

Supporting Information

Directional degradation of lignin model compounds by a palladium-catalyzed alkynylation at ambient environment

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General methods

Melting points were measured using a melting point instrument and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100-400 mesh silica gel plates (GF₂₅₄). The NHC-Pd catalysts IPr-Pd-Allyl-Cl, IPr-Pd-Cin-Cl, IPr-Pd-Im-Cl₂, and IPr-Pd-Py-Cl₂ were purchased from Beijing InnoChem Science & Technology Corporation Limited. The NHC-Pd catalysts IPr^{Ph2}-Pd-Cin-Cl and IPr^{tBu}-Pd-Cin-Cl were purchased from J&K Scientific. Unless otherwise noted, purchased chemicals were used without further purification. The structure of catalysts and ionic liquids are listed as follow (Fig 1):

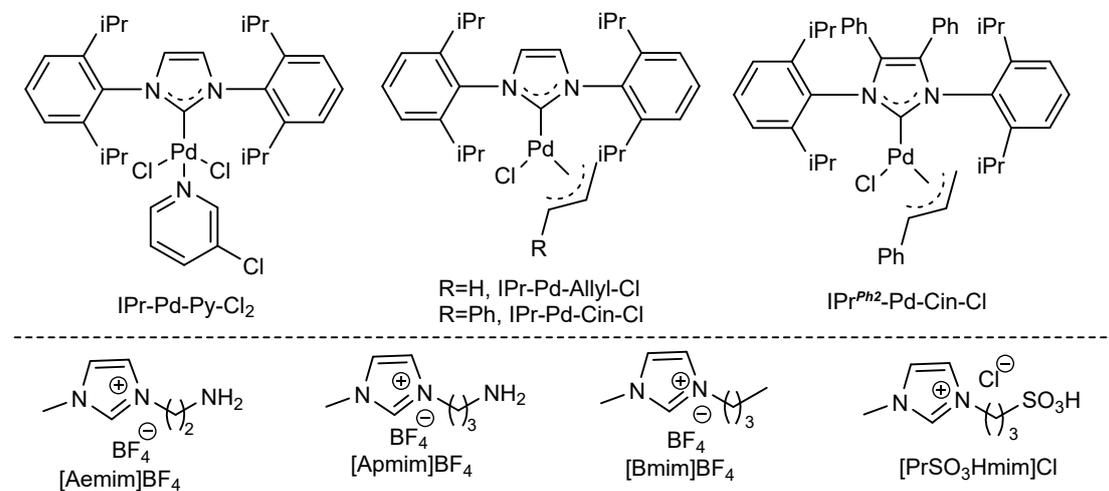
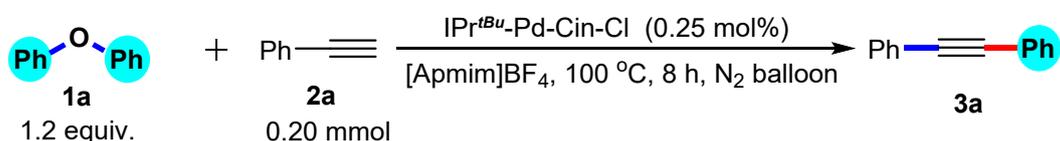


Fig 1 The structure of catalysts and ionic liquids

Typical procedure for the preparation of alkynes **3** and **4**

A mixture of IPr^{tBu}-Pd-Cin-Cl (0.25 mol %), ionic liquid [Apmim]BF₄ (3 mL) was added to an Schlenk tube equipped with a stir-bar. A balloon filled with N₂ was connected to the Schlenk tube *via* the side, then, diaryl ethers (**1**, 0.24 mmol), and alkynes (**2**, 0.20 mmol) were quickly added to the tube and stirred at 100 °C for 8 h. After the reaction was finished, the N₂ gas was released carefully and the reaction was quenched by water and extracted with CH₂Cl₂ three times. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired products.

General procedure for the recycling experiments ^a

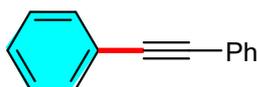


Run	GC yield of 3a ^b
1	92%
2	92%
3	92%
4	90%
5	88%
6	84%
7	75%
8	65%
9 ^c	92%

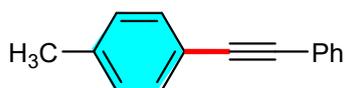
^a All runs were performed with **1a** (0.24 mmol), **2a** (0.20 mmol), IPr^{tBu}-Pd-Cin-Cl (0.25 mol %), [Apmim]BF₄ (3 mL) at 100 °C for 8 h. ^b Determined by GC using dodecane as the internal standard. ^c 0.5 mL of [Apmim]BF₄ was added.

After each run, the reaction mixture was cooled to room temperature and extractions were carried out using ethyl ether (3×5 mL) from the ionic liquid phase. Under these conditions, neither the ionic liquid nor catalyst was extracted. Upon extractions, the catalytic system was then treated under vacuum in order to remove the volatiles. The corresponding amounts of diphenyl ether (**1a**) and ethynylbenzene (**2a**) were then added for starting a new run. The results shown that the catalytic system could be typically recovered and reused for subsequent reactions for six times with no appreciable decrease in yields. However, after seven runs, the yield of **3a** sharply decreased from 84% to 75%. Gratifyingly, when added 0.5 mL of [Apmim]BF₄ to the catalytic system, the recovered IL phase exhibited the activity as well as the fresh one.

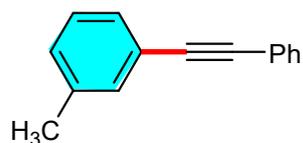
Characterization data for all products



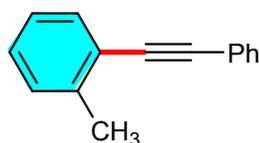
Diphenylacetylene (3a)^[1]: Yield: 86% as a white solid; m.p: 58.4-59.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, $J = 7.3, 2.6$ Hz, 4H), 7.43 - 7.33 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 131.64, 128.37, 128.28, 123.31, 89.40.



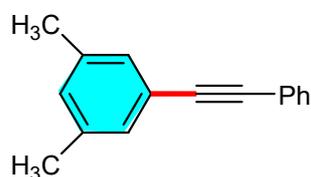
1-Methyl-4-(phenylethynyl)benzene (3b)^[1]: Yield: 82% as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dq, $J = 3.8, 2.3, 1.8$ Hz, 2H), 7.55 - 7.46 (m, 2H), 7.42 (d, $J = 1.6$ Hz, 1H), 7.40 - 7.34 (m, 2H), 7.25 - 7.18 (m, 2H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 138.44, 131.57, 129.19, 128.39, 128.14, 123.55, 120.26, 89.65, 88.81, 21.57. MS (EI) m/z 82, 95, 115, 163, 165, 189, 192.



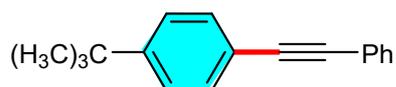
1-Methyl-3-(phenylethynyl)benzene (3c)^[1]: Yield: 80% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, $J = 7.7, 1.9$ Hz, 2H), 7.43 (s, 1H), 7.41 (d, $J = 6.9$ Hz, 2H), 7.39 (d, $J = 1.5$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 138.05, 132.24, 131.65, 129.20, 128.74, 128.37, 128.29, 128.20, 123.47, 123.16, 89.64, 89.11, 21.26. MS (EI) m/z 83, 95, 115, 163, 165, 189, 192.



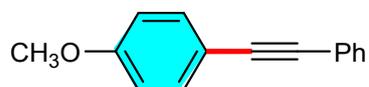
1-Methyl-2-(phenylethynyl)benzene (3d)^[1]: Yield: 81% as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.63 - 7.56 (m, 3H), 7.43 - 7.38 (m, 3H), 7.33 - 7.27 (m, 2H), 7.26 - 7.19 (m, 1H), 2.59 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.24, 132.57, 131.90, 131.58, 129.53, 128.51, 128.46, 128.37, 128.24, 125.65, 123.62, 123.09, 93.42, 88.42, 20.82. MS (EI) m/z 82, 94, 115, 139, 163, 165, 192.



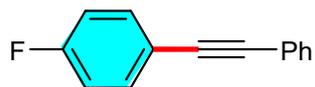
1,3-Dimethyl-5-phenylethynyl-benzene (3e)^[1]: Yield: 77% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.61 - 7.55 (m, 2H), 7.41 - 7.36 (m, 3H), 7.23 (s, 2H), 7.02 (s, 1H), 2.36 (q, $J = 0.7$ Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 137.93, 131.63, 130.25, 129.34, 128.40, 128.14, 123.52, 122.91, 89.79, 88.75, 21.16. MS (EI) m/z 76, 89, 103, 128, 152, 165, 178, 189, 191, 206.



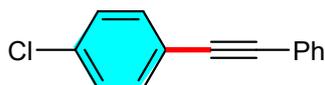
4-*t*-Butyl diphenylacetylene (3f)^[1]: Yield: 78% as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 21.0 Hz, 4H), 7.49 - 7.36 (m, 5H), 1.42 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.60, 131.68, 131.47, 128.53, 128.14, 125.43, 123.68, 120.41, 89.71, 88.90, 31.27. MS (EI) m/z 61, 73, 95, 133, 152, 178, 191, 204, 219, 234.



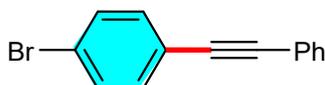
1-Methoxy-4-phenylethyne (3g)^[1]: Yield: 75% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, J = 7.9, 1.8 Hz, 2H), 7.53 - 7.48 (m, 2H), 7.41 - 7.32 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.65, 133.09, 131.48, 128.34, 127.97, 123.63, 115.41, 114.03, 89.41, 88.11, 55.32. MS (EI) m/z 63, 88, 115, 139, 150, 165, 193, 208.



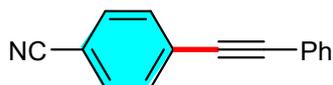
1-Fluoro-4-(2-phenylethynyl)benzene (3h)^[1]: Yield: 88% as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.60 - 7.52 (m, 4H), 7.39 (dd, J = 5.5, 3.5 Hz, 2H), 7.38 (s, 1H), 7.12 - 7.04 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 162.50 (d, J = 254.2 Hz), 133.51 (d, J = 8.6 Hz), 133.48, 132.55, 131.60, 128.42 (d, J = 8.5 Hz), 123.13, 119.43, 115.78 (d, J = 21.4 Hz), 89.10, 88.34. MS (EI) m/z 63, 85, 98, 120, 144, 170, 194, 196.



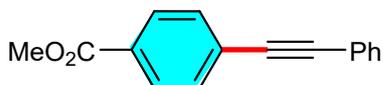
1-Chloro-4-(phenylethynyl)benzene (3i)^[1]: Yield: 85% as colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.60 - 7.55 (m, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.44 - 7.32 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 134.31, 132.86, 131.66, 128.74, 128.53, 128.45, 122.99, 121.84, 90.40, 88.32. MS (EI) m/z 63, 75, 88, 93, 106, 126, 151, 176, 186, 212.



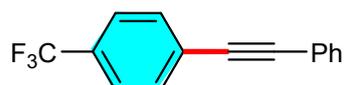
1-Bromo-4-(phenylethynyl)benzene (3j)^[1]: Yield: 84% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.60 - 7.55 (m, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.41 - 7.32 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 133.06, 131.66, 131.64, 128.55, 128.45, 122.96, 122.52, 122.29, 90.56, 88.37. MS (EI) m/z 75, 88, 99, 129, 151, 176, 207, 229, 256.



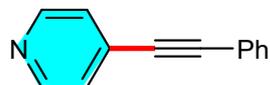
4-(2-Phenyleth-1-ynyl)benzonitrile (3k)^[2]: Yield: 90% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.70 - 7.60 (m, 4H), 7.60 - 7.53 (m, 2H), 7.41 (dd, J = 5.1, 1.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 132.10, 131.83, 129.17, 128.55, 128.25, 122.25, 118.57, 111.49, 93.82, 87.78. MS (EI) m/z 75, 88, 101, 151, 176, 201, 203.



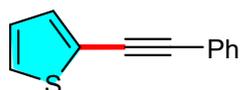
Methyl 4-(phenylethynyl)benzoate (3l)^[1]: Yield: 93% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.60 - 7.54 (m, 2H), 7.43 - 7.35 (m, 3H), 3.95 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.58, 131.75, 131.52, 129.54, 129.49, 128.78, 128.46, 128.03, 122.72, 92.38, 88.65, 52.24. MS (EI) *m/z* 75, 88, 102, 126, 151, 176, 205, 236.



1-(Phenylethynyl)-4-(trifluoromethyl)benzene (3m)^[2]: Yield: 94% as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.70 - 7.56 (m, 6H), 7.45 - 7.36 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 131.80 (q, *J* = 4.6 Hz), 129.93 (q, *J* = 32.6 Hz), 128.86, 128.48, 127.15, 125.15 (q, *J* = 272.3 Hz), 125.28, 125.24, 122.63, 122.59, 91.78, 87.99. MS (EI) *m/z* 75, 85, 98, 123, 176, 196, 227, 246.

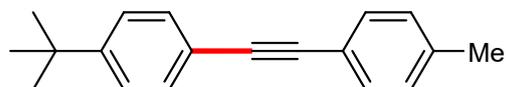


4-(Phenylethynyl)pyridine (3n)^[1]: Yield: 72% as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 6.1 Hz, 2H), 7.57 (dt, *J* = 4.8, 2.7 Hz, 2H), 7.43 - 7.36 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 149.78, 131.89, 131.47, 129.23, 128.52, 125.55, 122.11, 93.99, 86.68. MS (EI) *m/z* 76, 98, 126, 151, 179.

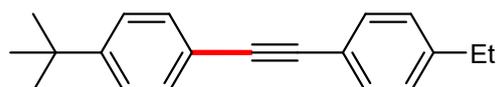


2-(Phenylethynyl)thiophene (3o)^[1]: Yield: 63% as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dt, *J* = 5.1, 2.6 Hz, 2H), 7.41 (dd, *J* = 5.1, 2.1 Hz, 3H), 7.35 (ddd, *J* = 9.1, 4.4, 1.3 Hz, 2H), 7.07 (dd, *J* = 5.3, 3.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 132.00, 131.50, 128.52, 128.48,

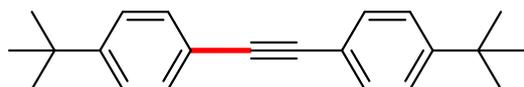
127.36, 127.21, 123.40, 123.01, 93.18, 82.77. MS (EI) m/z 63, 74, 92, 113, 126, 139, 152, 184.



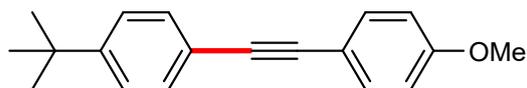
1-(Tert-butyl)-4-(p-tolylethynyl)benzene (4a)^[3]: Yield: 80% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J = 16.3, 8.4 Hz, 4H), 7.43 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 1.40 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.36, 138.20, 131.54, 131.36, 129.15, 125.39, 120.55, 120.52, 88.99, 88.95, 34.82, 31.26, 21.56. MS (EI) m/z 76, 94, 102, 116, 139, 165, 178, 218, 233, 248.



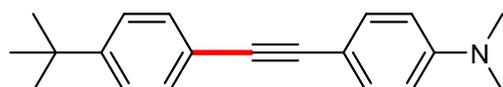
1-(Tert-butyl)-4-((4-ethylphenyl)ethynyl)benzene (4b)^[3]: Yield: 83% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.56 - 7.50 (m, 4H), 7.42 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.39 (s, 9H), 1.31 (t, J = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 151.35, 144.51, 131.62, 131.35, 127.93, 125.36, 120.76, 120.56, 89.01, 88.93, 34.81, 31.24, 28.88, 15.41. MS (EI) m/z 77, 89, 101, 116, 165, 178, 202, 217, 231, 247, 262.



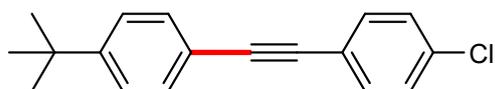
1-Tert-butyl-4-[2-(4-tert-butylphenyl)ethynyl]benzene (4c)^[3]: Yield: 77% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.54 - 7.49 (m, 4H), 7.43 - 7.39 (m, 4H), 1.38 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 151.34, 131.34, 125.34, 120.55, 88.92, 34.80. MS (EI) m/z 57, 76, 101, 130, 178, 217, 245, 260, 275, 290.



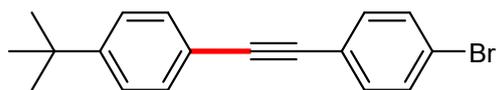
1-(1,1-Dimethylethyl)-4-[2-(4-methoxyphenyl)ethynyl]benzene (4d)^[3]: Yield: 78% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 8.8, 5.9 Hz, 4H), 7.39 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 159.51, 151.19, 133.02, 131.19, 125.32, 120.59, 115.69, 113.99, 88.68, 88.20, 55.31, 34.77, 31.21. MS (EI) m/z 76, 94, 110, 124, 165, 189, 221, 234, 249, 264.



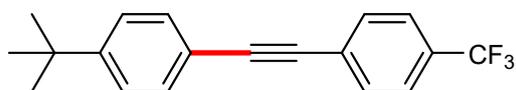
4-((4-(Tert-butyl)phenyl)ethynyl)-*N,N*-dimethylaniline (4e)^[3]: Yield: 72% as a yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.51 - 7.35 (m, 6H), 6.69 (d, J = 8.9 Hz, 2H), 3.02 (s, 6H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.66, 150.03, 132.69, 131.03, 125.26, 121.14, 111.89, 110.39, 89.87, 87.42, 40.27, 34.74, 31.25. MS (EI) m/z 116, 131, 152, 178, 202, 234, 247, 262, 277.



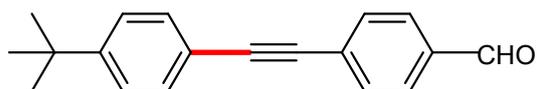
1-Chloro-4-[[4-(1,1-dimethylethyl)phenyl]ethynyl] (4g)^[3]: Yield: 73% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.55 - 7.24 (m, 8H), 1.37 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.83, 134.06, 132.80, 131.37, 128.67, 125.43, 122.07, 119.93, 90.55, 87.66, 34.84, 31.19. MS (EI) m/z 112, 201, 225, 253, 268.



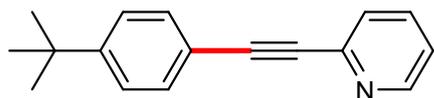
1-Bromo-4-[[4-(1,1-dimethylethyl)phenyl]ethynyl] (4h)^[3]: Yield: 77% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (ddd, J = 35.4, 8.4, 3.1 Hz, 8H), 1.38 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.86, 133.06, 131.63, 131.42, 125.48, 122.56, 122.30, 119.95, 90.80, 87.79, 34.87, 31.23. MS (EI) m/z 94, 135, 202, 297, 312.



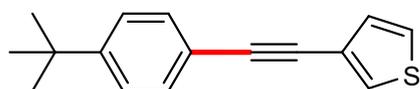
1-[2-[4-(1,1-Dimethylethyl)phenyl]ethynyl]-4-(trifluoromethyl)benzene (4i)^[4]: Yield: 75% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.69 - 7.62 (m, 4H), 7.55 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 1.39 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 152.27, 131.79, 131.55, 129.75 (q, J = 32.6 Hz), 127.43, 125.51, 125.40, 125.26 (q, J = 3.6 Hz), 124.05 (q, J = 272.1 Hz), 119.59, 92.08, 87.46, 34.88, 31.16. (EI) m/z 51, 75, 91, 104, 129, 143, 178, 202, 247, 259, 272, 287, 302.



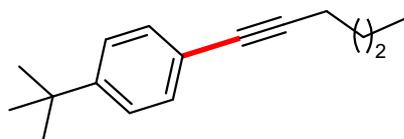
1-(tert-butyl)-4-(*p*-tolylethynyl)benzene (4j)^[4]: Yield: 69% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 10.02 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 1.36 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 191.34, 152.41, 135.28, 132.71, 132.07, 131.60, 129.88, 129.59, 129.49, 125.54, 119.49, 93.84, 88.08, 34.90, 31.18. MS (EI) m/z 95, 109, 123, 151, 178, 202, 219, 247, 262.



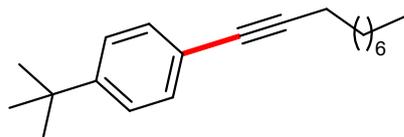
2-[2-[4-(1,1-Dimethylethyl)phenyl]ethynyl]pyridine (4k)^[4]: Yield: 62% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, $J = 4.9$ Hz, 1H), 7.66 (td, $J = 7.6, 1.9$ Hz, 1H), 7.54 (dd, $J = 14.3, 8.1$ Hz, 3H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.22 (dd, $J = 7.6, 4.9$ Hz, 1H), 1.34 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 152.34, 150.03, 143.69, 136.13, 131.83, 127.12, 125.43, 122.58, 119.23, 89.55, 88.12, 34.87, 31.16. MS (EI) m/z 78, 96, 110, 139, 152, 180, 192, 204, 220, 235.



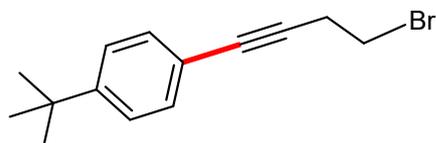
3-[2-[4-(1,1-Dimethylethyl)phenyl]ethynyl]thiophene (4l)^[4]: Yield: 65% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, $J = 3.0, 1.1$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 2H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.33 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.24 (dd, $J = 5.0, 1.3$ Hz, 1H), 1.37 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.51, 131.30, 129.97, 128.36, 125.39, 125.30, 122.57, 120.21, 89.06, 83.88, 34.82, 31.23. (EI) m/z 98, 112, 139, 165, 184, 197, 210, 225, 240.



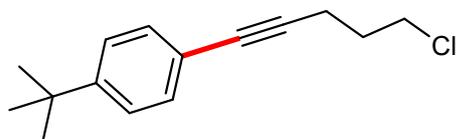
1-(Tert-butyl)-4-(pent-1-yn-1-yl)benzene (4n)^[4]: Yield: 65% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.28 (m, 4H), 2.43 (t, $J = 7.0$ Hz, 2H), 1.64 - 1.59 (m, 2H), 1.54 - 1.47 (m, 2H), 1.33 (s, 9H), 0.98 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.58, 131.23, 125.16, 121.11, 89.62, 34.66, 31.21, 30.95, 22.02, 19.13, 13.66. MS (EI) m/z 115, 141, 199, 214.



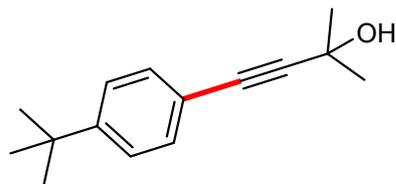
1-(Tert-butyl)-4-(pent-1-yn-1-yl)benzene (4o)^[4]: Yield: 73% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.40 - 7.31 (m, 4H), 2.43 (t, J = 7.1 Hz, 2H), 1.63 (dd, J = 8.7, 6.3 Hz, 2H), 1.49 - 1.30 (m, 19H), 0.95 - 0.90 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.69, 131.36, 125.28, 121.25, 89.81, 34.78, 32.01, 31.34, 29.38, 29.30, 29.08, 29.00, 22.82, 19.58, 14.26. MS (EI) m/z 73, 96, 133, 190, 207, 253, 281.



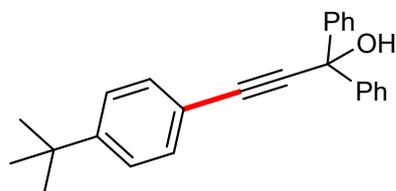
1-(3-Bromo-1-propyn-1-yl)-4-(1,1-dimethylethyl)benzene (4p)^[5]: Yield: 57% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (q, J = 8.6 Hz, 4H), 3.55 (t, J = 7.4 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 1.33 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.34, 131.39, 125.28, 120.10, 85.81, 82.50, 34.74, 31.19, 29.67, 23.95. MS (EI) m/z 128, 141, 249, 266.



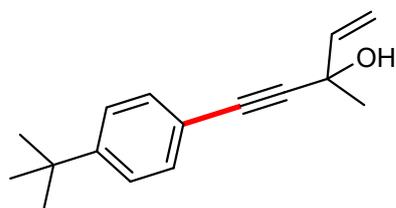
1-(Tert-butyl)-4-(5-chloropent-1-yn-1-yl)benzene (4q)^[5]: Yield: 68% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 - 7.28 (m, 4H), 3.74 (t, J = 6.4 Hz, 2H), 2.63 (t, J = 6.8 Hz, 2H), 2.08 (t, J = 6.6 Hz, 2H), 1.33 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.99, 131.29, 125.24, 120.56, 87.29, 43.79, 34.71, 31.57, 31.19, 16.91. MS (EI) m/z 128, 141, 219, 234.



4-(4-(Tert-butyl)phenyl)-2-methylbut-3-yn-2-ol (4r)^[5]: Yield: 54% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (q, *J* = 8.5 Hz, 4H), 2.23 (s, 1H), 1.64 (s, 6H), 1.33 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.49, 131.36, 125.25, 119.71, 93.15, 82.22, 65.66, 34.74, 31.57, 31.18. MS (EI) *m/z* 79, 115, 159, 201, 216.

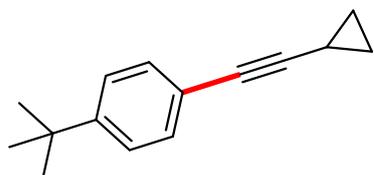


3-(4-(Tert-butyl)phenyl)-1,1-diphenylprop-2-yn-1-ol (4s)^[5]: Yield: 71% as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.81 - 7.27 (m, 14H), 3.04 (s, 1H), 1.39 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 152.07, 145.23, 131.61, 128.35, 127.74, 126.15, 126.06, 125.41, 119.47, 91.19, 87.47, 74.93, 34.88, 31.25. MS (EI) *m/z* 148, 178, 207, 339, 340.

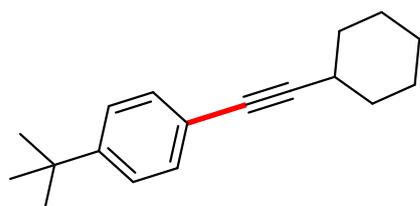


5-(4-(Tert-butyl)phenyl)-3-methylpent-1-en-4-yn-3-ol (4t)^[5]: Yield: 60% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.45 - 7.27 (m, 4H), 6.09 (dd, *J* = 17.0, 10.2 Hz, 1H), 5.62 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.1 Hz, 1H), 2.40 (s, 1H), 1.68 (s, 3H), 1.34 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 151.70, 142.17, 131.44, 125.28, 119.55, 113.65, 90.26, 84.93, 68.72,

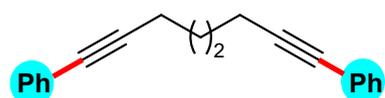
34.77, 31.18, 30.13. MS (EI) m/z 115, 143, 213, 227.



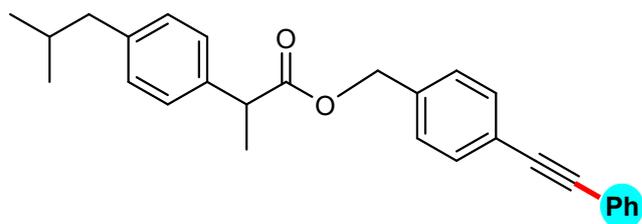
1-(Tert-butyl)-4-(cyclopropylethynyl)benzene (4u)^[5]: Yield: 67% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.39 - 7.25 (m, 4H), 1.47 (s, 1H), 1.33 (s, 9H), 0.93 - 0.77 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 150.61, 131.33, 125.16, 120.89, 92.59, 34.67, 31.20, 8.60. MS (EI) m/z 115, 128, 155, 183, 198.



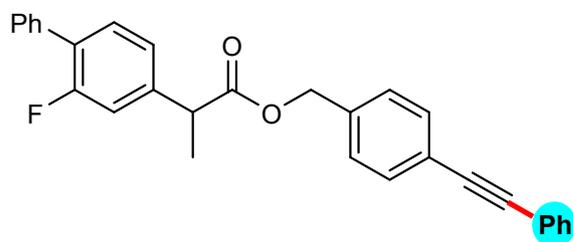
1-(Tert-butyl)-4-(cyclohexylethynyl)benzene (4v)^[5]: Yield: 72% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 4H), 2.60 (s, 1H), 1.91-1.37 (m, 10H), 1.32 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 150.54, 131.25, 125.13, 121.12, 93.71, 34.66, 32.79, 31.21, 29.68, 25.97, 24.91. MS (EI) m/z 141, 225, 240.



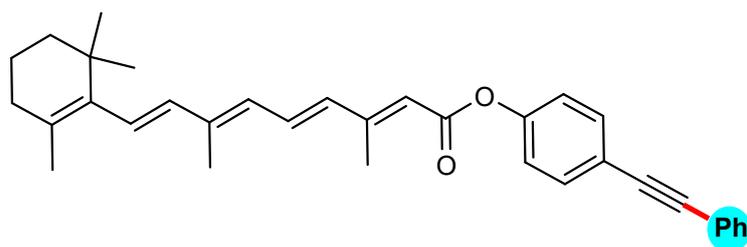
1,7-Diphenylhepta-1,6-diyne (6)^[6]: Yield: 77% as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.43 - 7.36 (m, 4H), 7.30 - 7.22 (m, 6H), 2.49 - 2.43 (m, 4H), 1.83 - 1.73 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 131.62, 128.25, 127.61, 124.01, 89.89, 81.00, 27.95, 19.08. MS (EI) m/z 89, 115, 128, 165, 215, 229, 258.



4-(Phenylethynyl)benzyl 2-(4-isobutylphenyl)propanoate (8a): Yield: 73% as a white solid; mp = 44.5-45.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 - 7.49 (m, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.33 (dd, $J = 5.1, 2.1$ Hz, 3H), 7.19 (t, $J = 7.5$ Hz, 4H), 7.09 (d, $J = 6.1$ Hz, 2H), 5.10 (s, 2H), 3.75 (q, $J = 7.2$ Hz, 1H), 2.45 (d, $J = 7.3$ Hz, 2H), 1.85 (dp, $J = 13.6, 6.8$ Hz, 1H), 1.51 (d, $J = 7.1$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.49, 140.70, 137.53, 136.24, 131.68, 131.66, 129.40, 128.41, 128.39, 127.71, 127.26, 123.18, 122.98, 89.74, 89.08, 65.87, 45.17, 45.07, 30.27, 22.44, 18.41. HRMS-ESI (m/z): calcd for $\text{C}_{28}\text{H}_{28}\text{O}_2$, $[\text{M}+\text{H}]^+$: 397.2162, found 397.2161.

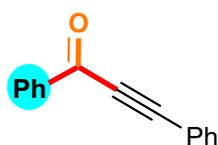


4-(phenylethynyl)benzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (8b): Yield: 78% as a white oil; ^1H NMR (400 MHz, CDCl_3) δ 7.55 - 7.46 (m, 6H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.39 - 7.27 (m, 5H), 7.25 - 7.21 (m, 2H), 7.15 - 7.09 (m, 2H), 5.17 - 5.08 (m, 2H), 3.80 (q, $J = 7.2$ Hz, 1H), 1.54 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.75, 160.97, 158.50, 141.64, 141.57, 135.93, 135.52, 131.79, 131.70, 130.91, 130.88, 129.04, 129.01, 128.54, 128.44, 127.99, 127.76, 123.67, 123.64, 123.26, 123.16, 115.49, 115.25, 89.96, 89.04, 66.29, 45.08, 45.06, 18.36. HRMS-ESI (m/z): calcd for $\text{C}_{30}\text{H}_{23}\text{FO}_2$, $[\text{M}+\text{H}]^+$: 435.1755, found 435.1750.



