Supporting Information

Visible-light-induced triple catalysis for a ring-opening cyanation of cyclopropyl ketones

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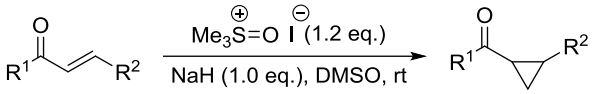
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. All the solvents were treated according to general methods. ^{1}H NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz with complete proton decoupling. The high resolution mass spectra (HRMS) were recorded on Bruker microTOF II ESI-TOF using a positive electrospray ionization (ESI^+).

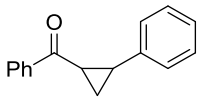
2. Preparation of Substrates

The cyclopropyl ketones (**1a**~**1t**, **4a**~**4f**, **6a**~**6i**) are prepared by the following procedure according to literature reports[1]. Substrates **4g**~**4h** were prepared according to literature[2].



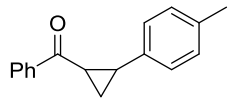
Procedure A: To a two-necked round flask, sodium hydride (60% in mineral oil, 1.0 equiv.) was added. Then, dry DMSO and trimethylsulfoxonium iodide (1.2 equiv.) were added to the flask at room temperature under an Ar atmosphere. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 mins, during which time the solution became clear. Chalcone (1.0 equiv.) was then added in one portion to the clear solution. The reaction solution was stirred at room temperature for 5 h. After completion of the reaction (TLC), the reaction was quenched with ice cold water and the mixture was diluted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (petroleum ether/ethyl acetate) as eluent to afford cyclopropyl ketone products.

Phenyl(2-phenylcyclopropyl)methanone (1a)



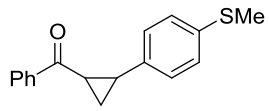
White solid; 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.57-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 6.7 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 2.93-2.88 (m, 1H), 2.73-2.68 (m, 1H), 1.95-1.91 (m, 1H), 1.62-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 140.4, 137.7, 132.9, 128.5, 128.1, 126.6, 126.2, 30.0, 29.3, 19.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}NaO$: 245.0937, found: 245.0945.

Phenyl(2-(*p*-tolyl)cyclopropyl)methanone (1b)



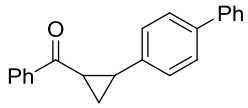
White solid; 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.56-7.52 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.12-7.05 (m, 4H), 2.88-2.84 (m, 1H), 2.69-2.64 (m, 1H), 1.93-1.88 (m, 1H), 1.55-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 137.8, 137.5, 136.3, 132.9, 129.3, 128.6, 128.2, 126.2, 30.0, 29.4, 21.1, 19.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{16}NaO$: 259.1093, found: 259.1096.

(2-(4-(Methylthio)phenyl)cyclopropyl)(phenyl)methanone (1c)



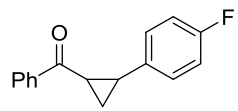
White solid; 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.58-7.53 (m, 1H), 7.46 (dd, J = 8.4, 7.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.88-2.84 (m, 1H), 2.68-2.63 (m, 1H), 2.47 (s, 3H), 1.94-1.89 (m, 1H), 1.55-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 137.7, 137.5, 136.6, 133.0, 128.6, 128.1, 127.1, 126.8, 29.7, 29.4, 19.1, 16.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}NaOS$: 291.0814, found: 291.0810.

(2-([1,1'-Biphenyl]-4-yl)cyclopropyl)(phenyl)methanone (1d)



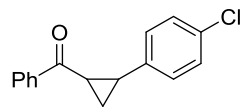
White solid; 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.56 (dd, J = 13.9, 7.7 Hz, 5H), 7.49-7.42 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.3 Hz, 2H), 2.97-2.92 (m, 1H), 2.77-2.72 (m, 1H), 1.99-1.94 (m, 1H), 1.63-1.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 140.8, 139.7, 139.6, 137.7, 133.0, 128.8, 128.6, 128.2, 127.3, 127.3, 127.0, 126.7, 29.8, 29.5, 19.3. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{22}H_{18}NaO$: 321.1250, found: 321.1247.

(2-(4-Fluorophenyl)cyclopropyl)(phenyl)methanone (1e)



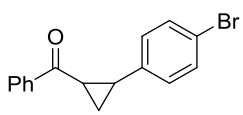
White solid; 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.14 (dd, J = 8.3, 5.3 Hz, 2H), 6.99 (t, J = 8.5 Hz, 2H), 2.87-2.83 (m, 1H), 2.71-2.66 (m, 1H), 1.93-1.88 (m, 1H), 1.52-1.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 161.7 (d, J = 246.4 Hz), 137.7, 136.1 (d, J = 3.0 Hz), 133.0, 128.6, 128.1, 127.8 (d, J = 8.1 Hz), 115.4 (d, J = 21.2 Hz), 29.2, 29.2, 19.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}FNaO$: 263.0843, found: 263.0841.

(2-(4-Chlorophenyl)cyclopropyl)(phenyl)methanone (1f)



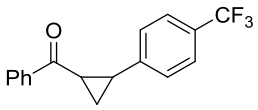
White solid; 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.57 (*t*, J = 7.4 Hz, 1H), 7.46 (dd, J = 8.4, 6.9 Hz, 2H), 7.28-7.25 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.88-2.84 (m, 1H), 2.69-2.64 (m, 1H), 1.94-1.89 (m, 1H), 1.54-1.49 (m , 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 139.0, 137.6, 133.1, 132.3, 128.7, 128.7, 128.1, 127.6, 29.3, 29.2, 19.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}ClNaO$: 279.0547, found: 279.0545.

(2-(4-Bromophenyl)cyclopropyl)(phenyl)methanone (1g)



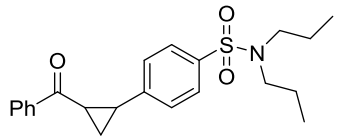
White solid; 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 21.2, 7.8 Hz, 4H), 7.05 (d, J = 8.0 Hz, 2H), 2.89-2.84 (m, 1H), 2.68-2.63 (m, 1H), 1.94-1.90 (m, 1H), 1.54-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 139.6, 137.6, 133.1, 131.6, 128.7, 128.1, 127.97, 120.3, 29.3, 29.3, 19.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}BrNaO$: 323.0042, found: 323.0043.

Phenyl(2-(4-(trifluoromethyl)phenyl)cyclopropyl)methanone (1h)



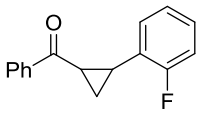
White solid; 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 8.2 Hz, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 2.97-2.92 (m, 1H), 2.77-2.72 (m, 1H), 1.99-1.95 (m, 1H), 1.61-1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 144.7, 137.5, 133.2, 128.7, 128.2, 126.5, 125.5 (q, J = 4.0 Hz), 124.5 (q, J = 273.7 HZ), 29.5, 29.2, 19.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{14}F_3NaO$: 313.0811, found: 313.0813.

4-(2-Benzoylcyclopropyl)-*N, N*-dipropylbenzenesulfonamide (1i)



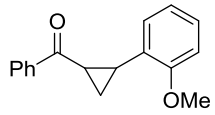
Yellow oil; 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 7.28 (d, J = 8.6 Hz, 2H), 3.09-3.05 (m, 4H), 2.98-2.94 (m, 1H), 2.77-2.72 (m, 1H), 1.99-1.94 (m, 1H), 1.62-1.52 (m, 5H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 145.4, 138.3, 137.4, 133.2, 128.7, 128.1, 127.4, 126.6, 50.1, 29.6, 29.1, 22.1, 19.7, 11.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{22}H_{27}NNaO_3S$: 408.1604, found: 408.1608.

(2-(2-Fluorophenyl)cyclopropyl)(phenyl)methanone (1j)



Yellow oil; 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.23-7.18 (m, 1H), 7.10 (dd, J = 5.4, 3.3 Hz, 2H), 7.03 (dd, J = 10.4, 8.2 Hz, 1H), 2.96-2.92 (m, 1H), 2.86-2.81 (m, 1H), 1.93-1.88 (m, 1H), 1.61-1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 161.8 (d, J = 247.5 Hz), 137.7, 133.0, 128.6, 128.2, 128.1 (d, J = 8.1 Hz), 127.5 (d, J = 13.1 Hz), 127.3 (d, J = 4.0 Hz), 124.1 (d, J = 4.0 Hz), 115.5 (d, J = 22.2 Hz), 27.4, 23.8, 23.7, 17.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.3. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}FNaO$: 263.0843, found: 263.0842.

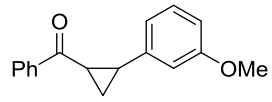
(2-(2-Methoxyphenyl)cyclopropyl)(phenyl)methanone (1k)



Colorless oil; 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 8.5 Hz, 1H), 7.05 (t, J = 4.5 Hz, 1H), 6.92 (q, J = 5.5, 3.9 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 3.76 (s, 3H), 2.90-2.79 (m, 2H), 1.92-1.88 (m, 1H), 1.58-1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 158.5, 138.1, 132.7, 128.8, 128.5, 128.2, 127.8, 126.3, 120.5, 110.4, 55.3,

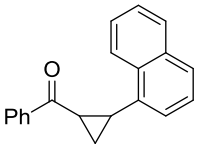
27.9, 25.6, 17.4. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_2$: 275.1043, found: 275.1044.

(2-(3-Methoxyphenyl)cyclopropyl)(phenyl)methanone (1l)



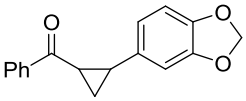
Colorless oil; 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.55 (t, J = 8.1 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.1 Hz, 1H), 6.79-6.72 (m, 3H), 3.80 (s, 3H), 2.93-2.88 (m, 1H), 2.71-2.66 (m, 1H), 1.95-1.90 (m, 1H), 1.58-1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 159.9, 142.2, 137.7, 133.0, 129.7, 128.6, 128.2, 118.5, 112.3, 111.8, 55.3, 30.1, 29.4, 19.3. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_2$: 275.1043, found: 275.1041.

(2-(Naphthalen-1-yl)cyclopropyl)(phenyl)methanone (1m)



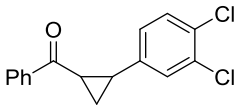
White solid; 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.8 Hz, 1H), 8.05-8.03 (m, 2H), 7.86 (dd, J = 7.5, 1.7 Hz, 1H), 7.77 (d, 1H), 3.28-3.23 (m, 1H), 2.91-2.86 (m, 1H), 2.00-1.95 (m, 1H), 1.77-1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 137.8, 136.2, 133.6, 133.0, 128.6, 128.6, 128.3, 127.7, 126.3, 126.0, 125.4, 124.1, 123.9, 27.7, 27.4, 17.9. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{20}H_{16}Na$: 295.1093, found: 295.1090.

(2-(Benzo[*d*][1,3]dioxol-5-yl)cyclopropyl)(phenyl)methanone (1n)



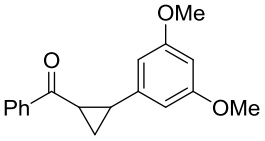
White solid; 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 6.74 (d, J = 7.9 Hz, 1H), 6.69-6.64 (m, 2H), 5.93 (s, 2H), 2.84-2.80 (m, 1H), 2.66-2.61 (m, 1H), 1.90-1.86 (m, 1H), 1.50-1.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 147.9, 146.4, 137.8, 134.4, 132.9, 128.6, 128.1, 119.8, 108.3, 106.6, 101.1, 30.1, 29.2, 19.0. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{18}H_{16}NaO_3$: 287.1043, found: 287.1045.

(2-(3,4-Dichlorophenyl)cyclopropyl)(phenyl)methanone (1o)



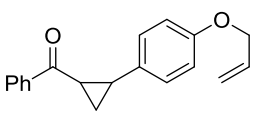
White solid; 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 8.3 Hz, 1H), 7.24 (s, 1H), 7.02 (dd, J = 8.4, 1.9 Hz, 1H), 2.90-2.85 (m, 1H), 2.68-2.63 (m, 1H), 1.94-1.89 (m, 1H), 1.54-1.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 140.9, 137.4, 133.2, 132.7, 130.5, 130.5, 128.7, 128.2, 128.1, 125.9, 29.2, 28.5, 19.2. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{16}H_{12}Cl_2NaO$: 313.0157, found: 313.0157.

(2-(3,5-Dimethoxyphenyl)cyclopropyl)(phenyl)methanone (1p)



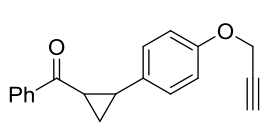
Yellow oil; 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 6.7 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 6.34 (s, 3H), 3.79 (s, 6H), 2.92-2.87 (m, 1H), 2.66-2.61 (m, 1H), 1.92-1.87 (m, 1H), 1.56-1.51 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 161.0, 143.0, 137.7, 133.0, 128.6, 128.2, 104.4, 98.4, 55.4, 30.2, 29.3, 19.2. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{18}H_{18}NaO_3$: 305.1148, found: 305.1149.

(3-(4-(Allyloxy)phenyl)cyclopropyl)(phenyl)methanone (1q)



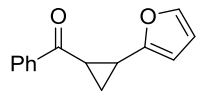
White solid; 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.19 (m, 1H), 7.18-7.15 (m, 2H), 6.96-6.92 (m, 2H), 6.08-5.99 (m, 1H), 5.44-5.39 (m, 1H), 5.32-5.29 (m, 1H), 4.60-4.57 (m, 2H), 2.87-2.83 (m, 1H), 2.69-2.64 (m, 1H), 1.91-1.86 (m, 1H), 1.53-1.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 162.5, 140.8, 132.5, 130.9, 130.4, 128.6, 126.5, 126.2, 118.2, 114.5, 68.91, 29.6, 28.9, 19.0. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{19}H_{18}NaO_2$: 301.1199, found: 301.1191.

Phenyl(2-(4-(prop-2-yn-1-yloxy)phenyl)cyclopropyl)methanone (1r)



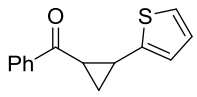
White solid; 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.31 (dd, J = 8.2, 6.8 Hz, 2H), 7.25-7.16 (m, 3H), 7.03-7.00 (m, 2H), 4.75 (d, J = 2.4 Hz, 2H), 2.87-2.83 (m, 1H), 2.69-2.64 (m, 1H), 2.54 (t, J = 2.4 Hz, 1H), 1.92-1.87 (m, 1H), 1.54-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 161.2, 140.7, 131.5, 130.3, 128.6, 126.6, 126.2, 114.6, 77.8, 76.2, 55.9, 29.7, 29.0, 19.0. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{19}H_{16}NaO_2$: 299.1043, found: 299.1042.

(2-(Furan-2-yl)cyclopropyl)(phenyl)methanone (1s)



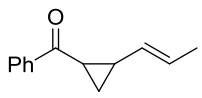
Yellow solid; 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.56 (dd, J = 8.1, 6.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 1.8 Hz, 1H), 6.32-6.30 (m , 1H), 6.12 (d, J = 3.2 Hz, 1H), 3.05-3.00 (m, 1H), 2.72-2.67 (m, 1H), 1.84-1.79 (m, 1H), 1.62-1.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 153.8, 141.1, 137.6, 133.0, 128.6, 128.2, 110.6, 105.2, 26.6, 22.8, 17.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{14}H_{12}NaO_2$: 235.0730, found: 235.0731.

Phenyl(2-(thiophen-2-yl)cyclopropyl)methanone (1t)



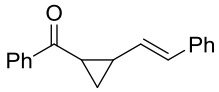
White solid; 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.12 (dd, J = 5.0, 1.2 Hz, 1H), 6.93 (dd, J = 5.1, 3.5 Hz, 1H), 6.89-6.88 (m, 1H), 2.96-2.85 (m, 2H), 1.97-1.92 (m, 1H), 1.57-1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 144.8, 137.6, 133.1, 128.6, 128.2, 127.1, 124.1, 123.2, 30.0, 25.1, 20.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{14}H_{12}NaOS$: 251.0501, found: 251.0505.

(*E*)-Phenyl(2-(prop-1-en-1-yl)cyclopropyl)methanone (4a)



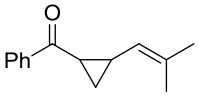
White solid; 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.97 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.45 (m, 2H), 5.69-5.61 (m, 1H), 5.22-5.14 (m, 1H), 2.65-2.61 (m, 1H), 2.17-2.10 (m, 1H), 2.37-2.31 (m, 1H), 1.70-1.65 (m , 4H), 1.16-1.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 138.0, 132.7, 131.2, 128.5, 128.1, 126.3, 29.2, 26.7, 18.2, 17.9. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{13}H_{14}NaO$: 209.0937, found: 209.0934.

(*E*)-Phenyl(2-styrylcyclopropyl)methanone (4b)



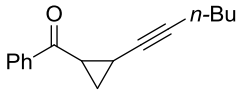
White solid; 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.7, 3.1 Hz, 2H), 7.57-7.44 (m, 3H), 7.34-7.27 (m, 4H), 7.23-7.19 (m, 1H), 6.57 (d, J = 15.7 Hz, 1H), 5.94-5.87 (m, 1H), 2.82-2.77 (m, 1H), 2.37-2.31 (m, 1H), 1.86-1.80 (m , 1H), 1.32-1.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 137.9, 137.0, 132.9, 130.6, 130.5, 128.7, 128.6, 128.1, 127.4, 126.0, 29.7, 27.2, 18.5. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{16}NaO$: 271.1093, found: 271.1086.

(2-(2-Methylprop-1-en-1-yl)cyclopropyl)(phenyl)methanone (4c)



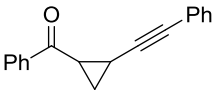
Colorless oil; 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.57-7.53 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 4.79-4.75 (m, 1H), 2.63-2.59 (m, 1H), 2.29-2.22 (m, 1H), 1.71 (s, 6H), 1.10-1.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 138.0, 134.4, 132.7, 128.5, 128.0, 125.2, 26.9, 26.5, 25.6, 18.9, 18.4. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{14}H_{14}NaO$: 223.1093, found: 223.1094.

(2-(Hex-1-yn-1-yl)cyclopropyl)(phenyl)methanone (4d)



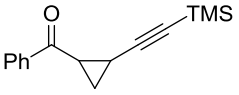
Yellow oil; 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.60-7.56 (m, 1H), 7.51-7.47 (m, 2H), 2.91-2.87 (m, 1H), 2.18-2.14 (m, 2H), 2.02-1.98 (m, 1H), 1.64-1.59 (m, 1H), 1.49-1.37 (m, 4H), 1.33-1.28 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 137.5, 133.0, 128.6, 128.2, 80.3, 78.4, 31.0, 27.0, 22.0, 19.7, 18.5, 14.0, 13.6. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{18}NaO$: 249.1250, found: 249.1253.

Phenyl(2-(phenylethynyl)cyclopropyl)methanone (4e)



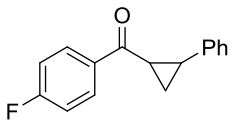
Yellow solid; 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.03 (m, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.45-7.27 (m, 5H), 3.29-3.27 (m, 1H), 2.22-2.12 (m, 1H), 1.62-1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 137.0, 134.0, 131.9, 129.3, 129.0, 128.8, 128.6, 123.0, 90.9, 78.1, 26.7, 19.6, 13.4. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{14}NaO$: 269.0937, found: 269.0930.

Phenyl(2-((trimethylsilyl)ethynyl)cyclopropyl)methanone (4f)



White solid; 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.61-7.57 (m, 1H), 7.49 (dd, J = 8.2, 6.8 Hz, 2H), 3.00-2.96 (m, 1H), 2.10-2.06 (m, 1H), 1.65-1.60 (m, 1H), 1.41-1.36 (m, 1H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 137.5, 133.4, 128.9, 128.5, 106.9, 82.8, 27.3, 20.2, 14.3, 0.3. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{15}H_{18}NaOSi$: 265.1019, found: 265.1010.

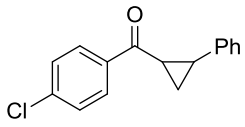
(4-Fluorophenyl)(2-phenylcyclopropyl)methanone (6a)



White solid; 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.25-7.21 (m, 1H), 7.18-7.10 (m, 4H), 2.86-2.82 (m, 1H), 2.72-2.67 (m, 1H), 1.94-1.90 (m, 1H), 1.59-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 165.7 (d, J = 255.5 Hz), 140.4, 134.1 (d, J = 3.0 Hz), 130.8 (d, J = 9.1 Hz), 128.6, 126.7, 126.2, 115.7 (d, J = 22.2 Hz), 30.1, 29.3, 19.3. ^{19}F NMR (376 MHz,

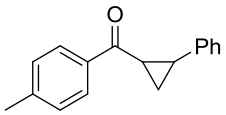
$CDCl_3$) δ -105.53. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{16}H_{14}FNaO$: 263.0843, found: 263.0848.

(4-Chlorophenyl)(2-phenylcyclopropyl)methanone (6b)



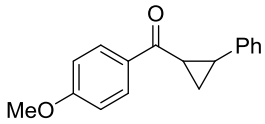
White solid; 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.4, 1.3 Hz, 2H), 7.43-7.41 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.25-7.21 (m, 1H), 7.17 (d, J = 7.5 Hz, 2H), 2.85-2.81 (m, 1H), 2.72-2.67 (m, 1H), 1.95-1.90 (m, 1H), 1.60-1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 140.3, 139.4, 136.0, 129.6, 128.9, 128.7, 126.8, 126.2, 30.3, 29.3, 19.4. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{16}H_{14}ClNaO$: 279.0547, found: 279.0549.

(3-Phenylcyclopropyl)(*p*-tolyl)methanone (6c)



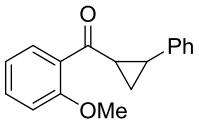
White solid; 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 3H), 7.18-7.16 (m, 2H), 2.90-2.86 (m, 1H), 2.70-2.66 (m, 1H), 2.40 (s, 3H), 1.92-1.88 (m, 1H), 1.55-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 143.7, 140.7, 135.2, 129.3, 128.6, 128.3, 126.6, 126.3, 29.8, 29.2, 21.7, 19.1. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{16}NaO$: 259.1093, found: 259.1088.

(4-Methoxyphenyl)(2-phenylcyclopropyl)methanone (6d)



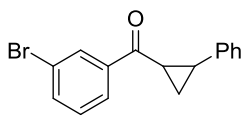
White solid; 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 2H), 7.31-7.27 (m, 2H), 7.23-7.15 (m, 3H), 6.92 (d, J = 8.9 Hz, 2H), 3.84 (s, 2H), 2.87-2.82 (m, 1H), 2.68-2.64 (m, 1H), 1.91-1.86 (m, 1H), 1.52-1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.5, 140.8, 130.8, 130.4, 128.6, 126.5, 126.3, 113.8, 55.5, 29.5, 28.9, 18.9. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_2$: 275.1043, found: 275.1043.

(2-Methoxyphenyl)(2-phenylcyclopropyl)methanone (6e)



White solid; 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.60 (m, 1H), 7.45-7.41 (m, 1H), 7.31-7.27 (m, 2H), 7.22-7.16 (m, 3H), 6.99 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.72 (s, 3H), 3.01-2.96 (m, 1H), 2.68-2.61 (m, 1H), 1.96-1.90 (m, 1H), 1.48-1.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 158.7, 141.2, 133.3, 130.0, 129.3, 128.4, 126.3, 120.6, 111.7, 55.6, 33.8, 30.7, 19.3. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}NaO_2$: 275.1043, found: 275.1044.

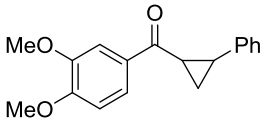
(3-Bromophenyl)(2-phenylcyclopropyl)methanone (6f)



White solid; 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, J = 1.9 Hz, 1H), 7.91-7.89 (m, 1H), 7.68-7.66 (m, 1H), 7.35-7.30 (m, 3H), 7.26-7.23 (m, 1H), 7.18-7.15 (m, 2H), 2.85-2.80 (m, 1H), 2.75-2.70 (m, 1H),

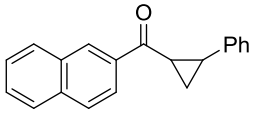
1.94-1.89 (m, 1H), 1.61-1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 140.1, 139.5, 135.8, 131.2, 130.2, 128.7, 126.8, 126.7, 126.3, 123.0, 30.5, 29.4, 19.7. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{16}H_{14}BrNaO$: 323.0042, found: 323.0039.

(3,4-Dimethoxyphenyl)(2-phenylcyclopropyl)methanone (6g)



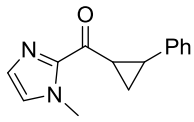
White solid; 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.26-7.23 (m, 1H), 7.21-7.17 (m, 2H), 6.88 (d, J = 8.4 Hz, 1H), 3.93 (d, J = 4.3 Hz, 6H), 2.88-2.84 (m, 1H), 2.70-2.65 (m, 1H), 1.92-1.87 (m, 1H), 1.55-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 153.3, 149.1, 140.7, 130.9, 128.6, 126.6, 126.3, 122.9, 110.2, 110.0, 56.1, 56.0, 29.6, 28.9, 19.0. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{18}NaO_3$: 305.1148, found: 305.1148.

Naphthalen-2-yl(2-phenylcyclopropyl)methanone (6h)



White solid; 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.12 (dd, J = 8.6, 1.7 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.94 (t, J = 8.8 Hz, 2H), 7.67-7.57 (m, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.33-7.28 (m, 3H), 3.15-3.10 (m, 1H), 2.87-2.82 (m, 1H), 2.06-2.02 (m, 1H), 1.71-1.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 140.6, 135.6, 135.1, 132.6, 129.8, 129.6, 128.7, 128.5, 128.4, 127.8, 126.8, 126.7, 126.4, 124.0, 30.1, 29.5, 19.5. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{20}H_{16}NaO$: 295.1093, found: 295.1095.

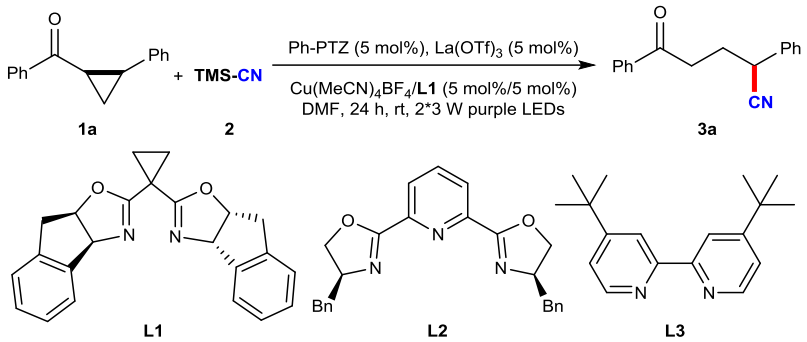
(1-Methyl-1H-imidazol-2-yl)(2-phenylcyclopropyl)methanone (6i)



White solid; 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.20-7.14 (m, 4H), 7.02 (s, 1H), 3.99 (d, J = 2.2 Hz, 3H), 3.64-3.59 (m, 1H), 2.71-2.66 (m, 1H), 1.83-1.78 (m, 1H), 1.56-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 143.6, 140.5, 129.4, 128.5, 127.1, 126.5, 126.3, 36.3, 29.7, 29.4, 20.2. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{14}H_{14}N_2NaO$: 295.1093, found: 295.1090.

3. Details for the Condition Optimization

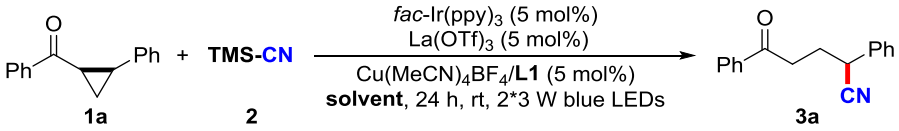
Table S1. Condition optimization[a]



Entry	Variation from the standard conditions	Yield (%)[b]
1	none	80
2	no Ph-PTZ, $La(OTf)_3$, [Cu], or light	-
3	$Cu(OAc)_2$ instead of $Cu(MeCN)_4BF_4$	18
4	**L2** instead of **L1**	36
5	**L3** instead of **L1**	-
6	10 mol % of **L1** was used	85 (80)[c]
7	$Mg(OTf)_2$ instead of $La(OTf)_3$	25
8	$Sc(OTf)_3$ instead of $La(OTf)_3$	-
9	$Ru(bpy)_3Cl_2$ $6H_2O$ instead of Ph-PTZ	6
10	*fac*-$Ir(ppy)_3$ instead of Ph-PTZ	77

[a]Reaction conditions: 0.20 mmol of **1a**, 0.60 mmol of **2**, $La(OTf)_3$ (5 mol%), $Cu(MeCN)_4BF_4$ (5 mol%), **L1** (5 mol%), Ph-PTZ (5 mol%) and anhydrous DMF (2.0 mL) at rt for 24 h under the irradiation of 2*3 W purple LEDs. [b]Determined by the ^1H NMR spectrum of reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield. DMF = *N*,*N*-dimethylformamide.

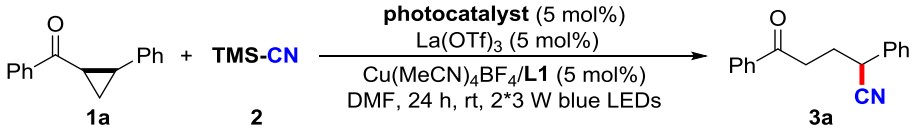
Table S2. The effect of solvents[a]



Entry	Solvent	Yield/%[b]
1	THF	NR
2	Dioxane	NR
3	CH_3CN	trace
4	CH_2Cl_2	64
5	$CHCl_3$	NR
6	Toluene	trace
7	CH_3OH	61
8	DMF	77
9	DMSO	25

[a]Reaction conditions: 0.20 mmol of **1a**, 0.60 mmol of **2**, $La(OTf)_3$ (5 mol%), $Cu(MeCN)_4BF_4$ (5 mol%), **L1** (5 mol%), *fac*-$Ir(ppy)_3$ (5 mol%), solvent (2 mL) at rt for 24 h under the irradiation of 2*3 W blue LEDs. [b]Determined by ^1H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. The effect of photocatalysts[a]

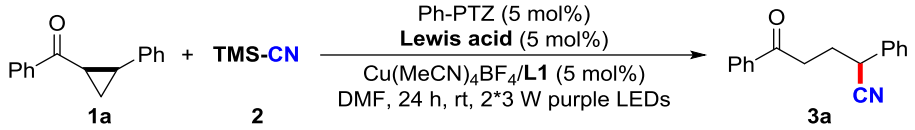


1a 2 3a

Entry	Photocatalyst	Yield/%[b]
1	*fac*-Ir(ppy)$_3$	77
2	Ru(bpy)$_3$Cl$_2$•6H$_2$O	6
3	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	NR
4	Ir(4-Fppy)$_2$(bpy)PF$_6$	NR
5[c]	Ph-PTZ	80

[a]Reaction conditions: 0.20 mmol of **1a**, 0.60 mmol of **2**, La(OTf)$_3$ (5 mol%), Cu(MeCN)$_4$BF$_4$ (5 mol%), **L1** (5 mol%), photocatalyst (5 mol%), DMF (2 mL) at rt for 24 h under the irradiation of 2*3 W blue LEDs. [b]Determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]Irradiation of 2*3 W purple LEDs.

Table S4. The effect of Lewis acids[a]

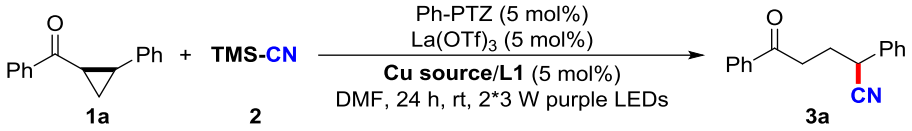


1a 2 3a

Entry	Lewis acid	Yield/%[b]
1	La(OTf)$_3$	80
2	Gd(OTf)$_3$	50
3	Sc(OTf)$_3$	NR
4	Yb(OTf)$_3$	NR
5	Sm(OTf)$_3$	NR
6	Mg(OTf)$_2$	25
7	Ga(OTf)$_3$	NR
8	In(OTf)$_3$	NR

[a]Reaction conditions: 0.20 mmol of **1**, 0.60 mmol of **2**, Lewis acid (5 mol%), Cu(MeCN)$_4$BF$_4$ (5 mol%), **L1** (5 mol%), Ph-PTZ (5 mol%), DMF (2 mL) at rt for 24 h under the irradiation of 2*3 W purple LEDs. [b]Determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. The effect of Cu sources[a]



Entry	Cu source	Yield/%[b]
1	$Cu(MeCN)_4BF_4$	80
2	CuCl	NR
3	CuBr	5
4	CuOAc	34
5	$Cu(OAc)_2$	18
6	CuCN	29
7	CuF_2	29
8	$Cu(OTf)_2$	NR

[a]Reaction conditions: 0.20 mmol of **1**, 0.60 mmol of **2**, $La(OTf)_3$ (5 mol%), Cu source (5 mol%), **L1** (5 mol%), Ph-PTZ (5 mol%), DMF (2 mL) at rt for 24 h under the irradiation of 2*3 W purple LEDs. [b]Determined by ^1H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

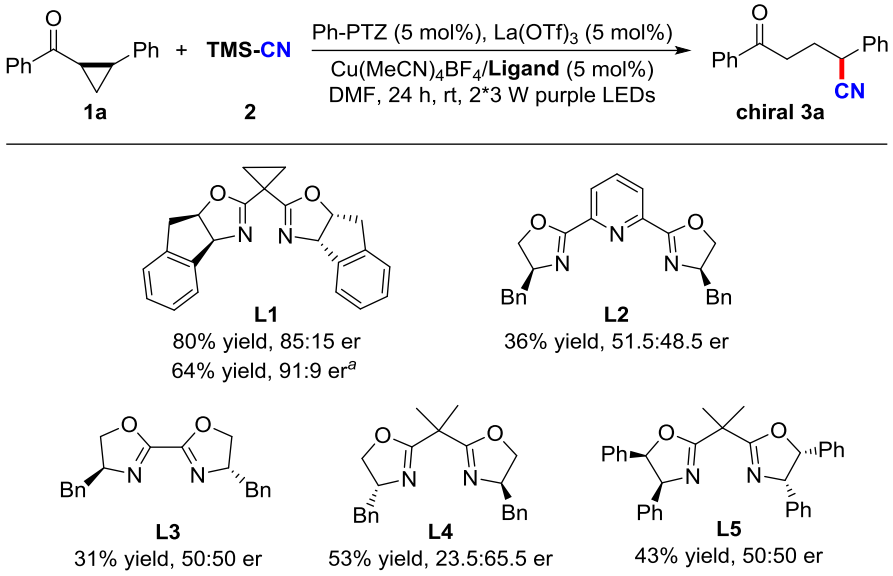
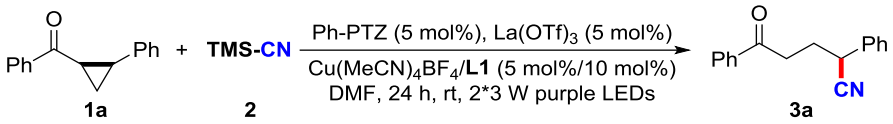


Figure S1. Preliminary trials on the asymmetric ring-opening cyanation. Reaction conditions: 0.20 mmol of **1a**, 0.60 mmol of **2**, $La(OTf)_3$ (5 mol%), $Cu(MeCN)_4BF_4$ (5 mol%), ligand (5 mol%), Ph-PTZ (5 mol%), DMF (2 mL) at rt for 24 h under the irradiation of 2*3 W purple LEDs; yields were determined by the ^1H NMR of the reaction mixture by using 1,3,5-trimethoxybenzene as an internal standard; ee values were determined by chiral HPLC. [a]The reaction was performed in CH_2Cl_2 (2 mL).

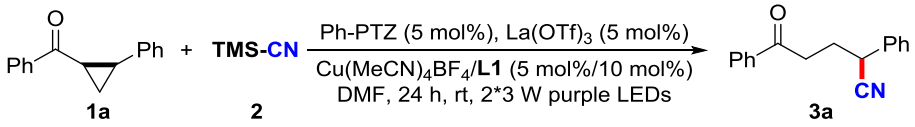
4. General Procedure for Ring-Opening Cyanation



1a 2 3a

Procedure B: $Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.01 mmol), **L1** (7.1 mg, 0.02 mmol) and anhydrous DMF (2 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar in an argon-filled glove box. Then the resulting mixture was stirred at room temperature for 20 mins followed by the addition of $La(OTf)_3$ (5.9 mg, 0.01 mmol). The solution continued to stir for 10 mins at room temperature. The vial was closed and the Schlenk tube was removed from the glove box. To the resulting mixture were added phenyl ketone **1a** (0.2 mmol, 44.5 mg), photocatalyst **Ph-PTZ** (2.8 mg, 0.01 mmol). The mixture was degassed by a "freeze-pump-thaw" procedure (3 times). After that, TMSCN (**2**, 76 μL, 0.6 mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from 2*3 W purple LEDs at room temperature for 24 h. Upon the completion of reaction as monitored by TLC, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 100:1~10:1) directly to give the desired product **3a** as a colorless oil in 80% yield.

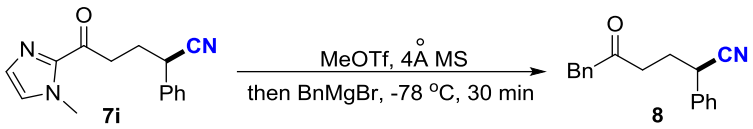
General Procedure for the Scaled-up Reaction



1a 2 3a

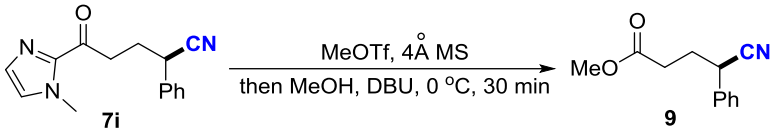
Procedure C: $Cu(CH_3CN)_4BF_4$ (155 mg, 0.5 mmol), **L1** (355 mg, 1.0 mmol) and anhydrous DMF (100 mL) were added to a 250 mL Schlenk flask equipped with a magnetic stir bar in an argon-filled glove box. Then the resulting mixture was stirred at room temperature for 30 mins followed by the addition of $La(OTf)_3$ (295 mg, 0.5 mmol). The solution continued to stir 10 mins at room temperature. The vial was closed and the Schlenk tube was removed from the glove box. To the resulting mixture were added phenyl ketone **1a** (10 mmol, 2.2 g), photocatalyst **Ph-PTZ** (140 mg, 0.5 mmol). The mixture was degassed by a "freeze-pump-thaw" procedure (3 times). After that, TMSCN (**2**, 3.8 mL, 30 mmol) was added into the mixture. At last, the mixture was stirred at a distance of ~1 cm from 2*3 W purple LEDs at room temperature for 24 h. Upon the completion of reaction as monitored by TLC, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 100:1~10:1) directly to give the desired product **3a** as a white soild in 85% yield with recovered **Ph-PTZ** (petroleum ether/ethyl acetate 200:1~100:1) in 83% yield.

Procedure for the Synthesis of 8



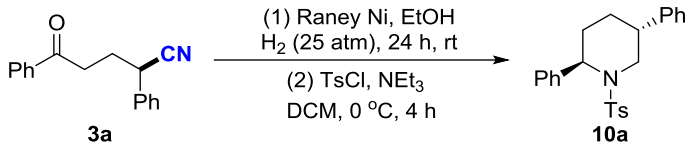
Procedure D[3]**:** Compound **7i** (53.4 mg, 0.2 mmol), 4Å molecular sieves (100 mg) and anhydrous acetonitrile (2 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar under an Ar atmosphere. The solution was stirred vigorously for 2 hours at room temperature. Then MeOTf (40 μL, 0.34 mmol) was added. After 2 h another 0.6 equiv. of MeOTf was added and the reaction stirred an additional 30 minutes. Then the suspension was filtered through a short plug of oven dried Celite. The Celite was washed with EtOAc and the solvent was removed by vacuum. The resulting oil and 4 mL THF were added to a 10 mL Schlenk flask under Ar. Then the reaction mixture was cooled to -78 ℃ before benzylmagnesium bromide (2.5 eq.) was added dropwisely. After the reaction was complete judged by TLC analysis, the mixture was extracted with diethyl ether and saturated $NaHCO_3$ solution. Combined organic dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to afford **8** as a colorless oil in 79% yield.

Procedure for the Synthesis of 9



Procedure E[3]: Compound **7i** (53.4 mg, 0.2 mmol), 4Å molecular sieves (100 mg), and anhydrous acetonitrile (2 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar under an Ar atmosphere. The solution was stirred vigorously for 2 hours at room temperature. Then MeOTf (40 μL, 0.34 mmol) was added. After 2 h another 0.6 equiv. of MeOTf was added and the reaction stirred an additional 30 minutes. Then the reaction mixture was cooled to 0 °C before MeOH (81 μL, 20.0 mmol) and DBU (60 μL, 0.40 mmol) was added slowly. The reaction was then stirred for 30 mins and quenched by 1 M HCl and extracted with EtOAc and the combined organic dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford **9** as a colorless oil in 83% yield.

Procedure for the Synthesis of 10a



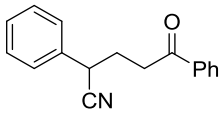
Procedure F[4,5]: Raney nickel that was washed with ethanol (3 times) was added to a solution of **3a** (99.7 mg, 0.40 mmol) in 2 mL EtOH. After the autoclave was flushed 3 times, it was pressurised with 25 bar of H_2 and stirred for 24 h at room temperature. Then the mixture was vented, and filtered through Celite, eluting with EtOAc and combined organic was concentrated in vacuo. The resulting crude product was dissolved in 2 mL CH_2Cl_2 under an Ar atmosphere. Then the reaction mixture was cooled to 0 ℃ before tosyl chloride and trimethylamine was added. The solution was warmed to room temperature and stirred for 4 h. The reaction was then quenched by 2 mL H_2O and extracted with ethyl acetate. Combined organic dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) directly to give **10a** (>20:1 dr.) in 78% isolated yield as a white solid over two steps. The relative configuration of **10a** was given out according to Klussmann's work because the sampe reductive cyclozation procedure and nearly the same starting material (*p*-MeO-Bz group) were used[5].

Procedure for the Synthesis of 10b

Procedure G[6,7]: To a solution of **3a** (99.7 mg, 0.40 mmol) in DMSO (1 mL) was added hydrogen peroxide (30%, 128 μL, 1.12 mmol) and K_2CO_3 (8.4 mg, 0.06 mmol) at 0 °C. The resulting solution was warmed to room temperature and stirred for 2 h. The reaction was then quenched by 2 mL H_2O and extracted with diethyl ether. Combined organic dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was dissolved in 4 mL $CHCl_3$ under an Ar atmosphere followed by the addition of a drop of BF_3 etherate. The solution was stirred vigorously for 30 minutes at room temperature. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) directly to give the desired product **10b** in 69% isolated yield as a white solid over two steps.

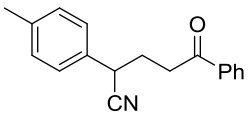
5. Spectral Data of Products

5-Oxo-2,5-diphenylpentanenitrile (3a)



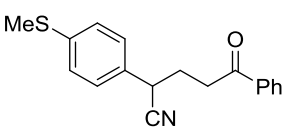
Colorless oil; 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95-7.92 (m, 2H), 7.66-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 4H), 7.39-7.33 (m, 1H), 4.30 (dd, J = 8.3, 6.8 Hz, 1H), 3.15 (t, J = 7.3 Hz, 2H), 2.30-2.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.3, 136.3, 136.0, 133.3, 129.1, 128.7, 128.0, 127.8, 127.4, 121.2, 35.2, 35.2, 29.3. IR (in KBr): 3163, 3032, 2935, 2241, 1683, 1401 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{15}NNaO$: 272.1046, found: 272.1043.

5-Oxo-5-phenyl-2-(p-tolyl)pentanenitrile (3b)



Colorless oil; 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, J = 2.0 Hz, 2H), 7.65-7.61 (m, 1H), 7.52 (t, J = 2.0 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 4.24 (t, J = 7.5 Hz, 1H), 3.13 (t, J = 7.2 Hz, 2H), 2.29 (s, 3H), 2.25-2.14 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.8, 137.8, 136.8, 133.8, 133.5, 130.1, 129.2, 128.3, 127.8, 121.8, 35.7, 35.3, 29.7, 21.1. IR (in KBr): 2987, 2926, 2241, 1684, 1400, 1181 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO$: 286.1202, found: 286.1196.

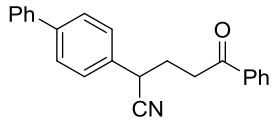
2-(4-(Methylthio)phenyl)-5-oxo-5-phenylpentanenitrile (3c)



White solid; 68% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 6.8 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.26 (t, J = 2.0 Hz, 1H), 3.14 (t, J = 7.2 Hz, 2H), 2.26-2.15 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.8, 138.7, 136.8, 133.8, 132.9, 129.2, 128.5, 128.3, 126.8, 121.7, 35.7, 35.1, 29.6, 15.0. IR (in KBr): 2987,

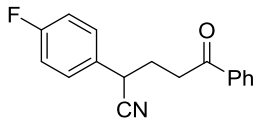
29237, 2242, 1682, 1649, 1400.39, 1240 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{17}NNaOS$: 318.0923, found: 318.0919.

2-([1,1'-Biphenyl]-4-yl)-5-oxo-5-phenylpentanenitrile (3d)



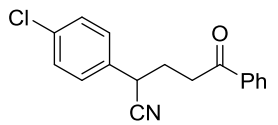
White solid; 82% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, J = 7.7 Hz, 2H), 7.74-7.63 (m, 5H), 7.55-7.46 (m, 6H), 7.38 (t, J = 7.3 Hz, 1H), 4.36 (t, J = 7.5 Hz, 1H), 3.19 (t, J = 7.2 Hz, 2H), 2.32-2.21 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d6) δ 198.8, 140.4, 139.9, 136.8, 135.6, 133.8, 129.5, 129.3, 128.5, 128.4, 128.2, 127.9, 127.2, 121.7, 35.8, 35.4, 29.6. IR (in KBr): 2988, 2256, 1647, 1398, 1046, 998 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{23}H_{19}NNaO$: 348.1359, found: 348.1348.

2-(4-Fluorophenyl)-5-oxo-5-phenylpentanenitrile (3e)



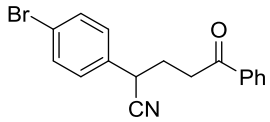
Colorless oil; 70% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 7.7 Hz, 2H), 7.66-7.62 (m, 1H), 7.54-7.47 (m, 4H), 7.25 (t, J = 8.6 Hz, 2H), 4.33 (t, J = 7.5 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.23 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 198.7, 162.2 (d, J = 245.4 Hz), 136.8, 133.8, 132.7 (d, J = 3.0 Hz), 130.1 (d, J = 8.1 Hz), 129.2, 128.3, 121.6, 116.4 (d, J = 21.2 Hz), 35.7, 35.0, 29.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.18. IR (in KBr): 3174, 2242, 1684, 1510, 1401, 837 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{14}FNNaO$: 290.0952, found: 290.0949.

2-(4-Chlorophenyl)-5-oxo-5-phenylpentanenitrile (3f)



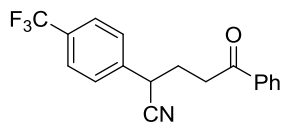
Colorless oil; 81% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.95-7.92 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.44 (m, 6H), 4.34 (dd, J = 8.3, 6.7 Hz, 1H), 3.14 (t, J = 7.2 Hz, 2H), 2.21 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.7, 136.7, 135.5, 133.8, 133.2, 129.9, 129.6, 129.2, 128.3, 121.4, 35.6, 35.1, 29.5. IR (in KBr): 3176, 2242, 1647, 1401, 1093 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{14}ClNNaO$: 306.0656, found: 306.0654.

2-(4-Bromophenyl)-5-oxo-5-phenylpentanenitrile (3g)



Colorless oil; 69% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 7.5 Hz, 2H), 7.66-7.61 (m, 3H), 7.54-7.50 (m, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.33 (t, J = 7.5 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.29-2.16 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 198.3, 136.3, 135.5, 133.4, 132.0, 129.5, 128.8, 127.9, 121.3, 120.9, 35.2, 34.7, 29.0. IR (in KBr): 2986, 2942, 2243, 1742, 1377, 1241, 1047 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{14}FNNaO$: 350.0151, found: 350.0153.

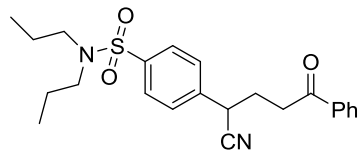
5-Oxo-5-phenyl-2-(4-(trifluoromethyl)phenyl)pentanenitrile (3h)



Colorless oil; 74% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.95 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.69-7.62 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H), 4.48 (t, J = 7.5 Hz, 1H), 3.18 (t, J = 7.2 Hz, 2H), 2.30-2.23 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.6, 141.1, 136.7, 133.8, 129.2 (q, J = 31.3

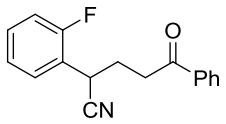
Hz), 129.2, 128.9, 128.3, 126.5 (q, J = 4.0 Hz), 124.5 (q, J = 273.7 Hz), 121.1, 35.7, 35.6, 29.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.16. IR (in KBr): 2987, 2938, 2244, 1684, 1401, 1327, 1125 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{18}H_{14}F_3NNaO$: 340.0920, found: 340.0908.

4-(1-Cyano-4-oxo-4-phenylbutyl)-*N*,*N*-dipropylbenzenesulfonamide (3i)



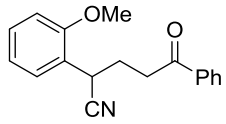
Yellow oil; 69% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94-7.92 (m, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.64 (dd, J = 15.4, 7.7 Hz, 3H), 7.51 (t, J = 7.7 Hz, 2H), 4.47 (t, J = 7.5 Hz, 1H), 3.18-3.13 (m, 2H), 3.01 (dd, J = 8.5, 6.6 Hz, 4H), 2.29-2.22 (m, 2H), 1.50-1.41 (m, 4H), 0.79 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.6, 141.0, 139.7, 136.7, 133.8, 129.2, 129.0, 128.3, 128.1, 121.1, 50.2, 35.6, 35.6, 29.5, 22.1, 11.4. IR (in KBr): 2977, 2938, 2877, 2244, 1684, 1400, 1240, 1047. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{23}H_{28}N_2NaO_3$: 435.1713, found: 435.1707.

2-(2-Fluorophenyl)-5-oxo-5-phenylpentanenitrile (3j)



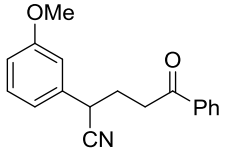
Yellow oil; 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99-7.90 (m, 2H), 7.69-7.61 (m, 1H), 7.55-7.51 (m, 3H), 7.47-7.41 (m, 1H), 7.32-7.25 (m, 2H), 4.48 (dd, J = 8.5, 6.8 Hz, 1H), 3.22-3.17 (m, 2H), 2.35-2.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.2, 159.7 (d, J = 247.5 Hz), 136.3, 133.4, 130.6 (d, J = 9.1 Hz), 129.6 (d, J = 4.0 Hz), 128.8, 127.9, 125.3 (d, J = 3.0 Hz), 122.8 (d, J = 14.1 Hz), 120.2, 116.0 (d, J = 21.2 Hz), 35.2, 29.8 (d, J = 2.0 Hz), 27.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ -117.47. IR (in KBr): 2852, 2246, 1683, 1400, 1235, 996. cm^{-1} HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}FNNaO$: 290.0952, found: 290.0945.

2-(2-Methoxyphenyl)-5-oxo-5-phenylpentanenitrile (3k)



Colorless oil; 59% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, J = 8.0 Hz, 2H), 7.65-7.62 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.42-7.30 (m, 2H), 7.11-6.95 (m, 2H), 4.37 (t, J = 7.5 Hz, 1H), 3.75 (s, 3H), 3.15-3.10 (m, 2H), 2.33-2.12 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.4, 156.2, 136.3, 133.3, 129.7, 128.8, 128.4, 127.8, 123.3, 121.0, 120.9, 111.6, 55.6, 35.2, 29.9, 27.1. IR (in KBr): 3193, 2845, 2241, 1682, 1400, 1248, 1026 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151, found: 302.1148.

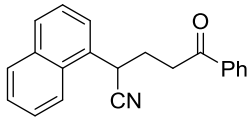
2-(3-Methoxyphenyl)-5-oxo-5-phenylpentanenitrile (3l)



Colorless oil; 64% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 8.0 Hz, 2H), 7.66-7.62 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.01-6.97 (m, 2H), 6.92 (dd, J = 8.3, 2.5 Hz, 1H), 4.26 (t, J = 7.5 Hz, 1H), 3.76 (s, 3H), 3.15 (t, J = 7.2 Hz, 2H), 2.38-2.13 (m, 2H). ^{13}C NMR

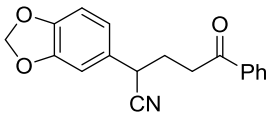
(100 MHz, DMSO-d_6) δ 198.8, 160.1, 137.9, 136.8, 133.8, 130.7, 129.2, 128.3, 121.6, 119.9, 114.0, 113.7, 55.6, 35.7, 35.7, 29.6. IR (in KBr): 3089, 2800, 2245, 1696, 1375, 1250, 959 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151, found: 302.1151.

2-(Naphthalen-1-yl)-5-oxo-5-phenylpentanenitrile (3m)



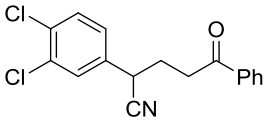
Colorless oil; 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 8.6 Hz, 1H), 8.02-7.94 (m, 4H), 7.71 (dd, J = 7.2, 1.2 Hz, 1H), 7.67-7.50 (m, 6H), 5.10 (dd, J = 9.5, 5.5 Hz, 1H), 3.38-3.34 (m, 1H), 3.31-3.23 (m, 1H), 2.44-2.24 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 199.0, 136.8, 134.1, 133.8, 132.4, 130.3, 129.5, 129.2, 128.4, 127.4, 126.8, 126.1, 125.8, 123.4, 121.8, 36.0, 33.1, 28.9. IR (in KBr): 2986, 2242, 1649, 1377, 1028, 939 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{21}H_{17}NNaO$: 322.1202, found: 322.1199.

2-(Benzo[*d*][1,3]dioxol-5-yl)-5-oxo-5-phenylpentanenitrile (3n)



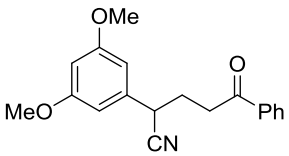
Colorless oil; 73% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.02 (s, 1H), 6.94- 6.87 (m, 2H), 6.04 (s, 2H), 4.19 (t, J = 7.6 Hz, 1H), 3.12 (t, J = 7.2 Hz, 2H), 2.26-2.13 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.8, 148.3, 147.5, 136.8, 133.8, 130.0, 129.2, 128.3, 121.8, 121.4, 109.0, 108.3, 101.8, 35.6, 35.3, 29.6. IR (in KBr): 3235, 2240, 1681, 1504, 1400, 1033 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{15}NNaO_3$: 316.0944, found: 316.0944.

2-(3,4-Dichlorophenyl)-5-oxo-5-phenylpentanenitrile (3o)



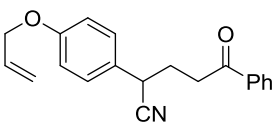
Colorless oil; 65% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96-7.93 (m, 2H), 7.75-7.61 (m, 3H), 7.55-7.44 (m, 3H), 4.38 (t, J = 8.2 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.34-2.18 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.2, 137.0, 136.3, 133.4, 131.7, 131.2, 130.9, 129.7, 128.8, 127.9, 127.9, 120.5, 35.2, 34.4, 28.7. IR (in KBr): 2986, 2935, 2243, 1683, 1470, 1400, 1032 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{13}Cl_2NNaO$: 340.0266, found: 340.0264.

2-(3,5-Dimethoxyphenyl)-5-oxo-5-phenylpentanenitrile (3p)



Colorless oil; 84% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 6.52 (d, J = 34.8 Hz, 2H), 4.20 (t, J = 7.5 Hz, 1H), 3.14 (t, J = 7.2 Hz, 2H), 2.50-2.16 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 198.9, 161.3, 138.6, 136.8, 133.8, 129.2, 128.3, 121.6, 106.0, 100.1, 55.8, 35.8, 35.7, 29.4. IR (in KBr): 2988, 2841, 2242, 1649, 1560, 1048, 997 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_3$: 332.1257, found: 332.1256.

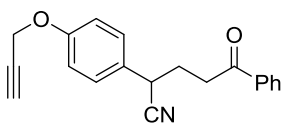
2-(4-(Allyloxy)phenyl)-5-oxo-5-phenylpentanenitrile (3q)



Colorless oil; 73% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93-7.89 (m, 2H), 7.42 (d, J = 4.3 Hz, 4H), 7.38-7.33 (m, 1H), 7.06-7.03 (m,

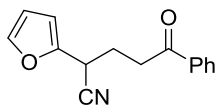
2H), 6.09-5.99 (m, 1H), 5.43-5.38 (m, 1H), 5.30-5.26 (m, 1H), 4.66-4.64 (m, 2H), 4.28 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.10-3.05 (m, 2H), 2.25-2.14 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.1, 162.6, 136.5, 133.6, 130.6, 129.8, 129.6, 128.5, 127.9, 121.7, 118.4, 115.0, 68.9, 35.7, 35.3, 29.9. IR (in KBr): 3290, 2986, 2940, 2242, 1676, 1600, 1377 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{20}H_{19}NNaO_2$: 328.1308, found: 328.1303.

5-Oxo-5-phenyl-2-(4-(prop-2-yn-1-yloxy)phenyl)pentanenitrile (3r)



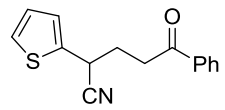
Colorless oil; 77% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95-7.91 (m, 2H), 7.42 (d, *J* = 4.3 Hz, 4H), 7.38-7.33 (m, 1H), 7.11-7.07 (m, 2H), 4.91 (d, *J* = 2.4 Hz, 2H), 4.28 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.63 (t, *J* = 2.3 Hz, 1H), 3.11-3.07 (m, 2H), 2.26-2.15 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.2, 161.5, 136.5, 130.6, 130.3, 129.6, 128.5, 127.9, 121.7, 115.2, 79.2, 79.1, 56.2, 35.8, 35.4, 29.9. IR (in KBr): 2986, 2938, 2241, 1676, 1599, 1374, 992 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{20}H_{17}NNaO_2$: 326.1151, found: 326.1154.

2-(Furan-2-yl)-5-oxo-5-phenylpentanenitrile (3s)



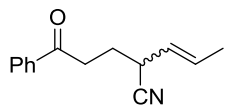
Yellow oil; 65% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96-7.93 (m, 2H), 7.71 (t, *J* = 1.4 Hz, 1H), 7.67-7.62 (m, 1H), 7.55-7.51 (m, 2H), 6.48 (d, *J* = 1.4 Hz, 2H), 4.51 (t, *J* = 7.5 Hz, 1H), 3.18 (t, *J* = 2.0 Hz, 2H), 2.27 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.6, 148.1, 144.1, 136.7, 133.8, 129.3, 128.3, 119.6, 111.4, 108.6, 35.4, 29.7, 26.2. IR (in KBr): 2988, 2250, 1681, 1649, 1399, 1047, 1027, 1001 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{15}H_{13}NNaO_2$: 262.0838, found: 262.0840.

5-Oxo-5-phenyl-2-(thiophen-2-yl)pentanenitrile (3t)



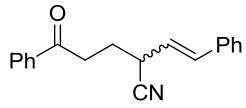
Yellow oil; 76% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96-7.93 (m, 2H), 7.66-7.61 (m, 1H), 7.56-7.49 (m, 3H), 7.18-7.16 (m, 1H), 7.04 (dd, *J* = 5.1 Hz, 3.5 Hz, 1H), 4.67 (t, *J* = 7.5 Hz, 1H), 3.19 (t, *J* = 2.0 Hz, 2H), 2.38-2.18 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.6, 138.3, 136.7, 133.9, 129.3, 128.3, 127.8, 127.1, 126.8, 121.0, 35.6, 31.0, 29.9. IR (in KBr): 2987, 2244, 1681, 1399, 1028, 999 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{15}H_{13}NNaOS$: 278.0610, found: 278.0610.

2-(3-Oxo-3-phenylpropyl)pent-3-enenitrile (5a, *E*/*Z* = 2.5:1)



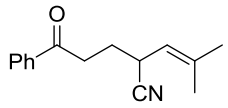
Colorless oil; 57% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99-7.95 (*E*+*Z*, m, 2H), 7.66-7.61 (*E*+*Z*, m, 1H), 7.56-7.50 (*E*+*Z*, m, 2H), 5.86-5.37 (*E*+*Z*, m, 2H), 3.63-3.54 (*E*+*Z*, m, 1H), 3.17-3.09 (*E*+*Z*, m, 2H), 2.38 (*E*, q, *J* = 7.2 Hz, 2H), 2.00-1.95 (*Z*, m, 2H), 1.68-1.66 (*Z*, m, 3H), 1.27 (*E*, dd, *J* = 7.1, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.6, 199.0, 137.0, 136.9, 133.8, 133.6, 132.0, 129.6, 129.2, 129.2, 128.4, 128.3, 126.8, 125.7, 122.2, 121.2, 37.6, 35.4, 32.9, 27.5, 27.3, 26.4, 18.9, 17.8. IR (in KBr): 2986, 2941, 2241, 1684, 1399, 1239, 1047 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{14}H_{15}NNaO$: 236.1046, found: 236.1043.

5-Oxo-5-phenyl-2-styrylpentanenitrile (5b, *E*/*Z* = 3:1)



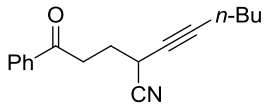
Yellow oil; 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99-7.97 (*Z*, m, 1H), 7.95-7.92 (*E*, m, 2H), 7.67-7.62 (*E*+*Z*, m, 1H), 7.55-7.48 (m, 4H), 7.43-7.27 (*E*+*Z*, m, 5H), 6.77-6.74 (*E*+*Z*, d, *J* = 11.3 Hz, 1H), 6.37 (*Z*, dd, *J* = 15.9, 6.7 Hz, 1H), 5.73 (*E*, dd, *J* = 11.3, 9.7 Hz, 1H), 4.03-3.94 (*E*, dd, *J* = 7.0, 1.3 Hz, 1H), 3.89 (*Z*, dd, *J* = 7.0, 1.3 Hz, 1H), 3.26-3.17 (*E*+*Z*, m, 2H), 2.16-1.99 (*E*+*Z*, m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.0, 198.9, 136.9, 136.8, 136.1, 135.6, 133.8, 133.7, 133.0, 129.2, 128.9, 128.6, 128.3, 127.0, 125.8, 124.5, 121.1, 121.0, 35.5, 35.4, 33.2, 29.1, 27.4, 27.3. IR (in KBr): 2250, 1681, 1650, 1400, 1026, 998 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{19}H_{17}NNaO$: 298.1202, found: 298.1196.

4-Methyl-2-(3-oxo-3-phenylpropyl)pent-3-enenitrile (5c)



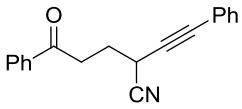
Colorless oil; 63% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98-7.96 (m, 2H), 7.68-7.64 (m, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 5.15 (d, *J* = 9.0 Hz, 1H), 3.78-3.72 (m, 1H), 3.15 (t, *J* = 7.1 Hz, 2H), 2.04-1.90 (m, 2H), 1.71 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.2, 138.1, 136.9, 133.8, 129.3, 128.3, 121.9, 119.1, 35.4, 28.8, 27.6, 25.6, 18.4. IR (in KBr): 3128, 2253, 1643, 1400, 1026, 998 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{15}H_{17}NNaO$: 250.1202, found: 250.1203.

2-(3-Oxo-3-phenylpropyl)oct-3-ynenitrile (5d)



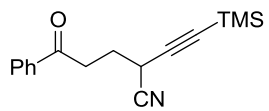
Colorless oil; 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 4.18-4.14 (m, 1H), 3.22 (t, *J* = 7.2 Hz, 2H), 2.21-2.09 (m, 4H), 1.42-1.27 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.5, 136.7, 133.8, 129.2, 128.3, 128.3, 119.0, 85.2, 73.1, 35.3, 30.3, 27.9, 22.2, 21.8, 17.9, 13.8. IR (in KBr): 3193, 2959, 2869, 2245, 1685, 1400, 1047 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{17}H_{19}NNaO$: 276.1359, found: 276.1353.

5-Oxo-5-phenyl-2-(phenylethynyl)pentanenitrile (5e)



Yellow oil; 76% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.48-7.44 (m, 2H), 7.42-7.36 (m, 3H), 4.52 (t, *J* = 6.9 Hz, 1H), 3.32 (t, *J* = 7.2 Hz, 2H), 2.29 (q, *J* = 8.4, 7.8 Hz, 2H). ^{13} NMR (100 MHz, DMSO-d_6) δ 198.1, 136.3, 133.4, 131.7, 129.3, 128.8, 128.7, 128.7, 128.0, 121.0, 118.1, 83.5, 82.1, 34.9, 27.2, 22.4. IR (in KBr): 2987, 2252, 1648, 1399, 1046, 998 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{19}H_{15}NNaO$: 296.1046, found: 296.1039.

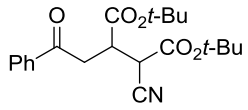
5-Oxo-5-phenyl-2-((trimethylsilyl)ethynyl)pentanenitrile (5f)



Colorless oil; 66% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.24 (t, *J* = 7.0 Hz, 1H), 3.16 (dd, *J* = 8.3, 6.3 Hz, 2H), 2.15-2.08 (m, 2H), 0.07

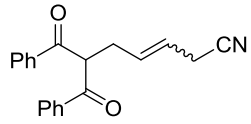
(s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.3, 137.6, 134.8, 130.2, 129.3, 119.3, 99.4, 90.4, 36.1, 28.4, 23.9, 0.9. IR (in KBr): 3180, 2986, 2185, 1685, 1399, 1046 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{16}H_{19}NNaOSi$: 292.1128, found: 292.1125.

