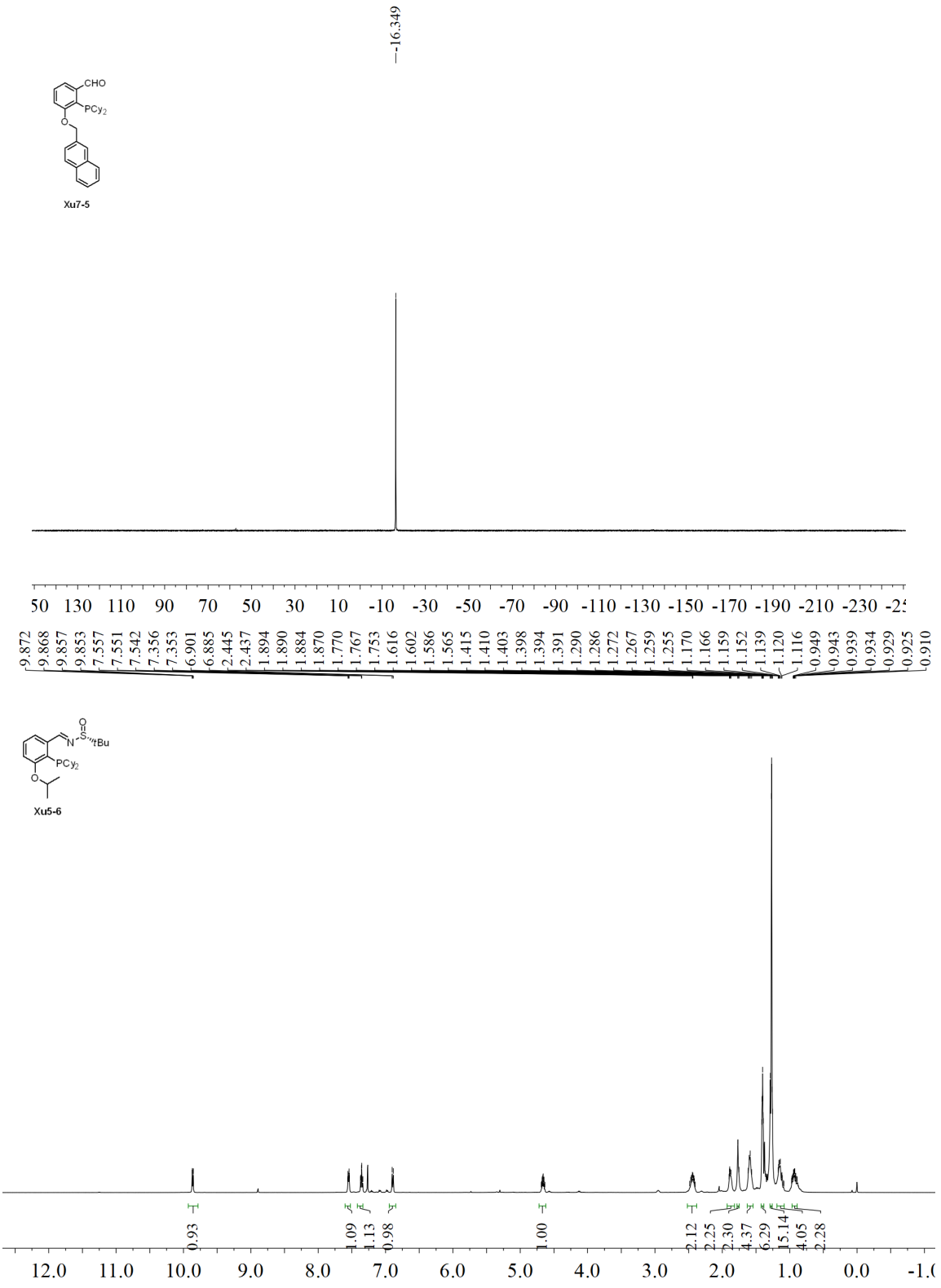
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N
S
O
tBu
PCy2
O
Xu5-6
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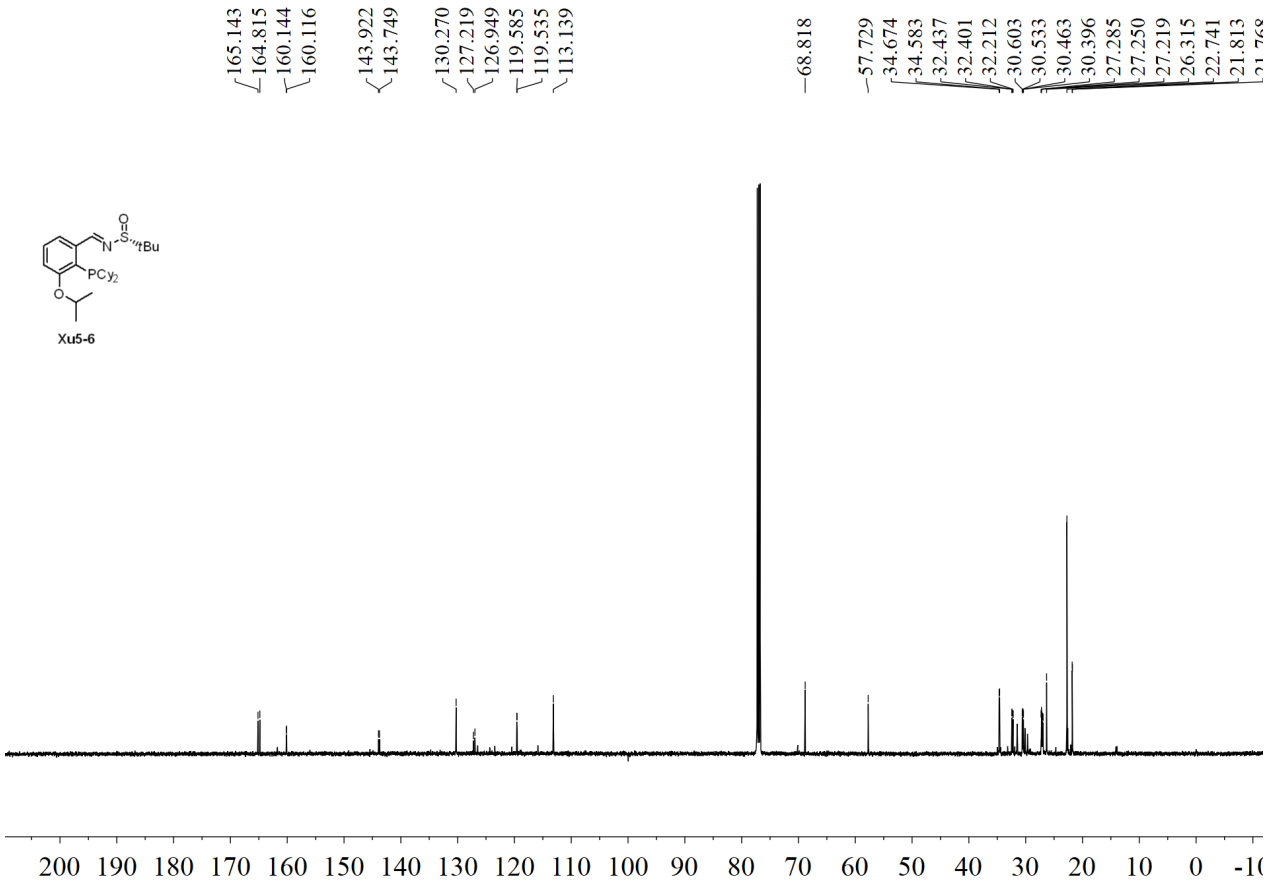
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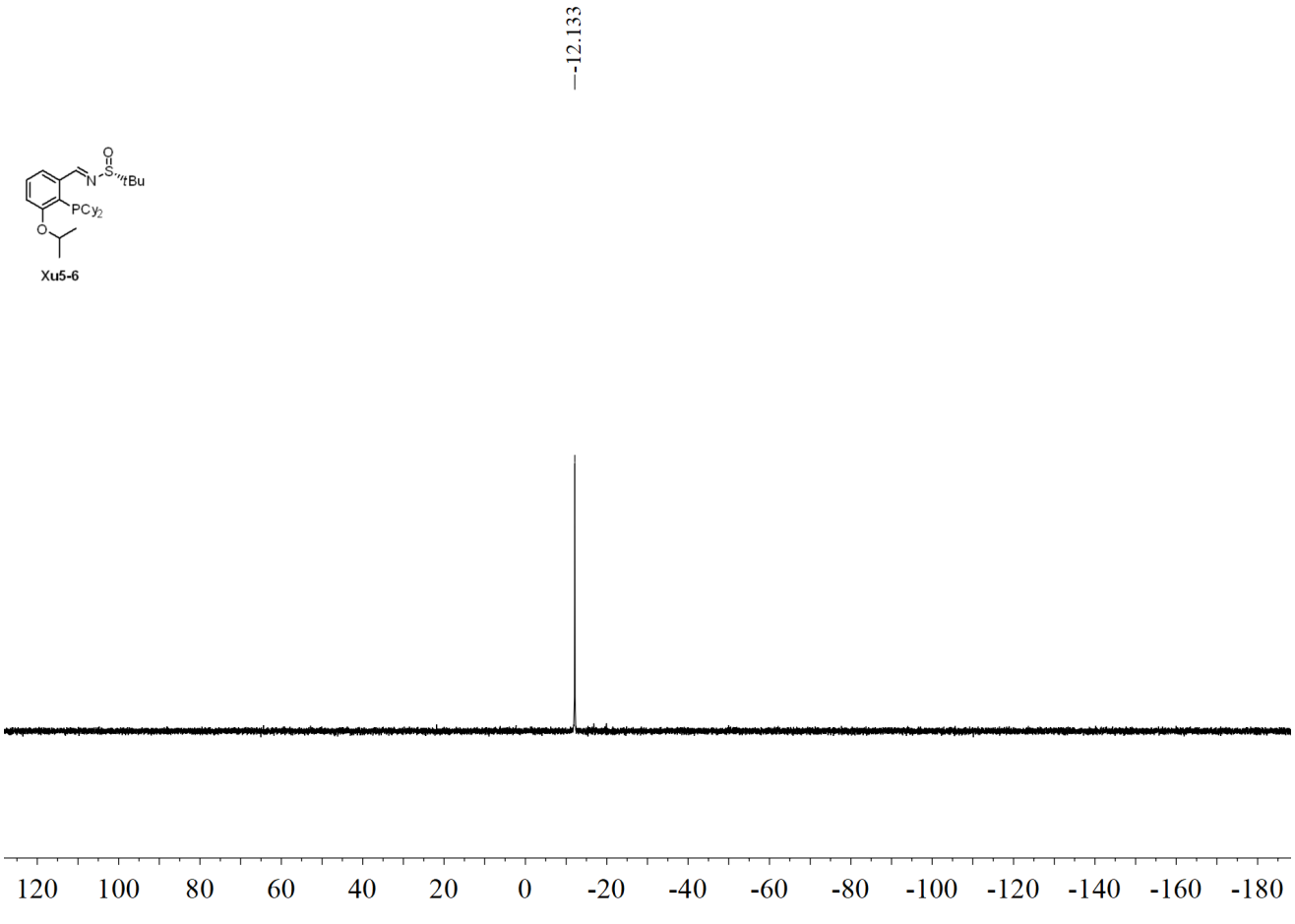
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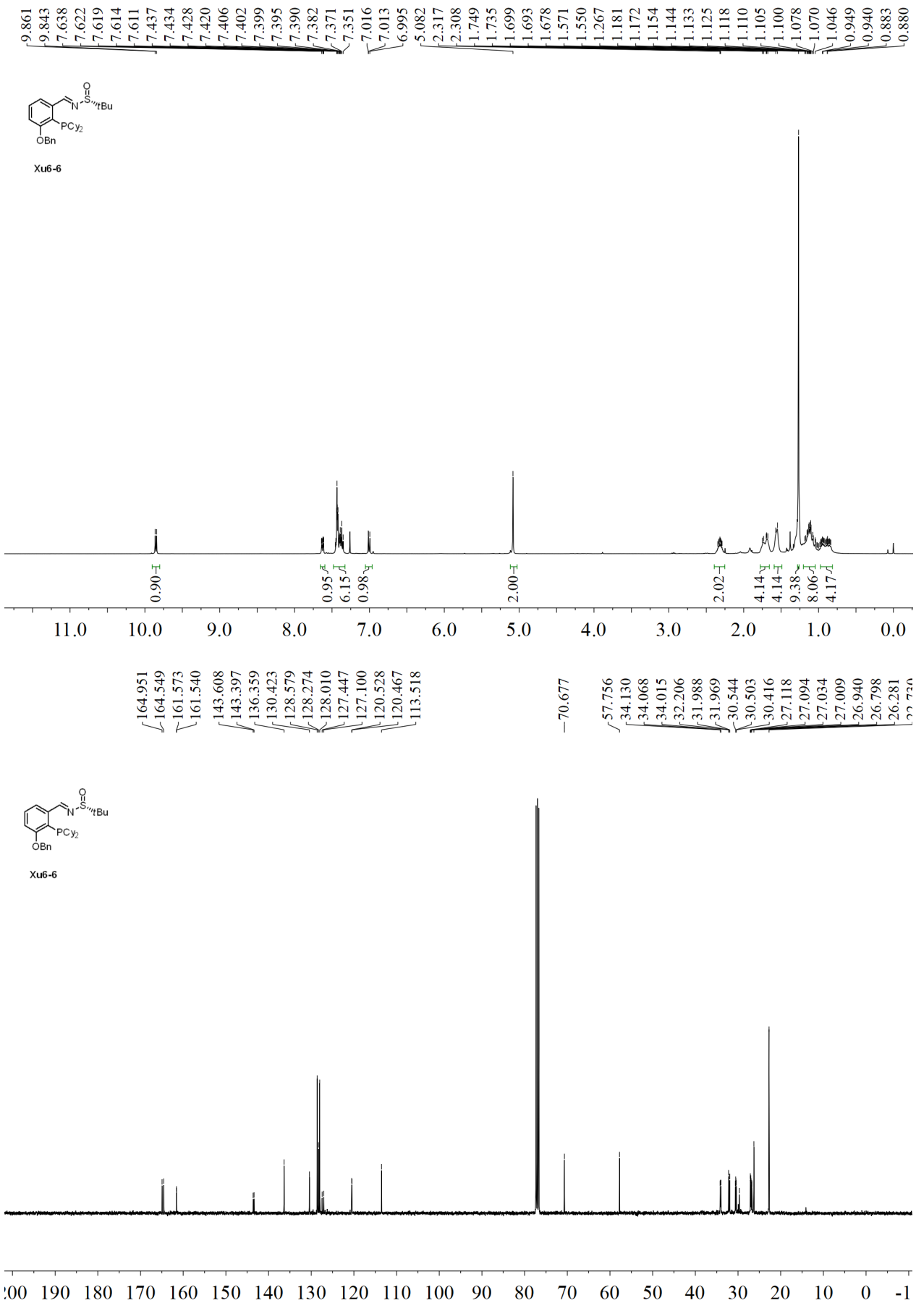
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tBu
PCy2
OBn
Xu6-6
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2.02
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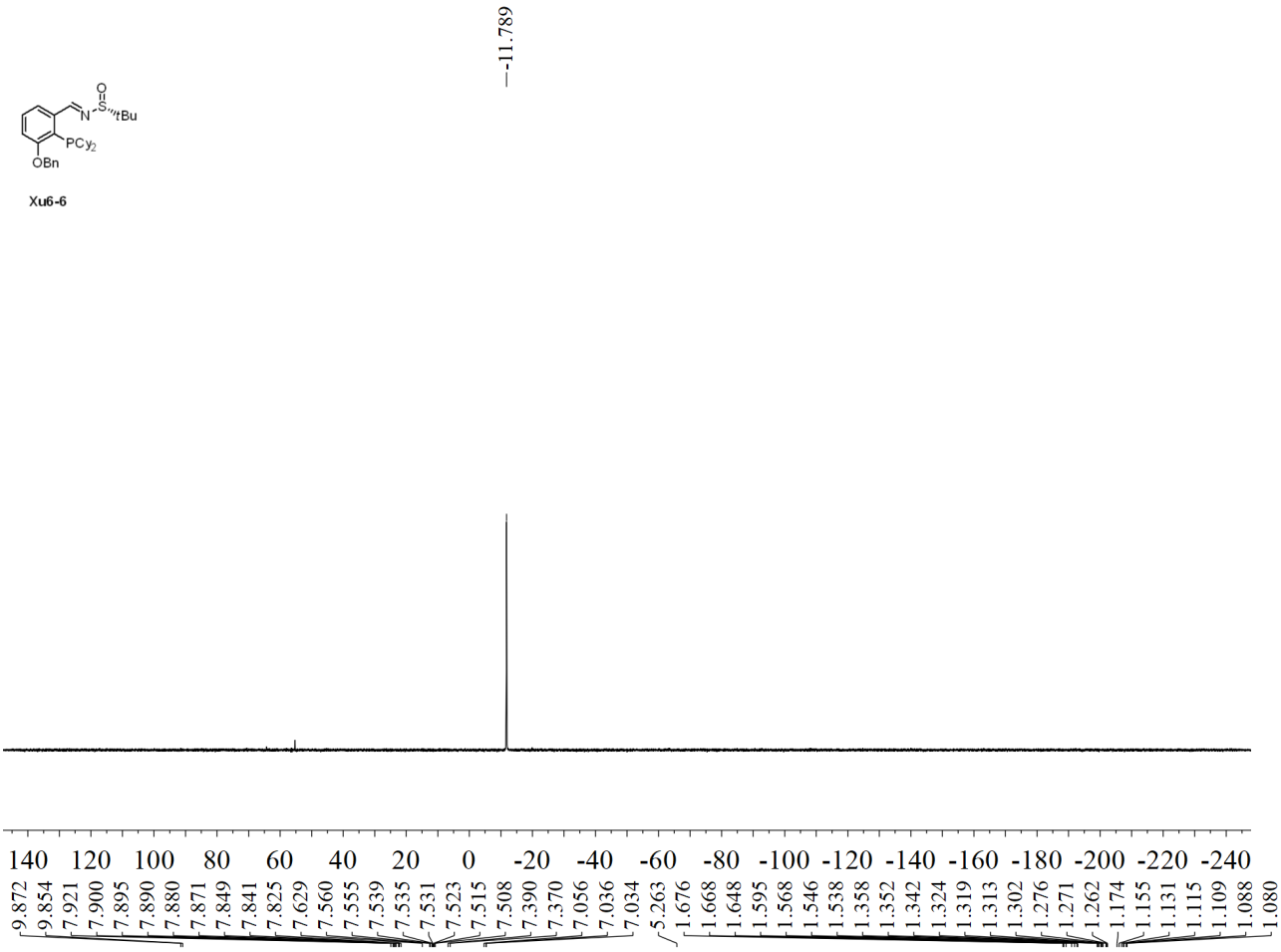
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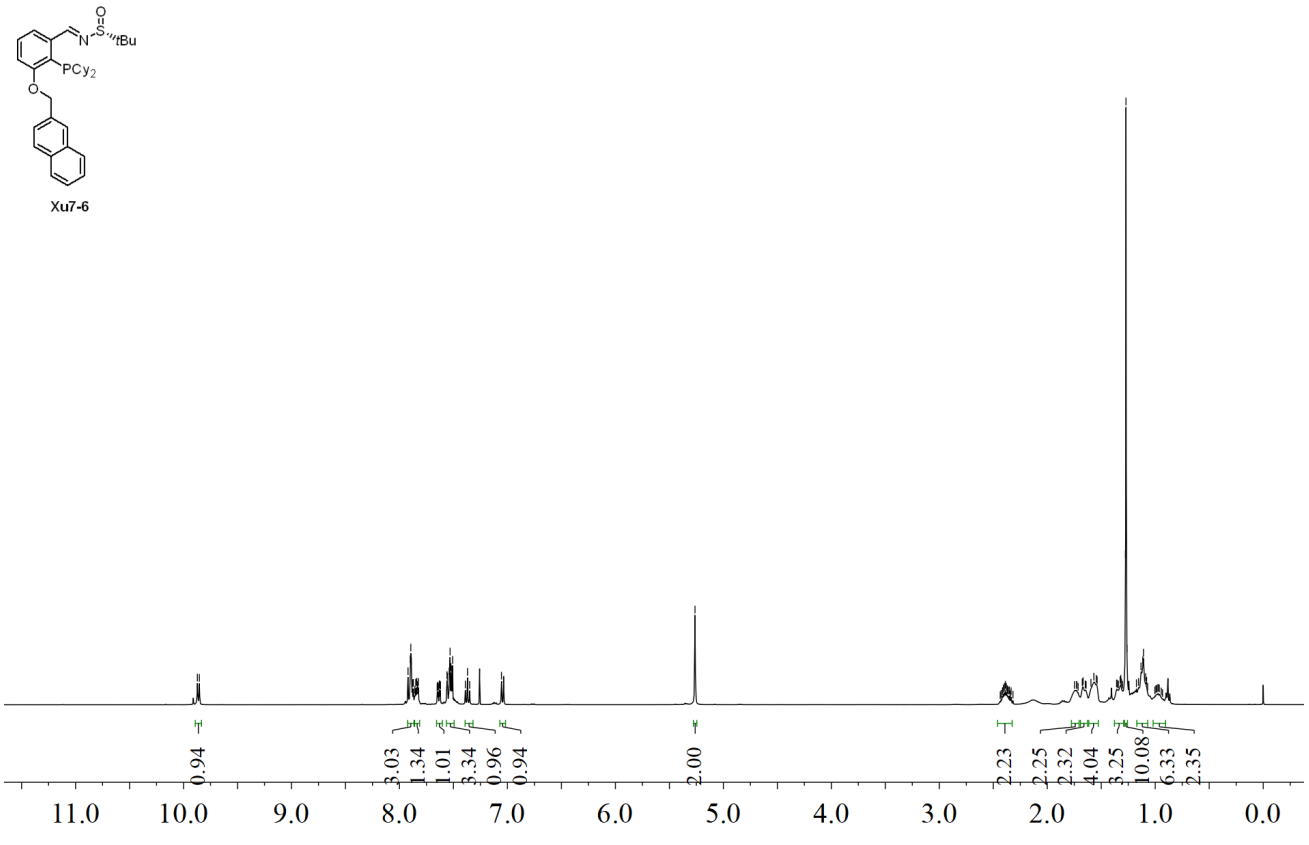
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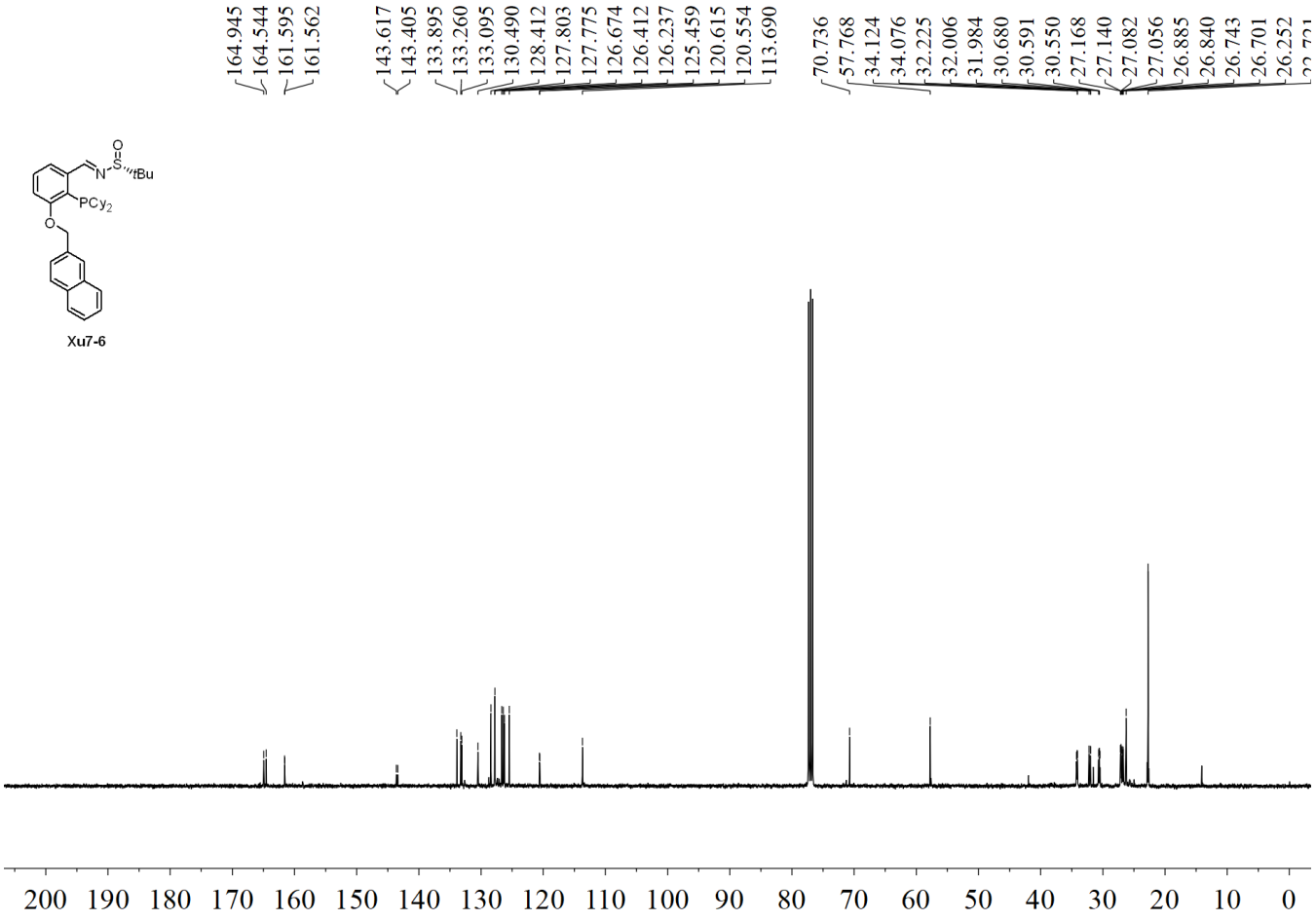
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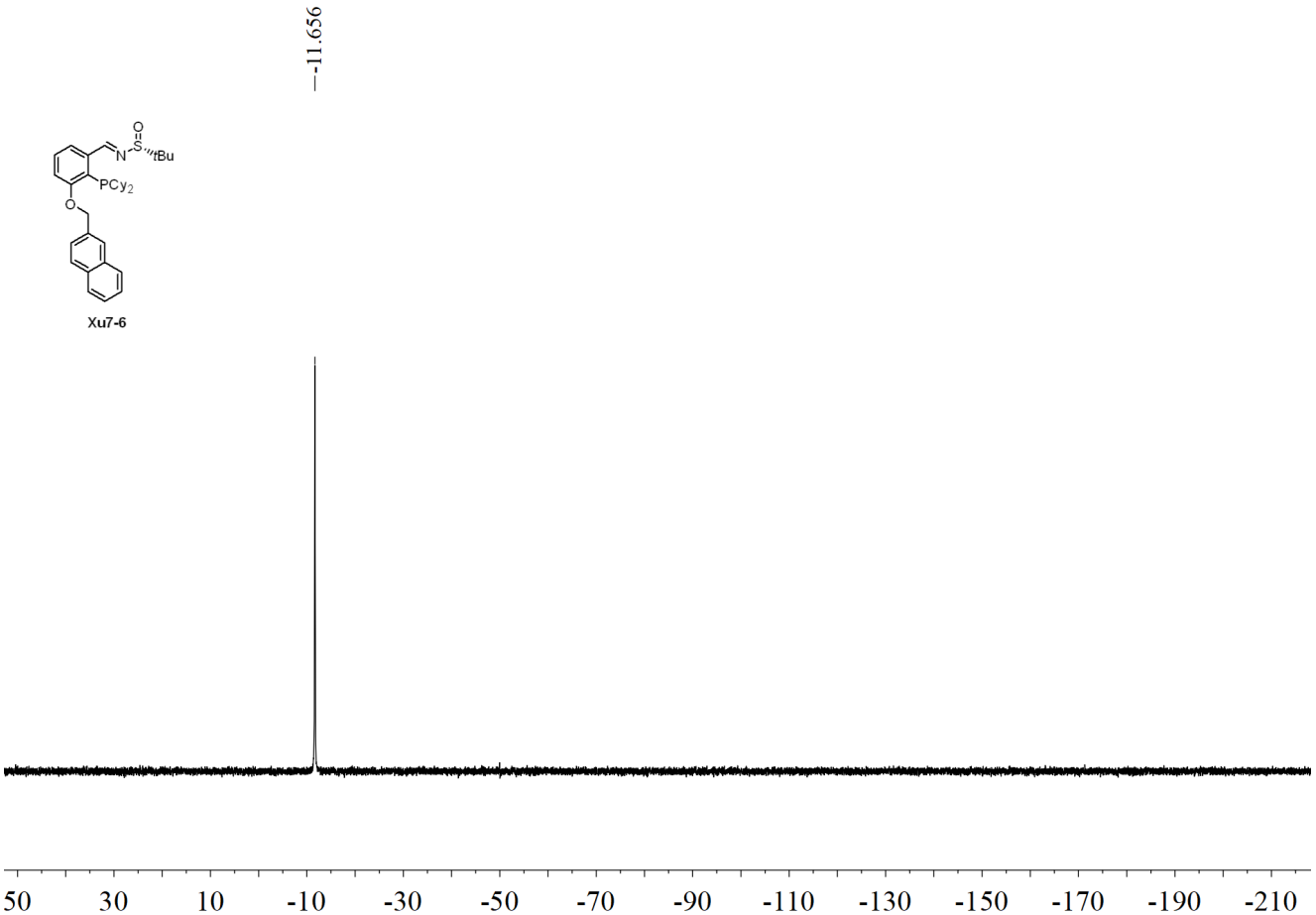
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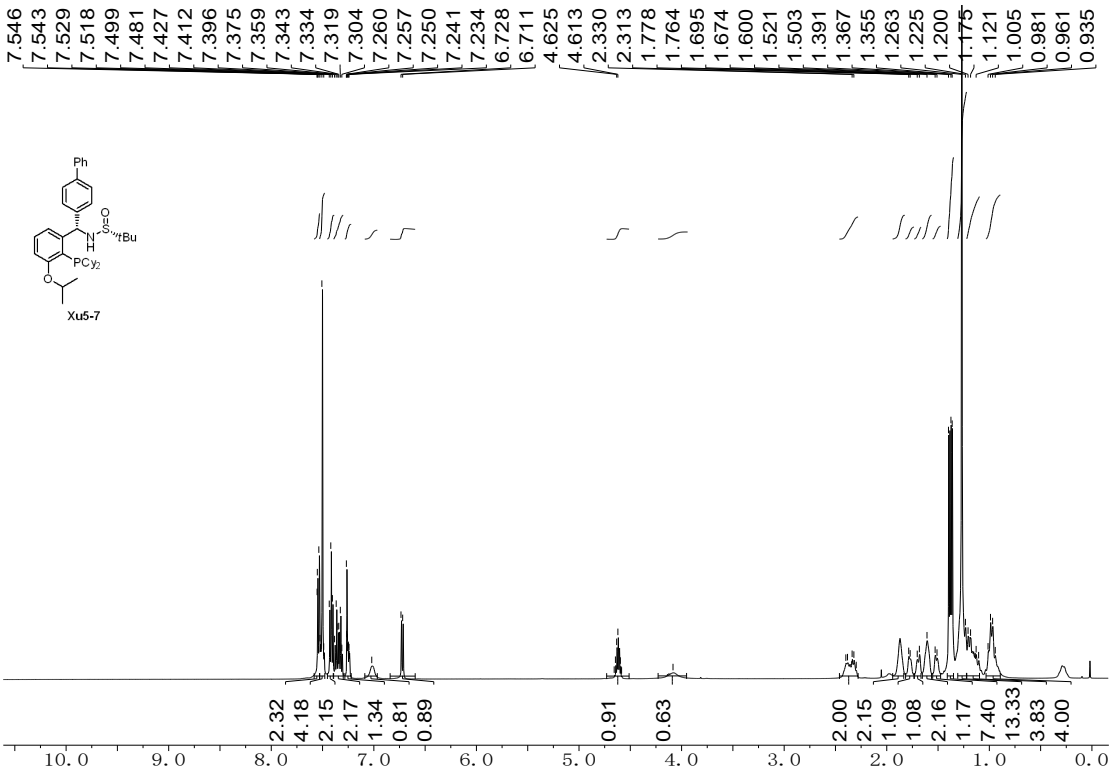
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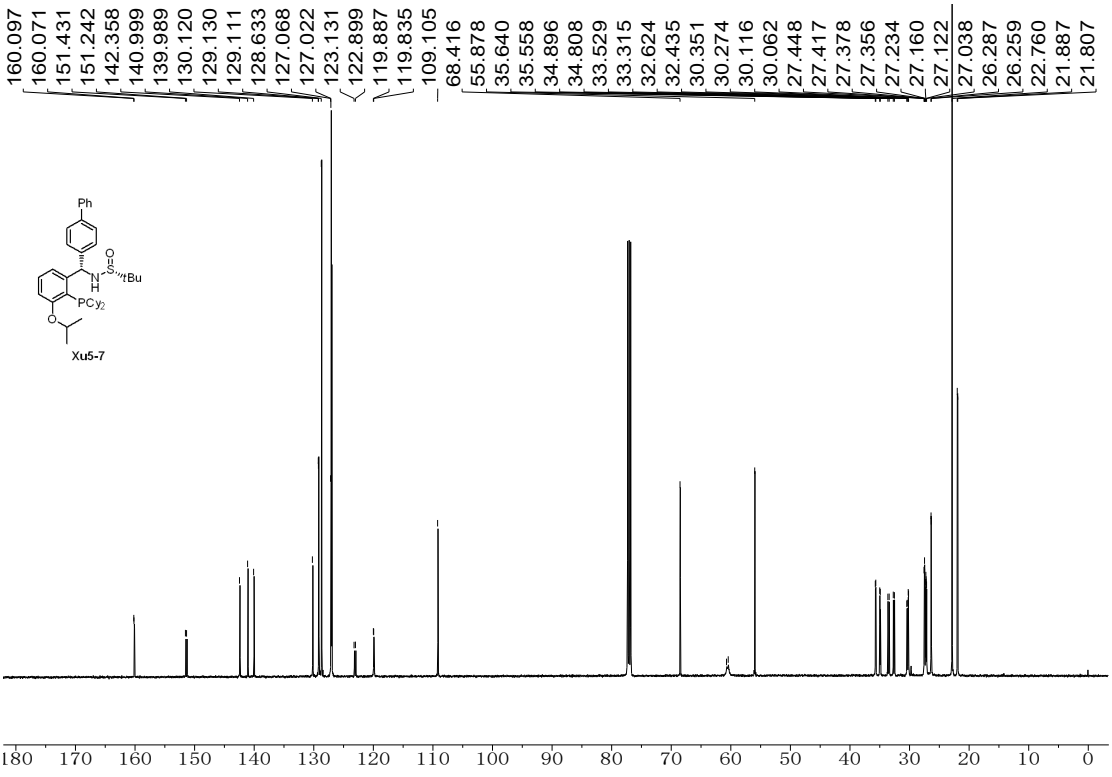
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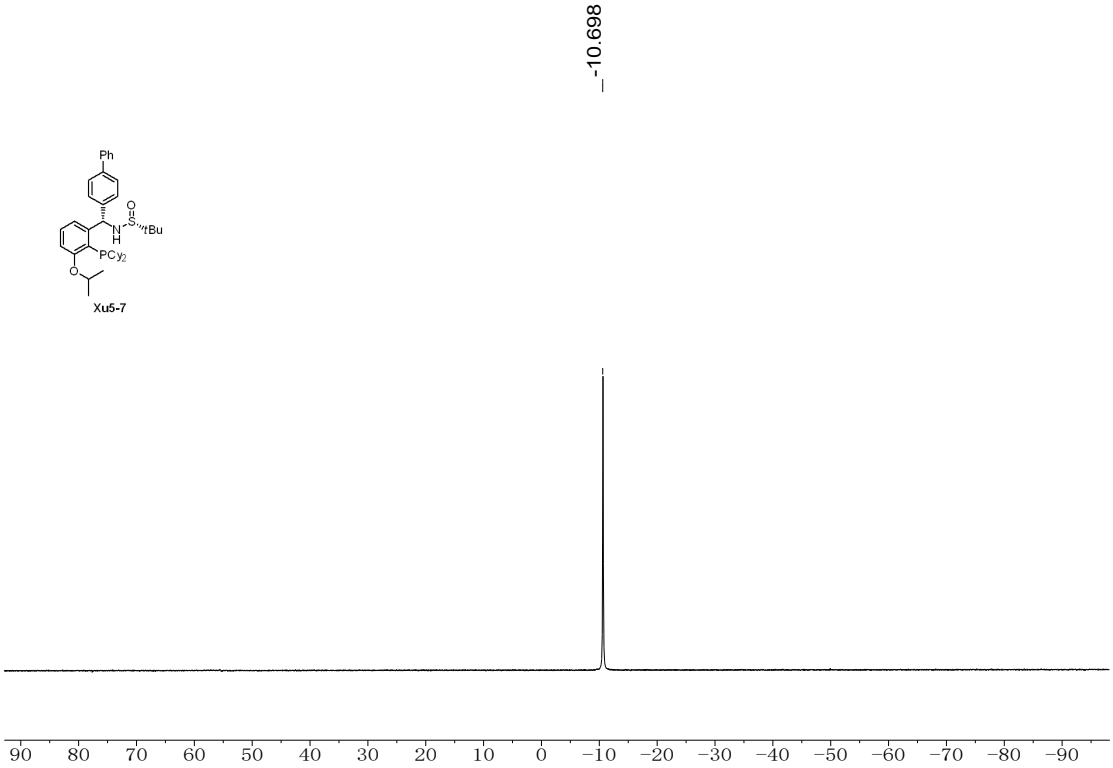
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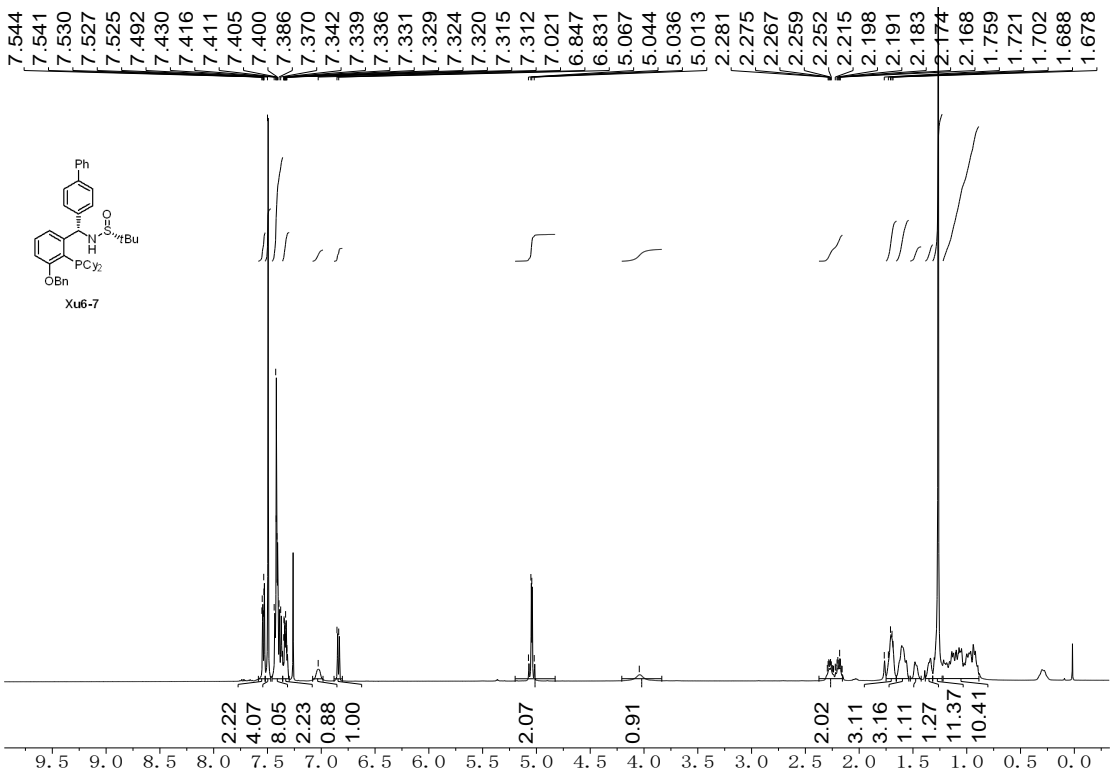
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S
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N
H
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OBn
Xu6-7
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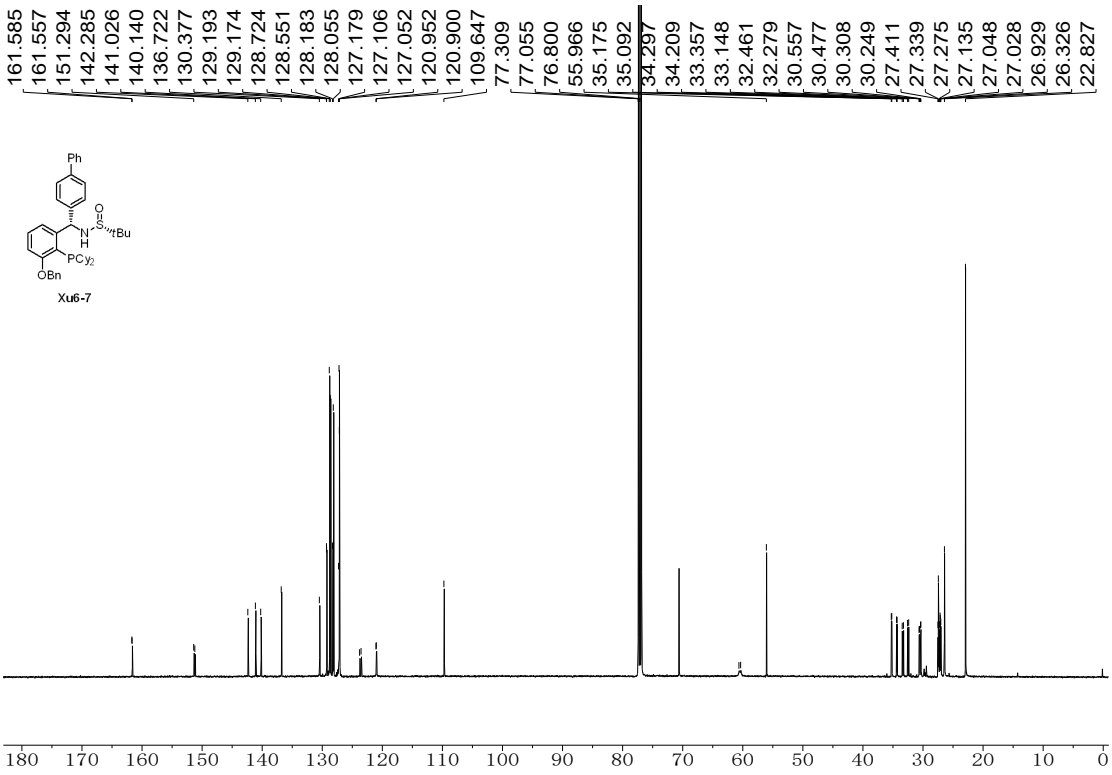
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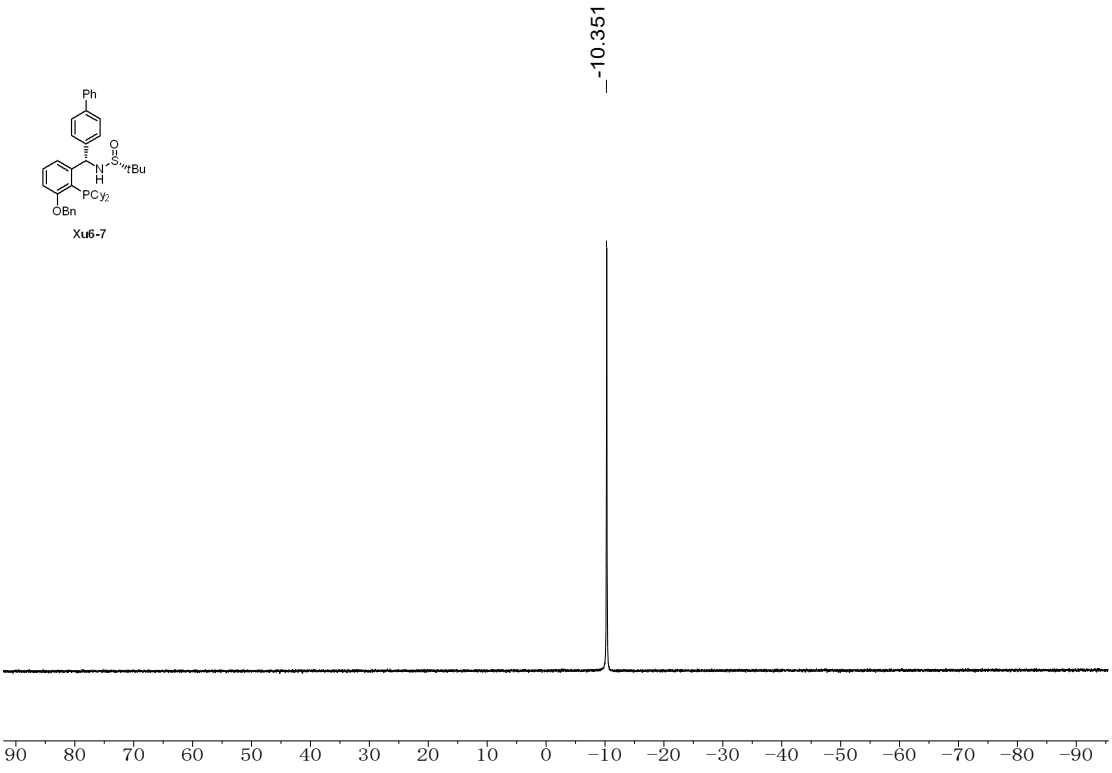
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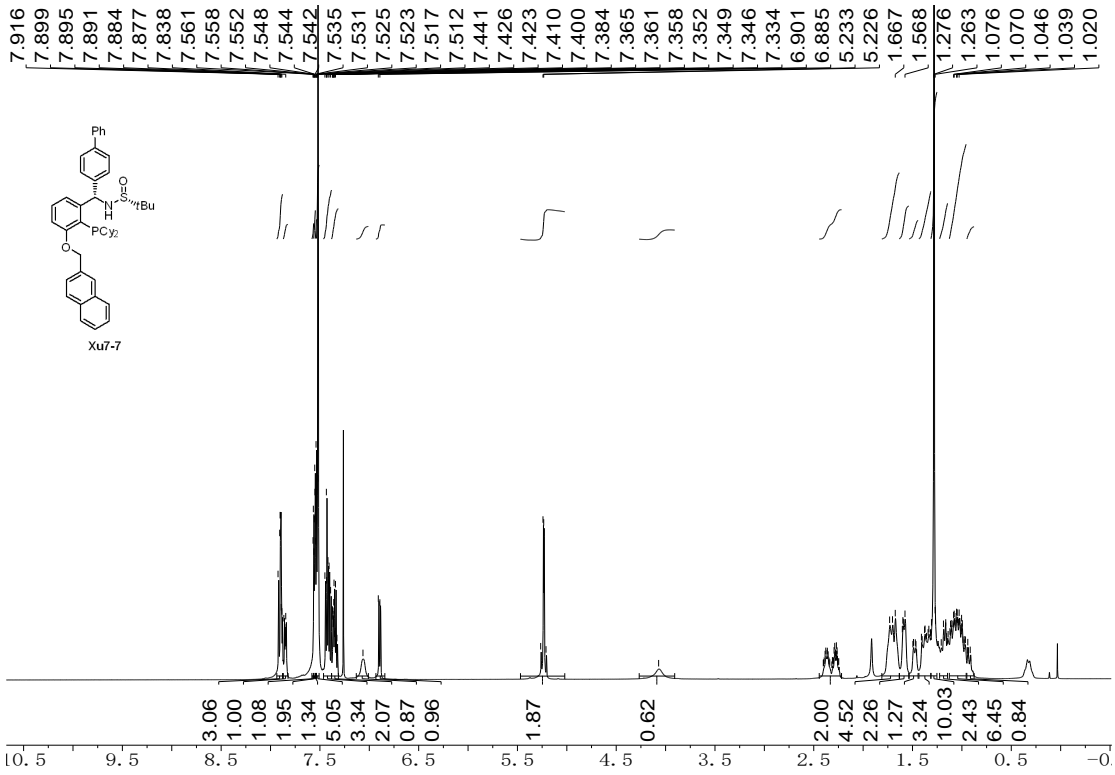
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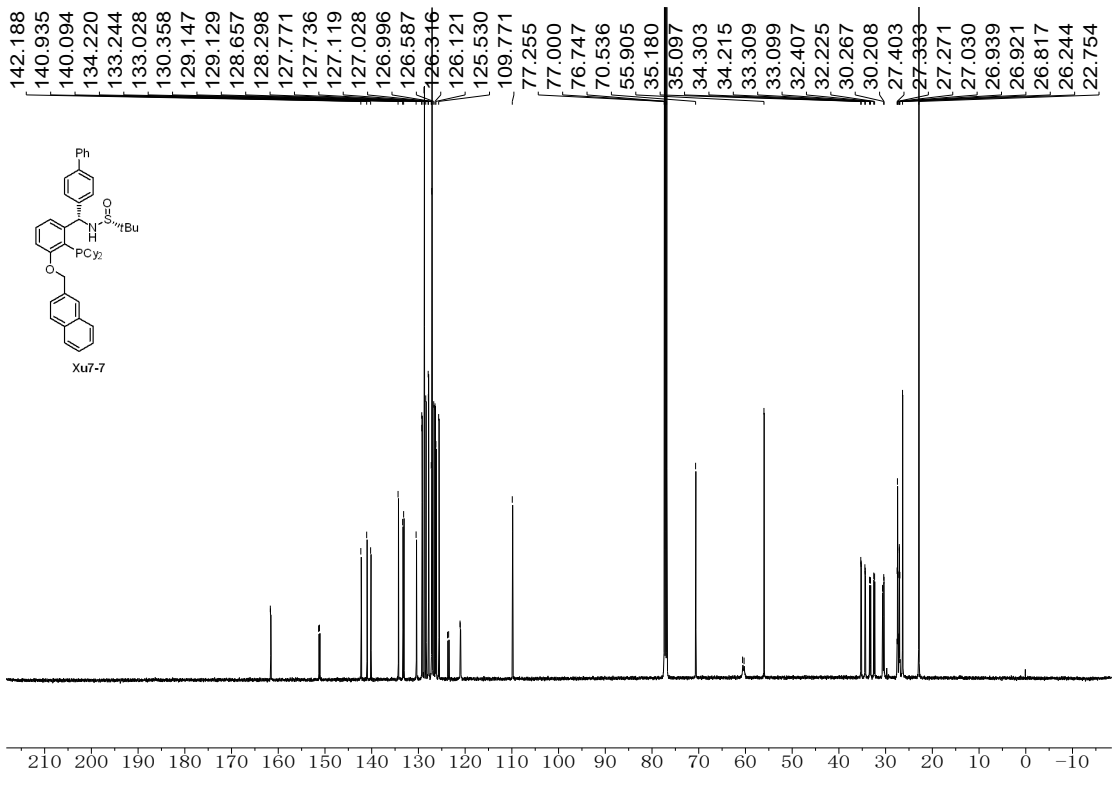
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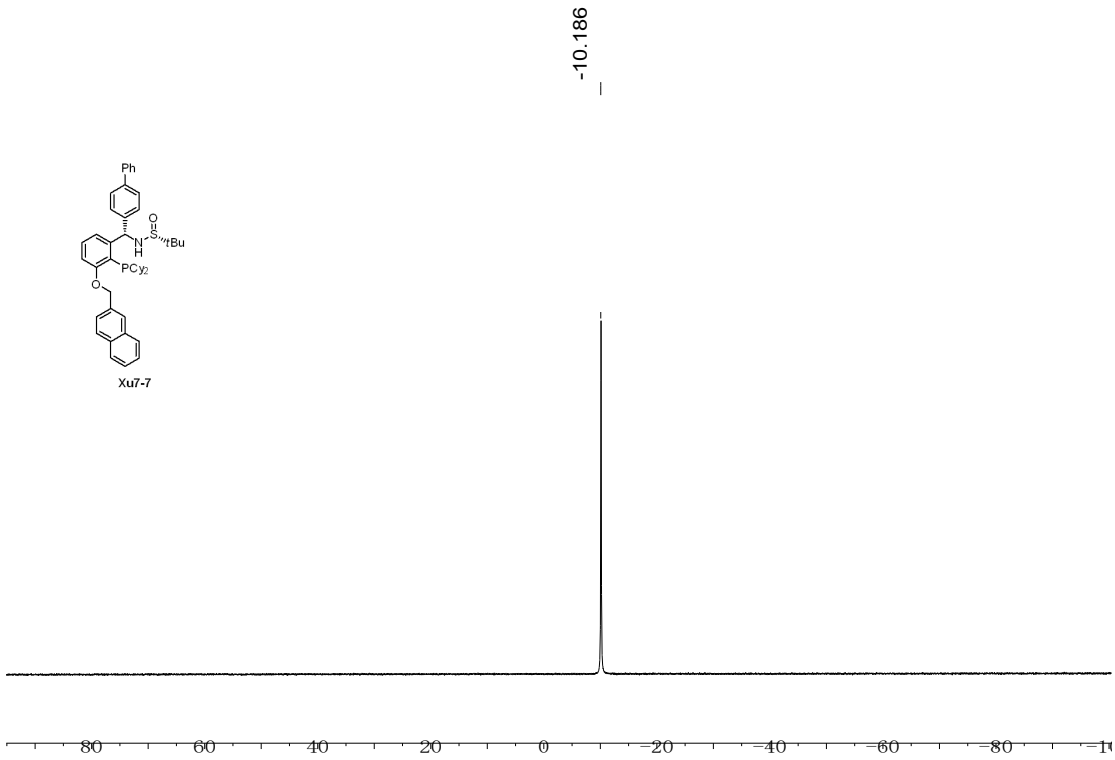
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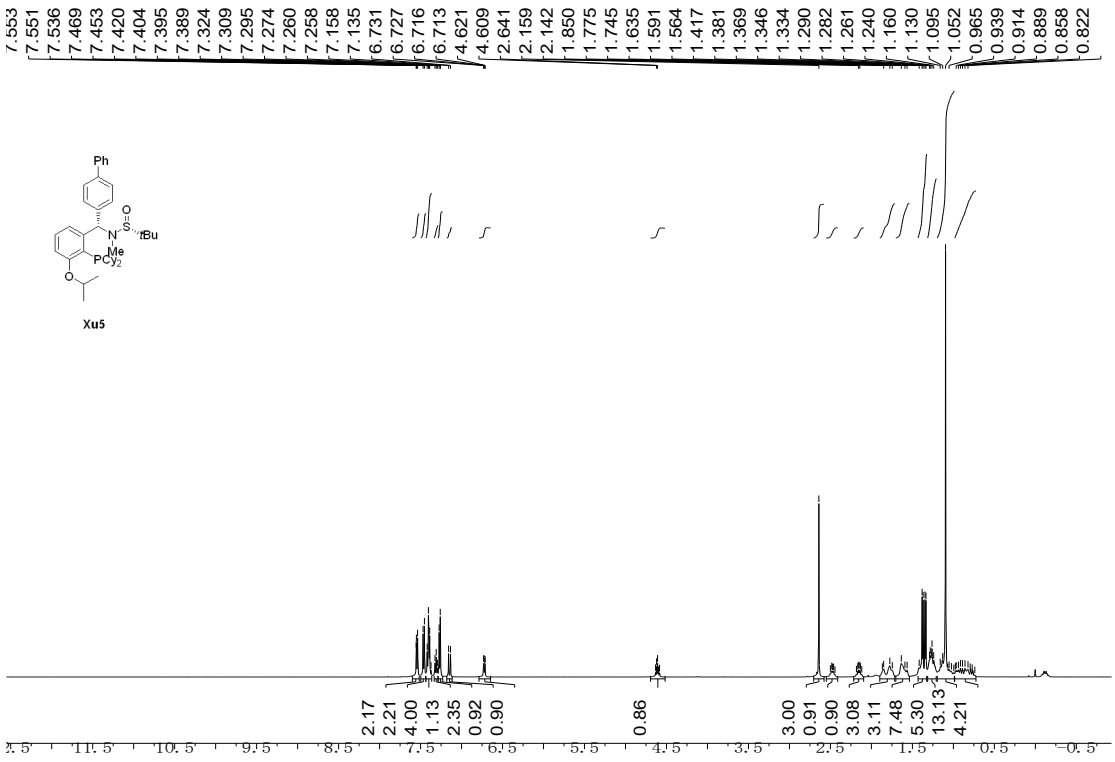
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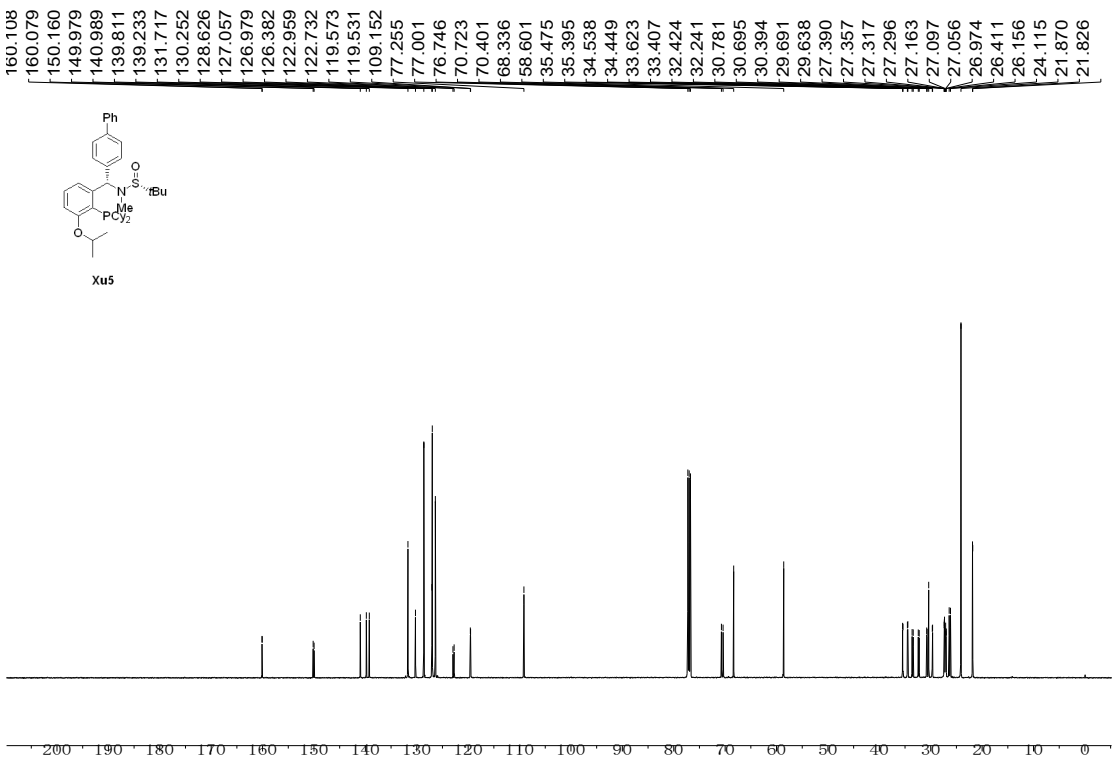
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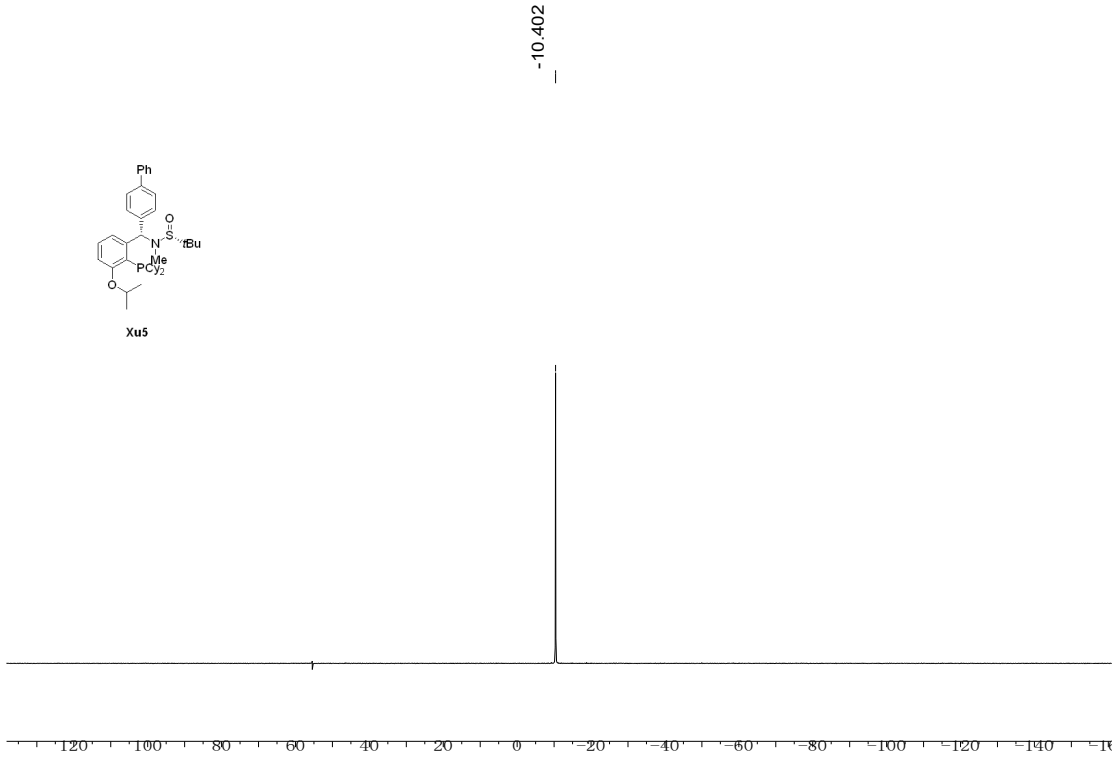
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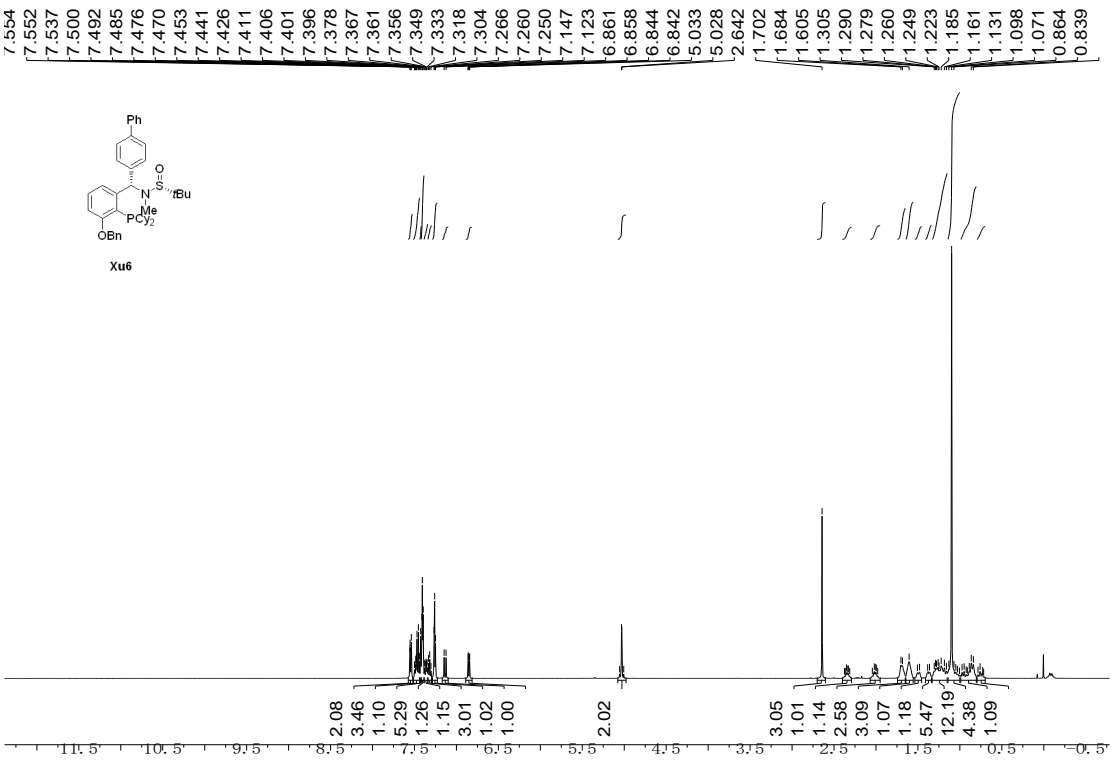
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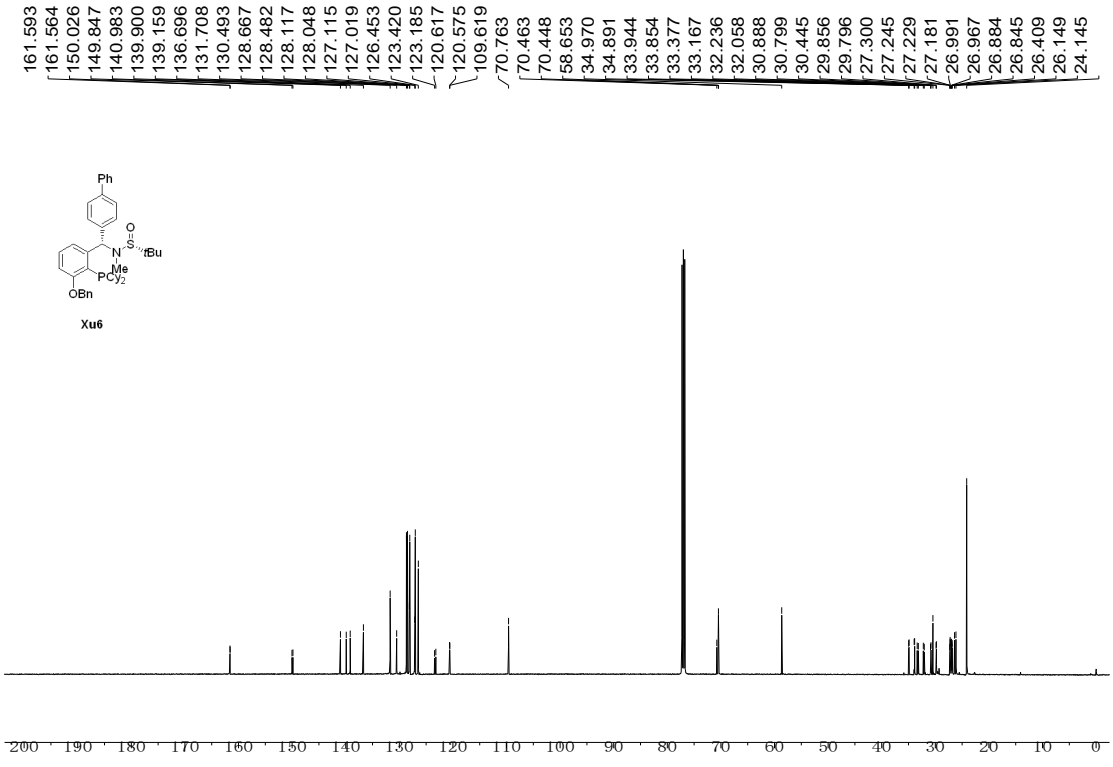
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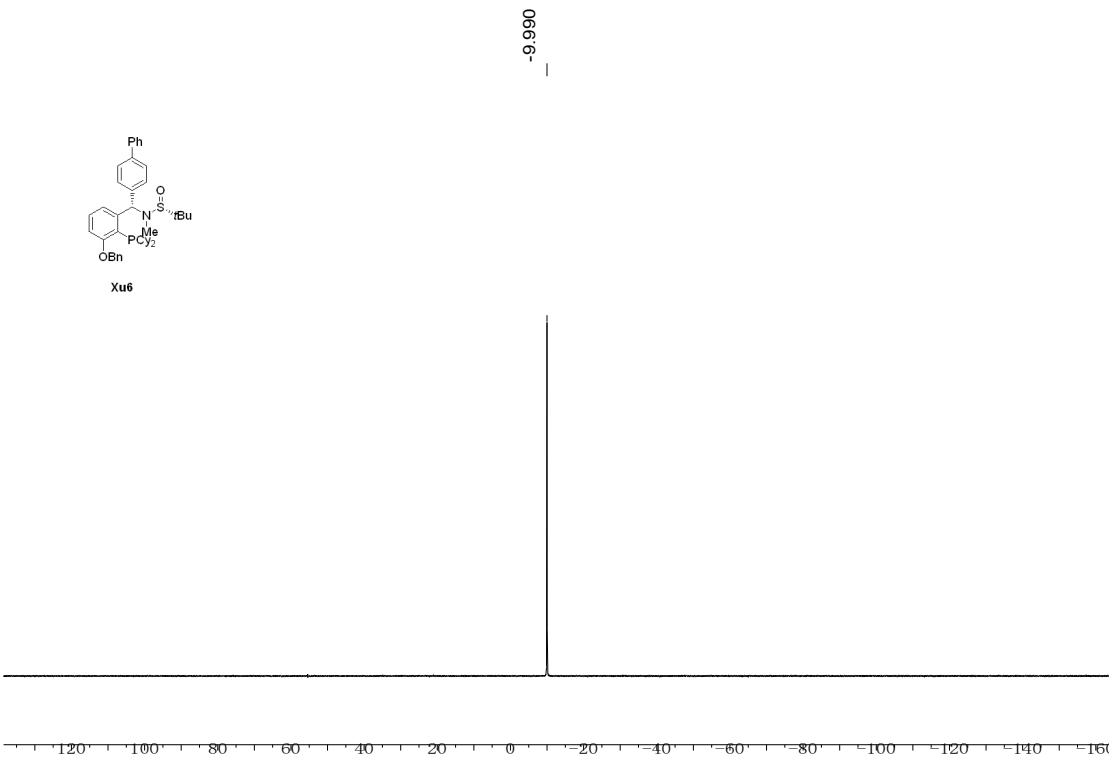
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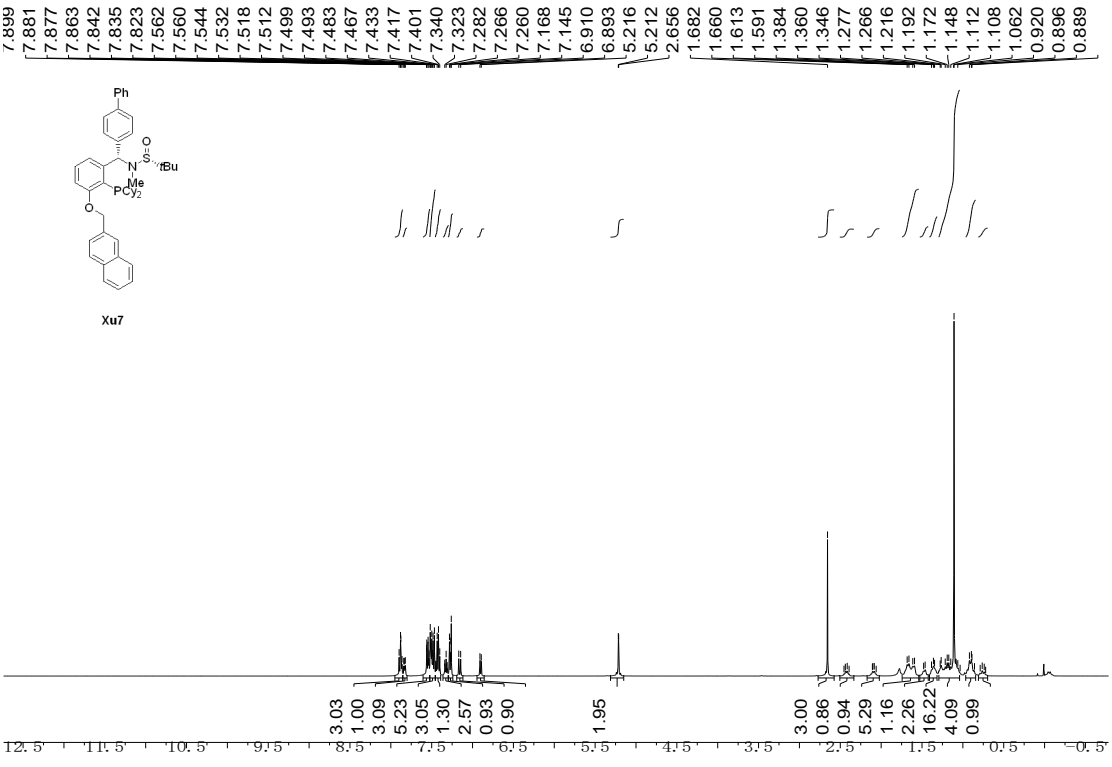
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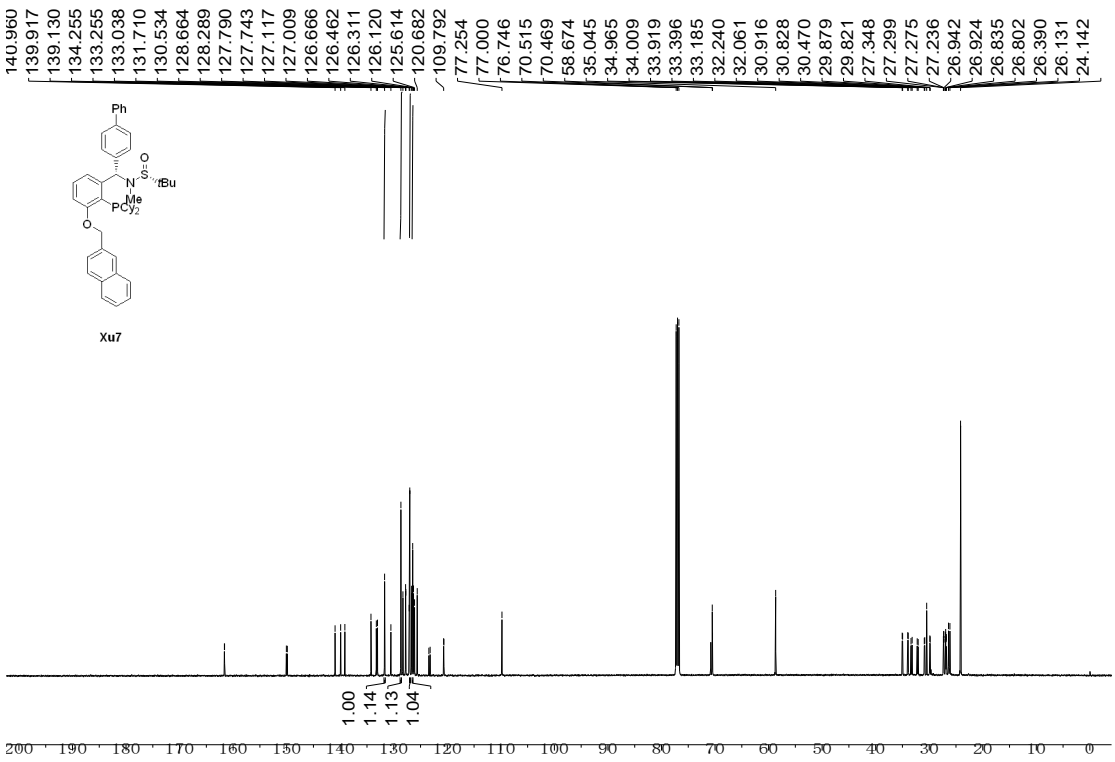
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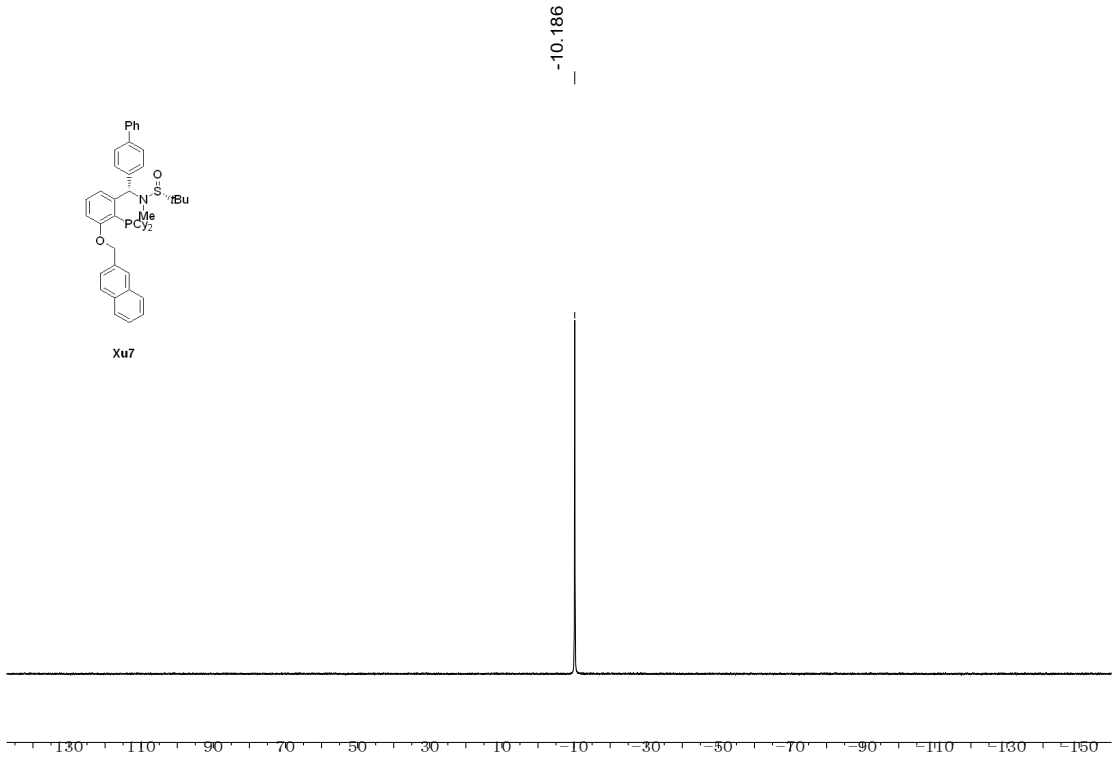
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-30
-50
-70
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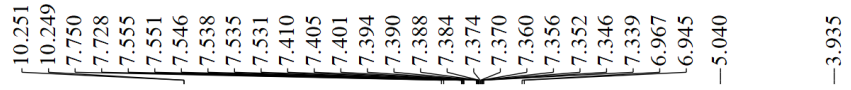
-110
-130
-150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7.538
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7.401
7.394
7.390
7.388
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7.346
7.339
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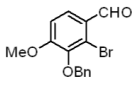
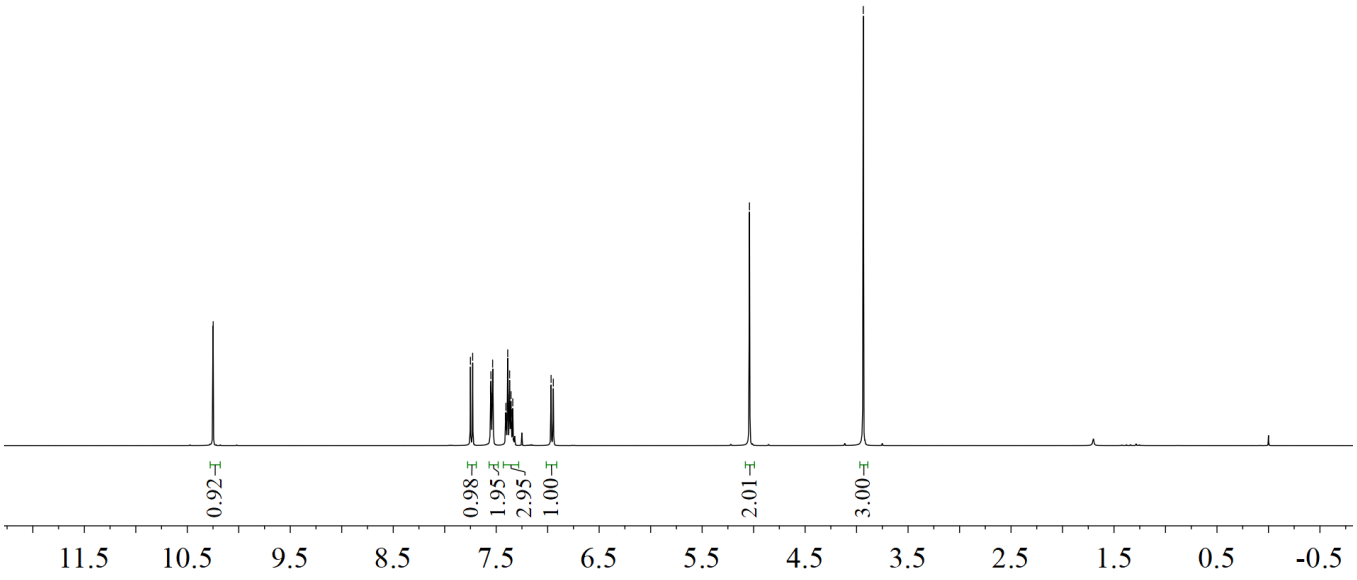
6.945
5.040
3.935


CHO
MeO
Br
OBn

Xu8-2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1.95
2.95
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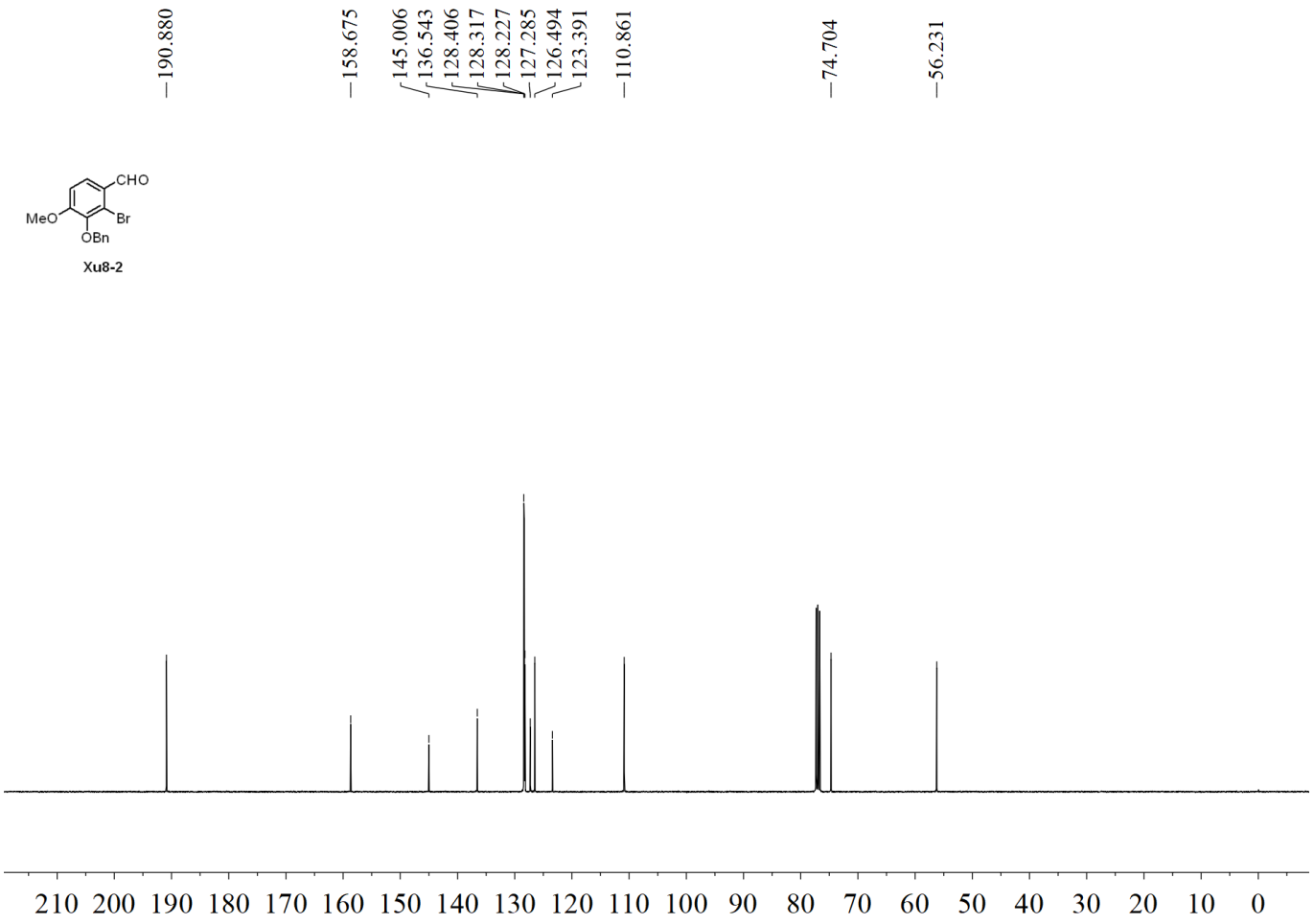
2.01
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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128.317
128.227
127.285
126.494
123.391
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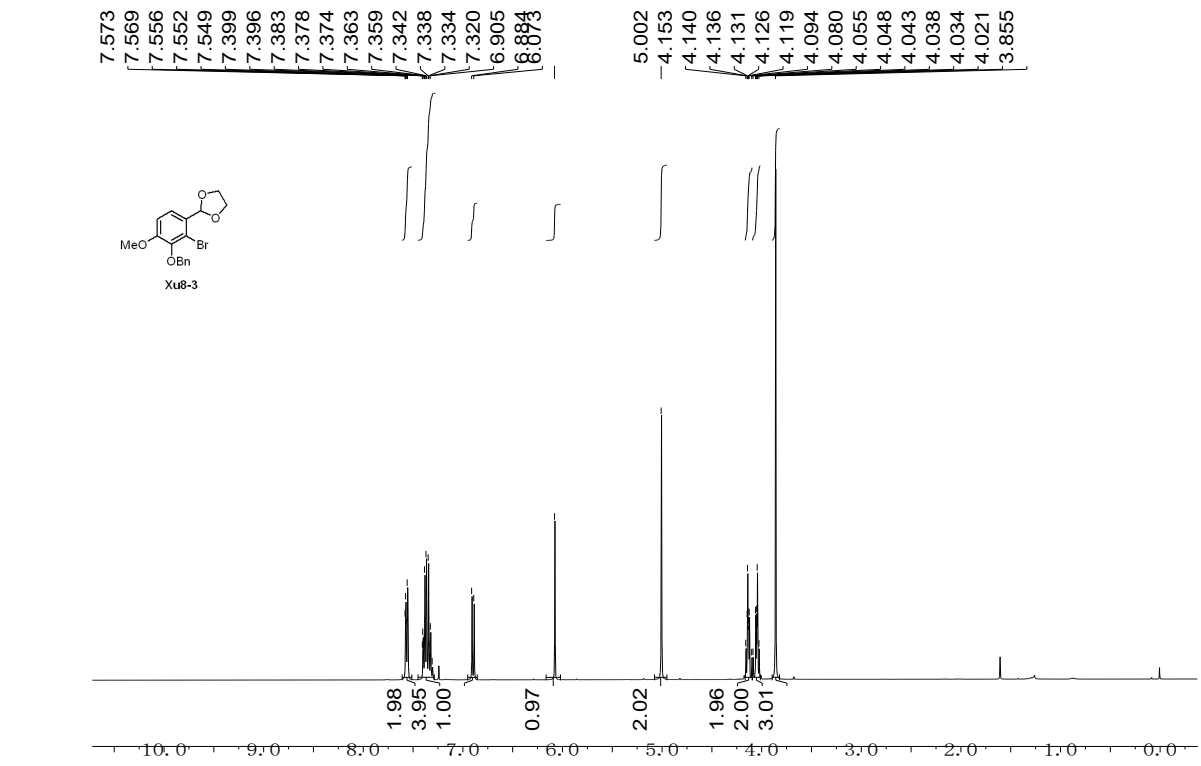
56.231
CHO
MeO
Br
OBn
Xu8-2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.374
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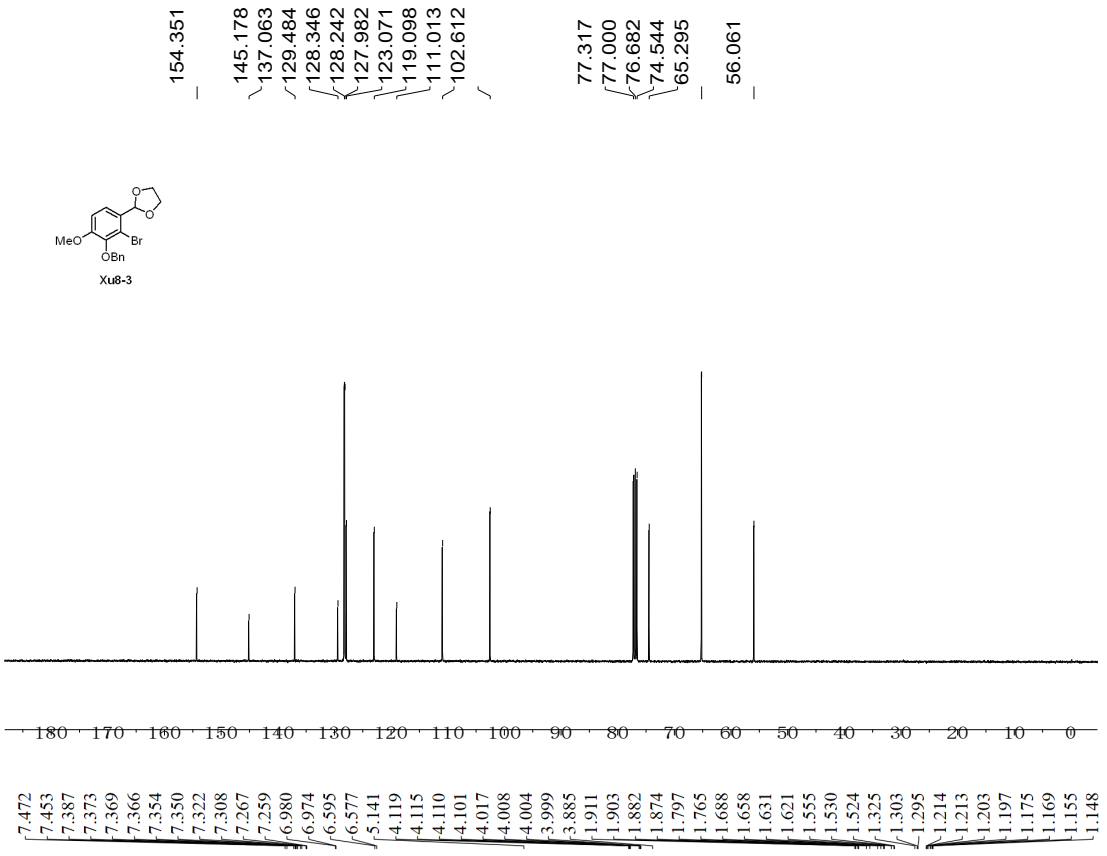
7.342
7.338
7.334
7.320
6.905
6.884
6.073
5.002
4.153
4.140
4.136
4.131
4.126
4.119
4.094
4.080
4.055
4.048
4.043
4.038
4.034
4.021
3.855
MeO
Br
OBn
Xu8-3
1.98
3.95
1.00
0.97
2.02
1.96
2.00
3.01
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0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123.071
119.098
111.013
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77.000
76.682
74.544
65.295
56.061
MeO
Br
OBn
Xu8-3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.472
7.453
7.387
7.373
7.369
7.366
7.354
7.350
7.322
7.308
7.267
7.259
6.980
6.974
6.595
6.577
5.141
4.119
4.115
4.110
4.101
4.017
4.008
4.004
3.999
3.885
1.911
1.903
1.882
1.874
1.797
1.765
1.688
1.658
1.631
1.621
1.555
1.530
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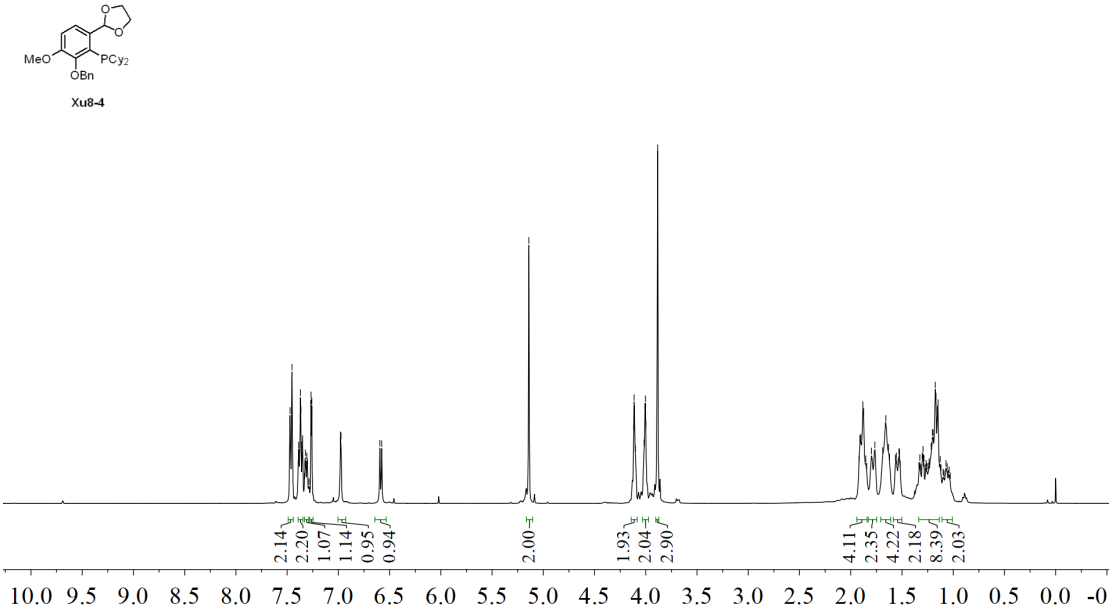
1.155
1.148