4-(Phenylethynyl)phenyl (2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)

nona-2,4,6,8-tetraenoate (8c): Yield: 75% as a yellow solid; mp =128.5 - 129 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (ddd, $J = 6.8, 5.1, 2.0$ Hz, 4H), 7.34 (dd, $J = 5.1, 2.3$ Hz, 3H), 7.17 - 7.03 (m, 3H), 6.35 (dd, $J = 21.7, 15.3$ Hz, 2H), 6.25 - 6.10 (m, 2H), 5.98 (s, 1H), 2.42 (d, $J = 1.1$ Hz, 3H), 2.03 (d, $J = 1.0$ Hz, 5H), 1.73 (s, 3H), 1.66 - 1.58 (m, 2H), 1.51 - 1.43 (m, 2H), 1.04 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.14, 156.07, 150.72, 140.63, 137.69, 137.20, 134.68, 132.70, 132.25, 131.63, 130.31, 129.41, 129.26, 128.38, 128.29, 123.23, 121.96, 120.52, 116.89, 89.28, 88.84, 39.61, 34.30, 33.16, 29.00, 21.82, 19.24, 14.15, 13.02. HRMS-ESI (m/z): calcd for $\text{C}_{34}\text{H}_{37}\text{O}_2$, $[\text{M}+\text{H}]^+$: 477.2788, found 477.2787.



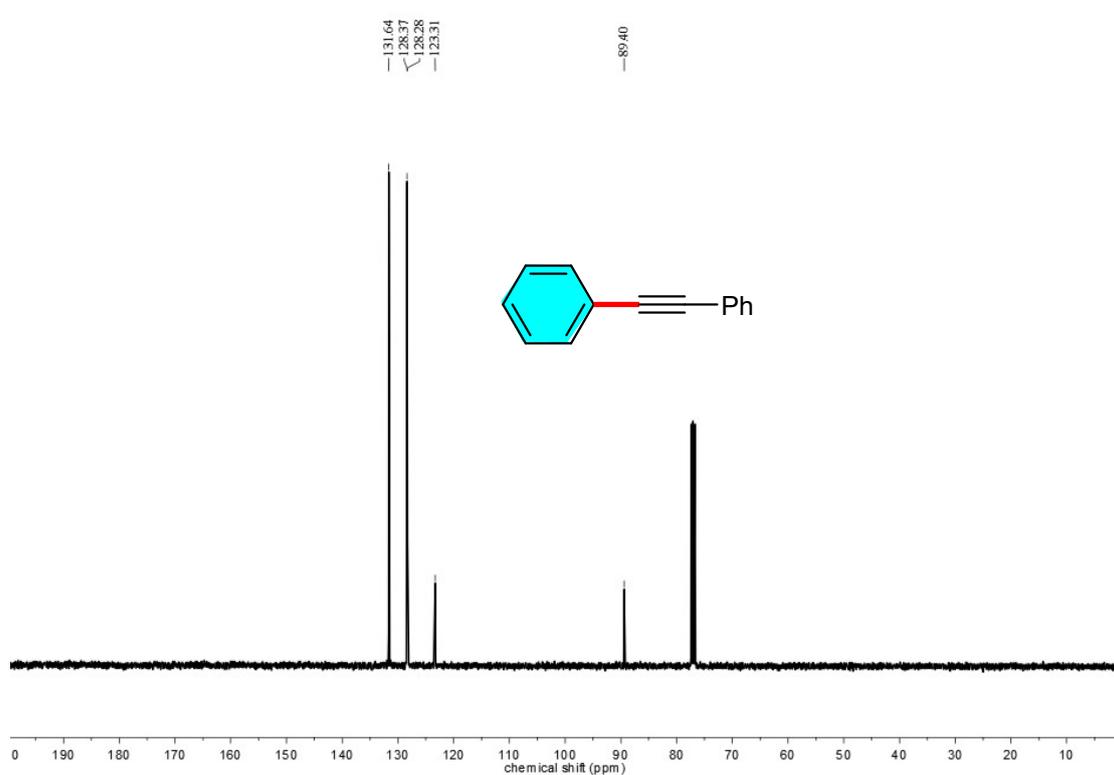
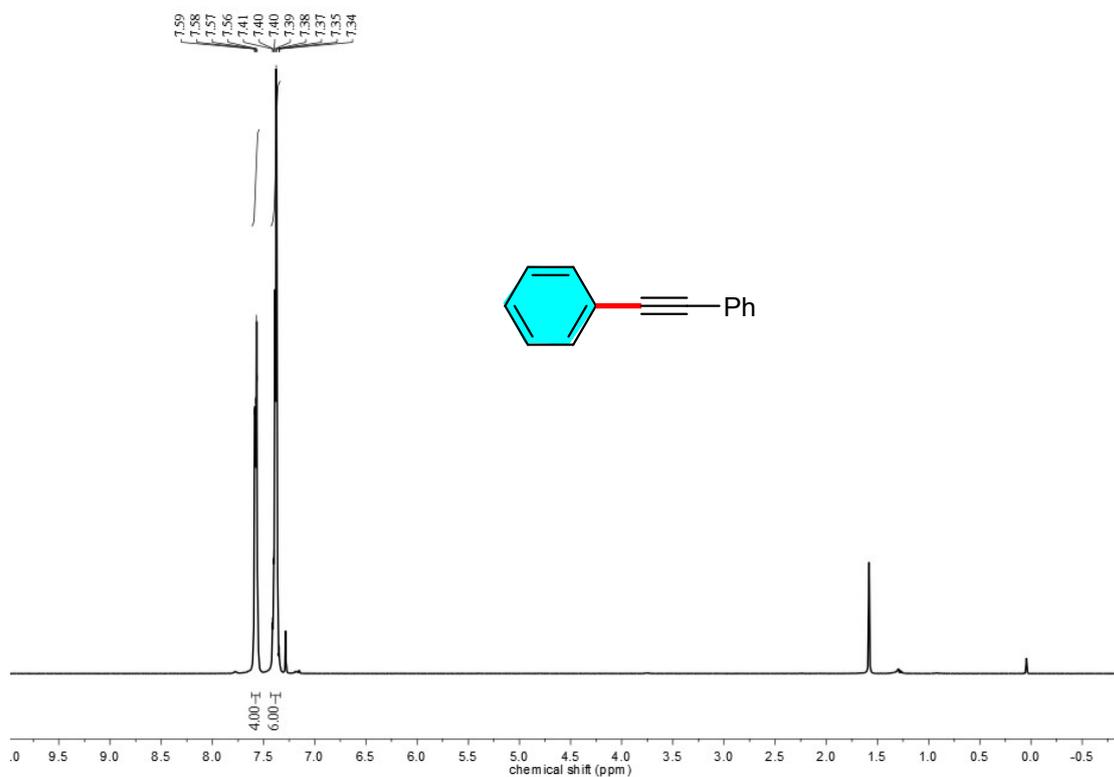
1,3-Diphenylprop-2-yn-1-one (9)^[7]: Yield: 65% as a as a yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3)

δ 8.28 - 8.22 (m, 2H), 7.73 - 7.66 (m, 2H), 7.62 (tt, $J = 6.8, 1.4$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.48 - 7.44 (m, 1H), 7.46 - 7.37 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.0, 136.9, 134.3, 133.2, 130.8, 129.6, 128.9, 128.6, 120.1, 93.2, 87.0; MS (EI) m/z 75, 115, 129, 178, 206.

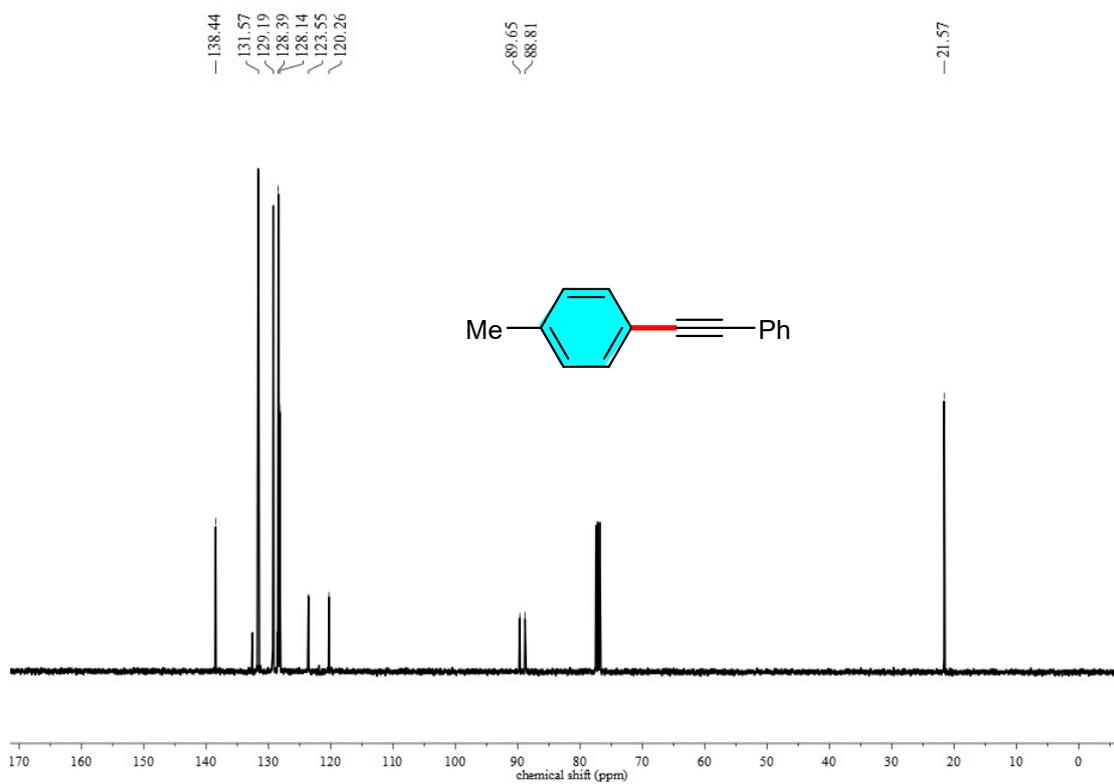
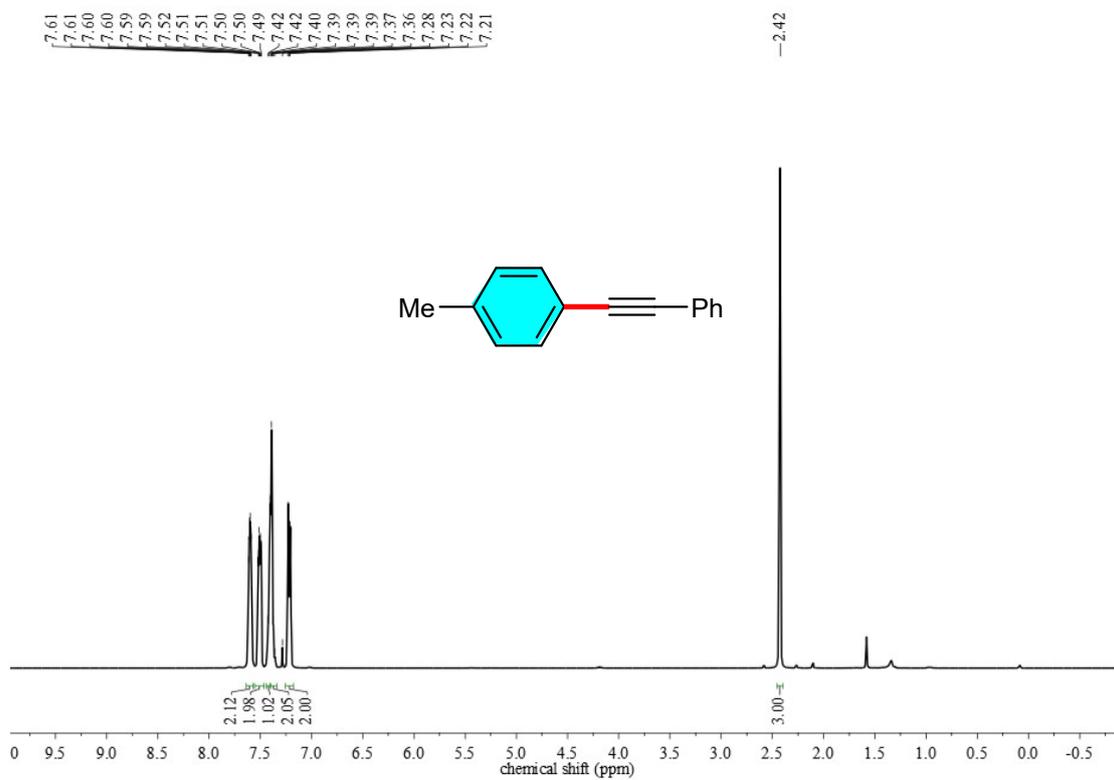
- [1] D. N. Sawant, P. J. Tambade, Y. S. Wagh and B. M. Bhanage, FeCl₃/PPh₃-Catalyzed Sonogashira Coupling Reaction of Aryl Iodides with Terminal Alkynes [J]. *Tetrahedron. Lett.*, 2010, **51**, 2758.
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^1H and ^{13}C NMR spectra of all compounds

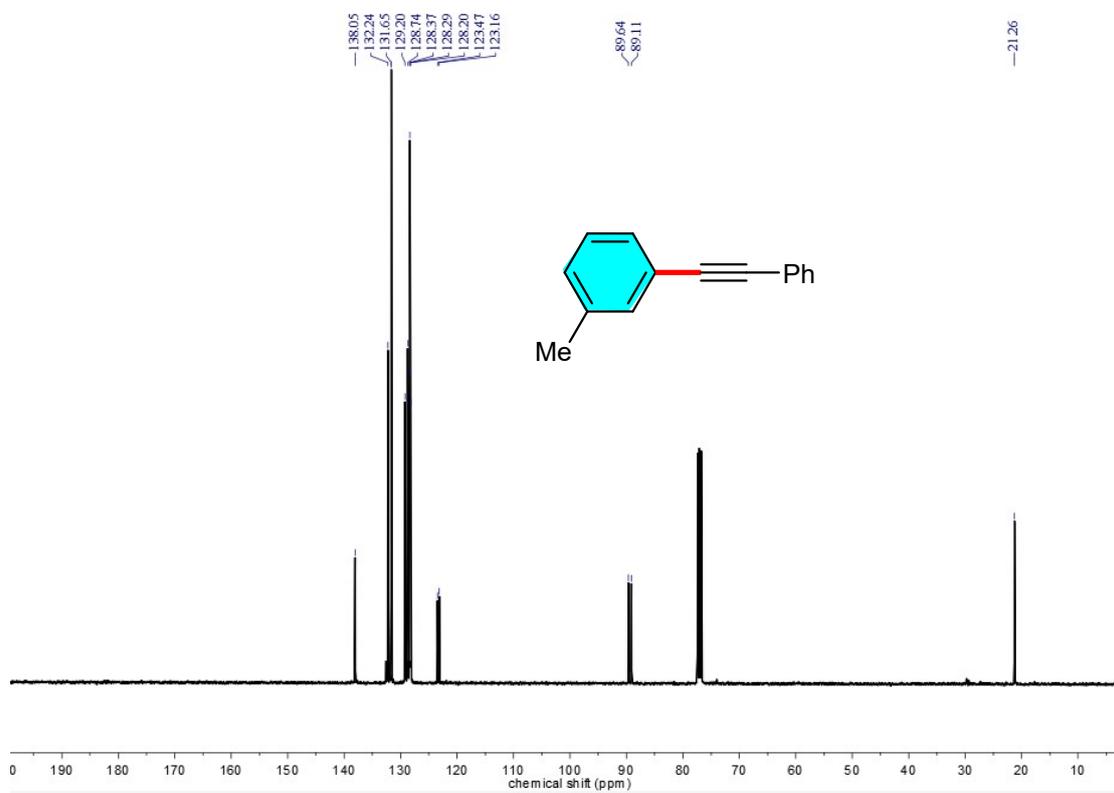
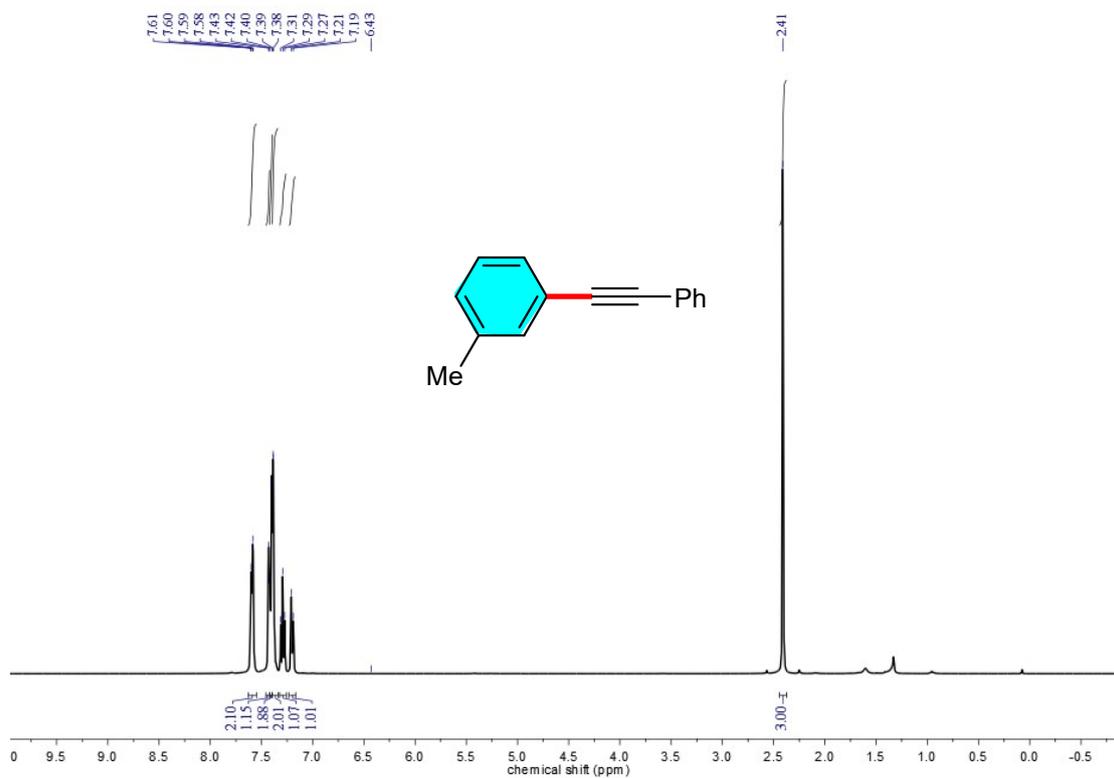
NMR spectrum of compound **3a** in CDCl_3 (400 MHz)



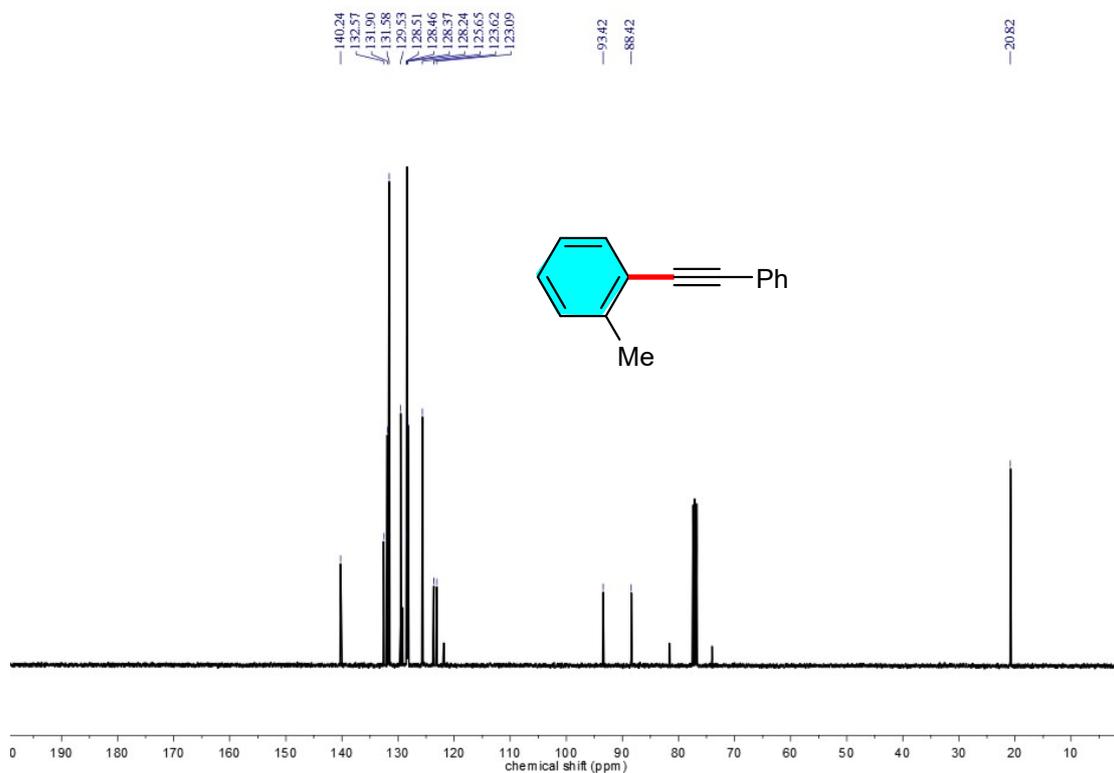
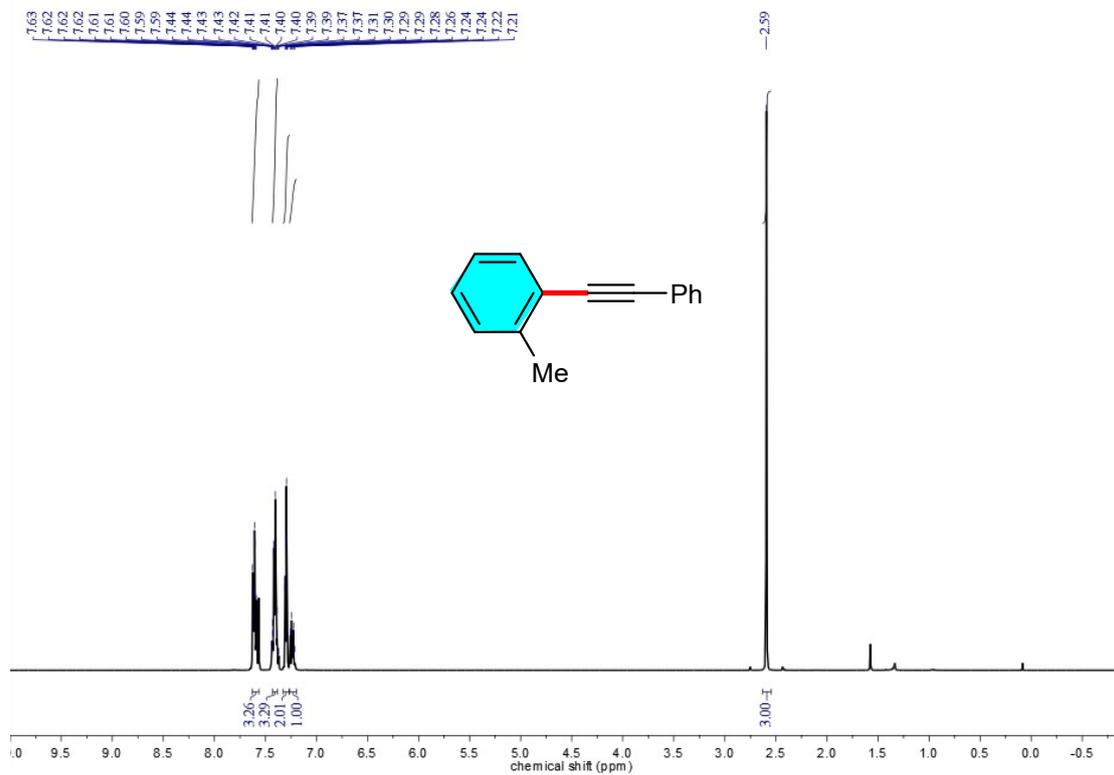
NMR spectrum of compound **3b** in CDCl₃ (400 MHz)



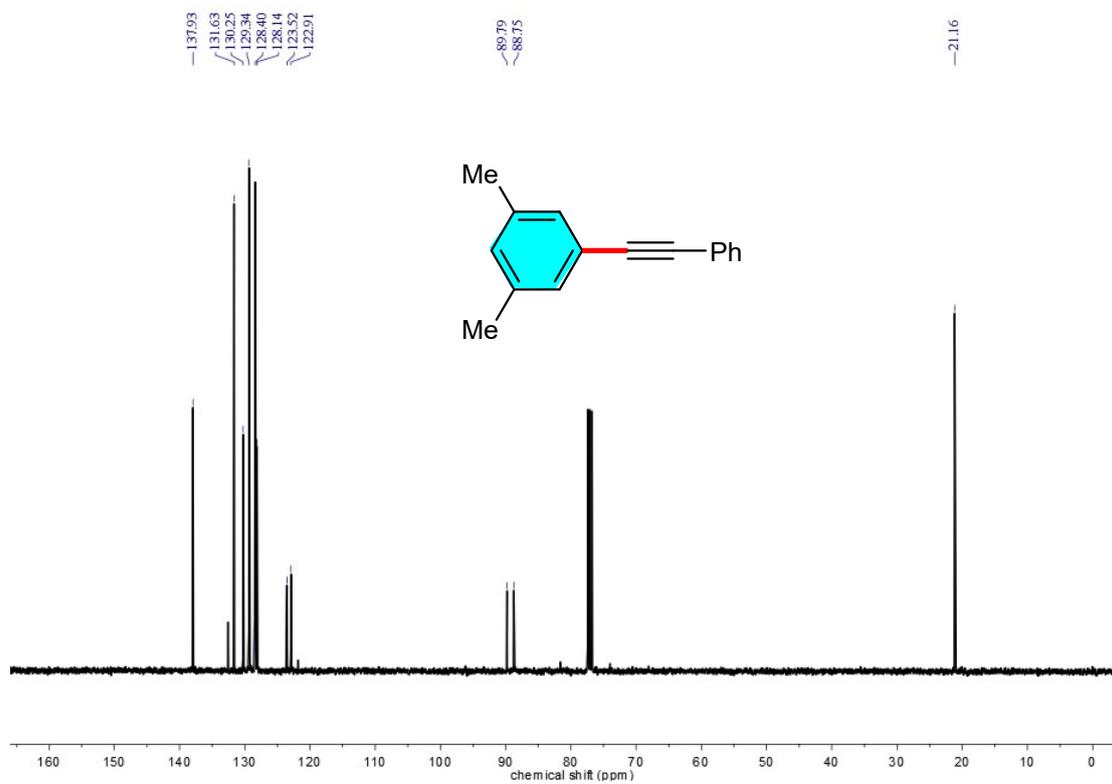
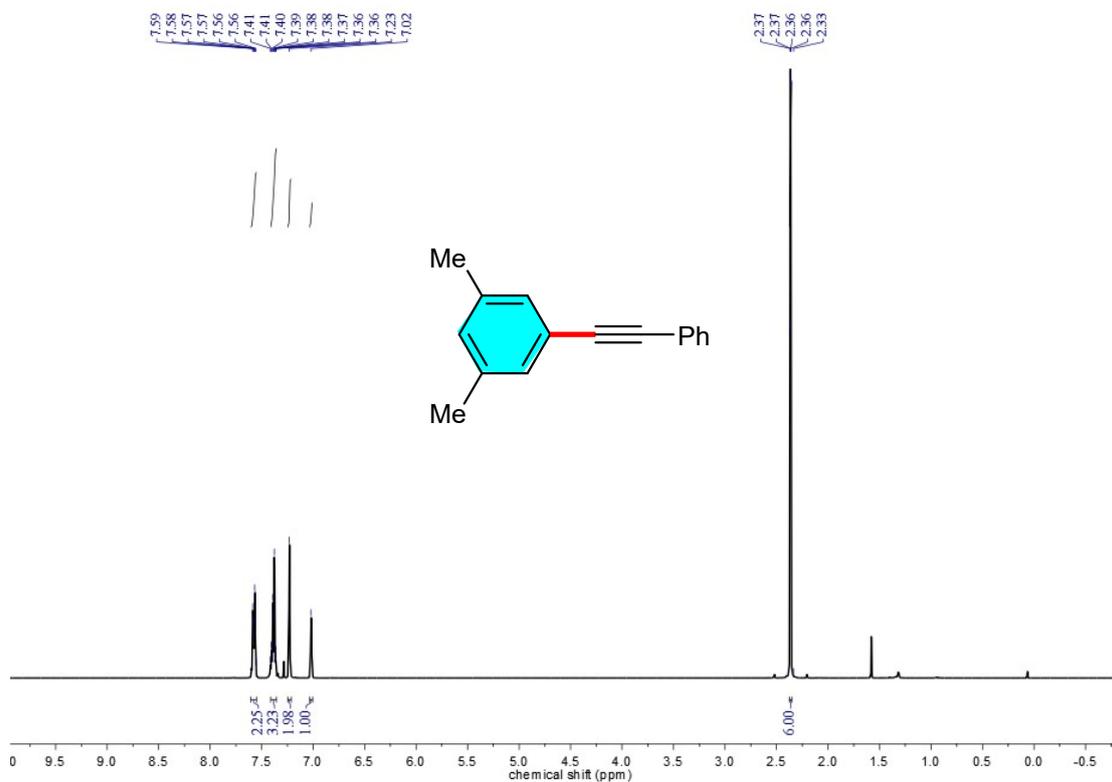
NMR spectrum of compound **3c** in CDCl₃ (400 MHz)



