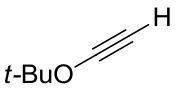
Contents

Method and Materials

General. Unless otherwise stated, reactions were performed under argon using freshly purified solvents, which were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All Reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Flash chromatography was performed with indicated solvents using silica gel (particle size 40-63 μm) purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova-400 MHz or 500 MHz spectrometer. Chemical shift are reported relative to internal chloroform ($CDCl_3$: ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.36 ppm) and benzene (C_6D_6: ^{1}H, δ = 7.15 ppm, ^{13}C, δ = 128.62 ppm). Coupling constants are in Hz and are reported as d (doublet), t (triplet), q (quartet), and m (multiplet). Mass spectra were acquired on an Agilent Technologies 1200 series LC/MS using indicated ionization methods.

Materials. Chemicals were purchased from Aldrich, Fisher or Alfa Aesar, TCI, and Chemical Strem and used without purification.



***tert*-Butyl acetylenyl ether**.[1] **CAUTION: terminal ynol ethers have been reported to explode upon heating in neat form.[2] Avoid heating *t*-butoxy acetylene. We have never experienced an explosion with the aryl-substituted ynol ethers, even after heating to >100 °C, but caution is still recommended.** Potassium hydride in mineral oil was washed by anhydrous hexane four times and dried under high vacuum pump for 30 minutes. To a 1000 ml flask charged with potassium hydride (53.5 g, 400 mmol) and equipped with a gas outlet, was added ether (100 ml) then *tert*-butanol (19.13 ml, 200 mmol) in 200 ml ether under argon at room temperature. After bubbling ceased, trichloroethene (17.4 ml, 196 mmol) in 150 ml ether was added dropwise at -40 °C. The cooling bath was removed, and the reaction was stirred for 1-2 h until the mixture turned brown. The suspension was cooled to -78 °C, and a 2.5M butyllithium solution (200 ml, 500 mmol) in THF was added. The reaction mixture was allowed to warm to -50 °C over about 30 min and then was stirred at that temperature for 1 hour. Water was added to quench the reaction at -50 °C, and the crude product was extracted by ether 3 times, dried with anhydrous sodium sulfate and filtered. Following the procedure described by Pericàs et al.[3] the crude reaction mixture was fractionally distilled on a rotary evaporator. Thus, solvent was removed from 300 to 200 torr with a room temperature water bath. The desired ynol ether was collected from 200 to 40 torr and a room temperature water bath. The product was further purified via redistillation from calcium hydride, again using a rotary evaporator and a room temperature water bath. The ether was obtained by collecting the fraction at 120 torr as a 30% by weight solution in hexanes and ether. The anhydrous mixture could be stored under argon at -20 °C in a Schlenk flask for half year.

General Method

Coupling reaction:

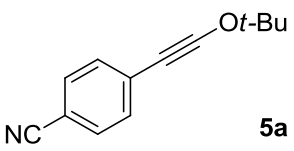
Method A. All solid reagents, aryl iodides (0.3 mmol), $Pd_2(dba)_3$ (15.6 mg, 0.015 mmol), PPh_3 (15.9 mg, 0.06 mmol), CuI (7.5 mg, 0.039 mmol), and 150 mg 4 Å molecular sieves were combined in vials and purged with argon. To the reaction, 0.6 ml diisopropylethyl amine and 0.6 ml *tert*-butyl acetylenyl ether were added at room temperature. If the aryl iodides were liquid, they were added after amine was added. The reaction was monitored via TLC for the completion (12-24 h), and the reaction mixtures were directly loaded to the aluminum plug and washed off with ethyl acetate and hexane (1:10) yielding the products and dibenzylideneacetone. The mixture can be used directly in next step. For electron deficient substrates, they have higher reactivity and shorter reaction time, and extending the reaction time may lead to hydrolysis of desired product.

Method B. Same as Method A except diisopropyl amine was used instead of diisopropylethyl amine. The reaction was monitored via TLC for the completion, and the reaction mixtures were directly loading to the aluminum column and washed off with ethyl acetate and hexane (1:10), yielding the pure products *tert*-butyl arylacetylenyl ether.

Method C. Same as Method B except tri(2-furyl)phosphine was used. The reaction was monitored via TLC for the completion, and the reaction mixtures were directly loading to the aluminum column and washed off with ethyl acetate and hexane (1:10), yielding the pure products tert-butyl arylacetylenyl ether.

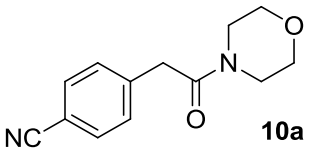
Ketene Formation and Morpholine Trapping (Table 2):

The *tert*-butyl arylacetylenyl ethers (products from coupling reaction) were dissolved in 2.0 ml toluene and 0.2 ml morpholine was added at room temperature under argon. The reaction was heated to 75 °C for 3 hours. The reaction mixture was concentrated under reduced pressure, and the pure morpholine amides were obtained following flash chromatography on silica gel with ethyl acetate and hexane (3:2).



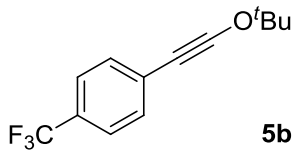
5a

tert-Butyl 4-nitrile-phenylacetylenyl ether (5a). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.4 Hz, 2H), 7.37 (d, J= 8.4 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.2, 131.9, 130.7, 119.35, 109.5, 100.6, 88.8, 43.1, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



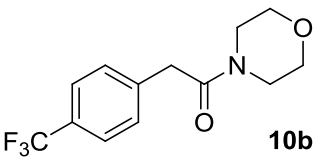
10a

4-Nitrile-phenylacetate morpholine amide (10a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.4 Hz, 2H), 7.35 (d, J= 8.4 Hz, 2H), 3.76 (s, 2H), 3.62-3.68 (m, 4H), 3.58 (t, J = 9.6 Hz, 2H), 3.45 (t, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 169.1, 140.35, 132.6, 129.9, 118.8, 66.8, 66.5, 46.6, 42.5, 40.3. ESI MS m/z: 231.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



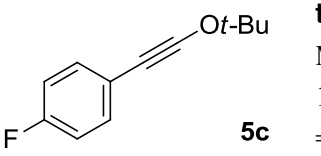
5b

tert-Butyl 4-trifluoromethyl-phenylacetylenyl ether (5b). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J = 8.0 Hz, 2H), 7.41 (d, J= 8.0 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.6, 129.7, 128.2 (q, J = 32.3), 125.4 (q, J = 3.8), 124.6 (q, J = 270.3) 98.4, 88.2, 42.7, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.6.



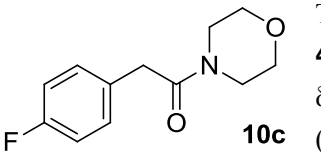
10b

4-Trifluoromethyl-phenylacetate morpholine amide (10b). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J = 8.0 Hz, 2H), 7.35 (d, J= 8.0, 2H), 3.76 (s, 2H), 3.65 (s, 4H), 3.55 (t, J = 4.8Hz, 2H), 3.45 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.0, 139.2, 129.6 (q, J = 32.3 Hz), 129.5, 126.0 (q, J = 3.8 Hz), 124.4 (q, J = 270.5 Hz), 67.1, 66.7, 46.7, 42.5, 40.5. ESI MS m/z: 274.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



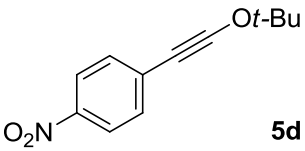
5c

tert-Butyl 4-flouro-phenylacetylenyl ether (5c). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.33 (m, 2H), 6.94 (tt, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.6 (d, J = 245 Hz), 133.2 (d, J = 7.9 Hz), 120.9 (d, J = 3.3 Hz), 115.5 (d, J = 21.8 Hz), 95.2, 87.2, 42.0, 27.4. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



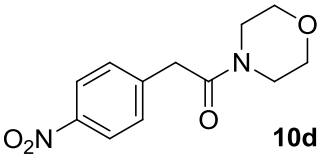
10c

4-flouro-phenylacetate morpholine amide (10c). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.20-7.23 (m, 2H), 7.03 (tt, J_1 = 8.0 Hz, J_2 = 2.5 Hz, 2H), 3.70 (s, 2H), 3.66 (s, 4H), 3.53 (t, J = 5.0 Hz, 2H), 3.45 (t, J = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 161.8 (d, J = 245 Hz), 130.4 (d, J = 3.3 Hz), 130.1 (d, J = 7.9 Hz), 115.6 (d, J = 22.4 Hz), 66.8, 66.4, 46.4, 42.1, 39.7. ESI MS m/z: 224.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.5.



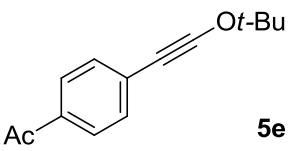
5d

tert-Butyl 4-nitro-phenylacetylenyl ether (5d). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 9.2 Hz, 2H), 7.41 (d, J = 9.2 Hz, 2H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9, 133.0, 131.8, 123.9, 101.8, 89.2, 43.4, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.6.



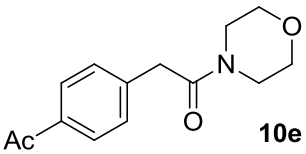
10d

4-Nitro-phenylacetate morpholine amide (10d). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 3.81 (s, 2H), 3.63-3.69 (m, 4H), 3.60 (t, J = 5.2 Hz, 2H), 3.47 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 147.3, 142.7, 130.3, 124.1, 67.1, 66.7, 46.7, 42.6, 40.3. ESI MS m/z: 250.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



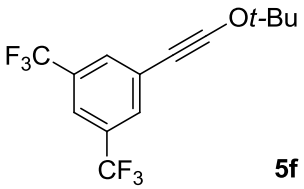
5e

tert-Butyl 4-aceto-phenonylacetylenyl ether (5e). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.79 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 133.1, 130.7, 117.1, 114.1, 94.4, 86.7, 55.6, 42.5, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



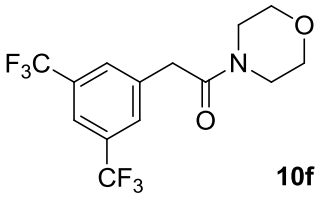
10e

4-Aceto-phenonylacetate morpholine amide (10e). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.76 (s, 2H), 3.63 (s, 4H), 3.51 (t, J = 4.8 Hz, 2H), 3.42 (t, J = 4.8 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.9, 169.1, 140.6, 136.2, 129.3, 129.1, 67.1, 66.7, 46.8, 42.5, 40.9, 26.9. ESI MS m/z: 248.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



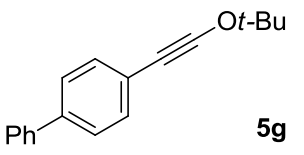
5f

tert-Butyl 3,5-bis-(trifluoromethyl)-phenylacetylenyl ether (5f). Method A. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 2H), 7.66 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.9 (q, J = 33.1 Hz), 131.4, 127.7, 123.5 (q, J = 271.2 Hz), 119.8, 99.0, 89.0, 41.6, 27.6. ESI MS m/z: 252.0, $[M\text{-}Bu\text{-}H]^-$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



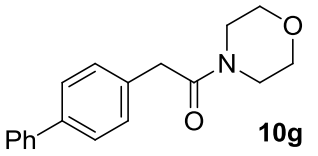
10f

3,5-bis-(trifluoromethyl)-phenylacetate morpholine amide (10f). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (s, 1H), 7.69 (s, 2H), 3.81 (s, 2H), 3.66 (m, 4H), 3.65 (t, J = 5.2 Hz, 2H), 3.51 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 137.2, 131.7 (q, J = 33.1 Hz), 129.5, 123.2 (q, J = 271.3 Hz), 121.0, 66.7, 66.4, 46.2, 42.3, 39.4. ESI MS m/z: 342.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



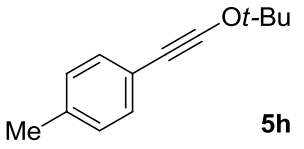
5g

tert-Butyl 4-biphenylacetylenyl ether (5g). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (dt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 7.52 (dt, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 7.42-7.47 (m, 4H), 7.35 (tt, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H) 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 139.3, 132.1, 129.1, 127.6, 127.23, 127.17, 124.1, 96.6, 87.3, 43.0, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



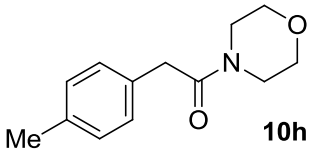
10g

4-biphenylacetate morpholine amide (10g). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.42-7.47 (m, 4H), 7.18-7.23 (m, 4H), 7.12 (tt, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 3.44 (t, J = 4.8 Hz, 2H), 3.40 (s, 2H), 3.22 (t, J = 4.8 Hz, 2H), 3.02 (t, J = 2.0 Hz, 2H), 2.76 (t, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ: 169.3, 141.8, 140.8, 135.4, 130.1, 129.7, 128.3, 128.1, 127.9, 67.3, 66.9, 47.0, 42.8, 41.0. ESI MS m/z: 282.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



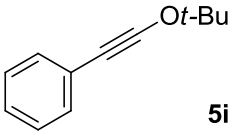
5h

tert-Butyl 4-methyl-phenylacetylenyl ether (5h). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, J = 6.4 Hz, 2H), 7.06 (d, J = 6.0 Hz, 2H), 2.32 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4, 131.6, 129.2, 121.8, 95.2, 86.9, 42.9, 27.5, 21.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.8.



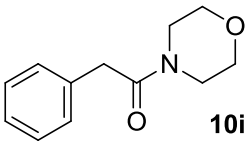
10h

4-Methyl-phenylacetate morpholine amide (10h). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.09 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 7.6 Hz, 2H), 3.42 (t, J = 4.4 Hz, 2H), 3.37 (s, 2H), 3.19 (t, J = 4.4 Hz, 2H), 2.98 (t, J = 4.8 Hz, 2H), 2.75 (t, J = 4.8 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: 169.6, 136.9, 133.3, 130.2, 129.4, 67.3, 66.9, 47.0, 42.8, 41.1, 21.6. ESI MS m/z: 220.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.5.



5i

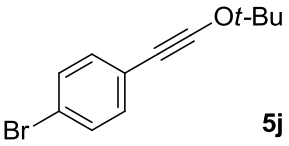
tert-Butyl phenylacetylenyl ether (5i). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.36 (m, 2H), 7.18-7.28 (m, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.7, 128.5, 126.6, 125.1, 95.9, 87.1, 43.1, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



10i

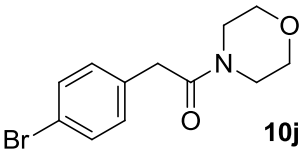
Phenylacetate morpholine amide (10i). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.33 (m, 2H), 7.21-7.25 (m, 3H), 3.72 (s, 2H), 3.63 (s, 4H), 3.43 (dt, J_1 = 19.2 Hz, J_2 = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 135.1, 129.1, 128.8, 127.2, 67.1, 66.7, 46.8, 42.4, 41.1. ESI MS m/z: 206.1, $[M+H]^+$. TLC (ethyl acetate:hexane =

3:2) r.f. = 0.5.



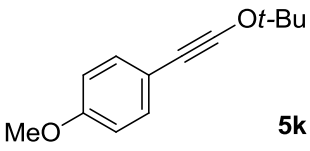
5j

tert-Butyl 4-bromo-phenylacetylenyl ether (5j). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.2, 131.6, 124.1, 120.3, 96.9, 87.6, 42.4, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



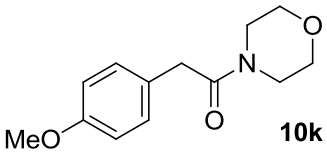
10j

4-Bromo-phenylacetate morpholine amide (10j). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.65 (s, 2H), 3.63 (s, 4H), 3.52 (t, J = 4.8 Hz, 2H), 3.41 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 134.1, 132.1, 130.7, 121.2, 67.1, 66.7, 46.7, 42.5, 40.3. ESI MS m/z: 284.0, 286.0, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



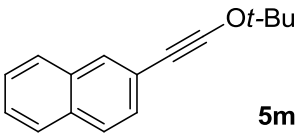
5k

tert-Butyl 4-methoxyl-phenylacetylenyl ether (5k). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H) 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 133.1, 117.1, 114.1, 94.4, 86.7, 55.6, 42.5, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.6.



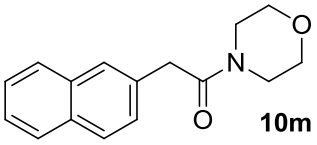
10k

4-methoxyl-phenylacetate morpholine amide (10k). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.66 (s, 2H), 3.63 (s, 4H), 3.46 (dt, J_1 = 22.0 Hz, J_2 = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 158.8, 129.9, 127.1, 114.5, 67.1, 66.8, 55.6, 46.8, 42.5, 40.3. ESI MS m/z: 236.0, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



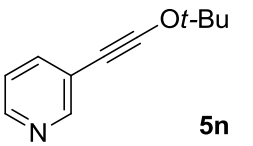
5m

tert-Butyl 2-naphthalenylacetylenyl ether (5m). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.77 (d, J = 6.4 Hz, 1H), 7.71-7.74 (m, 2H), 7.40-7.46 (m, 3H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.6, 132.2, 130.4, 129.5, 128.0, 127.6, 126.5, 125.9, 122.4, 96.3, 87.4, 43.6, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



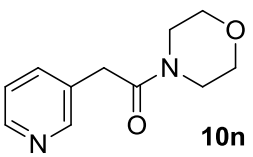
10m

2-Naphthalenylacetate morpholine amide (10m). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.58-7.61 (m, 3H), 7.52 (s, 1H), 7.36 (d, J = 6.4 Hz, 1H), 7.21-7.27 (m, 2H), 3.50 (s, 2H), 3.44 (t, J = 3.6 Hz, 2H), 3.19 (t, J = 3.6 Hz, 2H), 2.93 (t, J = 3.6 Hz, 2H), 2.74 (t, J = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ: 179.1, 169.3, 134.7, 133.9, 133.5, 129.3, 128.1, 127.9, 127.0, 126.5, 67.3, 66.9, 46.9, 42.8, 41.7. ESI MS m/z: 256.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



5n

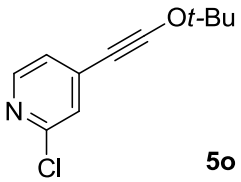
tert-Butyl pyridinyl-3-acetylenyl ether (5n). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (s, 1H), 8.40 (d, J = 4.0 Hz, 1H), 7.60 (dt, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 1H), 7.17 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 147.0, 138.5, 123.2, 122.3, 98.6, 88.2, 40.1, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



10n

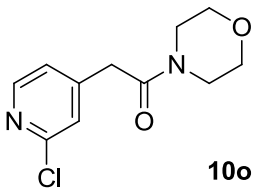
Pyridinyl-3-acetate morpholine amide (10n). ^{1}H NMR (400 MHz, C_6D_6) δ: 8.47 (d, J = 1.2 Hz, 1H), 8.45 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.37 (d, J = 6.0 Hz, 1H), 6.73 (dd, J_1 = 6.0 Hz, J_2 = 4.0 Hz, 1H), 3.33 (t, J = 4.0 Hz, 2H), 3.15 (t, J = 4.0 Hz, 2H), 3.05 (s, 2H), 2.99 (t, J = 4.0 Hz, 2H), 2.59 (t, J = 4.0 Hz, 2H); ^{13}C NMR (100

MHz, C_6D_6) δ: 168.5, 151.2, 149.3, 136.9, 131.8, 124.0, 67.2, 66.9, 46.6, 42.7, 37.7. ESI MS m/z: 207.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



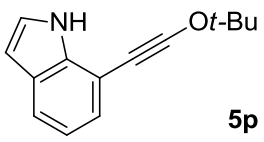
5o

tert-Butyl 2-chloro-4-pyridinylacetylenyl ether (5o). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, J = 5.2 Hz, 1H), 7.21 (s, 1H), 7.08 (d, J = 5.2 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 149.4, 137.0, 125.9, 124.5, 102.3, 89.7, 41.6, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



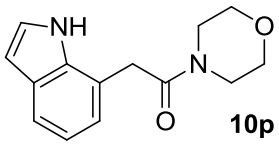
10o

2-Chloro-4-pyridinylacetate morpholine amide (10o). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J = 5.2 Hz, 1H), 7.24 (s, 1H), 7.11 (d, J = 4.8 Hz, 1H) 3.68 (s, 2H), 3.60-3.67 (m, 6H), 3.45 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.6, 152.3, 150.2, 147.3, 125.1, 123.4, 67.1, 66.8, 46.8, 42.7, 39.6. ESI MS m/z: 241.0, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.2. These products are not stable to prolonged storage.



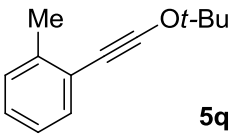
5p

tert-Butyl 7-indolylacetylenyl ether (5p). Method B. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (bs, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.23 (dd, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 1H), 7.22 (t, J = 3.2 Hz, 1H), 7.04 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H), 6.55 (dd, J_1 = 3.2 Hz, J_2 = 2.0 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 127.0, 125.1, 123.8, 119.8, 119.5, 107.4, 103.1, 98.8, 87.1, 38.5, 27.2. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



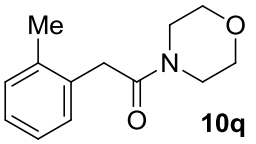
10p

7-Indolylacetate morpholine amide (10p). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.68 (bs, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 2.8 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.55 (dd, J_1 = 3.2 Hz, J_2 = 2.0 Hz, 1H), 3.98 (s, 2H), 3.53-3.61 (m, 6H), 3.42 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 135.8, 128.7, 125.2, 122.4, 120.3, 119.9, 117.1, 102.5, 66.9, 66.6, 47.2, 42.6, 39.6. ESI MS m/z: 245.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



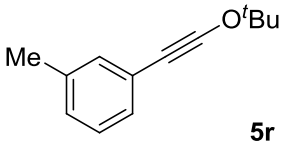
5q

tert-Butyl 2-methyl-phenylacetylenyl ether (5q). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.34 (m, 1H), 7.16-7.18 (m, 1H), 7.06-7.13 (m, 2H), 2.41 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 131.9, 129.5, 126.5, 125.8, 124.8, 99.8, 87.0, 42.1, 27.5, 21.4. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.8.



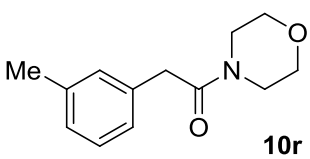
10q

2-Methyl-phenylacetate morpholine amide (10q). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11-7.19 (m, 5H), 3.68 (s, 4H), 3.67 (s, 2H) 3.55 (t, J = 4.8 Hz, 2H), 3.40 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 136.5, 133.7, 130.7, 128.9, 127.4, 126.6, 67.2, 66.8, 46.7, 42.4, 38.6, 20.0. ESI MS m/z: 220.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



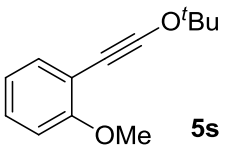
5r

tert-Butyl 3-methyl-phenylacetylenyl ether (5r). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12-7.18 (m, 3H), 7.00-7.03 (m, 1H), 2.31 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.1, 132.3, 128.8, 128.4, 127.5, 124.8, 95.6, 87.0, 43.2, 27.5, 21.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.8.



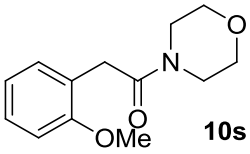
10r

3-Methyl-phenylacetate morpholine amide (10r). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (t, J = 8.0 Hz, 1H), 7.06 (s, 1H), 7.02 (t, J = 8.0 Hz, 2H) 3.69 (s, 2H), 3.63 (s, 4H), 3.45 (dt, J_1 = 23.6 Hz, J_2 = 3.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 138.8, 134.9, 129.5, 128.9, 127.9, 125.8, 67.1, 66.8, 46.8, 42.4, 41.1, 21.7. ESI MS m/z: 220.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



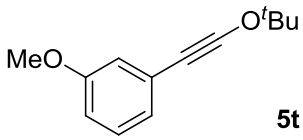
5s

tert-Butyl 2-methoxyl-phenylacetylenyl ether (5s). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 8.4 Hz, 1H), 6.83-6.89 (m, 2H), 3.86 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 133.1, 127.6, 120.7, 114.3, 110.8, 100.0, 87.2, 56.1, 39.2, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



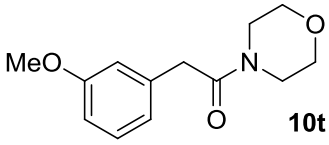
10s

2-Methoxyl-phenylacetate morpholine amide (10s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.25 (m, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H) 3.81 (s, 3H), 3.68 (s, 2H), 3.64 (s, 4H), 3.47 (dt, J_1 = 26.4 Hz, J_2 = 5.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 156.8, 130.2, 128.5, 123.7, 121.1, 110.7, 67.1, 66.9, 55.7, 46.7, 42.5, 34.4. ESI MS m/z: 236.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



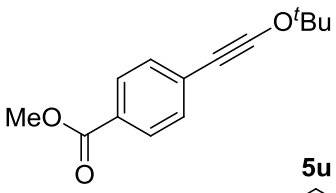
5t

tert-Butyl 3-methoxyl-phenylacetylenyl ether (5t). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (t, J = 8.0 Hz, 1H), 6.94 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.88 (dd, J_1 = 2.4 Hz, J_2 = 1.2 Hz, 1H), 6.76 (ddd, J_1 = 8.4 Hz, J_2 = 6.4 Hz, J_3 = 0.8 Hz, 1H), 3.79 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 129.4, 126.2, 124.3, 116.7, 113.0, 95.8, 87.3, 55.5, 43.1, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



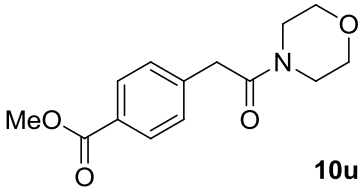
10t

3-Methoxyl-phenylacetate morpholine amide (10t). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18-7.22 (m, 1H), 6.75-6.79 (m, 3H), 3.76 (s, 3H), 3.67 (s, 2H), 3.60 (s, 4H), 3.45 (dt, J_1 = 24.0 Hz, J_2 = 4.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 160.1, 136.5, 130.0, 121.0, 114.4, 112.5, 67.0, 66.7, 55.4, 46.7, 42.3, 41.1. ESI MS m/z: 236.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



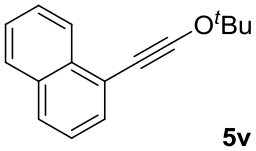
5u

tert-Butyl 4-methyl-carboxyl-phenylacetylenyl ether (5u). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 131.2, 130.3, 129.6, 127.7, 99.1, 88.0, 52.3, 43.3, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



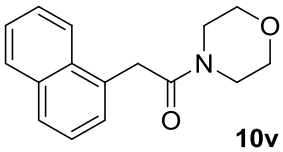
10u

4-Methyl-carboxyl-phenylacetate morpholine amide (10u). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.75 (s, 2H), 3.62 (s, 4H), 3.44 (dt, J_1 = 31.2 Hz, J_2 = 4.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 167.0, 140.3, 130.3, 129.2, 129.0, 67.0, 66.7, 52.4, 46.7, 42.5, 40.9. ESI MS m/z: 264.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.2.



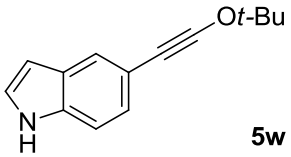
5v

tert-Butyl 1-naphthalenylacetylenyl ether (2v). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.47-7.58 (m, 3H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.0, 133.7, 129.9, 128.5, 126.9, 126.8, 126.5, 126.3, 125.7, 122.9, 100.5, 87.5, 41.3, 27.7. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.7.



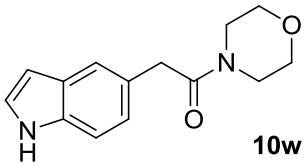
10v

1-Naphthalenylacetate morpholine amide (8v). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.96 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.18-7.35 (m, 4H), 3.80 (s, 2H), 3.45 (t, J = 4.4 Hz, 2H), 3.21 (t, J = 4.4 Hz, 2H), 2.95 (t, J = 3.6 Hz, 2H), 2.71 (t, J = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ: 169.5, 135.0, 133.2, 132.7, 129.7, 128.5, 127.2, 127.0, 126.7, 126.3, 124.7, 67.4, 67.0, 46.9, 42.8, 39.1. ESI MS m/z: 256.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.4.



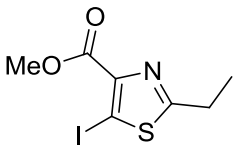
5w

tert-Butyl 5-indolylacetylenyl ether (2w). Method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (bs, 1H), 7.68 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.21 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.18 (t, J = 2.4 Hz, 1H), 6.48-6.50 (m, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9, 128.2, 126.3, 125.0, 124.3, 115.9, 111.2, 102.8, 93.4, 86.4, 43.8, 27.5. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.

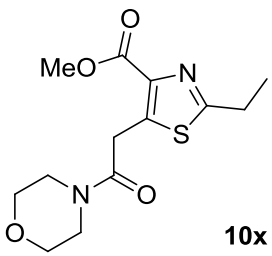


10w

5-Indolylacetate morpholine amide (8w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (bs, 1H), 7.48 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 2.8 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.49 (t, J = 2.0 Hz, 1H), 3.84 (s, 2H), 3.62-3.67 (m, 4H), 3.43-3.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 135.2, 128.6, 126.3, 125.1, 122.8, 120.6, 111.8, 102.7, 67.1, 66.8, 46.9, 42.5, 41.5. ESI MS m/z: 245.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.3.



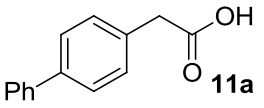
methyl 2-ethyl-5-iodothiazole-4-carboxylate. To a solution of thiazole (0.1 M in THF), the fresh made LDA (1.0 M in THF, 1.2 equiv.) was added rapidly at -78 °C; after stirring for 3 min at -78 °C, the I_2 solution (1.0 M in THF, 2.5 equiv.) was added. The reaction was stirring for another 5 min at -78 °C before adding sat. NaS_2O_3 (aq.) to quench the reaction at -78 °C. The aqueous phase was extracted with EtOAc for 3 times, and the organic layer was combined, dried through the Na_2SO_4 and concentrated to give the crude product. The pure product was obtained with a flash chromatograph. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.44 (q, J = 7.1 Hz, 1H), 2.75 (s, 1H), 1.43 (t, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 161.7, 147.6, 78.8, 62.2, 19.9, 14.7. ESI MS m/z: 297.9, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:1) r.f. = 0.7.



10x

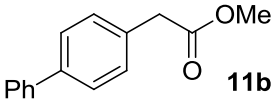
2-(2-ethyl-4-(methoxycarbonyl)thiazol-5-yl)acetate morpholine amide (10x). The coupling reaction was stopped after 50 min. Under the high vacuum pump the diisopropyl amine was removed from the crude product before morpholine was added and the mixture was heated. (0.1 mmol scale) ^{1}H NMR (500 MHz, Benzene-d6) δ: 4.16 (q, J = 7.1 Hz, 2H), 4.10 (s, 2H), 3.36 (t, J = 4.8 Hz, 2H), 3.18 (t, J = 4.9 Hz, 2H), 3.18 (t, J = 5.0 Hz, 2H), 2.90 (t, J = 5.0 Hz, 2H), 2.20 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Benzene-d6) δ: 167.2, 164.2, 163.5, 142.0, 141.9, 66.6, 66.4, 60.9, 45.9, 42.5, 31.9, 18.6, 14.4. ESI MS m/z: 299.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:1) r.f. = 0.3.

Ketene trapping with reagents other than morpholine.



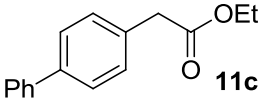
11a

4-Biphenylacetic acid (11a). Toluene (2.0 ml) with 0.2 ml water and then 0.2 ml TEA were added to *tert*-butyl 4-biphenylacetylenyl ether **5g** (18.7 mg, 0.074 mmol). The reaction was heated at 75 °C for 12h and then concentrated under reduced pressure. The residue was partitioned between 1.0 N HCl and EtOAc, and the organic layer was washed with brine, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. Flash chromatography on silica gel provided 14.7 mg pure acid as light yellow solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (t, J = 5.2 Hz, 4H), 7.44 (t, J = 6.0 Hz. 2H), 7.33-7.38 (m, 3H), 3.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.9, 141.0, 140.7, 132.6, 130.1, 129.1, 127.8, 127.7, 127.4, 41.0. ESI MS m/z: 213.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.6.



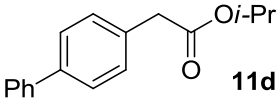
11b

Methyl 4-phenylbenzoate (11b). Anhydrous MeOH (2.5 ml) was added to 4-biphenylacetylenyl ether **5g** (14.6 mg, 0.058 mmol), and the solution was heated at 75 °C for 12h. Concentration under reduced pressure provided 13.1 mg pure ester in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (t, J = 8.4 Hz, 4H), 7.44 (t, J = 8.0 Hz. 2H), 7.33-7.38 (m, 3H), 3.73 (s, 3H), 3.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 141.1, 140.4, 133.3, 130.0, 129.1, 127.7, 127.6, 127.4, 52.5, 41.2. ESI MS m/z: 227.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.5.



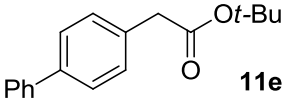
11c

Ethyl 4-phenylbenzoate (11c). Anhydrous EtOH (1.1 ml) was added to 4-biphenylacetylenyl ether **5g** (14.6 mg, 0.058 mmol), and the solution was heated at 75 °C for 12h. Concentration under reduced pressure provided pure ester in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.60 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.33-7.38 (m, 3H), 4.18 (q, J = 7.2 Hz, 2H), 3.67 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 141.1, 140.3, 133.5, 130.0, 129.1, 127.63, 127.58, 127.4, 61.3, 41.4, 14.5. ESI MS m/z: 241.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.5.



11d

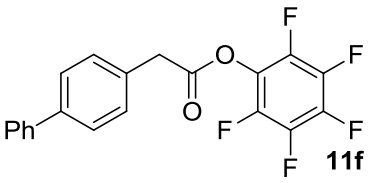
***Iso*-propyl 4-phenylbenzoate (11d).** Anhydrous *i*-PrOH (2.5 ml) was added to 4-biphenylacetylenyl ether **5g** (26.4 mg, 0.105 mmol) and the solution was heated at 75 °C for 12h. Concentration under reduced pressure provided 26.2 mg pure ester in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.61 (m, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.32-7.38 (m, 3H), 5.05 (dq, J_1 = 6.4 Hz, J_2 = 6.0 Hz, 1H), 3.63 (s, 2H), 1.26 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 141.2, 140.2, 133.7, 130.0, 129.1, 127.59, 127.56, 127.4, 68.6, 41.7, 22.1. ESI MS m/z: 254.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.5.



11e

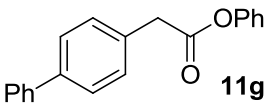
***Tert*-butyl 4-phenylbenzoate (11e).** Anhydrous *t*-BuOH (1.0 ml) was added to 4-biphenylacetylenyl ether **5g** (9.1 mg, 0.036 mmol), and the solution was heated at 75 °C for 6h. Concentration under reduced pressure provided 8.9 mg pure ester in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.60 (m, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.32-7.38 (m, 3H), 3.58 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 140.9, 139.7, 133.7, 129.6,

128.7, 127.18, 127.15, 127.0, 80.9, 42.2, 28.0. ESI MS m/z: 269.2, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.6.



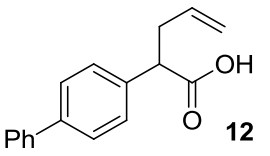
11f

Pentafluorophenyl 4-phenylbenzoate (11f). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (25.3 mg, 0.103 mmol), 2.0 ml toluene was added, followed by TEA (0.16 ml, 1.13 mmol) and 0.66 ml pentafluorophenol solution (0.63M in toluene, 1.03 mmol, freshly treated with 4 Å Molecular sieves). The reaction was heated to 75 °C for 5h. The crude product was washed by brine, dried with sodium sulfate anhydrous. 29.0 mg pure product was obtained following flash chromatography in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.63 (m, 4H), 7.43-7.48 (m, 4H), 7.37 (t, J = 7.2 Hz, 1H), 4.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 142.7, 141.1, 140.8, 140.2, 139.5, 136.9, 131.3, 130.0, 129.2, 128.0, 127.8, 127.4, 40.1. ESI MS m/z: 378.7, $[M-H]^-$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



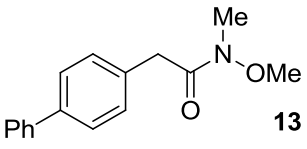
11g

Phenyl 4-phenylbenzoate (11g). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (20.3 mg, 0.081 mmol), 1.6 ml pre-mixed phenol (0.25M, 0.405 mmol) and TEA (0.5M, 0.81 mmol) toluene solution was added, followed by heating reaction at 75 °C for 5h. The crude product mixture was washed by saturated aqueous sodium hydrocarbonate and brine, and dried with anhydrous sodium sulfate. 20.8 mg pure product was obtained by flash chromatography (89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.0 Hz, 4H), 7.44-7.50 (m, 4H), 7.35-7.40 (m, 3H), 7.24 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.6 Hz, 2H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 151.1, 141.0, 140.7, 132.8, 130.0, 129.8, 129.1, 127.8, 127.7, 127.4, 126.2, 121.8, 41.4. ESI MS m/z: 287.0, $[M-H]^-$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.4.



12

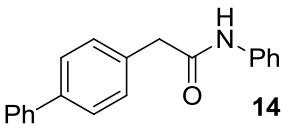
4-Biphenyl-2'-allylacetic acid (12). To 4 ml vial with *tert*-butyl 4-biphenylacetylenyl ether **5g** (11.0 mg, 0.046 mmol), 0.5 ml toluene was added, followed by TEA (52 μl, 0.23 mmol) and allylic alcohol (9.3 μl, 0.14 mmol). The reaction was heated at 75 °C for 5h, and then cooled to room temperature. TMSOTf (42 μl, 0.23 mmol) was added dropwise at room temperature, and the reaction was stirred for another 2h. The crude products were obtained by washing with 1.0 N HCl and brine, drying with anhydrous sodium sulfate, and concentrating via rotavap. After a flash chromatography, 10.3 mg pure product was afforded as white solid in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.58 (m, 4H), 7.38-7.45 (m, 4H), 7.34 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 5.71-5.81 (m, 1H), 5.12 (dd, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.04 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 3.70 (t, J = 7.6 Hz, 1H), 2.87 (m, 1H), 2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.4, 141.0, 140.9, 137.2, 135.2, 129.1, 128.8, 127.8, 127.7, 127.4, 117.7, 51.4, 37.4. ESI MS m/z: 253.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.7.



13

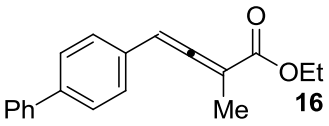
N-Methoxy-N-methyl-4-biphenylacetamide (13). To 4 ml vial with *tert*-butyl 4-biphenylacetylenyl ether **5g** (21.1 mg, 0.088 mmol), 1.2 ml toluene was added, followed by 0.88 ml pre-mixed Weinreb amide hydrochloride salt (1.0 M) and TEA (1.5 M) toluene solution. Then, the reaction was heated at 75 °C for 3h, and then 50 °C 10 hours. The crude products were obtained by washing with water and brine, drying with anhydrous sodium sulfate, and concentration under reduced pressure. After flash chromatography, 19.0 mg pure product was isolated in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.59

(m, 4H), 7.43 (t, J = 7.6 Hz. 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H) 3.82 (s, 2H), 3.66 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 141.2, 140.1, 134.3, 130.1, 129.1, 127.6, 127.5, 127.4, 61.7, 39.3, 32.6. ESI MS m/z: 256.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.5.



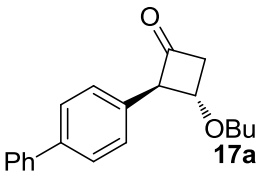
14

4-Biphenylacetanilide (14). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (28.4 mg, 0.113 mmol), 2.0 ml toluene was added, followed by aniline (0.2 ml, 2.25 mmol). The reaction was heated to 75 °C for 12h. The crude product was washed by 1 N HCl twice and brine, extracted with ethyl acetate, and dried by sodium sulfate. 31.0 mg pure product was isolated as light yellow solid after a flash chromatography in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.64 (m, 4H), 7.36-7.48 (m, 7H), 7.29 (t, J = 6.4 Hz, 2H), 7.23 (bs, 1H), 7.10 (t, J = 6.0 Hz, 1H), 3.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 140.9, 140.8, 137.9, 133.7, 130.3, 129.3, 129.2, 128.2, 127.8, 127.4, 124.8, 120.2, 44.8. ESI MS m/z: 288.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:1) r.f. = 0.7.



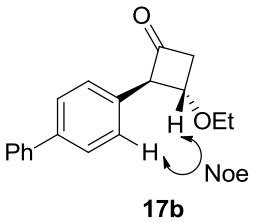
16

Ethyl 4-(4-biphenyl)-2-methyl-2,3-butadienoate (16). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (18.6 mg, 0.074 mmol) and (carbethoxyethylidene)triphenylphosphorane **15** (40.44 mg, 0.11 mmol), 1.5 ml toluene was added. The reaction mixture was heated to 75 °C for 12h. The crude products were obtained after washing with water and brine, drying with anhydrous sodium sulfate, and concentrating under reduced pressure. 12.9 mg pure product was afforded via flash chromatography as white solid in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.61 (m, 4H), 7.45 (t, J = 8.0 Hz, 2H), 7.33-7.37 (m, 3H), 6.52 (q, J = 2.8 Hz, 1H), 4.23 (qd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H), 2.02 (d, J = 2.8 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 212.9, 167.4, 140.94, 140.87, 131.9, 129.2, 128.1, 127.8, 127.7, 127.3, 99.9, 97.2, 61.5, 15.5, 14.6. ESI MS m/z: 279.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 3:2) r.f. = 0.8.



17a

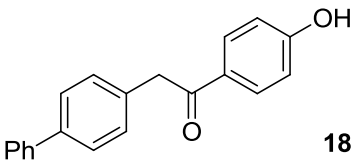
3-Butoxyl-2-(4-biphenyl)-cyclobutanone (17a). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (22.9 mg, 0.091 mmol), 1.0 ml vinyl butyl ether was added, and then the reaction was heated to 75 °C for 12h. The crude product was obtained following concentration under reduced pressure. 17.0 mg of product were obtained following flash chromatography in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.57 (m, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.29-7.35 (m, 3H), 4.46-4.49 (m, 1H), 4.39 (q, J = 6.4 Hz, 1H), 3.49-3.59 (m, 2H), 3.21-3.25 (m, 2H), 1.57-1.64 (m, 2H), 1.36-1.46 (m, 2H), 0.93 (t, J = 7.6 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.2, 140.7, 140.2, 134.0, 128.8, 127.6, 127.5, 127.3, 127.0, 71.3, 70.9, 70.0, 51.6, 31.7, 19.3, 13.9. ESI MS m/z: 295.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.6. Relative stereochemistry was assigned by analogy to **17b**.



17b

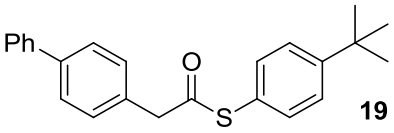
3-Ethoxyl-2-(4-biphenyl)-cyclobutanone (17b). Synthesized analogously to **17a**. 21.1 mg of product were isolated following flash chromatography in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.59 (m, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.30-7.37 (m, 3H), 4.50-4.52 (m, 1H), 4.43 (q, J = 6.4 Hz, 1H), 3.56-3.69 (m, 2H), 3.25-3.28 (m, 2H), 1.29 (t, J = 7.2 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.4, 140.9, 140.5, 134.2, 129.0, 127.9, 127.8, 127.6, 127.3, 71.6, 71.0, 65.9, 51.9, 15.5. ESI MS m/z: 267.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.6. Relative stereochemistry was assigned based on

an NOE between the oxygenated methine and the 2-position of the aryl ring.



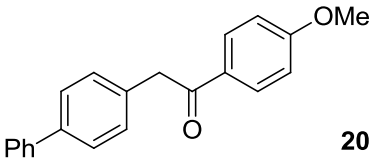
18

1-(4-hydroxylphenyl)-2-(4-biphenyl)ethanone (18). Methansulfonic acid (MSA) anhydride was added to commercially available MSA, and the mixture was heated at 90 °C for 1h. The water content was essential to this reaction, and it was monitored as 666.7 ppm using a Karl-Fischer apparatus. To 4 ml vial with phenyl 4-phenylbenzoate **11g** (17.1 mg, 0.113 mmol), 0.2 ml MSA (KF% = 666.7 ppm) was added, and the reaction was heated to 65 °C for 30h. Methanol was added to quench the reaction at room temperature, and the reaction system was neutralized by sodium carbonate solution. The crude product was extracted by warm DCM 6 times, and washed by brine. Flash chromatography provided the pure product (14.1mg, 82%) as white solid. ^{1}H NMR (400 MHz, CD_3OD + $CDCl_3$) δ: 7.98 (d, J = 8.8 Hz, 2H), 7.57 (t, J = 8.4 Hz, 4H), 7.41 (t, J = 8.0 Hz, 2H), 7.29-7.35 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 4.30 (s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 195.7, 162.3, 140.0, 138.3, 134.9, 131.1, 130.1, 128.9, 127.8, 127.3, 126.59, 126.56, 115.3, 43.9. ESI MS m/z: 289.1, $[M+H]^+$. TLC (MeOH:DCM = 1:10) r.f. = 0.4.



19

4'-tert-butyl-phenyl 4-phenylthiobenzoate (19). To 4 ml vial with 4-biphenylacetylenyl ether **5g** (28.0mg, 0.112 mmol), TEA (0.12 ml, 0.67 mmol) was added, followed by 4-*tert*-butylthiophenol (0.1 ml, 0.56 mmol). The reaction mixture was heated to 75 °C for 12 h, and the reaction was quenched with 1.0 ml 1 N HCl. Stirring was continued for 2h to hydrolyze thioketene acetal (ca. 50% of the reaction mixture) to the thioester. The crude product was obtained following extraction with ethyl acetate, washing with brine, and drying with anhydrous sodium sulfate. 30.4 mg pure product was isolated after flash chromatography (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.62 (m, 4H), 7.40-7.47 (m, 6H), 7.31-7.38 (m, 3H), 3.96 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1, 153.0, 141.0, 140.7, 134.4, 132.7, 130.4, 129.1, 127.74, 127.68, 127.4, 126.6, 124.6, 50.0, 35.1, 31.5. ESI MS m/z: 361.2, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.5.



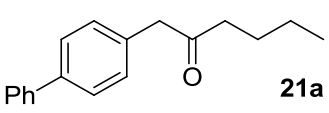
20

1-(4-methoxyphenyl)-2-(4-biphenyl)ethanone (20). To 4 ml vial, 1'-*tert*-butyl-phenyl 4-phenylthiobenzoate **19** (20.9 mg, 0.058 mmol), 4-methoxyphenylboronic acid (9.7 mg, 0.064 mmol) copper thiophene-2-carboxylate (16.6 mg, 0.087 mmol), $Pd_2(dba)_3$ (0.6 mg, 1 mol%), and TFP (0.4 mg, 3 mol%) were combined. THF (0.6 ml) was added to the solid mixture, and the reaction was heated to 50 °C for 12h. The crude product was washed by water and brine, and then dried with anhydrous sodium sulfate. After a flash chromatography, 13.9 mg pure product was isolated as a white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J = 8.8 Hz, 2H), 7.56 (m, 4H), 7.43 (t, J = 8.0 Hz, 2H), 7.31-7.36 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 4.28 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 196.5, 163.9, 141.2, 140.1, 134.3, 131.3, 130.2, 130.0, 129.1, 127.7, 127.6, 127.4, 114.1, 55.8, 45.2. ESI MS m/z: 303.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.4.

General Method for lanthanum promoted morpholine amide addition:

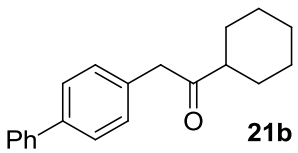
To $LaCl_3$▪2LiCl 0.6 M THF solution, 1.0 equivalent of Grignard reagent was added via syringe pump over 30 minutes at -20 °C, and the mixture was stirred at -20 °C for 1h. The pre-mixed $LaCl_3$ and Grignard solution was added to 4-biphenylacetate morpholine amide **10g** dissolved in THF (0.1 M) via syringe pump

over 30 minutes at -78 °C. The reaction was stirred at -78 °C for 2h, and it was quenched by saturated aqueous ammonium chloride. The crude product was extracted with ethyl acetate and washed by brine. Ketones **21a** – **21d** were purified using preparative TLC.



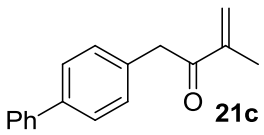
21a

1-butyl-2-(4-biphenyl)ethanone (21a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.61 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 3.73 (s, 2H), 2.45 (t, J = 7.6 Hz, 2H), 1.57 (tt, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 2H), 1.29 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.9, 141.1, 140.2, 133.7, 130.2, 129.1, 127.7, 127.6, 127.4, 50.0, 42.2, 26.2, 22.6, 14.2. ESI MS m/z: 253.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



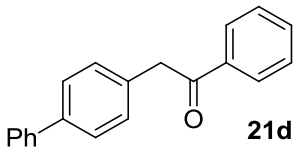
21b

1-cyclohexyl-2-(4-biphenyl)ethanone (21b). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.61 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 3.78 (s, 2H), 2.50 (tt, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 1H), 1.78-1.88 (m, 4H), 1.65-1.69 (m, 1H), 1.15-1.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.5, 141.1, 140.1, 133.8, 130.2, 129.1, 127.6, 127.5, 127.4, 50.6, 47.7, 28.9, 26.2, 26.0. ESI MS m/z: 279.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.5.



21c

1-*iso*-propenyl-2-(4-biphenyl)ethanone (21c). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.60 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 6.12 (s, 1H), 5.87 (d, J = 1.6 Hz, 1H), 4.06 (s, 2H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.6, 144.6, 141.2, 140.1, 134.3, 130.1, 129.1, 127.7, 127.5, 127.4, 126.1, 44.4, 18.2. ESI MS m/z: 237.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.5.

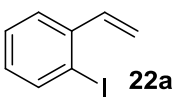


21d

1-phenyl-2-(4-biphenyl)ethanone (21d). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J = 7.2 Hz, 2H), 7.55-7.59 (m, 5H), 7.48 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.31-7.36 (m, 3H), 4.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.9, 141.1, 140.2, 136.9, 133.9, 133.6, 130.2, 129.1, 129.0, 128.9, 127.7, 127.5, 127.3, 45.4. ESI MS m/z: 273.2, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.

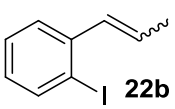
General Method for Wittig Reaction:

To a vigorously stirred slurry of phosphonium salt (1.15 equiv.) in THF was added n-butyllithium solution (2.5 M in hexane, 1.12 equiv.) at 0 °C. The reaction is allowed to stir for 15 min and then 2-iodoaryl-1-aldehyde solution in THF (1.0 equiv.) was added dropwise at 0 °C. After 15 min, the ice bath was removed and the reaction was allowed to stir for 2 h. The reaction was quenched with sat. ammonium chloride aq., and extracted with EtOAc. The combined organics was dried through the Na_2SO_4 and concentrated to get the crude product. The pure product was able to obtain via a flash chromatograph.



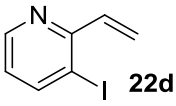
22a

1-iodo-2-vinylbenzene (22a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 7.51 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.00 - 6.84 (m, 2H), 5.63 (dd, J_1 = 17.3 Hz, J_2 = 1.0 Hz, 1H), 5.32 (dd, J_1 = 10.9 Hz, J_2 = 1.0 Hz, 1H). ^{1}H NMR and ^{13}C NMR was described.[4] ^{1}H NMR data was consistent.



22b

2-iodopropenylbenzene (22b). (as a 1:2 mixture of *Z/E* isomers) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.81 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 7.43 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.35 – 7.26 (m, 1+2H), 6.91 (m, 1+1H), 6.58 (dq, J_1 = 15.5 Hz, J_2 =1.7 Hz, 1H), 6.37 (dq, J_1 = 11.3 Hz, J_2 = 1.8 Hz, 1H), 6.11 (dq, J_1 = 15.5 Hz, J_2 = 6.7 Hz, 1H), 5.85 (dq, J_1 = 11.4 Hz, J_2 = 7.1 Hz, 1H), 1.93 (dd, J_1 = 6.7 Hz, J_2 = 1.7 Hz, 3H), 1.76 (dd, J_1 = 7.1 Hz, J_2 = 1.8 Hz, 3H). ^{1}H NMR and ^{13}C NMR was described.[5] ^{1}H NMR data was consistent.



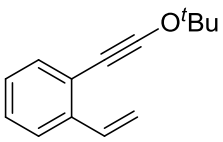
22d

3-iodo-2-vinylpyridine (22d). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 8.09 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.17 (dd, J_1 = 16.8 Hz, J_2 = 10.6 Hz, 1H), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 1H), 6.38 (dd, J_1 = 16.8 Hz, J_2 = 1.9 Hz, 1H), 5.51 (dd, J_1 = 10.6 Hz, J_2 = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 148.9, 147.3, 137.5, 123.9, 122.0, 96.1. ESI MS m/z: 231.9, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.5.

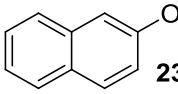
Preparation and characterization of compound **22c**,[6] **22e**[7] were described.

General Method for 6-π electrocyclization from 2-iodo-1-enylbenzene:

Same as Method C of coupling reaction except 16 mol% CuI was loaded in the reaction. The reaction was monitored via TLC for the completion, and the reaction mixtures were directly loading to the aluminum plug and washed off with ethyl acetate and hexane eluent. The yielding products were dissolved in toluene (0.03M) and heated to 120 °C over night. The mixture after the reaction was concentrated and further purified with flash chromatograph to yield the pure product.

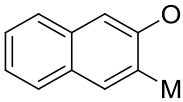


1-(tert-butoxyethynyl)-2-vinylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 – 7.50 (m, 1H), 7.40 – 7.32 (m, 1H), 7.26 – 7.11 (m, 3H), 5.76 (d, J = 17.7 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 136.0, 132.7, 127.7, 126.8, 124.8, 124.0, 114.9, 100.4, 87.4, 41.6, 27.6. TLC (ethyl acetate:hexane = 1:10) r.f. = 0.8.



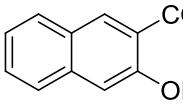
23a

naphthalen-2-ol (23a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (t, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.44 (ddd, J_1 = 8.2 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1H), 7.34 (ddd, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 1.3 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 7.11 (dd, J_1 = 8.8 Hz, J_2 = 2.6 Hz, 1H), 5.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.4, 134.7, 130.0, 129.0, 127.9, 126.7, 126.5, 123.8, 117.9, 109.6. ESI MS m/z: 145.0, $[M+H]^{+\cdot}$ TLC (ethyl acetate:hexane = 1:10) r.f. = 0.4.



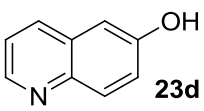
23b

3-methylnaphthalen-2-ol (23b). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.60 (s, 1H), 7.38 (dd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, 1H), 7.31 (dd, J_1 = 8.2 Hz, J_2 = 6.8 Hz, 1H), 7.09 (s, 1H), 4.94 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 133.5, 129.5, 129.3, 127.1, 126.5, 126.0, 125.7, 123.6, 109.1, 16.7. ESI MS m/z: 159.0, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.4.



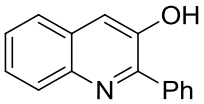
23c

methyl 3-hydroxy-2-naphthoate (23c). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.44 (s, 1H), 8.48 (s, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.50 (dd, J_1 = 8.3 Hz, J_2 = 6.8 Hz, 1H), 7.37 – 7.28 (m, 2H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 156.4, 138.0, 132.6, 129.3, 129.3, 127.1, 126.4, 124.1, 114.3, 111.8, 52.7. ESI MS m/z: 203.0, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:5) r.f. = 0.4.



23d

quinolin-6-ol (23d). ^{1}H NMR (400 MHz, CD_3OD) δ: 8.60 (dd, J_1 = 4.3 Hz, J_2 = 1.7 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 9.1 Hz, 1H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 4.3 Hz, 1H), 7.35 (dd, J_1 = 9.1 Hz, J_2 = 2.8 Hz, 1H), 7.14 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ: 157.4, 147.9, 144.0, 136.6, 131.4, 130.4, 123.5, 122.5, 109.6. ESI MS m/z: 146.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:3) r.f. = 0.4.



23e

2-phenylquinolin-3-ol (23e). ^{1}H NMR (400 MHz, CD_3OD) δ: 9.67 (s, 1H), 8.23 (s, 1H), 8.04 (d, J = 7.1 Hz, 2H), 8.01 (d, J = 7.7 Hz, 1H), 7.88 – 7.77 (m, 3H), 7.58 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.23 (t, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ: 170.9, 142.1, 137.9, 135.2, 130.3, 130.0, 129.7, 129.0, 128.0, 123.4, 122.2, 122.0, 110.7. ESI MS m/z: 222.1, $[M+H]^+$. TLC (ethyl acetate:hexane = 1:3) r.f. = 0.4.

