Electronic Supplementary Material (ESI) for ChemComm.

Access to Polysubstituted Indoles or Benzothiophenes via Palladium-Catalyzed Cross-Coupling of Furfural Tosylhydrazones with 2-Iodoanilines or 2-Iodothiophenols

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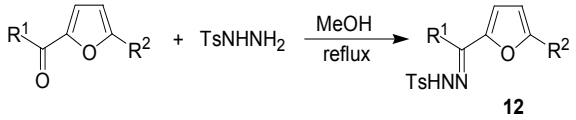
General Experimental details

IR spectra were recorded with FT-IR as a thin film or using KBr pellets and are expressed in cm^{-1}. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in Hz; splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet). Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer. Mass spectra were obtained from high resolution ESI mass spectrometer. All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (100-200 Mesh) using petroleum ether and ethyl acetate as the eluent.

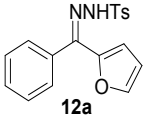
General procedures of tosylhydrazones 12:

p-Tosylhydrazide (939 mg, 5.05 mmol) was added to a solution of 2-acyl-furans (5 mmol) in methanol (10 mL). The mixture was reflux for 12 h. The solution was then cooled to room temperature, and the crude products could be obtained as precipitates. The precipitates were washed by petroleum ether then removed in vacuo to afford the pure products **12**.



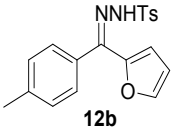
Characterization of 12

N'-(Furan-2-yl(phenyl)methylene)-4-methylbenzenesulfonohydrazide (12a)



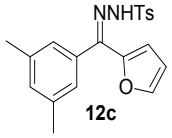
Yellow solid (1.62 g, 95%), mp 144-145 ℃; IR (KBr) 3316, 3046, 1632, 1449, 1340, 1163, 1104, 619, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 6.9 Hz, 2H), 7.48-7.50 (m, 4H), 7.34-7.26 (m, 3H), 7.22-7.20 (m, 2H), 6.36 (br, 1H), 6.26 (br, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 145.7, 144.6, 144.1, 135.5, 130.5, 129.7, 128.3, 128.2, 128.1, 128.0, 113.8, 111.5, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{16}N_2NaO_3S$: $[M + Na]^+$ 363.0779, found: 363.0776.

N'-(Furan-2-yl(p-tolyl)methylene)-4-methylbenzenesulfonohydrazide (12b)



Yellow solid (1.68 g, 95%), mp 140-141 ℃; IR (KBr) 3398, 3046, 2908, 1621, 1454, 1345, 1107, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.38-7.30 (m, 5H), 7.16 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 3.1 Hz, 1H), 6.54 (d, J = 3.1 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 144.3, 144.0, 139.8, 135.6, 133.3, 130.3, 129.6, 128.9, 128.7, 128.1, 116.5, 111.6, 21.6, 21.3; HRMS (ESI) m/z calcd for $C_{19}H_{18}N_2NaO_3S$: $[M + Na]^+$ 377.0936, found: 377.0930.

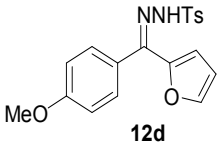
N'-((3,5-Dimethylphenyl)(furan-2-yl)methylene)-4-methylbenzenesulfonohydrazide (12c)



12c

Yellow solid (1.66 g, 90%), mp 148-149 ℃; IR (KBr) 3452, 2916, 1635, 1452, 1109, 619 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 7.83-7.70 (m, 3H), 7.41 (d, J = 7.8 Hz, 2H), 7.15 (s, 1H), 6.88 (s, 2H), 6.50 (d, J = 2.5 Hz, 1H), 6.25 (d, J = 2.5 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 150.9, 146.2, 144.9, 143.2, 137.8, 136.2, 131.1, 131.0, 129.4, 127.7, 126.1, 113.4, 111.7, 21.0, 20.9; HRMS (ESI) m/z calcd for $C_{20}H_{20}N_2NaO_3S$: $[M + Na]^+$ 391.1092, found: 391.1087.

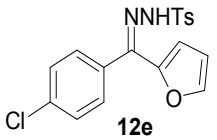
N'-(Furan-2-yl(4-methoxyphenyl)methylene)-4-methylbenzenesulfonohydrazide (12d)



12d

Yellow solid (1.92 g, 93%), mp 180-181 ℃; IR (KBr) 3372, 3046, 1512, 1455, 1339, 1166, 587 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 1.3 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 3.2 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 147.2, 144.3, 144.0, 141.5, 135.6, 130.1, 129.6, 128.6, 128.1, 116.5, 113.6, 111.6, 55.4, 21.6; HRMS (ESI) m/z calcd for $C_{19}H_{18}N_2NaO_4S$: $[M + Na]^+$ 393.0885, found: 393.0879.

N'-((4-Chlorophenyl)(furan-2-yl)methylene)-4-methylbenzenesulfonohydrazide (12e)

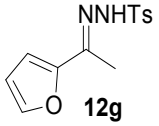


12e

Yellow solid (1.68 g, 90%), mp 170-171 ℃; IR (KBr) 3329, 3050, 1632, 1489, 1344, 1165, 1102, 974, 835, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.89 (d, J = 7.4 Hz, 2H), 7.65 (s, 1H), 7.47-7.31 (m, 6H), 6.59 (br, 1H), 6.56 (br, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 144.6, 144.2, 140.1, 135.8, 135.5, 134.6, 130.0, 129.6, 128.5, 128.1, 116.6, 111.7, 21.6; HRMS (ESI) m/z calcd for $C_{18}H_{15}ClN_2NaO_3S$: $[M + Na]^+$ 397.0390,

found: 397.0384.

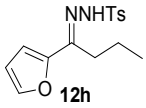
N'-(1-(Furan-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (12g)



12g

Yellow solid (1.36 g, 98%), mp 154-155 ℃; IR (KBr) 3045, 1607, 1454, 1338, 1165, 1021, 904, 814, 749, 704, 552 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.43 (s, 1H), 7.32 (d, J = 7.8 Hz, 2H), 6.69 (d, J = 2.3 Hz, 1H), 6.41 (d, J = 2.3 Hz, 1H), 2.41 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 145.0, 144.2, 143.8, 135.4, 129.6, 128.1, 111.7, 110.3, 21.6, 12.6; HRMS (ESI) m/z calcd for $C_{13}H_{14}N_2NaO_3S$: $[M + Na]^+$ 301.0623, found: 301.0617.

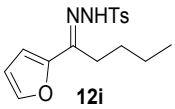
N'-(1-(Furan-2-yl)butylidene)-4-methylbenzenesulfonohydrazide (12h)



12h

Yellow solid (1.5 g, 98%), mp 117.1-117.2 ℃; IR (KBr) 3465, 3044, 1578, 1487,1460, 1376, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.56 (s, 0.8H), 7.43 (s, 0.2H), 7.30-7.26 (m, 2H), 6.70 (d, J = 2.8 Hz, 1H), 6.51 (d, J = 2.8 Hz, 0.8H), 6.41 (br, 0.2H), 2.47 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 1.60-1.52 (m, 2H), 0.93 (t, J = 7.6 Hz, 0.6H), 0.84 (t, J = 7.6 Hz, 2.4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.8, 141.6, 129.9, 129.4, 128.0, 36.3, 21.6, 20.7, 13.6; HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2NaO_3S$: $[M + Na]^+$ 329.0936, found: 329.0935.

N'-(1-(Furan-2-yl)pentylidene)-4-methylbenzenesulfonohydrazide (12i)

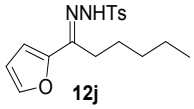


12i

Yellow solid (1.57 g, 98%), mp 140.4-140.5 ℃; IR (KBr) 3463, 3033, 1594, 1489, 1453, 1386, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 2.8 Hz, 1H), 6.39 (br, J = 2.8 Hz, 1H), 2.50 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.48-1.41 (m, 2H), 1.34-1.25 (m, 2H), 0.83 (J = 7.6 Hz, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 151.3, 148.8, 144.1, 143.7, 135.4, 129.6, 128.0, 111.6, 110.2, 28.0, 26.5, 22.7, 21.6, 13.8; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_2NaO_3S$: $[M + Na]^+$ 343.1092, found: 343.1090.

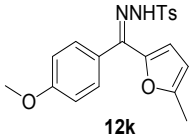
N'-(1-(Furan-2-yl)hexylidene)-4-methylbenzenesulfonohydrazide (12j)



12j

White solid (1.60 g, 96%), mp 89-90 ℃; IR (KBr) 3046, 1567, 1454, 1362, 1107, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.52 (d, J = 2.0 Hz, 0.6H), 7.49 (d, J = 2.0 Hz, 0.4H), 7.43-7.28 (m, 2H), 6.69 (d, J = 3.2 Hz, 0.6H), 6.67 (d, J = 3.2 Hz, 0.4H), 6.51-6.50 (dd, J = 3.2, 2.0 Hz, 0.6H), 6.40 (dd, J = 3.2, 2.0 Hz, 0.4H), 2.5-2.44 (m, 2H), 2.41 (s, 3H), 1.57-1.43 (m, 2H), 1.30-1.14 (m, 4H), 0.85-0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.8, 141.8, 135.7, 129.4, 128.1, 114.1, 111.5, 110.2, 34.4, 31.2, 27.1, 25.6, 22.4, 13.9; HRMS (ESI) m/z calcd for $C_{17}H_{22}N_2NaO_3S$: $[M + Na]^+$ 357.1249, found: 357.1243.

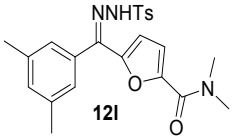
N'-((4-Methoxyphenyl)(5-methylfuran-2-yl)methylene)-4-methylbenzenesulfonohydrazide (12k)



12k

Yellow solid (1.69 g, 88%), mp 159-160 ℃; IR (KBr) 3315, 3045, 2949, 1508, 1454, 1343, 1253, 1167, 1025, 552 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.13 (d, J = 3.1 Hz, 1H), 5.98 (d, J = 3.1 Hz, 1H), 3.88 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 155.2, 149.4, 146.0, 144.0, 135.6, 130.0, 129.6, 128.0, 121.6, 115.6, 114.9, 107.9, 55.4, 21.61, 14.0; HRMS (ESI) m/z calcd for $C_{20}H_{20}N_2NaO_4S$: $[M + Na]^+$ 407.1041, found: 407.1036.

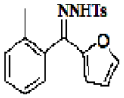
5-((3,5-Dimethylphenyl)(2-tosylhydrazono)methyl)-N,N-dimethylfuran-2-carboxamide (12l)



12l

Yellow solid (1.75 g, 80%), mp 121-122 ℃; IR (KBr) 3451, 1629, 1438, 1109, 619 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 10.72 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.17 (s, 1H), 7.00 (d, J = 3.6 Hz, 1H), 6.94 (s, 2H), 6.38 (d, J = 3.6 Hz, 1H), 3.18 (s, 3H), 2.98 (s, 3H), 2.40 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 158.6, 151.6, 148.3, 145.3, 143.4, 137.8, 135.9, 131.3, 130.5, 129.3, 127.7, 126.2, 117.1, 113.6, 38.6, 38.4, 21.0, 20.8; HRMS (ESI) m/z calcd for $C_{23}H_{25}N_3NaO_4S$: $[M + Na]^+$ 462.1463, found: 462.1458.

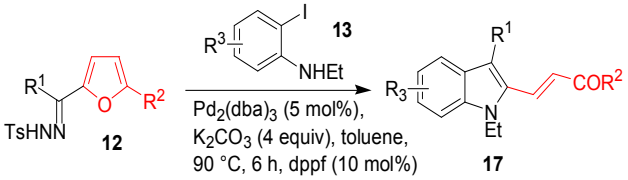
N'-(furan-2-yl(o-tolyl)methylene)-4-methylbenzenesulfonohydrazide(12m)



12m

Yellow solid (1.52 g, 86%), mp 154.0-154.1℃; IR (KBr) 3459, 3022, 1481, 1458, 758 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 7.86 (d, J = 7.6 Hz, 2H), 7.50 (s, 1H), 7.42-7.29 (m, 6H), 6.97 (d, J = 7.6 Hz, 2H), 6.38 (d, J = 2.0 Hz, 1H), 6.22 (J = 2.0 Hz, 1H), 2.45 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 150.4, 146.1, 144.7, 144.1, 136.6, 135.5, 131.2, 130.6, 129.6, 129.2, 128.2, 127.9, 126.9, 113.5, 111.5; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O_3$: $[M + H]^+$355.1111, found: 355.1114.

General procedure for the synthesis of indoles 17

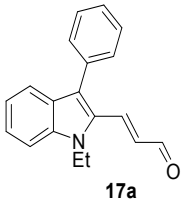


$Pd_2(dba)_3$ (23 mg, 0.025 mmol), dppf (28 mg, 0.05 mmol), K_2CO_3 (276 mg, 2.0 mmol), and **12** (1.0 mmol) were suspended in toluene (3 mL) in a Schlenk tube under nitrogen, and **13** (0.50 mmol) was added. The mixture was stirred at 90 °C for 6 h, cooled to room temperature, and filtered through a short column of silica gel (ethyl acetate). The solvent was removed in vacuo, and the crude residue was purified by column chromatography (ethyl

acetate/petroleum ether = 1:10) to give **17**.

Characterization of 17

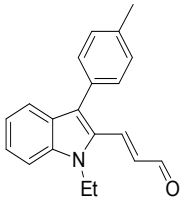
(E)-3-(1-Ethyl-3-phenyl-1H-indol-2-yl)acrylaldehyde (17a, E/Z*>99:1*)



17a

Yellow oil (104 mg, 76%), IR (film) 3128, 1673, 1608, 1534, 1451, 1399, 1118, 1009, 967, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 16.3 Hz, 1H), 7.54-7.35 (m, 7H), 7.16-7.13 (m, 1H), 6.50 (dd, J = 16.3, 7.5 Hz, 1H), 4.41 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 140.9, 138.9, 133.8, 130.5, 129.6, 128.8, 127.6, 127.4, 127.2, 125.6, 125.5, 121.1, 120.9, 109.7, 39.3, 15.4; HRMS (ESI) m/z calcd for $C_{19}H_{17}NNaO$: $[M + Na]^+$ 298.1208, found: 298.1202.

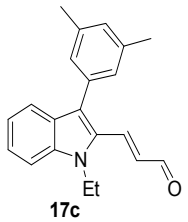
(E)-3-(1-Ethyl-3-(p-tolyl)-1H-indol-2-yl)acrylaldehyde (17b, E/Z*=95:5*)



17b

Yellow oil (112 mg, 78%), IR (film) 3122, 1673, 1605, 1401, 1399, 1118, 1013, 963, 745, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 16.3 Hz, 1H), 7.39-7.35 (m, 2H), 7.34-7.29 (m, 4H), 7.13 (dd, J = 8.0, 6.4 Hz, 1H), 6.50 (dd, J = 16.3, 7.6 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 141.1, 139.0, 137.4, 130.8, 130.3, 129.6, 129.5, 127.2, 127.2, 125.7, 125.6, 121.2, 120.8, 109.7, 39.2, 21.3, 15.4; HRMS (ESI) m/z calcd for $C_{20}H_{19}NNaO$: $[M + Na]^+$ 312.1364, found: 312.1359.

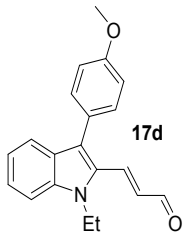
(E)-3-(3-(3,5-Dimethylphenyl)-1-ethyl-1H-indol-2-yl)acrylaldehyde (17c, E/Z*>99:1*)



17c

Yellow oil (125 mg, 83%), IR (film) 2979, 2920, 2729, 1726, 1670, 1117, 743 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 12.6 Hz, 2H), 7.58 (s, 1H), 7.38-7.36 (m, 2H), 7.14 (t, J = 7.2 Hz, 1H), 7.07 (s, 2H), 6.51 (dd, J = 16.3, 7.6 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 2.39 (s, 6H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 141.3, 138.9, 138.4, 133.6, 129.6, 129.3, 128.3, 127.2, 127.0, 126.1, 125.6, 121.3, 120.8, 109.6, 39.3, 21.4, 15.4; HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO$: $[M + Na]^+$ 326.1521, found: 326.1515.

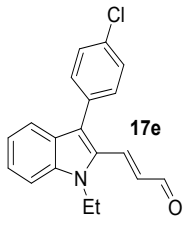
(E)-3-(1-Ethyl-3-(4-methoxyphenyl)-1H-indol-2-yl)acrylaldehyde (17d, E/Z*>99:1*)



17d

Yellow oil (117 mg, 77%), IR (film), 2975, 1656, 1246, 1018, 971, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.62-7.57 (m, 1H), 7.45-7.37 (m, 4H), 7.17 (ddd, J = 8.0, 6.4, 1.5 Hz, 1H), 7.10-7.06 (m, 2H), 6.54 (dd, J = 16.3, 7.5 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 3.92 (s, 3H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 159.2, 141.0, 138.9, 131.6, 129.5, 127.3, 127.0, 126.0, 125.6, 125.5, 121.2, 120.8, 114.4, 109.6, 55.4, 39.2, 15.4; HRMS (ESI) m/z calcd for $C_{20}H_{19}NNaO_2$: $[M + Na]^+$ 328.1313, found: 328.1308.

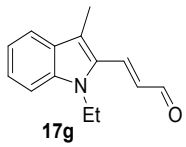
(E)-3-(3-(4-Chlorophenyl)-1-ethyl-1H-indol-2-yl)acrylaldehyde (17e, E/Z*=97:3*)



17e

Yellow oil (92 mg, 60%), IR (film) 2972, 1725, 1674, 1527, 1481, 1284, 1093, 967, 838, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, J = 7.5 Hz, 1H), 7.59-7.46 (m, 4H), 7.43-7.36 (m, 4H), 7.20-7.11 (m, 1H), 6.50 (dd, J = 16.3, 7.5 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 140.3, 138.8, 133.6, 132.3, 131.7, 129.6, 129.2, 127.8, 127.0, 125.7, 123.8, 121.2, 120.8, 109.8, 39.3, 15.4; HRMS (ESI) m/z calcd for $C_{19}H_{16}ClNNaO$: $[M + Na]^+$ 332.0818, found: 332.0813.

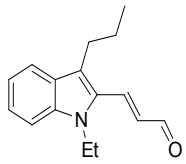
(E)-3-(1-Ethyl-3-methyl-1H-indol-2-yl)acrylaldehyde (17g, E/Z=98:2)



17g

Yellow oil (89 mg, 84%), IR (film) 2904, 1670, 1400, 1012, 941, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, J = 7.5 Hz, 1H), 7.63-7.59 (m, 2H), 7.34-7.29 (m, 2H), 7.14-7.11 (m, 1H), 6.62 (dd, J = 16.0, 7.5 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.50 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 140.0, 138.4, 128.6, 128.2, 127.5, 125.2, 120.3, 120.0, 119.0, 109.5, 38.5, 15.5, 10.7; HRMS (ESI) m/z calcd for $C_{14}H_{15}NNaO$: $[M + Na]^+$ 236.1051, found: 236.1046.

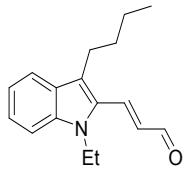
(E)3-(1-Ethyl-3-propyl-1H-indol-2-yl)-propenal (17h, E/Z>99:1)



17h

Yellow oil (74 mg, 61%), IR (film) 2857, 2719, 1676, 1457, 1421, 1345, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 16.0 Hz, 1H), 7.32 (br, 2H), 7.13-7.11 (m, 1H), 6.57 (dd, J = 16.0, 7.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 1.73-1.67 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 140.1, 138.8, 129.5, 127.7, 126.7, 125.2, 124.8, 120.5, 120.0, 109.6, 38.8, 27.1, 24.2, 15.4, 14.2, HRMS (ESI) m/z calcd for $C_{16}H_{19}NNaO$: $[M + Na]^+$ 264.1359, found: 264.1359.

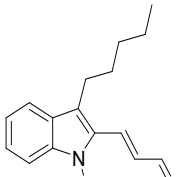
3-(3-Butyl-1-ethyl-1H-indol-2-yl)-propenal (17i, E/Z*>99:1*)



17i

Yellow oil (91 mg, 72%), IR (film) 2857, 2719, 1676, 1457, 1421, 1345, 741 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.31 (br, 2H), 7.14-7.11 (m, 1H), 6.58 (dd, J = 16.0, 7.6 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 1.66-1.62 (m, 2H), 1.45-1.37 (m, 5H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 138.8, 129.4, 127.7, 126.7, 125.3, 125.0, 120.5, 120.0, 109.6, 38.8, 33.2, 25.0, 22.9, 15.4, 14.0; HRMS (ESI) m/z calcd for $C_{16}H_{19}NNaO$: $[M + Na]^+$278.1515, found: 278.1520.

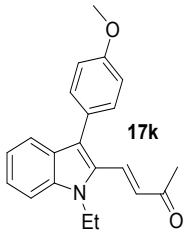
(E)-3-(1-Ethyl-3-pentyl-1H-indol-2-yl)acrylaldehyde (17j, E/Z*=95:5*)



17j

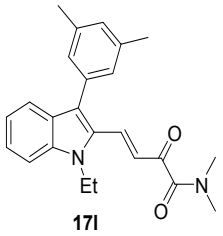
Yellow oil (115 mg, 86%), IR (film) 2929, 1672, 1609, 1524, 1455, 1141, 970, 814, 742, 703, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 16.2 Hz, 1H), 7.32 (d, J = 3.8 Hz, 2H), 7.15-7.11 (m, 1H), 6.57 (dd, J = 16. 2, 7.5 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.06-2.85 (m, 2H), 1.66 (t, J = 7.2 Hz, 3H), 1.44-1.35 (m, 6H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 140.1, 138.8, 129.4, 129.0, 127.6, 126.7, 125.2, 120.5, 120.0, 109.6, 38.8, 31.9, 30.7, 25.2, 22.6, 15.4, 14.1; HRMS (ESI) m/z calcd for $C_{18}H_{23}NNaO$: $[M + Na]^+$ 292.1677, found: 292.1672.

(E)-4-(1-Ethyl-3-(4-methoxyphenyl)-1H-indol-2-yl)but-3-en-2-one (17k, E/Z*>75:25*)



Yellow oil (86 mg, 54%), IR (film) 2905, 1662, 1586, 1401, 1248, 1026, 966, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 16.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.40-7.37 (m, 2H), 7.35-7.30 (m, 1H), 7.17-7.09 (m, 2H), 7.06-7.01 (m, 2H), 6.49 (d, J = 16.5 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 2.26 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 159.0, 138.4, 132.0, 131.5, 130.7, 129.8, 127.5, 126.6, 126.4, 124.8, 123.5, 120.8, 114.3, 109.6, 55.4, 39.0, 27.7, 15.5; HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO_2$: $[M + Na]^+$ 342.1470, found: 342.1464.

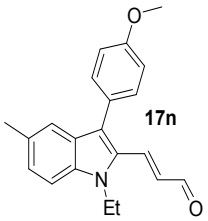
(E)-4-(3-(3,5-Dimethylphenyl)-1-ethyl-1H-indol-2-yl)-N,N-dimethyl-2-oxobut-3-enamide (17l, E/Z*>99:1*)



17l

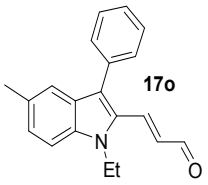
Yellow oil (106 mg, 57%), IR (film) 2917, 1740, 1568, 1137, 1016, 919, 747, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 16.7 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.42-7.38 (m, 2H), 7.19-7.05 (m, 4H), 6.71 (d, J = 16.7 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 3.03 (s, 3H), 3.01 (s, 3H), 2.42 (s, 6H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 167.2, 139.2, 138.2, 136.9, 133.6, 129.7, 129.2, 128.3, 127.1, 126.8, 125.7, 121.6, 121.4, 120.8, 109.7, 39.3, 37.2, 34.3, 21.4, 15.4; HRMS (ESI) m/z calcd for $C_{24}H_{26}N_2NaO_2$: $[M + Na]^+$ 397.1892, found: 397.1886.

(E)-3-(1-Ethyl-3-(4-methoxyphenyl)-5-methyl-1H-indol-2-yl)acrylaldehyde (17n, E/Z*=94:6*)



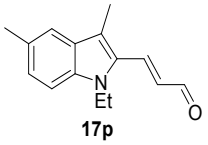
Yellow oil (86 mg, 54%), IR (film) 2972, 1605, 1462, 1384, 1279, 1249, 1158, 1090, 993, 876, 824, 681, 637, 587, 556, 478 cm^{-1}; H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 16.3 Hz, 1H), 7.39-7.35 (m, 3H), 7.29 (d, *J* = 8. 6 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.48 (dd, *J* = 16.3, 7.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 2.41 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 159.2, 141.2, 137.5, 131.6, 130.3, 129.6, 127.5, 126.7, 126.2, 125.2, 125.0, 120.4, 114.4, 109.4, 55.4, 39.2, 21.4, 15.4; HRMS (ESI) m/z calcd for $C_{21}H_{22}NO_2$: $[M + H]^+$ 320.1651, found: 320.1659.

(E)-3-(1-Ethyl-5-methyl-3-phenyl-1H-indol-2-yl)acrylaldehyde (17o, E/Z*=80:20*)



Yellow oil (72 mg, 50%), IR (film) 2977, 1739, 1673, 1564, 1534, 1454, 1313, 1121, 986, 797, 699, 592 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 7. 6 Hz, 1H), 7.55 (d, *J* = 16.3 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.47-7.38 (m, 4H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.21 (dd, *J* = 8.5, 1.3 Hz, 1H), 6.48 (dd, *J* = 16.3, 7.6 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 141.1, 137.5, 134.0, 130.5, 130.4, 129.6, 128.8, 127.5, 127.5, 127.4, 127.0, 125.1, 120.4, 109.4, 39.3, 21.4, 15.4; HRMS (ESI) m/z calcd for $C_{20}H_{20}NO$: $[M + H]^+$ 290.1545, found: 290.1553.

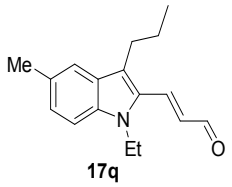
(E)-3-(1-Ethyl-3,5-dimethyl-1H-indol-2-yl)-propenal (17p, E/Z*>99:1*)



Yellow oil (85 mg, 75%), IR (film) 2852, 2725, 1651,1460, 1429, 834, 791, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 9.66 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.40 (s, 1H),

7.22-7.14 (m, 2H), 6.60 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 3H), 1.46 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 140.1, 137.0, 129.8, 129.3, 128.3, 127.1, 127.0, 119.6, 118.6, 109.3, 38.6, 21.4, 15.5, 10.7；HRMS (ESI) m/z calcd for $C_{15}H_{17}NNaO$: $[M + Na]^+$ 250.1202, found: 250.1211.

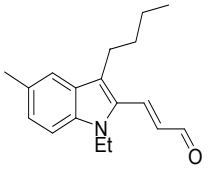
(E)-3-(1-Ethyl-5-methyl-3-propyl-1H-indol-2-yl)-propenal (17q, , E/Z*=96:4*)



17q

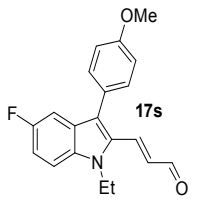
Yellow oil (91 mg, 71%), IR(film) 2851, 2750, 1662, 1468, 1423, 1374, 867, 791, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 16.6 Hz, 1H), 7.41 (s, 1H), 7.20-7.14 (m, 2H), 6.55 (dd, *J* = 16.6, 7.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 1.72-1.66 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 140.2, 137.4, 129.6, 129.3, 127.9, 127.2, 126.3, 124.4, 119.8, 109.3, 38.9, 27.1, 24.2, 21.4, 15.4, 14.3; HRMS (ESI) m/z calcd for $C_{17}H_{21}NNaO$: $[M + Na]^+$ 278.1515, found: 278.1515.

3-(3-Butyl-1-ethyl-5-methyl-1H-indol-2-yl)-propenal (17r, E/Z*=99:1*)



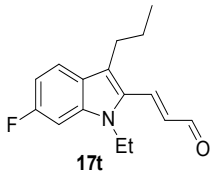
Yellow oil (104.9 mg, 78%), IR (film) 2903, 2718, 1687,1455, 1432, 844, 786, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 16.0 Hz, 1H), 7.40 (s, 1H), 7.20-7.12 (m, 2H), 6.54 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 1.64-1.61 (m, 2H), 1.45-1.34 (m, 5H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 140.2, 137.4, 129.5, 129.3, 127.8, 127.2, 126.3, 124.6, 119.8, 109.4, 38.8, 33.2, 25.0, 22.9, 21.5, 15.4, 14.1; HRMS (ESI) m/z calcd for $C_{18}H_{24}NO$: $[M + H]^+$ 270.1858, found: 270.1850.

(E)-3-(1-Ethyl-5-fluoro-3-(4-methoxyphenyl)-1H-indol-2-yl)acrylaldehyde (17s, E/Z*>99:1*)



Yellow oil (100 mg, 67%), IR (film), 2932, 1650, 1236, 1012, 973,820, 680, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 16.3 Hz, 1H), 7.35-7.32 (m, 3H), 7.25-7.22 (m, 1H), 7.14 – 7.03 (m, 3H), 6.50 (dd, *J* = 16.3, 7.5 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 159.3, 140.6, 135.4, 131.4, 131.3, 130.8, 127.7, 125.6, 114.5, 114.2, 110.6, 110.5, 105.6, 105.3, 55.4, 39.4, 15.5; HRMS (ESI) m/z calcd for $C_{20}H_{19}FNO_2$: $[M + H]^+$ 324.1400, found: 324.1388.

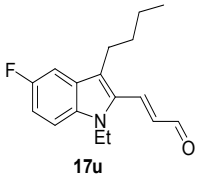
3-(1-Ethyl-6-fluoro-3-propyl-1H-indol-2-yl)-propenal (17t, E/Z>99:1)



17t

Yellow oil (67.34 mg, 52%), IR (film) 2917, 2851, 1675, 1486, 1469, 1370, 850, 796, 751, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.26-7.30 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 1H), 6.60 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.30 (q, *J* = 7.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.73-1.68 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.03 (*J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 139.7, 135.3, 130.8, 127.5, 123.9, 114.1, 113.8, 110.5, 110.4, 104.9, 104.7, 39.0, 27.1, 24.0, 15.4, 14.2; HRMS (ESI) m/z calcd for $C_{16}H_{17}FNO$: $[M - H]^-$ 258.1300, found: 258.1133.

