Supporting Information

Delineating Physical Organic Parameters in Site-Selective C–H Functionalization of Indoles

Youyoung Kim[†,‡,§], Yoonsu Park[†,‡,§], and Sukbok Chang[‡,†,*]

[†]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 34141, Korea

[‡]Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon, 34141, Korea

[§] Contributed equally to this work.

I. General Methods

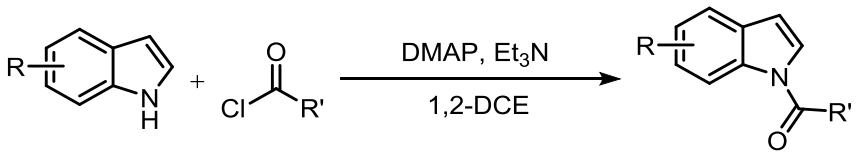
Unless otherwise stated, all commercial reagents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) or treatment with acidic anisaldehyde stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using a proper eluent system. ^{1}H NMR was recorded on Agilent Technologies DD2 (600 MHz), Bruker Avance 400 (400 MHz) or Bruker Avance 300 (300 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. The following abbreviations were used to describe peak splitting patterns when appropriate: br (broad), s (singlet), d (doublet), t (triplet), hept (heptet), dd (doublet of doublet), td (triplet of doublet), m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Agilent Technologies DD2 (150 MHz), Bruker Avance 400 (100 MHz) or Bruker Avance 300 (75 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the appropriate solvent peak. ^{19}F NMR was recorded on Agilent Technologies DD2 (564 MHz), Bruker Avance 400 (376 MHz). Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method. X-ray diffraction data was collected on a Bruker SMART APEX II coated with Paraton-*N* oil under a stream of N_2 (g) at 120 K. Melting point was measured with Buchi Melting Point M-565. If necessary, regiomeric ratios were measured by using a high performance liquid chromatography from Shimadzu with a binary mobile phase gradient (Hx/THF = 8:2 or 9:1) elution (0.8 mL/min) and a Chiral-pak IA-3 or ID-3. Photodiode array (PDA) detection was monitored at 254 nm.

Safety Statement

No unexpected or unusually high safety hazards were encountered in these methods. Although tosyl azide is one of the more stable azide compounds, it is still regarded as a potential explosive and should be carefully stored at -30 °C.

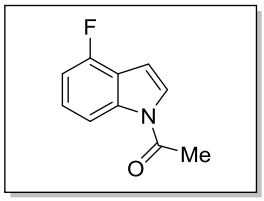
II. Procedures for the Preparation of Starting Materials

1. General Procedure for the Preparation of *N*-Protected Indoles[S1]



To a solution of indoles (2.5 mmol), 4-(dimethylamino)pyridine (31 mg, 0.25 mmol) and triethylamine (0.52 mL, 3.8 mmol) in dry 1,2-dichloroethane (10 mL) was added acyl chloride (3.0 mmol) dropwise at 0 °C. The reaction mixture was stirred at 80°C for overnight. After the reaction was cooled to room temperature, the solvent was removed under reduced pressure and the residue was partitioned between EtOAc and brine. The organic layer was collected, and the aqueous layer was extracted by EtOAc for two times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the desired *N*-protected indoles.

1-Acetyl-4-fluoroindole



White solid; **m.p.** 50 – 52 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 3.7 Hz, 1H), 7.31 – 7.22 (m, 1H), 6.98 – 6.92 (m, 1H), 6.73 (d, *J* = 3.7 Hz, 1H), 2.62 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.8, 155.7 (d, *J* = 248.0 Hz), 137.7 (d, *J* = 9.2 Hz), 126.1 (d, *J* = 7.2 Hz), 125.3, 119.3 (d, *J* = 21.9 Hz), 112.8, 109.2 (d, *J* = 18.4 Hz), 104.8, 24.1; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -122.0; **IR** (cm^{-1}) 3150, 3129, 1692, 1485, 1432, 1268, 1210, 1038, 922, 735, 674, 594; **High Resolution MS** (EI): Calculated for $C_{10}H_8FNO$ $[M]^+$: 177.0590, Found: 177.0588.

2. Synthesis of Deuterated Indole[S2,S3]

For kinetic studies, deuterated indole substrate was synthesized according to the reported procedures.

3. Preparation of Silver Carboxylates[S4-6]

General Procedure 1 (GP1)

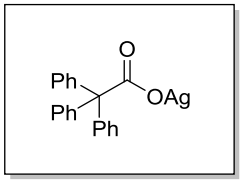
Acid (20.9 mmol) was added to a solution of NaOH (724 mg, 18.1 mmol) in H_2O (10 mL) in 50 mL beaker equipped with a magnetic stir bar. After stirring at room temperature for 15 min, a solution of $AgNO_3$ (2.56 g, 15.1 mmol) in H_2O (10 mL) was added dropwise and stirring was continued for

additional 15 min. The product was collected on a filter and then washed with water (20 mL x 2) and hexane (20 mL x 2), respectively. Subsequent drying under reduced pressure afforded the silver carboxylate.

General Procedure 2 (GP2)

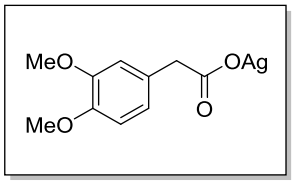
Ag_2O (0.69 g, 3.0 mmol) was added to a 50% aqueous solution of acid (7.0 mmol) in 20 mL vial equipped with a magnetic stir bar. During the reaction, white precipitate appeared which was collected on a filter and then washed with water (20 mL x 2). Subsequent drying under reduced pressure afforded the silver carboxylate.

