Supporting Information

Silver-mediated radical 5-*exo*-*dig* cyclization of 2-alkynylbenzonitriles: Synthesis of phosphinylated 1-indenones

Xiao-Tong Zhu,[a,b,c] Qi Zhao,[a] Feng Liu,[a] Ai-Fang Wang,[a] Pei-Jun Cai,*[,b] Wen-Juan Hao,[a] Shu-Jiang Tu,*[,a] and Bo Jiang*[,a]

[a]School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, 221116, P. R. China;

[b]School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou, 221116, P. R. China;

[c]Department of Chemistry, Xuzhou Medical University, Xuzhou 221004, P. R. China.

Email: jiangchem@jsnu.edu.cn; laotu@jsnu.edu.cn; pjcai@cumt.edu.cn

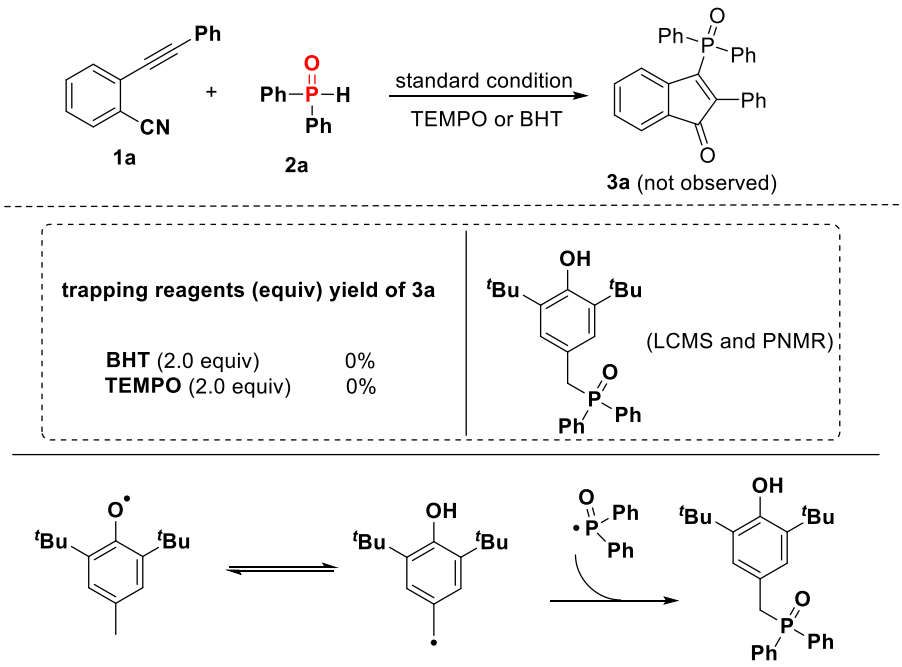
Context

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-d_6) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Mechanistic Study

TEMPO or BHT as the radical trapping reagent—General procedure

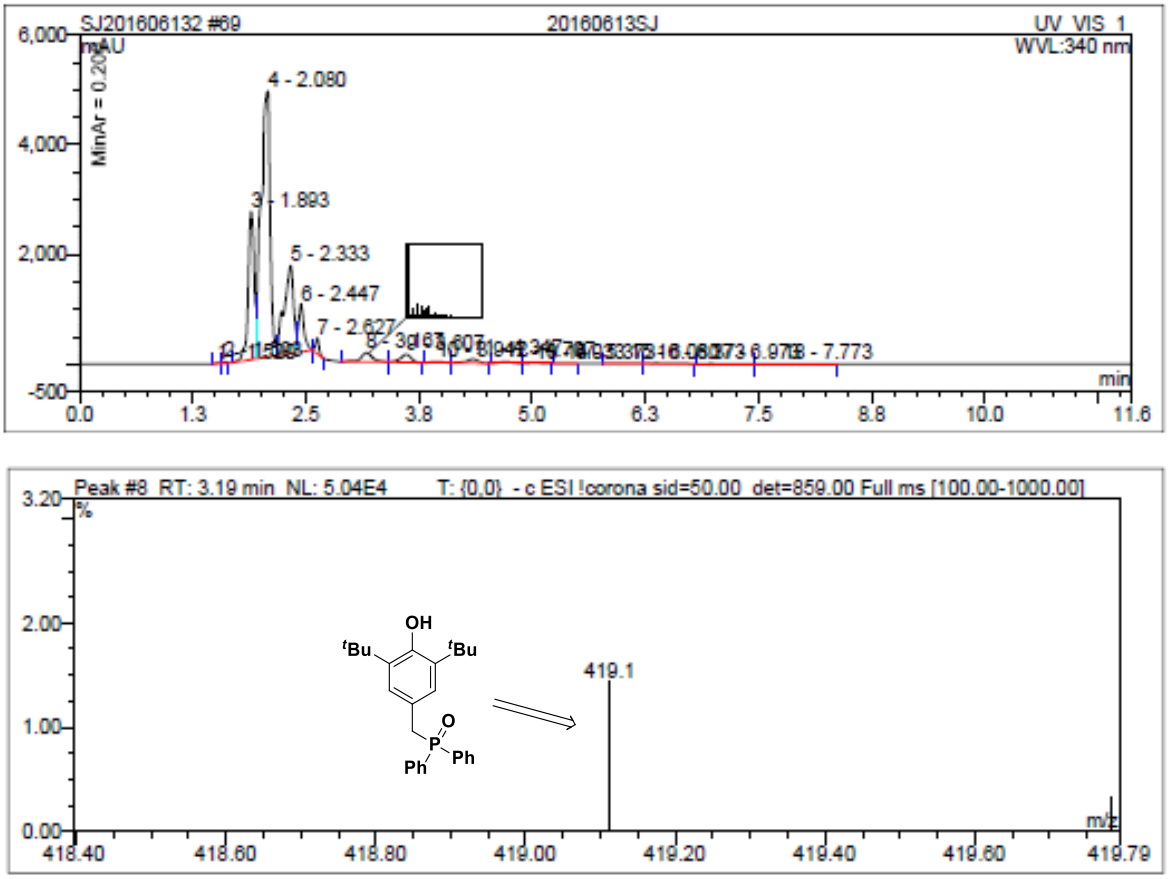


Scheme 1. Radical-Trapping Experiment

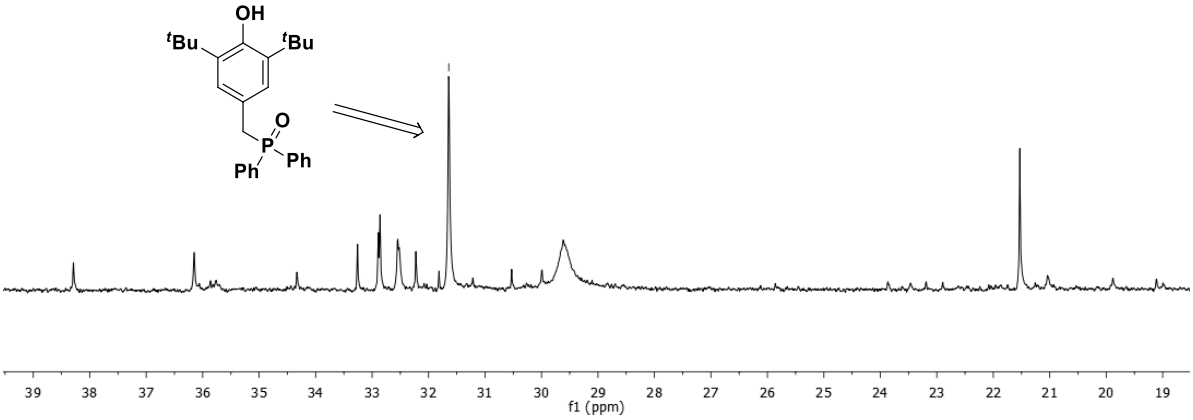
A mixture of 2-(phenylethynyl)benzonitrile (**1a**, 1.0 equiv, 0.2 mmol) with diphenylphosphine oxide (**2a,** 4.0 equiv, 0.80 mmol)), $AgNO_3$ (2.0 equiv, 0.4 mmol) and TEMPO or BHT (2.0 equiv, 0.4 mmol) in CH_3CN-H_2O (2.0 mL, V/V = 3:1) was heated at 80 ^{o}C for 4 hours. After completion of the reaction, the solution further detected by LC-MS analysis and ^{31}P NMR.[1]

Reference

1. Y. Gao, G. Lu, P. Zhang, L. Zhang, G. Tang and Y. Zhao, *Org. Lett.*, 2016, **18**, 1242.



LCMS spectra of intermediate



^{31}P NMR spectra of intermediate

General Procedure for the preparation of 2-alkynylbenzonitriles 1 [2-4]

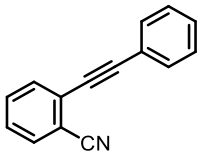
Example for the synthesis of **1a**: ***2-(phenylethynyl)benzonitrile***

A mixture of 2-bromobenzonitrile (1.0 equiv, 5 mmol), ethynylbenzene (1.2 equiv, 6.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 equiv, 0.1 mmol) and CuI (0.01 equiv, 0.05 mmol) in Et_3N (20 mL) was heated at 50 ℃ under Ar atmosphere for 2 h. After completion of the reaction as indicated by TLC, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate (2×10 mL). The combined organic layers were washed with water (2×10 mL) and brine (1×10 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired product **1a** as a yellow liquid. Other 2-alkynylbenzonitriles (**1b**-**1x**) were prepared under the similar reaction conditions.

Reference

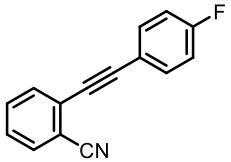
1. M. J. Wu, L. J. Chang, L. M. Wei and C. F. Lin, *Tetrahedron*, 1999, **55**, 13193.
2. Y. H, X.-Y, Zhang and X.-S, Fan, *Chem. Commun*., 2014, **50**, 5641.
3. C. F. Lin, J. H. Yang, P. C. Hsieh, W. D. Lu and M. J. Wu, *J. Chin. Chem. Soc*., 2001, **48**, 211.

2-(phenylethynyl)benzonitrile (1a) [2,3]



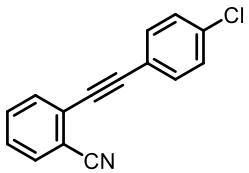
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66-7.60 (m, 4H, Ar-H), 7.57-7.53 (m, 1H, Ar-H), 7.43-7.34 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 134.3, 133.9, 133.2, 132.7, 132.5, 132.1, 132.0, 129.3, 128.5, 128.3, 127.2, 122.0, 117.6, 115.3, 96.0, 85.7. IR (KBr, ν, cm^{-1}) 3062, 2228, 1598, 1495, 1443, 1282, 1164, 917, 757. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_9N$ $[M+H]^+$ 204.0813, found 204.0800.

2-((4-fluorophenyl)ethynyl)benzonitrile (1b) [3]



Yellow solid, Mp: 86-87 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67 (d, J = 8.0 Hz, 1H, Ar-H), 7.62-7.55 (m, 4H, Ar-H), 7.43-7.39 (m, 1H, Ar-H), 7.10-7.04 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 163.1 (d, ^1J = 249.6 Hz), 134.0 (d, ^4J = 8.5 Hz), 132.7, 132.4, 132.0, 128.3, 127.1, 118.2 (d, ^3J = 3.5 Hz), 117.6, 115.9 (d, ^2J = 22.1 Hz), 115.3, 94.9, 85.4. IR (KBr, ν, cm^{-1}) 3052, 2228, 1592, 1508, 1445, 1220, 1160, 834, 756. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8FN$ $[M+H]^+$ 222.0719, found 222.0723.

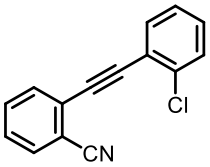
2-((4-chlorophenyl)ethynyl)benzonitrile (1c) [3]



Yellow solid, Mp: 60-61 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.63 (d, J = 8.0 Hz, 1H, Ar-H), 7.60-7.54 (m, 2H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.42-7.37 (m, 1H, Ar-H), 7.30 (d, J = 8.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 135.3, 134.3, 134.0, 133.2, 132.6, 132.5, 132.1, 128.8, 128.6, 127.7, 120.5, 117.5, 115.2,

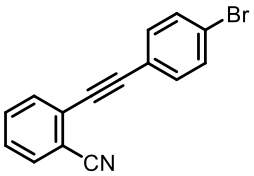
94.7, 86.6. IR (KBr, ν, cm^{-1}) 3064, 2228, 1588, 1493, 1435, 1282, 1086, 831, 756. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8ClN$ $[M+H]^+$ 238.0424, found 238.0429.

2-((2-chlorophenyl)ethynyl)benzonitrile (1d)



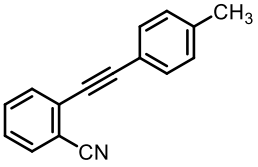
White solid, Mp: 99-100 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.70-7.65 (m, 3H, Ar-H), 7.61-7.56 (m, 1H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 7.34-7.25 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 136.2, 133.9, 132.8, 132.5, 132.4, 130.3, 129.4, 128.6, 126.8, 126.6, 122.1, 117.5, 115.2, 92.4, 90.2. IR (KBr, ν, cm^{-1}) 3121, 2228, 1586, 1489, 1443, 1287, 1055, 956, 750. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8ClN$ $[M+H]^+$ 238.0424, found 238.0417.

2-((4-bromophenyl)ethynyl)benzonitrile (1e)



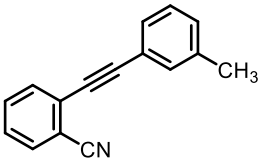
Yellow solid, Mp: 77-78 °C. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68 (d, J = 8.0 Hz, 1H, Ar-H), 7.63-7.56 (m, 2H, Ar-H), 7.53-7.41 (m, 5H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 133.4, 132.7, 132.4, 132.1, 131.8, 128.5, 126.9, 123.7, 121.0, 117.5, 115.4, 94.8, 86.6. IR (KBr, ν, cm^{-1}) 3123, 2229, 1509, 1491, 1468, 1068, 1011, 820, 762. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8BrN$ $[M+H]^+$ 281.9918, found 281.9930.

2-(p-tolylethynyl)benzonitrile (1f) [2,3]



Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.62-7.50 (m, 2H, Ar-H), 7.46 (d, J = 7.6 Hz, 2H, Ar-H), 7.43-7.34 (m, 2H, Ar-H), 7.14 (d, J = 7.6 Hz, 2H, Ar-H), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 139.6, 134.3, 134.0, 133.2, 132.6, 132.5, 132.0, 131.9, 129.3, 128.2, 127.7, 119.0, 115.0, 96.3, 85.2, 21.6. IR (KBr, ν, cm^{-1}) 3030, 2228, 2170, 1591, 1478, 1443, 1380, 1281, 1163, 955, 762. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{11}N$ $[M+H]^+$ 218.0970, found 218.0979.

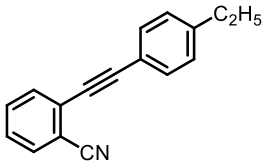
2-(m-tolylethynyl)benzonitrile (1g) [3]



Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.64-7.58 (m, 2H, Ar-H), 7.56-7.52 (m, 1H, Ar-H), 7.42-7.35 (m, 3H, Ar-H), 7.27-7.23 (m, 1H, Ar-H), 7.19 (d, J = 7.6 Hz, 1H, Ar-H), 2.35 (s, 3H, CH_3). ^{13}C NMR

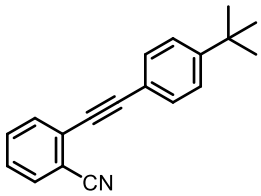
(100 MHz, $CDCl_3$; δ, ppm) 138.2, 134.3, 134.0, 132.6, 132.5, 132.1, 130.2, 129.1, 128.4, 128.2, 121.8, 117.6, 115.2, 96.3, 85.4, 21.3. IR (KBr, ν, cm^{-1}) 3064, 2229, 2209, 1600, 1489, 1445, 1284, 1164, 1094, 785. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{11}N$ $[M+H]^+$ 218.0970, found 218.0976.

2-((4-ethylphenyl)ethynyl)benzonitrile (1h)



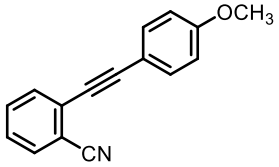
Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.65-7.59 (m, 2H, Ar-H), 7.58- 7.50 (m, 2H, Ar-H), 7.43-7.35 (m, 2H, Ar-H), 7.18 (d, J = 8.0 Hz, 2H, Ar-H), 2.68-2.63 (m, 2H, CH_2), 1.25-1.21 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 145.9, 134.3, 134.0, 133.2, 132.7, 132.5, 132.1, 128.1, 127.8, 127.4, 119.2, 117.7, 115.1, 96.4, 85.2, 29.0, 15.4. IR (KBr, ν, cm^{-1}) 2966, 2228, 2218, 1591, 1511, 1442, 1282, 1184, 835, 761. HR-MS (APCI-TOF) m/z calcd for $C_{17}H_{13}N$ $[M+H]^+$ 232.1126, found 232.1119.

2-((4-(tert-butyl)phenyl)ethynyl)benzonitrile (1i)



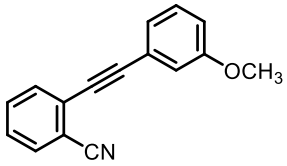
White solid, Mp: 87-88 ^oC; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67-7.65 (m, 1H, Ar-H), 7.63-7.61 (m, 1H, Ar-H), 7.58-7.53 (m, 3H, Ar-H), 7.41-7.37 (m, 3H, Ar-H), 1.34 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.7, 132.6, 132.3, 132.0, 131.8, 128.0, 127.5, 125.5, 119.0, 117.6, 115.3, 96.4, 85.1, 34.9, 31.2. IR (KBr, ν, cm^{-1}) 2960, 2228, 1590, 1507, 1440, 1267, 1105, 835, 771. HR-MS (APCI-TOF) m/z calcd for $C_{19}H_{17}N$ $[M+H]^+$ 260.1439, found 260.1441.

2-((4-methoxyphenyl)ethynyl)benzonitrile (1j) [3,4]



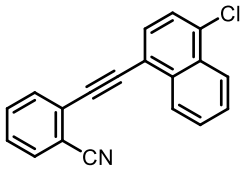
Yellow solid, Mp: 78-79 ^oC. ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66 (d, J = 7.6 Hz, 1H, Ar-H), 7.59-7.54 (m, 4H, Ar-H), 7.40-7.36 (m, 1H, Ar-H), 6.92-6.88 (m, 2H, Ar-H), 3.84 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 160.4, 133.6, 132.6, 132.3, 131.8, 127.8, 127.7, 117.7, 115.0, 114.1(4),114.1(0), 96.4, 84.6, 55.4. IR (KBr, ν, cm^{-1}) 2960, 2228, 2219, 1589, 1478, 1438, 1289, 1179, 1023, 828, 764. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{11}NO$ $[M+H]^+$ 234.0919, found 234.0925.

2-((3-methoxyphenyl)ethynyl)benzonitrile (1k)



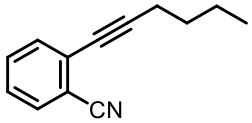
Light yellow solid, Mp: 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67-7.61 (m, 2H, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.42-7.38 (m, 1H, Ar-H), 7.30-7.26 (m, 1H, Ar-H), 7.21 (d, J = 7.6 Hz, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 6.94 (d, J = 8.4 Hz, 1H, Ar-H), 3.82 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 159.4, 132.7, 132.4, 132.2, 129.6, 128.3, 127.1, 124.6, 123.0, 117.6, 116.6, 116.0, 115.3, 95.9, 85.4, 55.4. IR (KBr, ν, cm^{-1}) 2998, 2224, 2205, 1573, 1490, 1427, 1264, 1186, 954, 760. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{11}NO$ $[M+H]^+$ 234.0919, found 234.0914.

2-((4-chloronaphthalen-1-yl)ethynyl)benzonitrile (1l)



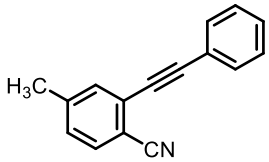
White solid, Mp: 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66 (d, J = 8.0 Hz, 2H, Ar-H), 7.61-7.56 (m, 3H, Ar-H), 7.53 (d, J = 8.4 Hz, 2H, Ar-H), 7.43-7.39 (m, 1H, Ar-H), 7.34 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 135.4, 133.2, 132.7, 132.5, 132.1, 128.9, 128.5, 126.9, 120.5, 117.5, 115.3, 94.8, 86.5. IR (KBr, ν, cm^{-1}) 3162, 2228, 1493, 1400, 1085, 1013, 831, 755. HR-MS (APCI-TOF) m/z calcd for $C_{19}H_{10}ClN$ $[M+H]^+$ 288.0580, found 288.0568.

2-(hex-1-yn-1-yl)benzonitrile (1m)



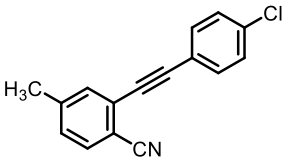
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.61-7.56 (m, 1H, Ar-H), 7.51 (d, J = 7.6 Hz, 1H, Ar-H), 7.42-7.39 (m, 1H, Ar-H), 7.30- 7.26 (m, 1H, Ar-H), 2.42-2.38 (m, 2H, CH_2), 1.59-1.52 (m, 2H, CH_2), 1.48-1.39 (m, 2H, CH_2), 0.89-0.86 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 134.3, 134.0, 133.1, 132.4, 132.3, 132.2, 127.9, 127.7, 127.6, 125.1, 117.7, 117.1, 115.7, 115.1, 97.8, 30.4, 21.9, 19.2, 13.6. IR (KBr, ν, cm^{-1}) 2959, 2230, 1593, 1482, 1430, 1047, 761. HR-MS (APCI-TOF) m/z calcd for $C_{13}H_{13}N$ $[M+H]^+$ 184.1126, found 184.1125.

4-methyl-2-(phenylethynyl)benzonitrile (1n)



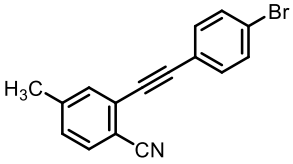
White solid, Mp: 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.63-7.58 (m, 2H, Ar-H), 7.53 (d, J = 8.0 Hz, 1H, Ar-H), 7.42 (s, 1H, Ar-H), 7.41-7.34 (m, 3H, Ar-H), 7.19 (d, J = 7.6 Hz, 1H, Ar-H), 2.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 143.4, 132.7, 132.5, 132.0, 129.3, 129.2, 128.5, 127.0, 122.2, 117.9, 112.3, 95.5, 85.8, 21.7. IR (KBr, ν, cm^{-1}) 3122, 2225, 1594, 1496, 1445, 1401, 1284, 822, 760. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{11}N$ $[M+H]^+$ 218.0970, found 218.0982.

2-((4-chlorophenyl)ethynyl)-4-methylbenzonitrile (1o)



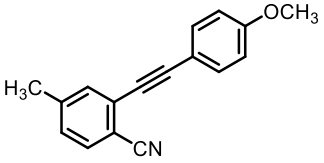
Yellow solid, Mp: 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.52-7.45 (m, 4H, Ar-H), 7.40 (d, J = 8.4 Hz, 1H, Ar-H), 7.34-7.30 (m, 1H, Ar-H), 7.22-7.16 (m, 1H, Ar-H), 2.38 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 143.5, 135.3, 134.0, 133.7, 133.2, 132.7, 132.5, 129.5, 128.8, 126.6, 120.7, 117.8, 112.3, 94.2, 86.7, 21.6. IR (KBr, ν, cm^{-1}) 3099, 2222, 1601, 1494, 1088, 1014, 845, 814. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{10}ClN$ $[M+H]^+$ 252.0580, found 252.0570.

2-((4-bromophenyl)ethynyl)-4-methylbenzonitrile (1p)



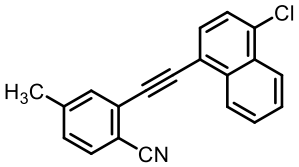
Yellow solid, Mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.59- 7.55 (m, 2H, Ar-H), 7.52-7.48 (m, 3H, Ar-H), 7.41-7.38 (m, 1H, Ar-H), 7.22 (d, J = 7.2 Hz, 1H, Ar-H), 2.42 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 143.4, 133.1, 132.7, 132.6, 132.0, 131.7, 131.6, 129.5, 123.7, 122.8, 122.1, 121.9, 112.4, 95.0, 87.6, 21.7. IR (KBr, ν, cm^{-1}) 3125, 2225, 1595, 1482, 1401, 1282, 1068, 1010, 839, 825. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{10}BrN$ $[M+H]^+$ 296.0075, found 296.0090.

2-((4-methoxyphenyl)ethynyl)-4-methylbenzonitrile (1q)



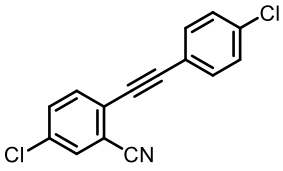
White solid, Mp: 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.55-7.51 (m, 3H, Ar-H), 7.40 (s, 1H, Ar-H), 7.16 (d, J = 7.6 Hz, 1H, Ar-H), 6.88 (d, J = 8.8 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 160.3, 143.3, 133.6, 132.5, 132.4, 128.8, 127.4, 118.0, 114.2, 114.1, 112.0, 95.8, 84.8, 55.4, 21.7. IR (KBr, ν, cm^{-1}) 2952, 2223, 2204, 1597, 1510, 1454, 1252, 1169, 1028, 836, 823. HR-MS (APCI-TOF) m/z calcd for $C_{17}H_{13}NO$ $[M+H]^+$ 248.1075, found 248.1066.

2-((4-chloronaphthalen-1-yl)ethynyl)-4-methylbenzonitrile (1r)



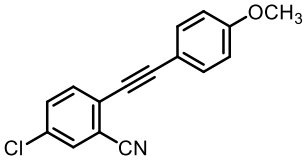
Yellow solid, Mp: 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.55-7.48 (m, 4H, Ar-H), 7.42 (s, 1H, Ar-H), 7.34-7.31 (m, 2H, Ar-H), 7.22-7.19 (m, 2H, Ar-H), 2.40 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 145.4, 143.5, 135.3, 134.0, 133.7, 133.2, 132.7, 132.5, 129.5, 128.8, 128.5, 126.6, 125.0, 120.6, 117.8, 112.7, 112.3, 94.2, 86.7, 21.6. IR (KBr, ν, cm^{-1}) 3069, 2230, 1601, 1495, 1396, 1273, 1087, 826. HR-MS (APCI-TOF) m/z calcd for $C_{20}H_{12}ClN$ $[M+H]^+$ 302.0737, found 302.0745.

5-chloro-2-((4-chlorophenyl)ethynyl)benzonitrile (1s)



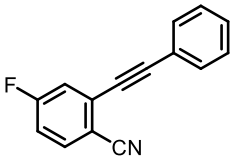
Light yellow solid, Mp: 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.65-7.63 (m, 1H, Ar-H), 7.61-7.42 (m, 4H, Ar-H), 7.37-7.26 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 135.7, 134.5, 134.3, 134.2, 133.9, 133.2, 133.0, 132.4, 128.9, 125.4, 120.2, 116.7, 116.3, 95.9, 85.6. IR (KBr, ν, cm^{-1}) 3099, 2233, 1491, 1397, 1270, 1087, 878, 827. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_7Cl_2N$ $[M+H]^+$ 272.0034, found 272.0041.

5-chloro-2-((4-methoxyphenyl)ethynyl)benzonitrile (1t) [3]



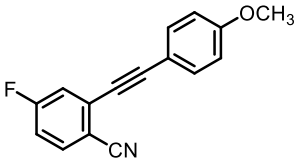
White solid, Mp: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.60 (s, 1H, Ar-H), 7.54-7.50 (m, 4H, Ar-H), 6.88 (d, J = 8.4 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 160.6, 133.7, 133.6, 132.9, 132.8, 132.2, 126.2, 116.5, 116.3, 114.2, 113.7, 97.5, 83.8, 55.4. IR (KBr, ν, cm^{-1}) 3015, 2215, 1604, 1568, 1480, 1443, 1291, 1251, 1149, 878, 838. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{10}ClNO$ $[M+H]^+$ 268.0529, found 268.0533.

4-fluoro-2-(phenylethynyl)benzonitrile (1u)



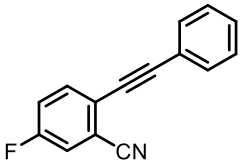
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66-7.57 (m, 3H, Ar-H), 7.44-7.34 (m, 4H, Ar-H), 7.31-7.22 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 161.3 (d, ^1J = 251.5 Hz), 134.9 (d, ^4J = 8.1 Hz), 134.2 (d, ^4J = 8.4 Hz), 131.9, 129.3, 128.5, 123.7 (d, ^3J = 3.9 Hz), 122.0, 121.8, 120.6, 120.4, 119.7 (d, ^2J = 25.1 Hz), 116.8, 95.8, 84.6. IR (KBr, ν, cm^{-1}) 3073, 2236, 2217, 1595, 1497, 1411, 1265, 1144, 941, 760. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8FN$ $[M+H]^+$ 222.0719, found 222.0716.

4-fluoro-2-((4-methoxyphenyl)ethynyl)benzonitrile (1v)



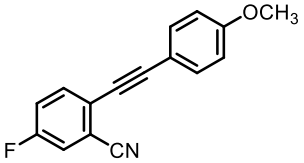
White solid, Mp: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66-7.62 (m, 1H, Ar-H), 7.55 (d, J = 8.4 Hz, 2H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.10-7.06 (m, 1H, Ar-H), 6.89 (d, J = 8.4 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 164.5 (d, ^1J = 254.8 Hz), 160.7, 134.8 (d, ^4J = 9.9 Hz), 133.8, 130.3 (d, ^4J = 11.0 Hz), 118.9 (d, ^2J = 23.9 Hz), 117.1, 115.8 (d, ^2J = 22.8 Hz), 114.2, 113.5, 111.3 (d, ^3J = 3.3 Hz), 97.8, 83.8 (d, ^3J = 3.0 Hz), 55.4. IR (KBr, ν, cm^{-1}) 3082, 2228, 2208, 1596, 1457, 1442, 1250, 1085, 958, 828. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{10}FNO$ $[M+H]^+$ 252.0825, found 252.0822.

5-fluoro-2-(phenylethynyl)benzonitrile (1w)



Yellow solid, Mp: 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68-7.65 (m, 1H, Ar-H), 7.63-7.58 (m, 2H, Ar-H), 7.43-7.36 (m, 3H, Ar-H), 7.32-7.30 (m, 1H, Ar-H), 7.14-7.09 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 164.4 (d, J = 255.1 Hz), 134.9 (d, J = 10.0 Hz), 132.1, 129.9 (d, J = 10.9 Hz), 129.7, 128.5, 121.5, 119.3 (d, J = 24.0 Hz), 116.9, 116.3 (d, J = 22.7 Hz), 111.6 (d, J = 3.4 Hz), 97.3, 84.6 (d, J = 3.1 Hz). IR (KBr, ν, cm^{-1}) 3081, 2227, 1567, 1474, 1420, 1213, 1135, 956, 825, 755. HR-MS (APCI-TOF) m/z calcd for $C_{15}H_8FN$ $[M+H]^+$ 222.0719, found 222.0740.

5-fluoro-2-((4-methoxyphenyl)ethynyl)benzonitrile (1x) [3]



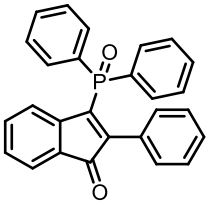
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.59-7.56 (m, 1H, Ar-H), 7.55-7.52 (m, 2H, Ar-H), 7.37-7.34 (m, 1H, Ar-H), 7.30-7.25 (m, 1H, Ar-H), 6.91-6.88 (m, 2H, Ar-H), 3.84 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 161.0 (d, J = 250.8 Hz), 160.5, 133.8 (d, J = 8.4 Hz), 133.5, 124.2 (d, J = 3.8 Hz), 120.4 (d, J = 21.8 Hz), 119.6 (d, J = 25.1 Hz), 116.6 (d, J = 3.0 Hz), 116.4 (d, J = 9.3 Hz), 114.2, 113.9, 96.1 (d, J = 1.6 Hz), 83.6, 55.4. IR (KBr, ν, cm^{-1}) 3114, 2231, 1607, 1484, 1399, 1283, 1146, 944, 826, 760. HR-MS (APCI-TOF) m/z calcd for $C_{16}H_{10}FNO$ $[M+H]^+$ 252.0825, found 252.0846.

General Procedure for the Synthesis of Products 3

Example for the synthesis of **3a**: ***3-(diphenylphosphoryl)-2-phenyl-1H-inden-1-one***

To a sealed 10-mL tube, 2-(phenylethynyl)benzonitrile (**1a**, 1.0 equiv, 0.20 mmol), diphenylphosphine oxide (**2a**, 4.0 equiv, 0.80 mmol), silver nitrate (2.0 equiv), and acetonitrile (1.5 mL) as well as water (0.5 mL) were continuously added. Then, the reaction system was heated at 80 °C (4.0 hours) until TLC revealed that conversion of the starting material **1a** was completed. Next, the reaction mixture was cooled to room temperature and 20 mL of ethyl acetate was poured into this reaction system, which were washed with water (2 x 10 mL). The resulting organic phase was concentrated under vacuum and purified by flash column chromatography (silica gel, mixtures of petroleum ether / ethyl acetat = 4:1 (V/V)) to afford the desired product **3a** as a yellow solid.

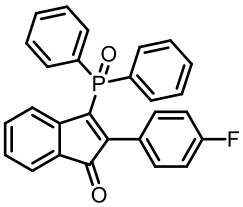
3-(diphenylphosphoryl)-2-phenyl-1H-inden-1-one (3a)



54 mg, 67%; A yellow solid, Mp: 203-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.57 (d, J = 6.8 Hz, 1H, Ar-H), 7.42-7.38 (m, 2H, Ar-H), 7.31-7.27 (m, 4H, Ar-H), 7.24-7.20 (m, 3H, Ar-H),

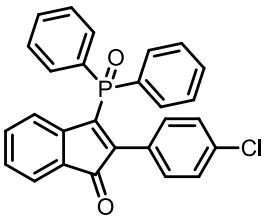
7.07-7.02 (m, 1H, Ar-H), 6.96-6.93 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.2 (d, $^3J_{C-P}$ = 15.5 Hz), 145.8, 145.7, 145.1, 145.0, 144.1 (d, $^1J_{C-P}$ = 97.2 Hz), 134.8, 132.2, 132.1 (d, $^2J_{C-P}$ = 9.7 Hz), 131.3 (d, $^2J_{C-P}$ = 10.1 Hz), 131.0, 129.7 (d, $^4J_{C-P}$ = 1.1 Hz), 129.3, 129.1 (d, $^4J_{C-P}$ = 2.8 Hz), 128.8(1), 128.8(0), 128.6 (d, $^3J_{C-P}$ = 12.5 Hz), 128.5, 127.5, 124.8, 123.9. IR (KBr, ν, cm^{-1}) 3132, 1723, 1594, 1438, 1191. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{19}O_2P$ $[M+H]^+$ 406.1123, found 407.1237.

3-(diphenylphosphoryl)-2-(4-fluorophenyl)-1H-inden-1-one (3b)



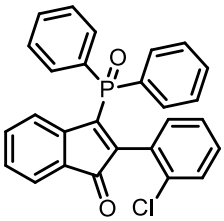
61 mg, 72%; A yellow solid, Mp: 189-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.57 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 7.34-7.29 (m, 4H, Ar-H), 7.25-7.20 (m, 2H, Ar-H), 7.12-7.10 (m, 1H, Ar-H), 7.01- 6.97 (m, 2H, Ar-H), 6.68-6.64 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.0 (d, $^3J_{C-P}$ = 15.0 Hz), 162.8 (d, $^1J_{C-F}$ = 248.0 Hz), 161.6, 144.9, 144.8, 134.8, 132.2 (d, $^4J_{C-P}$ = 2.7 Hz), 131.5 (d, $^1J_{C-P}$ = 105.7 Hz), 131.7 (d, $^4J_{C-F}$ = 8.5 Hz), 131.3 (d, $^2J_{C-P}$ = 10.2 Hz), 131.0, 128.9, 128.7 (d, $^3J_{C-P}$ = 12.5 Hz), 125.2 (d, $^3J_{C-F}$ = 3.0 Hz), 124.8, 124.0, 114.6 (d, $^2J_{C-F}$ = 21.7 Hz). IR (KBr, *v*, cm^{-1}) 3072, 1726, 1559, 1458, 1229, 1162. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{18}FO_2P$ $[M+H]^+$ 424.1028, found 425.1100.

2-(4-chlorophenyl)-3-(diphenylphosphoryl)-1H-inden-1-one (3c)



67 mg, 76%; An orange-red solid, Mp: 211-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67-7.62 (m, 4H, Ar-H), 7.58 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.34-7.30 (m, 4H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 7.15 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.94-6.89 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.8 (d, $^3J_{C-P}$ = 15.3 Hz), 144.8, 144.7, 144.6, 143.4, 134.9, 134.8, 132.2 (d, $^4J_{C-P}$ = 2.7 Hz), 131.9, 131.3 (d, $^2J_{C-P}$ = 10.2 Hz), 131.0, 129.0, 128.7 (d, $^3J_{C-P}$ = 12.5 Hz), 127.7, 124.9, 124.1. IR (KBr, *v*, cm^{-1}): 3051, 1713, 1591, 1437, 1198. HRMS (APCI-TOF) m/z calcd for $C_{27}H_{18}ClO_2P$ $[M+H]^+$ 440.0733, found 441.0801.

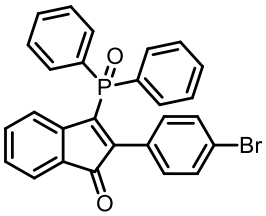
2-(2-chlorophenyl)-3-(diphenylphosphoryl)-1H-inden-1-one (3d)



64 mg, 73%; A yellow solid, Mp: 204-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.83-7.78 (m, 2H, Ar-H), 7.65-7.55 (m, 3H, Ar-H), 7.50-7.28 (m, 7H, Ar-H), 7.24-7.17 (m, 2H, Ar-H), 7.09 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.01-6.97 (m, 1H, Ar-H), 6.82-6.78 (m, 1H, Ar-H), 6.72 (d, *J* = 7.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.6 (d, $^3J_{C-P}$ = 14.8 Hz), 144.7, 144.6, 132.6 (d, $^1J_{C-P}$ = 105.1 Hz), 132.4 (d, $^4J_{C-P}$ = 2.6 Hz), 132.2 (d, $^4J_{C-P}$ = 2.6 Hz), 131.5 (d, $^2J_{C-P}$ = 10.5 Hz), 131.3 (d, $^2J_{C-P}$ = 10.3 Hz), 131.2, 129.7, 129.4 (d, $^4J_{C-P}$ = 2.6 Hz),

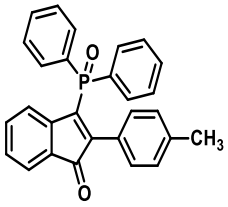
129.1, 128.8 (d, $^{3}J_{C\text{-}P}$ = 13.5 Hz), 128.6, 128.4 (d, $^{3}J_{C\text{-}P}$ = 12.6 Hz), 126.1, 124.6 (d, $^{1}J_{C\text{-}P}$ = 105.9 Hz). IR (KBr, *v*, cm^{-1}) 3123, 1717, 1559, 1457, 1196, 924. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{18}ClO_2P$ $[M+H]^+$ 440.0733, found 441.0813.

2-(4-bromophenyl)-3-(diphenylphosphoryl)-1H-inden-1-one (3e)



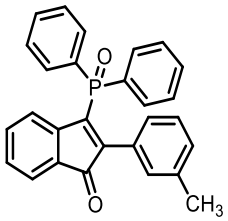
69 mg, 71%; An orange solid, Mp: 208-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.67-7.62 (m, 4H, Ar-H), 7.57 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.34-7.30 (m, 4H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 7.17 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.08 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 195.7 (d, $^{1}J_{C\text{-}P}$ = 15.2 Hz), 144.8, 144.7, 144.6(0), 144.6(1), 134.9, 132.2, 131.7 (d, $^{1}J_{C\text{-}P}$ = 109.7 Hz), 131.4 (d, $^{2}J_{C\text{-}P}$ = 10.1 Hz), 130.6, 129.0, 128.7 (d, $^{3}J_{C\text{-}P}$ = 12.5 Hz), 128.1 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz), 124.9, 124.1, 123.2. IR (KBr, *v*, cm^{-1}) 3049, 1713, 1559, 1457, 1198. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{18}BrO_2P$ $[M+H]^+$ 484.0228, found 485.0328.

3-(diphenylphosphoryl)-2-(p-tolyl)-1H-inden-1-one (3f)



55 mg, 66%; A yellow solid, Mp: 218-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.67-7.62 (m, 4H, Ar-H), 7.56 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.43-7.39 (m, 2H, Ar-H), 7.30-7.28 (m, 4H, Ar-H), 7.24-7.16 (m, 3H, Ar-H), 6.85 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.74 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.18 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.4 (d, $^{3}J_{C\text{-}P}$ = 15.7 Hz), 146.0(2), 146.0(0), 145.2, 145.1, 138.6, 134.7, 131.9, 131.8 (d, $^{1}J_{C\text{-}P}$ = 87.2 Hz), 131.4, 129.6, 129.4, 128.9 (d, $^{4}J_{C\text{-}P}$ = 3.7 Hz), 128.6 (d, $^{3}J_{C\text{-}P}$ = 12.2 Hz), 128.2, 128.1, 126.2 (d, $^{4}J_{C\text{-}P}$ = 2.3 Hz), 124.7, 123.9, 21.3. IR (KBr, *v*, cm^{-1}) 3050, 1734, 1596, 1458, 1396, 1183. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{21}O_2P$ $[M+H]^+$ 420.1279, found 421.1361.

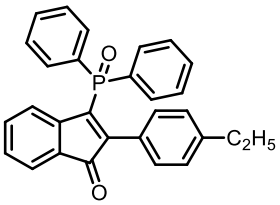
3-(diphenylphosphoryl)-2-(m-tolyl)-1H-inden-1-one (3g)



55 mg, 65%; A yellow solid, Mp: 201-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.56 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.41-7.37 (m, 2H, Ar-H), 7.31-7.27 (m, 4H, Ar-H), 7.24-7.19 (m, 3H, Ar-H), 6.93- 6.81 (m, 3H, Ar-H), 6.67 (s, 1H, Ar-H), 2.06 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.3 (d, $^{3}J_{C\text{-}P}$ = 15.6 Hz), 146.0, 145.9, 136.9, 134.8, 132.1, 131.6 (d, $^{1}J_{C\text{-}P}$ = 106.4 Hz), 131.2 (d, $^{2}J_{C\text{-}P}$ = 10.1 Hz), 130.5(2), 130.5(1), 129.4, 129.0 (d, $^{4}J_{C\text{-}P}$ = 2.9 Hz), 128.8 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz), 128.7, 128.5 (d, $^{3}J_{C\text{-}P}$ = 12.5 Hz) ,

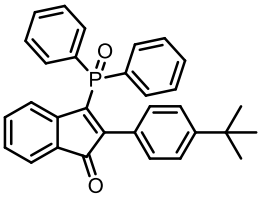
127.5, 126.6, 124.8, 123.9, 21.1. IR (KBr, *v*, cm^{-1}) 3048, 1720, 1558, 1439, 1193. HRMS (APCI-TOF) m/z calcd for $C_{28}H_{21}O_2P$ $[M+H]^+$ 420.1279, found 421.1354.

3-(diphenylphosphoryl)-2-(4-ethylphenyl)-1H-inden-1-one (3h)



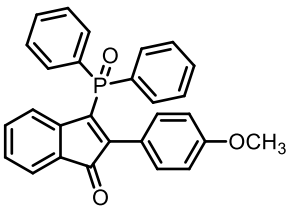
54 mg, 62%; A yellow solid, Mp: 195-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.67-7.62 (m, 4H, Ar-H), 7.57 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.41-7.37 (m, 2H, Ar-H), 7.30-7.27 (m, 3H, Ar-H), 7.22-7.18 (m, 4H, Ar-H), 6.88 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.77 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.50-2.44 (m, 2H, CH_2), 1.15-1.11 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.6 (d, $^3J_{C-P}$ = 14.4 Hz), 146.0, 145.2, 145.1, 144.8, 134.8, 132.0(2), 132.0(0), 131.8, 131.7 (d, $^1J_{C-P}$ = 80.9 Hz), 129.7, 129.2, 128.8 (d, $^4J_{C-P}$ = 3.8 Hz), 128.5 (d, $^3J_{C-P}$ = 12.5 Hz), 127.0, 126.4, 126.3, 124.7, 123.9, 28.7, 15.4. IR (KBr, *v*, cm^{-1}) 3132, 1717, 1595, 1436, 1183. HRMS (APCI-TOF) m/z calcd for $C_{29}H_{23}O_2P$ $[M+H]^+$ 434.1436, found 435.1510.

2-(4-(tert-butyl)phenyl)-3-(diphenylphosphoryl)-1H-inden-1-one (3i)



50 mg, 54%; An orange-red solid, Mp: 204-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.67-7.62 (m, 4H, Ar-H), 7.57 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.39-7.36 (m, 2H, Ar-H), 7.29-7.27 (m, 3H, Ar-H), 7.25 – 7.18 (m, 4H, Ar-H), 6.96-6.88 (m, 4H, Ar-H), 1.20 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.5 (d, $^3J_{C-P}$ = 16.9 Hz), 151.4, 145.8, 145.7, 145.2, 145.1, 134.8, 132.0 (d, $^4J_{C-P}$ = 2.2 Hz), 131.6 (d, $^1J_{C-P}$ = 105.8 Hz), 131.4 (d, $^2J_{C-P}$ = 10.1 Hz), 129.4, 128.8 (d, $^4J_{C-P}$ = 3.8 Hz), 128.6, 128.5 (d, $^3J_{C-P}$ = 12.5 Hz), 126.1 (d, $^4J_{C-P}$ = 2.6 Hz), 124.7, 124.4, 123.9, 34.5, 31.1. IR (KBr, *v*, cm^{-1}) 2960, 1717, 1559, 1457, 1362, 1190. HR-MS (APCI-TOF) m/z calcd for $C_{31}H_{27}O_2P$ $[M+H]^+$ 462.1749, found 463.1826.

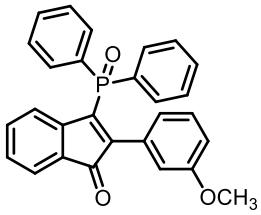
3-(diphenylphosphoryl)-2-(4-methoxyphenyl)-1H-inden-1-one (3j)



50 mg, 56%; An orange-red solid, Mp: 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.70-7.65 (m, 4H, Ar-H), 7.56 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.43-7.39 (m, 2H, Ar-H), 7.32-7.28 (m, 4H, Ar-H), 7.22-7.17 (m, 2H, Ar-H), 7.06 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.98 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.49 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.70 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.5 (d, $^3J_{C-P}$ = 15.6 Hz), 160.0, 145.6, 145.5, 145.3, 145.2, 144.6, 143.0, 134.7, 132.0, 131.8 (d, $^1J_{C-P}$ = 109.3 Hz), 131.4, 128.9, 128.8(2), 128.8(0), 128.7, 128.6 (d, $^3J_{C-P}$ =

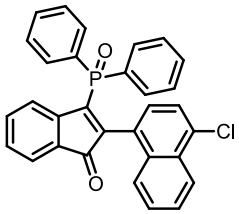
12.4 Hz), 128.5, 124.5, 123.9, 121.5 (d, $^4J_{C-P}$ = 3.0 Hz), 113.1, 55.2. IR (KBr, *v*, cm^{-1}) 3057, 1716, 1606, 1457, 1396, 1196. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{21}O_3P$ $[M+H]^+$ 436.1228, found 437.1353.

3-(diphenylphosphoryl)-2-(3-methoxyphenyl)-1H-inden-1-one (3k)



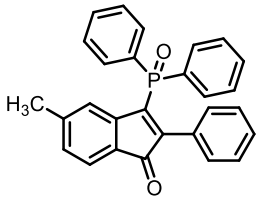
52 mg, 60%; A yellow solid, Mp: 159-160 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69-7.64 (m, 4H, Ar-H), 7.57 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.43-7.39 (m, 2H, Ar-H), 7.32-7.28 (m, 4H, Ar-H), 7.24-7.21 (m, 3H, Ar-H), 6.94-6.90 (m, 1H, Ar-H), 6.61-6.57 (m, 2H, Ar-H), 6.46 (s, 1H, Ar-H), 3.63 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.0 (d, $^3J_{C-P}$ = 16.2 Hz), 158.4, 145.8, 145.7, 134.8, 131.6 (d, $^1J_{C-P}$ = 101.5 Hz), 131.3 (d, $^2J_{C-P}$ = 10.2 Hz), 128.8, 128.7 (d, $^2J_{C-P}$ = 10.4 Hz), 128.6 (d, $^3J_{C-P}$ = 12.5 Hz), 124.9, 123.9, 122.1, 114.9, 114.8, 55.0. IR (KBr, *v*, cm^{-1}) 3028, 1716, 1559, 1458, 1228, 1182. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{21}O_3P$ $[M+H]^+$ 436.1228, found 437.1310.

2-(4-chloronaphthalen-1-yl)-3-(diphenylphosphoryl)-1H-inden-1-one (3l)



60 mg, 61%; A yellow-orange solid, Mp: 211-212 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67-7.62 (m, 5H, Ar-H), 7.57 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.34-7.30 (m, 5H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 7.15 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.94-6.89 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.8 (d, $^1J_{C-P}$ = 15.3 Hz), 145.5, 144.8(5), 144.8(0), 144.6(3), 144.6(0), 144.5, 134.9, 134.8 (d, $^4J_{C-P}$ = 3.5 Hz),132.2 (d, $^4J_{C-P}$ = 2.8 Hz), 131.4 (d, $^1J_{C-P}$ = 106.0 Hz), 131.0 (d, $^4J_{C-P}$ = 1.2 Hz), 129.0, 128.7 (d, $^3J_{C-P}$ = 12.5 Hz), 127.7 (d, $^4J_{C-P}$ = 4.6 Hz), 124.9, 124.0. IR (KBr, *v*, cm^{-1}) 3038, 1713, 1591, 1486, 1197. HR-MS (APCI-TOF) m/z calcd for $C_{31}H_{20}ClO_2P$ $[M+H]^+$ 490.0889, found 491.0971.

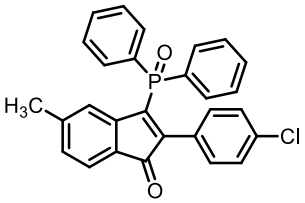
3-(diphenylphosphoryl)-5-methyl-2-phenyl-1H-inden-1-one (3n)



46 mg, 55%; A yellow solid, Mp: 195-196 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67-7.61 (m, 4H, Ar-H), 7.46 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.42-7.38 (m, 2H, Ar-H), 7.30-7.28 (m, 4H, Ar-H), 7.08 (s, 1H, Ar-H), 7.08-7.00 (m, 2H, Ar-H), 6.96-6.93 (m, 4H, Ar-H), 2.21 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.7 (d, $^3J_{C-P}$ = 15.4 Hz), 146.3 (d, $^4J_{C-P}$ = 5.5 Hz), 146.1, 145.5 (d, $^2J_{C-P}$ = 7.9 Hz), 133.0 (d, $^4J_{C-P}$ = 2.8 Hz), 132.4, 132.1 (d, $^4J_{C-P}$ = 2.1 Hz), 131.9, 131.8 (d, $^2J_{C-P}$ = 10.4 Hz), 131.7 (d, $^1J_{C-P}$ = 106.3 Hz), 131.4 (d, $^2J_{C-P}$ = 10.0 Hz), 129.1 (d, $^1J_{C-P}$ = 101.8 Hz), 129.4 (d, $^4J_{C-P}$ = 2.6 Hz), 129.2 (d, $^3J_{C-P}$ = 12.8 Hz), 128.9, 128.4 (d, $^3J_{C-P}$ = 14.9 Hz),

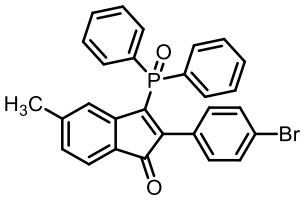
128.3, 127.4, 126.5 (d, $^4J_{C-P}$ = 3.5 Hz), 126.1, 124.0, 125.7, 118.3, 22.2. IR (KBr, *v*, cm^{-1}) 3123, 1716, 1734, 1521, 1399, 1187. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{21}O_2P$ $[M+H]^+$ 420.1279, found 421.1355.