MeO
PCy2
OBn
Xu8-4
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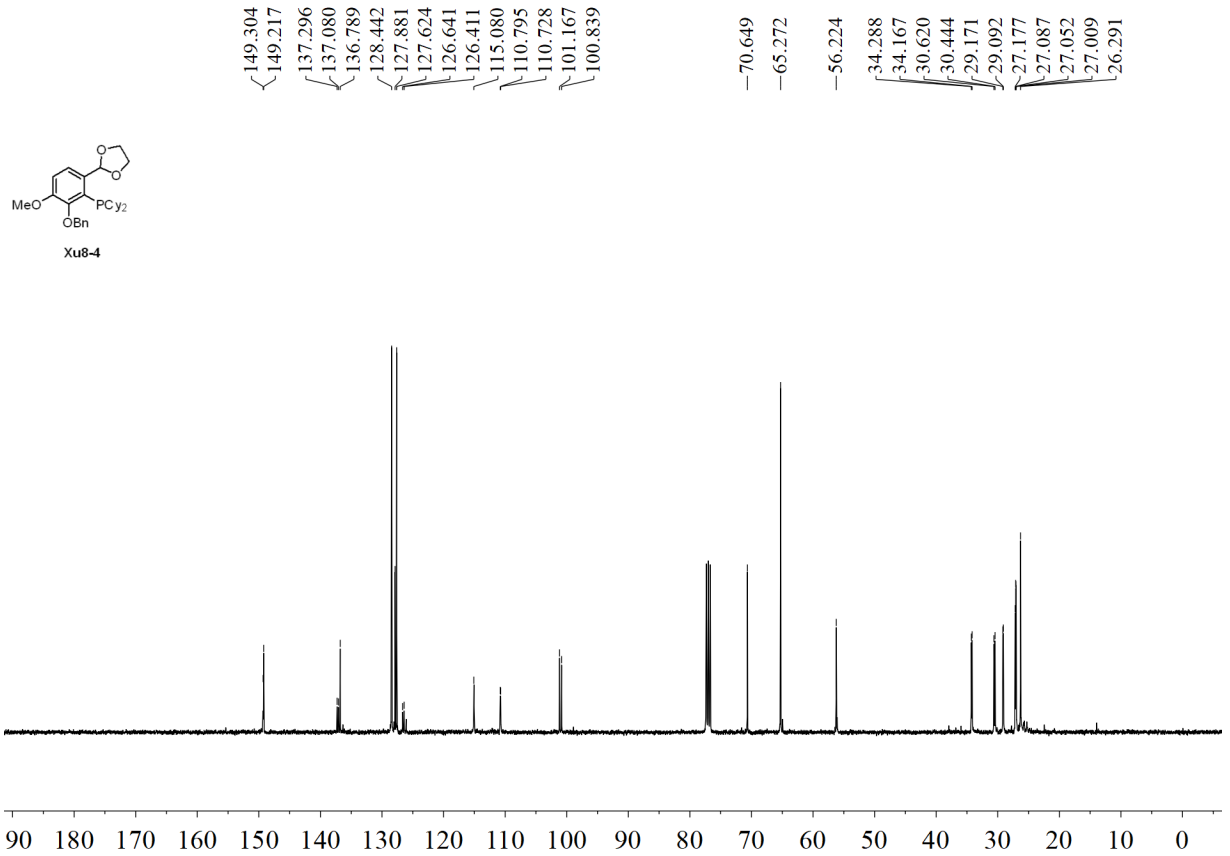
2.20
1.07
1.14
0.95
0.94
2.00
1.93
2.04
2.90
4.11
2.35
4.22
2.18
8.39
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0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127.881
127.624
126.641
126.411
115.080
110.795
110.728
101.167
100.839
70.649
65.272
56.224
34.288
34.167
30.620
30.444
29.171
29.092
27.177
27.087
27.052
27.009
26.291
MeO
PCy2
OBn
Xu8-4
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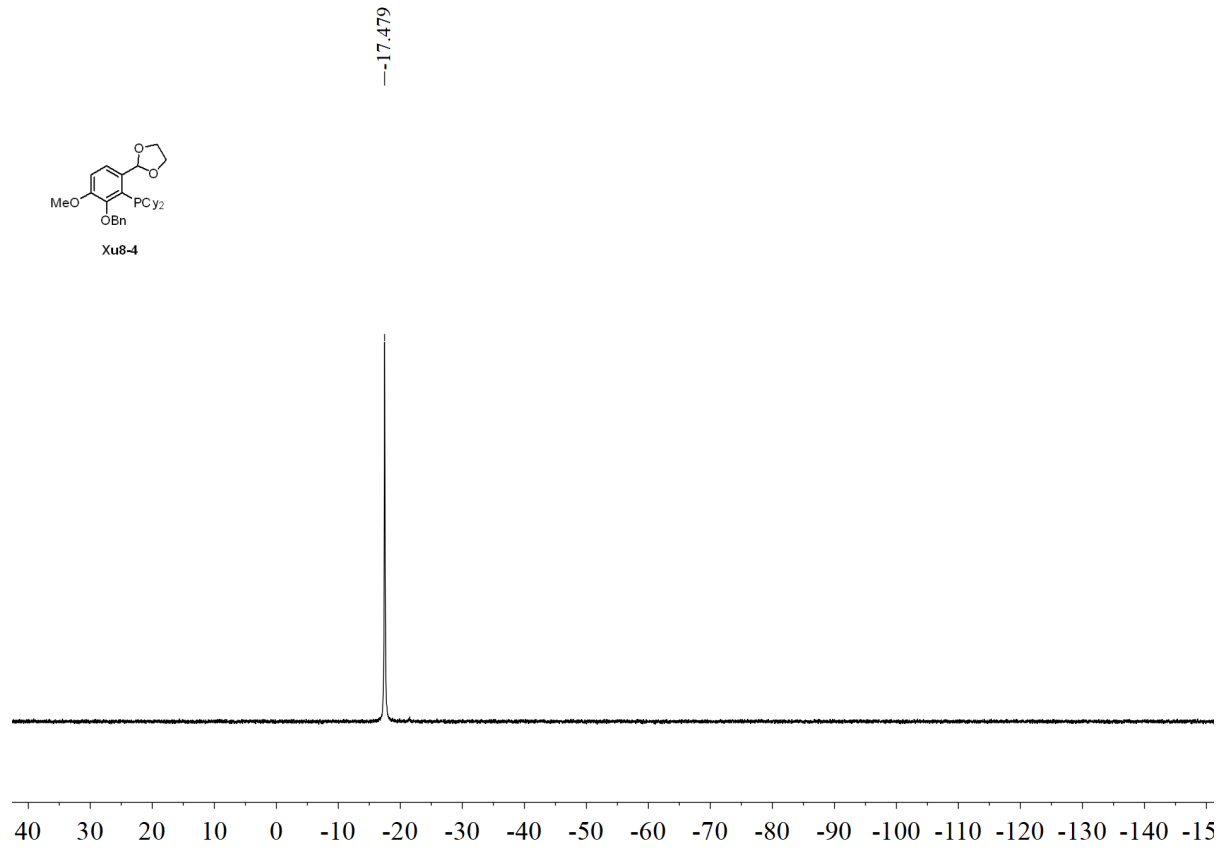
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OBn
Xu8-4
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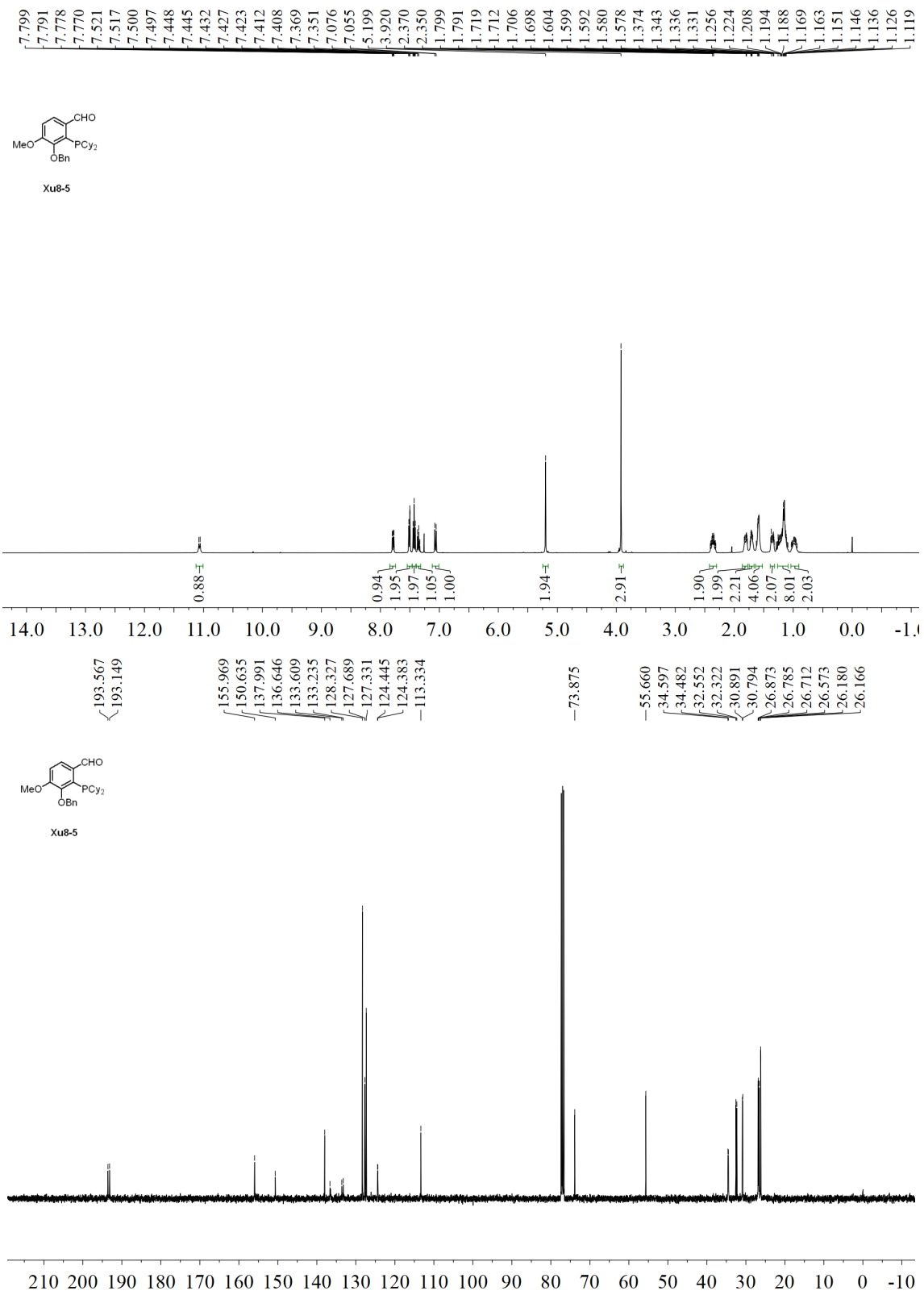
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7.778
7.770
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7.517
7.500
7.497
7.448
7.445
7.432
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7.423
7.412
7.408
7.369
7.351
7.076
7.055
5.199
3.920
2.370
2.350
1.799
1.791
1.719
1.712
1.706
1.698
1.604
1.599
1.592
1.580
1.578
1.374
1.343
1.336
1.331
1.256
1.224
1.208
1.194
1.188
1.169
1.163
1.151
1.146
1.136
1.126
1.119
CHO
MeO
PCy2
OBn
Xu8-5
0.88
0.94
1.95
1.97
1.05
1.00
1.94
2.91
1.90
1.99
2.21
4.06
2.07
8.01
2.03
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
193.567
193.149
155.969
150.635
137.991
136.646
133.609
133.235
128.327
127.689
127.331
124.445
124.383
113.334
73.875
55.660
34.597
34.482
32.552
32.322
30.891
30.794
26.873
26.785
26.712
26.573
26.180
26.166
CHO
MeO
PCy2
OBn
Xu8-5
210
200
190
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120
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100
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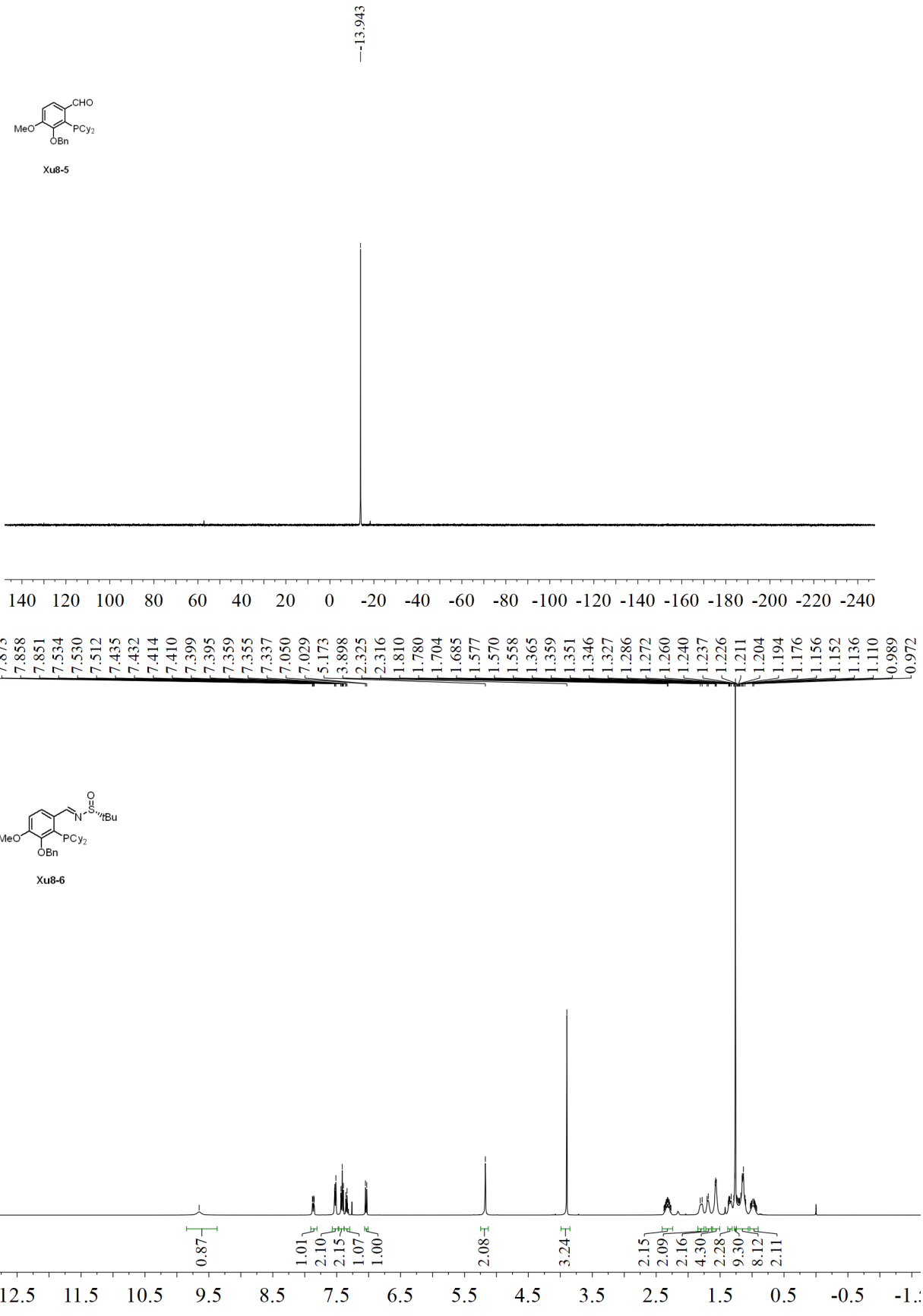
10
0
-10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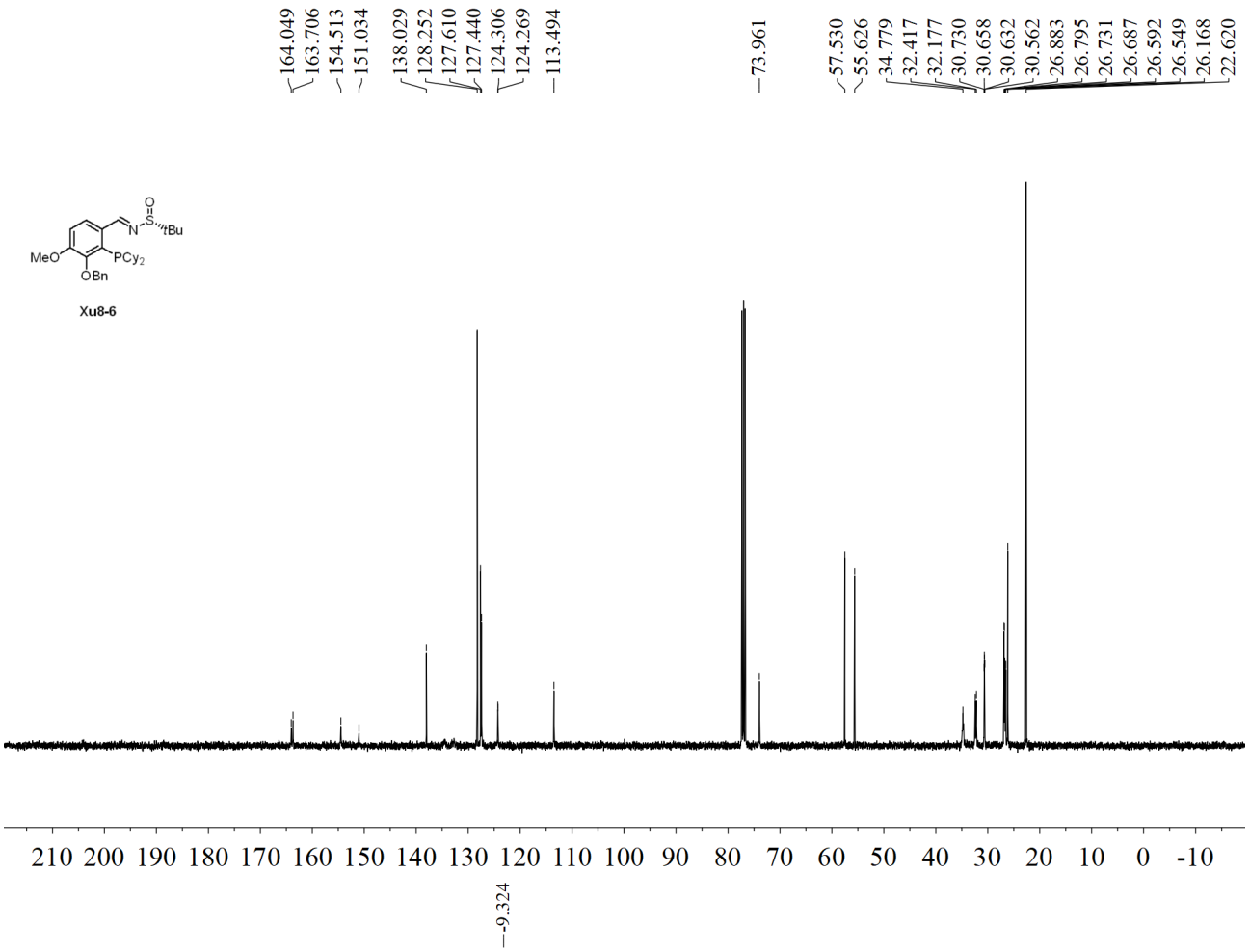
CHO
MeO
PCy2
OBn
Xu8-5
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
7.880 7.873 7.858 7.851 7.534 7.530 7.512 7.435 7.432 7.414 7.410 7.399 7.395 7.359 7.355 7.337 7.050 7.029 5.173 3.898 2.325 2.316 1.810 1.780 1.704 1.685 1.577 1.570 1.558 1.365 1.359 1.351 1.346 1.327 1.286 1.272 1.260 1.240 1.237 1.226 1.211 1.204 1.194 1.176 1.156 1.152 1.136 1.110 0.989 0.972
N
S
O
tBu
MeO
PCy2
OBn
Xu8-6
0.87 1.01 2.10 2.15 1.07 1.00 2.08 3.24 2.15 2.09 2.16 4.30 2.28 9.30 8.12 2.11
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5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127.440
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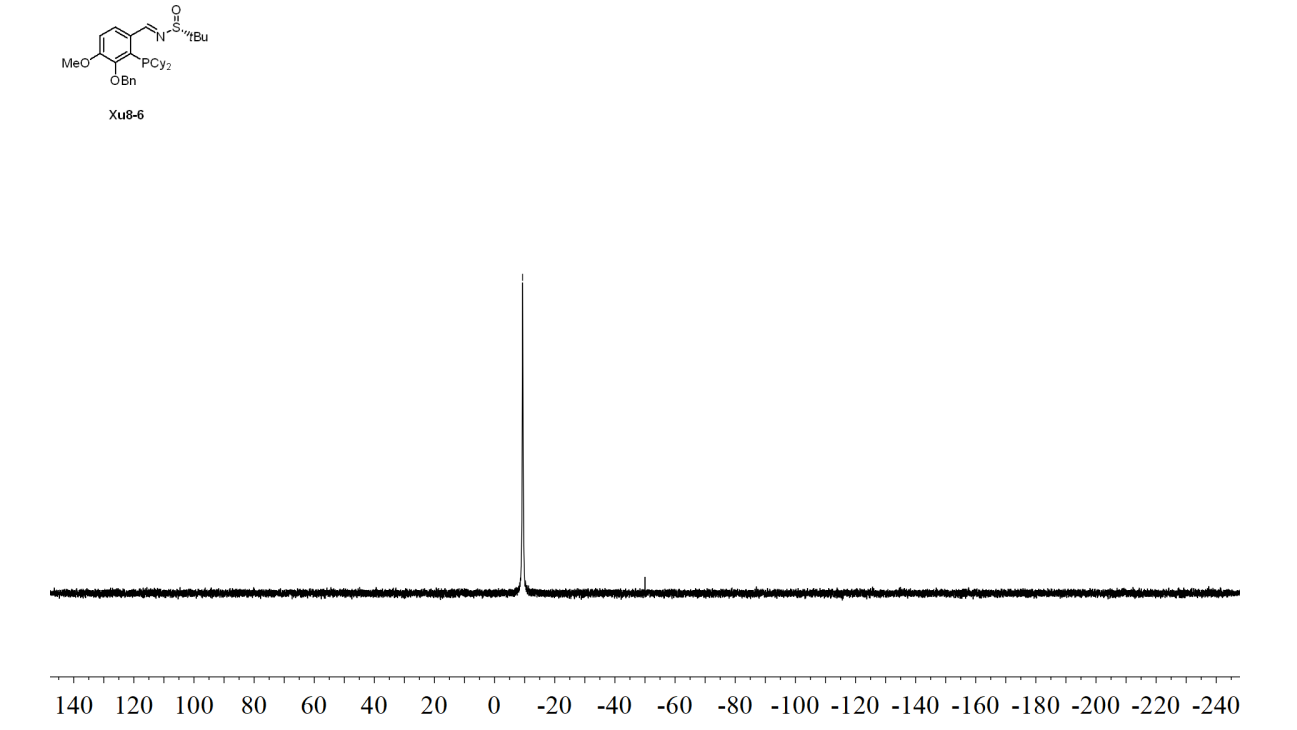
124.269
113.494
73.961
57.530
55.626
34.779
32.417
32.177
30.730
30.658
30.632
30.562
26.883
26.795
26.731
26.687
26.592
26.549
26.168
22.620
MeO
OBn
PCy2
tBu
Xu8-6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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tBu
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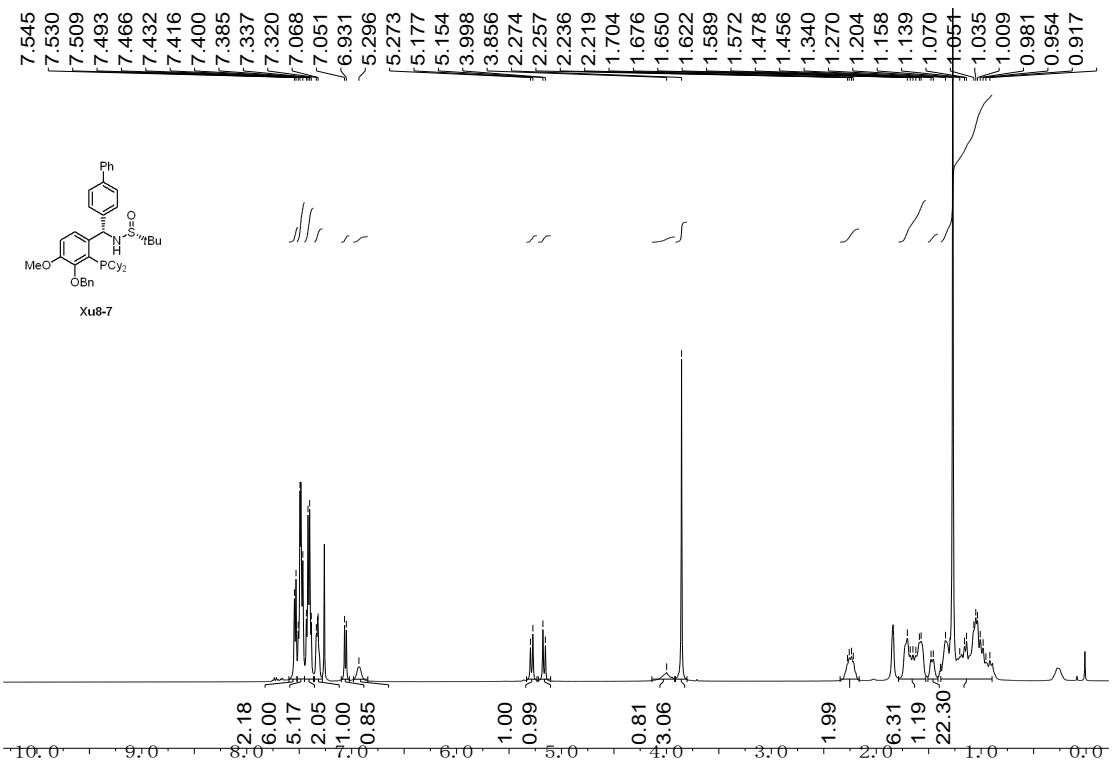
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7.432
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7.400
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7.337
7.320
7.068
7.051
6.931
5.296
5.273
5.177
5.154
3.998
3.856
2.274
2.257
2.236
2.219
1.704
1.676
1.650
1.622
1.589
1.572
1.478
1.456
1.340
1.270
1.204
1.158
1.139
1.070
1.051
1.035
1.009
0.981
0.954
0.917
Ph
MeO
OBn
PCy2
tBu
Xu8-7
2.18
6.00
5.17
2.05
1.00
0.85
1.00
0.99
0.81
3.06
1.99
6.31
1.19
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8.0
7.0
6.0
5.0
4.0
3.0
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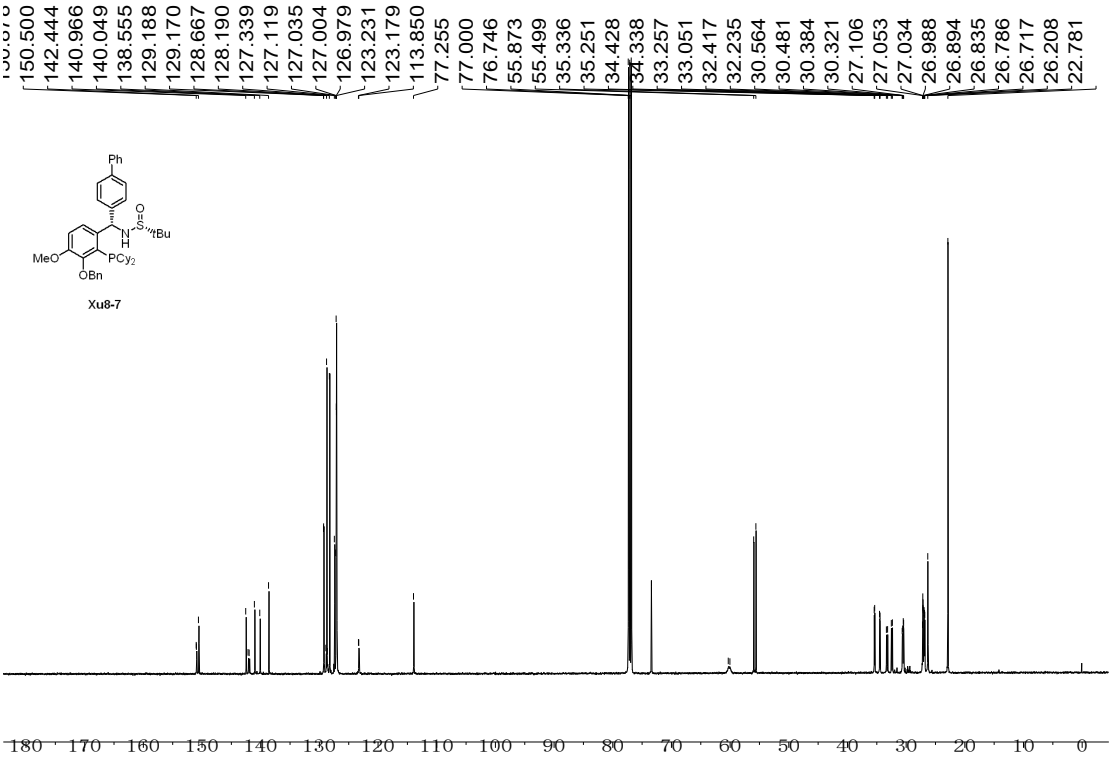
1.0
0.0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128.667
128.190
127.339
127.119
127.035
127.004
126.979
123.231
123.179
113.850
77.255
77.000
76.746
55.873
55.499
35.336
35.251
34.428
34.338
33.257
33.051
32.417
32.235
30.564
30.481
30.384
30.321
27.106
27.053
27.034
26.988
26.894
26.835
26.786
26.717
26.208
22.781
Ph
MeO
OBn
PCy2
tBu
Xu8-7
180
170
160
150
140
130
120
110
100
90
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70
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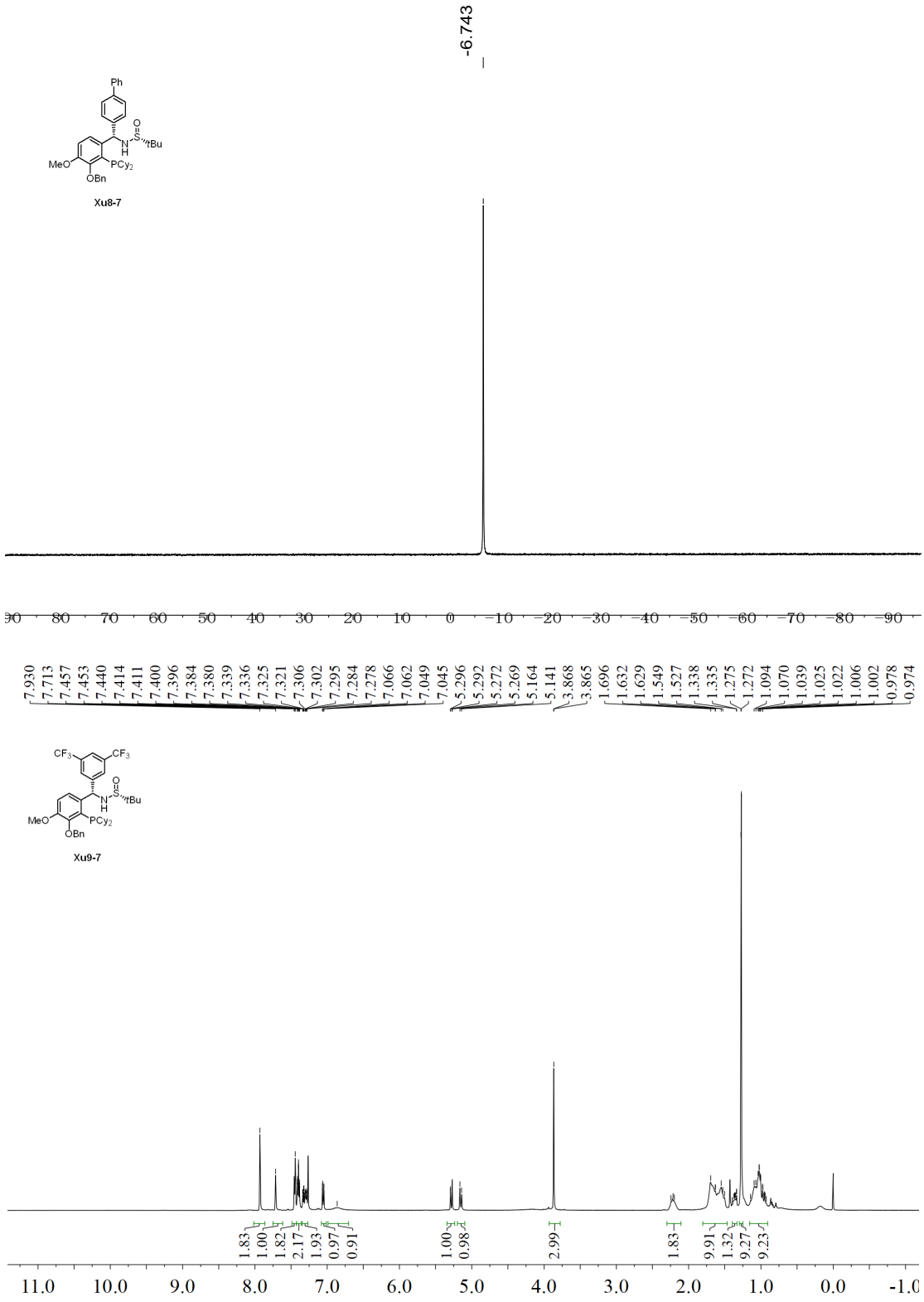
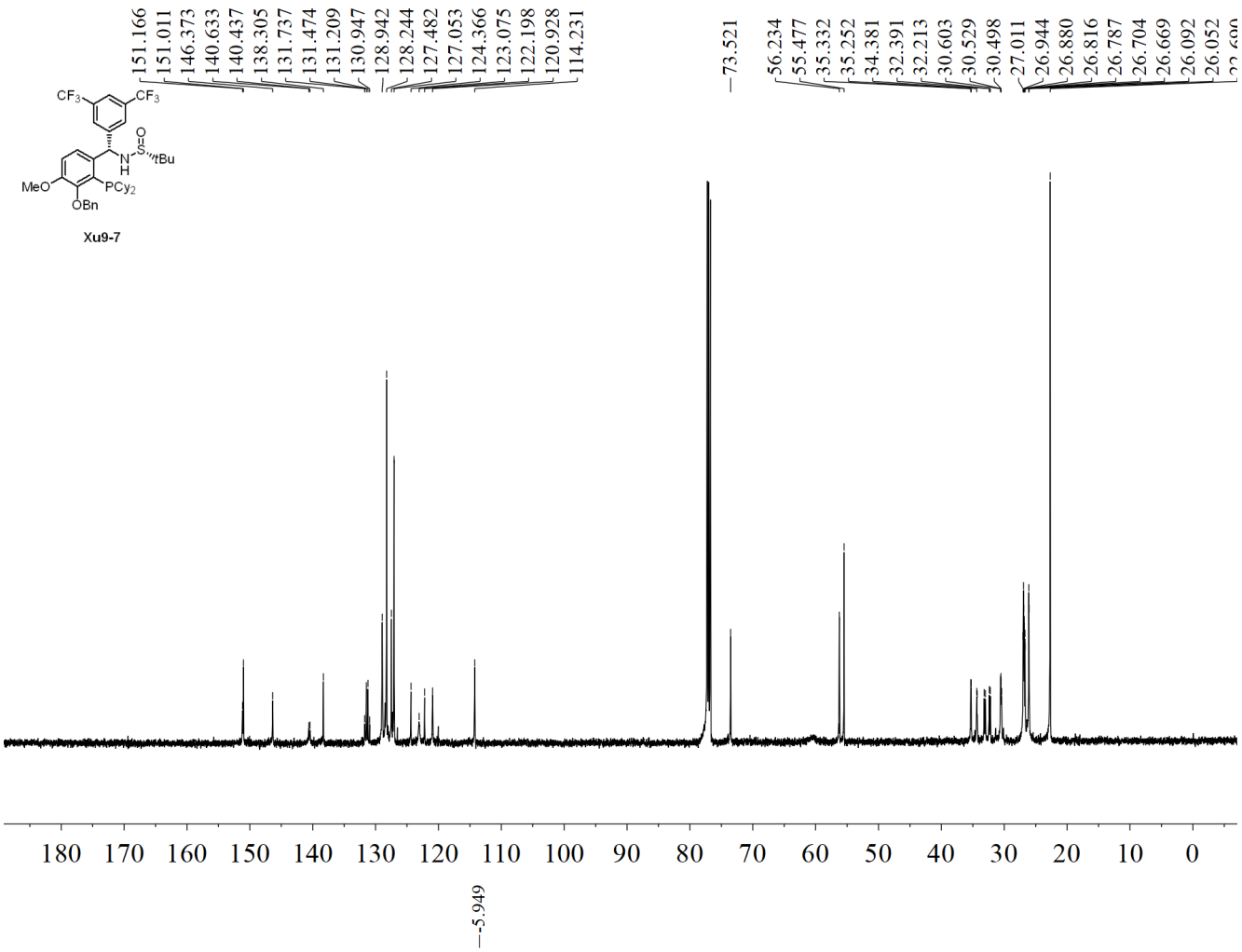
30
20
10
0


-6.743
Xu8-7
Xu9-7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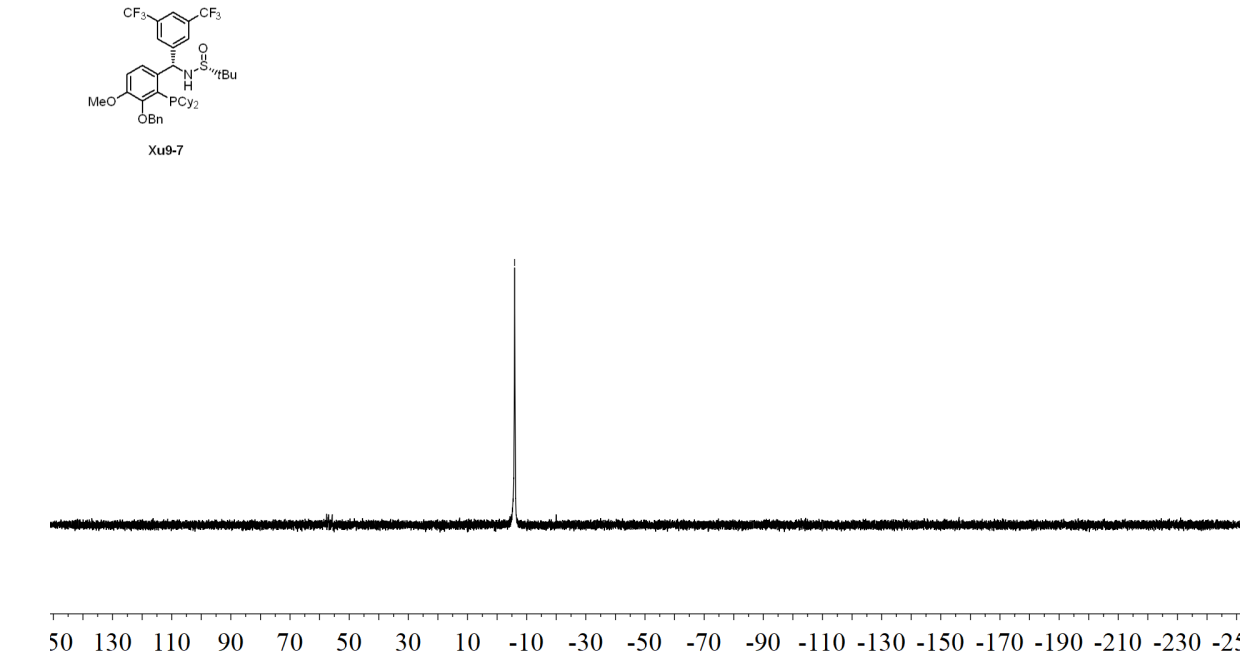
151.011
146.373
140.633
140.437
138.305
131.737
131.474
131.209
130.947
128.942
128.244
127.482
127.053
124.366
123.075
122.198
120.928
114.231
73.521
56.234
55.477
35.332
35.252
34.381
32.391
32.213
30.603
30.529
30.498
27.011
26.944
26.880
26.816
26.787
26.704
26.669
26.092
26.052
CF3
CF3
MeO
PCy2
OBn
tBu
Xu9-7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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CF3
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PCy2
OBn
tBu
Xu9-7
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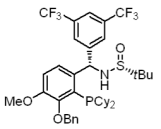
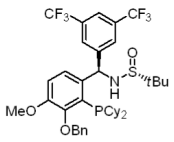


Xu9-7



(*R*, *R*$_S$)-Xu9-7

151.320
151.292
151.229
146.093
141.565
141.372
138.313
131.625
131.362
131.099
130.835
128.865
128.299
127.542
127.118
124.474
122.663
122.606
122.307
120.748
114.649
73.626
59.855
59.605
56.304
55.575
35.348
35.268
34.703
34.624
33.192
32.990
32.490
32.311
30.743
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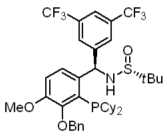
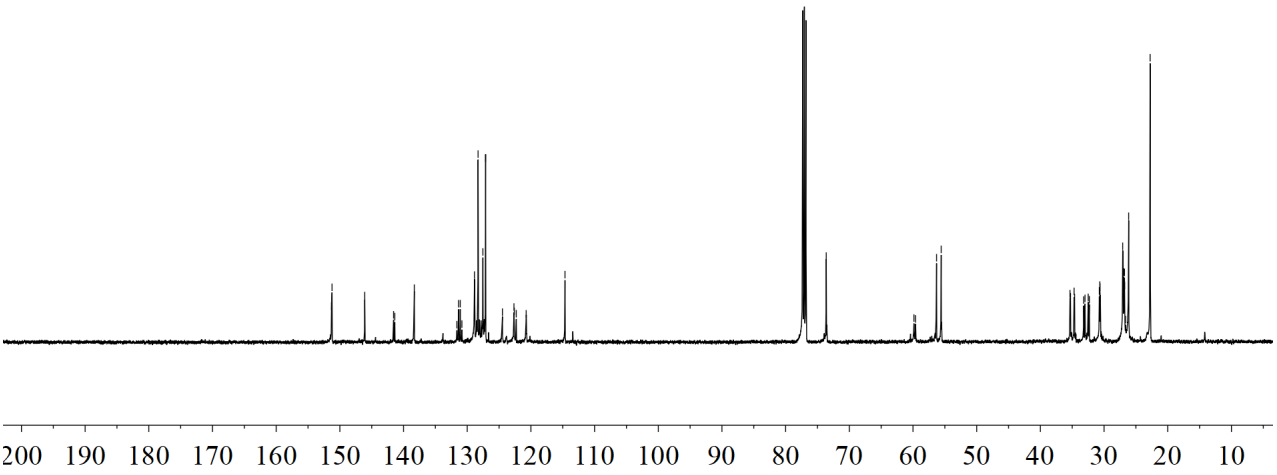
26.133
22.763



(*R*, *R*$_S$)-Xu9-7



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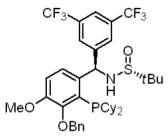
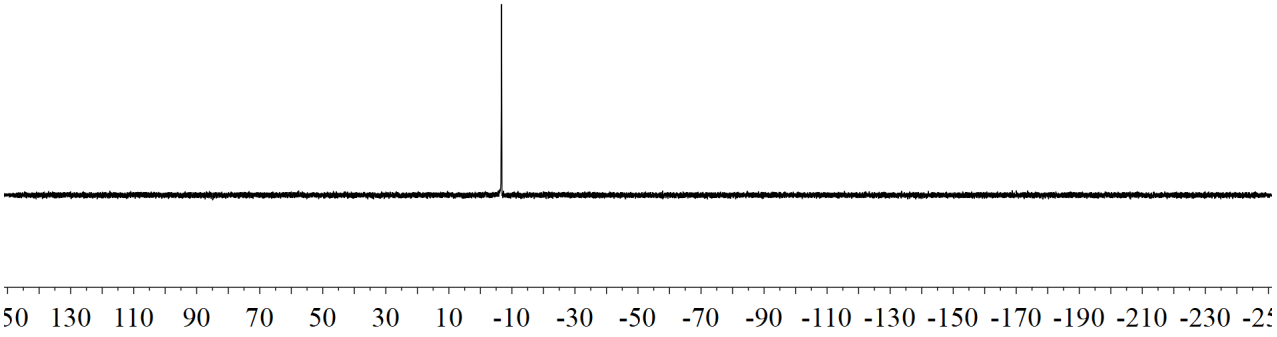
-6.695



(*R*, *R*$_S$)-Xu9-7



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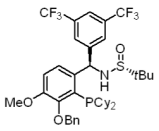
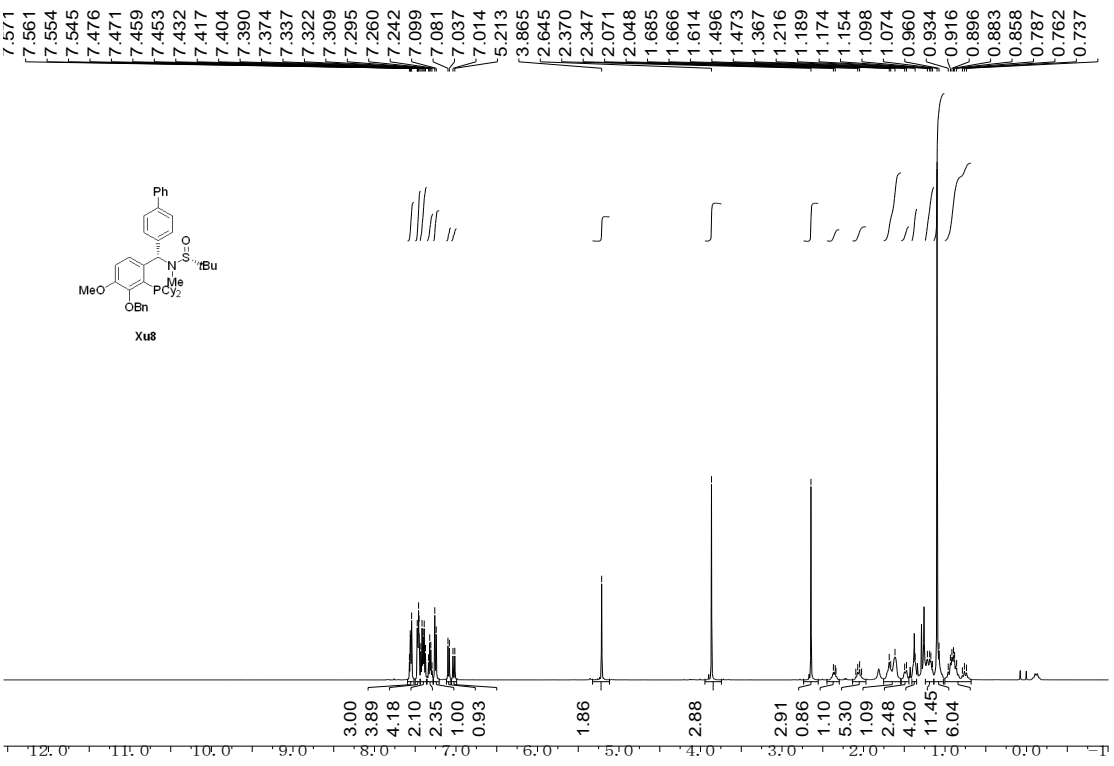


(*R*, *R*$_S$)-Xu9-7

-62.793
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210

Xu8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7.014
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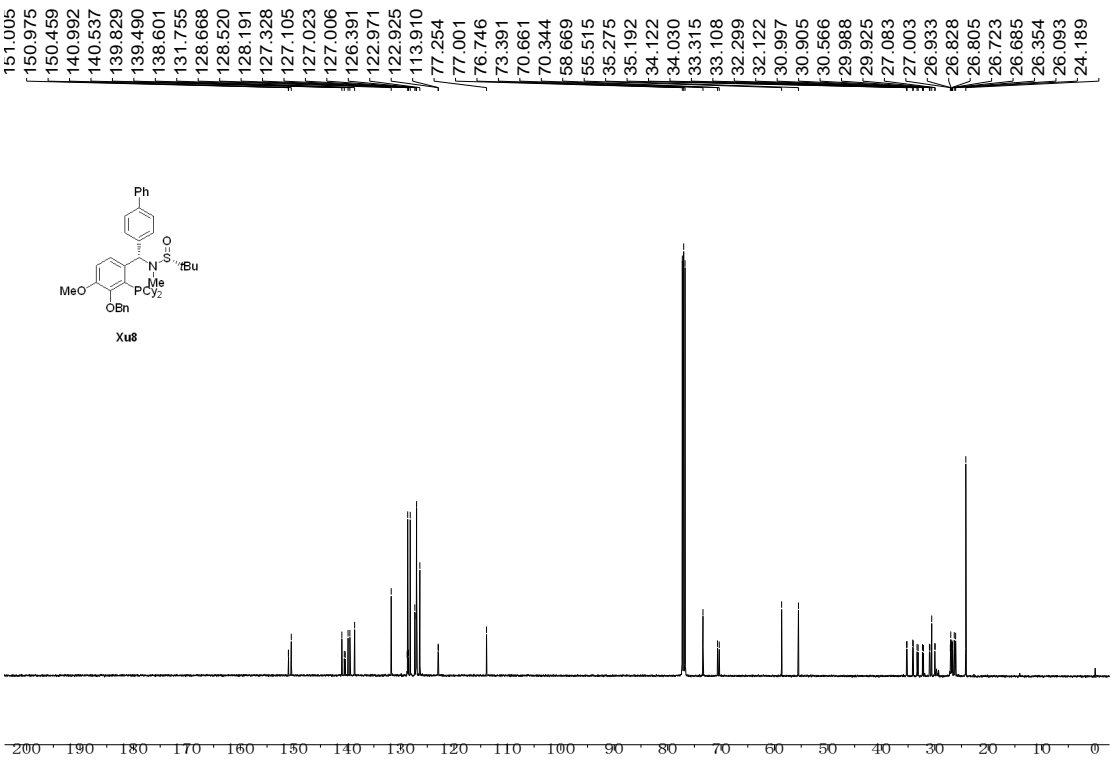
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26.685
26.354
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MeO
OBn
PCy2
Me
N
S
O
tBu
Xu8
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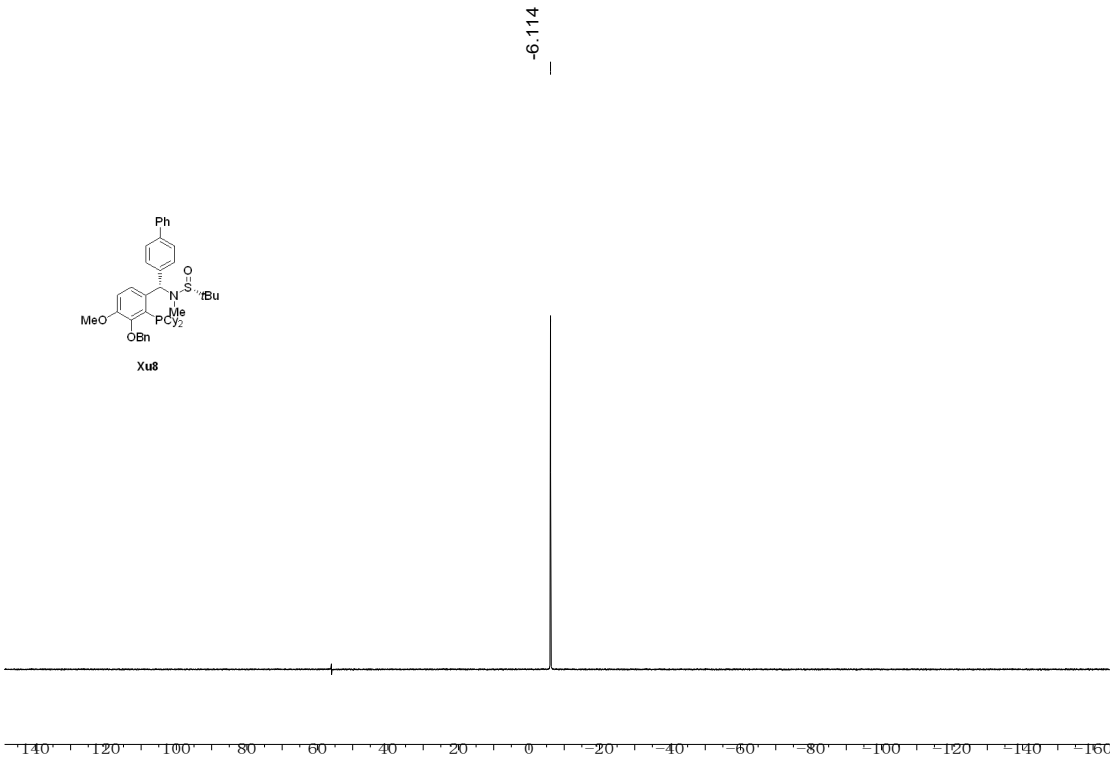
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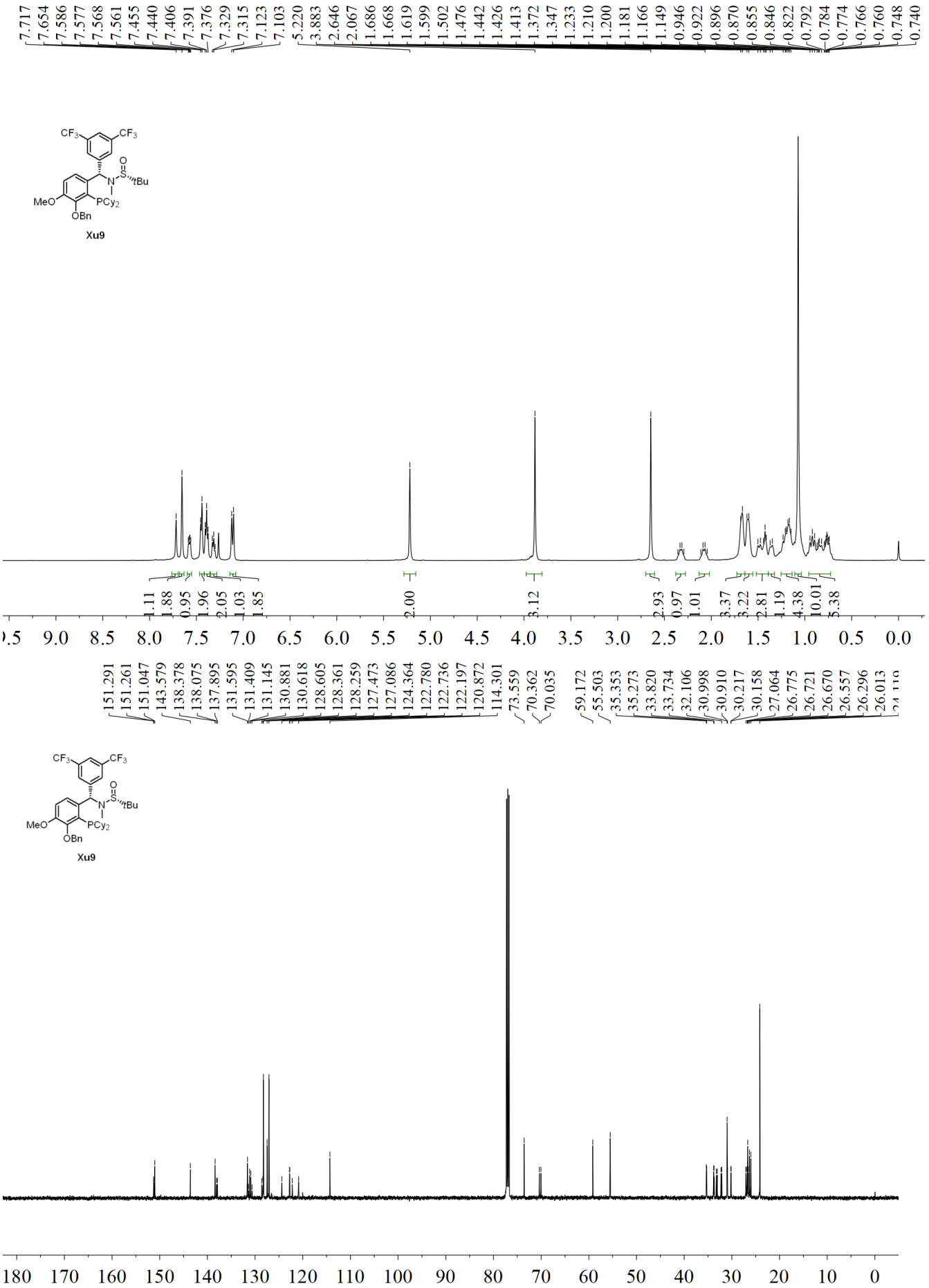
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PCy2
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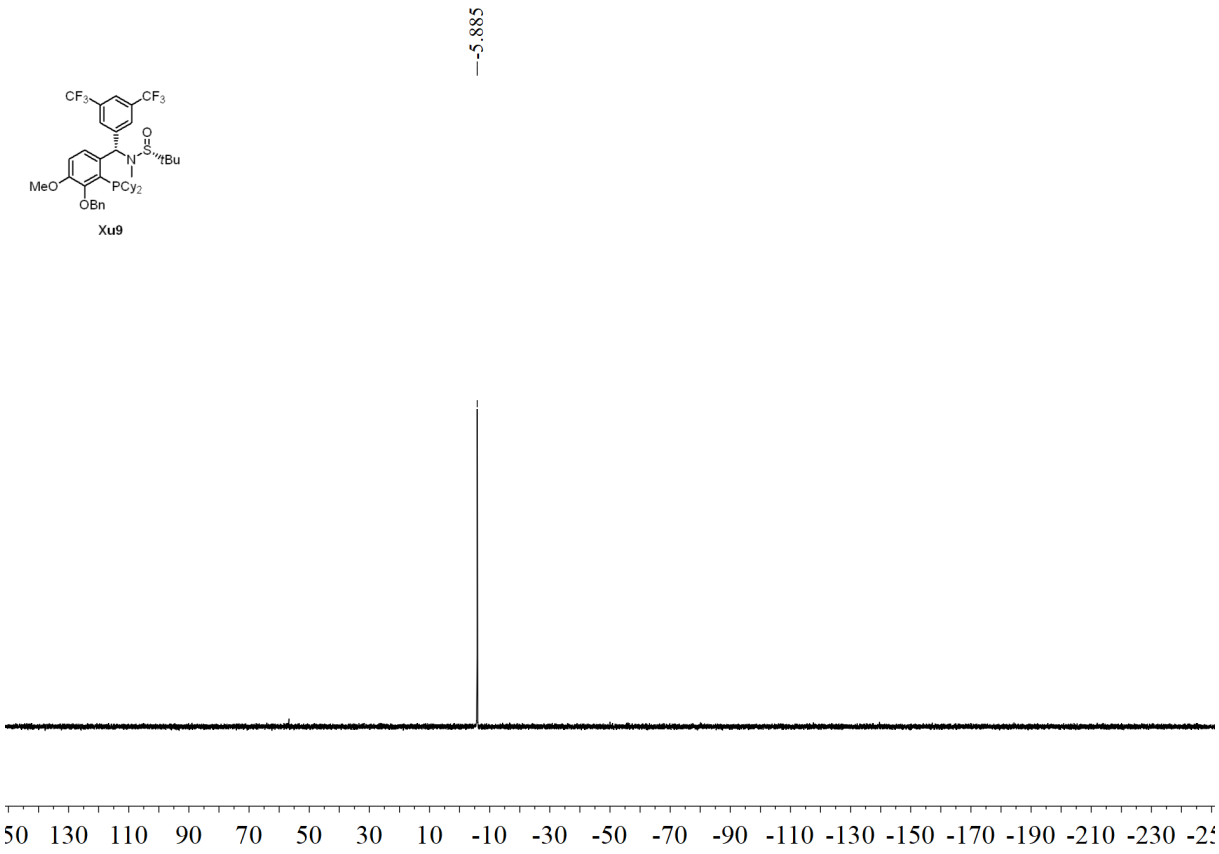
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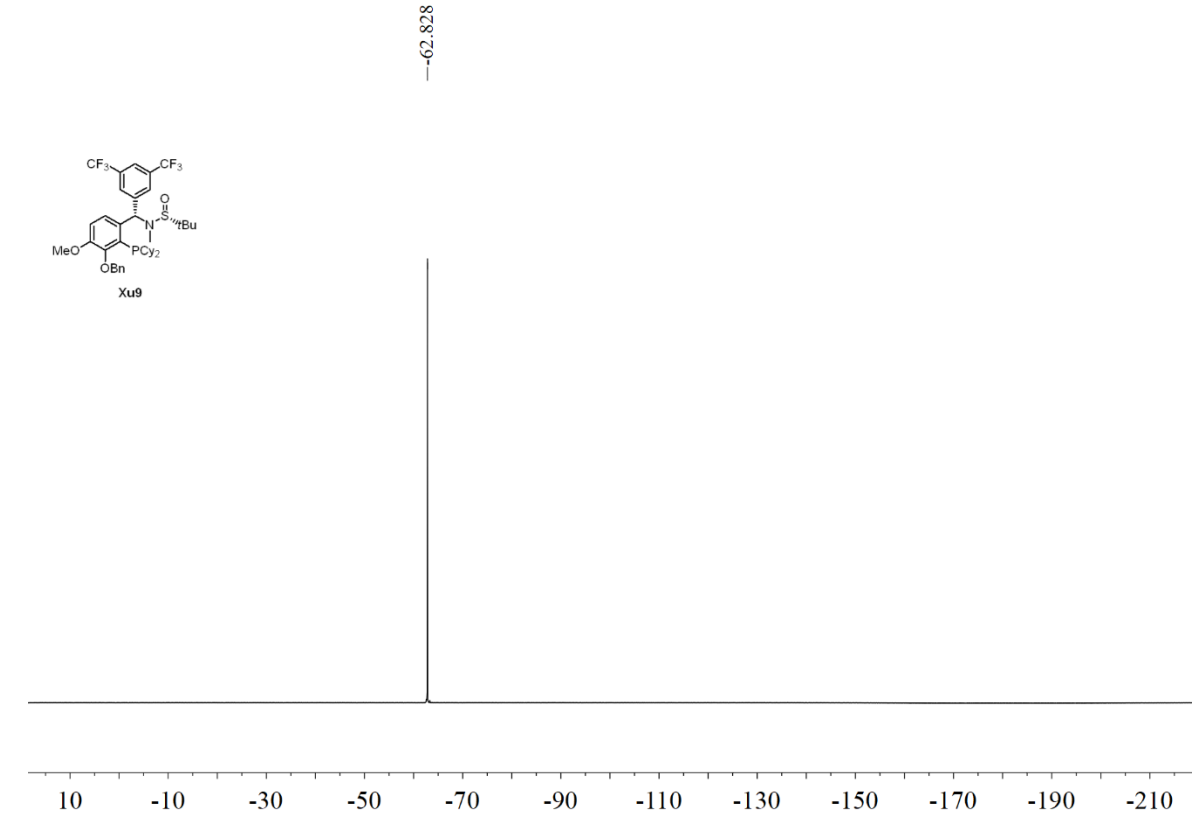
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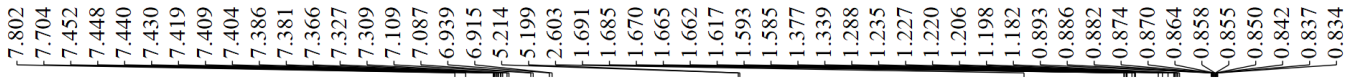
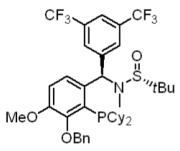
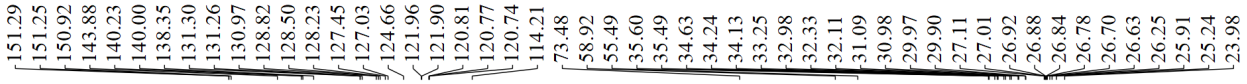
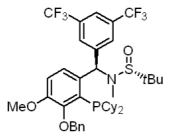




(*R*, *R*$_S$)-Xu9





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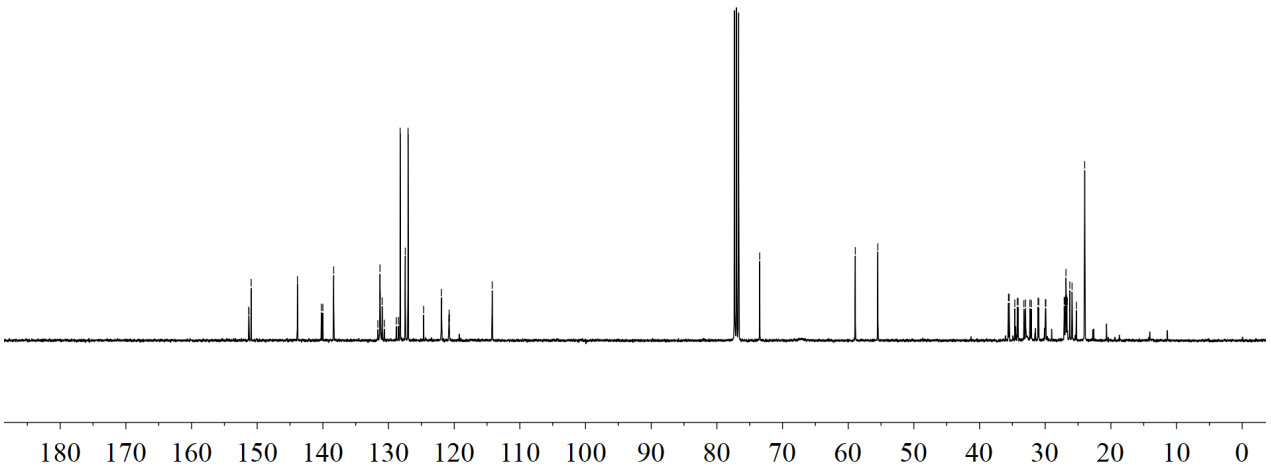
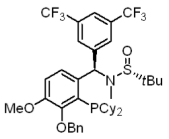
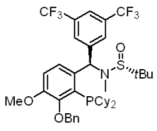
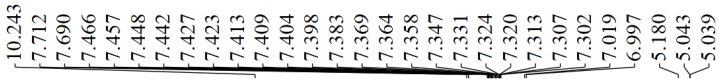




(*R*, *R*$_S$)-Xu9



(*R*, *R*$_S$)-Xu9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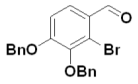
5.039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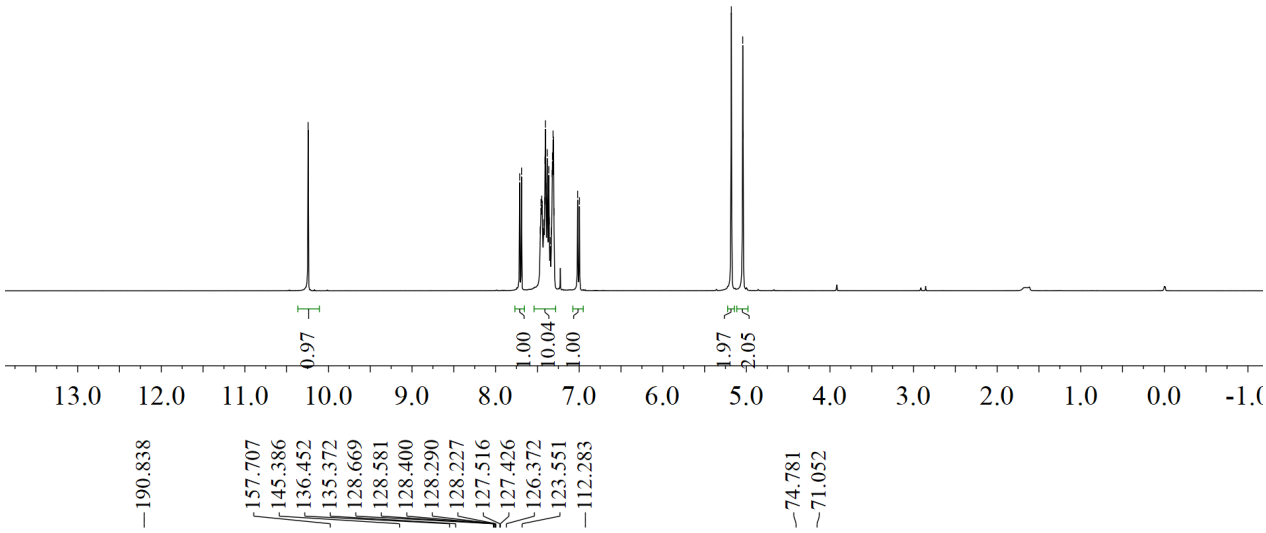
Br
OBn
O

Xu10-2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3.0
2.0
1.0
0.0

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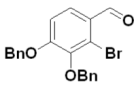
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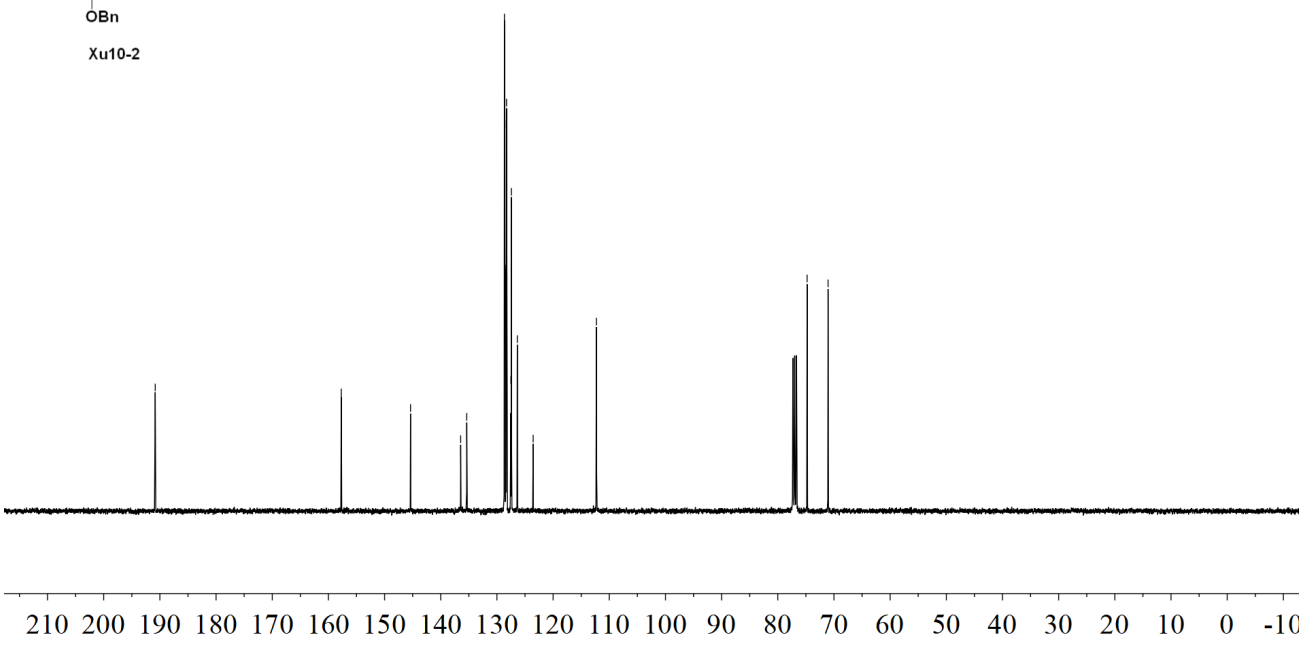
Br
OBn
O

Xu10-2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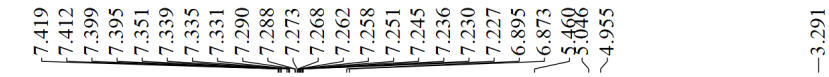
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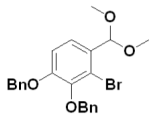
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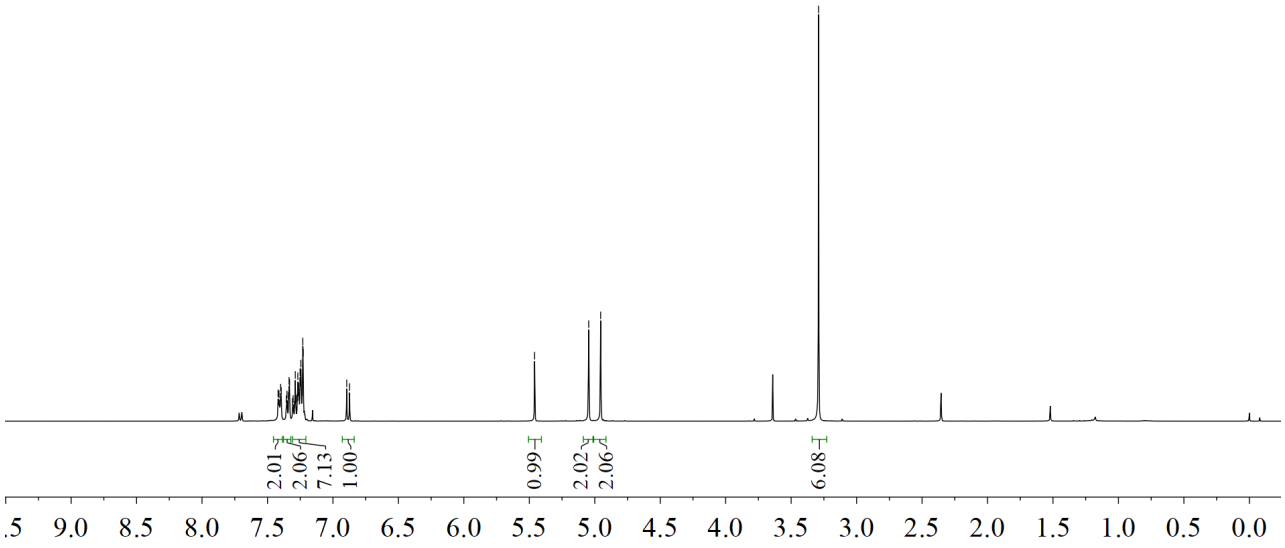
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6.08
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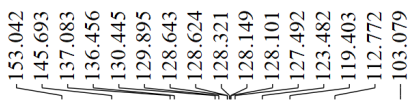
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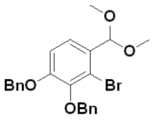
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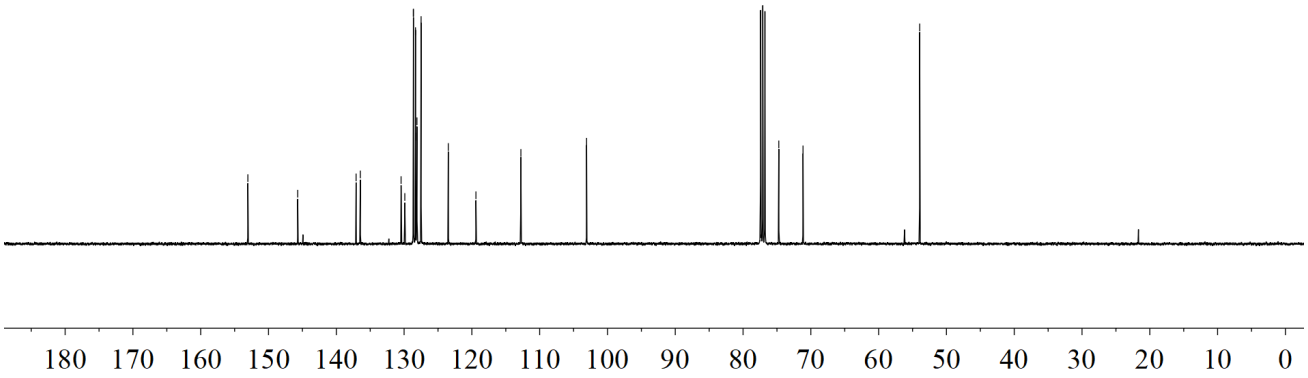
Xu10-3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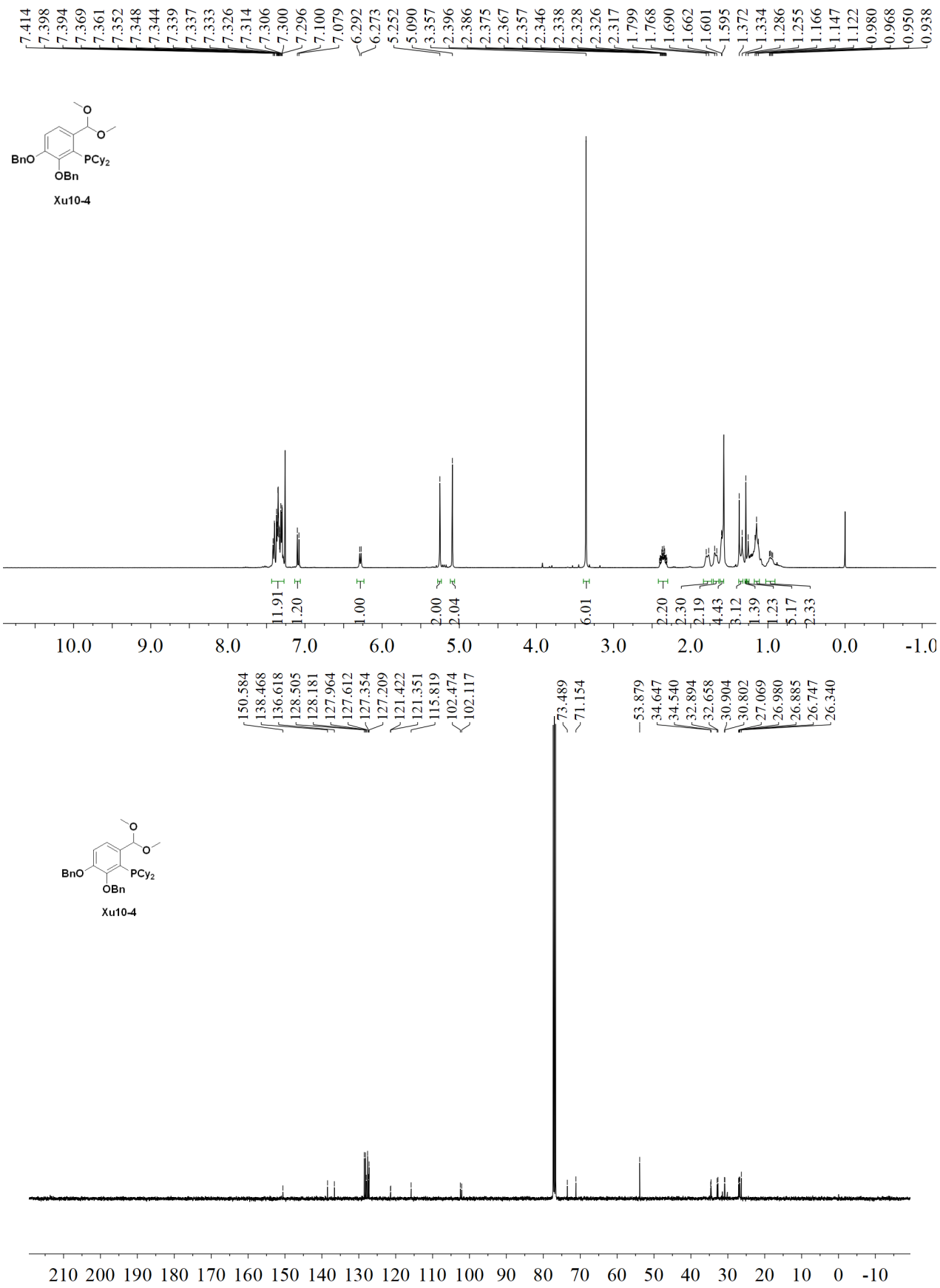
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BnO
PCy2
OBn
Xu10-4
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10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
150.584 138.468 136.618 128.505 128.181 127.964 127.612 127.354 127.209 121.422 121.351 115.819 102.474 102.117
73.489 71.154
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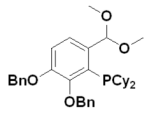
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PCy2
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Xu10-4