Silver 2,2,2-triphenylacetate (GP1)



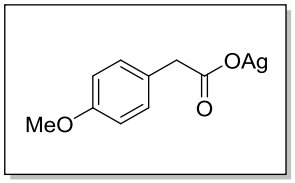
White solid; **m.p.** 215 – 217 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.24 – 7.10 (m, 15H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 177.6, 146.4 (3C), 130.4 (6C), 127.0 (6C), 125.6 (3C), 69.2; **IR** (cm^{-1}) 3010, 1561, 1541, 1484, 1441, 1330, 744, 697, 671.

Silver 2-(3,4-dimethoxyphenyl)acetate (GP1)



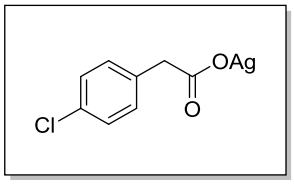
White solid; **m.p.** 185 – 187 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.87 – 6.78 (m, 2H), 6.73 (dd, J = 8.1, 1.9 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 3.39 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 175.5, 148.4, 147.1, 130.7, 121.2, 113.3, 111.7, 55.7, 55.5, 43.6; **IR** (cm^{-1}) 2985, 1508, 1382, 1259, 1231, 1147, 1138, 1021, 794, 709, 647, 542.

Silver 2-(4-methoxyphenyl)acetate (GP1)



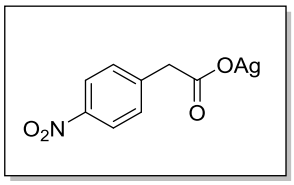
White solid; **m.p.** 206 – 208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 3.71 (s, 3H), 3.40 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 157.5, 130.2 (2C), 129.8, 113.3 (2C), 55.0, 42.7; **IR** (cm^{-1}) 2983, 1611, 1506, 1390, 1244, 1181, 1026, 813, 792, 704, 521.

Silver 2-(4-chlorophenyl)acetate (GP1)



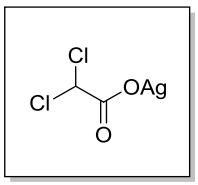
Grey solid; **m.p.** 231 – 233 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.29 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 3.45 (s, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 174.6, 137.3, 131.1 (2C), 130.3, 127.7 (2C), 43.2; **IR** (cm^{-1}) 1532, 1489, 1367, 1087, 1015, 856, 807, 754, 736, 676.

Silver 2-(4-nitrophenyl)acetate (GP1)



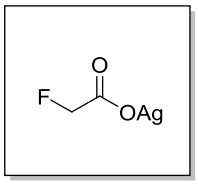
White solid; **m.p.** 243 – 245 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.11 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 3.61 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 173.7, 146.7, 145.8, 130.6 (2C), 123.1 (2C), 43.8; **IR** (cm^{-1}) 1523, 1378, 1345, 1308, 1110, 849, 823, 732, 722.

Silver 2,2-dichloroacetate (GP1)



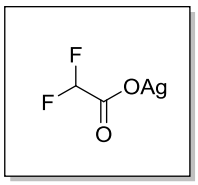
Grey solid; **m.p.** 210 – 212 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 6.18 (s, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 166.3, 70.1; **IR** (cm^{-1}) 3007, 1594, 1568, 1367, 1201, 816, 713, 660.

Silver 2-fluoroacetate (GP2)



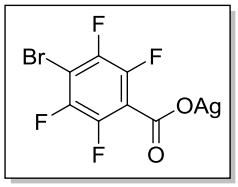
White solid; **m.p.** 246 – 248 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 4.64 (d, J = 49.3 Hz, 2H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.6, 80.32 (d, J = 180.4 Hz); **^{19}F NMR** (564 MHz, DMSO-d_6) δ 32.4 (t, J = 49.3 Hz); **IR** (cm^{-1}) 2959, 1539, 1406, 1323, 1045, 933, 690, 585, 554.

Silver 2,2-difluoroacetate (GP2)



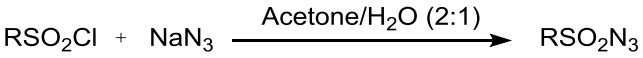
White solid; **m.p.** 251 – 253 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 5.85 (t, J = 55.7 Hz, 1H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 165.8, 110.1 (t, J = 248.8 Hz); **^{19}F NMR** (564 MHz, DMSO-d_6) δ -121.5 (d, J = 55.7 Hz); **IR** (cm^{-1}) 1582, 1448, 1320, 1112, 1045, 949, 814, 593.

Silver 4-bromo-2,3,5,6-tetrafluorobenzoate (GP1)



White solid; **m.p.** 244 – 246 °C; **^{19}F NMR** (564 MHz, DMSO-d_6) δ -134.5 (m), -141.8 (m); **^{13}C NMR** (100 MHz, DMSO-d_6) 160.5, 144.1 (dddd, J = 245.5, 16.8, 3.8, 2.3 Hz), 142.0 (dddd, J = 245.2, 14.1, 9.3, 3.8 Hz), 122.64 – 121.84 (m), 97.29 – 96.62 (m); **IR** (cm^{-1}) 1634, 1551, 1470, 1360, 973, 836, 804, 748, 691, 474.

4. General Procedure for the Preparation of Sulfonyl Azides[S7]



To a solution of sodium azide (1.0 g, 15 mmol) in water (5 mL) was added dropwise a solution of sulfonyl chloride (10 mmol) in acetone (10 mL) at 0 ºC. The reaction mixture was allowed to stir at room temperature for overnight and the acetone was removed under reduced pressure. Water was added, and the reaction mixture was extracted with EtOAc for three times. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The crude product can be used without any further purification.