2-(4-chlorophenyl)-3-(diphenylphosphoryl)-5-methyl-1H-inden-1-one (3o)



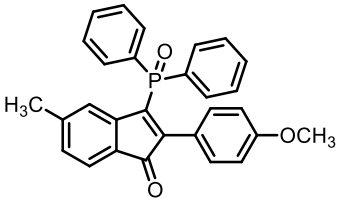
56 mg, 62%; A yellow-orange solid, Mp: 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.66-7.61 (m, 4H, Ar-H), 7.47-7.44 (m, 3H, Ar-H), 7.34-7.30 (m, 4H, Ar-H), 7.02 (d, *J* = 6.0 Hz, 2H, Ar-H), 6.92-6.86 (m, 4H, Ar-H), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 195.3 (d, $^3J_{C-P}$ = 14.3 Hz), 162.7, 146.3, 146.2, 145.3, 145.2, 134.7, 132.2 (d, $^1J_{C-P}$ = 96.3 Hz), 132.6, 132.2, 131.9, 131.0 (d, $^4J_{C-P}$ = 4.6 Hz), 130.3, 131.4 (d, $^2J_{C-P}$ = 9.9 Hz), 129.1, 129.0 (d, $^3J_{C-P}$ = 12.3 Hz), 128.7 (d, $^3J_{C-P}$ = 12.3 Hz), 128.3 (d, $^1J_{C-P}$ = 108.2 Hz), 127.9 (d, $^4J_{C-P}$ = 2.1 Hz), 127.6, 126.4 (d, $^4J_{C-P}$ = 2.9 Hz), 126.1, 125.3, 124.6, 124.1, 123.0, 113.5, 22.2. IR (KBr, *v*, cm^{-1}) 3123, 1717, 1559, 1437, 1399, 1190. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{20}ClO_2P$ $[M+H]^+$ 454.0889, found 455.0942.

2-(4-bromophenyl)-3-(diphenylphosphoryl)-5-methyl-1H-inden-1-one (3p)



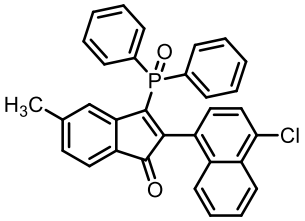
63 mg, 63%; A orange-red solid, Mp: 216-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.71-7.66 (m, 3H, Ar-H), 7.51 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.47 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.40 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.37-7.33 (m, 3H, Ar-H), 7.09-7.01 (m, 4H, Ar-H), 6.95 (d, *J* = 8.0 Hz, 1H, Ar-H), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.2 (d, $^3J_{C-P}$ = 15.2 Hz), 146.3, 132.5 (d, $^1J_{C-P}$ = 108.2 Hz), 132.2 (d, $^4J_{C-P}$ = 2.7 Hz), 132.0, 131.1 (d, $^1J_{C-P}$ = 106.0 Hz), 131.4 (d, $^2J_{C-P}$ = 10.1 Hz), 130.5, 129.8, 129.1, 128.7 (d, $^3J_{C-P}$ = 12.4 Hz), 126.2, 124.1, 122.1, 90.2, 89.4, 22.4. IR (KBr, *v*, cm^{-1}) 2920, 1718, 1594, 1438, 1191. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{20}BrO_2P$ $[M+H]^+$ 498.0384, found 499.0461.

3-(diphenylphosphoryl)-2-(4-methoxyphenyl)-5-methyl-1H-inden-1-one (3q)



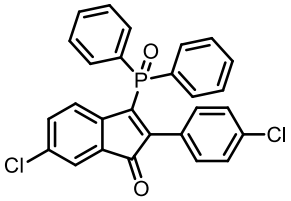
45 mg, 50%; An orange-red solid, Mp: 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.45-7.39 (m, 3H, Ar-H), 7.32-7.28 (m, 4H, Ar-H), 6.98-6.91 (m, 4H, Ar-H), 6.47 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.69 (s, 1H, OCH_3), 2.17 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 196.0 (d, $^3J_{C-P}$ = 15.6 Hz), 159.9, 146.2 (d, $^4J_{C-P}$ = 5.5 Hz), 146.0, 145.7 (d, $^2J_{C-P}$ = 8.2 Hz), 142.1 (d, $^1J_{C-P}$ = 98.6 Hz), 132.0 (d, $^1J_{C-P}$ = 108.0 Hz), 131.9 (d, $^4J_{C-P}$ = 2.8 Hz), 131.3, 128.5 (d, $^4J_{C-P}$ = 2.4 Hz), 126.5 (d, $^4J_{C-P}$ = 4.0 Hz), 125.8, 123.9, 121.7 (d, $^4J_{C-P}$ = 3.2 Hz), 113.1, 55.2, 26.9, 22.1. IR (KBr, *v*, cm^{-1}) 3123, 1717, 1601, 1506, 1399, 1254, 1183. HR-MS (APCI-TOF) m/z calcd for $C_{29}H_{23}O_3P$ $[M+H]^+$ 450.1385, found 451.1448.

2-(4-chloronaphthalen-1-yl)-3-(diphenylphosphoryl)-5-methyl-1H-inden-1-one (3r)



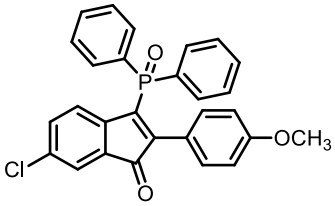
56 mg, 56%; A yellow solid, Mp: 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66-7.61 (m, 5H, Ar-H), 7.48-7.44 (m, 3H, Ar-H), 7.34-7.30 (m, 4H, Ar-H), 7.02 (d, J = 6.0 Hz, 2H, Ar-H), 6.92-6.86 (m, 5H, Ar-H), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.7 (d, $^3J_{C\text{-}P}$ = 16.0 Hz), 146.3, 134.7, 132.2 (d, $^2J_{C\text{-}P}$ = 10.7 Hz), 132.0 (d, $^1J_{C\text{-}P}$ = 108.2 Hz), 131.6, 131.4, 130.9, 128.7 (d, $^3J_{C\text{-}P}$ = 11.6 Hz), 128.6 (d, $^1J_{C\text{-}P}$ = 108.7 Hz), 127.9, 127.6, 126.4, 126.1, 125.3, 124.6, 124.1, 123.0, 113.6, 22.2. IR (KBr, ν, cm^{-1}) 3038, 1715, 1549, 1460, 1283, 1194. HR-MS (APCI-TOF) m/z calcd for $C_{32}H_{22}ClO_2P$ $[M+H]^+$ 504.1046, found 505.1104.

6-chloro-2-(4-chlorophenyl)-3-(diphenylphosphoryl)-1H-inden-1-one (3s)



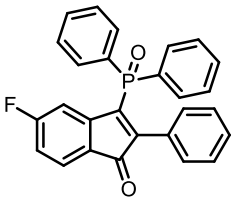
69 mg, 73%; A yellow-orange solid, Mp: 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66-7.61 (m, 4H, Ar-H), 7.53 (s, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.35-7.30 (m, 4H, Ar-H), 7.22 (d, J = 8.0 Hz, 1H, Ar-H), 7.11 (d, J = 8.0 Hz, 1H, Ar-H), 6.94-6.87 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.7 (d, $^3J_{C\text{-}P}$ = 15.1 Hz), 144.6, 144.5, 142.9, 142.8, 135.3, 134.6 (d, $^1J_{C\text{-}P}$ = 102.4 Hz), 134.3, 133.1, 132.0 (d, $^1J_{C\text{-}P}$ = 93.3 Hz), 131.4 (d, $^2J_{C\text{-}P}$ = 10.1 Hz), 131.3, 131.1, 130.3, 129.0, 128.8 (d, $^3J_{C\text{-}P}$ = 12.5 Hz), 127.7, 127.2, 125.7, 124.5, 26.9. IR (KBr, ν, cm^{-1}) 3008, 1720, 1594, 1486, 1185. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{17}Cl_2O_2P$ $[M+H]^+$ 474.0343, found 475.0409.

6-chloro-3-(diphenylphosphoryl)-2-(4-methoxyphenyl)-1H-inden-1-one (3t)



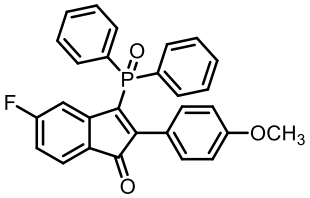
60 mg, 64%; An orange-red solid, Mp: 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.52 (s, 1H, Ar-H), 7.44-7.41 (m, 2H, Ar-H), 7.33-7.29 (m, 4H, Ar-H), 7.18 (d, J = 8.0 Hz, 1H, Ar-H), 7.02-6.96 (m, 3H, Ar-H), 6.49 (d, J = 8.0 Hz, 2H, Ar-H), 3.70 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.4 (d, $^3J_{C\text{-}P}$ = 15.8 Hz), 160.2, 134.7, 133.9, 132.1, 131.7 (d, $^1J_{C\text{-}P}$ = 92.5 Hz), 131.4 (d, $^4J_{C\text{-}P}$ = 4.3 Hz), 130.4 (d, $^4J_{C\text{-}P}$ = 3.6 Hz), 128.7 (d, $^3J_{C\text{-}P}$ = 12.4 Hz), 126.5, 124.8 (d, $^1J_{C\text{-}P}$ = 107.7 Hz), 124.3, 121.1 (d, $^4J_{C\text{-}P}$ = 2.9 Hz), 113.2, 55.5. IR (KBr, ν, cm^{-1}) 3010, 1719, 1608, 1505, 1457, 1301, 1182. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{20}ClO_3P$ $[M+H]^+$ 470.0839, found 471.0909.

3-(diphenylphosphoryl)-5-fluoro-2-phenyl-1H-inden-1-one (3u)



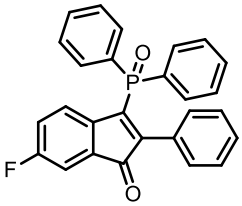
60 mg, 71%; A yellow solid, Mp: 194-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.70-7.65 (m, 4H, Ar-H), 7.61-7.58 (m, 1H, Ar-H), 7.47-7.43 (m, 2H, Ar-H), 7.35-7.31 (m, 4H, Ar-H), 7.12-7.07 (m, 1H, Ar-H), 7.03-6.98 (m, 5H, Ar-H), 6.92-6.88 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.2 (d, $^3J_{C-P}$ = 15.2 Hz), 166.9 (d, $^1J_{C-F}$ = 254.7 Hz), 132.4, 131.9 (d, $^1J_{C-P}$ = 108.1 Hz), 131.4, 129.6 (d, $^4J_{C-P}$ = 1.2 Hz), 129.0 (d, $^3J_{C-P}$ = 12.6 Hz), 128.7 (d, $^3J_{C-P}$ = 12.6 Hz), 127.5, 125.7 (d, $^2J_{C-P}$ = 10.1 Hz), 124.7 (d, $^3J_{C-F}$ = 3.2 Hz), 124.6, 122.4, 114.8 (d, $^2J_{C-F}$ = 23.2 Hz), 113.7 (d, $^2J_{C-F}$ = 25.8 Hz). IR (KBr, ν, cm^{-1}) 3050, 1723, 1592, 1463, 1193. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{18}FO_2P$ $[M+H]^+$ 424.1082, found 425.1096.

3-(diphenylphosphoryl)-5-fluoro-2-(4-methoxyphenyl)-1H-inden-1-one (3v)



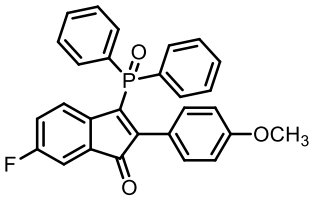
62 mg, 68%; An orange-red solid, Mp: 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69-7.64 (m, 4H, Ar-H), 7.57-7.53 (m, 1H, Ar-H), 7.45-7.41 (m, 2H, Ar-H), 7.34-7.30 (m, 4H, Ar-H), 6.99 (d, J = 8.4 Hz, 2H, Ar-H), 6.85-6.80 (m, 2H, Ar-H), 6.50 (d, J = 8.4 Hz, 2H, Ar-H), 3.70 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.6 (d, $^3J_{C-P}$ = 15.2 Hz), 166.8 (d, $^1J_{C-F}$ = 254.5 Hz), 160.3, 148.4 (d, $^4J_{C-F}$ = 8.8 Hz), 148.3, 132.2, 131.8 (d, $^1J_{C-P}$ = 93.7 Hz), 131.4 (d, $^4J_{C-P}$ = 4.8 Hz), 128.7 (d, $^3J_{C-P}$ = 12.5 Hz), 125.6 (d, $^2J_{C-P}$ = 10.2 Hz), 124.8, 124.7, 121.2 (d, $^3J_{C-F}$ = 2.9 Hz), 114.4 (d, $^2J_{C-F}$ = 23.2 Hz), 113.4, 55.2. IR (KBr, ν, cm^{-1}) 3055, 1727, 1592, 1468, 1255, 1182. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{20}FO_3P$ $[M+H]^+$ 454.1134, found 455.1210.

3-(diphenylphosphoryl)-6-fluoro-2-phenyl-1H-inden-1-one (3w)



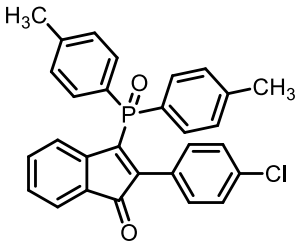
61 mg, 72%; A yellow solid, Mp: 205-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.85 (d, J = 8.8 Hz, 1H, Ar-H), 7.69-7.64 (m, 4H, Ar-H), 7.50-7.42 (m, 2H, Ar-H), 7.38-7.30 (m, 4H, Ar-H), 7.27-7.23 (m, 1H, Ar-H), 7.20-7.12 (m, 1H, Ar-H), 7.11-7.02 (m, 1H, Ar-H), 7.00-6.88 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.9 (d, $^3J_{C-P}$ = 14.0 Hz), 163.2 (d, $^1J_{C-F}$ = 250.0 Hz), 145.8, 131.8 (d, $^1J_{C-P}$ = 92.6 Hz), 131.7 (d, $^1J_{C-P}$ = 100.3 Hz), 129.6, 128.9 (d, $^3J_{C-F}$ = 2.6 Hz), 128.7 (d, $^3J_{C-P}$ = 12.6 Hz), 127.5, 126.1 (d, $^4J_{C-F}$ = 7.7 Hz), 120.2 (d, $^2J_{C-F}$ = 22.4 Hz), 112.2 (d, $^2J_{C-F}$ =24.6 Hz). IR (KBr, ν, cm^{-1}) 3042, 1726, 1559, 1474, 1282, 1189. HR-MS (APCI-TOF) m/z calcd for $C_{27}H_{18}FO_2P$ $[M+H]^+$ 424.1028, found 425.1100.

3-(diphenylphosphoryl)-6-fluoro-2-(4-methoxyphenyl)-1H-inden-1-one (3x)



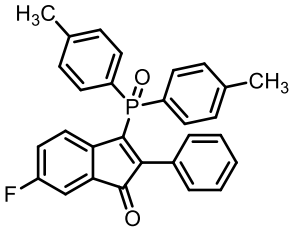
60 mg, 66%; An orange-red solid, Mp: 156-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.68-7.63 (m, 4H, Ar-H), 7.44-7.40 (m, 2H, Ar-H), 7.33-7.28 (m, 4H, Ar-H), 7.25 (s, 1H, Ar-H), 7.08-7.05 (m, 1H, Ar-H), 6.95 (d, J = 8.8 Hz, 2H, Ar-H), 6.90-6.86 (m, 1H, Ar-H), 6.48 (d, J = 8.8 Hz, 2H, Ar-H), 3.70 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.3 (d, $^3J_{C\text{-}P}$ = 16.9 Hz), 163.0 (d, $^1J_{C\text{-}F}$ = 249.5 Hz), 160.1, 145.7, 140.7 (d, $^2J_{C\text{-}P}$ = 9.5 Hz), 131.8 (d, $^1J_{C\text{-}P}$ = 77.9 Hz), 131.7 (d, $^1J_{C\text{-}P}$ = 85.3 Hz), 128.7 (d, $^3J_{C\text{-}P}$ = 12.5 Hz), 125.7 (d, $^4J_{C\text{-}F}$ = 7.6 Hz), 121.2 (d, $^3J_{C\text{-}F}$ = 2.9 Hz), 120.1 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 113.1, 112.1 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 55.2. IR (KBr, ν, cm^{-1}) 3012, 1717, 1504, 1474, 1252, 1194. HR-MS (APCI-TOF) m/z calcd for $C_{28}H_{20}FO_3P$ $[M+H]^+$ 454.1134, found 455.1213.

2-(4-chlorophenyl)-3-(di-p-tolylphosphoryl)-1H-inden-1-one (3y)



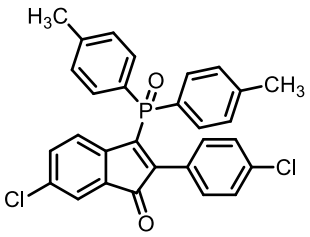
61 mg, 65%; A yellow-orange solid, Mp: 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.56 (d, J = 6.8 Hz, 1H, Ar-H), 7.53-7.47 (m, 4H, Ar-H), 7.24-7.20 (m, 3H, Ar-H), 7.11 (d, J = 6.4 Hz, 4H, Ar-H), 6.92 (d, J = 8.4 Hz, 2H, Ar-H), 6.83 (d, J = 8.4 Hz, 2H, Ar-H), 2.36 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.2 (d, $^3J_{C\text{-}P}$ = 14.6 Hz), 143.1, 134.9, 134.6, 131.4 (d, $^2J_{C\text{-}P}$ = 10.3 Hz), 130.9, 129.4 (d, $^3J_{C\text{-}P}$ = 13.1 Hz), 128.3 (d, $^1J_{C\text{-}P}$ = 107.8 Hz), 127.5, 125.0, 123.9, 21.6. IR (KBr, ν, cm^{-1}) 3034, 1717, 1559, 1457, 1184, 1114. HR-MS (APCI-TOF) m/z calcd for $C_{29}H_{22}ClO_2P$ $[M+H]^+$ 468.1046, found 469.1132.

3-(di-p-tolylphosphoryl)-6-fluoro-2-phenyl-1H-inden-1-one (3z)



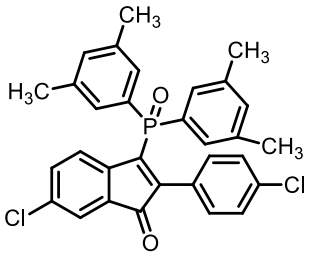
65 mg, 72%; A yellow solid, Mp: 193-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.52-7.47 (m, 4H, Ar-H), 7.32-7.29 (m, 1H, Ar-H), 7.25-7.23 (m, 1H, Ar-H), 7.08-7.06 (m, 5H, Ar-H), 6.95- 6.92 (m, 3H, Ar-H), 6.87 (d, J = 7.6 Hz, 2H, Ar-H), 2.32 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 195.3 (d, $^3J_{C\text{-}P}$ = 15.6 Hz), 163.2 (d, $^1J_{C\text{-}F}$ = 249.8 Hz), 147.2, 142.9, 131.4 (d, $^2J_{C\text{-}P}$ = 10.7 Hz), 130.6, 129.6 (d, $^3J_{C\text{-}P}$ = 12.9 Hz), 129.4 (d, $^3J_{C\text{-}P}$ = 12.9 Hz), 128.5 (d, $^1J_{C\text{-}P}$ = 109.3 Hz), 127.4, 126.2 (d, $^4J_{C\text{-}F}$ = 6.9 Hz), 122.3, 120.2 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 112.0 (d, $^2J_{C\text{-}F}$ = 24.5 Hz), 100.0 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 21.6. IR (KBr, ν, cm^{-1}) 3048, 1724, 1558, 1472, 1275, 1190. HR-MS (APCI-TOF) m/z calcd for $C_{29}H_{22}FO_2P$ $[M+H]^+$ 452.1341, found 453.1430.

6-chloro-2-(4-chlorophenyl)-3-(di-p-tolylphosphoryl)-1H-inden-1-one (3aa)



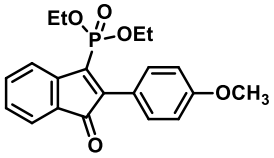
67 mg, 67%; An orange-red solid, Mp: 236-237 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.52-7.45 (m, 5H, Ar-H), 7.23-7.20 (m, 2H, Ar-H), 7.12 (d, J = 6.8 Hz, 4H, Ar-H), 6.93 (d, J = 8.0 Hz, 2H, Ar-H), 6.82 (d, J = 8.4 Hz, 2H, Ar-H), 2.36 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.9 (d, $^3J_{C\text{-}P}$ = 14.6 Hz), 143.3, 134.8, 134.6 (d, $^1J_{C\text{-}P}$ = 109.5 Hz), 131.3 (d, $^2J_{C\text{-}P}$ = 10.2 Hz), 130.8, 130.3, 129.5 (d, $^3J_{C\text{-}P}$ = 12.7 Hz), 127.6, 127.4, 127.1, 125.9, 124.3, 21.6. IR (KBr, ν, cm^{-1}) 3058, 1713, 1541, 1457, 1180, 1116. HR-MS (APCI-TOF) m/z calcd for $C_{29}H_{21}Cl_2O_2P$ $[M+H]^+$ 502.0656, found 503.0708.

3-(bis(3,5-dimethylphenyl)phosphoryl)-6-chloro-2-(4-chlorophenyl)-1H-inden-1-one (3bb)

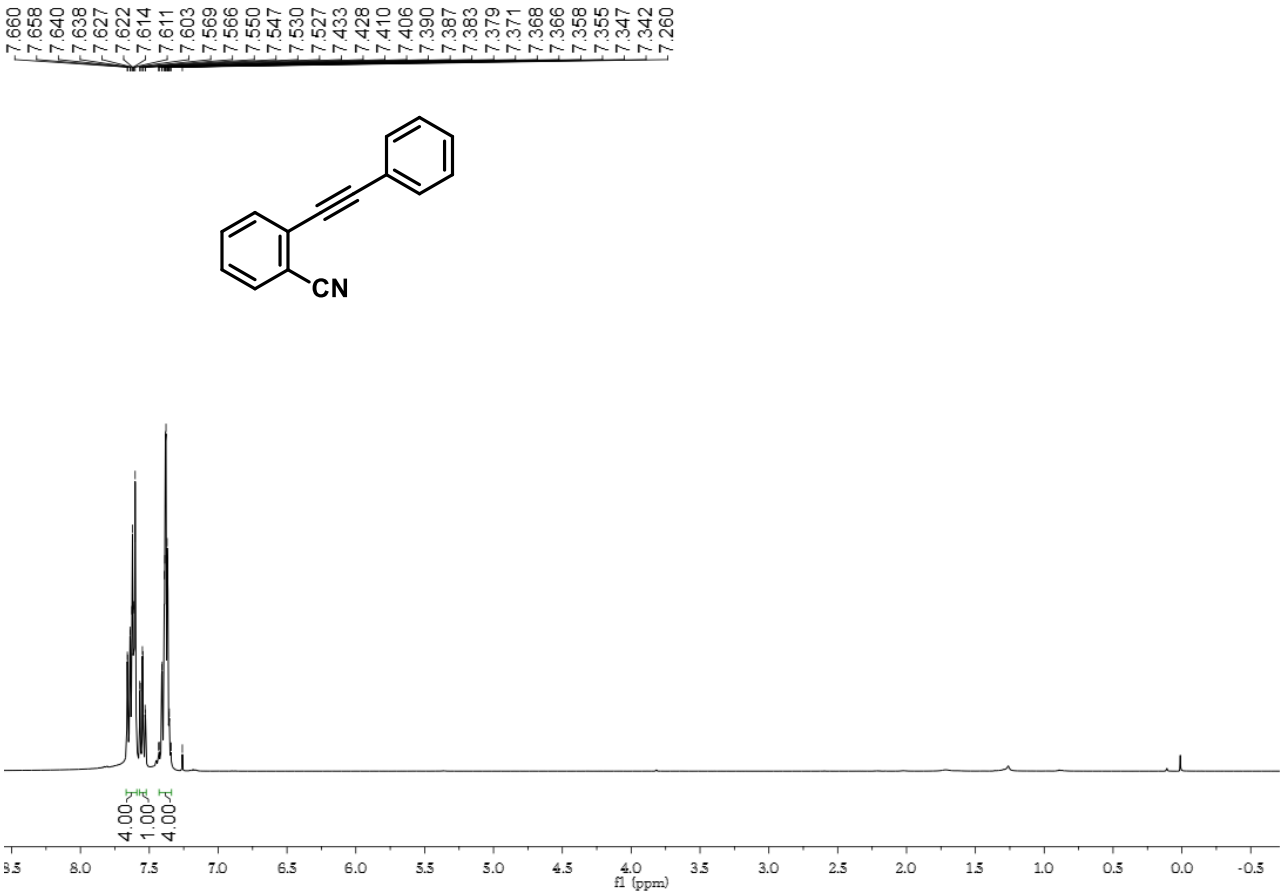


72 mg, 68%; A yellow-orange solid, Mp: 223-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.51 (s, 1H, Ar-H), 7.26-7.20 (m, 4H, Ar-H), 7.17 (s, 2H, Ar-H), 7.07 (s, 2H, Ar-H), 6.93 (d, J = 8.4 Hz, 2H, Ar-H), 6.85 (d, J = 8.4 Hz, 2H, Ar-H), 2.23 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.9 (d, $^3J_{C\text{-}P}$ = 15.3 Hz), 144.1 (d, $^2J_{C\text{-}P}$ = 7.6 Hz), 143.1 (d, $^2J_{C\text{-}P}$ = 7.8 Hz), 138.6 (d, $^3J_{C\text{-}P}$ = 13.2 Hz), 134.6 (d, $^1J_{C\text{-}P}$ = 100.1 Hz), 134.8, 134.0, 130.5, 130.3 (d, $^4J_{C\text{-}P}$ = 3.6 Hz), 128.9 (d, $^2J_{C\text{-}P}$ = 10.2 Hz), 127.5 (d, $^4J_{C\text{-}P}$ = 2.4 Hz), 127.3, 126.0, 124.3, 21.2. IR (KBr, ν, cm^{-1}) 3050, 1715, 1559, 1458, 1274, 1190. HR-MS (APCI-TOF) m/z calcd for $C_{31}H_{25}Cl_2O_2P$ $[M+H]^+$ 530.0969, found 531.1046.

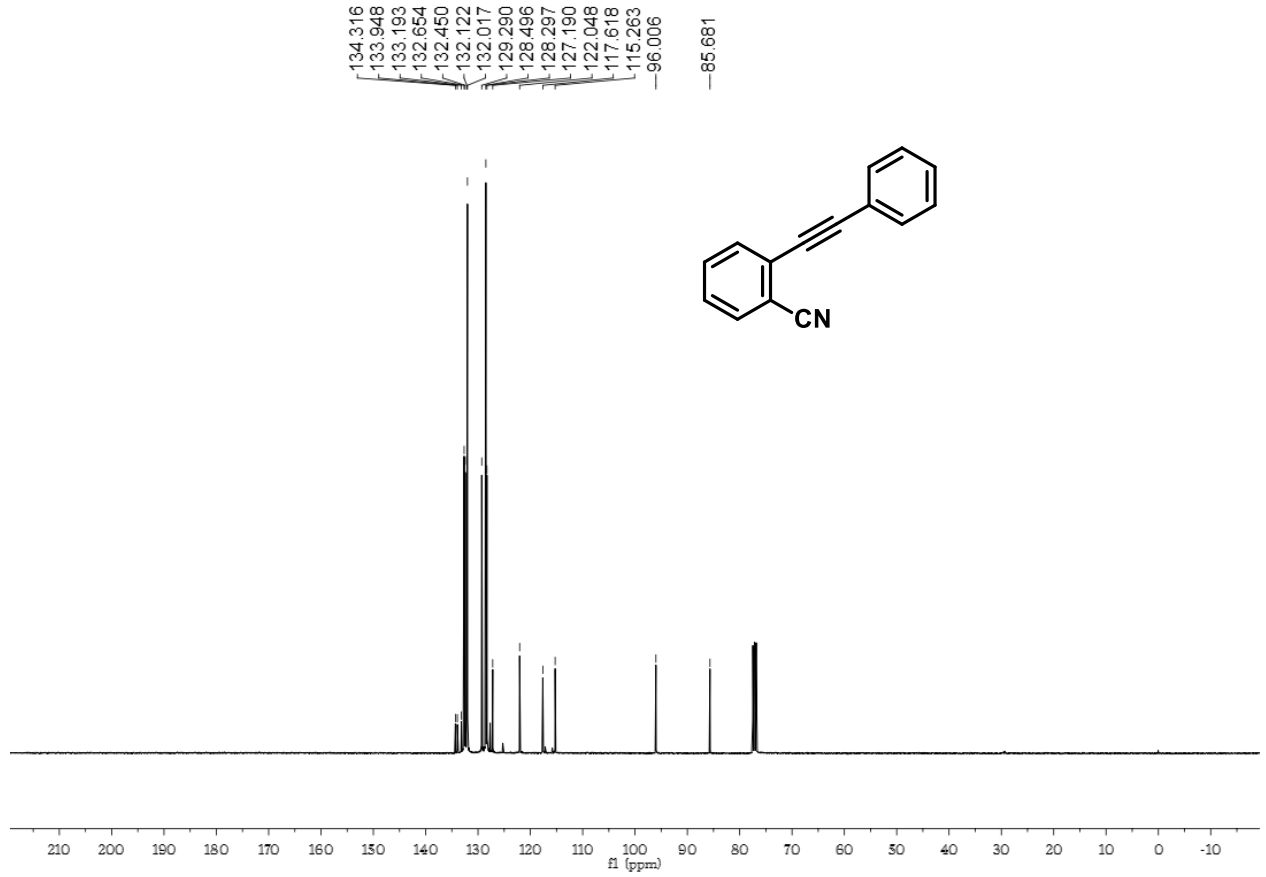
diethyl (2-(4-methoxyphenyl)-1-oxo-1H-inden-3-yl)phosphonate (3cc)



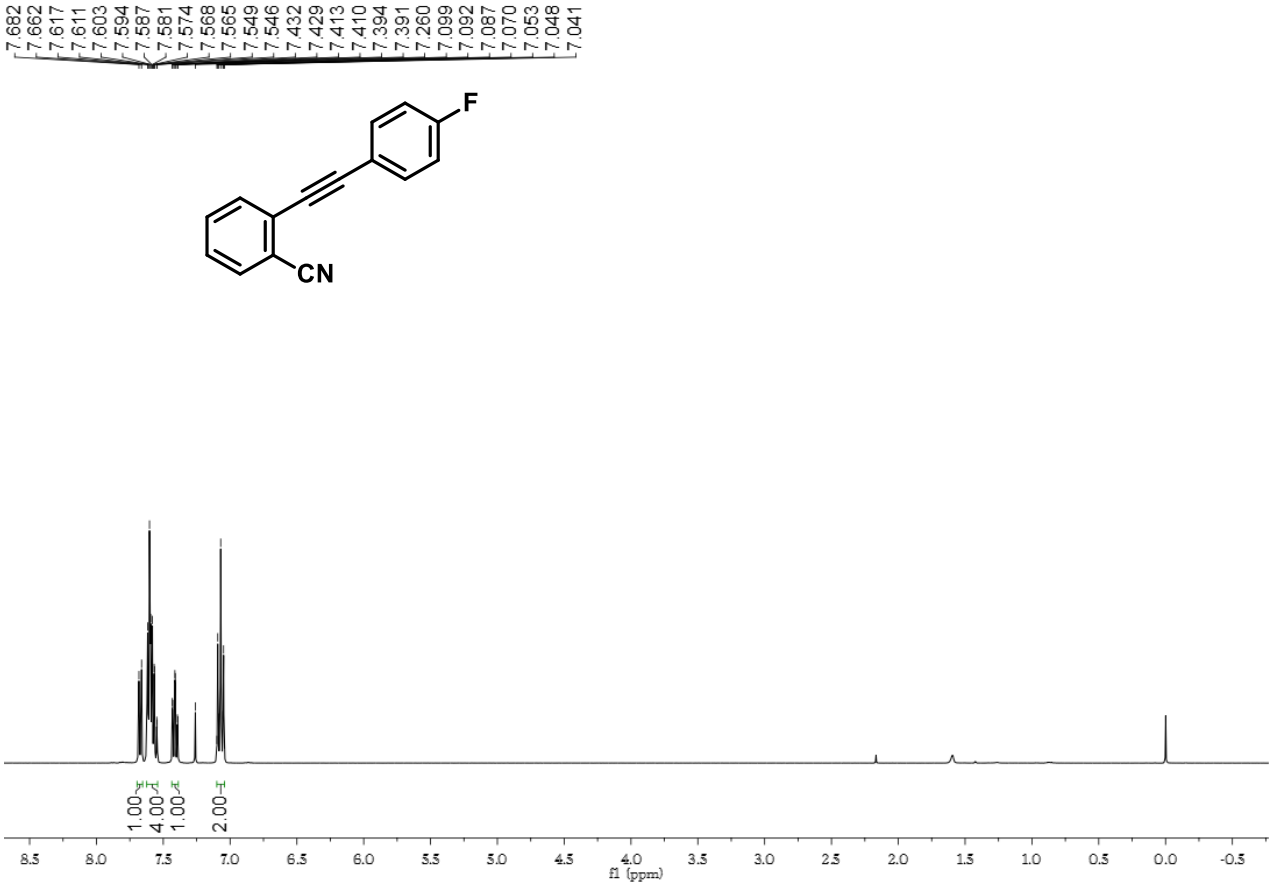
30 mg, 40%; A red liquid. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.70 (d, J = 7.6 Hz, 1H, Ar-H), 7.55-7.43 (m, 4H, Ar-H), 7.27-7.23 (m, 1H, Ar-H), 6.97-6.94 (m, 2H, Ar-H), 4.16-4.06 (m, 2H, CH_2), 4.04-3.94 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 1.21-1.17 (m, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.5 (d, $^3J_{C\text{-}P}$ = 21.9 Hz), 160.8, 144.8 (d, $^2J_{C\text{-}P}$ = 11.6 Hz), 144.4 (d, $^2J_{C\text{-}P}$ = 8.3 Hz), 138.2 (d, $^1J_{C\text{-}P}$ = 189.1 Hz), 135.0, 132.1 (d, $^4J_{C\text{-}P}$ = 1.7 Hz), 128.8 (d, $^3J_{C\text{-}P}$ = 6.2 Hz), 128.6, 123.8, 122.1 (d, $^3J_{C\text{-}P}$ = 4.0 Hz), 113.3, 62.4 (d, $^2J_{C\text{-}P}$ = 5.6 Hz), 55.3, 16.1 (d, $^3J_{C\text{-}P}$ = 6.6 Hz). IR (KBr, ν, cm^{-1}) 3031, 2711, 1718, 1589, 1457, 1392, 1253, 1015, 978. HR-MS (APCI-TOF) m/z calcd for $C_{20}H_{21}O_5P$ $[M+H]^+$ 373.1205, found 373.1209.



