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Stereodivergent Synthesis via Iridium-Catalyzed Asymmetric Double Allylic Alkylation of Cyanoacetate

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Supporting Information

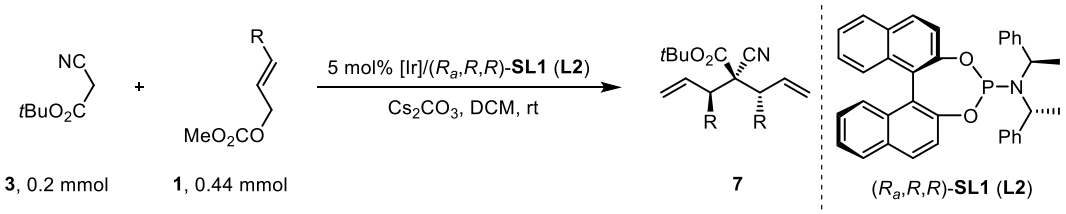
Table of Contents

I. General Remarks.....S2
II. General Procedure for Synthesis of Gem-Allylic Cyanoacetates.....S2-S14
III. Preliminary Investigate Synthesis of Bisallylated Cyanoacetates Bearing Continues Three Stereocenters with Two Different Allyl Carbonates.....S14-S15
IV. General Procedure for Synthesis of Monoallylated Cyanoacetates and Krapcho Decarboxylation.....S15-S19
V. Optimization of the Asymmetric Double Allylation Reaction Conditions.....S19-S20
VI. Stereodivergent Synthesis of Bisallylated Cyanoacetates Bearing Continues Three Stereocenters.....S21-S29
VII. Synthesis of (*S*,*s*,*R*)-*meso*-**7d**.....S30-S31
VIII. Gram Scales and Synthetic Transformations.....S31-S35
IX. References.....S35
X. NMR and HPLC Spectra.....S36-S139
XI. X-ray Structures of (*S*,*S*)-**7j**, (*S*,*R*,*S*)-**8A**, *meso*-(*S*,*s*,*R*)-**7d**, and (3*S*,4*S*,5*R*)-**12**.....S140-S141

I. General Remarks

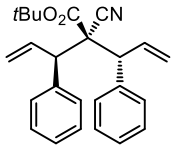
^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal CF_3COOH signal at -76.55 ppm. The data are reported as (s = single, d = double, t = triple, q = quarter, m = multiple or unresolved, br s = broad single, coupling constant(s) in Hz, integration). Commercially obtained reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. The enantiomeric excesses (ee) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent 1200 Series chromatographs using a Diacel chiral column (25 cm). Optical rotations were measured on an Rudolph Research Analytical Autopol VI polarimeter with [α]D values reported in degrees; concentration (c) is in g/100 mL. All reactions were reacted under Ar_2 atmosphere. Allylic carbonates **2** were prepared according to the literature procedure.[1] Chiral ligands (*R*$_a$,*R*,*R*)-**SL1** (**L2**) and (*R*$_a$,*R*,*R*)-**SL7** (**L3**) were prepared according to the literature procedure.[2] The absolute configuration of (*S*,*S*)-**7j**, (*S*,*R*,*S*)-**8A**, *meso*-(*S*,*s*,*R*)-**7d**, and (3*S*,4*S*,5*R*)-(*S*)-**12** were determined by X-ray analysis.

II. General Procedure for Synthesis of Gem-Allylic Cyanoacetates



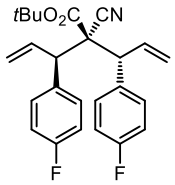
A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (*R*$_a$,*R*,*R*)-**SL1** (**L2**) (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5

mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. allylic carbonates (0.44 mmol), Cyanoacetates (0.20 mmol), Cs_2CO_3 (0.40 mmol), DCM (2 mL) were then added, reacted at room temperature. Once starting material was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude **7**, and dr was determined by crude ^{1}H NMR. The crude product was purified by silica-gel column chromatography to give **7**.



7a

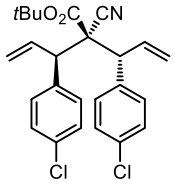
***tert*-butyl (*R*)-2-cyano-3-phenyl-2-((*R*)-1-phenylallyl)pent-4-enoate (7a):** Yield (97%); white solid, mp 92–94 °C; $[\alpha]^{25}_D$ = -108.66 (*c* 1.64, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.26 (m, 7H), 7.25 – 7.21 (m, 1H), 6.64 (ddd, *J* = 17.0, 10.1 Hz, 9.9 Hz, 1H), 6.20 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.31 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.20 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.13 (dd, *J* = 16.9, 1.4 Hz, 1H), 3.91 (d, *J* = 9.3 Hz, 1H), 3.83 (d, *J* = 9.9 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 138.8, 138.4, 134.6, 134.3, 129.09, 129.06, 128.49, 128.45, 127.9, 127.6, 119.7, 119.6, 118.5, 84.0, 58.6, 55.3, 53.4, 27.2.; HRMS (ESI+) Calcd. For $C_{25}H_{27}NNaO_2^+$ ([M+Na]$^+$): 396.1934, found: 396.1923. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.78 and 6.61 min.



7b

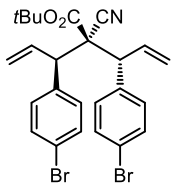
***tert*-butyl (*R*)-2-cyano-3-(4-fluorophenyl)-2-((*R*)-1-(4-fluorophenyl)allyl)pent-4-enoate (7b):** Yield (97%); pale yellow solid, mp 54–56 °C; $[\alpha]^{25}_D$ = -87.68 (*c* 1.25, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 7.04 – 6.94 (m, 4H), 6.59 (ddd, *J* = 17.2, 10.0,

10.0 Hz, 1H), 6.17 (ddd, *J* = 17.2, 10.2, 9.2 Hz, 1H), 5.32 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.23 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.20 (dd, *J* = 17.2, 1.0 Hz, 1H), 5.13 (dd, *J* = 17.2, 1.0 Hz, 1H), 3.90 (d, *J* = 9.2 Hz, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 162.3 (d, *J* = 246 Hz), 162.2 (d, *J* = 245 Hz), 134.5 (d, *J* = 3 Hz), 134.14, 134.10 (d, *J* = 3 Hz), 133.8, 130.7 (d, *J* = 7 Hz), 130.6 (d, *J* = 8 Hz), 120.0, 119.9, 118.2, 115.4 (d, *J* = 21 Hz), 115.3 (d, *J* = 22 Hz), 84.3, 58.7, 54.3, 52.5, 27.2.; ^{19}F NMR (376 MHz, Chloroform-d) δ -114.16 – -114.39 (m), -114.46 – -114.71 (m). HRMS (APCI+) Calcd. For $C_{25}H_{26}F_2NO_2^+$ ([M+H]$^+$): 410.1926, found: 410.1922. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.28 and 5.72 min.



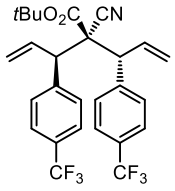
7c

***tert*-butyl (*R*)-3-(4-chlorophenyl)-2-((*R*)-1-(4-chlorophenyl)allyl)-2-cyanopent-4-enoate (7c):** Yield (96%); white solid, mp 58–60 °C; $[\alpha]^{25}_D$ = -120.96 (*c* 1.46, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 5H), 7.26 – 7.24 (m, 1H), 6.56 (ddd, *J* = 17.0, 10.0 Hz, 10.0 Hz, 1H), 6.15 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.33 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.24 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.21 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.14 (dd, *J* = 16.9, 1.2 Hz, 1H), 3.88 (d, *J* = 9.4 Hz, 1H), 3.79 (d, *J* = 10.0 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 137.1, 136.7, 133.9, 133.7, 133.5, 130.4, 130.4, 128.7, 128.6, 120.28, 120.25, 118.1, 84.6, 58.3, 54.5, 52.6, 27.2.; HRMS (ESI+) Calcd. For $C_{25}H_{25}NNaO_2^+$ ([M+Na]$^+$): 464.1155, found: 464.1133. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak ID, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 4.95 and 5.94 min.



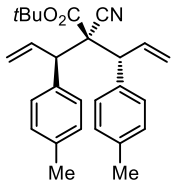
7d

***tert*-butyl (*R*)-3-(4-bromophenyl)-2-((*R*)-1-(4-bromophenyl)allyl)-2-cyanopent-4-enoate (7d):** Yield (99%); white solid, mp 98–100 °C; $[\alpha]^{25}_{D}$ = -114.83 (*c* 1.51, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 4H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 2H), 6.56 (ddd, *J* = 17.0, 10.0 Hz, 10.0 Hz, 1H), 6.15 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.32 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.24 (dd, *J* = 10.1, 1.2 Hz, 1H), 5.20 (dd, *J* = 16.9, 1.0 Hz, 1H), 5.14 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.87 (d, *J* = 9.3 Hz, 1H), 3.77 (d, *J* = 10.0 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 137.6, 137.2, 133.8, 133.5, 131.7, 131.6, 130.8, 130.7, 122.0, 121.8, 120.4, 120.3, 118.1, 84.6, 58.2, 54.6, 52.7, 27.3.; HRMS (APCI+) Calcd. For $C_{25}H_{26}Br_2NO_2^+$ ($[M+H]^+$): 530.0325, found: 530.0337. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.021 and 7.65 min.



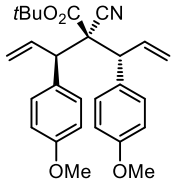
7e

***tert*-butyl (*R*)-2-cyano-3-(4-(trifluoromethyl)phenyl)-2-((*R*)-1-(4-(trifluoromethyl)phenyl)allyl)pent-4-enoate (7e):** Yield (91%); pale yellow solid, mp 59–61 °C; $[\alpha]^{25}_{D}$ = -88.82 (*c* 0.93, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 6H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.61 (ddd, *J* = 17.0, 10.0 Hz, 10.0 Hz, 1H), 6.19 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.38 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.262 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.257 (dd, *J* = 16.9, 1.0 Hz, 1H), 5.17 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.99 (d, *J* = 9.4 Hz, 1H), 3.90 (d, *J* = 10.0 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 142.5, 142.1, 133.3, 133.1, 130.3 (q, *J* = 32 Hz), 130.1 (q, *J* = 34 Hz), 129.51, 129.49, 125.5 (q, *J* = 4 Hz), 125.4 (q, *J* = 4 Hz), 123.93 (q, *J* = 271 Hz), 123.90 (q, *J* = 271 Hz), 121.0, 120.8, 117.9, 84.9, 58.0, 54.9, 53.1, 27.1.; ^{19}F NMR (376 MHz, Chloroform-d) δ -62.67, -62.77. HRMS (APCI+) Calcd. For $C_{27}H_{26}F_6NO_2^+$ ($[M+H]^+$): 510.1862, found: 510.1875. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 4.14 and 4.71 min.



7f

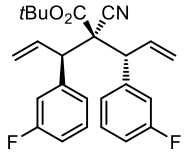
***tert*-butyl (*R*)-2-cyano-3-(*p*-tolyl)-2-((*R*)-1-(*p*-tolyl)allyl)pent-4-enoate (7f):** Yield (99%); pale yellow syrupy liquid; $[\alpha]^{25}_{D}$ = -118.70 (*c* 0.58, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H), 7.13 – 7.06 (m, 4H), 6.60 (ddd, *J* = 17.0, 10.0 Hz, 10.0 Hz, 1H), 6.19 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.28 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.18 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.12 (dd, *J* = 16.9, 1.5, 1H), 3.87 (d, *J* = 9.4 Hz, 1H), 3.77 (d, *J* = 10.0 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 137.5, 137.2, 135.8, 135.5, 134.9, 134.6, 129.2, 129.0, 128.92, 128.85, 119.33, 119.28, 118.6, 83.8, 58.7, 55.0, 53.0, 27.2, 21.1, 21.0.; HRMS (ESI+) Calcd. For $C_{27}H_{31}NNaO_2^+$ ($[M+Na]^+$): 424.2247, found: 424.2238. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.59 and 12.39 min.



7g

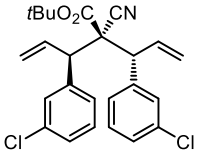
***tert*-butyl (*R*)-2-cyano-3-(4-methoxyphenyl)-2-((*R*)-1-(4-methoxyphenyl)allyl)pent-4-enoate (7g):** Yield (81%); pale yellow syrupy liquid; $[\alpha]^{25}_{D}$ = -126.00 (*c* 0.55, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 6.86 – 6.80 (m, 4H), 6.59 (ddd, *J* = 17.0, 10.1, 10.0 Hz, 1H), 6.18 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.28 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.19 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.18 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.11 (d, *J* = 16.9, 1.7 Hz, 1H), 3.86 (d, *J* = 9.3 Hz, 1H), 3.79 (s, 3H), 3.78 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 159.1, 159.0, 134.8, 134.5, 131.0, 130.6, 130.1, 130.0, 119.19, 119.16, 118.7, 113.83, 113.77, 83.8, 59.1, 55.3, 55.2, 54.4, 52.6, 27.3.; HRMS (ESI+) Calcd. For $C_{27}H_{31}NNaO_4^+$ ($[M+Na]^+$): 456.2145, found: 456.2135. 18:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 238 nm); t_r = 7.48 and

10.19 min.



7h

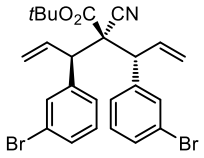
***tert*-butyl (*R*)-2-cyano-3-(3-fluorophenyl)-2-((*R*)-1-(3-fluorophenyl)allyl)pent-4-enoate (7h):** Yield (95%); pale yellow syrupy liquid; $[\alpha]^{25}_{D}$ = -94.44 (*c* 0.72, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 1H), 7.26 – 7.24 (m, 1H), 7.21 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.04 – 6.92 (m, 3H), 6.57 (ddd, *J* = 17.0, 10.0, 9.9 Hz, 1H), 6.17 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.35 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.25 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.23 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.16 (dd, *J* = 16.9, 1.5 Hz, 1H), 3.90 (d, *J* = 9.4 Hz, 1H), 3.81 (d, *J* = 9.9 Hz, 1H), 1.05 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 162.62 (d, *J* = 245 Hz), 162.55 (d, *J* = 245 Hz), 140.9 (d, *J* = 7 Hz), 140.5 (d, *J* = 7 Hz), 133.7, 133.4, 130.1 (d, *J* = 9 Hz), 130.0 (d, *J* = 8 Hz), 125.0 (d, *J* = 3 Hz), 124.7 (d, *J* = 3 Hz), 120.4, 120.3, 118.0, 116.2 (d, *J* = 34 Hz), 115.9 (d, *J* = 34 Hz), 114.9 (d, *J* = 21 Hz), 114. (d, *J* = 29 Hz), 114.6 (d, *J* = 29 Hz), 84.6, 58.2, 54.8 (d, *J* = 2 Hz), 52.9 (d, *J* = 2 Hz), 27.2.; ^{19}F NMR (376 MHz, Chloroform-d) δ -112.48 – -112.59 (m), -112.59 – -112.68 (m). HRMS (ESI+) Calcd. For $C_{25}H_{25}F_2NNaO_2^+$ ($[M+Na]^+$): 432.1746, found: 432.1740. 20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0 mL/min, λ = 238 nm); t_r = 6.60 and 8.11 min.



7i

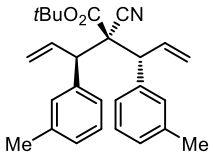
***tert*-butyl (*R*)-3-(3-chlorophenyl)-2-((*R*)-1-(3-chlorophenyl)allyl)-2-cyanopent-4-enoate (7i):** Yield (86%); pale yellow solid, mp 78–80 °C; $[\alpha]^{25}_{D}$ = -90.81 (*c* 0.74, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (dt, *J* = 5.4, 2.1 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.26 – 7.22 (m, 3H), 6.57 (ddd, *J* = 17.0, 10.3, 10.0 Hz, 1H), 6.17 (ddd, *J* = 16.9, 10.2, 9.5 Hz, 1H), 5.35 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 16.9, 1.3 Hz, 1H), 3.88 (d, *J* = 9.5

Hz, 1H), 3.78 (d, *J* = 10.0 Hz, 1H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 140.5, 140.1, 134.3, 134.2, 133.7, 133.4, 129.9, 129.8, 129.5, 128.8, 128.1, 127.8, 127.6, 127.0, 120.5, 117.8, 84.8, 58.2, 54.8, 52.9, 27.3.; HRMS (ESI+) Calcd. For $C_{25}H_{25}Cl_2NNaO_2^+$ ([M+Na]$^+$): 464.1155, found: 464.1156. 17:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.98 and 7.84 min.



7j

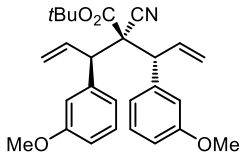
***tert*-butyl (*R*)-3-(3-bromophenyl)-2-((*R*)-1-(3-bromophenyl)allyl)-2-cyanopent-4-enoate (7j):** Yield (88%); pale yellow solid, mp 108–110 °C; $[\alpha]^{25}_D$ = -82.36 (*c* 1.27, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 1.9 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.30 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.19 (dt, *J* = 11.0, 7.8 Hz, 2H), 6.56 (ddd, *J* = 17.0, 10.2, 10.0 Hz, 1H), 6.17 (ddd, *J* = 16.8, 10.1, 9.5 Hz, 1H), 5.34 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.4 Hz, 1H), 5.17 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.86 (d, *J* = 9.5 Hz, 1H), 3.76 (d, *J* = 10.0 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 140.8, 140.4, 133.6, 133.3, 132.3, 131.7, 131.1, 130.8, 130.1, 130.1, 128.0, 127.4, 122.6, 122.4, 120.6, 120.5, 117.8, 84.9, 58.2, 54.8, 52.8, 27.3.; HRMS (APCI+) Calcd. For $C_{25}H_{26}Br_2NO_2^+$ ([M+H]$^+$): 530.0325, found: 530.0313. 18:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.99 and 8.55 min.



7k

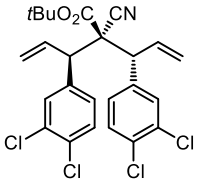
***tert*-butyl (*R*)-2-cyano-3-(*m*-tolyl)-2-((*R*)-1-(*m*-tolyl)allyl)pent-4-enoate (7k):** Yield (93%); white solid, mp 82–84 °C; $[\alpha]^{25}_D$ = -96.06 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.15 – 7.10 (m, 2H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.63 (ddd, *J* = 16.9, 10.1, 9.9 Hz, 1H), 6.21 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.29 (dd, *J* = 10.1, 1.7

Hz, 1H), 5.201 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.198 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.13 (dd, *J* = 16.9, 1.5 Hz, 1H), 3.87 (d, *J* = 9.4 Hz, 1H), 3.77 (d, *J* = 9.9 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 138.7, 138.3, 138.0, 137.9, 134.8, 134.5, 129.9, 129.6, 128.6, 128.38, 128.36, 128.2, 126.1, 125.9, 119.44, 119.39, 118.4, 83.8, 58.5, 55.3, 53.4, 27.2, 21.4, 21.3.; HRMS (ESI+) Calcd. For $C_{27}H_{31}NNaO_2^+$ ([M+Na]$^+$): 424.2247, found: 424.2238. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.58 and 8.90 min.



7l

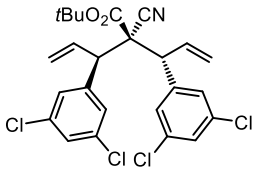
***tert*-butyl (*R*)-2-cyano-3-(3-methoxyphenyl)-2-((*R*)-1-(3-methoxyphenyl)allyl)pent-4-enoate (7l):** Yield (92%); white solid, mp 103–105 °C; $[\alpha]^{25}_D$ = -99.07 (*c* 0.75, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 1H), 7.20 – 7.16 (m, 1H), 7.03 – 6.99 (m, 1H), 6.97 – 6.92 (m, 2H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.60 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 6.18 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.30 (dd, *J* = 10.0, 1.7 Hz, 1H), 5.21 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.12 (dd, *J* = 17.0, 1.7 Hz, 1H), 3.87 (d, *J* = 9.3 Hz, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 159.52, 159.48, 140.2, 139.7, 134.5, 134.3, 129.44, 129.42, 121.34, 121.29, 119.6, 119.5, 115.0, 114.3, 113.6, 113.2, 84.0, 58.4, 55.3, 55.21, 55.19, 53.5, 27.2.; HRMS (ESI+) Calcd. For $C_{27}H_{31}NNaO_4^+$ ([M+Na]$^+$): 456.2145, found: 456.2138. 10:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.72 and 9.24 min.



7m

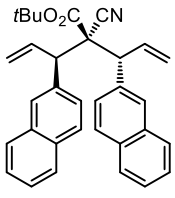
***tert*-butyl (*R*)-2-cyano-3-(3,4-dichlorophenyl)-2-((*R*)-1-(3,4-dichlorophenyl)allyl)pent-4-enoate (7m):** Yield (98%); white solid, mp 64–66 °C; $[\alpha]^{25}_D$ = -118.04 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.45 (d, *J* = 2.1 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.52 (ddd, *J* = 17.0, 10.0. 9.9 Hz, 1H), 6.14 (ddd, *J* = 16.8, 10.2, 9.5 Hz, 1H), 5.36 (dd, *J* = 10.0, 1.4 Hz, 1H), 5.30 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.30 (dd, *J* = 16.8, 1.2 Hz, 1H), 3.86 (d, *J* = 9.5 Hz, 1H), 3.75 (d, *J* = 9.9 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 138.5, 138.3, 133.1, 132.8, 132.7, 132.5, 132.2, 132.0, 131.3, 130.6, 130.54, 130.46, 128.6, 128.1, 121.1, 121.0, 117.6, 85.3, 58.0, 54.1, 52.3, 27.3.; HRMS (ESI+) Calcd. For $C_{25}H_{23}Cl_4NNaO_2^+$ ([M+Na]$^+$): 532.0375, found: 532.0360. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.07 and 6.66 min.



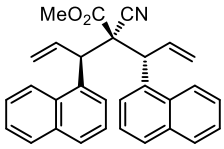
7n

***tert*-butyl (*R*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*R*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate (7n):** Yield (97%); white solid, mp 88–90 °C; $[\alpha]^{25}_D$ = -86.52 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 2.0 Hz, 3H), 7.27 (t, *J* = 1.9 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 2H), 6.50 (ddd, *J* = 16.9, 10.1, 9.9 Hz, 1H), 6.13 (ddd, *J* = 16.9, 10.1, 9.6 Hz, 1H), 5.37 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.33 (dd, *J* = 10.1, 1.1 Hz, 1H), 5.23 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.21 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.72 (d, *J* = 9.9 Hz, 1H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 141.5, 141.2, 135.1, 135.0, 132.9, 132.5, 128.3, 128.0, 127.51, 127.49, 121.4, 121.3, 117.2, 85.5, 57.6, 54.5, 52.5, 27.3.; HRMS (ESI+) Calcd. For $C_{25}H_{23}Cl_4NNaO_2^+$ ([M+Na]$^+$): 532.0375, found: 532.0368. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 210 nm); t_r = 5.00 and 5.86 min.



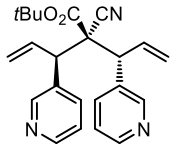
7o

***tert*-butyl (*R*)-2-cyano-3-(naphthalen-2-yl)-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate (7o):** Yield (97%); white solid, mp 116–118 °C; $[\alpha]^{25}_D$ = -155.41 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.76 (m, 8H), 7.61 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.43 (m, 5H), 6.79 (ddd, *J* = 17.0, 10.0 Hz, 10.0 Hz, 1H), 6.35 (ddd, *J* = 16.9, 10.0 Hz, 9.8 Hz, 1H), 5.37 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.29 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.23 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.20 (dd, *J* = 16.9, 1.2 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 4.06 (d, *J* = 10.0 Hz, 1H), 0.84 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 136.1, 135.9, 134.5, 134.4, 133.3, 133.2, 132.9, 132.7, 128.3, 128.23, 128.20, 128.1, 128.0, 127.9, 127.6, 127.5, 126.9, 126.7, 126.2, 126.12, 126.05, 126.0, 120.0, 119.8, 118.5, 84.1, 58.6, 55.5, 53.6, 27.1.; HRMS (ESI+) Calcd. For $C_{33}H_{31}NNaO_2^+$ ($[M+Na]^+$): 496.2247, found: 496.2242. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 232 nm); t_r = 10.70 and 21.76 min.



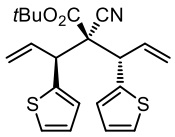
7p

***tert*-butyl (*R*)-2-cyano-3-(naphthalen-1-yl)-2-((*R*)-1-(naphthalen-1-yl)allyl)pent-4-enoate (7p):** Yield (77%); white solid, mp 80–82 °C; $[\alpha]^{25}_D$ = -123.58 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.88 (dt, *J* = 7.9, 1.9 Hz, 2H), 7.85 – 7.76 (m, 2H), 7.75 – 7.64 (m, 2H), 7.62 – 7.51 (m, 3H), 7.49 – 7.37 (m, 4H), 6.64 (ddd, *J* = 16.7, 9.8. 9.5 Hz, 1H), 6.06 (ddd, *J* = 16.9, 10.2, 9.2 Hz, 1H), 5.37 (dd, *J* = 16.7, 1.2 Hz, 1H), 5.36 (dd, *J* = 9.8, 1.2 Hz, 1H), 5.21 (d, *J* = 9.5 Hz, 1H), 5.03 (d, *J* = 9.2 Hz, 1H), 4.83 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.65 (dd, *J* = 16.9, 1.2 Hz, 1H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 135.5, 135.4, 134.8, 134.3, 134.1, 133.9, 132.3, 130.7, 129.2, 128.9, 128.6, 128.1, 126.6, 126.3, 125.9, 125.8, 125.6, 125.3, 125.2, 125.1, 122.6, 122.4, 119.4, 118.2, 118.1, 59.3, 52.7, 48.5, 46.0.; HRMS (ESI+) Calcd. For $C_{30}H_{25}NNaO_2^+$ ($[M+Na]^+$): 454.1778, found: 454.1771. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak IE, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 11.46 and 17.56 min.



7q

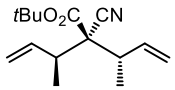
***tert*-butyl (*R*)-2-cyano-3-(pyridin-3-yl)-2-((*R*)-1-(pyridin-3-yl)allyl)pent-4-enoate (7q):** Yield (33%); pale yellow solid, mp 106–108 °C; $[\alpha]^{25}_{D}$ = -112.50 (*c* 0.84, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (ddt, *J* = 14.3, 4.8, 2.5 Hz, 4H), 7.88 (ddd, *J* = 8.0, 2.4, 1.6 Hz, 1H), 7.74 – 7.66 (m, 1H), 7.30 – 7.24 (m, 2H), 6.60 (ddd, *J* = 17.0, 10.0, 9.9 Hz, 1H), 6.17 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.40 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.27 (dd, *J* = 10.0, 1.4 Hz, 1H), 5.18 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.97 (d, *J* = 9.4 Hz, 1H), 3.89 (d, *J* = 9.9 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 150.5, 150.2, 149.3, 149.1, 136.4, 135.9, 134.3, 133.9, 133.1, 132.7, 123.4, 123.3, 121.1, 121.0, 117.7, 85.2, 58.3, 52.8, 50.7, 27.2.; HRMS (APCI+) Calcd. For $C_{23}H_{26}N_3O_2^+$ ($[M+H]^+$): 376.2020, found: 376.2031. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 220 nm); t_r = 27.78 and 36.47 min.



7r

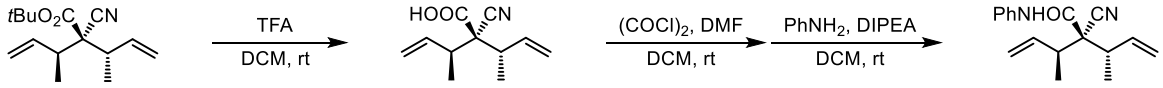
***tert*-butyl (*R*)-2-cyano-3-(naphthalen-1-yl)-2-((*R*)-1-(naphthalen-1-yl)allyl)pent-4-enoate (7r):** Yield (83%); pale yellow solid, mp 96–98 °C; $[\alpha]^{25}_{D}$ = -97.75 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.19 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.46 (ddd, *J* = 16.9, 10.0, 9.8 Hz, 1H), 6.15 (ddd, *J* = 16.8, 10.2, 9.2 Hz, 1H), 5.34 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.251 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.246 (dd, *J* = 16.8, 1.4 Hz, 1H), 5.34 (dd, *J* = 16.9, 1.2 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 4.16 (d, *J* = 9.8 Hz, 1H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 140.32, 140.25, 133.9, 133.8, 126.8, 126.6, 126.5, 126.4, 124.9, 124.8, 120.1, 119.7, 118.4, 84.3, 59.6, 50.3, 48.7, 27.3.; HRMS (ESI+) Calcd. For $C_{21}H_{23}NNaO_2S_2^+$ ($[M+Na]^+$): 408.1062, found: 408.1056. >20:1 dr. The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0

mL/min, λ = 220 nm); t_r = 9.26 and 10.42 min.



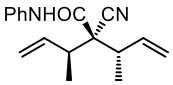
7s

***tert*-butyl (*S*)-2-((*S*)-but-3-en-2-yl)-2-cyano-3-methylpent-4-enoate (7s):** Yield (87%); pale yellow liquid; $[\alpha]^{25}_D$ = -9.03 (*c* 1.03, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 (ddd, *J* = 17.2, 11.6, 8.7 Hz, 1H), 5.82 (ddd, *J* = 17.2, 10.4, 9.0 Hz, 1H), 5.203 (dd, *J* = 11.6, 1.6 Hz, 1H), 5.196 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.12 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.4, 1.2 Hz, 1H), 2.75 (dq, *J* = 9.0, 6.9 Hz, 1H), 2.75 (dq, *J* = 8.7, 6.8 Hz, 1H), 1.51 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 136.7, 136.4, 118.3, 118.2, 117.8, 84.1, 58.4, 42.7, 41.6, 27.9, 17.2, 16.5.; HRMS (ESI+) Calcd. For $C_{15}H_{23}NNaO_2^+$ ([M+Na]$^+$): 272.1621, found: 272.1615. >20:1 dr. The product was transformed to **16** (*vide infra*) and then analyzed by HPLC to determine the enantiomeric excess: 95% ee.



(*S*,*S*)-**7s** **15** **16**, 74% yield, 95% ee

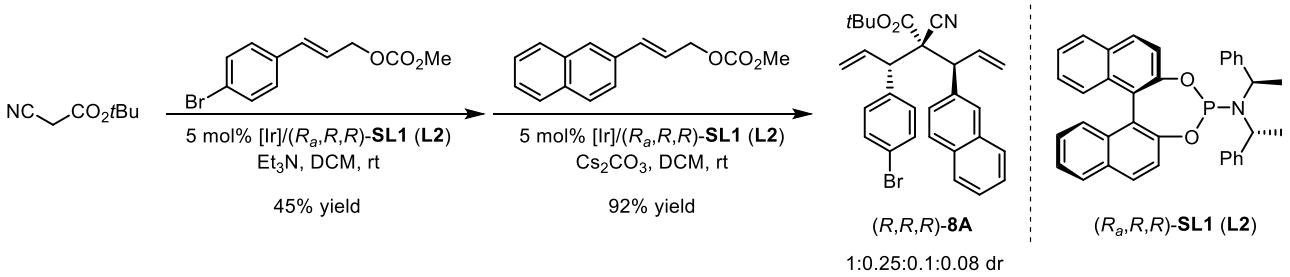
To a solution of (*S*,*S*)-**7s** (0.20 mmol) in DCM (2.0 mL) was added TFA (1.0 mL) under Ar_2 at rt and the reaction mixture was stirred for 2 h, then concentrated in vacuo to give crude **11** without purified by flash chromatography. To a solution of crude **15** in DCM (2.0 mL) was added $(COCl)_2$ (0.80 mmol, 4.0 equiv.) and DMF (20 μL) under Ar_2 and the reaction mixture stirred for 1 h, then concentrated in vacuo. After that, DCM (2 mL), diisopropylethylamine (0.40 mmol) and aniline (0.30 mmol) was added under Ar_2, the reaction mixture stirred for 8 h at rt. The reaction was quenched with H_2O and extracted with CH_2Cl_2 (3 x 3 mL) and the combined organics were washed with 10% $NaHCO_3$ (1 x 10 mL), and brine (10 mL). The combined organics were combined and dried over Na_2SO_4 and concentrated under vacuum and purified by silica-gel flash chromatography.



16

(*S*,*Z*)-2-((*S*)-but-3-en-2-yl)-2-cyano-3-methyl-N-phenylpent-4-enimidic acid (16): Yield (74%); Pale yellow liquid; $[\alpha]^{32}_{D}$ = -16.60 (*c* 3.56, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.54 – 7.46 (m, 2H), 7.40 – 7.32 (m, 2H), 7.23 – 7.14 (m, 1H), 5.96 (ddd, *J* = 17.5, 9.9, 8.6 Hz, 1H), 5.84 (ddd, *J* = 17.1, 10.3, 8.7 Hz, 1H), 5.33 – 5.21 (m, 2H), 5.20 – 5.10 (m, 2H), 3.01 – 2.82 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 136.7, 136.5, 136.4, 129.1, 125.5, 120.7, 112.0, 118.7, 118.0, 58.7, 42.4, 41.9, 17.0, 16.4.; HRMS (ESI+) Calcd. For $C_{17}H_{21}N_2O$ ($[M+H]^+$): 269.1648, found: 269.1646. The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralcel OJ-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 240 nm); t_r = 8.45 and 9.51 min.

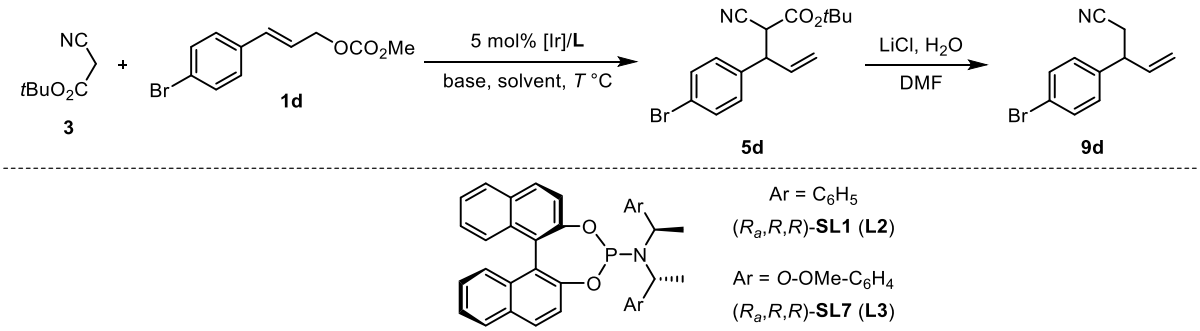
III. Preliminary Investigate Synthesis of Bisallylated Cyanoacetates Bearing Continues Three Stereocenters with Two Different Allylic Carbonates.



A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (*R*$_a$,*R*,*R*)-**SL1** (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. Allylic carbonate **1d** (0.20 mmol), cyanoacetate **3** (0.20 mmol), Et_3N (0.20 mmol), DCM (2 mL) were then added, and then reacted at room temperature for 12 h under Ar_2 atmosphere. The crude product was purified by silica-gel column chromatography to give the mono-allylic cyanoacetate **5d**. Then under Ar_2 atmosphere, $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %),

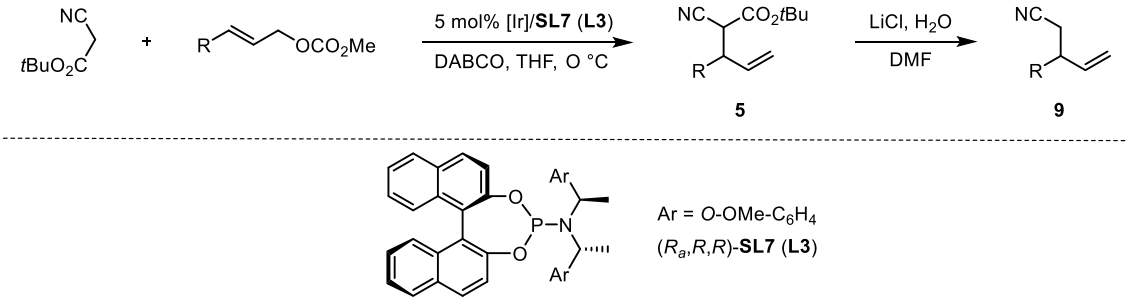
phosphoramidite ligand (R_a,*R*,*R*)-**SL1** (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL) were heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give Ir-compless. To this Schlenk tube allylic carbonate **1m** (0.20 mmol), mono-allylic cyanoacetate **5d**, Cs_2CO_3 (0.20 mmol), DCM (2 mL) were then added, and then reacted at room temperature under Ar_2 atmosphere. Once starting material was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude **8A**. The crude product was purified by silica-gel column chromatography to give **8A**.

IV. Optimization of the Asymmetric Monoallylation Reaction Conditions and General Procedure for Synthesis of Mono-Allylic Cyanoacetates and Krapcho Decarboxylation



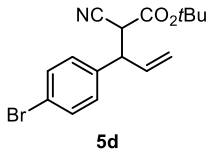
Entry[a]	Ligand	Base	Solvent	*T* (°C)	Yield of **5d** (%)[b]	Ee of **9d** (%)[c]
1[d]	(R_a,*R*,*R*)-**SL1** (**L2**)	Et_3N[d]	DCM	room temp.	47	90
2[d]	(R_a,*R*,*R*)-**SL1** (**L2**)	DABCO	DCM	room temp.	43	88
3[d]	(R_a,*R*,*R*)-**SL1** (**L2**)	DABCO	THF	room temp.	34	90
4	(R_a,*R*,*R*)-**SL7** (**L3**)	DABCO	THF	reflux	43	86
5	(R_a,*R*,*R*)-**SL7** (**L3**)	DABCO	THF	room temp.	56	94
6[e]	(R_a,*R*,*R*)-**SL7** (**L3**)	Et_3N	THF	room temp.	47	93
7	(R_a,*R*,*R*)-**SL7** (**L3**)	DABCO	THF	0 °C	68	99

[a] All the reactions were carried out with 0.2 mmol of **3**, 0.1 mmol of **1d** and 0.04 mmol base in 2 mL of solvent. [b] Isolated yields. [c] Ee was determined by chiral HPLC analysis. [d] 0.2 mmol Et_3N was used. [e] 0.2 mmol of **3** and 0.2 mmol **1d** was used.



A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.01 mmol, 2.5 mol %), phosphoramidite ligand **SL7** (0.02 mmol, 5 mol %), degassed THF (1.0 mL) and degassed *n*-propylamine (1.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. allylic carbonates (0.40 mmol), Cyanoacetates (0.80 mmol), DABCO (0.08 mmol), DCM (4 mL) were then added, reacted at room temperature. Once starting material **1** was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude **5**. The crude product was purified by silica-gel column chromatography to give **5**.

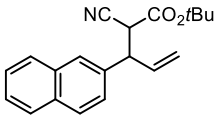
A Schlenk tube was evacuated and backfilled with argon for three times, then added LiCl (0.35 mmol), **5** (0.10 mmol), DMF (0.75 mL), and H_2O (7 μL). The mixture was stirred under reflux for 1 h. After the reaction was complete, a saturated aqueous solution of NH_4Cl (5 mL) was added. The aqueous layer was extracted three times with ether (2 mL). The combined organic layer was dried with Na_2SO_4 filtered, and evaporated to give crude **9**. The crude product was purified by silica-gel column chromatography to give **9**.



5d

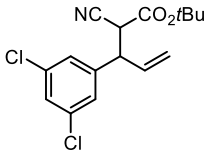
***tert*-butyl 3-(4-bromophenyl)-2-cyanopent-4-enoate (Mixture of Diastereomers) (5d):** Yield (68%); pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 4H), 7.24 – 7.14 (m, 4H), 6.17 – 5.99 (m, 2H), 5.35 – 5.20 (m, 4H), 4.02 – 3.94 (m, 2H), 3.75 (d, *J* = 7.2 Hz, 1H), 3.67 (d, *J* = 6.9 Hz, 1H), 1.39 (s, 9H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 137.6, 136.8, 135.7, 134.4,

132.0, 131.9, 129.9, 129.5, 122.0, 121.8, 119.5, 118.4, 115.5, 84.51, 84.47, 49.1, 48.8, 44.8, 44.4, 27.7, 27.6.; HRMS (ESI+) Calcd. For $C_{16}H_{18}BrNNaO_2^+$ ([M+Na]$^+$): 358.0413, found: 358.0412.



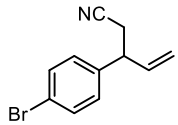
5o

***tert*-butyl 2-cyano-3-(naphthalen-2-yl)pent-4-enoate (Mixture of Diastereomers) (5o):** Yield (64%); pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 8H), 7.50 – 7.38 (m, 6H), 6.31 – 6.09 (m, 2H), 5.37 – 5.26 (m, 4H), 4.22 – 4.13 (m, 2H), 3.86 (d, *J* = 7.6 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 1H), 1.34 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.74, 163.73, 136.2, 135.9, 135.3, 135.0, 133.3, 132.9, 132.8, 128.7, 128.6, 127.9, 127.8, 127.63, 127.62, 127.4, 126.8, 126.4, 126.3, 126.22, 126.18, 125.7, 125.4, 119.3, 118.2, 115.8, 115.7, 84.30, 84.25, 49.9, 49.7, 45.0, 44.6, 27.64, 27.61.; HRMS (ESI+) Calcd. For $C_{20}H_{21}NNaO_2^+$ ([M+Na]$^+$): 330.1465, found: 330.1468.



5n

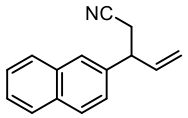
***tert*-butyl 2-cyano-3-(3,5-dichlorophenyl)pent-4-enoate (Mixture of Diastereomers) (5n):** Yield (50%); pale yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.26 – 7.16 (m, 4H), 6.15 – 5.96 (m, 2H), 5.42 – 5.24 (m, 4H), 4.03 – 3.91 (m, 2H), 3.77 (d, *J* = 7.1 Hz, 1H), 3.68 (d, *J* = 7.0 Hz, 1H), 1.42 (s, 9H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.13, 163.10, 141.8, 141.1, 135.4, 135.3, 134.7, 133.6, 128.2, 128.0, 126.8, 126.4, 120.3, 119.1, 115.1, 115.0, 84.9, 84.8, 49.0, 48.6, 44.5, 44.1, 27.63, 27.61.; HRMS (ESI+) Calcd. For $C_{16}H_{17}Cl_2NNaO_2^+$ ([M+Na]$^+$): 348.0529, found: 348.0529.



9d

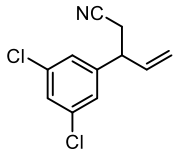
3-(4-bromophenyl)pent-4-enenitrile (9d): Yield (72%); colorless liquid; ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.54 – 7.44 (m, 2H), 7.16 – 7.03 (m, 2H), 5.99 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.27 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.20 (dd, *J* = 17.2, 0.8 Hz, 1H), 3.67 (dt, *J* = 6.8, 6.7 Hz, 1H), 2.74 (dd, *J* = 16.2, 6.7 Hz, 1H), 2.68 (dd, *J* = 16.2, 6.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.2, 137.2, 132.1, 129.1, 121.5, 117.8, 117.3, 44.8, 23.8.; HRMS (ESI+) Calcd. For $C_{11}H_{10}BrNNa^+$ ([M+Na]$^+$): 257.9889, found: 257.9883. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee for (*S*)-**9d**, 99% ee for (*R*)-**9d** (Chiralcel OD-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 19.61 and 23.67 min.



9o

3-(naphthalen-2-yl)pent-4-enenitrile (9o): Yield (80%); colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 3H), 7.70 – 7.66 (m, 1H), 7.52 – 7.44 (m, 2H), 7.33 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.11 (ddd, *J* = 17.2, 10.4, 6.9 Hz, 1H), 5.30 (dd, *J* = 10.4, 1.0 Hz, 1H), 5.25 (dd, *J* = 17.2, 1.1 Hz, 1H), 3.86 (td, *J* = 7.2, 6.9 Hz, 1H), 2.83 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.79 (dd, *J* = 16.8, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.7, 137.6, 133.4, 132.7, 128.8, 127.8, 127.6, 126.4, 126.08, 126.06, 125.2, 118.2, 117.1, 45.5, 23.8.; HRMS (ESI+) Calcd. For $C_{15}H_{13}NNa^+$ ([M+Na]$^+$): 230.0940, found: 230.0941. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee for (*S*)-**9o**, 99% ee for (*R*)-**9o** (Chiralcel OJ-H, *i*-propanol/hexane = 10/9, flow rate 1.0 mL/min, λ = 220 nm); t_r = 36.09 and 37.82 min.

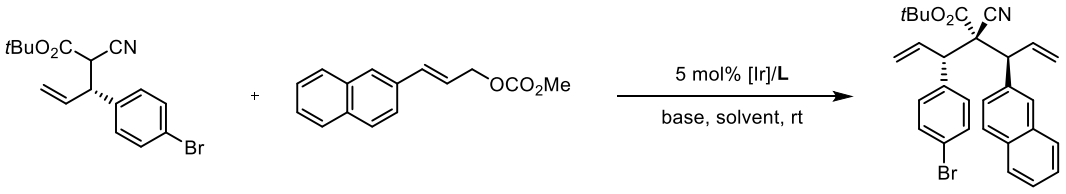


9n

3-(3,5-dichlorophenyl)pent-4-enenitrile (9n): Yield (75%); colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 1.9 Hz, 1H), 7.13 (dd, *J* = 1.9, 0.5 Hz, 2H), 5.96 (ddd, *J* = 17.2, 10.4, 6.9 Hz, 1H), 5.33 (dd, *J* = 10.4, 0.4 Hz, 1H), 5.24 (dd, *J* = 17.2, 0.8 Hz, 1H), 3.66 (dt, *J* = 7.2, 6.9 Hz, 1H), 2.81 – 2.70 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.75 – 2.64 (dd, *J* = 9.2, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 136.3, 135.5, 127.9, 126.0, 118.1, 117.4, 44.8, 23.6.; HRMS (ESI+) Calcd. For

$C_{11}H_9Cl_2NNa^+$ ([M+Na]$^+$): 248.0004, found: 248.0015. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee for (*S*)-**9n**, 95% ee for (*R*)-**9n** (Chiralpak IE, *i*-propanol/hexane = 1/99, flow rate 1.0 mL/min, λ = 206 nm); t_r = 11.92 and 12.69 min.

V. Optimization of the Asymmetric Double Allylation Reaction Conditions

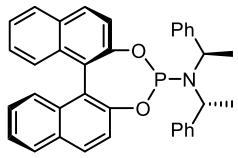


5d **1o** (*R*,*R*,*R*)-**8A**

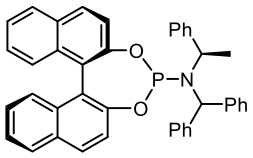
Entry[a]	Ligand	Base	Solvent	Yield of **8A** (%)[b]	dr of **8A** (%)[c]
1	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	THF	93	1:0.18:0.03:0.02
2	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	toluene	90	1:0.25:0.05:0.01
3	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	Et_2O	93	1:0.33:0.06:0.02
4	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	MeOH	90	1:0.40:0.31:0.05
5	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	MeCN	83	1:0.36:0.05:0.02
6	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	DMF	95	1:0.41:0.10:0.03
7	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	DCM	93	1:0.24:0.10:0.01
8	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	DCE	94	1:0.25:0.09:0.01
9	(R_a,*R*,*R*)-**SL1**	*t*BuOK	THF	38	1:0.19:0.03:0.01
10	(R_a,*R*,*R*)-**SL1**	NaOH	THF	46	1:0.19:0.07:0.03
11	(R_a,*R*,*R*)-**SL1**	DBU	THF	30	1:0.17:0.03:0.01
12	(R_a,*R*,*R*)-**SL1**	*n*BuLi	THF	88	1:0.22:0.10:0.01
13	(R_a,*R*,*R*)-**SL1**	LiHDMS	THF	33	1:0.39:0.03:0.03
14	(R_a,*R*,*R*)-**SL1**	NaHDMS	THF	56	1:0.20:0.05:0.02
15	(R_a,*R*,*R*)-**SL1**	Et_3N	THF	96	1:0.24:0.11:0.01
16[d]	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	DCM	91	1:0.15:0.08:0.01
17[d]	(R_a,*R*,*R*)-**SL1**	Cs_2CO_3	DCM/THF = 1:1	86	1:0.15:0.08:0.01
18	(R_a,*R*,*R*)-**SL2**	Cs_2CO_3	THF	<5	/
19	(R_a,*R*,*R*)-**SL3**	Cs_2CO_3	THF	<5	/
20[d]	(R_a,*R*,*R*)-**SL2**	Cs_2CO_3	DCM	75	1:0.35:0.04:0.02
21[d]	(R_a,*R*,*R*)-**SL3**	Cs_2CO_3	DCM	85	1:0.27:0.04:0.01
22[d]	(R_a,*R*,*R*)-**SL4**	Cs_2CO_3	DCM	88	1:0.45:0.04:0.03
23[d]	(R_a,*R*,*R*)-**SL5**	Cs_2CO_3	DCM	92	1:0.17:0.05:0.02
24[d]	(R_a,*R*,*R*)-**SL6**	Cs_2CO_3	DCM	83	1:0.18:0.06:0.02
25[d]	(R_a,*R*,*R*)-**SL7**	Cs_2CO_3	DCM	94	1:0.15:0.03:0

26[d]	(R_a,*R*,*R*)-**SL8**	Cs_2CO_3	DCM	75	1:0.12:0.03:0.01
27[d]	(R_a,*R*,*R*)-**SL9**	Cs_2CO_3	DCM	81	1:0.14:0.05:0.02
28[d]	(R_a,*R*,*R*)-**SL10**	Cs_2CO_3	DCM	84	1:0.13:0.04:0.02
29[d]	(R_a,*R*,*R*)-**SL11**	Cs_2CO_3	DCM	90	1:0.21:0.05:0.02
30[d]	(R_a,*R*,*R*)-**SL12**	Cs_2CO_3	DCM	46	1:0.17:0.05:0.03
31[d]	(R_a,*R*,*R*)-**SL13**	Cs_2CO_3	DCM	78	1:0.20:0.05:0.02
32[d]	(R_a,*R*,*R*)-**SL14**	Cs_2CO_3	DCM	47	1:0.09:0.03:0.01
33	(R_a,*R*,*R*)-**SL14**	Cs_2CO_3	DCM	60	1:0.09:0.05:0.01
34	(R_a,*R*,*R*)-**SL7**	Cs_2CO_3	DCM	95	1:0.16:0.03:0

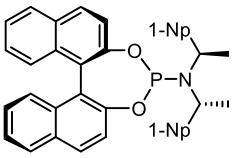
[a] All reactions were carried out with 0.20 mmol **5d**, 0.2 mmol **1o** and 0.2 mmol base in 2 mL of solvent. [b] Yields refer to the isolated products after chromatographic purification. [c] The dr value was determined by ^{1}H NMR analysis. [d] Reaction was carried out at 0 °C.



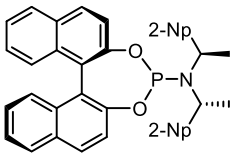
(R_a,*R*,*R*)-**SL1** (**L2**)



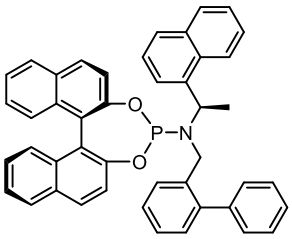
(R_a,*R*)-**SL2**



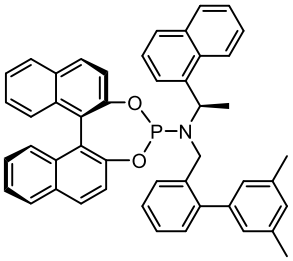
(R_a,*R*,*R*)-**SL3**



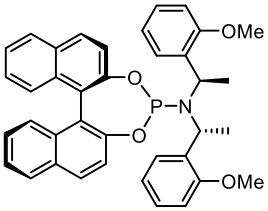
(R_a,*R*,*R*)-**SL4**



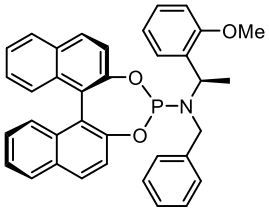
(R_a,*R*,*R*)-**SL5**



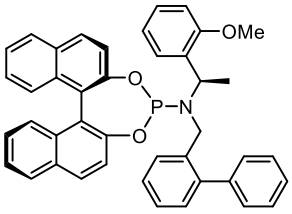
(R_a,*R*,*R*)-**SL6**



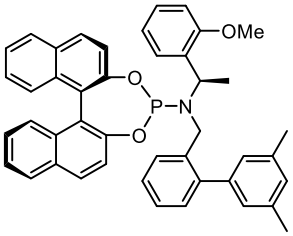
(R_a,*R*,*R*)-**SL7** (**L3**)



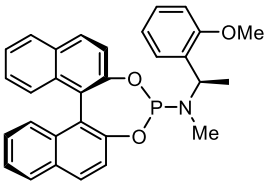
(R_a,*R*,*R*)-**SL8**



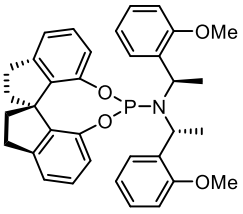
(R_a,*R*,*R*)-**SL9**



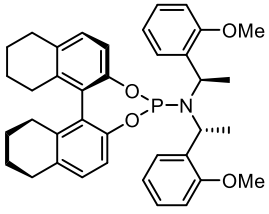
(R_a,*R*,*R*)-**SL10**



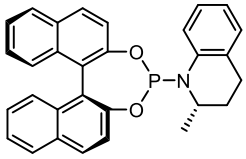
(R_a,*R*,*R*)-**SL11**



(*S*,*R*,*R*)-**SL12**

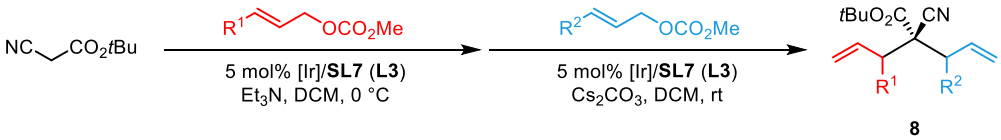


(R_a,*R*,*R*)-**SL13**



(S_a,*S*)-**SL14**

VI. Stereodivergent Synthesis of Bisallylated Cyanoacetates Bearing Continues Three Stereocenters



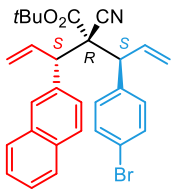
8

General Procedure for Synthesis of Bisallylated Cyanoacetates:

(*S*,*R*,*S*)-**8A** as example

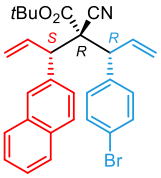
A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (S_a,*S*,*S*)-**SL7** (**L3**) (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. Allylic carbonate **1o** (0.50 mmol), cyanoacetate **3** (1.00 mmol), DABCO (0.10 mmol), THF (10 mL) were then added, and then reacted at 0 °C for 12 h under Ar_2 atmosphere. The crude product was purified by silica-gel column chromatography to give the mono-allylic cyanoacetate **5o**.

Then under Ar_2 atmosphere, $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (S_a,*S*,*S*)-**SL7** (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL) were heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give Ir-compless. To this Schlenk tube allylic carbonate **1d** (0.20 mmol), mono-allylic cyanoacetate **5o** (0.20 mmol), Cs_2CO_3 (0.20 mmol), DCM (2 mL) were then added, and then reacted at room temperature under Ar_2 atmosphere. Once starting material was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude (*S*,*R*,*S*)-**8A**. The crude product was purified by silica-gel column chromatography to give (*S*,*R*,*S*)-**8A**.



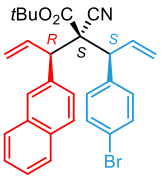
(*S*,*R*,*S*)-**8A**

***tert*-butyl (2*R*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*S*,*R*,*S*)-8A):** Yield (94%); White solid, mp 88–90 °C; $[\alpha]^{25}_{D}$ = 126.46 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.25 – 7.21 (m, 2H), 6.62 (ddd, *J* = 17.0, 10.0, 9.8 Hz, 1H), 6.30 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.35 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.244 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.35 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.17 (dd, *J* = 16.9, 2.0 Hz, 1H), 4.08 (d, *J* = 9.4 Hz, 1H), 3.84 (d, *J* = 9.8 Hz, 1H), 0.86 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 137.4, 135.9, 134.3, 133.8, 133.2, 132.7, 131.6, 130.8, 128.2, 128.1, 127.9, 127.4, 126.6, 126.2, 126.1, 122.0, 120.2, 120.1, 118.3, 84.3, 58.4, 54.7, 53.5, 27.1.; HRMS (ESI+) Calcd. For $C_{29}H_{28}BrNNaO_2^+$ ([M+Na]$^+$): 524.1196, found: 524.1179; dr = 1:0.12:0.02:0.



(*S*,*R*,*R*)-**8A**

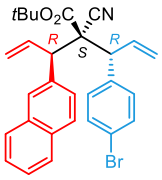
***tert*-butyl (2*R*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*S*,*R*,*R*)-8A):** Yield (98%); White solid, mp 88–90 °C; $[\alpha]^{25}_{D}$ = 31.96 (*c* 1.12, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (ddd, *J* = 8.8, 4.3, 2.4 Hz, 4H), 7.51 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.30 – 7.26 (m, 2H), 6.46 (dddd, *J* = 16.9, 10.2, 8.8 Hz, 1H), 6.37 (dddd, *J* = 16.9, 10.2, 8.8 Hz, 1H), 5.30 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.18 (dd, *J* = 16.9, 2.3 Hz, 1H), 5.17 (dd, *J* = 16.9, 2.2 Hz, 1H), 4.05 (d, *J* = 8.8 Hz, 1H), 3.92 (d, *J* = 8.8 Hz, 1H), 0.79 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 138.1, 136.2, 135.9, 135.7, 133.1, 132.7, 131.4, 130.9, 128.2, 128.0, 127.9, 127.5, 126.8 126.2, 126.1, 121.7, 120.1, 120.0, 118.4, 84.1, 58.3, 56.2, 55.5, 26.9.; dr = 1:0.04:0.04:0.



(*R*,*S*,*S*)-**8A**

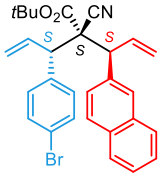
***tert*-butyl (2*R*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate**

((*R*,*S*,*S*)-8A): Yield (99%); White solid, mp 84–86 °C; $[\alpha]^{25}_{D}$ = -20.39 (*c* 1.27, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (ddd, *J* = 8.8, 3.6, 2.4 Hz, 4H), 7.51 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.29 – 7.26 (m, 2H), 6.46 (ddd, *J* = 16.9, 10.0, 8.8 Hz, 1H), 6.36 (ddd, *J* = 16.8, 10.0, 8.9 Hz, 1H), 5.30 (dd, *J* = 10.0, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.0, 1.6 Hz, H), 5.18 (dd, *J* = 16.8, 2.0 Hz, 1H), 5.17 (dd, *J* = 16.9, 2.0 Hz, H), 4.05 (d, *J* = 8.8 Hz, 1H), 3.92 (d, *J* = 8.9 Hz, 1H), 0.79 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 138.1, 136.2, 135.9, 135.7, 133.1, 132.7, 131.4, 130.9, 128.2, 128.0, 127.9, 127.5, 126.8, 126.2, 126.1, 121.7, 120.1, 120.0, 118.4, 84.1, 58.3, 56.2, 55.5, 26.9.; dr = 1:0.03:0.02:0.



(*R*,*S*,*R*)-**8A**

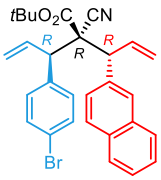
***tert*-butyl (2*S*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*R*,*S*,*R*)-8A):** Yield (95%); White solid, mp 84–86 °C; $[\alpha]^{25}_{D}$ = -159.26 (*c* 1.36, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.47 – 7.43 (m, 4H), 7.25 – 7.21 (m, 2H), 6.62 (ddd, *J* = 17.0, 10.0. 9.8 Hz, 1H), 6.30 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.35 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.244 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.240 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.18 (dd, *J* = 16.9, 2.1 Hz, 1H), 4.08 (d, *J* = 9.4 Hz, 1H), 3.84 (d, *J* = 9.8 Hz, 1H), 0.86 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 137.4, 135.9, 134.3, 133.8, 133.2, 132.7, 131.6, 130.8, 128.2, 128.1, 127.9, 127.4, 126.6, 126.2, 126.1, 122.0, 120.2, 120.1, 118.3, 84.3, 58.4, 54.7, 53.5, 27.1.; dr = 1:0.12:0.02:0.



(*S*,*S*,*S*)-**8A**

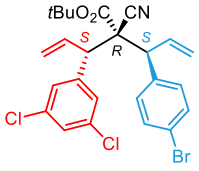
***tert*-butyl (2*S*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*S*,*S*,*S*)-8A):** Yield (92%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = 146.88 (*c* 1.12, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.73 (m, 4H), 7.48 – 7.38 (m, 5H), 7.34 – 7.30 (m, 2H), 6.72 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 6.20 (ddd, *J* = 16.9, 10.2, 9.6 Hz, 1H), 5.34 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.26 (dd, *J* = 17.0,

1.0 Hz, 1H), 5.21 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.15 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.98 (d, *J* = 10.0 Hz, 1H), 3.94 (d, *J* = 9.6 Hz, 1H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 137.7, 135.7, 134.1, 134.0, 133.2, 132.9, 131.5, 130.9, 128.2, 128.1, 127.9, 127.6, 126.8, 126.2, 126.1, 121.7, 120.2, 120.0, 118.2, 84.4, 58.4, 55.3, 52.8, 27.2.; dr = 1:0.18:0.05:0.02.



(*R*,*R*,*R*)-**8A**

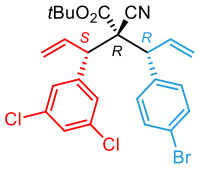
***tert*-butyl (2*R*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*R*,*R*,*R*)-8A):** Yield (95%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = -124.13 (*c* 1.04, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 4H), 7.47 – 7.41 (m, 5H), 7.35 – 7.30 (m, 2H), 6.72 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1H), 6.20 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.34 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.25 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.21 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 16.9, 2.1 Hz, 1H), 3.98 (d, *J* = 9.3 Hz, 1H), 3.96 (d, *J* = 10.0 Hz, 1H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 137.7, 135.7, 134.1, 134.0, 133.2, 132.9, 131.6, 131.5, 130.9, 128.2, 128.1, 127.9, 127.6, 126.8, 126.2, 126.1, 121.7, 120.2, 120.0, 118.2, 84.4, 58.4, 55.3, 52.8, 27.2.; dr = 1:0.16:0.03:0.



(*S*,*R*,*S*)-**8B**

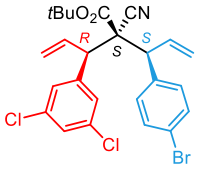
***tert*-butyl (2*R*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*S*,*R*,*S*)-8B):** Yield (83%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = 86.85 (*c* 1.08, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.42 (m, 2H), 7.29 (d, *J* = 1.9 Hz, 2H), 7.27 – 7.26 (m, 1H), 7.22 – 7.17 (m, 2H), 6.53 (ddd, *J* = 17.0, 10.0, 9.8 Hz, 1H), 6.10 (ddd, *J* = 17.0, 10.3, 9.4 Hz, 1H), 5.33 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.3, 1.2 Hz, 1H), 5.20 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.16 (dd, *J* = 17.0, 1.6 Hz, 1H), 3.85 (d, *J* = 9.4 Hz, 1H), 3.75 (d, *J* = 9.8 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 141.8, 136.9, 135.0, 133.3, 133.0, 131.7, 130.7, 127.8, 127.5, 122.1, 121.1, 120.5, 117.6, 85.0,

57.9, 54.6, 52.6, 27.3.; HRMS (ESI+) Calcd. For $C_{25}H_{24}BrCl_2NNaO_2^+$ ([M+Na]$^+$): 542.0260, found: 542.0257; dr = 1:0.07:0.03:0.



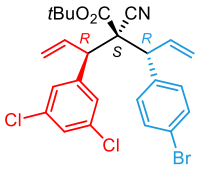
(*S*,*R*,*R*)-**8B**

***tert*-butyl (2*R*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*S*,*R*,*R*)-8B):** Yield (94%); Pale yellow solid, mp 63–65 °C; $[\alpha]^{25}_D$ = -21.50 (*c* 1.27, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.41 (m, 2H), 7.26 – 7.23 (m, 5H), 6.28 (ddd, *J* = 16.8, 10.2, 9.2 Hz, 1H), 6.26 (ddd, *J* = 16.8, 10.4, 9.2 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.32 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.17 (dd, *J* = 16.8, 2.0 Hz, 1H), 5.16 (dd, *J* = 16.8, 2.0 Hz, 1H), 3.82 (d, *J* = 9.2 Hz, 1H), 3.81 (d, *J* = 9.2 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 142.0, 137.6, 135.2, 134.8, 134.7, 131.5, 130.8, 127.8, 127.6, 121.9, 121.0, 120.4, 117.7, 84.8, 57.8, 55.5, 55.1, 27.1.; dr = 1:0.07:0.03:0.01.



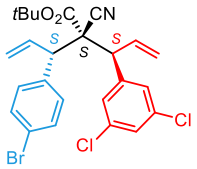
(*R*,*S*,*S*)-**8B**

***tert*-butyl (2*S*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*R*,*S*,*S*)-8B):** Yield (91%); Pale yellow solid, mp 63–65 °C; $[\alpha]^{25}_D$ = 20.82 (*c* 1.22, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.22 (m, 5H), 6.27 (dtd, *J* = 16.9, 10.4, 8.9 Hz, 1H), 6.27 (ddd, *J* = 16.9, 10.2, 9.2 Hz, 1H), 6.27 (ddd, *J* = 17.2, 10.2, 9.2 Hz, 1H), 5.32 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.17 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.16 (dd, *J* = 16.9, 2.0 Hz, 1H), 3.82 (d, *J* = 9.2 Hz, 1H), 3.81 (d, *J* = 9.2 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 142.0, 137.6, 135.2, 134.8, 134.7, 131.5, 130.8, 127.8, 127.6, 121.9, 121.0, 120.4, 117.7, 84.8, 57.8, 55.5, 55.1, 27.1.; dr = 1:0.04:0.02:0.



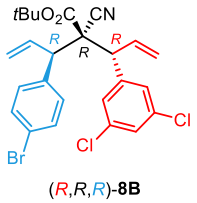
(*R*,*S*,*R*)-**8B**

***tert*-butyl (2*S*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*R*,*S*,*R*)-8B):** Yield (91%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = -85.43 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.29 (d, *J* = 1.9 Hz, 2H), 7.26 (d, *J* = 2.1 Hz, 1H), 7.21 – 7.18 (m, 2H), 6.53 (ddd, *J* = 17.0, 10.0, 9.9 Hz, 1H), 6.10 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.33 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.22 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.16 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.85 (d, *J* = 9.4 Hz, 1H), 3.75 (d, *J* = 9.9 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 141.8, 136.9, 134.9, 133.3, 133.0, 131.7, 130.7, 127.8, 127.5, 122.1, 121.1, 120.5, 117.6, 85.0, 57.9, 54.6, 52.7, 27.3.; dr = 1:0.07:0.03:0.



(*S*,*S*,*S*)-**8B**

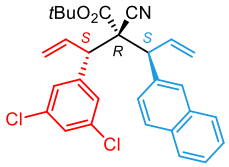
***tert*-butyl (2*S*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*S*,*S*,*S*)-8B):** Yield (99%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = 88.98 (*c* 0.89, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.19 (d, *J* = 1.9 Hz, 2H), 6.52 (ddd, *J* = 16.9, 10.0. 9.9 Hz, 1H), 6.18 (ddd, *J* = 16.9, 10.2, 9.5 Hz, 1H), 5.36 (dd, *J* = 10.0, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.23 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.28 (dd, *J* = 16.9, 1.4 Hz, 1H), 3.86 (d, *J* = 9.5 Hz, 1H), 3.73 (d, *J* = 9.9 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 141.5, 137.3, 135.0, 133.6, 132.7, 131.6, 130.8, 128.2, 127.5, 121.9, 121.1, 120.6, 117.6, 85.1, 57.9, 54.5, 52.7, 27.3.; dr = 1:0.19:0.02:0.01.



(*R*,*R*,*R*)-**8B**

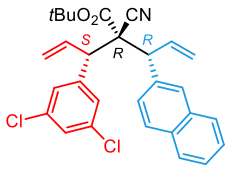
***tert*-butyl (2*R*,3*R*)-3-(4-bromophenyl)-2-cyano-2-((*R*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate**

((*R*,*R*,*R*)-8B): Yield (97%); Pale yellow liquid; $[\alpha]^{25}_{D}$ = -97.83 (*c* 0.92, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 2H), 7.31 – 7.28 (m, 3H), 7.19 (d, *J* = 1.9 Hz, 2H), 6.52 (ddd, *J* = 16.9, 10.1. 9.6 Hz, 1H), 6.18 (ddd, *J* = 16.9, 10.2, 9.9 Hz, 1H), 5.36 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.28 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.23 (dd, *J* = 10.2, 1.0 Hz, 1H), 5.18 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.87 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 9.9 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 141.5, 137.3, 135.0, 133.6, 132.7, 131.6, 130.8, 128.1, 127.5, 121.9, 121.0, 120.6, 117.6, 85.1, 57.8, 54.5, 52.7, 27.3.; dr = 1:0.19:0.02:0.01.



(*S*,*R*,*S*)-**8C**

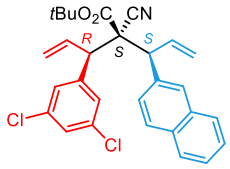
***tert*-butyl (2*R*,3*S*)-3-(4-bromophenyl)-2-cyano-2-((*S*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoate ((*S*,*R*,*S*)-8C):** Yield (93%); White solid, mp 88–90 °C; $[\alpha]^{25}_{D}$ = 80.56 (*c* 0.90, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.48 – 7.44 (m, 3H), 7.32 (d, *J* = 1.9 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.70 (dd, *J* = 17.0, 10.0, 9.9 Hz, 1H), 6.15 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.34 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.25 (dd, *J* = 17.0, 0.8 Hz, 1H), 5.34 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.17 (dd, *J* = 16.8, 1.6 Hz, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.93 (d, *J* = 9.3 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 142.0, 135.4, 134.9, 133.9, 133.23, 133.21, 132.9, 128.3, 128.2, 128.0, 127.8, 127.6, 126.8, 126.3, 126.2, 121.0, 120.2, 117.8, 84.8, 58.1, 55.3, 52.7, 27.3.; HRMS (ESI+) Calcd. For $C_{29}H_{27}Cl_2NNaO_2^+$ ($[M+Na]^+$): 514.1311, found: 514.1307; dr = 1:0.07:0.04:0.



(*S*,*R*,*R*)-**8C**

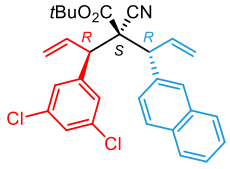
***tert*-butyl (2*R*,3*S*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*S*,*R*,*R*)-8C):** Yield (98%); White solid, mp 98–100 °C; $[\alpha]^{25}_{D}$ = -34.00 (*c* 0.84, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 9.2, 2.3 Hz, 4H), 7.50 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.29 (d, *J* = 1.9 Hz, 2H), 7.26 (d, *J* = 1.8 Hz, 1H), 6.44 (ddd, *J* = 16.9, 10.2, 8.9 Hz, 1H), 6.32 (ddd, *J* =

16.9, 10.2, 8.9 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 4.03 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 8.9 Hz, 1H), 0.85 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 142.3, 136.0, 135.7, 134.9, 134.8, 133.1, 132.7, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 126.7, 126.24, 126.17, 120.9, 120.2, 117.9, 84.5, 58.1, 56.3, 55.2, 27.0.; dr = 1:0.03:0.03:0.



(*R*,*S*,*S*)-**8C**

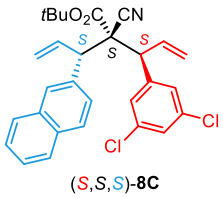
***tert*-butyl (2*S*,3*R*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*S*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*R*,*S*,*S*)-8C):** Yield (96%); White solid, mp 99–101 °C; $[\alpha]^{25}_{D}$ = 35.64 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 9.2, 2.2 Hz, 4H), 7.50 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.29 (d, *J* = 1.9 Hz, 2H), 7.26 – 7.24 (m, 2H), 6.44 (ddd, *J* = 16.9, 10.2, 8.9 Hz, 1H), 6.32 (ddd, *J* = 16.9, 10.2, 8.9 Hz, 1H), 5.35 (d, *J* = 10.2 Hz, 2H), 5.31 (dd, *J* = 10.2, 1.2 Hz, 2H), 5.209 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.203 (dd, *J* = 16.9, 1.2 Hz, 1H), 4.03 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 8.9 Hz, 1H), 0.85 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 142.3, 136.0, 135.7, 134.9, 134.8, 133.1, 132.7, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 126.7, 126.2, 126.2, 120.9, 120.2, 118.0, 84.6, 58.1, 56.3, 55.2, 27.0.; dr = 1:0.03:0.02:0.01.



(*R*,*S*,*R*)-**8C**

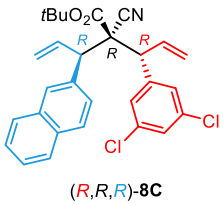
***tert*-butyl (2*S*,3*R*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*R*,*S*,*R*)-8C):** Yield (93%); White solid, mp 88–90 °C; $[\alpha]^{25}_{D}$ = -106.00 (*c* 1.12, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.48 – 7.43 (m, 3H), 7.32 (d, *J* = 1.9 Hz, 2H), 7.26 (t, *J* = 1.9 Hz, 1H), 6.70 (dd, *J* = 17.0, 10.0, 9.9 Hz, 1H), 6.15 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.34 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.25 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.24 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.17 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.93 (d, *J* = 9.4 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 142.0, 135.4, 134.9, 133.9, 133.2, 133.2, 132.9, 128.3, 128.2, 128.0, 127.8,

127.6, 126.8, 126.3, 126.2, 121.0, 120.2, 117.8, 84.8, 58.1, 55.3, 52.7, 27.3.; dr = 1:0.08:0.04:0.



(*S*,*S*,*S*)-**8C**

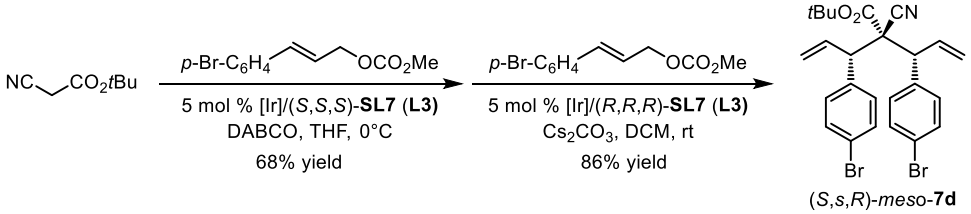
***tert*-butyl (2*S*,3*S*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*S*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*S*,*S*,*S*)-8C):** Yield (88%); White solid, mp 105–107 °C; $[\alpha]^{25}_{D}$ = 143.60 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.77 (m, 4H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.45 (ddd, *J* = 7.5, 3.5, 1.9 Hz, 2H), 7.29 (t, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 1.9 Hz, 2H), 6.59 (ddd, *J* = 17.0, 10.0. 9.6 Hz, 1H), 6.33 (ddd, *J* = 16.9, 10.1, 9.9 Hz, 1H), 5.39 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.30 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.26 (dd, *J* = 10.1, 1.2 Hz, 1H), 5.39 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.08 (d, *J* = 9.6 Hz, 1H), 3.81 (d, *J* = 9.9 Hz, 1H), 0.89 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 141.7, 135.7, 135.0, 134.2, 133.2, 133.1, 132.7, 128.21, 128.18, 128.1, 127.9, 127.6, 127.5, 126.5, 126.2, 126.1, 120.9, 120.3, 117.9, 84.8, 58.1, 54.7, 53.5, 27.1; dr = 1:0.15:0.03:0.01.



(*R*,*R*,*R*)-**8C**

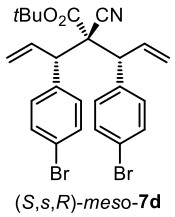
***tert*-butyl (2*R*,3*R*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*R*)-1-(naphthalen-2-yl)allyl)pent-4-enoate ((*R*,*R*,*R*)-8C):** Yield (96%); White solid, mp 105–107 °C; $[\alpha]^{25}_{D}$ = -127.44 (*c* 1.33, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.77 (m, 4H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.29 (t, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 2H), 6.59 (ddd, *J* = 17.0, 10.8, 9.8 Hz, 1H), 6.33 (ddd, *J* = 16.9, 10.0, 9.5 Hz, 1H), 5.39 (dd, *J* = 10.0, 1.4 Hz, 1H), 5.29 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.26 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.2 Hz, 1H), 4.08 (d, *J* = 9.5 Hz, 1H), 3.81 (d, *J* = 9.8 Hz, 1H), 0.89 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 141.7, 135.7, 135.0, 134.2, 133.2, 133.1, 132.7, 128.21, 128.18, 128.1, 127.9, 127.6, 127.5, 126.5, 126.2, 126.1, 120.9, 120.3, 117.9, 84.8, 58.1, 54.7, 53.5, 27.1.; dr = 1:0.15:0.03:0.01.