5. Preparation of IrCp*$(CF_3CO_2)_2$[S8]

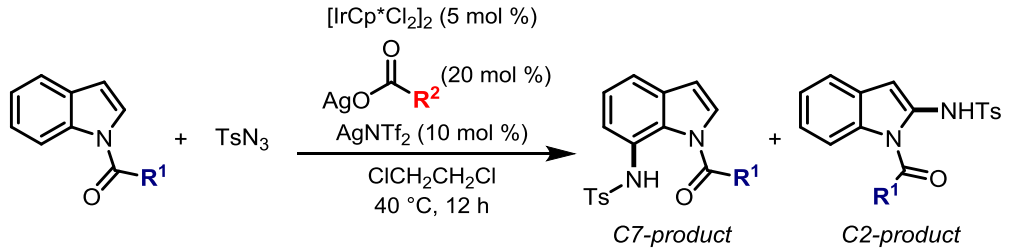
Pentamethylcyclopentadienyl iridium bistrifluoroacetate complex was synthesized according to the reported procedures.

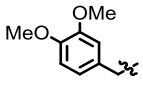
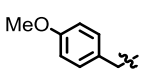
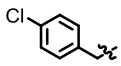
III. Procedure for the Optimization Study

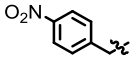
1. Procedure for Reaction Optimization

To a screw capped vial with a spinvane triangular-shaped Teflon spinbar were added *N*-acylindole (0.20 mmol), *p*-toluenesulfonyl azide (34 μL, 0.22 mmol), catalyst, and additive in 1,2-dichloroethnae (0.5 mL) under Ar-purged conditions. The reaction mixture was stirred in a pre-heated oil bath or a heating block at the 40 °C for 12 h. The reaction mixture was cooled to room temperature and filtered through a plug of celite and then washed with EtOAc. The solvents were removed under reduced pressure and the crude yield and regiomeric ratios were measured by ^{1}H NMR using dibromomethane as an internal standard or by HPLC using quinoline as an internal standard in case the regiomeric ratio exceeds 19:1.

Table S1. Directing Groups and Silver Carboxylates Screen[a]



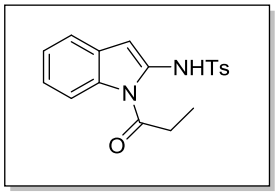
entry	R^1	R^2	1st trial yield (%) (C7 / C2)	2nd trial yield (%) (C7 / C2)	average yield (%) (C7-product)	average yield (%) (C2-product)	ratio (C7:C2)	measured $\Delta\Delta G^{\ddagger}$ (kcal/mol)
1	Me	Me	47.0 / 34.0	48.0 / 36.0	47.5	35.0	1.4 : 1	0.19
2	Me	CH_2F	19.0 / 55.3	21.6 / 58.3	20.3	56.8	1 : 2.8	-0.64
3	Me	CHF_2	6.0 / 76.0	6.0 / 71.0	6.0	73.5	1 : 12.3	-1.56
4	Me	CF_3	1.4 / 83.8	1.2 / 77.1	1.3	80.5	1 : 61.9	-2.57
5	Me	Et	54.0 / 37.0	49.0 / 31.0	51.5	34.0	1.5 : 1	0.26
6	Me	^{i}Pr	50.0 / 31.0	51.0 / 31.0	50.5	31.0	1.6 : 1	0.30
7	Me	^{t}Bu	51.0 / 21.0	52.0 / 21.0	51.5	21.0	2.5 : 1	0.56
8	Me	CH_2Ph	41.0 / 46.0	40.0 / 44.0	40.5	45.0	1 : 1.1	-0.07
9	Me	$CH(Ph)_2$	33.0 / 45.0	33.0 / 48.0	33.0	46.5	1 : 1.4	-0.21
10	Me	$C(Ph)_3$	34.0 / 48.5	33.0 / 46.0	33.5	47.3	1 : 1.4	-0.21
11	Me		38.0 / 41.5	39.0 / 38.0	38.5	39.8	1 : 1.0	-0.02
12	Me		41.0 / 43.5	40.0 / 46.0	40.5	44.8	1 : 1.1	-0.06
13	Me		38.0 / 43.0	39.0 / 47.5	38.5	45.3	1 : 1.2	-0.10