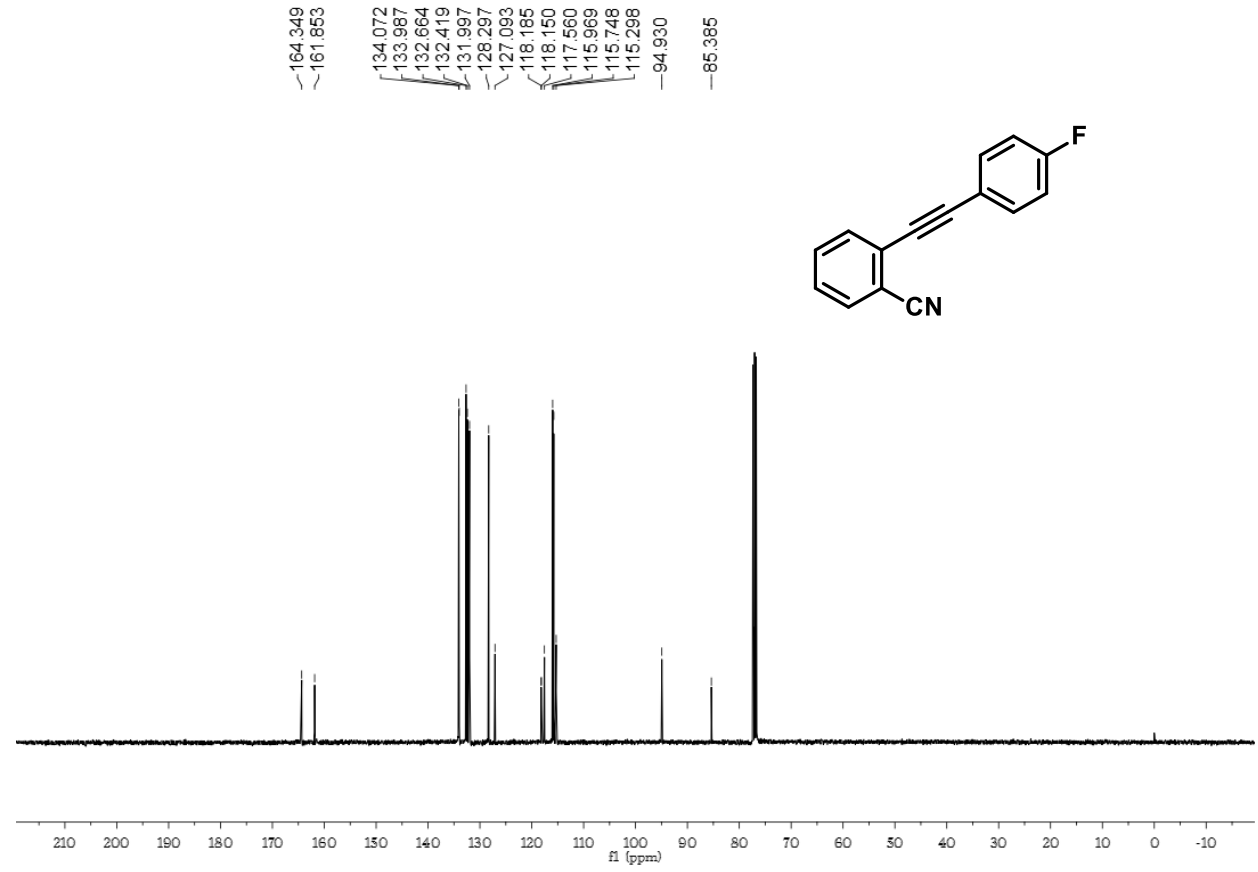
^{1}H NMR Spectrum of Compound 1a



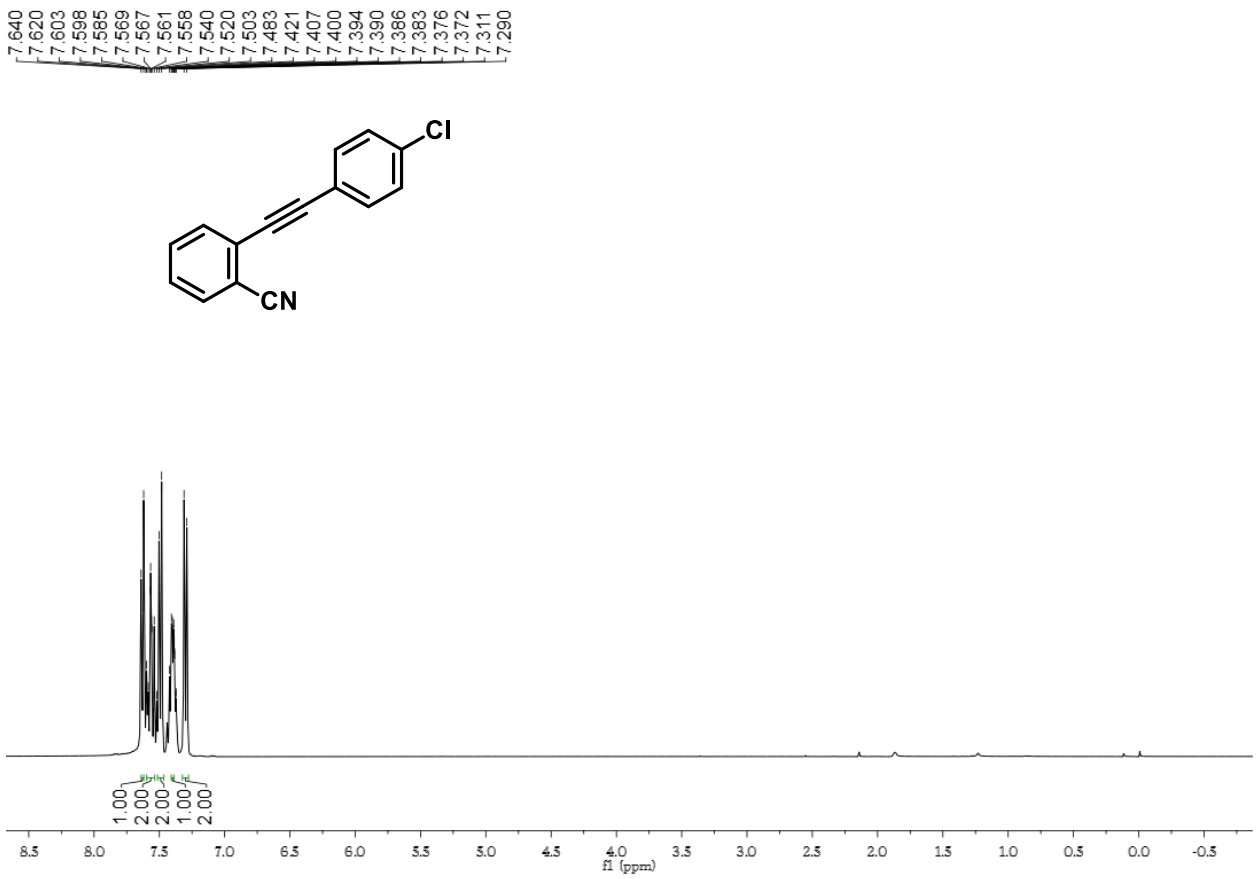
^{13}C NMR Spectrum of Compound 1a



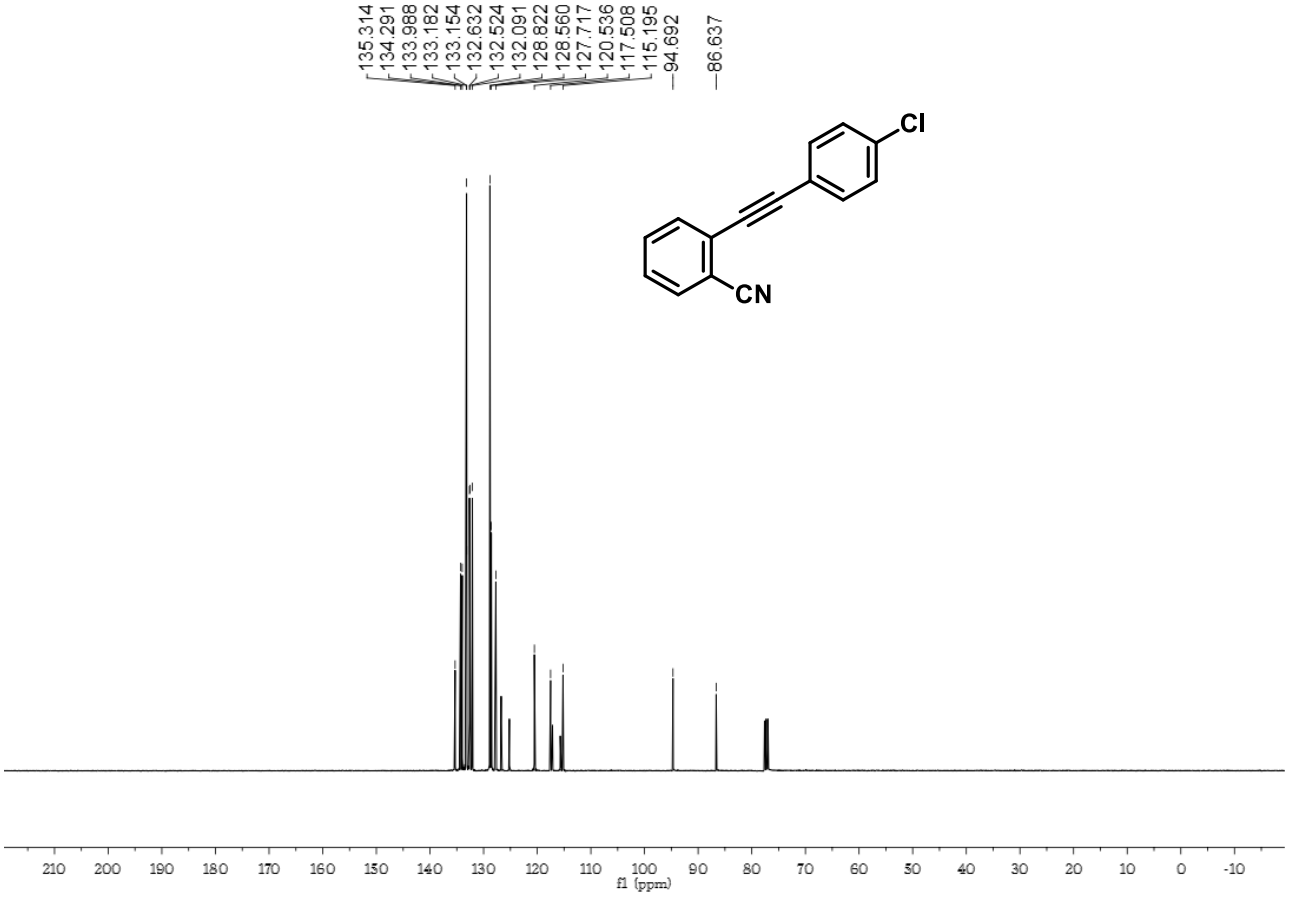
^{1}H NMR Spectrum of Compound 1b



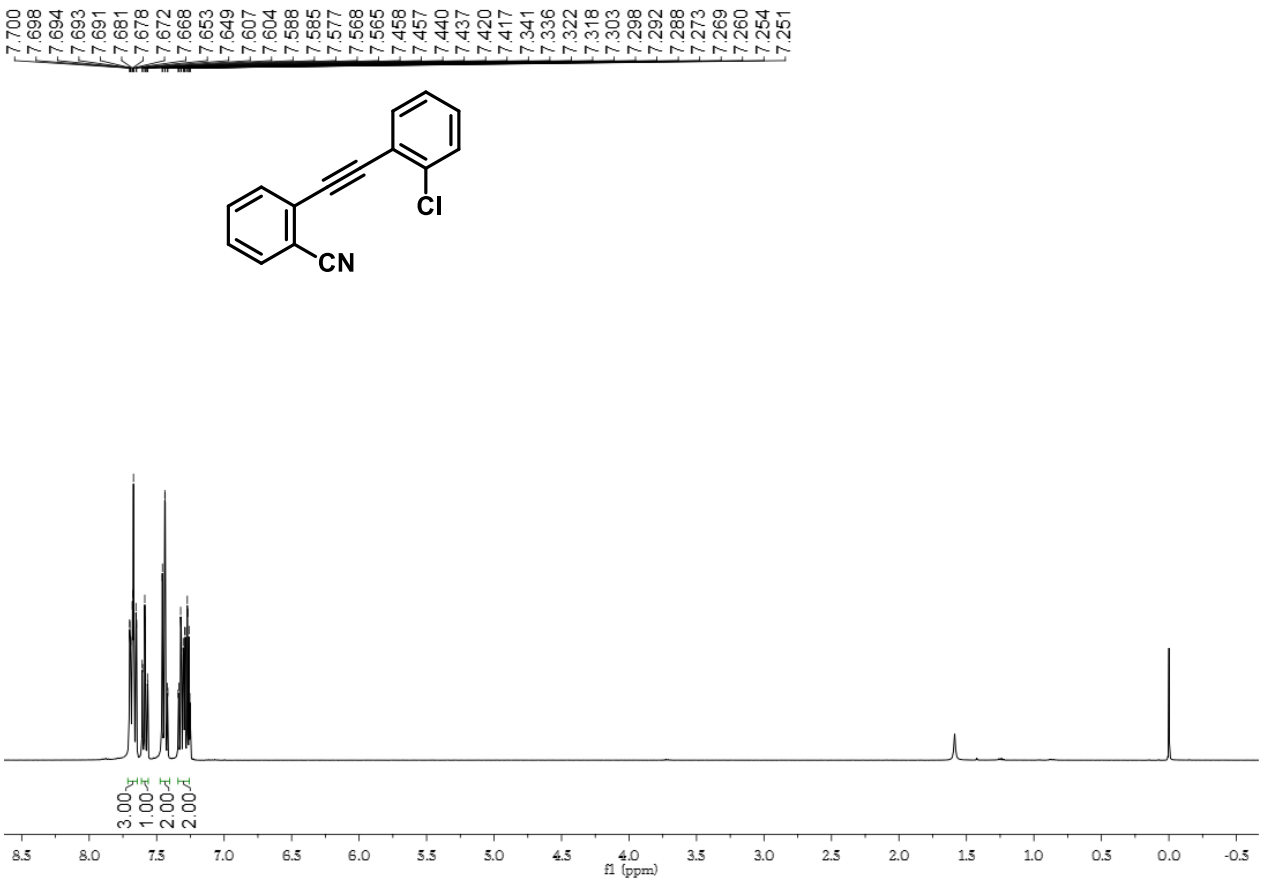
^{13}C NMR Spectrum of Compound 1b



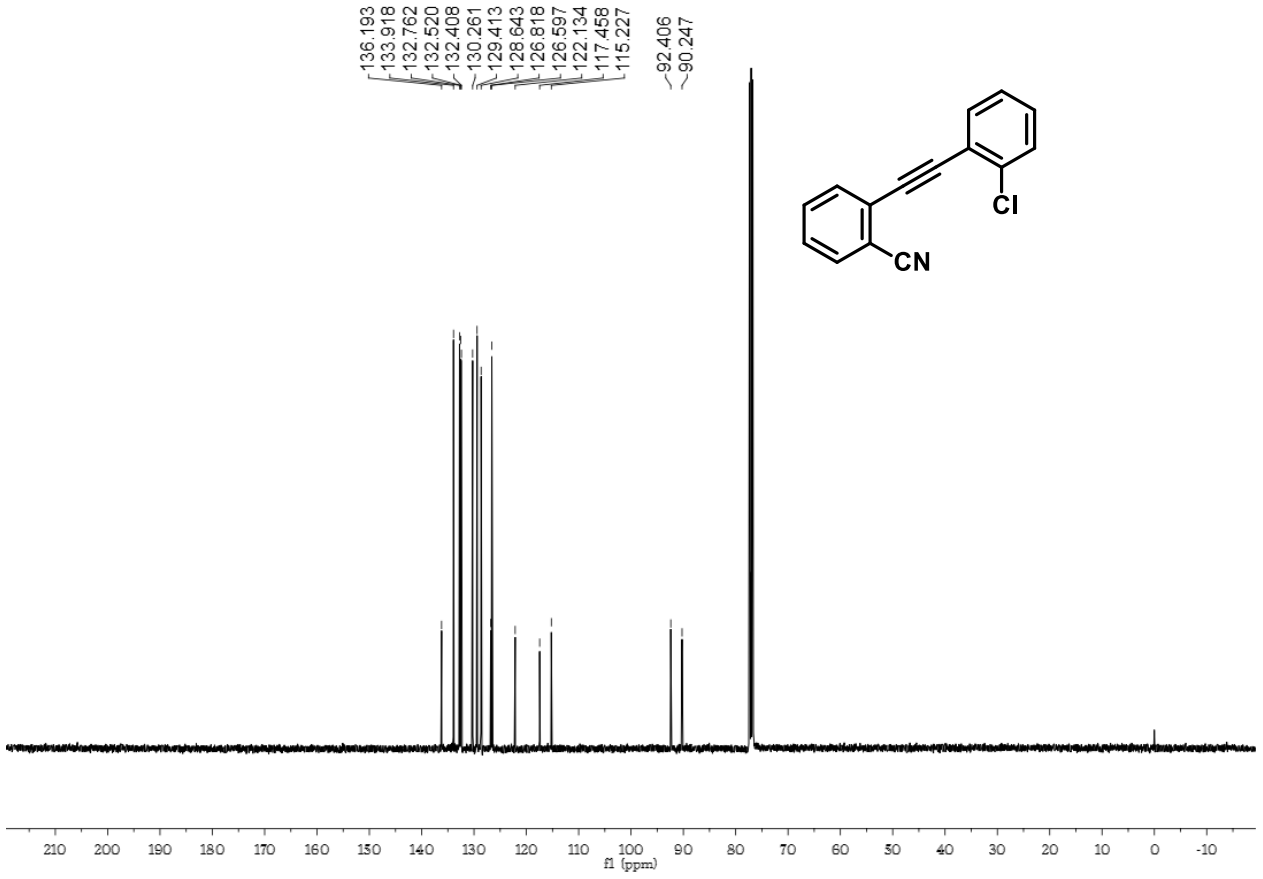
^{1}H NMR Spectrum of Compound 1c



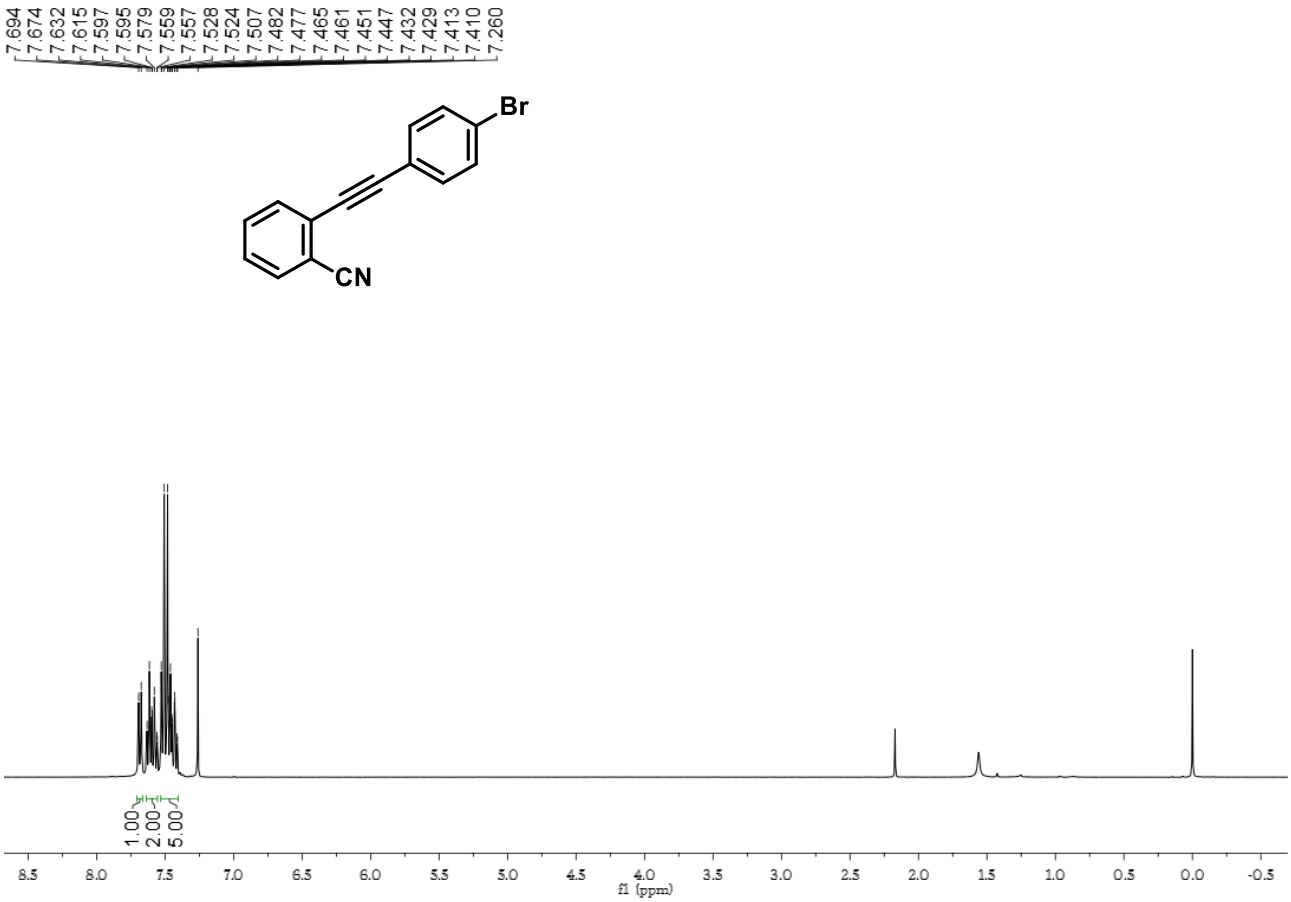
^{13}C NMR Spectrum of Compound 1c



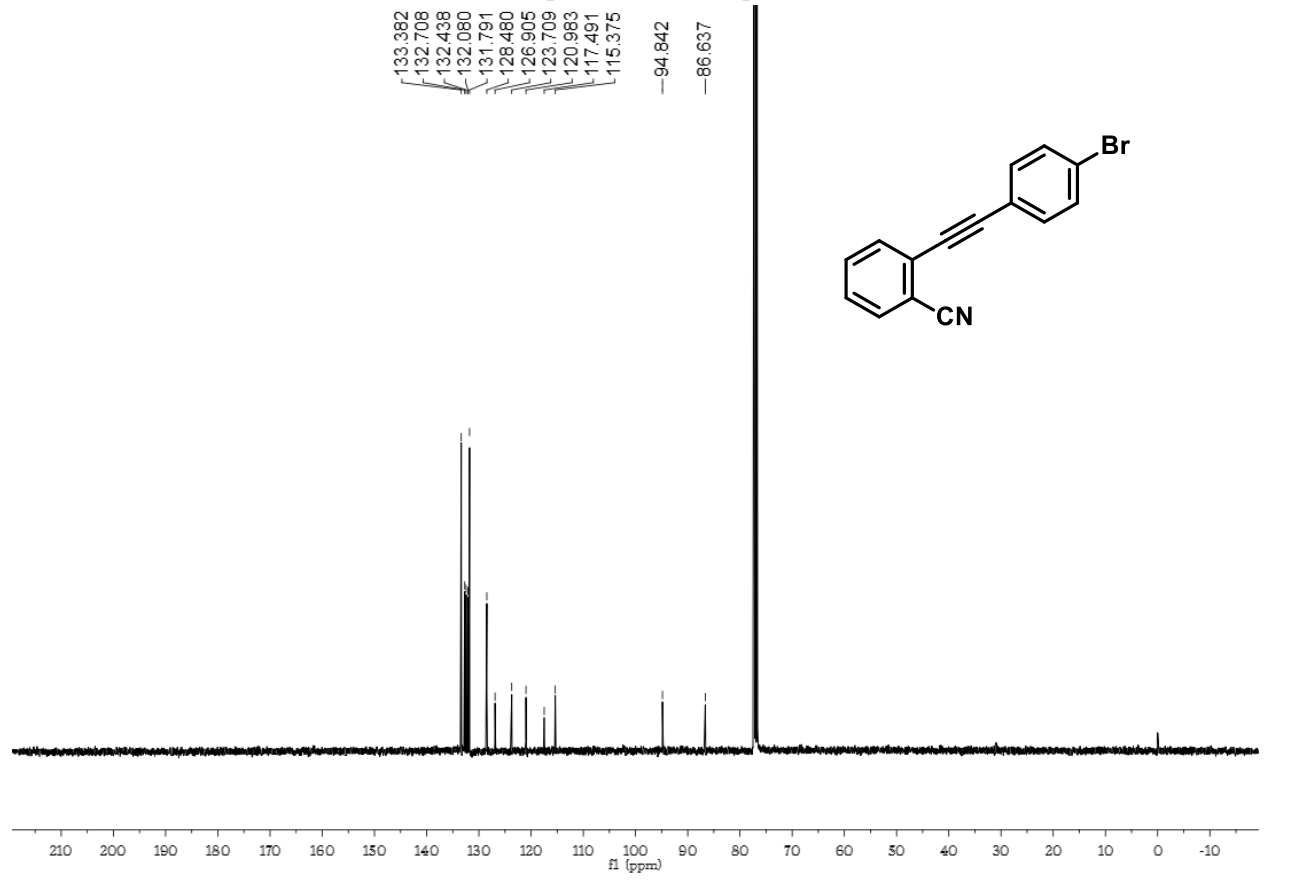
^{1}H NMR Spectrum of Compound 1d



^{13}C NMR Spectrum of Compound 1d

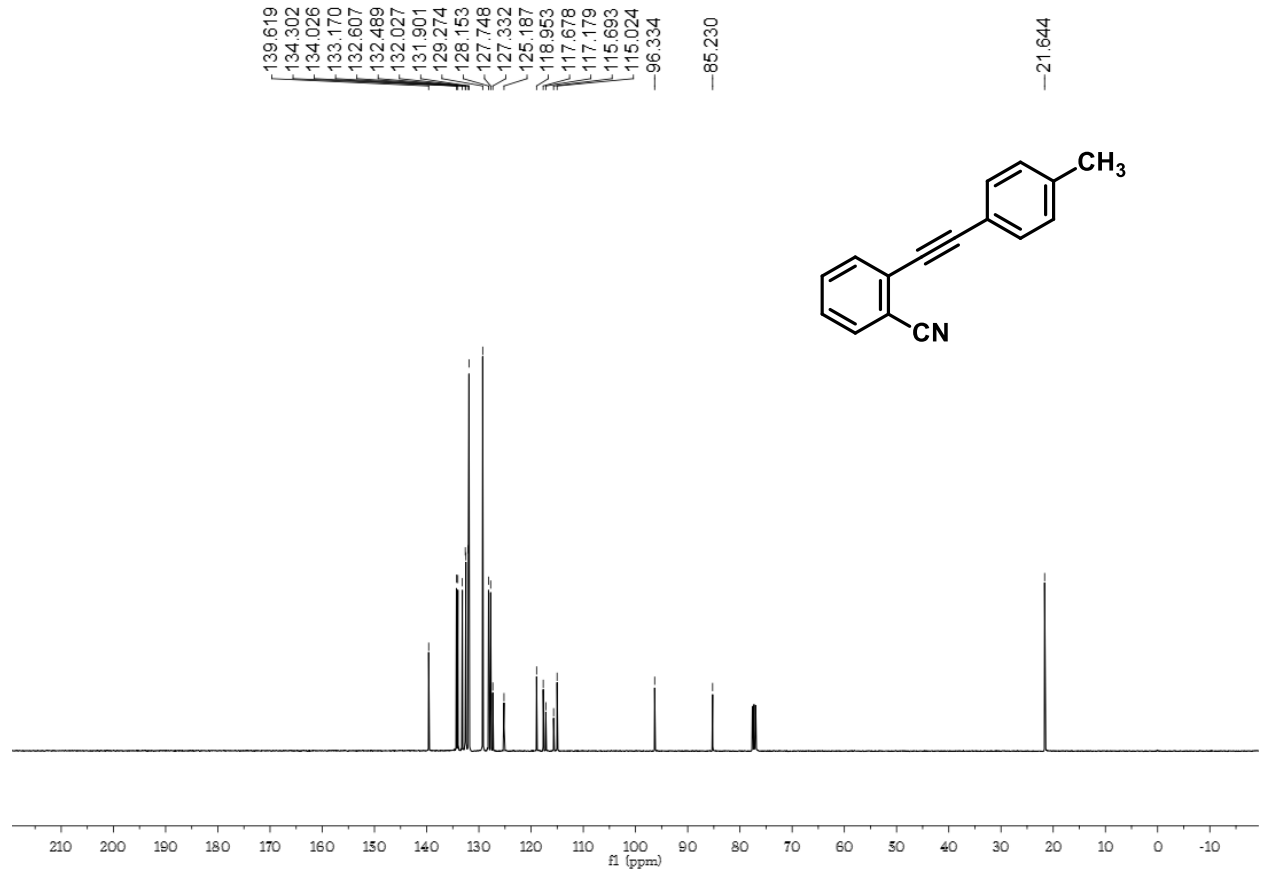


^{1}H NMR Spectrum of Compound 1e

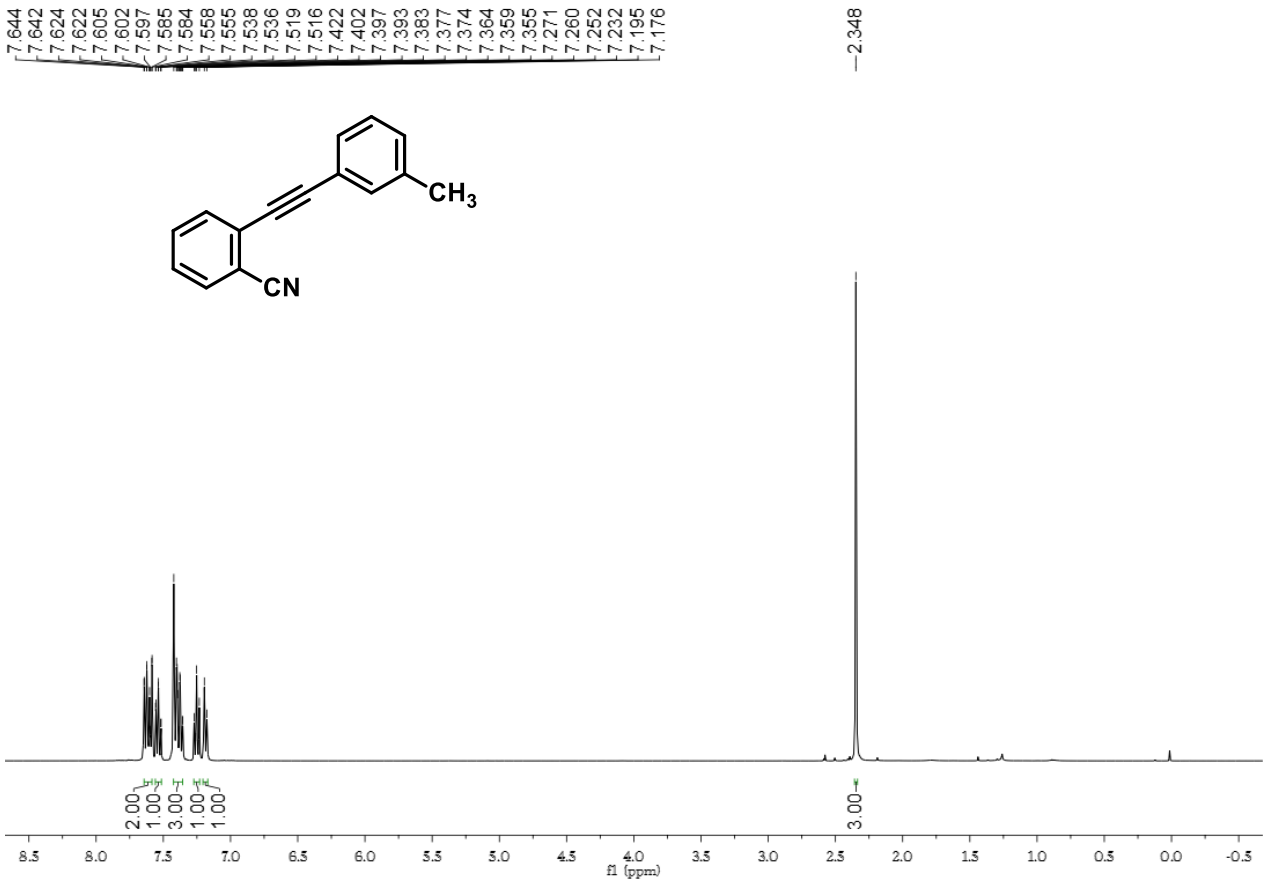


^{13}C NMR Spectrum of Compound 1e

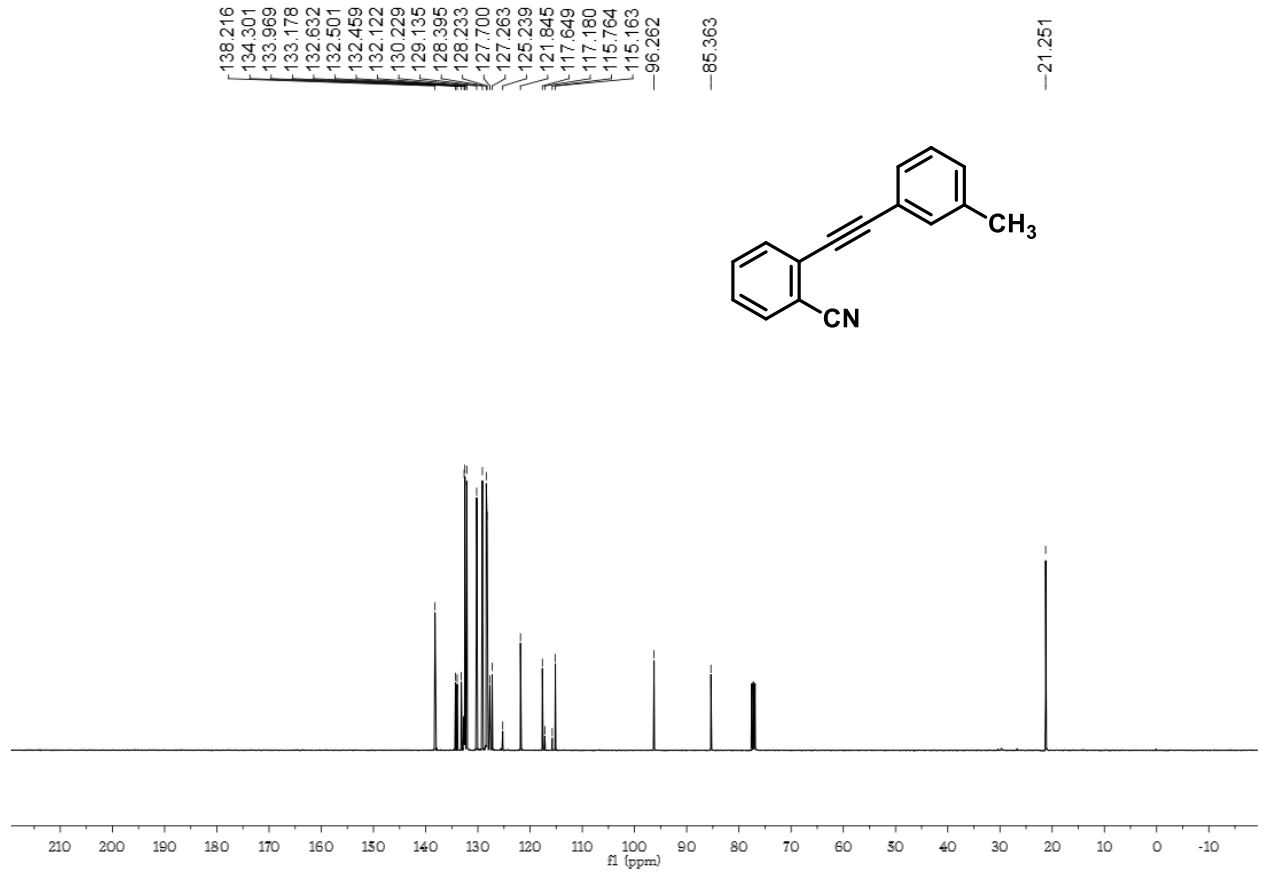
^{1}H NMR Spectrum of Compound 1f



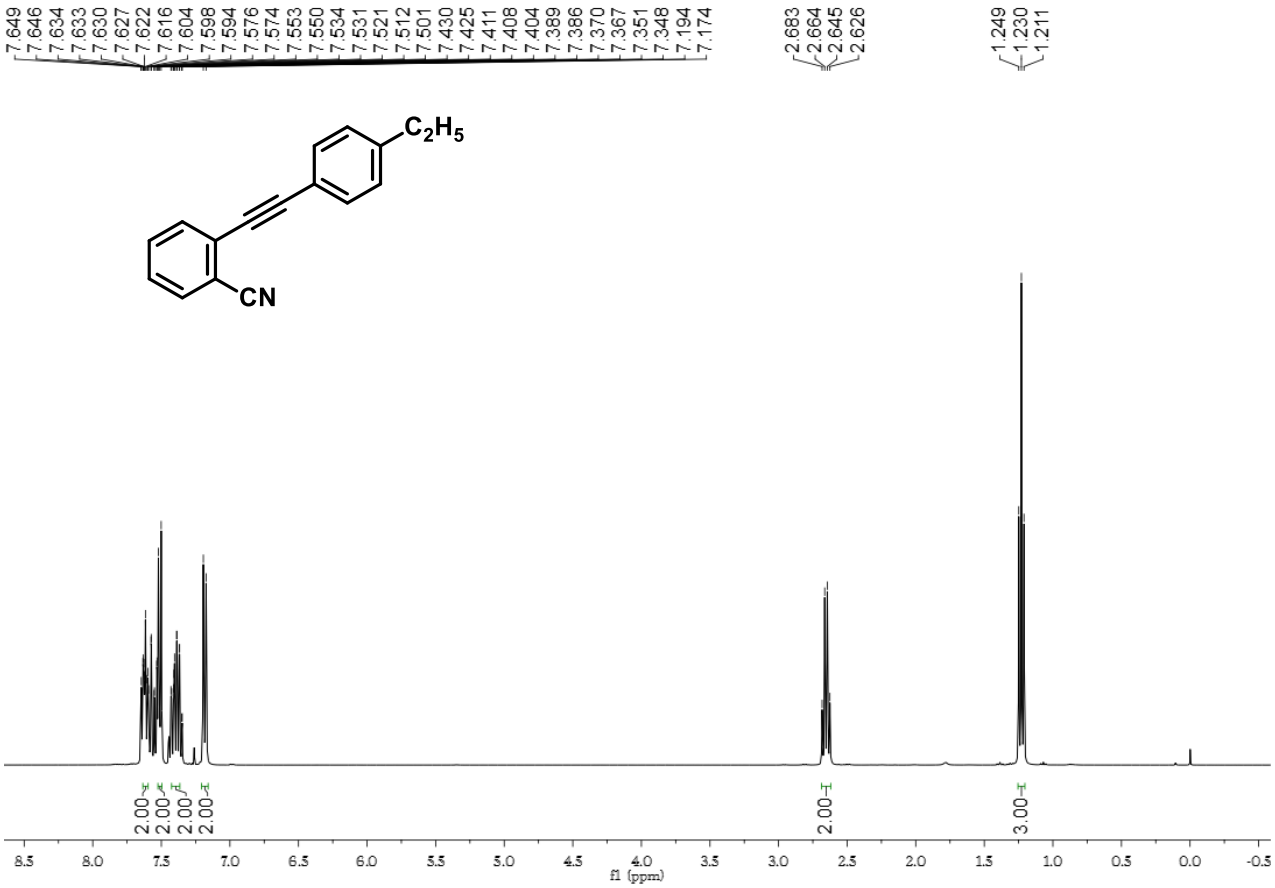
^{13}C NMR Spectrum of Compound 1f



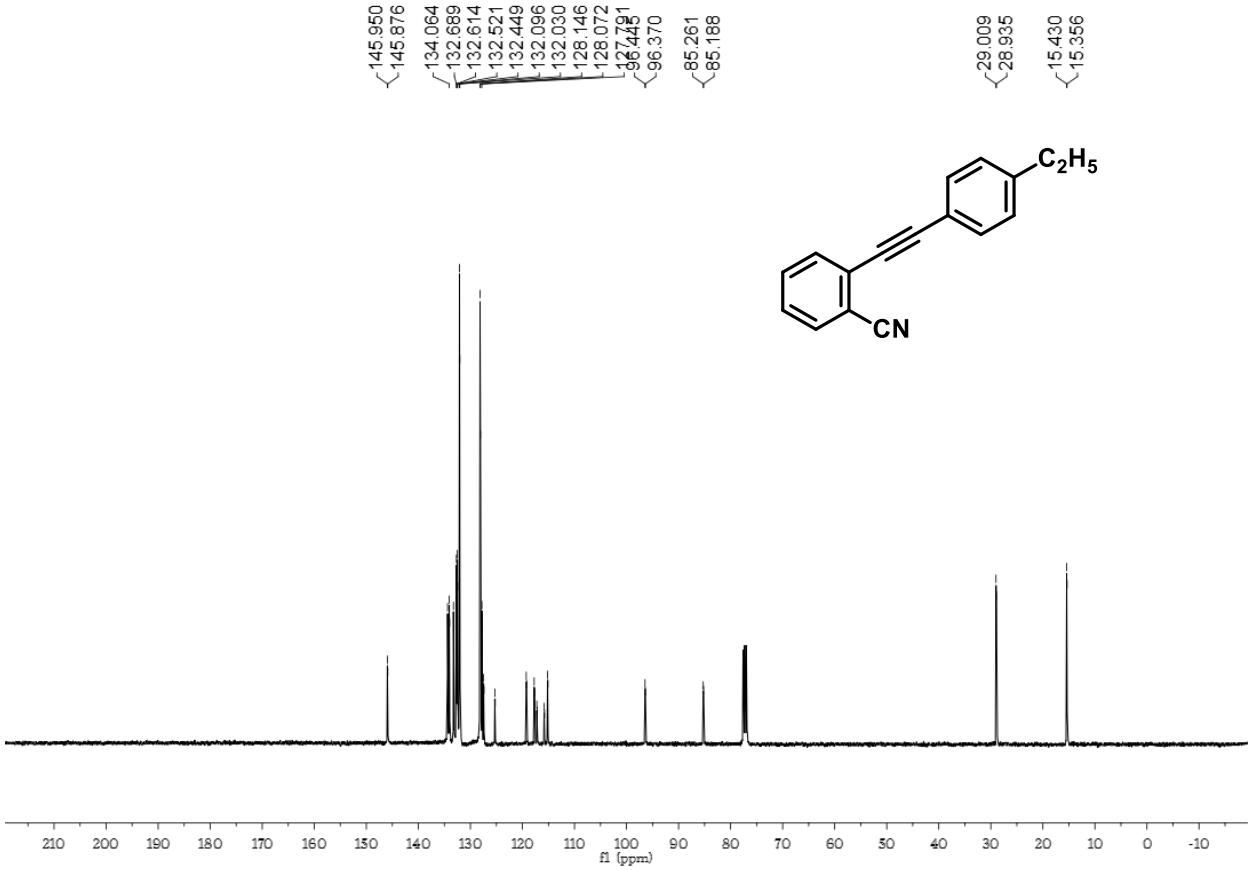
^{1}H NMR Spectrum of Compound 1g



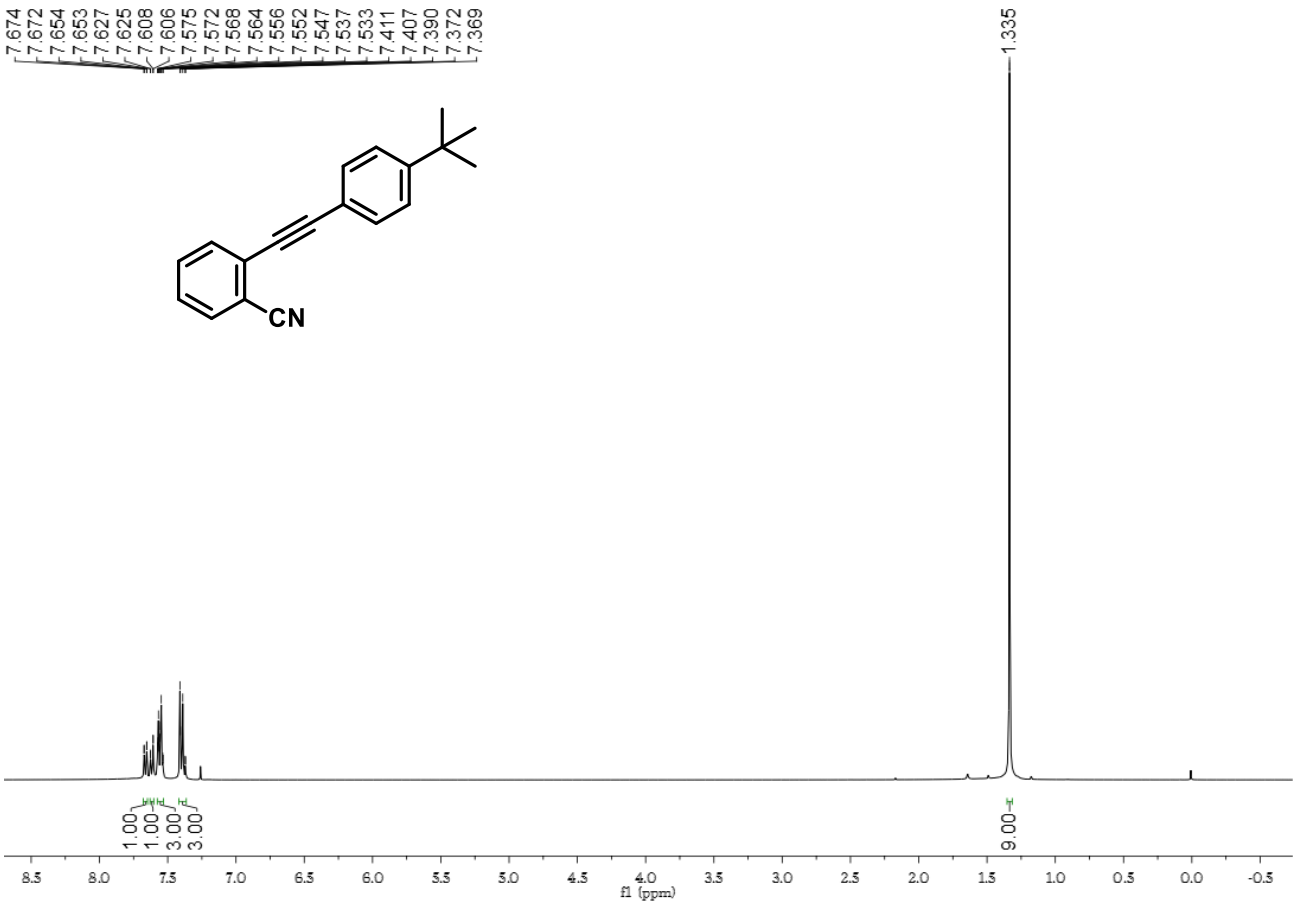
^{13}C NMR Spectrum of Compound 1g



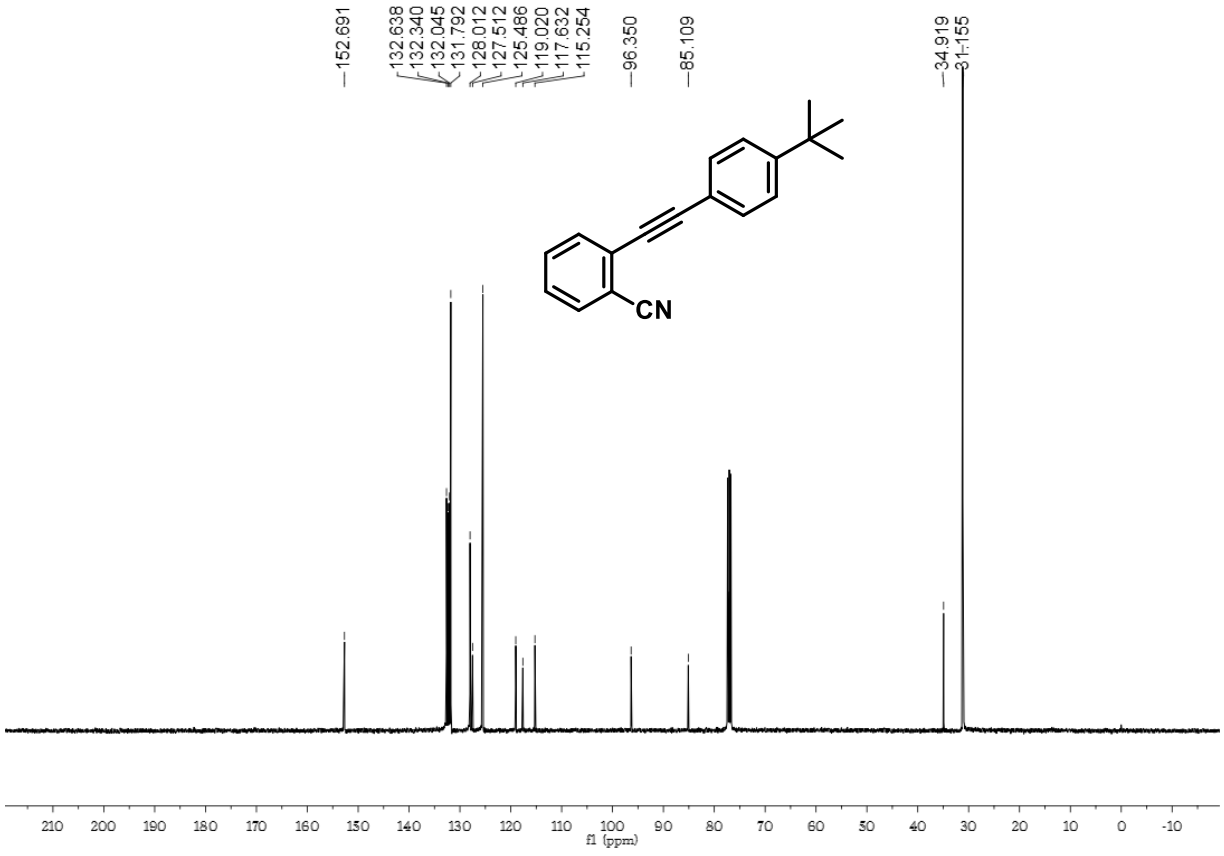
^{1}H NMR Spectrum of Compound 1h



^{13}C NMR Spectrum of Compound 1h

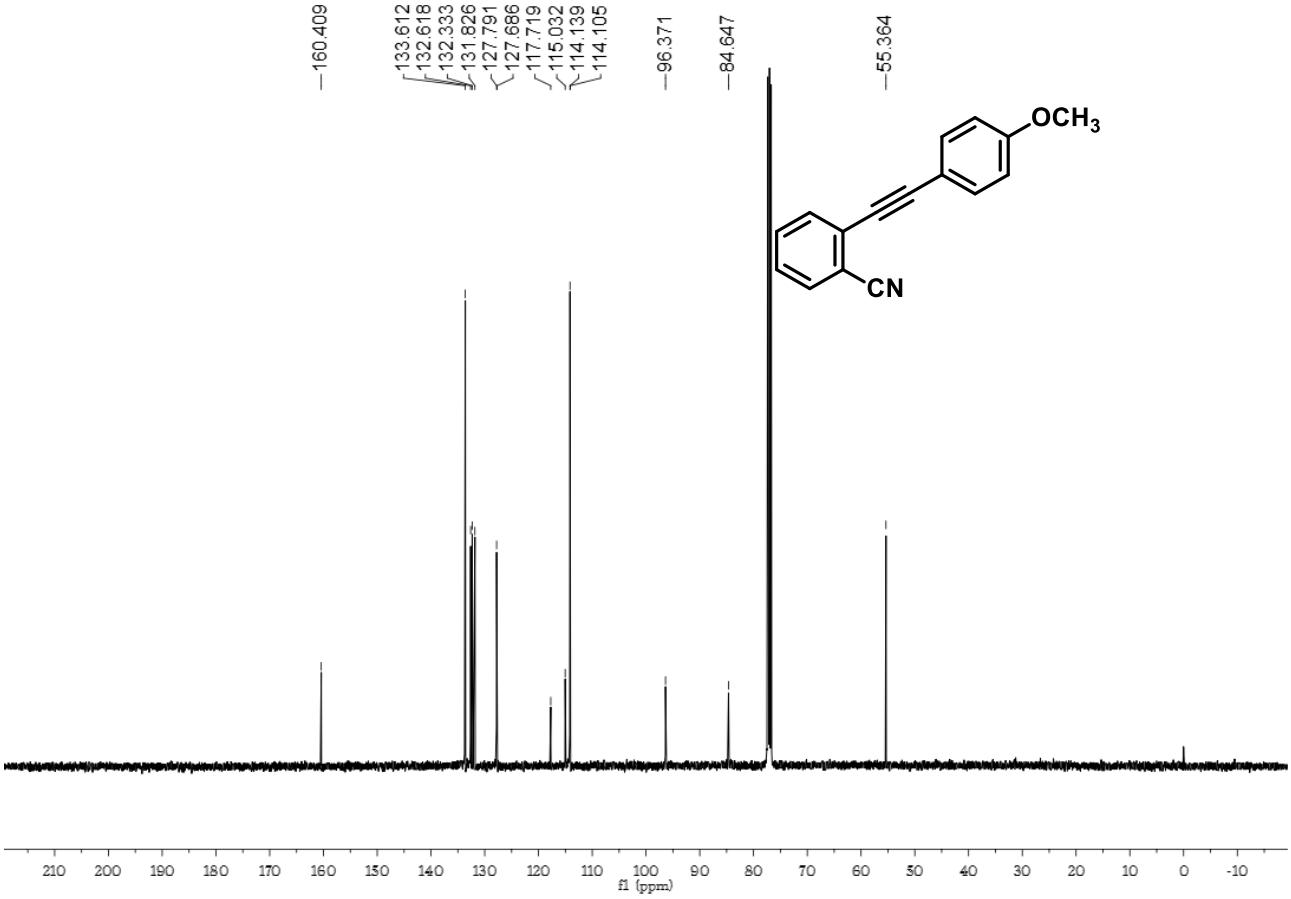


^{1}H NMR Spectrum of Compound 1i

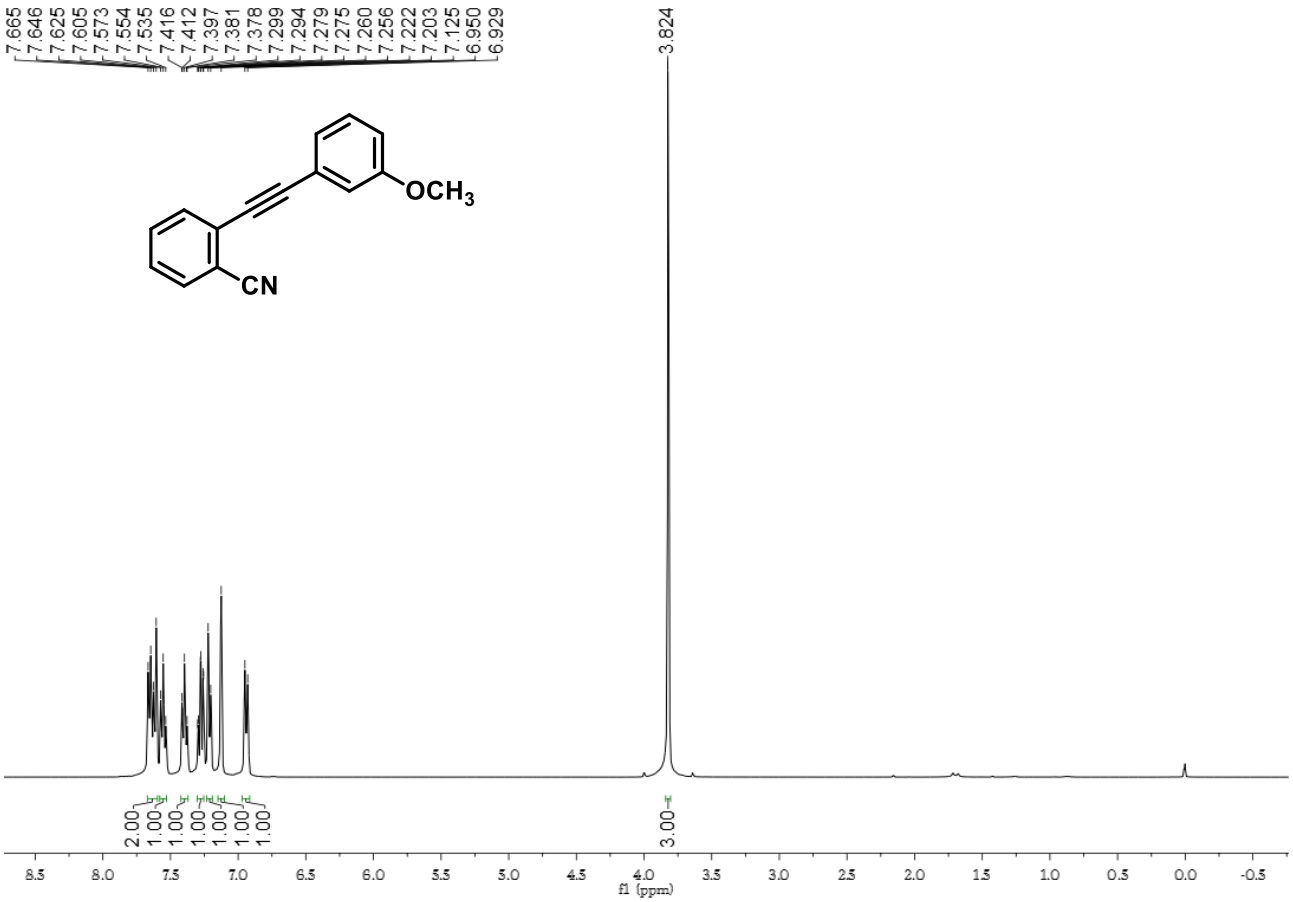


^{13}C NMR Spectrum of Compound 1i