References:

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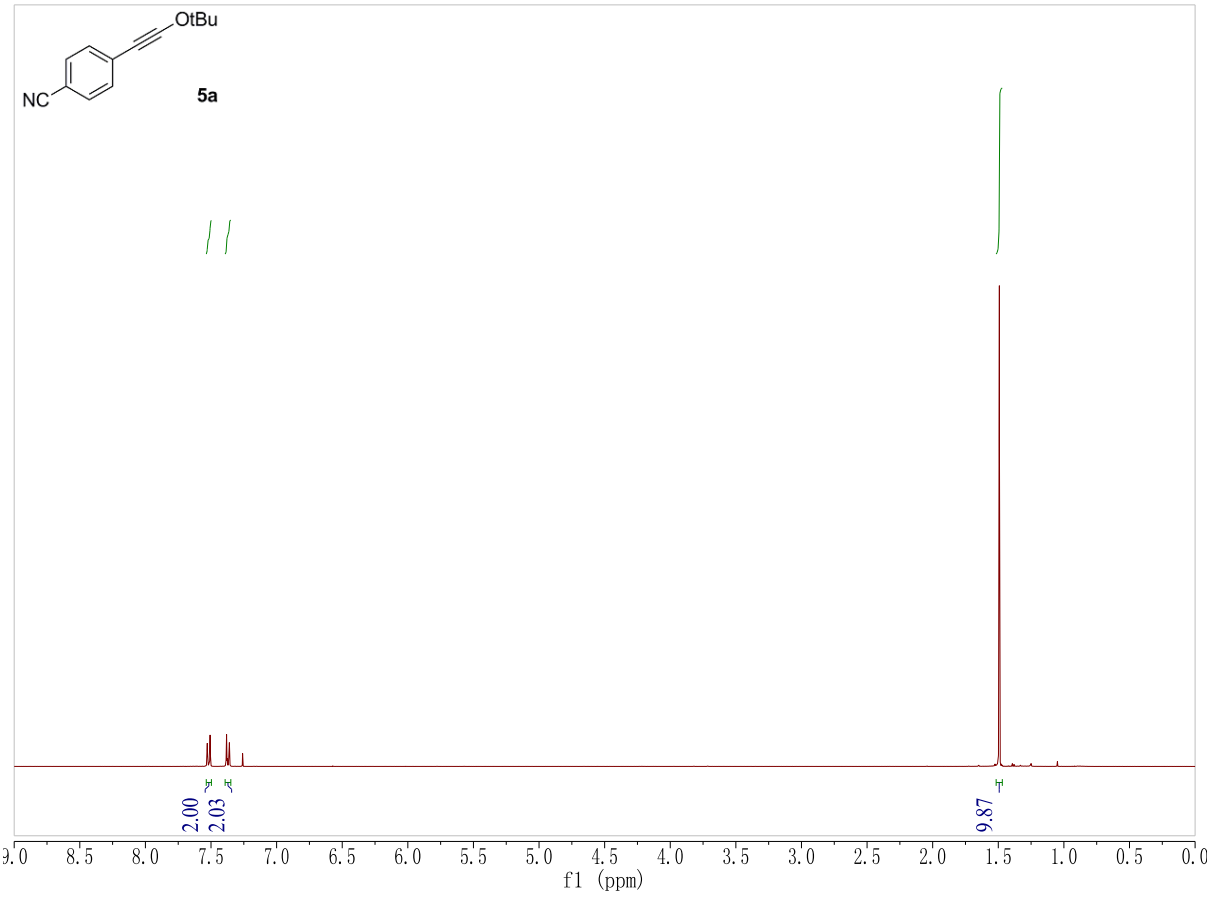
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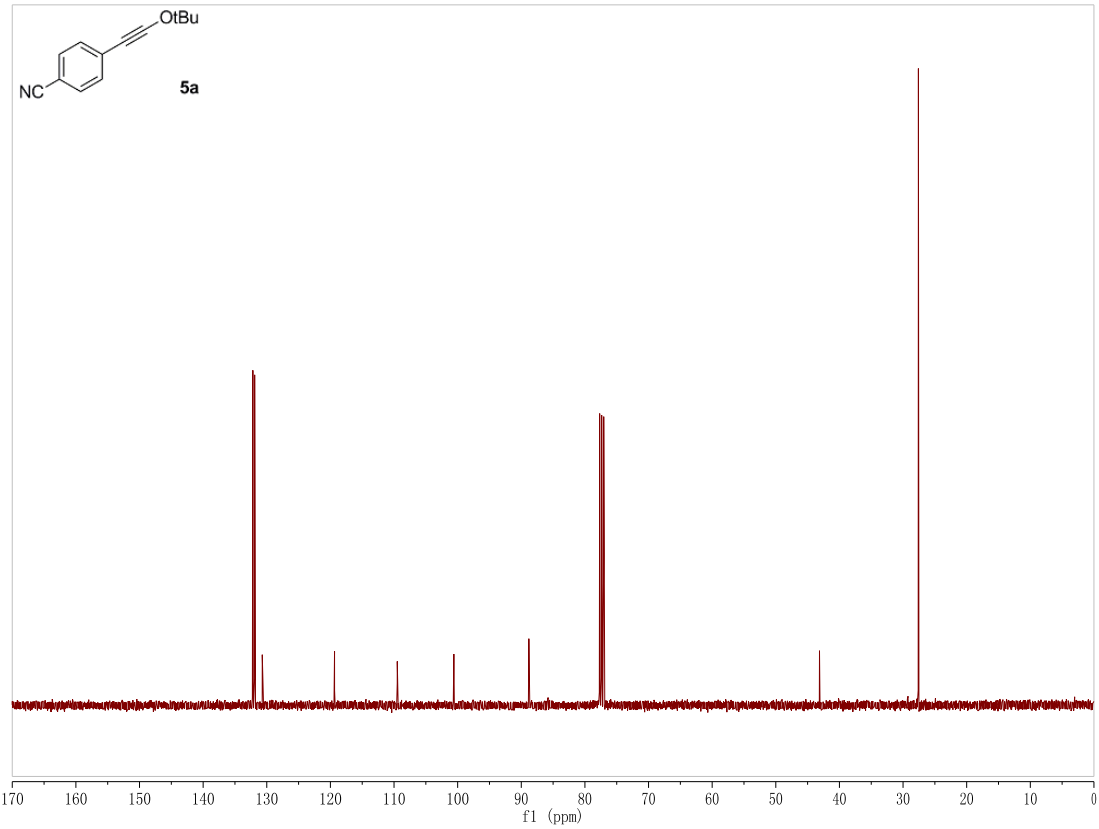
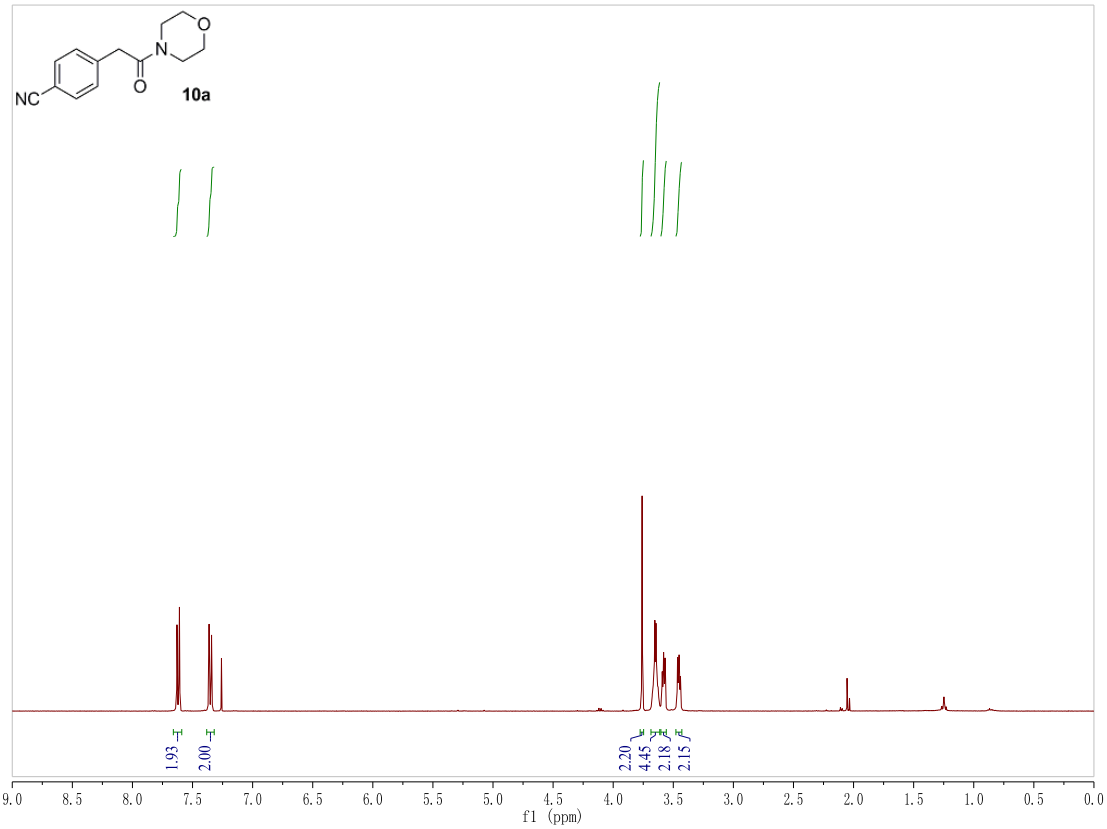
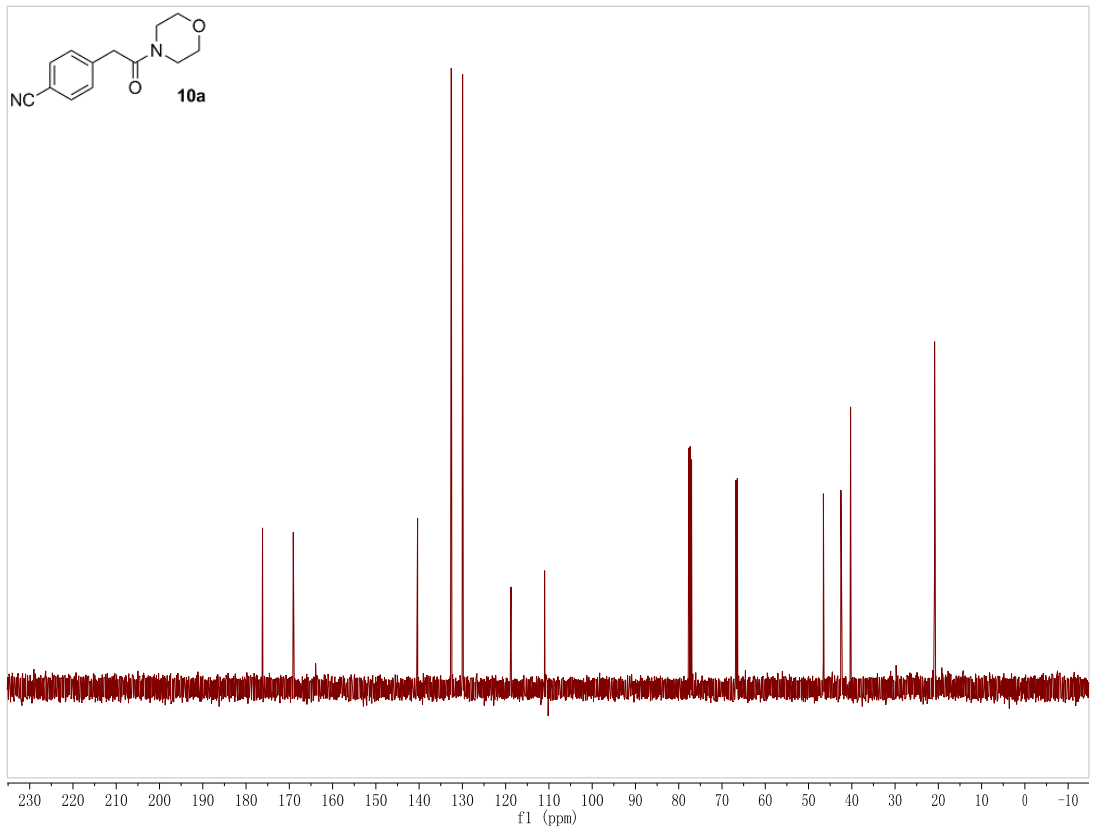
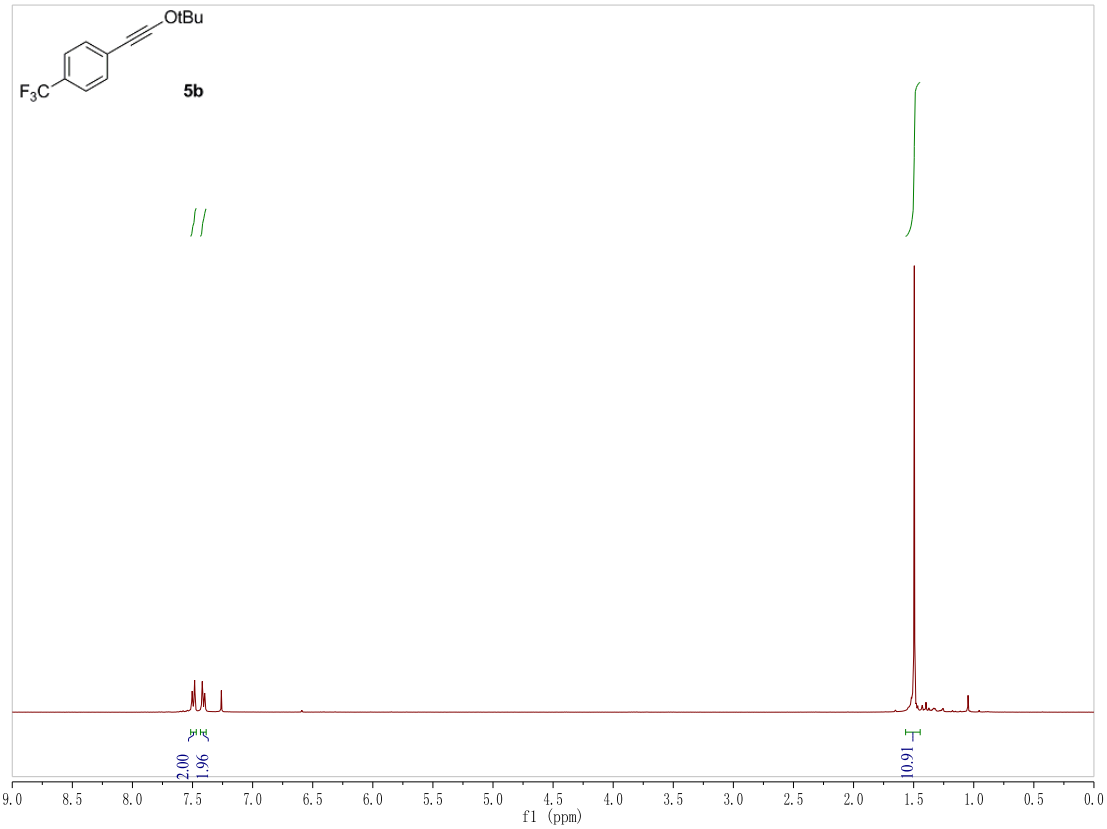
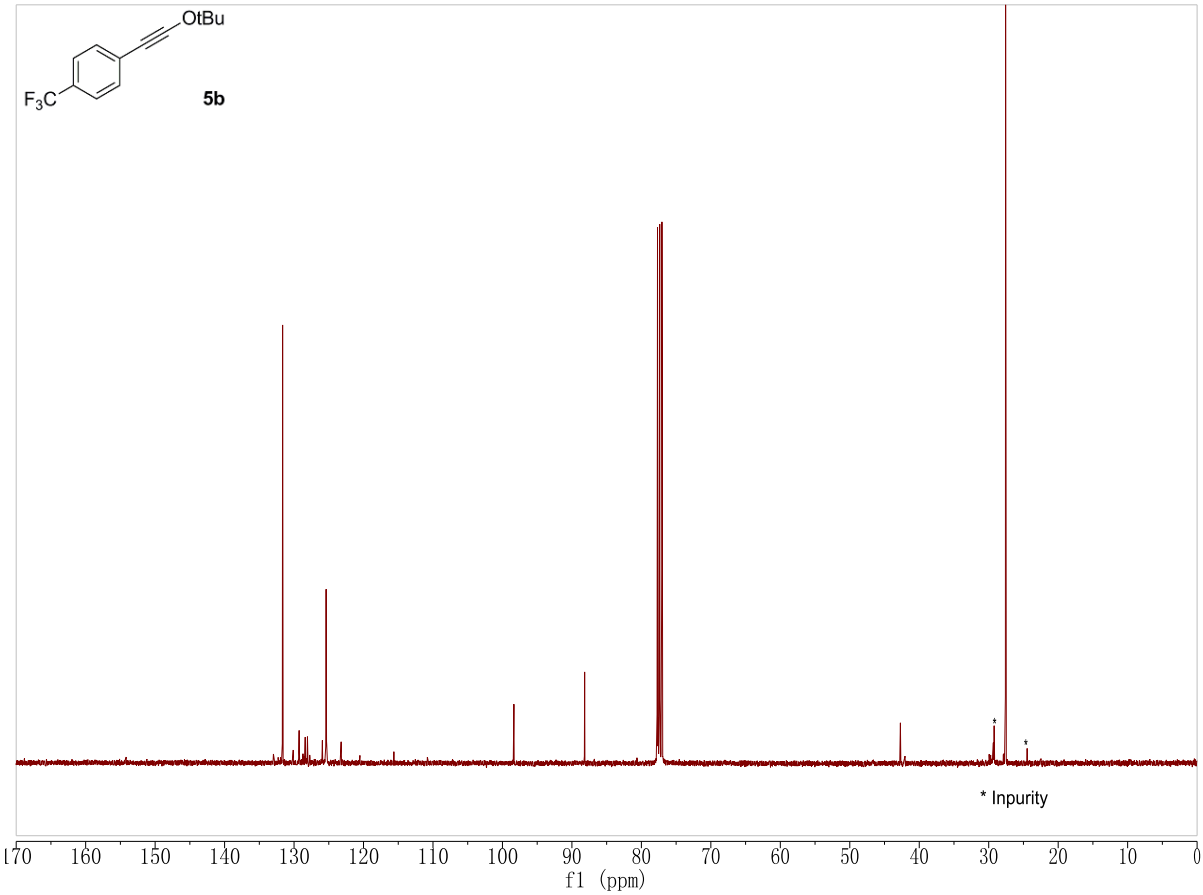
NC
5a
2.00
2.03
9.87
f1 (ppm)

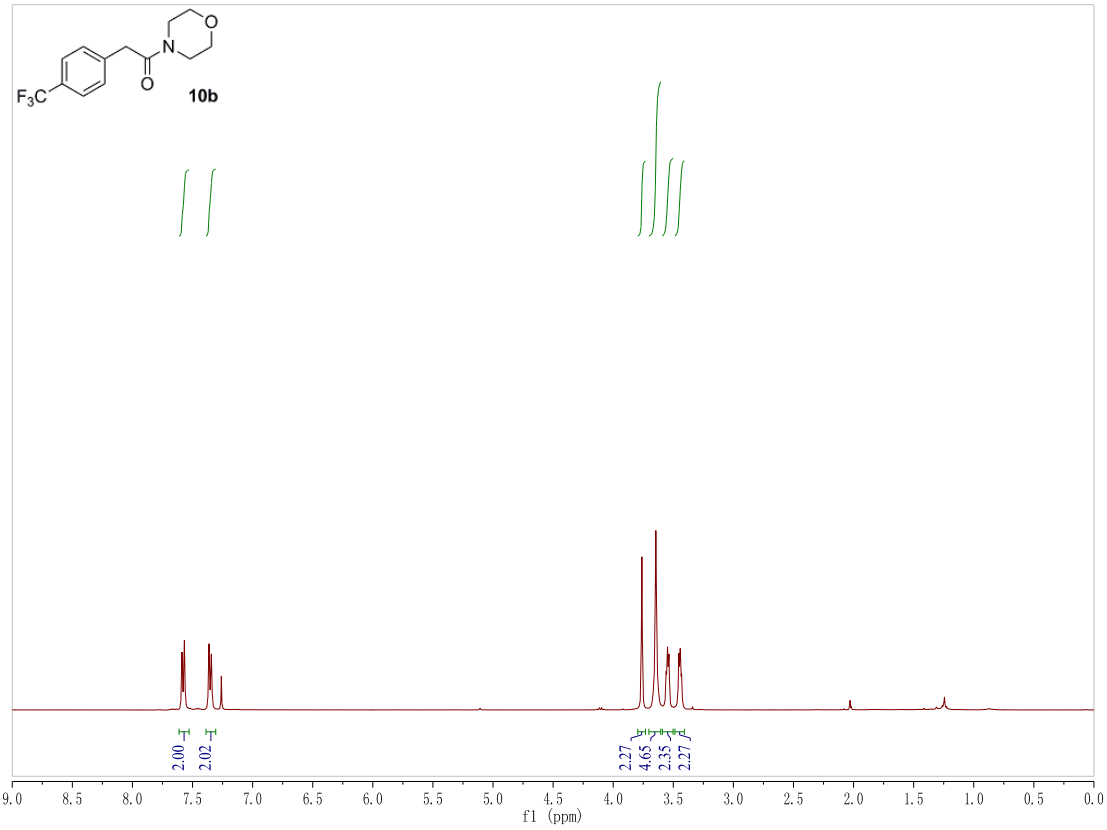

OtBu
NC
5a
f1 (ppm)

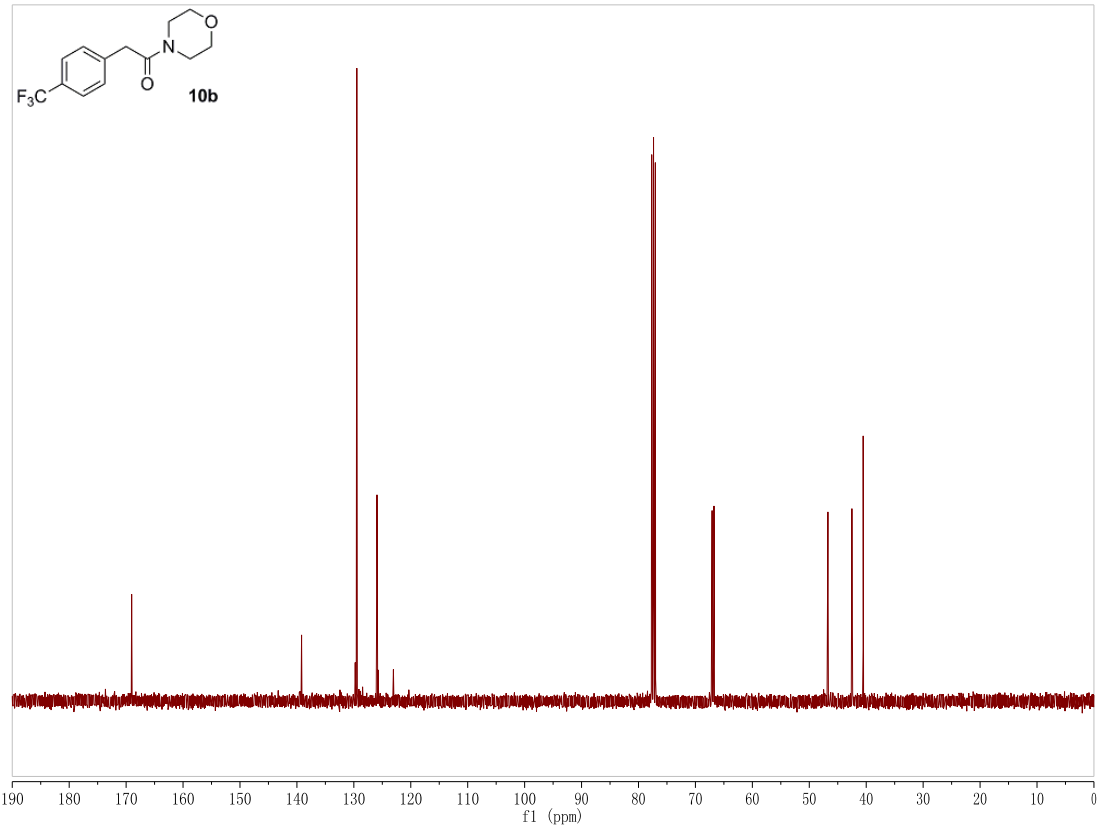

NC
O
N
O
10a
1.93
2.00
2.20
4.45
2.18
2.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

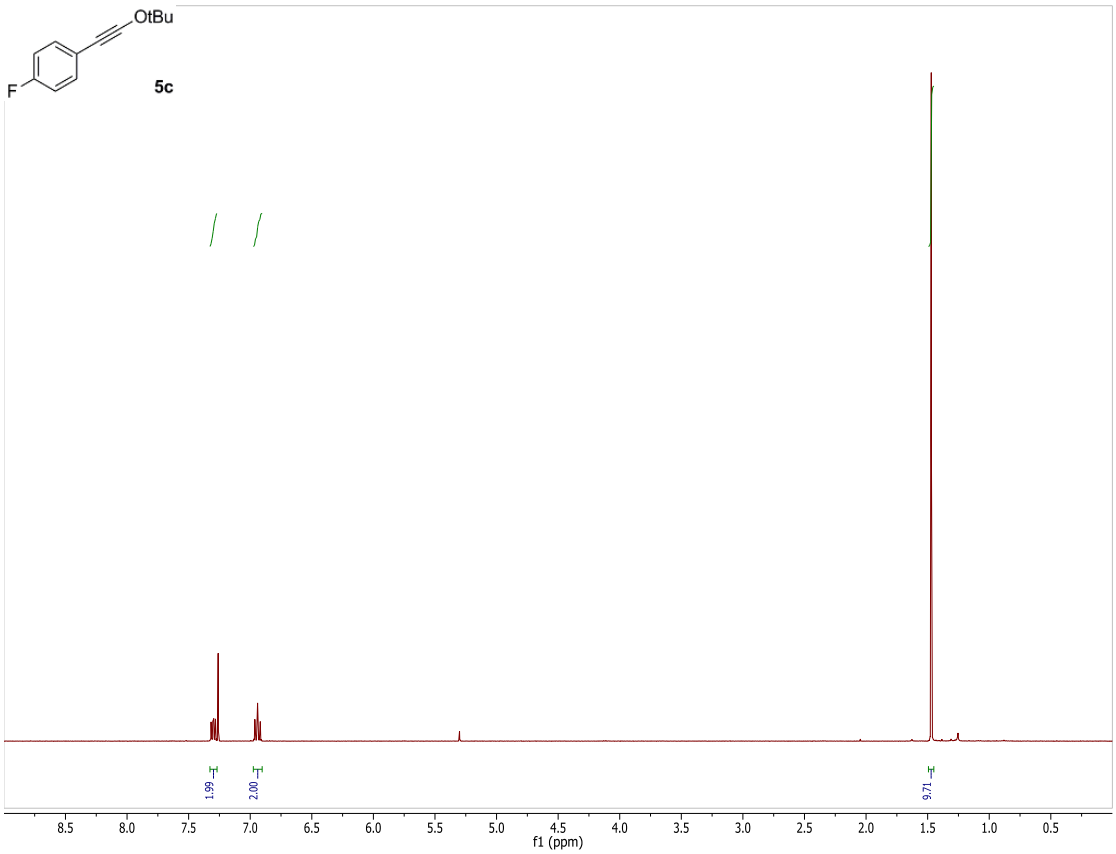

NC
O
N
O
10a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

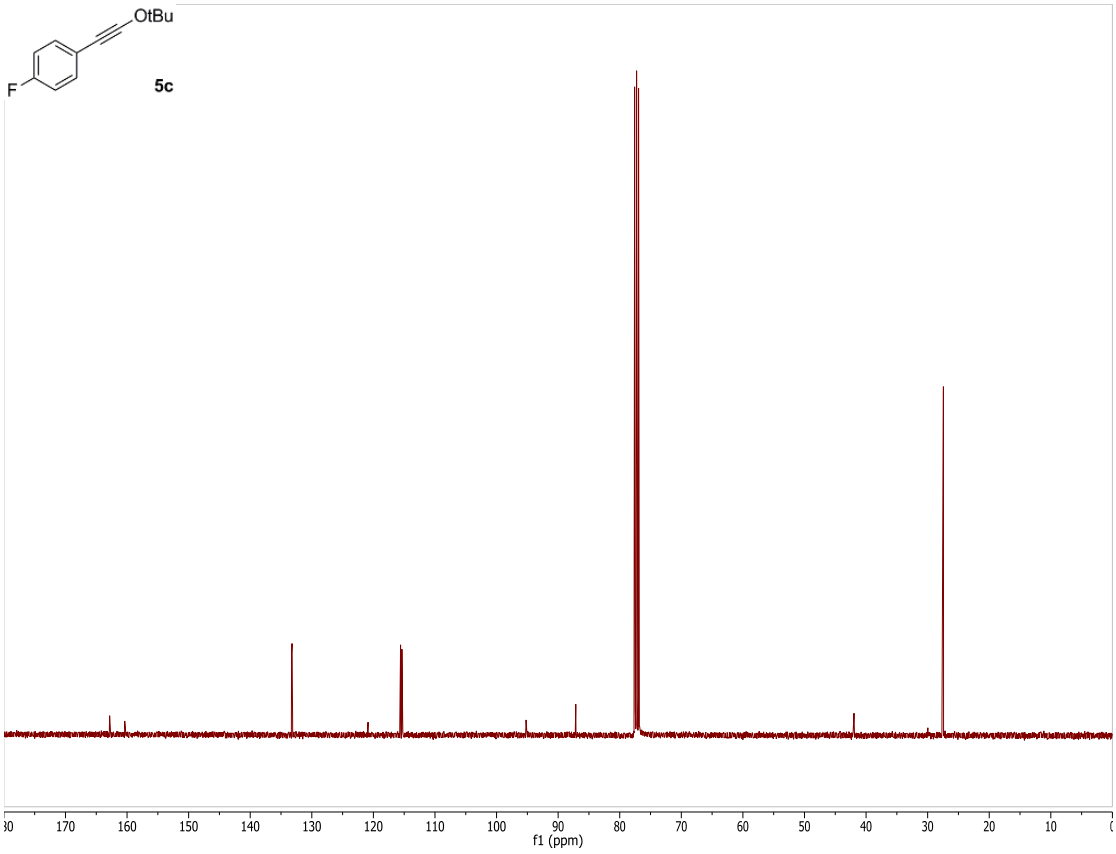

OtBu
F3C
5b
2.00
1.96
10.91
f1 (ppm)

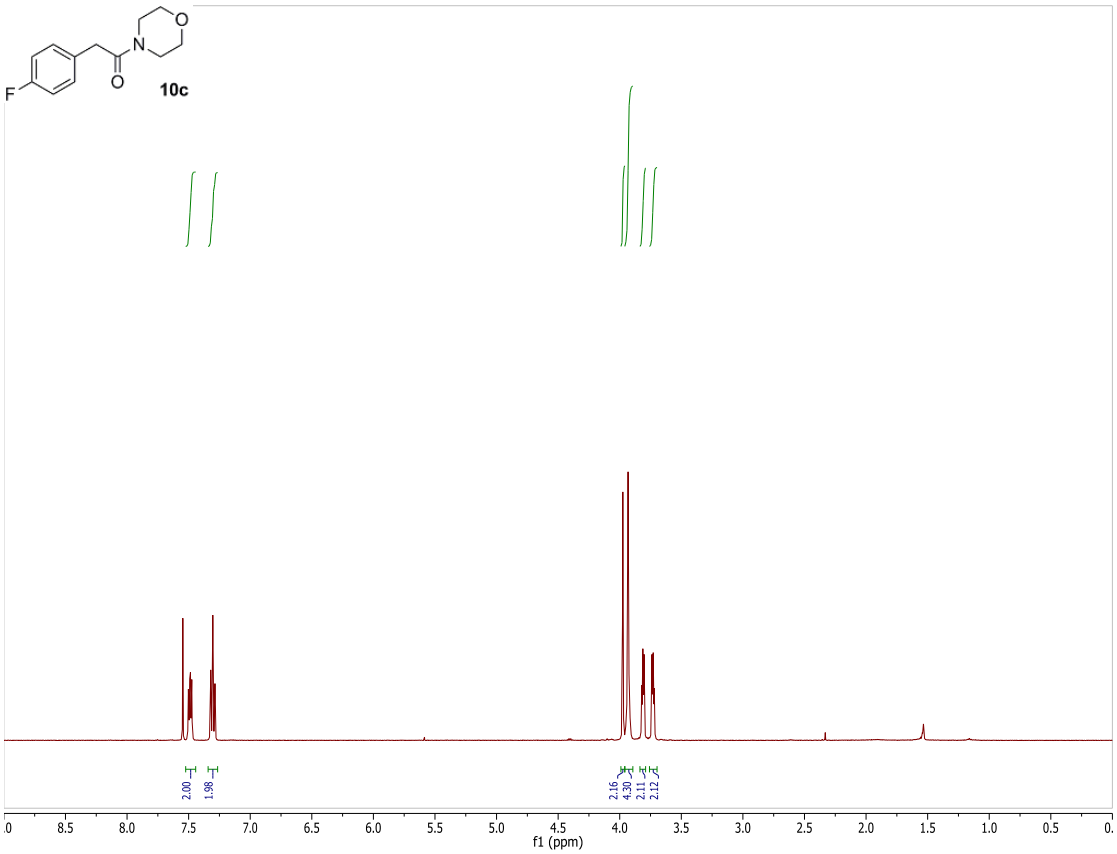

OtBu
F3C
5b
* Inpurity
f1 (ppm)

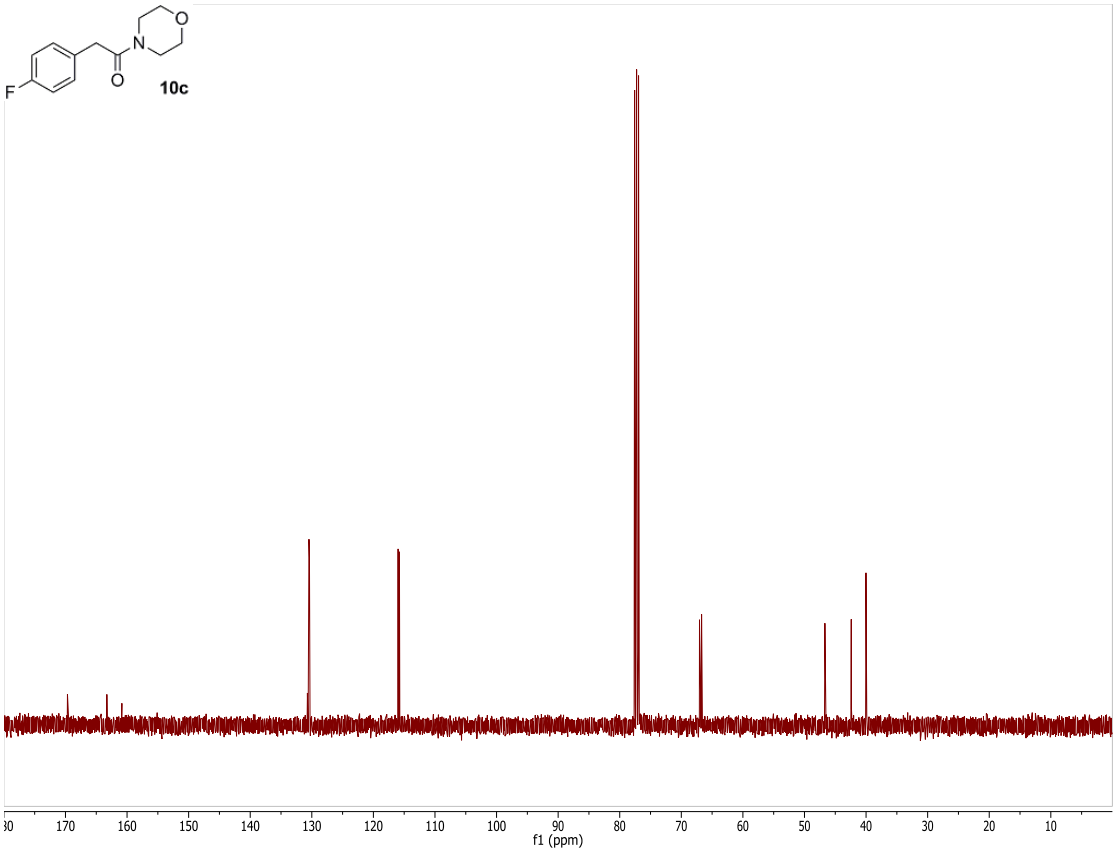

F3C
O
N
O
10b
2.00
2.02
2.27
4.65
2.35
2.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

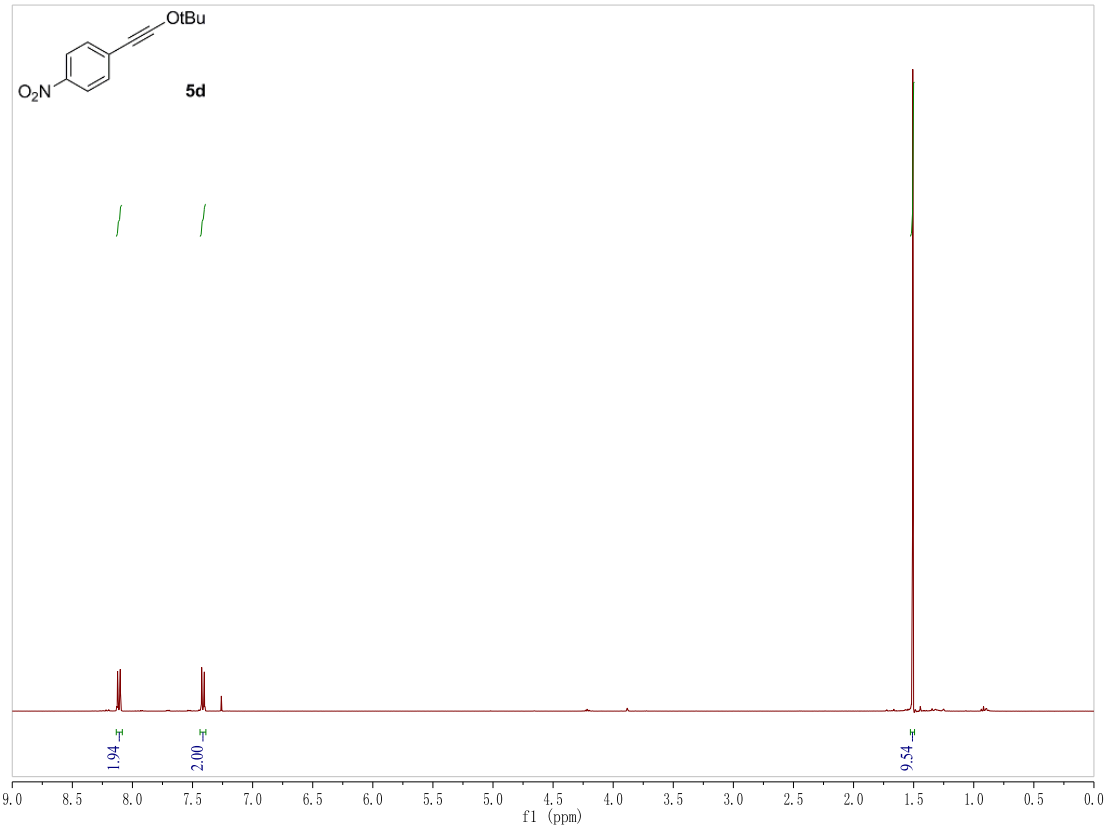

F3C
O
N
O
10b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

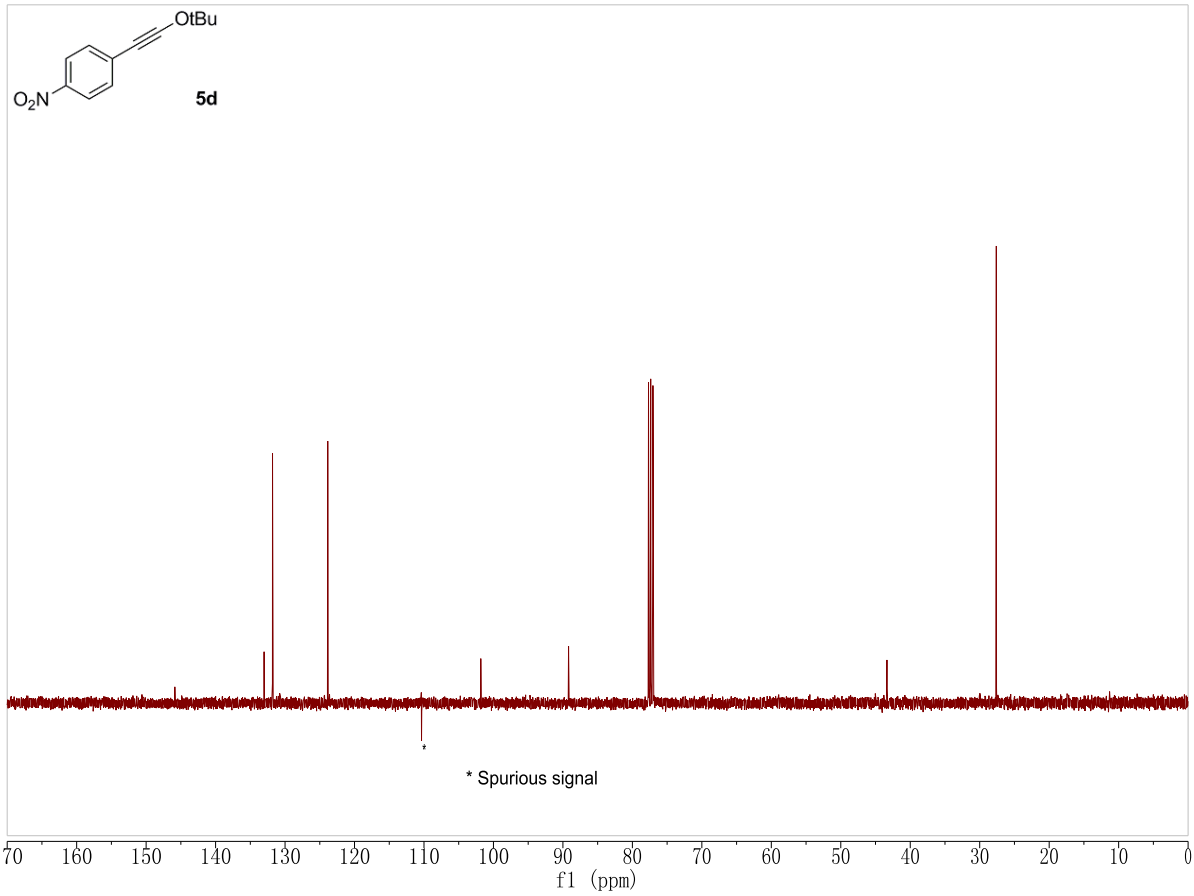

OtBu
F
5c
1.99
2.00
9.71
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

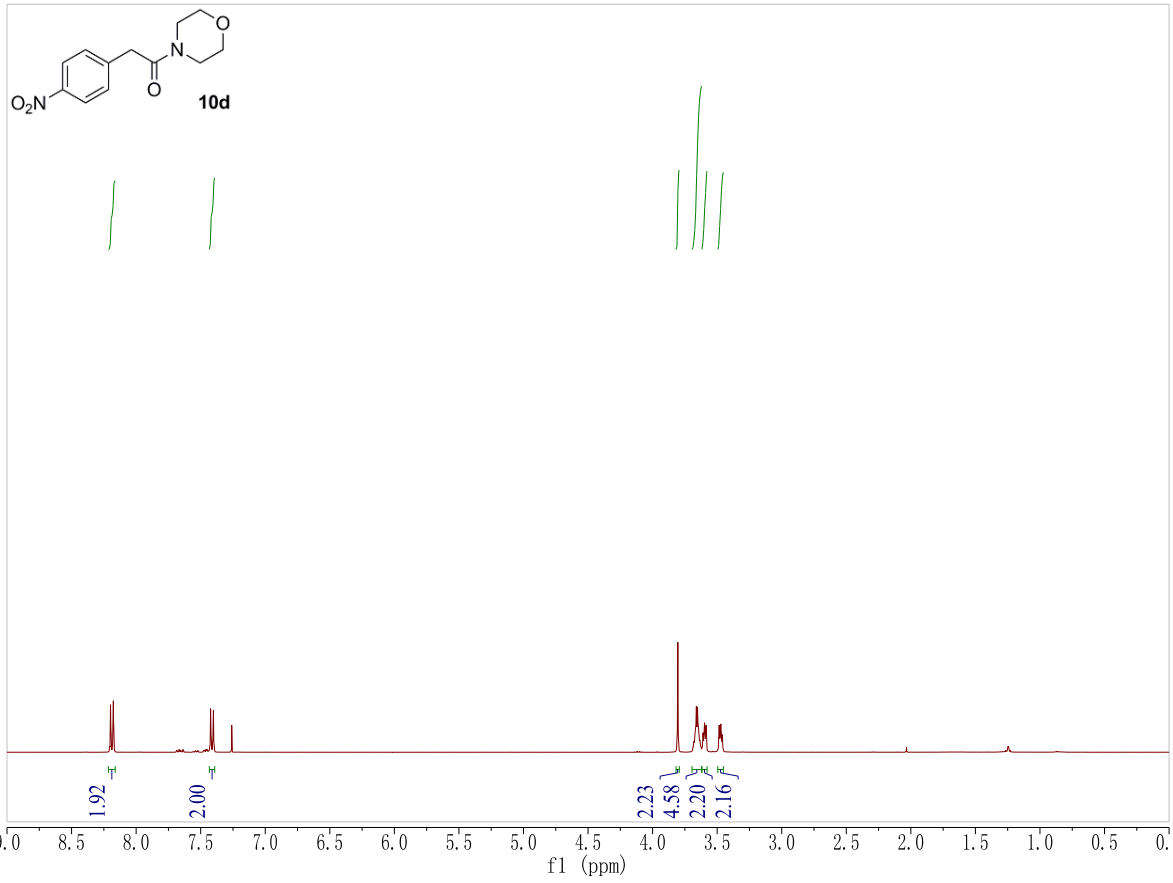

OtBu
F
5c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

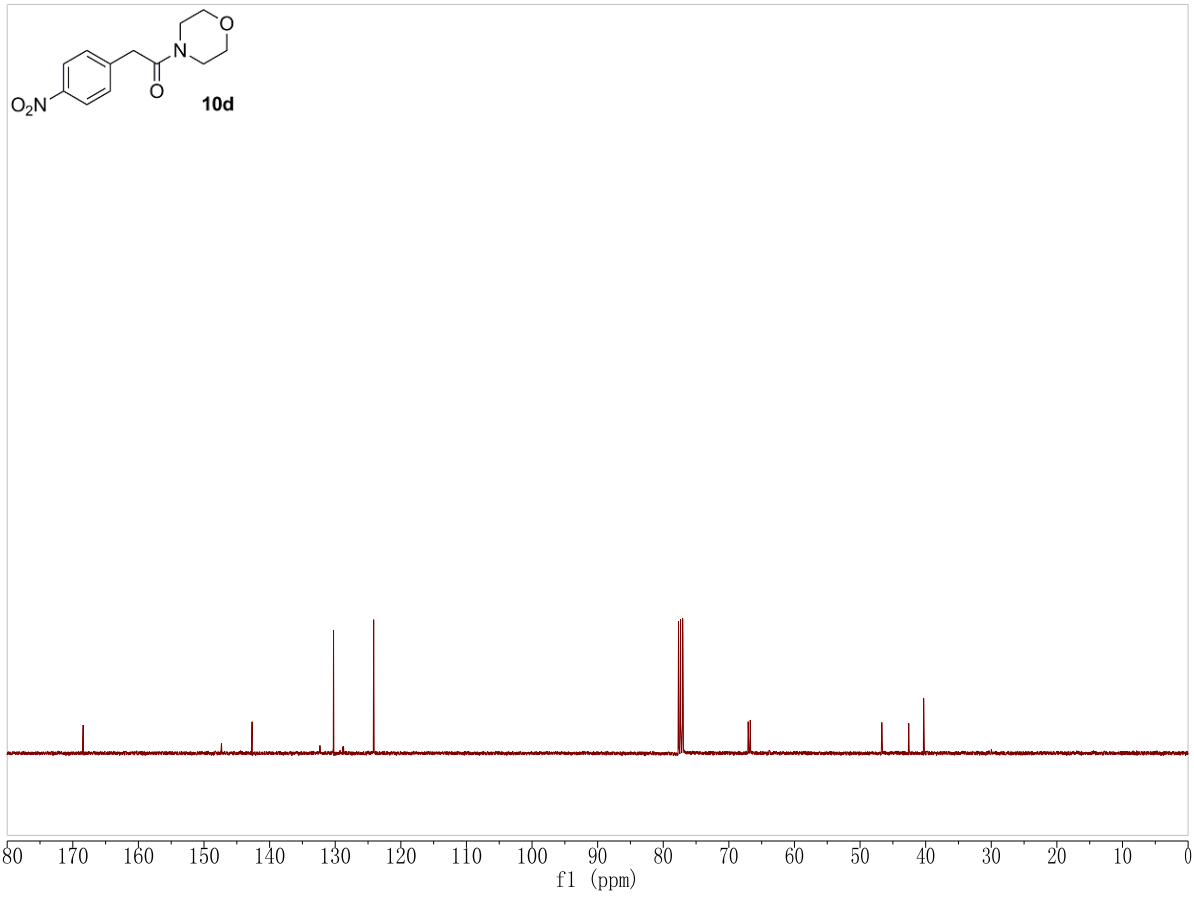

10c
2.00
1.98
2.16
4.30
2.11
2.12
f1 (ppm)

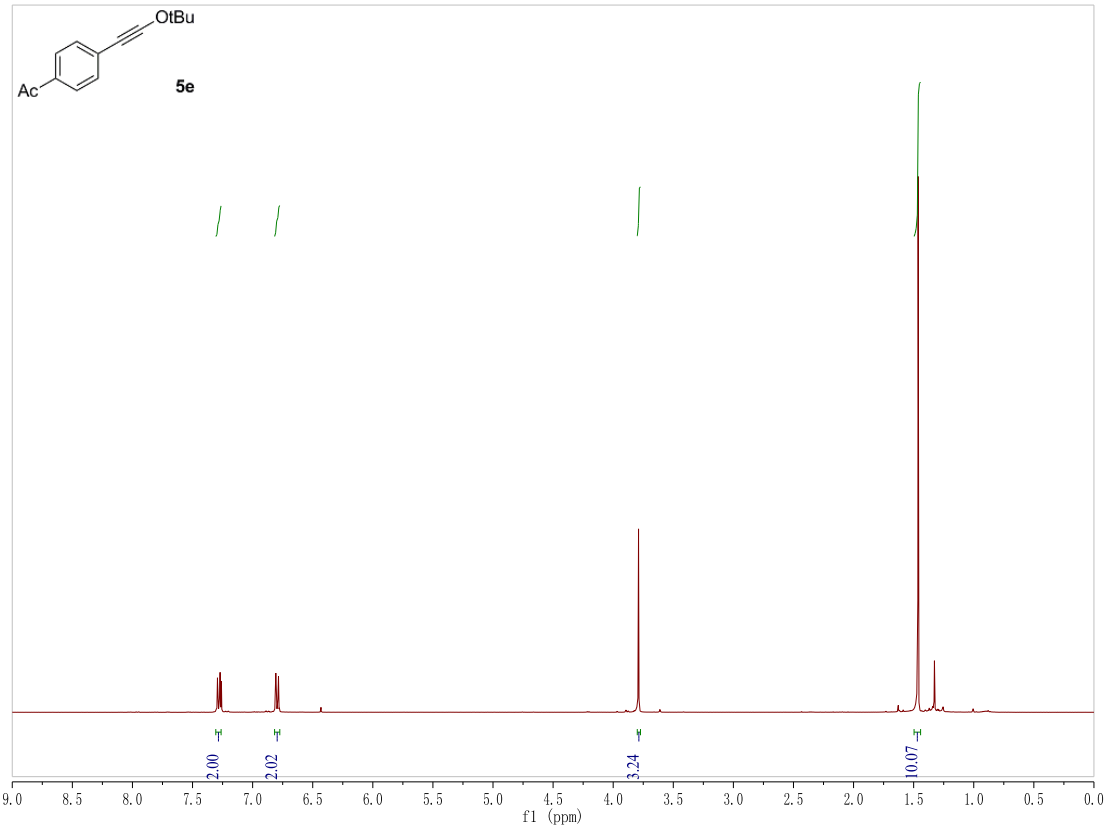

10c
f1 (ppm)

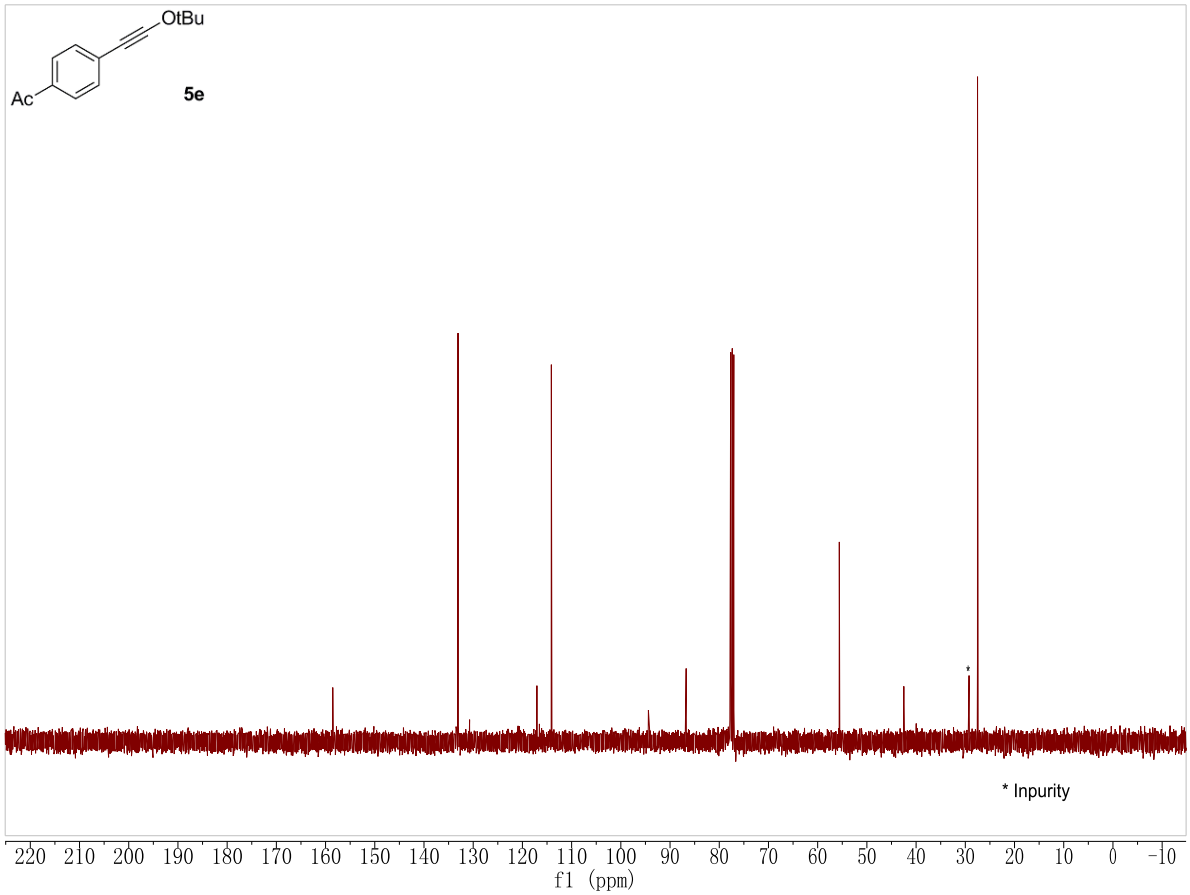

OtBu
O2N
5d
1.94
2.00
9.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

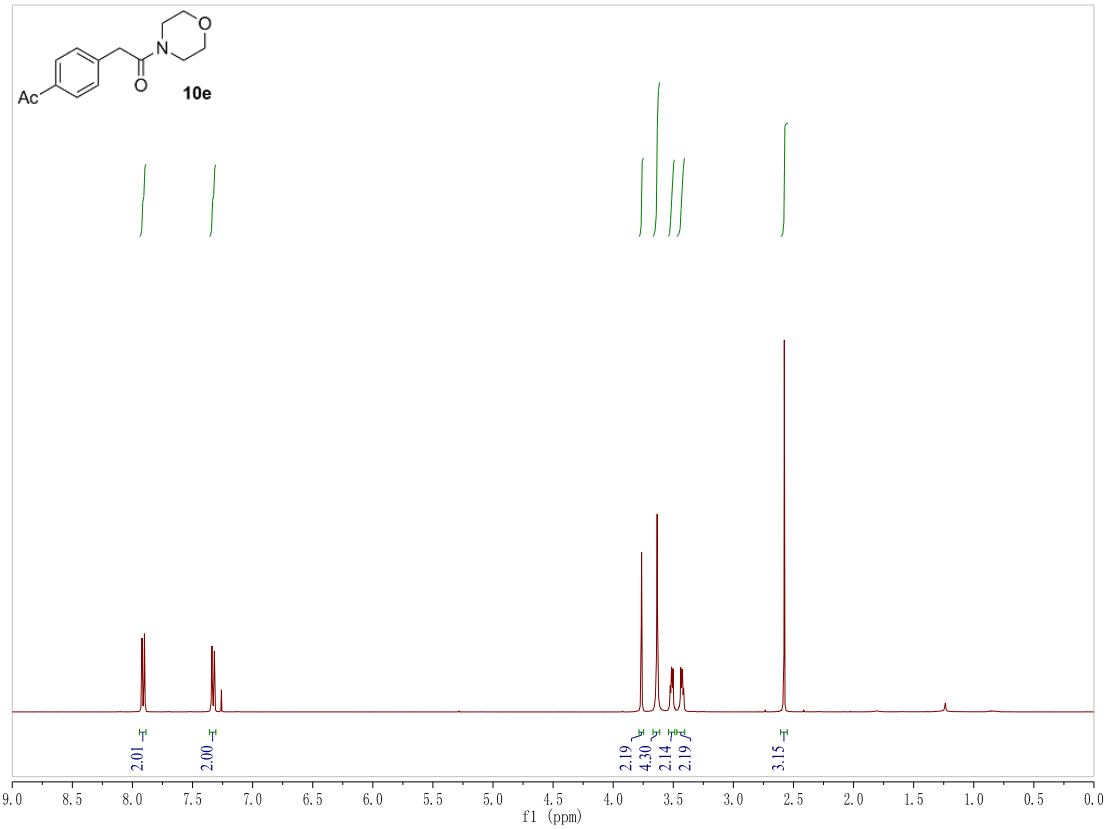

OtBu
O2N
5d
* Spurious signal
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

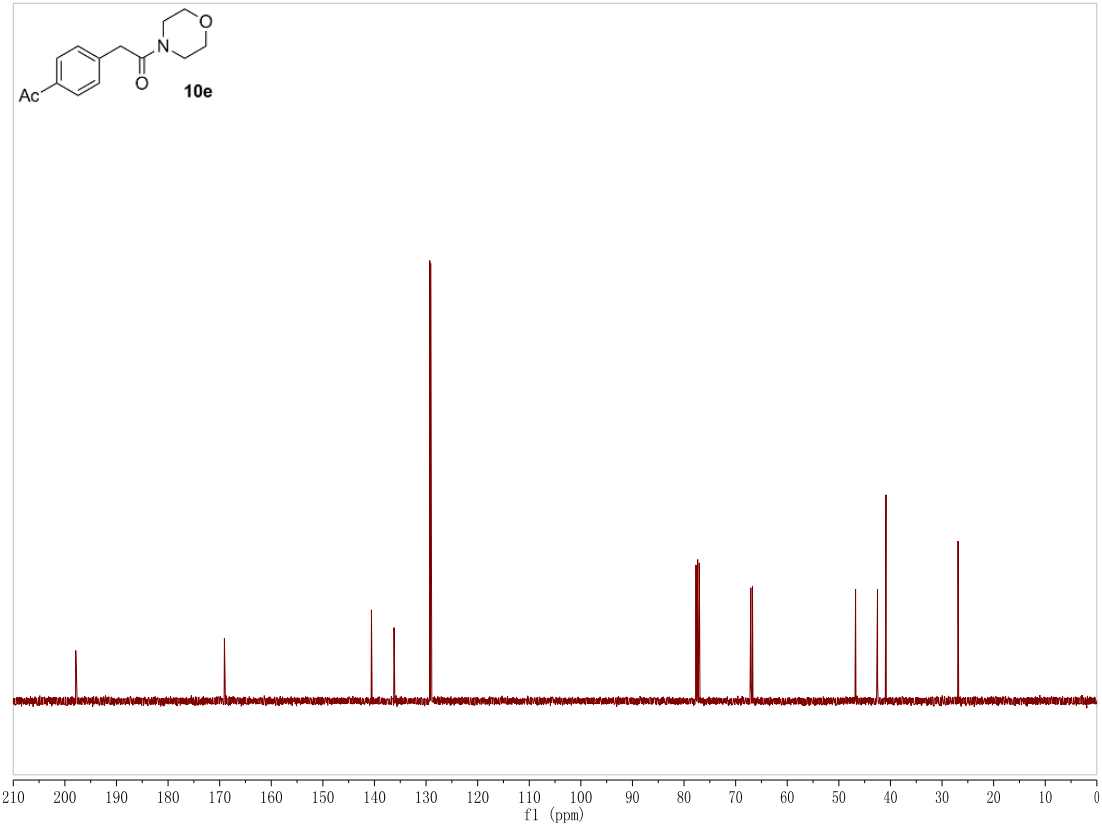

10d
1.92
2.00
2.23
4.58
2.20
2.16
f1 (ppm)

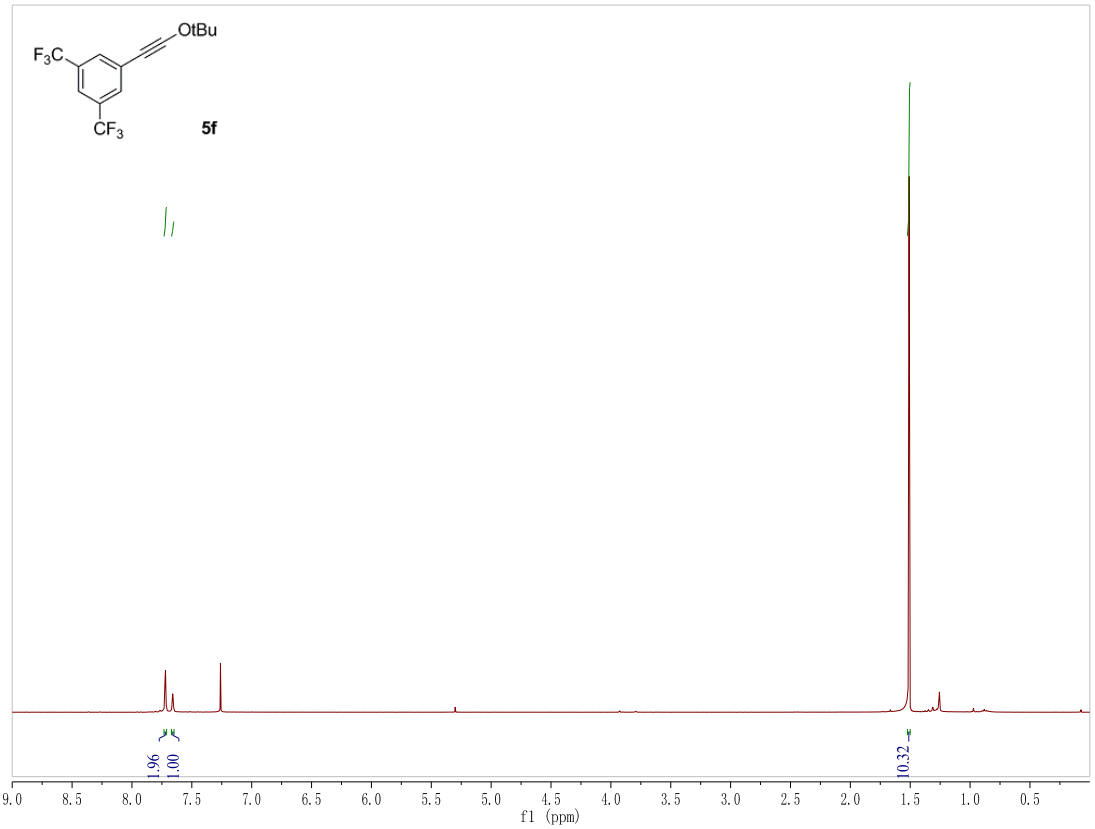

10d
f1 (ppm)