3-(3-Butyl-1-ethyl-5-fluoro-1H-indol-2-yl)-propenal (17u, E/Z>99:1)

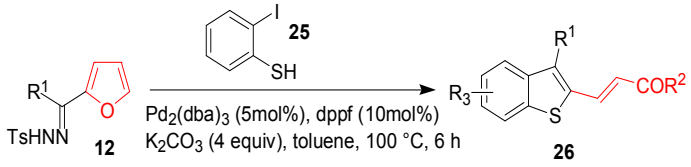


17u

Yellow oil (65.5 mg, 48%), IR (film) 2912, 2732, 1690,1439, 1422, 825, 773, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 9.71 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 16.4 Hz, 1H), 7.29-7.25 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 1H), 6.60 (dd, *J* = 16.4, 7.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H),

2.90 (t, J = 7.6 Hz, 2H), 1.68-1.61 (m, 2H), 1.47-1.40 (m, 5H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 157.8, 139.7, 135.3, 130.7, 127.8, 127.5, 124.2, 113.9, 110.5, 104.7, 39.0, 33.0, 25.0, 22.8, 15.4, 14.0; HRMS (ESI) m/z calcd for $C_{17}H_{21}FNO$: $[M + H]^+$ 274.1607, found: 274.1611.

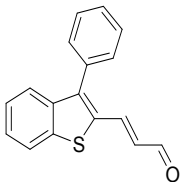
General procedure for the synthesis of thiophenes 26



$Pd_2(dba)_3$ (23 mg, 0.025 mmol), dppf (28 mg, 0.05 mmol), K_2CO_3 (276 mg, 2.0 mmol), and **12** (1.0 mmol) were suspended in toluene (3 mL) in a Schlenk tube under nitrogen, and **25** (0.50 mmol) was added. The mixture was stirred at 100 °C for 6 h, cooled to room temperature, and filtered through a short column of silica gel (ethyl acetate). The solvent was removed in vacuo, and the crude residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to give **26**.

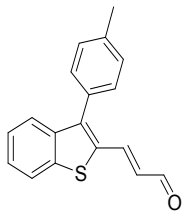
Characterization of 26

3-(3-Phenyl-benzo[b]thiophen-2-yl)-propenal (26a, E/Z > 99:1)



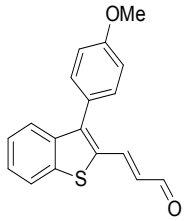
Yellow oil (67.32 mg, 51%), IR (KBr) 3058, 3019, 2852, 2729, 1677, 1468, 1447, 751, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 8.0 Hz, 1H), 8.04-7.97 (m, 1H), 7.64 (br, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.30 (br, 2H), 7.11 (d, J = 16.0 Hz, 1H), 7.03-6.95 (m, 3H), 6.40 (dd, J = 16.0 Hz, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 147.5, 146.7, 138.0, 135.2, 133.8, 133.1, 132.3, 131.5, 129.8, 128.6, 128.2, 128.0, 127.7, 124.1; HRMS (ESI) m/z calcd for $C_{17}H_{11}OS$: $[M - H]^-$ 263.0536, found: 263.0556.

3-(3-p-Tolyl-benzo[b]thiophen-2-yl)-propenal (26b, E/Z > 99:1)



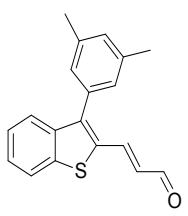
Yellow oil (85 mg, 58%), IR (KBr) 3055, 3026, 2853, 2729, 1676, 1448, 1428, 817, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 8.0 Hz, 1H), 8.0-7.94 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.09-6.92 (m, 5H), 6.36 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 147.8, 136.5, 140.1, 135.5, 135.2, 133.5, 133.1, 131.7, 131.2, 129.4, 128.1, 127.8, 127.7, 123.8, 21.3; HRMS (ESI) m/z calcd for $C_{18}H_{13}OS$: $[M - H]^-$ 277.0693, found: 277.0821.

3-[3-(4-Methoxy-phenyl)-benzo[b]thiophen-2-yl]-propenal (26c, E/Z*>80:20*)



Yellow oil (90 mg, 61%), IR (KBr) 3058, 3006, 2837, 2730, 1675, 1447, 1427, 836, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 8.0 Hz, 0.8H), 9.38 (d, *J* = 8.0 Hz, 0.2H), 8.00-7.94 (m, 0.8H), 7.67-7.41 (m, 3.2H), 7.31-7.20 (m, 0.2H), 7.06-6.91 (m, 3H), 6.80 (d, *J* = 8.8 Hz, 1.6H), 6.35 (dd, *J* = 15.2 Hz, 8.0 Hz, 0.8H), 6.11 (d, *J* = 12.0 Hz, 0.2H), 5.98 (dd, *J* = 15.2 Hz, 8.0 Hz, 0.2H), 3.84 (s, 0.6H), 3.77 (s, 2.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9 193.7, 160.9, 160.8, 151.7, 148.4, 148.0, 146.1, 136.5, 135.6, 133.9, 133.1, 133.0, 132.5, 131.2, 131.1, 130.8, 130.7, 130.4, 130.0, 129.7, 129.1, 128.3, 127.8, 127.7, 123.7, 122.8, 55.3; HRMS (ESI) m/z calcd for $C_{18}H_{13}O_2S$: $[M - H]^-$ 293.0642, found: 293.0653.

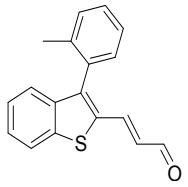
3-[3-(3,5-Dimethyl-phenyl)-benzo[b]thiophen-2-yl]-propenal (26d, E/Z > 99:1)



Yellow oil (48.18 mg, 33%), IR (KBr) 3010, 2854, 1675, 1447, 1428, 821, 751, 700 cm^{-1};

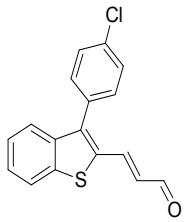
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.0 Hz, 1H), 1.73 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32-7.28 (m, 1H), 7.13-7.07 (m, 4H), 5.98-5.92 (m, 1H), 2.38 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 152.5, 148.4, 138.3, 137.0, 135.6, 134.0, 131.9, 131.5, 131.1, 129.7, 129.6, 128.4, 127.3, 121.9, 21.3; HRMS (ESI) m/z calcd for $C_{19}H_{15}OS$: $[M - H]^-$ 291.0849, found: 291.0865.

3-(3-o-Tolyl-benzo[b]thiophen-2-yl)-propenal (26e，E/Z = 96:4)



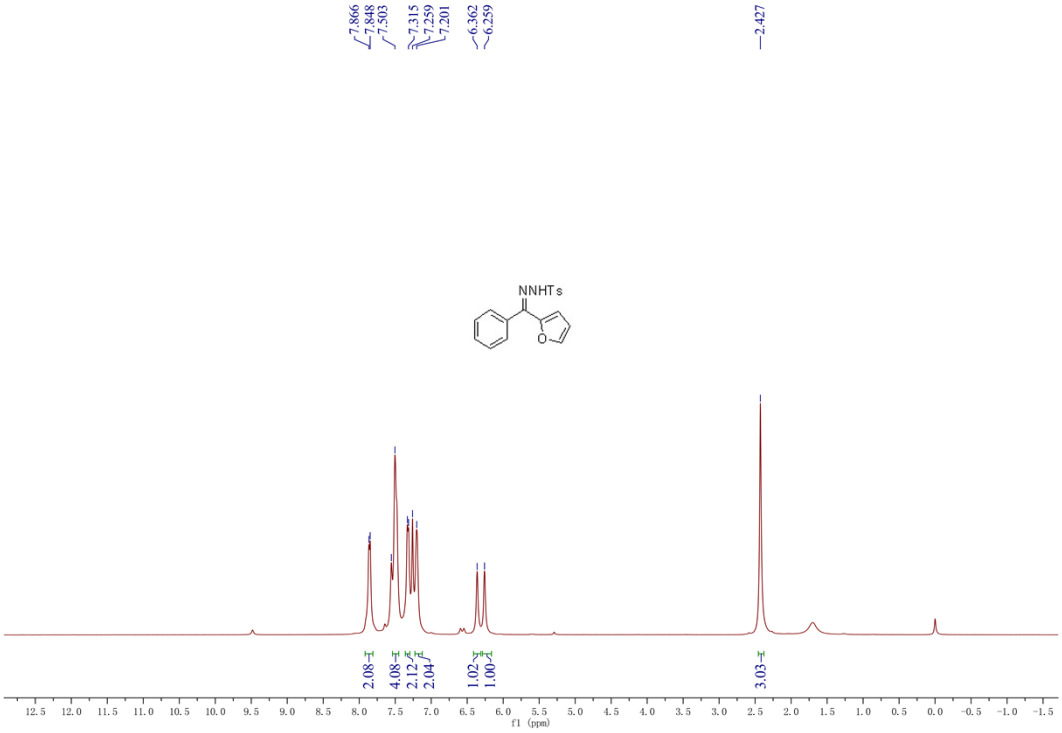
Yellow oil (86.18 mg, 62%), IR (KBr) 3015, 2853, 1673, 1485, 1447, 879, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.41-7.27 (m, 5H), 6.68-6.61 (m, 1H), 5.90-5.83 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 193.7, 152.1, 147.5, 137.9, 136.7, 134.7, 134.2, 131.7, 130.8, 130.7, 130.6, 129.8, 129.4, 129.3, 128.6, 126.0, 121.2, 19.5; HRMS (ESI) m/z calcd for $C_{18}H_{13}OS$: $[M - H]^-$ 277.0686, found: 277.0674.

3-[3-(4-Chloro-phenyl)-benzo[b]thiophen-2-yl]-propenal (26f，E/Z = 78:22)

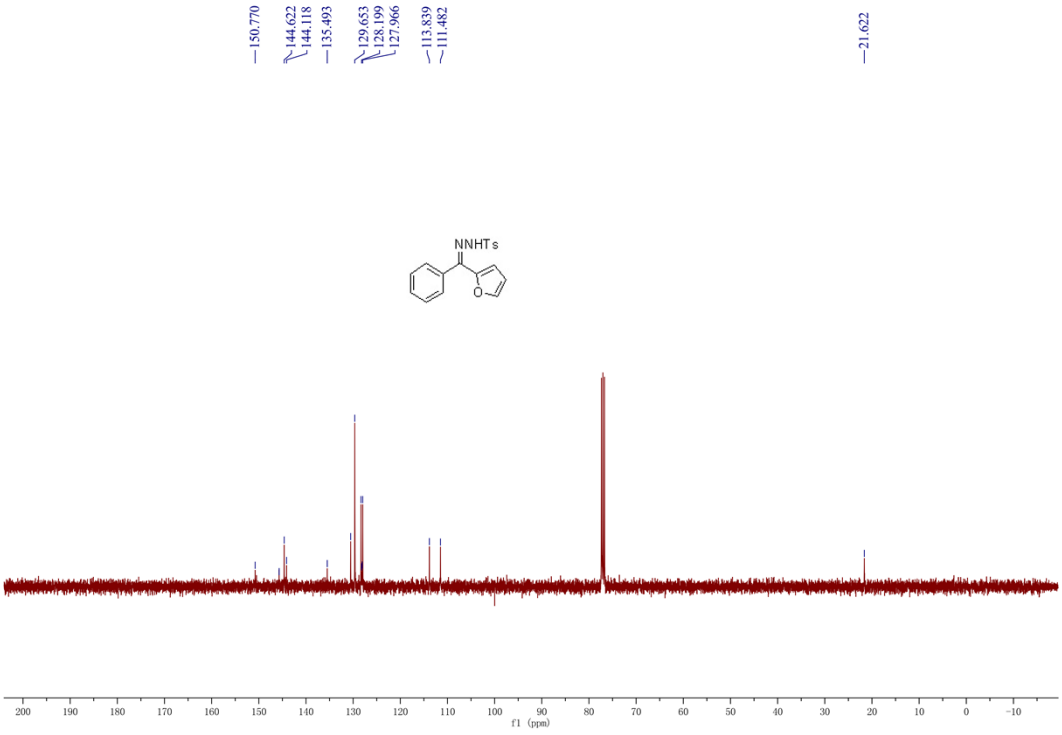


Yellow oil(74.5 mg, 50%), IR (KBr) 3059, 2853, 2740, 1674, 1448, 1428, 831, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 8.0 Hz, 0.78H), 9.38 (d, *J* = 8.0 Hz, 0.22H), 7.99-7.92 (m, 0.78H), 7.66 (d, *J* = 7.6 Hz, 0.22H), 7.56-7.22 (m, 5H), 7.06-6.96 (m, 2.78H), 6.38 (dd, *J* = 15.2 Hz, 8.0 Hz, 0.78H), 6.16 (d, *J* = 11.6 Hz, 0.22H), 6.00-5.98 (m, 0.22H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 193.5, 150.1, 147.1, 145.4, 136.6, 136.5, 134.6, 134.1, 134.0, 133.3, 132.5, 131.8, 131.6, 131.1, 131.0, 130.8, 129.4, 128.9, 128.8, 128.4, 127.8, 124.3, 123.8; HRMS (ESI) m/z calcd for $C_{17}H_{10}ClOS$: $[M-H]^-$ 297.0139, found: 297.0161.