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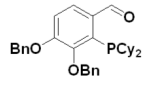
5.221 5.172 2.374 2.365 2.355 2.346 2.337 1.827 1.815 1.797 1.787 1.721 1.714 1.695 1.686 1.603 1.583 1.343 1.335 1.265 1.257 1.213 1.172 1.152 1.128 1.121 1.004 0.992 0.971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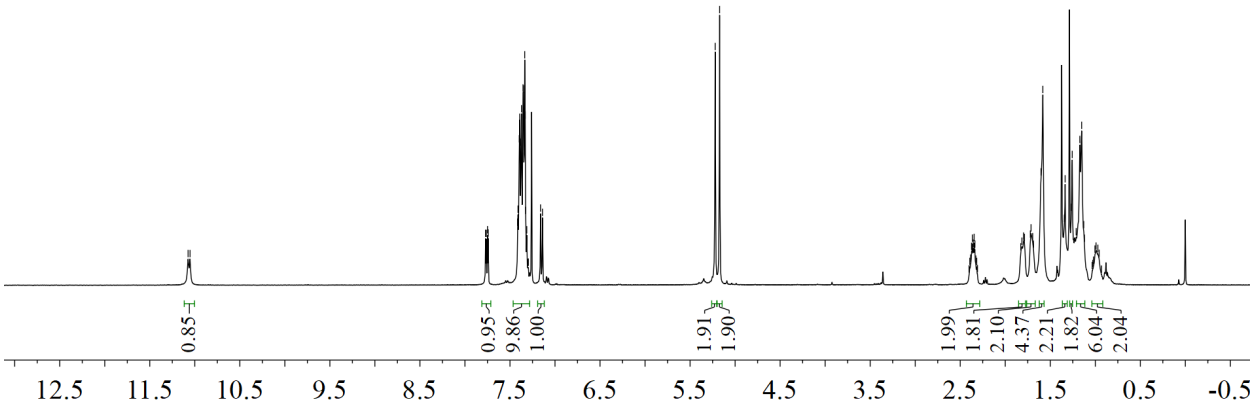
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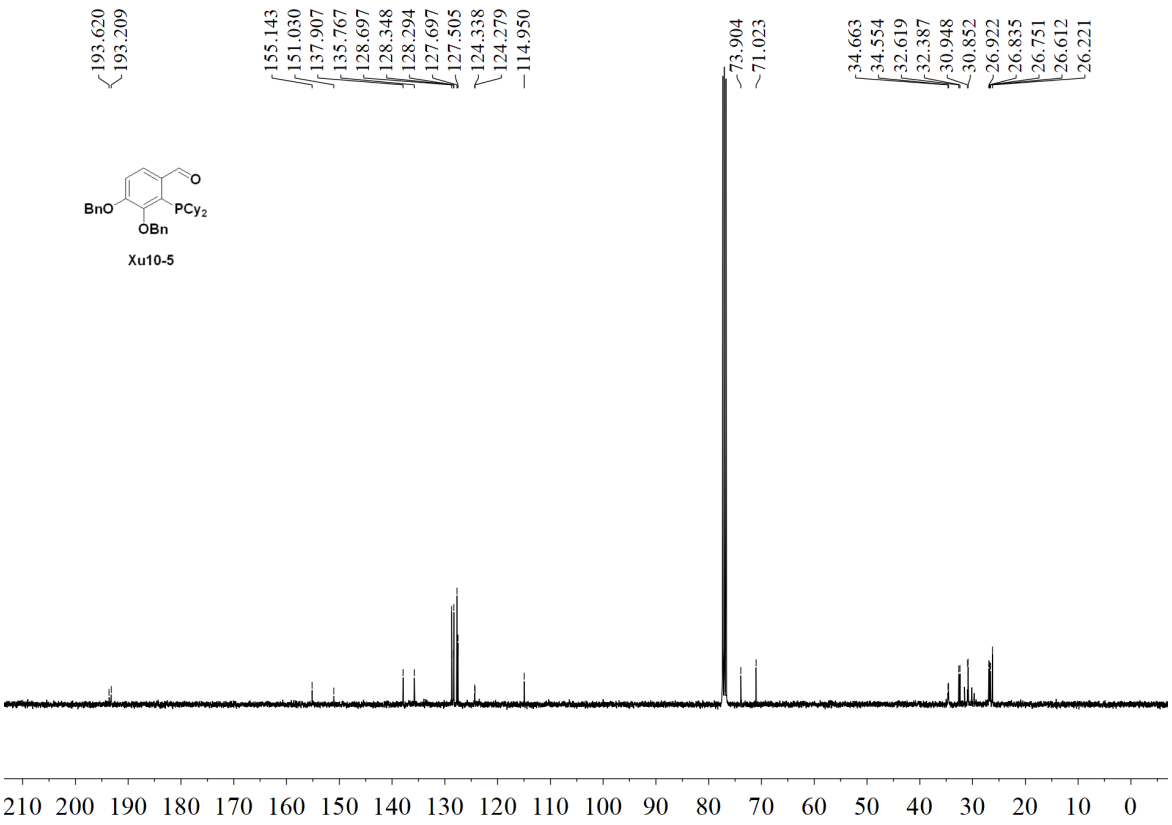
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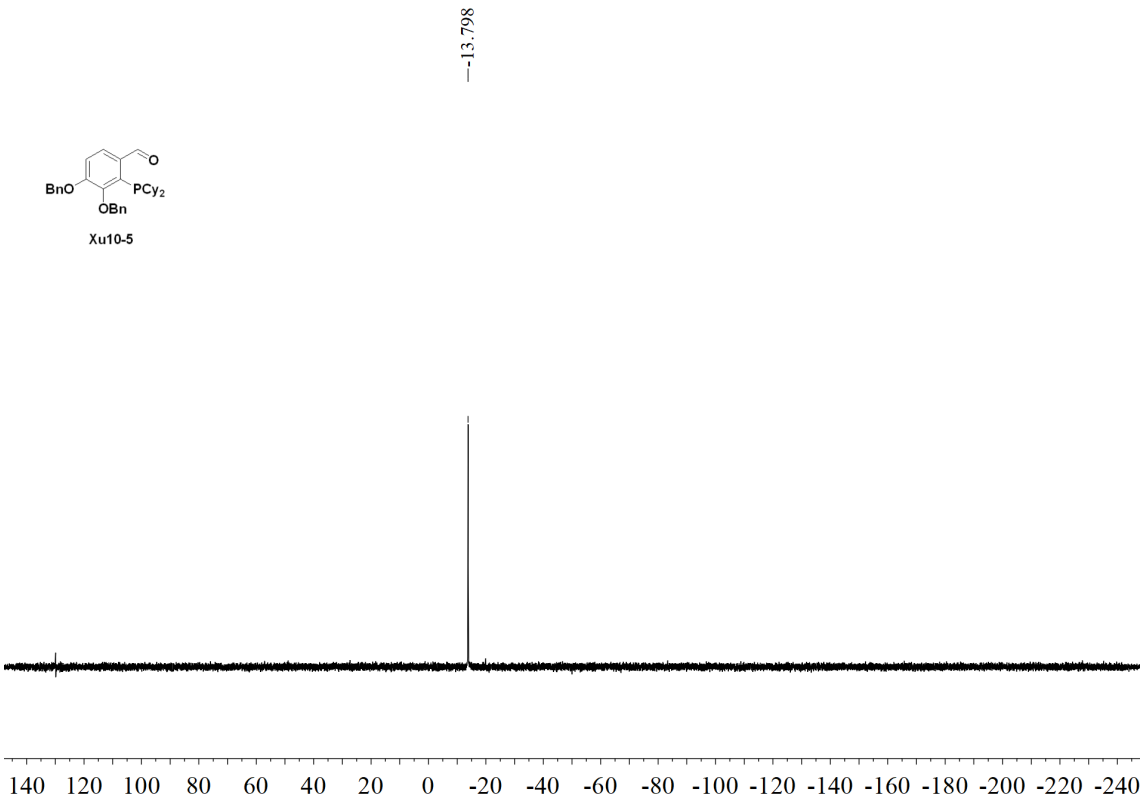
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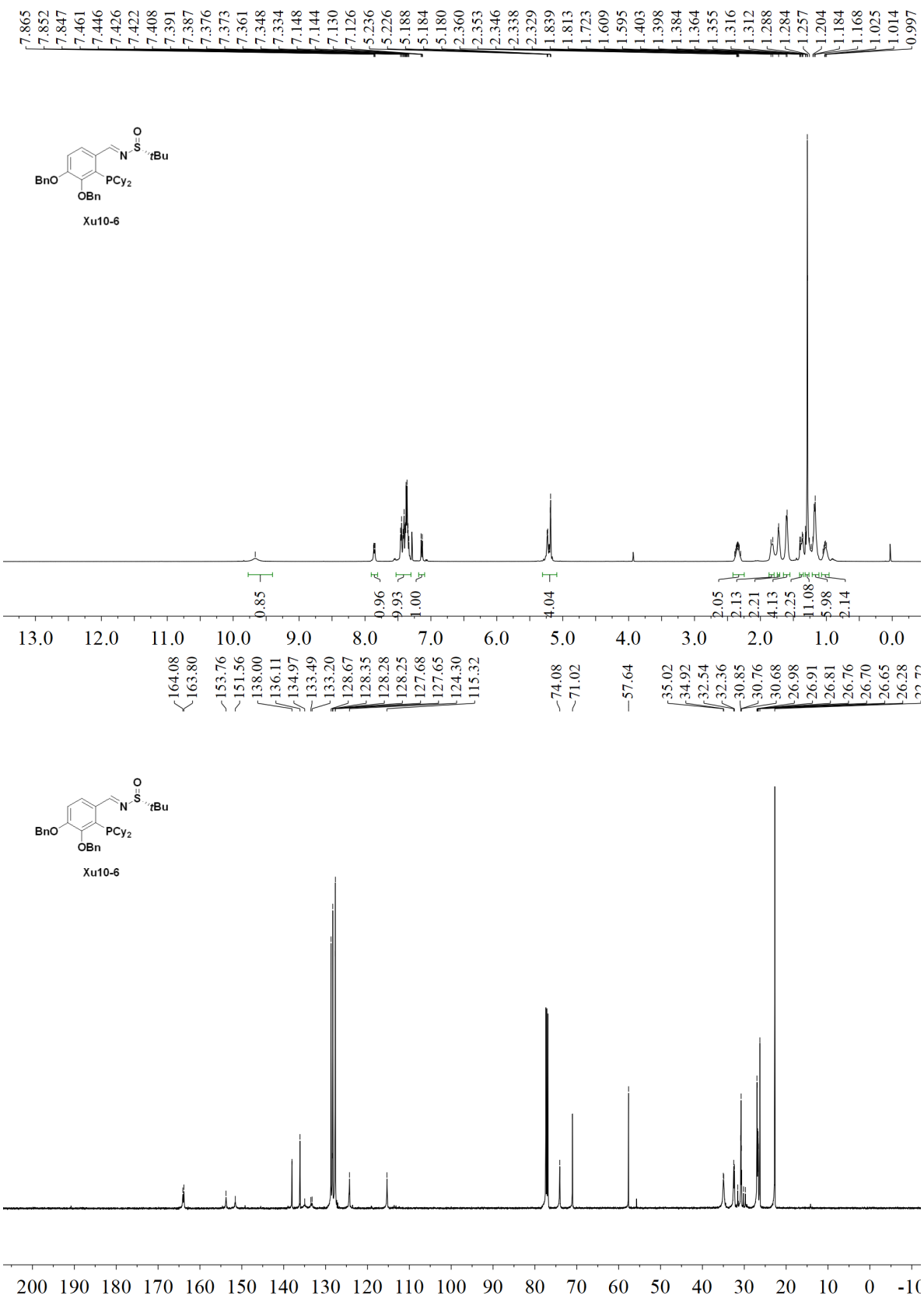
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Xu10-6
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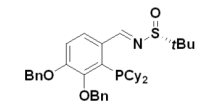
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OBn