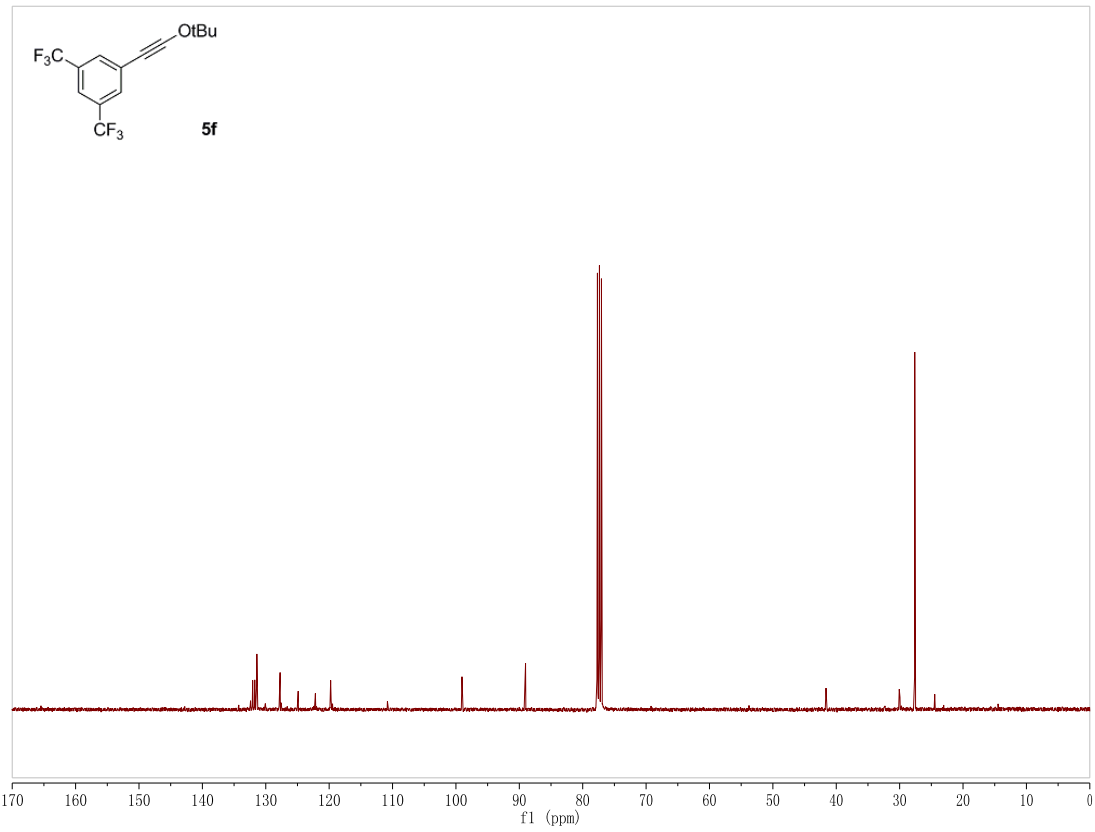

OtBu
Ac
5e
2.00
2.02
3.24
10.07
f1 (ppm)

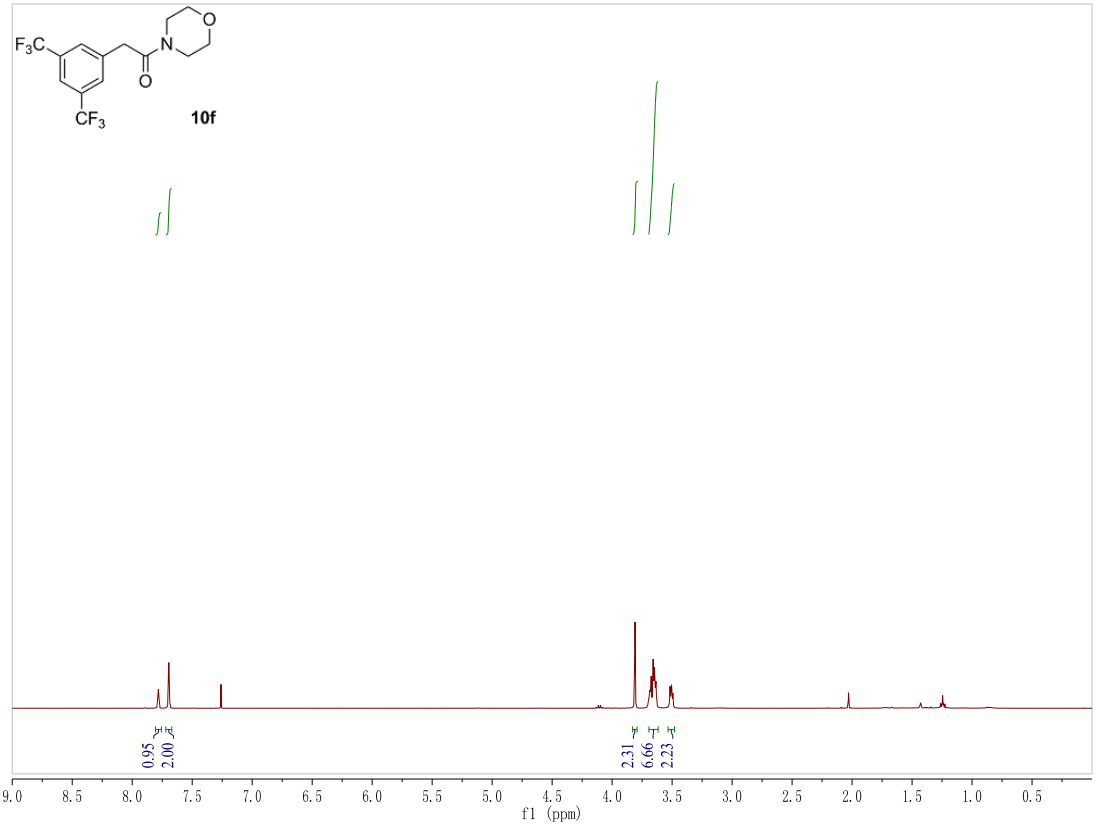

OtBu
Ac
5e
* Inpurity
f1 (ppm)

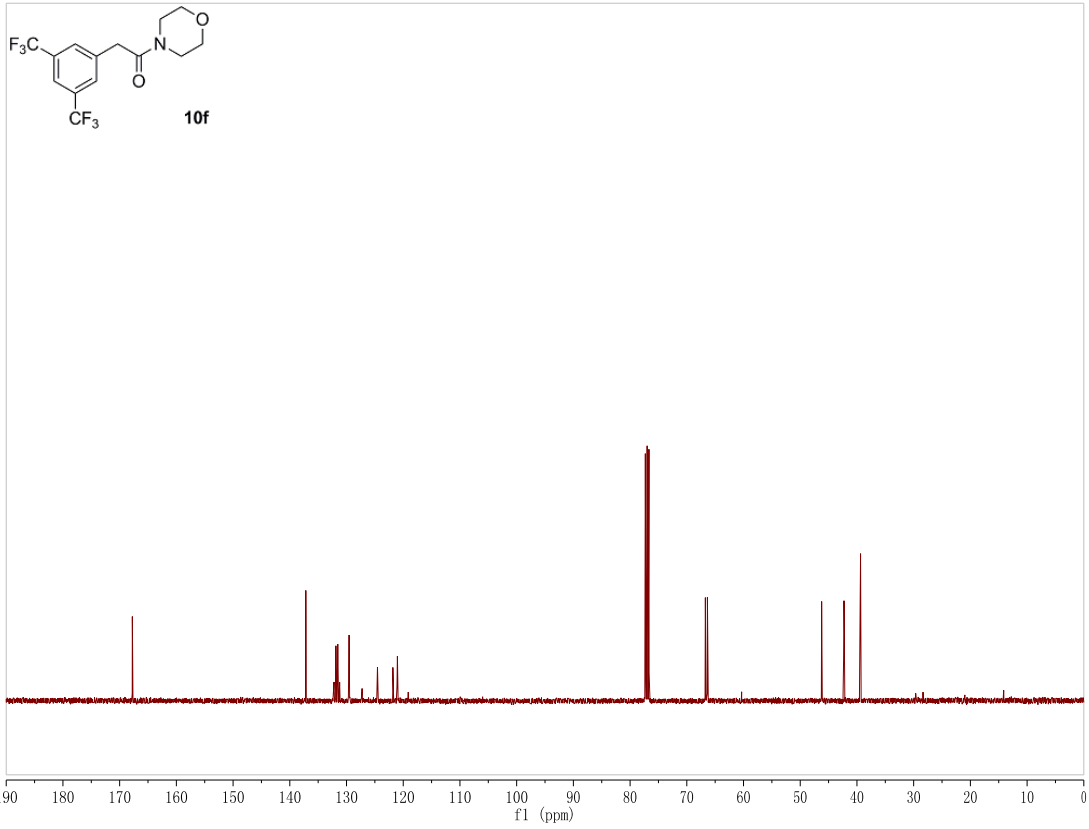

Ac
10e
2.01
2.00
2.19
4.30
2.14
2.19
3.15
f1 (ppm)

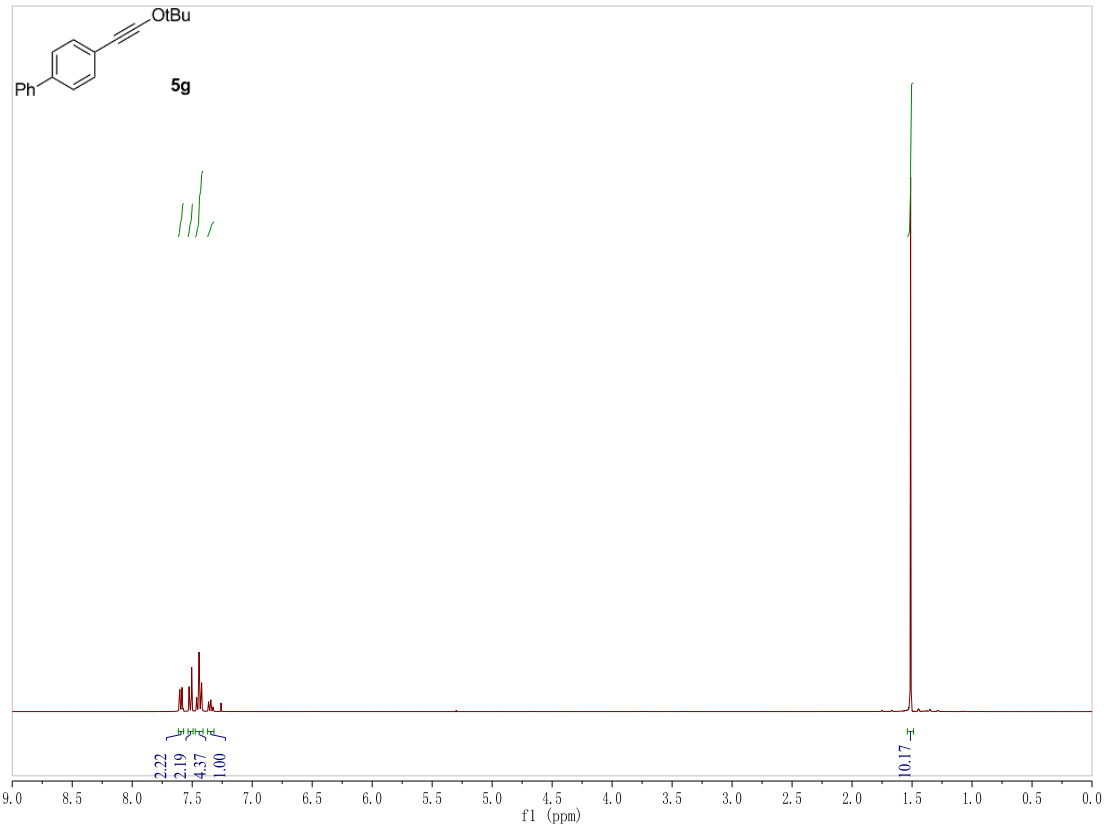

Ac
10e
f1 (ppm)

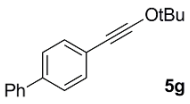

OtBu
F3C
CF3
5f
1.96
1.00
10.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

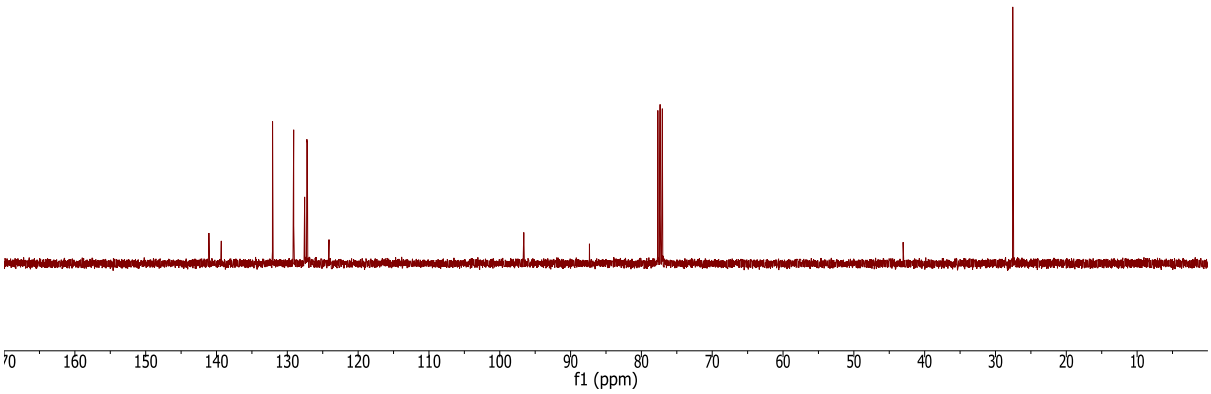

OtBu
F3C
CF3
5f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

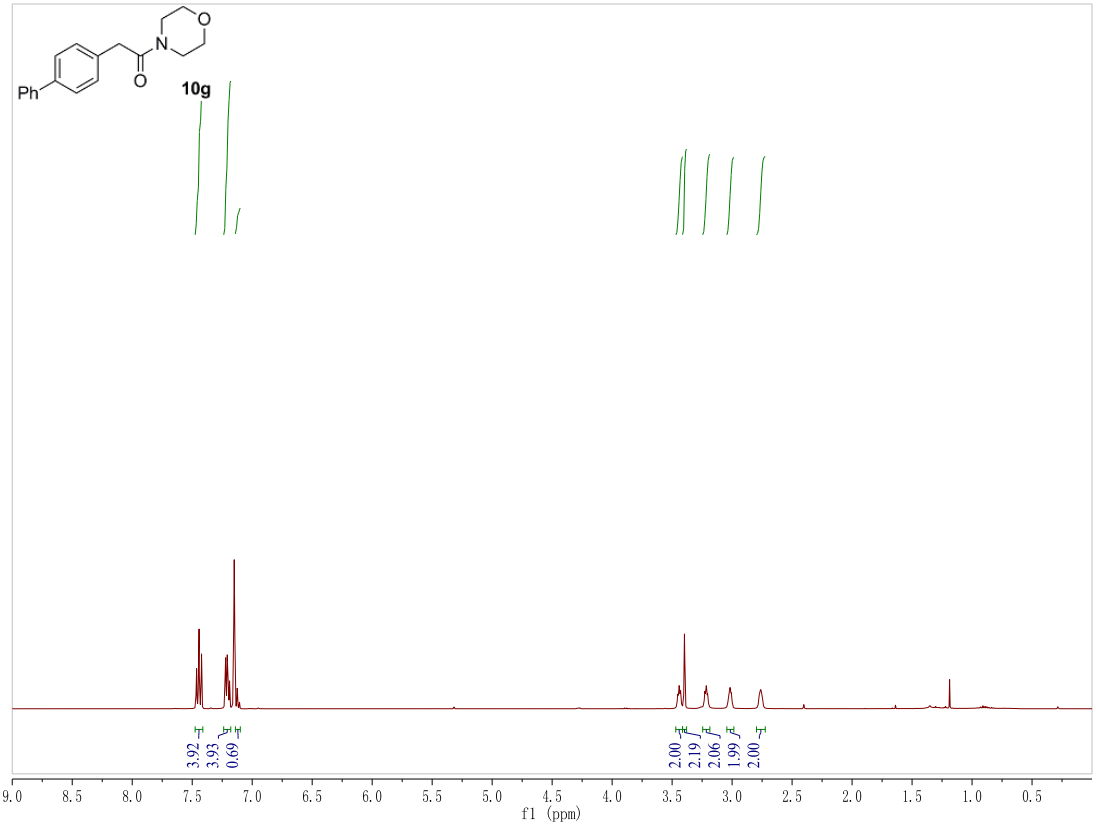

F3C
CF3
O
N
O
10f
0.95
2.00
2.31
6.66
2.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

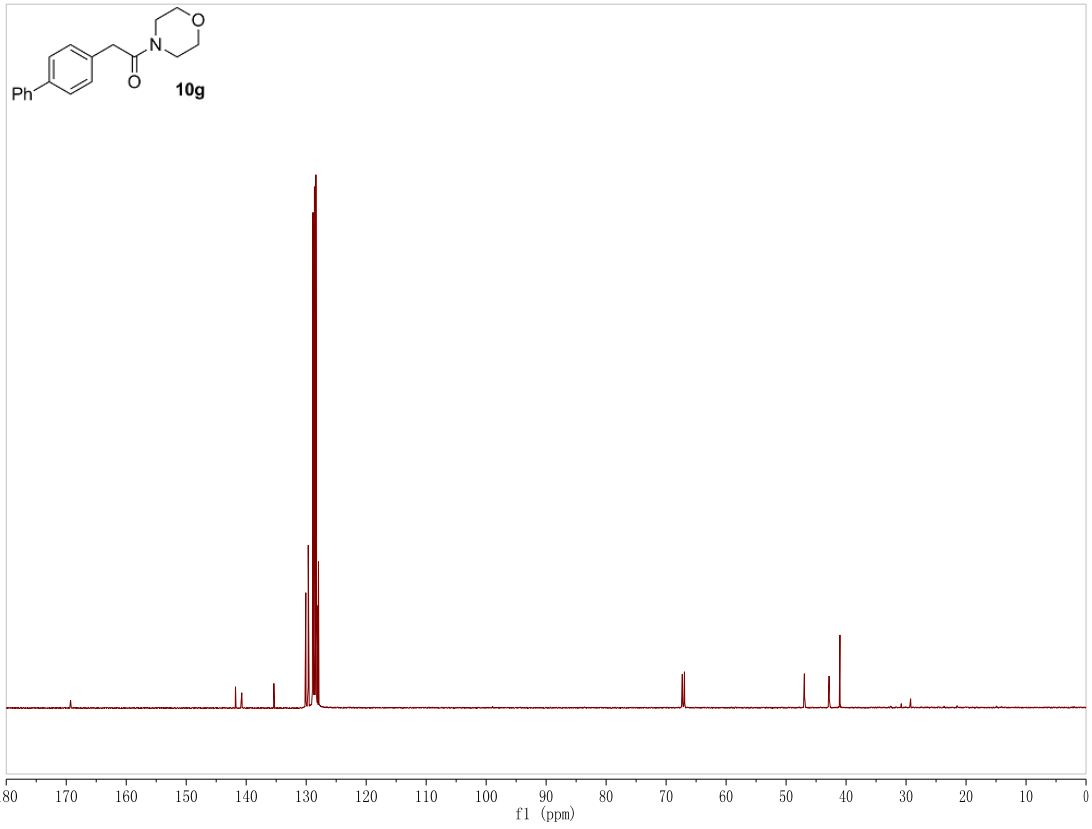

F3C
CF3
O
N
O
10f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

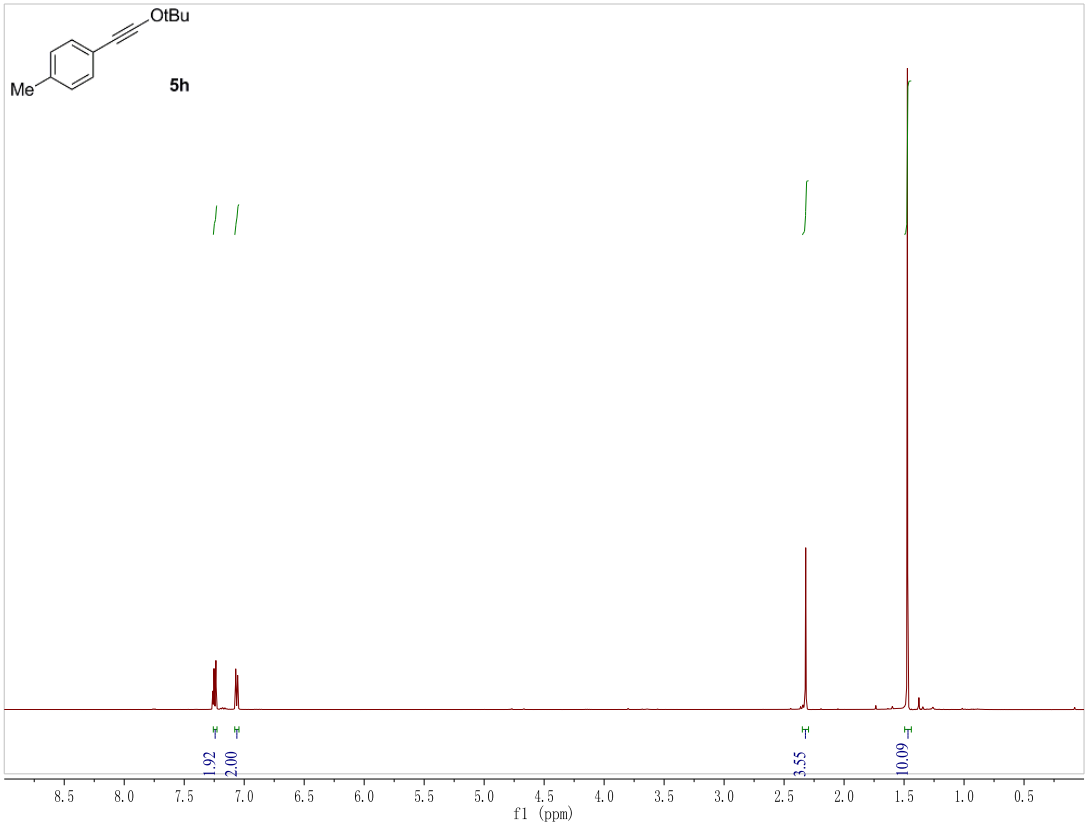

OtBu
Ph
5g
2.22
2.19
4.37
1.00
10.17
f1 (ppm)

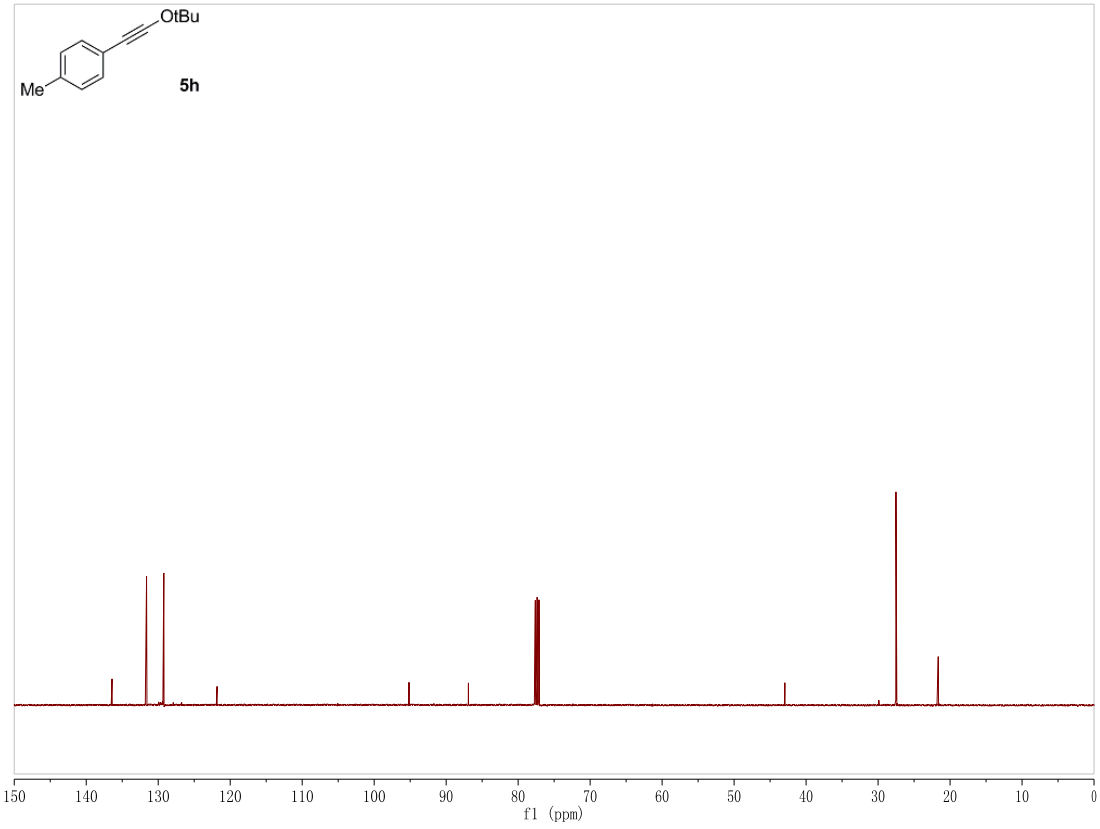

OtBu
Ph
5g

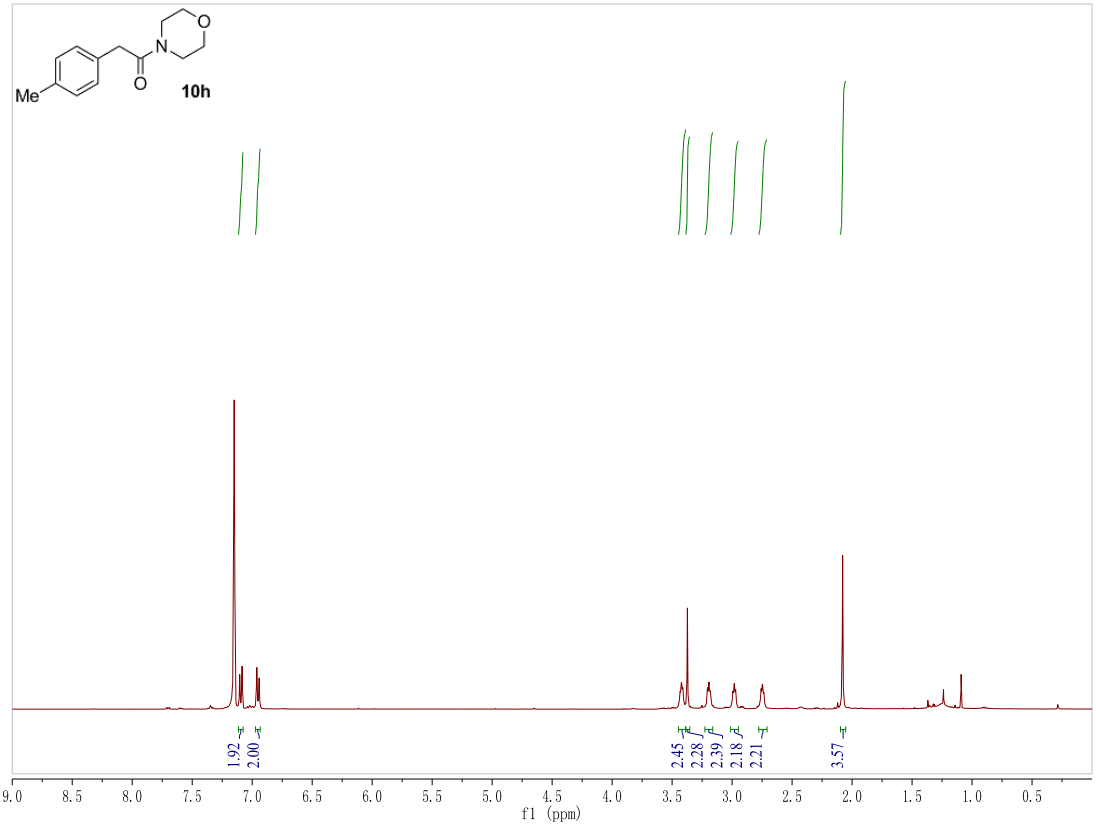

f1 (ppm)

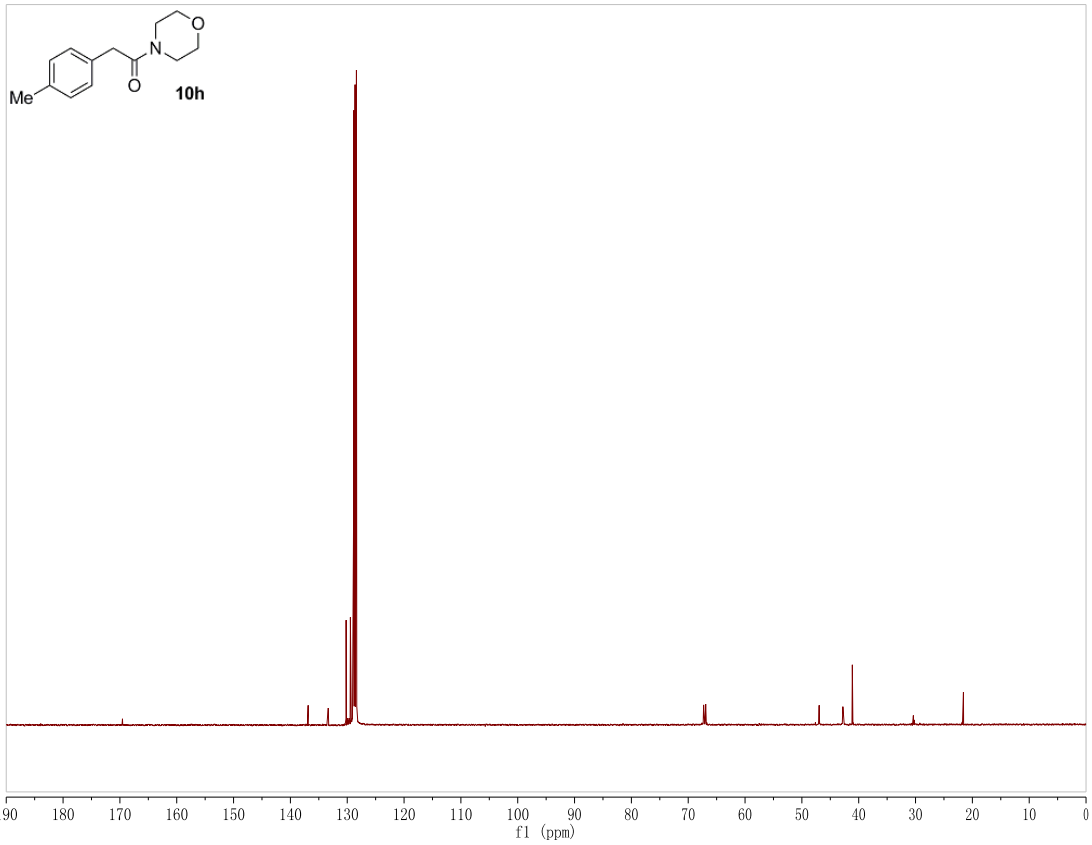

Ph
10g
3.92
3.93
0.69
2.00
2.19
2.06
1.99
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

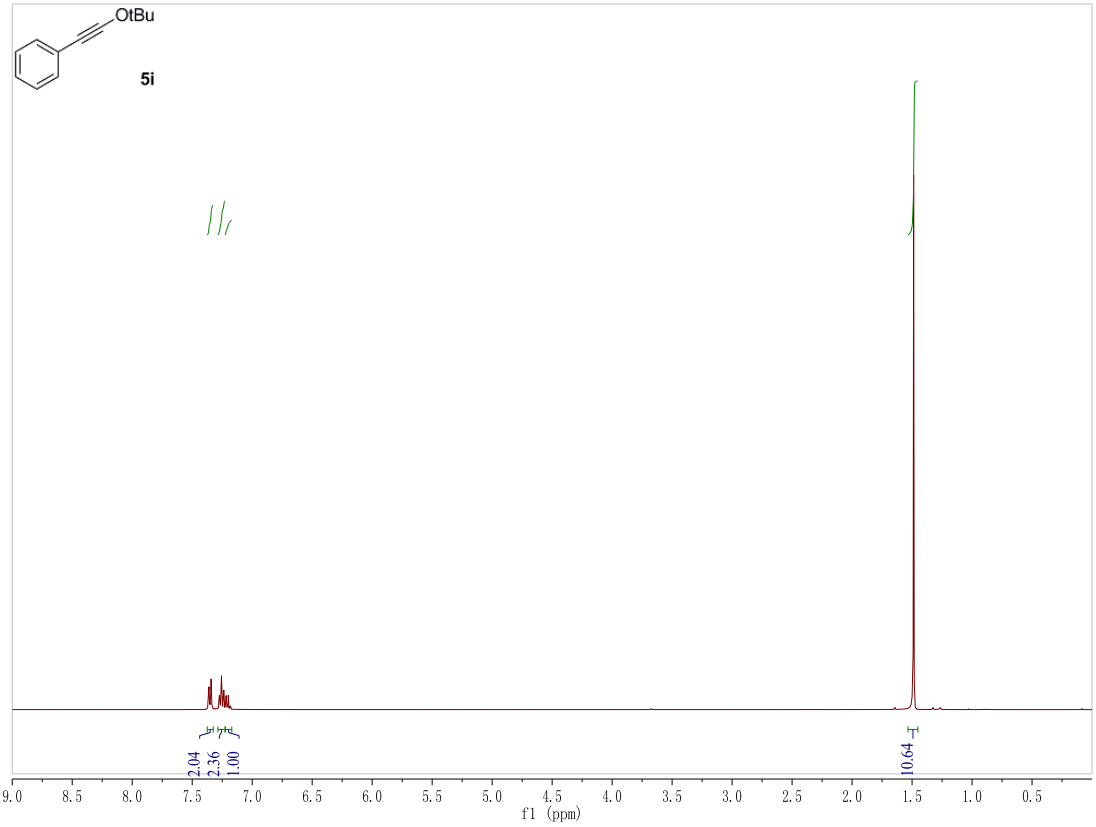

Ph
10g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

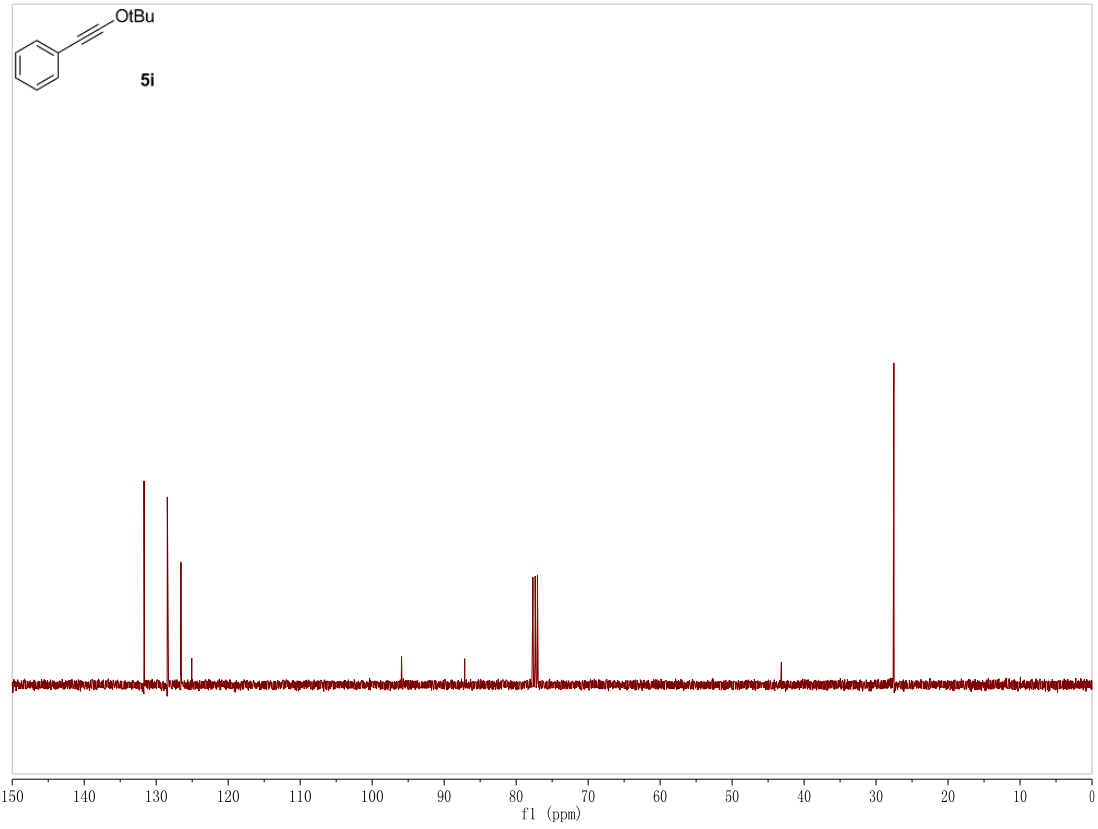

OtBu
Me
5h
1.92
2.00
3.55
10.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

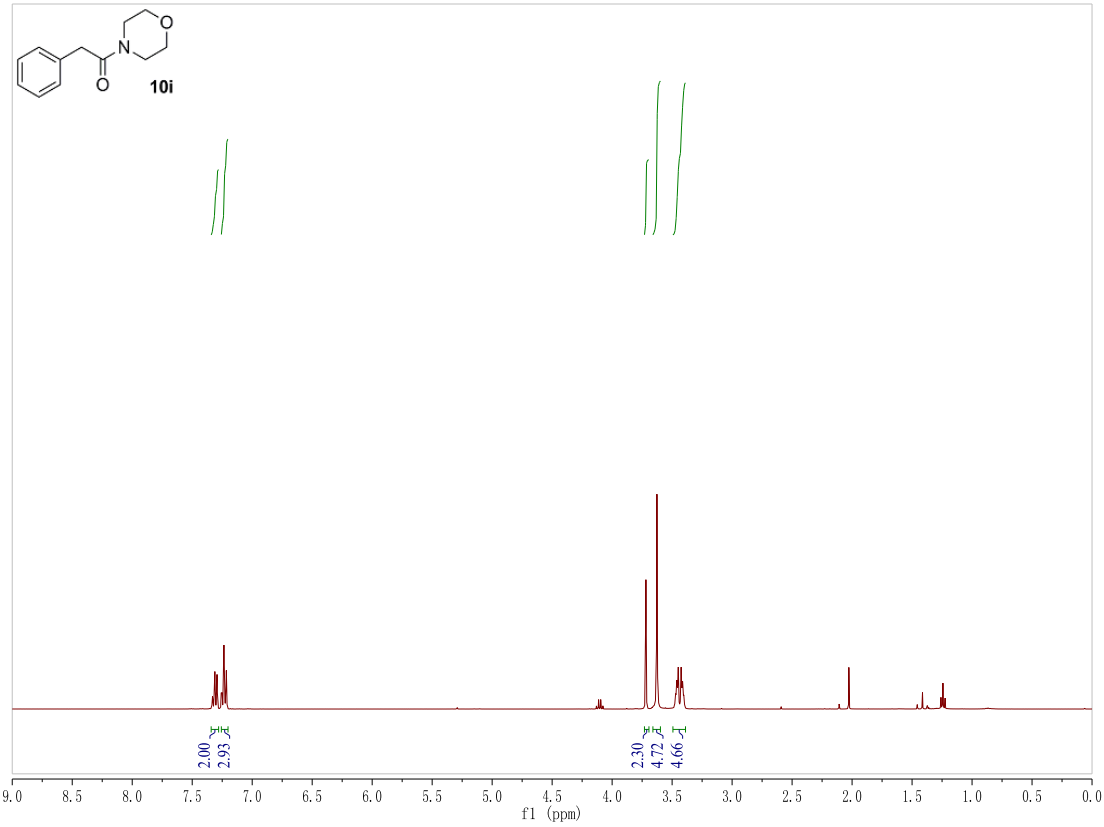

OtBu
Me
5h
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

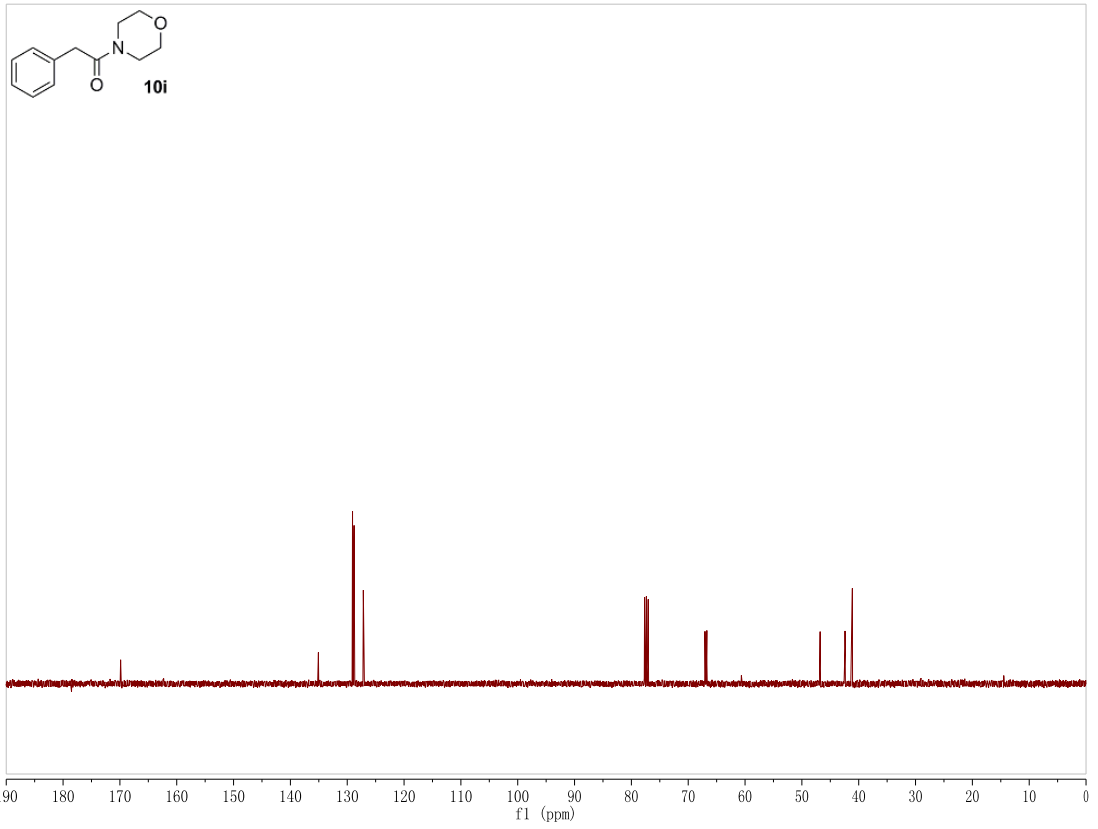

Me
10h
1.92
2.00
2.45
2.28
2.39
2.18
2.21
3.57
f1 (ppm)

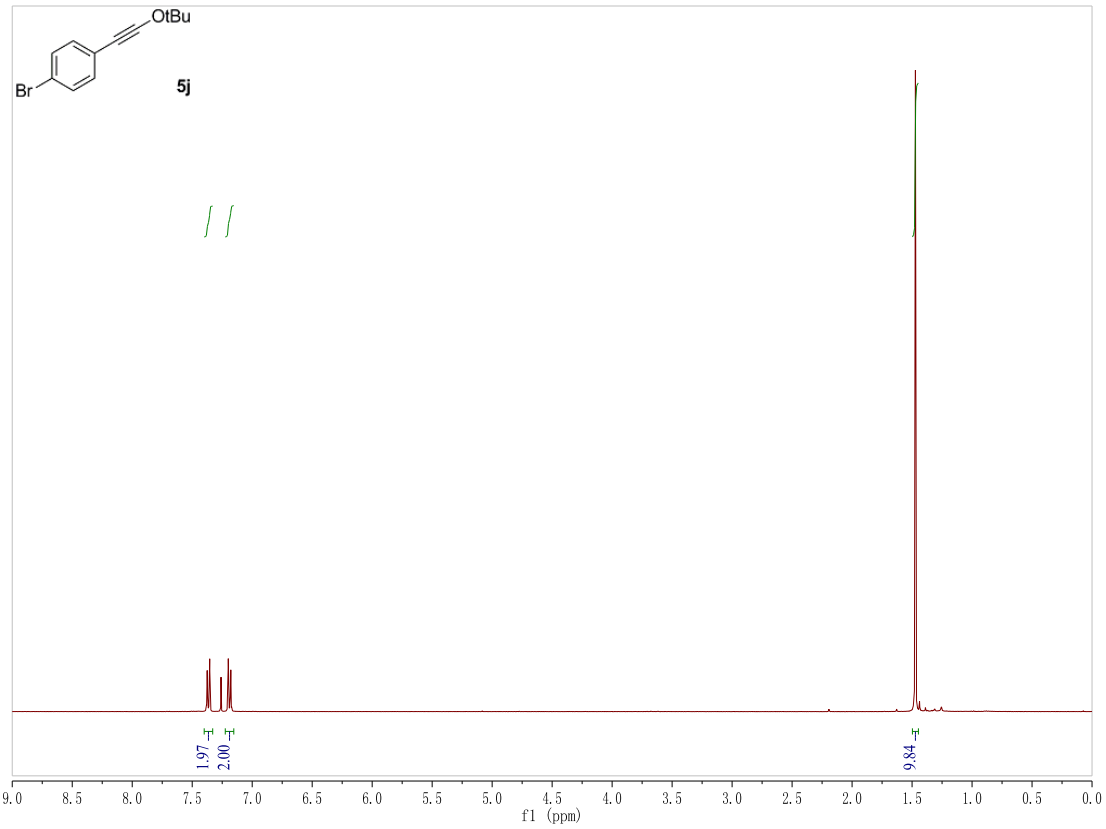

Me
10h
f1 (ppm)

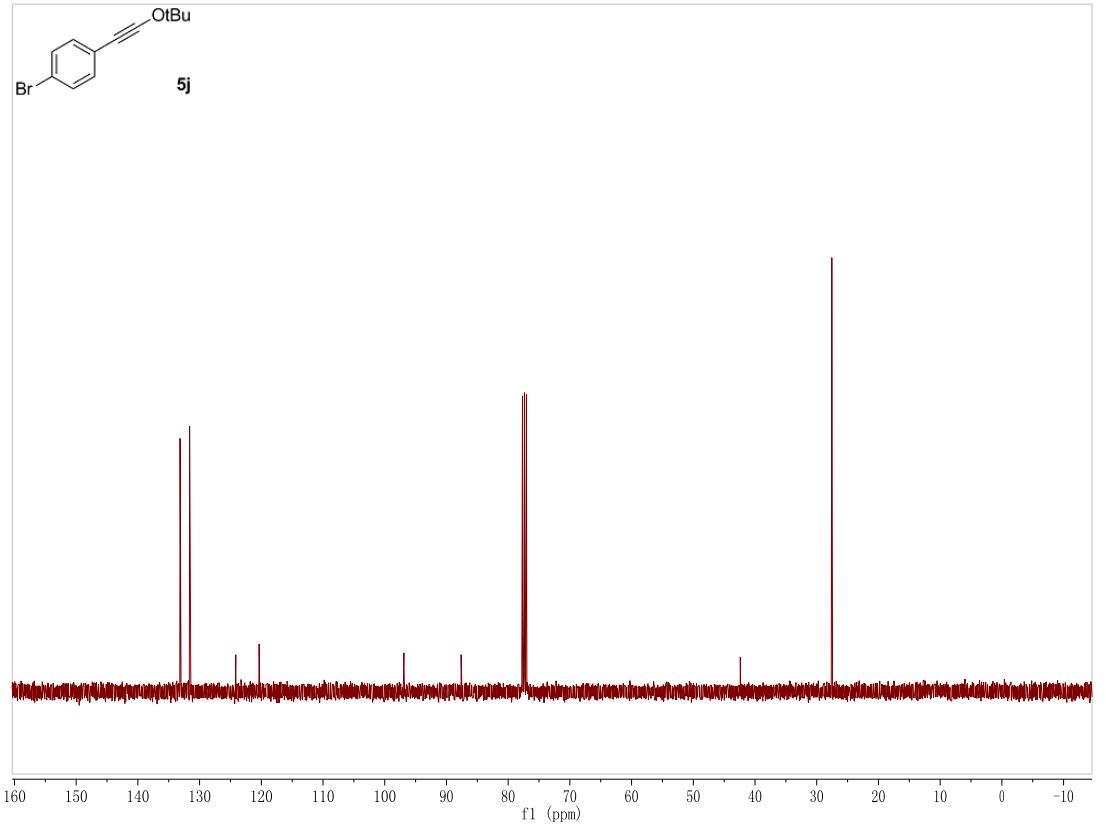

OtBu
5i
2.04
2.36
1.00
10.64
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

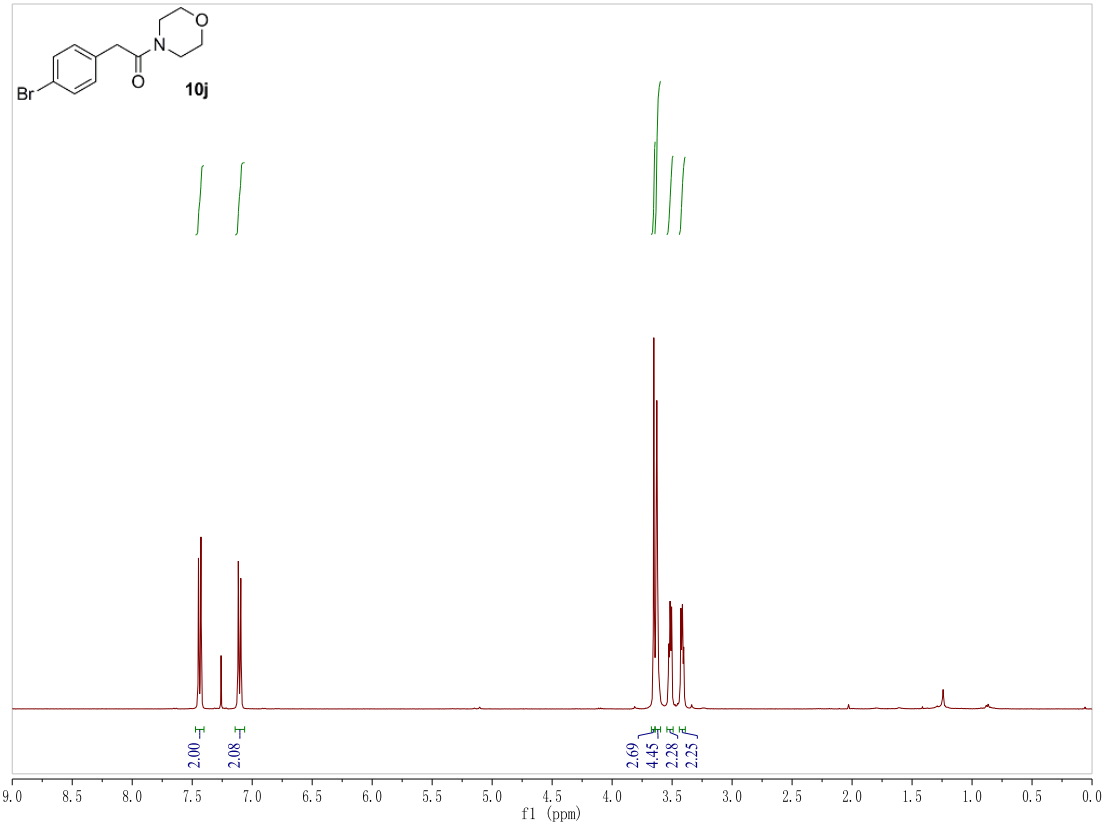

OtBu
5i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

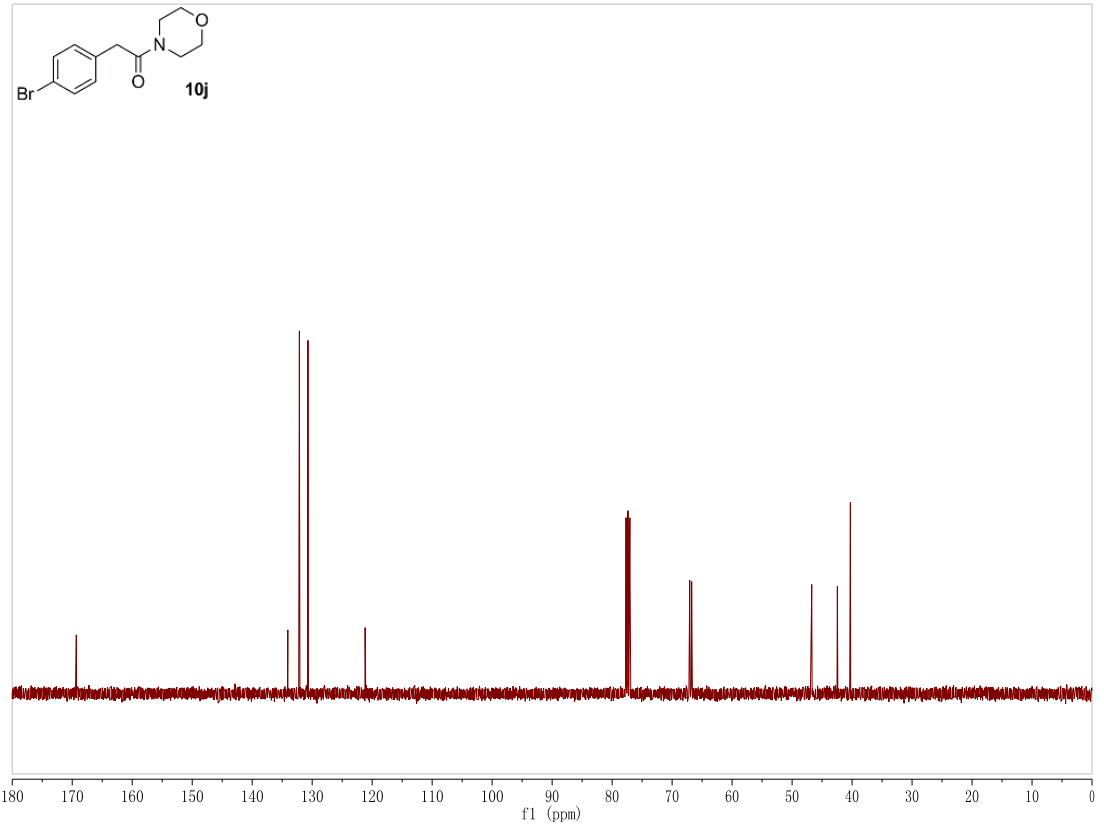

10i
2.00
2.93
2.30
4.72
4.66
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

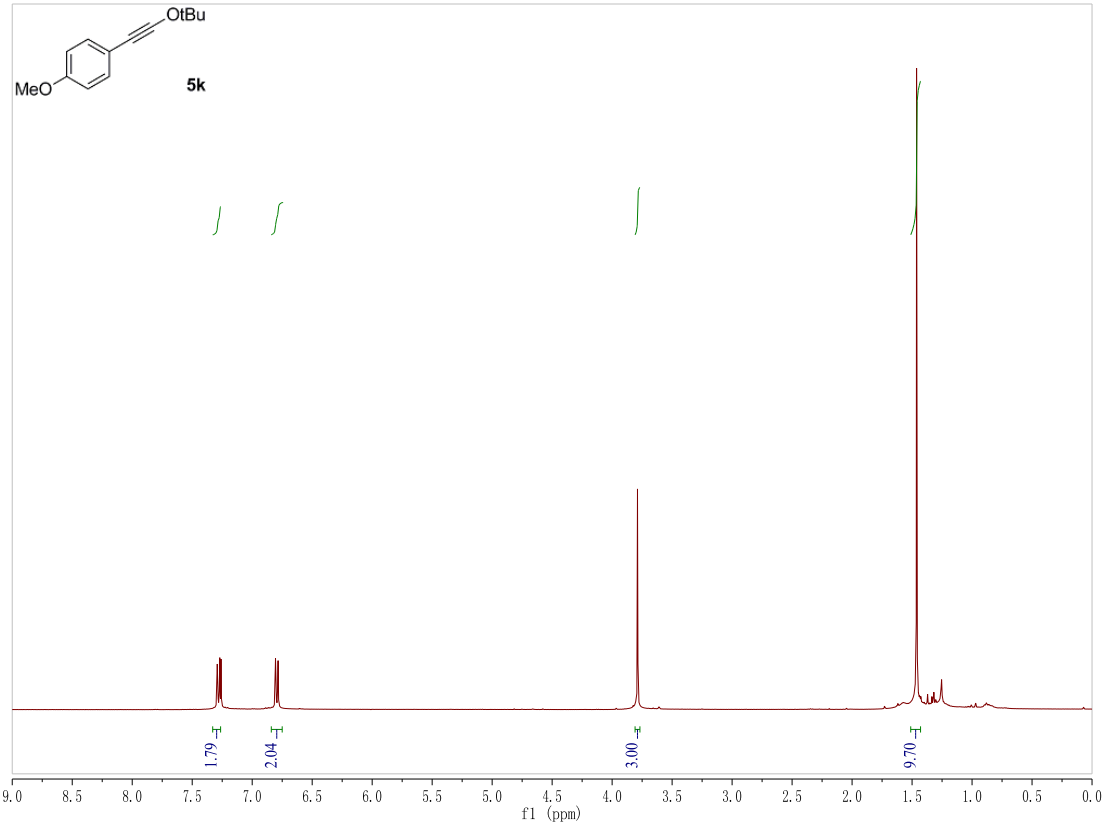

10i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

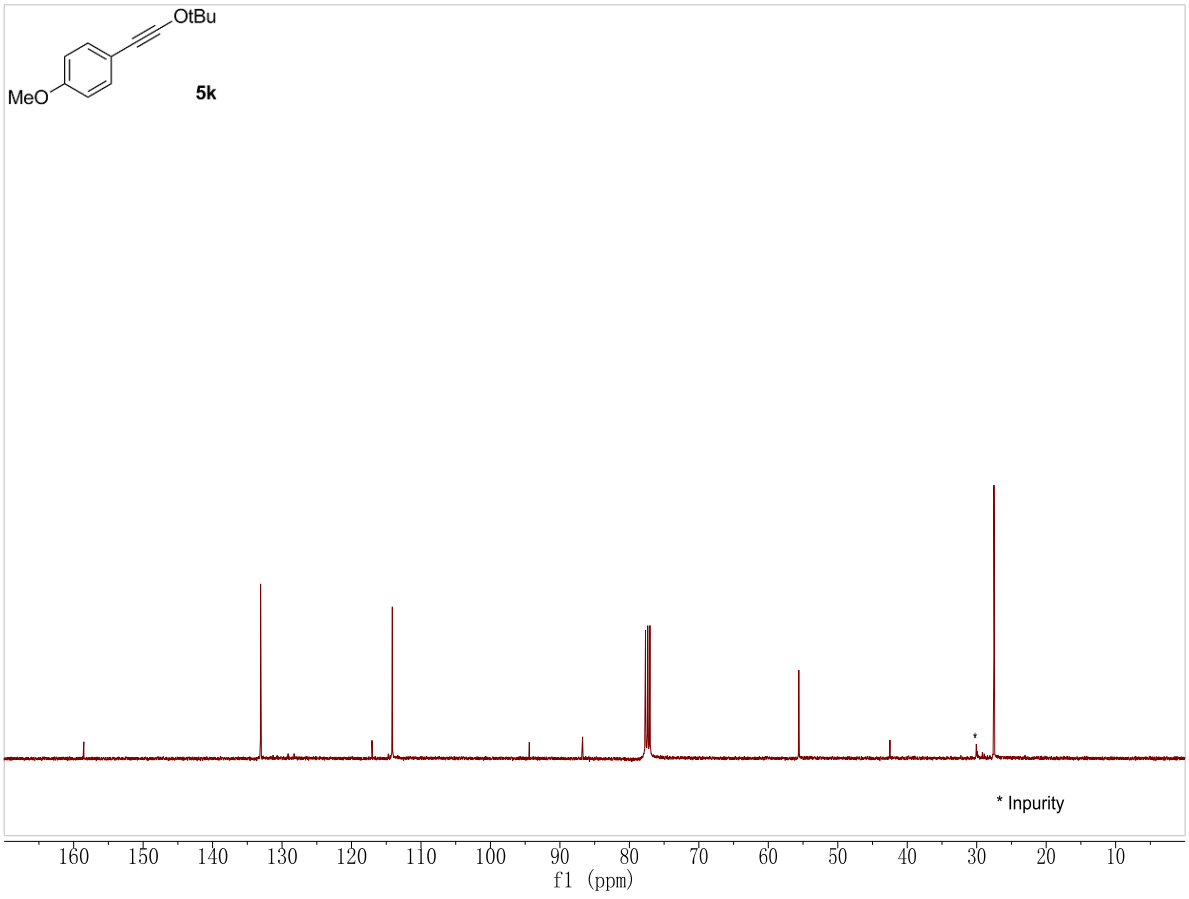

OtBu
Br
5j
1.97
2.00
9.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

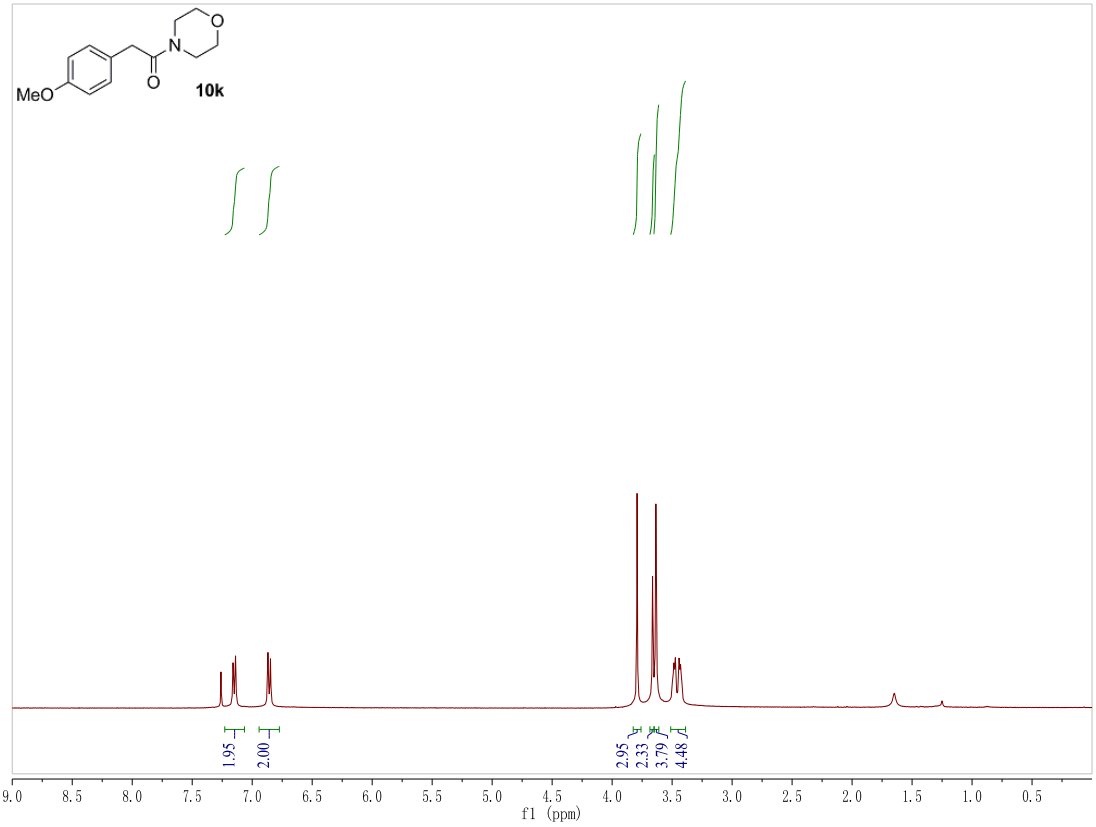

OtBu
Br
5j
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

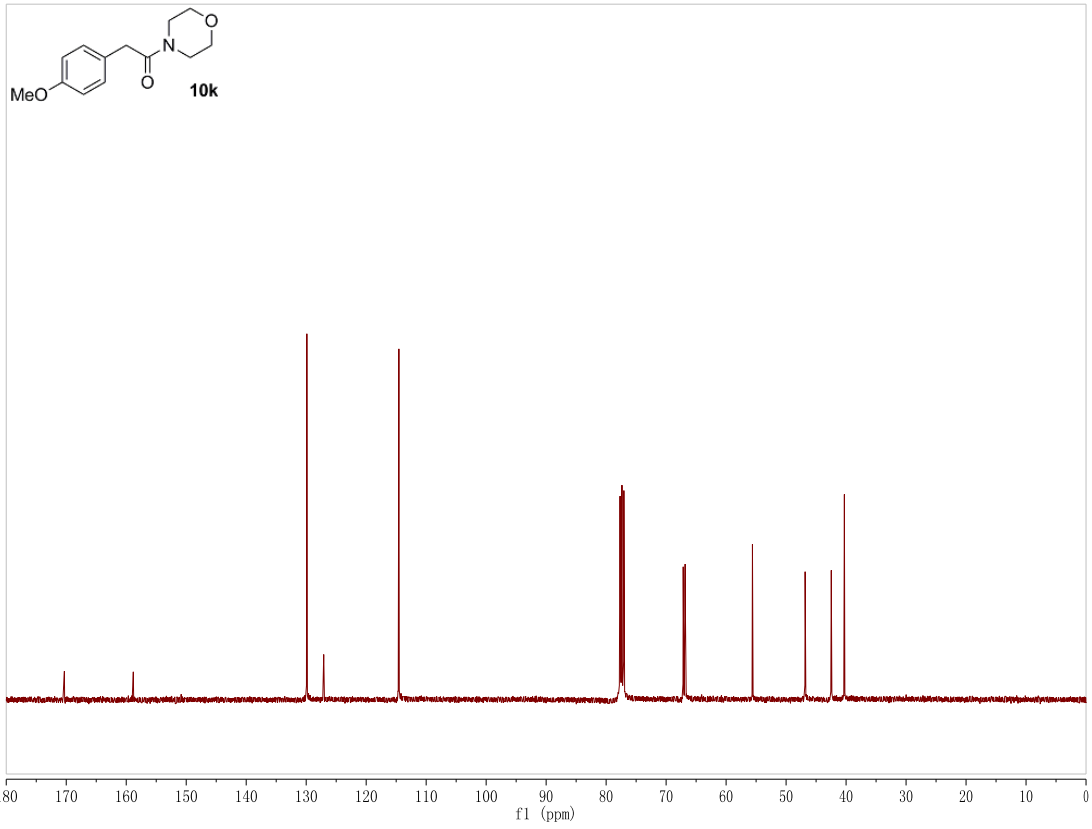

Br
O
N
O
10j
2.00
2.08
2.69
4.45
2.28
2.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