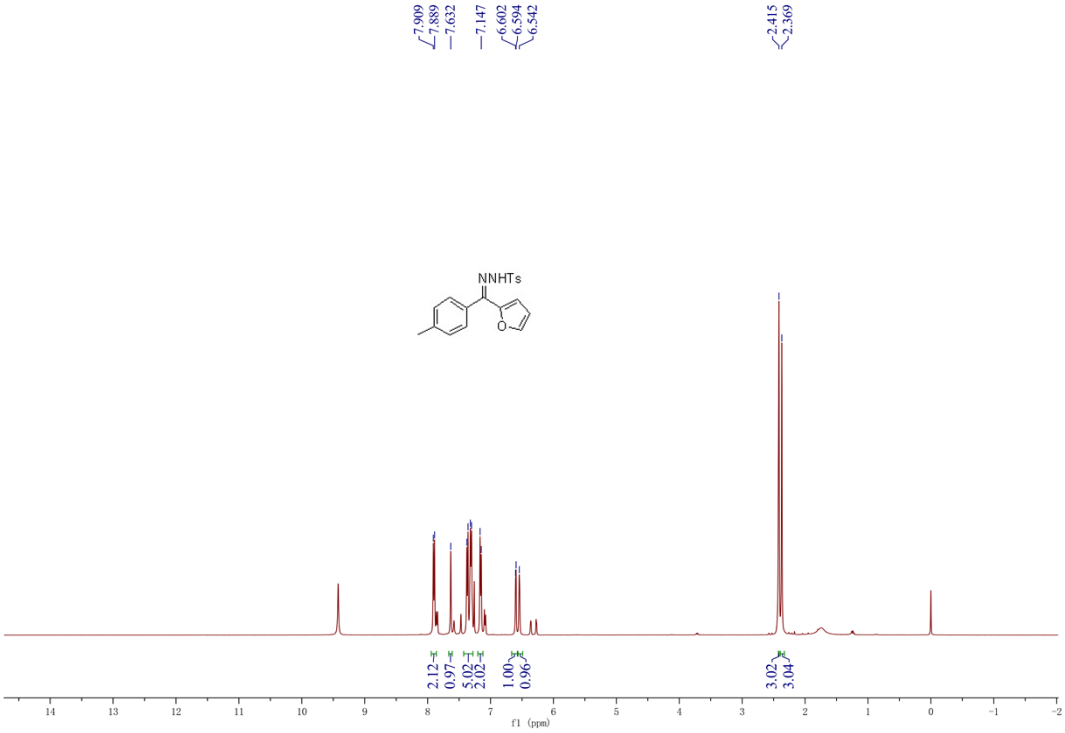
^{1}H NMR of **12a**



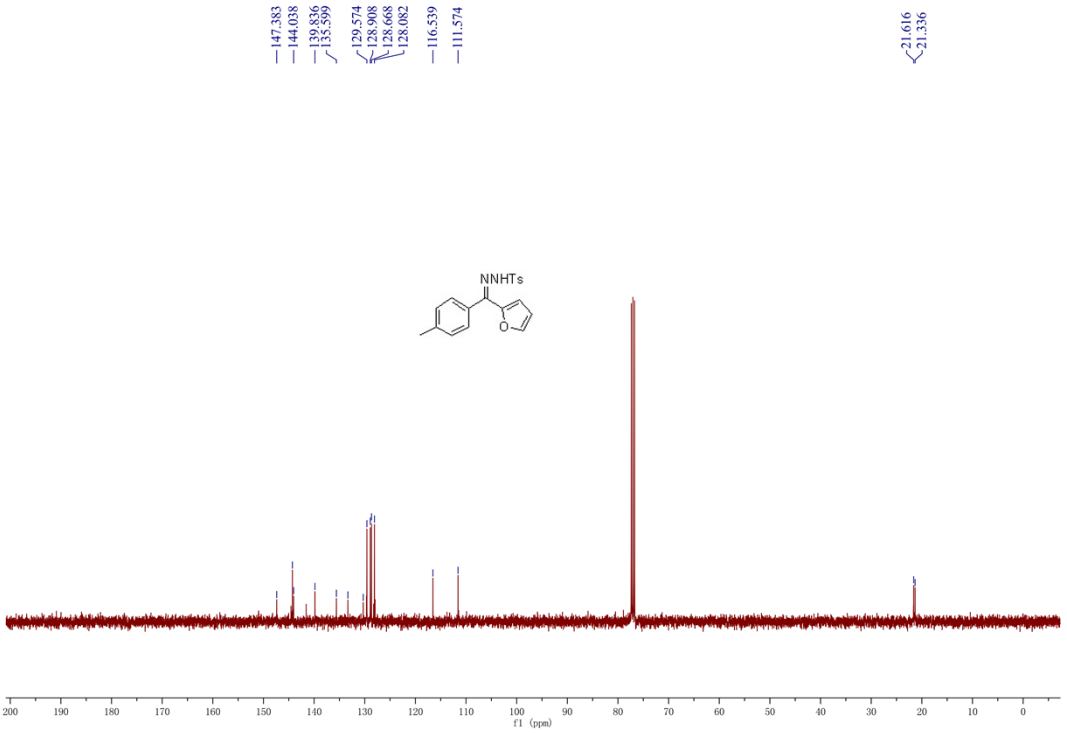
^{13}C NMR of **12a**



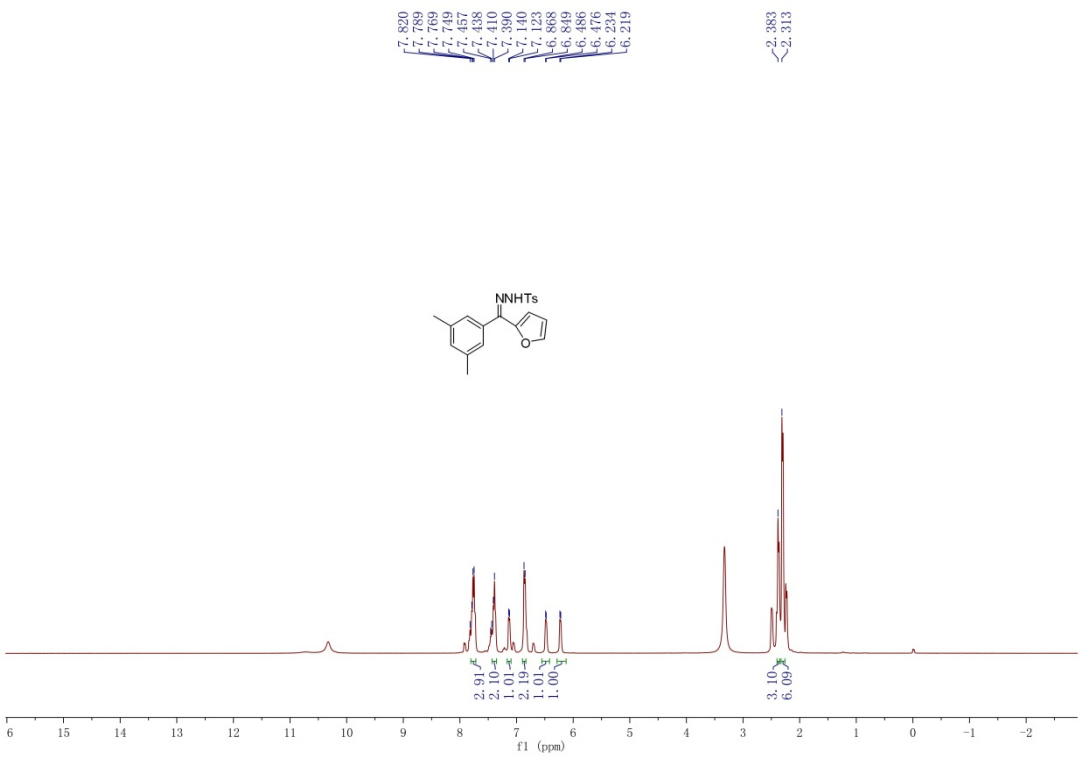
^{1}H NMR of **12b**



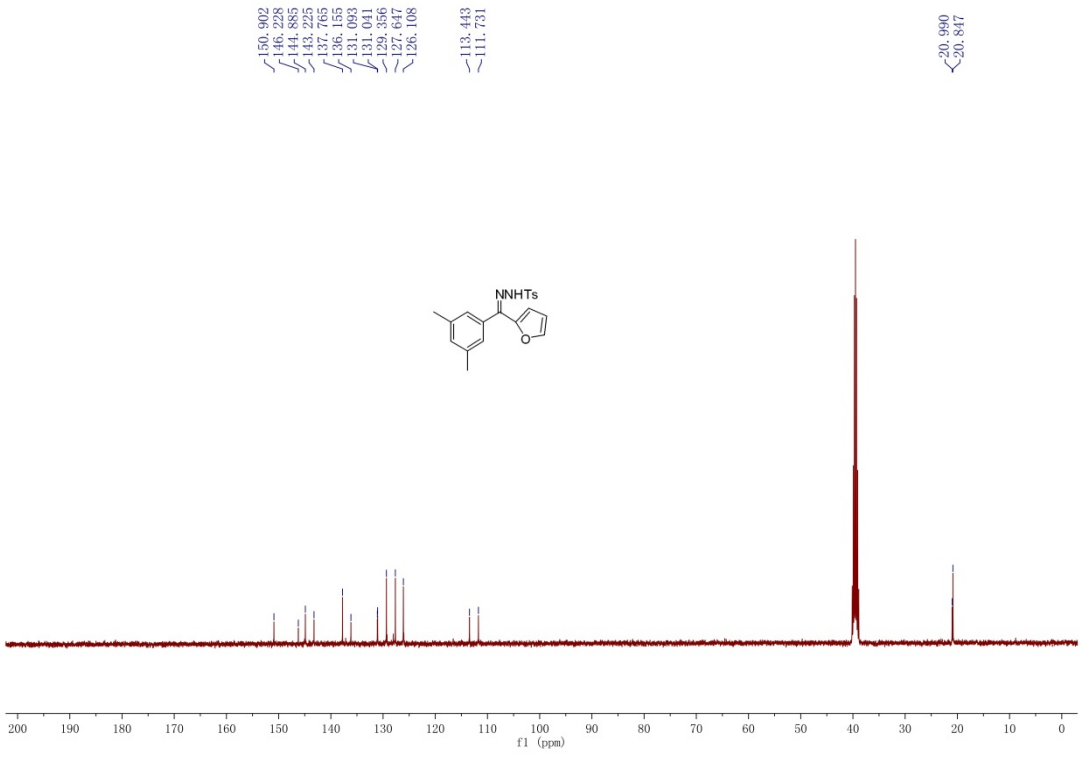
^{13}C NMR of **12b**



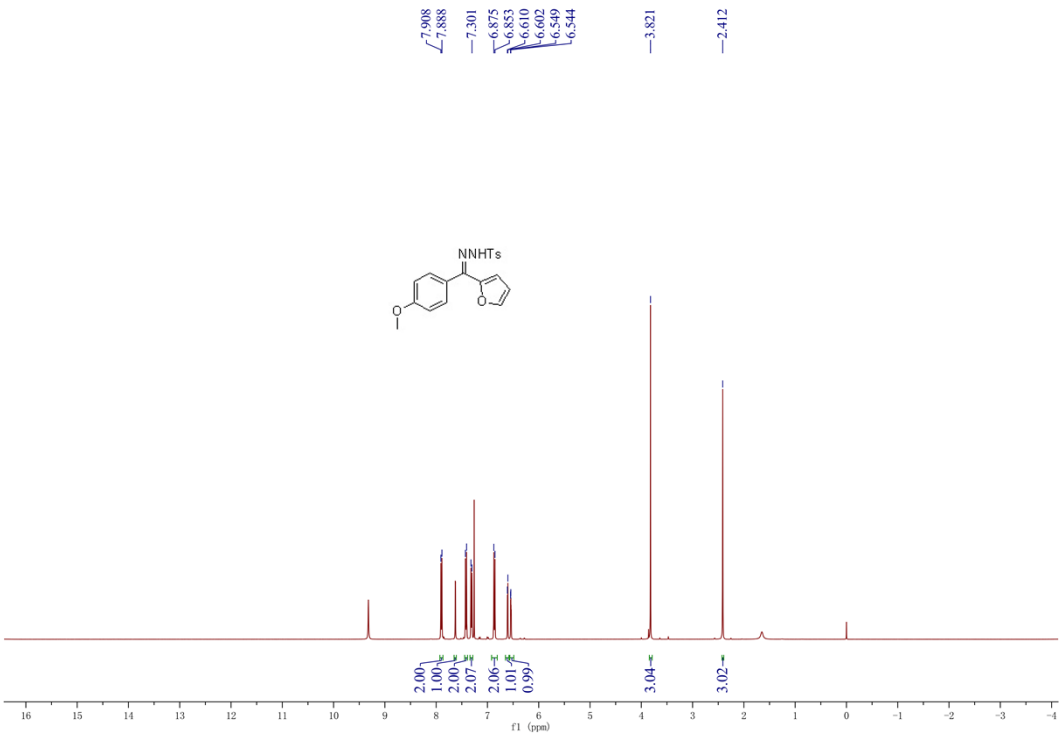
^{1}H NMR of **12c**



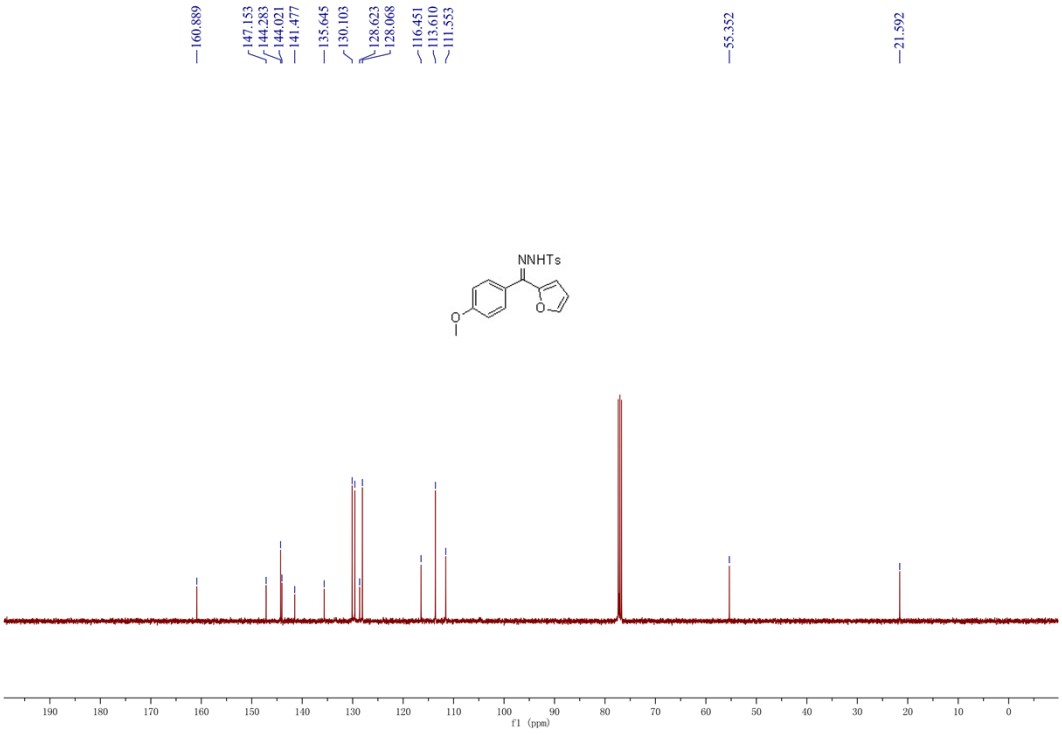
^{13}C NMR of **12c**



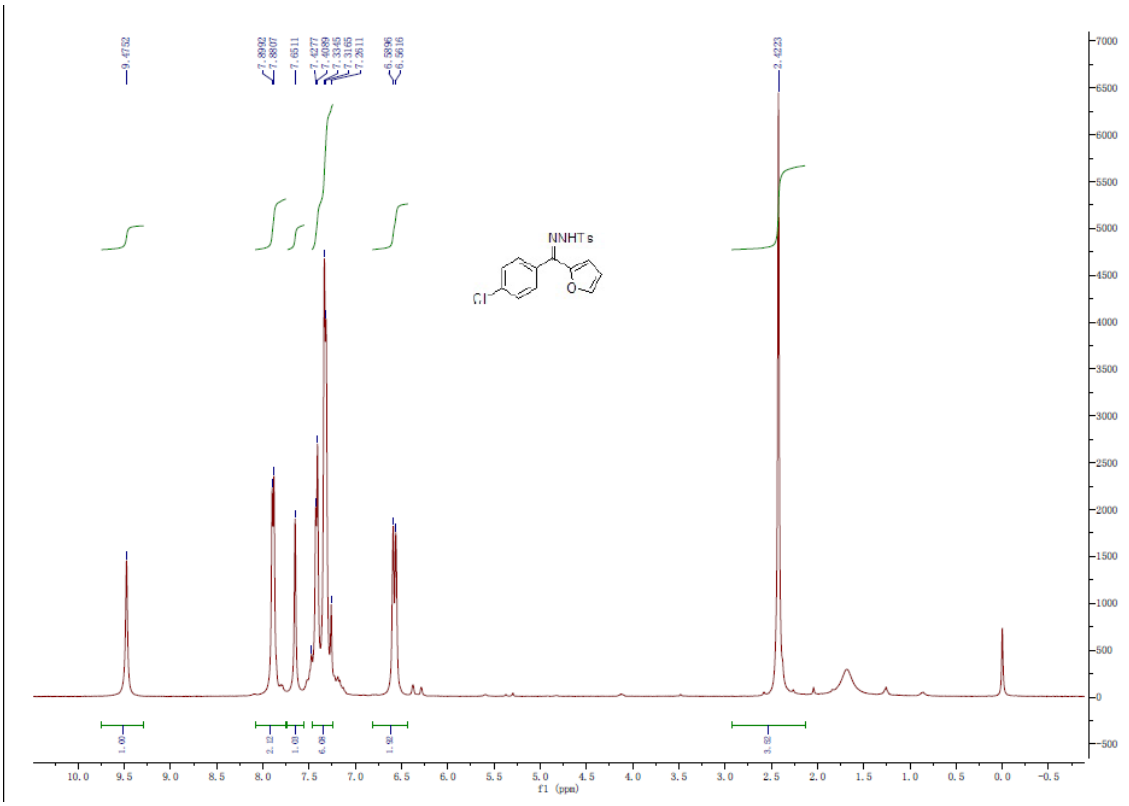
^{1}H NMR of **12d**



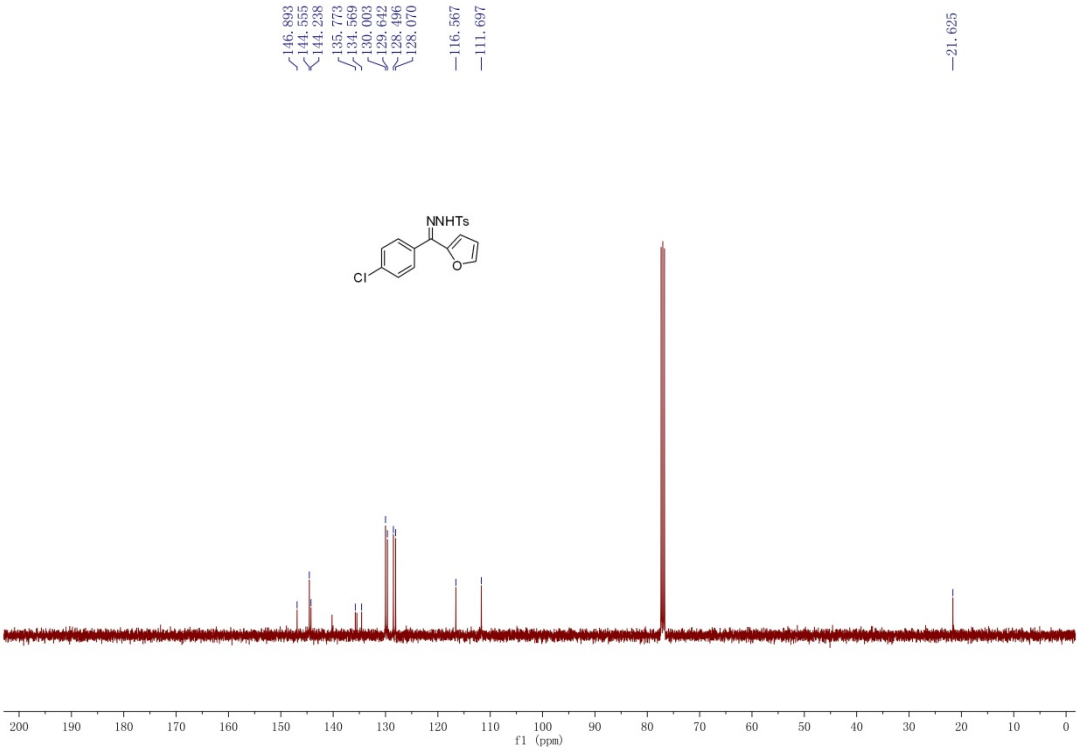
^{13}C NMR of **12d**



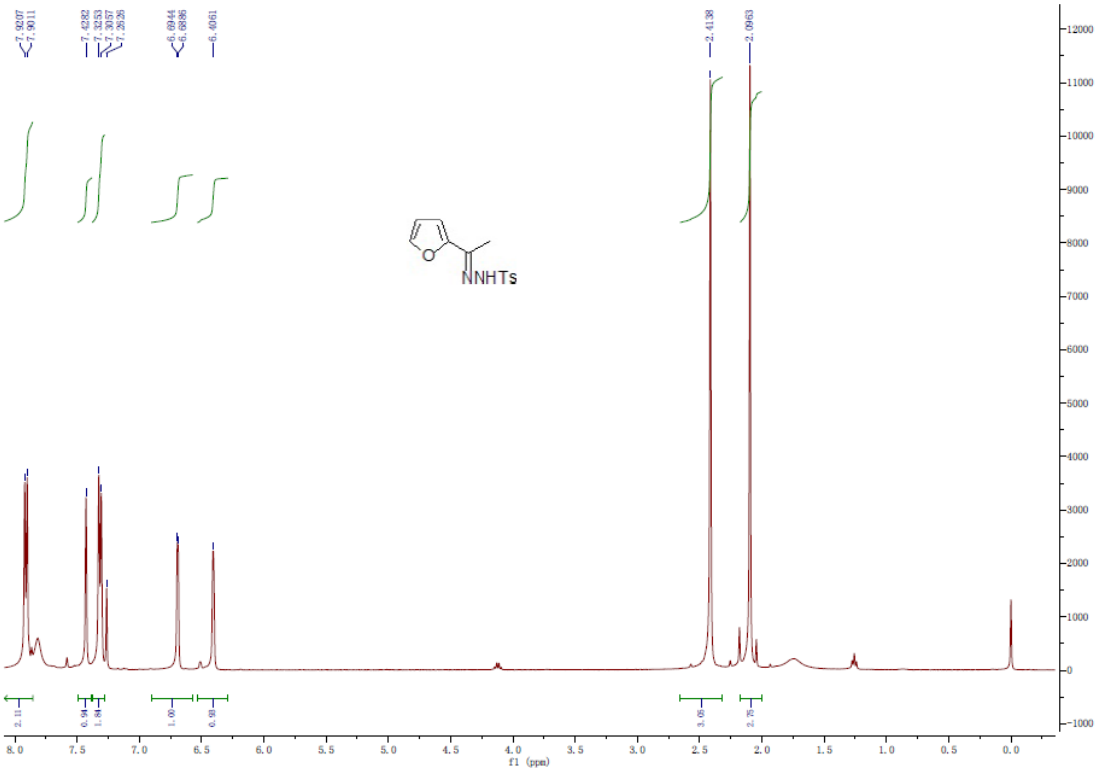
^{1}H NMR of **12e**



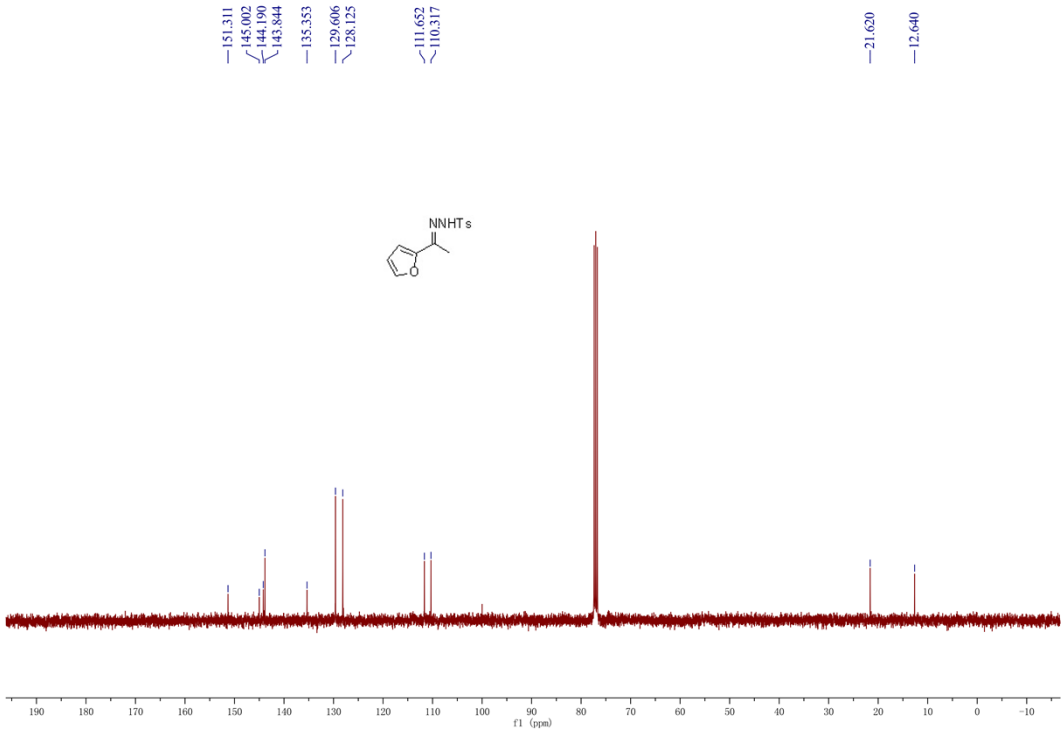
^{13}C NMR of **12e**



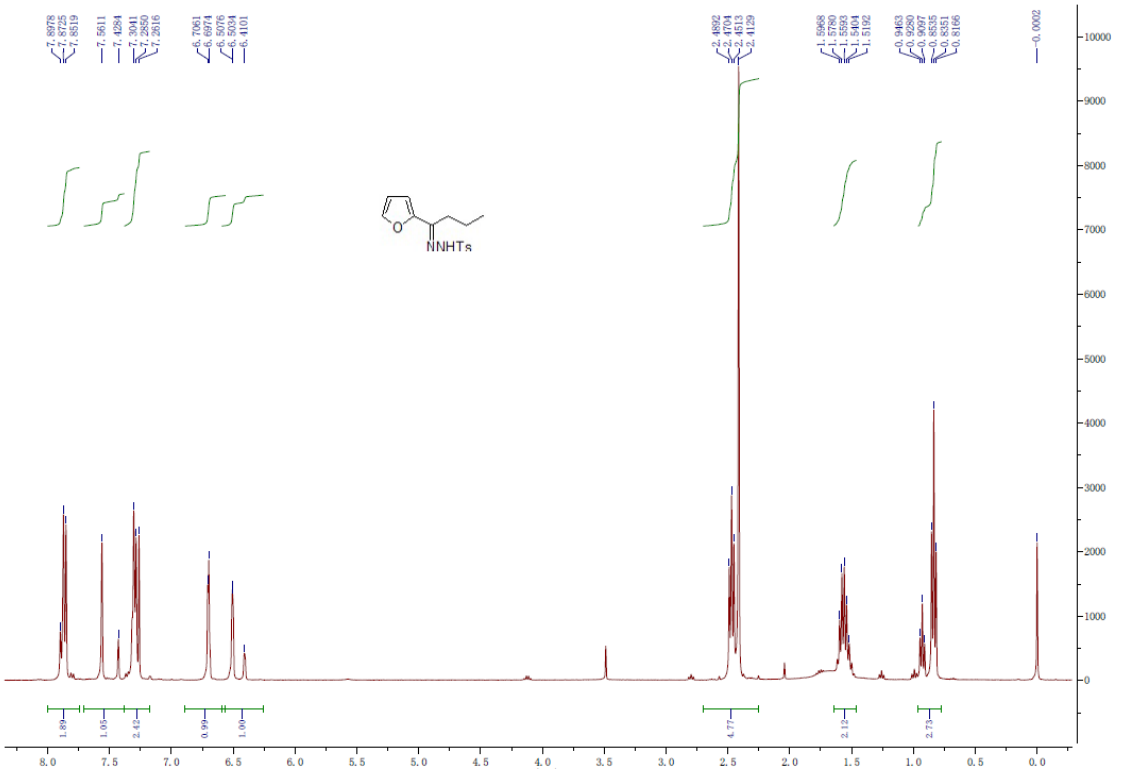
^{1}H NMR of **12g**



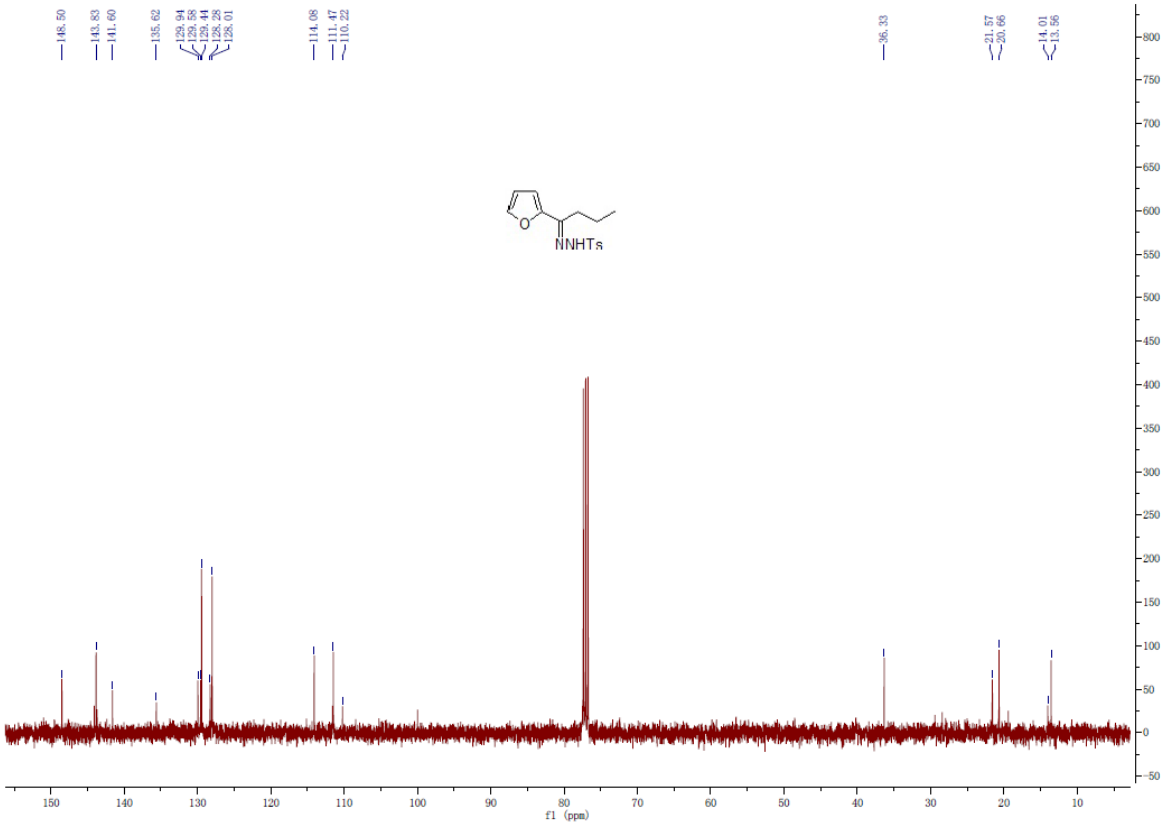
^{13}C NMR of **12g**



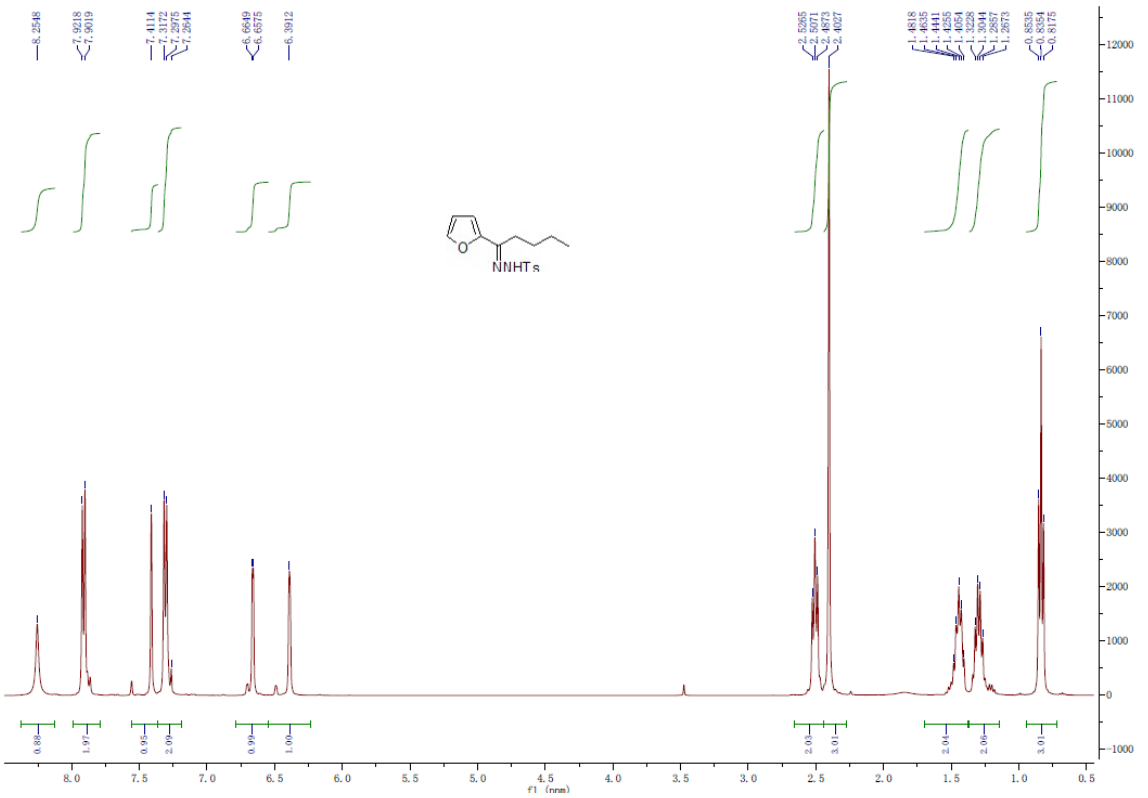
^{1}H NMR of **12h**



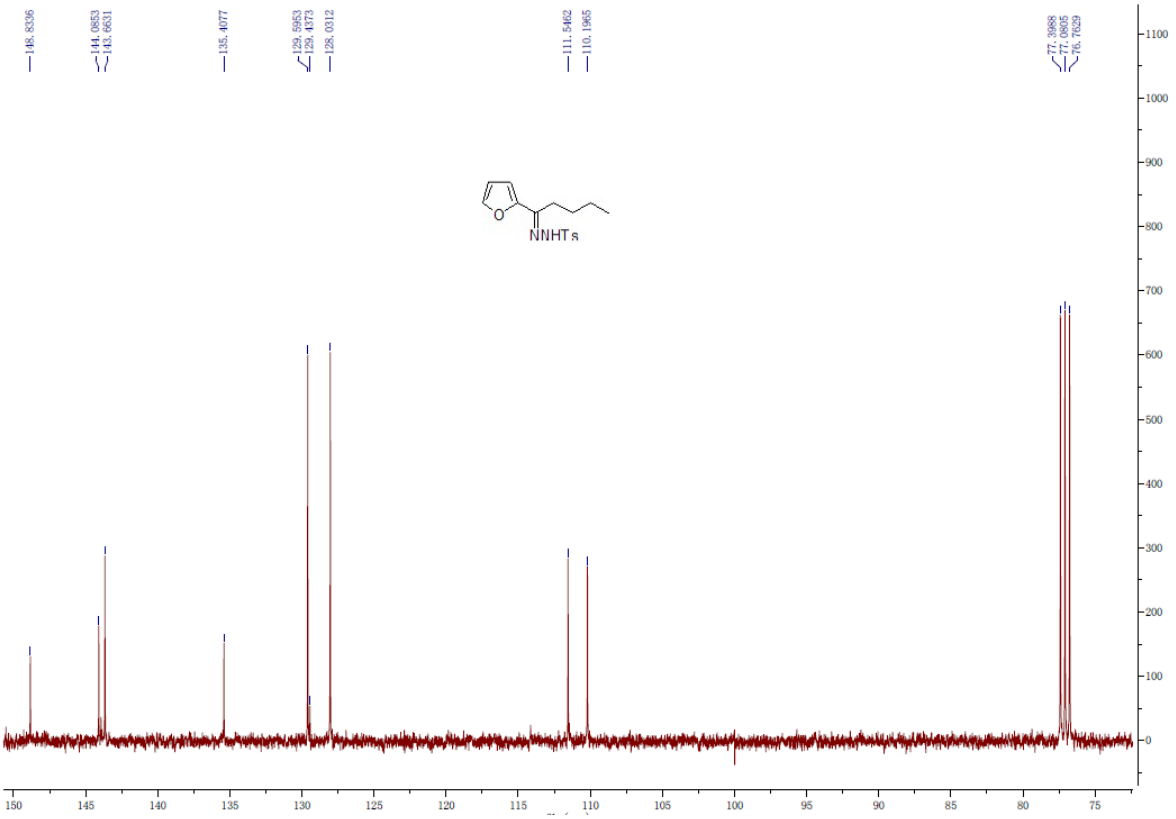