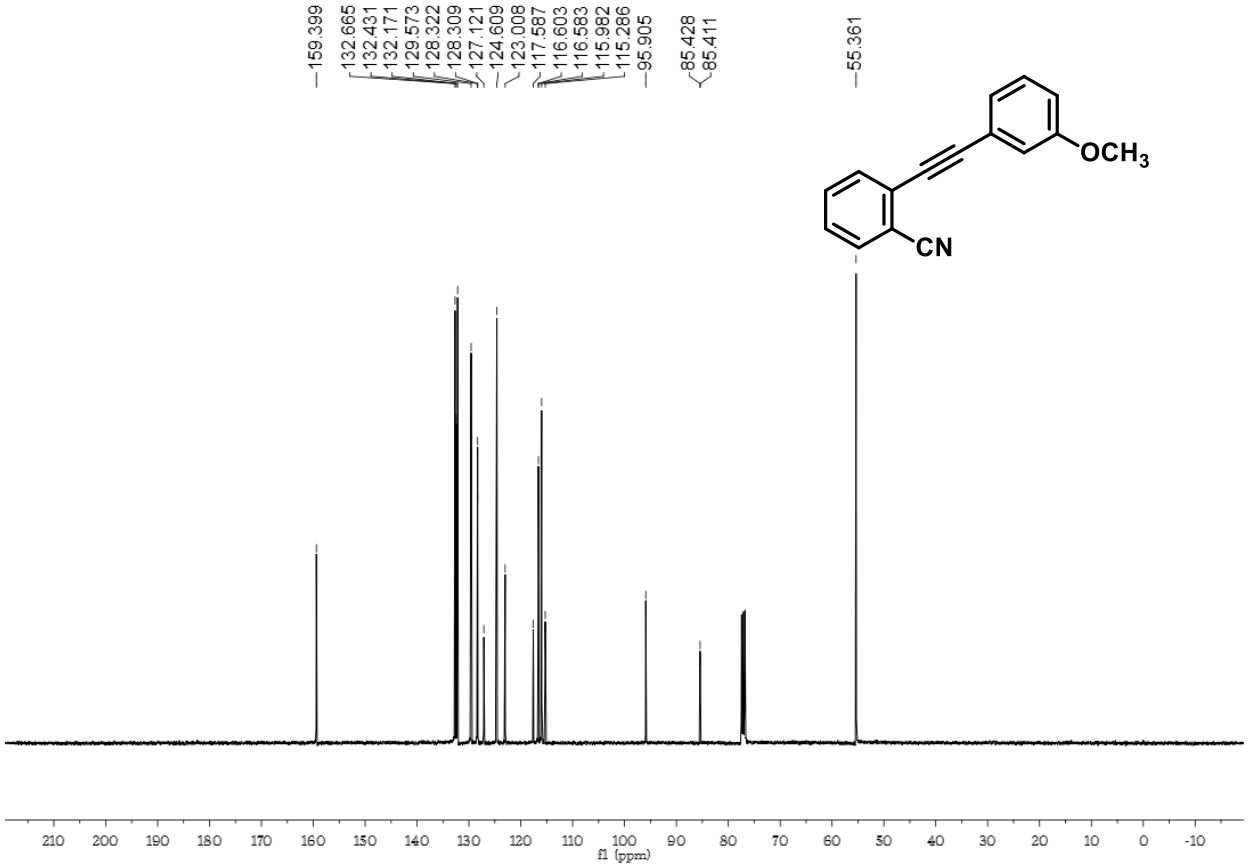
^{1}H NMR Spectrum of Compound 1j



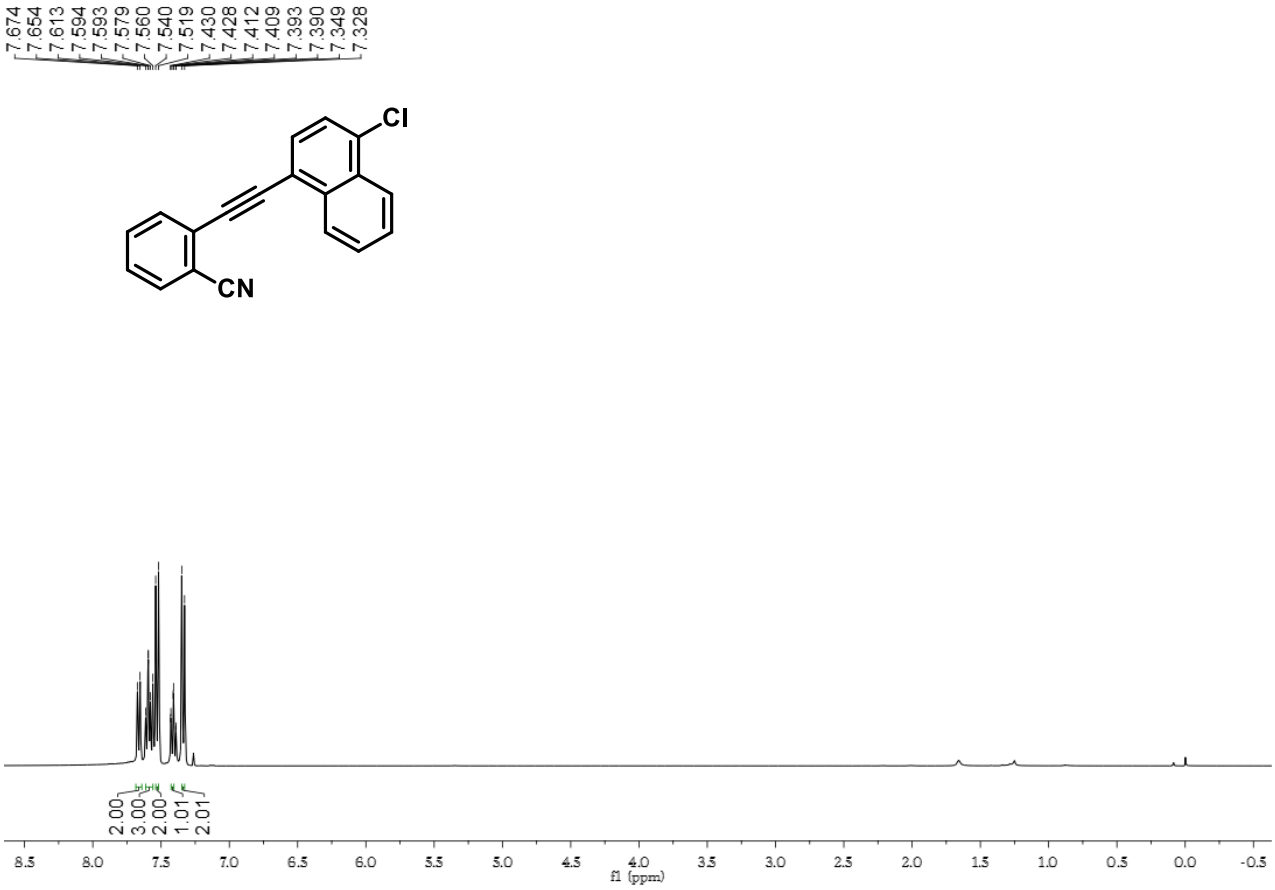
^{13}C NMR Spectrum of Compound 1j



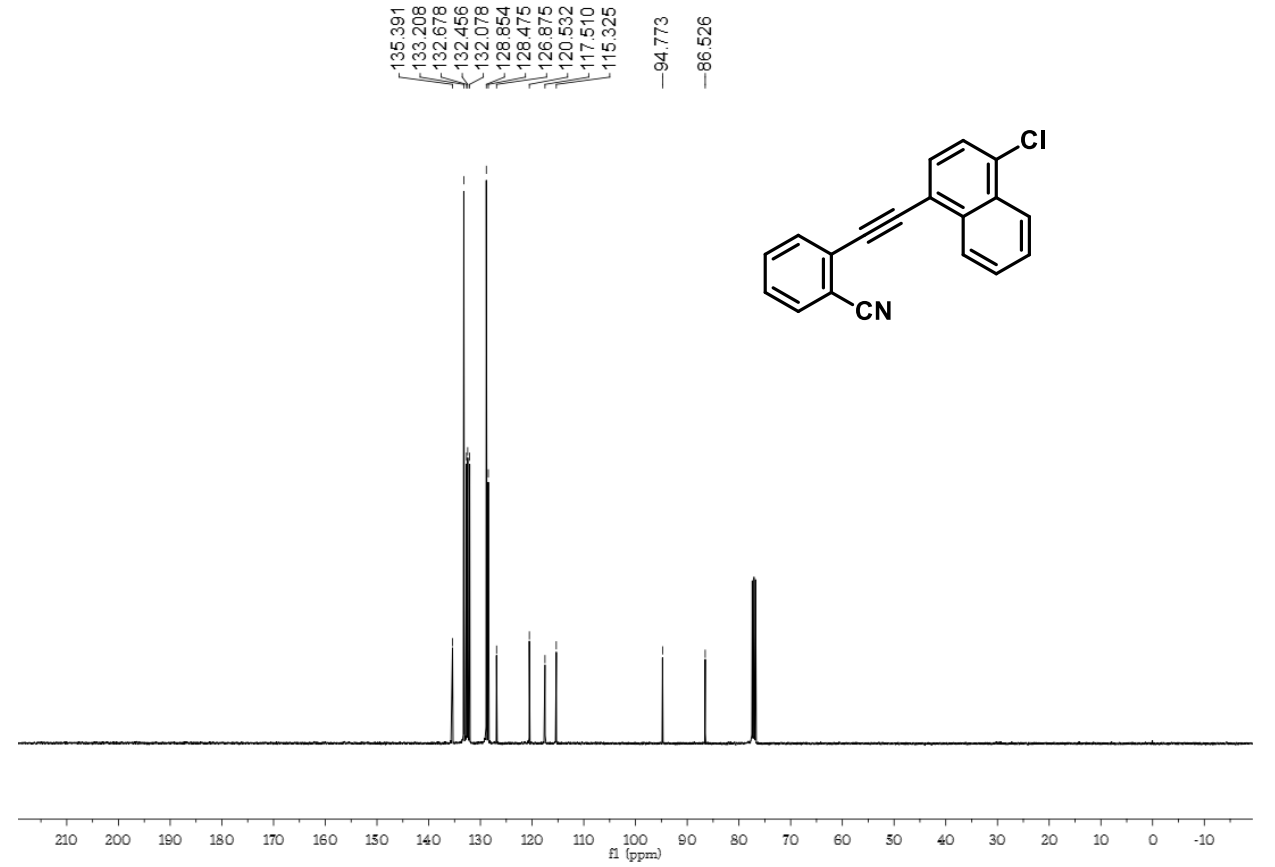
^{1}H NMR Spectrum of Compound 1k



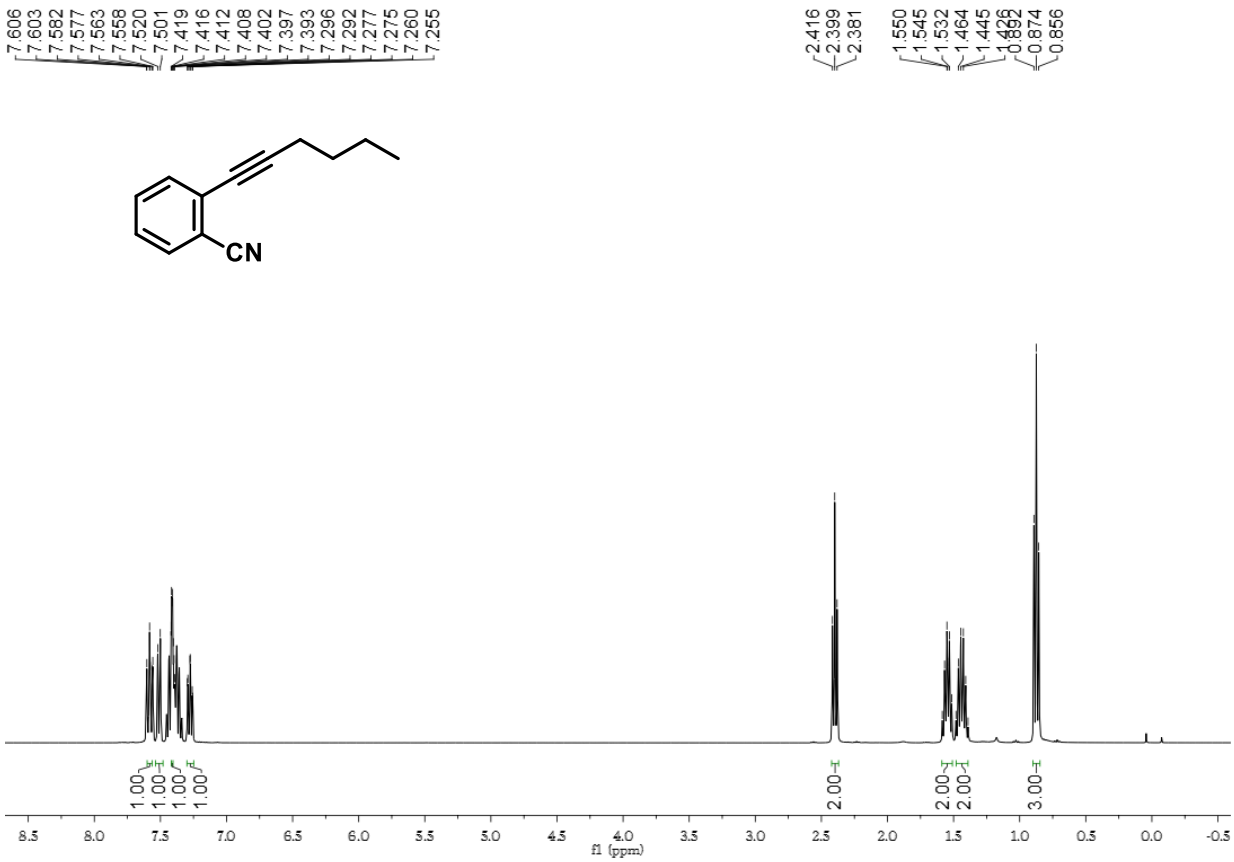
^{13}C NMR Spectrum of Compound 1k



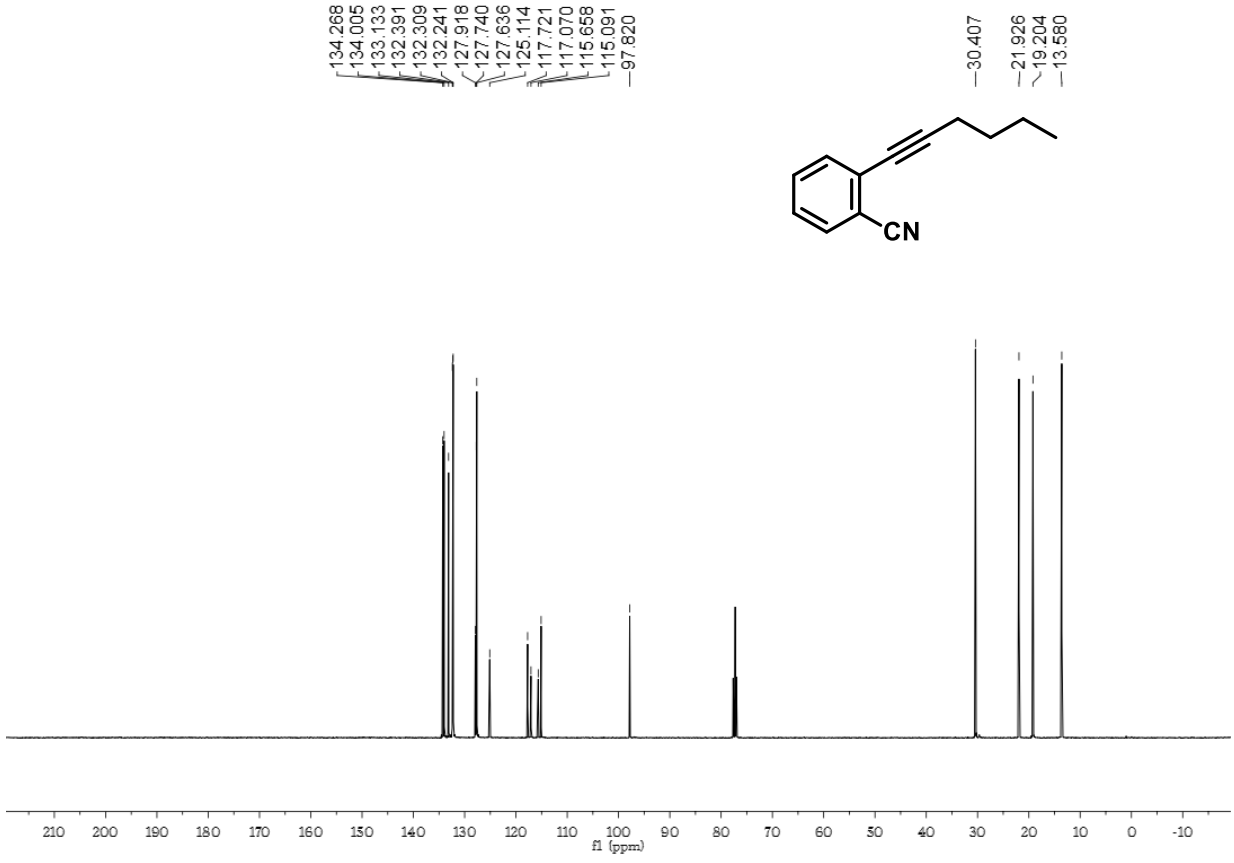
^{1}H NMR Spectrum of Compound 1l



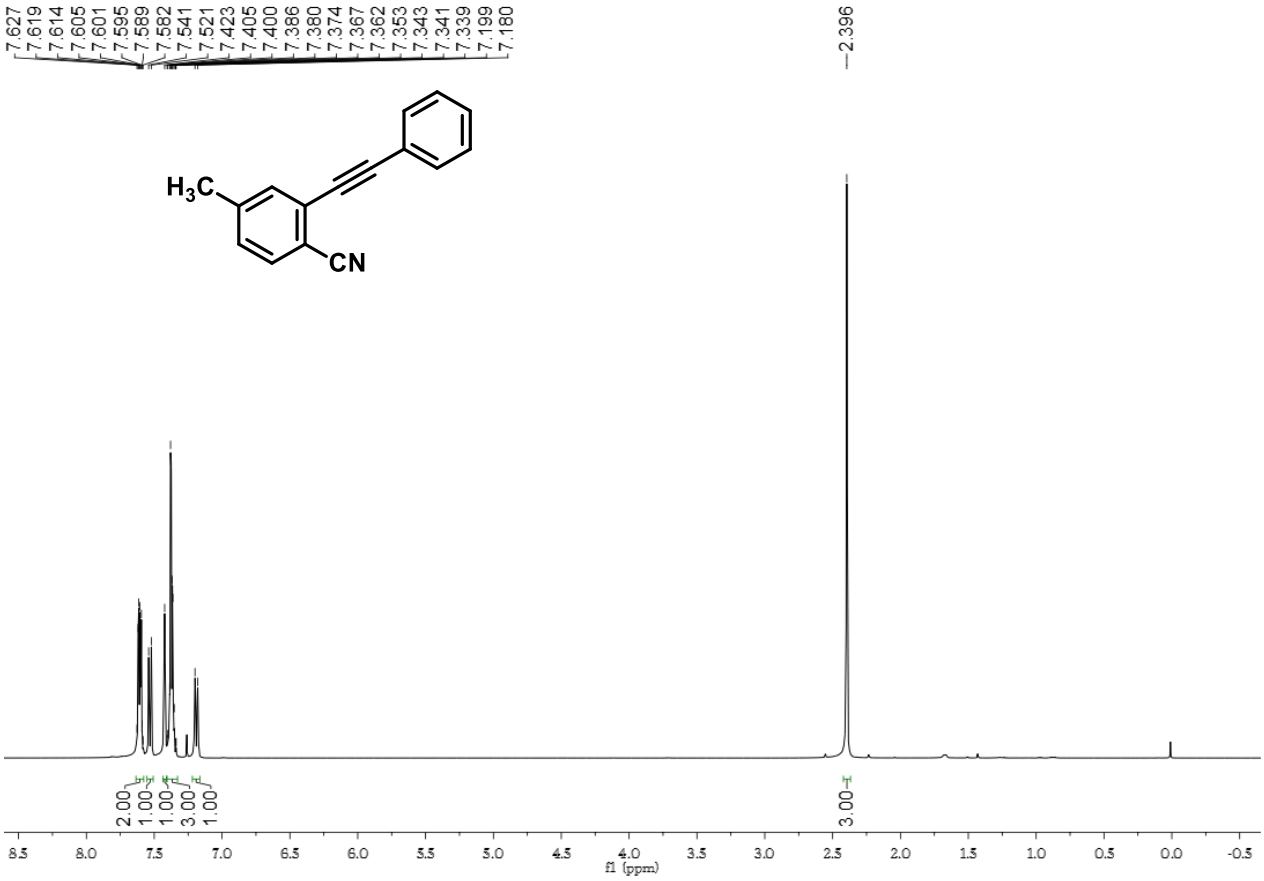
^{13}C NMR Spectrum of Compound 1l



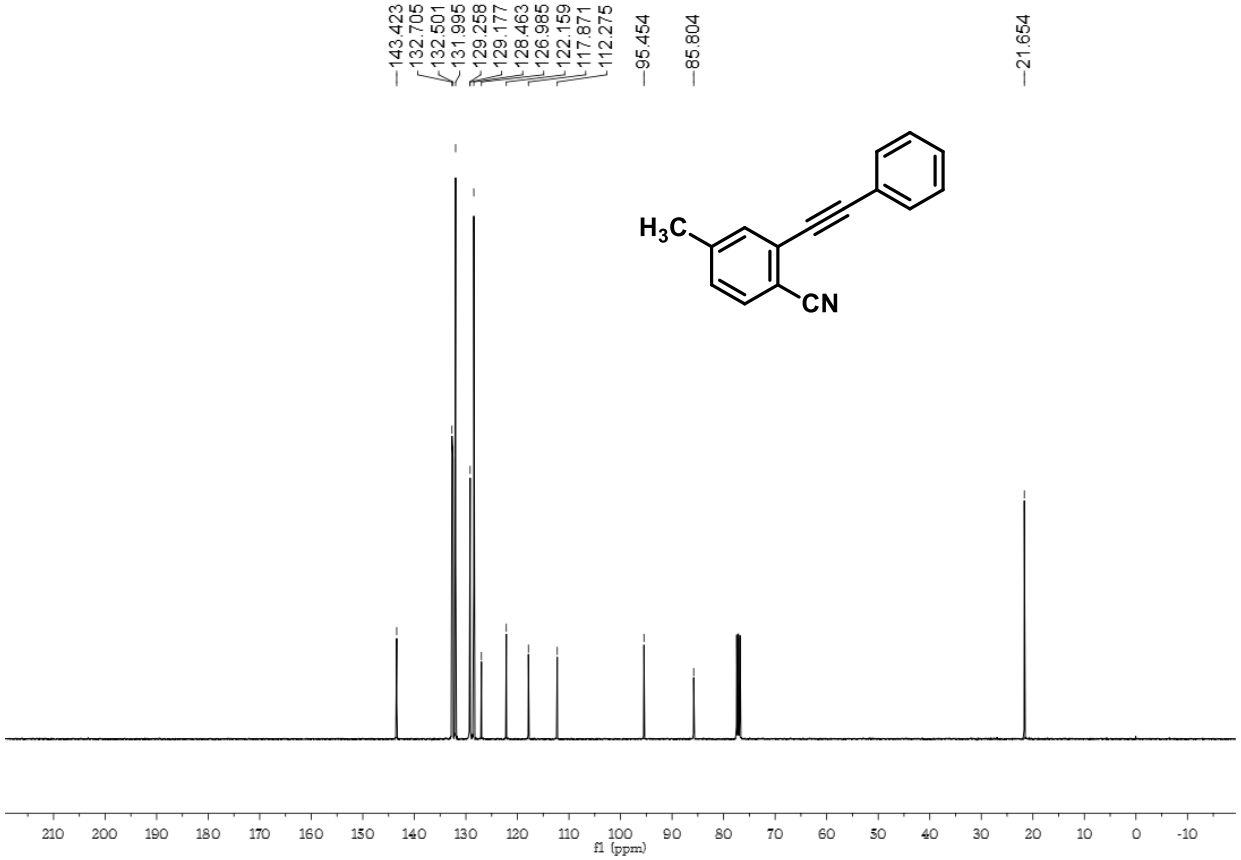
^{1}H NMR Spectrum of Compound 1m



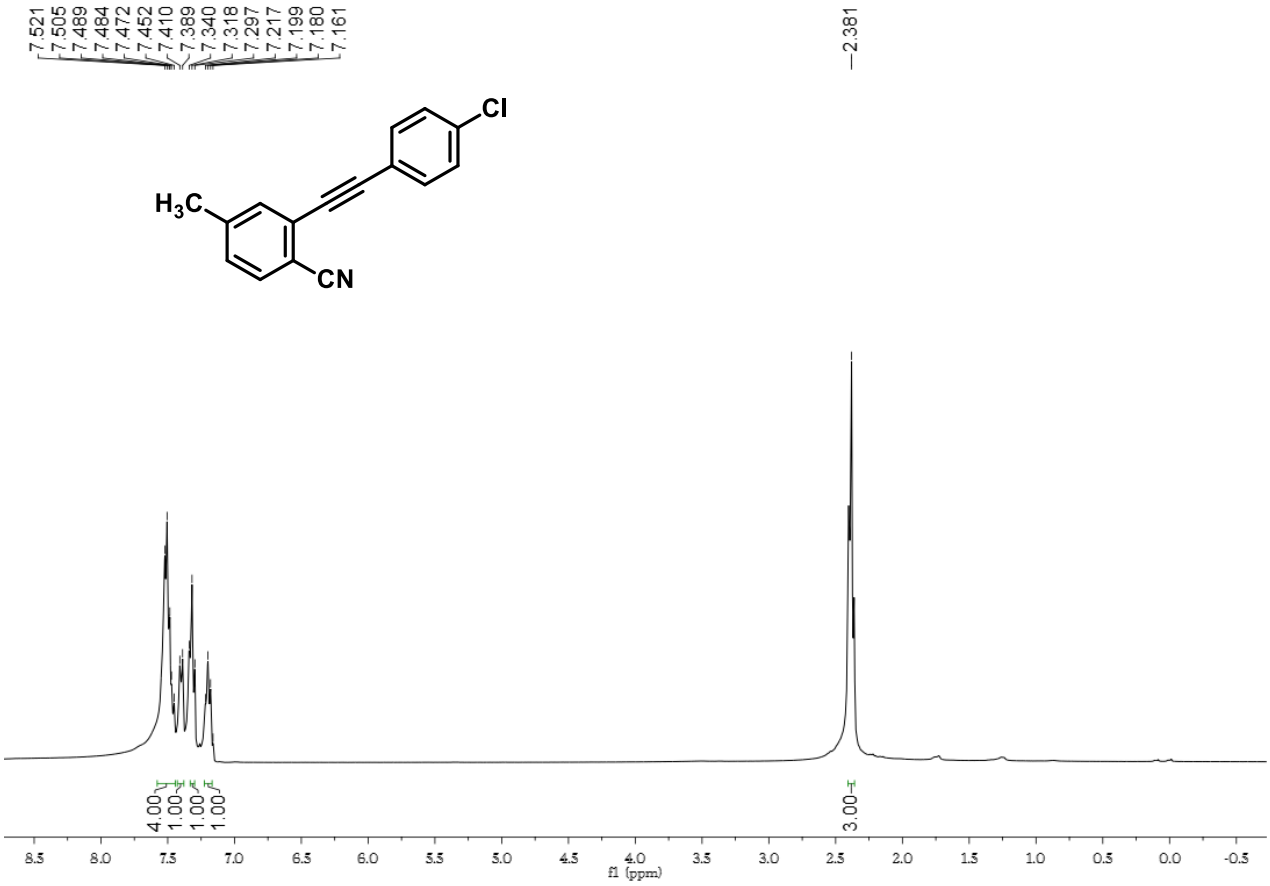
^{13}C NMR Spectrum of Compound 1m



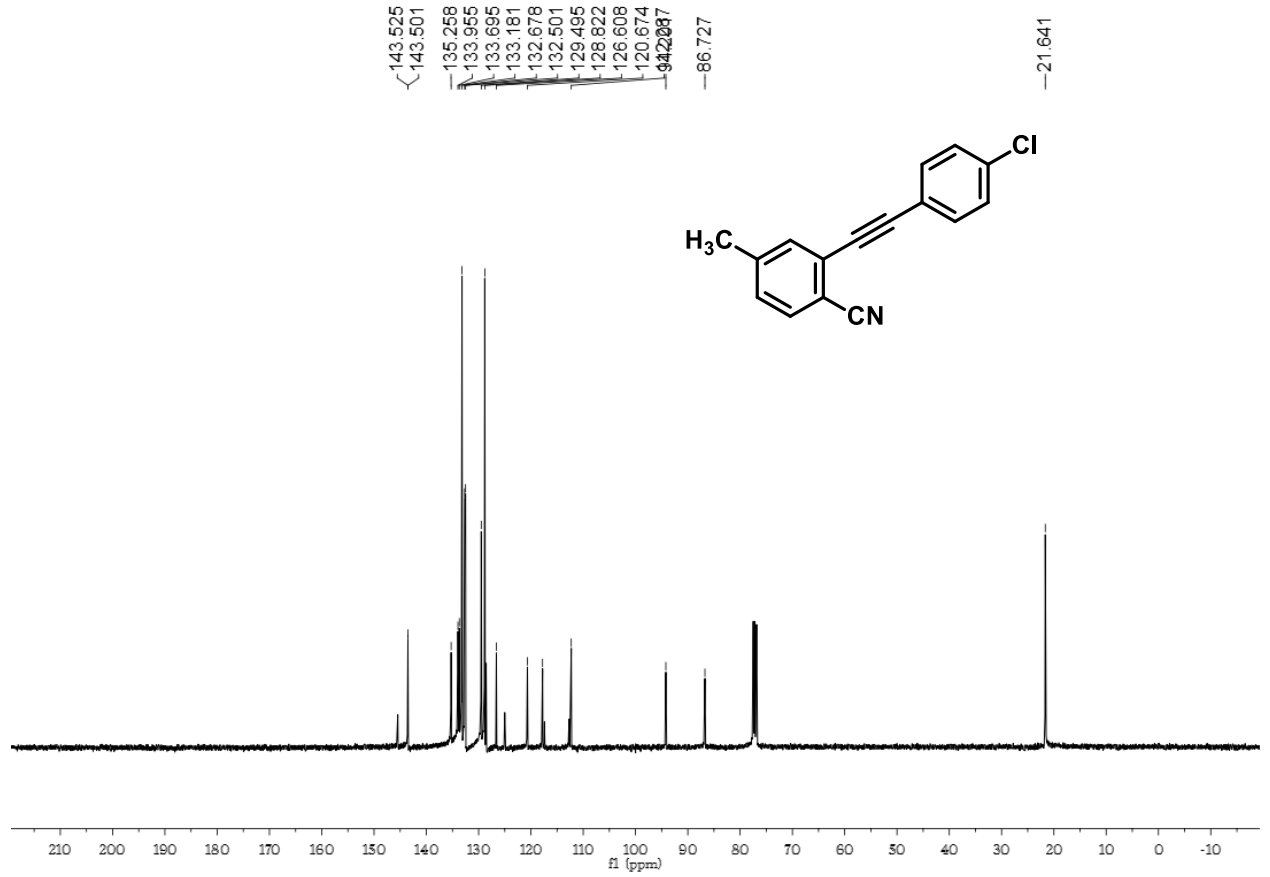
^{1}H NMR Spectrum of Compound 1n



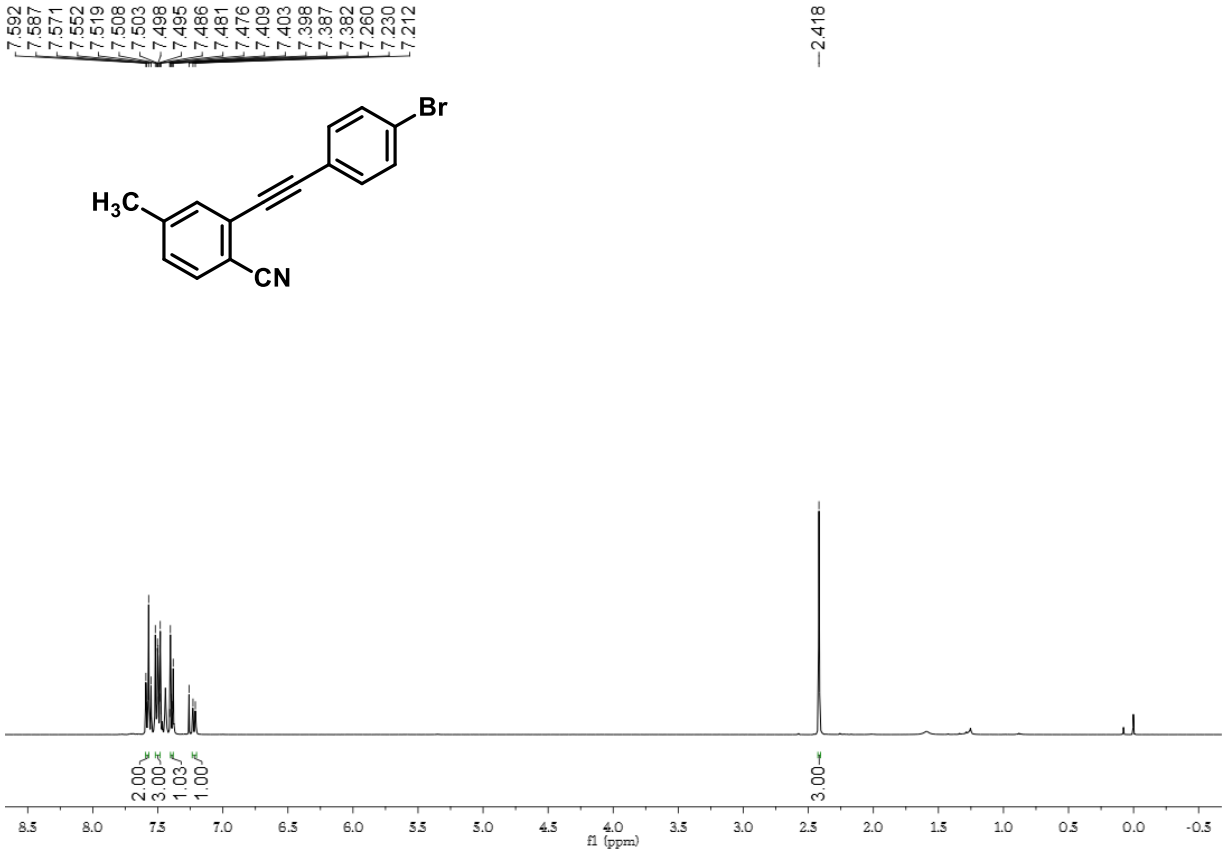
^{13}C NMR Spectrum of Compound 1n



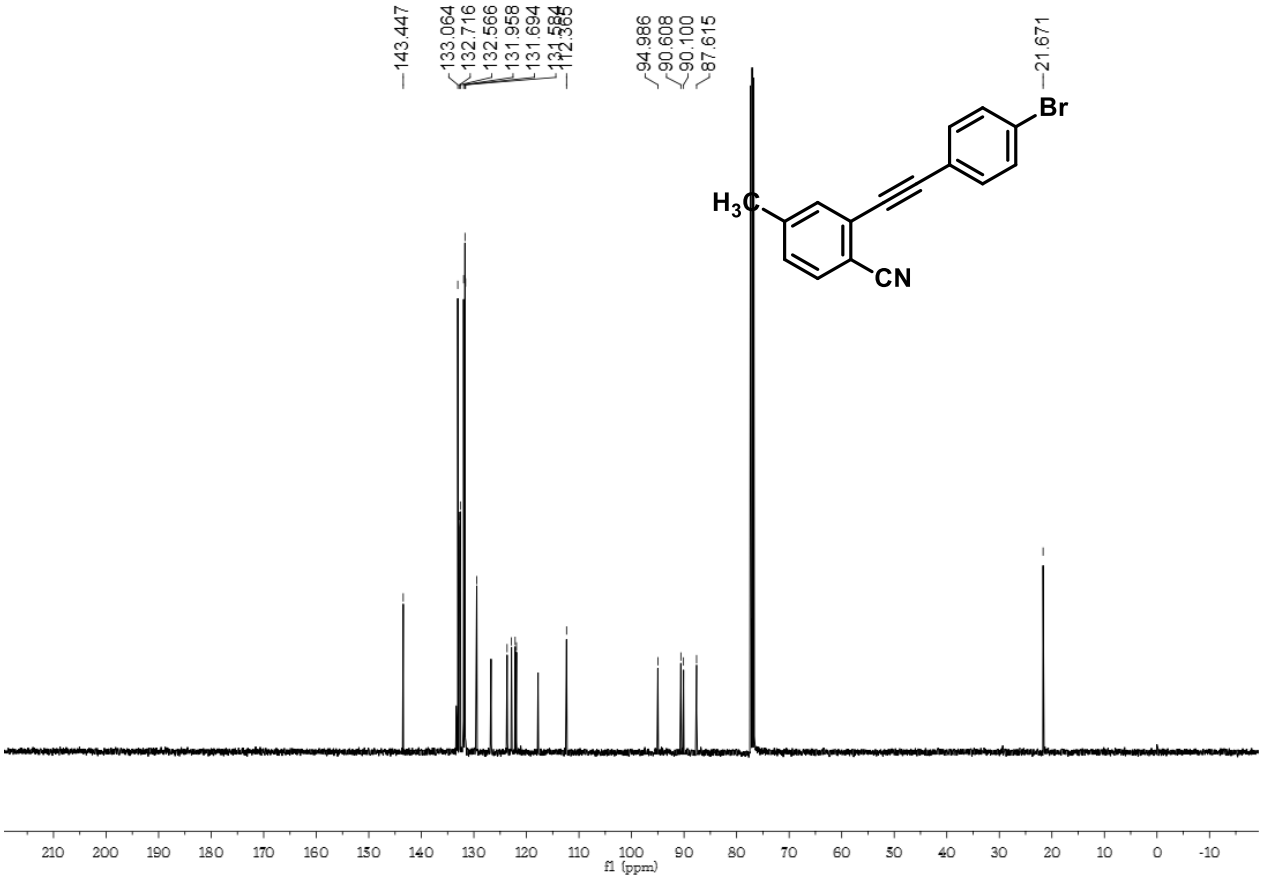
^{1}H NMR Spectrum of Compound 1o



^{13}C NMR Spectrum of Compound 1o

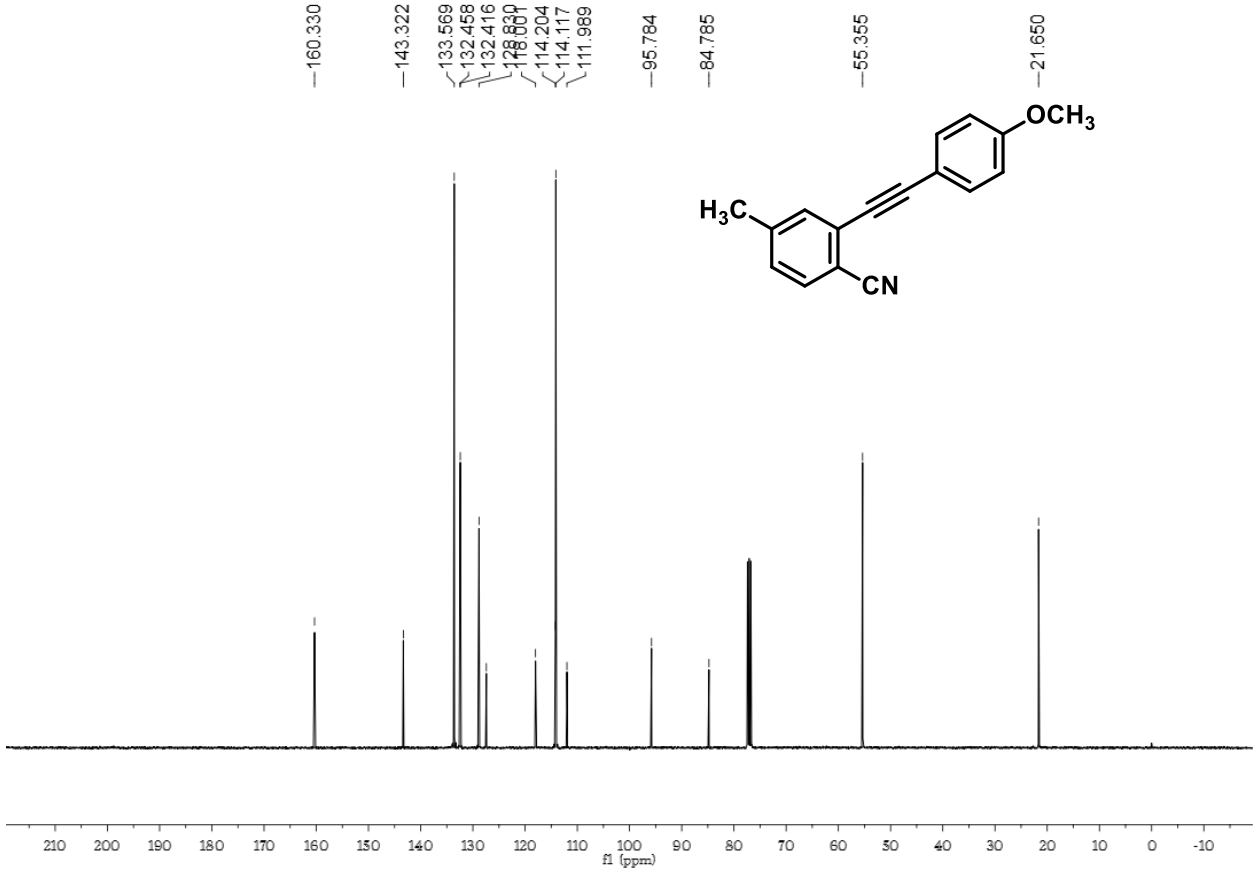


^{1}H NMR Spectrum of Compound 1p

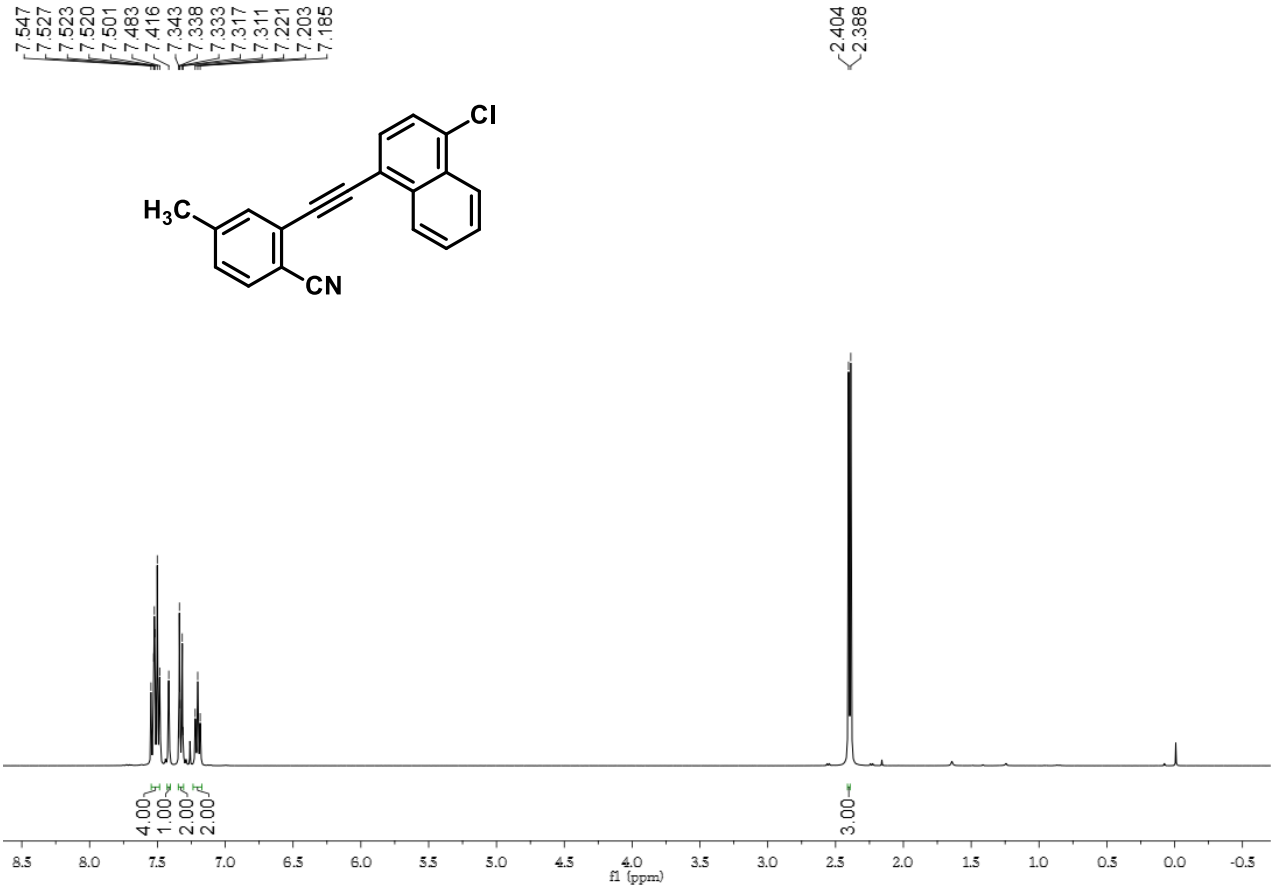


^{13}C NMR Spectrum of Compound 1p

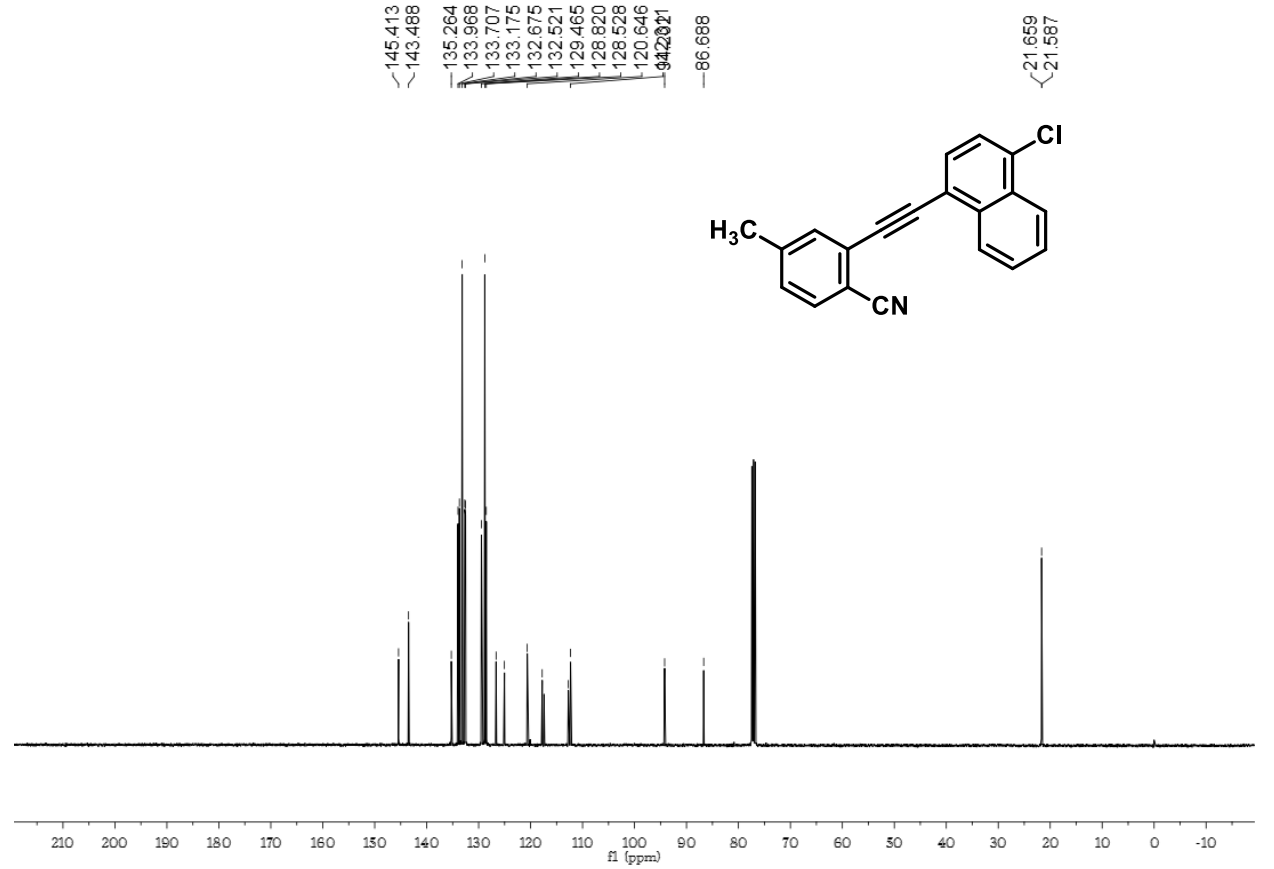
^{1}H NMR Spectrum of Compound 1q



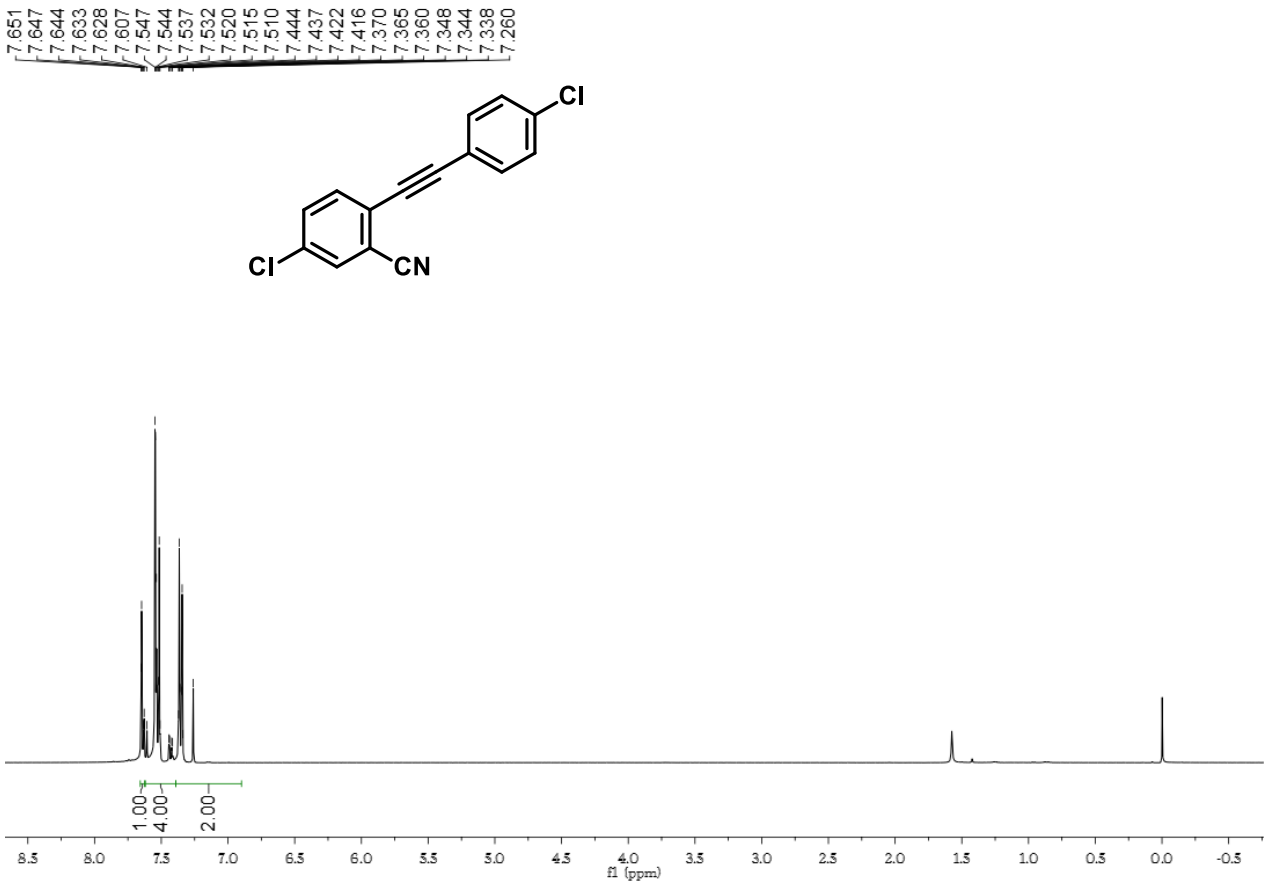
^{13}C NMR Spectrum of Compound 1q



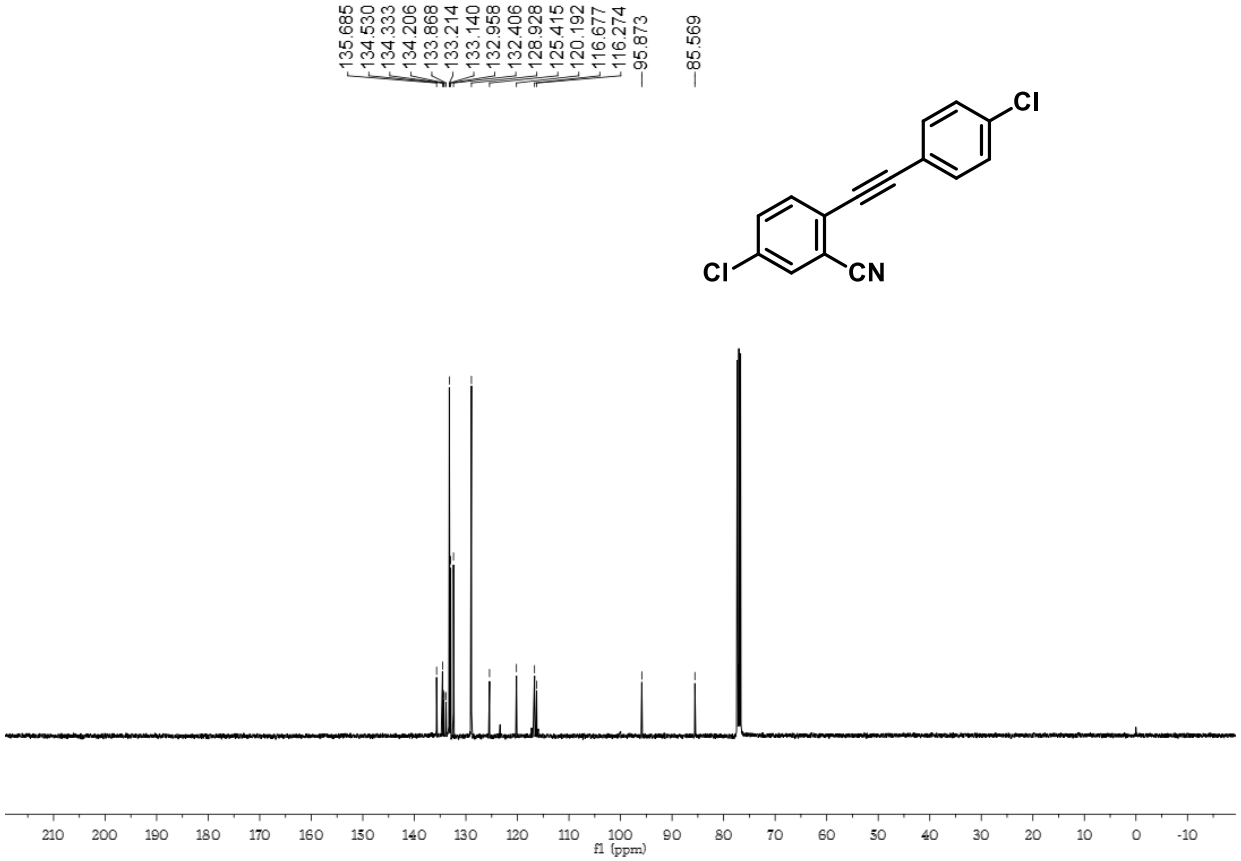
^{1}H NMR Spectrum of Compound 1r