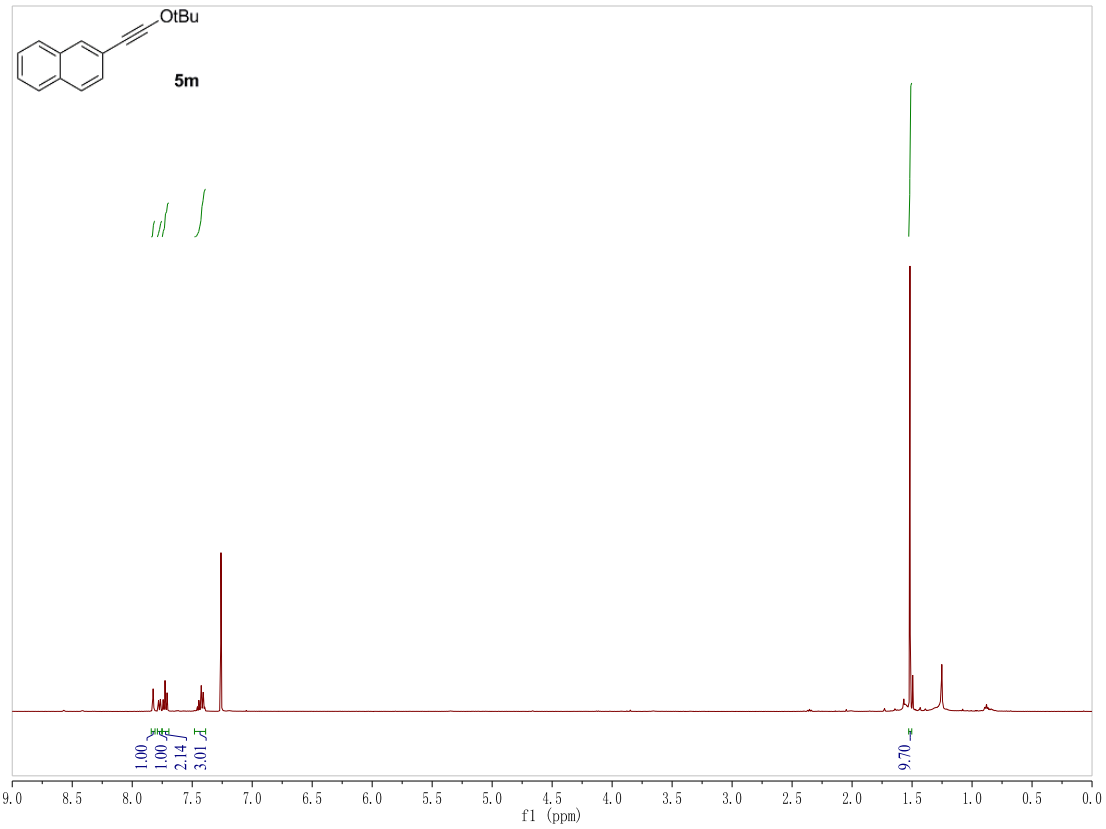

Br
O
N
O
10j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

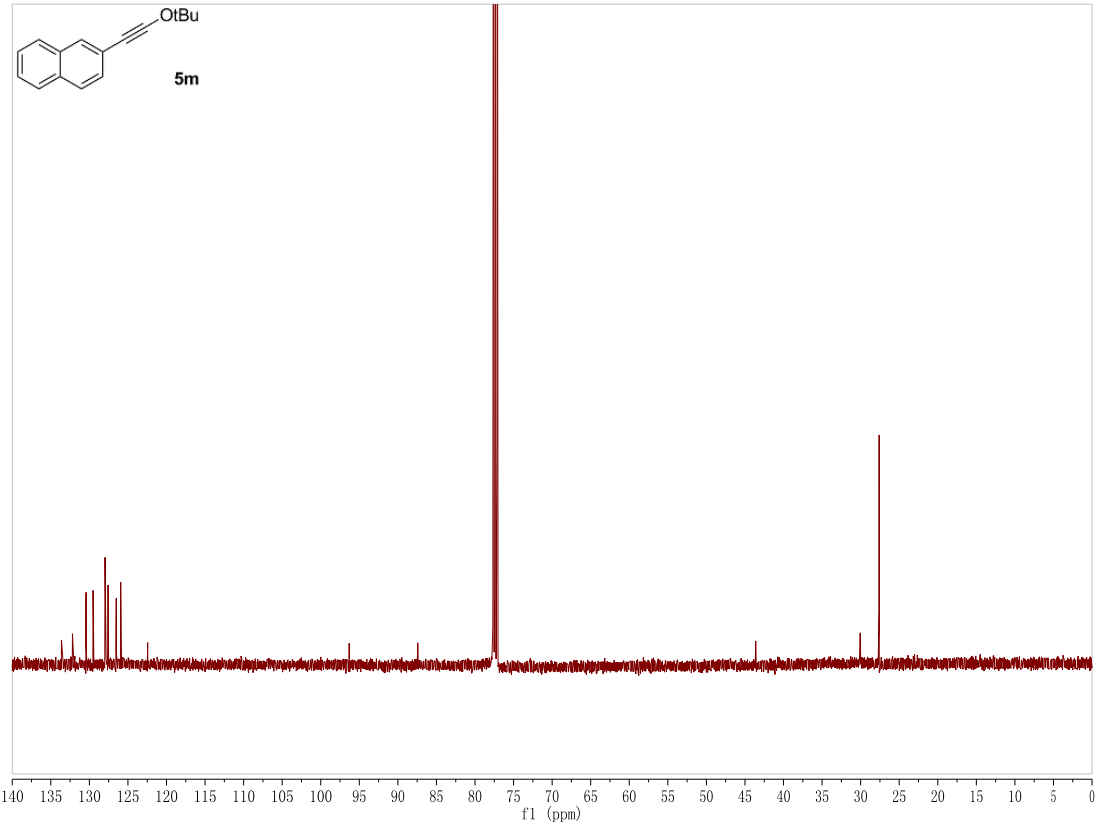

OtBu
MeO
5k
1.79
2.04
3.00
9.70
f1 (ppm)

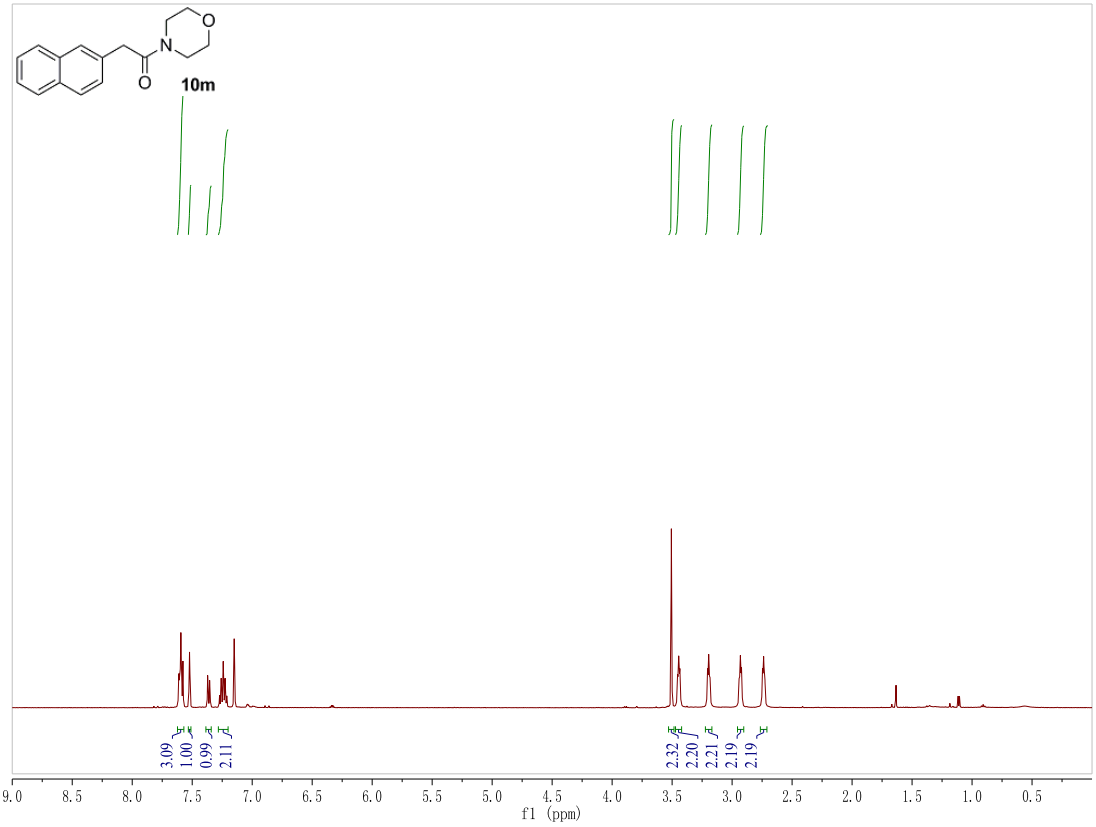

OtBu
MeO
5k
* Inpurity
f1 (ppm)

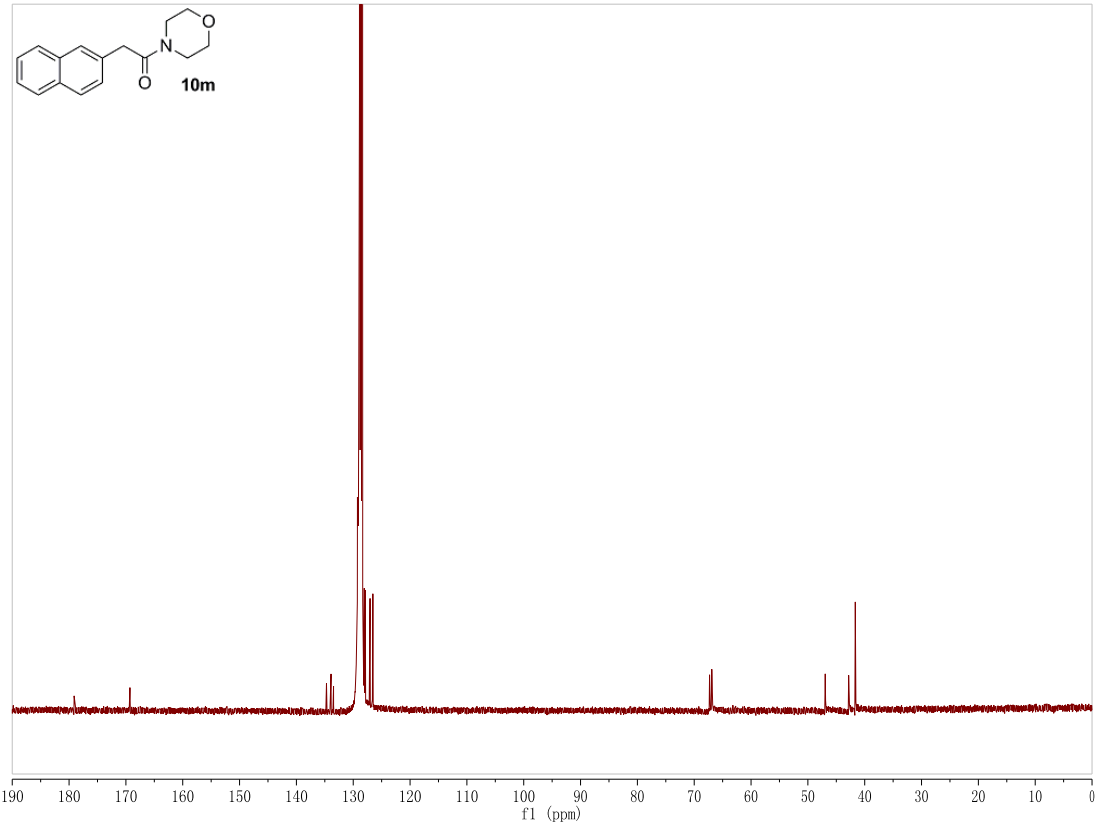

MeO
10k
1.95
2.00
2.95
2.33
3.79
4.48
f1 (ppm)

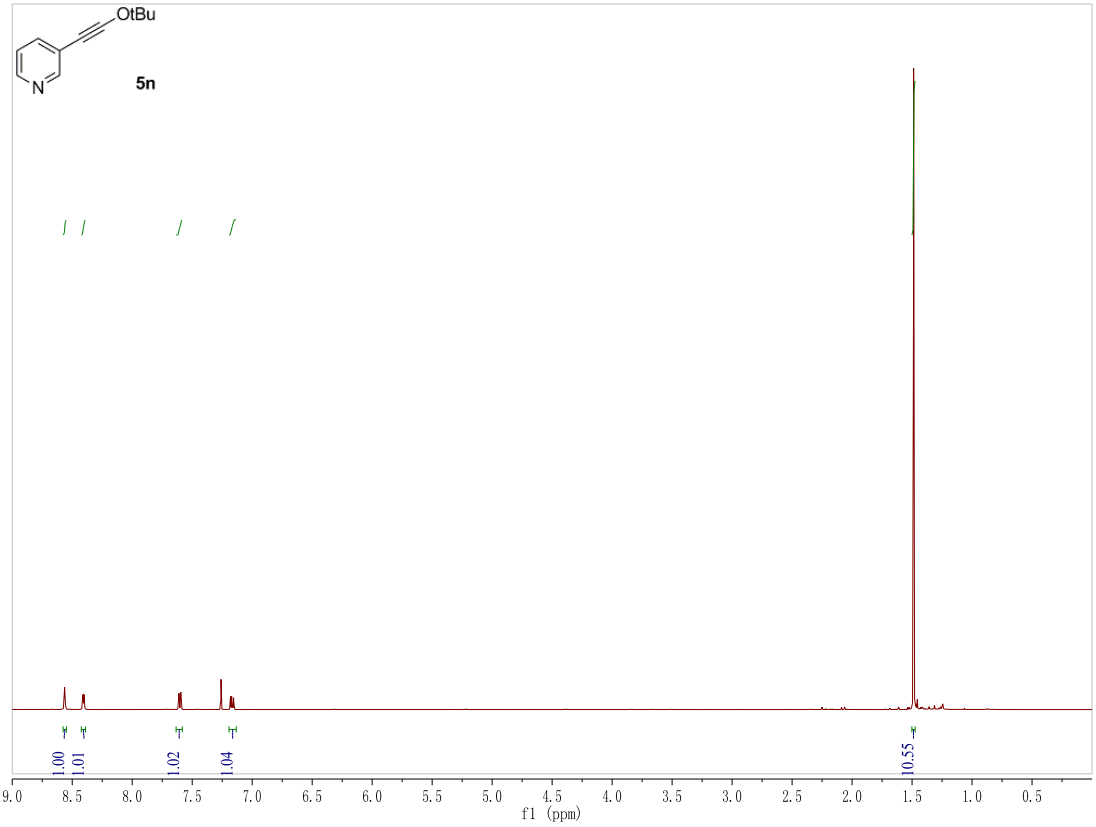

MeO
10k
f1 (ppm)

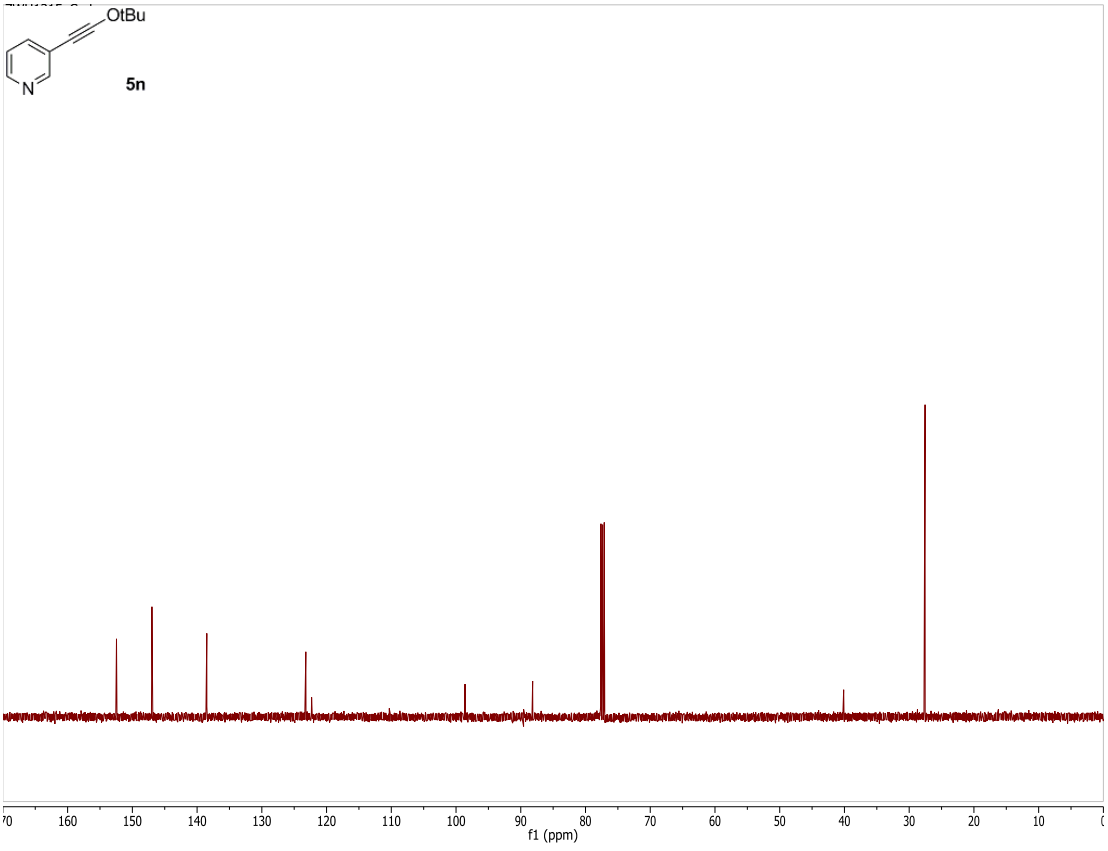

OtBu
5m
1.00
1.00
2.14
3.01
9.70
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

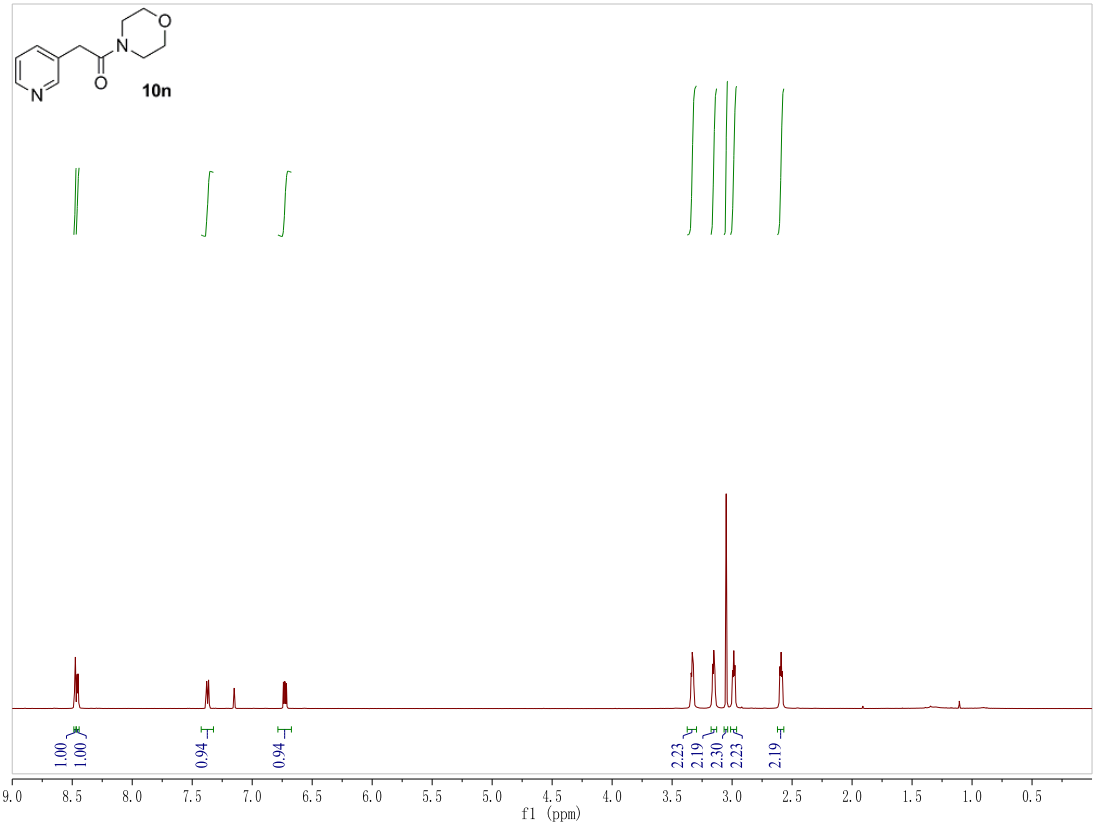

OtBu
5m
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

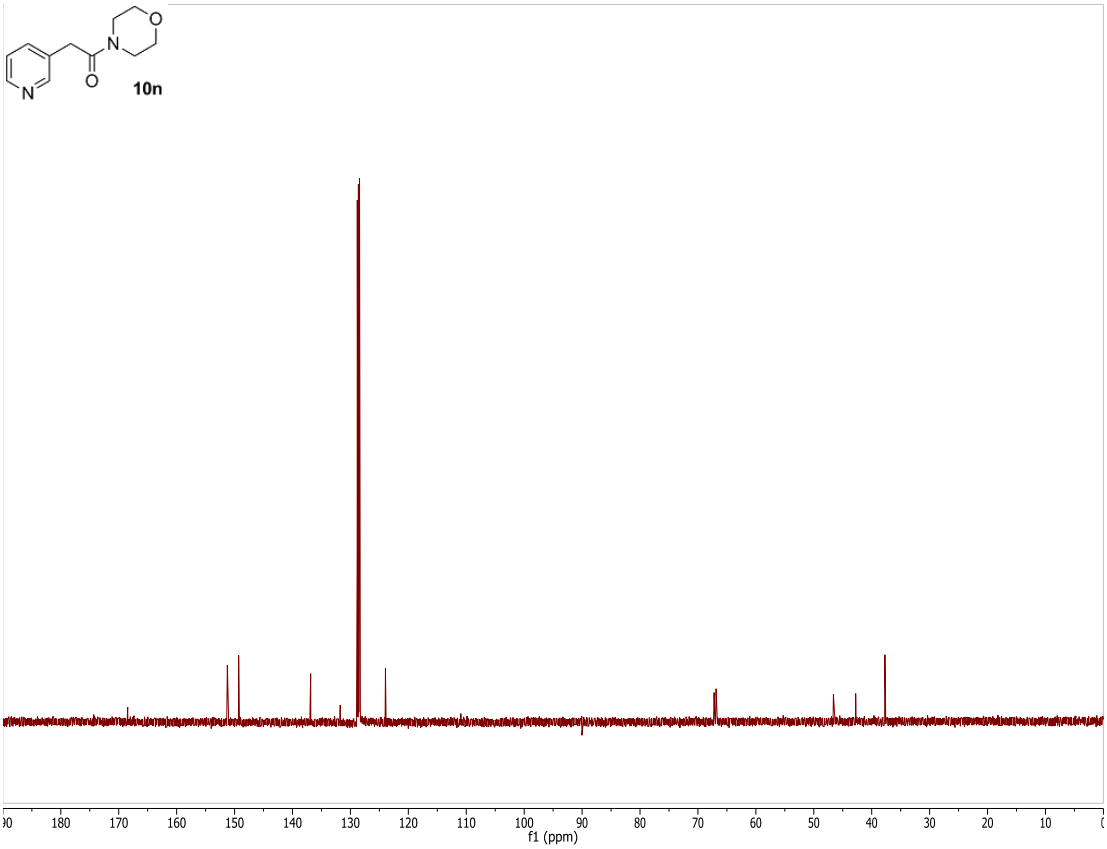

10m
3.09
1.00
0.99
2.11
2.32
2.20
2.21
2.19
2.19
f1 (ppm)

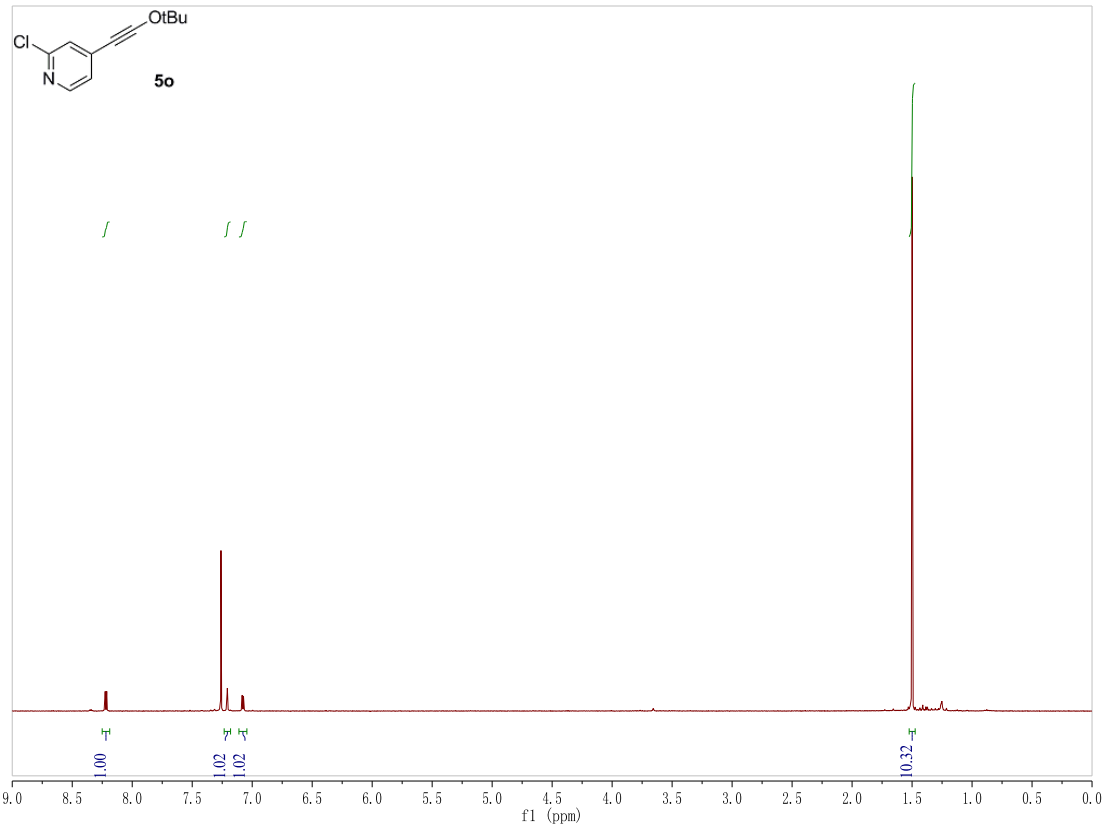

10m
f1 (ppm)

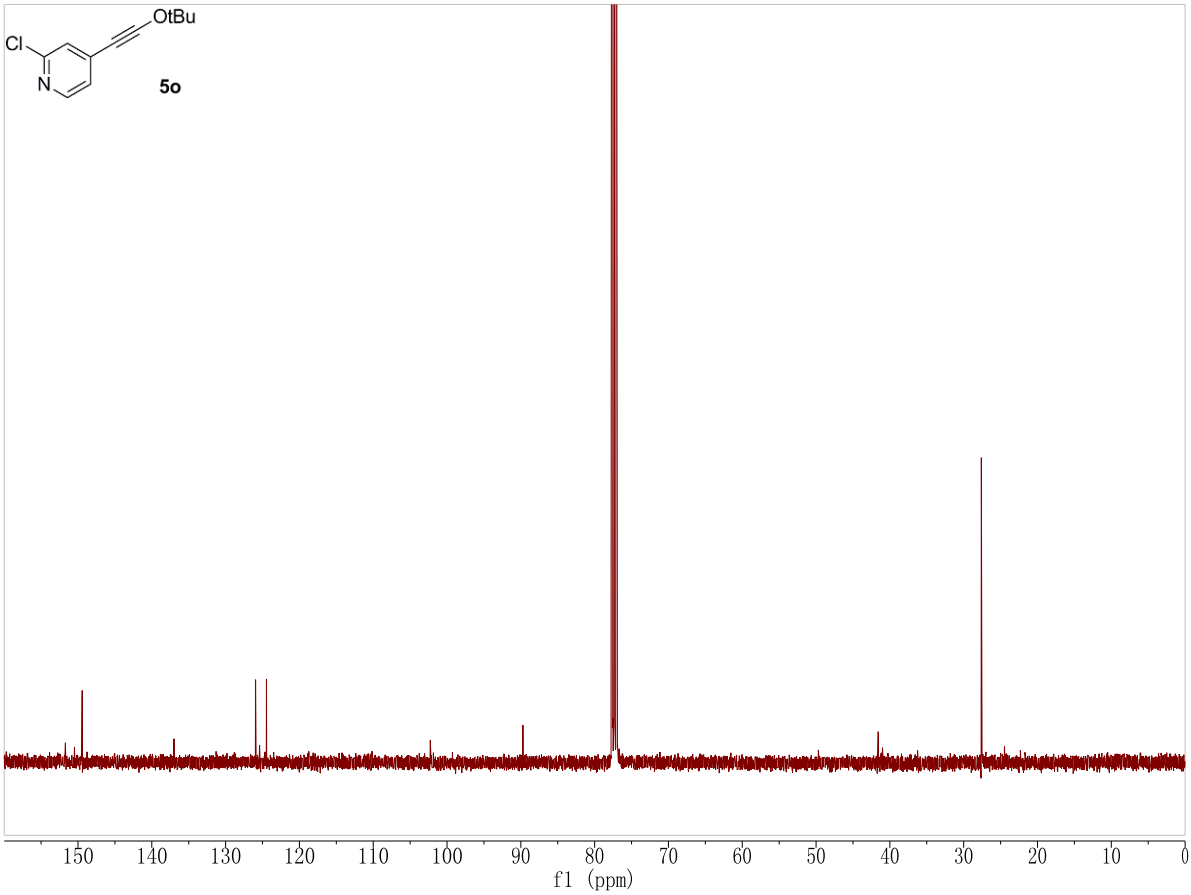

OtBu
N
5n
1.00
1.01
1.02
1.04
10.55
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

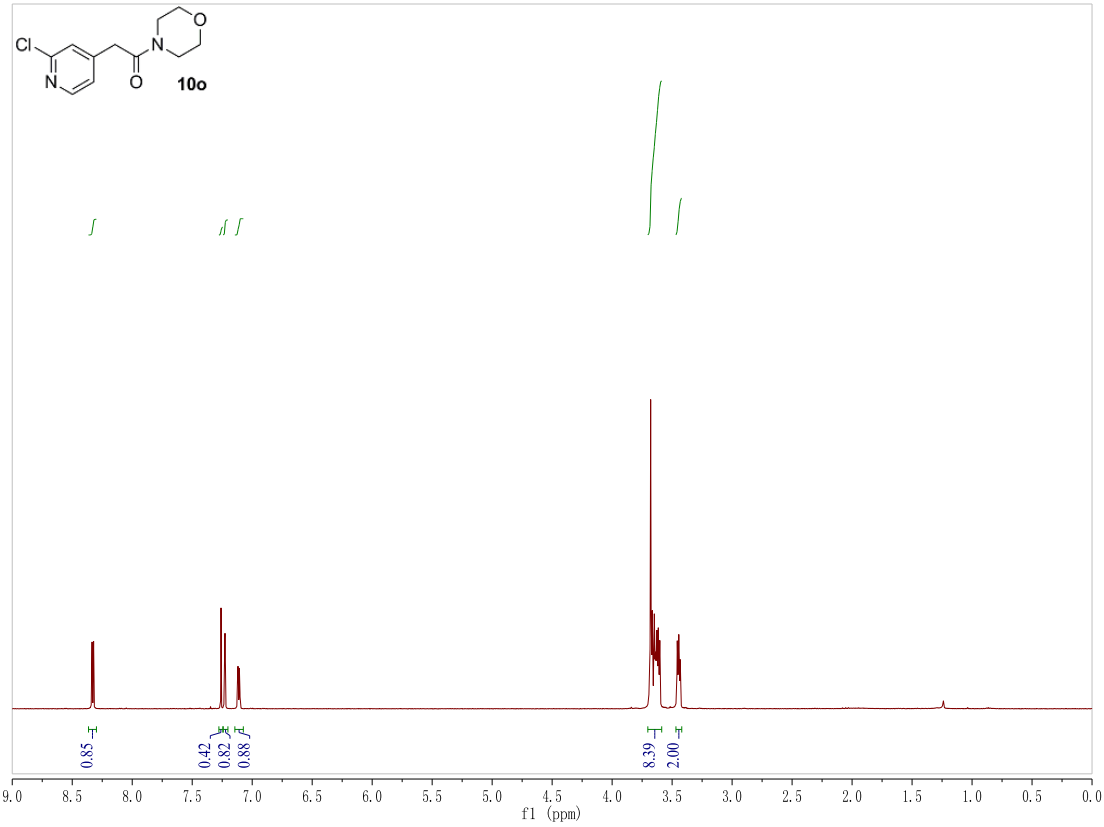

OtBu
N
5n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

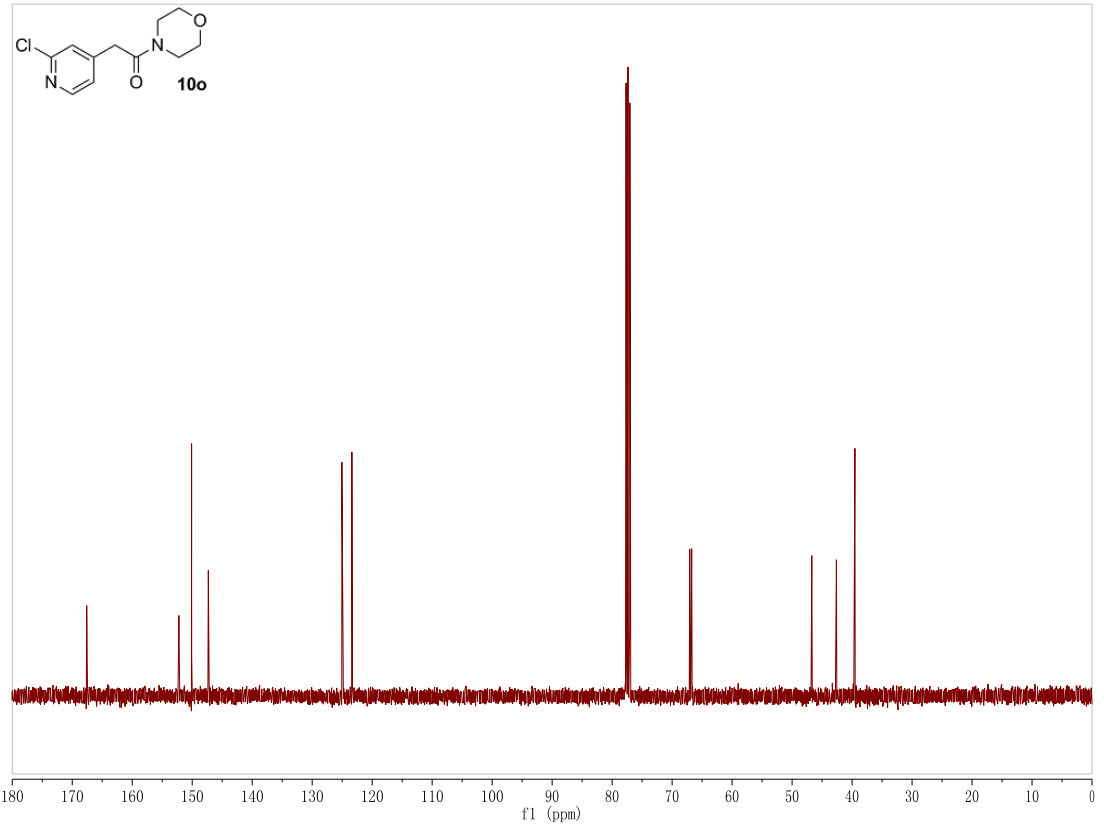

10n
1.00
1.00
0.94
0.94
2.23
2.19
2.30
2.23
2.19
f1 (ppm)

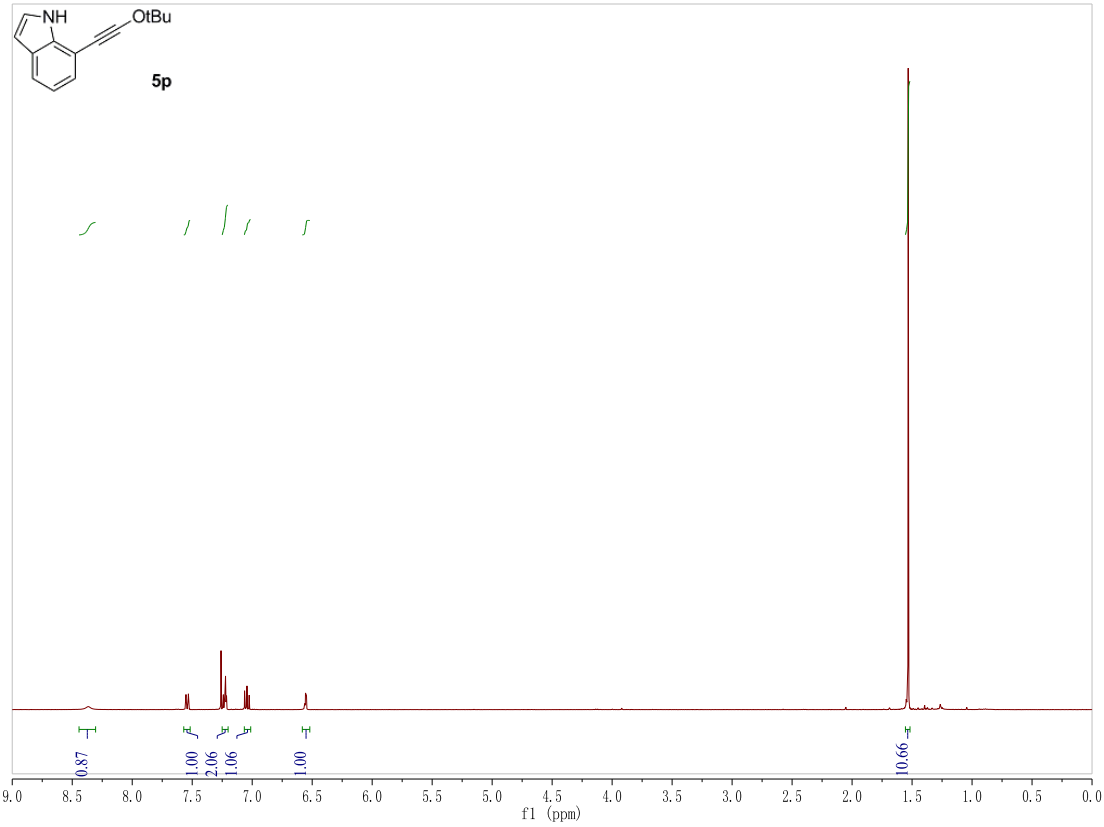

10n
f1 (ppm)

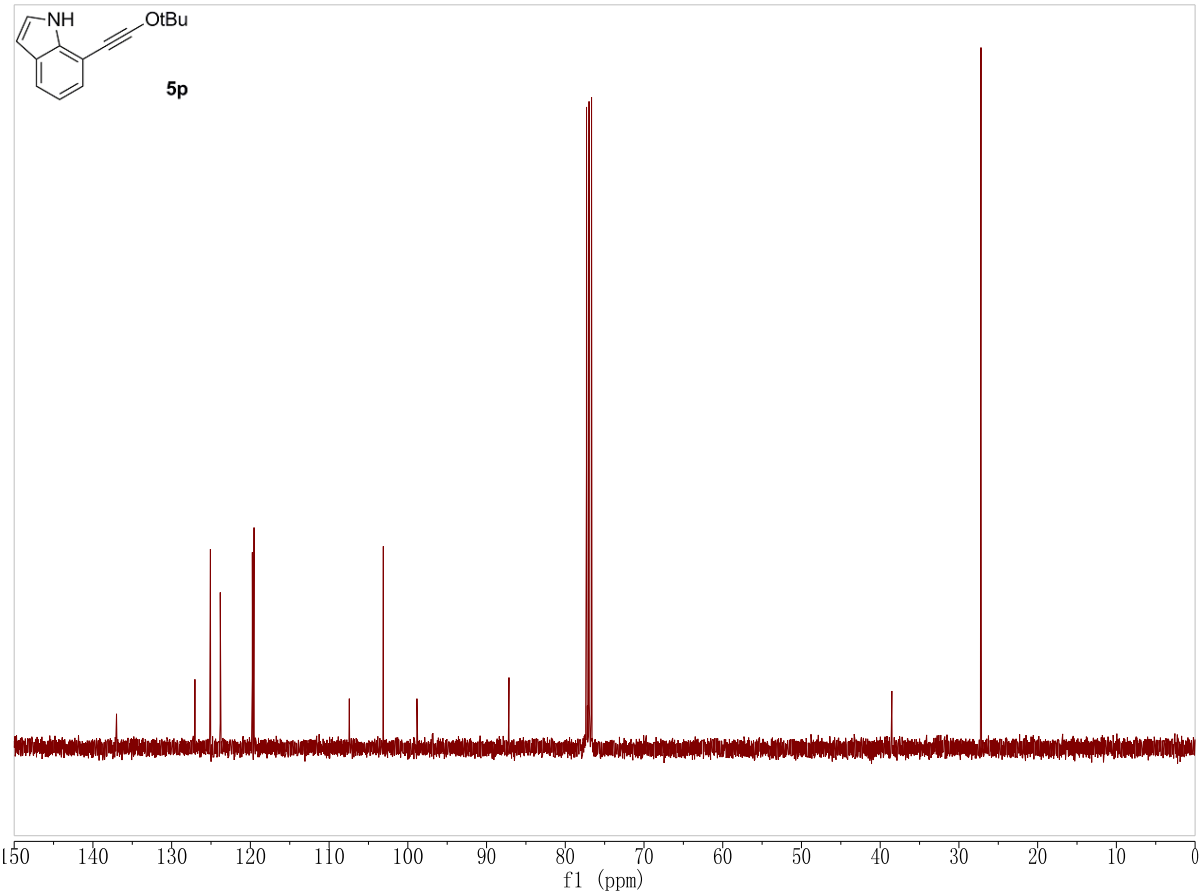

OtBu
Cl
N
5o
1.00
1.02
1.02
10.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

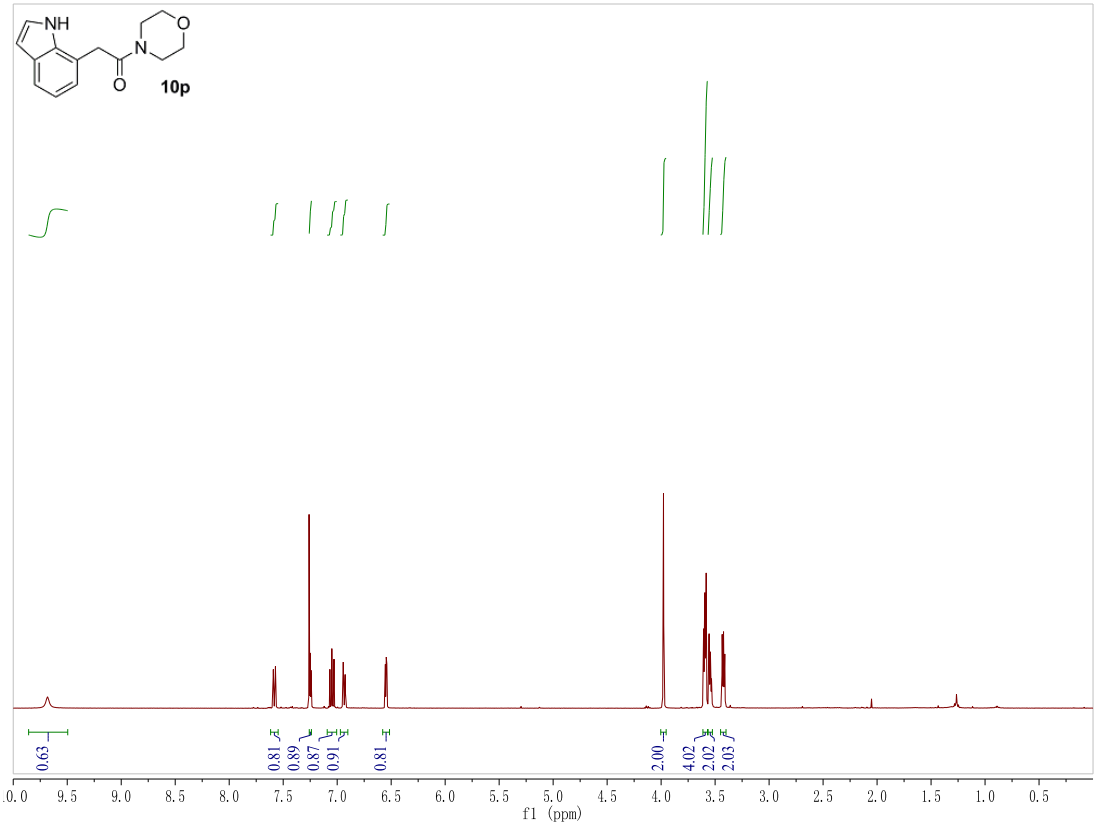

OtBu
Cl
N
5o
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

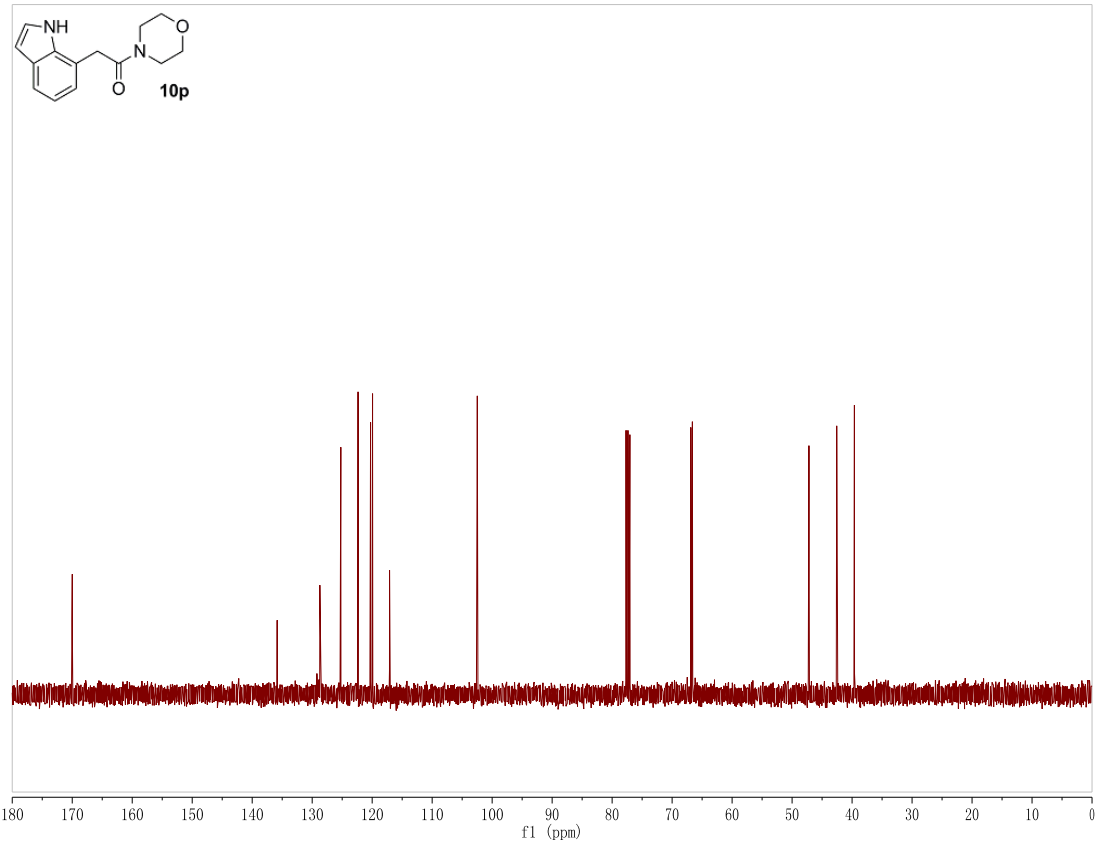

Cl
N
O
N
O
10o
0.85
0.42
0.82
0.88
8.39
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

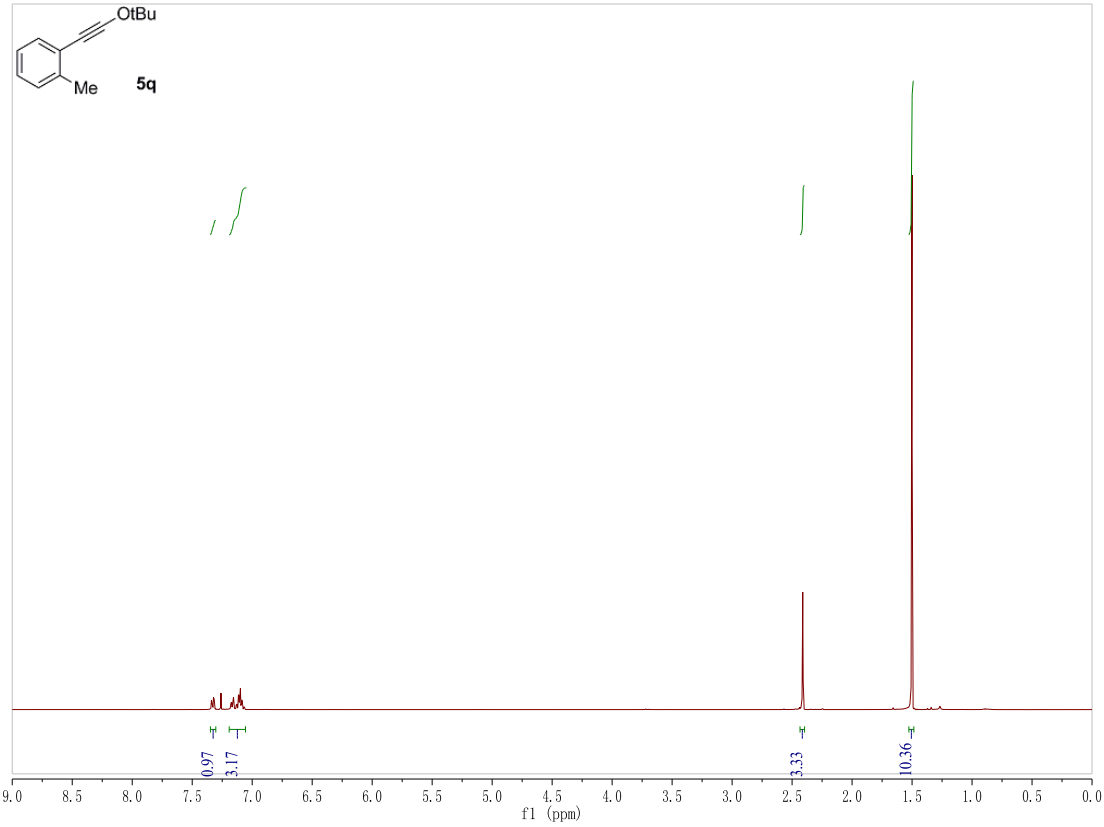

Cl
N
O
N
O
10o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

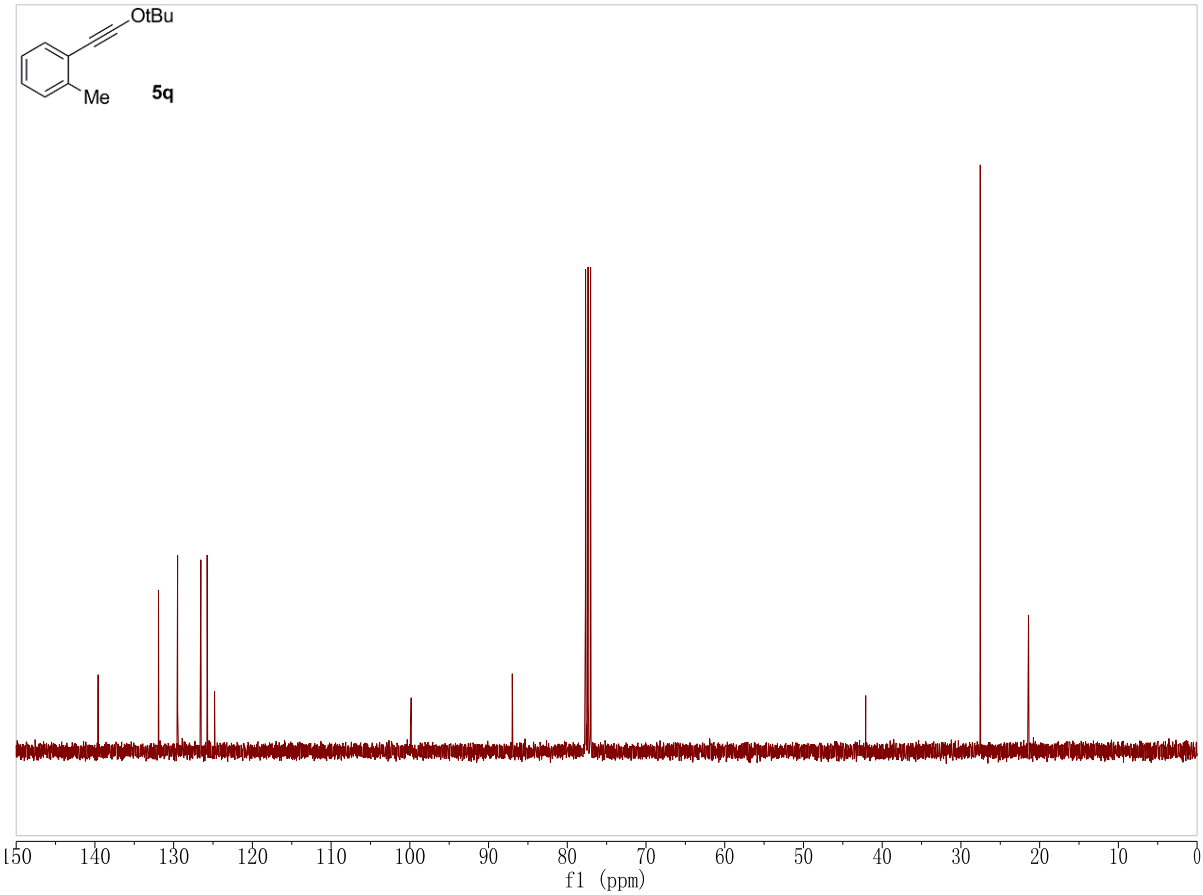

NH
OtBu
5p
0.87
1.00
2.06
1.06
1.00
10.66
f1 (ppm)