^{13}C NMR of **12h**



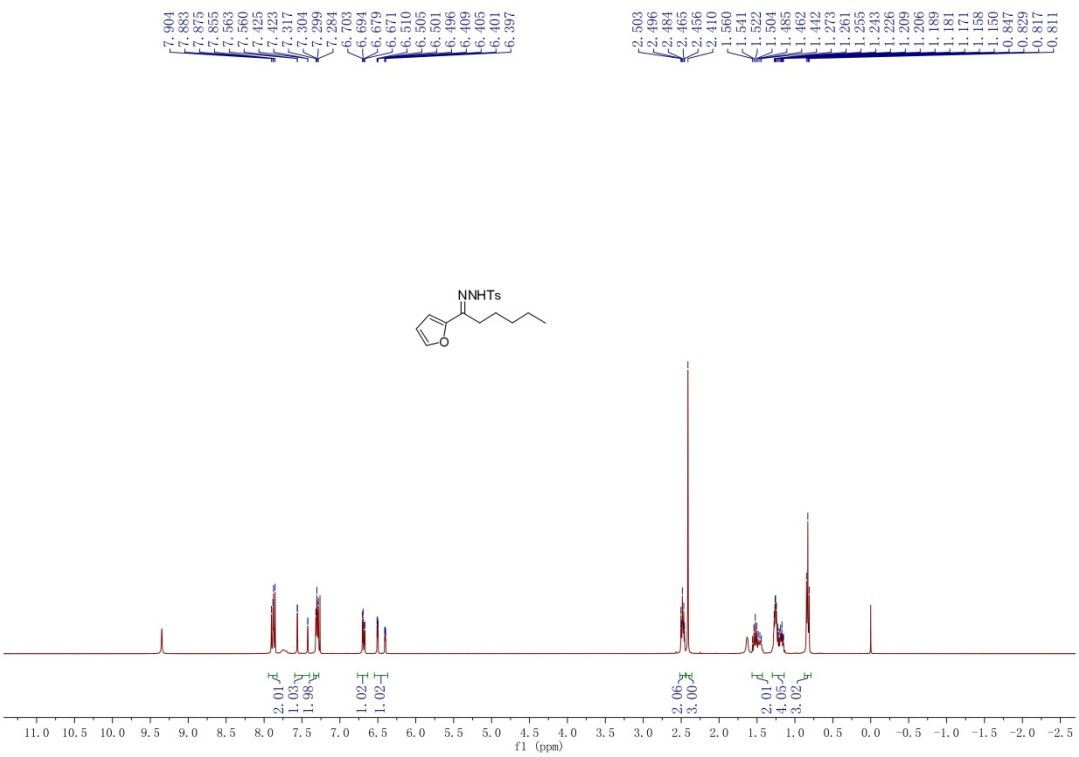
^{1}H NMR of **12i**



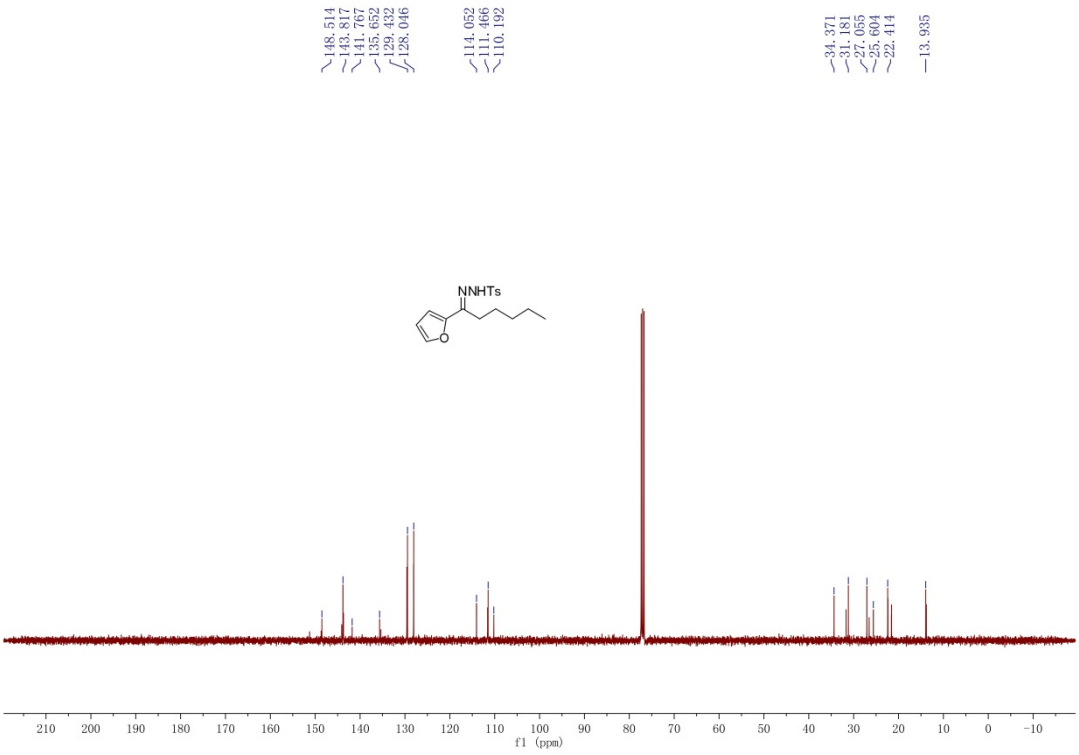
^{13}C NMR of **12i**



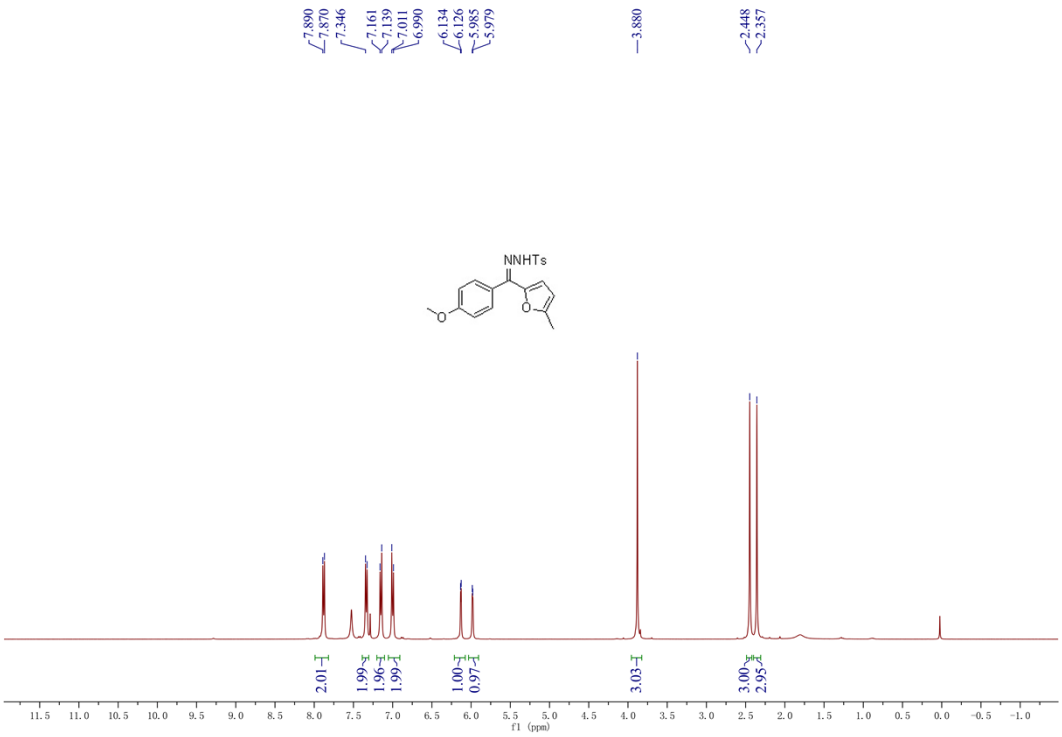
^{1}H NMR of **12j**



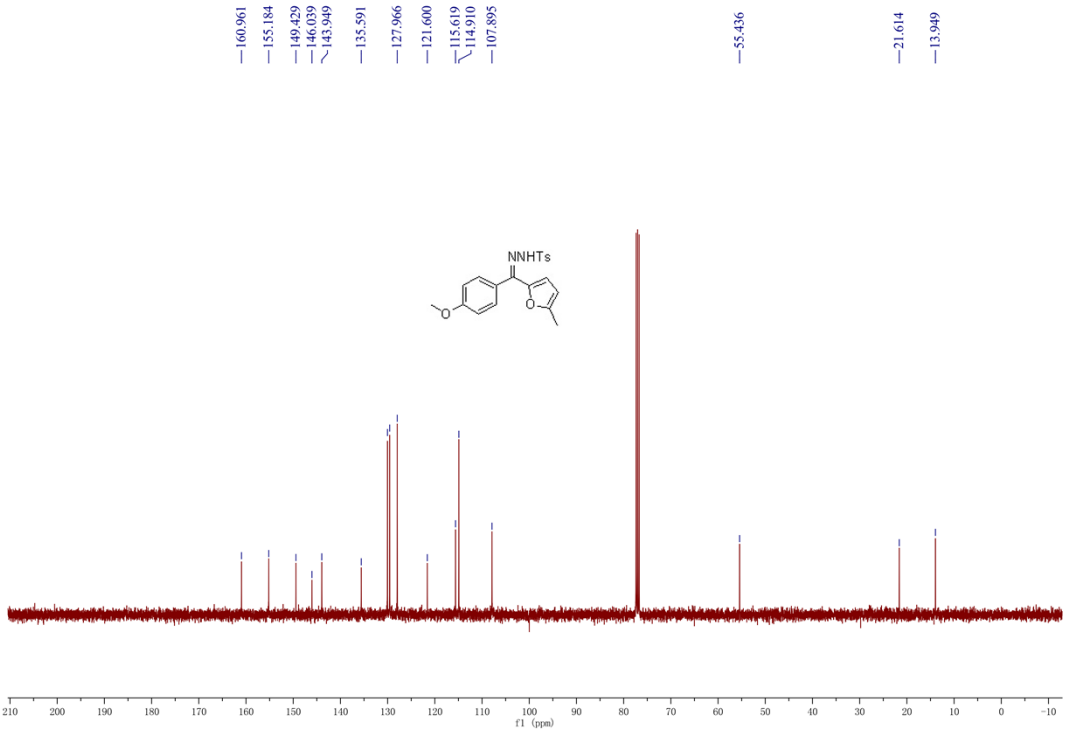
^{13}C NMR of **12j**



^{1}H NMR of **12k**

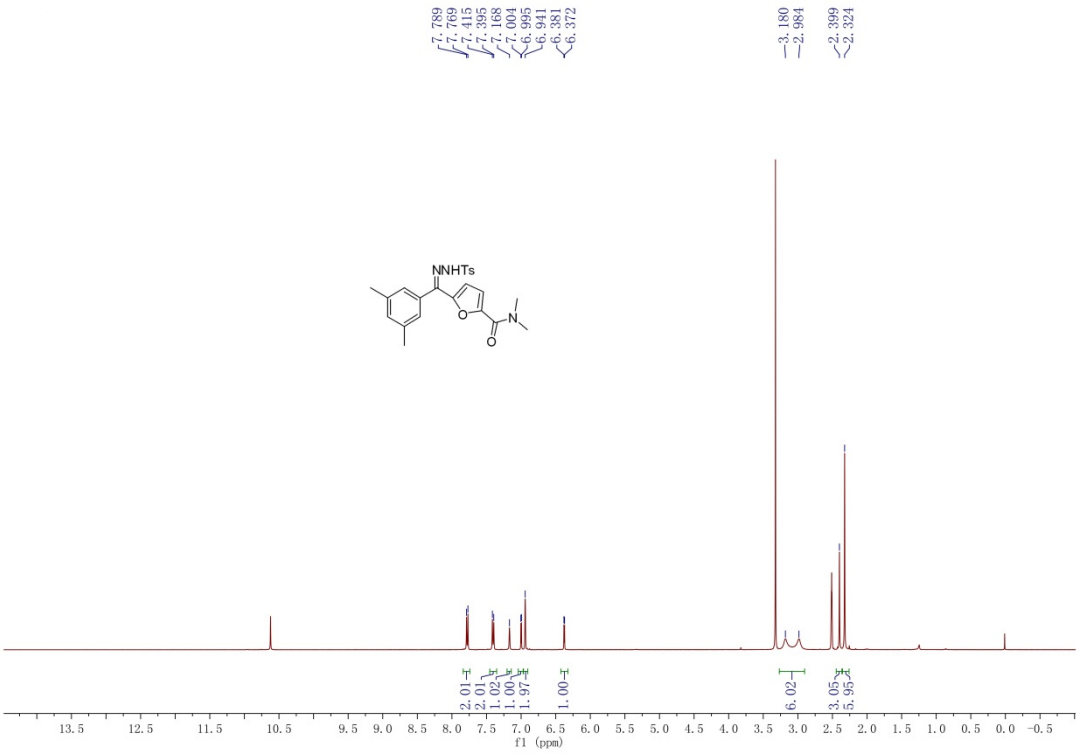


^{13}C NMR of **12k**

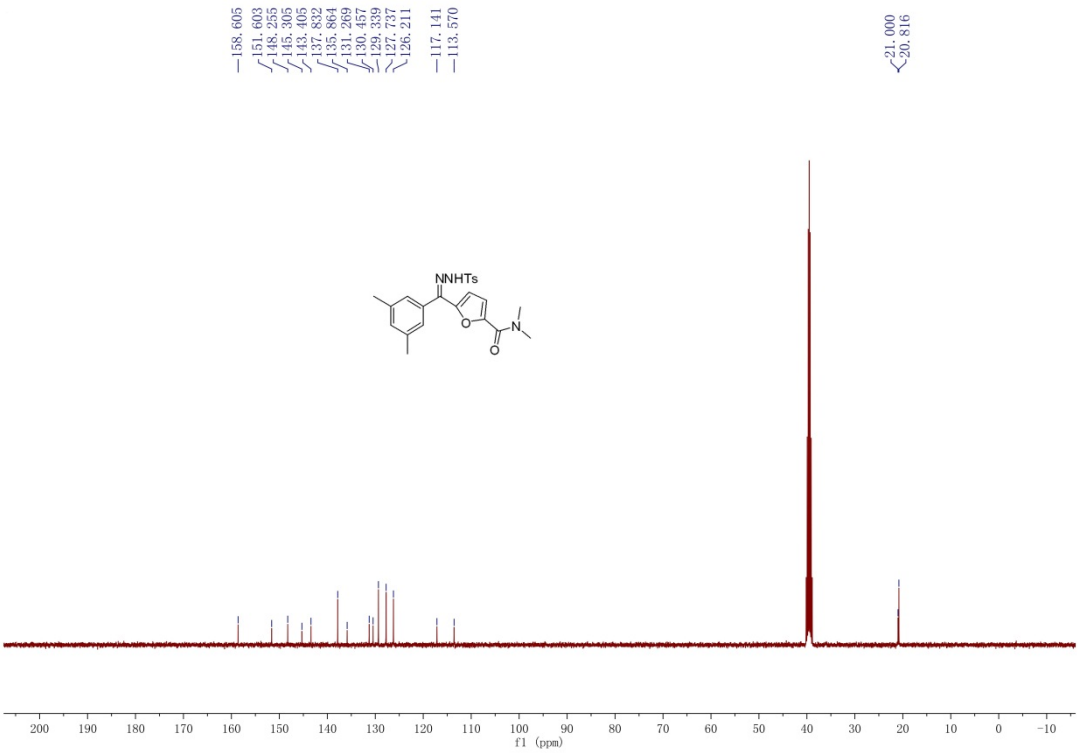


^{1}H NMR of **12l**

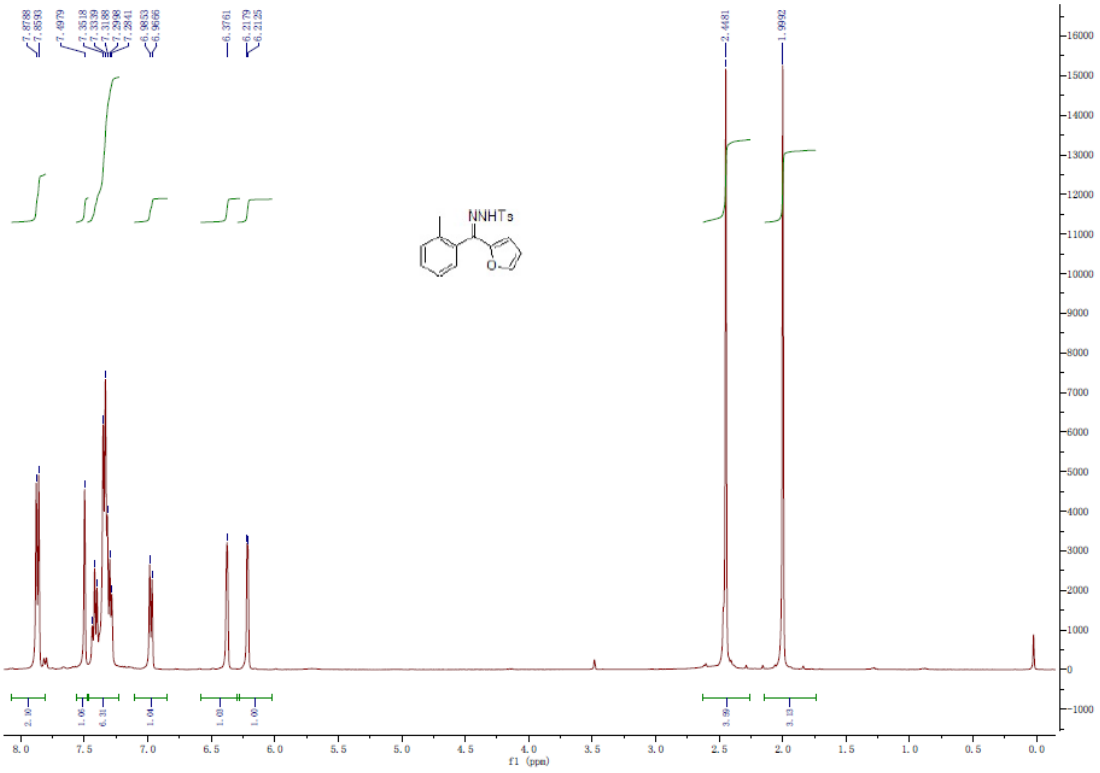
^{1}H NMR of **12l**



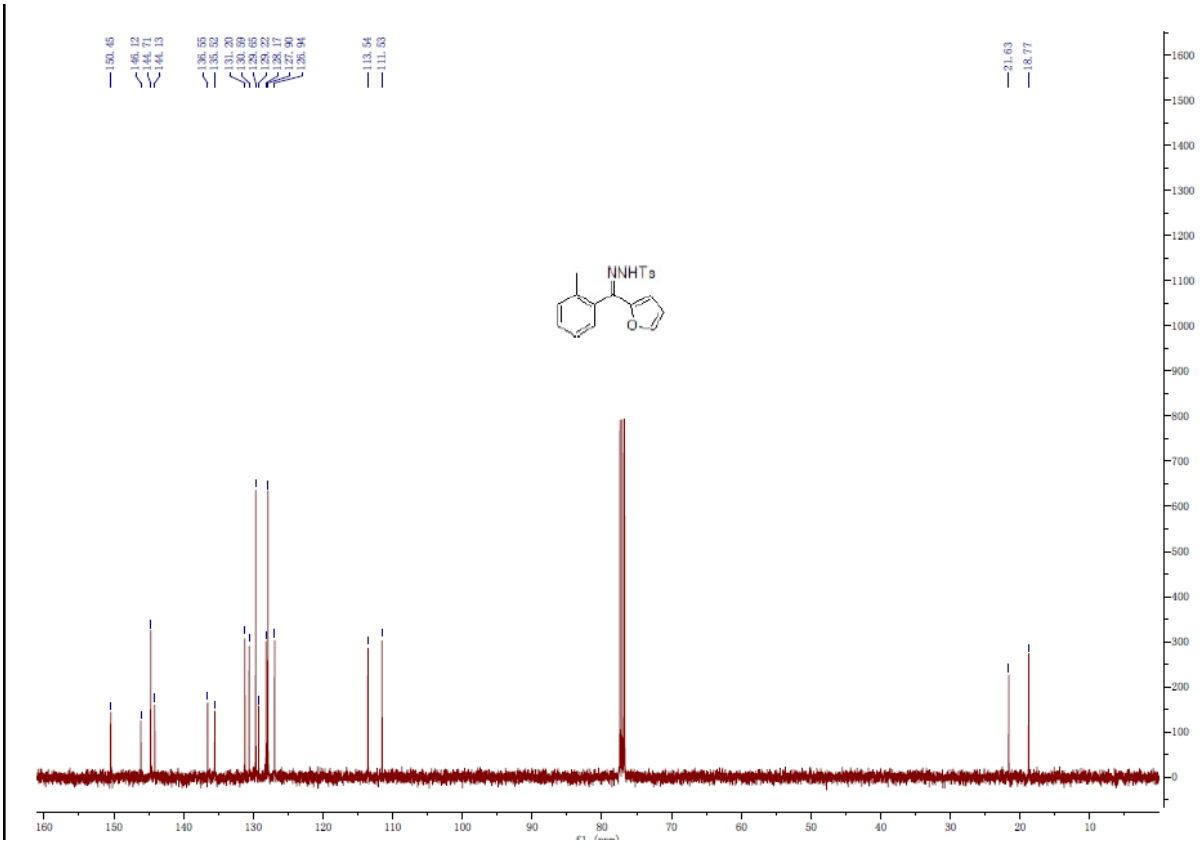
^{13}C NMR of **12l**



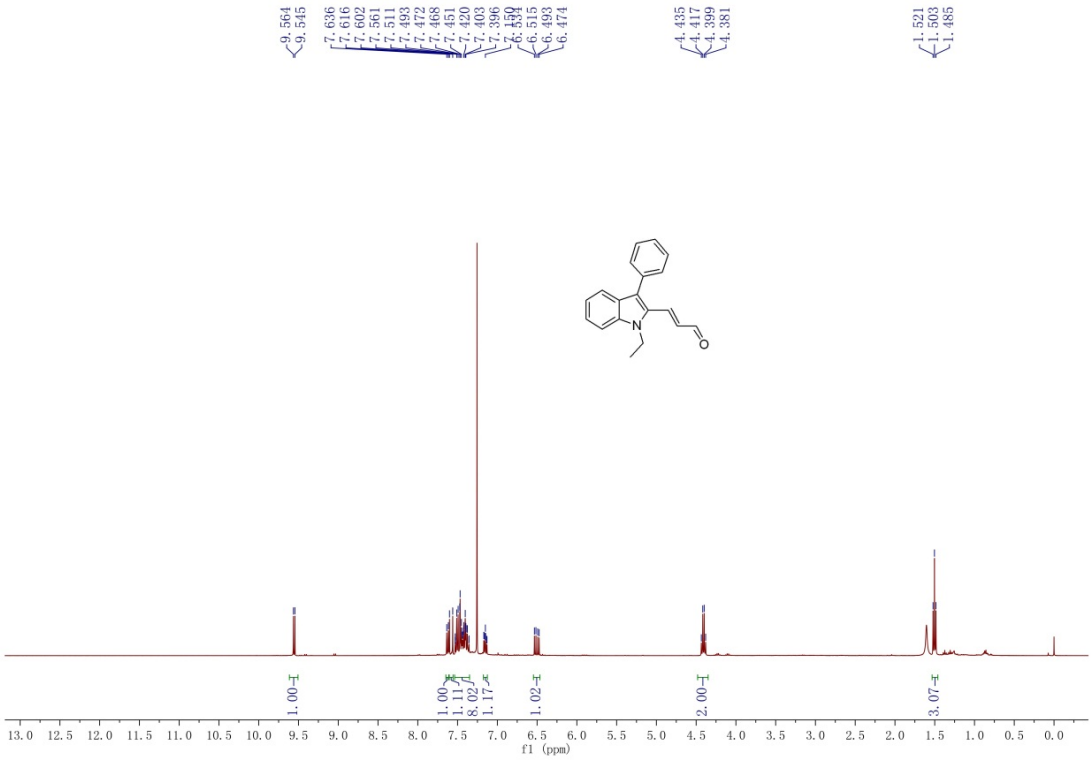
^{1}H NMR of **12m**



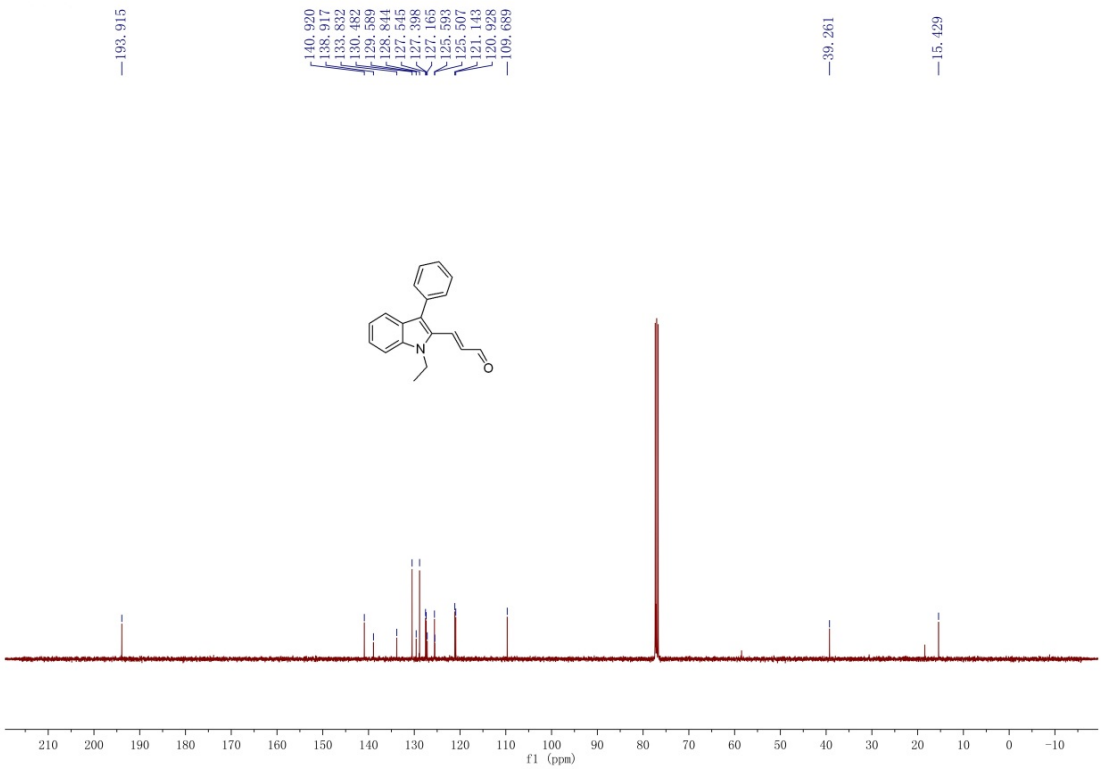
^{13}C NMR of **12m**



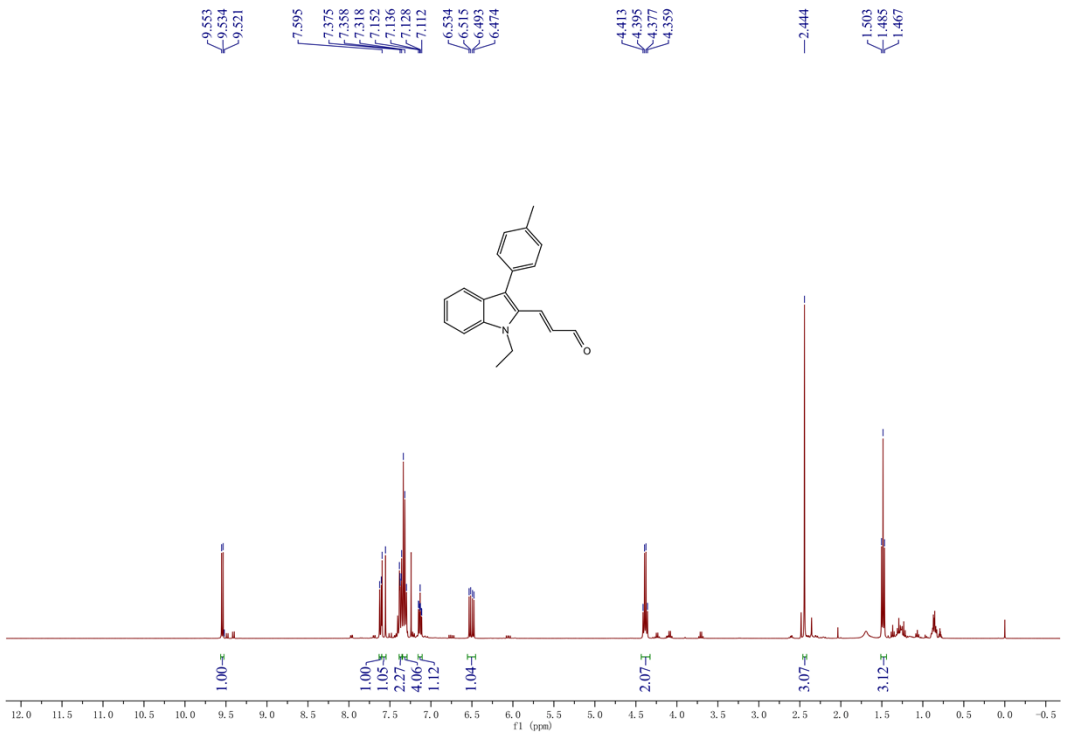
^{1}H NMR of **17a**



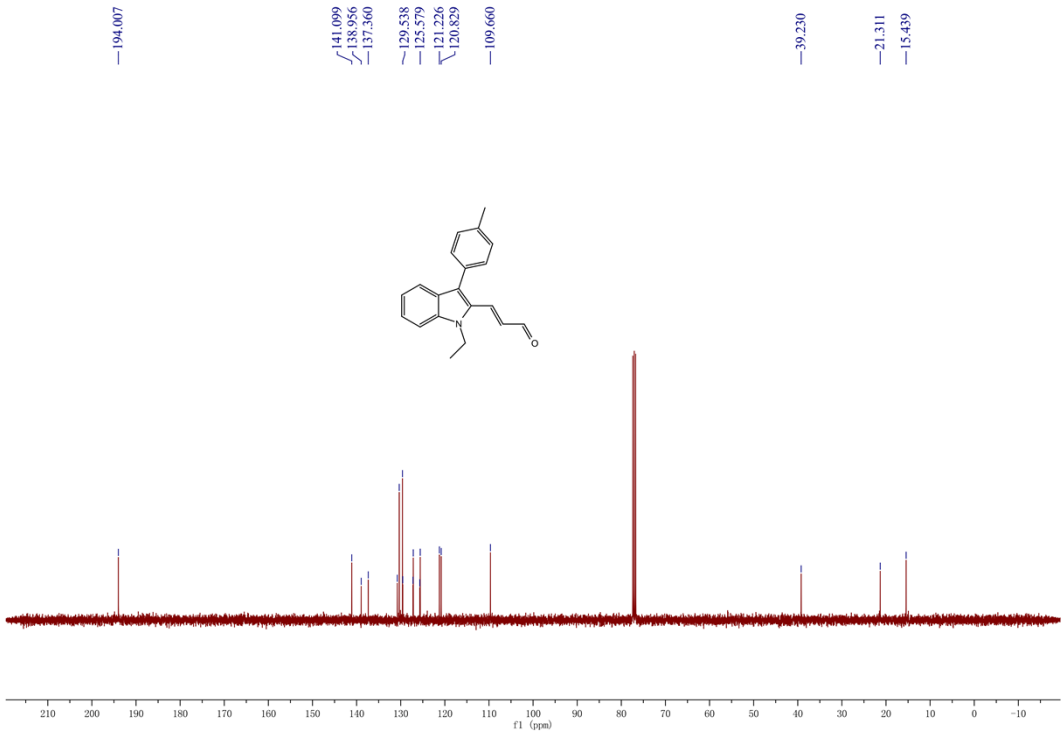
^{13}C NMR of **17a**



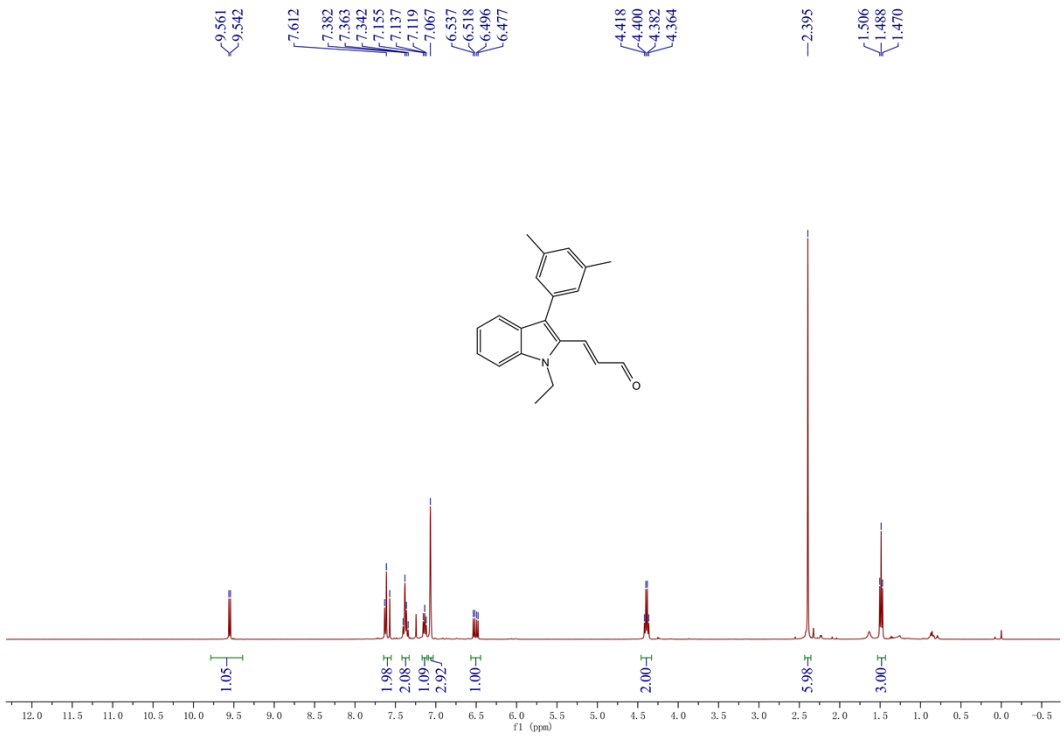
