Visible-light photoredox synthesis of internal alkynes containing quaternary carbons

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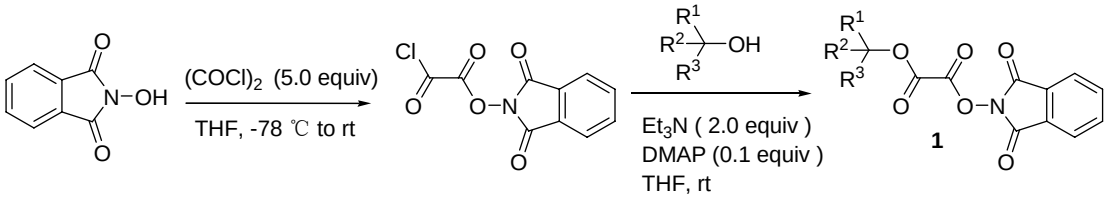
General experimental procedures

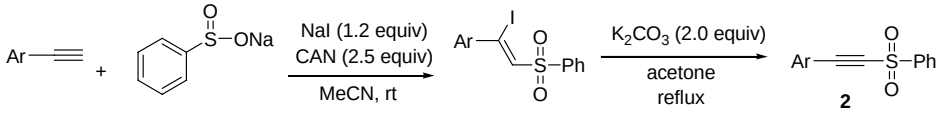
Reactions were carried out under Ar atmosphere in anhydrous solvents. All commercially reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) and products were obtained by column chromatography on silica gel. Proton magnetic resonance spectra (^{1}H NMR) were recorded in the solvent of $CDCl_3$ using tetramethylsilane (TMS) as the internal standard (^{1}H NMR: TMS at 0.00 ppm) and referencing to the residual proton resonance of $CDCl_3$ (7.26 ppm) and carbon magnetic resonance spectra (^{13}C NMR) were recorded in the solvent of $CDCl_3$ referencing to the carbon resonance of $CDCl_3$ (77.2 ppm).

General procedure for synthesis of tert-alkyl *N*-phthalimidoyl oxalates[1]



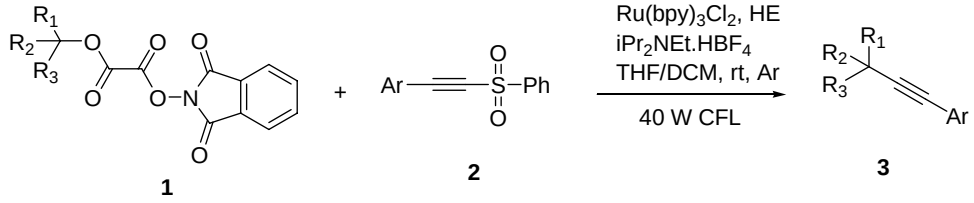
A round-bottom flask was charged with *N*-hydroxyphthalimide (12 mmol, 1.96 g), followed by the addition of THF (200 ml). The resulting solution was then cooled to –78 °C and oxalyl chloride (60 mmol, 5.20 ml) was added dropwise. The solution was then allowed to warm to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure to yield as a white solid. A round-bottom flask was charged with alcohol (2 mmol, 1.0 equiv), and DMAP (0.2 mmol, 24 mg) followed by the addition of Et_3N (4 mmol, 0.54 ml). Then, the chloro *N*-phthalimidoyl oxalate (4 mmol, 1.01 g) was dissolved in 50 ml THF and was added via cannula. The resulting heterogeneous mixture was allowed to stir at room temperature for 2 h. The volatiles were removed under reduced pressure, and the resulting crude residue was dissolved in a small quantity of CH_2Cl_2 then poured into a mass of hexanes. The resulting heterogeneous mixture was filtered through a cotton plug and washed with hexanes. The filtrate was concentrated under reduced pressure to provide **(1)**.

General procedure for synthesis of alkynyl sulfones[2]



To a mixture of arylacetylene (2 mmol), sodium benzenesulfinate (2.4 mmol, 394 mg) and NaI (2.4 mmol, 360 mg) in anhydrous MeCN was added a solution of CAN (5 mmol, 1100 mg) in the same solvent under an argon atmosphere and the reaction was stirred at room temperature overnight. After the completion of the reaction, the reaction mixture was extracted with CH_2Cl_2, and the CH_2Cl_2 layer was separated, washed with sat. $Na_2S_2O_3$, brine and dried over anhydrous Na_2SO_4. The residue after removing the solvent was refluxed with K_2CO_3 (4 mmol, 552 mg) in anhydrous acetone for about 3 hours. After the completion of the reaction, the reaction mixture was washed with H_2O and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo using a rotary evaporator, and the residue was purified by the chromatography to afford the target product **(2)** .

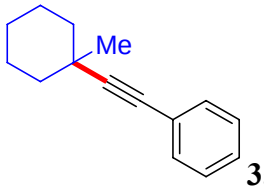
General procedure for synthesis of compounds 3a-ac and their characterization data.



Oxalate (**1**) (0.15 mmol), alkyne sulfone (**2**) (0.1 mmol), $Ru(bpy)_3Cl_2$ (1 μmol, 1 mg), Hantzsch ester (0.15 mmol, 38 mg), $^{i}Pr_2NEt{\cdot}HBF_4$ (0.12 mmol, 26 mmg) were added to a Schlenk tube charged with a magnetic stir bar. A mixed solvent of THF/CH_2Cl_2 (2 mL, 1:1) was added to the tube. The resulting solution was freezed with liquid nitrogen, and the tube was degassed by alternating vacuum evacuation then allowing it to warm to room temperature for three cycles. The tube was filled with argon and then sealed, and irradiated with a 40 W fluorescent lamp (approximately 2 cm away from the light source). After 8 h, the resulting solution was concentrated and purified

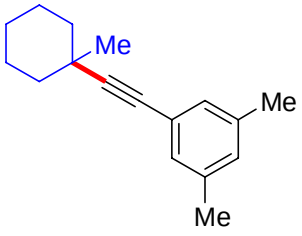
directly by silica gel column chromatography to give the desired product (**3a-ac**).

Characterization data of compounds 3a-ac



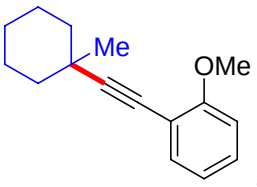
3a

1-(2-(1-Methylcyclohexyl)ethynyl)benzene (3a). Eluent: petroleum. Yield 17 mg (82%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.39 (m, 2H), 7.30-7.28 (m, 2H), 7.26-7.25 (m, 1H), 1.83-1.55 (m, 8H), 1.28 (s, 3H), 1.26-1.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.4, 96.9, 81.8, 39.6, 33.3, 30.4, 26.0, 23.5. EI-MS: M^+ m/z 198.2.



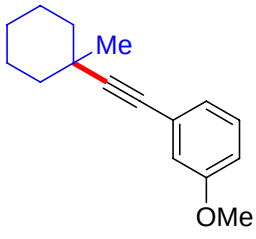
3b

1,3-Dimethyl-5-(2-(1-methylcyclohexyl)ethynyl)benzene (3b). Eluent: petroleum. Yield 13 mg (53%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05 (s, 2H), 6.90 (s, 1H), 2.28 (s, 6H), 1.83-1.57 (m, 8H), 1.27 (s, 3H), 1.22 (dd, 2H, J = 12.4 Hz, J = 3.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.7, 129.3, 129.3, 123.9, 96.1, 82.1, 40.0, 33.2, 30.4, 26.0, 23.5, 21.2. EI-MS: M^+ m/z 226.3.



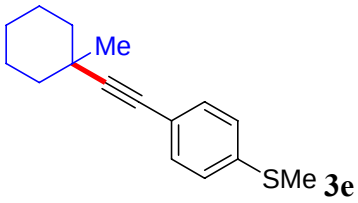
3c

1-Methoxy-2-(2-(1-methylcyclohexyl)ethynyl)benzene (3c). Eluent: petroleum. Yield 20 mg (84%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (dd, 2H, J = 7.5 Hz, J = 1.7 Hz), 6.91-6.82 (m, 2H), 3.87 (s, 3H), 1.92-1.50 (m, 8H), 1.30 (s, 3H), 1.29-1.22 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 133.5, 128.8, 120.4, 113.6, 110.9, 101.1, 77.9, 56.0, 39.7, 33.6, 30.3, 26.1, 23.5. EI-MS: M^+ m/z 228.3.



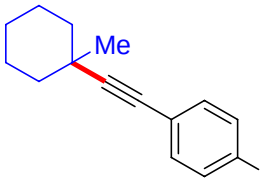
3d

1-Methoxy-3-(2-(1-methylcyclohexyl)ethynyl)benzene (3d). Eluent: petroleum. Yield 21 mg (89%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (t, 1H, *J* = 7.9 Hz), 7.01 (d, 1H, *J* = 7.5 Hz), 6.94 (s, 1H), 6.82 (dd, 1H, *J* = 8.3 Hz, *J* = 2.6 Hz), 3.80 (s,3H), 1.82 (d, 2H, *J* = 12.4 Hz), 1.76-1.57 (m, 6H), 1.28 (s, 3H), 1.23 (dd, 2H, *J* = 12.4 Hz, *J* = 3.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 129.3, 125.4, 124.3, 116.5, 114.1, 96.7, 81.8, 55.3, 39.6, 33.2, 30.3, 26.0, 23.5. EI-MS: M^+ m/z 228.3.



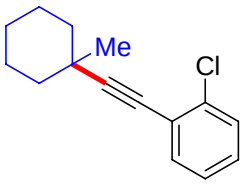
3e

Methyl(4-(2-(1-methylcyclohexyl)ethynyl)phenyl)sulfane (3e). Eluent: petroleum. Yield 10 mg (39%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (dd, 2H, *J* = 8.3 Hz, *J* = 2.7 Hz), 7.15 (dd, 2H, *J* = 8.2 Hz, *J* = 2.6 Hz), 2.47 (s, 3H), 1.79 (d, 2H, *J* = 12.8 Hz), 1.73-1.52 (m, 6H), 1.27 (s, 3H), 1.22-1.10 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.9, 132.0, 126.1, 120.9, 96.9, 81.5, 39.6, 33.3, 30.4, 26.0, 23.5, 15.8. EI-MS: M^+ m/z 244.1.



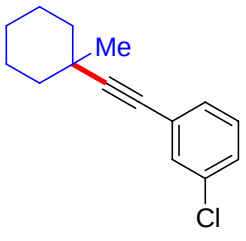
3f

1-Fluoro-4-(2-(1-methylcyclohexyl)ethynyl)benzene (3f). Eluent: petroleum. Yield 11 mg (48%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.35 (m, 2H), 6.99-6.94 (m, 2H), 1.79 (d, 2H, *J* = 12.7 Hz), 1.76-1.52 (m, 6H), 1.27 (s, 3H), 1.25-1.14 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 133.4, 120.4, 115.3, 96.4, 80.7, 39.6, 33.2, 30.3, 26.0, 23.5. EI-MS: M^+ m/z 216.3.



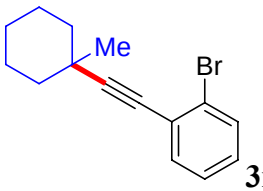
3g

1-Chloro-2-(2-(1-methylcyclohexyl)ethynyl)benzene (3g). Eluent: petroleum. Yield 18 mg (74%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.41 (m, 1H), 7.41-7.33 (m, 1H), 7.21-7.13 (m, 2H), 1.86-1.59 (m, 8H), 1.31 (s, 3H), 1.26-1.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 133.2, 129.2, 128.4, 126.3, 124.1, 102.6, 78.8, 39.5, 33.6, 30.3, 26.0, 23.5. EI-MS: M^+ m/z 232.3.



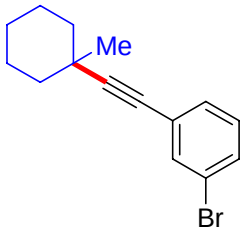
3h

1-Chloro-3-(2-(1-methylcyclohexyl)ethynyl)benzene (3h). Eluent: petroleum. Yield 21 mg (86%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (s, 1H), 7.29-7.27 (m, 1H), 7.22 (dd, 2H, J = 7.8 Hz, J = 4.4 Hz), 1.80 (d, 2H, J = 13.1 Hz), 1.71-1.65 (m, 6H), 1.27 (s, 3H), 1.23 (dd, 2H, J = 12.4 Hz, J = 3.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.0, 131.6, 129.8, 129.4, 127.7, 126.1, 98.3, 80.6, 39.5, 33.3, 30.2, 26.0, 23.5. EI-MS: M^+ m/z 232.1.



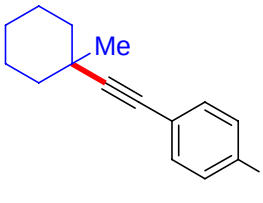
3i

1-Bromo-2-(2-(1-methylcyclohexyl)ethynyl)benzene (3i). Eluent: petroleum. Yield 19 mg (71%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (dd, 1H, J = 8.1 Hz, J = 1.1 Hz), 7.44 (dd, 1H, J = 7.7 Hz, J = 1.7 Hz), 7.22 (td, 1H, J = 7.5 Hz, J = 1.0 Hz), 7.10 (td, 1H, J = 7.6 Hz, J = 1.6 Hz), 1.88-1.58 (m, 8H), 1.31 (s, 3H), 1.28-1.20 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.3, 132.3, 128.6, 126.9, 126.3, 125.8, 102.0, 80.6, 39.5, 33.9, 30.3, 26.0, 23.5. EI-MS: M^+ m/z 276.2.



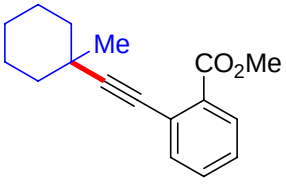
3j

1-Bromo-3-(2-(1-methylcyclohexyl)ethynyl)benzene (3j). Eluent: petroleum. Yield 20 mg (72%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, 1H, *J* = 1.1 Hz), 7.40-7.37 (m, 1H), 7.32 (dd, 1H, *J* = 7.6 Hz, *J* = 1.0 Hz), 7.14 (t, 1H, *J* = 7.9 Hz), 1.80 (d, 2H, *J* = 12.9 Hz), 1.73-1.59 (m, 6H), 1.27 (s, 3H), 1.25-1.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.5, 130.6, 130.2, 129.6, 126.4, 122.0, 98.4, 80.5, 39.5, 33.3, 30.2, 26.0, 23.5. EI-MS: M^+ m/z 276.0.



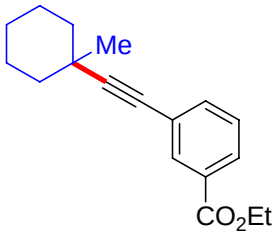
3k

1-Bromo-4-(2-(1-methylcyclohexyl)ethynyl)benzene (3k). Eluent: petroleum. Yield 17 mg (58%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (dd, 2H, *J* = 8.4 Hz, *J* = 2.2 Hz), 7.26 (dd, 2H, *J* = 4.5 Hz, *J* = 2.5 Hz), 1.79 (d, 2H, *J* = 12.6 Hz), 1.73-1.55 (m, 6H), 1.26 (s, 3H), 1.23-1.11 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.2, 131.4, 123.3, 121.4, 98.1, 80.8, 39.5, 33.3, 30.2, 26.0, 23.5. EI-MS: M^+ m/z 276.1.



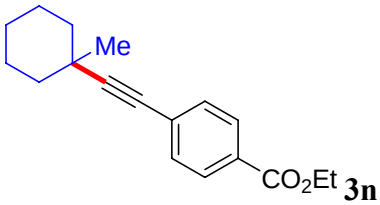
3l

Methyl 2-(2-(1-methylcyclohexyl)ethynyl)benzoate (3l). Eluent: petroleum. Yield 22 mg (84%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (dd, 1H, *J* = 7.8 Hz, *J* = 1.2 Hz), 7.51 (dd, 1H, *J* = 7.8 Hz, *J* = 1.1 Hz), 7.43-7.39 (m, 1H), 7.32-7.28 (m, 1H), 3.91 (s, 3H), 1.78-1.57 (m, 8H), 1.30 (s, 3H), 1.25-1.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5, 134.7, 132.3, 131.4, 130.2, 127.2, 124.4, 102.2, 80.4, 52.1, 39.5, 33.6, 30.3, 26.0, 23.5. EI-MS: M^+ m/z 256.3.



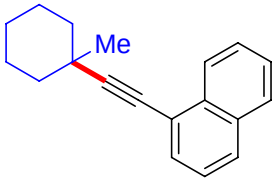
3m

Methyl 3-(2-(1-methylcyclohexyl)ethynyl)benzoate (3m). Eluent: petroleum. Yield 25 mg (92%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07-8.06 (m, 1H), 7.93-7.91 (m, 1H), 7.58-7.56 (m, 1H), 7.35 (t, 1H, *J* = 7.8 Hz), 4.38 (q, 2H, *J* = 7.1 Hz), 1.83-1.59 (m, 8H), 1.40 (t, 3H, *J* = 7.1 Hz), 1.28 (s, 3H), 1.26-1.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 135.8, 132.7, 130.6, 128.4, 128.3, 124.7, 97.9, 81.0, 61.2, 39.5, 33.3, 30.3, 26.0, 23.5, 14.4. EI-MS: M^+ m/z 270.3.



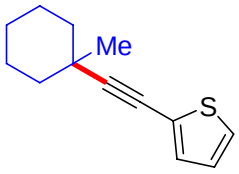
3n

Ethyl 4-(2-(1-methylcyclohexyl)ethynyl)benzoate (3n). Eluent: petroleum. Yield 24 mg (85%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.3 Hz), 4.37 (q, 2H, *J* = 7.1 Hz), 1.82 (d, 2H, *J* = 12.8 Hz), 1.79-1.52 (m, 6H), 1.39 (q, 3H, *J* = 7.1 Hz), 1.28 (s, 3H), 1.24 (dd, 2H, *J* = 12.3 Hz, *J* = 3.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 131.5, 129.4, 129.1, 129.1, 100.3, 81.4, 61.1, 39.5, 33.4, 30.2, 26.0, 23.5, 14.4. EI-MS: M^+ m/z 270.4.



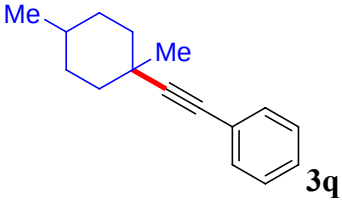
3o

1-(2-(1-Methylcyclohexyl)ethynyl)naphthalene (3o). Eluent: petroleum. Yield 19 mg (73%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, 1H, *J* = 8.3 Hz), 7.81 (dd, 2H, *J* = 24.8 Hz, *J* = 8.1 Hz), 7.65 (d, 1H, *J* = 7.2 Hz), 7.61-7.46 (m, 2H), 7.43-7.39 (m, 1H), 1.97-1.66 (m, 8H), 1.41 (s, 3H), 1.39-1.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.6, 133.3, 130.1, 128.3, 127.9, 126.6, 126.4, 126.3, 125.3, 122.0, 102.1, 79.7, 39.8, 33.8, 30.7, 26.1, 23.7. EI-MS: M^+ m/z 248.4.



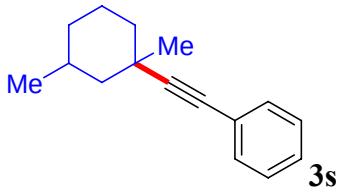
3p

2-(2-(1-Methylcyclohexyl)ethynyl)thiophene (3p). Eluent: petroleum. Yield 10 mg (44%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (dd, 1H, J = 3.0 Hz, J = 1.1 Hz), 7.25-7.20 (m, 1H), 7.08 (dd, 1H, J = 4.9 Hz, J = 1.1 Hz), 1.79 (d, 2H, J = 12.9 Hz), 1.76-1.54 (m, 6H), 1.26 (s, 3H), 0.93-0.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 130.3, 127.3, 125.0, 123.3, 96.3, 84.6, 39.6, 33.3, 29.8, 26.0, 23.5. EI-MS: M^+ m/z 204.1.



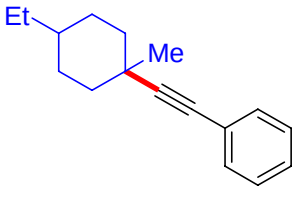
3q

1-(2-(1,4-Dimethylcyclohexyl)ethynyl)benzene (3q). Eluent: petroleum. Yield 17 mg (77%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.35 (m, 2H), 7.30-7.25 (m, 3H), 1.82 (d, 2H, J = 12.7 Hz), 1.61-1.54 (m, 2H), 1.47-1.37 (m, 4H), 1.27 (s, 3H), 1.26-1.22 (m, 1H), 0.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.4, 96.6, 82.0, 39.7, 33.0, 32.5, 32.3, 30.5, 22.7. EI-MS: M^+ m/z 212.2.



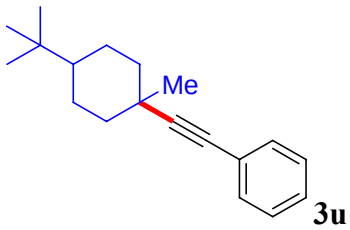
3s

1-(2-(1,3-Dimethylcyclohexyl)ethynyl)benzene (3s). Eluent: petroleum. Yield 16 mg (71%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (dt, 2H, J = 4.2 Hz, J = 2.5 Hz), 7.33-7.20 (m, 3H), 1.92-1.55 (m, 6H), 1.28 (s, 3H), 1.18-1.07 (m, 1H), 0.91 (s, 3H), 0.91-70.89 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 128.2, 127.4, 124.4, 96.5, 82.2, 48.21, 39.30, 34.83, 33.75, 30.83, 29.63, 23.63, 22.64. EI-MS: M^+ m/z 212.3.



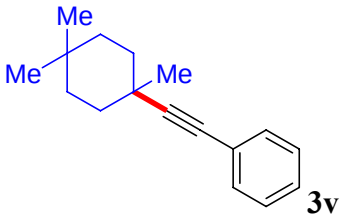
3t

1-(2-(4-Ethyl-1-methylcyclohexyl)ethynyl)benzene (3t). Eluent: petroleum. Yield 14 mg (61%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.32 (m, 2H), 7.31-7.26 (m, 3H), 1.88-1.81 (m, 2H), 1.65 (dd, 2H, *J* = 13.5 Hz, *J* = 3.2 Hz), 1.44-1.33 (m, 2H) 1.28 (s, 3H), 1.24 (dd, 4H, *J* = 13.2 Hz, *J* = 8.7 Hz), 1.08 (m, 1H), 0.89 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 128.2, 127.4, 124.4, 96.7, 82.0, 39.6, 39.2, 33.4, 30.5, 29.9, 29.8, 11.6. EI-MS: M^+ m/z 226.2.



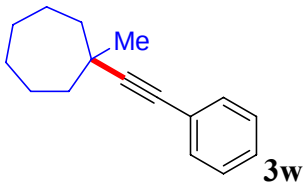
3u

1-(2-(4-*tert*-Butyl-1-methylcyclohexyl)ethynyl)benzene (3u). Eluent: petroleum. Yield 22 mg (84%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.38 (m, 2H), 7.28-7.25 (m, 3H), 1.88 (d, 2H, *J* = 13.0 Hz), 1.66 (d, 2H, *J* = 13.4 Hz), 1.52 (dd, 2H, *J* = 12.6 Hz, *J* = 2.7 Hz), 1.52-1.50 (m, 1H), 1.27 (s, 3H), 1.21 (dd, 2H, *J* = 12.9 Hz, *J* = 3.2 Hz), 0.89 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 128.2, 127.4, 124.4, 96.5, 82.2, 47.7, 40.1, 33.2, 32.5, 30.3, 27.7, 24.4. EI-MS: M^+ m/z 254.4.



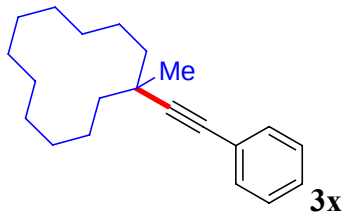
3v

1-(2-(1,4,4-Trimethylcyclohexyl)ethynyl)benzene (3v). Eluent: petroleum. Yield 17 mg (73%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.37 (m, 2H), 7.29-7.24 (m, 3H), 1.66 (dd, 4H, *J* = 16.3 Hz, *J* = 6.7 Hz), 1.44 (dd, 2H, *J* = 15.2 Hz, *J* = 11.9 Hz), 1.30 (s, 3H), 1.29-1.22 (m, 2H), 0.95 (s, 3H), 0.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.3, 96.7, 81.5, 36.4, 35.5, 33.0, 32.5, 30.0, 29.7. EI-MS: M^+ m/z 226.4.