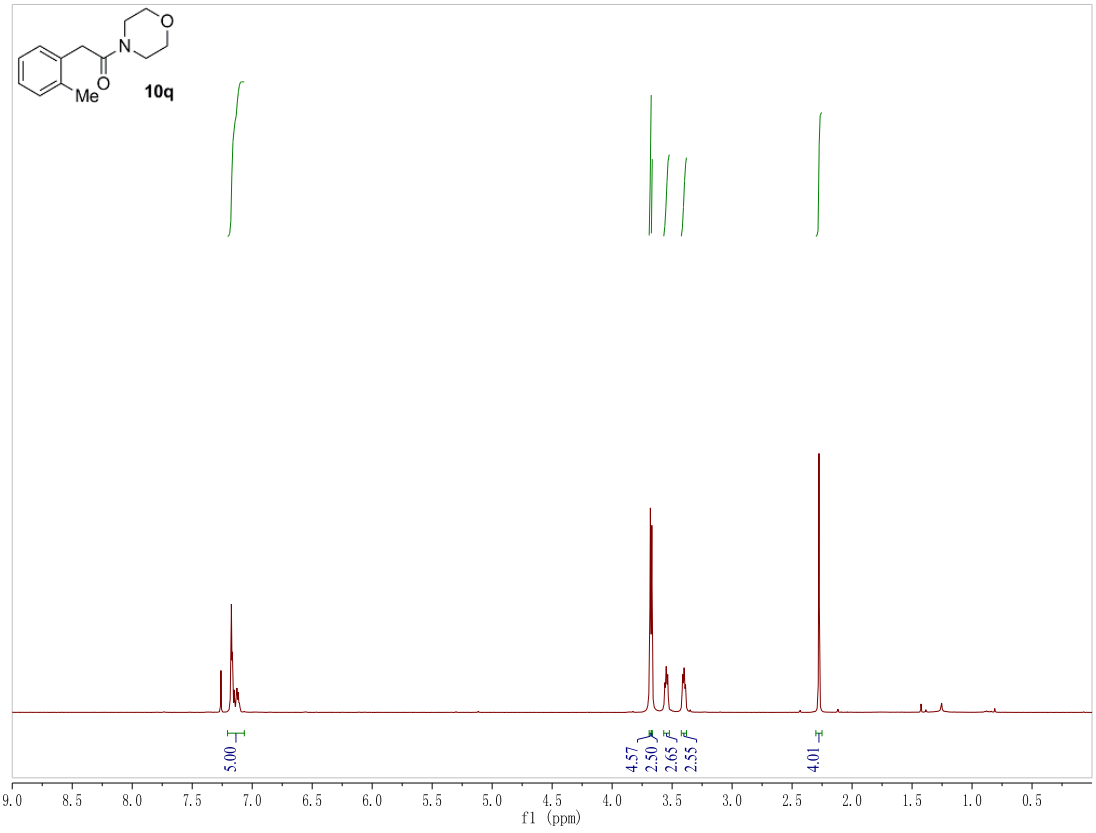

NH
OtBu
5p
f1 (ppm)

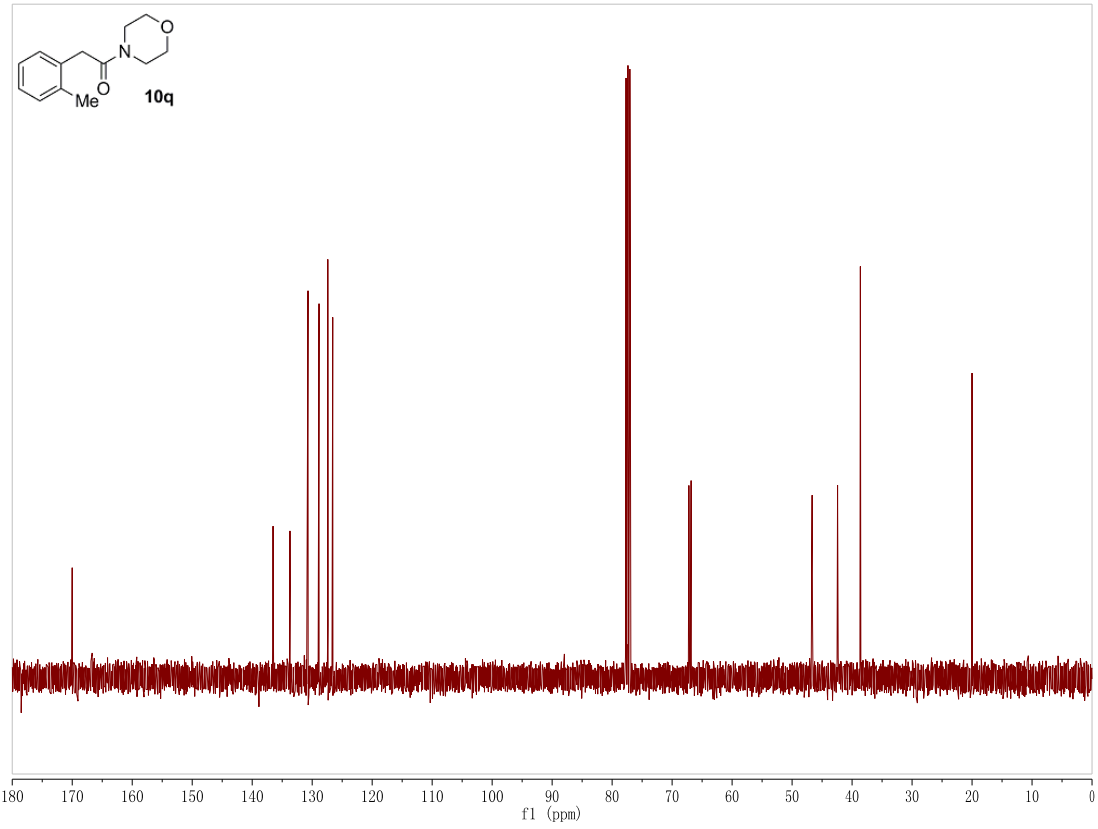

NH
O
N
O
10p
0.63
0.81
0.89
0.87
0.91
0.81
2.00
4.02
2.02
2.03
f1 (ppm)

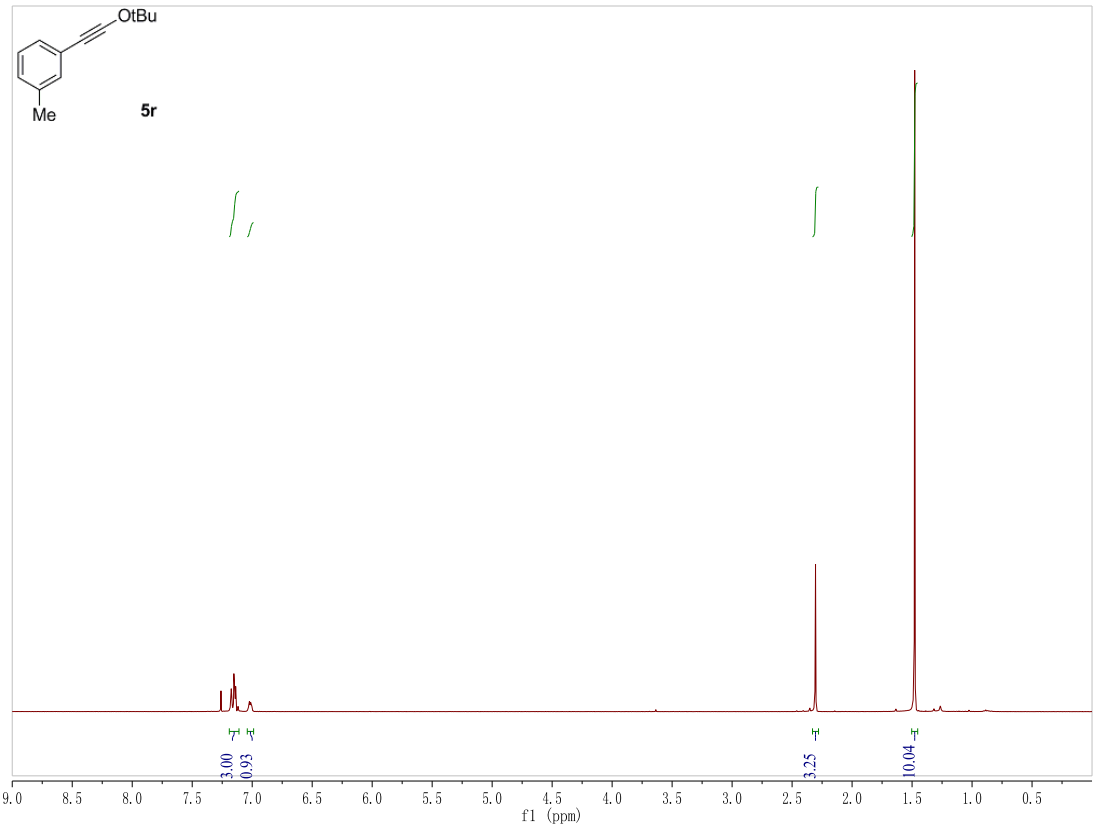

NH
O
N
O
10p
f1 (ppm)

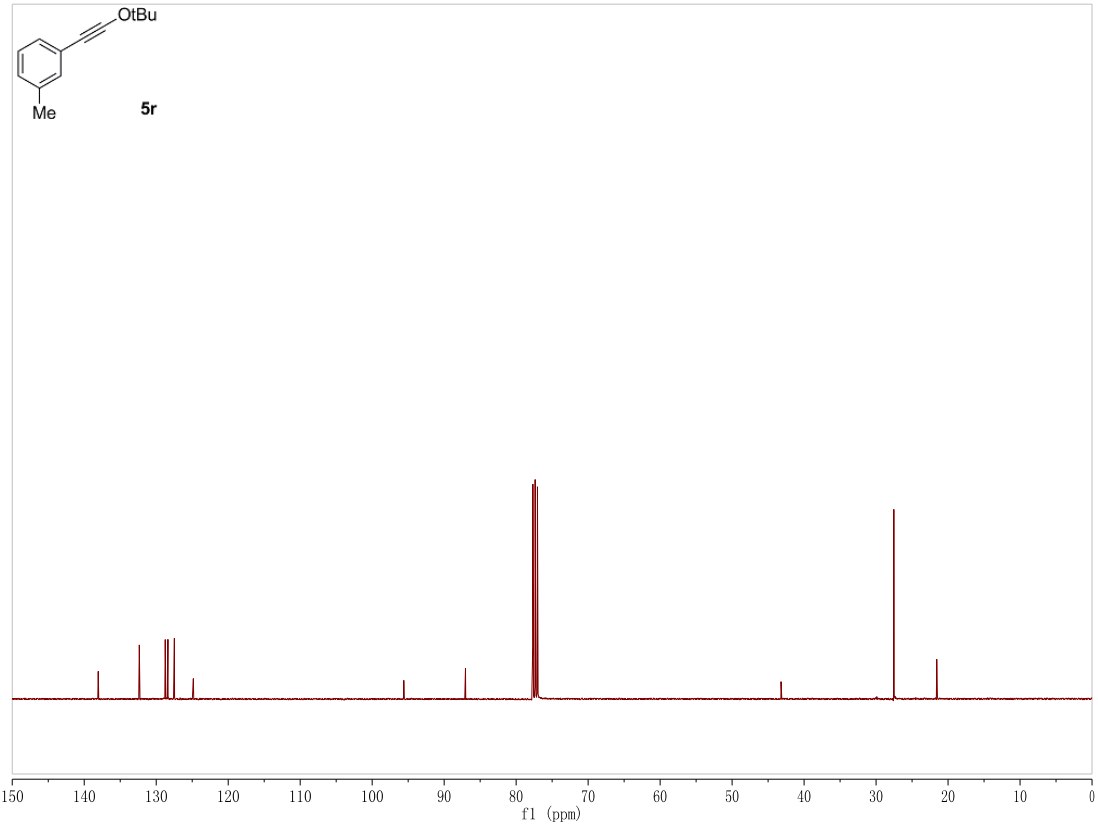

OtBu
Me
5q
0.97
3.17
3.33
10.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

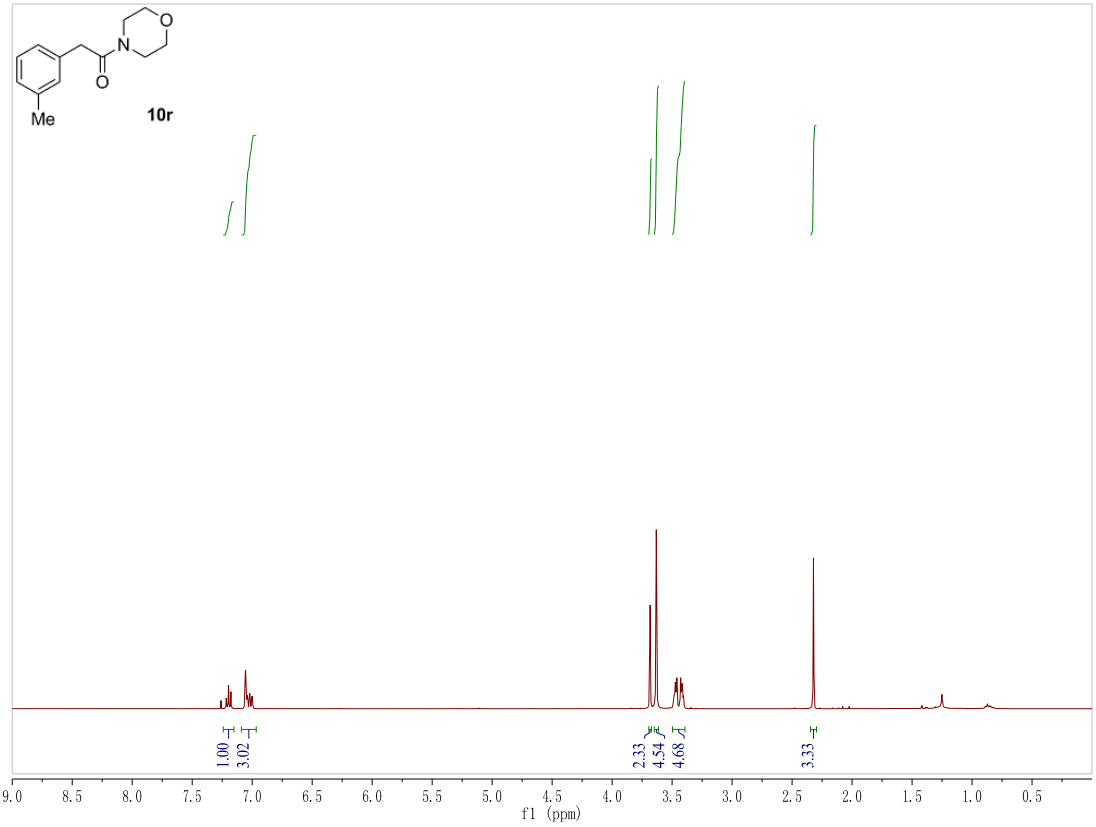

OtBu
Me
5q
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

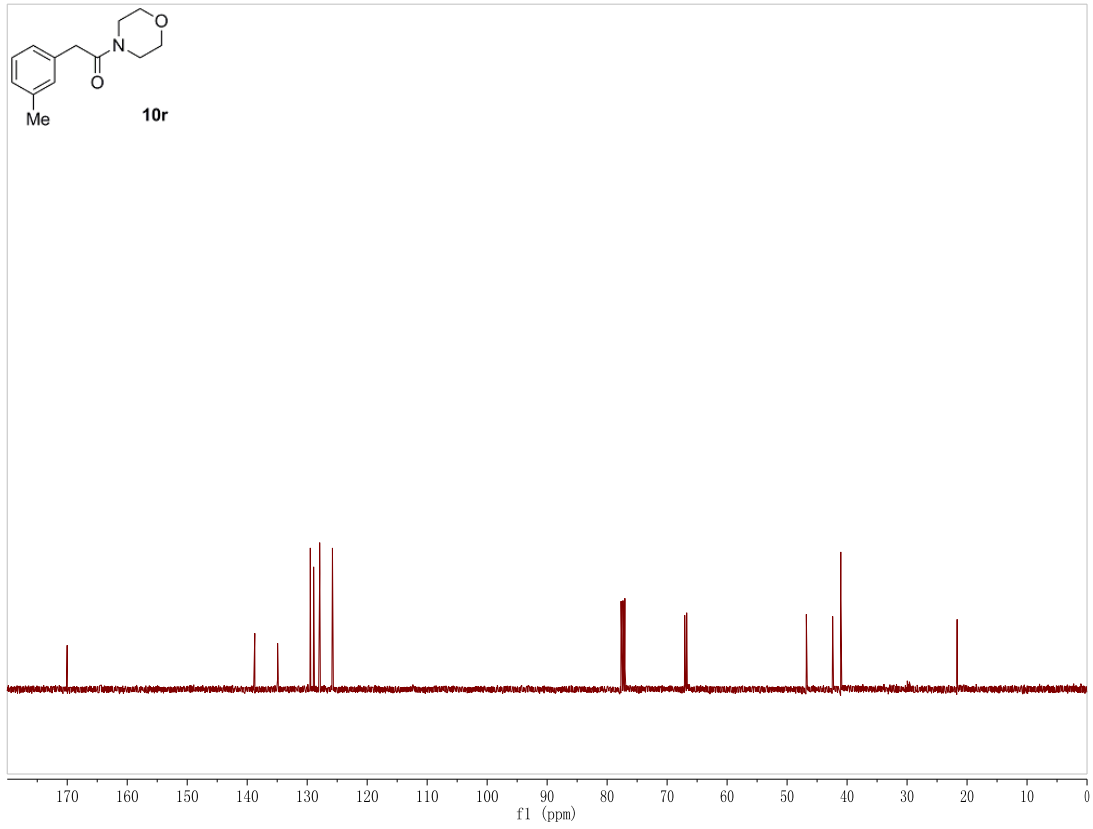

10q
Me
O
N
O
5.00
4.57
2.50
2.65
2.55
4.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

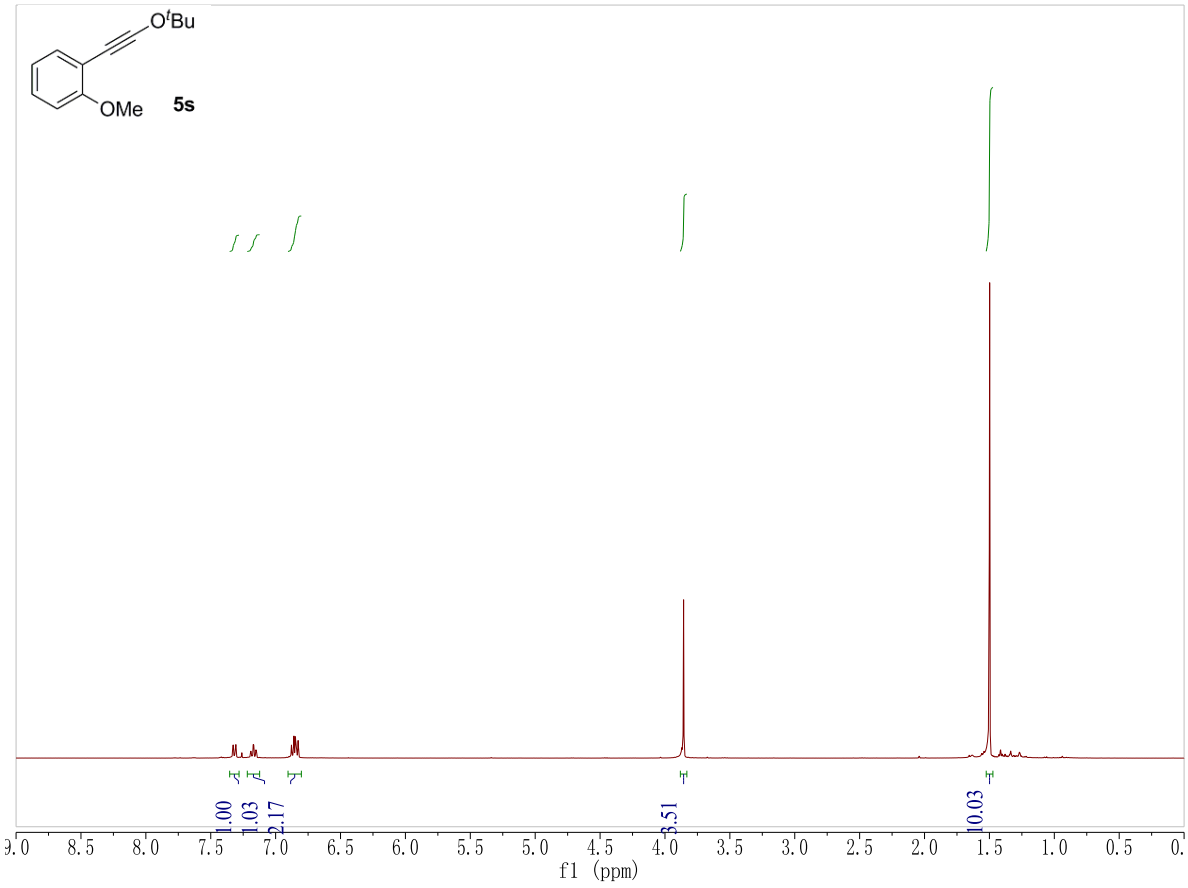

10q
Me
O
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

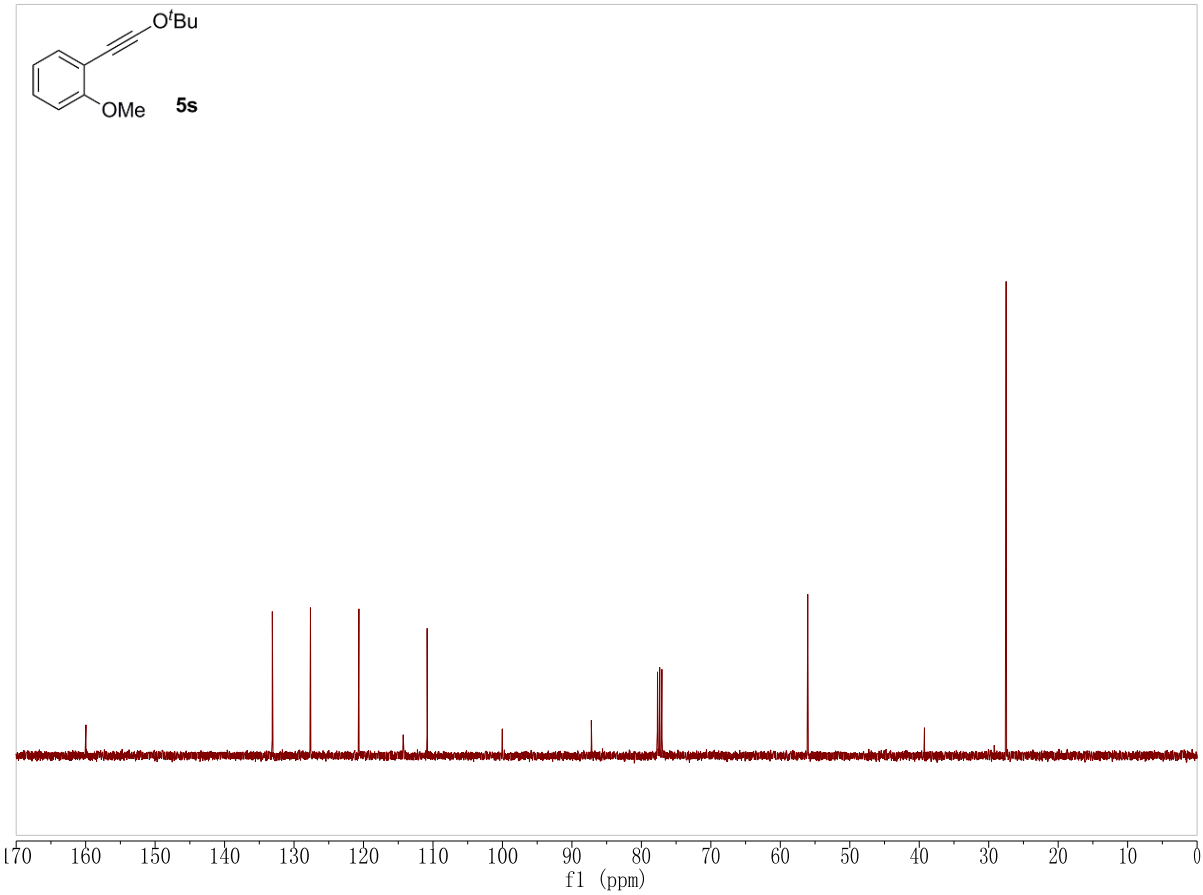

OtBu
Me
5r
3.00
0.93
3.25
10.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

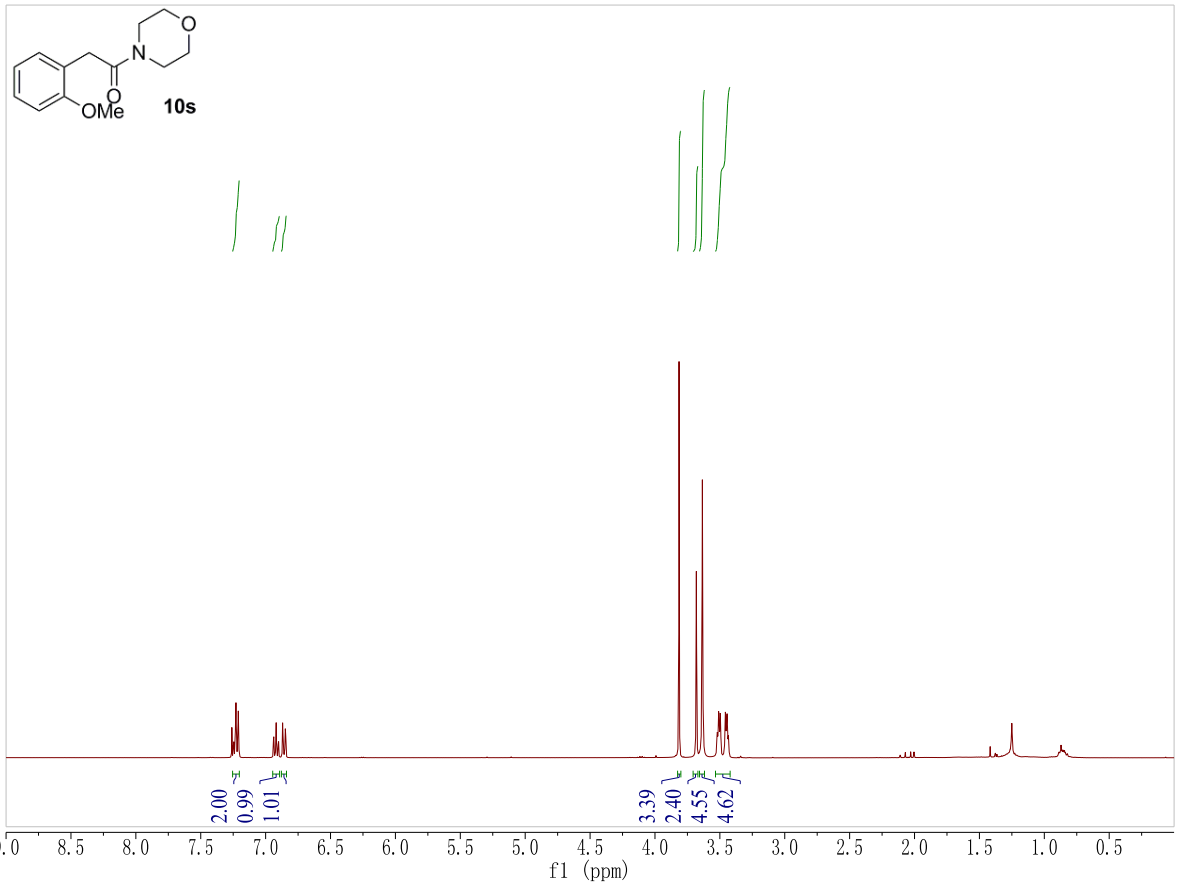

OtBu
Me
5r
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

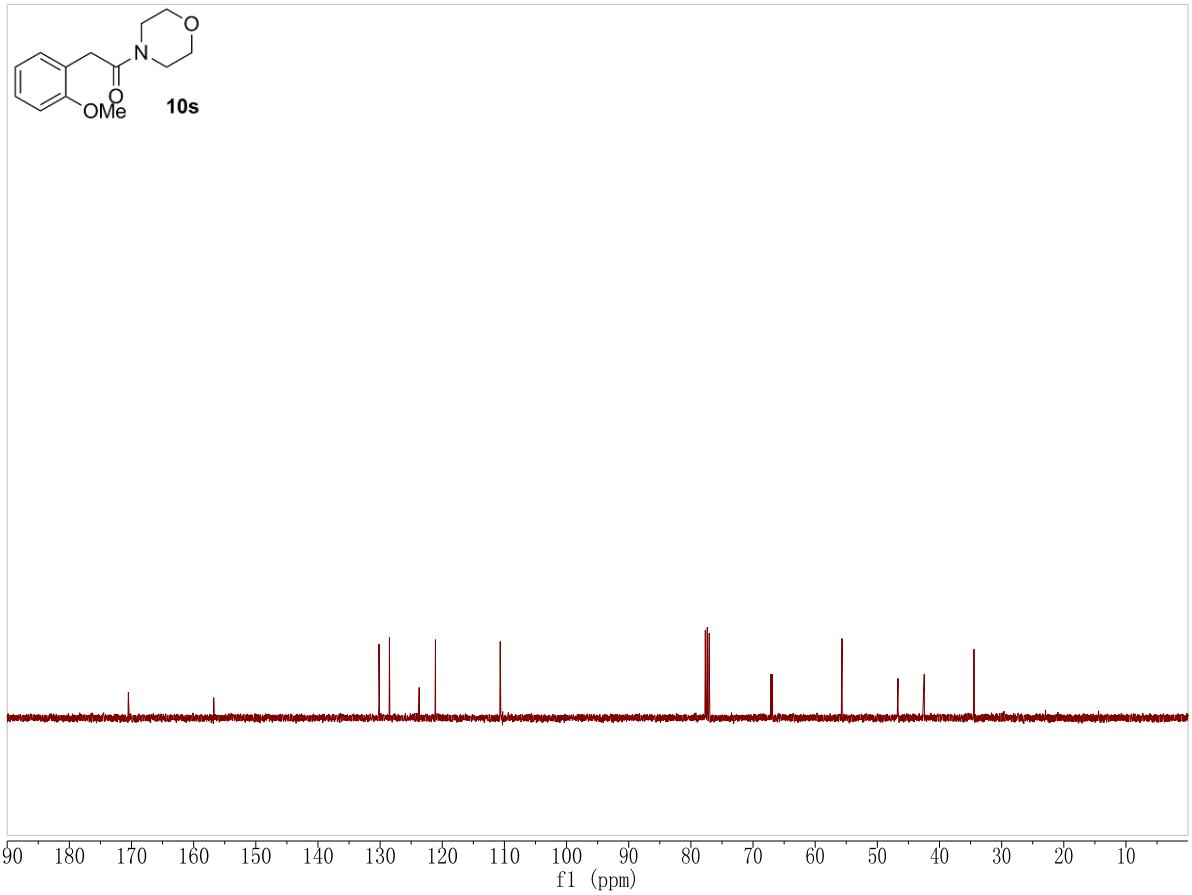

Me
10r
1.00
3.02
2.33
4.54
4.68
3.33
f1 (ppm)

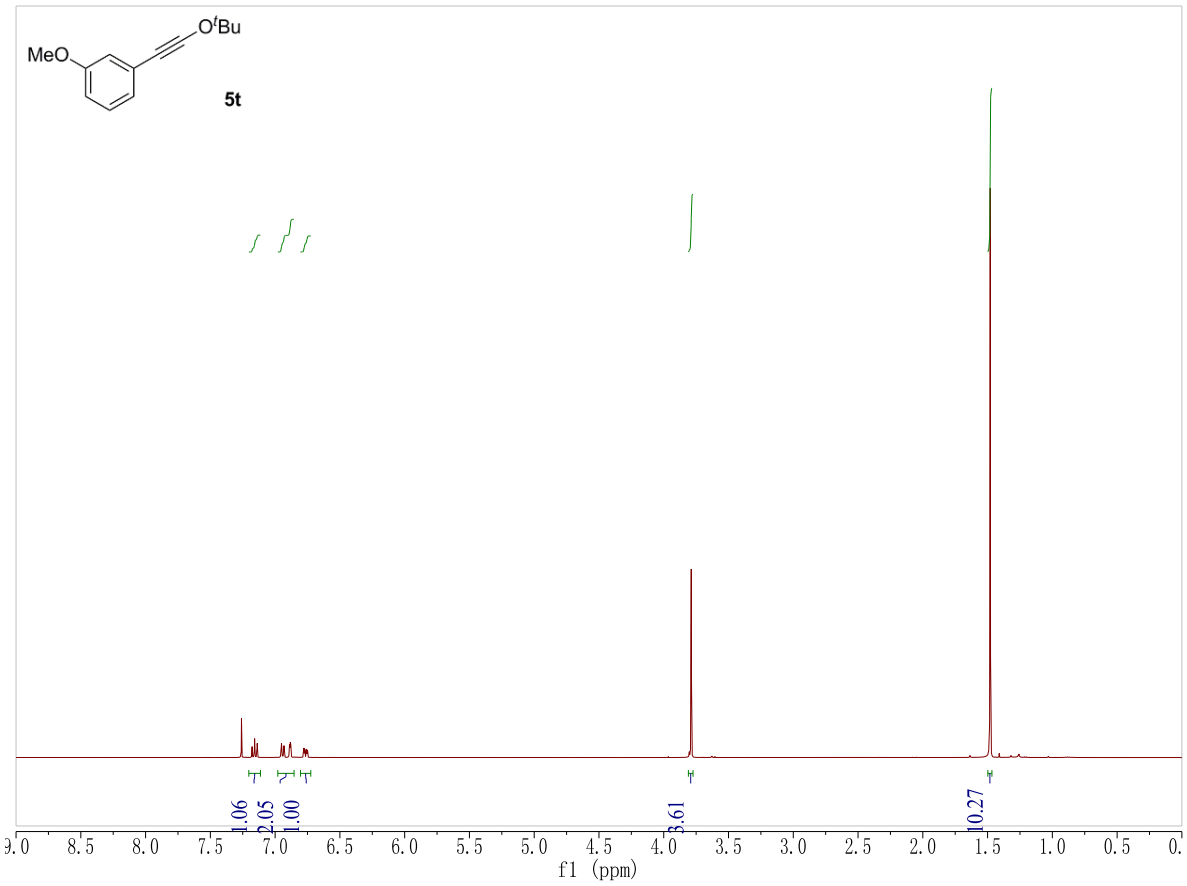

Me
10r
f1 (ppm)

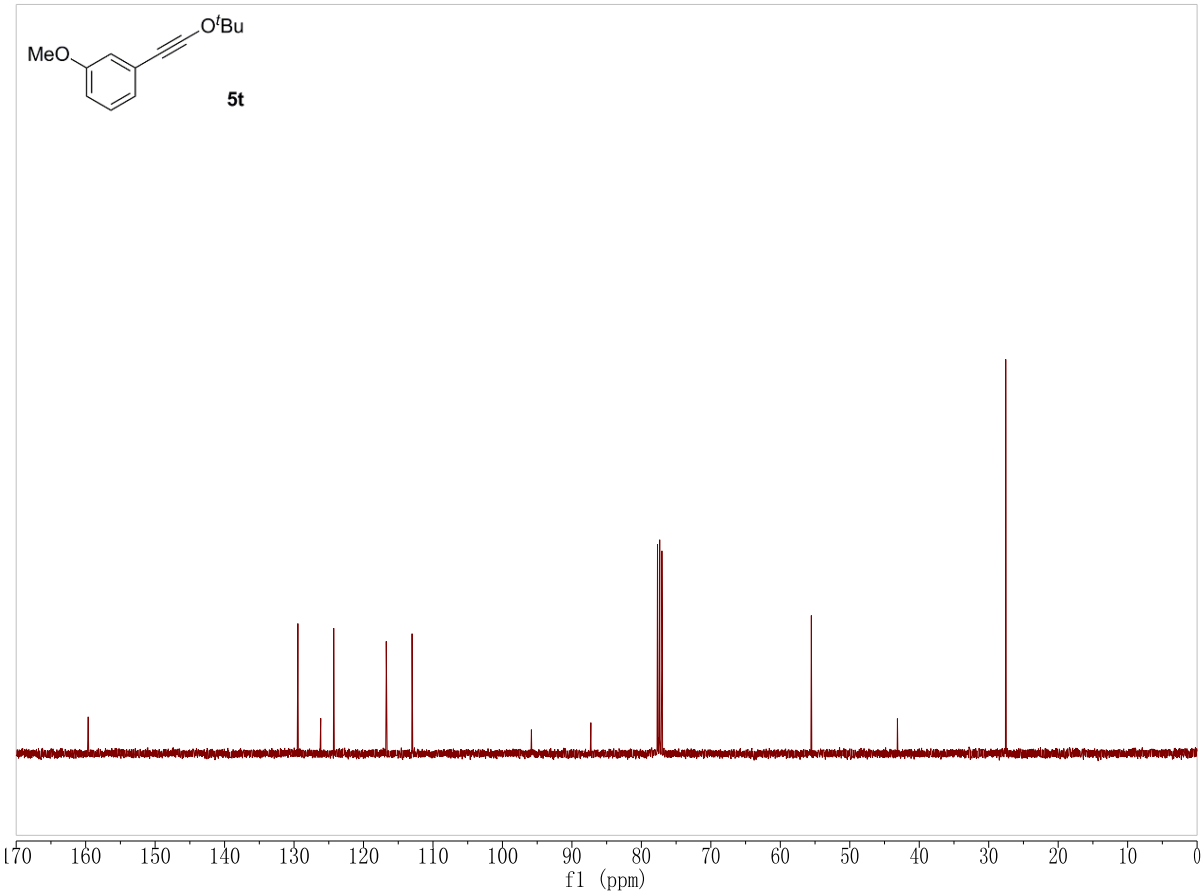

O^{t}Bu
OMe
5s
1.00
1.03
2.17
3.51
10.03
f1 (ppm)

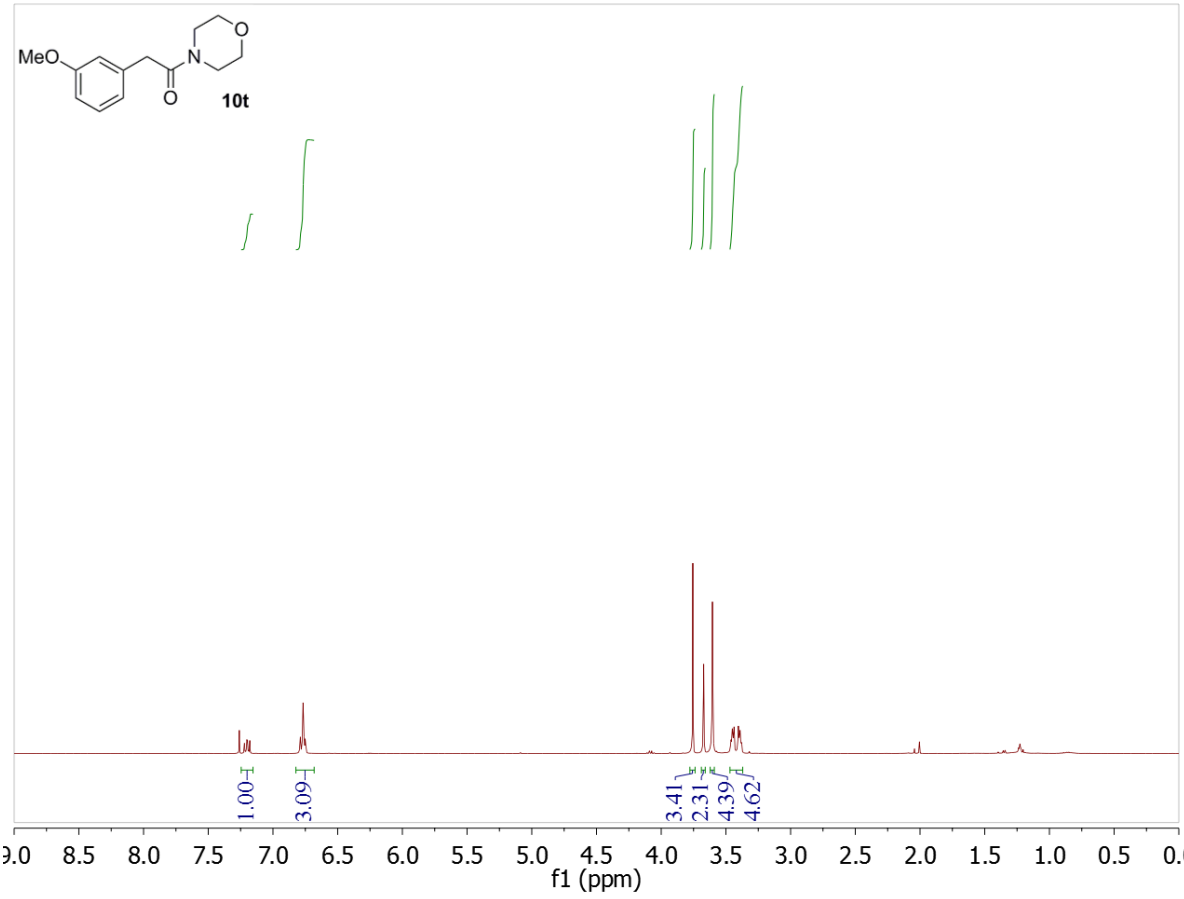

O^{t}Bu
OMe
5s
f1 (ppm)

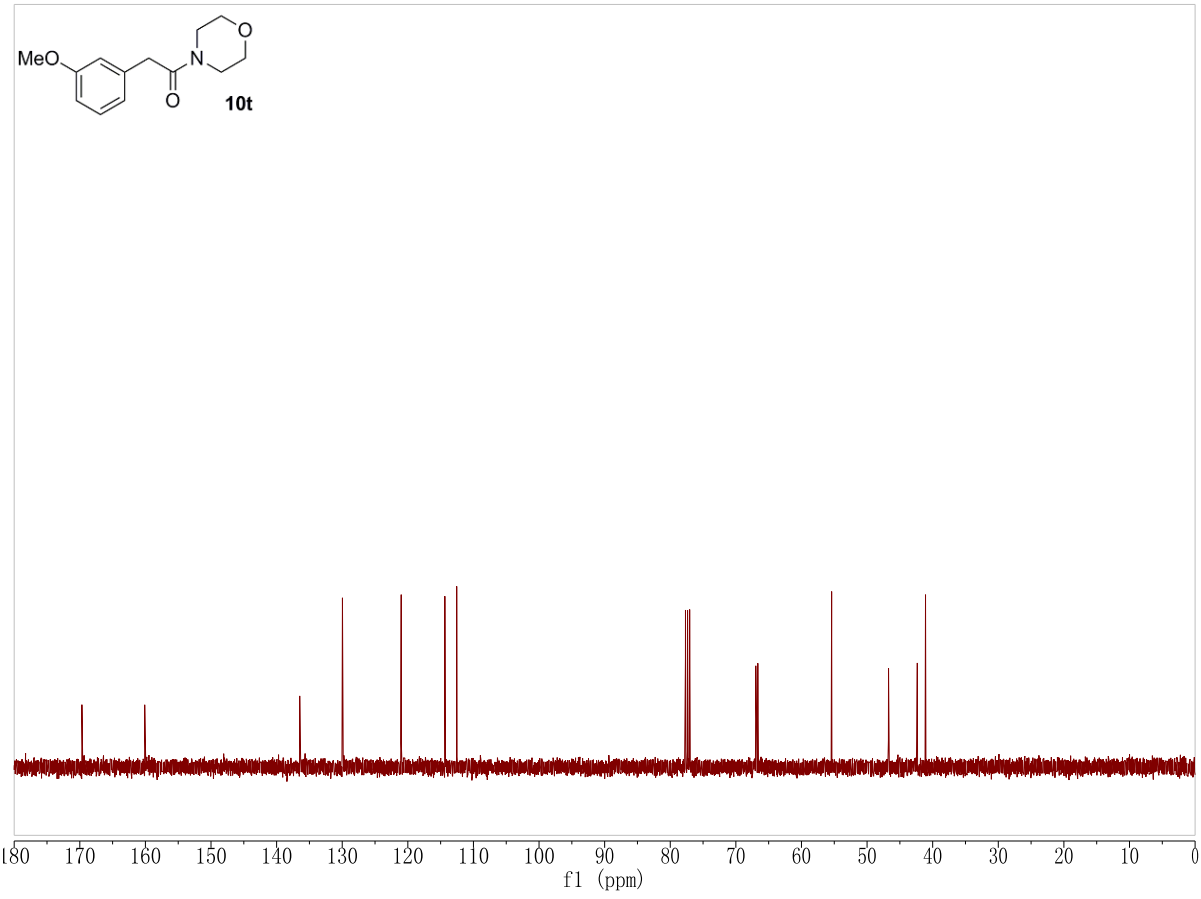

10s
2.00
0.99
1.01
3.39
2.40
4.55
4.62
f1 (ppm)

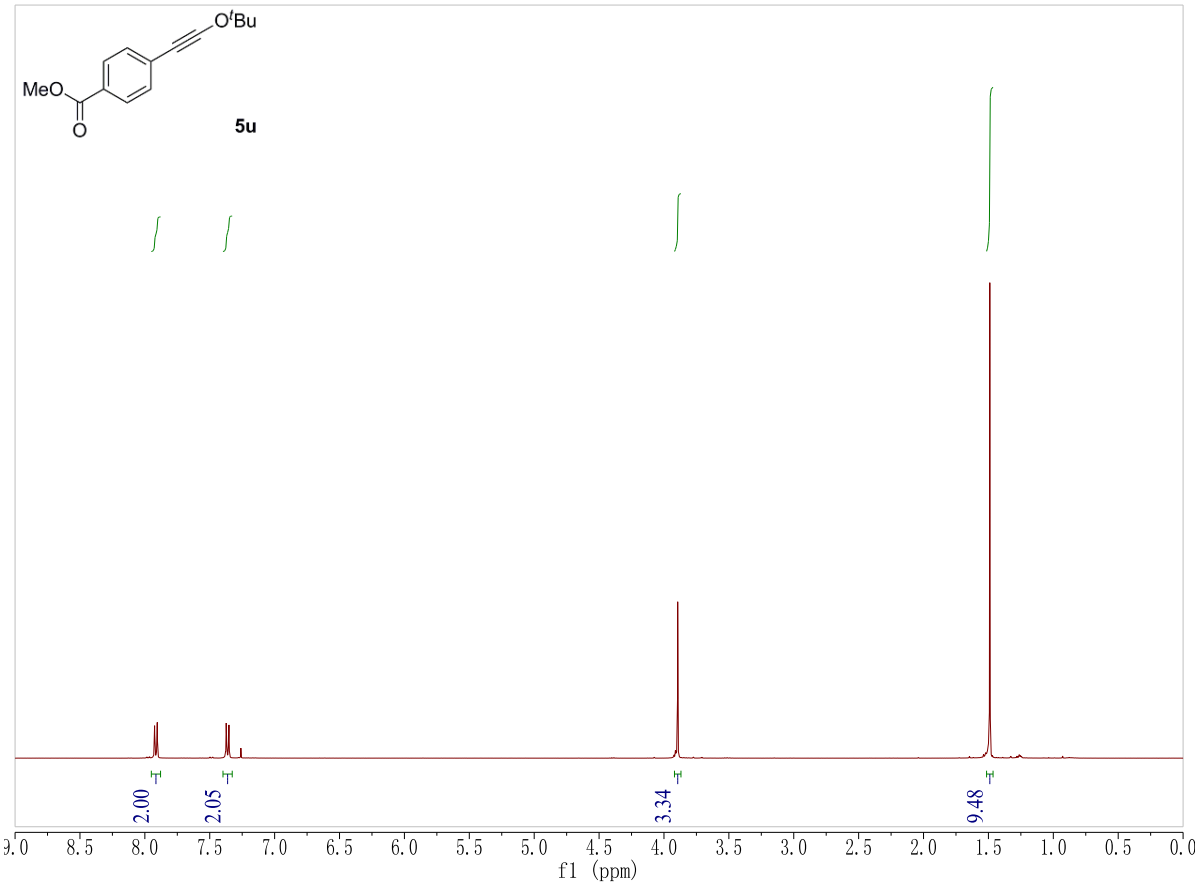

10s
f1 (ppm)

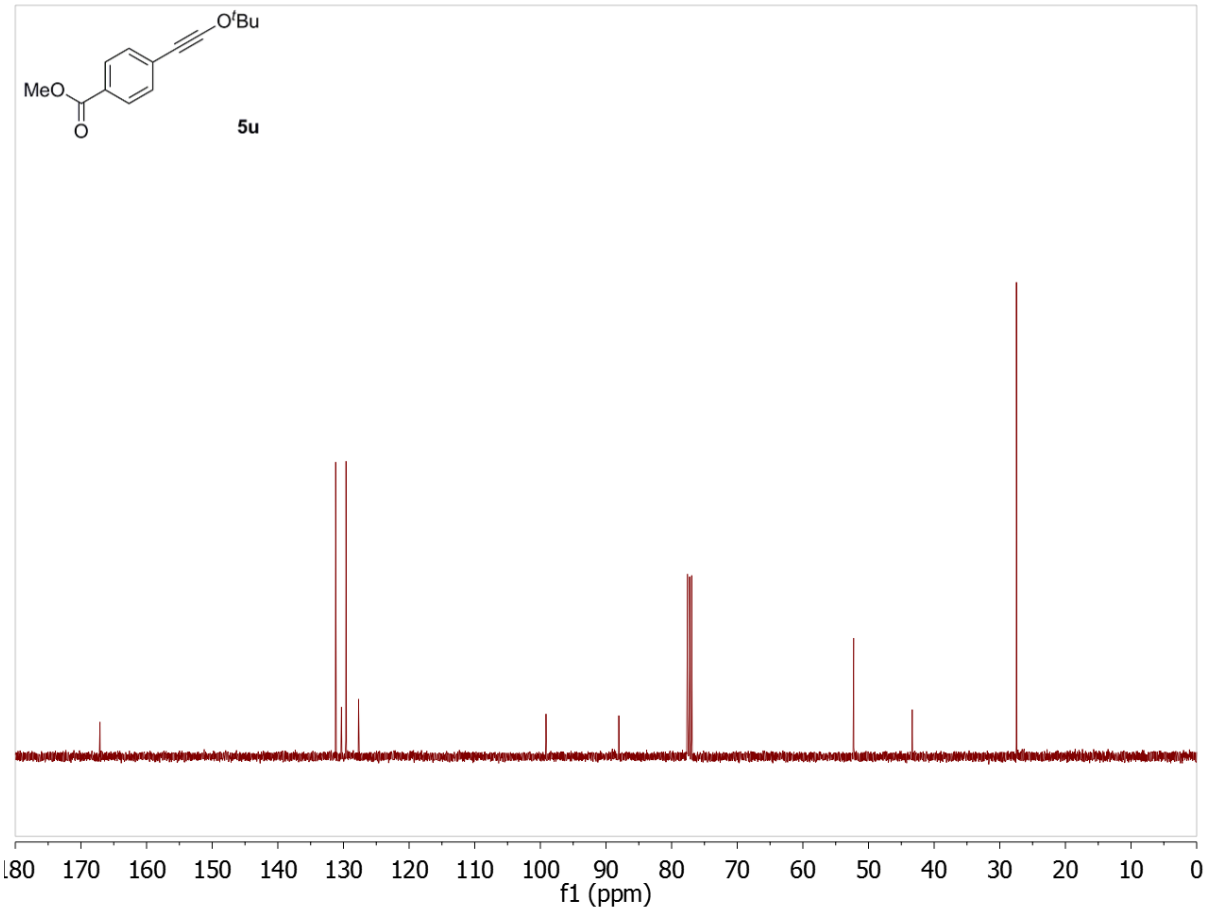

MeO
O^{t}Bu
5t
1.06
2.05
1.00
3.61
10.27
f1 (ppm)

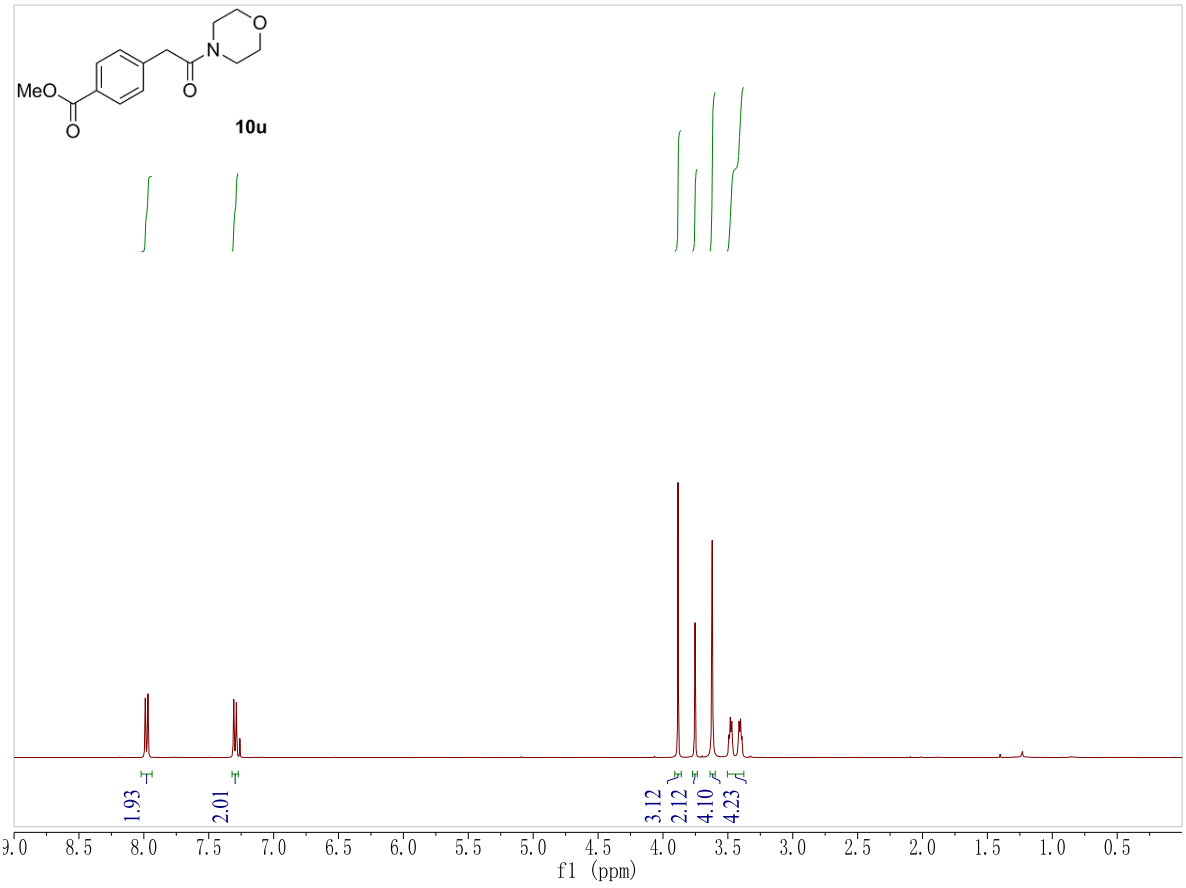

MeO
O^{t}Bu
5t
f1 (ppm)

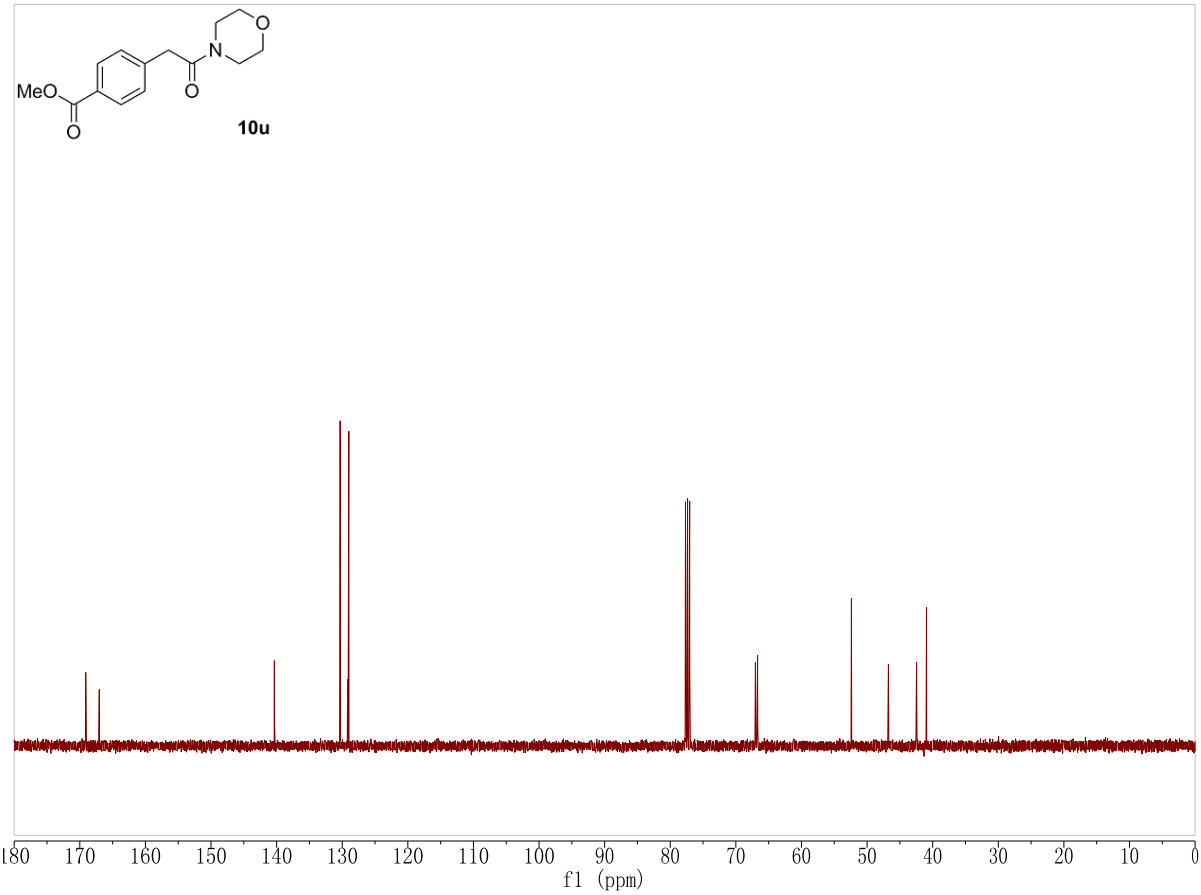

MeO
O
N
O
10t
1.00
3.09
3.41
2.31
4.39
4.62
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

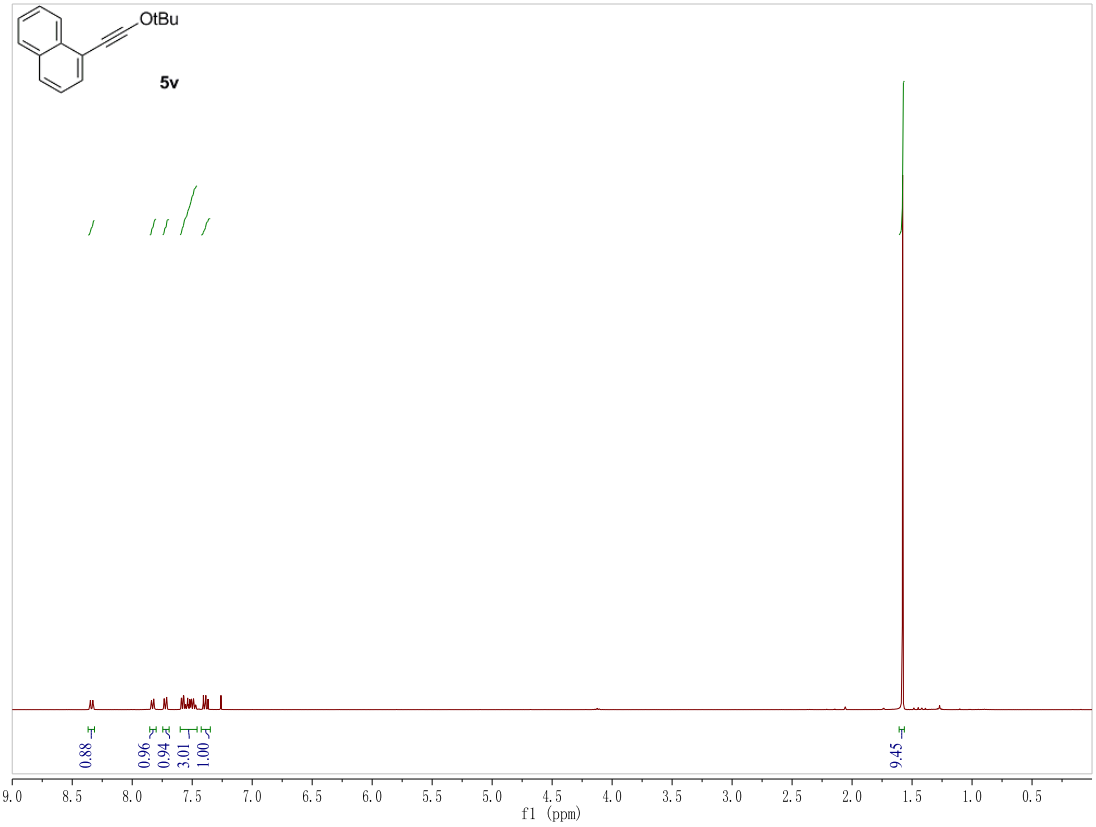

MeO
O
N
O
10t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

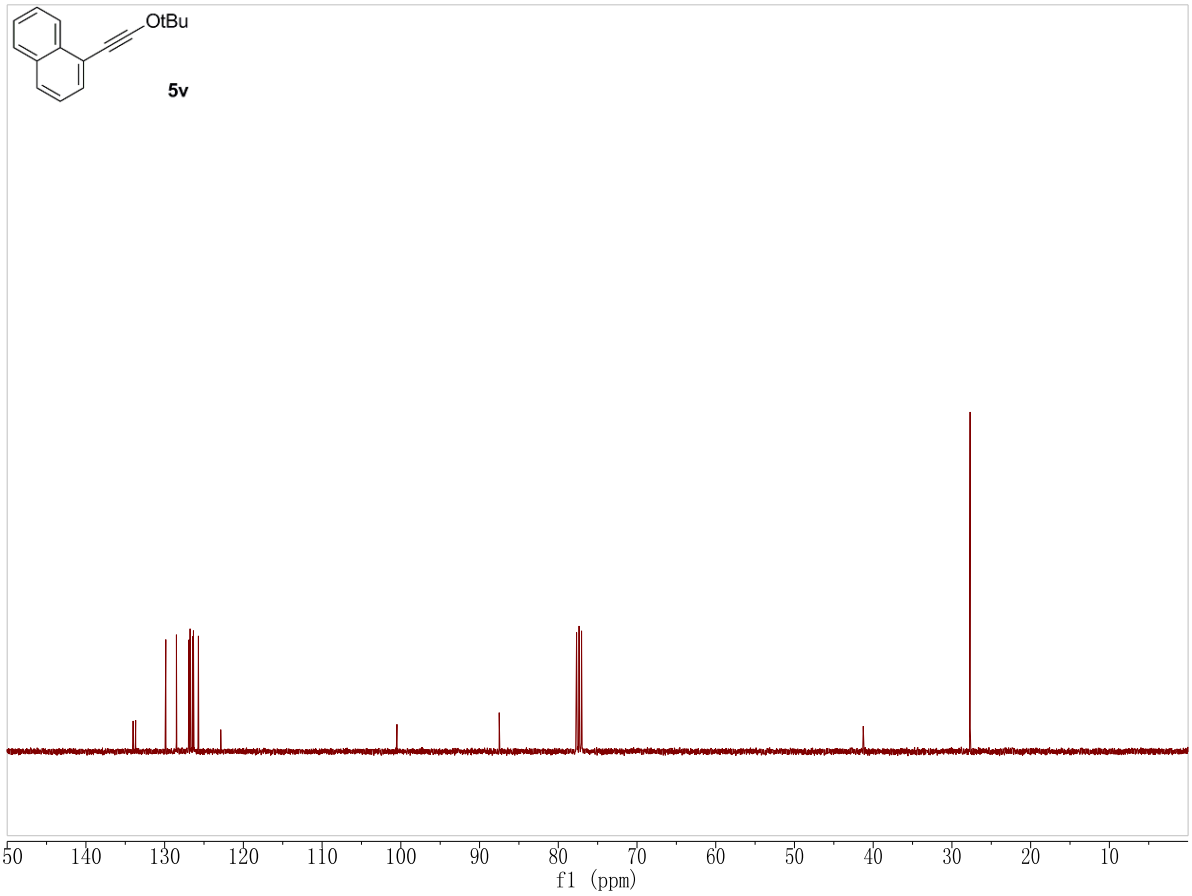

O^{t}Bu
MeO
O
5u
2.00
2.05
3.34
9.48
f1 (ppm)