^{1}H NMR of **17b**



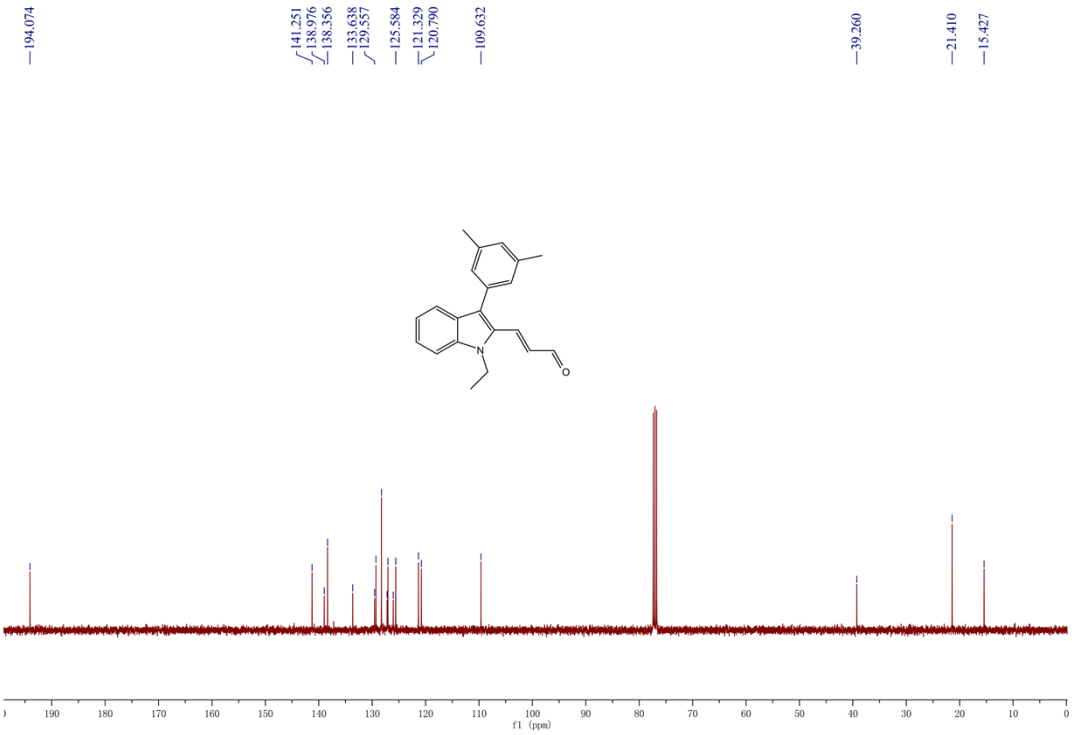
^{13}C NMR of **17b**



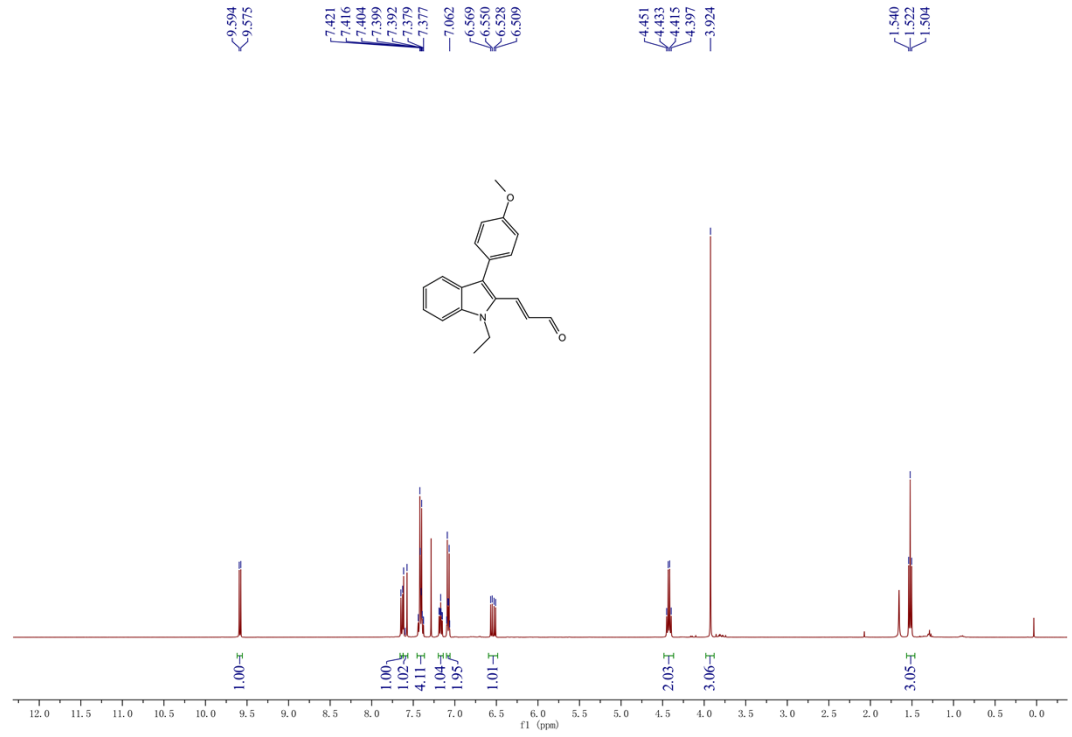
^{1}H NMR of **17c**



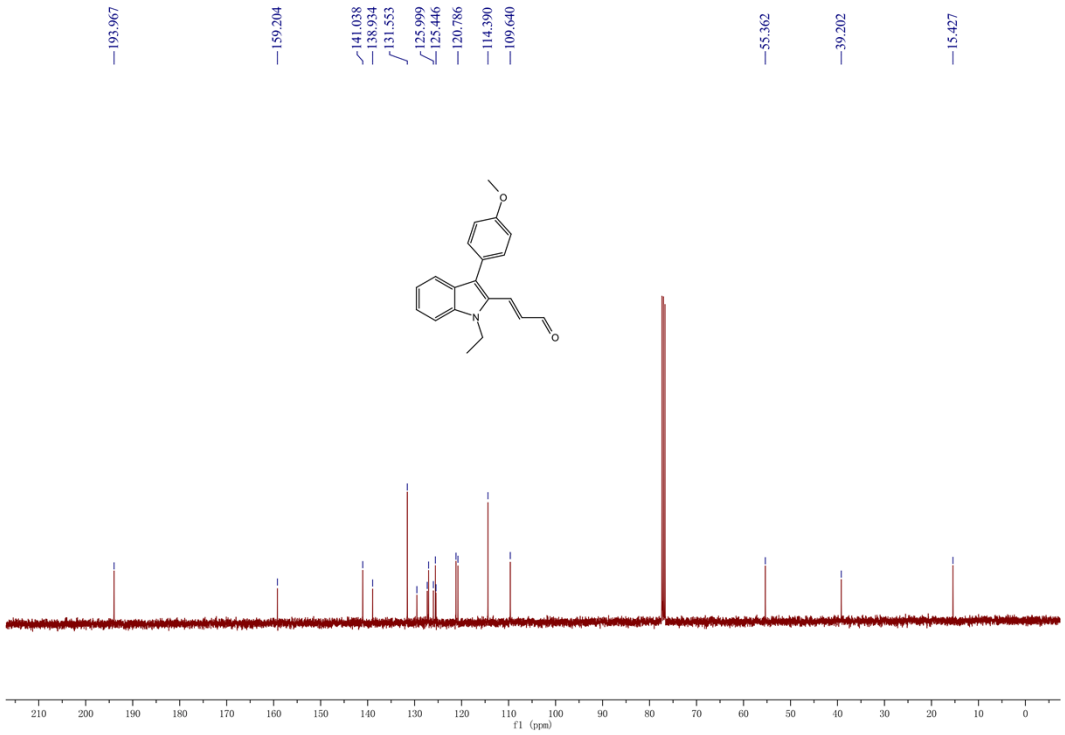
^{13}C NMR of **17c**



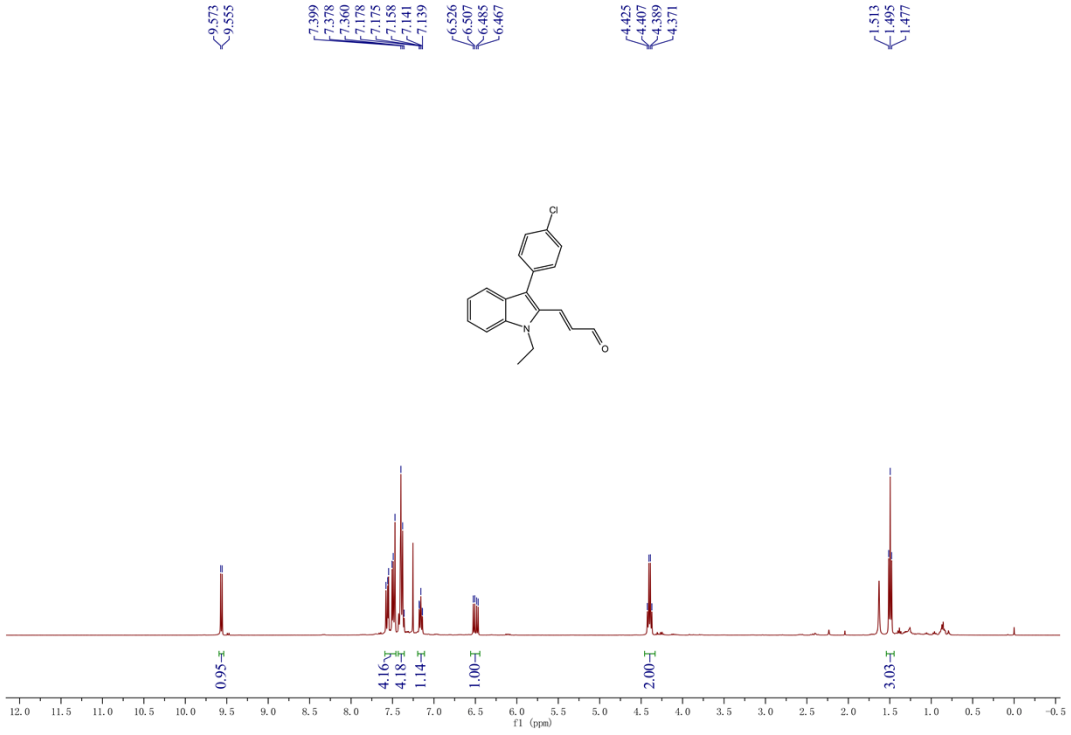
^{1}H NMR of **17d**



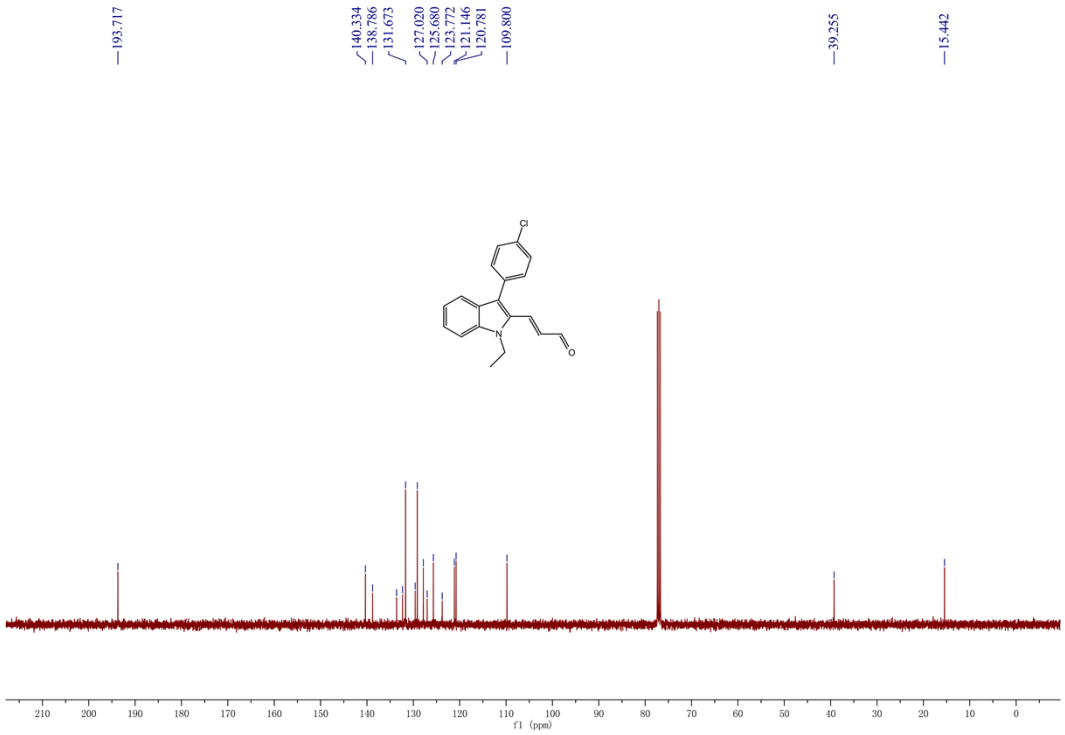
^{13}C NMR of **17d**



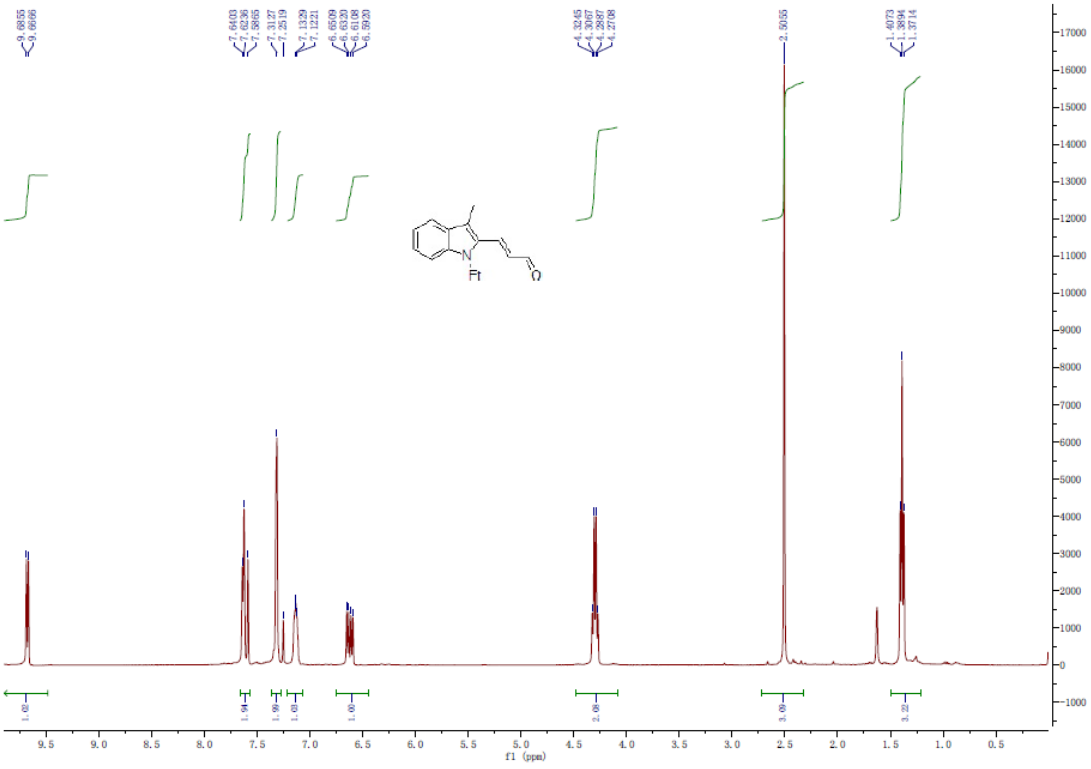
^{1}H NMR of **17e**



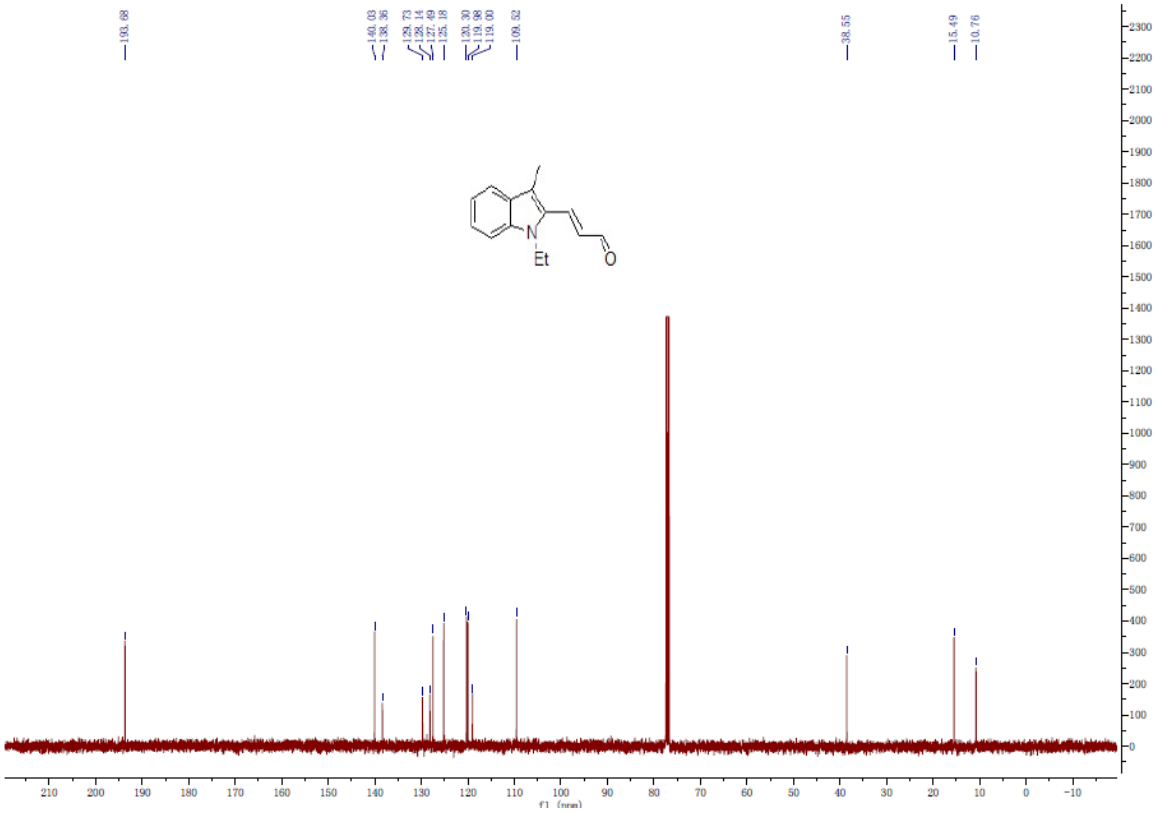
^{13}C NMR of **17e**



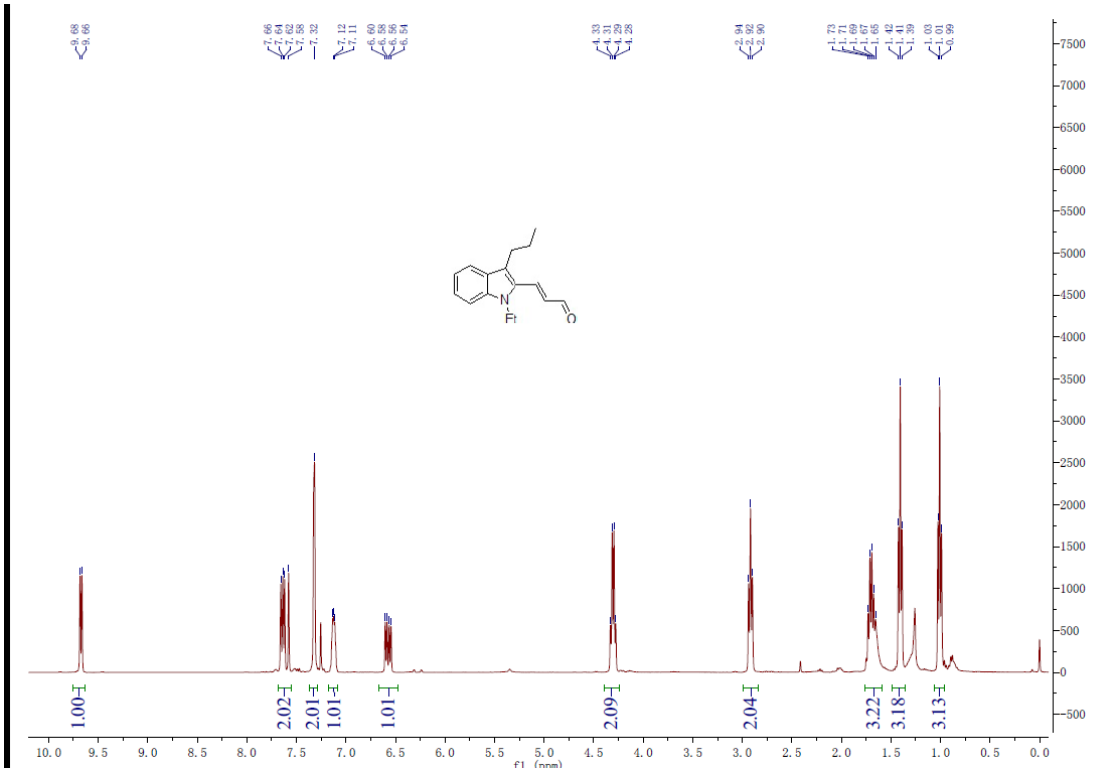
^{1}H NMR of **17g**



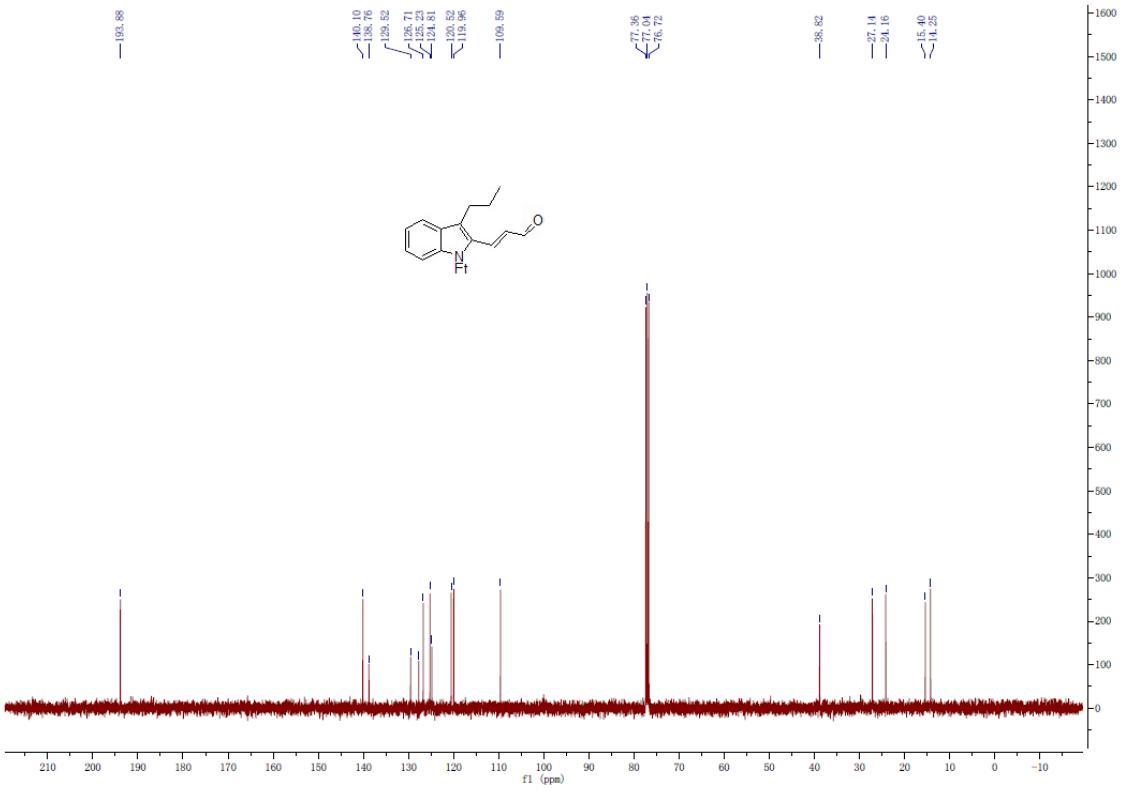
^{13}C NMR of **17g**



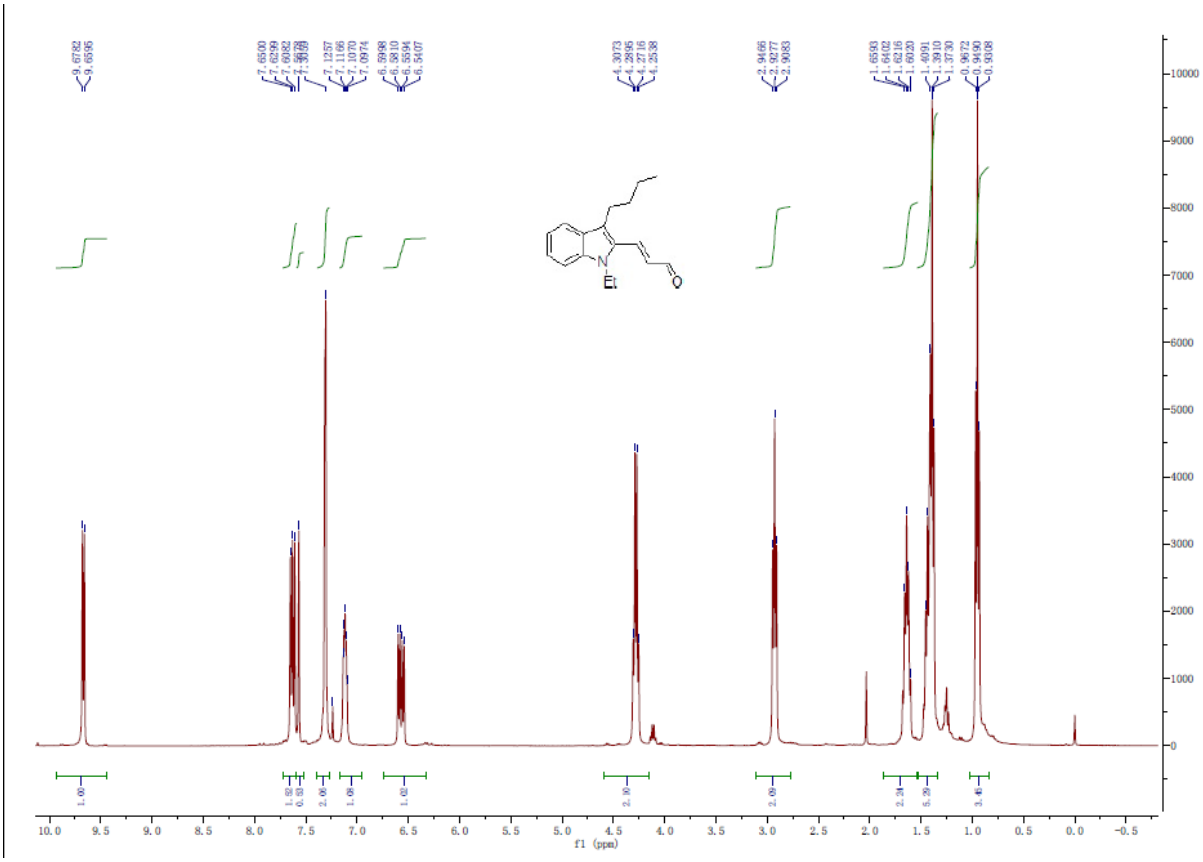
^{1}H NMR of **17h**



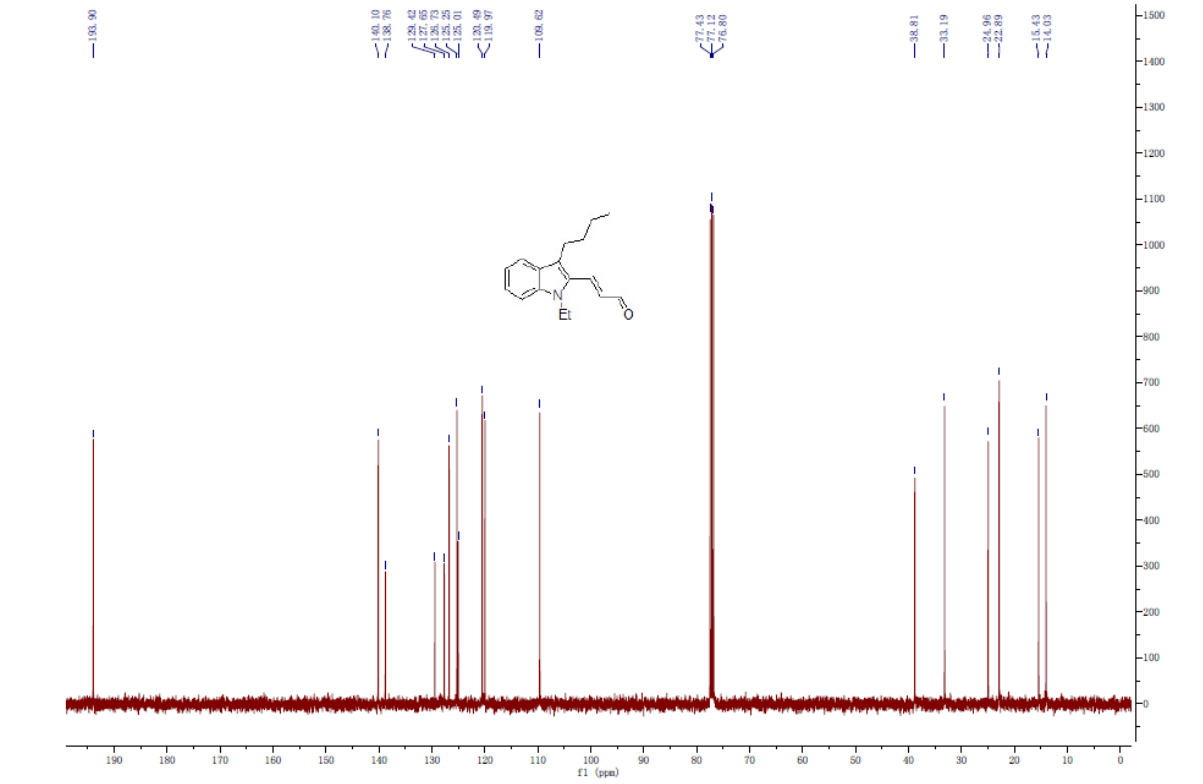
^{13}C NMR of **17h**


193.88
140.10
138.76
129.52
126.71
125.23
124.81
120.52
119.96
109.59
77.36
77.04
76.72
38.62
27.14
24.16
15.40
14.25
O
N
Ts
f1 (ppm)