VII. Synthesis of (*S,s,R*)-*meso*-7d



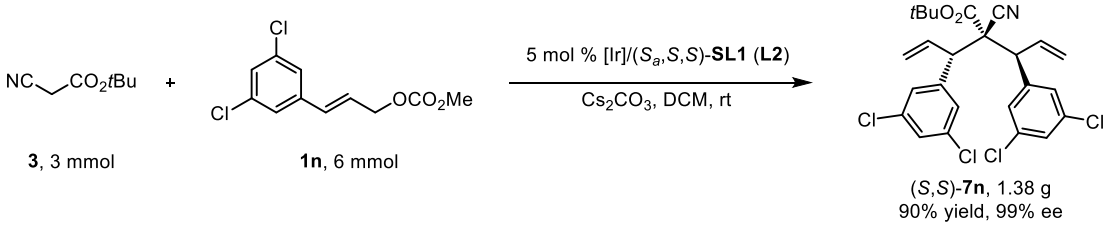
A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (S_a,*S,S*)-**SL7** (**L3**) (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. Allylic carbonate **1d** (0.50 mmol), cyanoacetate **3** (1.00 mmol), DABCO (0.10 mmol), THF (10 mL) were then added, and then reacted at 0 °C for 12 h under Ar_2 atmosphere. The crude product was purified by silica-gel column chromatography to give the mono-allylic cyanoacetate **5d**.

Then under Ar_2 atmosphere, $[Ir(COD)Cl]_2$ (0.005 mmol, 2.5 mol %), phosphoramidite ligand (R_a,*R,R*)-**SL7** (**L3**) (0.01 mmol, 5 mol %), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL) were heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give Ir-compless. To this Schlenk tube allylic carbonate **1d** (0.20 mmol), mono-allylic cyanoacetate **5d** (0.20 mmol), Cs_2CO_3 (0.20 mmol), DCM (2 mL) were then added, and then reacted at room temperature under Ar_2 atmosphere. Once starting material was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude (*S,s,R*)-*meso*-**7d**. The crude product was purified by silica-gel column chromatography to give (*S,s,R*)-*meso*-**7d**.

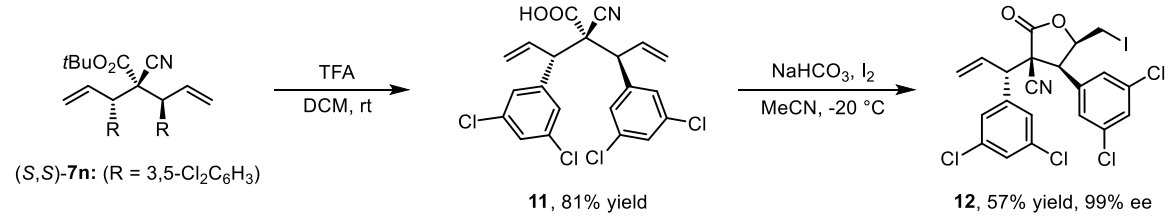


***tert*-butyl (2*s*,3*S*)-3-(4-bromophenyl)-2-((*R*)-1-(4-bromophenyl)allyl)-2-cyanopent-4-enoate ((*S*,*s*,*R*)-*meso*-7d):** Yield (86%); White solid, mp 158–160 °C; $[\alpha]^{25}_{D}$ = 0.03 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 4H), 7.26 – 7.19 (m, 4H), 6.30 (ddd, *J* = 16.9, 10.2, 8.9 Hz, 2H), 5.27 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.26 (dd, *J* = 10.3, 1.2 Hz, 1H), 5.14 (dd, *J* = 16.9, 0.9 Hz, 1H), 5.13 (dd, *J* = 16.9, 1.2 Hz, 1H), 3.83 (d, *J* = 8.9 Hz, 2H), 0.94 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 137.8, 135.4, 131.5, 130.9, 121.8, 120.2, 118.1, 84.4, 58.0, 55.4, 27.1.

VIII. Gram Scales and Synthetic Transformations

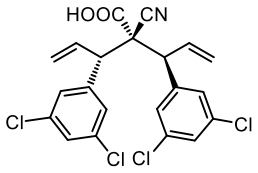


A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.075 mmol, 2.5 mol %), phosphoramidite ligand (*R*$_a$,*R*,*R*)-**SL7** (**L3**) (0.15 mmol, 5 mol %), degassed THF (7.5 mL) and degassed *n*-propylamine (7.5 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed under vacuum to give a pale yellow solid. allylic carbonates **1n** (6.00 mmol), Cyanoacetates **3** (3.00 mmol), Cs_2CO_3 (6.00 mmol), DCM (30 mL) were then added, reacted at room temperature. Once starting material was consumed (monitored by TLC), the mixture was added water, and extracted with dichloromethane (3×). The dichloromethane layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to give crude (*S*,*S*)-**7n**. The crude product was purified by silica-gel column chromatography to give (*S*,*S*)-**7n** in 90% yield with 99% ee.



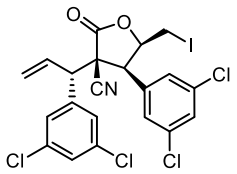
To a solution of (*S*,*S*)-**7n** (0.20 mmol) in DCM (2.0 mL) was added TFA (1.0 mL) under Ar_2 at rt and the reaction mixture was stirred for 2 h before concentrated in vacuo and purified by flash chromatography (CH_2Cl_2 to 5% MeOH:CH_2Cl_2) to yield **11** (81%) as a foamy solid.

To a solution of **11** (0.10 mmol) in MeCN (1.0 mL) was added $NaHCO_3$ (0.20 mmol, 2.0 equiv.) and I_2 (0.30 mmol, 3.0 equiv.) under Ar_2 and the flask was covered with aluminum foil and the reaction mixture stirred in the dark for 5 h before being uncovered to reveal a brown precipitate. The reaction was quenched with 10% $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 x 3 mL) and the combined organics were washed with 10% $NaHCO_3$ (1 x 10 mL), and brine (10 mL). The combined organics were combined and dried over Na_2SO_4 and concentrated under vacuum and purified by silica-gel flash chromatography to yield **12**.



11

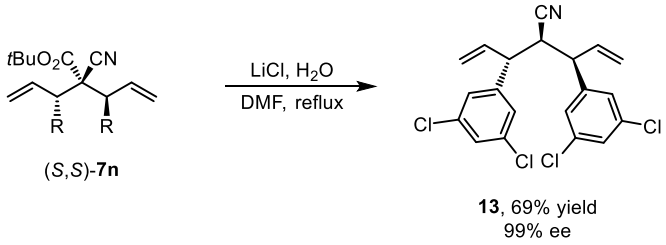
(*S*)-2-cyano-3-(3,5-dichlorophenyl)-2-((*S*)-1-(3,5-dichlorophenyl)allyl)pent-4-enoic acid (11): Yield (81%); Pale yellow foamy solid, m.p. 86–88 °C; $[\alpha]^{25}_D$ = 115.71 (*c* 0.91, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (dt, *J* = 16.8, 1.7 Hz, 2H), 7.22 (dd, *J* = 19.6, 1.9 Hz, 4H), 6.79 (bs, 1H), 6.35 (ddd, *J* = 16.9, 10.1, 9.6 Hz, 1H), 6.10 (ddd, *J* = 16.8, 10.0, 9.8 Hz, 1H), 5.38 (dd, *J* = 10.1, 1.1 Hz, 1H), 5.32 (dd, *J* = 10.0, 1.2 Hz, 1H), 5.25 (d, *J* = 16.8, 1.1 Hz, 1H), 5.20 (d, *J* = 16.9, 1.2 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.80 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 141.1, 140.6, 135.3, 135.2, 132.4, 132.0, 128.6, 128.4, 127.5, 127.3, 127.2, 121.8, 121.7, 58.0, 54.3, 52.2.; HRMS (ESI+) Calcd. For $C_{21}H_{14}Cl_4NNa_2O_2$ ($[M+2Na-H]^+$): 497.9569, found: 497.9573.



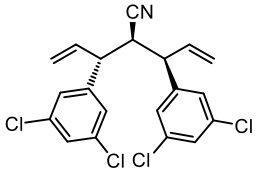
12

(3*S*,4*S*,5*R*)-4-(3,5-dichlorophenyl)-3-((*S*)-1-(3,5-dichlorophenyl)allyl)-5-(iodomethyl)-2-oxotetrahyd

rofuran-3-carbonitrile (12): Yield (57%); white solid, mp 232–234 °C; $[\alpha]^{25}_{D}$ = -50.14 (*c* 0.74, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 1.8 Hz, 1H), 7.38 (t, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 2H), 7.10 (d, *J* = 1.8 Hz, 2H), 6.30 (ddd, *J* = 16.8, 10.0, 9.3 Hz, 1H), 5.61 (d, *J* = 10.0 Hz, 1H), 5.50 (d, *J* = 16.8 Hz, 1H), 4.96 (ddd, *J* = 9.4, 5.7, 5.5 Hz, 1H), 3.95 (d, *J* = 5.5 Hz, 1H), 3.72 (d, *J* = 9.3 Hz, 1H), 3.36 (dd, *J* = 10.3, 5.7 Hz, 1H), 2.76 (dd, *J* = 10.3, 9.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 138.5, 136.2, 135.7, 134.9, 132.5, 130.1, 129.3, 126.9, 122.9, 114.0, 80.1, 57.1, 52.9, 52.7, -1.3.; HRMS (ESI+) Calcd. For $C_{21}H_{14}Cl_4INNaO_2^+$ ($[M+Na]^+$): 601.8716, found: 601.8692. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak ID, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 210 nm); t_r = 6.00 and 8.41 min.



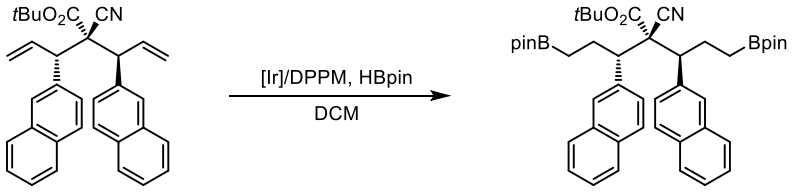
A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.01 mmol, 5 mol %), bis(diphenylphosphino)methane (dppm) (10 mol %) and anhydrous DCM (2 mL), and the reaction mixture was stirred for 30 min. After that, (*S*,*S*)-**7n** (0.20 mmol) was added in one portion under Ar_2. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, 1.0 mmol) was added at room temperature, and the resulting solution was stirred overnight. The reaction mixture was quenched with MeOH (1 mL) and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to afford the product **13**.



13

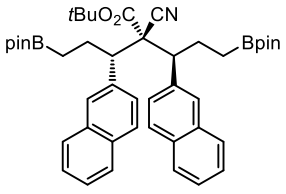
(*R*)-3-(3,5-dichlorophenyl)-2-((*R*)-1-(3,5-dichlorophenyl)allyl)pent-4-enenitrile (13): Yield (69%);

Pale yellow liquid; $[\alpha]^{25}_{D}$ = -62.25 (*c* 0.89, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (q, *J* = 1.9 Hz, 2H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 4H), 6.11 (ddd, *J* = 16.9, 10.2, 9.0 Hz, 1H), 5.90 (ddd, *J* = 16.9, 10.2, 8.6 Hz, 1H), 5.42 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.33 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.25 (dd, *J* = 16.9, 1.5 Hz, 1H), 5.24 (dd, *J* = 16.9, 1.3 Hz, 1H), 3.54 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.41 (dd, *J* = 9.3, 8.6 Hz, 1H), 3.12 (dd, *J* = 9.3, 5.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 142.4, 135.9, 135.64, 135.55, 133.8, 128.2, 128.0, 126.5, 126.2, 121.0, 119.8, 117.9, 49.5, 48.0, 42.8.; HRMS (ESI+) Calcd. For $C_{20}H_{15}Cl_4NNa^+$ ($[M+Na]^+$): 431.9851, found: 431.9860. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.13 and 6.45 min.



(*S*,*S*)-**7o** **14**, 71% yield, 99% ee

A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added $[Ir(COD)Cl]_2$ (0.01 mmol, 5 mol %), bis(diphenylphosphino)methane (dppm) (10 mol %) and anhydrous DCM (2 mL), and the reaction mixture was stirred for 30 min. After that, (*S*,*S*)-**7o** (0.20 mmol) was added in one portion under Ar_2. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, 1.0 mmol) was added at room temperature, and the resulting solution was stirred overnight. The reaction mixture was quenched with MeOH (1 mL) and concentrated under reduced pressure. The residue was purified by fast silica-gel (inactivated by Et_3N) column chromatography to afford the product **14**.



14

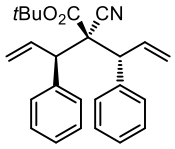
***tert*-butyl (*S*)-2-cyano-3-(naphthalen-2-yl)-2-((*S*)-1-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (14):** Yield (71%); white solid, mp 92–95 °C; $[\alpha]^{25}_{D}$ = 30.13 (*c* 0.76, CH_2Cl_2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 4H), 7.77 – 7.68 (m, 4H), 7.60 – 7.50 (m, 2H), 7.46 – 7.40 (m, 4H), 3.49 (dd, *J* = 12.1, 3.2 Hz, 1H), 3.33 (dd, *J* = 12.0, 2.9 Hz, 1H), 2.48 – 2.32 (m, 1H), 2.11 – 2.03 (m, 1H), 1.91 – 1.70 (m, 1H), 1.59 – 1.44 (m, 1H), 1.18 (s, 6H), 1.18 (s, 6H), 1.02 (s, 6H), 1.00 (s, 6H), 0.89 (s, 9H), 0.67 – 0.58 (m, 1H), 0.53 – 0.45 (m, 1H), 0.42 – 0.33 (m, 1H), 0.28 – 0.18 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 136.7, 135.7, 133.3, 133.04, 133.03, 132.7, 129.0, 128.2, 128.0, 127.8, 127.6, 127.5, 127.3, 127.21, 127.19, 125.9, 125.8, 125.74, 125.71, 125.6, 119.1, 83.3, 82.9, 82.7, 60.4, 53.6, 52.0, 27.0, 25.7, 24.82, 24.77, 24.6, 24.5, 9.0.; HRMS (ESI+) Calcd. For $C_{45}H_{57}B_2NNaO_6^+$ ($[M+Na]^+$): 752.4264, found: 752.4269. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); t_r = 13.08 and 18.84 min.

IX. References

1. a) B. M. Trost, J. R. Miller, Jr. C. M. Hoffman, *J. Am. Chem. Soc.* **2011**, *133*, 8165; b) M. Yasumoto, H. Ueki, V. A. Soloshonok, *J. Fluorine Chem.* **2007**, *128*, 736; c) K. Morisaki, Y. Kondo, M. Sawa, H. Morimoto, T. Ohshima, *Chem. Pharm. Bull.* **2017**, *65*, 1089; d) L.-M. Shi, X.-S. Sun, C. Shen, Z.-F. Wang, H.-Y. Tao, C.-J. Wang, *Org. Lett*. **2019**, *21*, 4842.

2. a) C. R. Smith, D. J. Mans, T. V. Rajanbabu, *Org. Synth*. **2008**, *85*, 238. b) K. Tissot-Croset, D. Polet, S. Gille, C. Hawner, A. Alexakis, *Synthesis*, **2004**, 2586.

X. NMR and HPLC Data



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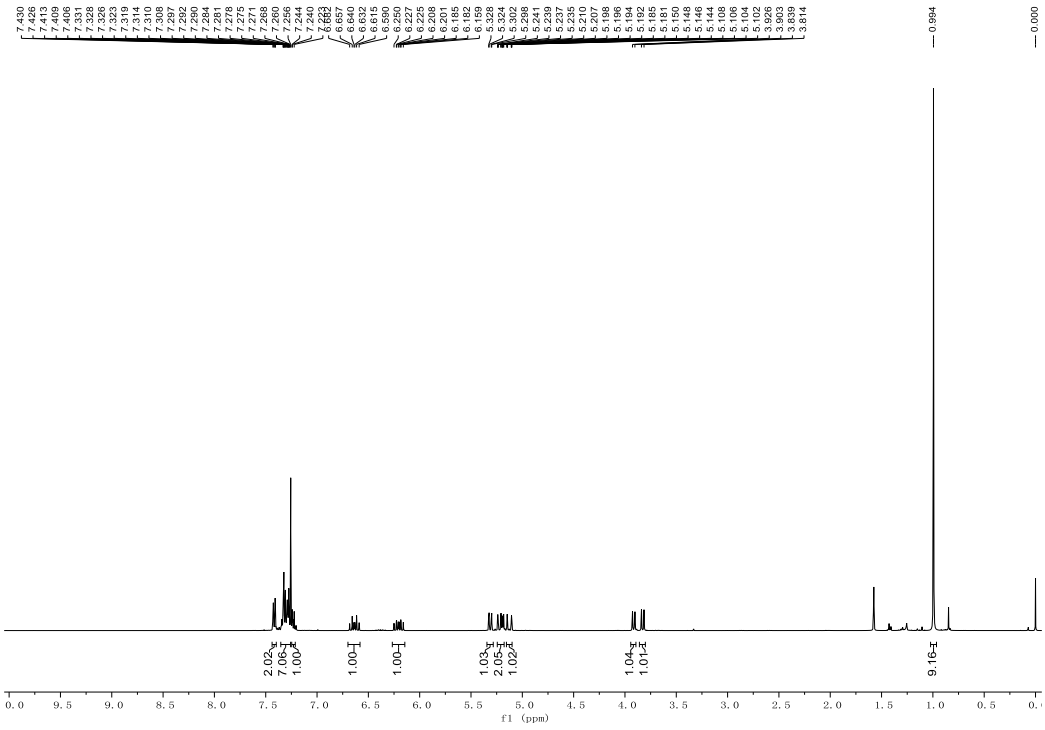

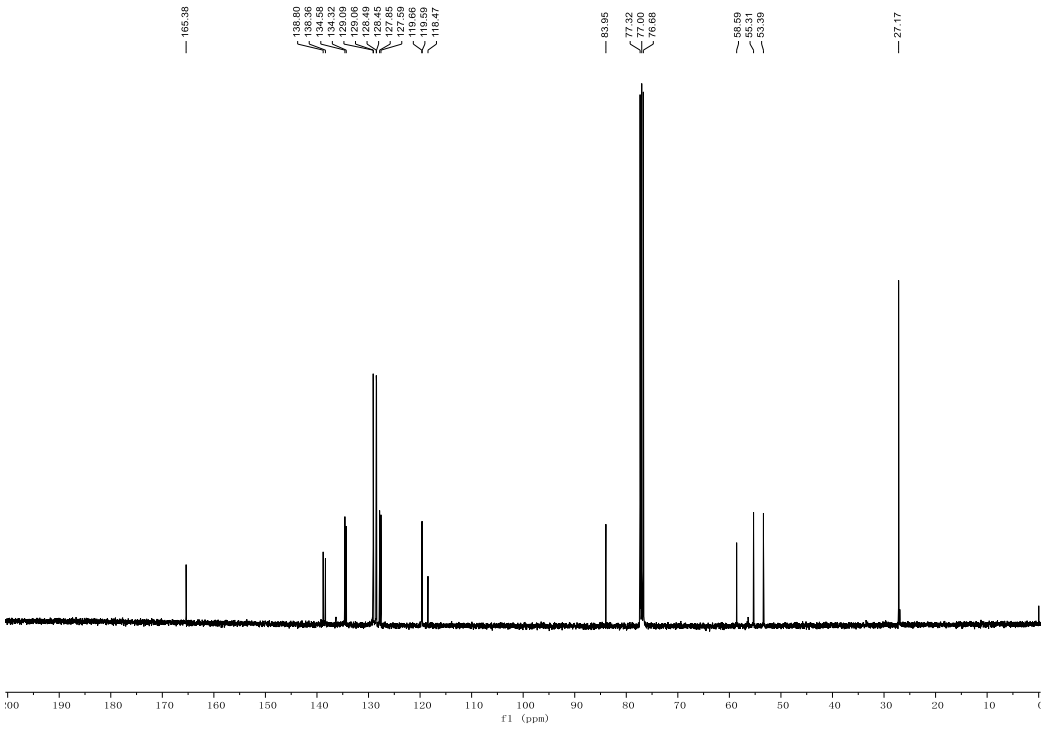

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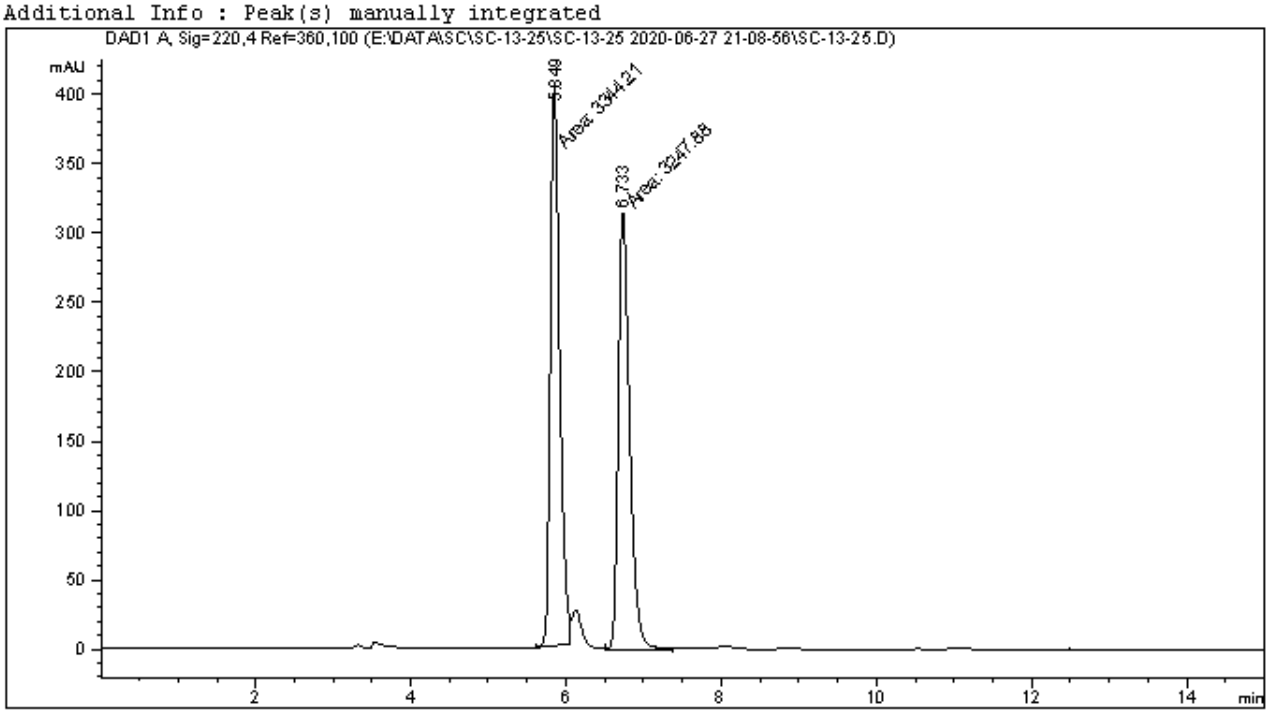


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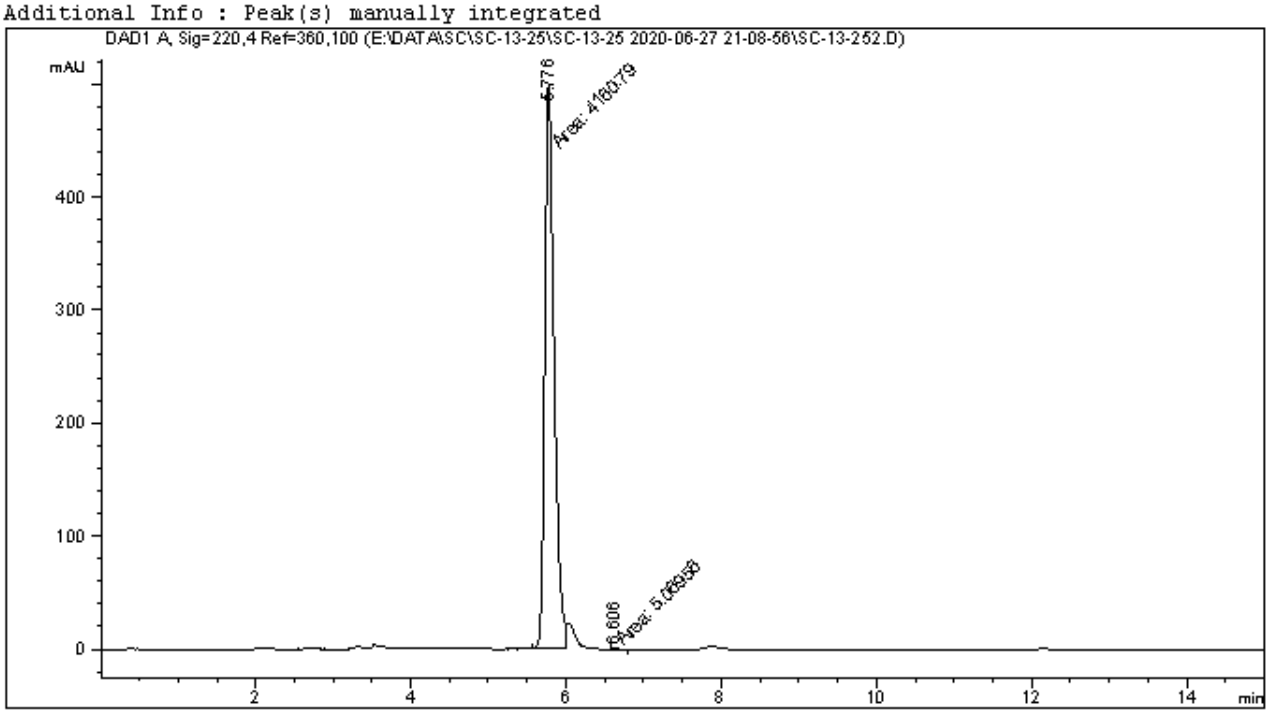


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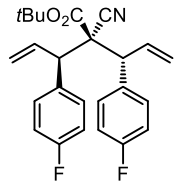

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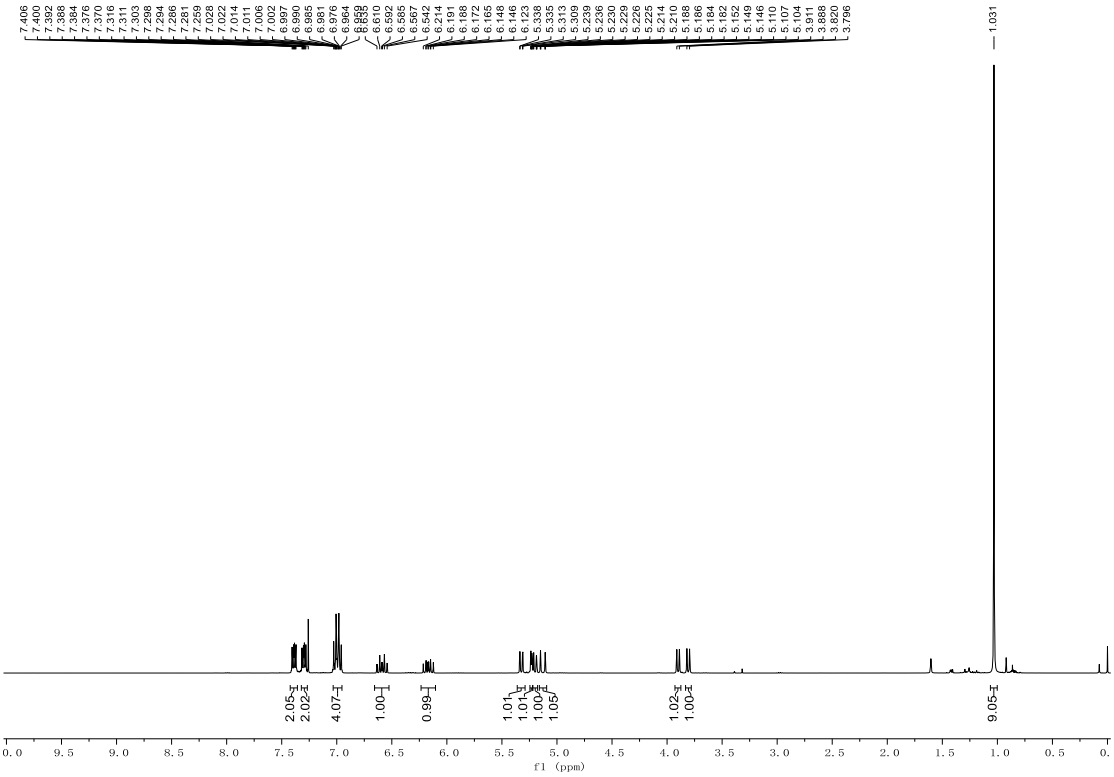

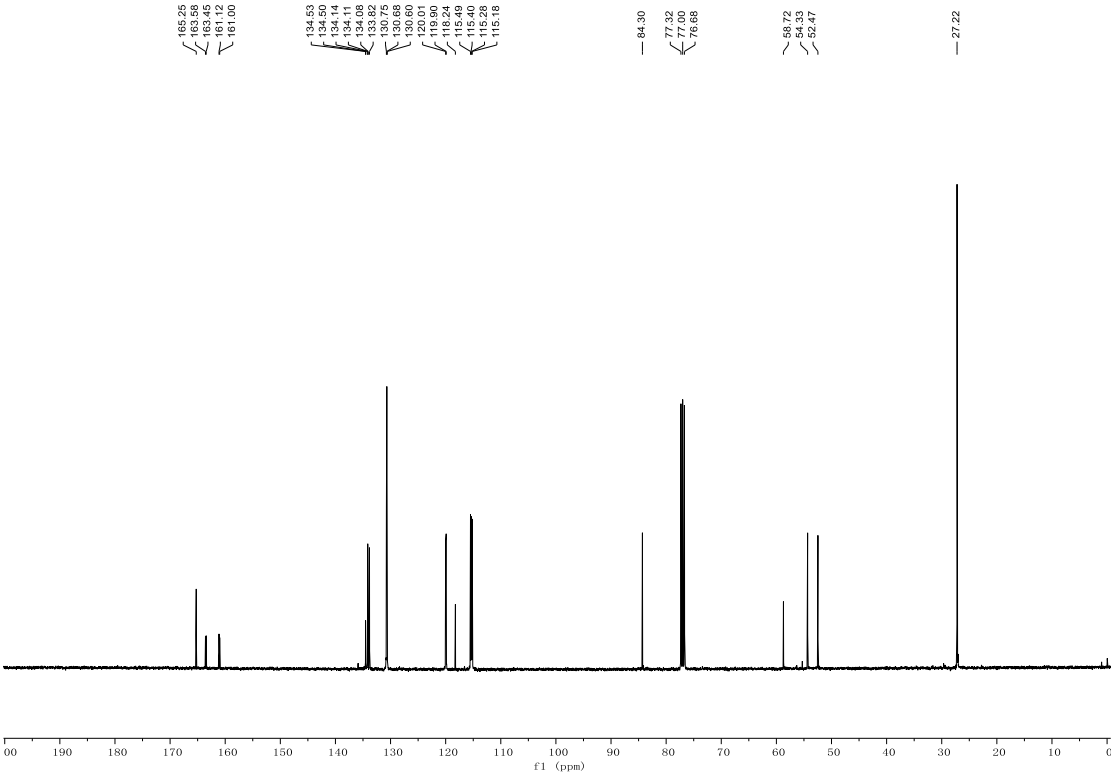

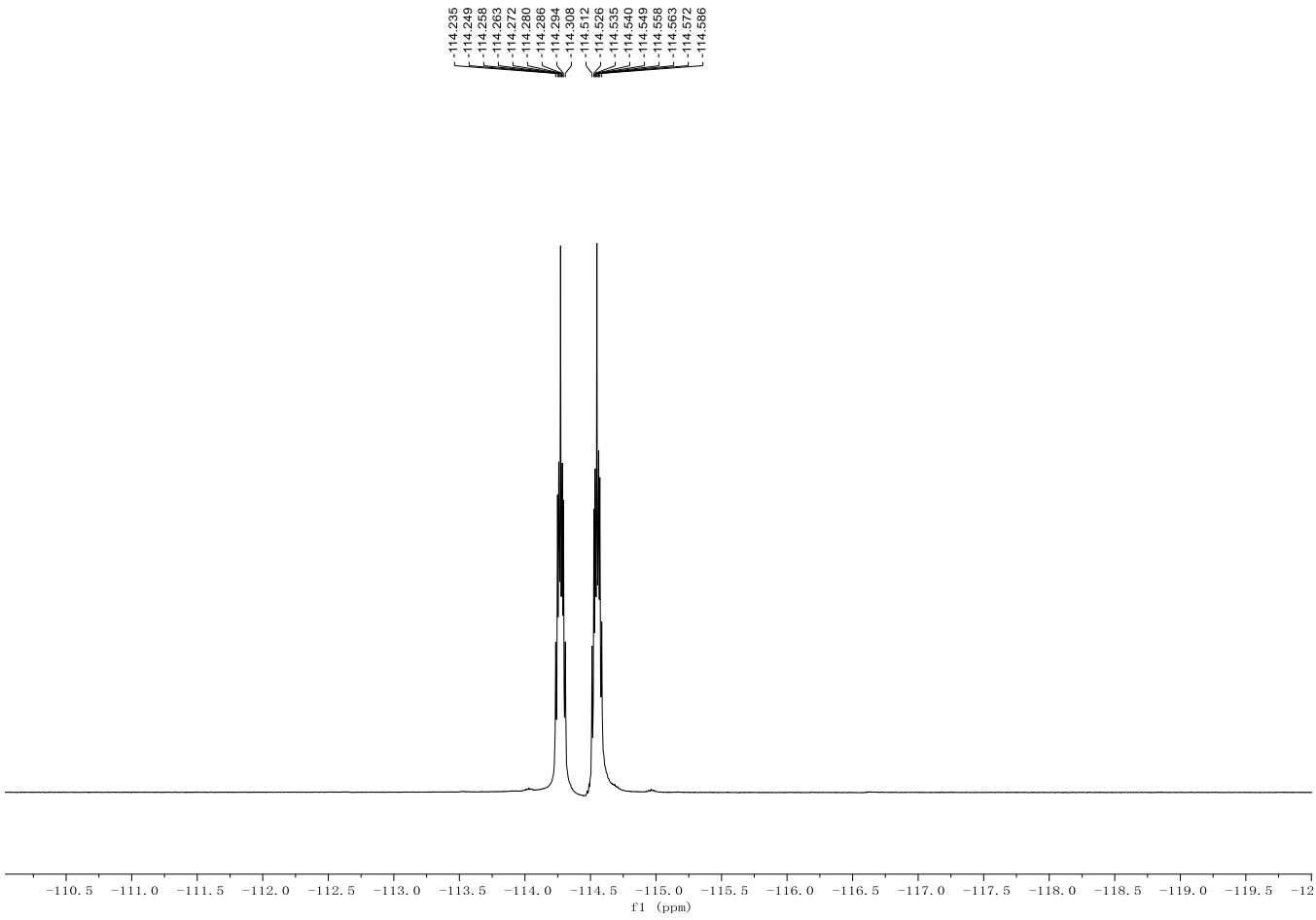
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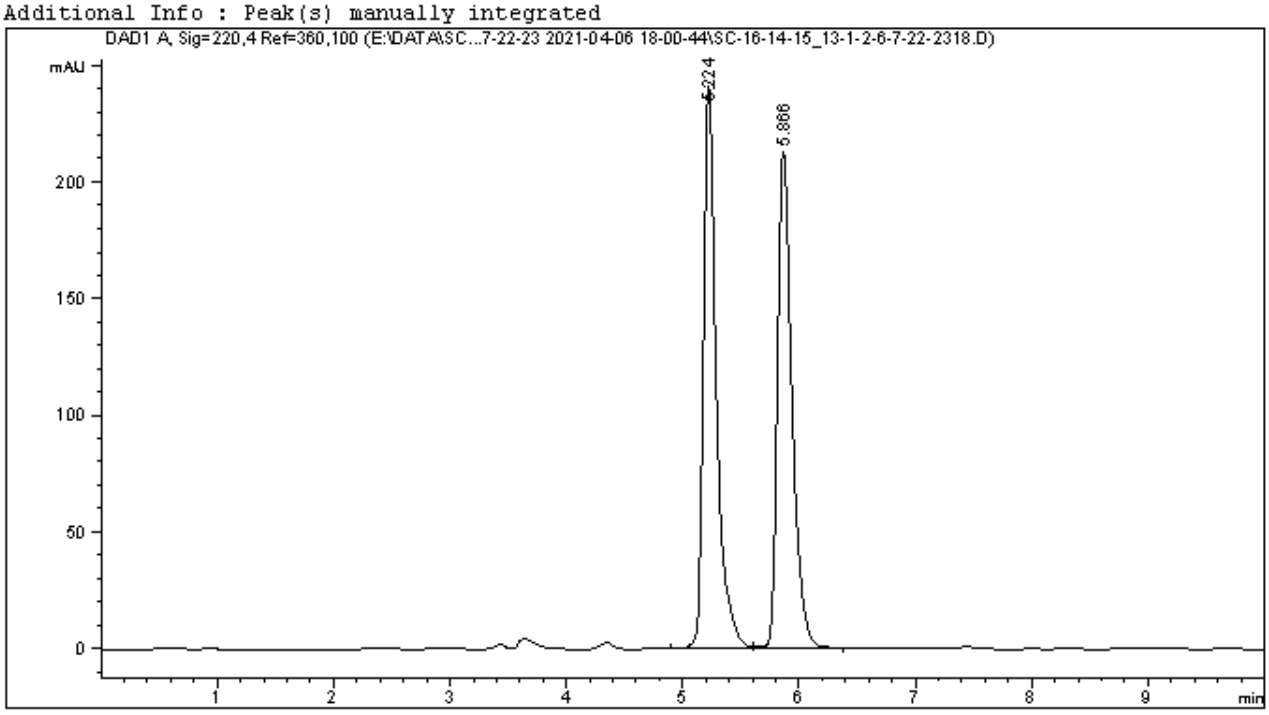


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Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
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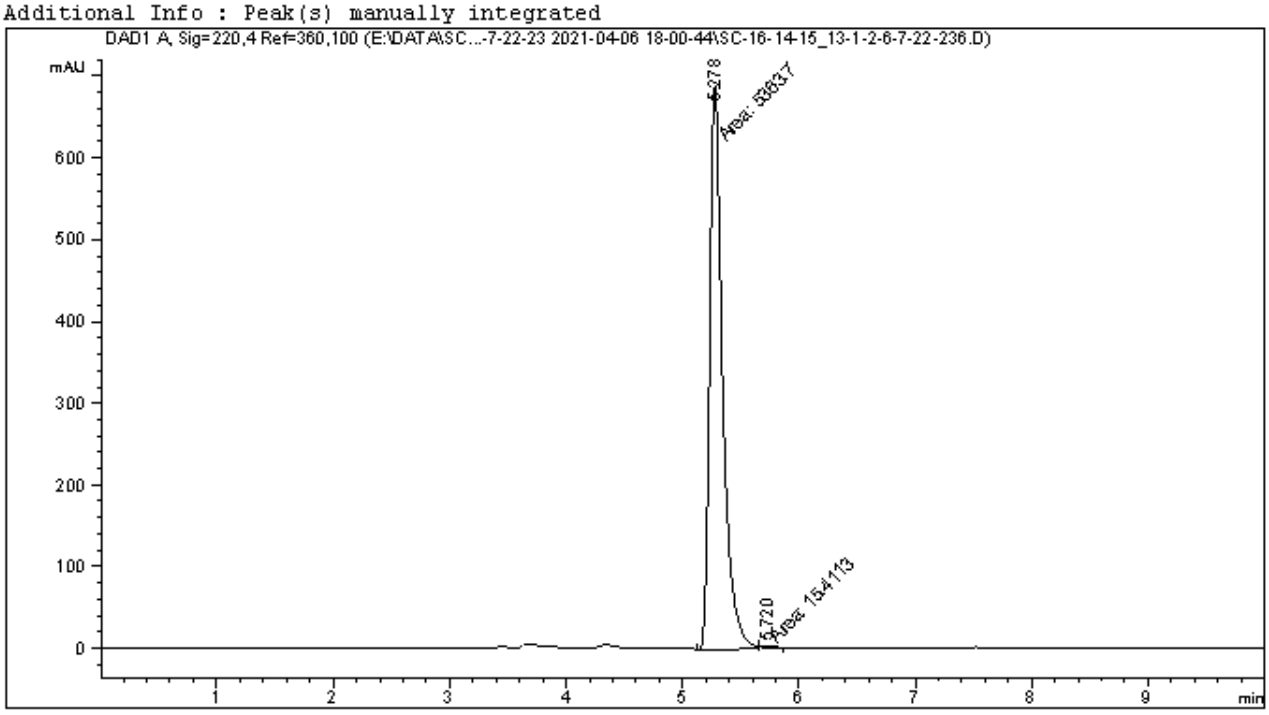
    Injection Date  : 4/6/2021 7:09:34 PM                  Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M
    Last changed    : 4/6/2021 6:00:45 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:47:05 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



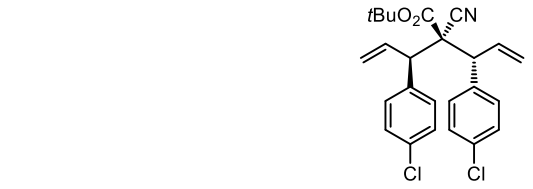

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

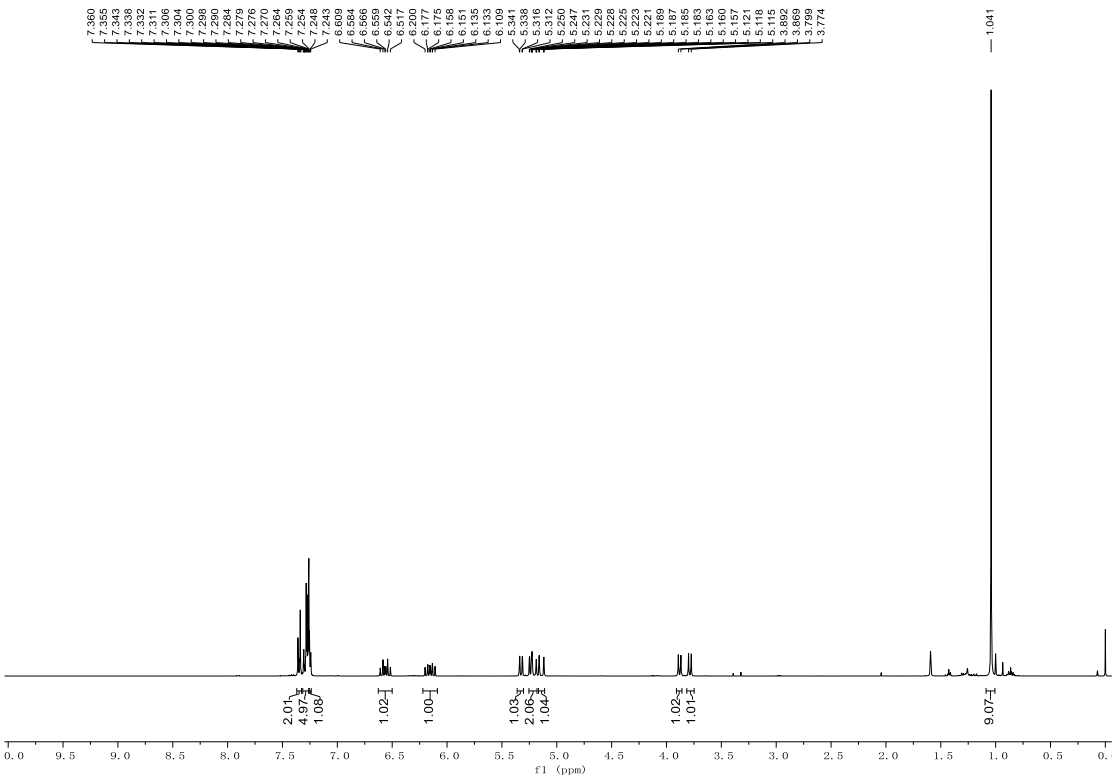

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

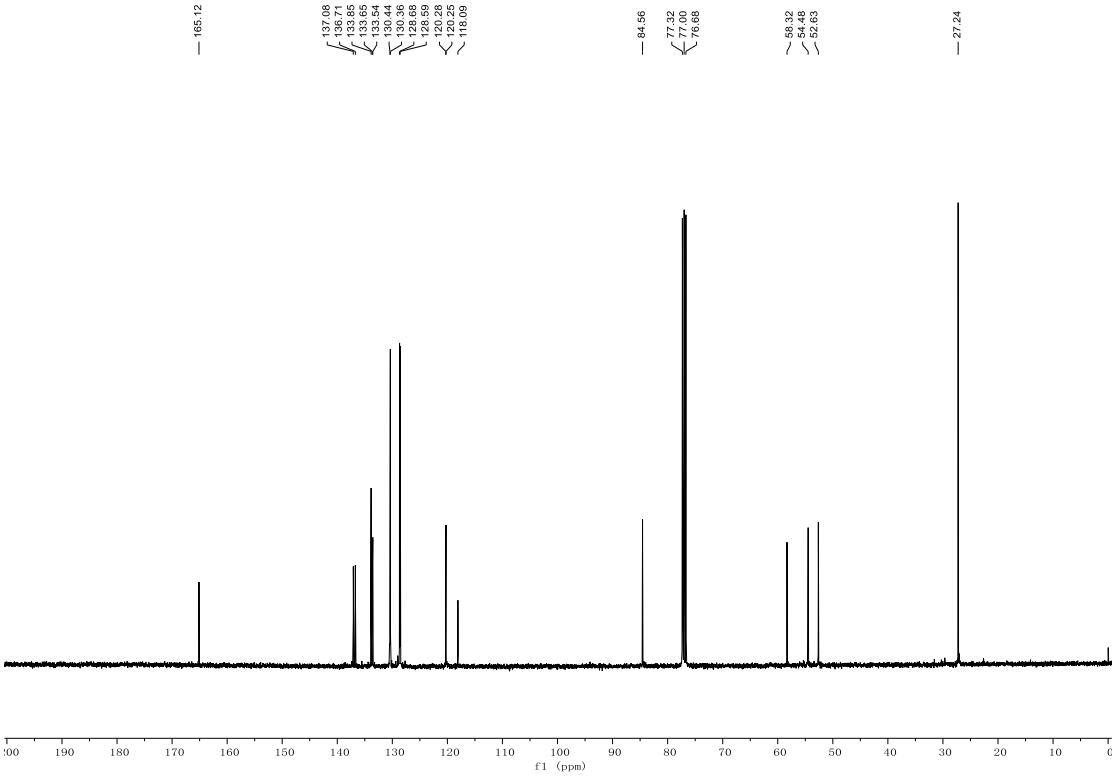
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.278 MF    0.1298 5363.69922  688.66479  99.7135
       2   5.720 MM    0.1314   15.41134    1.95500   0.2865

    Totals :                  5379.11056  690.61980
```


tBuO2C
CN
Cl
Cl

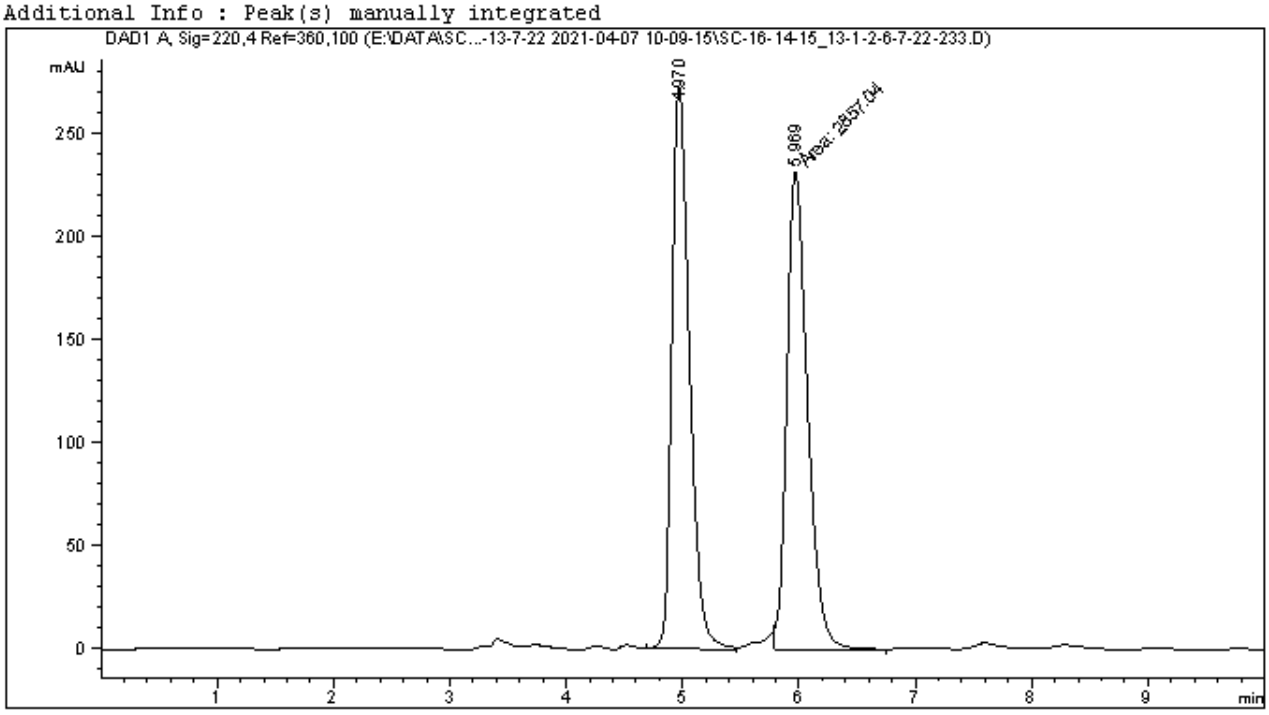
7c


7.360
7.355
7.343
7.338
7.332
7.311
7.306
7.304
7.300
7.298
7.290
7.284
7.279
7.276
7.270
7.264
7.259
7.254
7.248
7.243
6.569
6.564
6.566
6.559
6.542
6.517
6.200
6.177
6.175
6.158
6.151
6.135
6.133
6.109
5.341
5.338
5.316
5.312
5.266
5.247
5.231
5.229
5.228
5.225
5.223
5.221
5.189
5.187
5.185
5.183
5.163
5.160
5.157
5.121
5.116
5.115
3.892
3.869
3.799
3.774
1.041
2.01
4.97
1.08
1.02
1.00
1.03
2.06
1.04
1.02
1.01
9.07
f1 (ppm)


165.12
137.08
135.71
133.85
133.65
133.54
130.44
130.36
128.68
128.59
120.28
120.25
118.09
84.56
77.32
77.00
76.68
58.32
54.48
52.63
27.24
f1 (ppm)

Data File E:\DATA\SC...2-23\SC-13-7-22 2021-04-07 10-09-15\SC-16-14-15_13-1-2-6-7-22-233.D
Sample Name: SC-13-7-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260                              Location :   63
    Injection Date  : 4/7/2021 10:44:29 AM                  Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23\SC-13-7-22 2021-04-07 10-09-15\SC-3
                      -ID-98-2-DAD-1ML-10MIN.M
    Last changed    : 4/7/2021 10:09:15 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23\SC-13-7-22 2021-04-07 10-09-15\SC-3
                      -ID-98-2-DAD-1ML-10MIN.M (Sequence Method)
    Last changed    : 4/7/2021 5:07:59 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

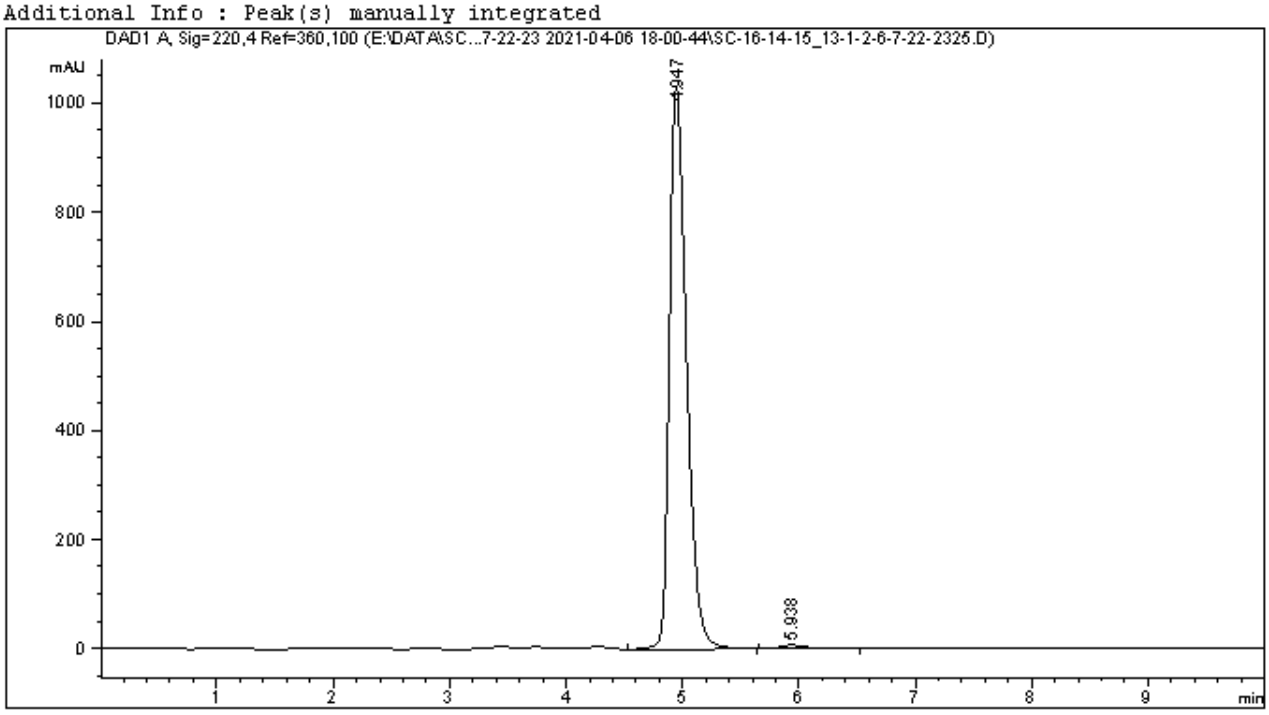

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.970 BV    0.1605 2866.67163  273.07132  50.0842
       2   5.969 FM    0.2053 2857.03687  231.89261  49.9158

    Totals :                   5723.70850  504.96393
```

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2325.D
Sample Name: SC-13-7B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  26
    Acq. Instrument : 1260                             Location :  66
    Injection Date  : 4/7/2021 1:05:46 AM                  Inj :  1
                                                     Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-3-ID-98-2-
                      DAD-1ML-10MIN.M
    Last changed    : 4/6/2021 8:42:31 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-3-ID-98-2-
                      DAD-1ML-10MIN.M (Sequence Method)
    Last changed    : 4/7/2021 5:11:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



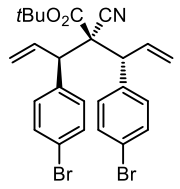

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

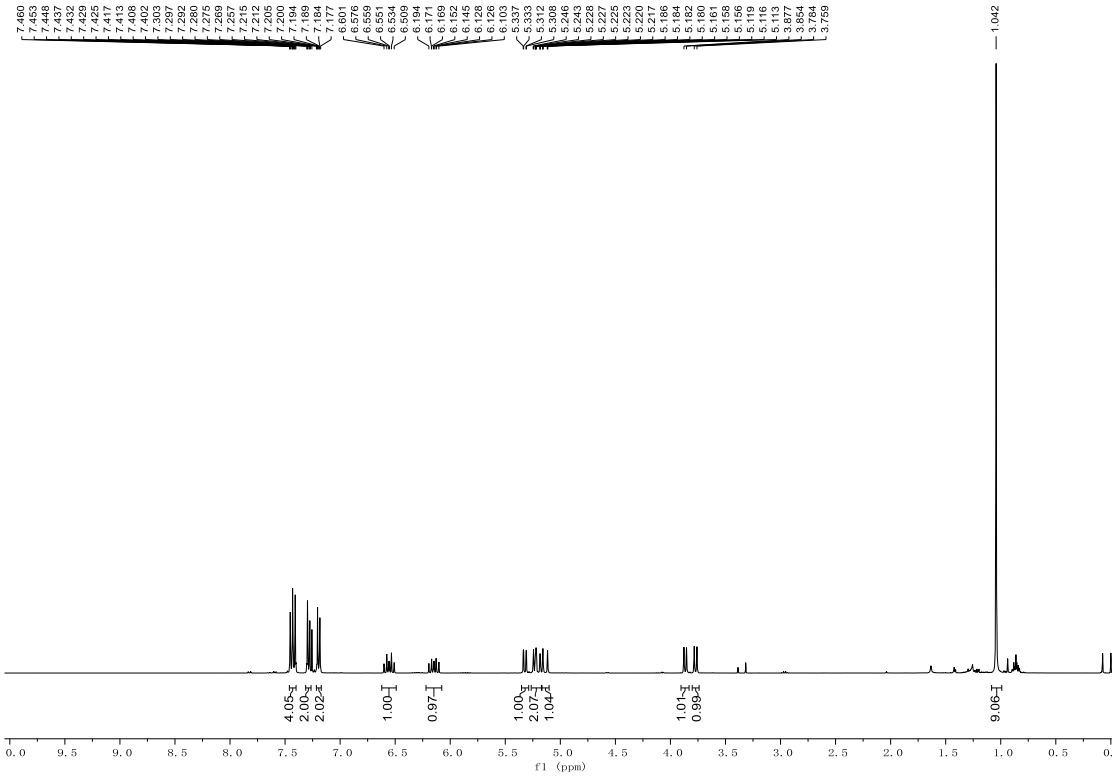

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

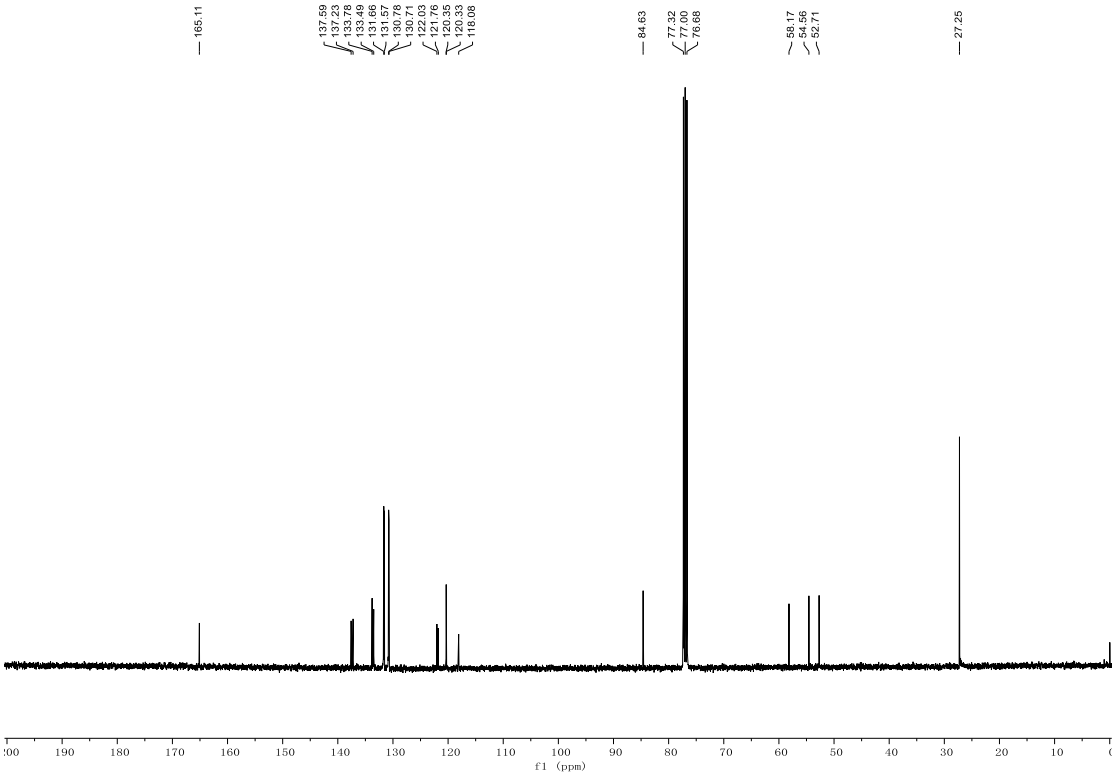
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.947 BB    0.1561 1.05210e4  1030.69934  99.1167
       2   5.938 BB    0.1999   93.76121    6.67556   0.8833

    Totals :                  1.06148e4  1037.37490
```


tBuO2C
CN
Br
Br

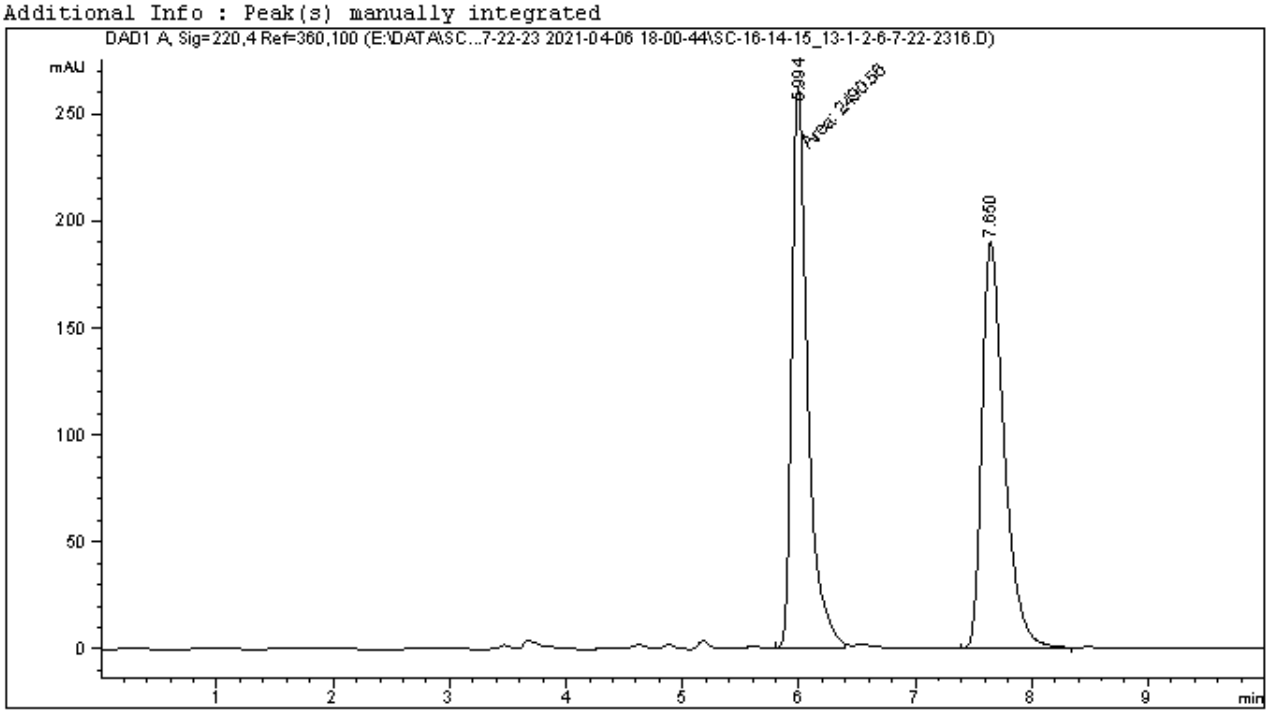
7d


7.460
7.453
7.448
7.437
7.432
7.429
7.425
7.417
7.413
7.408
7.402
7.393
7.287
7.282
7.280
7.275
7.269
7.257
7.215
7.212
7.205
7.200
7.194
7.189
7.184
7.177
6.601
6.576
6.559
6.551
6.534
6.509
6.194
6.171
6.169
6.152
6.145
6.128
6.126
6.103
5.337
5.333
5.312
5.308
5.246
5.243
5.228
5.227
5.225
5.223
5.220
5.217
5.186
5.184
5.182
5.160
5.161
5.158
5.156
5.119
5.116
5.113
3.877
3.864
3.784
3.759
1.042
4.05
2.00
2.02
1.00
0.97
1.00
2.07
1.04
1.01
0.99
9.06
f1 (ppm)


165.11
137.59
137.23
133.78
133.49
131.66
131.57
130.78
130.71
121.93
121.76
120.35
120.33
118.08
84.63
77.32
77.00
76.68
58.17
54.56
52.71
27.25
f1 (ppm)

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2316.D
Sample Name: SC-13-2-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  17
    Acq. Instrument : 1260                              Location :  86
    Injection Date  : 4/6/2021 10:24:04 PM                  Inj :  1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M
    Last changed    : 4/6/2021 6:00:45 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:47:05 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

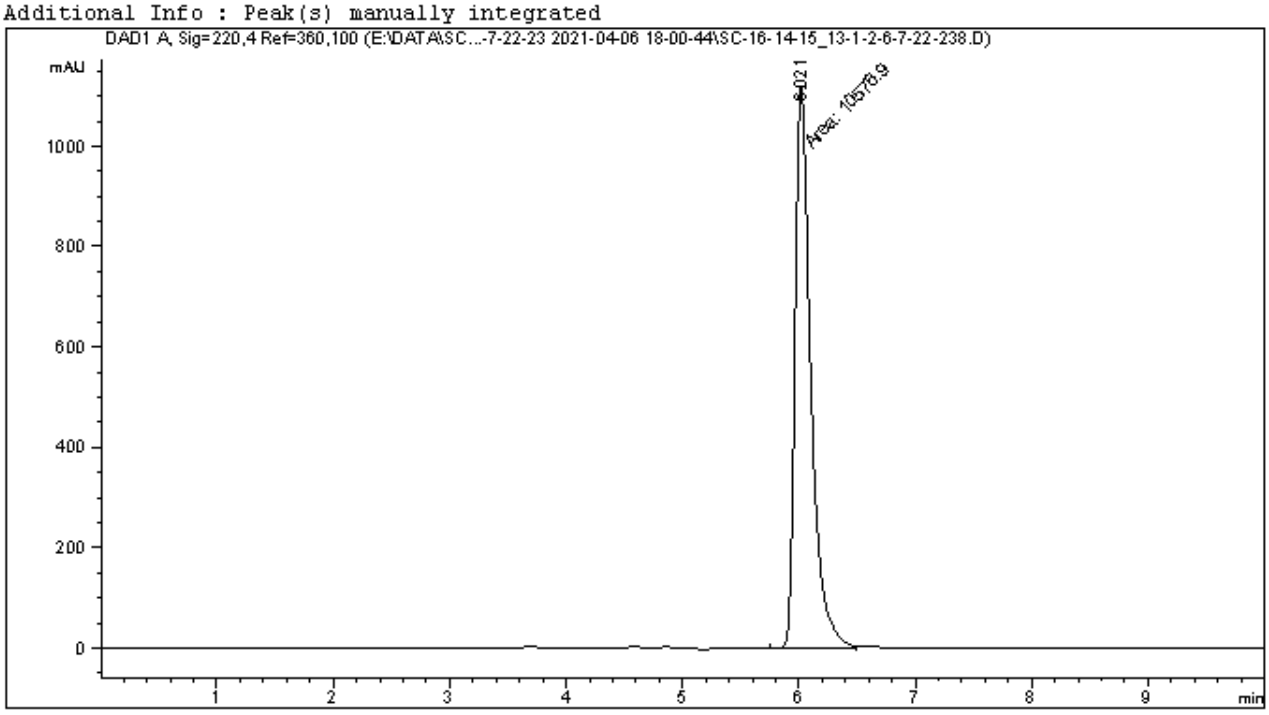

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.994 MF    0.1583 2490.56177  262.17987  49.7241
       2   7.650 BB    0.2001 2518.20166  189.42445  50.2759

    Totals :                   5008.76343  451.60432
```

Data File E:\DATA\SC...3-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-238.D
Sample Name: SC-13-2B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   9
    Acq. Instrument : 1260                             Location :   88
    Injection Date  : 4/6/2021 7:32:29 PM                  Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M
    Last changed    : 4/6/2021 6:00:45 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-10MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:47:05 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



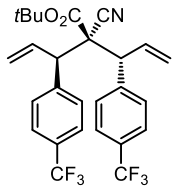

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

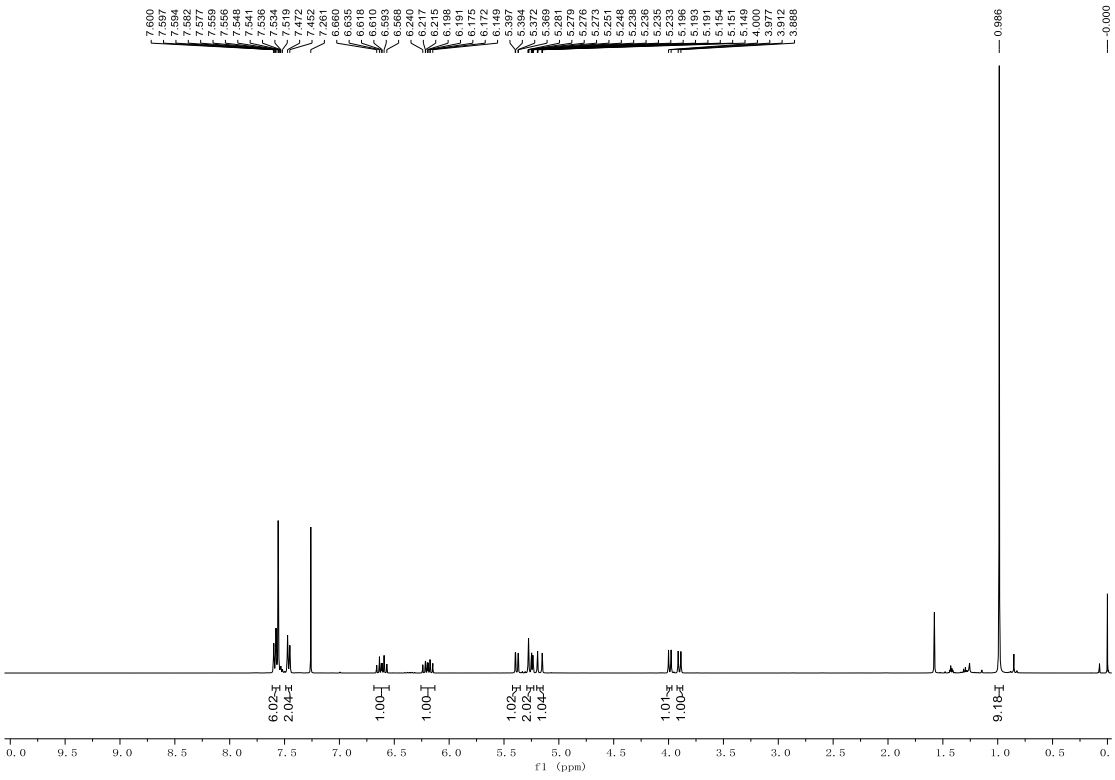

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

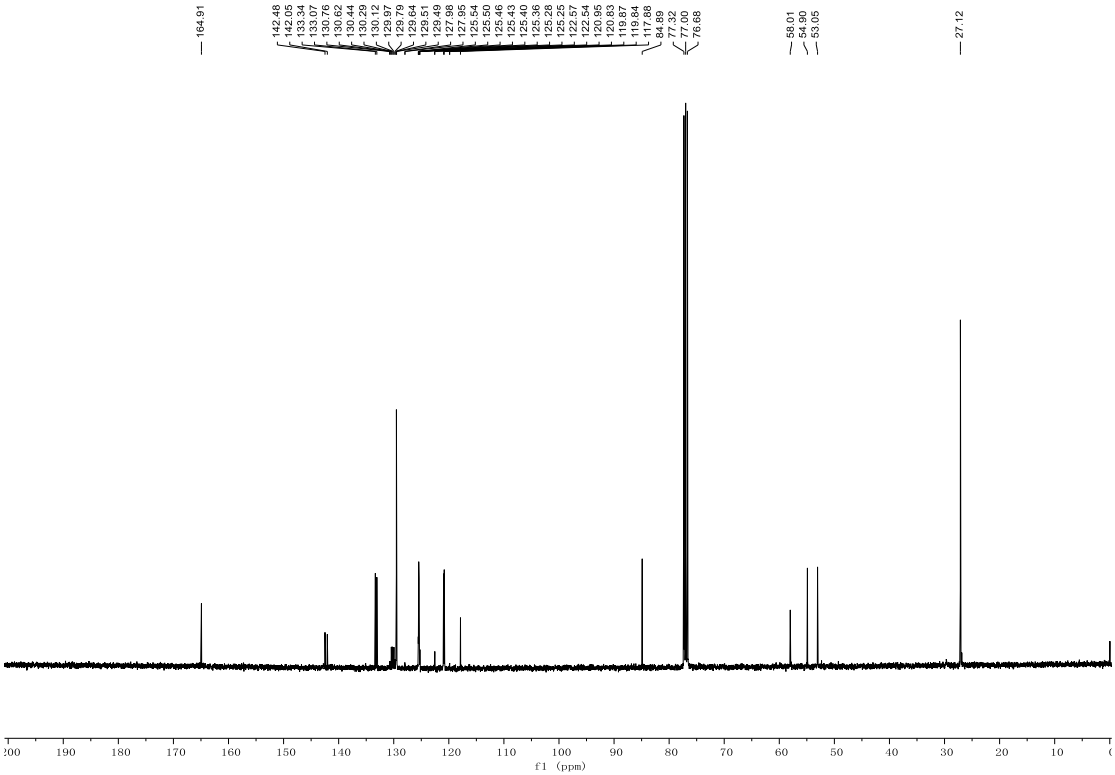
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.021 MF    0.1576 1.05769e4  1118.70166 100.0000