^{13}C NMR Spectrum of Compound 1r

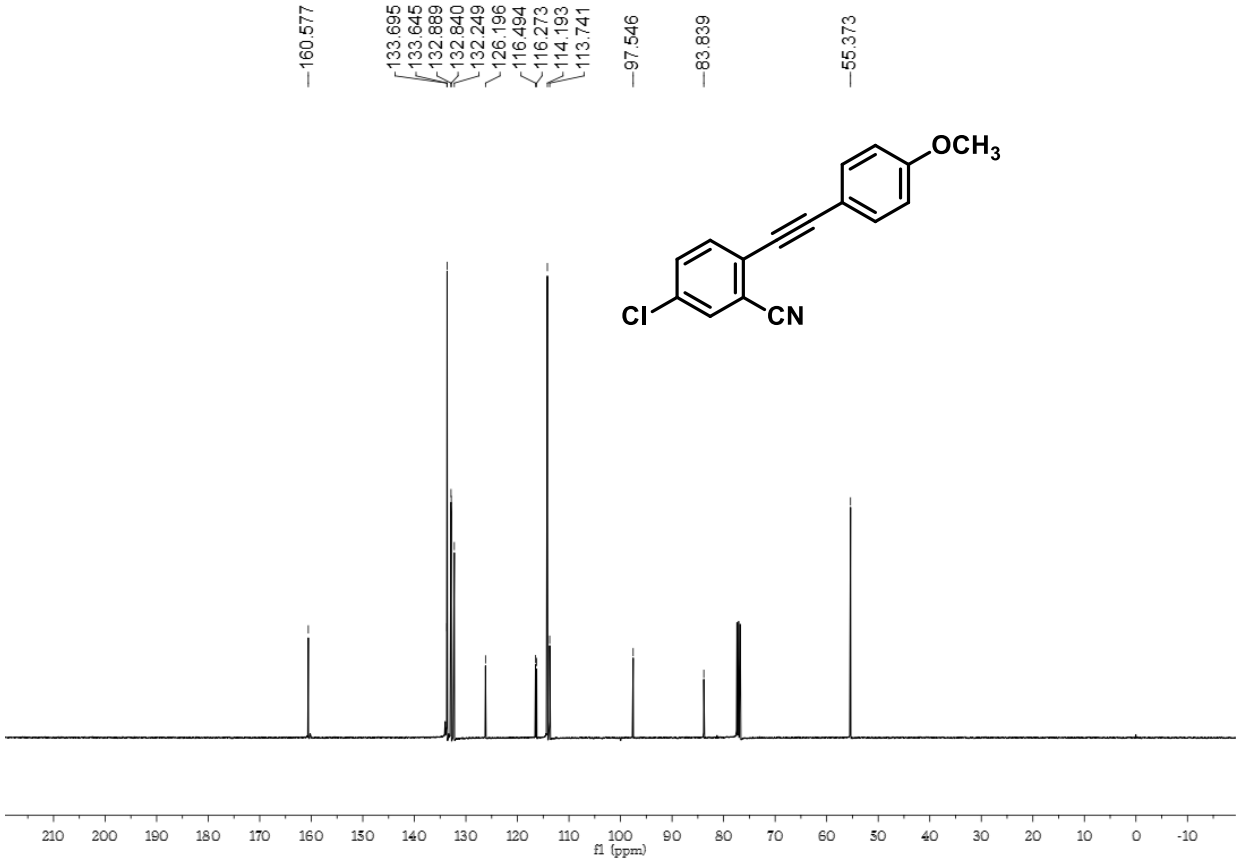


^{1}H NMR Spectrum of Compound 1s

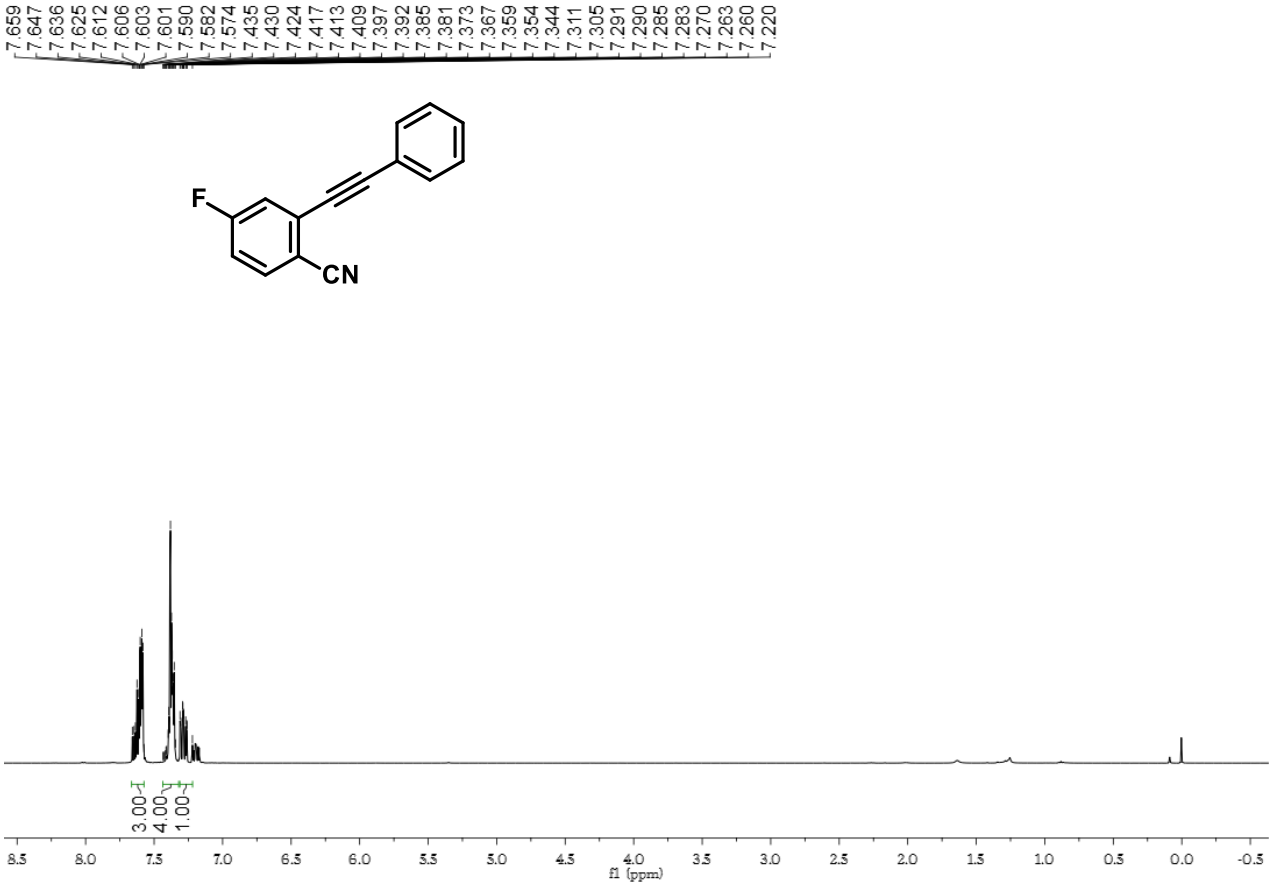


^{13}C NMR Spectrum of Compound 1s

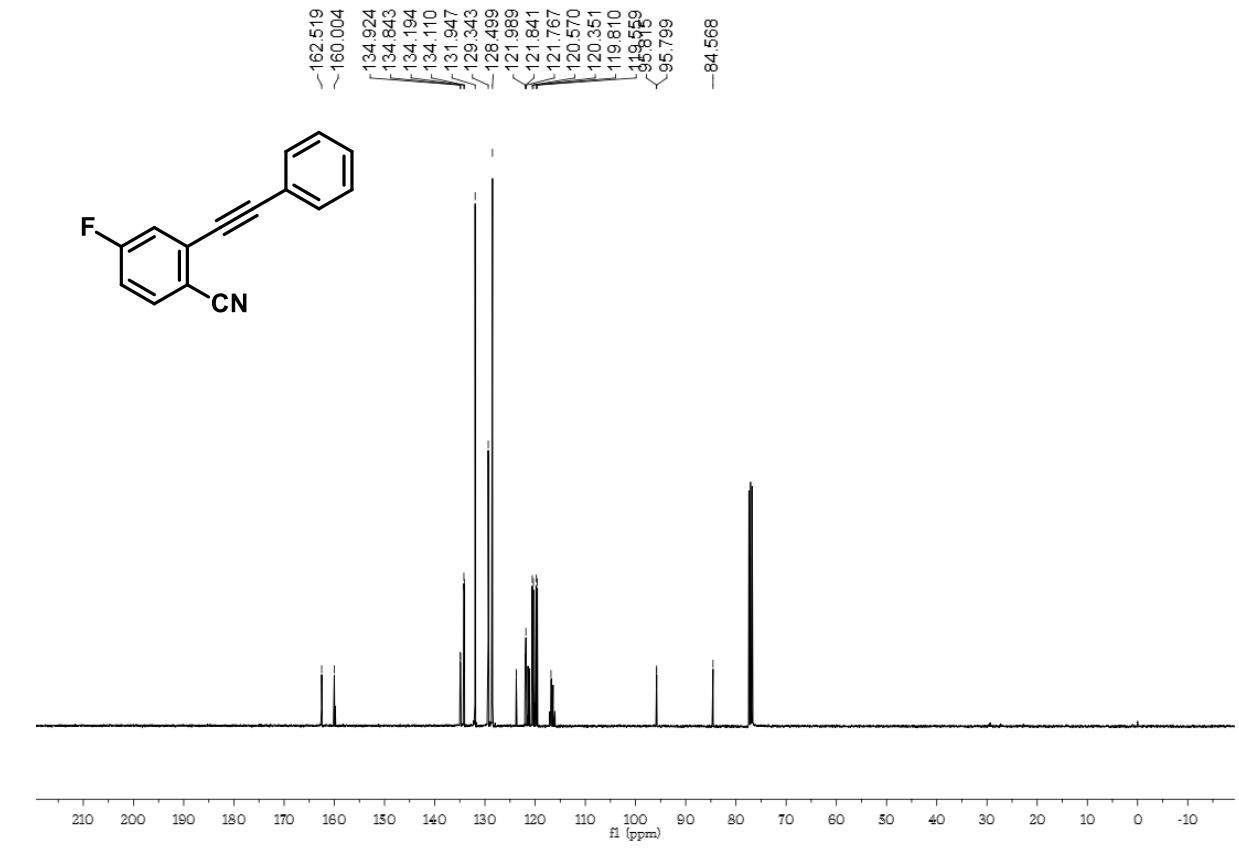
^{1}H NMR Spectrum of Compound 1t



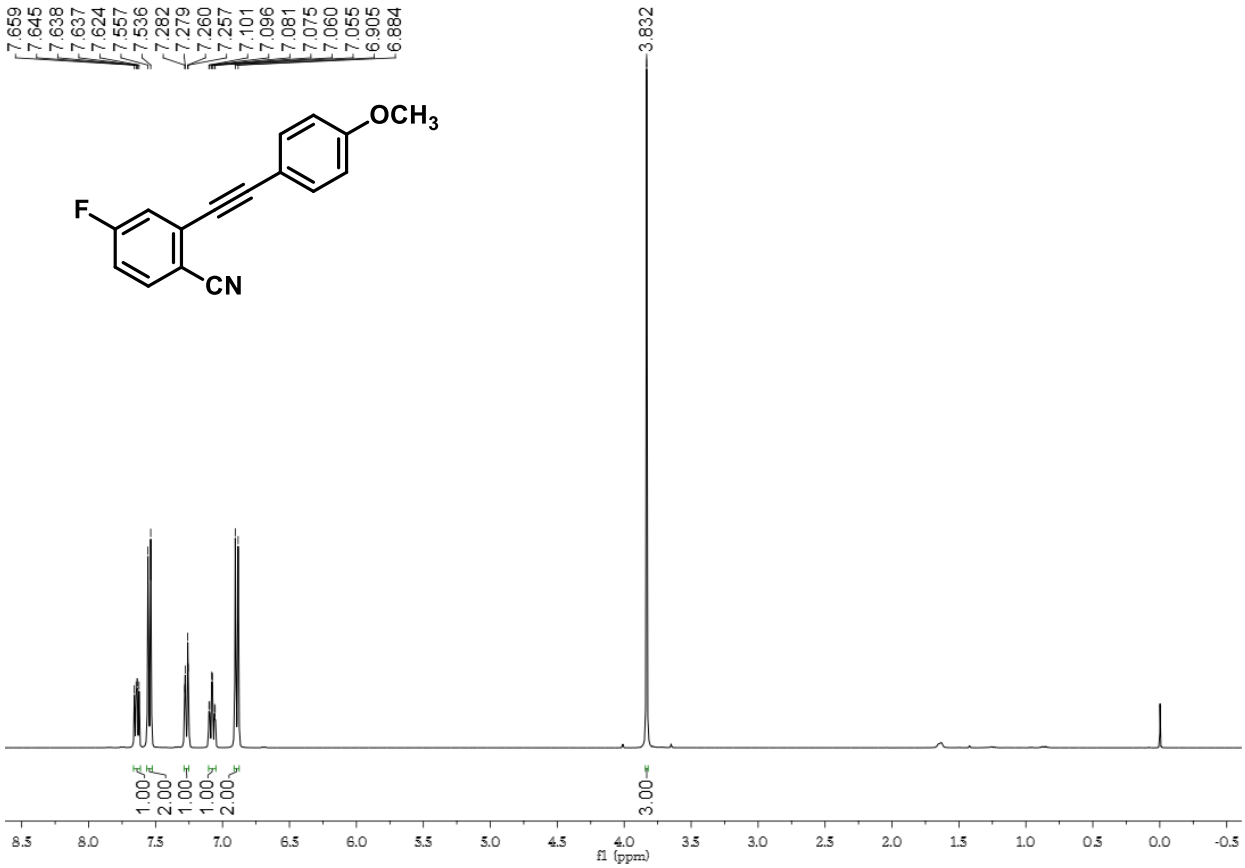
^{13}C NMR Spectrum of Compound 1t



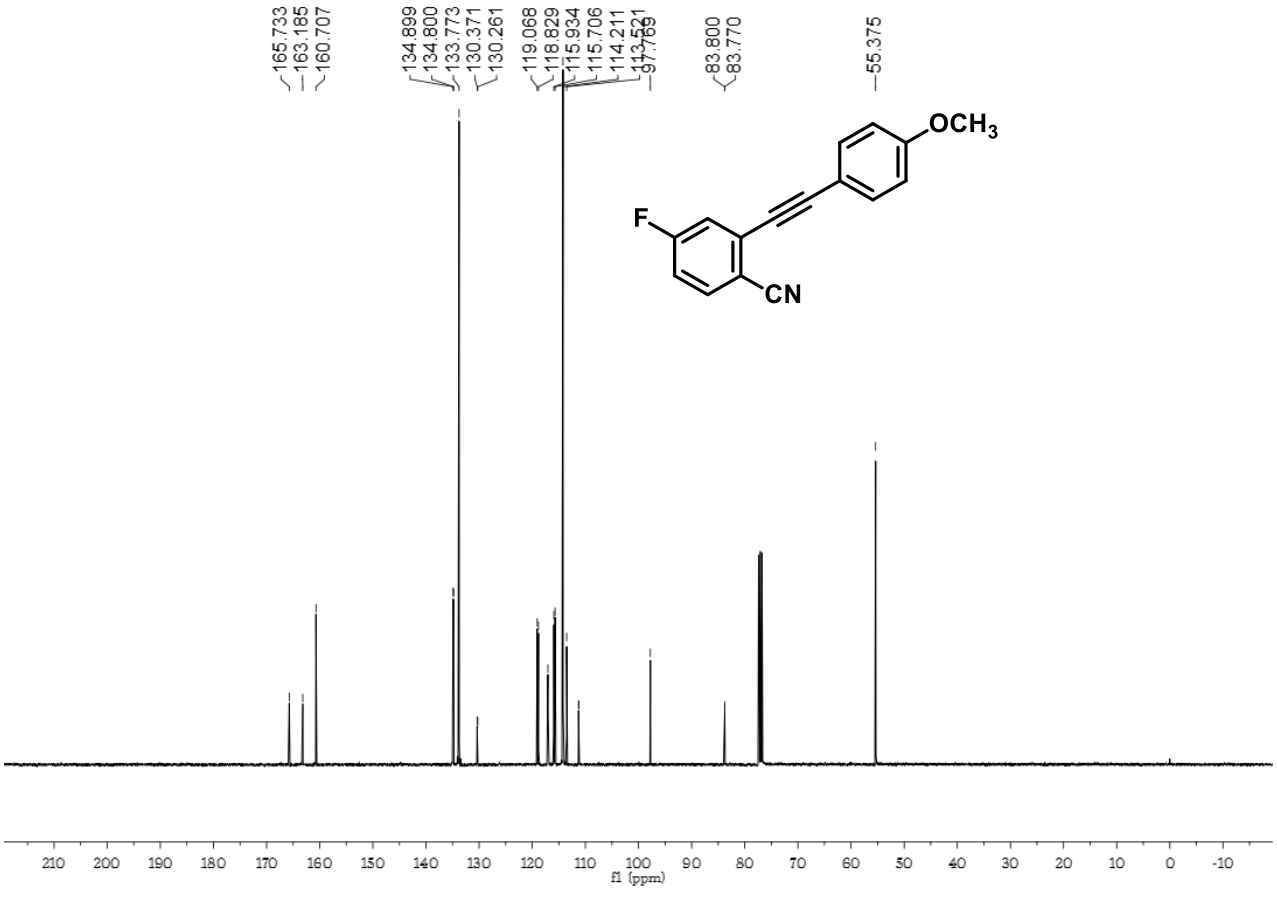
^{1}H NMR Spectrum of Compound 1u



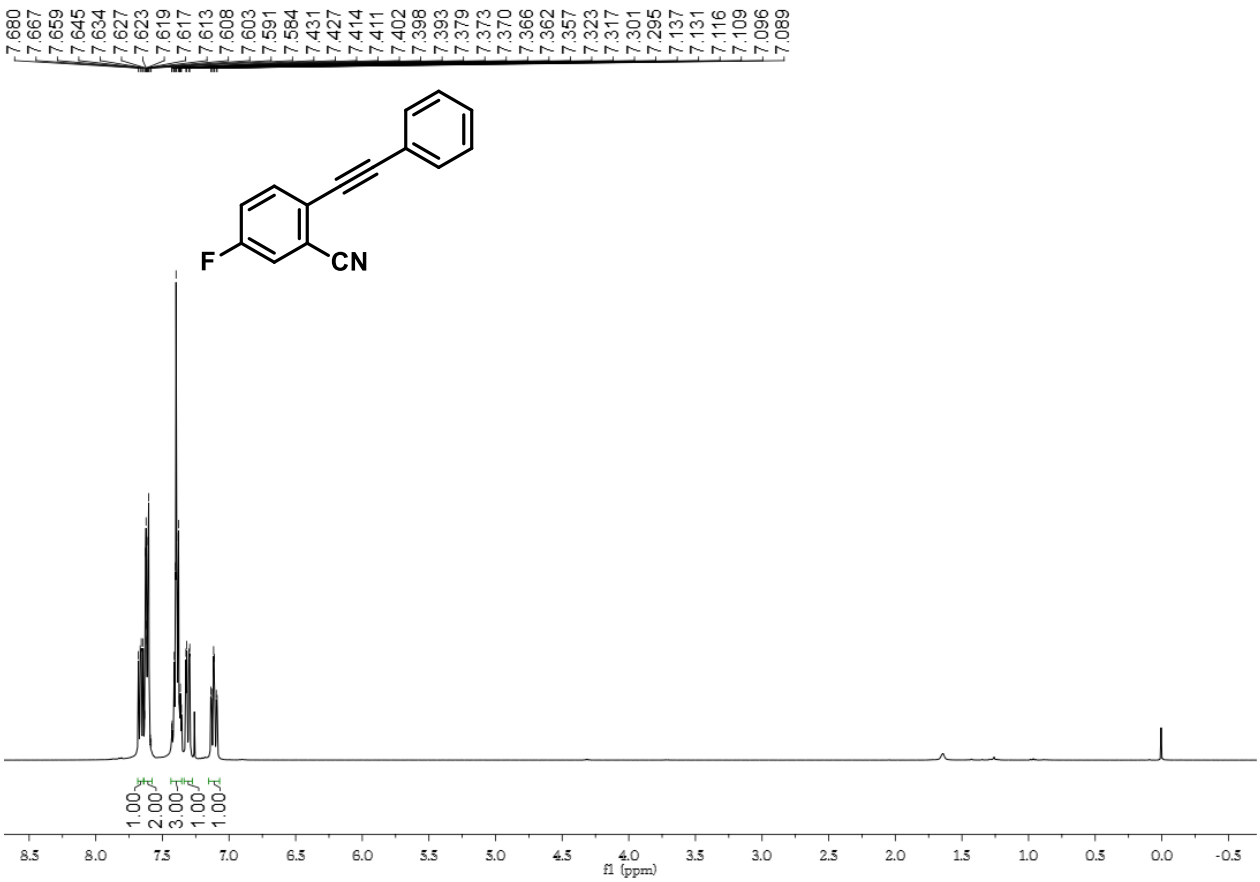
^{13}C NMR Spectrum of Compound 1u



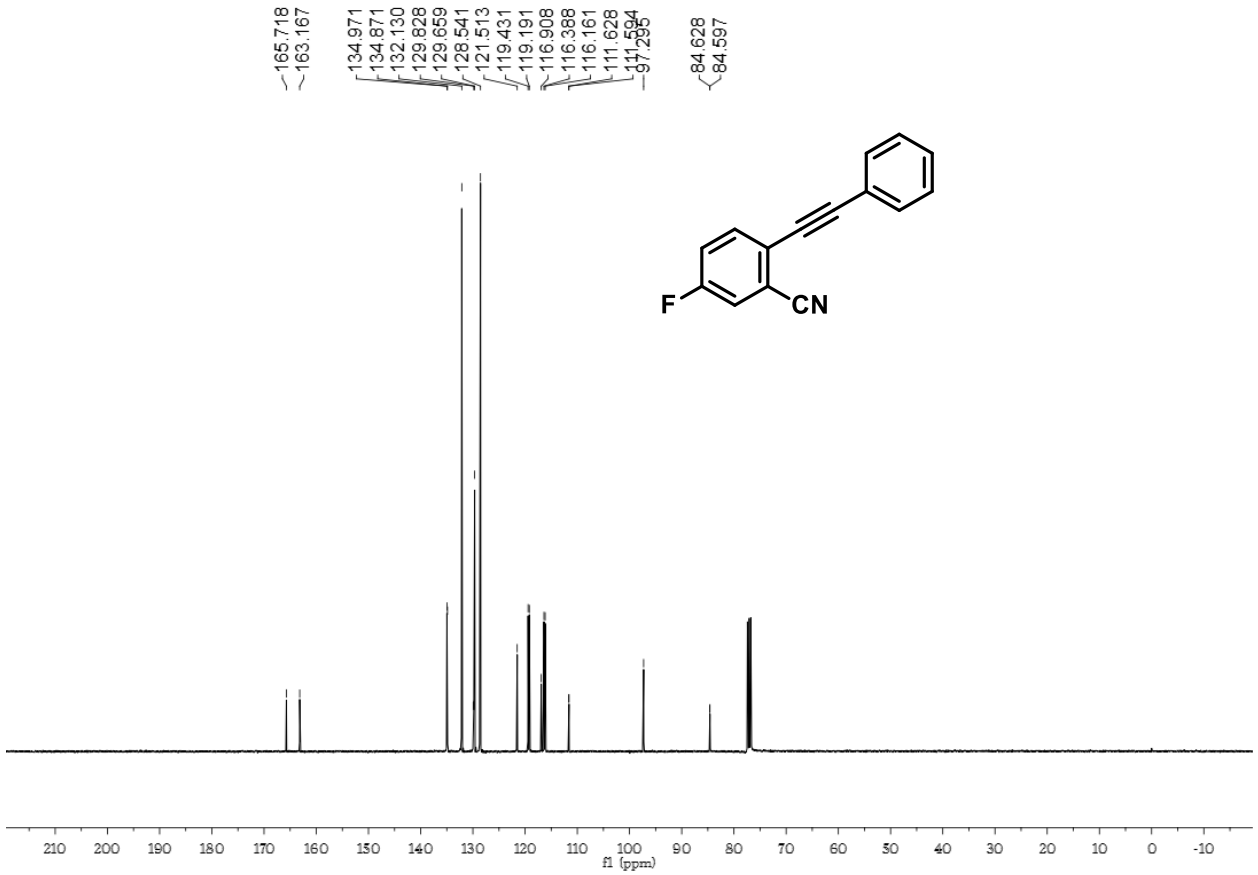
^{1}H NMR Spectrum of Compound 1v



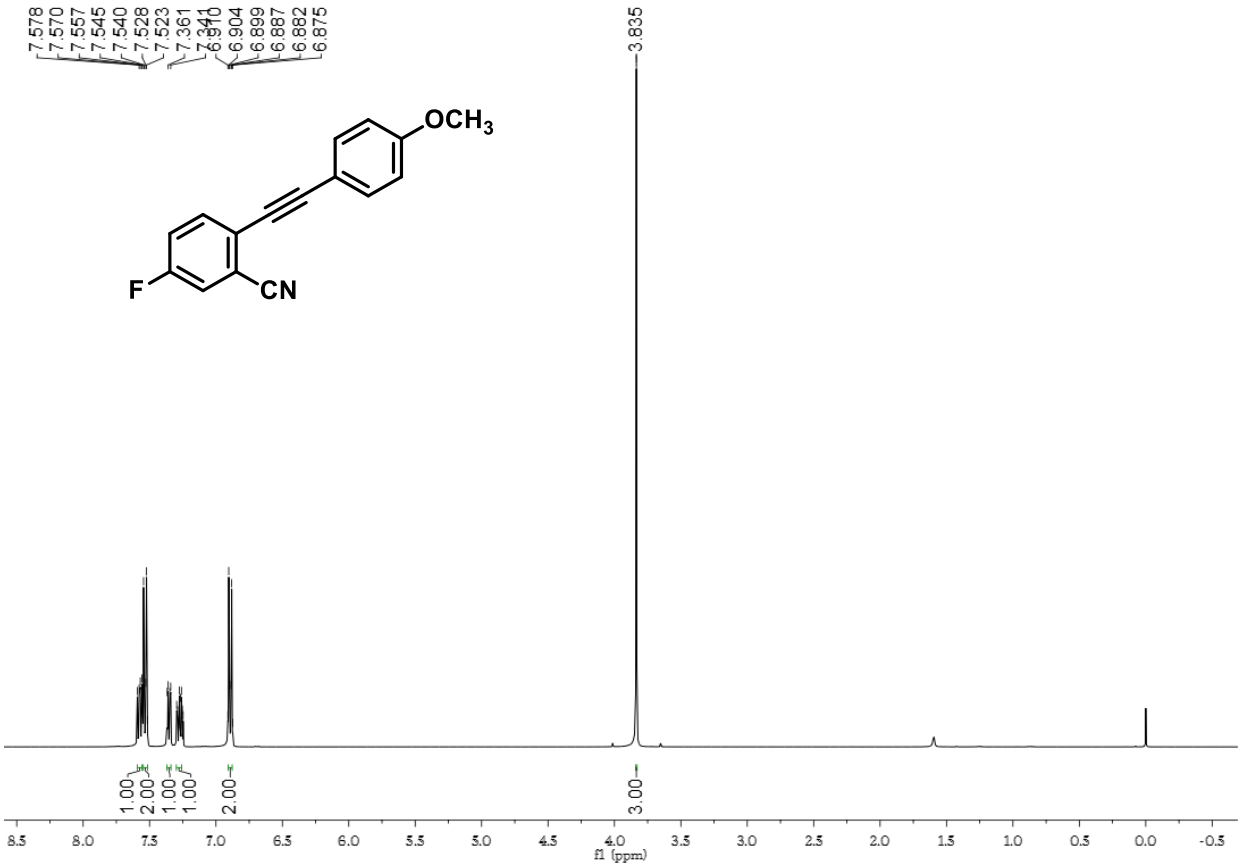
^{13}C NMR Spectrum of Compound 1v



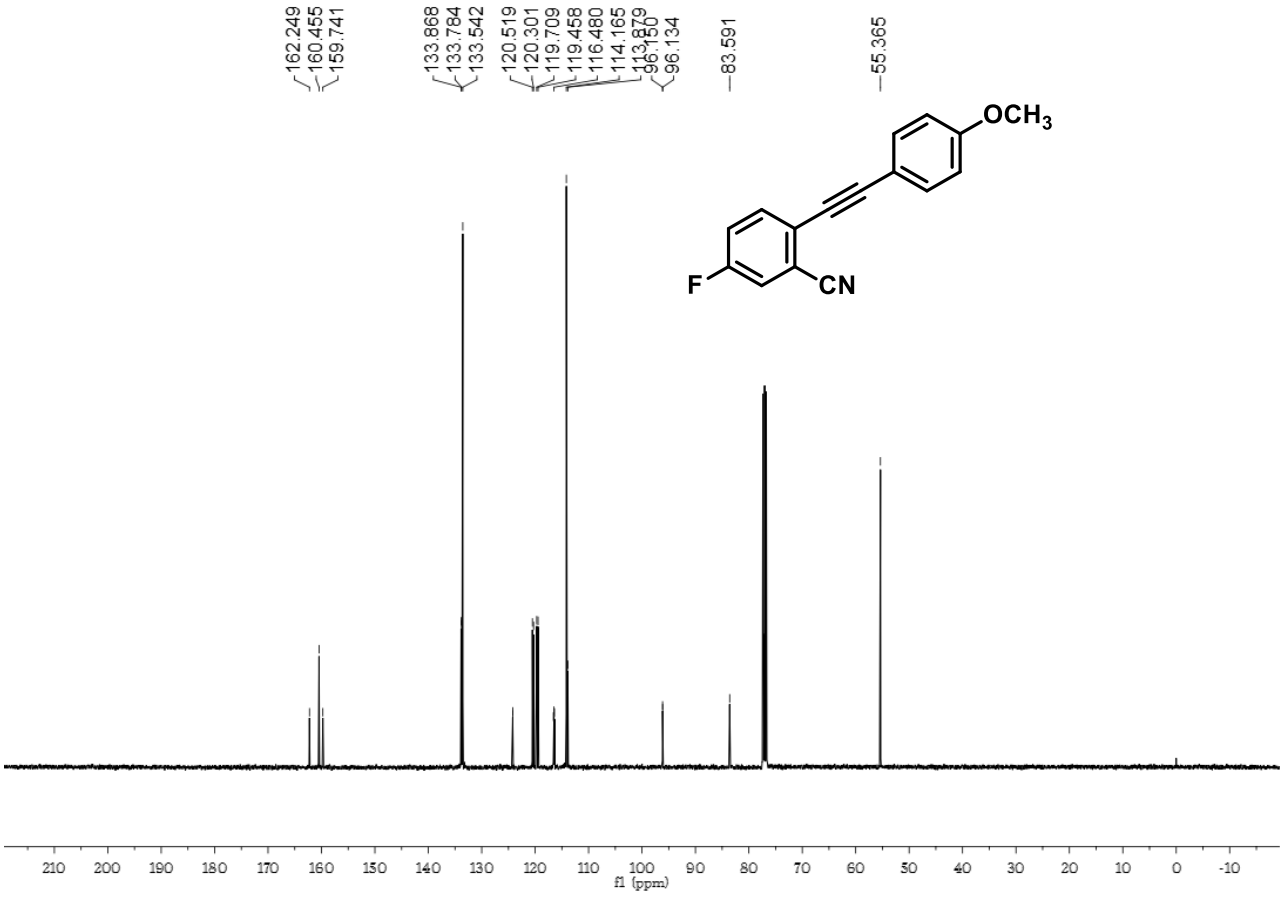
^{1}H NMR Spectrum of Compound 1w



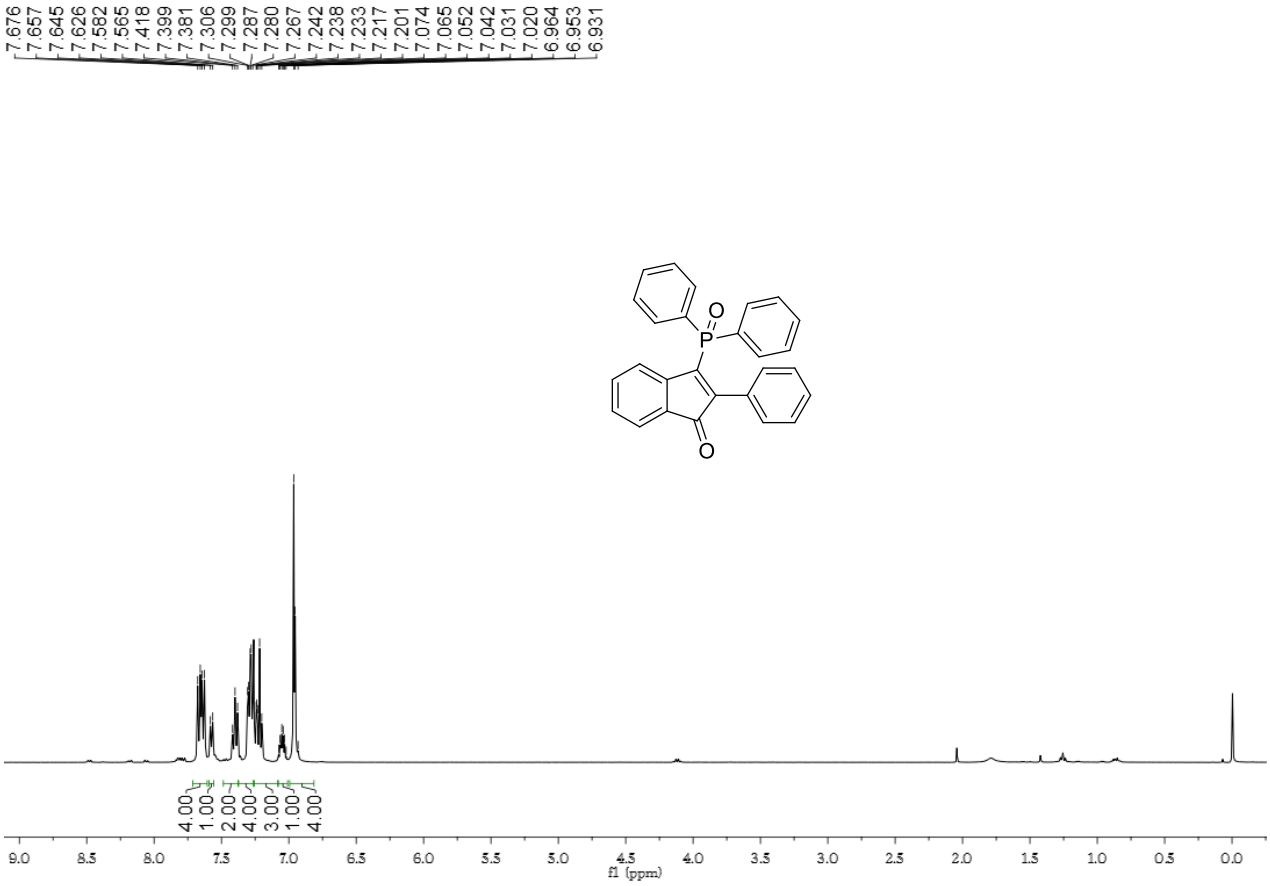
^{13}C NMR Spectrum of Compound 1w



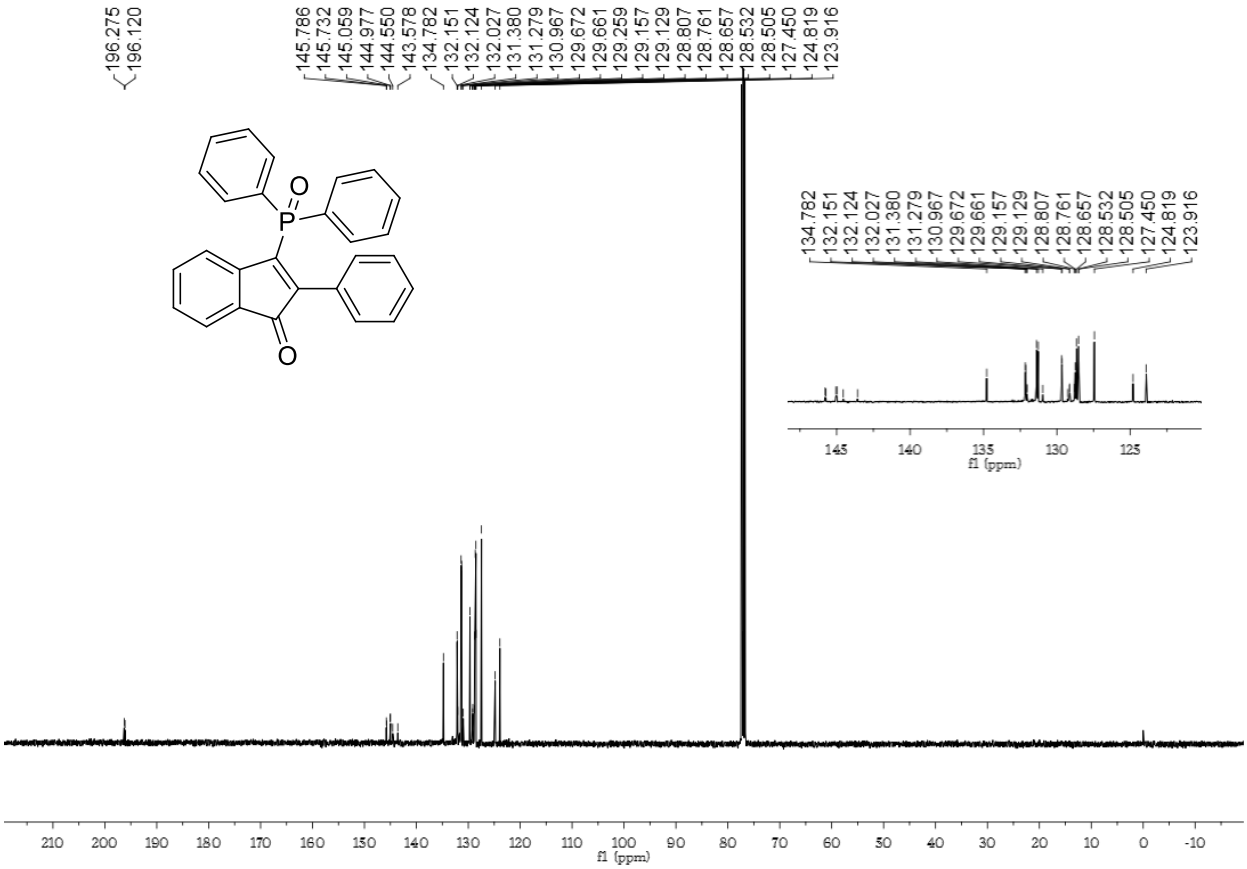
^{1}H NMR Spectrum of Compound 1x



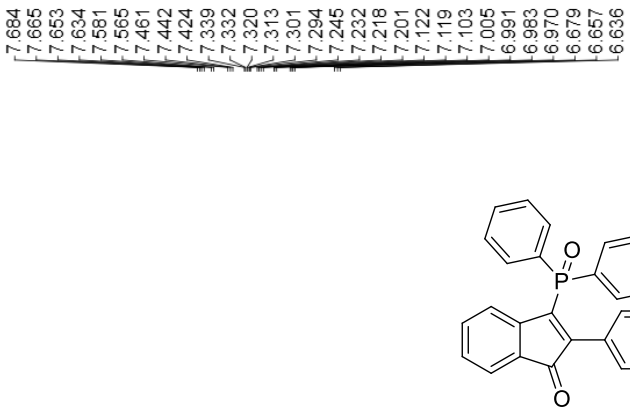
^{13}C NMR Spectrum of Compound 1x



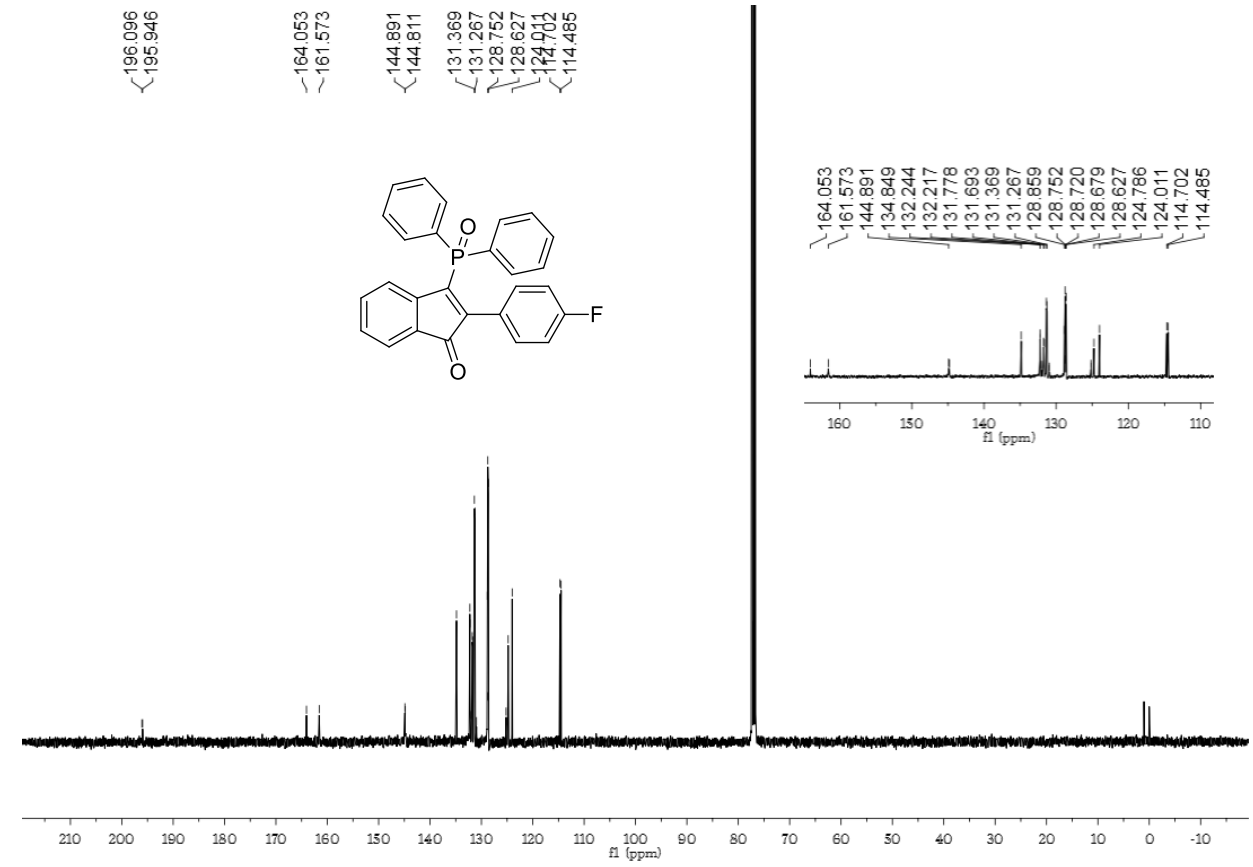
^{1}H NMR Spectrum of Compound 3a



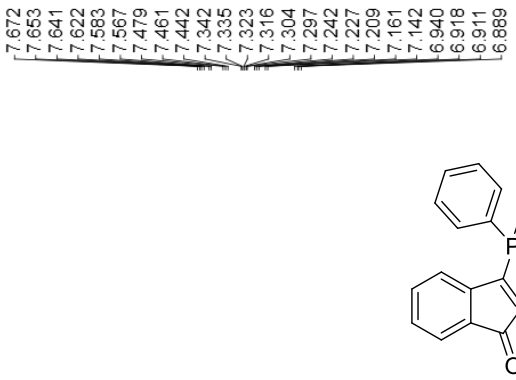
^{13}C NMR Spectrum of Compound 3a



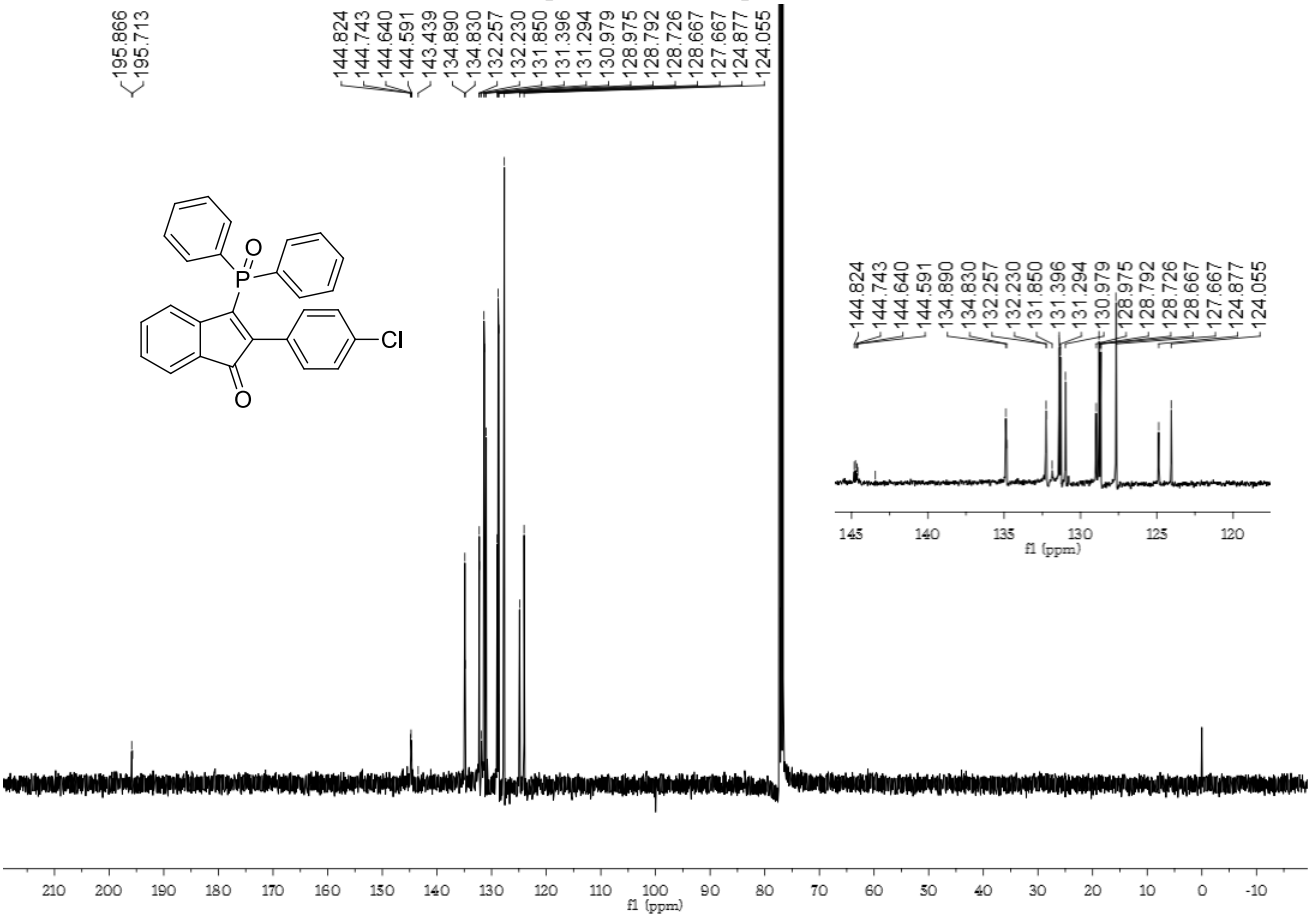
^{1}H NMR Spectrum of Compound 3b



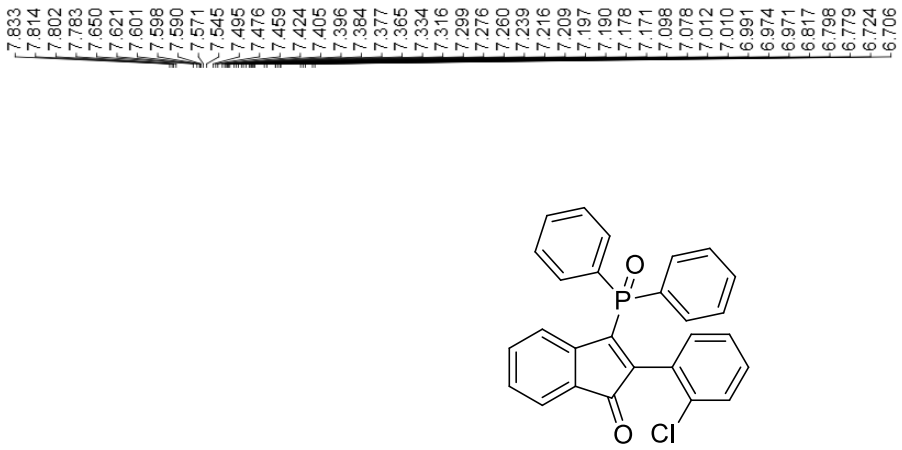
^{13}C NMR Spectrum of Compound 3b



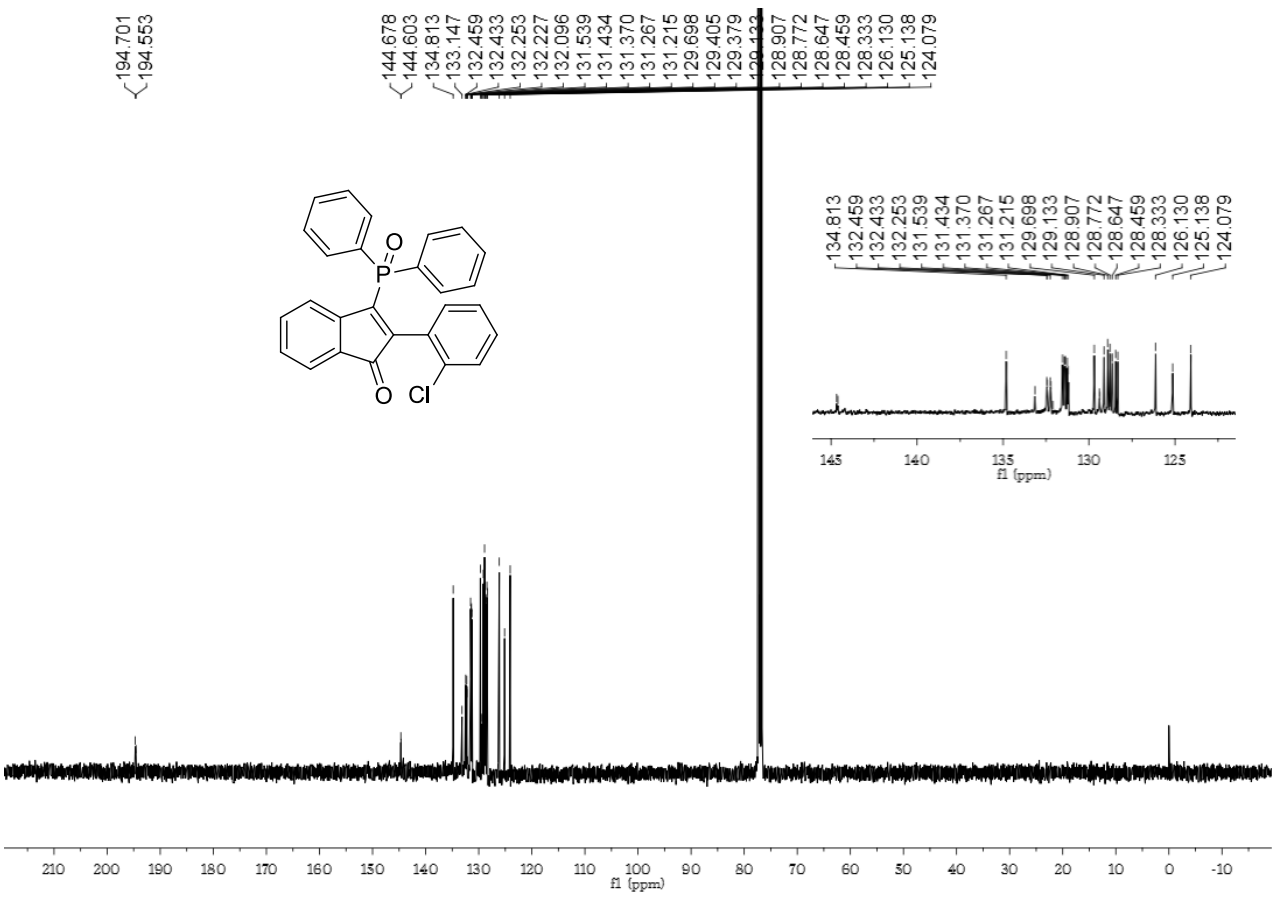