Di-tert-butyl 2-cyano-3-(2-oxo-2-phenylethyl)succinate (5g, 3:1 dr)



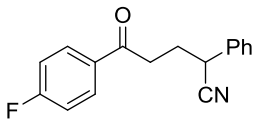
Colorless oil; 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (minor, dd, J = 8.3, 1.4 Hz, 1H), 7.92 (major, dd, J = 7.8, 1.4 Hz, 1H), 7.72-7.65 (major+minor, m, 1H), 7.61-7.57 (major+minor, m, 1H), 7.51-7.43 (major, m, 2H), 4.27 (major, d, J = 6.0 Hz, 1H), 3.51-3.47 (major, m, 1H), 3.45-3.42 (minor, m, 1H), 3.40 (minor, d, J = 1.2 Hz, 1H), 2.89 (major, dd, J = 17.4, 6.9 Hz, 1H), 2.78 (major, dd, J = 17.4, 4.7 Hz, 1H), 2.67-2.63 (minor, m, 1H), 2.58 (minor, d, J = 5.4 Hz, 1H), 1.49 (minor, d, J = 1.3 Hz, 3H), 1.46 (major, d, J = 1.3 Hz, 9H), 1.30 (major, d, J = 1.3 Hz, 9H), 1.11 (minor, d, J = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.9, 192.2, 171.6, 170.8, 169.3, 166.9, 139.0, 136.4, 134.4, 134.2, 131.9, 129.2, 129.1, 128.9, 128.5, 126.8, 82.0, 82.0, 81.7, 81.6, 48.1, 43.5, 38.0, 33.4, 30.3, 28.1, 28.0, 27.8, 27.6, 25.9. IR (in KBr): 2981, 2936, 2252, 1731, 1691, 1645, 1397, 1150 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{21}H_{27}NNaO_5$: 396.1781, found: 396.1777.

6-Benzoyl-7-oxo-7-phenylhept-3-enenitrile (5h, *E*/*Z* = 2:1)



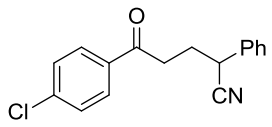
Colorless oil; 85% yield. (*E*)-**5h**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 -7.97 (m, 4H), 7.69-7.61 (m, 2H), 7.53 (t, J = 7.7 Hz, 4H), 5.93 (t, J = 6.4 Hz, 1H), 5.85-5.77 (m, 1H), 5.47-5.40 (m, 1H), 3.21 (dd, J = 5.5, 1.6 Hz, 2H), 2.67 (t, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 136.1, 134.3, 131.3, 129.5, 128.9, 121.6, 118.9, 55.0, 31.9, 19.8. (*Z*)-**5h**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 - 7.99 (m, 4H), 7.68-7.64 (m, 2H), 7.54 (t, J = 7.8 Hz, 4H), 5.94 (t, J = 6.5 Hz, 1H), 5.70-5.64 (m, 1H), 5.43-5.37 (m, 1H), 3.33-3.30 (m, 2H), 2.69 (t, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 136.0, 134.3, 131.8, 129.6, 128.9, 120.5, 119.5, 54.7, 27.3, 15.5. IR (in KBr): 3029, 2237, 1676, 1401, 1168, 1036 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{20}H_{17}NNaO_2$: 326.1151, found: 326.1152.

5-(4-Fluorophenyl)-5-oxo-2-phenylpentanenitrile (7a)



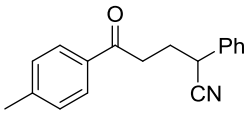
Yellow oil; 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05-8.00 (m, 2H), 7.45-7.40 (m, 4H), 7.38-7.31 (m, 3H), 4.29 (dd, J = 8.4, 6.8 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.27-2.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.0, 165.1 (d, J = 252.5 Hz) , 136.0, 133.1, 133.1, 130.9 (d, J = 9.1 Hz), 129.1, 128.1, 127.4, 121.3, 115.8 (d, J = 22.2 Hz), 35.3, 35.2, 29.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.86. IR (in KBr): 3214, 2241, 1645, 1400, 1157, 1096 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^+$ calcd for $C_{17}H_{14}FNNaO$: 290.0952, found: 290.0949.

5-(4-Fluorophenyl)-5-oxo-2-phenylpentanenitrile (7b)



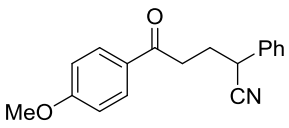
Colorless oil; 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96-7.93 (m, 2H), 7.60-7.56 (m, 2H), 7.42 (d, J = 4.3 Hz, 4H), 7.39-7.33 (m, 1H), 4.29 (dd, J = 8.4, 6.7 Hz, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.27-2.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.4, 138.3, 136.0, 135.0, 129.8, 129.1, 128.9, 128.1, 127.4, 121.2, 35.3, 35.2, 29.2. IR (in KBr): 2241, 1639, 1400, 1091, 988 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{17}H_{14}ClNNaO$: 306.0656, found: 306.0653.

5-Oxo-2-phenyl-5-(p-tolyl)pentanenitrile (7c)



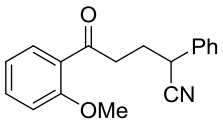
Colorless oil; 88% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 4.3 Hz, 4H), 7.36 (q, J = 4.1 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 4.28 (dd, J = 8.3, 6.8 Hz, 1H), 3.11 (t, J = 7.5 Hz, 2H), 2.36 (s, 3H), 2.24-2.17 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.3, 144.2, 136.5, 134.3, 129.8, 129.6, 128.5, 128.4, 127.9, 121.7, 35.7, 35.6, 29.8, 21.6. IR (in KBr): 3032, 2985, 2939, 2241, 1680, 1608, 1401, 1375, 1047 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{18}H_{17}NNaO$: 286.1202, found: 286.1198.

5-(4-Methoxyphenyl)-5-oxo-2-phenylpentanenitrile (7d)



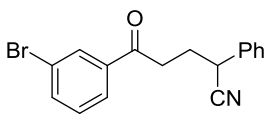
Colorless oil; 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, J = 8.9 Hz, 2H), 7.42 (d, J = 4.4 Hz, 4H), 7.38-7.33 (m, 1H), 7.03 (d, J = 8.9 Hz, 2H), 4.28 (dd, J = 8.4, 6.8 Hz, 1H), 3.83 (s, 3H), 3.10-3.06 (t, J = 2.0 Hz, 2H), 2.26-2.15 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.6, 163.2, 136.1, 130.2, 129.3, 129.1, 128.0, 127.4, 121.2, 113.9, 55.5, 35.3, 34.8, 29.5. IR (in KBr): 3031, 2937, 2842, 2241, 1675, 1600, 1400, 1171, 1112 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151, found: 302.1149.

5-(2-Methoxyphenyl)-5-oxo-2-phenylpentanenitrile (7e)



Colorless oil; 89 % yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57-7.51 (m, 2H), 7.45-7.39 (m, 4H), 7.38-7.33 (m, 1H), 7.15 (d, J = 8.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 4.28 (dd, J = 8.0, 6.9 Hz, 1H), 3.83 (s, 3H), 3.04 (t, J = 7.4 Hz, 2H), 2.20-2.13 (m, 2H). ^{13} NMR (100 MHz, DMSO-d_6) δ 200.5, 158.7, 136.5, 134.4, 130.0, 129.5, 128.5, 127.9, 127.8, 121.7, 121.0, 112.9, 56.2, 35.7, 35.7, 30.1. IR (in KBr): 3031, 2940, 2844, 2241, 1669, 1400, 1024 cm^{-1}. HRMS (ESI) for: m/z [M + Na]$^{+}$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151, found: 302.1151.

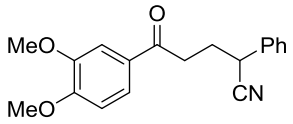
5-(3-Bromophenyl)-5-oxo-2-phenylpentanenitrile (7f)



Colorless oil; 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.42 (d, J = 4.3 Hz, 4H), 7.38-7.34 (m, 1H), 4.28 (dd, J = 8.4, 6.8 Hz, 1H), 3.16 (t, J = 7.2 Hz, 2H), 2.25-2.18 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.8, 138.8, 136.5, 136.4, 131.5, 130.8, 129.6, 128.5, 127.9, 127.4, 122.6, 121.7, 35.9, 35.7,

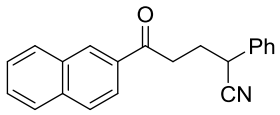
29.6. IR (in KBr): 3131, 2240, 1684, 1400, 1163, 994 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{14}FNNaO$: 350.0151, found: 350.0146.

5-(3,4-Dimethoxyphenyl)-5-oxo-2-phenylpentanenitrile (7g)



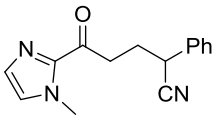
Colorless oil; 89% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (dd, J = 8.4, 2.1 Hz, 1H), 7.43 (d, J = 4.3 Hz, 5H), 7.41-7.34 (m, 1H), 7.06 (d, J = 8.5 Hz, 1H), 4.29 (dd, J = 8.5, 6.7 Hz, 1H), 3.83 (d, J = 13.8 Hz, 6H), 3.14-3.09 (m, 2H), 2.25-2.16 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 153.2, 148.6, 136.1, 129.2, 129.2, 129.1, 128.1, 127.4, 122.7, 121.3, 110.9, 110.0, 55.8, 55.5, 35.3, 34.8, 29.7. IR (in KBr): 3007, 2936, 2844, 2240, 1672, 1514, 1415, 1153 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_3$: 332.1257, found: 332.1261.

5-(Naphthalen-2-yl)-5-oxo-2-phenylpentanenitrile (7h)



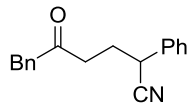
Colorless oil; 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.02-7.95 (m, 3H), 7.68-7.59 (m, 2H), 7.49-7.41 (m, 4H), 7.40-7.34 (m, 1H), 4.34 (dd, J = 8.4, 6.8 Hz, 1H), 3.34-3.28 (m, 2H), 2.34-2.23 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.7, 136.6, 135.6, 134.1, 132.6, 130.2, 130.1, 129.6, 129.2, 128.8, 128.5, 128.1, 127.9, 127.4, 123.9, 121.8, 35.8, 35.8, 29.9. IR (in KBr): 3137, 2925, 2852, 2240, 1678, 1400, 1181 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{21}H_{17}NNaO$: 322.1202, found: 322.1201.

5-(1-Methyl-1*H*-imidazol-2-yl)-5-oxo-2-phenylpentanenitrile (7i)



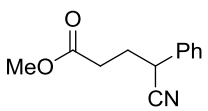
Colorless oil; 89% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (s, 1H), 7.45-7.39 (m, 4H), 7.38-7.34 (m, 1H), 4.32 (t, J = 7.4 Hz, 1H), 3.89 (s, 3H), 3.17-3.13 (m, 2H), 2.24-2.17 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.6, 142.6, 136.4, 129.5, 129.1, 128.6, 128.5, 127.9, 121.7, 36.1, 35.7, 29.7. IR (in KBr): 2923, 2852, 2244, 1676, 1402, 1027 cm^{-1}. HRMS (ESI) for: m/z $[M + H]^+$ calcd for $C_{15}H_{16}N_3O$: 254.1288, found: 254.1291.

5-Oxo-2,6-diphenylhexanenitrile (8)



Colorless oil; 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43-7.39 (m, 2H), 7.37-7.29 (m, 5H), 7.26-7.21 (m, 1H), 7.18-7.16 (m, 2H), 4.18 (dd, J = 8.2, 6.8 Hz, 1H), 3.77 (s, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.10-1.99 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 207.1, 136.3, 135.1, 130.1, 129.5, 128.7, 128.5, 127.8, 127.0, 121.6, 49.2, 39.1, 35.5, 29.3. IR (in KBr): 2923, 2851, 2244, 1648, 1400, 1026 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{18}H_{17}NNaO$: 286.1202 found: 286.1202.

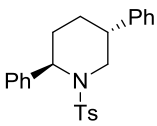
Methyl 4-cyano-4-phenylbutanoate (9)



Colorless oil; 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43-7.39 (m, 2H), 7.37-7.29 (m, 5H), 7.26-7.21 (m, 1H), 7.18-7.16 (m, 2H), 4.18 (dd, J = 8.2, 6.8 Hz, 1H), 3.77 (s, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.10-1.99 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 207.1, 136.3, 135.1, 130.1, 129.5, 128.7, 128.5, 127.8, 127.0,

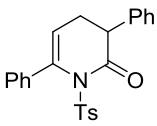
121.6, 49.2, 39.1, 35.5, 29.3. IR (in KBr): 2361, 1736, 1640, 1400, 1160, 1090 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{12}H_{13}NNaO_2$: 226.0838 found: 226.0846.

***syn*-2,5-Diphenyl-1-tosylpiperidine (10a)**



White solid; 78% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 12H), 7.13 (d, J = 7.9 Hz, 2H), 4.21 (dd, J = 7.9 Hz, 3.6 Hz, 1H), 4.12-4.00 (m, 1H), 3.11-3.02 (m, 2H), 2.38 (s, 3H), 2.04-1.94 (m, 3H), 1.74-1.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.8, 141.0, 135.2, 129.1, 128.5, 127.9, 127.7, 127.6, 127.2, 127.2, 126.7, 60.8, 51.8, 40.5, 32.8, 28.1, 21.4. IR (in KBr): 3161, 2361, 1648, 1340, 1096 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{24}H_{25}NNaO_2$: 414.1498 found: 414.1489.

3,6-Diphenyl-3,4-dihydropyridin-2(1*H*)-one (10b)



White solid; 69% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 23.6 Hz, 1H), 7.44-7.40 (m, 2H), 7.38-7.24 (m, 8H), 5.51-5.49 (m, 1H), 3.78 (dd, J = 9.7, 7.3 Hz, 1H), 2.84-2.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 138.9, 137.2, 134.9, 128.9, 128.8, 128.7, 128.2, 127.3, 124.9, 102.2, 46.4, 29.2. IR (in KBr): 2360, 2336, 1647, 1339, 1093 cm^{-1}. HRMS (ESI) for: m/z $[M + Na]^+$ calcd for $C_{17}H_{15}NNaO$: 272.1046 found: 272.1039.

6. Preliminary Mechanistic Investigation

6.1 Stern-Volmer quenching studies

Voltammetric experiments was conducted on a GU Instruments Electrochemical Workstation model GU/07078C. CV measurement of starting material was carried out in 0.1 M of Bu_4NPF_6/DMF at a scan rate of 100 mV/s with the protection of Ar. The electrochemical cell contained a glassy carbon, a Pt wire electrode and a SCE reference electrode.

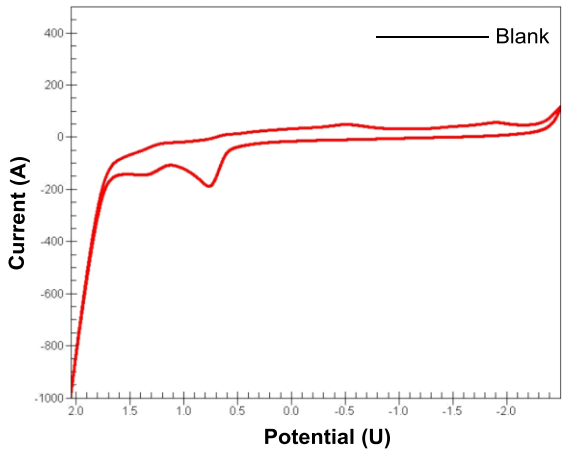


Figure S2. Cyclic voltammogram of background

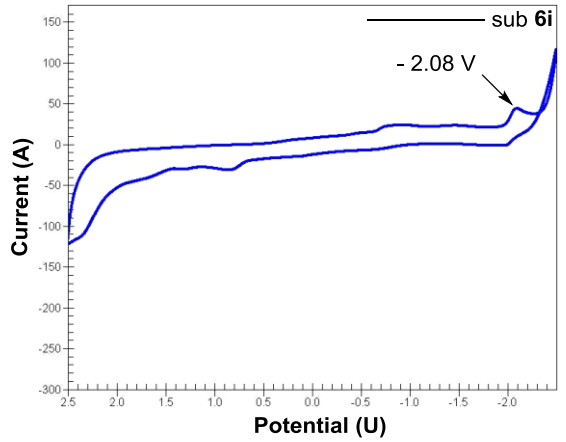


Figure S3. Cyclic voltammogram of substrate **6i**

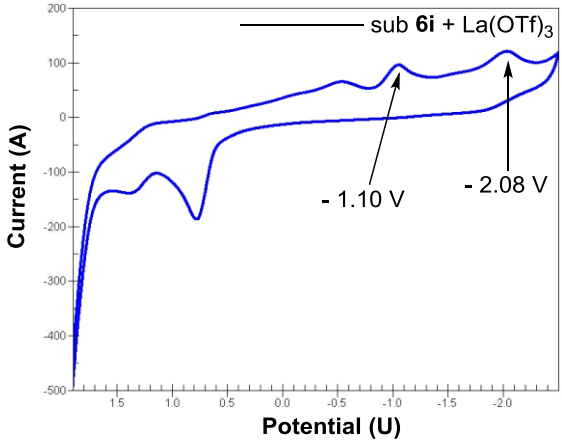
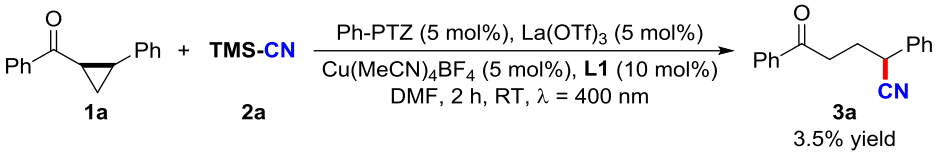


Figure S4. Cyclic voltammogram of substrate **6i**/$La(OTf)_3$ (1:1)

6.2 Determination of quantum yield



Procedure H: A cuvette was charged with $Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.01 mmol), **L1** (7.1 mg, 0.02 mmol), $La(OTf)_3$ (5.9 mg, 0.01 mmol), phenyl ketone **1a** (0.2 mmol, 44.5 mg), TMSCN **2a** (76 μL, 0.6 mmol), photocatalyst **Ph-PTZ** (2.8 mg, 0.01 mmol) and 2.0 mL of anhydrous DMF. The sample was irradiated (λ = 400 nm, slit width = 3.0 nm, slit height 5.0 mm with intensity of 5.65 mW cm^2) for 7200 s. After irradiation, the yield of product formed was determined by ^1H NMR based on 1,3,5-trimethoxybenzene standard. The quantum yield was determined as follows.

ϕ = Mole number for product/Mole number for absorption of photons = 0.055

$$\Phi = \frac{n_{\mathbf{3a}} N_A / t}{f\ P\ \lambda / hc}$$

n_{3a}: the mole number of the product **3a**; t: reaction time (7200 s); NA: 6.02×10^{23} /mol; f: $1\text{-}10^{-A}$ (400 nm, A = 1.468); P: P = E*S (E: illumination intensity, E = 5.65 mW/cm^2; S: the area that irradiated S = 0.15 cm^2); λ: wavelength (λ = 4.0×10^{-7} m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^8 m/s).

7. References

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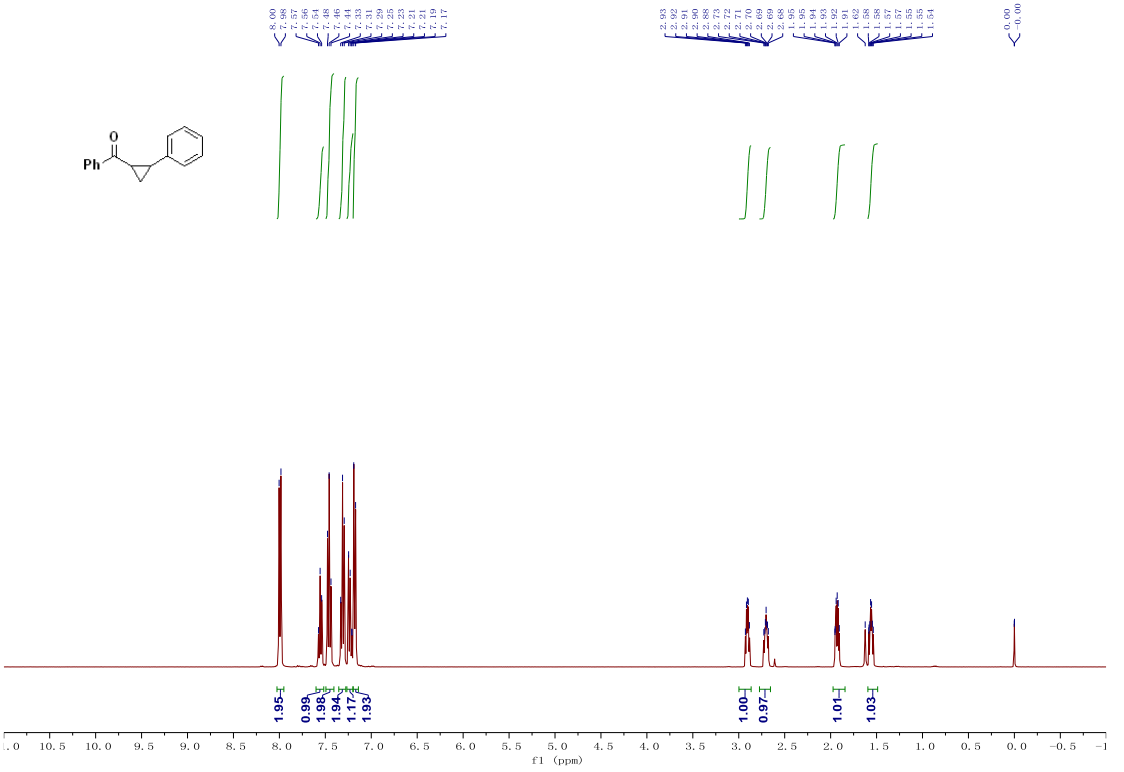
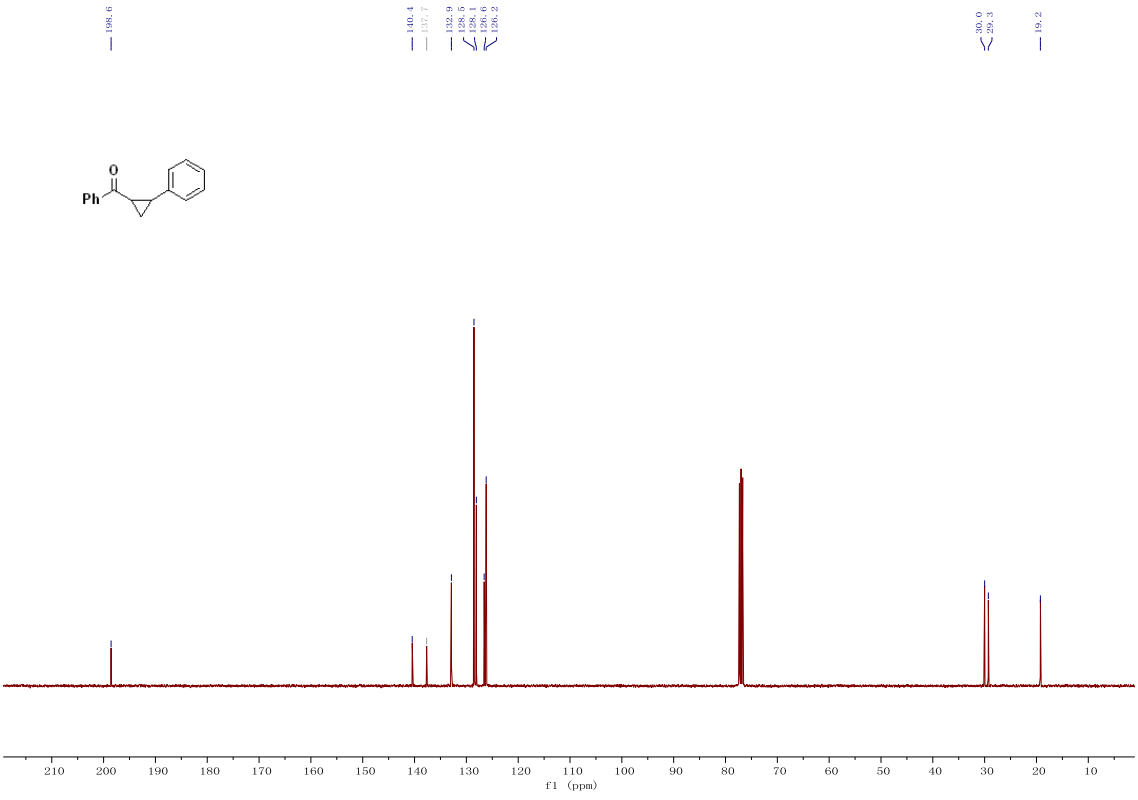
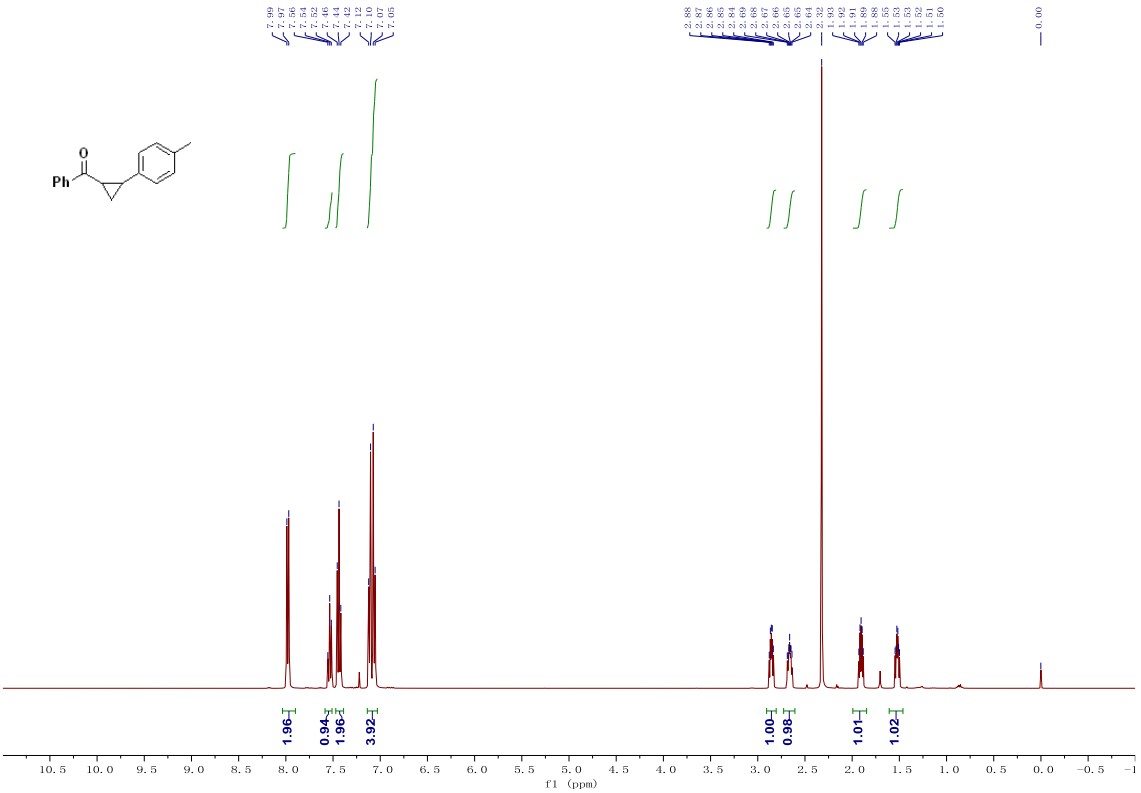
8. Copies of NMR Spectra

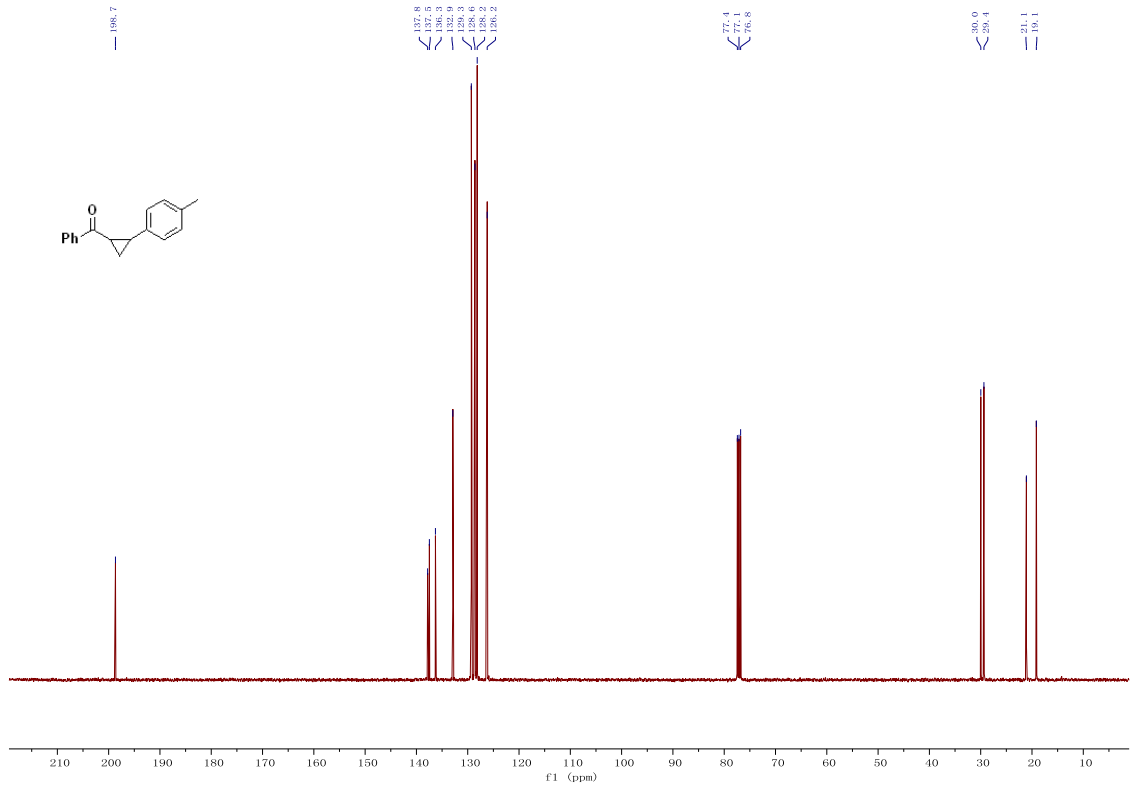
^{1}H and ^{13}C NMR of compound **1a**



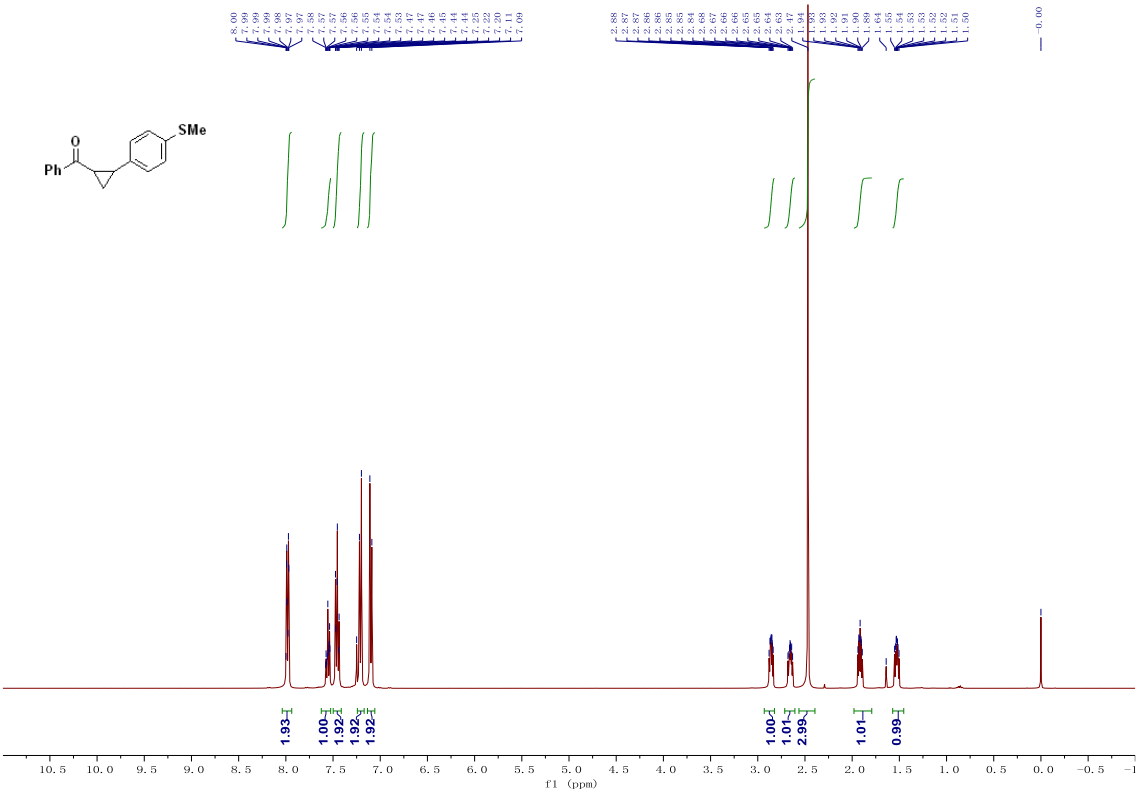


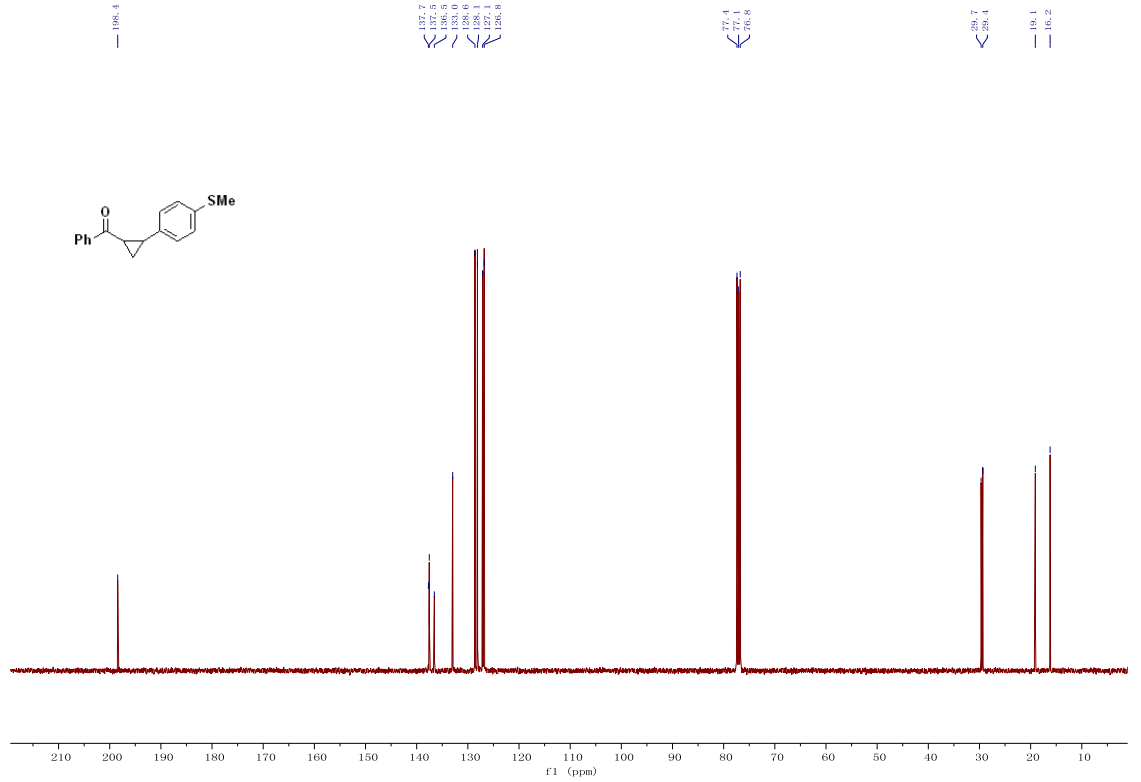
^{1}H and ^{13}C NMR of compound **1b**



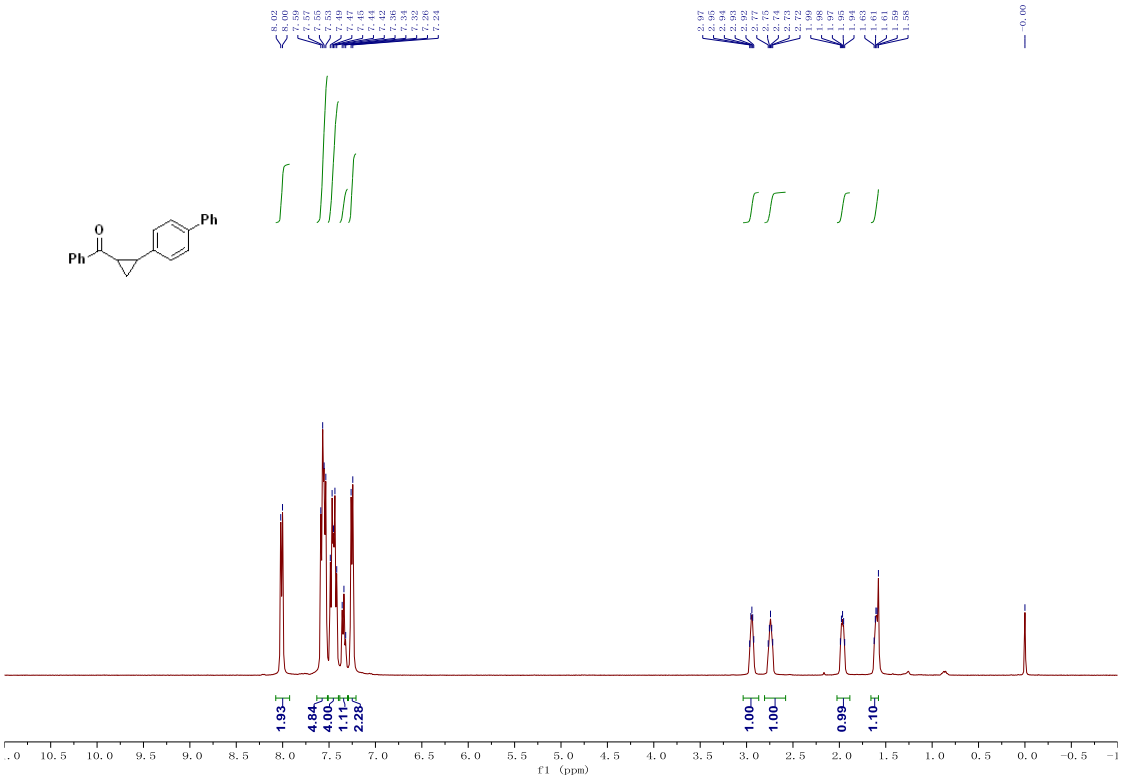


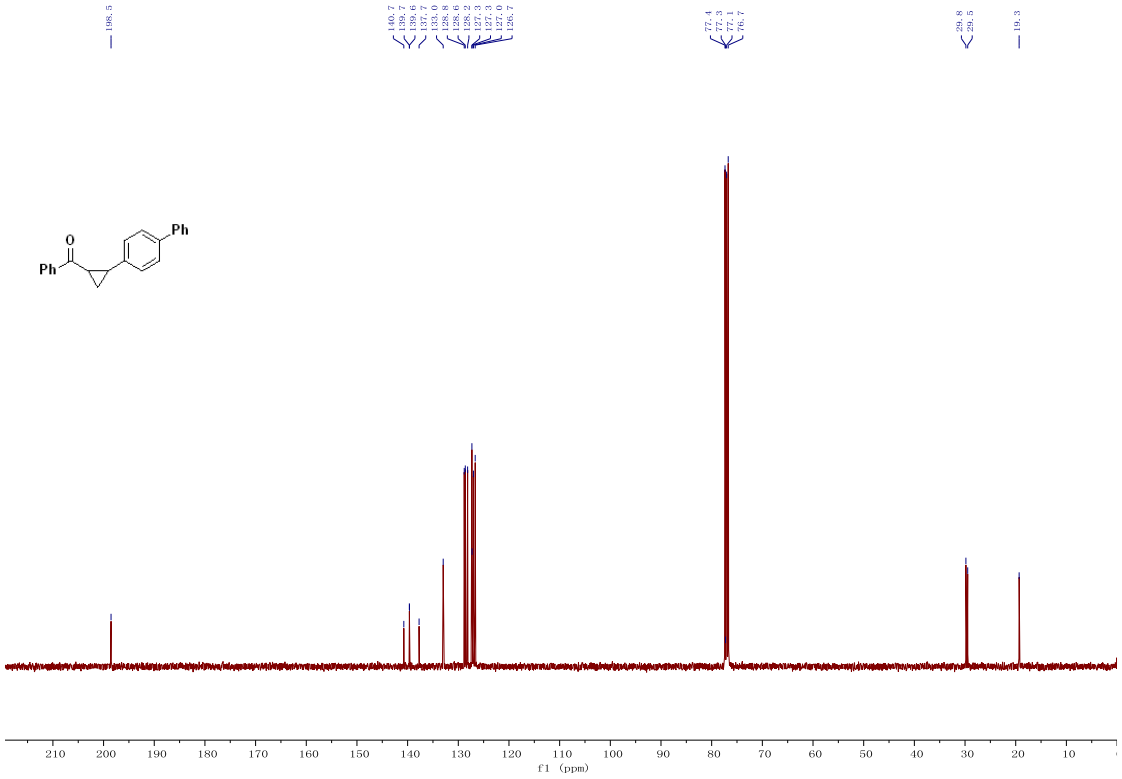
^{1}H and ^{13}C NMR of compound **1c**



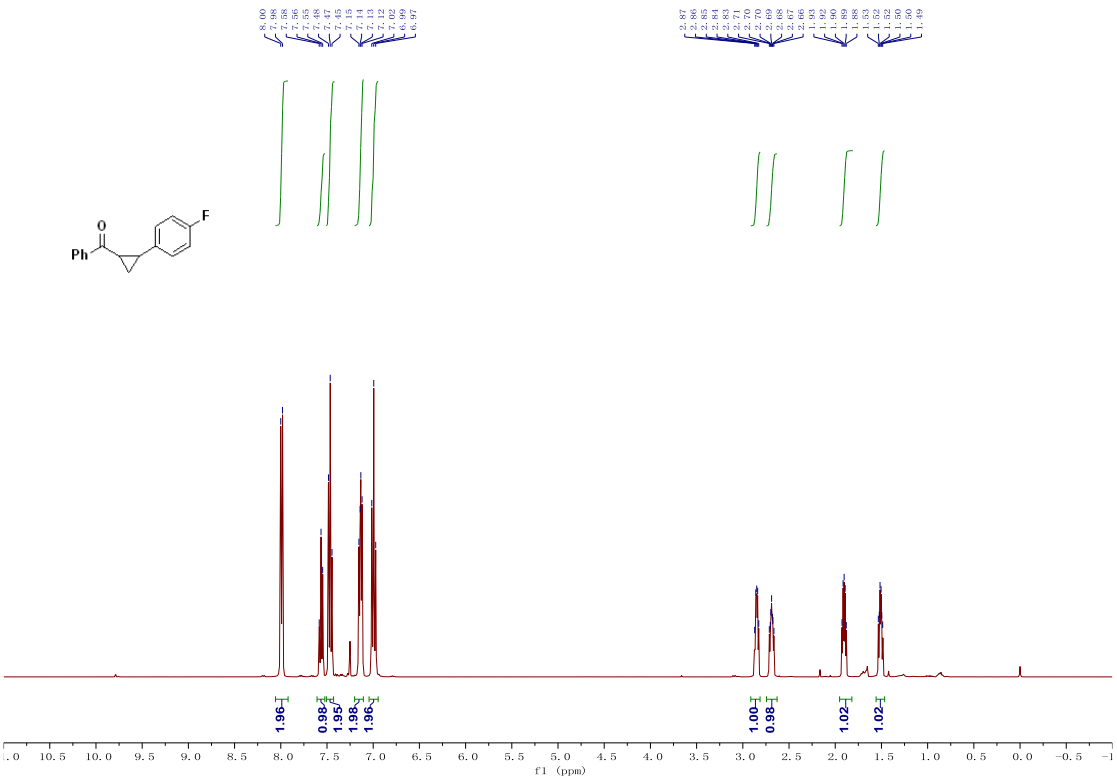


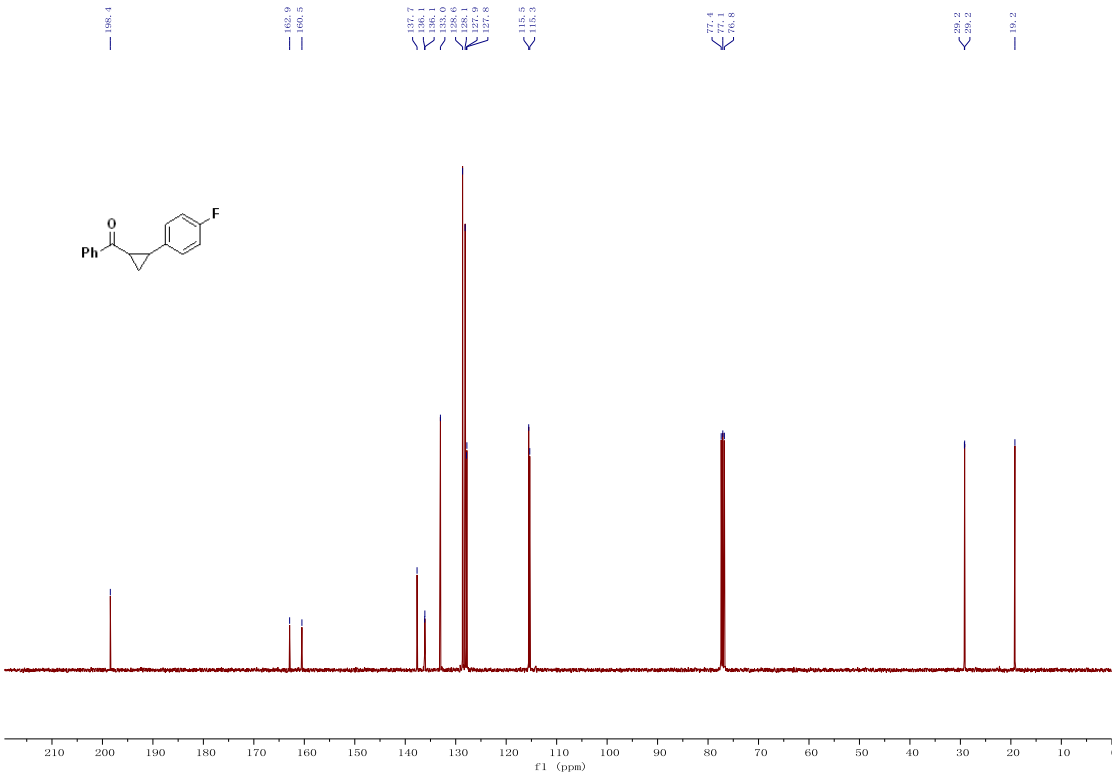
^{1}H and ^{13}C NMR of compound **1d**

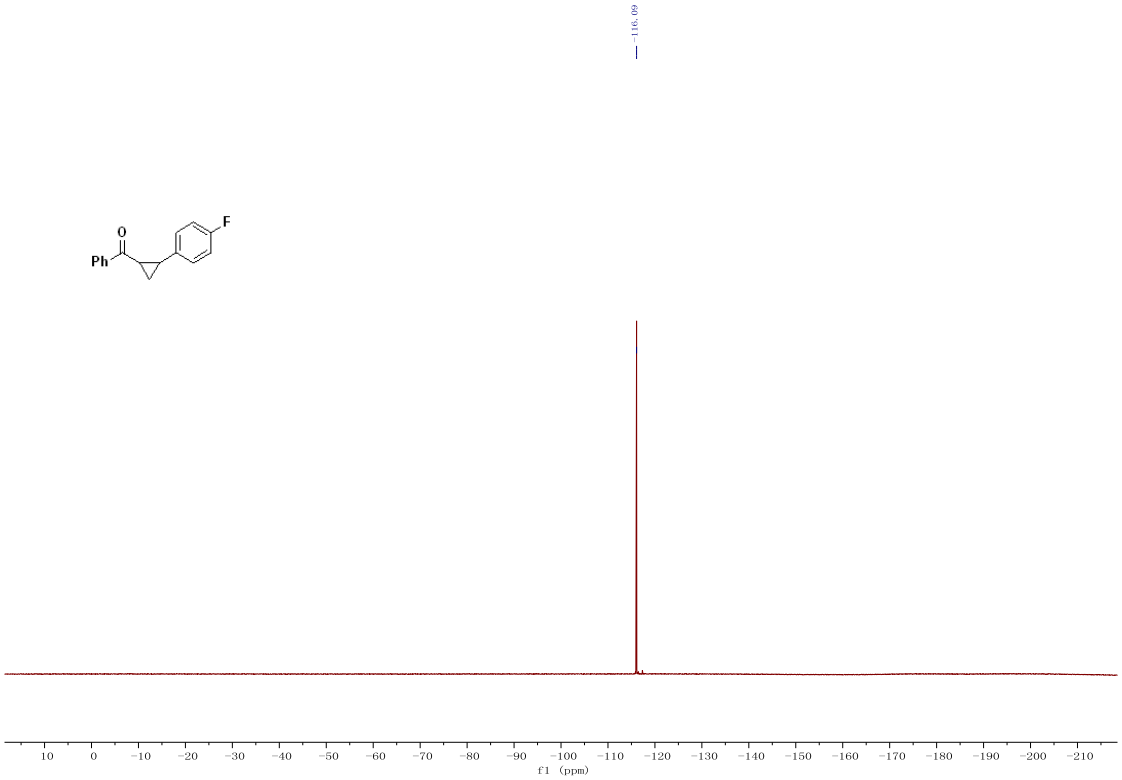




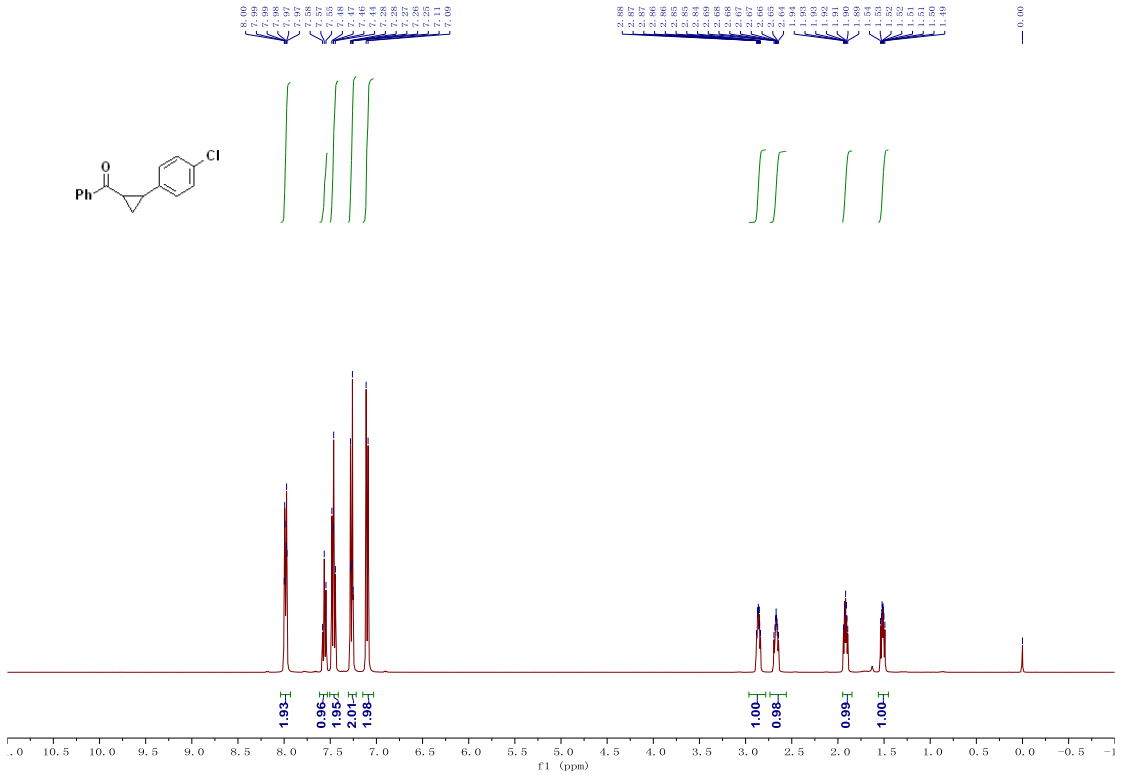
^{1}H ,^{13}C and ^{19}F NMR of compound **1e**

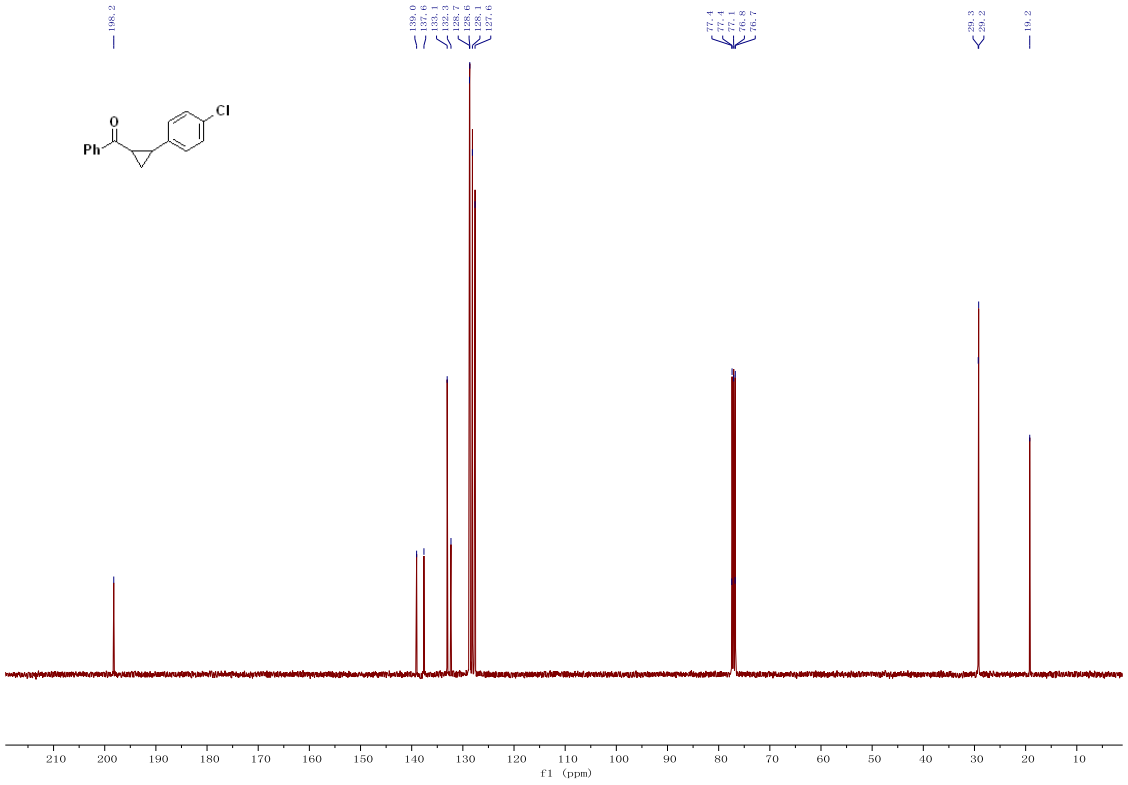




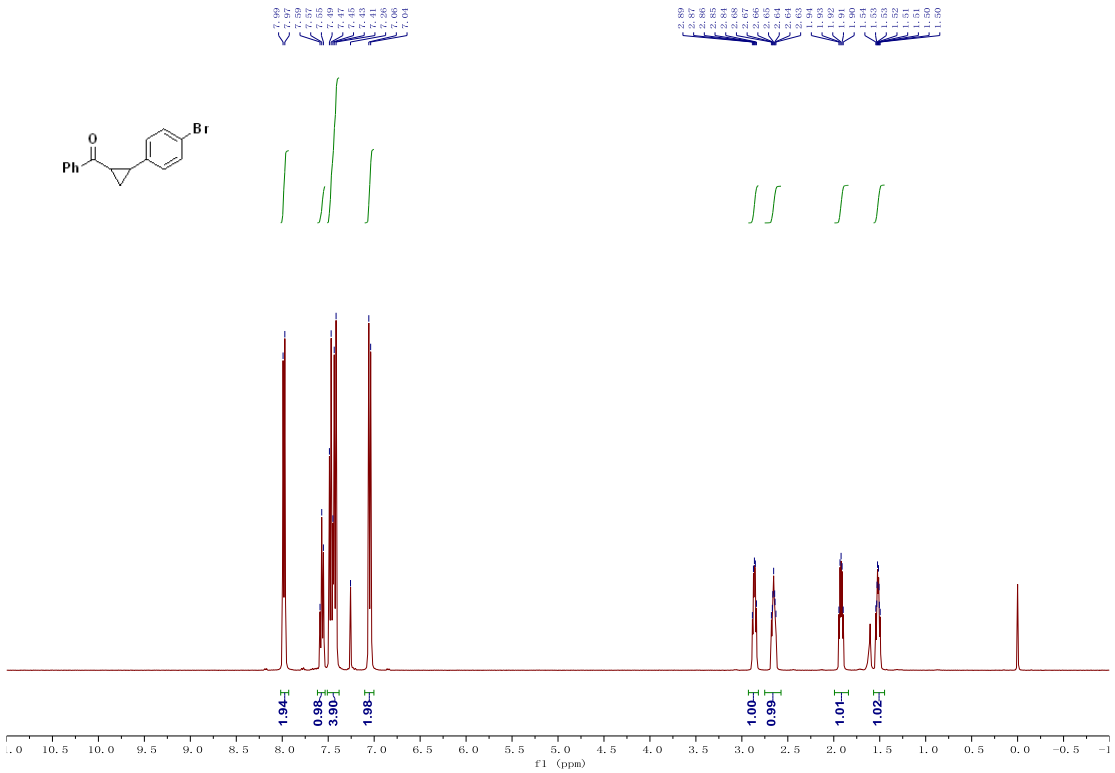


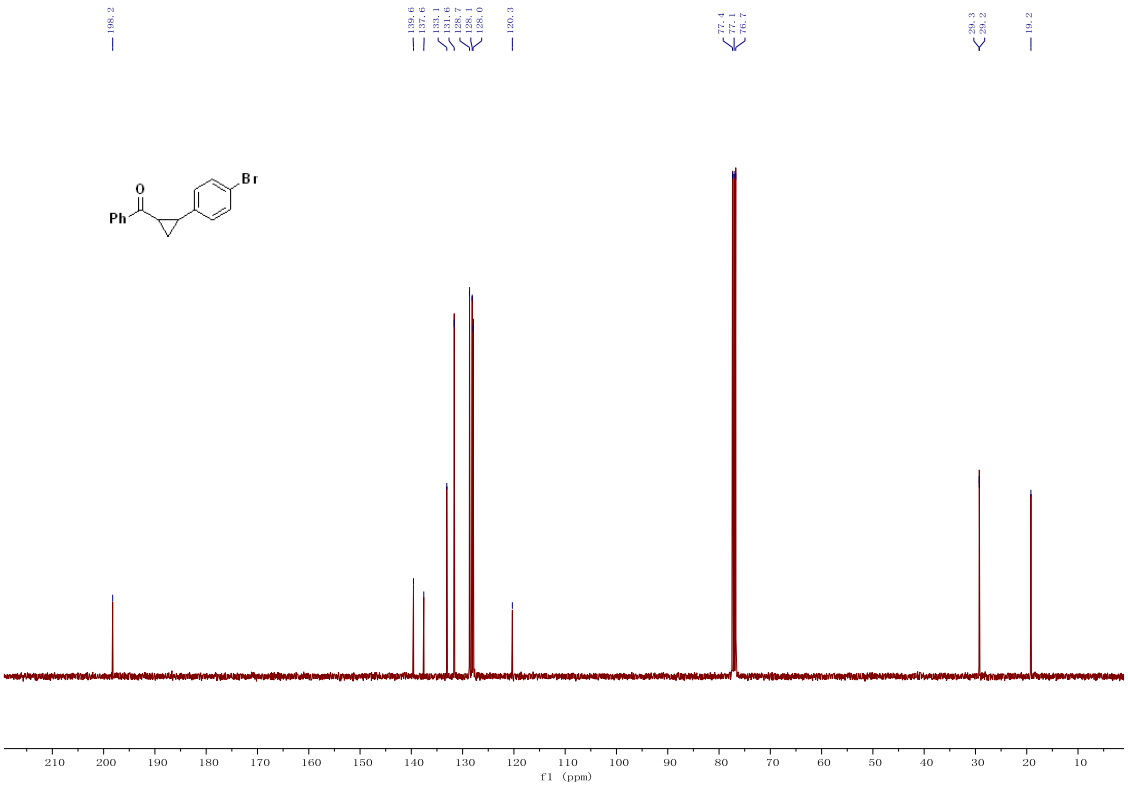
^{1}H and ^{13}C NMR of compound **1f**



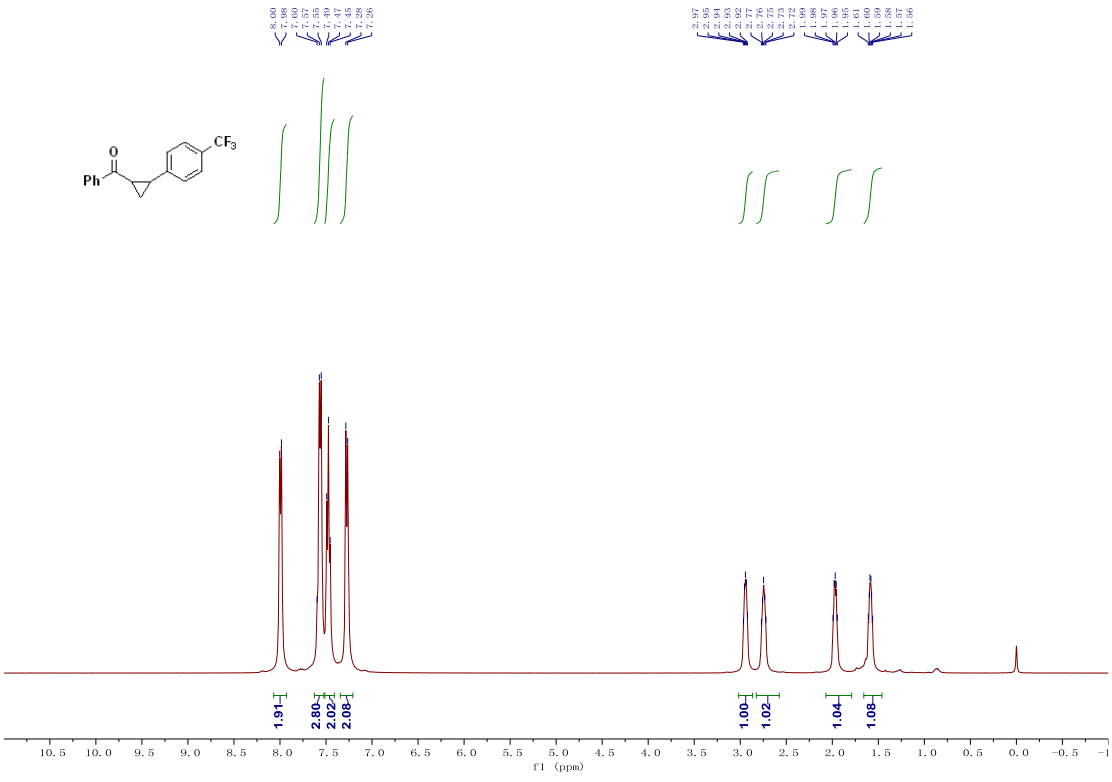


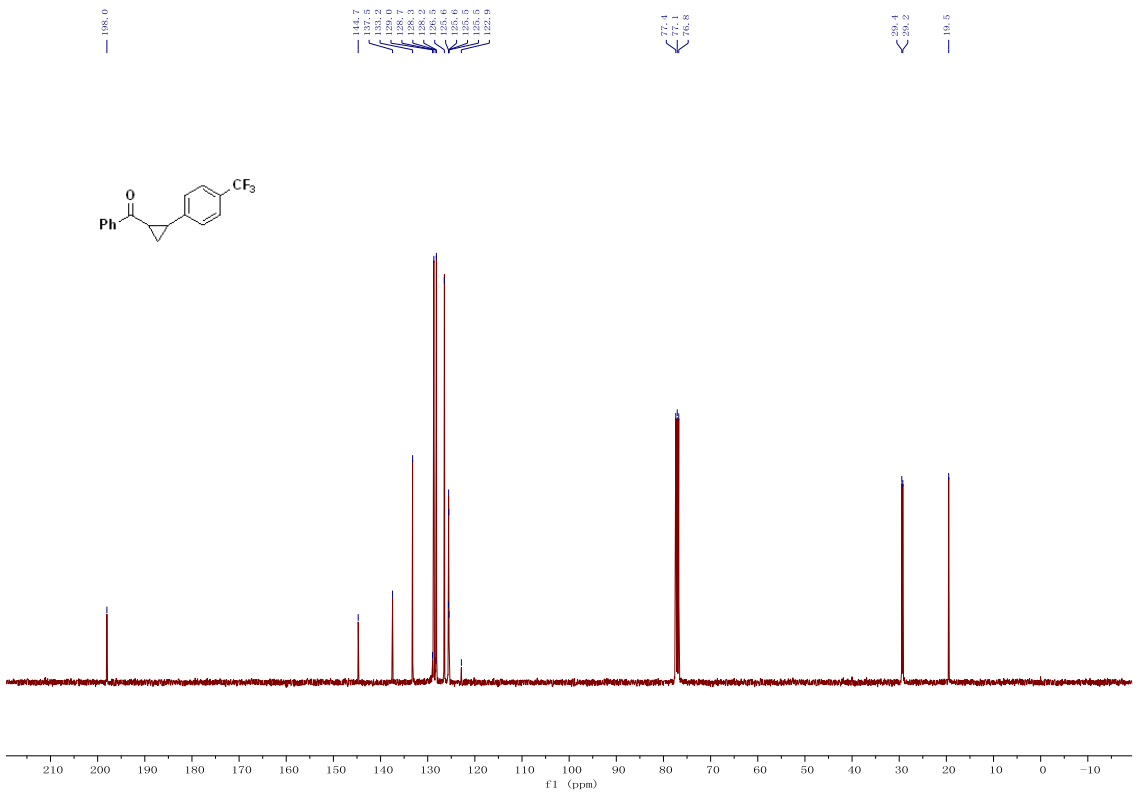
^{1}H and ^{13}C NMR of compound **1g**

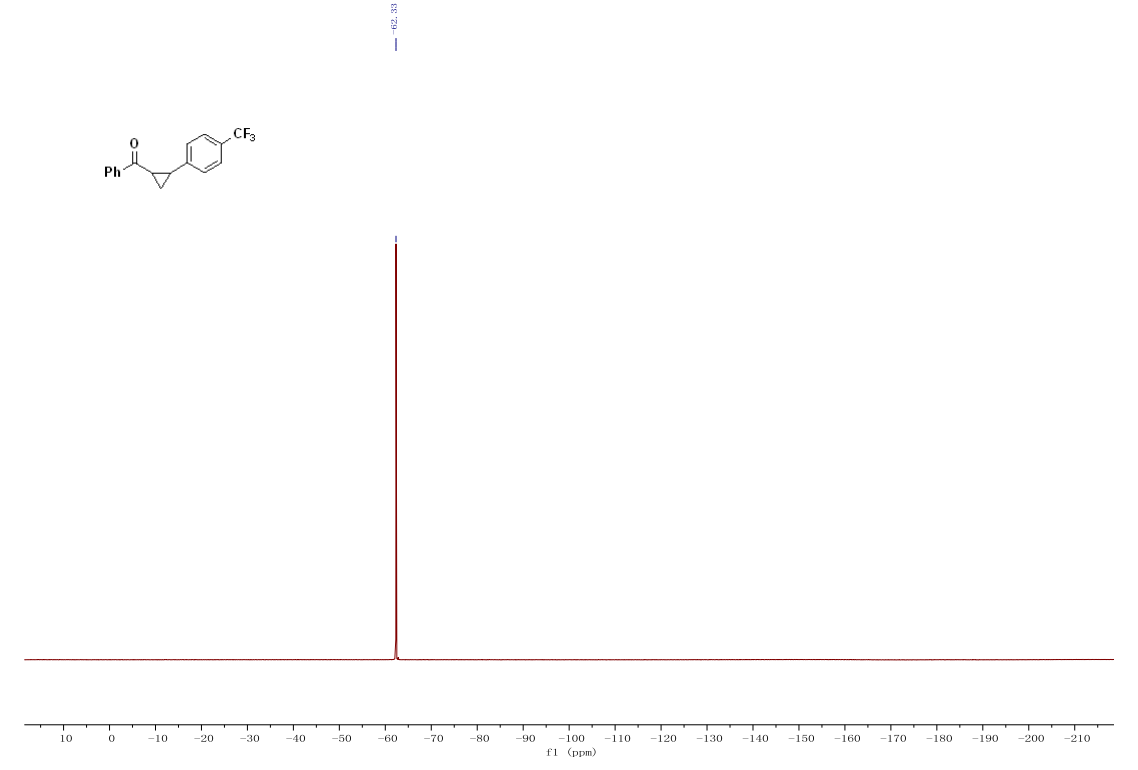




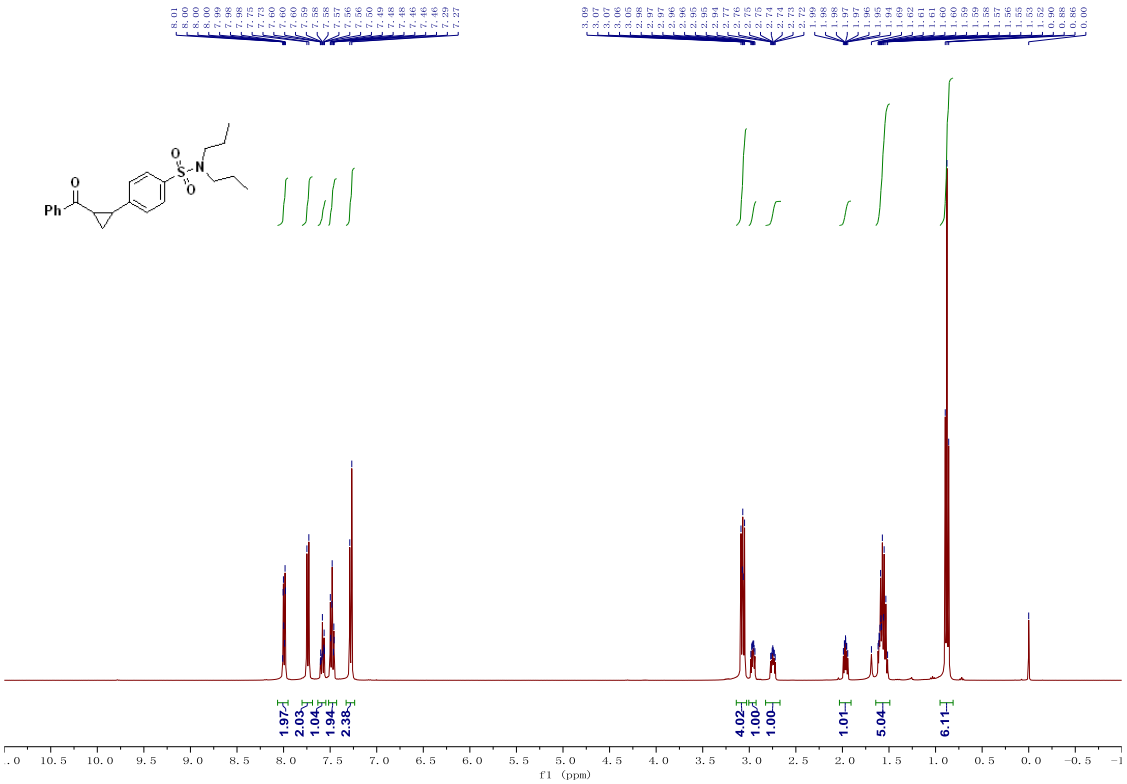
^{1}H ,^{13}C and ^{19}F NMR of compound **1h**