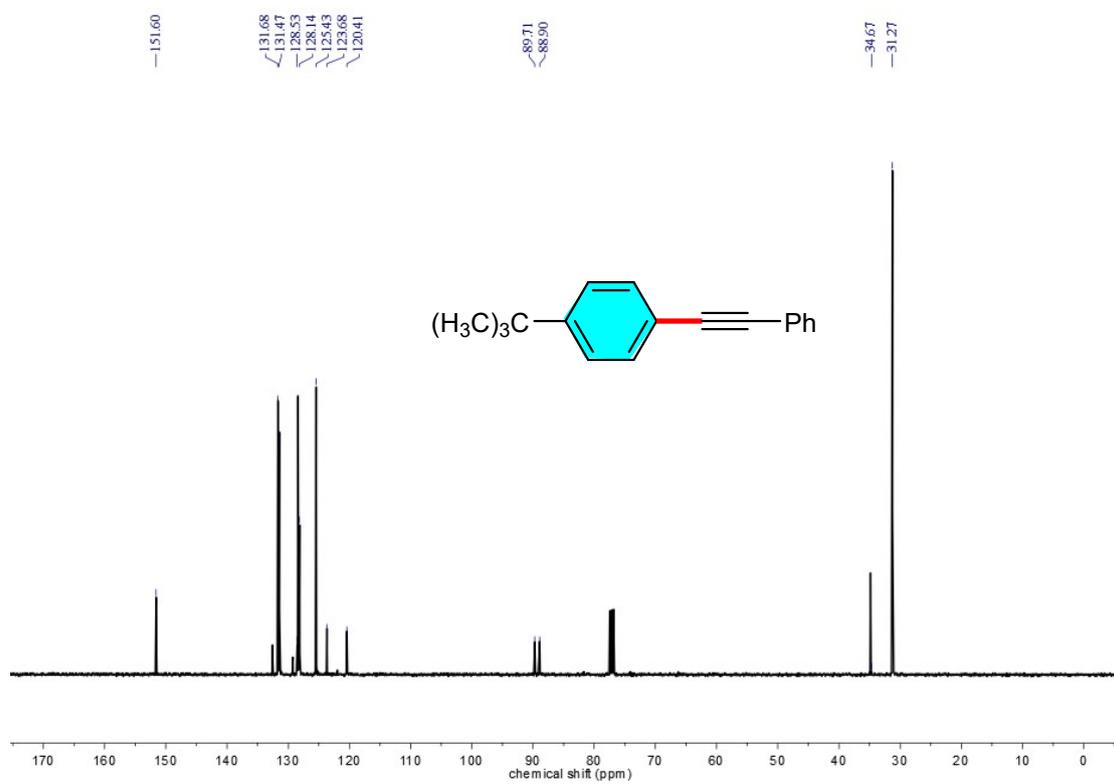
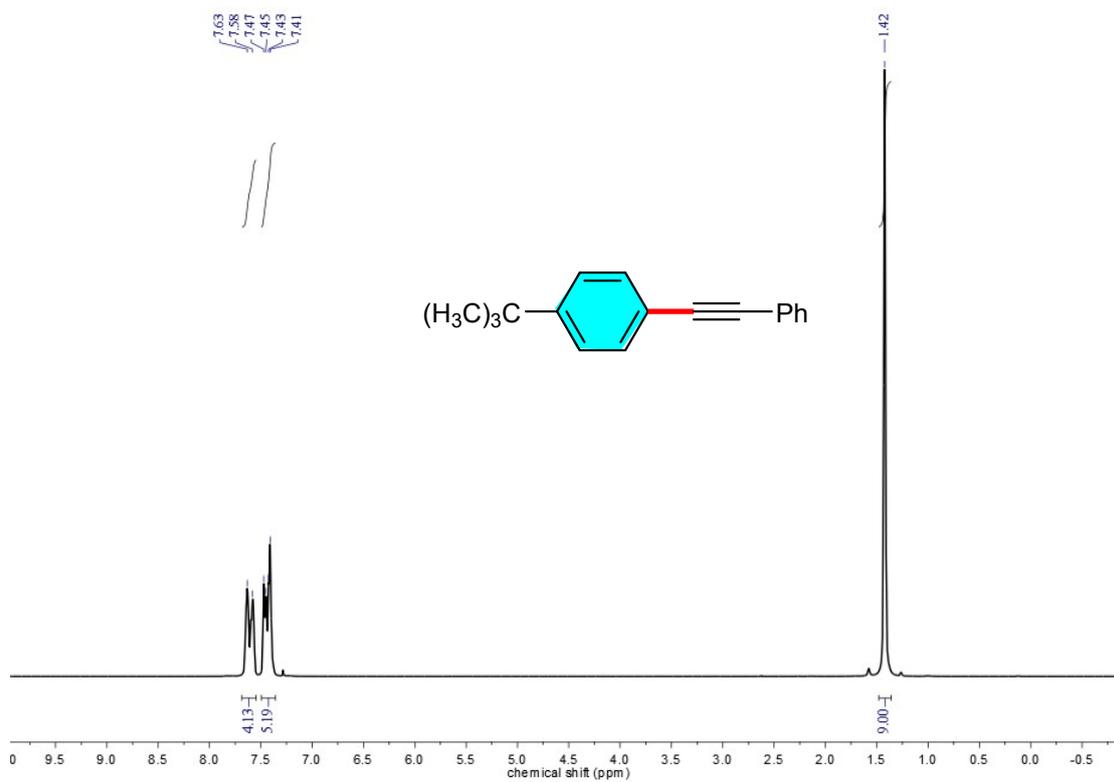
NMR spectrum of compound **3d** in CDCl₃ (400 MHz)



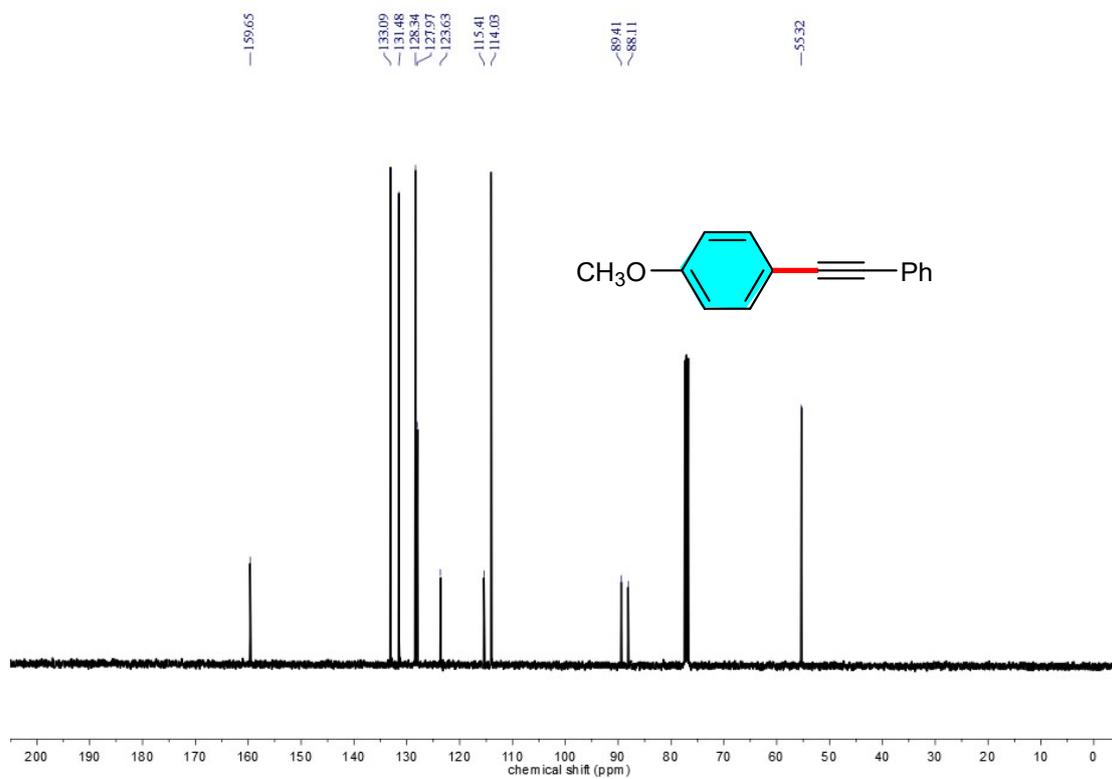
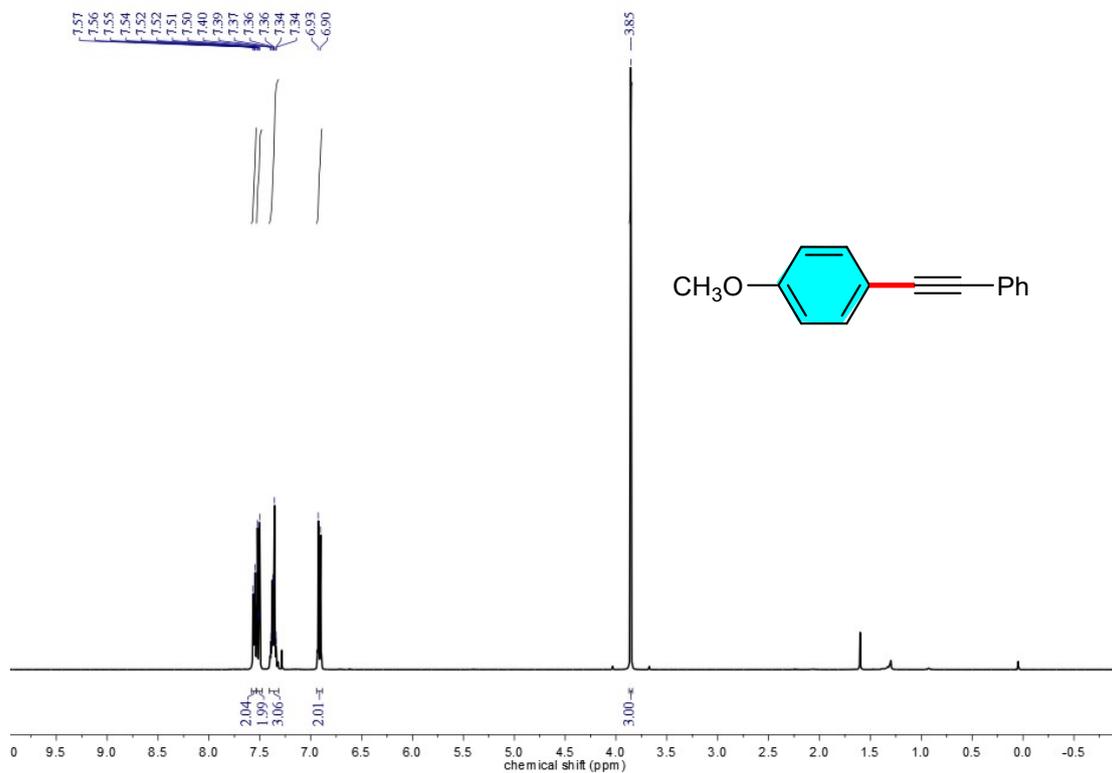
NMR spectrum of compound **3e** in CDCl₃ (400 MHz)



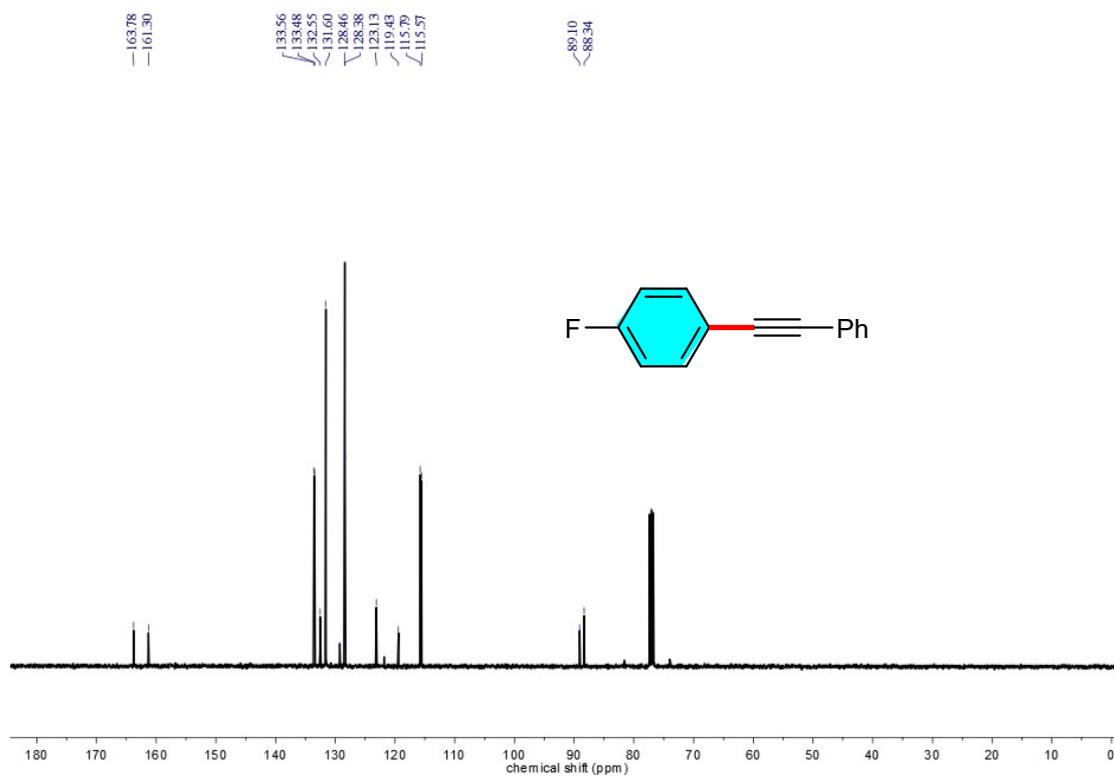
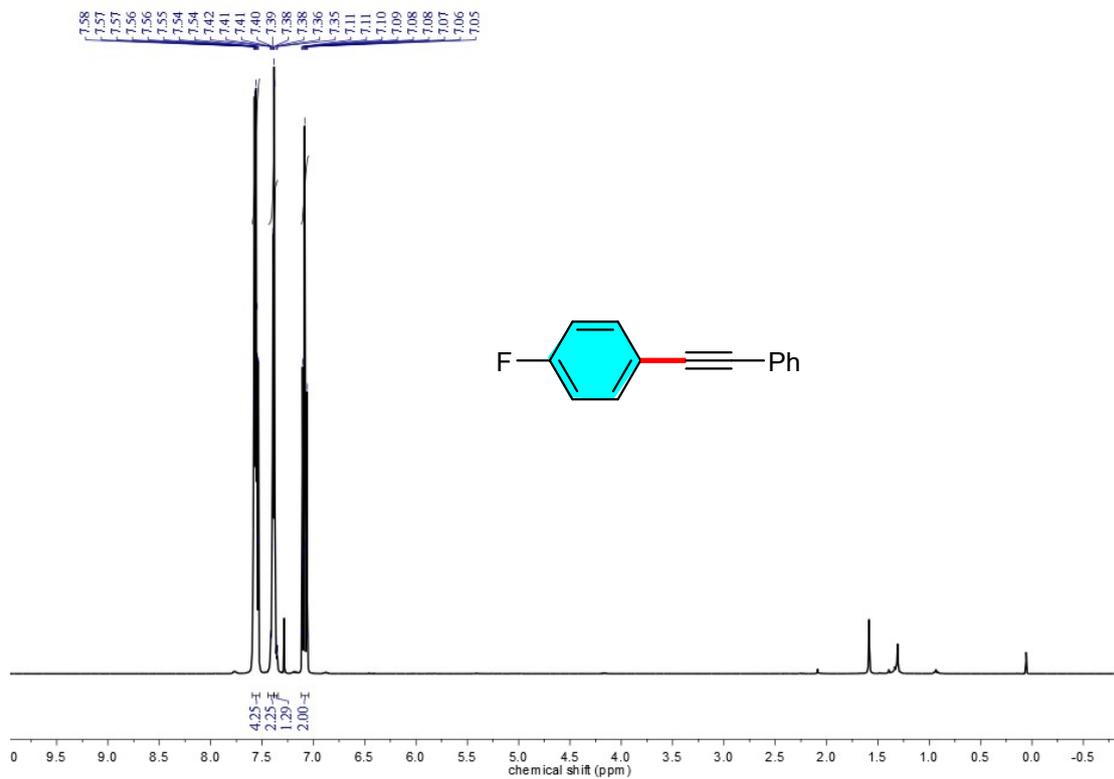
NMR spectrum of compound **3f** in CDCl₃ (400 MHz)



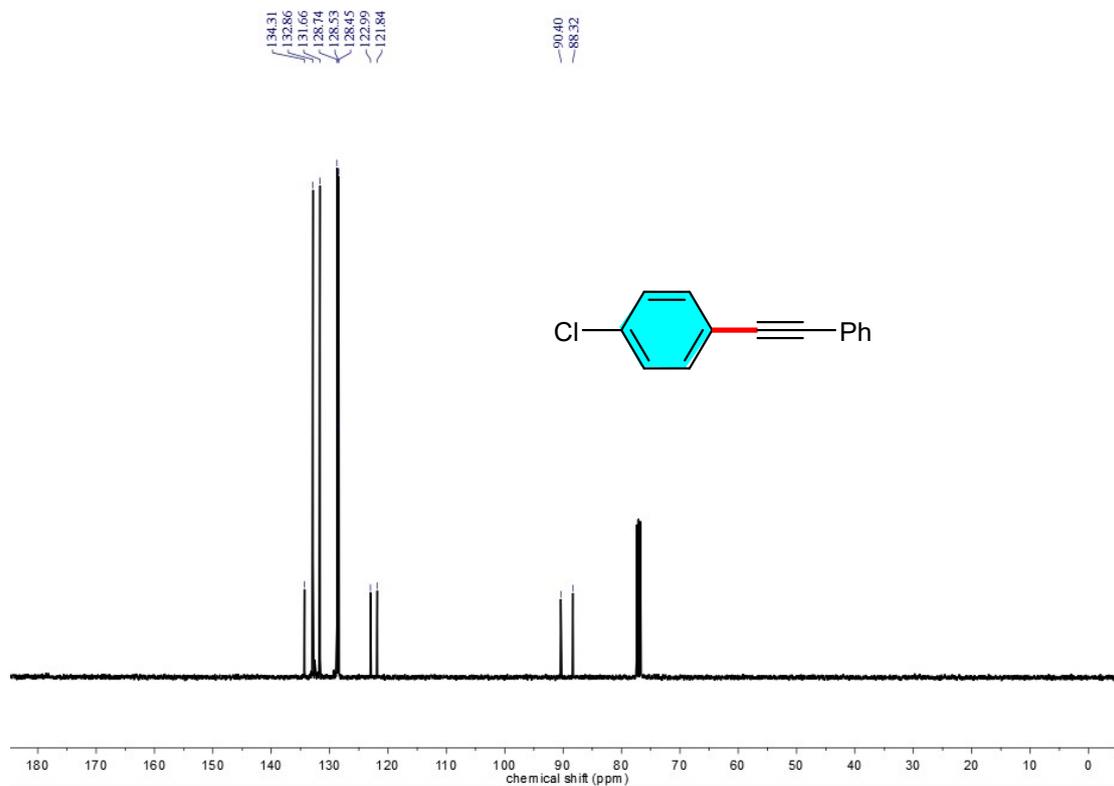
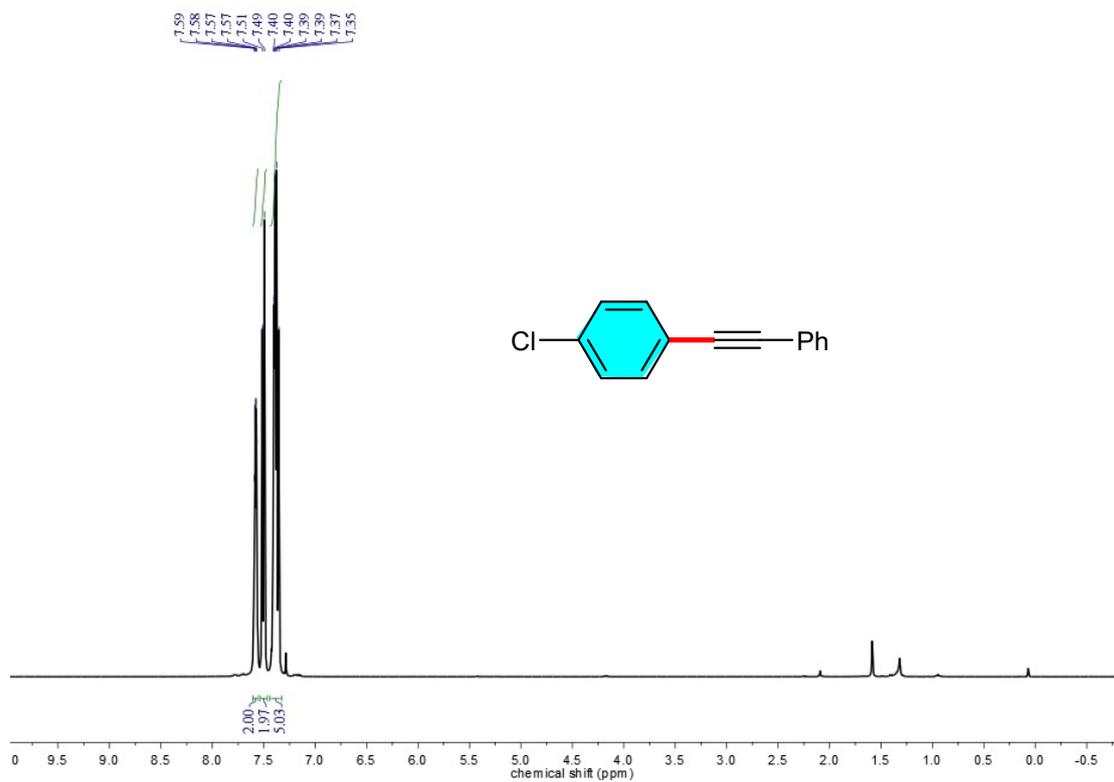
NMR spectrum of compound **3g** in CDCl₃ (400 MHz)



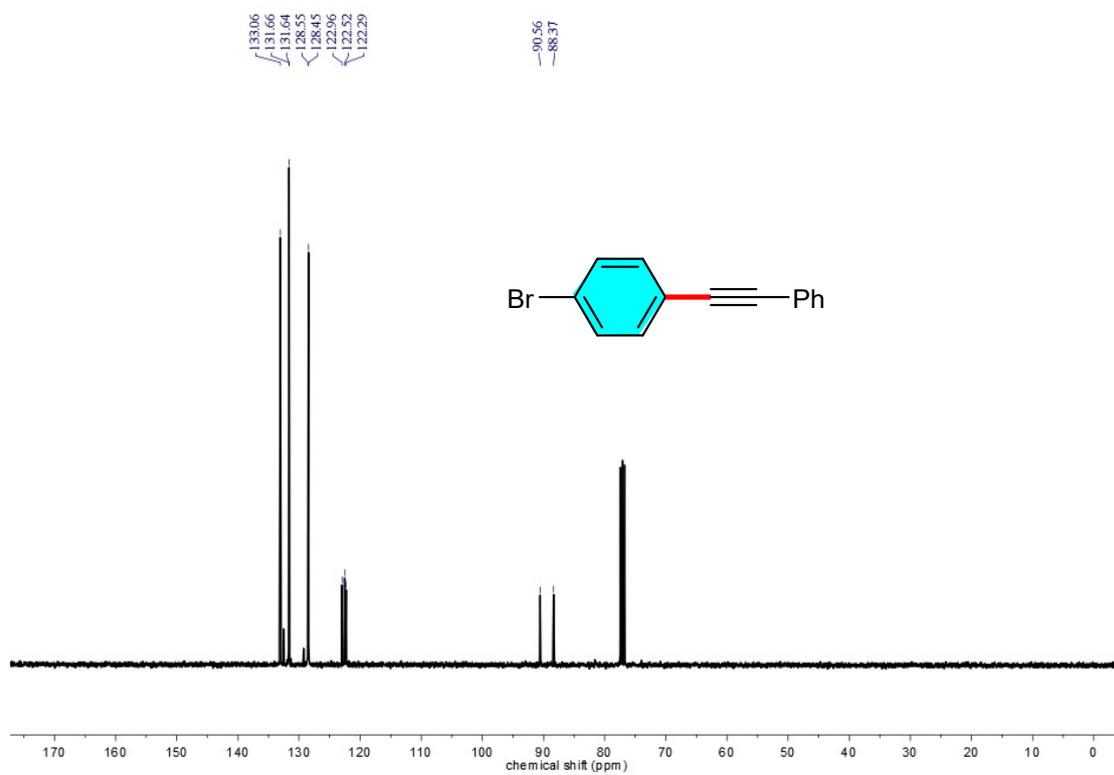
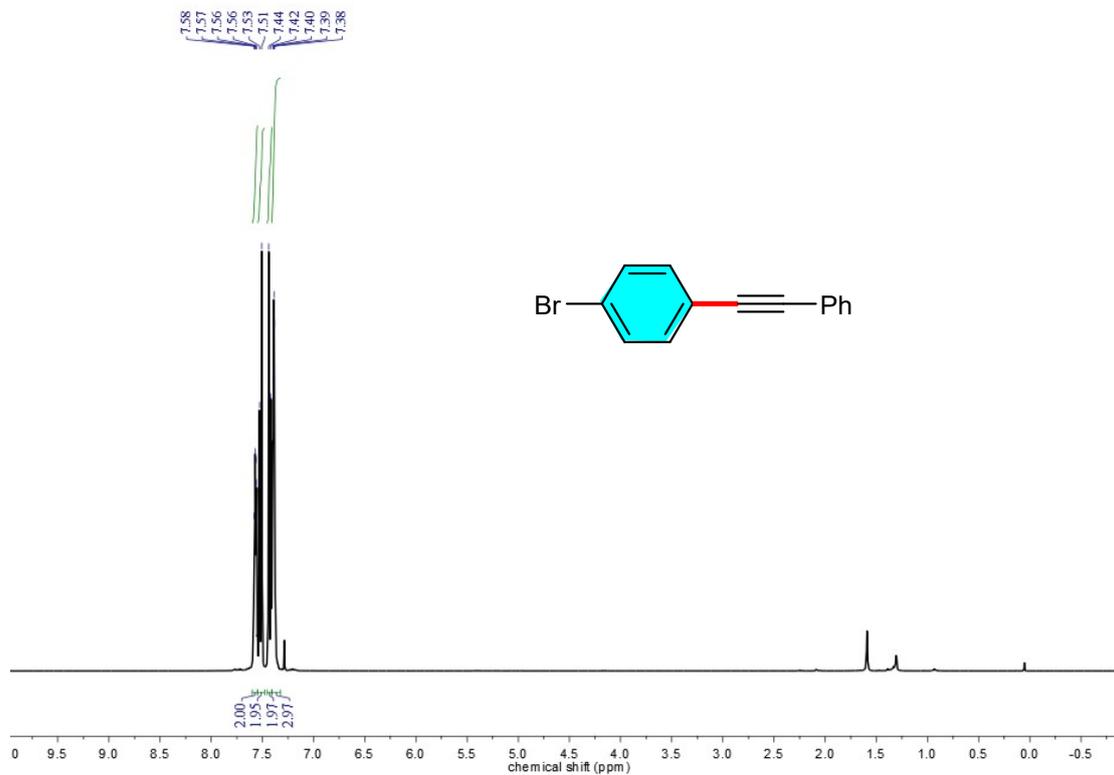
NMR spectrum of compound **3h** in CDCl₃ (400 MHz)



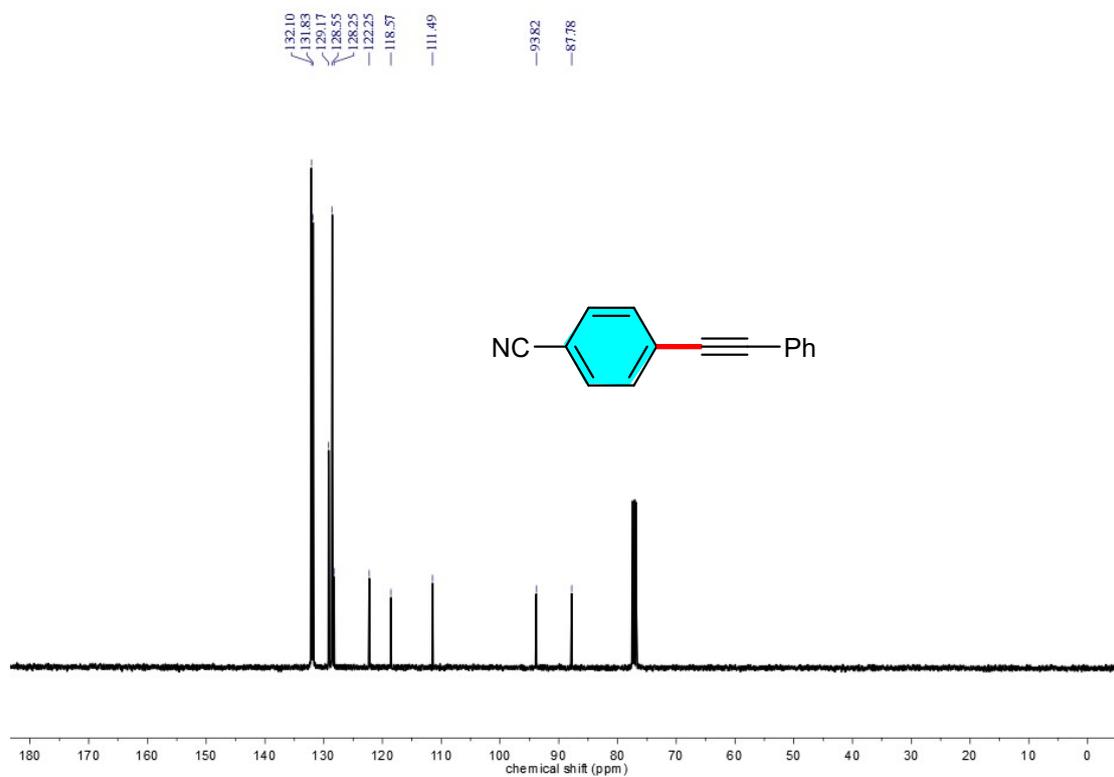
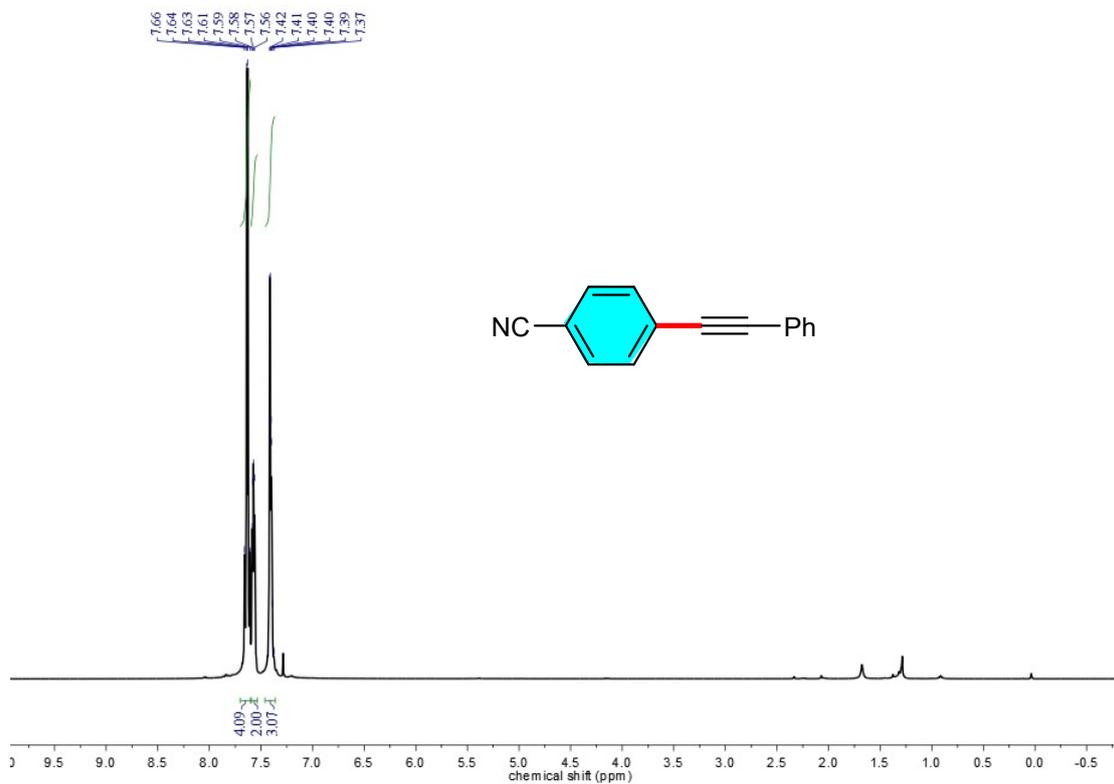
NMR spectrum of compound **3i** in CDCl₃ (400 MHz)