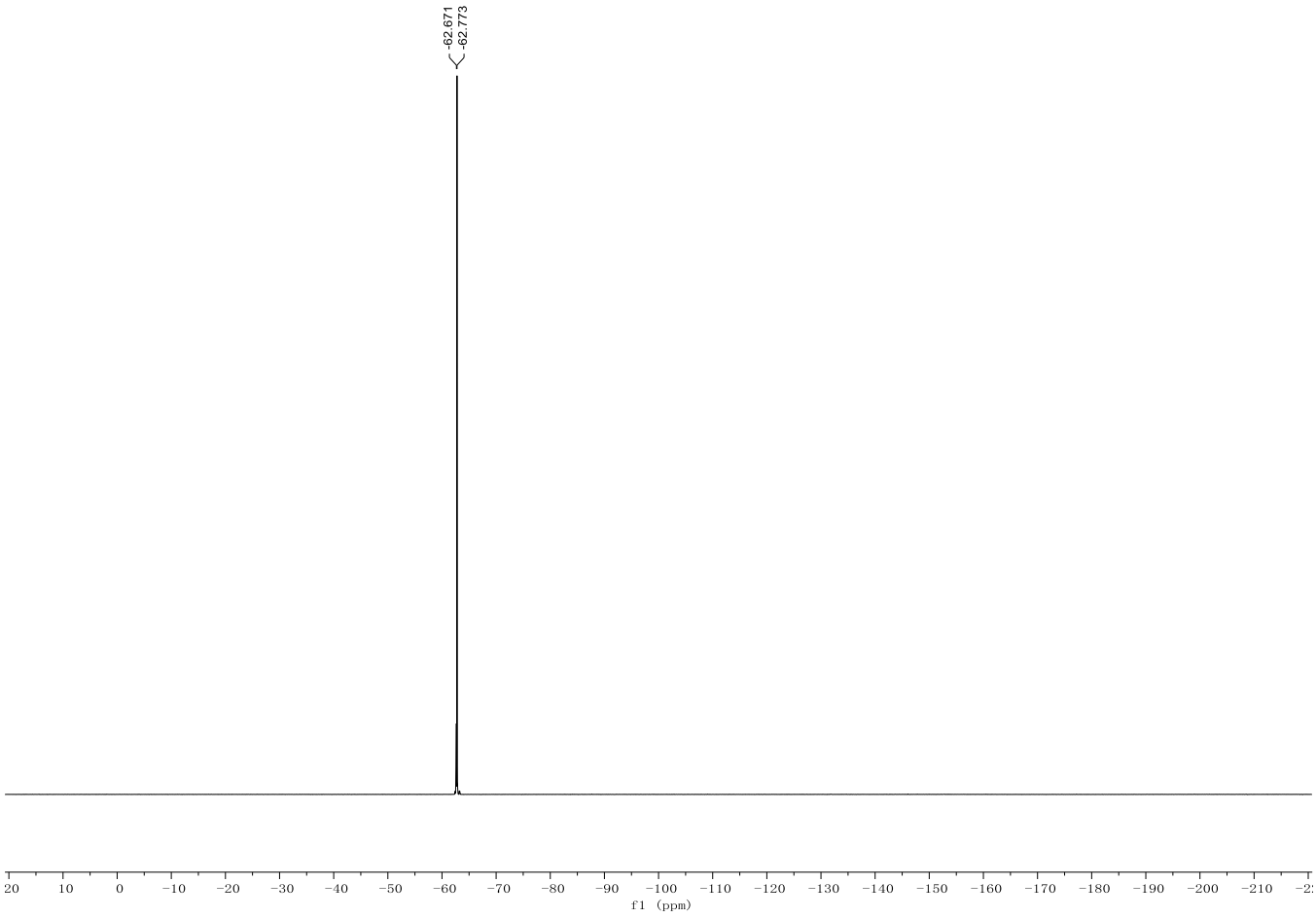
    Totals :                  1.05769e4  1118.70166
```


tBuO2C
CN
CF3
CF3

7e

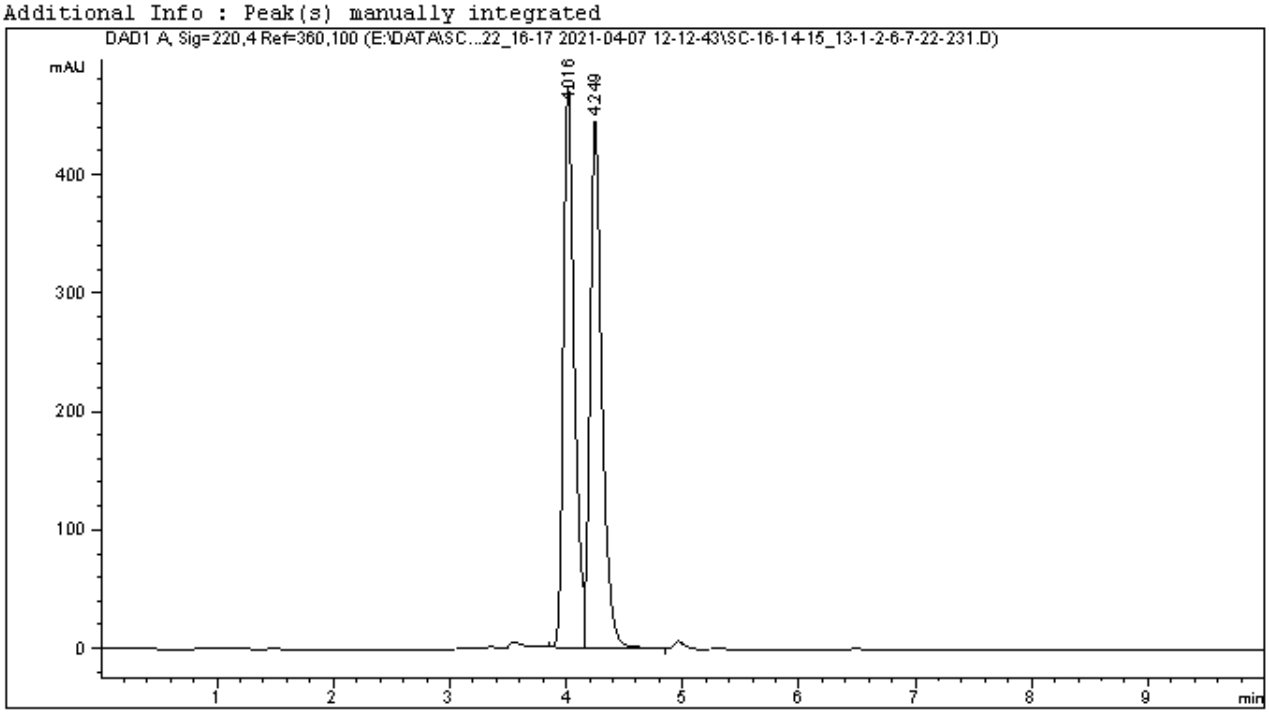

7.600
7.597
7.594
7.582
7.577
7.569
7.556
7.548
7.541
7.536
7.534
7.519
7.472
7.452
7.261
6.660
6.635
6.618
6.610
6.593
6.568
6.240
6.217
6.215
6.198
6.191
6.175
6.172
6.149
5.397
5.394
5.372
5.369
5.281
5.279
5.276
5.273
5.251
5.248
5.238
5.236
5.235
5.233
5.196
5.193
5.191
5.154
5.151
5.149
4.000
3.977
3.912
3.888
0.986
0.000
6.02
2.04
1.00
1.00
1.02
2.02
1.04
1.01
1.00
9.18
f1 (ppm)


164.91
142.48
142.05
133.34
133.07
130.76
130.62
130.44
130.29
130.12
129.97
129.79
129.64
129.51
129.49
127.98
127.95
125.54
125.50
125.46
125.43
125.40
125.36
125.28
125.25
122.57
122.54
120.95
120.83
119.87
119.84
117.88
84.99
77.32
77.00
76.68
58.01
54.90
53.05
27.12
f1 (ppm)


-62.671
-62.773
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

Data File E:\DATA\SC...\SC-13-22_16-17 2021-04-07 12-12-43\SC-16-14-15_13-1-2-6-7-22-231.D
Sample Name: SC-13-22-RAC-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260                              Location :   61
    Injection Date  : 4/7/2021 12:24:54 PM                  Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23\SC-13-22_16-17 2021-04-07 12-12-43
                      \SC-4-IE-98-2-DAD-1ML-10MIN-2UL.M
    Last changed    : 4/7/2021 12:12:43 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23\SC-13-22_16-17 2021-04-07 12-12-43
                      \SC-4-IE-98-2-DAD-1ML-10MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:15:55 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

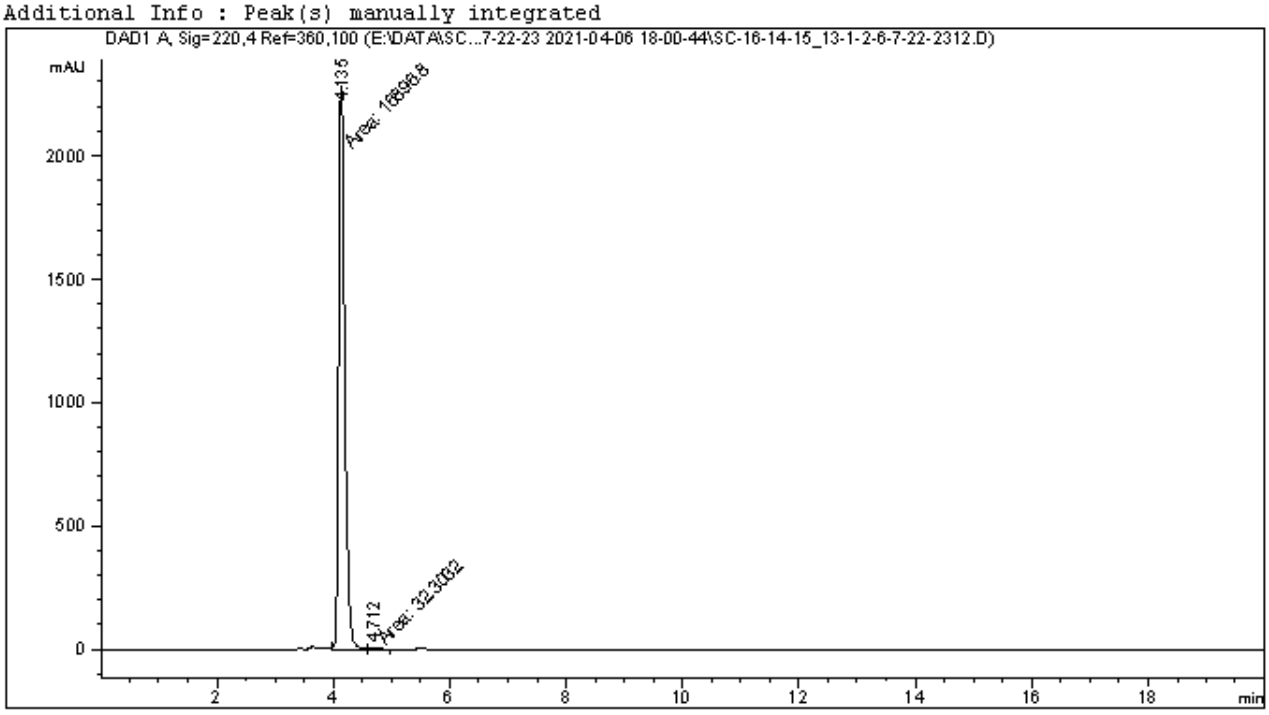

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.016 BV    0.0098 3114.95044  473.30215  49.7345
       2   4.249 VB    0.1057 3148.20605  443.89285  50.2655

    Totals :                   6263.15649  917.19501
```

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2312.D
Sample Name: SC-13-22B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  13
    Acq. Instrument : 1260                             Location :  62
    Injection Date  : 4/6/2021 9:08:31 PM                  Inj :  1
                                                     Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M
    Last changed    : 4/6/2021 8:40:39 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:18:50 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



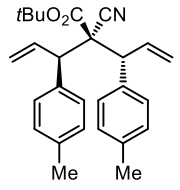

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

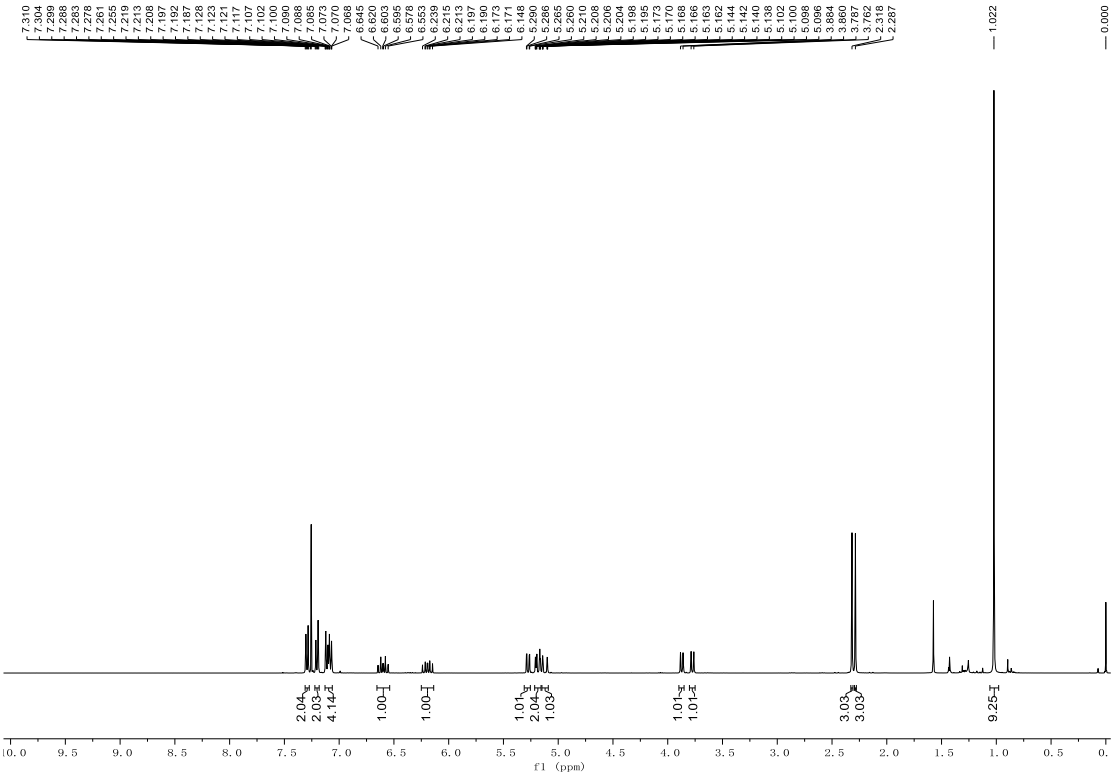

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

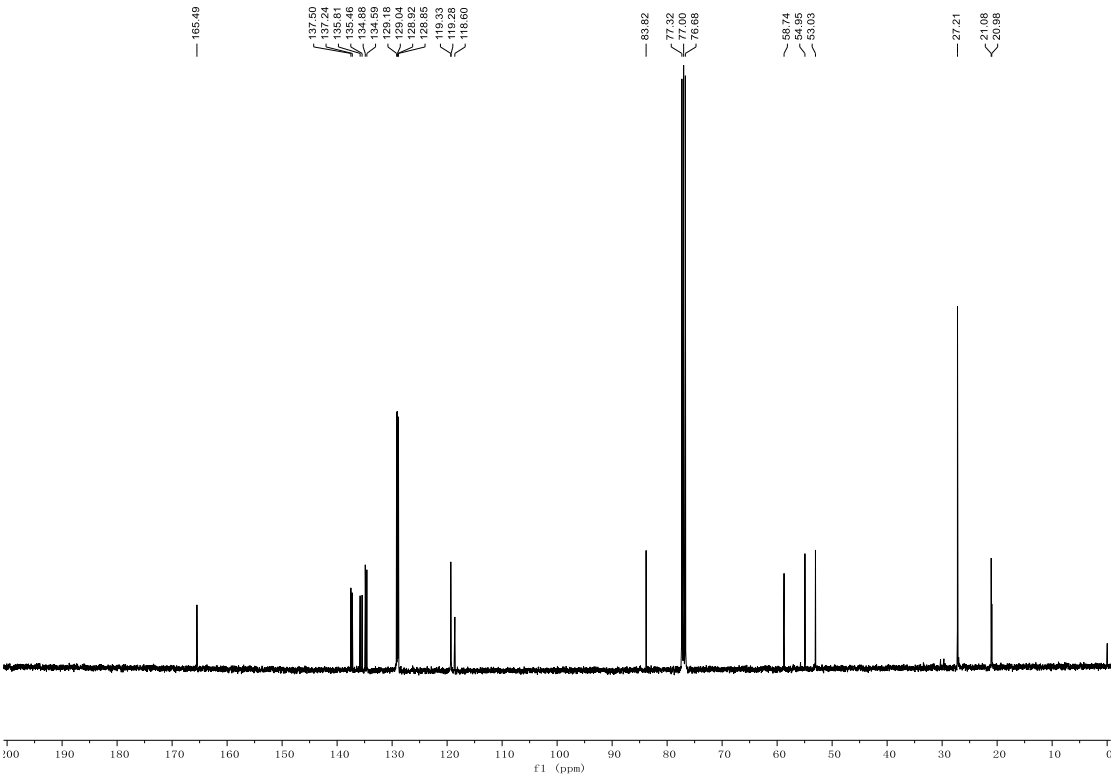
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.135 MF    0.1235 1.68968e4  2281.11060  99.8092
       2   4.712 FM    0.1640   32.30324    3.28293   0.1908

    Totals :                  1.69291e4  2284.39353
```



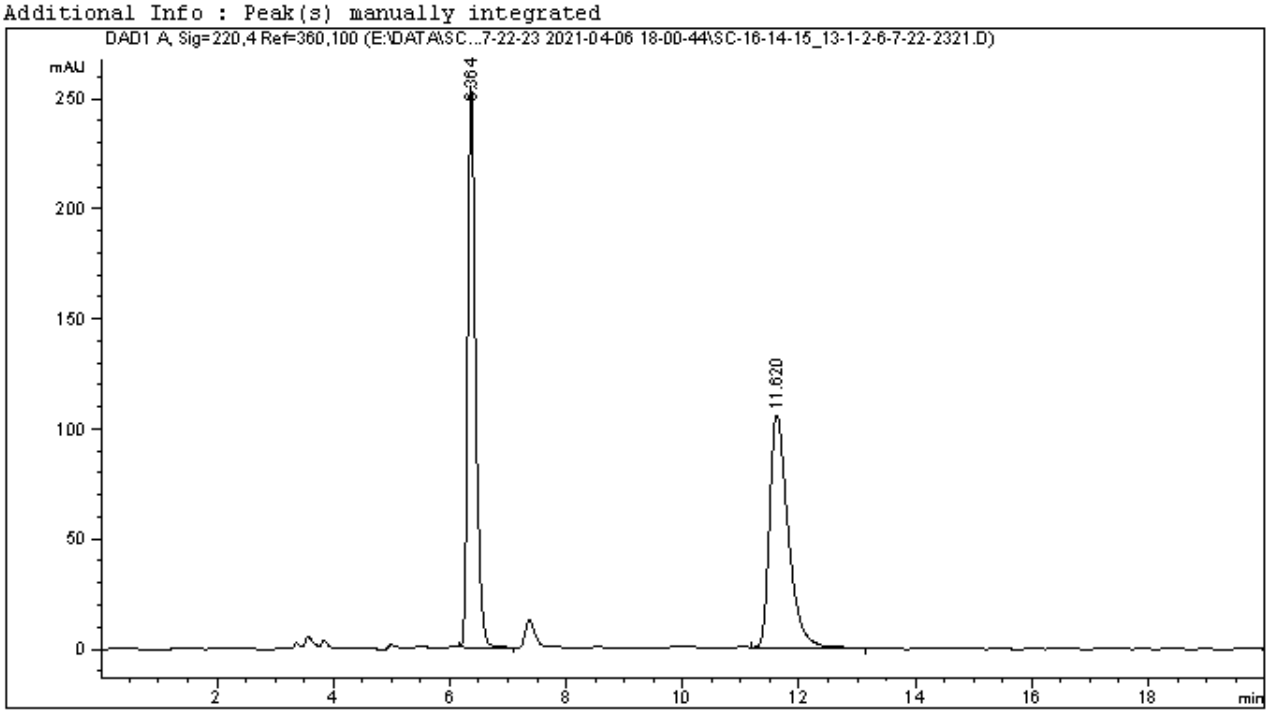
7f





Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2321.D
Sample Name: SC-13-23-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  22
    Acq. Instrument : 1260                            Location :  62
    Injection Date  : 4/7/2021 12:11:00 AM                 Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M
    Last changed    : 4/6/2021 8:40:39 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:02:56 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

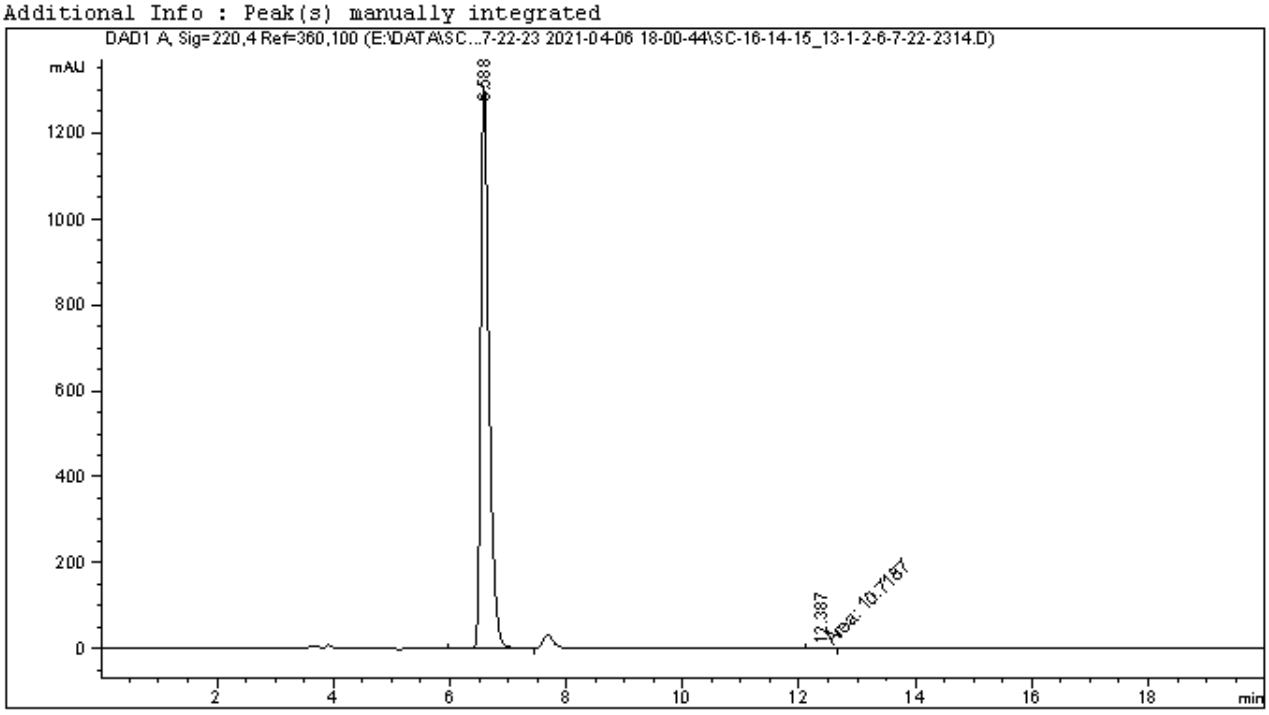

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.364 BB    0.1414 2389.66943  254.73019  50.4425
       2  11.620 BB    0.3365 2347.74023  105.97092  49.5575

    Totals :                  4737.40967  360.70111
```

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2314.D
Sample Name: SC-13-23B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  15
    Acq. Instrument : 1260                             Location :  64
    Injection Date  : 4/6/2021 9:51:23 PM                  Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M
    Last changed    : 4/6/2021 8:40:39 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:02:56 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



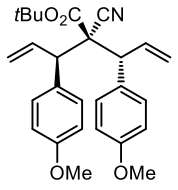

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

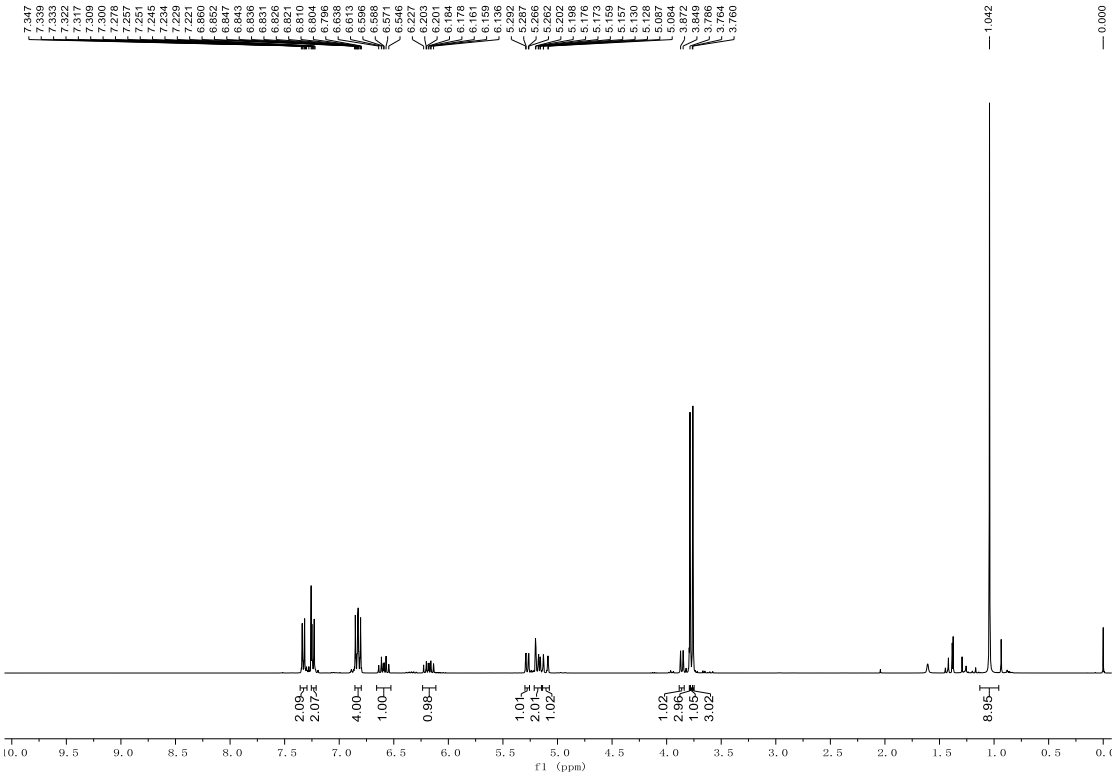

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

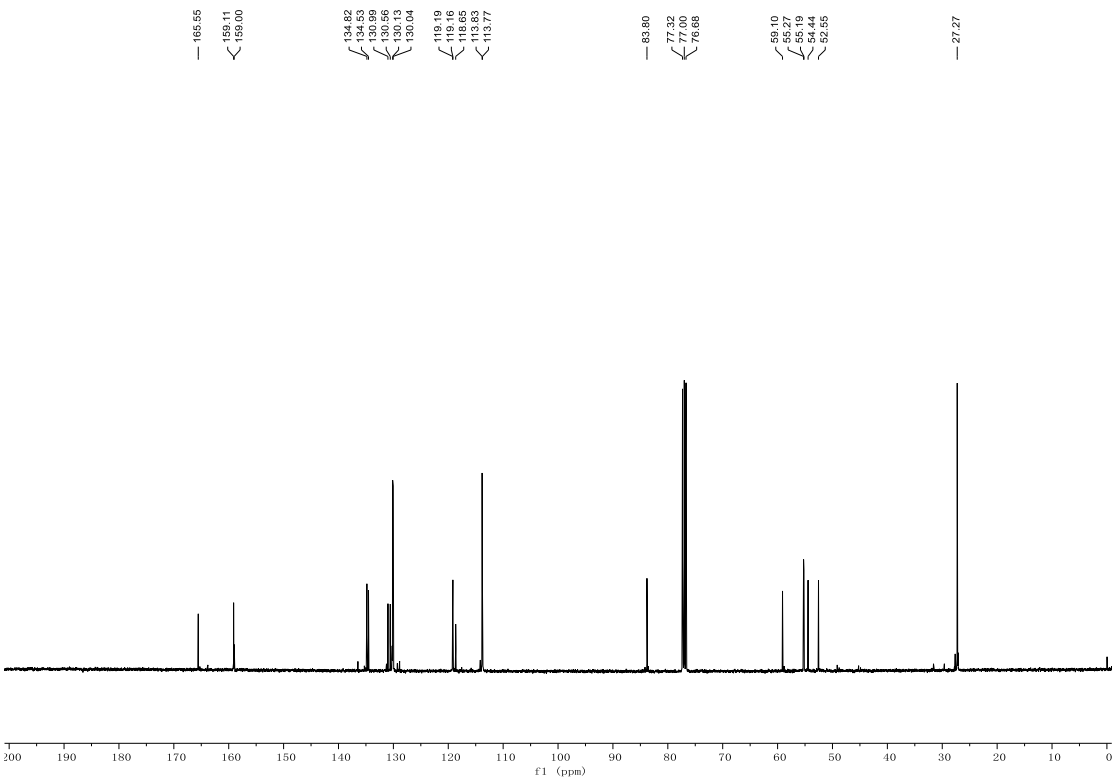
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.588 VB R  0.1497 1.29850e4  1308.11499  99.9175
       2  12.387 MM    0.3569   10.71871 5.00560e-1   0.0825

    Totals :                  1.29957e4  1308.61555
```


tBuO2C
CN
OMe
OMe

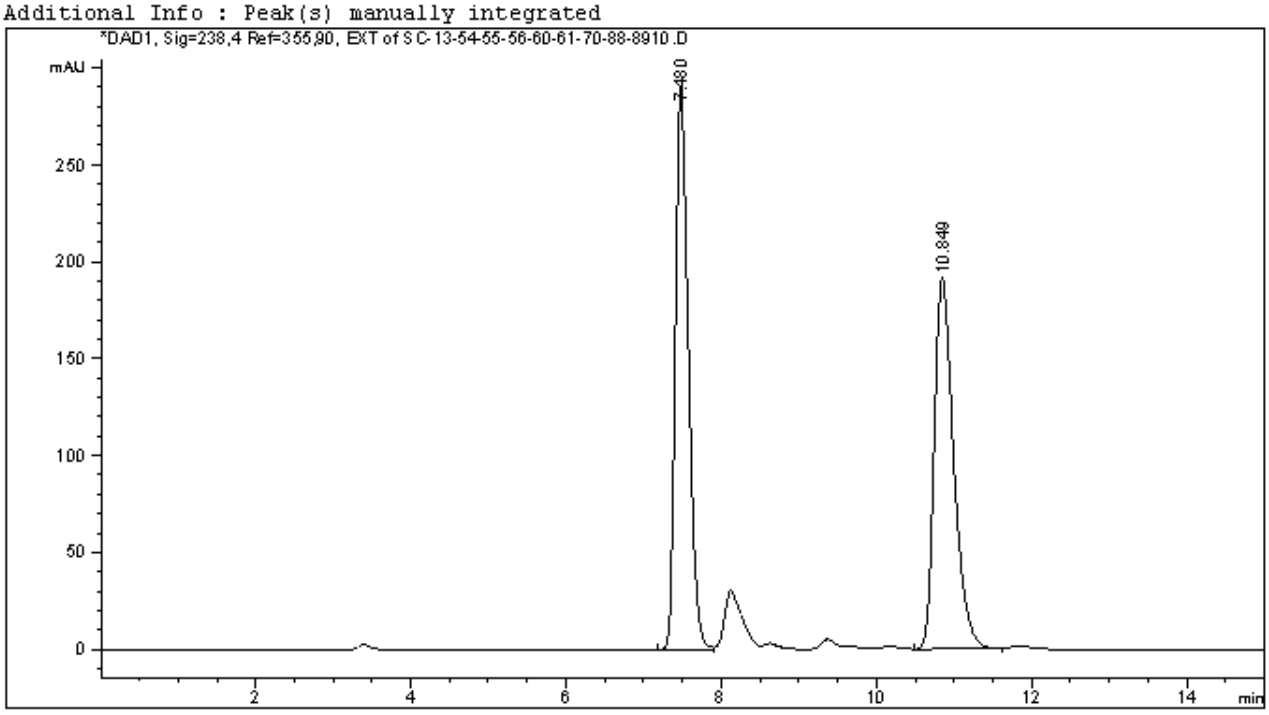
7g


7.347
7.339
7.333
7.322
7.317
7.309
7.300
7.278
7.257
7.251
7.245
7.234
7.229
7.221
6.860
6.852
6.847
6.843
6.836
6.831
6.826
6.821
6.810
6.804
6.798
6.788
6.613
6.596
6.588
6.571
6.546
6.227
6.203
6.201
6.184
6.178
6.161
6.159
6.136
5.292
5.287
5.266
5.262
5.202
5.198
5.176
5.173
5.159
5.157
5.130
5.088
5.087
5.084
3.872
3.849
3.786
3.764
3.760
1.042
0.000
2.09
2.07
4.00
1.00
0.98
1.01
2.01
1.02
1.02
2.96
1.05
3.02
8.95
f1 (ppm)


165.55
159.11
159.00
134.82
134.53
130.99
130.56
130.13
130.04
119.19
114.16
113.85
113.83
113.77
83.80
77.32
77.00
76.68
59.10
55.27
55.19
54.44
52.55
27.27
f1 (ppm)

Data File E:\DATA\SC...-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-8910.D
Sample Name: SC-13-88-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  11
    Acq. Instrument : 1260                             Location :  87
    Injection Date  : 10/21/2020 1:21:35 PM                 Inj :  1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-90-10-DAD-1ML-15MIN.M
    Last changed    : 10/21/2020 9:37:15 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-90-10-DAD-1ML-15MIN.M (Sequence Method)
    Last changed    : 4/5/2021 10:06:57 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

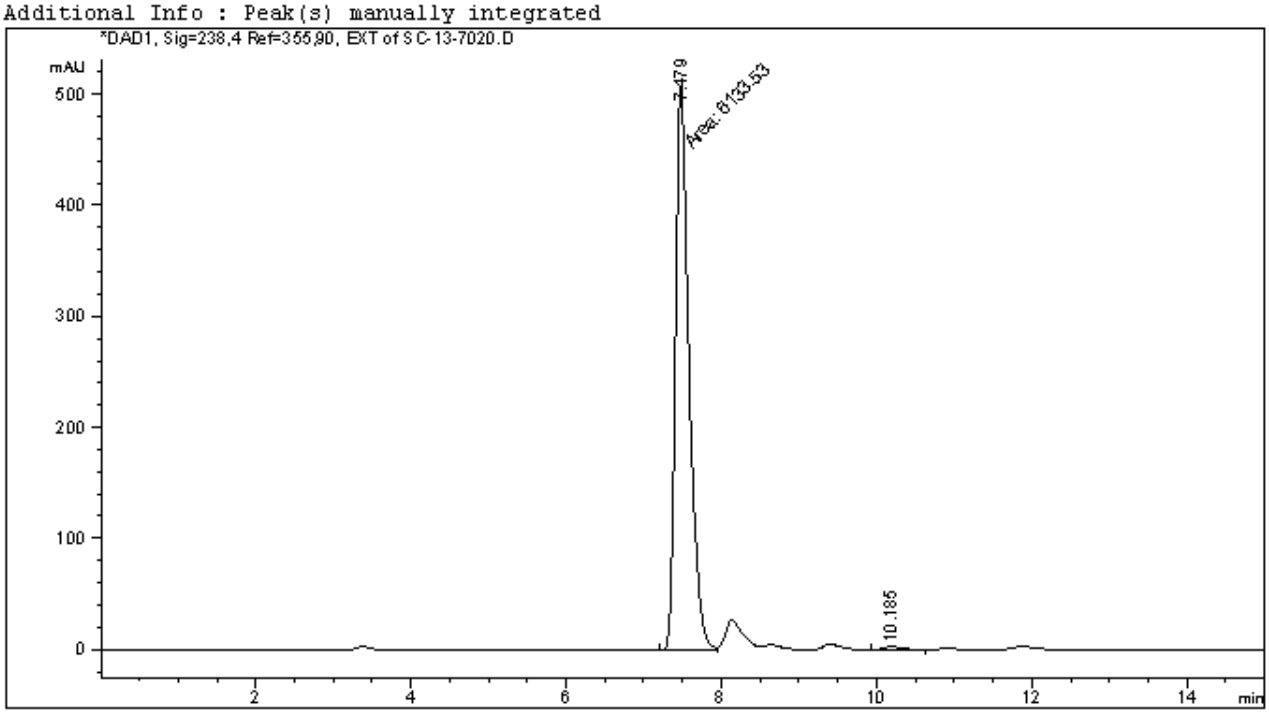

    Signal 1: DAD1, Sig=238,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.480 BV    0.1759 3355.95093  290.27252  50.3326
       2  10.849 BB    0.2631 3311.59668  191.19852  49.6674

    Totals :                  6667.54761  481.47104
```

Data File E:\DATA\SC...8-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-7020.D
Sample Name: SC-13-88B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  21
    Acq. Instrument : 1260                             Location :  94
    Injection Date  : 10/20/2020 7:53:11 AM                 Inj :  1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-90-10-DAD-1ML-15MIN.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-90-10-DAD-1ML-15MIN.M (Sequence Method)
    Last changed    : 4/7/2021 5:46:07 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



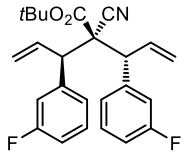

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

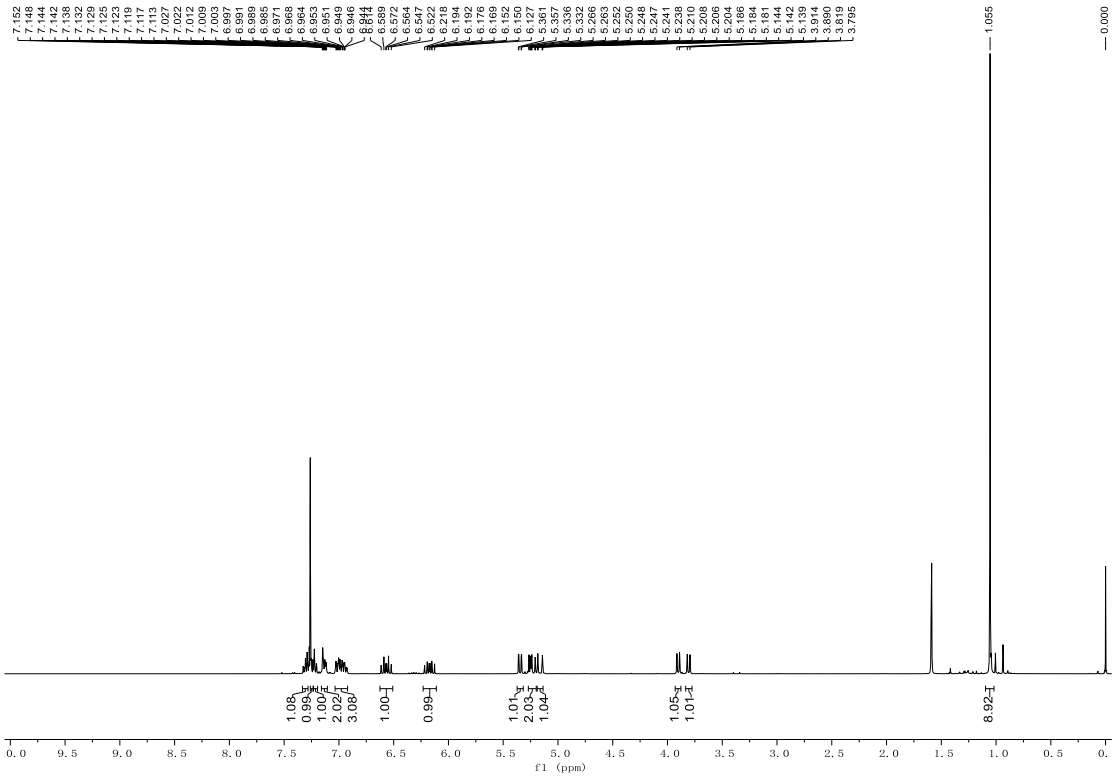

    Signal 1: DAD1, Sig=238,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

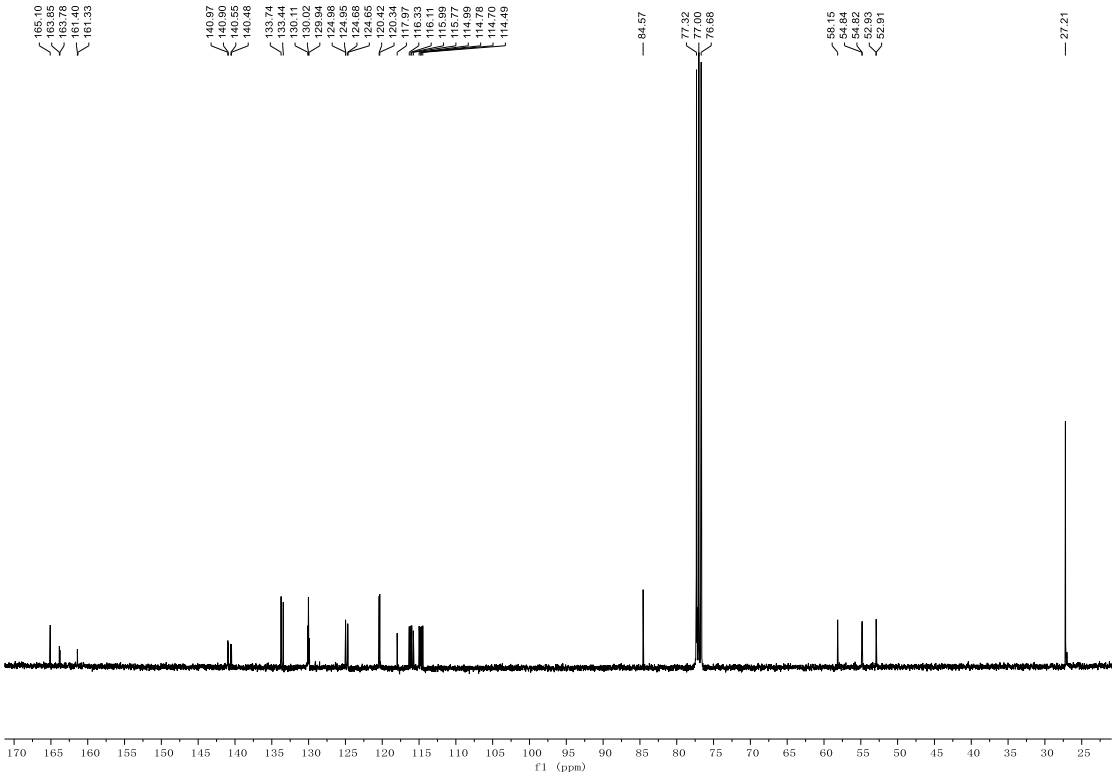
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.479 MF    0.2016 6133.53320  507.03662  99.4223
       2  10.185 BB    0.2142   35.63805    2.36017   0.5777

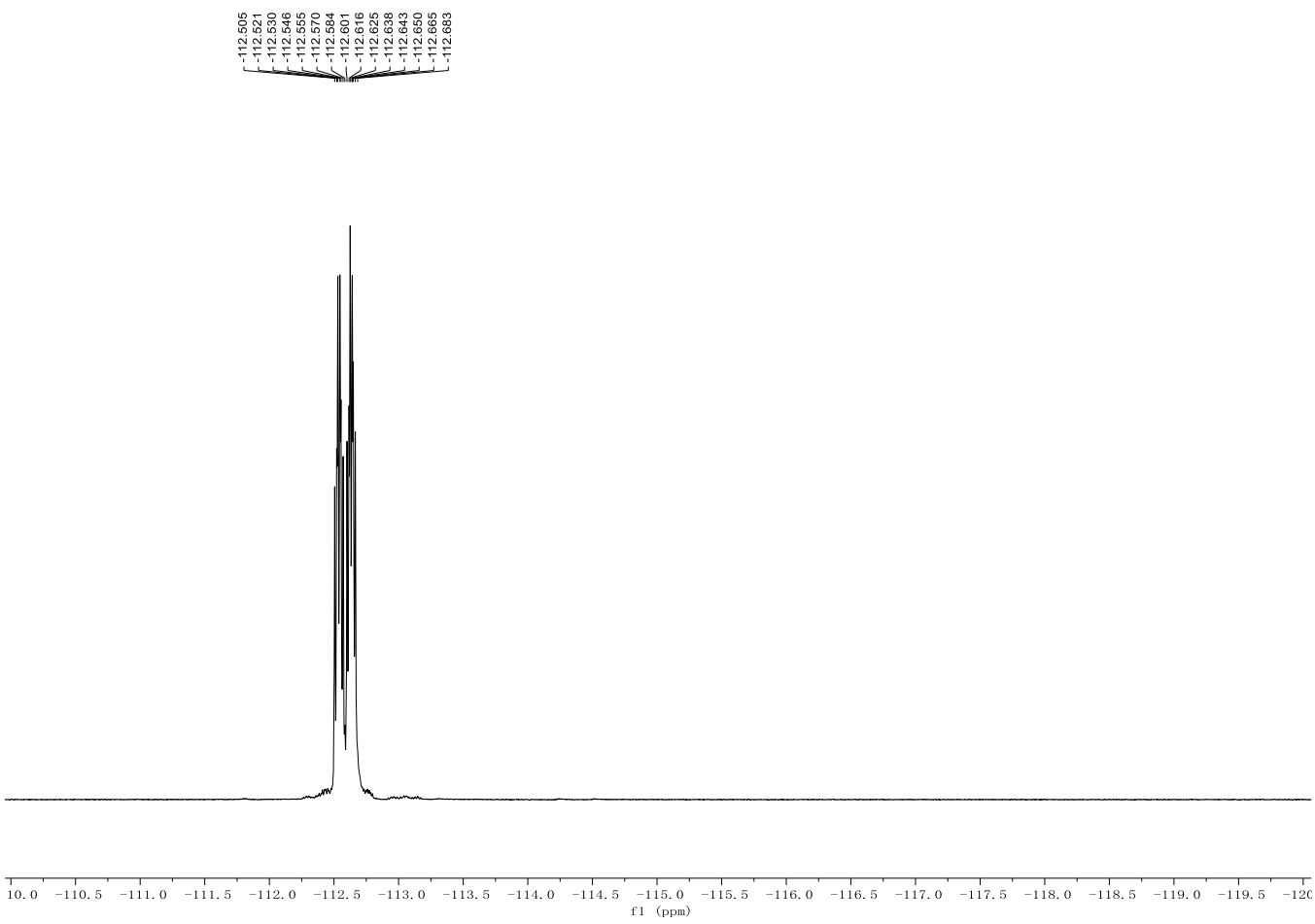
    Totals :                  6169.17125  509.39679
```


tBuO2C
CN
F
F

7h

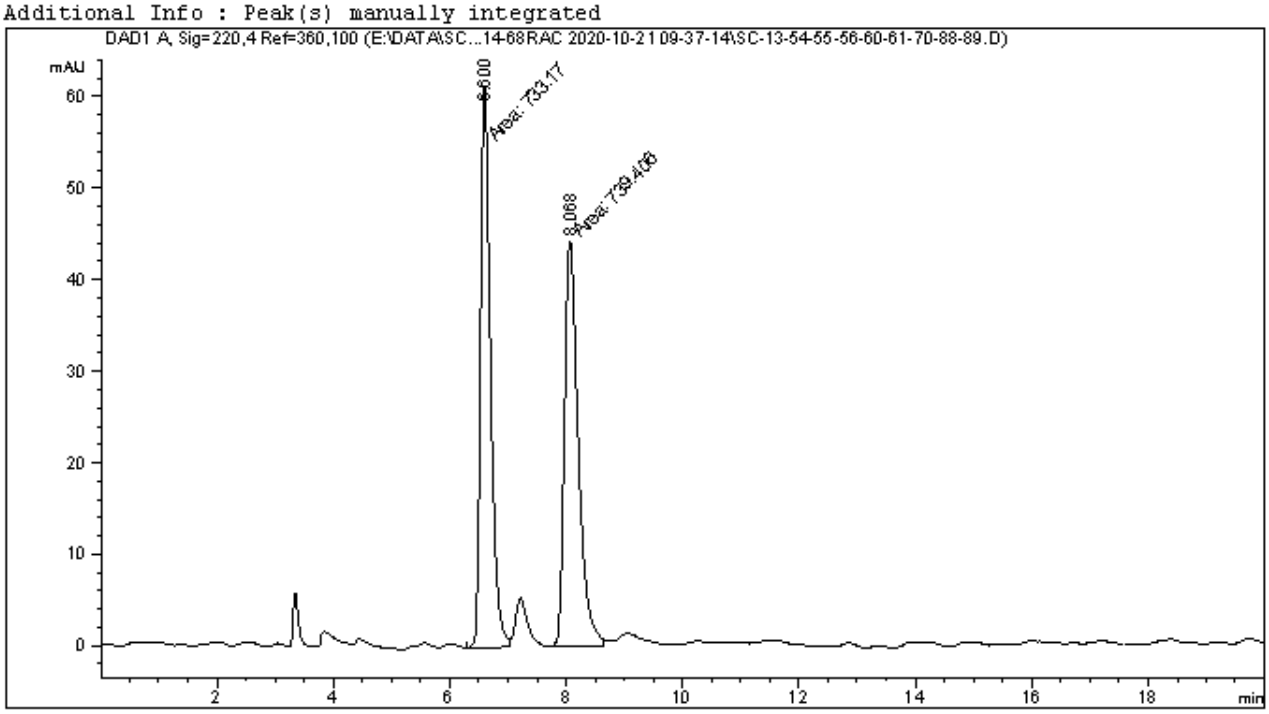

7.152
7.148
7.144
7.142
7.138
7.132
7.129
7.125
7.123
7.119
7.117
7.113
7.027
7.022
7.012
7.009
7.003
6.997
6.991
6.989
6.985
6.971
6.968
6.964
6.953
6.951
6.949
6.946
6.844
6.614
6.589
6.572
6.564
6.547
6.522
6.218
6.194
6.192
6.176
6.169
6.152
6.150
6.127
5.361
5.357
5.336
5.332
5.266
5.263
5.253
5.252
5.250
5.248
5.247
5.241
5.238
5.210
5.208
5.206
5.204
5.186
5.184
5.181
5.144
5.142
5.139
3.844
3.800
3.819
3.795
1.055
0.000
1.08
0.99
1.00
2.02
3.08
1.00
0.99
1.01
2.03
1.04
1.05
1.01
8.92
f1 (ppm)


165.10
163.85
163.78
161.40
161.33
140.97
140.90
140.55
140.48
133.74
133.44
130.11
130.02
129.94
124.98
124.95
124.68
124.65
120.42
120.34
117.97
116.33
116.11
115.99
115.77
114.99
114.78
114.70
114.49
84.57
77.32
77.00
76.68
58.15
54.84
54.82
52.93
52.91
27.21
f1 (ppm)


-112.505
-112.521
-112.530
-112.546
-112.555
-112.570
-112.584
-112.601
-112.616
-112.625
-112.638
-112.643
-112.650
-112.665
-112.683
10.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120
f1 (ppm)

Data File E:\DATA\SC...88-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-89.D
Sample Name: SC-13-54-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   81
    Injection Date  : 10/21/2020 9:38:38 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/21/2020 9:37:14 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 9:43:40 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

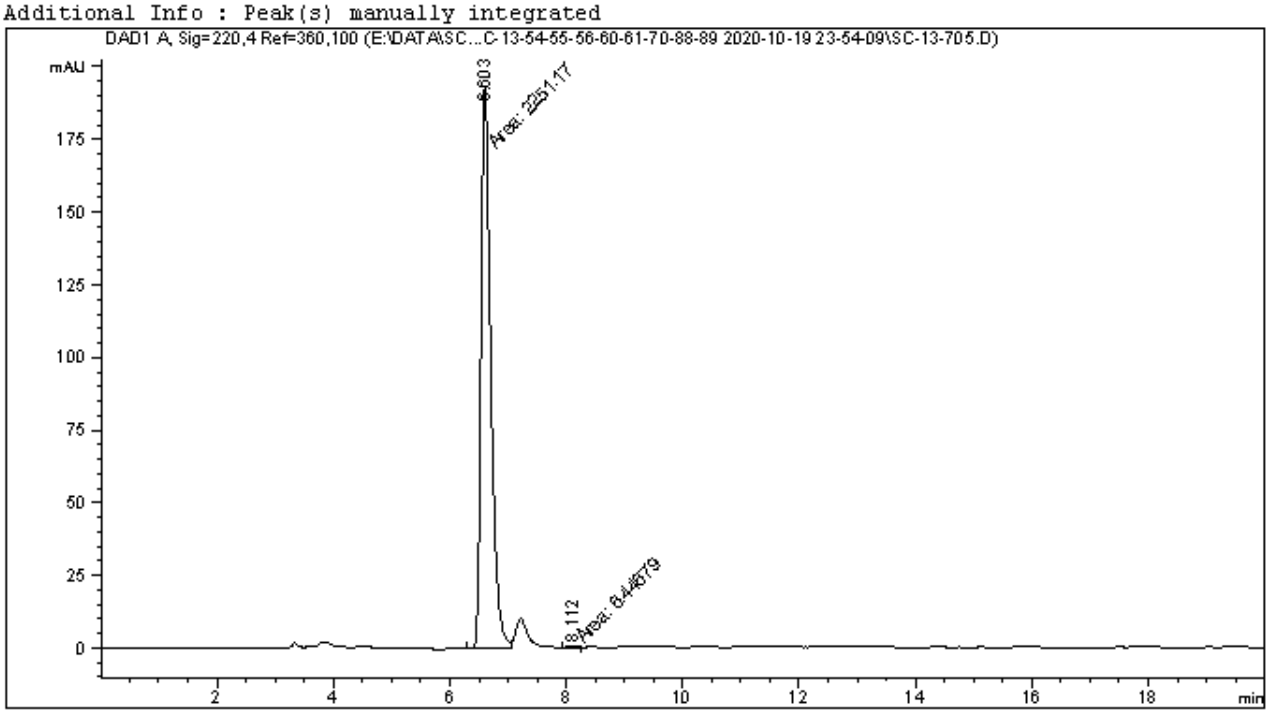

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.600 MF    0.1992  733.17047   61.33347  49.7883
       2   8.068 MM    0.2778  739.40637   44.36321  50.2117

    Totals :                  1472.57684  105.69667
```

Data File E:\DATA\SC...88-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-705.D
Sample Name: SC-13-54B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   6
    Acq. Instrument : 1260                             Location :   73
    Injection Date  : 10/20/2020 2:42:13 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:25:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



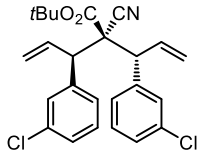

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

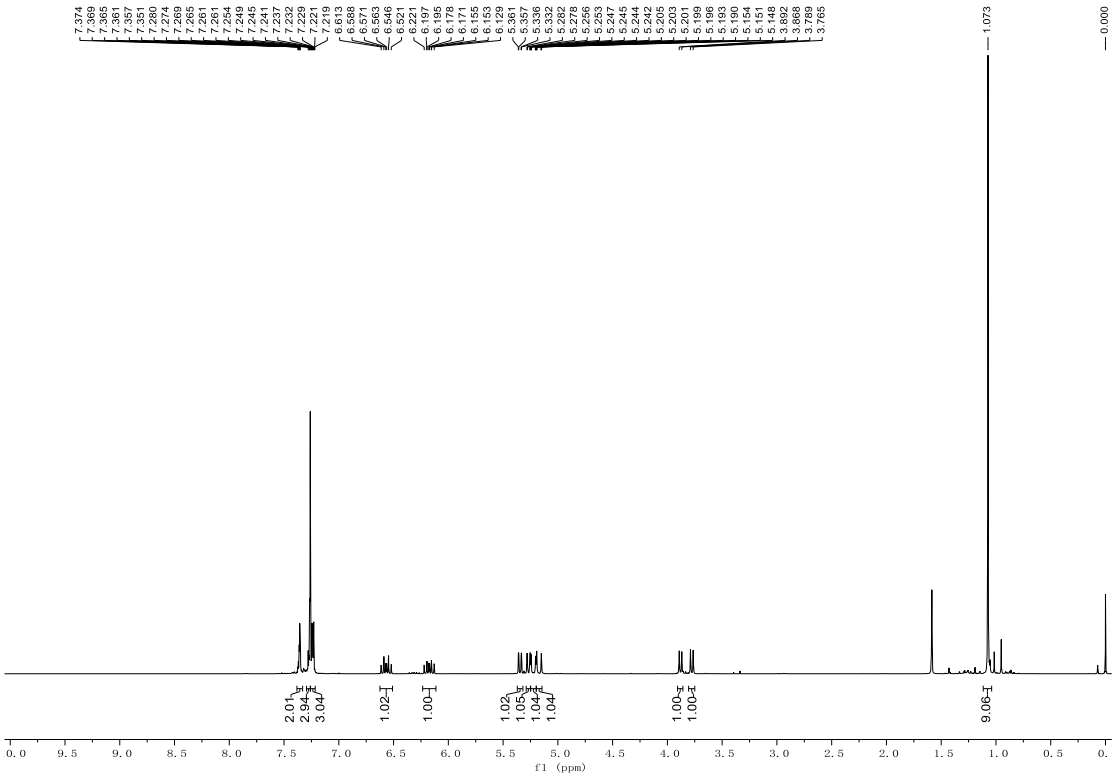

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

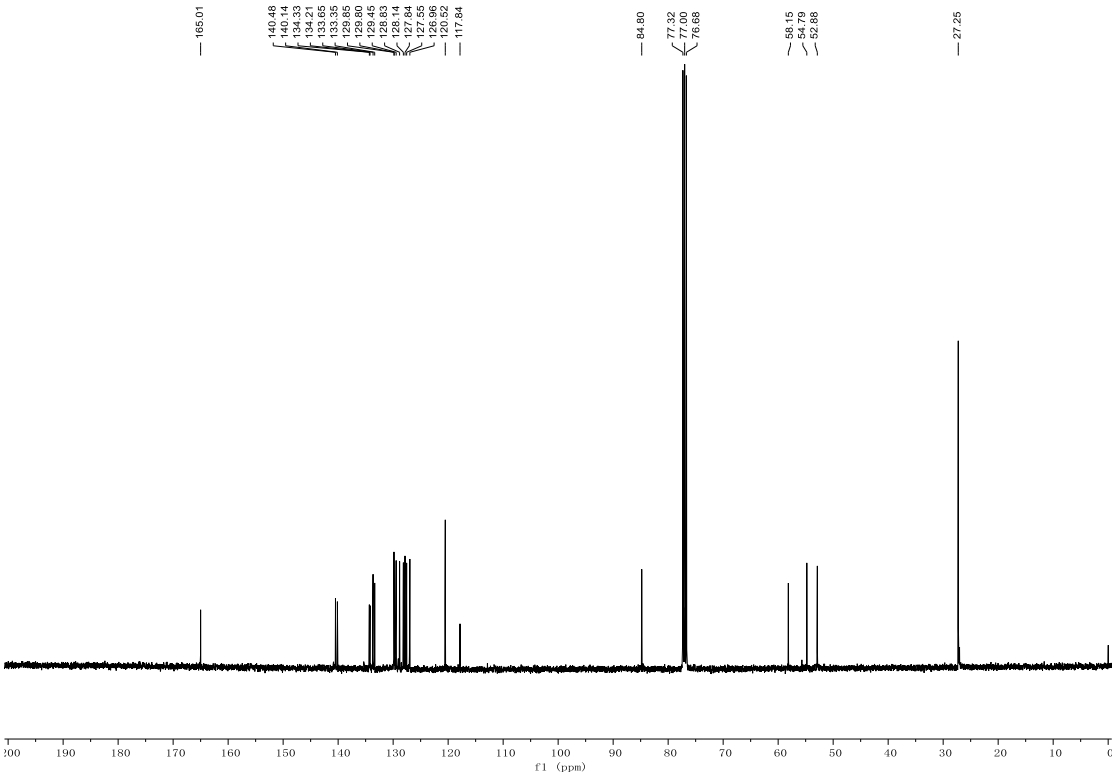
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.603 MF    0.1940 2251.17212  193.36316  99.7144
       2   8.112 MM    0.2504    6.44679 4.29162e-1   0.2856

    Totals :                  2257.61891  193.79232
```


tBuO2C
CN
Cl
Cl

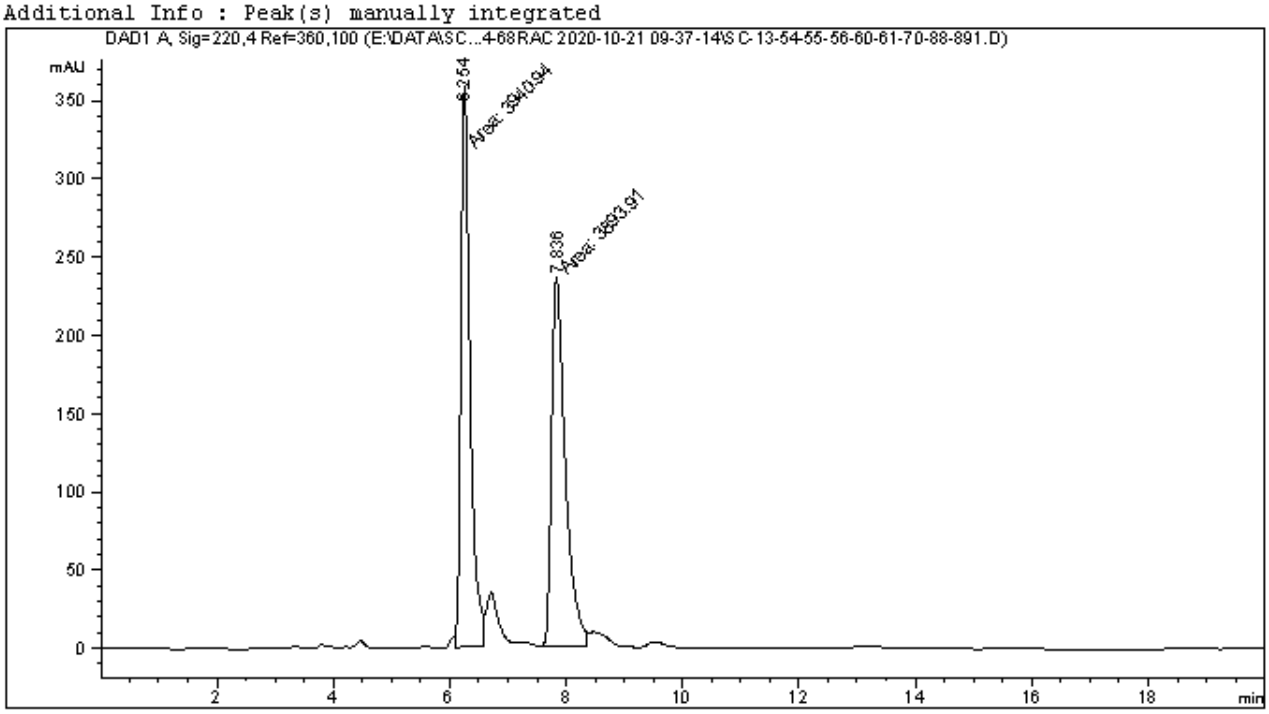
7i


7.374
7.369
7.365
7.361
7.357
7.351
7.280
7.274
7.269
7.265
7.261
7.261
7.254
7.249
7.245
7.241
7.237
7.232
7.229
7.221
7.219
6.613
6.588
6.571
6.563
6.546
6.521
6.221
6.197
6.195
6.178
6.171
6.155
6.153
6.129
5.361
5.357
5.336
5.332
5.282
5.278
5.256
5.253
5.247
5.245
5.244
5.242
5.205
5.203
5.201
5.199
5.196
5.193
5.190
5.154
5.151
5.148
3.892
3.868
3.789
3.765
1.073
0.000
2.01
2.94
3.04
1.02
1.00
1.02
1.05
1.04
1.04
1.00
1.00
9.06
f1 (ppm)


165.01
140.48
140.14
134.33
134.21
133.65
133.35
129.85
129.80
129.45
128.83
128.14
127.84
127.55
126.96
120.52
117.84
84.80
77.32
77.00
76.68
58.15
54.79
52.88
27.25
f1 (ppm)

Data File E:\DATA\SC...8-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-891.D
Sample Name: SC-13-55-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260                             Location :   82
    Injection Date  : 10/21/2020 9:59:58 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/21/2020 9:37:14 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 9:47:07 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

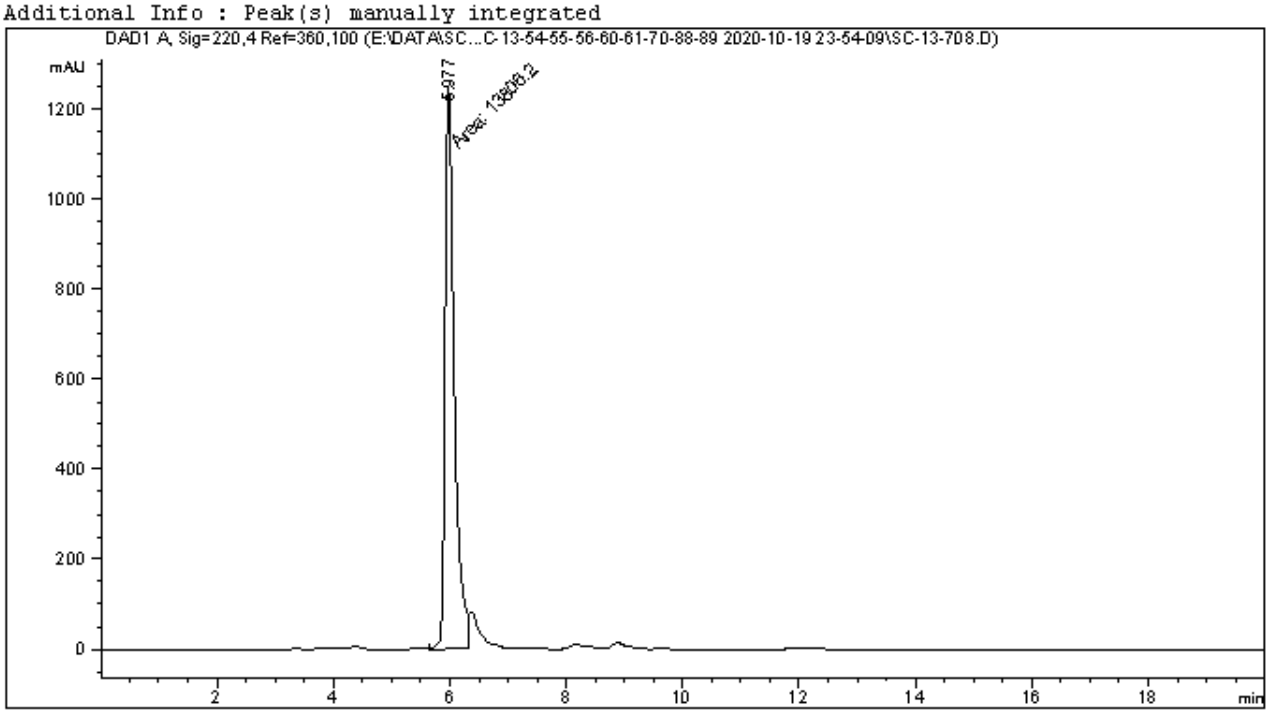

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.254 FM    0.1835 3940.93604  357.94888  50.3001
       2   7.836 MM    0.2757 3893.90527  235.40367  49.6999

    Totals :                   7834.84131  593.35255
```

Data File E:\DATA\SC...88-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-708.D
Sample Name: SC-13-55B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   9
    Acq. Instrument : 1260                             Location :   76
    Injection Date  : 10/20/2020 3:46:40 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:27:49 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



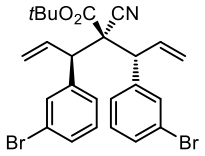

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

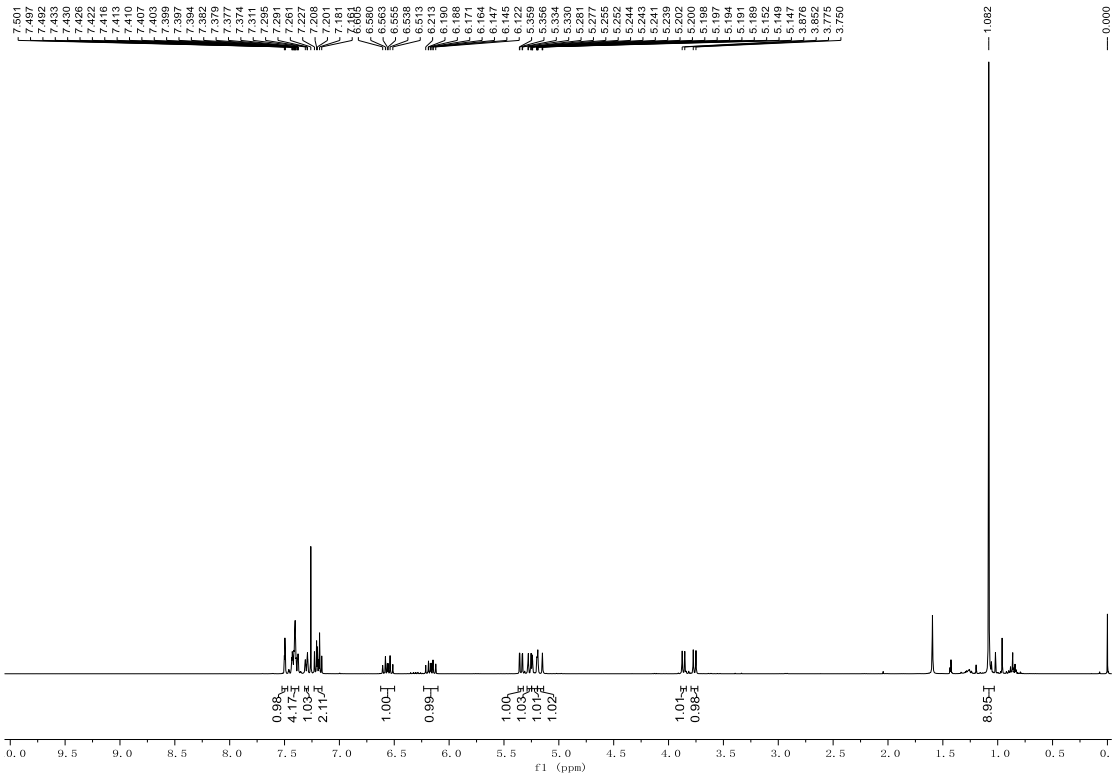

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

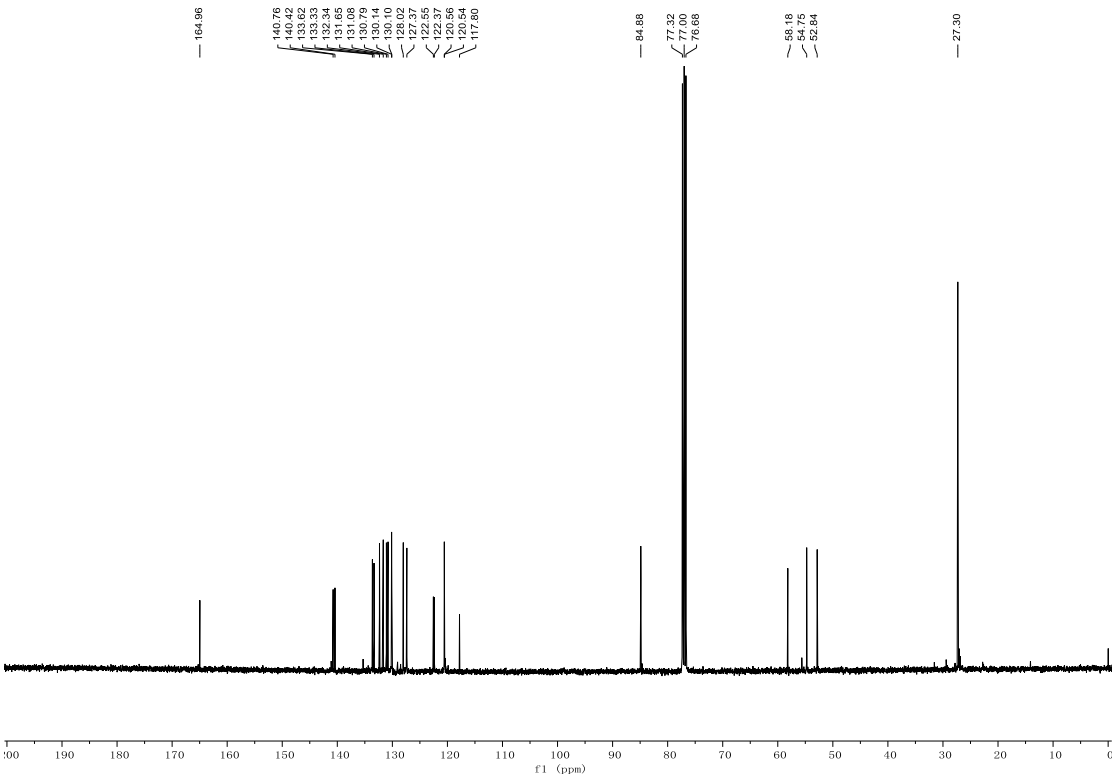
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.977 MF    0.1841 1.38062e4  1250.17249 100.0000

    Totals :                  1.38062e4  1250.17249
```



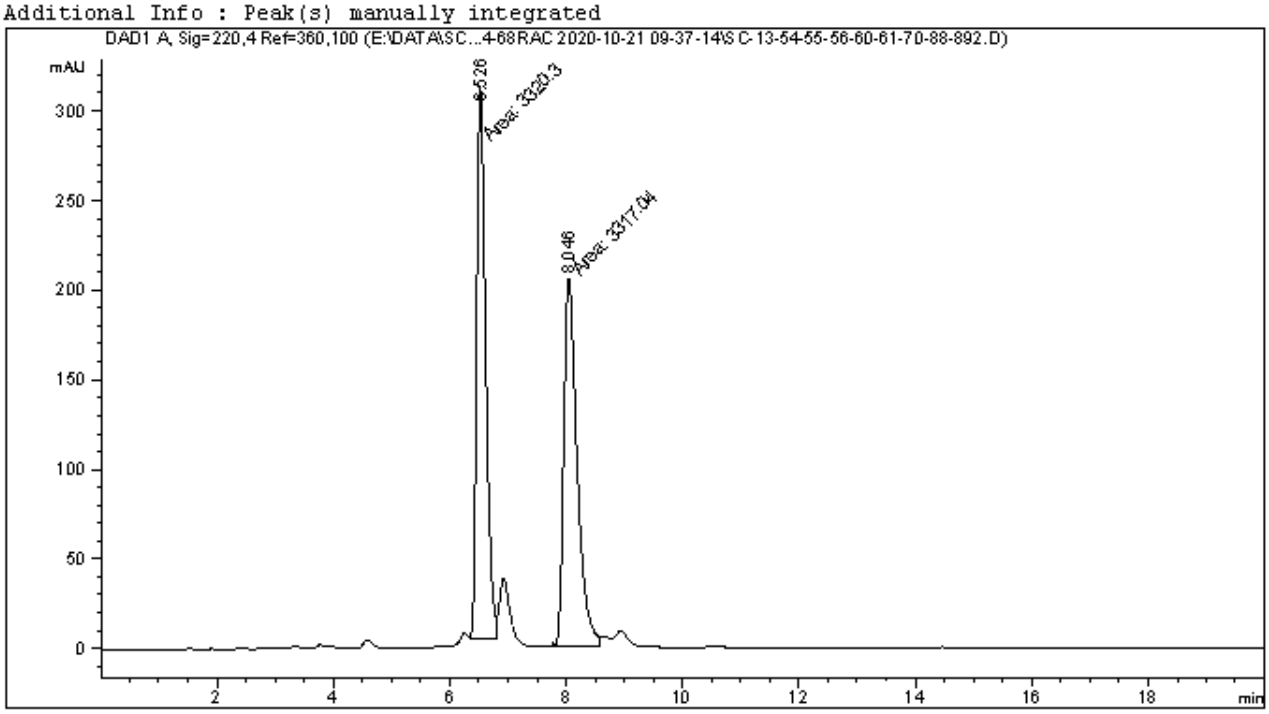
7j





Data File E:\DATA\SC...8-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-892.D
Sample Name: SC-13-56-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260                           Location :   83
    Injection Date  : 10/21/2020 10:21:22 AM              Inj :   1
                                                  Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/21/2020 9:37:14 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 9:49:19 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

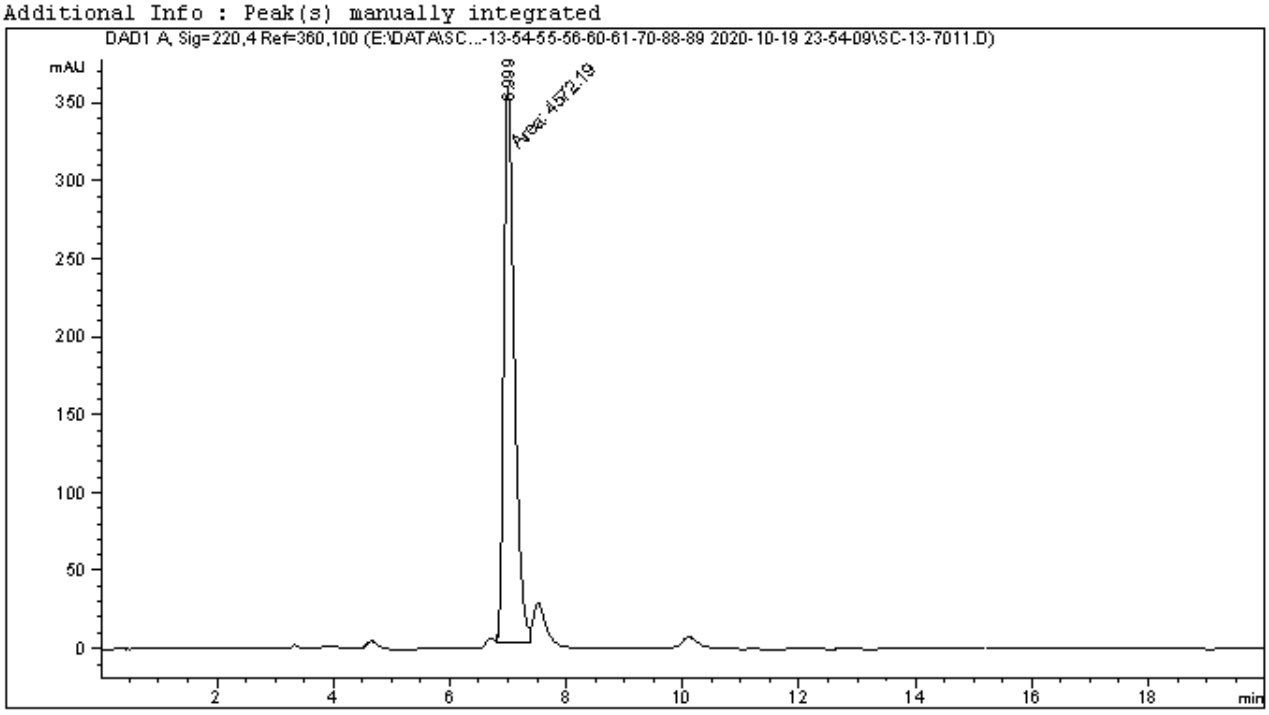

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.526 MM    0.1798 3320.29688  307.72296  50.0245
       2   8.046 MM    0.2691 3317.03979  205.41220  49.9755

    Totals :                   6637.33667  513.13516
```

Data File E:\DATA\SC...8-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-7011.D
Sample Name: SC-13-56B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  12
    Acq. Instrument : 1260                             Location :  79
    Injection Date  : 10/20/2020 4:51:16 AM                Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:31:11 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