14	Me		37.0 / 51.0	36.0 / 49.0	36.5	50.0	1 : 1.4	-0.20
15	Me	CH_2Cl	21.5 / 57.0	23.0 / 57.0	22.3	57.0	1 : 2.6	-0.58
16	Me	$CHCl_2$	5.8 / 77.8	5.7 / 76.6	5.8	77.2	1 : 13.3	-1.61
17	Me	C_2F_5	1.1 / 81.7	1.1 / 79.0	1.1	80.4	1 : 73.1	-2.67
18	Et	Me	53.0 / 28.0	53.0 / 28.0	53.0	28.0	1.9 : 1	0.40
19	Et	CH_2F	29.0 / 58.0	28.0 / 55.0	28.5	56.5	1 : 2.0	-0.43
20	Et	CHF_2	9.0 / 72.0	9.0 / 73.0	9.0	72.5	1 : 8.1	-1.30
21	Et	CF_3	2.9 / 67.2	3.1 / 68.3	3.0	67.8	1 : 22.6	-1.94
22	Et	^{t}Bu	64.0 / 22.0	62.0 /17.0	63.0	19.5	3.2 : 1	0.73
23	Et	$CHCl_2$	9.8 / 74.0	9.3 / 71.0	9.6	72.5	1 : 7.6	-1.26
24	Et	C_2F_5	2.9 / 70.9	2.5 / 65.2	2.7	68.0	1 : 25.2	-2.01
25	^{i}Pr	Me	55.0 / 21.0	53.0 / 21.0	54.0	21.0	2.6 : 1	0.59
26	^{i}Pr	CH_2F	31.5 / 50.3	32.7 / 48.0	32.1	49.2	1 : 1.5	-0.27
27	^{i}Pr	CHF_2	9.5 / 71.0	10.9 / 71.8	10.2	71.4	1 : 7.0	-1.21
28	^{i}Pr	CF_3	4.8 / 73.0	5.6 / 73.6	5.2	73.3	1 : 14.1	-1.65
29	^{i}Pr	^{t}Bu	71.9 / 19.0	71.4 / 16.0	71.7	17.5	4.1 : 1	0.88
30	^{i}Pr	$CHCl_2$	12.8 / 70.0	10.8 / 68.0	11.8	69.0	1 : 5.8	-1.10
31	^{i}Pr	C_2F_5	5.0 / 78.0	5.0 / 78.0	5.0	78.0	1 : 15.6	-1.71
32	^{t}Bu	CH_2F	88.0 / 5.0	86.0 / 5.0	87.0	5.0	17.4 : 1	1.78
33	^{t}Bu	CHF_2	65.0 / 24.0	65.0 / 25.0	65.0	24.5	2.7 : 1	0.61
34	^{t}Bu	CF_3	48.0 / 38.0	48.0 / 36.5	48.0	37.3	1.3 : 1	0.16
35	^{t}Bu	C_2F_5	45.0 / 38.3	45.4 / 39.3	45.2	38.8	1.2 : 1	0.10
36	^{t}Bu	$CHCl_2$	69.0 / 27.0	68.5 / 24.8	68.8	25.9	2.7 : 1	0.61
37	CF_2H	Me	n.d. / n.d.	n.d. / n.d.	n.d.	n.d.	-	-
38	CF_3	Me	n.d. / n.d.	n.d. / n.d.	n.d.	n.d.	-	-
39	Cy	Me	53.0 / 26.0	55.0 / 18.5	54.0	22.3	2.4 : 1	0.55
40	Pr	Me	55.0 / 27.0	56.0 / 29.8	55.5	28.4	2.0 : 1	0.41
41	Me	(4-CF_3)C_6H_4	26.3 / 43.3	28.5 / 53.7	27.4	48.5	1 : 1.8	-0.36
42	Me	(4-NO_2)C_6H_4	30.0 / 50.5	25.1 / 50.1	27.6	50.3	1 : 1.8	-0.38
43	Me	(4-F)C_6H_4	18.0 / 44.8	22.2 / 43.4	20.1	44.1	1 : 2.2	-0.49
44	Me	(4-Cl)C_6H_4	21.3 / 42.5	18.2 / 46.8	19.8	44.7	1 : 2.3	-0.51
45	Me	Ph	20.0 / 47.9	14.0 / 45.3	17.0	46.6	1 : 2.7	-0.63
46	Me	(4-Br)C_6F_4	12.3 / 75.6	12.6 / 75.0	12.5	75.3	1 : 6.0	-1.12

[a]Standard reaction conditions: *N*-acylindole (0.20 mmol), *p*-toluenesulfonyl azide (0.22 mmol, 1.1 equiv.), catalyst, and additives in 1,2-DCE (0.5 mL) at 40 °C for 12 h. Ratios, determined by ^{1}H NMR or HPLC analysis of the crude reaction mixture versus internal standard, are averaged over two experimental runs. n.d.= not detected.

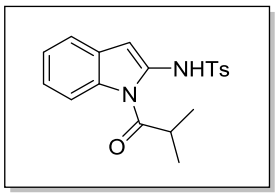
***N*-(1-Propionyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2 and Figure 3)

[Separation condition (HPLC): Chiral-pak ID-3, Hx/THF=9:1, 0.8 mL/min, 254 nm]



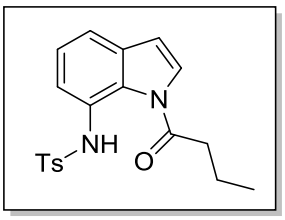
Brown solid; **m.p.** 145 – 147 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) 10.60 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 5.93 (s, 1H), 3.18 (q, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 174.9, 144.2, 136.3, 134.7, 131.1, 130.2 (2C), 127.5 (2C), 127.2, 125.2, 123.6, 121.0, 115.8, 105.2, 32.1, 21.5, 9.3; **IR** (cm^{-1}) 3206, 2986, 2920, 1717, 1622, 1592, 1354, 1309, 1150, 1132, 1086, 740, 667, 546; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_3S$ $[M]^+$: 342.1038, Found: 342.1036.

***N*-(1-Isobutyryl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2 and Figure 3)



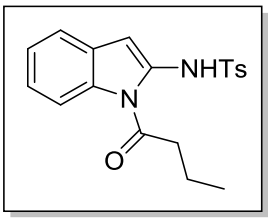
White solid; **m.p.** 126 – 128 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.73 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 – 7.10 (m, 1H), 5.91 (s, 1H), 4.00 (hept, J = 6.8 Hz, 1H), 2.39 (s, 3H), 1.15 (d, J = 6.8 Hz, 6H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 178.2, 143.8, 135.4, 134.6, 130.5, 129.8 (2C), 127.0 (2C), 126.7, 124.6, 122.9, 120.5, 114.5, 104.0, 35.3, 21.1, 18.7 (2C); **IR** (cm^{-1}) 3371, 2972, 2870, 1713, 1629, 1595, 1462, 1310, 1150, 1075, 757, 665, 548; **High Resolution MS** (EI): Calculated for $C_{19}H_{20}N_2O_3S$ $[M]^+$: 356.1195, Found: 356.1192.