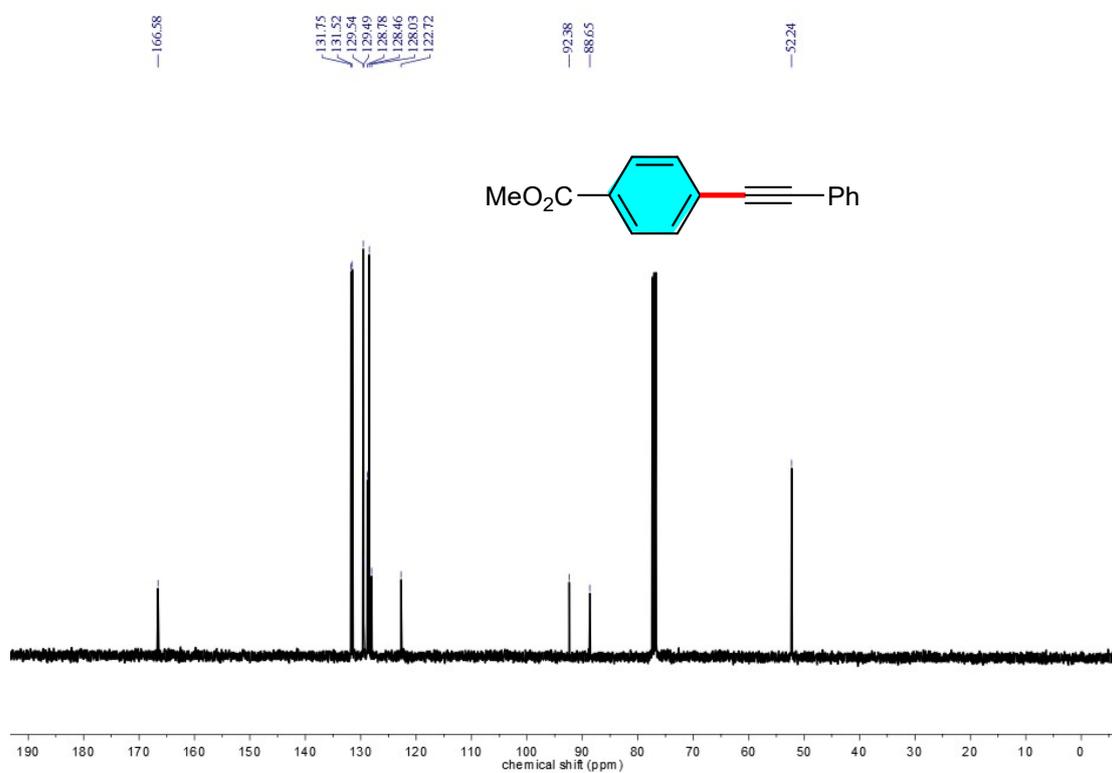
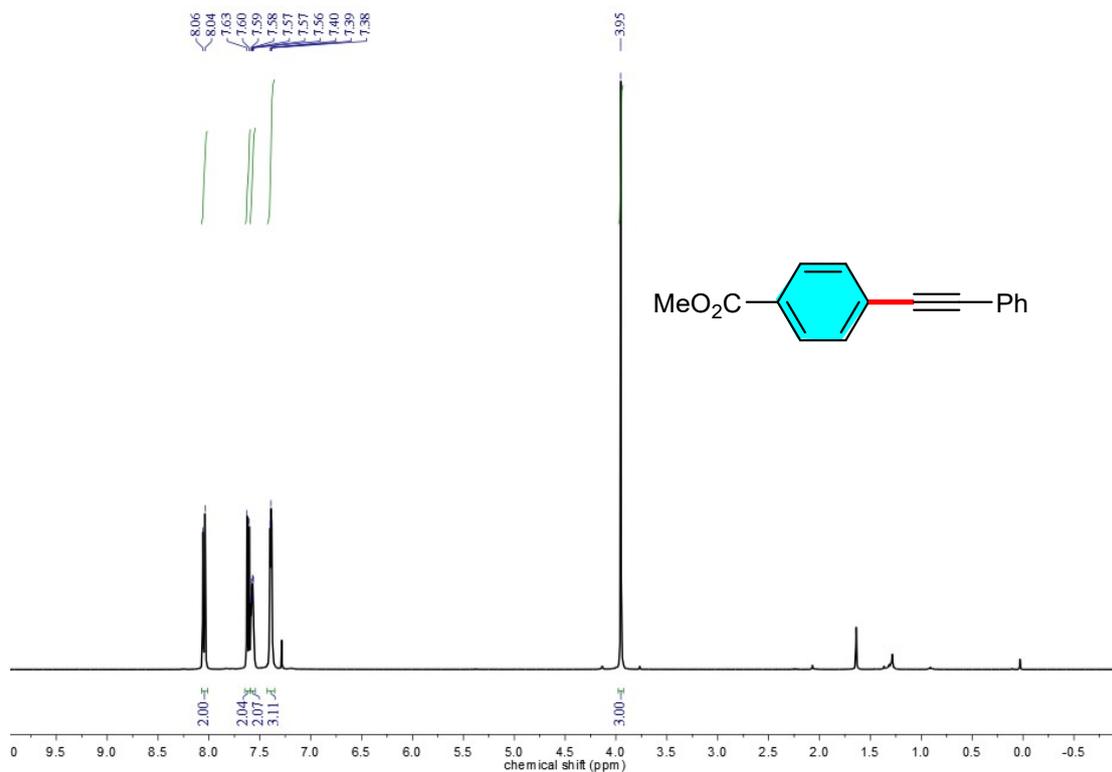
NMR spectrum of compound **3j** in CDCl₃ (400 MHz)



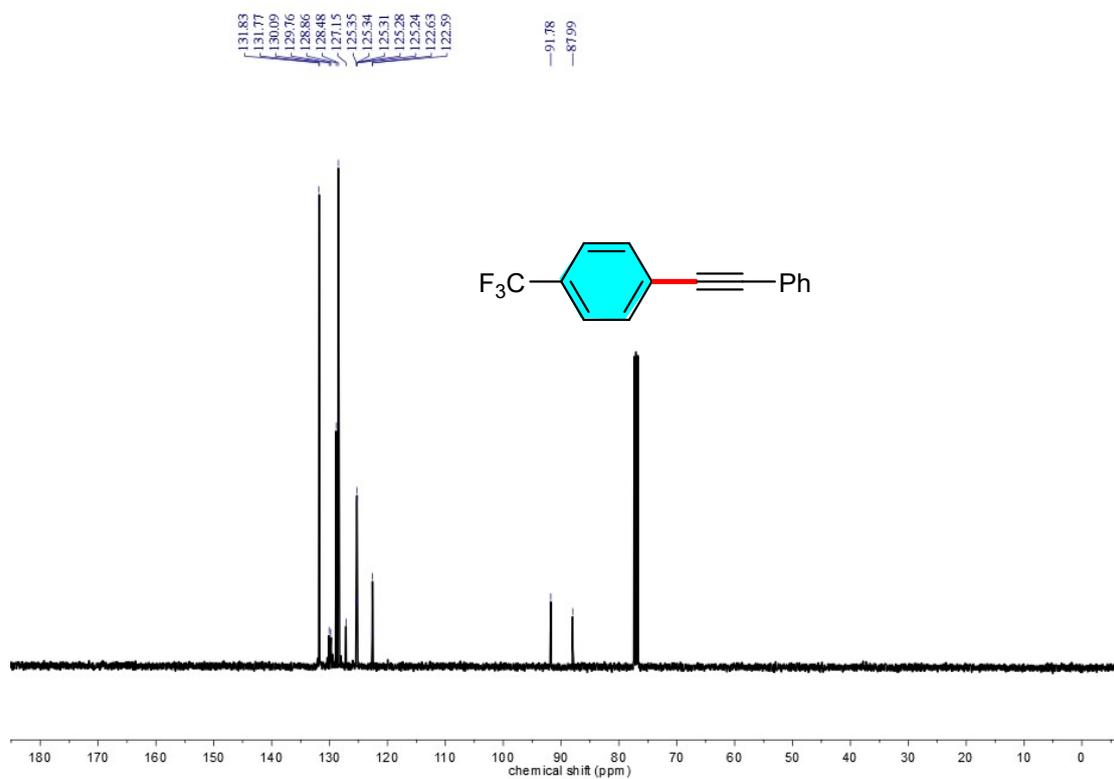
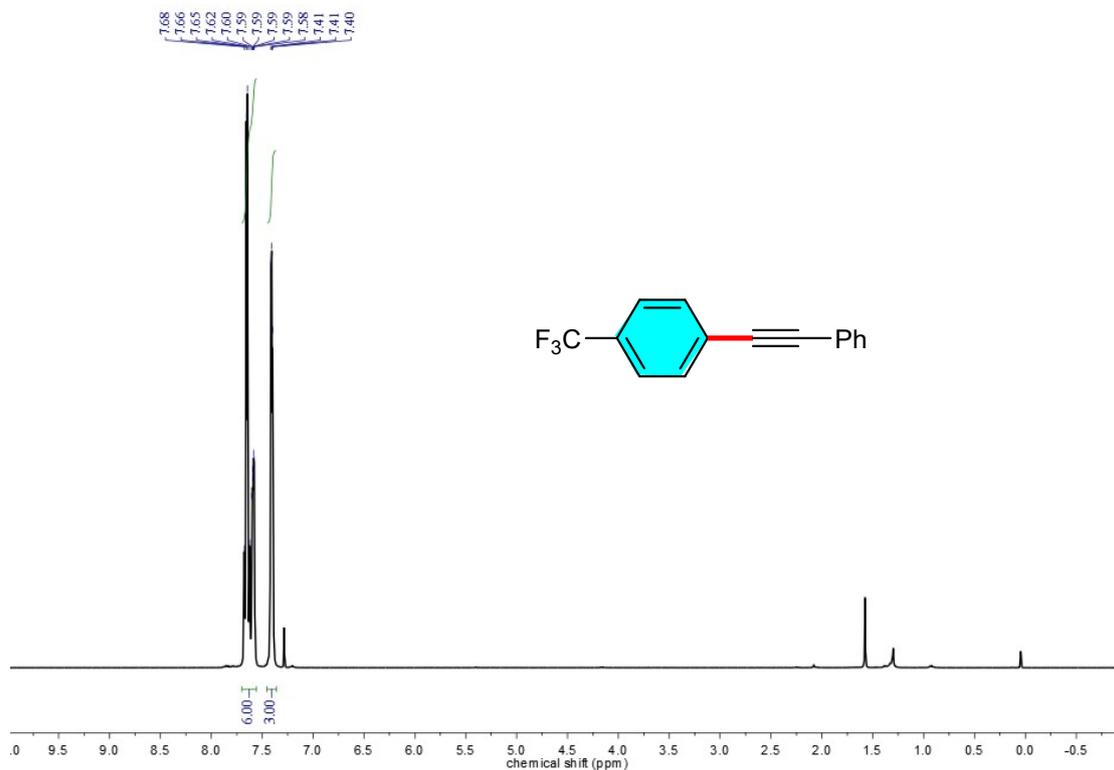
NMR spectrum of compound **3k** in CDCl₃ (400 MHz)



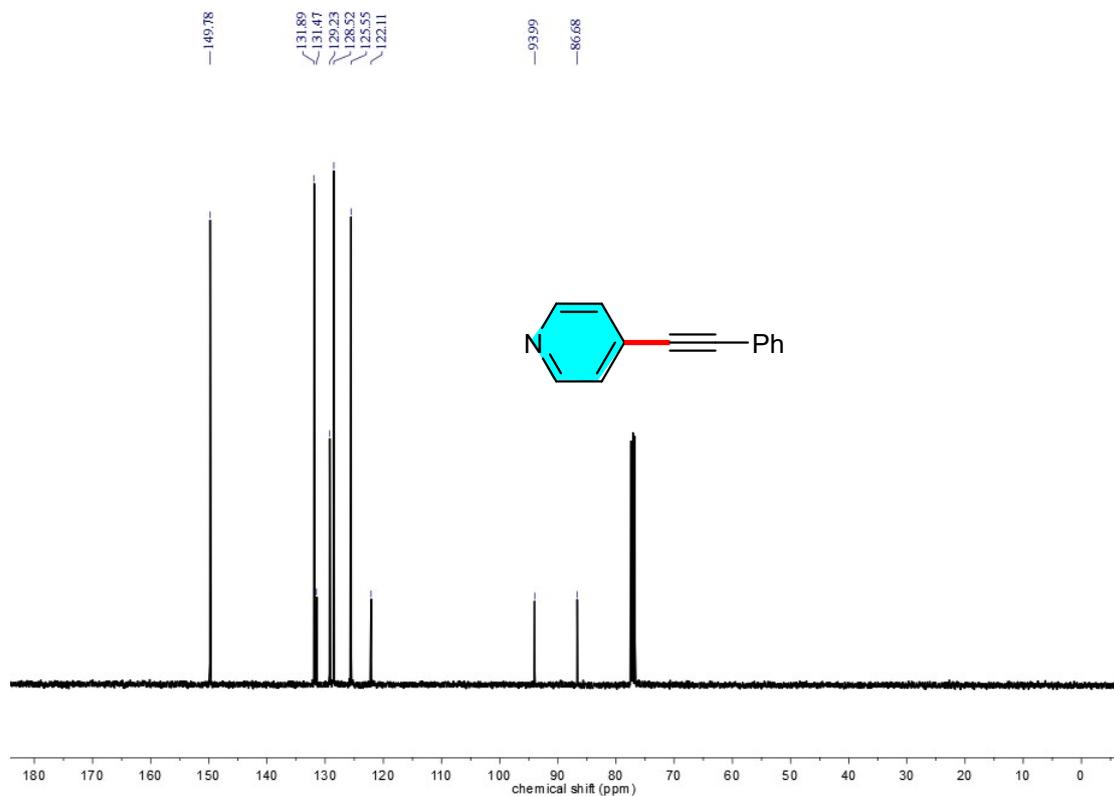
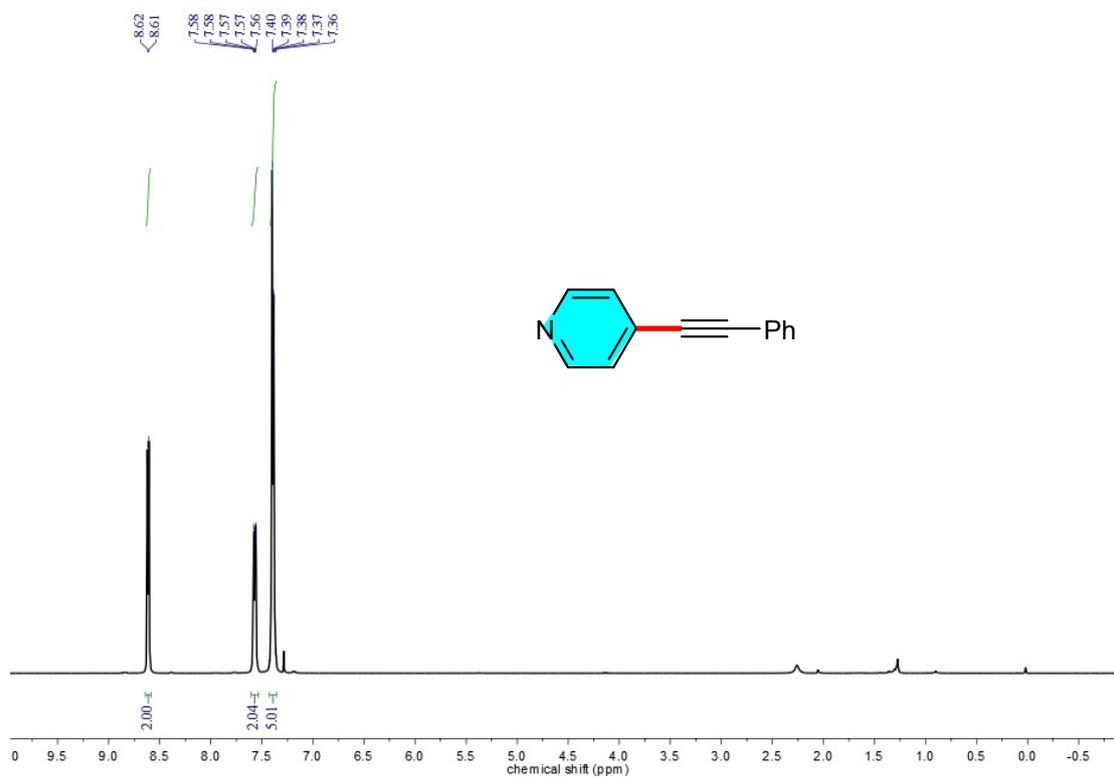
NMR spectrum of compound **31** in CDCl₃ (400 MHz)



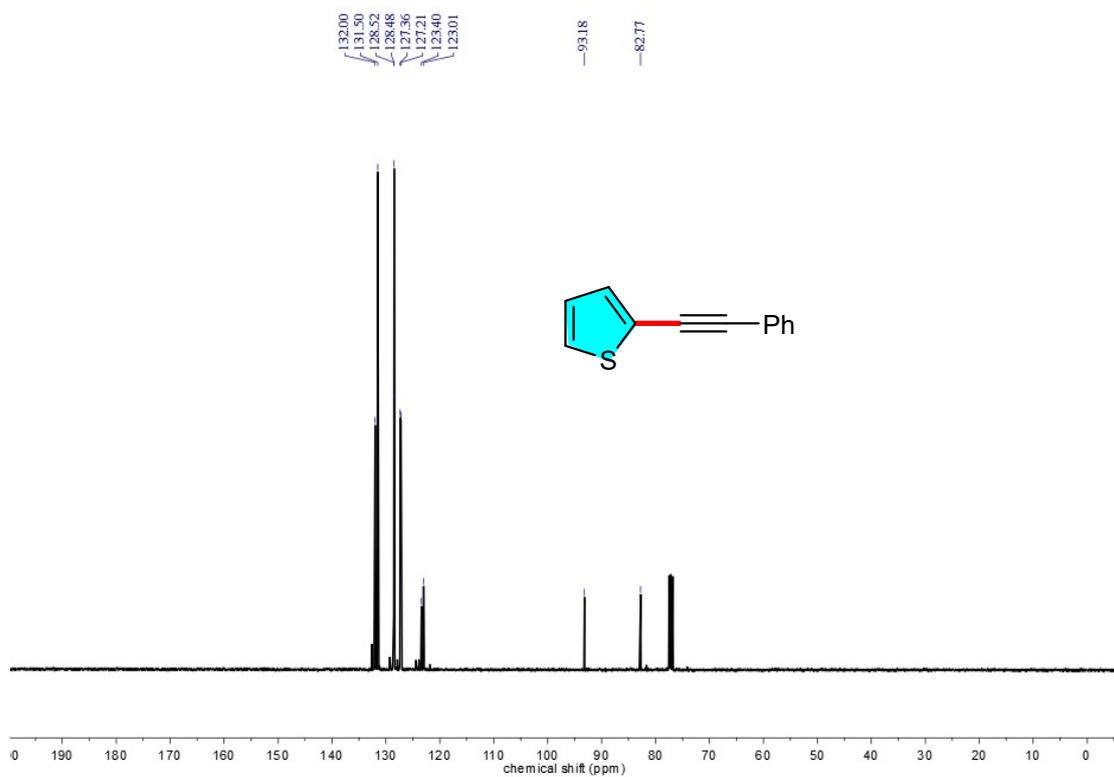
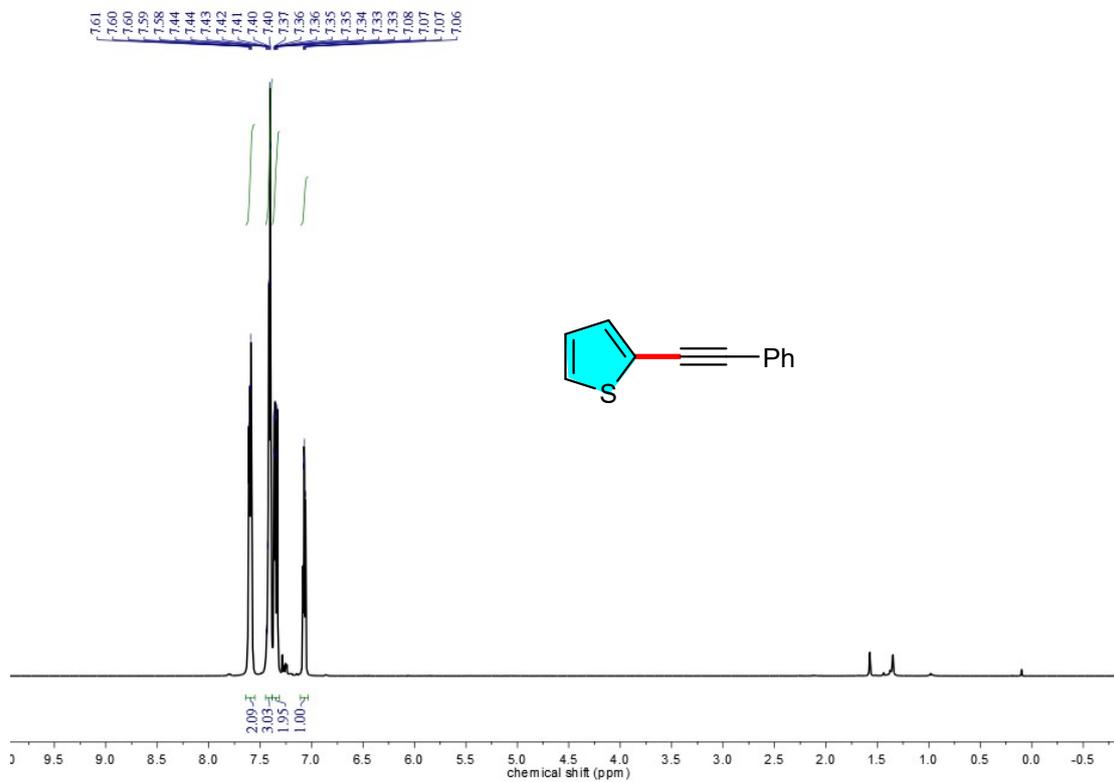
NMR spectrum of compound **3m** in CDCl₃ (400 MHz)



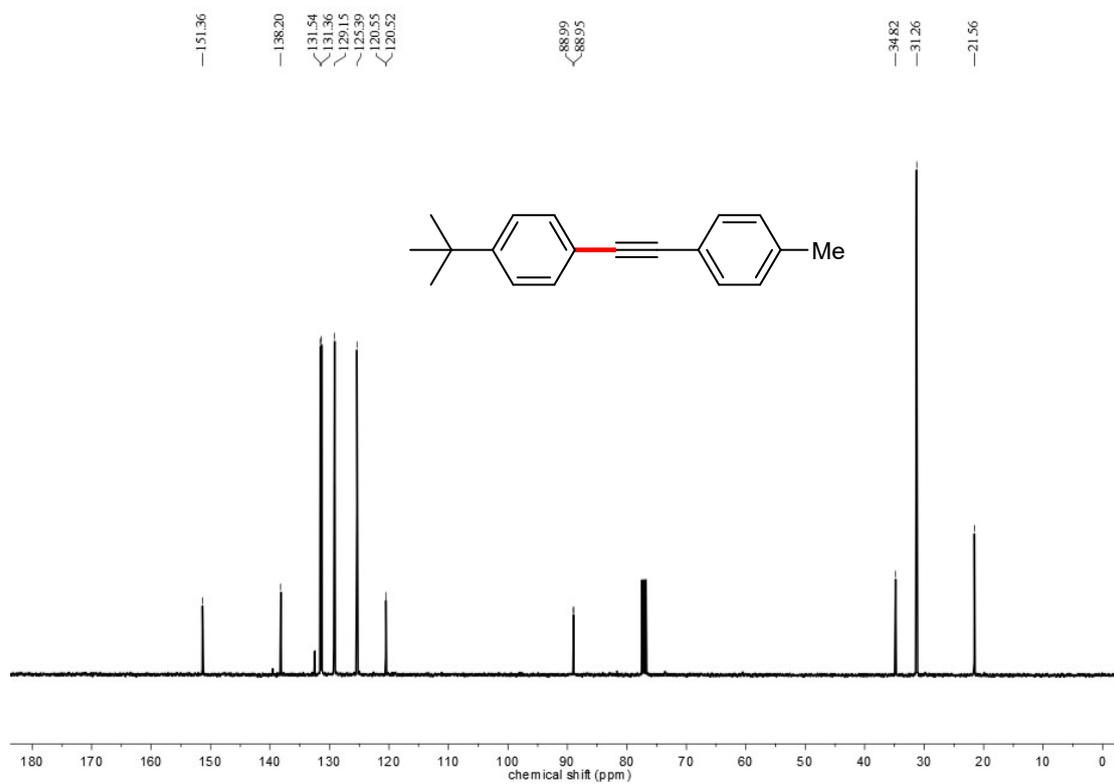
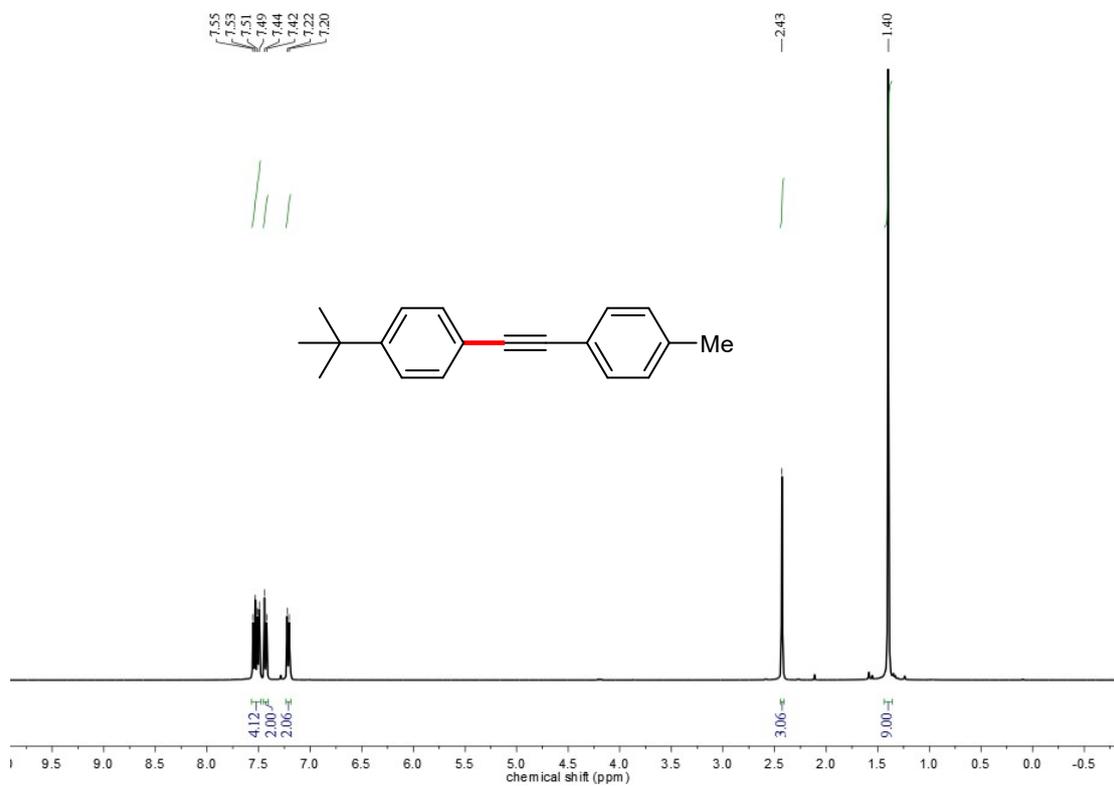
NMR spectrum of compound **3n** in CDCl₃ (400 MHz)



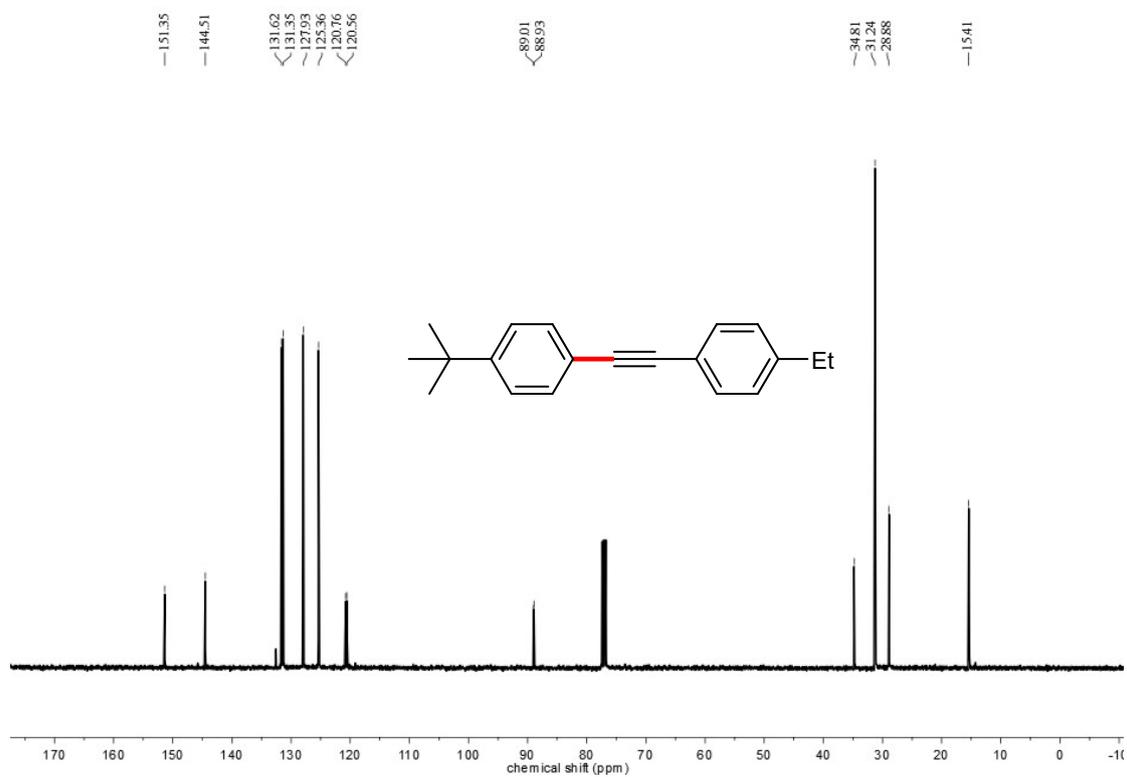
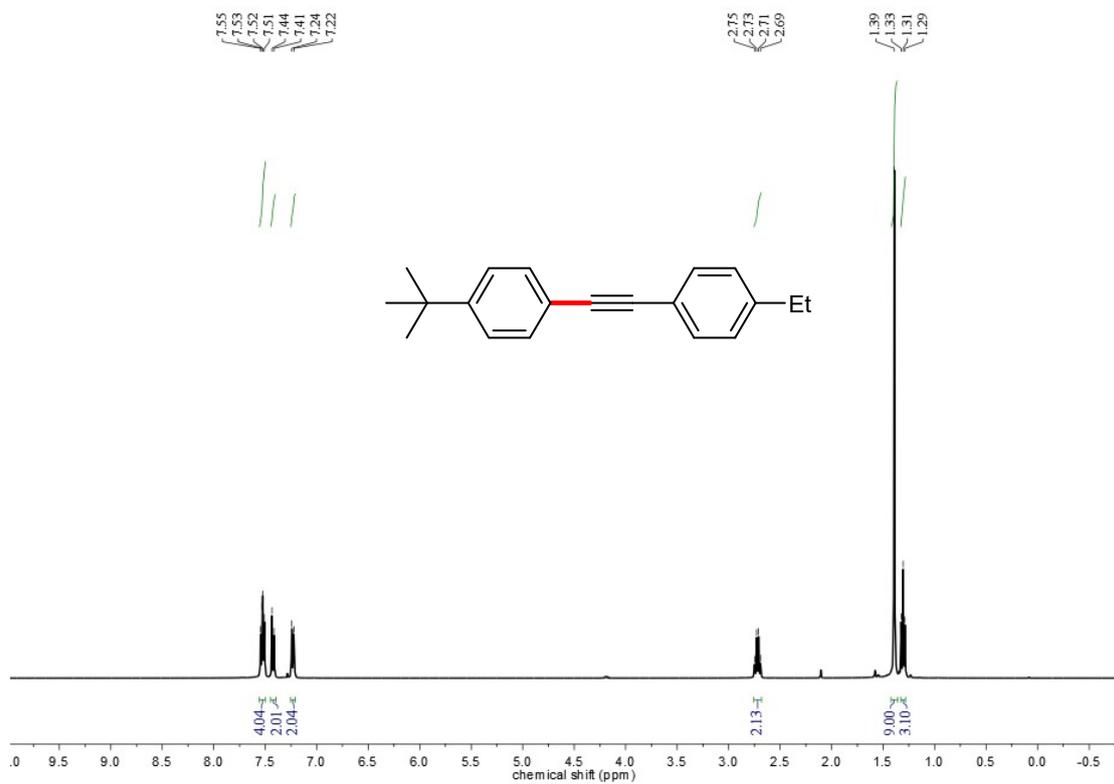
NMR spectrum of compound **3o** in CDCl₃ (400 MHz)