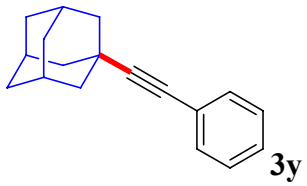
3w

1-Methyl-1-(2-phenylethynyl)cycloheptane (3w). Eluent: petroleum. Yield 18 mg (82%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.39 (m, 2H), 7.31-7.26 (m, 3H), 1.81 (dd, 2H, *J* = 7.6 Hz, *J* = 5.9 Hz), 1.76-1.51 (m, 10H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.3, 98.0, 81.1, 42.3, 36.1, 31.4, 28.3, 24.0. EI-MS: M^+ m/z 212.4.



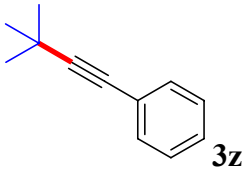
3x

1-Methyl-1-(2-phenylethynyl)cyclododecane (3x). Eluent: petroleum. Yield 23 mg (79%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.36 (m, 2H), 7.27-7.24 (m, 3H), 1.64-1.36 (m, 22H), 1.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.3, 96.3, 80.5, 34.9, 34.3, 27.4, 26.5, 26.2, 22.6, 22.2, 19.9. EI-MS: M^+ m/z 282.1.



3y

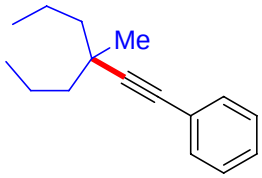
(3r,5r,7r)-1-(Phenylethynyl)adamantane (3y). Eluent: petroleum. Yield 9 mg (35%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, 2H, *J* = 8.5 Hz), 7.26-7.20 (m, 3H), 1.96 (s, 6H), 1.73-1.72 (m, 6H), 1.56 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 126.9, 98.5, 79.4, 43.0, 36.5, 28.7, 28.1. EI-MS: M^+ m/z 236.0.



3z

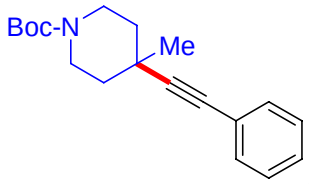
1-(3,3-Dimethylbut-1-ynyl)benzene (3z). Eluent: petroleum. Yield 7 mg (41%).

Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.32 (m, 2H), 7.30-7.26 (m, 3H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 128.2, 127.5, 121.1, 95.1, 79.9, 31.2, 29.8. EI-MS: M^+ m/z 158.3.



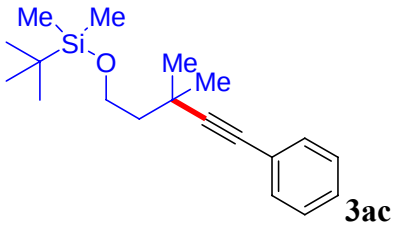
3aa

1-(3-Methyl-3-propylhex-1-ynyl)benzene (3aa). Eluent: petroleum. Yield 16 mg (72%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.33 (m, 2H), 7.29-7.25 (m, 3H), 1.53-1.38 (m, 8H), 1.22 (s, 3H). 0.95 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.2, 127.4, 124.3, 98.0, 81.1, 42.3, 36.1, 31.4, 28.3, 24.0. EI-MS: M^+ m/z 214.3.



3ab

***tert*-Butyl 4-methyl-4-(2-phenylethynyl)piperidine-1-carboxylate (3ab).** Eluent: petroleum. Yield 21 mg (69%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.37 (m, 2H), 7.31-7.27 (m, 3H), 4.04-3.99 (m, 2H), 3.17-3.11 (m, 4H), 1.75 (d, 2H, J = 12.4 Hz), 1.46 (s, 9H), 1.45-1.39 (m, 2H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 131.7, 128.3, 127.9, 123.6, 94.1, 79.4, 38.5, 33.5, 32.0, 29.7, 28.6. HRESI-MS: calcd for $C_{19}H_{26}NO_2^+$ $[M+H]^+$ m/z 300.1964; found, 300.11969.

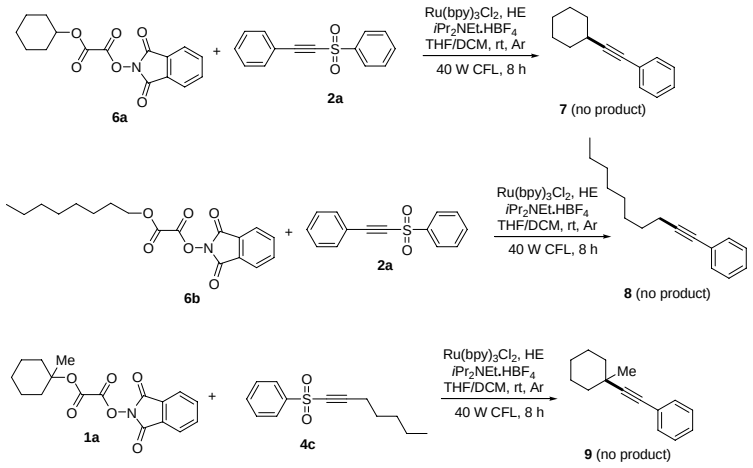


3ac

(3,3-Dimethyl-5-phenylpent-4-ynyloxy)(tert-butyl)dimethylsilane (3ac). Eluent: petroleum. Yield 20 mg (65%). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.26 (m, 5H), 3.94-3.83 (m, 2H), 1.83-1.71 (m, 2H), 1.31 (s, 6H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 128.2, 127.6, 124.0, 96.7, 80.7, 61.1, 45.7, 30.4, 29.9, 26.1, 18.4, 1.0. HRESI-MS: calcd for $C_{19}H_{31}OSi^+$ $[M+H]^+$ m/z

303.2144; found, 303.2136.

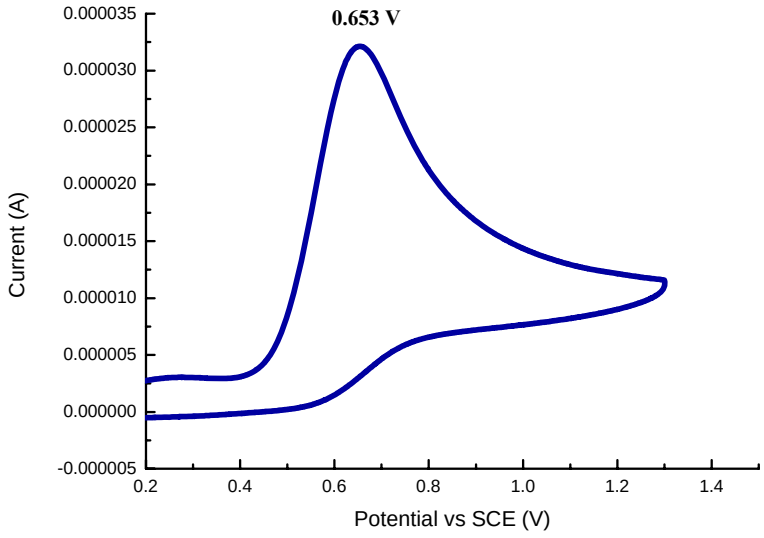
Extending experiments



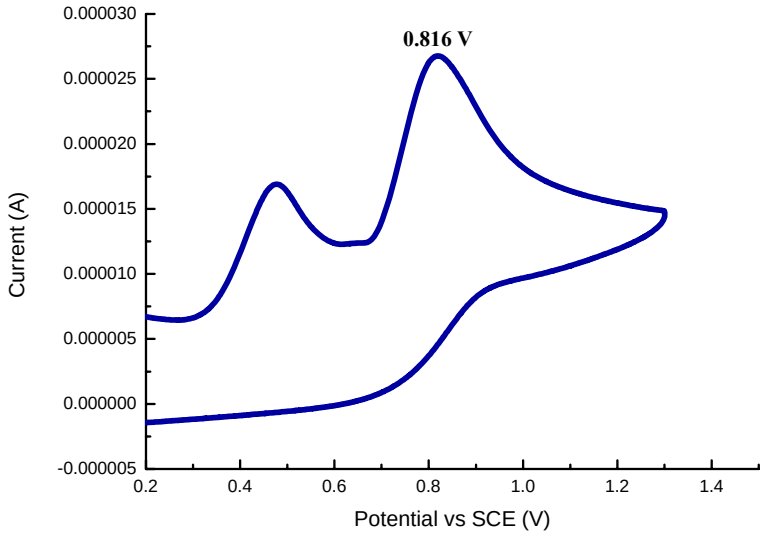
Cyclic voltammetry data

Cyclic voltammetry was performed using a CH Instruments Electrochemical Analyzer, a glassy carbon working electrode, a platinum mesh counter electrode, and a $Ag/AgNO_3$ (0.01M) reference electrode. Samples were prepared with a substrate concentration of 0.01 M in a 0.1 M tetraethylammonium hexafluorophosphate in acetonitrile electrolyte solution. Data was collected with a sweep rate of 100 mV/s.

Oxidation potential vs SCE (V) for DIPEA



Oxidation potential vs SCE (V) for HE



Fluorescent quenching experiments.

Quantum yield of $[Ru(bpy)_3]^{2+}$ have been reported by some research groups: 0.042-0.055 in H_2O[3] and 0.059-0.090 in CH_3CN.[4]

Reagent: $Ru(bpy)_3Cl_2$ was dissolved in DMF, the concentration of the solutions reached 10^{-5}mol/l. It was a standard solution. Hantzsch ester was dissolved in DMF, the concentration of the solutions reached 10^{-1}mol/l. It was a standard solution. $^{i}Pr_2NEt{\cdot}HBF_4$ was dissolved in DMF, the concentration of the solutions reached 10^{-1}mol/l. It was a standard solution.

Experiment:

UV-visible spectrum measurement ($Ru(bpy)_3Cl_2$)

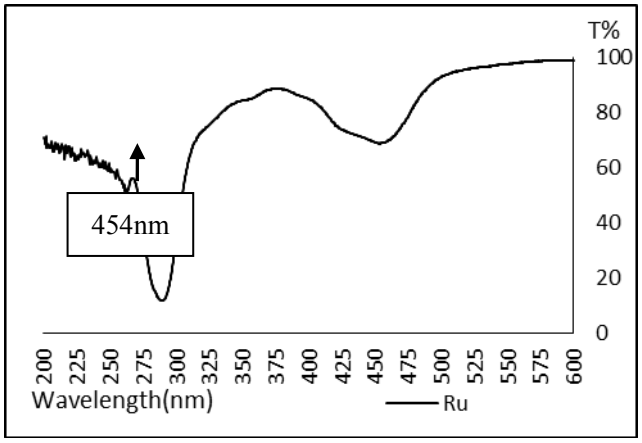


Fig **1** Absorption spectra of popop and $Ru(bpy)_3Cl_2$.

Fluorescence spectrum measurement

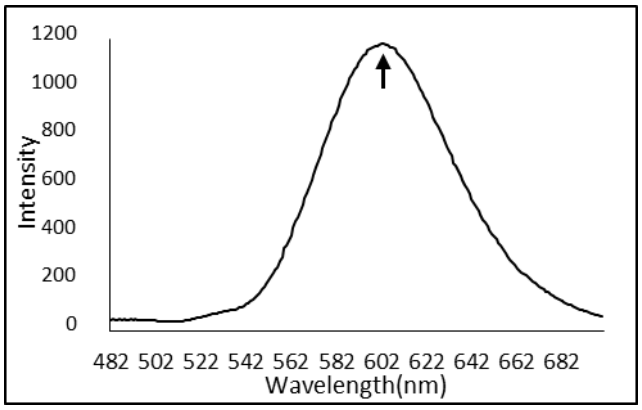


Fig **2** Fluorescence spectra of $Ru(bpy)_3Cl_2$.

Scan mode: Emission; EX Slit: 5.0 nm; EX WL: 454.0 nm; It's excitation spectral lines **λmax: 605 nm**

Fluorescence spectrum measurement

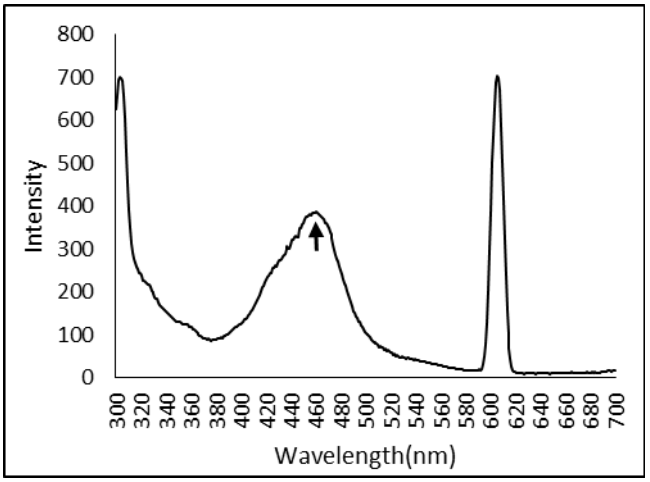


Fig **3** Fluorescence spectra of $Ru(bpy)_3Cl_2$.

Scan mode: Excitation; EX Slit: 5.0 nm; EX WL: 605.0 nm; It's excitation spectral lines **λmax: 460nm**

Fluorescence quenching

The fluorescence intensity were measured in the presence of different five concentrations (0.8×10^{-2}mol/l, 1.4×10^{-2}mol/l, 2.0×10^{-2}mol/l, 2.4×10^{-2}mol/l, 3.2×10^{-2}mol/l *i*$Pr_2NEt.HBF_4$), obtain a set of corresponding concentration fluorescence quenching

spectra.

The fluorescence intensity were measured in the presence of different five concentrations (0.8×10^{-2}mol/l, 1.4×10^{-2}mol/l, 2.0×10^{-2}mol/l, 2.4×10^{-2}mol/l, 3.2×10^{-2}mol/l Hantzsch ester), obtain a set of corresponding concentration fluorescence quenching spectra.

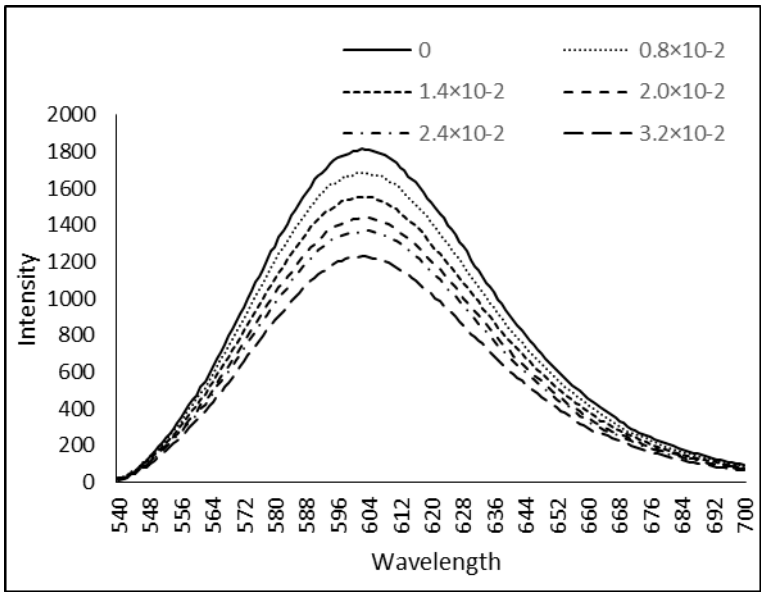


Fig **4** Fluorescence quenching of $Ru(bpy)_3Cl_2$ by various concentrations of $^{i}Pr_2NEt.HBF_4$.(Scan mode: Emission; EX Slit: 5.0 nm; EX WL: 460.0 nm.)

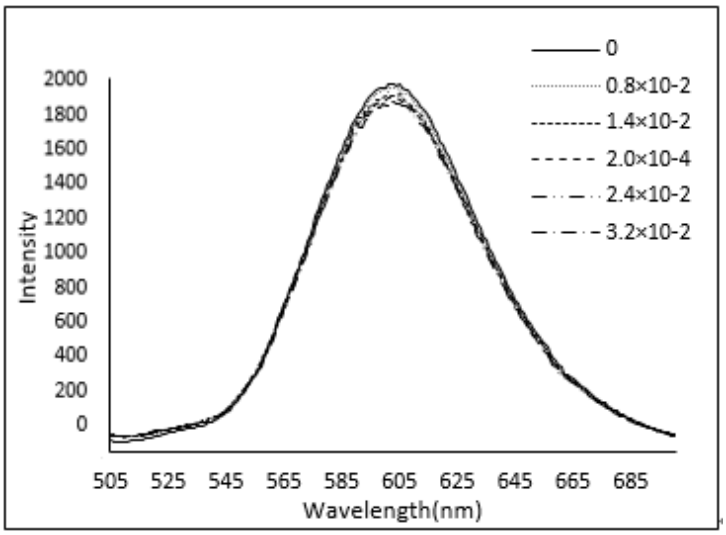


Fig **5** Fluorescence quenching of $Ru(bpy)_3Cl_2$ by various concentrations of HE.(Scan mode: Emission; EX Slit: 5.0 nm; EX WL: 460.0 nm.)

From figure 4/5, when we added different concentrations of $^{i}Pr_2NEt.HBF_4$, the

fluorescence intensity weakened regularly. But when we added different concentrations of HE, the fluorescence intensity didn't have significant change. Obviously, *i*$Pr_2NEt.HBF_4$ was a quencher in this experiment.

According to the above data, we thought the Stern−Volme plot for the fluorescence quenching of $Ru(bpy)_3Cl_2$ by various concentrations of $^{i}Pr_2NEt.HBF_4$ .We can see from the graph, I_0/I had a good linear relationship with [Q].

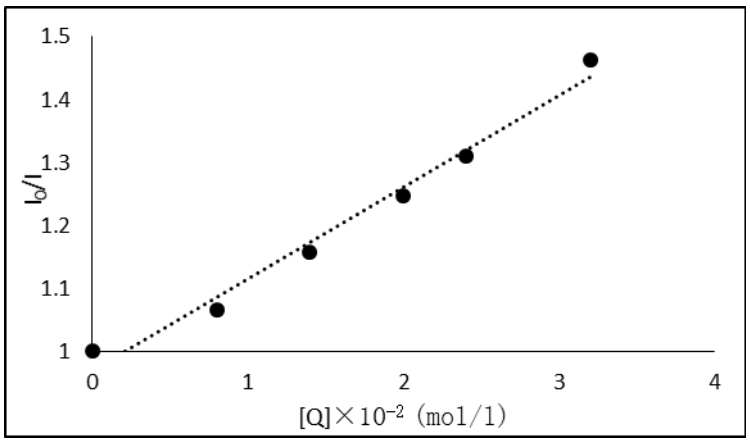
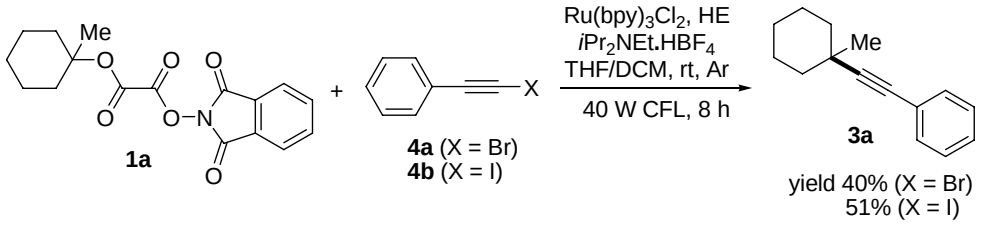


Fig 6 Sterm-Volmer plots for the fluorescence quenching of $Ru(bpy)_3Cl_2$ by various concentrations of $^{i}Pr_2NEt{\cdot}HBF_4$.

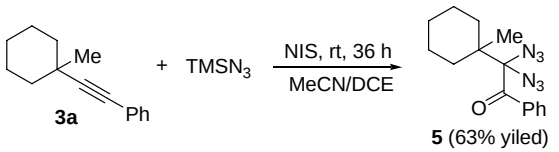
Coupling of 1a with 1-(2-bromoethynyl)benzene or 1-(2-iodoethynyl)benzene



Oxalate (**1a**) (0.15 mmol), 1-(2-bromoethynyl)benzene (**4a**) or 1-(2-iodoethynyl)benzene (**4b**) (0.1 mmol), $Ru(bpy)_3Cl_2$ (1 μmol, 1 mg), Hantzsch ester (0.15 mmol, 38 mg), $^{i}Pr_2NEt{\cdot}HBF_4$ (0.12 mmol, 26 mmg) were added to a Schlenk tube charged with a magnetic stir bar. A mixed solvent of THF/CH_2Cl_2 (2 mL, 1:1) was added to the tube. The resulting solution was freezed with liquid nitrogen, and the tube was degassed by alternating vacuum evacuation then allowing it to warm to room temperature for three cycles. The tube was filled with argon and then sealed, and irradiated with a 40 W fluorescent lamp (approximately 2 cm away from the light

source). After 8 h, the resulting solution was concentrated and purified directly by silica gel column chromatography to give the desired product (**3a**).

Synthesis of compounds 5.



5 (63% yiled)

To a solution of alkyne (**3a**) (0.2 mmol) in MeCN/DCE (1.0 mL/1.0 mL) was added $TMSN_3$ (0.44 mmol, 57.76 μl), and NIS (0.22 mmol, 49.5 mg) and stirred at room temperature under nitrogen. The reaction was monitored by TLC to establish completion. 10% $Na_2S_2O_3$ solution was added to the reaction mixture and extracted with ethyl acetate. The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated at the reduced pressure. Column chromatography on silica gel using hexane/ethyl acetate as an eluent afforded coupling product (**5**). Yield 38 mg (63%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.77 (m, 2H), 7.47-7.44 (m,3H), 1.60 (d, 2H, J = 12.8 Hz), 1.49-1.41 (m, 6H), 1.06 (s, 3H), 1.02-0.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.2, 133.7, 133.2, 130.4, 128.4, 88.5, 49.5, 34.3, 32.2, 27.0, 25.5. EI-MS: M^+ m/z 298.1.