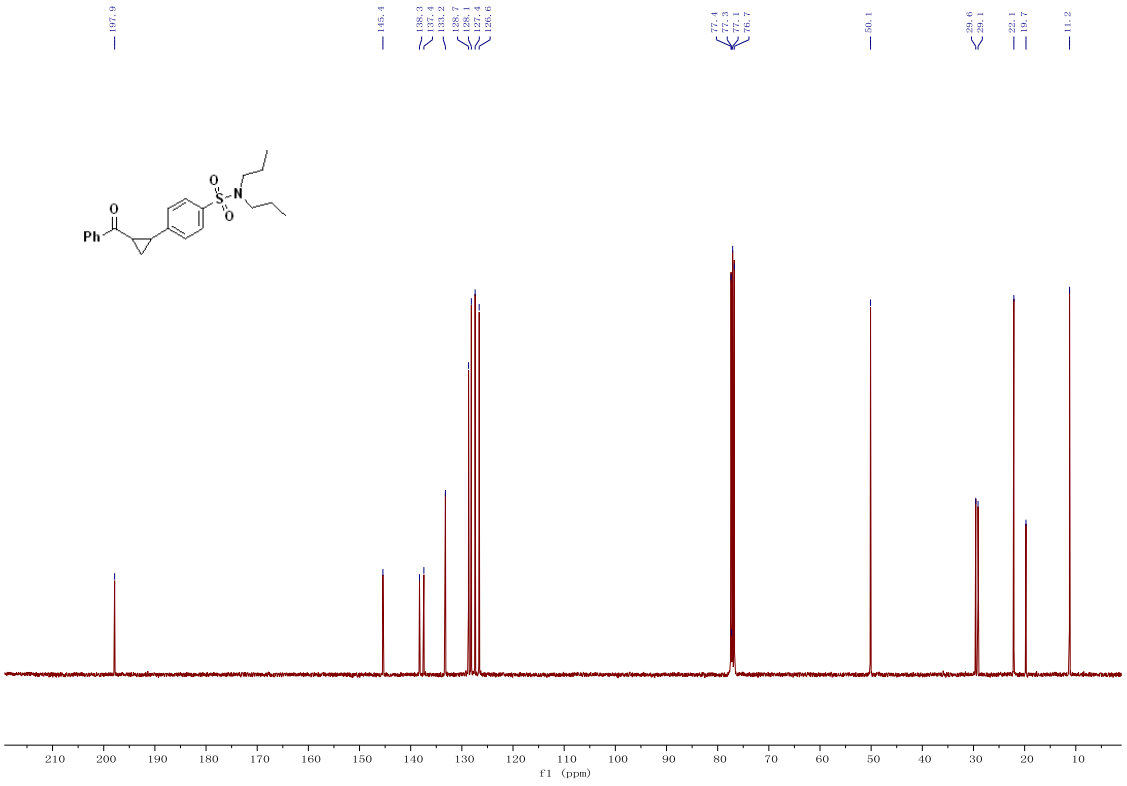



198.0
144.7
137.5
132.2
130.0
128.7
128.3
128.2
126.5
125.6
125.5
125.5
122.9
77.4
77.1
76.8
29.4
29.2
19.5
O
Ph
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

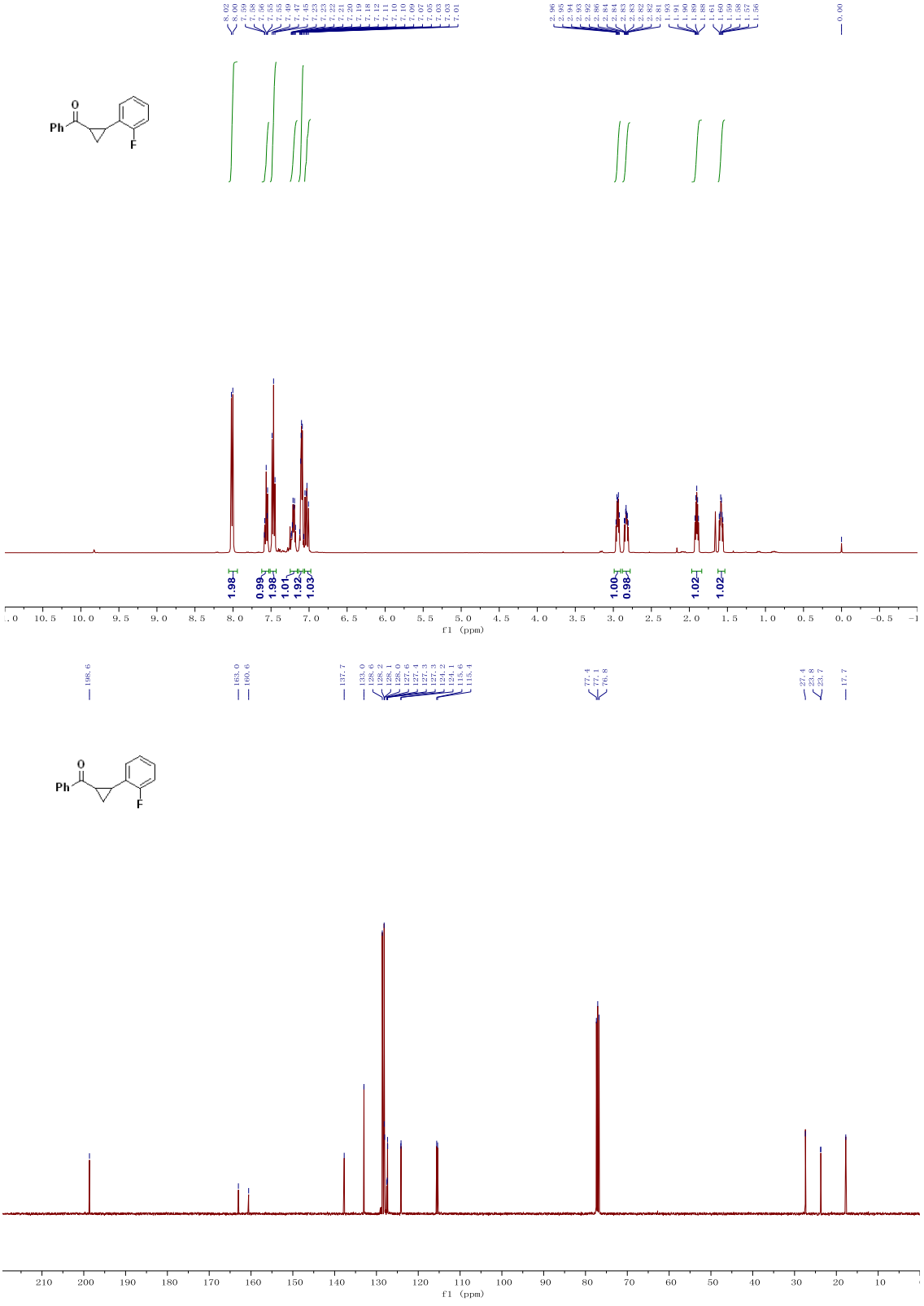

−62.33
O
Ph
CF3
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

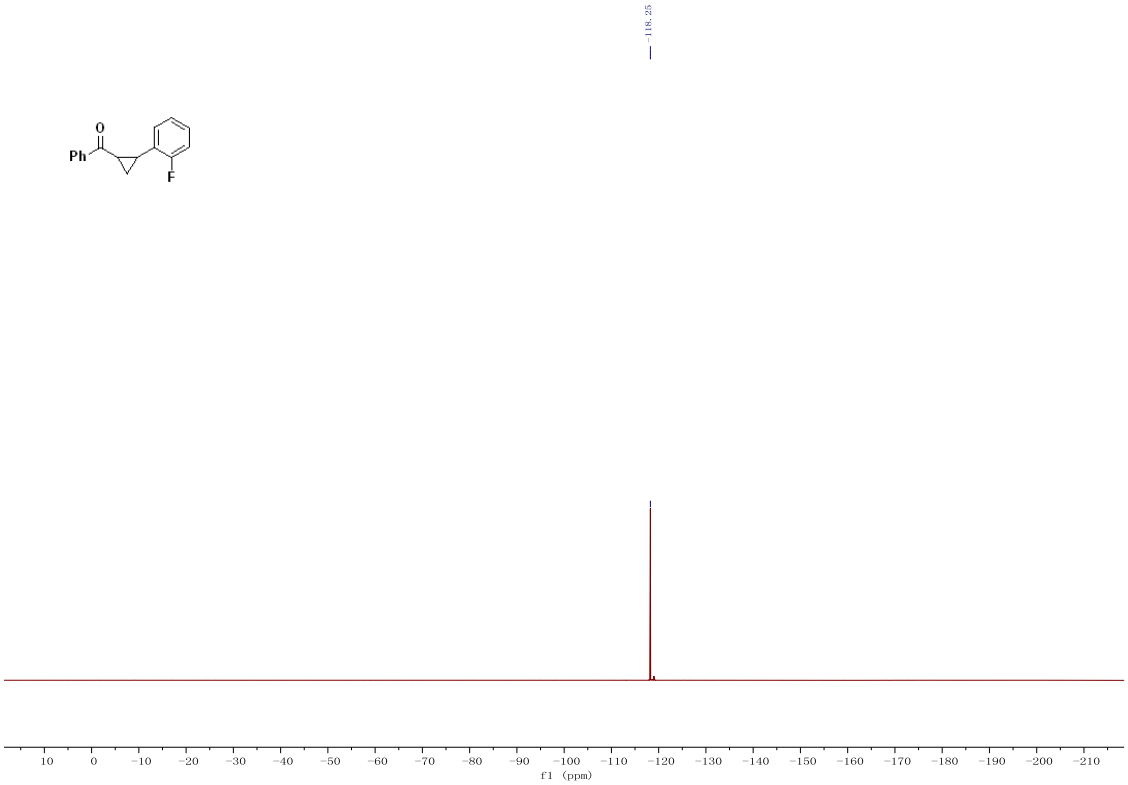
^{1}H and ^{13}C NMR of compound **1i**



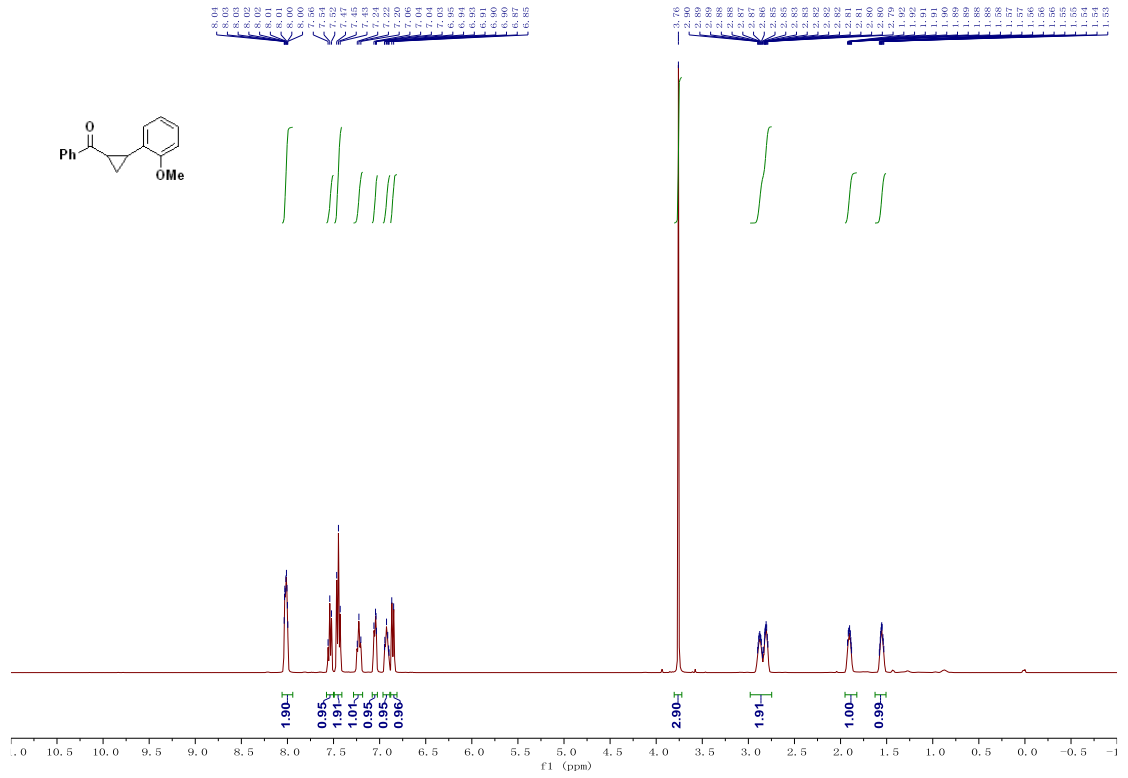


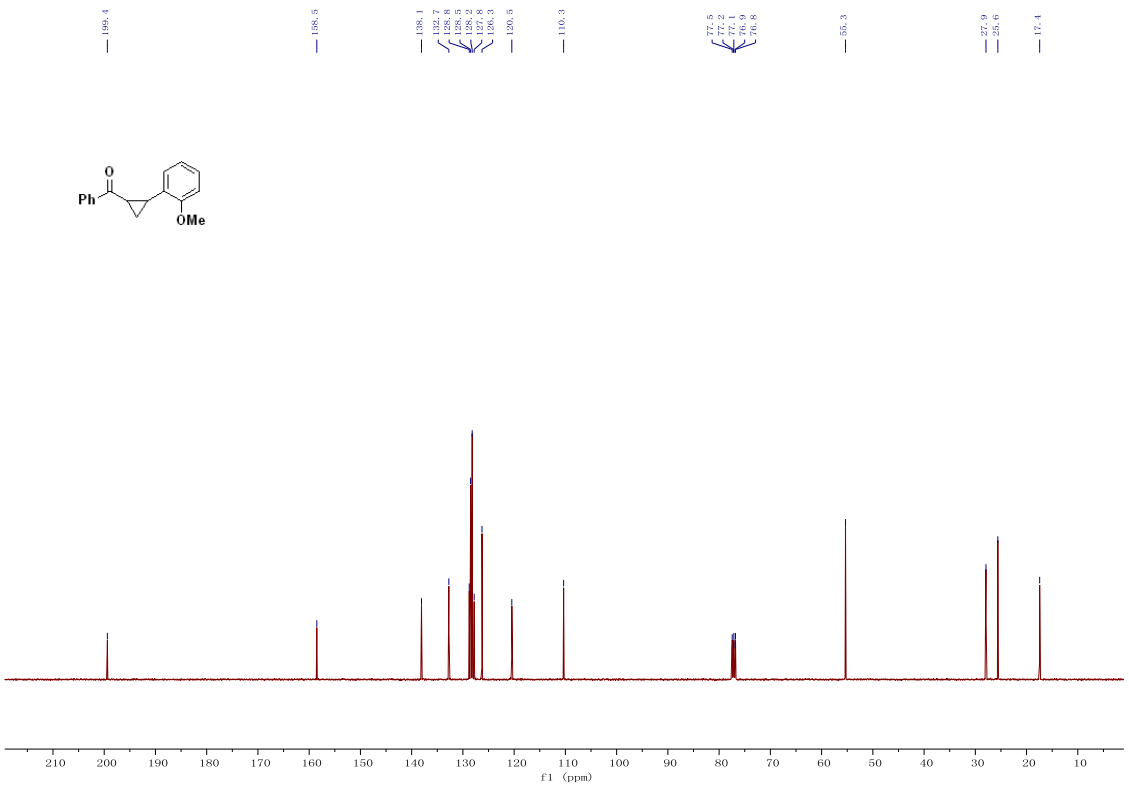
^{1}H ,^{13}C and ^{19}F NMR of compound **1j**