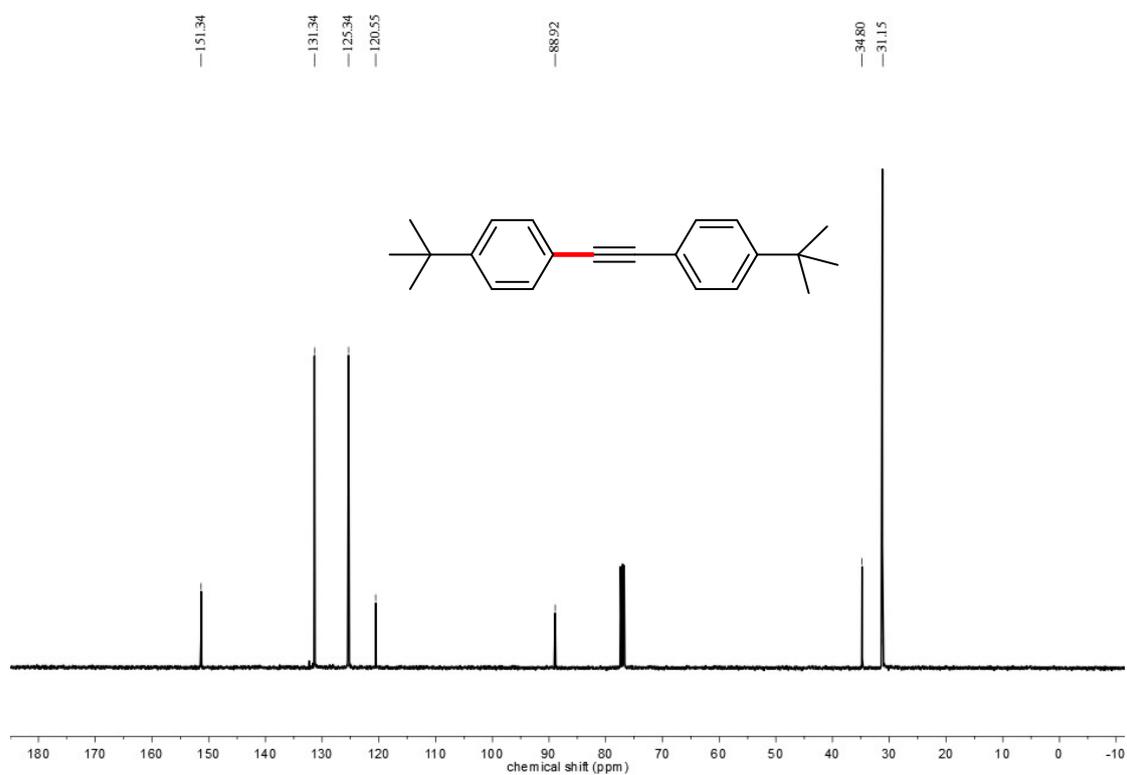
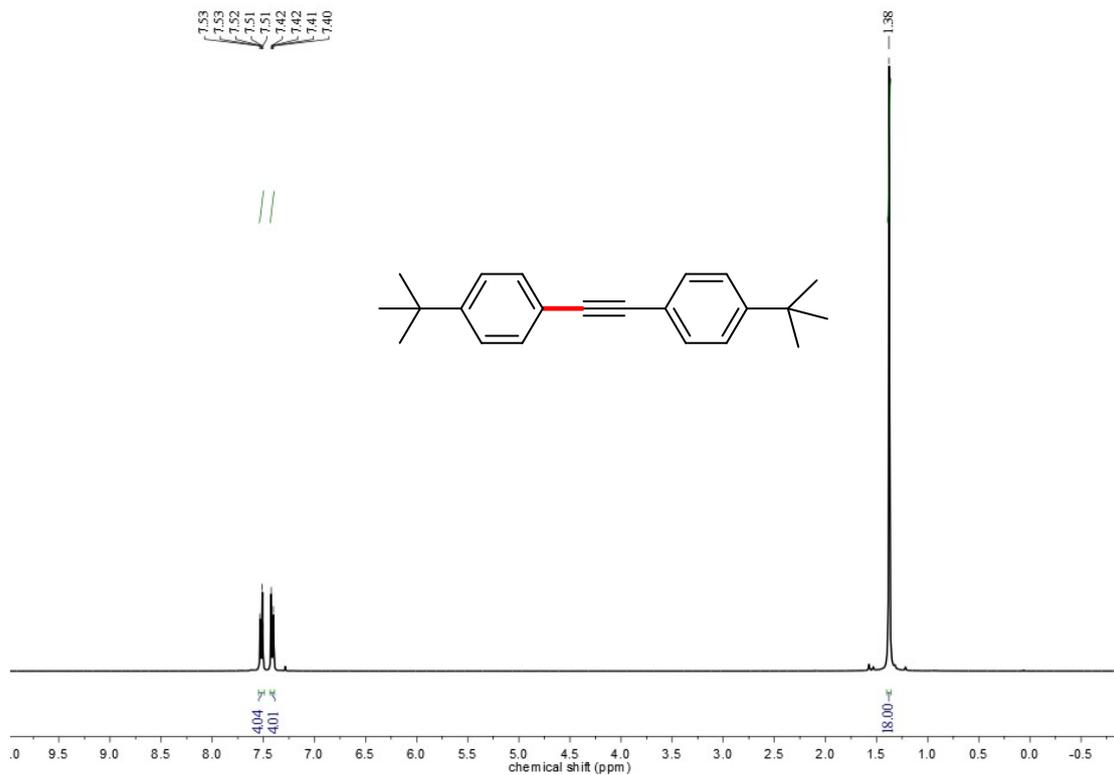
NMR spectrum of compound **4a** in CDCl₃ (400 MHz)



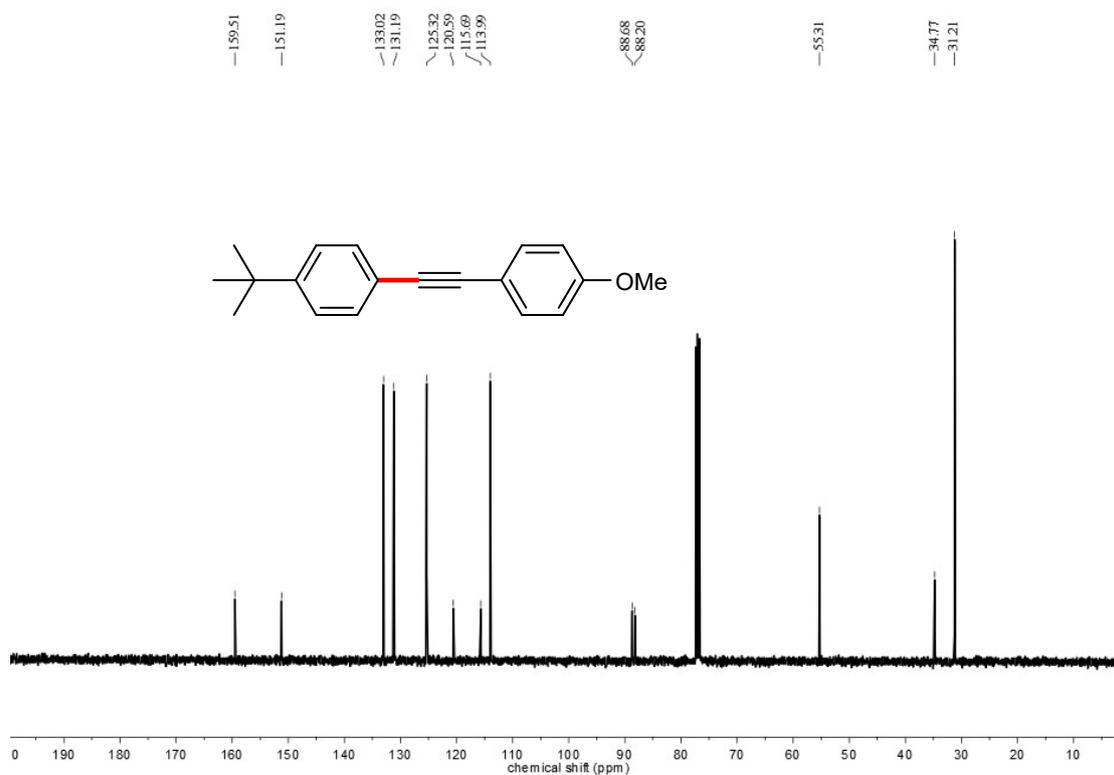
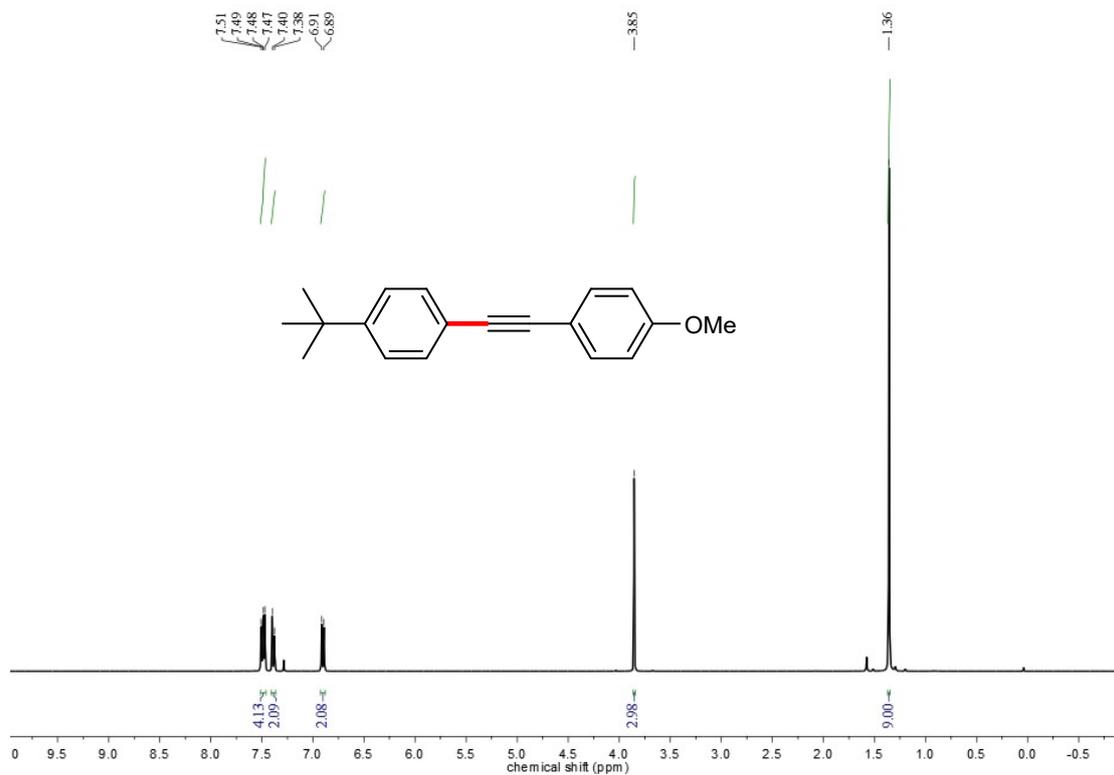
NMR spectrum of compound **4b** in CDCl₃ (400 MHz)



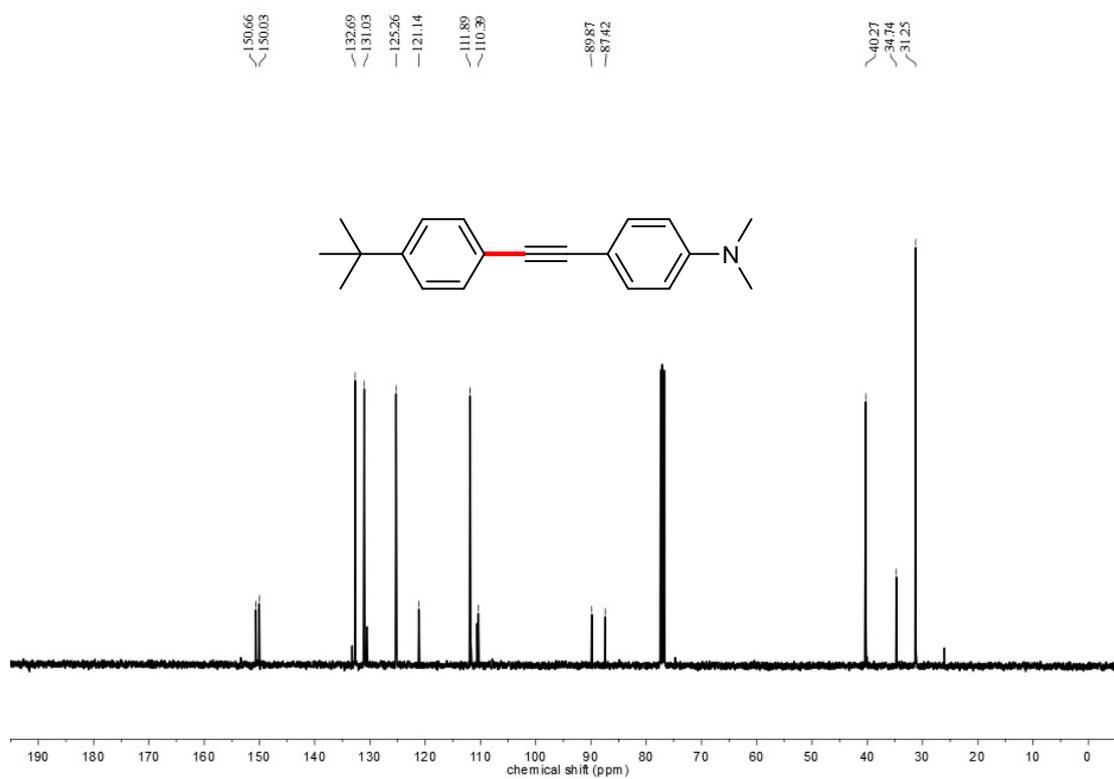
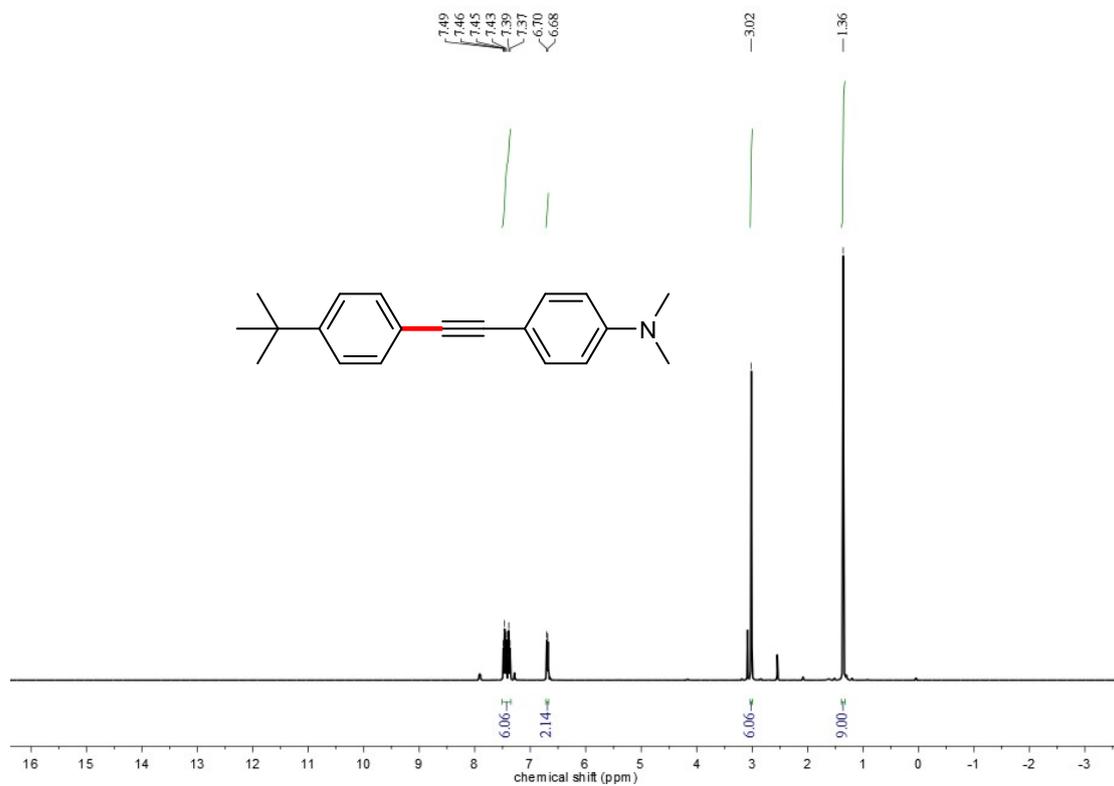
NMR spectrum of compound **4c** in CDCl₃ (400 MHz)



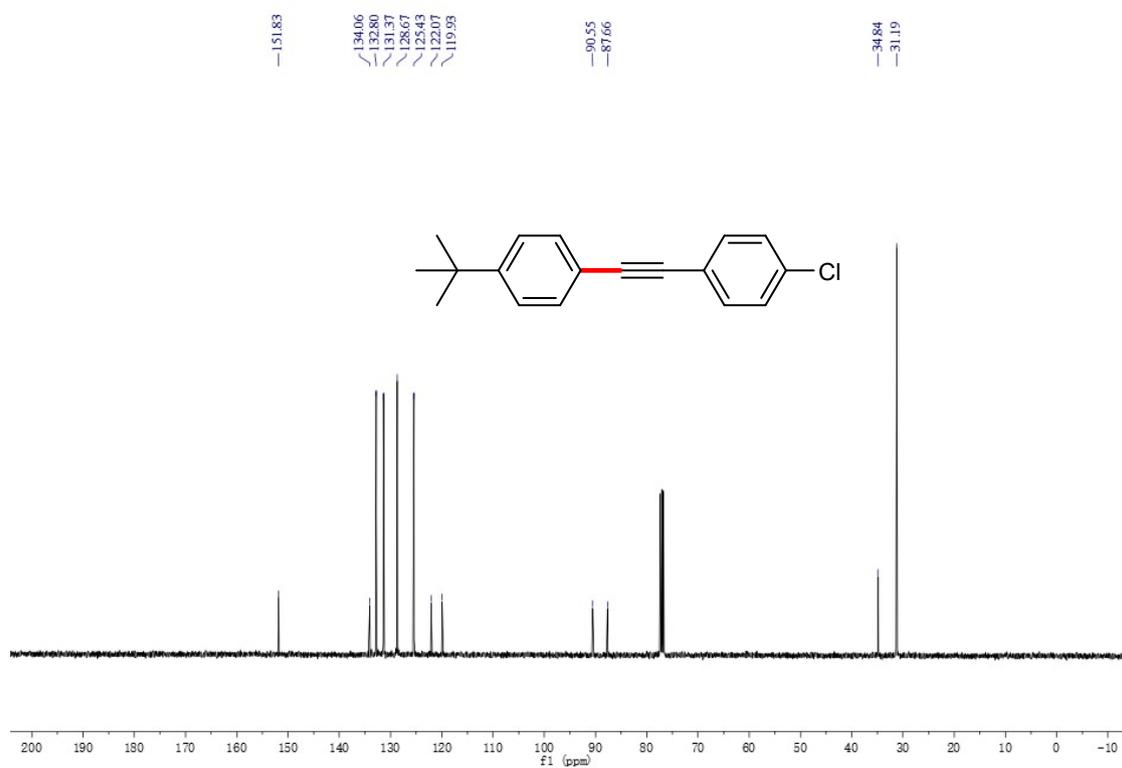
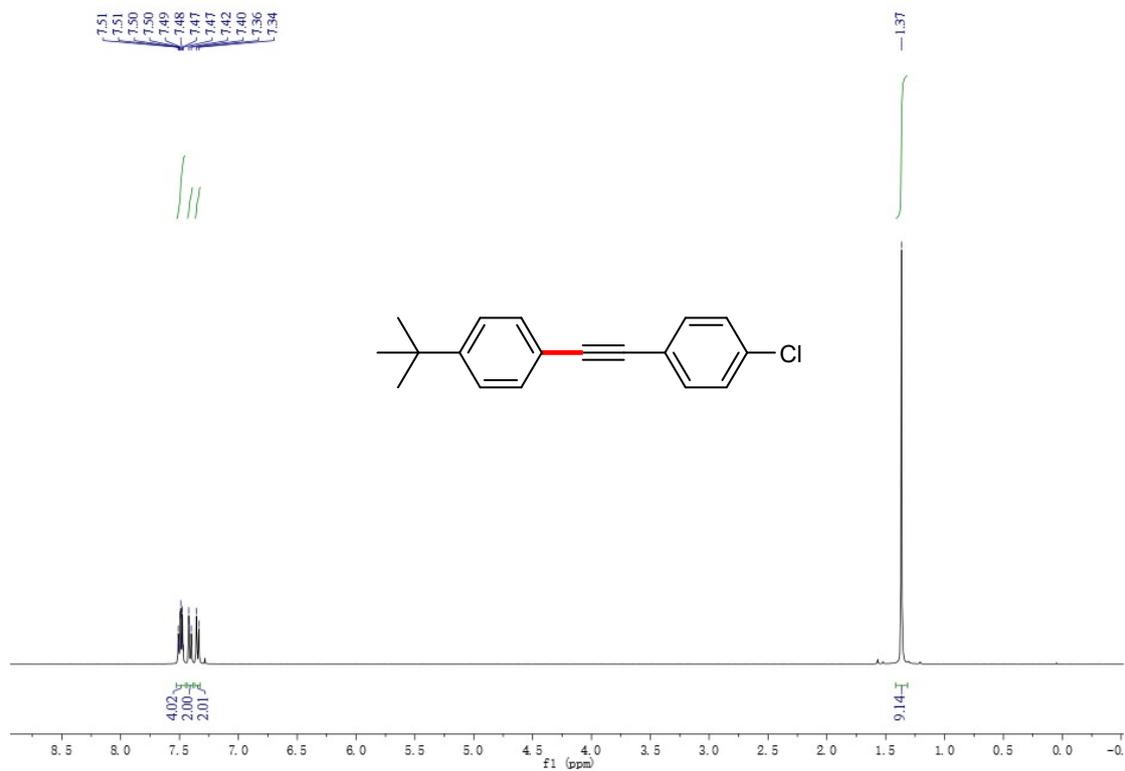
NMR spectrum of compound **4d** in CDCl₃ (400 MHz)



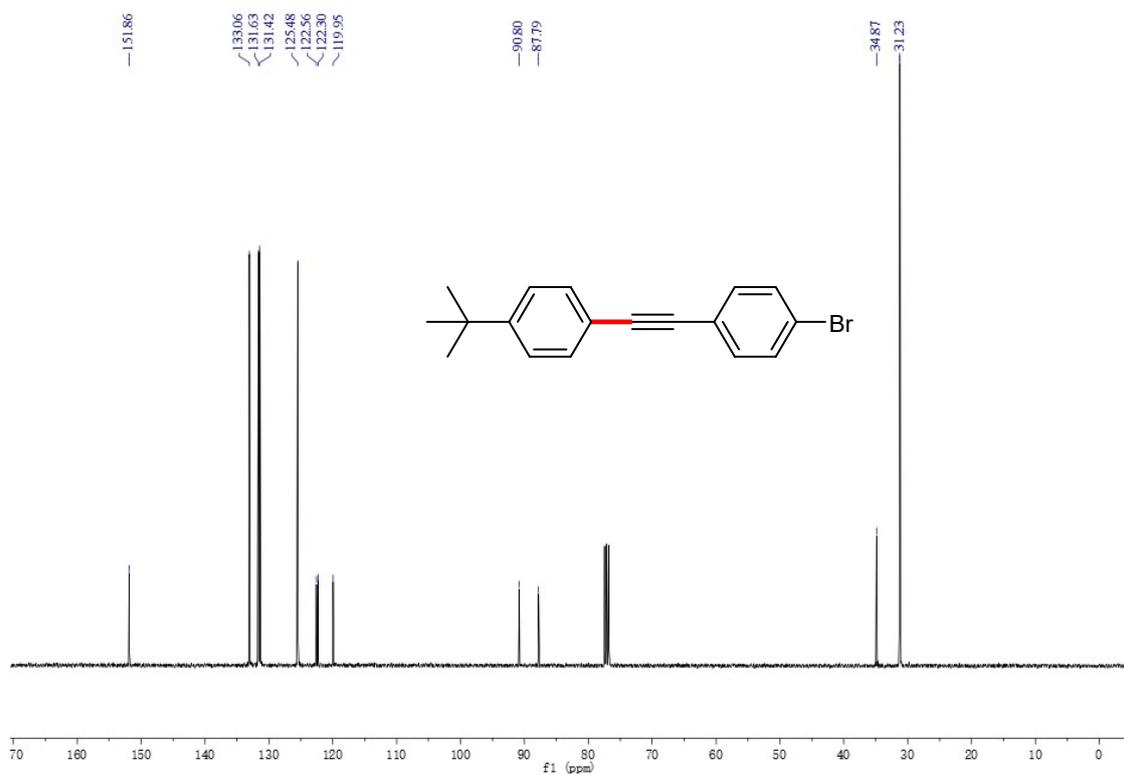
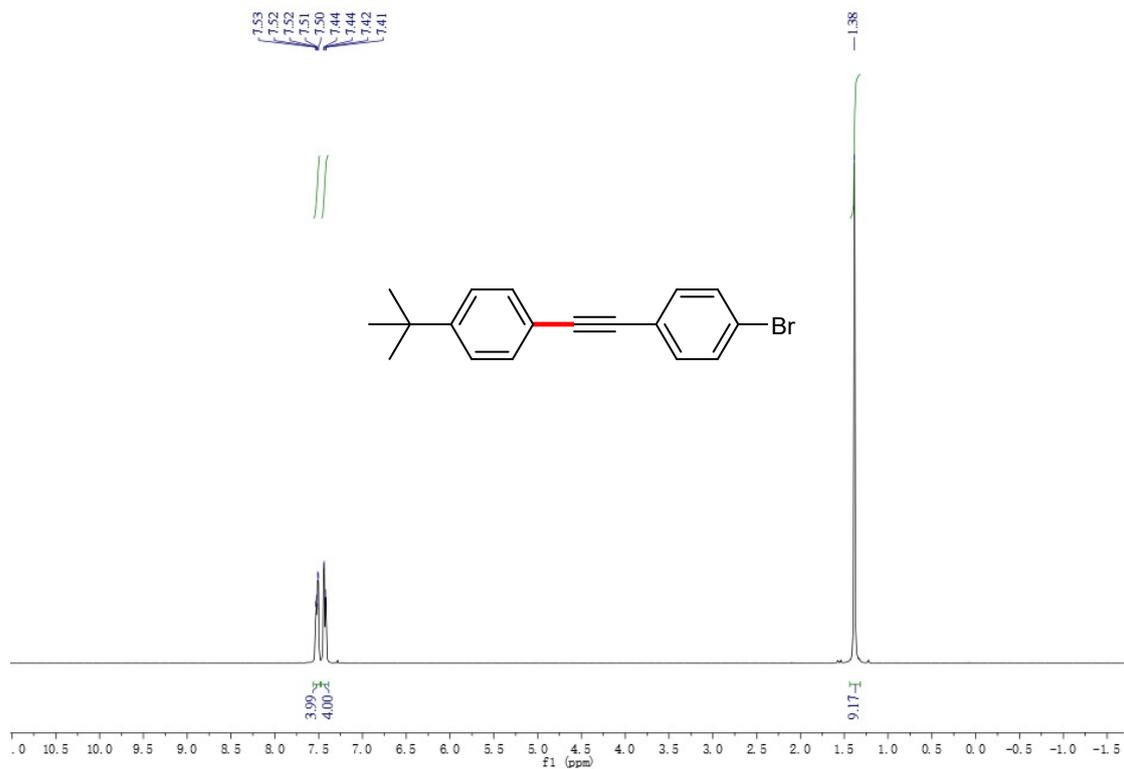
NMR spectrum of compound **4e** in CDCl₃ (400 MHz)