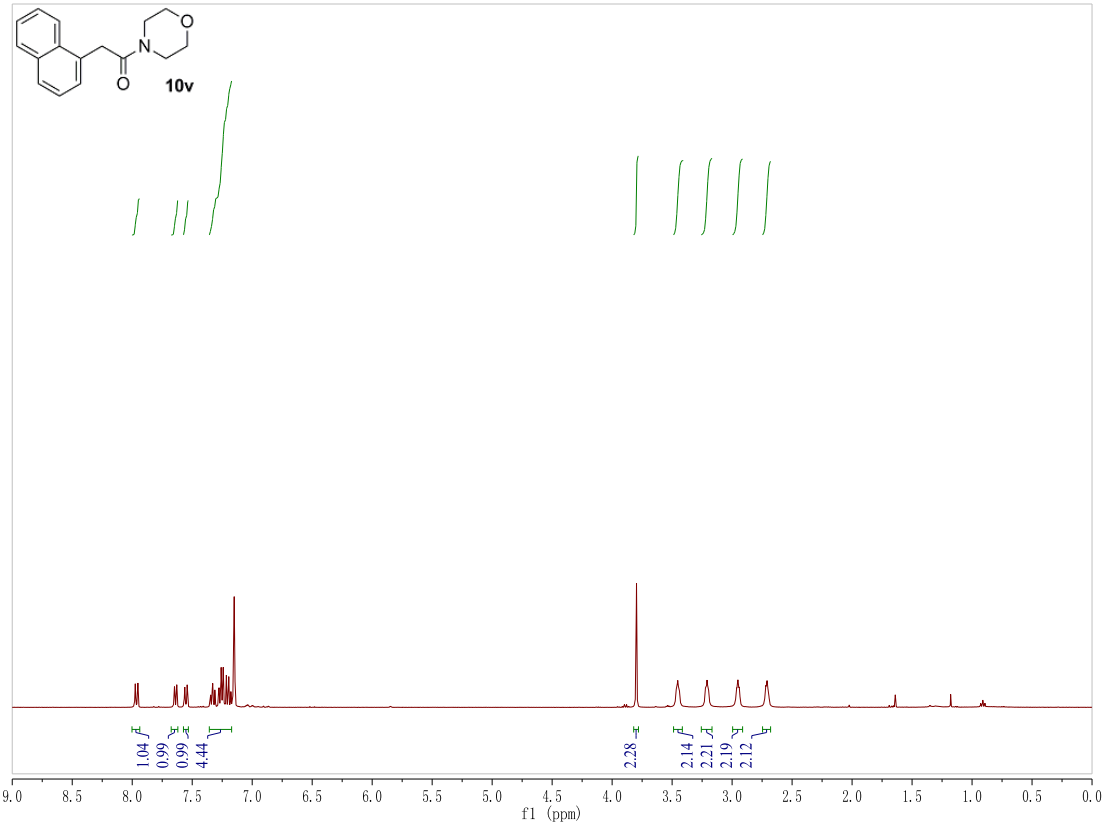

O^{t}Bu
MeO
O
5u
f1 (ppm)

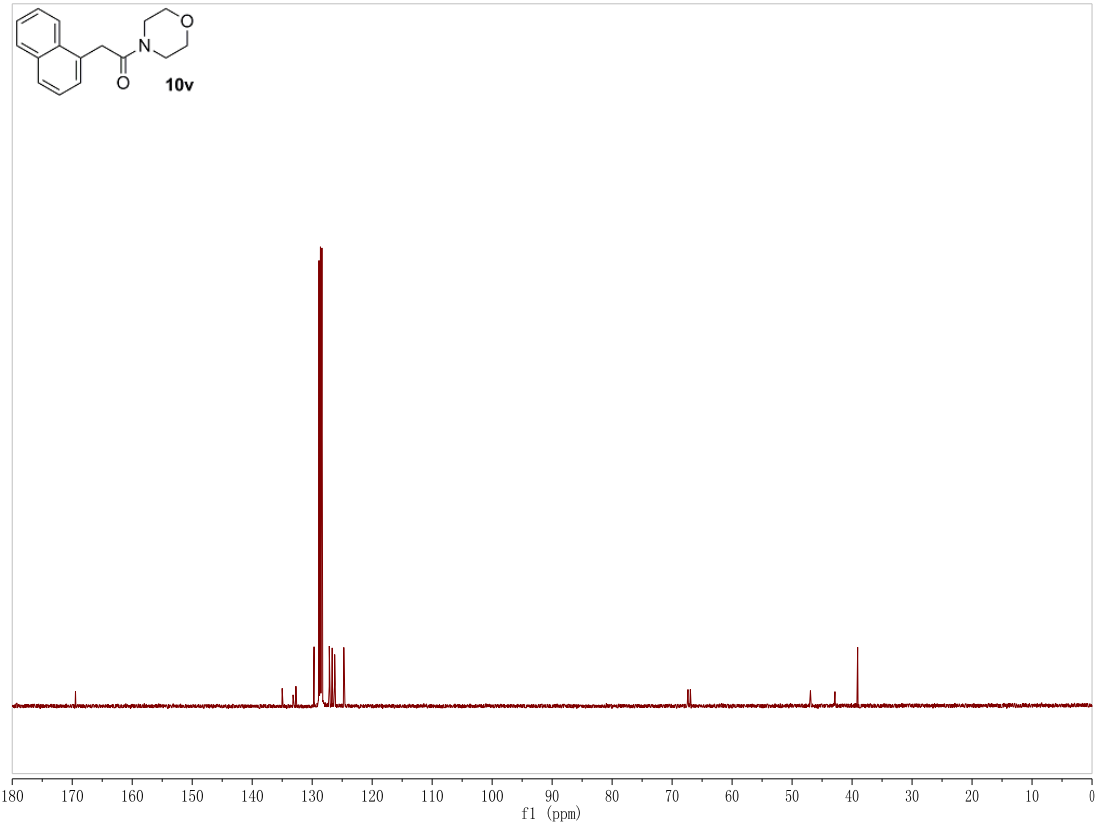

MeO
O
O
N
O
10u
1.93
2.01
3.12
2.12
4.10
4.23
f1 (ppm)

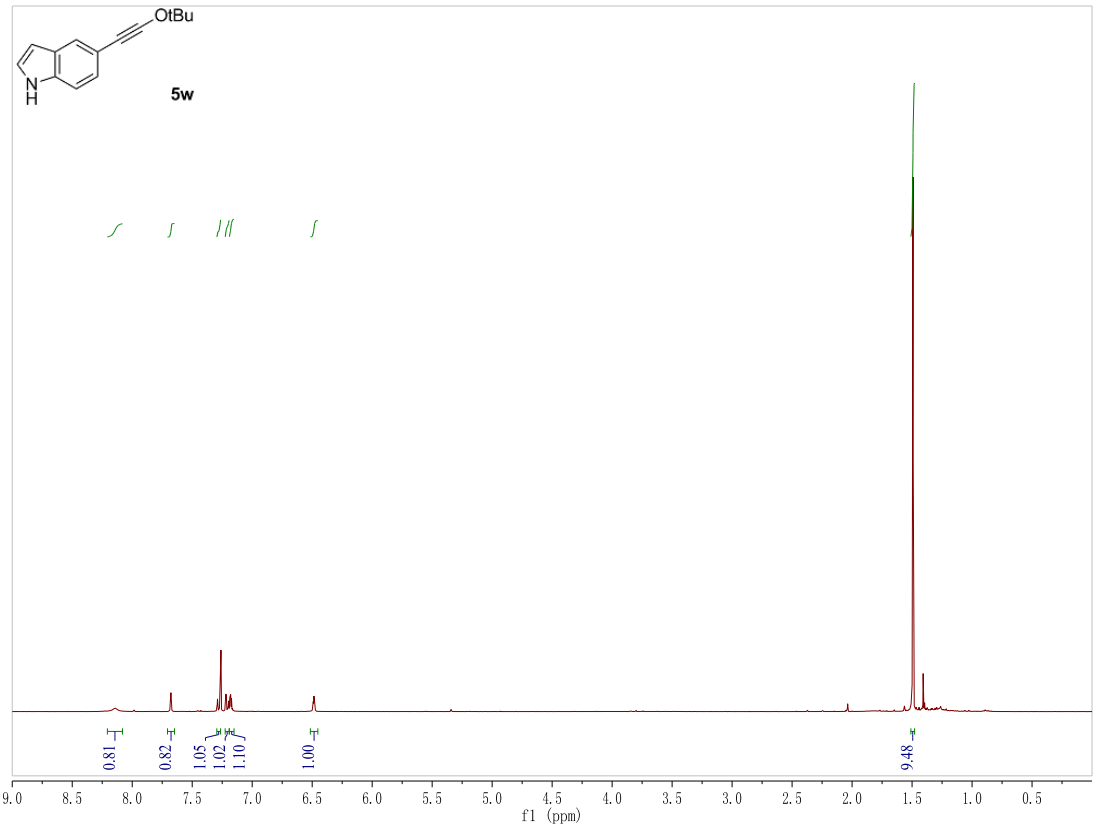

MeO
O
O
N
O
10u
f1 (ppm)

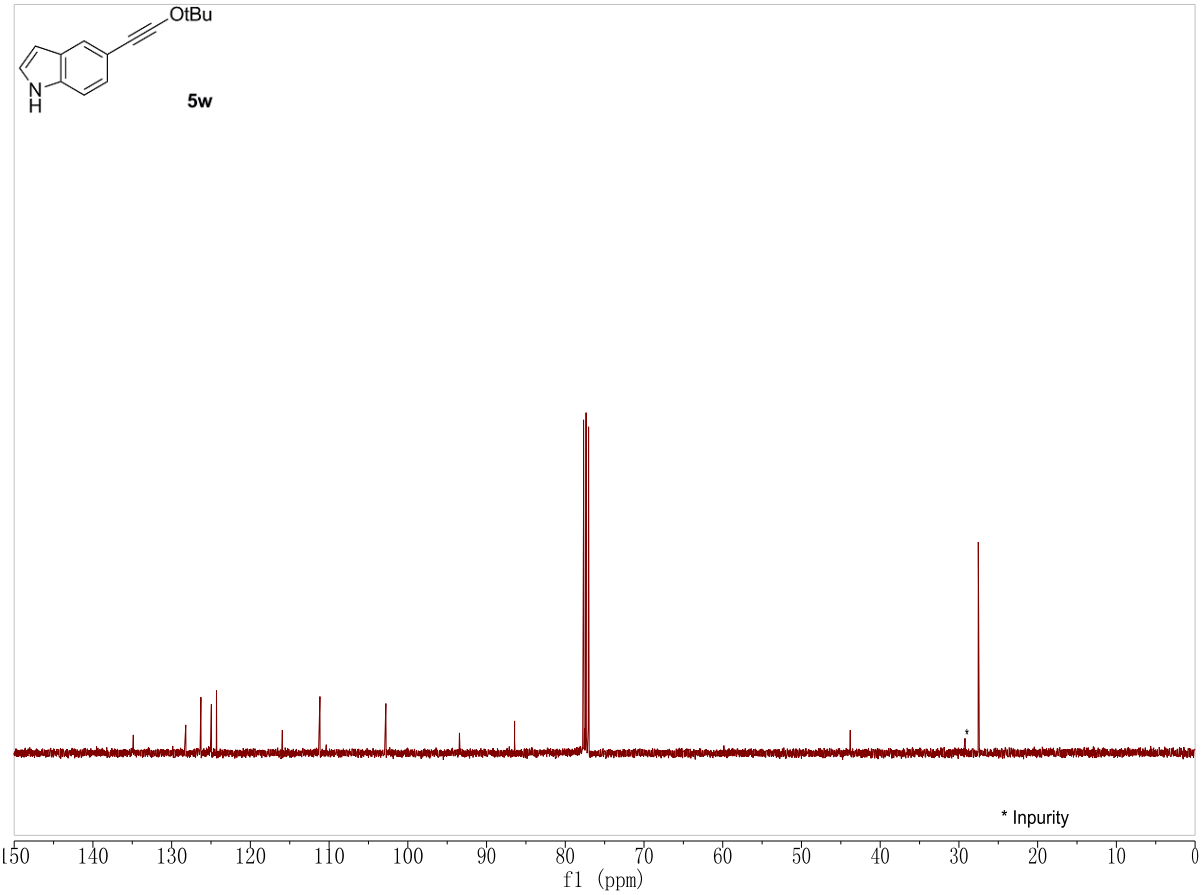

OtBu
5v
0.88
0.96
0.94
3.01
1.00
9.45
f1 (ppm)

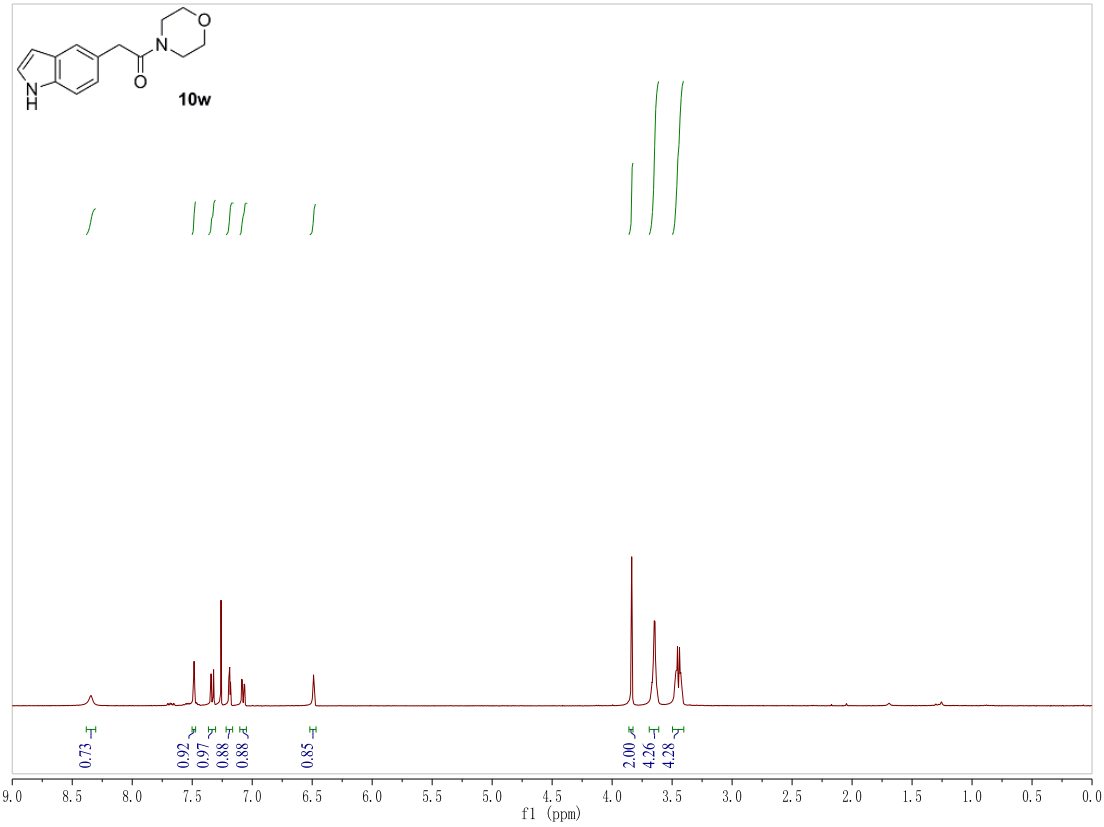

OtBu
5v
f1 (ppm)

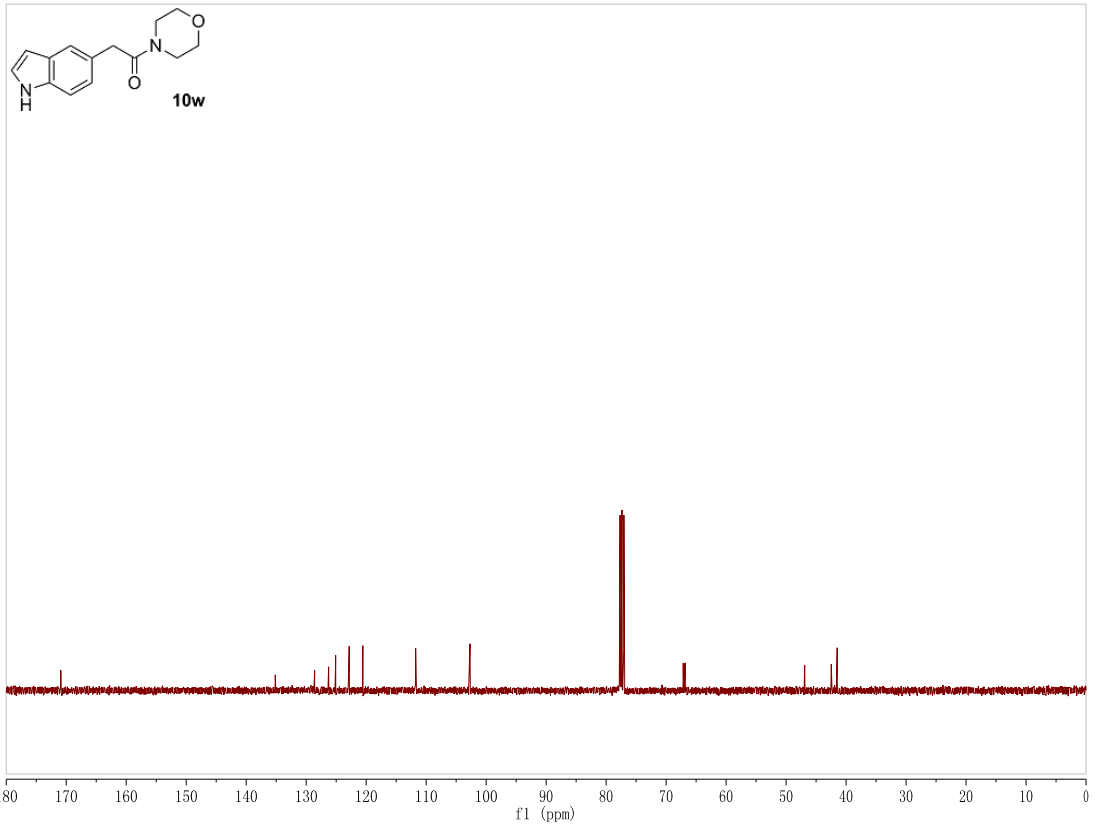

10v
1.04
0.99
0.99
4.44
2.28
2.14
2.21
2.19
2.12
f1 (ppm)

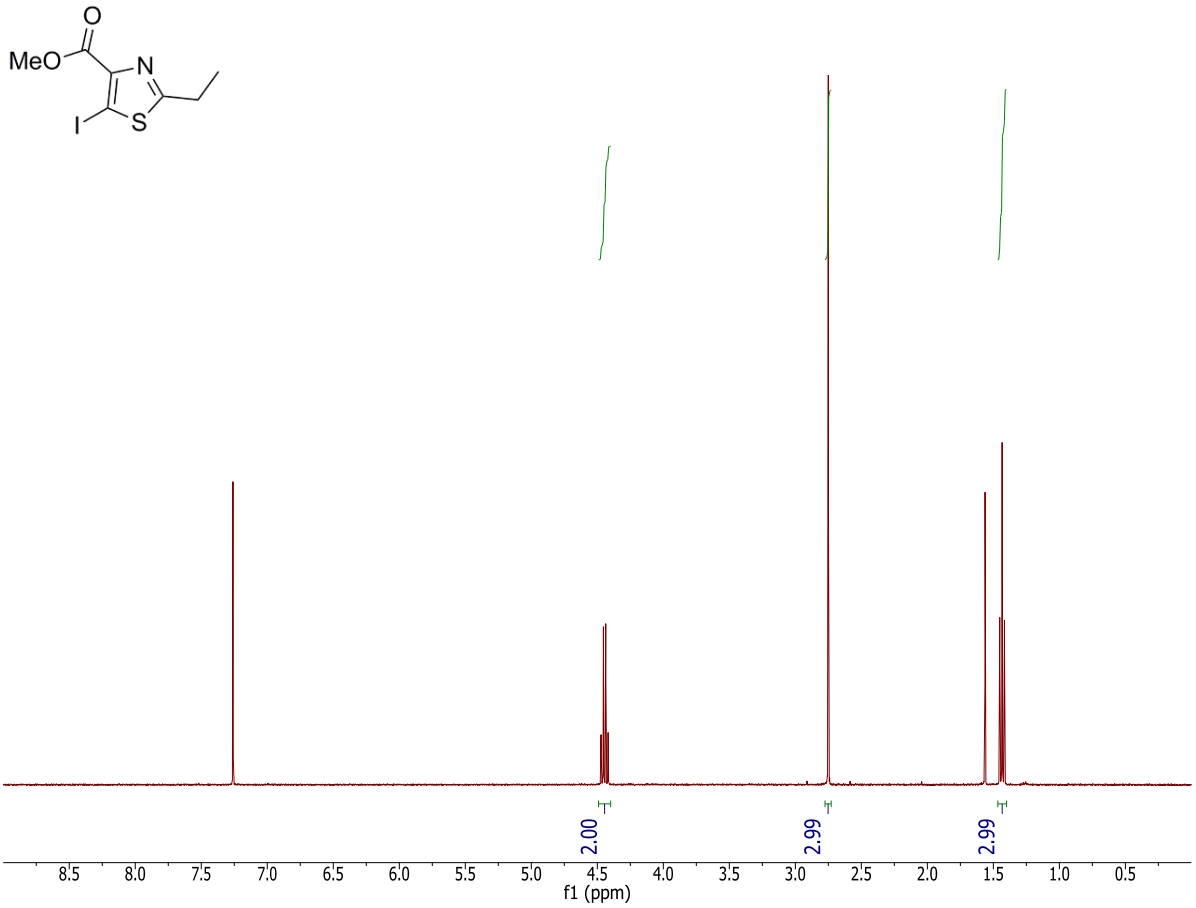

10v
f1 (ppm)

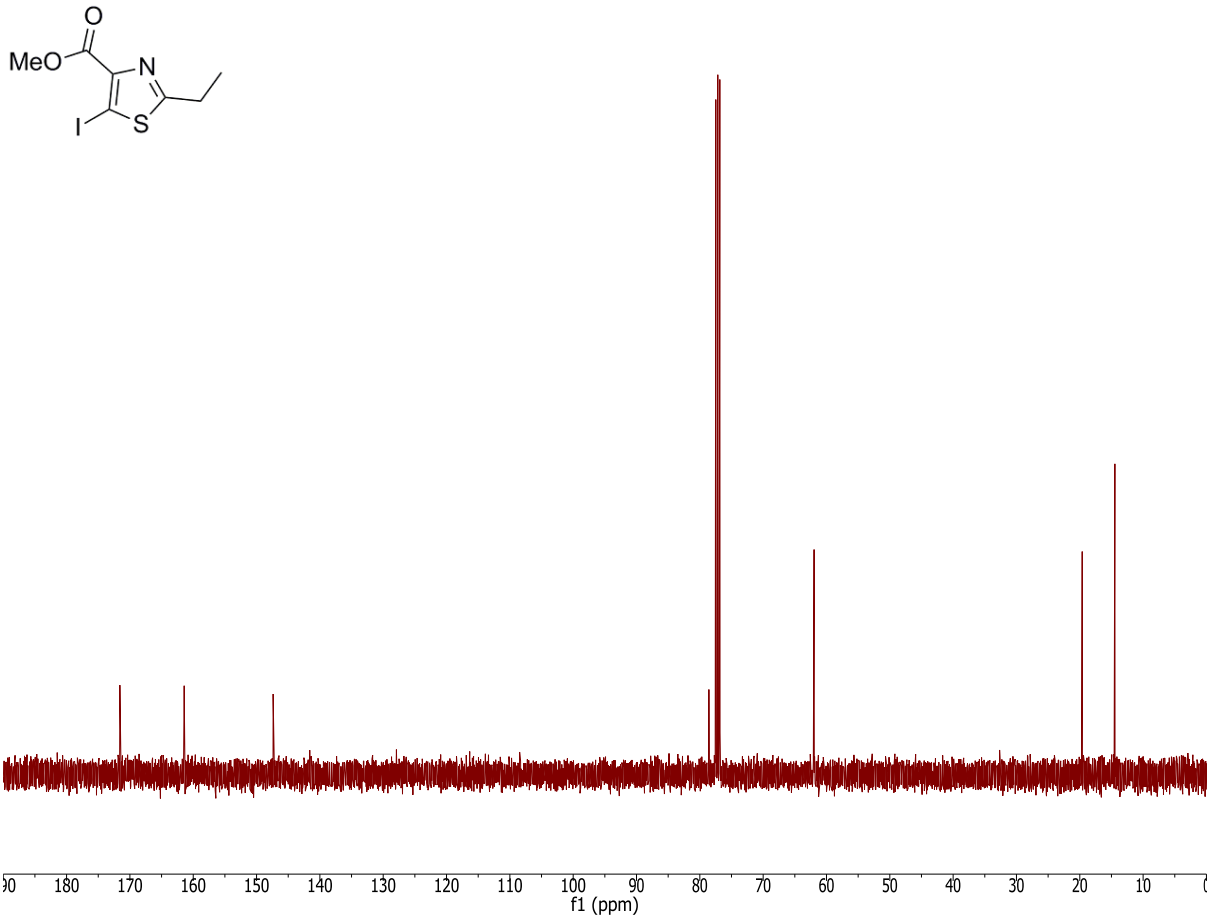

OtBu
N
H
5w
0.81
0.82
1.05
1.02
1.10
1.00
9.48
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

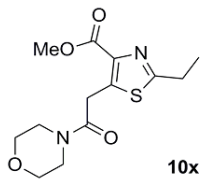

OtBu
N
H
5w
* Inpurity
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10w
0.73
0.92
0.97
0.88
0.88
0.85
2.00
4.26
4.28
f1 (ppm)

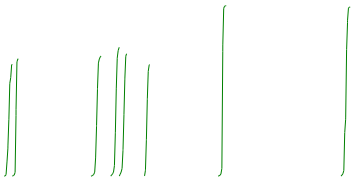

10w
f1 (ppm)

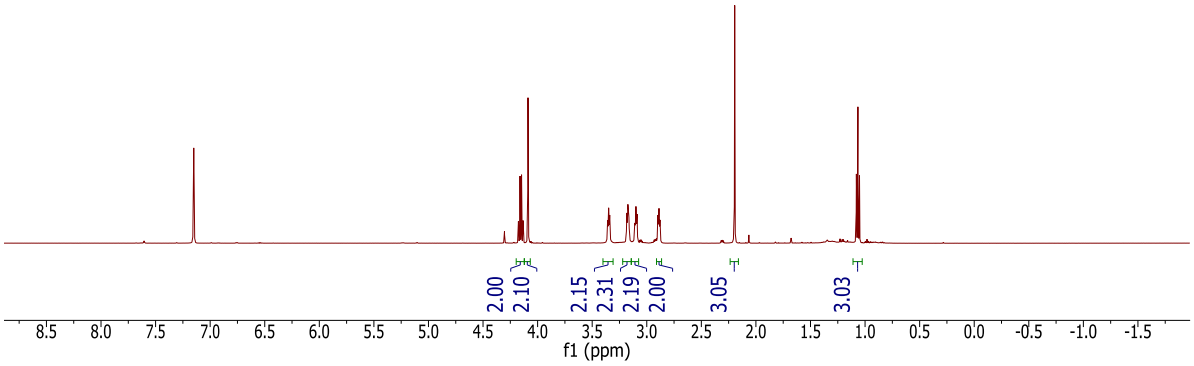

O
MeO
N
S
I
2.00
2.99
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

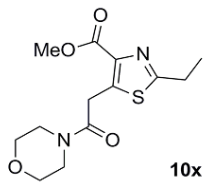

O
MeO
N
S
I
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO
O
N
S
N
O
O

10x

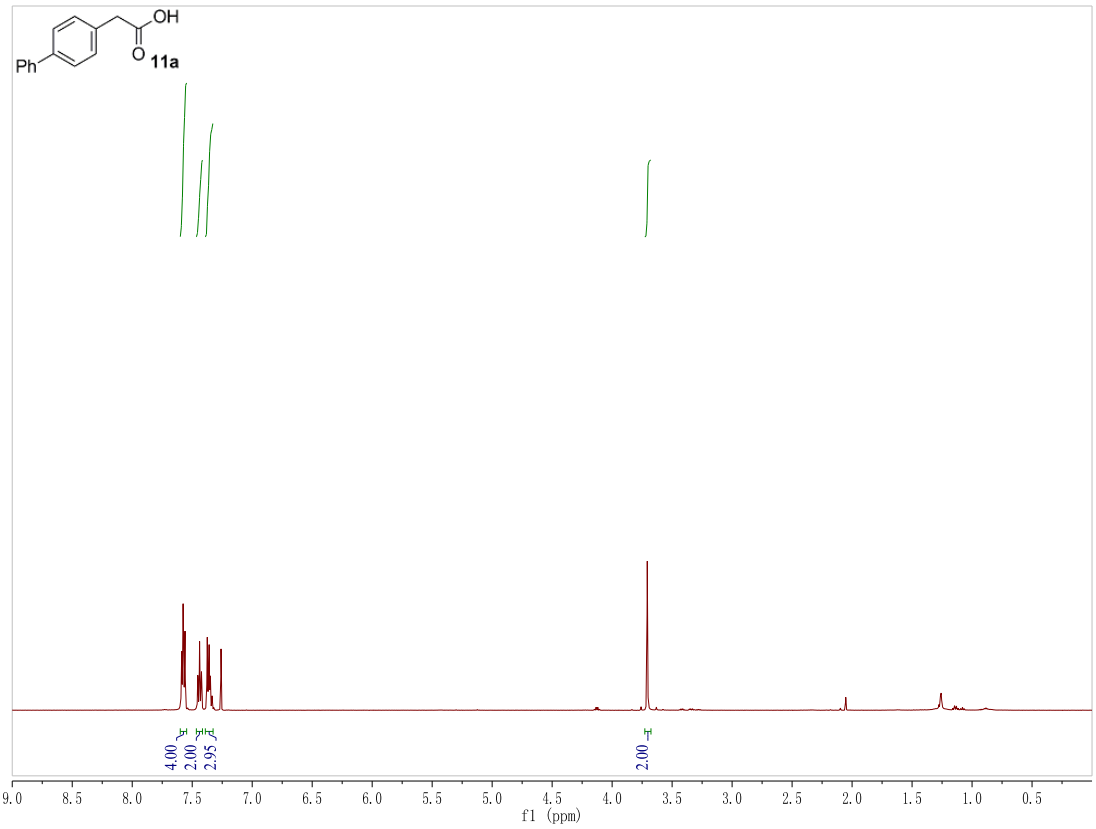


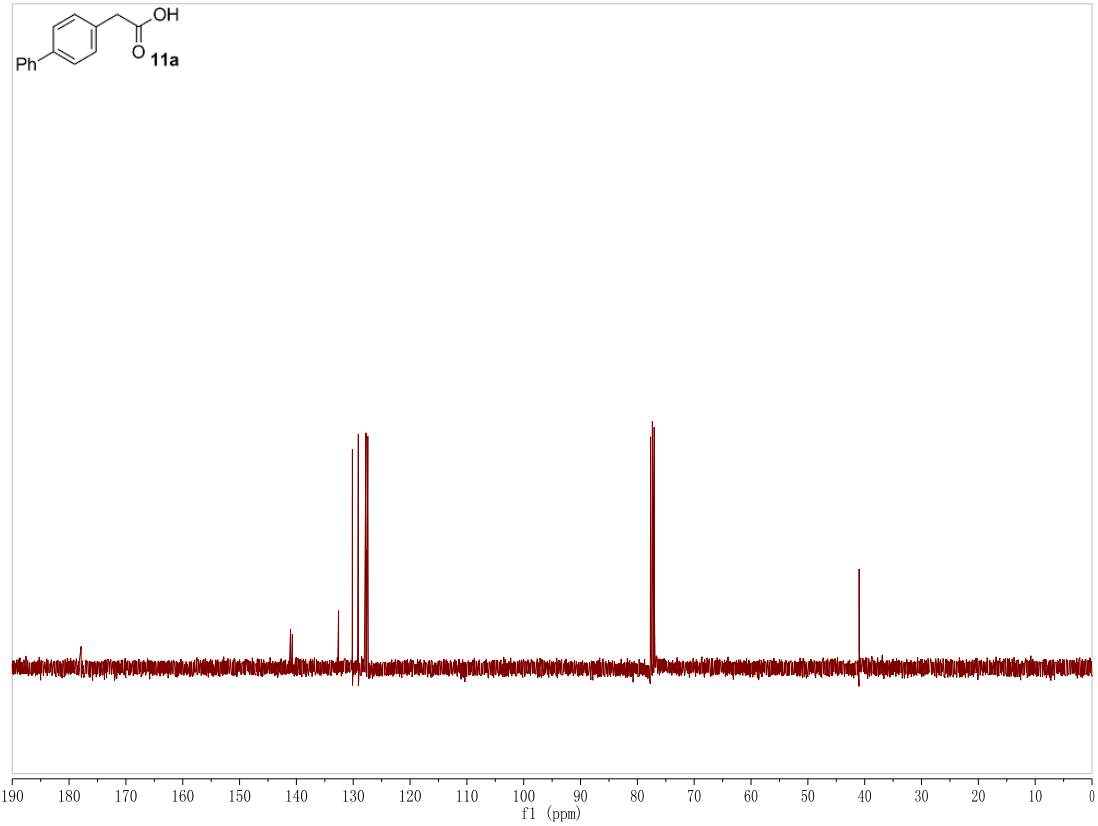

2.00
2.10
2.15
2.31
2.19
2.00
3.05
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

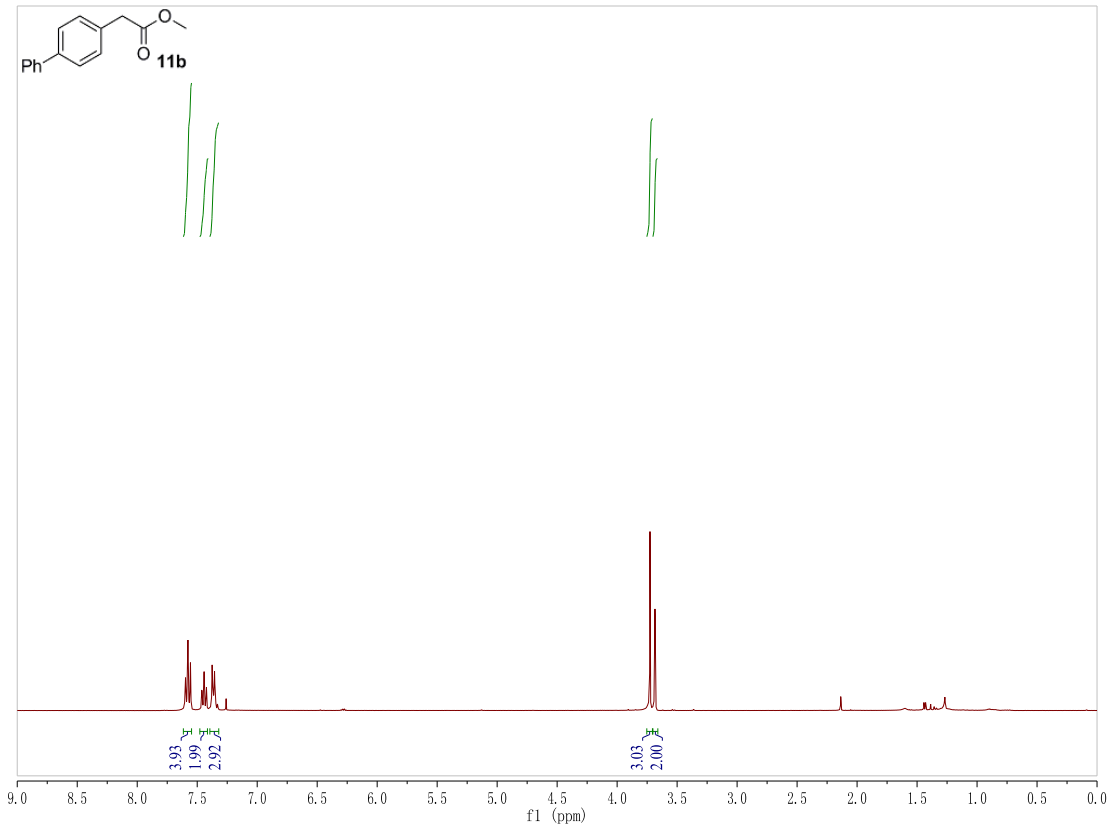

MeO
O
N
S
N
O
O

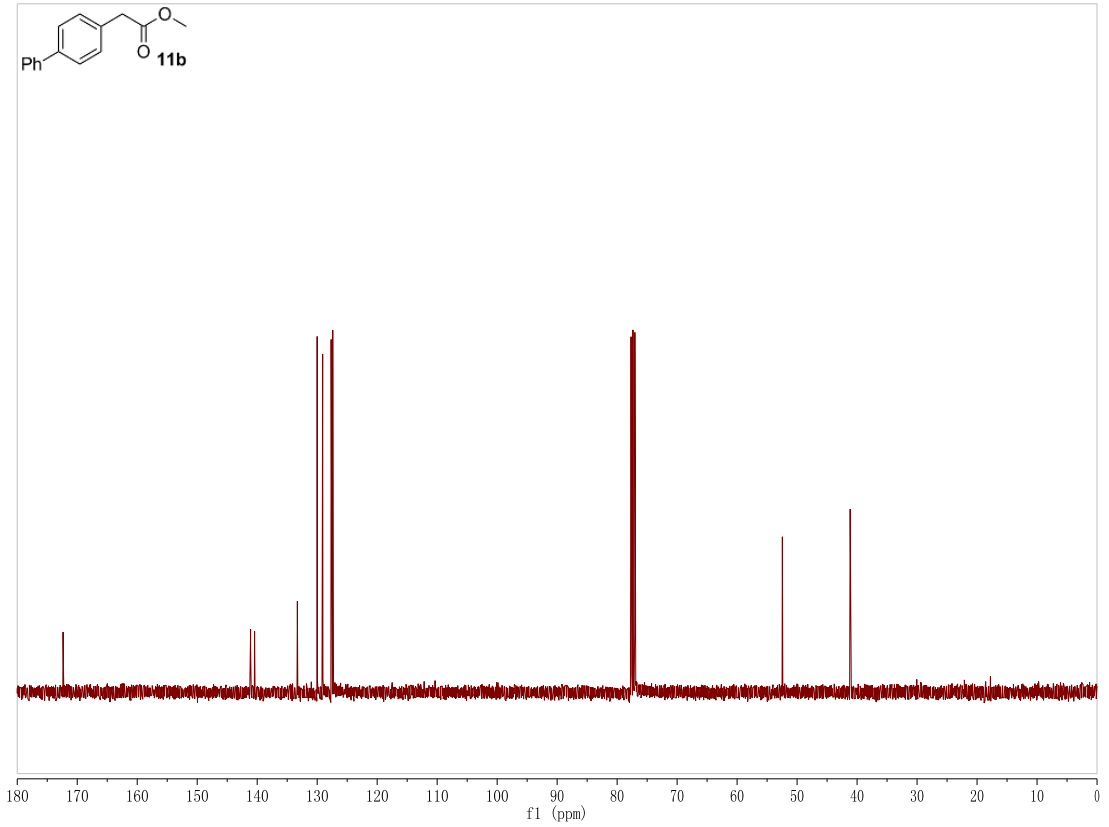
10x

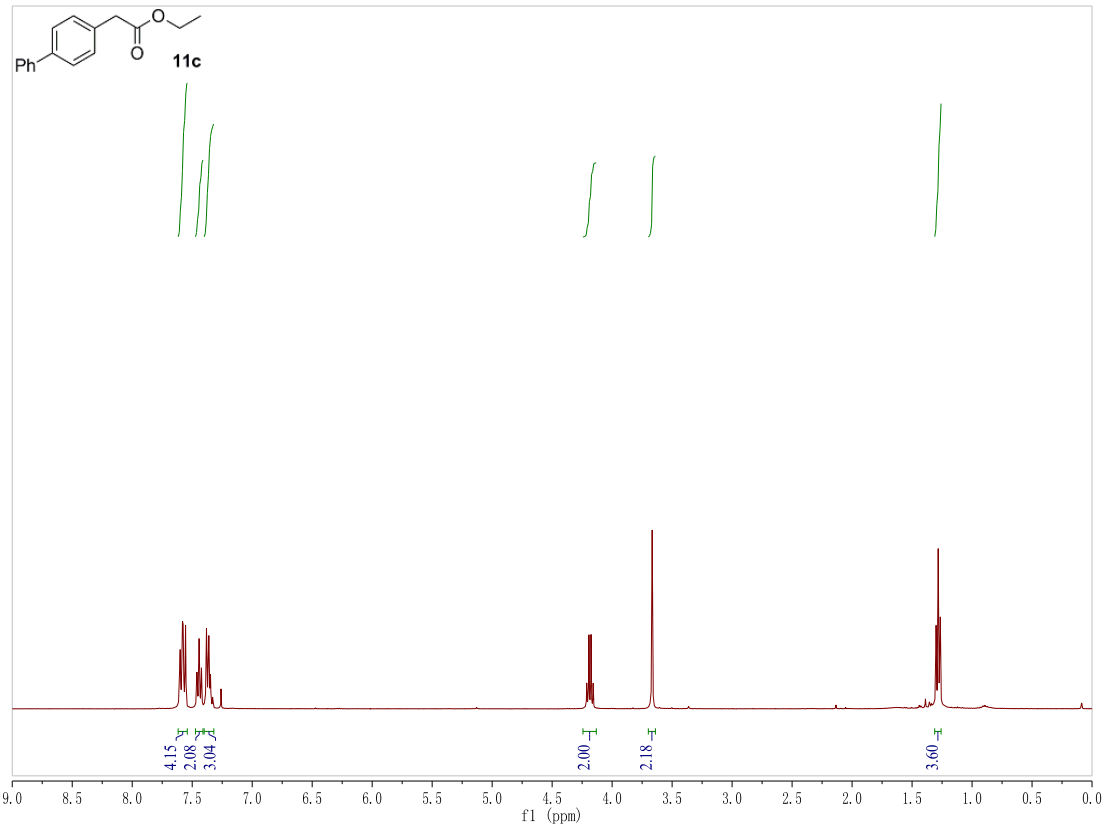
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

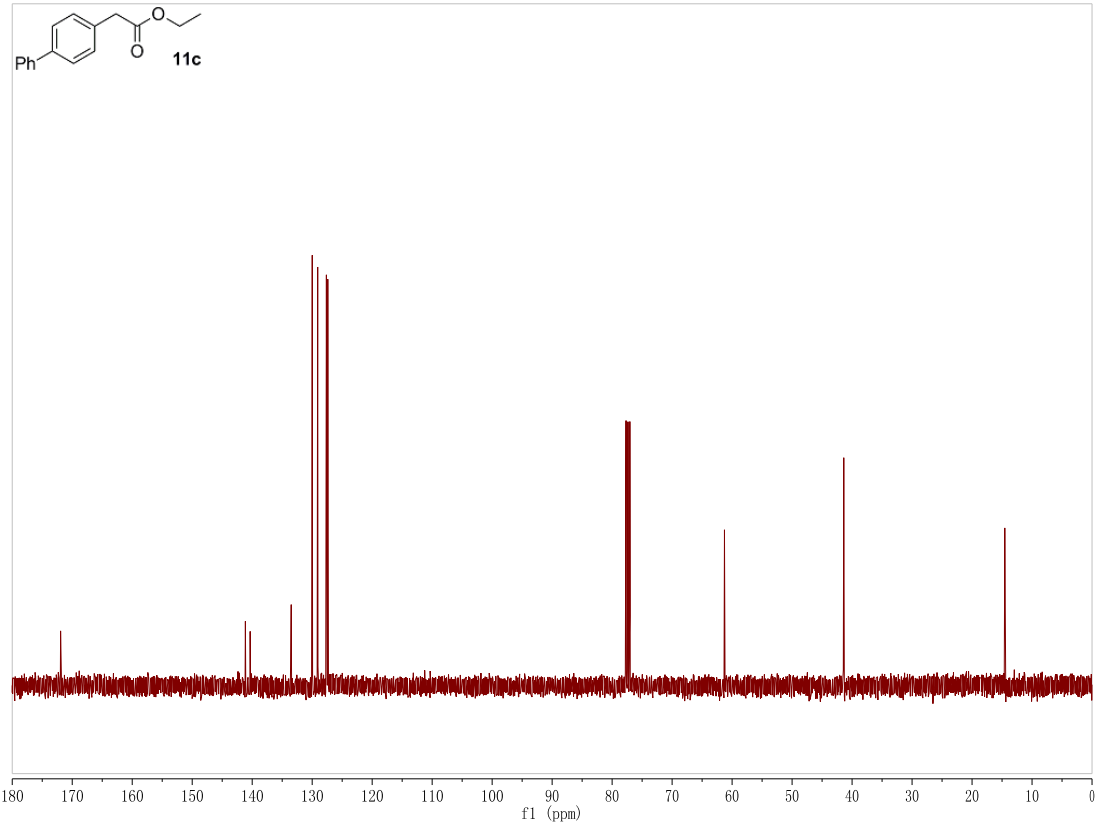

OH
O
Ph
11a
4.00
2.00
2.95
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

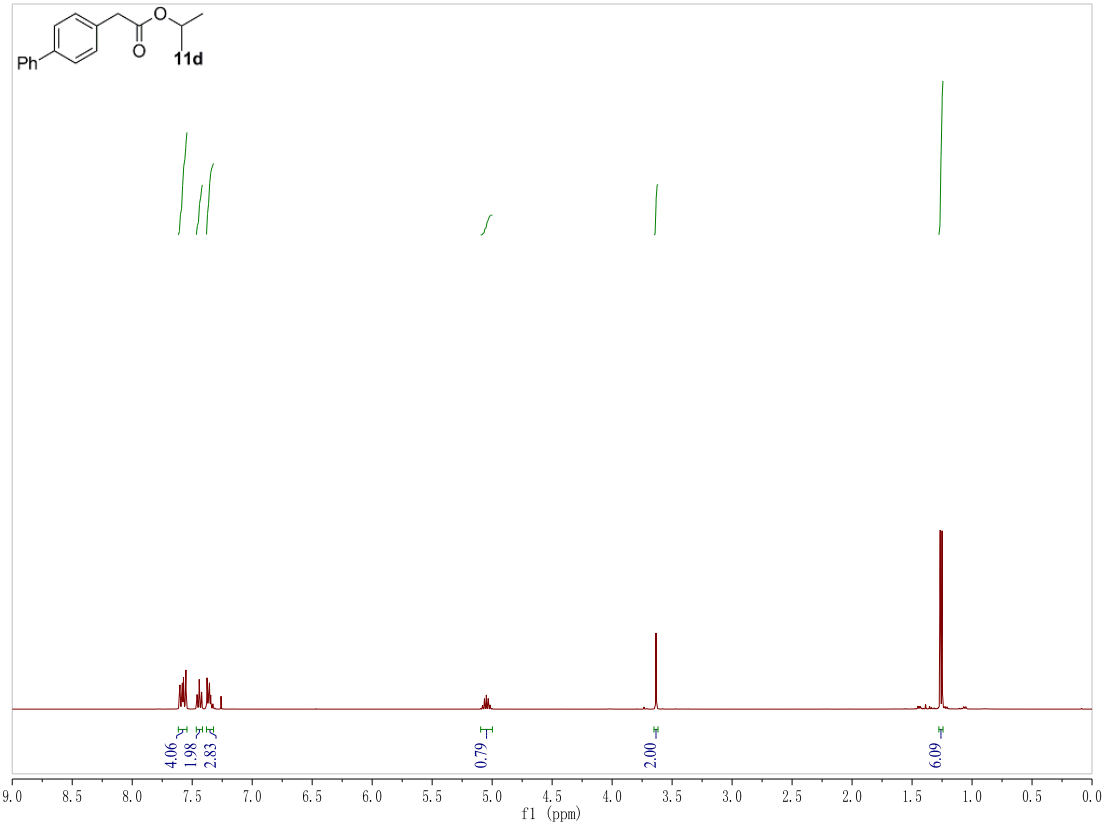

OH
O
Ph
11a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

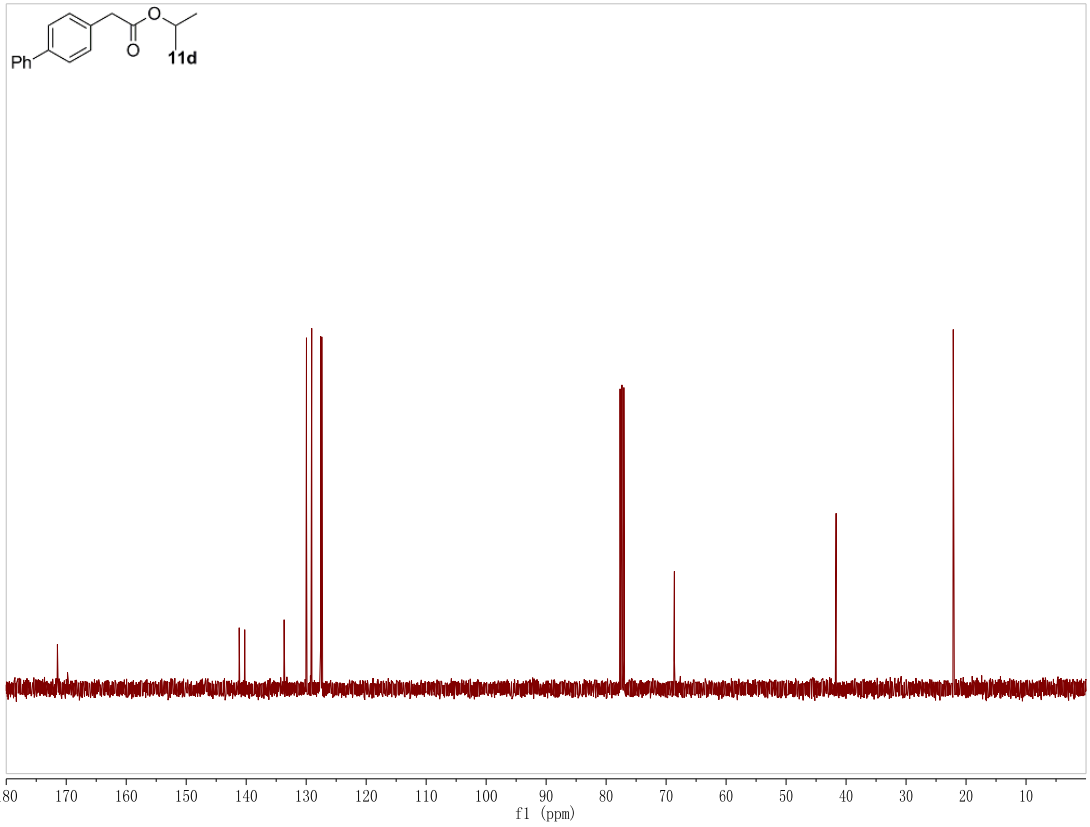

Ph
O
O
11b
3.93
1.99
2.92
3.03
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

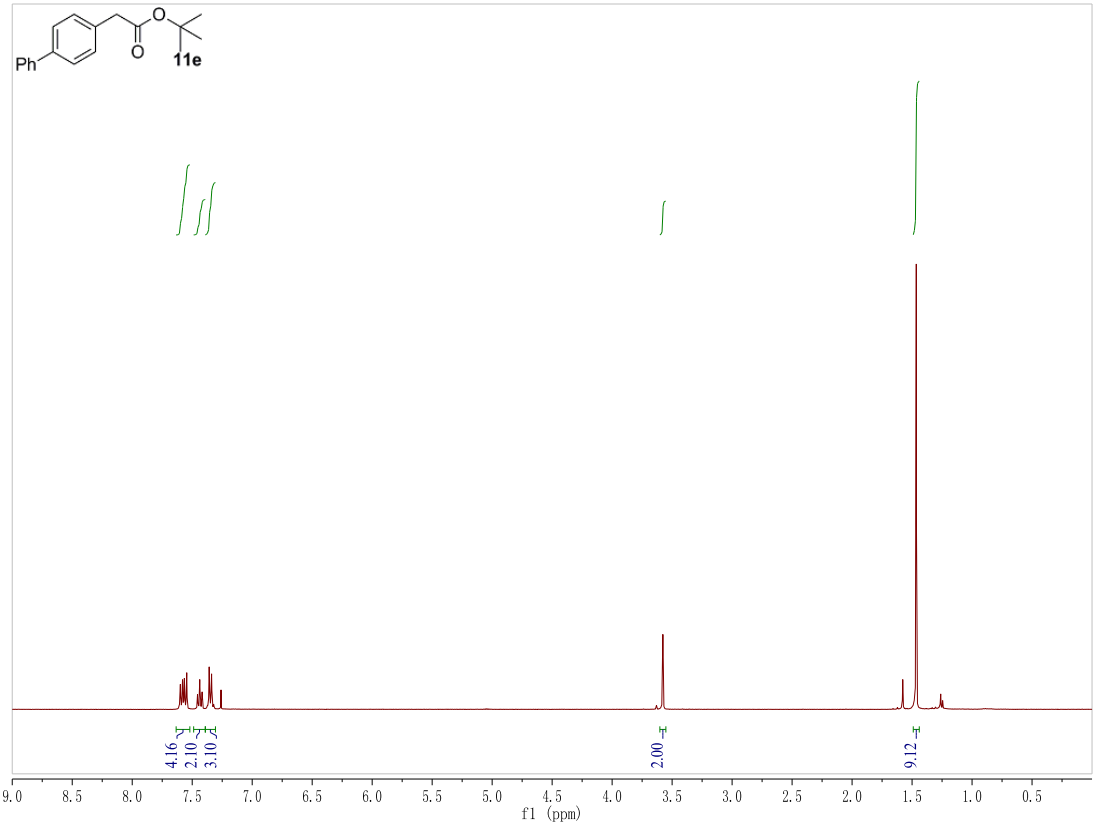

Ph
O
O
11b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

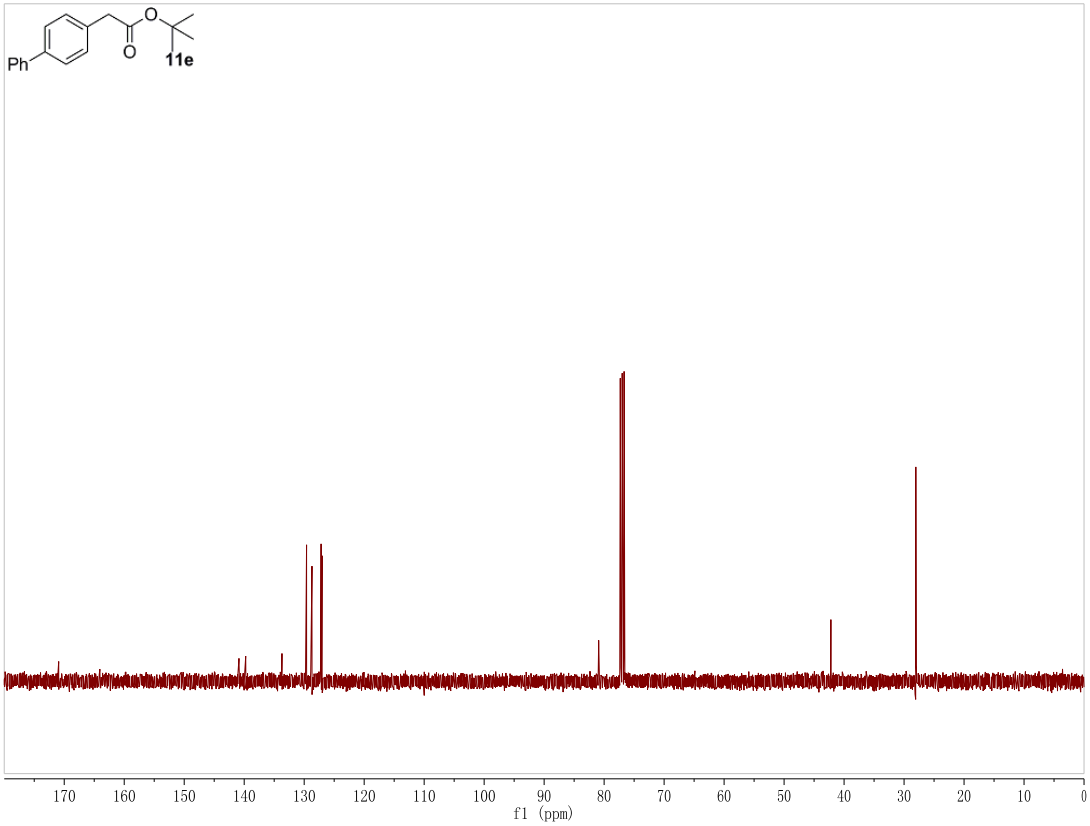

Ph
O
O
11c
4.15
2.08
3.04
2.00
2.18
3.60
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