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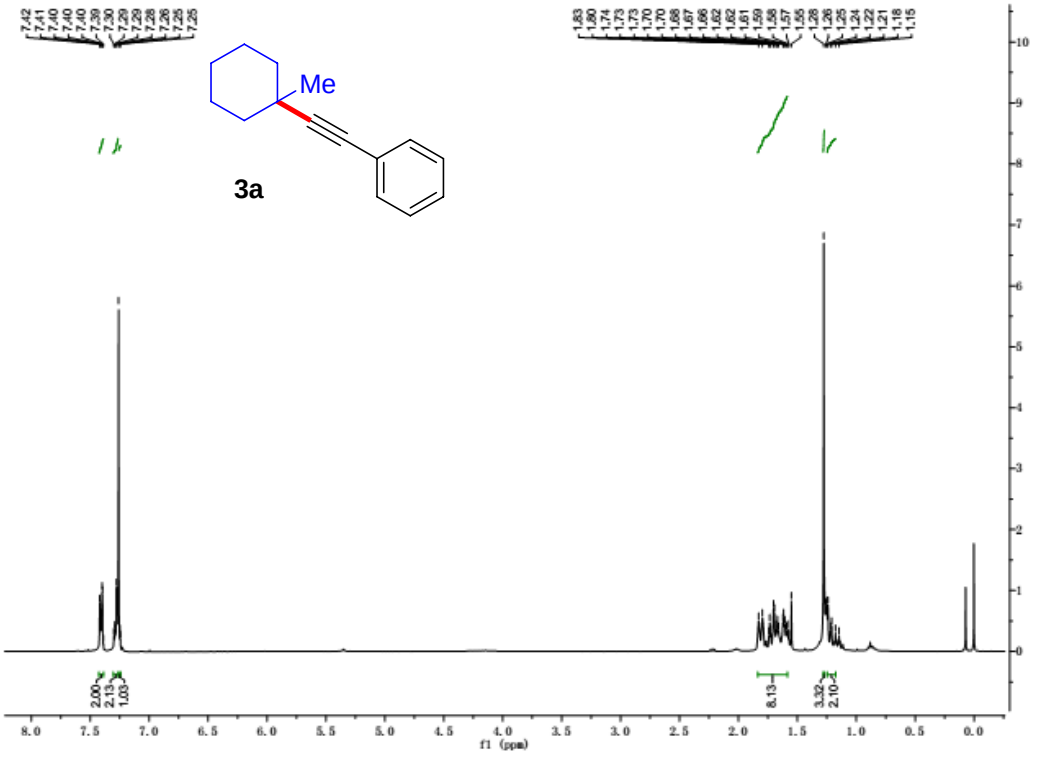
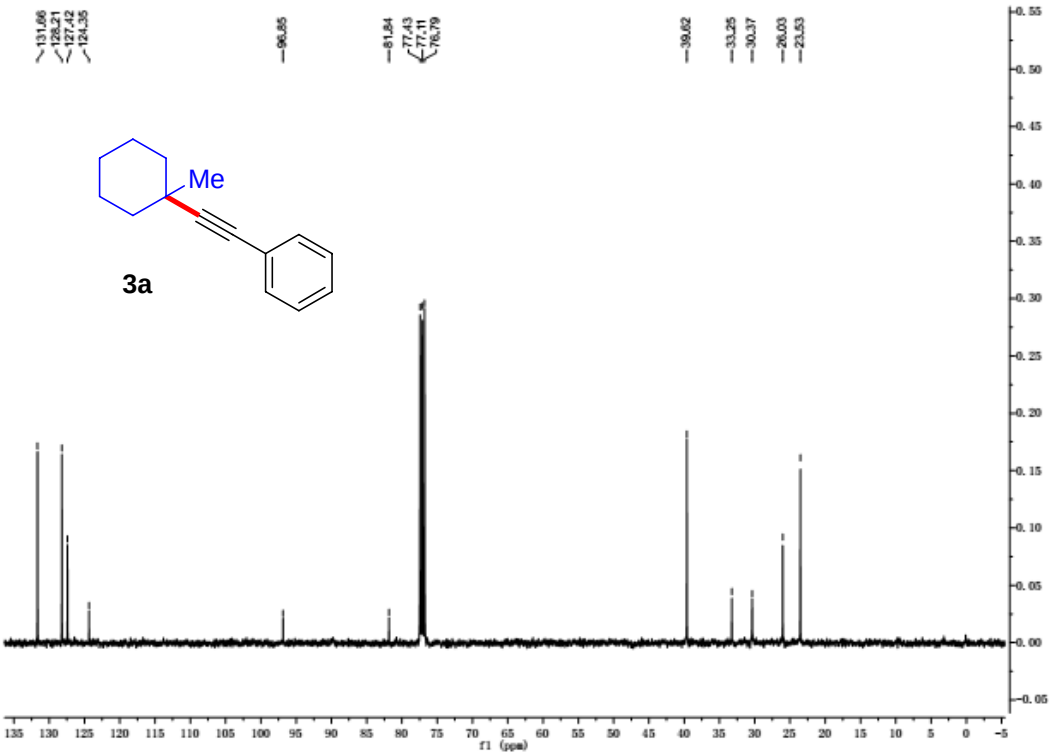
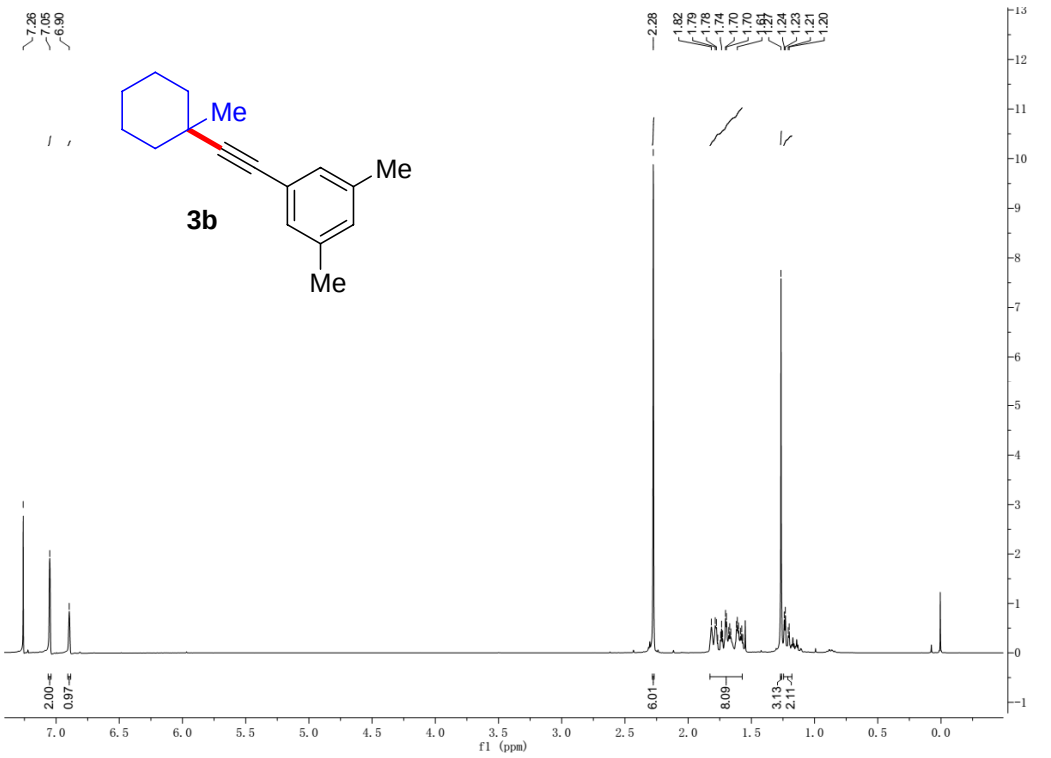
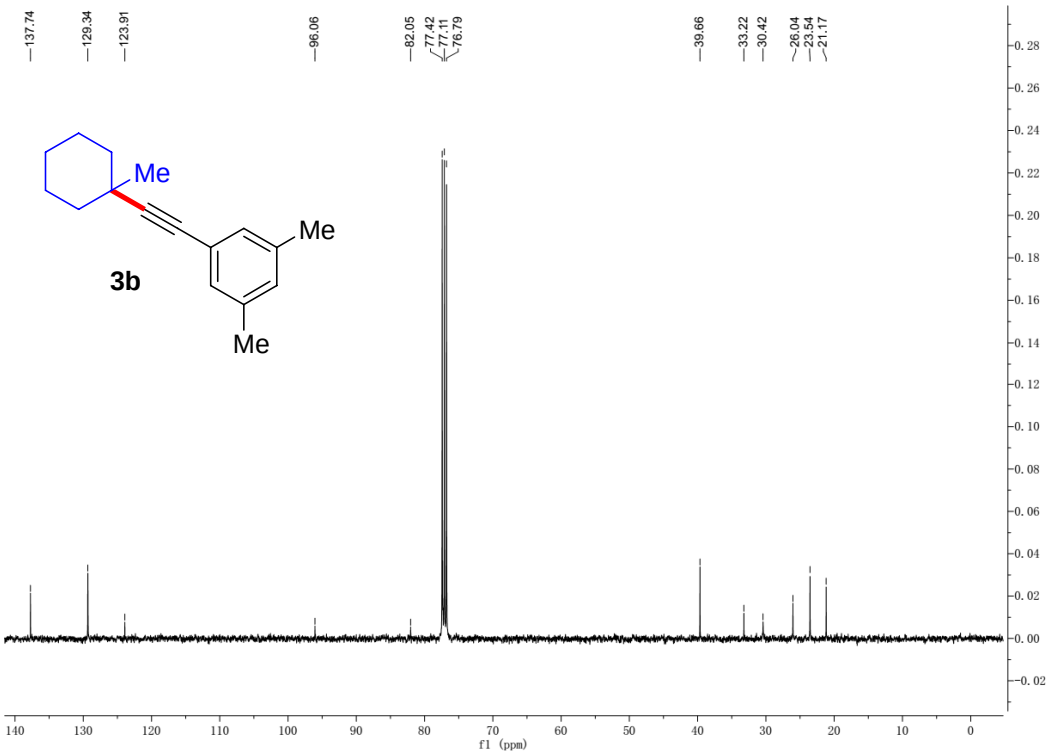
The ^{1}H and ^{13}C NMR spectra of compounds 3a-ac