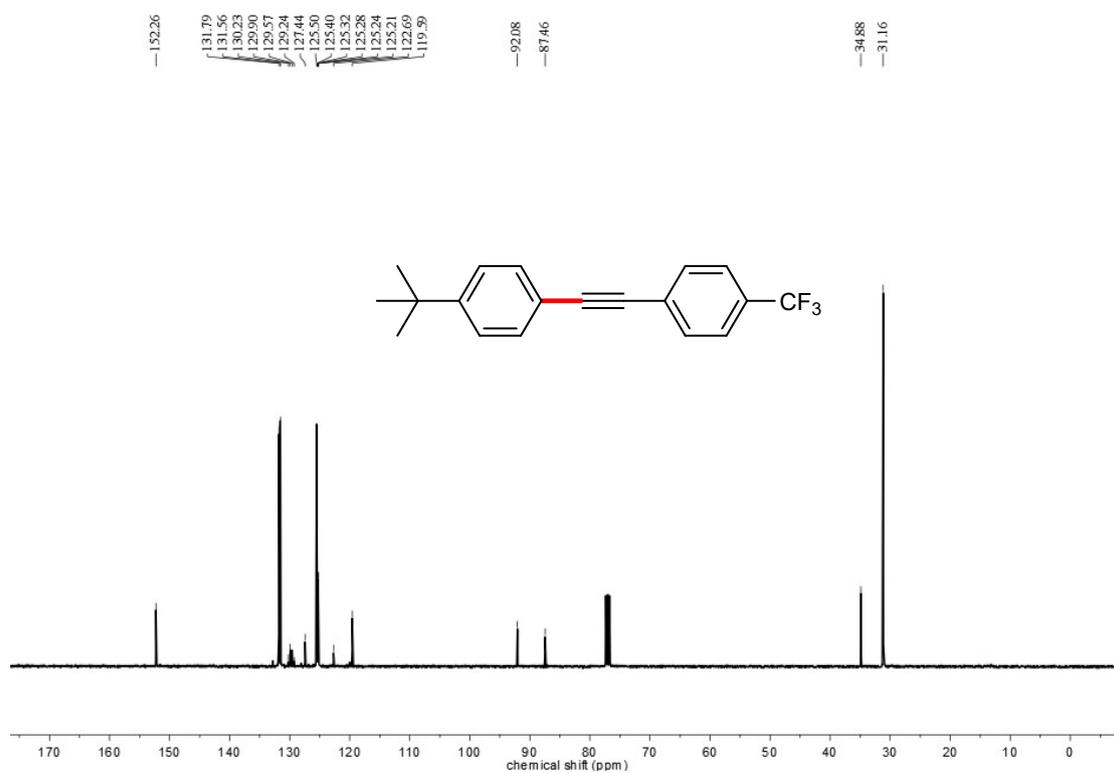
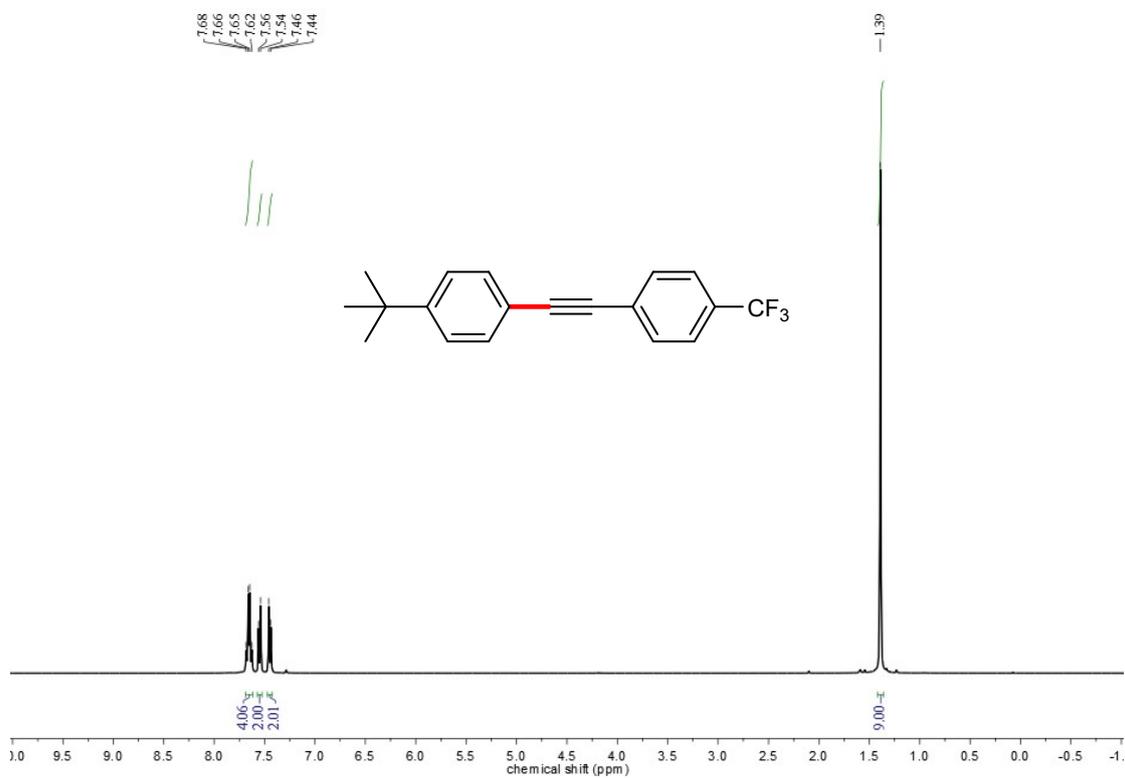
NMR spectrum of compound **4g** in CDCl₃ (400 MHz)



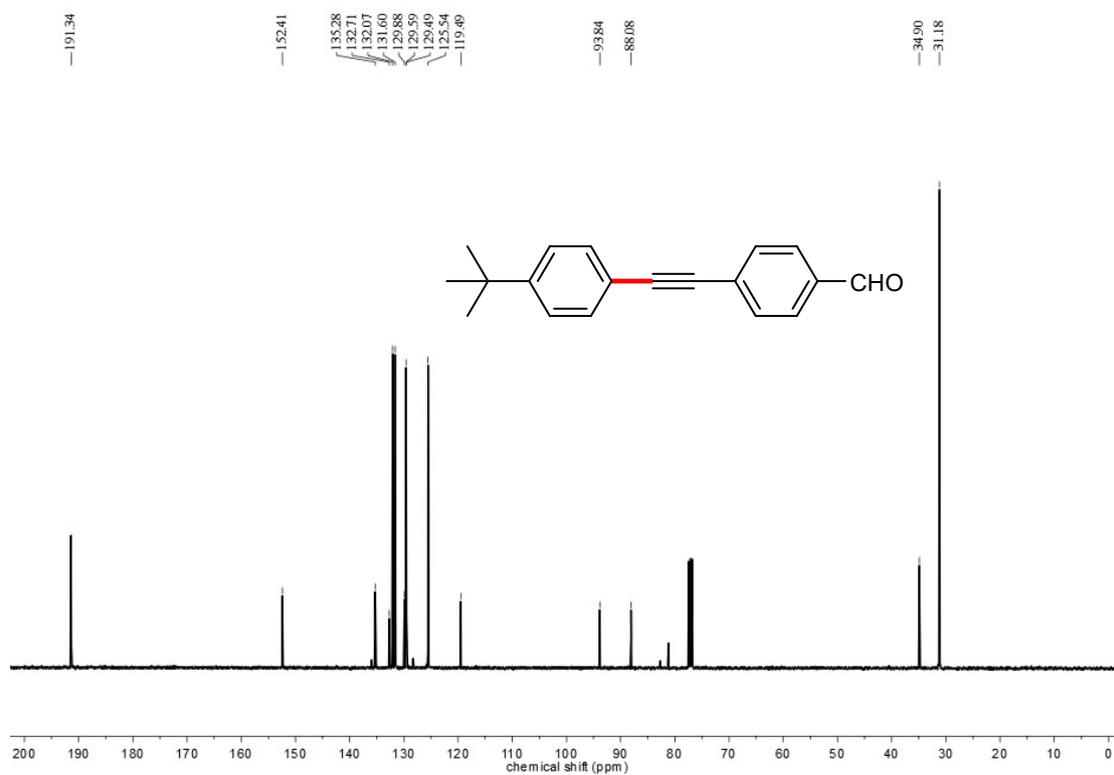
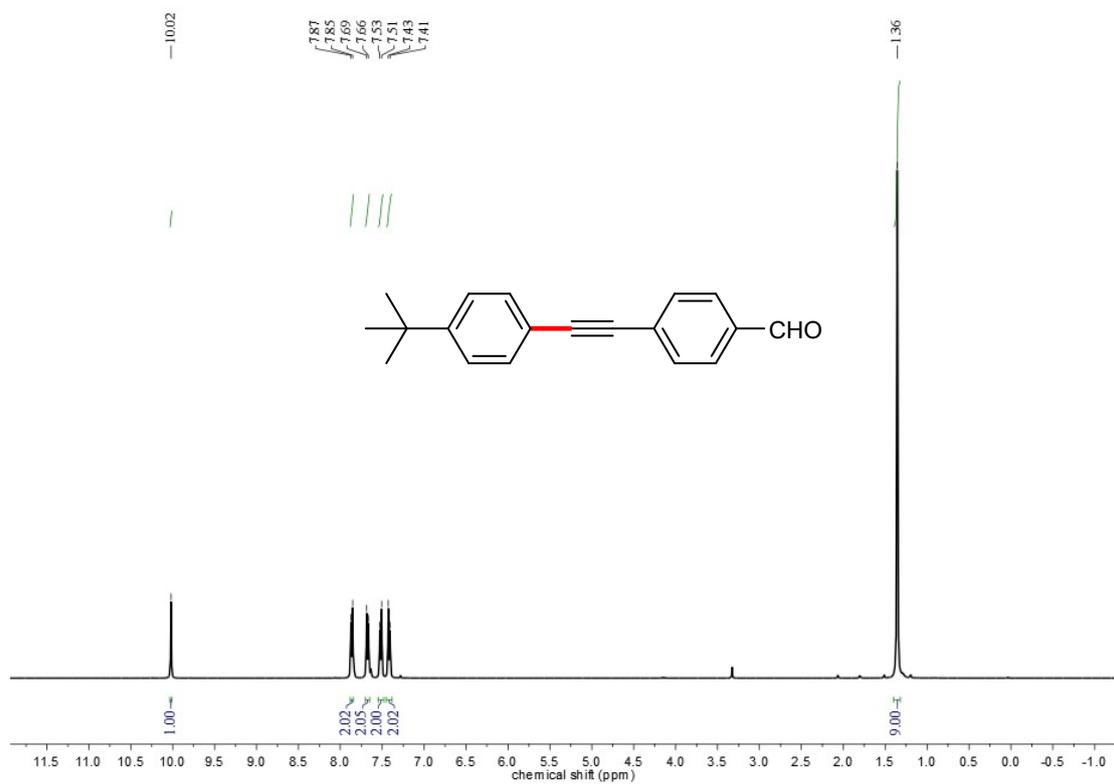
NMR spectrum of compound **4h** in CDCl₃ (400 MHz)



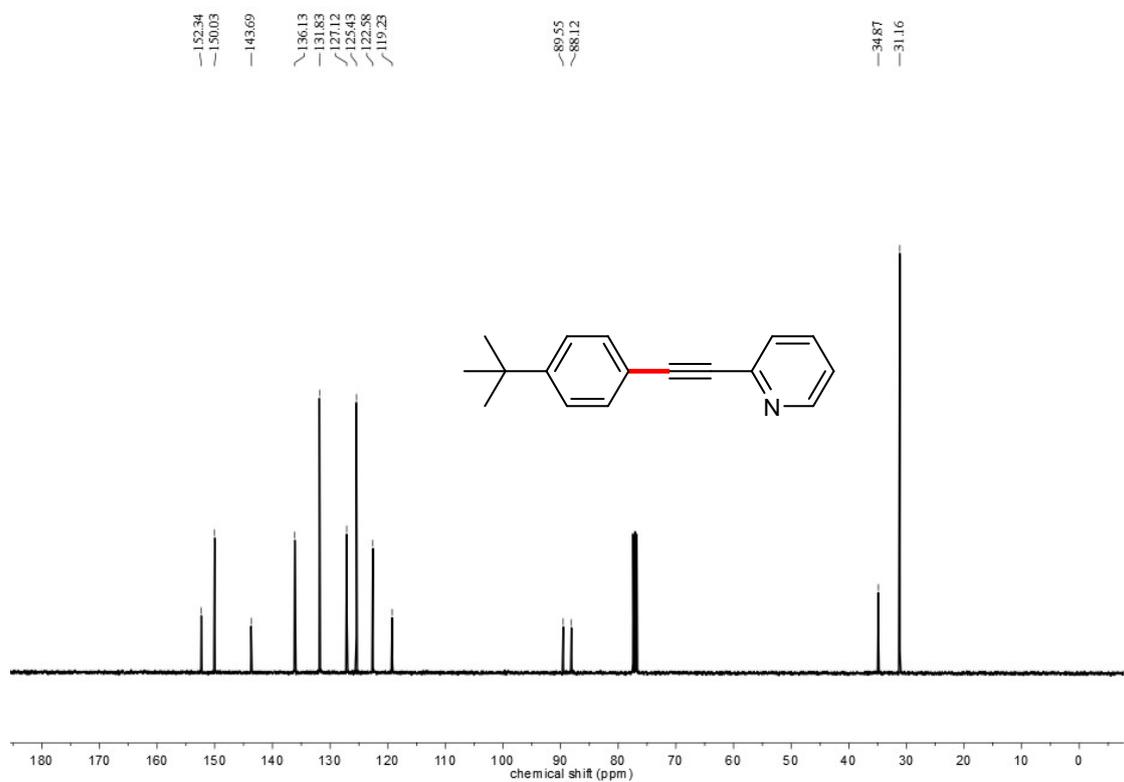
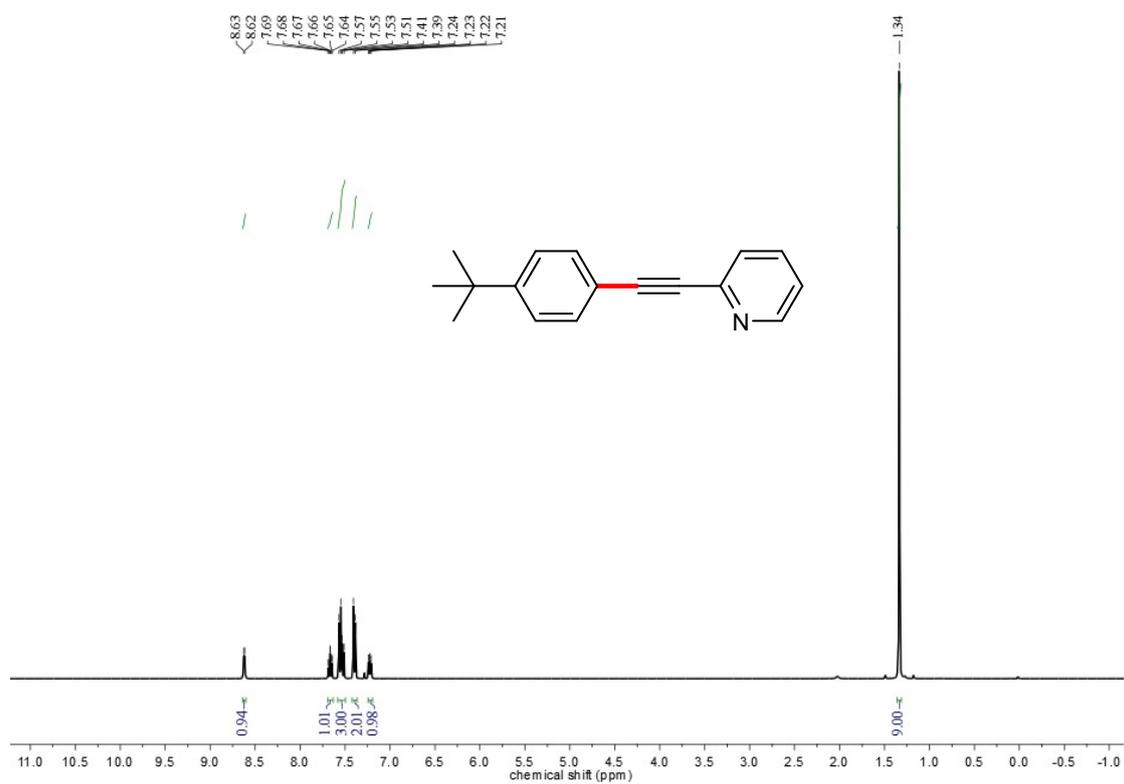
NMR spectrum of compound **4i** in CDCl₃ (400 MHz)



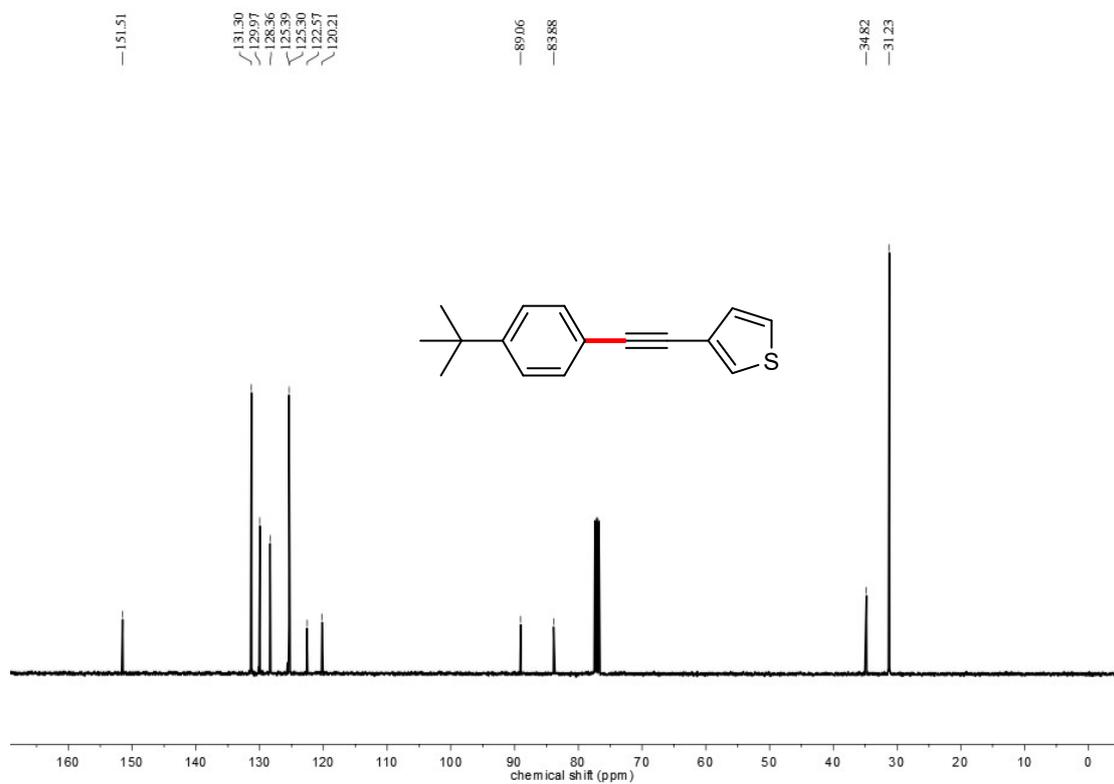
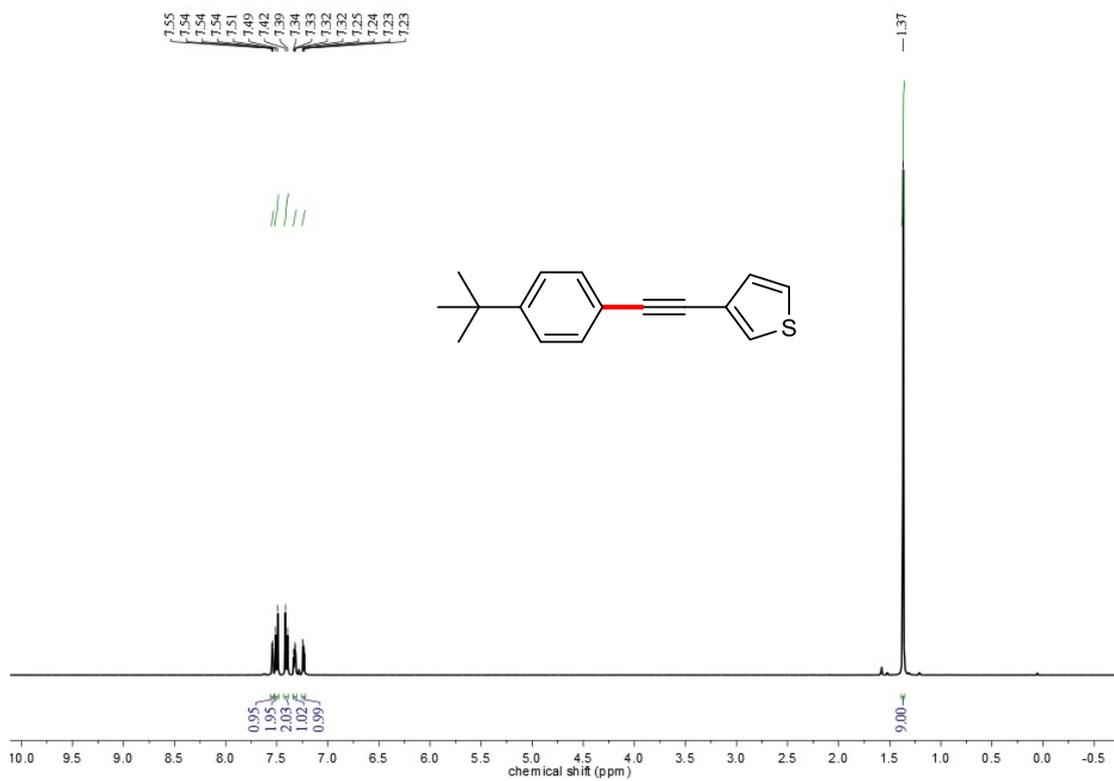
NMR spectrum of compound **4j** in CDCl₃ (400 MHz)



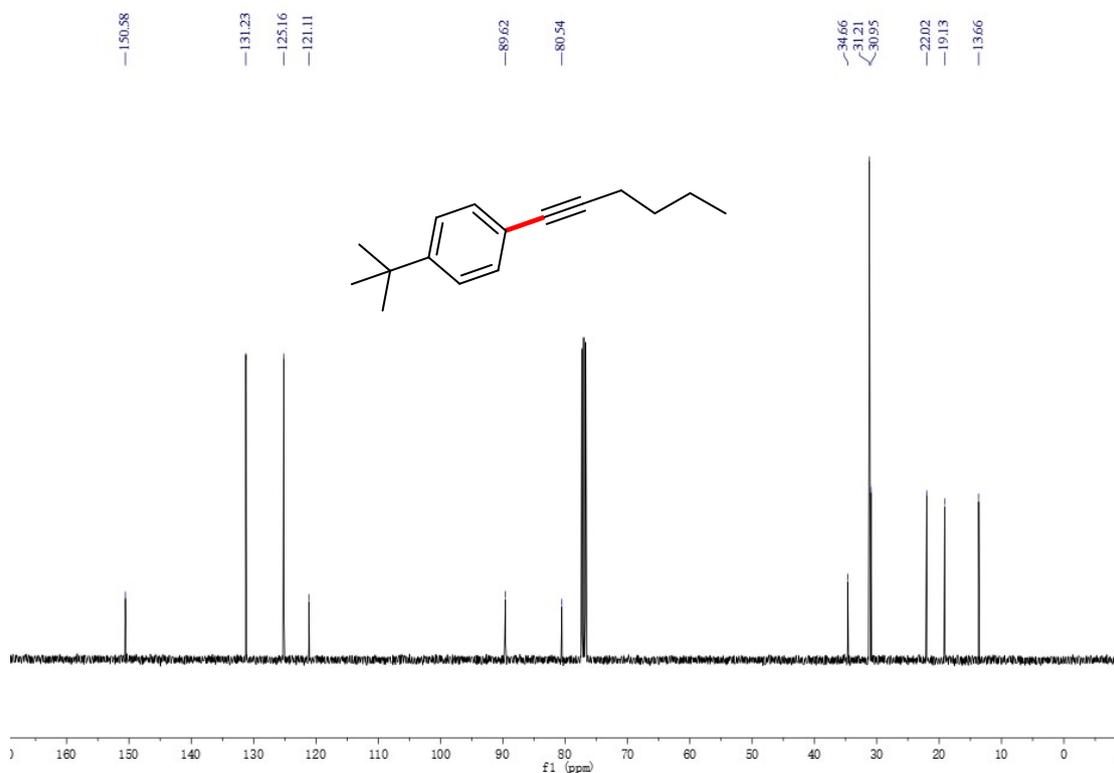
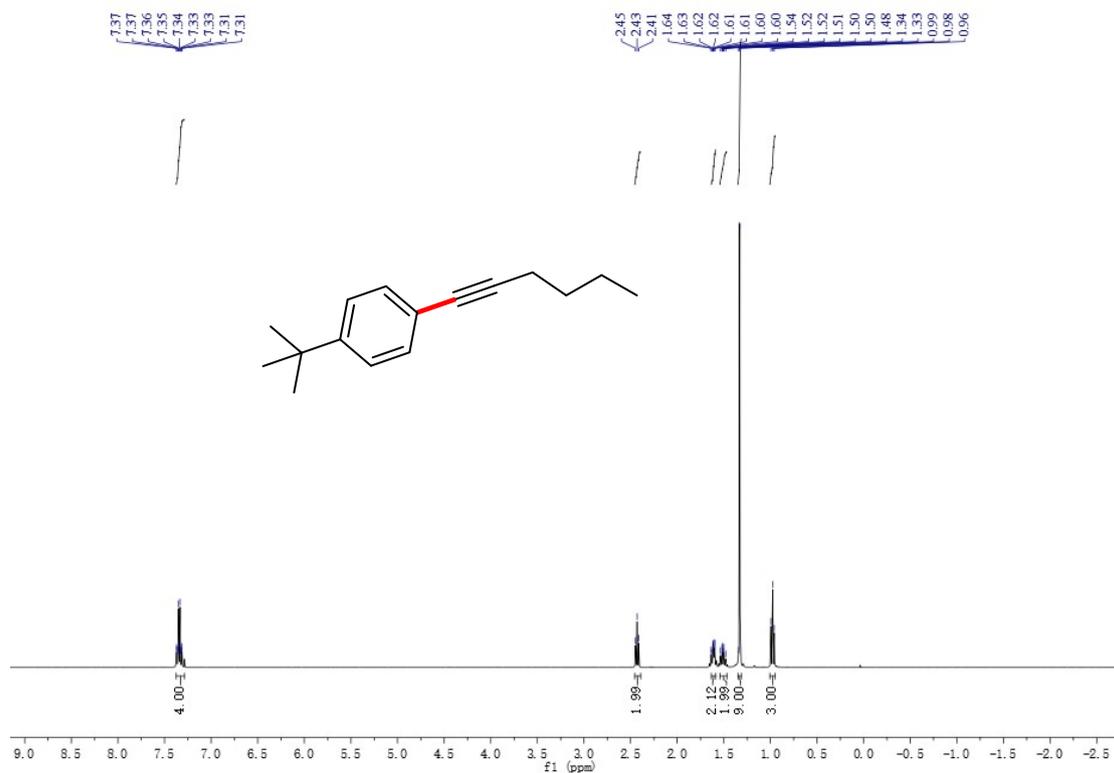
NMR spectrum of compound **4K** in CDCl₃ (400 MHz)



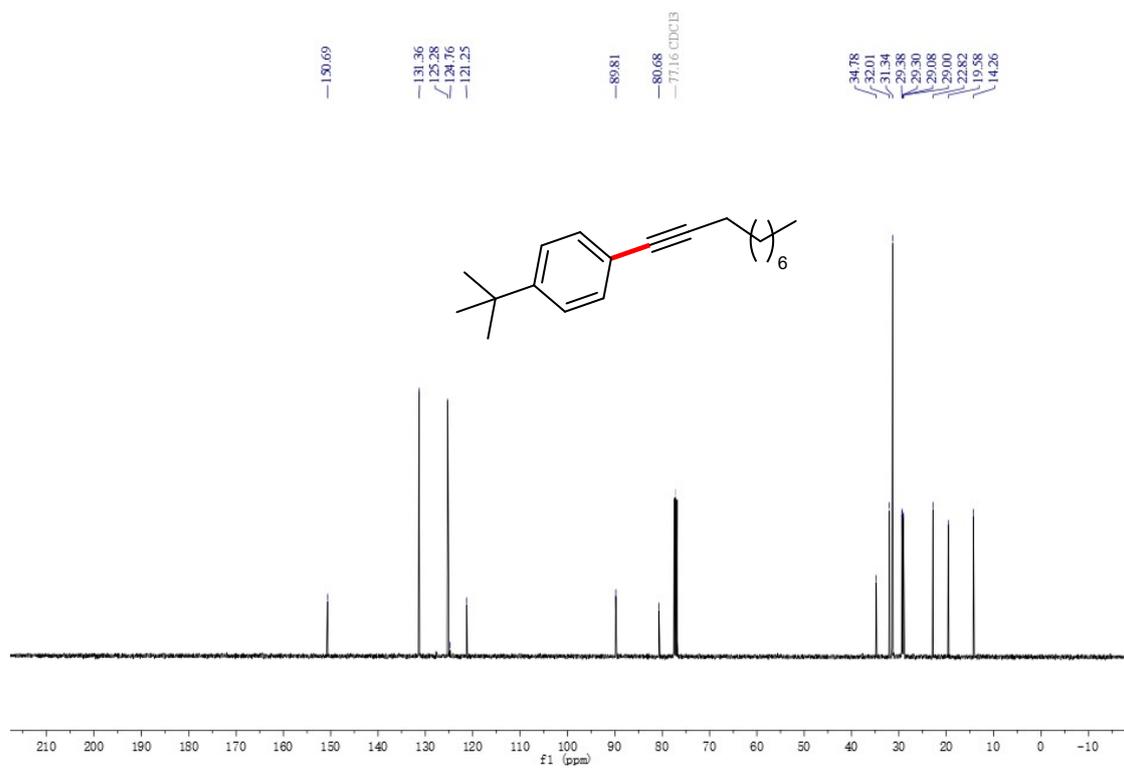
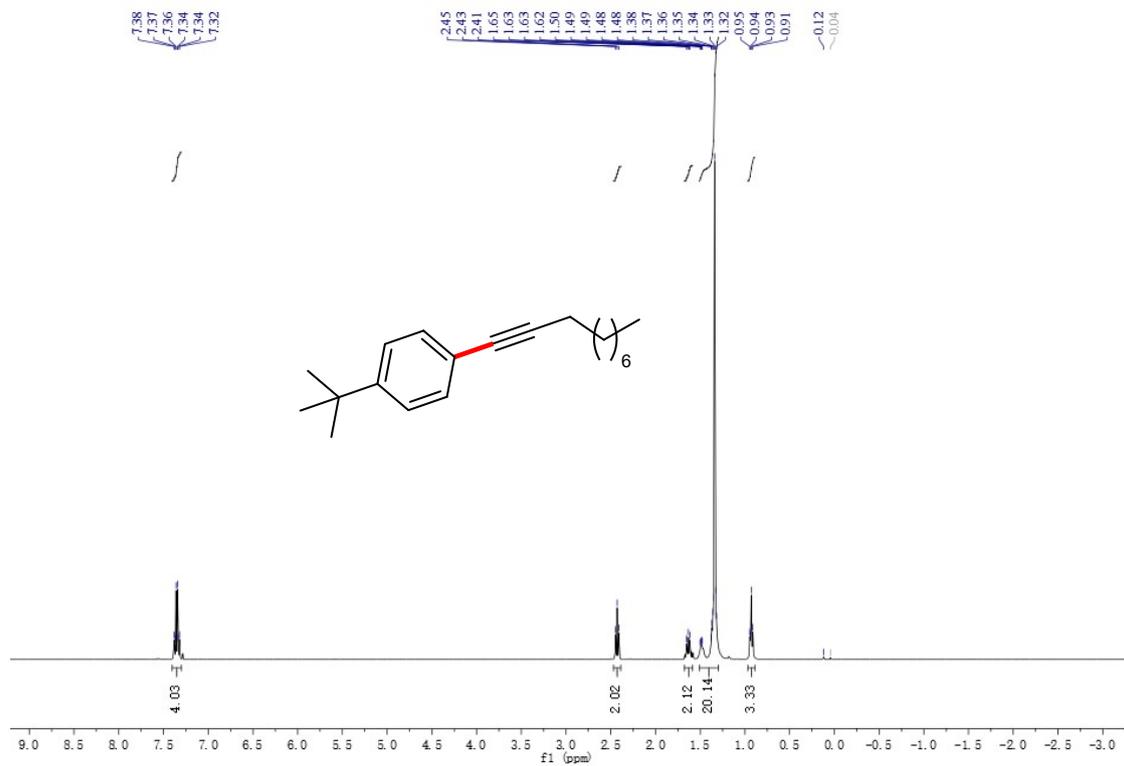
NMR spectrum of compound **4l** in CDCl₃ (400 MHz)