Xu10-6

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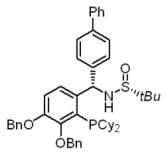
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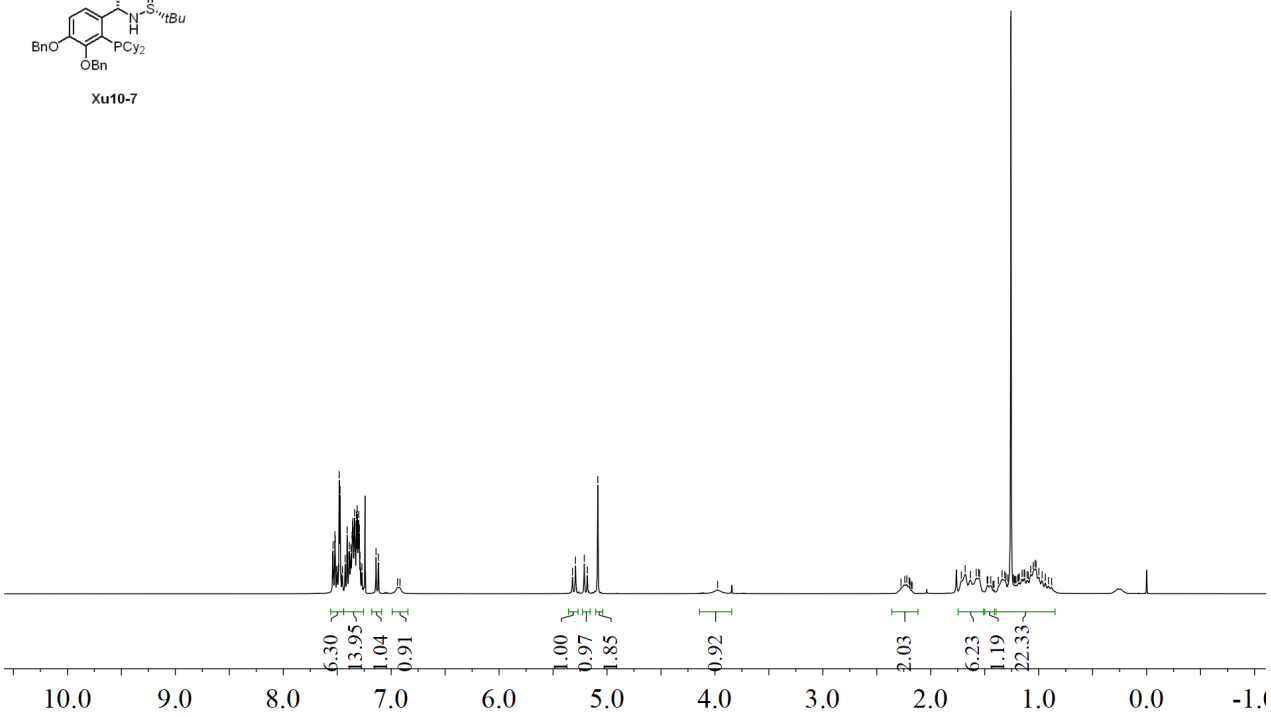
Xu10-7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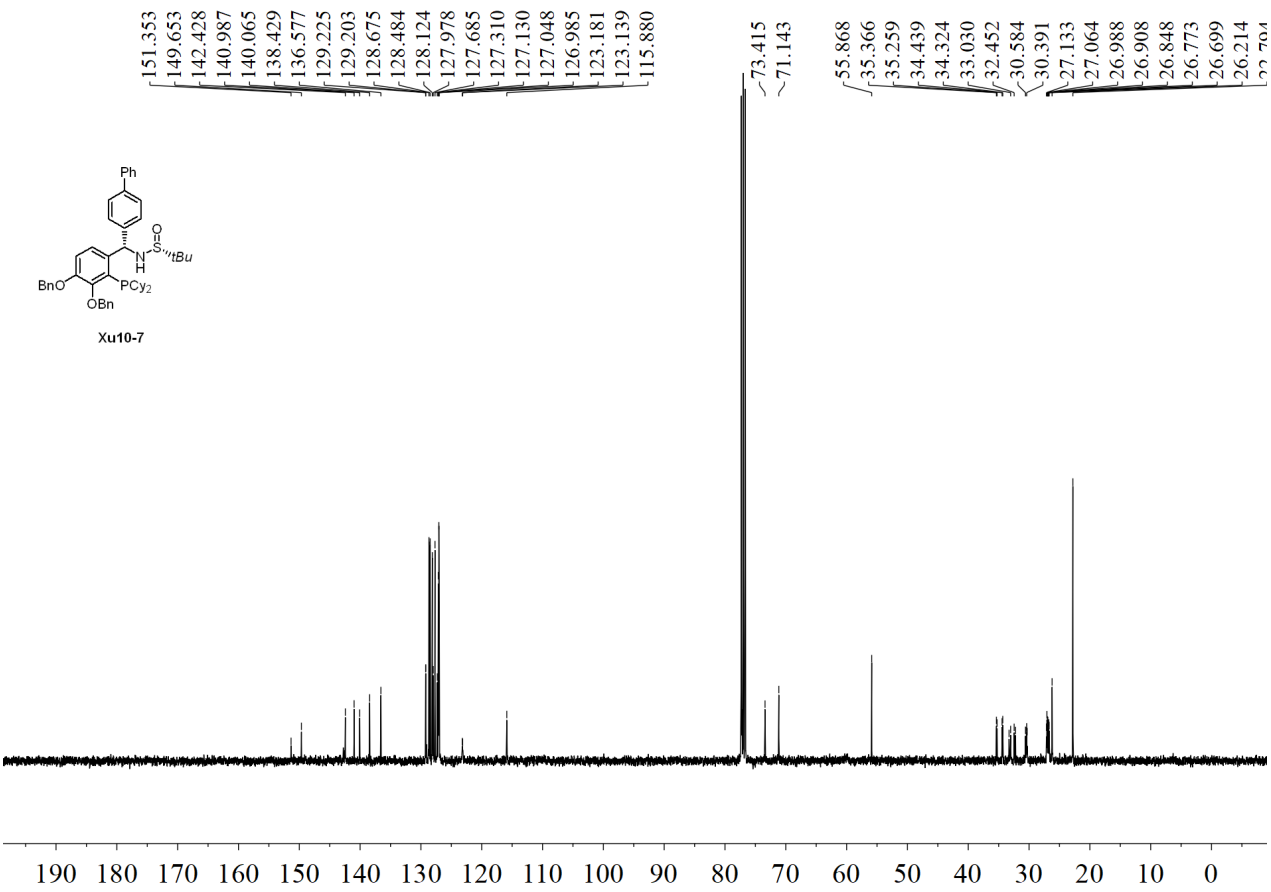
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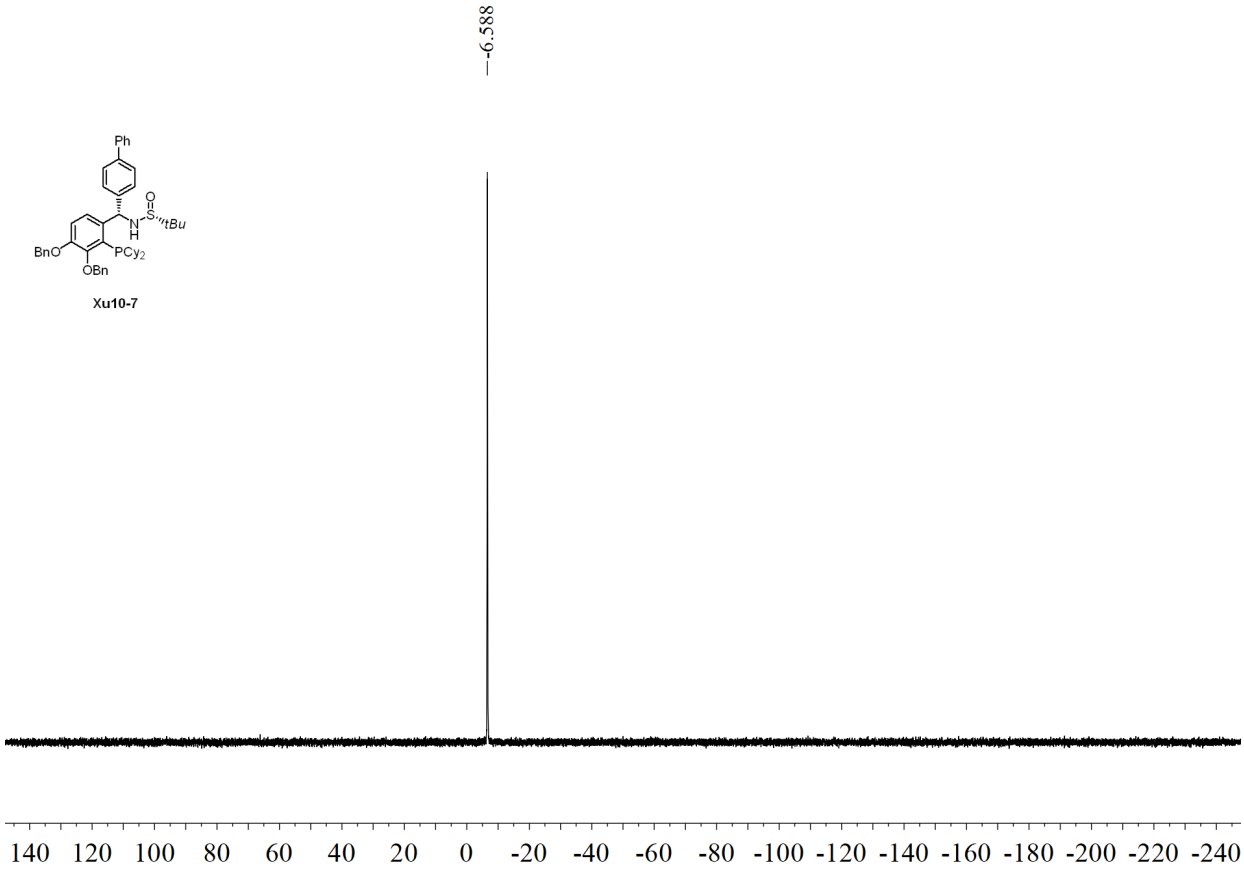
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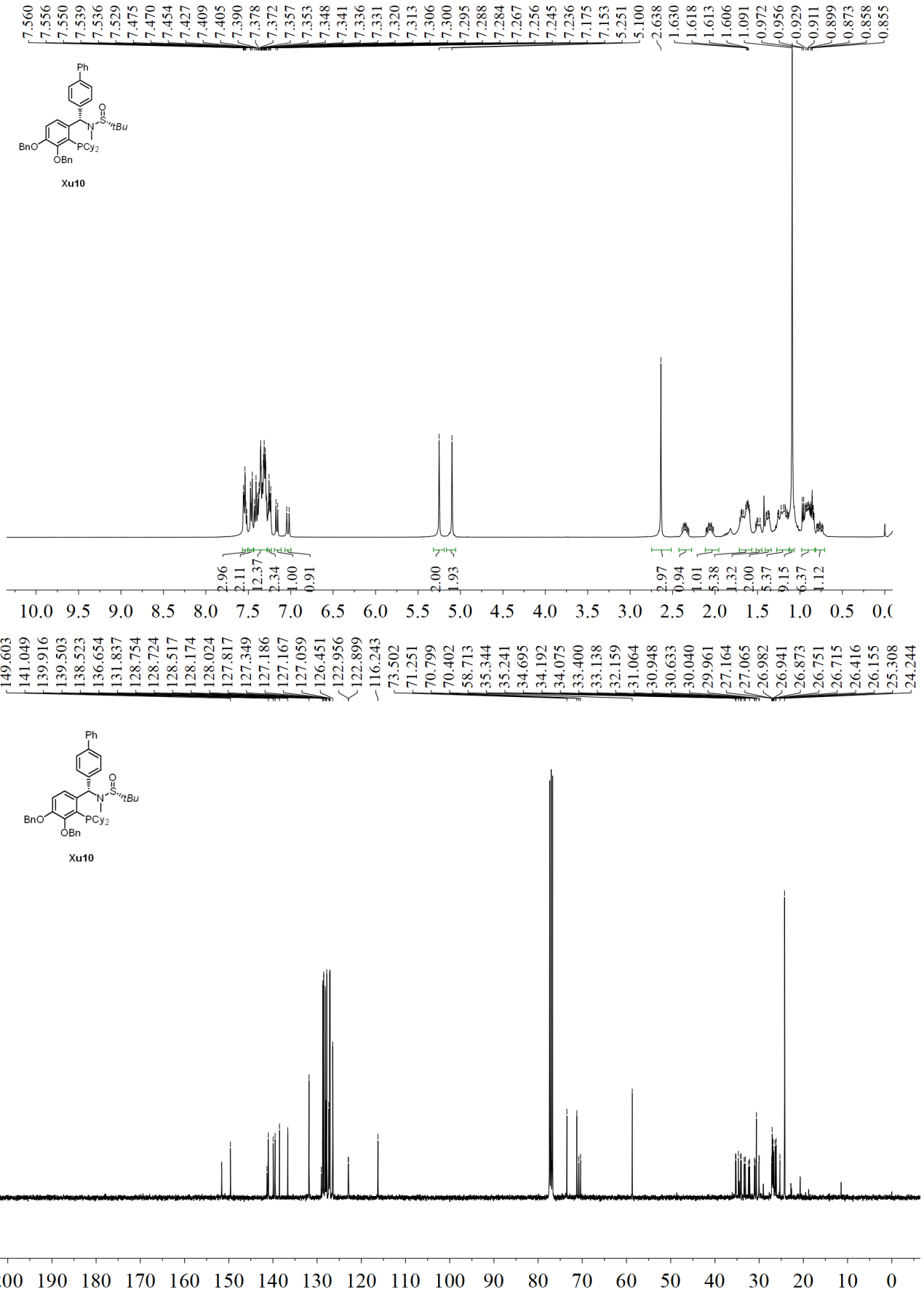
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S
tBu
N
BnO
PCy2
OBn
Xu10
2.96 2.11 12.37 2.34 1.00 0.91 2.00 1.93 2.97 0.94 1.01 5.38 1.32 2.00 5.37 9.15 6.37 1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
149.603 141.049 139.916 139.503 138.523 136.654 131.837 128.754 128.724 128.517 128.174 128.024 127.817 127.349 127.186 127.167 127.059 126.451 122.956 122.899 116.243 73.502 71.251 70.799 70.402 58.713 35.344 35.241 34.695 34.192 34.075 33.400 33.138 32.159 31.064 30.948 30.633 30.040 29.961 27.164 27.065 26.982 26.941 26.873 26.751 26.715 26.416 26.155 25.308 24.244
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PCy2
OBn
Xu10
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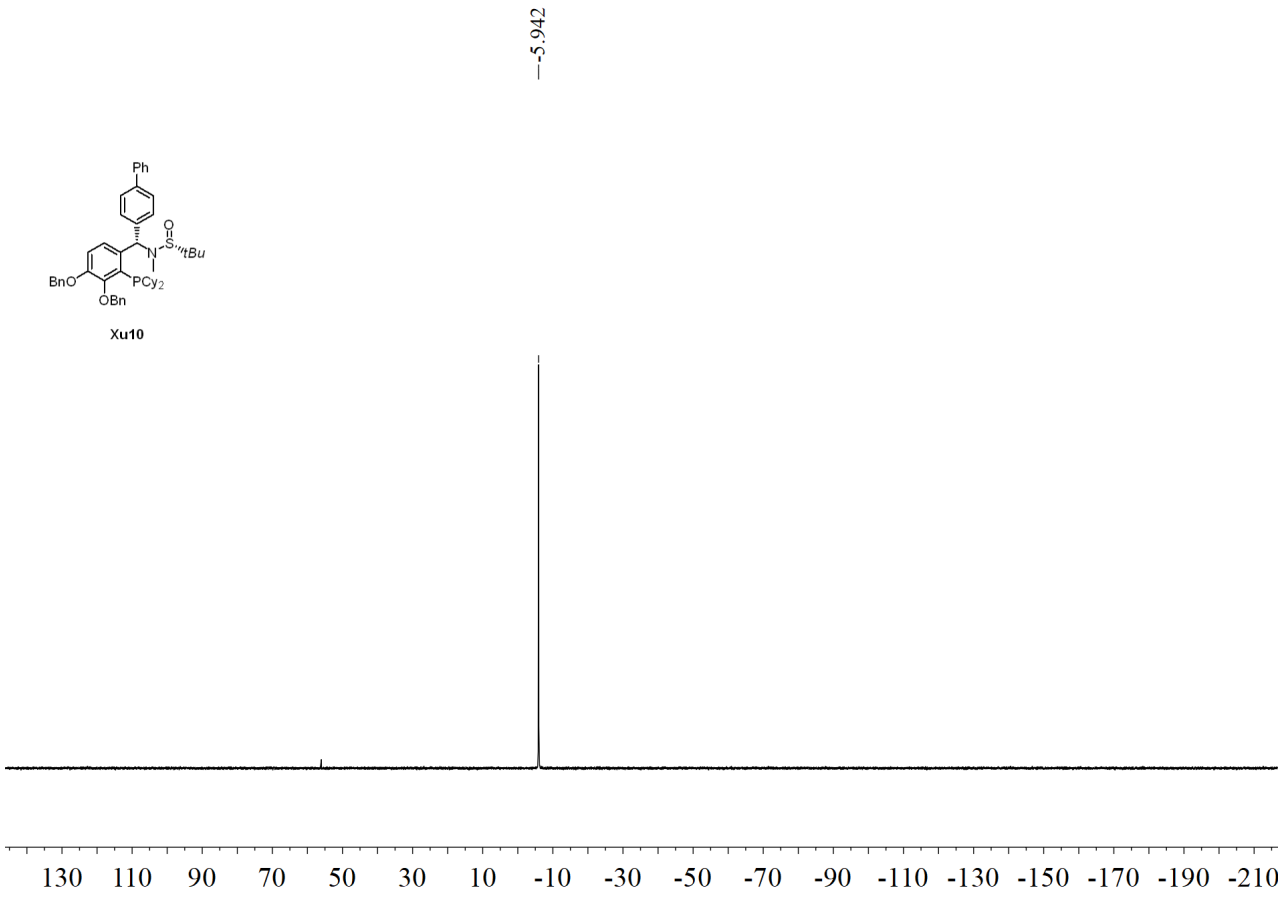
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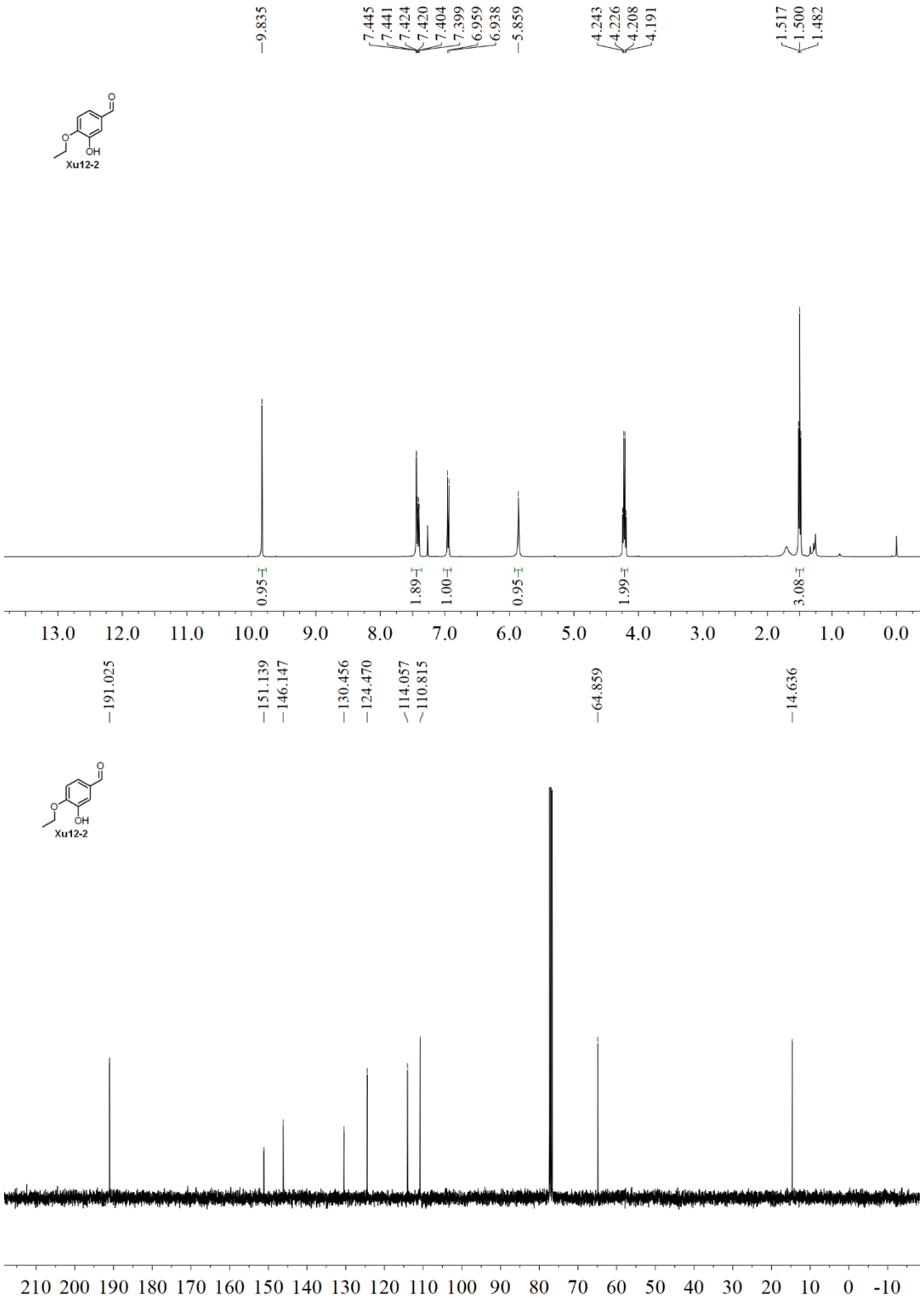
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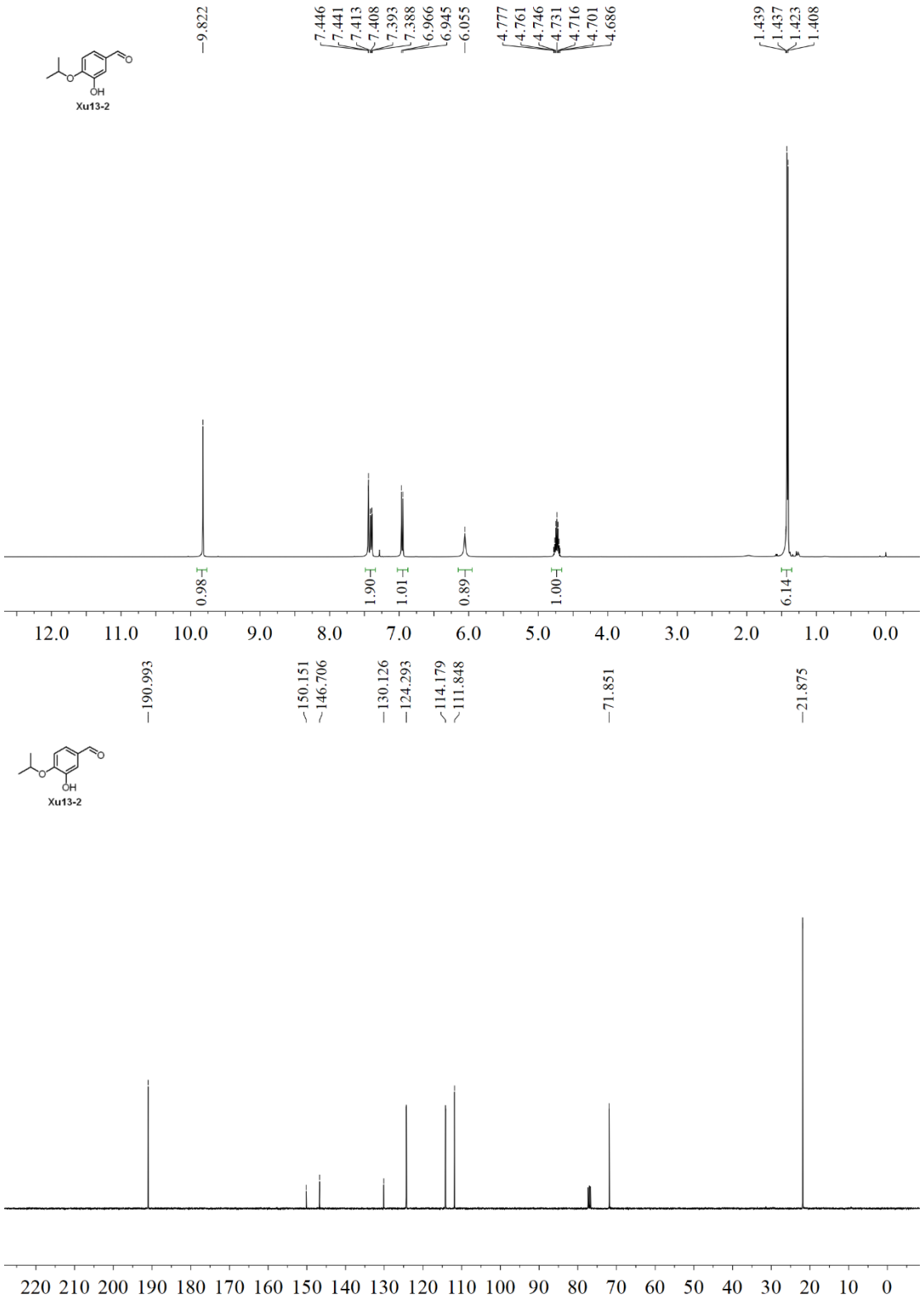
Xu12-2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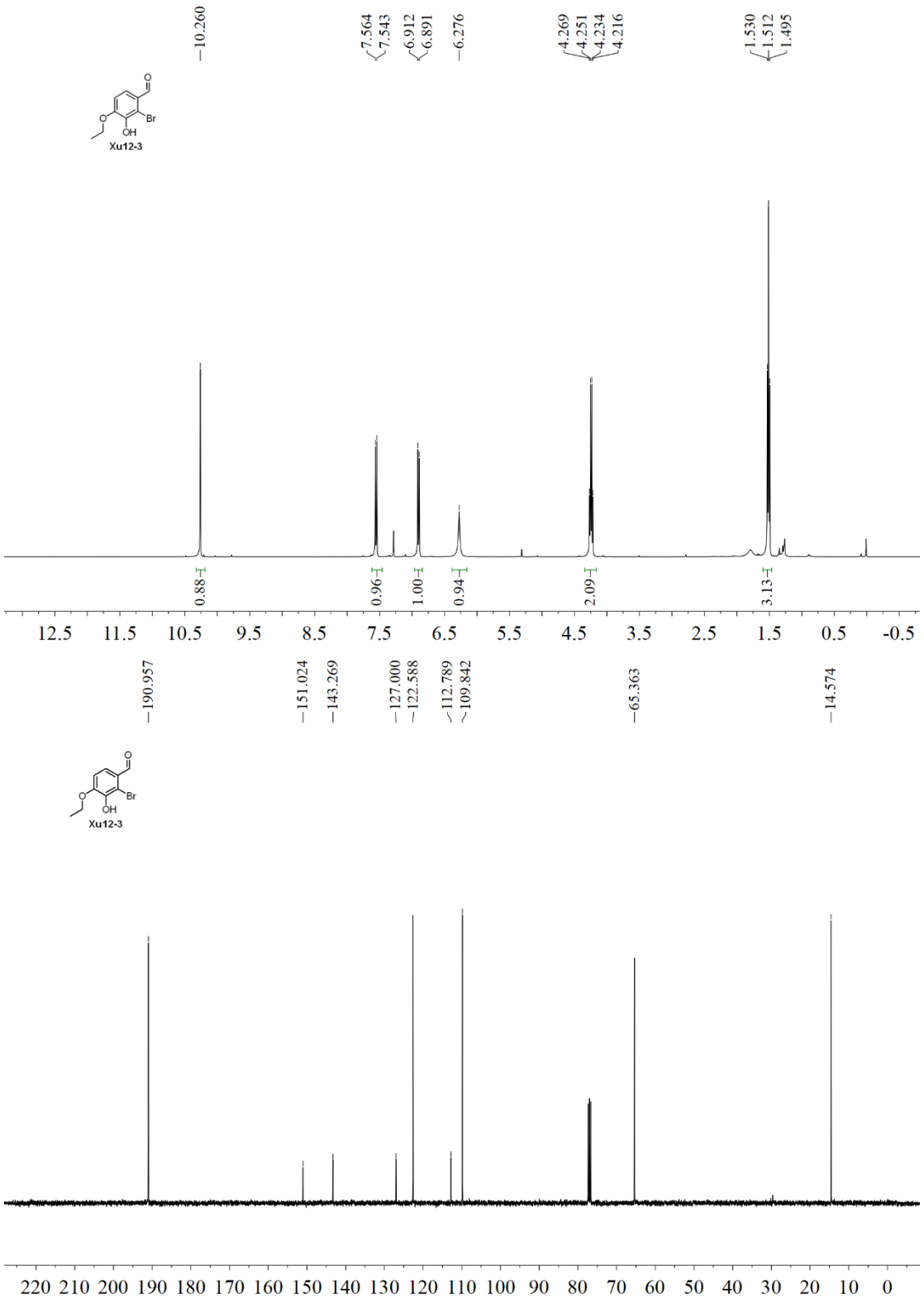
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3.13
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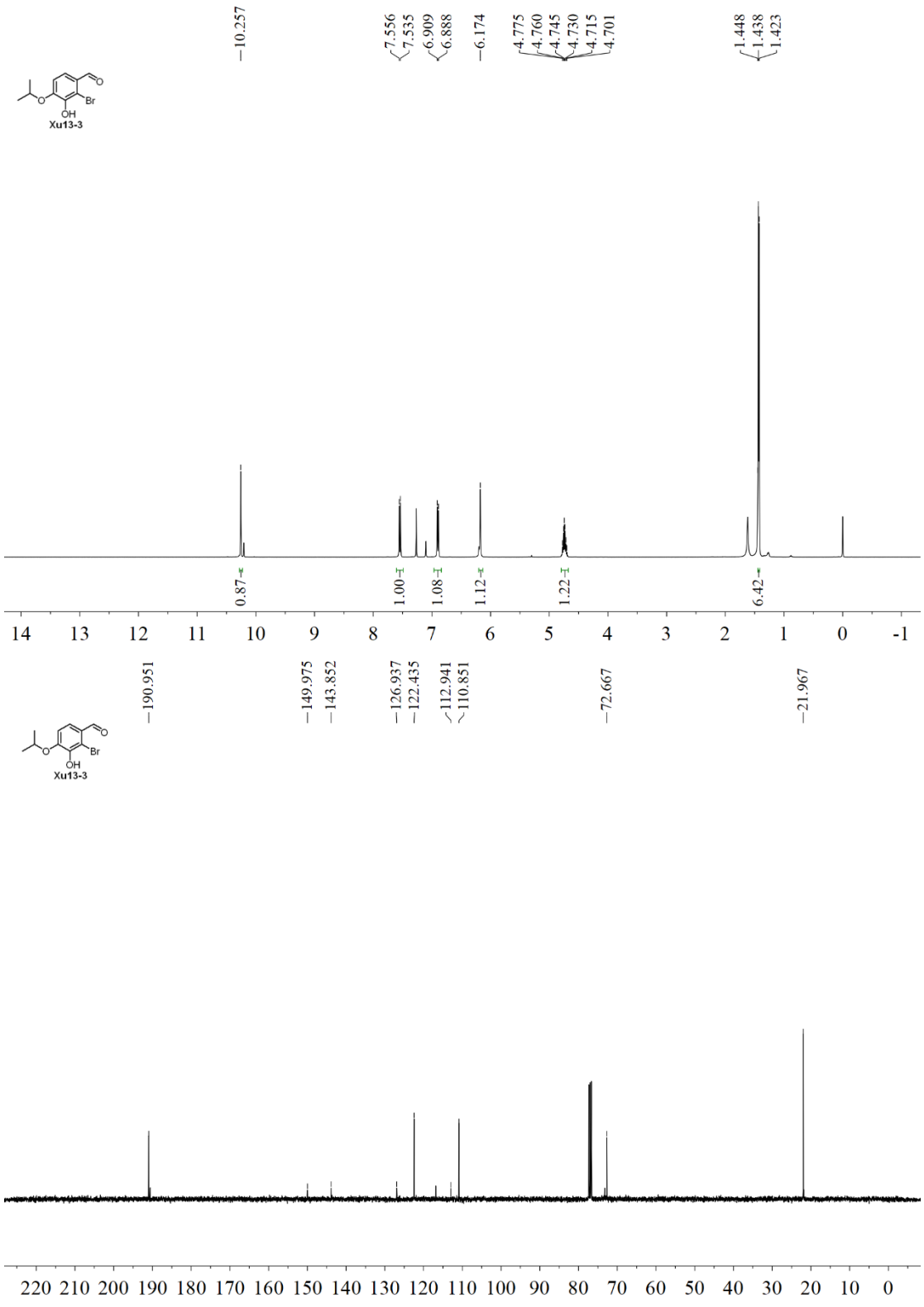
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1.438
1.423
Br
OH
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1.12
1.22
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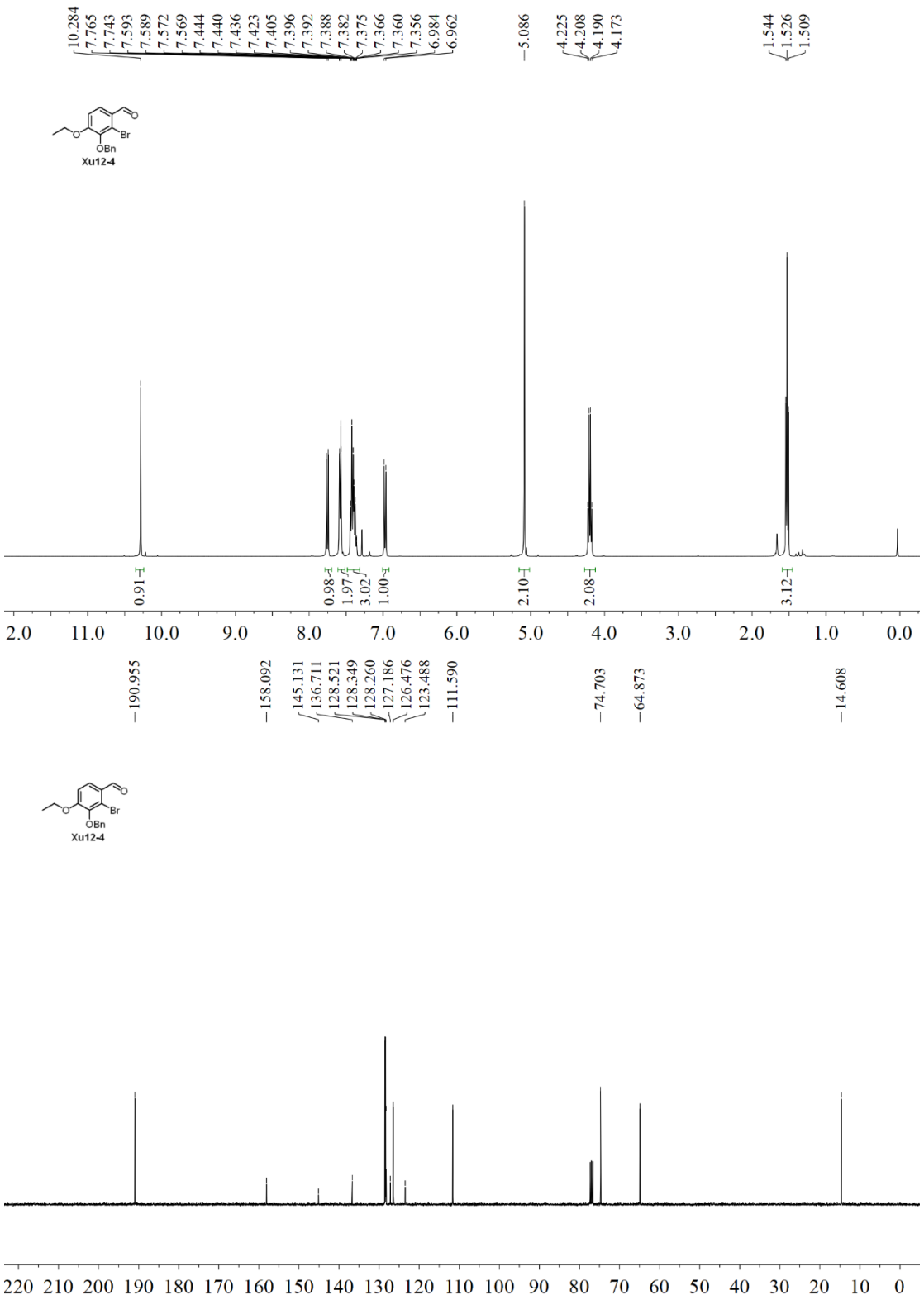
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4.208
4.190
4.173
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1.526
1.509
Br
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1.00
2.10
2.08
3.12
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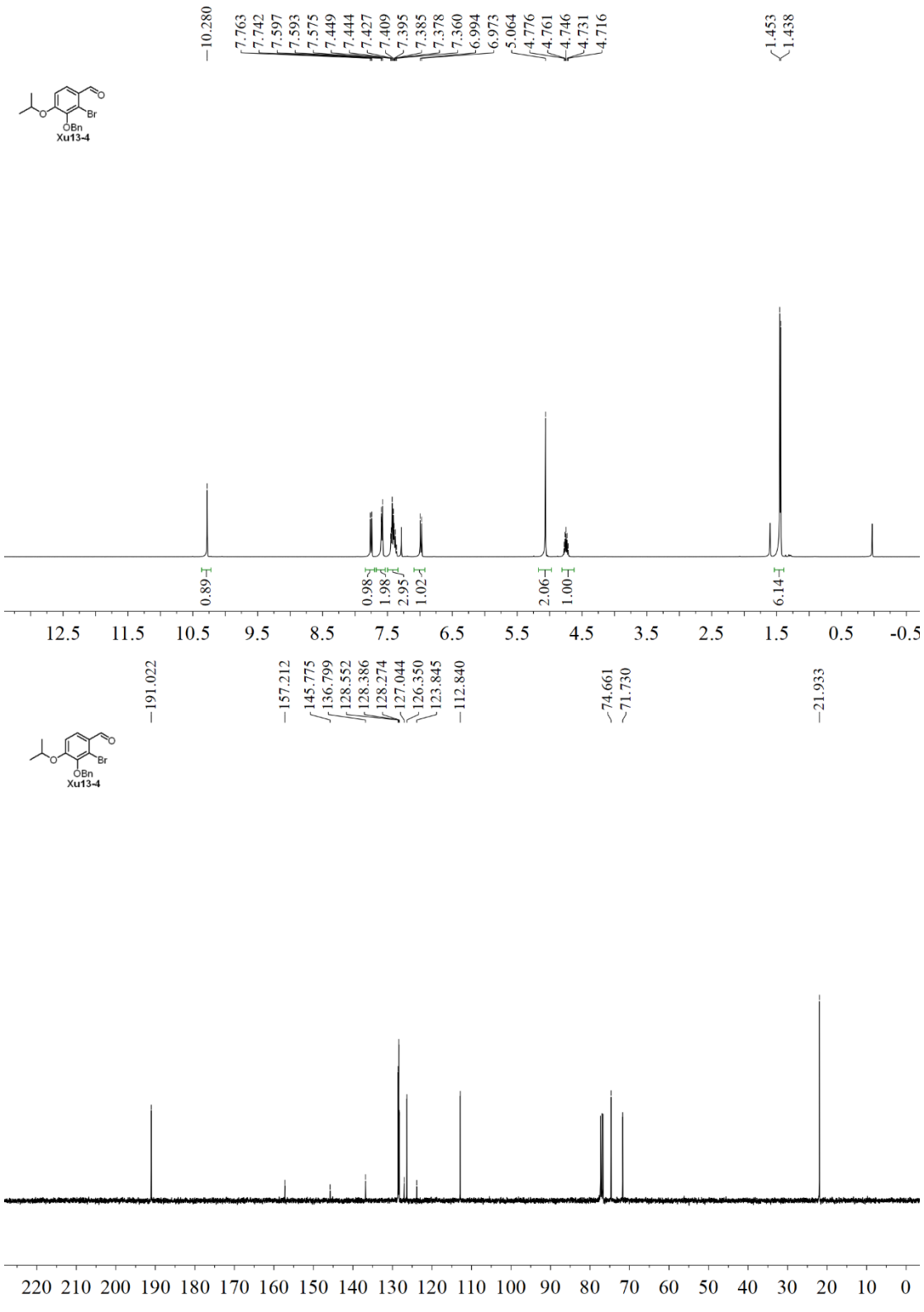
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1.438
Br
OBn
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2.06
1.00
6.14
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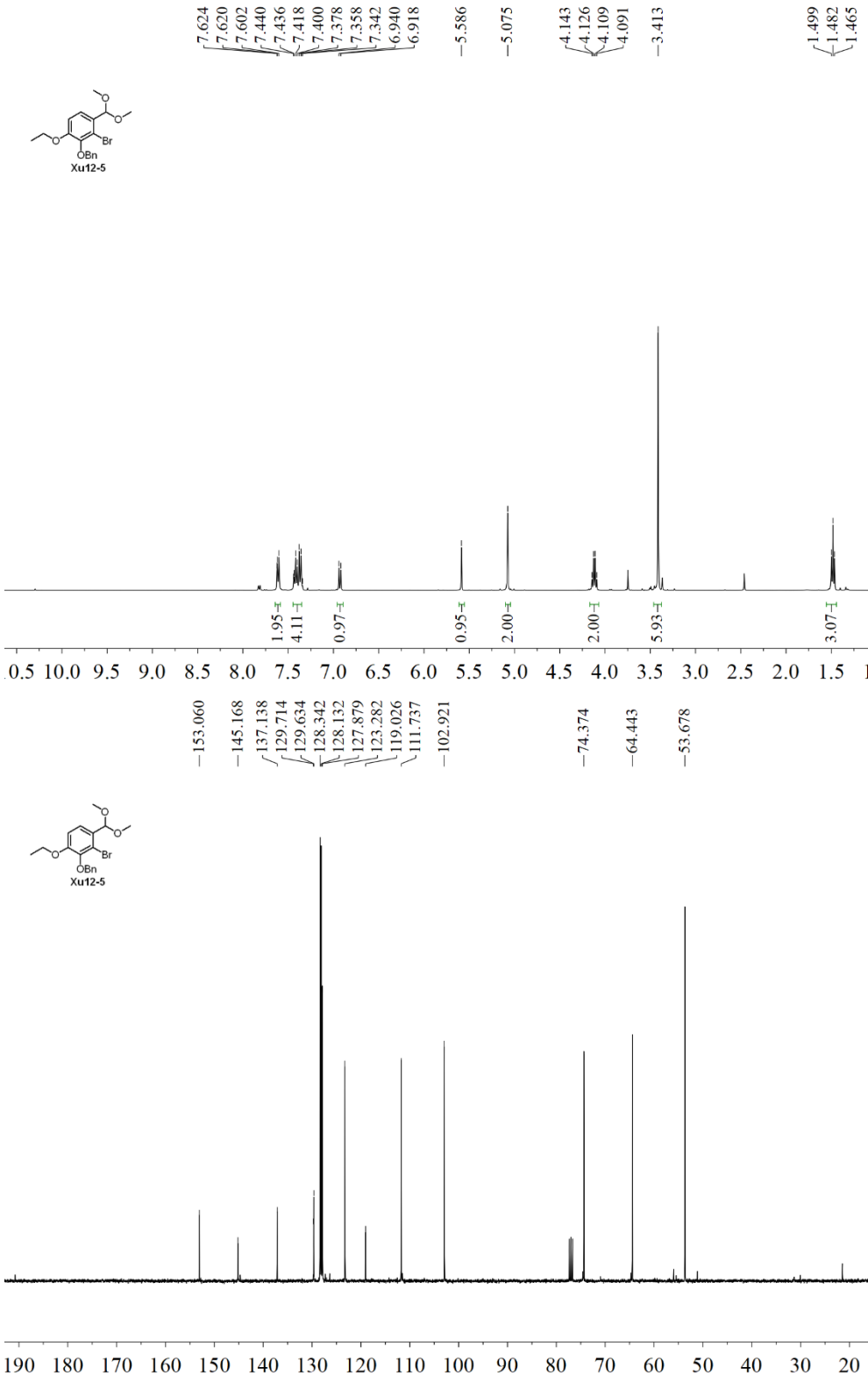
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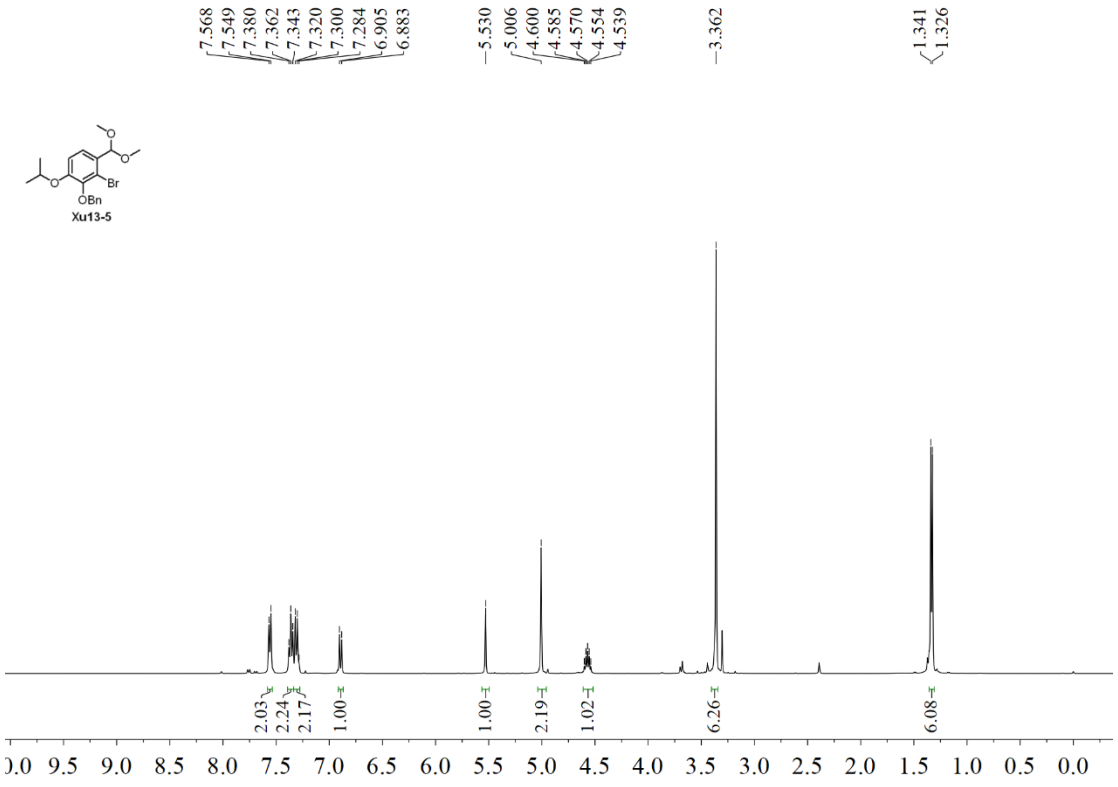
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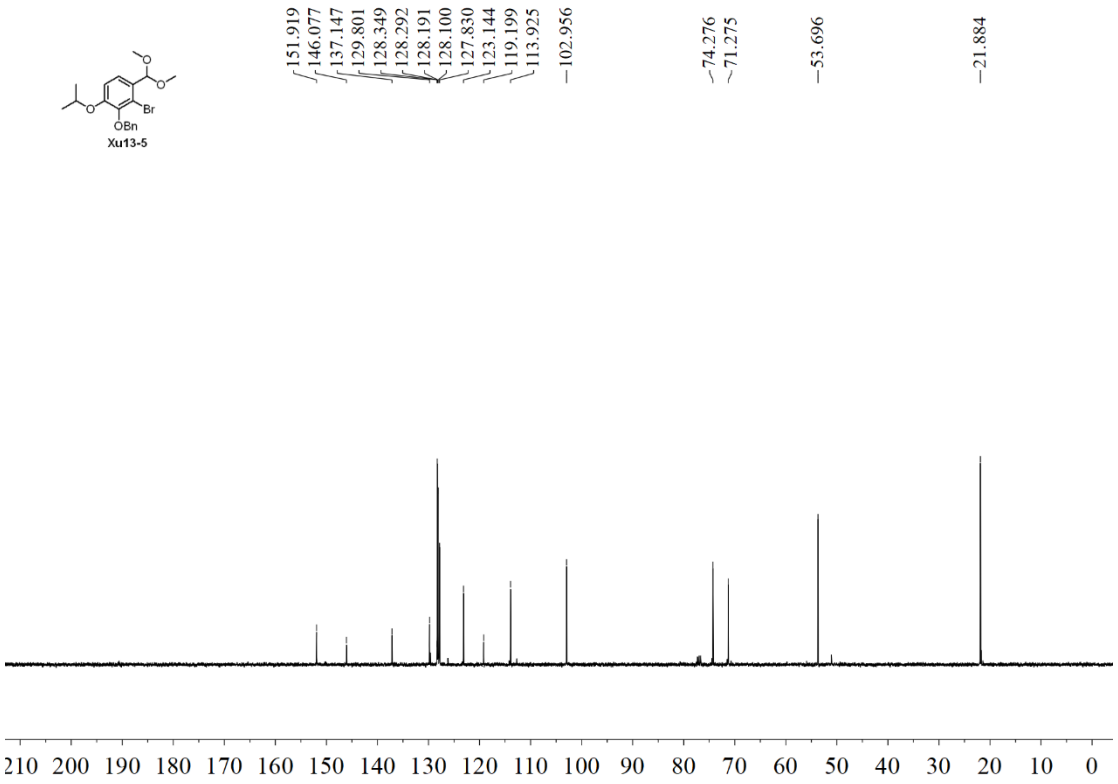
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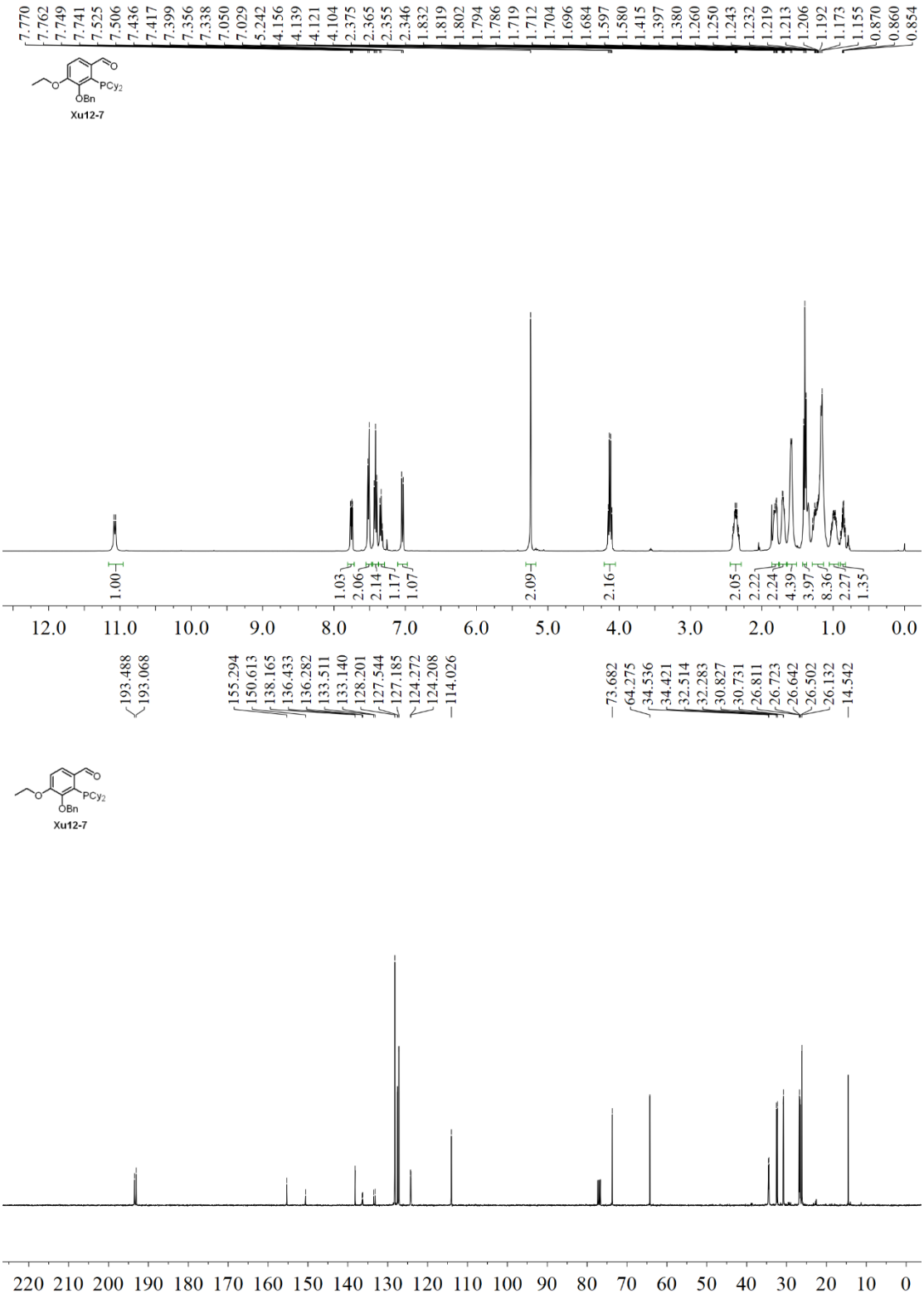
Xu13-5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Xu12-7
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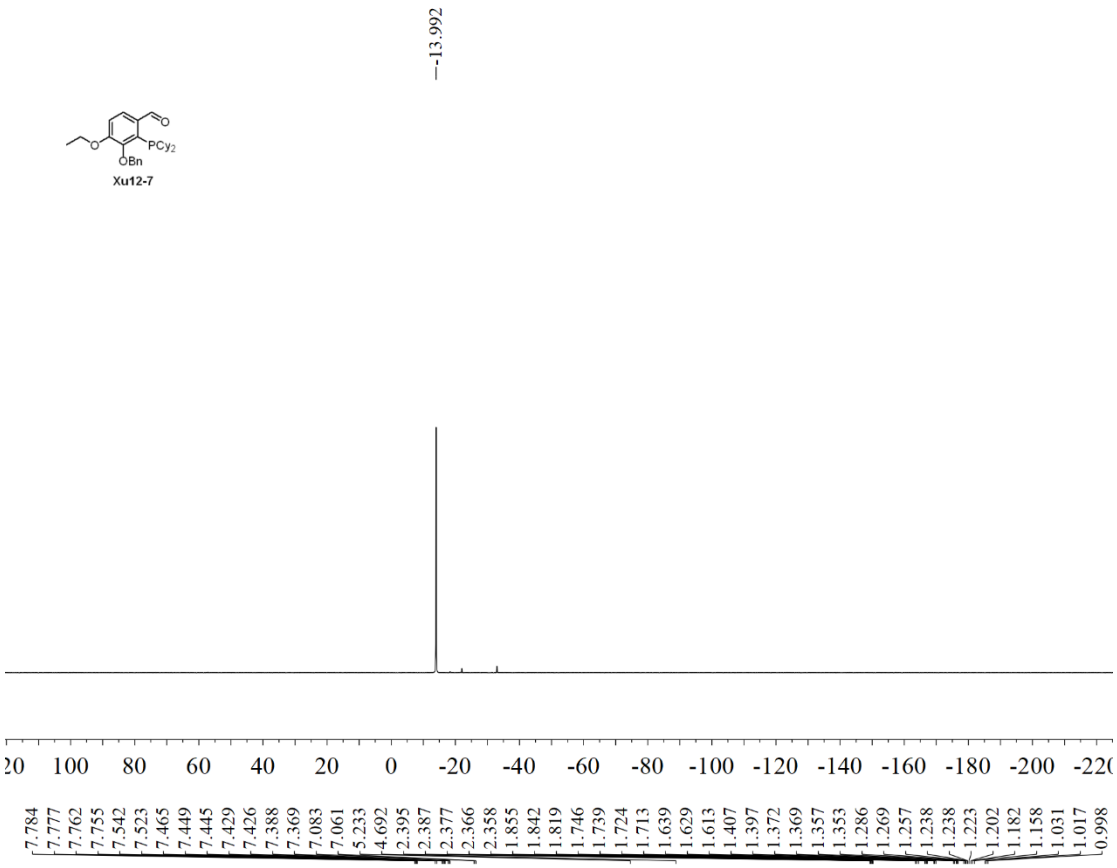
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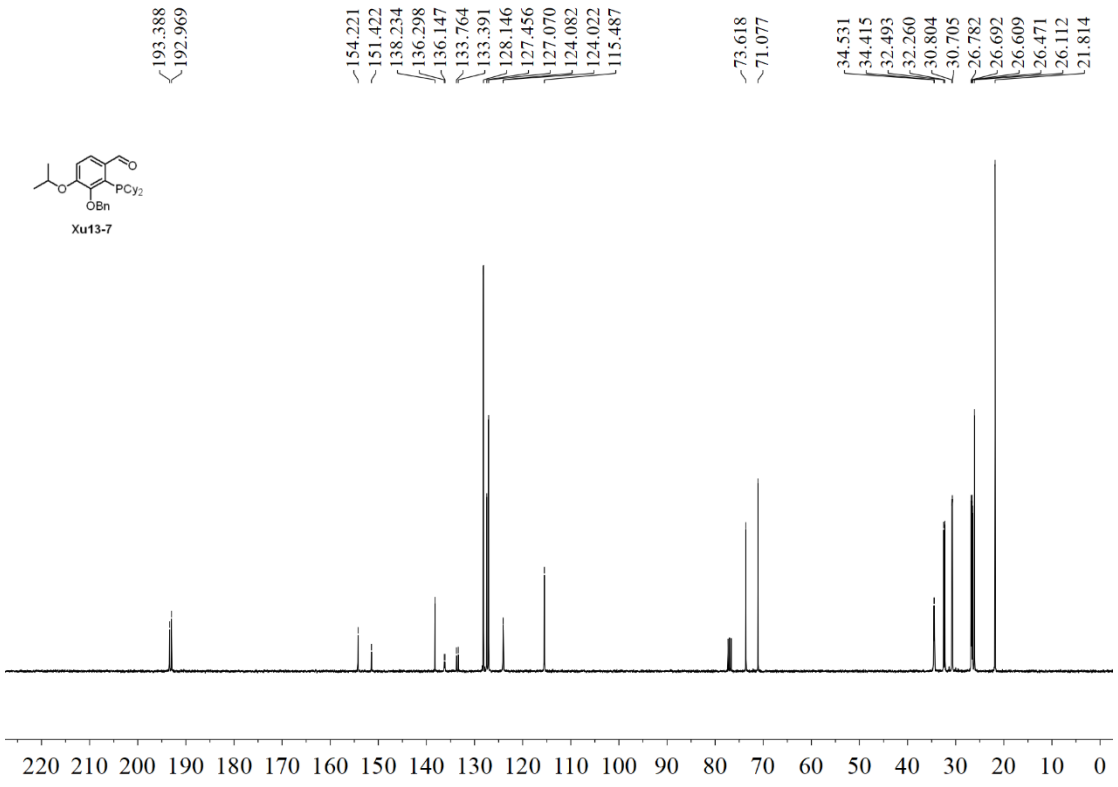
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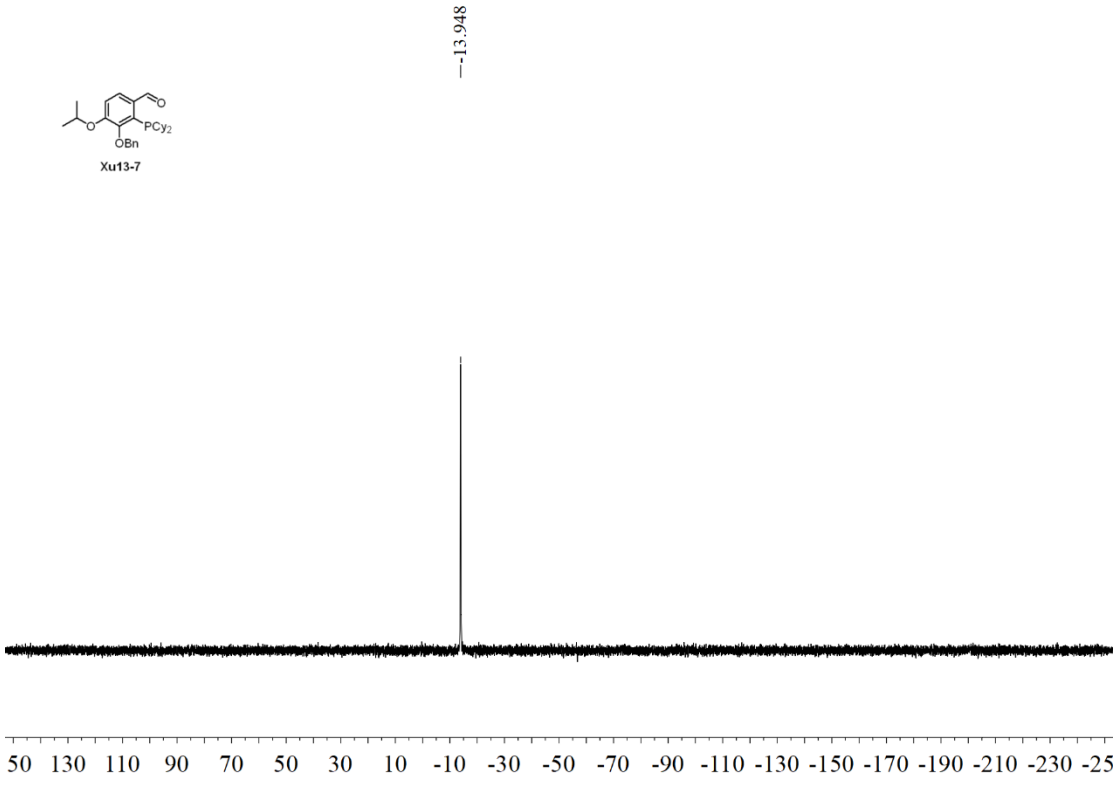
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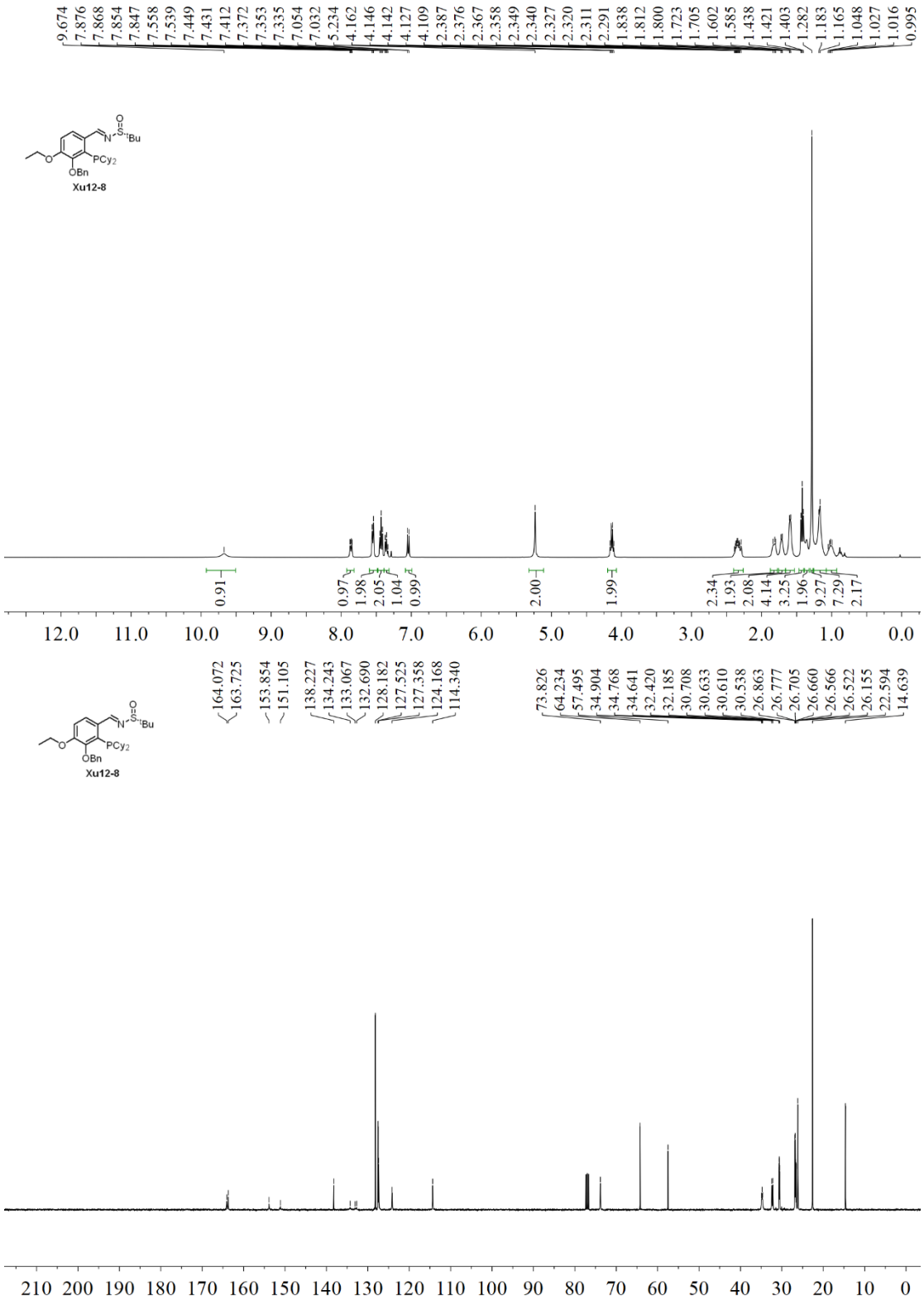
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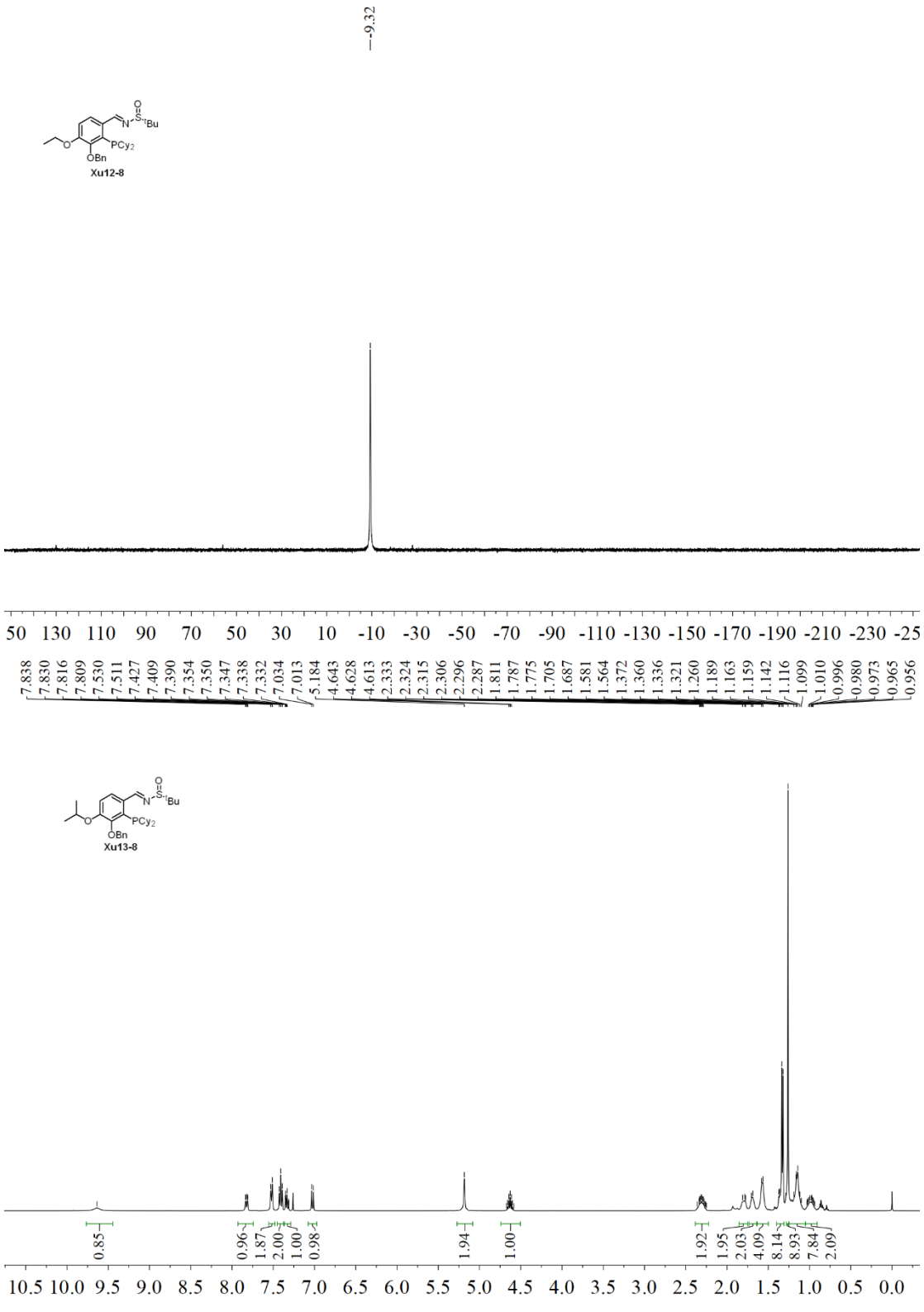
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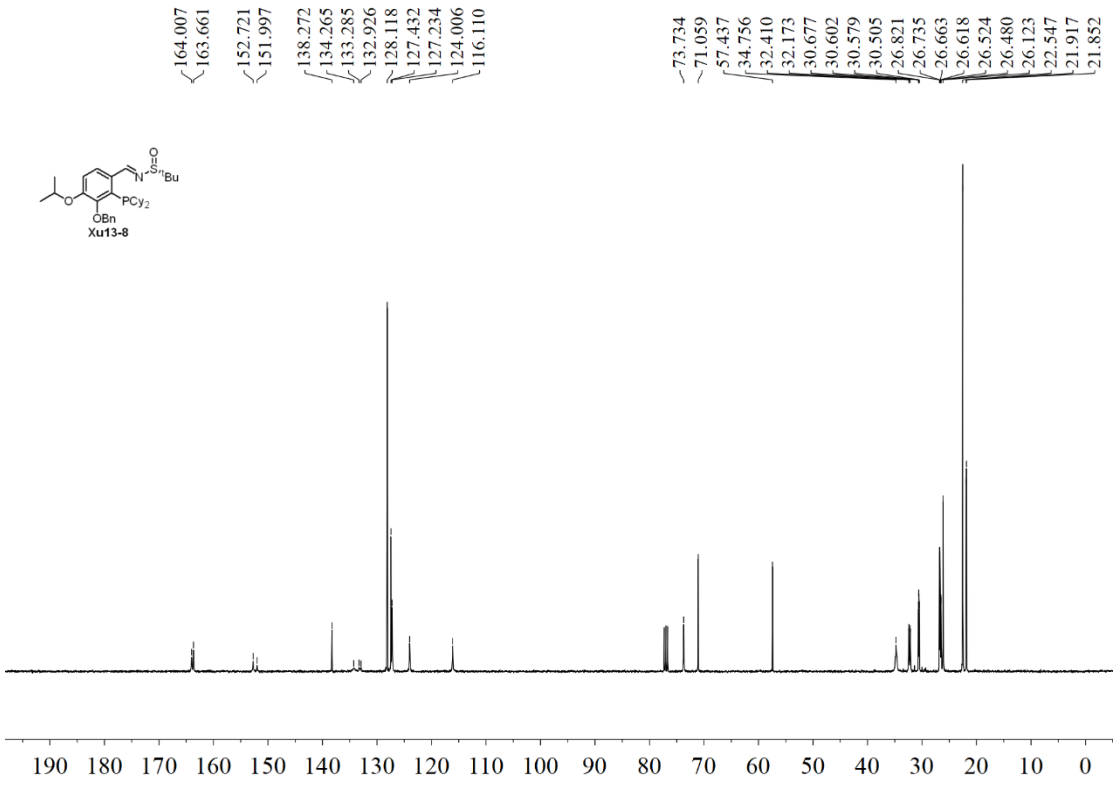
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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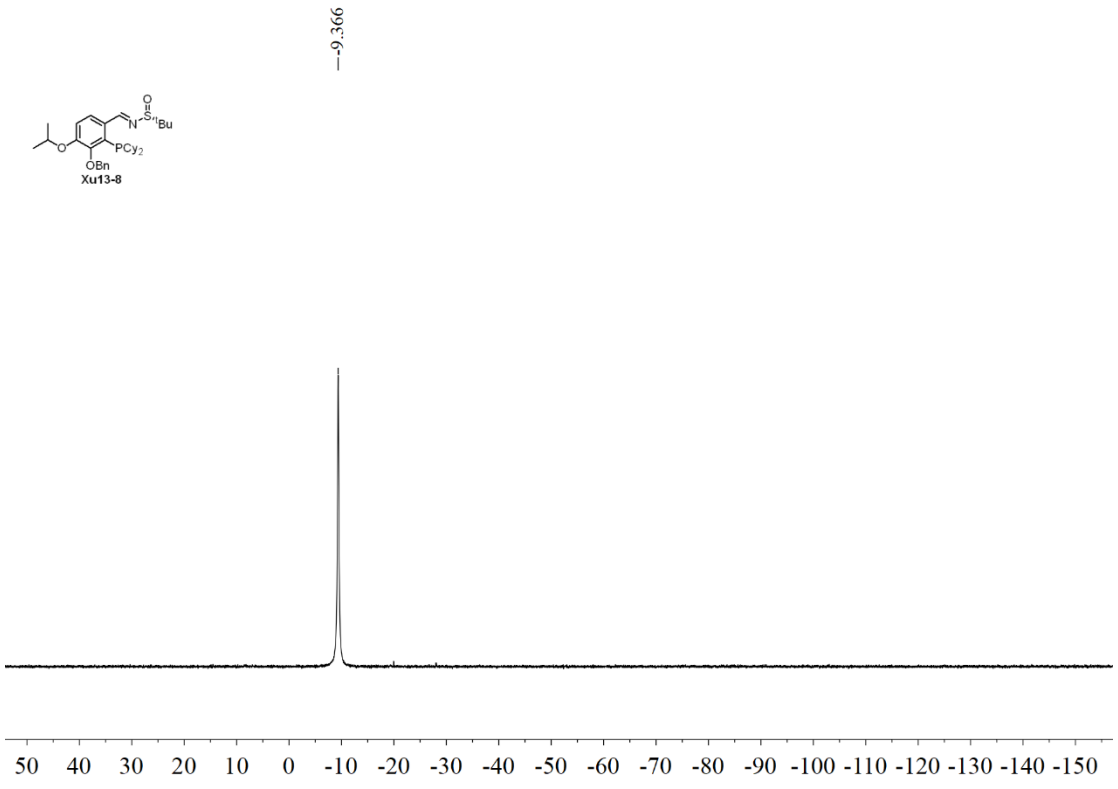
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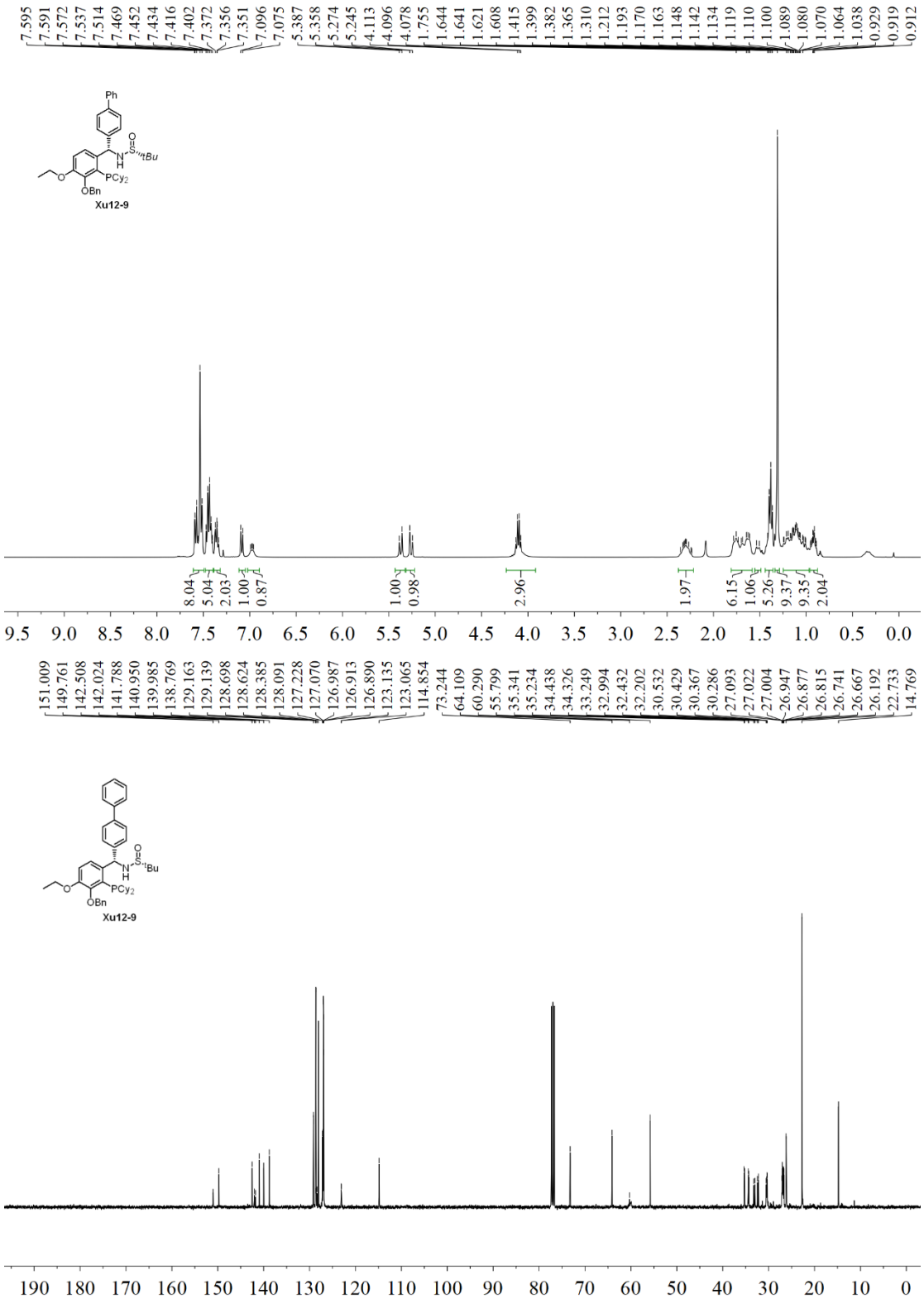
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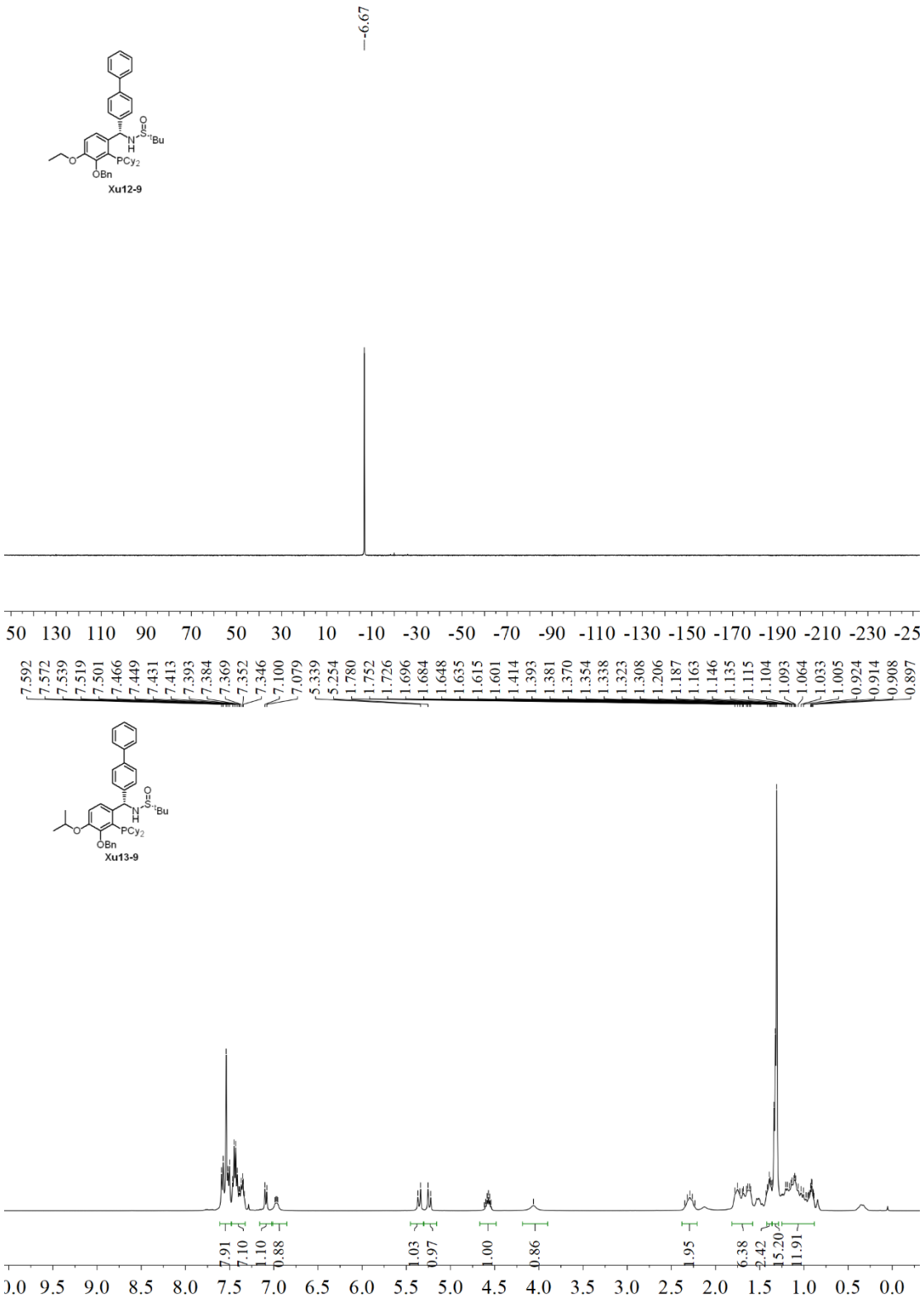
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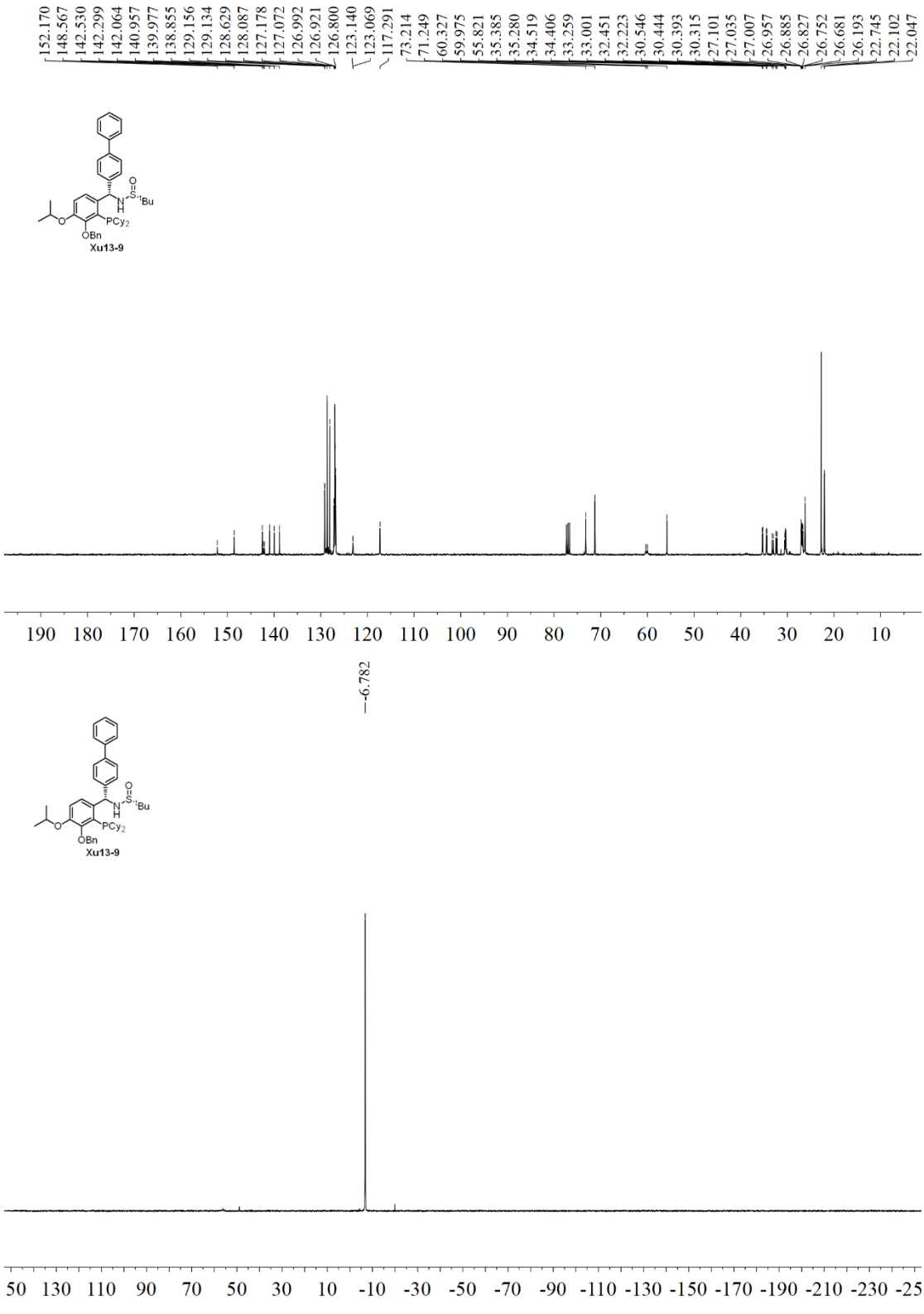
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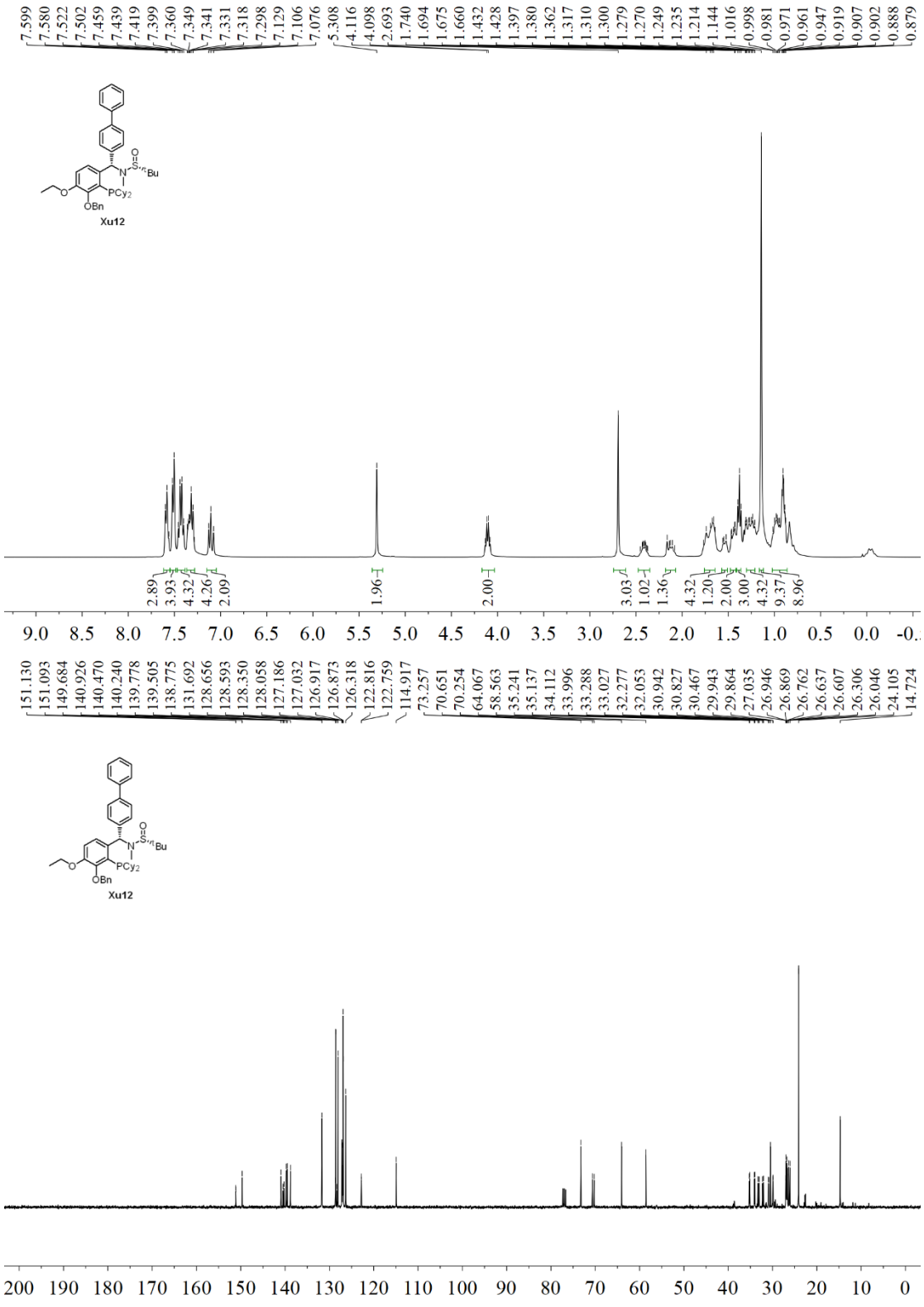
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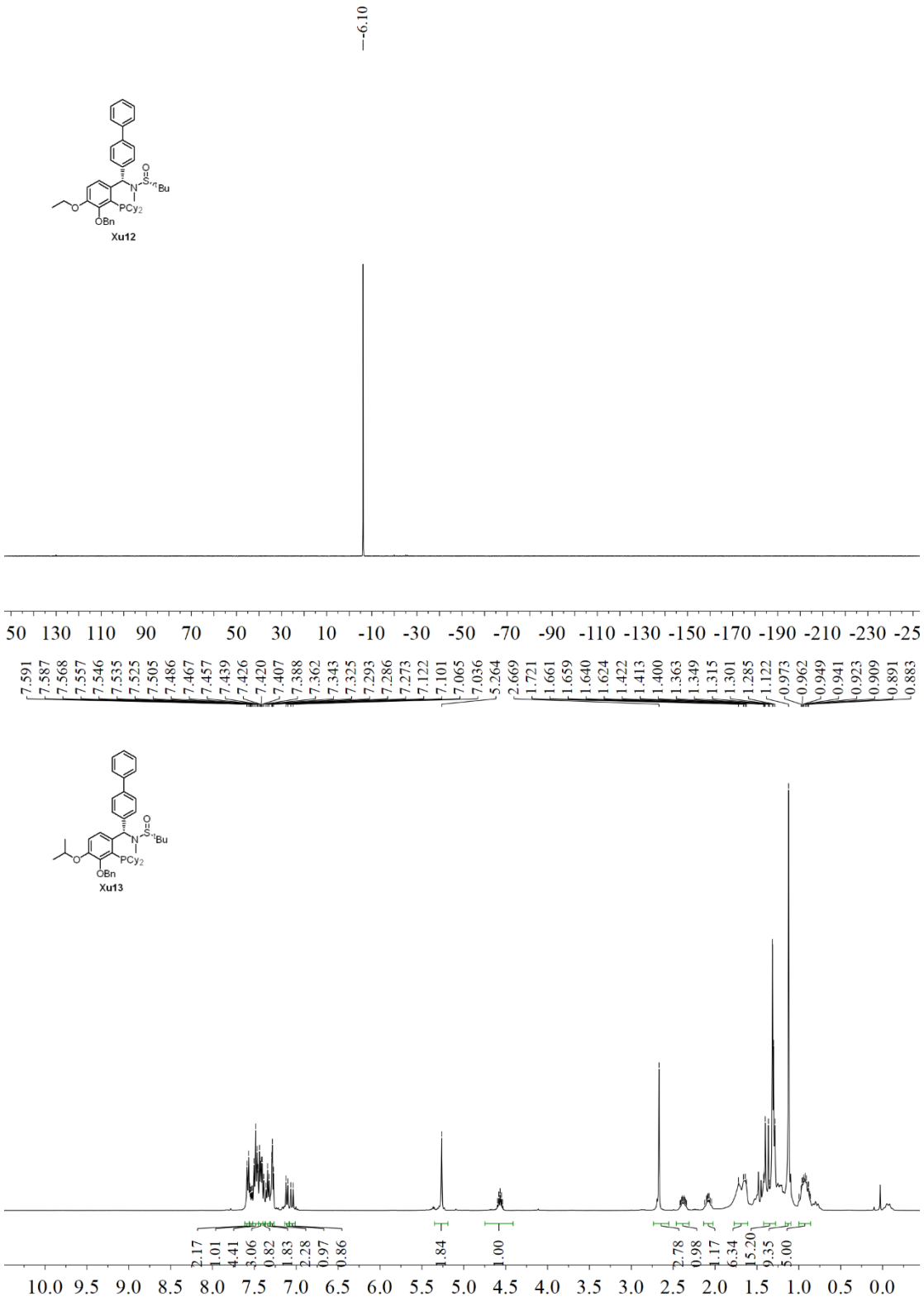
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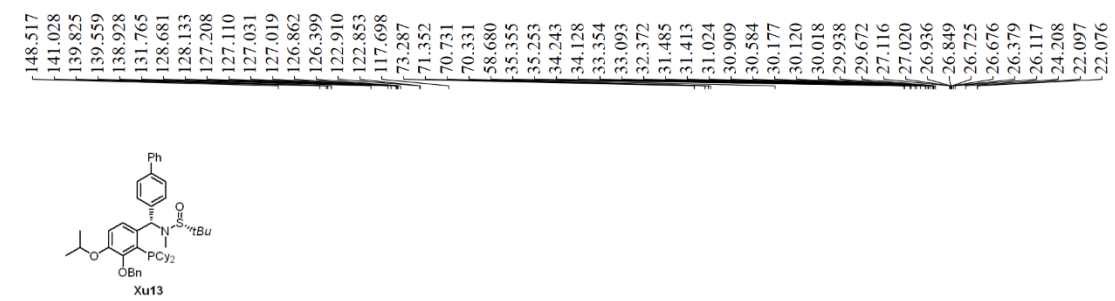
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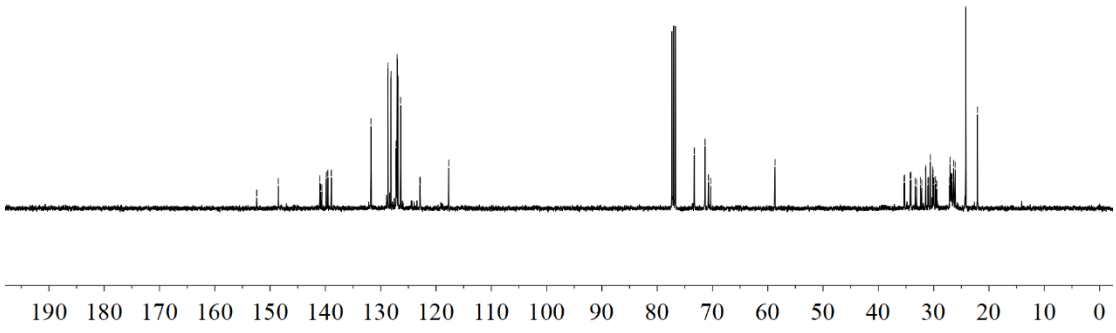
Xu13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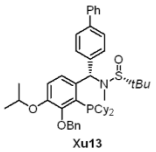
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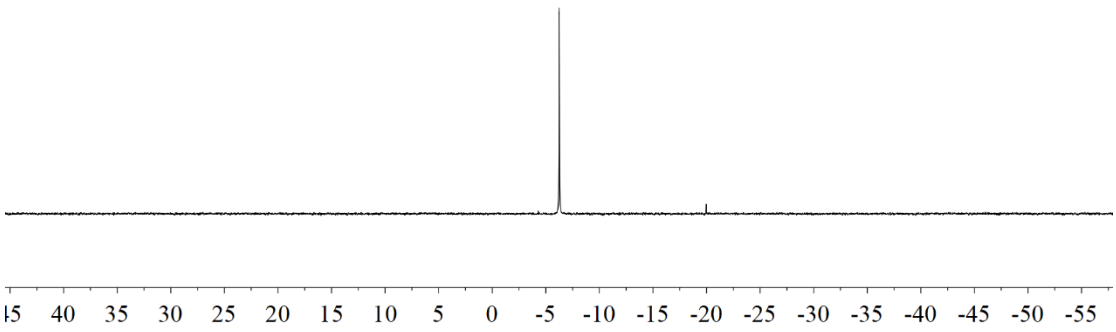
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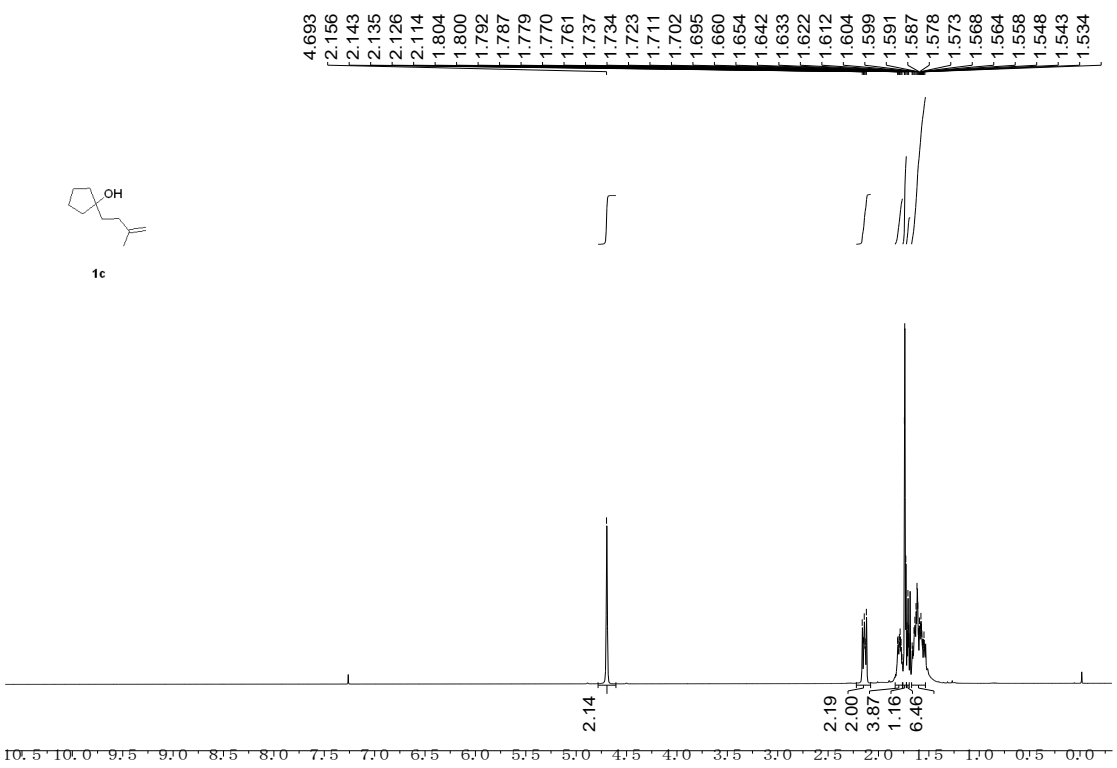
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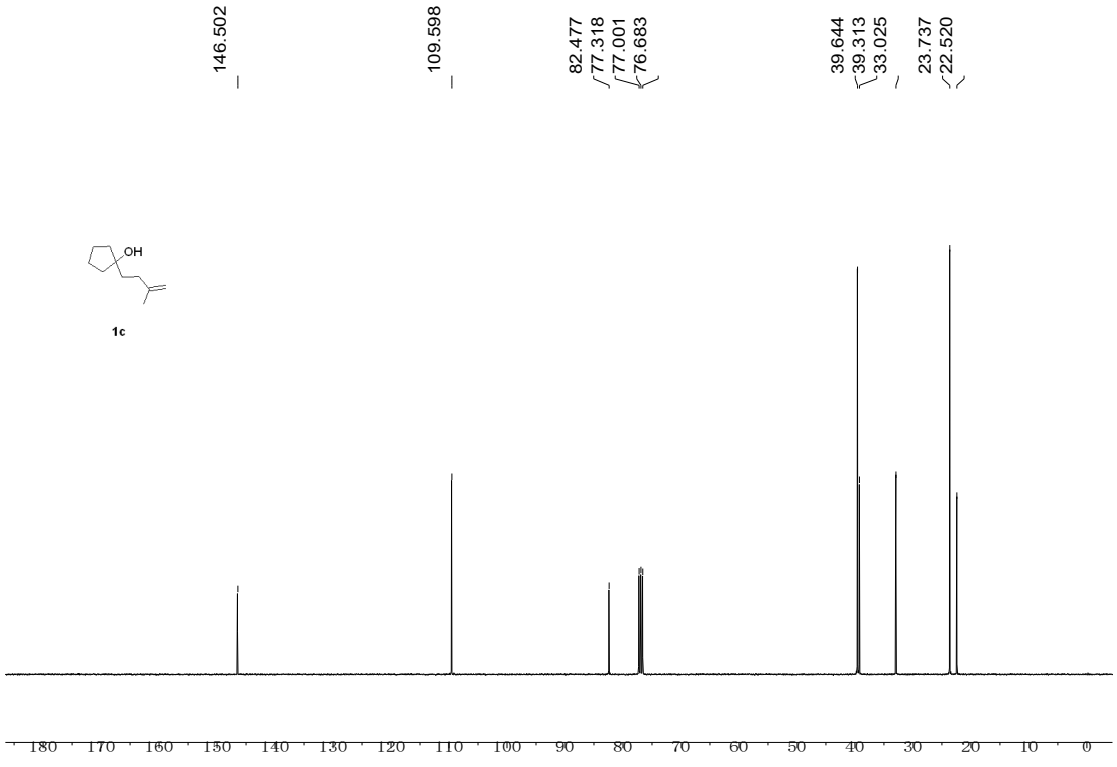
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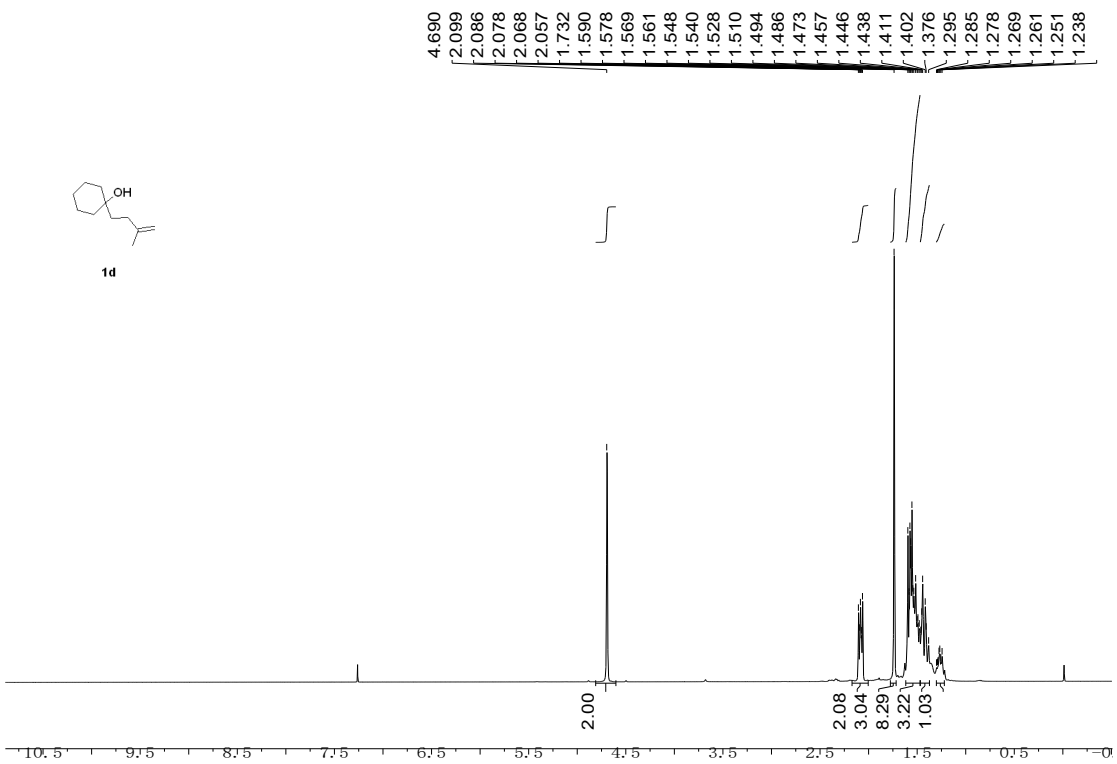
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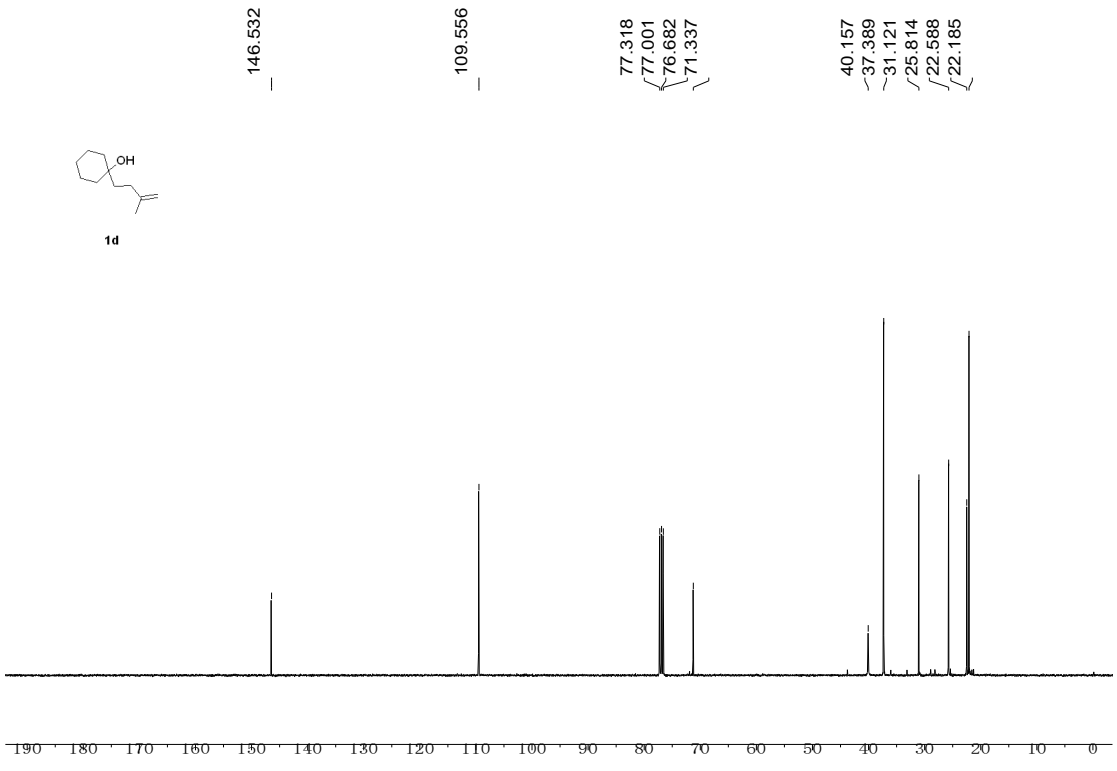
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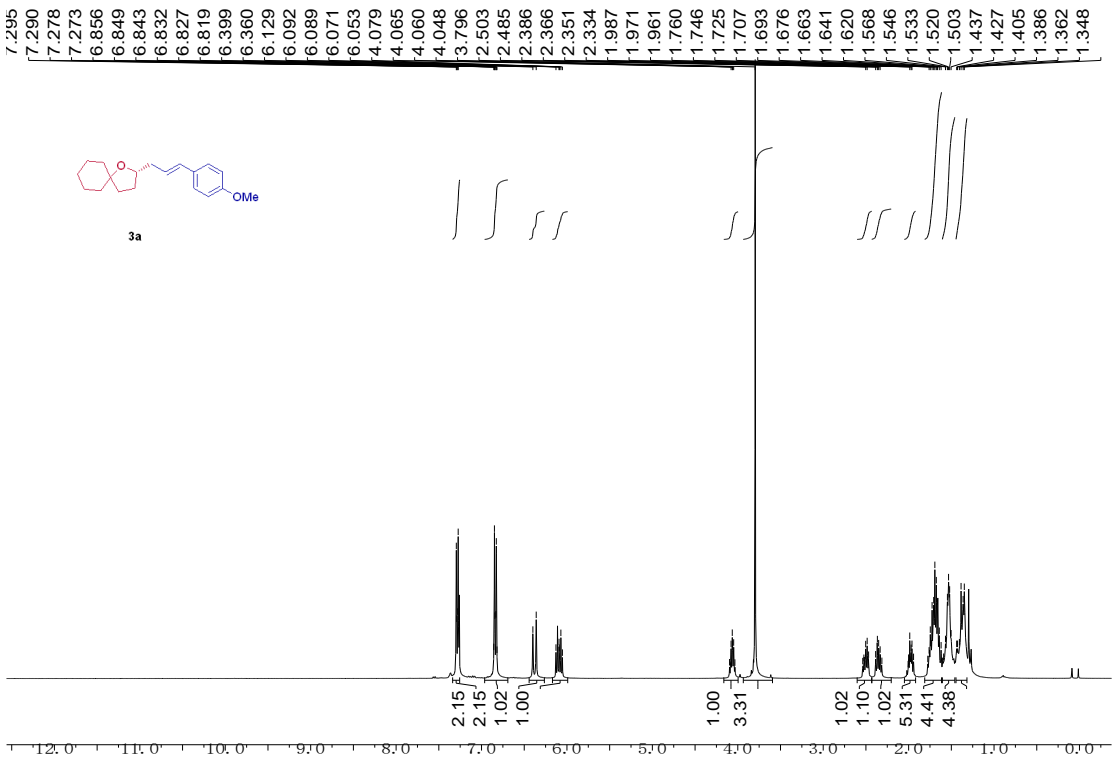
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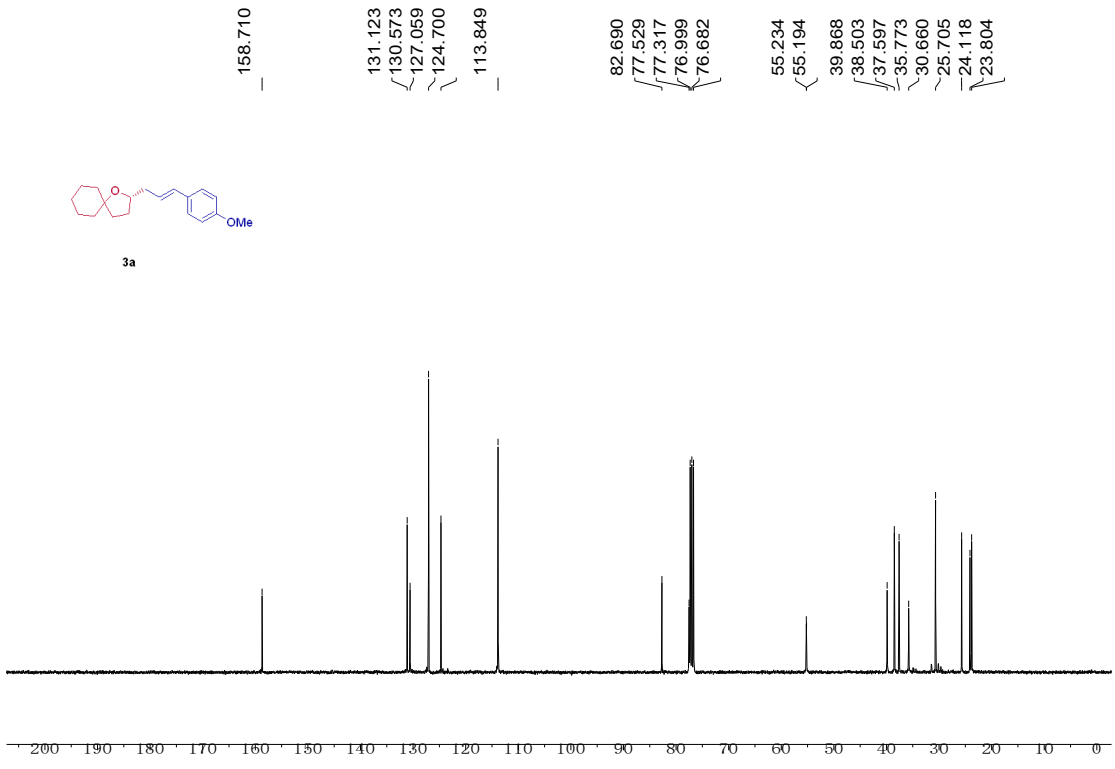
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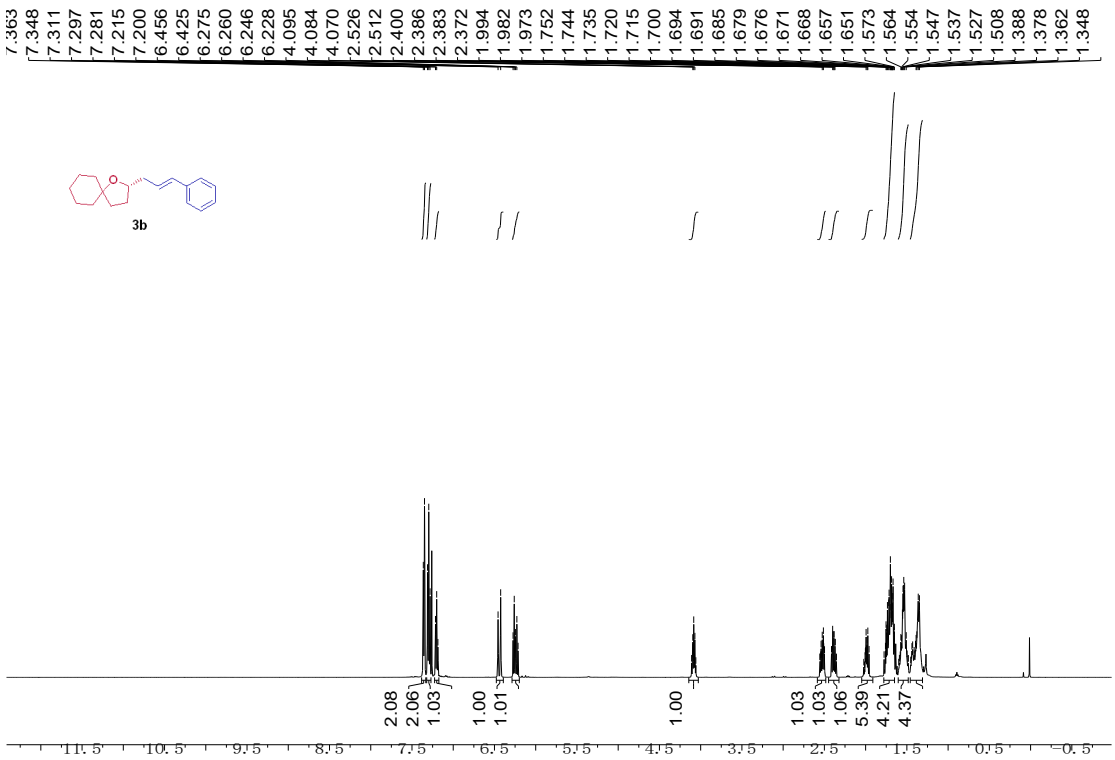
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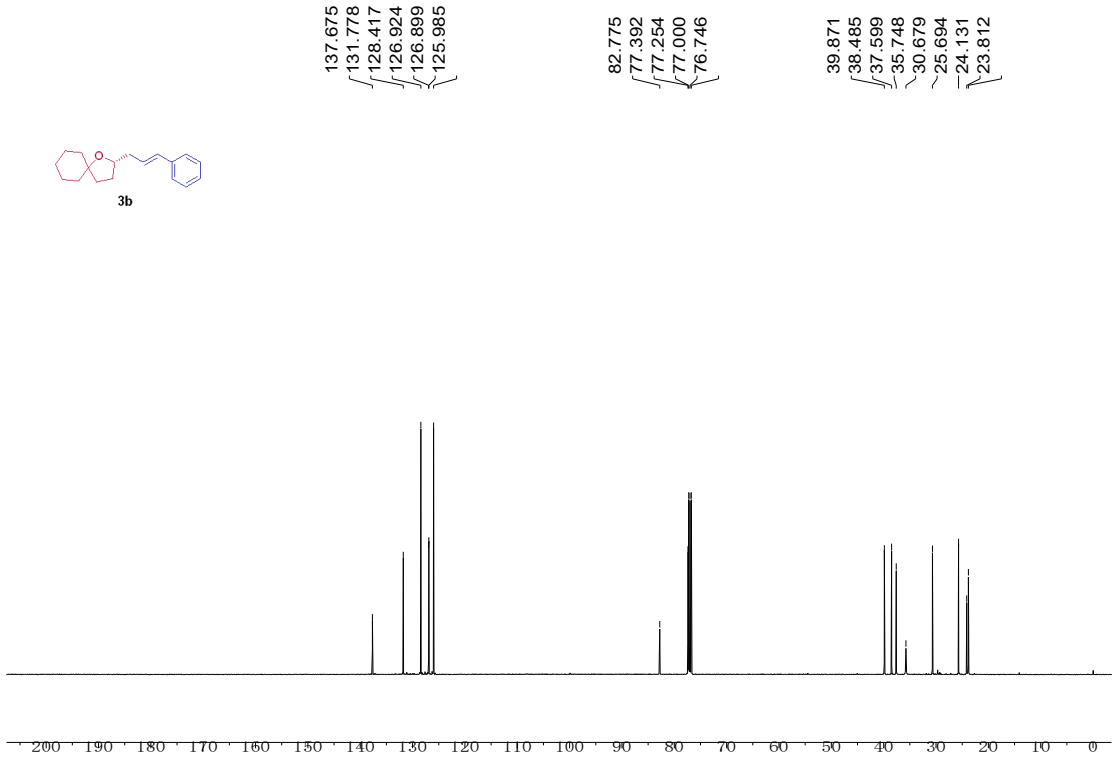
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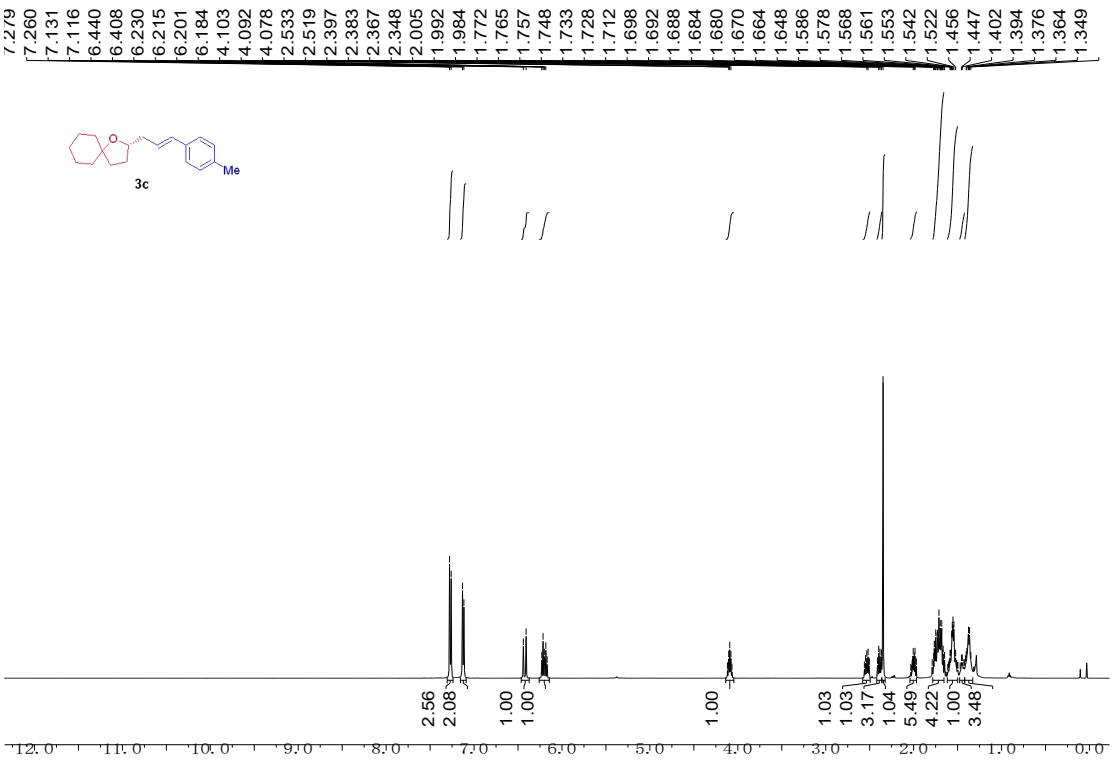
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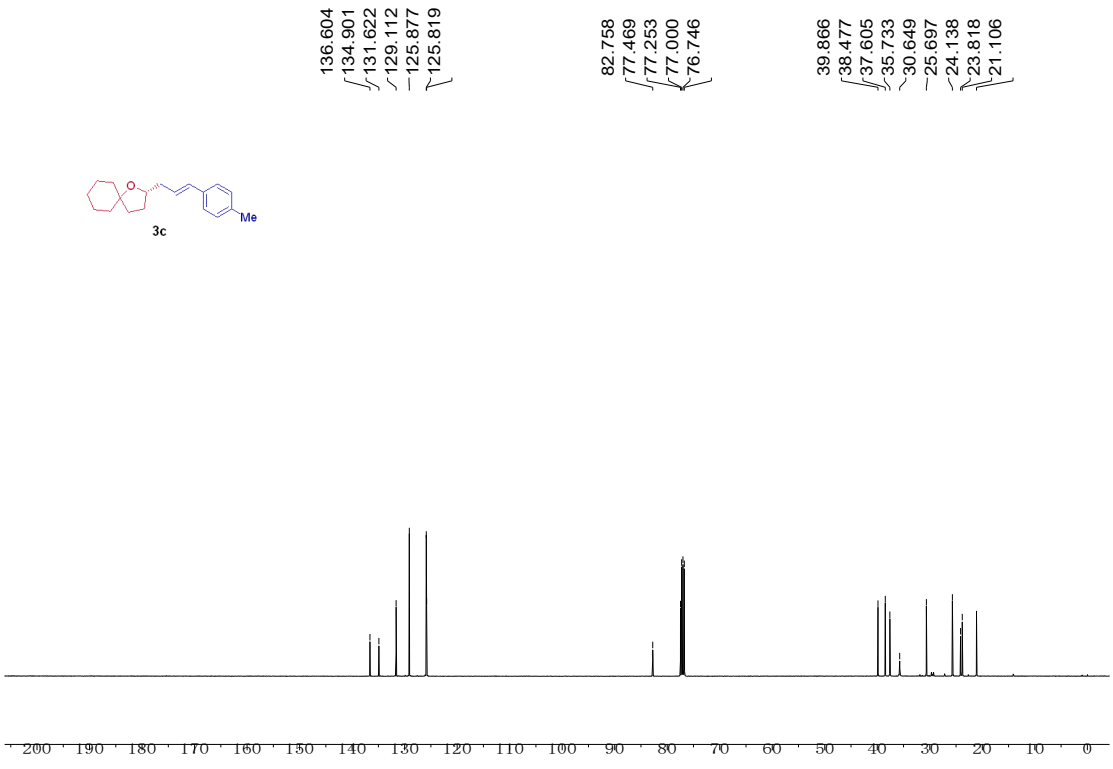
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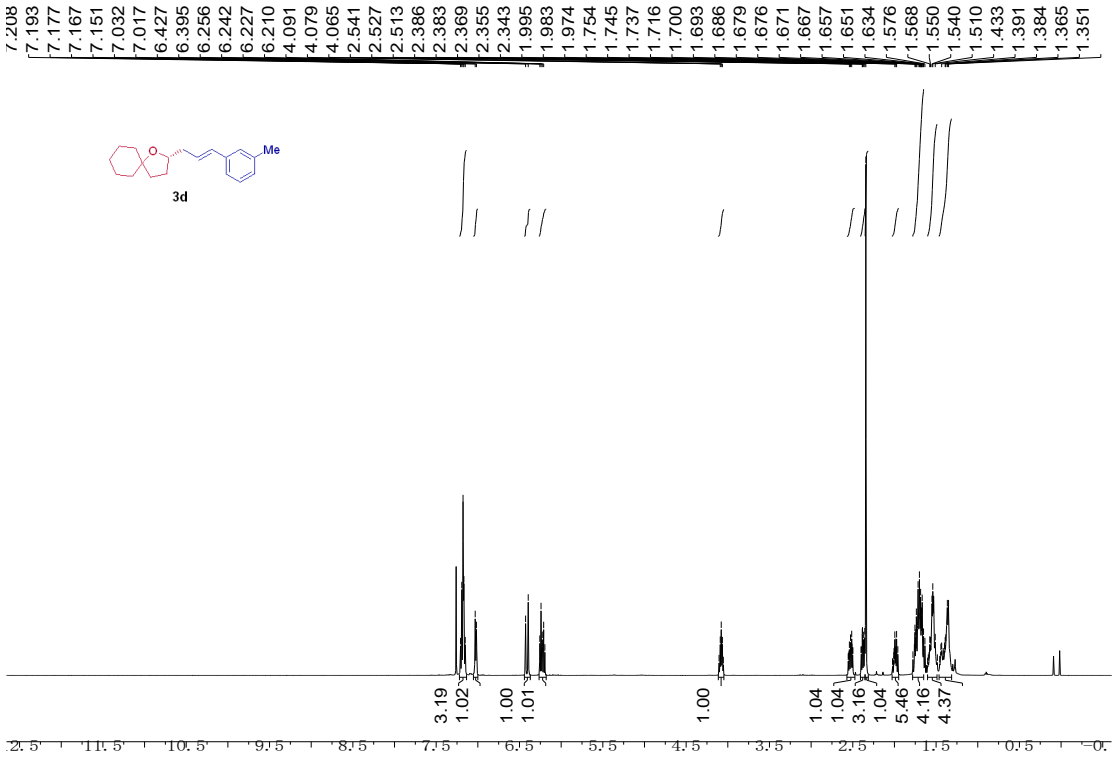
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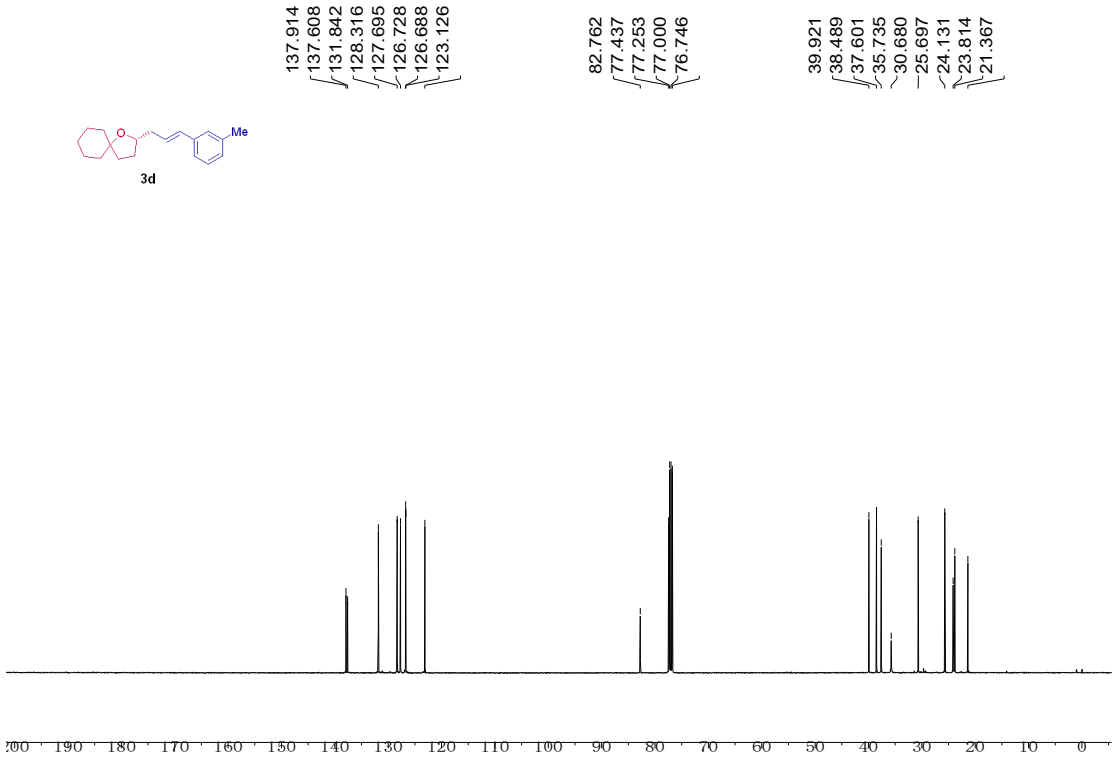
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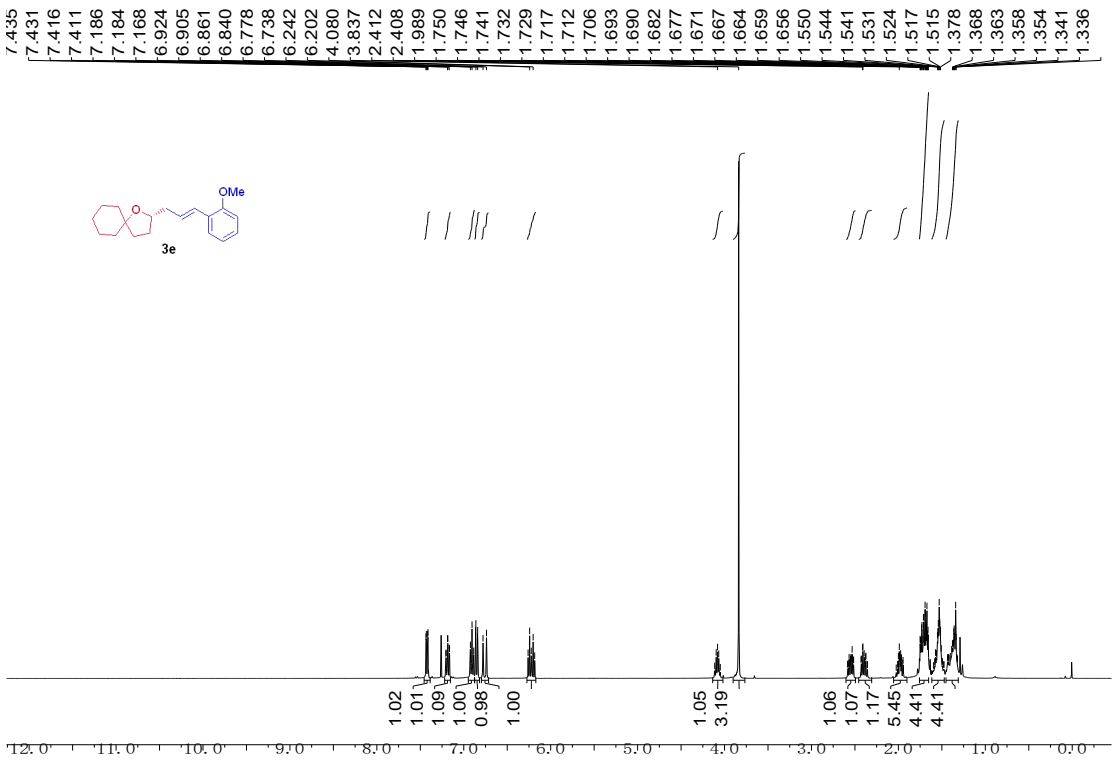
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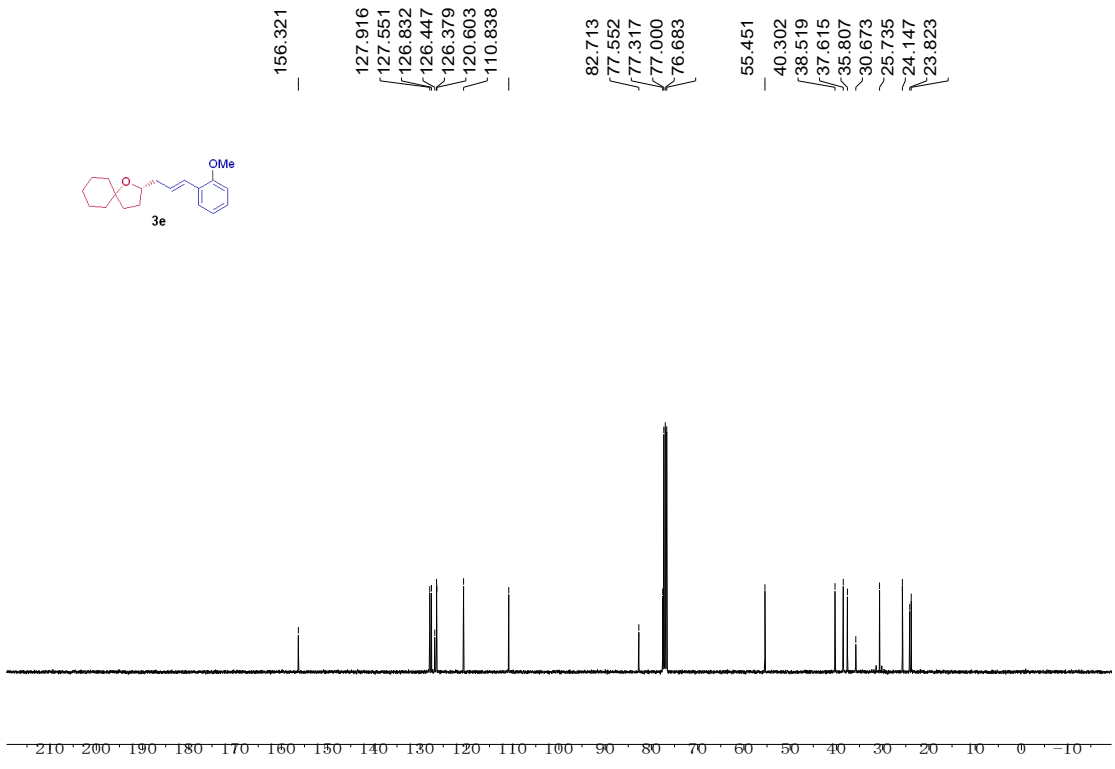
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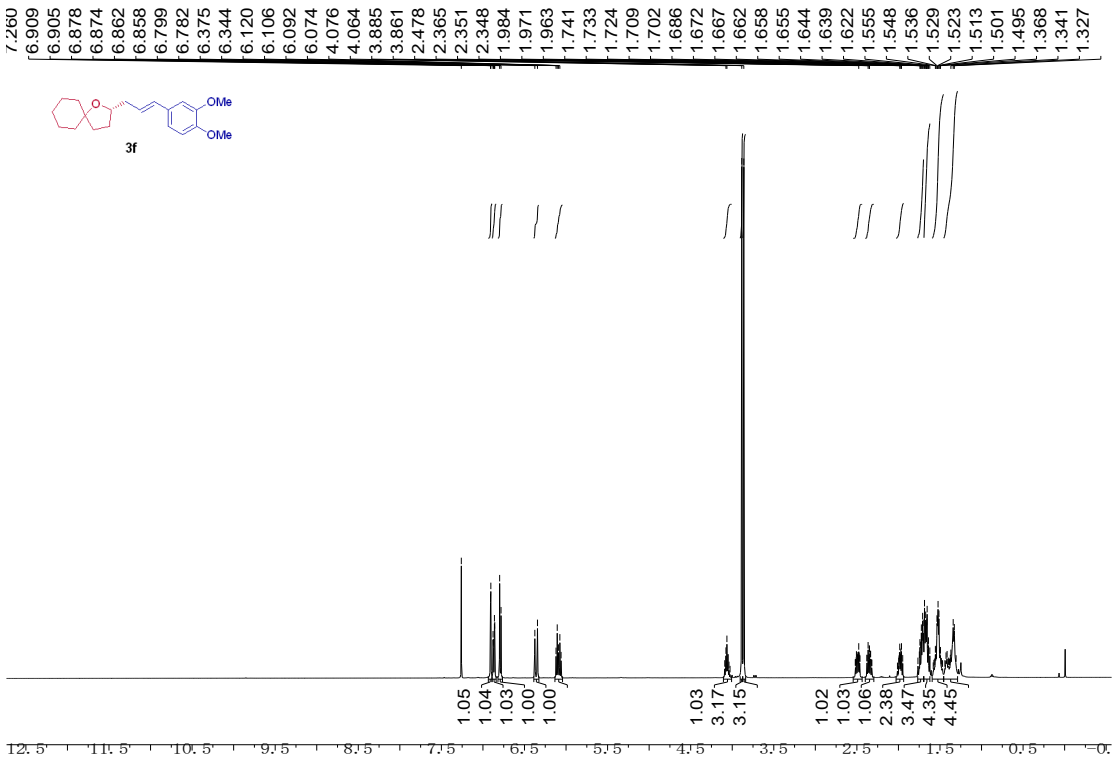
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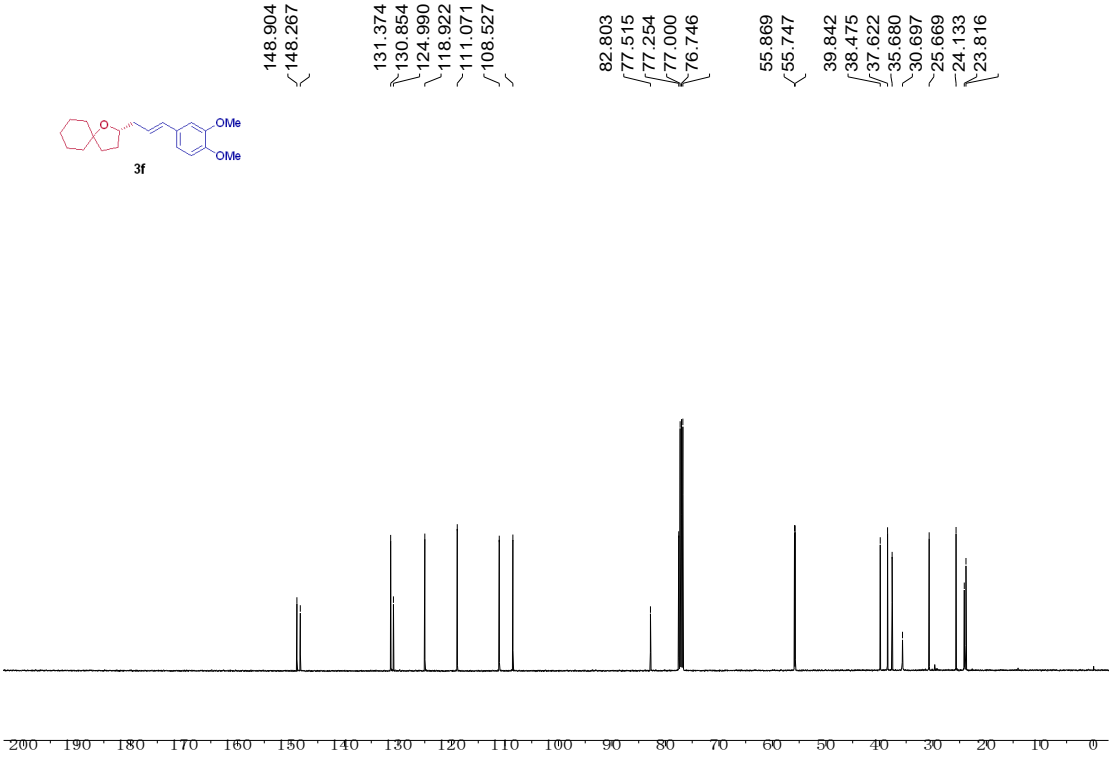
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OMe
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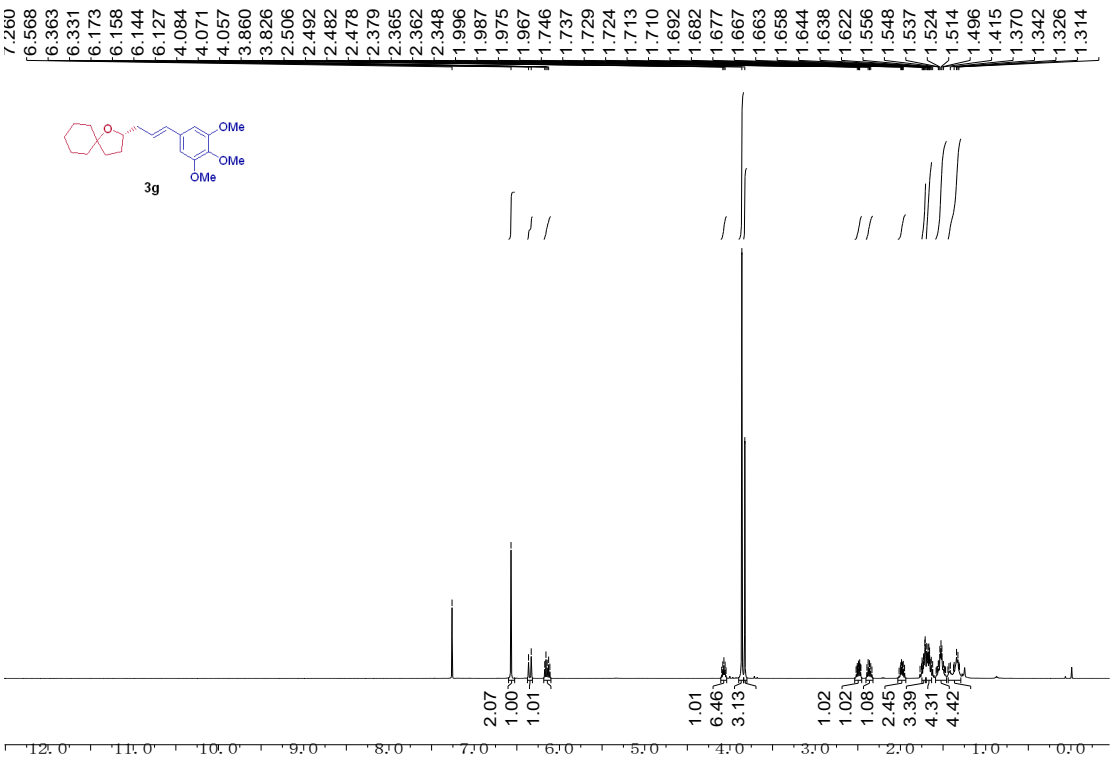
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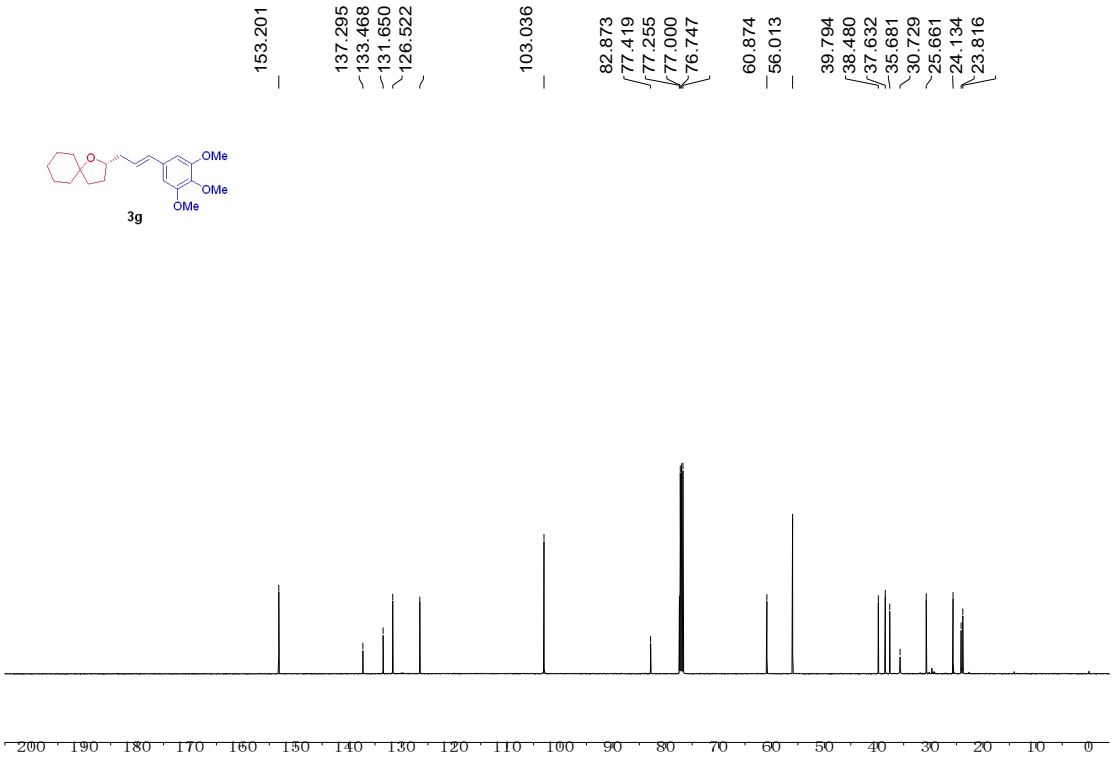
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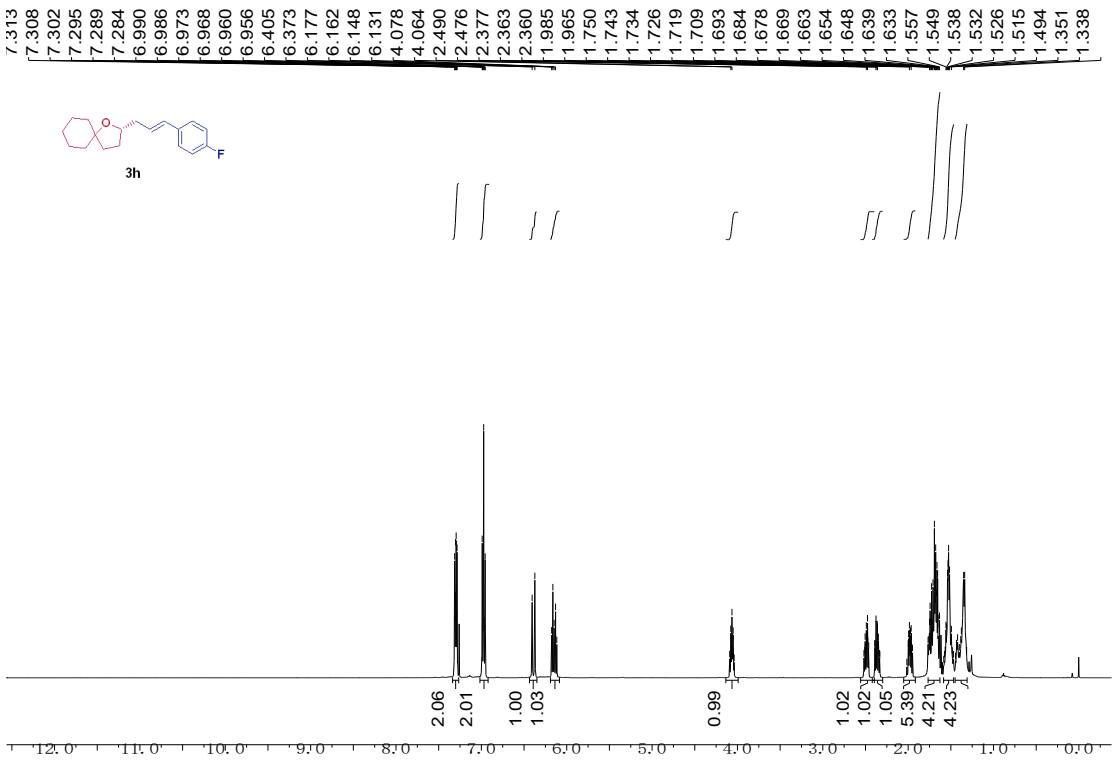
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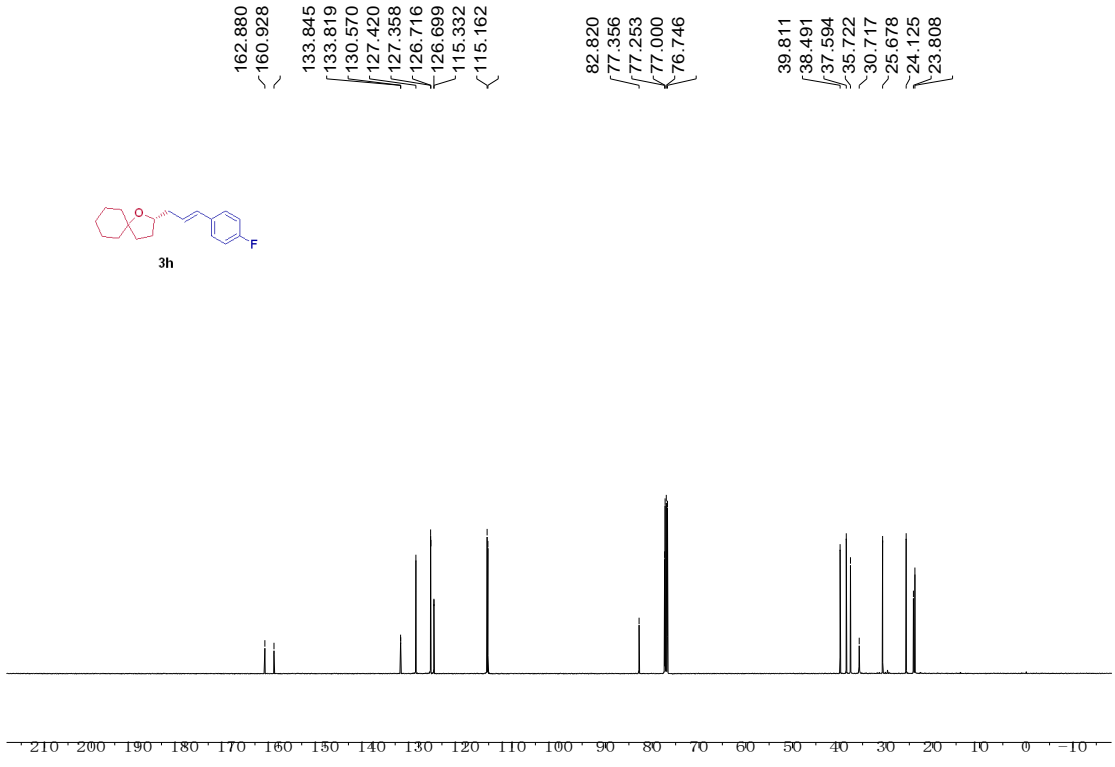
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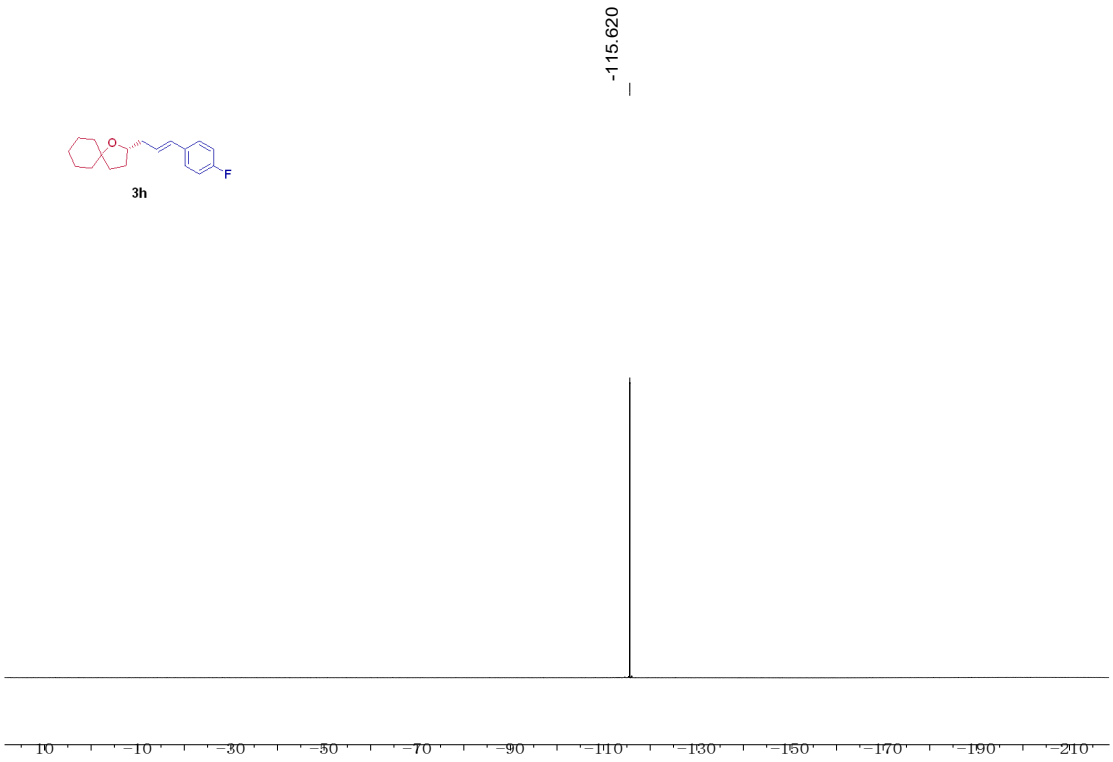
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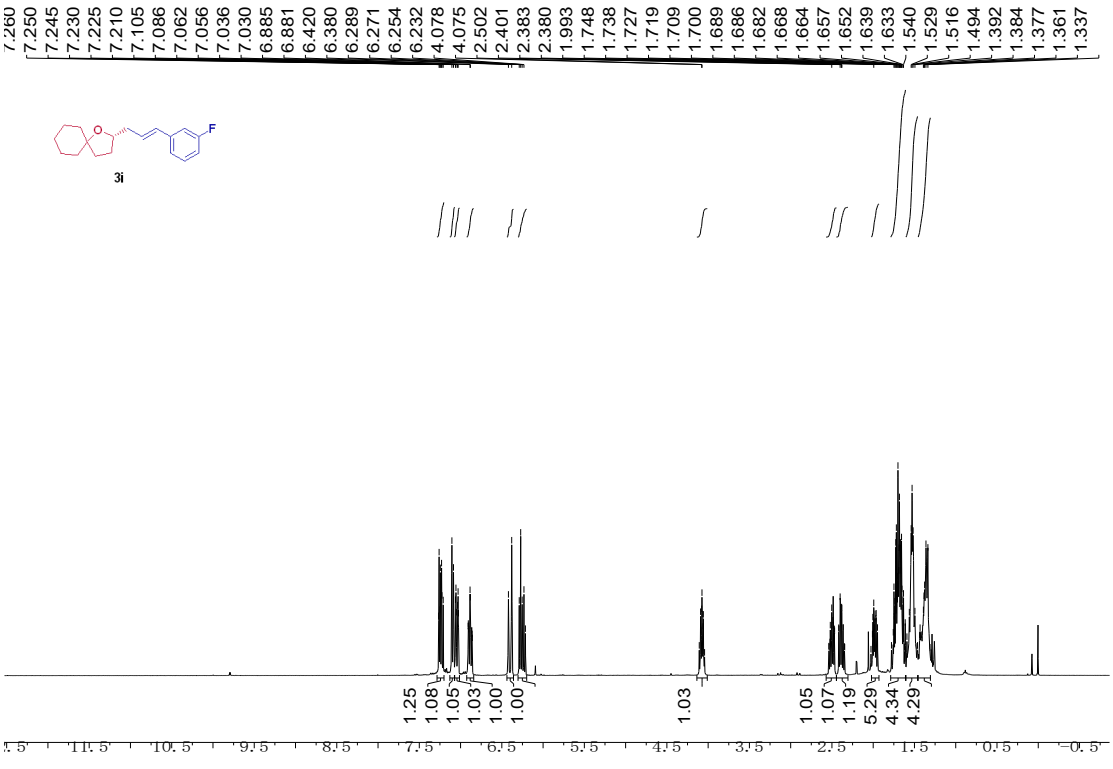
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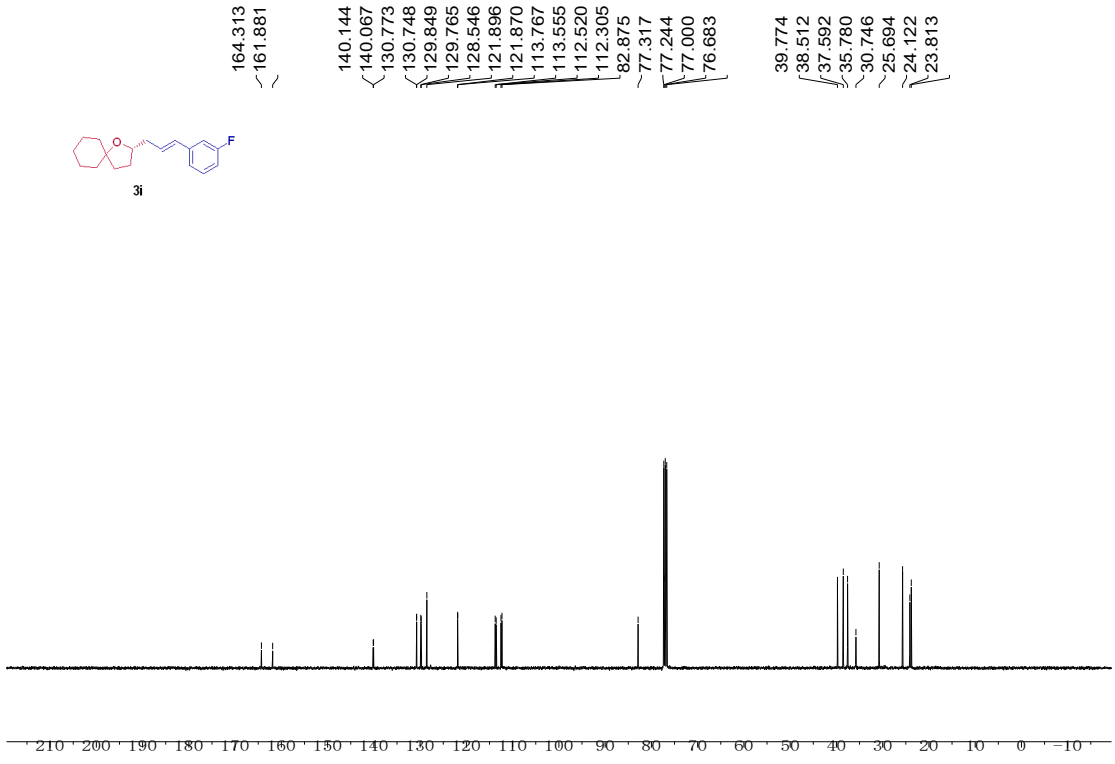
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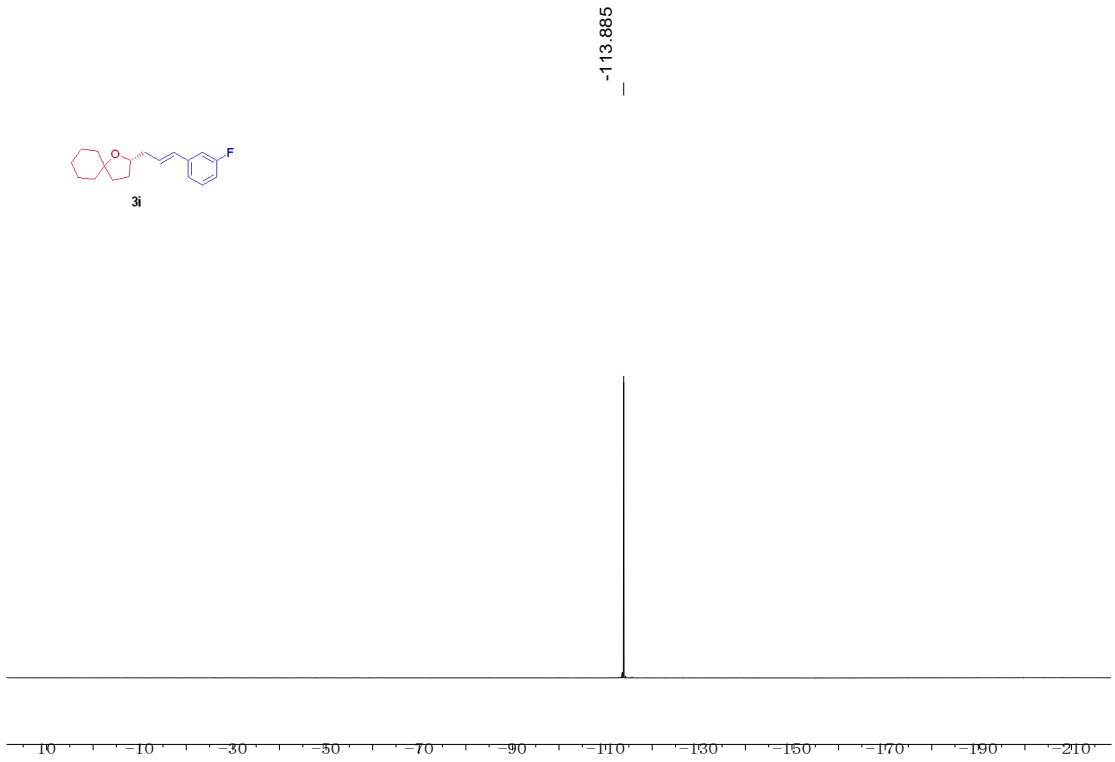
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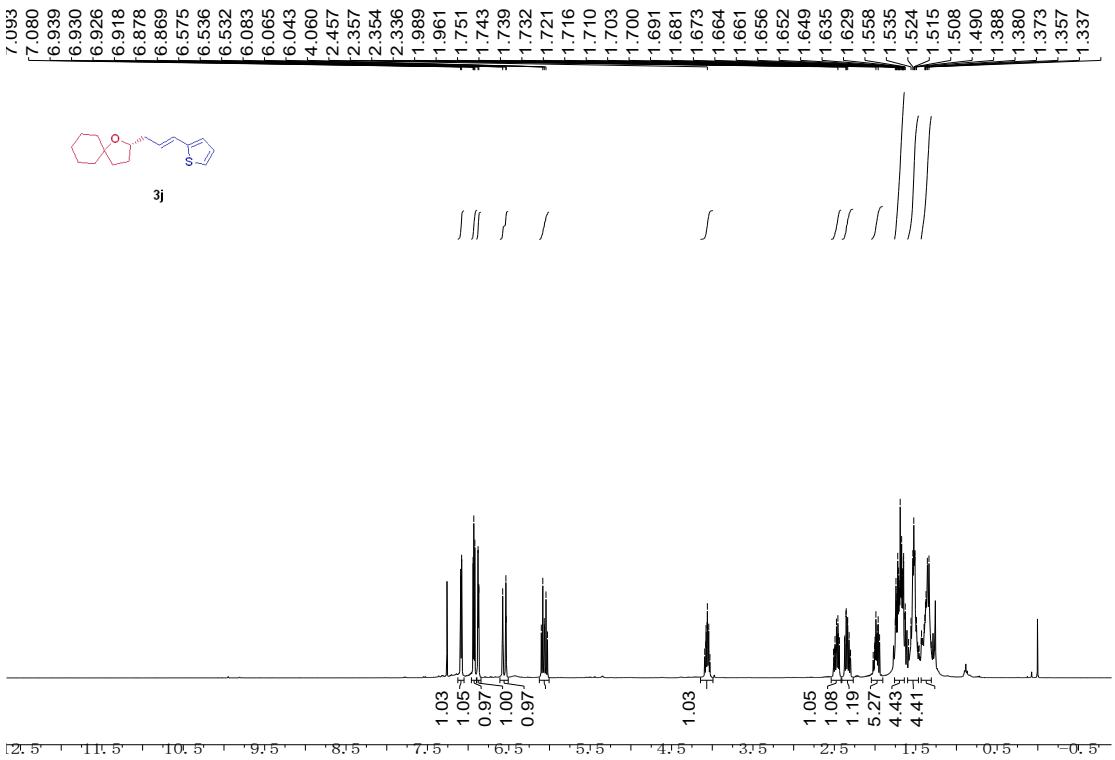
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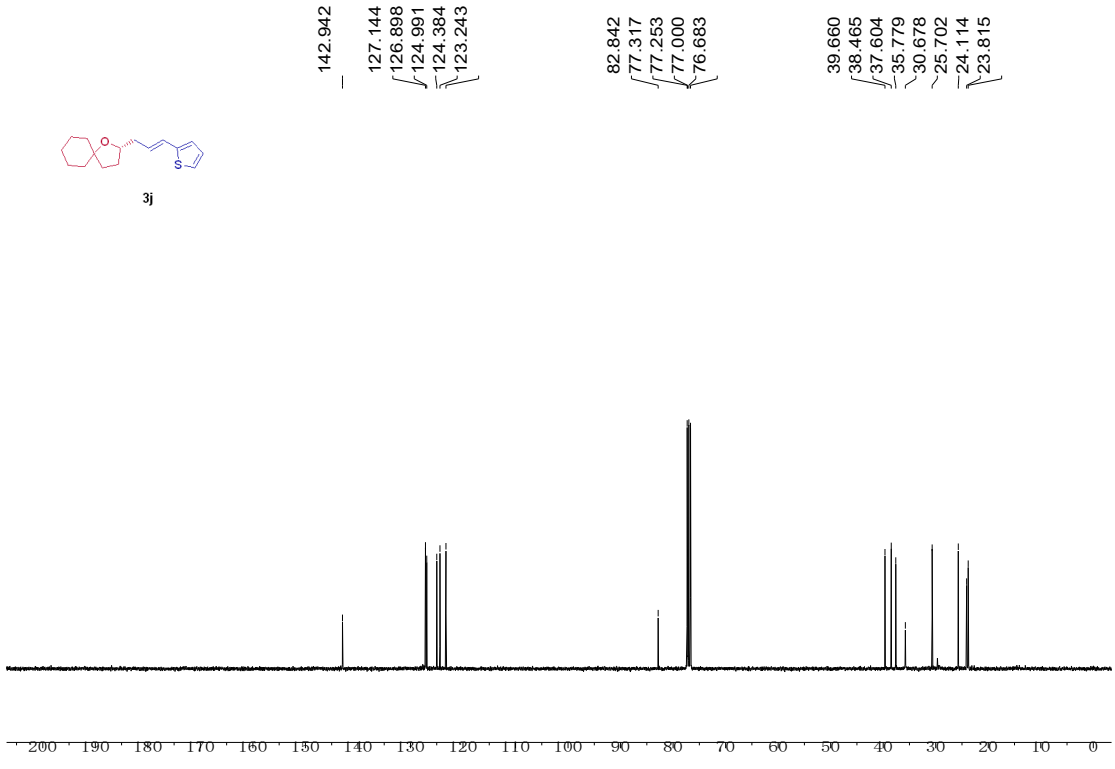
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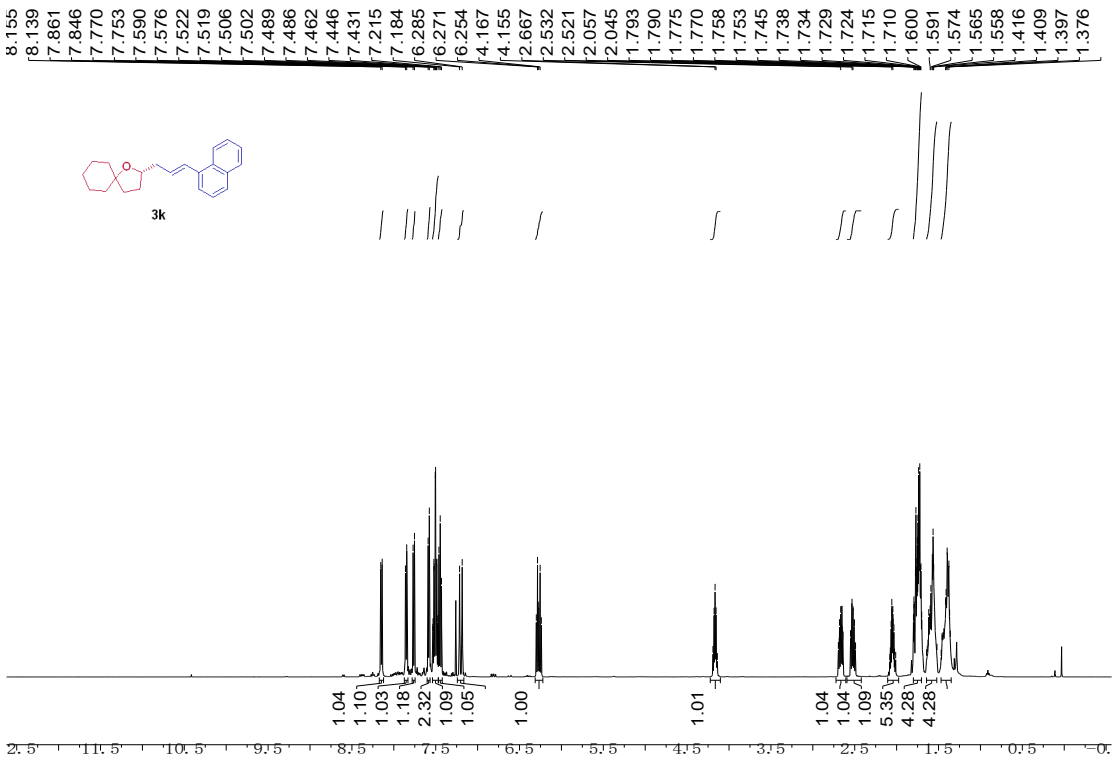
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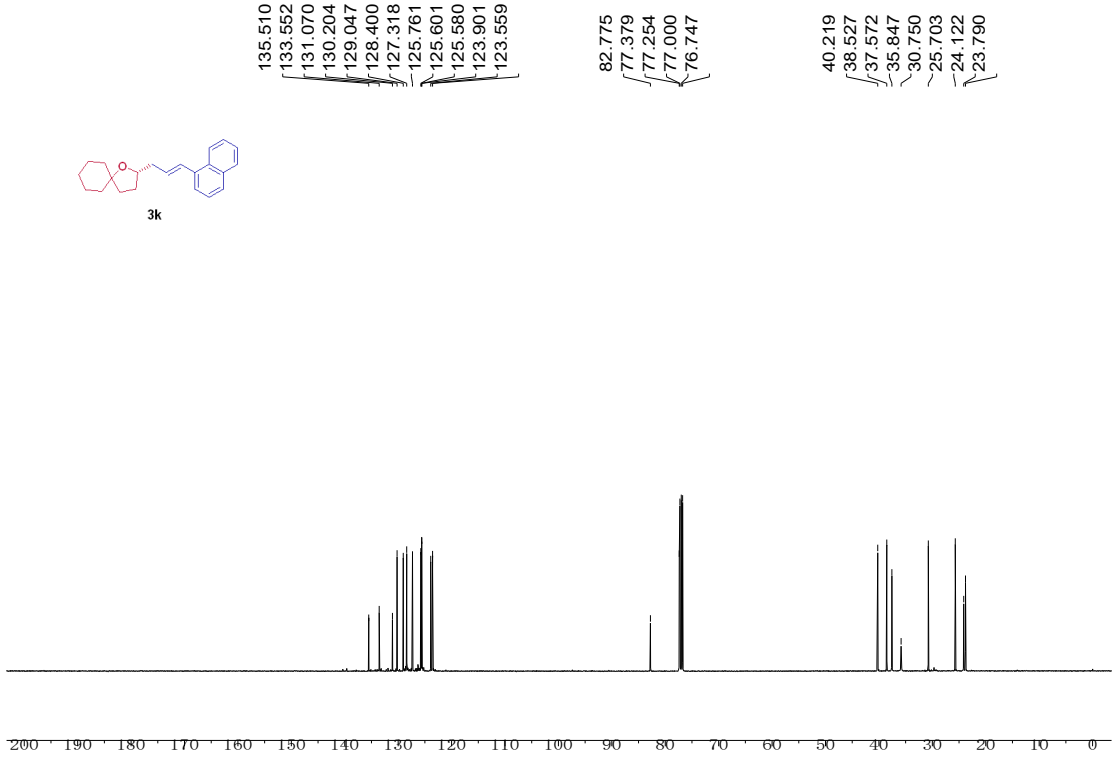
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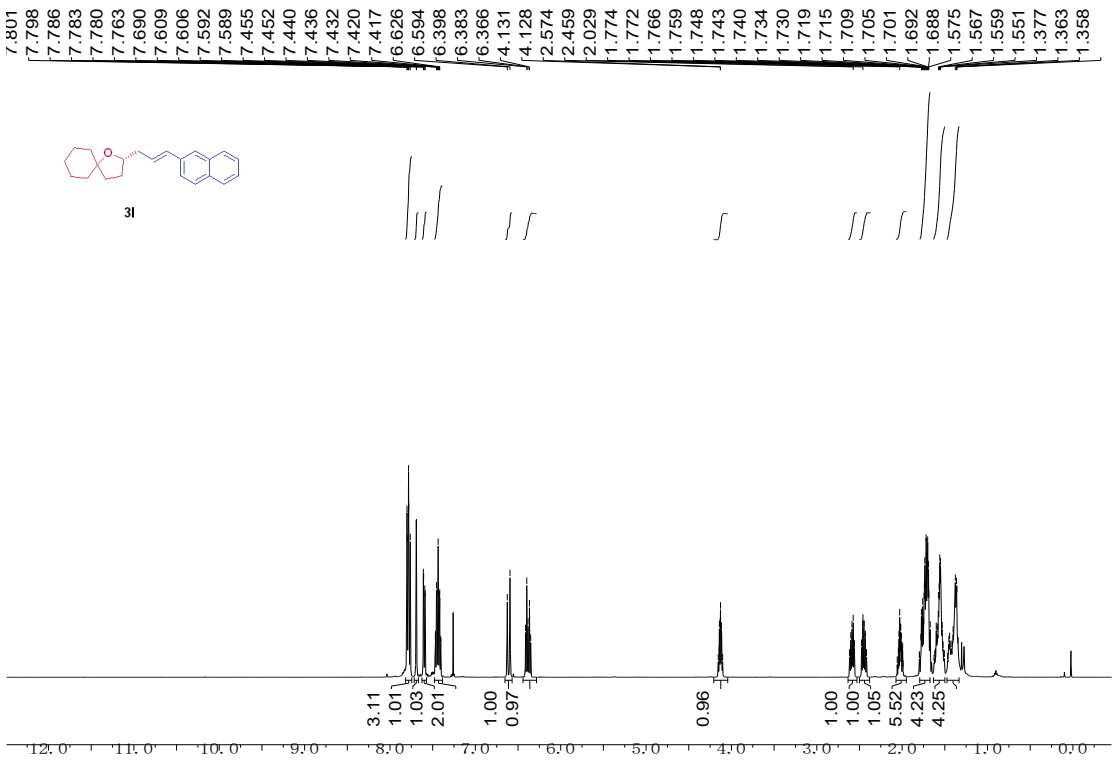
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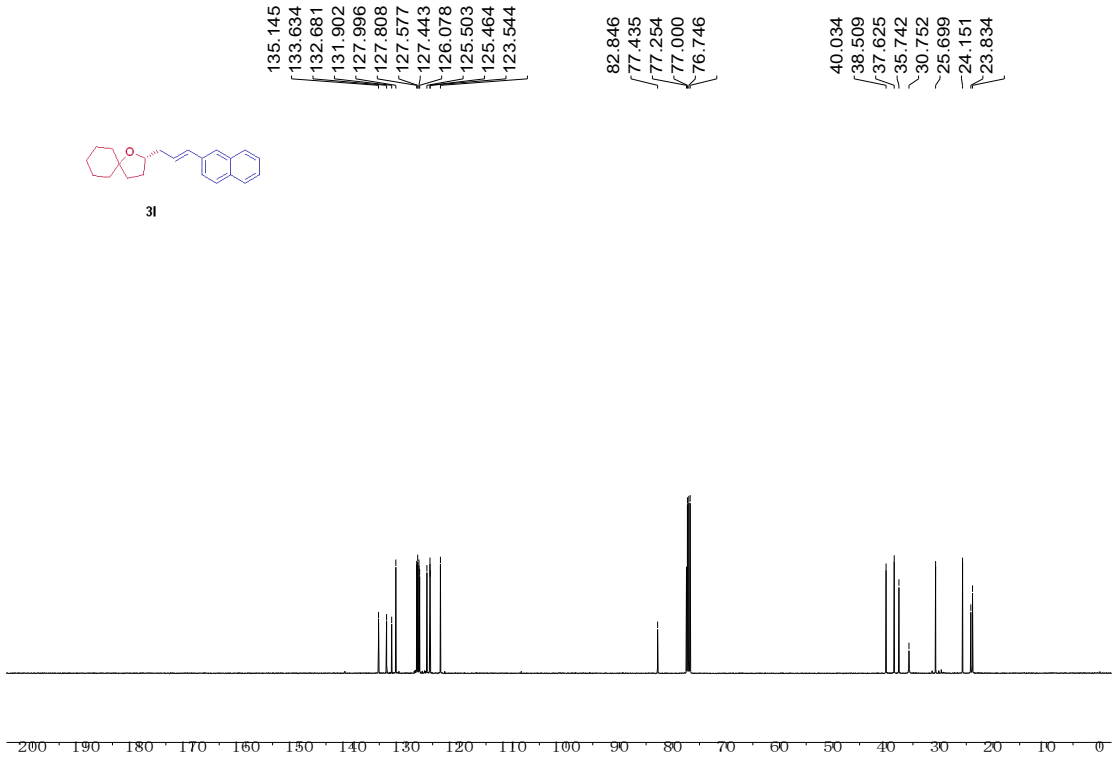
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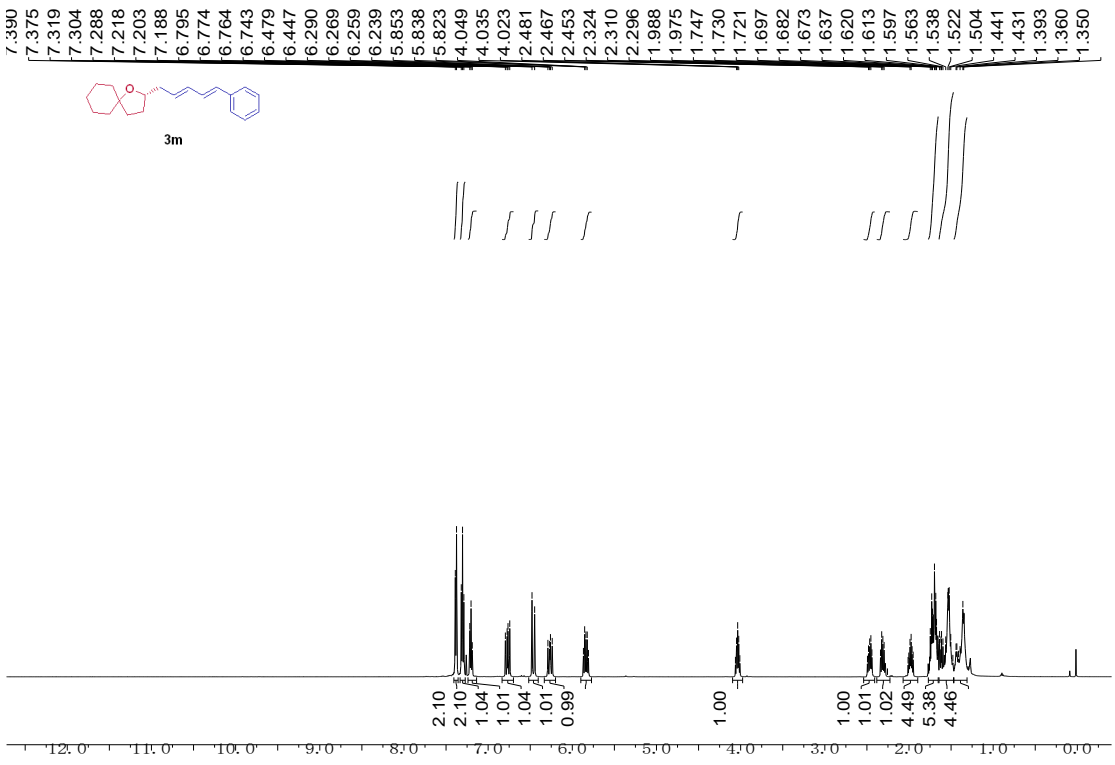
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1.04
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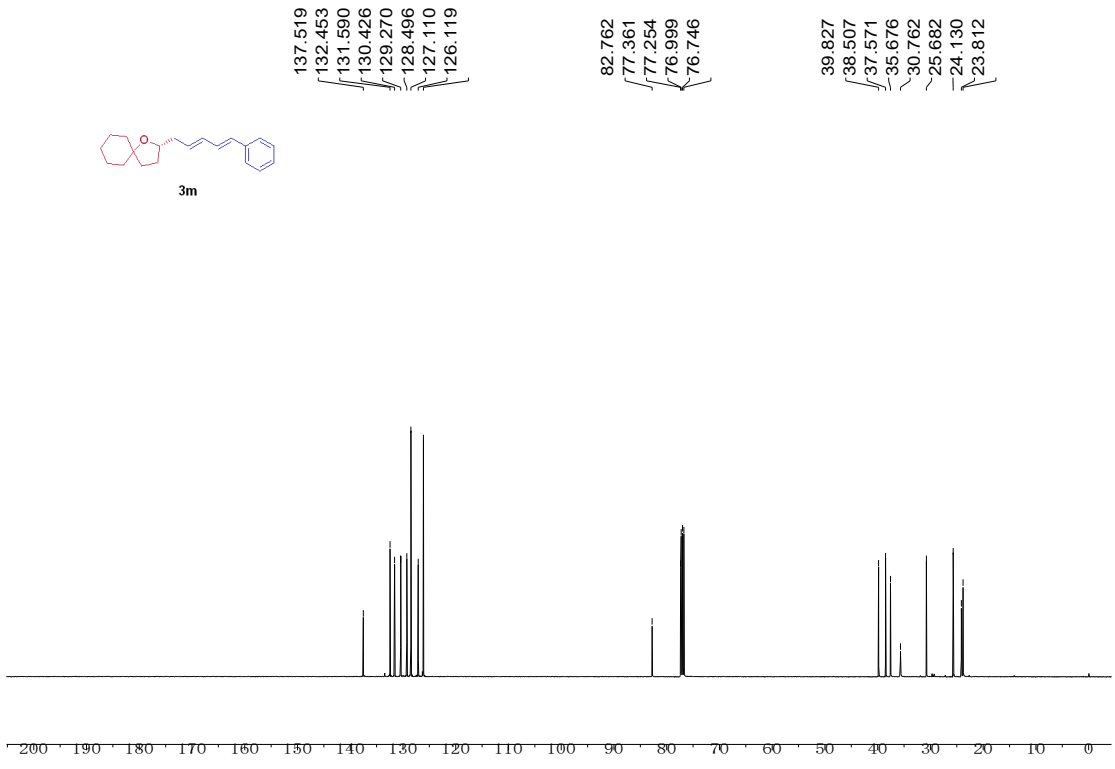
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24.130
23.812
3m
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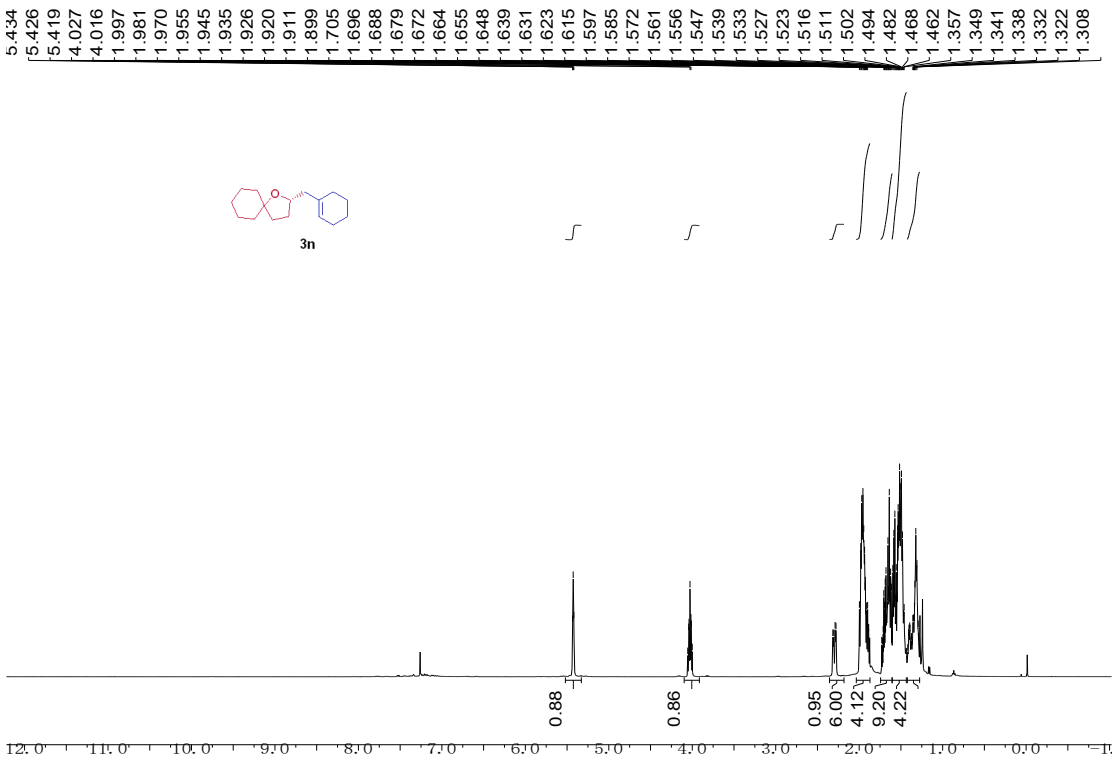
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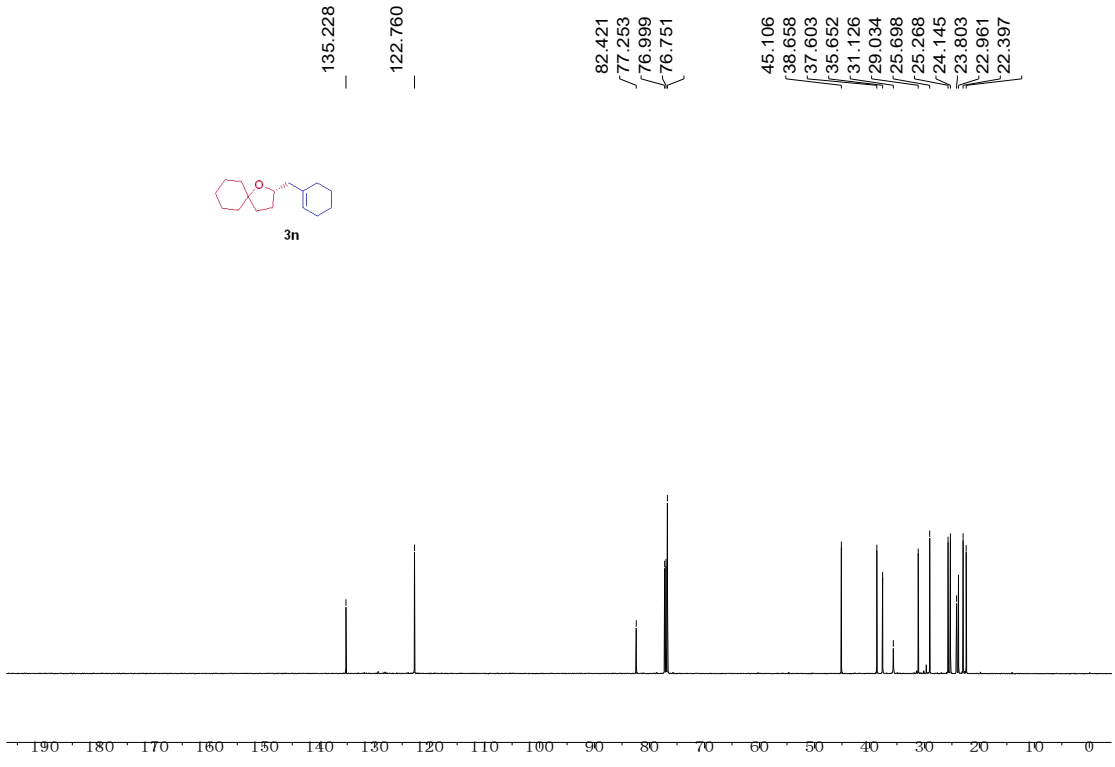
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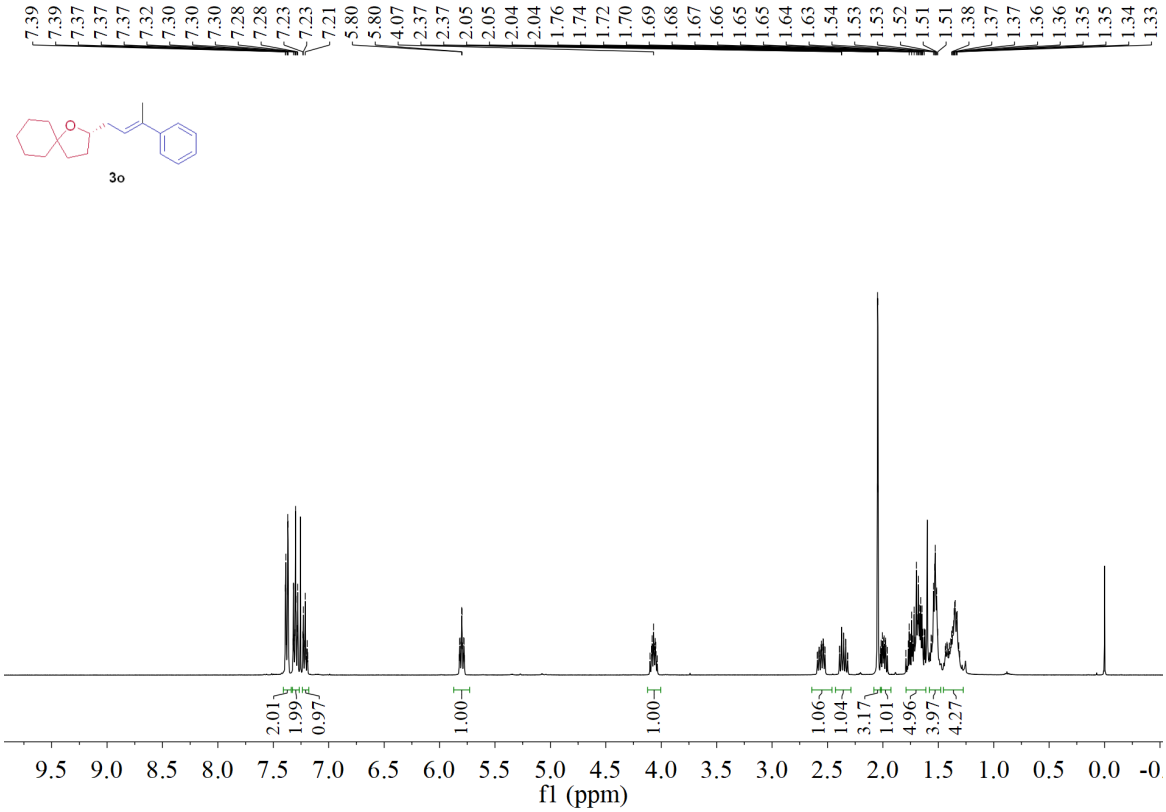
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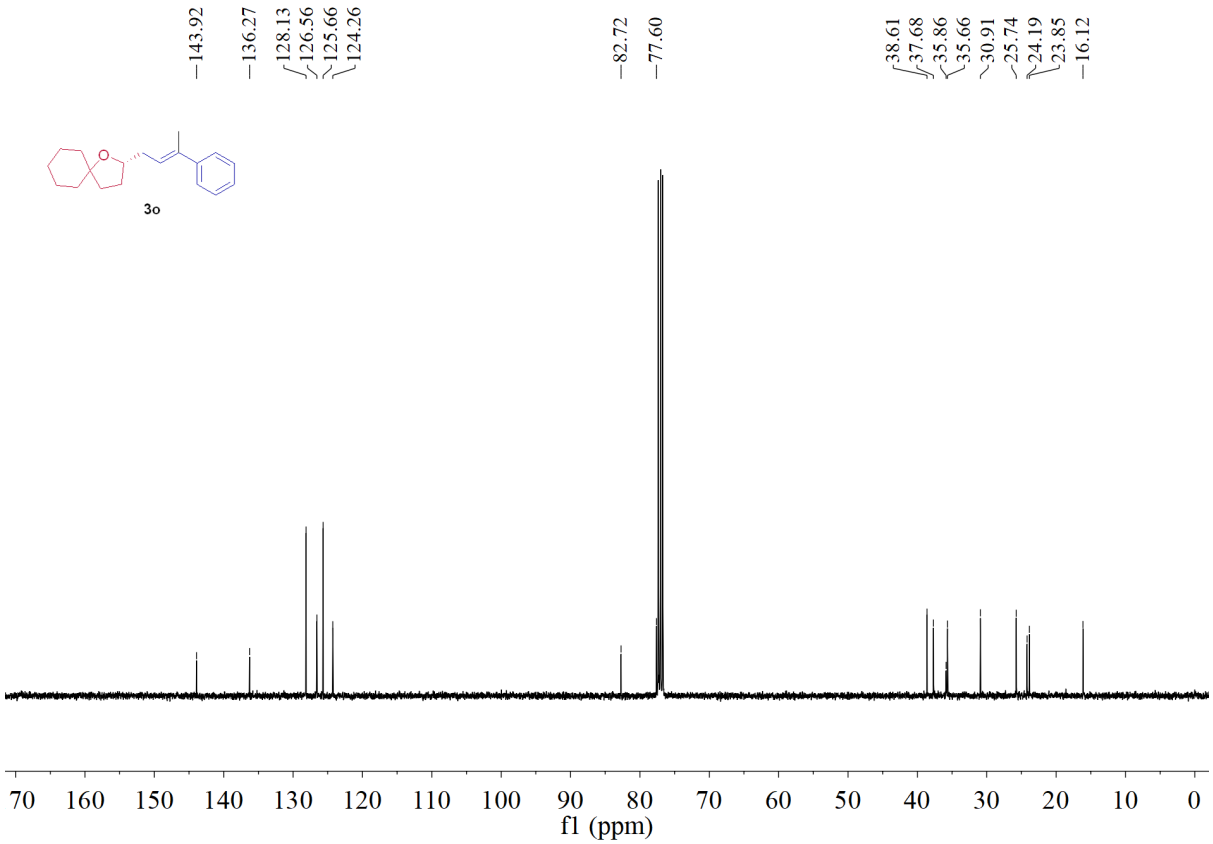
5.80 5.80 4.07 2.37 2.37 2.05 2.05 2.04 2.04 1.76 1.74 1.72 1.70 1.69 1.68 1.67 1.66 1.65 1.65 1.64 1.63 1.54 1.53 1.53 1.52 1.51 1.51 1.38 1.37 1.37 1.36 1.36 1.35 1.35 1.34 1.33
3o
2.01 1.99 0.97 1.00 1.00 1.06 1.04 3.17 1.01 4.96 3.97 4.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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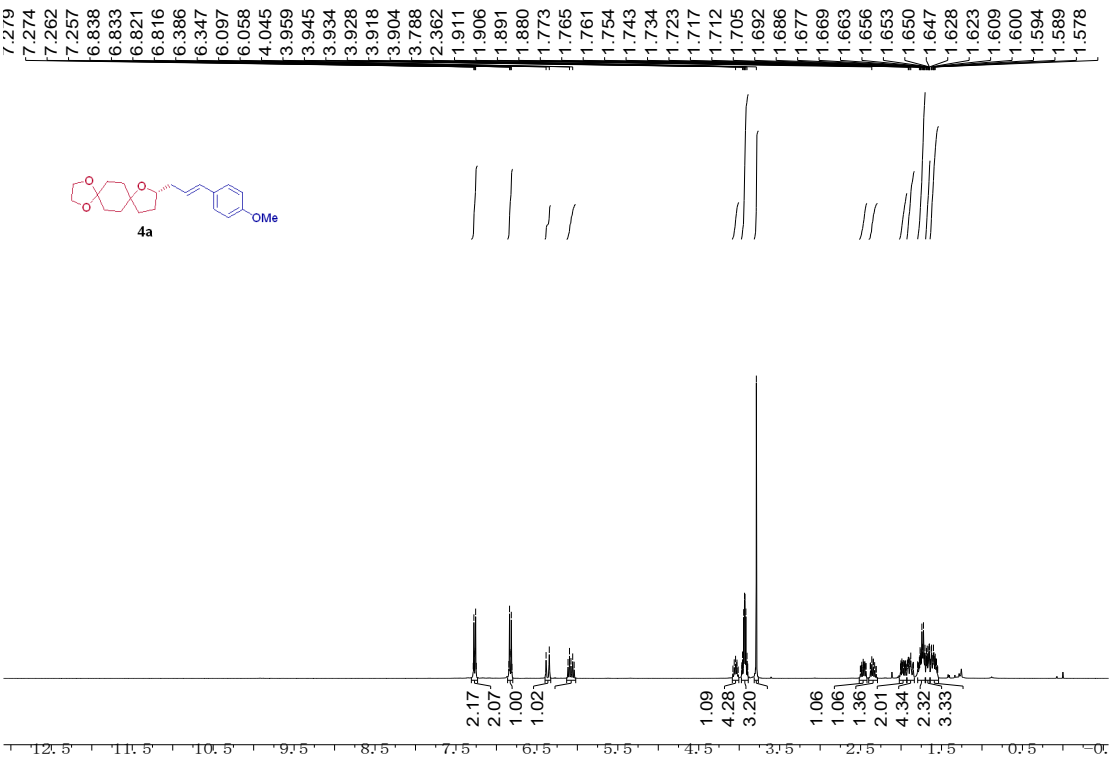
f1 (ppm)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1.589
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OMe
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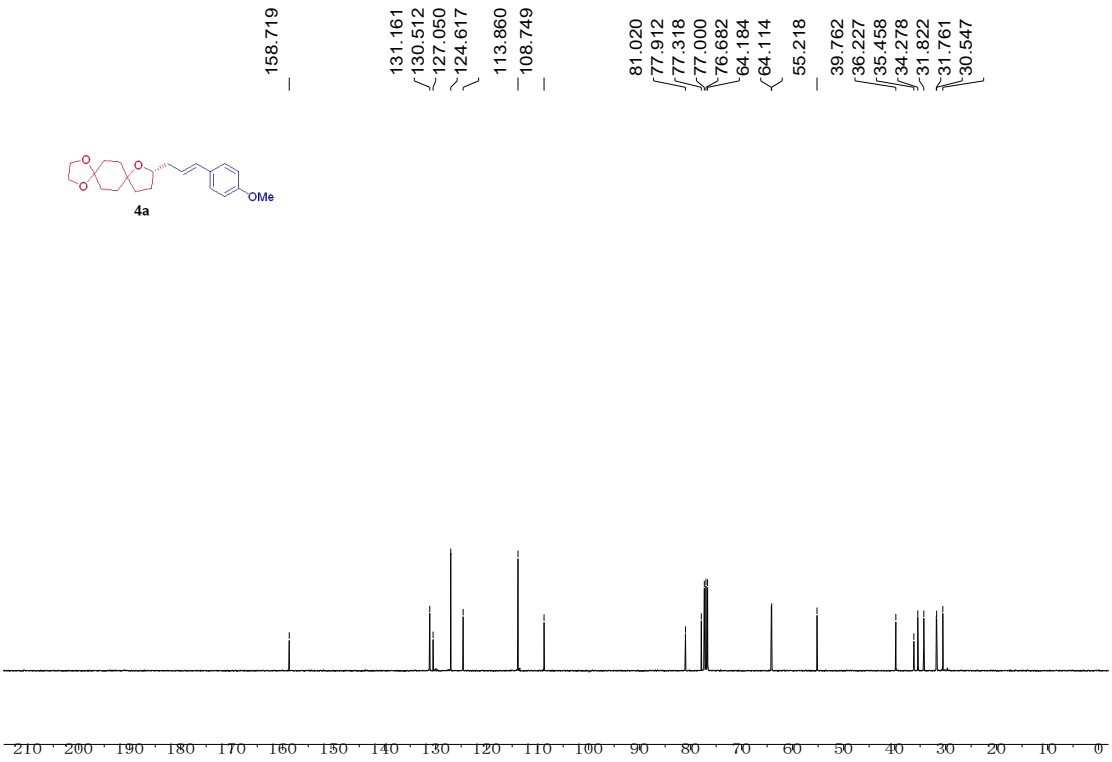
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OMe
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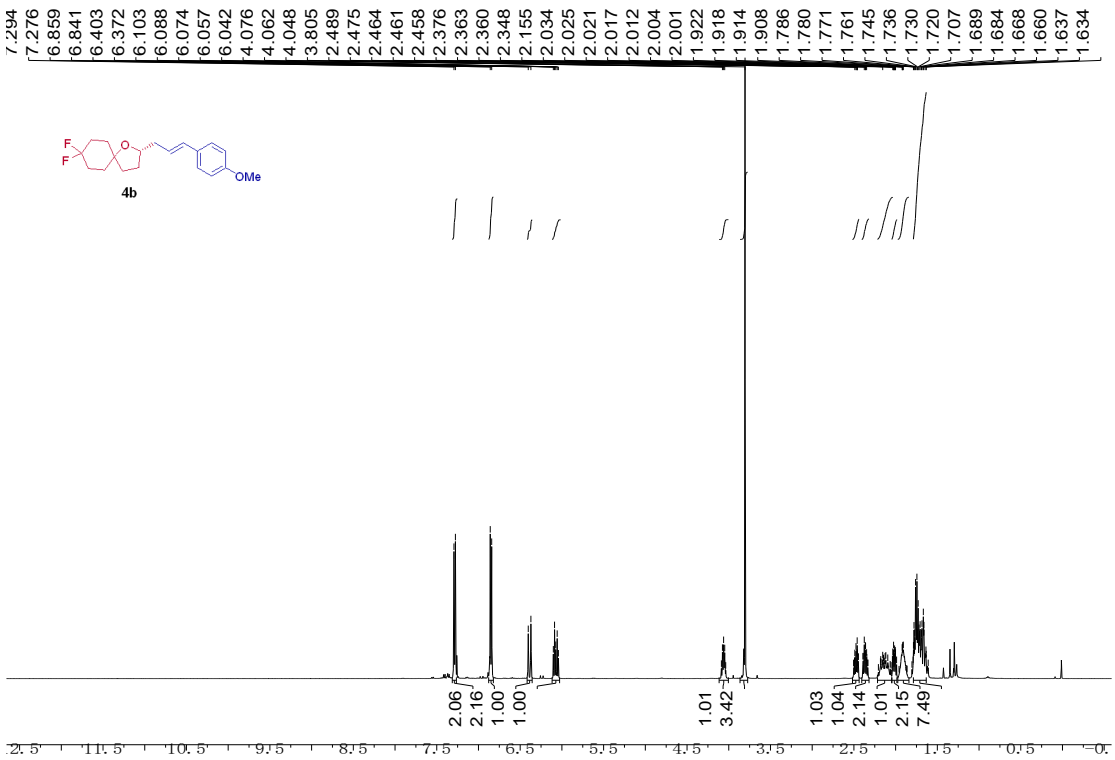
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1.634
F
F
O
OMe
4b
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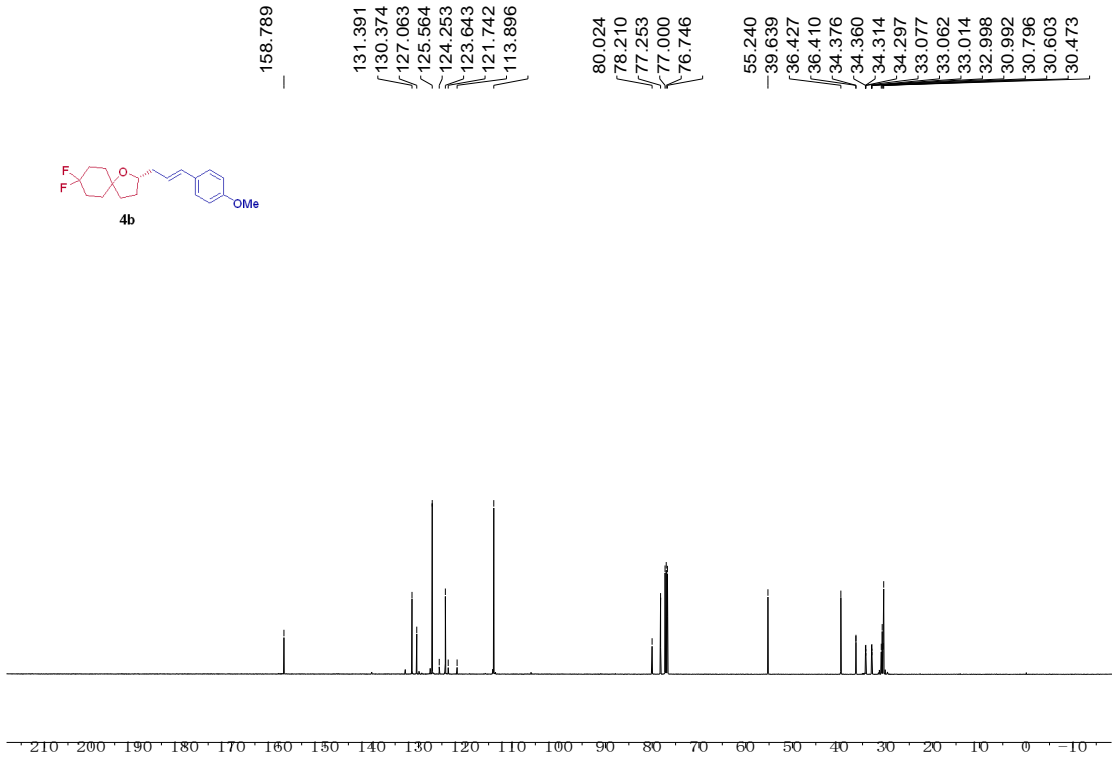
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34.360
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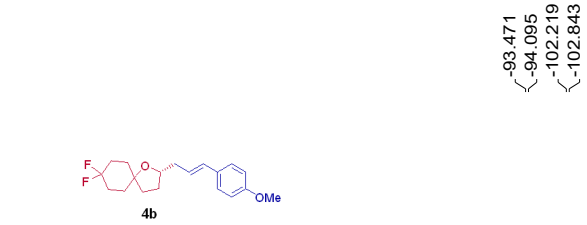
O
OMe
4b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O
OMe
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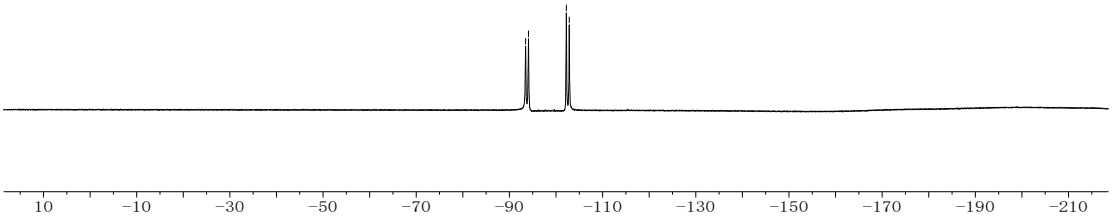
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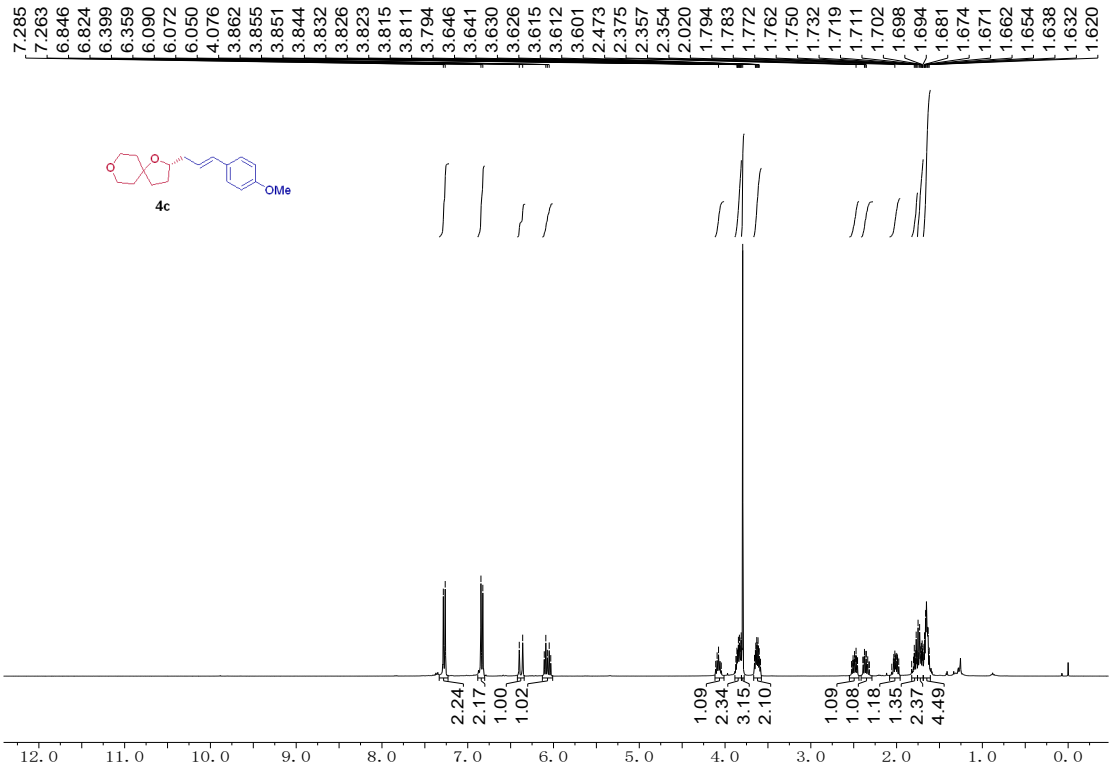
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O
O
OMe
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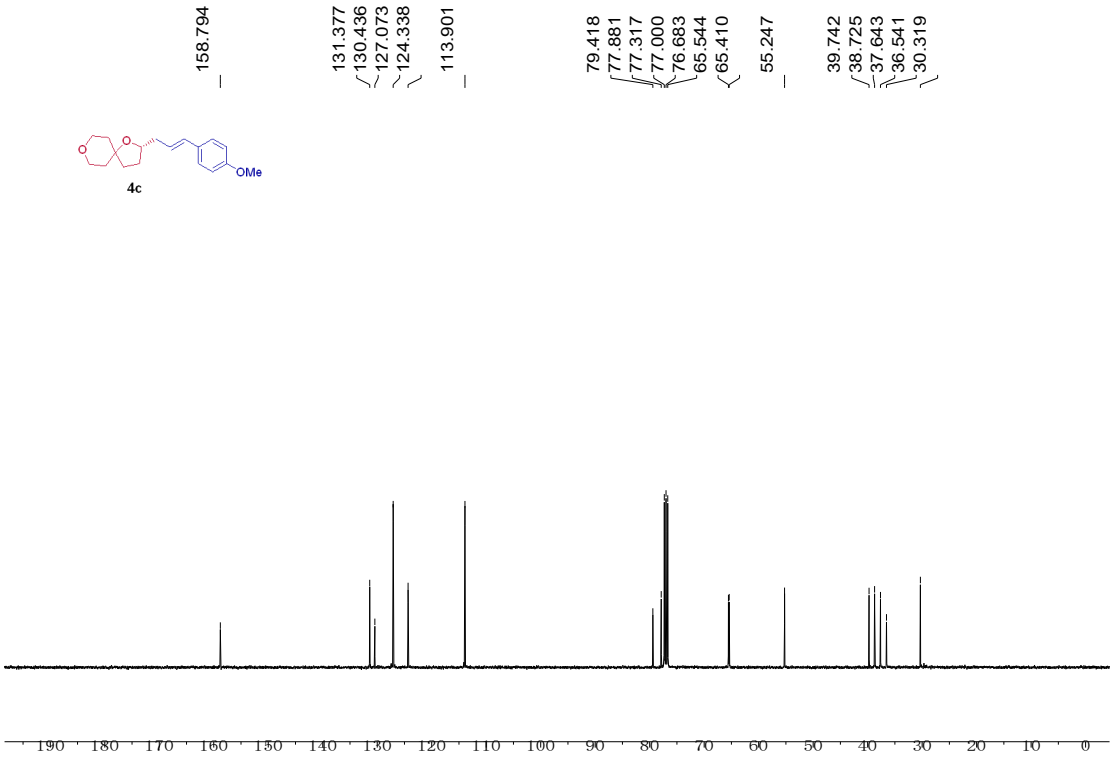
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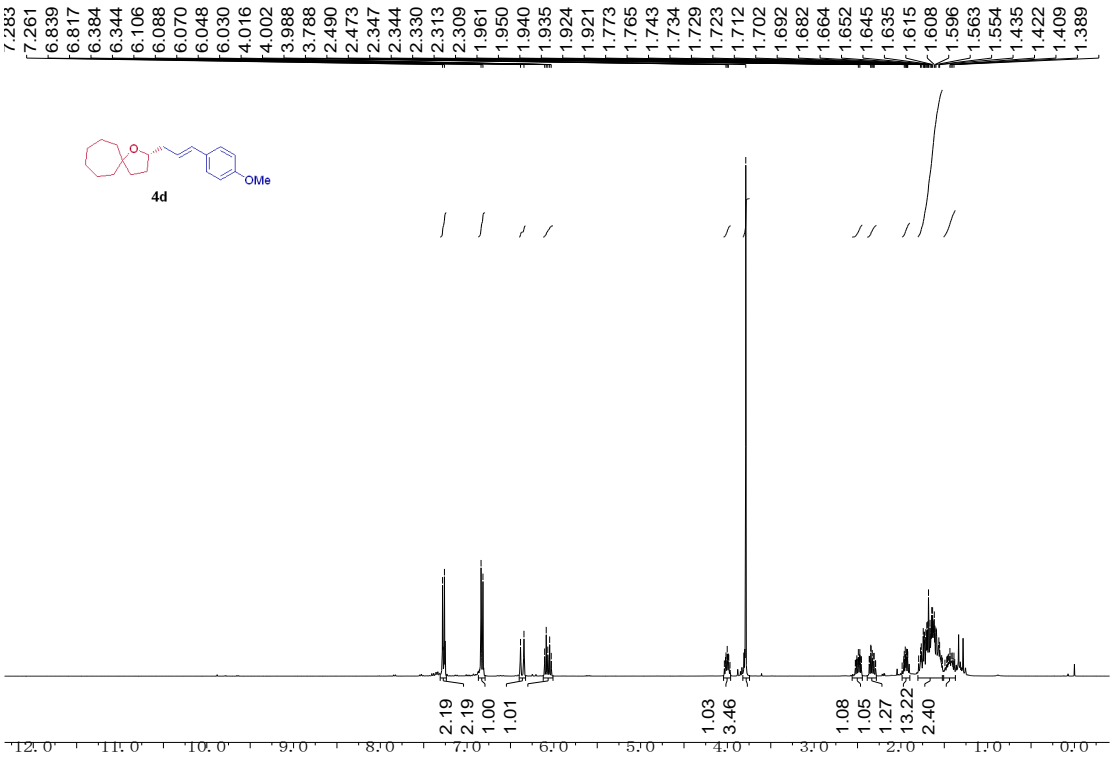
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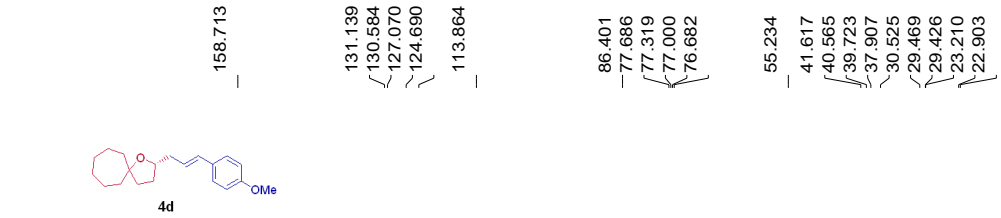
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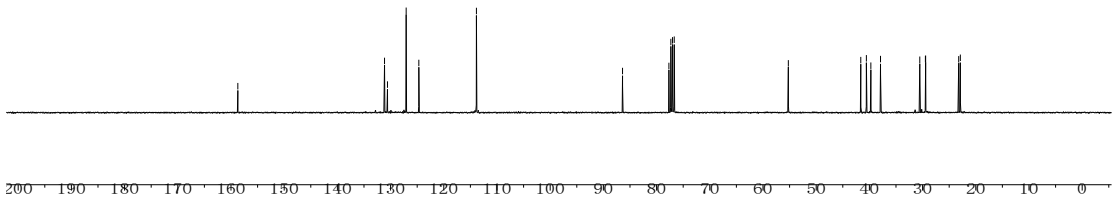
4d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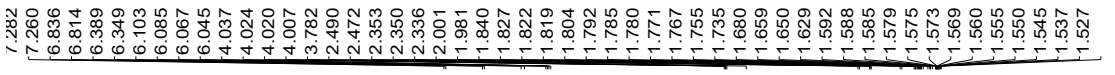
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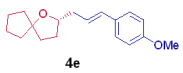
OMe