^{1}H NMR Spectrum of Compound 3c



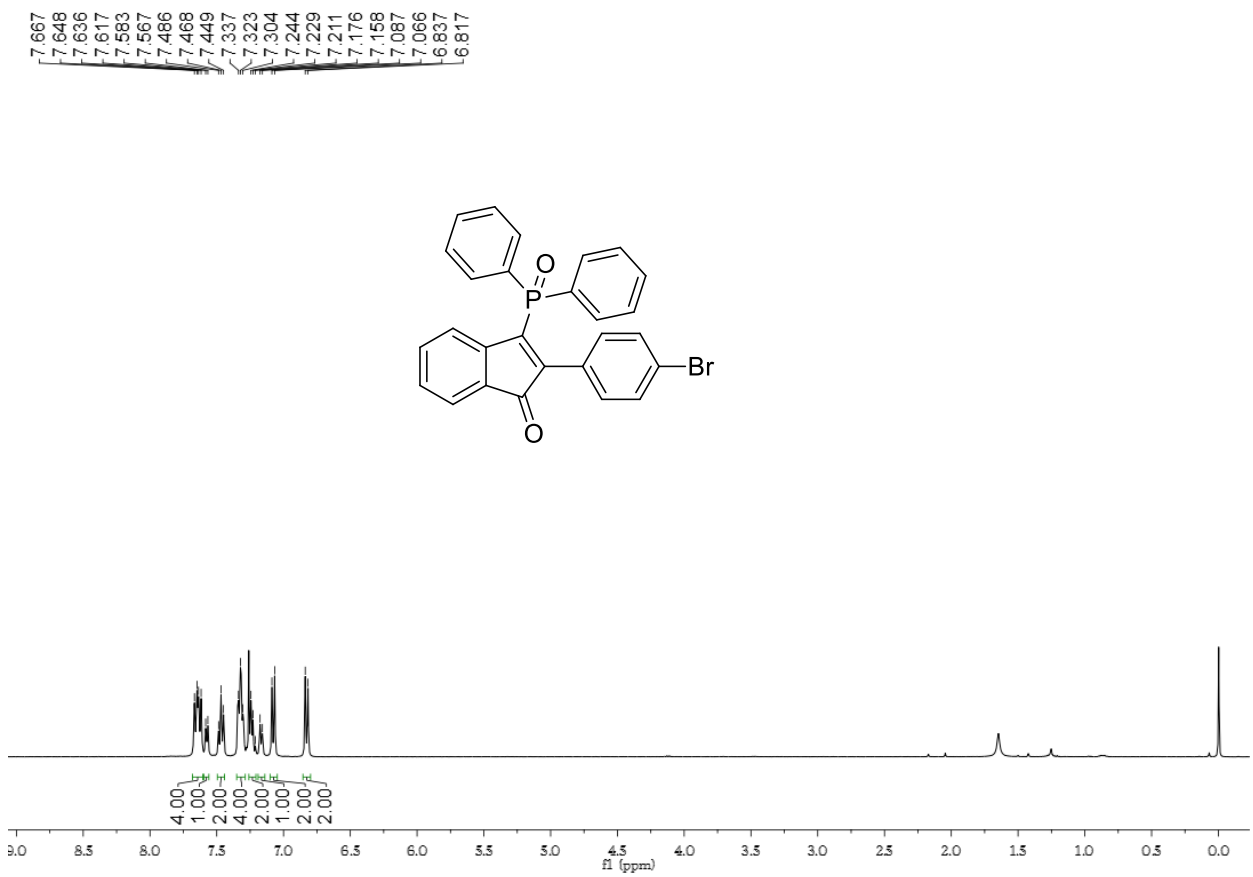
^{13}C NMR Spectrum of Compound 3c



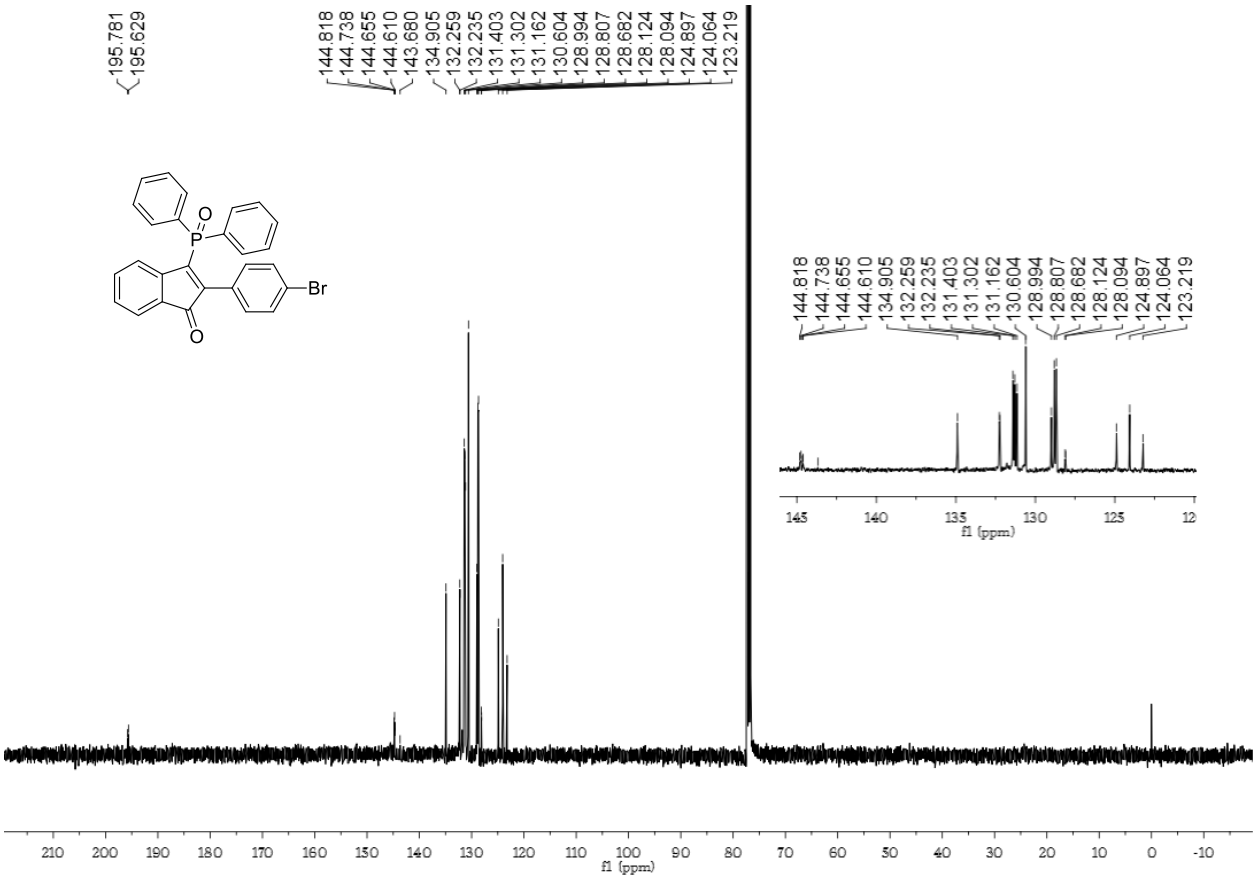
^{1}H NMR Spectrum of Compound 3d



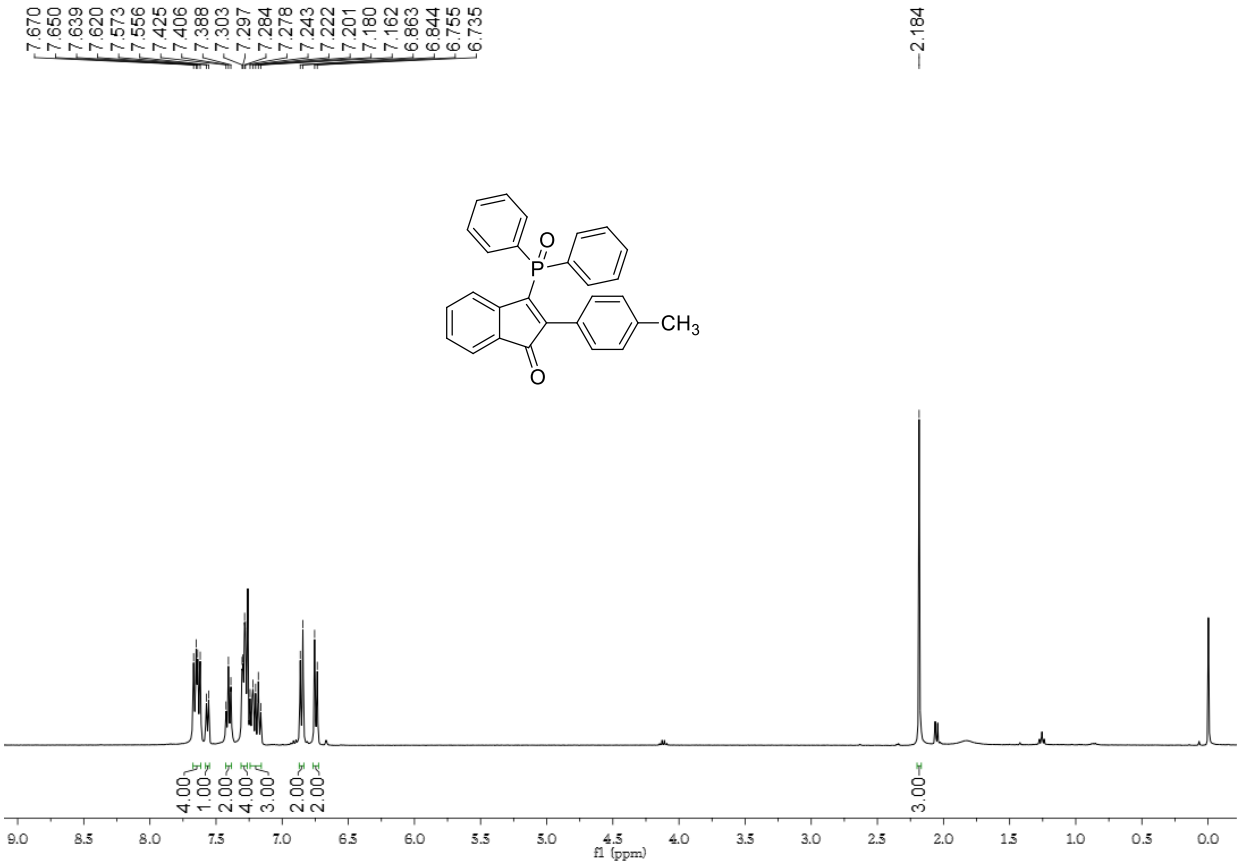
^{13}C NMR Spectrum of Compound 3d



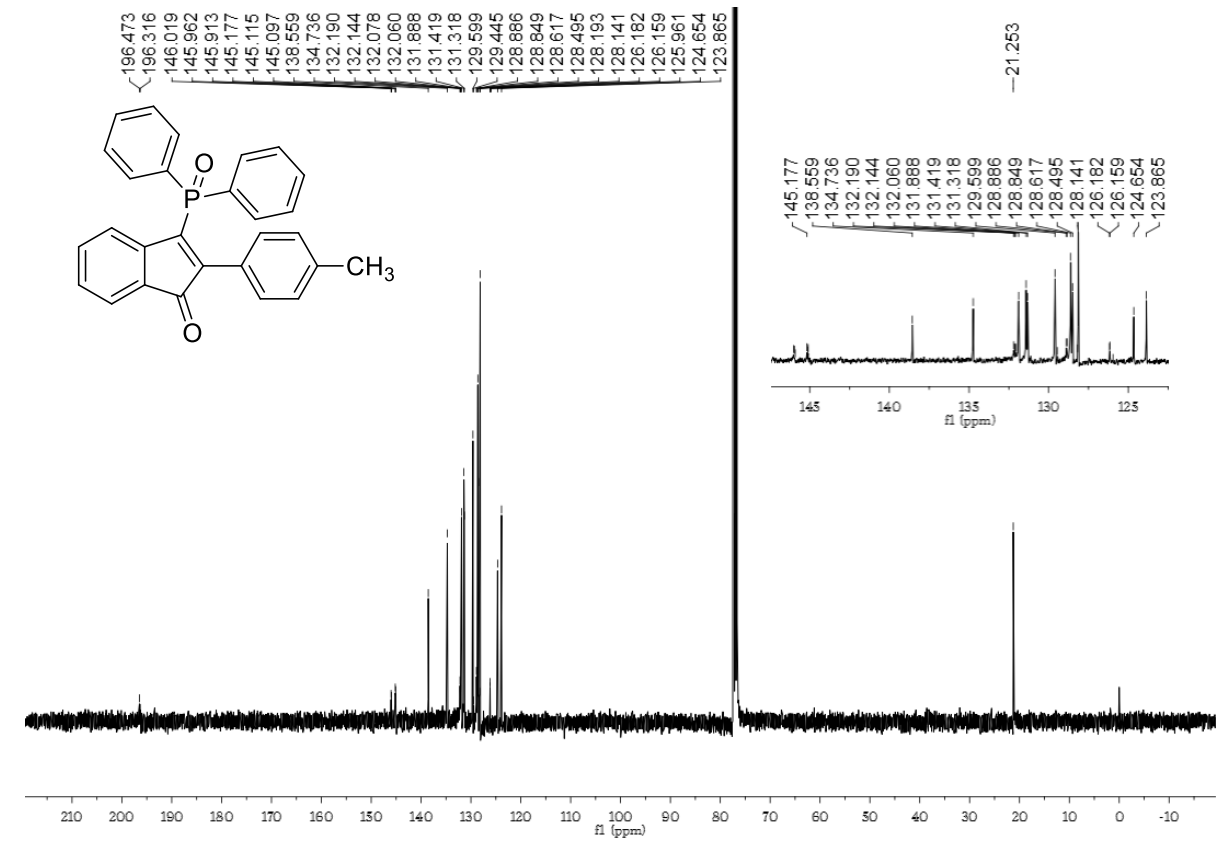
^{1}H NMR Spectrum of Compound 3e



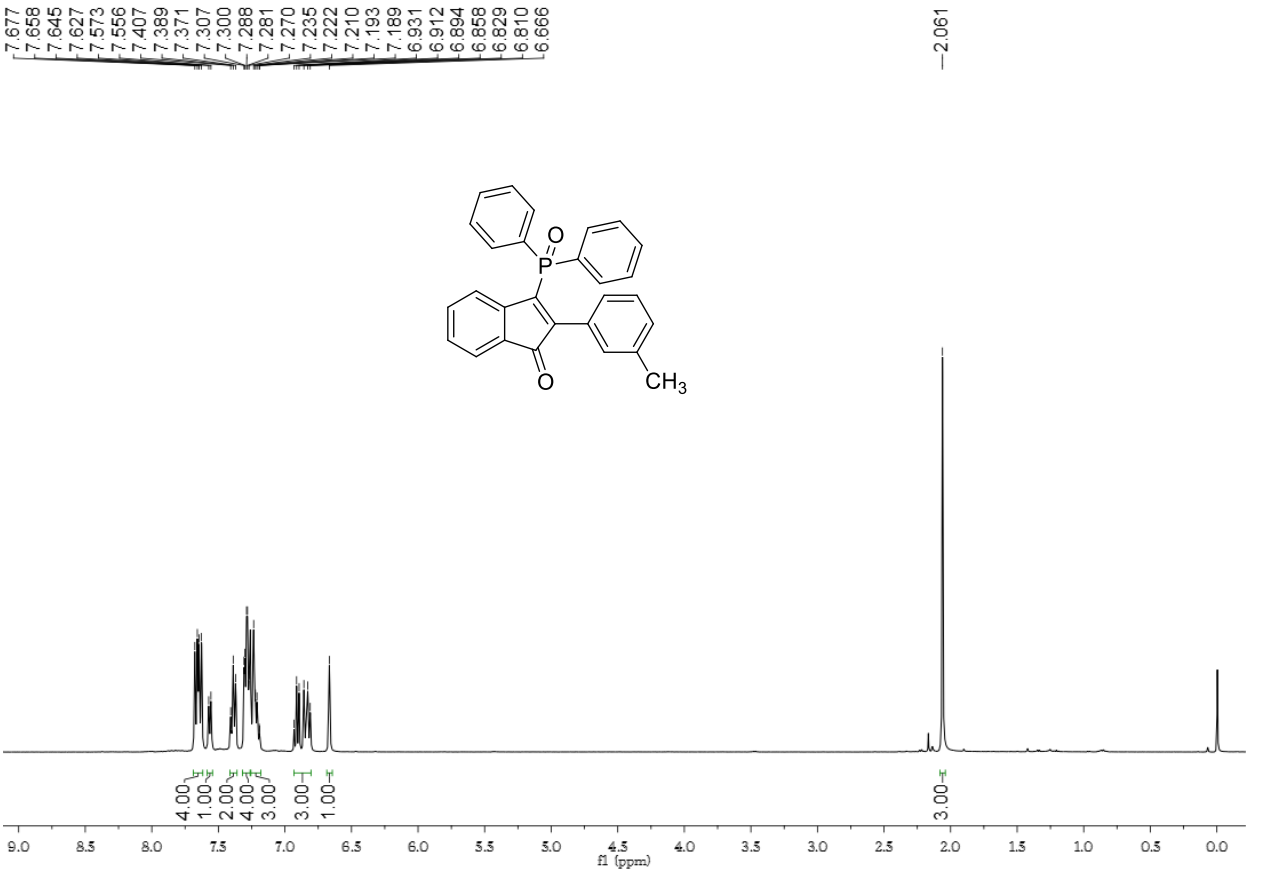
^{13}C NMR Spectrum of Compound 3e



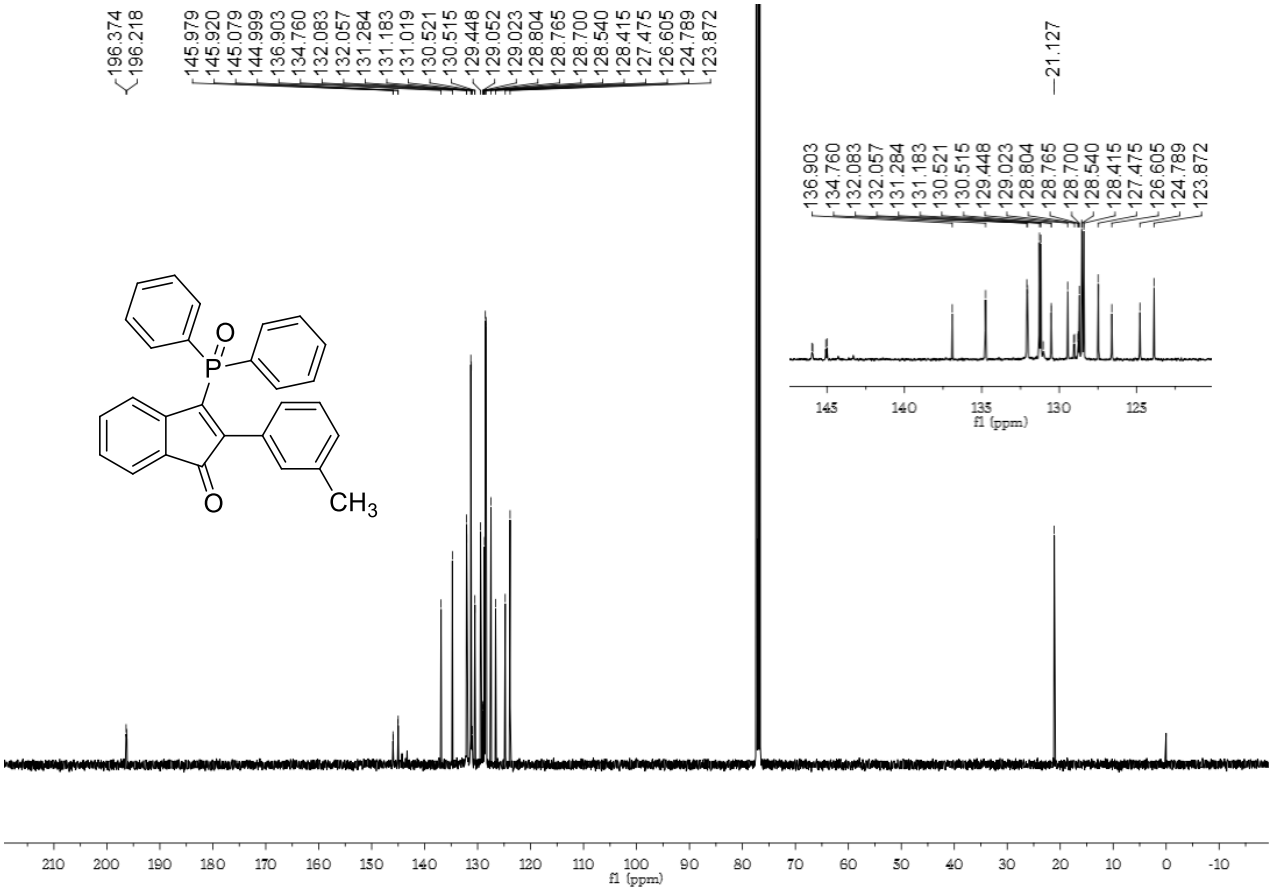
[1]H NMR Spectrum of Compound 3f



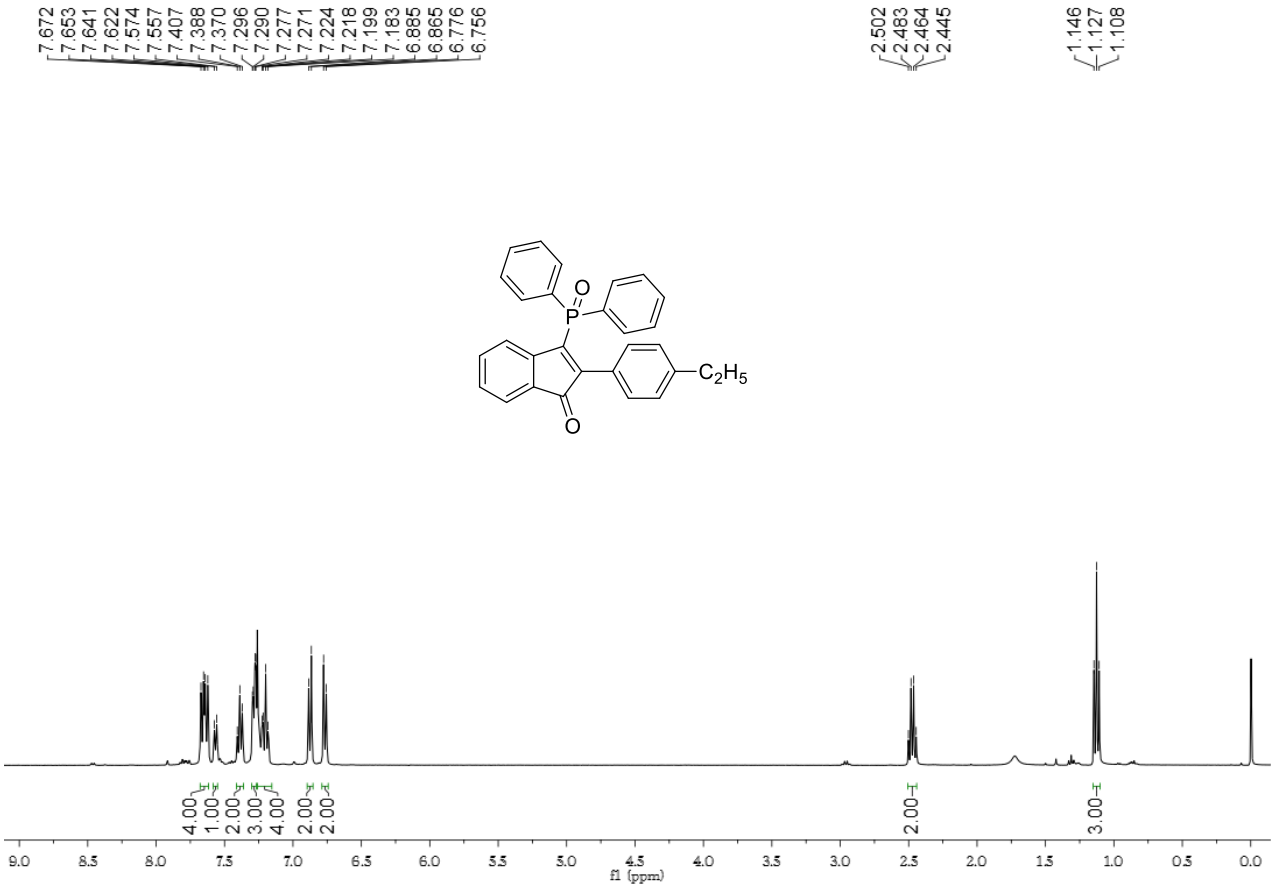
[13]C NMR Spectrum of Compound 3f



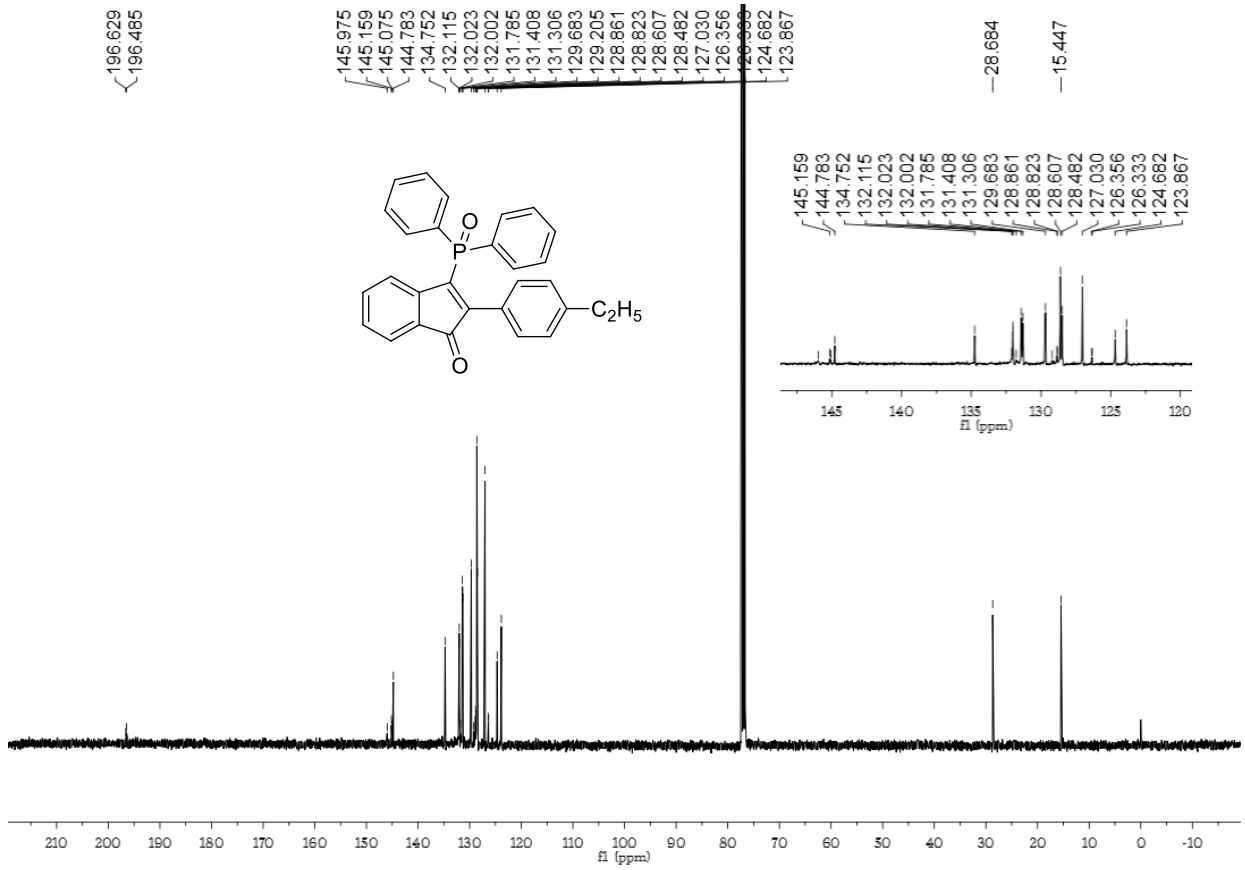
^{1}H NMR Spectrum of Compound 3g



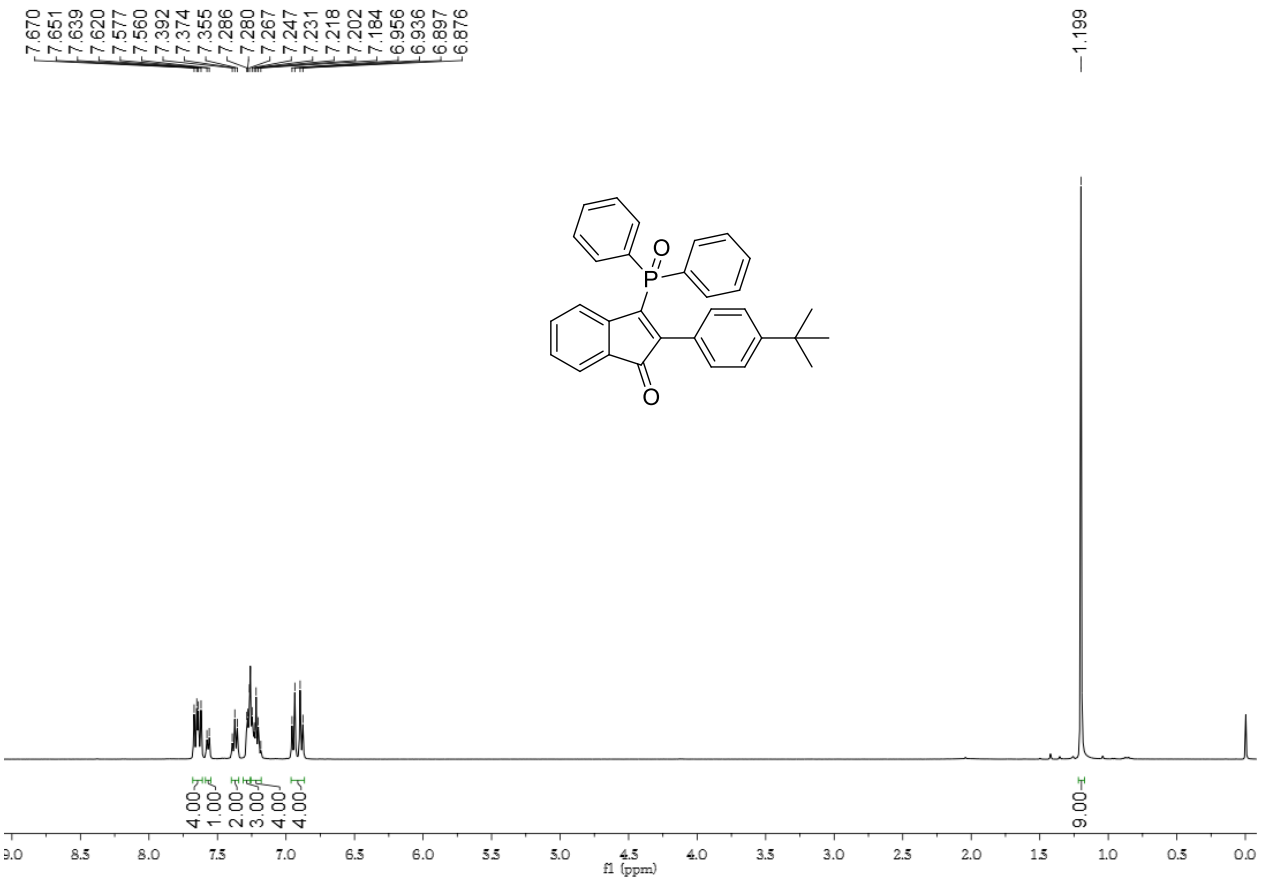
^{13}C NMR Spectrum of Compound 3g



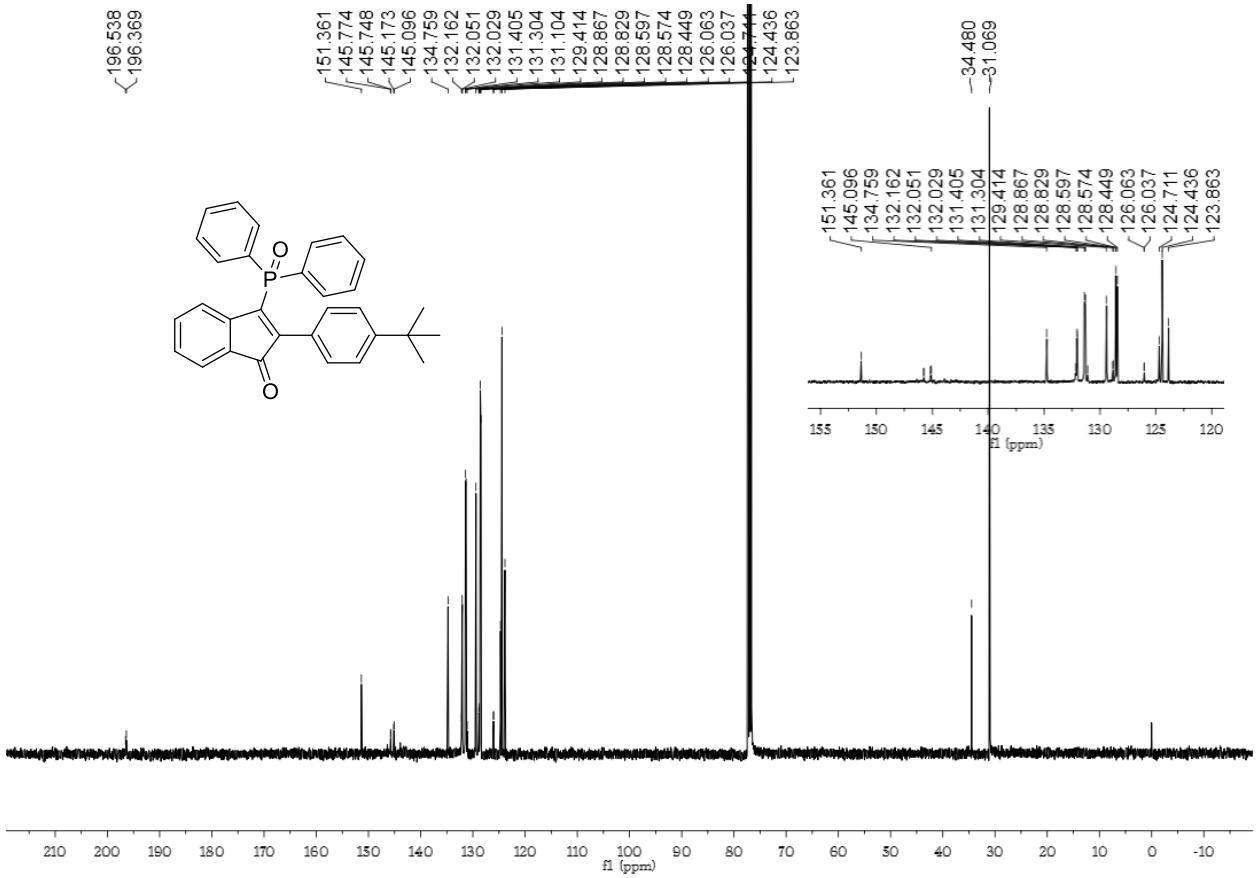
^{1}H NMR Spectrum of Compound 3h



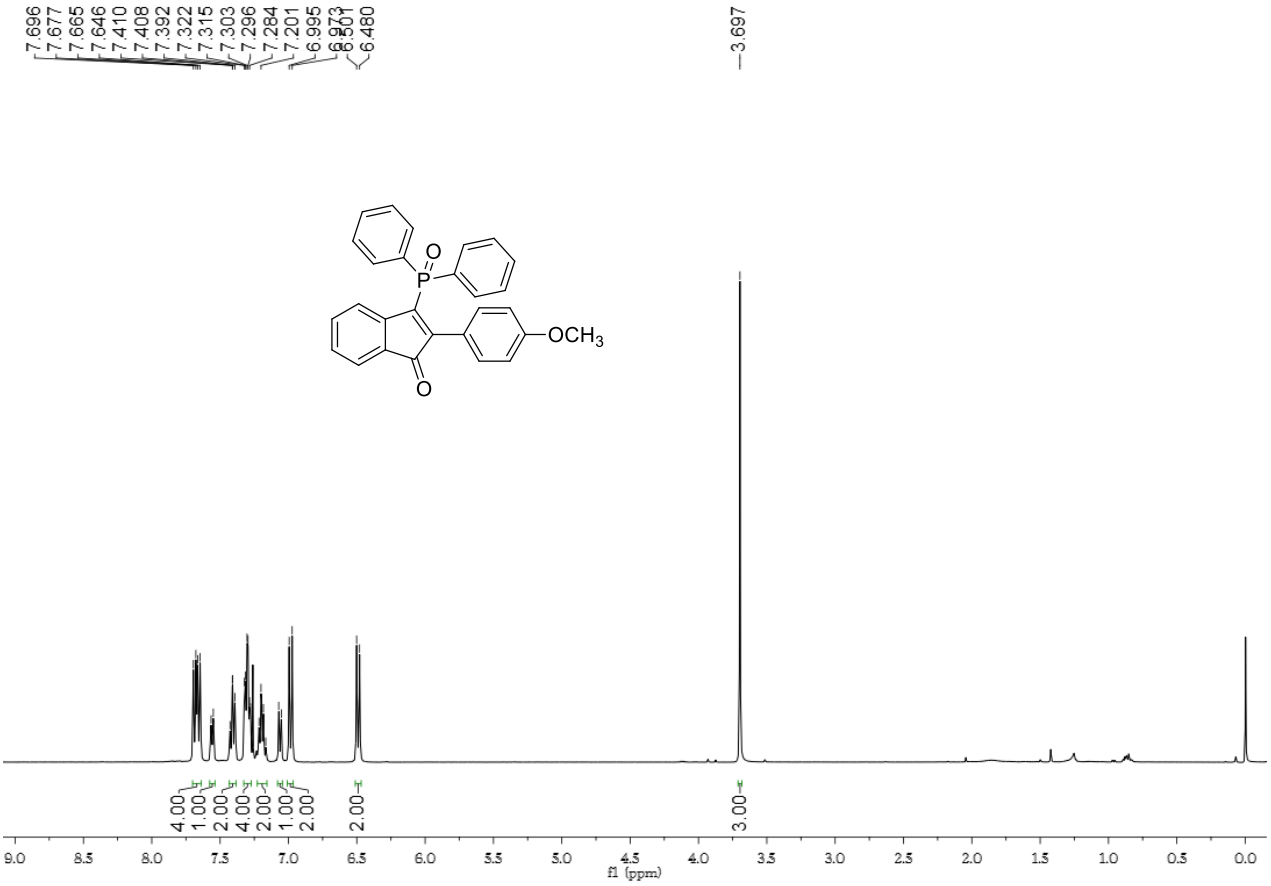
^{13}C NMR Spectrum of Compound 3h



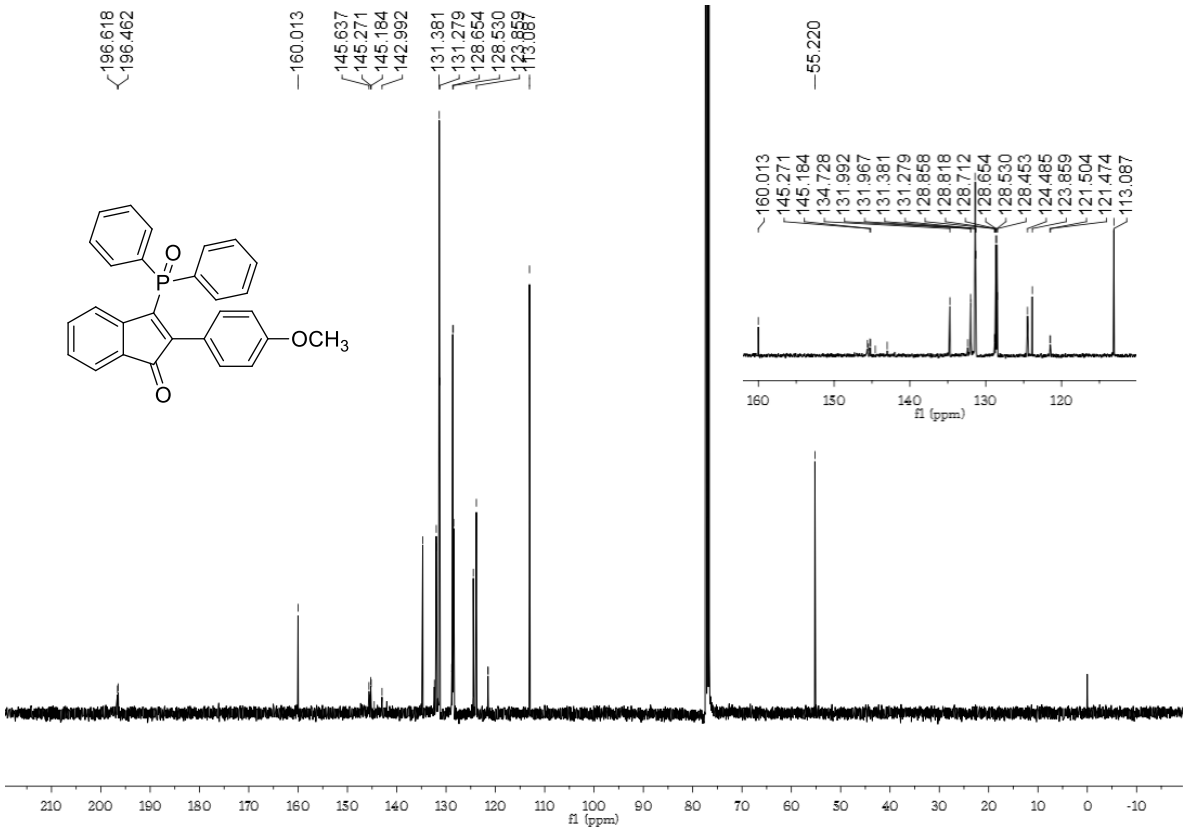
^{1}H NMR Spectrum of Compound 3i



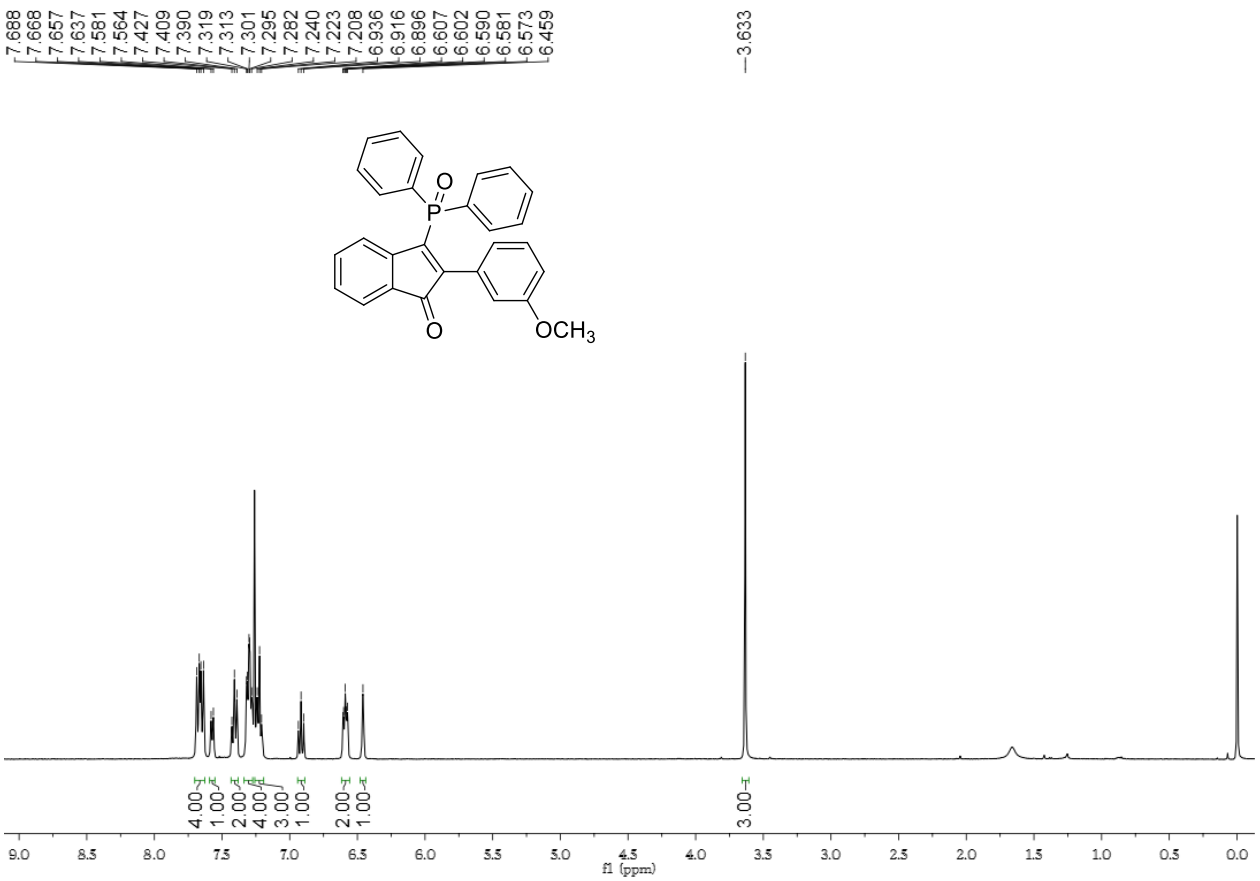
^{13}C NMR Spectrum of Compound 3i



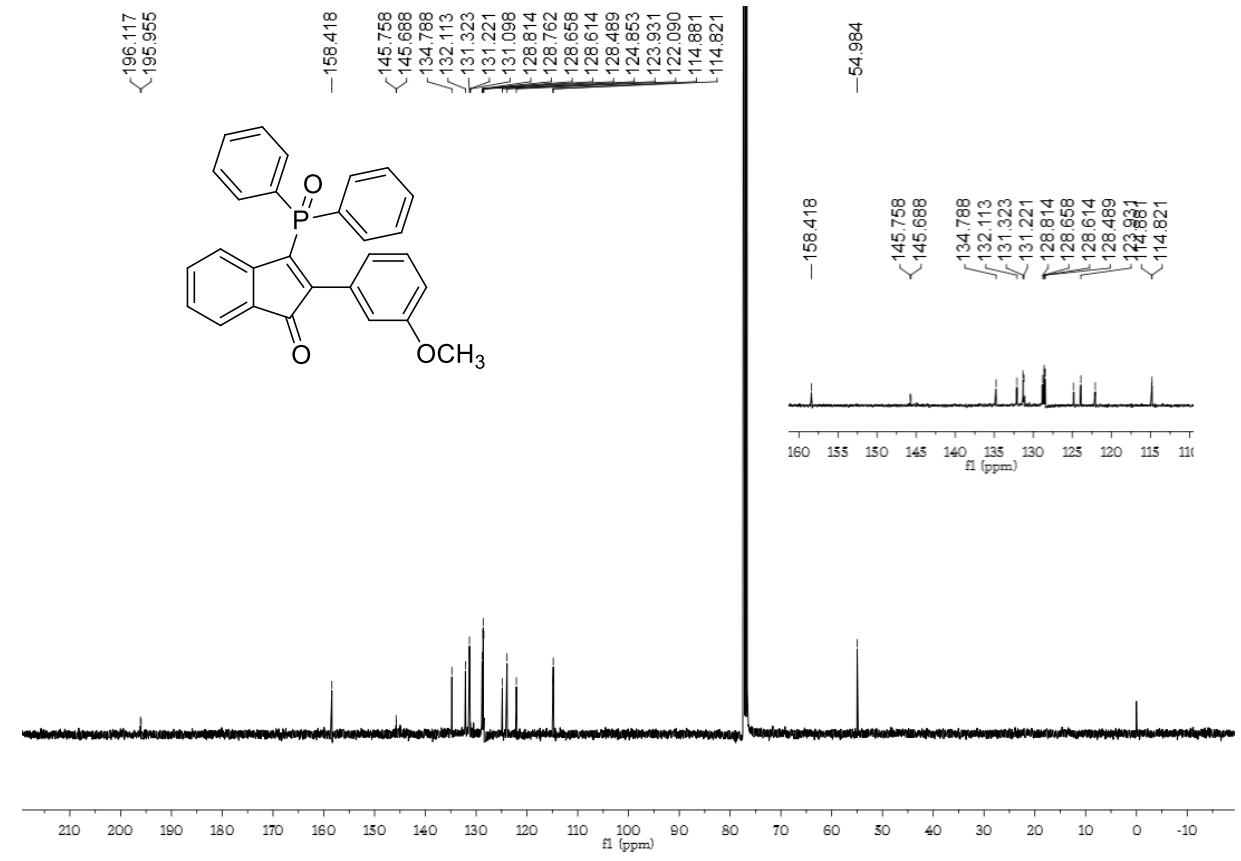
^{1}H NMR Spectrum of Compound 3j



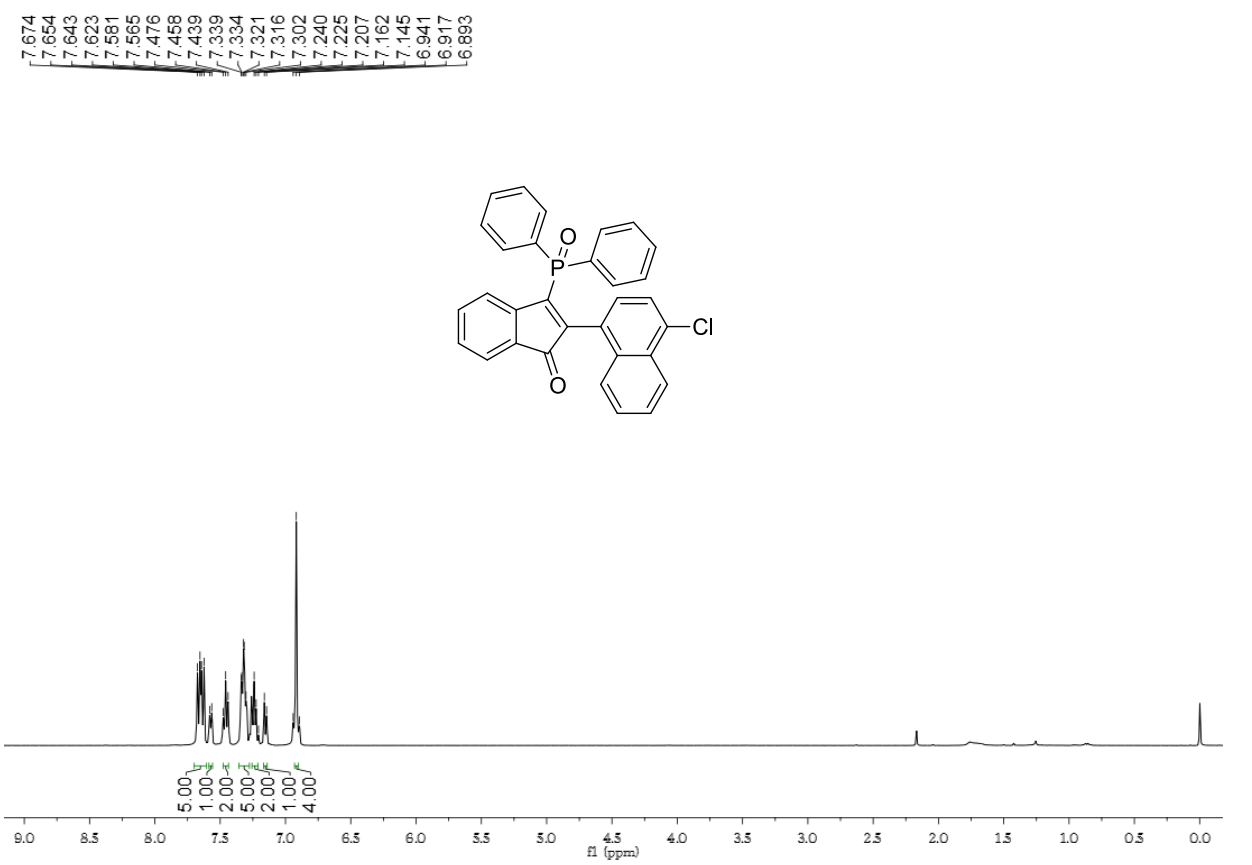
^{13}C NMR Spectrum of Compound 3j



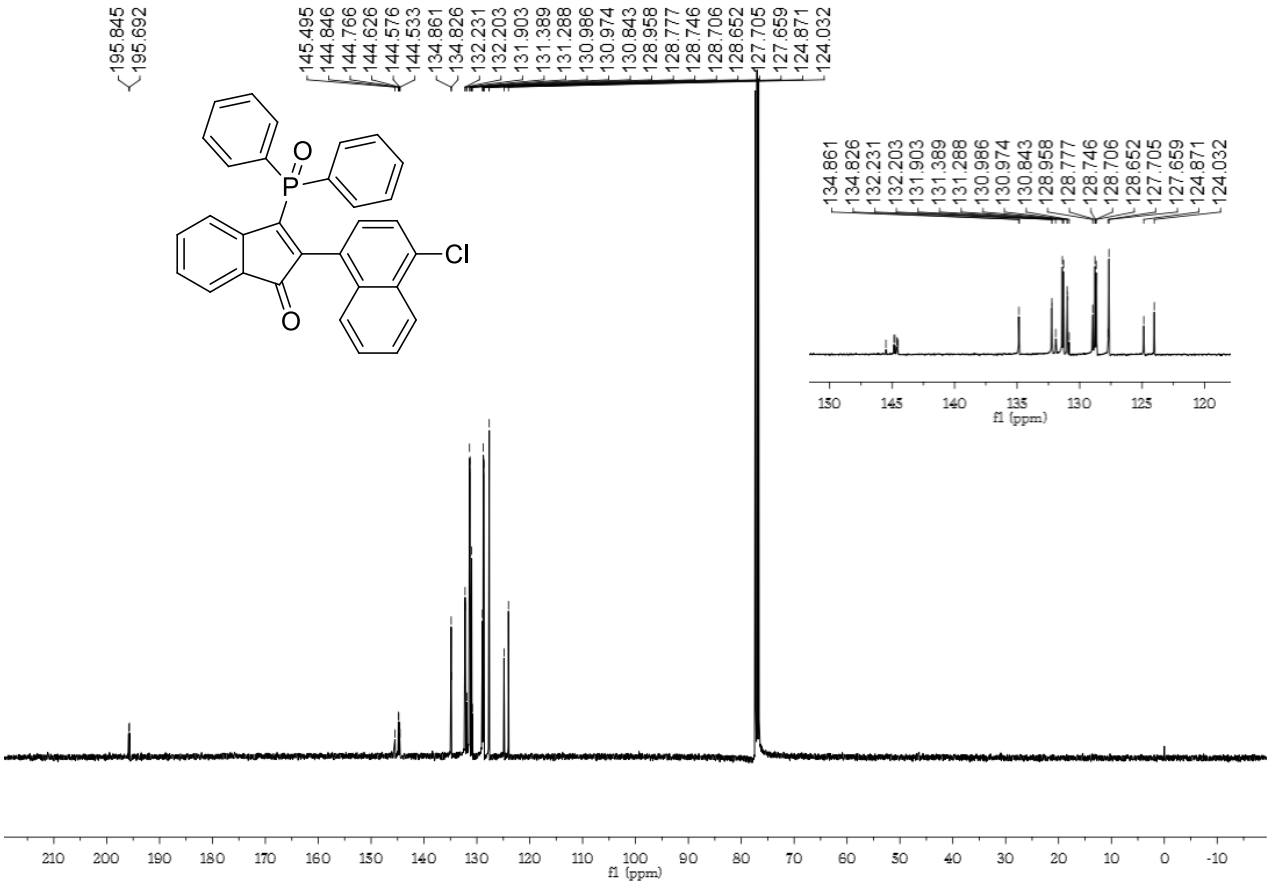
^{1}H NMR Spectrum of Compound 3k