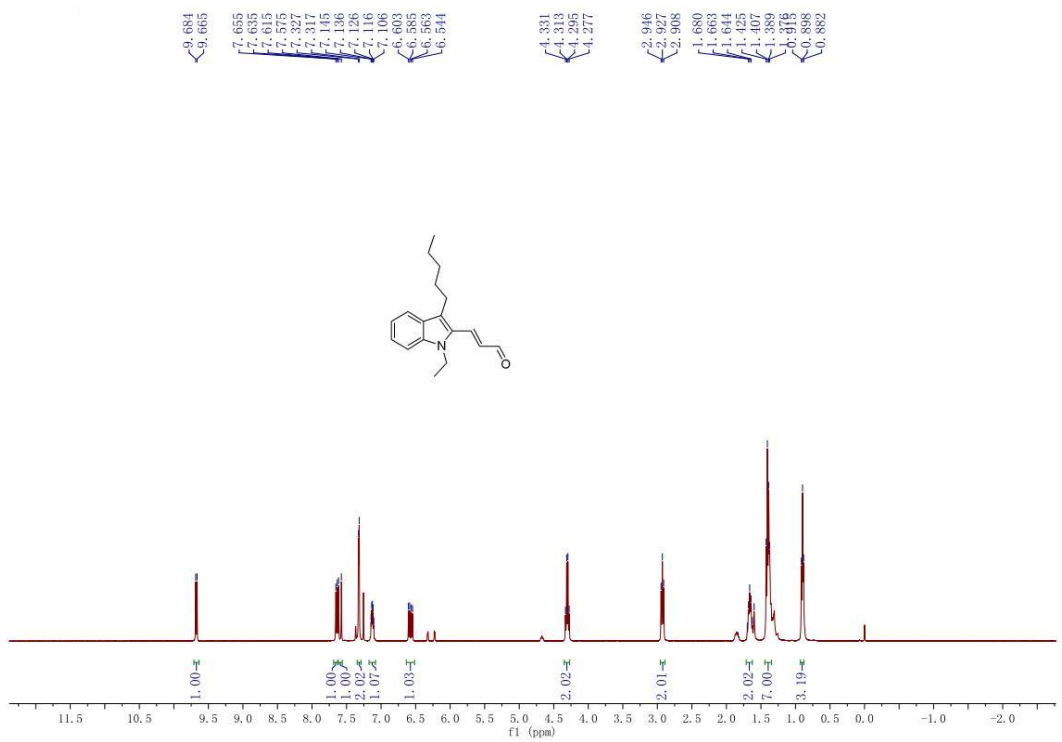
^{1}H NMR of **17i**



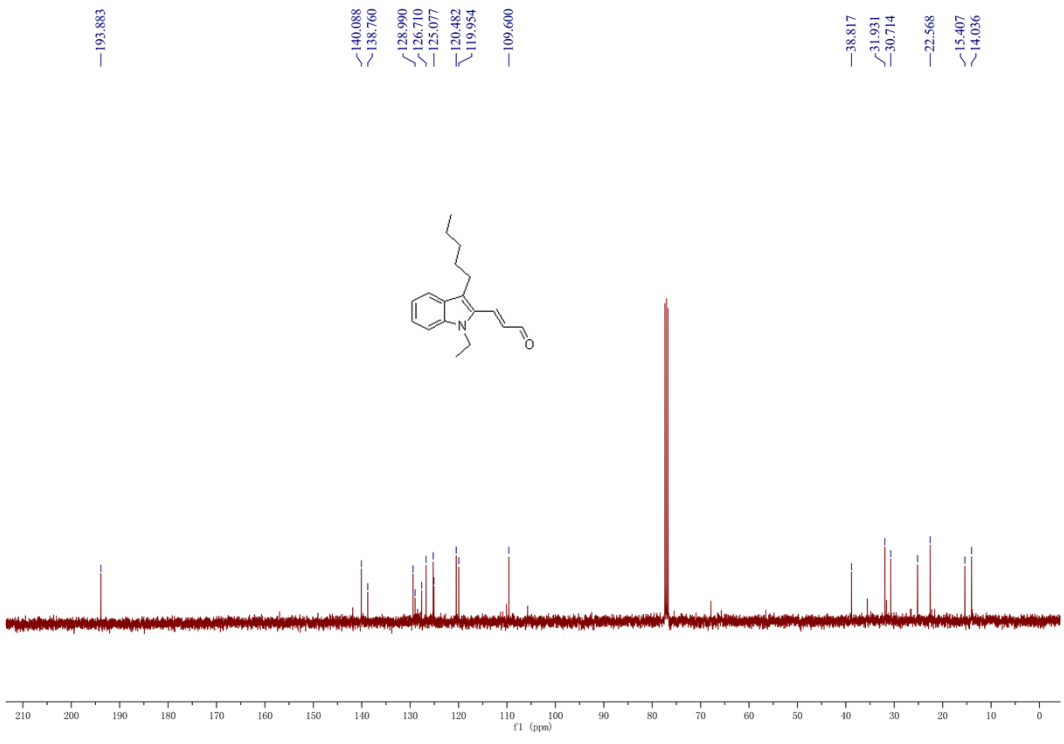
^{13}C NMR of **17i**



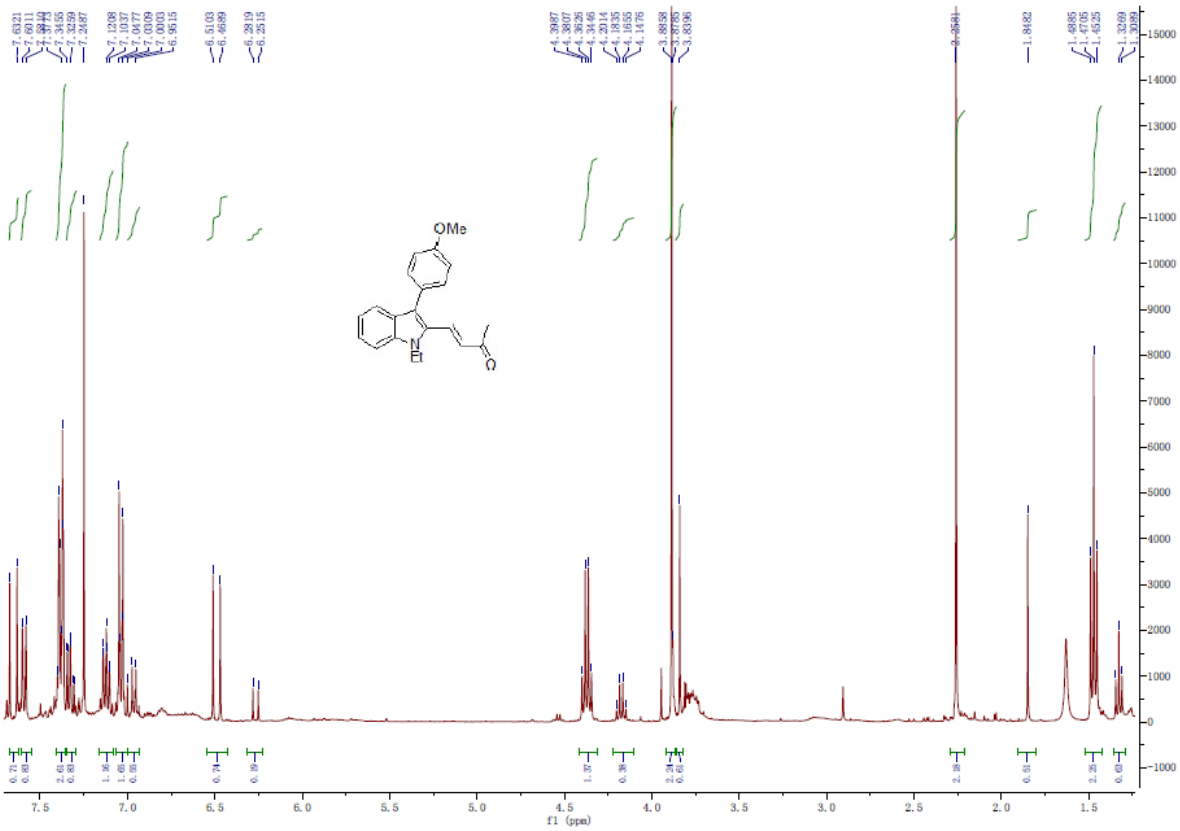
^{1}H NMR of **17j**



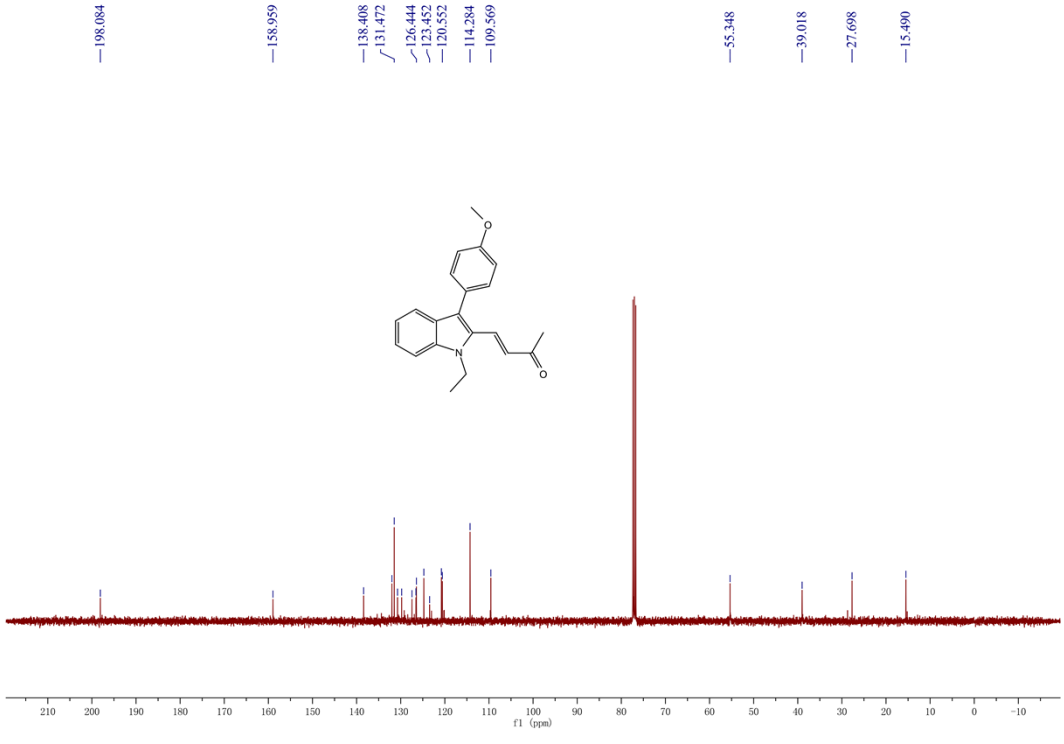
^{13}C NMR of **17j**



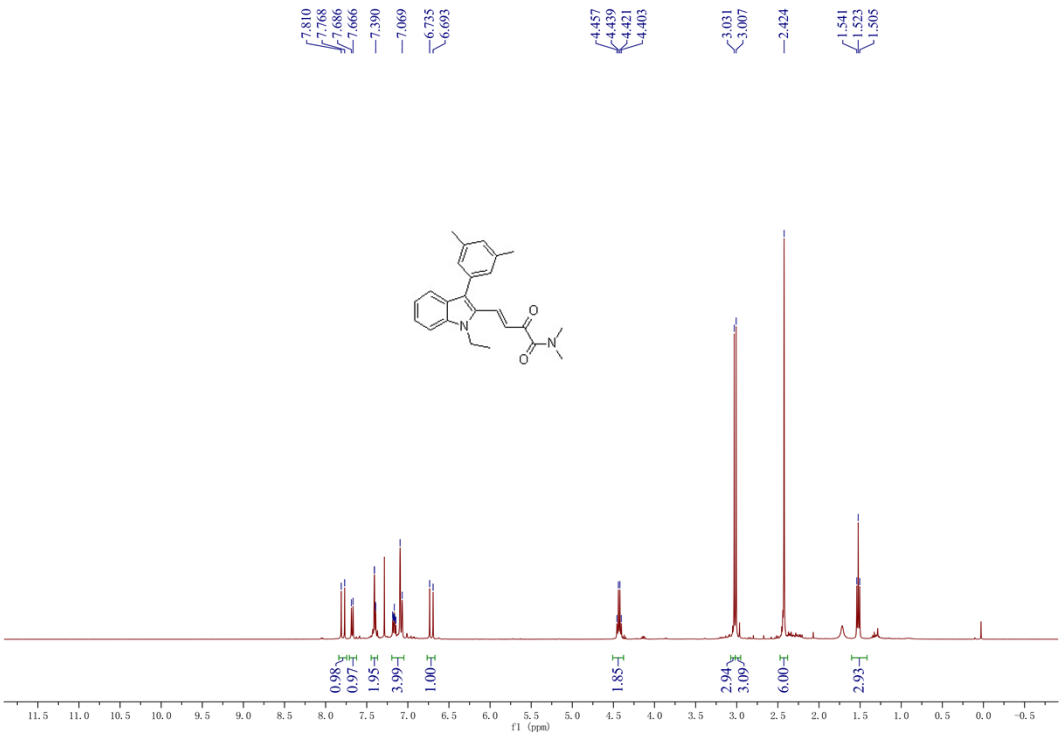
^{1}H NMR of **17k** (Z/E =1/4)



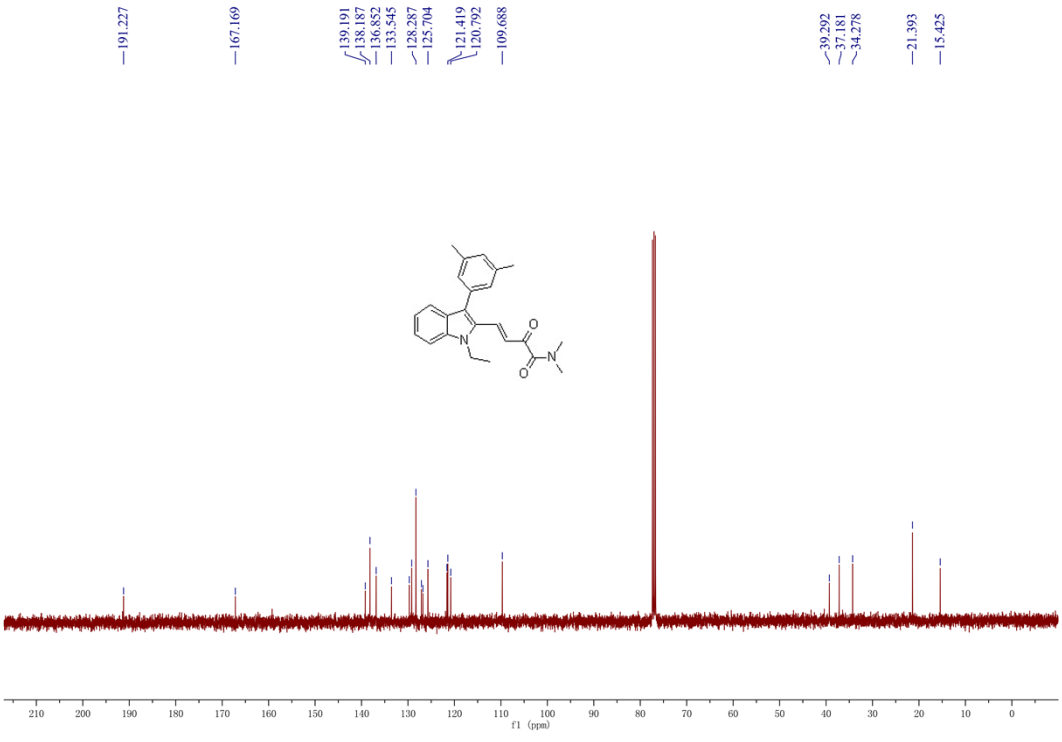
^{13}C NMR of **17K** (Z/E =1/4)



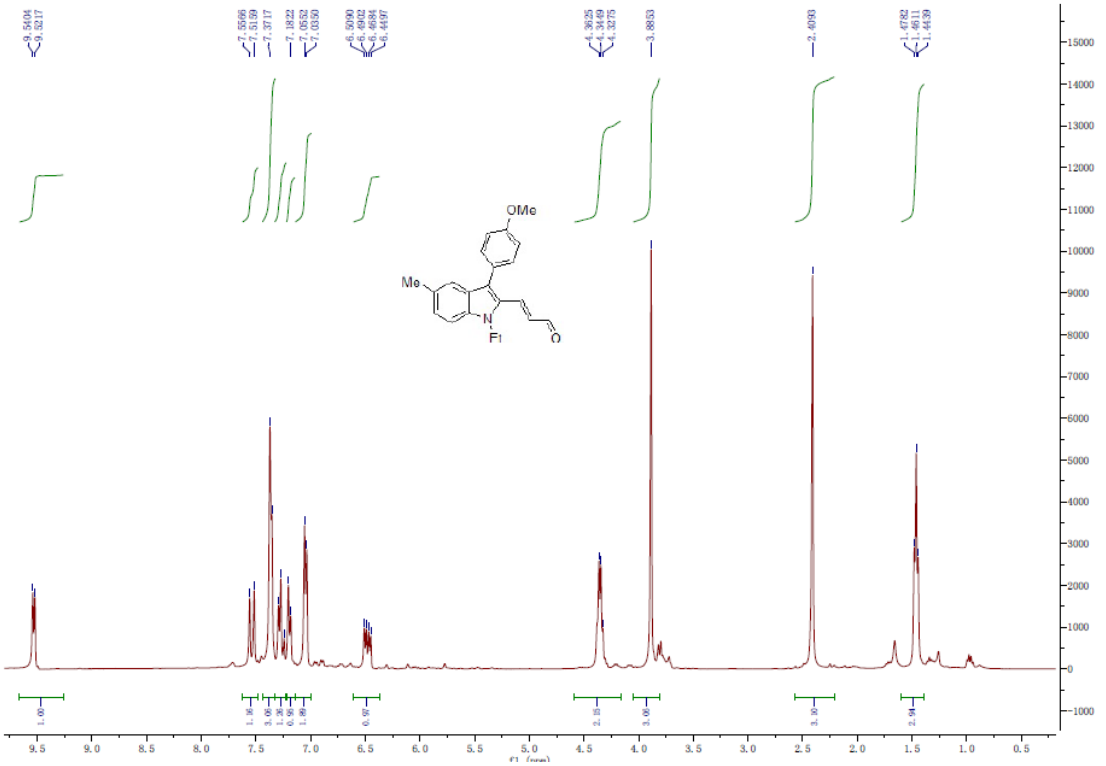
^{1}H NMR of **17l**



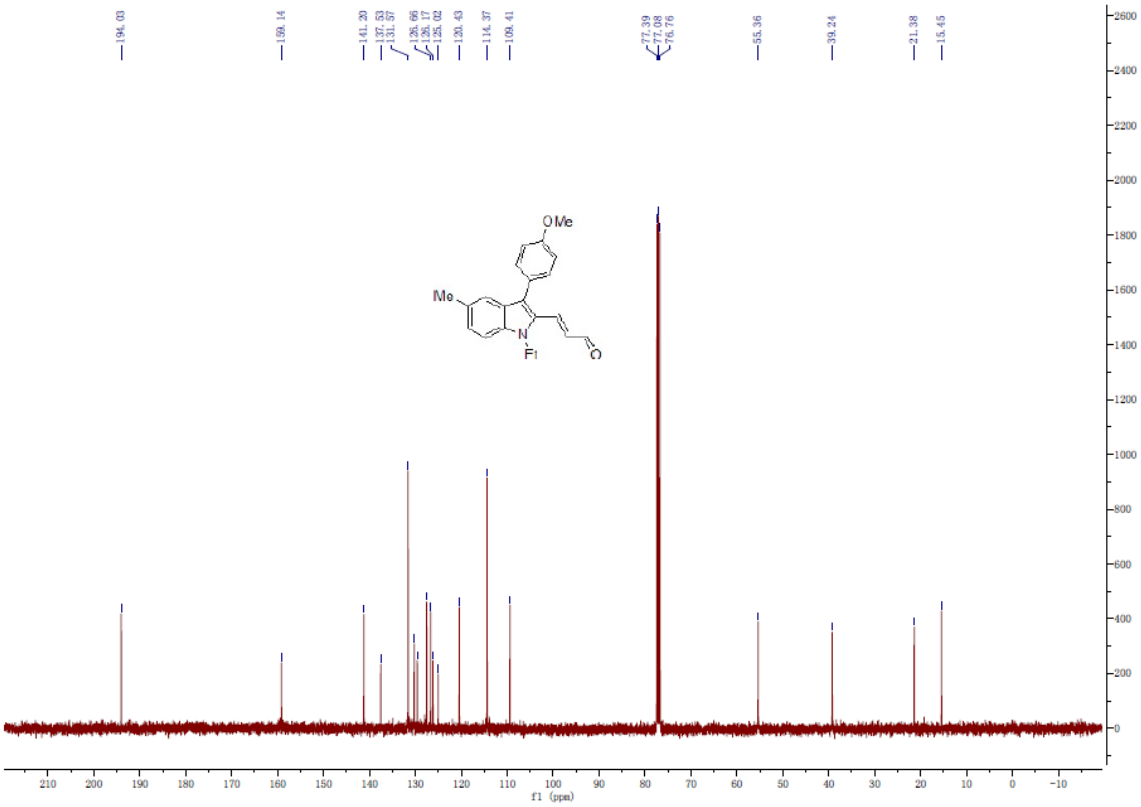
^{13}C NMR of **17l**



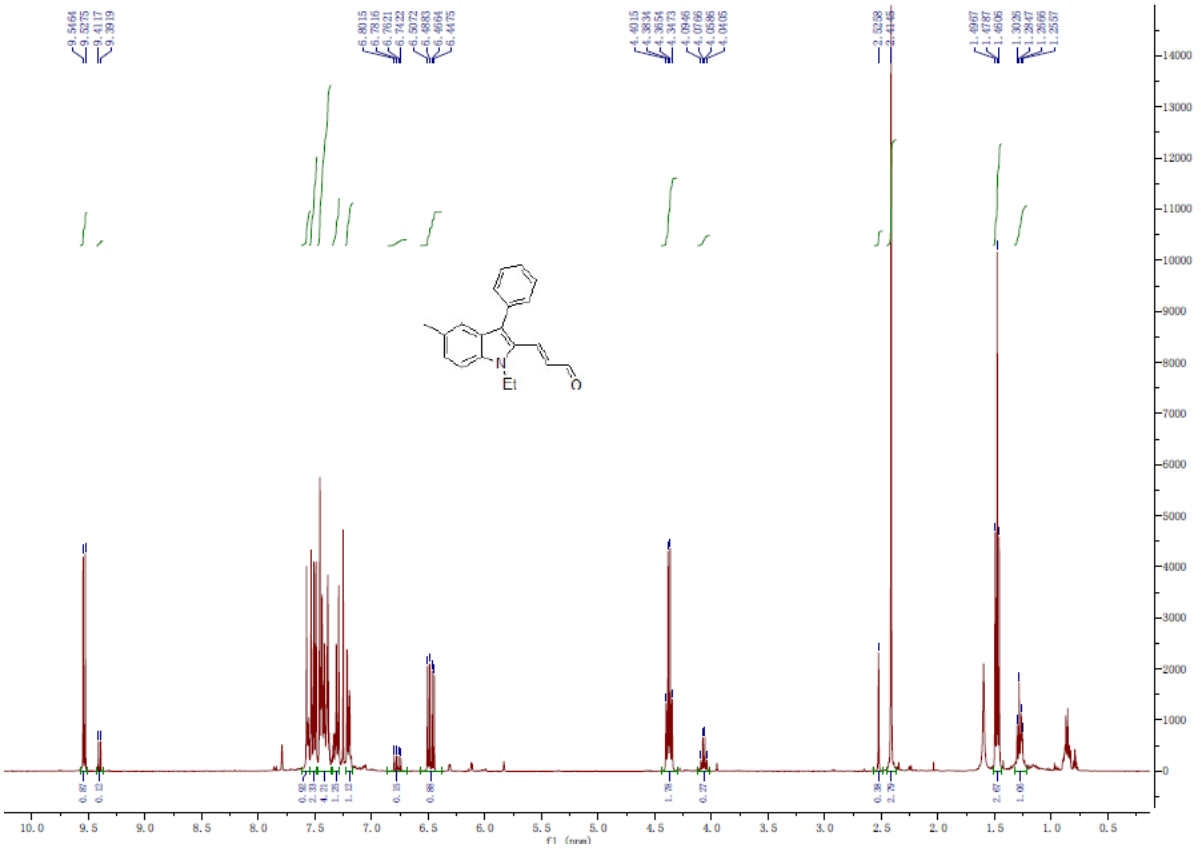
^{1}H NMR of **17n**



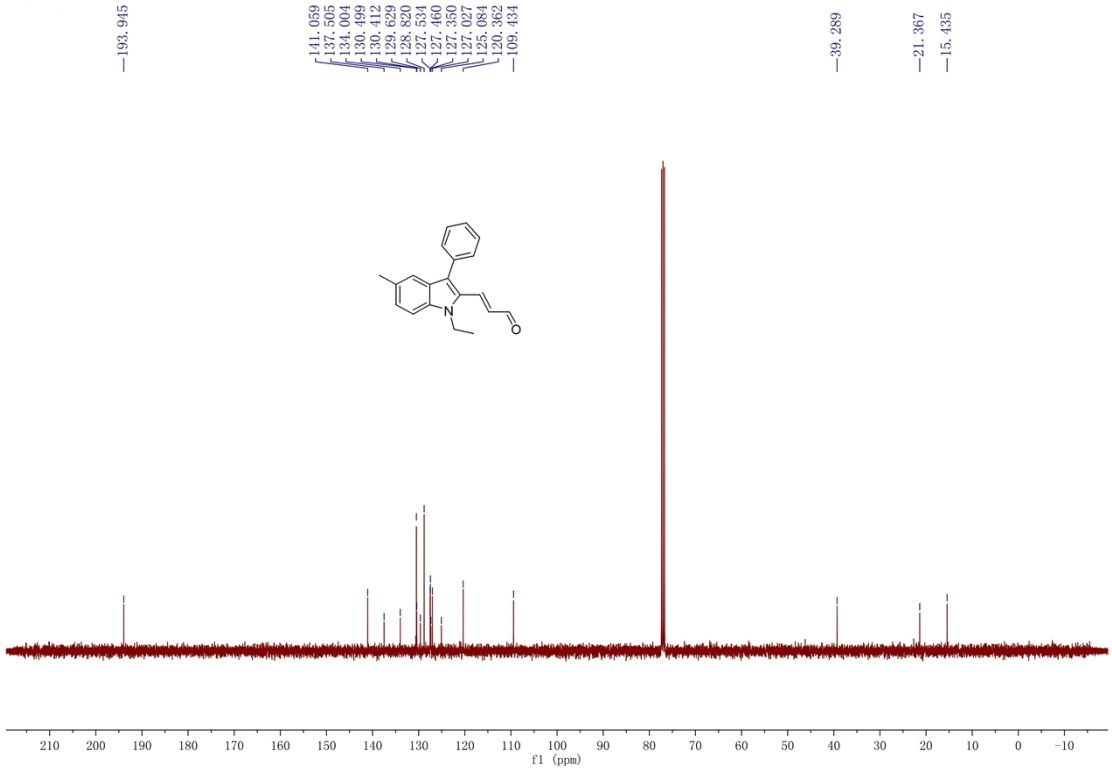
^{13}C NMR of **17n**



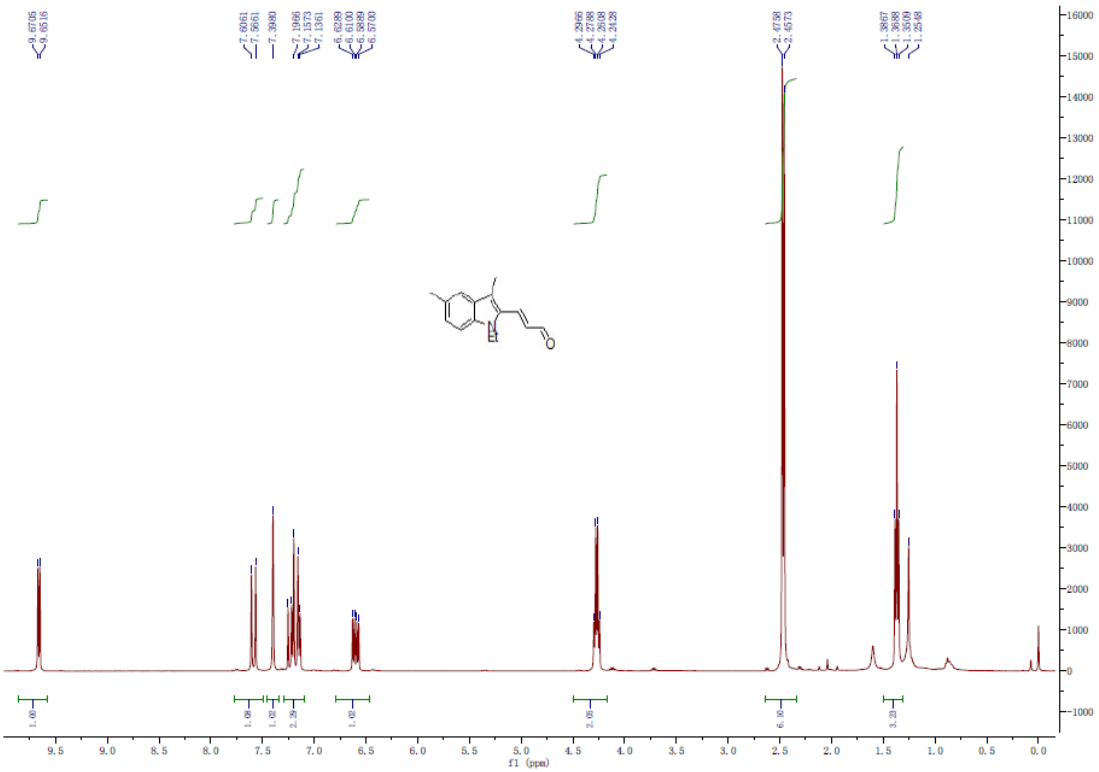
^{1}H NMR of **17o** (E/Z = 4/1)



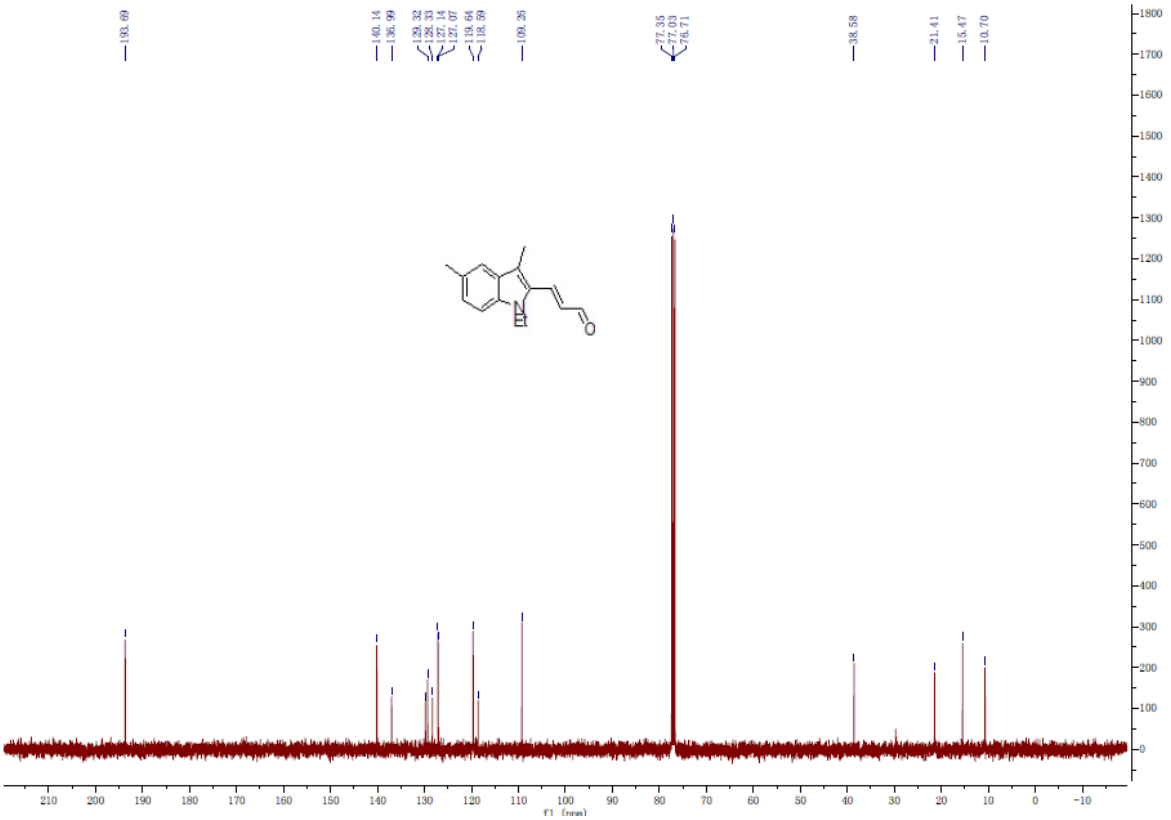
^{13}C NMR of **17o** (E/Z = 4/1)