4e

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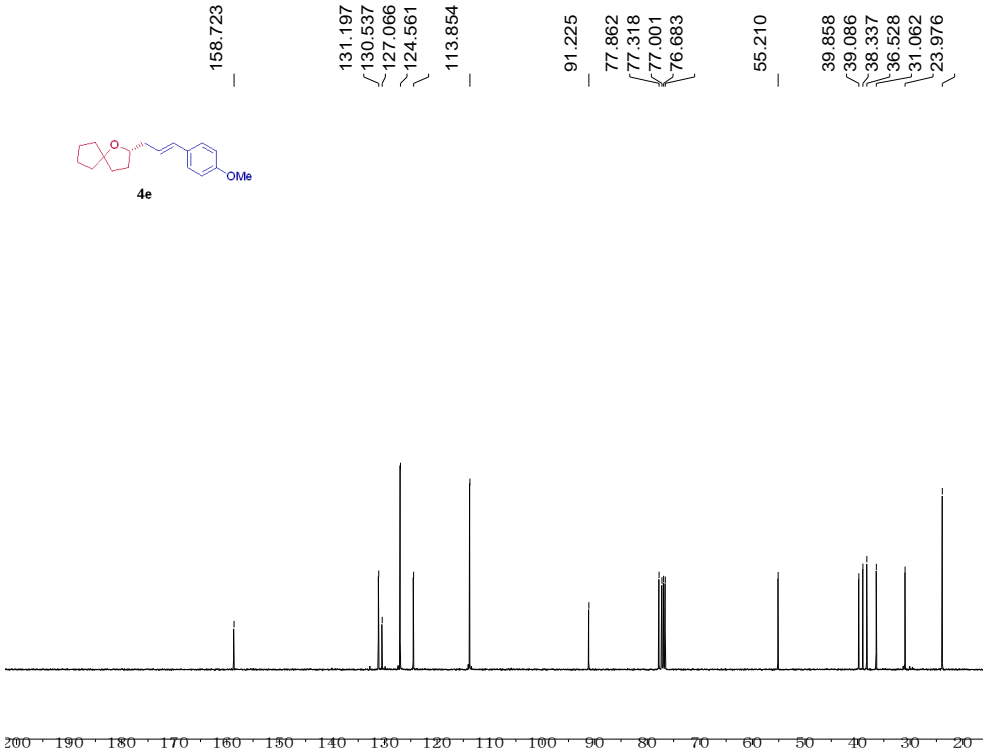
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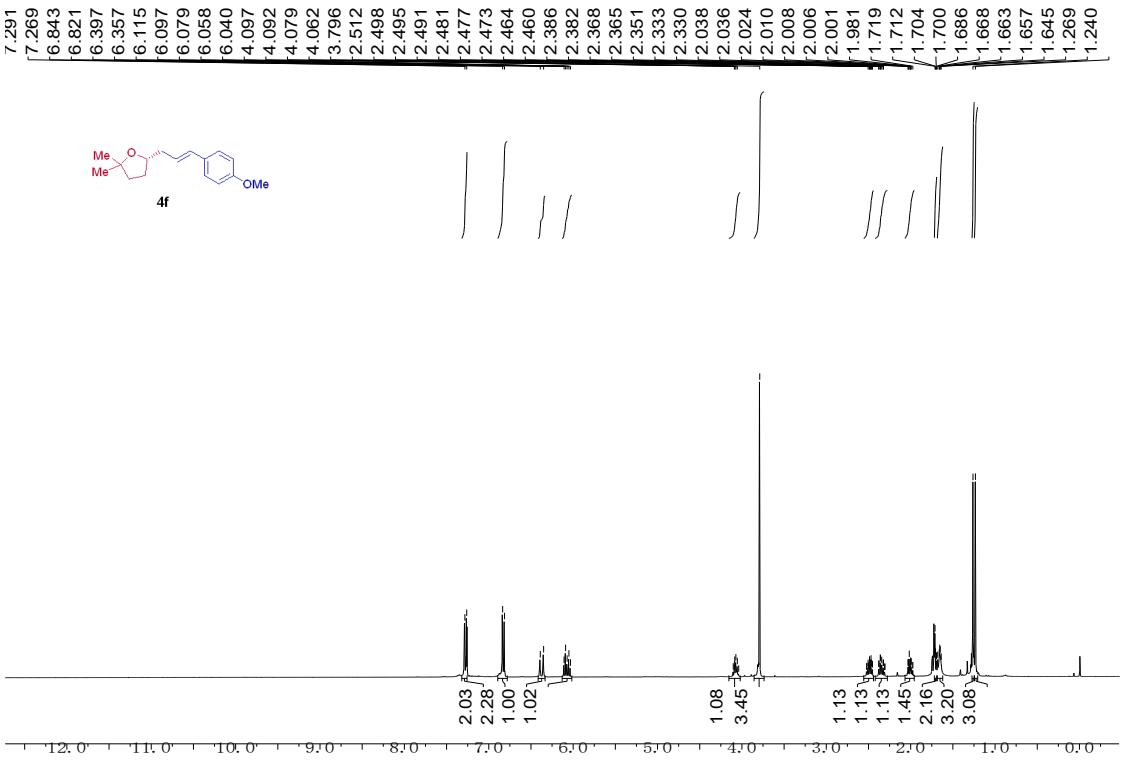
OMe
4e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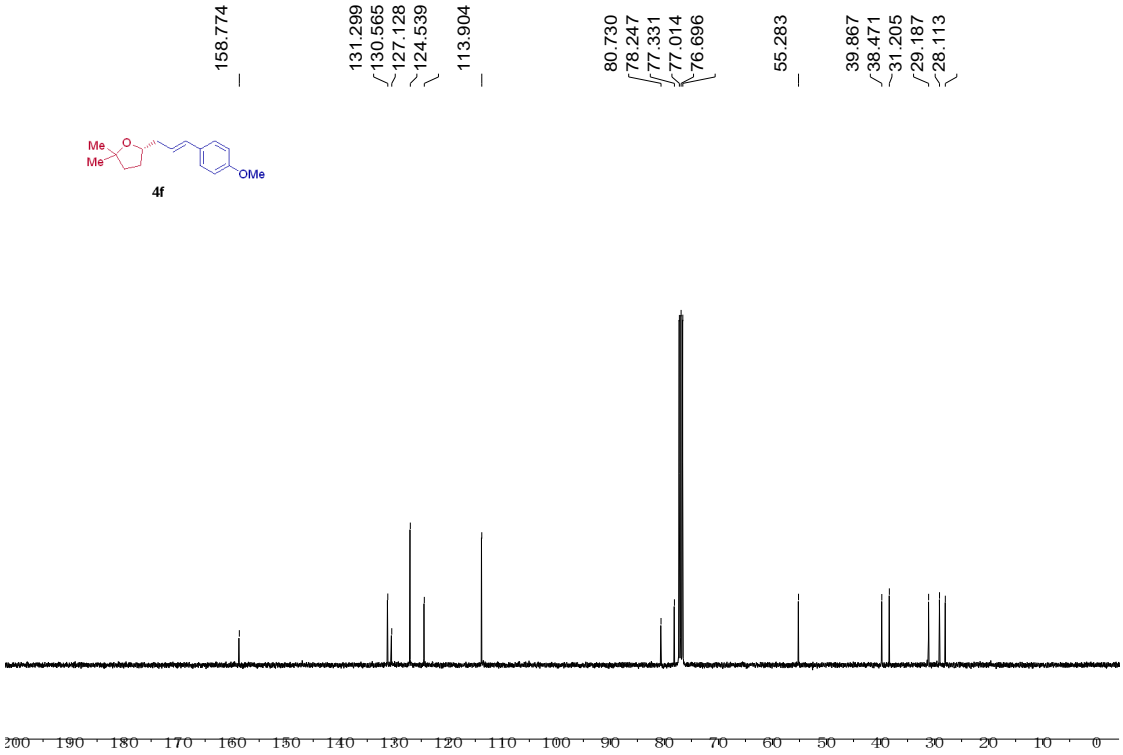
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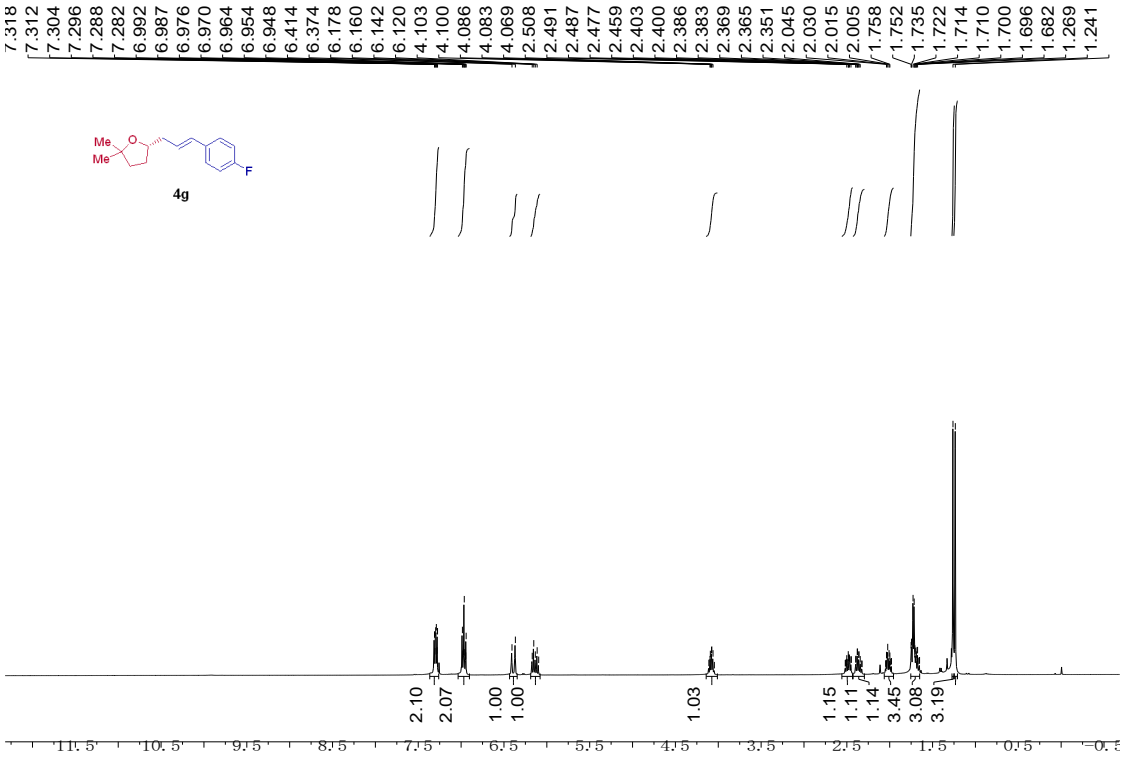
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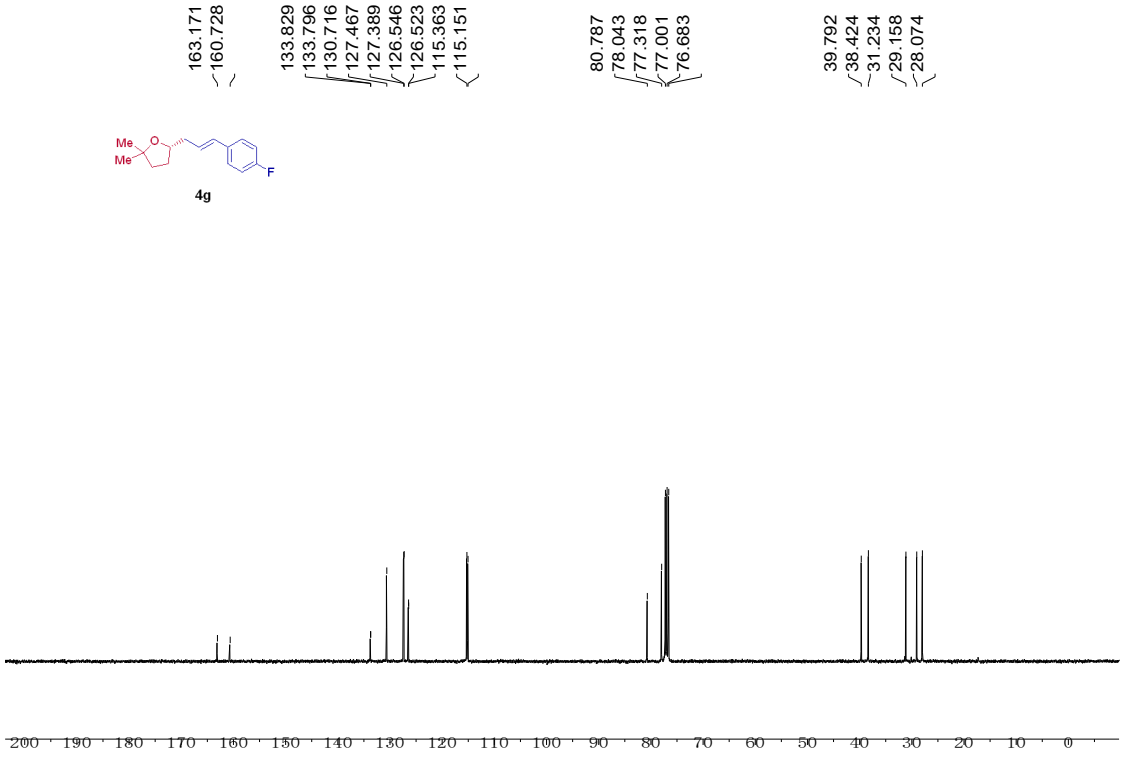
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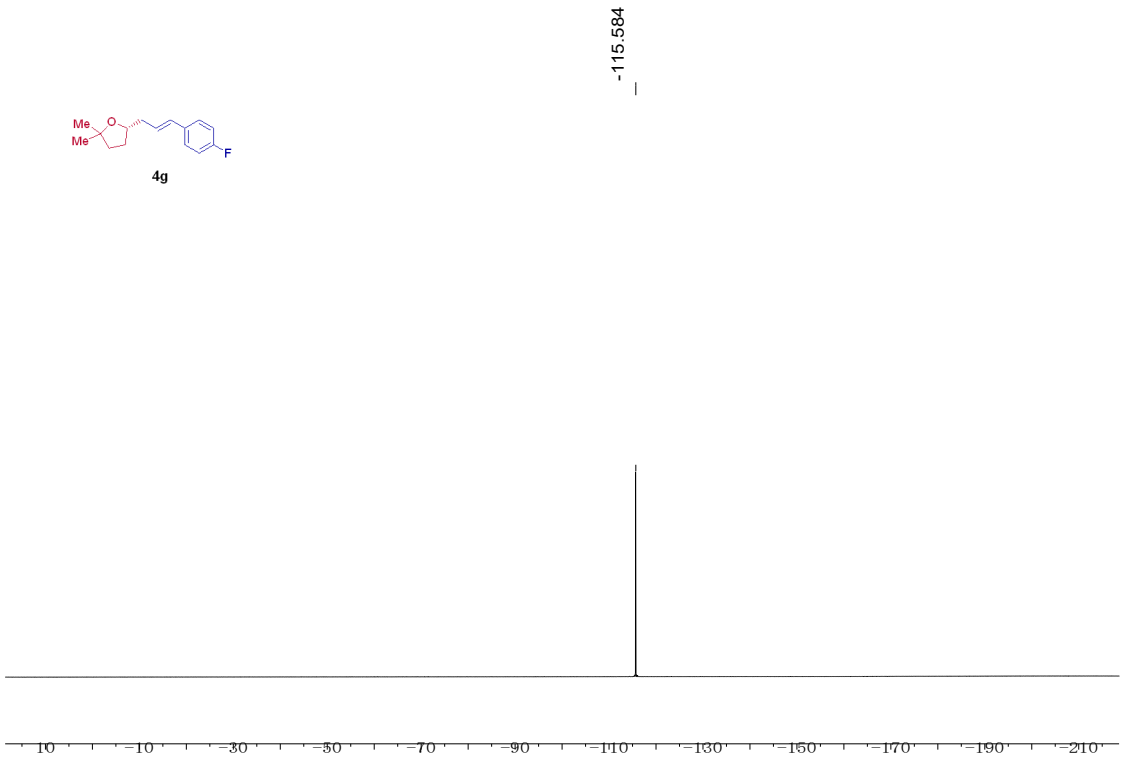
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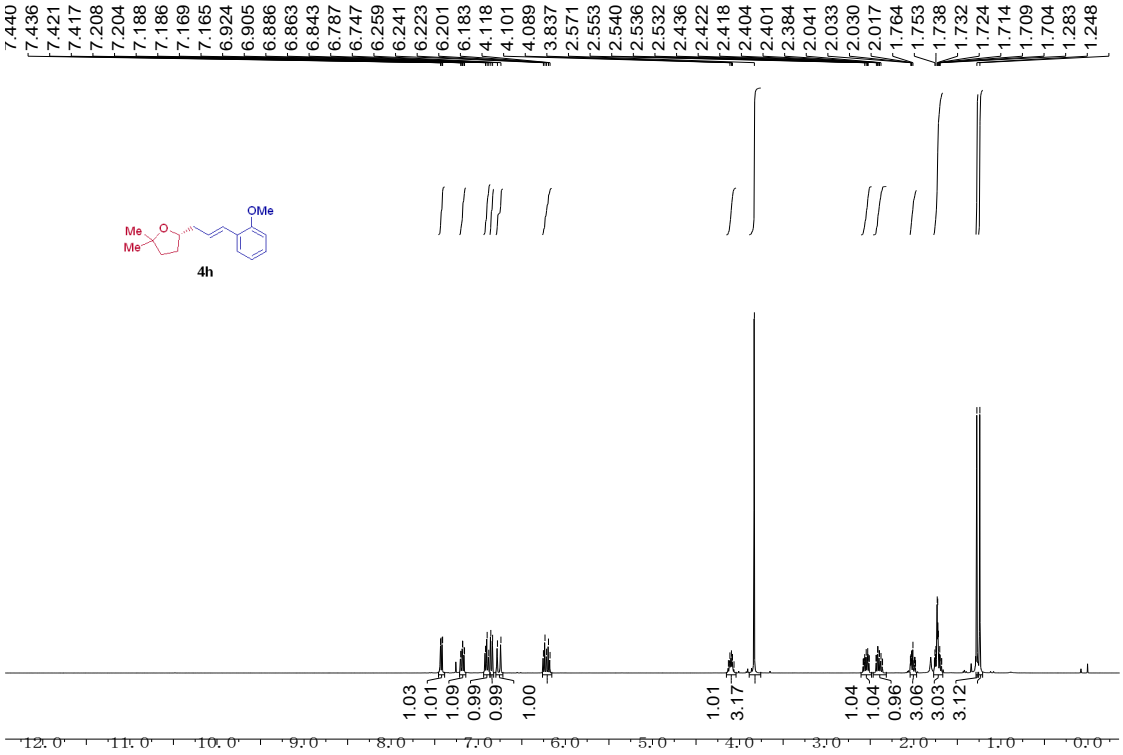
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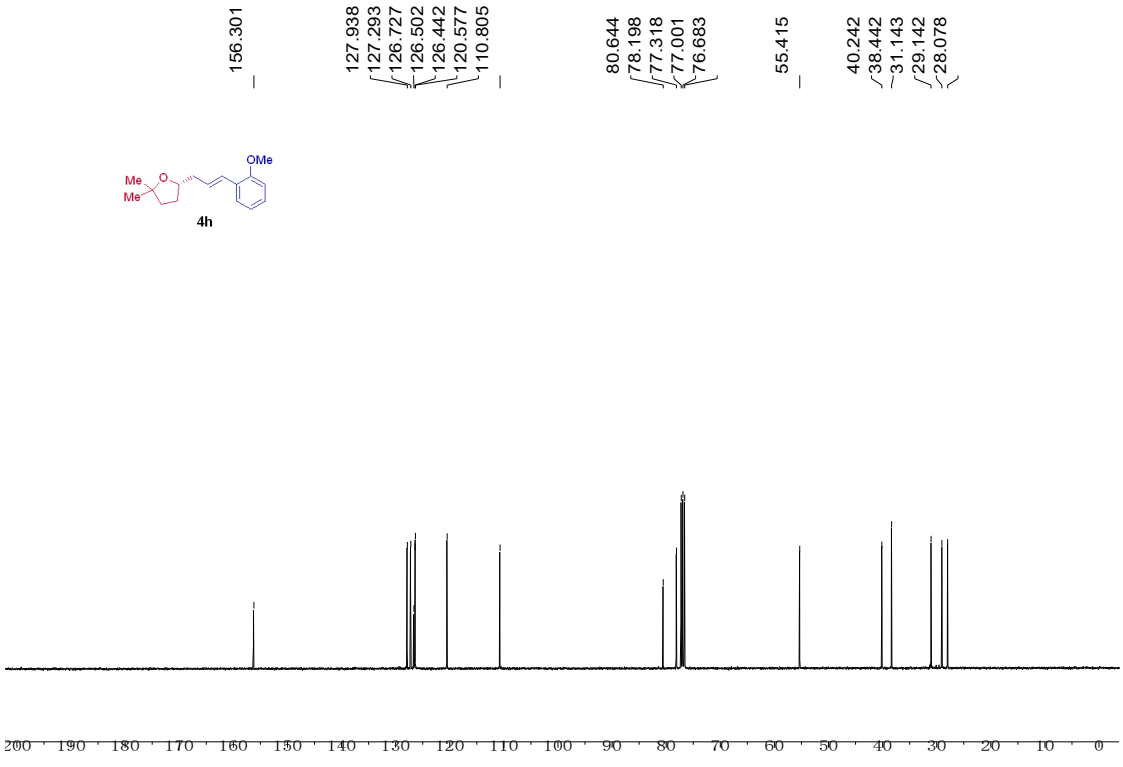
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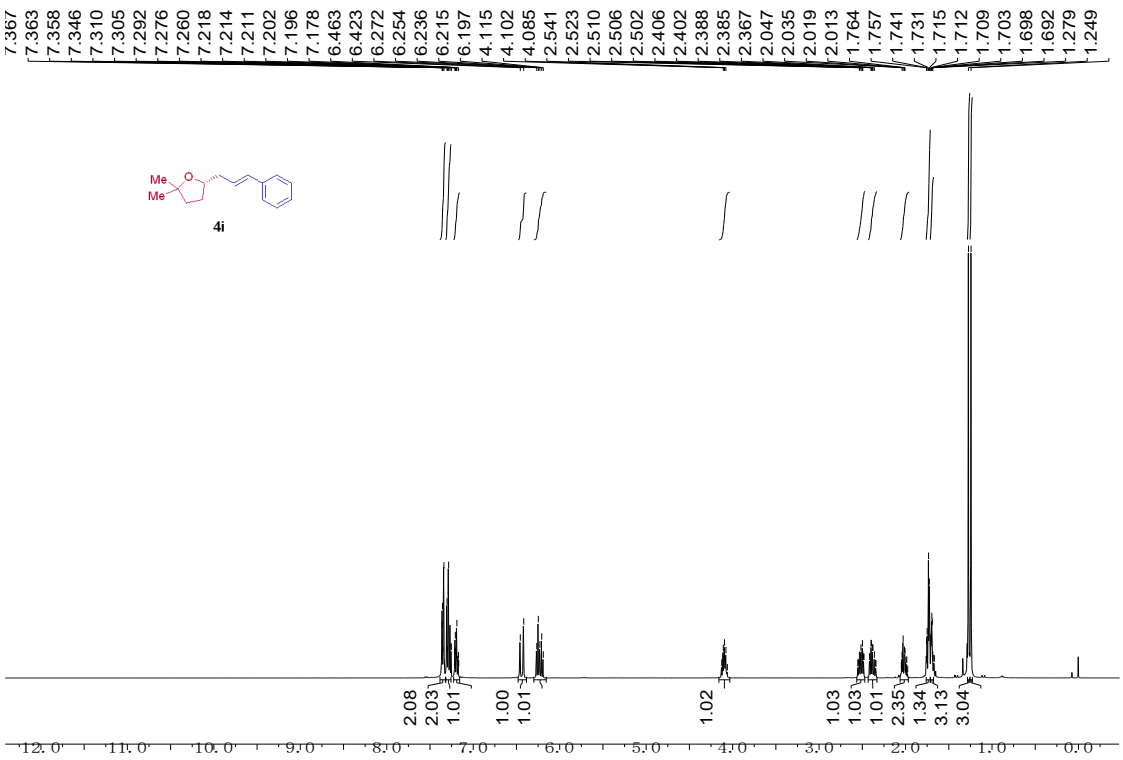
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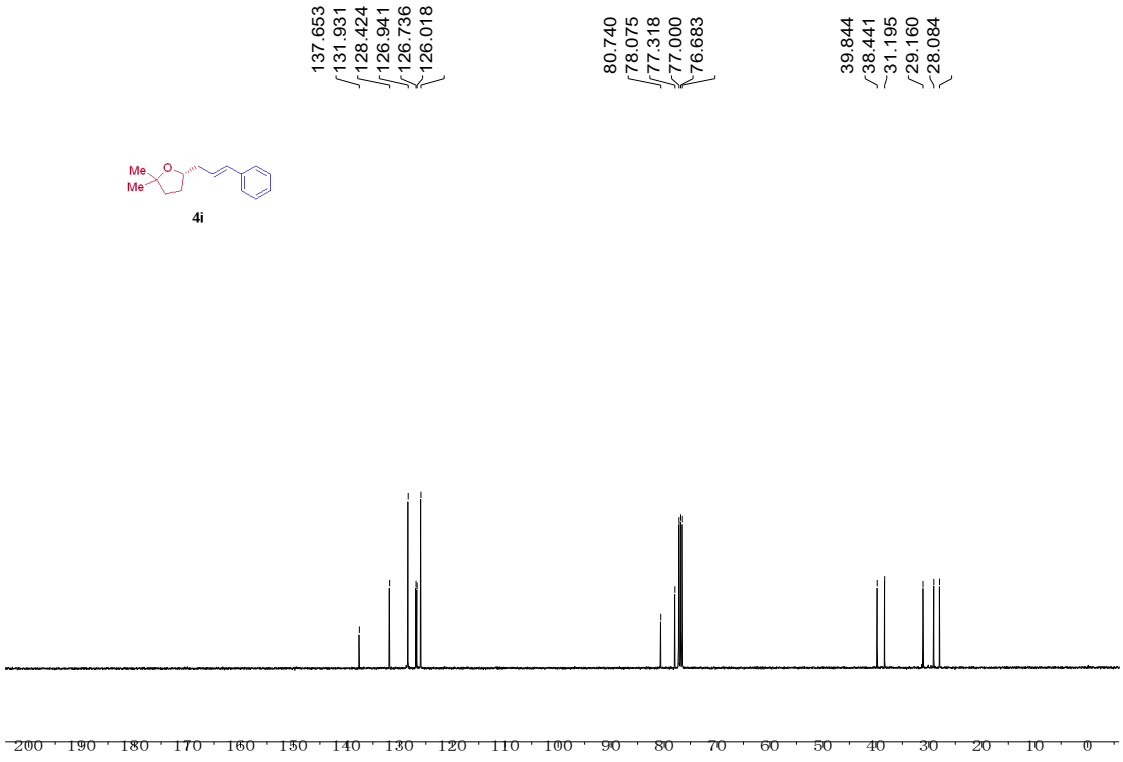
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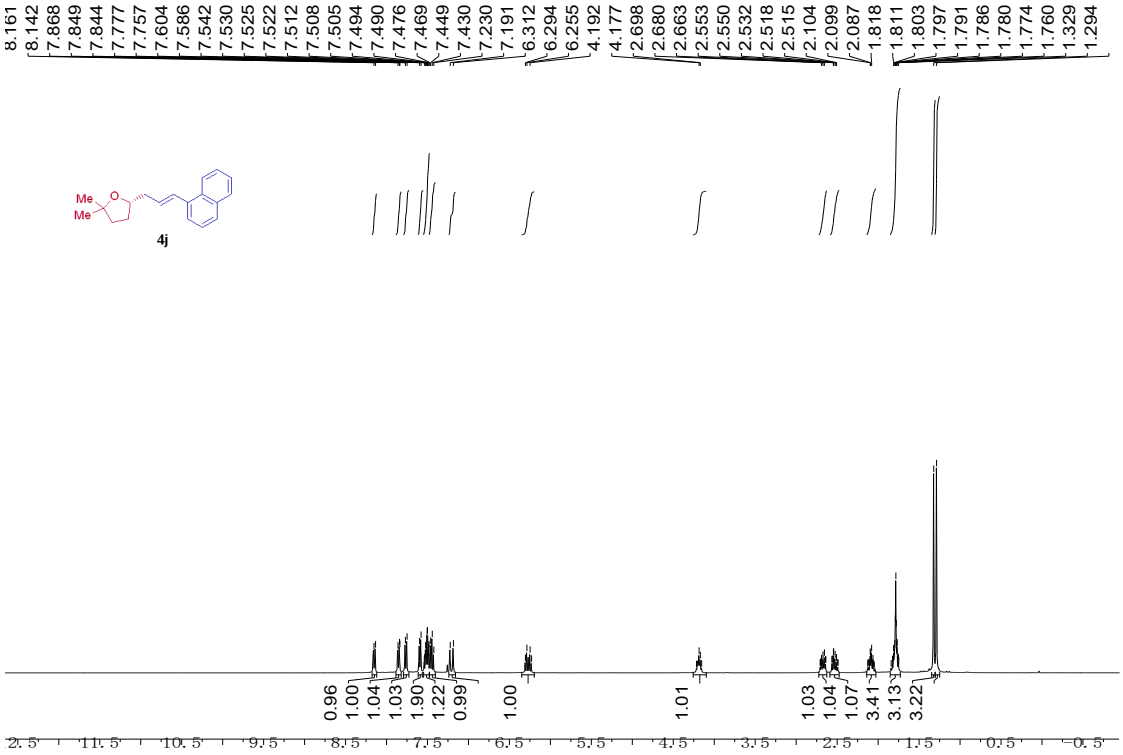
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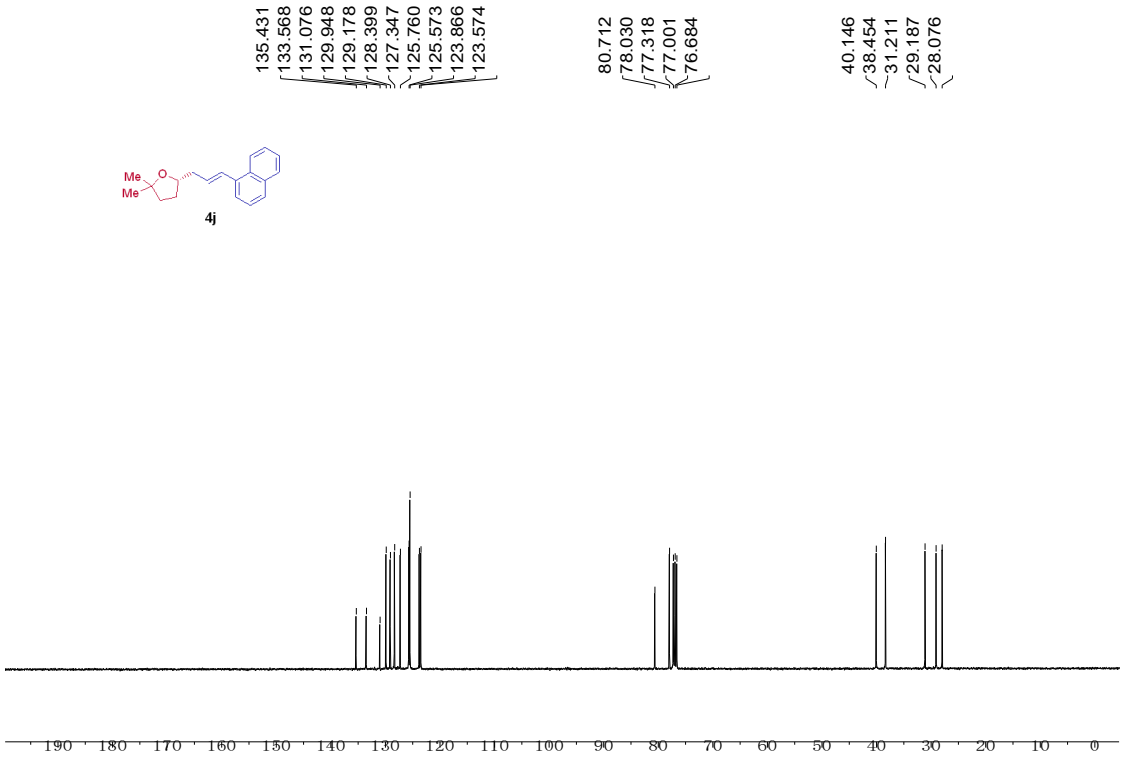
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O
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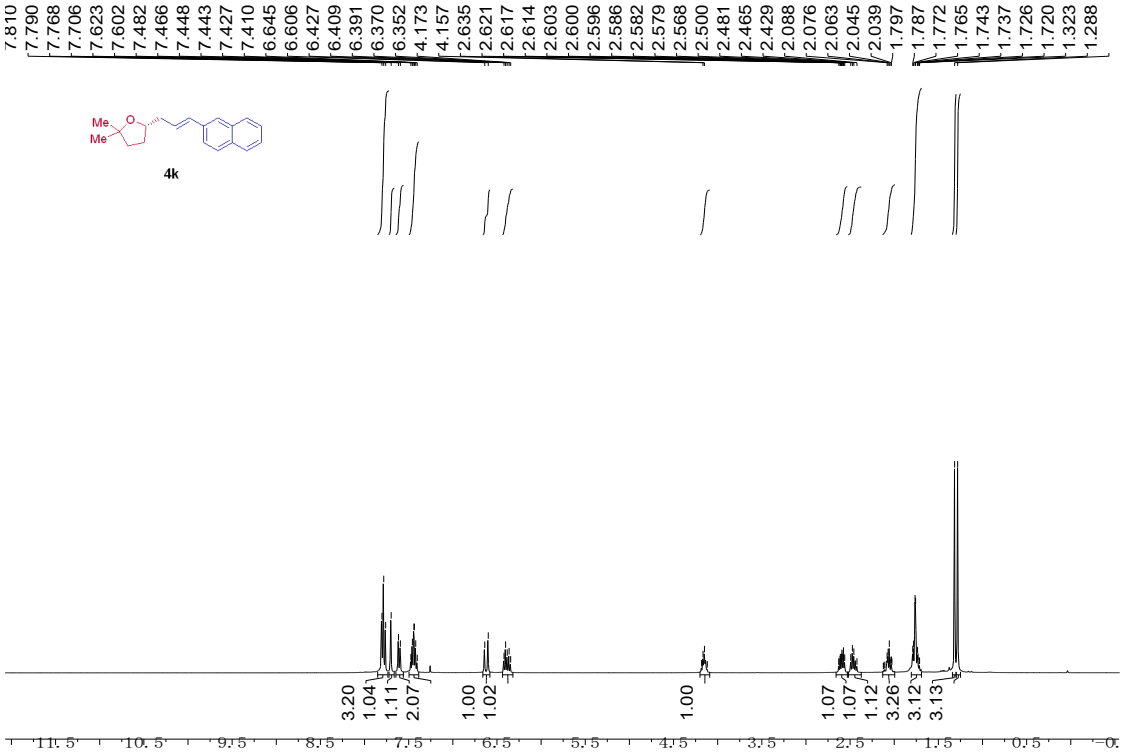
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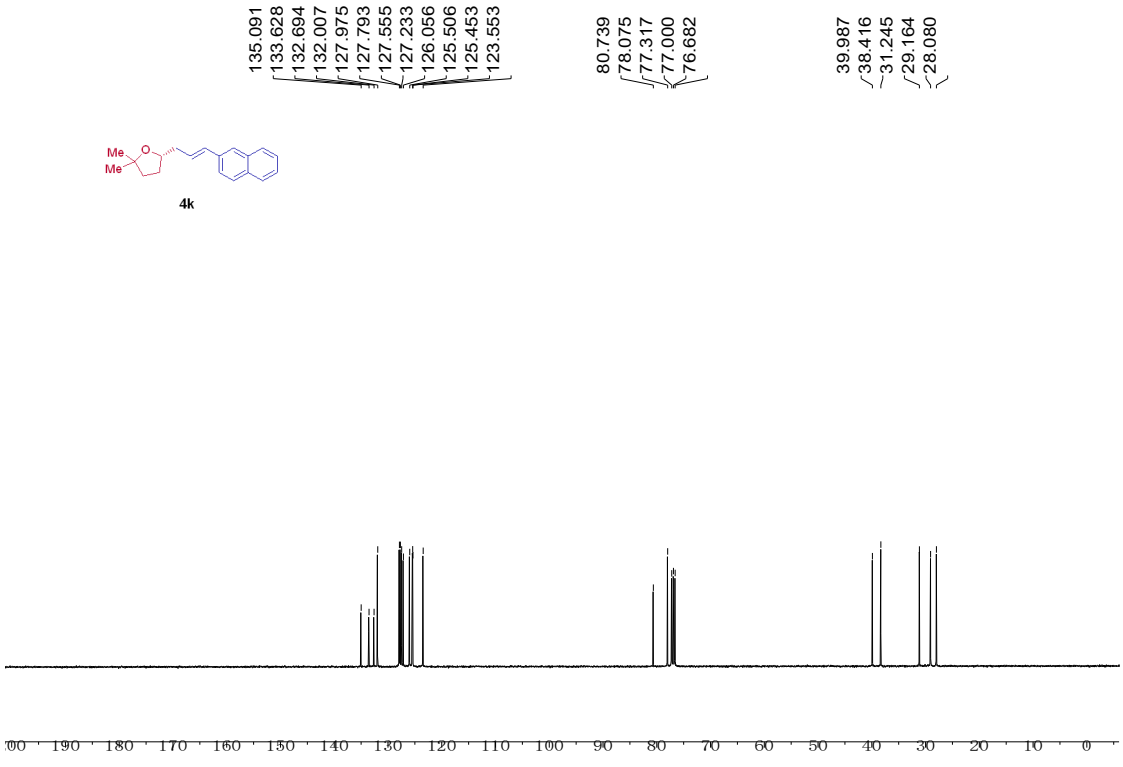
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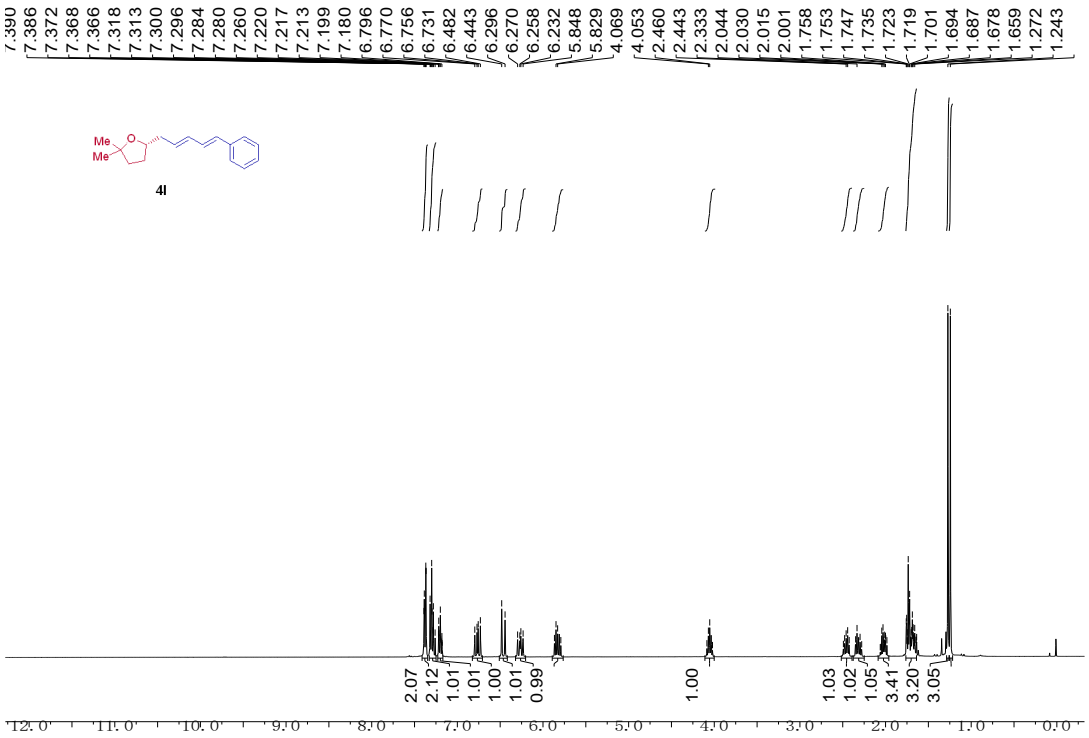
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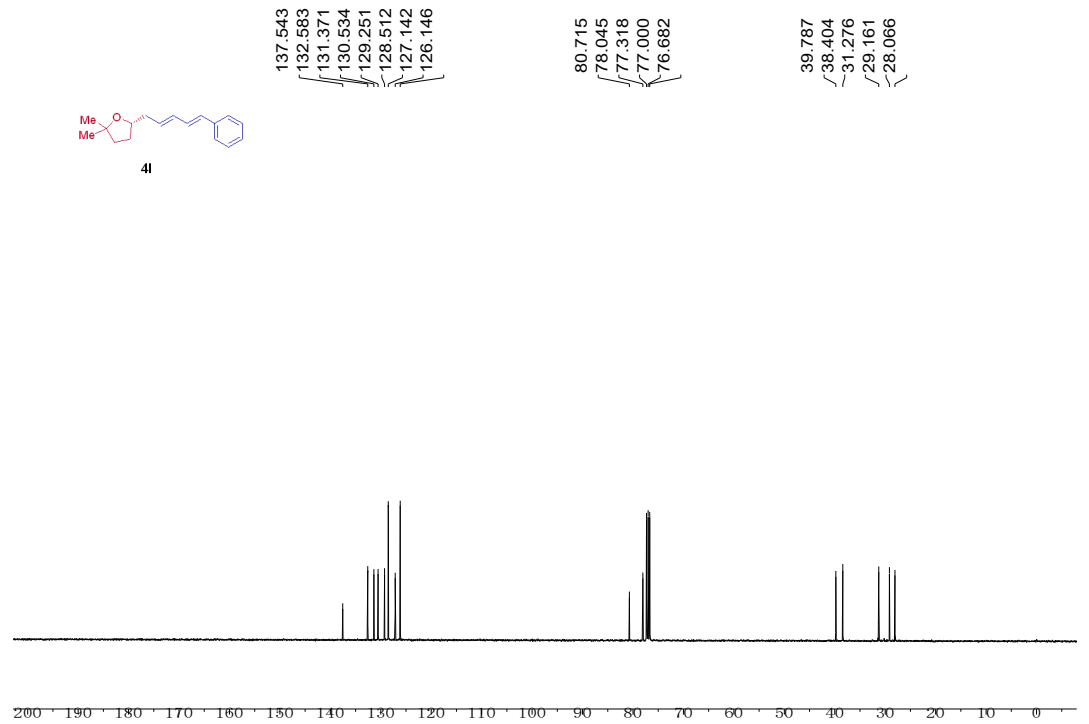
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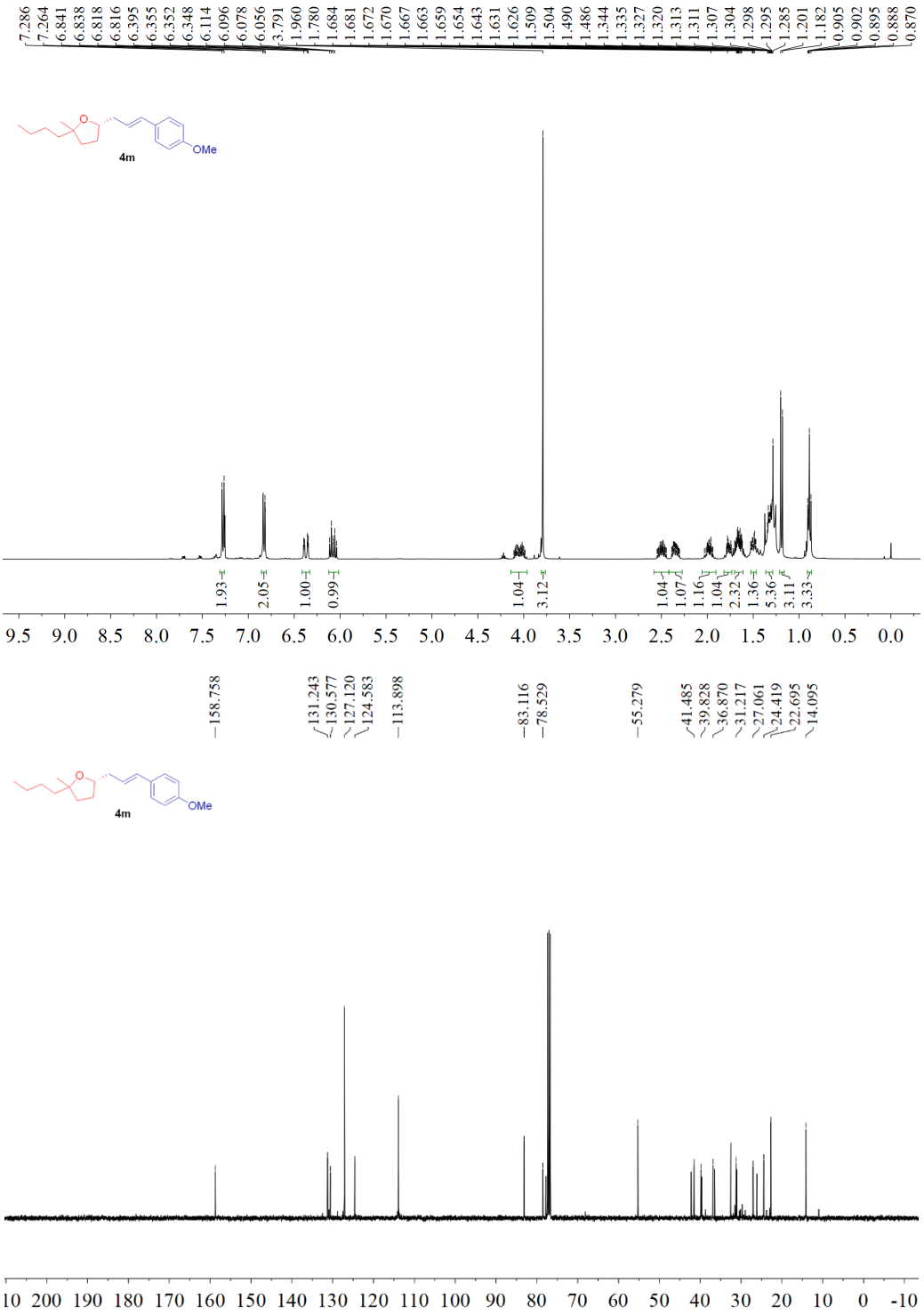
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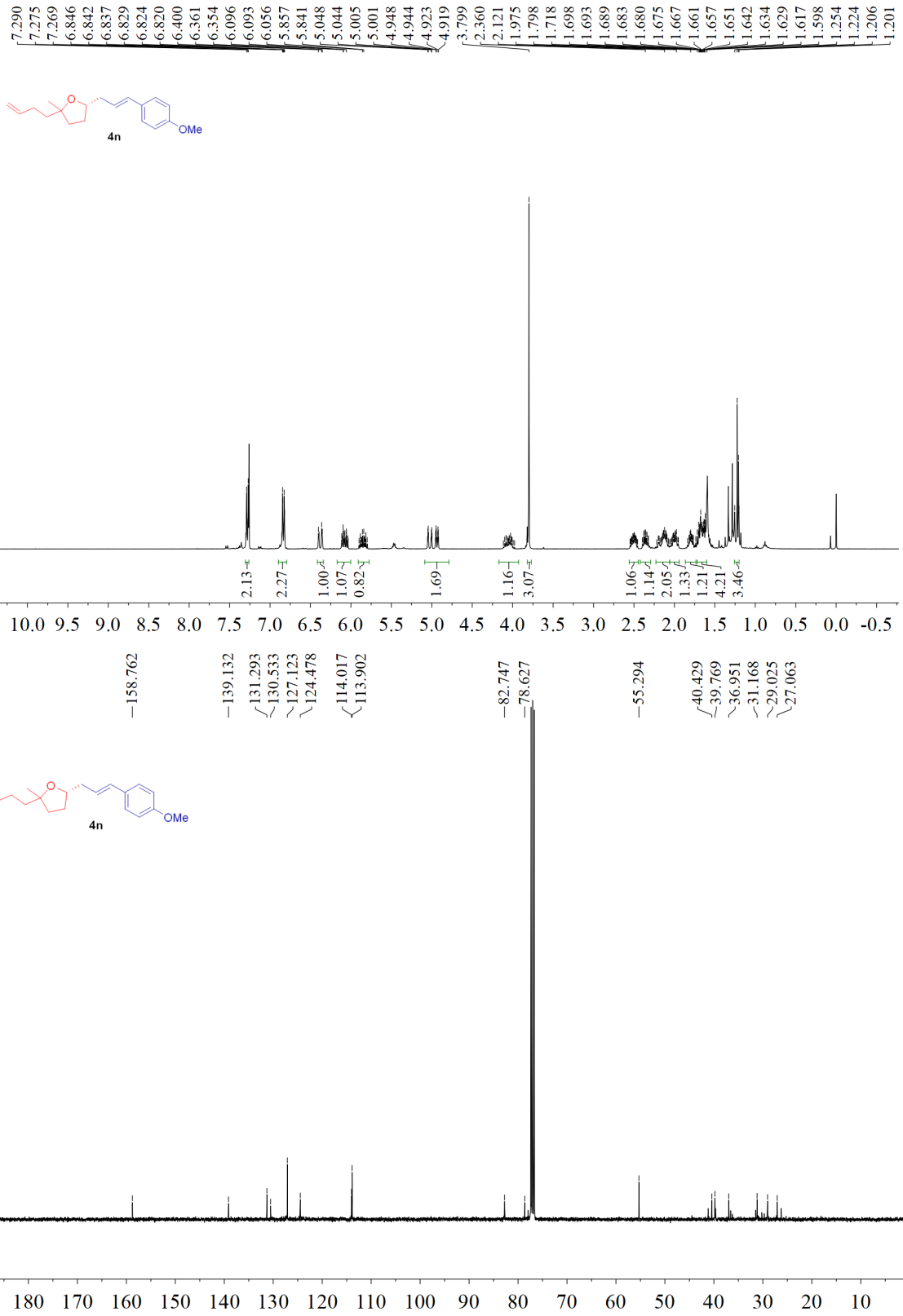
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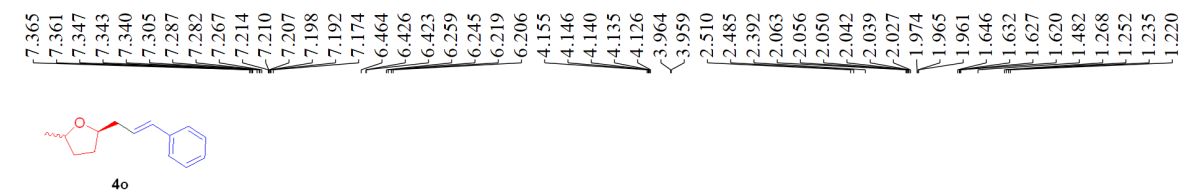
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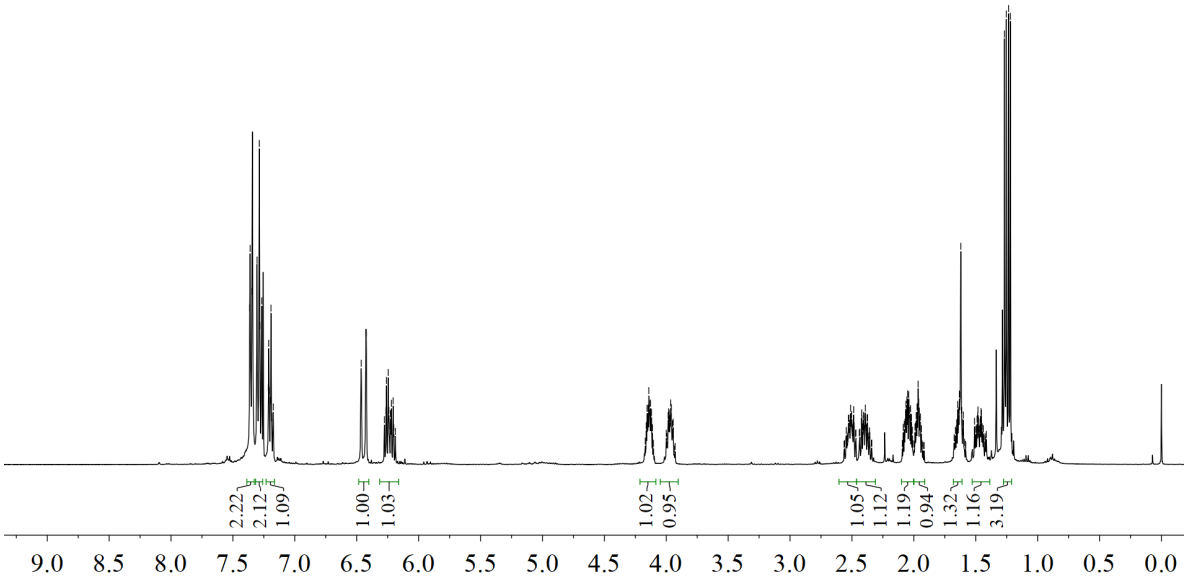
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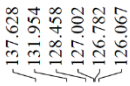
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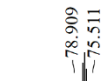
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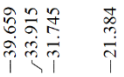
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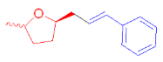