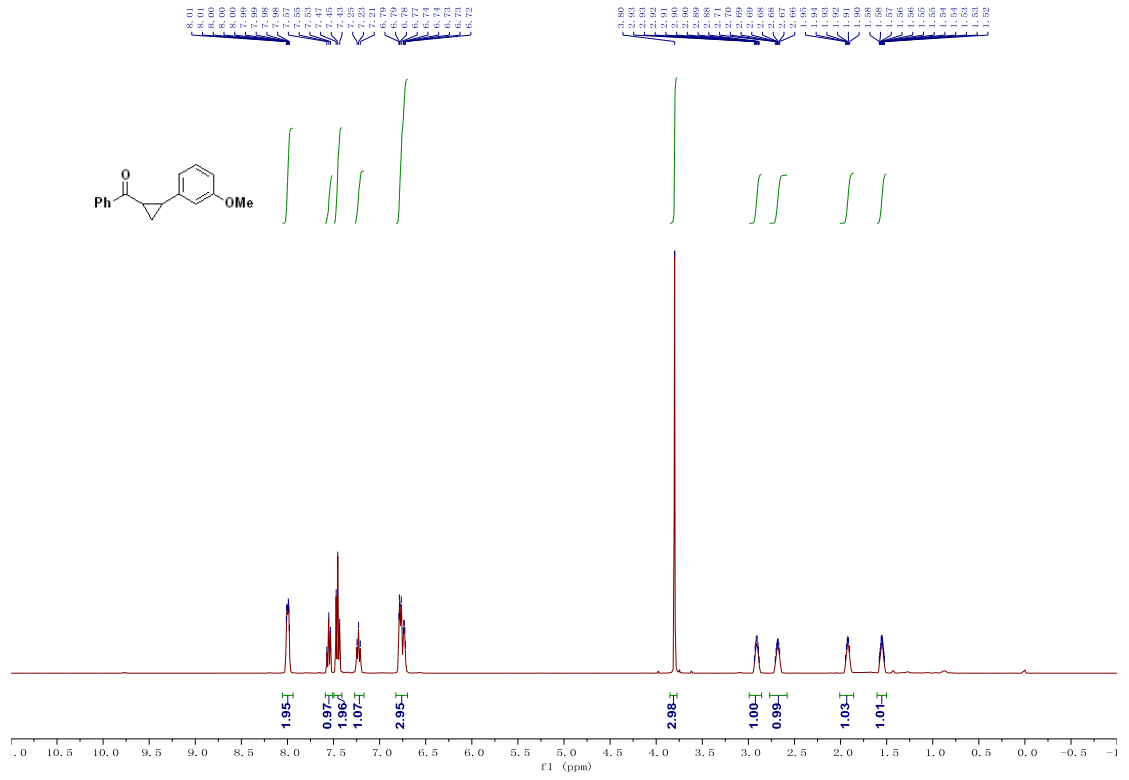


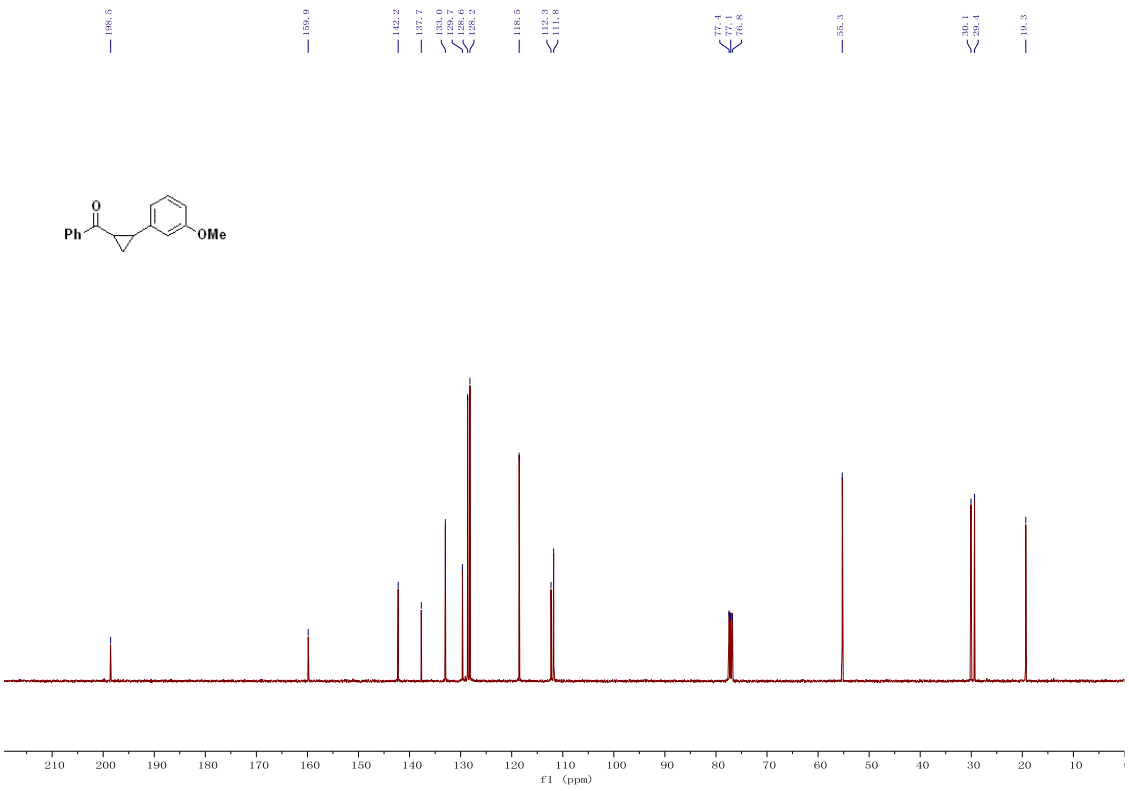
^{1}H and ^{13}C NMR of compound **1k**



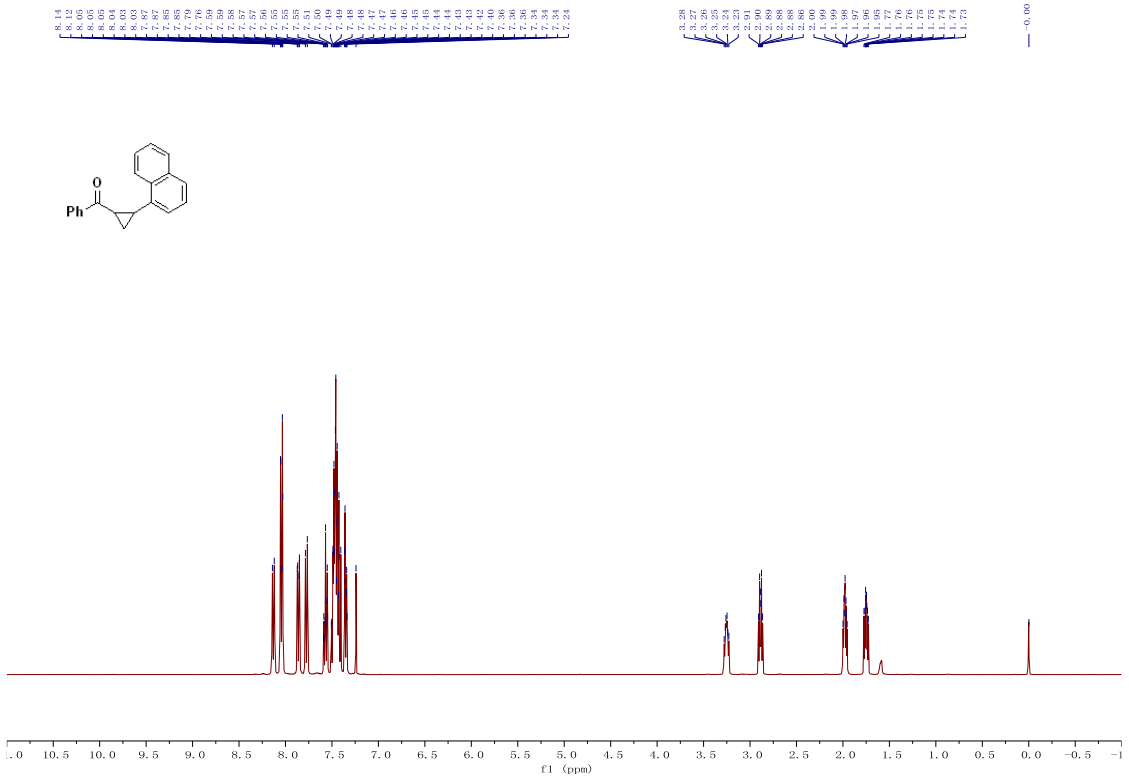


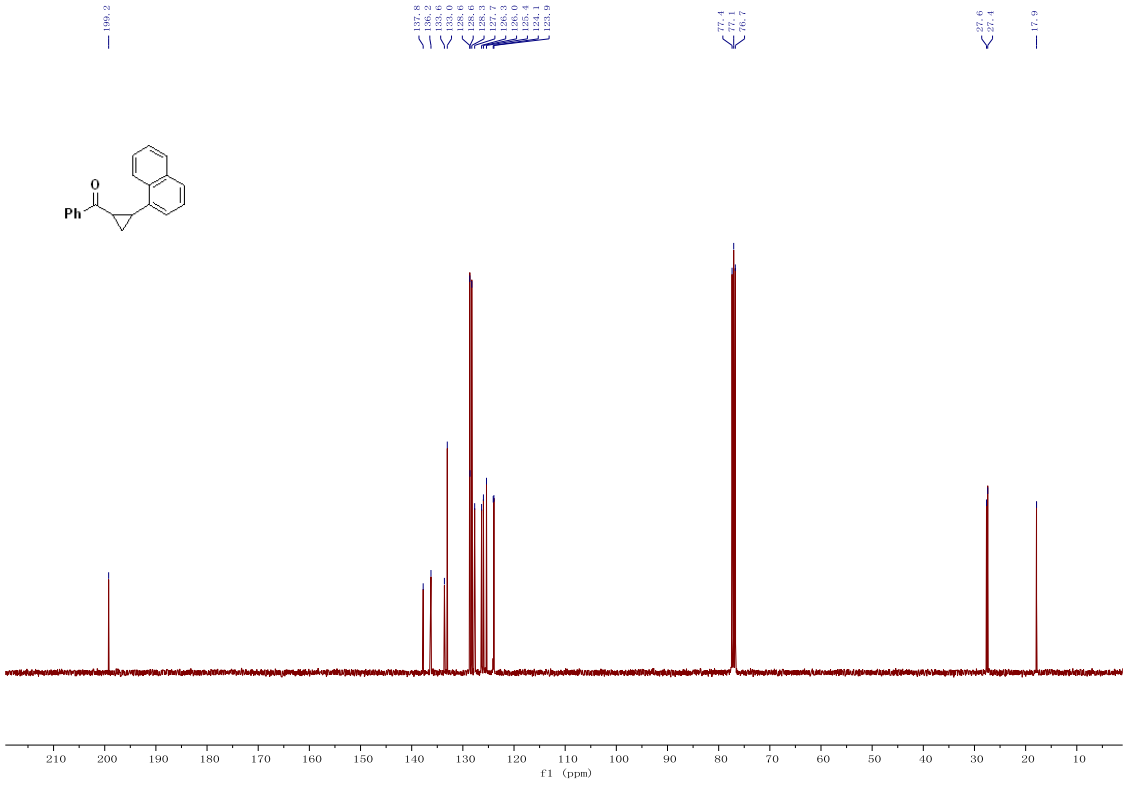
^{1}H and ^{13}C NMR of compound **1l**



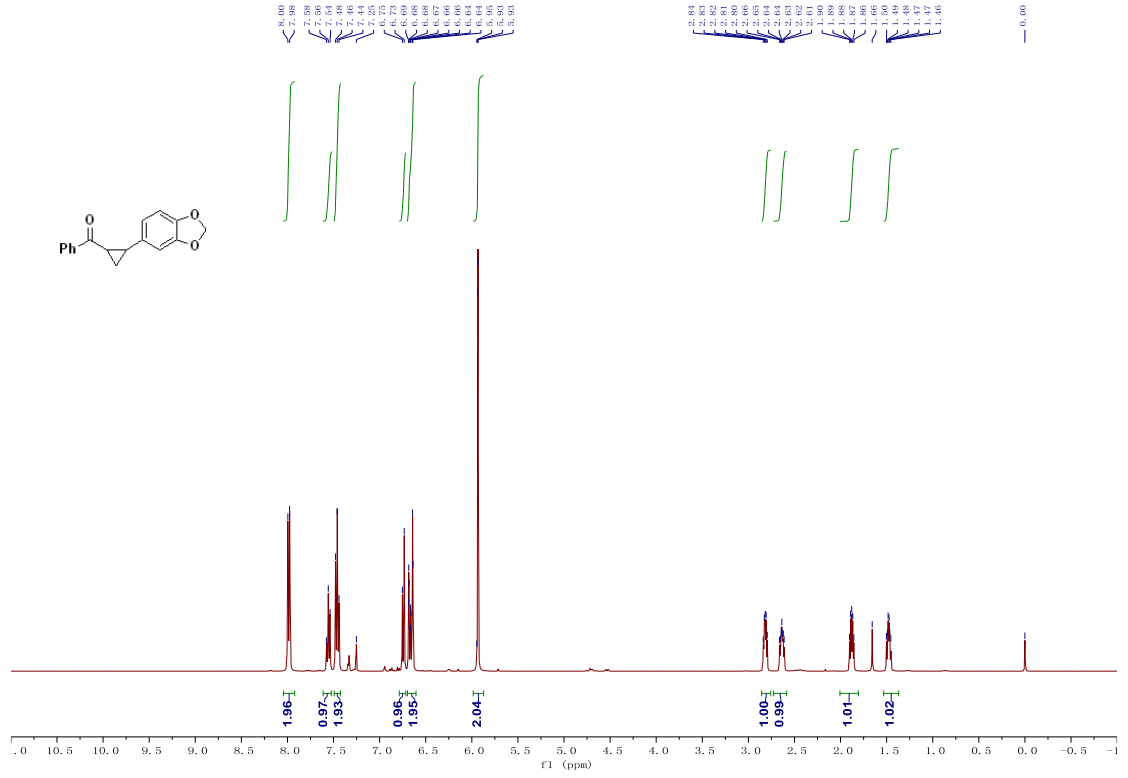


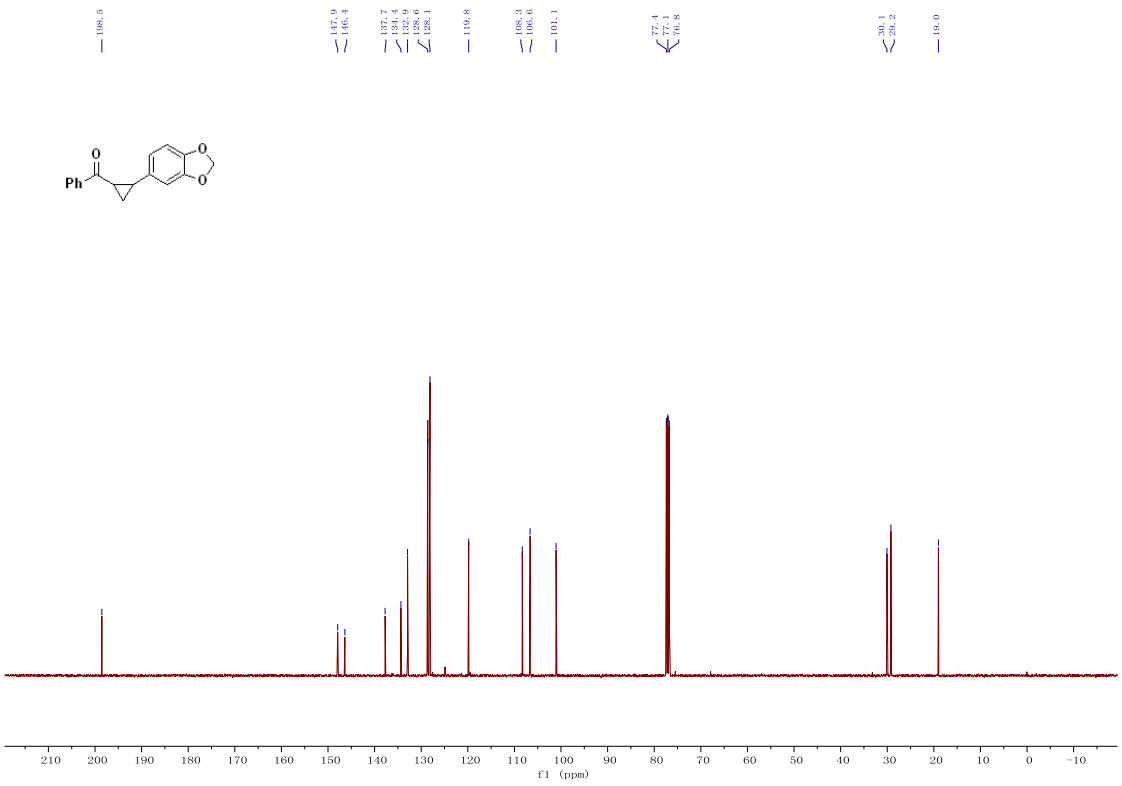
^{1}H and ^{13}C NMR of compound **1m**



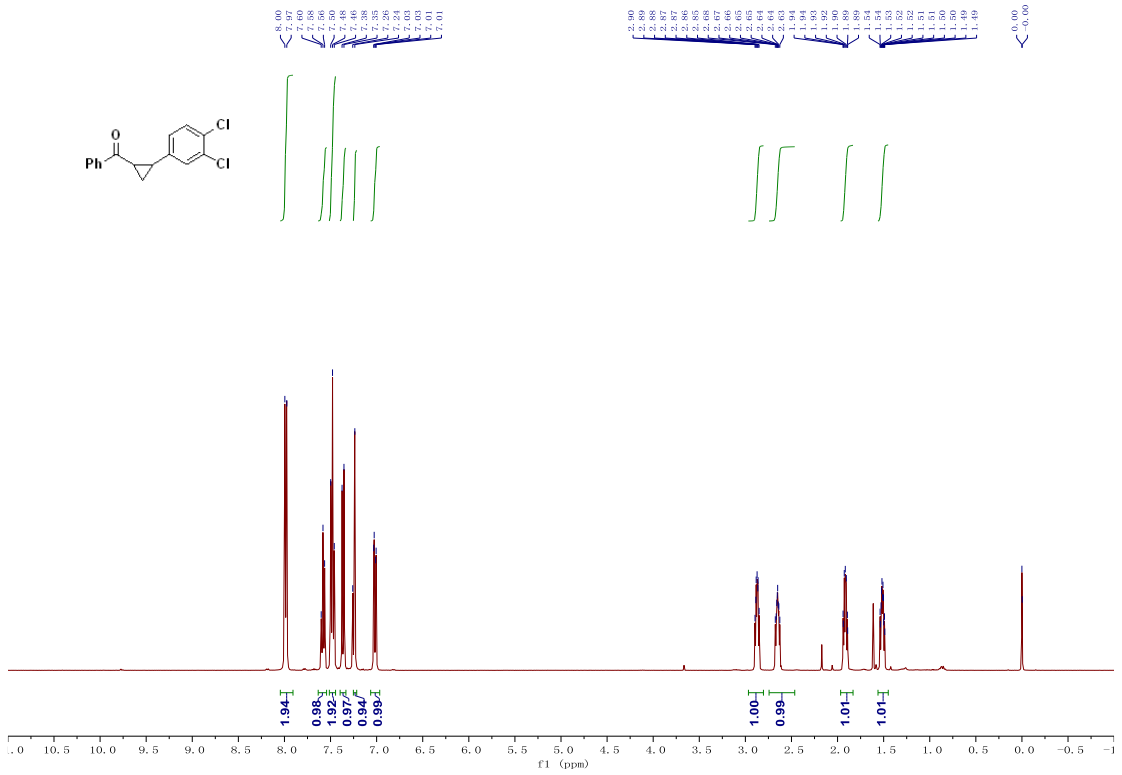


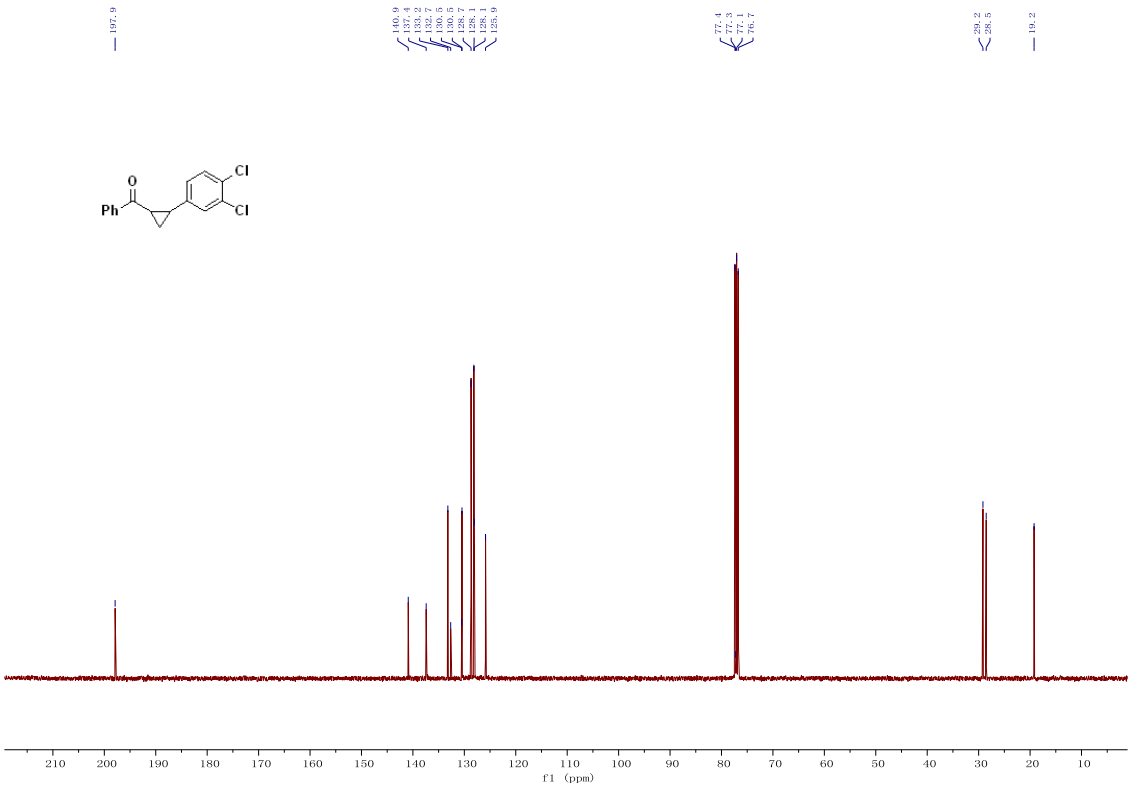
^{1}H and ^{13}C NMR of compound **1n**



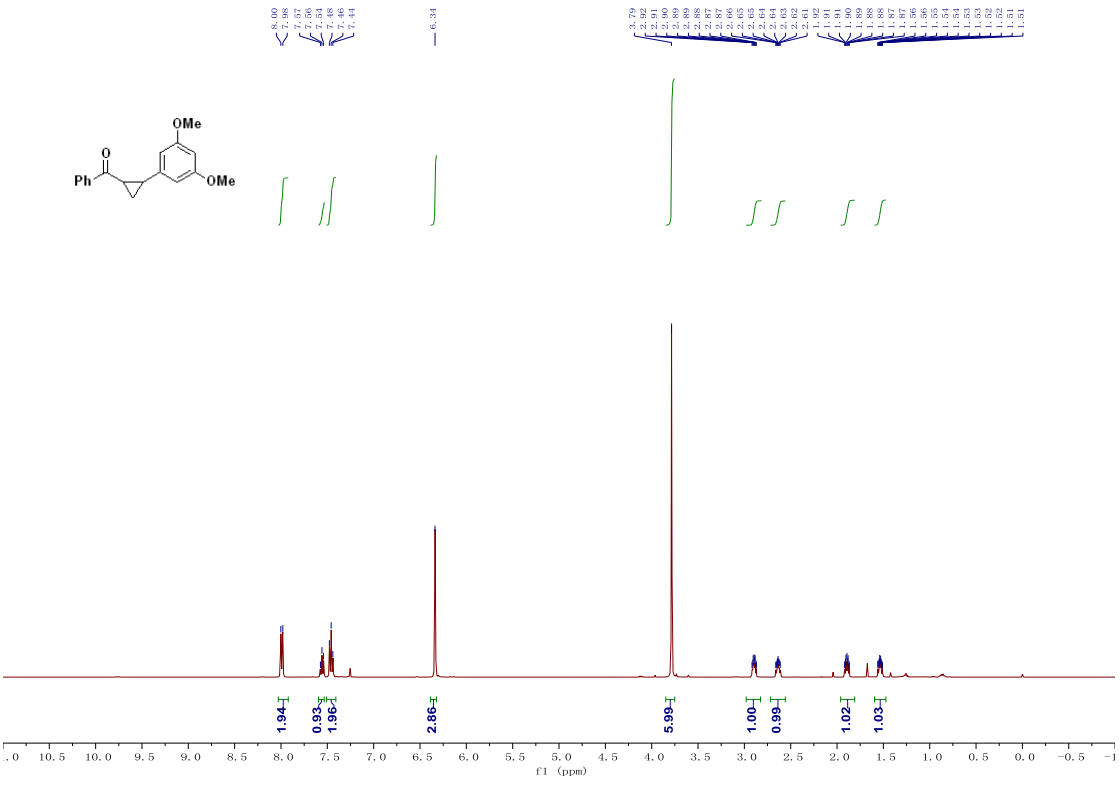


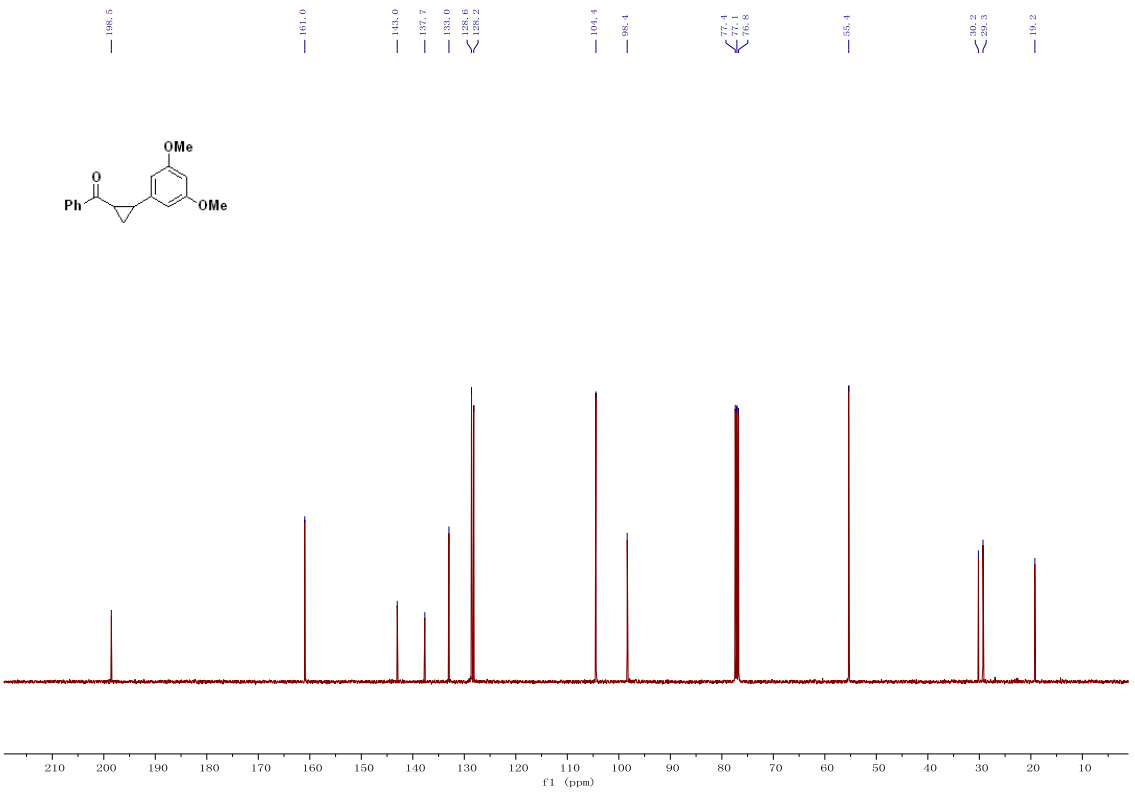
^{1}H and ^{13}C NMR of compound **1o**



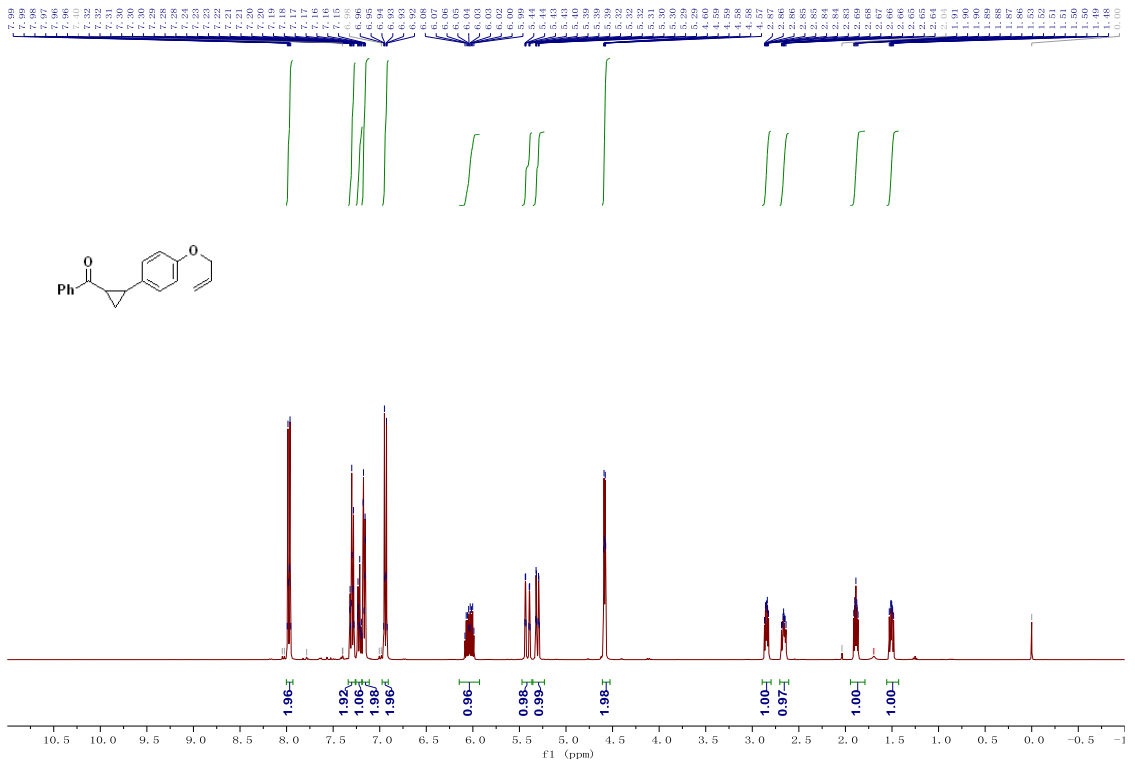


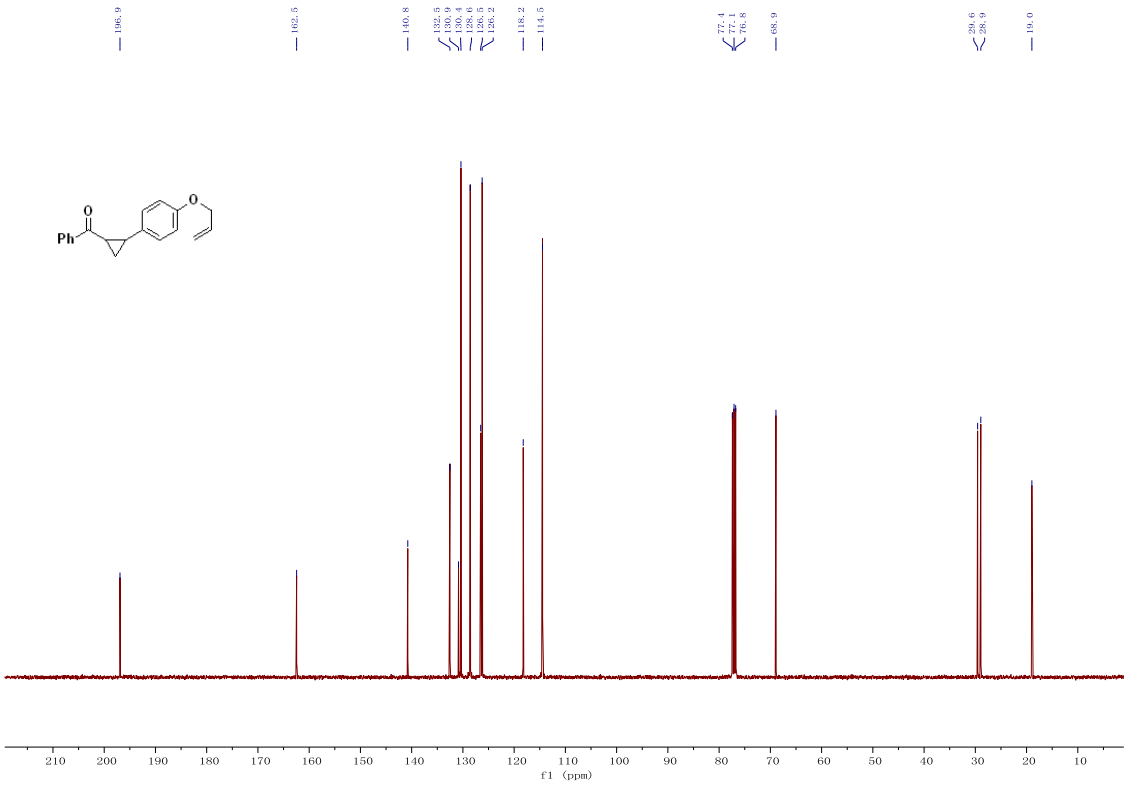
^{1}H and ^{13}C NMR of compound **1p**



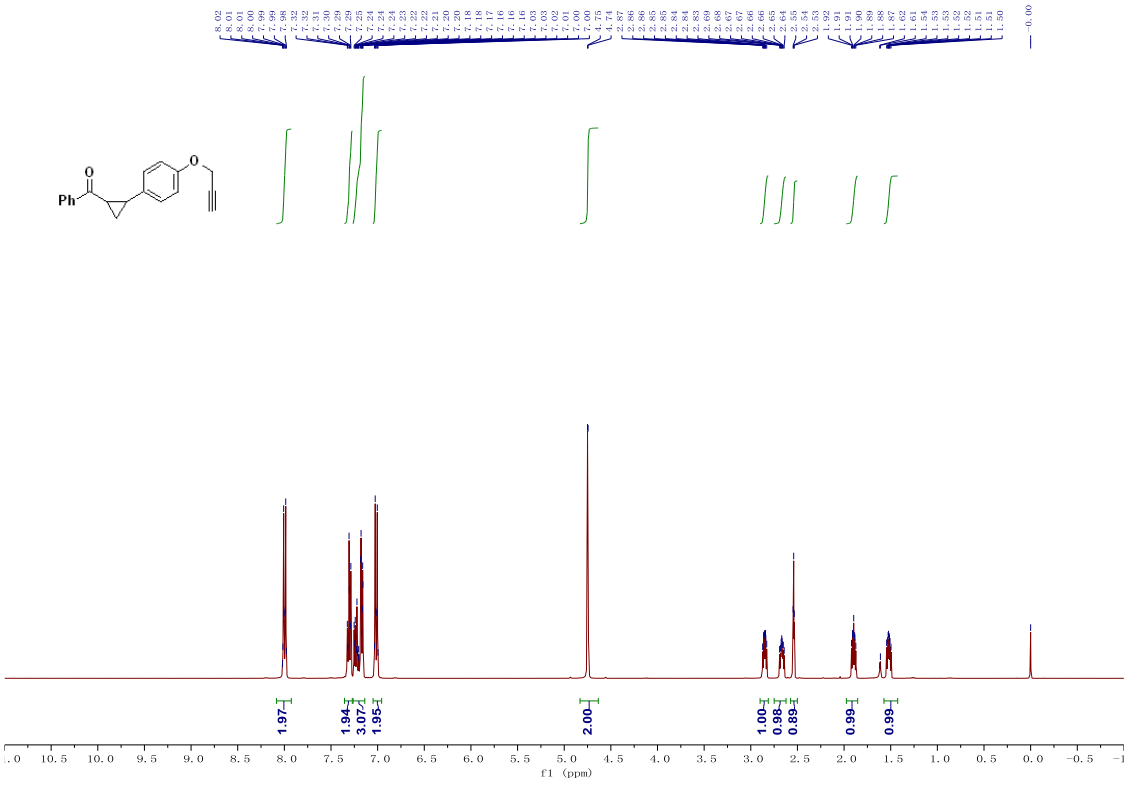


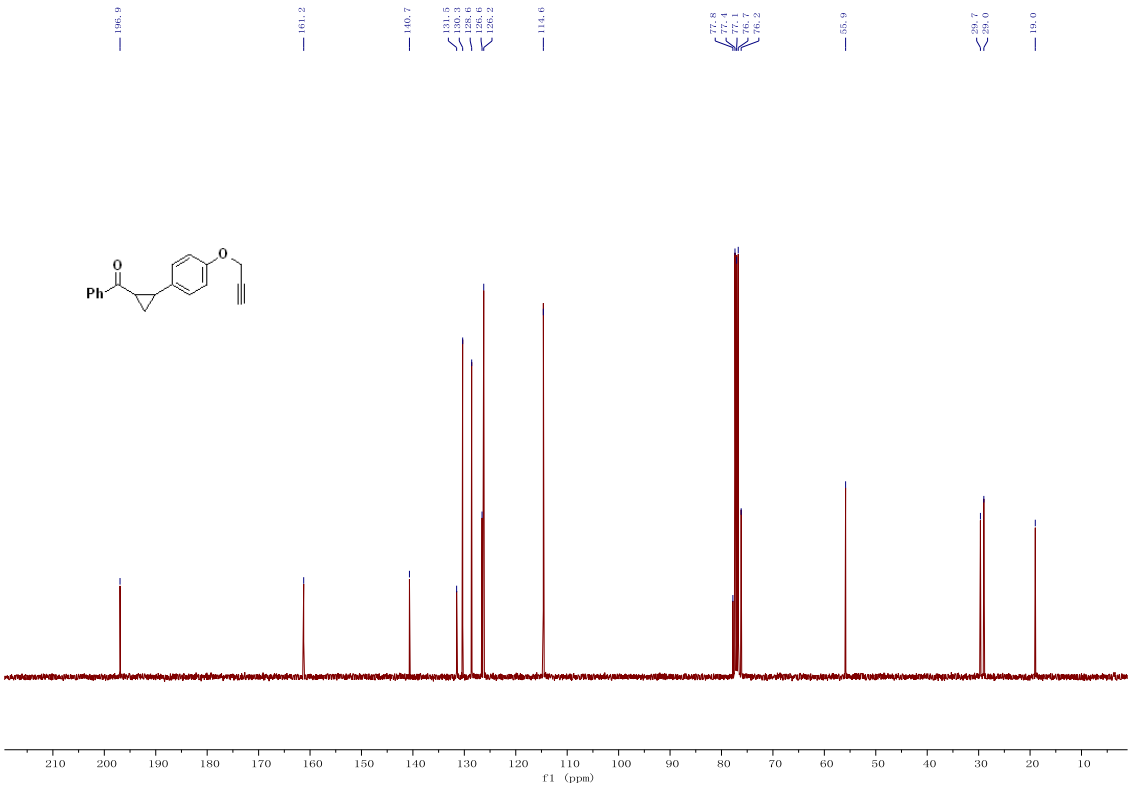
^{1}H and ^{13}C NMR of compound **1q**



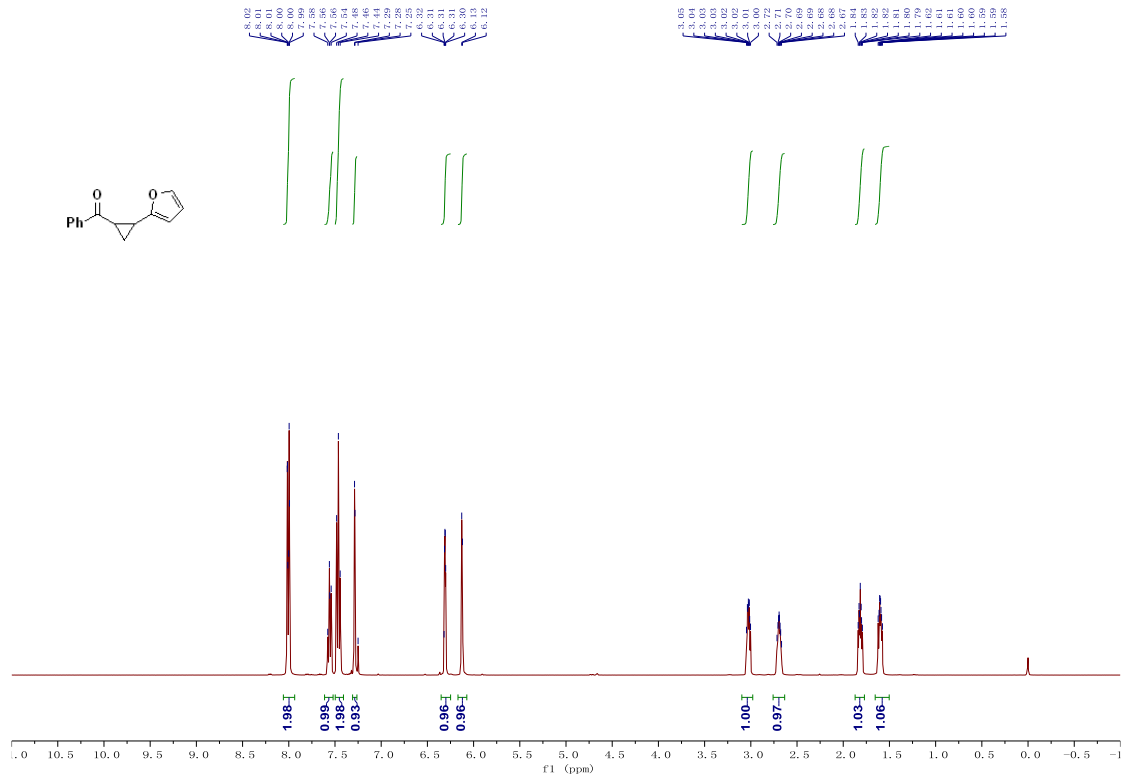


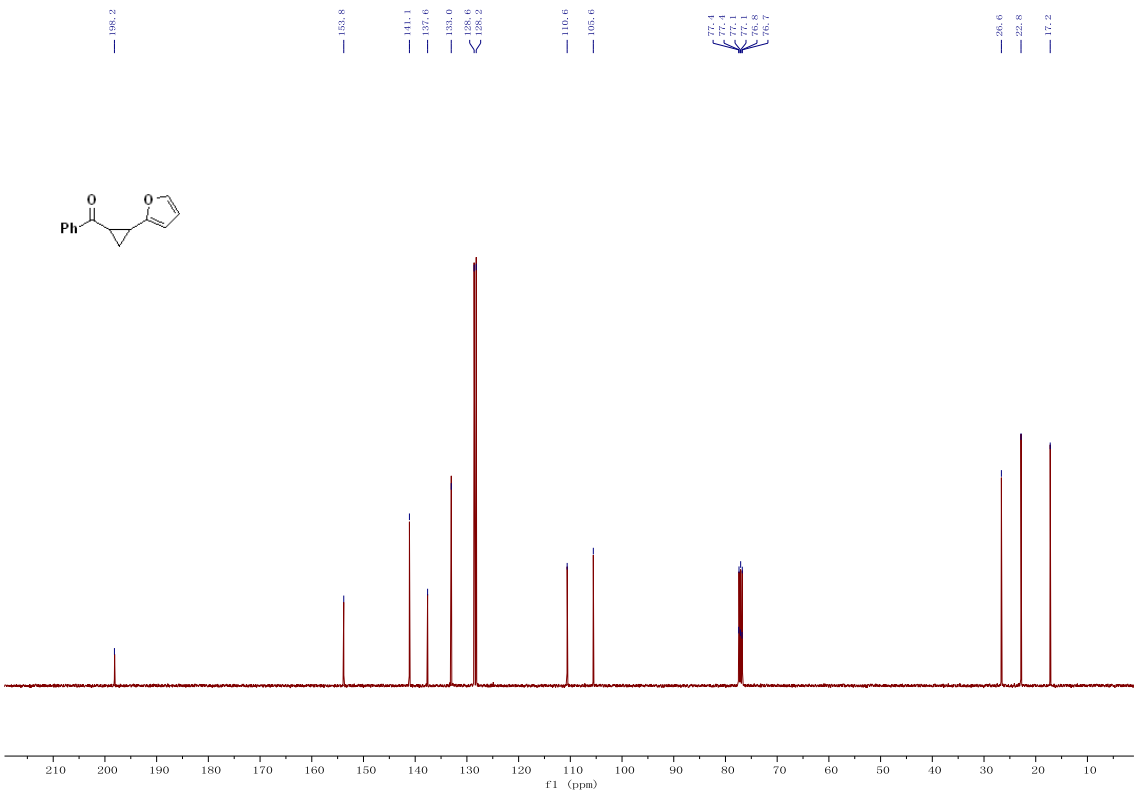
^{1}H and ^{13}C NMR of compound **1r**



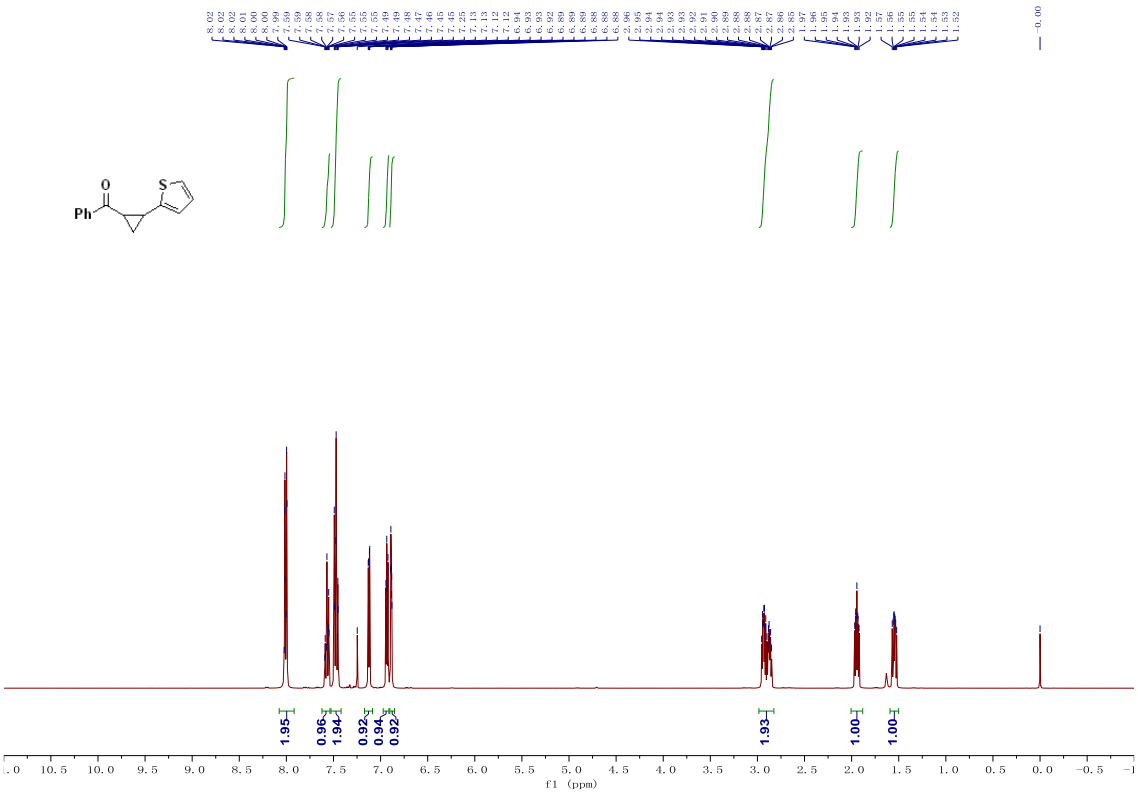


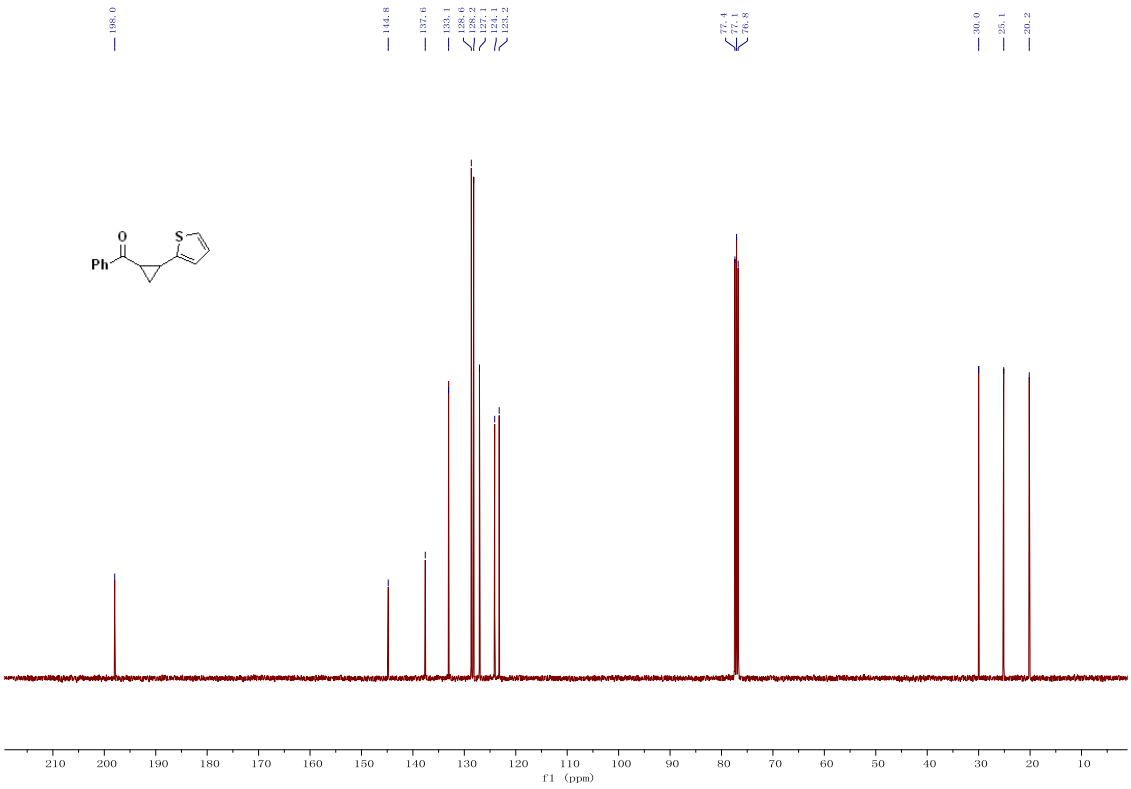
^{1}H and ^{13}C NMR of compound **1s**



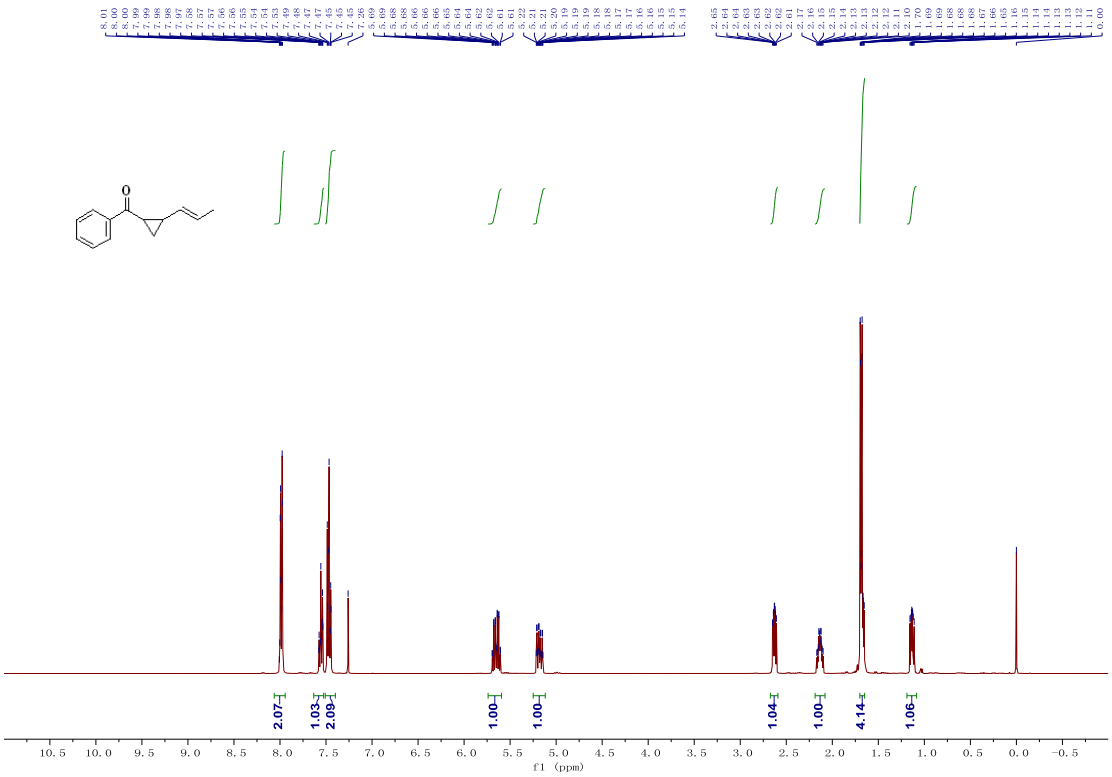


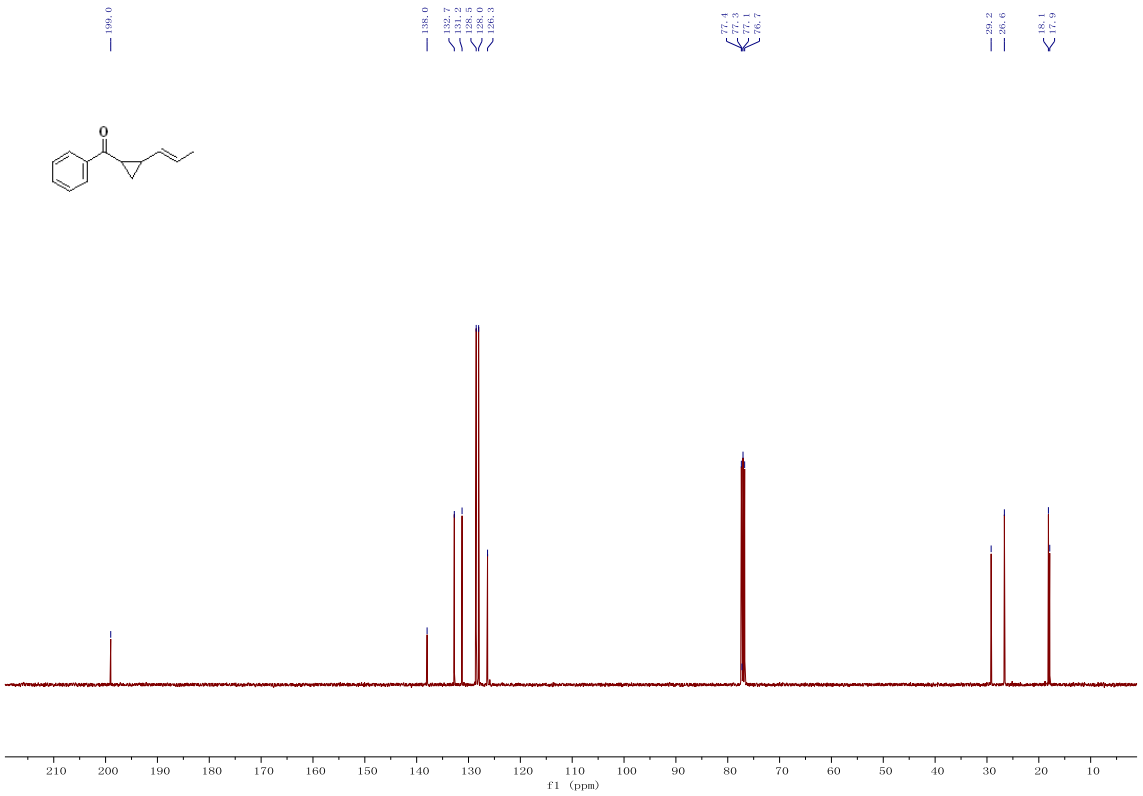
^{1}H and ^{13}C NMR of compound **1t**



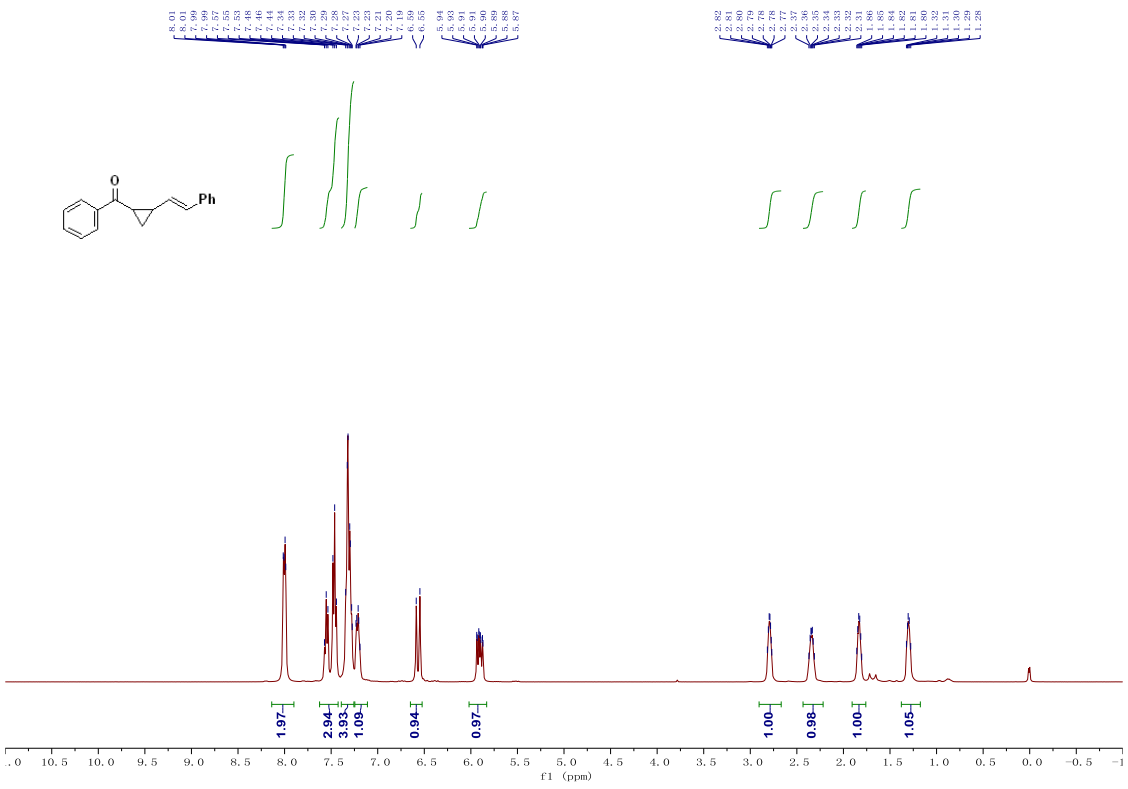


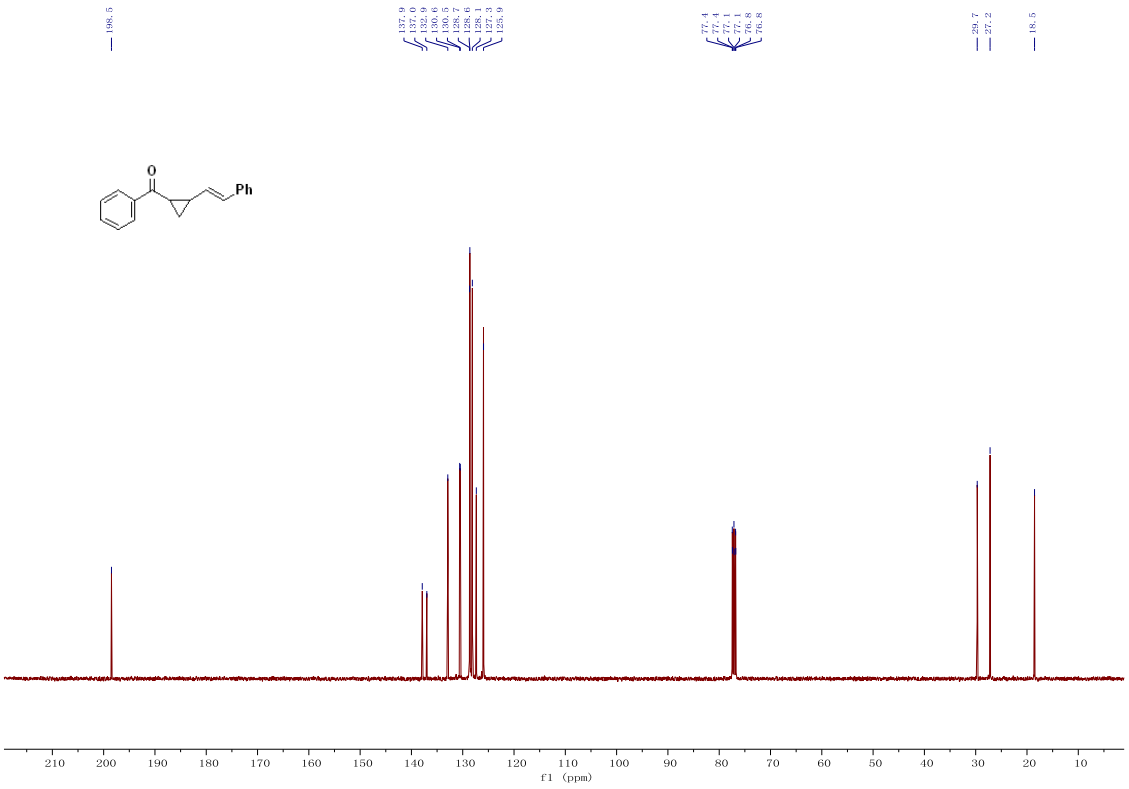
^{1}H and ^{13}C NMR of compound **4a**



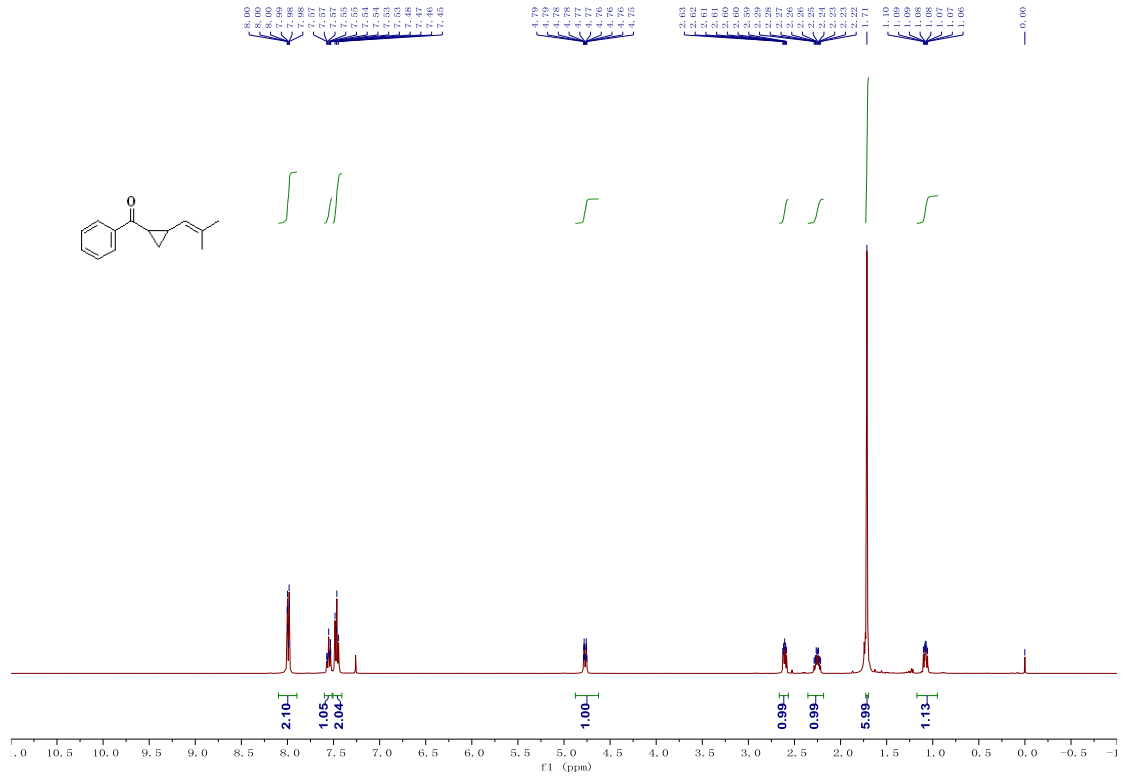


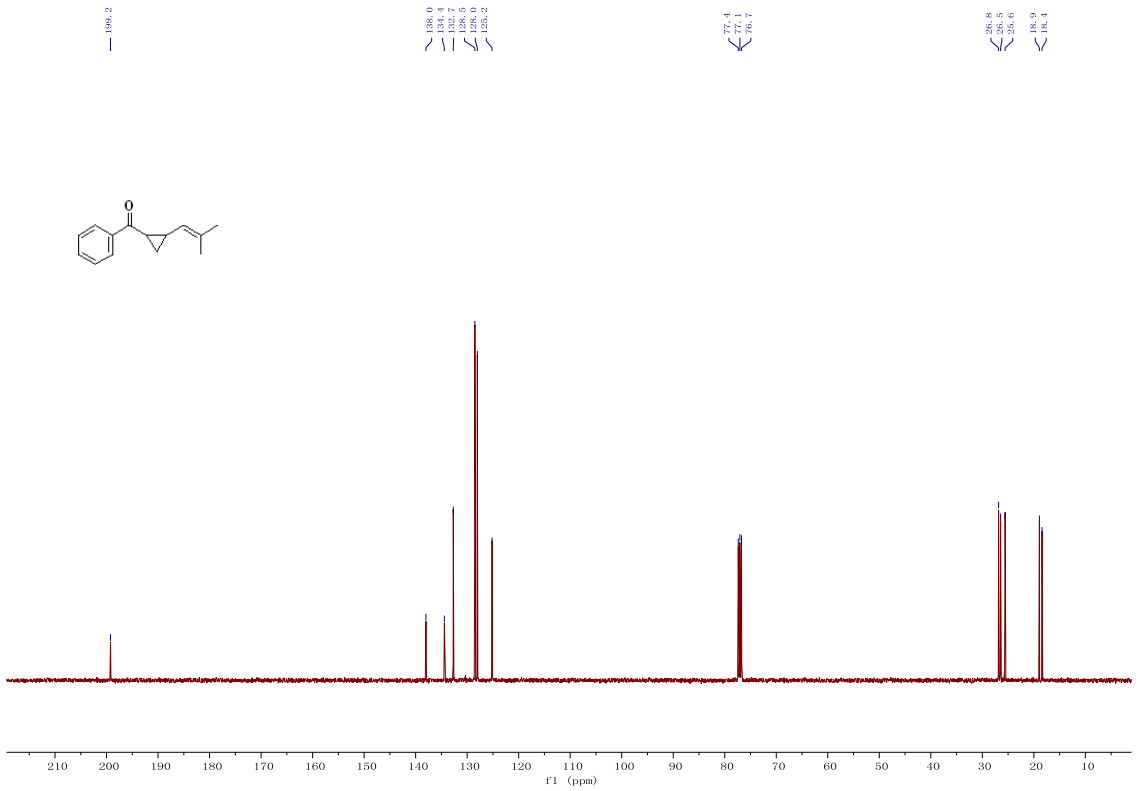
^{1}H and ^{13}C NMR of compound **4b**



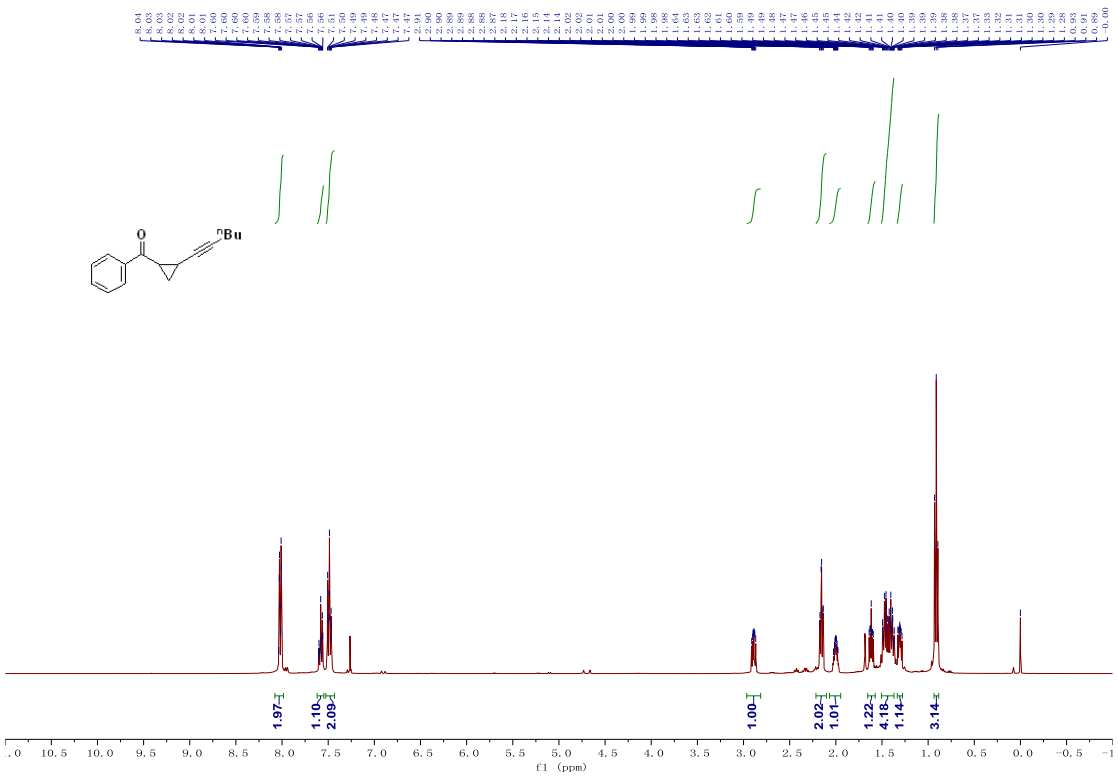


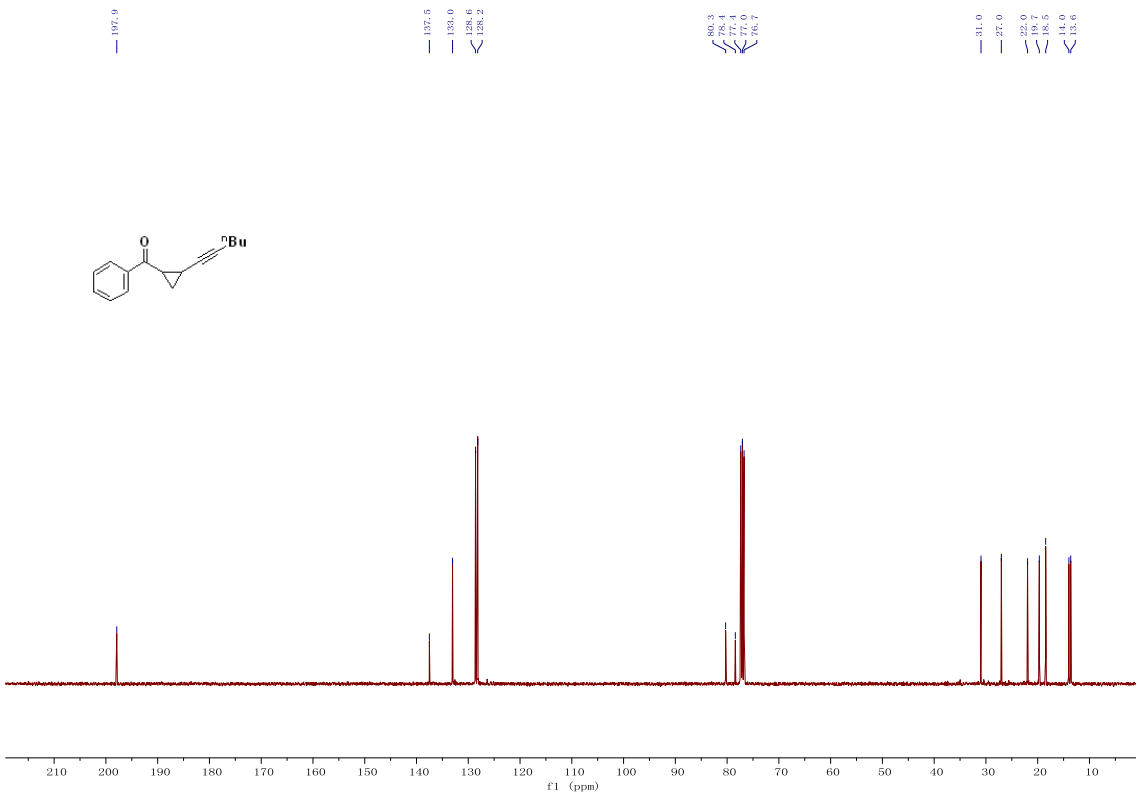
^{1}H and ^{13}C NMR of compound **4c**



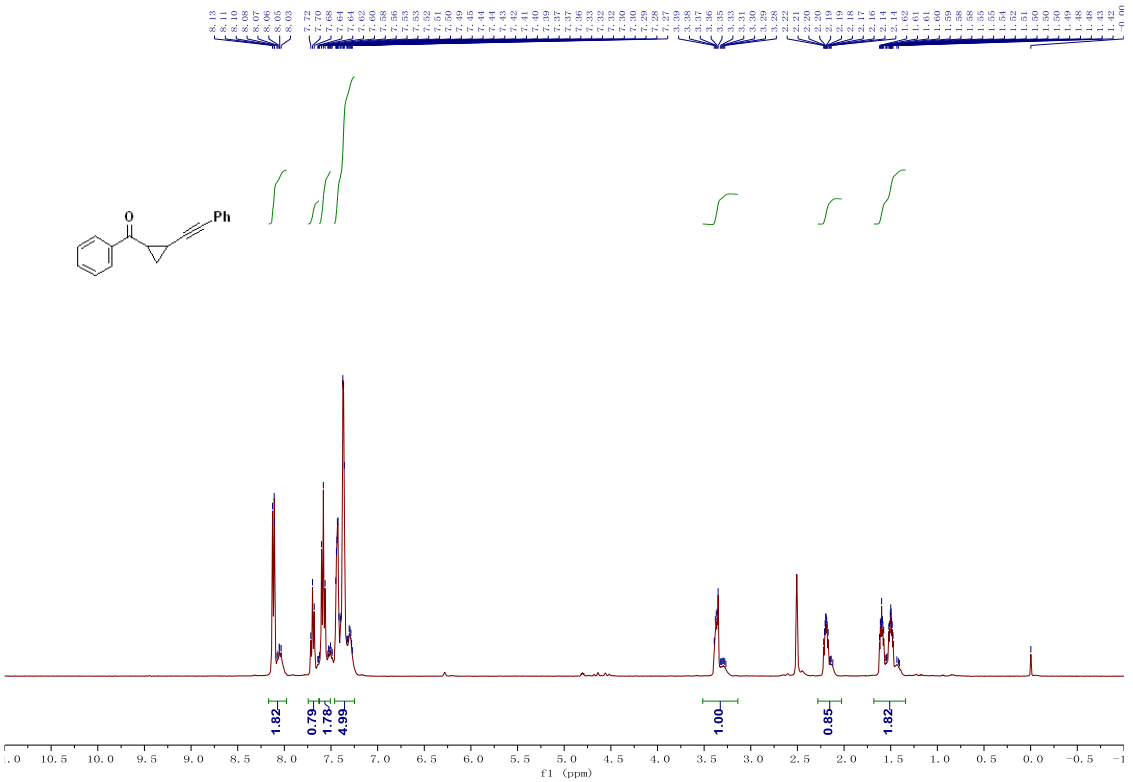


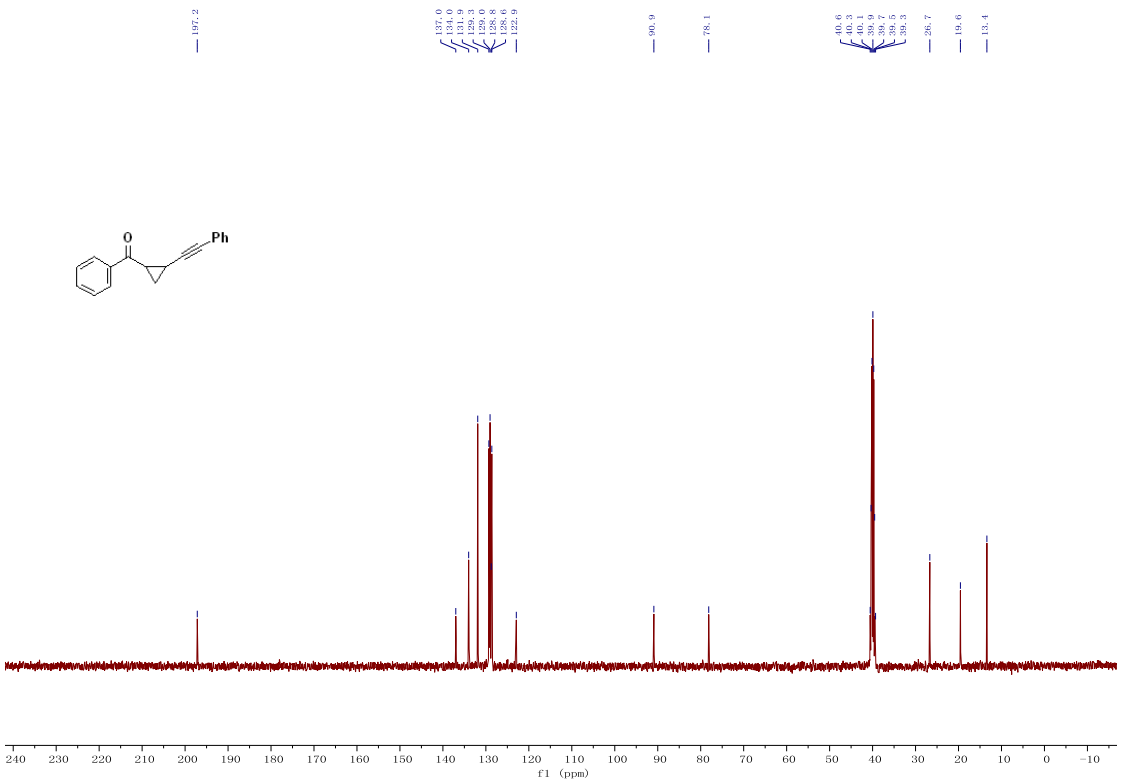
^{1}H and ^{13}C NMR of compound **4d**



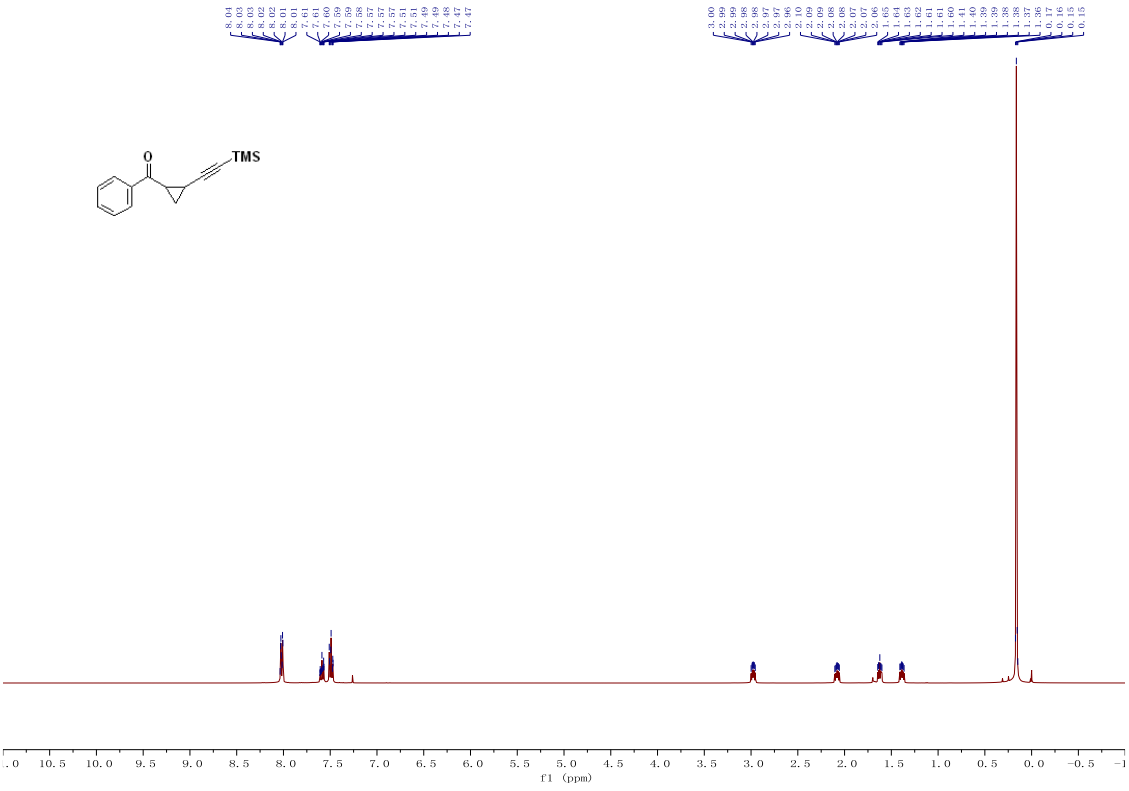


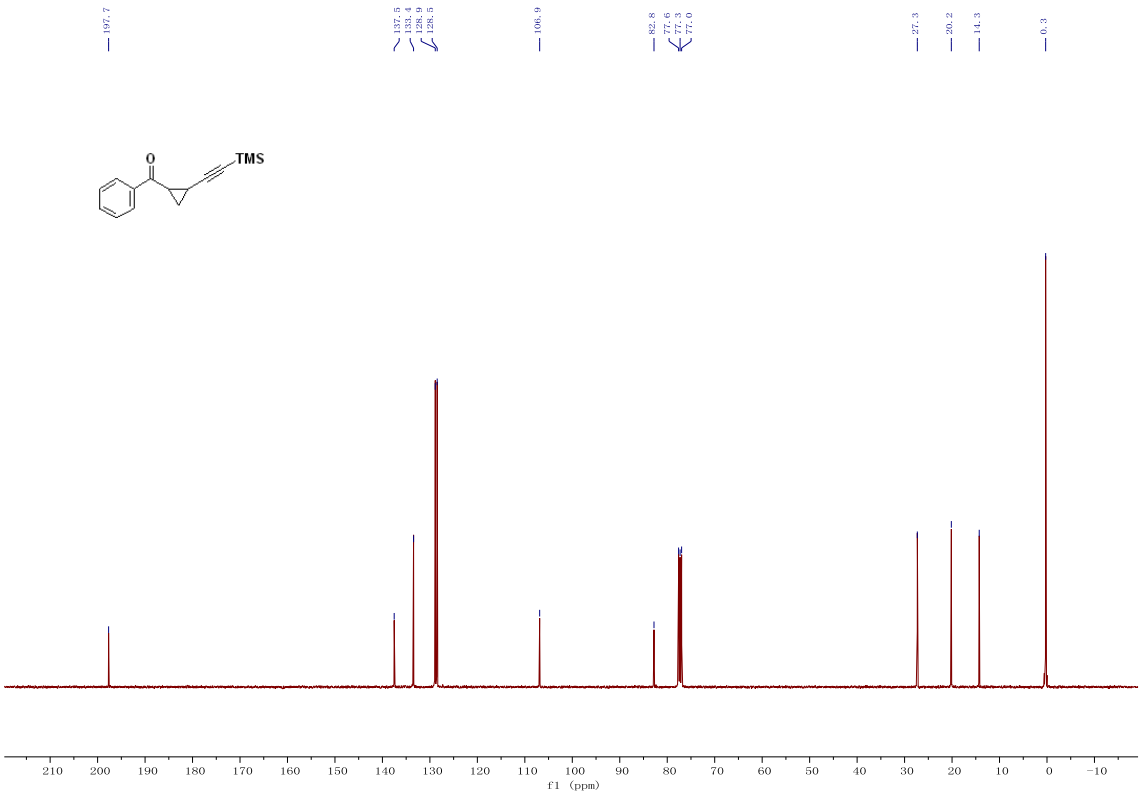
^{1}H and ^{13}C NMR of compound **4e**



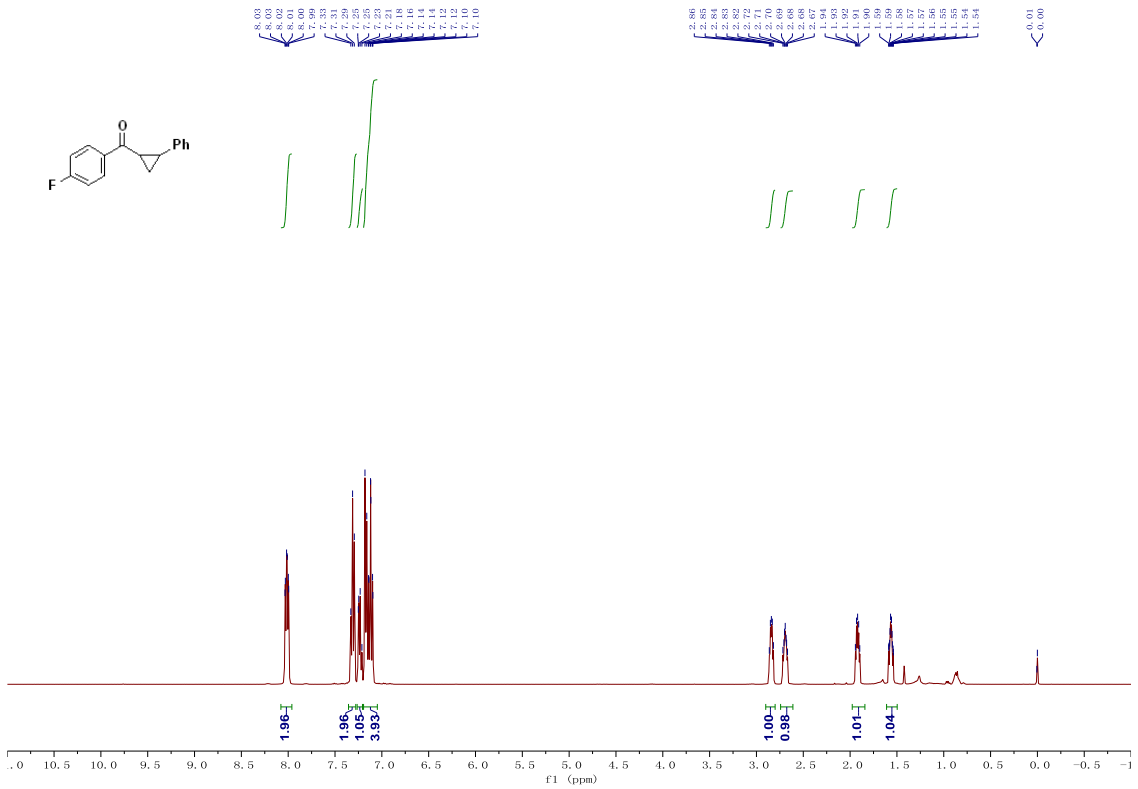


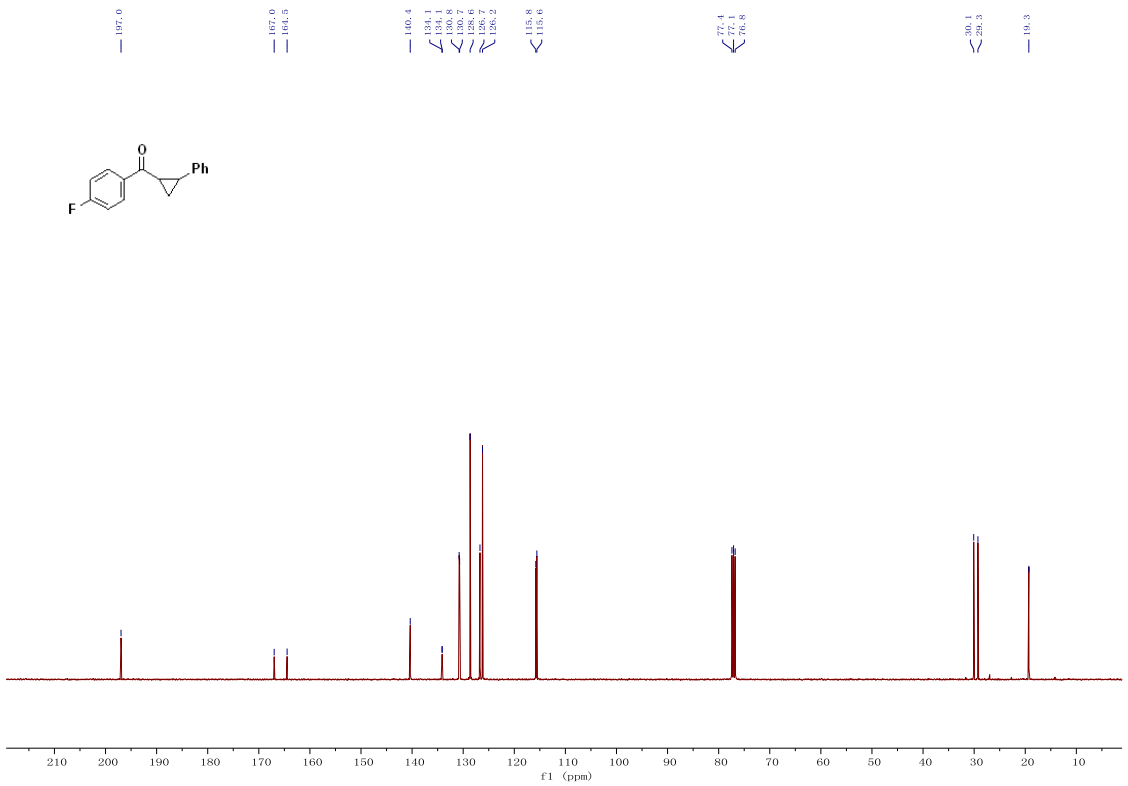
^{1}H and ^{13}C NMR of compound **4f**





^{1}H, ^{13}C and ^{19}F NMR of compound **6a**

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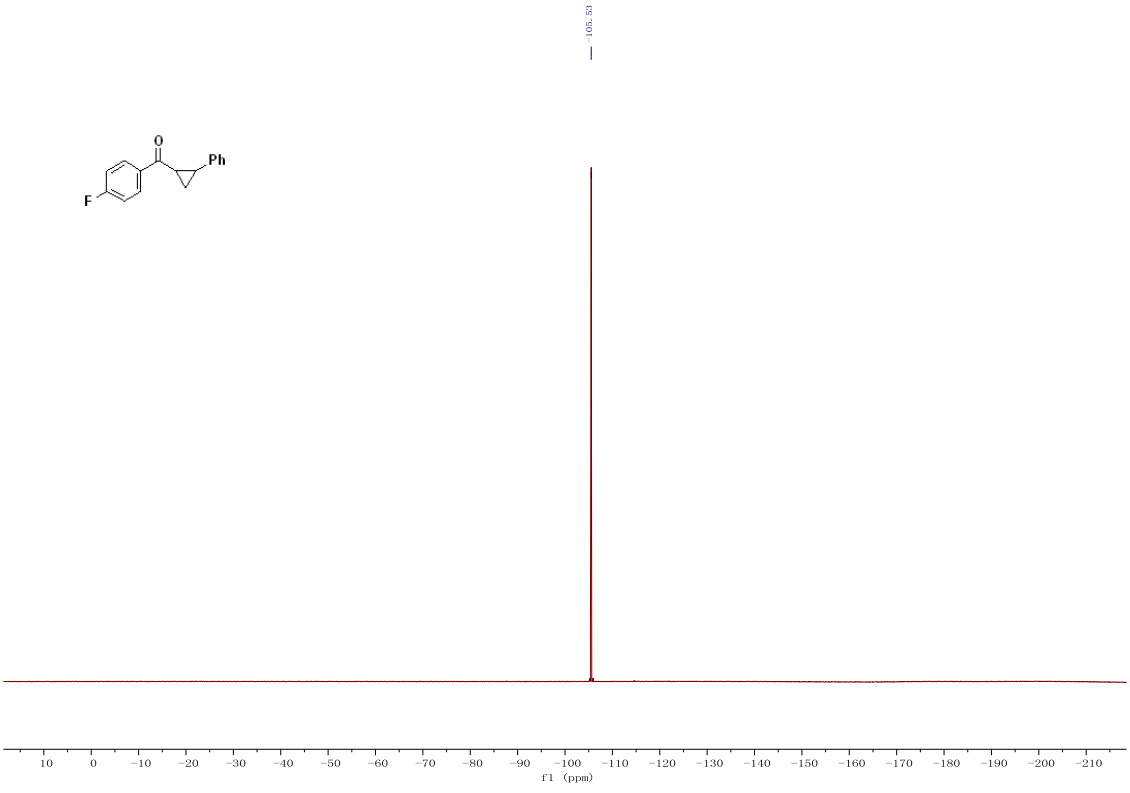
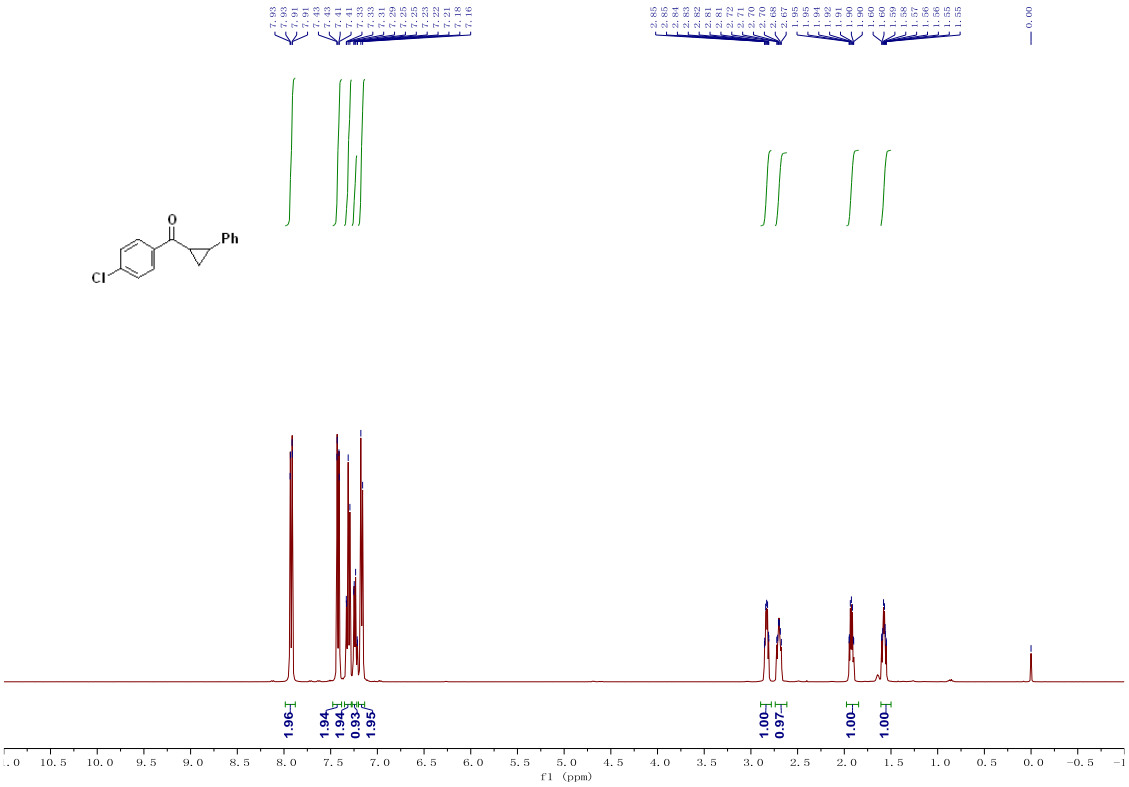
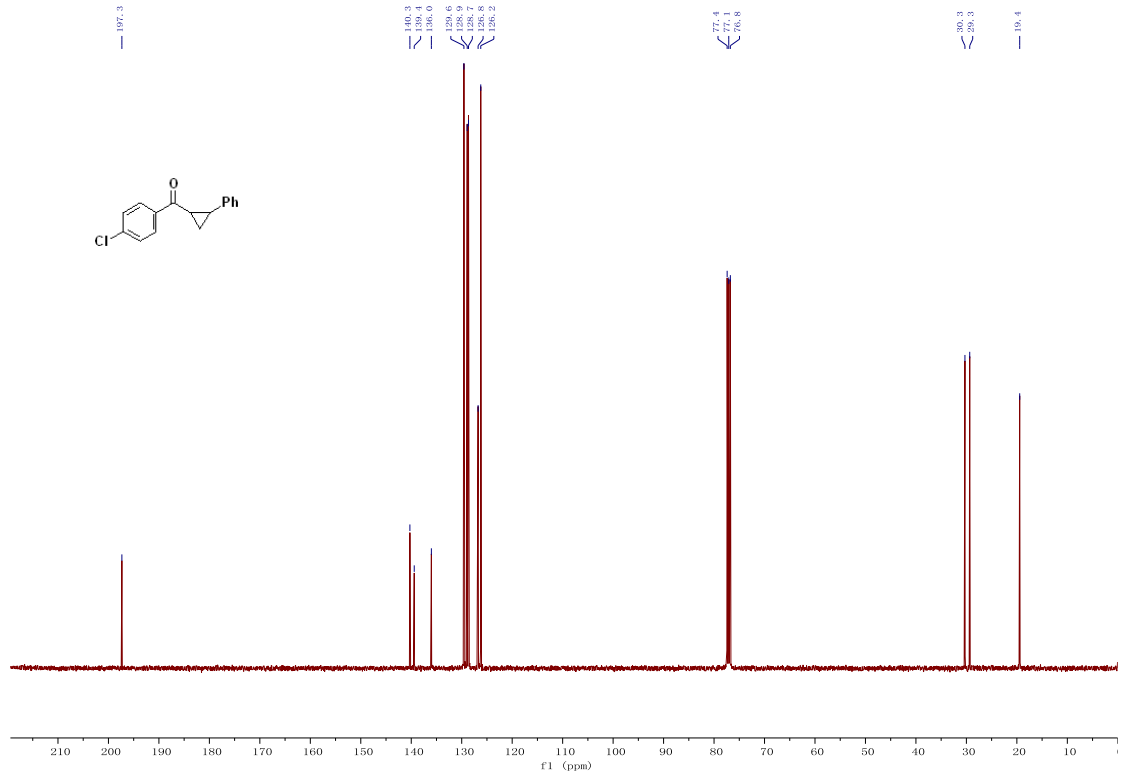
115.6
77.4
77.1
76.8
30.1
29.3
19.3
O
Ph
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