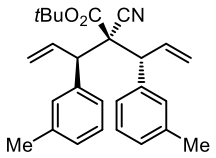

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

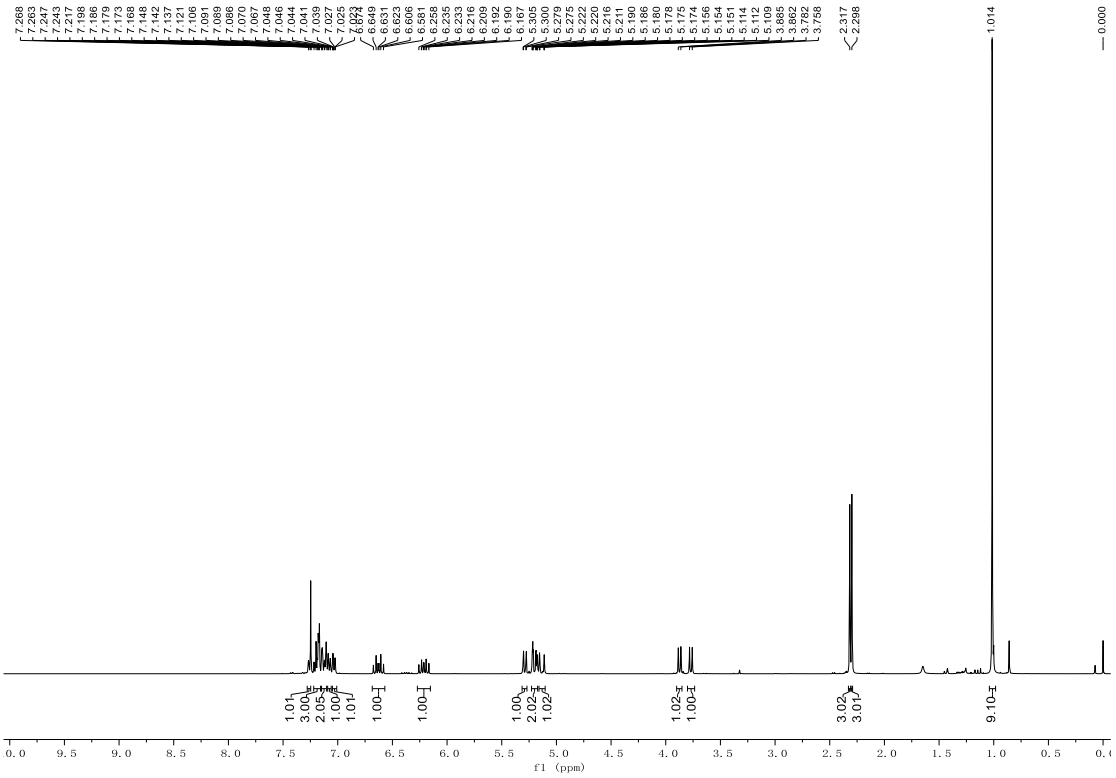

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

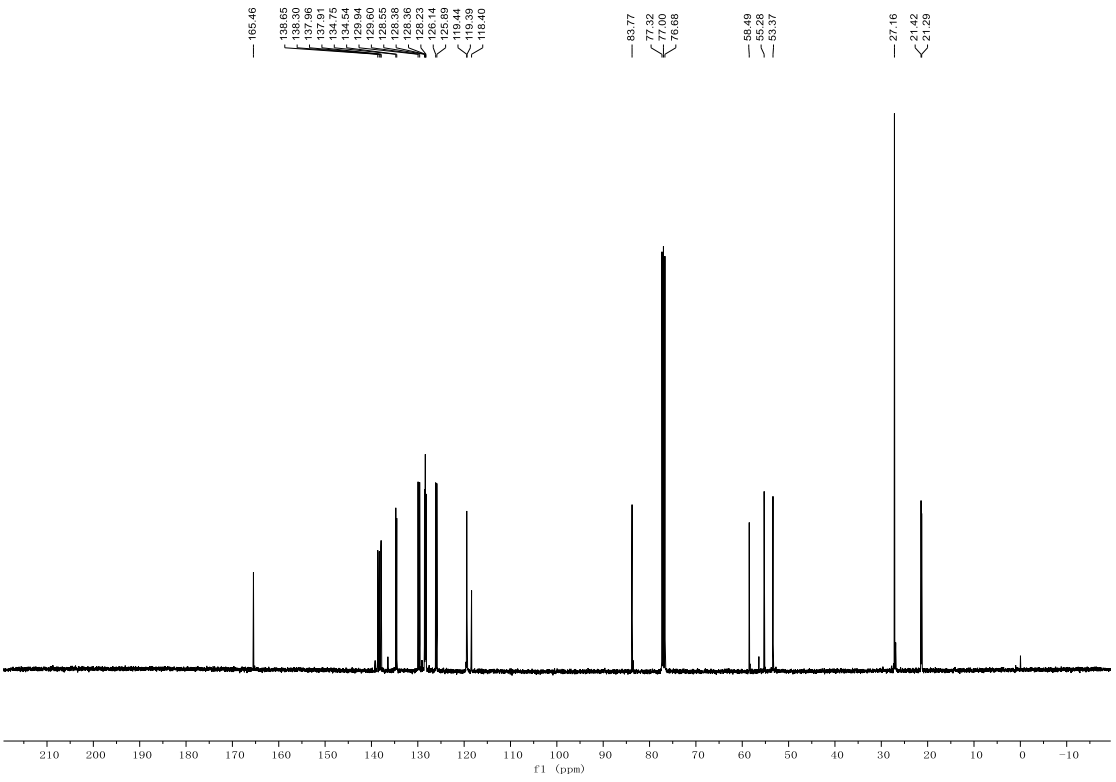
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.999 MM    0.2134 4572.18848  357.04721 100.0000

    Totals :                   4572.18848  357.04721
```



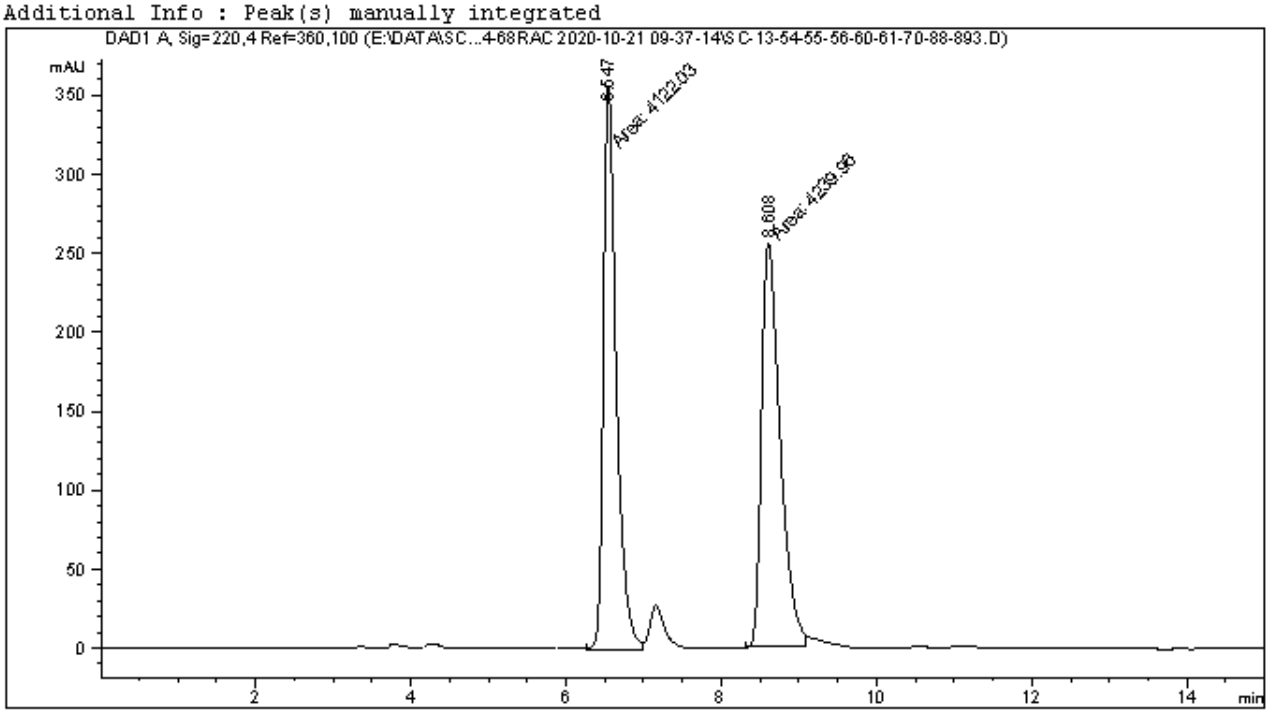
7k





Data File E:\DATA\SC...8-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-893.D
Sample Name: SC-13-60-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260                             Location :   84
    Injection Date  : 10/21/2020 10:42:40 AM               Inj :   1
                                                     Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/21/2020 10:56:52 AM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 9:49:19 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

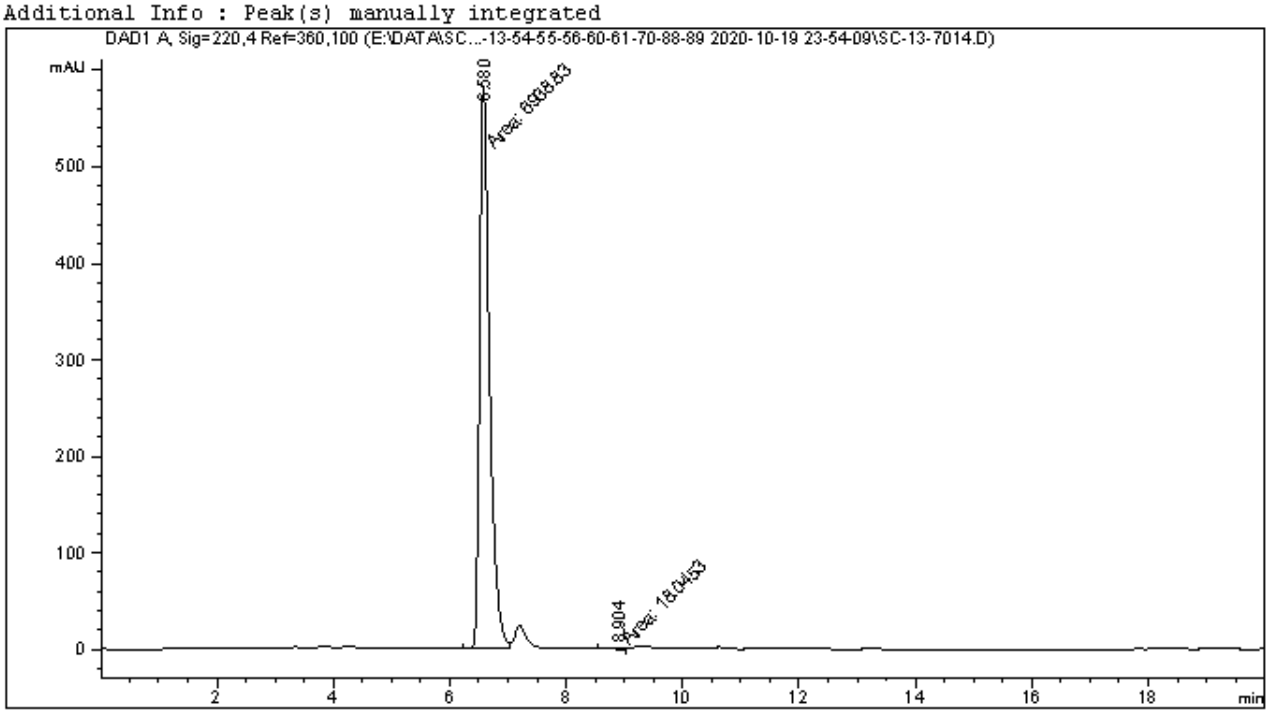
    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.547 MM    0.1927 4122.02734  356.43216  49.2948
       2   8.608 MM    0.2770 4239.95996  255.08609  50.7052
```

Data File E:\DATA\SC...8-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-7014.D
Sample Name: SC-13-60B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  15
    Acq. Instrument : 1260                             Location :   83
    Injection Date  : 10/20/2020 5:55:18 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:35:20 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



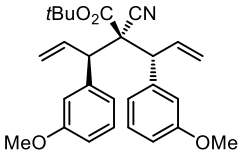

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

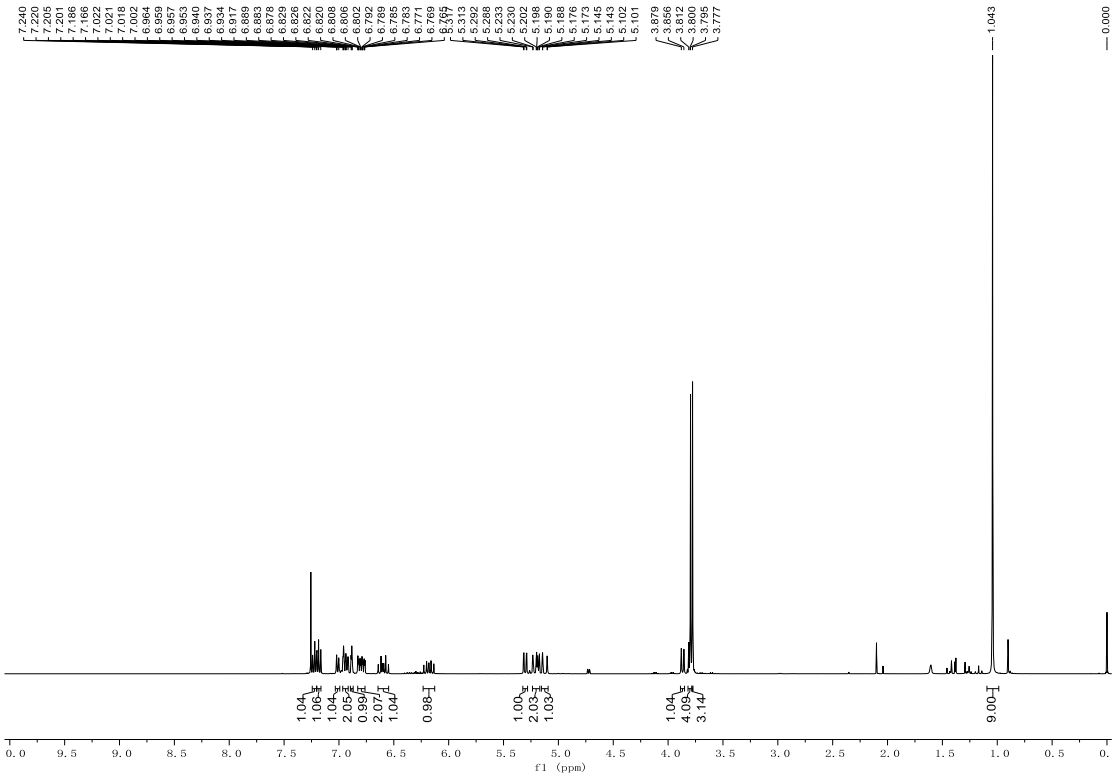

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

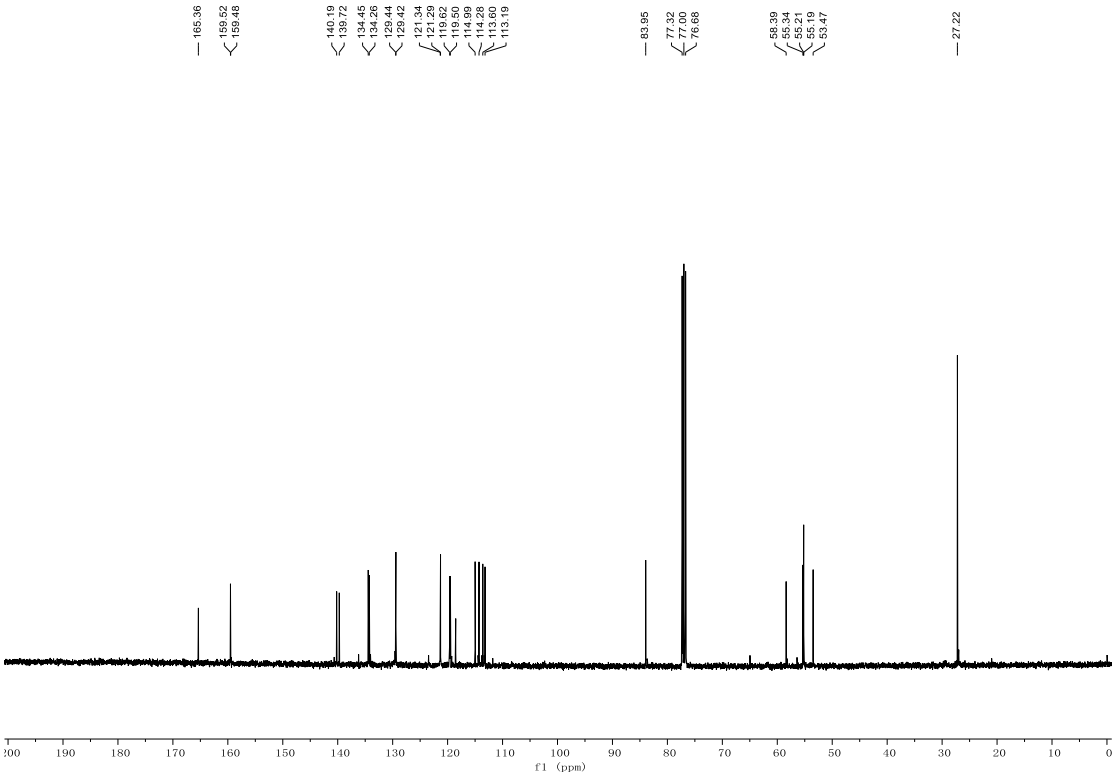
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.580 MF    0.1986 6938.83398  582.45392  99.7406
       2   8.904 MM    0.3685   18.04535 8.16098e-1   0.2594

    Totals :                  6956.87933  583.27002
```



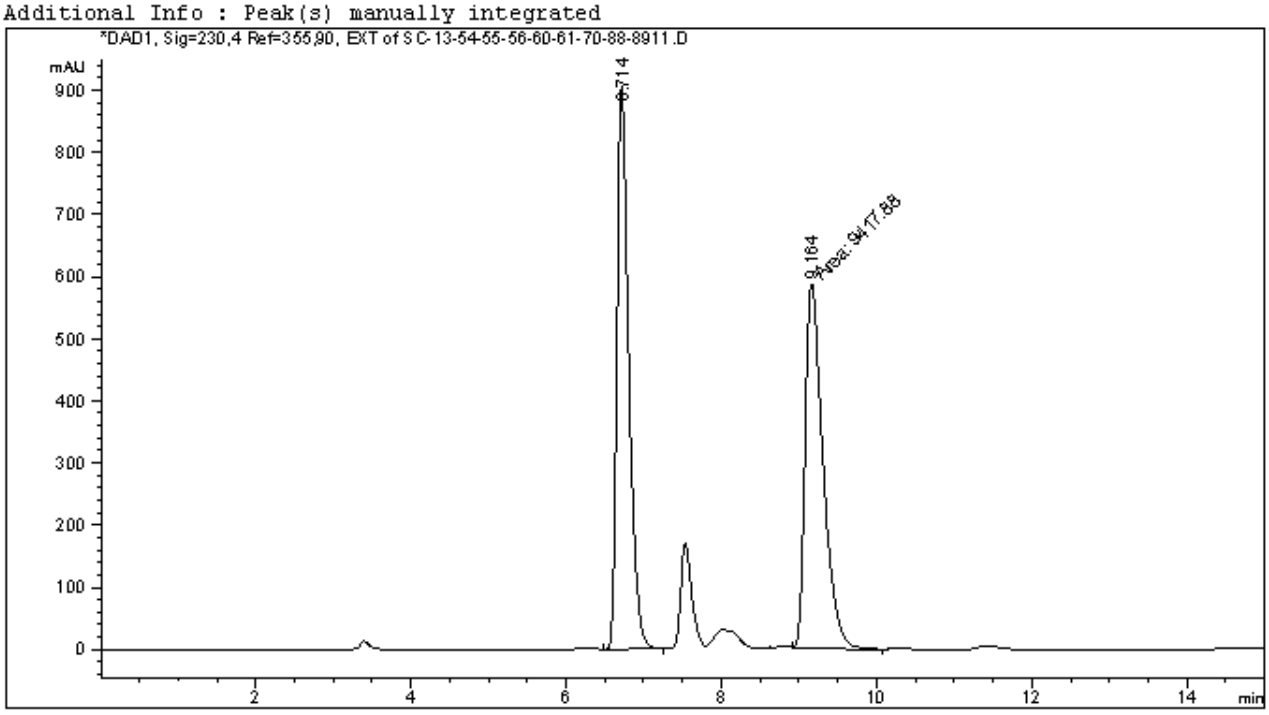
7l





Data File E:\DATA\SC...-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-8911.D
Sample Name: SC-13-89-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  12
    Acq. Instrument : 1260                             Location :  88
    Injection Date  : 10/21/2020 1:38:01 PM                 Inj :  1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-90-10-DAD-1ML-15MIN.M
    Last changed    : 10/21/2020 9:37:15 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-90-10-DAD-1ML-15MIN.M (Sequence Method)
    Last changed    : 4/5/2021 10:10:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

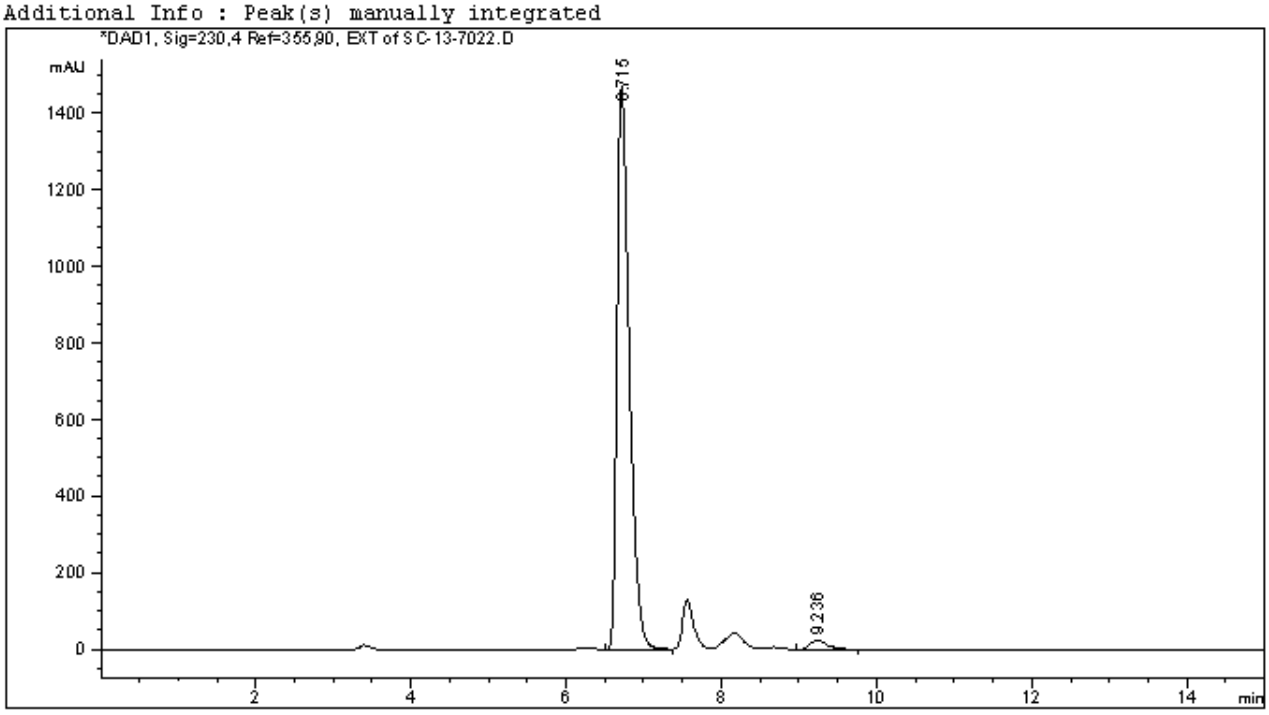

    Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.714 BB    0.1581 9551.91406  905.35913  50.3533
       2   9.164 FM    0.2671 9417.87891  587.76190  49.6467

    Totals :                  1.89698e4  1493.12103
```

Data File E:\DATA\SC...8-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-7022.D
Sample Name: SC-13-89B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  23
    Acq. Instrument : 1260                             Location :  97
    Injection Date  : 10/20/2020 8:26:06 AM                Inj :  1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-90-10-DAD-1ML-15MIN.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-90-10-DAD-1ML-15MIN.M (Sequence Method)
    Last changed    : 4/7/2021 5:48:47 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



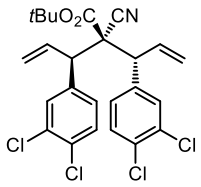

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

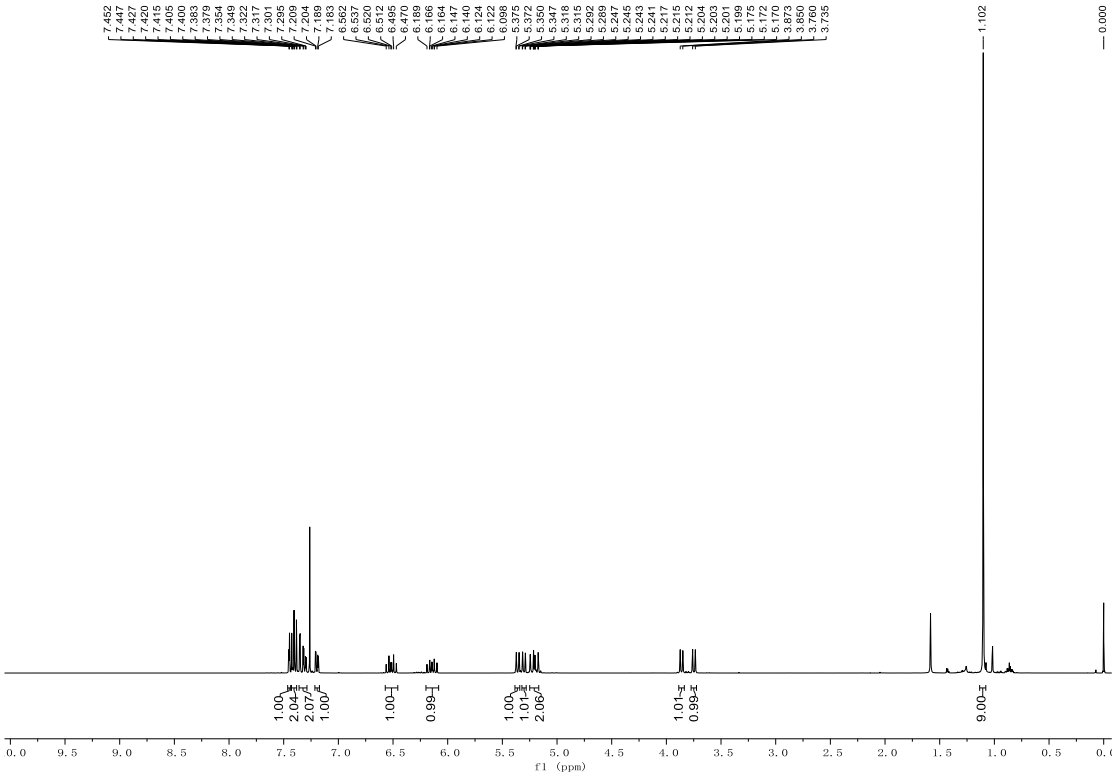

    Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

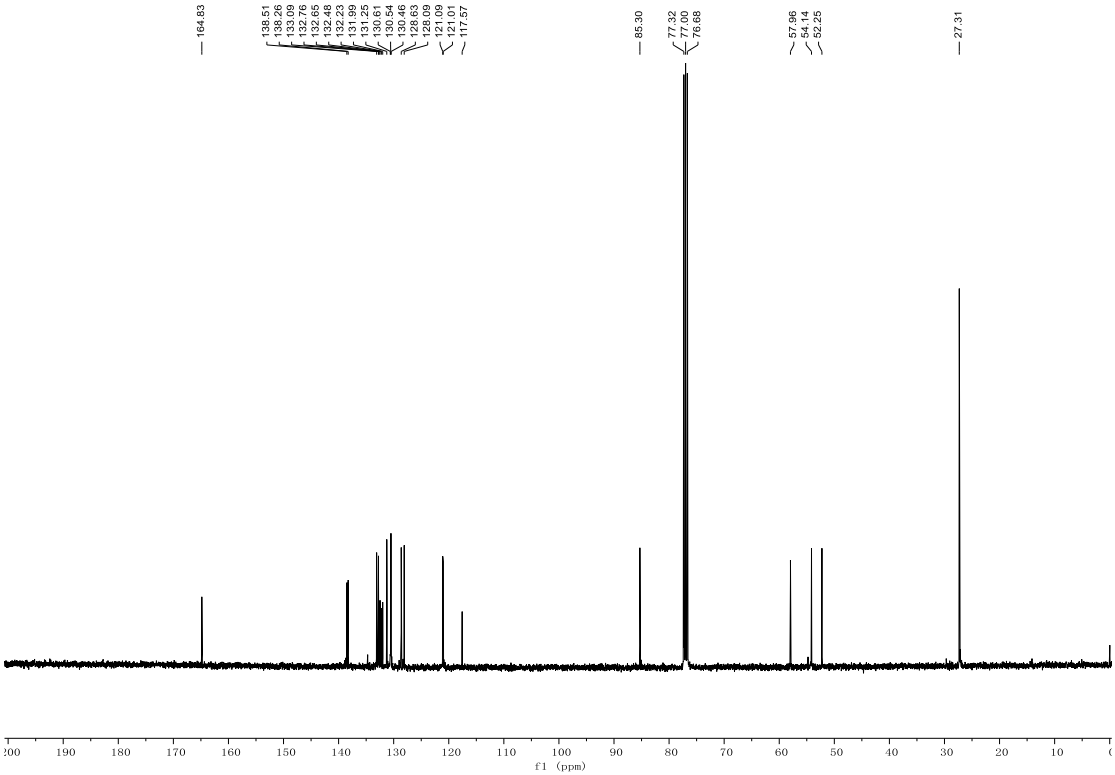
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.715 BB    0.1645 1.61862e4  1470.06201  97.8054
       2   9.236 BB    0.2234  363.18506   24.30026   2.1946

    Totals :                  1.65493e4  1494.36227
```


tBuO2C
CN
Cl
Cl
Cl
Cl

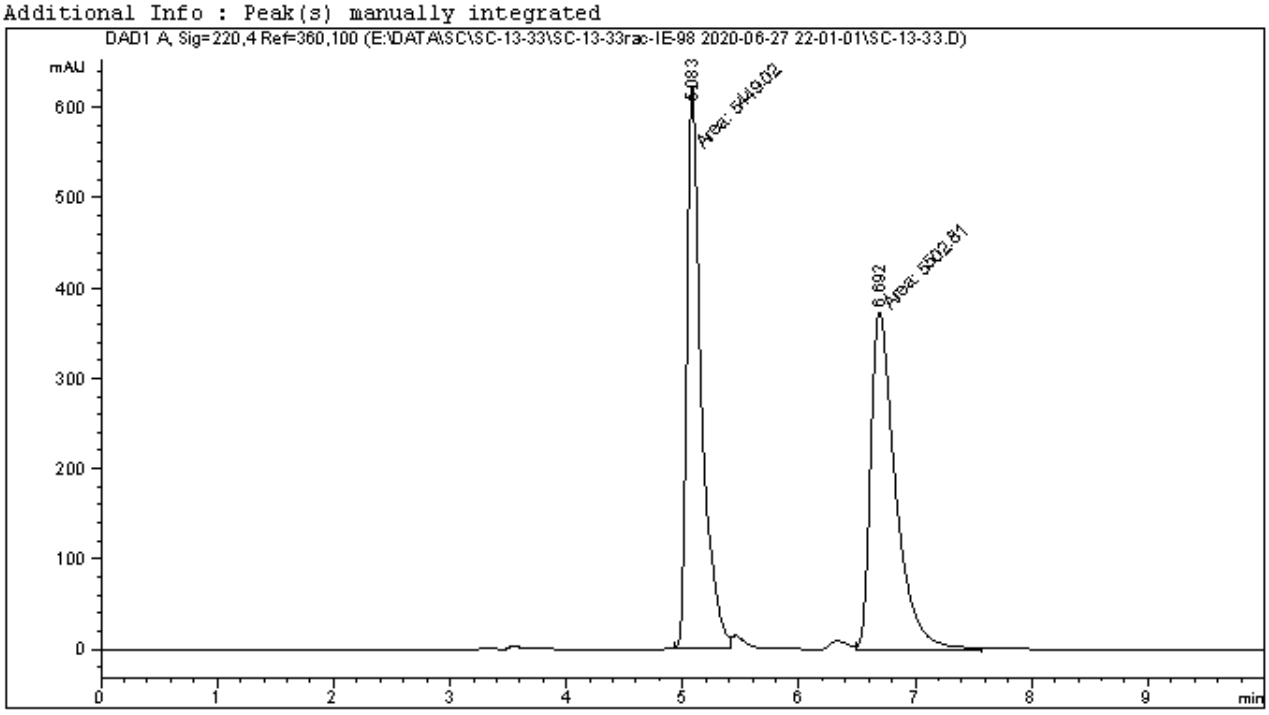
7m


7.452
7.447
7.427
7.420
7.415
7.405
7.400
7.383
7.379
7.354
7.349
7.322
7.317
7.301
7.295
7.209
7.204
7.189
7.183
6.562
6.537
6.520
6.512
6.495
6.470
6.189
6.166
6.164
6.147
6.140
6.124
6.122
6.098
5.375
5.372
5.350
5.347
5.318
5.315
5.292
5.289
5.247
5.245
5.243
5.241
5.217
5.215
5.212
5.204
5.203
5.201
5.199
5.175
5.172
5.170
3.873
3.855
3.760
3.735
1.102
0.000
1.00
2.04
2.07
1.00
1.00
0.99
1.00
1.01
2.06
1.01
0.99
9.00
f1 (ppm)


164.83
138.51
138.26
133.09
132.76
132.65
132.48
132.23
131.99
131.25
130.61
130.54
130.46
128.63
128.09
121.09
121.01
117.57
85.30
77.32
77.00
76.68
57.96
54.14
52.25
27.31
f1 (ppm)

Data File E:\DATA\SC\SC-13-33\SC-13-33rac-IE-98 2020-06-27 22-01-01\SC-13-33.D
Sample Name: SC-13-33Rac

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   92
    Injection Date  : 6/27/2020 10:02:23 PM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-33\SC-13-33rac-IE-98 2020-06-27 22-01-01\SC-4-IE-98-2-DAD-
                      1ML-20MIN-2UL.M
    Last changed    : 6/27/2020 10:01:01 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-33\SC-13-33rac-IE-98 2020-06-27 22-01-01\SC-4-IE-98-2-DAD-
                      1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/5/2021 9:35:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

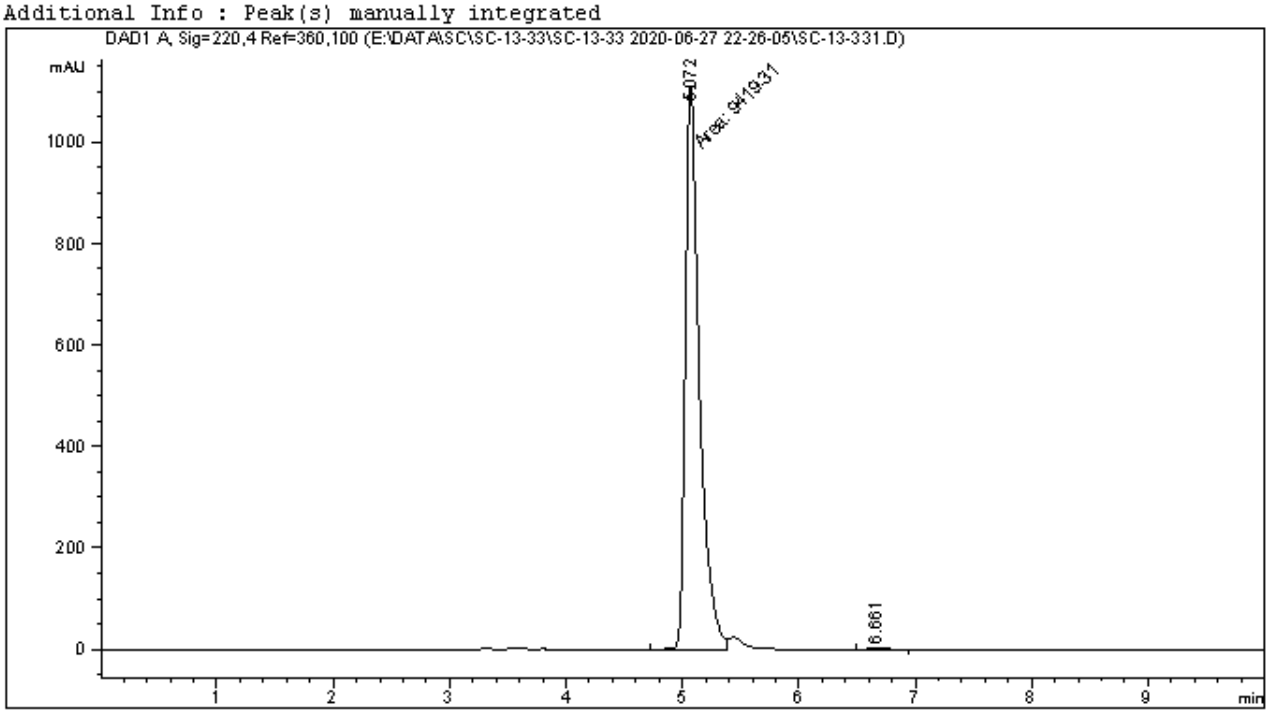

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.083 MM    0.1459 5449.01563  622.31415  49.7544
       2   6.692 MM    0.2461 5502.81201  372.69318  50.2456

    Totals :                  1.09518e4   995.00732
```

Data File E:\DATA\SC\SC-13-33\SC-13-33 2020-06-27 22-26-05\SC-13-331.D
Sample Name: SC-13-33B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260                             Location :   94
    Injection Date  : 6/27/2020 10:38:55 PM                Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-33\SC-13-33 2020-06-27 22-26-05\SC-4-IE-98-2-DAD-1ML-10MIN
                      -2UL.M
    Last changed    : 6/27/2020 10:26:05 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-33\SC-13-33 2020-06-27 22-26-05\SC-4-IE-98-2-DAD-1ML-10MIN
                      -2UL.M (Sequence Method)
    Last changed    : 4/5/2021 9:39:01 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



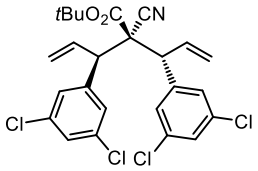

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

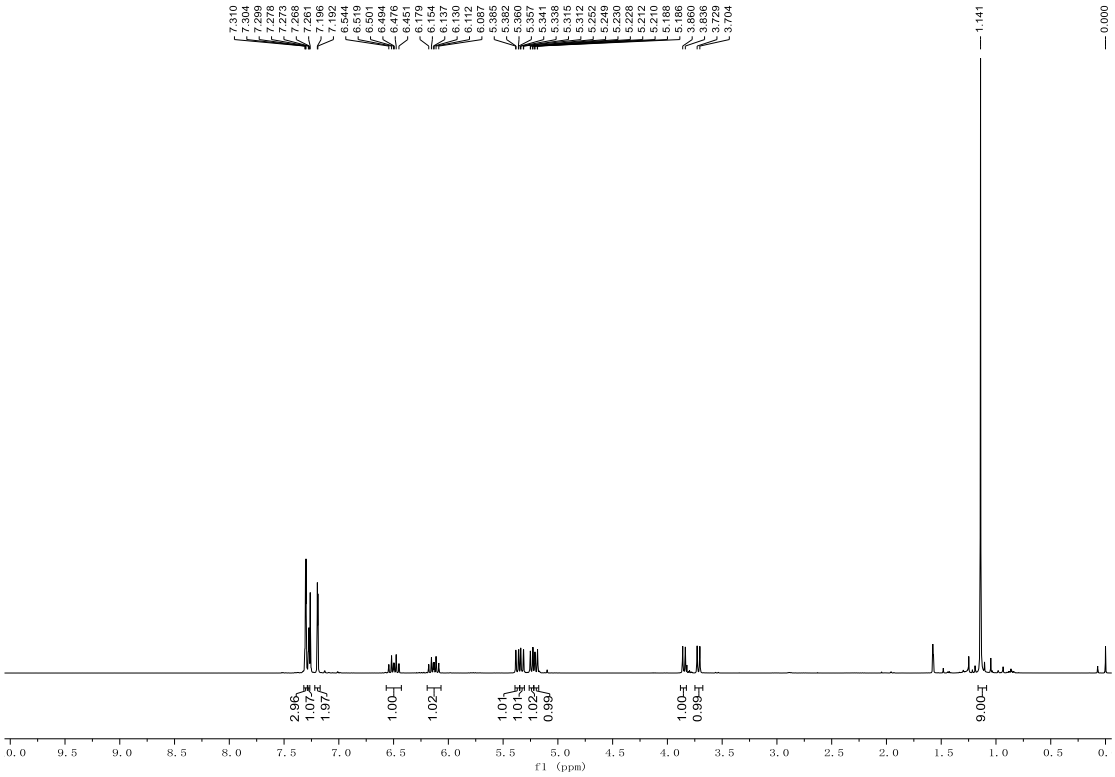

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

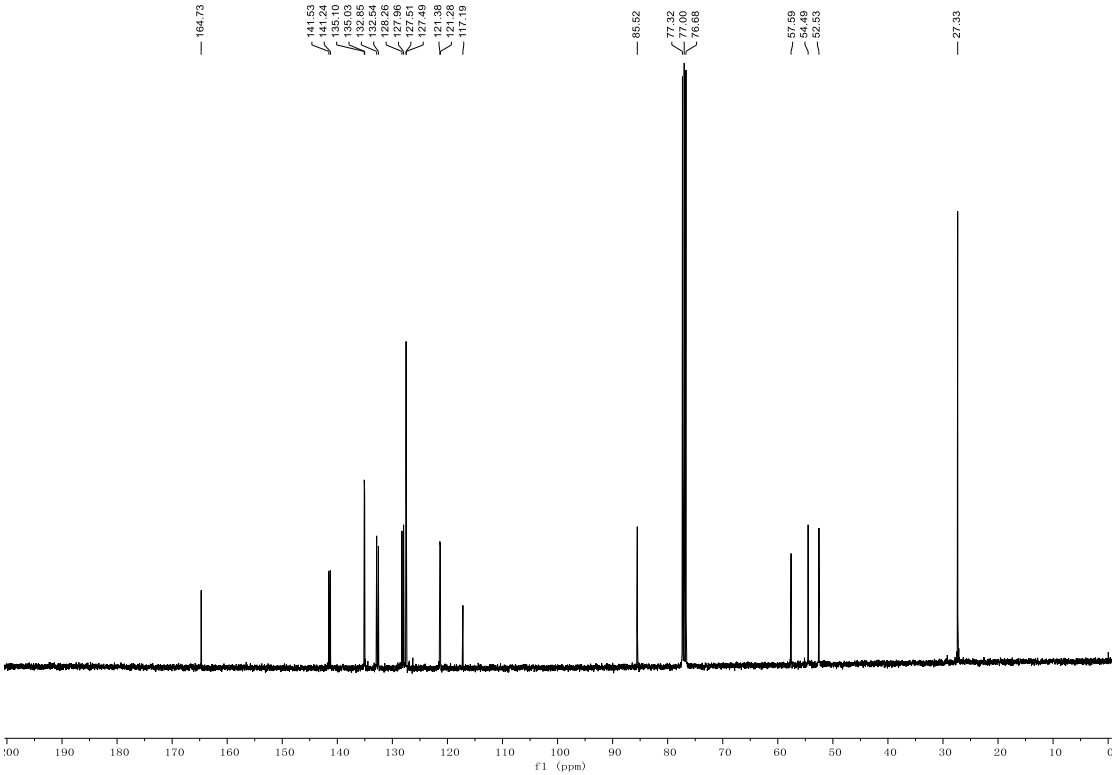
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.072 MF    0.1414 9419.30957 1110.15784  99.8016
       2   6.661 BB    0.1508   18.72850    1.51989   0.1984

    Totals :                  9438.03807 1111.67772
```


tBuO2C
CN
Cl
Cl
Cl
Cl

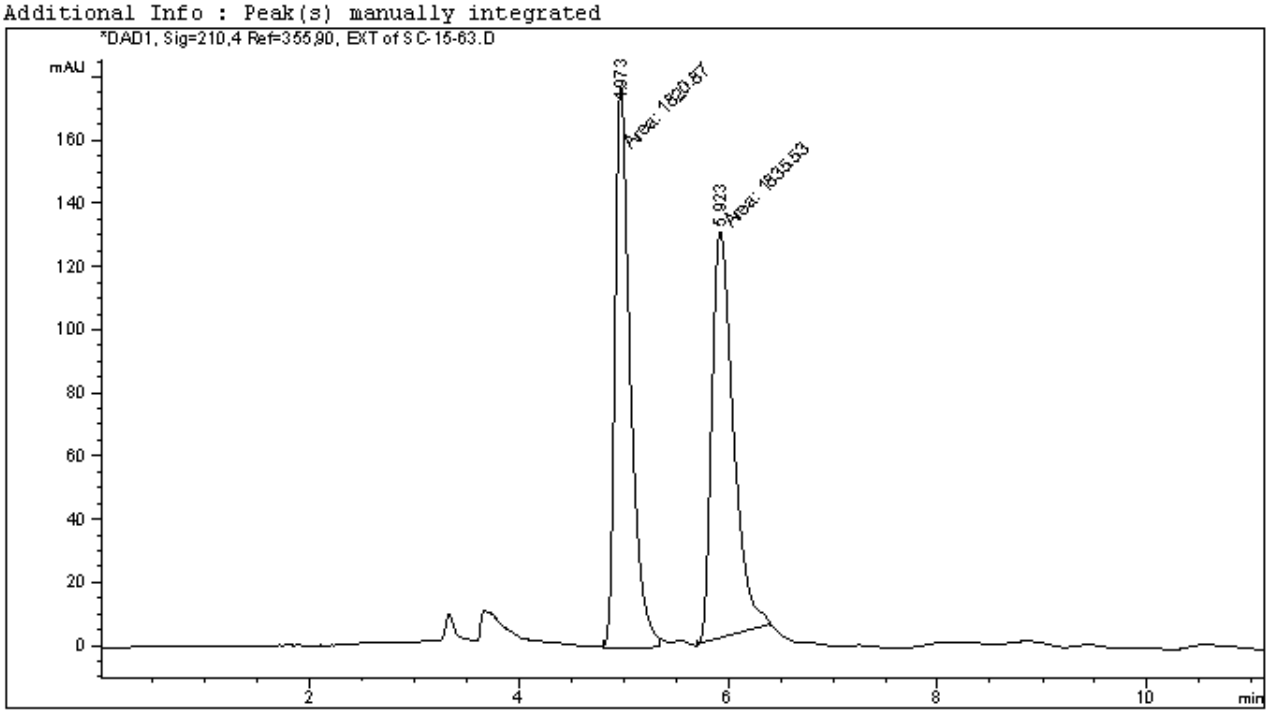
7n


7.310
7.304
7.299
7.278
7.273
7.266
7.261
7.196
7.192
6.544
6.519
6.501
6.494
6.476
6.451
6.179
6.154
6.137
6.130
6.112
6.087
5.365
5.362
5.360
5.357
5.341
5.338
5.315
5.312
5.252
5.249
5.230
5.228
5.212
5.210
5.188
5.186
3.860
3.836
3.729
3.704
1.141
0.000
2.96
1.07
1.97
1.00
1.02
1.01
1.01
1.02
0.99
1.00
0.99
9.00
f1 (ppm)


164.73
141.53
141.24
135.10
135.03
132.85
132.54
128.26
127.96
127.51
127.49
121.38
121.28
117.19
85.52
77.32
77.00
76.68
57.59
54.49
52.53
27.33
f1 (ppm)

Data File E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-15-63.D
Sample Name: SC-15-6-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260                             Location :   97
    Injection Date  : 11/24/2020 9:46:46 AM                 Inj :   1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-4-IE-98-2-DAD-1ML-10MIN-
                      2UL.M
    Last changed    : 11/24/2020 9:44:46 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-4-IE-98-2-DAD-1ML-10MIN-
                      2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:40:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1, Sig=210,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.973 MM    0.1708 1820.86536  177.71632  49.7994
       2   5.923 MM    0.2377 1835.53308  128.68147  50.2006

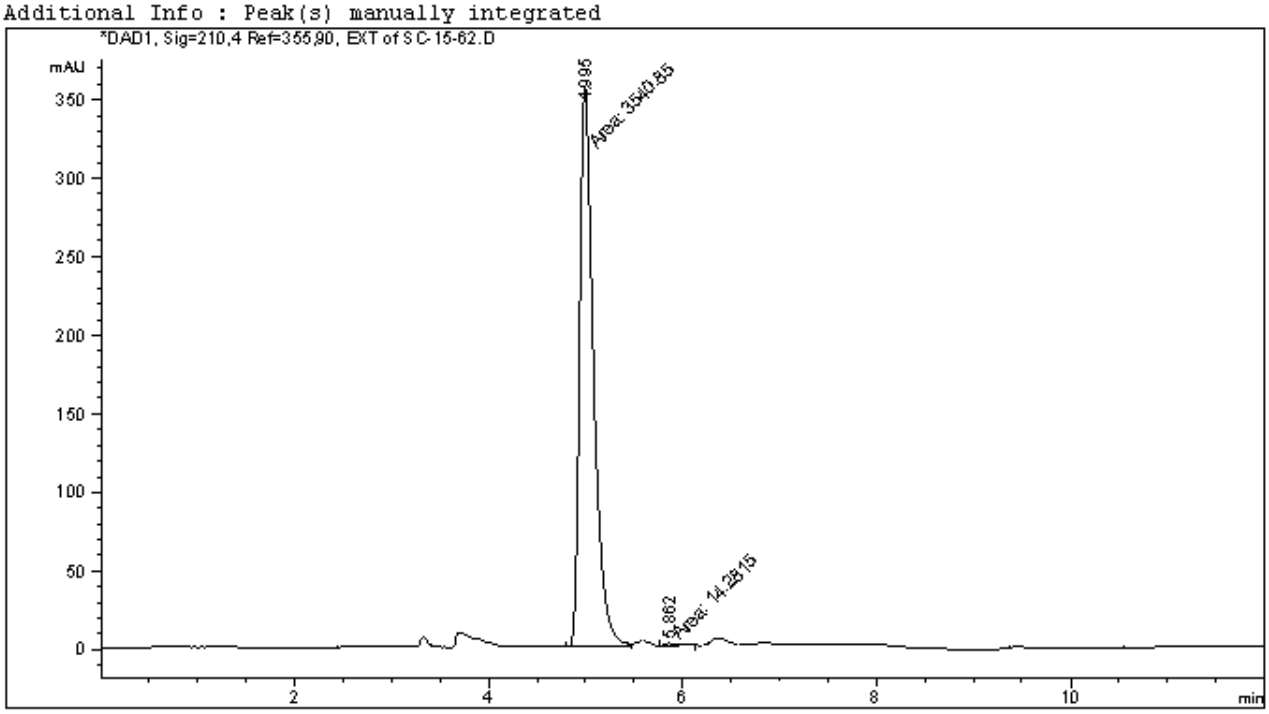
    Totals :                   3656.39844  306.39780
```

Data File E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-15-62.D
Sample Name: SC-15-6B

==========

Acq. Operator	: SYSTEM	Seq. Line :	3
Acq. Instrument	: 1260	Location :	99
Injection Date	: 11/24/2020 9:33:19 AM	Inj :	1
		Inj Volume :	2.000 µl

Acq. Method : E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-4-IE-98-2-DAD-1ML-10MIN-2UL.M
Last changed : 11/24/2020 9:44:46 AM by SYSTEM
(modified after loading)
Analysis Method : E:\DATA\SC\SC-15-6\SC-15-6 2020-11-24 09-08-48\SC-4-IE-98-2-DAD-1ML-10MIN-2UL.M (Sequence Method)
Last changed : 4/7/2021 4:40:37 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



==========

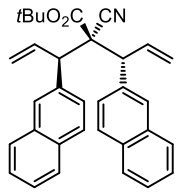
Area Percent Report

==========

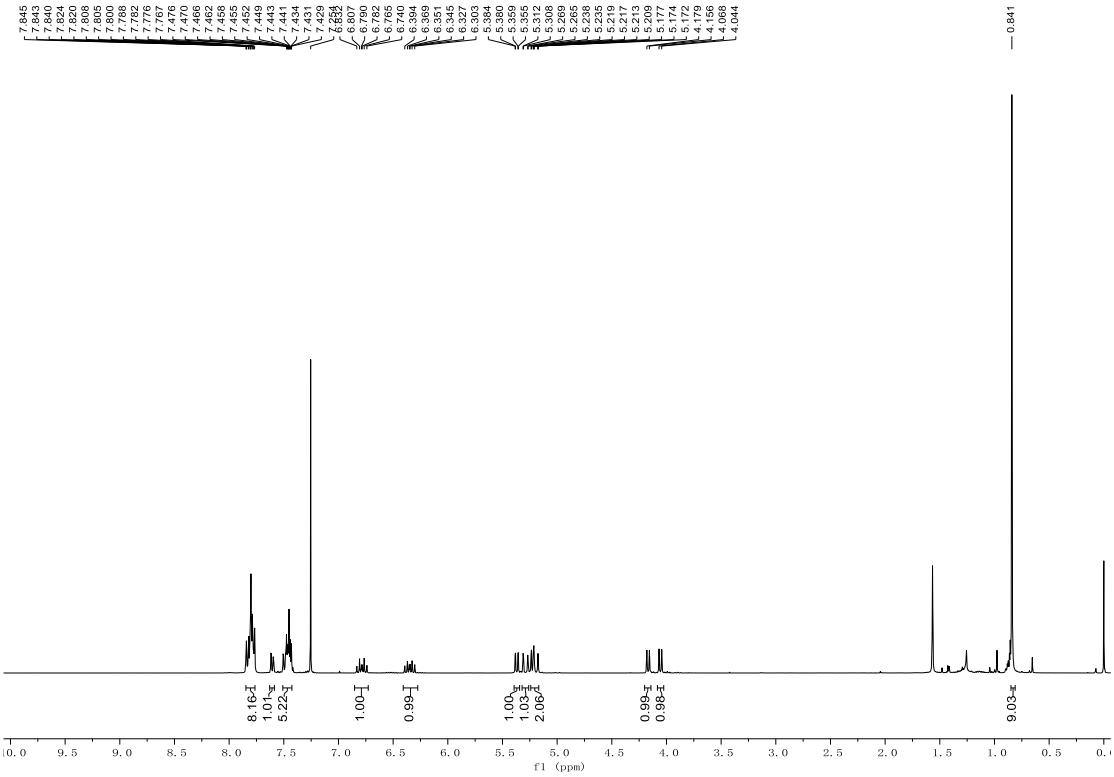
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

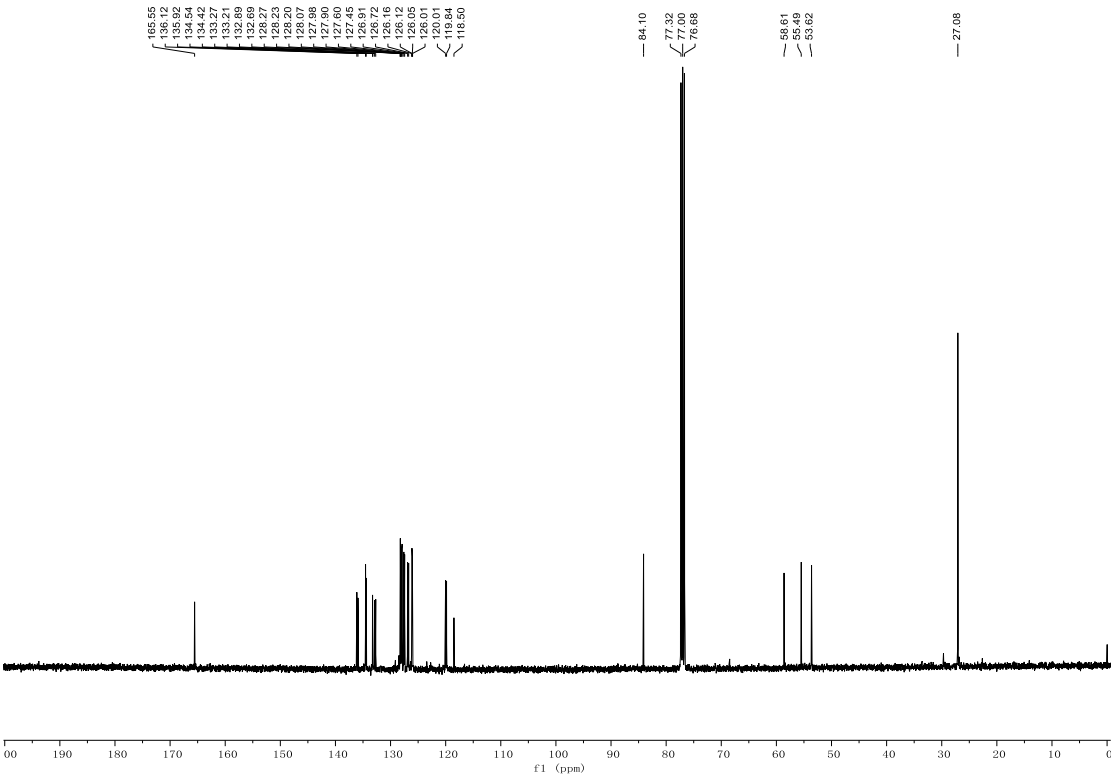
Signal 1: DAD1, Sig=210,4 Ref=355,90, EXT
Signal has been modified after loading from rawdata file!

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.995	MF	0.1655	3540.85229	356.55188	99.5983
2	5.862	MM	0.1810	14.28147	1.31520	0.4017


tBuO2C
CN

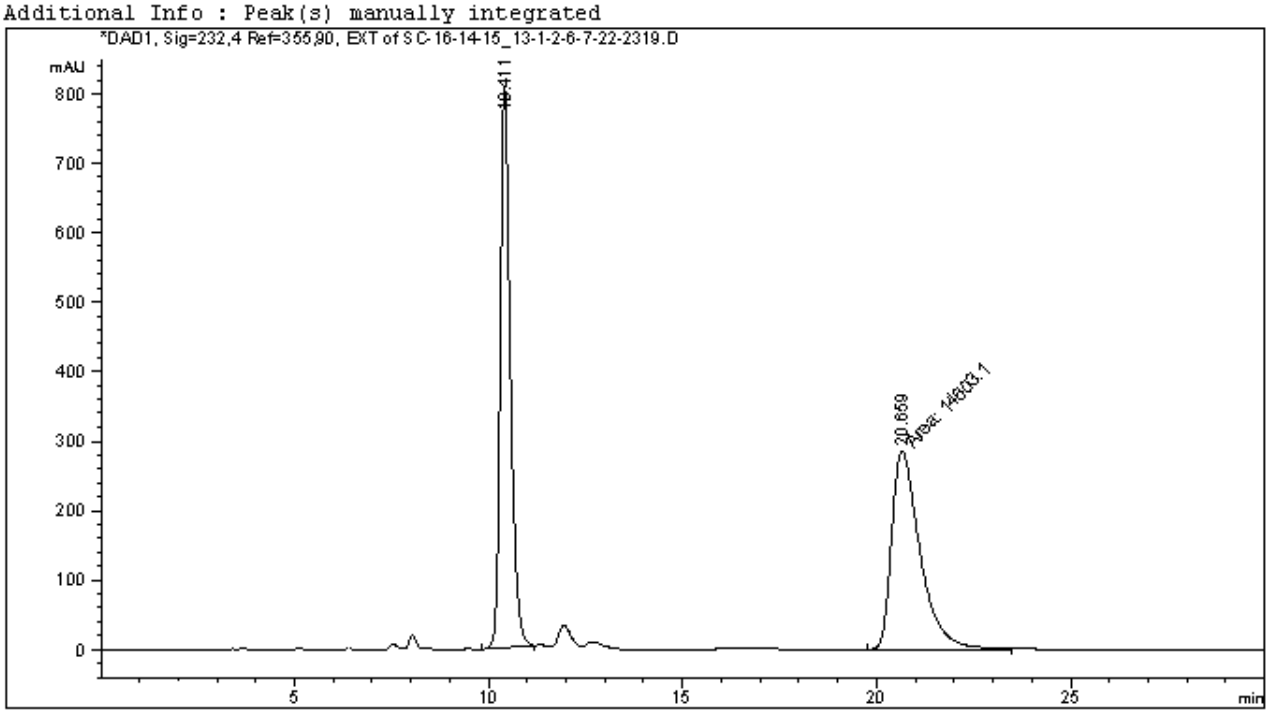
7o


7.845
7.843
7.840
7.824
7.820
7.808
7.805
7.800
7.788
7.782
7.776
7.767
7.476
7.470
7.466
7.462
7.458
7.455
7.452
7.449
7.443
7.441
7.434
7.431
7.429
7.254
6.832
6.807
6.790
6.782
6.765
6.740
6.394
6.369
6.351
6.345
6.327
6.303
5.384
5.380
5.359
5.355
5.312
5.308
5.269
5.265
5.238
5.235
5.219
5.217
5.213
5.209
5.177
5.174
5.172
4.179
4.156
4.068
4.044
0.841
8.16
1.01
5.22
1.00
0.99
1.00
1.03
2.06
0.99
0.98
9.03
f1 (ppm)


165.55
136.12
135.92
134.54
134.42
133.27
133.21
132.89
132.69
128.27
128.23
128.20
128.07
127.98
127.90
127.60
127.45
126.91
126.72
126.16
126.12
126.05
126.01
120.01
119.84
118.50
84.10
77.32
77.00
76.68
58.61
55.49
53.62
27.08
f1 (ppm)

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2319.D
Sample Name: SC-13-6-RAC-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  20
    Acq. Instrument : 1260                              Location :  87
    Injection Date  : 4/6/2021 11:18:11 PM                  Inj :  1
                                                    Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-30MIN-2UL.M
    Last changed    : 4/6/2021 6:00:45 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-30MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:57:35 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

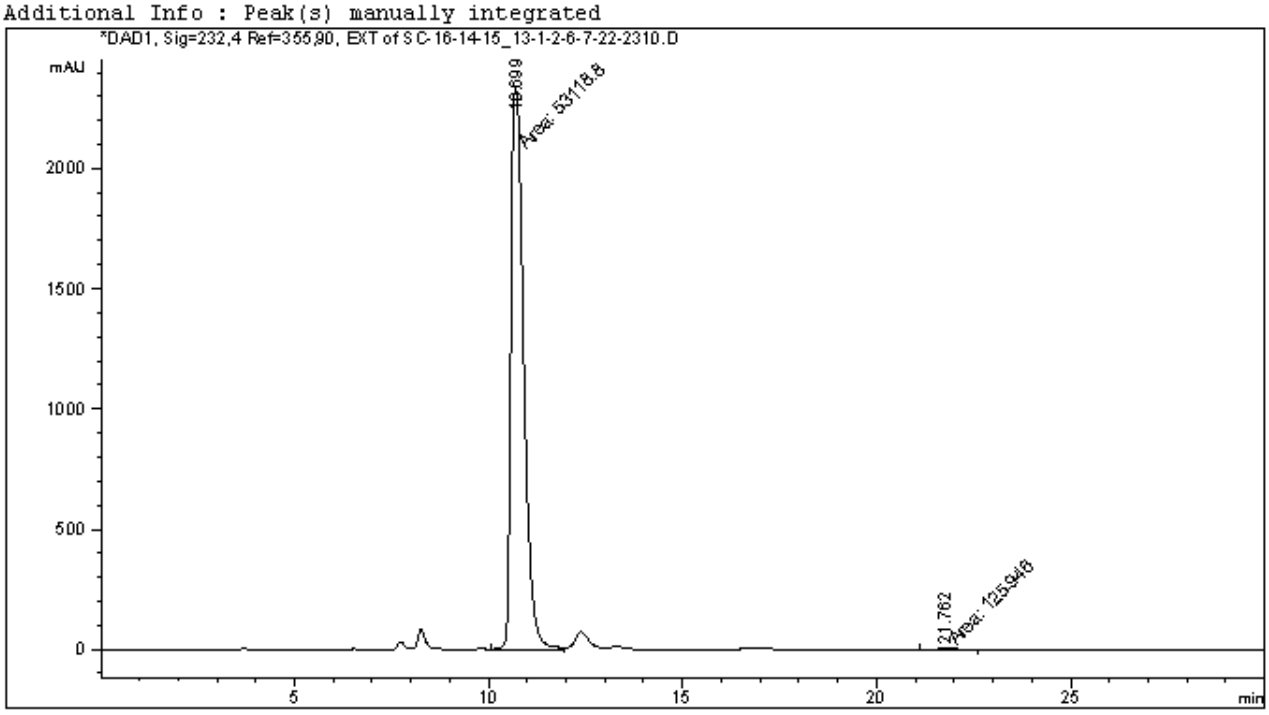

    Signal 1: DAD1, Sig=232,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.411 BB    0.2764 1.47660e4   807.28174  50.2772
       2  20.659 MM    0.8507 1.46031e4   286.10654  49.7228

    Totals :                  2.93691e4  1093.38828
```

Data File E:\DATA\SC...-1-2-6-7-22-23 2021-04-06 18-00-44\SC-16-14-15_13-1-2-6-7-22-2310.D
Sample Name: SC-13-6B

```
    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  11
    Acq. Instrument : 1260                             Location :  90
    Injection Date  : 4/6/2021 8:15:43 PM                  Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-30MIN-2UL.M
    Last changed    : 4/6/2021 6:00:45 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-14-15_13-1-2-6-7-22-23 2021-04-06 18-00-44\SC-4-IE-98-2-
                      DAD-1ML-30MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 4:57:35 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



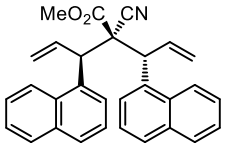

```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

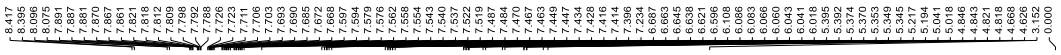

    Signal 1: DAD1, Sig=232,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

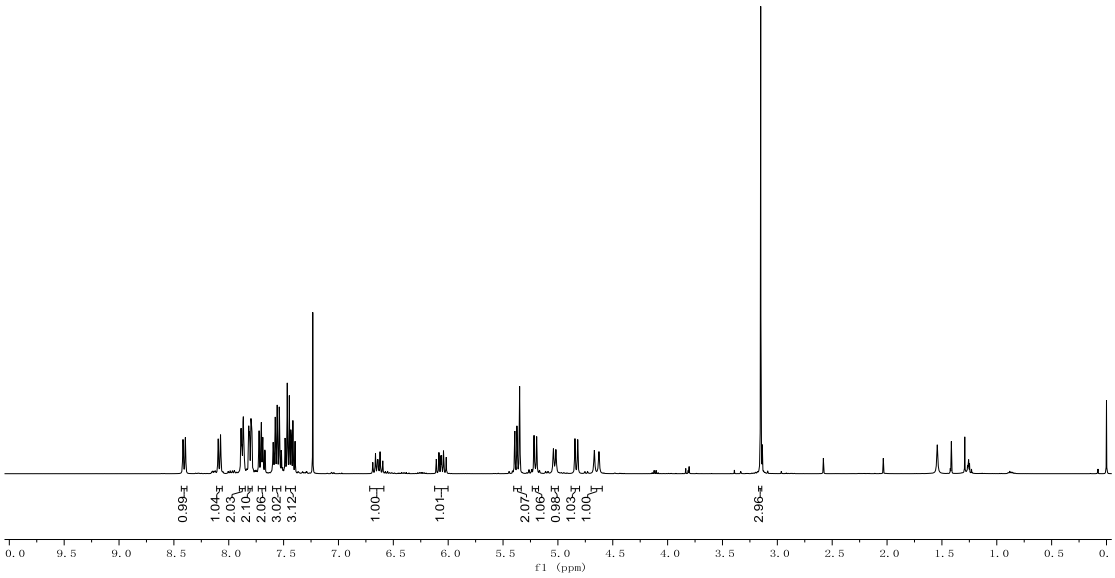
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.699 MF    0.3782 5.31188e4  2340.82568  99.7635
       2  21.762 MM    0.8464  125.94573    2.47996   0.2365

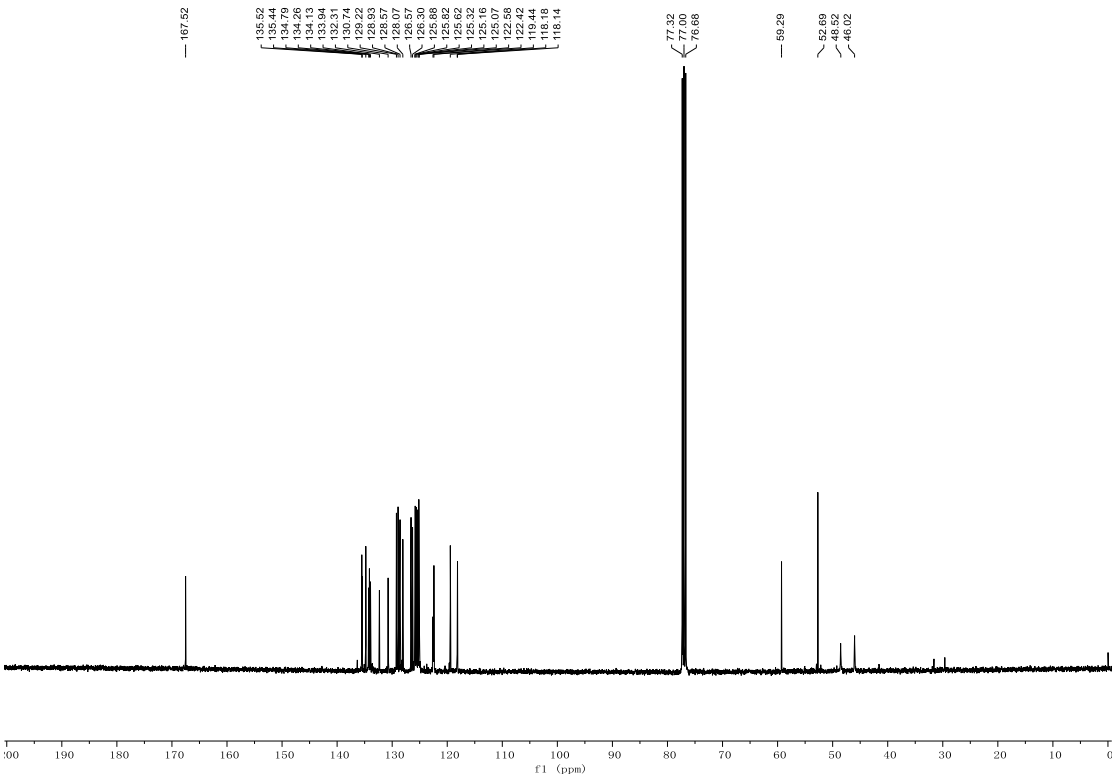
    Totals :                  5.32448e4  2343.30564
```


MeO2C
CN

7p

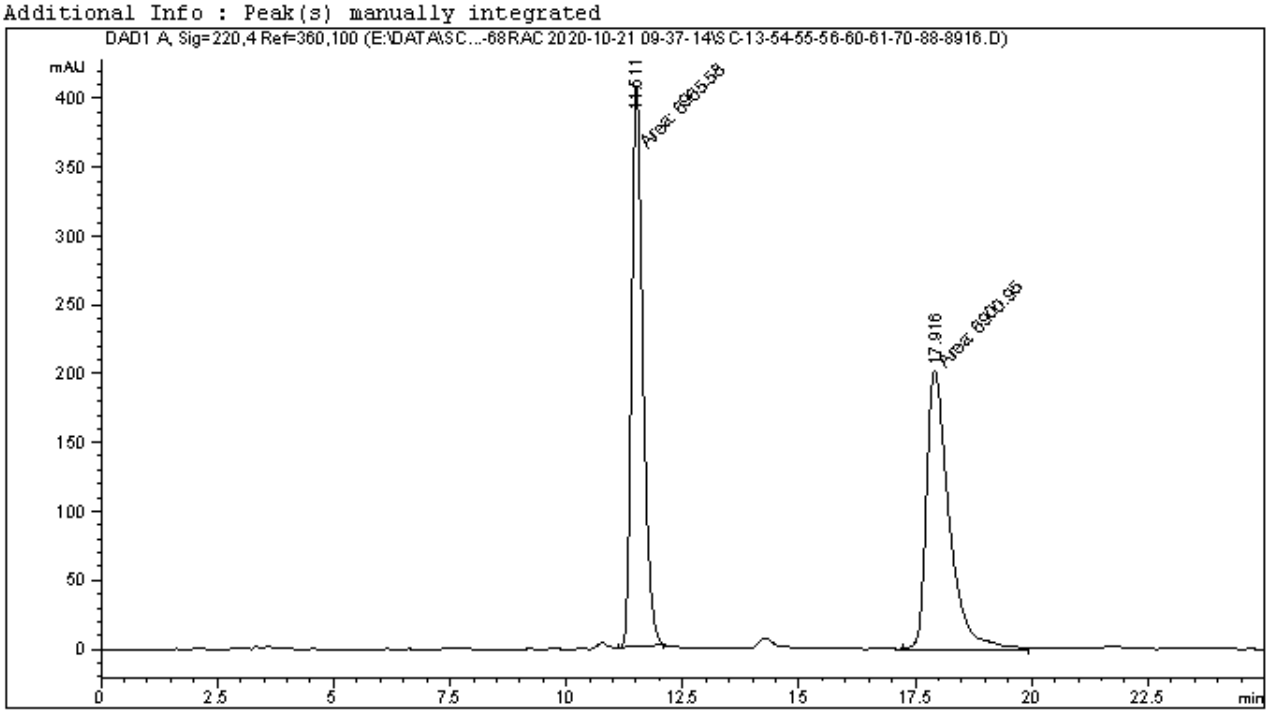



0.99
1.04
2.03
2.10
2.06
3.02
3.12
1.00
1.01
2.07
1.06
0.98
1.03
1.00
2.96
f1 (ppm)


167.52
135.52
135.44
134.79
134.26
134.13
133.94
132.31
130.74
129.22
128.93
128.57
128.07
126.37
126.30
125.88
125.82
125.62
125.32
125.16
125.07
122.58
122.42
118.44
118.18
118.14
77.32
77.00
76.68
59.29
52.69
48.52
46.02
f1 (ppm)

Data File E:\DATA\SC...-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-8916.D
Sample Name: SC-14-68-72-RAC-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :  17
    Acq. Instrument : 1260                             Location :  89
    Injection Date  : 10/21/2020 3:19:17 PM                Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-98-2-DAD-1ML-30MIN-2UL.M
    Last changed    : 10/21/2020 9:37:14 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-98-2-DAD-1ML-30MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 10:15:49 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

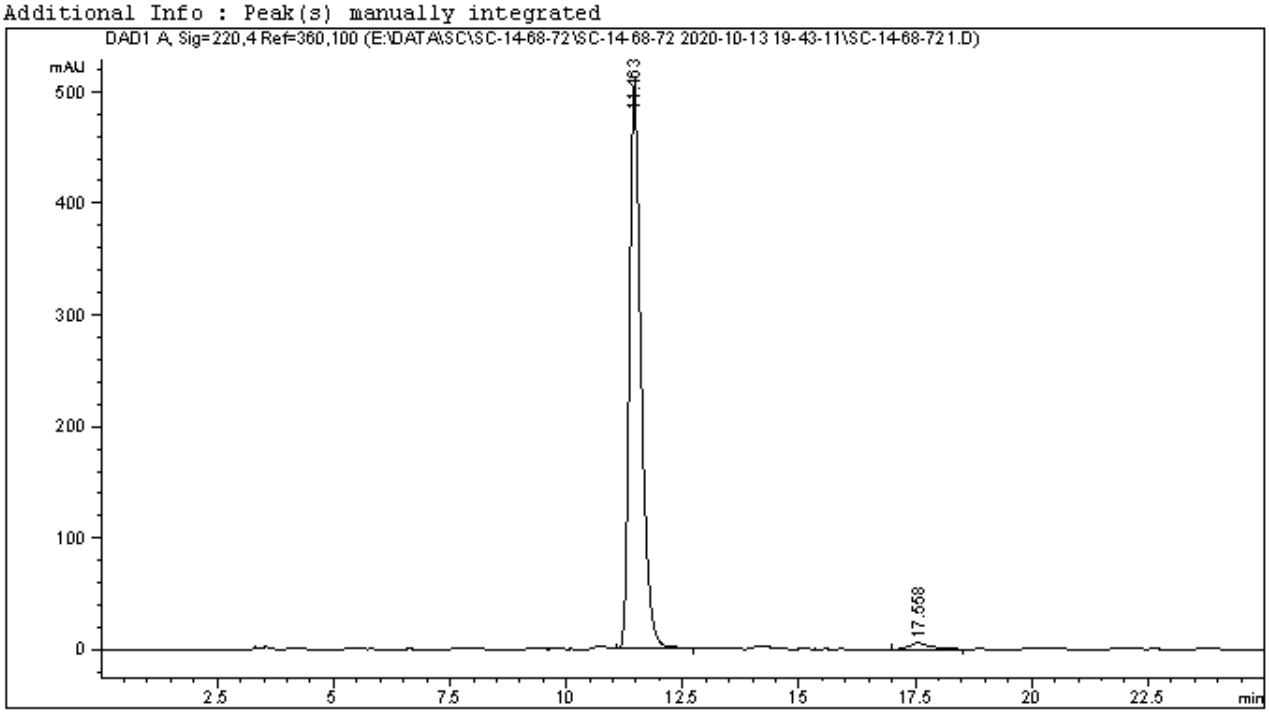

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.511 MM    0.2854 6965.58350  406.71854  50.2330
       2  17.916 MM    0.5670 6900.95313  202.86623  49.7670

    Totals :                  1.38665e4   609.58476
```

Data File E:\DATA\SC\SC-14-68-72\SC-14-68-72 2020-10-13 19-43-11\SC-14-68-721.D
Sample Name: SC-14-72

```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260                           Location :   73
    Injection Date  : 10/13/2020 8:10:59 PM              Inj :   1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-14-68-72\SC-14-68-72 2020-10-13 19-43-11\SC-4-IE-98-2-DAD-1ML
                      -30MIN-2UL.M
    Last changed    : 10/13/2020 8:07:08 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-14-68-72\SC-14-68-72 2020-10-13 19-43-11\SC-4-IE-98-2-DAD-1ML
                      -30MIN-2UL.M (Sequence Method)
    Last changed    : 4/5/2021 10:14:47 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