7.26
7.05
6.90
2.28
1.82
1.79
1.78
1.74
1.70
1.70
1.61
1.27
1.24
1.23
1.21
1.20
Me
Me
Me
3b
2.00
0.97
6.01
8.09
3.13
2.11
f1 (ppm)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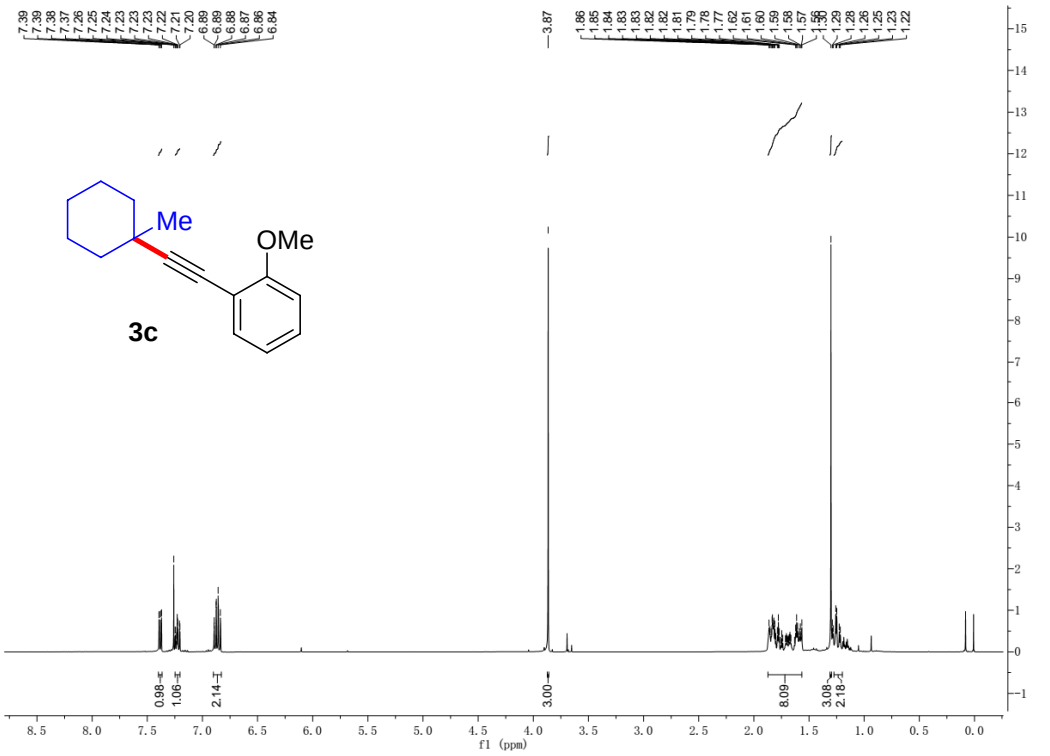
30.42
26.04
23.54
21.17
Me
Me
Me
3b
f1 (ppm)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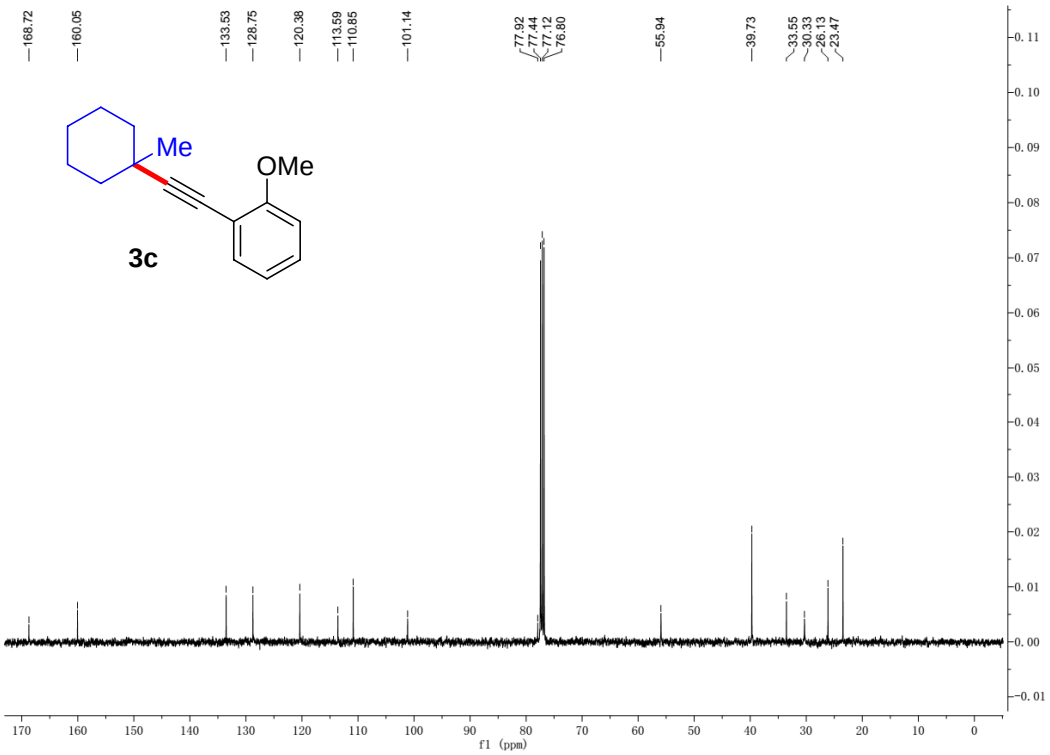
OMe
3c
f1 (ppm)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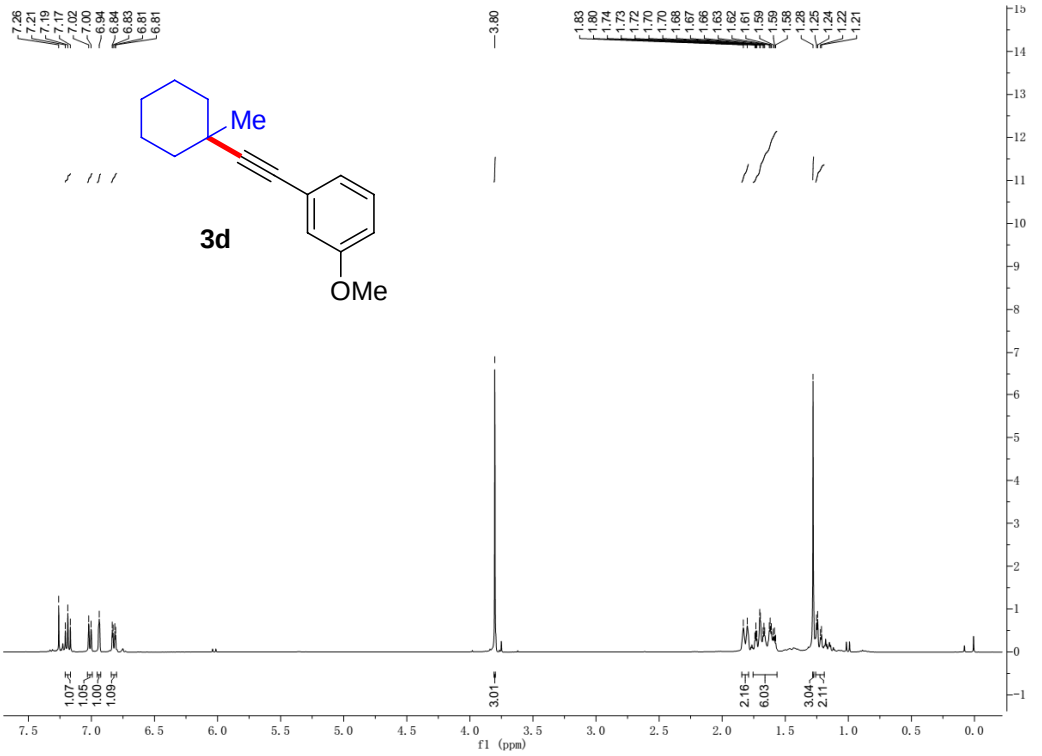
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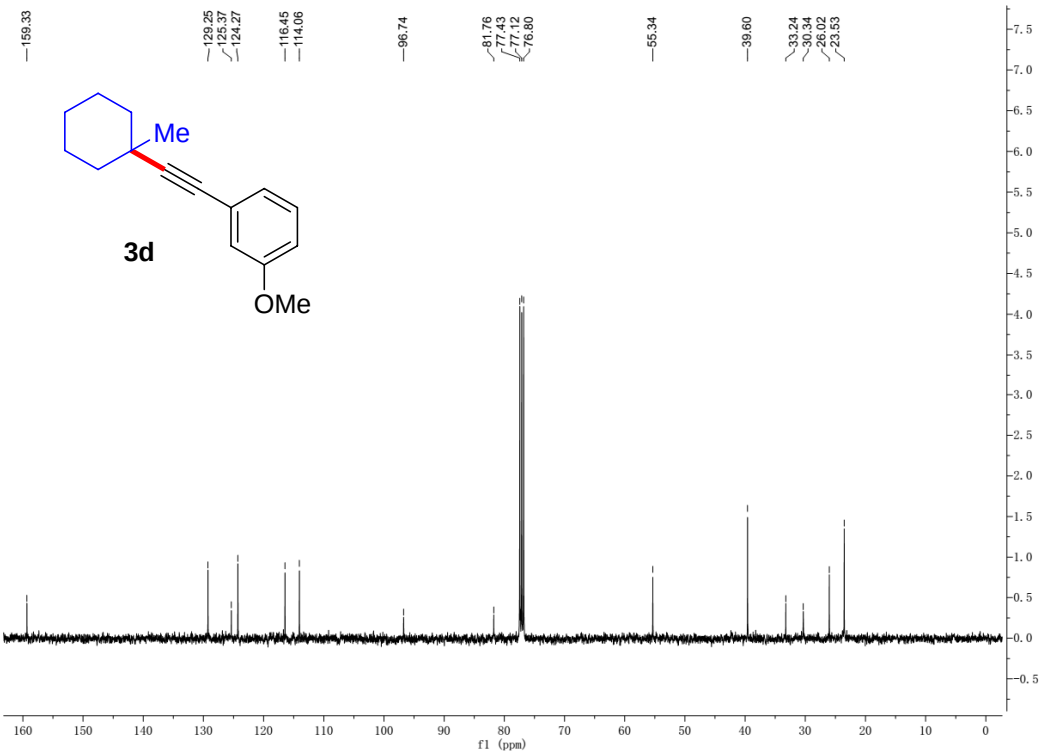
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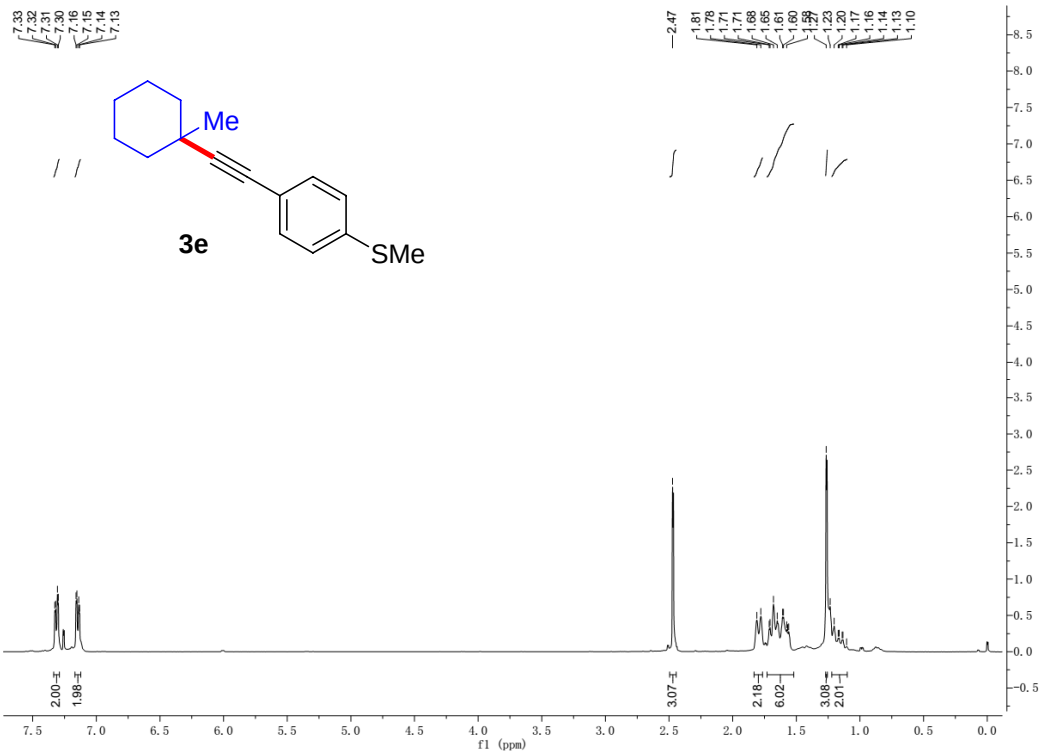
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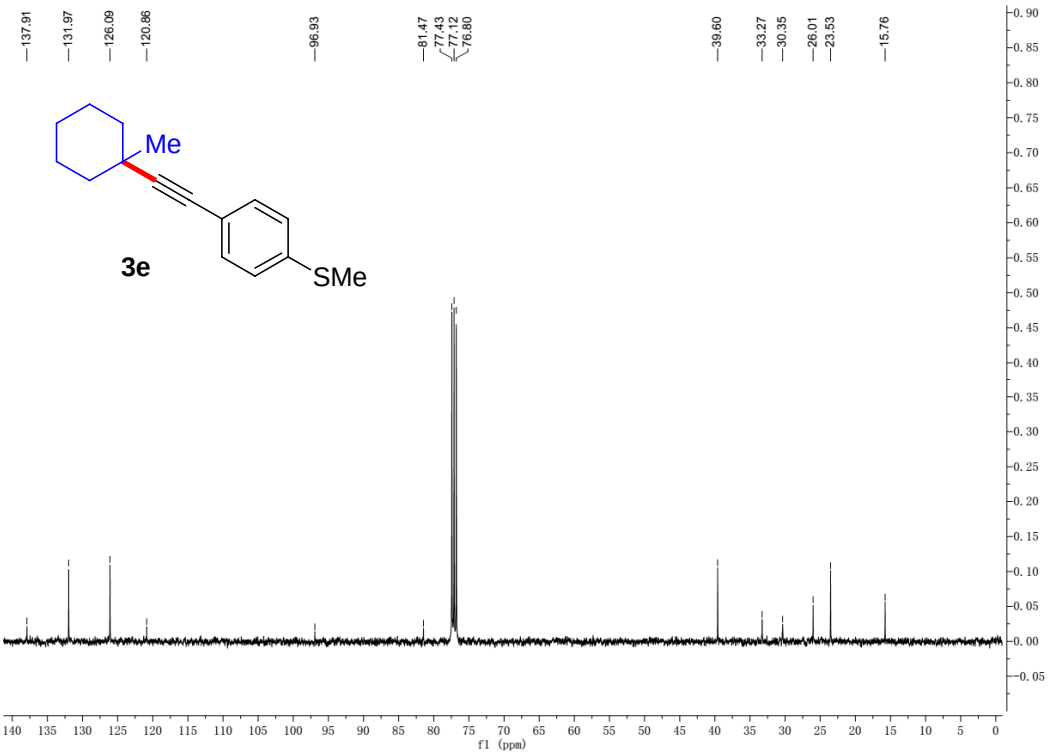
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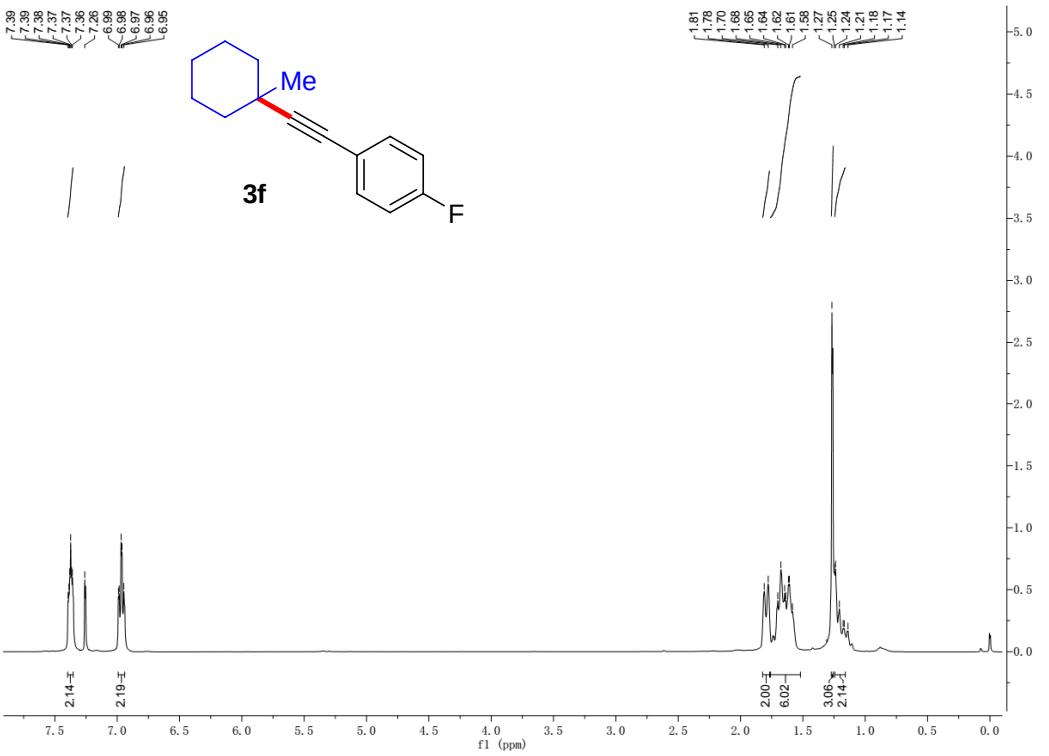
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F
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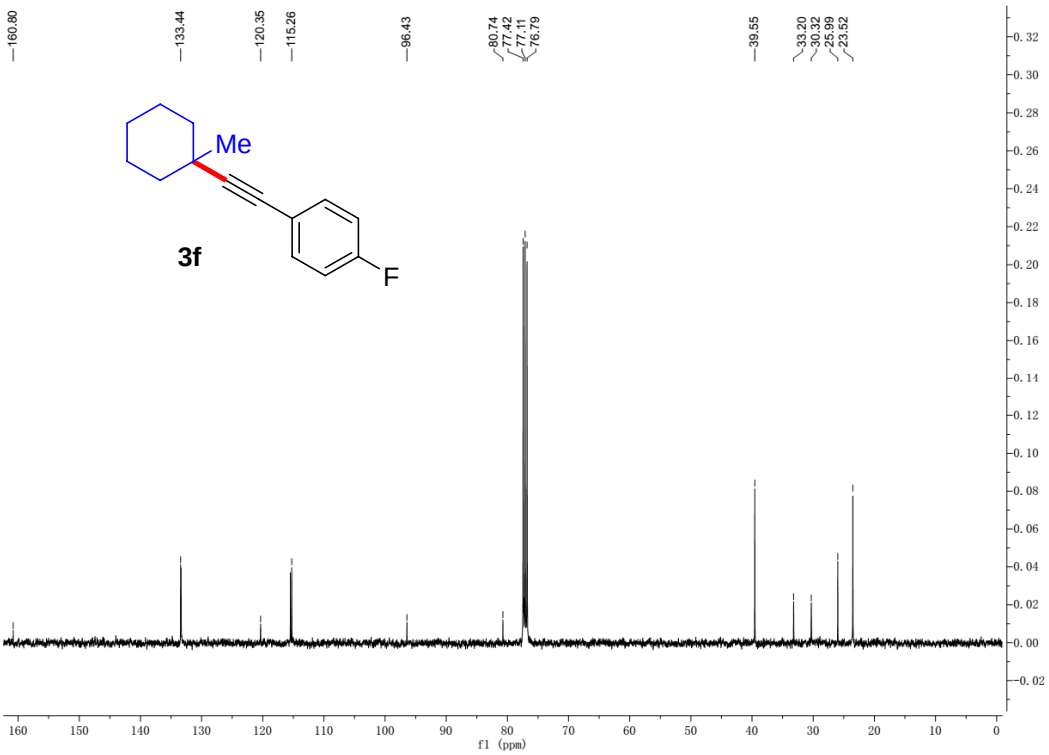
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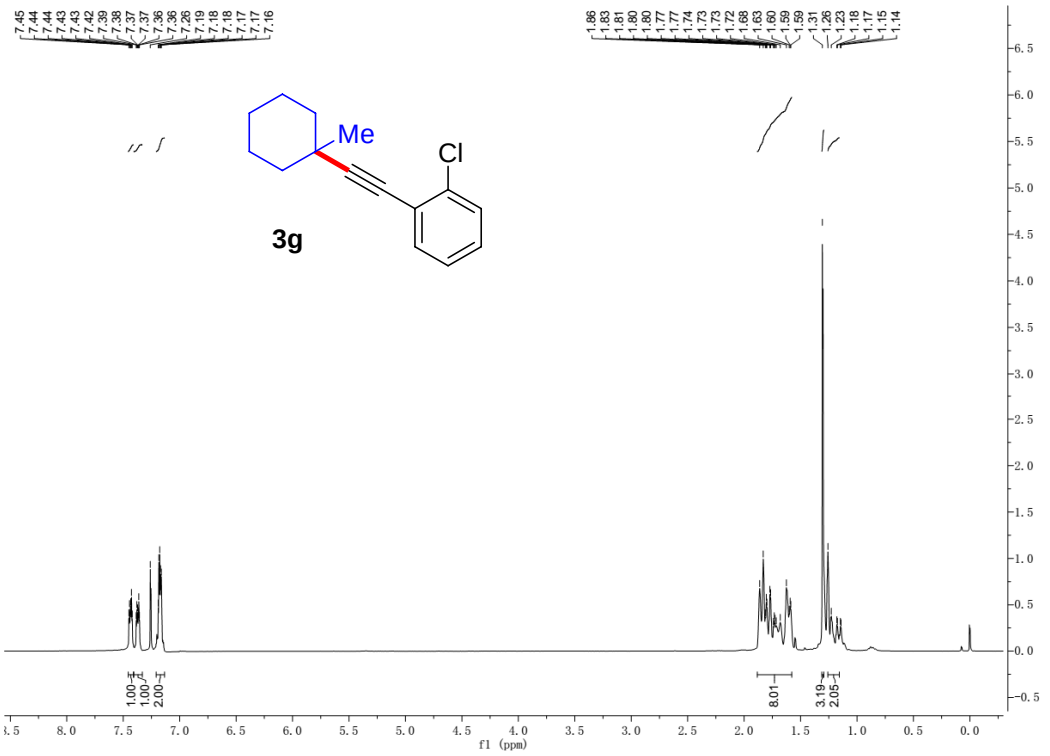
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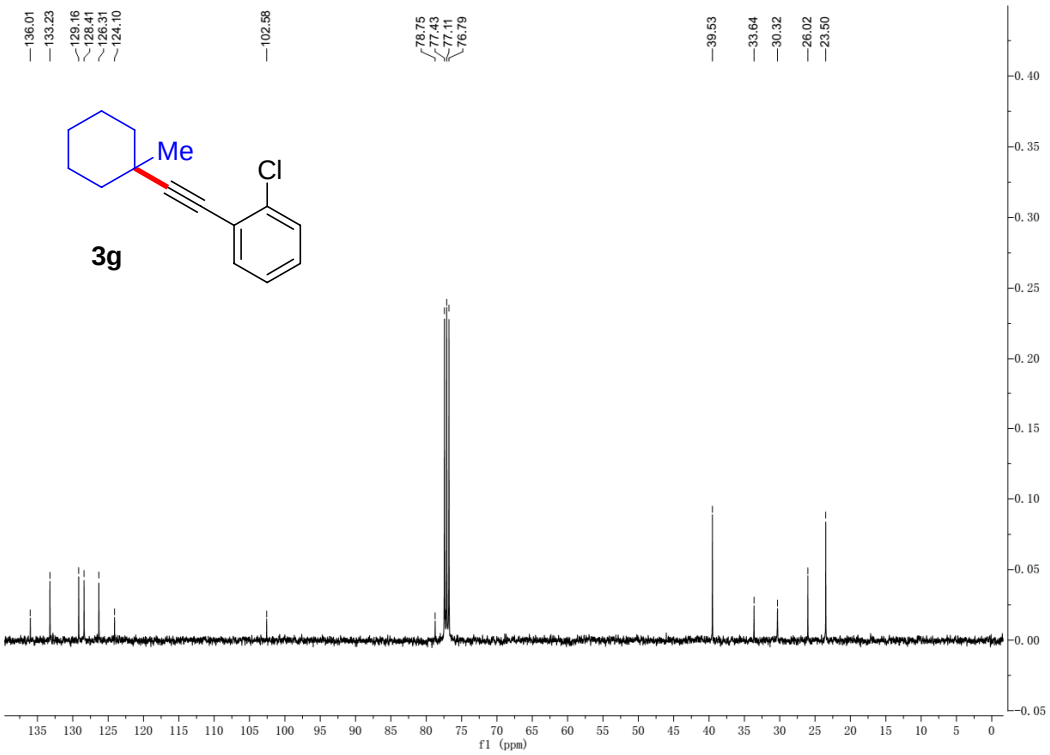
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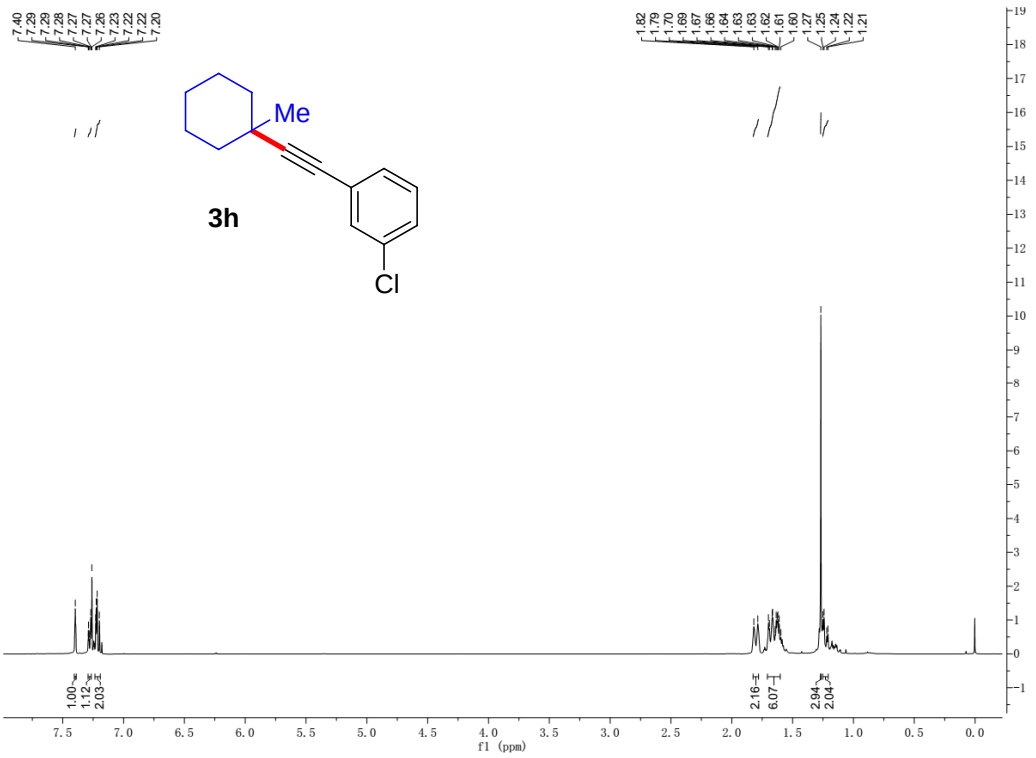
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1.70
1.69
1.67
1.66
1.64
1.63
1.63
1.62
1.61
1.60
1.27
1.25
1.24
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3h
Cl
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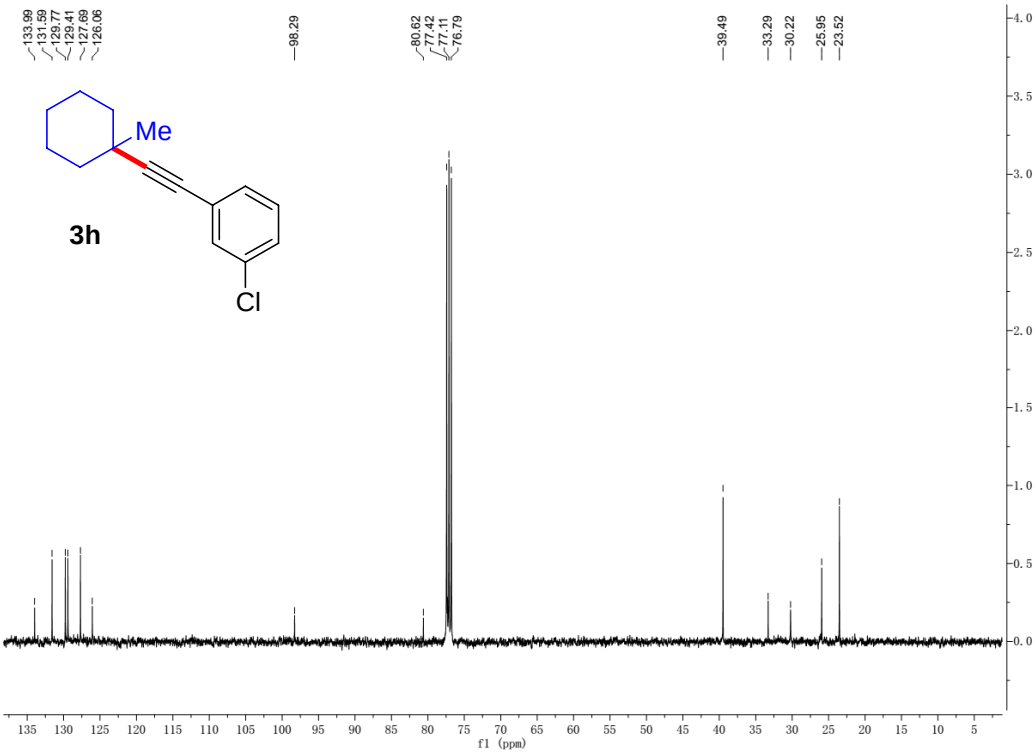
2.04
f1 (ppm)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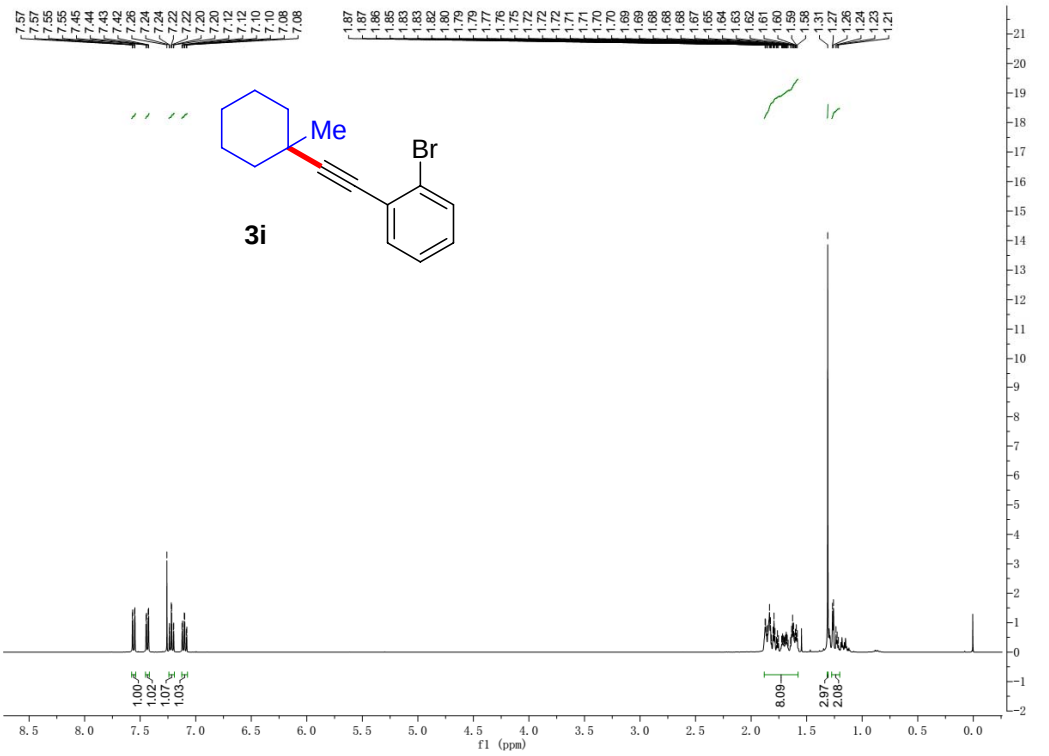
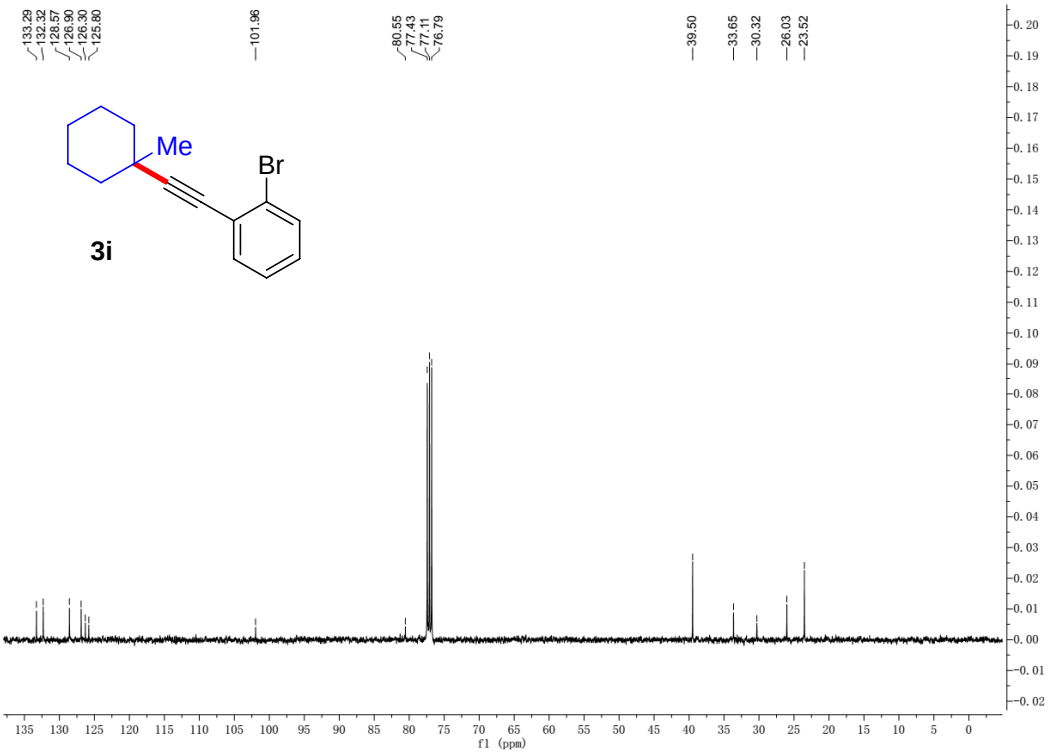
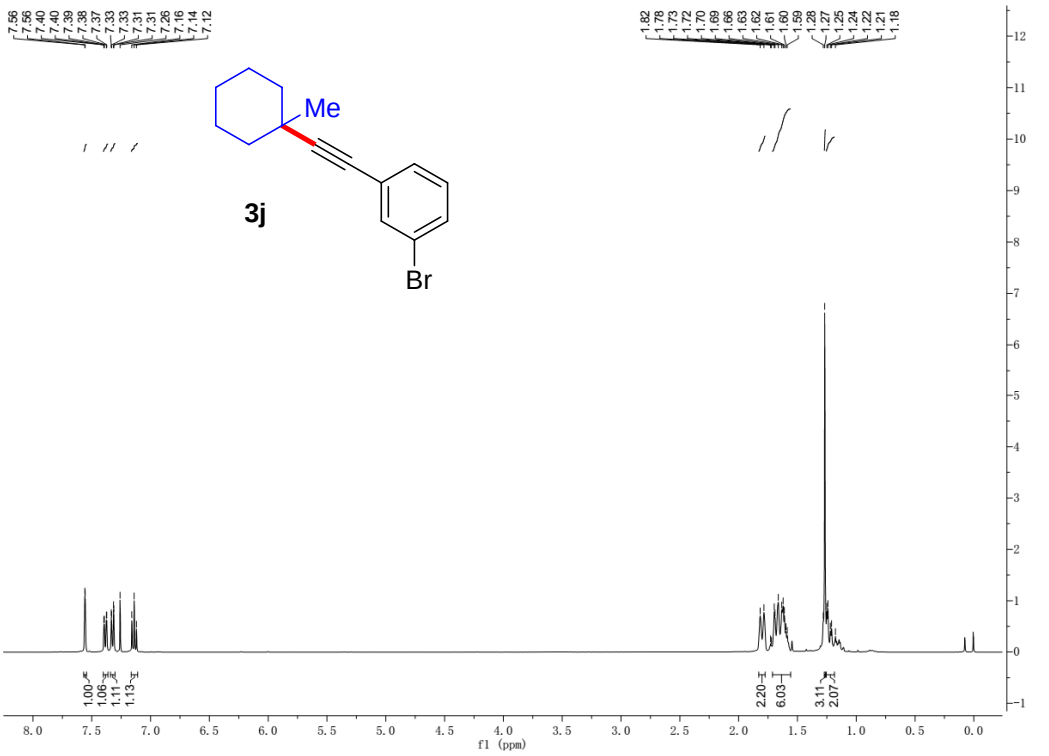
76.79
39.49
33.29
30.22
25.95
23.52
Me
3h
Cl
f1 (ppm)


Me
Br
3i
f1 (ppm)