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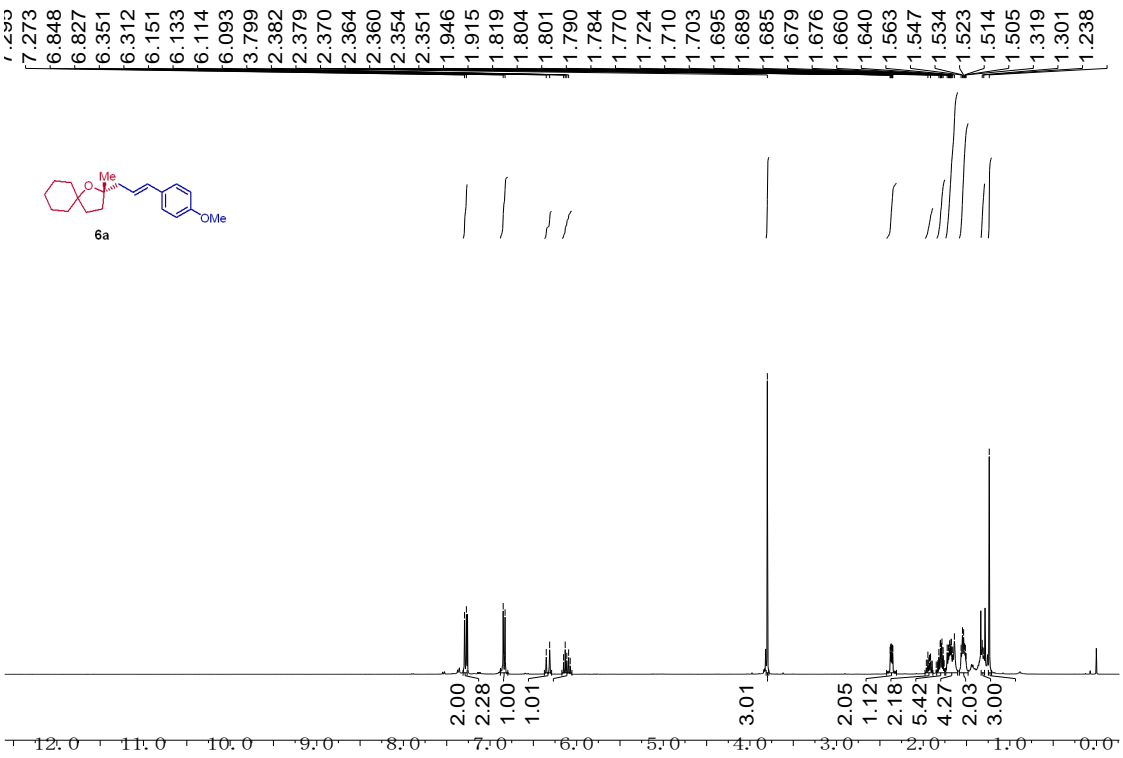
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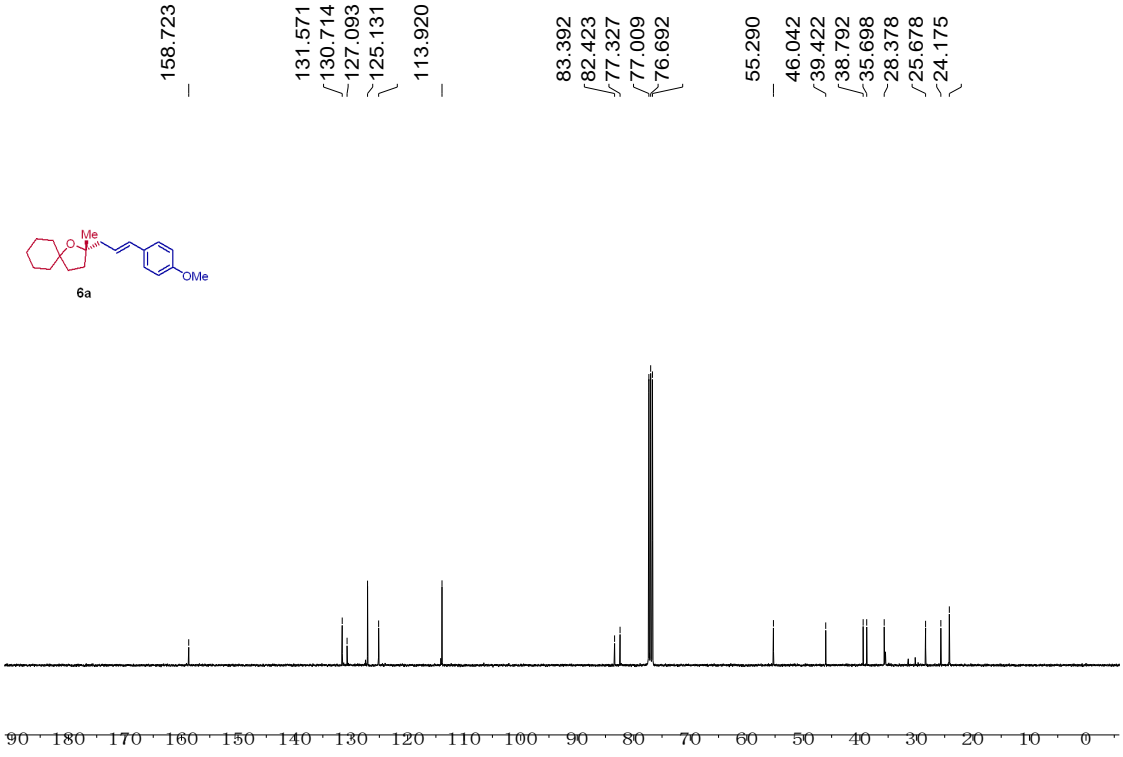
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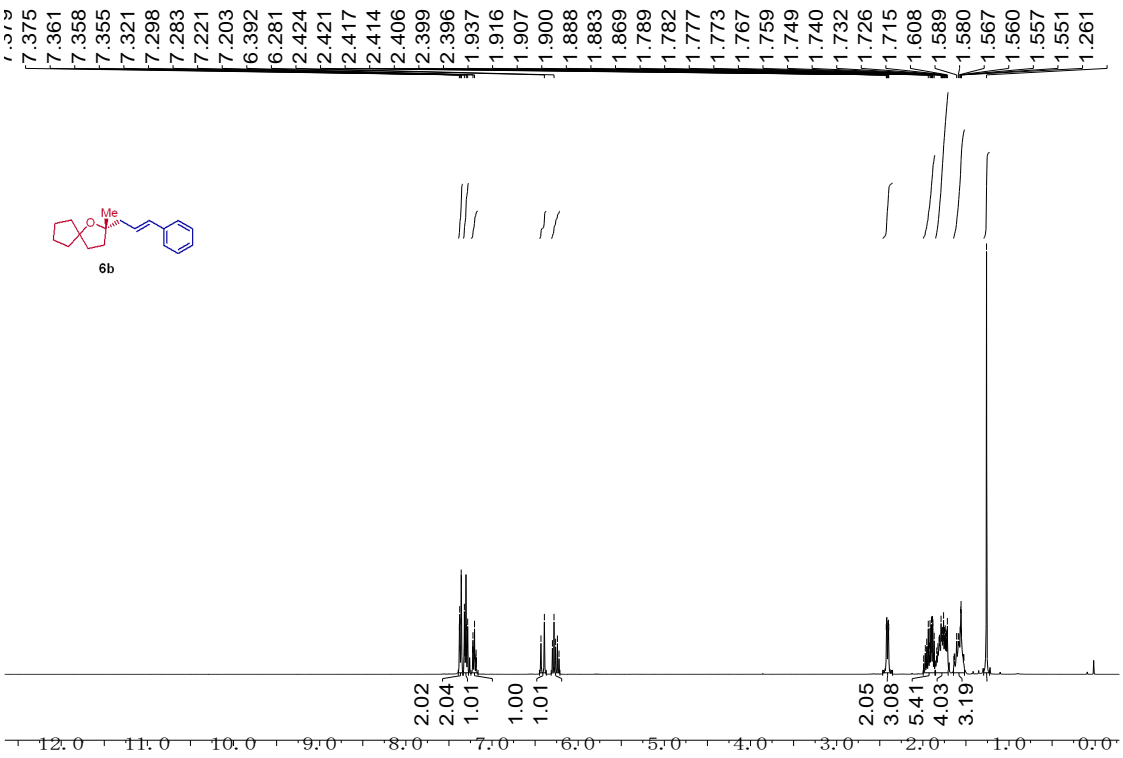
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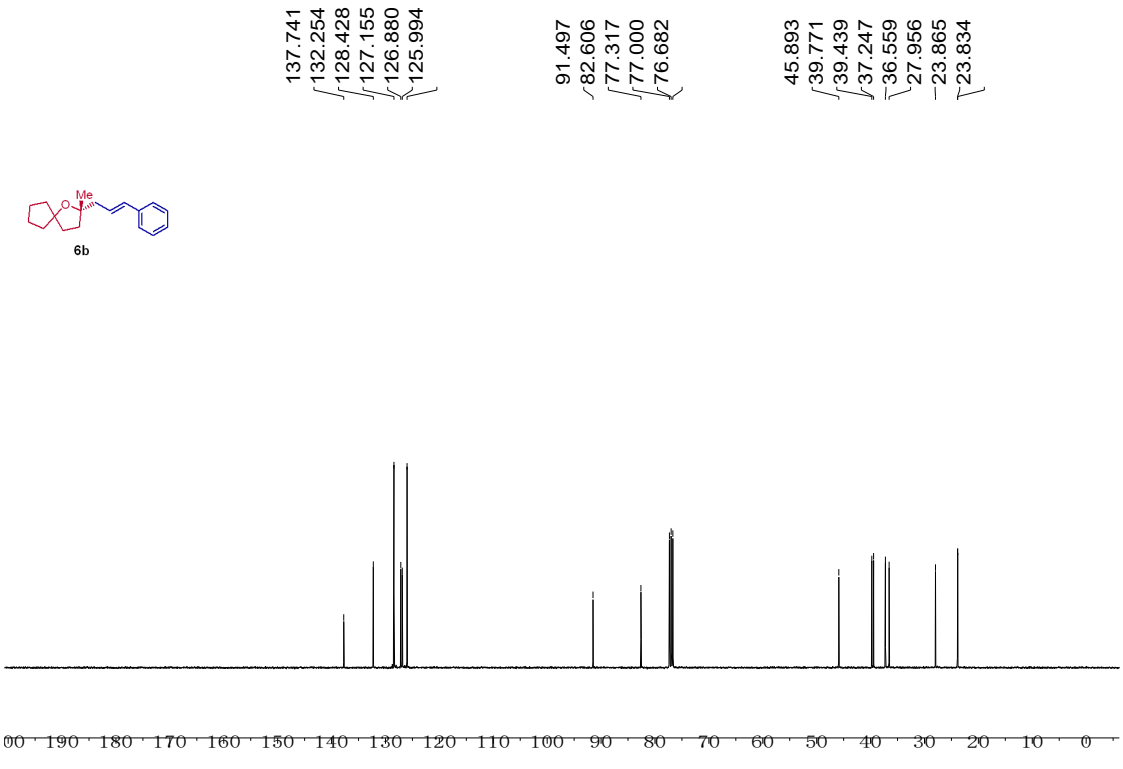
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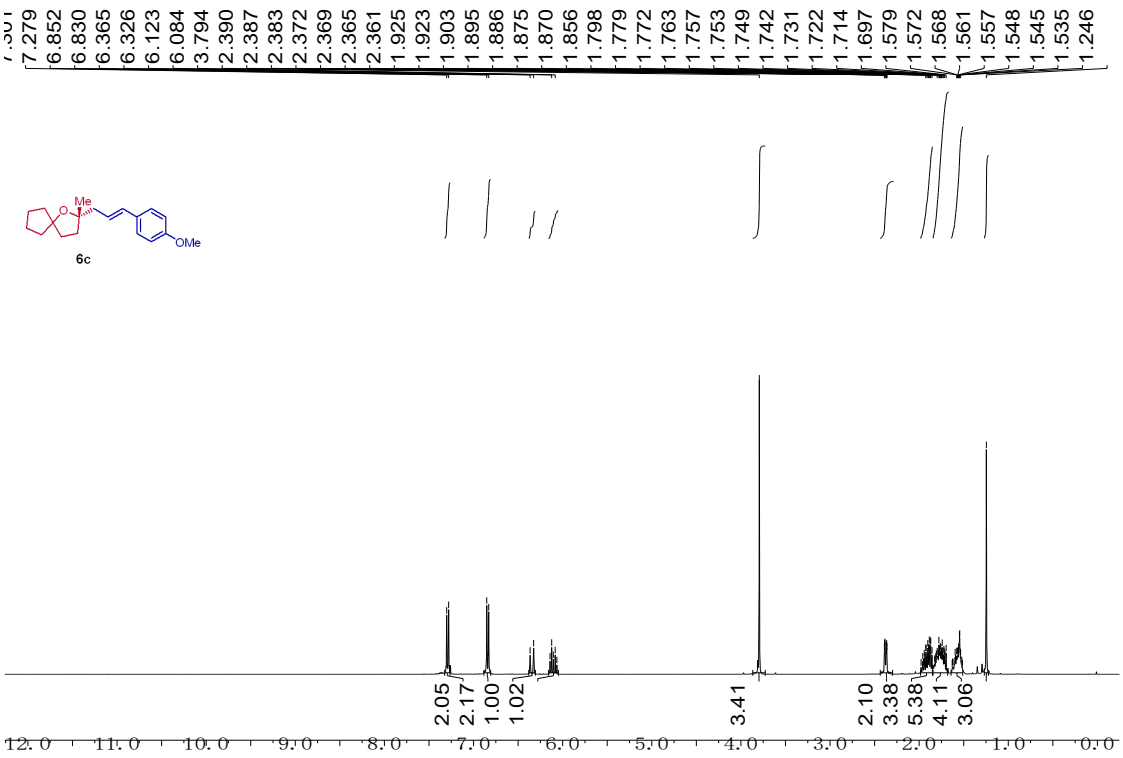
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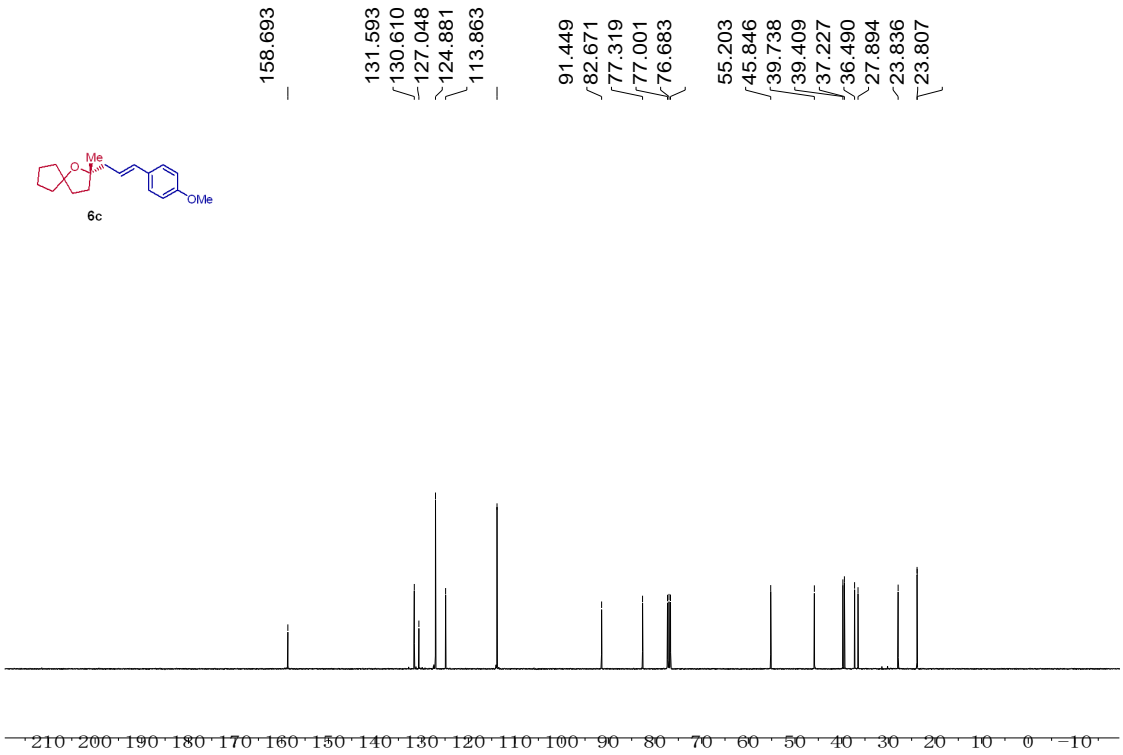
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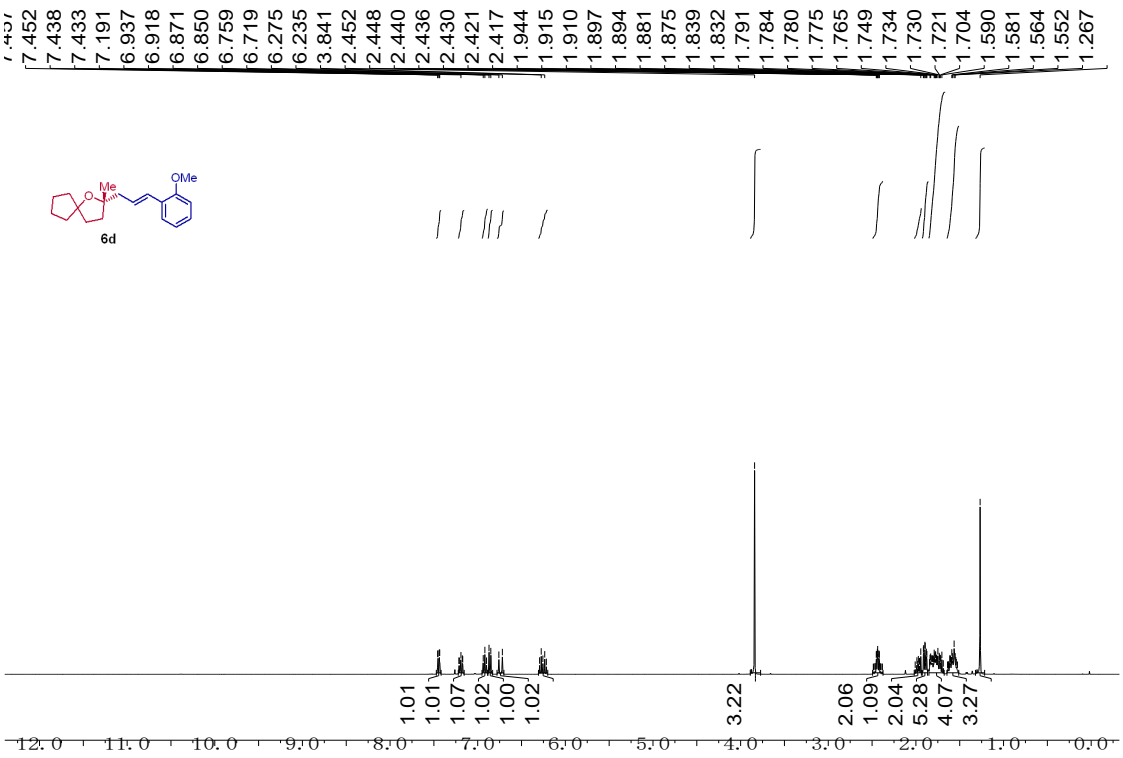
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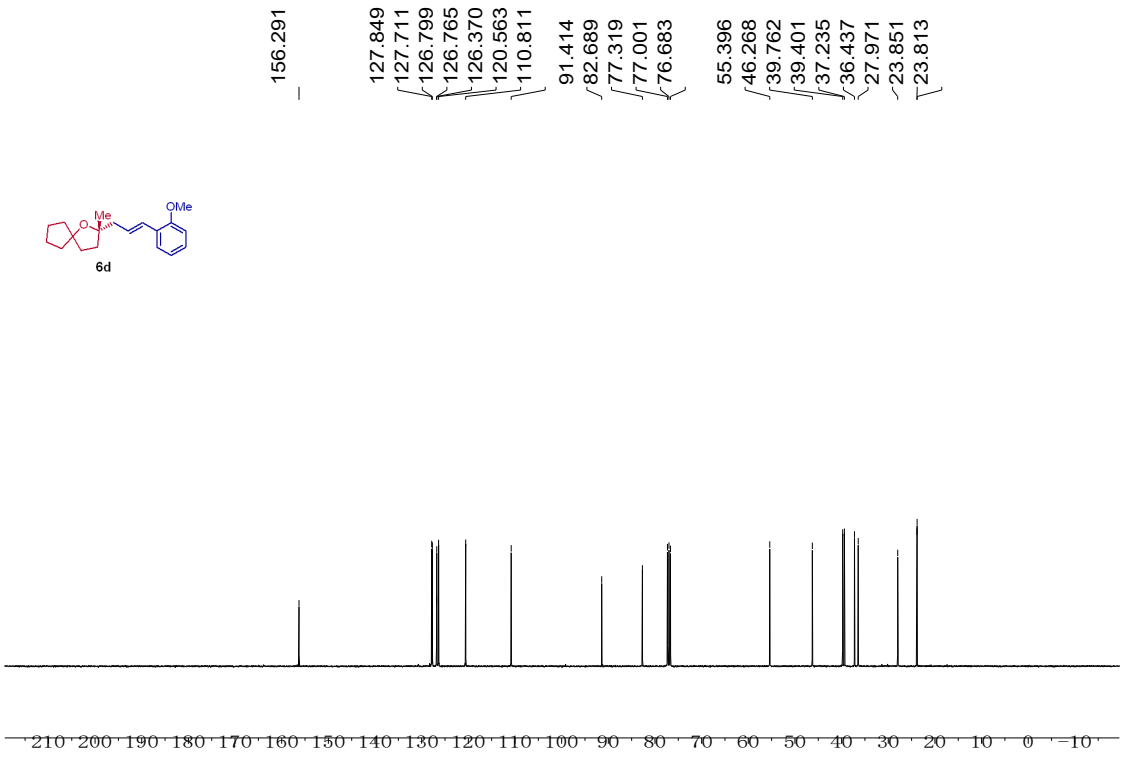
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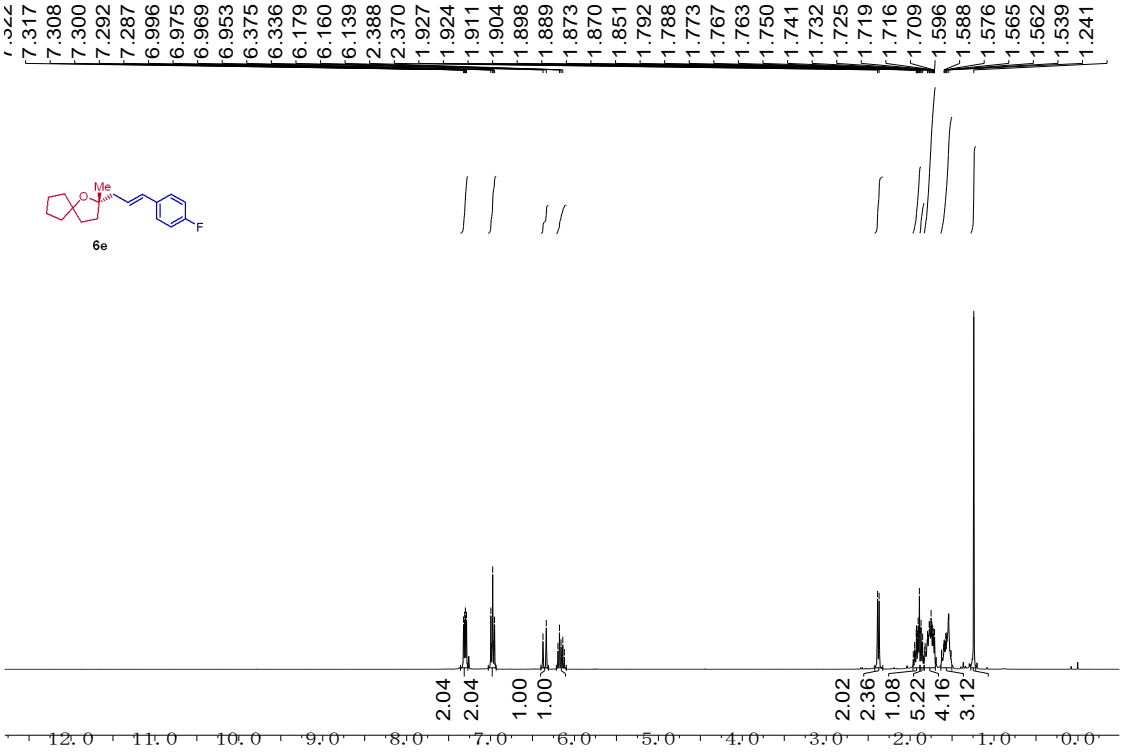
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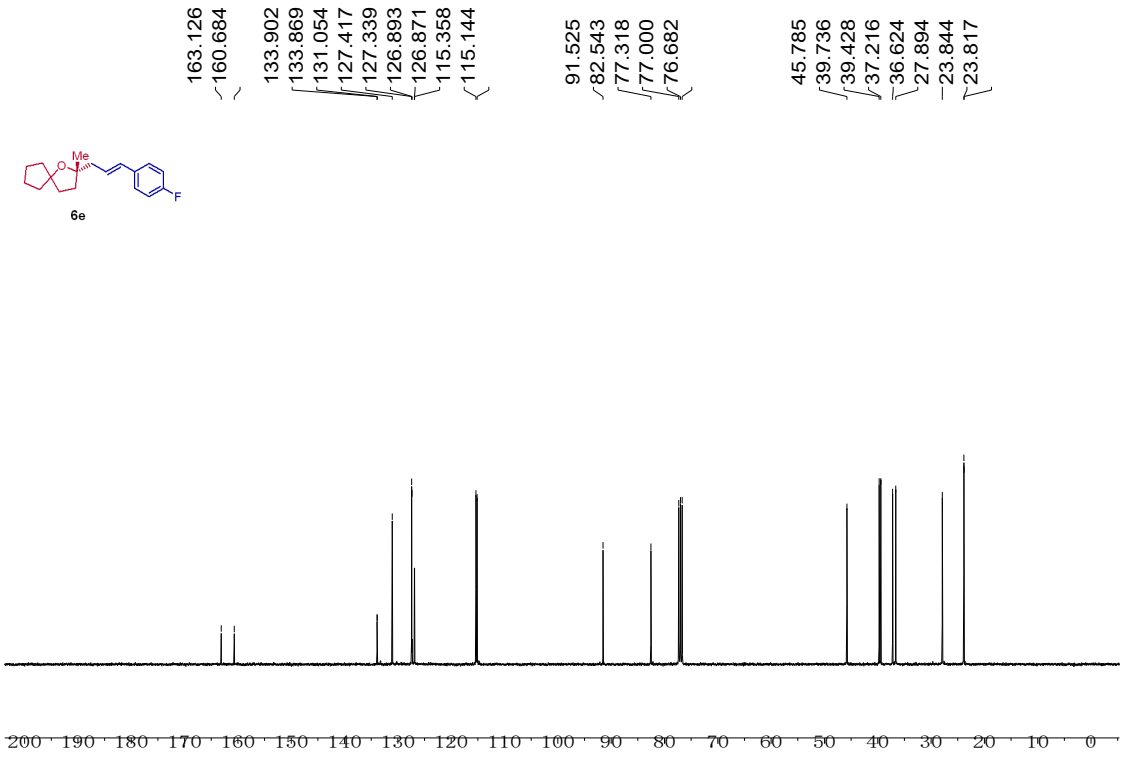
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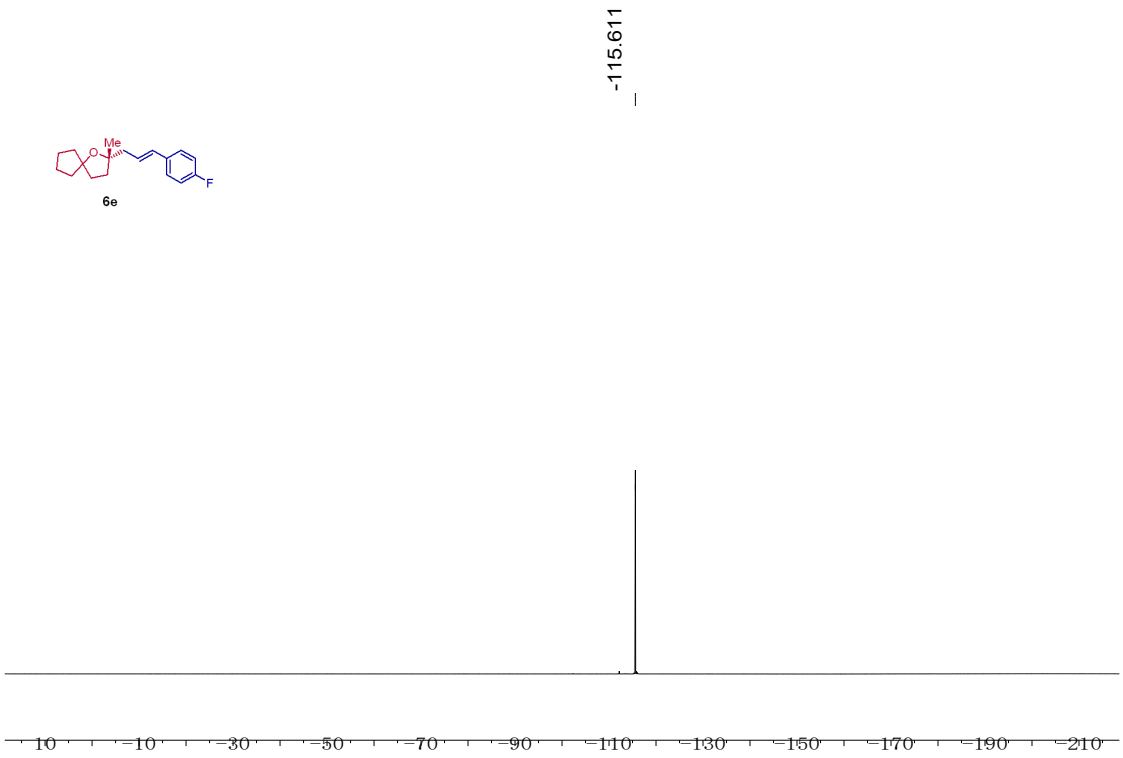
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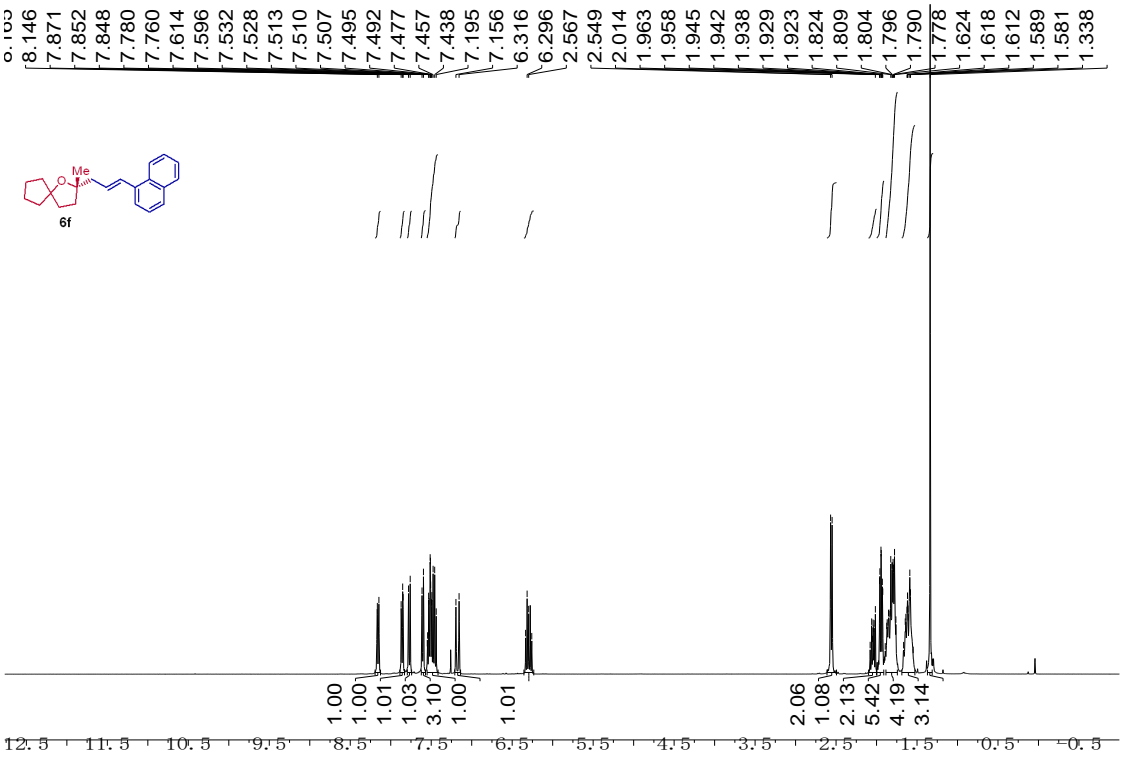
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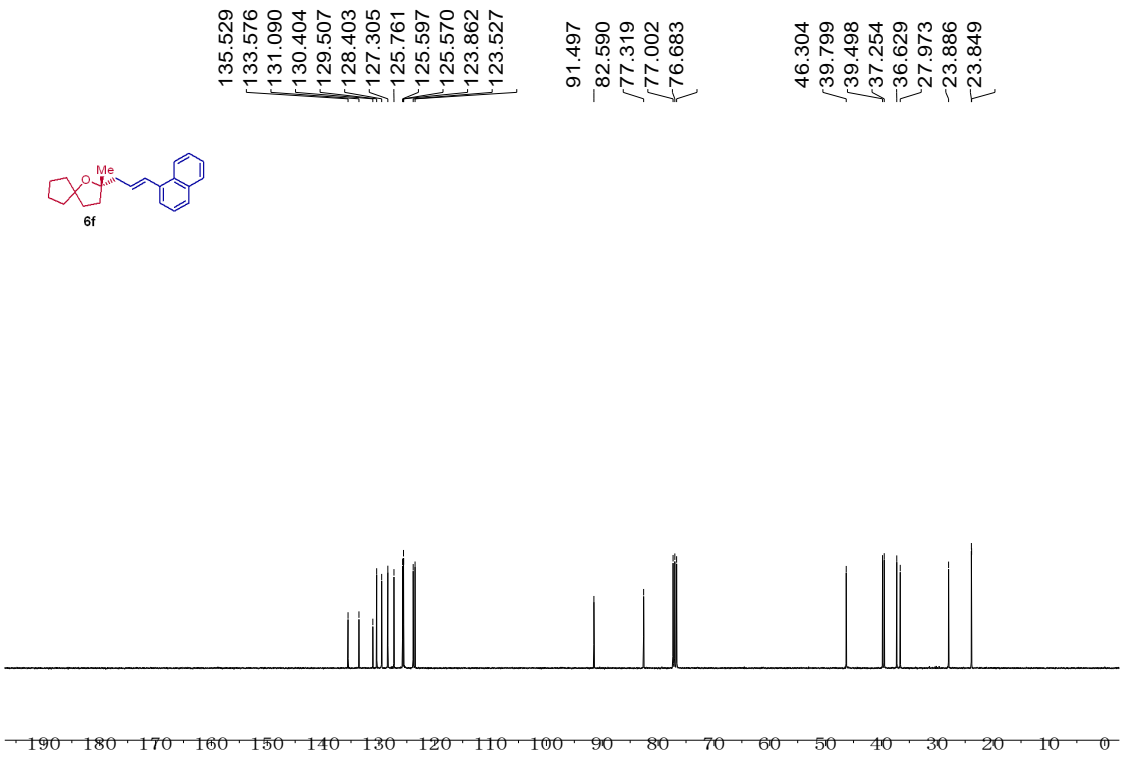
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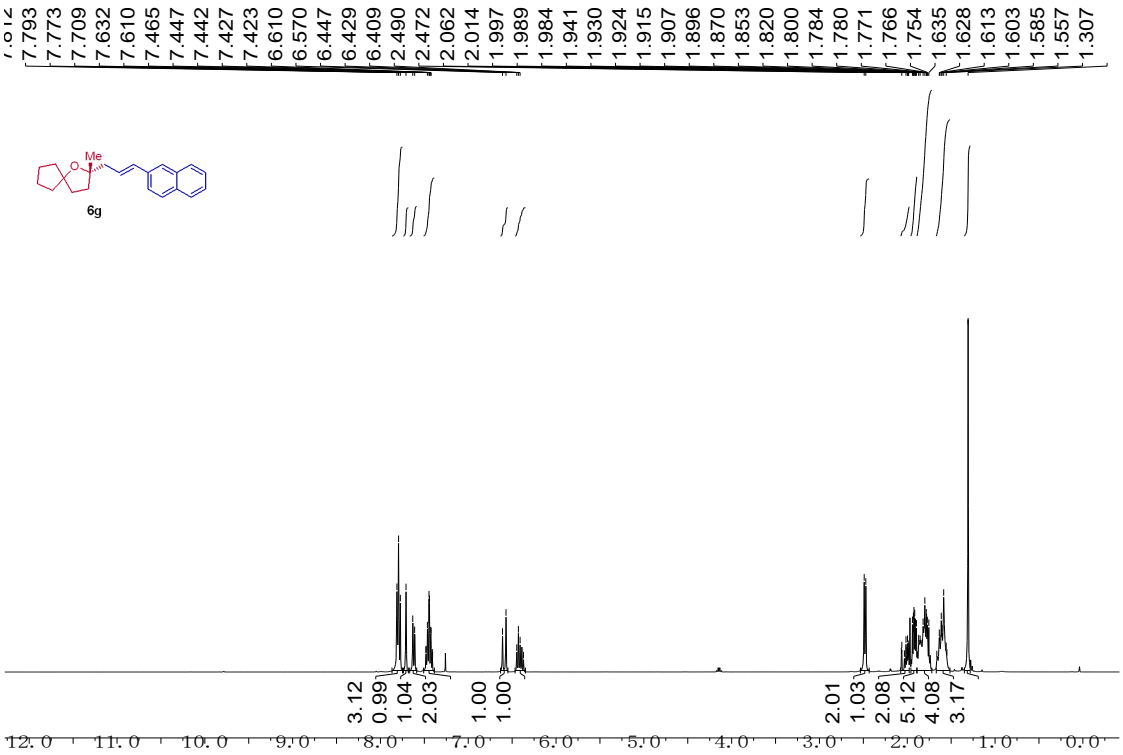
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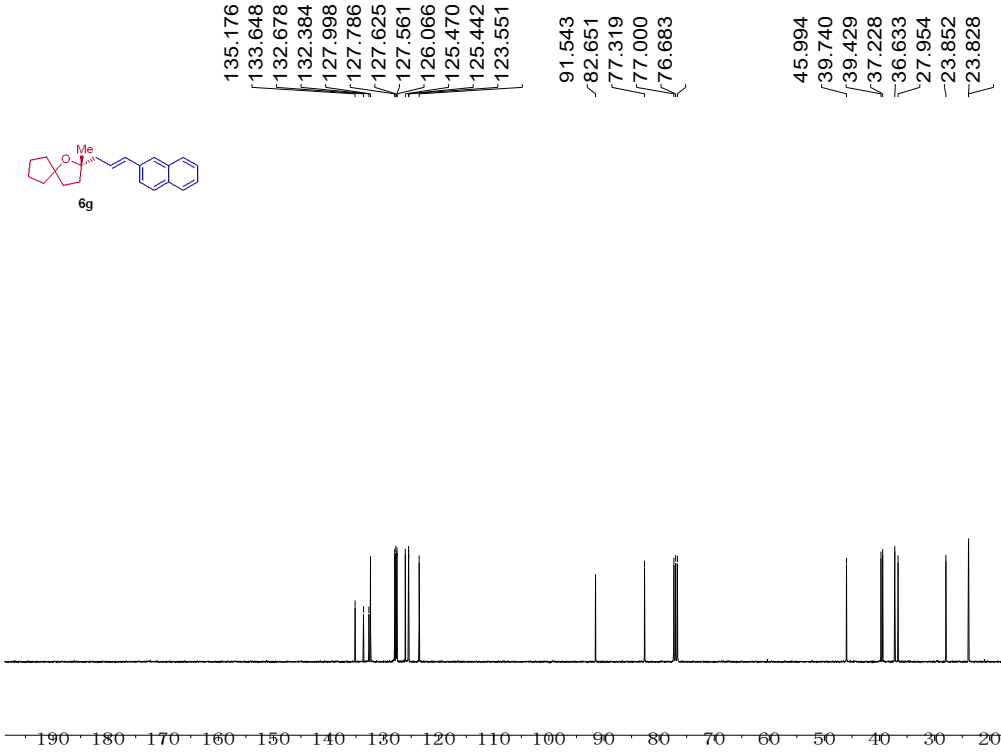
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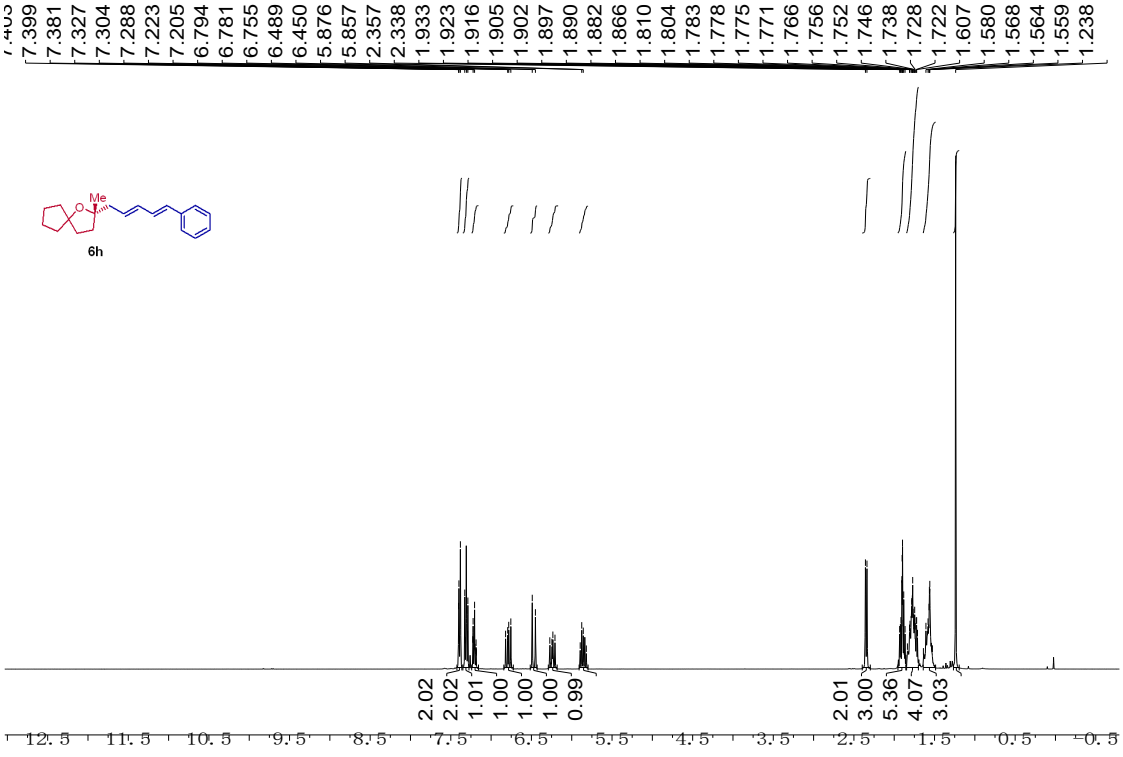
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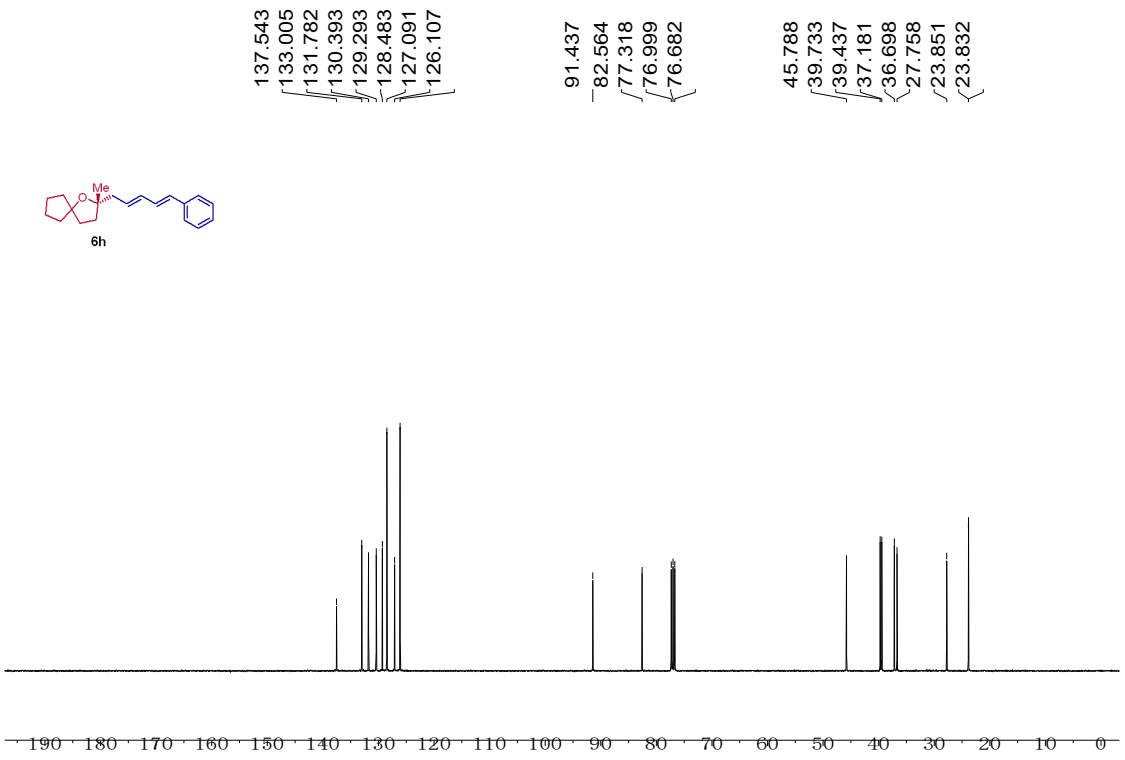
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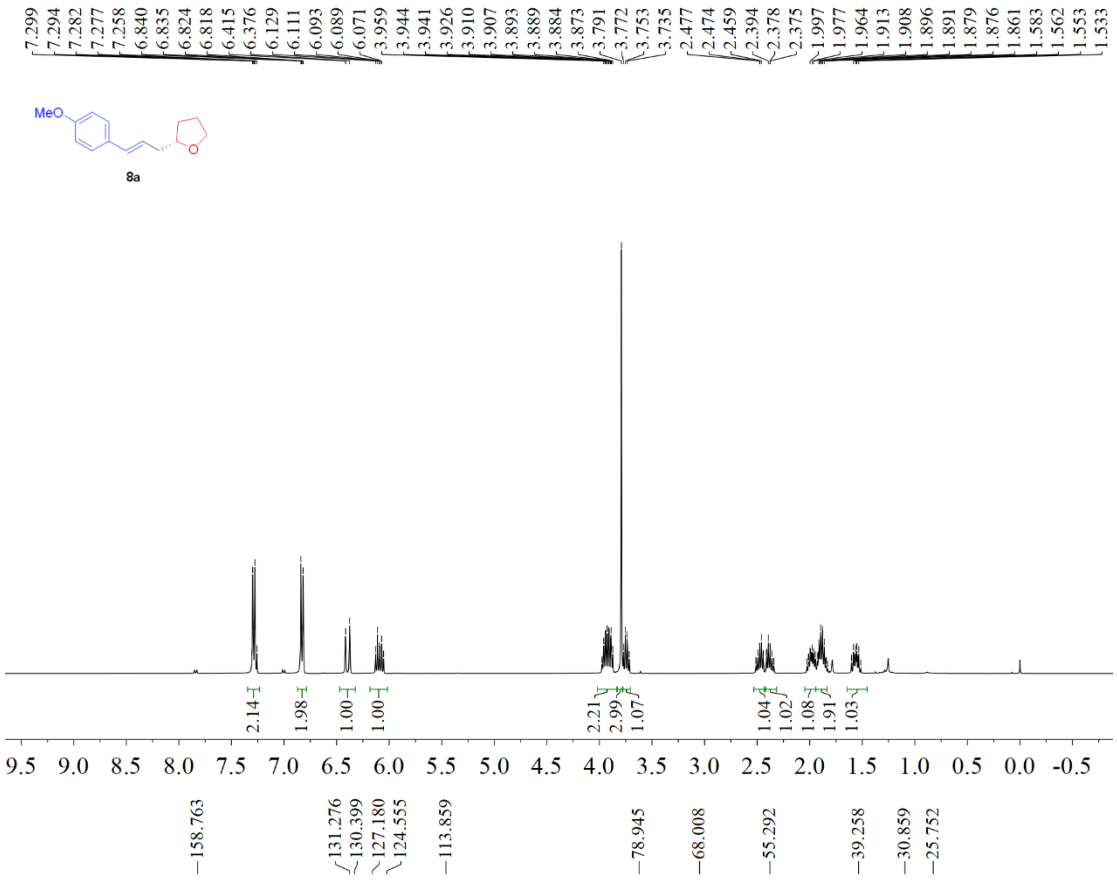
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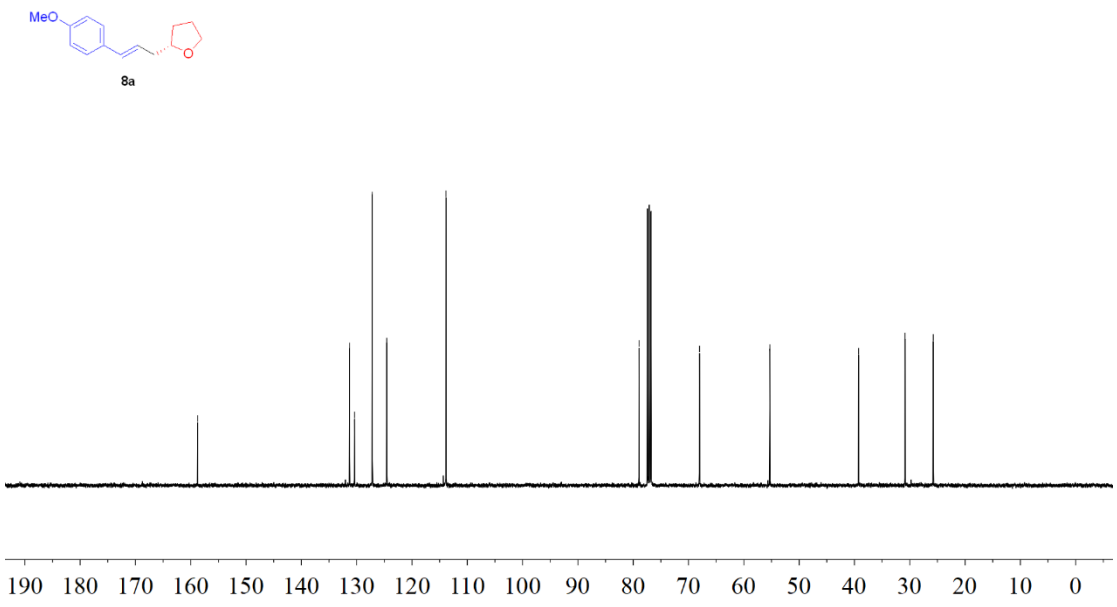
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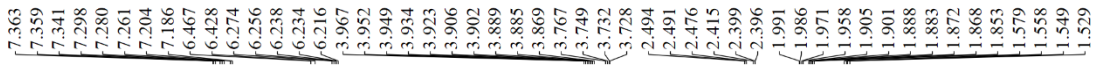
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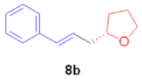
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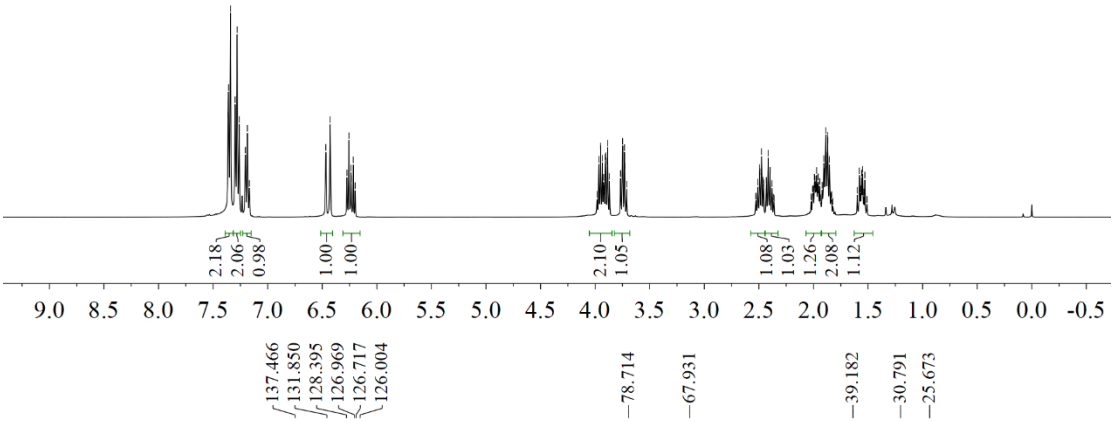
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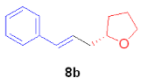
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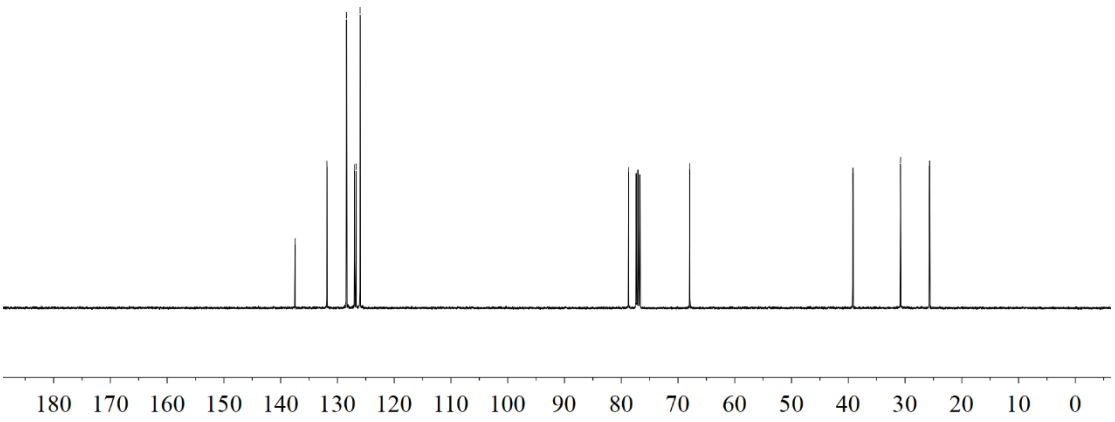
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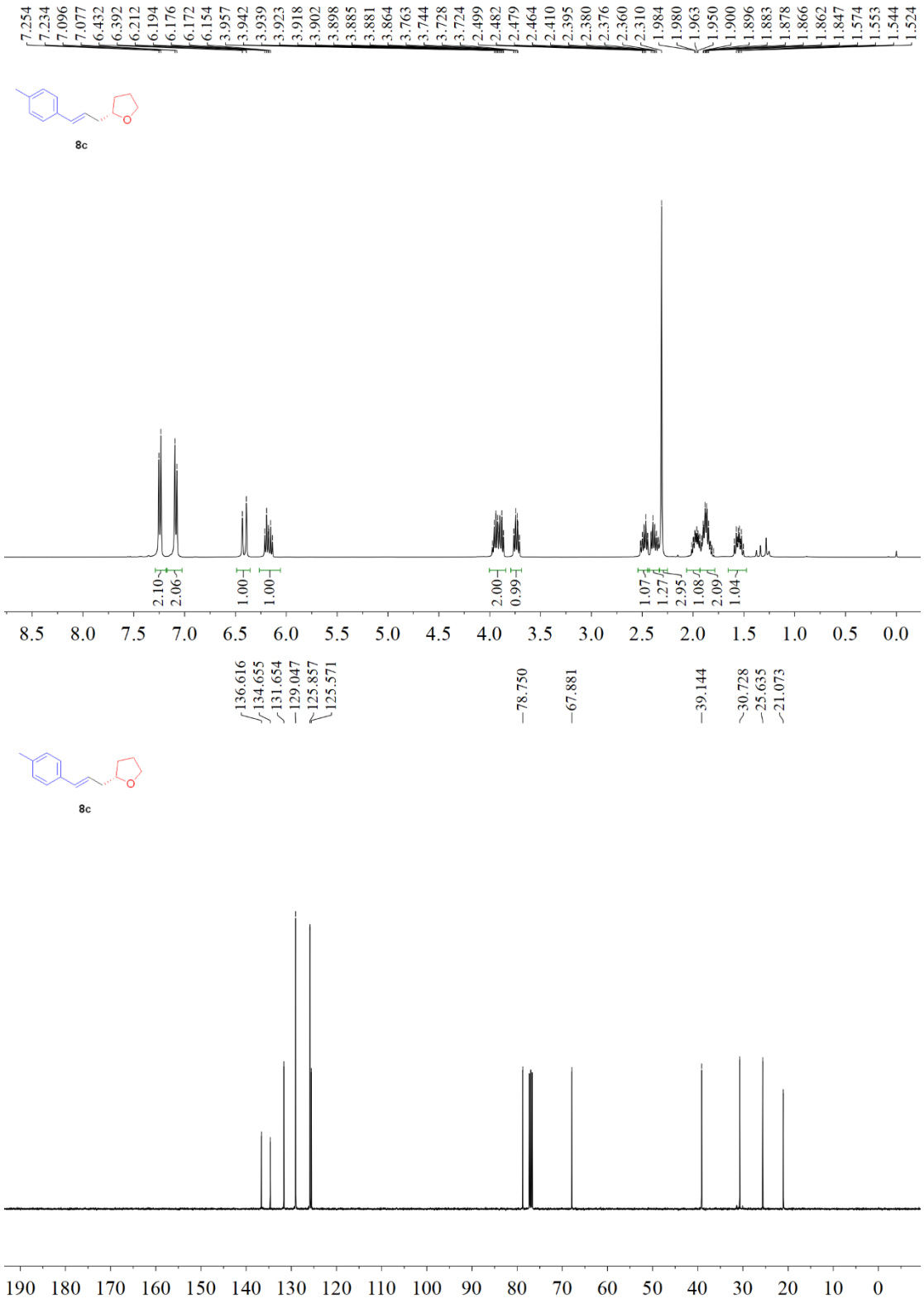
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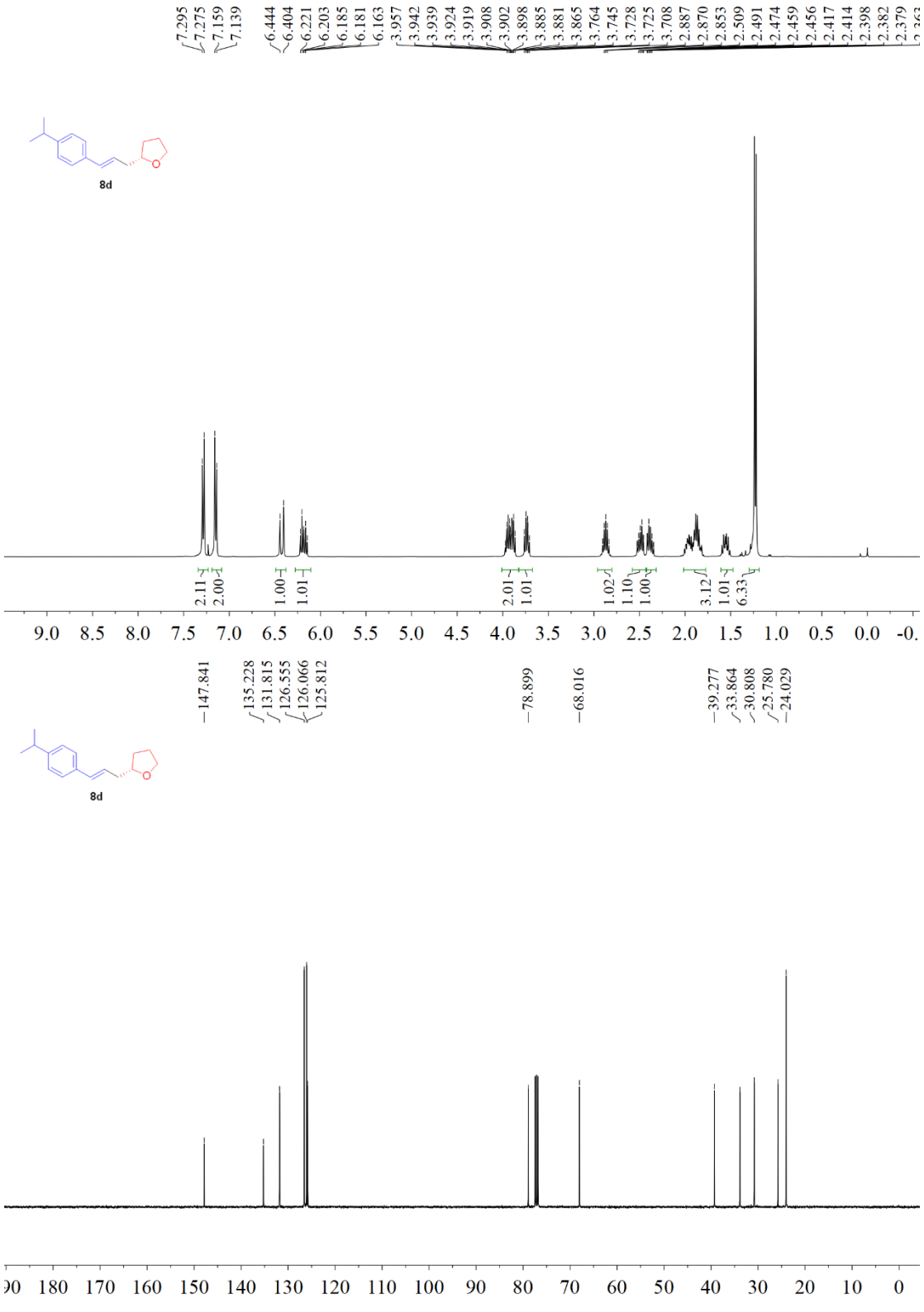
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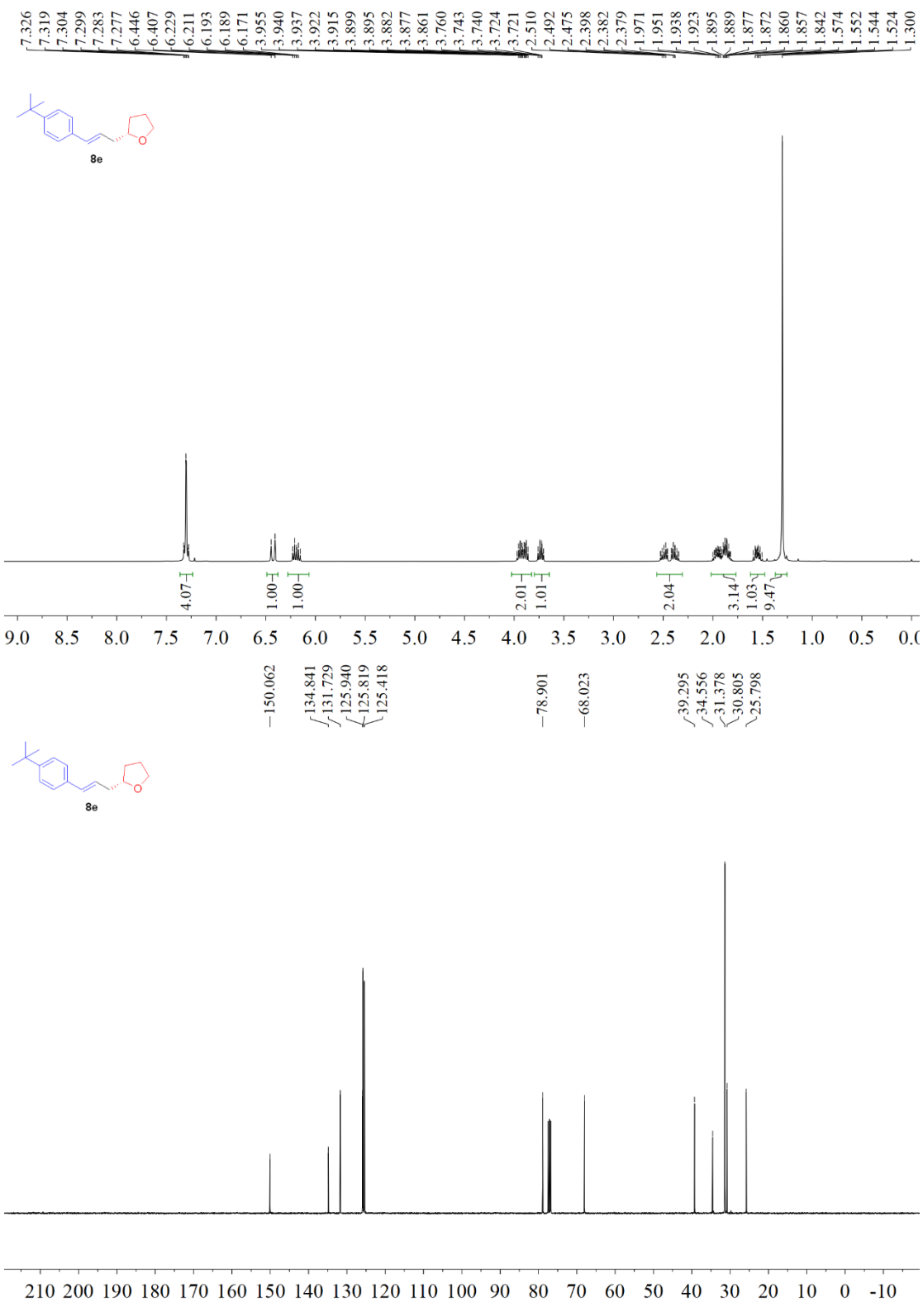
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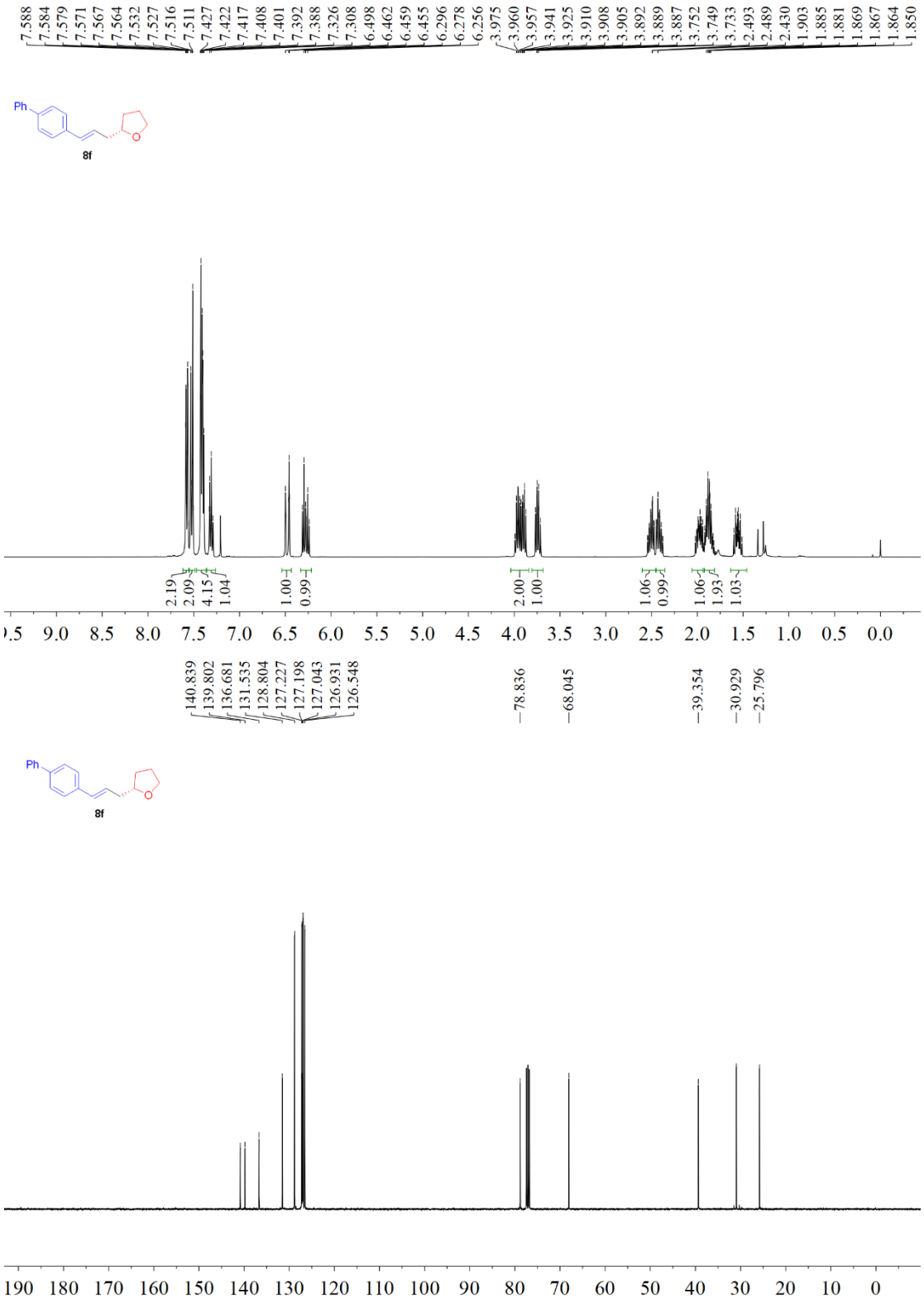
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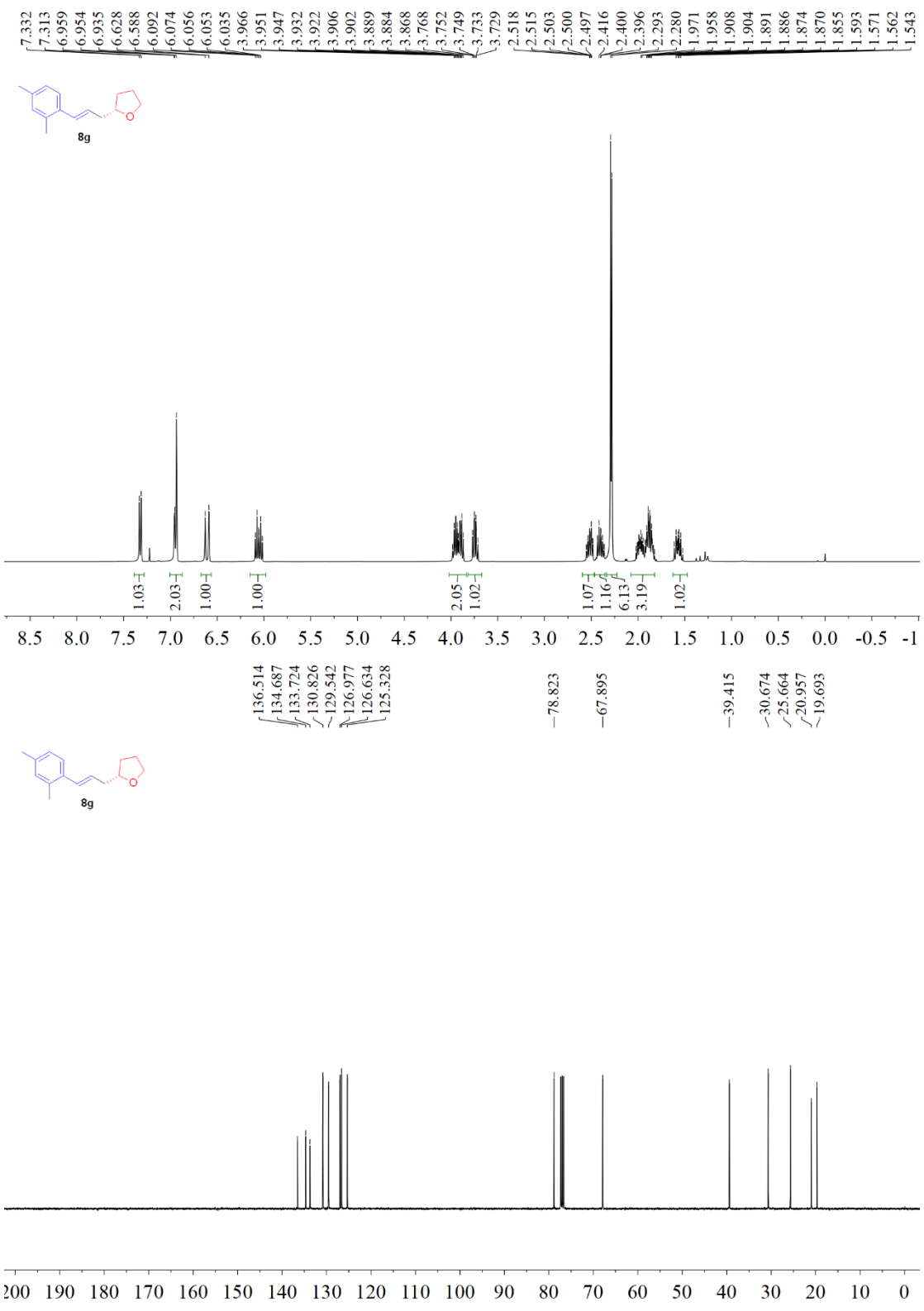
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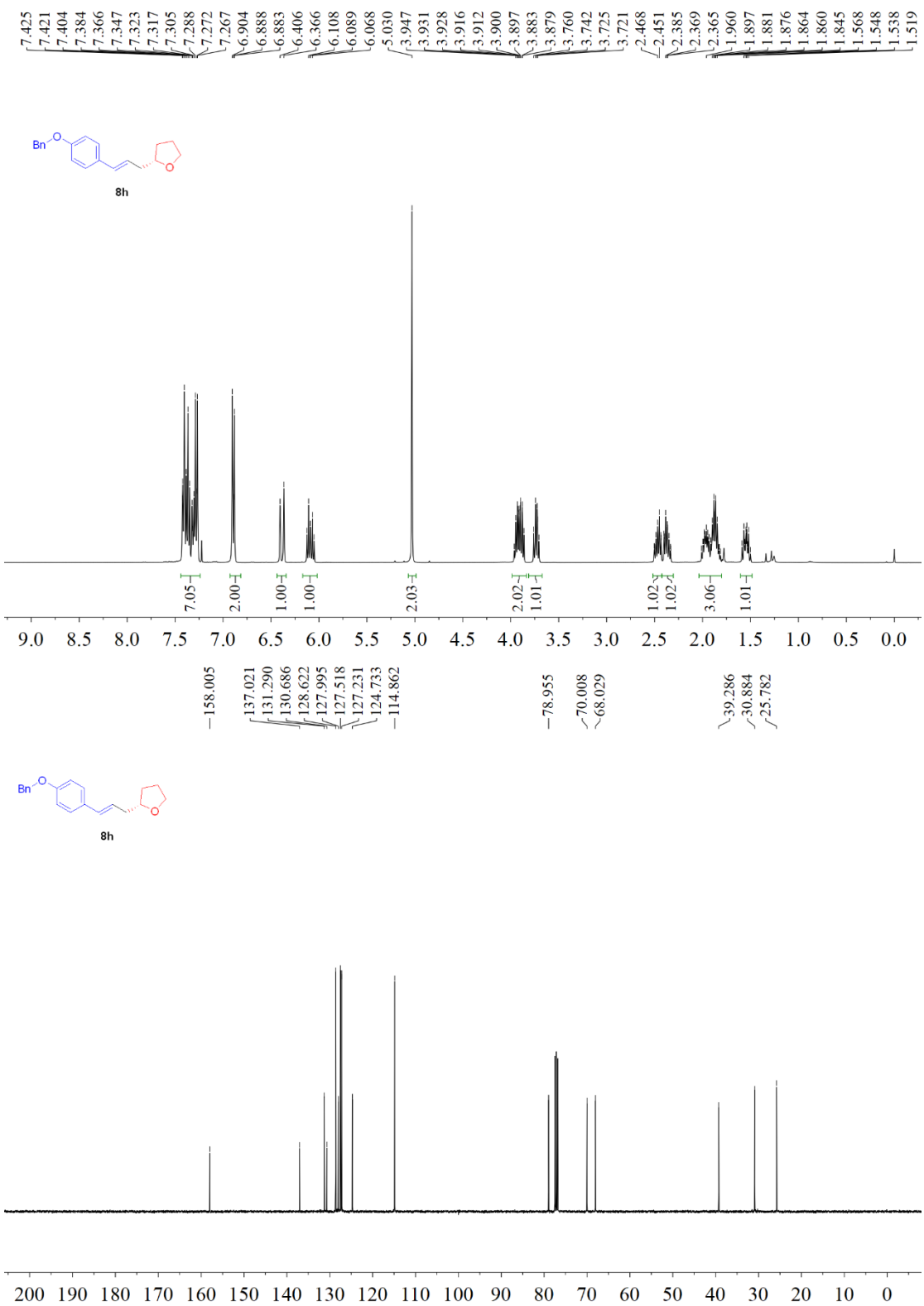
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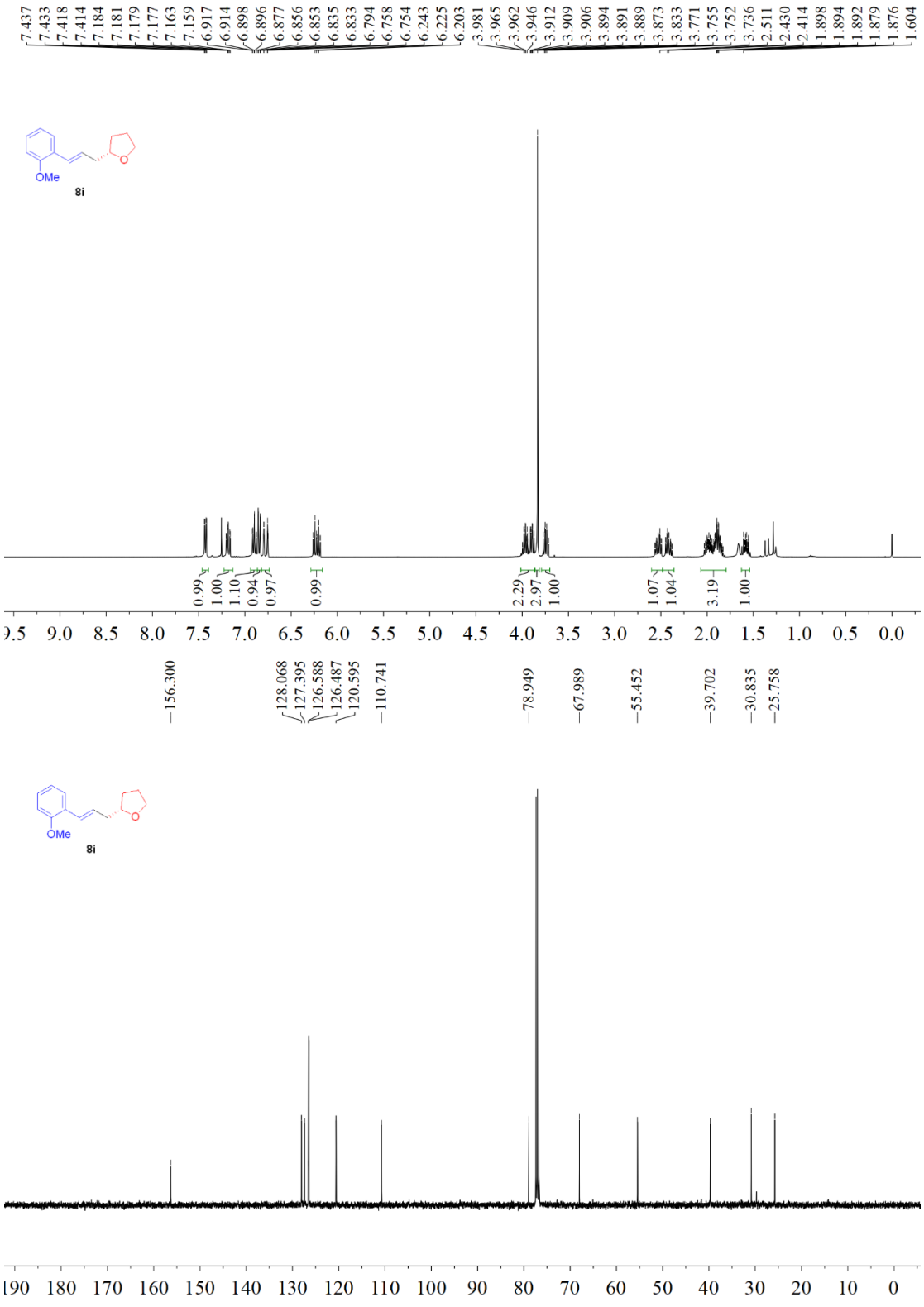
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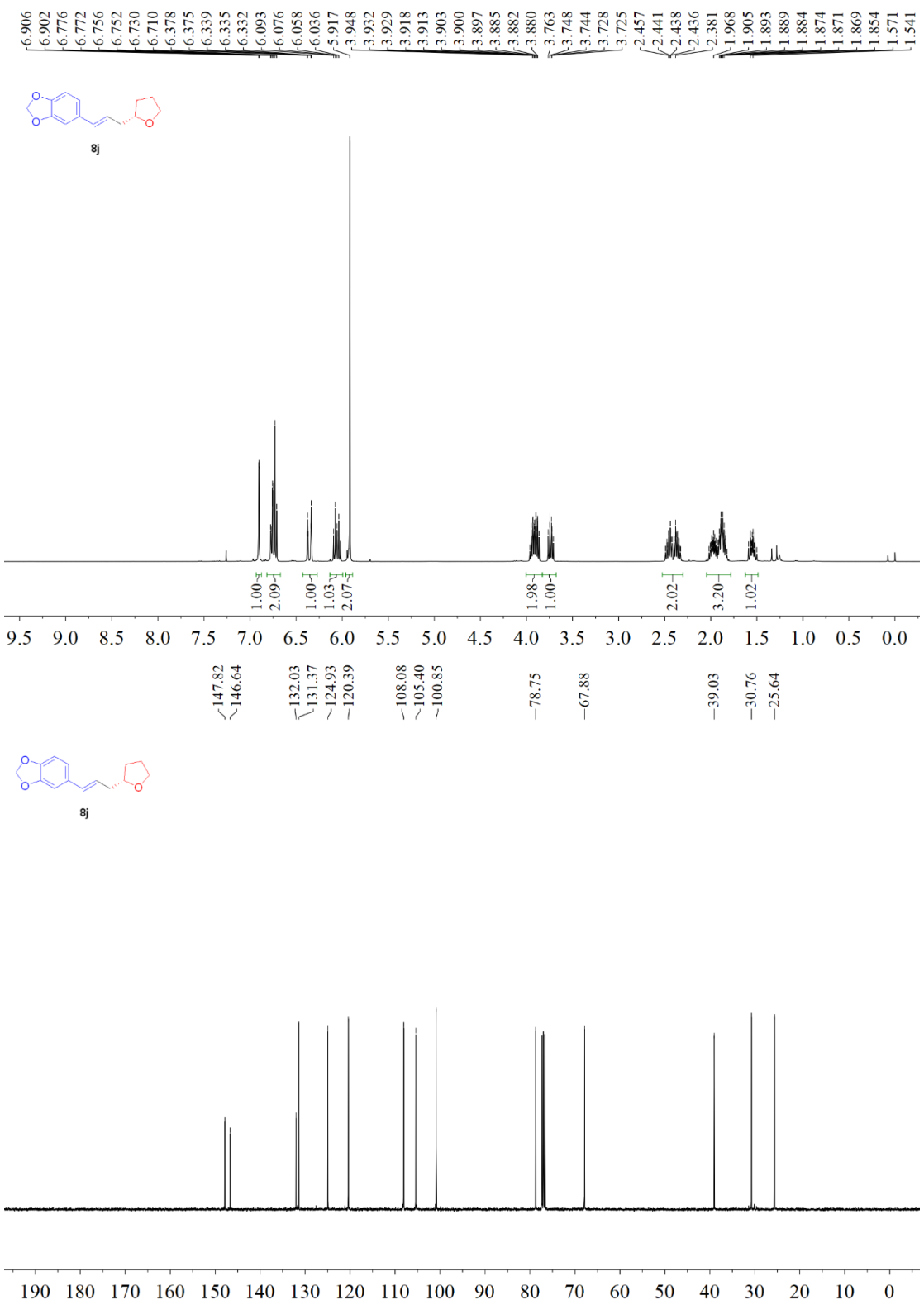
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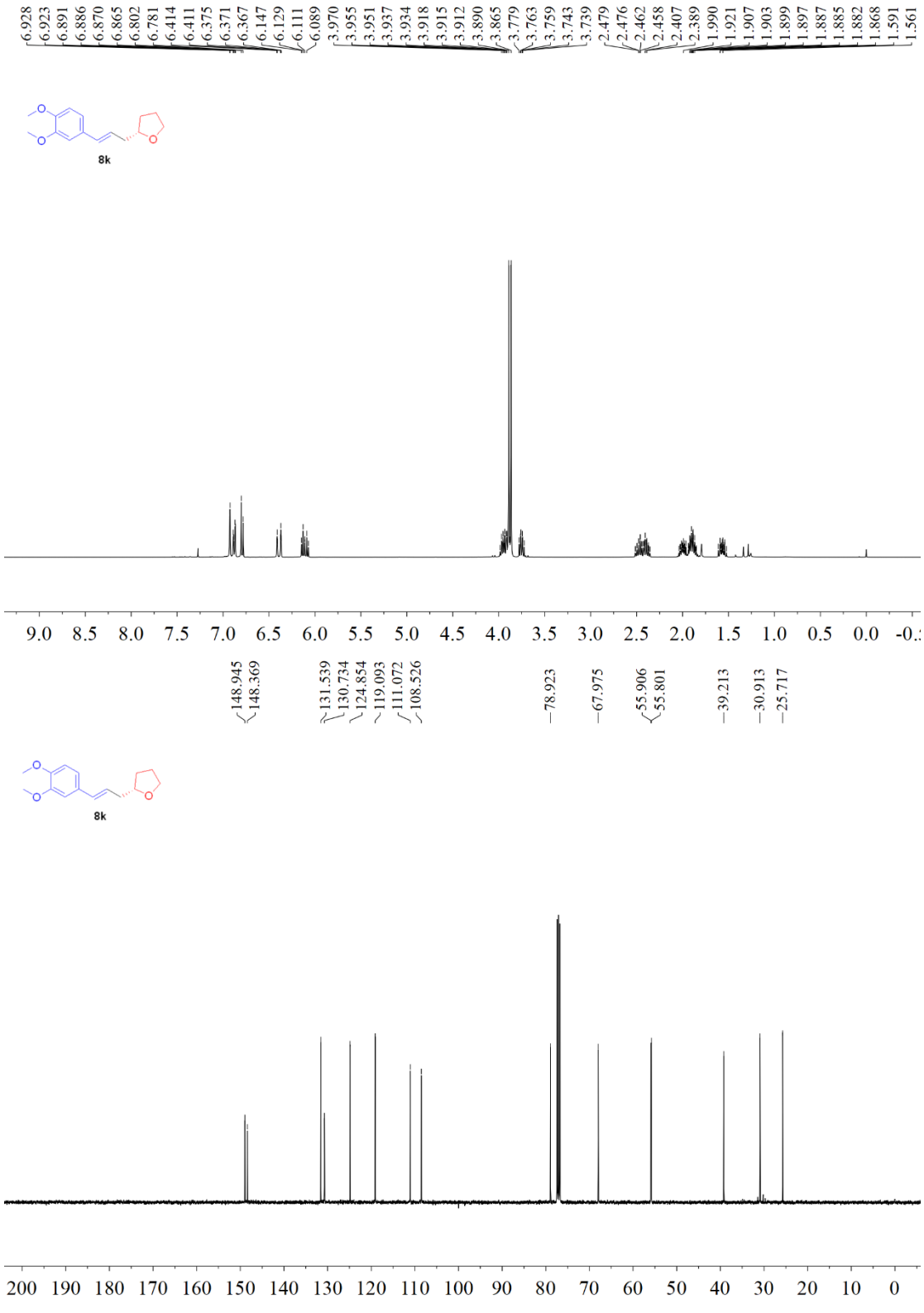
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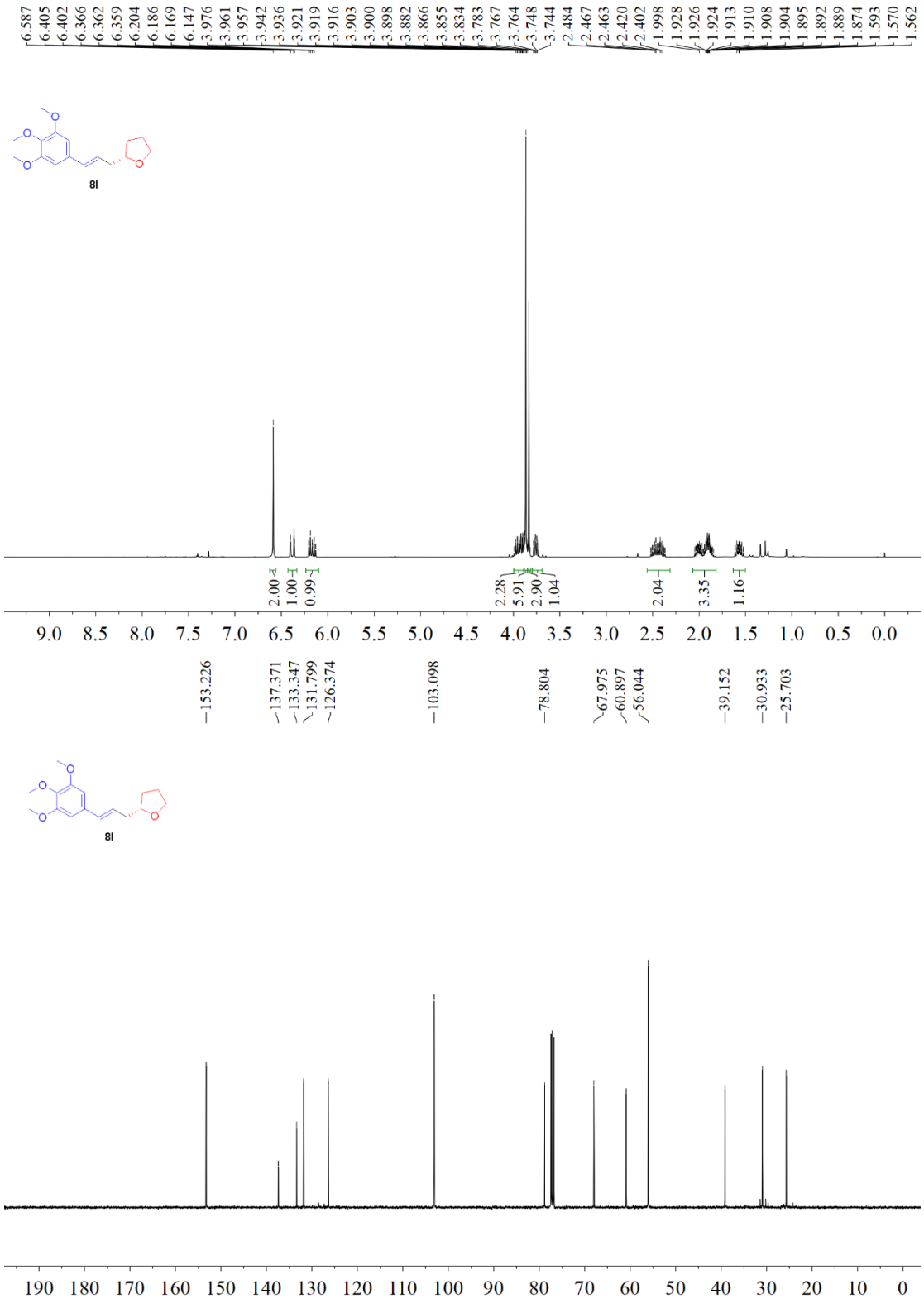
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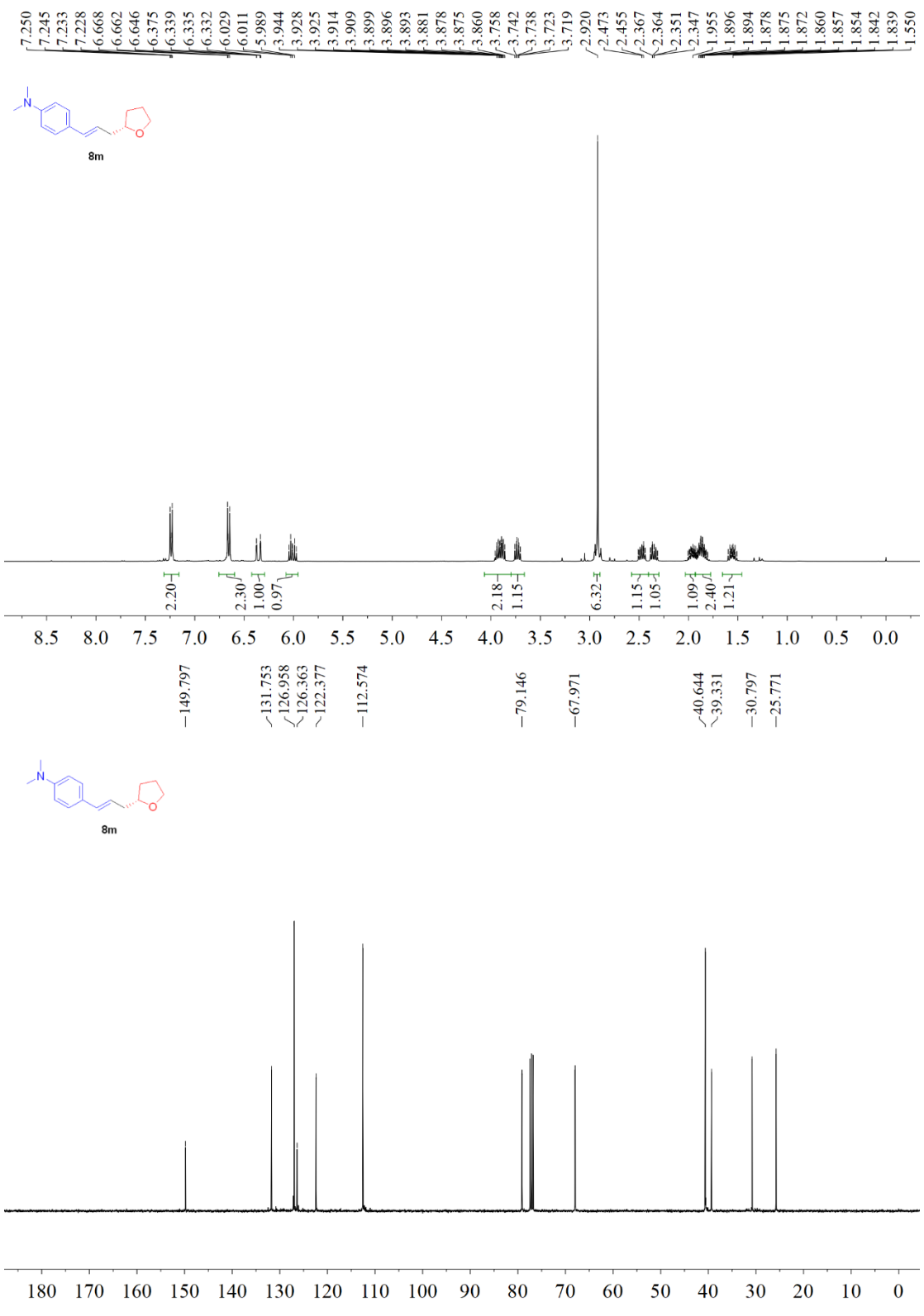
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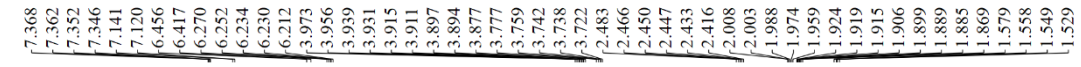
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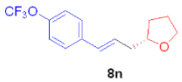
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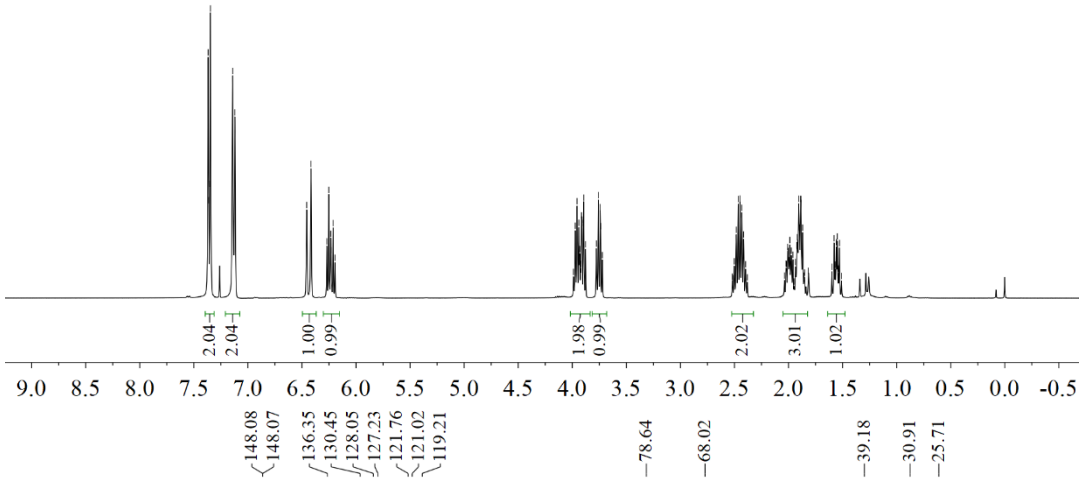
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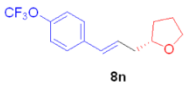
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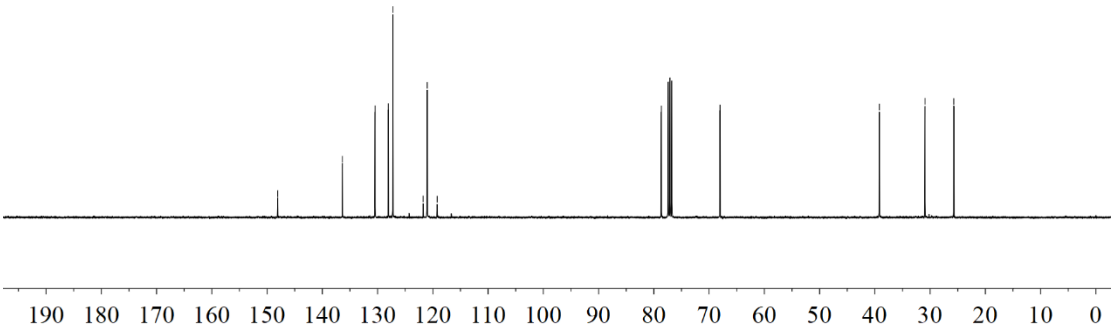
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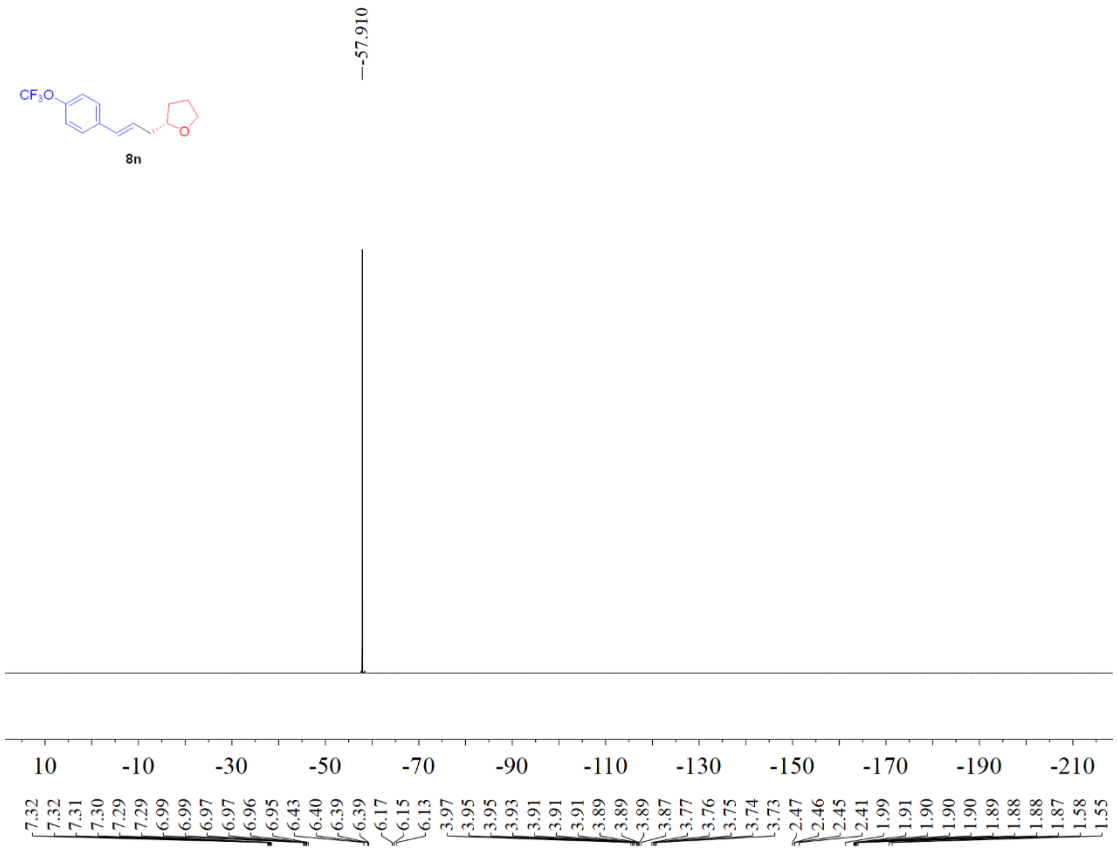
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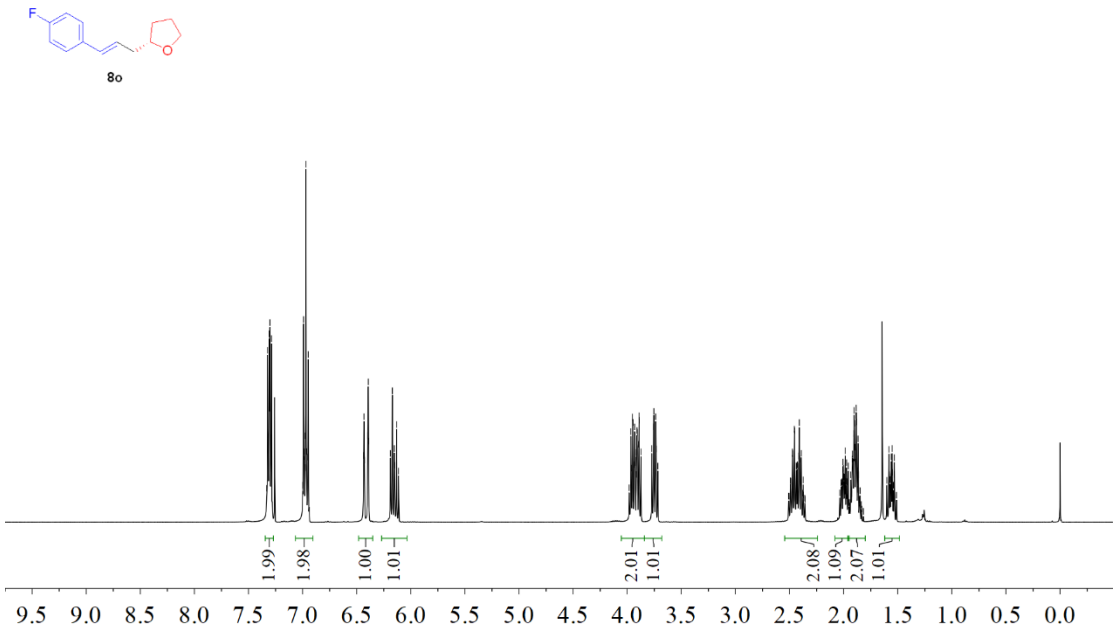
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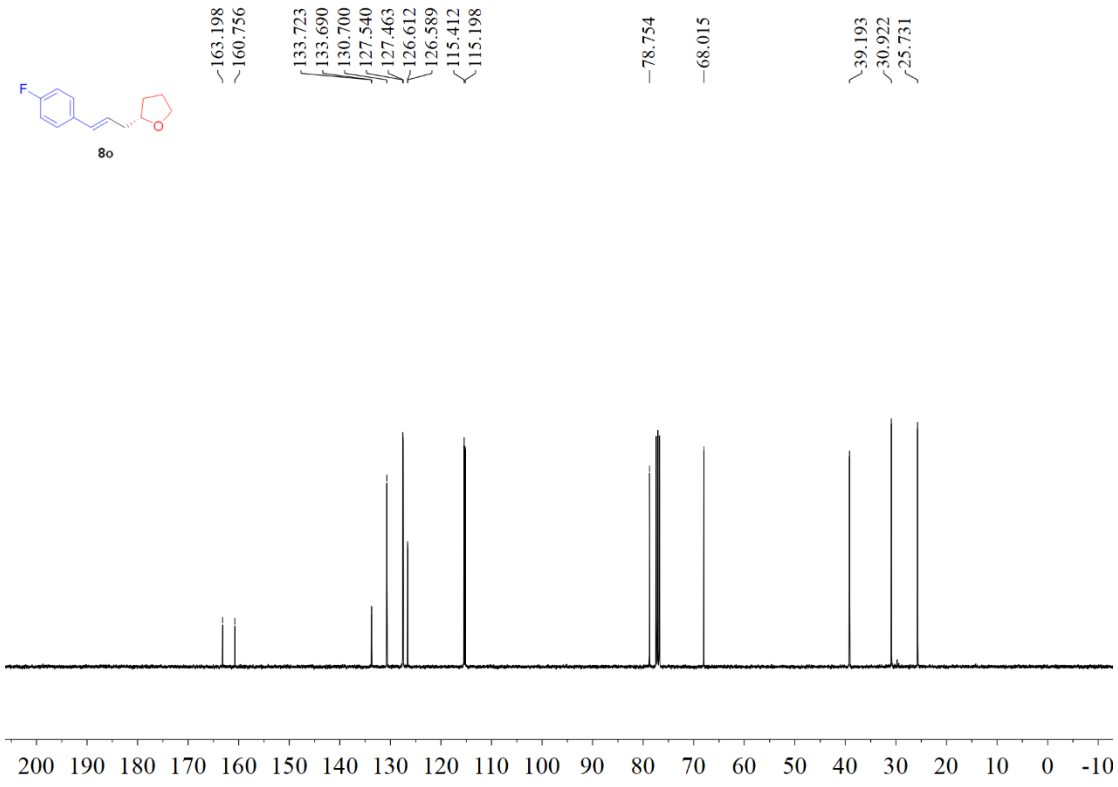
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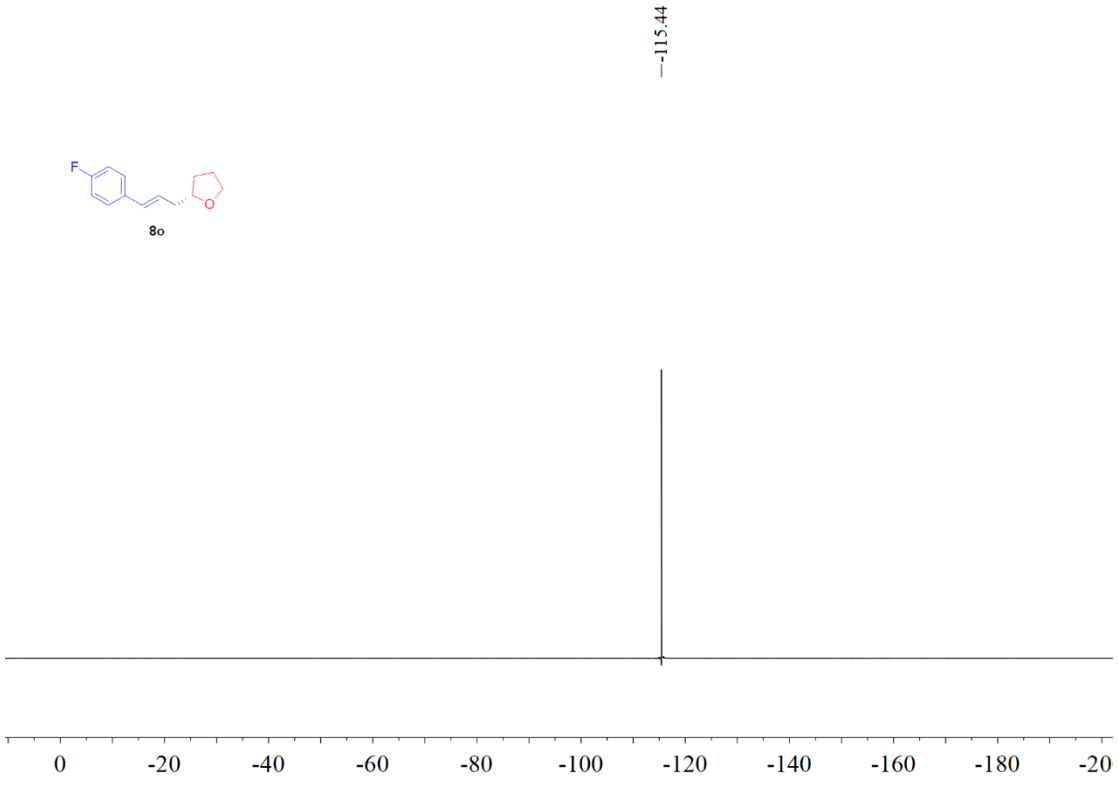
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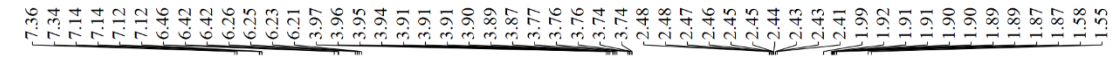
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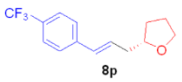
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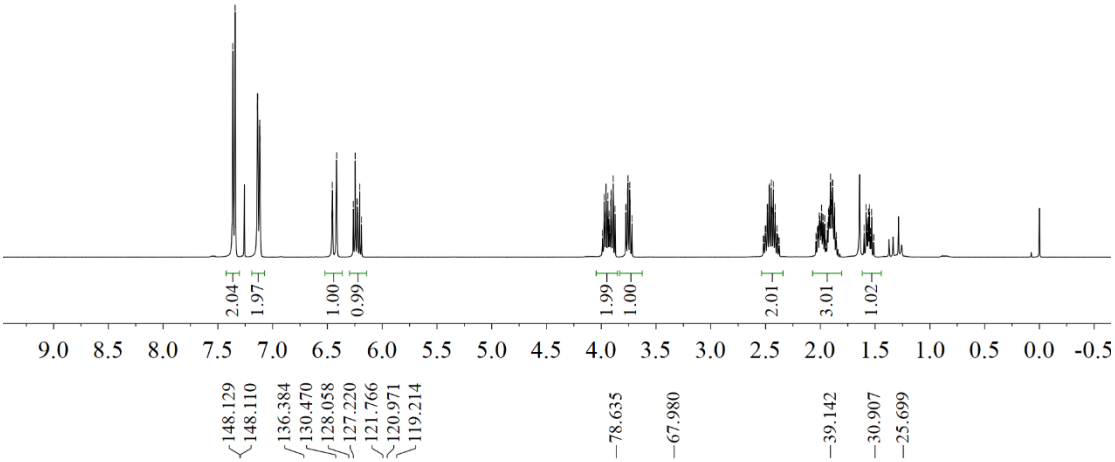
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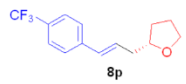
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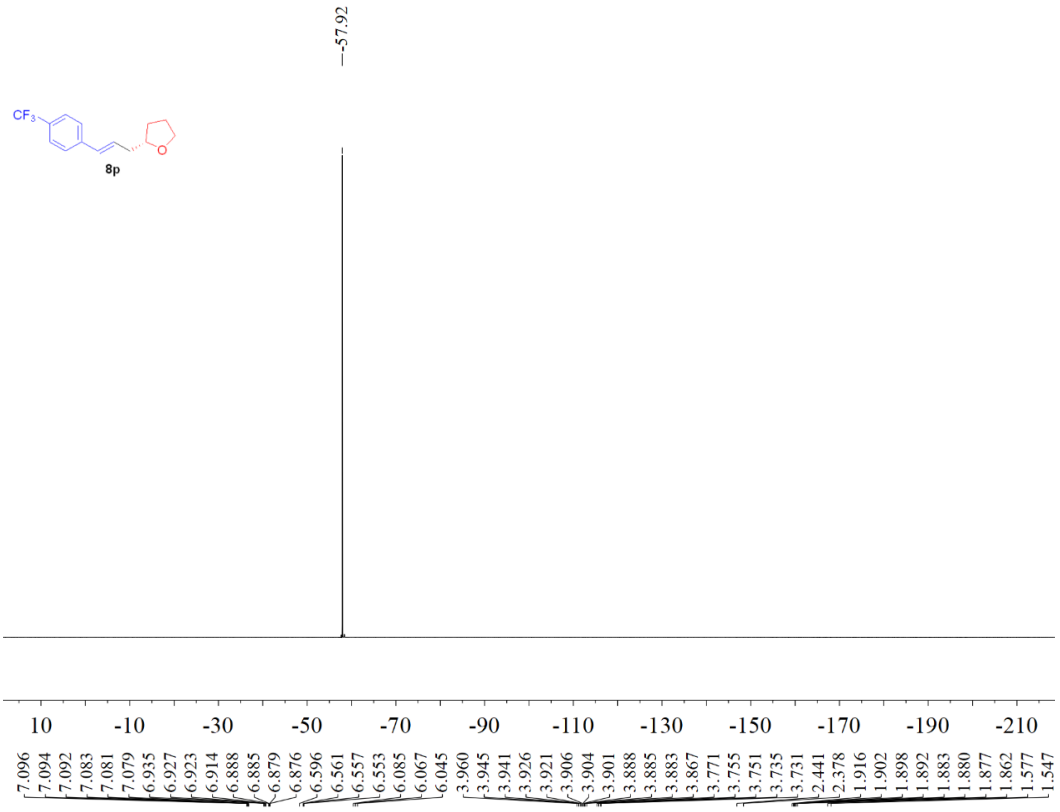
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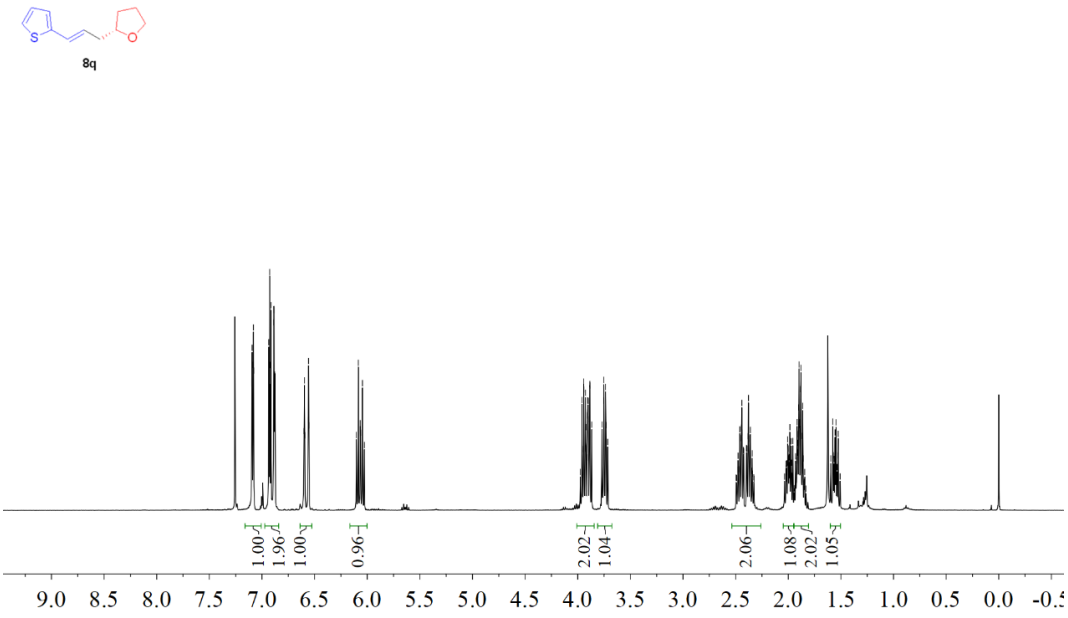
3.960 3.945 3.941 3.926 3.921 3.906 3.904 3.901 3.888 3.885 3.883 3.867 3.771 3.755 3.751 3.735 3.731 2.441 2.378 1.916 1.902 1.898 1.892 1.883 1.880 1.877 1.862 1.577 1.547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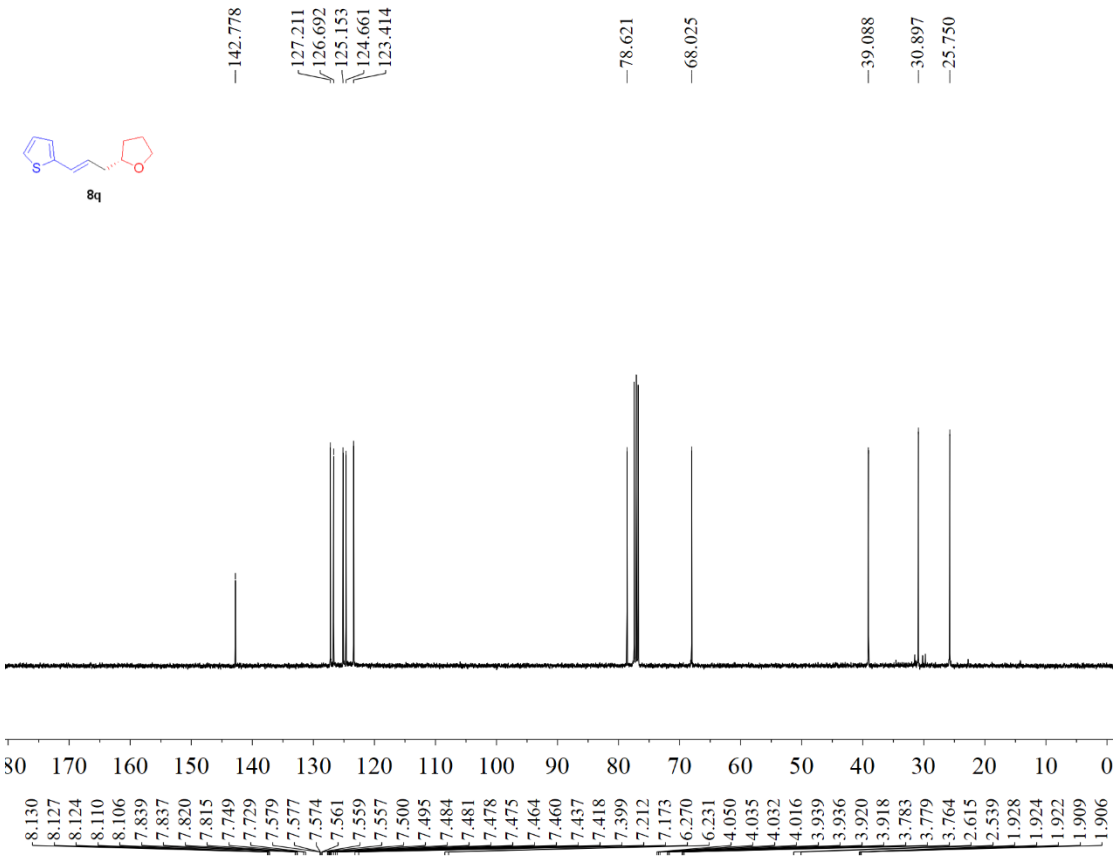
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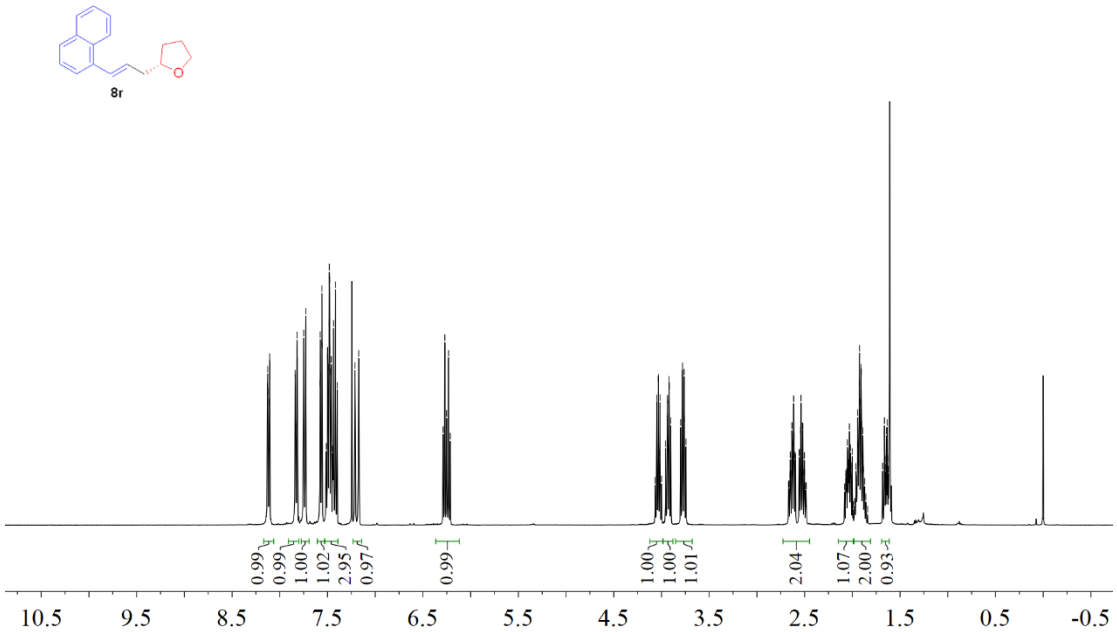
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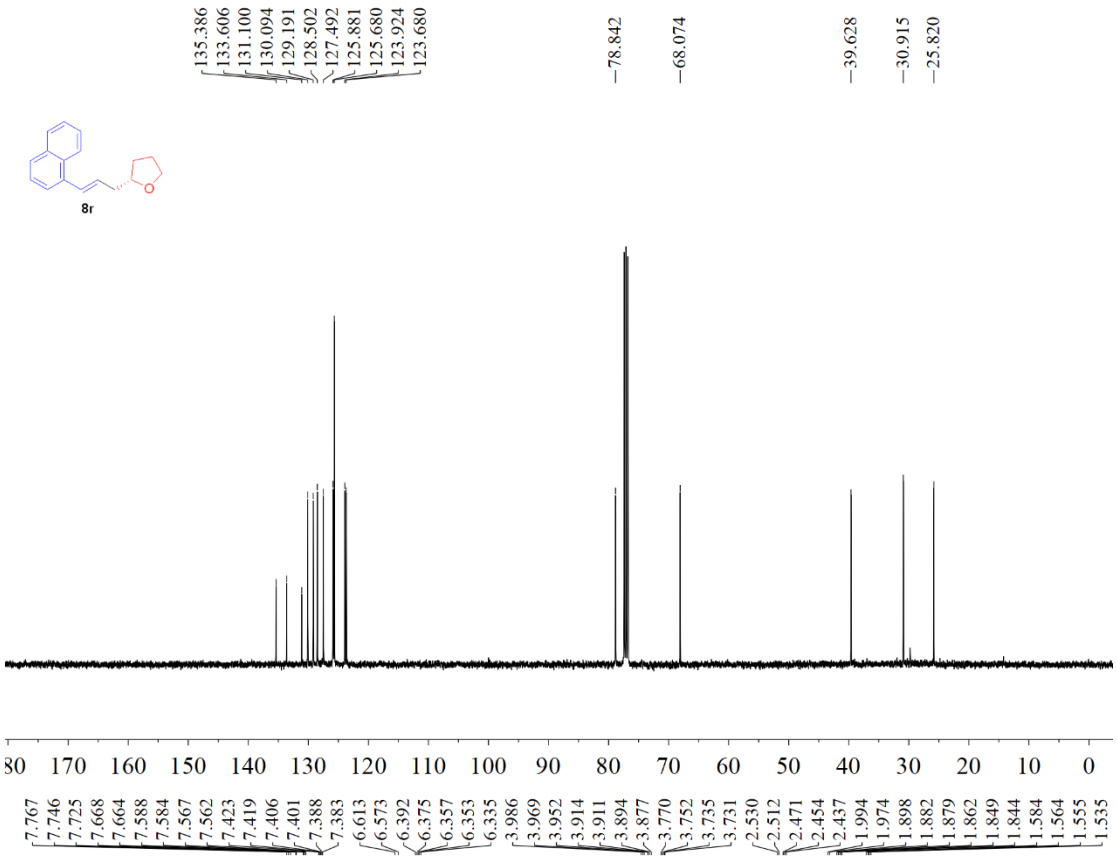
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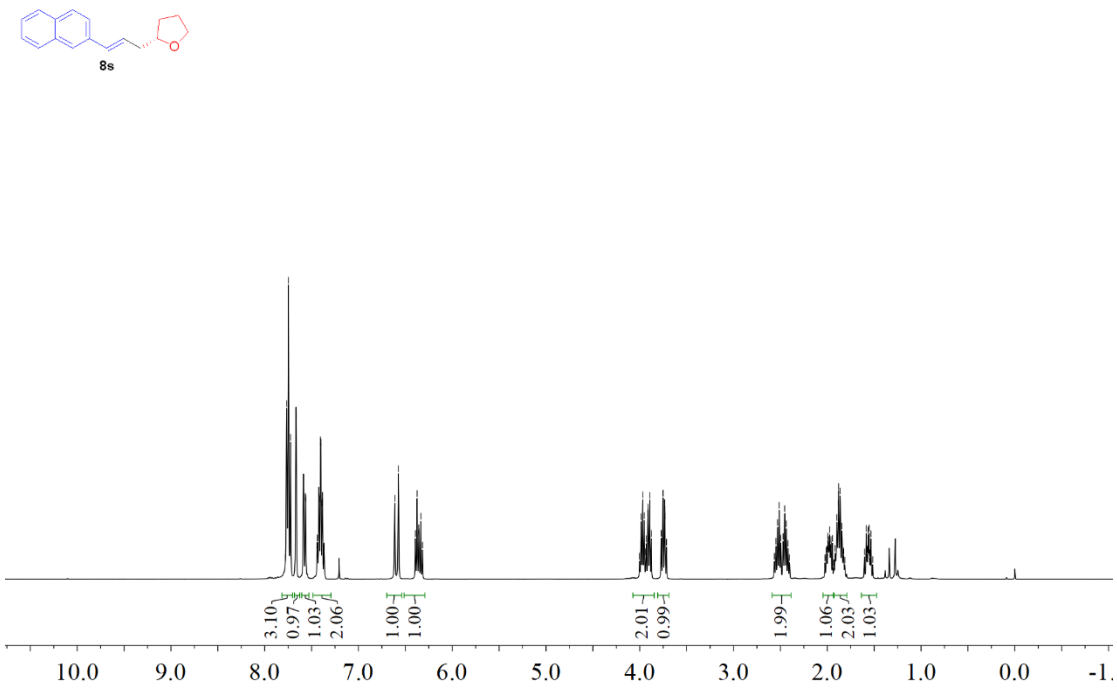
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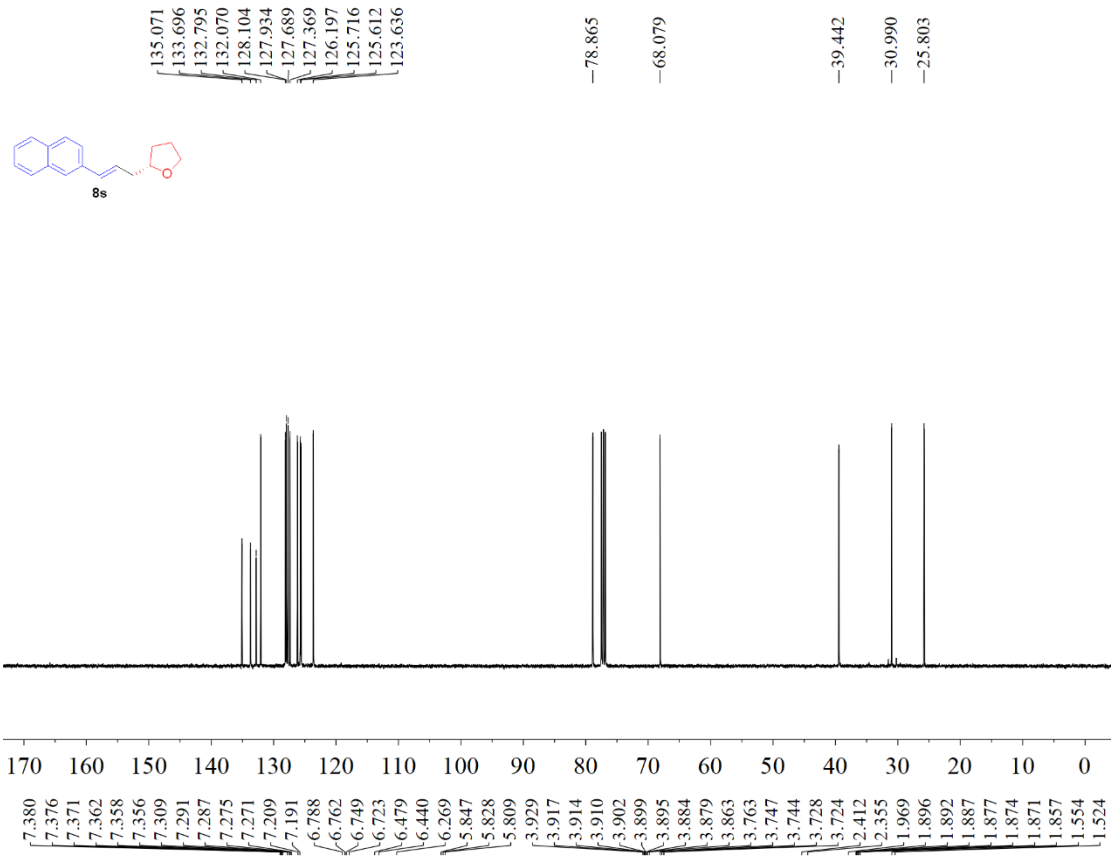
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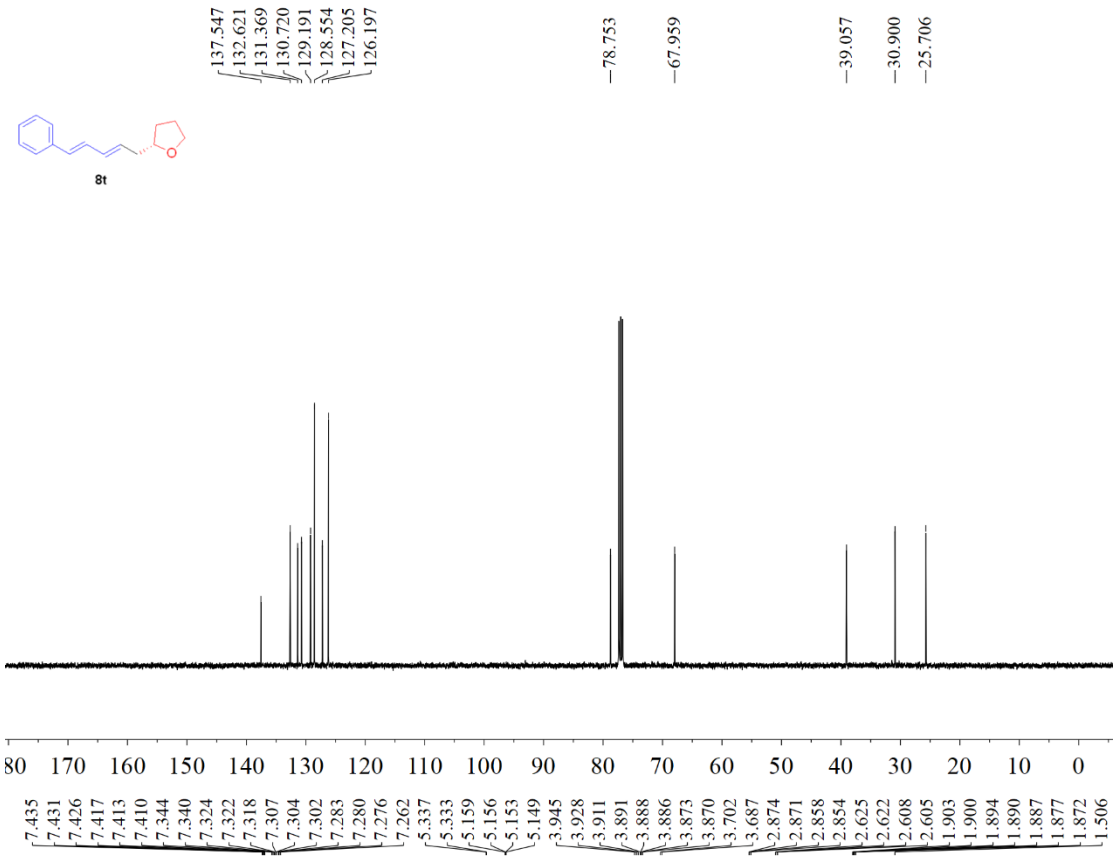
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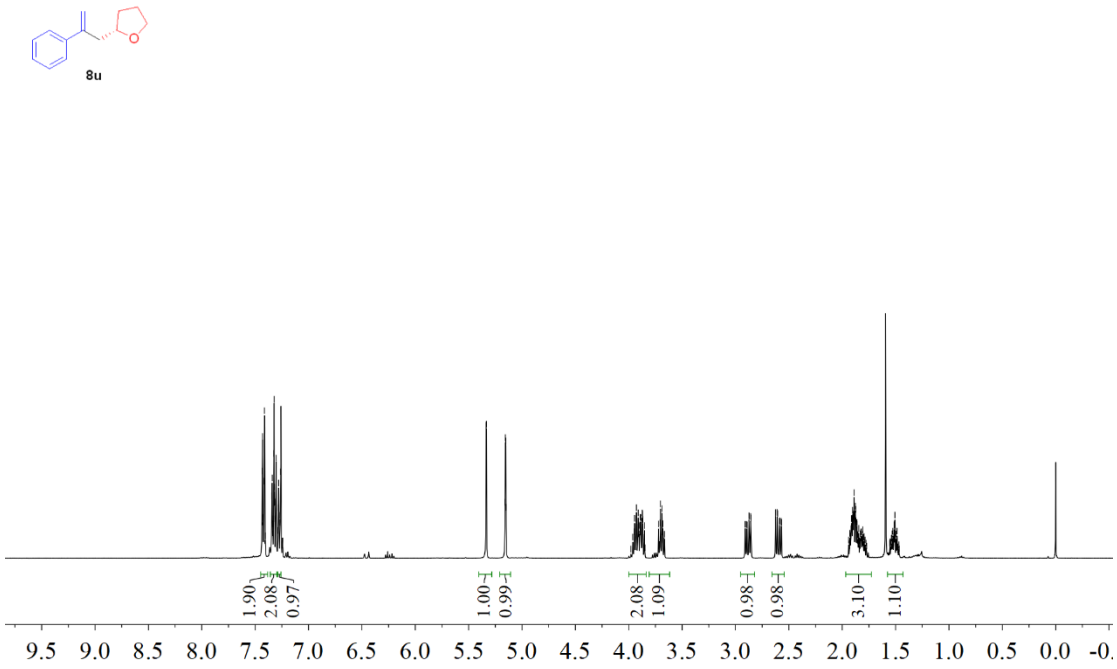
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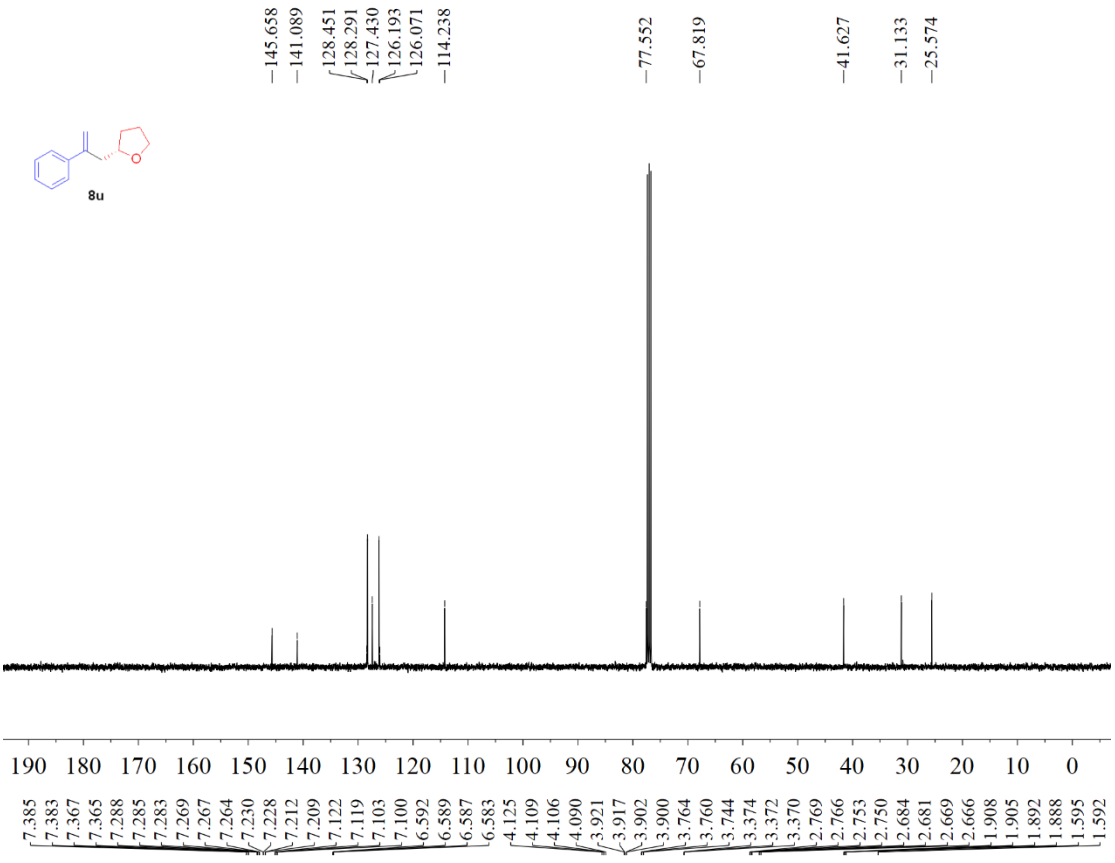
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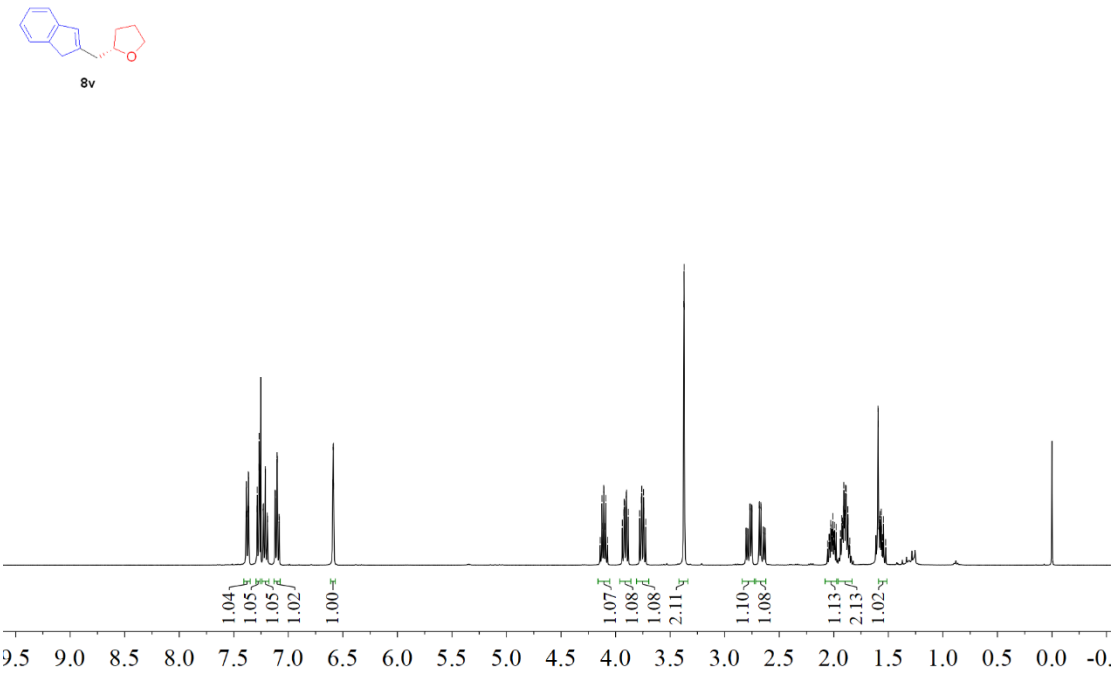
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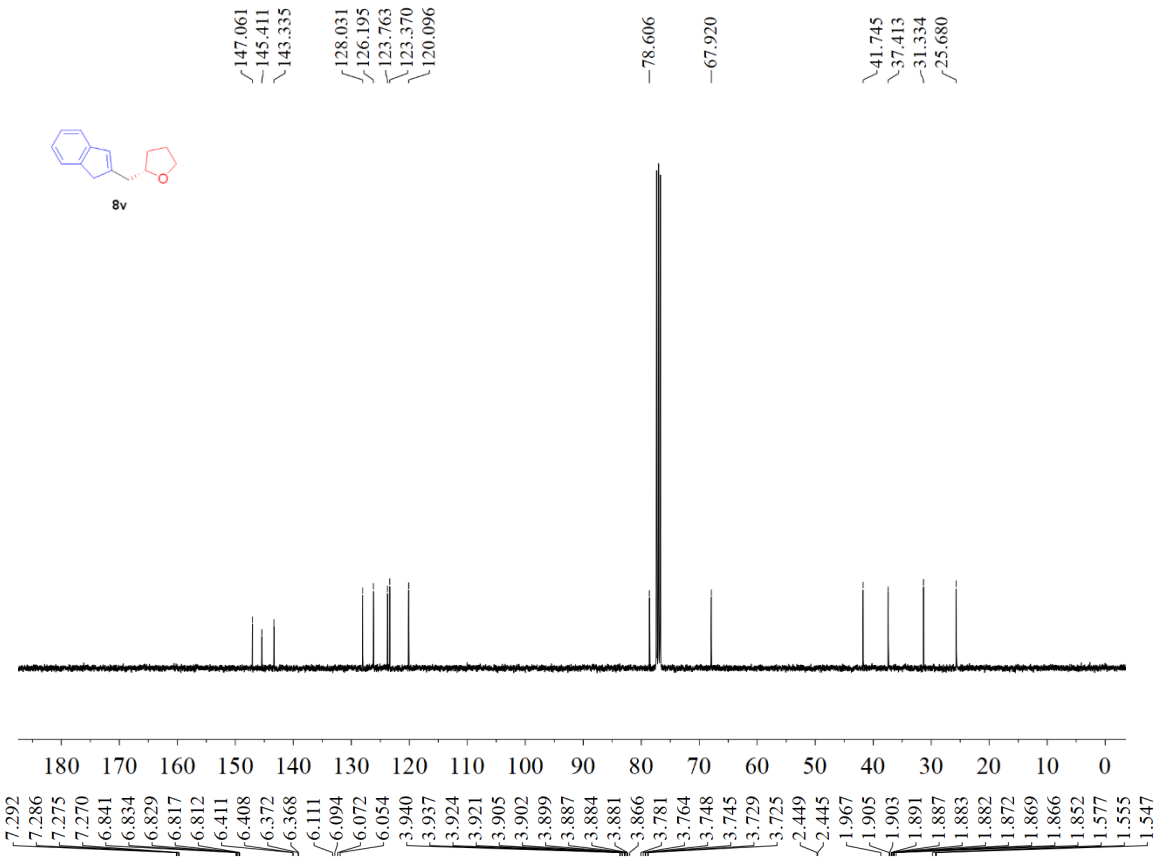
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8v
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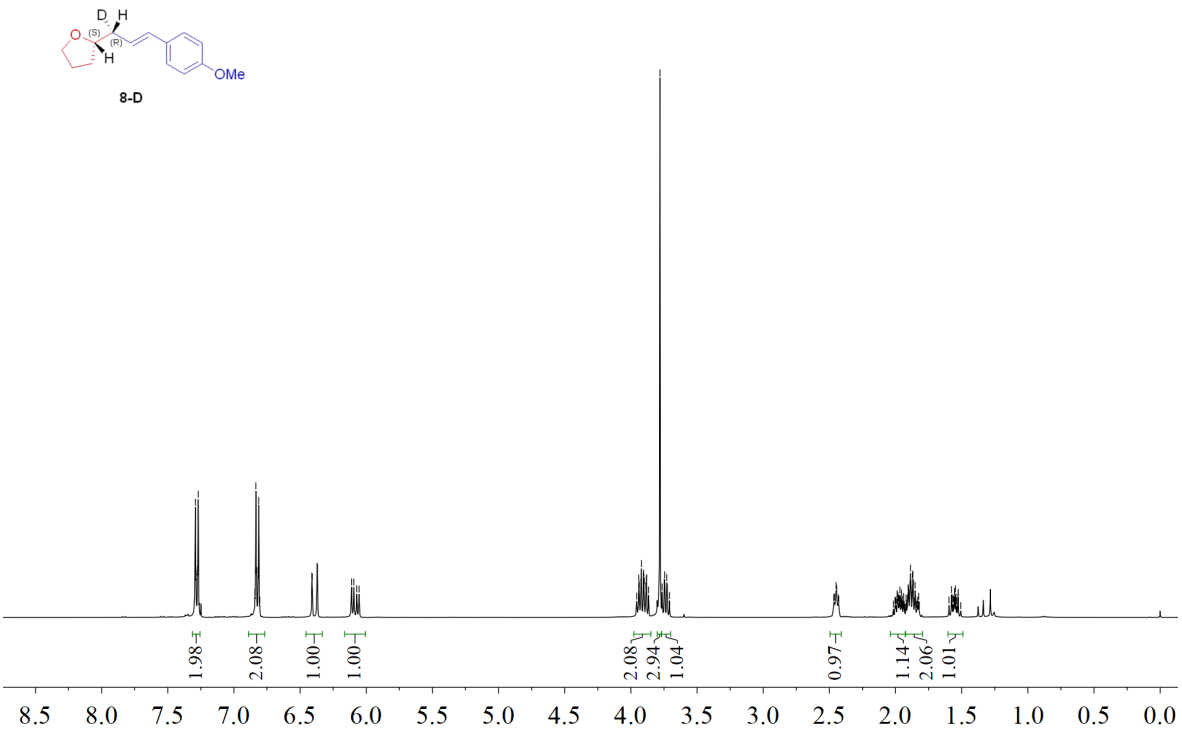
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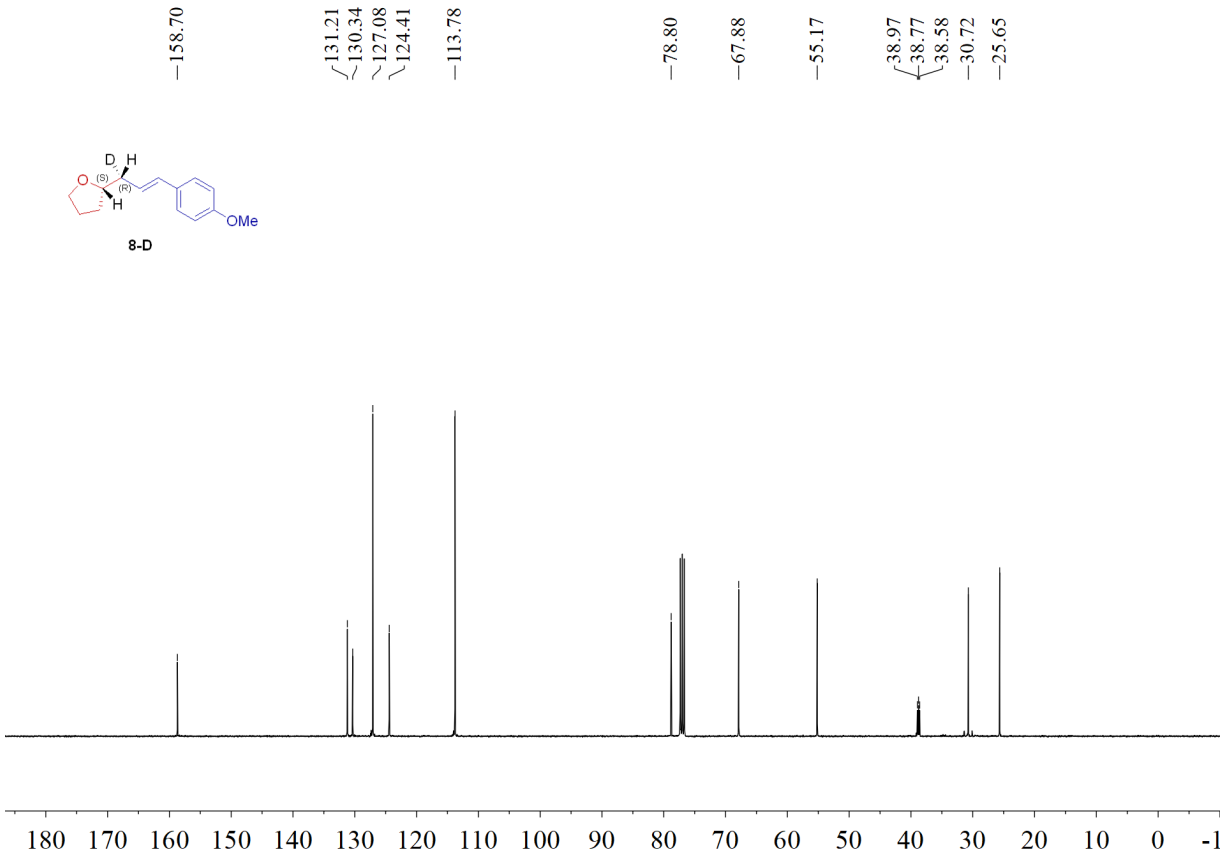
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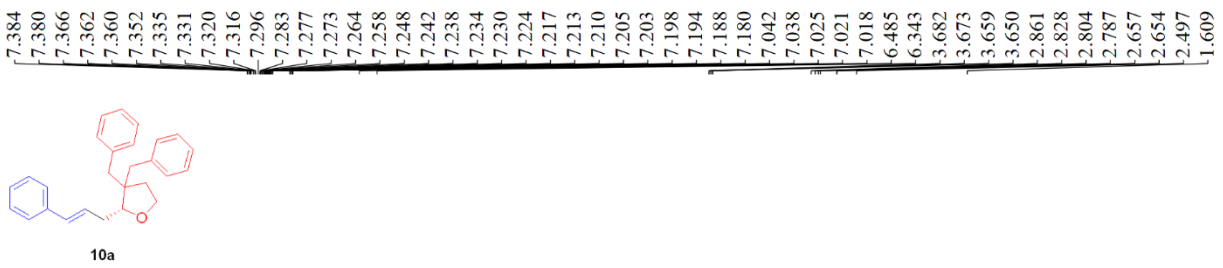
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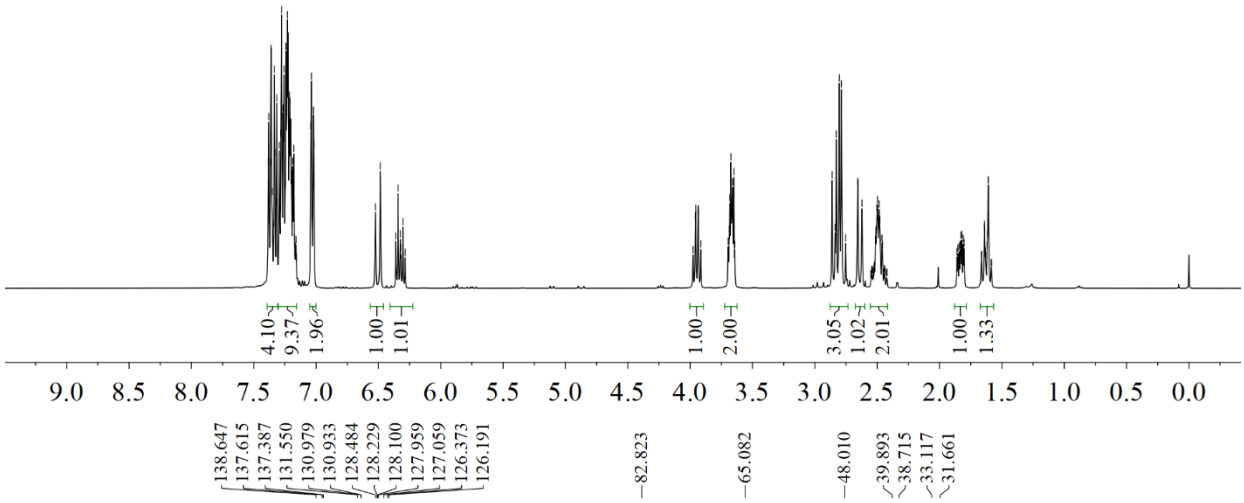
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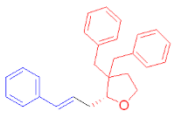