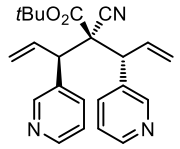

```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

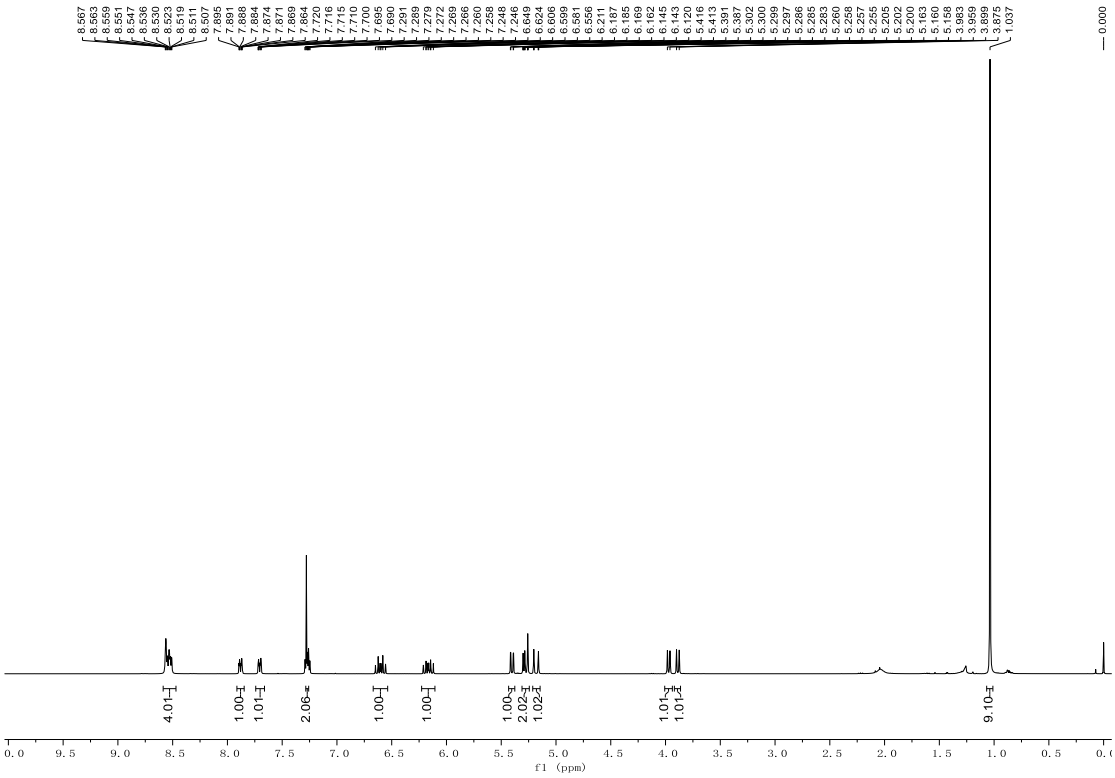

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

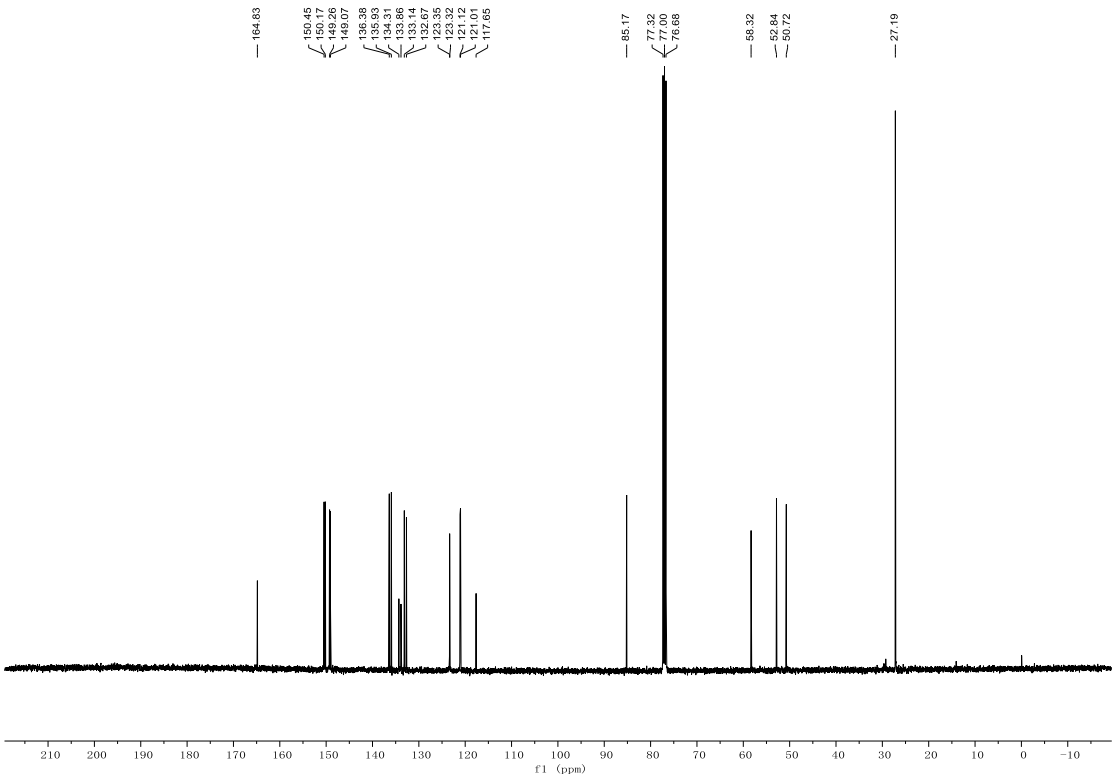
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.463 BB    0.2655 8922.01758  504.00177  98.1937
       2  17.558 BB    0.3642  164.12421    5.37574   1.8063

    Totals :                  9086.14178  509.37751
```


tBuO2C
CN
N
N

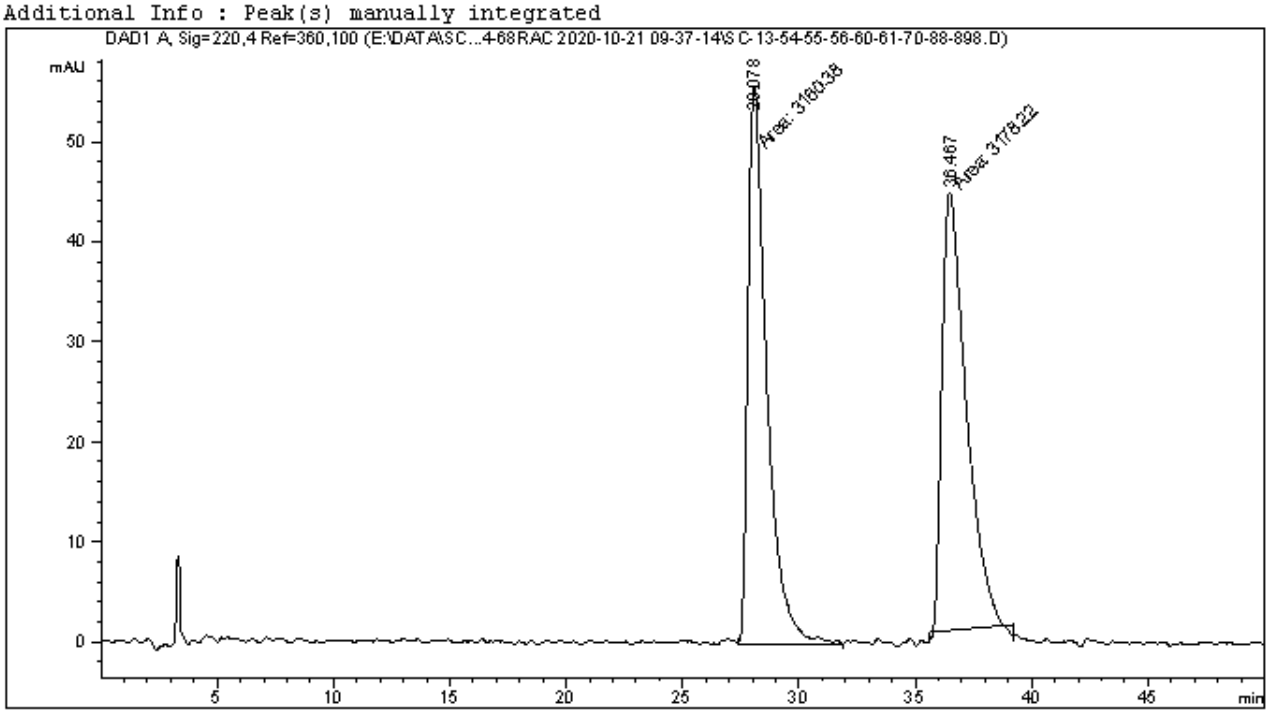
7q


8.567
8.563
8.559
8.551
8.547
8.536
8.530
8.523
8.519
8.511
8.507
7.895
7.891
7.888
7.884
7.874
7.871
7.869
7.864
7.720
7.716
7.715
7.710
7.700
7.695
7.690
7.291
7.289
7.279
7.272
7.269
7.266
7.260
7.258
7.248
7.246
6.649
6.624
6.606
6.599
6.591
6.585
6.211
6.187
6.185
6.169
6.162
6.145
6.143
6.130
5.416
5.413
5.391
5.387
5.302
5.300
5.299
5.297
5.286
5.285
5.283
5.260
5.258
5.257
5.255
5.205
5.202
5.200
5.163
5.160
5.158
3.983
3.959
3.899
3.875
1.037
0.000
4.01
1.00
1.01
2.06
1.00
1.00
1.00
2.02
1.02
1.01
1.01
9.10
f1 (ppm)


164.83
150.45
150.17
149.26
149.07
136.38
135.93
134.31
133.86
133.14
132.67
123.35
123.32
121.12
121.01
117.65
85.17
77.32
77.00
76.68
58.32
52.84
50.72
27.19
f1 (ppm)

Data File E:\DATA\SC...8-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-898.D
Sample Name: SC-13-70-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   9
    Acq. Instrument : 1260                             Location :   86
    Injection Date  : 10/21/2020 12:14:05 PM               Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-80-20-DAD-1ML-50min.M
    Last changed    : 10/21/2020 9:37:15 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-80-20-DAD-1ML-50min.M (Sequence Method)
    Last changed    : 4/5/2021 10:04:04 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

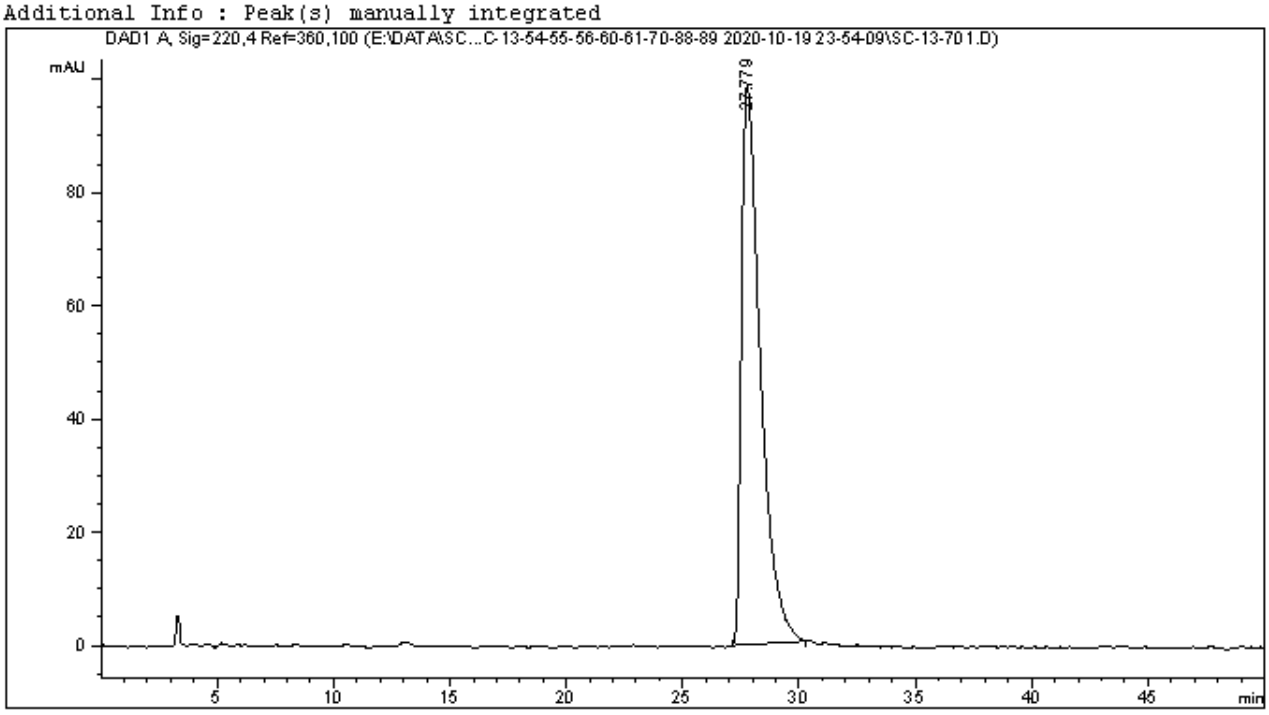

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.078 MM    0.9449 3160.38208   55.74611  49.8593
       2  36.467 MM    1.2106 3178.21851   43.75503  50.1407

    Totals :                  6338.60059   99.50114
```

Data File E:\DATA\SC...88-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-701.D
Sample Name: SC-13-70B

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260                           Location :   89
    Injection Date  : 10/20/2020 12:47:14 AM              Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-80-20-DAD-1ML-50min.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-80-20-DAD-1ML-50min.M (Sequence Method)
    Last changed    : 4/7/2021 5:40:09 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



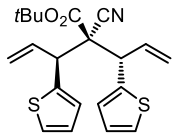

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

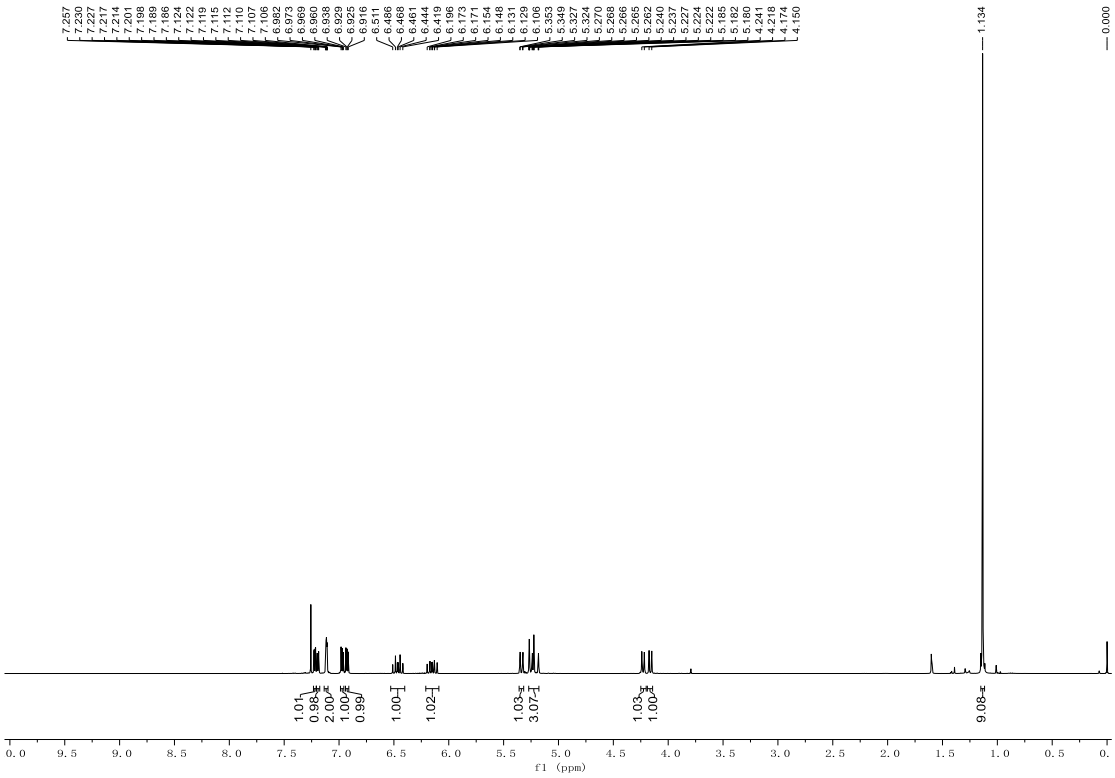

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

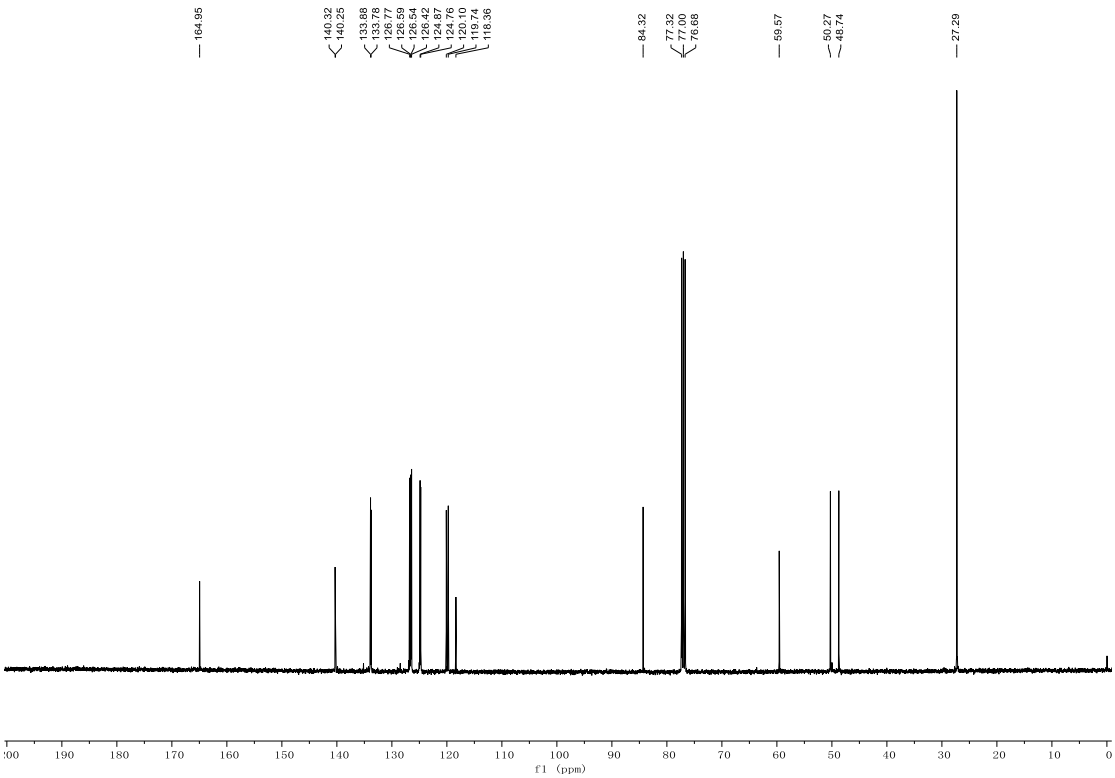
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.779 BB    0.7773 5584.47217   98.52300 100.0000

    Totals :                  5584.47217   98.52300
```


tBuO2C
CN
S
S

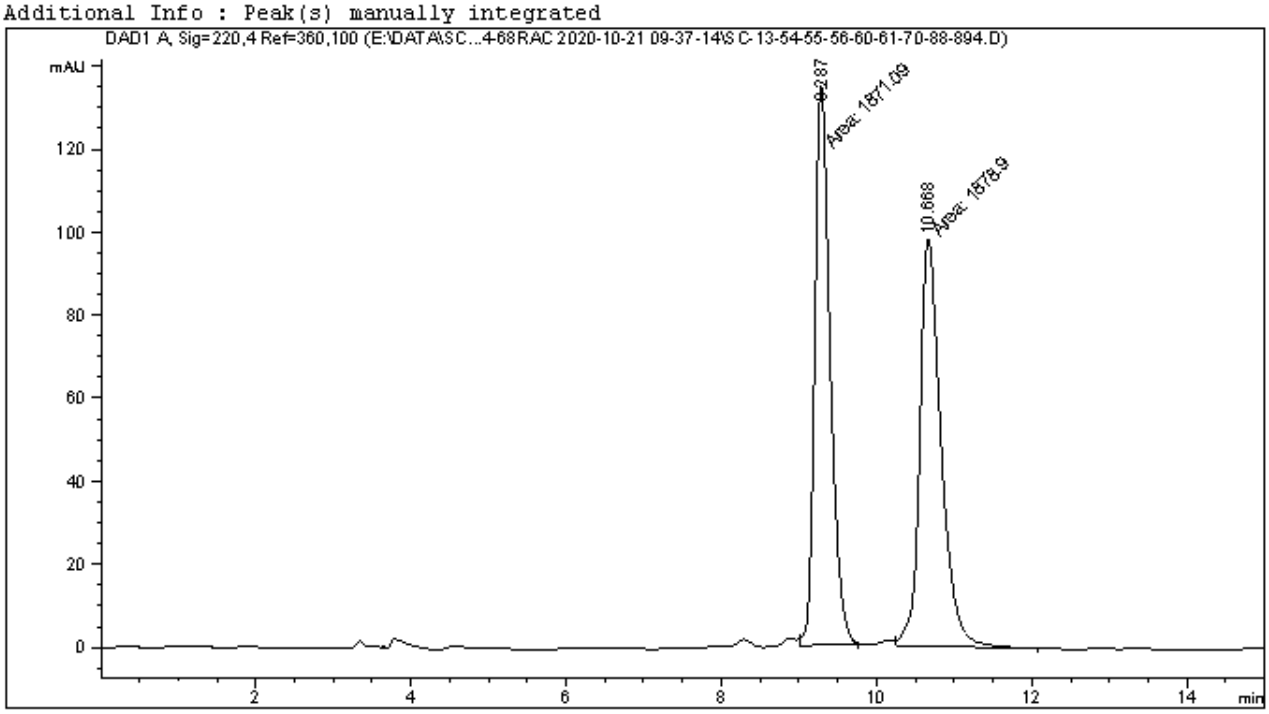
7r


7.257
7.230
7.227
7.217
7.214
7.201
7.198
7.189
7.186
7.124
7.122
7.119
7.115
7.112
7.110
7.107
7.106
6.982
6.973
6.969
6.960
6.938
6.929
6.925
6.916
6.511
6.486
6.468
6.461
6.444
6.419
6.196
6.173
6.171
6.154
6.148
6.131
6.129
6.106
5.353
5.349
5.327
5.324
5.270
5.268
5.266
5.265
5.262
5.240
5.237
5.227
5.224
5.222
5.185
5.182
5.180
4.241
4.218
4.174
4.150
1.134
0.000
1.01
0.98
2.00
1.00
0.99
1.00
1.02
1.03
3.07
1.03
1.00
9.08
f1 (ppm)


164.95
140.32
140.25
133.88
133.78
126.77
126.59
126.54
126.42
124.87
124.76
120.10
119.74
118.36
84.32
77.32
77.00
76.68
59.57
50.27
48.74
27.29
f1 (ppm)

Data File E:\DATA\SC...8-89--14-68RAC 2020-10-21 09-37-14\SC-13-54-55-56-60-61-70-88-894.D
Sample Name: SC-13-61-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   5
    Acq. Instrument : 1260                             Location :   85
    Injection Date  : 10/21/2020 10:59:03 AM               Inj :   1
                                                     Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/21/2020 10:56:52 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89--14-
                      68RAC 2020-10-21 09-37-14\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method
                      )
    Last changed    : 4/5/2021 9:49:19 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

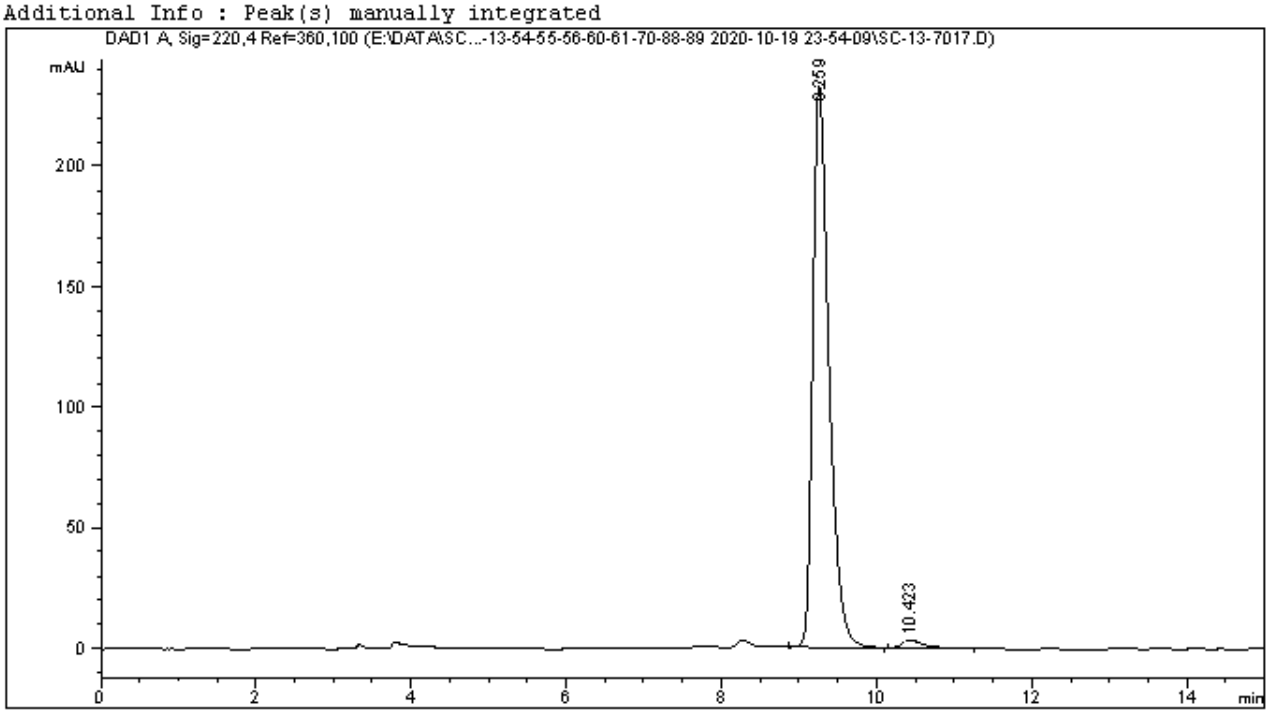

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.287 MM    0.2318 1871.09351  134.53082  49.8959
       2  10.668 FM    0.3194 1878.90137   98.04790  50.1041

    Totals :                  3749.99487  232.57872
```

Data File E:\DATA\SC...8-89\SC-13-54-55-56-60-61-70-88-89 2020-10-19 23-54-09\SC-13-7017.D
Sample Name: SC-13-61B

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  18
    Acq. Instrument : 1260                           Location :  86
    Injection Date  : 10/20/2020 6:59:23 AM              Inj :  1
                                                   Inj Volume : 2.000 µl
    Acq. Method     : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M
    Last changed    : 10/19/2020 11:54:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-13-54-55-56-60-61-70-88-89\SC-13-54-55-56-60-61-70-88-89 2020
                      -10-19 23-54-09\SC-4-IE-99-1-DAD-1ML-20MIN-2UL.M (Sequence Method)
    Last changed    : 4/7/2021 5:38:43 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



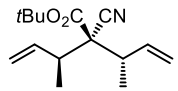

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

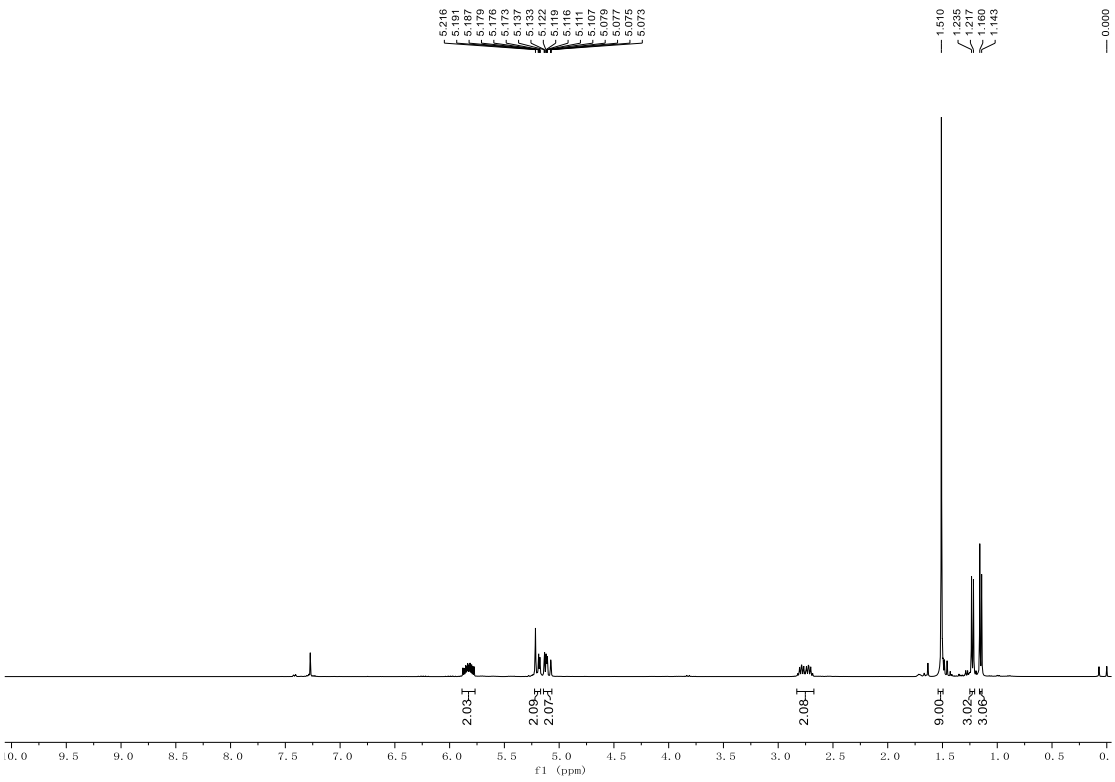

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

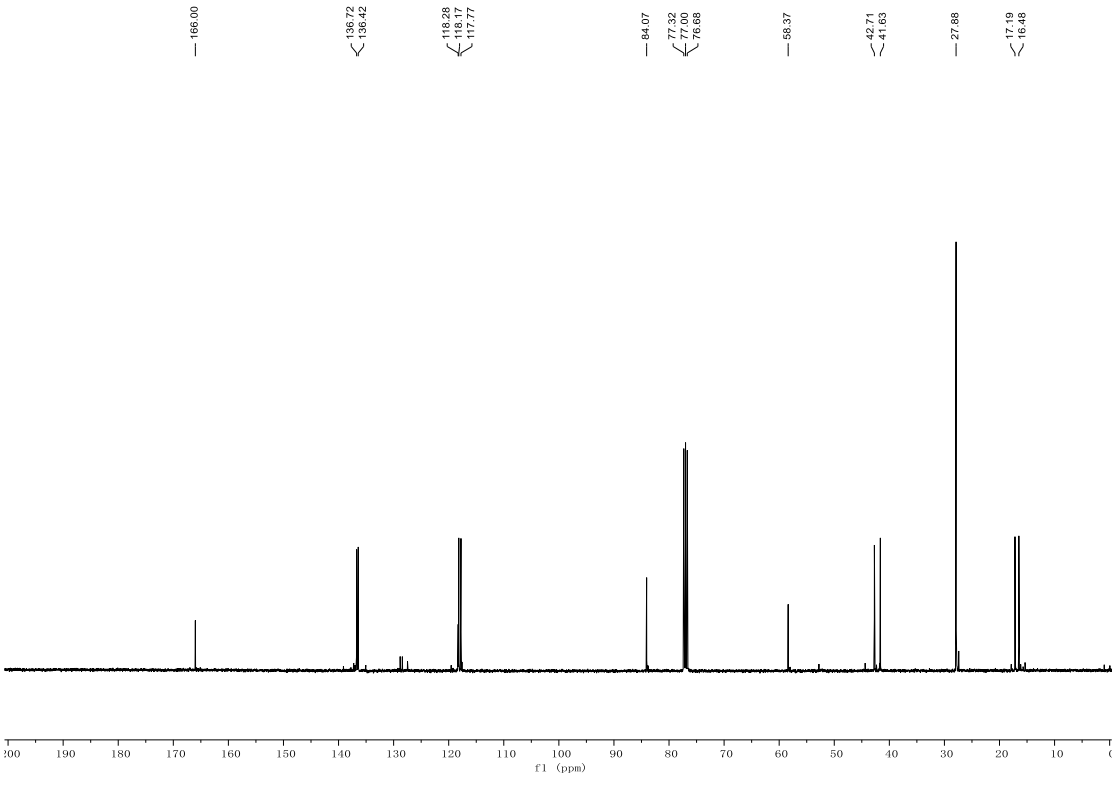
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.259 BB    0.2172 3372.66626  232.52678  98.1224
       2  10.423 BB    0.2561   64.53595    3.39007   1.8776

    Totals :                  3437.20221  235.91685
```


tBuO2C
CN

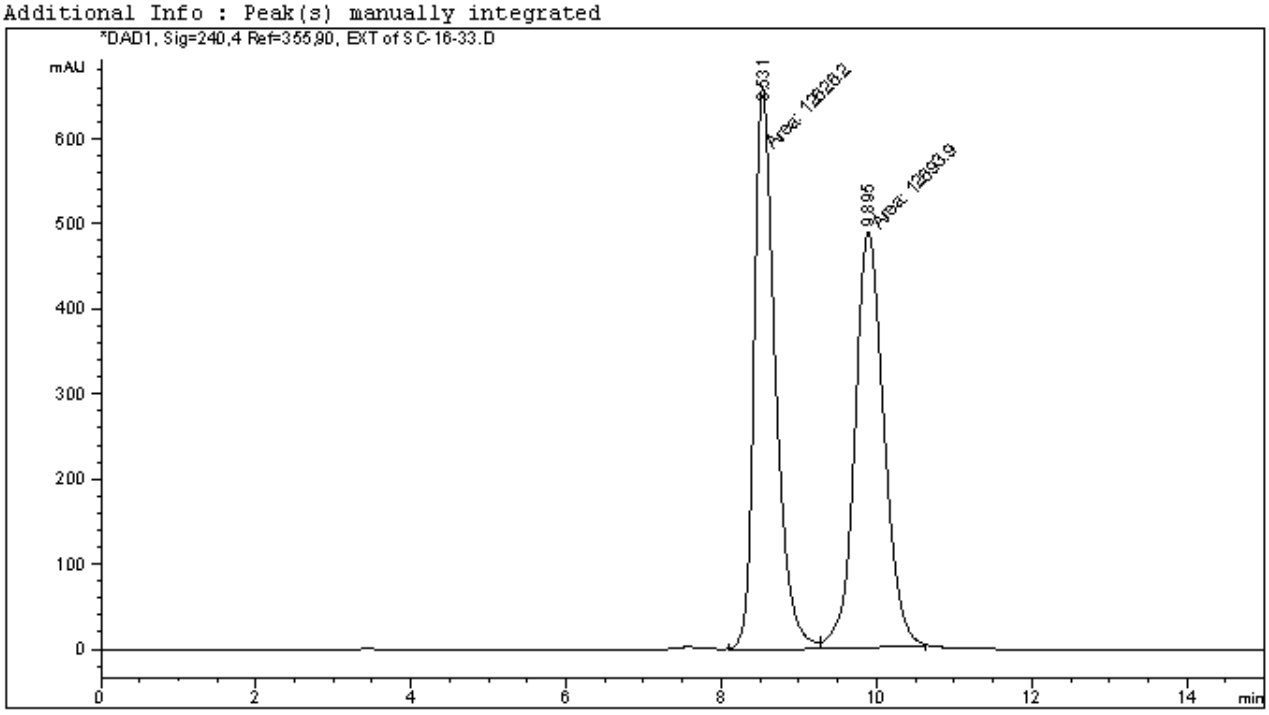
7s


5.216
5.191
5.187
5.179
5.178
5.173
5.137
5.133
5.122
5.119
5.116
5.111
5.107
5.079
5.077
5.075
5.073
1.510
1.235
1.217
1.166
1.143
0.000
2.03
2.09
2.07
2.08
9.00
3.02
3.06
f1 (ppm)


166.00
136.72
136.42
118.28
118.17
117.77
84.07
77.32
77.00
76.68
58.37
42.71
41.63
27.88
17.19
16.48
f1 (ppm)

Data File E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-16-33.D
Sample Name: SC-16-33-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   82
    Injection Date  : 5/13/2021 10:53:58 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-5-OJH-98-2-DAD-1ML-
                      20MIN.M
    Last changed    : 5/13/2021 10:52:29 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-5-OJH-98-2-DAD-1ML-
                      20MIN.M (Sequence Method)
    Last changed    : 5/13/2021 11:11:41 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

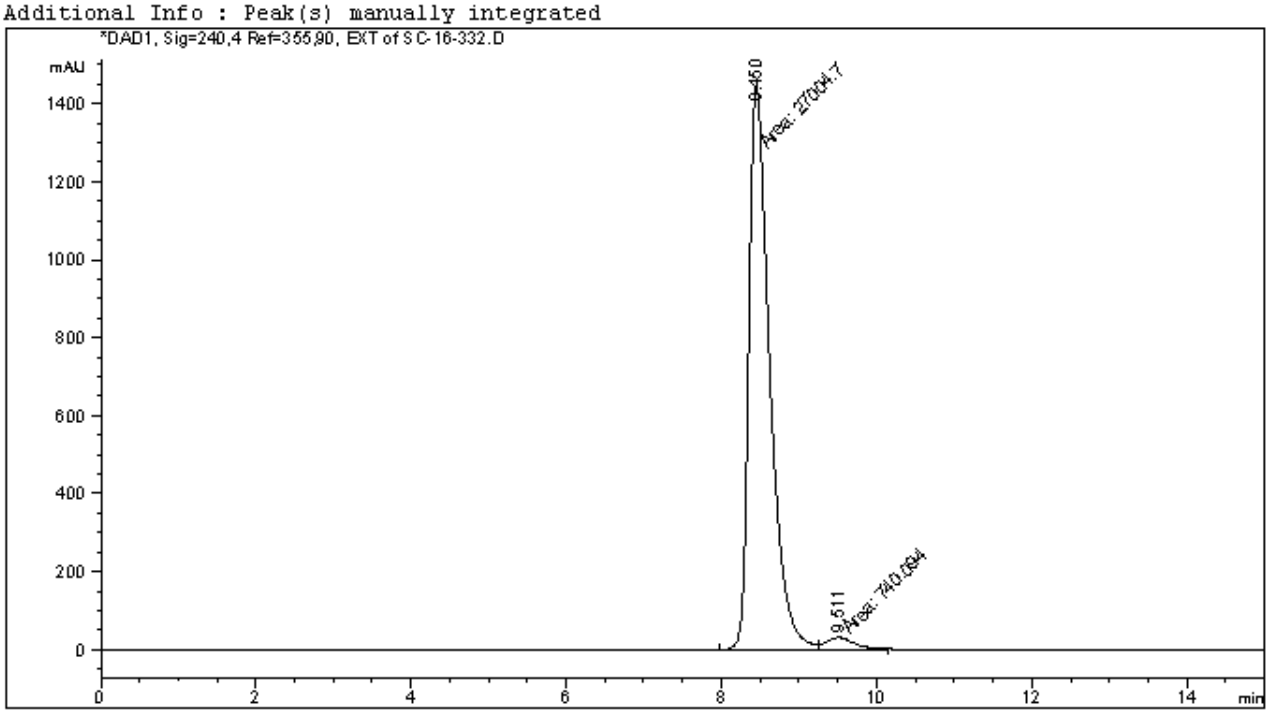

    Signal 1: DAD1, Sig=240,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.531 MF    0.3179 1.26262e4   661.92004  49.8663
       2   9.895 FM    0.4334 1.26939e4   488.19965  50.1337

    Totals :                   2.53202e4  1150.11969
```

Data File E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-16-332.D
Sample Name: SC-16-33B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260                             Location :   84
    Injection Date  : 5/13/2021 10:31:08 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-5-0JH-98-2-
                      DAD-1ML-20MIN.M
    Last changed    : 5/13/2021 9:47:05 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-5-0JH-98-2-
                      DAD-1ML-20MIN.M (Sequence Method)
    Last changed    : 5/13/2021 11:01:04 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



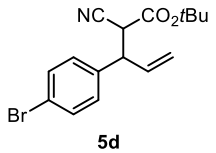

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

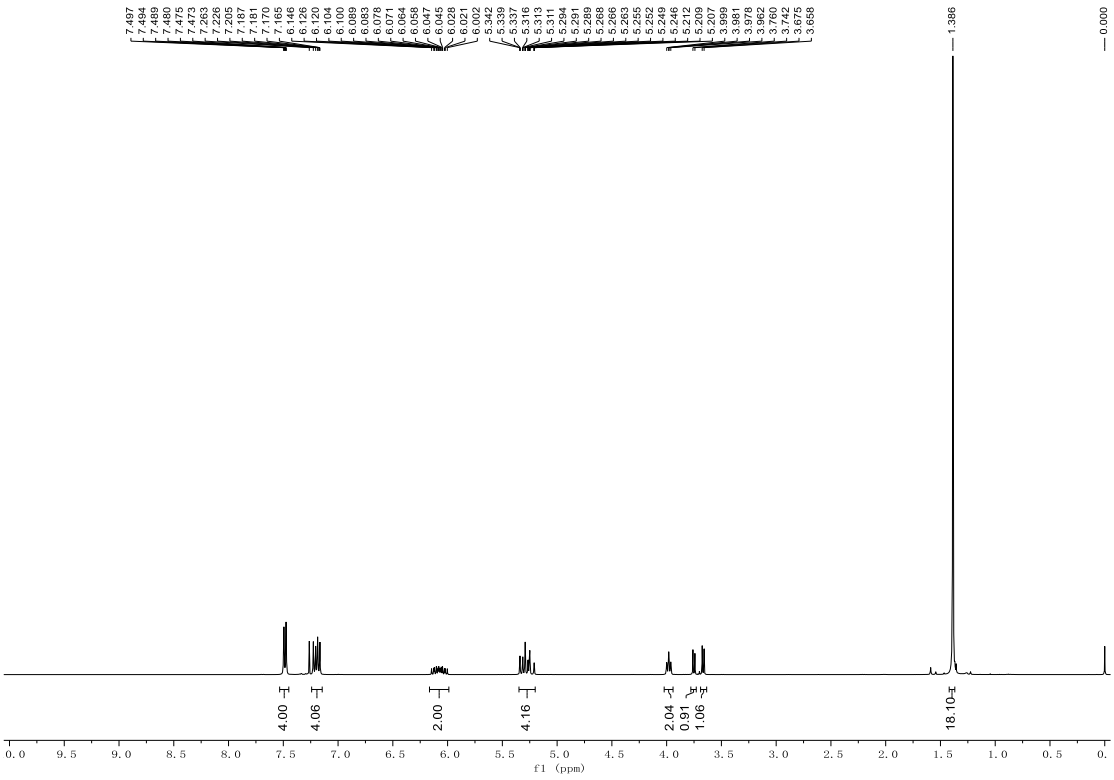

    Signal 1: DAD1, Sig=240,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.450 MF    0.3116 2.70047e4  1444.33252  97.3325
       2   9.511 FM    0.4116  740.09369   29.96502   2.6675

    Totals :                   2.77447e4  1474.29754
```


NC
CO2tBu
Br

5d


7.497
7.494
7.489
7.480
7.475
7.473
7.263
7.226
7.205
7.187
7.181
7.170
7.165
6.146
6.126
6.120
6.104
6.100
6.089
6.083
6.078
6.071
6.064
6.058
6.047
6.045
6.028
6.021
6.002
5.342
5.339
5.337
5.316
5.313
5.311
5.294
5.291
5.289
5.288
5.266
5.263
5.255
5.252
5.249
5.246
5.242
5.209
5.207
3.999
3.981
3.978
3.962
3.760
3.742
3.675
3.658
1.386
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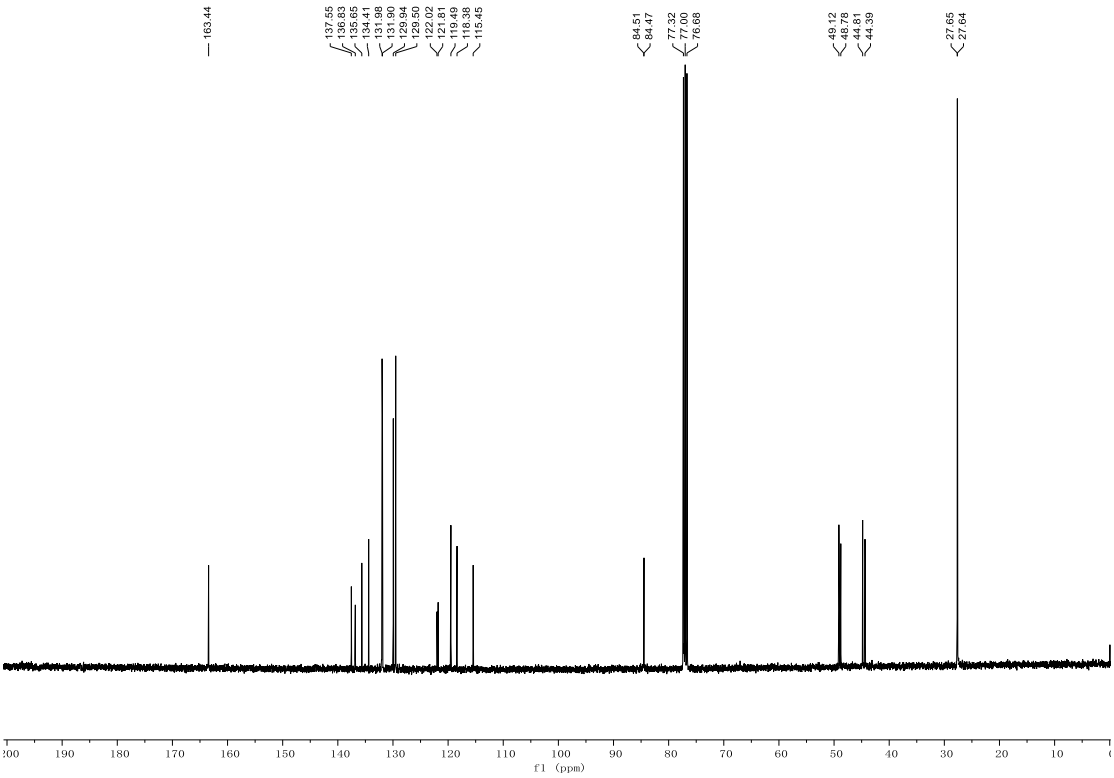
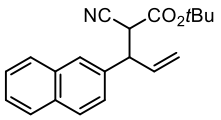
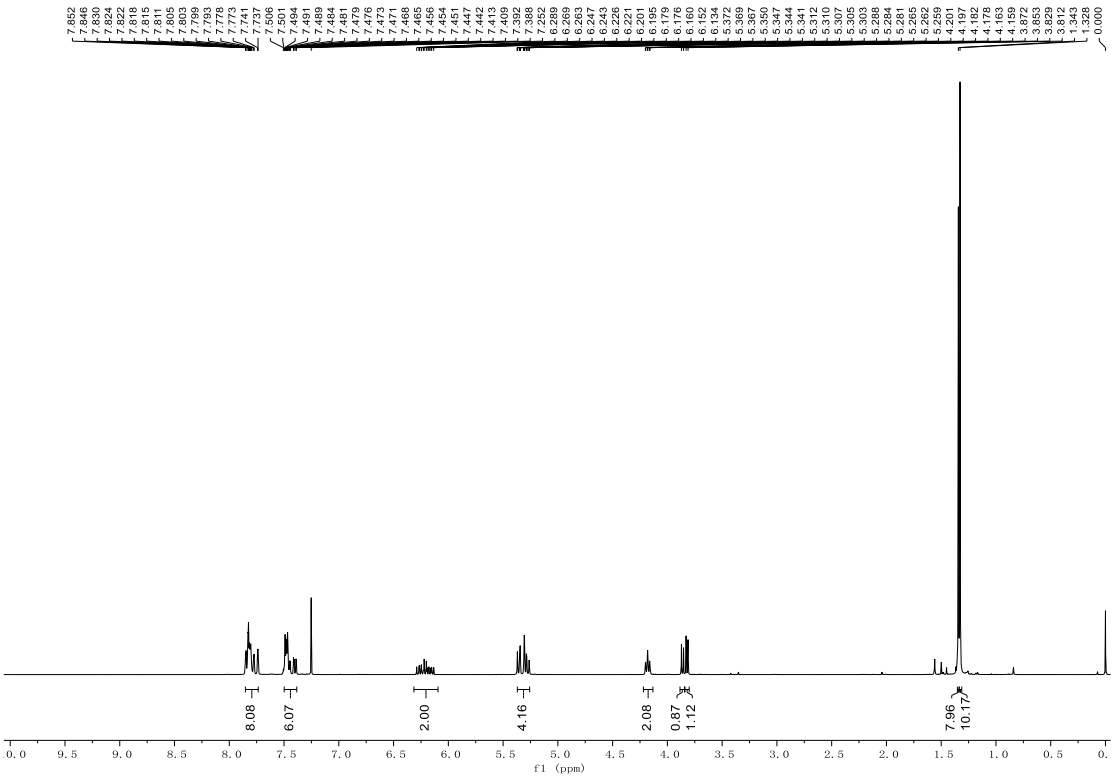
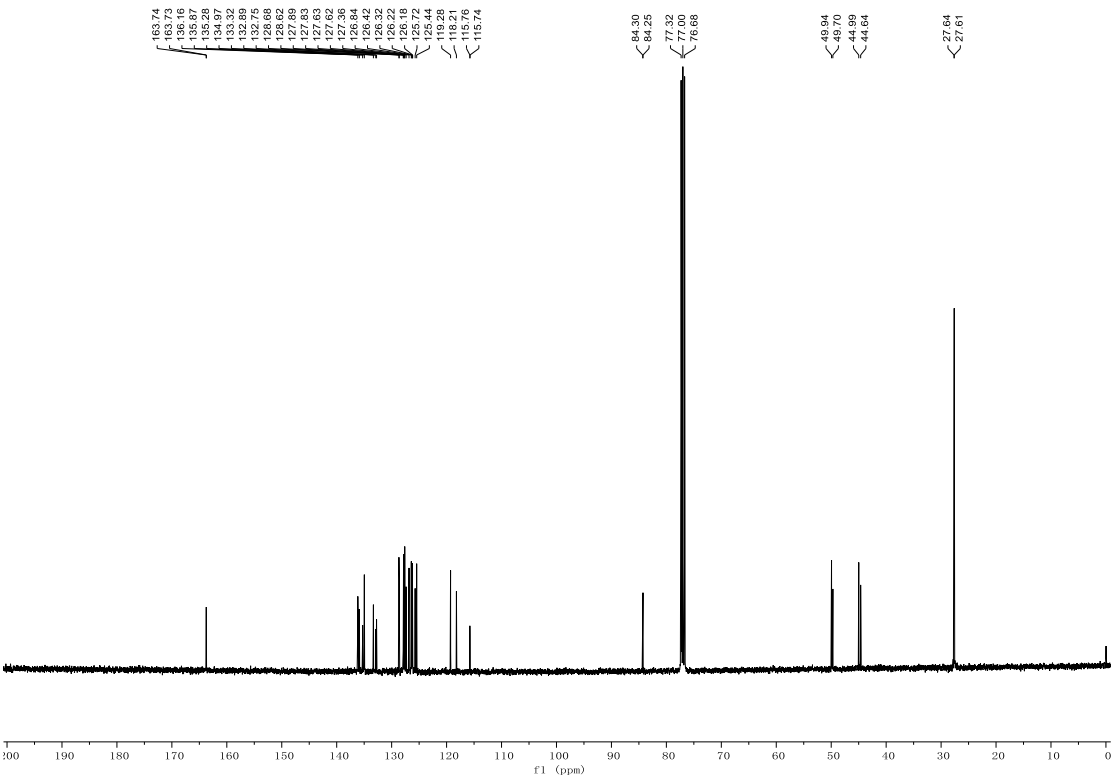
4.00
4.06
2.00
4.16
2.04
0.91
1.06
18.10
f1 (ppm)

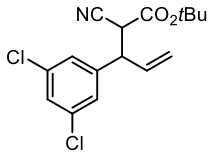

163.44
137.55
136.83
135.65
134.41
131.68
131.90
129.94
129.50
122.02
121.81
119.49
118.38
115.45
84.51
84.47
77.32
77.00
76.68
49.12
48.78
44.81
44.39
27.65
27.64
f1 (ppm)



5o



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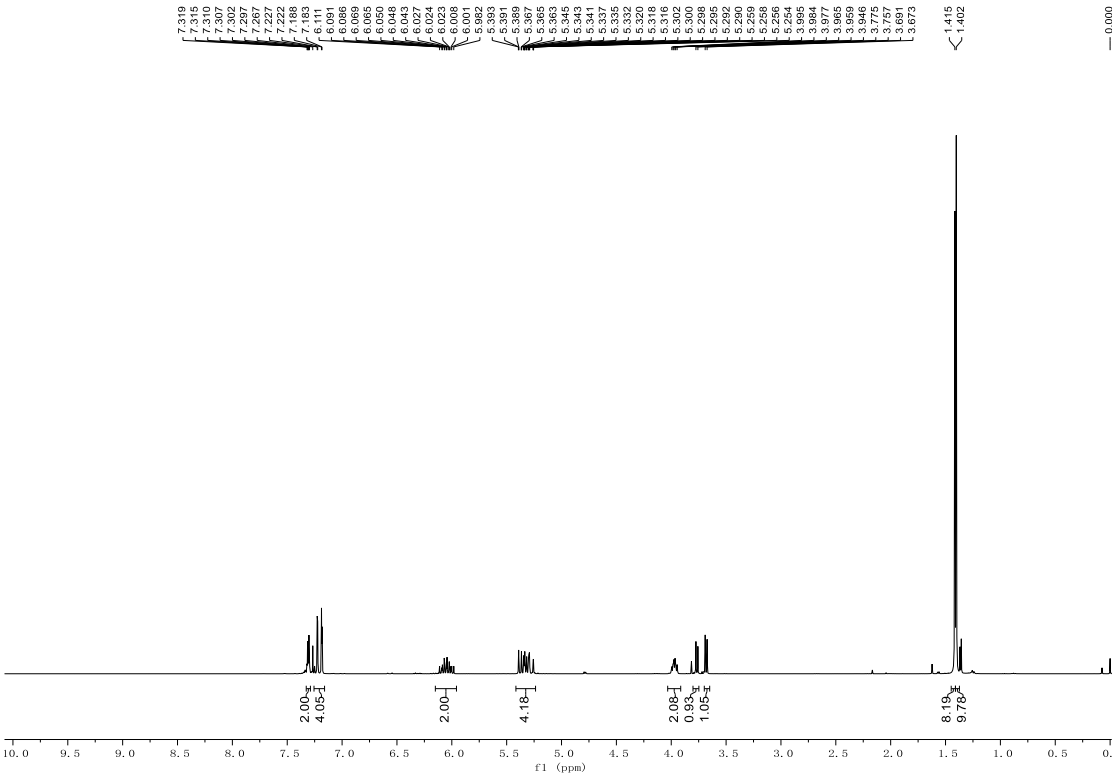
CO2tBu
Cl
Cl

5n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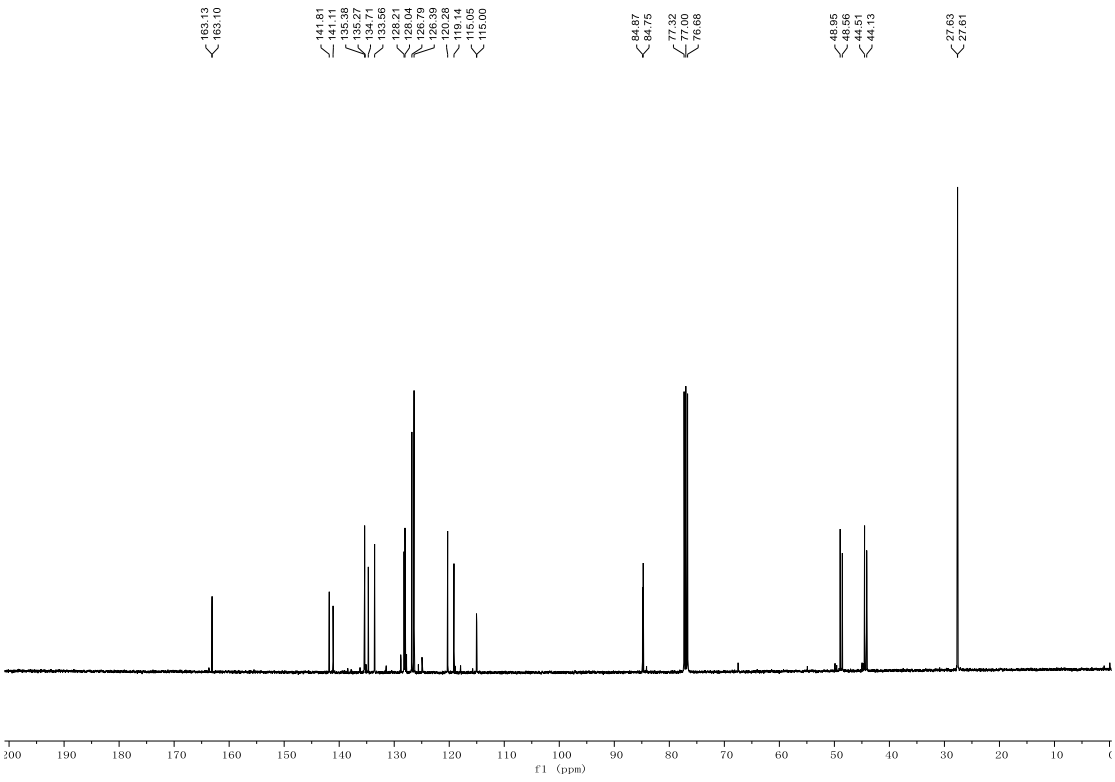
7.307
7.302
7.297
7.267
7.227
7.222
7.188
7.183
6.111
6.091
6.086
6.069
6.065
6.055
6.048
6.043
6.027
6.024
6.023
6.008
6.001
5.982
5.968
5.391
5.389
5.367
5.365
5.363
5.345
5.343
5.341
5.337
5.335
5.332
5.320
5.318
5.316
5.302
5.300
5.298
5.295
5.292
5.290
5.259
5.258
5.256
5.254
3.985
3.984
3.977
3.965
3.959
3.946
3.775
3.757
3.691
3.673
1.415
1.402
0.000
2.00
4.05
2.00
4.18
2.08
0.93
1.05
8.19
9.78
f1 (ppm)


163.13
163.10
141.81
141.11
135.38
135.27
134.71
133.56
128.21
128.04
126.79
126.39
120.28
119.14
115.05
115.00
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84.75
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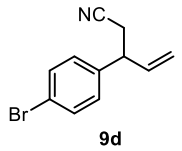
77.00
76.68
48.95
48.56
44.51
44.13
27.63
27.61
f1 (ppm)


NC
Br

9d

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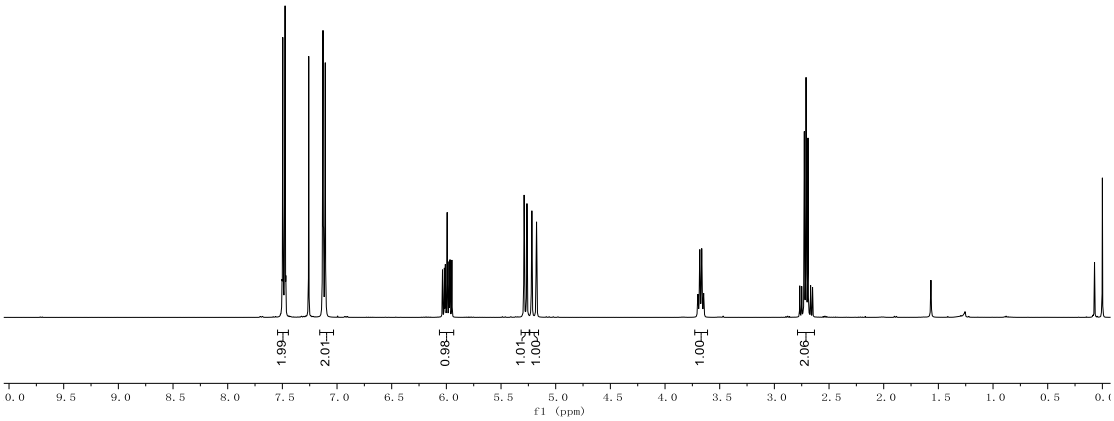
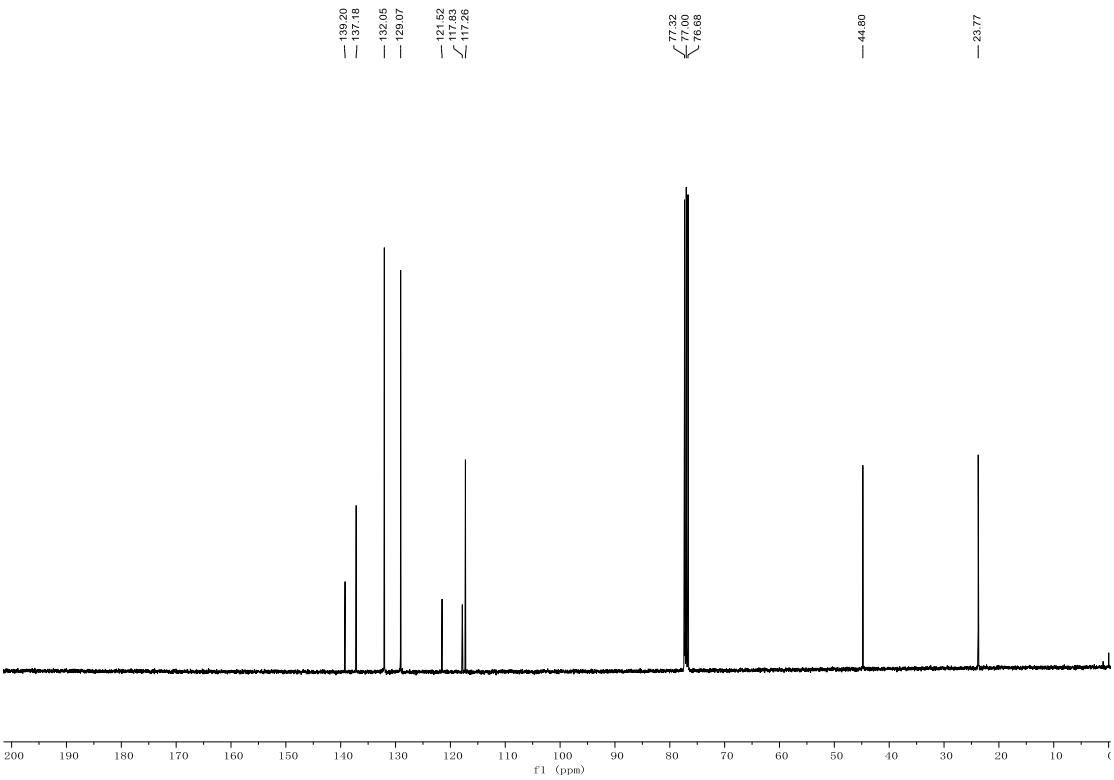
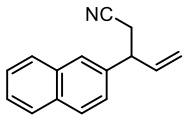
7.480
7.475
7.469
7.259
7.135
7.129
7.124
7.112
7.106
7.101
6.035
6.018
6.009
5.993
5.976
5.967
5.950
5.289
5.286
5.263
5.260
5.220
5.218
5.177
5.175
3.700
3.685
3.682
3.668
3.664
3.647
2.768
2.750
2.726
2.711
2.708
2.692
2.669
2.651
0.000


1.99
2.01
0.98
1.01
1.00
1.00
2.06
f1 (ppm)


139.20
137.18
132.05
129.07
121.52
117.83
117.26
77.32
77.00
76.68
44.80
23.77
f1 (ppm)


NC

9o

7.845
7.832
7.830
7.824
7.819
7.814
7.808
7.806
7.803
7.800
7.680
7.678
7.675
7.506
7.494
7.488
7.479
7.470
7.464
7.344
7.339
7.323
7.318
7.242
6.148
6.131
6.123
6.105
6.088
6.080
6.063
5.313
5.311
5.308
5.287
5.285
5.282
5.273
5.271
5.268
5.231
5.228
5.225
3.889
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3.853
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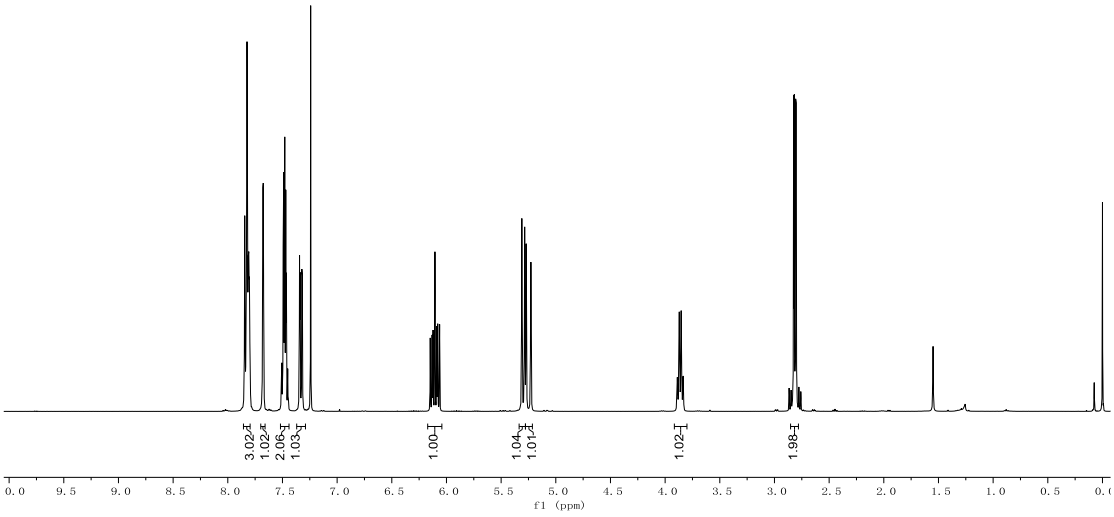
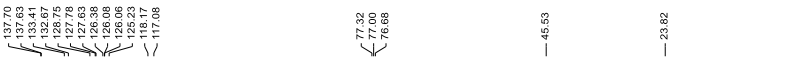
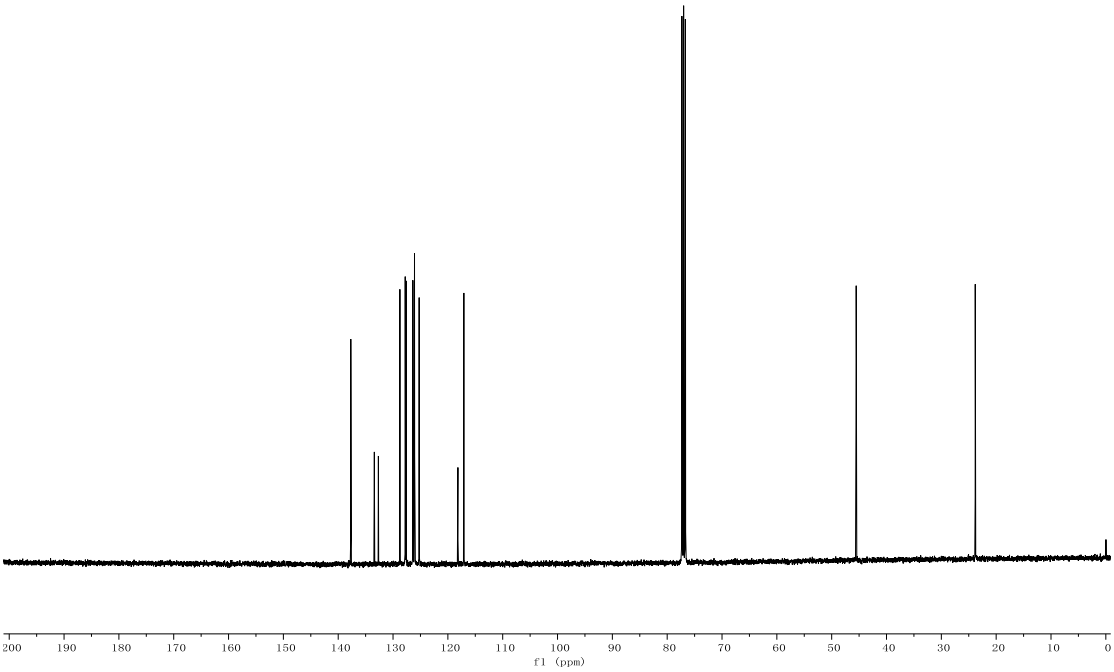
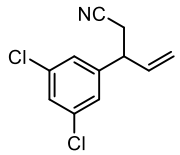
2.866
2.848
2.824
2.818
2.806
2.801
2.777
2.759
0.000

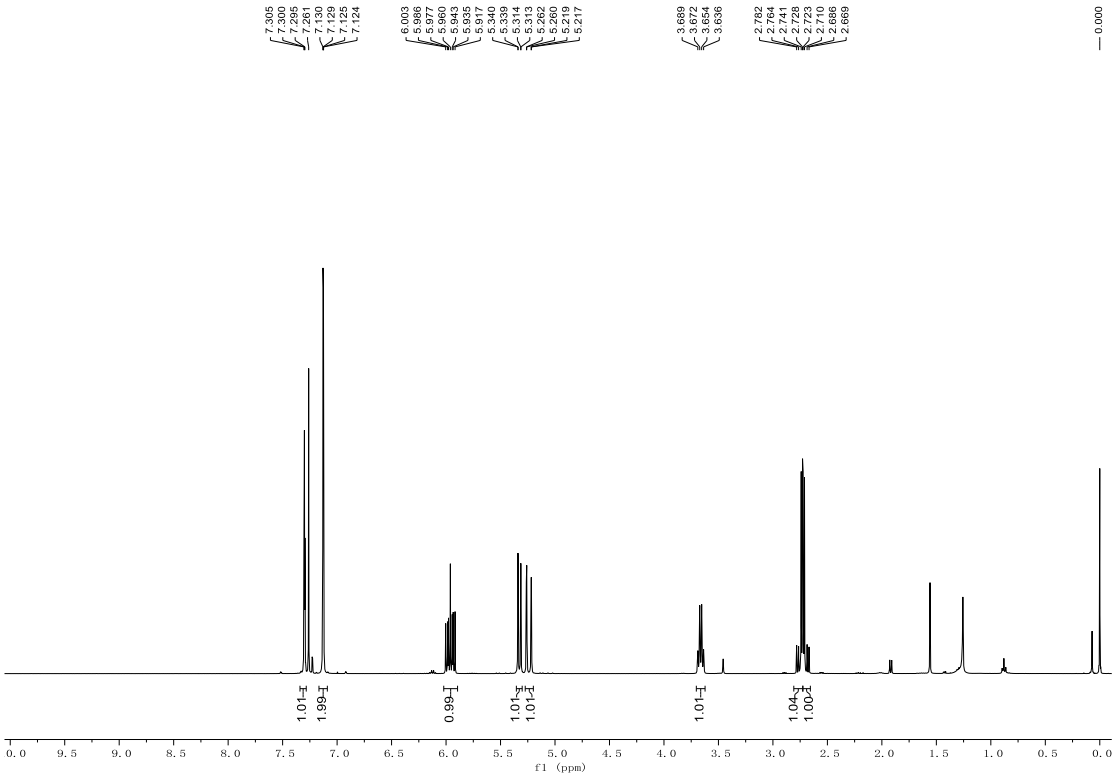

3.02
1.02
2.06
1.03
1.00
1.04
1.01
1.02
1.98
f1 (ppm)


137.70
137.63
133.41
132.67
128.75
127.78
127.63
126.38
126.08
126.06
125.23
118.17
117.08
77.32
77.00
76.68
45.53
23.82


f1 (ppm)


NC
Cl
Cl

9n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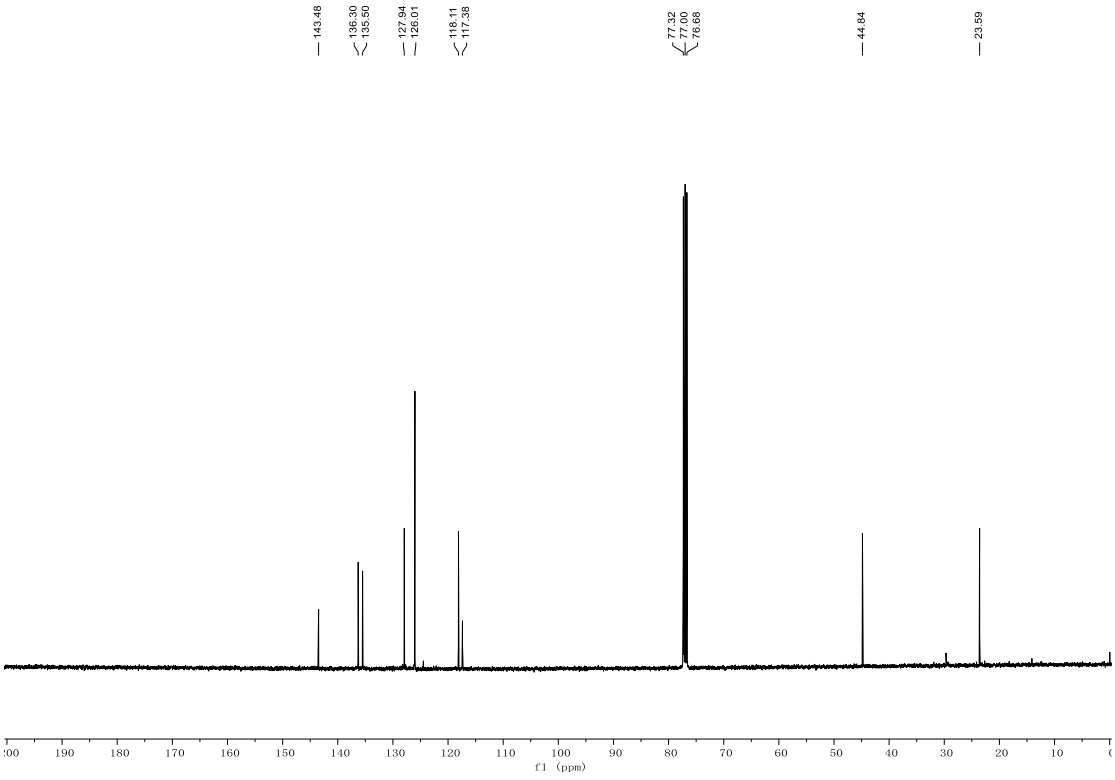
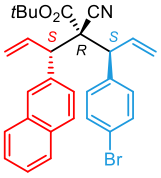
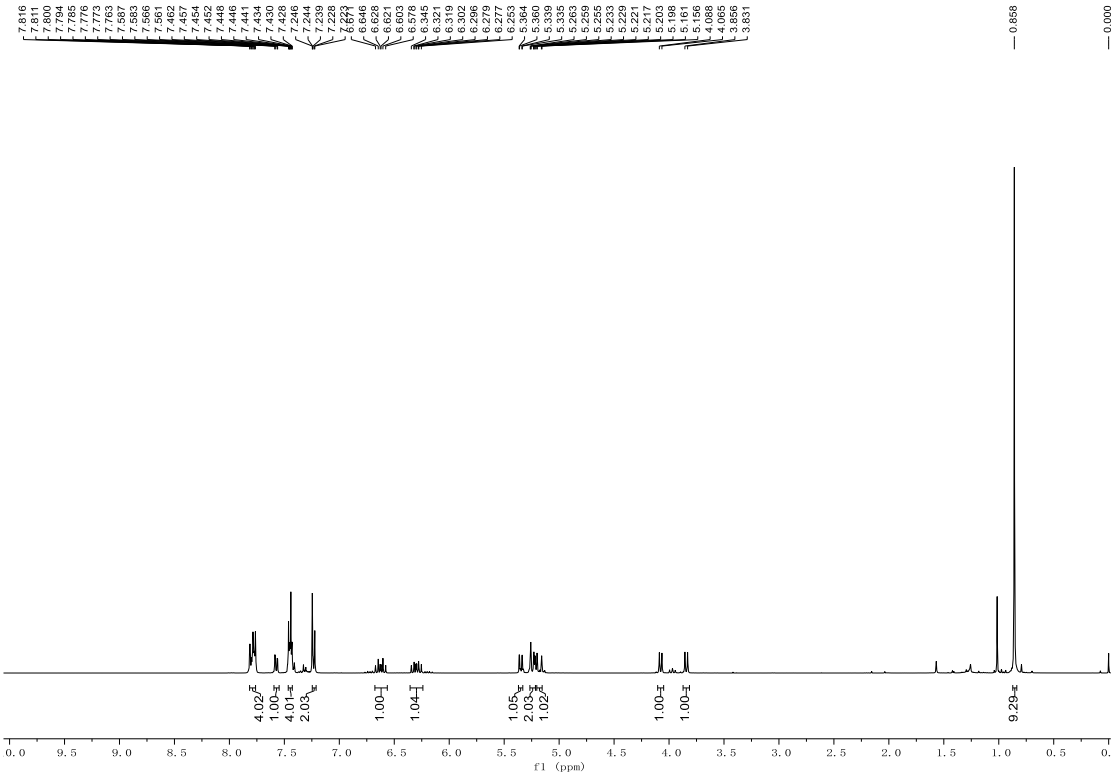
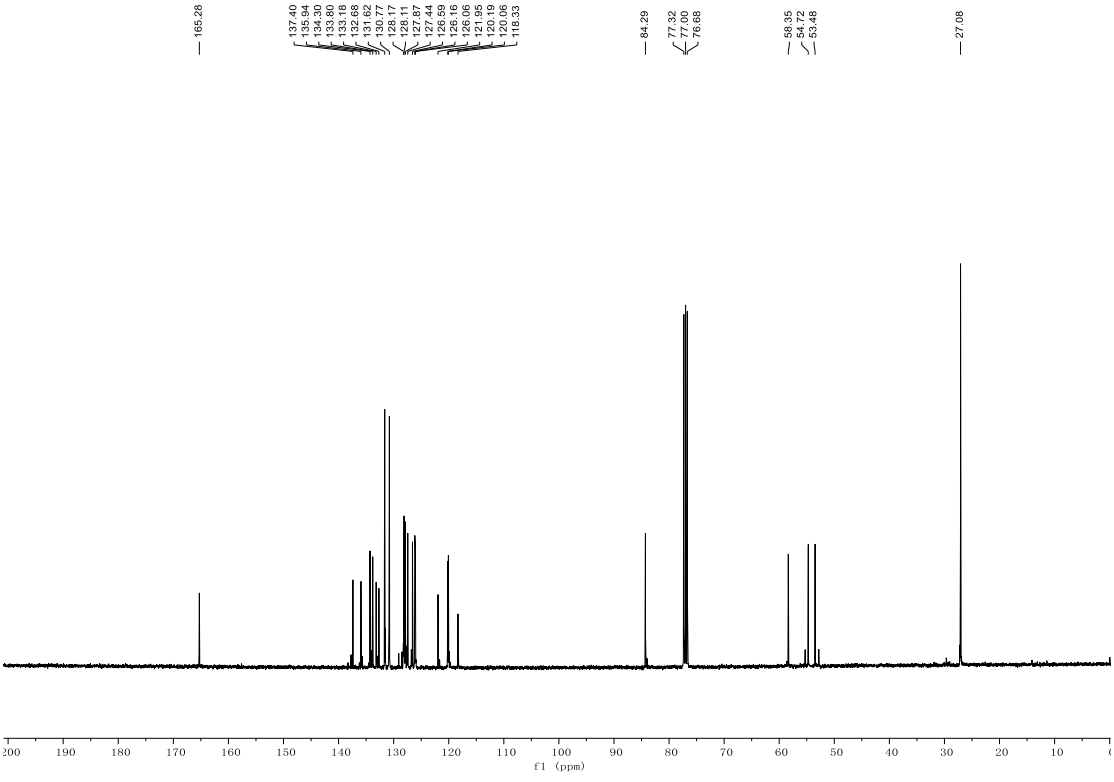
7.300
7.295
7.261
7.130
7.129
7.125
7.124
6.003
5.986
5.977
5.960
5.943
5.935
5.917
5.340
5.339
5.314
5.313
5.262
5.260
5.219
5.217
3.689
3.672
3.654
3.636
2.782
2.764
2.741
2.728
2.723
2.710
2.686
2.669
0.000
1.01
1.99
0.99
1.01
1.01
1.01
1.04
1.00
f1 (ppm)