Me
Br
3i
f1 (ppm)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7.26
7.16
7.14
7.12
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1.78
1.73
1.72
1.70
1.69
1.66
1.63
1.62
1.61
1.60
1.59
1.28
1.27
1.25
1.24
1.22
1.21
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6.03
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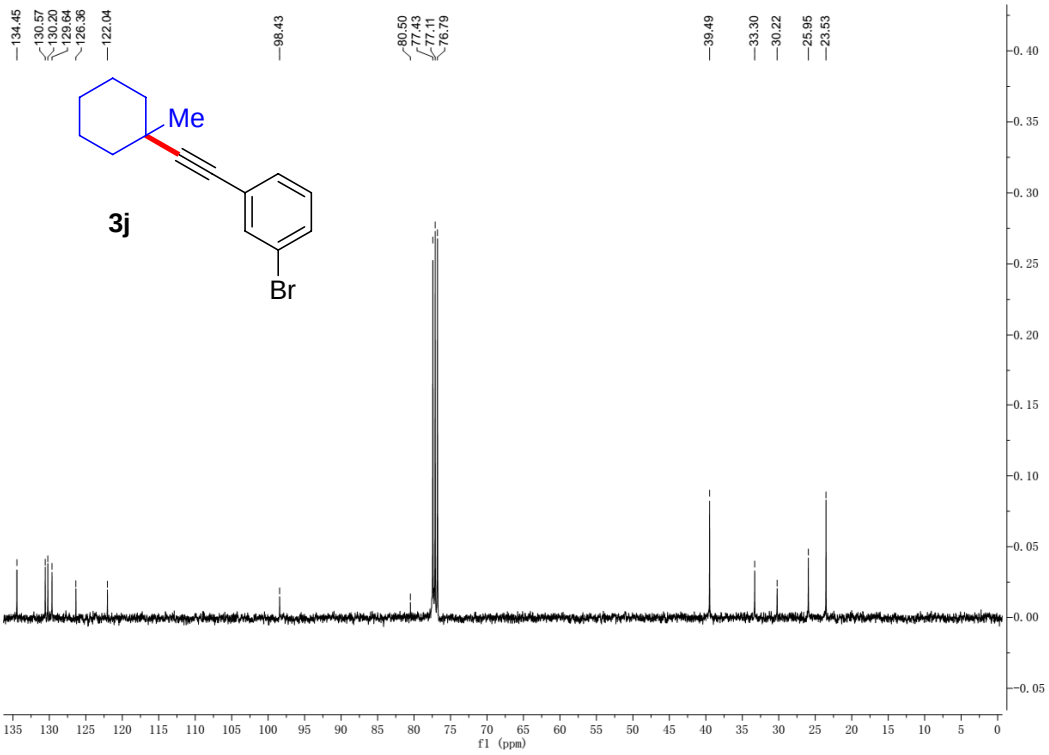
2.07
f1 (ppm)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33.30
30.22
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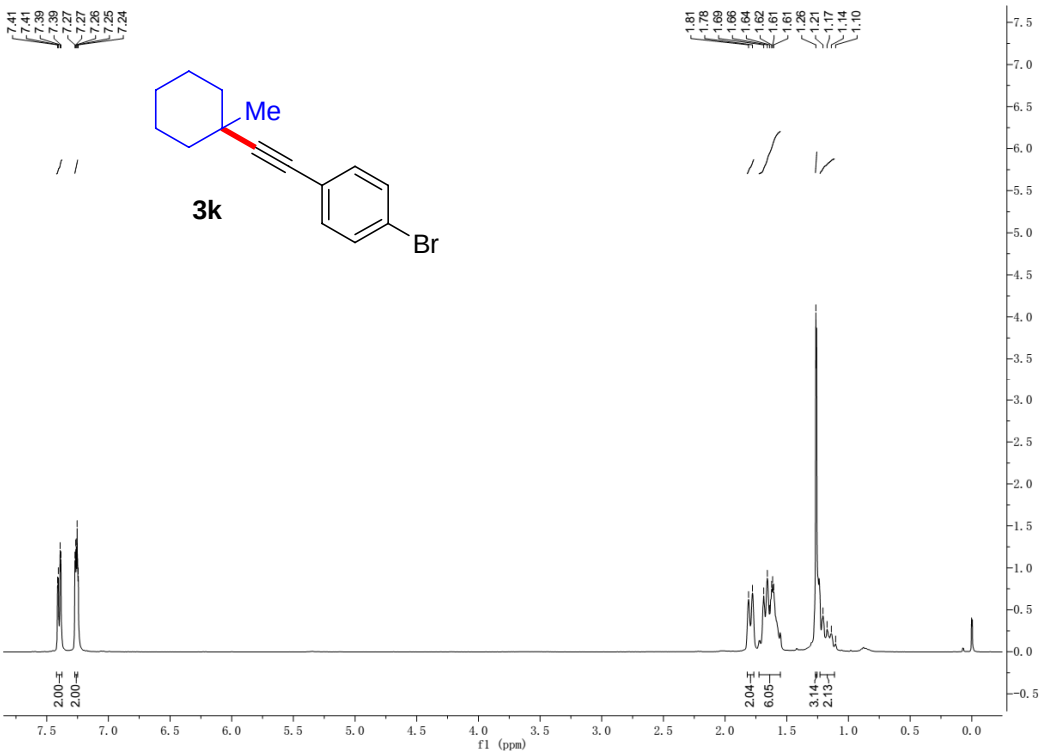
23.53
Me
Br
3j
f1 (ppm)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1.66
1.64
1.62
1.61
1.61
1.26
1.21
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Me
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2.00
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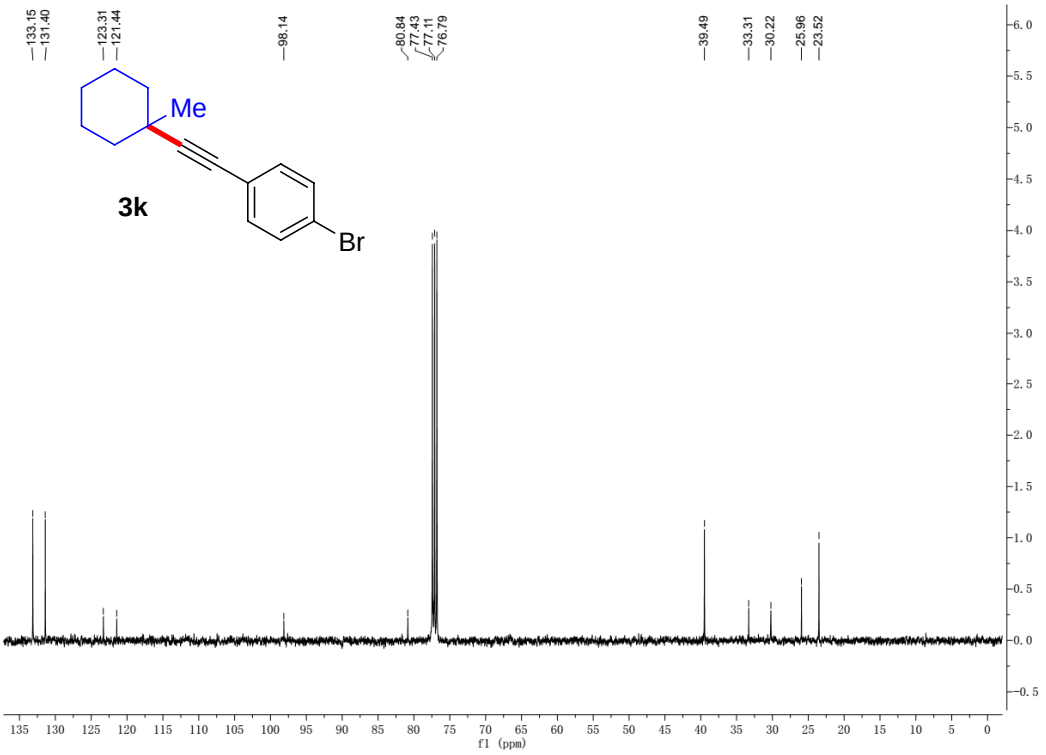
2.13
f1 (ppm)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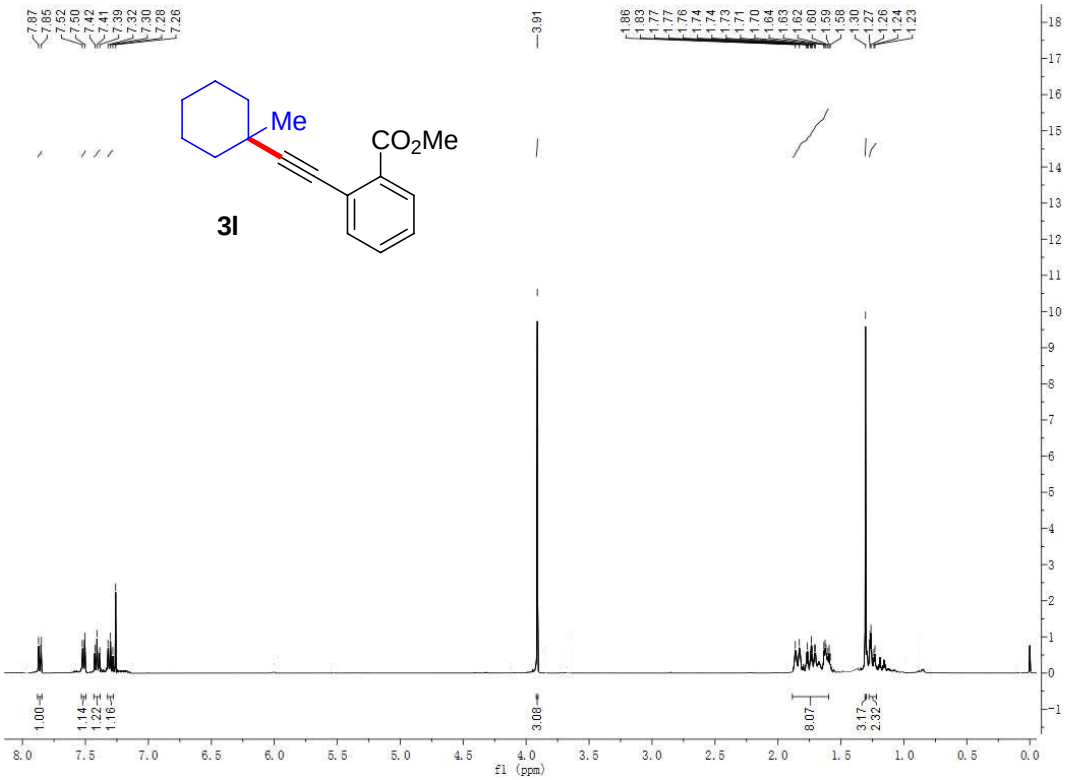
Me
3k
Br
f1 (ppm)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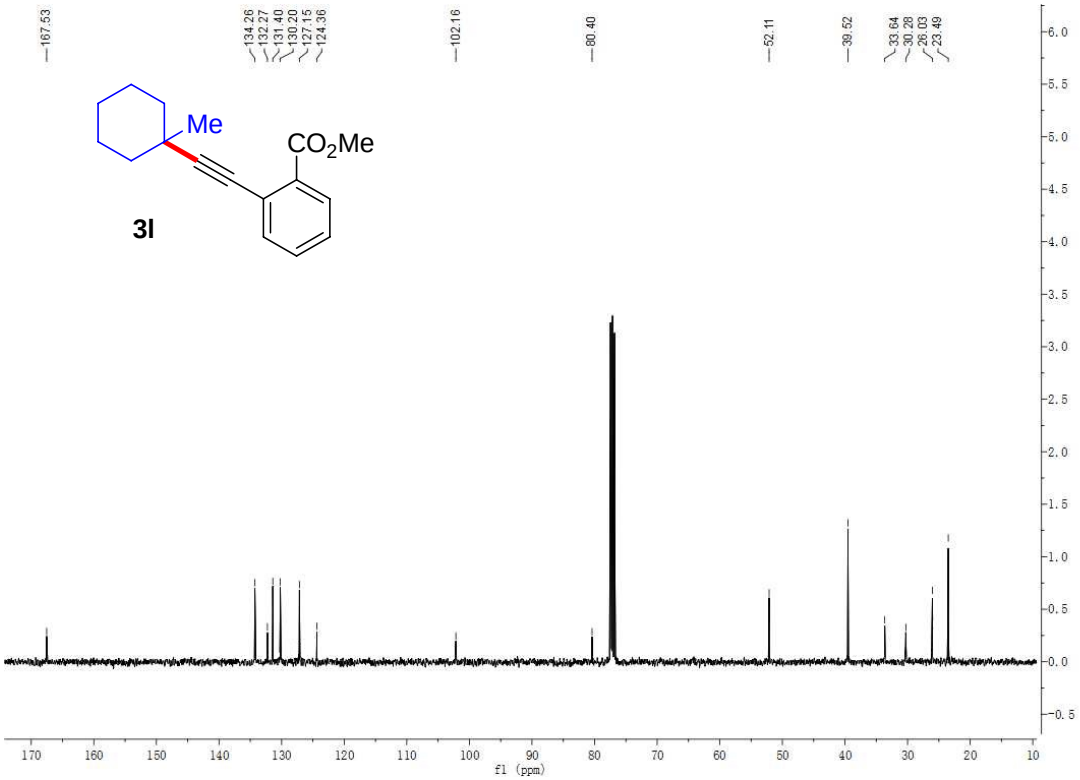
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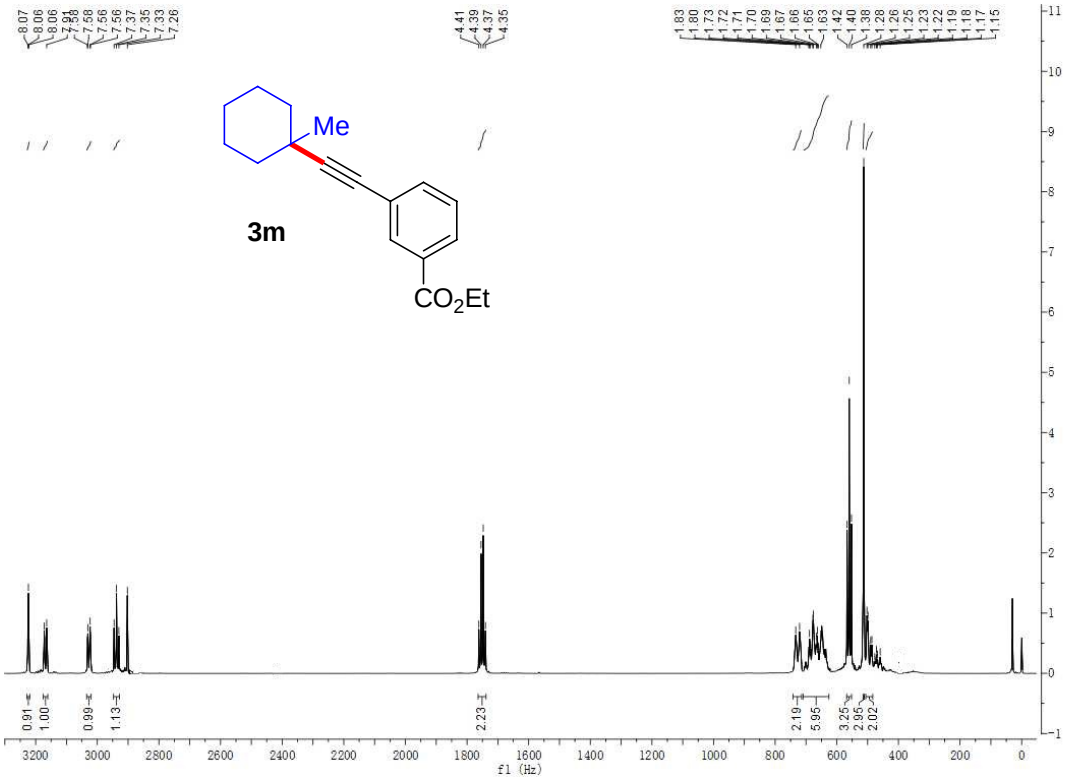
f1 (ppm)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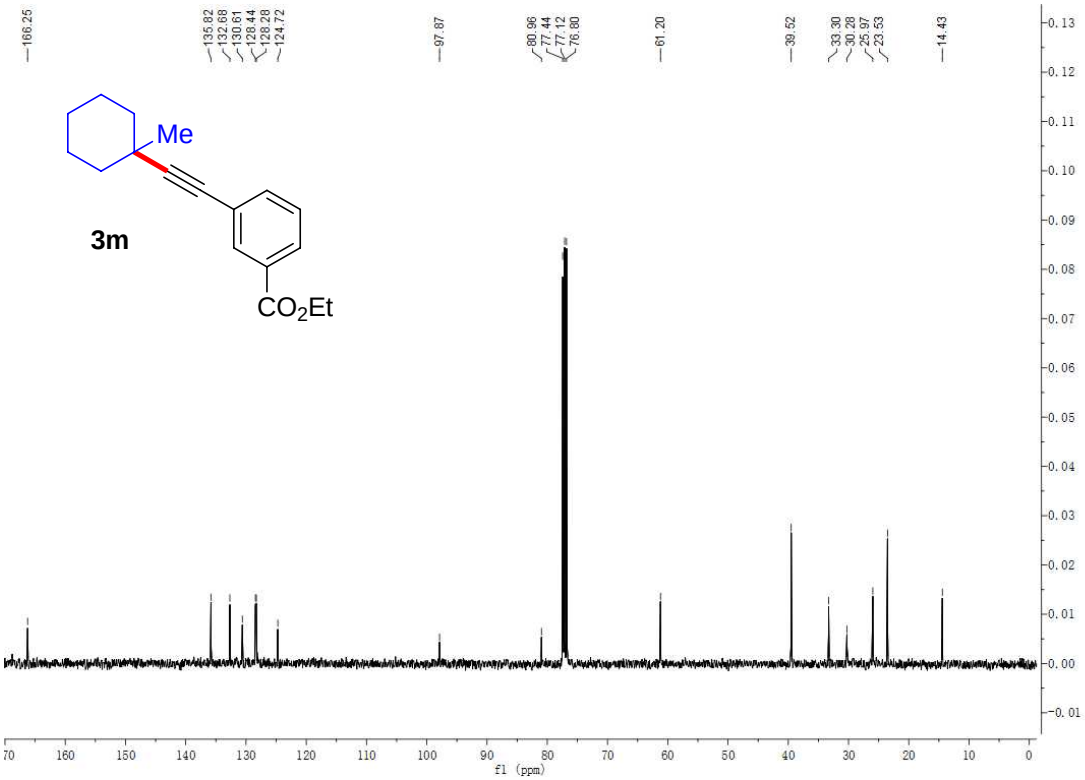
f1 (Hz)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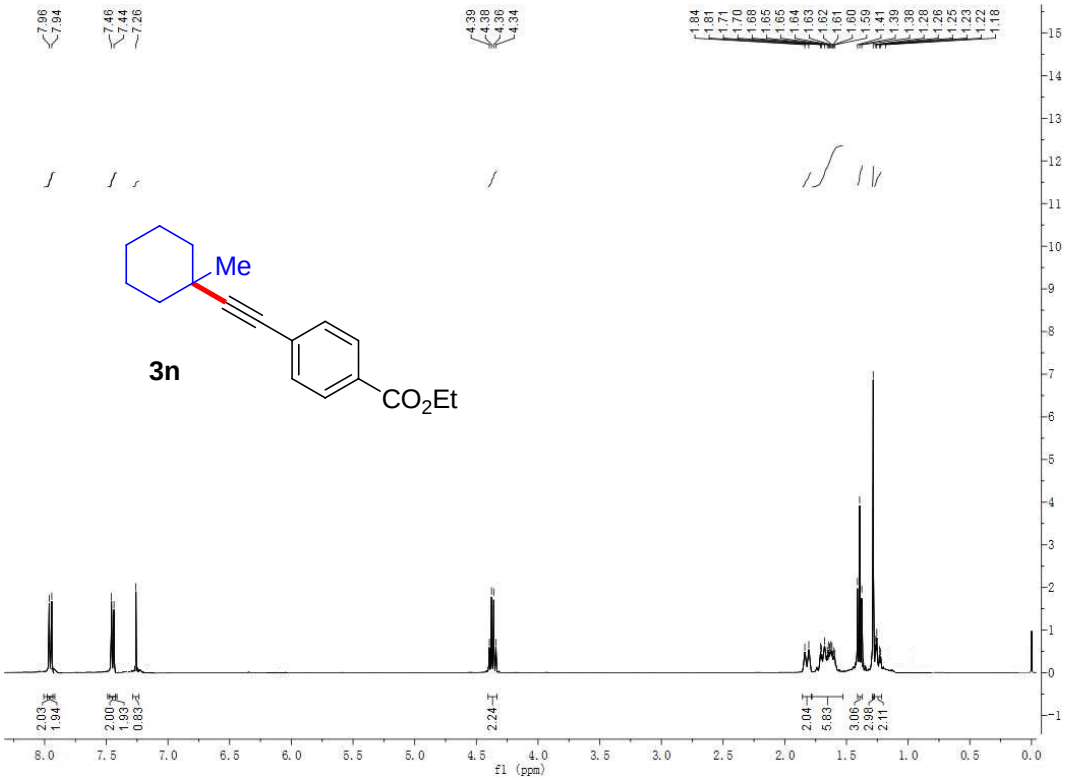
f1 (ppm)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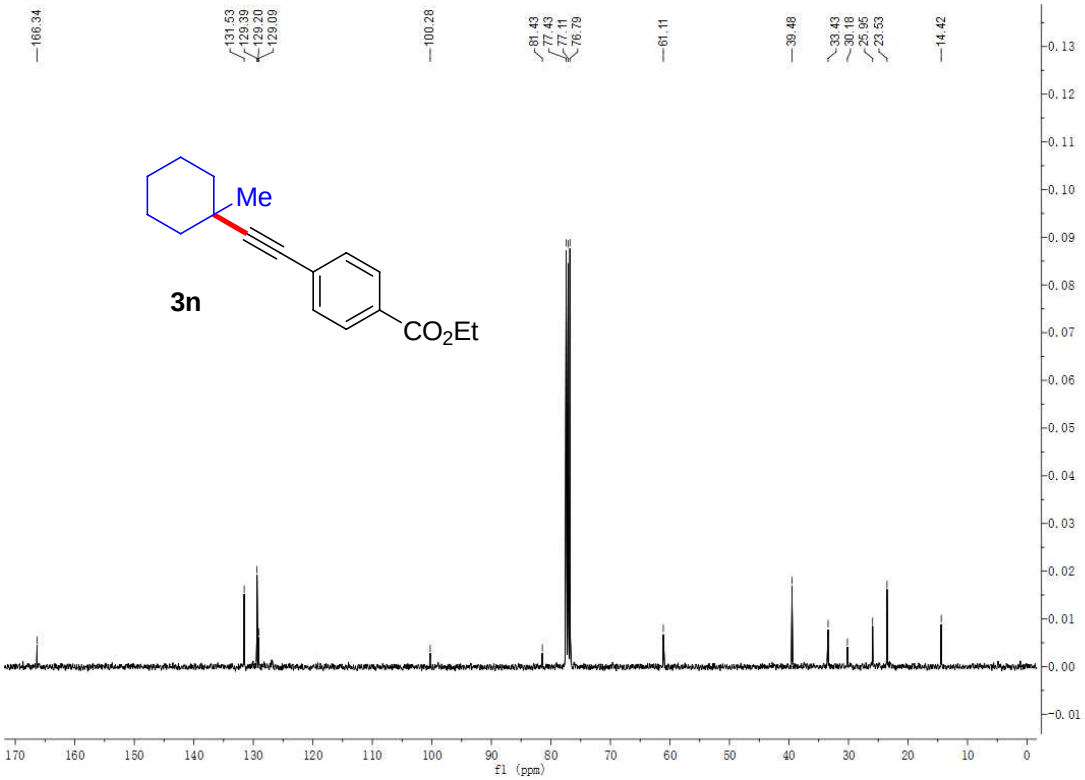
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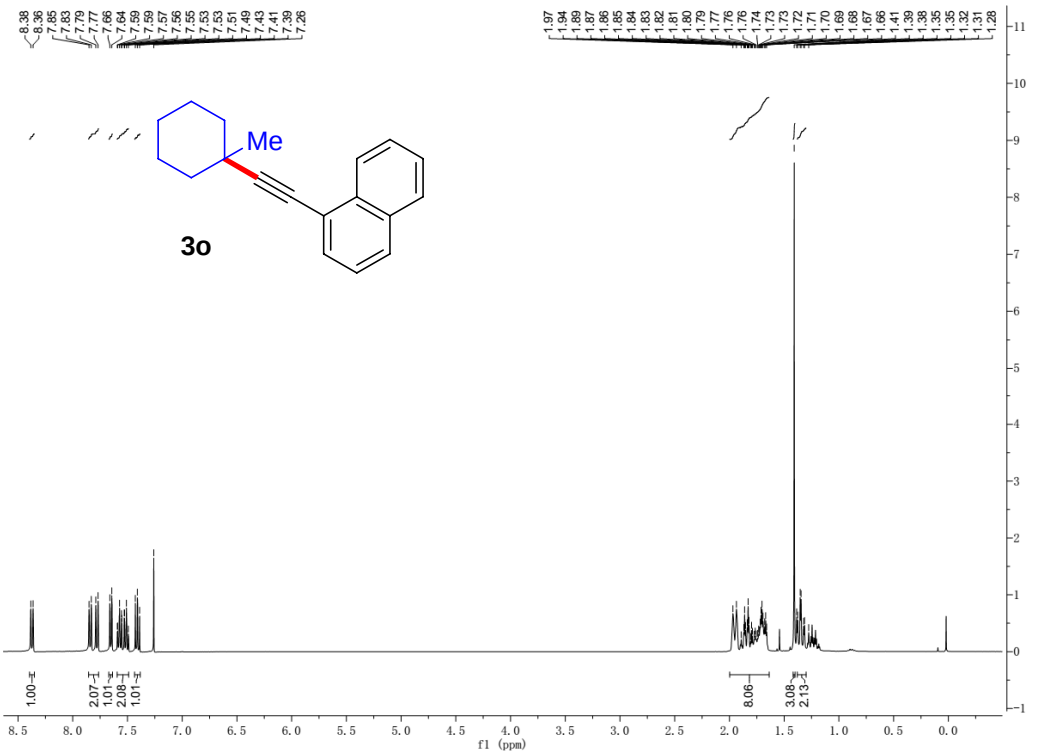
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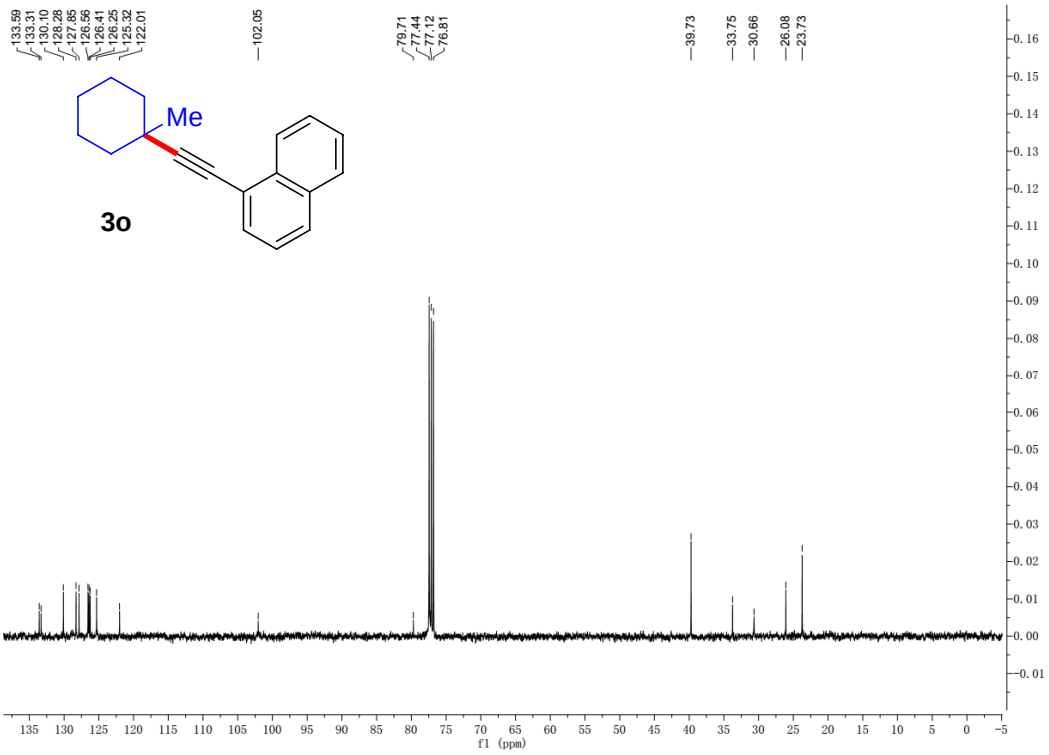
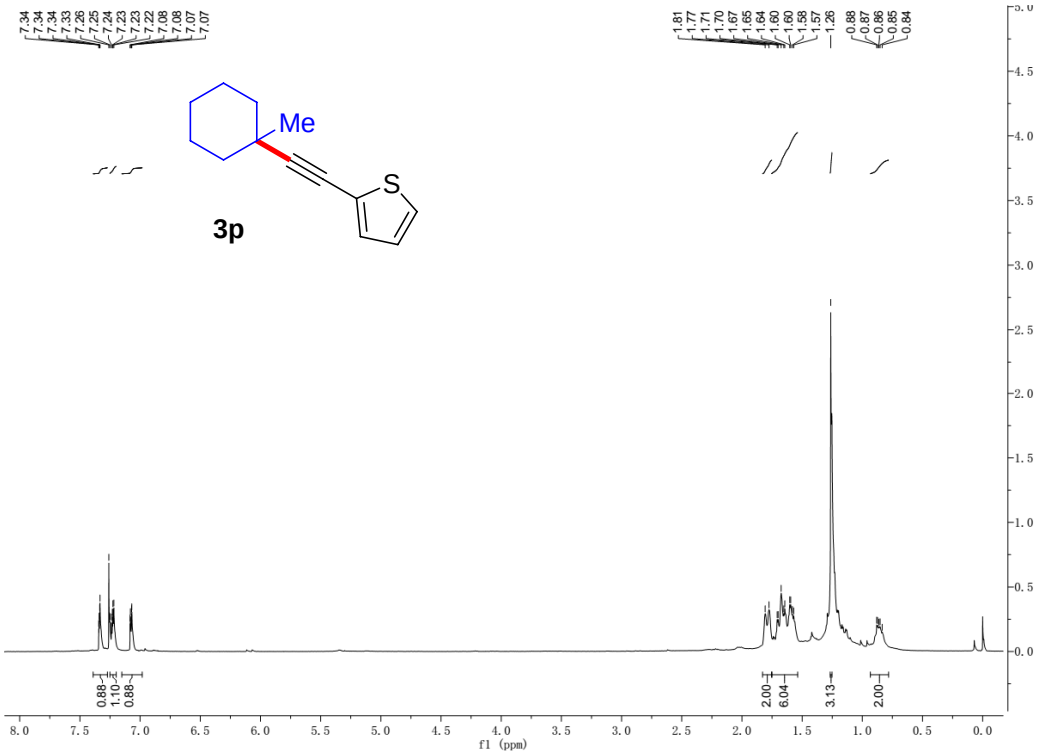
3o
f1 (ppm)