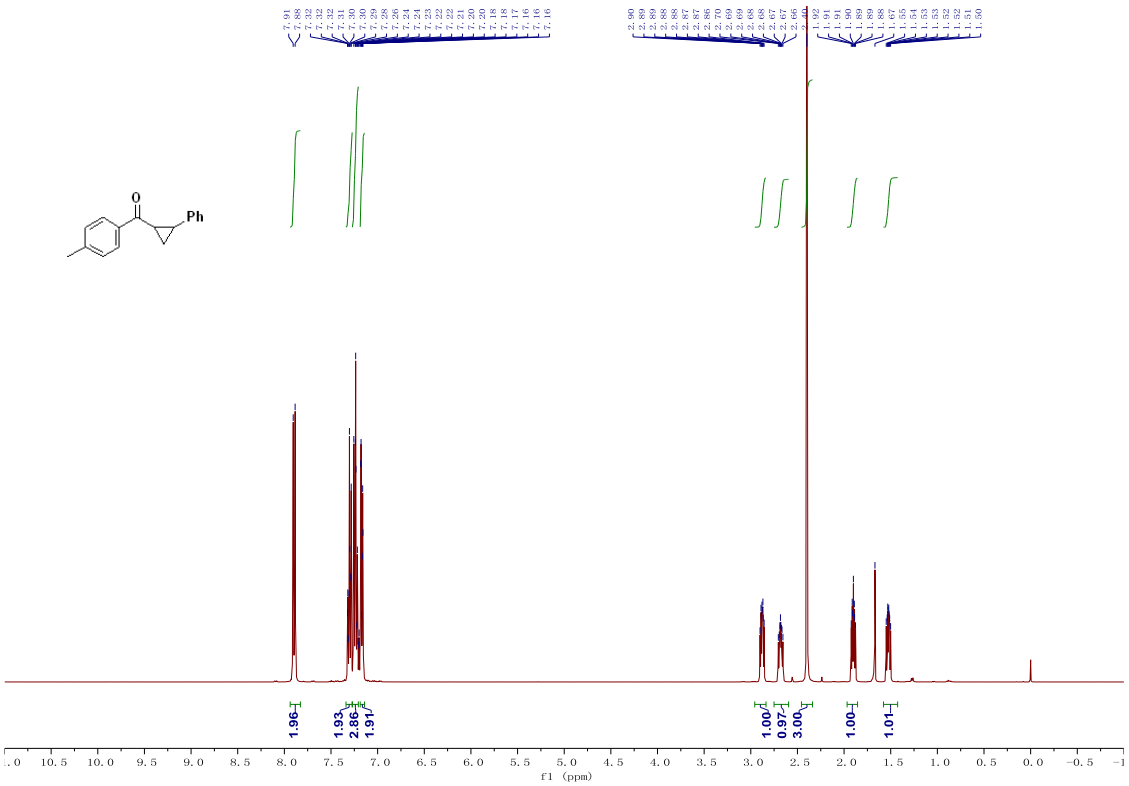

-105.53
O
Ph
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

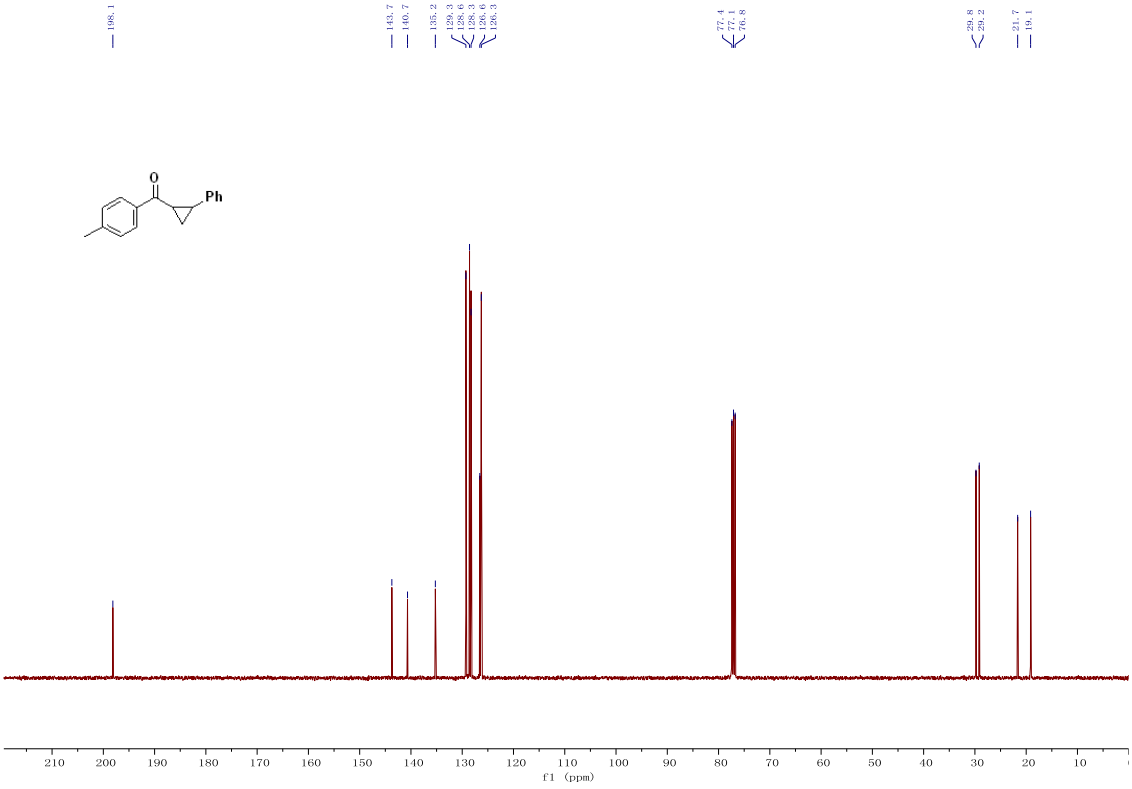
^{1}H and ^{13}C NMR of compound **6b**



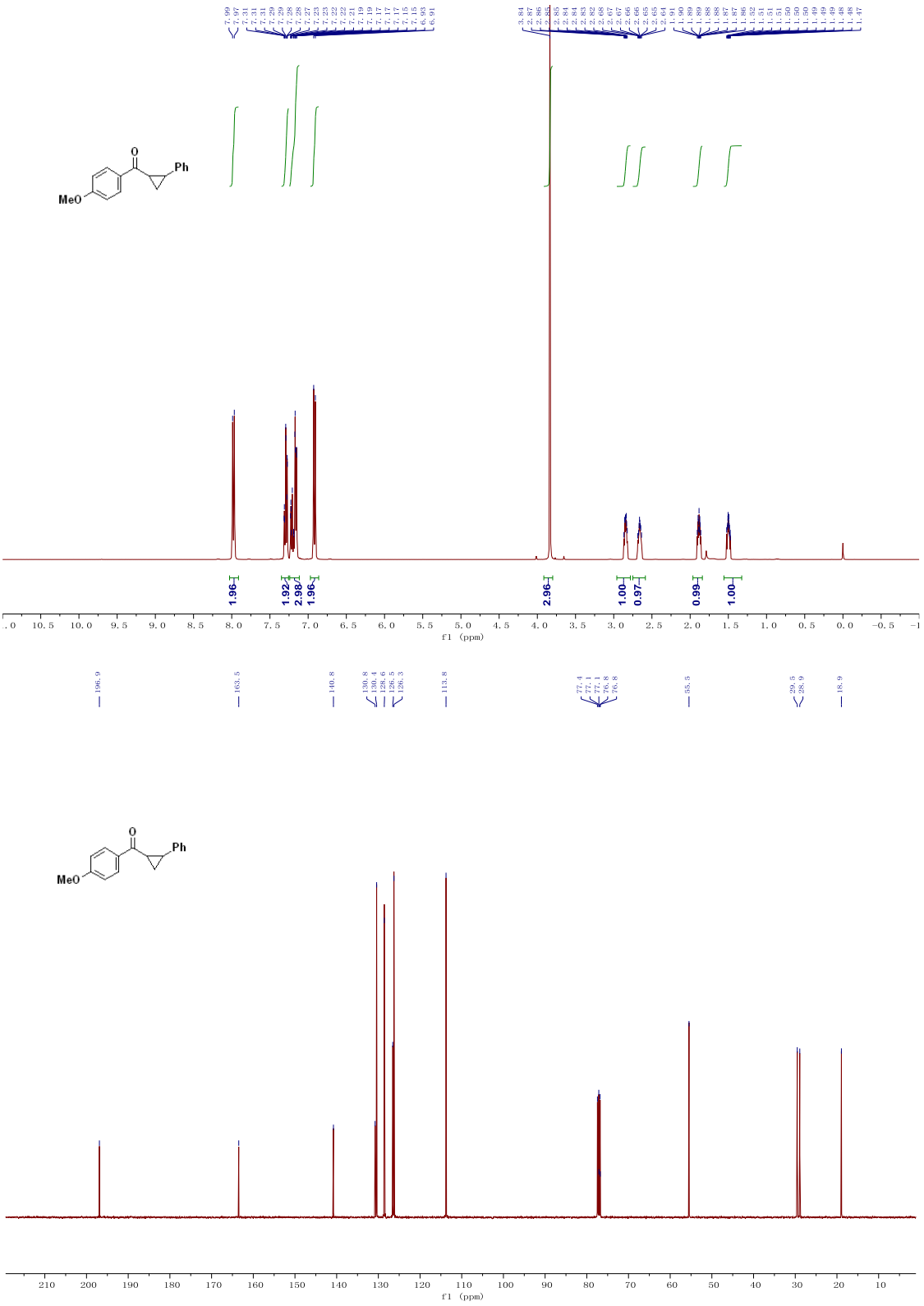


^{1}H and ^{13}C NMR of compound **6c**

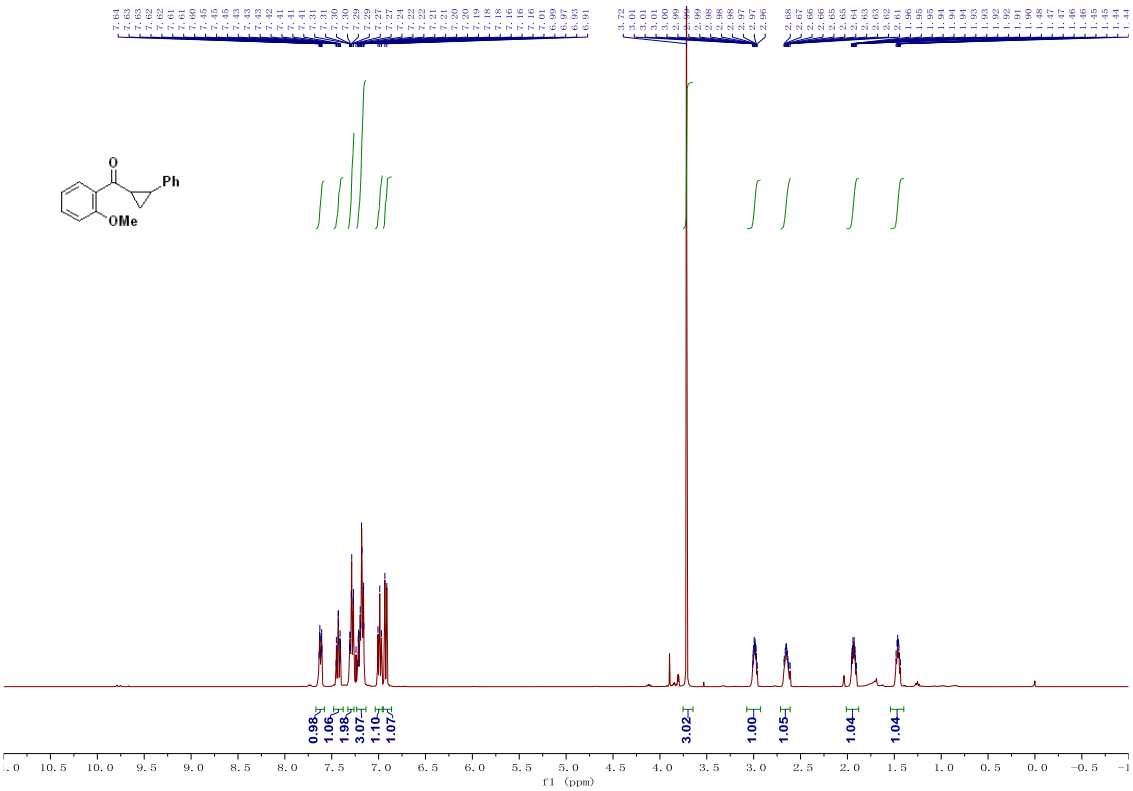


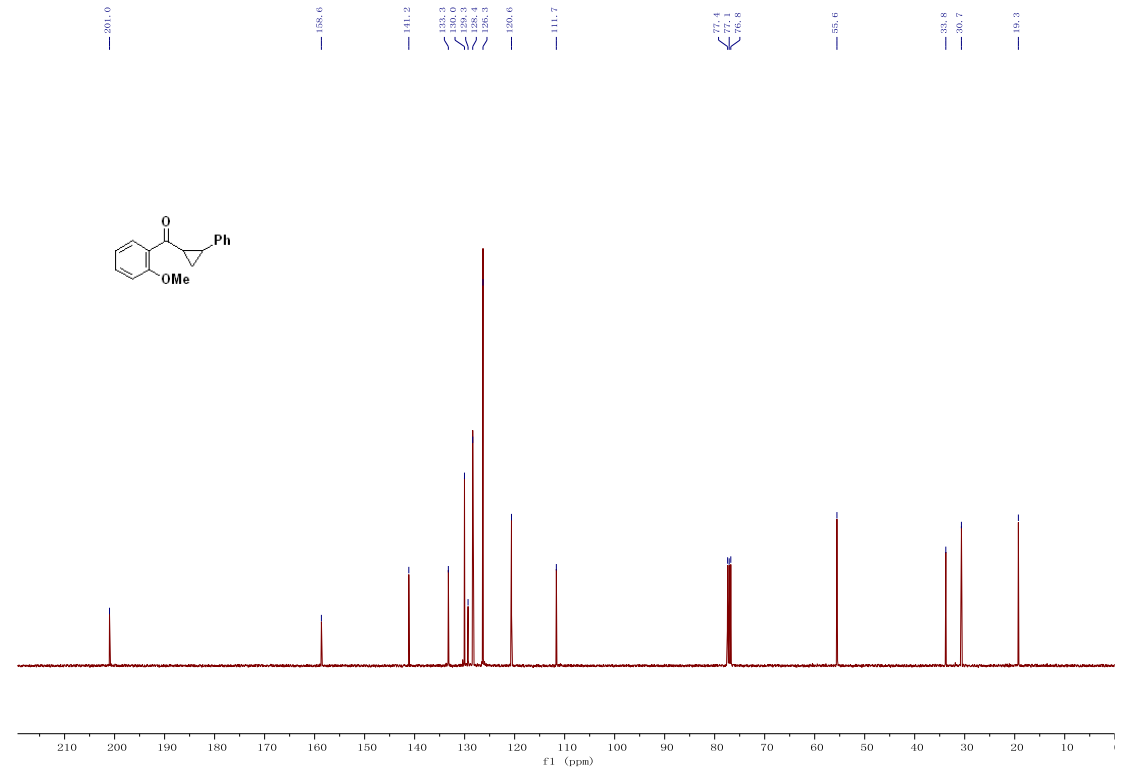


^{1}H and ^{13}C NMR of compound **6d**

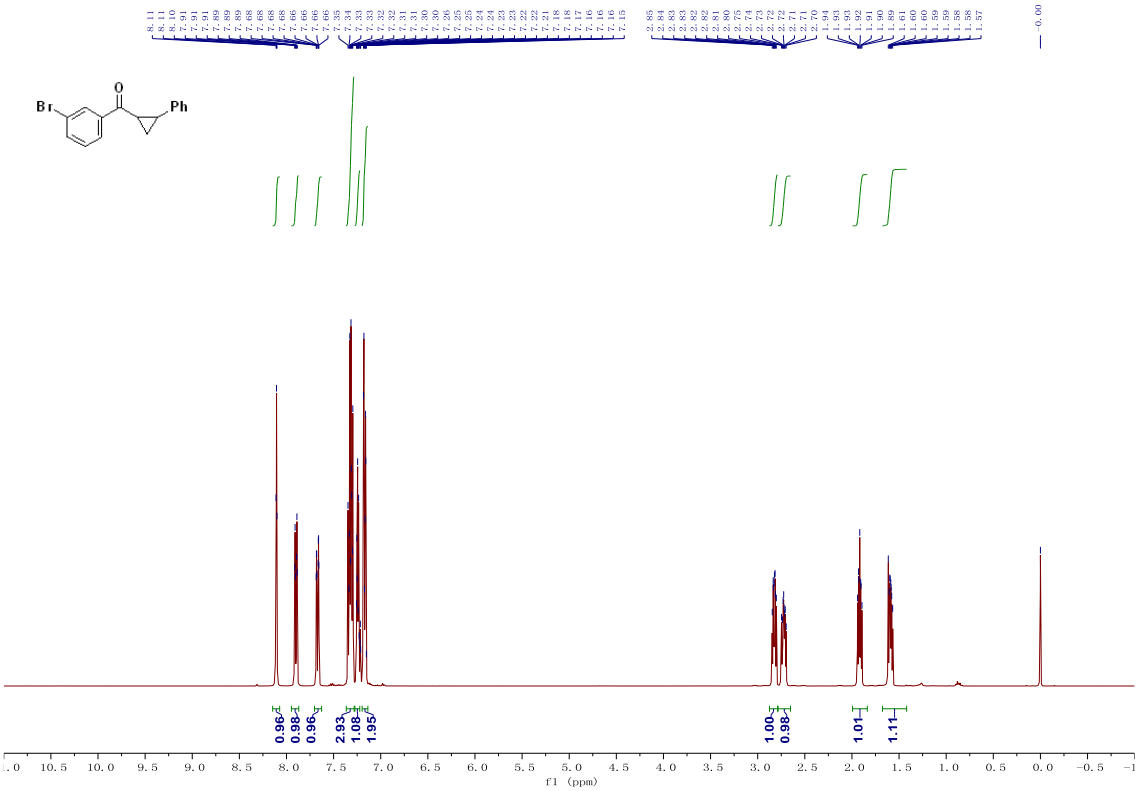


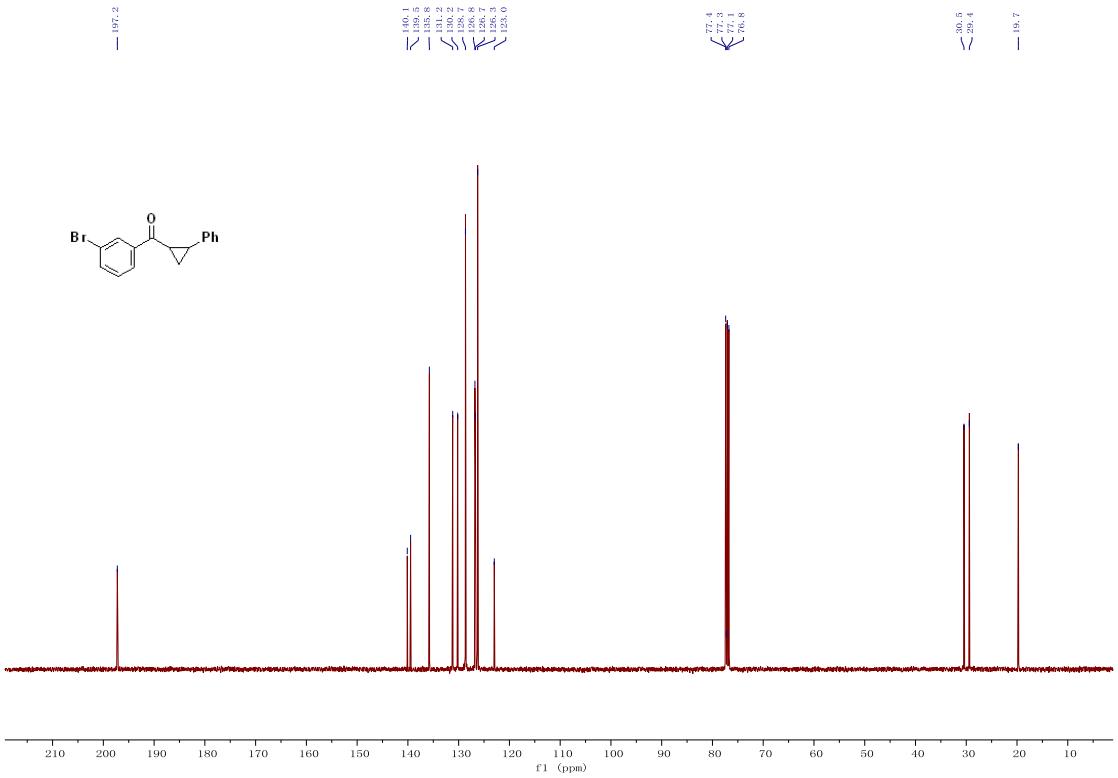
^{1}H and ^{13}C NMR of compound **6e**



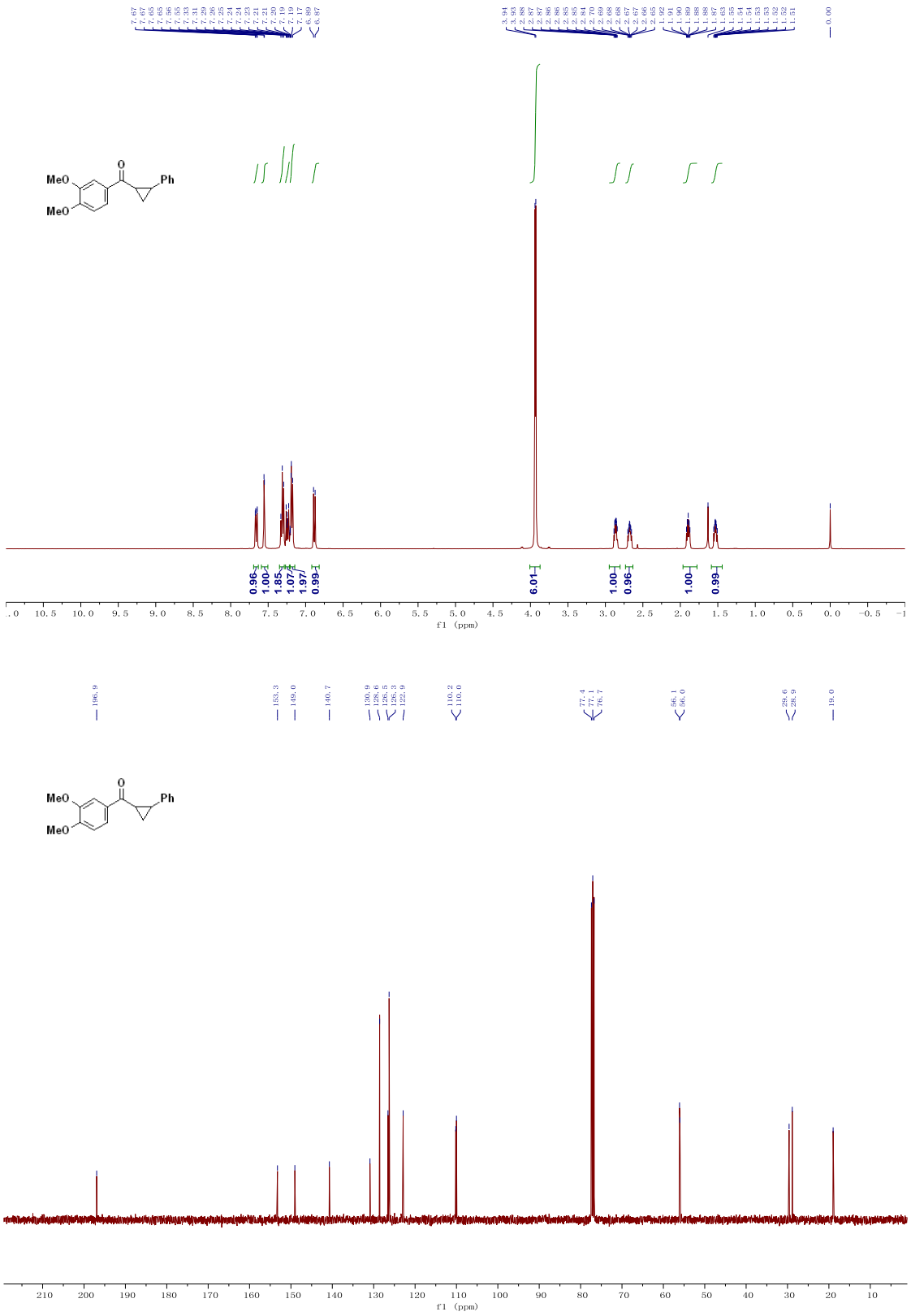


^{1}H and ^{13}C NMR of compound **6f**

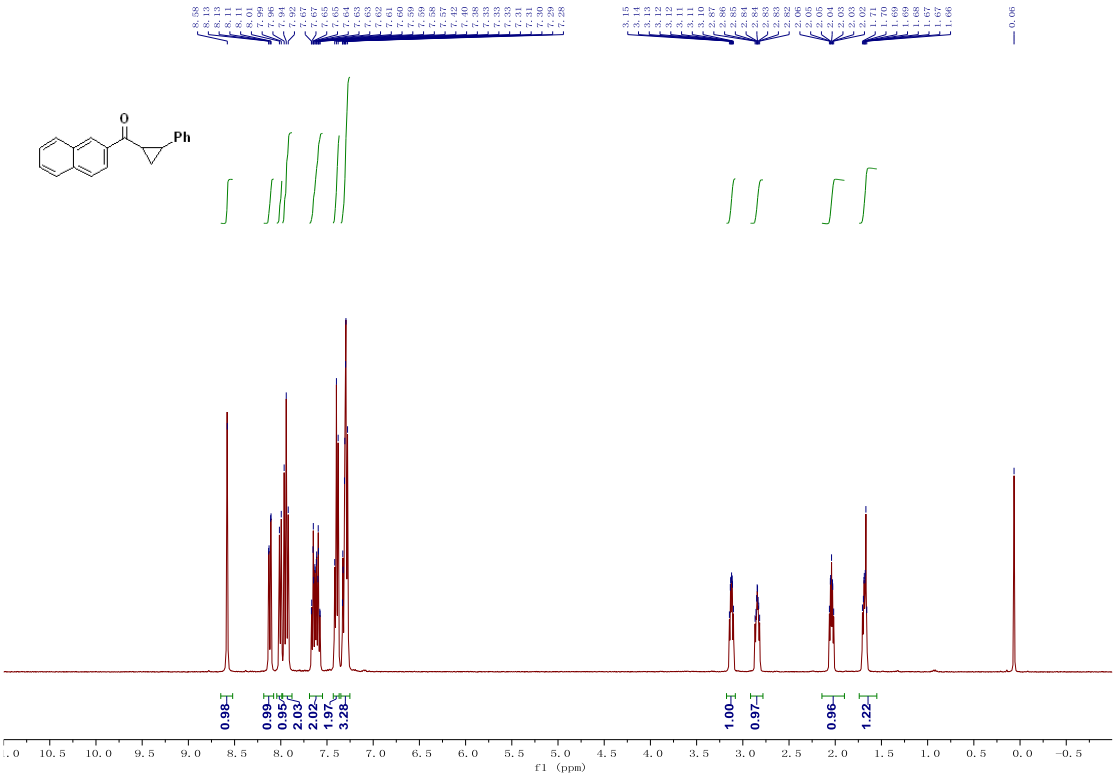


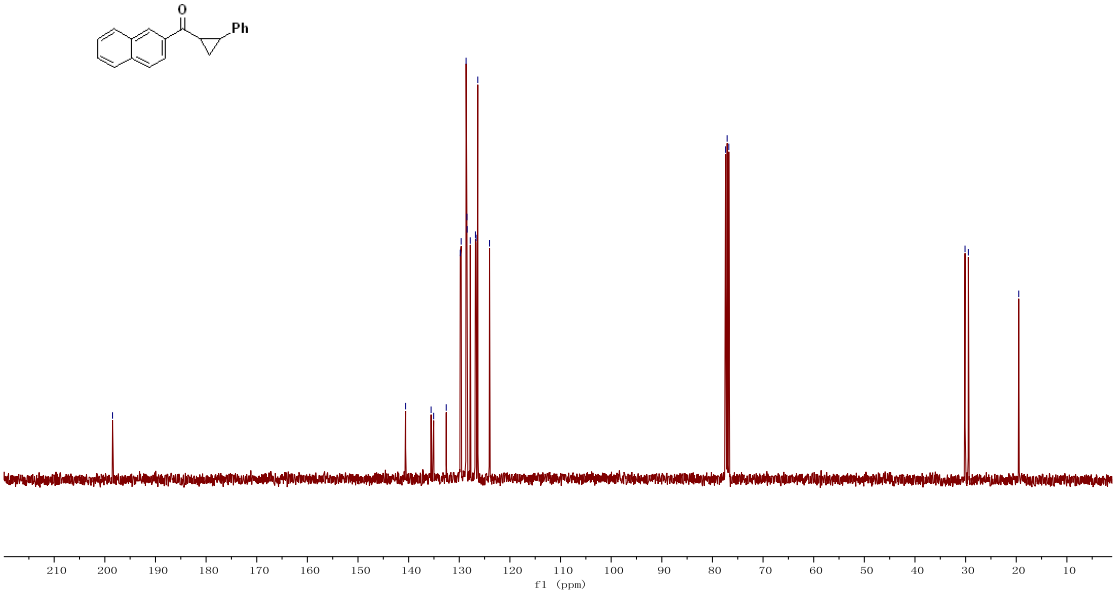


^{1}H and ^{13}C NMR of compound **6g**

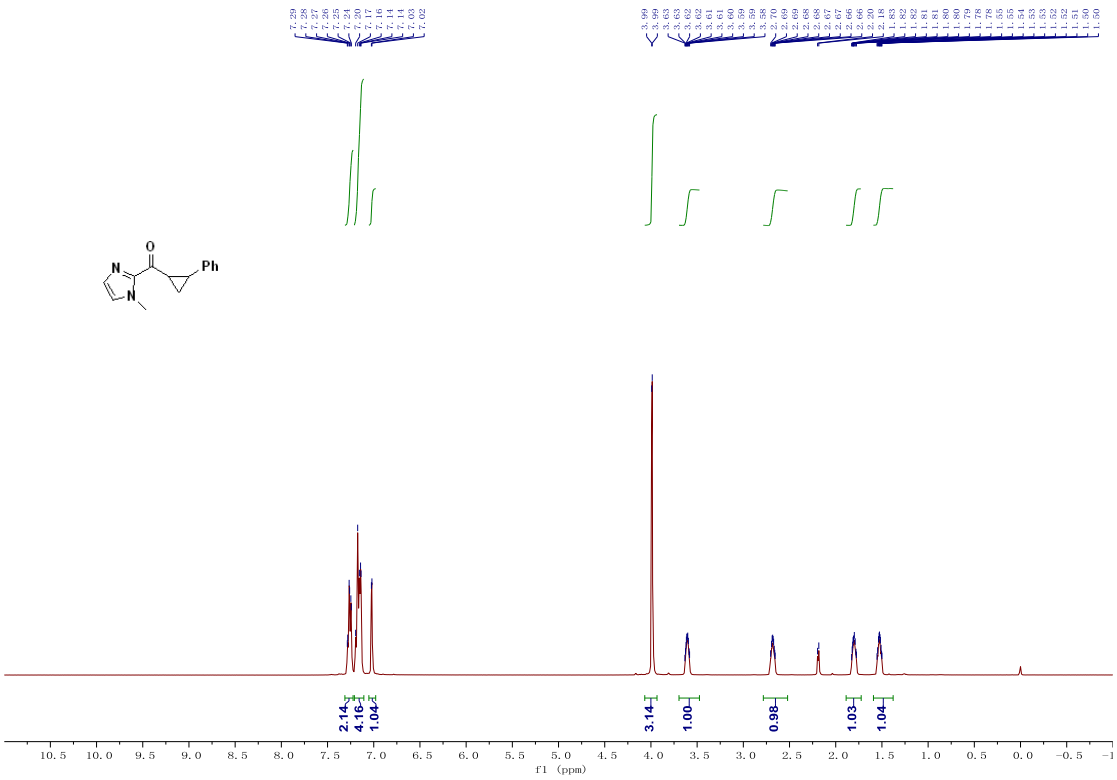


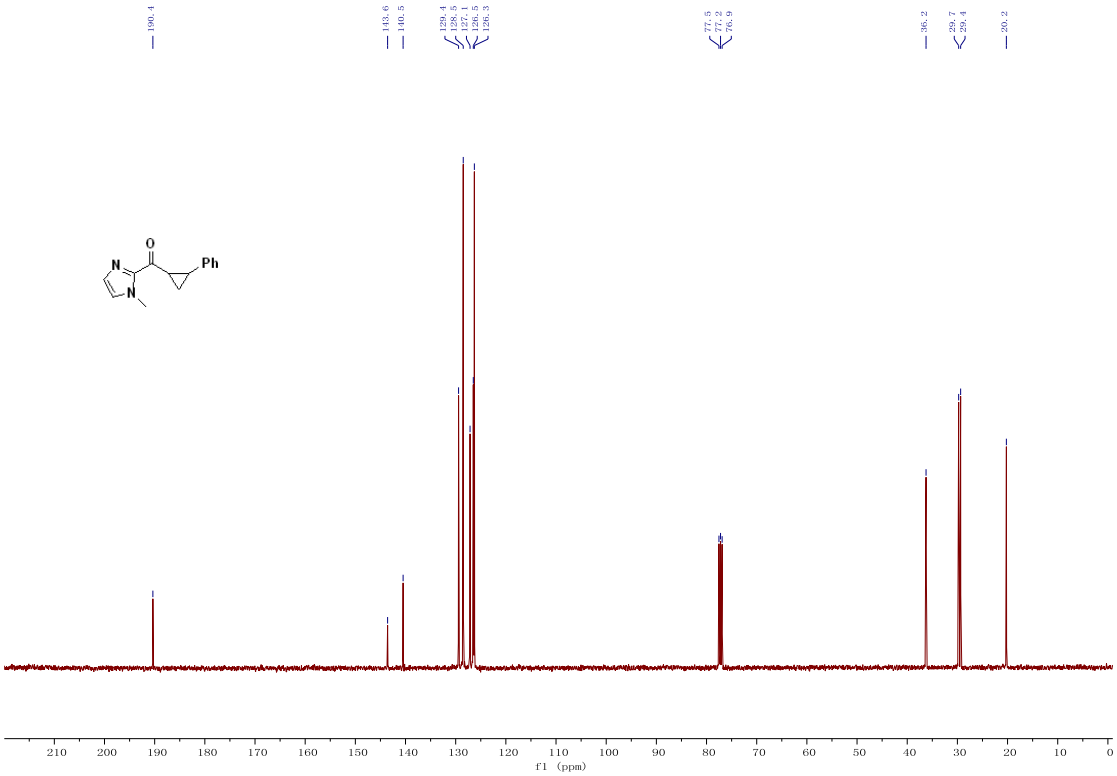
^{1}H and ^{13}C NMR of compound **6h**



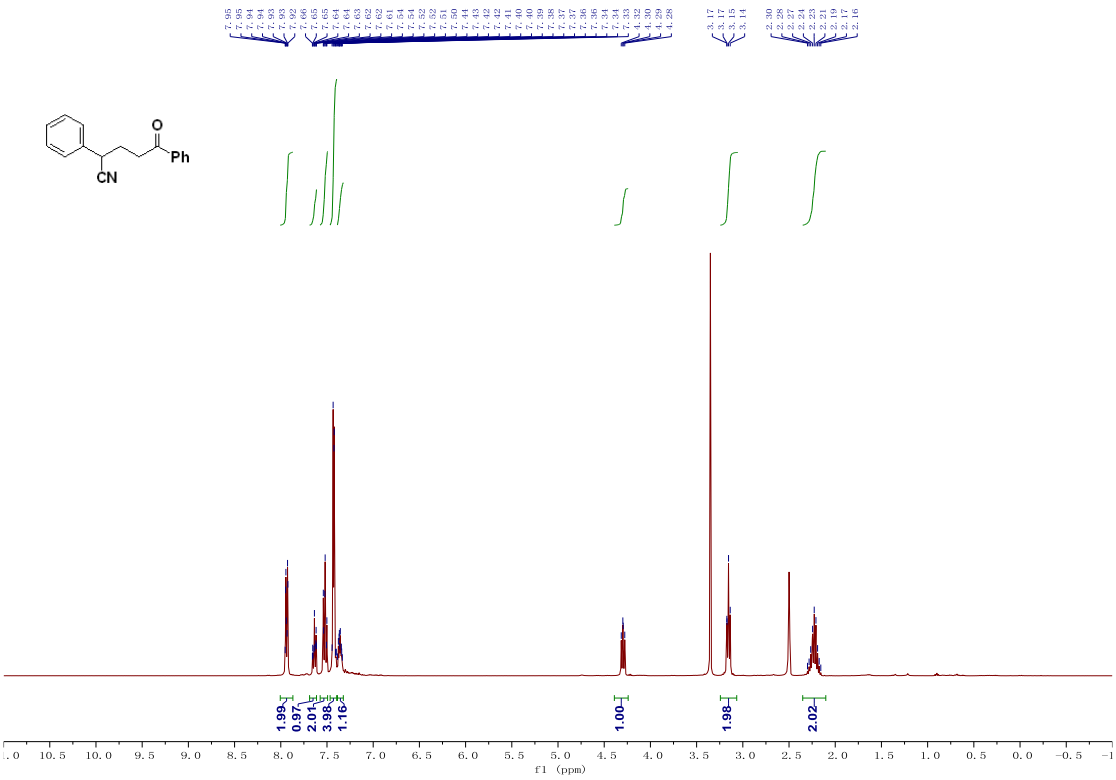


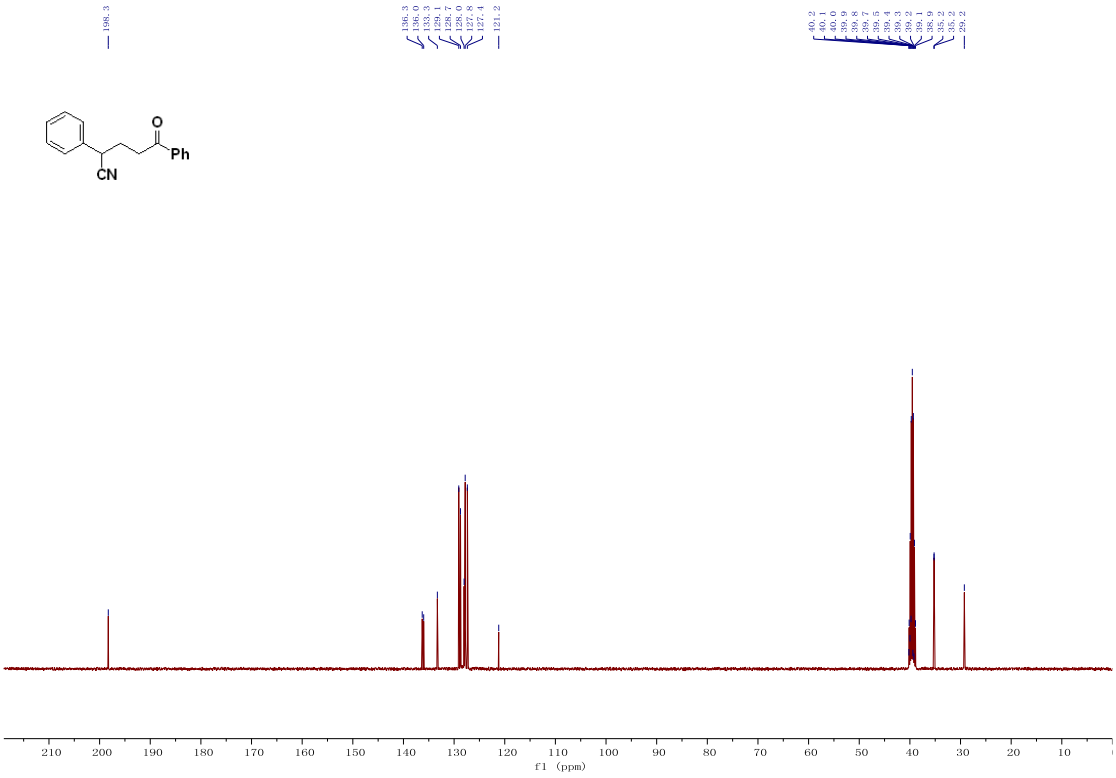
^{1}H and ^{13}C NMR of compound **6i**



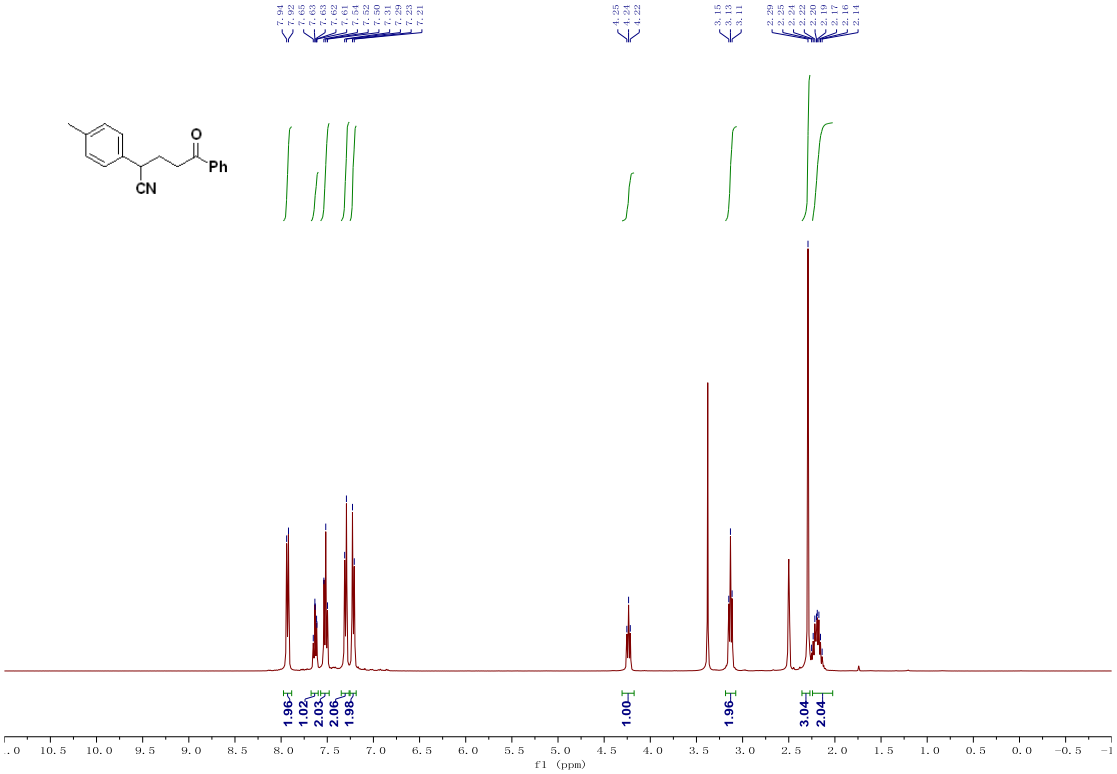


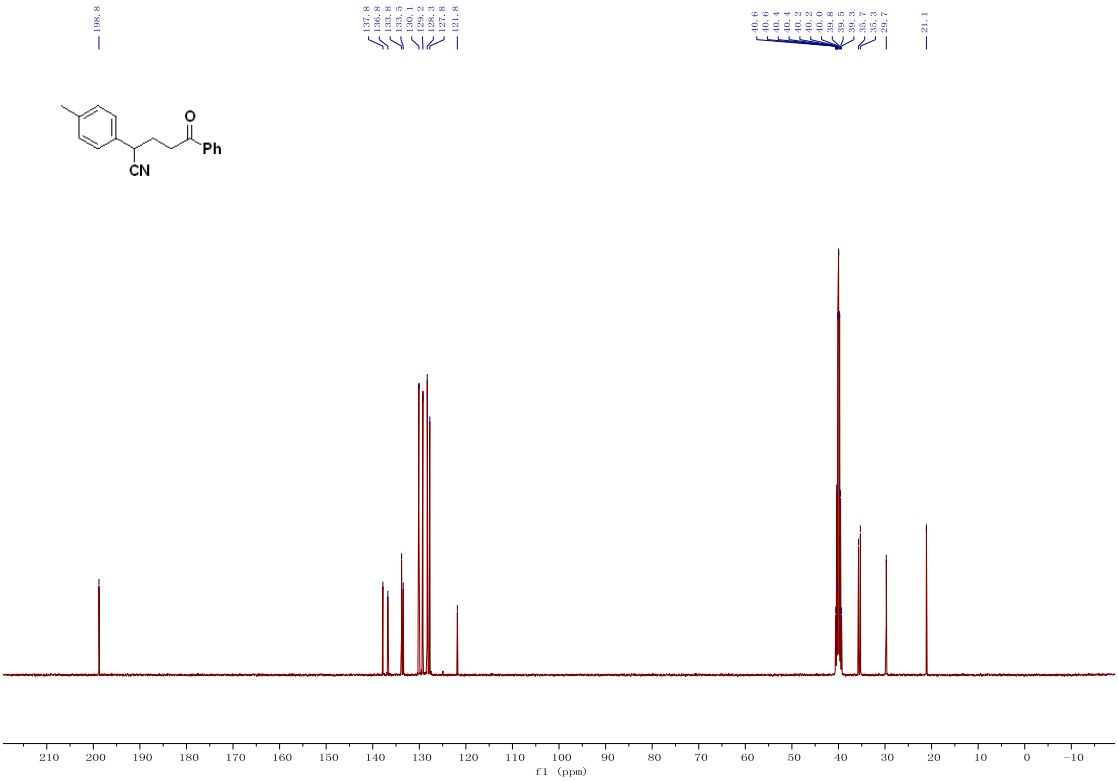
^{1}H and ^{13}C NMR of compound **3a**



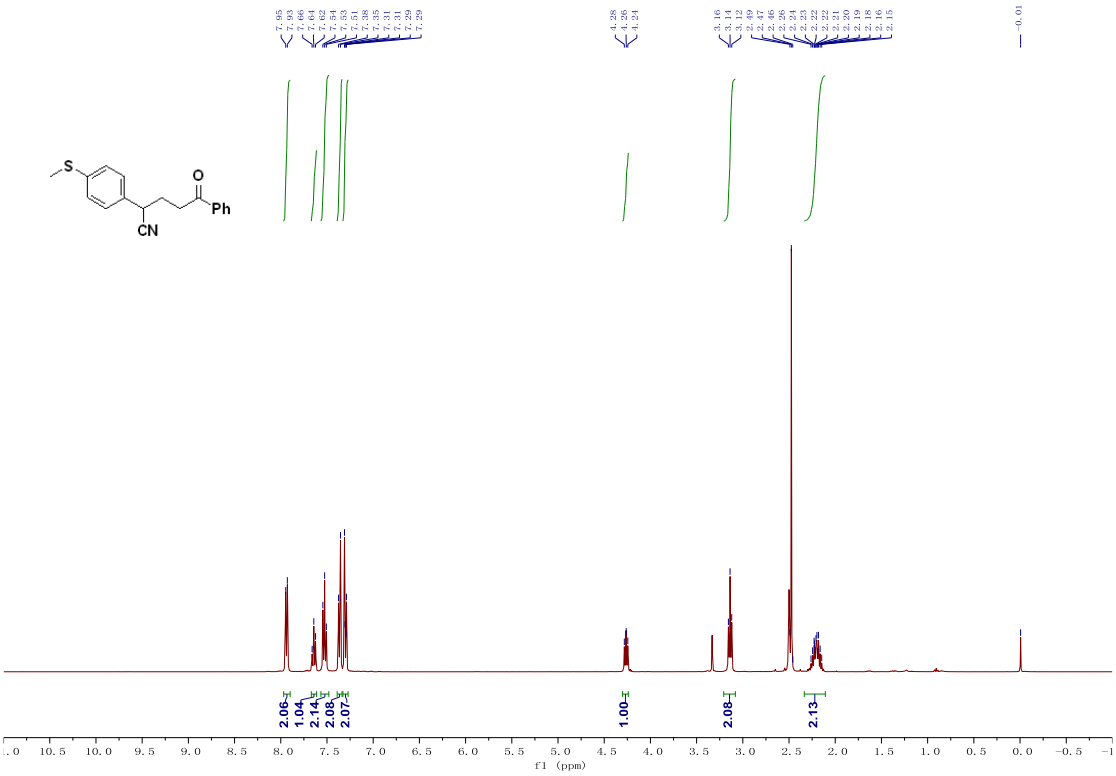


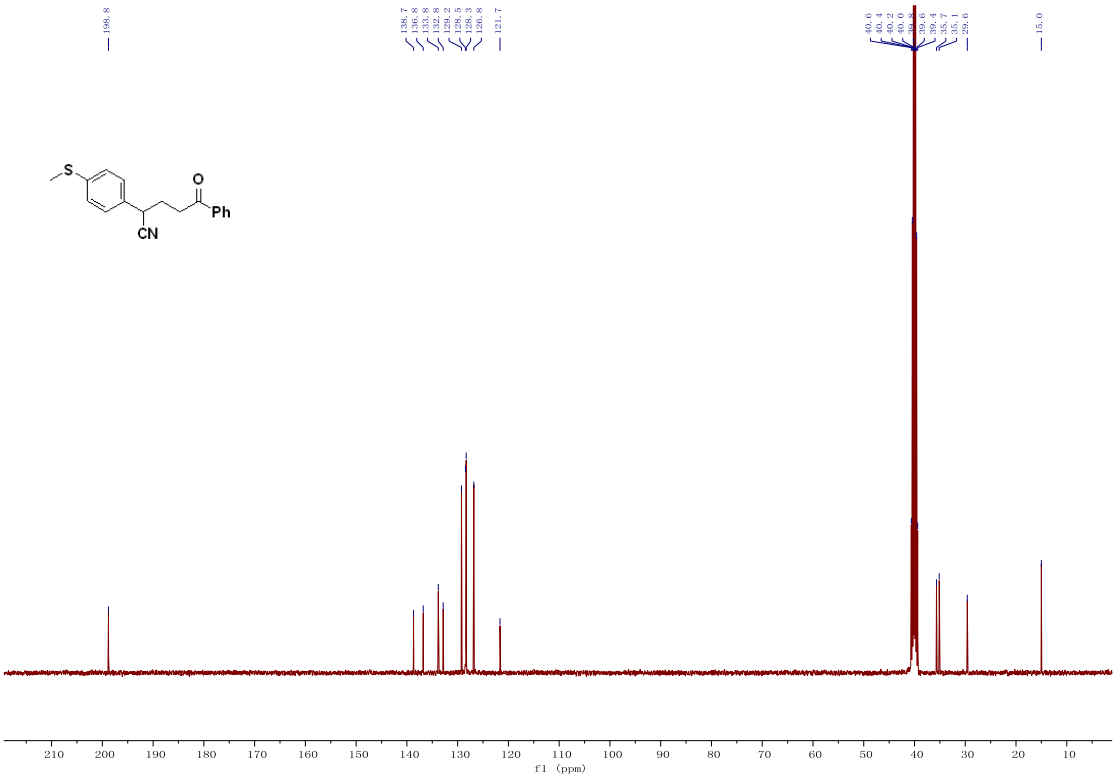
^{1}H and ^{13}C NMR of compound **3b**



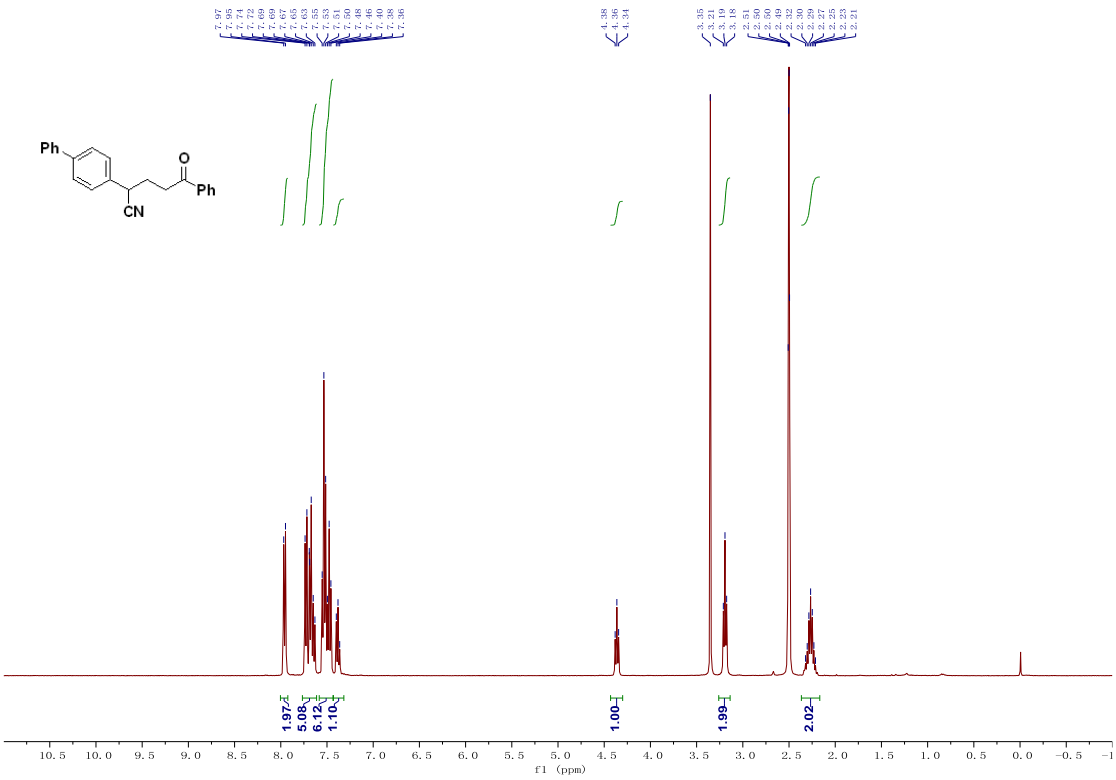


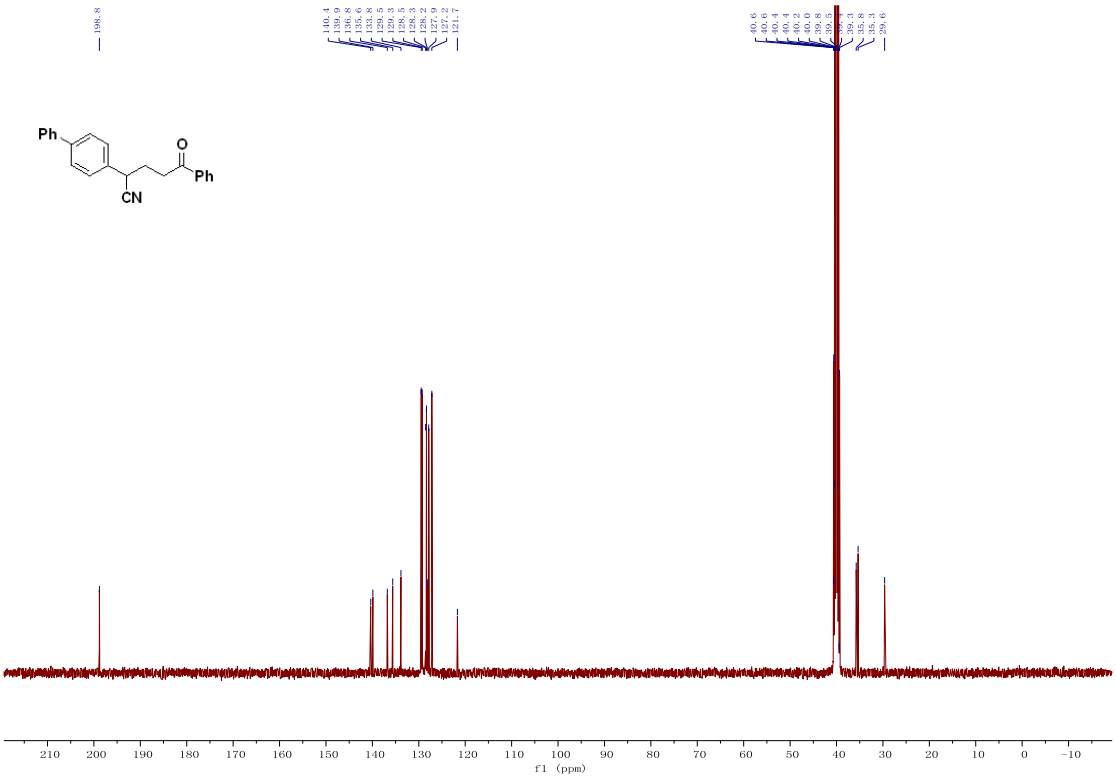
^{1}H and ^{13}C NMR of compound **3c**



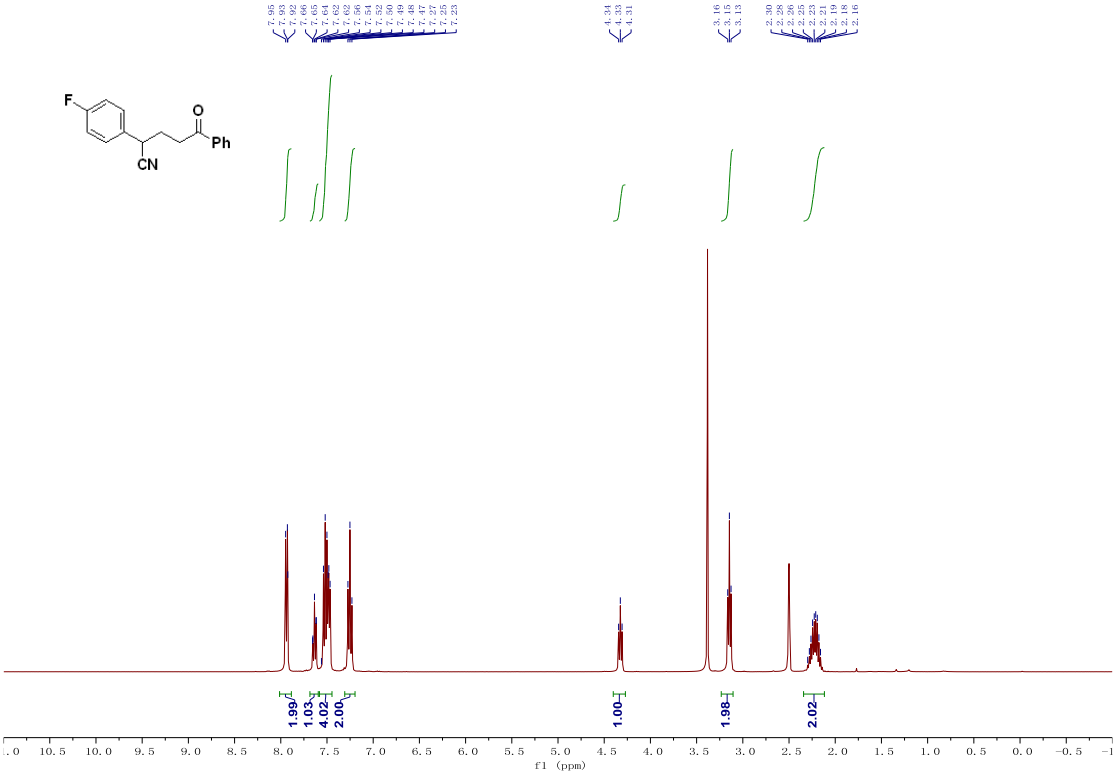


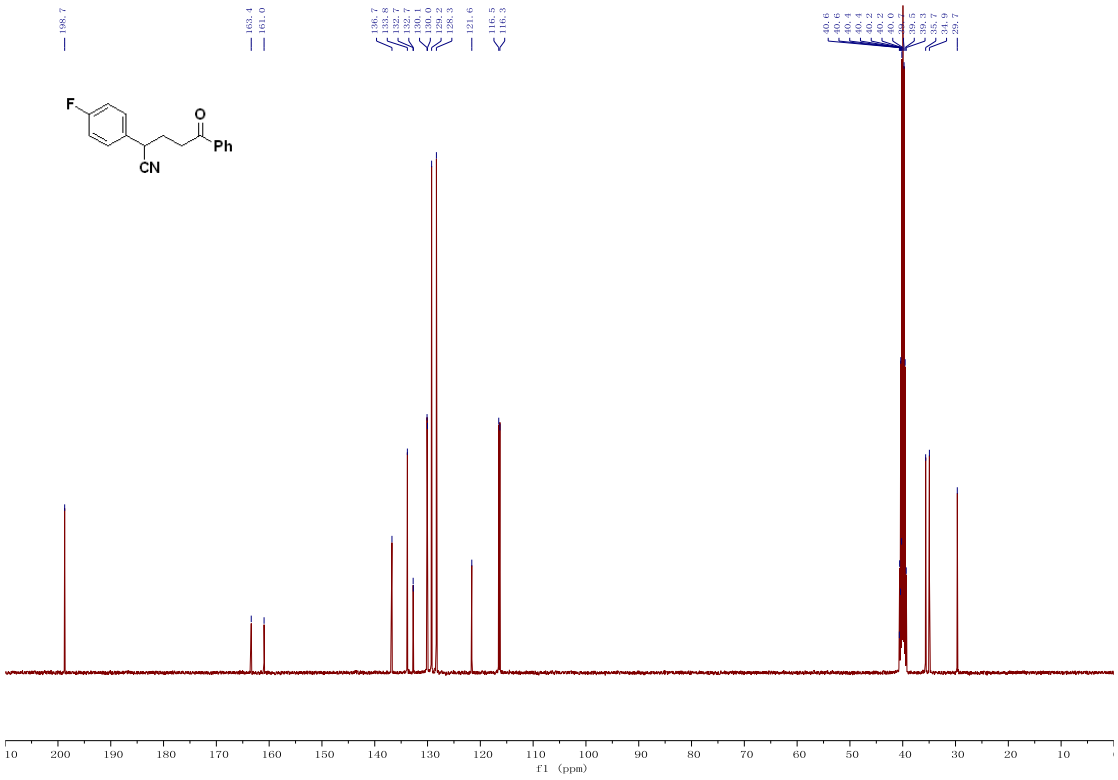
^{1}H and ^{13}C NMR of compound **3d**

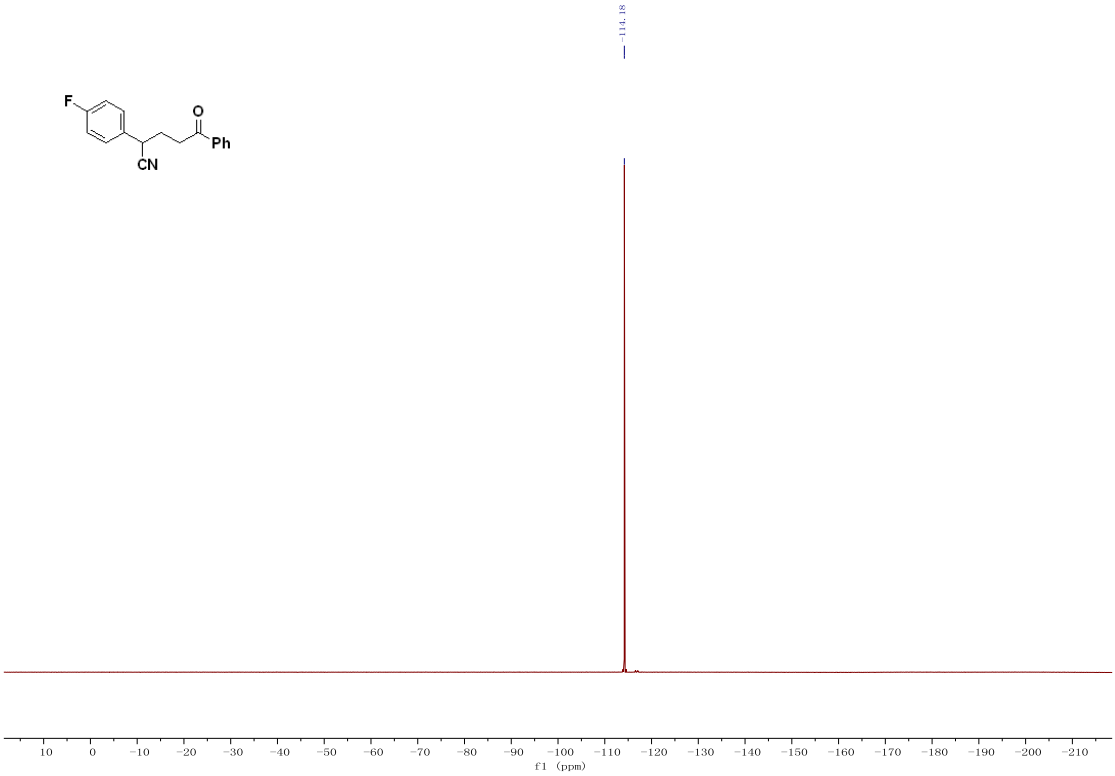




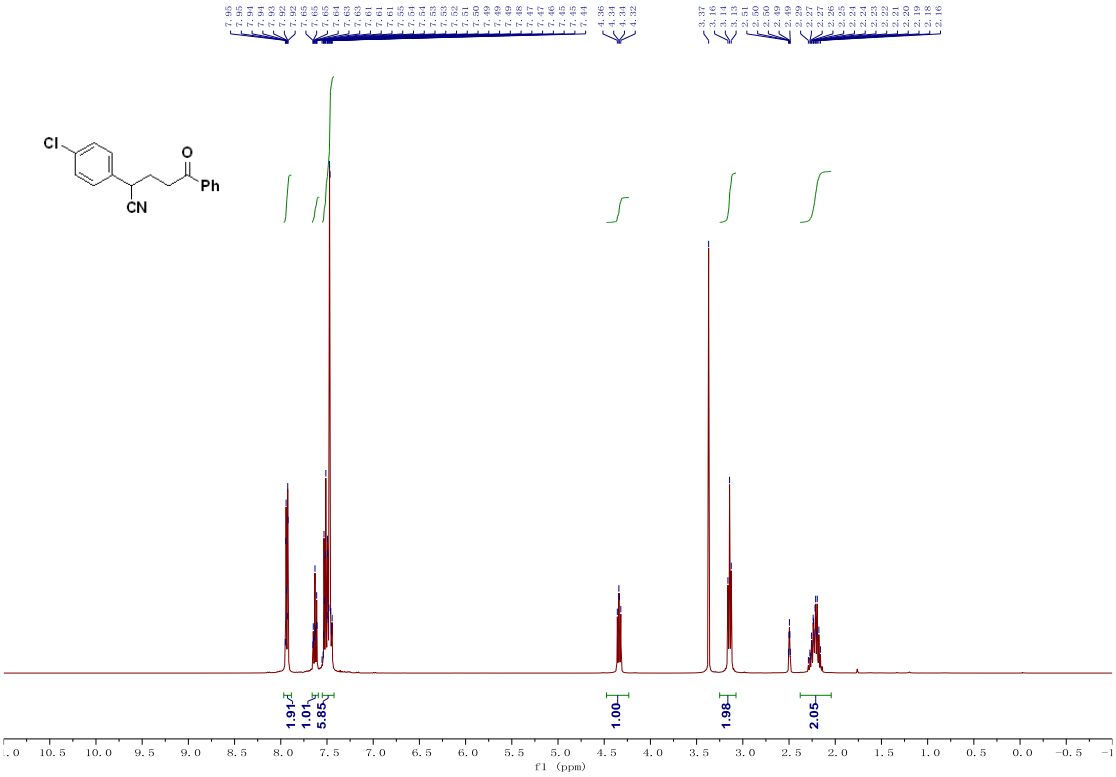
^{1}H, ^{13}C and ^{19}F NMR of compound **3e**