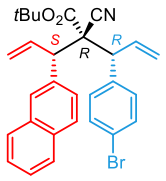

143.48
136.30
135.50
127.94
126.01
118.11
117.38
77.32
77.00
76.68
44.84
23.59
f1 (ppm)


tBuO2C
CN
S
R
S
Br

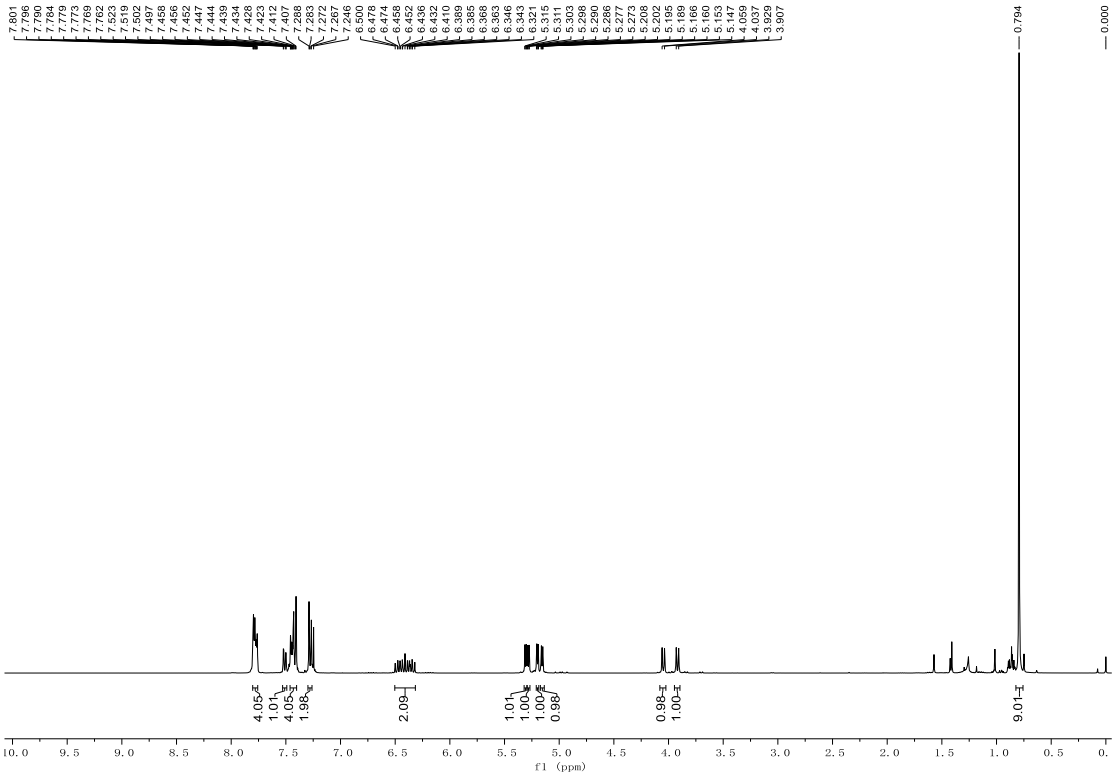
(*S*,*R*,*S*)-**8A**

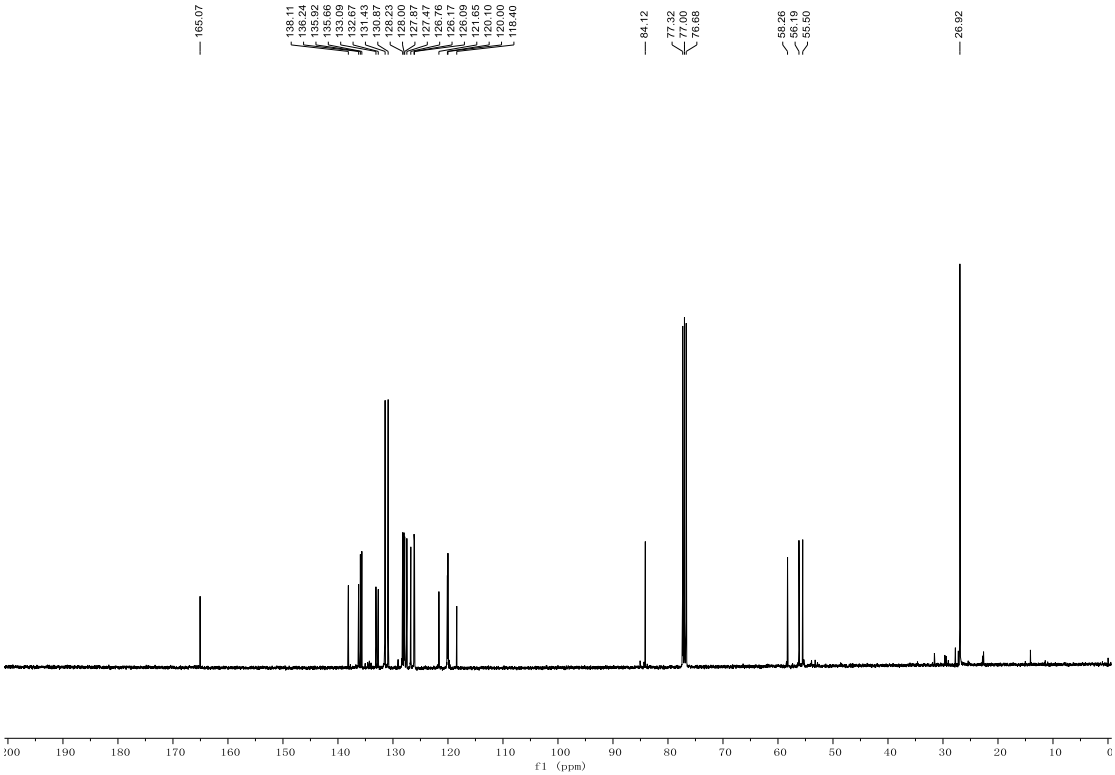

7.816
7.811
7.800
7.794
7.785
7.776
7.773
7.763
7.587
7.583
7.566
7.561
7.462
7.457
7.454
7.452
7.448
7.446
7.441
7.434
7.430
7.428
7.246
7.244
7.239
7.228
6.646
6.628
6.621
6.603
6.578
6.345
6.321
6.319
6.302
6.296
6.279
6.277
6.253
5.364
5.360
5.339
5.335
5.263
5.259
5.255
5.233
5.229
5.221
5.217
5.203
5.198
5.161
5.156
4.088
4.065
3.856
3.831
0.858
0.000
4.02
1.00
4.01
2.03
1.00
1.04
1.05
2.03
1.02
1.00
1.00
9.29
f1 (ppm)

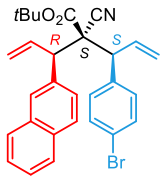

165.28
137.40
135.94
134.30
133.80
133.18
132.68
131.62
130.77
129.17
128.11
127.87
127.44
126.59
126.16
126.06
121.95
120.19
120.06
118.33
84.29
77.32
77.00
76.68
58.35
54.72
53.46
27.08
f1 (ppm)


tBuO2C
CN
S
R
R
Br

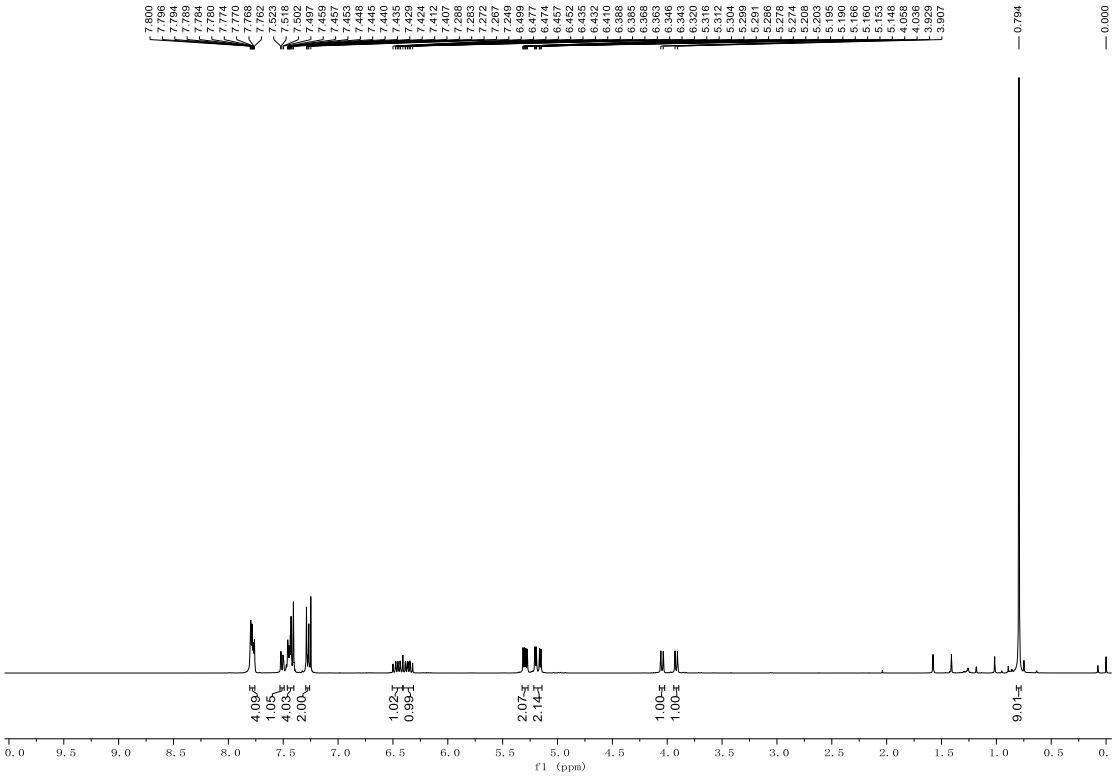
(*S*,*R*,*R*)-**8A**


7.801 7.796 7.790 7.784 7.779 7.773 7.769 7.762 7.523 7.519 7.502 7.497 7.458 7.456 7.452 7.447 7.444 7.439 7.434 7.428 7.423 7.412 7.407 7.288 7.283 7.272 7.267 7.246 6.500 6.478 6.474 6.458 6.452 6.436 6.432 6.410 6.389 6.385 6.368 6.363 6.346 6.343 6.321 5.315 5.311 5.303 5.298 5.290 5.286 5.277 5.273 5.208 5.202 5.195 5.189 5.166 5.160 5.153 5.147 5.059 4.037 3.929 3.907
0.794
0.000
4.05 1.01 4.05 1.98 2.09 1.01 1.00 1.00 0.98 0.98 1.00 9.01
f1 (ppm)


165.07
138.11 136.24 135.92 135.66 133.09 132.87 131.43 130.87 128.23 128.00 127.87 127.47 126.76 126.17 125.69 121.65 120.10 120.00 118.40
84.12
77.32 77.00 76.68
58.26 56.19 55.50
26.92
f1 (ppm)


tBuO2C
CN
R
S
S
Br

(*R*,*S*,*S*)-**8A**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7.796
7.794
7.789
7.784
7.780
7.774
7.770
7.768
7.762
7.523
7.518
7.502
7.497
7.459
7.457
7.453
7.448
7.445
7.440
7.435
7.429
7.424
7.412
7.407
7.288
7.283
7.272
7.267
7.249
7.249
6.477
6.474
6.457
6.452
6.435
6.432
6.410
6.388
6.385
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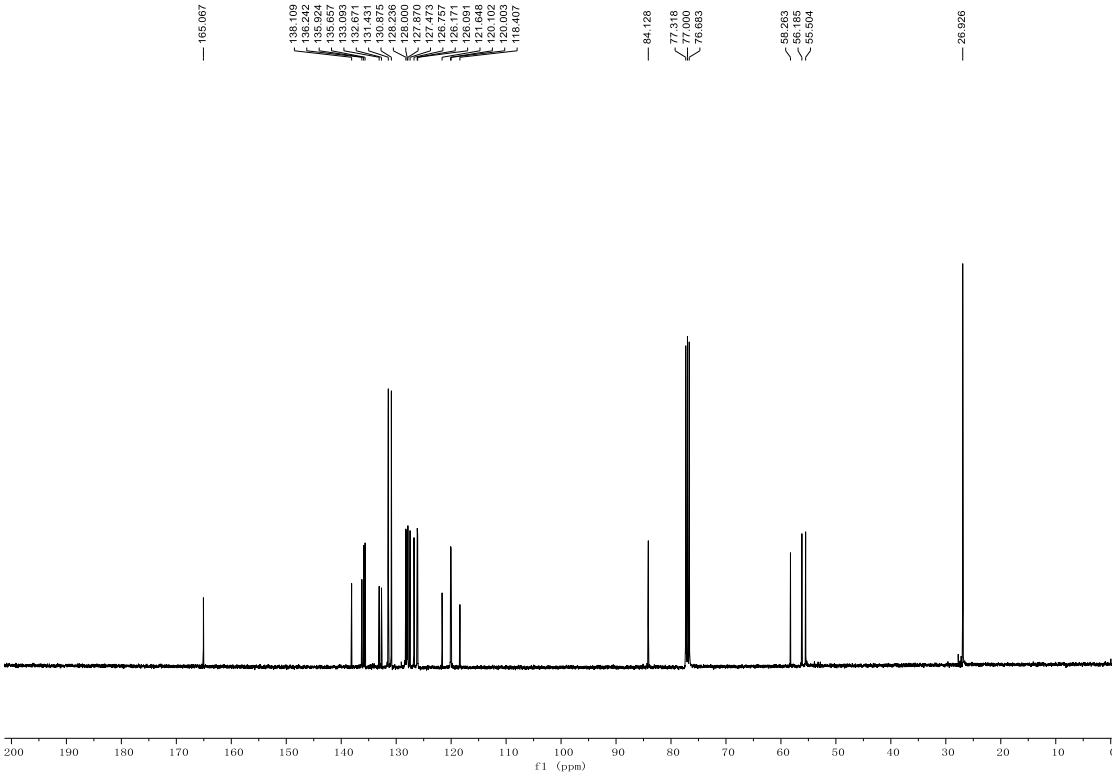
6.363
6.346
6.343
6.320
5.316
5.312
5.304
5.299
5.291
5.286
5.278
5.274
5.208
5.203
5.195
5.190
5.166
5.160
5.153
5.148
4.058
4.036
3.929
3.907
0.794
0.000
4.09
1.05
4.03
2.00
1.02
0.99
2.07
2.14
1.00
1.00
9.01
f1 (ppm)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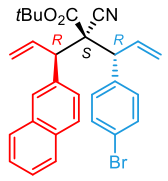
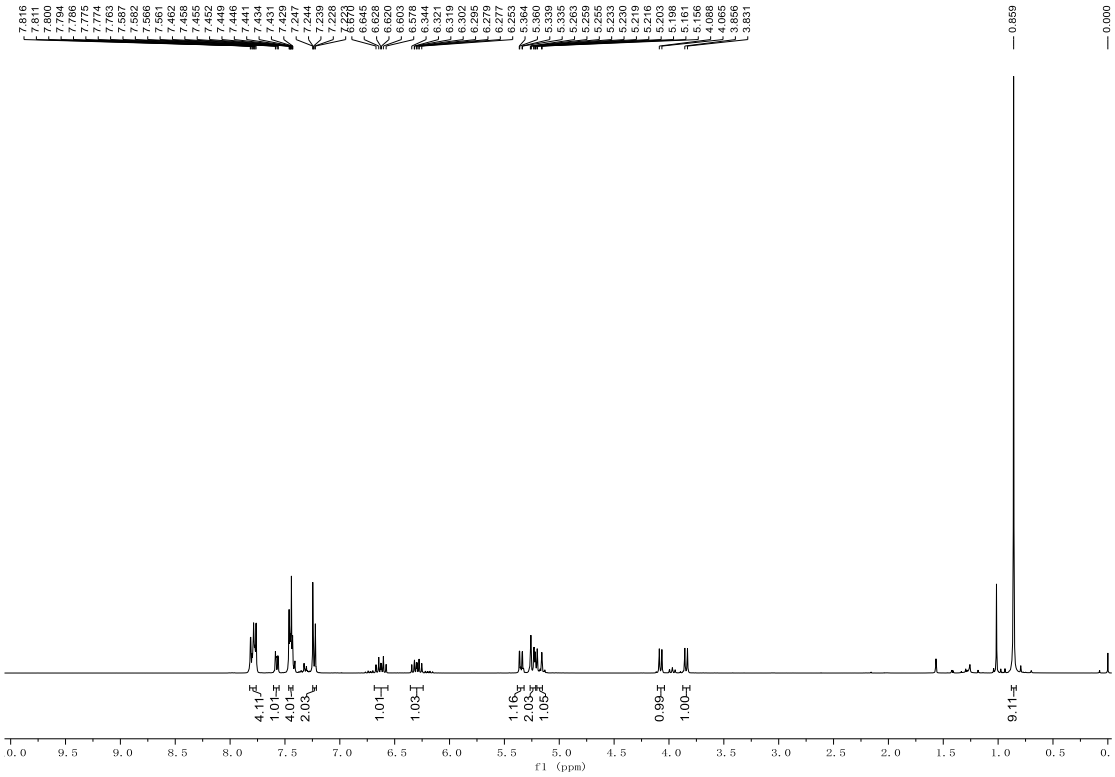
136.242
135.924
135.657
133.093
132.671
131.431
130.275
128.236
128.000
127.870
127.473
126.757
126.171
126.091
121.648
120.102
120.003
118.407
84.128
77.318
77.000
76.683
58.263
56.185
55.504
26.926
f1 (ppm)


tBuO2C
CN
R
S
R
Br

(*R*,*S*,*R*)-**8A**


7.816
7.811
7.800
7.794
7.786
7.775
7.774
7.763
7.587
7.582
7.566
7.561
7.462
7.458
7.455
7.452
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7.446
7.441
7.434
7.431
7.429
7.247
7.244
7.239
7.228
6.645
6.628
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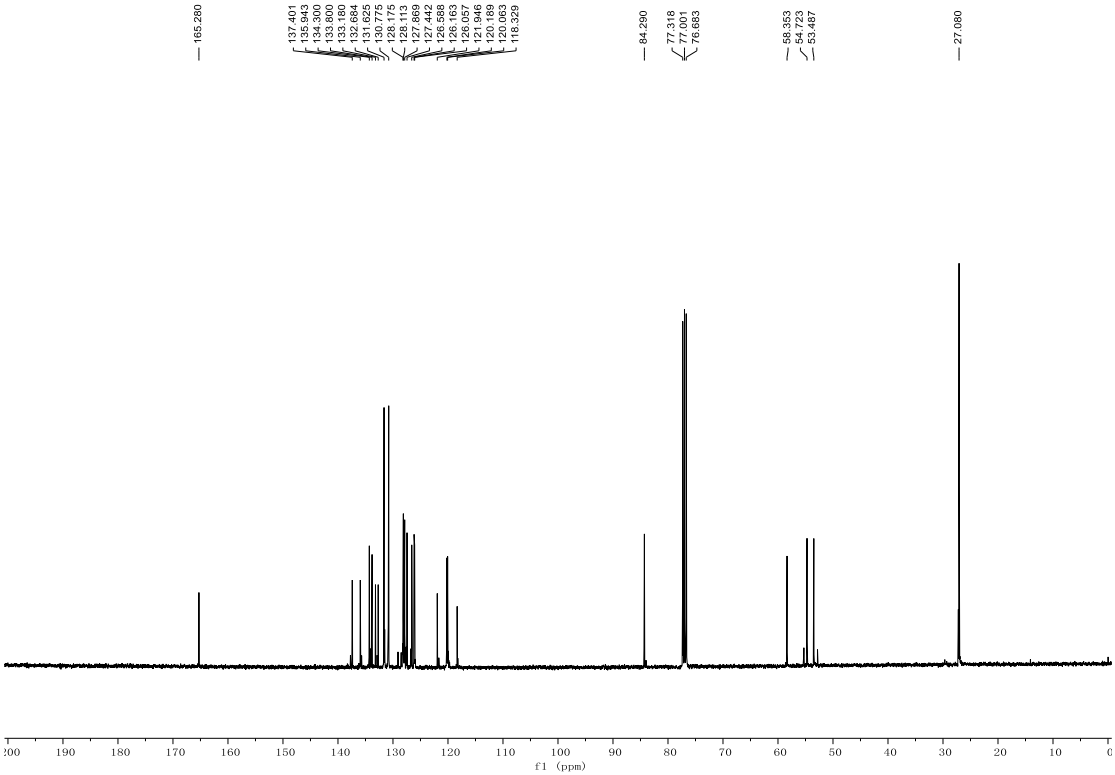
6.603
6.578
6.344
6.321
6.319
6.302
6.295
6.279
6.277
6.253
5.364
5.360
5.339
5.335
5.263
5.259
5.255
5.233
5.230
5.219
5.216
5.203
5.198
5.161
5.156
4.088
4.065
3.856
3.831
0.859
0.000
4.11
1.01
4.01
2.03
1.01
1.03
1.16
2.03
1.05
0.99
1.00
9.11
f1 (ppm)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134.300
133.800
133.180
132.684
131.625
130.775
128.175
128.113
127.869
127.442
126.588
126.163
126.057
121.646
120.189
120.063
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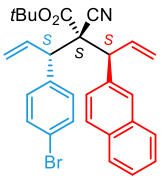
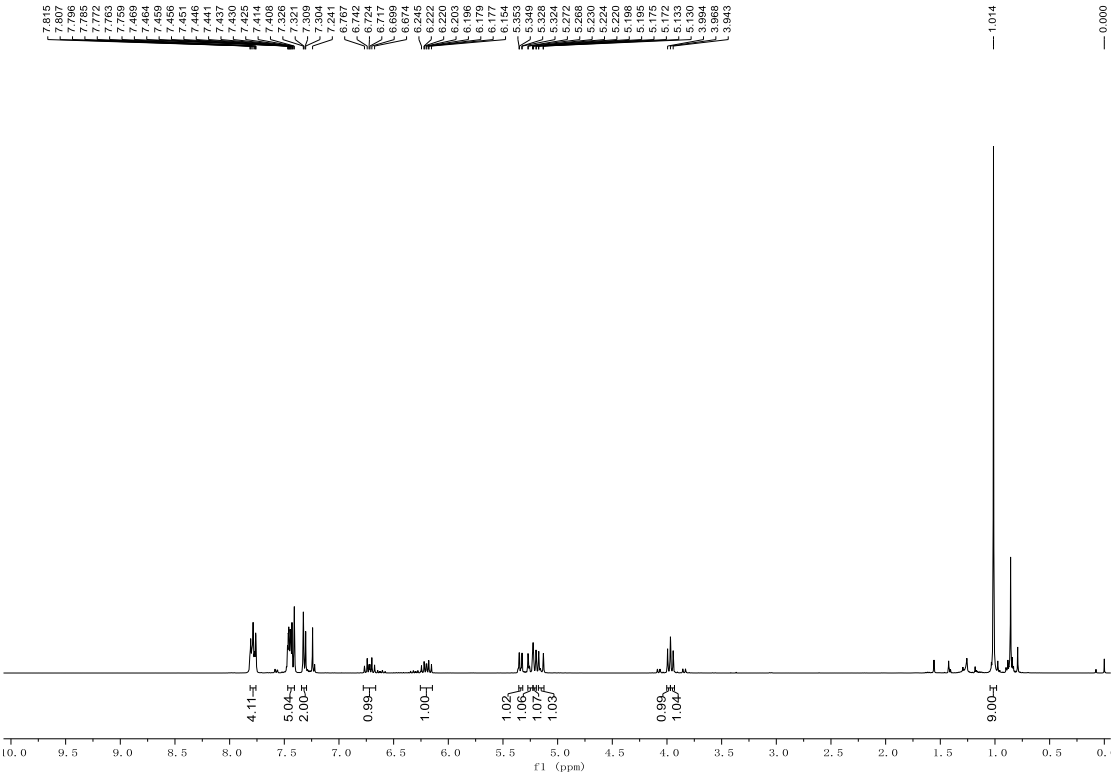
84.290
77.318
77.001
76.683
58.353
54.223
53.467
27.080
f1 (ppm)


tBuO2C
CN
S
S
S
Br

(*S*,*S*,*S*)-**8A**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7.786
7.772
7.763
7.759
7.469
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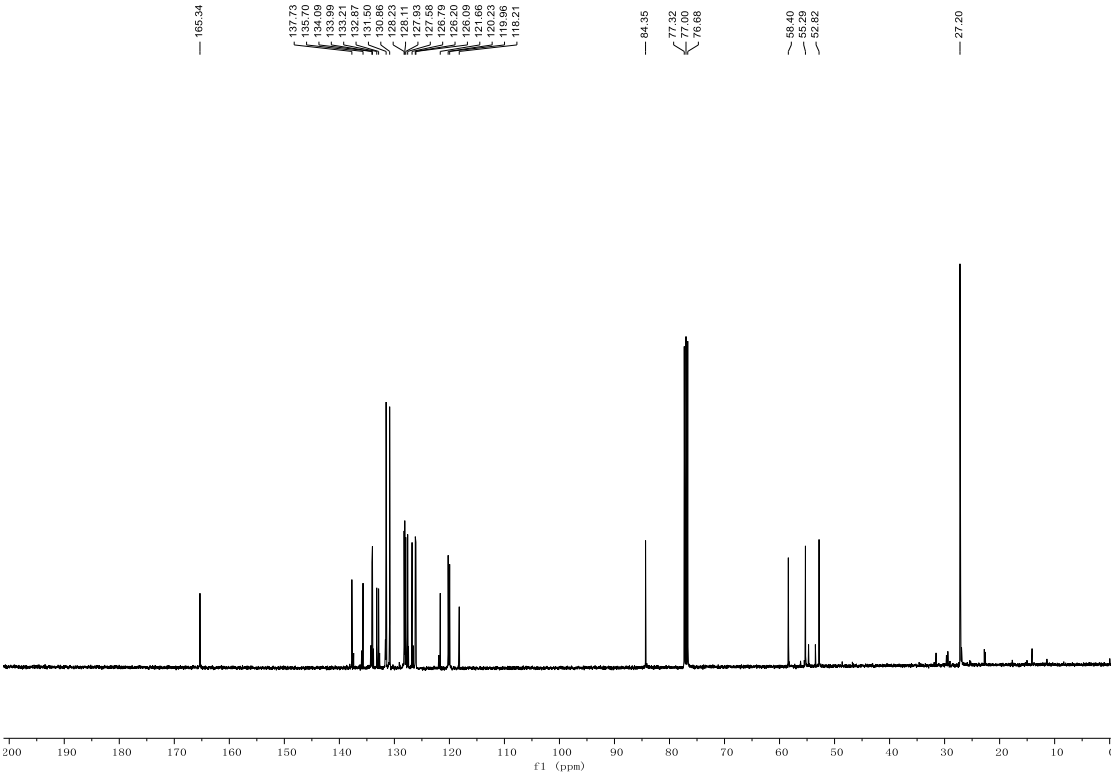
7.459
7.456
7.451
7.446
7.441
7.437
7.430
7.425
7.414
7.408
7.326
7.321
7.309
7.304
7.241
6.767
6.742
6.724
6.717
6.699
6.674
6.245
6.222
6.220
6.203
6.196
6.179
6.177
6.154
5.353
5.349
5.328
5.324
5.272
5.268
5.230
5.224
5.220
5.198
5.195
5.175
5.172
5.133
5.130
3.994
3.968
3.943
1.014
0.000
4.11
5.04
2.00
0.99
1.00
1.02
1.06
1.07
1.03
0.99
1.04
9.00
f1 (ppm)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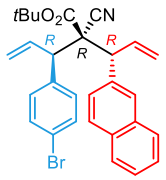
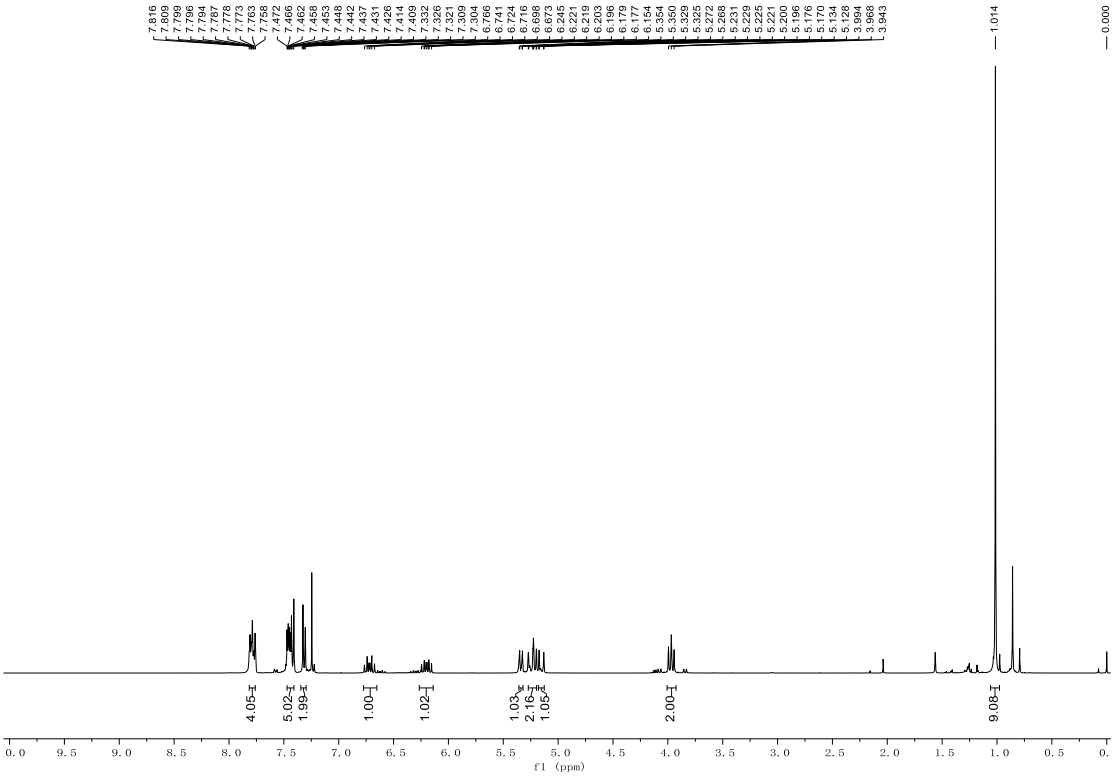
133.21
132.87
131.50
130.86
130.23
128.11
127.93
127.58
126.79
126.20
126.09
121.66
120.23
119.96
118.21
84.35
77.32
77.00
76.68
58.40
55.29
52.82
27.20
f1 (ppm)


tBuO2C
CN
R
R
R
Br

(*R*,*R*,*R*)-**8A**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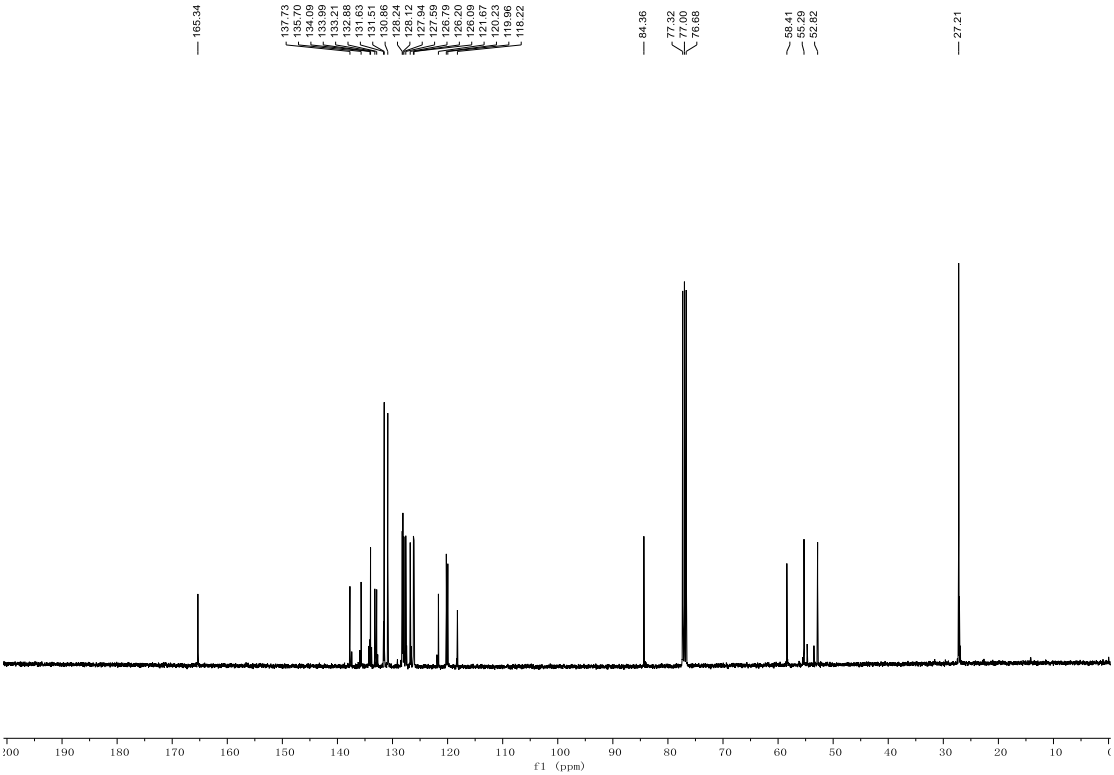
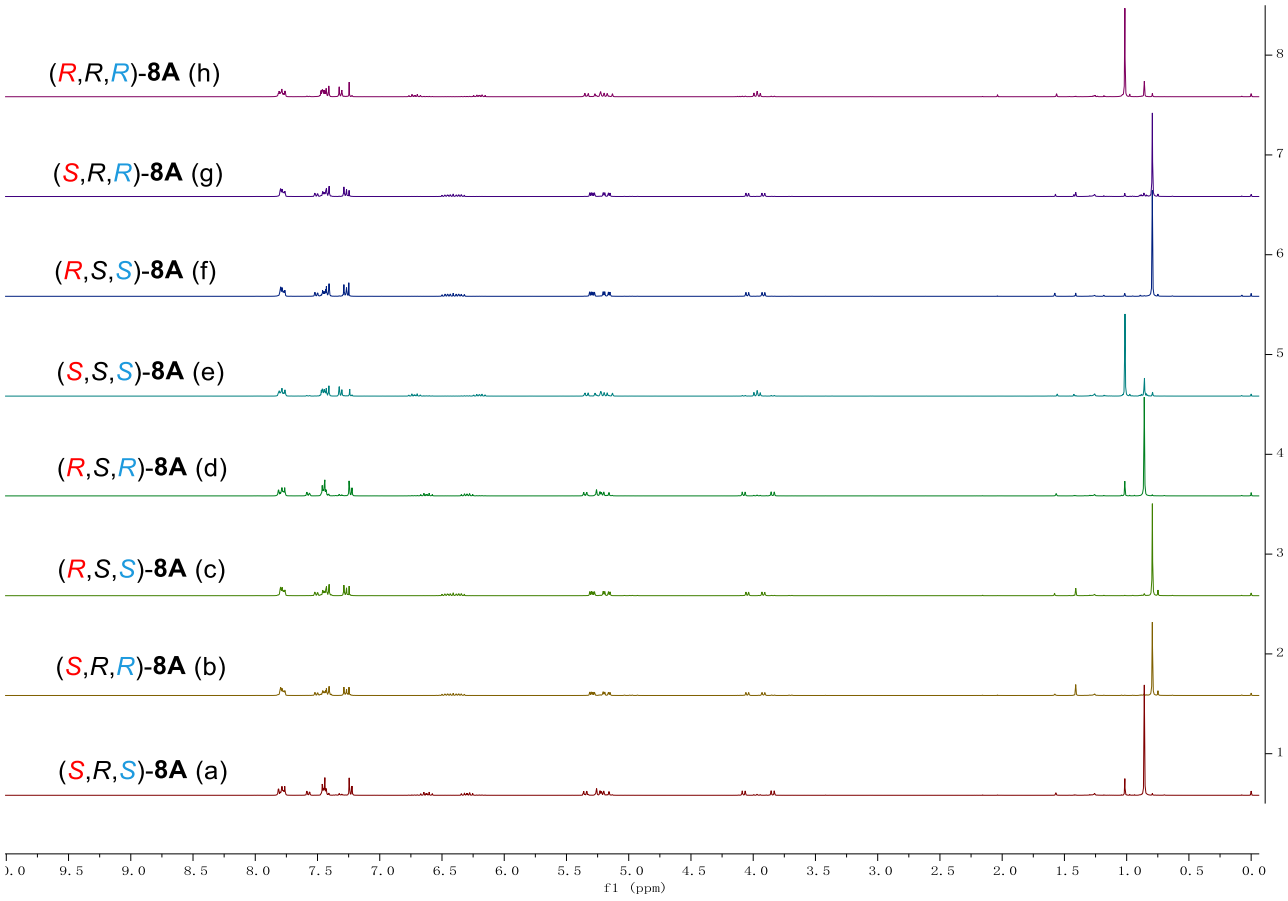
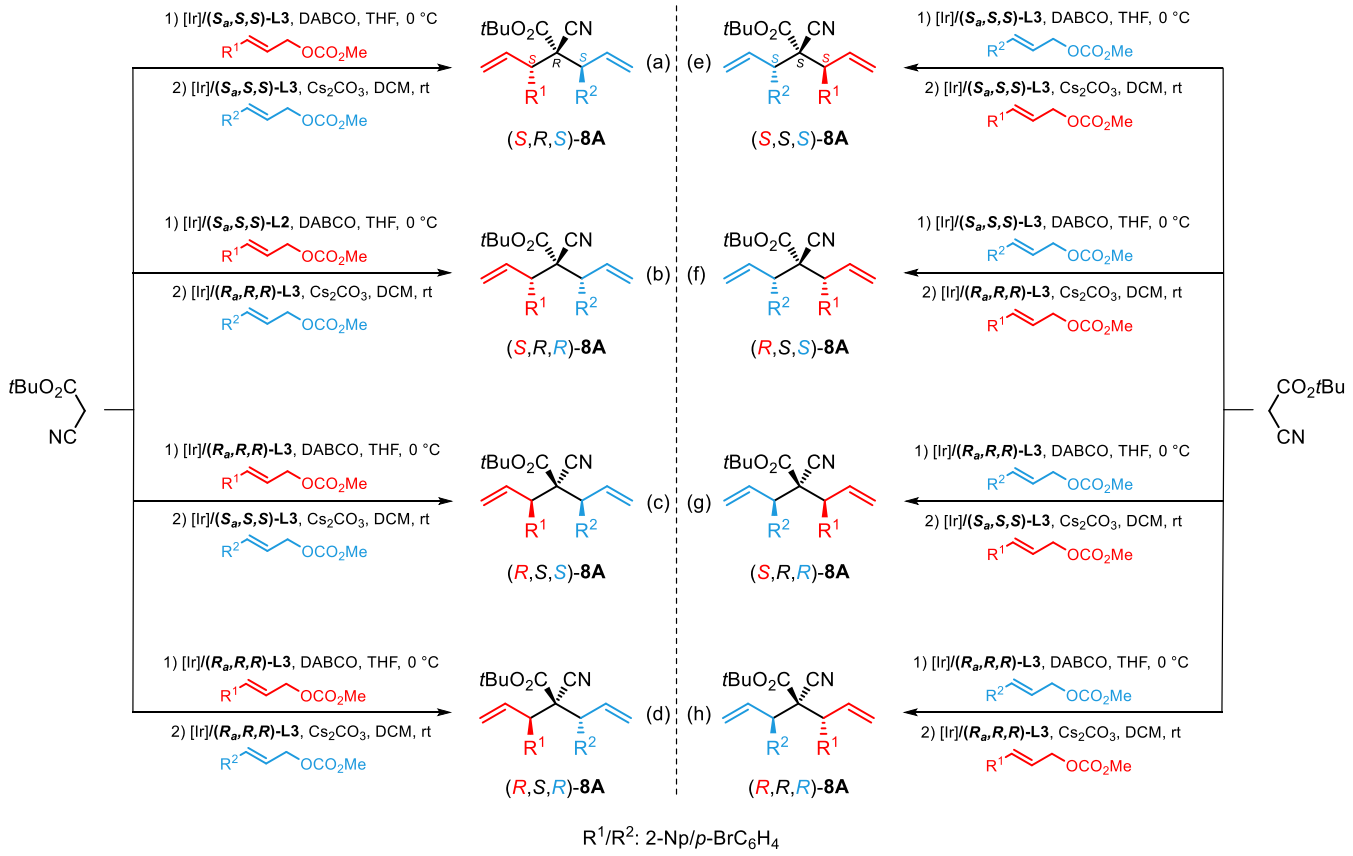
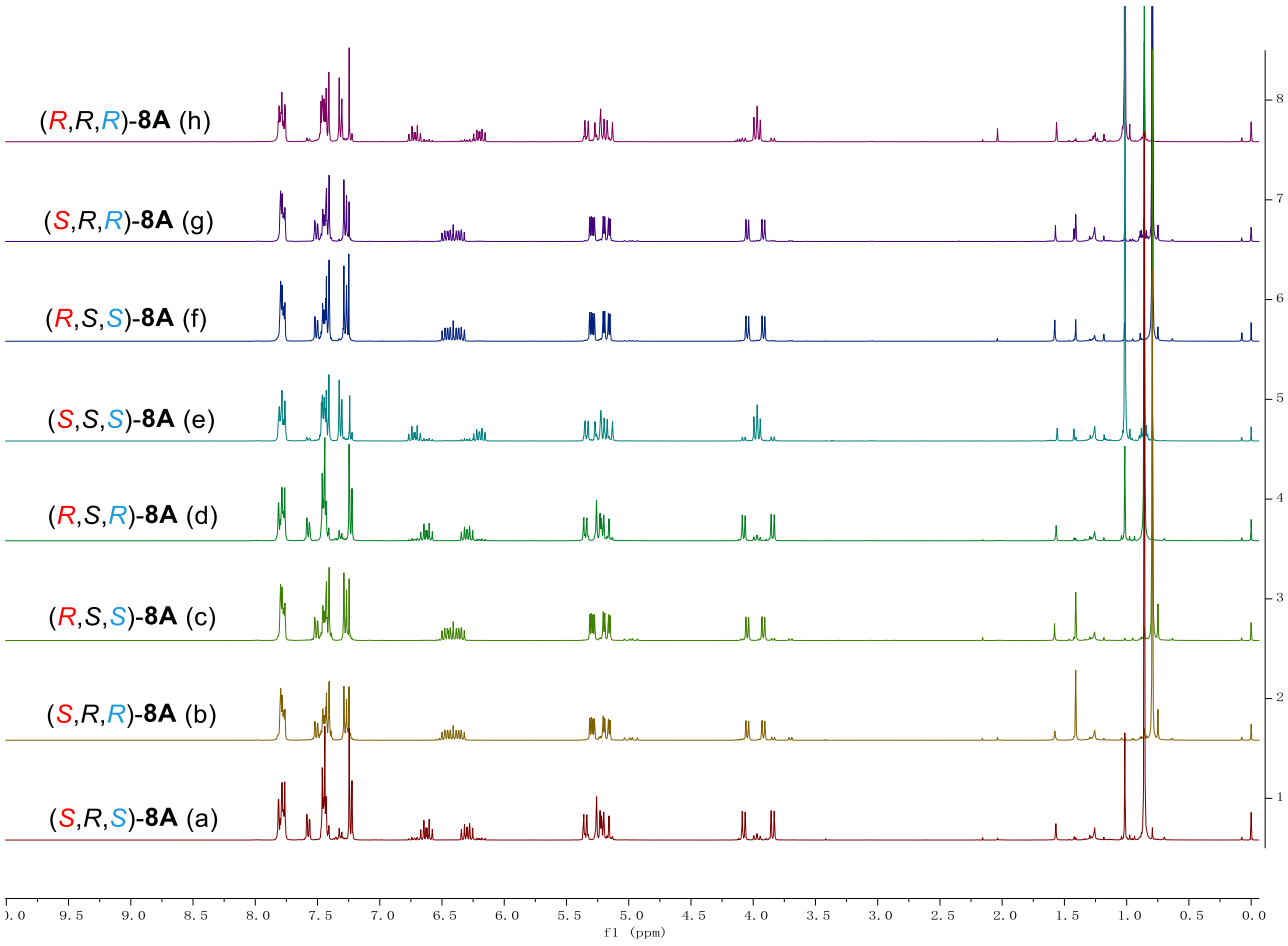
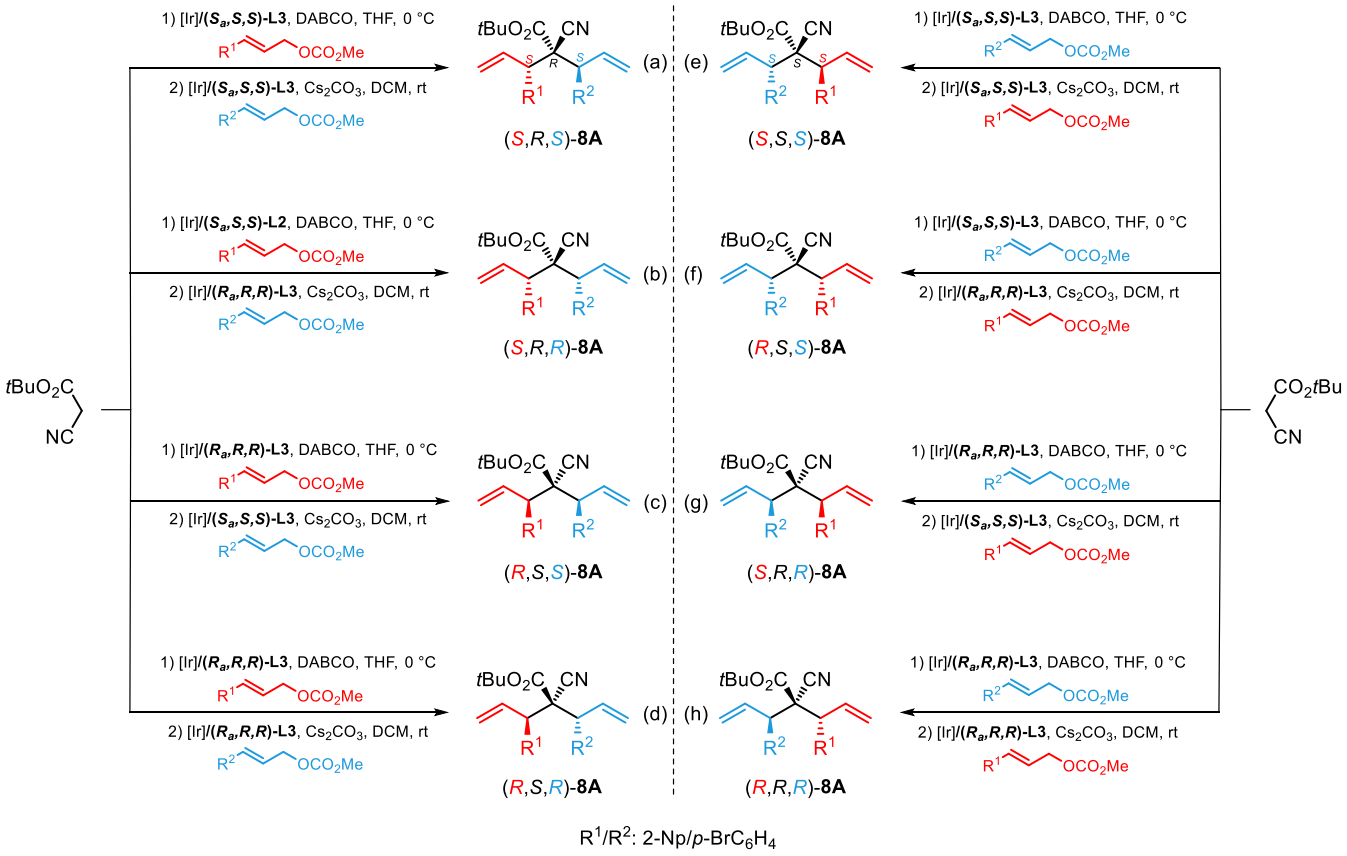
7.794
7.787
7.778
7.773
7.763
7.758
7.472
7.466
7.462
7.458
7.453
7.446
7.442
7.437
7.431
7.426
7.414
7.409
7.332
7.326
7.321
7.309
7.304
6.766
6.741
6.724
6.716
6.698
6.673
6.245
6.221
6.219
6.203
6.196
6.179
6.177
6.154
5.354
5.350
5.329
5.325
5.272
5.268
5.231
5.229
5.225
5.221
5.200
5.196
5.176
5.170
5.134
5.128
3.994
3.966
3.943
1.014
0.000
4.05
5.02
1.99
1.00
1.02
1.03
2.16
1.05
2.00
9.08
f1 (ppm)

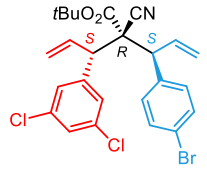

165.34
137.73
135.70
134.09
133.99
133.21
132.88
131.63
131.51
130.86
128.24
128.12
127.94
127.55
126.79
126.20
126.09
121.67
120.23
119.96
118.22
84.36
77.32
77.00
76.68
58.41
55.29
52.82
27.21
f1 (ppm)


(R,R,R)-8A (h)
(S,R,R)-8A (g)
(R,S,S)-8A (f)
(S,S,S)-8A (e)
(R,S,R)-8A (d)
(R,S,S)-8A (c)
(S,R,R)-8A (b)
(S,R,S)-8A (a)
f1 (ppm)

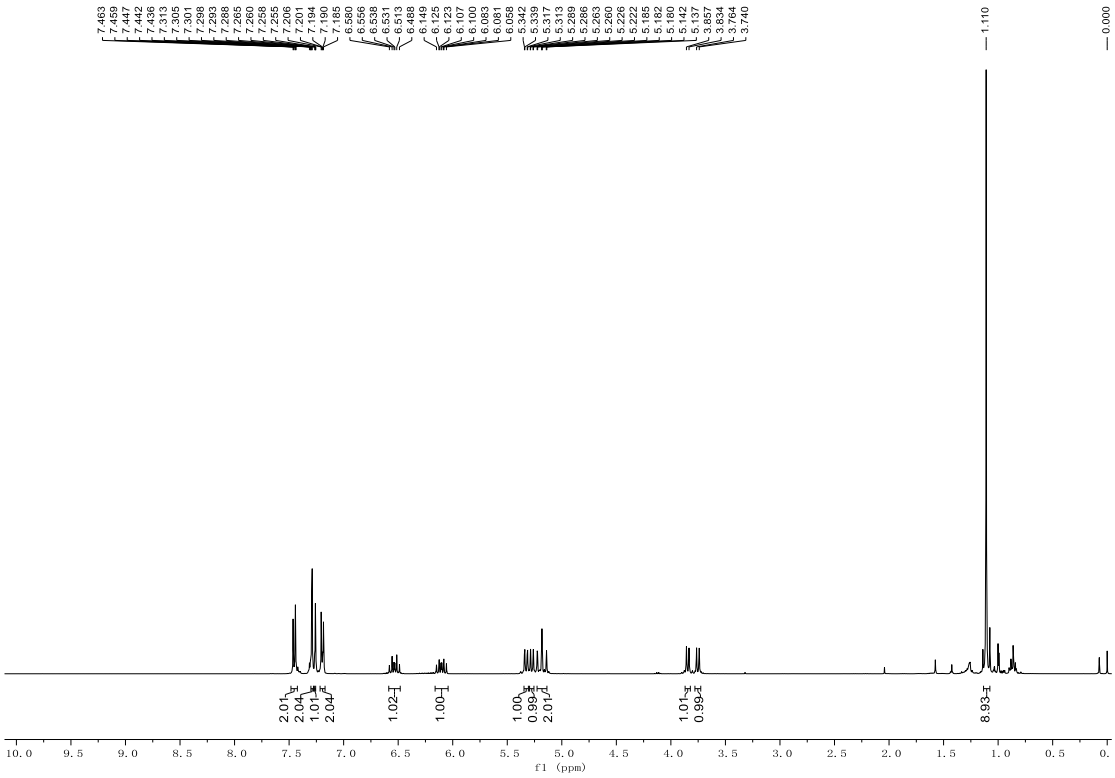

tBuO2C
NC
CO2tBu
CN
1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
OCO2Me
(S,R,S)-8A
(S,S,S)-8A
(S,R,R)-8A
(R,S,S)-8A
(R,S,R)-8A
(R,R,R)-8A
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
R1/R2: 2-Np/p-BrC6H4


(R,R,R)-8A (h)
(S,R,R)-8A (g)
(R,S,S)-8A (f)
(S,S,S)-8A (e)
(R,S,R)-8A (d)
(R,S,S)-8A (c)
(S,R,R)-8A (b)
(S,R,S)-8A (a)
f1 (ppm)


1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
tBuO2C CN
NC
CO2tBu
(S,R,S)-8A
(S,S,S)-8A
(S,R,R)-8A
(R,S,S)-8A
(R,S,R)-8A
(R,R,R)-8A
R1/R2: 2-Np/p-BrC6H4


tBuO2C
CN
S
R
S
Cl
Cl
Br

(*S*,*R*,*S*)-**8B**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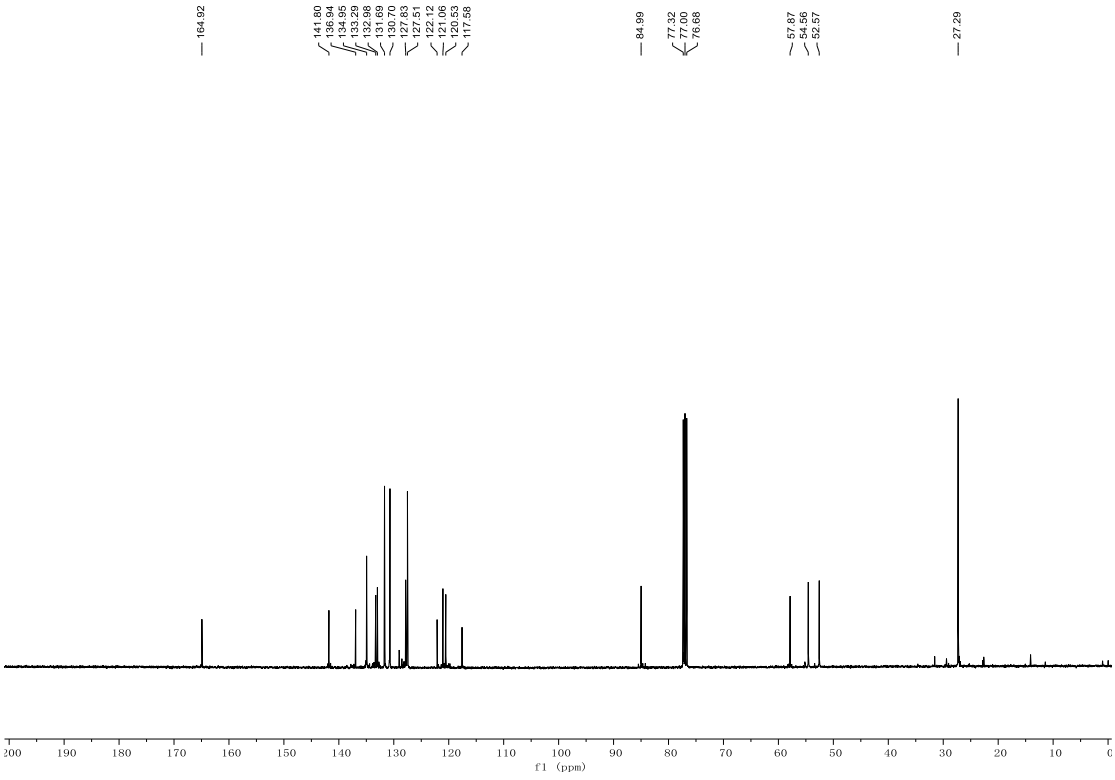
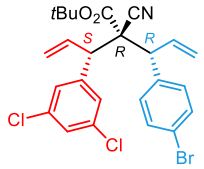
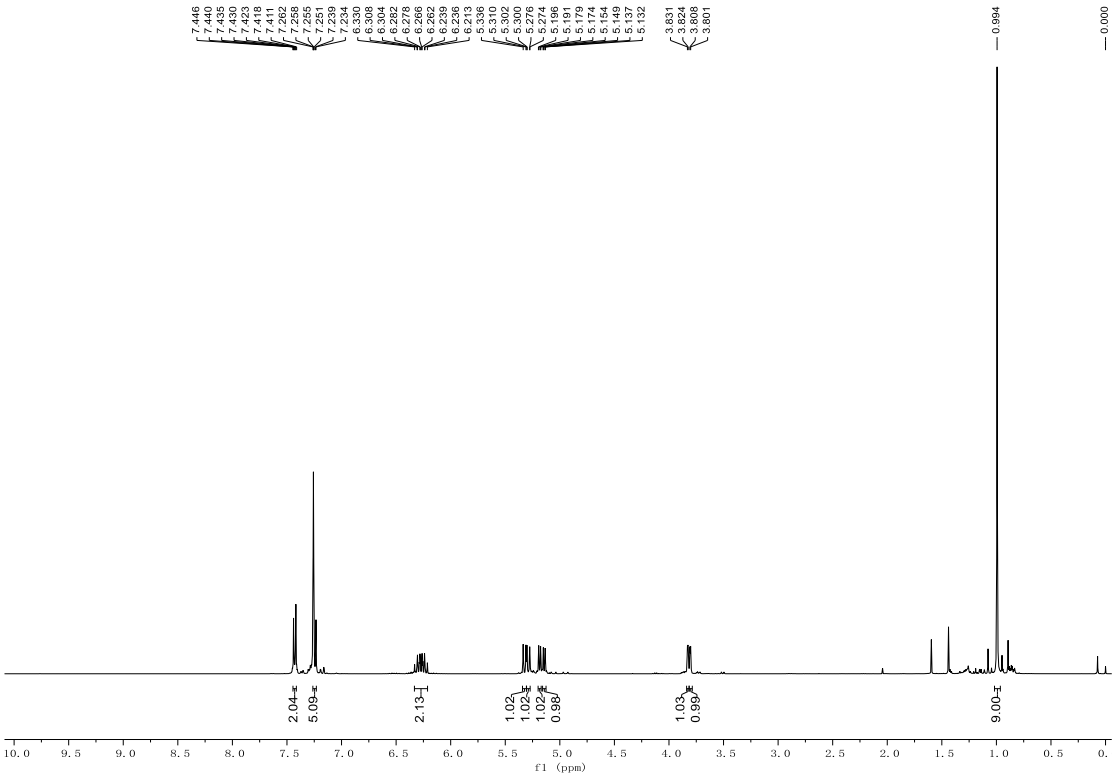
7.459
7.447
7.442
7.436
7.313
7.305
7.301
7.298
7.293
7.288
7.265
7.260
7.258
7.255
7.206
7.201
7.194
7.190
7.185
6.580
6.556
6.538
6.531
6.513
6.488
6.149
6.125
6.123
6.107
6.100
6.083
6.081
6.058
5.342
5.339
5.317
5.313
5.289
5.286
5.263
5.260
5.226
5.222
5.185
5.182
5.180
5.142
5.137
3.857
3.834
3.764
3.740
1.110
0.000
2.01
2.04
1.01
2.04
1.02
1.00
1.00
0.99
2.01
1.01
0.99
8.93
f1 (ppm)


164.92
141.80
136.94
134.95
133.29
132.96
131.68
130.70
127.83
127.51
122.12
121.06
120.53
117.58
84.99
77.32
77.00
76.68
57.87
54.56
52.57
27.29
f1 (ppm)


tBuO2C
CN
S
R
R
Cl
Cl
Br

(*S*,*R*,*R*)-**8B**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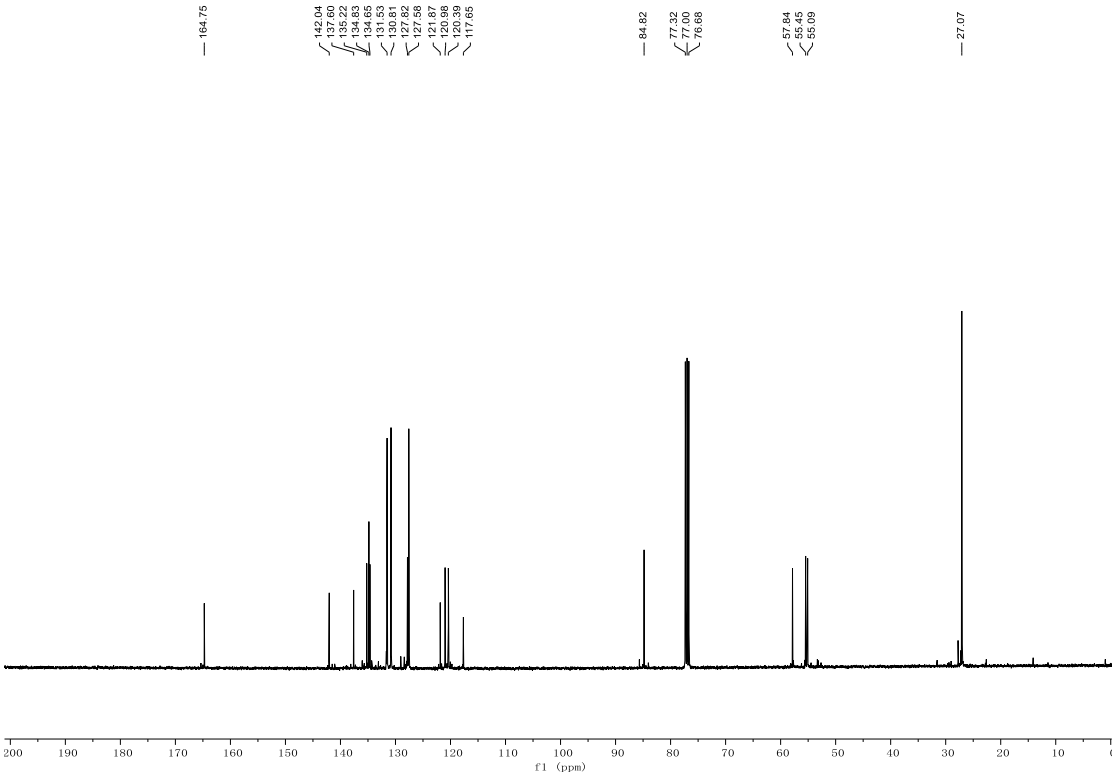
7.418
7.411
7.262
7.258
7.255
7.251
7.239
7.234
6.330
6.308
6.304
6.282
6.278
6.266
6.262
6.239
6.236
6.213
5.336
5.310
5.302
5.300
5.276
5.274
5.196
5.191
5.179
5.174
5.154
5.149
5.137
5.132
3.831
3.824
3.808
3.801
0.994
0.000
2.04
5.09
2.13
1.02
1.02
1.02
0.98
1.03
0.99
9.00
f1 (ppm)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134.65
131.53
130.81
127.82
127.58
121.87
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120.39
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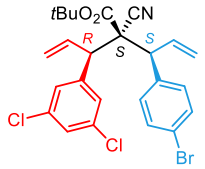
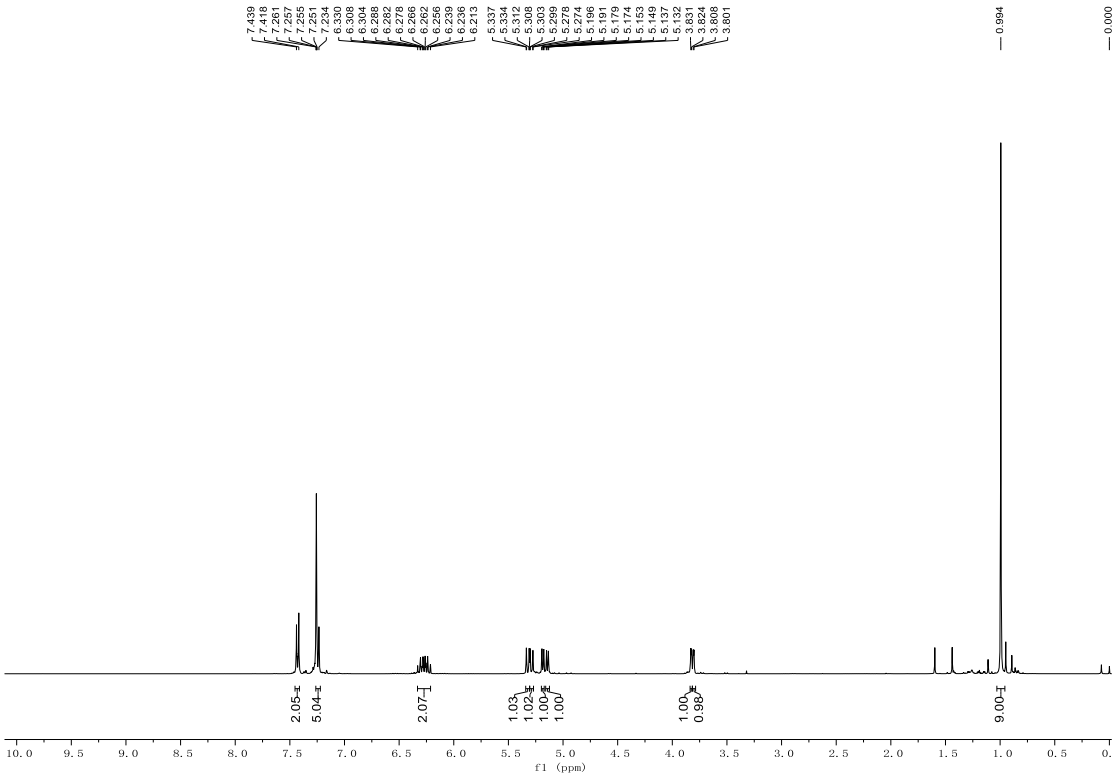
84.82
77.32
77.00
76.68
57.84
55.45
55.09
27.07
f1 (ppm)


tBuO2C
CN
R
S
S
Cl
Cl
Br

(*R*,*S*,*S*)-**8B**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6.308
6.304
6.288
6.282
6.278
6.266
6.262
6.256
6.239
6.236
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5.334
5.312
5.308
5.303
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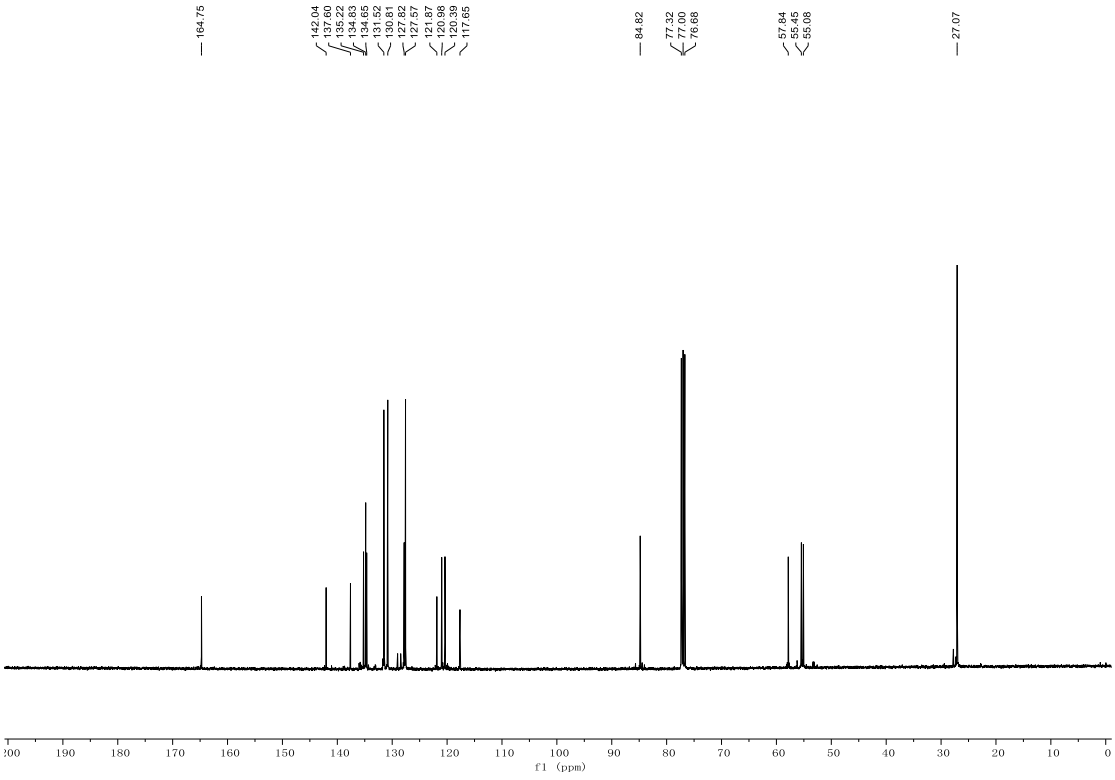
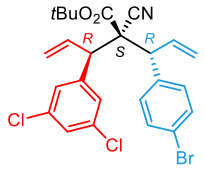
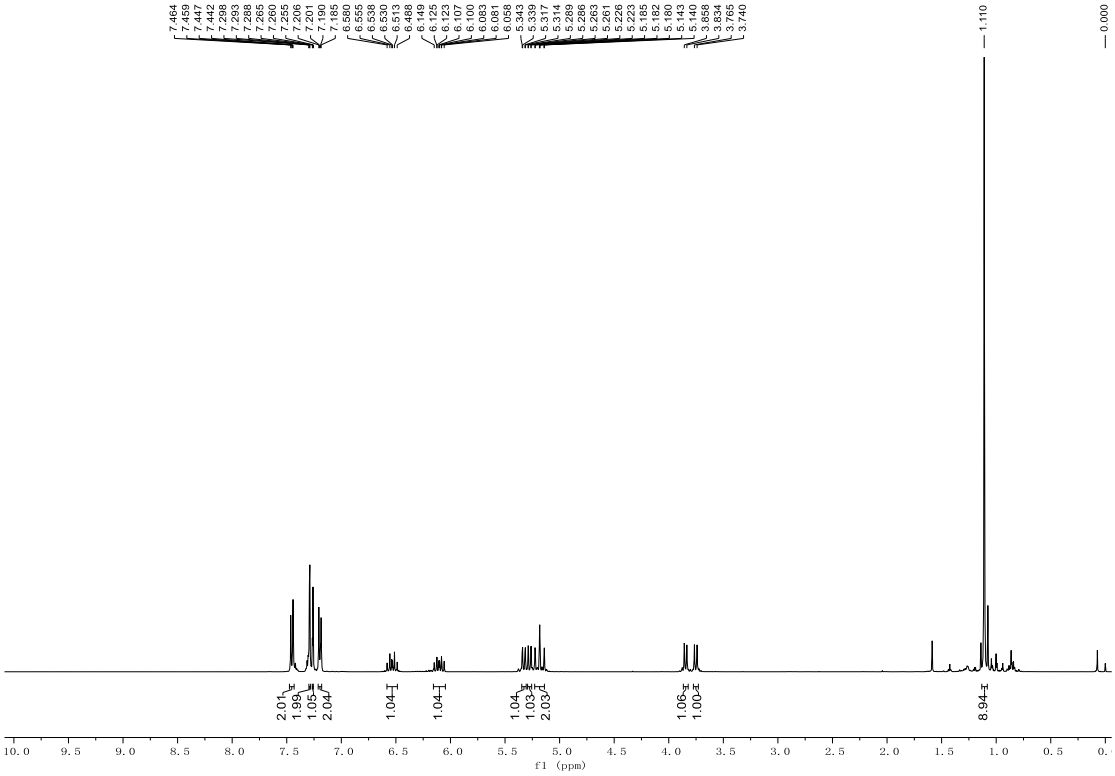
5.274
5.196
5.191
5.179
5.174
5.153
5.149
5.137
5.132
3.831
3.824
3.808
3.801
0.994
0.000
2.05
5.04
2.07
1.03
1.02
1.00
1.00
1.00
0.98
9.00
f1 (ppm)


164.75
142.04
137.60
135.22
134.83
134.65
131.52
130.81
127.82
127.57
121.87
120.98
120.39
117.65
84.82
77.32
77.00
76.68
57.84
55.45
55.08
27.07
f1 (ppm)


tBuO2C
CN
R
S
R
Cl
Cl
Br

(*R*,*S*,*R*)-**8B**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7.293
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7.260
7.255
7.206
7.201
7.190
7.185
6.580
6.555
6.538
6.530
6.513
6.498
6.449
6.125
6.123
6.107
6.100
6.083
6.081
6.058
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5.223
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5.182
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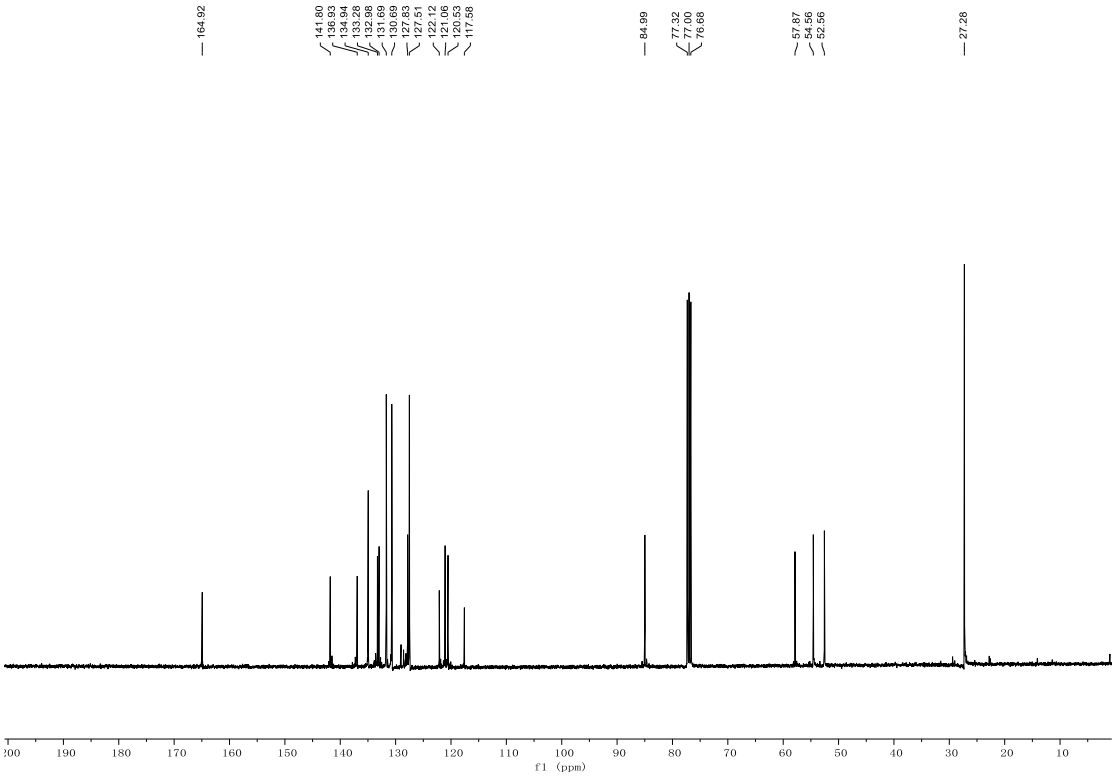
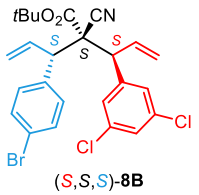
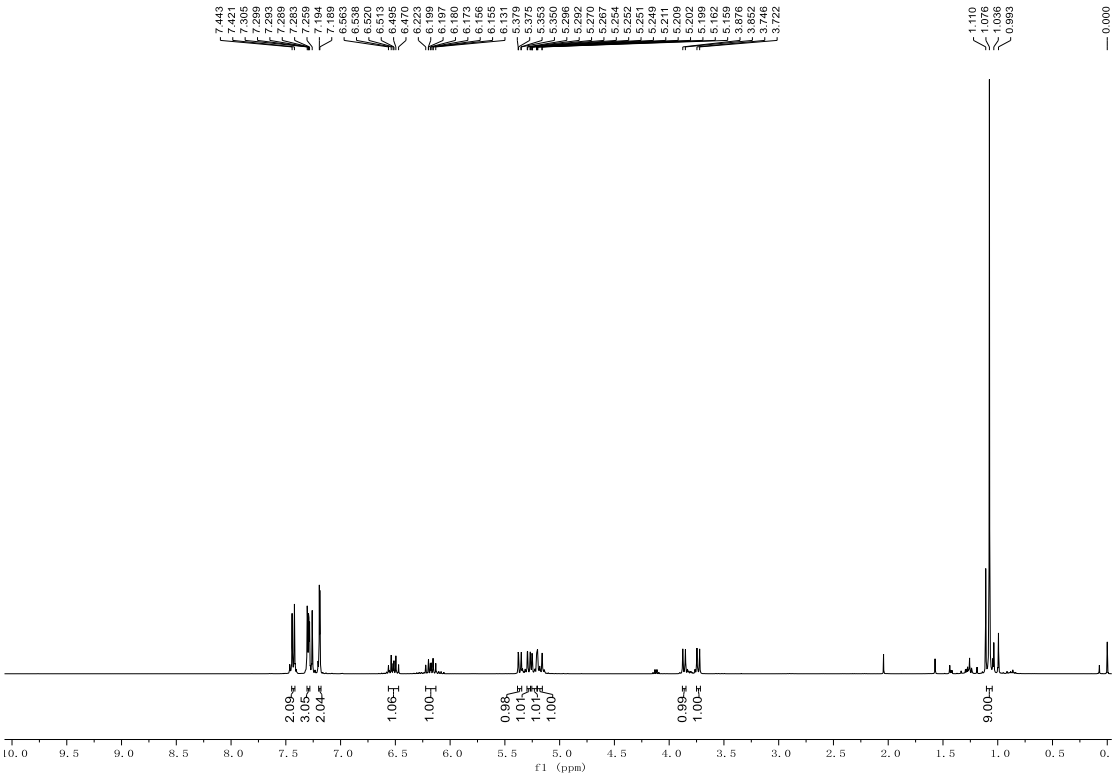
5.143
5.140
3.858
3.834
3.765
3.740
1.110
0.000
2.01
1.99
1.05
2.04
1.04
1.04
1.04
1.03
2.03
1.06
1.00
8.94
f1 (ppm)