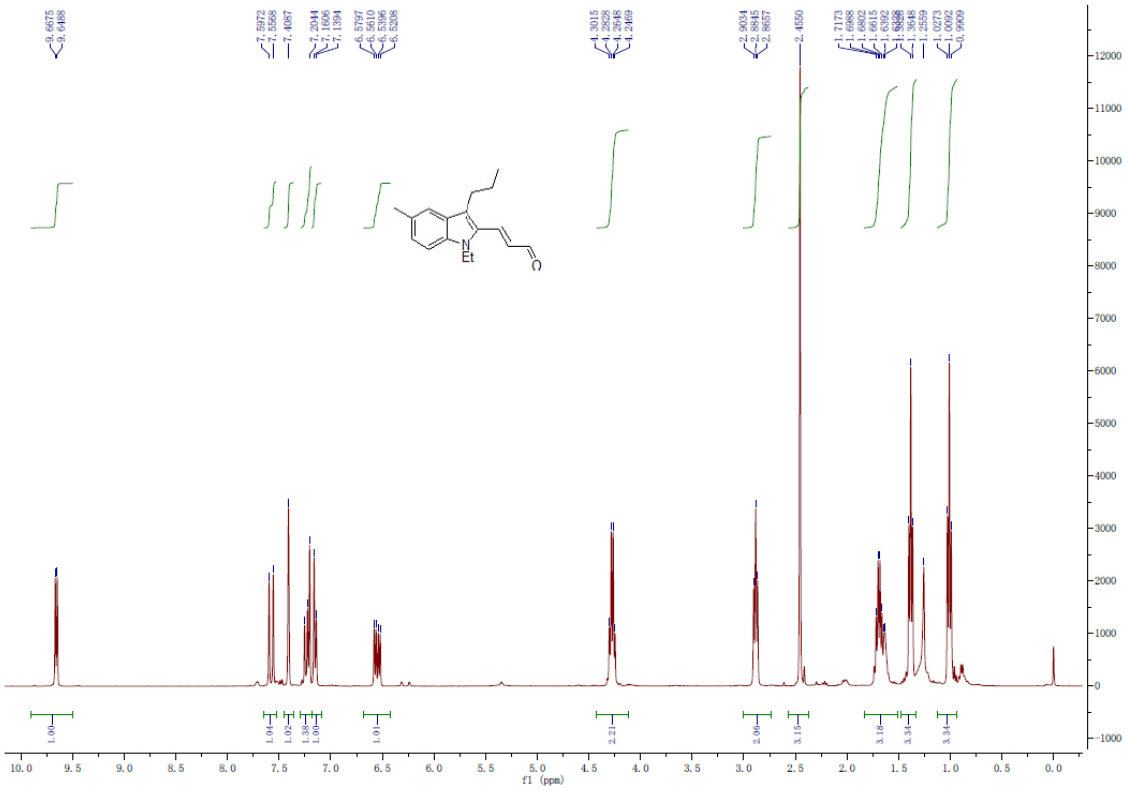
^{1}H NMR of **17p**



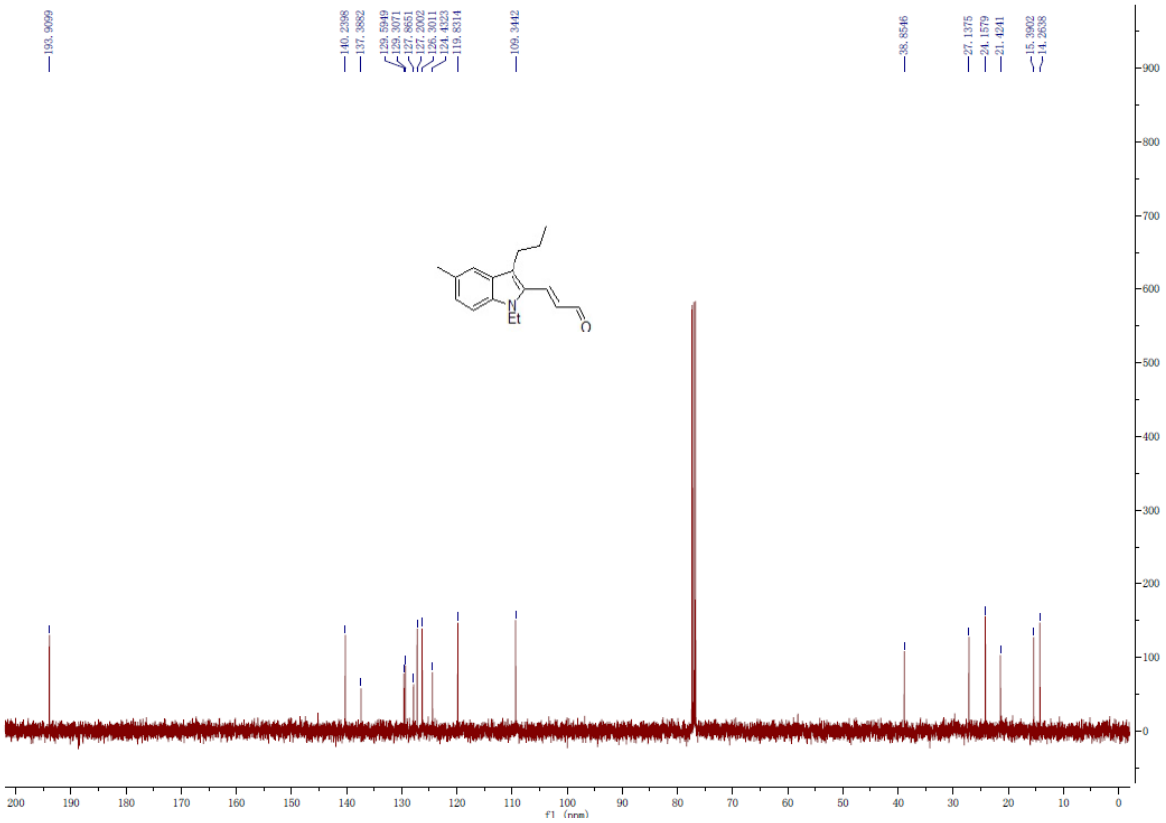
^{13}C NMR of **17p**



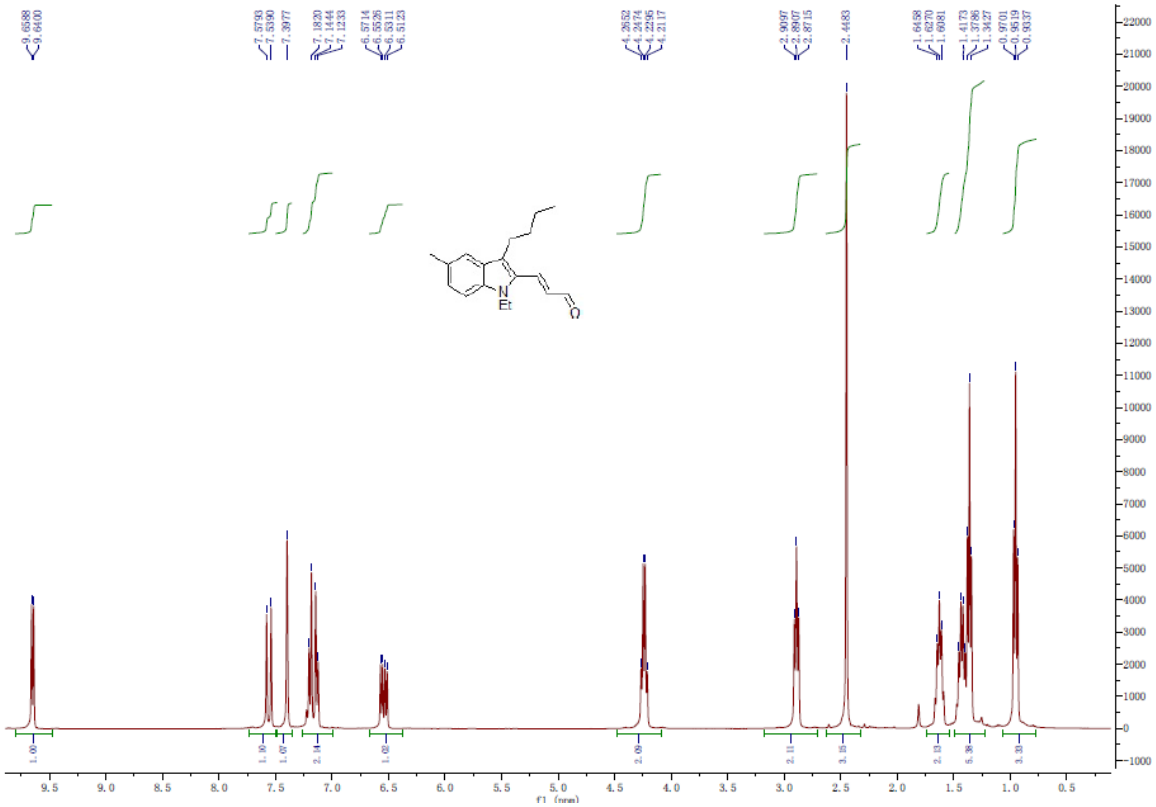
^{1}H NMR of **17q**



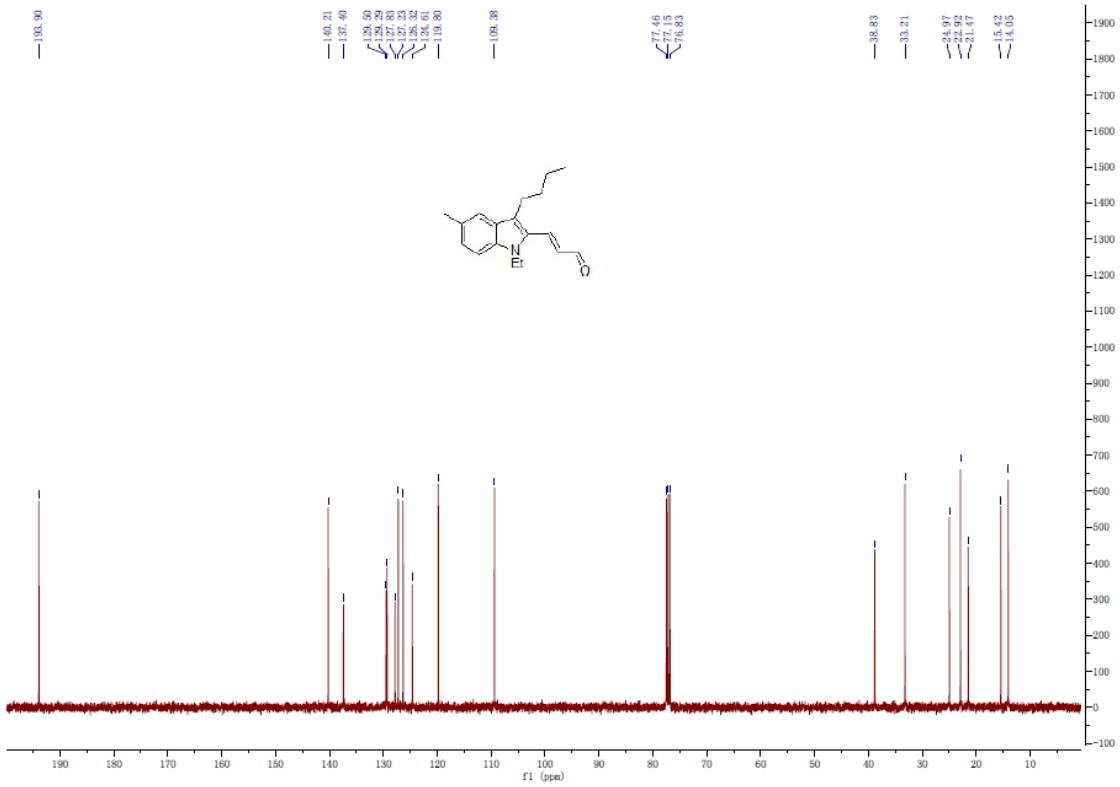
^{13}C NMR of **17q**



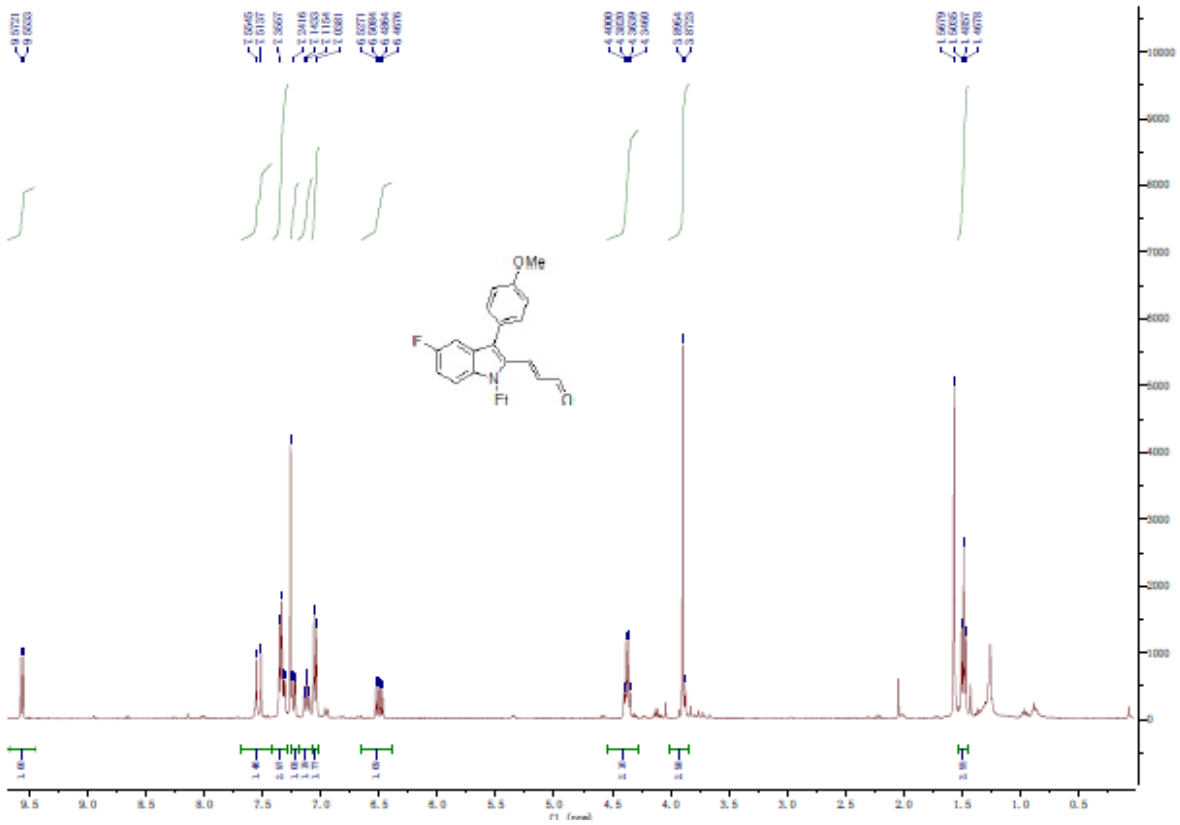
^{1}H NMR of **17r**



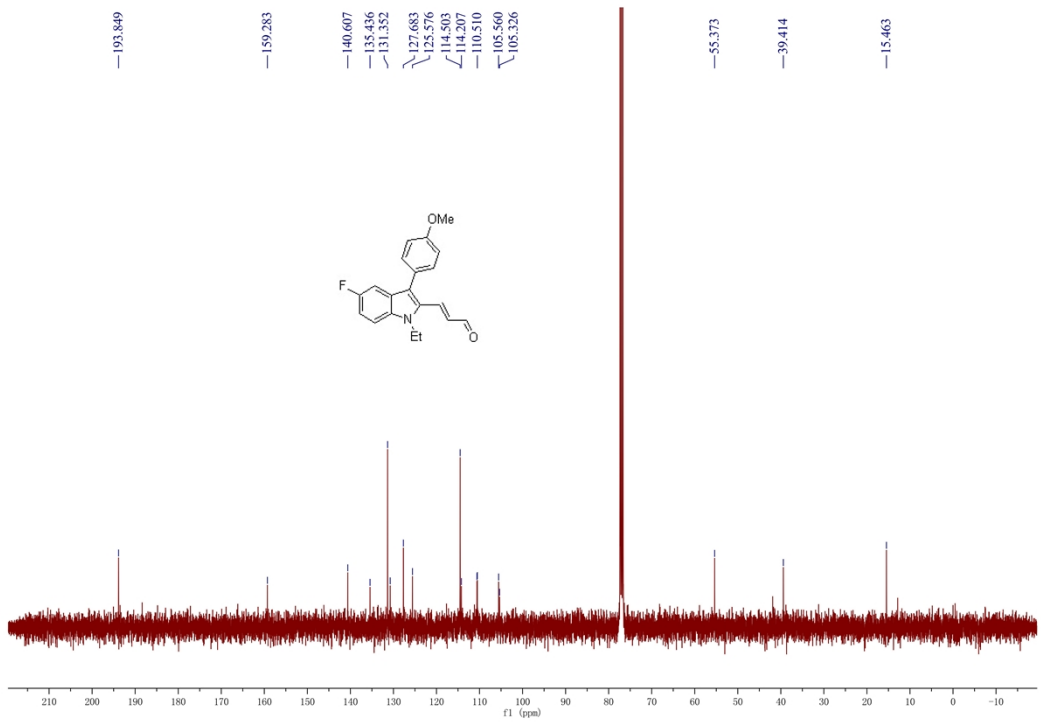
^{13}C NMR of **17r**



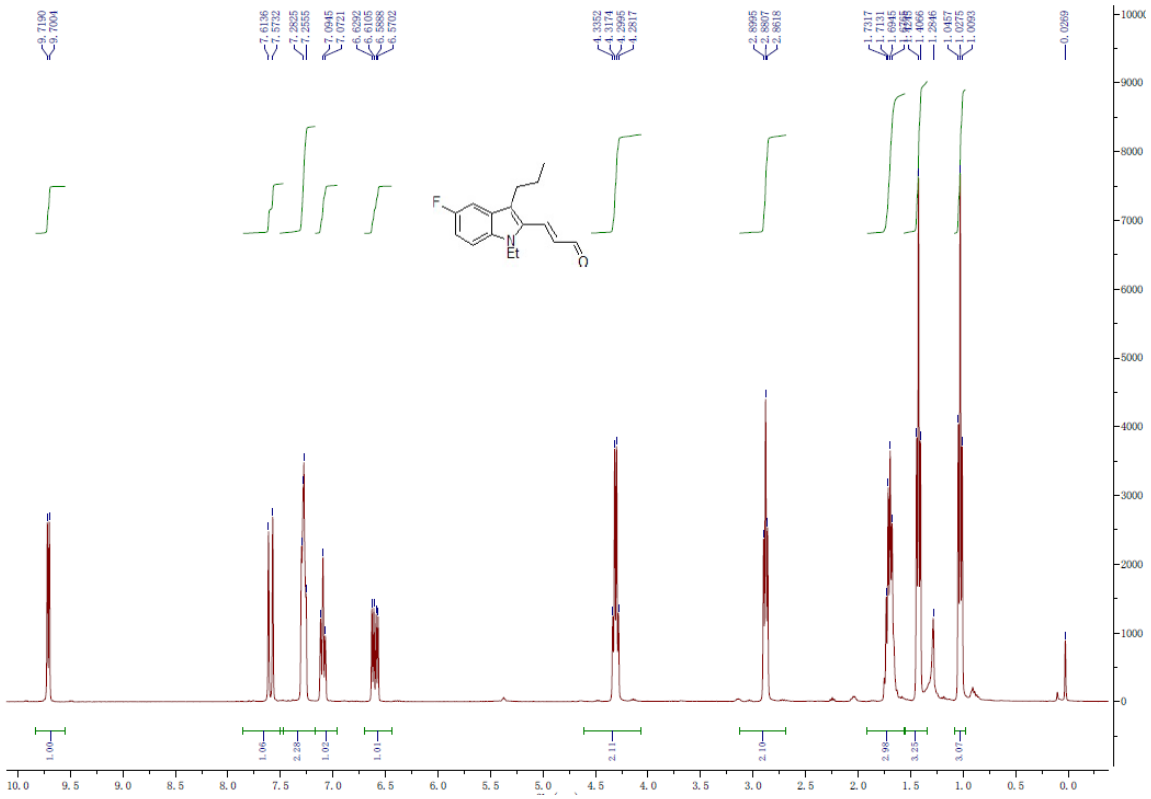
^{1}H NMR of **17s**



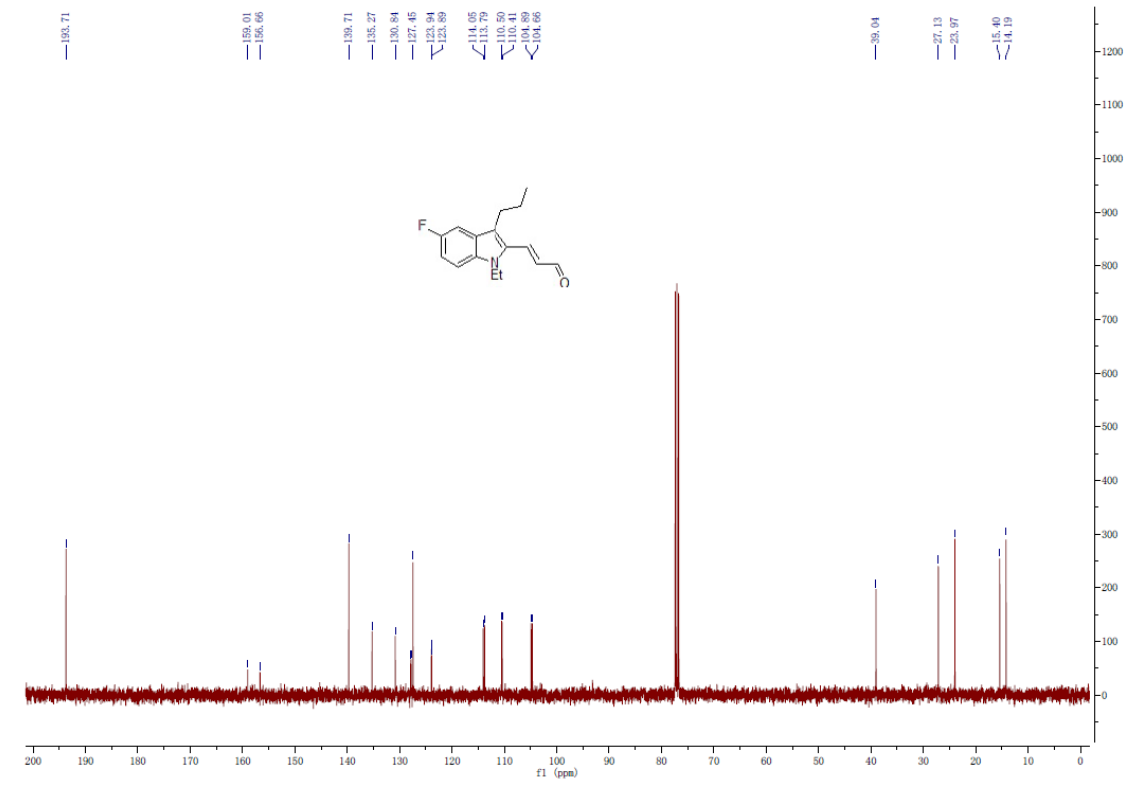
^{13}C NMR of **17s**



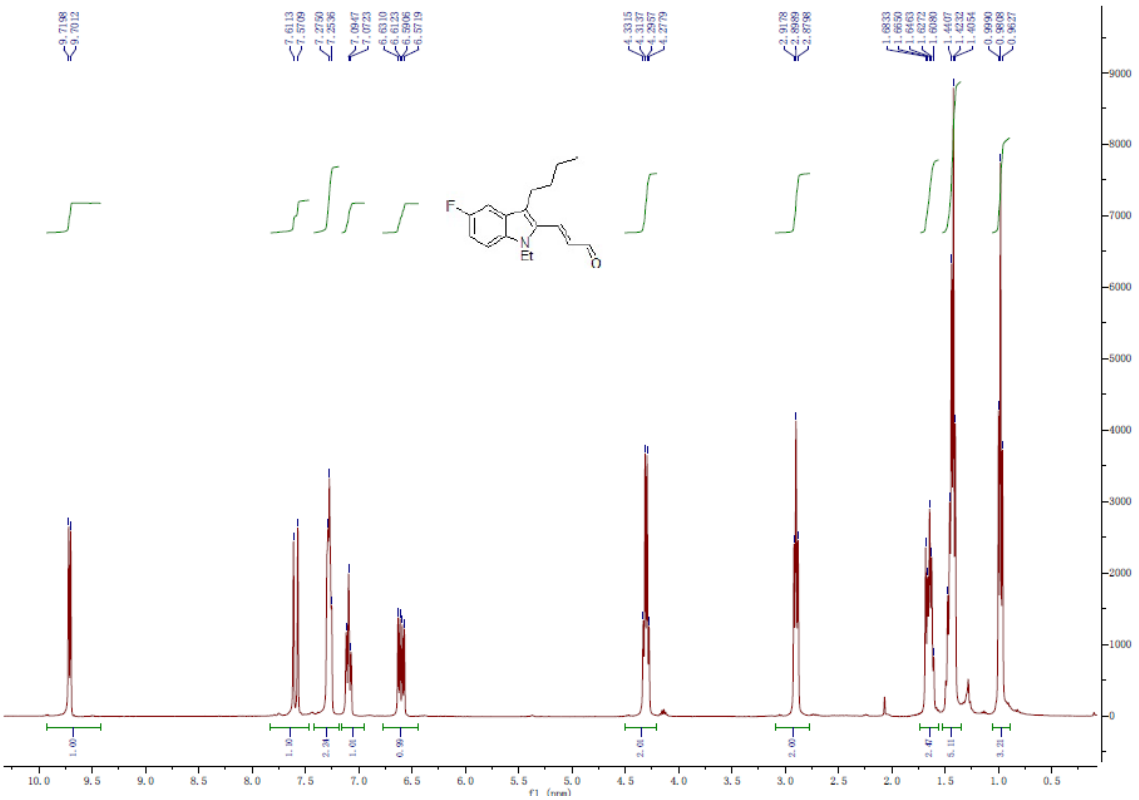
^{1}H NMR of **17t**



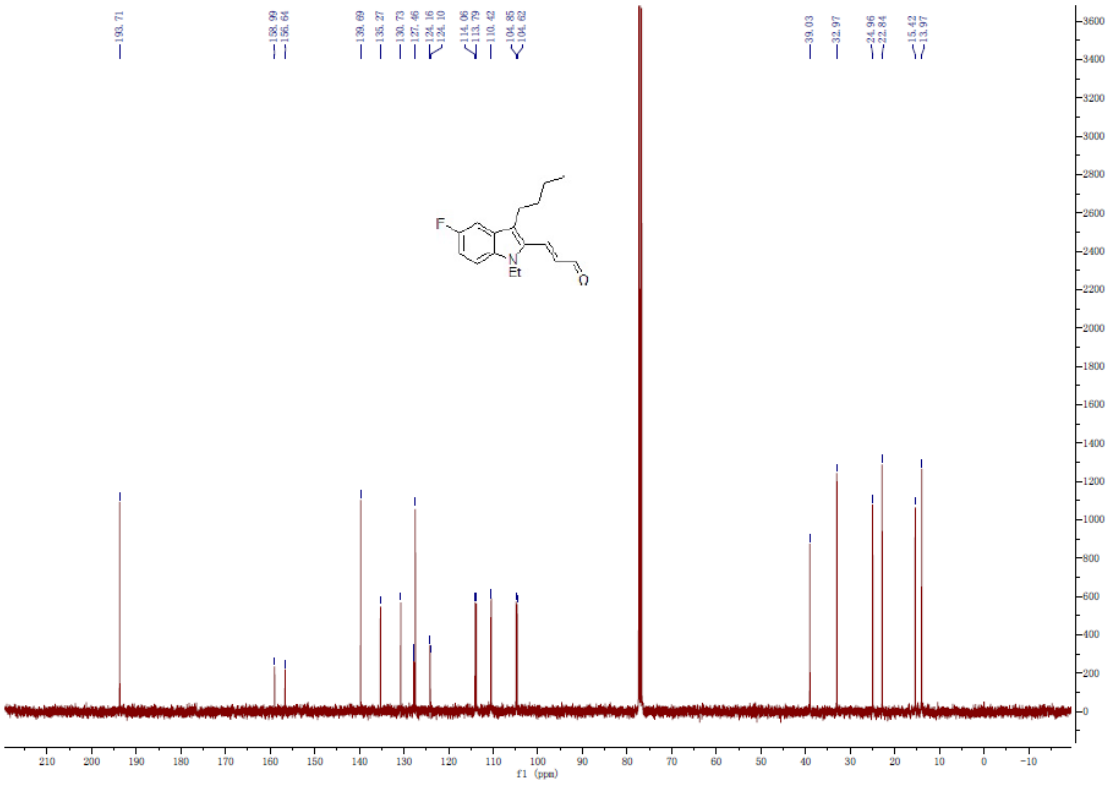
^{13}C NMR of **17t**



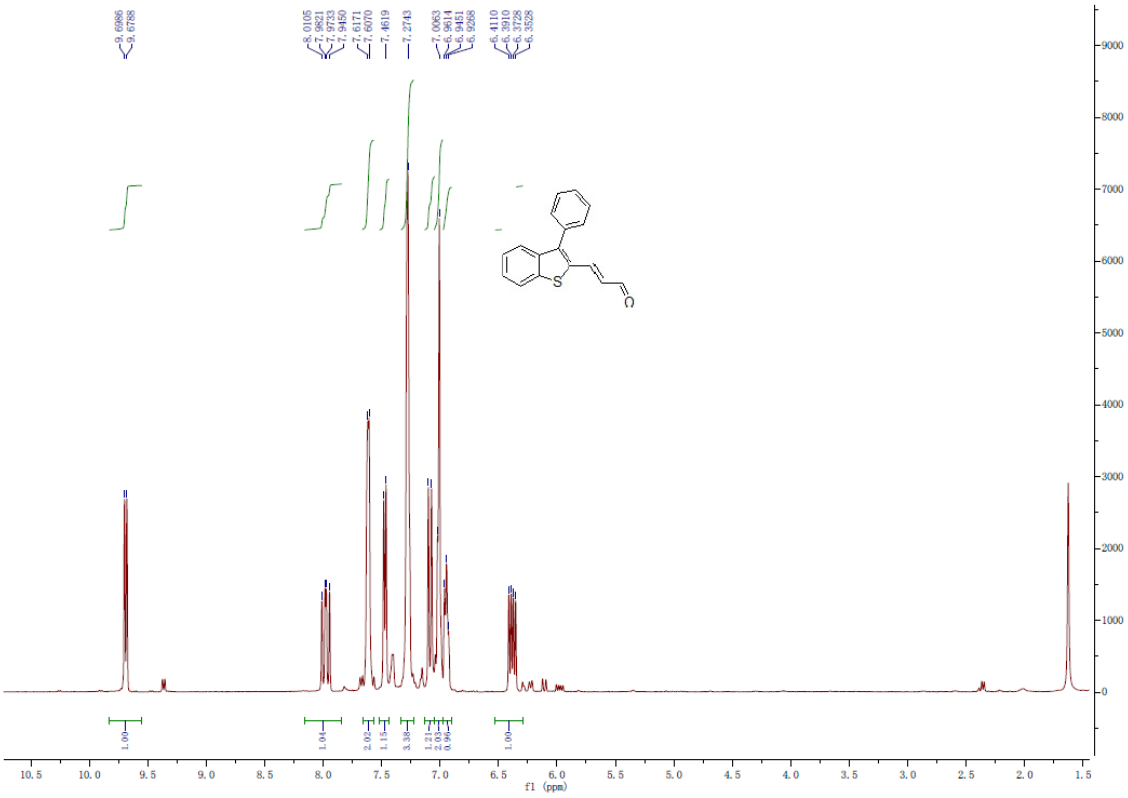
^{1}H NMR of **17u**