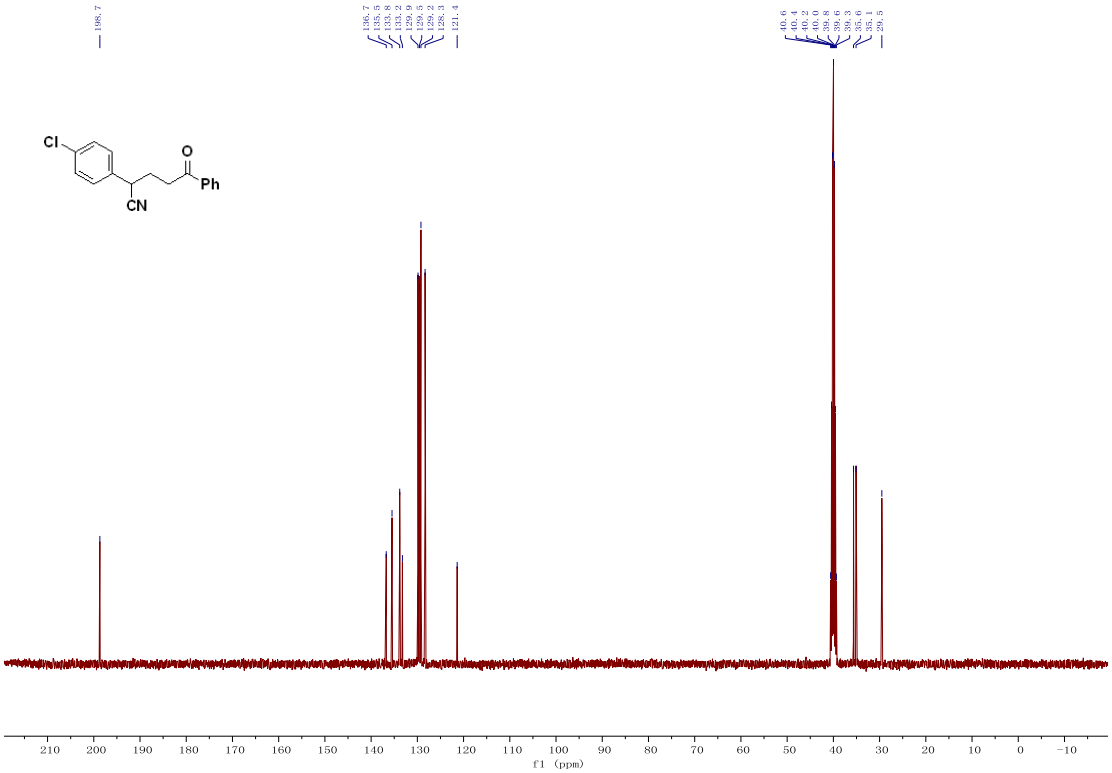




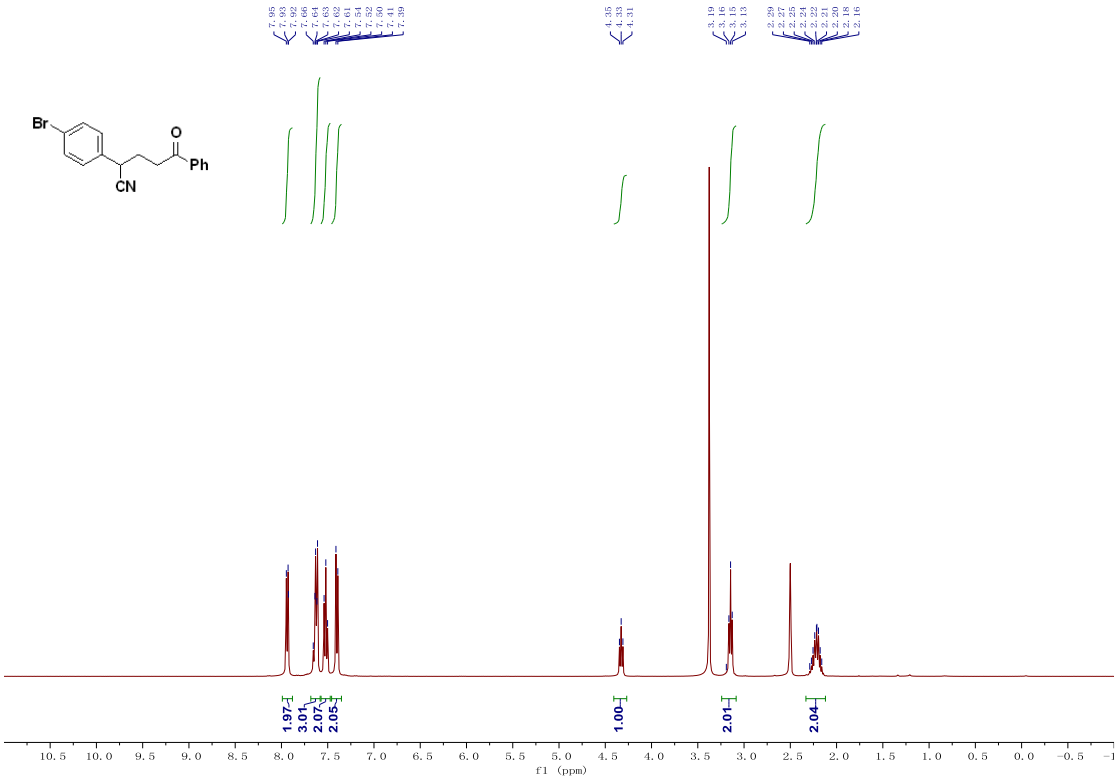


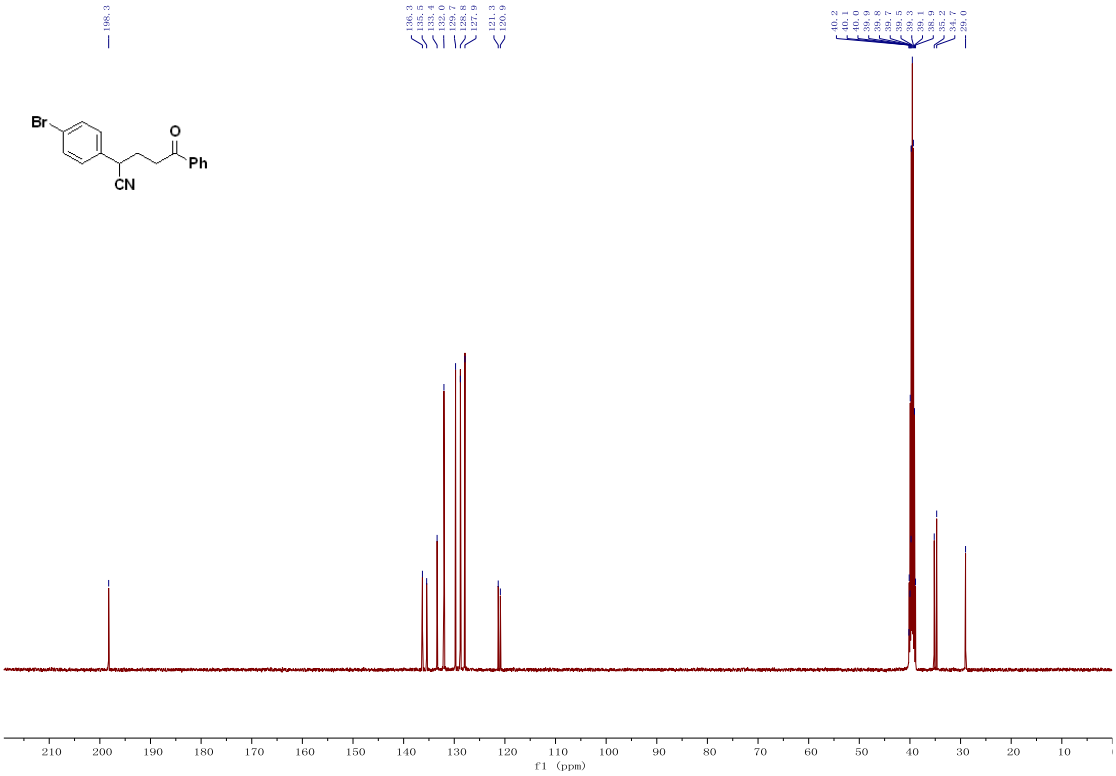
^{1}H and ^{13}C NMR of compound **3f**



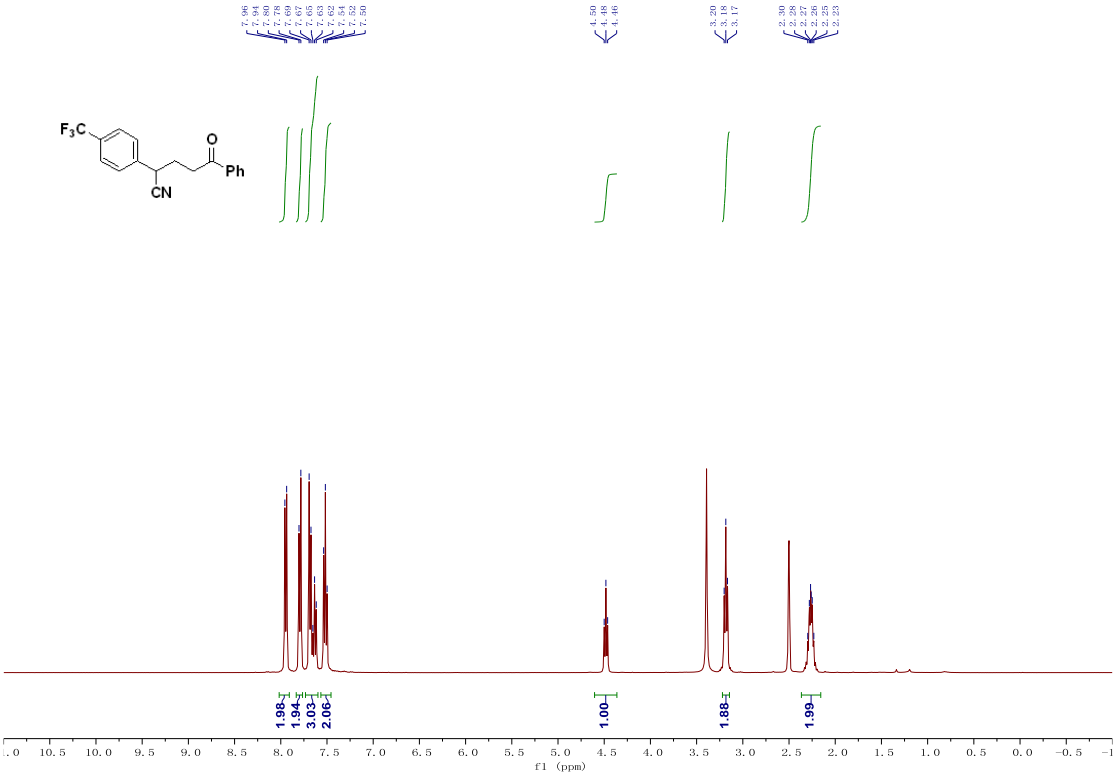


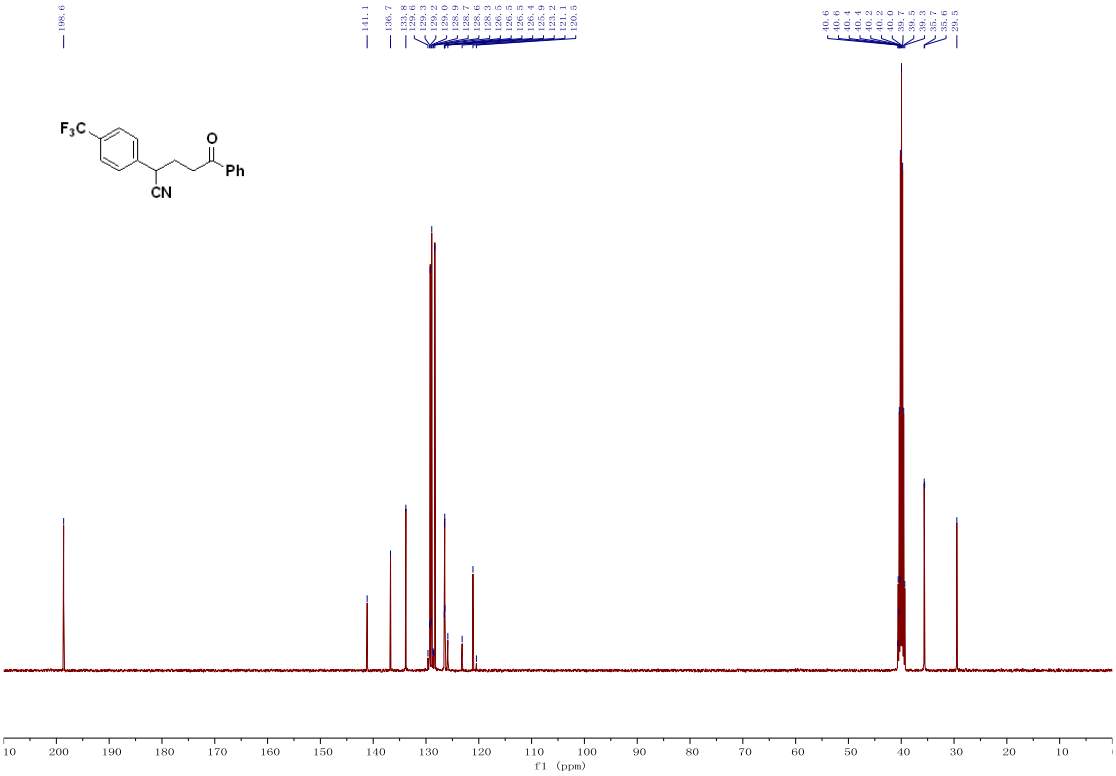
^{1}H and ^{13}C NMR of compound **3g**





^{1}H, ^{13}C and ^{19}F NMR of compound **3h**

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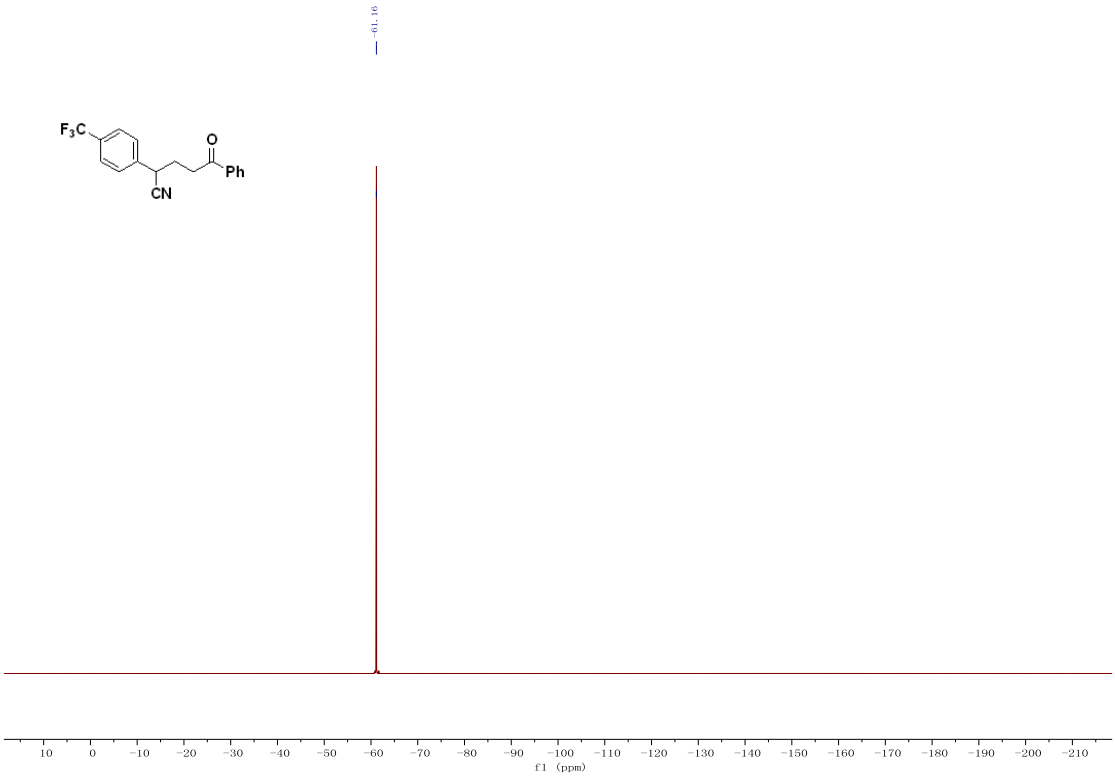
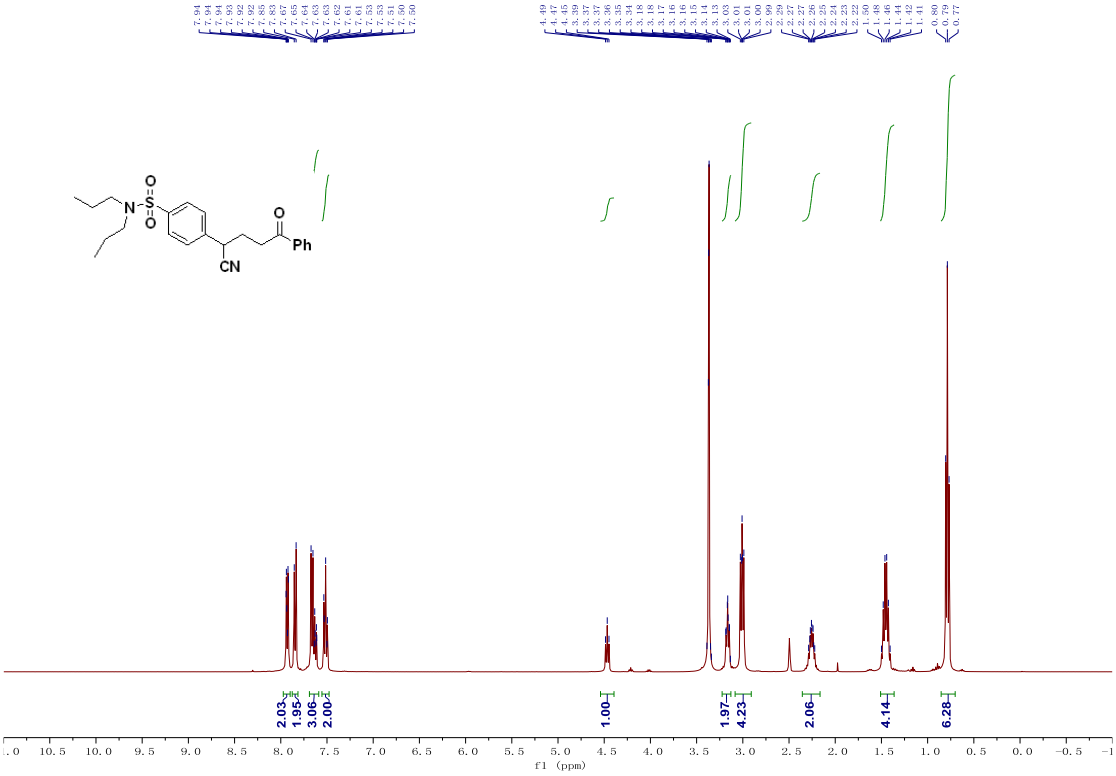
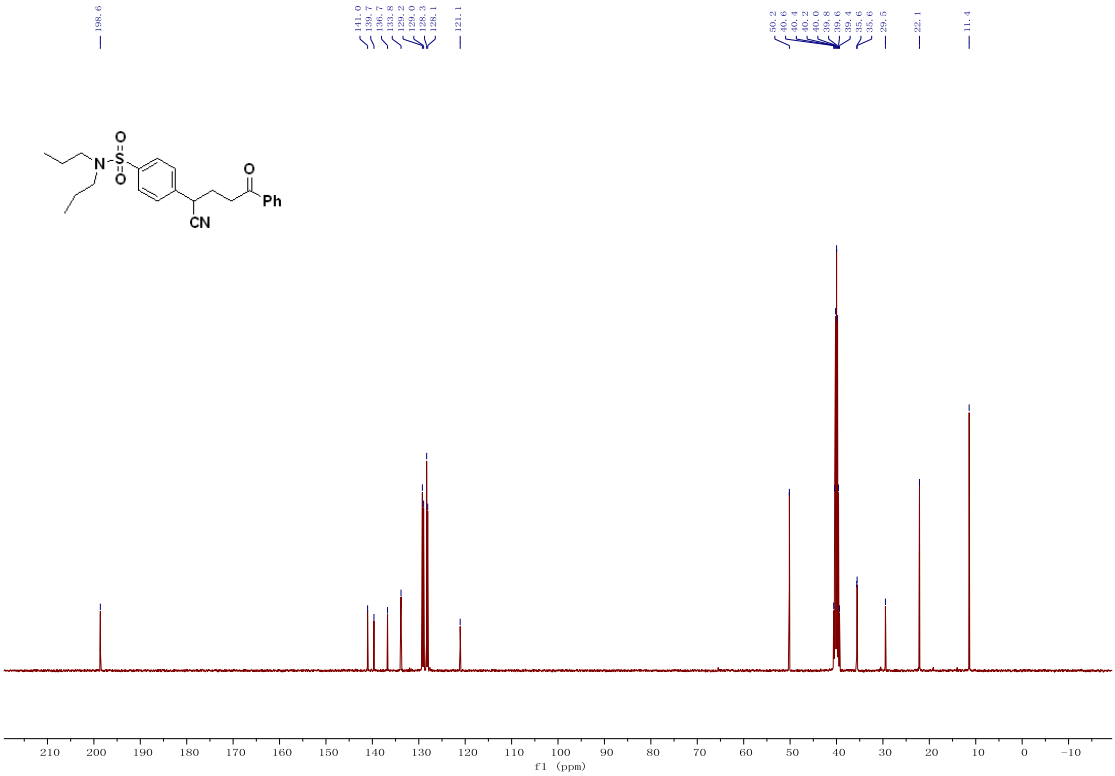
125.9
123.2
121.1
120.8
40.6
40.6
40.4
40.4
40.2
40.2
40.0
39.7
39.5
39.3
35.7
35.6
29.5
F3C
O
Ph
CN
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

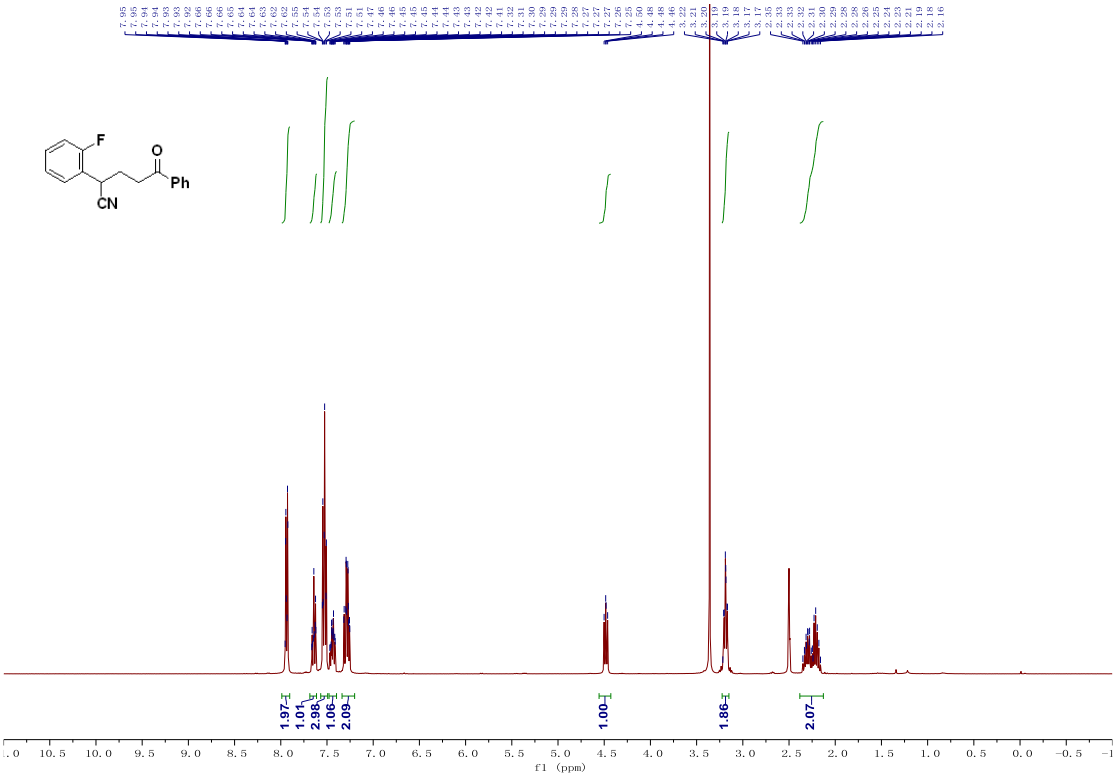

-61.16
F3C
O
Ph
CN
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

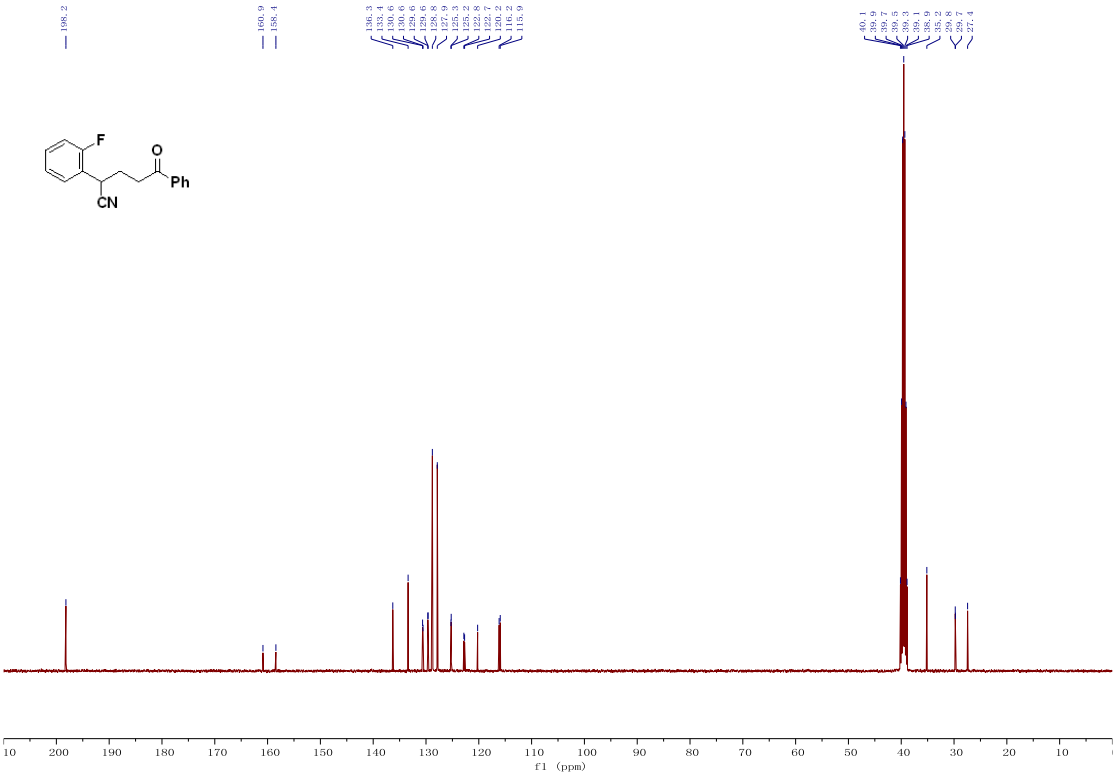
^{1}H and ^{13}C NMR of compound **3i**

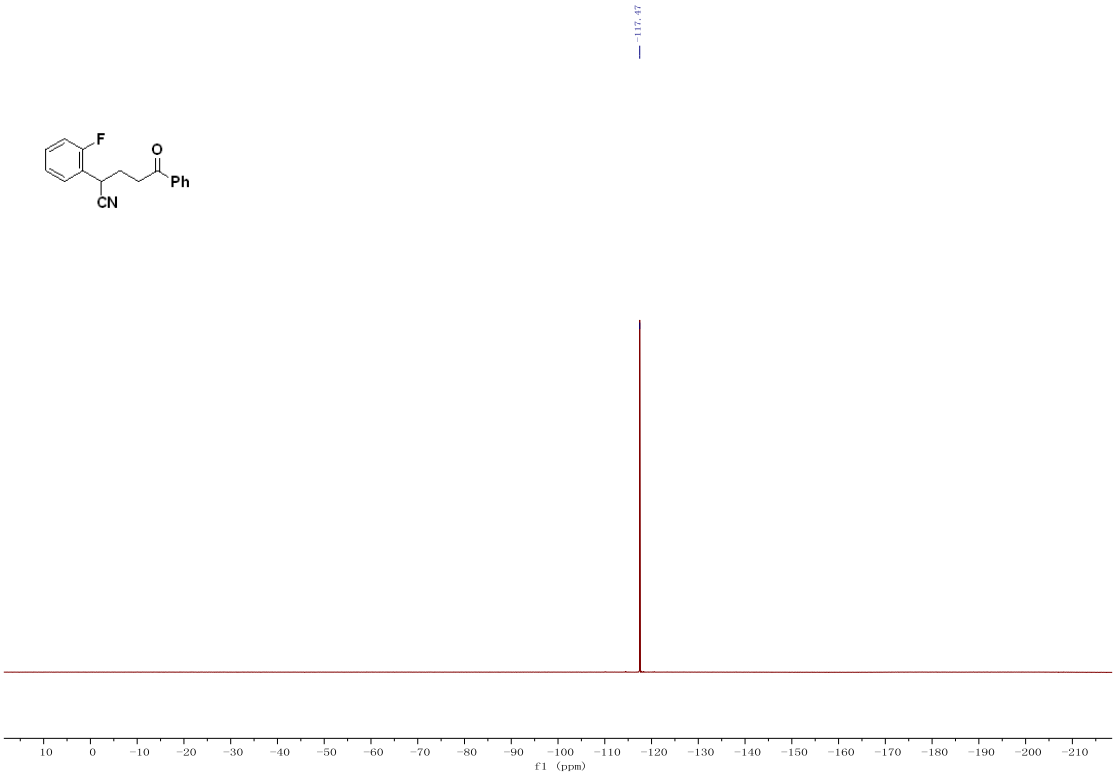




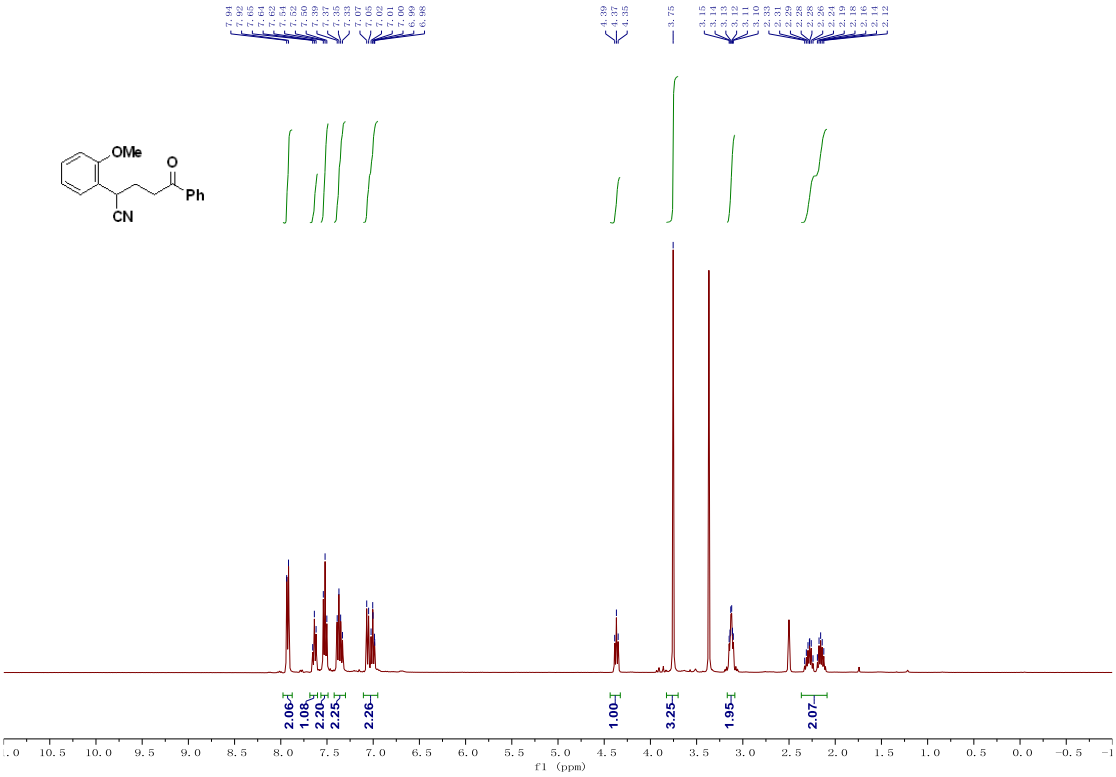
^{1}H, ^{13}C and ^{19}F NMR of compound **3j**