***N*-(1-Butyryl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide** (Figure 3)



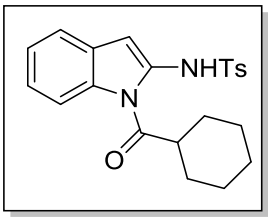
White solid; **m.p.** 115 – 117 °C; **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 10.49 (s, 1H), 7.56 – 7.46 (m, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.36 – 7.23 (m, 3H), 7.09 (d, J = 8.0 Hz, 3H), 6.60 (d, J = 3.9 Hz, 1H), 2.76 (t, J = 7.4 Hz, 2H), 1.79 (h, J = 7.3 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, CD_2Cl_2) δ 173.8, 144.0, 137.0, 133.7, 129.6 (2C), 128.5, 127.3 (2C), 126.9, 126.0, 125.7, 120.6, 118.6, 110.8, 38.7, 21.5, 18.7, 13.8; **IR** (cm^{-1}) 3067, 2970, 1686, 1330, 1202, 1160, 1087, 798, 774, 699, 558, 534; **High Resolution MS** (EI): Calculated for $C_{19}H_{20}N_2O_3S$ $[M]^+$: 356.1195, Found: 356.1195.

***N*-(1-Butyryl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Figure 3)



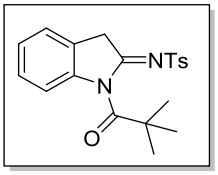
White solid; **m.p.** 119 – 121 °C; **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.32 – 7.24 (m, 3H), 7.22 – 7.14 (m, 1H), 5.93 (s, 1H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.69 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 173.7, 143.8, 135.9, 134.3, 130.6, 129.8 (2C), 127.0 (2C), 126.8, 124.8, 123.2, 120.6, 115.3, 104.8, 40.0, 21.1, 17.8, 13.5; **IR** (cm^{-1}) 3050, 2963, 2929, 1718, 1626, 1593, 1314, 1280, 1071, 837, 754, 546; **High Resolution MS** (EI): Calculated for $C_{19}H_{20}N_2O_3S$ $[M]^+$: 356.1195, Found: 356.1192.

***N*-(1-Cyclohexanecarbonyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Figure 3)



Yellow solid; **m.p.** 120 – 122 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.69 (s, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.24 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 5.87 (s, 1H), 3.73 (m, 1H), 2.38 (s, 3H), 1.93 – 1.70 (m, 4H), 1.50 – 1.10 (m, 6H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 176.9, 143.8, 135.7, 134.5, 130.4, 129.8 (2C), 127.0 (2C), 126.6, 124.6, 122.9, 120.5, 114.6, 104.1, 44.6, 28.7 (2C), 25.3, 25.1 (2C), 21.0; **IR** (cm^{-1}) 2928, 2853, 1717, 1628, 1595, 1463, 1314, 1279, 1153, 1073, 854, 778, 755, 549; **High Resolution MS** (EI): Calculated for $C_{22}H_{24}N_2O_3S$ $[M]^+$: 396.1508, Found: 396.1509.

***N*-(1-Pivaloylindolin-2-ylidene)-4-methylbenzenesulfonamide** (Figure 3)



White solid; **m.p.** 200 – 202 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.19 – 7.09 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.32 (s, 2H), 2.42 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 185.2, 169.5, 144.1, 142.1, 139.1, 130.0 (2C), 128.6, 127.2 (2C), 127.0, 125.4, 124.8, 111.7, 44.6, 36.7, 27.6 (3C), 21.8; **IR** (cm^{-1}) 3062, 2954, 2834, 1590, 1299, 1143, 1087, 774, 669, 544; **High Resolution MS** (EI): Calculated for $C_{20}H_{22}N_2O_3S$ $[M]^+$: 370.1351, Found: 370.1351.

2. HPLC Calibration for Yield Determination

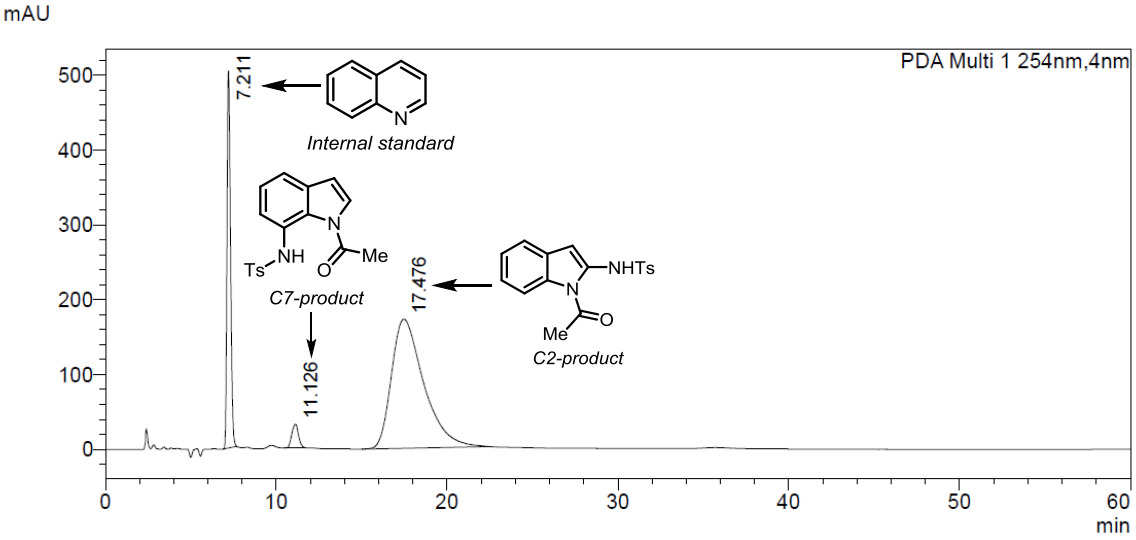
Preparation of HPLC Samples

Following the above procedure, to the crude residue was added internal standard (quinoline, 24 μL, 0.20 mmol), and the resulting mixture was then reconstituted in HPLC grade THF (10 mL). After sonication, an aliquot (100 μL) of this mixture was diluted with hexane/THF solution (1.6:1, 900 μL) to a concentration of approximately ~2.0 mM, and this solution was analyzed by HPLC to determine yield; typical HPLC traces are shown in Figure S1.