Me
3o
f1 (ppm)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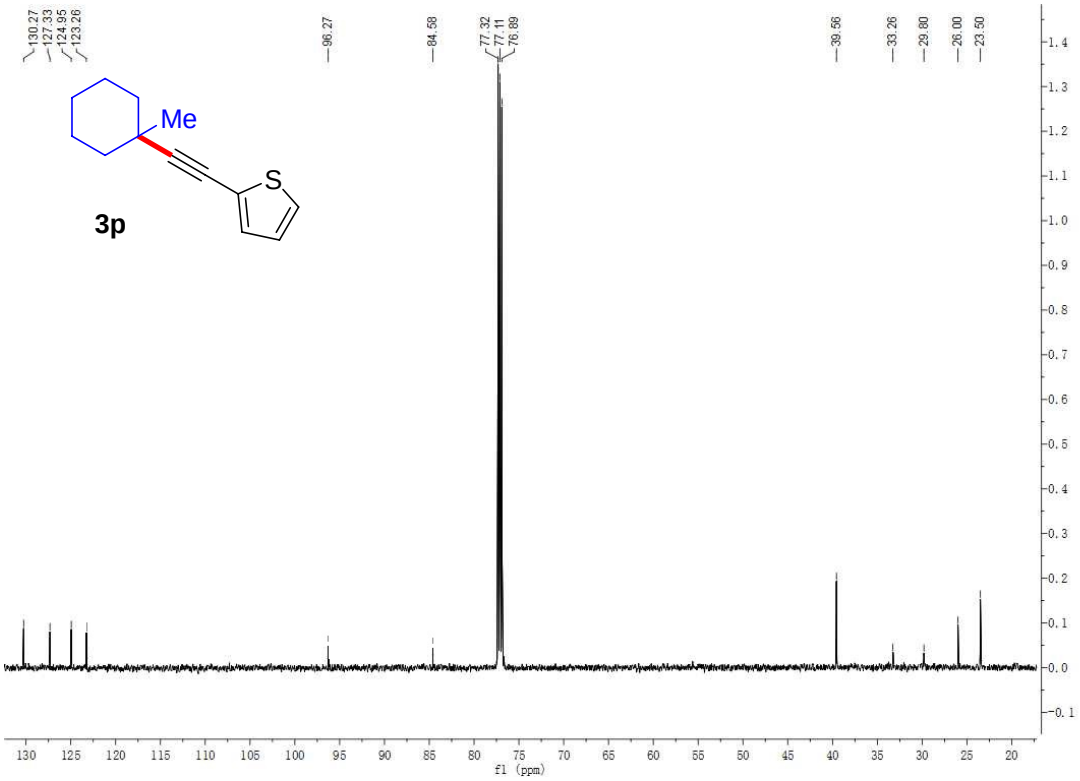
S
3p
f1 (ppm)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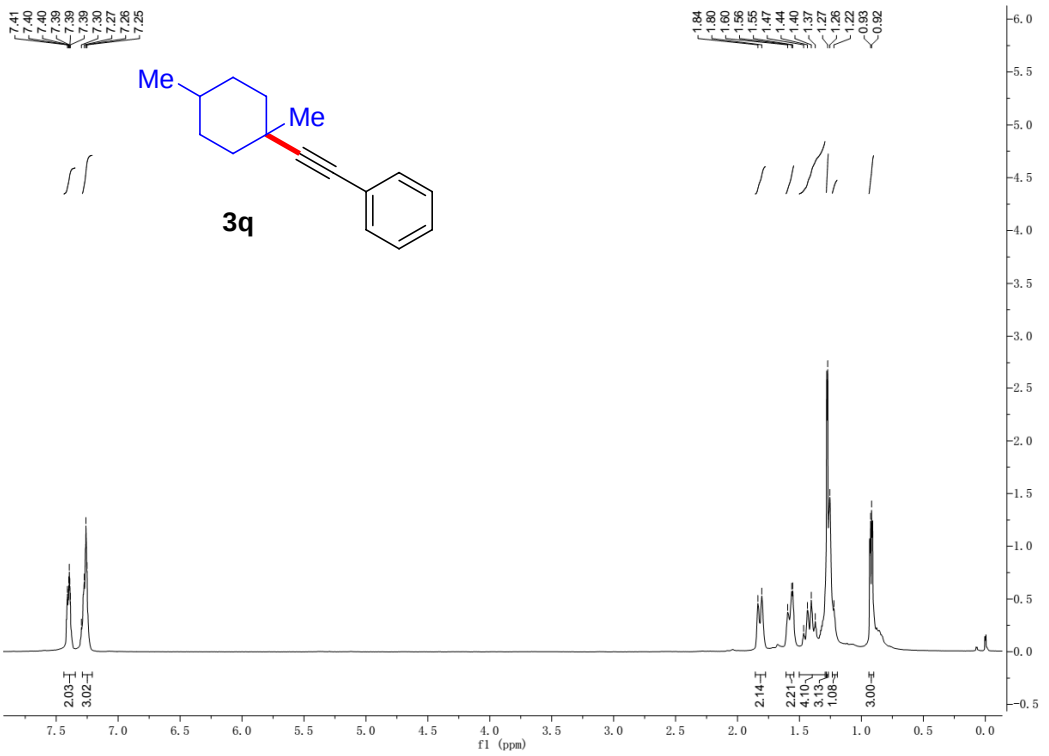
S
3p
f1 (ppm)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1.60
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1.55
1.47
1.44
1.40
1.37
1.27
1.26
1.22
0.93
0.92
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Me
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2.14
2.21
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3.13
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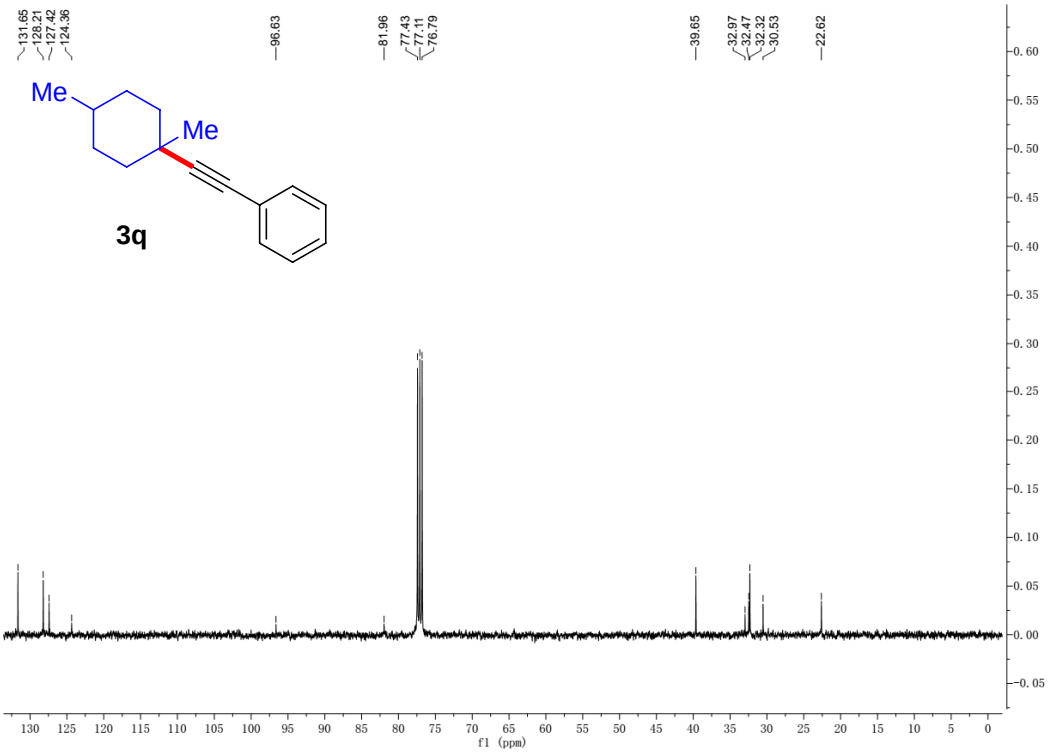
3.00
f1 (ppm)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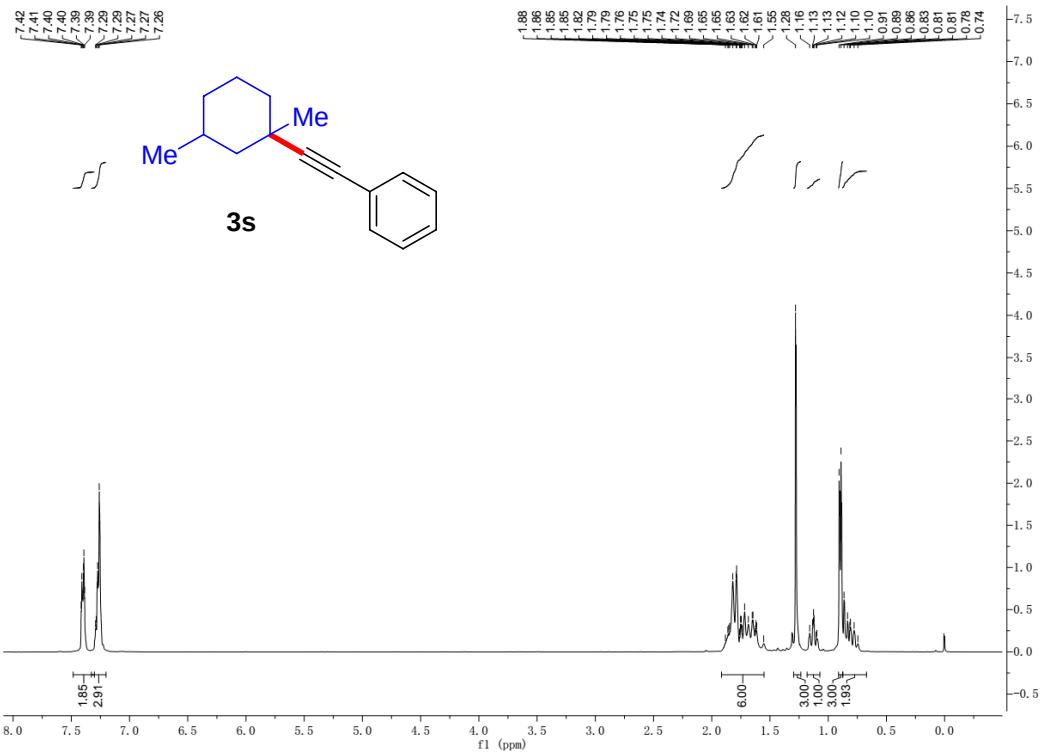
22.62
Me
Me
3q
f1 (ppm)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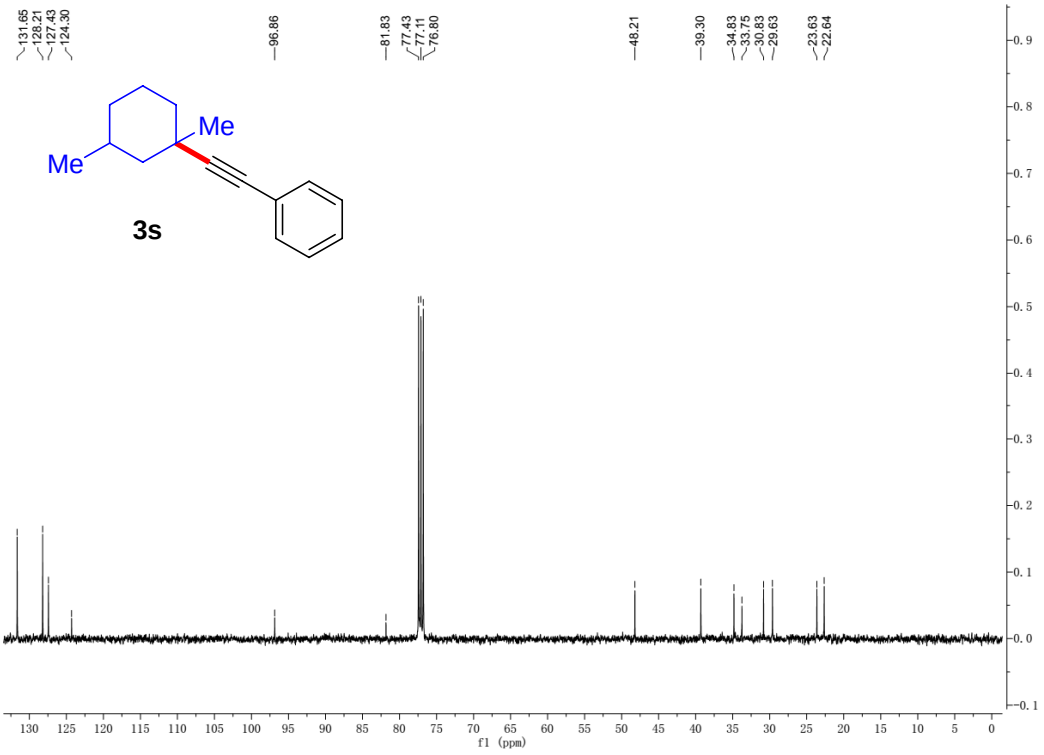
Me
3s
f1 (ppm)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Me
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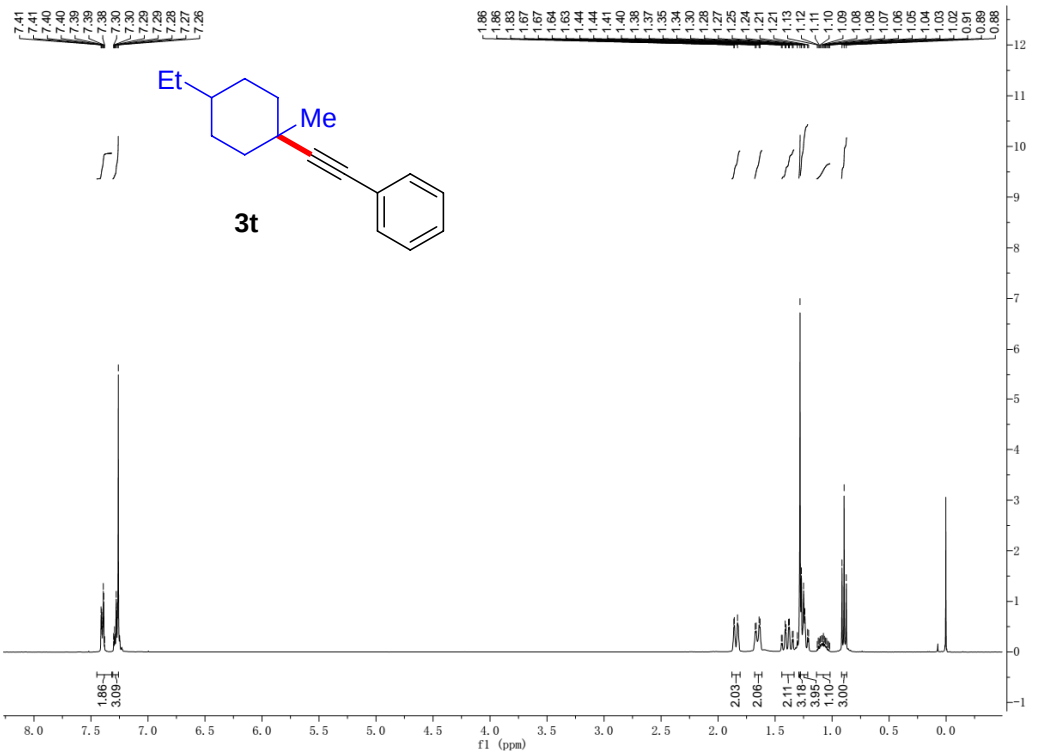
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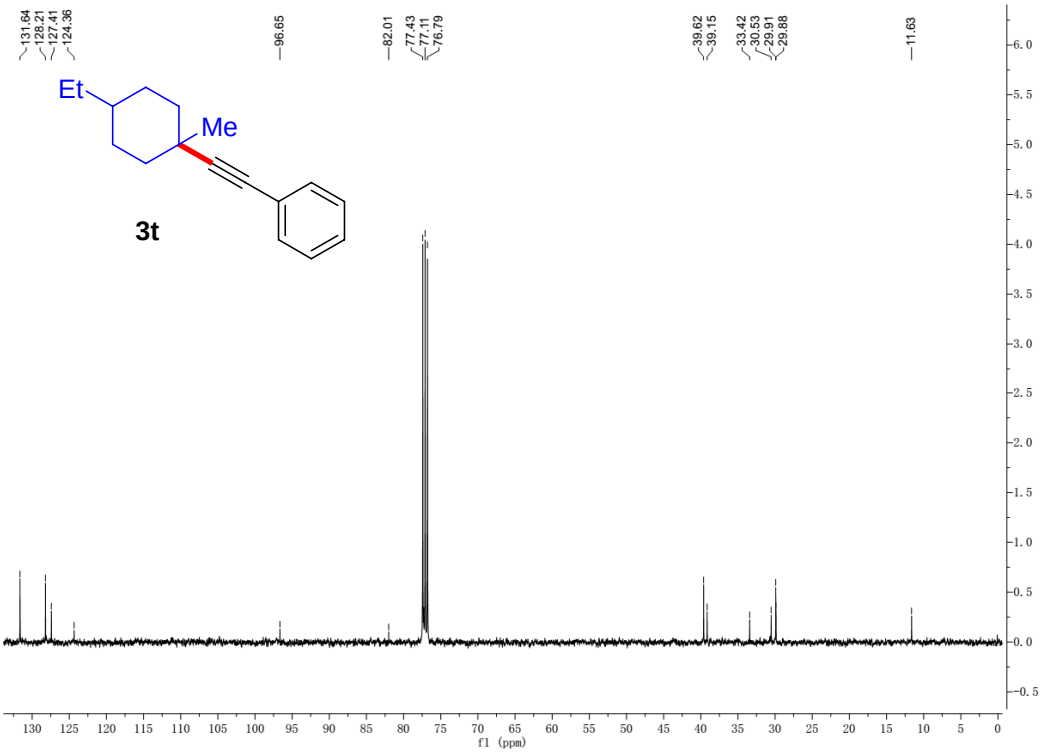
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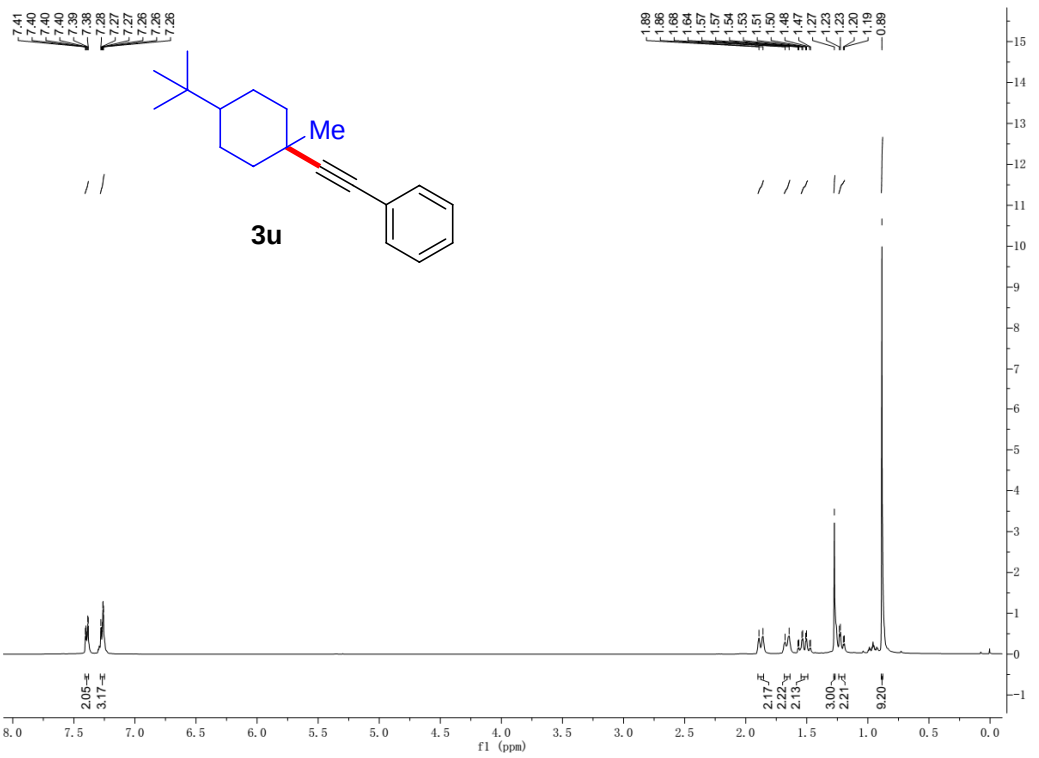
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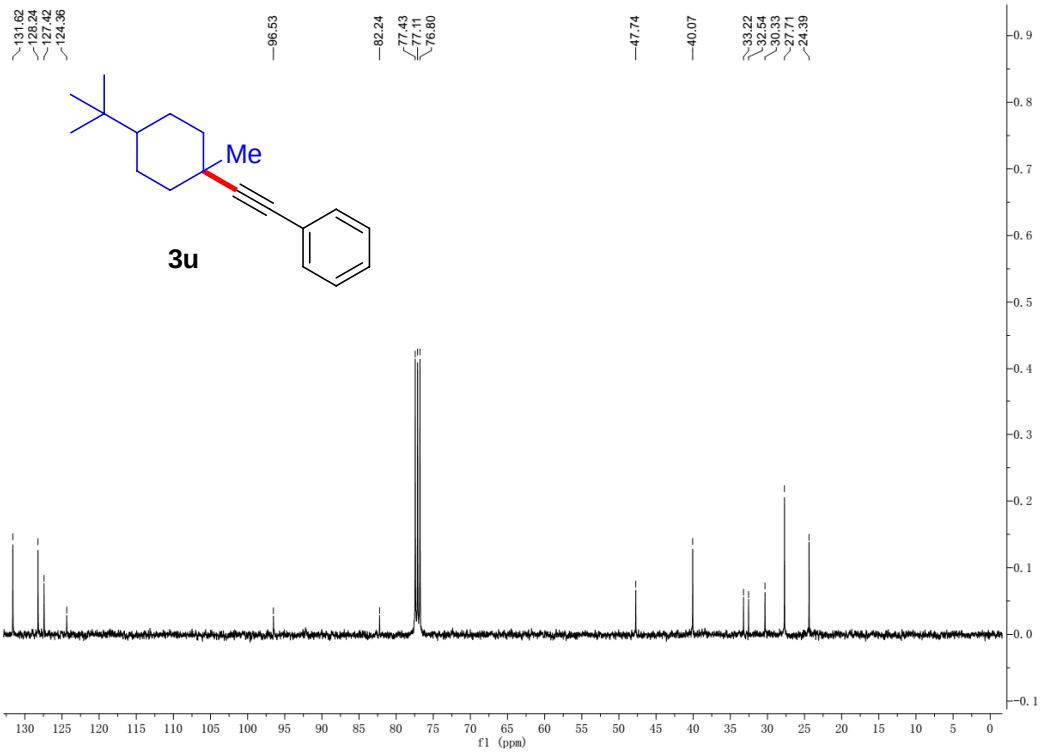