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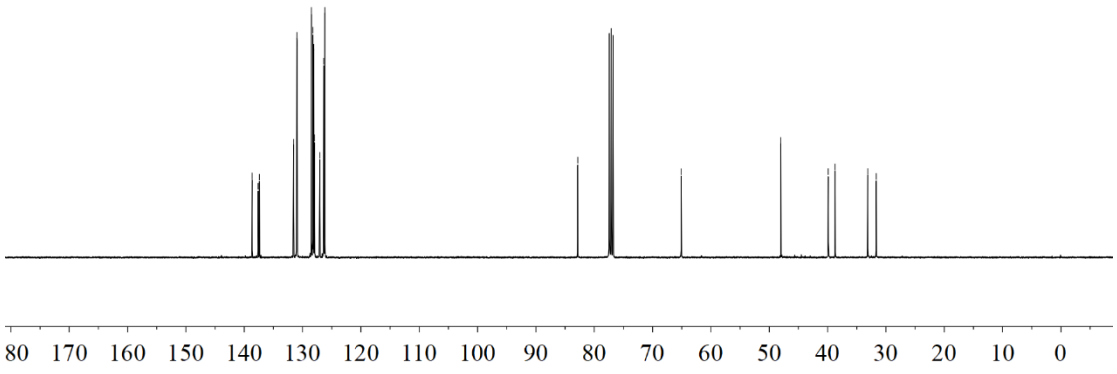
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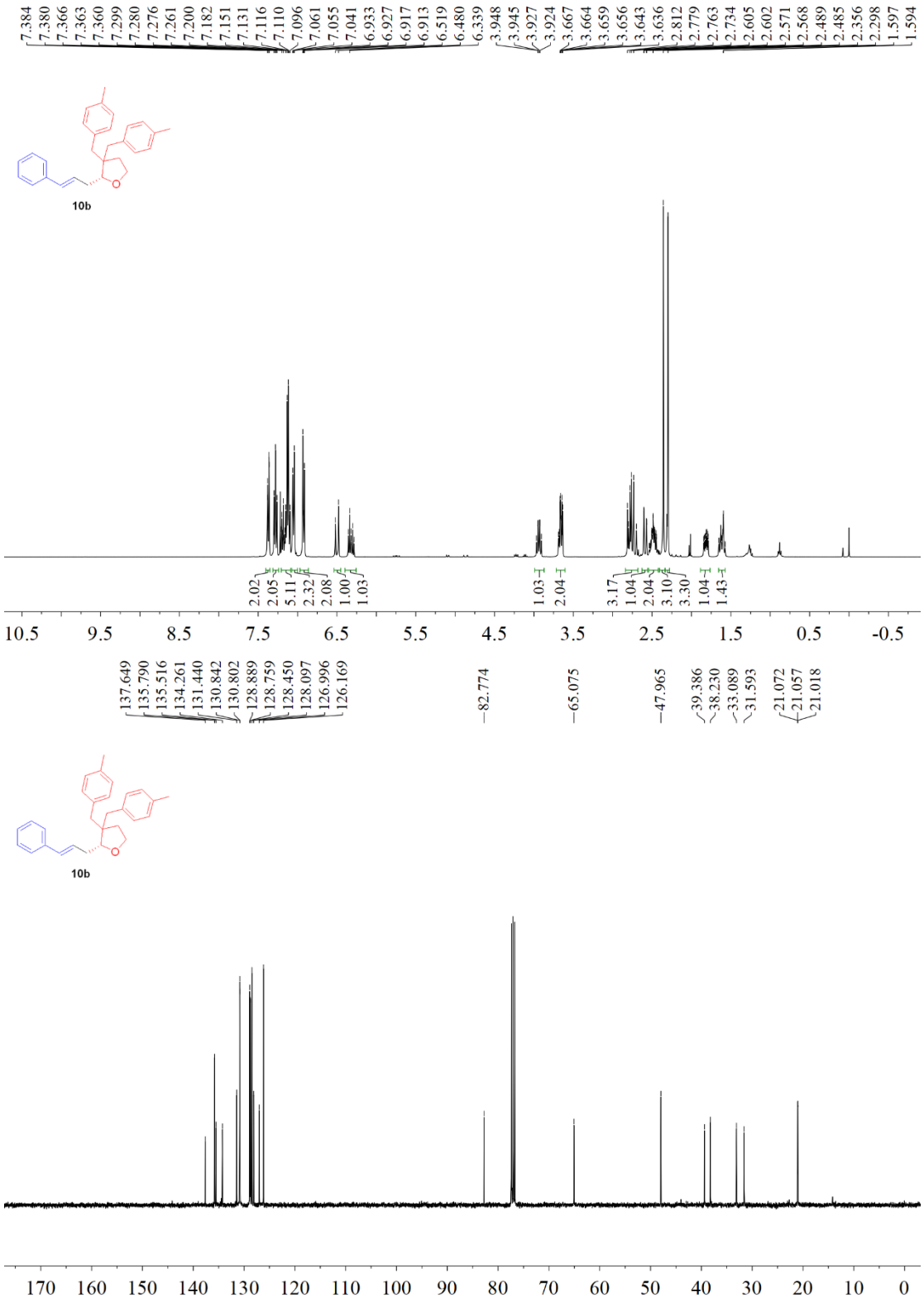
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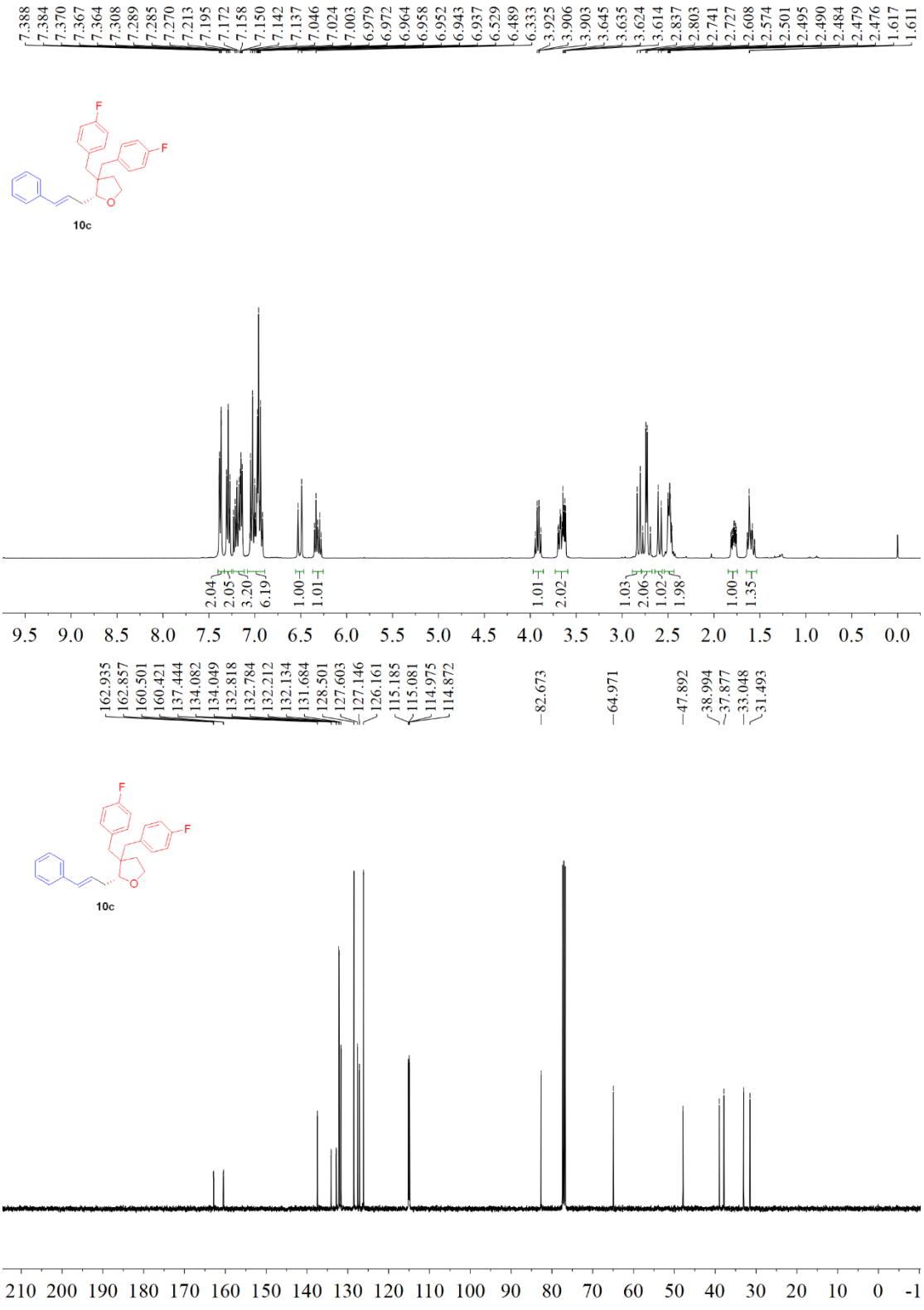
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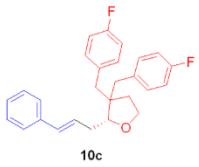
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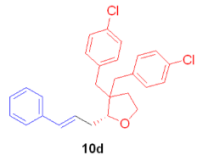
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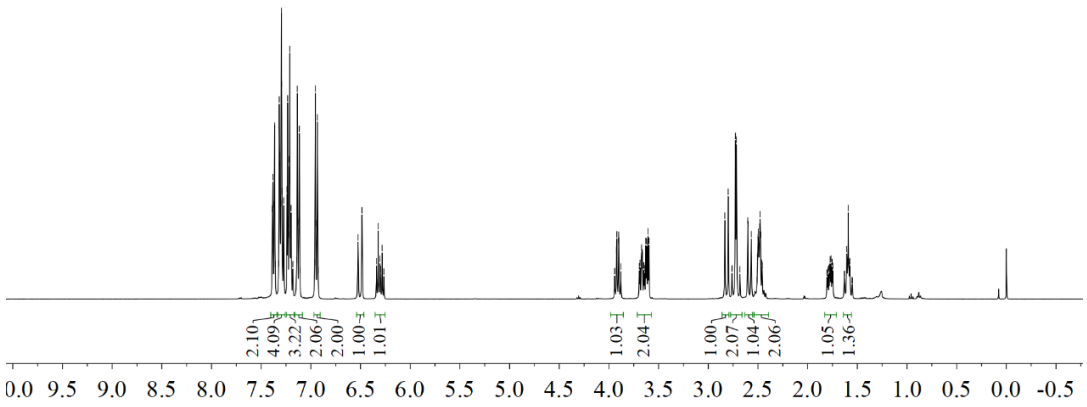
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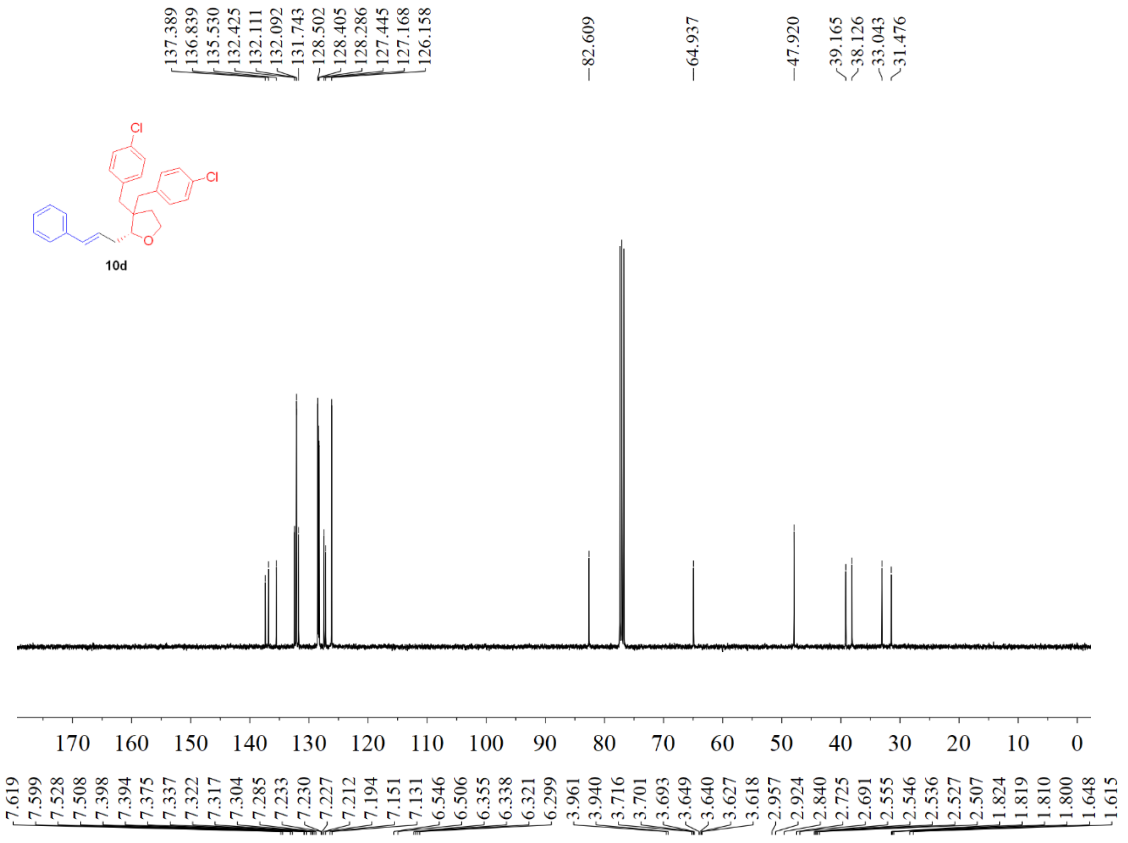
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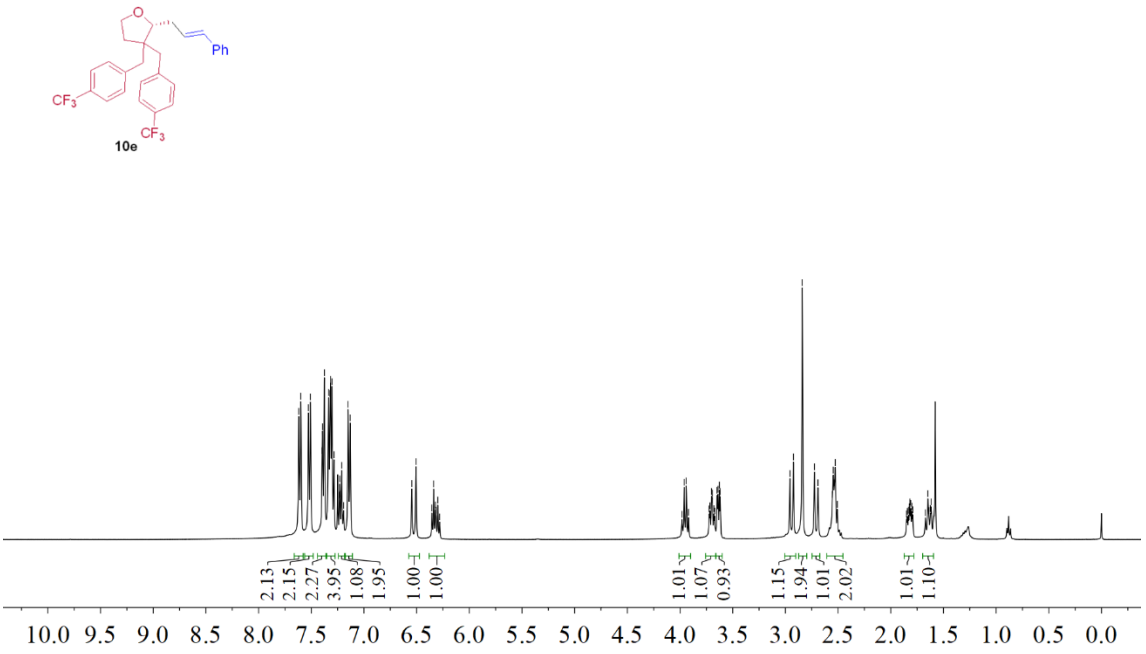
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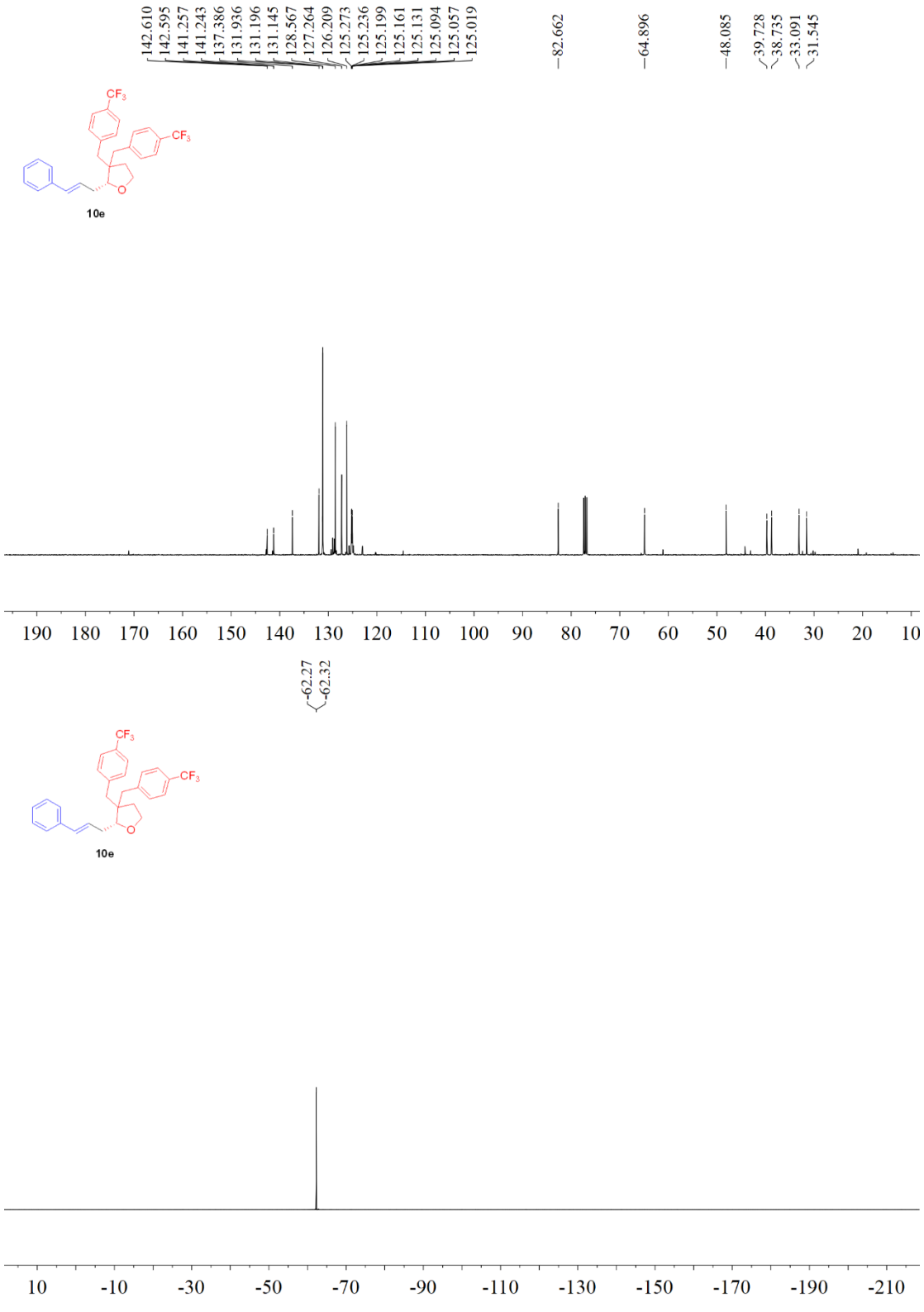
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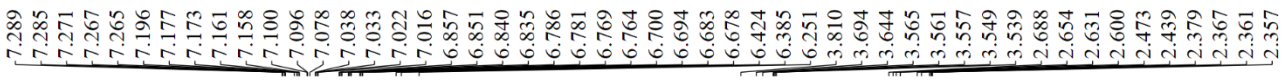
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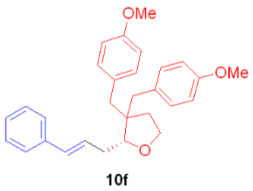
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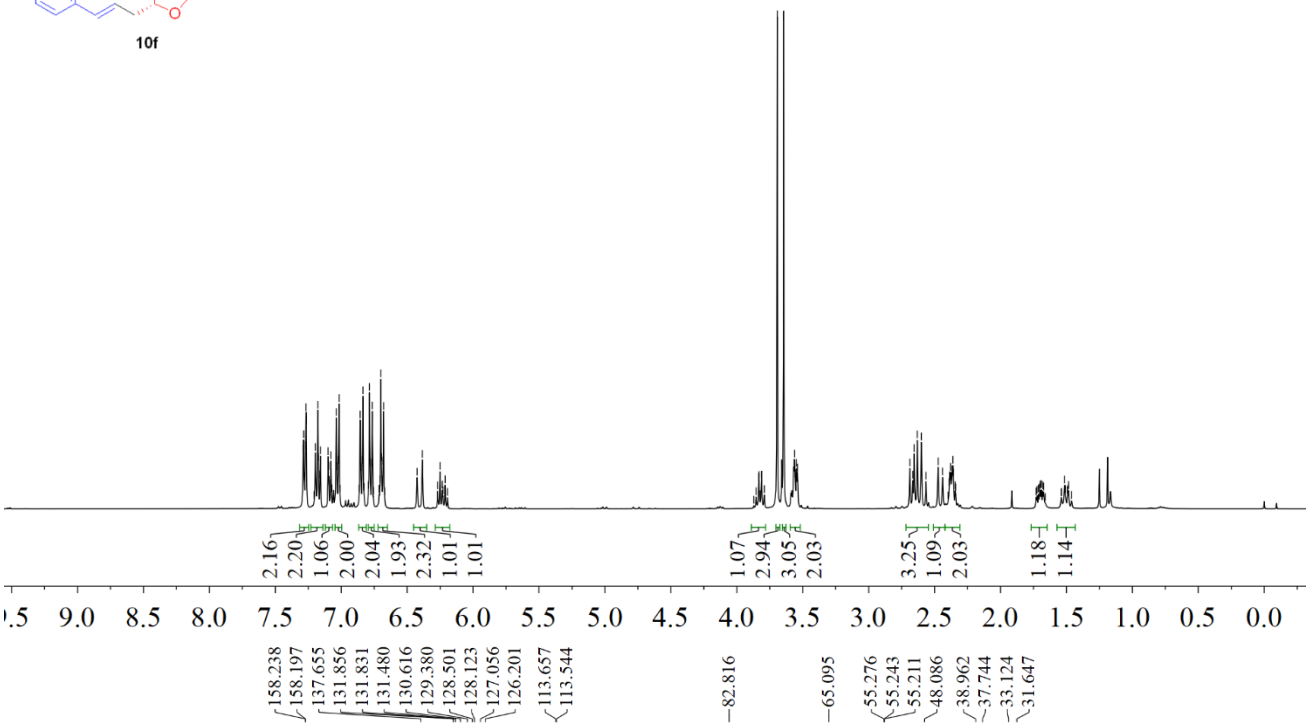
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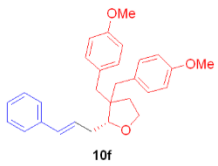
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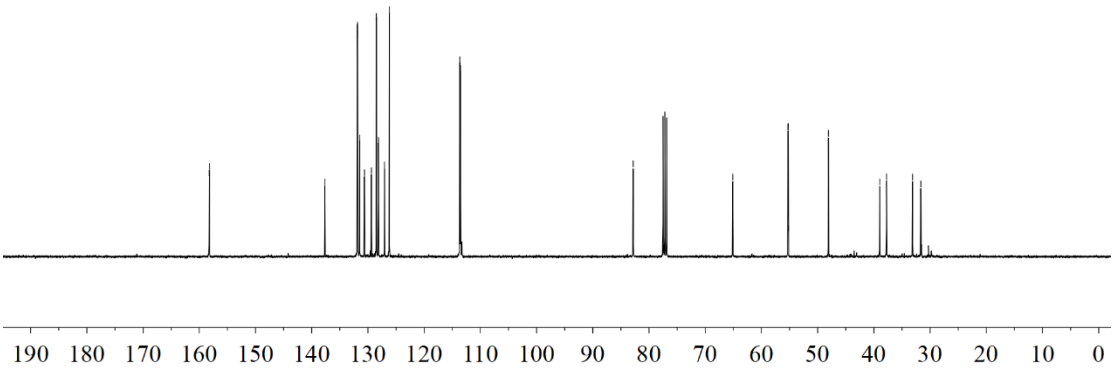
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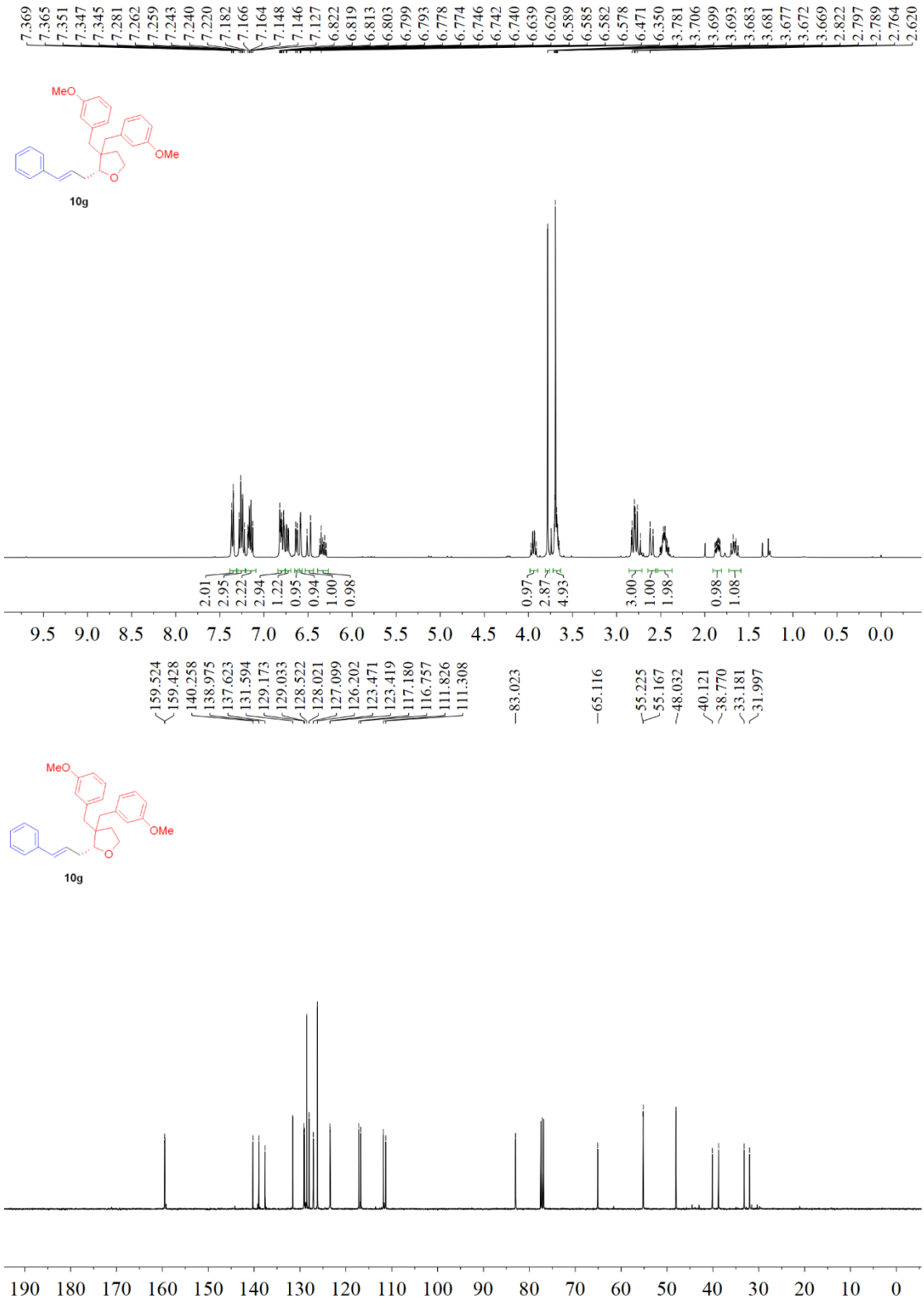
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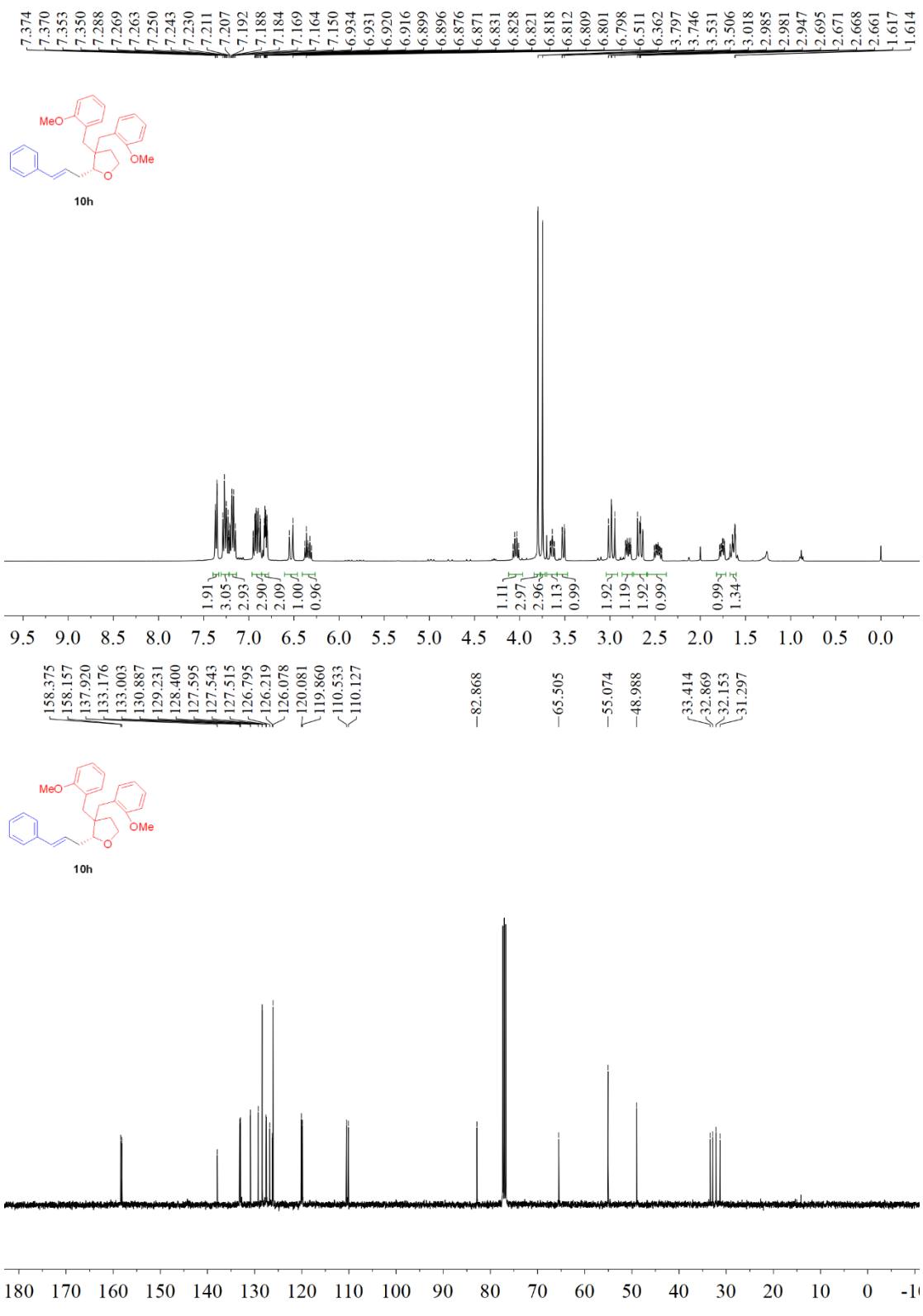
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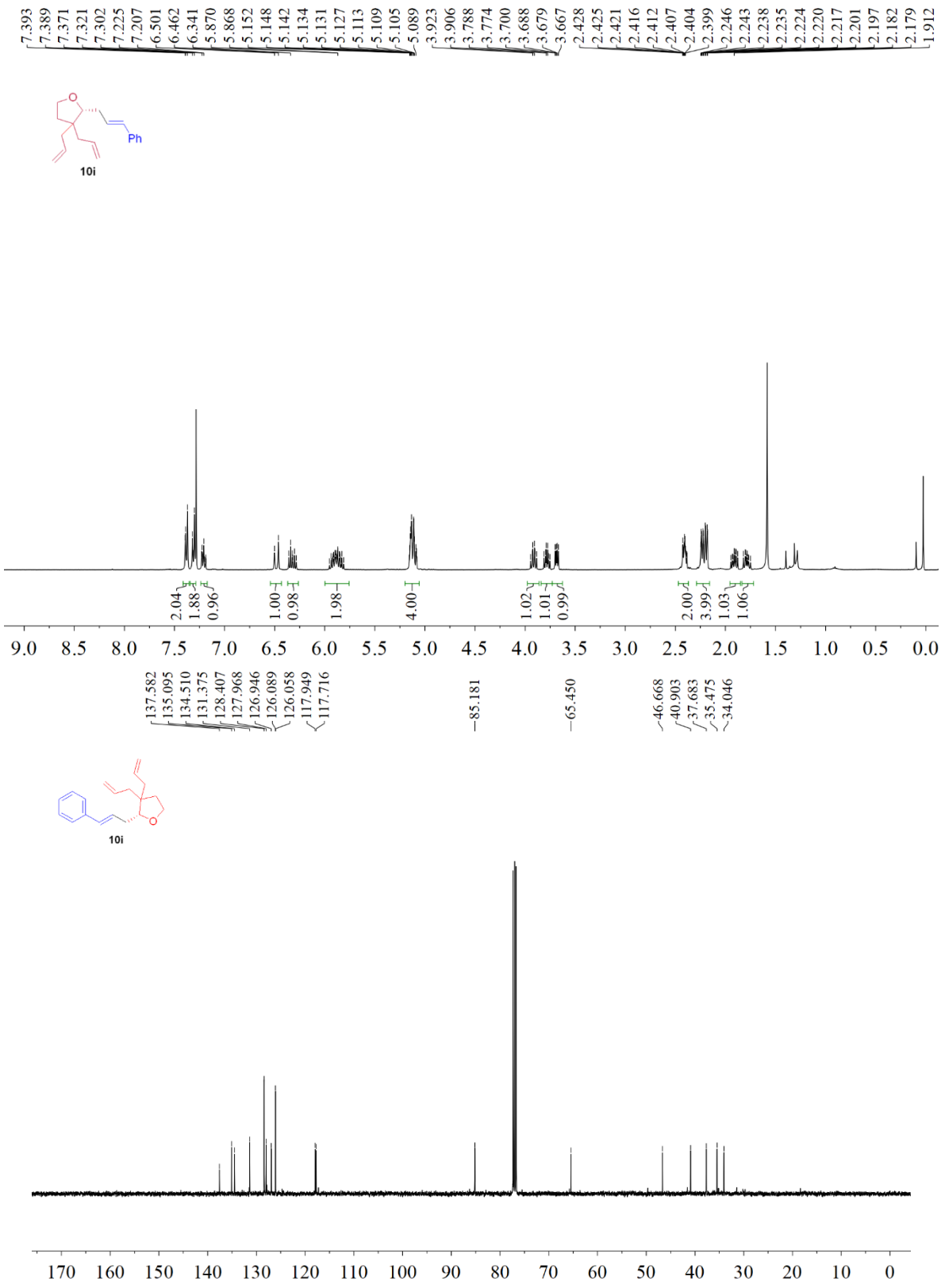
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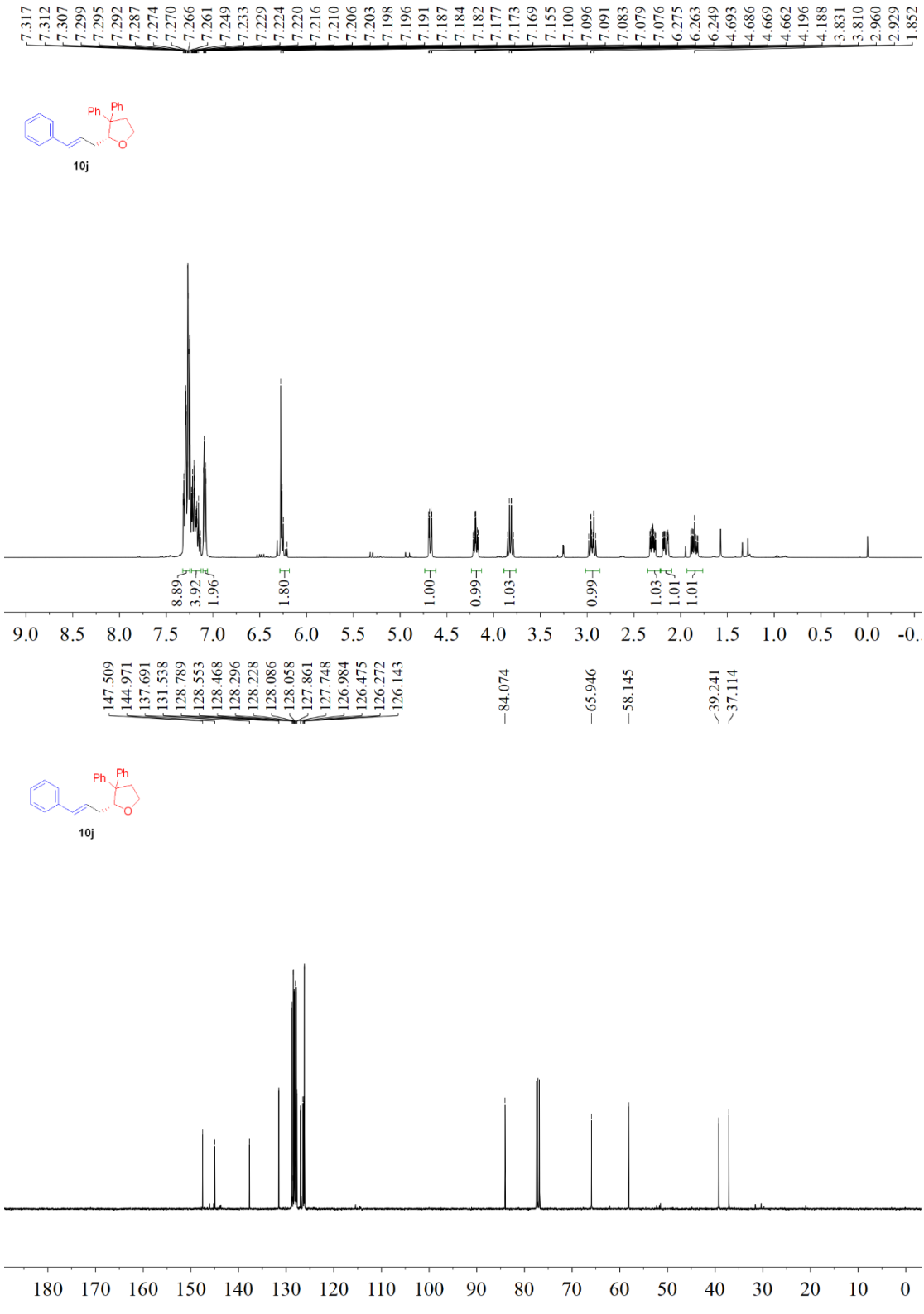
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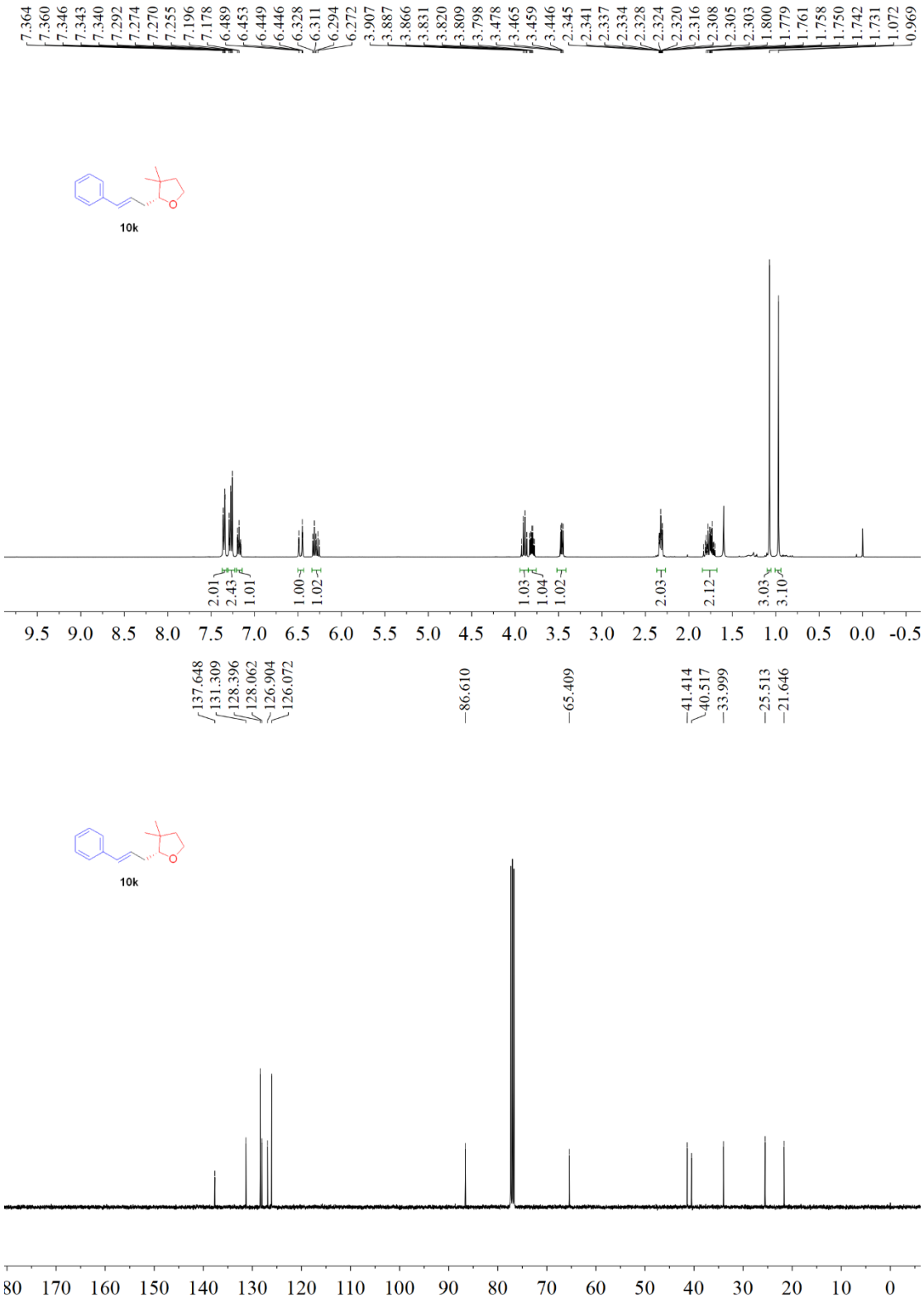
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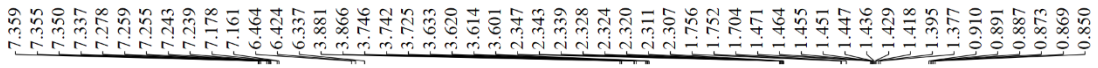
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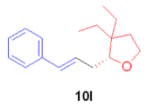