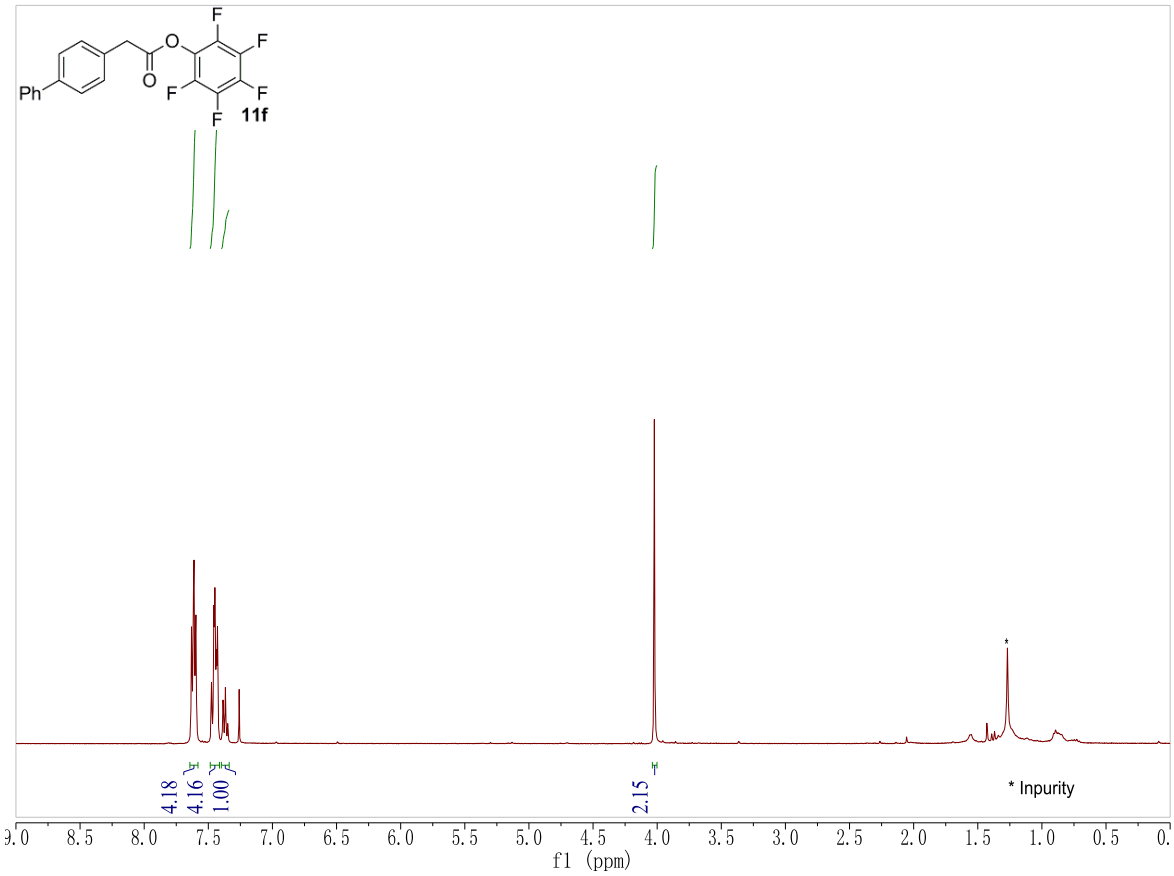

Ph
O
O
11c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

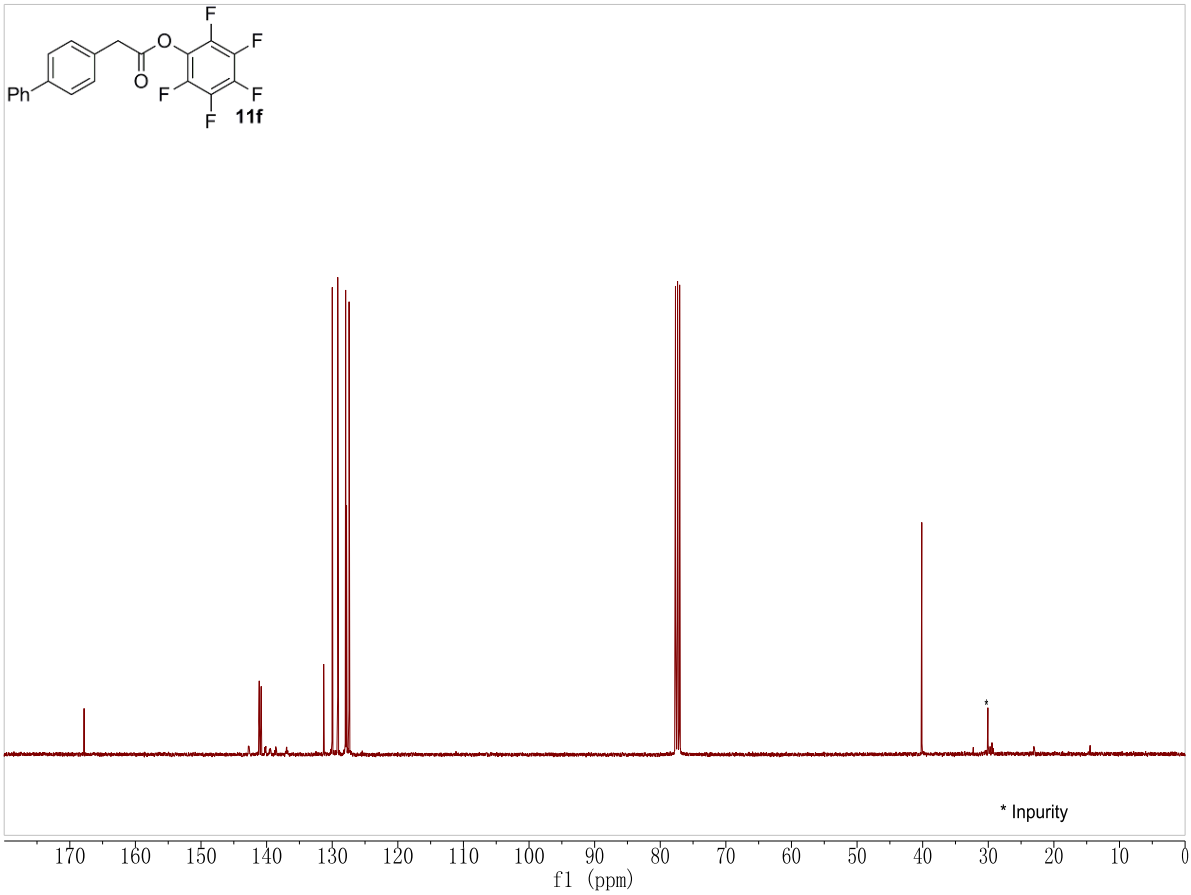

Ph
O
O
11d
4.06
1.98
2.83
0.79
2.00
6.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

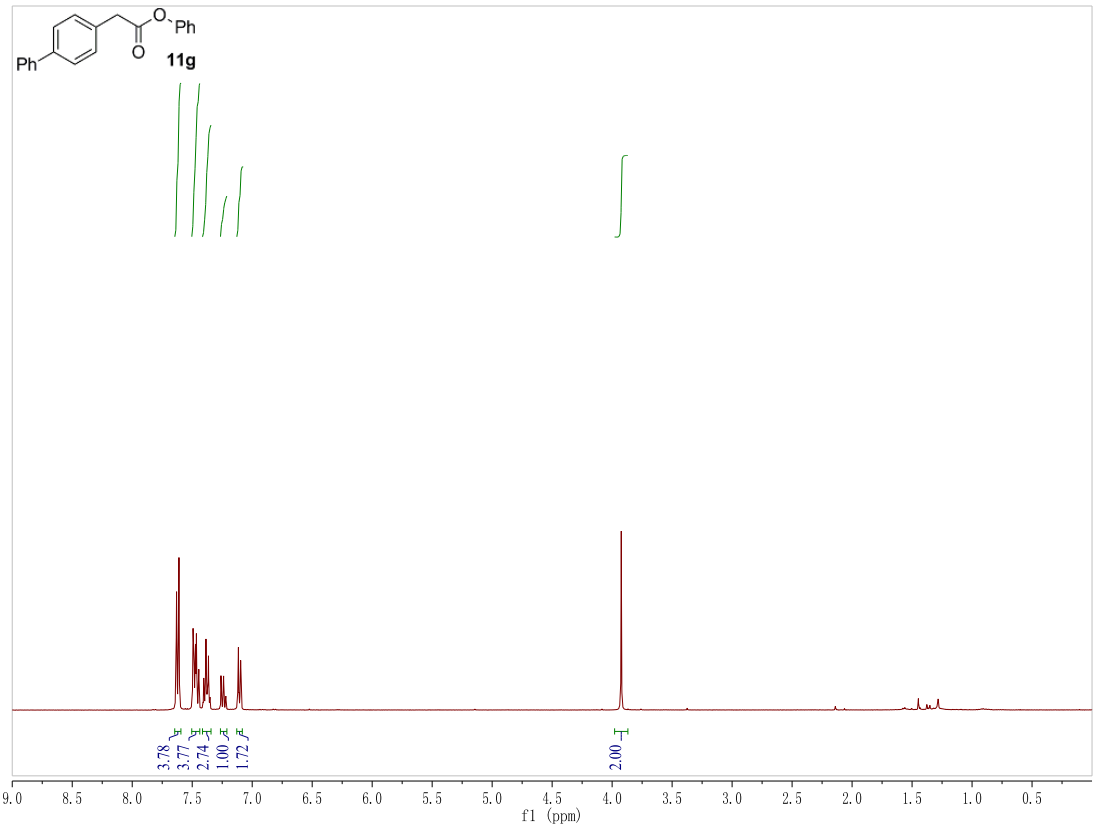

Ph
O
O
11d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

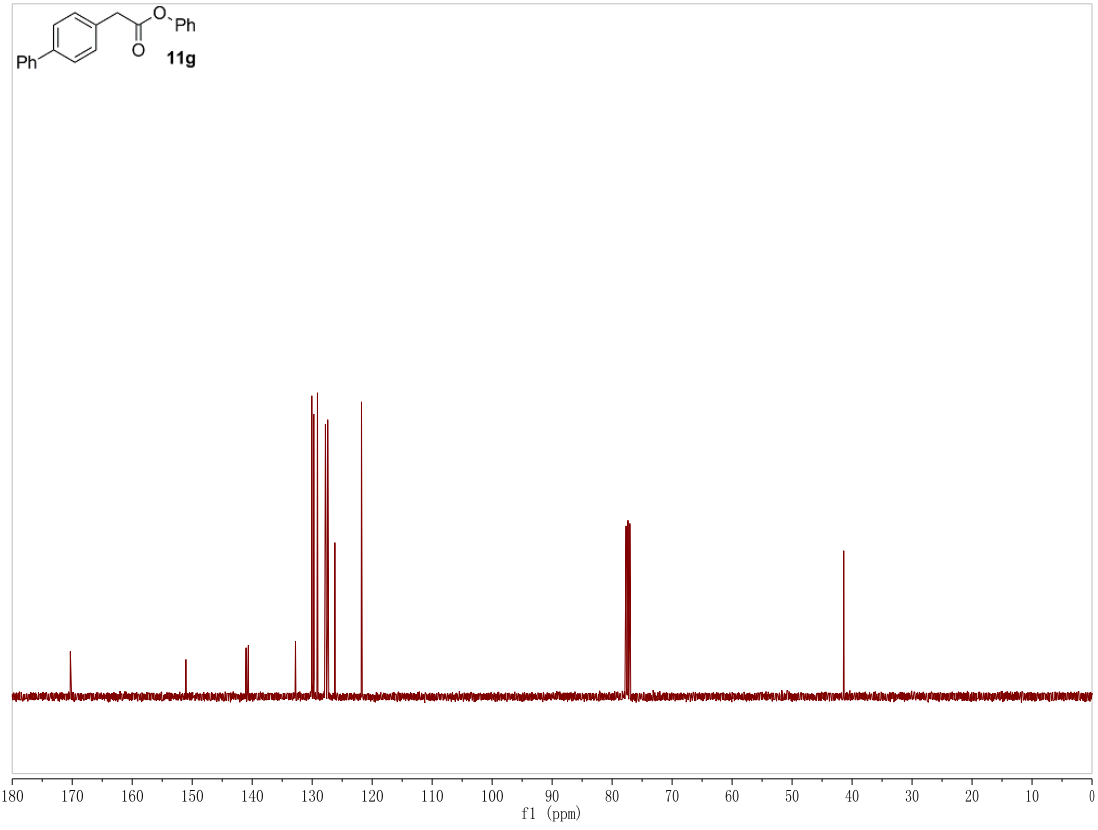

Ph
O
O
11e
4.16
2.10
3.10
2.00
9.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

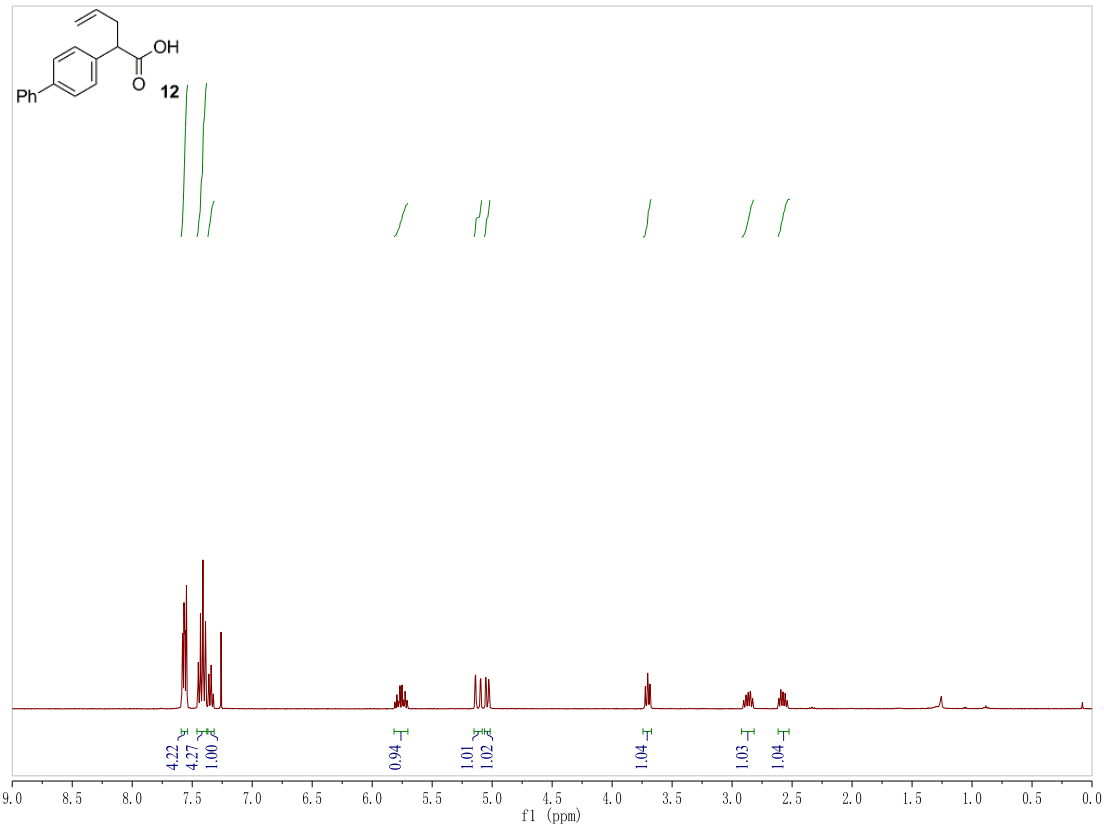

Ph
O
O
11e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

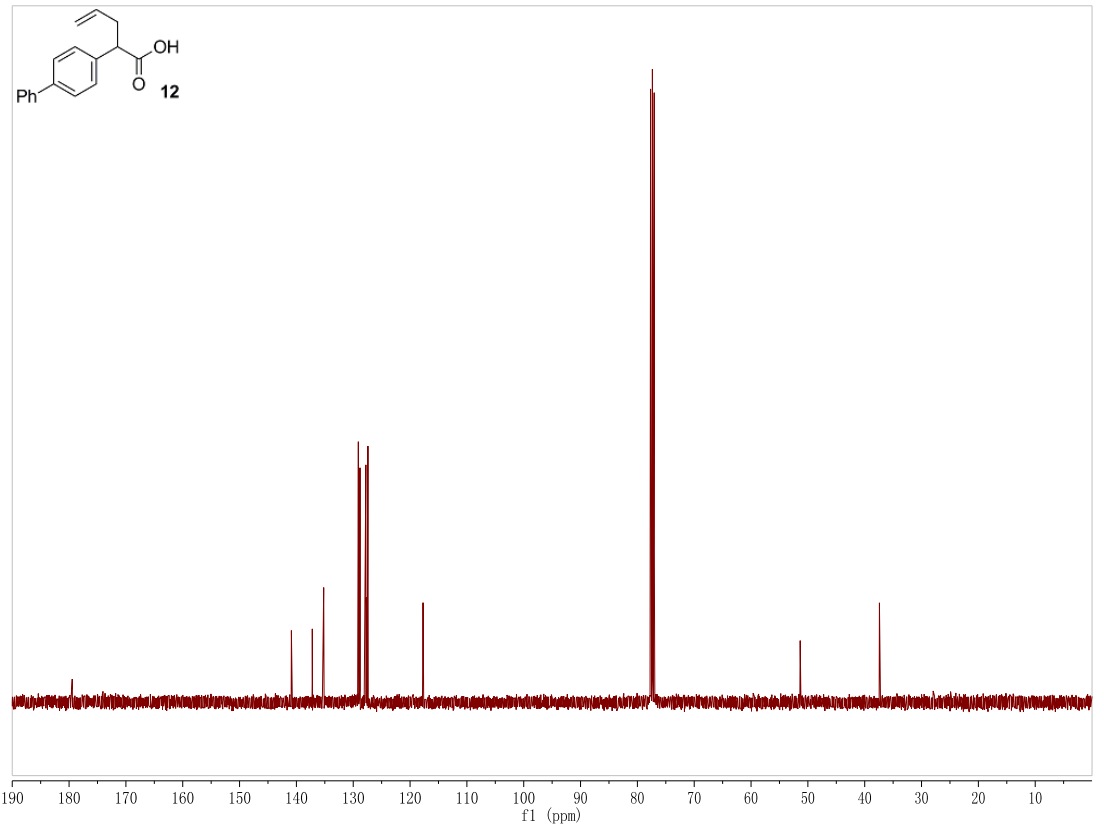

Ph
O
O
F
F
F
F
F
11f
4.18
4.16
1.00
2.15
* Inpurity
f1 (ppm)

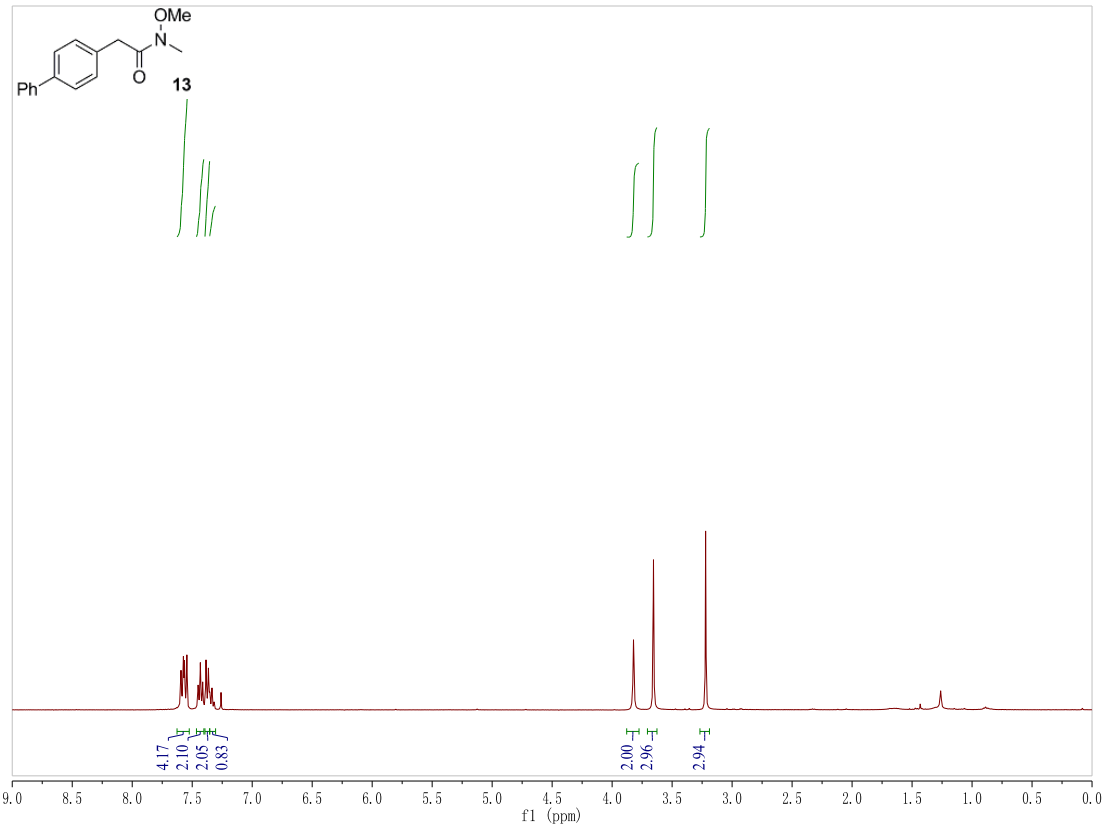

Ph
O
O
F
F
F
F
F
11f
* Inpurity
f1 (ppm)

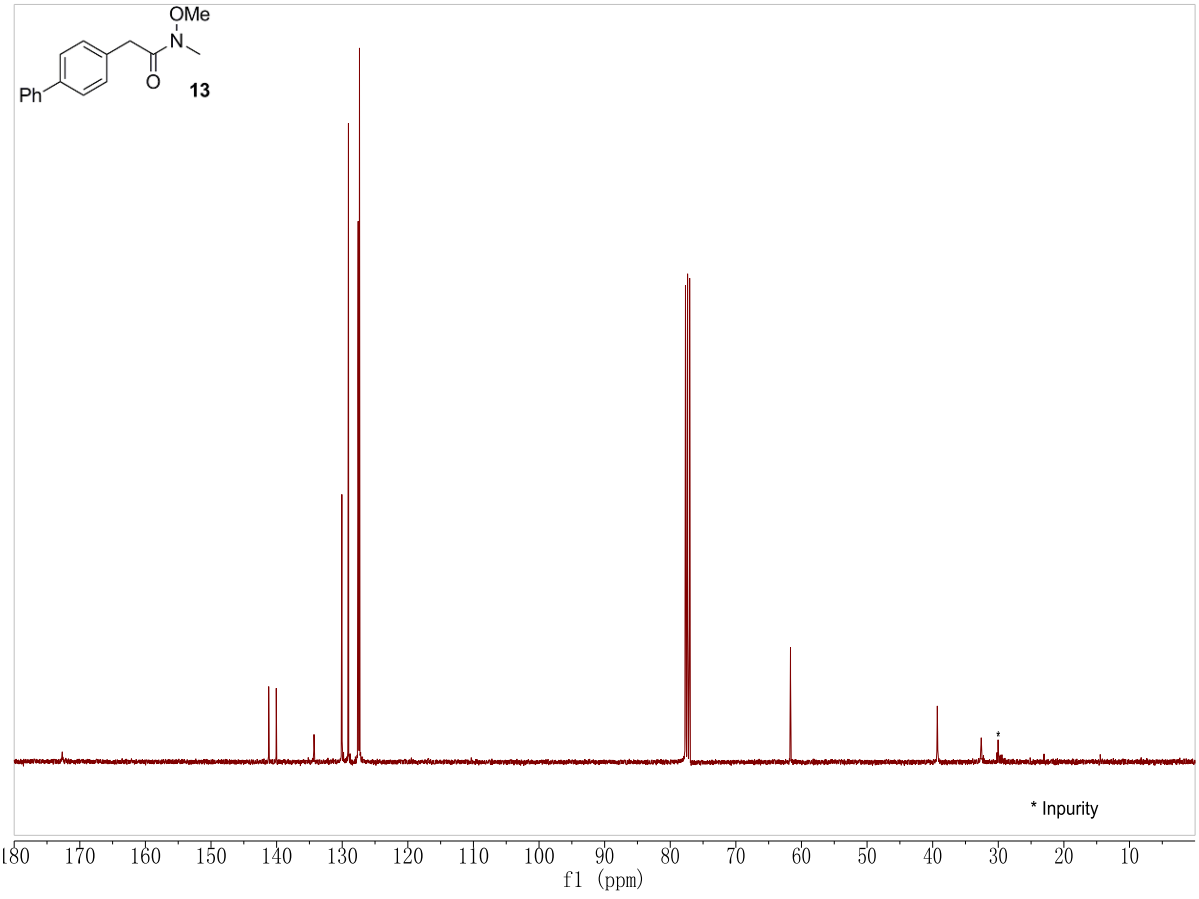

Ph
O
O
Ph
11g
3.78
3.77
2.74
1.00
1.72
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

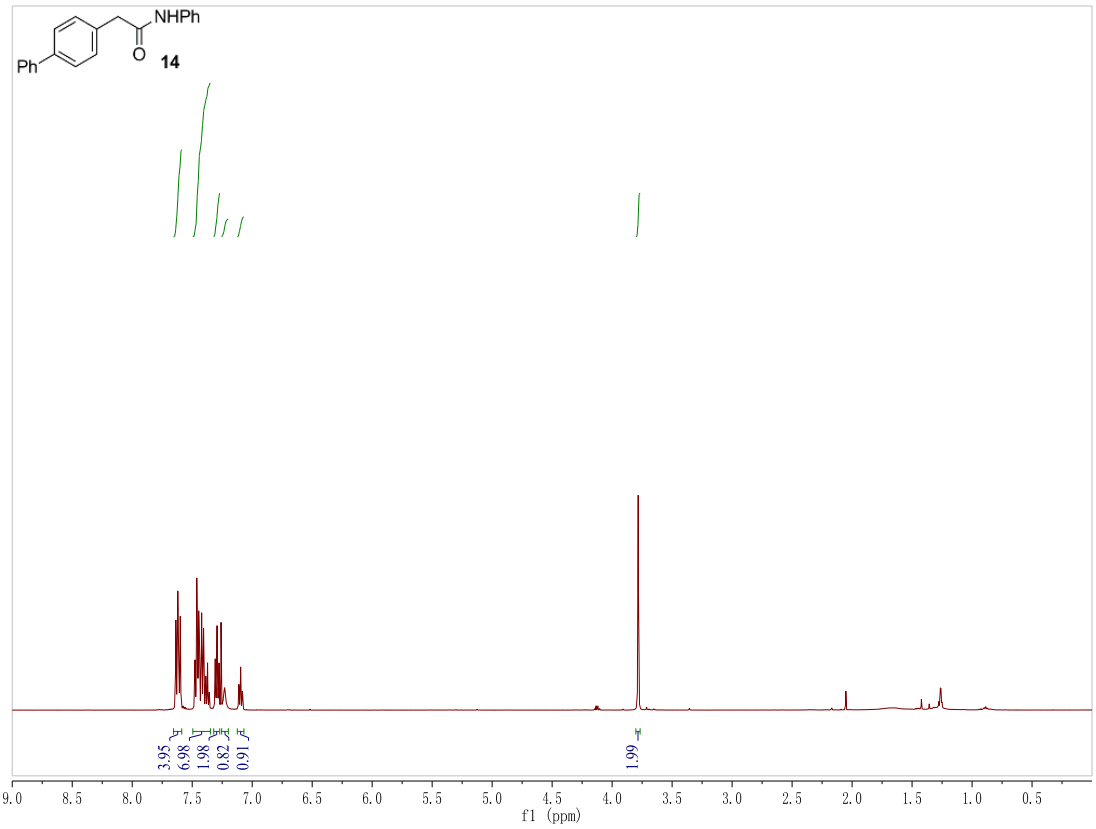

Ph
O
O
Ph
11g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

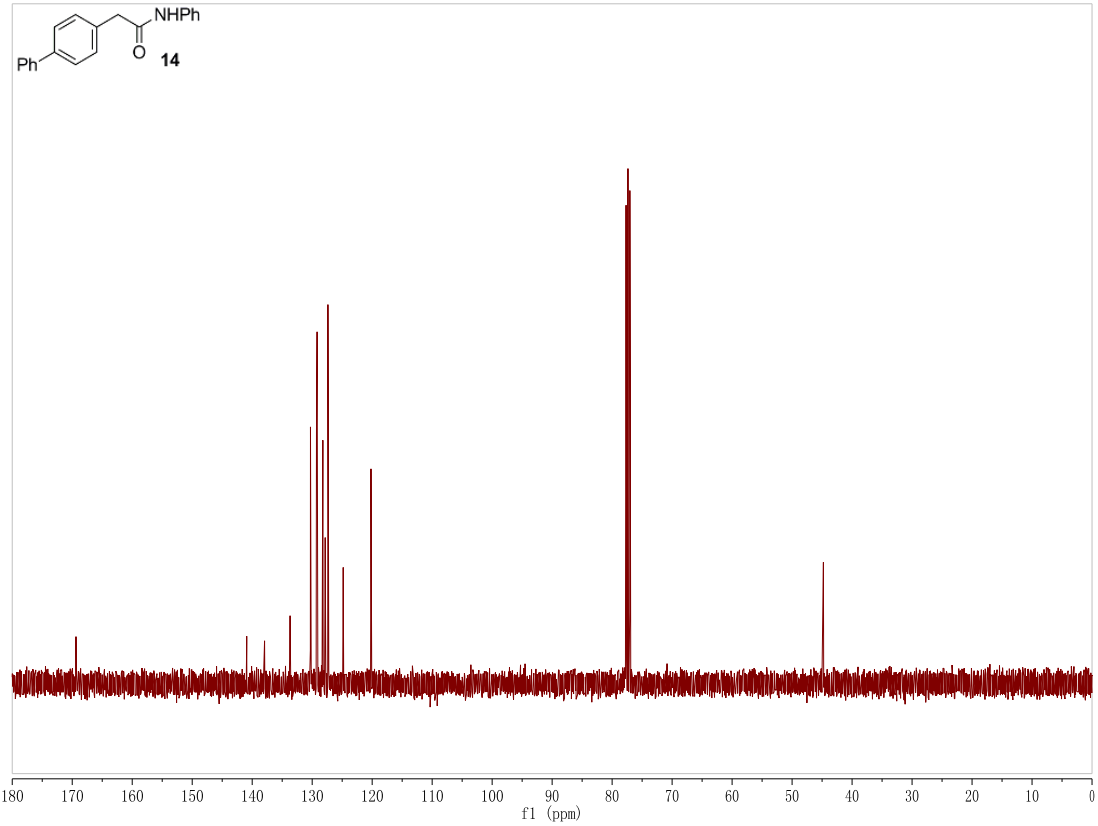

OH
O
Ph
12
4.22
4.27
1.00
0.94
1.01
1.02
1.04
1.03
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

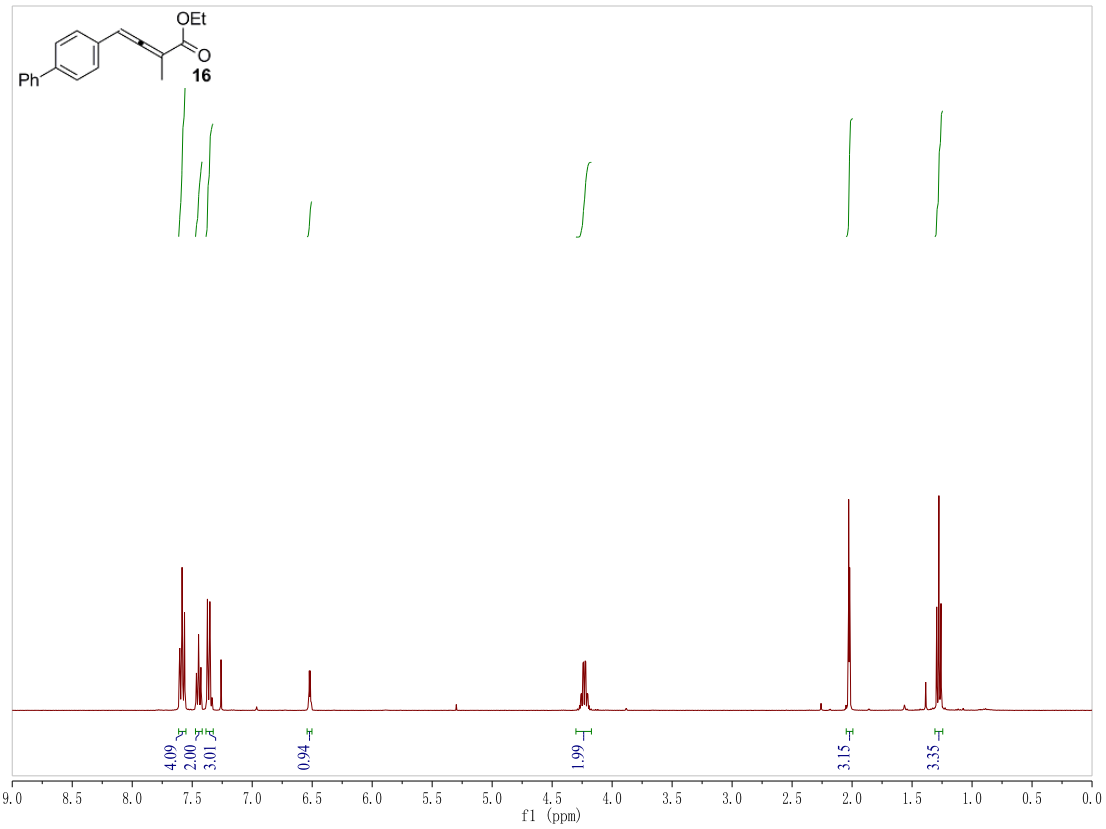

OH
O
Ph
12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

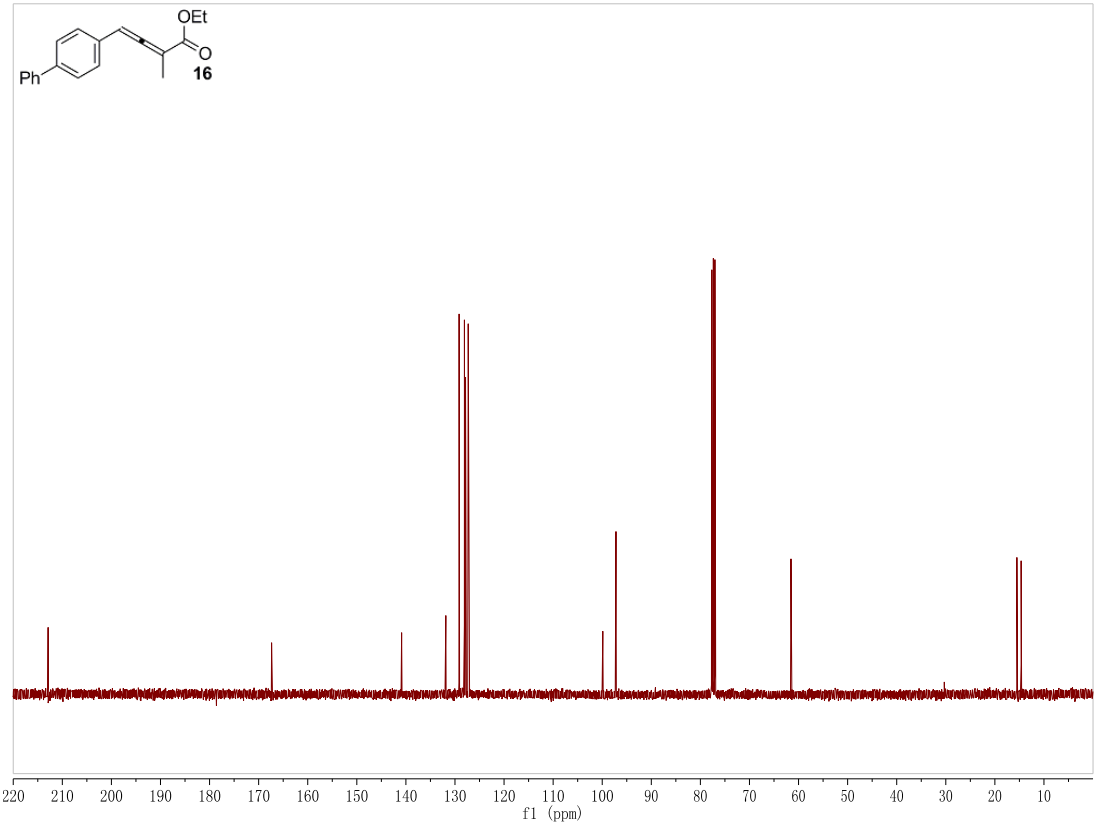

OMe
N
O
Ph
13
4.17
2.10
2.05
0.83
2.00
2.96
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

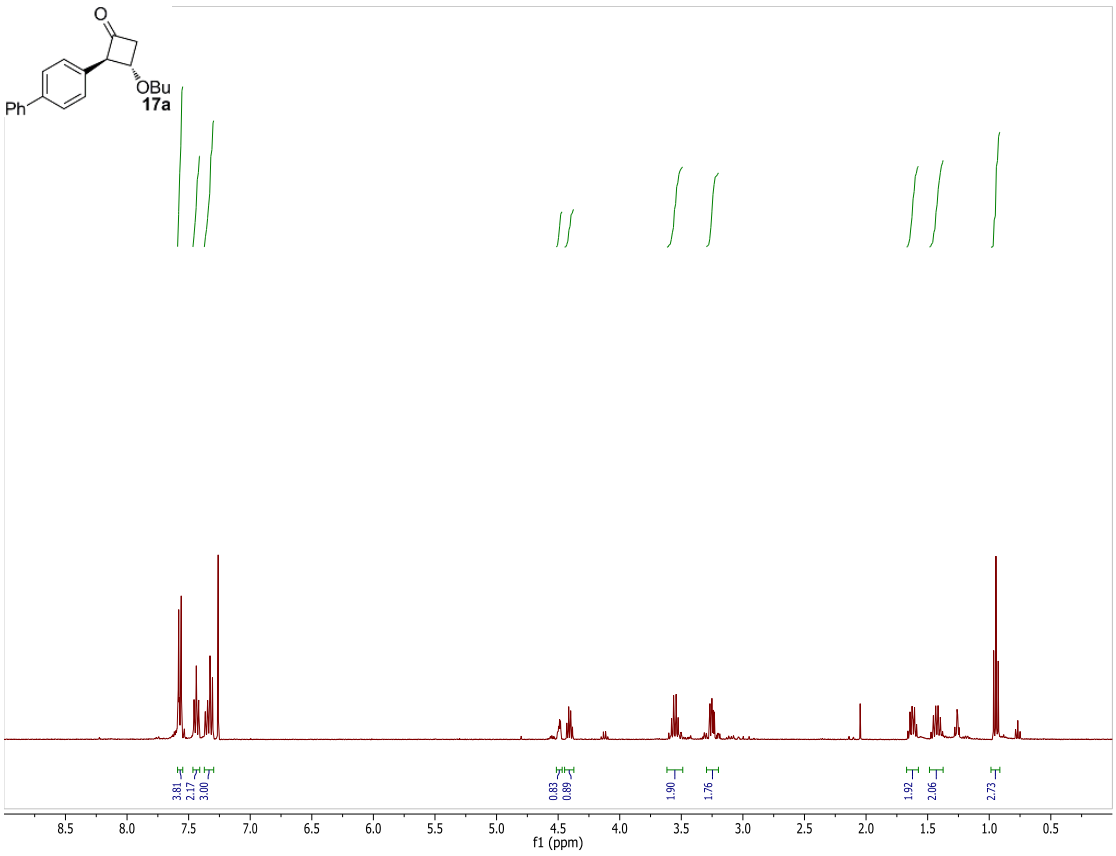

OMe
N
O
Ph
13
* Inpurity
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

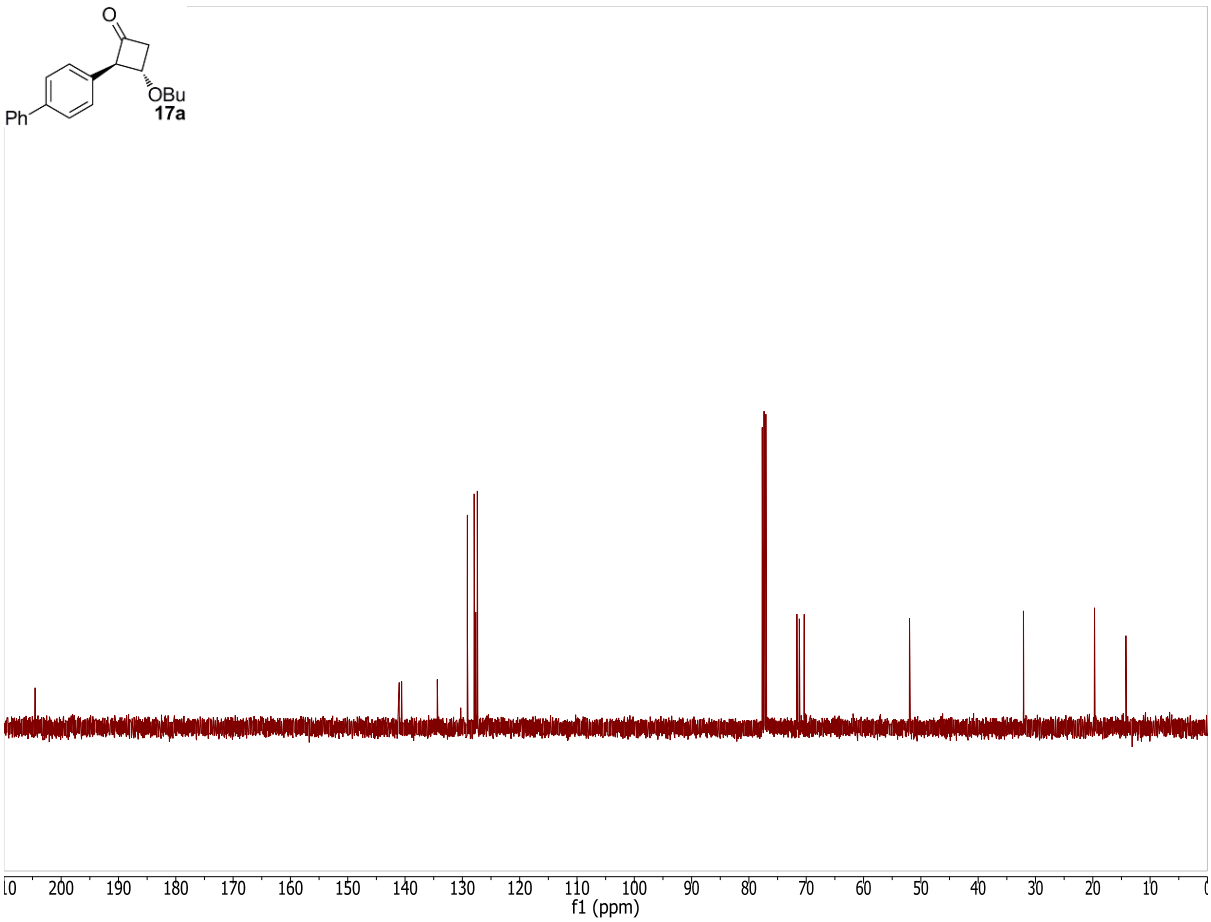

NHPh
O
Ph
14
3.95
6.98
1.98
0.82
0.91
1.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

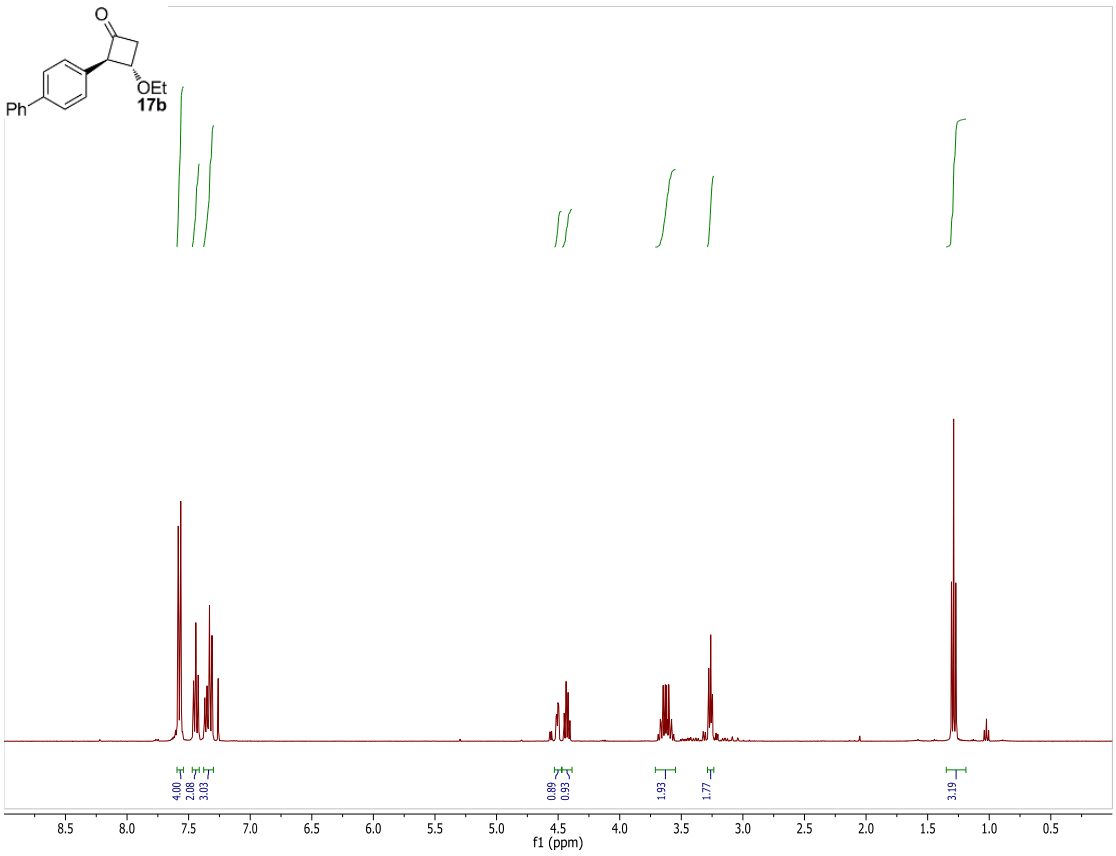

NHPh
O
Ph
14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

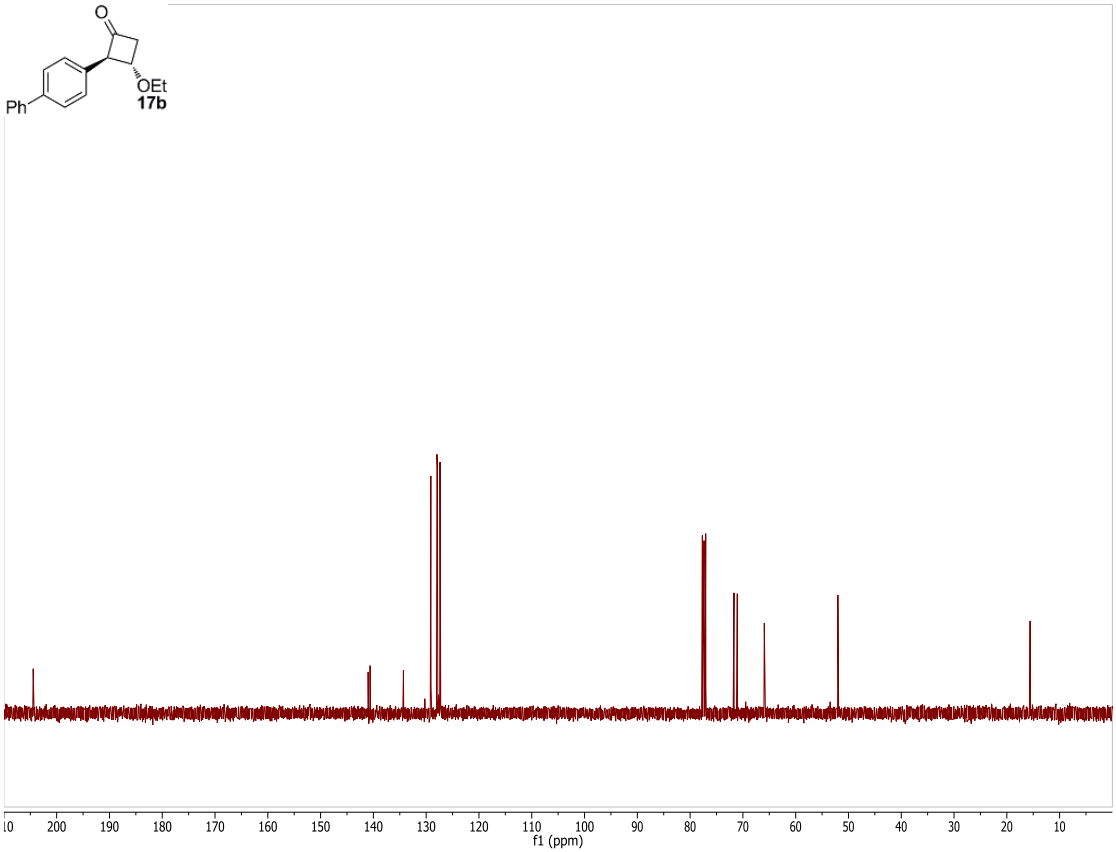

OEt
O
Ph
16
4.09
2.00
3.01
0.94
1.99
3.15
3.35
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

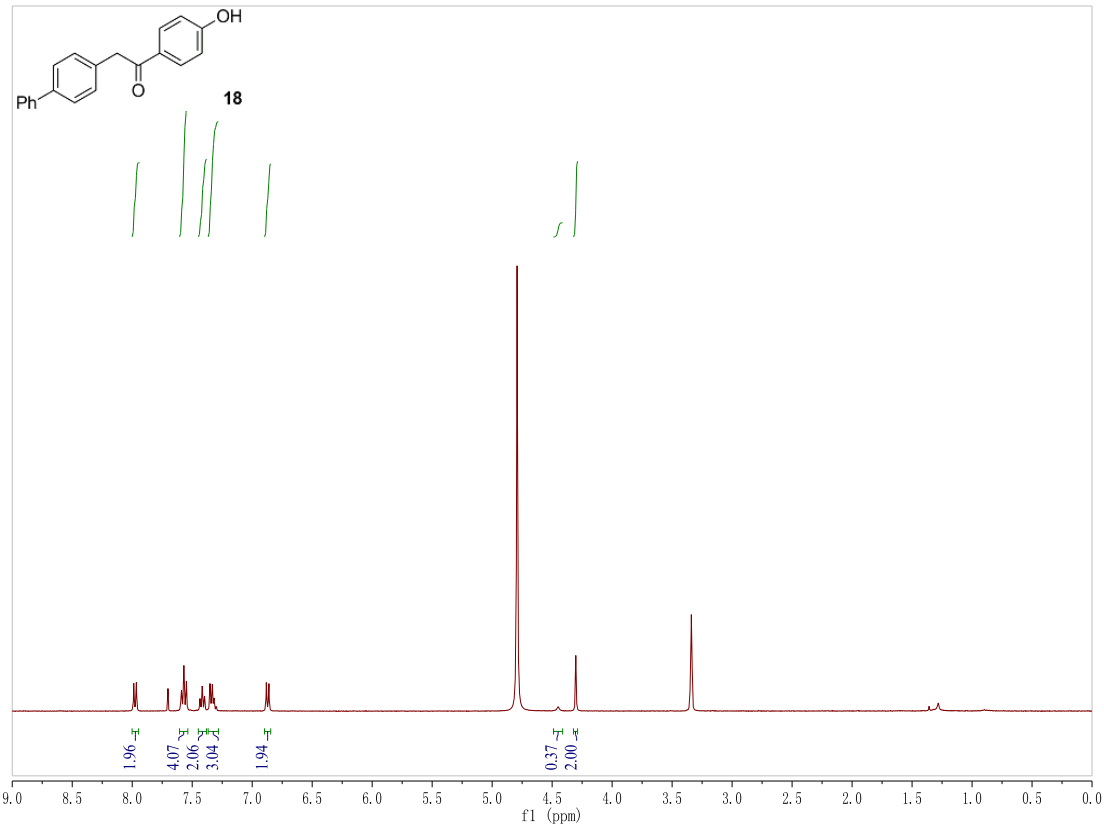

OEt
O
Ph
16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

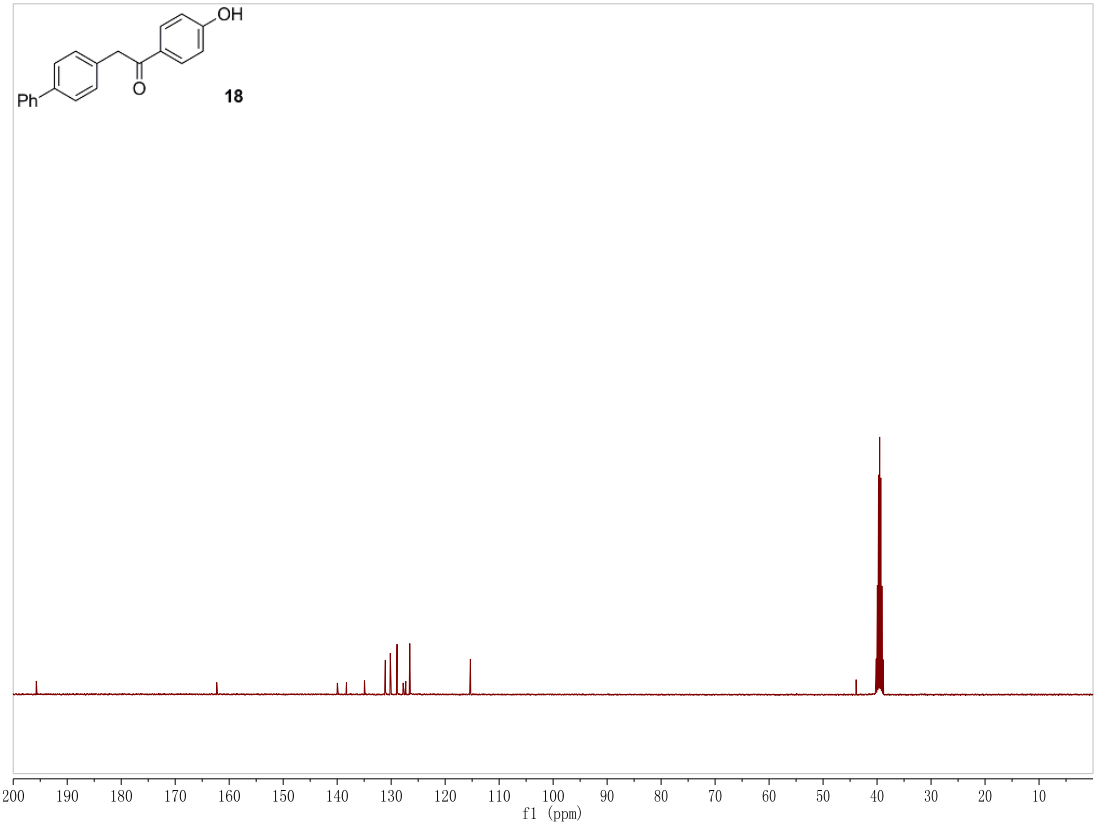

O
OBu
17a
Ph
3.81
2.17
3.00
0.83
0.89
1.90
1.76
1.92
2.06
2.73
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

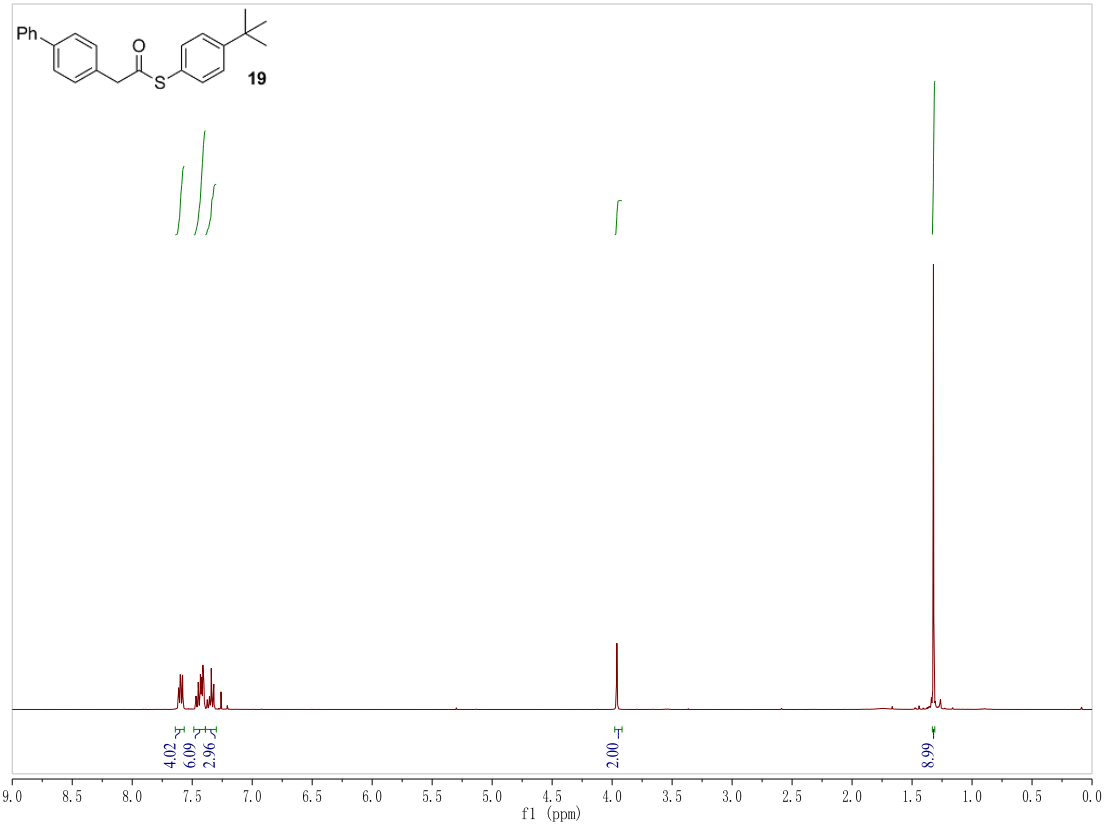

O
OBu
17a
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

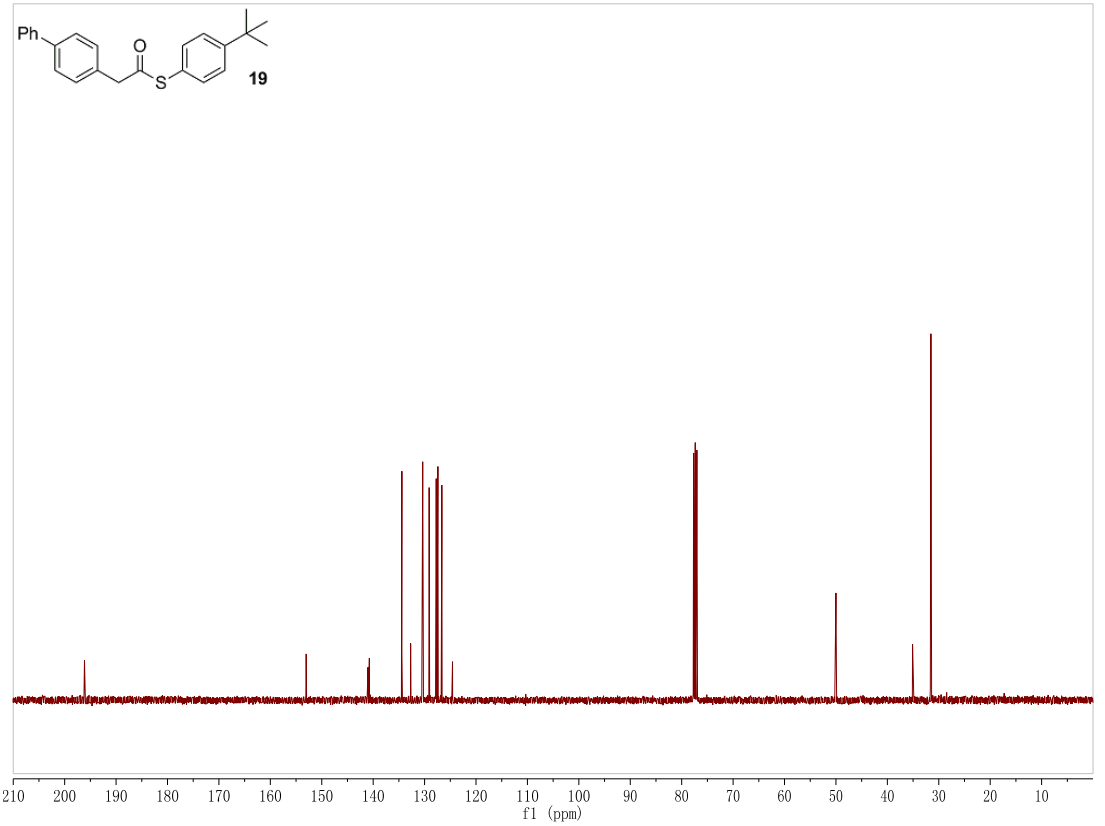

O
OEt
17b
Ph
4.00
2.08
3.03
0.89
0.93
1.93
1.77
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