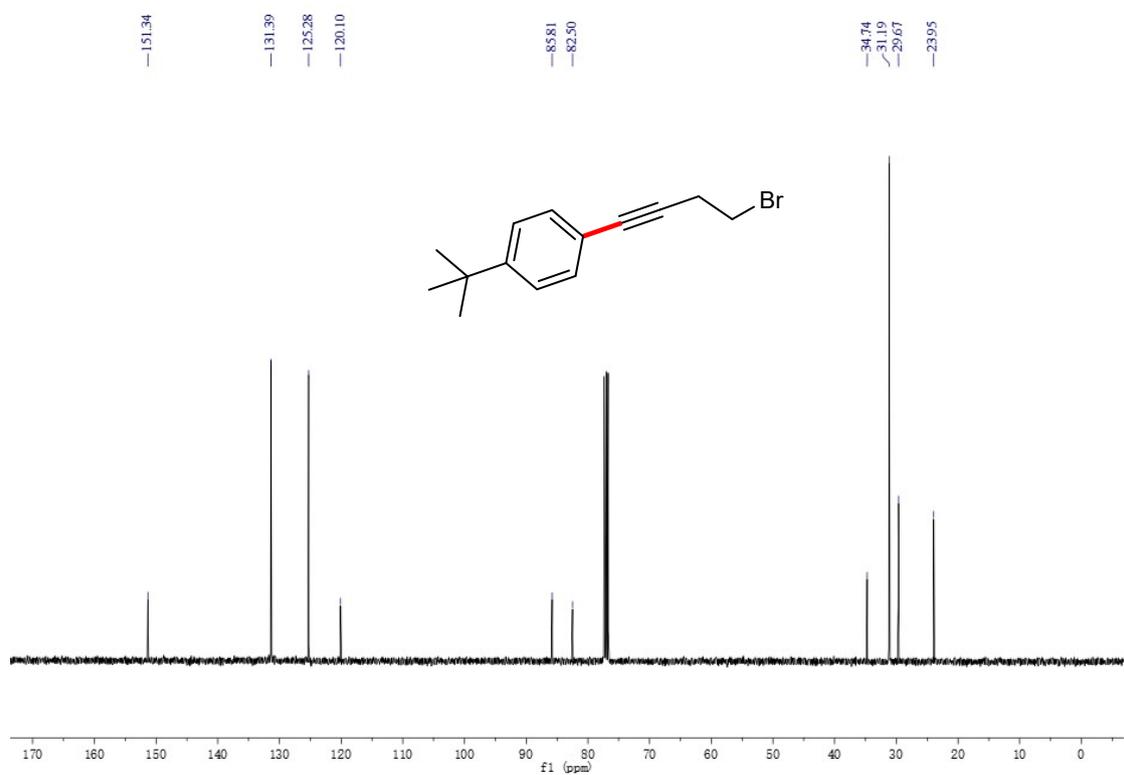
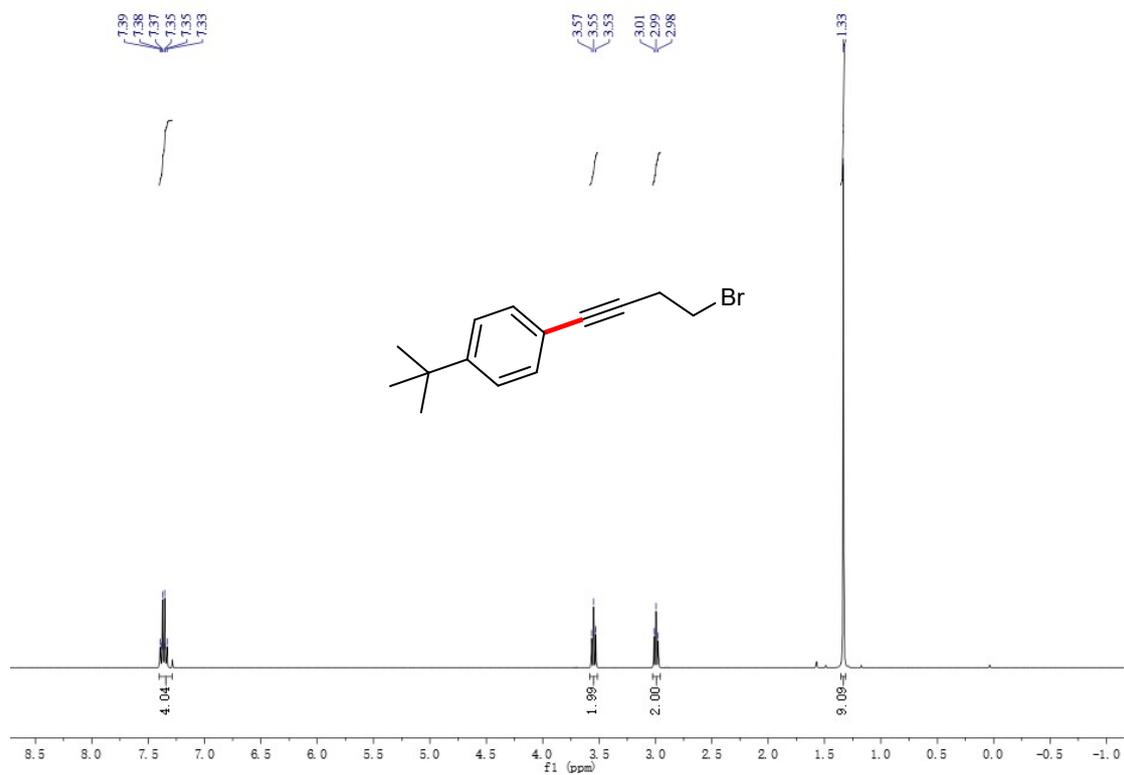
NMR spectrum of compound **4n** in CDCl₃ (400 MHz)



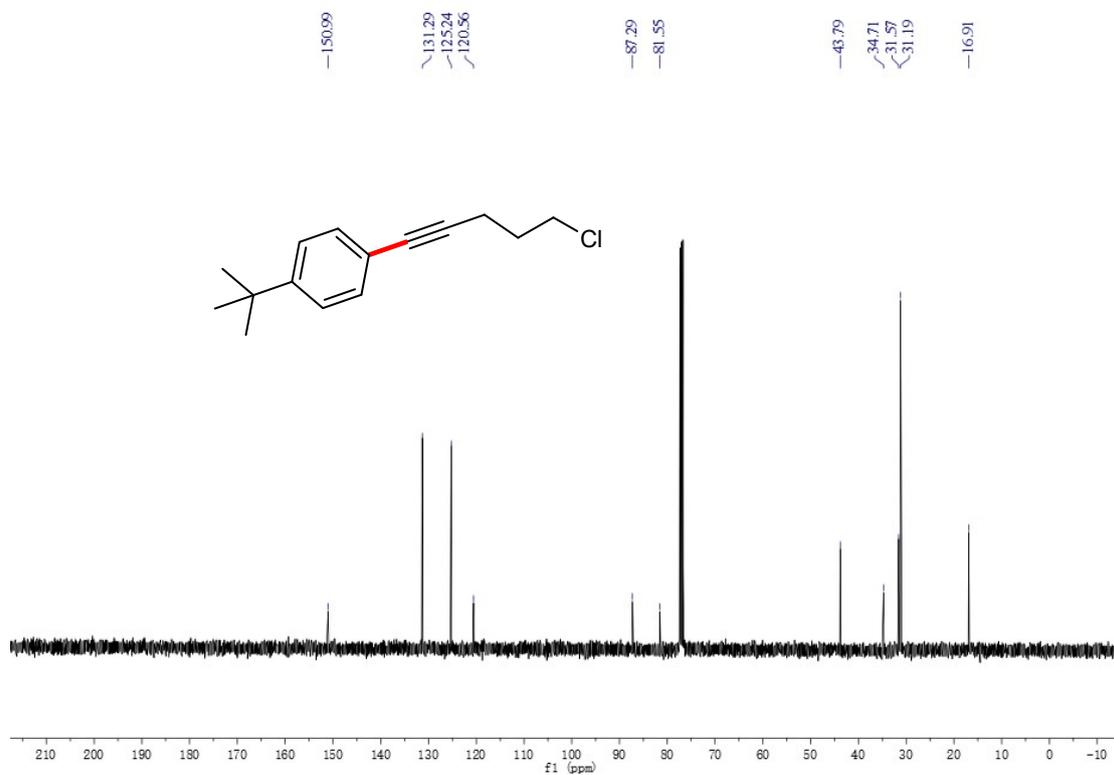
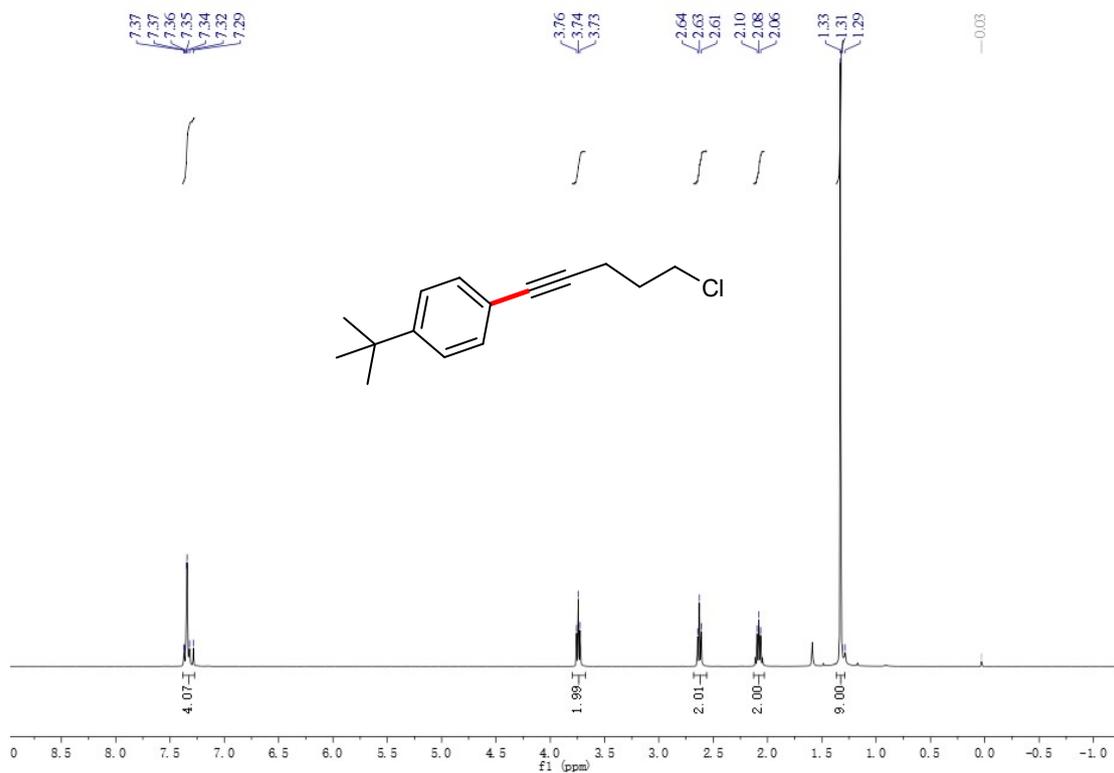
NMR spectrum of compound **4o** in CDCl₃ (400 MHz)



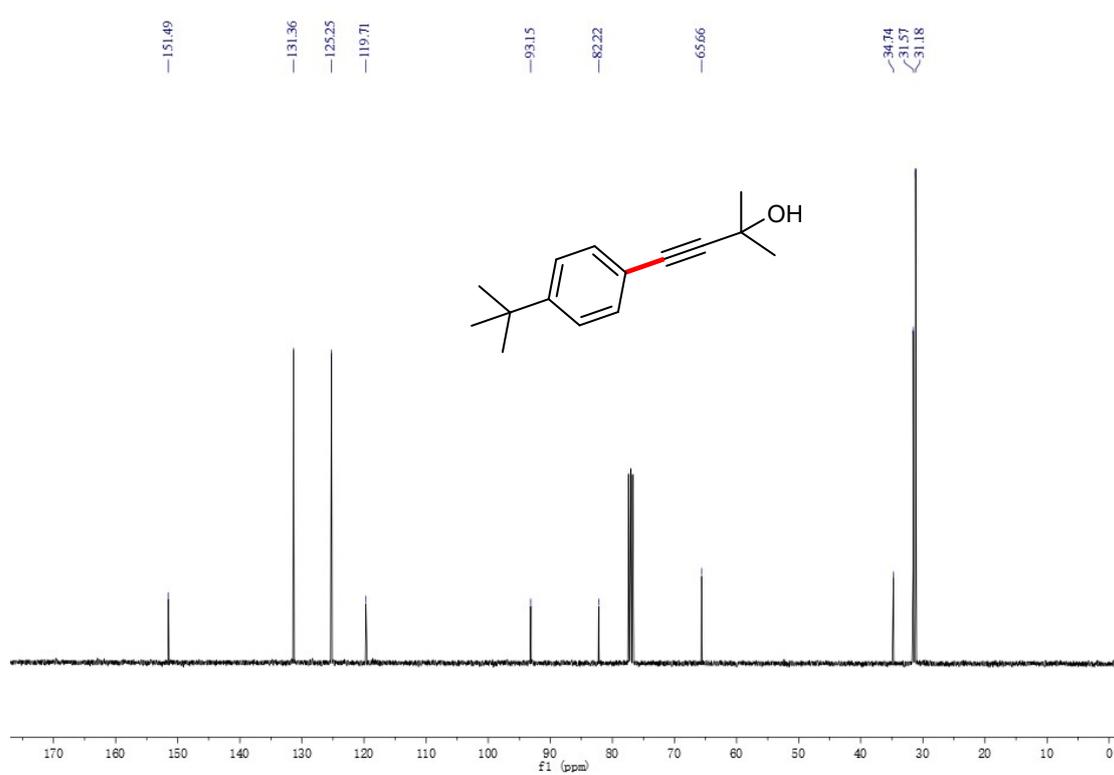
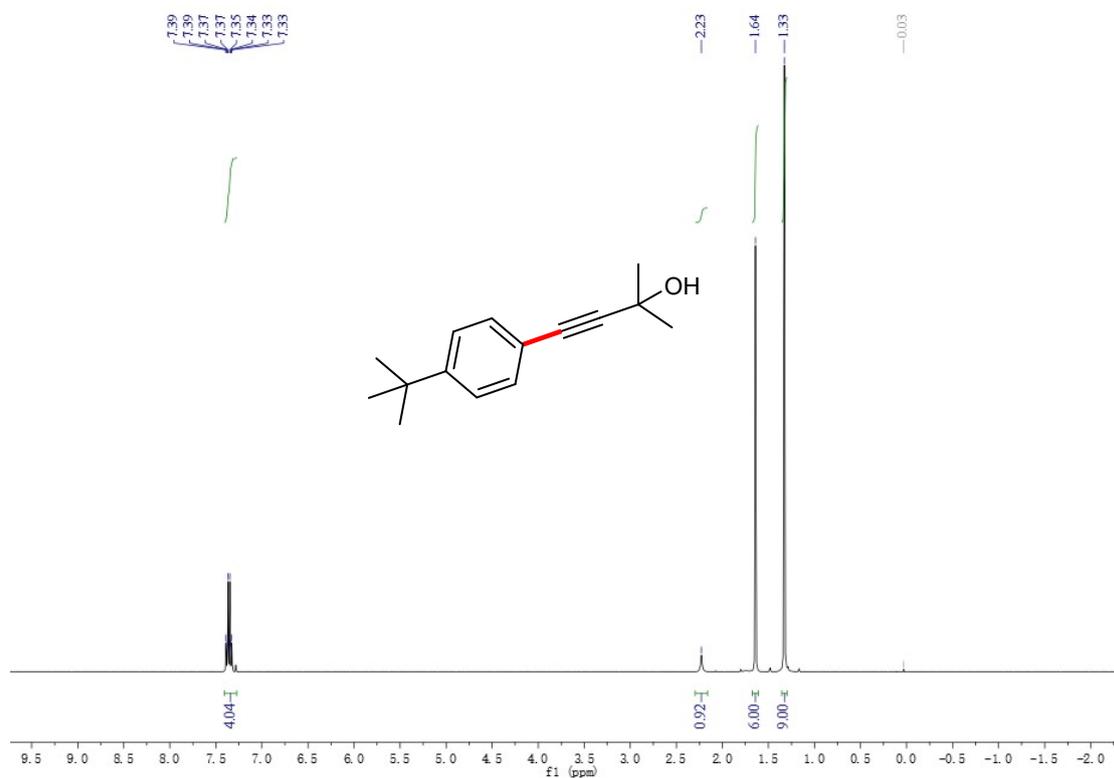
NMR spectrum of compound **4p** in CDCl₃ (400 MHz)



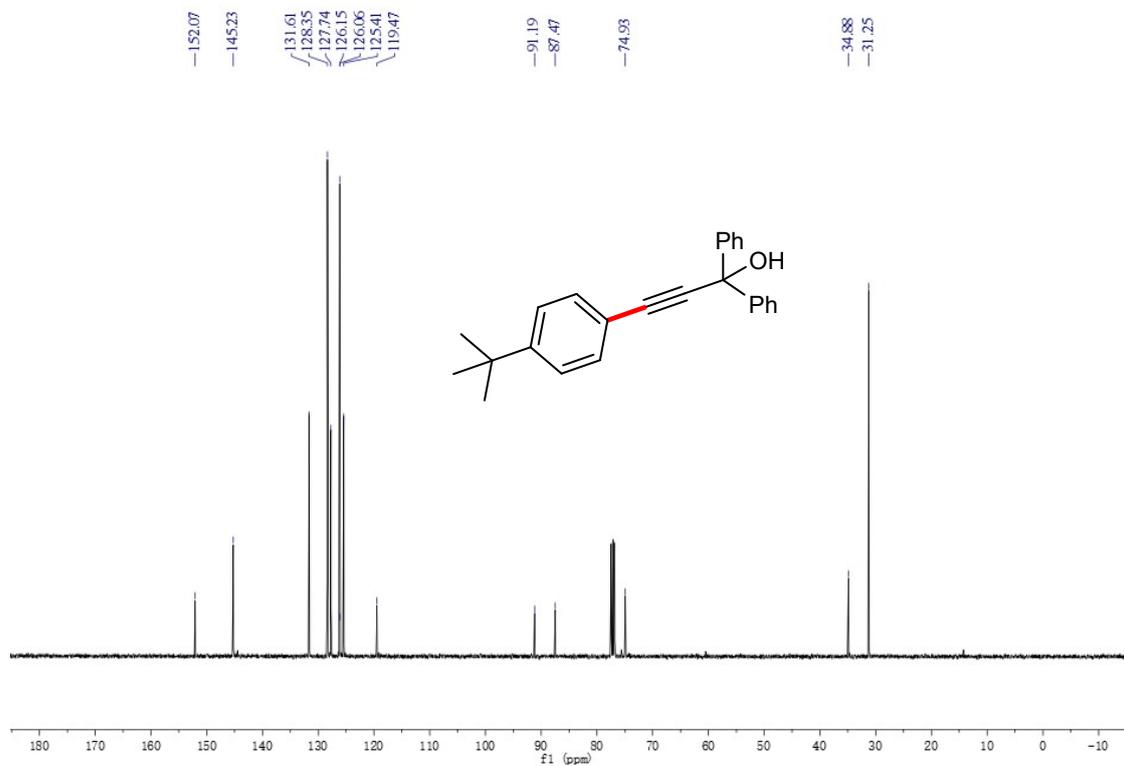
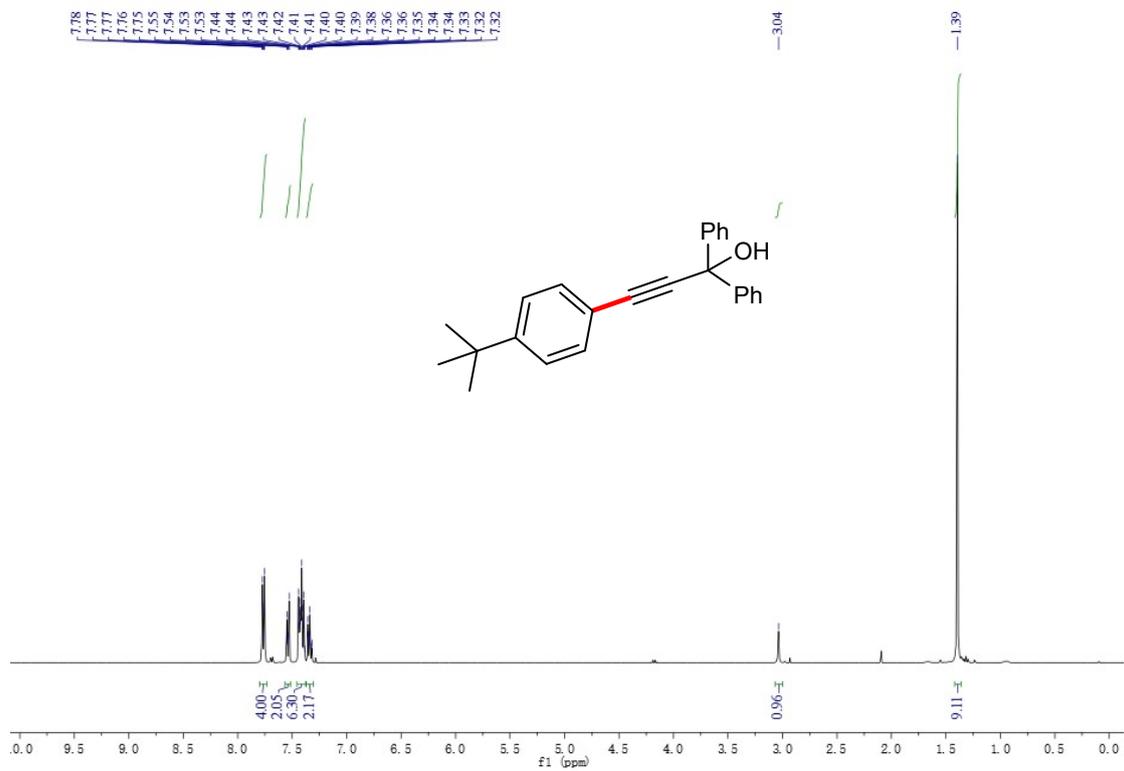
NMR spectrum of compound **4q** in CDCl₃ (400 MHz)



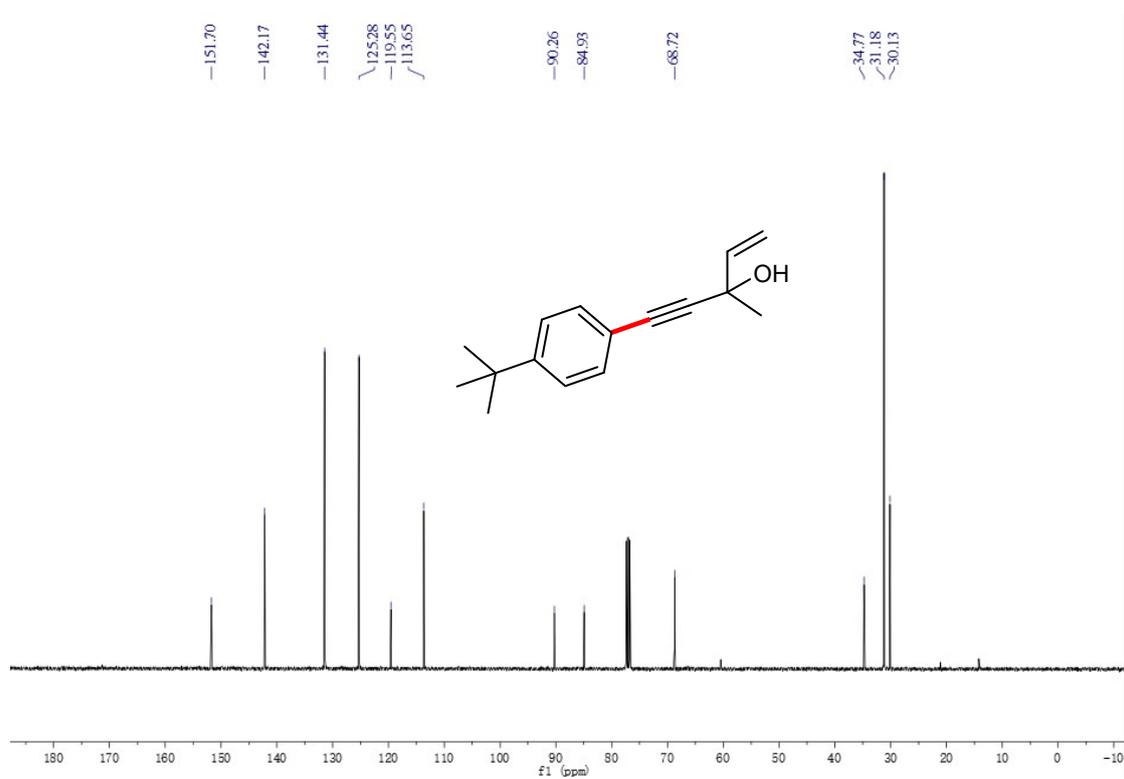
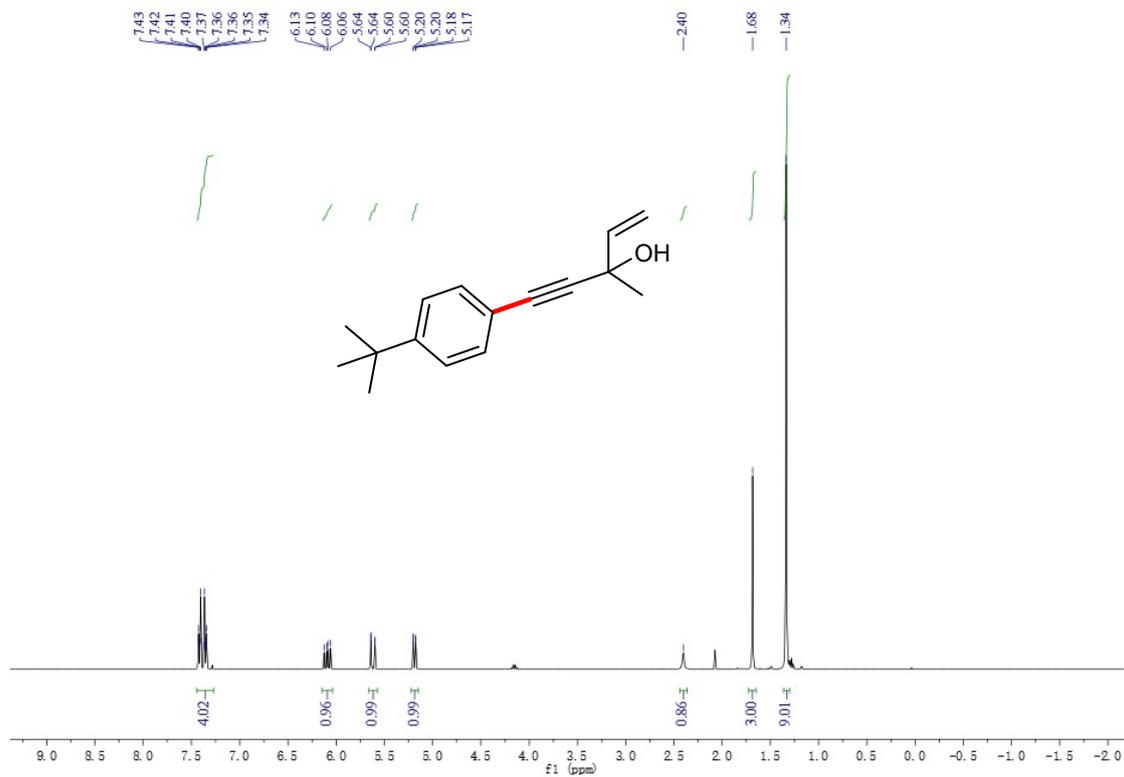
NMR spectrum of compound **4r** in CDCl₃ (400 MHz)



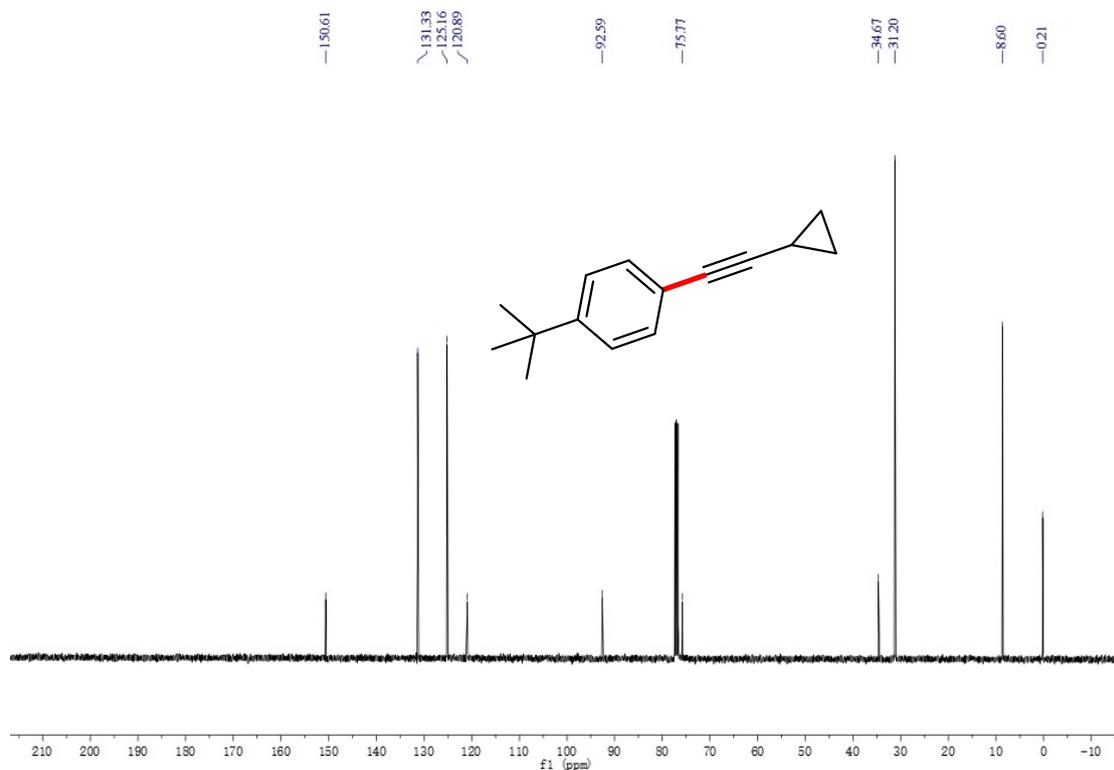
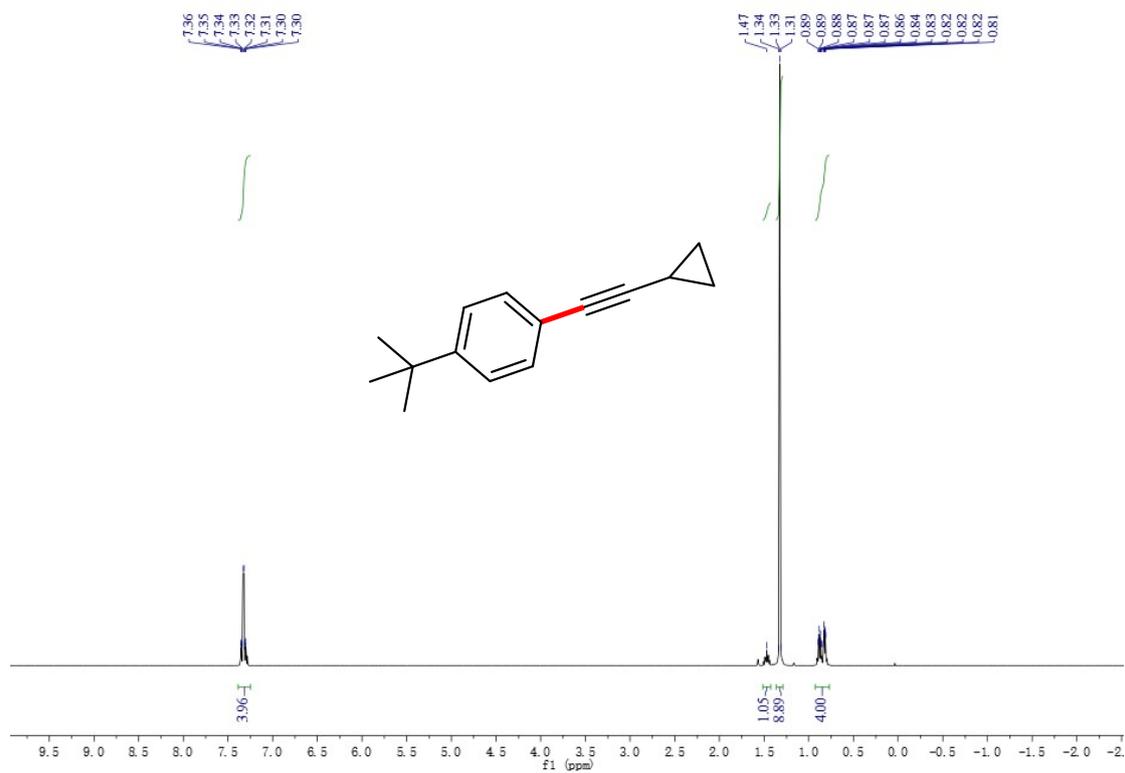
NMR spectrum of compound **4s** in CDCl₃ (400 MHz)