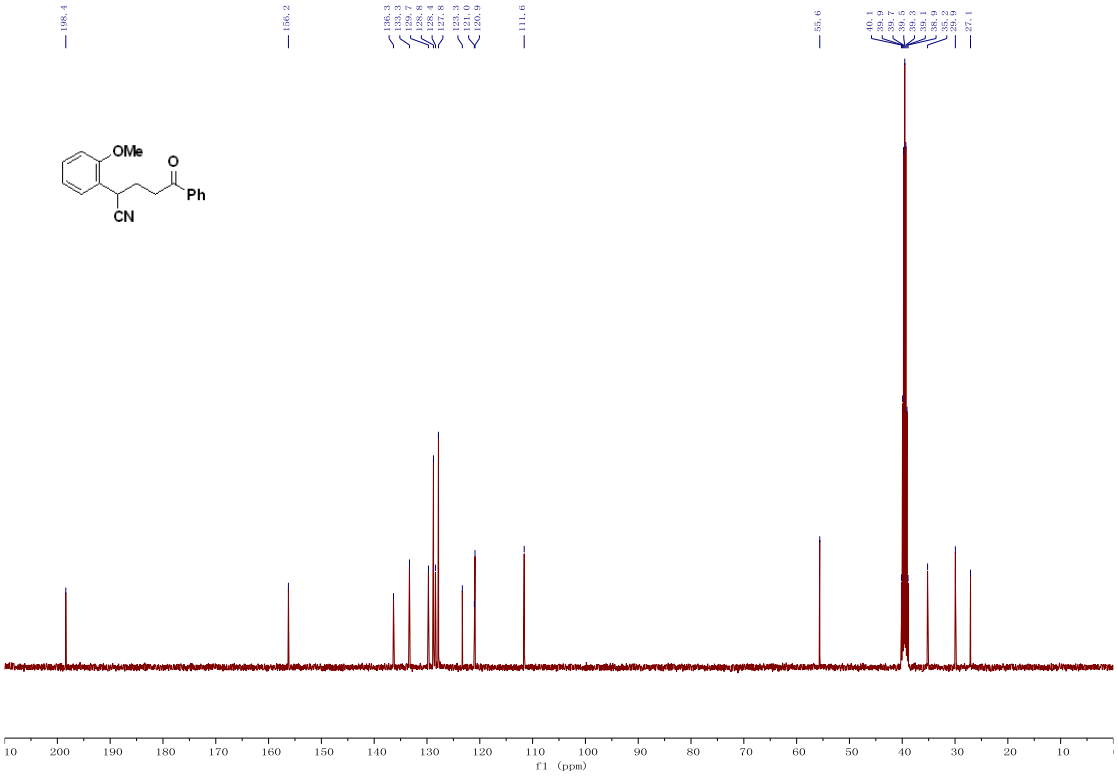




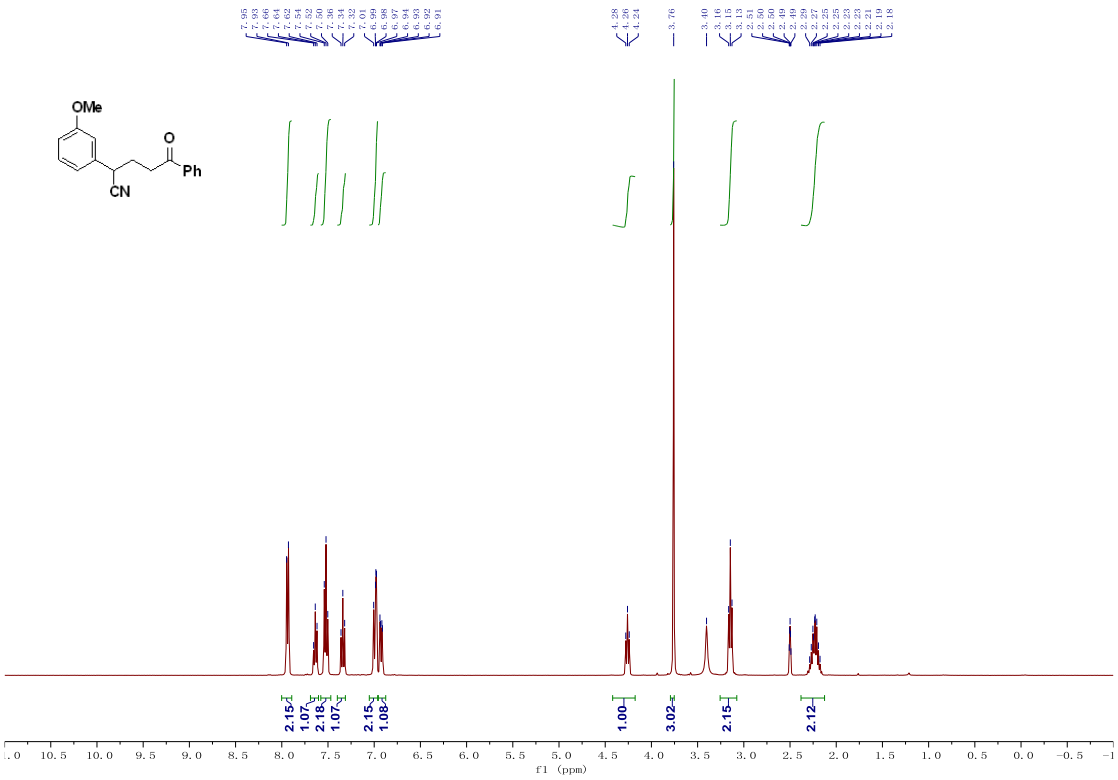


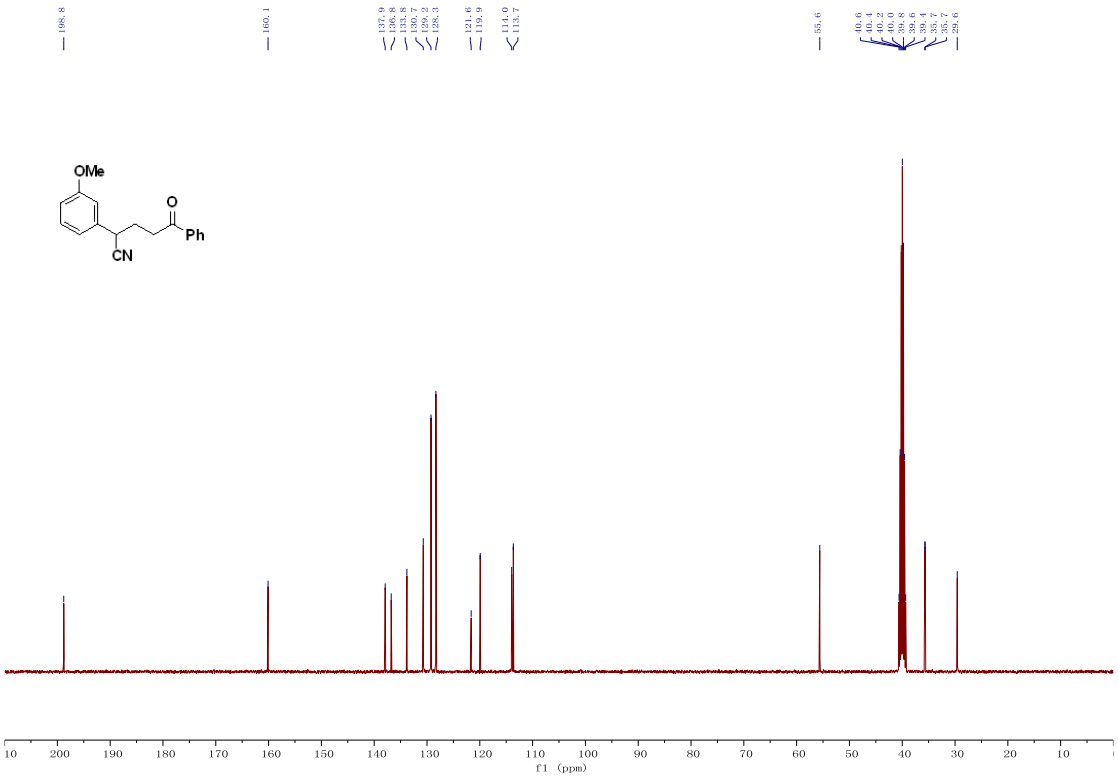
^{1}H and ^{13}C NMR of compound **3k**



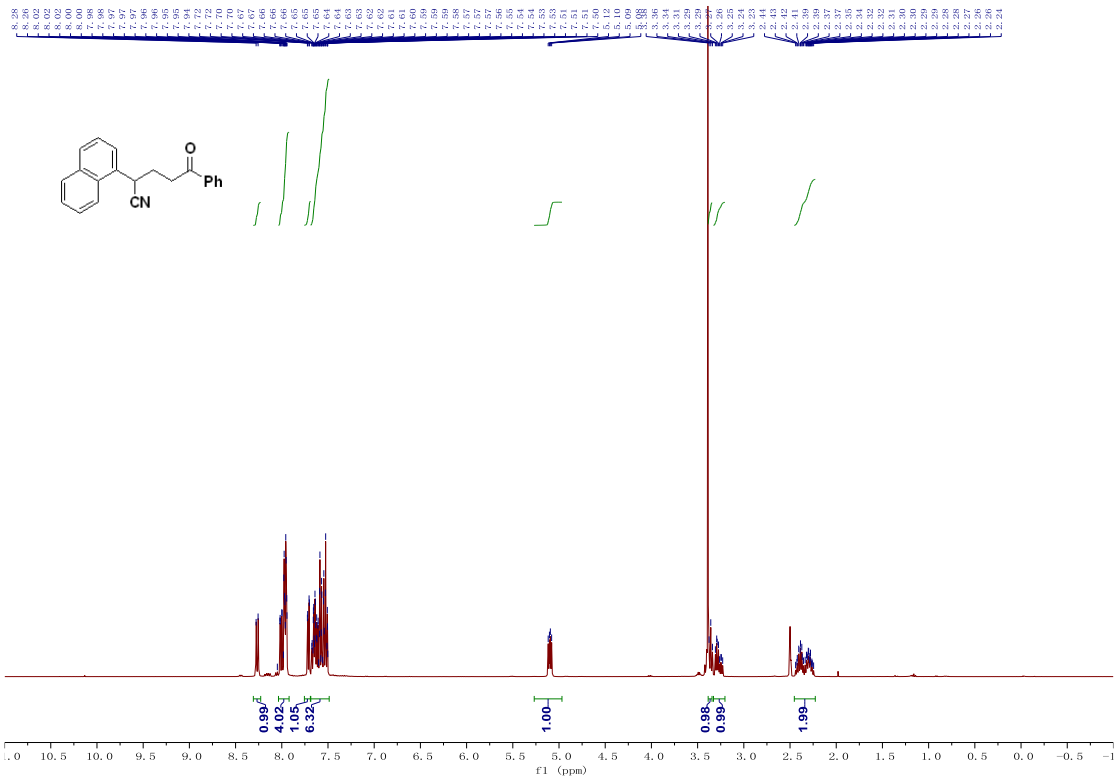


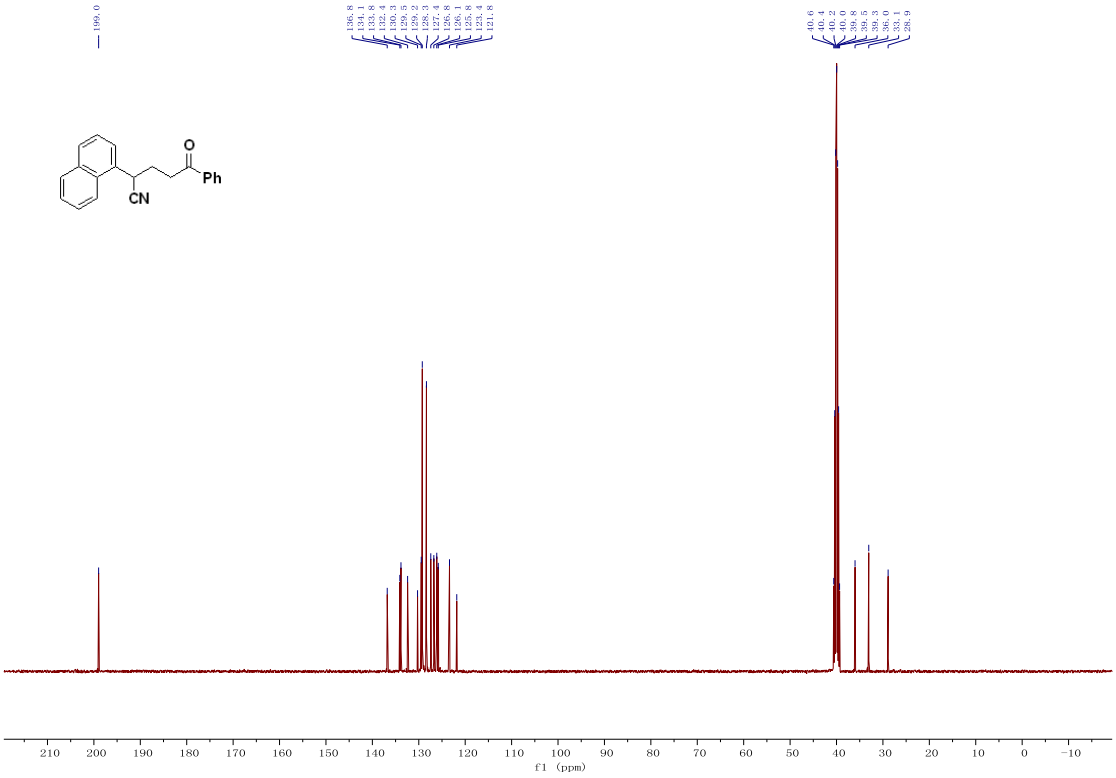
^{1}H and ^{13}C NMR of compound **3l**



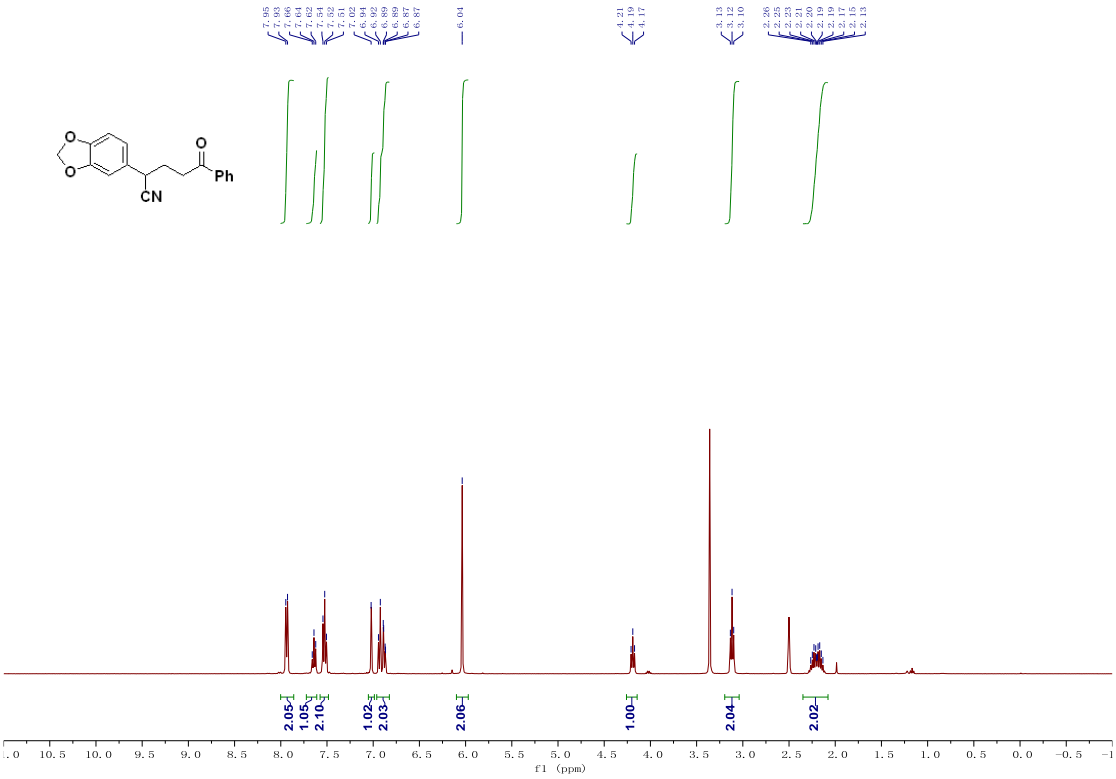


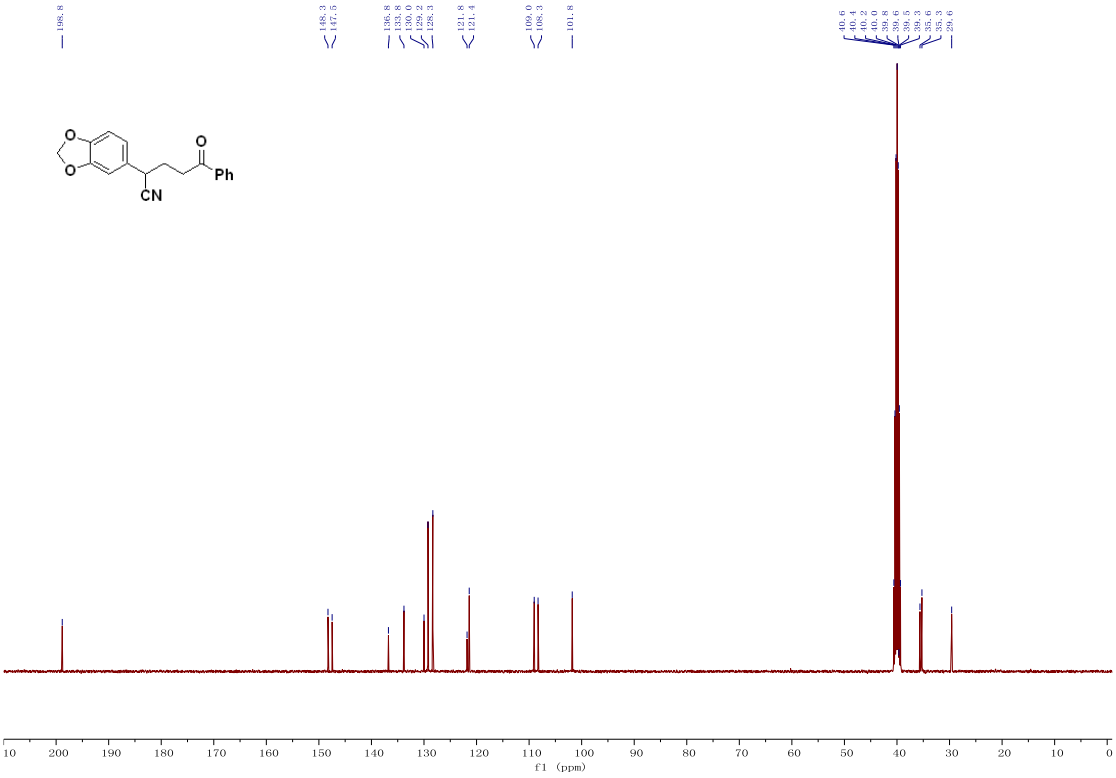
^{1}H and ^{13}C NMR of compound **3m**



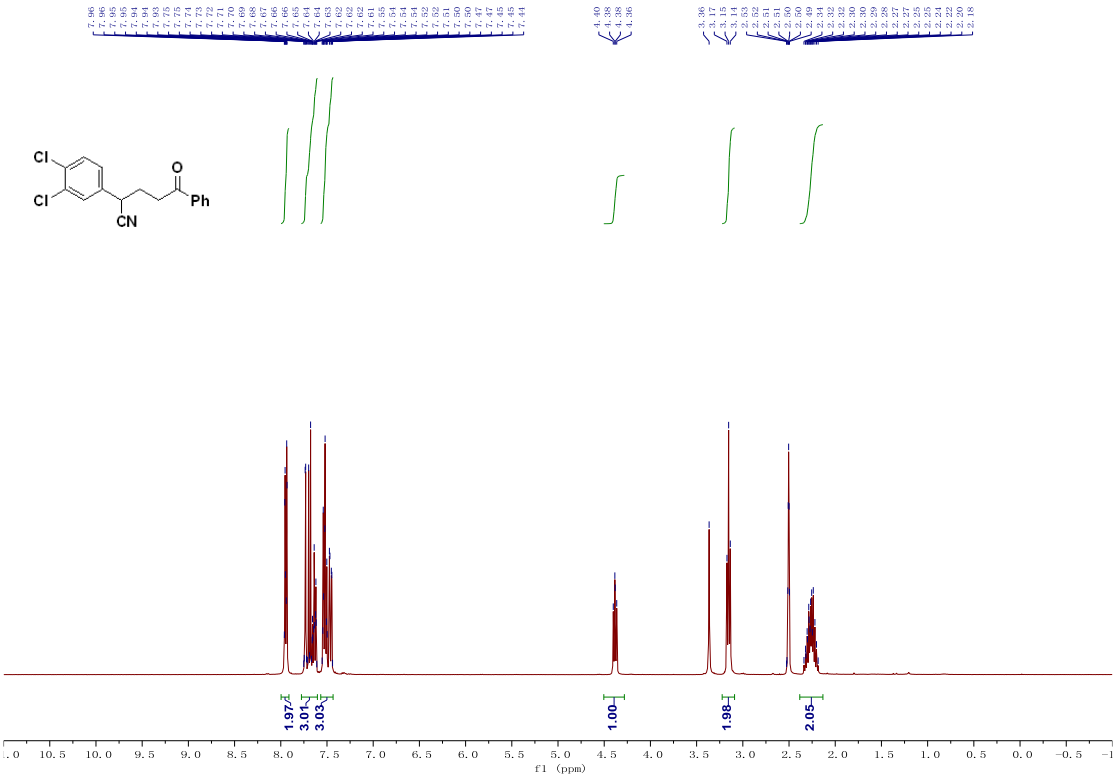


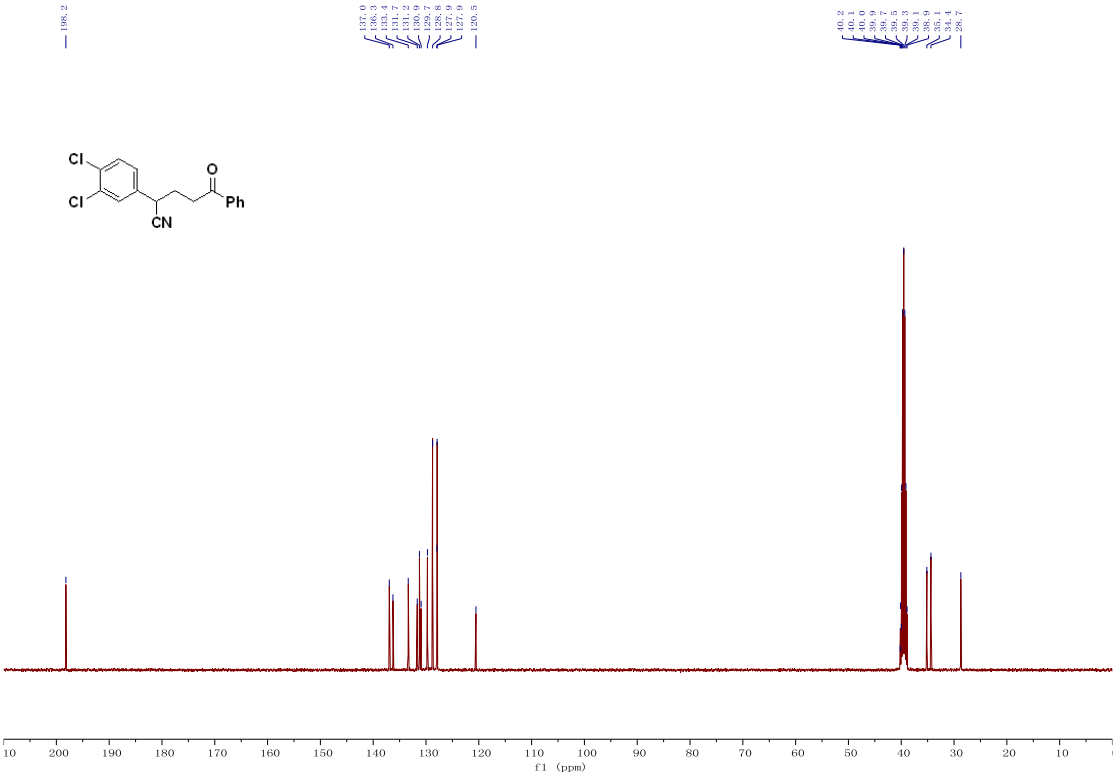
^{1}H and ^{13}C NMR of compound **3n**



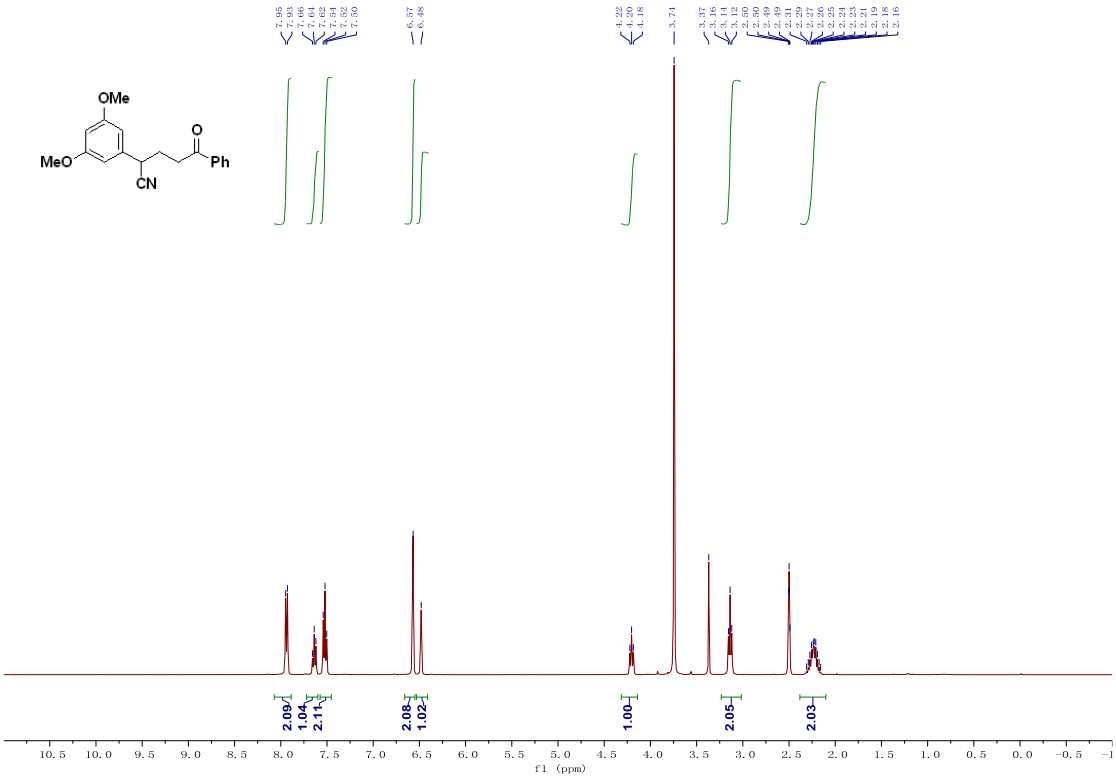


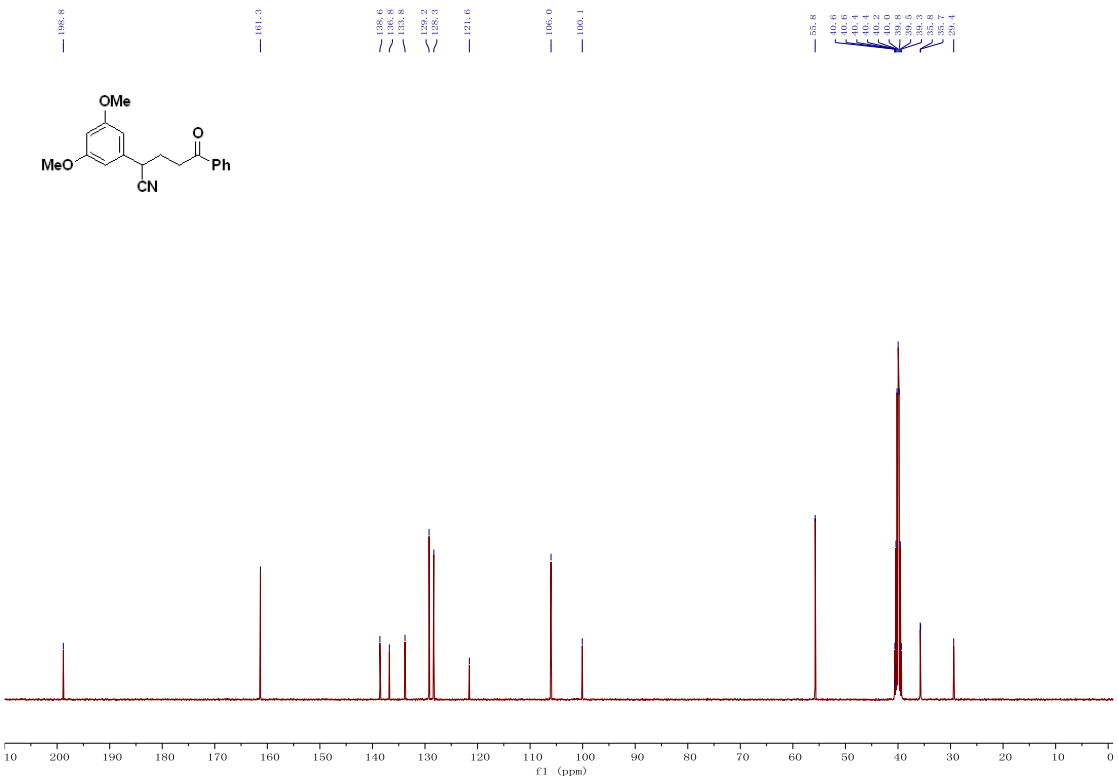
^{1}H and ^{13}C NMR of compound **3o**



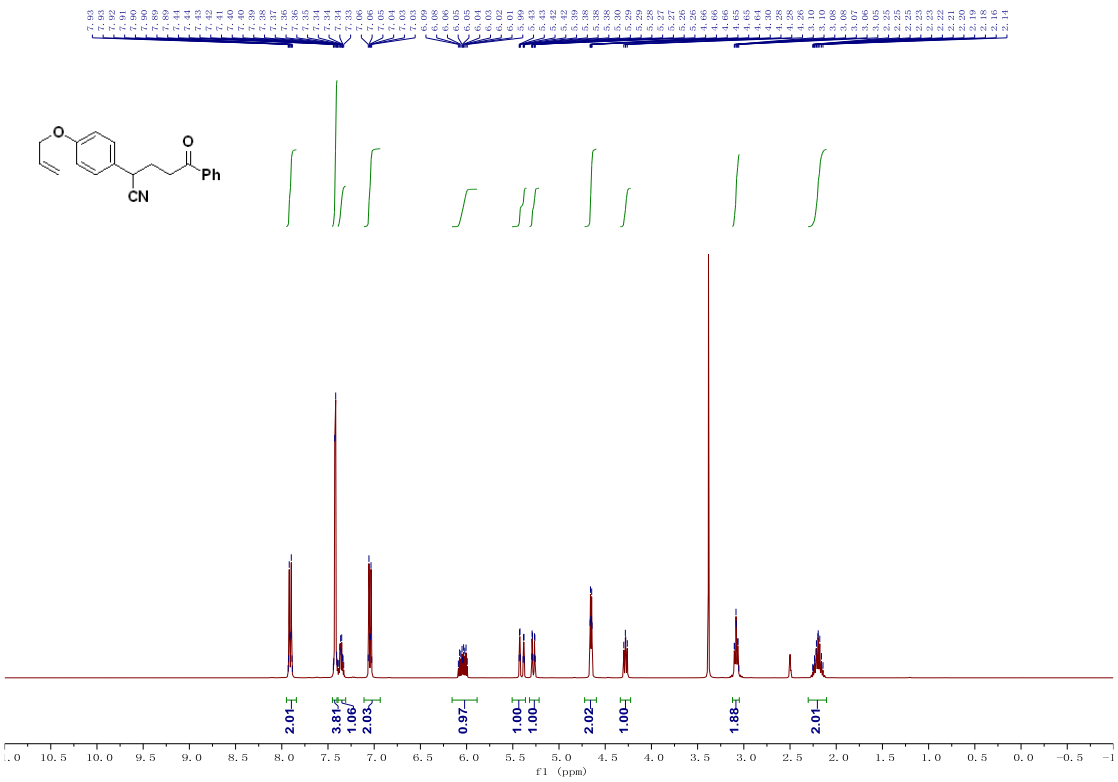


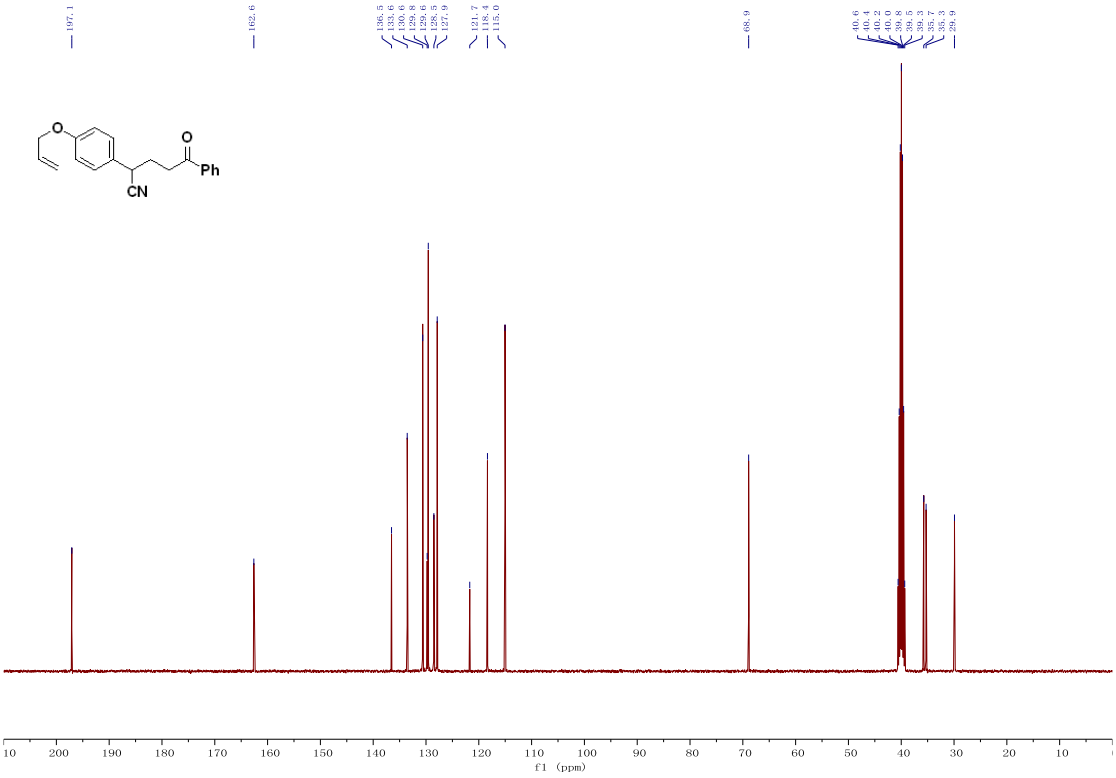
^{1}H and ^{13}C NMR of compound **3p**



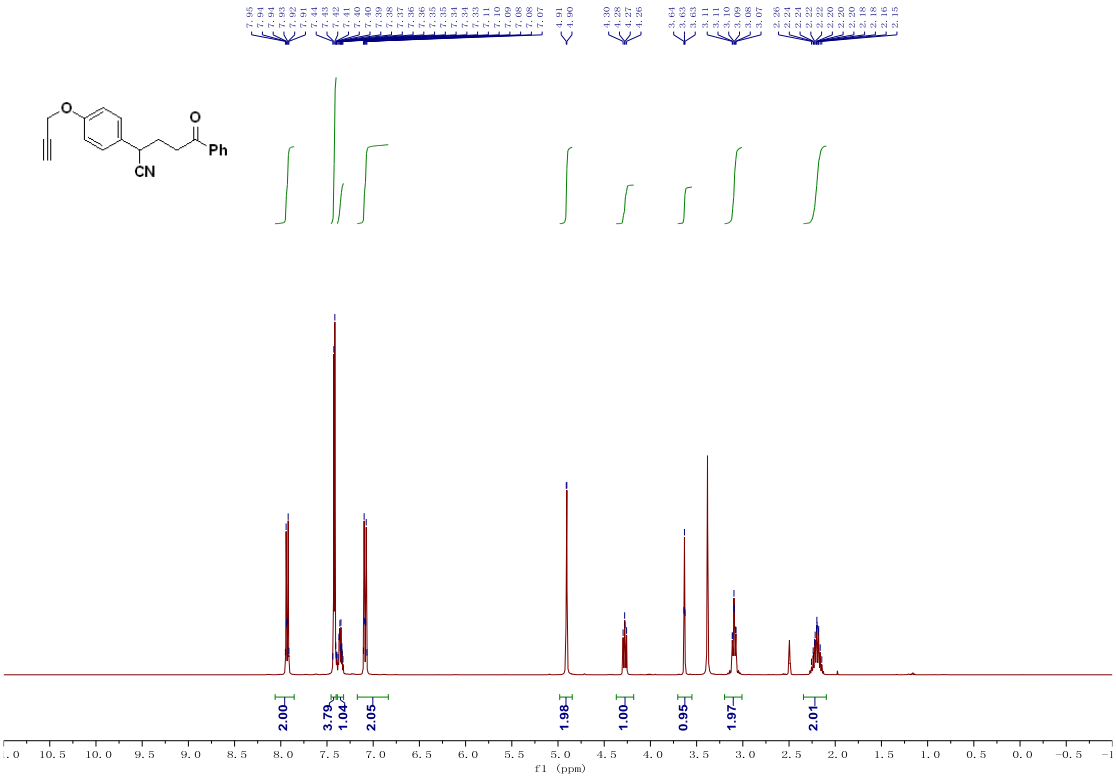


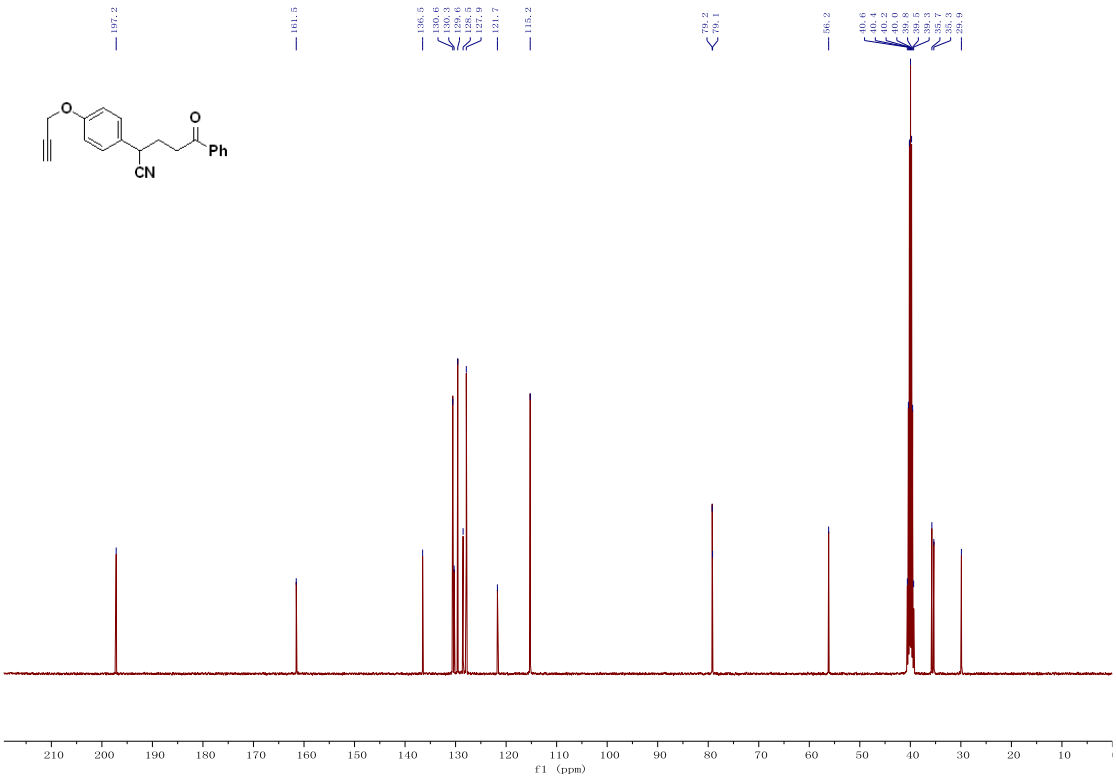
^{1}H and ^{13}C NMR of compound **3q**



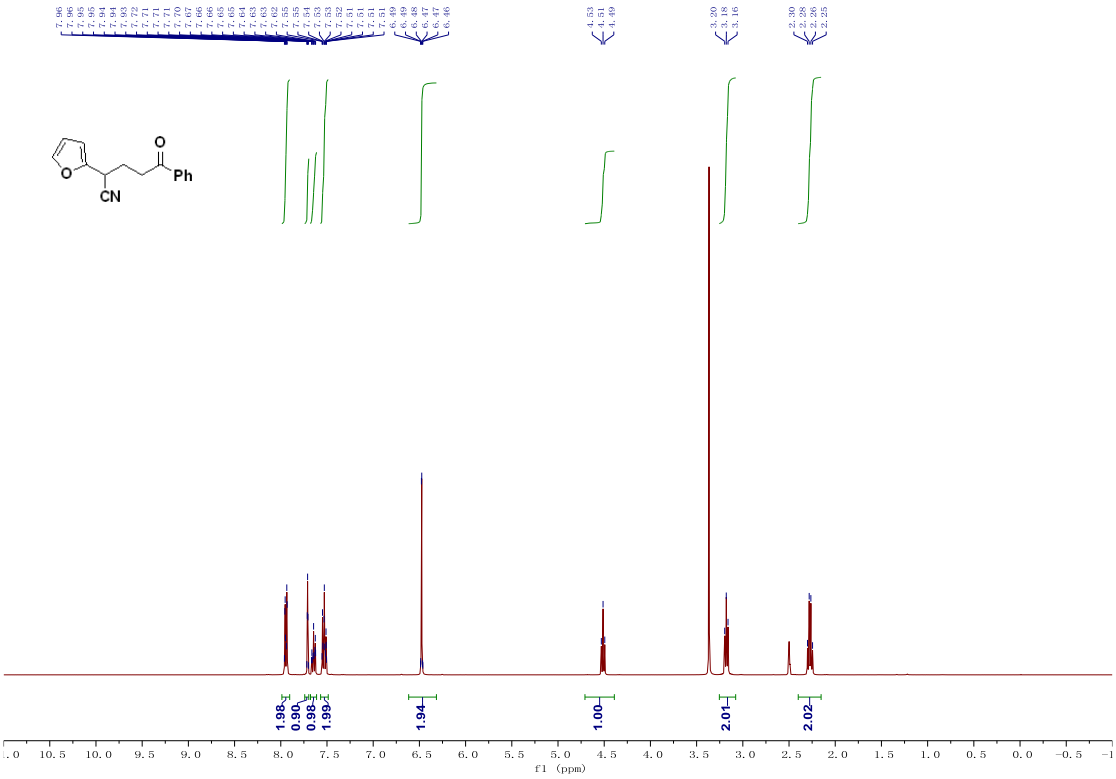


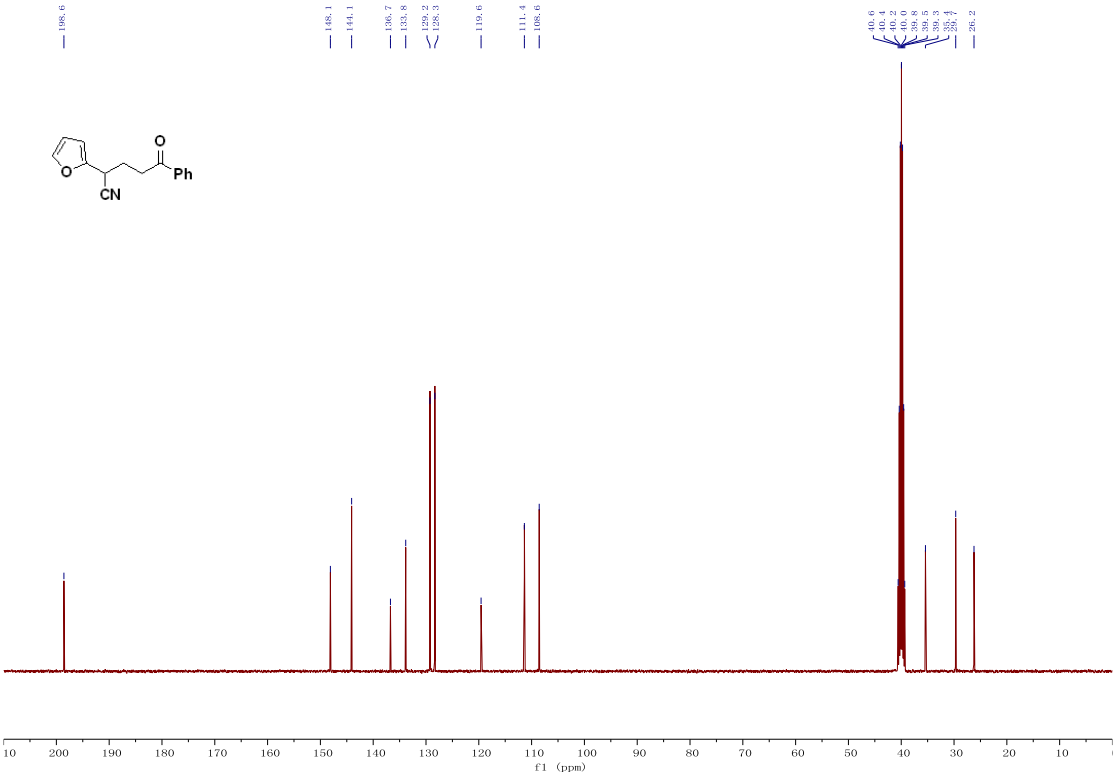
^{1}H and ^{13}C NMR of compound **3r**



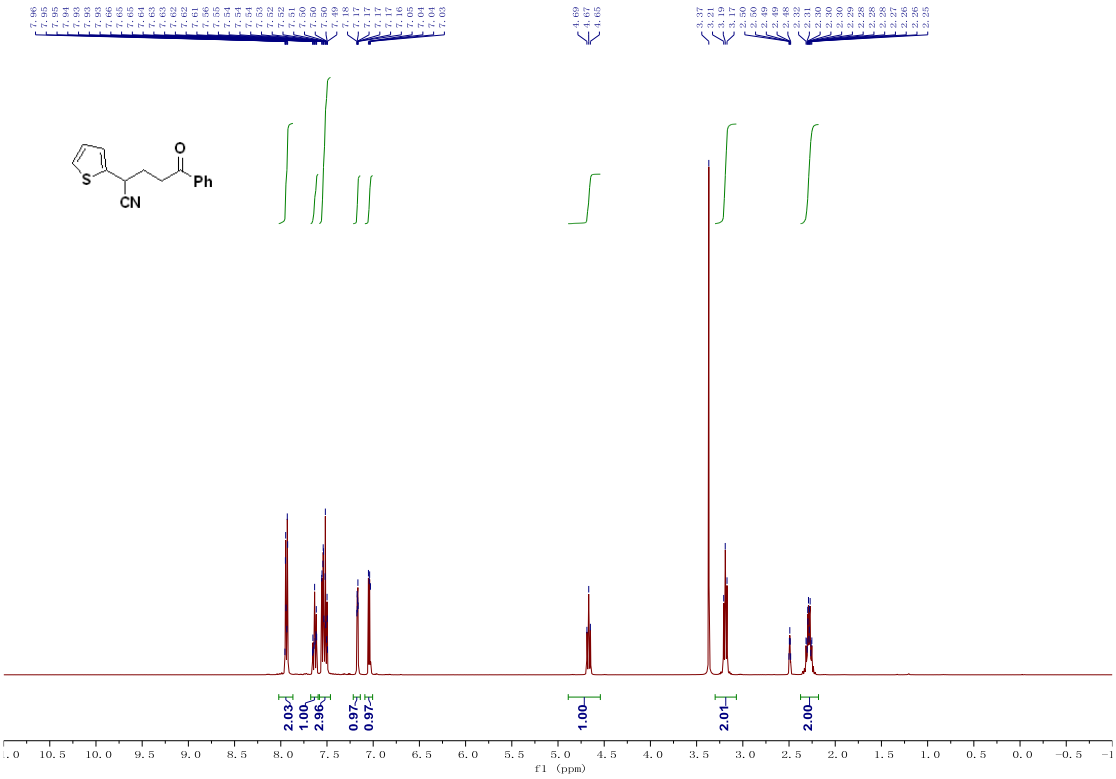


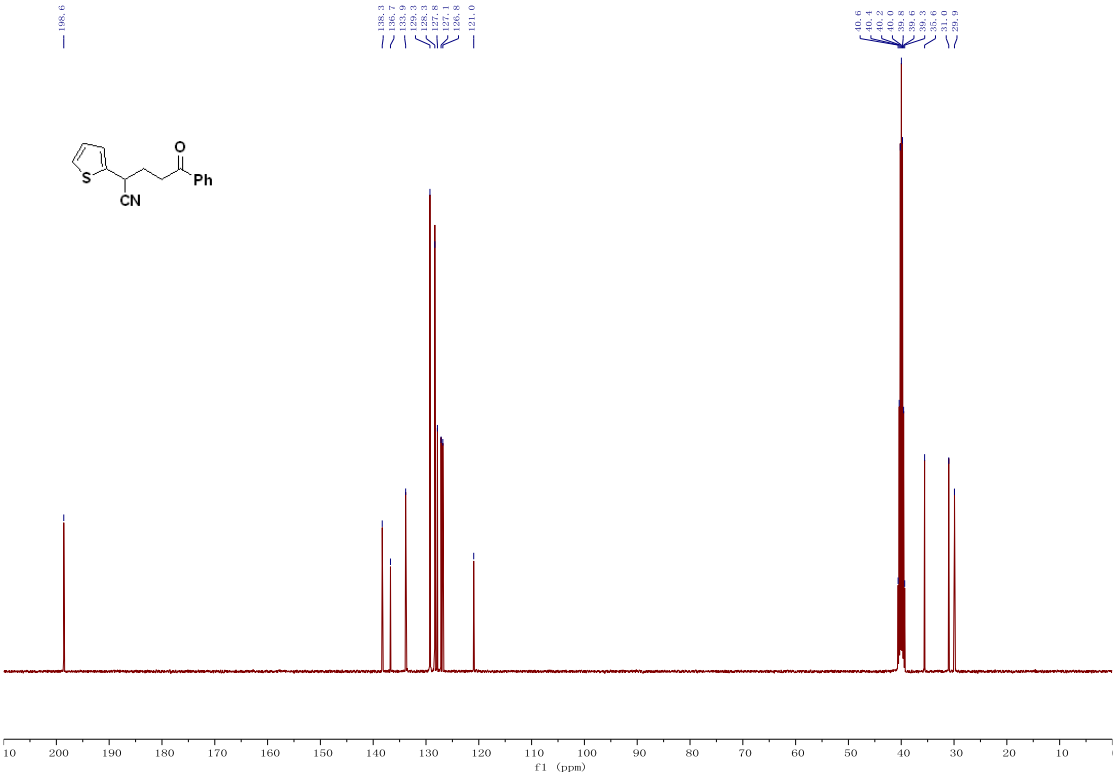
^{1}H and ^{13}C NMR of compound **3s**



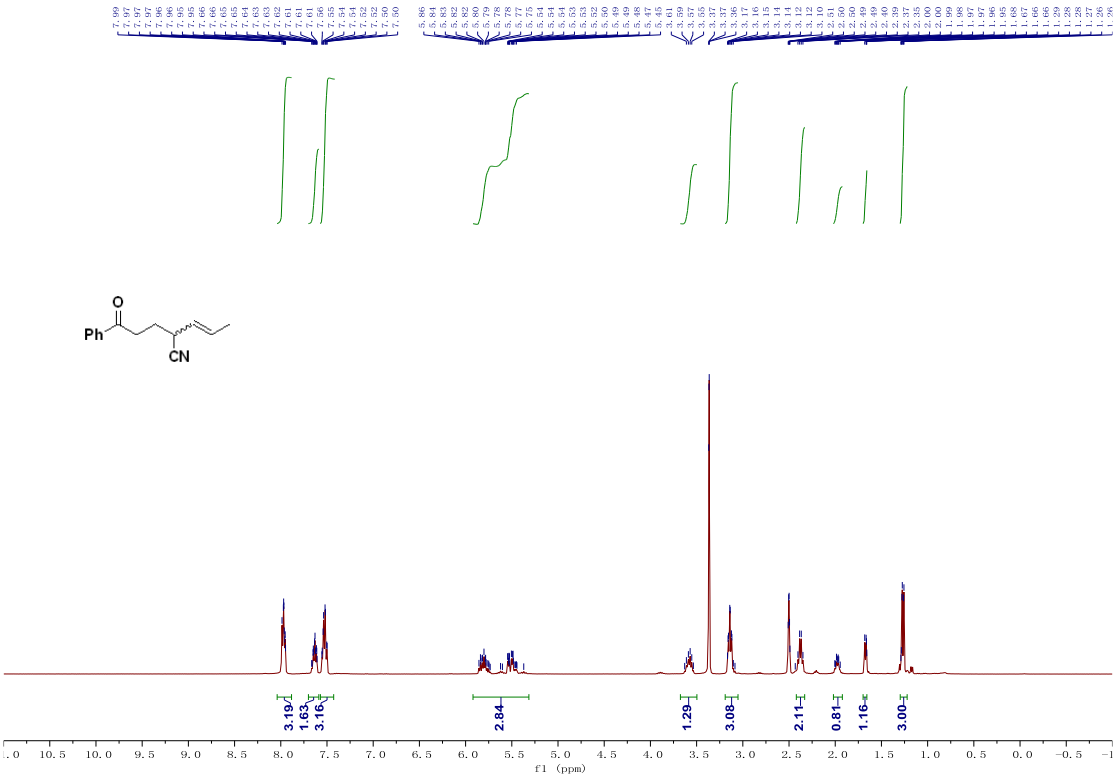


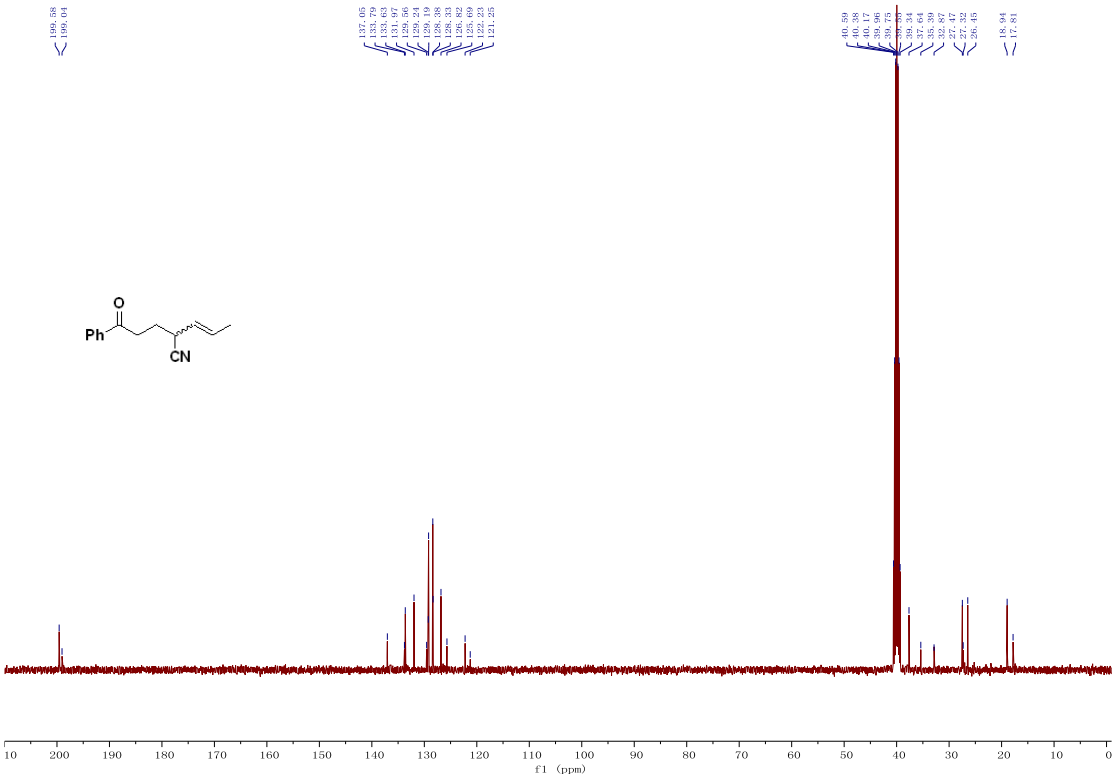
^{1}H and ^{13}C NMR of compound **3t**



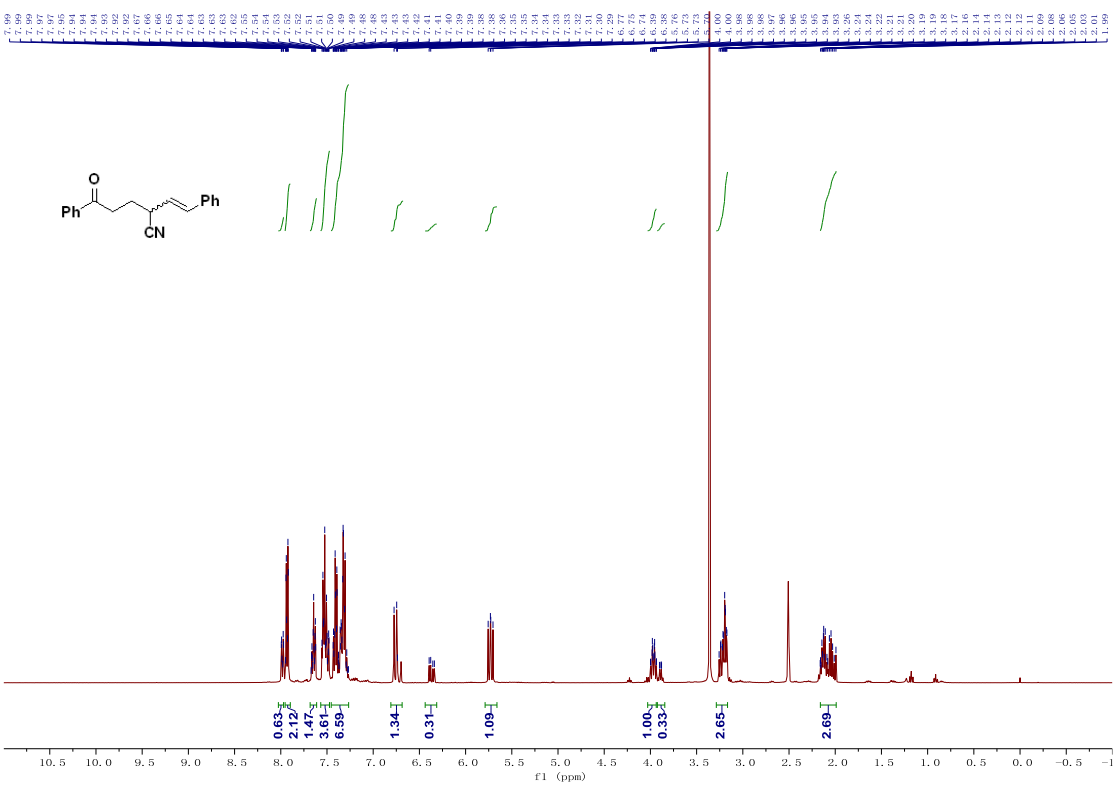


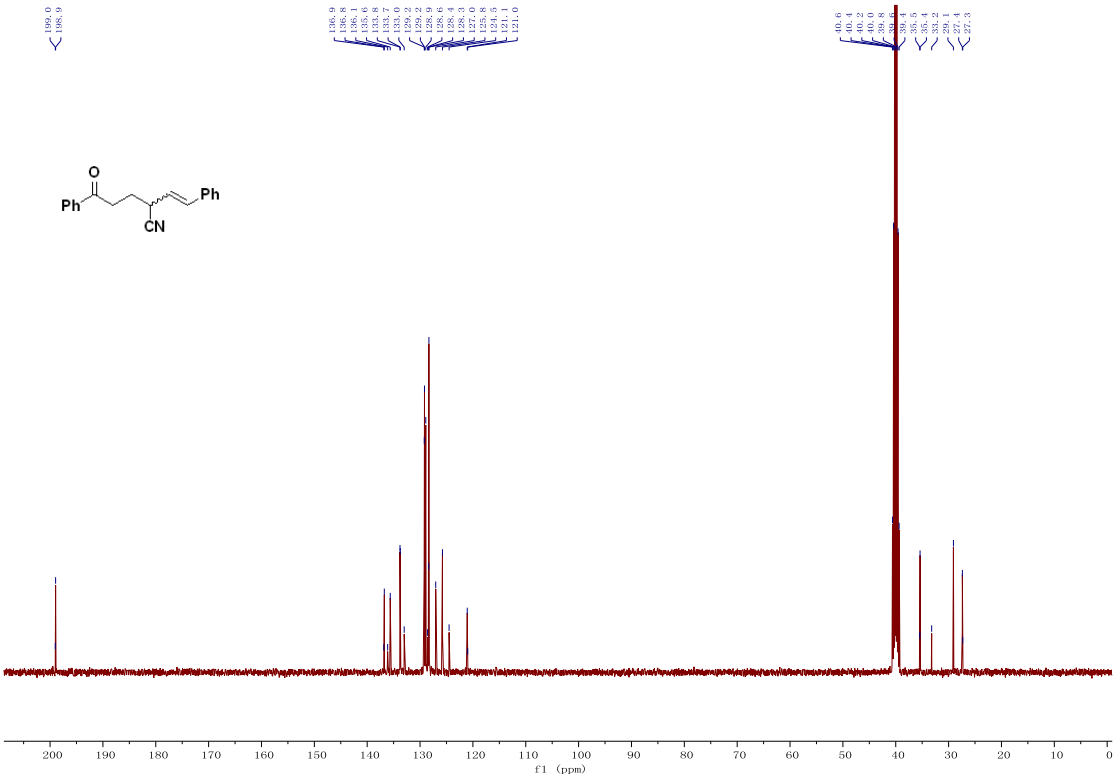
^{1}H and ^{13}C NMR of compound **5a**



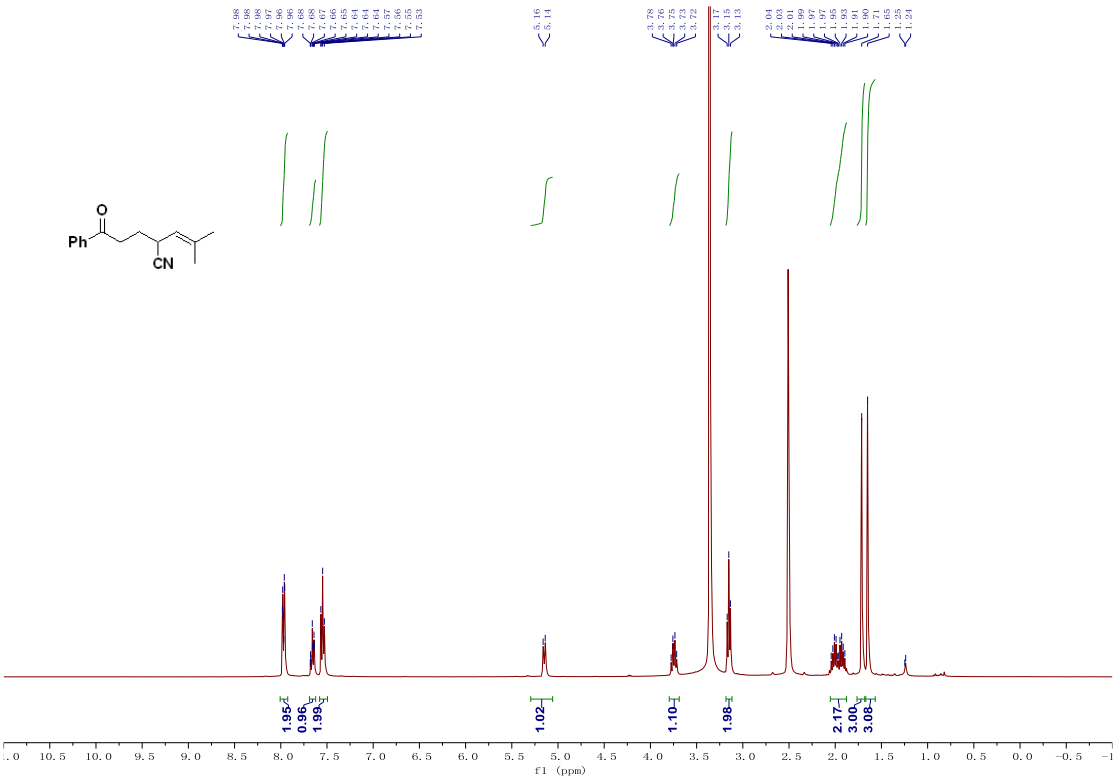


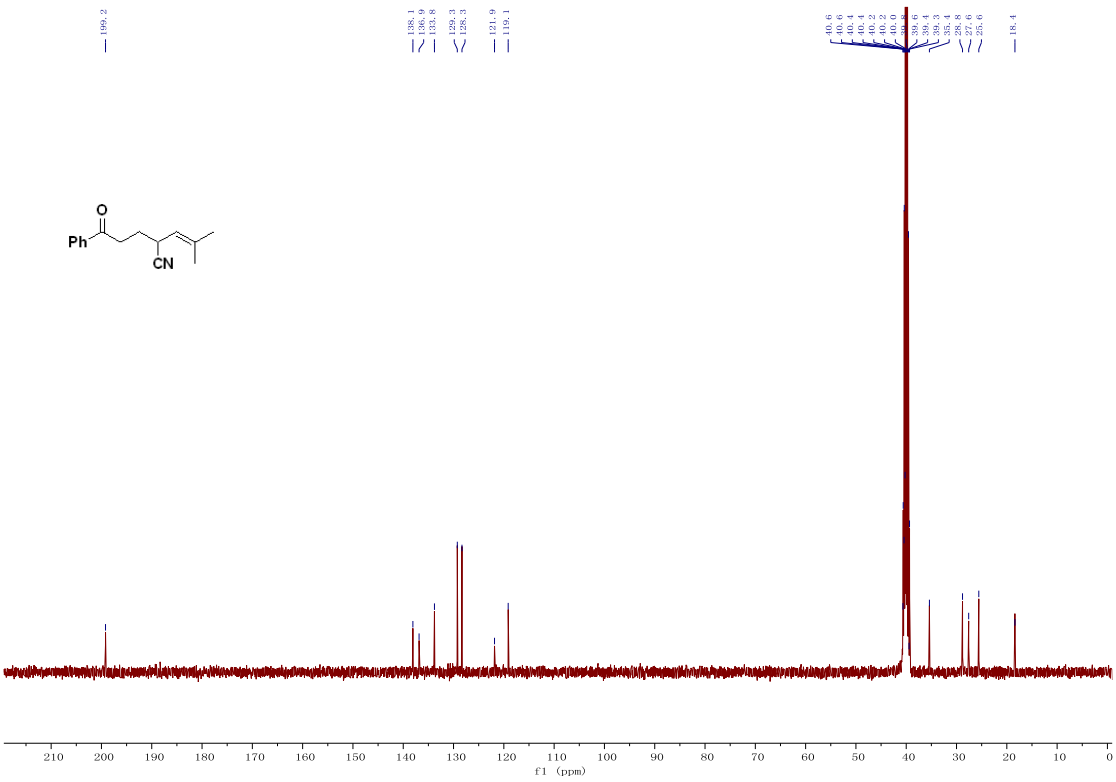
^{1}H and ^{13}C NMR of compound **5b**



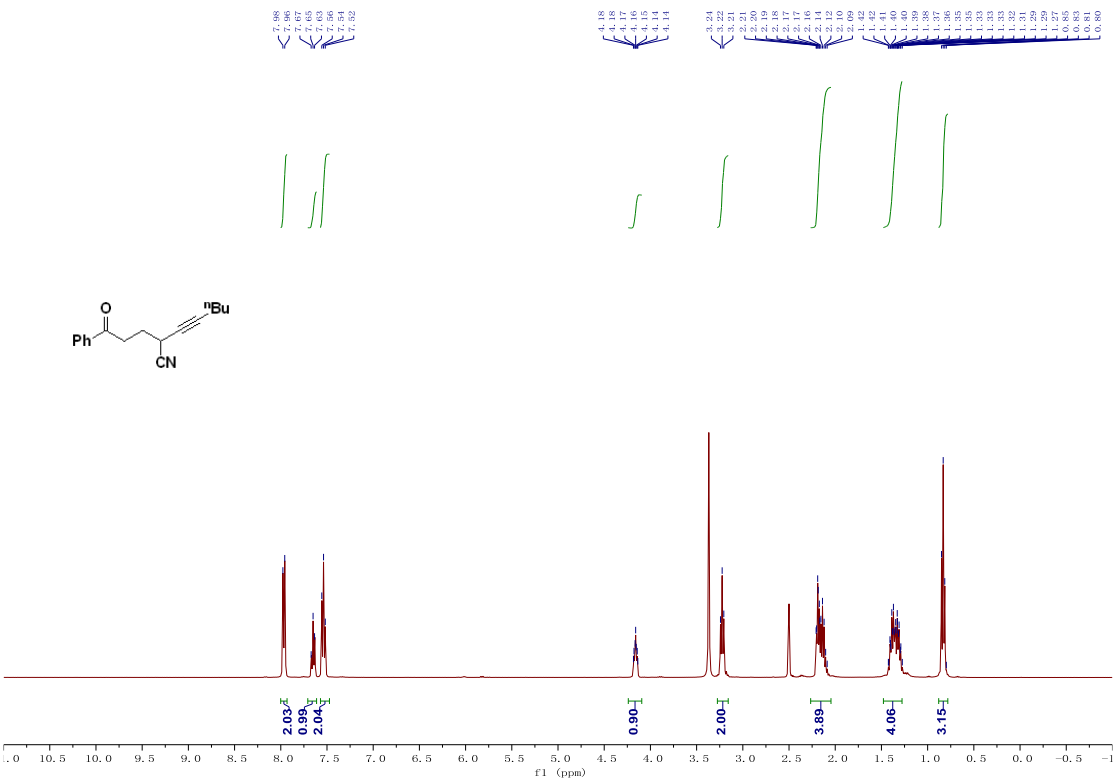


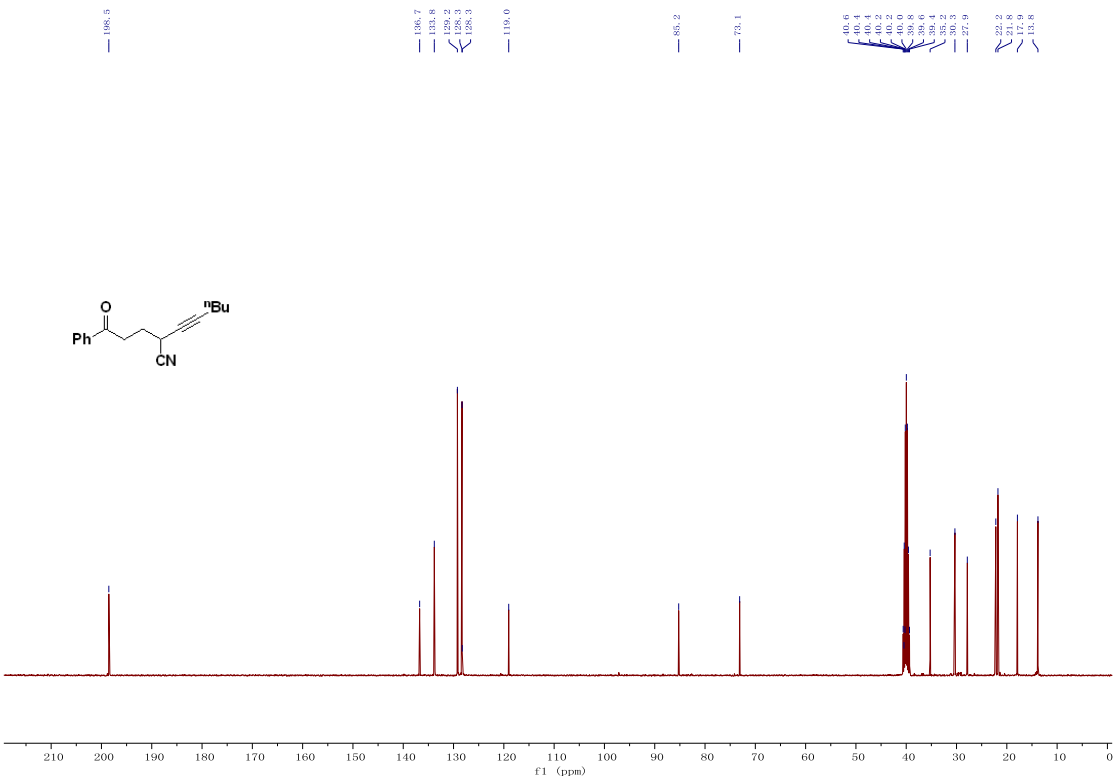
^{1}H and ^{13}C NMR of compound **5c**



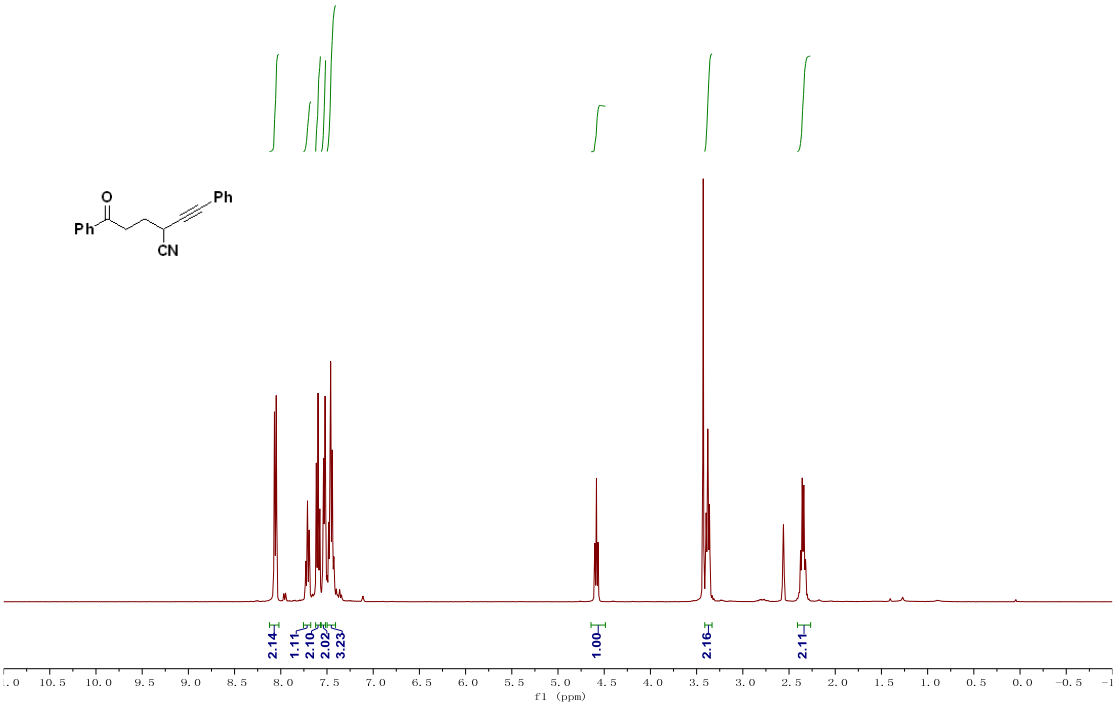


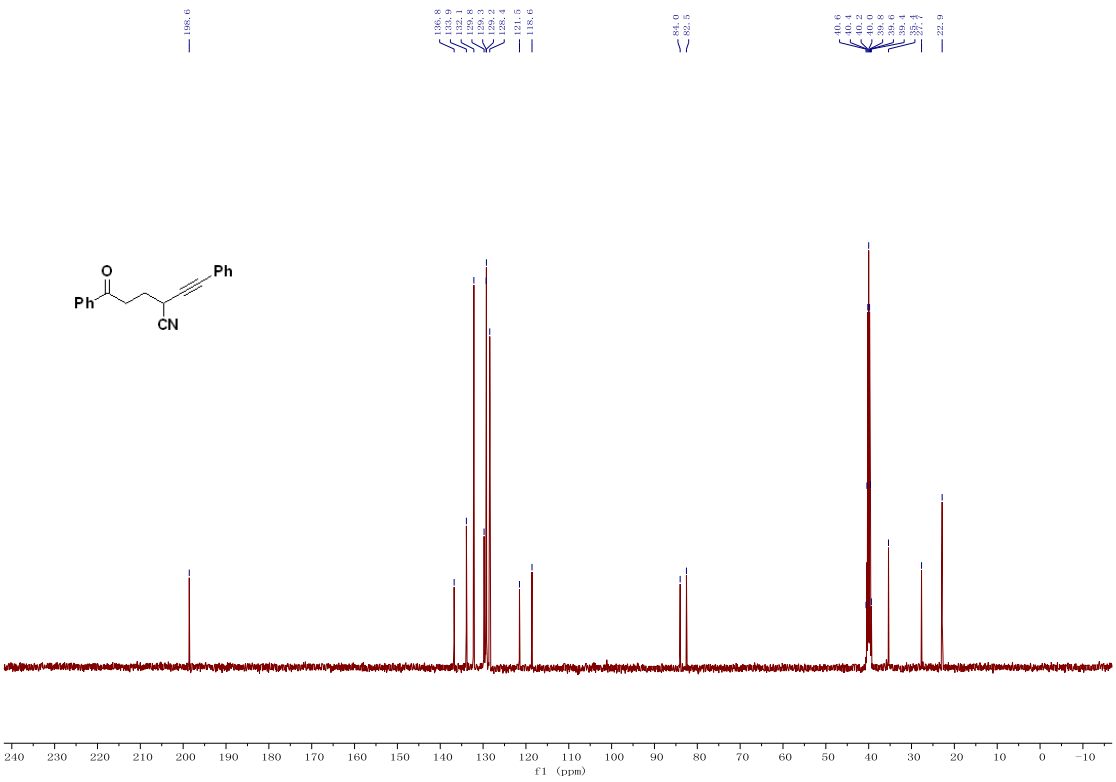
^{1}H and ^{13}C NMR of compound **5d**



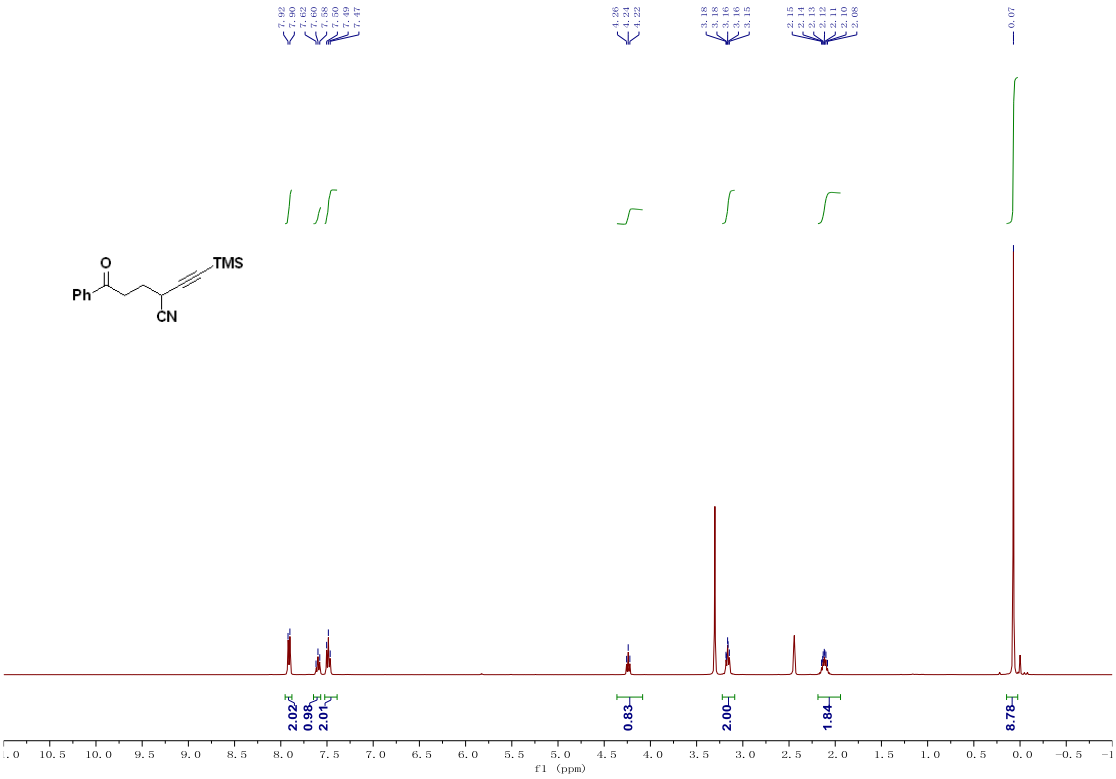


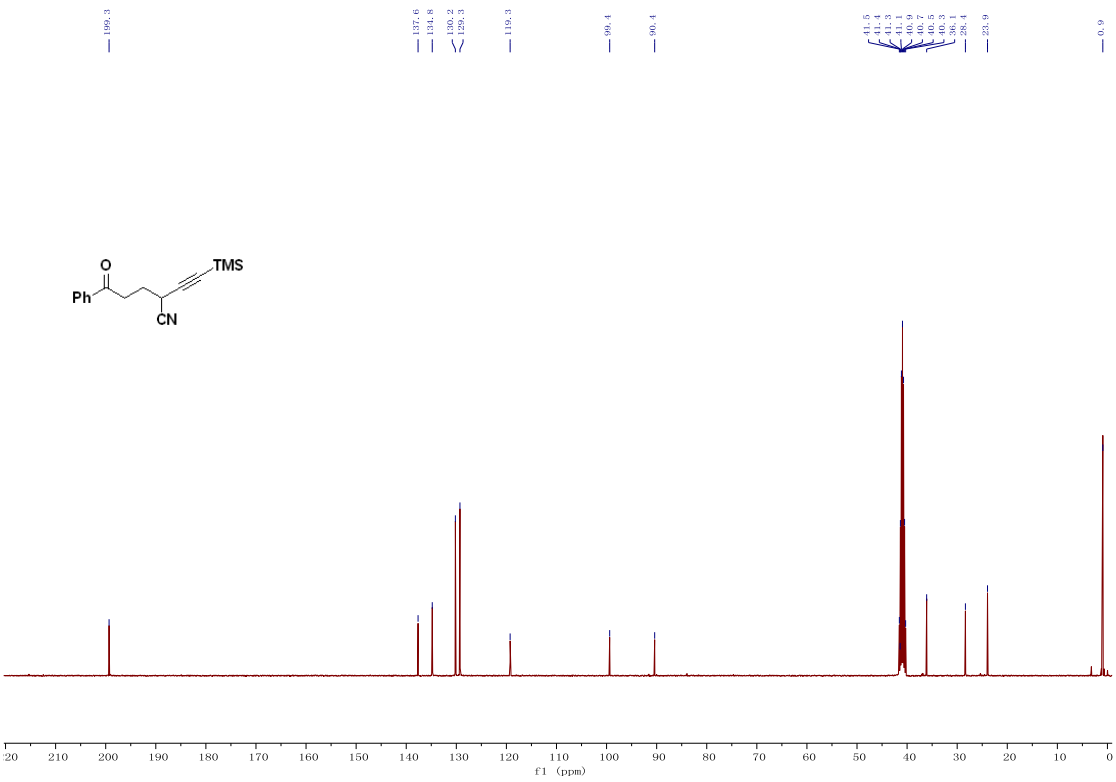
^{1}H and ^{13}C NMR of compound **5e**



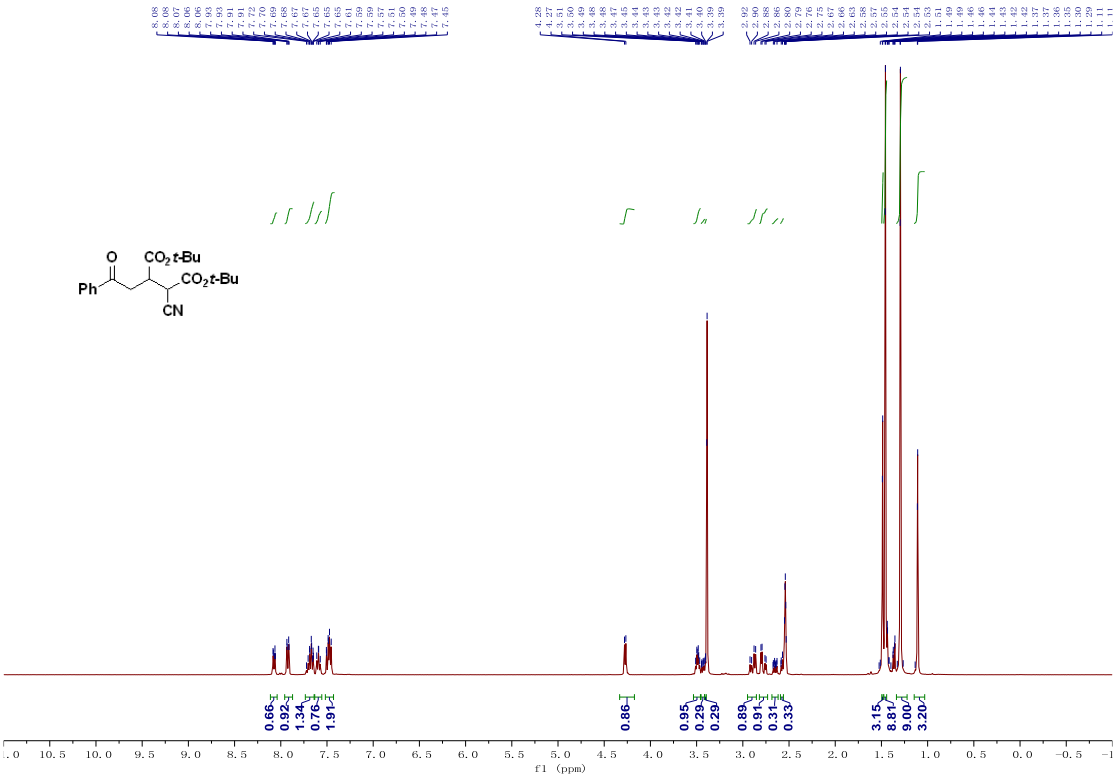


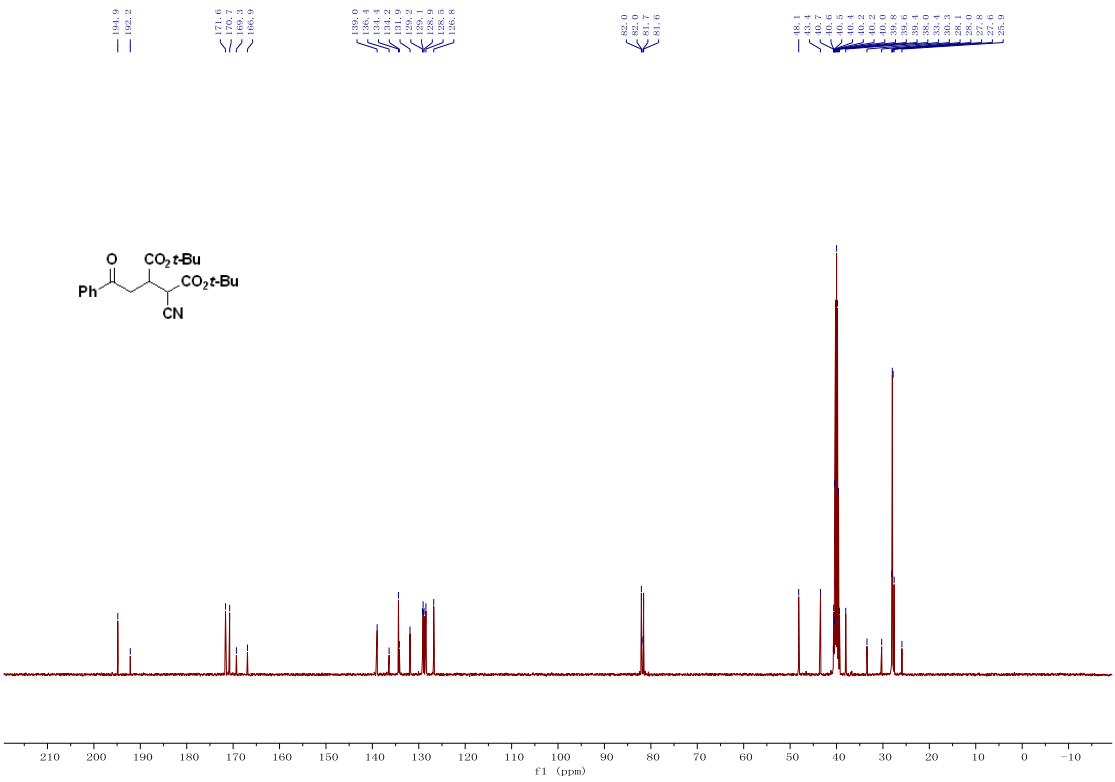
^{1}H and ^{13}C NMR of compound **5f**



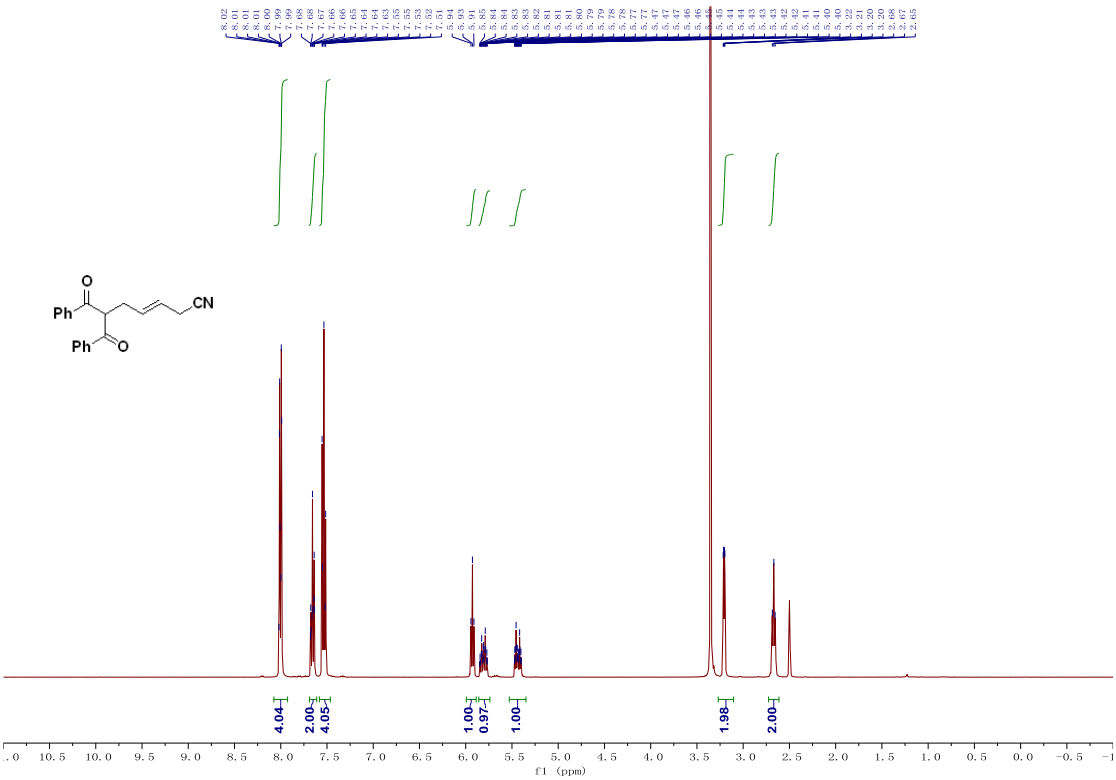


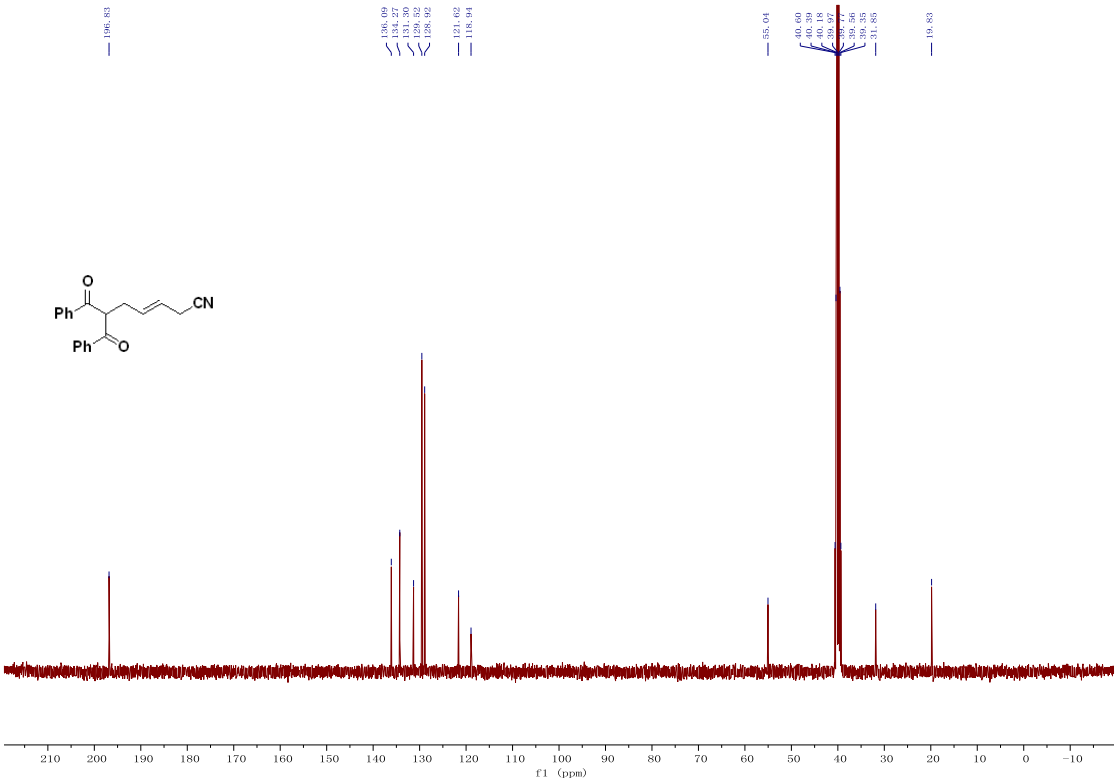
^{1}H and ^{13}C NMR of compound **5g**



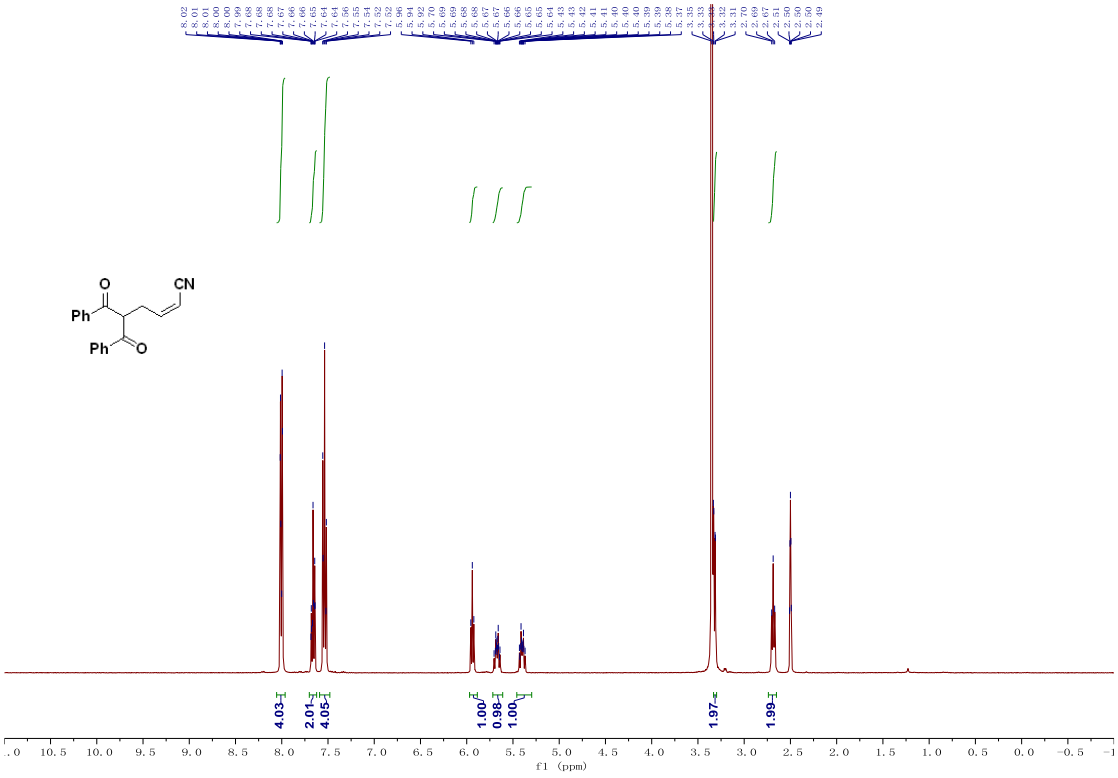


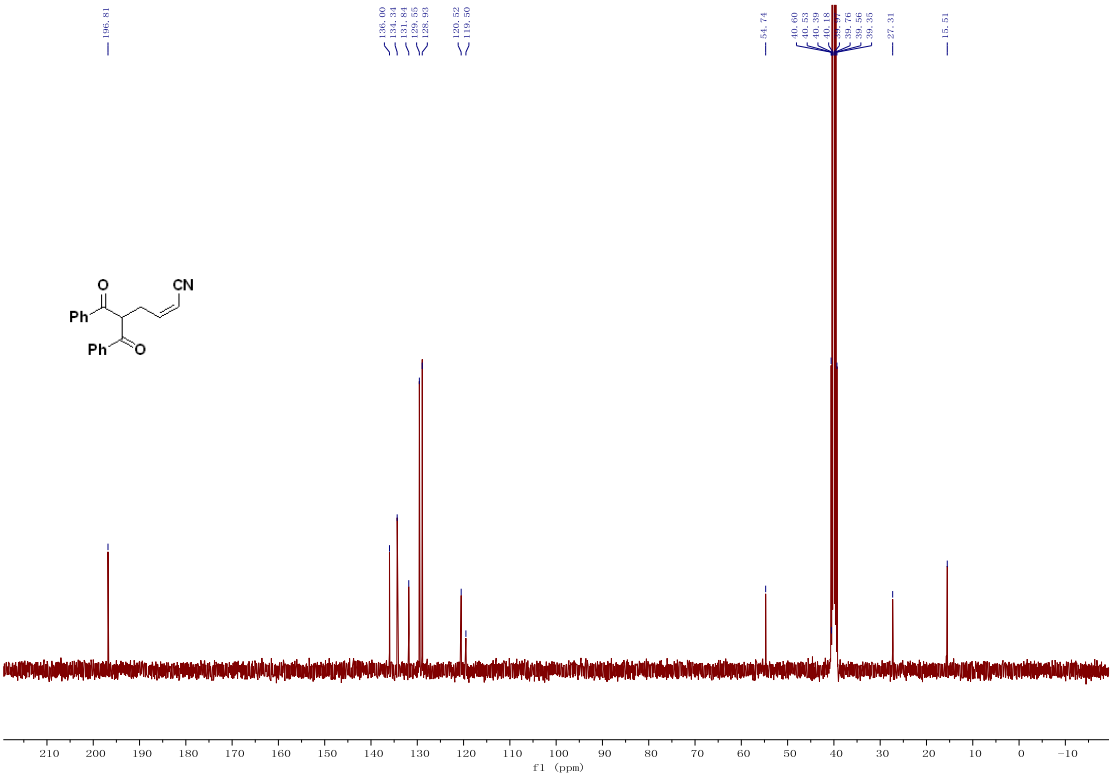
^{1}H and ^{13}C NMR of compound **(*E*)-5h**



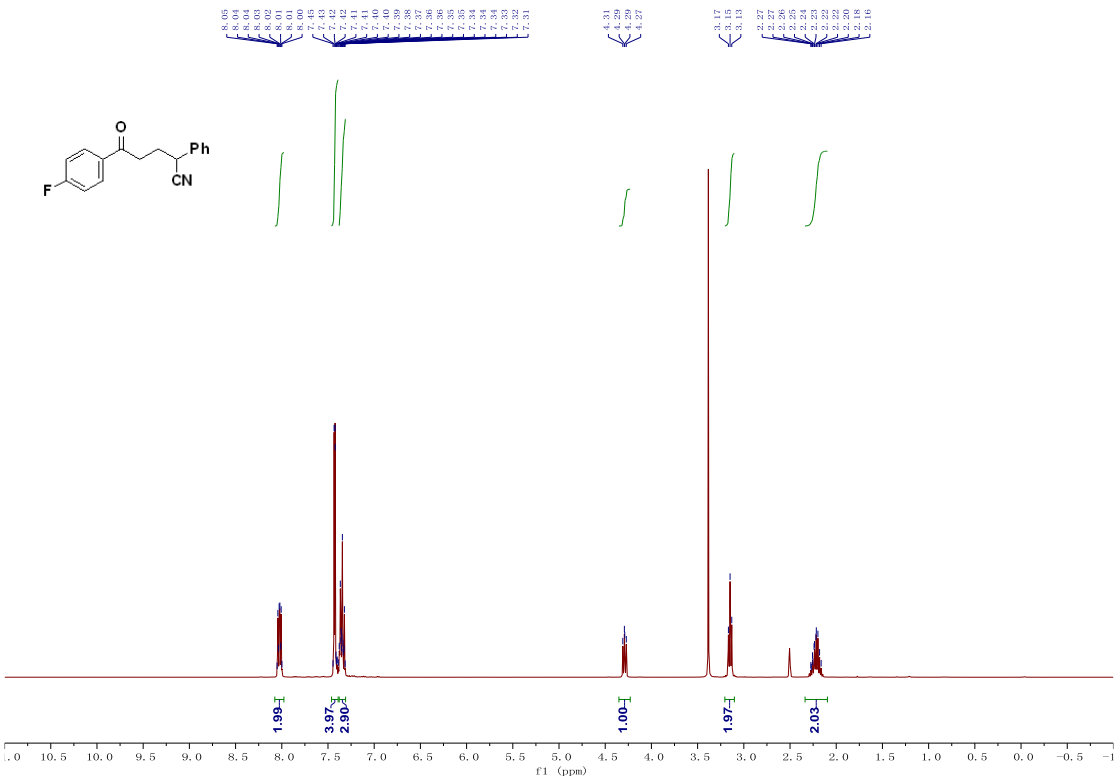


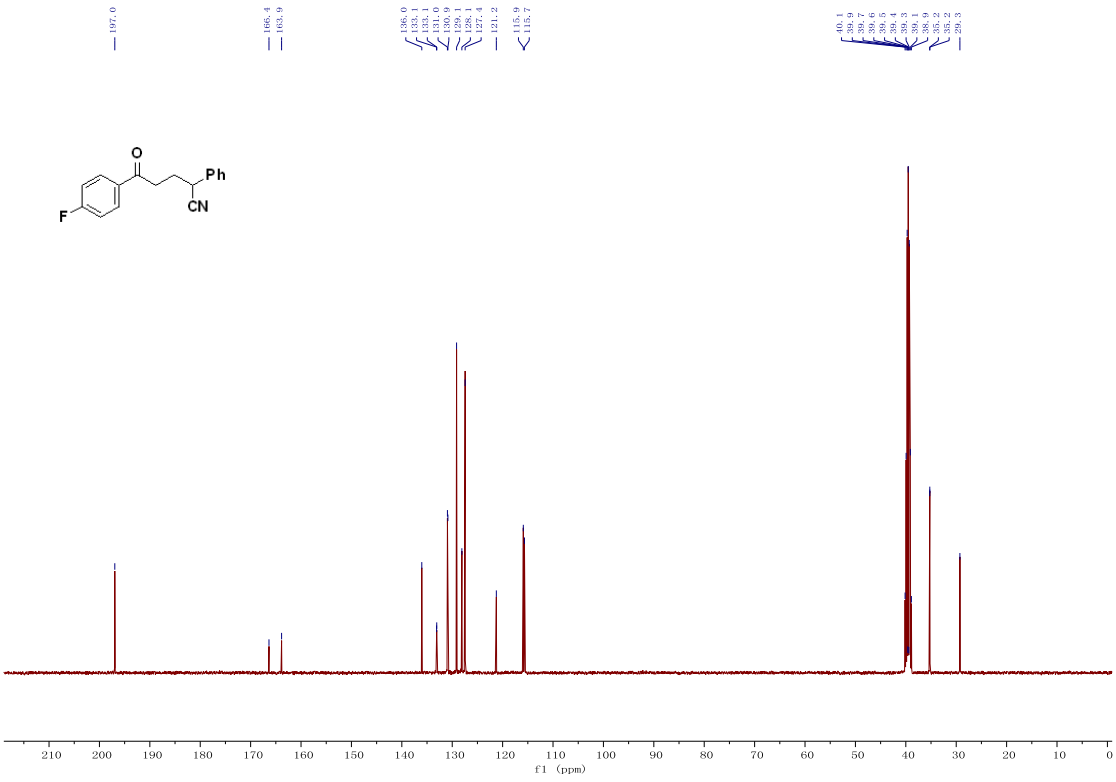
^{1}H and ^{13}C NMR of compound **(Z)-5h**