164.92
141.80
136.93
134.94
133.28
132.98
131.69
130.60
127.83
127.51
122.12
121.06
120.53
117.58
84.99
77.32
77.00
76.68
57.87
54.56
52.56
27.28
f1 (ppm)


tBuO2C
CN
S
S
S
Br
Cl
Cl

(*S*,S,*S*)-**8B**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7.288
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7.259
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6.513
6.495
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6.180
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6.155
6.131
5.379
5.375
5.353
5.350
5.296
5.292
5.270
5.267
5.254
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5.251
5.249
5.211
5.209
5.202
5.199
5.162
5.159
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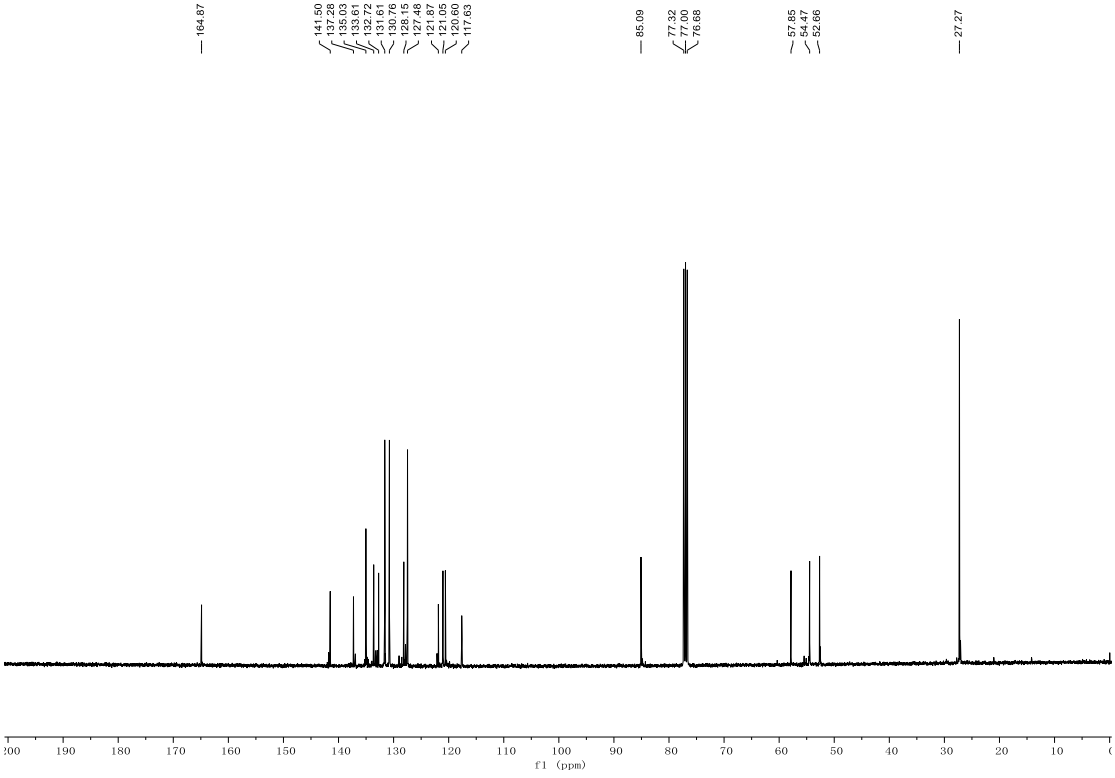
3.852
3.746
3.722
1.110
1.076
1.036
0.993
0.000
2.09
3.05
2.04
1.06
1.00
0.98
1.01
1.01
1.00
0.99
1.00
9.00
f1 (ppm)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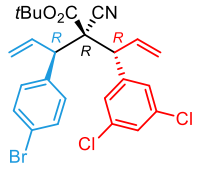
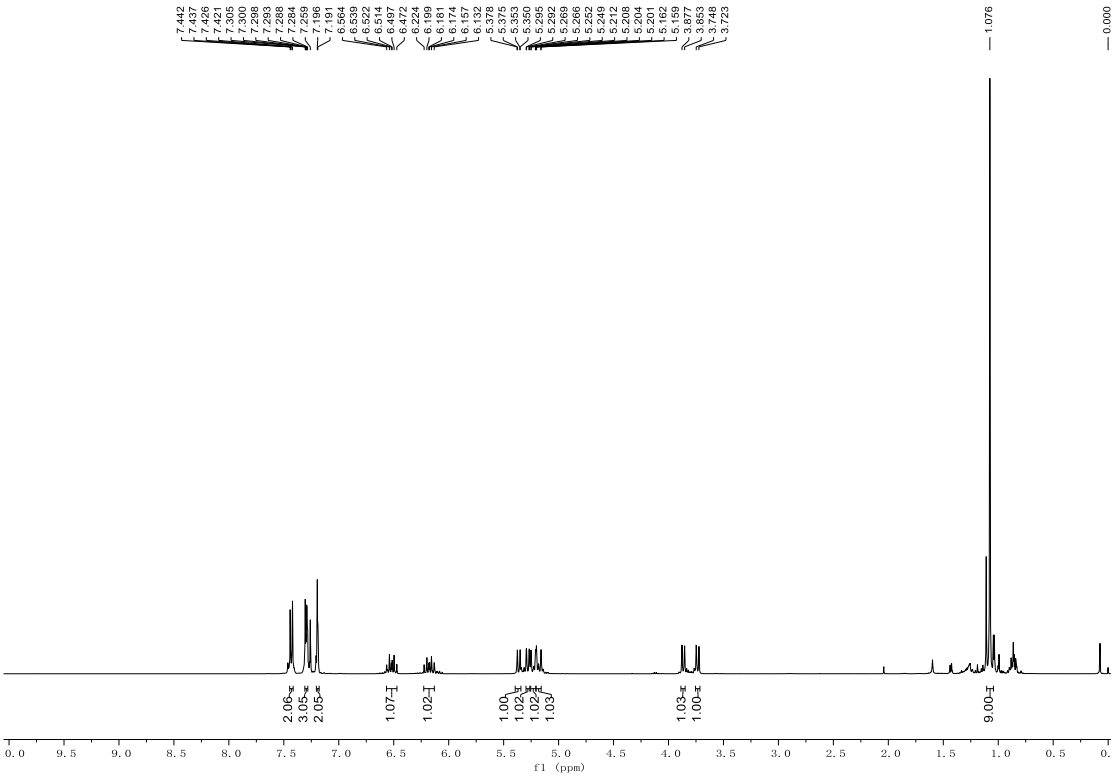
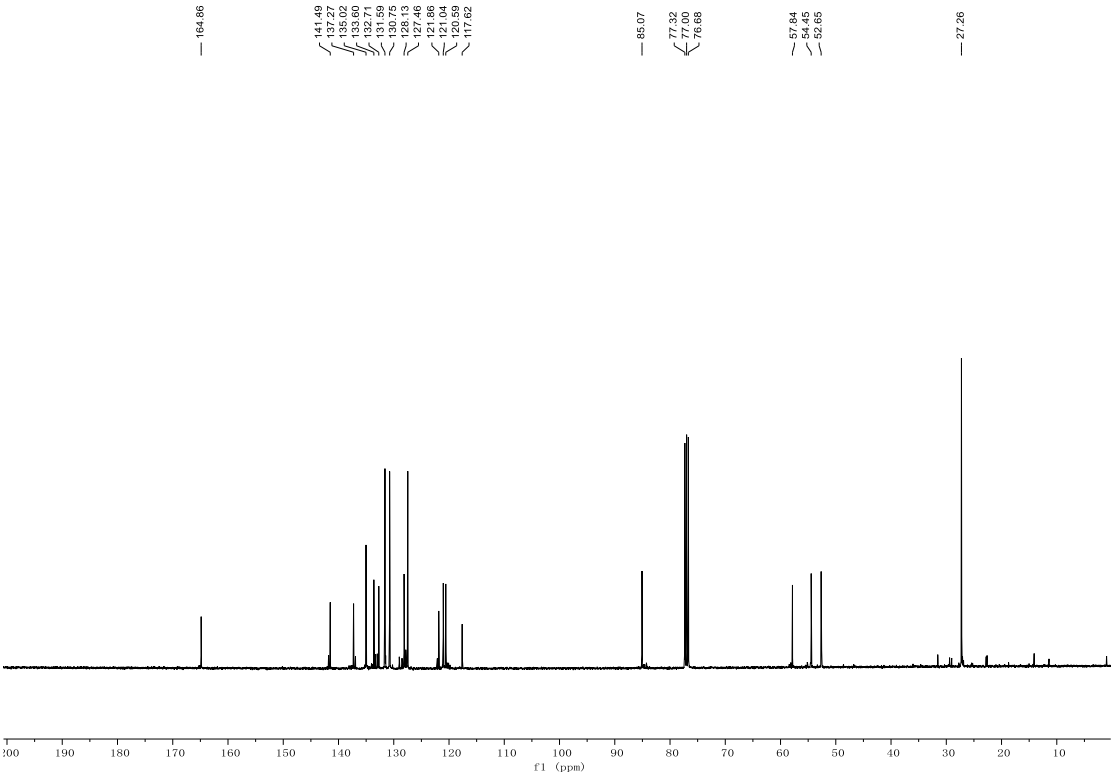
135.03
133.61
132.72
131.61
130.76
128.15
127.48
121.87
121.05
120.60
117.63
85.09
77.32
77.00
76.68
57.85
54.47
52.66
27.27
f1 (ppm)


tBuO2C
CN
R
R
R
Br
Cl
Cl

(*R*,*R*,*R*)-**8B**


7.442
7.437
7.426
7.421
7.305
7.300
7.298
7.293
7.288
7.284
7.259
7.196
7.191
6.564
6.539
6.522
6.514
6.497
6.472
6.224
6.199
6.181
6.174
6.157
6.132
5.378
5.375
5.353
5.350
5.295
5.292
5.269
5.266
5.252
5.249
5.212
5.208
5.204
5.201
5.162
5.159
3.877
3.853
3.748
3.723
1.076
0.000
2.06
3.05
2.05
1.07
1.02
1.00
1.02
1.02
1.03
1.03
1.00
9.00
f1 (ppm)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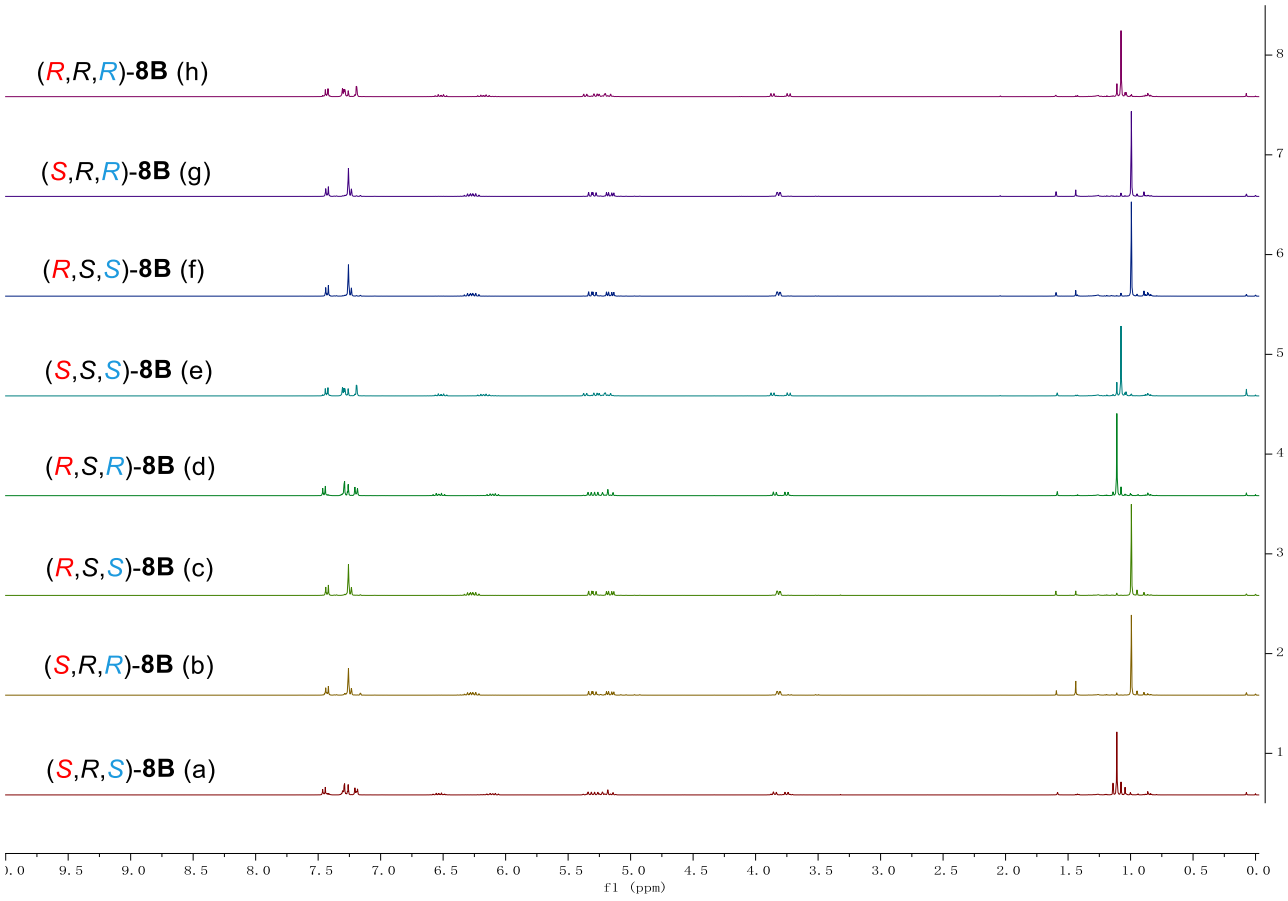
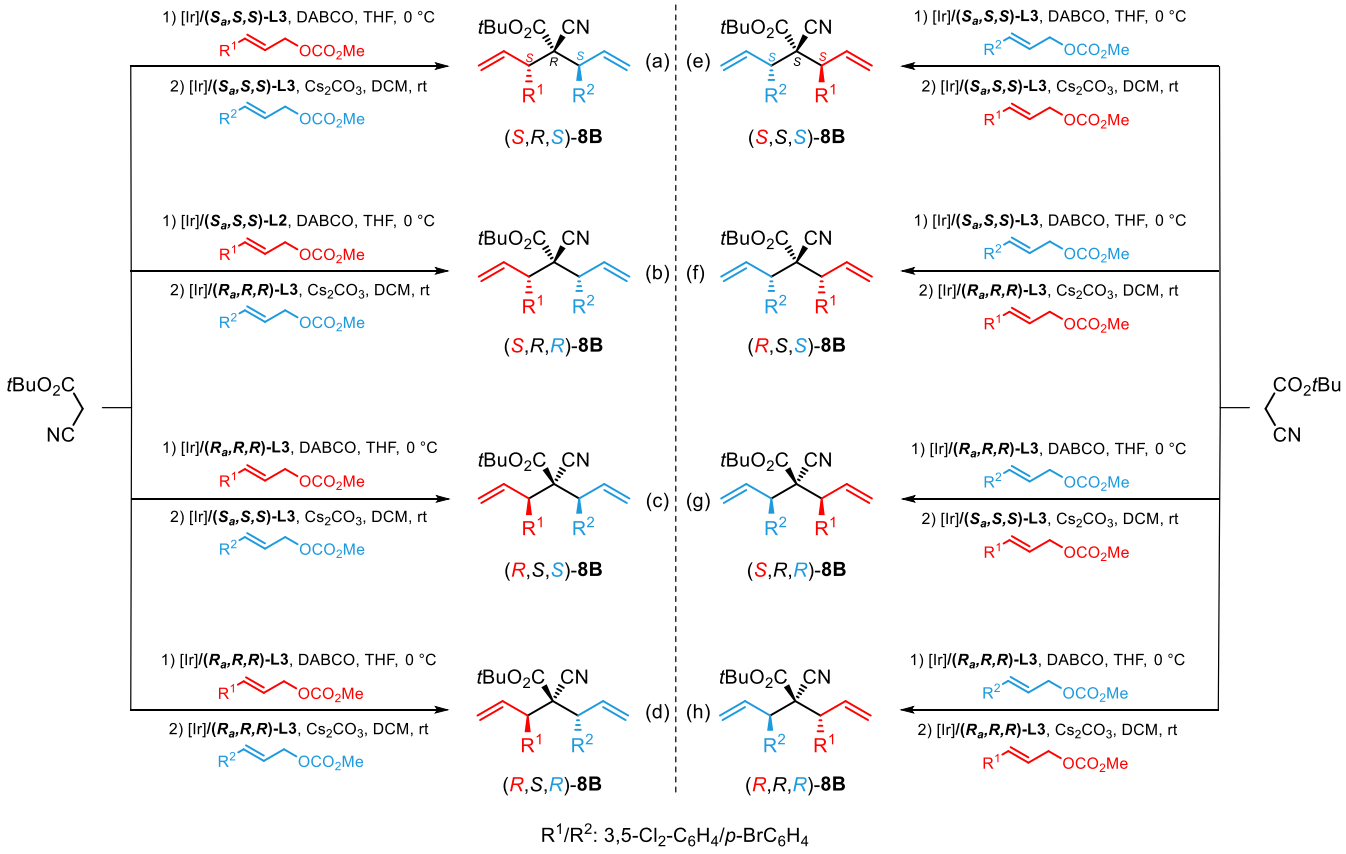
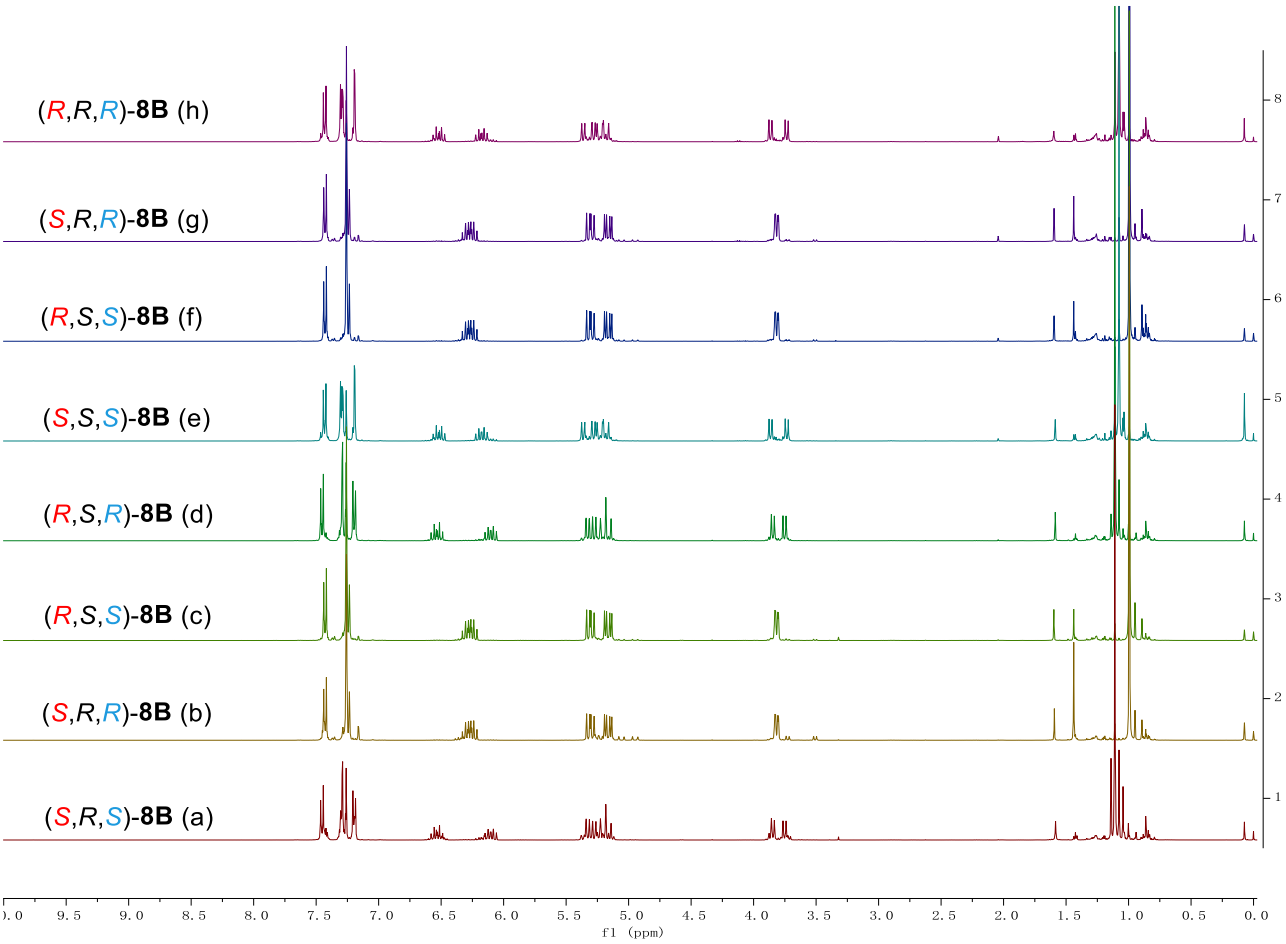
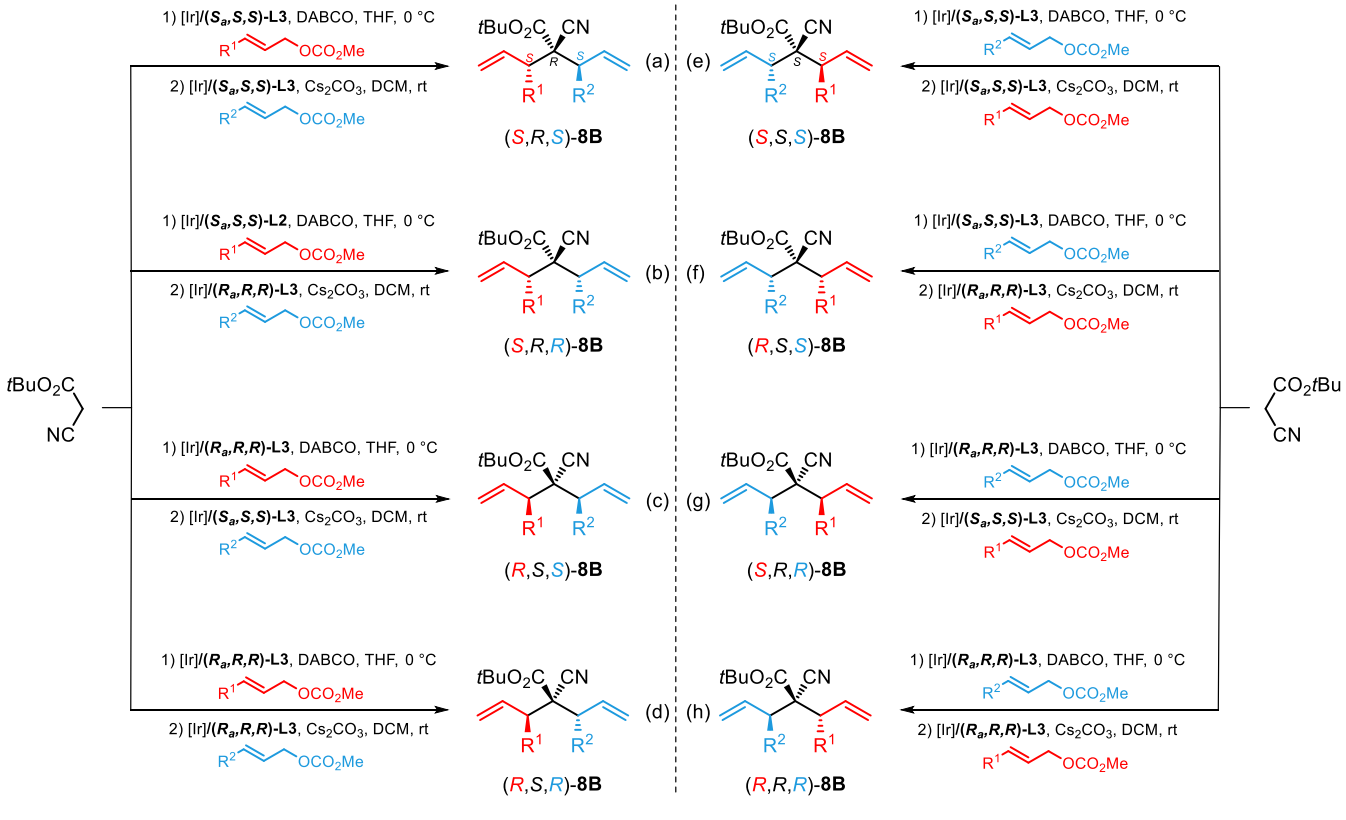
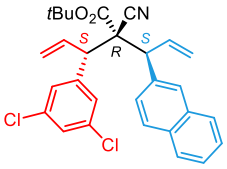
137.27
135.02
133.60
132.71
131.59
130.75
128.13
127.46
121.86
121.04
120.59
117.62
85.07
77.32
77.00
76.68
57.84
54.45
52.65
27.26
f1 (ppm)


(R,R,R)-8B (h)
(S,R,R)-8B (g)
(R,S,S)-8B (f)
(S,S,S)-8B (e)
(R,S,R)-8B (d)
(R,S,S)-8B (c)
(S,R,R)-8B (b)
(S,R,S)-8B (a)
f1 (ppm)

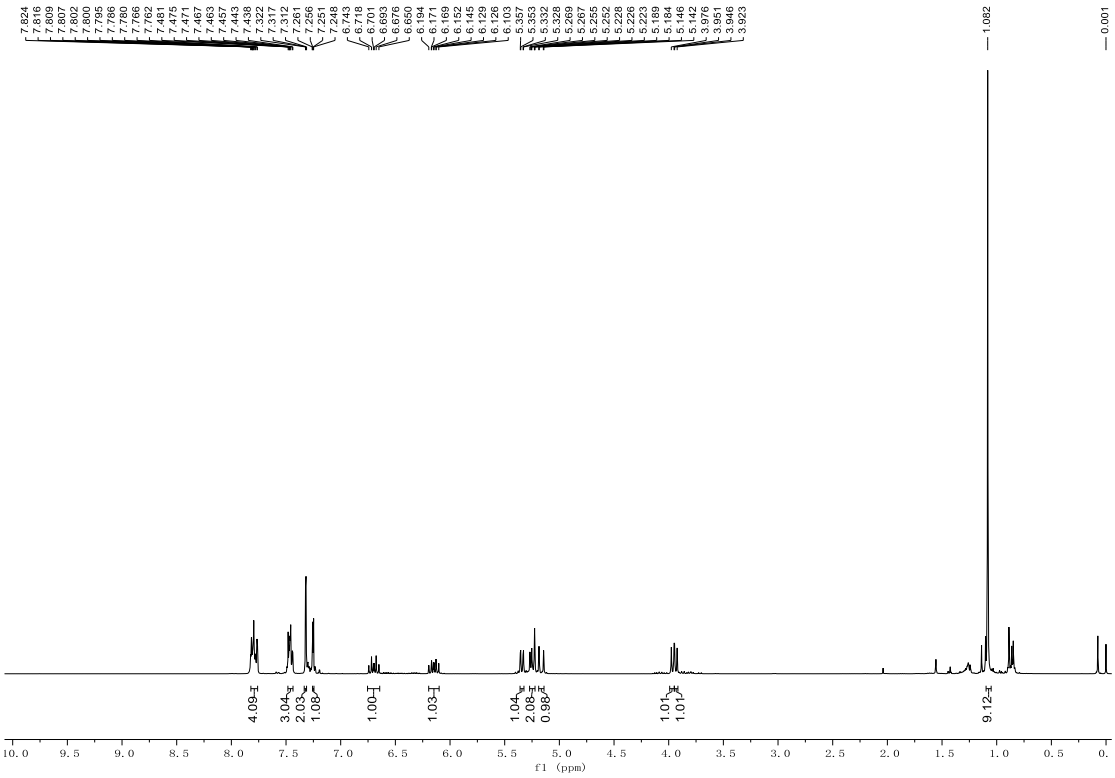

tBuO2C
NC
CO2tBu
CN
1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
OCO2Me
(a) (S,R,S)-8B
(b) (S,R,R)-8B
(c) (R,S,S)-8B
(d) (R,S,R)-8B
(e) (S,S,S)-8B
(f) (R,S,S)-8B
(g) (S,R,R)-8B
(h) (R,R,R)-8B
R1/R2: 3,5-Cl2-C6H4/p-BrC6H4

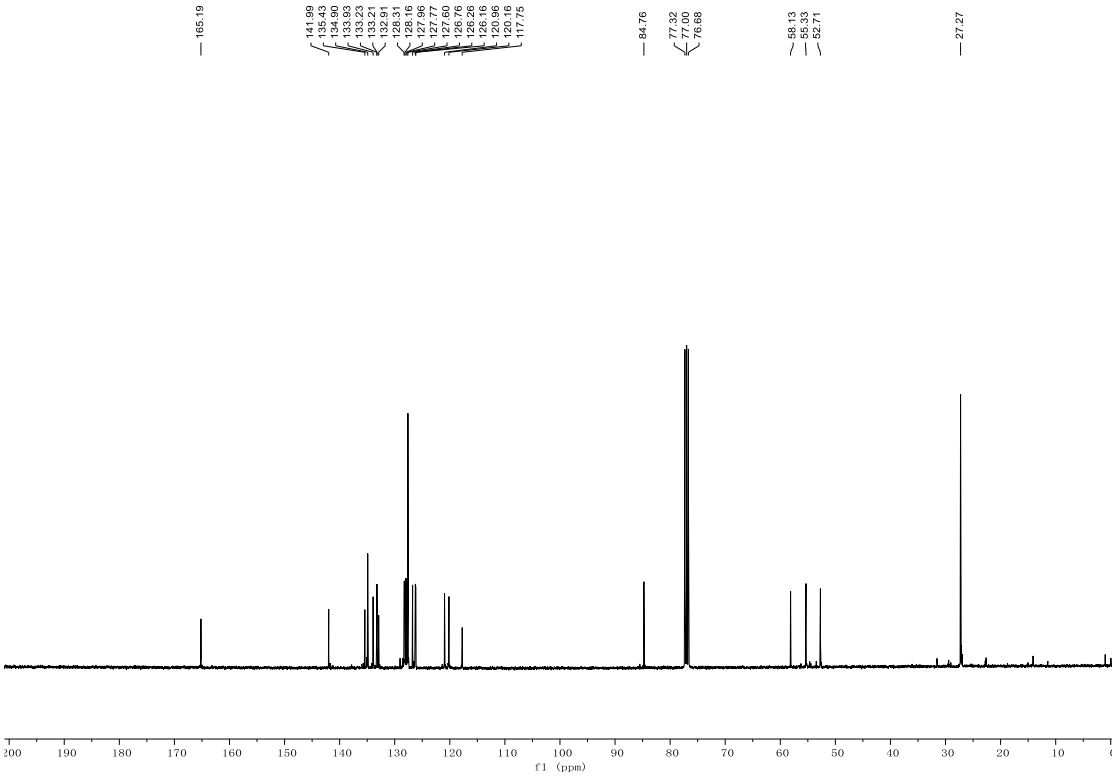

(R,R,R)-8B (h)
(S,R,R)-8B (g)
(R,S,S)-8B (f)
(S,S,S)-8B (e)
(R,S,R)-8B (d)
(R,S,S)-8B (c)
(S,R,R)-8B (b)
(S,R,S)-8B (a)
f1 (ppm)

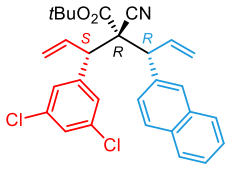

tBuO2C
NC
CO2tBu
CN
(a) (S,R,S)-8B
(b) (S,R,R)-8B
(c) (R,S,S)-8B
(d) (R,S,R)-8B
(e) (S,S,S)-8B
(f) (R,S,S)-8B
(g) (S,R,R)-8B
(h) (R,R,R)-8B
1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
R1/R2: 3,5-Cl2-C6H4/p-BrC6H4


tBuO2C
CN
S
R
S
Cl
Cl

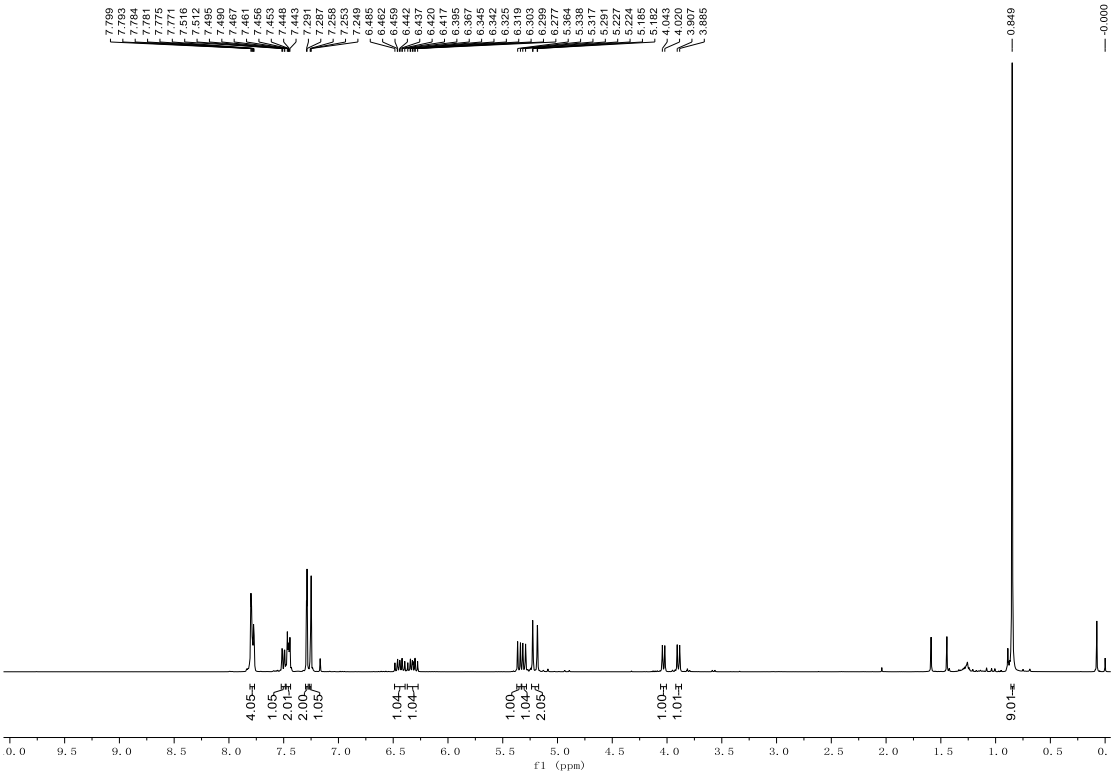
(*S*,*R*,*S*)-**8C**


7.824
7.816
7.809
7.807
7.802
7.800
7.795
7.786
7.780
7.766
7.762
7.481
7.475
7.471
7.467
7.463
7.457
7.443
7.438
7.322
7.317
7.312
7.261
7.256
7.251
7.248
6.743
6.718
6.701
6.693
6.676
6.655
6.194
6.171
6.169
6.152
6.145
6.129
6.126
6.103
5.357
5.353
5.332
5.328
5.269
5.267
5.255
5.252
5.228
5.226
5.223
5.189
5.184
5.146
5.142
3.976
3.951
3.946
3.923
1.082
0.001
4.09
3.04
2.03
1.08
1.00
1.03
1.04
2.08
0.98
1.01
1.01
9.12
f1 (ppm)


165.19
141.99
135.43
134.90
133.93
133.23
133.21
132.91
128.31
128.16
127.96
127.77
127.60
126.76
126.26
126.16
120.96
120.16
117.75
84.76
77.32
77.00
76.68
58.13
55.33
52.71
27.27
f1 (ppm)


tBuO2C
CN
S
R
R
Cl
Cl

(*S*,*R*,*R*)-**8C**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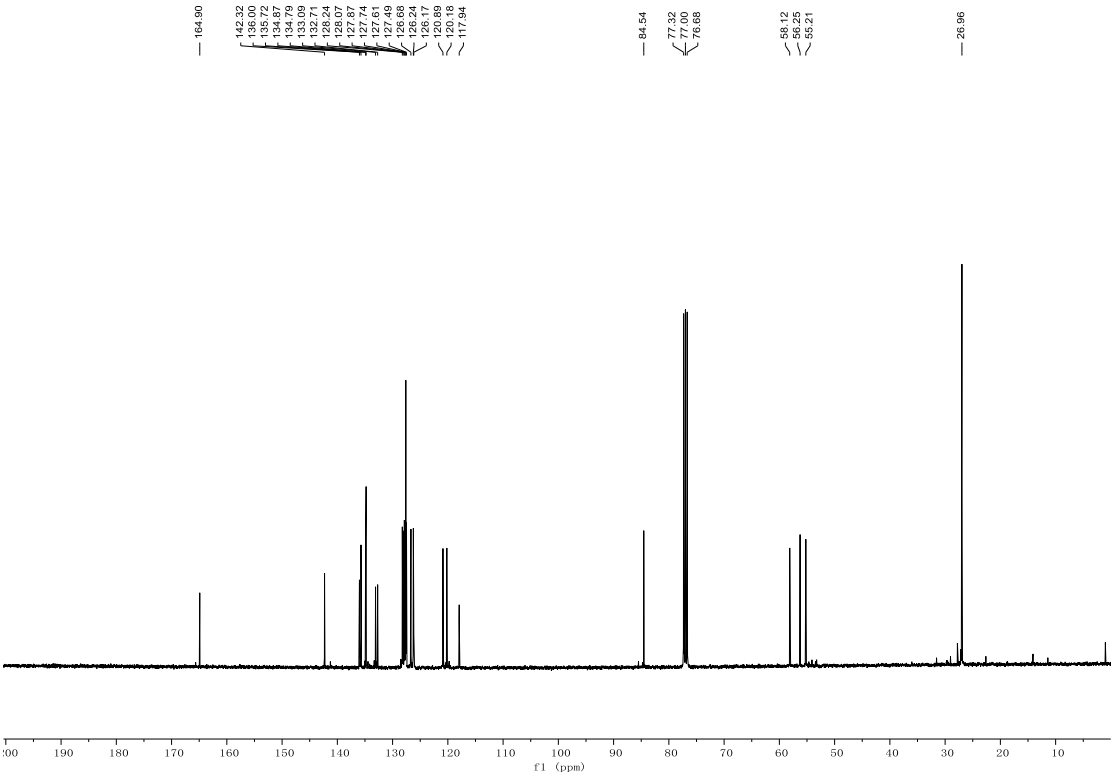
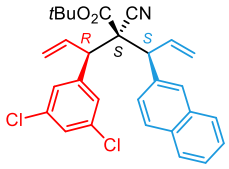
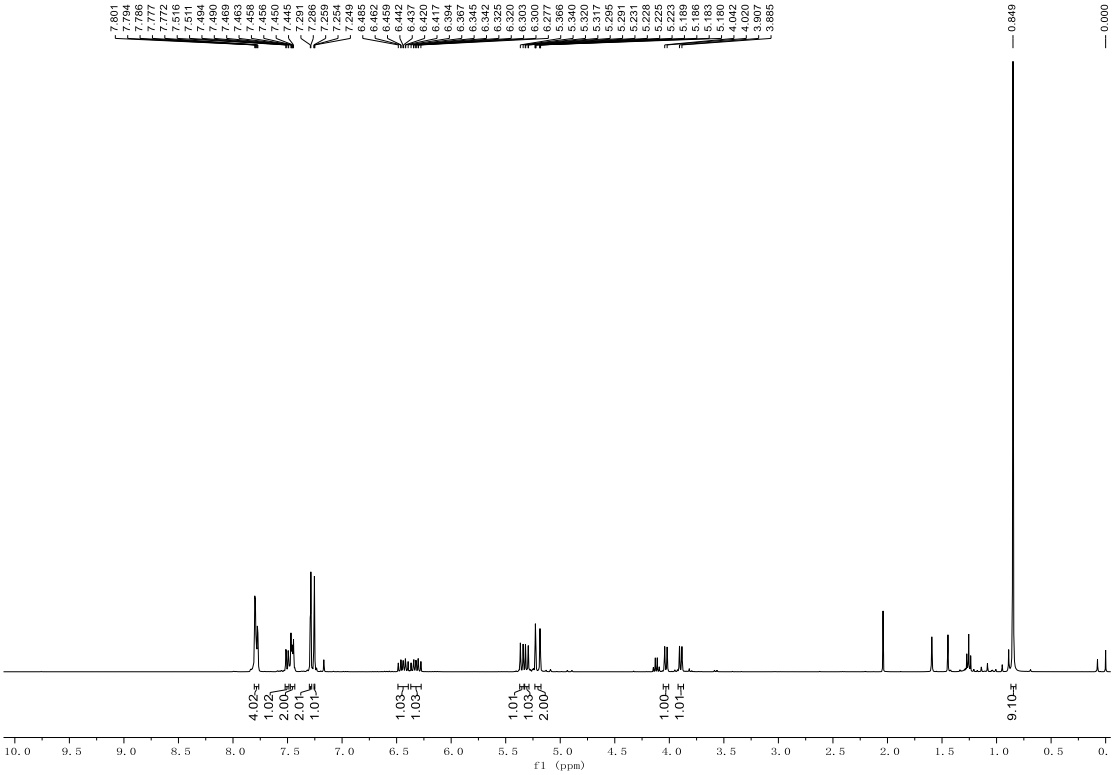
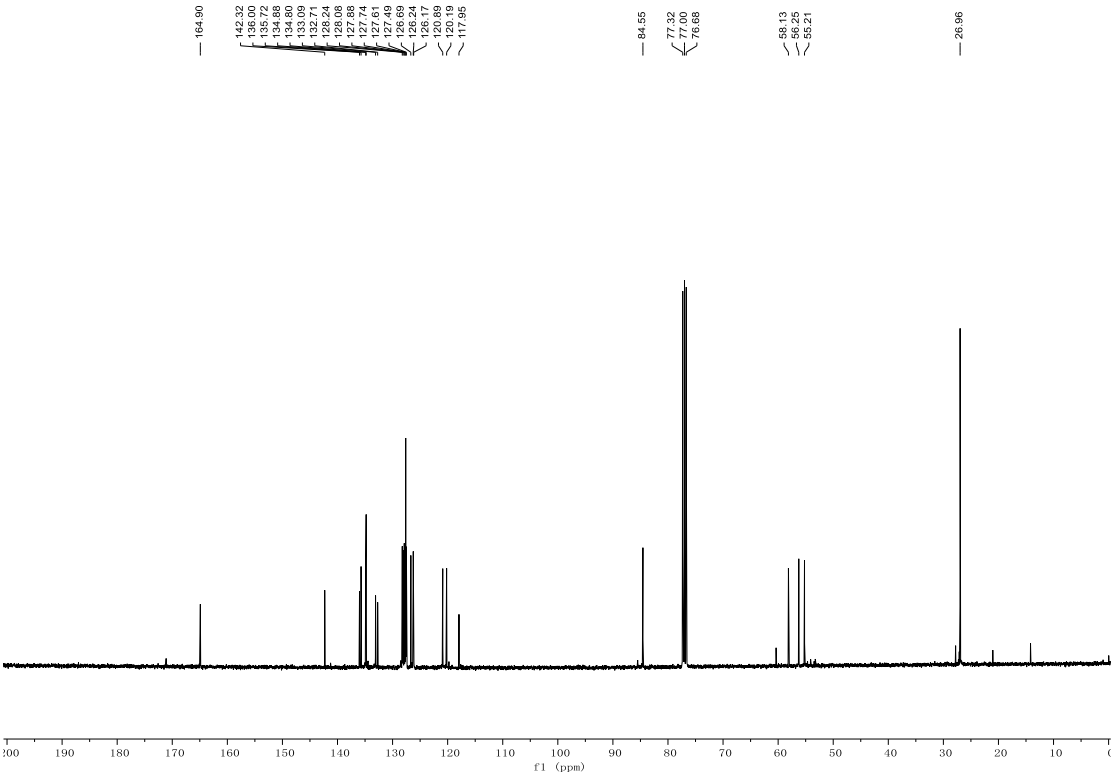
7.793
7.784
7.781
7.775
7.771
7.516
7.512
7.495
7.490
7.467
7.461
7.456
7.453
7.448
7.443
7.291
7.287
7.258
7.253
7.249
6.485
6.462
6.459
6.442
6.437
6.420
6.417
6.395
6.367
6.345
6.342
6.325
6.319
6.303
6.299
6.277
5.364
5.338
5.317
5.291
5.277
5.224
5.185
5.182
4.043
4.020
3.907
3.885
0.849
-0.000
4.05
1.05
2.01
2.00
1.05
1.04
1.04
1.00
1.04
2.05
1.00
1.01
9.01
f1 (ppm)

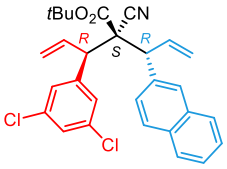

164.90
142.32
136.00
135.72
134.87
134.79
133.09
132.71
128.24
128.07
127.87
127.74
127.61
127.49
126.68
126.24
126.17
120.69
120.18
117.94
84.54
77.32
77.00
76.68
58.12
56.25
55.21
26.96
f1 (ppm)


tBuO2C
CN
R
S
S
Cl
Cl

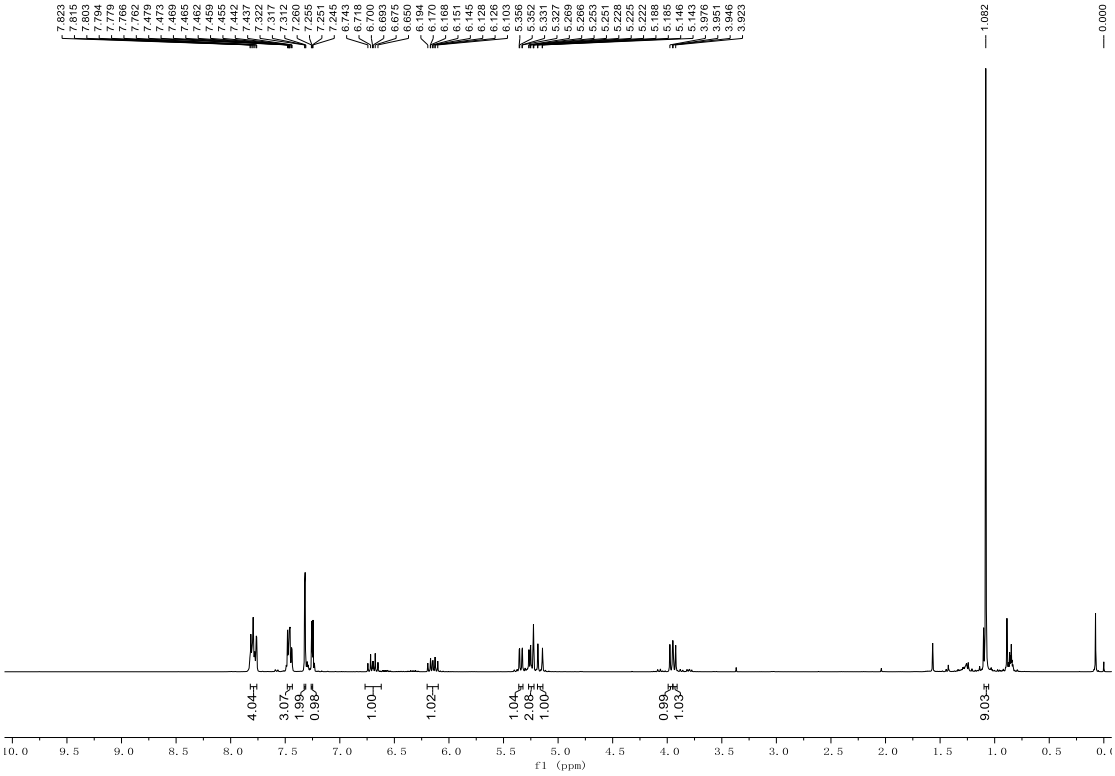
(*R*,*S*,*S*)-**8C**

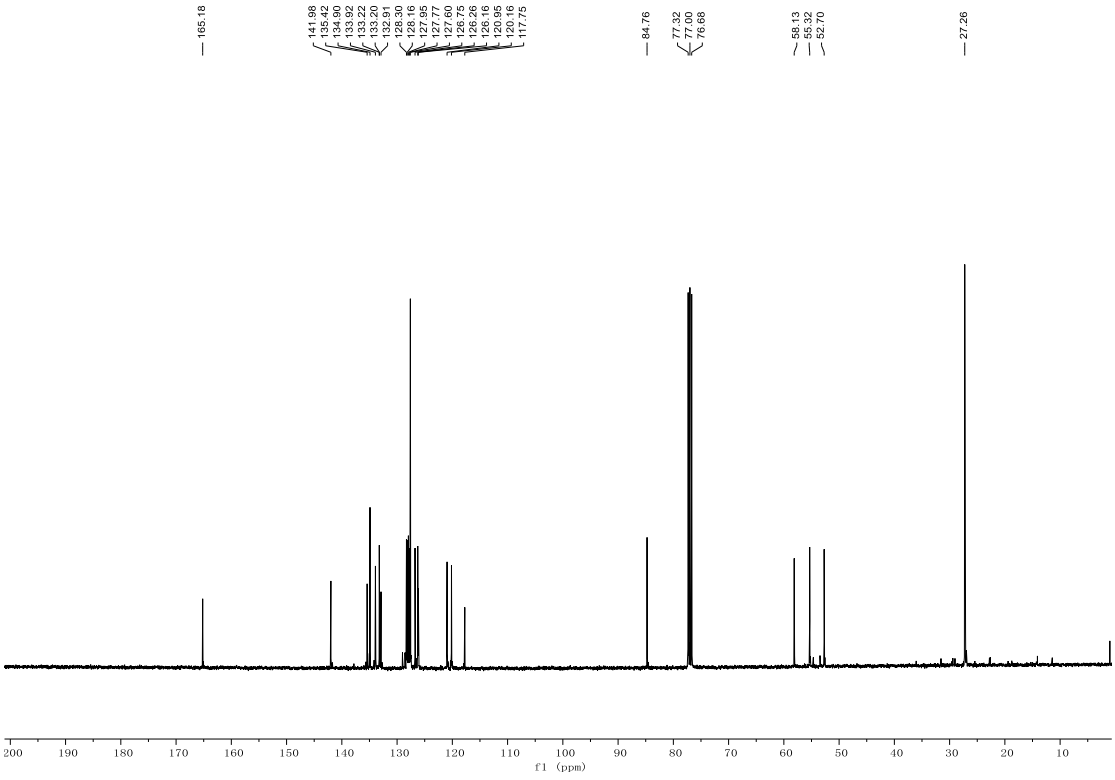

7.801
7.784
7.786
7.777
7.772
7.516
7.511
7.494
7.490
7.469
7.465
7.458
7.456
7.450
7.445
7.291
7.286
7.259
7.254
7.249
6.485
6.462
6.459
6.442
6.437
6.420
6.417
6.394
6.367
6.345
6.342
6.325
6.320
6.303
6.300
6.277
5.366
5.340
5.320
5.317
5.295
5.291
5.231
5.228
5.225
5.223
5.189
5.186
5.183
5.180
4.042
4.020
3.997
3.885
0.849
0.000
4.02
1.02
2.00
2.01
1.01
1.03
1.03
1.01
2.00
1.00
1.01
9.10
f1 (ppm)


164.90
142.32
136.00
135.72
134.88
134.80
133.09
132.71
128.24
128.06
127.88
127.74
127.61
127.49
126.69
126.24
126.17
120.89
120.19
117.95
84.55
77.32
77.00
76.68
58.13
56.25
55.21
26.96
f1 (ppm)


tBuO2C
CN
R
S
R
Cl
Cl

(*R*,*S*,*R*)-**8C**


7.823
7.815
7.803
7.794
7.779
7.766
7.762
7.479
7.473
7.469
7.465
7.462
7.459
7.455
7.442
7.437
7.322
7.317
7.312
7.266
7.255
7.251
7.245
6.743
6.718
6.700
6.693
6.675
6.655
6.194
6.170
6.168
6.151
6.145
6.128
6.126
5.403
5.356
5.352
5.331
5.327
5.269
5.266
5.253
5.251
5.228
5.225
5.222
5.188
5.185
5.146
5.143
3.976
3.951
3.946
3.923
1.082
0.000
4.04
3.07
1.99
0.98
1.00
1.02
1.04
2.08
1.00
0.99
1.03
9.03
f1 (ppm)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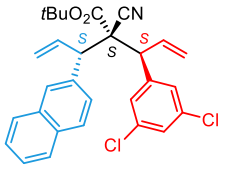
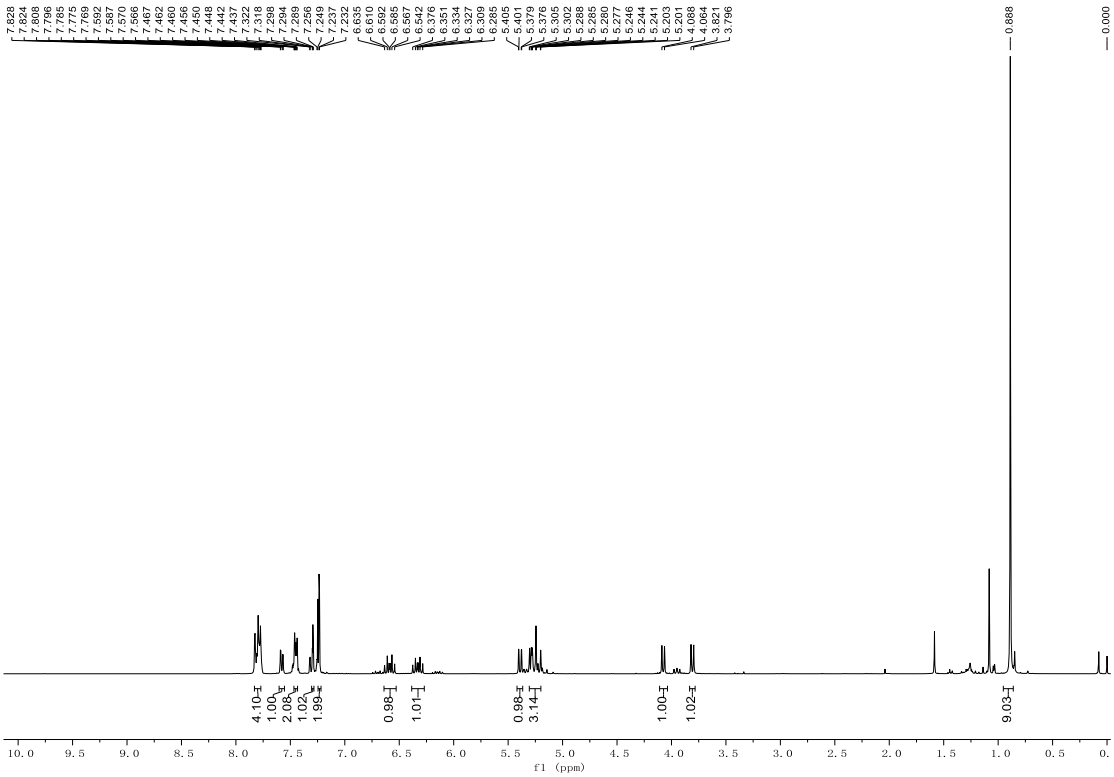
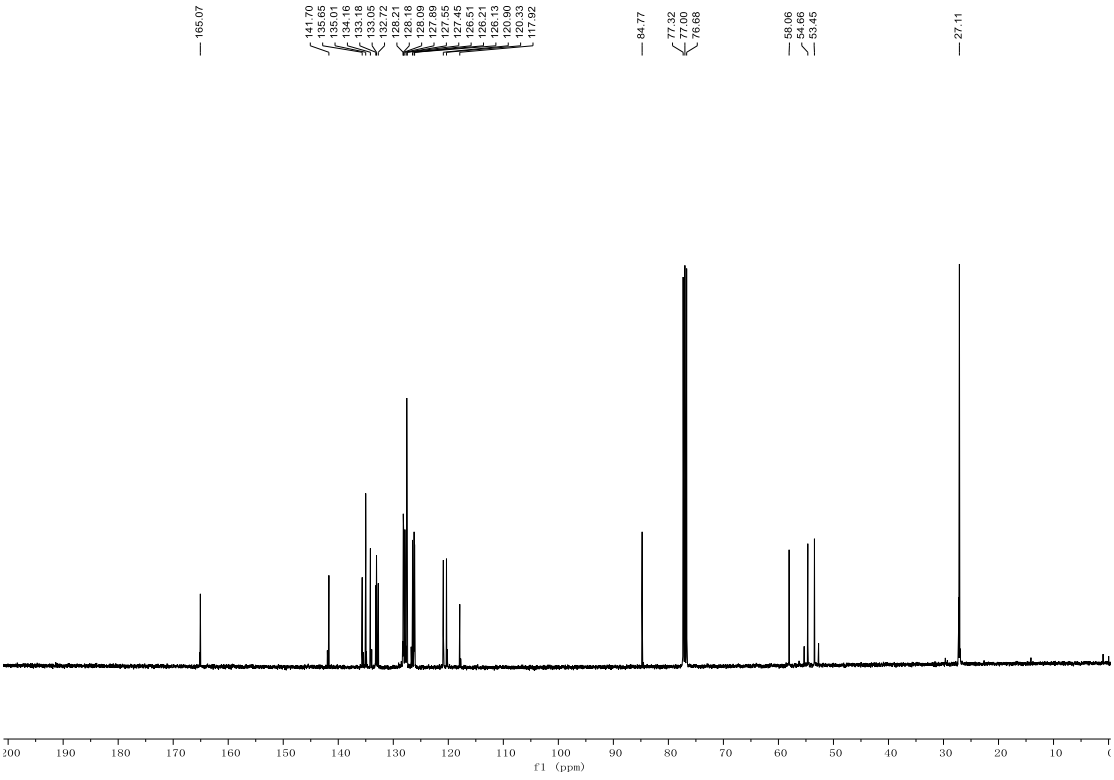
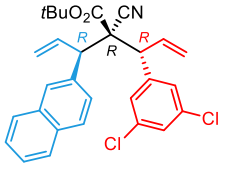
141.98
135.42
134.90
133.92
133.22
133.20
132.91
128.30
128.16
127.95
127.77
127.60
126.75
126.26
126.16
120.95
120.16
117.75
84.76
77.32
77.00
76.68
58.13
55.32
52.70
27.26
f1 (ppm)


tBuO2C
CN
S
S
S
Cl
Cl

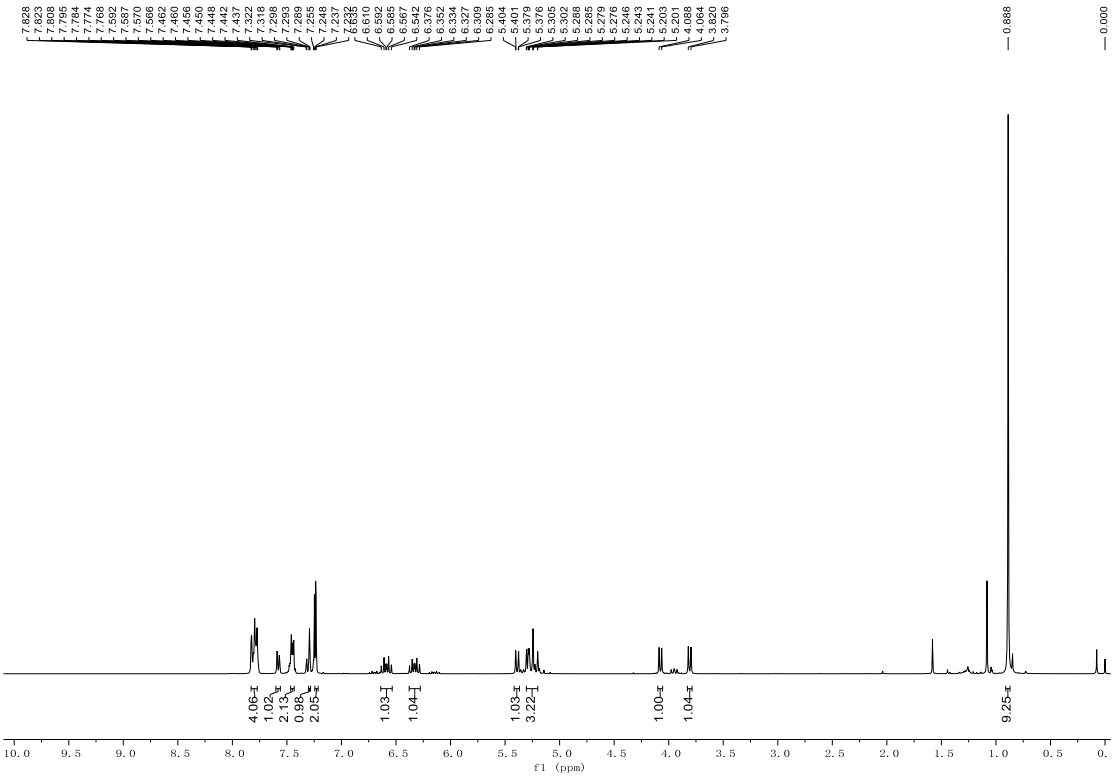
(*S*,*S*,*S*)-**8C**

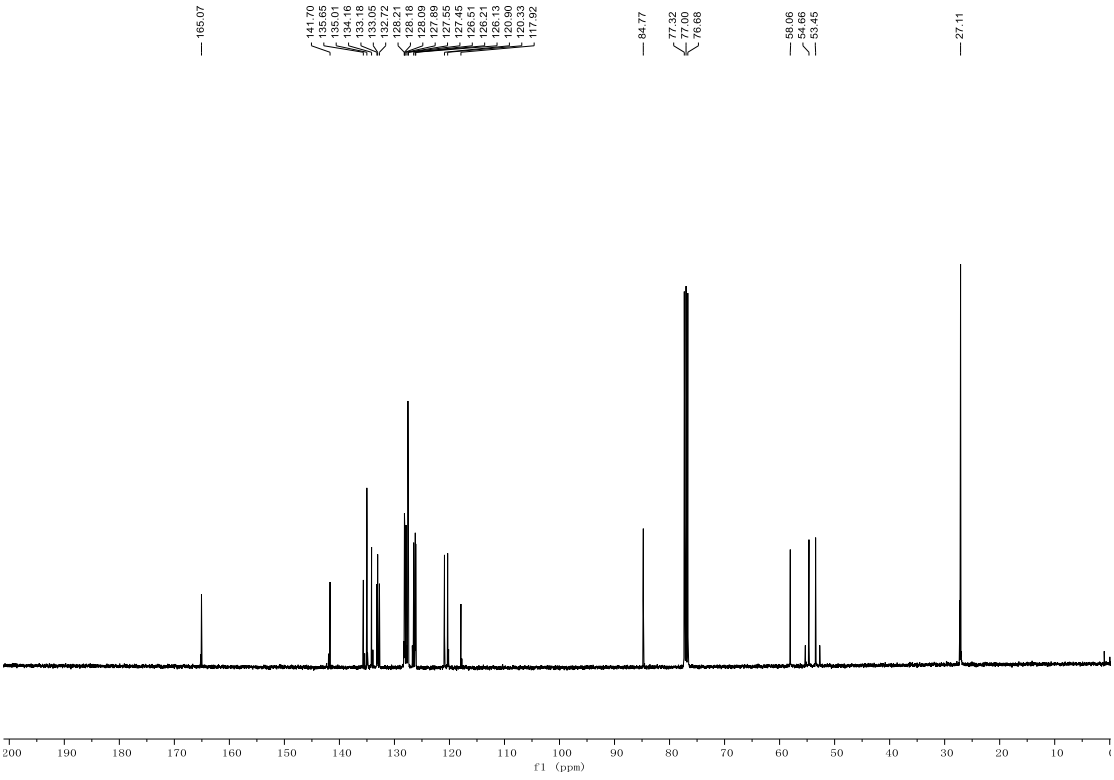

7.828
7.824
7.808
7.796
7.785
7.775
7.769
7.592
7.587
7.570
7.566
7.467
7.462
7.460
7.456
7.455
7.448
7.442
7.437
7.322
7.298
7.294
7.288
7.266
7.249
7.237
7.232
6.635
6.610
6.592
6.585
6.567
6.542
6.376
6.351
6.334
6.327
6.309
6.285
5.405
5.401
5.379
5.376
5.305
5.302
5.288
5.285
5.280
5.277
5.246
5.244
5.241
5.203
5.201
4.088
4.064
3.821
3.796
0.888
0.000
4.10
1.00
2.08
1.02
1.99
0.98
1.01
0.98
3.14
1.00
1.02
9.03
f1 (ppm)

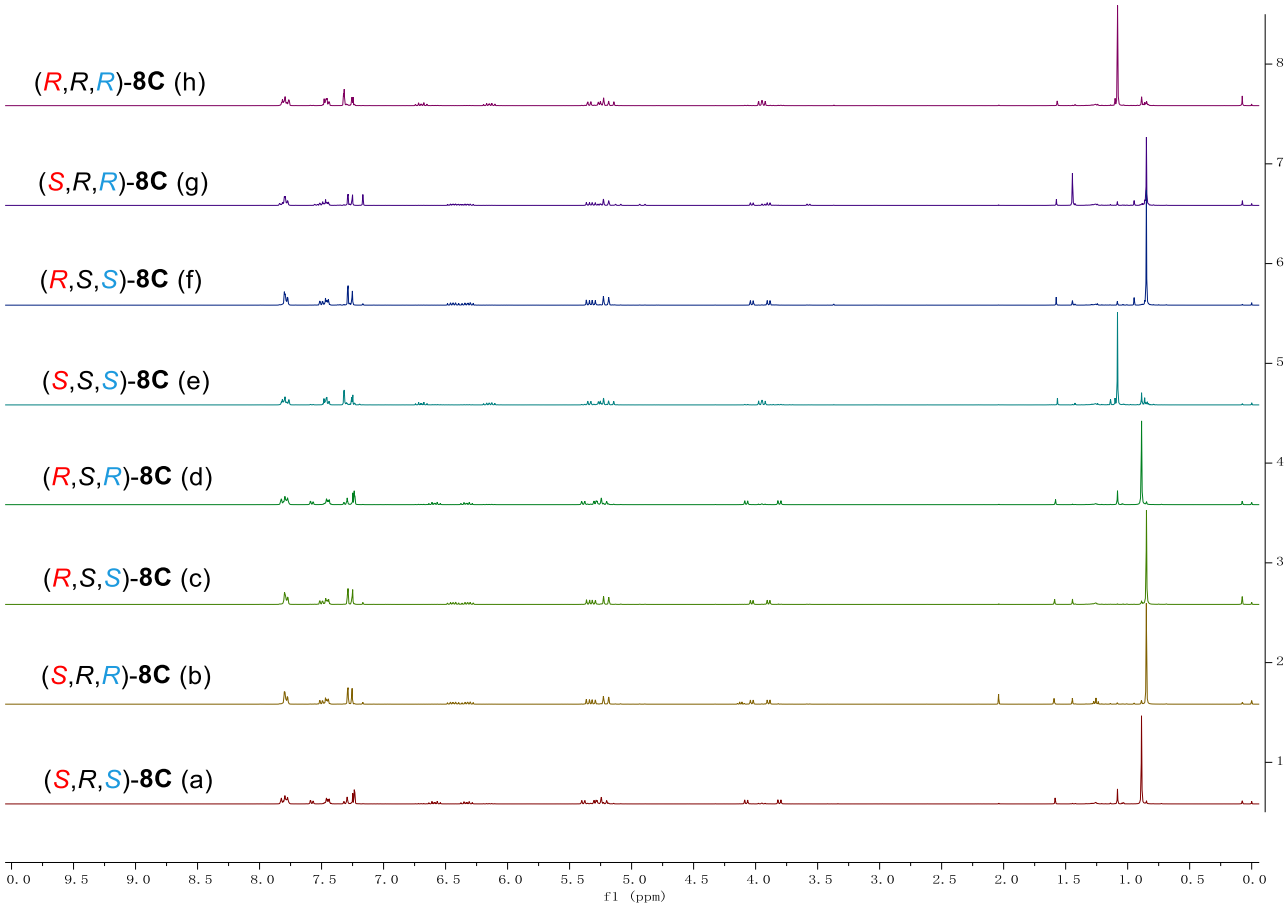

165.07
141.70
135.65
135.01
134.16
133.18
133.05
132.72
128.21
128.18
128.09
127.89
127.55
127.45
126.51
126.21
126.13
120.90
120.33
117.92
84.77
77.32
77.00
76.68
58.06
54.66
53.45
27.11
f1 (ppm)

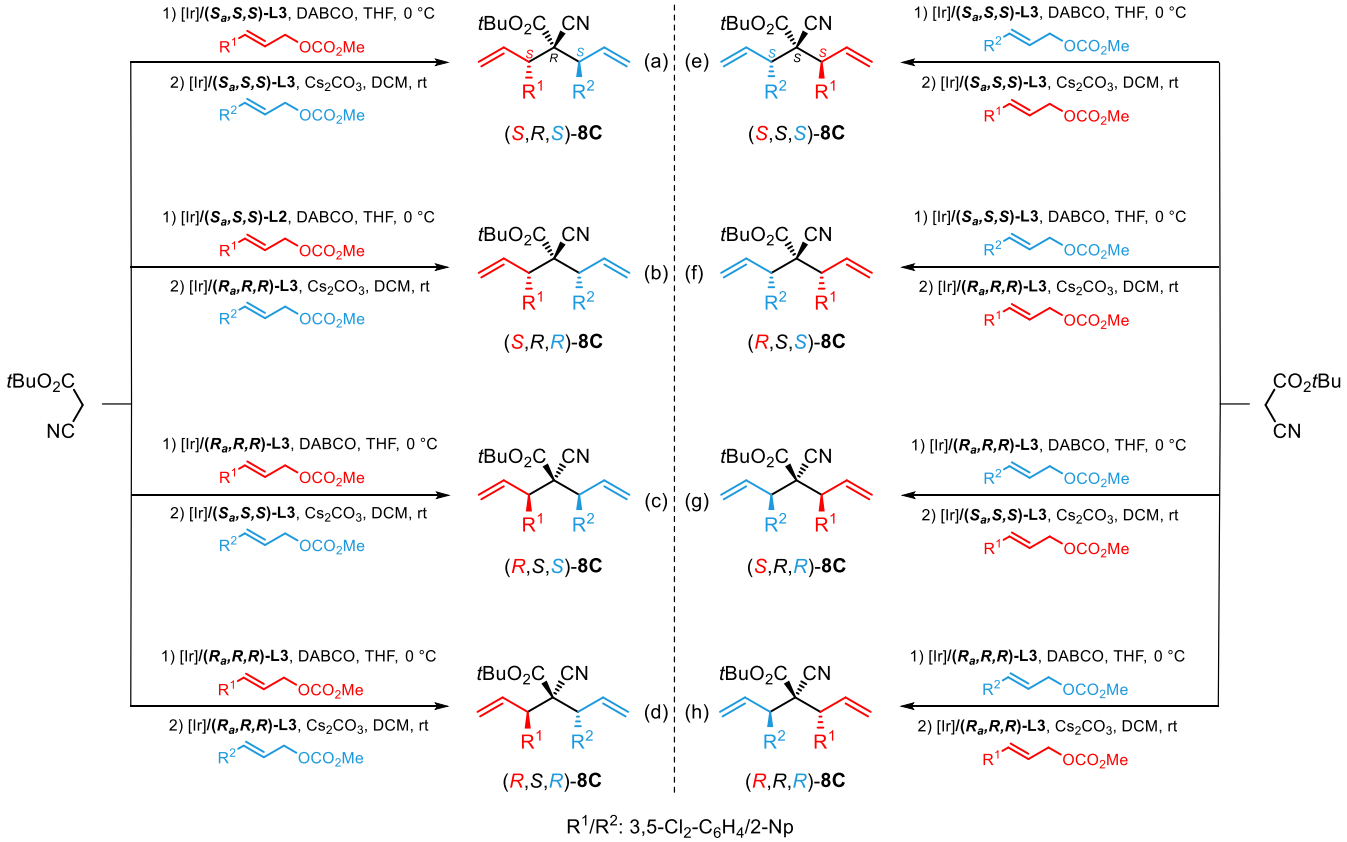

tBuO2C
CN
R
R
R
Cl
Cl

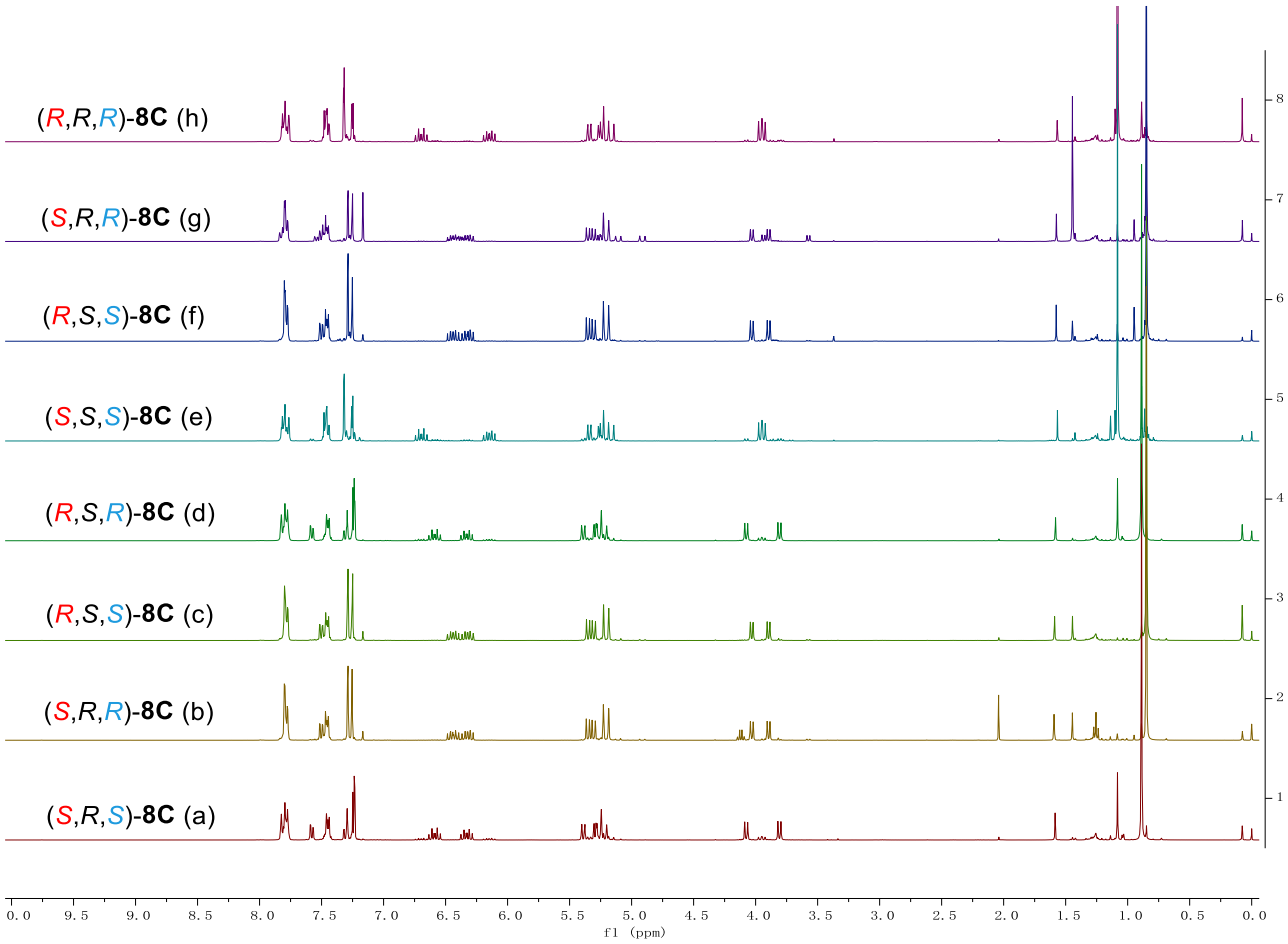
(*R*,*R*,*R*)-**8C**

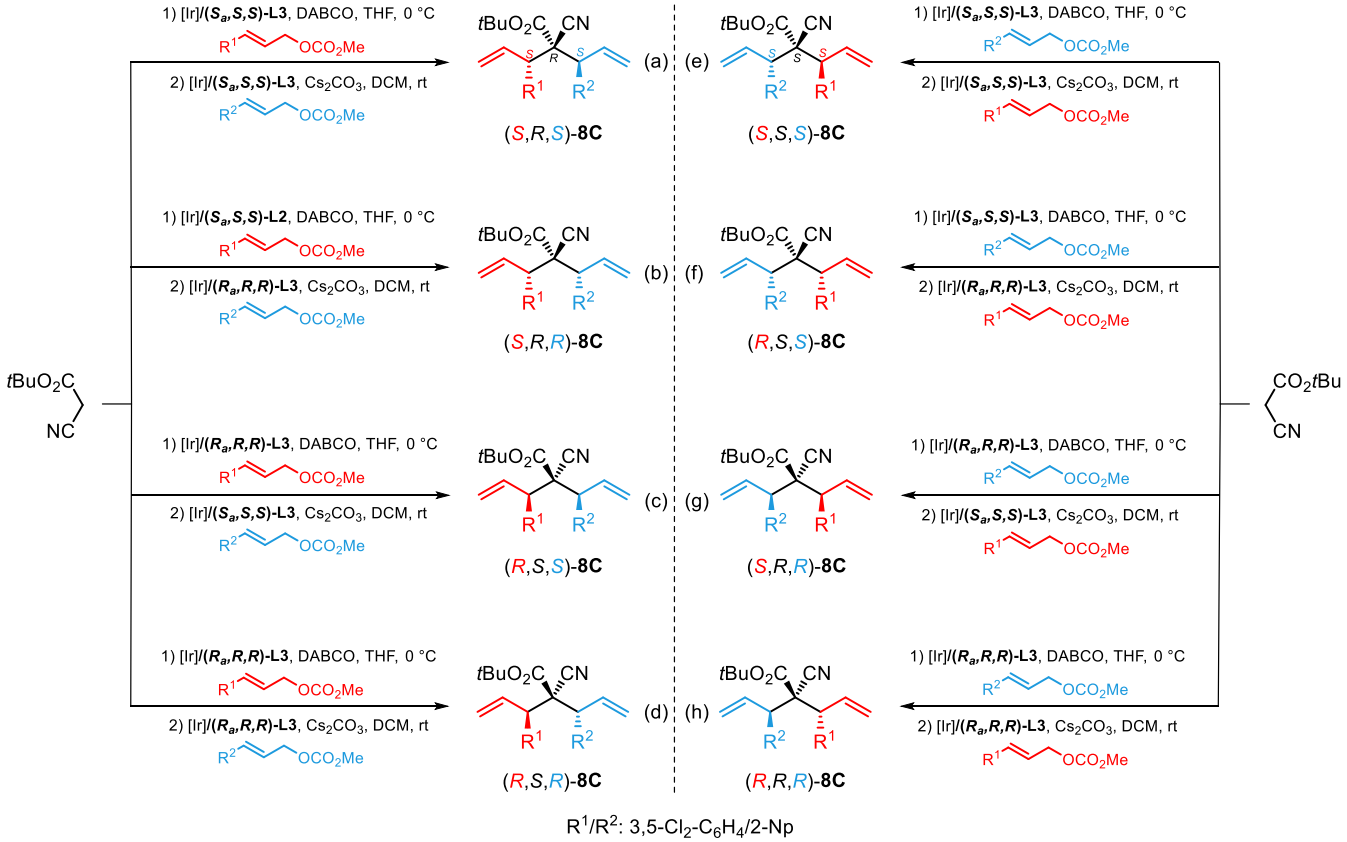

7.828
7.823
7.808
7.795
7.784
7.774
7.768
7.592
7.587
7.570
7.566
7.462
7.460
7.456
7.450
7.448
7.442
7.437
7.322
7.318
7.298
7.293
7.289
7.255
7.248
7.237
7.232
6.635
6.610
6.602
6.585
6.567
6.542
6.376
6.352
6.334
6.327
6.309
6.285
5.404
5.401
5.379
5.376
5.305
5.302
5.288
5.285
5.279
5.276
5.246
5.243
5.241
5.203
5.201
4.088
4.064
3.820
3.796
0.888
0.000
4.06
1.02
2.13
0.98
2.05
1.03
1.04
1.03
3.22
1.00
1.04
9.25
f1 (ppm)