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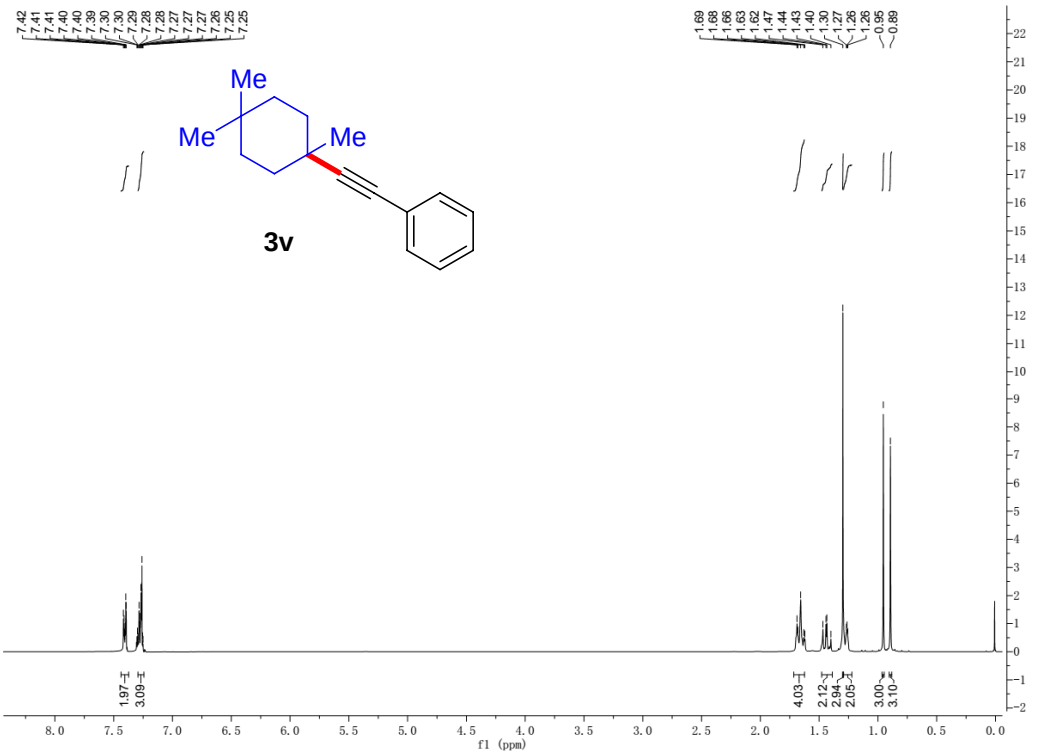
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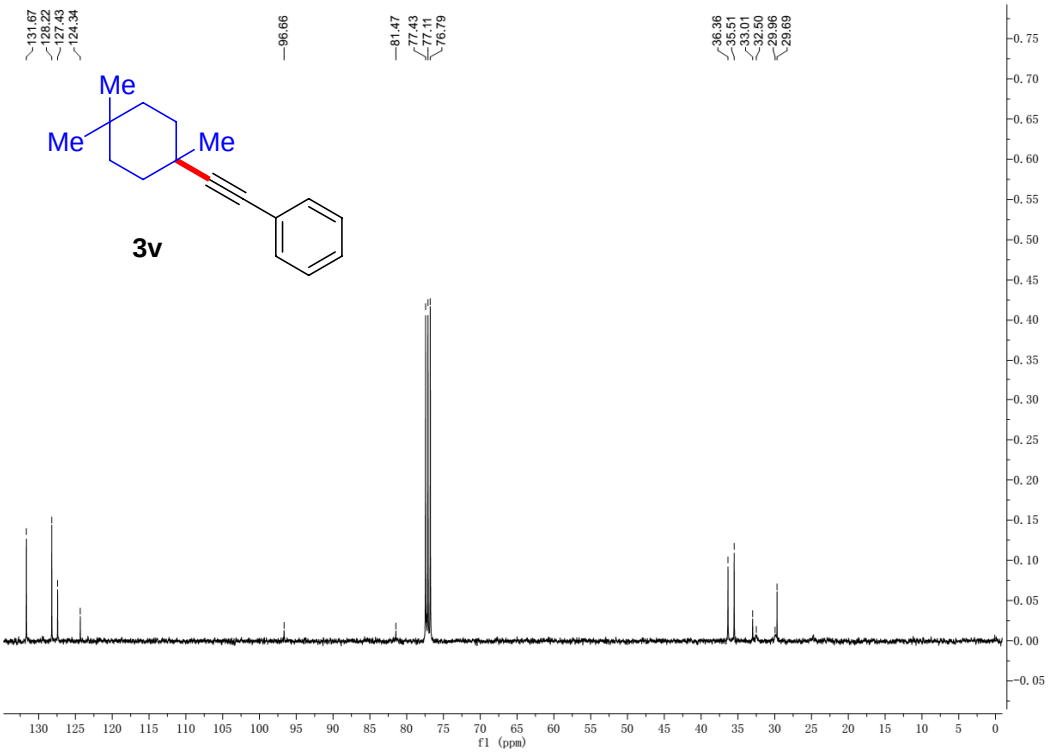
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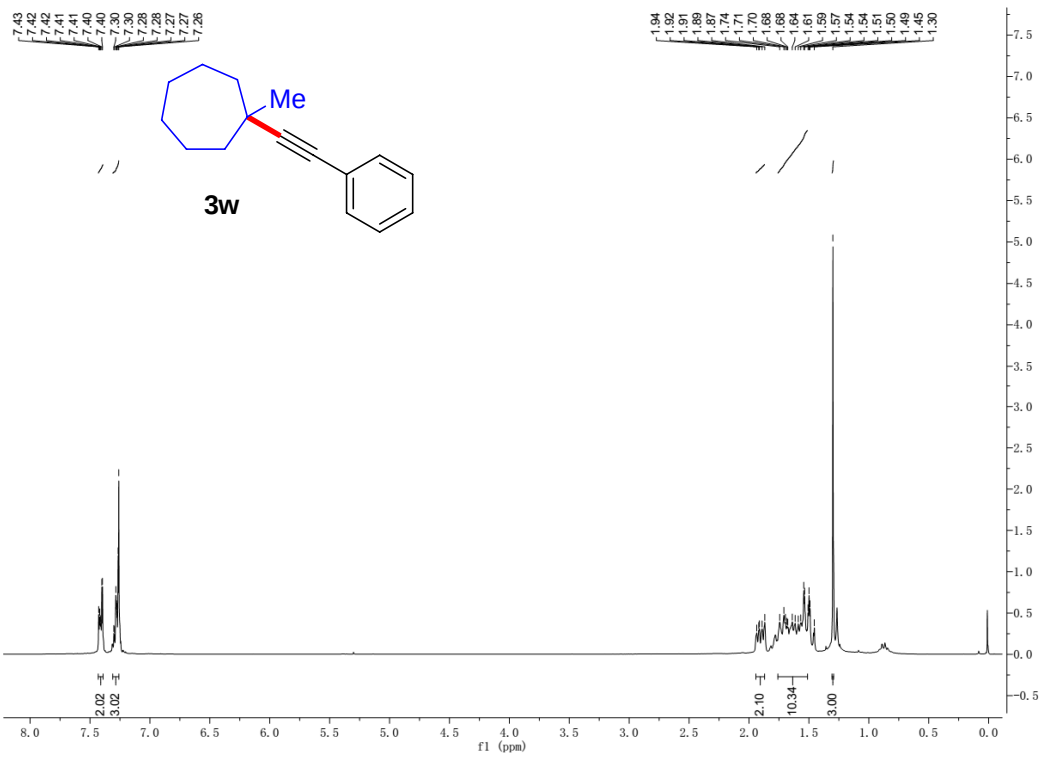
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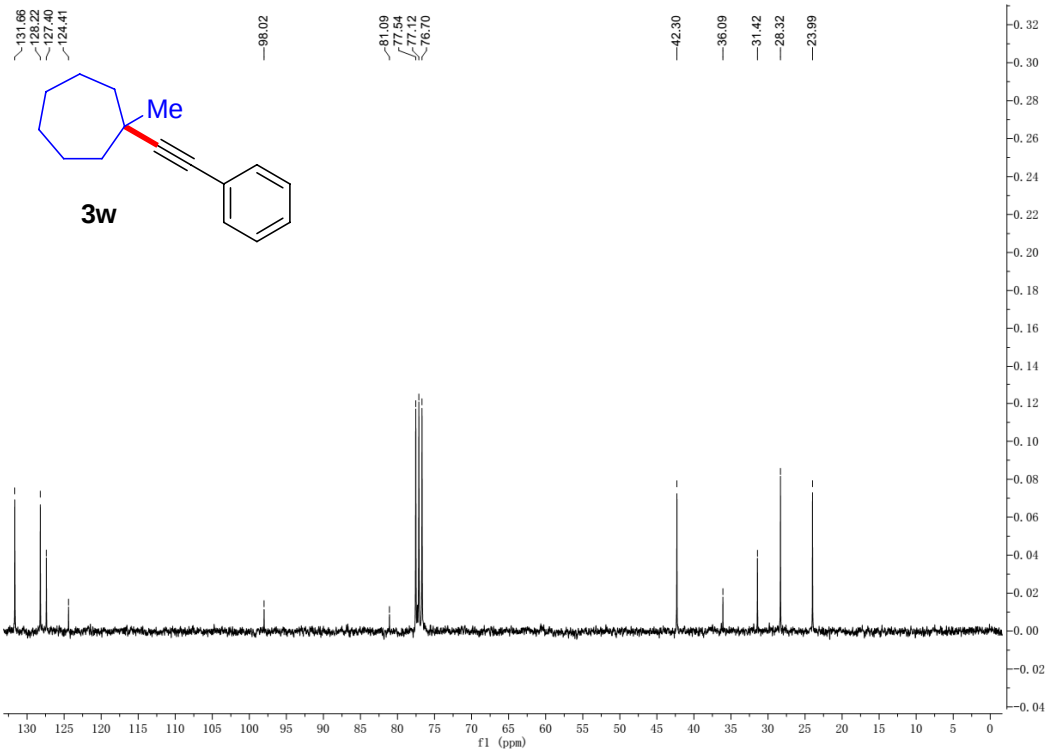
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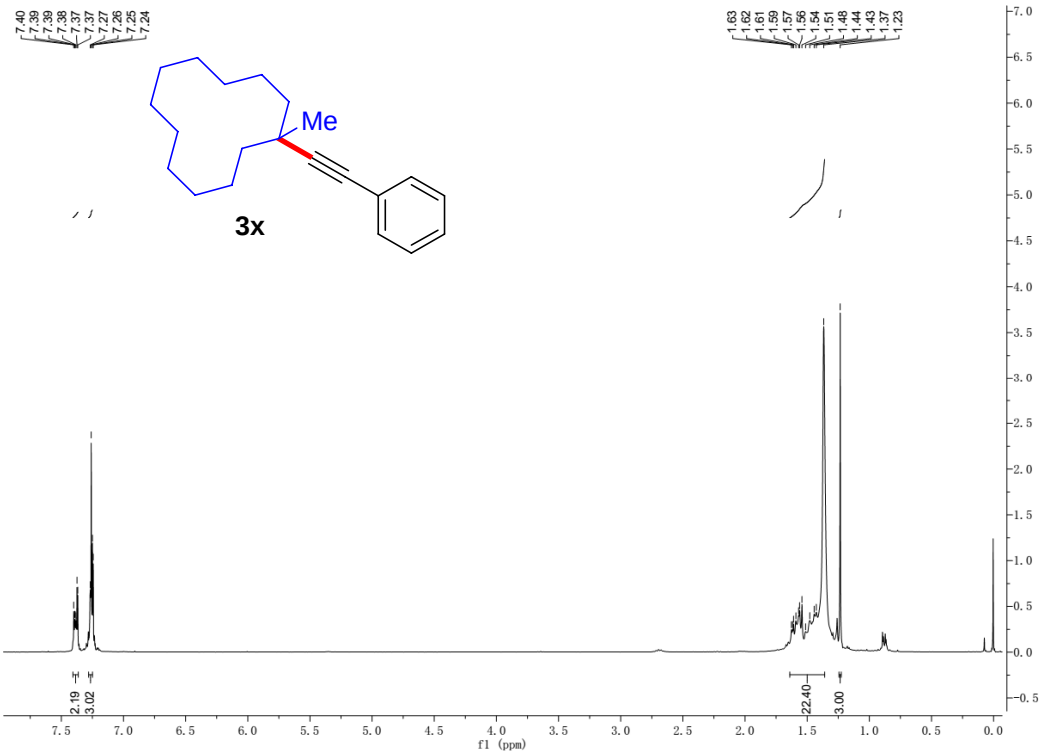
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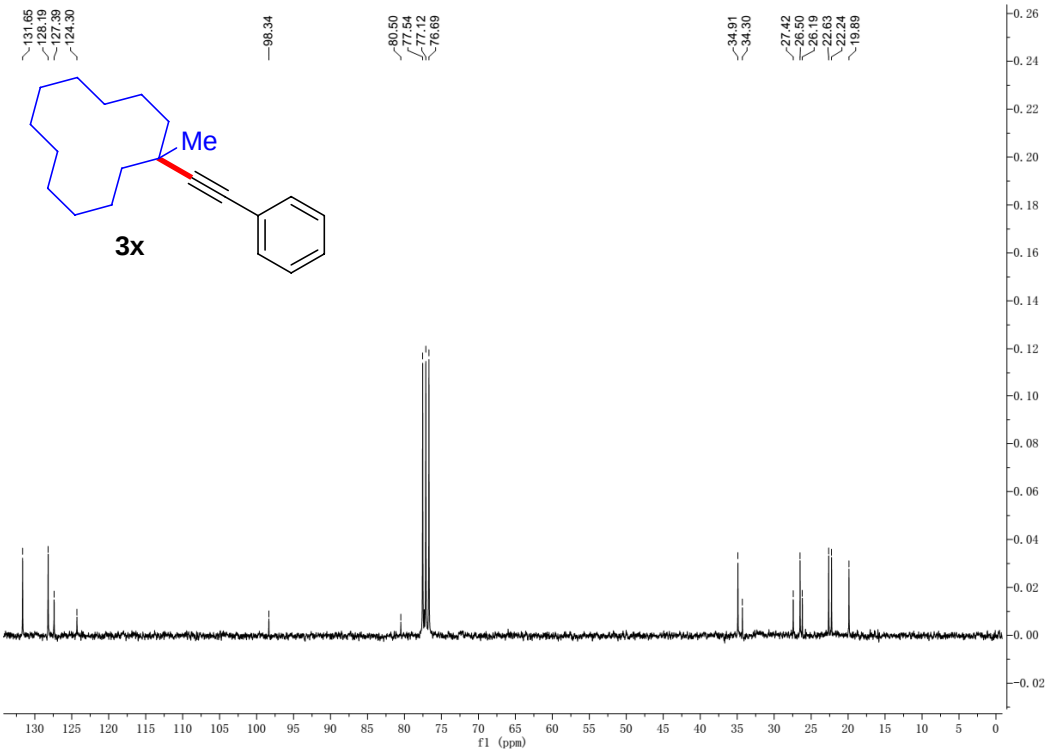
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3x
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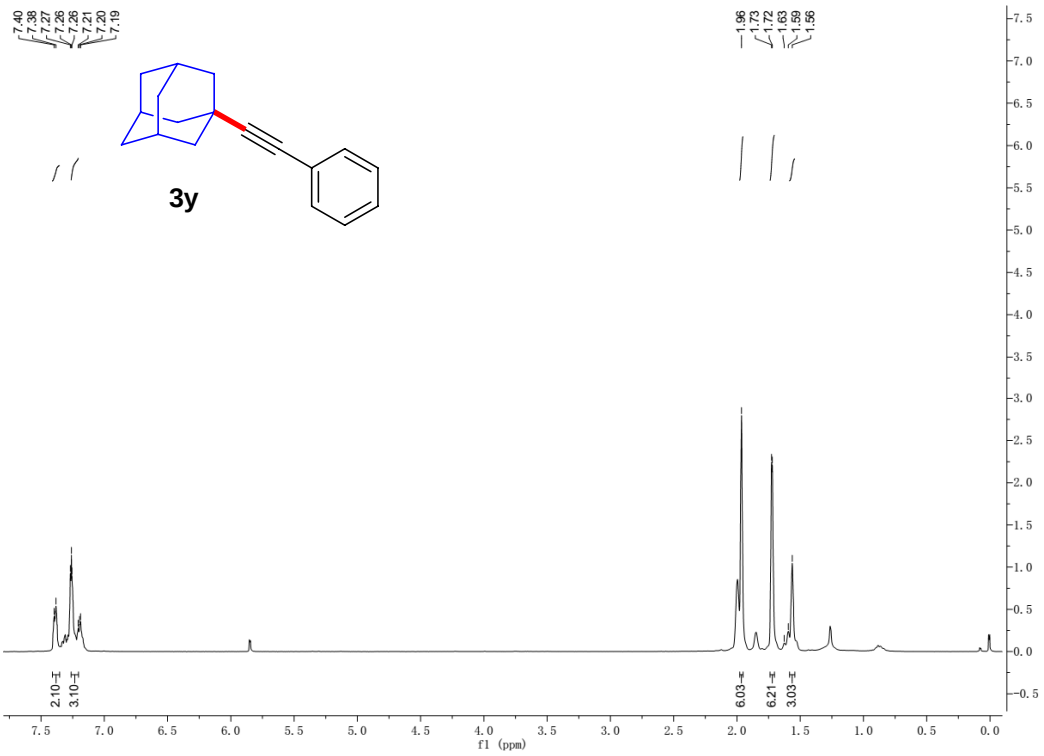
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1.59
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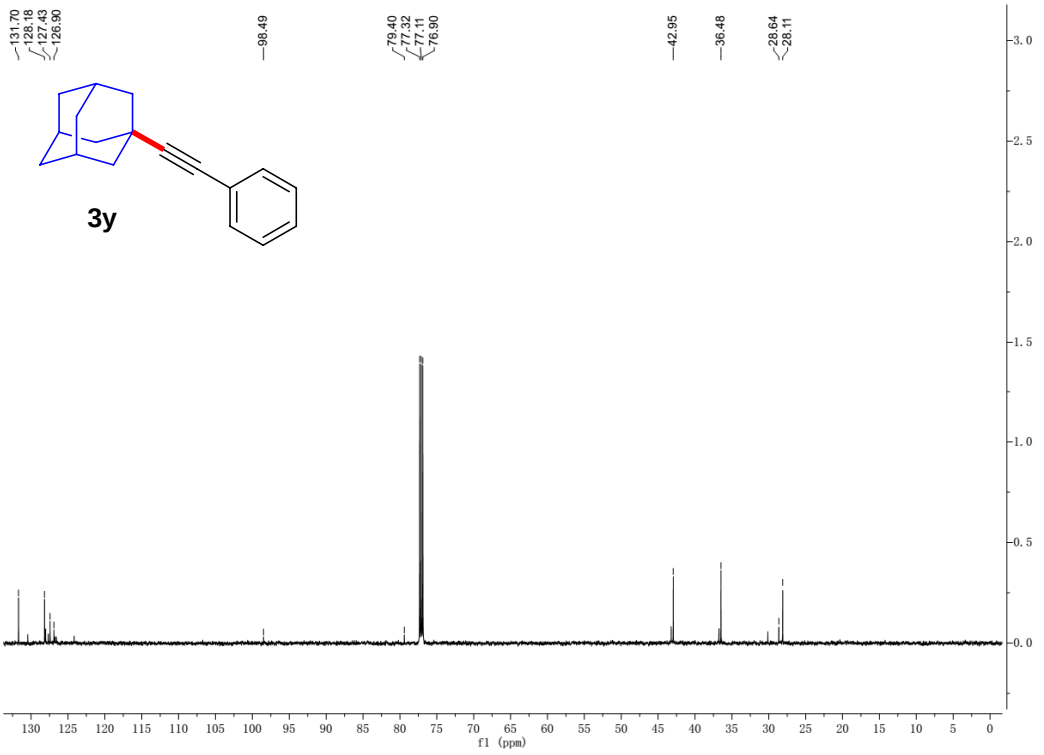
3y
2.10
3.10
6.03
6.21
3.03
f1 (ppm)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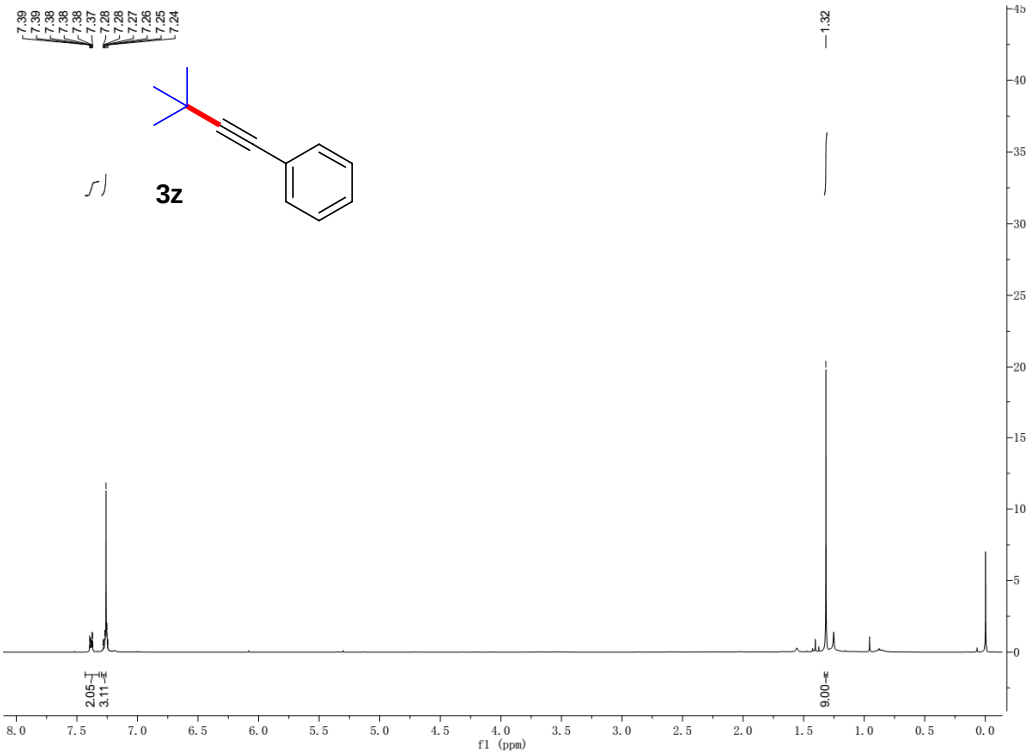
f1 (ppm)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7.28
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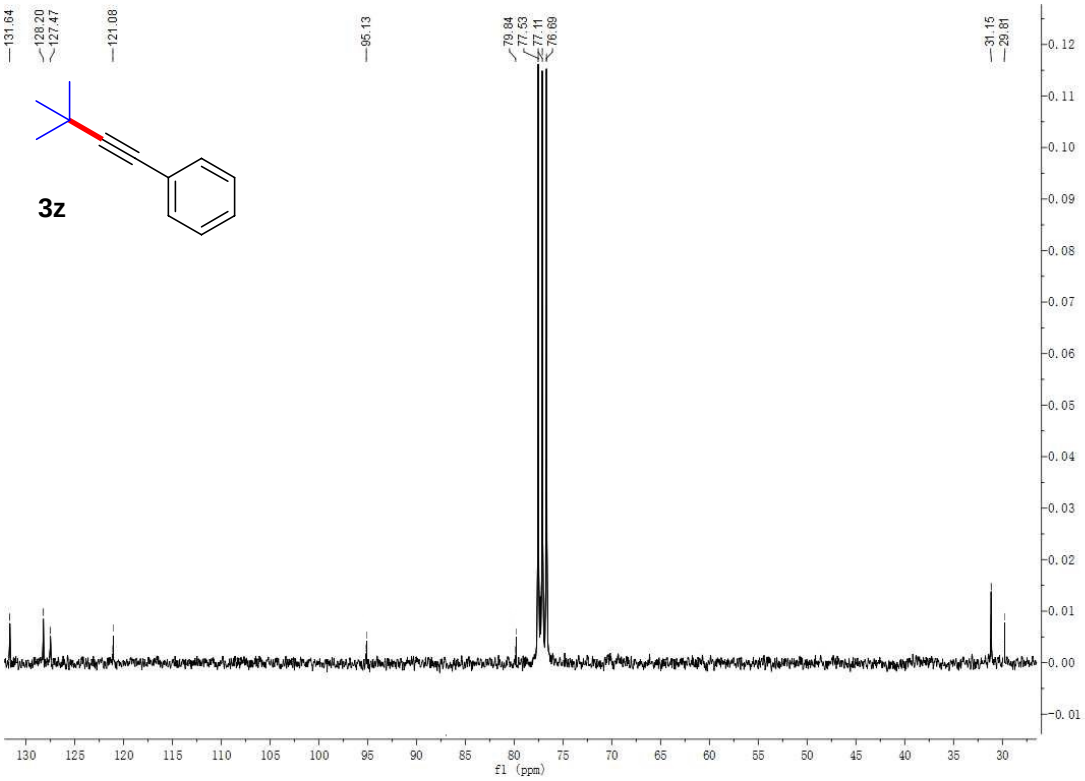
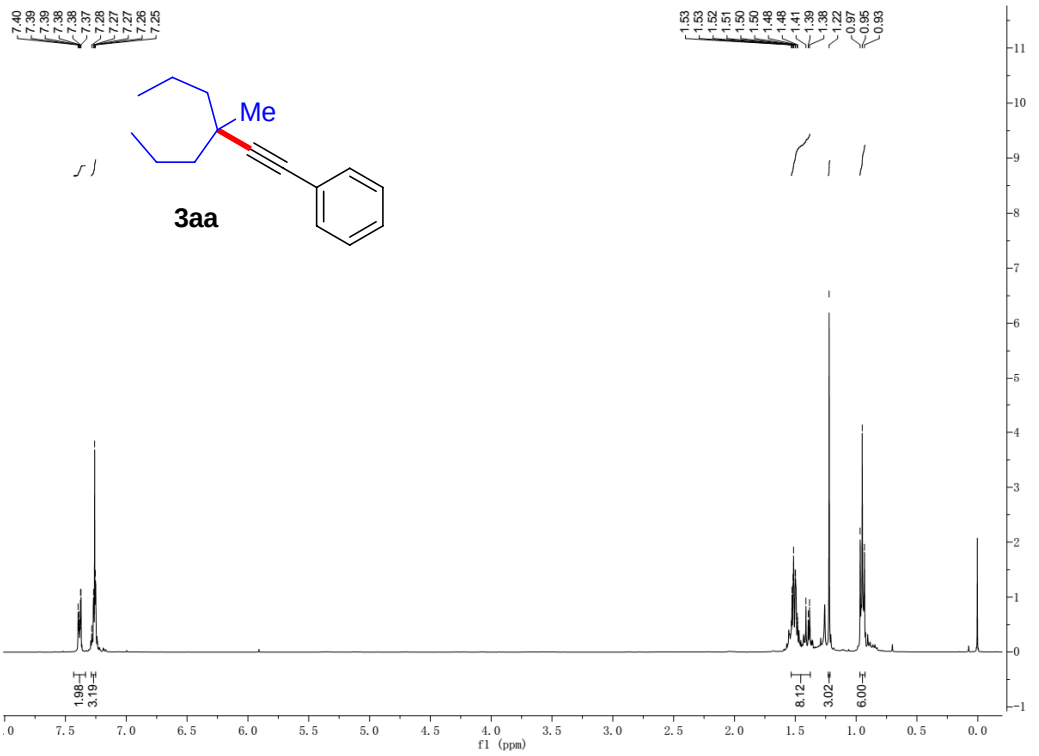
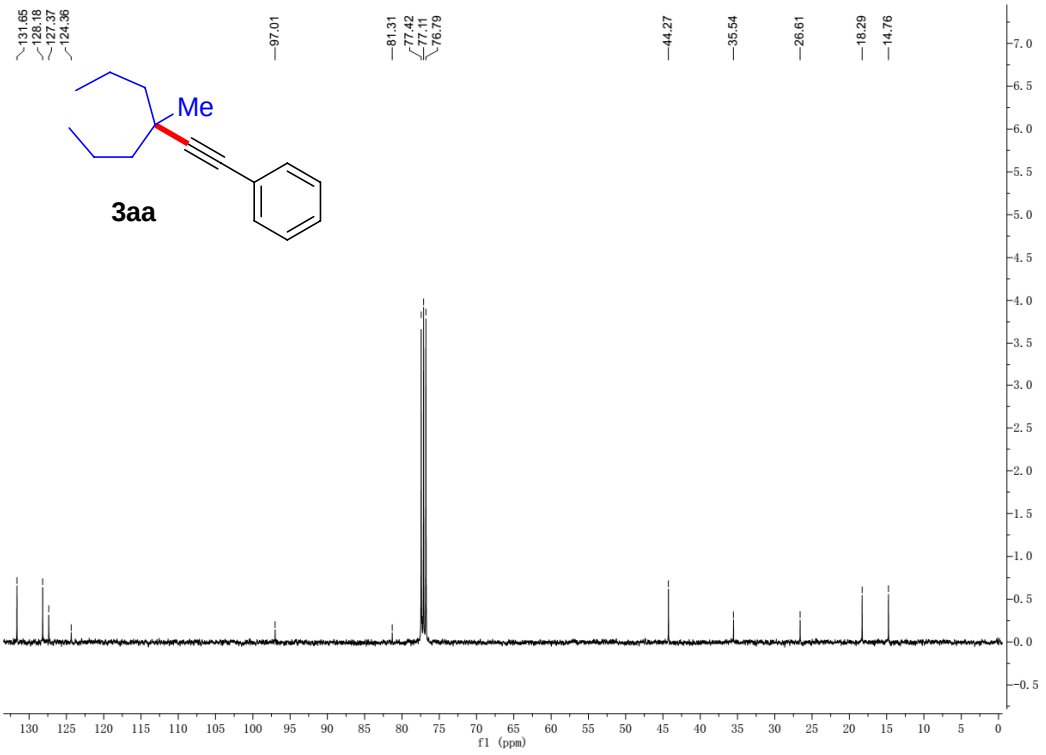
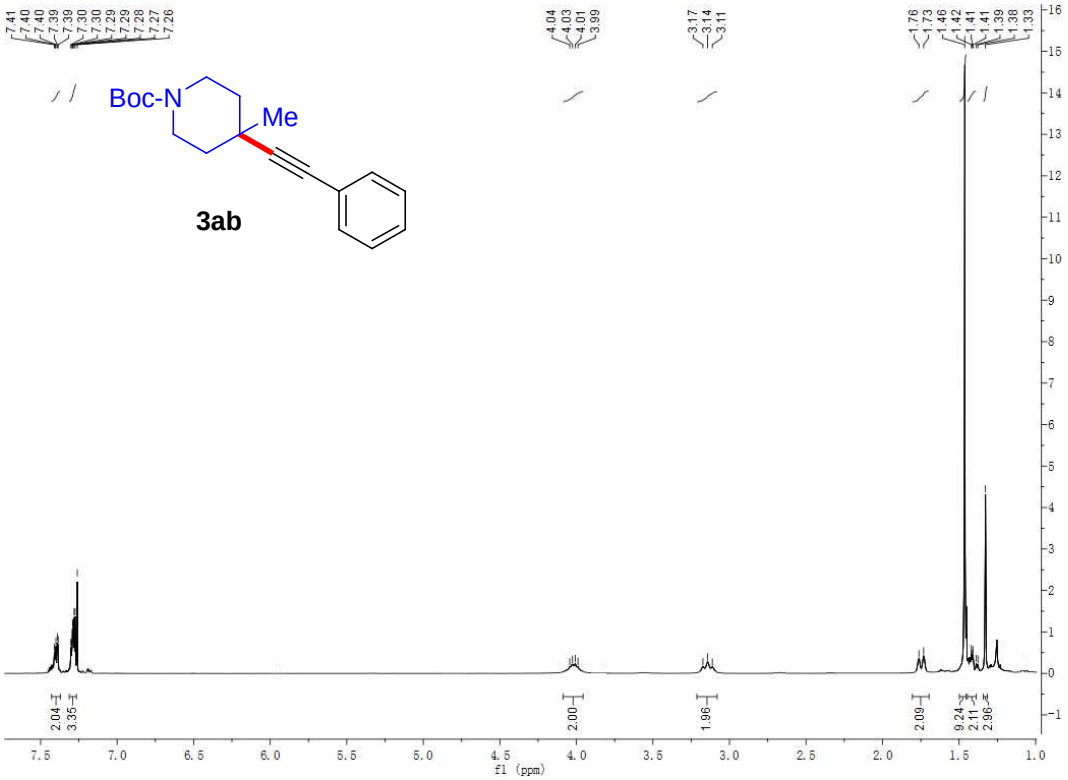
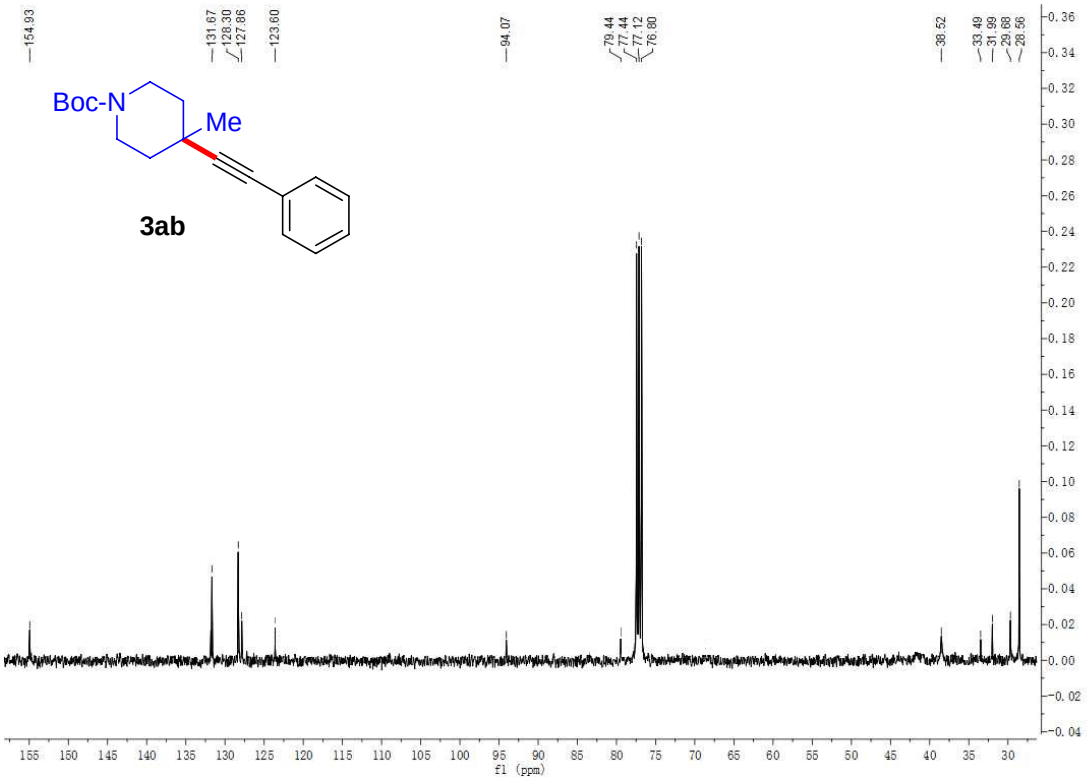
7.25
7.24
1.32
3z
2.05
3.11
9.00
f1 (ppm)