Construction of Calibration Curves

The regiomeric ratios exceeding ratio of 19:1 were obtained by HPLC. UV response area (λ = 254 nm) relative to quinoline as internal standard was determined for all components of the model reaction system, and calibration curves across 6 concentrations were generated for each. Reaction samples during optimization were analyzed within the linear range at a concentration of ~2.0 mM.

<Chromatogram>

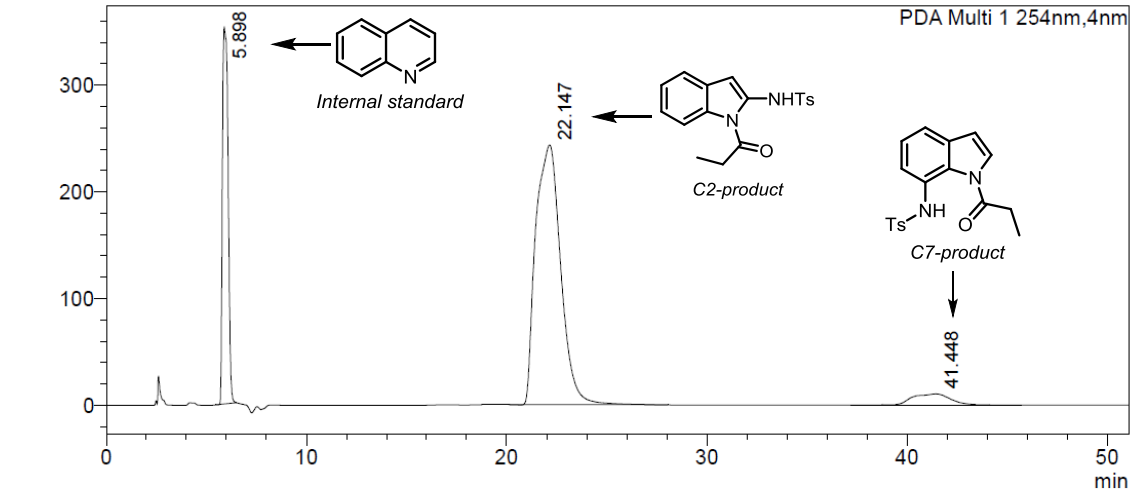


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.211	7142155	503850	0.000		M	
2	11.126	864668	31740	0.000		M	
3	17.476	22641802	172549	0.000		M	
Total		30648625	708139				

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.898	6963289	352708	0.000		M	
2	22.147	21134618	243378	0.000		M	
3	41.448	1373553	10451	0.000		M	
Total		29471460	606537				

Figure S1. Sample HPLC trace of reaction used to determine yield; the internal standard and each regioisomer are identified on the traces (up: Table S1, entry 17, down: Table S1, entry 21).

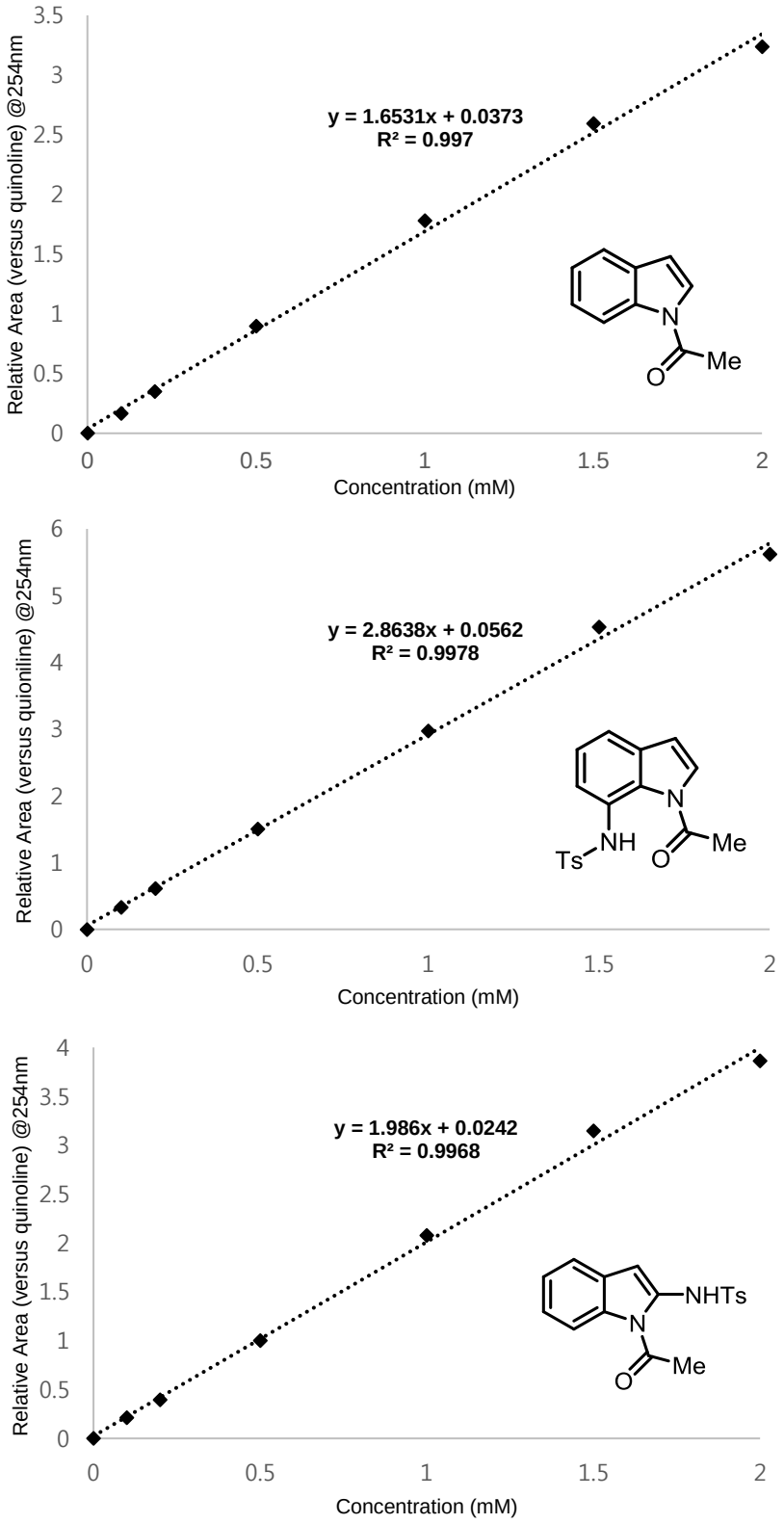


Figure S2. Calibration curves of *N*-acetylindole and regioisomeric products.