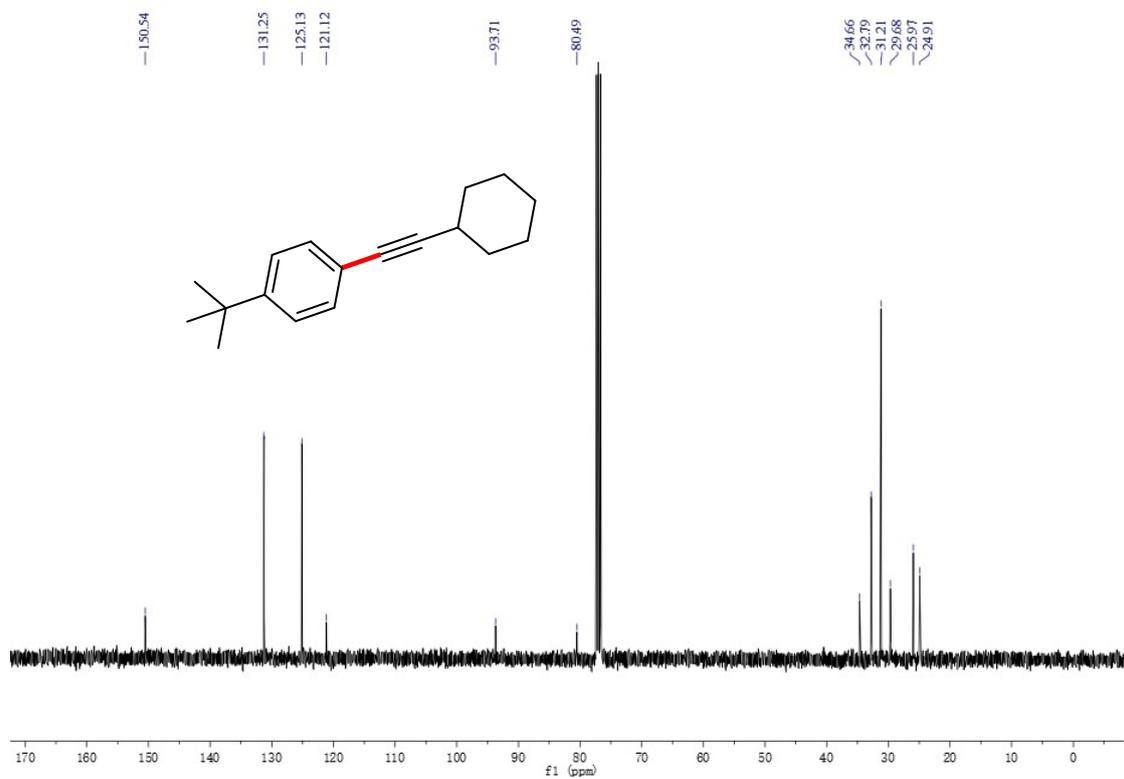
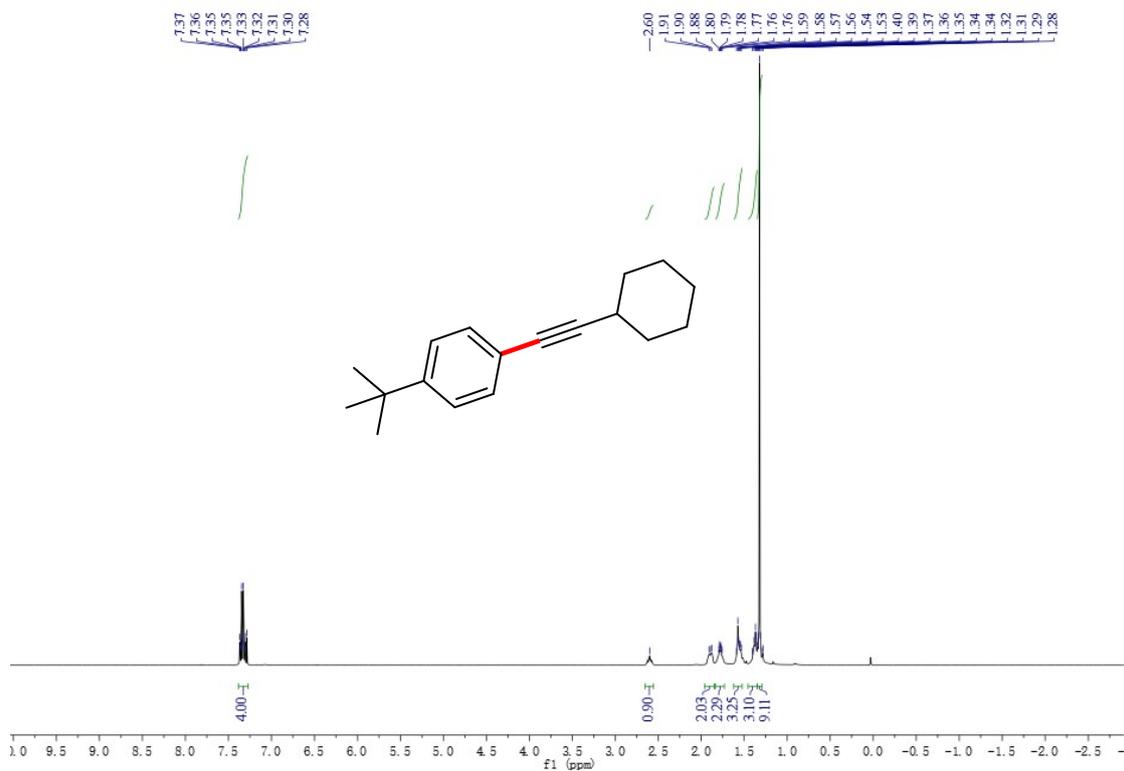
NMR spectrum of compound **4t** in CDCl₃ (400 MHz)



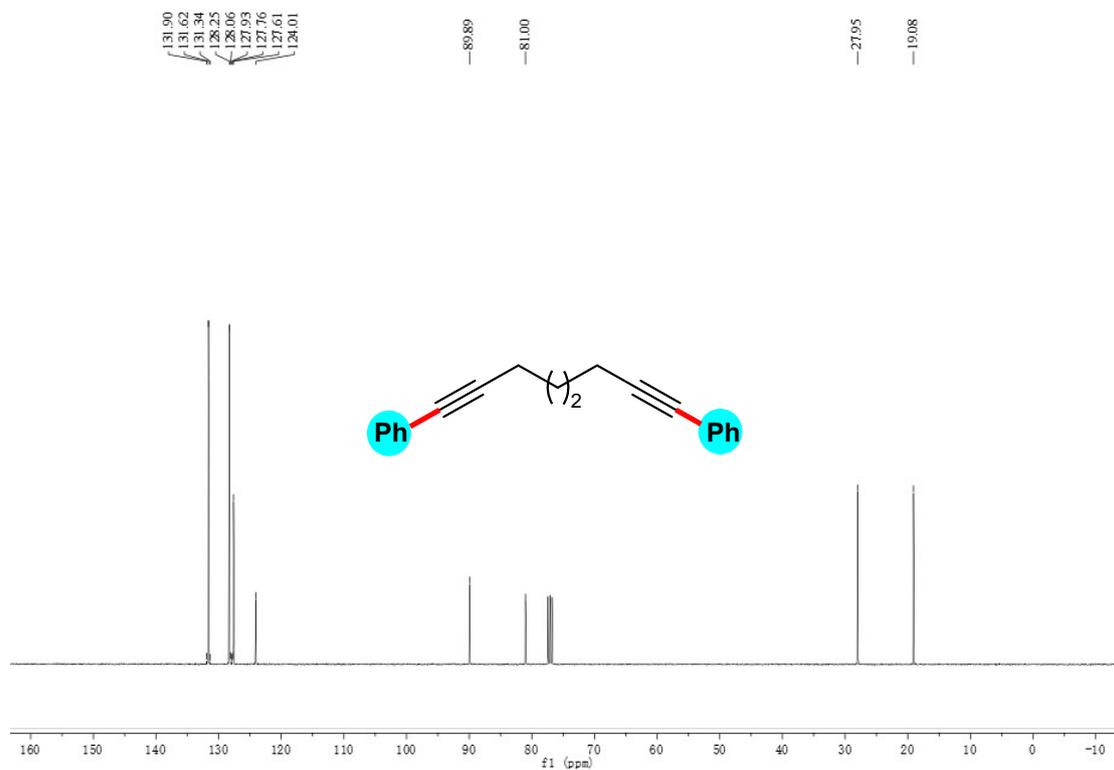
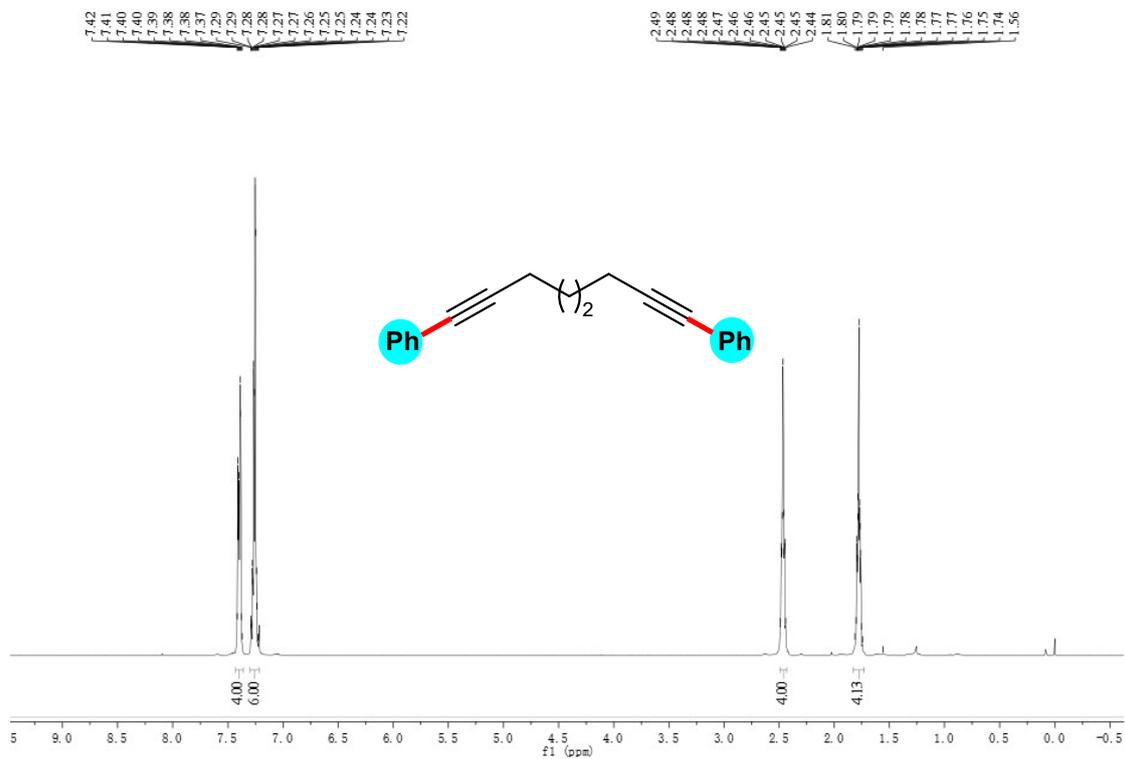
NMR spectrum of compound **4u** in CDCl₃ (400 MHz)



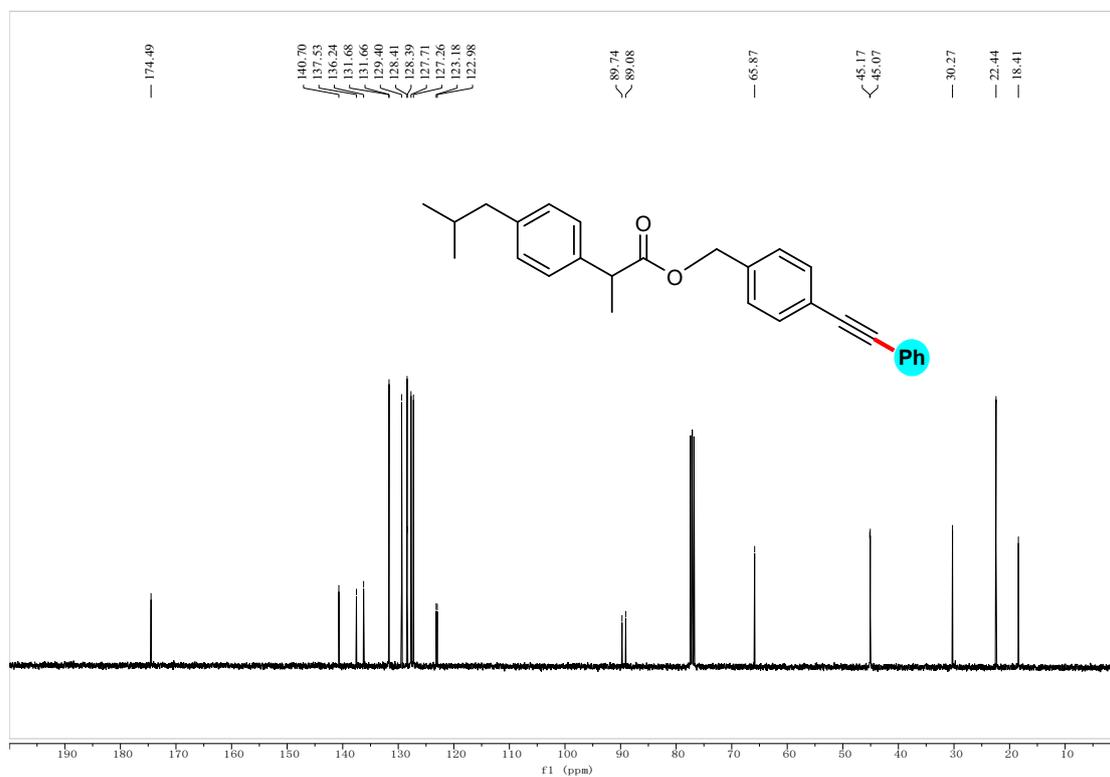
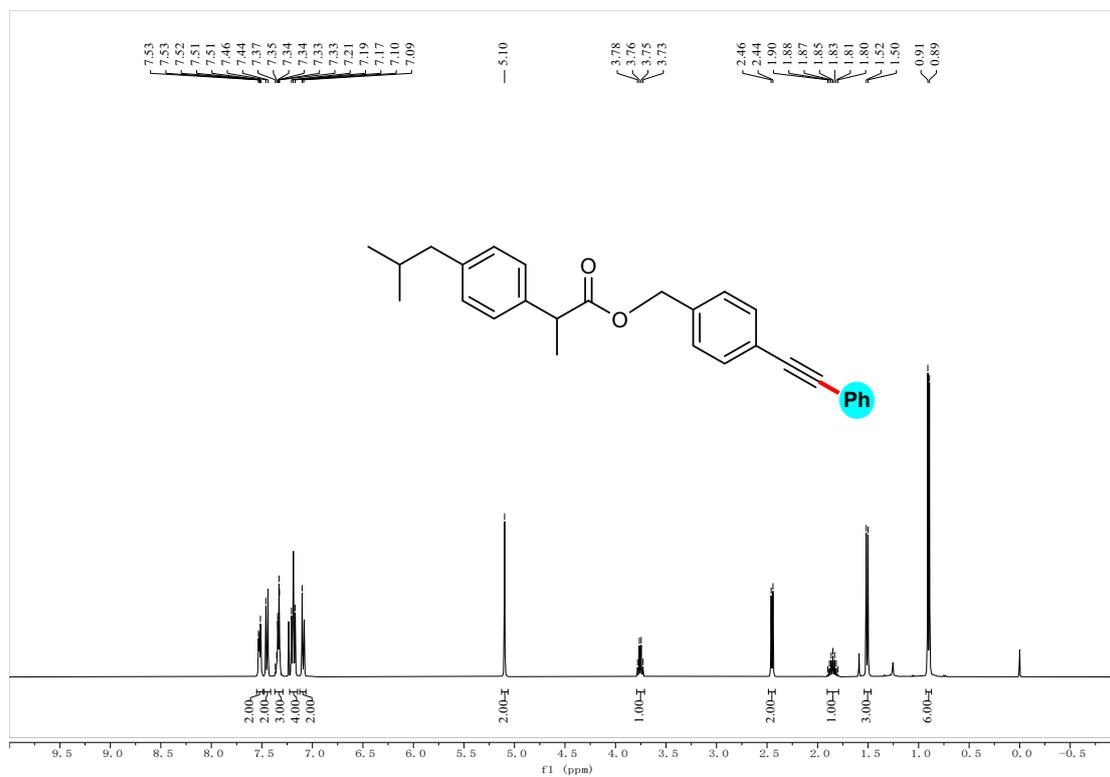
NMR spectrum of compound **4v** in CDCl₃ (400 MHz)



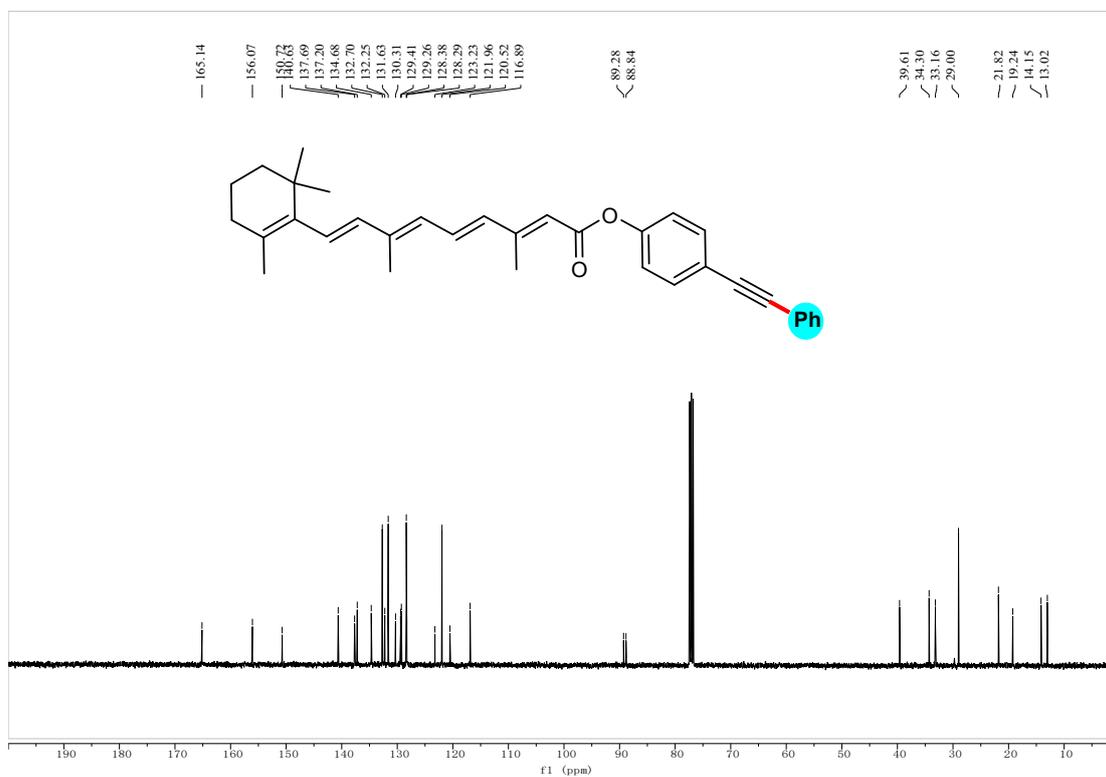
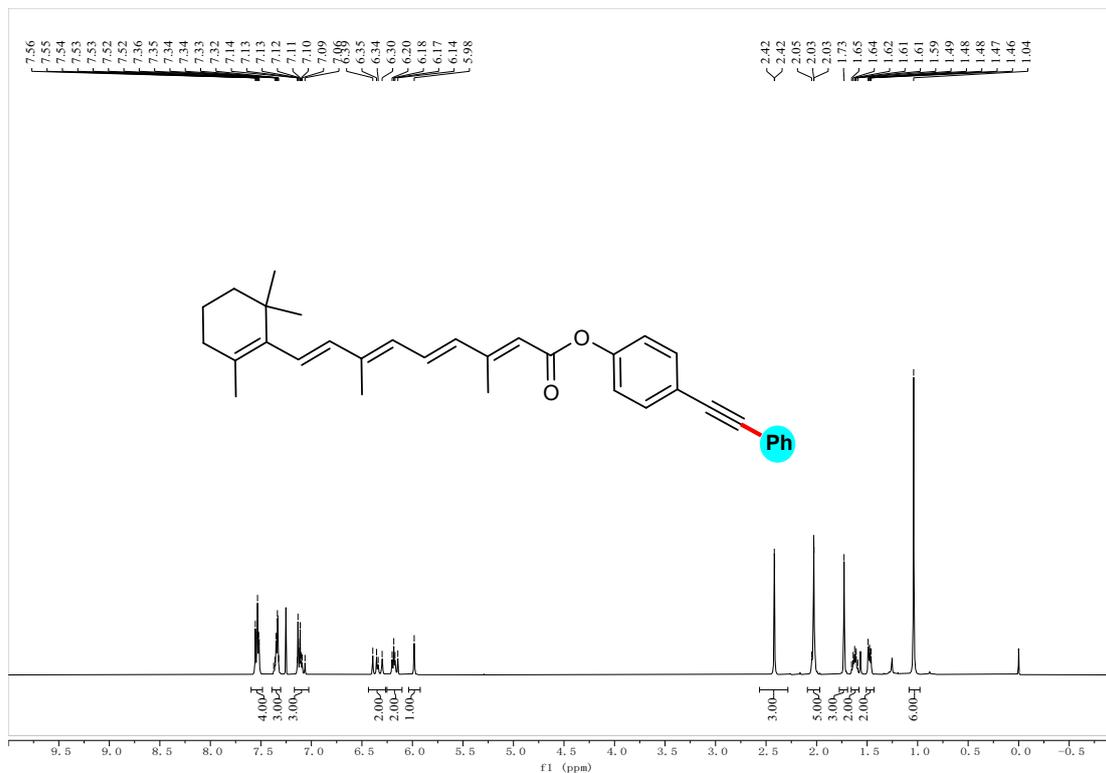
NMR spectrum of compound **6** in CDCl₃ (400 MHz)



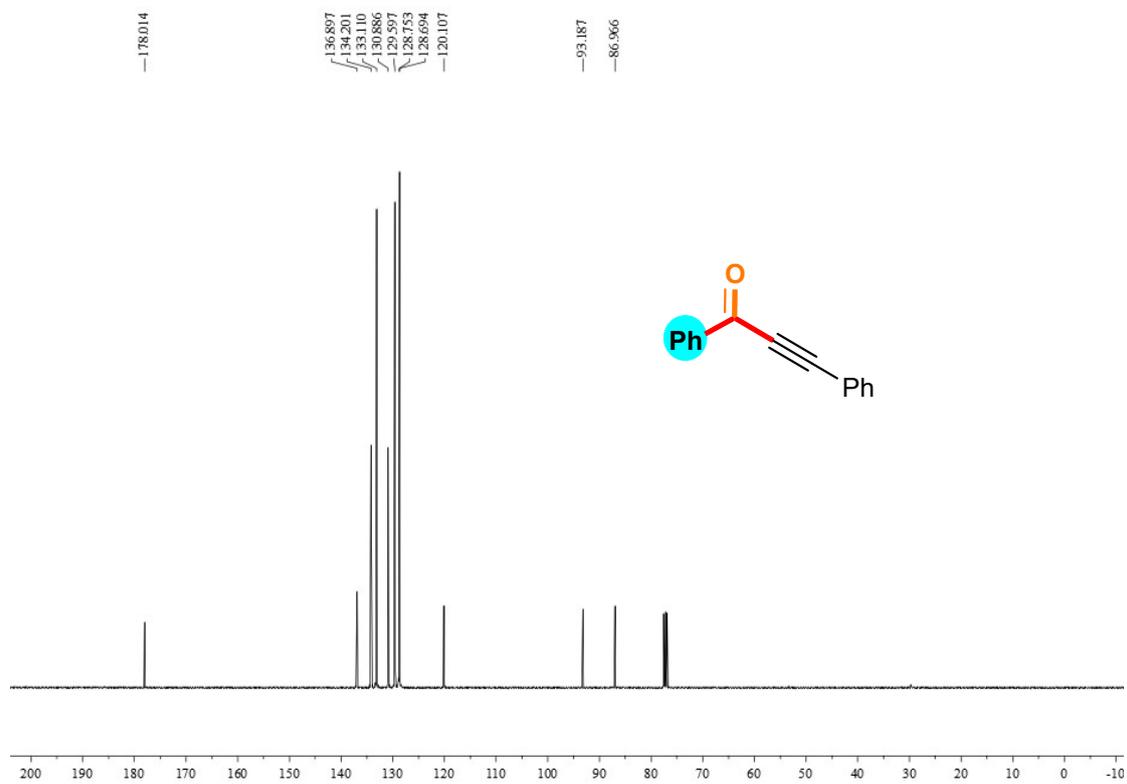
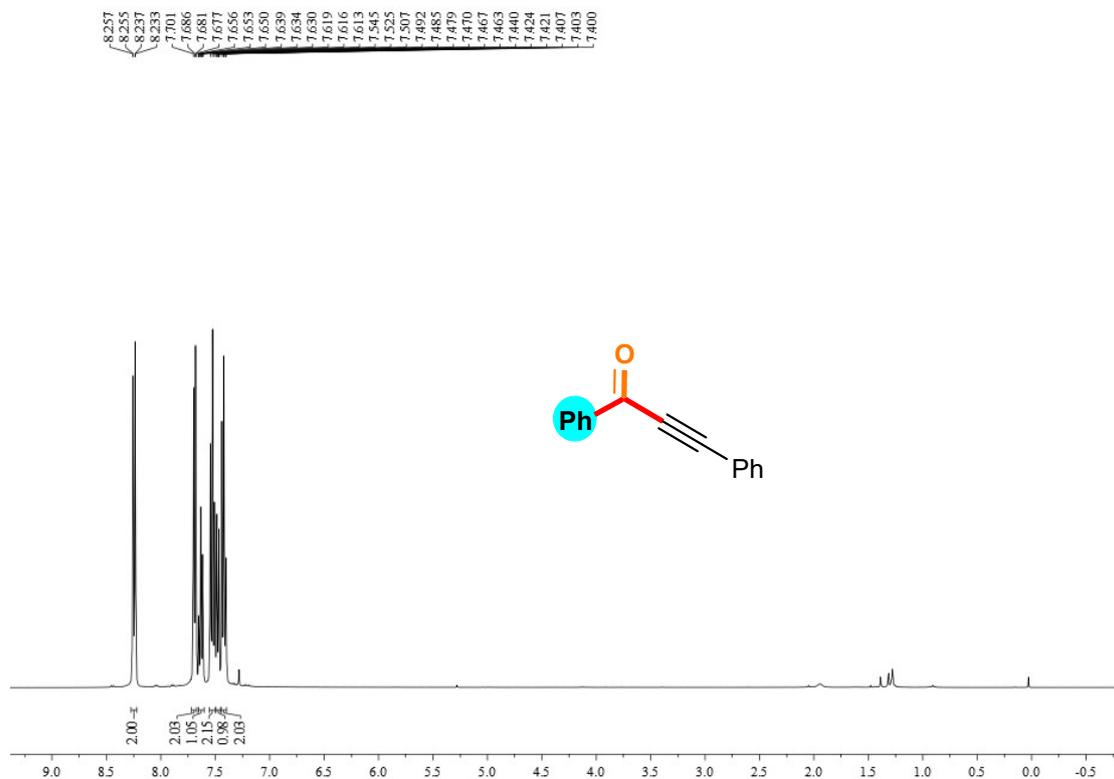
NMR spectrum of compound **8a** in CDCl₃ (400 MHz)



NMR spectrum of compound **8c** in CDCl₃ (400 MHz)

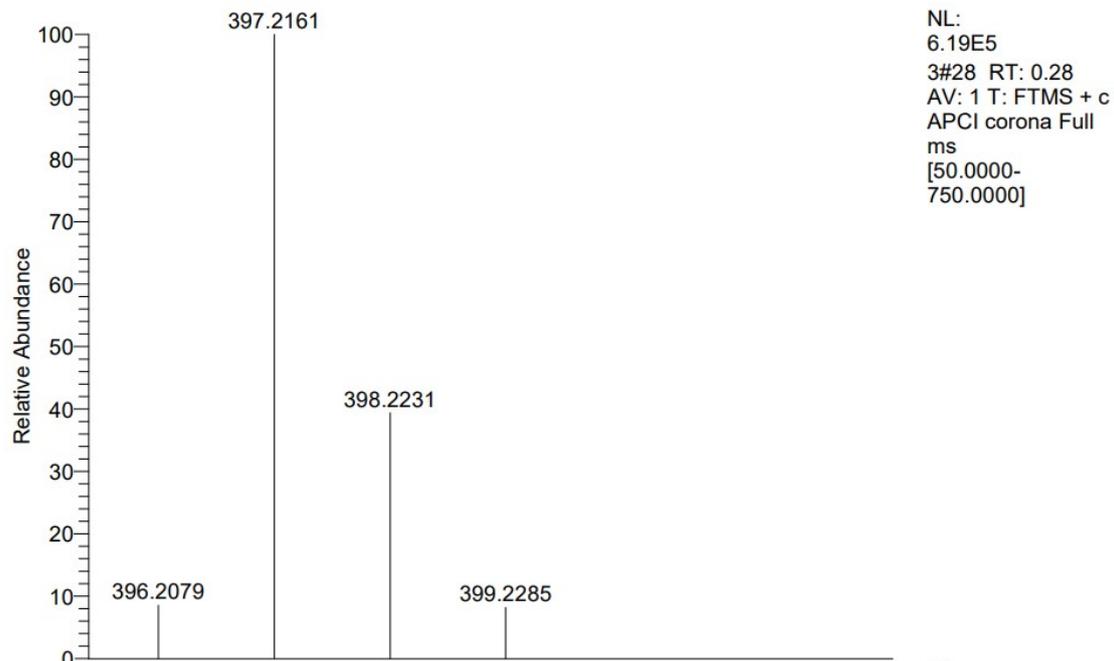


NMR spectrum of compound **9** in CDCl₃ (400 MHz)



HR-MS spectra of new compounds

HR-MS spectrum of compound **8a**



HR-MS spectrum of compound **8b**



HR-MS spectrum of compound **8c**