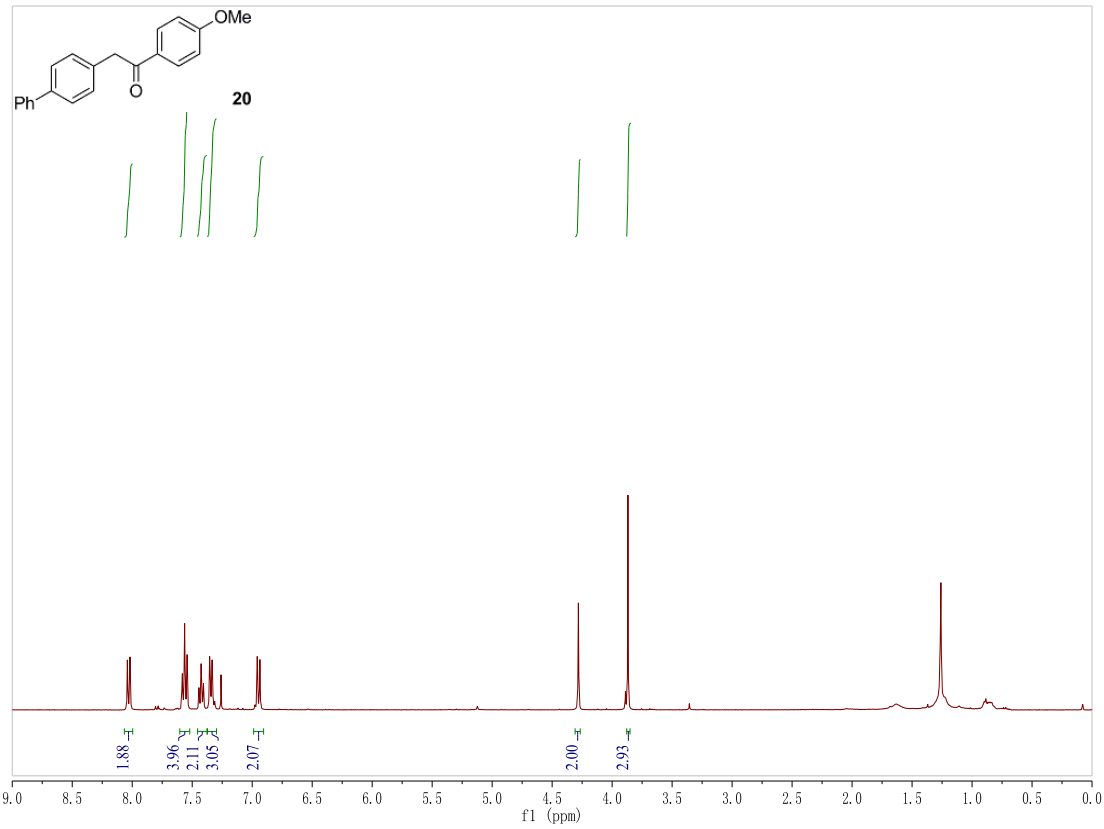

O
OEt
17b
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

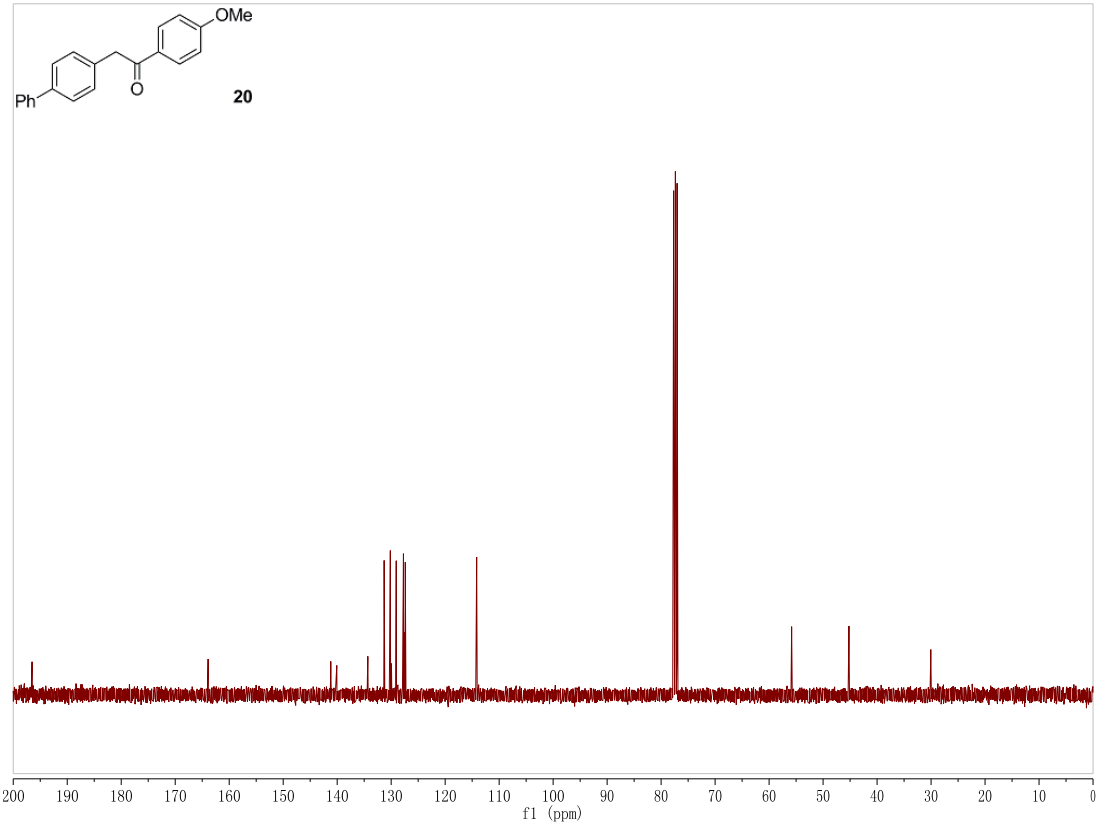

OH
O
Ph
18
1.96
4.07
2.06
3.04
1.94
0.37
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

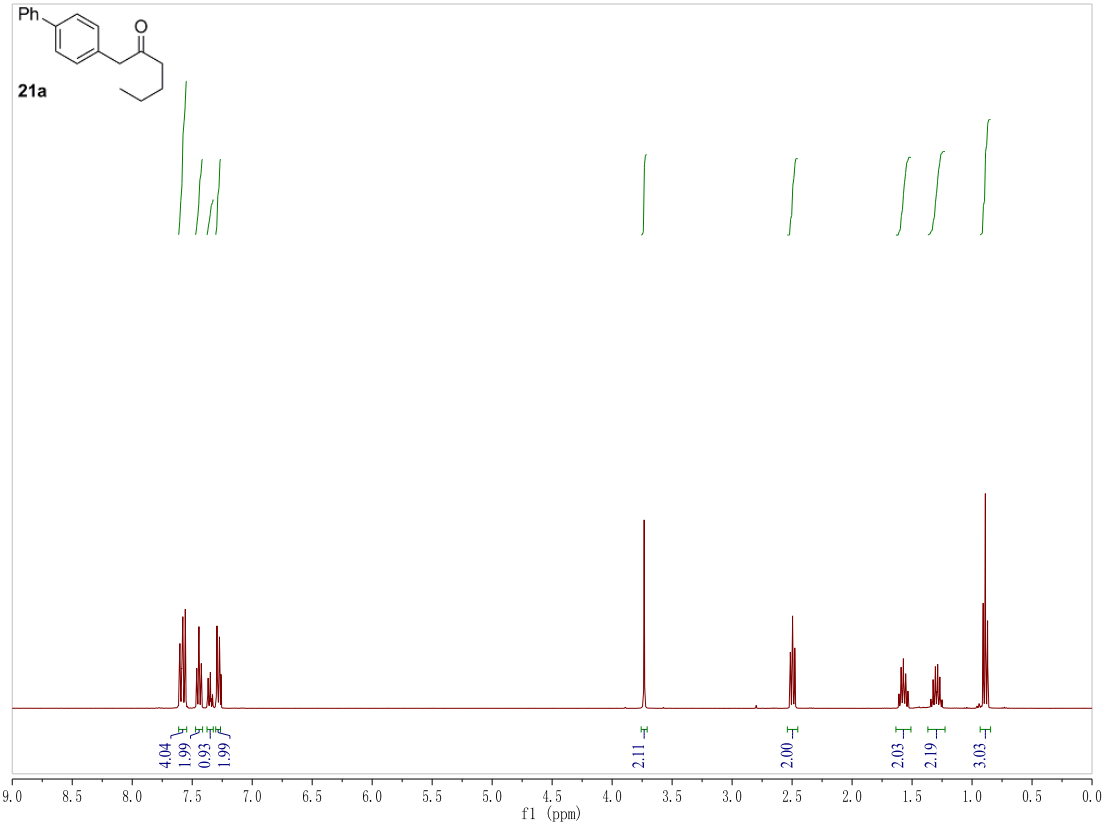

OH
O
Ph
18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

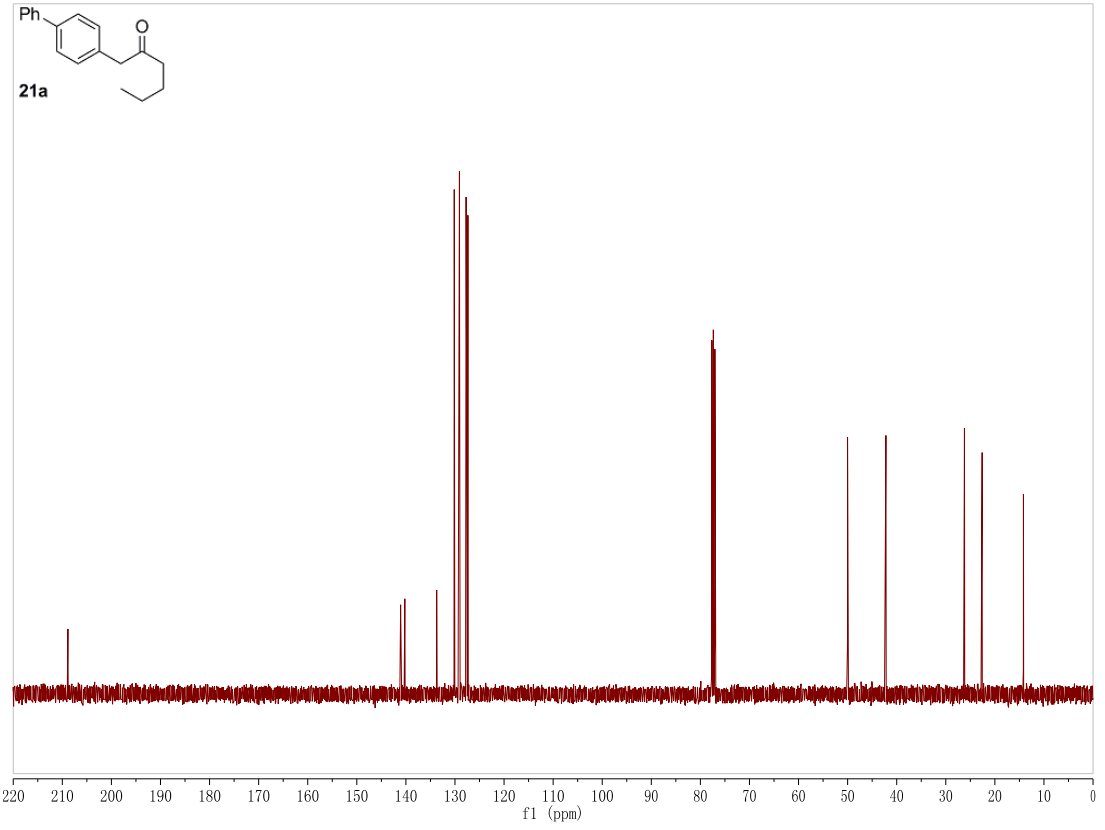

Ph
O
S
19
4.02
6.09
2.96
2.00
8.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

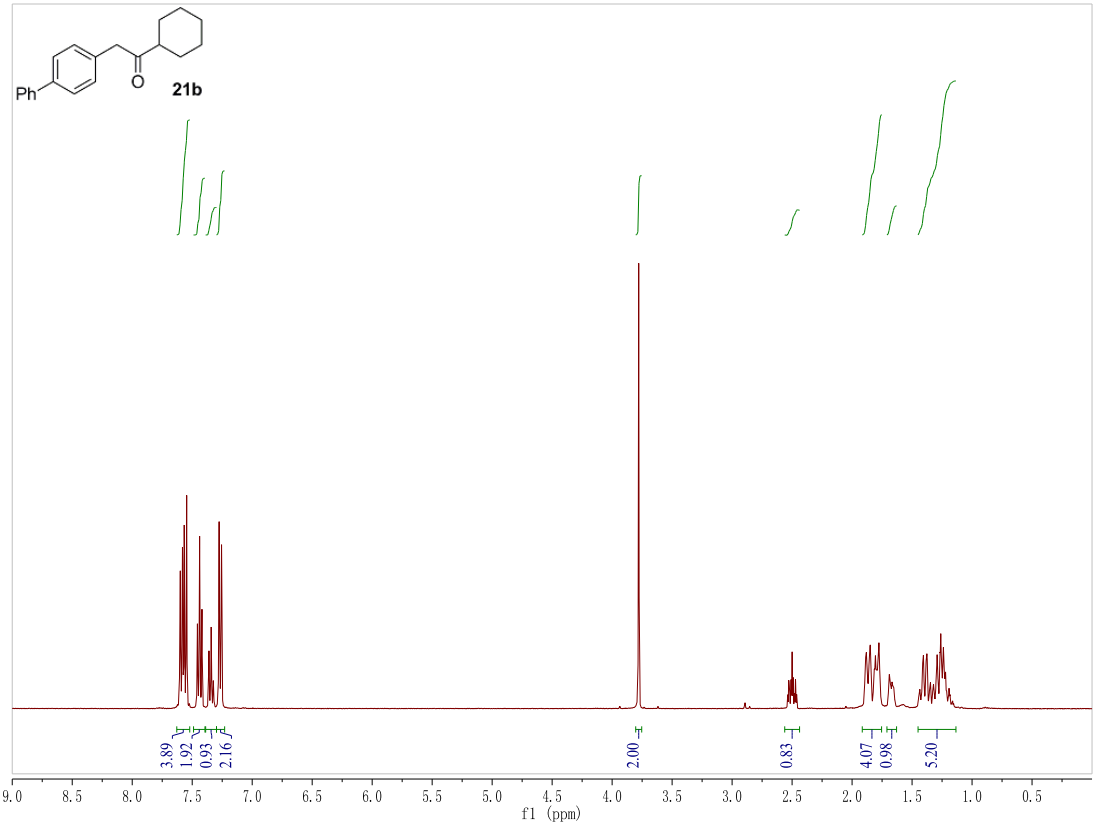

Ph
O
S
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

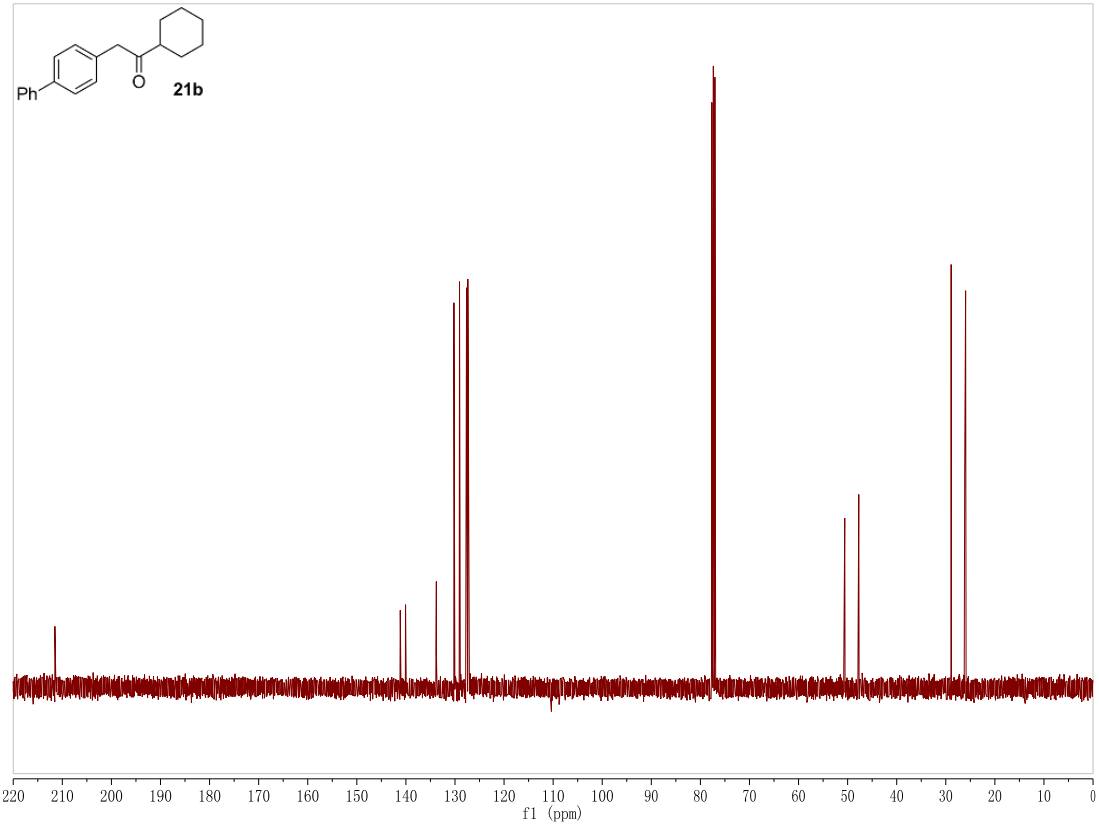

OMe
Ph
O
20
1.88
3.96
2.11
3.05
2.07
2.00
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

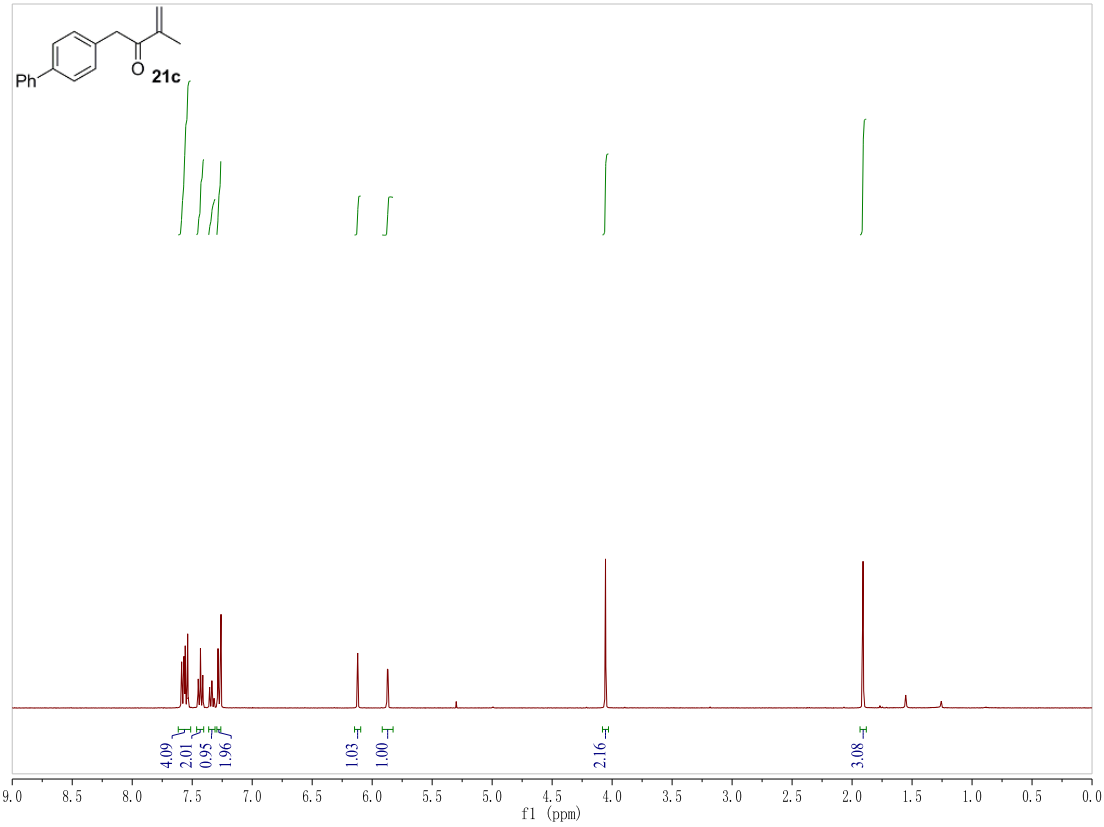

OMe
Ph
O
20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

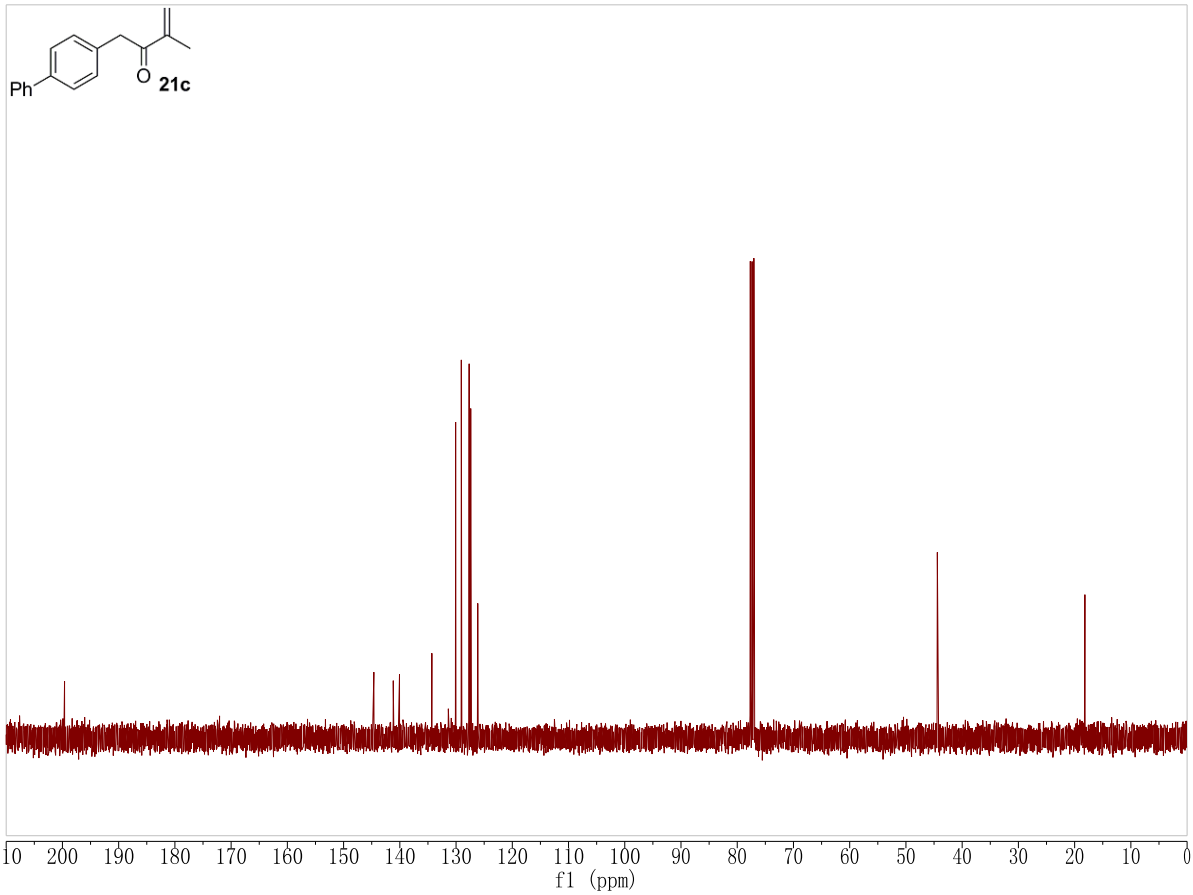

Ph
O
21a
4.04
1.99
0.93
1.99
2.11
2.00
2.03
2.19
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

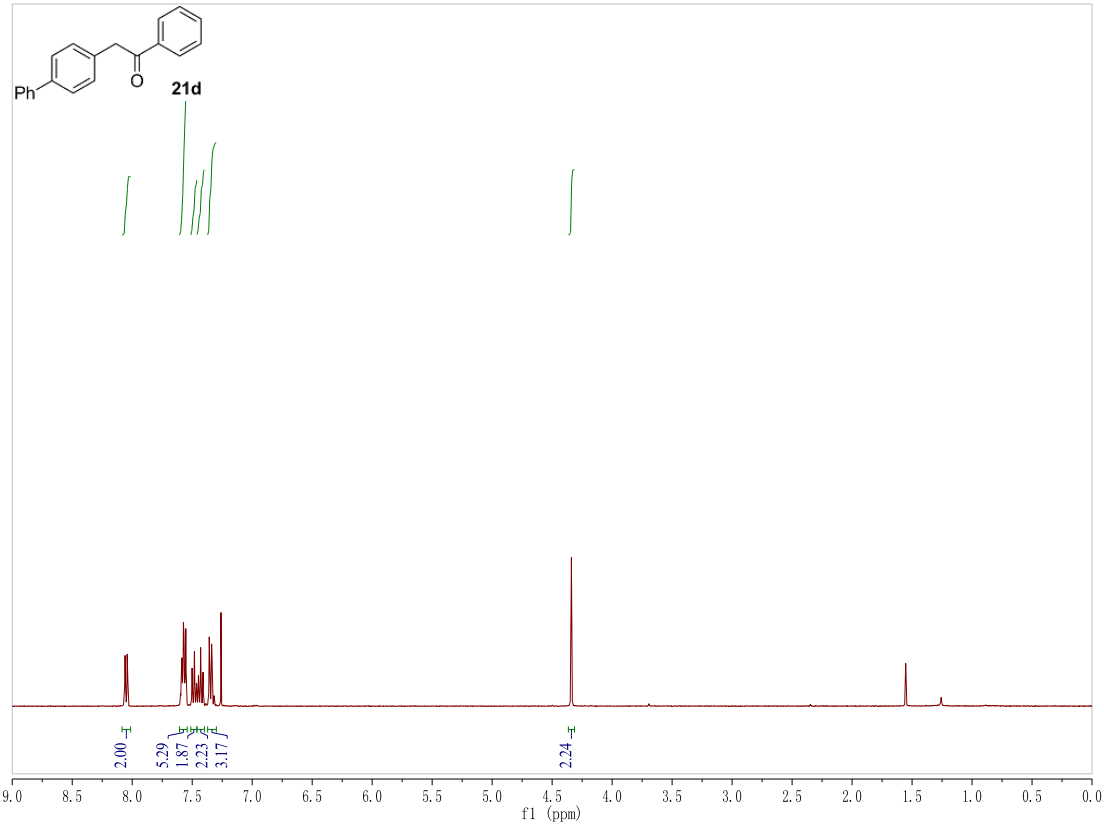

Ph
O
21a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

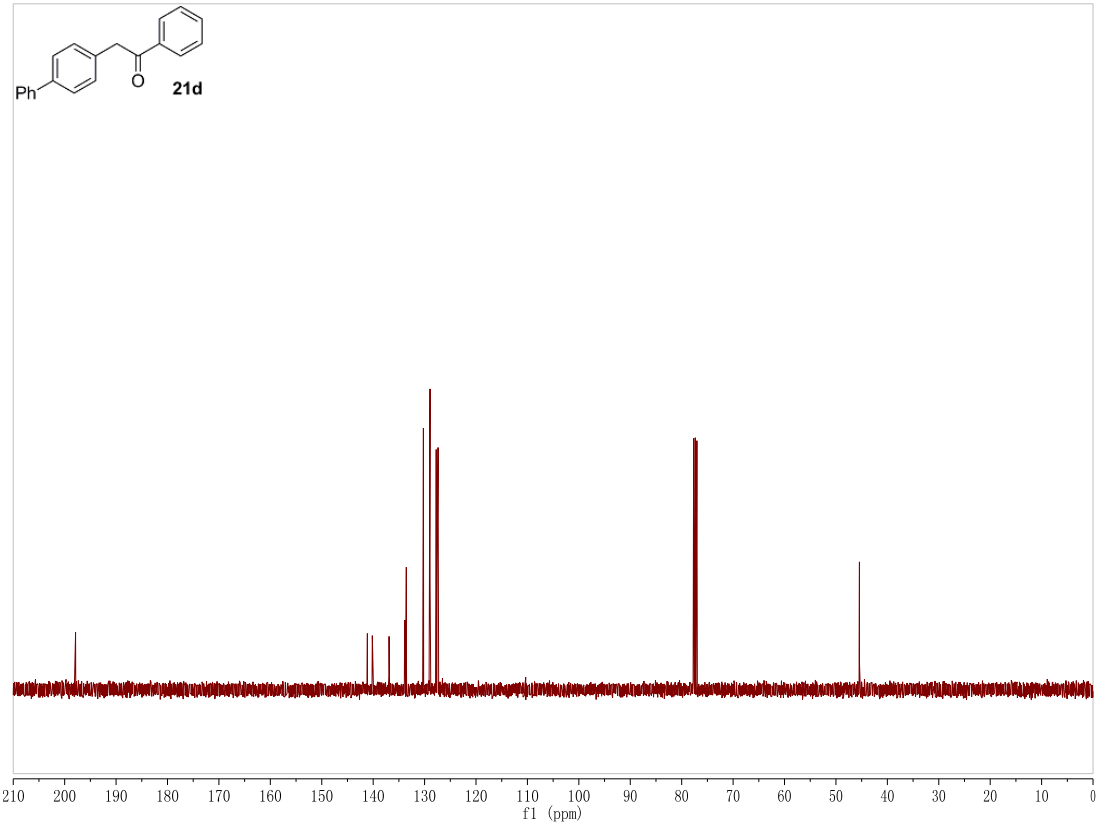

Ph
O
21b
3.89
1.92
0.93
2.16
2.00
0.83
4.07
0.98
5.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

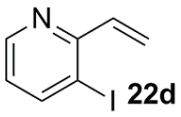

Ph
O
21b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
21c
4.09
2.01
0.95
1.96
1.03
1.00
2.16
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

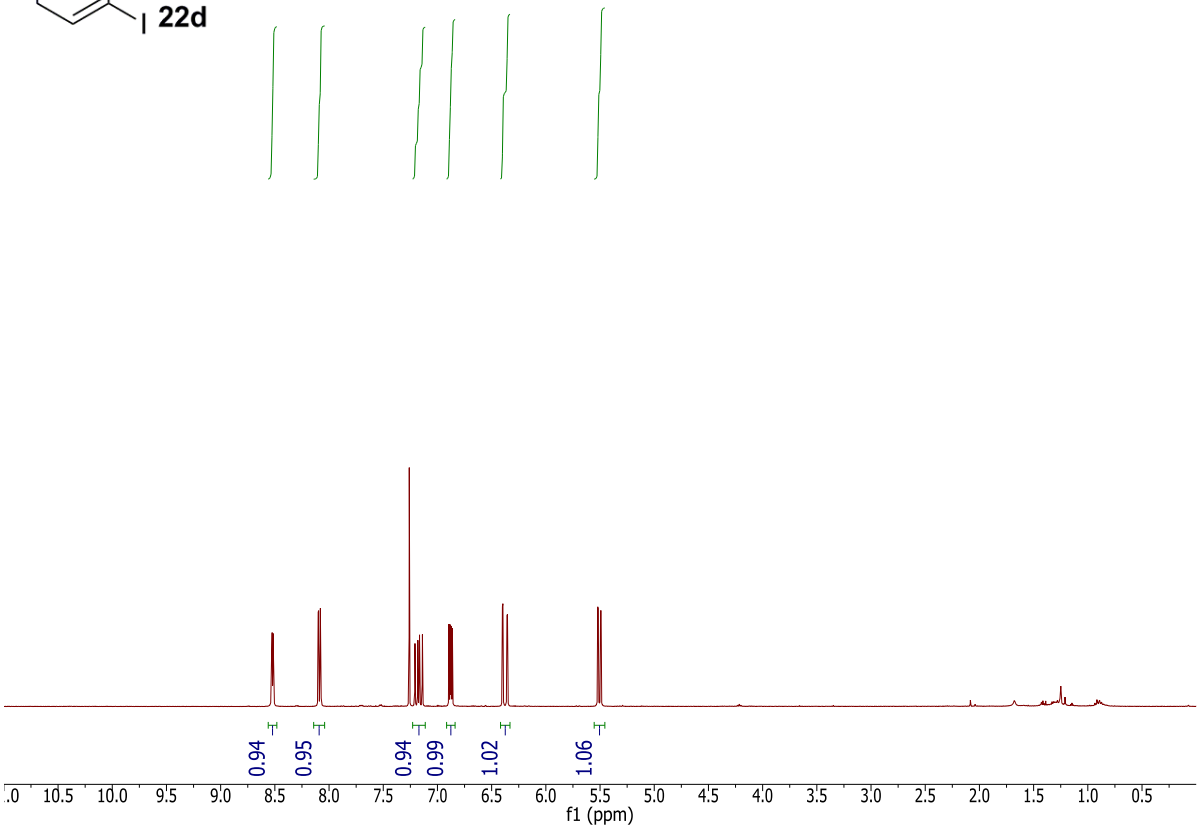

Ph
O
21c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

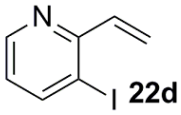

Ph
O
21d
2.00
5.29
1.87
2.23
3.17
2.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
O
21d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

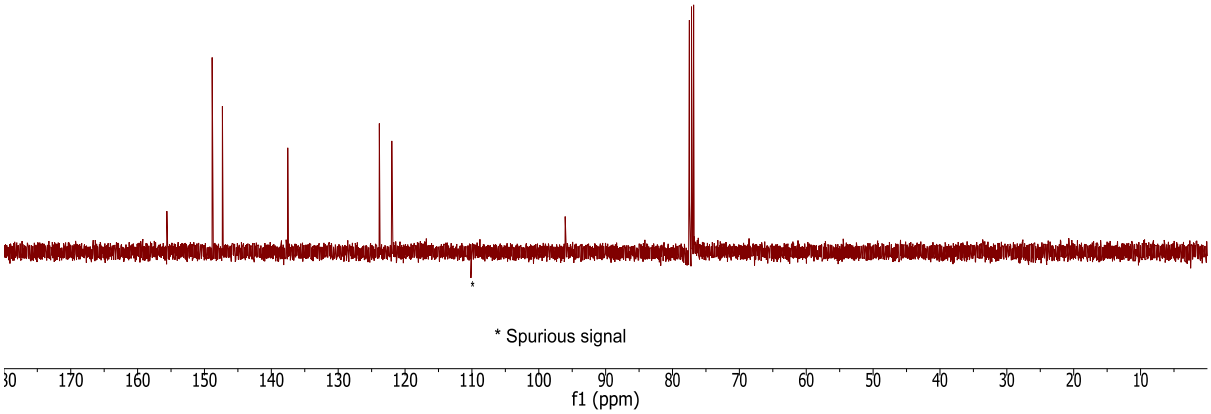


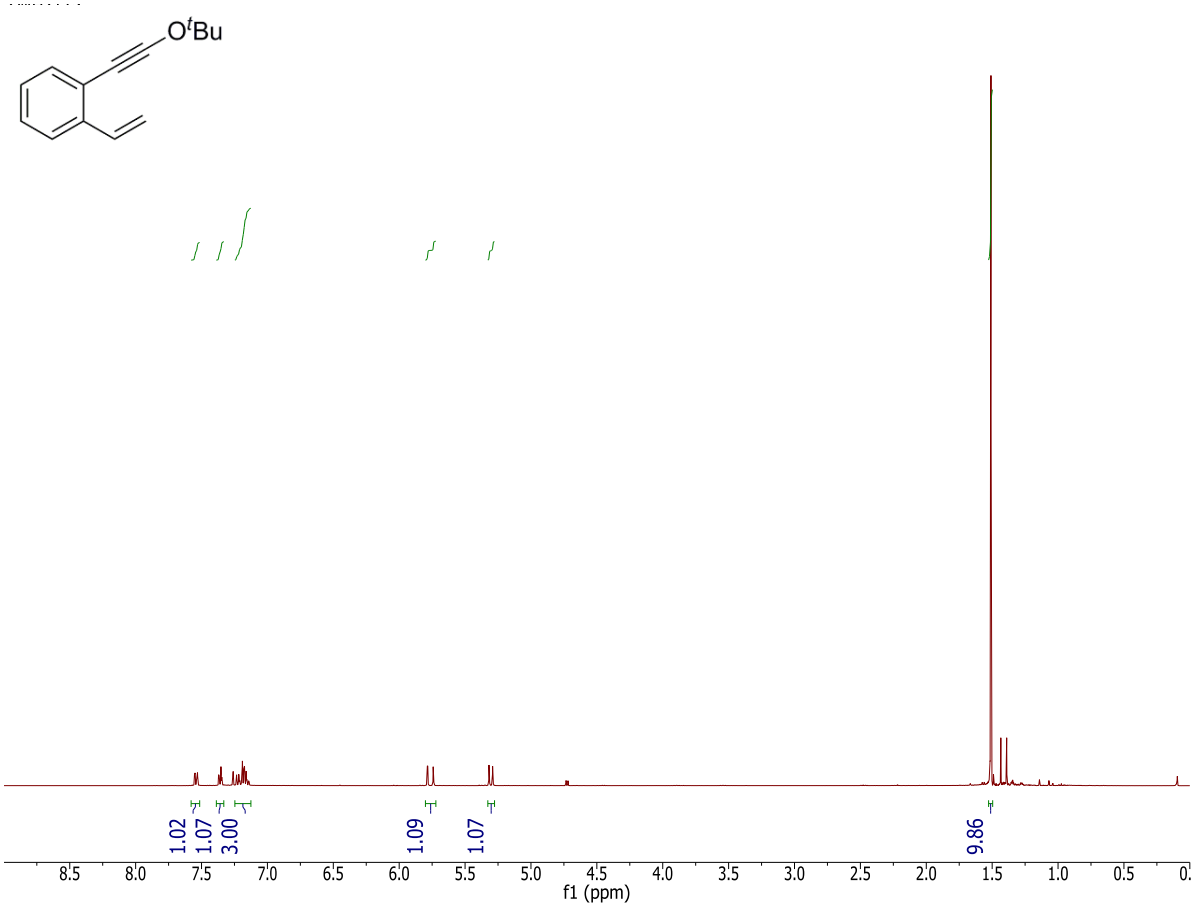
22d

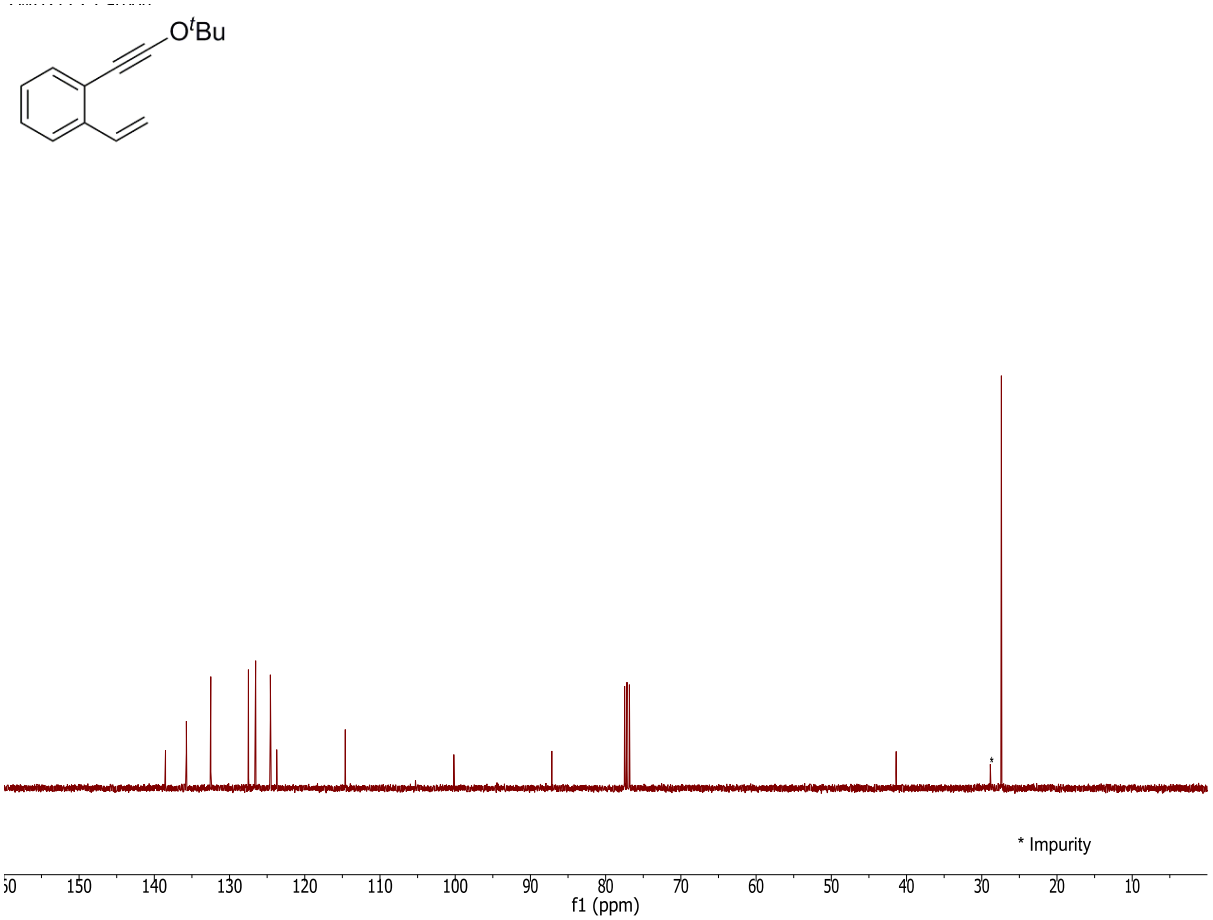


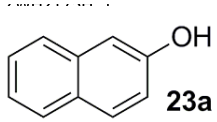


22d

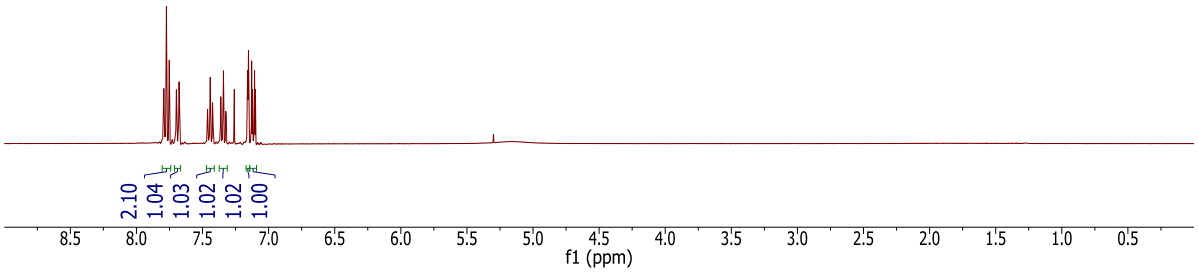


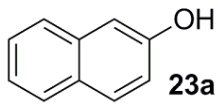

O^{t}Bu
1.02
1.07
3.00
1.09
1.07
9.86
f1 (ppm)


O^{t}Bu
* Impurity
f1 (ppm)

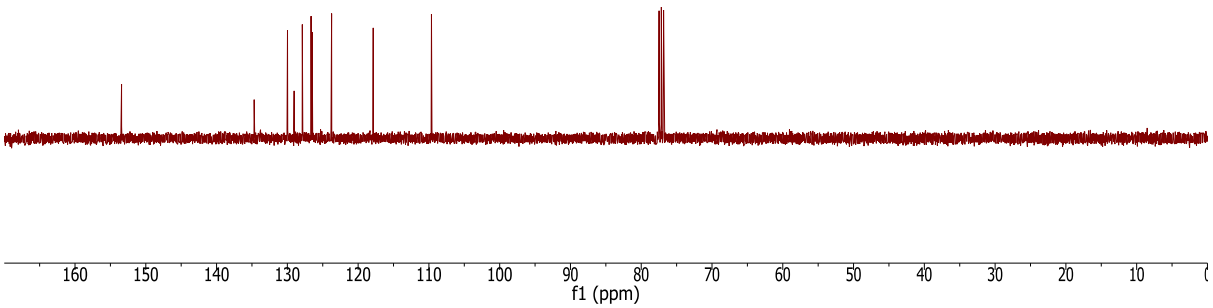

OH

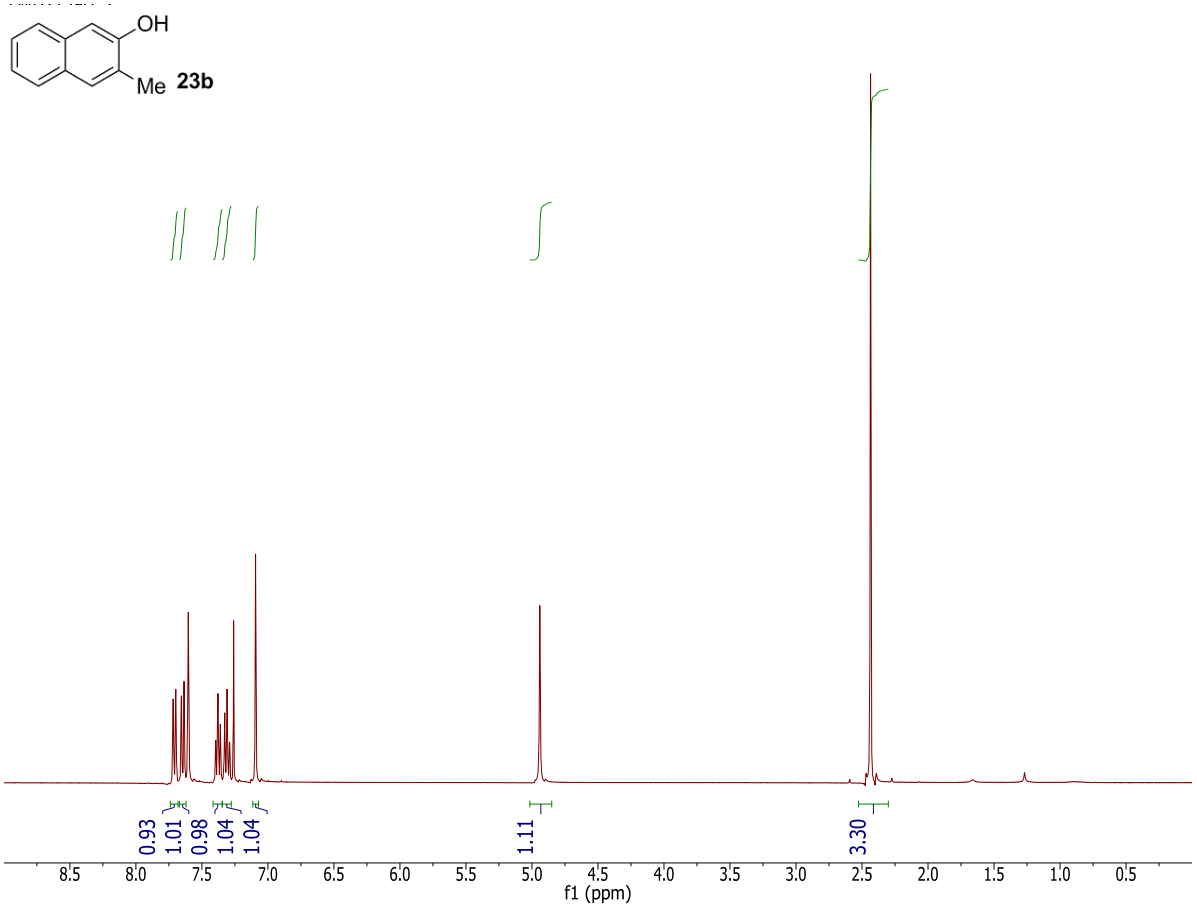
23a

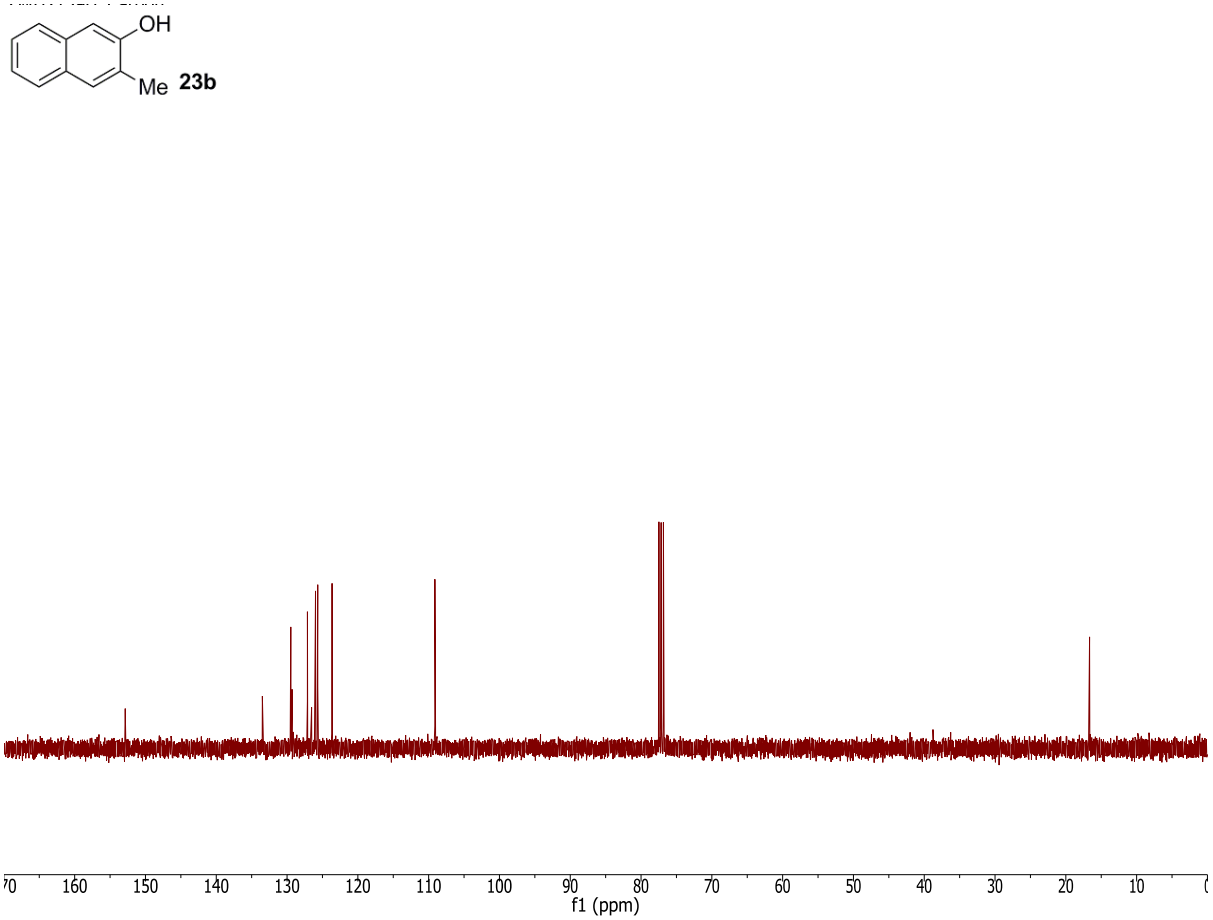

2.10
1.04
1.03
1.02
1.02
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

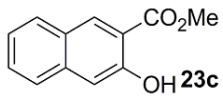

OH

23a

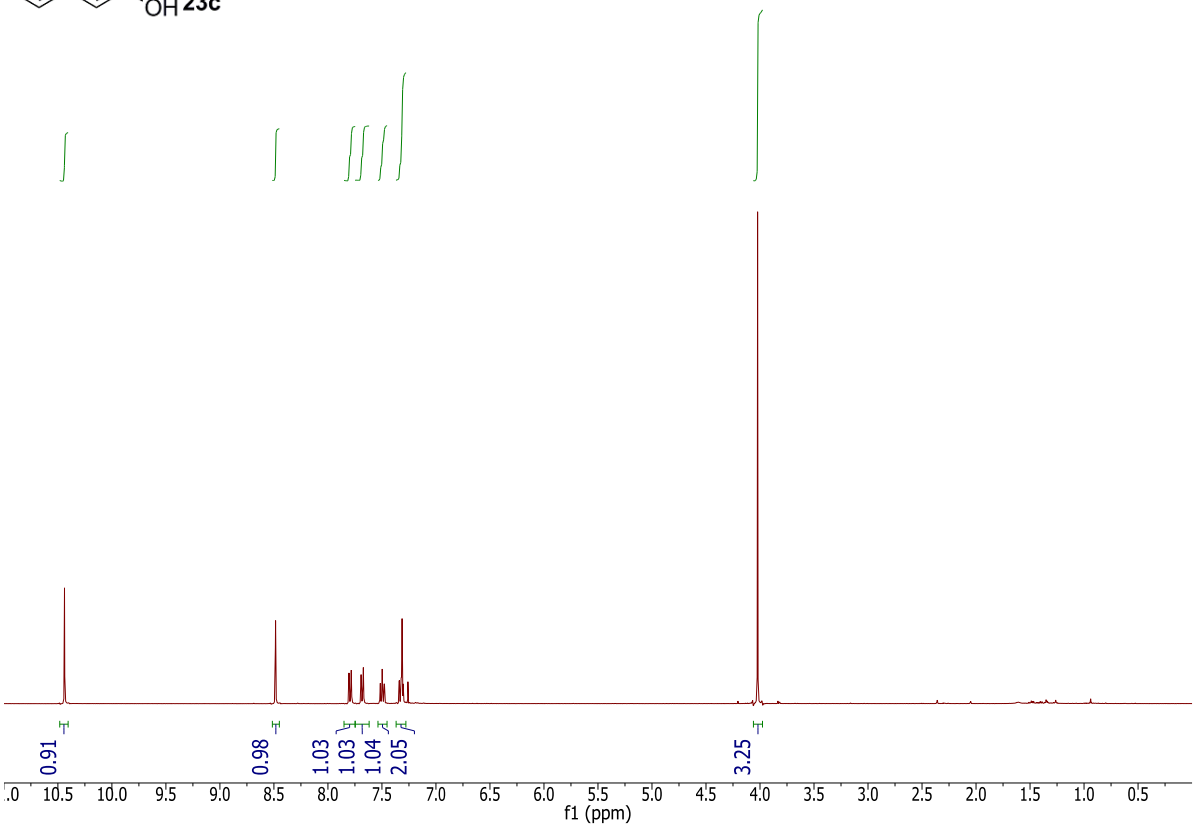

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

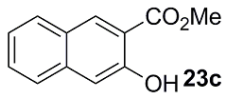

OH
Me
23b
0.93
1.01
0.98
1.04
1.04
1.11
3.30
f1 (ppm)


OH
Me
23b
f1 (ppm)

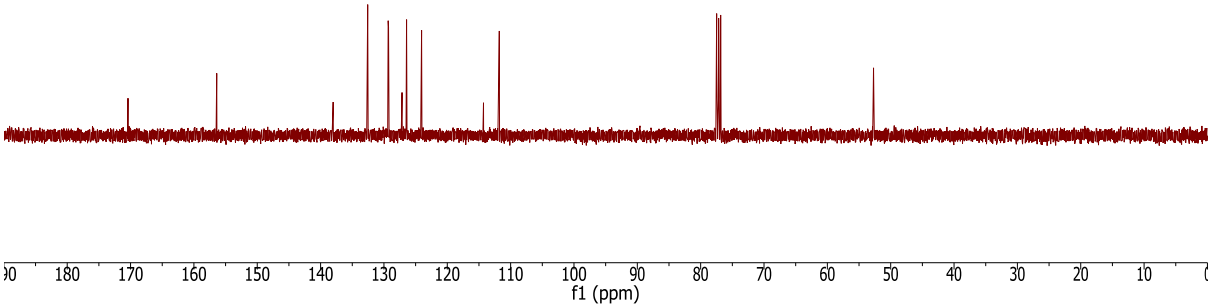


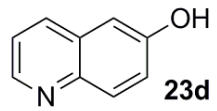
23c



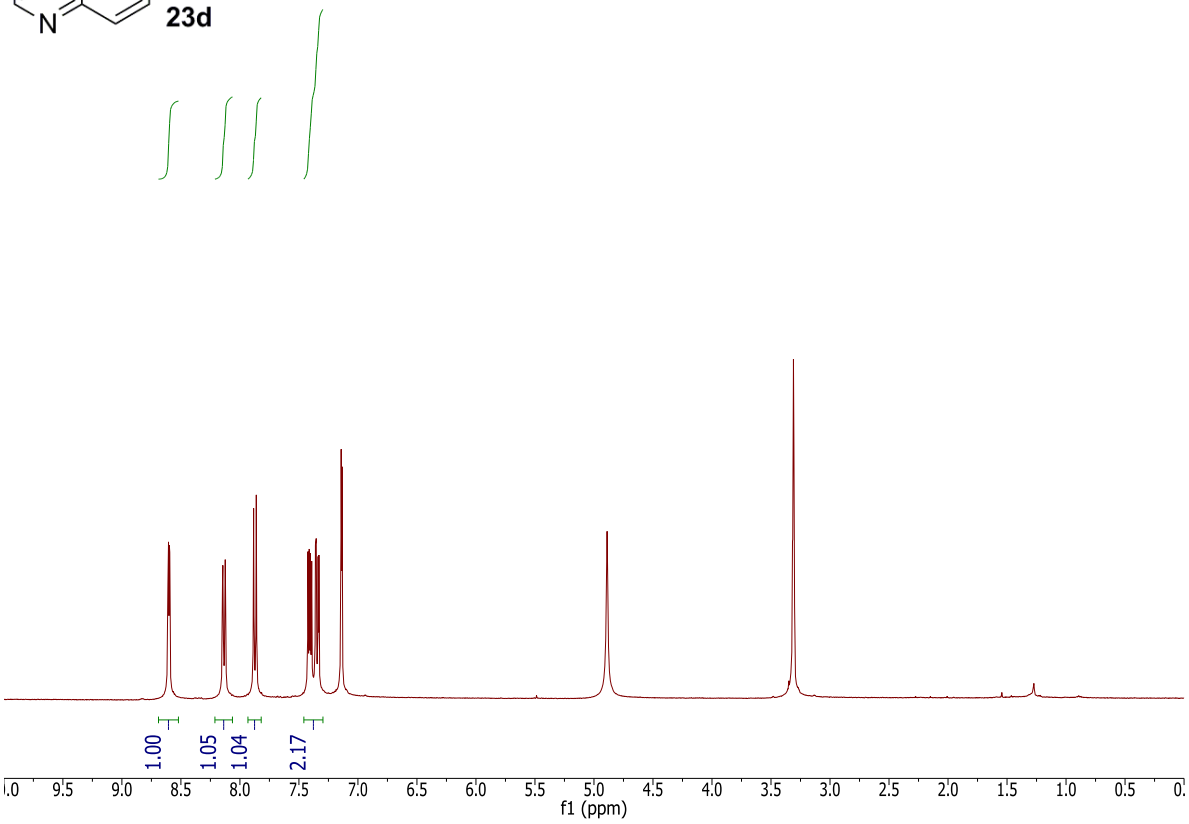


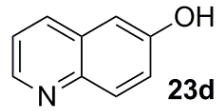
23c



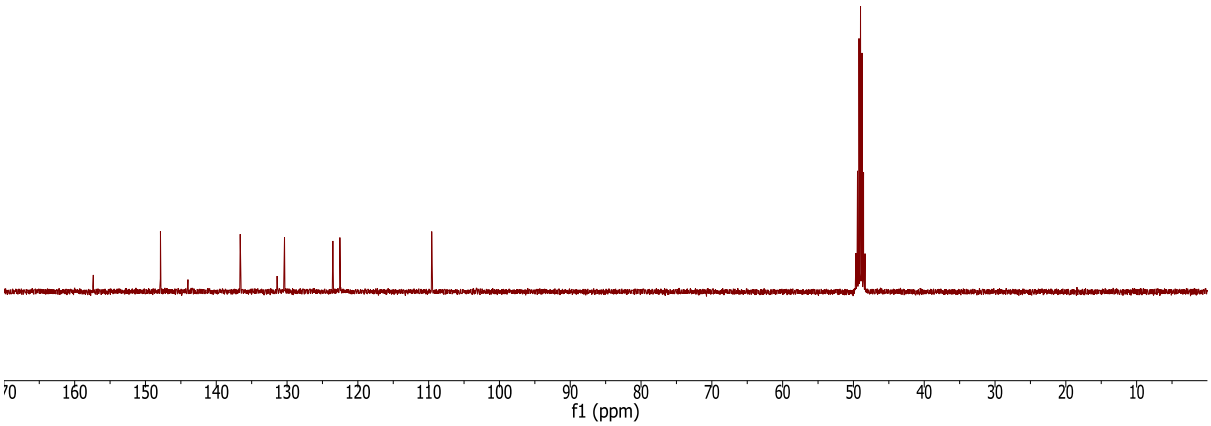


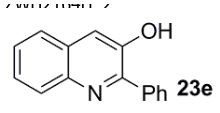
23d



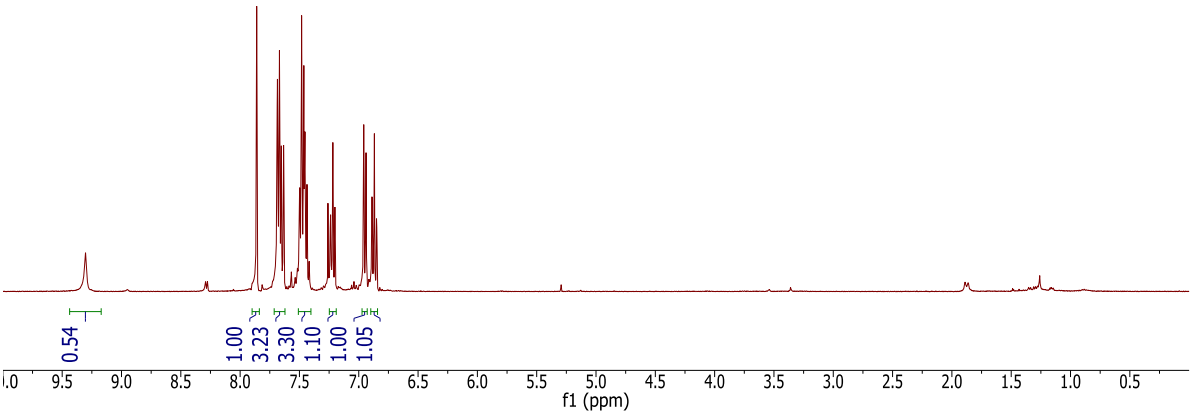


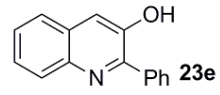
23d





23e





23e