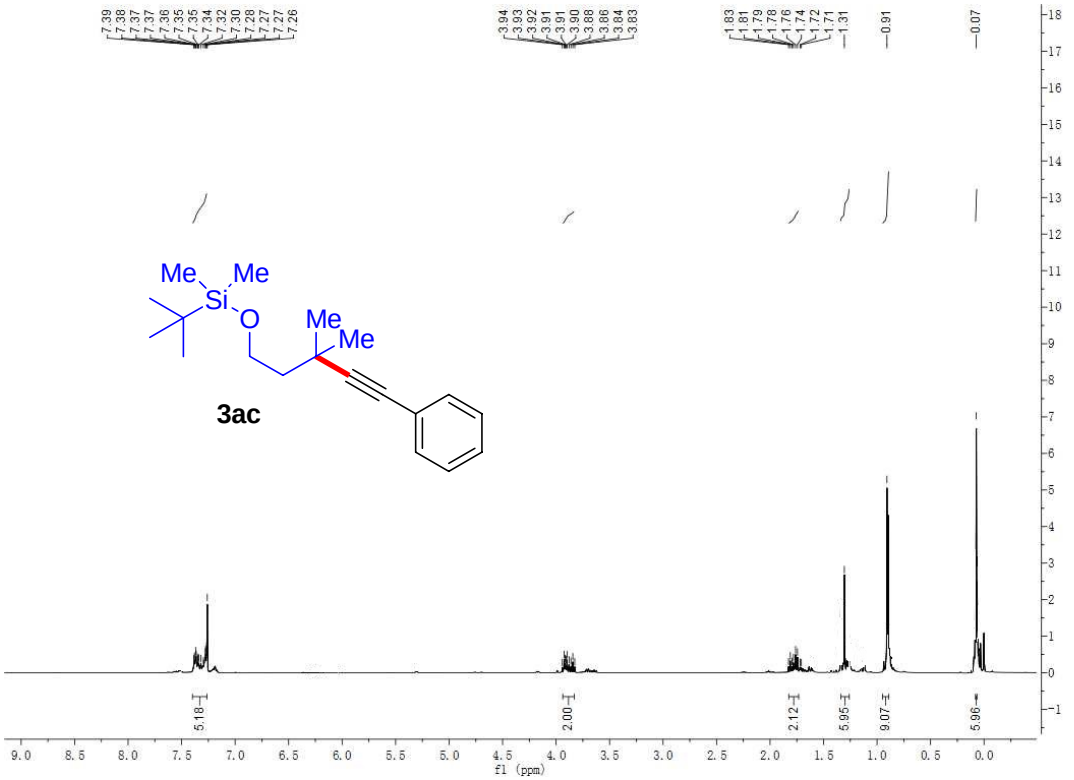

131.64
128.20
127.47
121.08
95.13
79.84
77.53
77.11
76.69
31.15
29.81
3z
f1 (ppm)

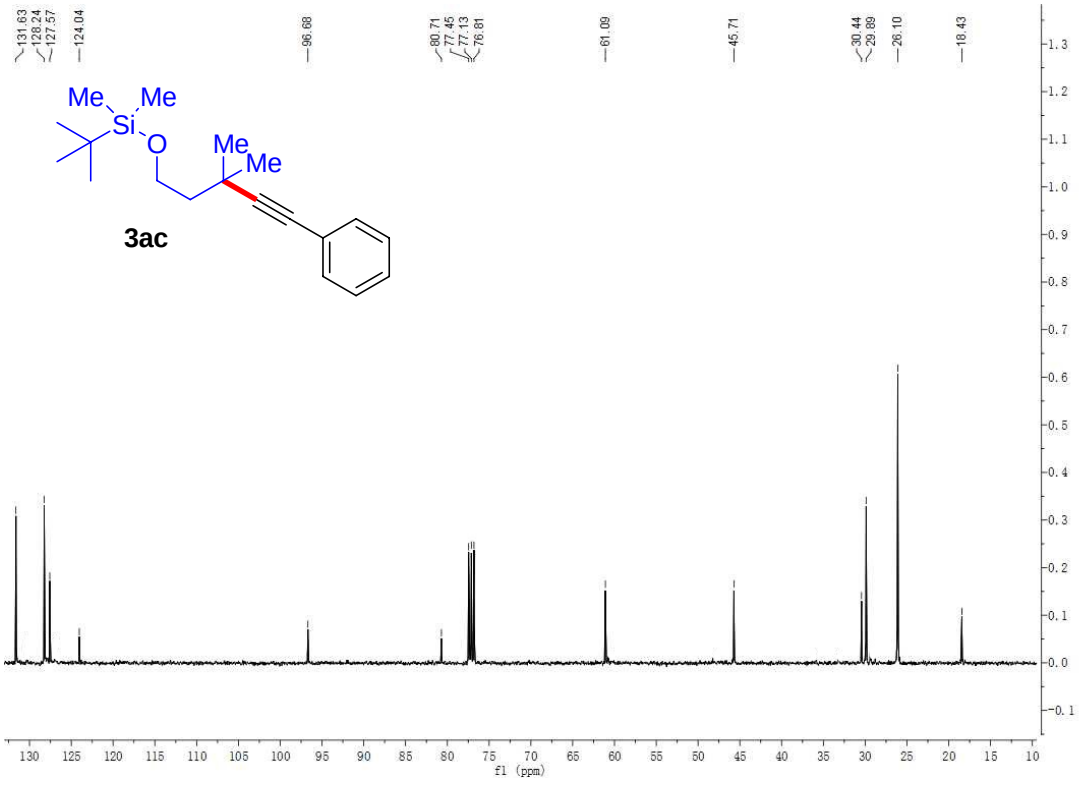

Me
3aa
f1 (ppm)

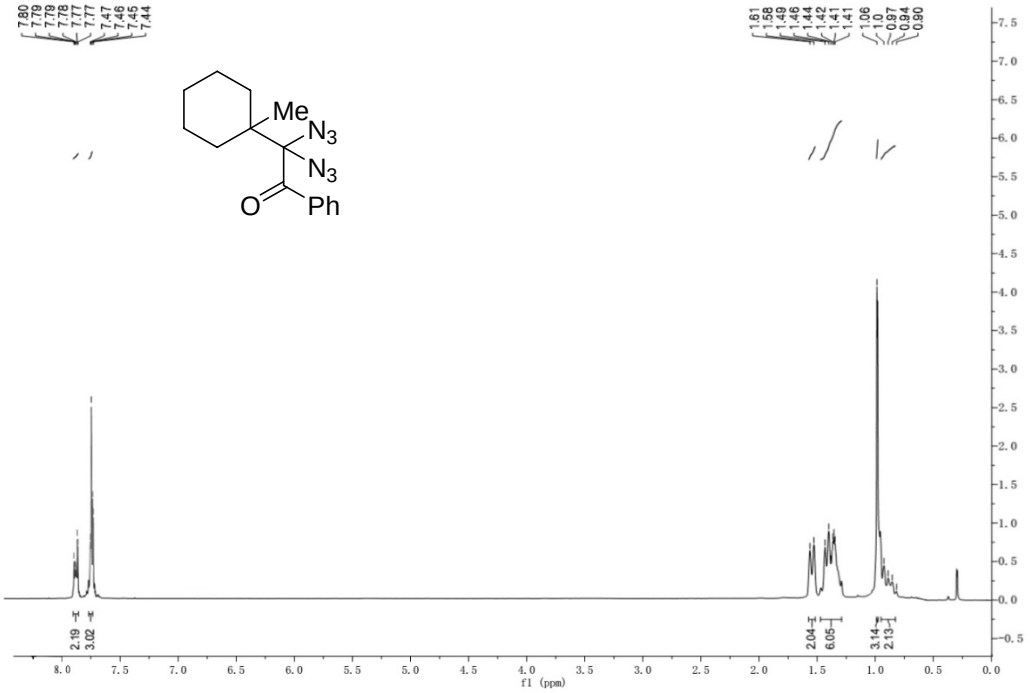

Me
3aa
f1 (ppm)

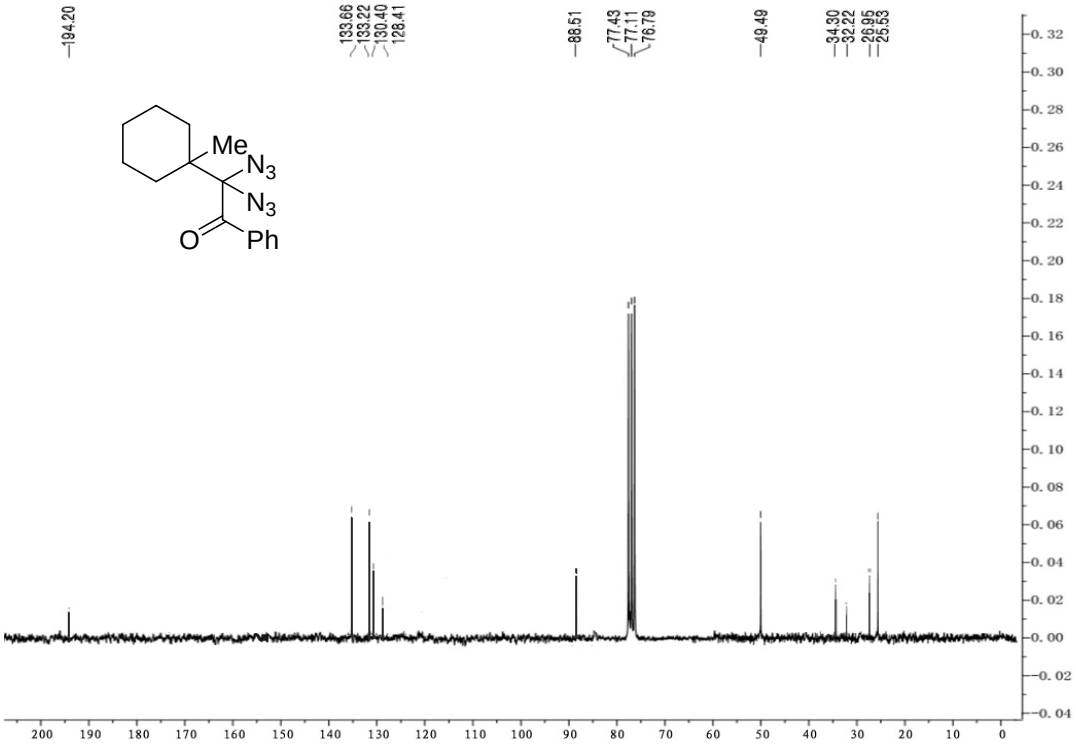

Boc-N
Me
3ab


Boc-N
Me
3ab


Me
Me
Si
O
Me
Me
3ac


Me
Me
Si
O
Me
Me
3ac


7.80
7.79
7.79
7.78
7.77
7.77
7.47
7.46
7.45
7.44
1.61
1.58
1.49
1.46
1.44
1.42
1.41
1.41
1.06
1.0
0.97
0.84
0.80
Me
N3
N3
O
Ph
2.19
3.02
2.04
6.05
3.14
2.13
f1 (ppm)


194.20
133.66
133.22
130.40
128.41
88.51
77.43
77.11
76.79
49.49
34.30
32.22
26.95
25.53
Me
N3
N3
O
Ph