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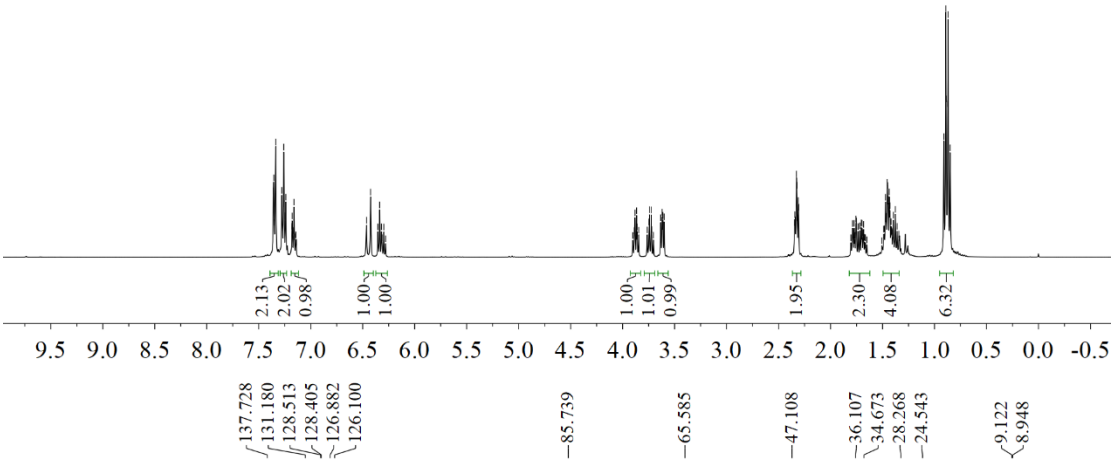
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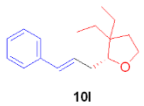

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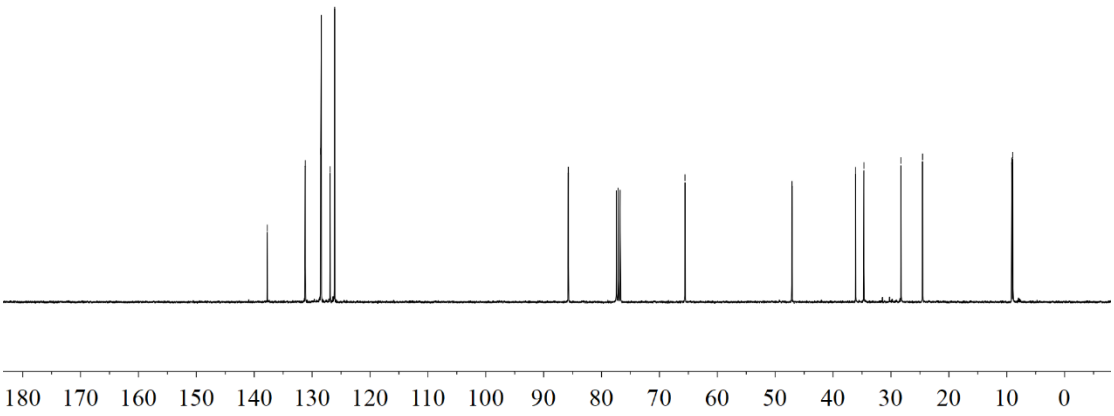
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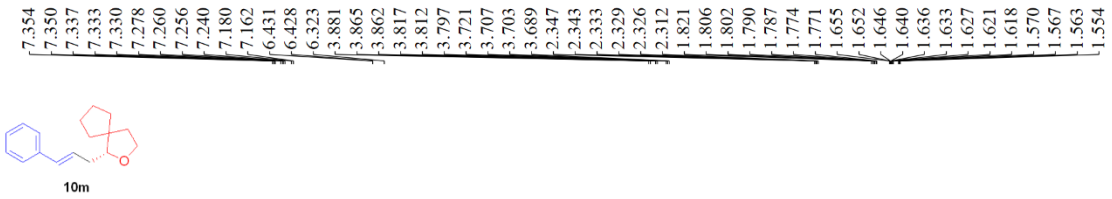
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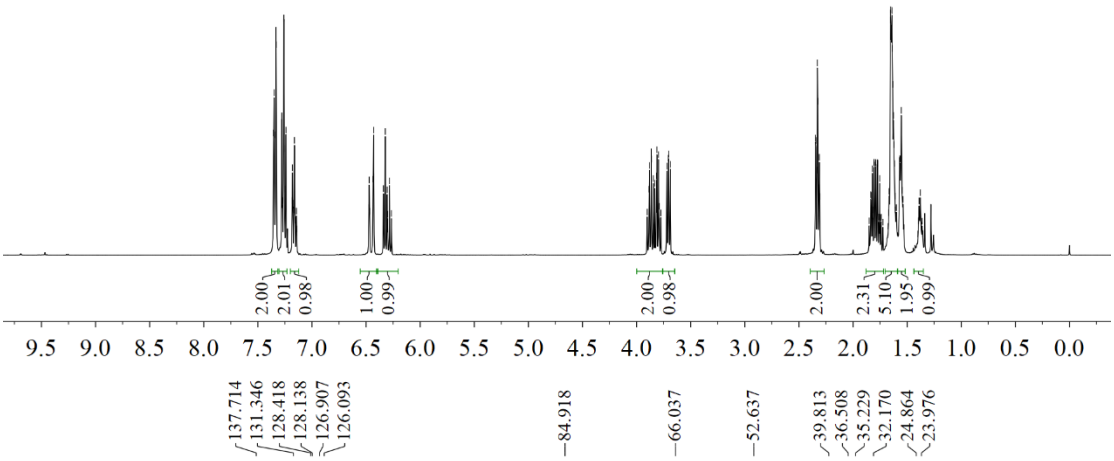
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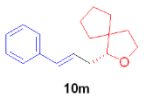
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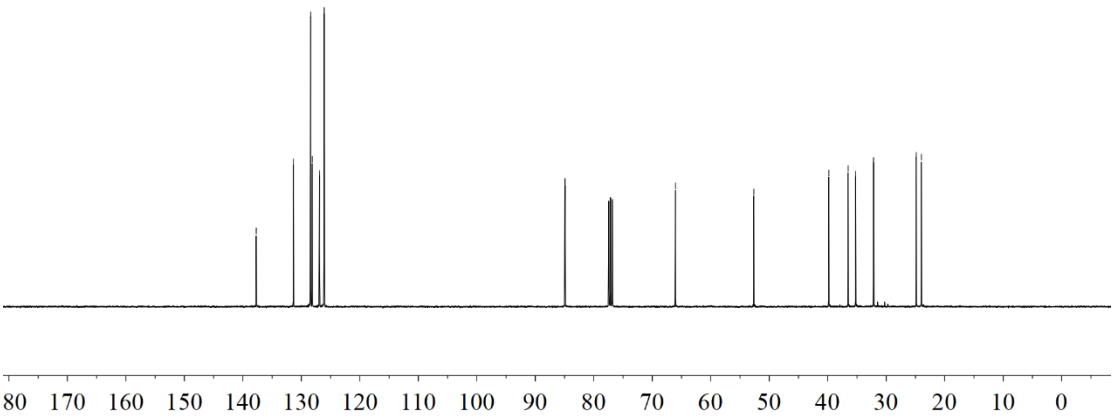
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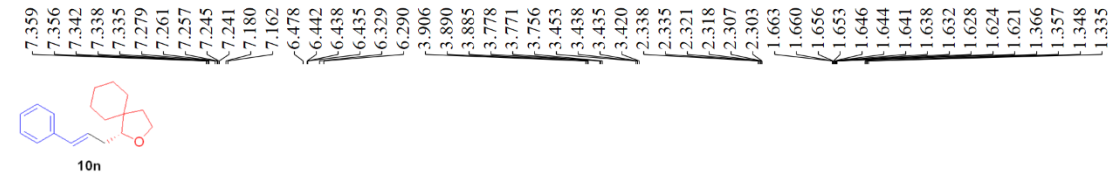
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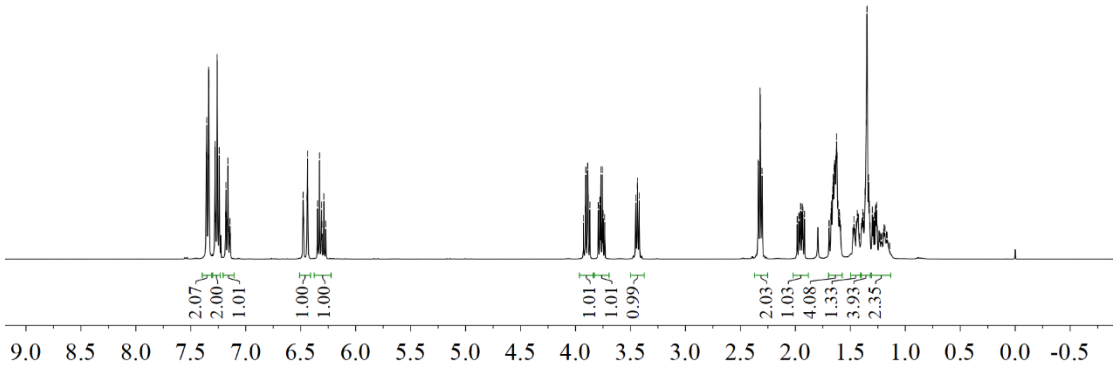
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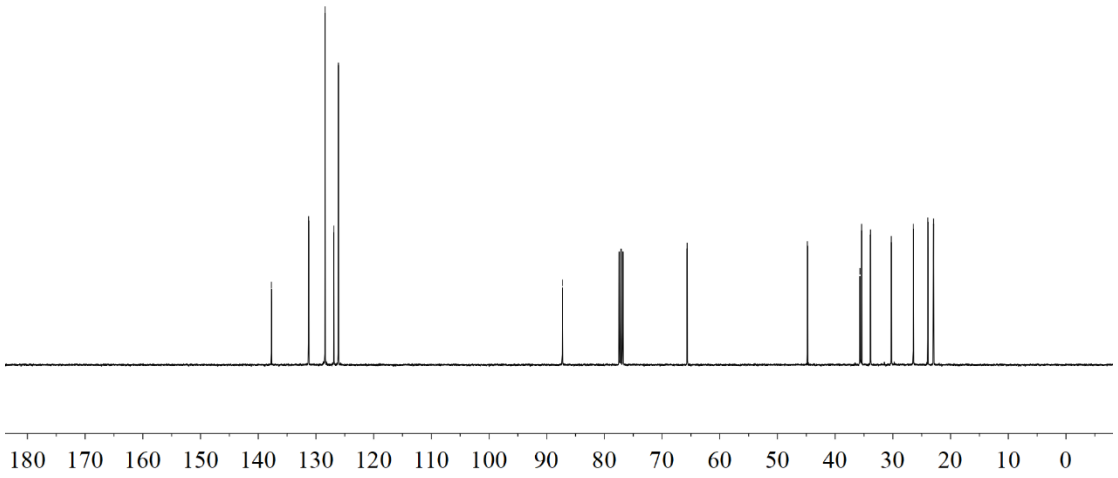
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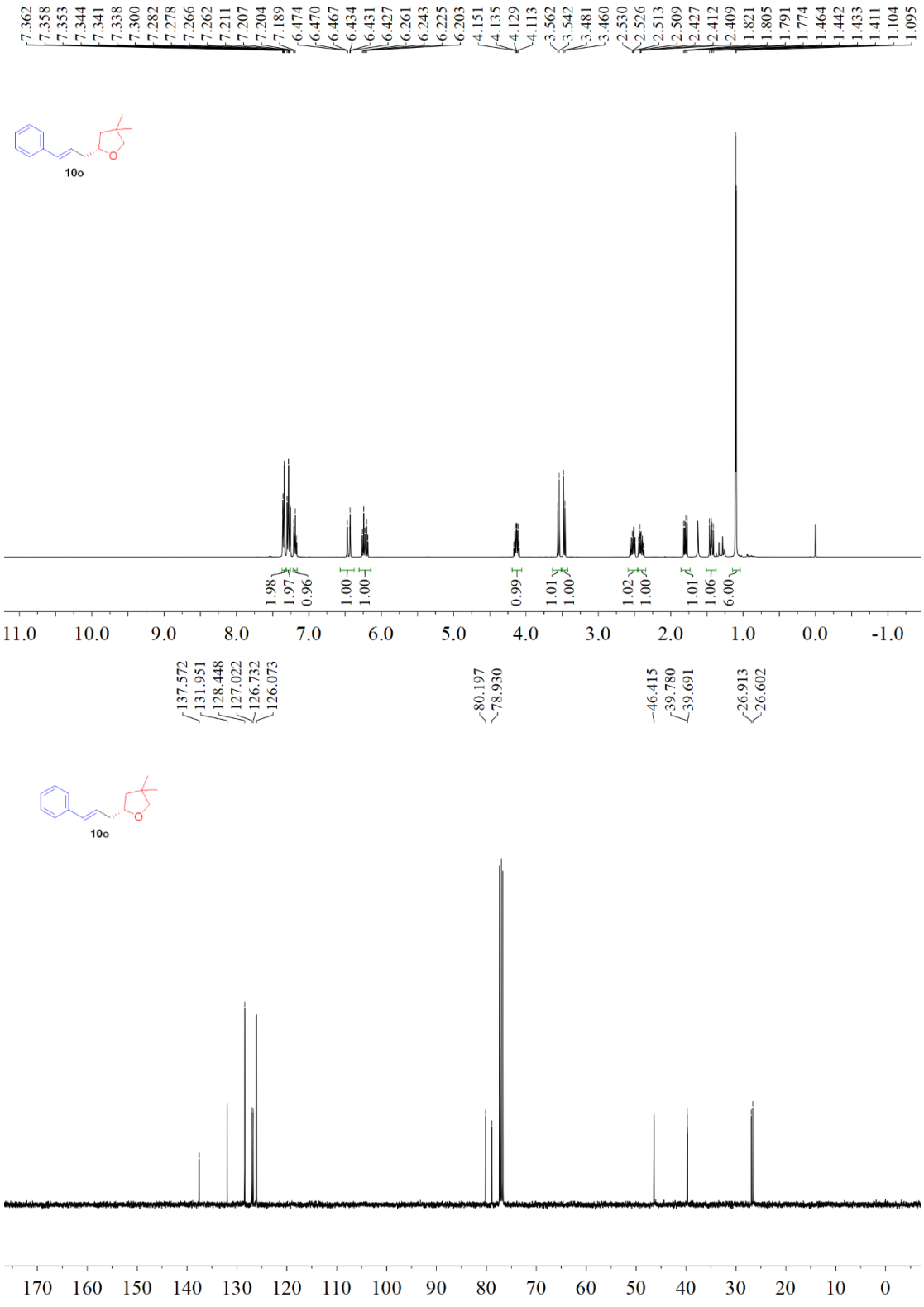
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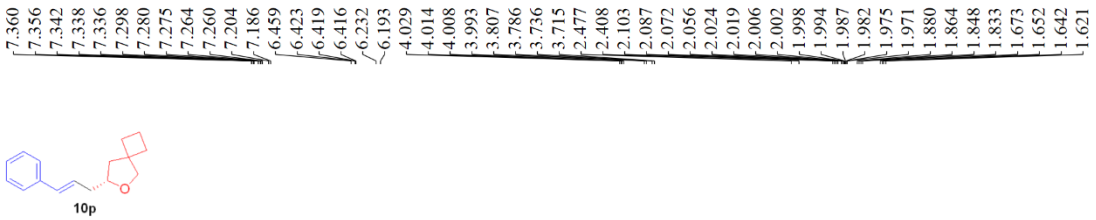
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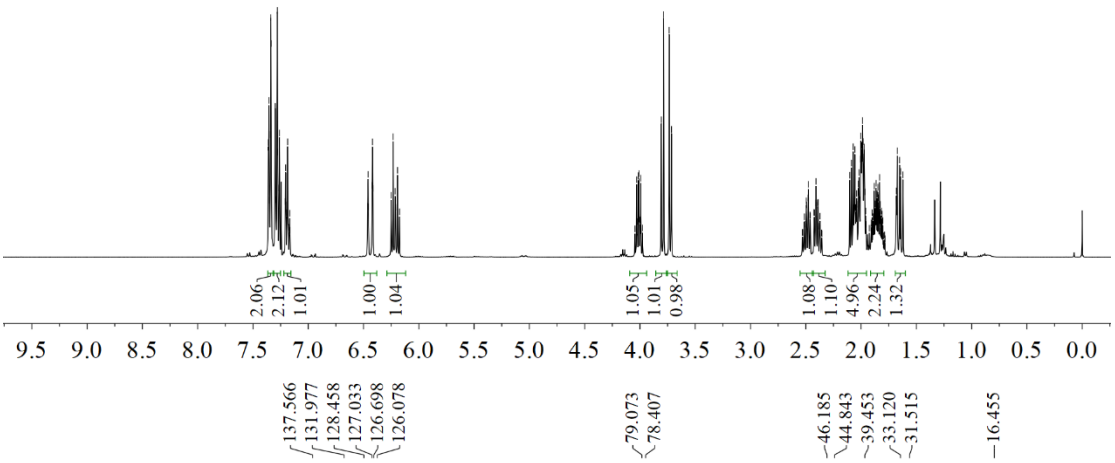
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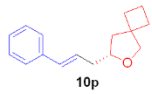
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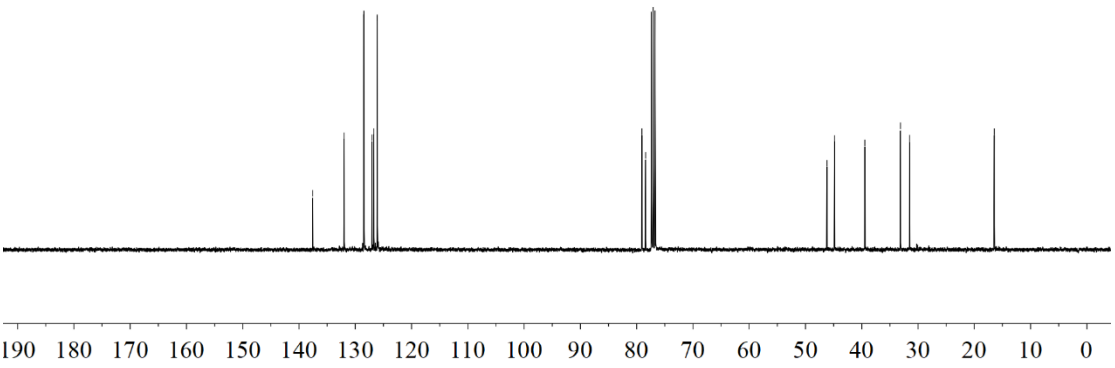
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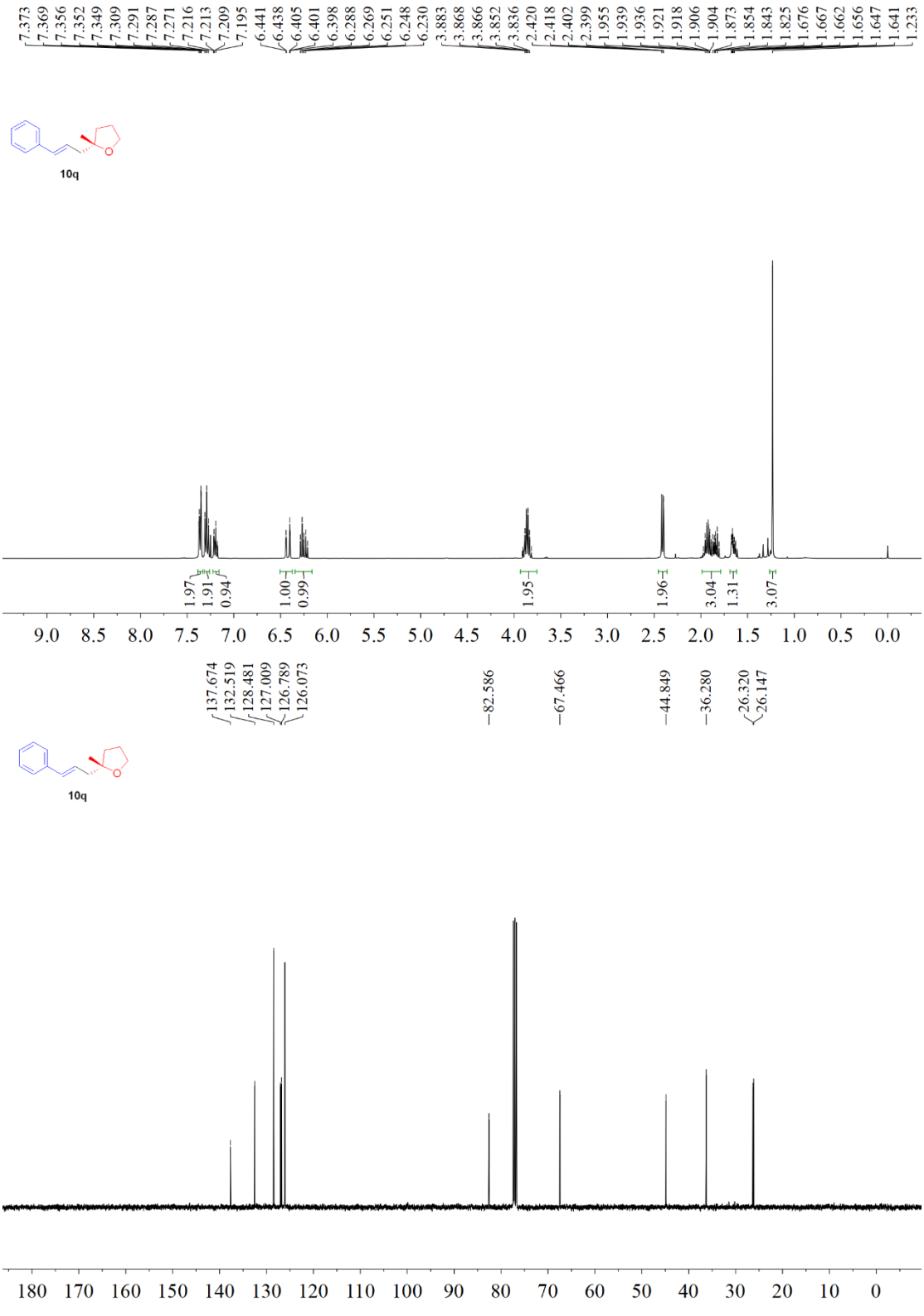
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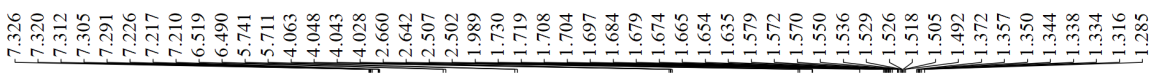
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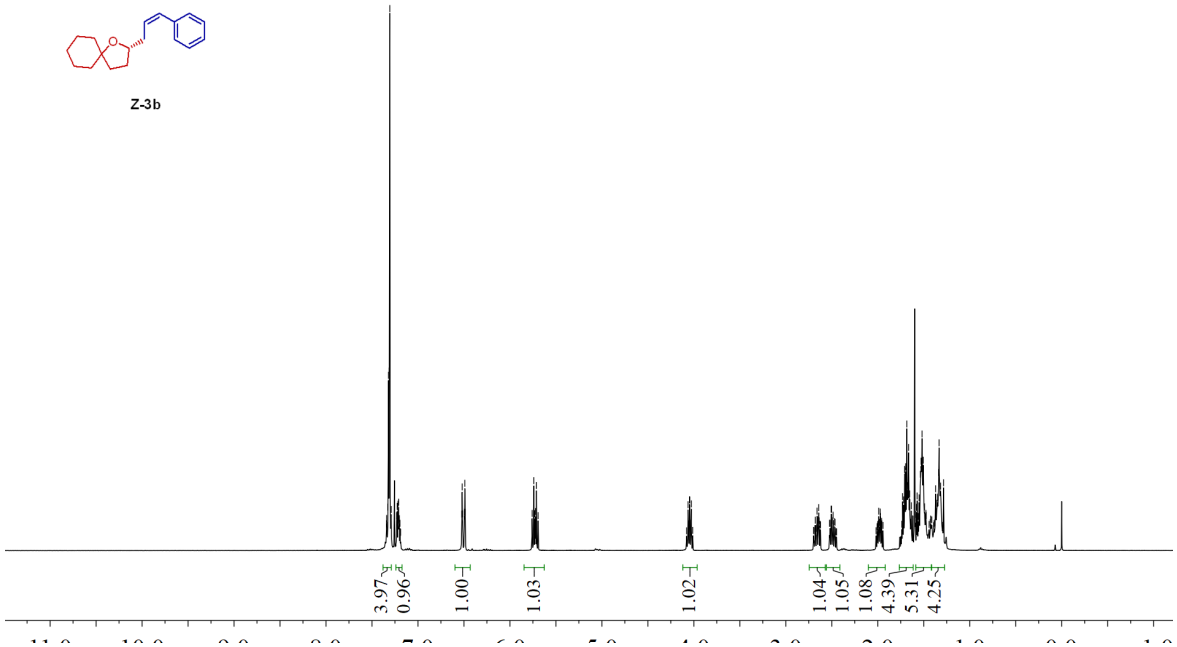
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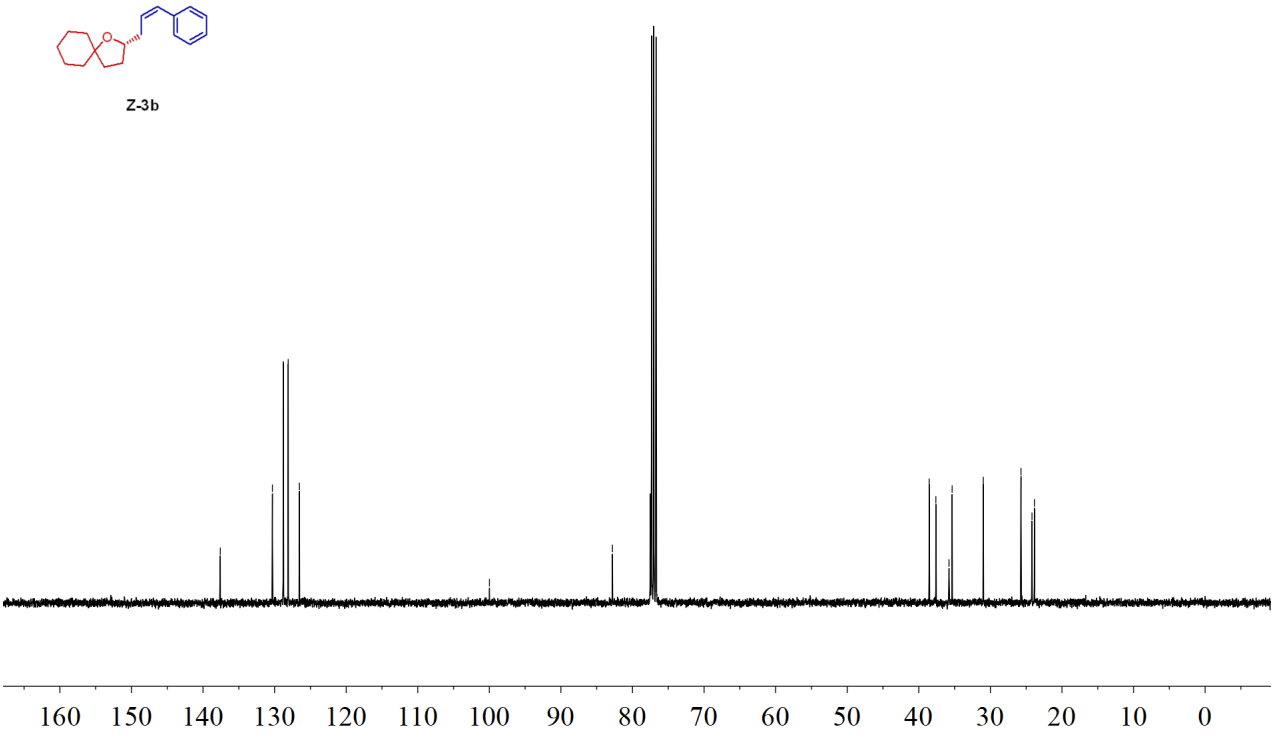
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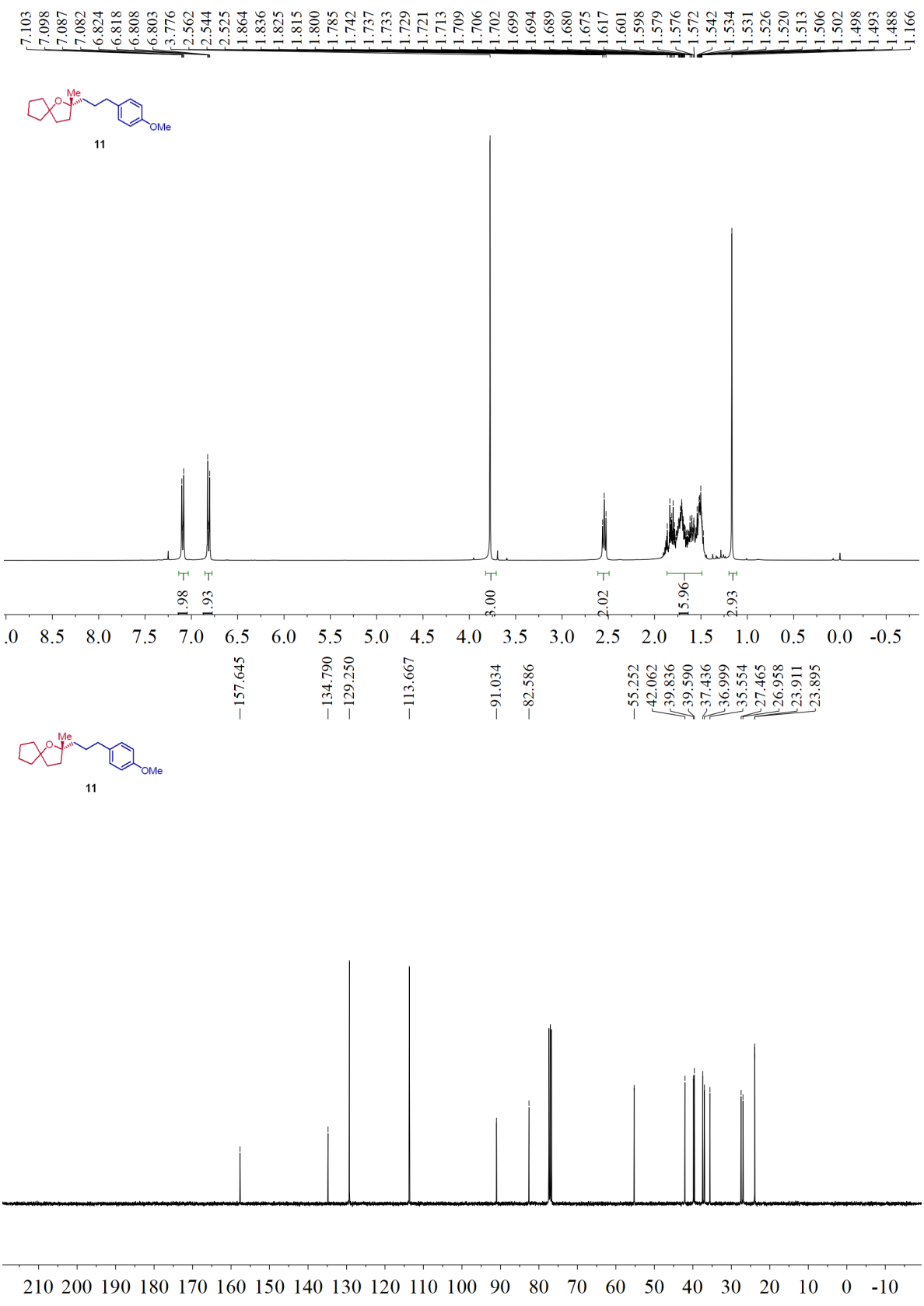
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O
OMe
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1.93
3.00
2.02
15.96
2.93
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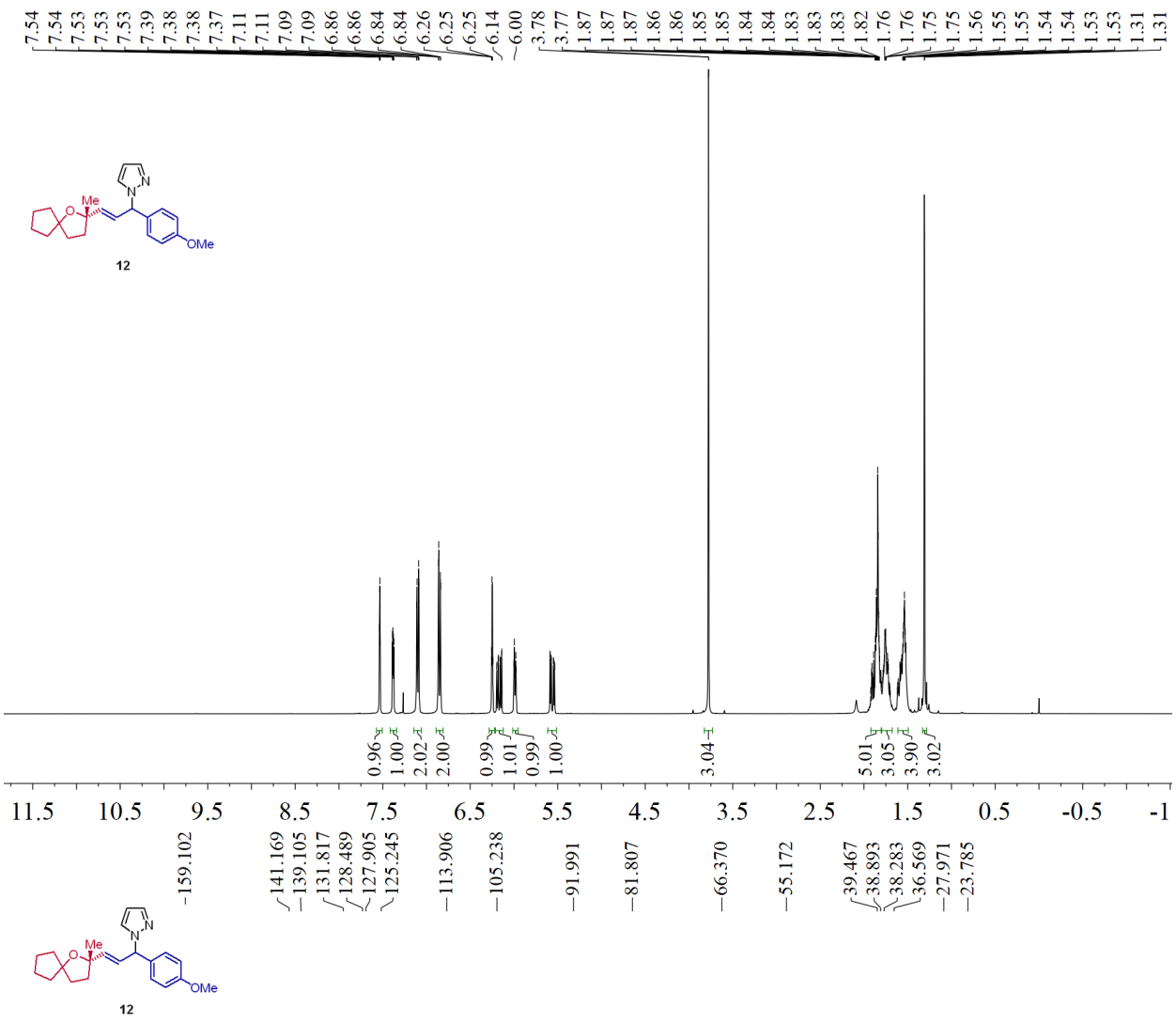
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Me
O
N
N
OMe
12
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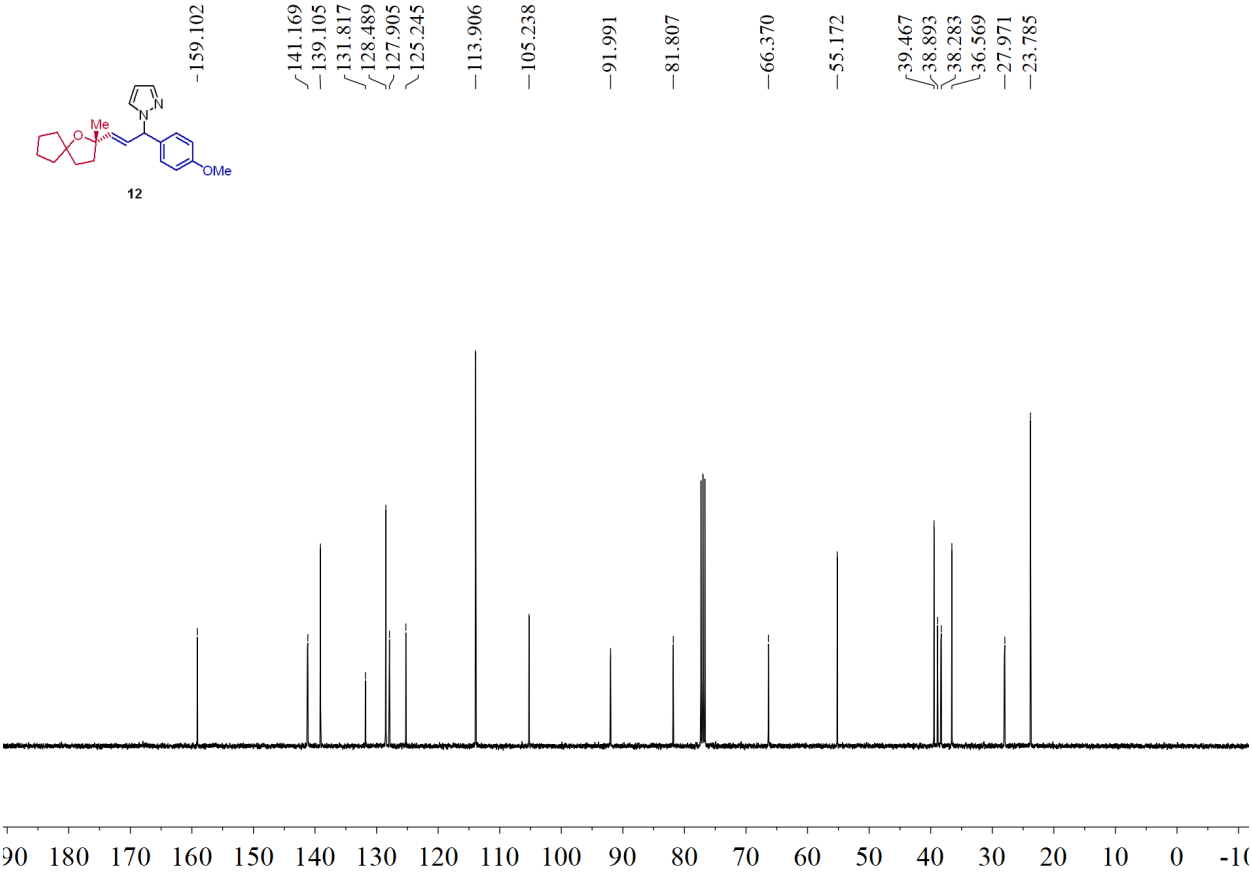
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38.283
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N
OMe
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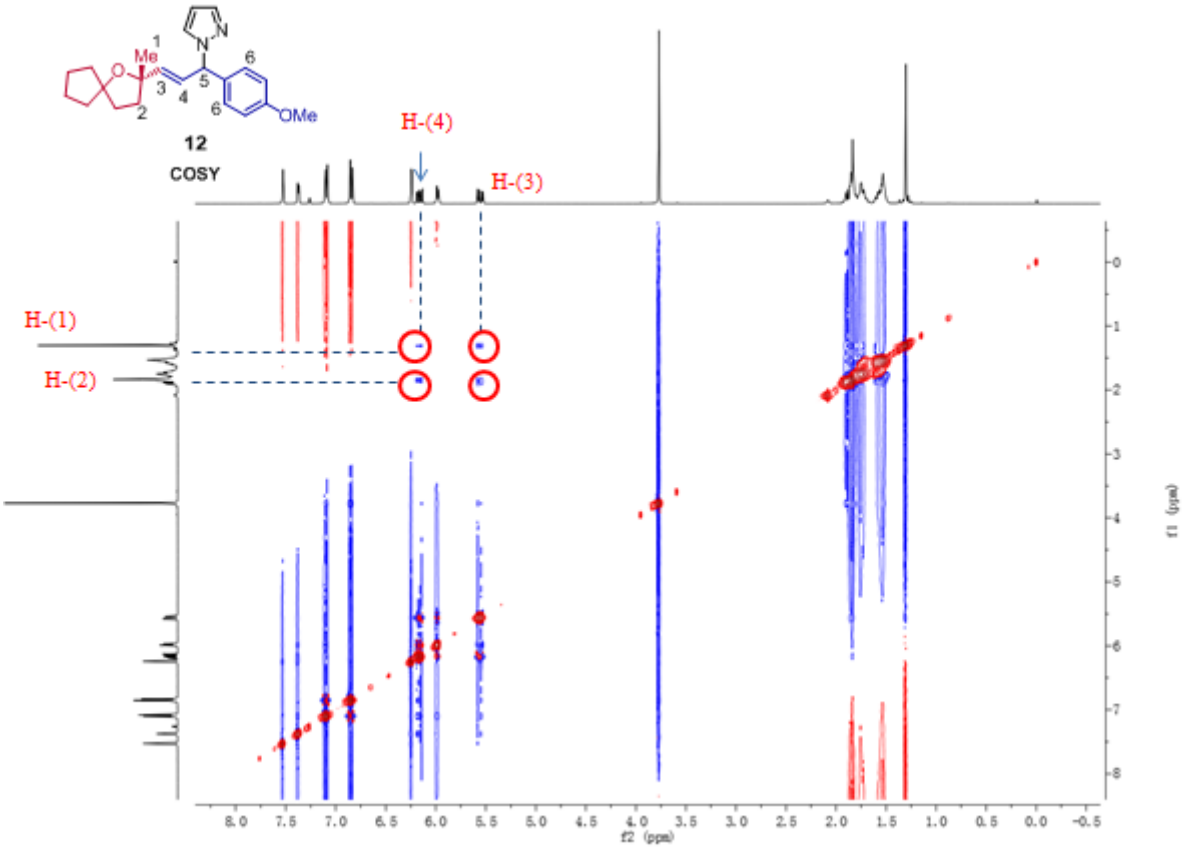
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COSY
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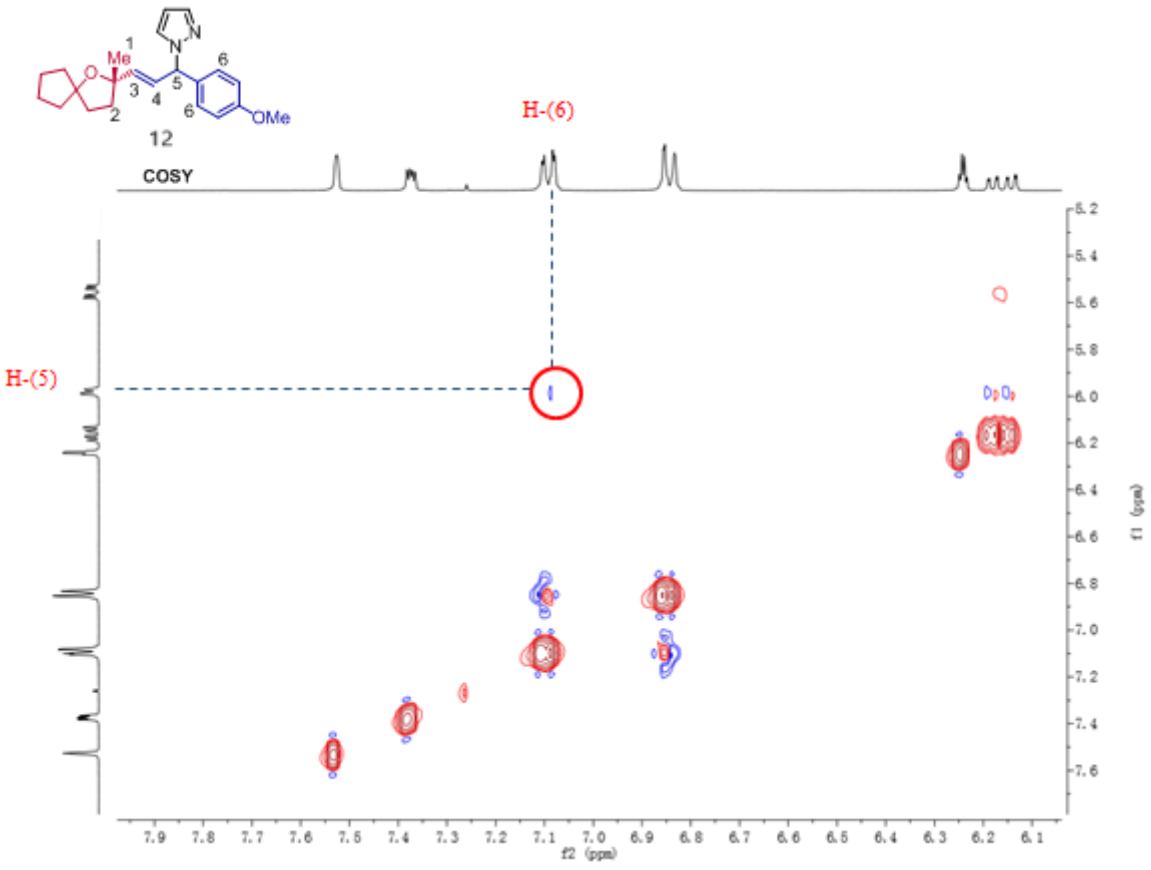
H-(3)
H-(1)
H-(2)
Me
OMe
f2 (ppm)
f1 (ppm)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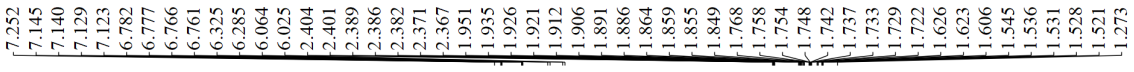
COSY
H-(6)
H-(5)
f2 (ppm)
f1 (ppm)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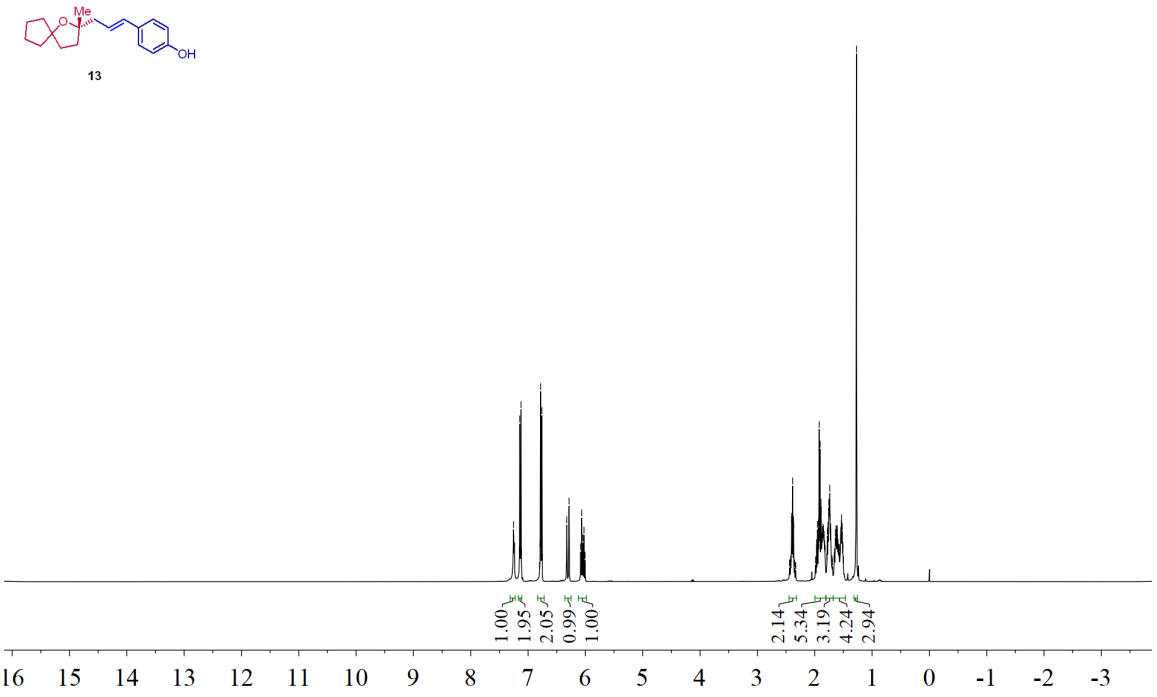
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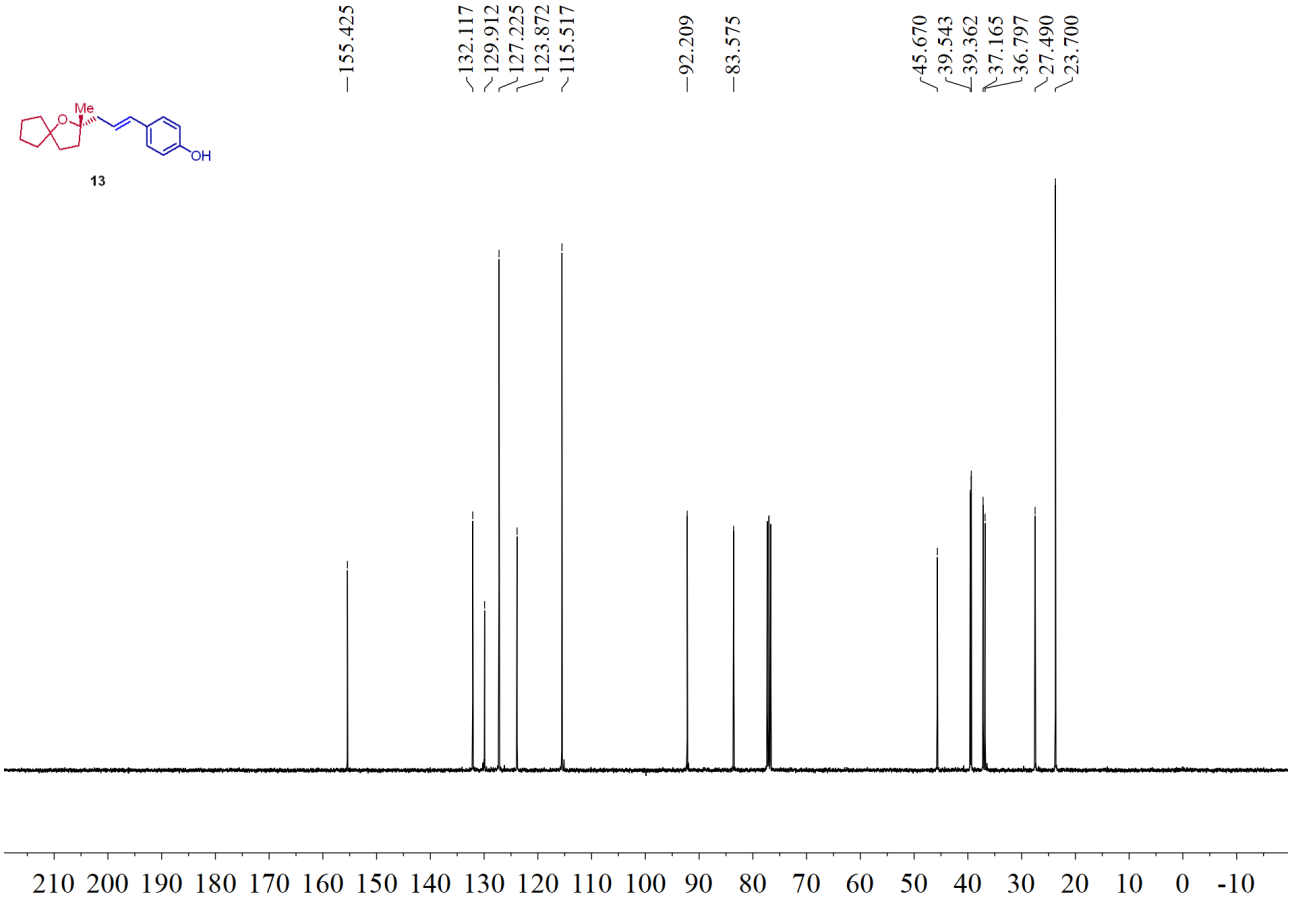

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