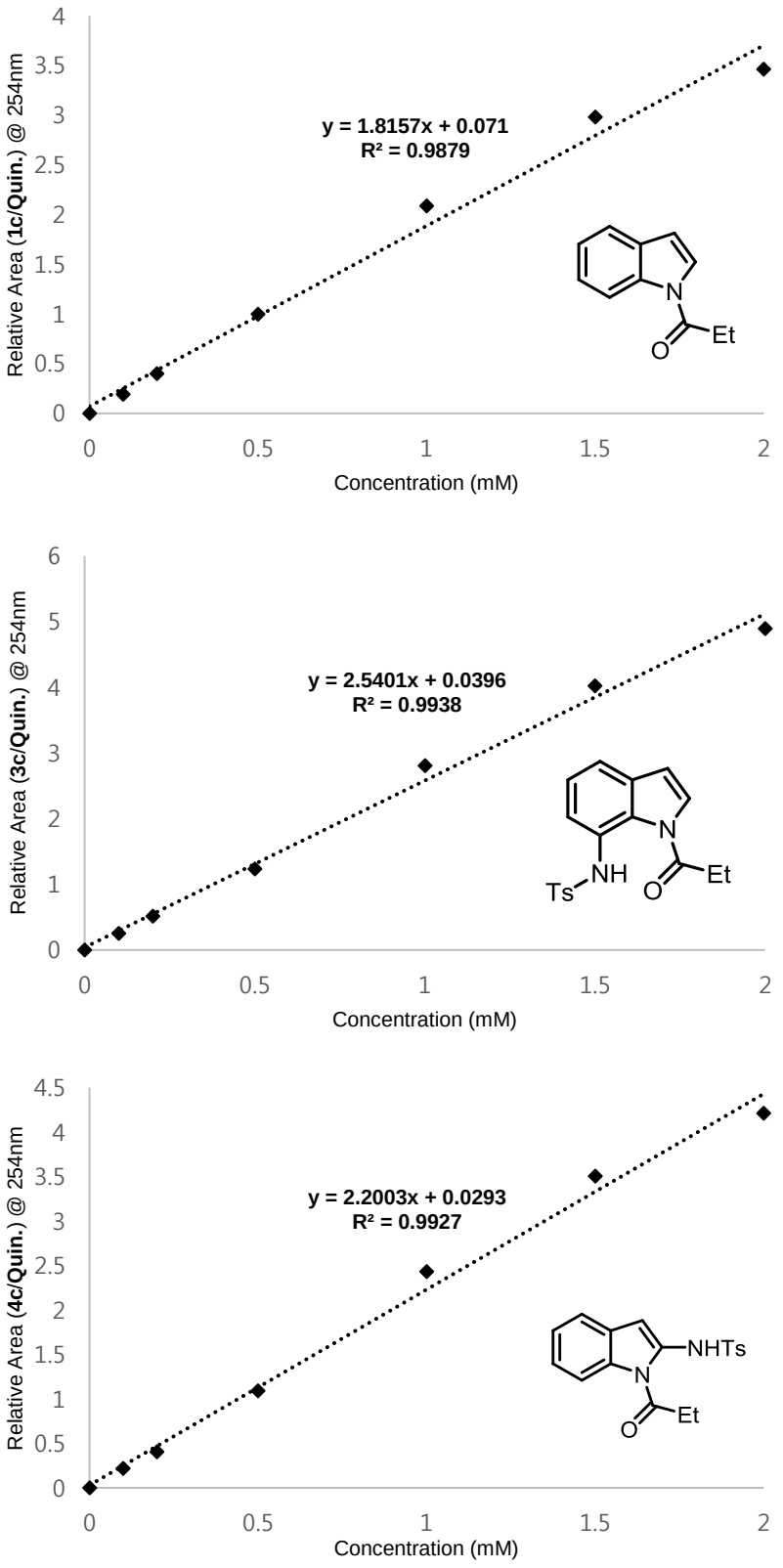
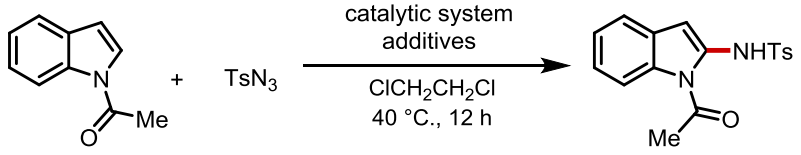


Figure S3. Calibration curves of *N*-propionylindole and regioisomeric products.

3. Further Optimizations for Improved Catalytic Reaction

To afford high yields of **4**, further studies were conducted according to the above general procedure (page S7). The crude yield was measured by ^{1}H NMR using dibromomethane as an internal standard.