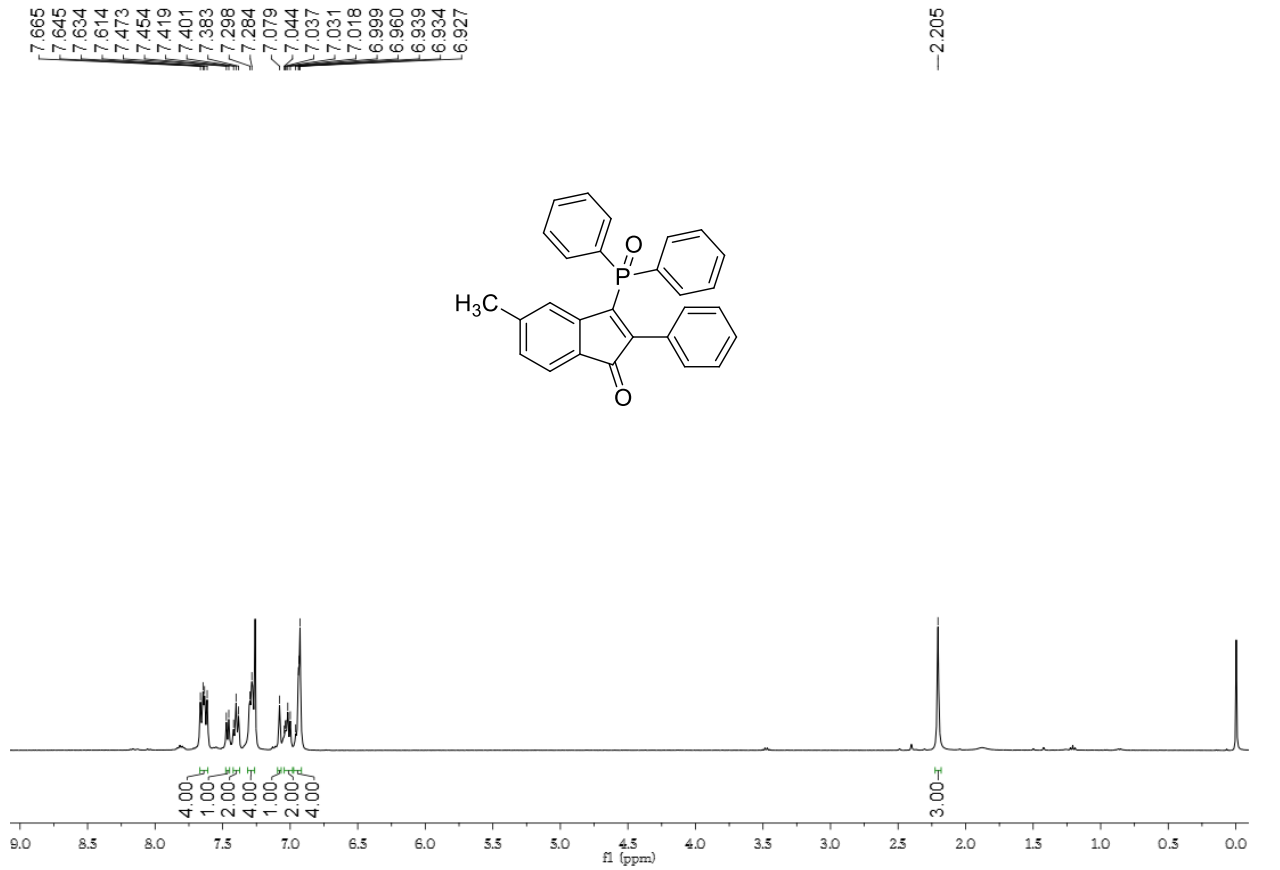
^{13}C NMR Spectrum of Compound 3k



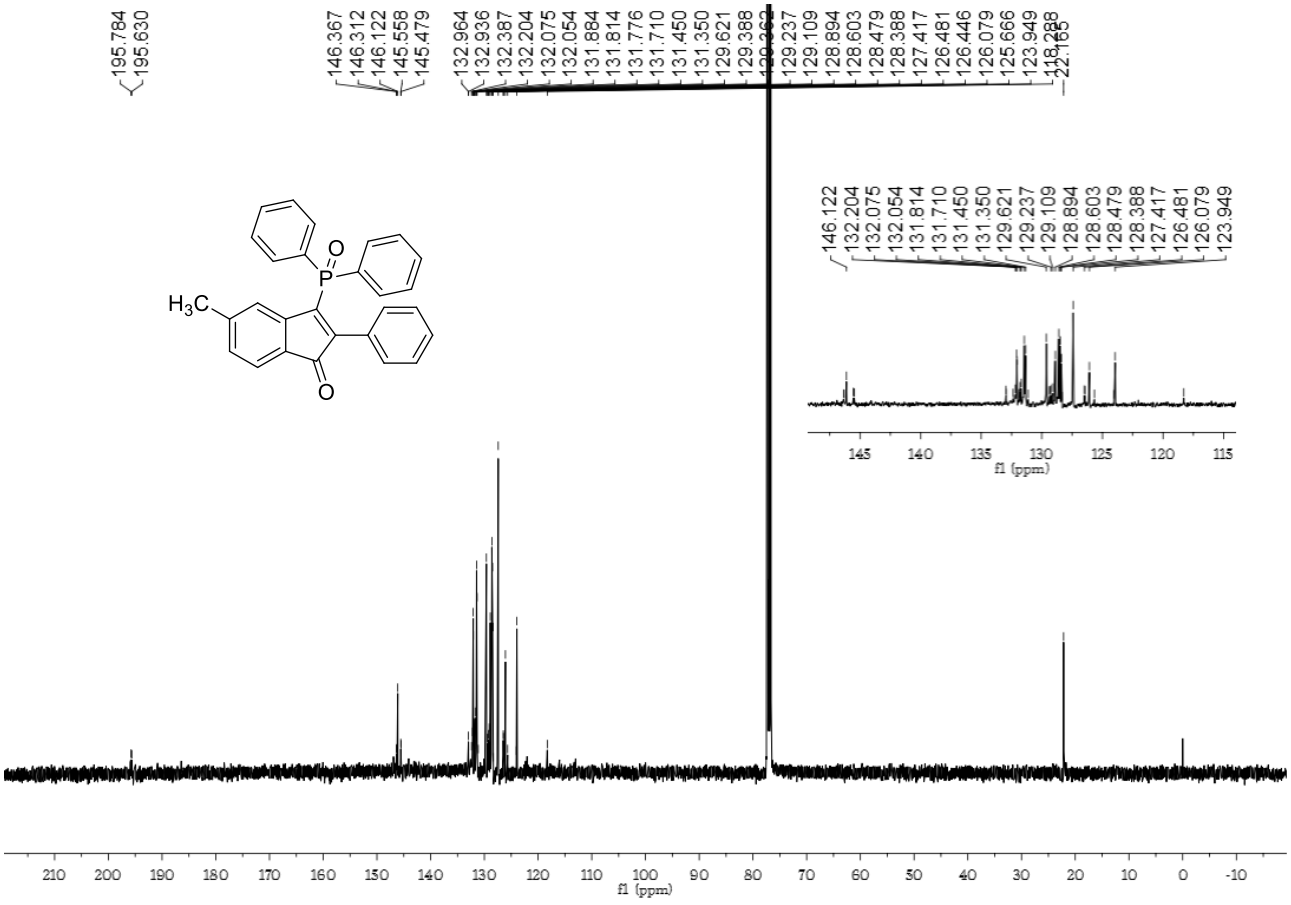
^{1}H NMR Spectrum of Compound 3l



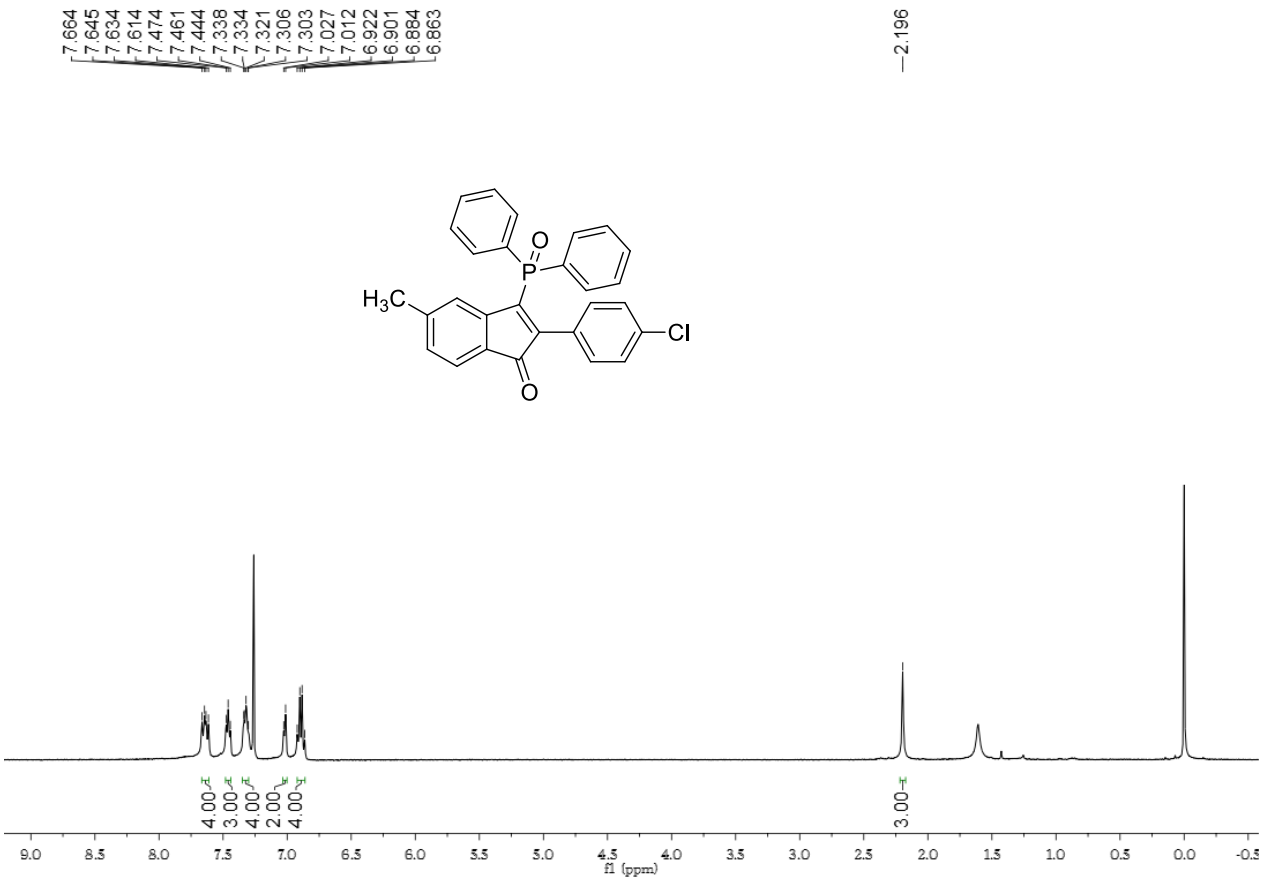
^{13}C NMR Spectrum of Compound 3l



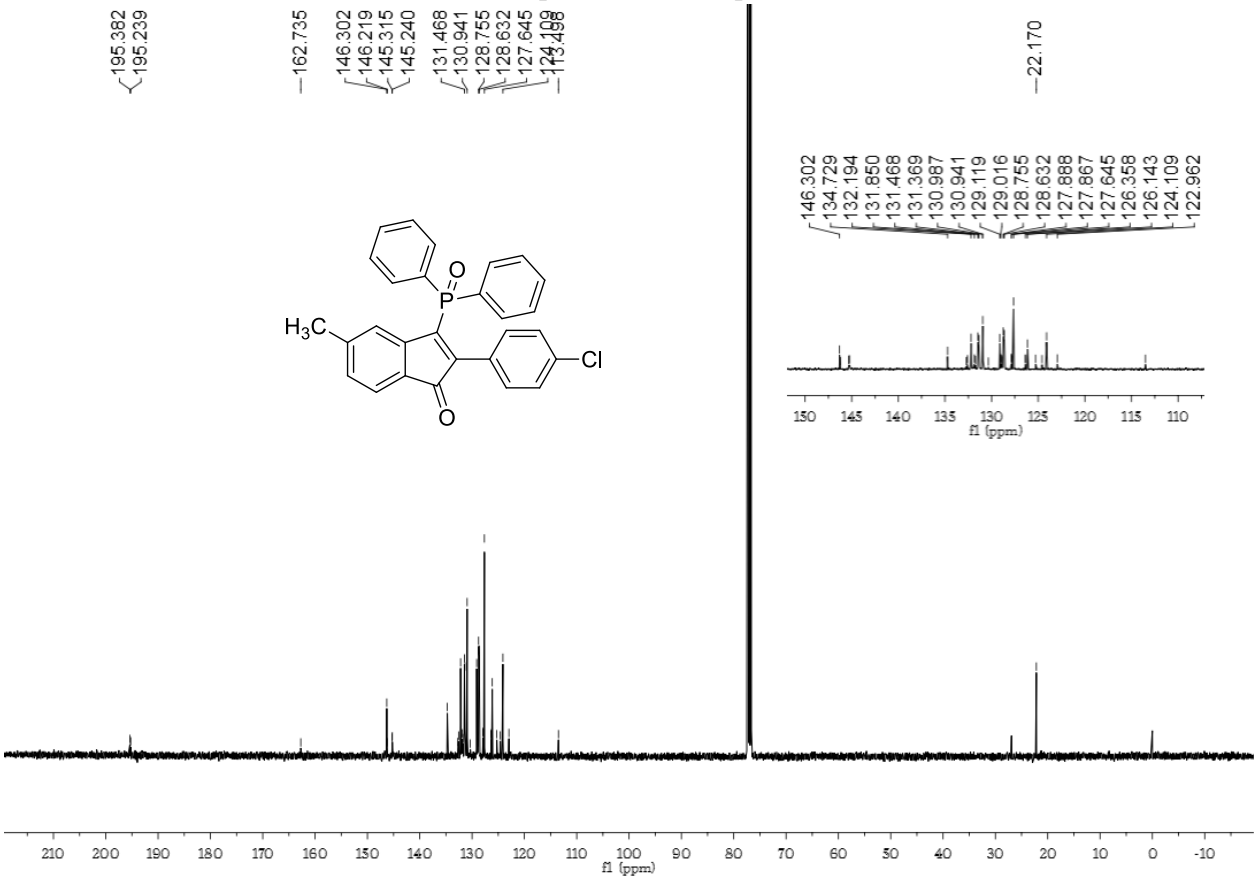
^{1}H NMR Spectrum of Compound 3n



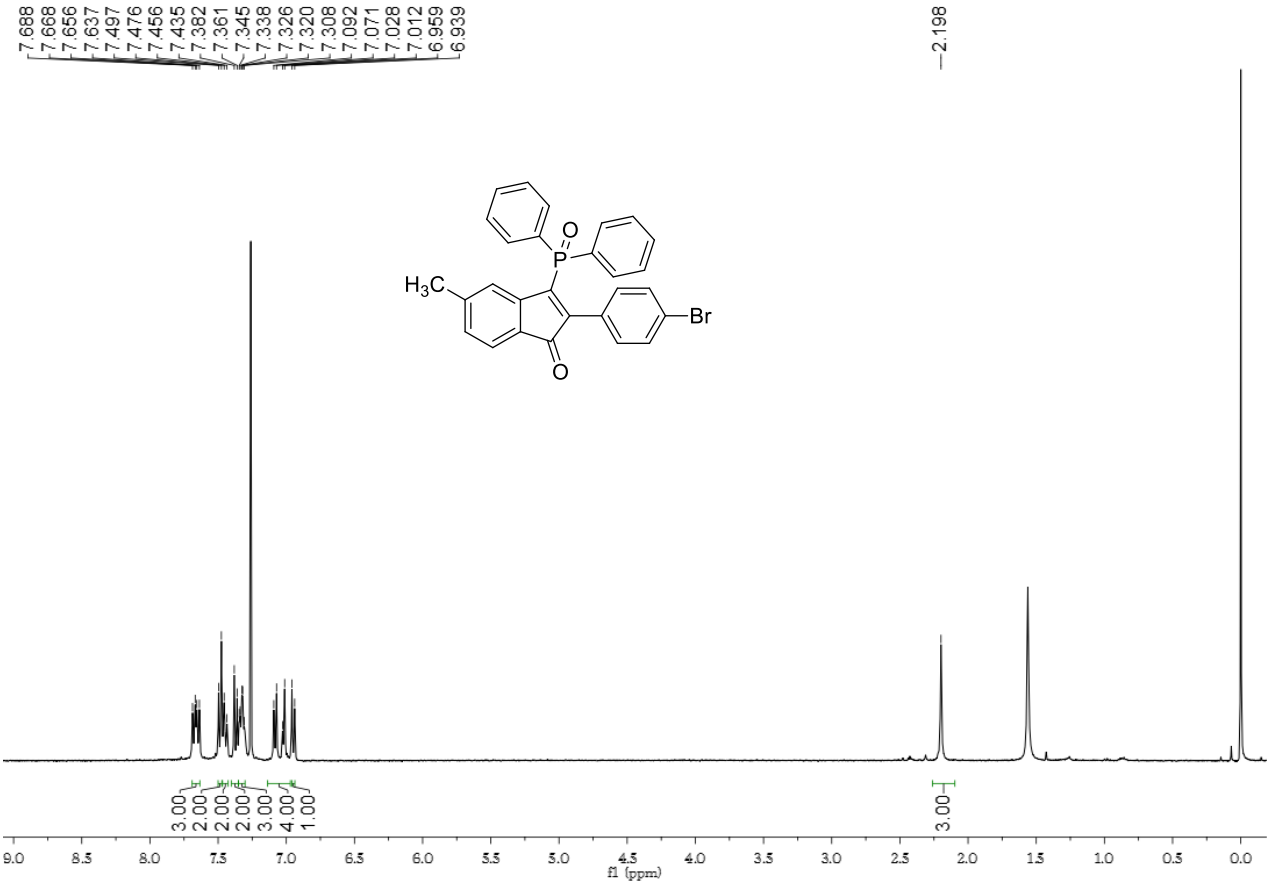
^{13}C NMR Spectrum of Compound 3n



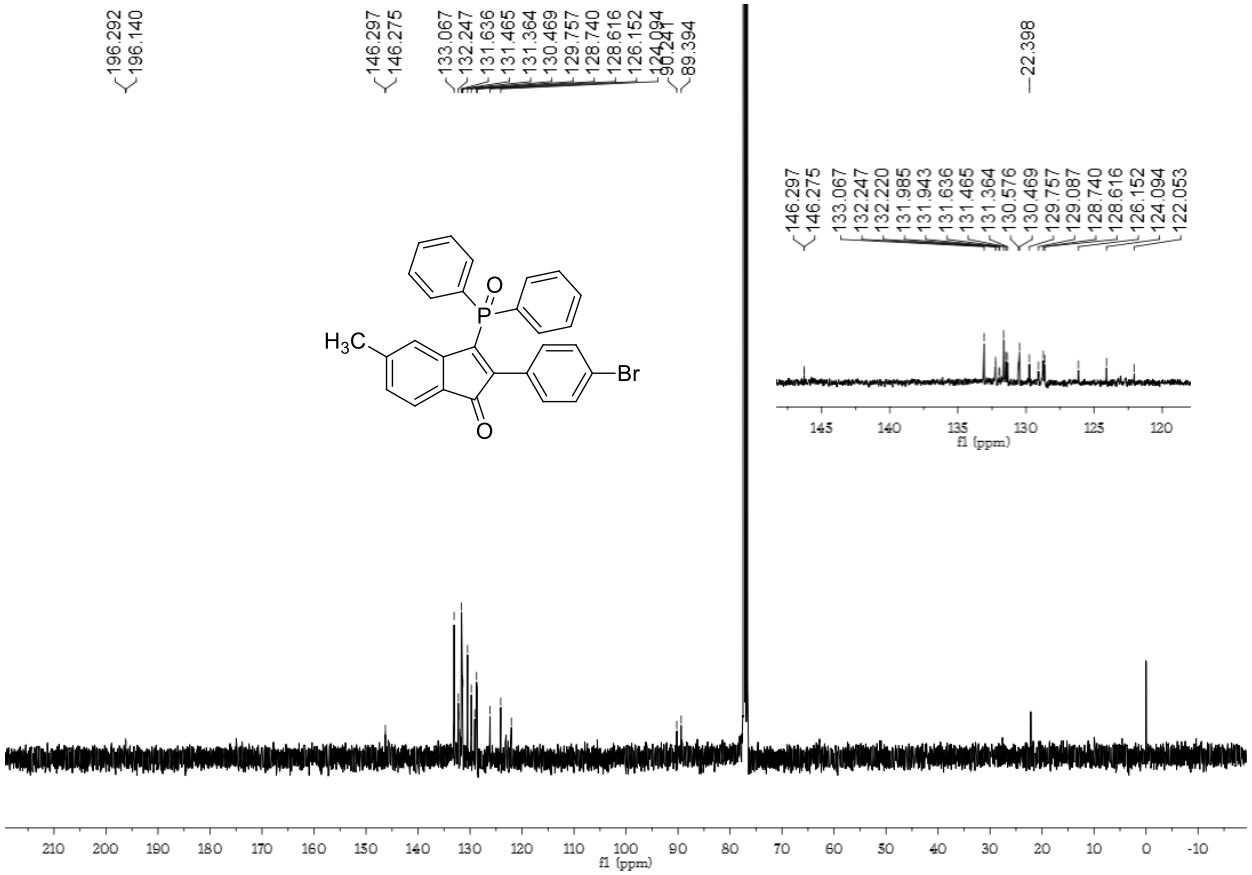
^{1}H NMR Spectrum of Compound 3o



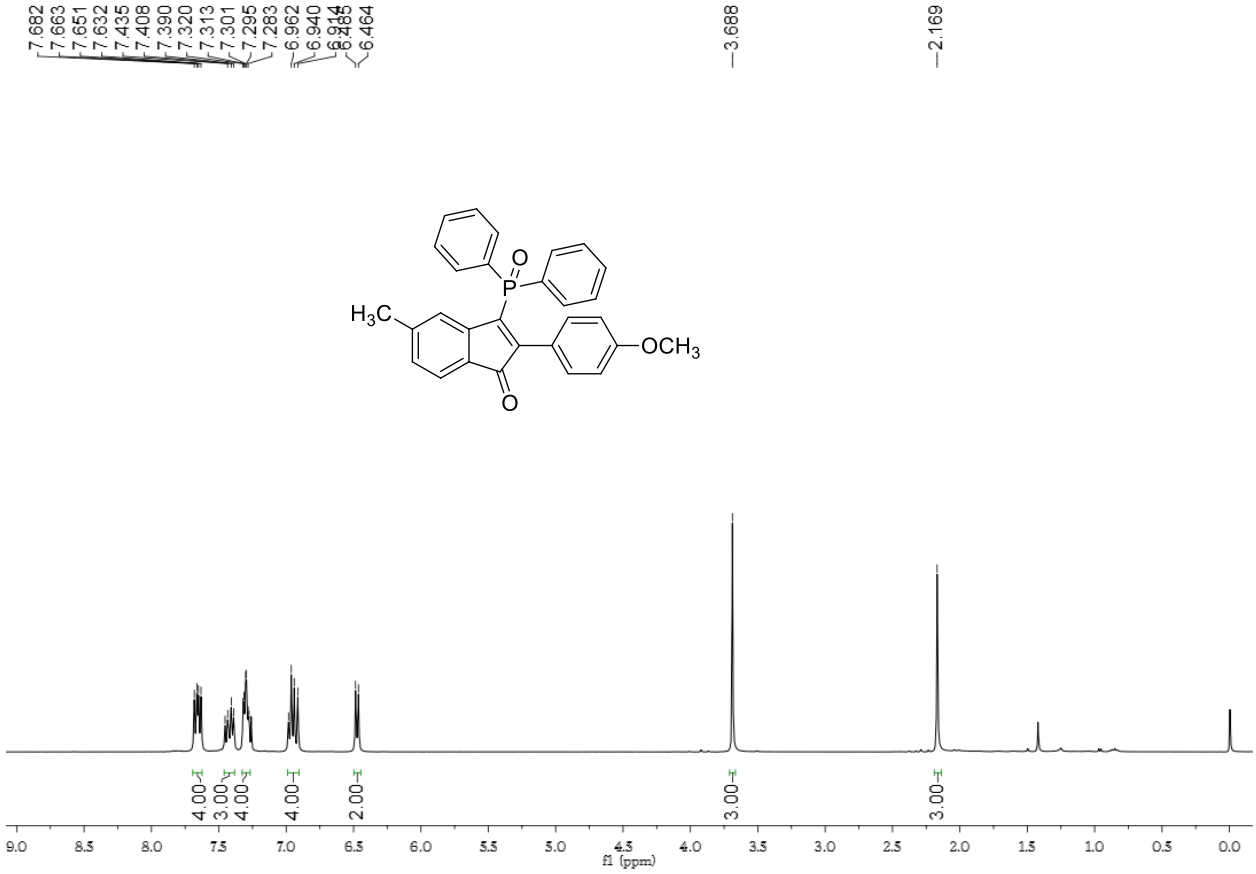
^{13}C NMR Spectrum of Compound 3o



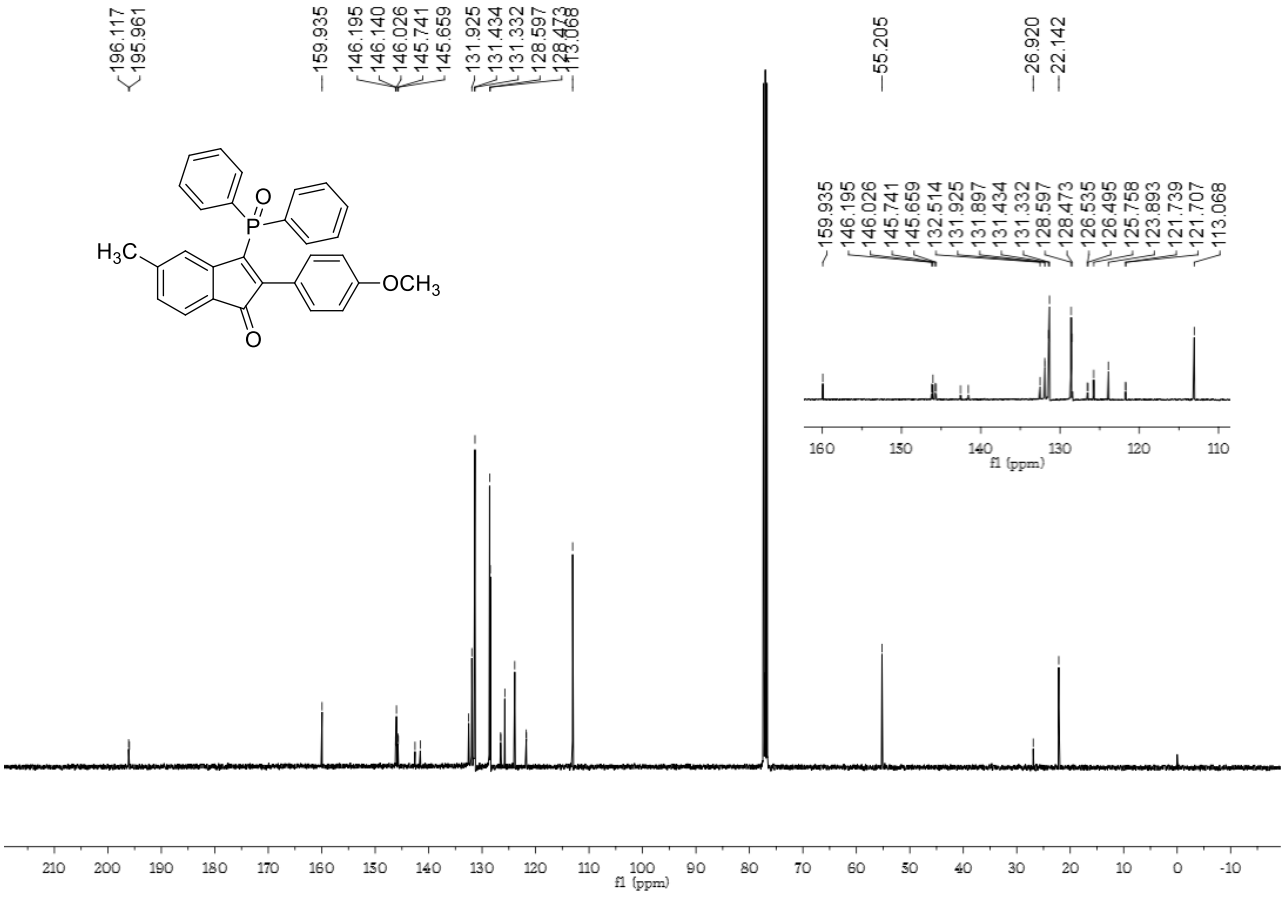
^{1}H NMR Spectrum of Compound 3p



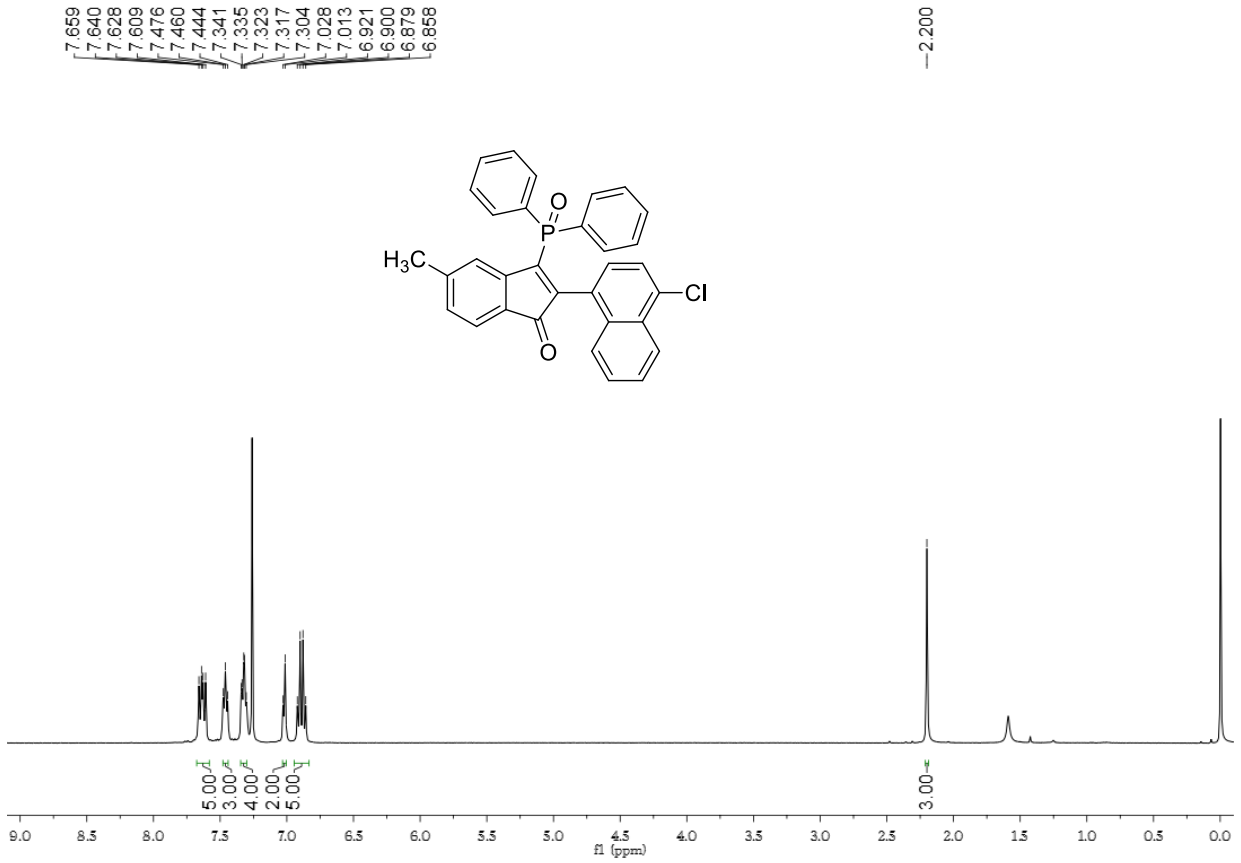
^{13}C NMR Spectrum of Compound 3p



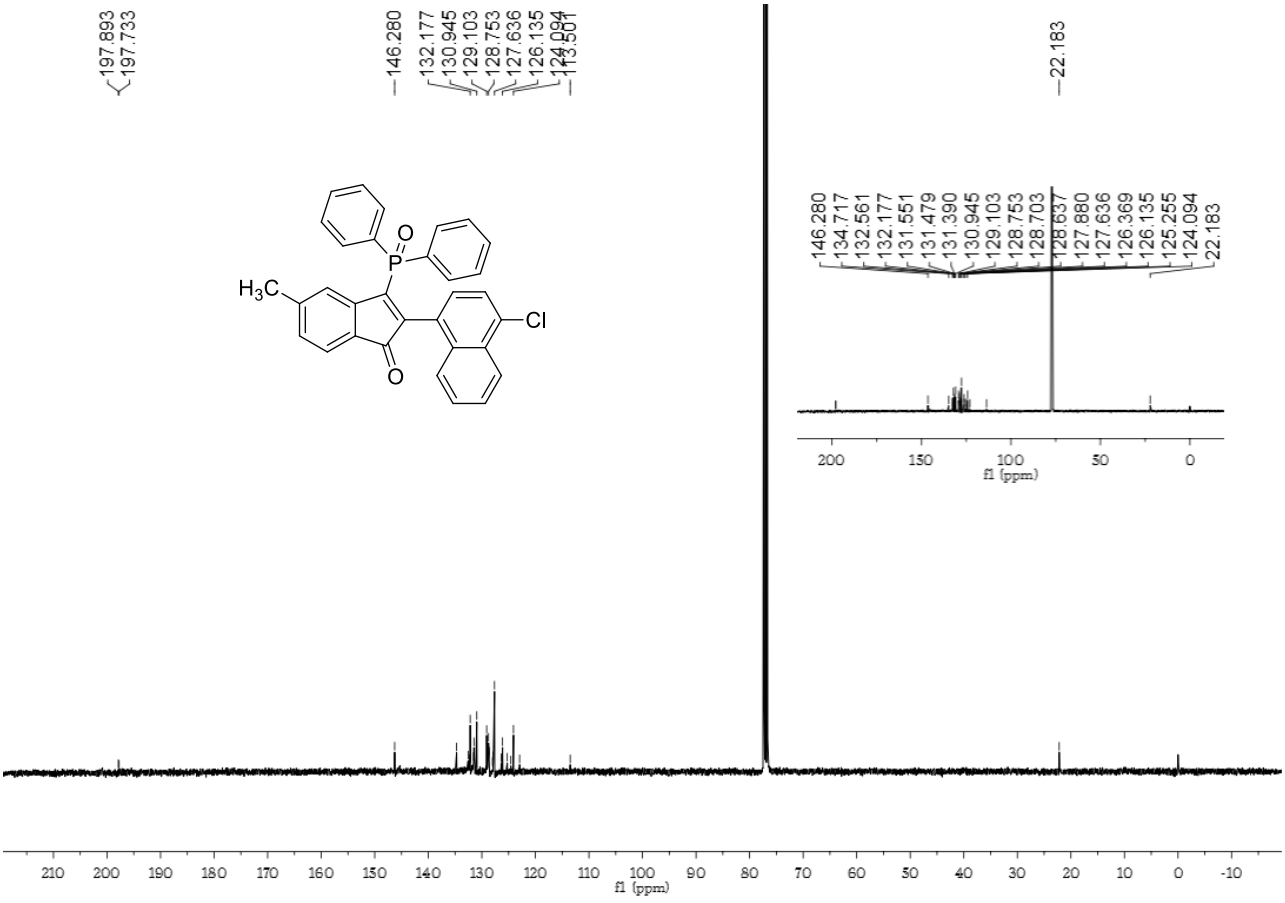
^{1}H NMR Spectrum of Compound 3q



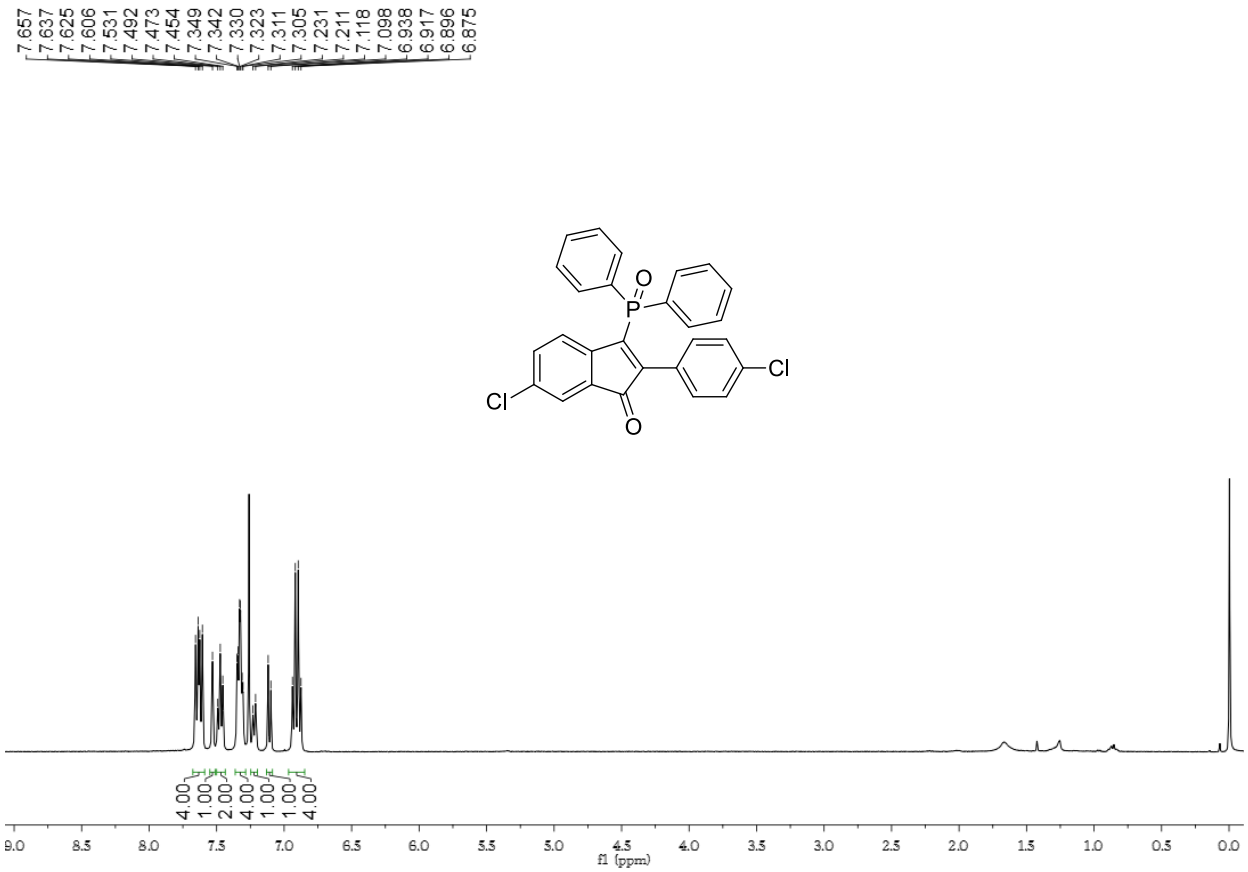
^{13}C NMR Spectrum of Compound 3q



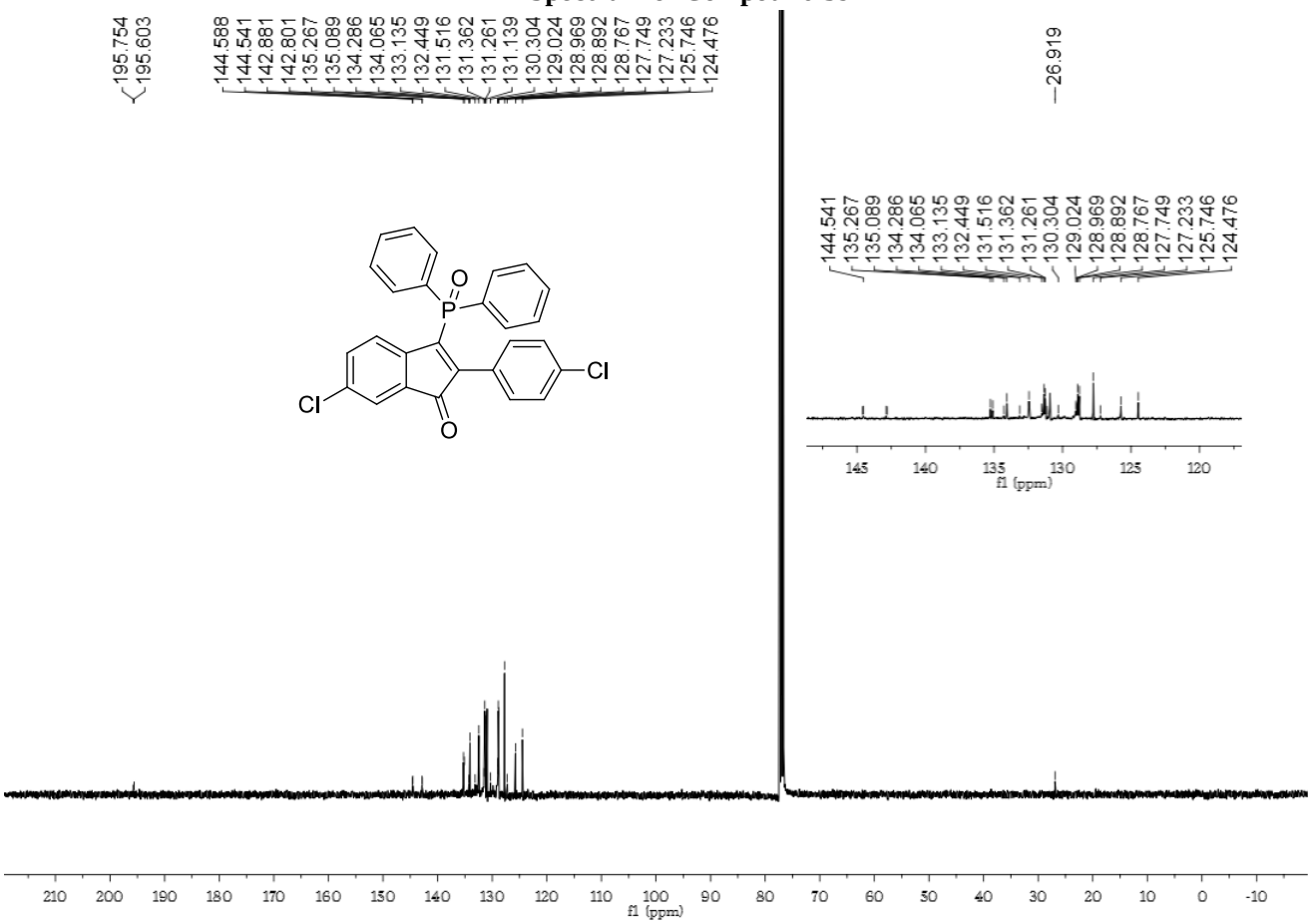
^{1}H NMR Spectrum of Compound 3r



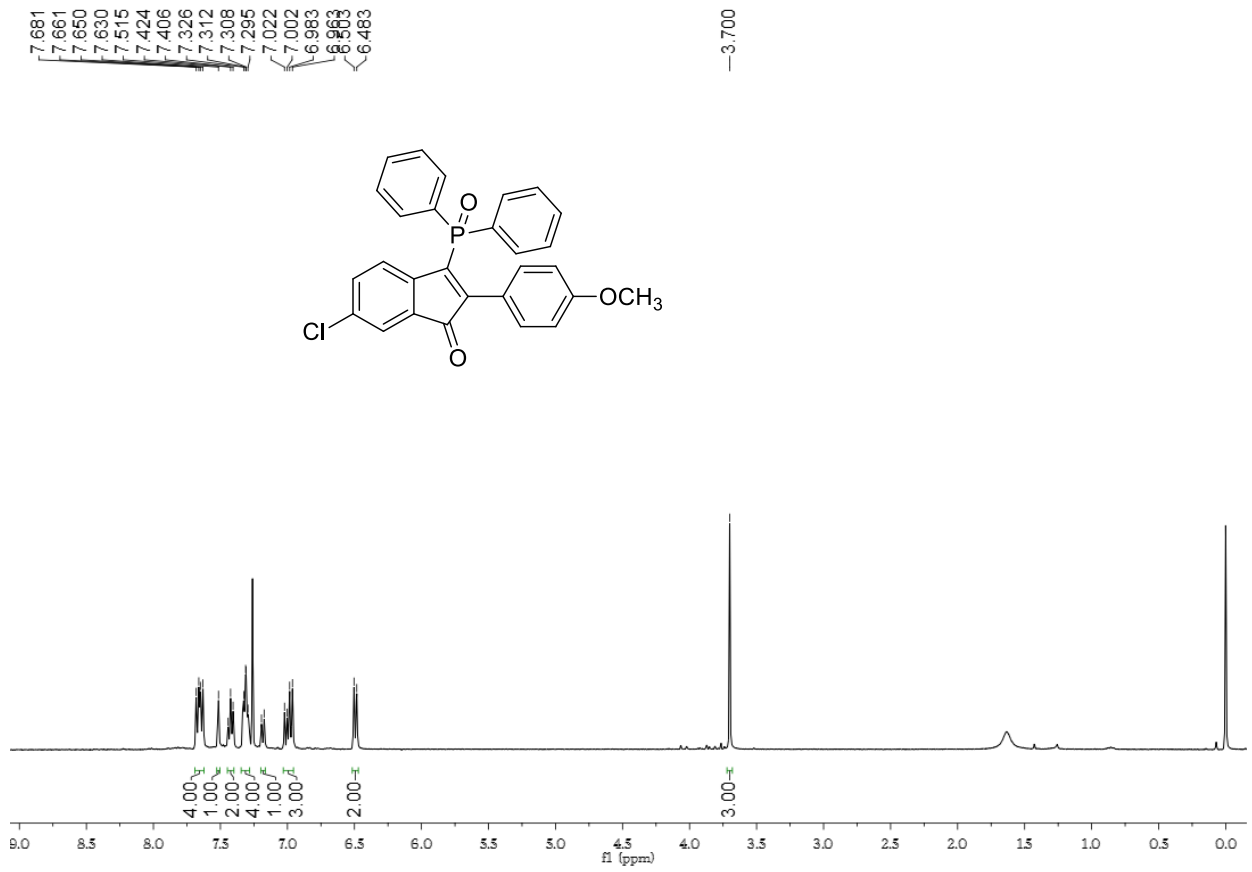
^{13}C NMR Spectrum of Compound 3r



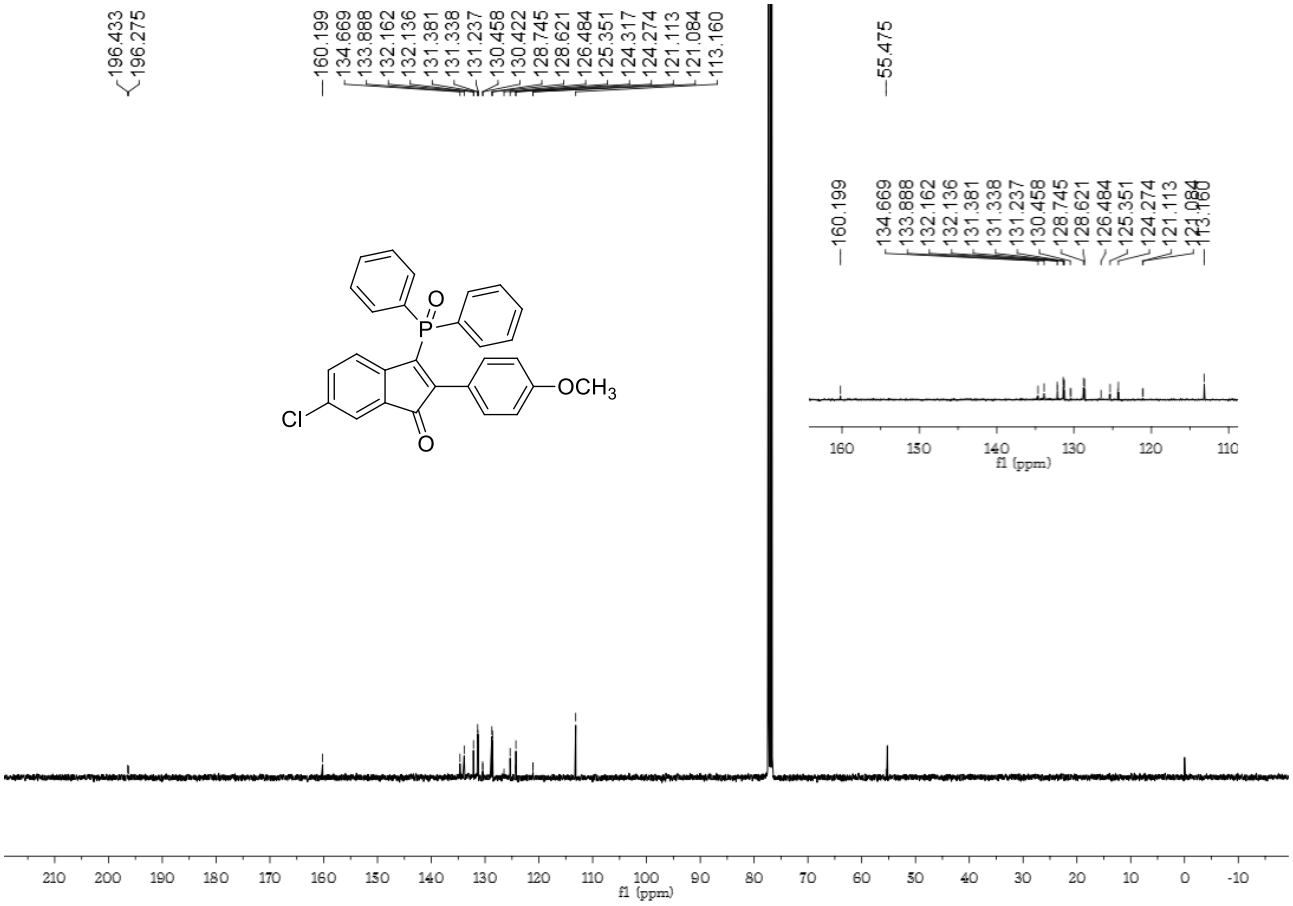
^{1}H NMR Spectrum of Compound 3s



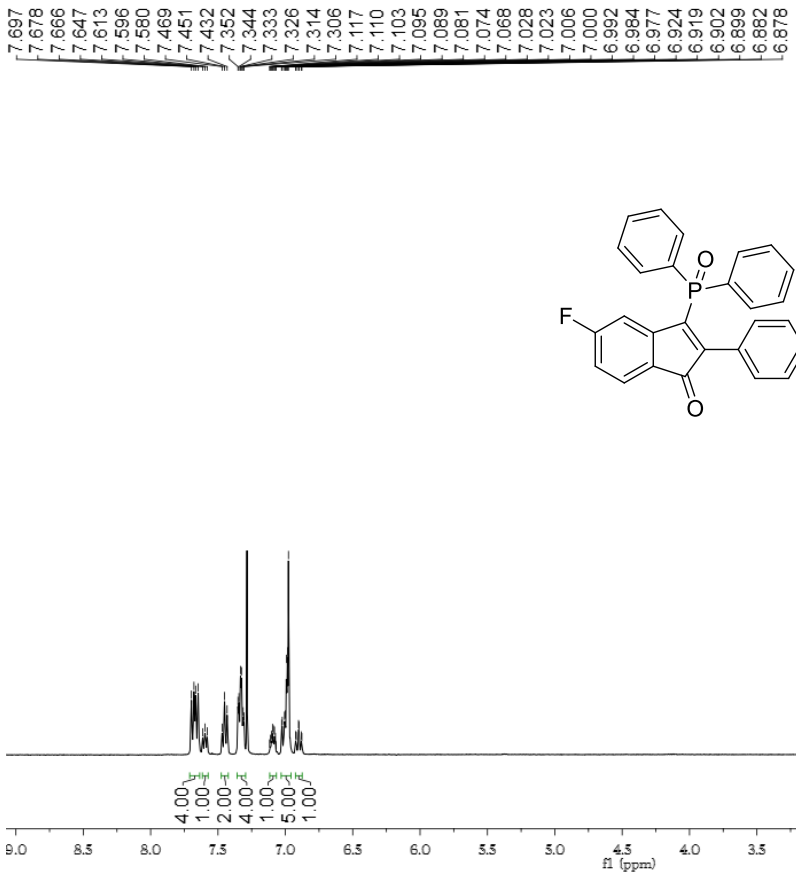
^{13}C NMR Spectrum of Compound 3s



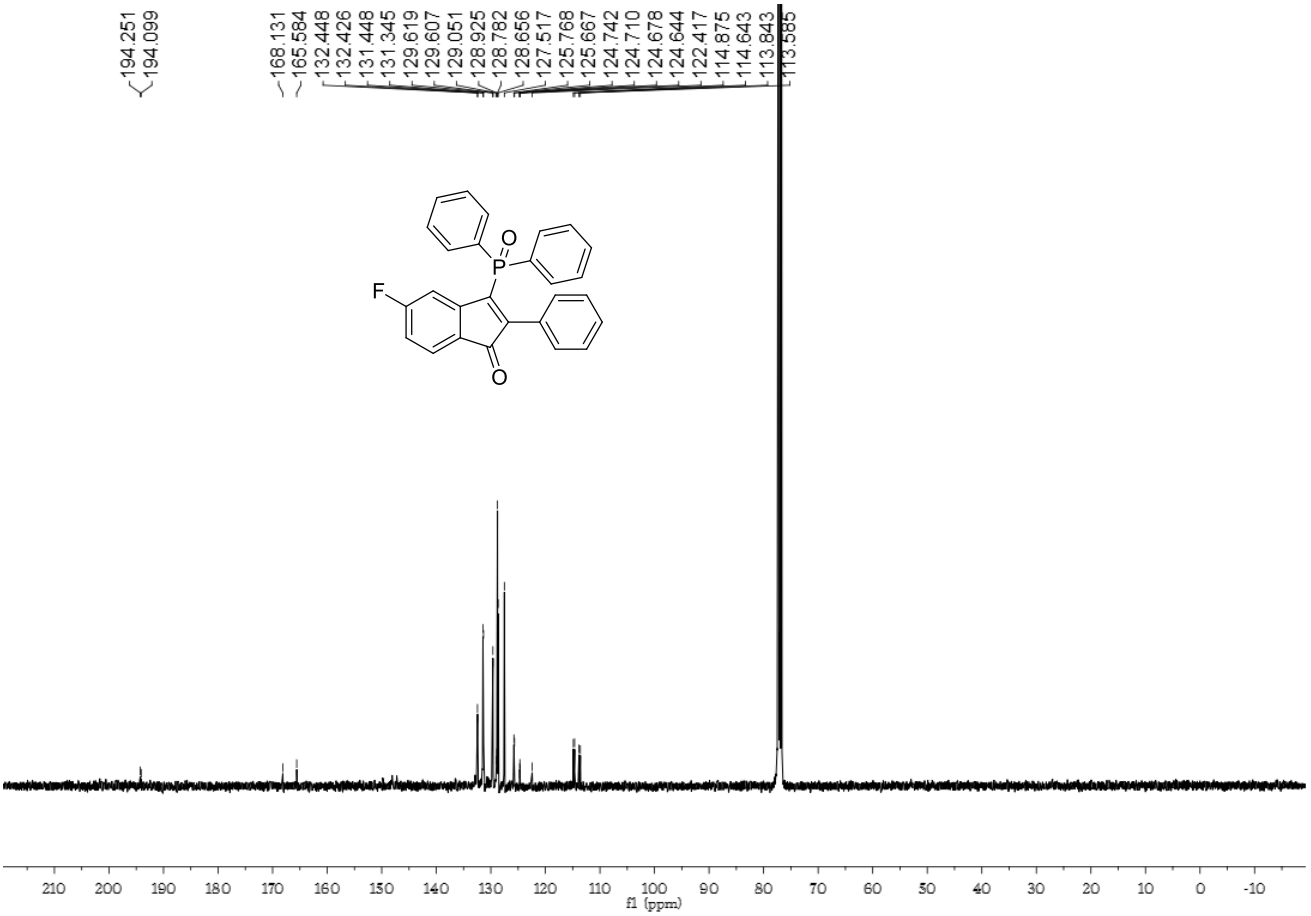
^{1}H NMR Spectrum of Compound 3t



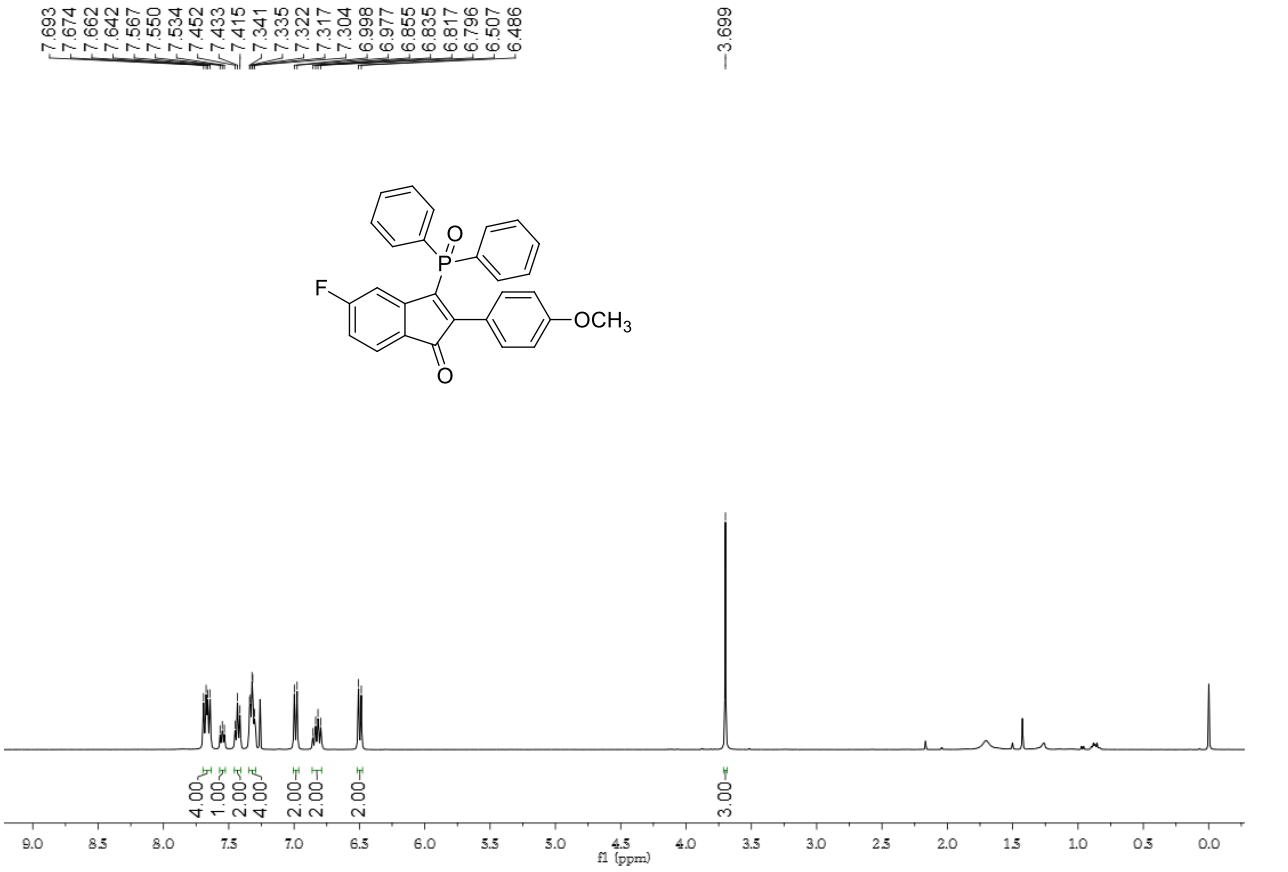