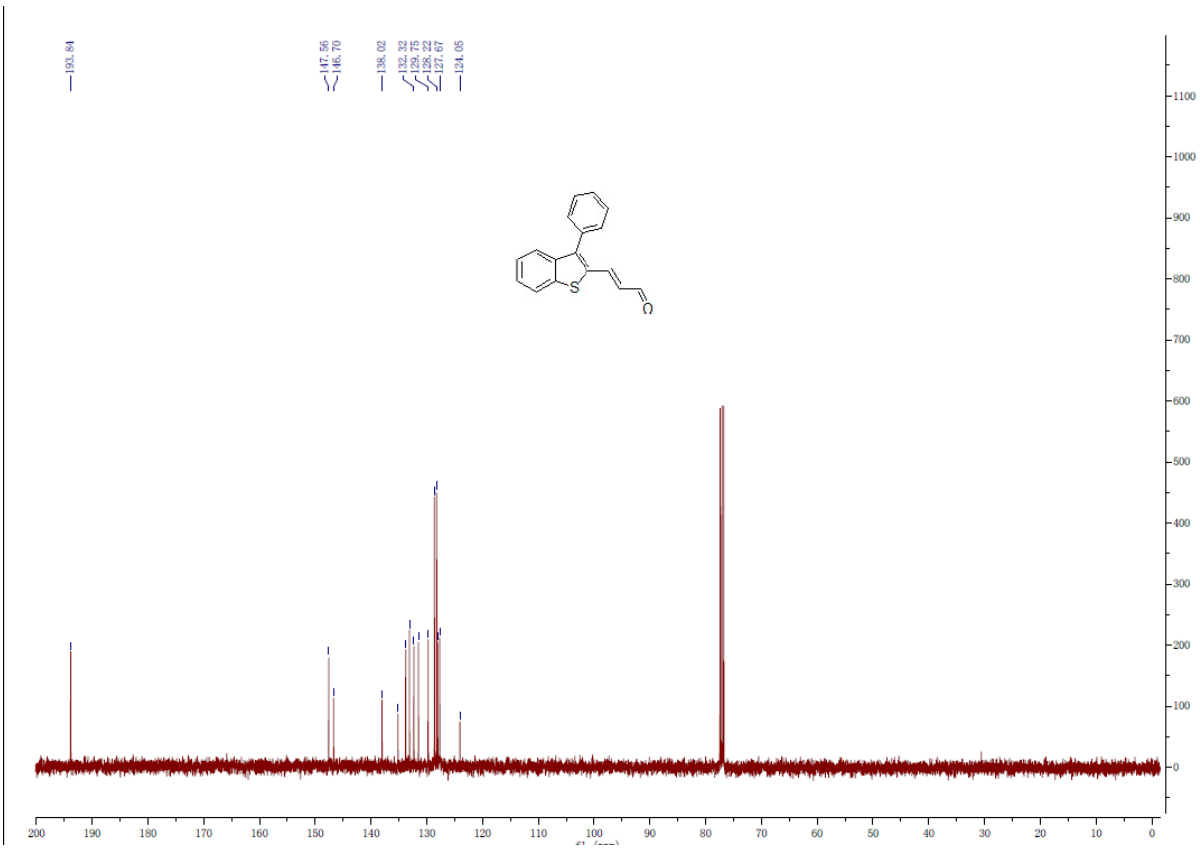
^{13}C NMR of **17 u**



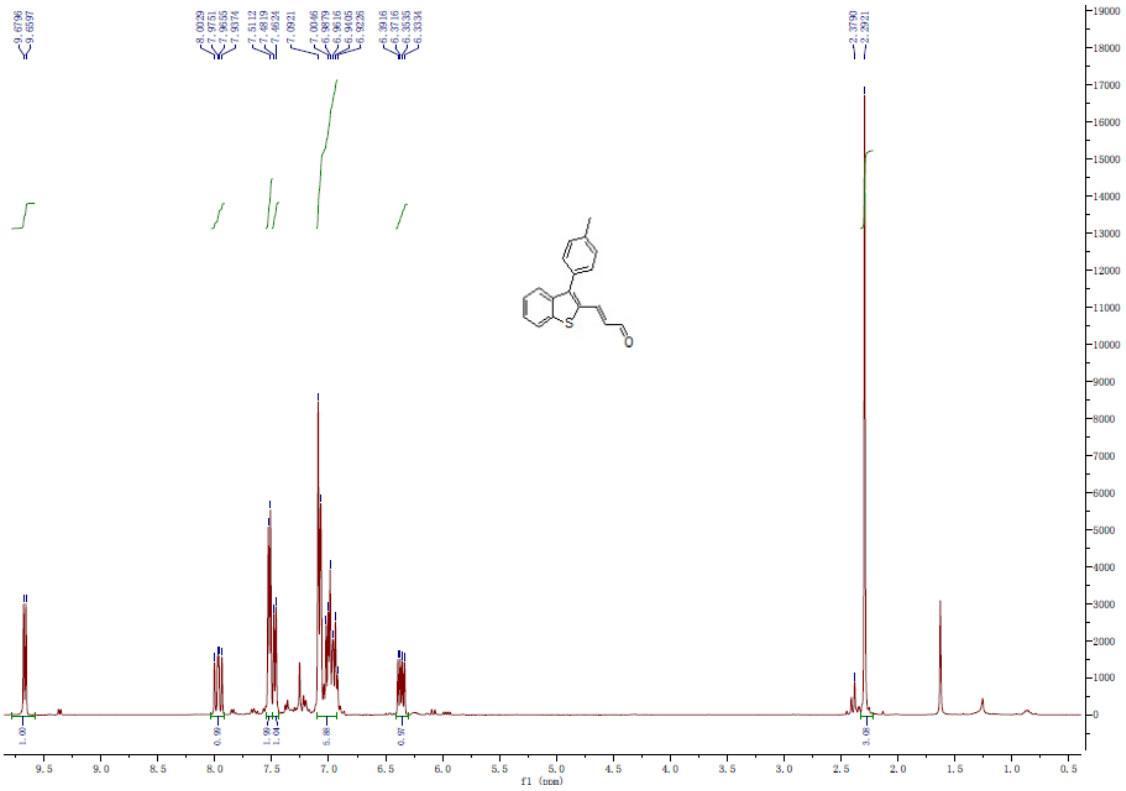
^{1}H NMR of **26a**



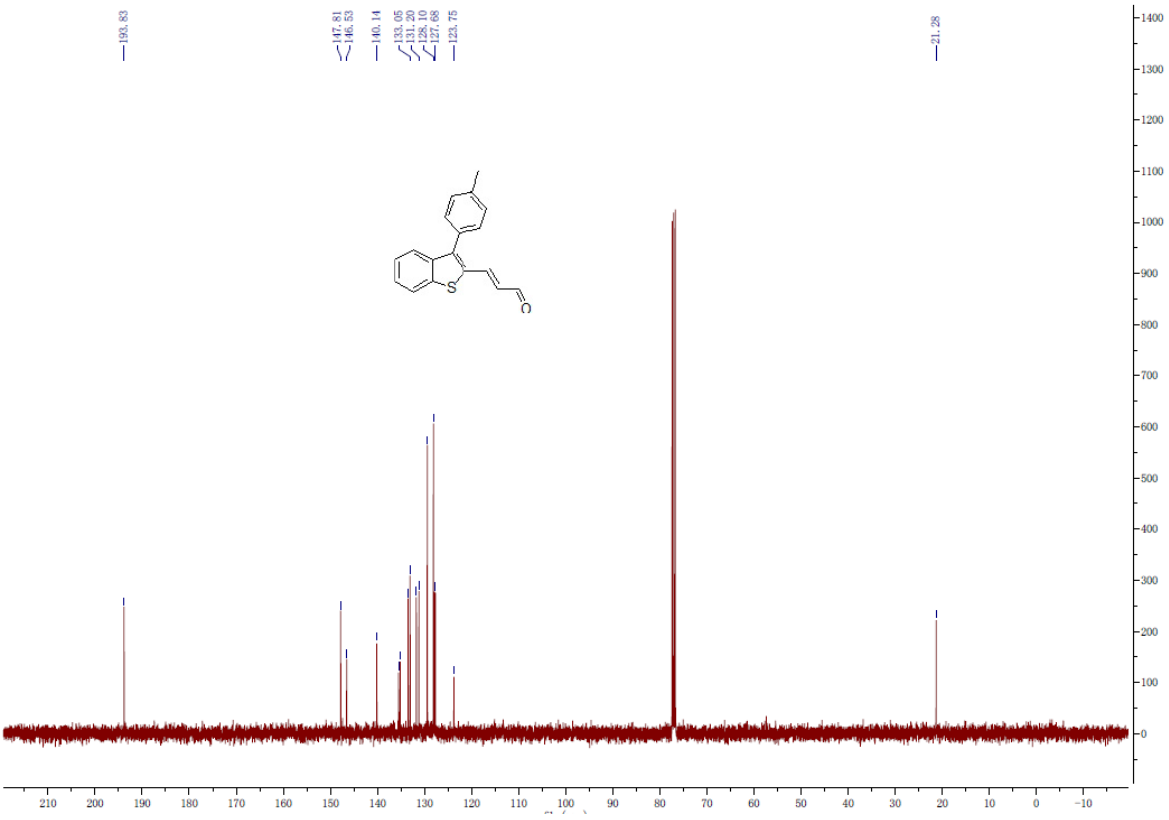
^{13}C NMR of **26a**



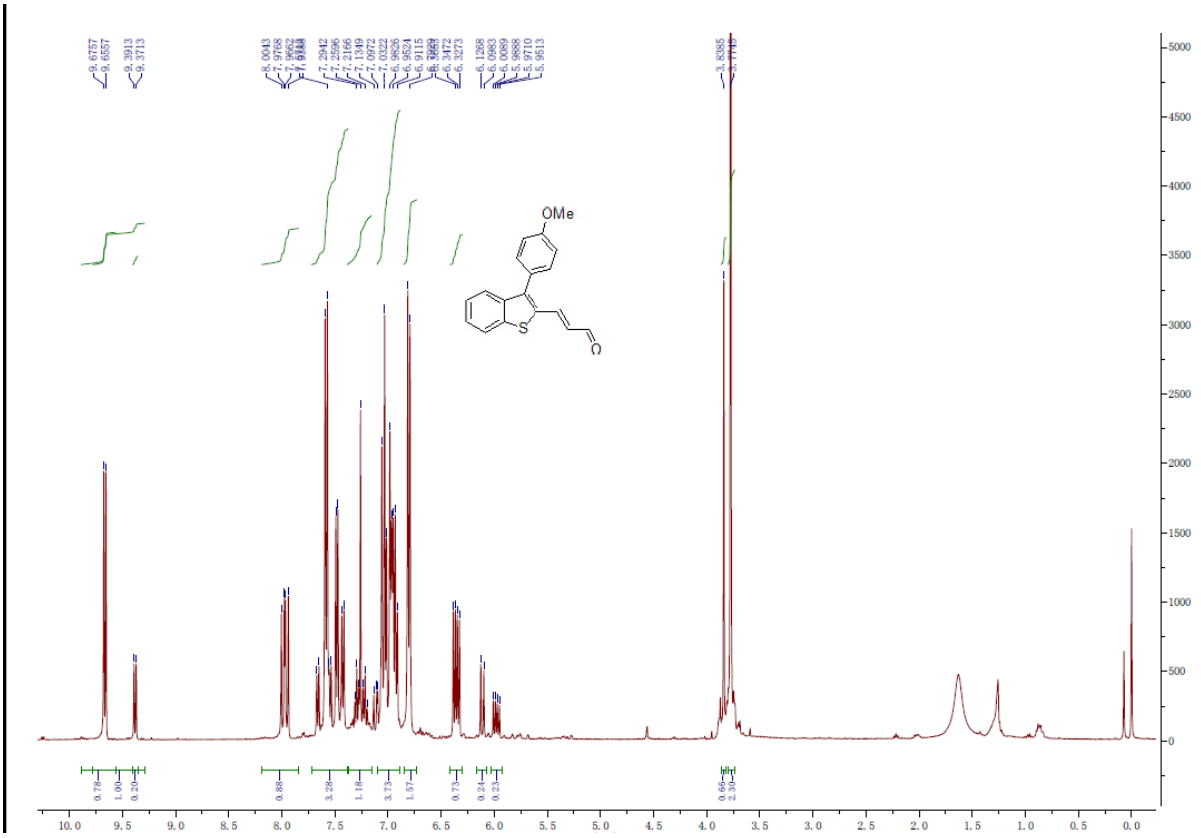
^{1}H NMR of **26b**



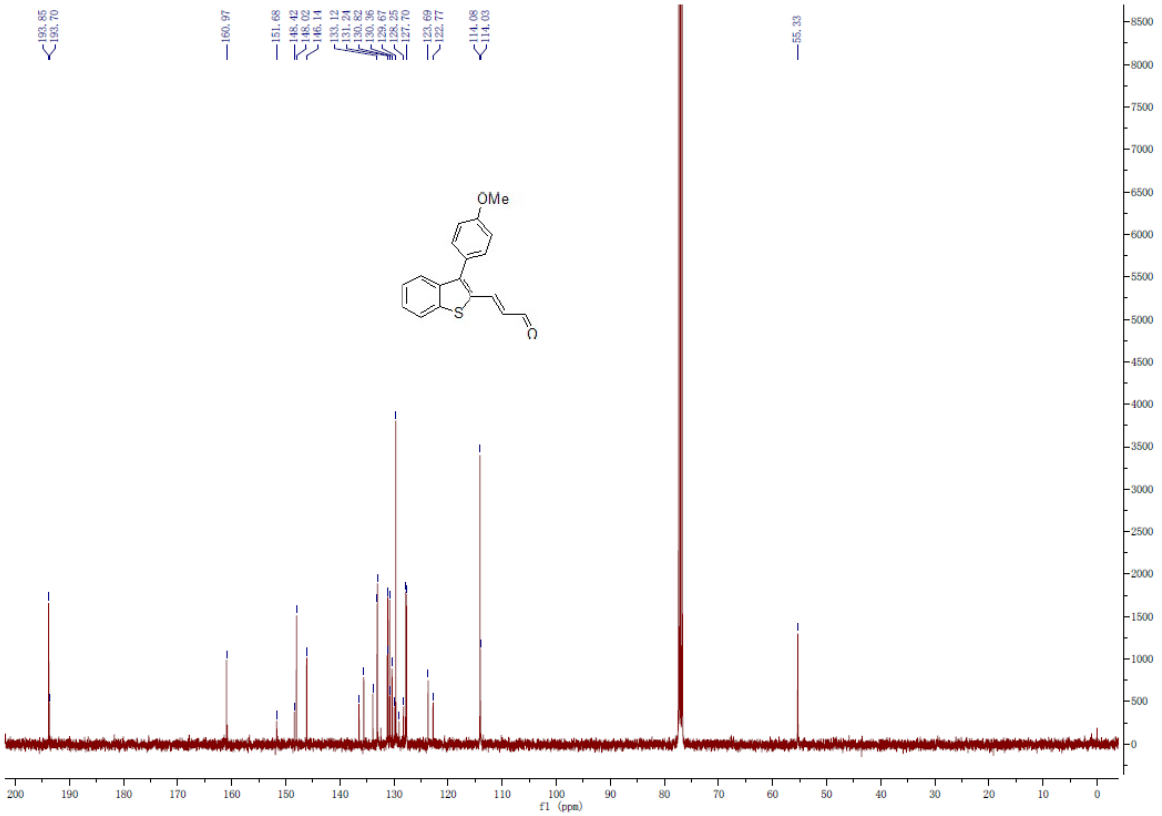
^{13}C NMR of **26b**



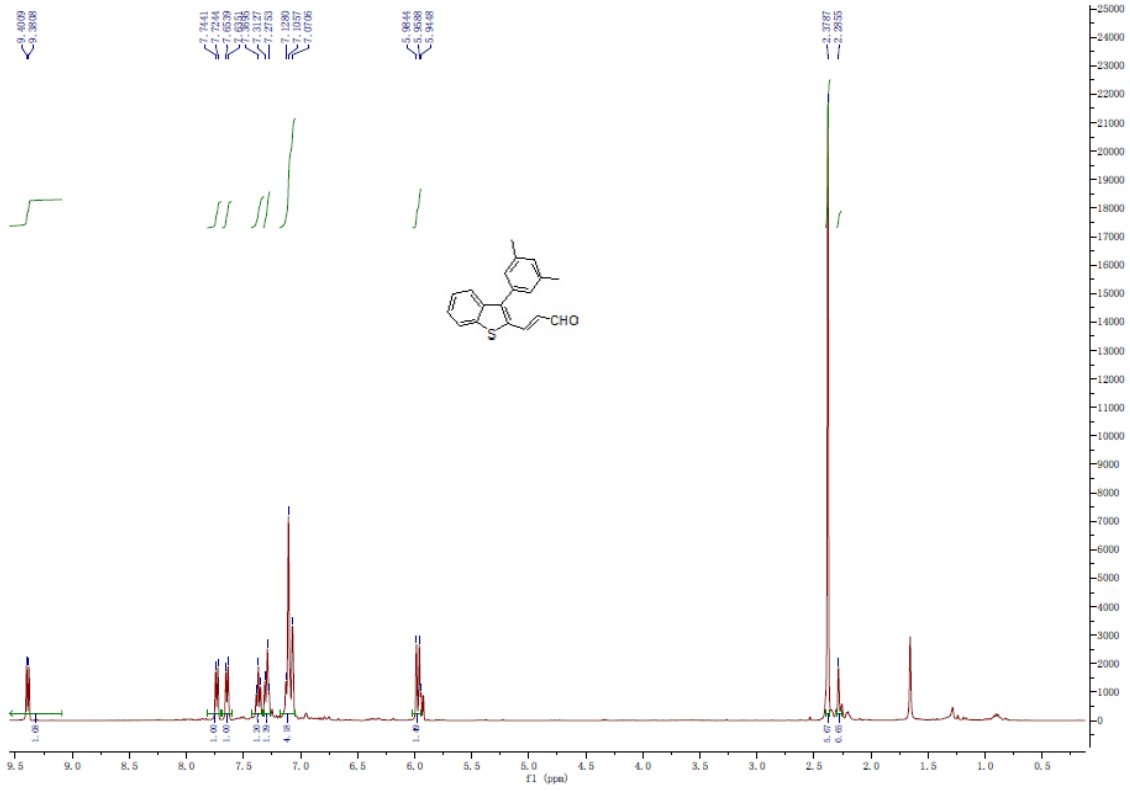
^{1}H NMR of **26c**



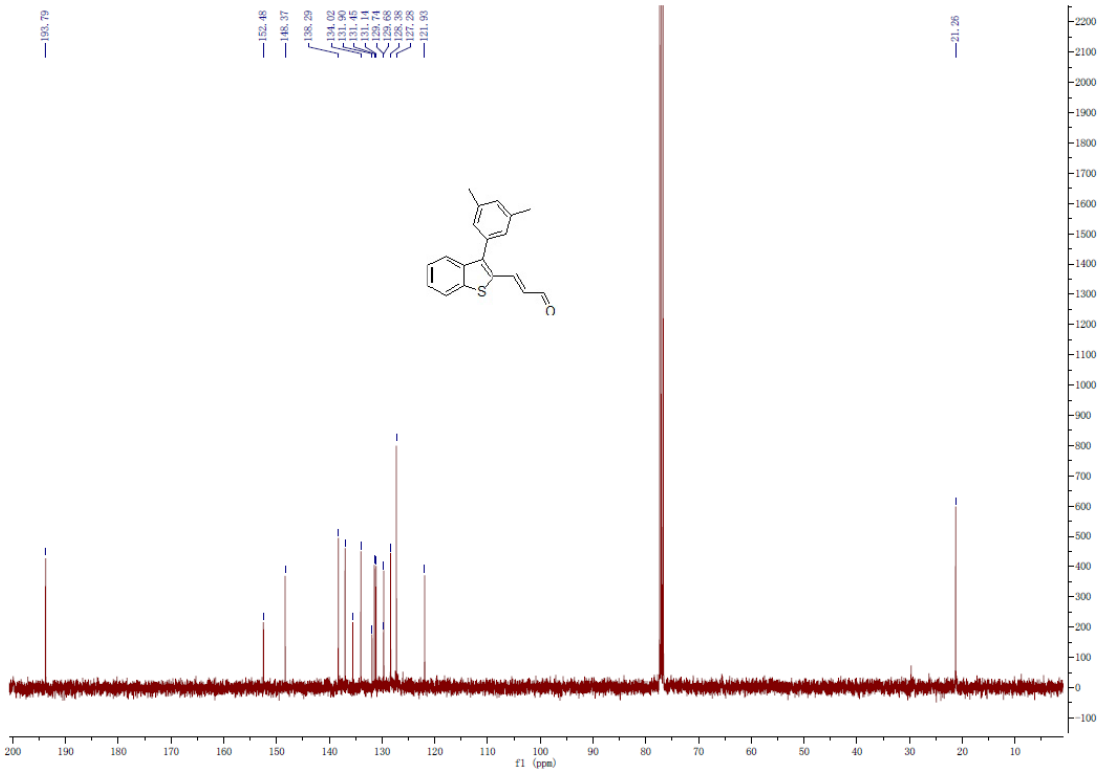
^{13}C NMR of **26c**



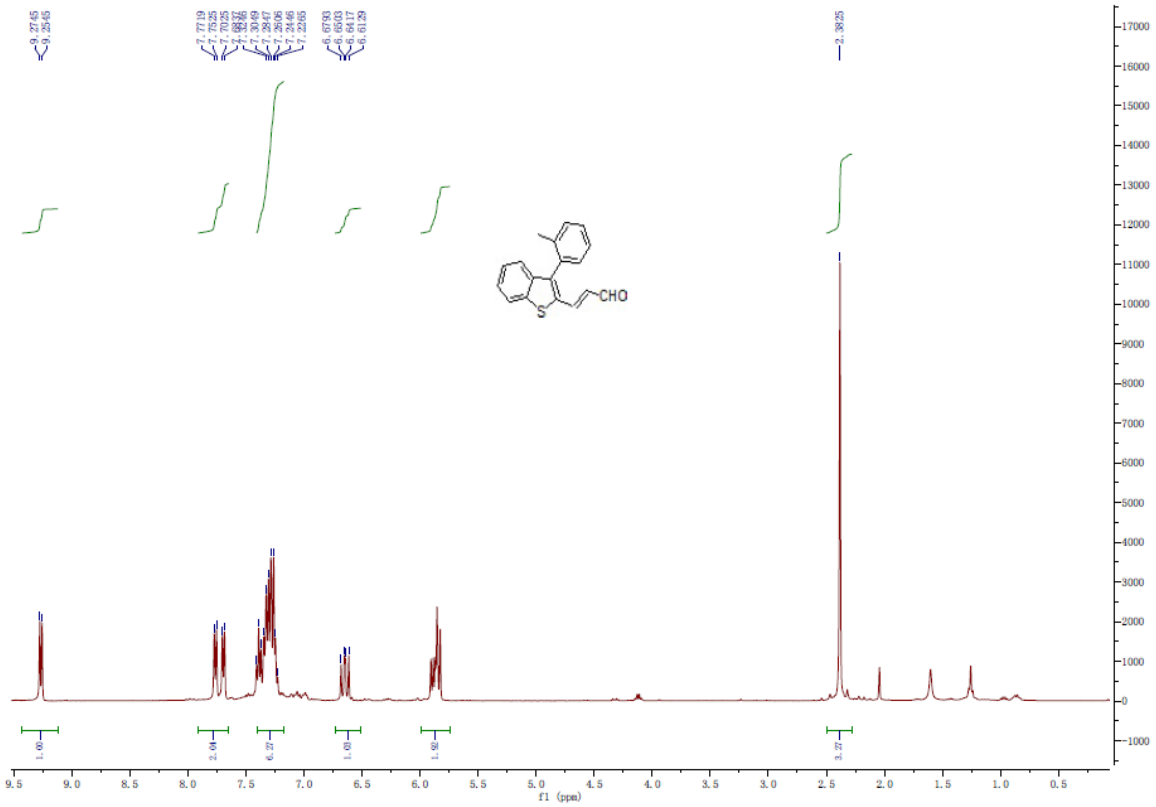
^{1}H NMR of **26d**



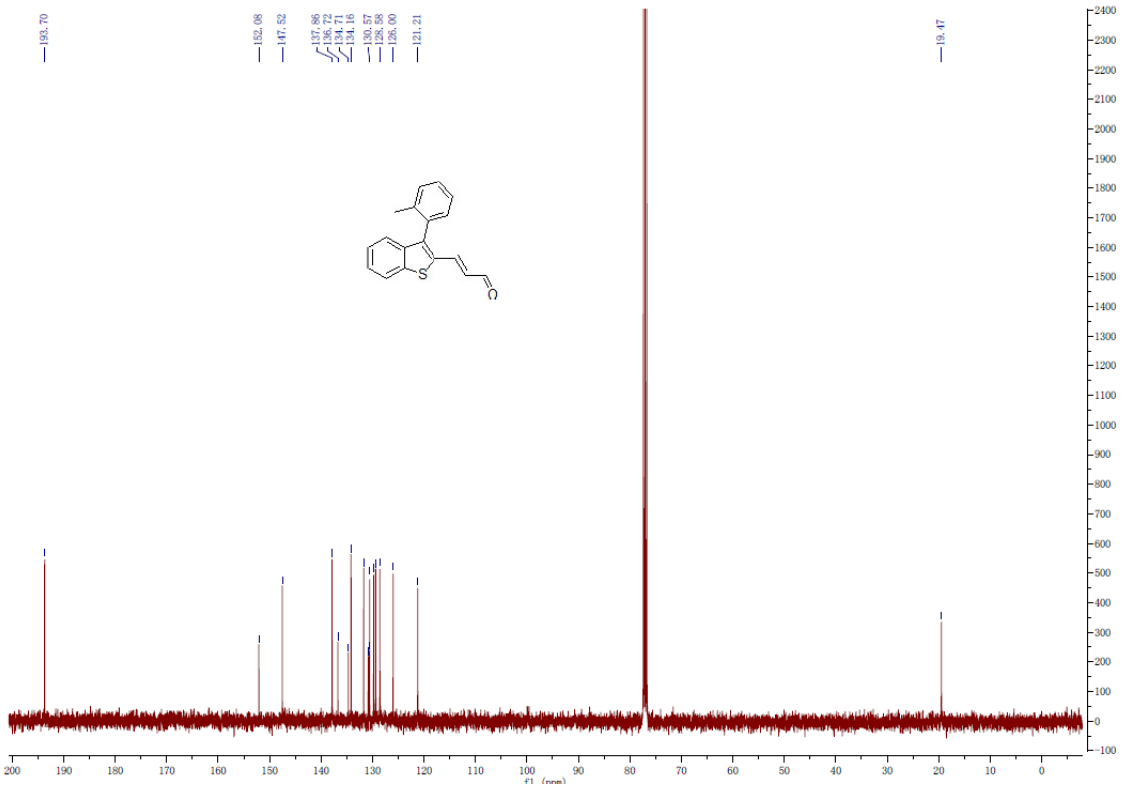
^{13}C NMR of **26d**



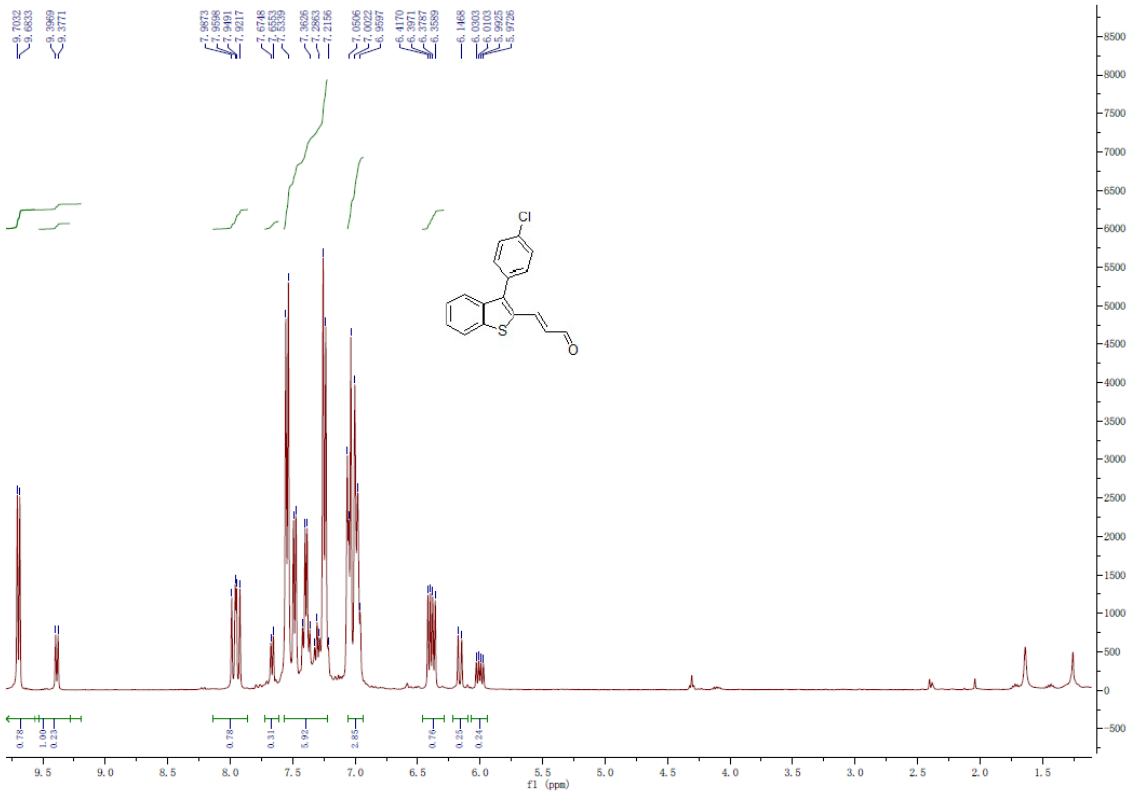
^{1}H NMR of **26e**



^{13}C NMR of **26e**



^{1}H NMR of **26f**



^{13}C NMR of **26f**