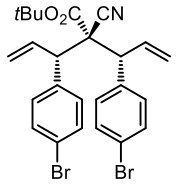

165.07
141.70
135.65
135.01
134.16
133.18
133.05
132.72
128.21
128.18
128.09
127.89
127.55
127.45
126.51
126.21
126.13
120.90
120.33
117.92
84.77
77.32
77.00
76.68
58.06
54.66
53.45
27.11
f1 (ppm)


(R,R,R)-8C (h)
(S,R,R)-8C (g)
(R,S,S)-8C (f)
(S,S,S)-8C (e)
(R,S,R)-8C (d)
(R,S,S)-8C (c)
(S,R,R)-8C (b)
(S,R,S)-8C (a)
f1 (ppm)

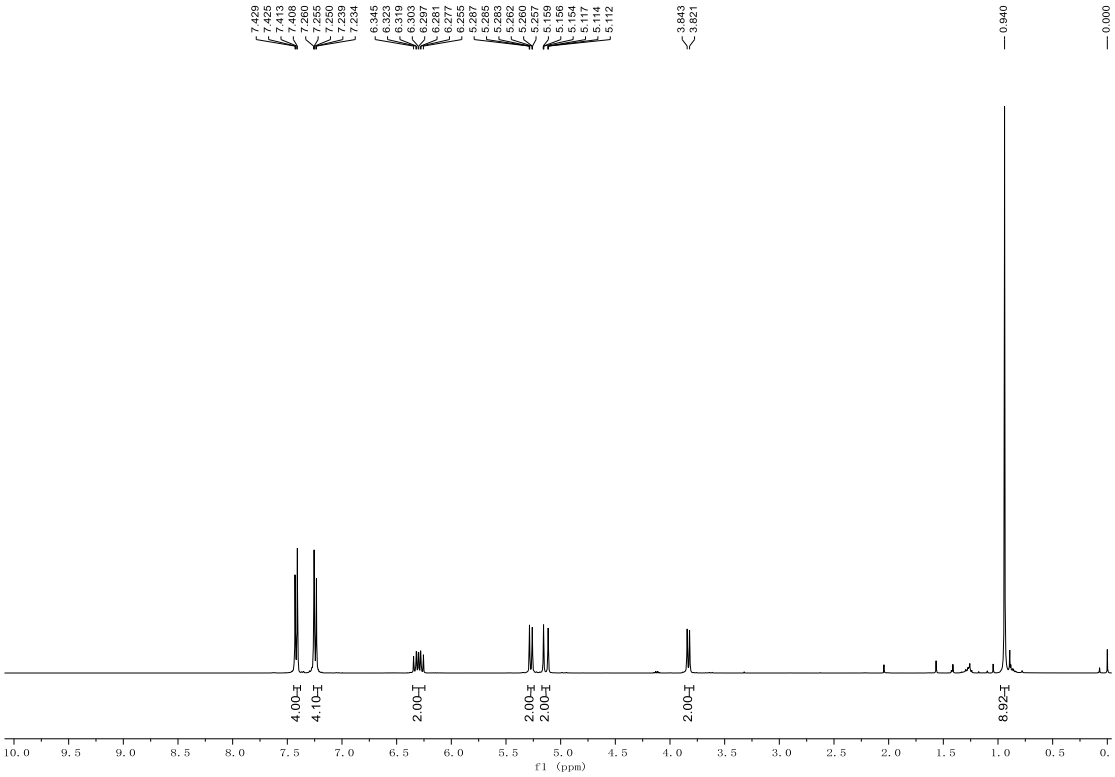

tBuO2C
NC
CO2tBu
CN
1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
OCO2Me
(a) (S,R,S)-8C
(b) (S,R,R)-8C
(c) (R,S,S)-8C
(d) (R,S,R)-8C
(e) (S,S,S)-8C
(f) (R,S,S)-8C
(g) (S,R,R)-8C
(h) (R,R,R)-8C
R1/R2: 3,5-Cl2-C6H4/2-Np

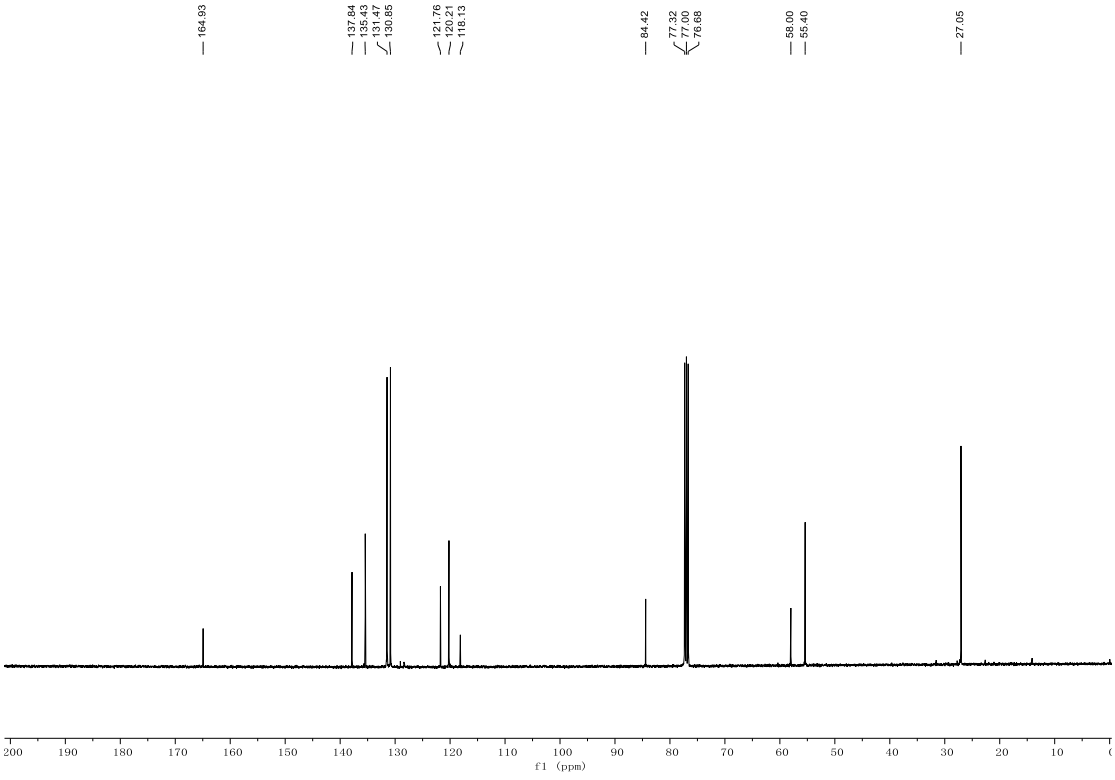

(R,R,R)-8C (h)
(S,R,R)-8C (g)
(R,S,S)-8C (f)
(S,S,S)-8C (e)
(R,S,R)-8C (d)
(R,S,S)-8C (c)
(S,R,R)-8C (b)
(S,R,S)-8C (a)
f1 (ppm)

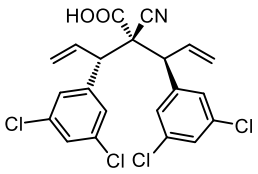

tBuO2C
NC
CO2tBu
CN
1) [Ir]/(Sa,S,S)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Sa,S,S)-L2, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Sa,S,S)-L3, Cs2CO3, DCM, rt
1) [Ir]/(Ra,R,R)-L3, DABCO, THF, 0 °C
2) [Ir]/(Ra,R,R)-L3, Cs2CO3, DCM, rt
OCO2Me
(a) (S,R,S)-8C
(b) (S,R,R)-8C
(c) (R,S,S)-8C
(d) (R,S,R)-8C
(e) (S,S,S)-8C
(f) (R,S,S)-8C
(g) (S,R,R)-8C
(h) (R,R,R)-8C
R1/R2: 3,5-Cl2-C6H4/2-Np


tBuO2C
CN
Br
Br

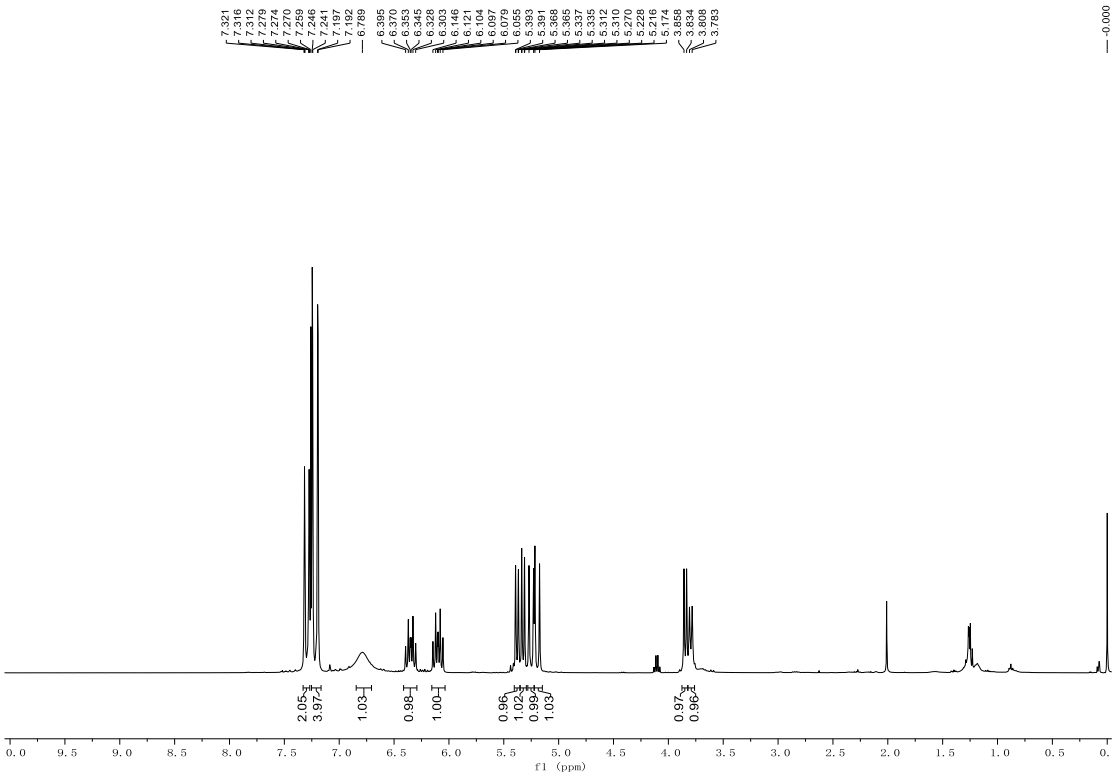
(*S*,*s*,*R*)-*meso*-**7d**

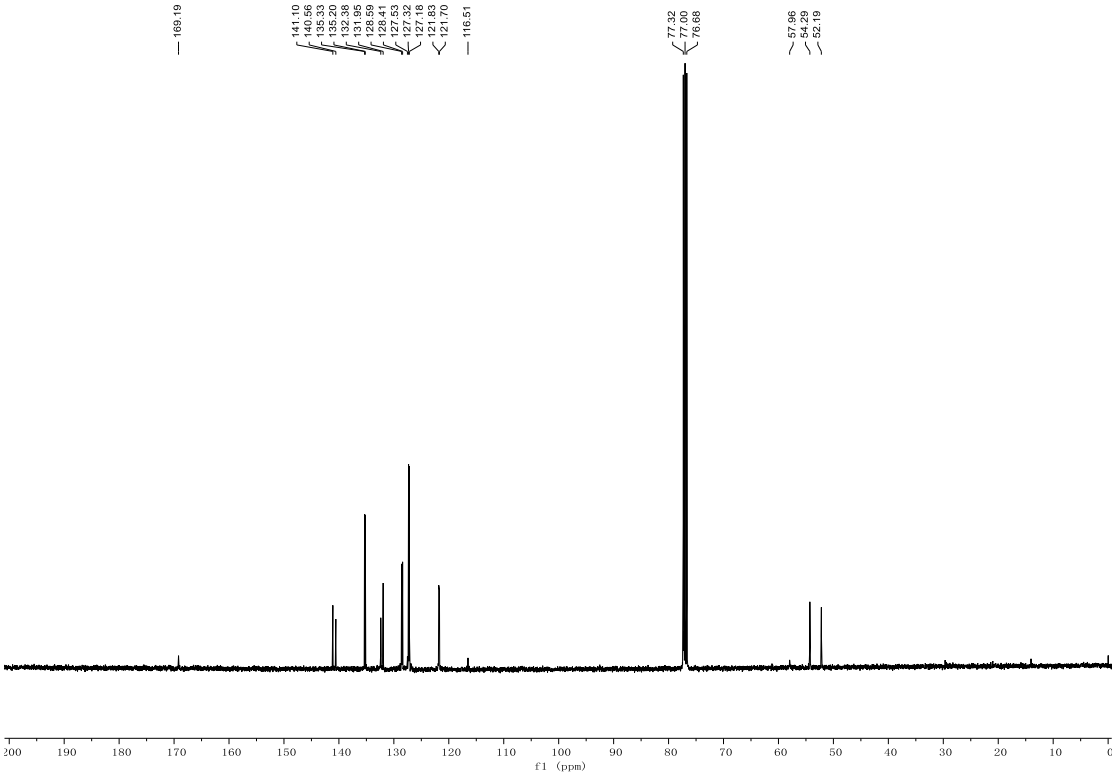

7.429
7.425
7.413
7.408
7.260
7.255
7.250
7.239
7.234
6.345
6.323
6.319
6.303
6.297
6.291
6.277
6.255
5.287
5.285
5.283
5.262
5.260
5.257
5.158
5.156
5.154
5.117
5.114
5.112
3.843
3.821
0.940
0.000
4.00
4.10
2.00
2.00
2.00
2.00
8.92
f1 (ppm)

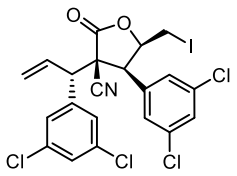

164.93
137.84
135.43
131.47
130.85
121.76
120.21
118.13
84.42
77.32
77.00
76.68
58.00
55.40
27.05
f1 (ppm)


HOOC
CN
Cl
Cl
Cl
Cl

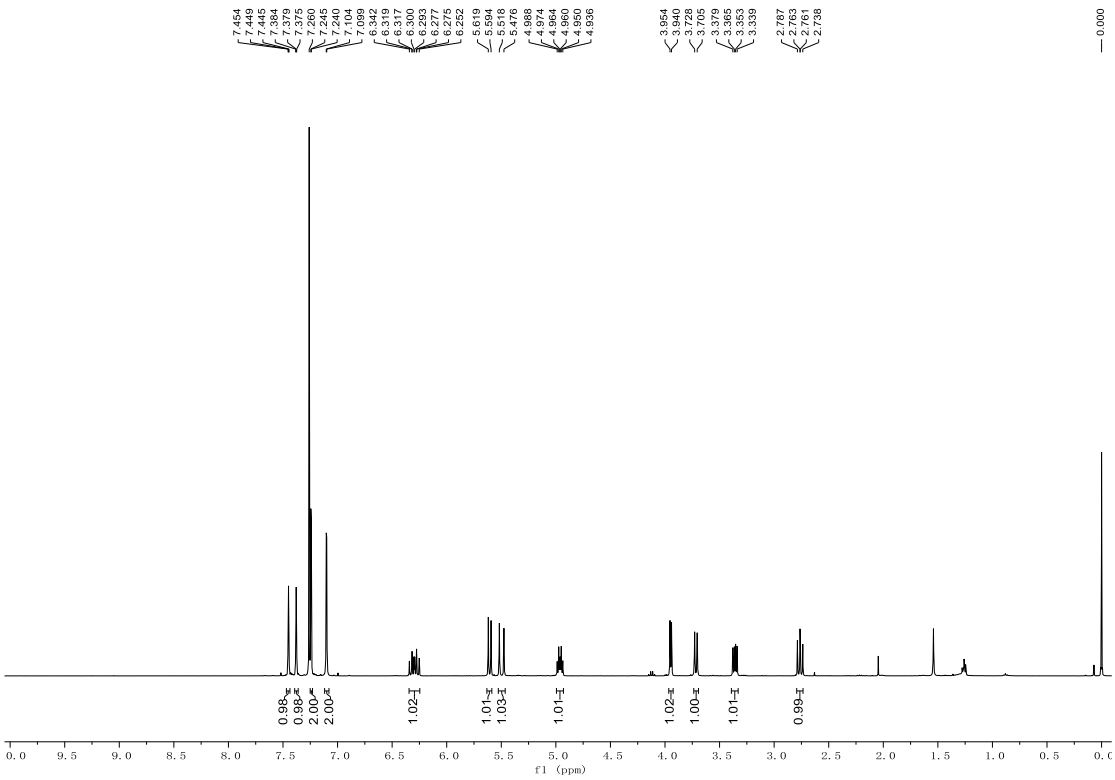
11

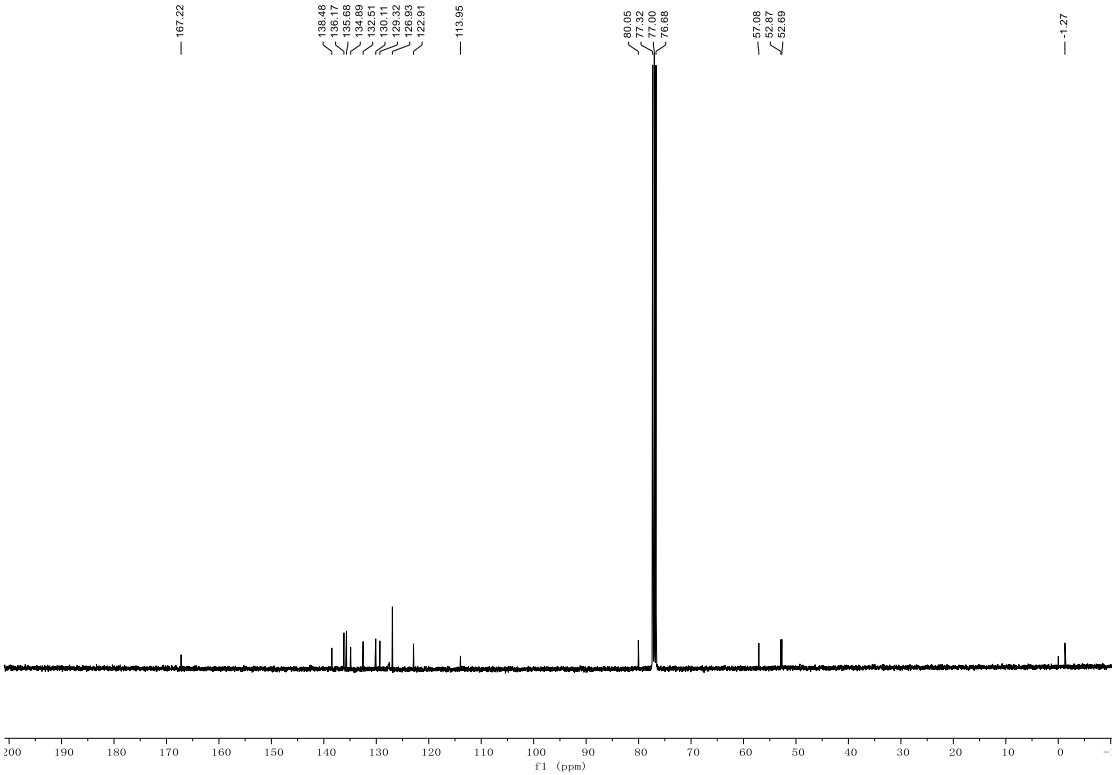

7.321
7.316
7.312
7.279
7.274
7.270
7.259
7.246
7.241
7.197
7.192
6.789
6.395
6.370
6.353
6.345
6.328
6.303
6.146
6.121
6.104
6.097
6.079
6.055
5.393
5.391
5.388
5.365
5.337
5.335
5.312
5.310
5.270
5.228
5.216
5.174
3.858
3.834
3.808
3.783
0.000
2.05
3.97
1.03
0.98
1.00
0.96
1.02
0.99
1.03
0.97
0.96
f1 (ppm)


169.19
141.10
140.56
135.33
135.20
132.38
131.95
128.59
128.41
127.53
127.32
127.18
121.83
121.70
116.51
77.32
77.00
76.68
57.96
54.29
52.19
f1 (ppm)


O
O
I
CN
Cl
Cl
Cl
Cl

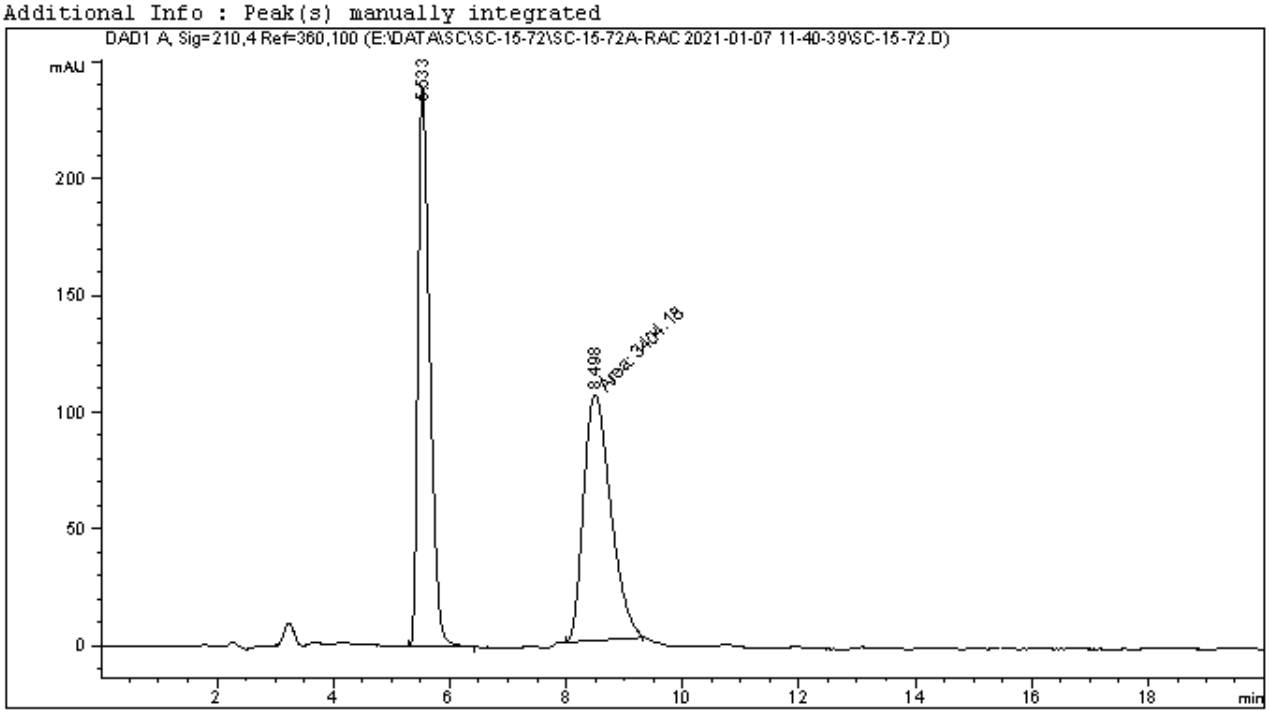
12


7.454
7.449
7.445
7.384
7.379
7.375
7.260
7.245
7.240
7.104
7.099
6.342
6.319
6.317
6.300
6.293
6.277
6.275
6.252
5.619
5.594
5.518
5.476
4.988
4.974
4.964
4.960
4.950
4.936
3.954
3.940
3.728
3.705
3.379
3.365
3.353
3.339
2.787
2.763
2.761
2.738
0.000
0.98
0.98
2.00
2.00
1.02
1.01
1.03
1.01
1.02
1.00
1.01
0.99
f1 (ppm)


167.22
138.48
136.17
135.68
134.89
132.51
130.11
129.32
128.93
122.91
113.95
80.05
77.32
77.00
76.68
57.08
52.87
52.69
-1.27
f1 (ppm)

Data File E:\DATA\SC\SC-15-72\SC-15-72A-RAC 2021-01-07 11-40-39\SC-15-72.D
Sample Name: SC-15-72A-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   86
    Injection Date  : 1/7/2021 11:42:01 AM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-72\SC-15-72A-RAC 2021-01-07 11-40-39\SC-3-ID-80-20-DAD-1ML
                      -20MIN.M
    Last changed    : 1/7/2021 11:40:39 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-72\SC-15-72A-RAC 2021-01-07 11-40-39\SC-3-ID-80-20-DAD-1ML
                      -20MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:06:55 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

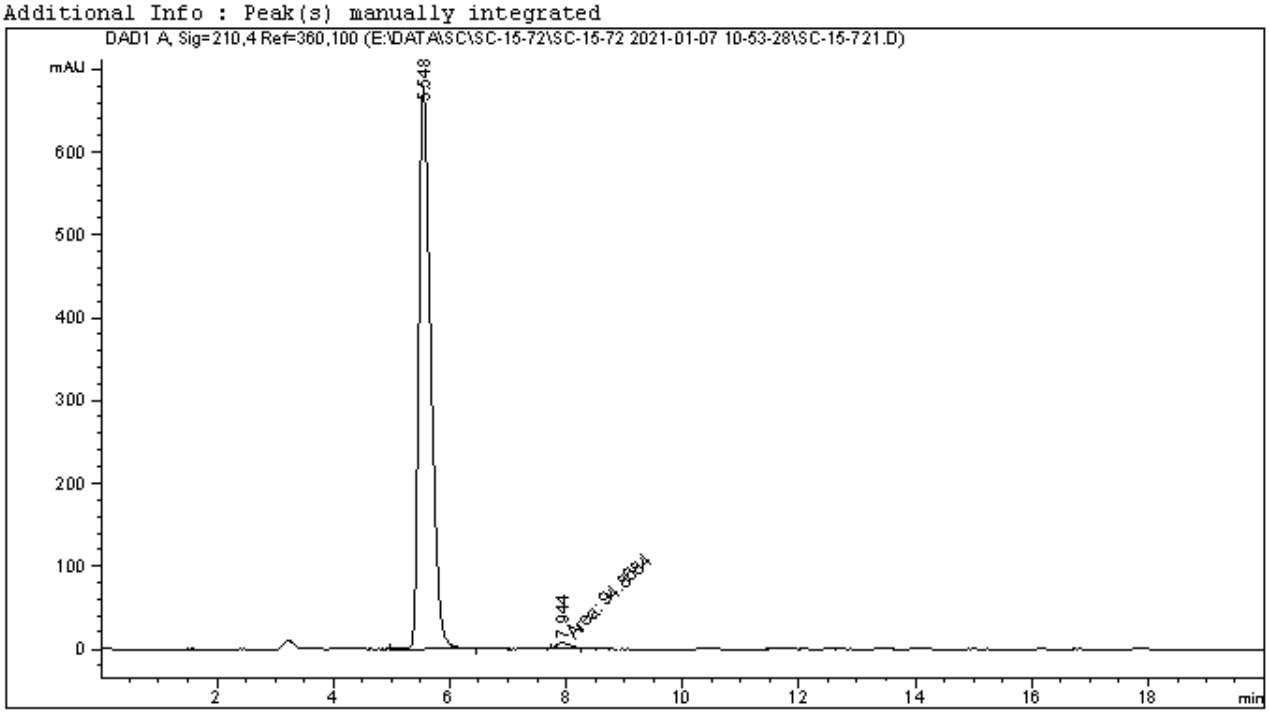

    Signal 1: DAD1 A, Sig=210,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.533 BB    0.2107 3381.61597  239.52287  49.8338
       2   8.498 MM    0.5399 3404.17749  105.07890  50.1662

    Totals :                   6785.79346  344.60178
```

Data File E:\DATA\SC\SC-15-72\SC-15-72 2021-01-07 10-53-28\SC-15-721.D
Sample Name: SC-15-72B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260                             Location :   85
    Injection Date  : 1/7/2021 11:16:14 AM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-72\SC-15-72 2021-01-07 10-53-28\SC-3-ID-80-20-DAD-1ML-
                      20MIN.M
    Last changed    : 1/7/2021 10:53:28 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-72\SC-15-72 2021-01-07 10-53-28\SC-3-ID-80-20-DAD-1ML-
                      20MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:07:34 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



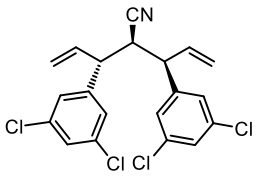

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

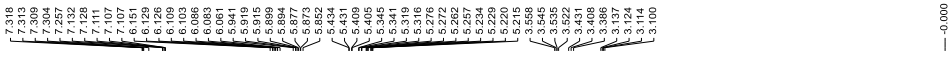

    Signal 1: DAD1 A, Sig=210,4 Ref=360,100

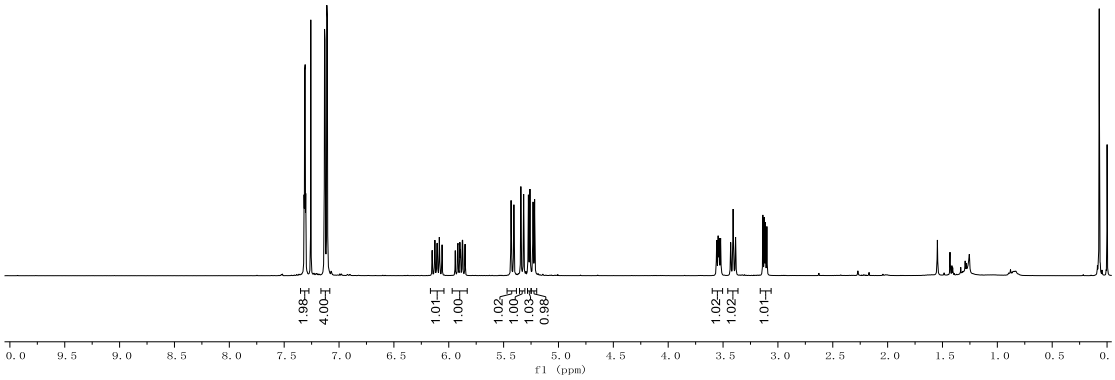
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.548 VB R  0.2162 9727.44336  678.94696  99.0342
       2   7.944 MM    0.2569   94.86842    6.15471   0.9658

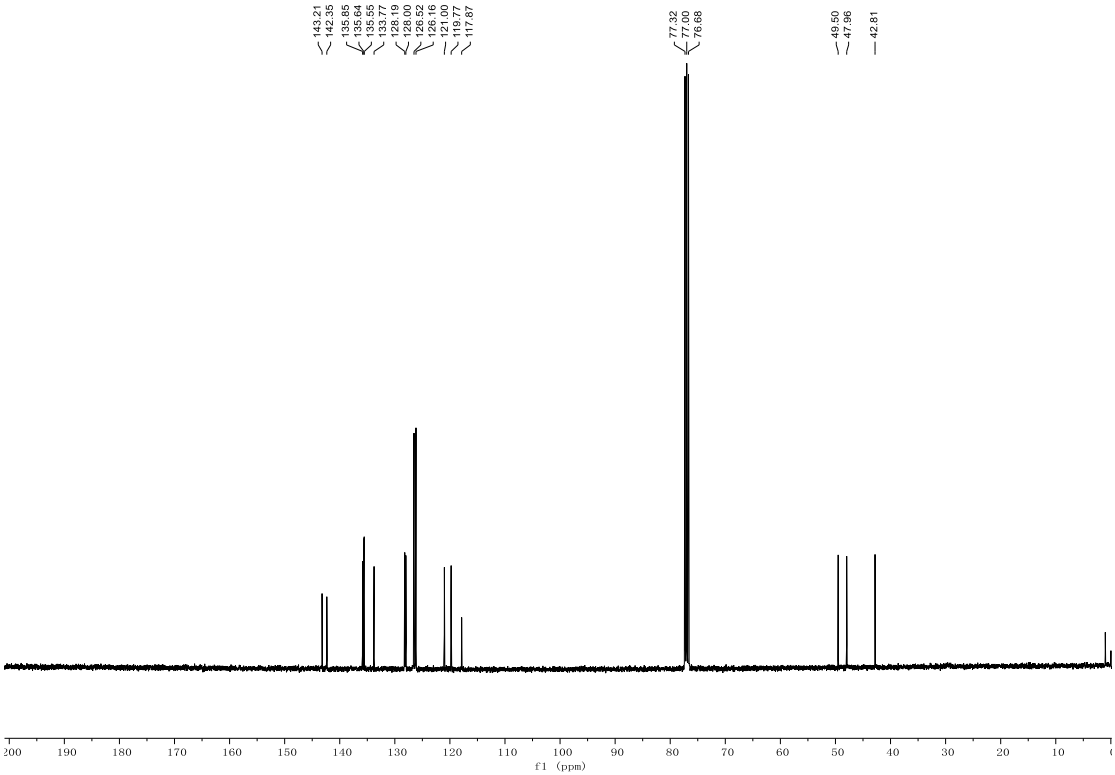
    Totals :                  9822.31178  685.10167
```


CN
Cl
Cl Cl
Cl

13

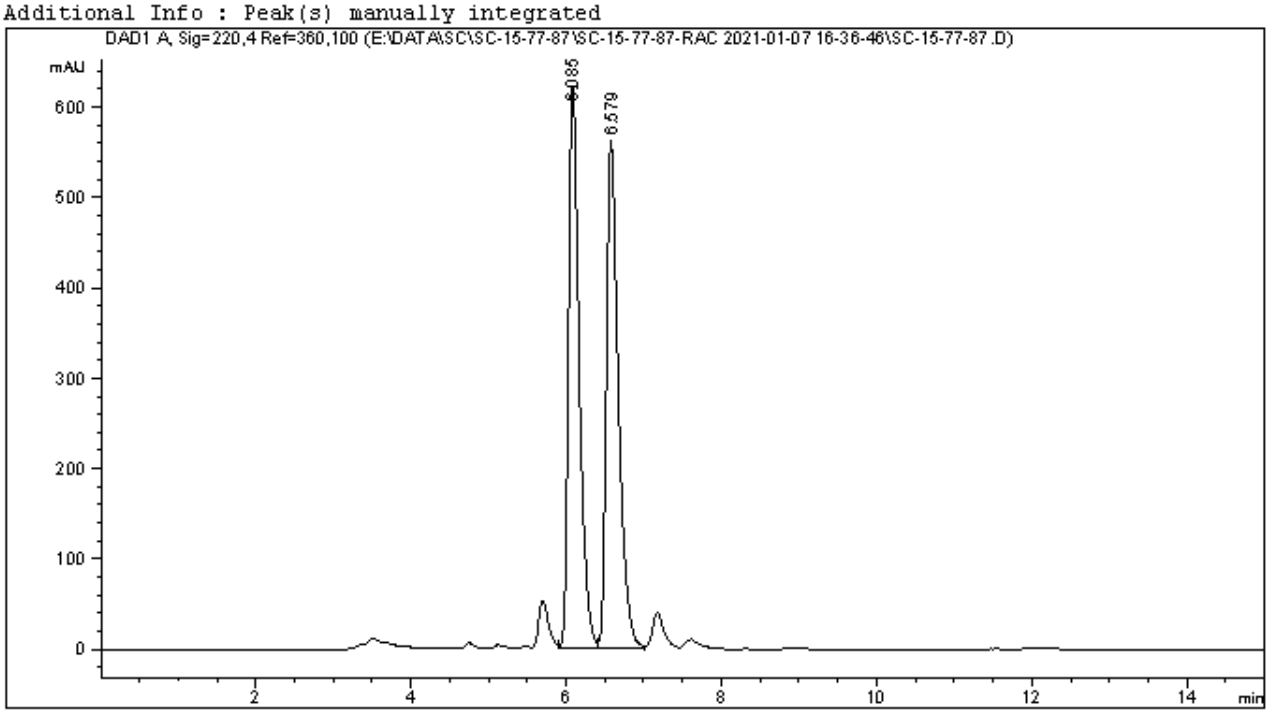

7.318
7.313
7.309
7.304
7.257
7.132
7.128
7.111
7.107
7.097
7.151
6.129
6.126
6.109
6.103
6.086
6.083
6.061
5.941
5.919
5.915
5.899
5.894
5.877
5.873
5.852
5.434
5.431
5.409
5.405
5.345
5.341
5.319
5.316
5.276
5.272
5.262
5.257
5.234
5.229
5.220
5.215
3.558
3.545
3.535
3.522
3.431
3.408
3.386
3.137
3.124
3.114
3.100
0.000


1.98
4.00
1.01
1.00
1.02
1.00
1.03
0.98
1.02
1.02
1.01
f1 (ppm)


143.21
142.35
135.85
135.64
135.55
133.77
128.19
128.00
126.52
126.16
121.00
119.77
117.87
77.32
77.00
76.68
49.50
47.96
42.81
f1 (ppm)

Data File E:\DATA\SC\SC-15-77-87\SC-15-77-87-RAC 2021-01-07 16-36-46\SC-15-77-87.D
Sample Name: SC-15-77-87-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   81
    Injection Date  : 1/7/2021 4:38:09 PM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-77-87\SC-15-77-87-RAC 2021-01-07 16-36-46\SC-4-IE-95-5-DAD
                      -1ML-30MIN.M
    Last changed    : 1/7/2021 4:45:42 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\SC\SC-15-77-87\SC-15-77-87-RAC 2021-01-07 16-36-46\SC-4-IE-95-5-DAD
                      -1ML-30MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:11:38 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

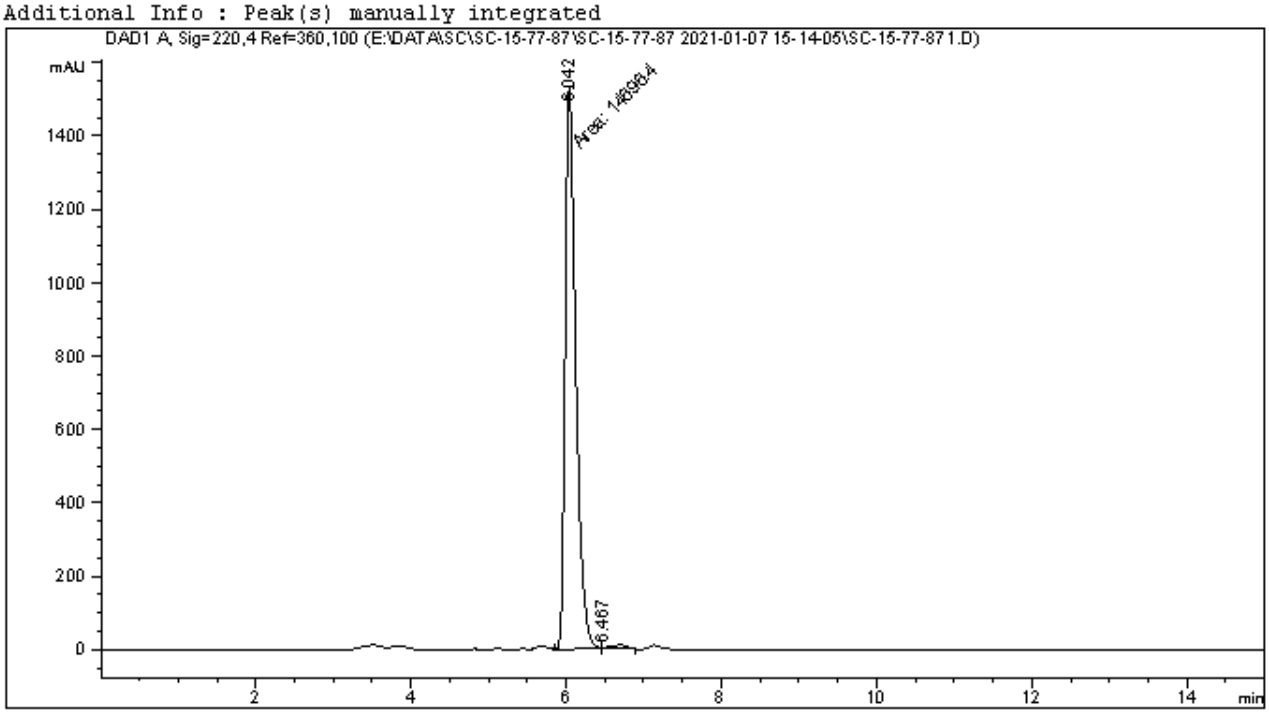

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.085 VV    0.1459 6015.66504  621.84479  50.1198
       2   6.579 VV    0.1603 5986.90430  561.77594  49.8802

    Totals :                   1.20026e4  1183.62073
```

Data File E:\DATA\SC\SC-15-77-87\SC-15-77-87 2021-01-07 15-14-05\SC-15-77-871.D
Sample Name: SC-15-87

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260                           Location :   83
    Injection Date  : 1/7/2021 3:31:50 PM                 Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-77-87\SC-15-77-87 2021-01-07 15-14-05\SC-4-IE-95-5-DAD-1ML
                      -30MIN.M
    Last changed    : 1/7/2021 3:19:09 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-77-87\SC-15-77-87 2021-01-07 15-14-05\SC-4-IE-95-5-DAD-1ML
                      -30MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:13:23 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



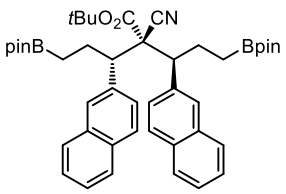

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

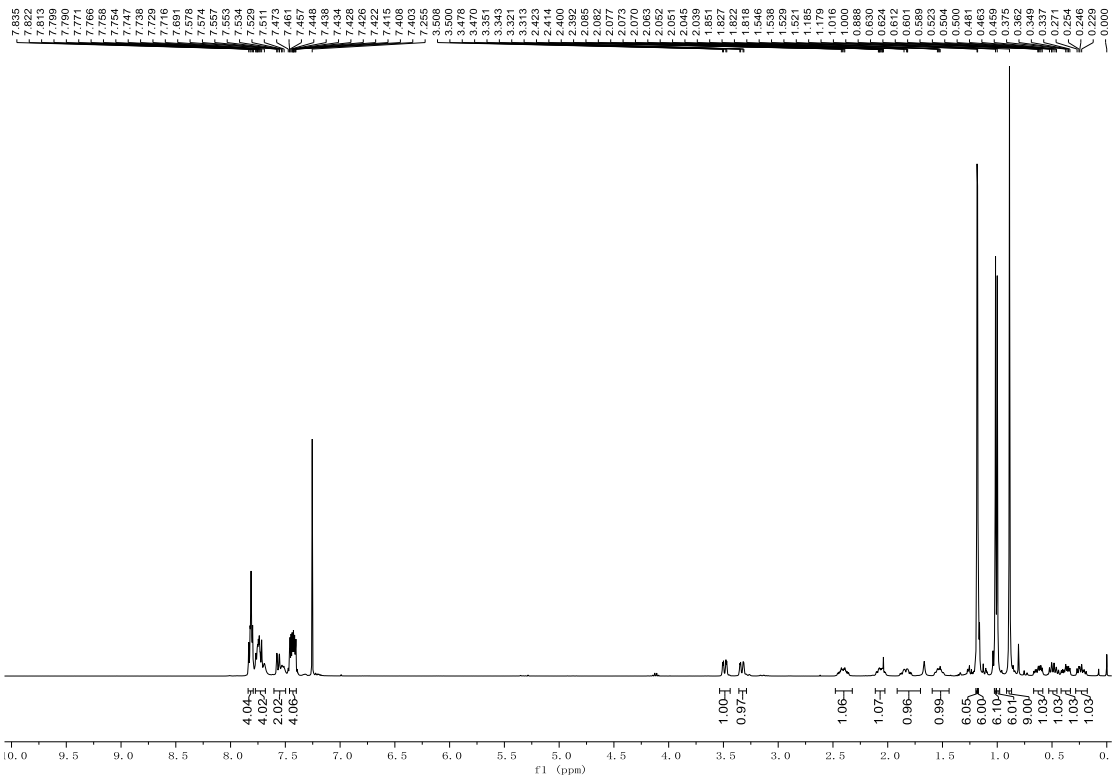

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

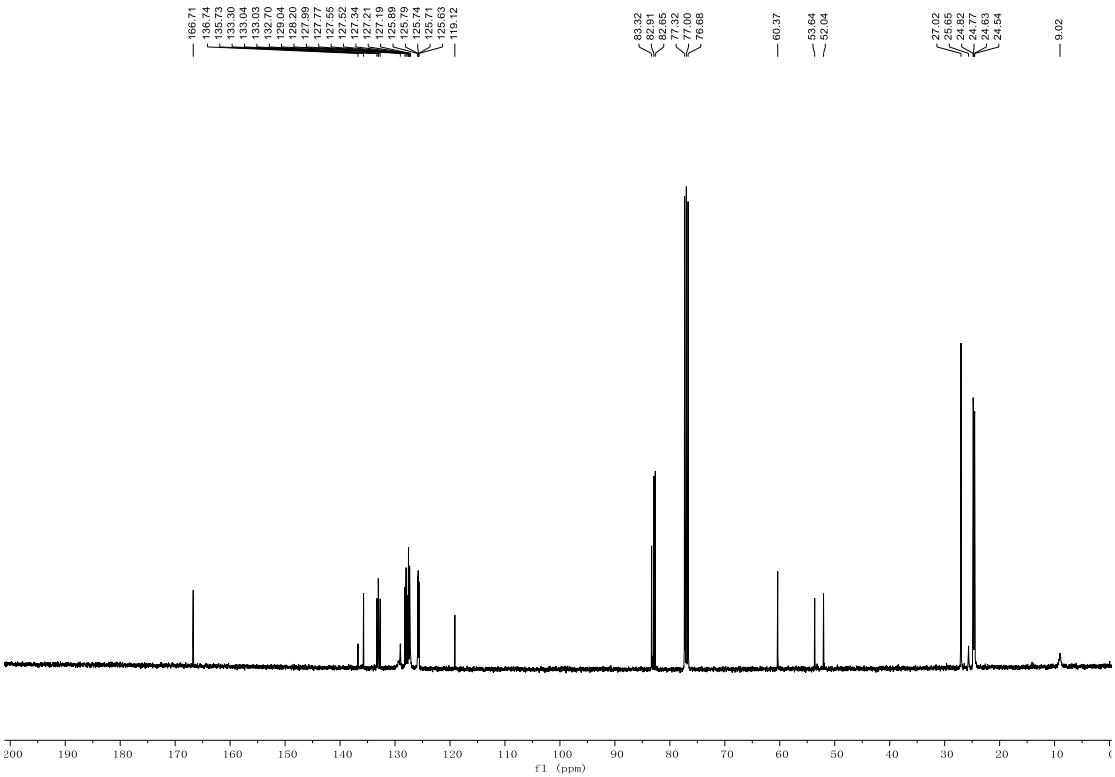
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.042 MF    0.1596 1.46964e4  1534.73291  98.9340
       2   6.467 FM R  0.1436  158.35353    2.72323   1.0660

    Totals :                  1.48548e4  1537.45614
```



14

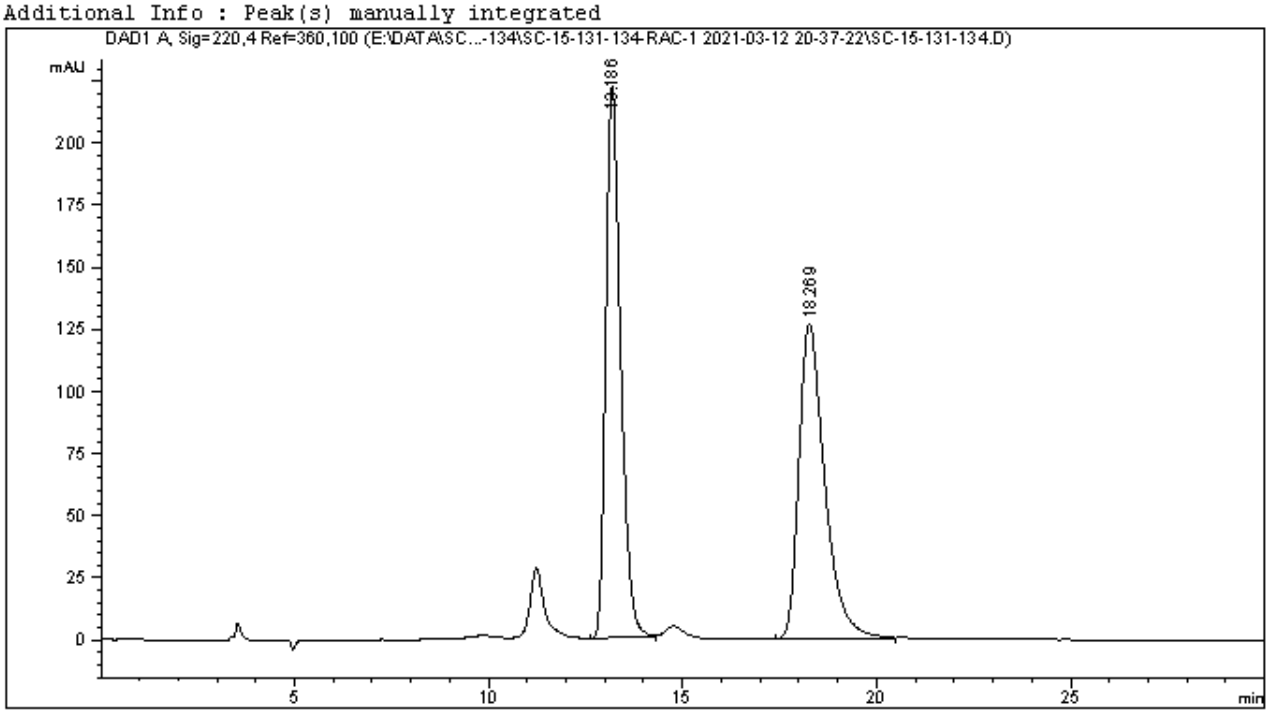




S-134

Data File E:\DATA\SC\SC-15-131-134\SC-15-131-134-RAC-1 2021-03-12 20-37-22\SC-15-131-134.D
Sample Name: SC-15-131-134-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   81
    Injection Date  : 3/12/2021 8:38:43 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-131-134\SC-15-131-134-RAC-1 2021-03-12 20-37-22\SC-4-IE-95
                      -5-DAD-1ML-30MIN.M
    Last changed    : 3/12/2021 8:37:22 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-131-134\SC-15-131-134-RAC-1 2021-03-12 20-37-22\SC-4-IE-95
                      -5-DAD-1ML-30MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:16:12 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

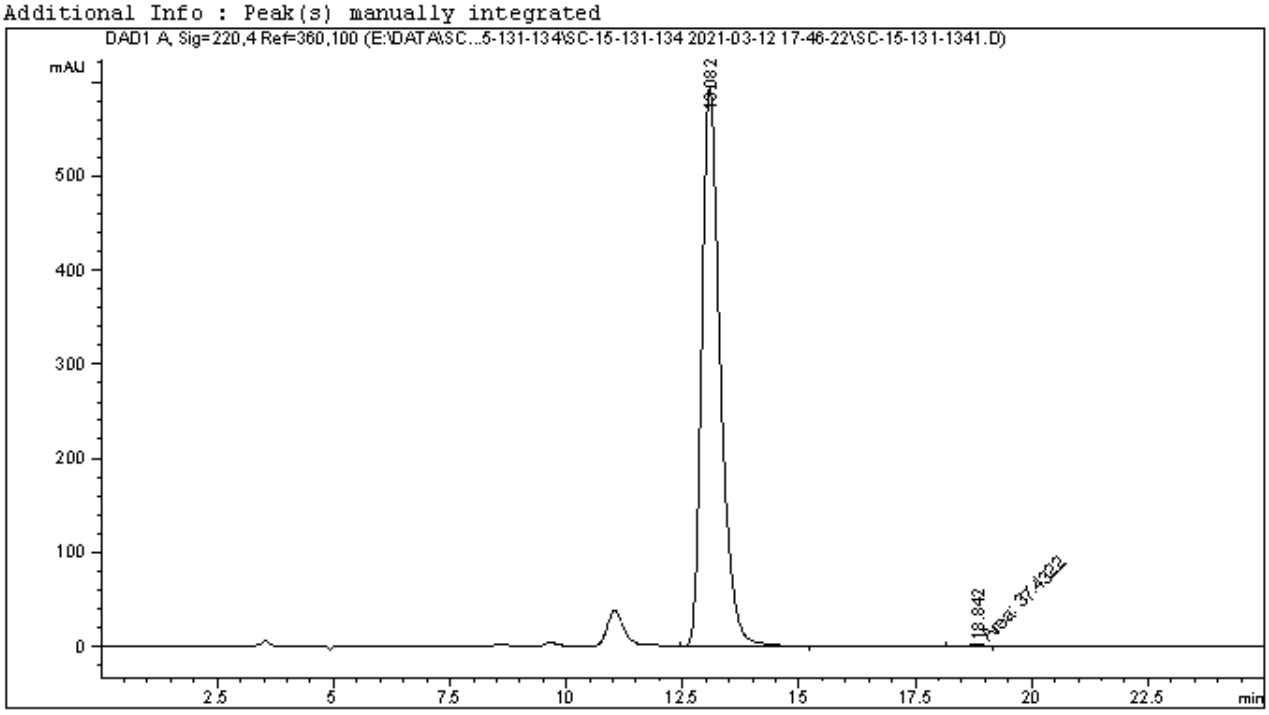

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.186 BB    0.4028 5895.11279  221.96712  50.1374
       2  18.269 BB    0.6893 5862.80615  126.82327  49.8626

    Totals :                  1.17579e4   348.79038
```

Data File E:\DATA\SC\SC-15-131-134\SC-15-131-134 2021-03-12 17-46-22\SC-15-131-1341.D
Sample Name: SC-15-134

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260                           Location :   83
    Injection Date  : 3/12/2021 6:14:03 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-15-131-134\SC-15-131-134 2021-03-12 17-46-22\SC-4-IE-95-5-DAD
                      -1ML-30MIN.M
    Last changed    : 3/12/2021 5:48:10 PM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-15-131-134\SC-15-131-134 2021-03-12 17-46-22\SC-4-IE-95-5-DAD
                      -1ML-30MIN.M (Sequence Method)
    Last changed    : 4/7/2021 6:17:13 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



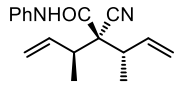

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

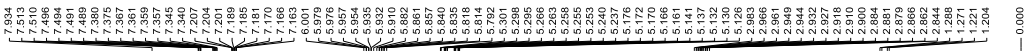

    Signal 1: DAD1 A, Sig=220,4 Ref=360,100

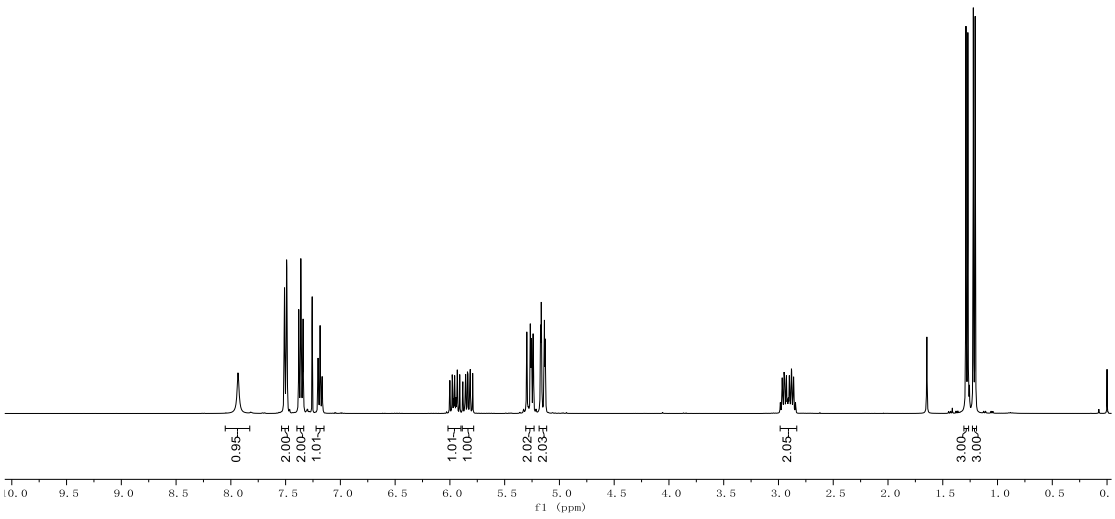
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.082 BB    0.4177 1.64576e4   595.02911  99.7731
       2  18.842 MM    0.5628   37.43217    1.10849   0.2269

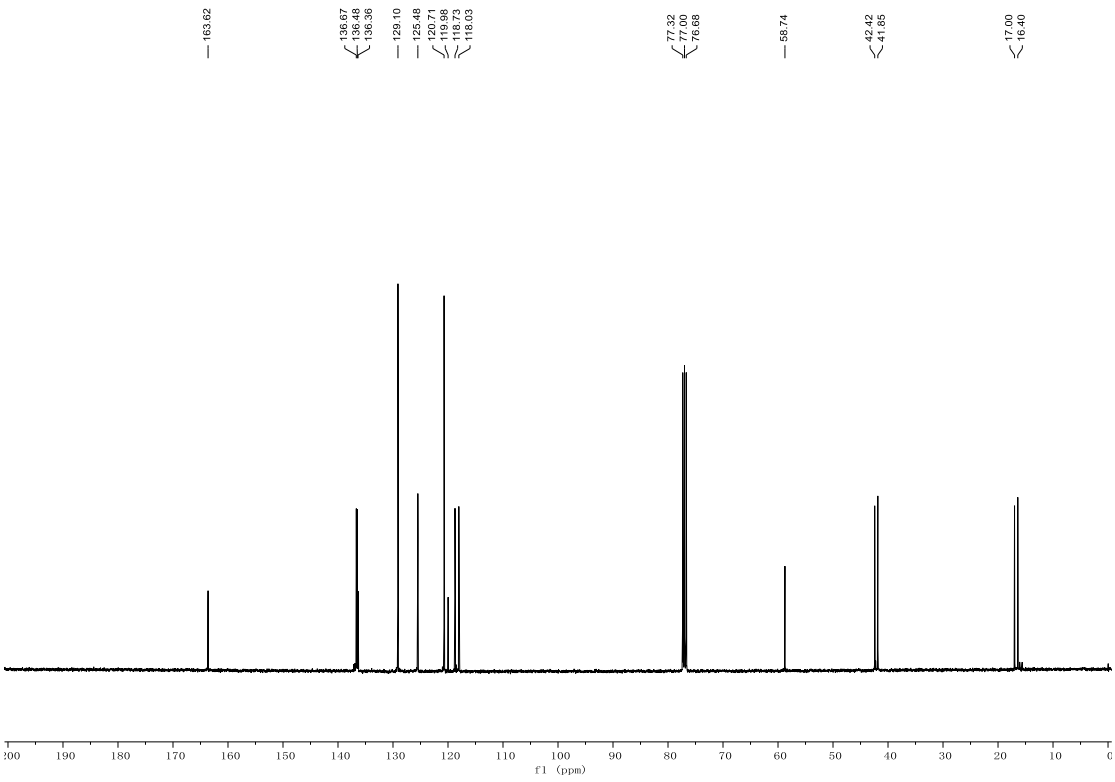
    Totals :                  1.64951e4   596.13760
```


PhNHOC
CN

16

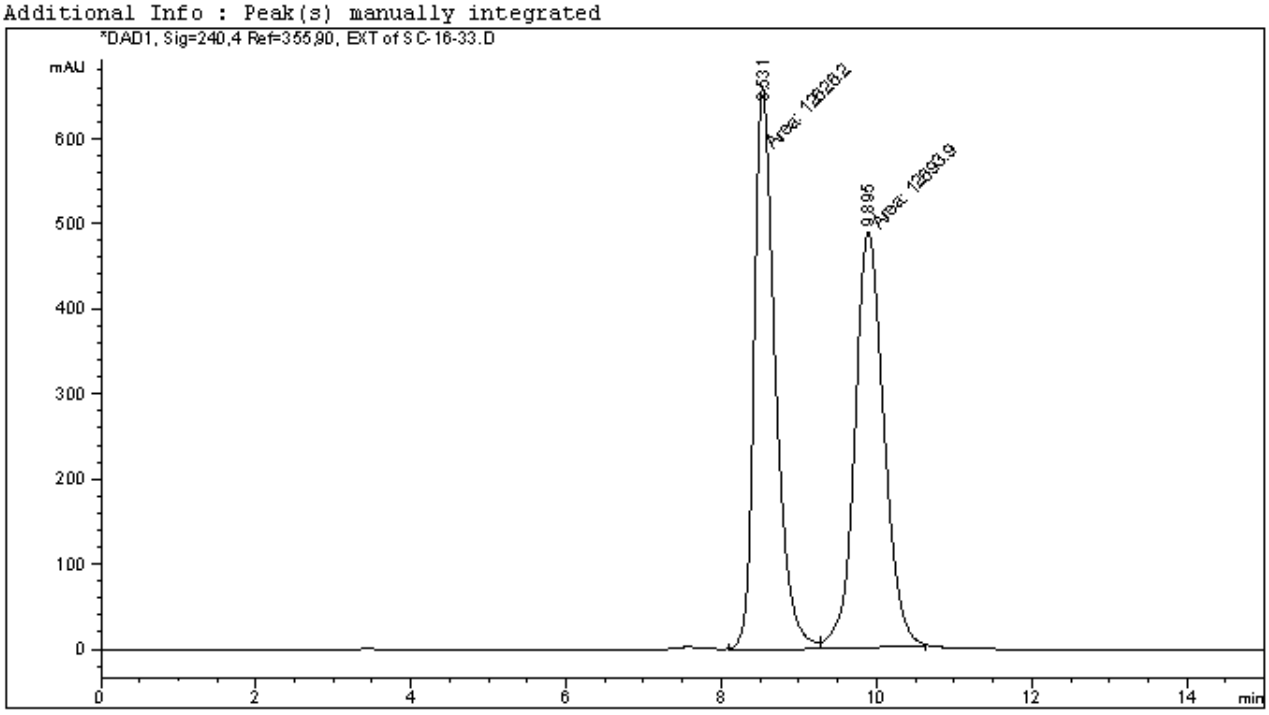



0.95
2.00
2.00
1.01
1.01
1.00
2.02
2.03
2.05
3.00
3.00
f1 (ppm)


163.62
136.67
136.48
136.36
129.10
125.48
120.71
119.98
118.73
118.03
77.32
77.00
76.68
58.74
42.42
41.85
17.00
16.40
f1 (ppm)

Data File E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-16-33.D
Sample Name: SC-16-33-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : 1260                             Location :   82
    Injection Date  : 5/13/2021 10:53:58 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-5-OJH-98-2-DAD-1ML-
                      20MIN.M
    Last changed    : 5/13/2021 10:52:29 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-33\SC-16-33-RAC 2021-05-13 10-52-29\SC-5-OJH-98-2-DAD-1ML-
                      20MIN.M (Sequence Method)
    Last changed    : 5/13/2021 11:11:41 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

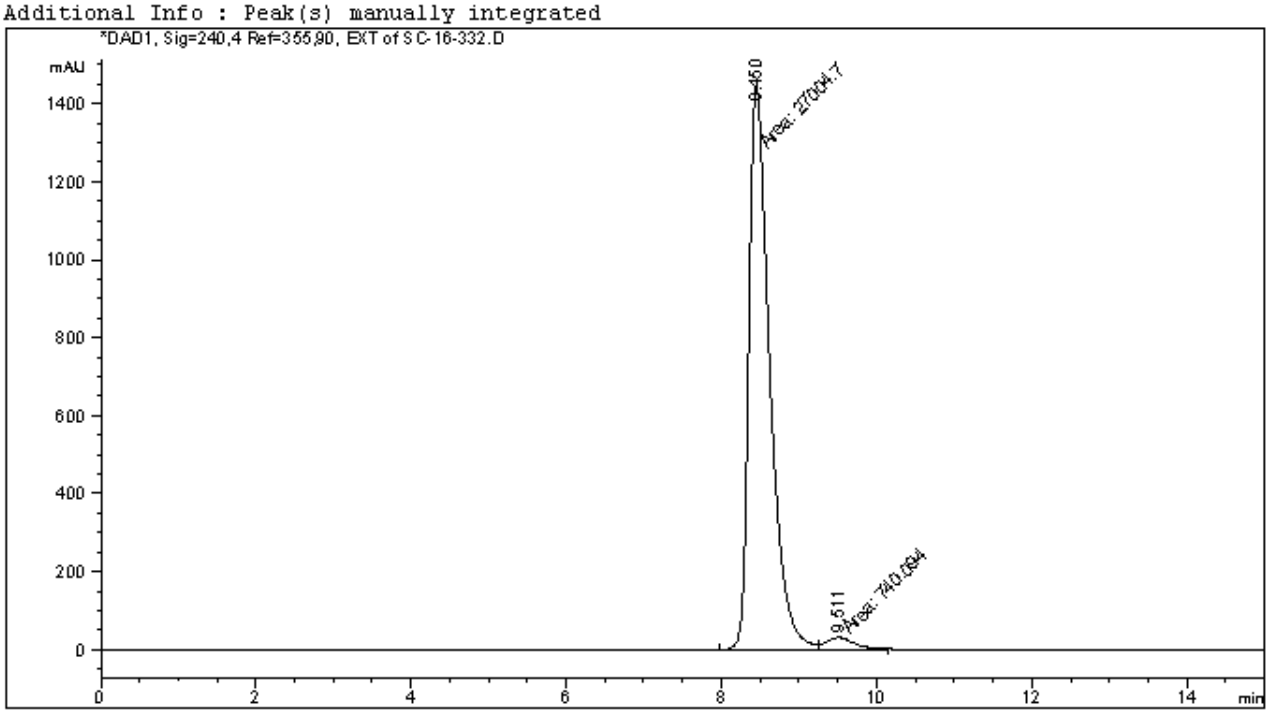

    Signal 1: DAD1, Sig=240,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.531 MF    0.3179 1.26262e4   661.92004  49.8663
       2   9.895 FM    0.4334 1.26939e4   488.19965  50.1337

    Totals :                   2.53202e4  1150.11969
```

Data File E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-16-332.D
Sample Name: SC-16-33B

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   3
    Acq. Instrument : 1260                             Location :   84
    Injection Date  : 5/13/2021 10:31:08 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-5-0JH-98-2-
                      DAD-1ML-20MIN.M
    Last changed    : 5/13/2021 9:47:05 AM by SYSTEM
    Analysis Method : E:\DATA\SC\SC-16-33\SC-16-33-RAC-0J-98 2021-05-13 09-47-05\SC-5-0JH-98-2-
                      DAD-1ML-20MIN.M (Sequence Method)
    Last changed    : 5/13/2021 11:01:04 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

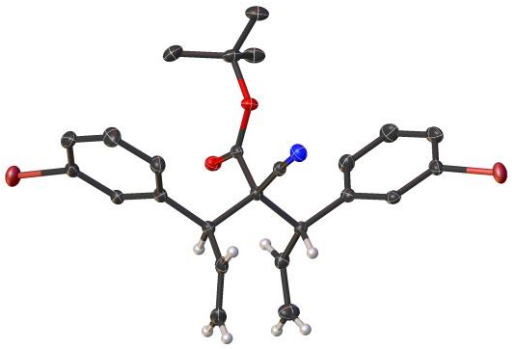
    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1, Sig=240,4 Ref=355,90, EXT
     Signal has been modified after loading from rawdata file!

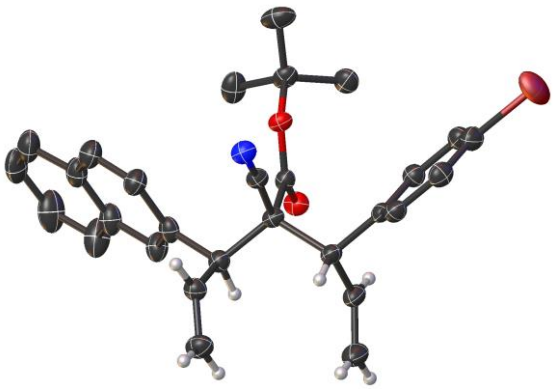
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.450 MF    0.3116 2.70047e4  1444.33252  97.3325
       2   9.511 FM    0.4116  740.09369   29.96502   2.6675

    Totals :                   2.77447e4  1474.29754
```

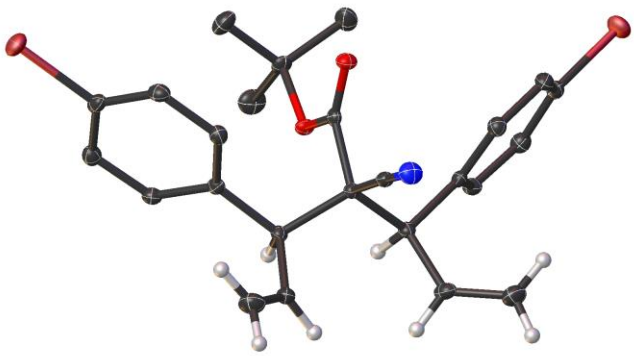
XI. X-ray Structures of (*S*,*S*)-**7j**, (*S*,*R*,*S*)-**8A**, *meso*-(*S*,*s*,*R*)-**7d**, and (3*S*,4*S*,5*R*)-(*S*)-**12**



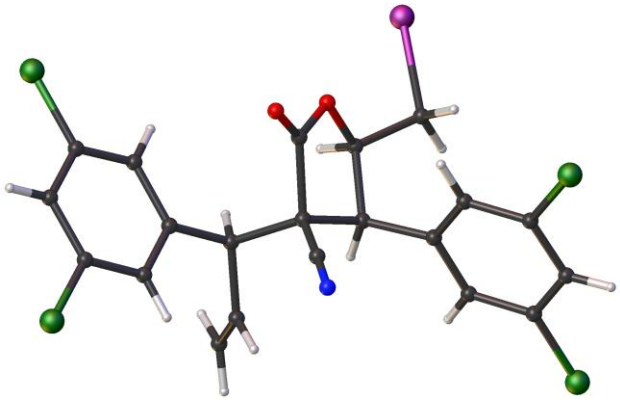
Crystal data for (*S*,*S*)-**7j**: $C_{25}H_{25}Br_2NO_2$, M_r = 531.28, T = 296 K, monoclinic, space group $P12_11$, a = 10.68950(10), b = 11.14220(10), c = 10.92190(10) Å, β = 112.4700(10) º, V = 1202.09(2) Å^3, Z = 2, 4759 unique reflections, final R_1 = 0.0192 and wR_2 = 0.0498 for 4773 observed [I>2σ(I)] reflections, Flack χ = -0.016(6). CCDC 2096475 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



Crystal data for (*S*,*R*,*S*)-**8A**: $C_{29}H_{28}BrNO_2$, M_r = 502.43, T = 296 K, orthorhombic, space group $P2_12_12_1$, a = 7.53030(10), b = 8.69550(10), c = 39.2876(3) Å, V = 2572.54(5) Å^3, Z = 4, 5020 unique reflections, final R_1 = 0.0279 and wR_2 = 0.0731 for 5128 observed [I>2σ(I)] reflections, Flack χ = -0.026(6). CCDC 2096476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



Crystal data for *meso*-(*S*,*s*,*R*)-**7d**: $C_{25}H_{25}Br_2NO_2$, M_r = 531.28, T = 296 K, monoclinic, space group $P2_1/m$, a = 5.982, b = 20.17050(10), c = 9.655 Å, β = 104.4620(10) °, V = 1128.058(8) Å^3, Z = 2, 2075 unique reflections, final R_1 = 0.0205 and wR_2 = 0.0514 for 2083 observed [I>2σ(I)] reflections, CCDC 2096474 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



Crystal data for (3*S*,4*S*,5*R*)-(*S*)-**12**: $C_{21}H_{14}Cl_4INO_2$, M_r = 581.03, T = 296 K, triclinic, space group $P1$, a = 8.2099(3), b = 11.6051(4), c = 12.1577(5) Å, α = 87.954(3) °, β = 80.589(3) °, γ = 89.897(3) °, V = 1142.02(7) Å^3, Z = 2, 6921 unique reflections, final R_1 = 0.0738 and wR_2 = 0.2072 for 7558 observed [I>2σ(I)] reflections, Flack χ = 0.001(8). CCDC 2096478 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).