^{13}C NMR Spectrum of Compound 3t



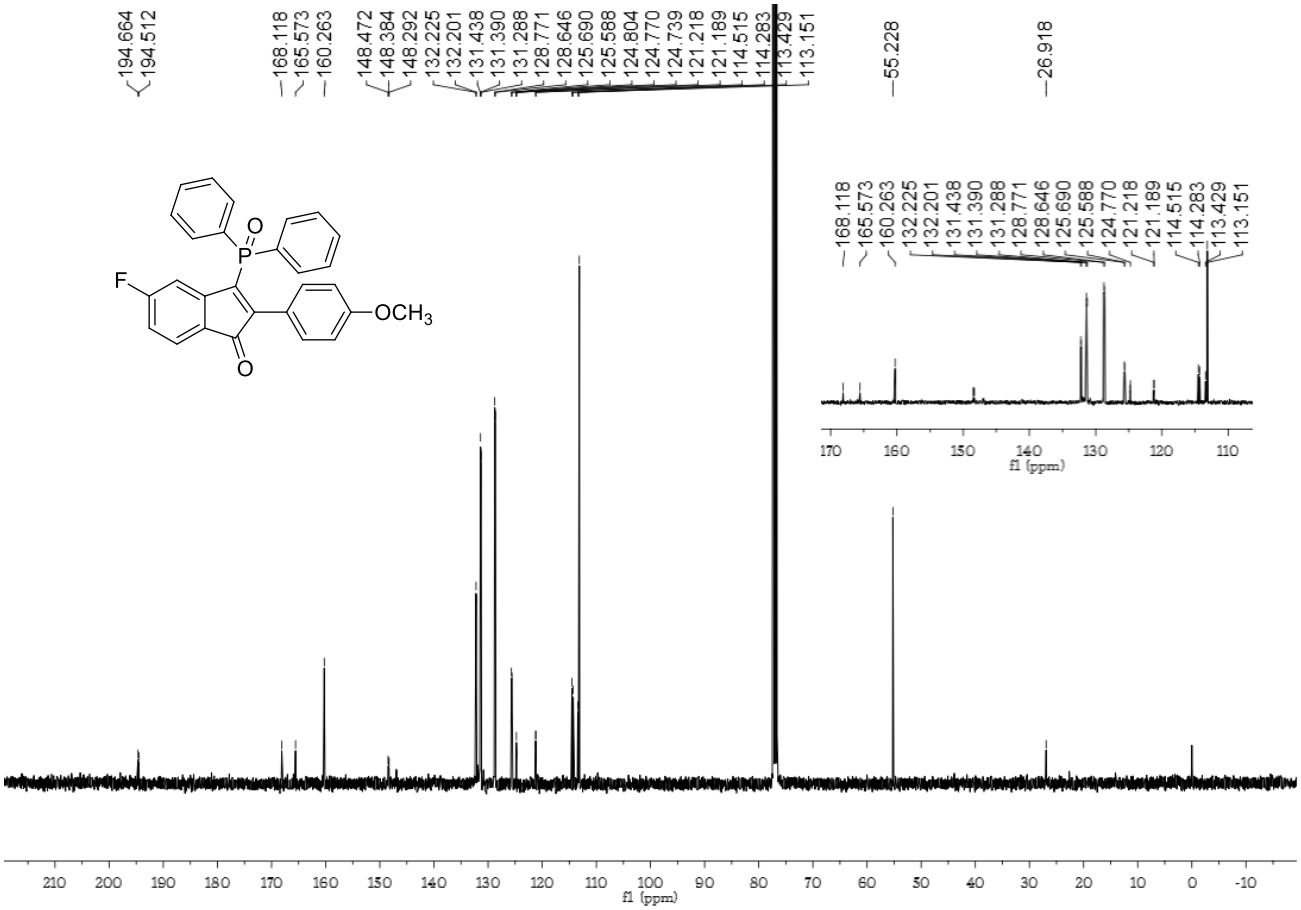
^{1}H NMR Spectrum of Compound 3u



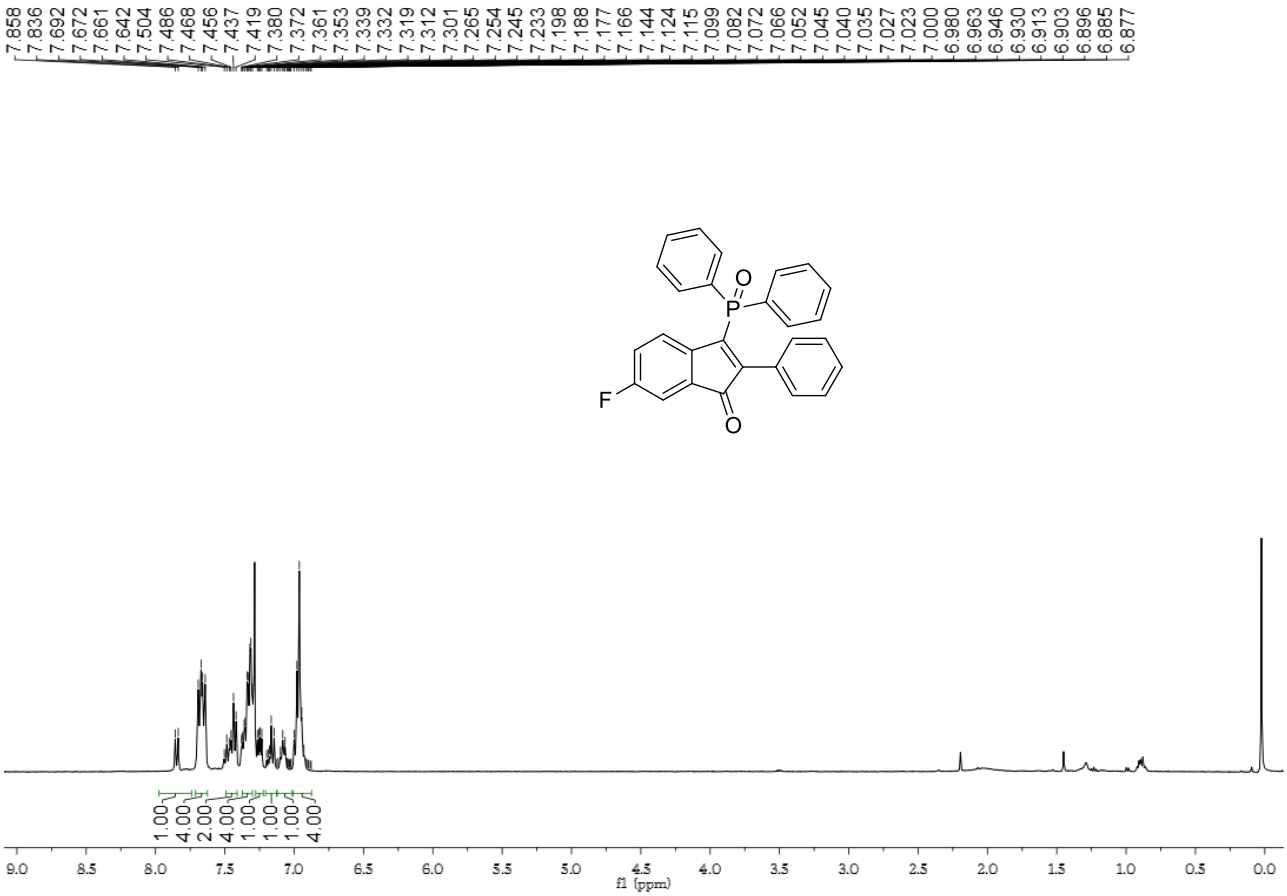
^{13}C NMR Spectrum of Compound 3u



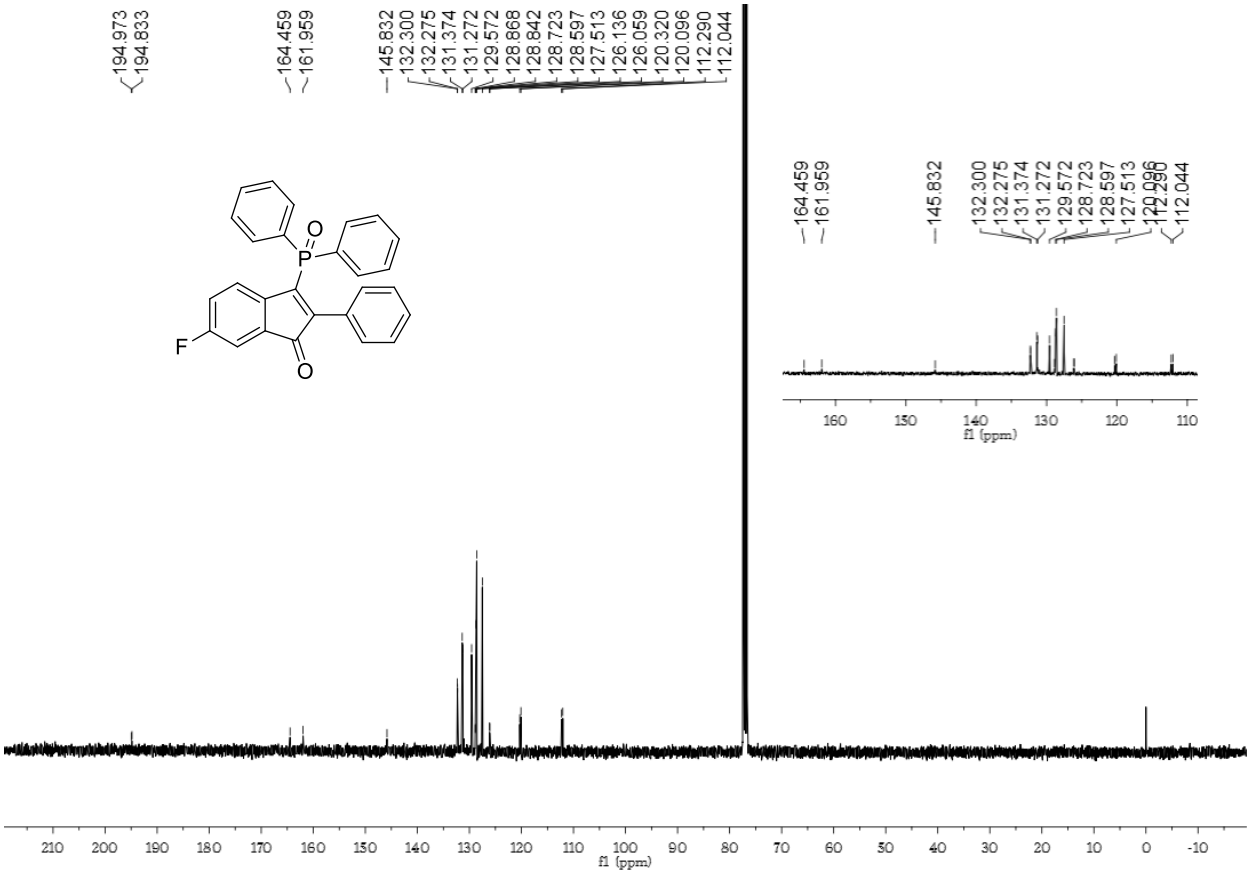
^{1}H NMR Spectrum of Compound 3v



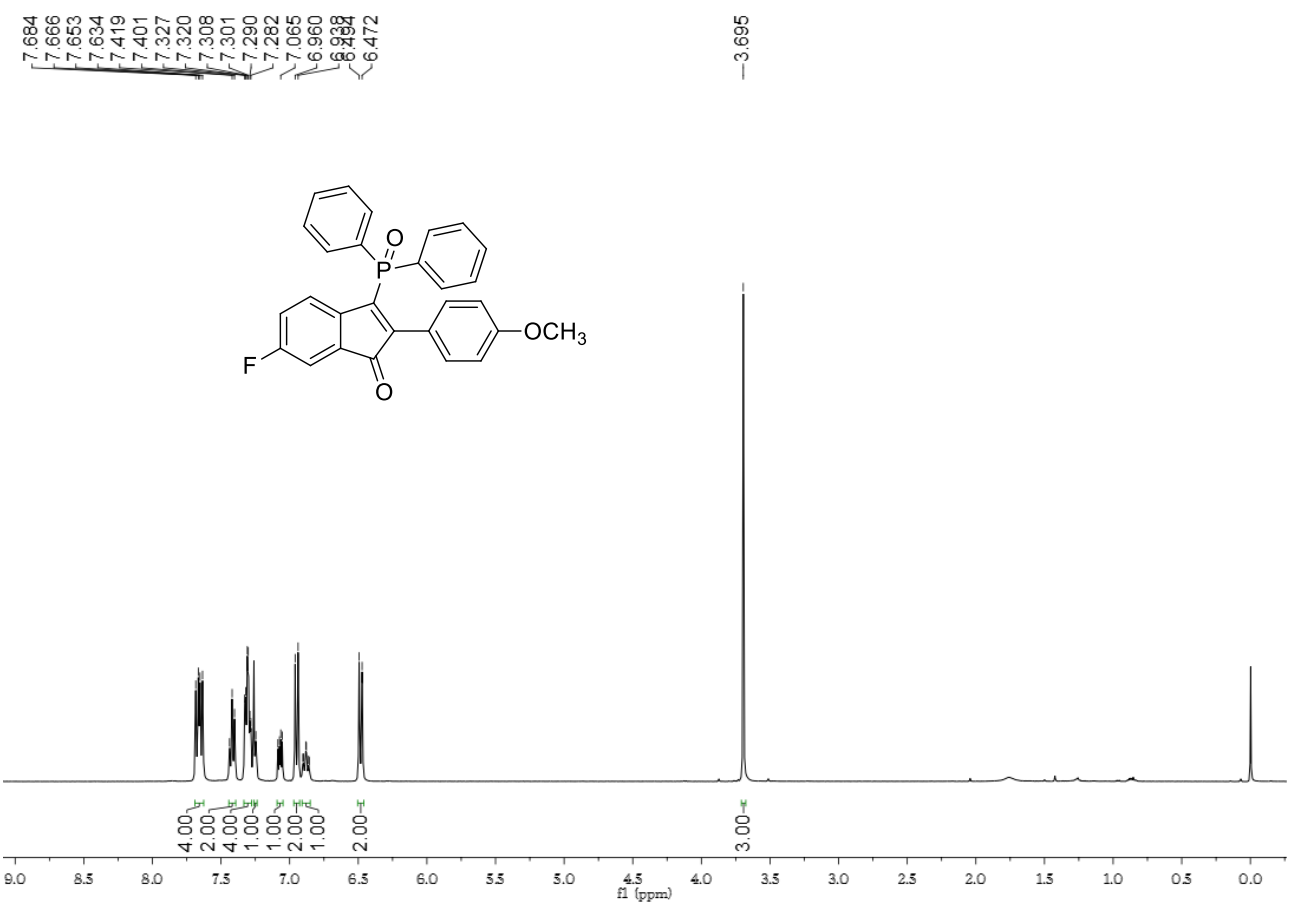
^{13}C NMR Spectrum of Compound 3v



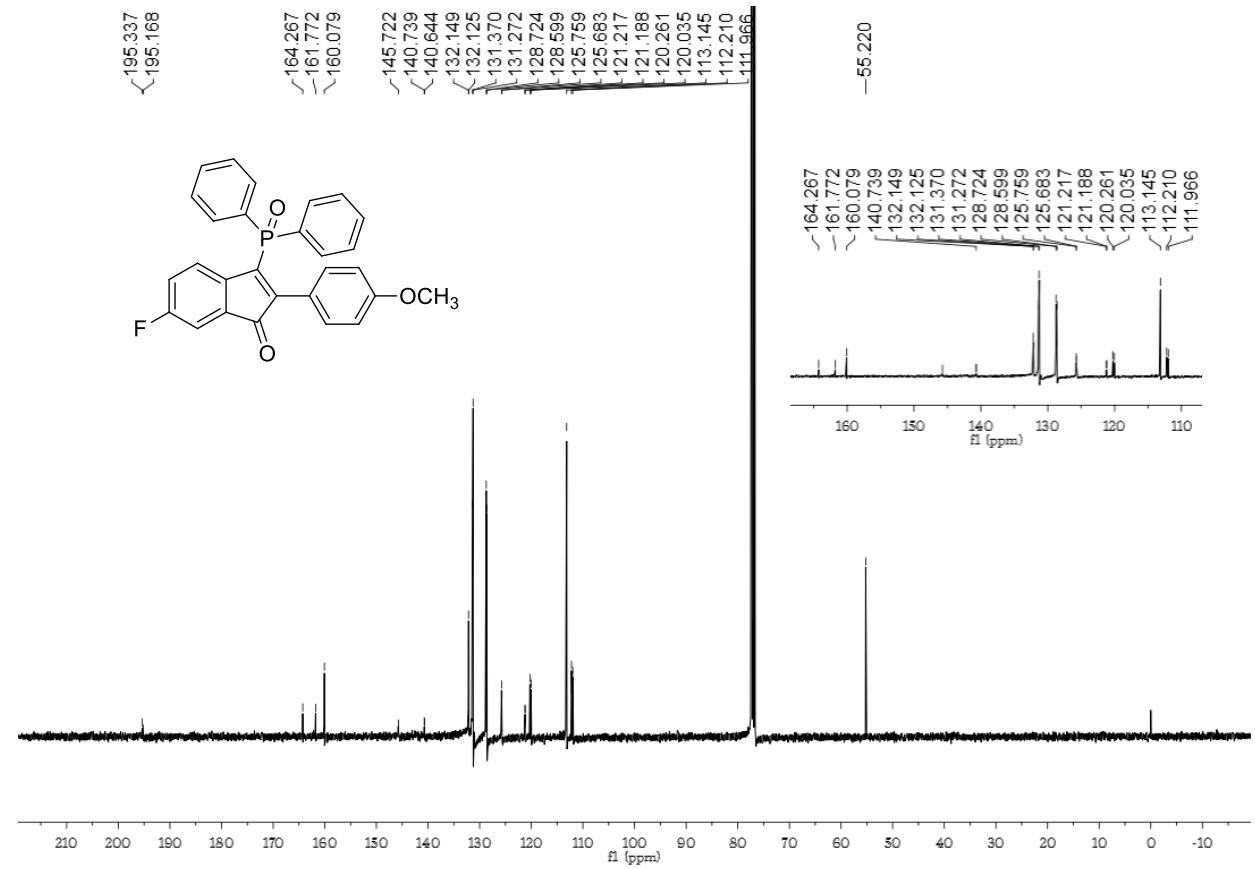
^{1}H NMR Spectrum of Compound 3w



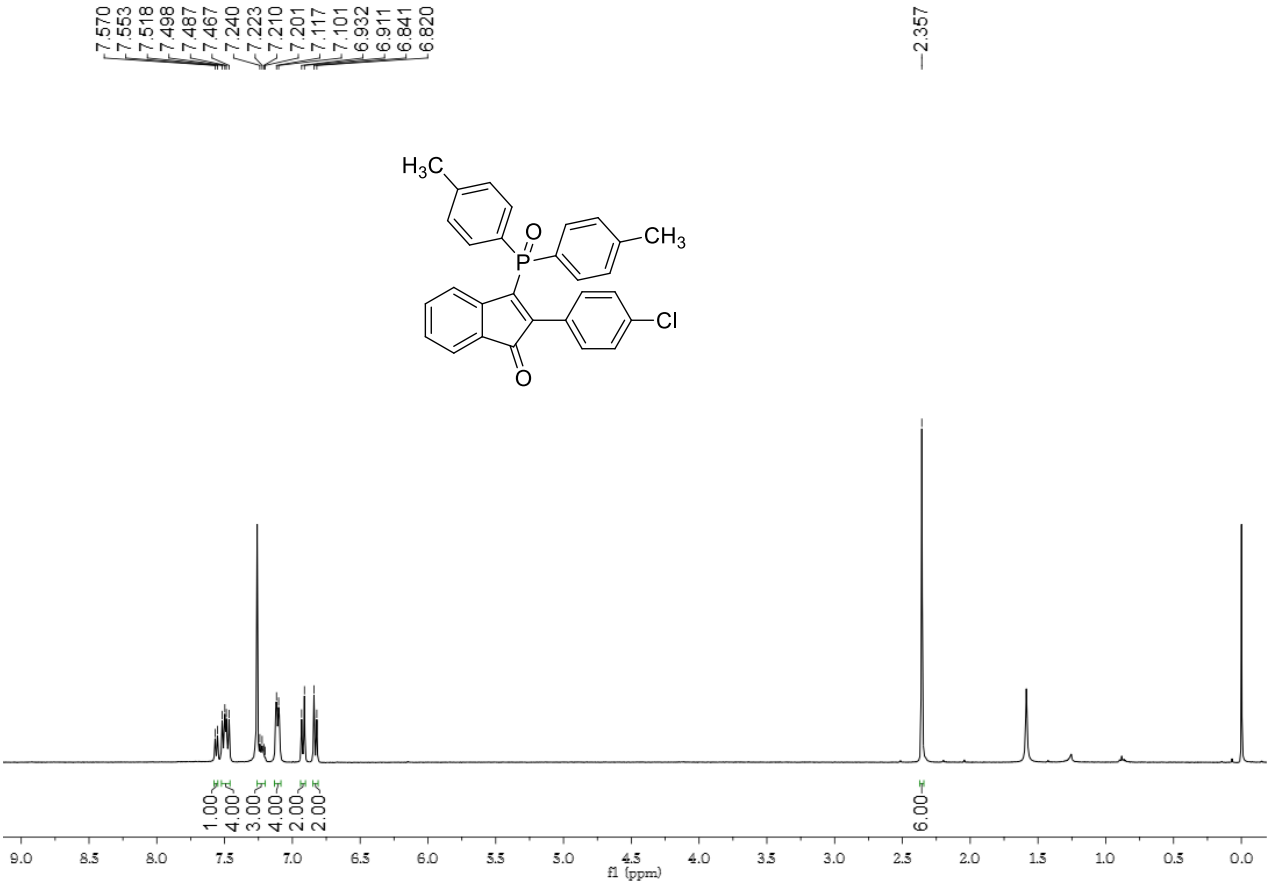
^{13}C NMR Spectrum of Compound 3w



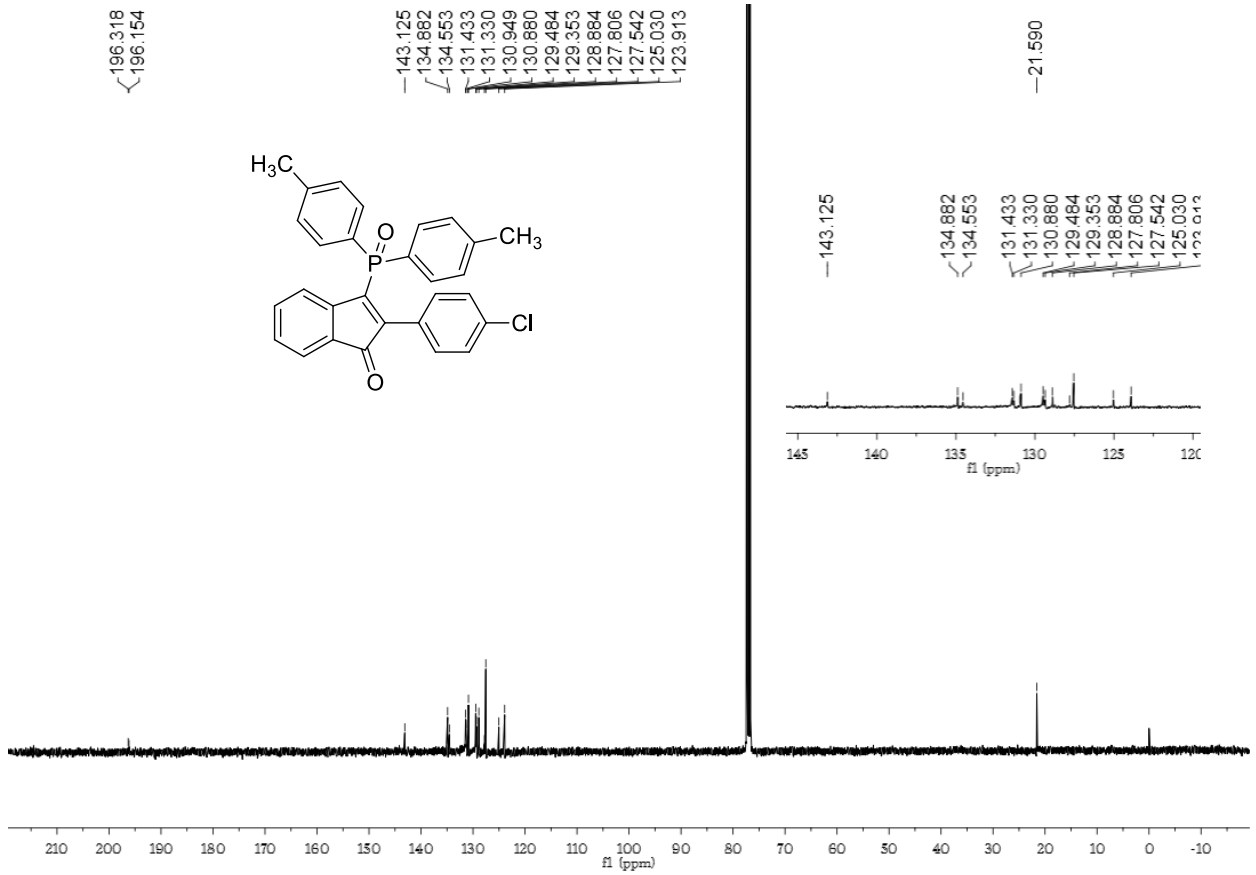
^{1}H NMR Spectrum of Compound 3x



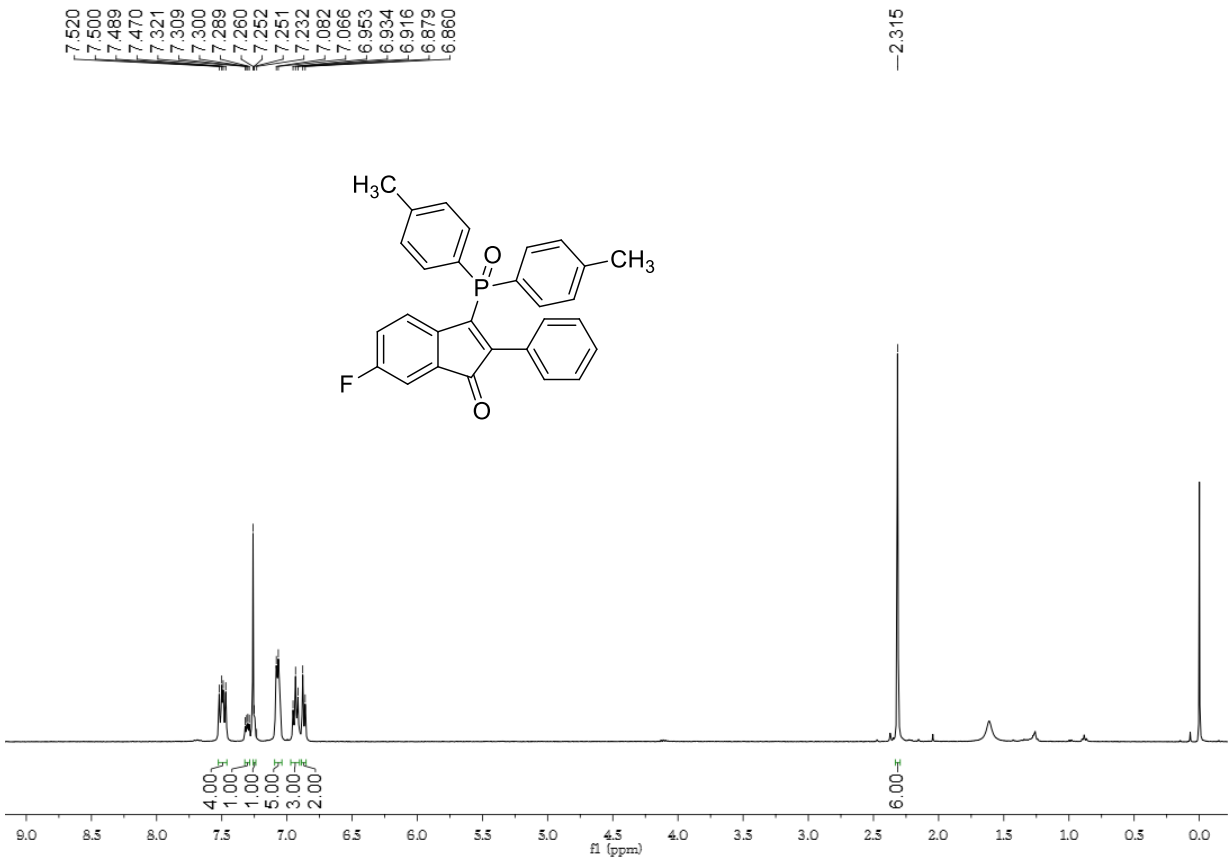
^{13}C NMR Spectrum of Compound 3x



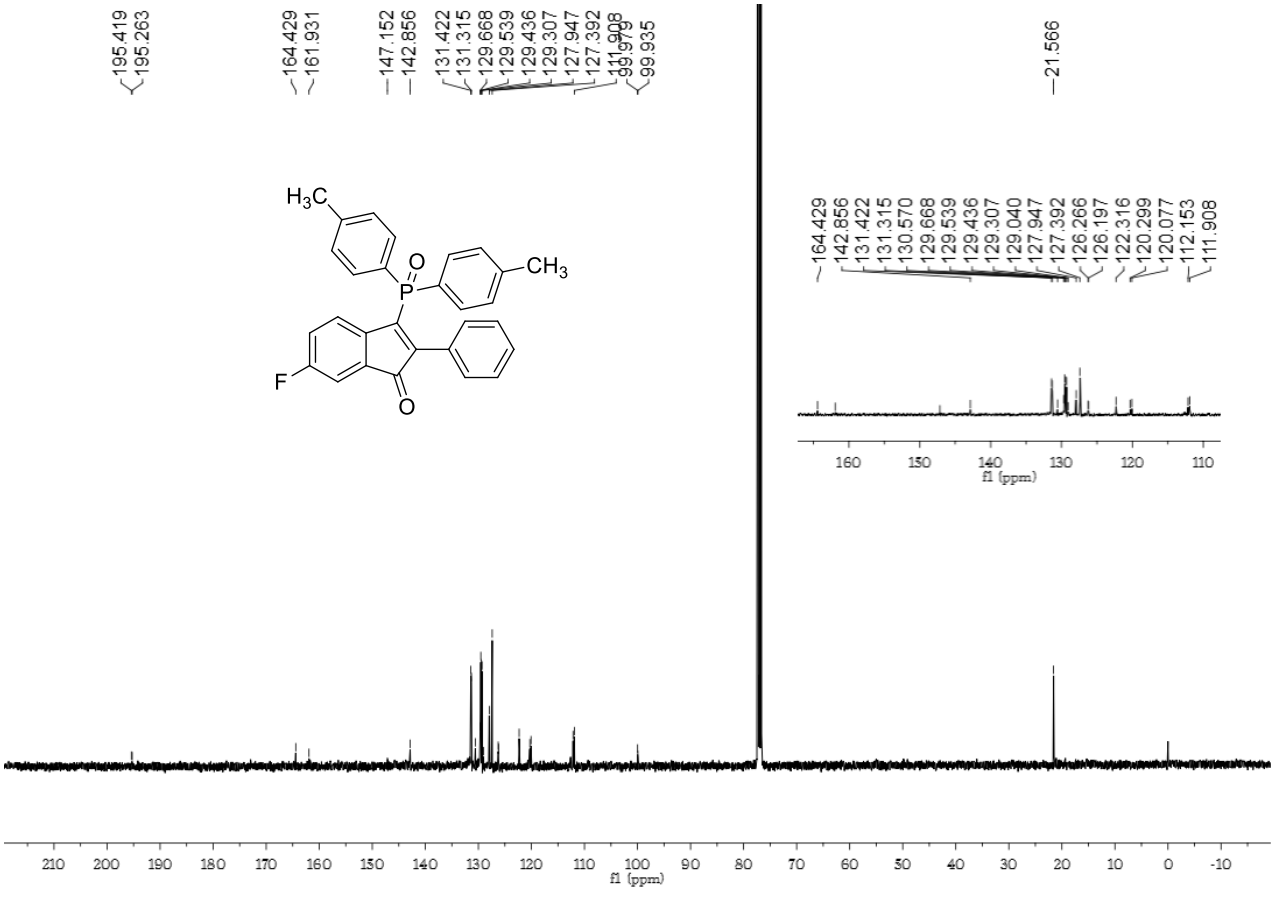
^{1}H NMR Spectrum of Compound 3y



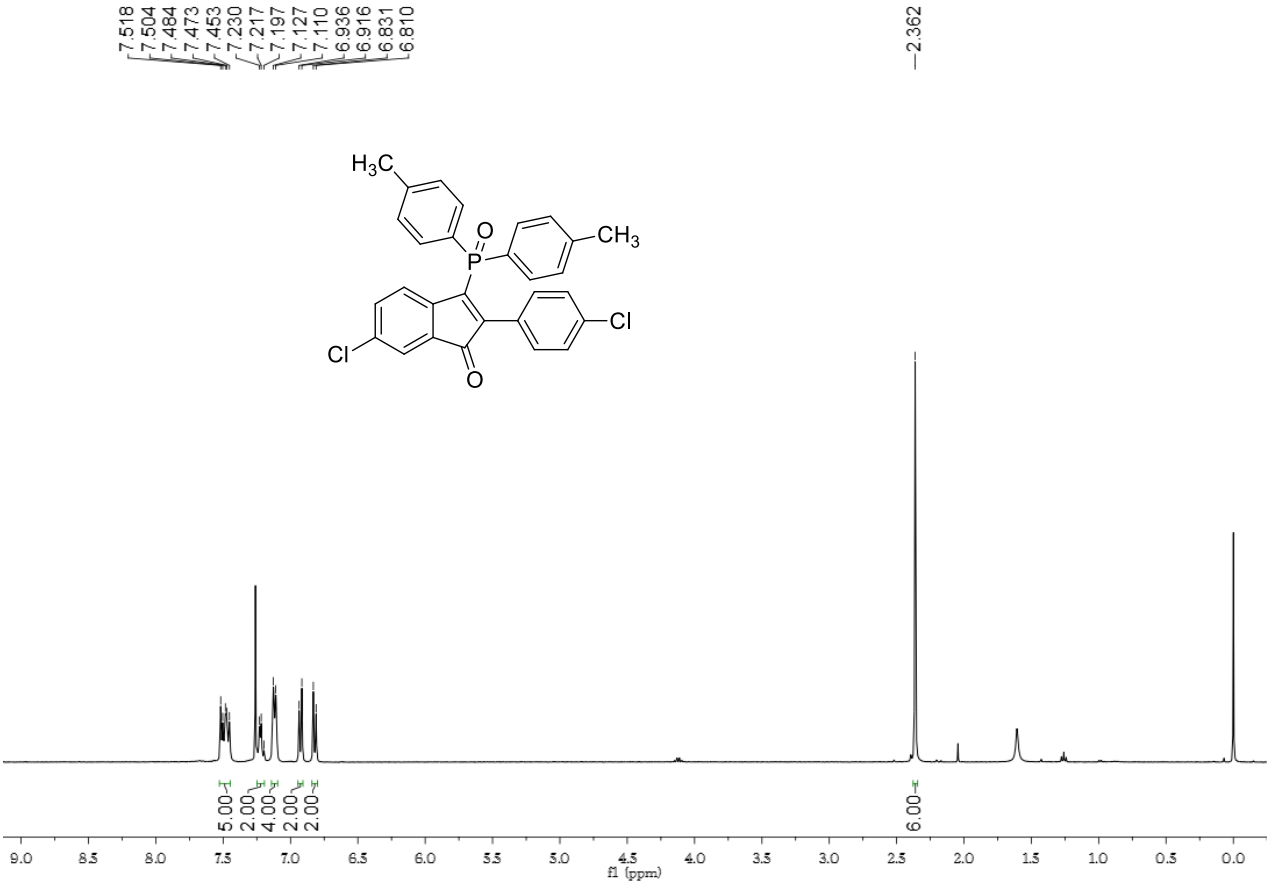
^{13}C NMR Spectrum of Compound 3y



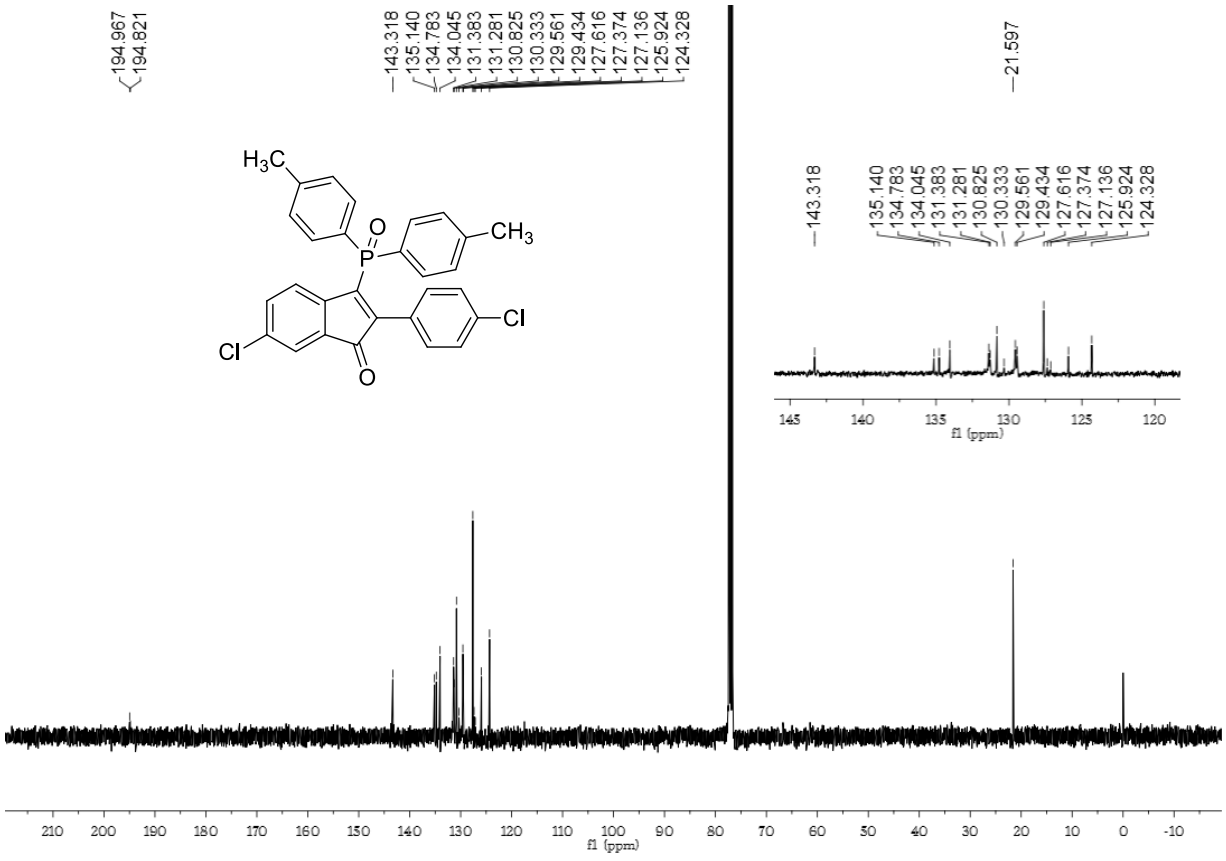
^{1}H NMR Spectrum of Compound 3z



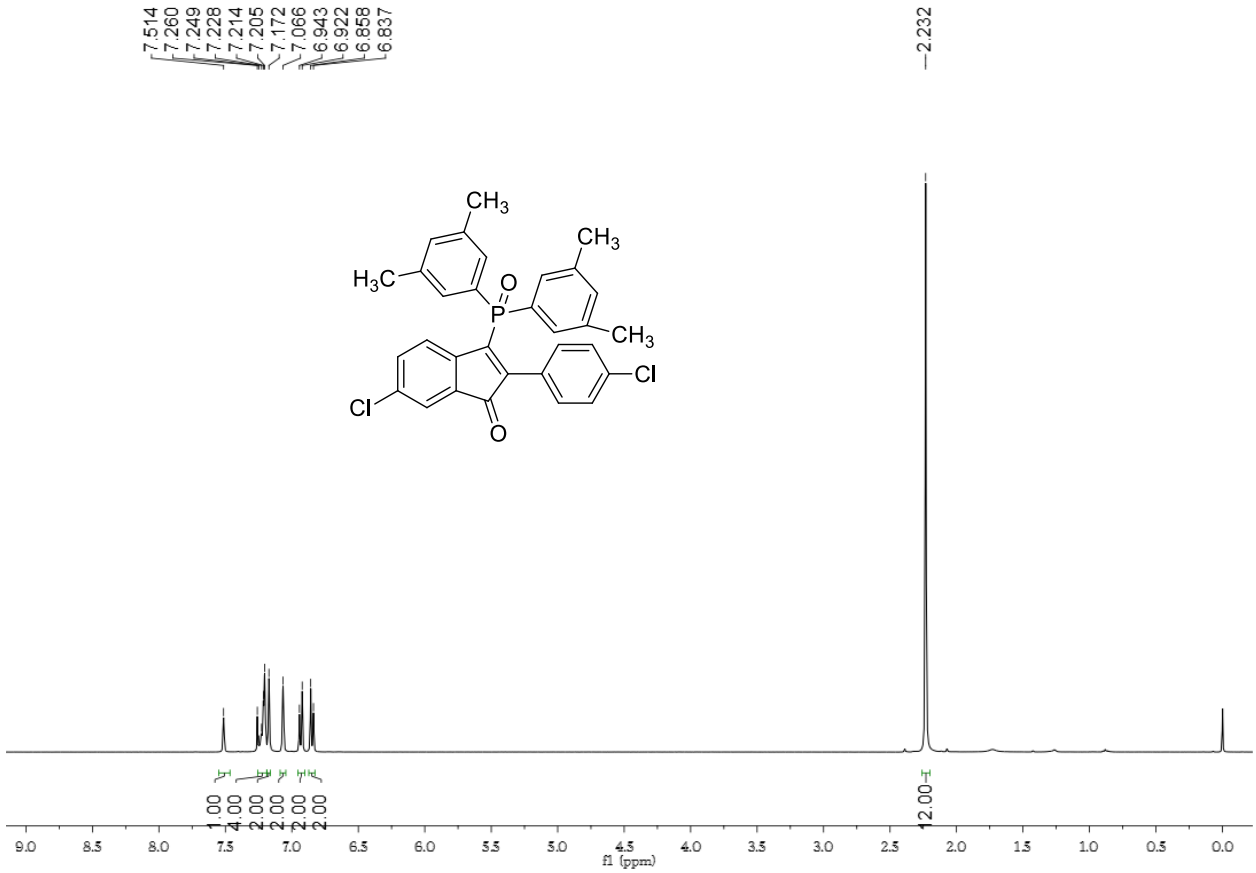
^{13}C NMR Spectrum of Compound 3z



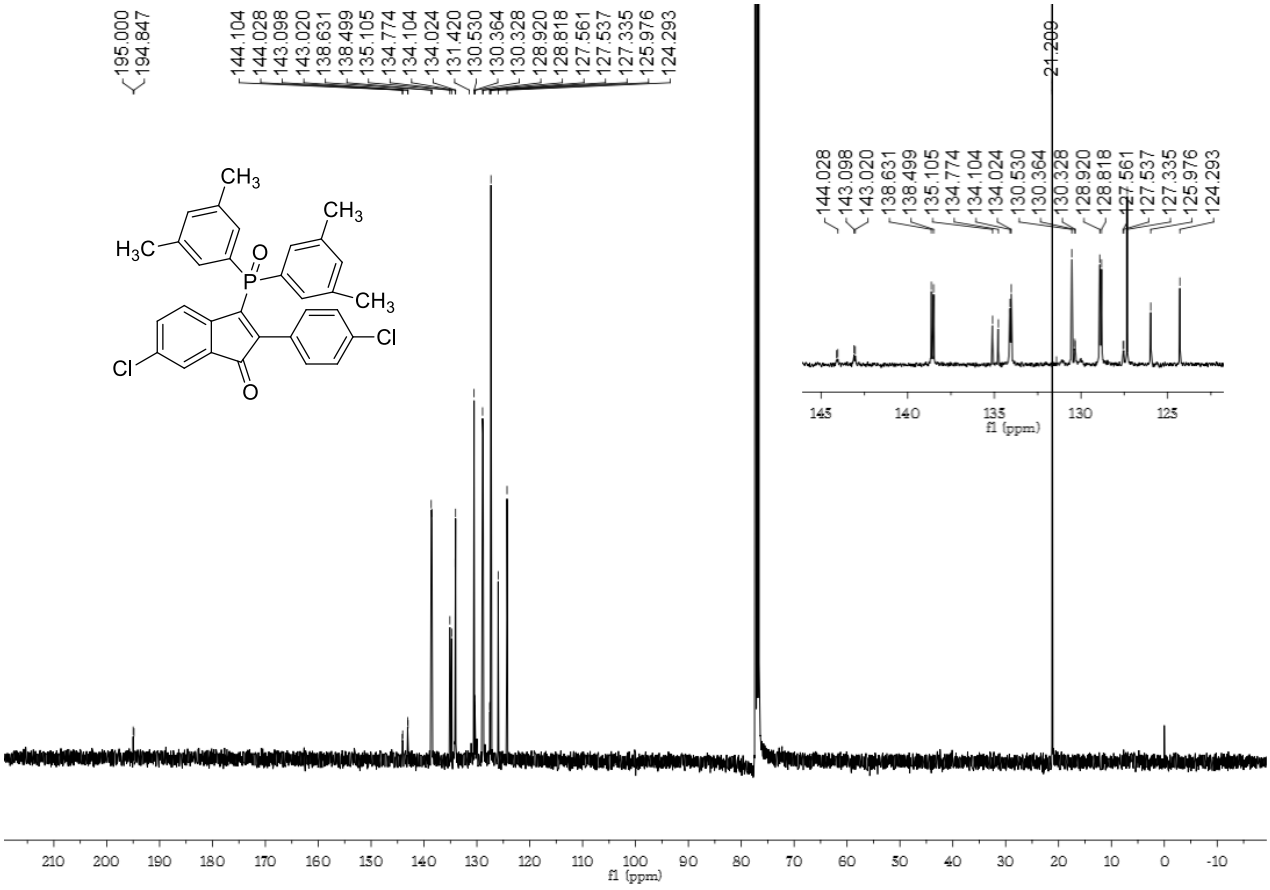
^{1}H NMR Spectrum of Compound 3aa



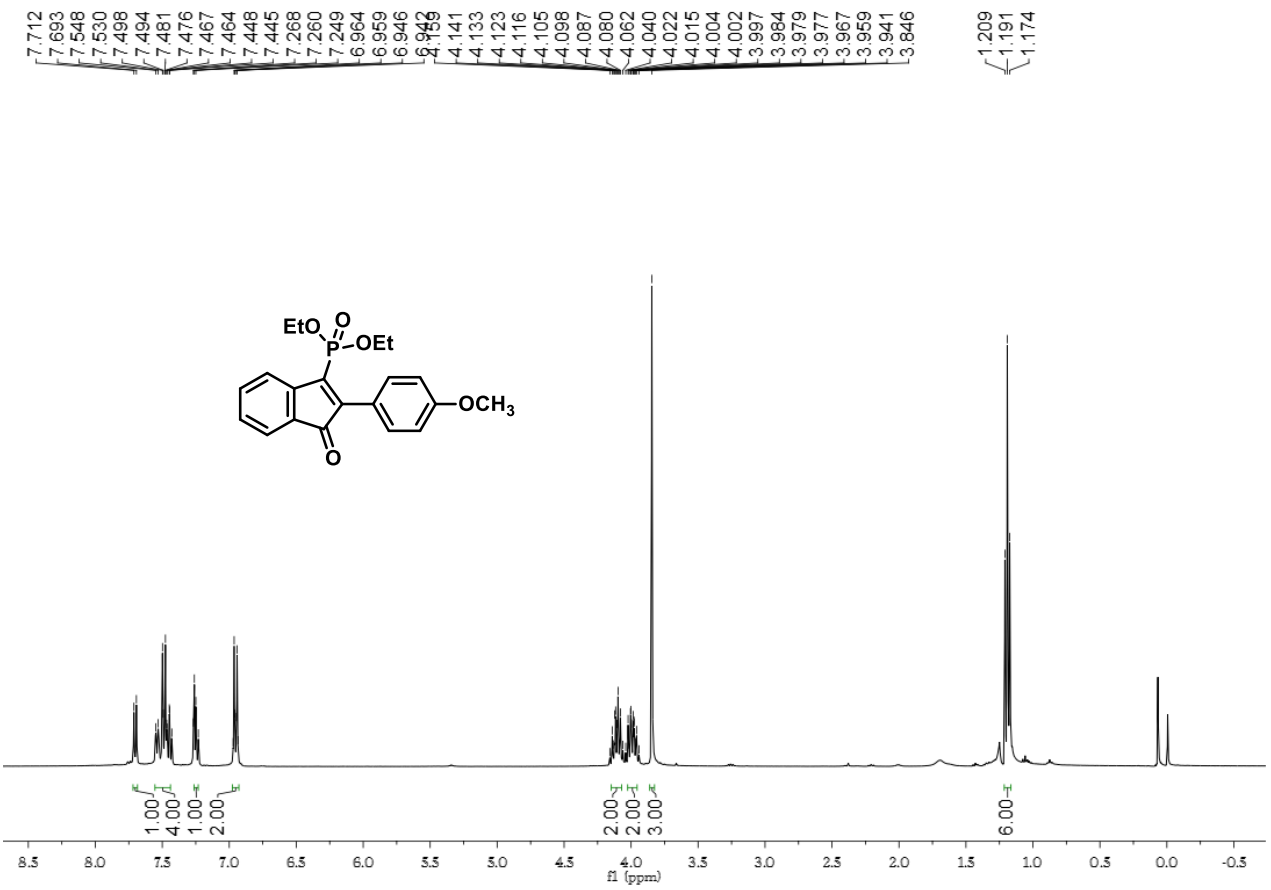
^{13}C NMR Spectrum of Compound 3aa



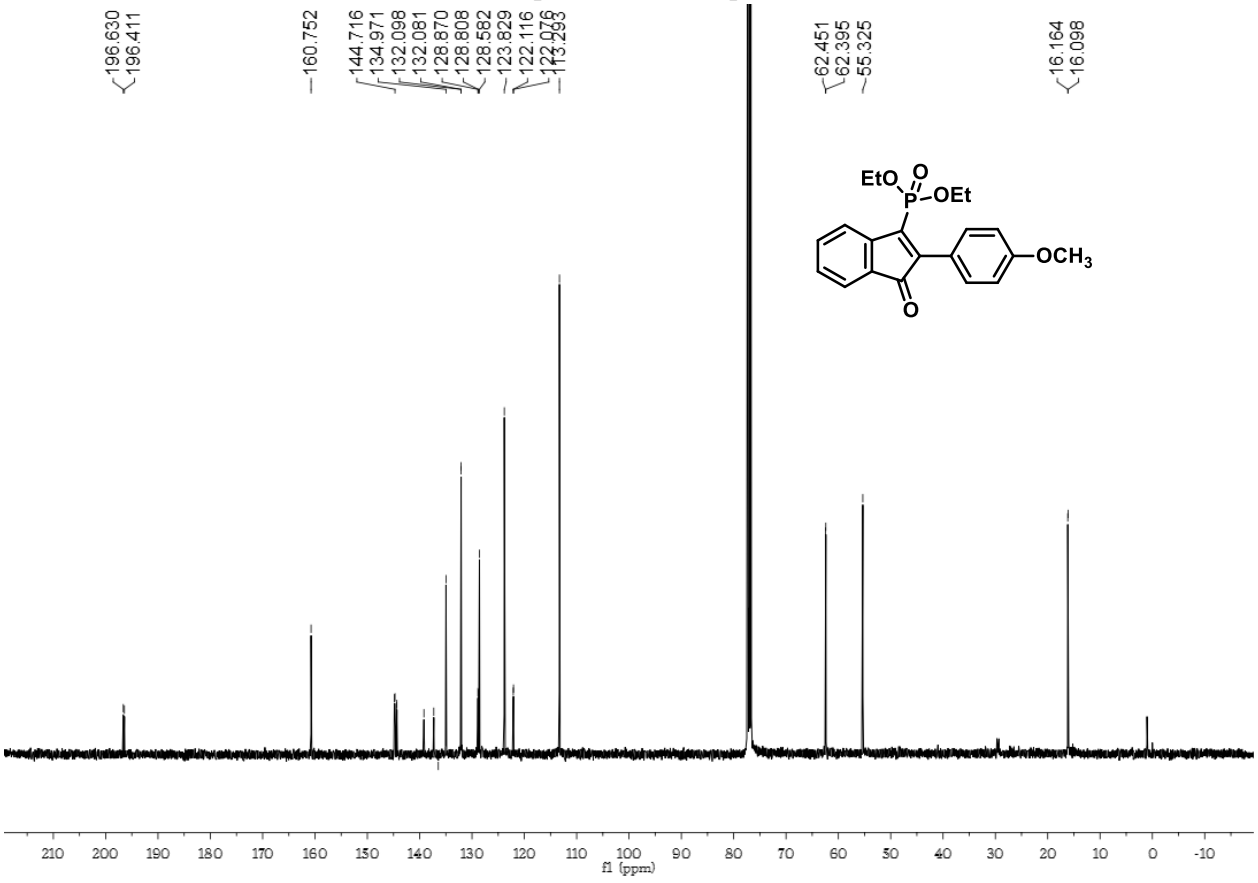
^{1}H NMR Spectrum of Compound 3bb



^{13}C NMR Spectrum of Compound 3bb



^{1}H NMR Spectrum of Compound 3cc



^{13}C NMR Spectrum of Compound 3cc