^{1}H, ^{13}C NMR and ^{19}F of compound **7a**

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166.4
163.9
138.0
133.1
133.1
131.6
130.9
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128.1
127.4
121.2
115.9
115.7
40.1
39.9
39.7
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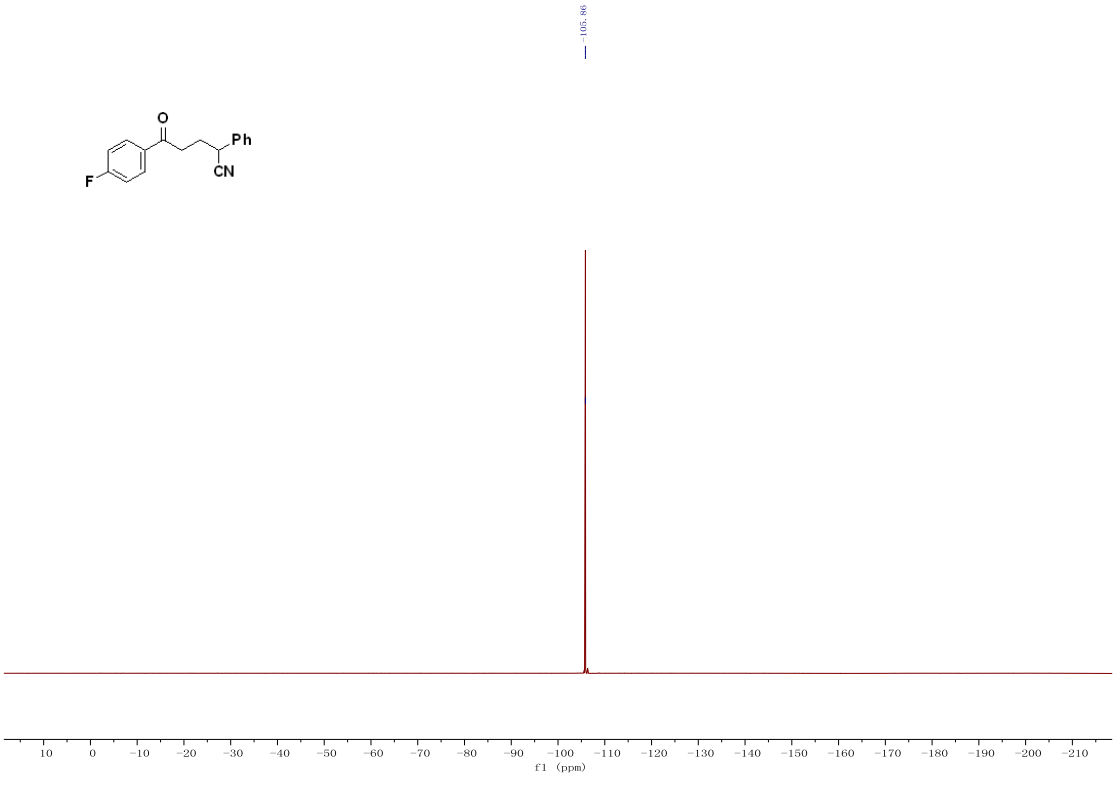
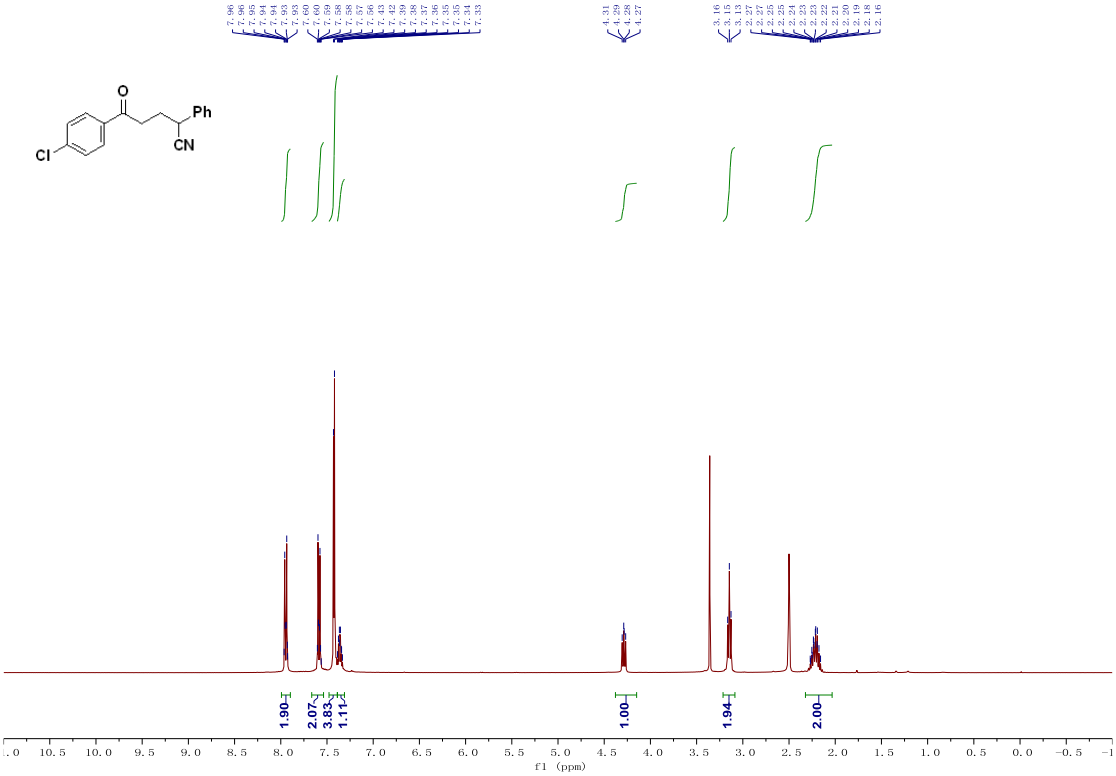
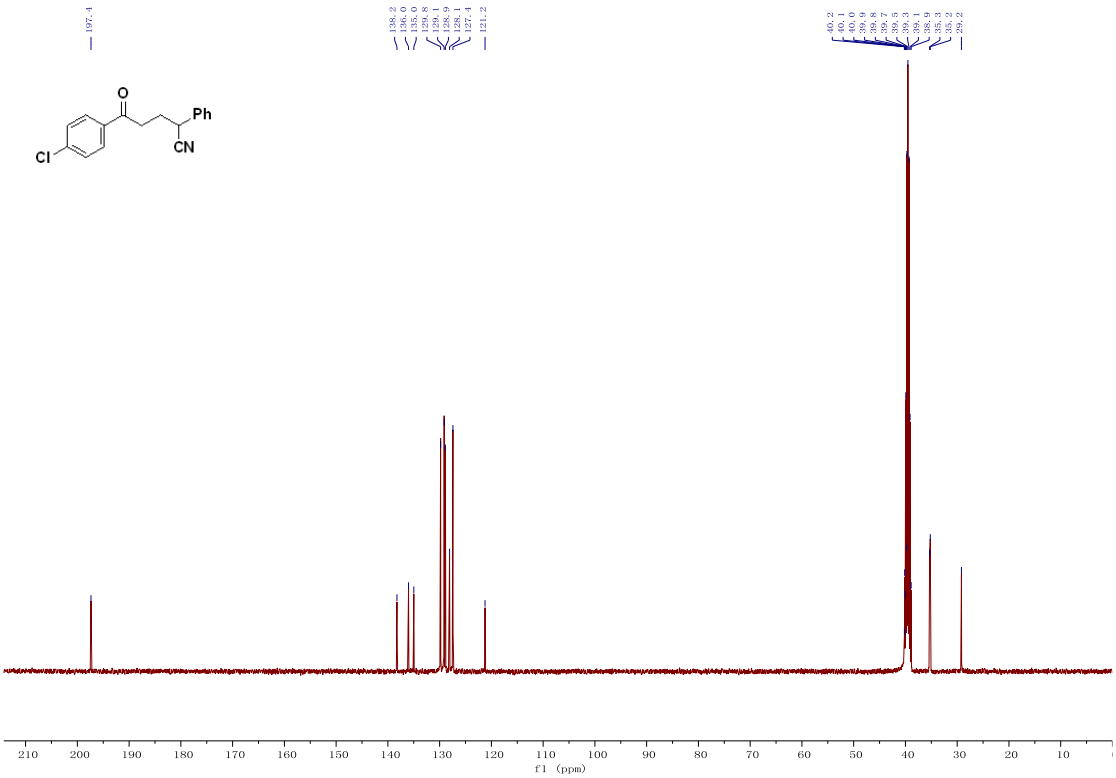
39.3
39.1
38.9
35.2
29.3
O
Ph
CN
F
f1 (ppm)

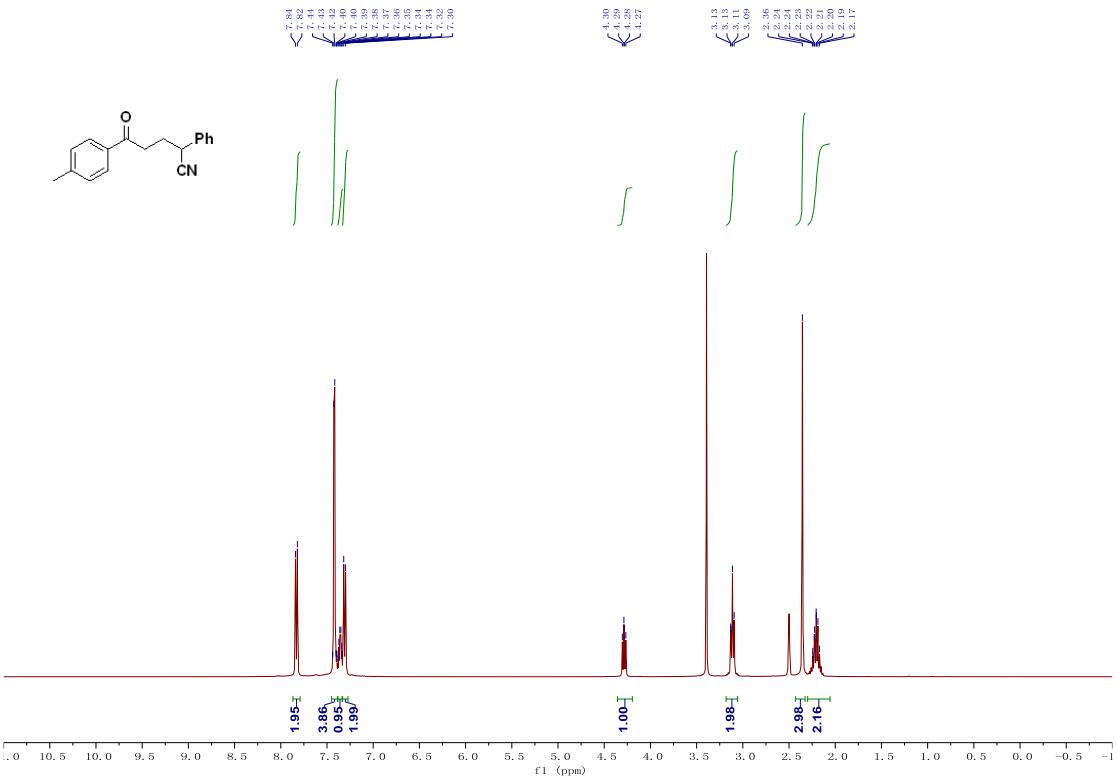

105.86
O
Ph
CN
F
f1 (ppm)

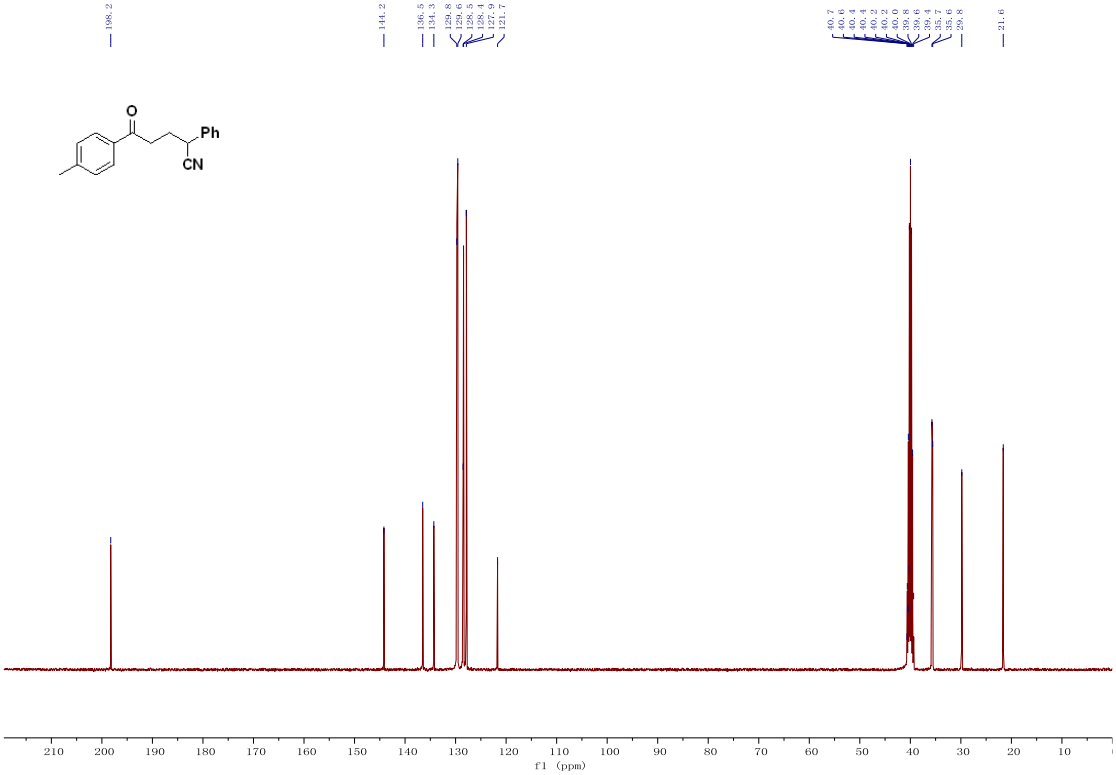
^{1}H and ^{13}C NMR of compound **7b**



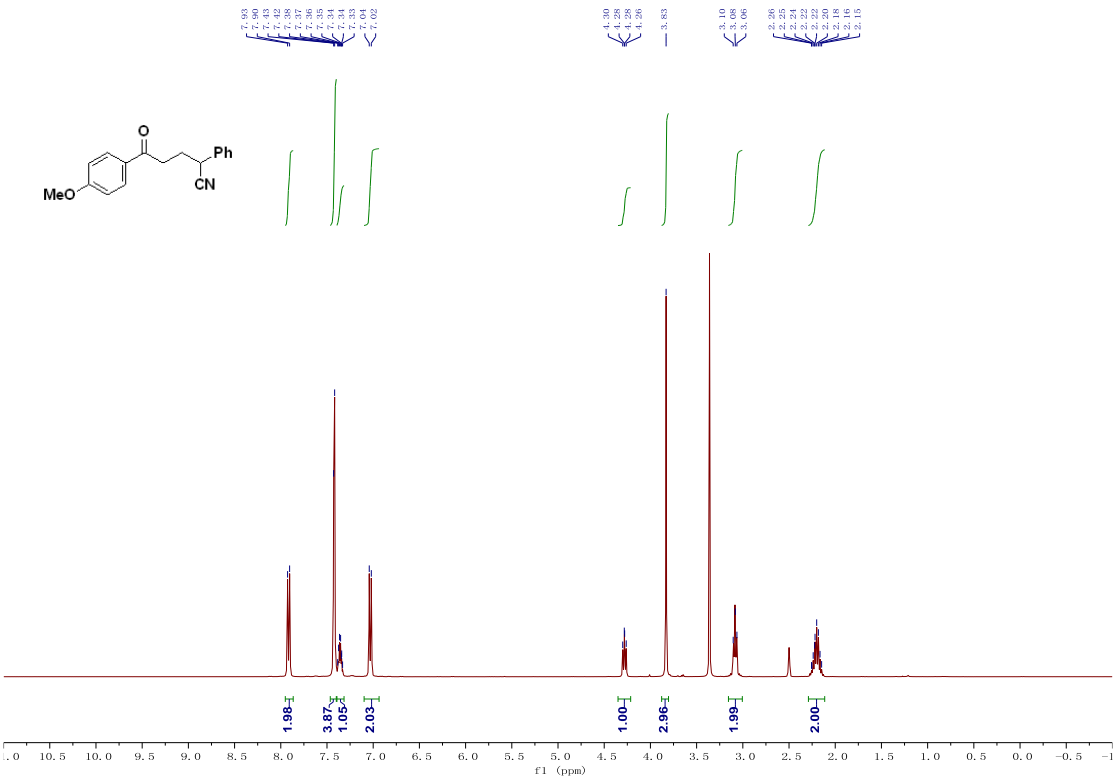


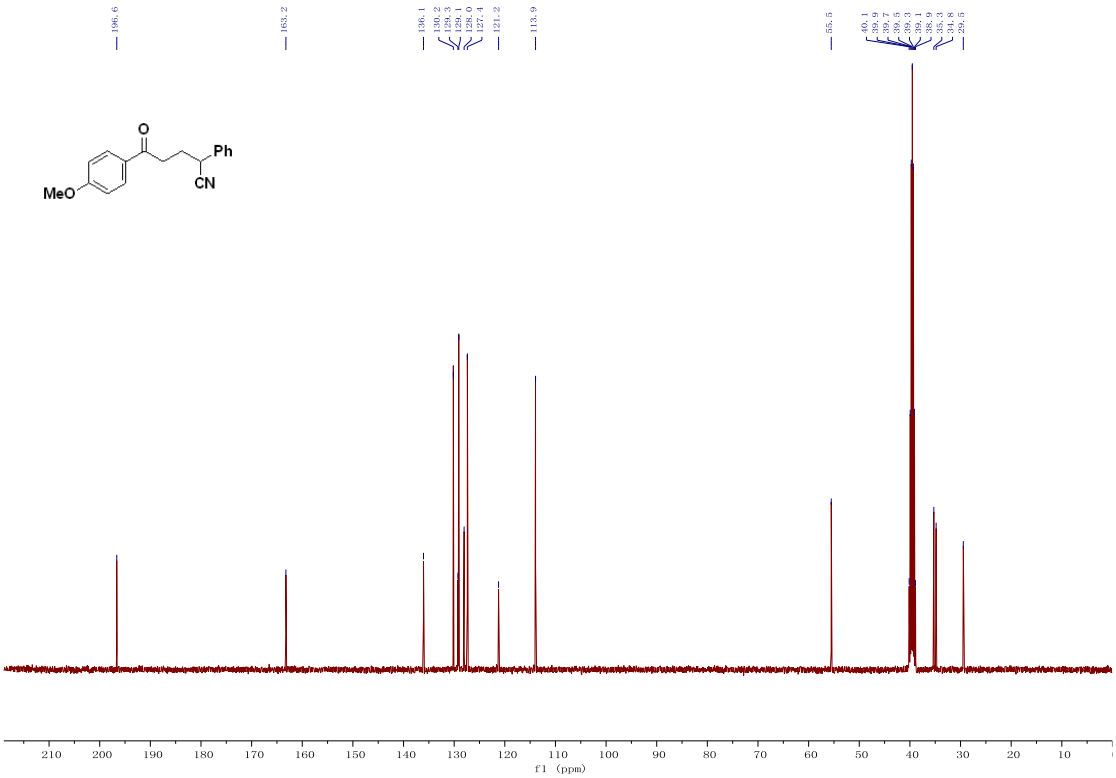
^{1}H and ^{13}C NMR of compound **7c**



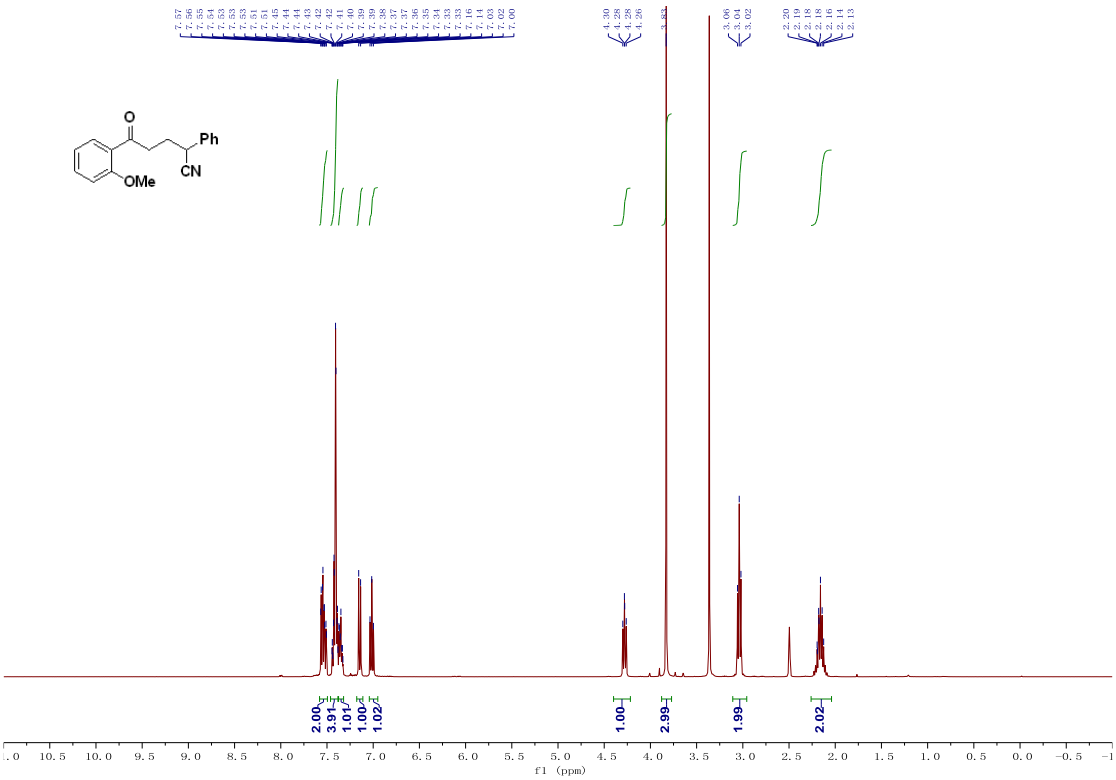


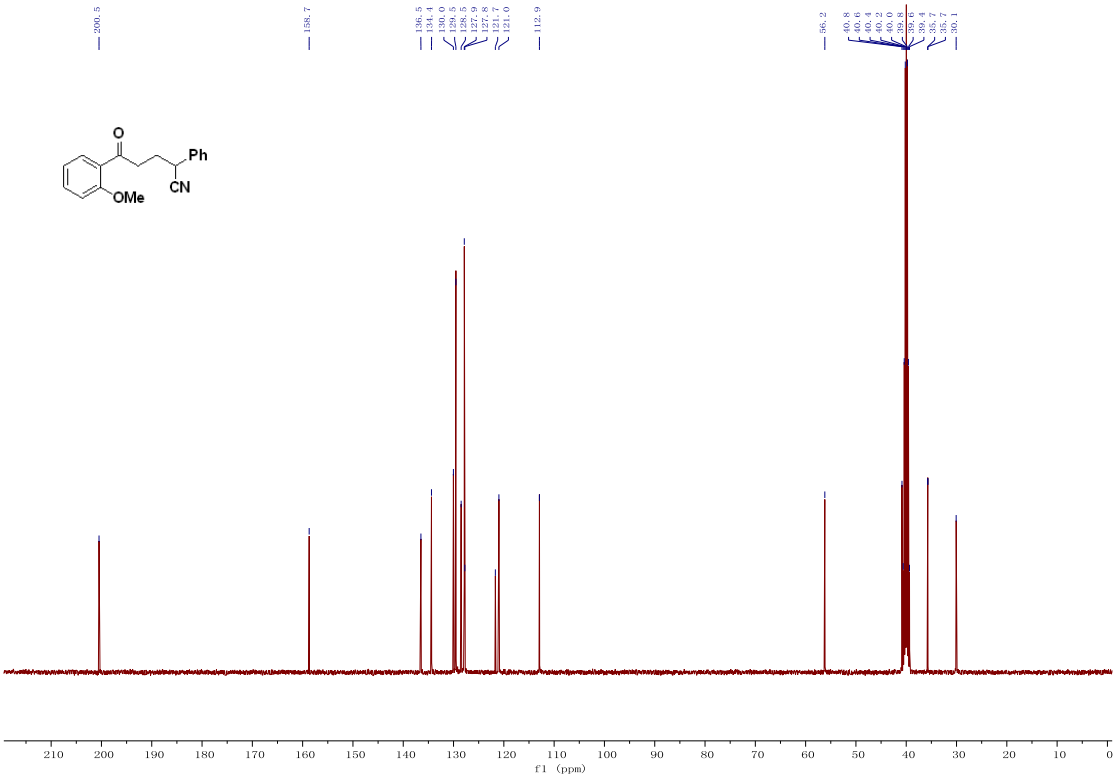
^{1}H and ^{13}C NMR of compound **7d**



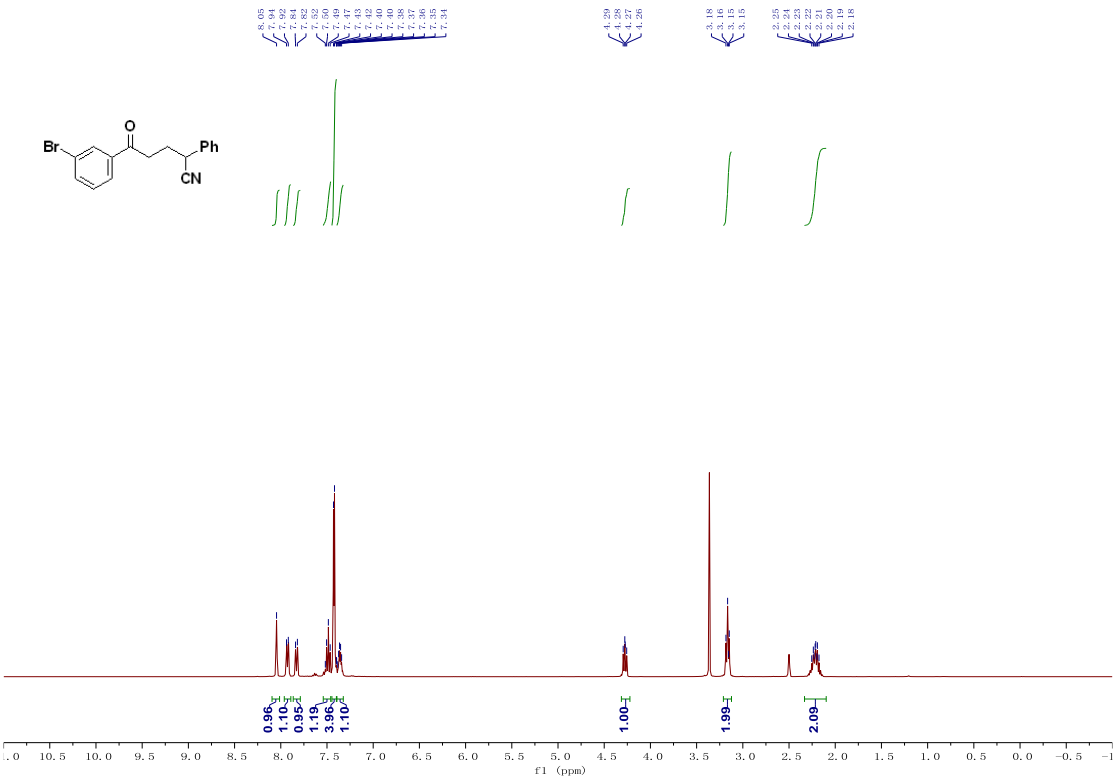


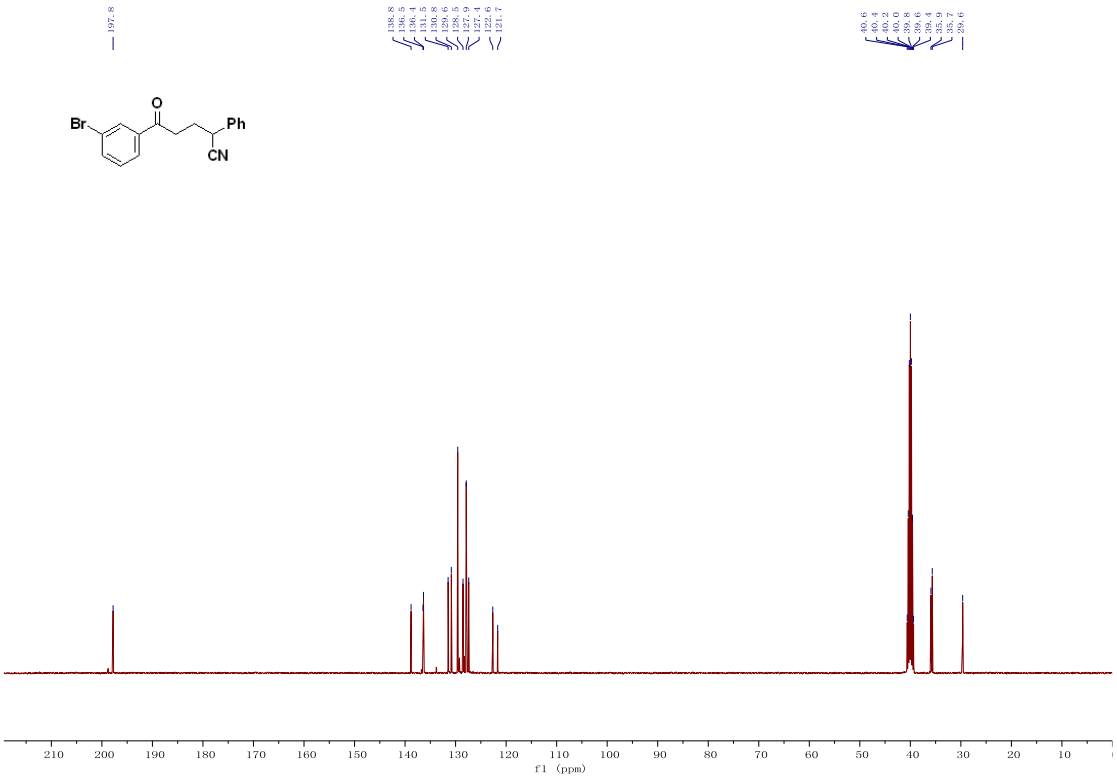
^{1}H and ^{13}C NMR of compound **7e**



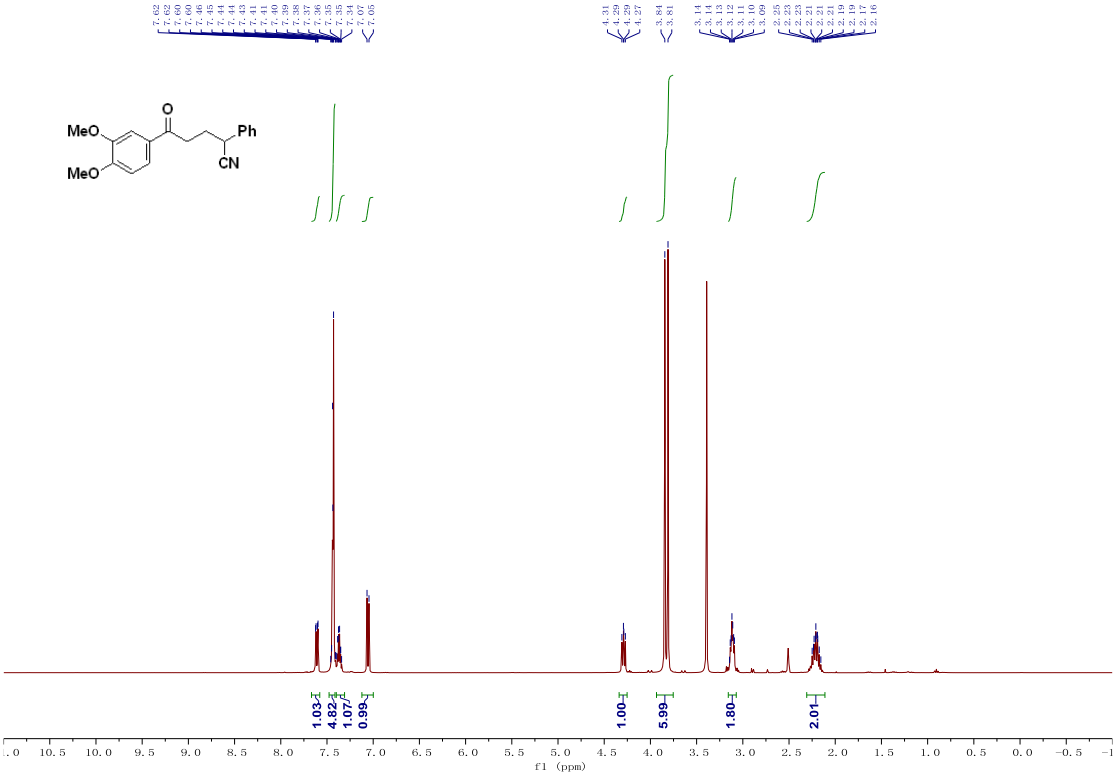


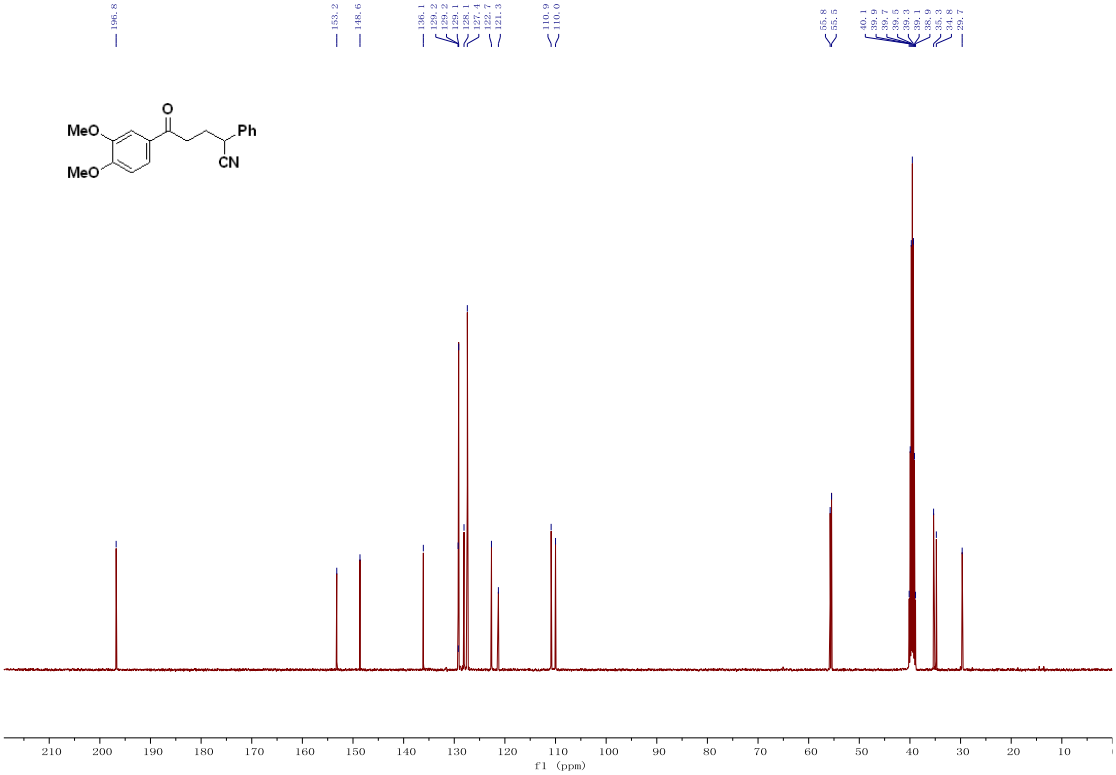
^{1}H and ^{13}C NMR of compound **7f**



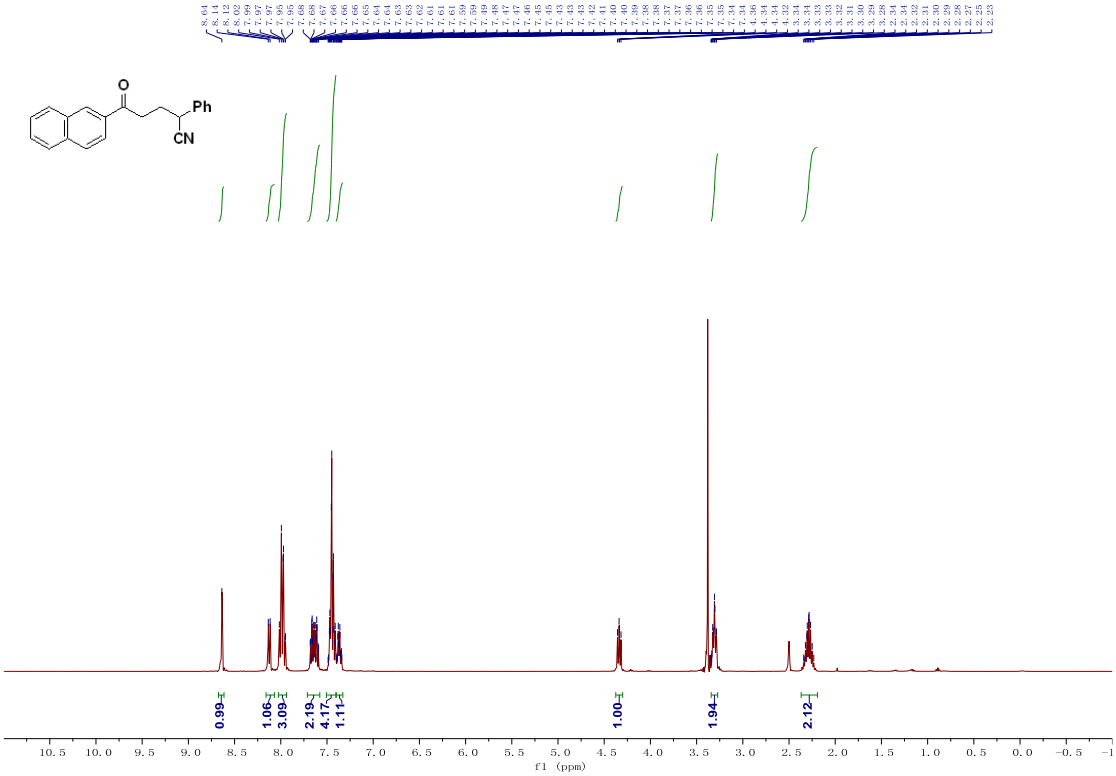


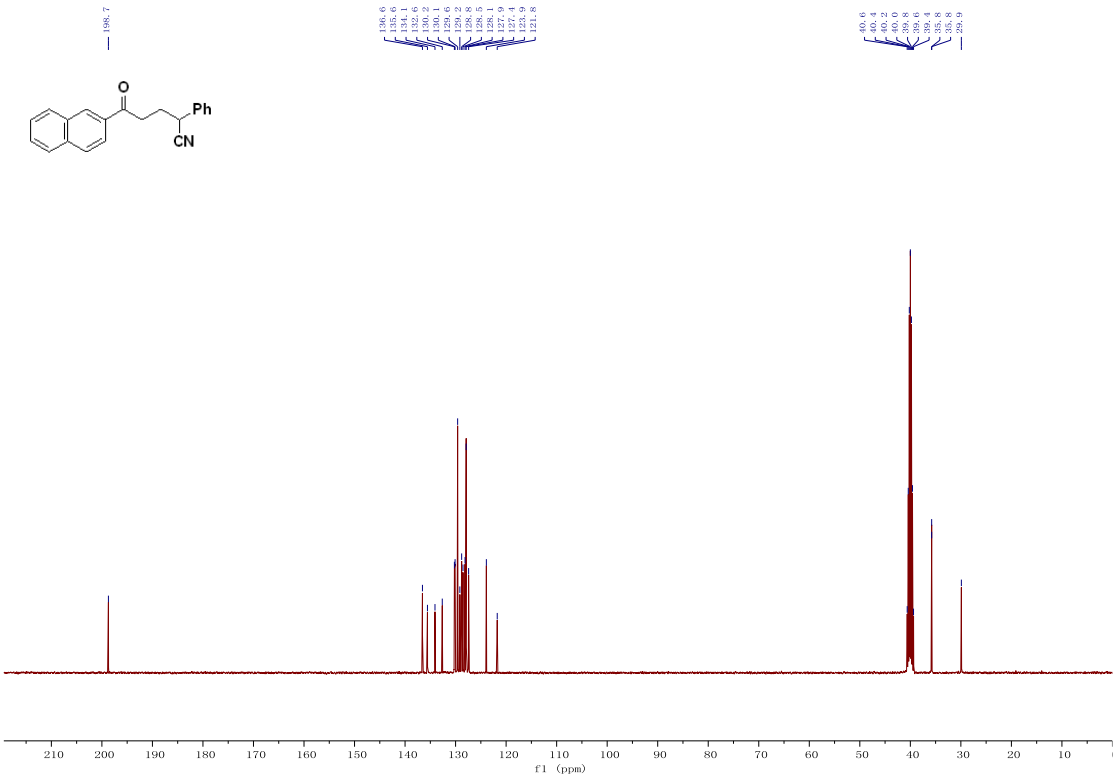
^{1}H and ^{13}C NMR of compound **7g**



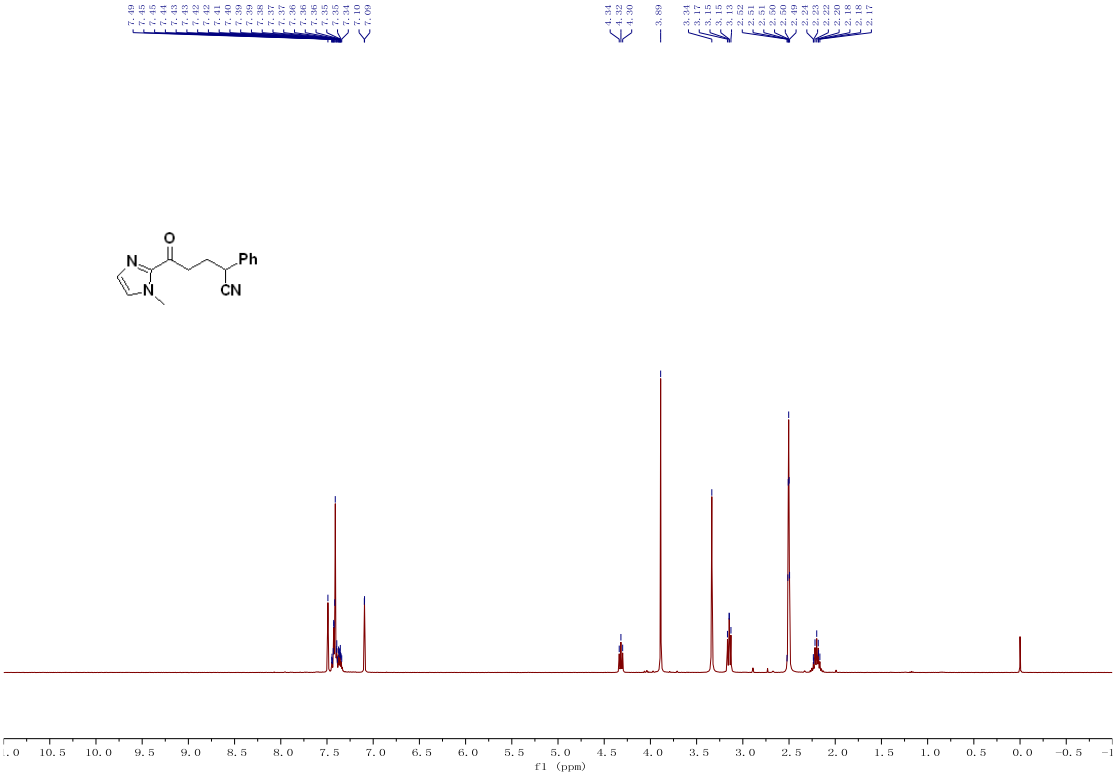


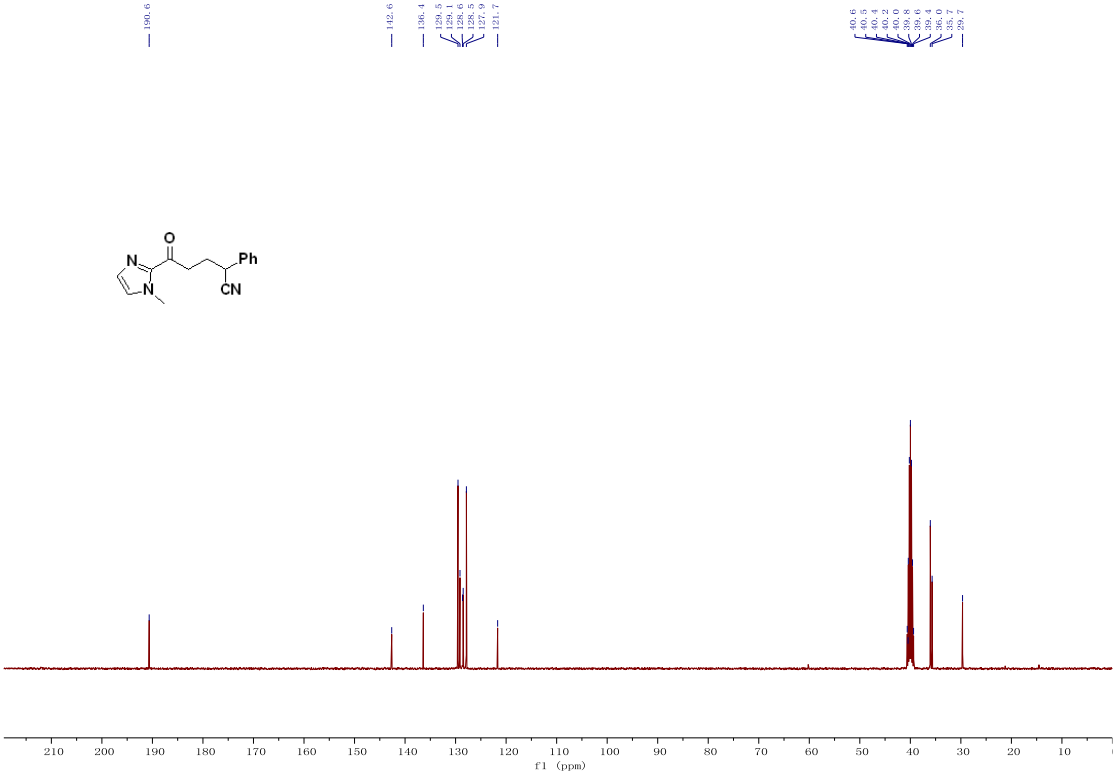
^{1}H and ^{13}C NMR of compound **7h**



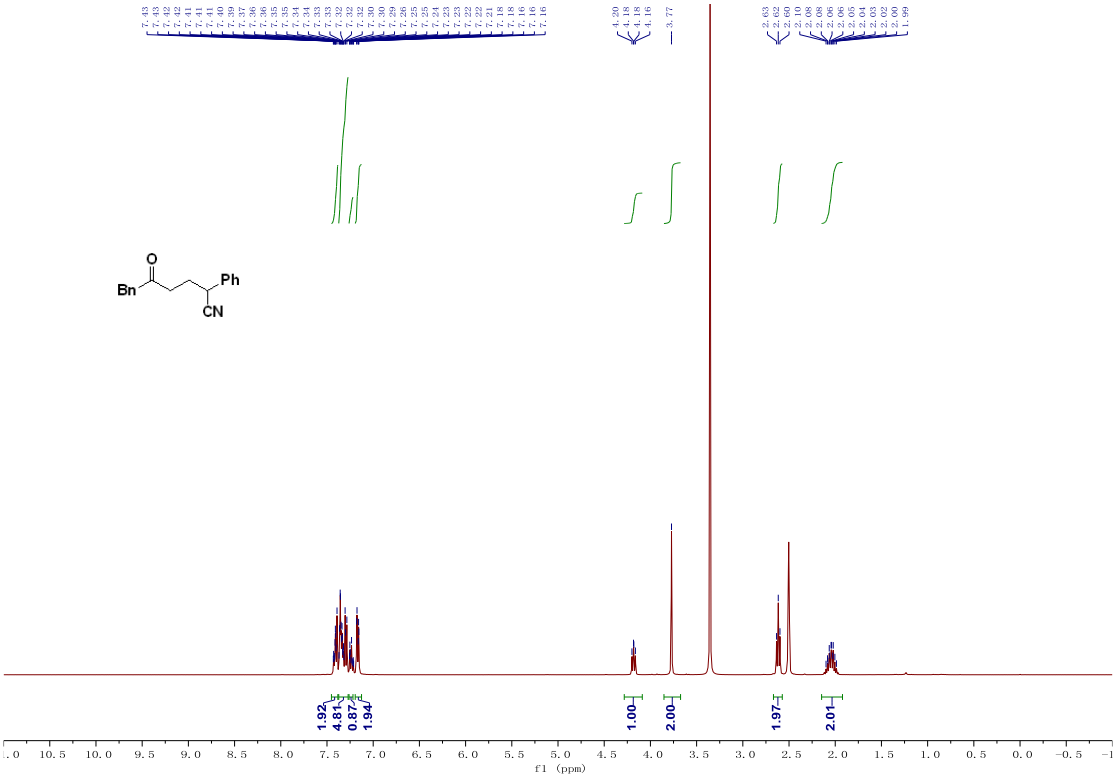


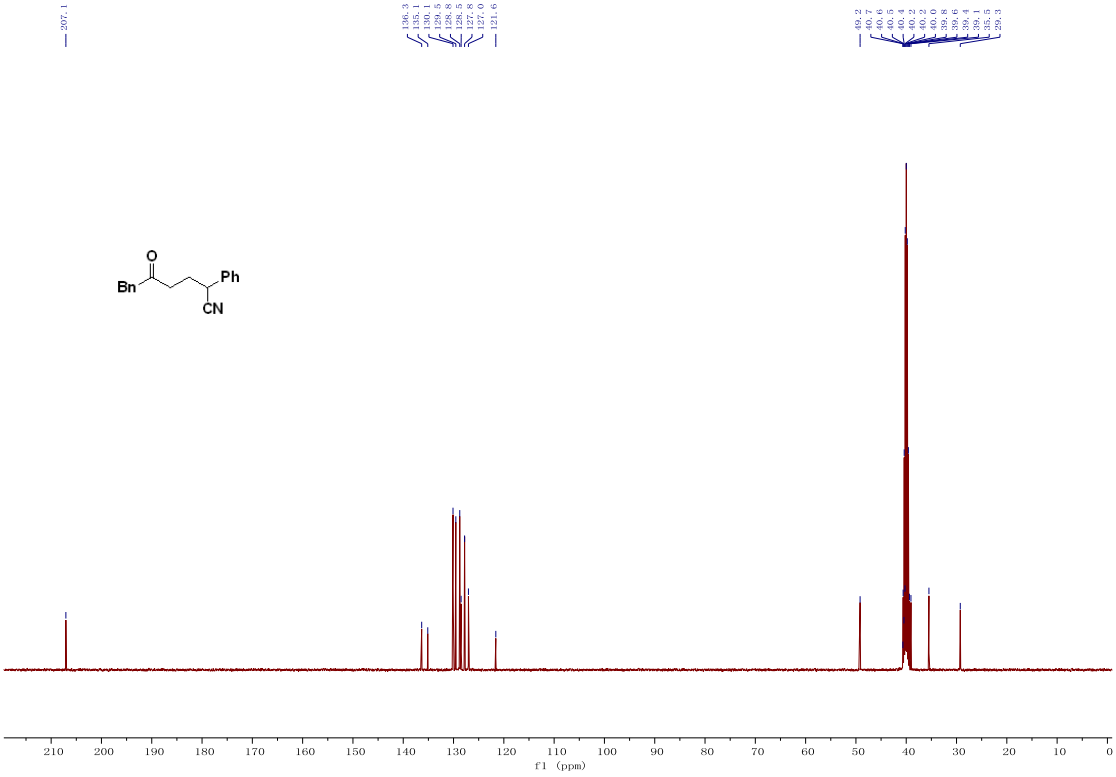
^{1}H and ^{13}C NMR of compound **7i**



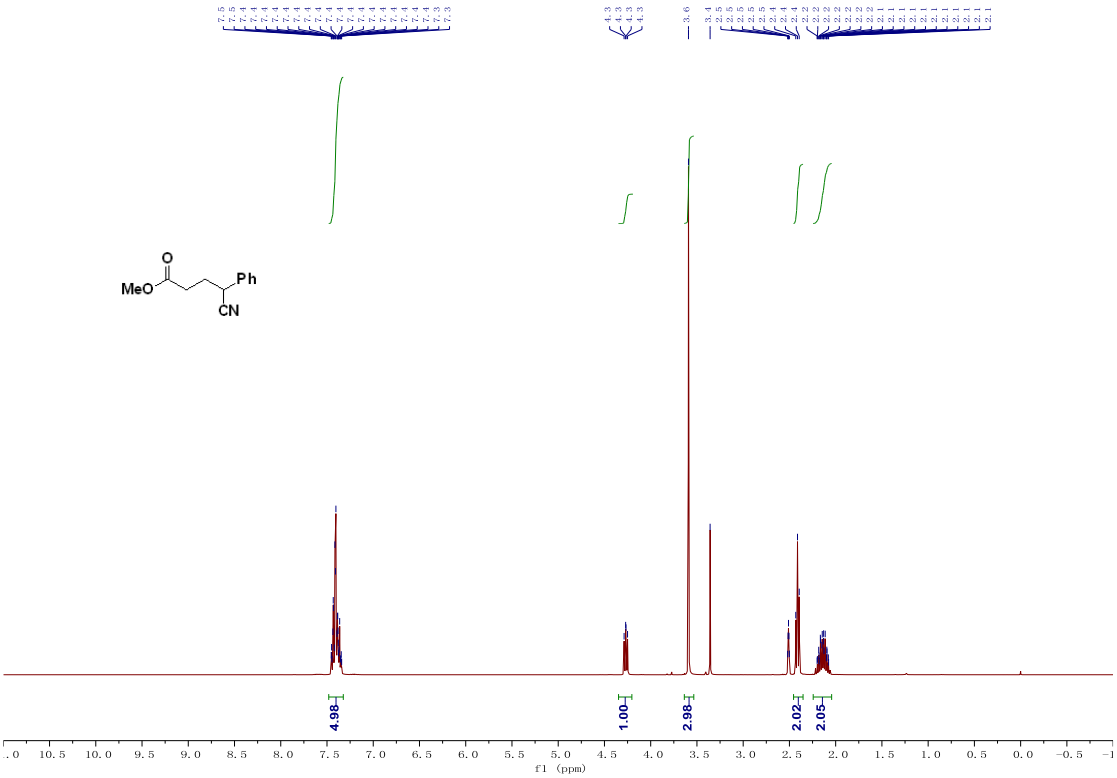


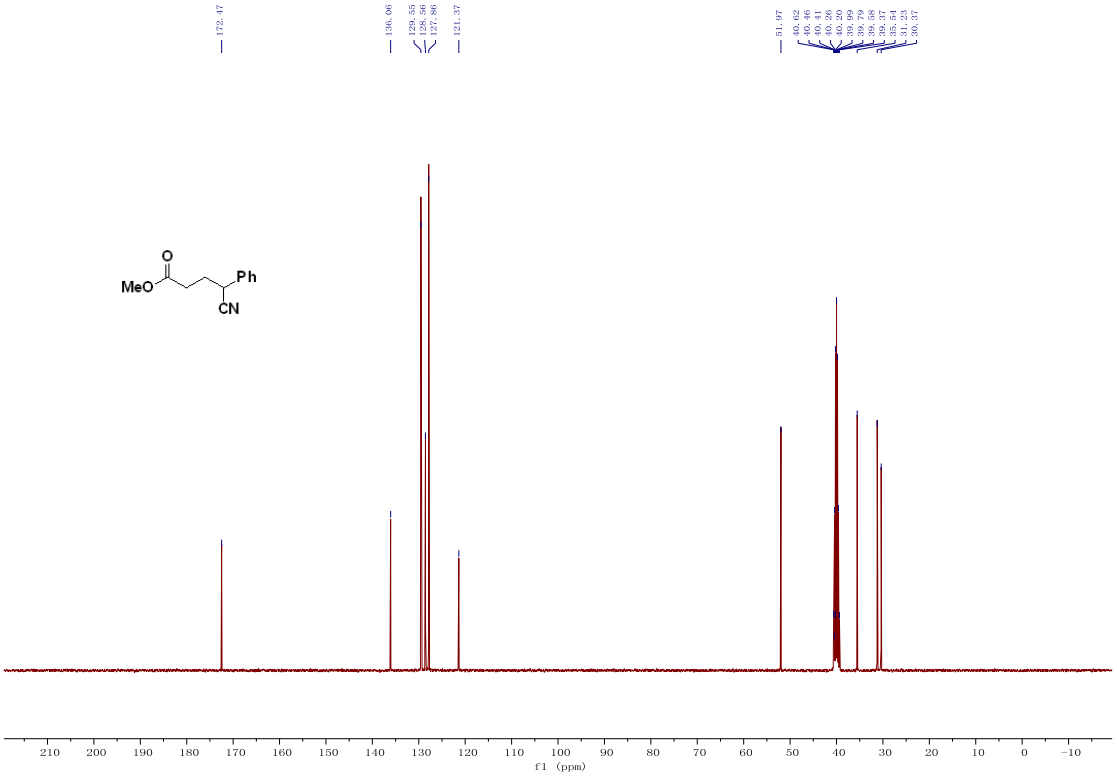
^{1}H and ^{13}C NMR of compound **8**



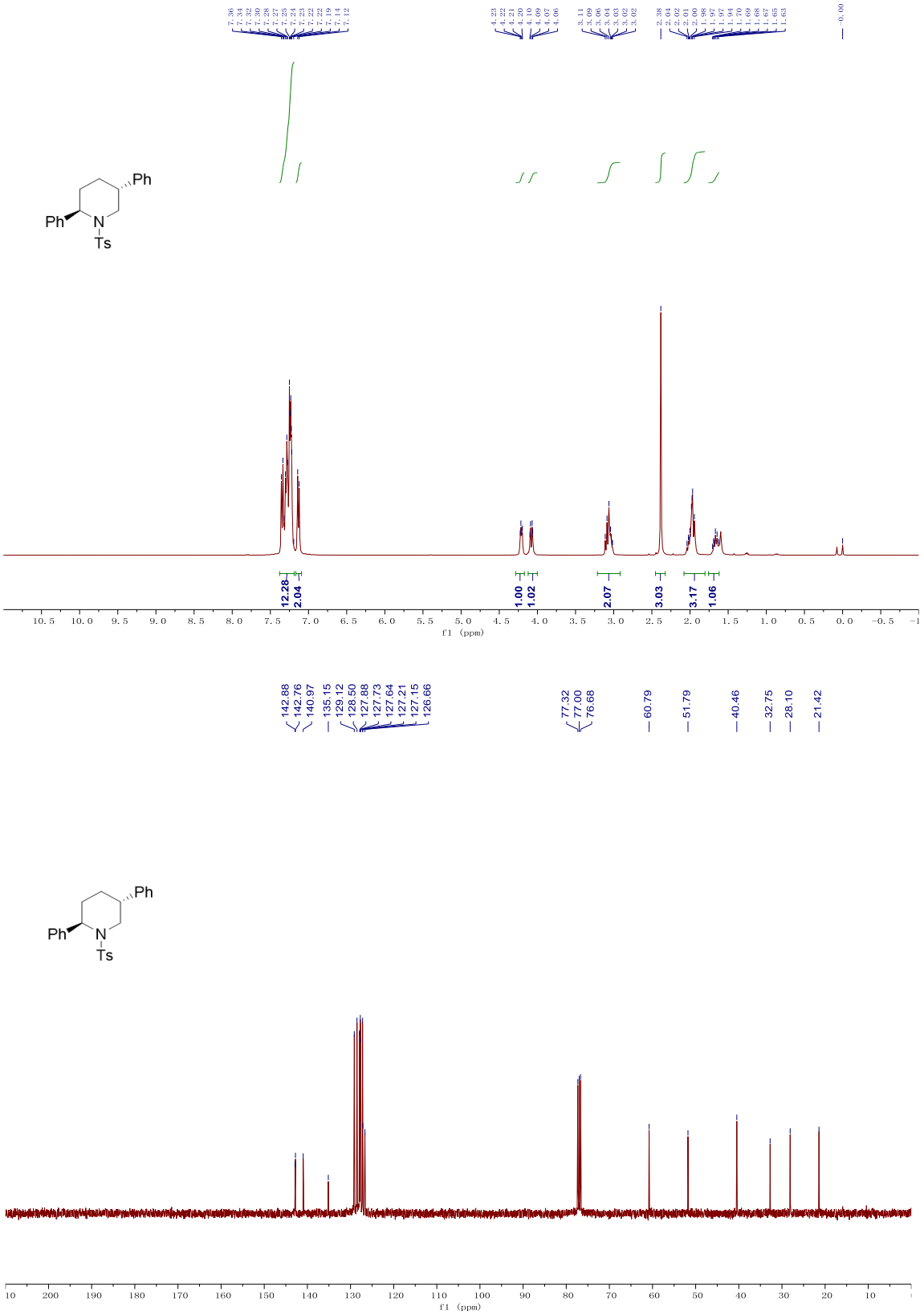


^{1}H and ^{13}C NMR of compound **9**

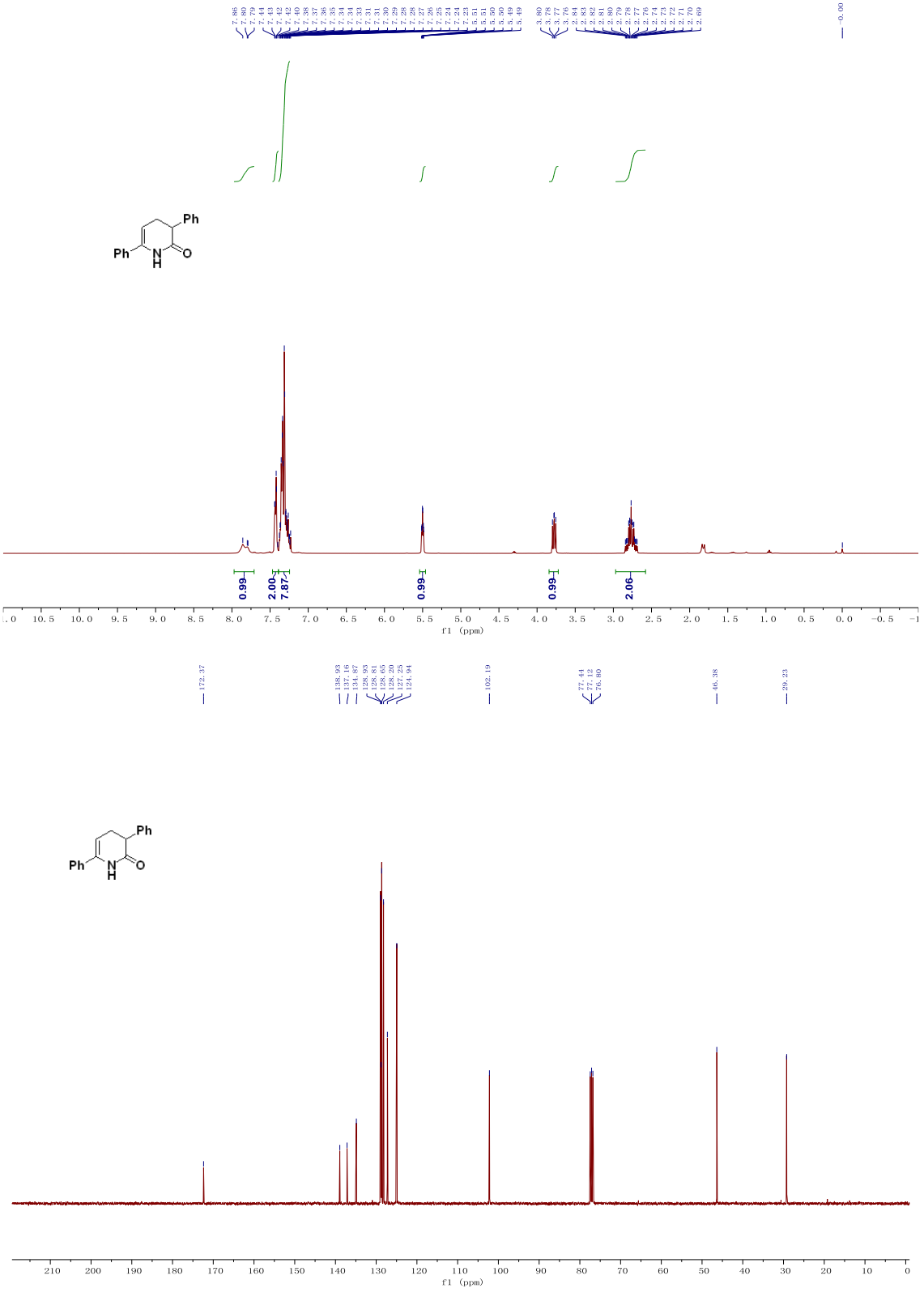




^{1}H and ^{13}C NMR of compound **10a**



^{1}H and ^{13}C NMR of compound **10b**

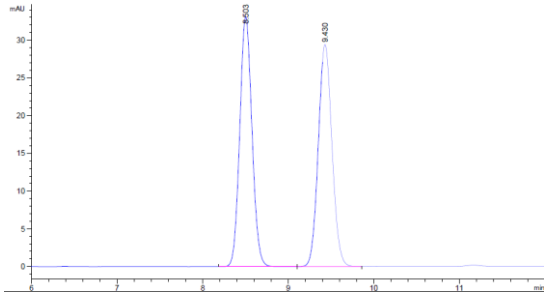


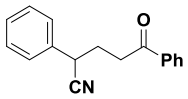
9. Copies of HPLC Spectra

Chiral HPLC spectrum of racemic 3a

(Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C,

t_R (major) = 8.50 min, t_R (minor) = 9.43 min)



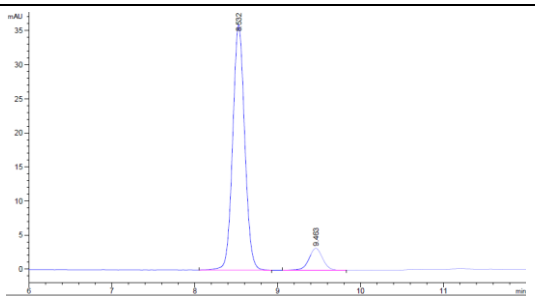


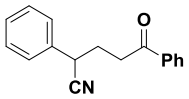
racemic 3a

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.503	BB	0.1556	328.17474	33.11584	50.1666
2	9.430	BB	0.1732	325.99469	29.43109	49.8334

Chiral HPLC spectrum of chiral 3a

$[\alpha]_D^{25}$ = -0.91 (c = 0.98 in $CHCl_3$)





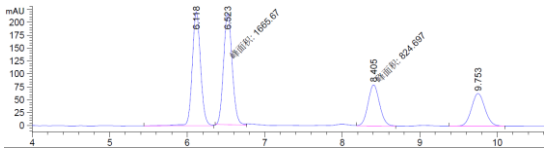
chiral 3a

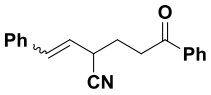
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.532	BB	0.1551	361.60907	36.01597	90.8381
2	9.463	BB	0.1750	36.47187	3.20037	9.1619

Chiral HPLC spectrum of racemic 5b

(Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C,

t_R (major) = 6.52 min, 8.41 min, t_R (minor) = 6.12 min, 9.75min)



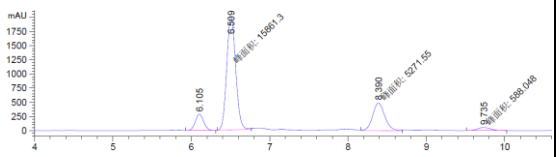


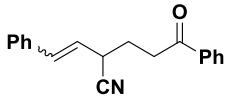
racemic 5b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.118	BV	0.1151	1645.58997	220.53731	33.6756
2	6.523	MM	0.1289	1665.67285	215.35829	34.0866
3	8.405	MM	0.1728	824.69739	79.56264	16.8767
4	9.753	BB	0.1855	750.63397	62.76193	15.3611

Chiral HPLC spectrum of chiral 5b

$[\alpha]_D^{25}$ = -0.83 (c = 1.0 in $CHCl_3$)



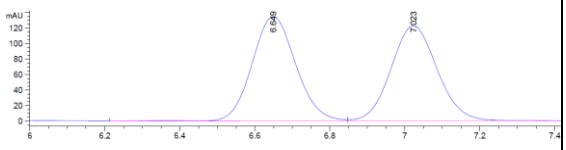


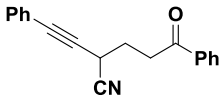
chiral 5b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.105	BB	0.1140	2110.49243	286.26221	8.8559
2	6.509	MM	0.1317	1.58613e4	2007.94373	66.5564
3	8.390	MM	0.1799	5271.55176	488.47827	22.1202
4	9.735	MM	0.1923	588.04791	50.97087	2.4675

Chiral HPLC spectrum of racemic 5e

(Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C, t_R (major) = 6.65 min, t_R (minor) = 7.02 min)



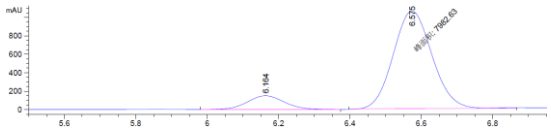


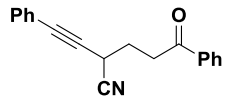
racemic 5e

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.649	VV R	0.1262	1090.61487	135.06433	50.8930
2	7.023	VB	0.1321	1052.34277	122.63476	49.1070

Chiral HPLC spectrum of chiral 5e

$[\alpha]_D^{25}$ = -1.26 (c = 1.0 in $CHCl_3$)





chiral 5e

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.164	BB	0.1112	1057.82129	148.30142	11.7010
2	6.575	MM	0.1254	7982.62598	1060.86011	88.2990