Table S2. Optimization of the Reaction Condition[a]



1 **2** **4**

entry	catalytic system (mol %)	additives (mol %)	yield (%)
1	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	-	n.d
2	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (10)	AgOTFA (20)	78
3	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (10)	NaOTFA (20)	61
4	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (10)	LiOTFA (20)	55
5	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (10)	$Cu(OTFA)_2$ (20)	<5
6	$[IrCp^*Cl_2]_2$ (5) / $NaNTf_2$ (10)	AgOTFA (20)	87
7	$IrCp^*(OTFA)_2$ (10)	$AgNTf_2$ (10)	75
8	**$IrCp^*(OTFA)_2$ (10)**	**$NaNTf_2$ (10)**	**93**
9	$IrCp^*(OTFA)_2$ (10)	-	10
10	-	$NaNTf_2$ (10)	n.d

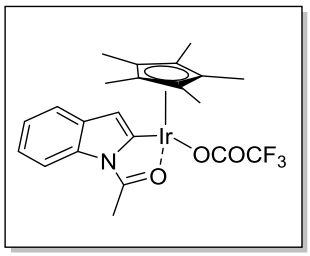
[a]Standard reaction conditions: *N*-acetylindole **1** (23 μL, 0.20 mmol), **2** (34 μL, 0.22 mmol, 1.1 equiv.), catalyst, and additives in 1,2-DCE (0.5 mL) at 40 °C for 12 h.

IV. Experimental Procedures of Mechanistic Studies

1. Preparation of Iridacycle

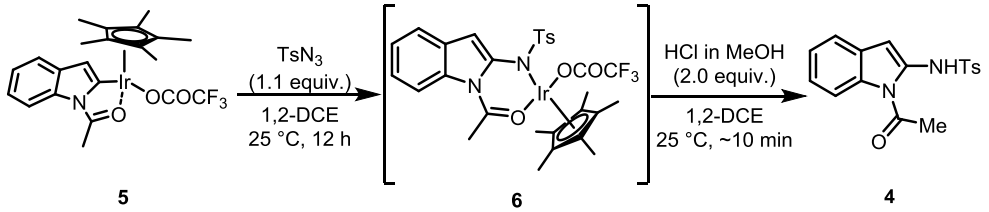
A solution of *N*-acetylindole (**1**, 70 uL, 0.50 mmol), $[IrCp^*Cl_2]_2$ (0.20 g, 0.25 mmol), lithium carbonate (37 mg, 0.50 mmol), and silver trifluoroacetate (0.11 g, 0.50 mmol) in 1,2-dichloroethane (2.5 mL) was stirred for 12 h at 50 °C under argon atmosphere. Another portion of silver trifluoroacetate (0.11 g, 0.50 mmol) was added and the mixture was allowed to stir for additional 12 h at 50 °C. The resulting crude mixture was filtered through a pad of celite washing with 1,2-dichloroethane (15 mL), and concentrated under reduced pressure. The crude mixture was reconstituted in methylene chloride (1.0 mL) for the preparation of concentrated solution, then eluting with a solution of hexane/EtOAc (2:1) on preparative thin layer chromatography silica plate. After repeating the elution three times, the yellowish silica containing the product was collected and then washed with EtOAc. The filtrate was dried under reduced pressure to give the desired iridacycle as a yellow solid.

Iridacycle (Scheme 3, **5**)



Yellow solid (153 mg, 51%); **m.p.** 165 – 167 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.12 – 7.06 (m, 1H), 6.59 (s, 1H), 2.91 (s, 3H), 1.73 (s, 15H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 179.3, 162.3, 161.9 (q, *J* = 35.4 Hz), 137.6, 136.0, 124.9, 122.3, 120.0, 115.9 (q, *J* = 291.8 Hz), 113.9, 112.8, 87.5 (5C), 21.9, 9.9 (5C); **^{19}F NMR** (564 MHz, CD_2Cl_2) δ -75.0; **IR** (cm^{-1}) 2919, 1705, 1693, 1553, 1476, 1179, 1129, 1021, 753, 720; **High Resolution MS** (EI): Calculated for $C_{20}H_{23}IrNO^+$ $[M\text{-}CO_2CF_3]^+$: 486.1403, Found: 486.1401.

2. Stoichiometric Amidation of Iridacycle with Tosyl Azide



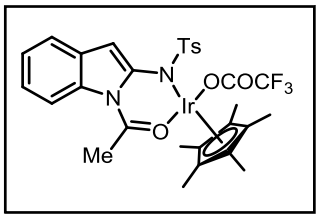
5 **6** **4**

To a J-Young NMR tube were added ***Iridacycle*** (**5**, 60 mg, 0.10 mmol), *p*-toluenesulfonyl azide (17 μL, 0.11 mmol) and methylene chloride-d_2 (0.5 mL) under argon atmosphere. The NMR tube was gently shaken and kept at 25 °C. The reaction progress was followed by ^{1}H and ^{19}F NMR spectroscopy until complete conversion to ***Ir-Amido complex*** was reached (approximately for 12 h). The crude yield of **6**

(71%) was measured by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. The reaction mixture was then quenched by hydrochloric acid in methanol solution. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with hexane/EtOAc as an eluent to give the desired amidated product (**4**, 61%).

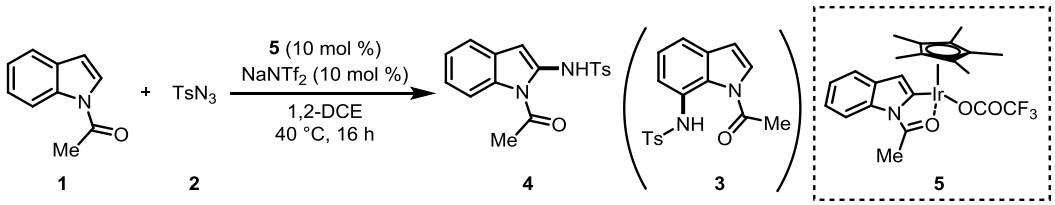
Ir-Amido Complex (Scheme 3, **6**)

After confirming the complete conversion to ***Ir-Amido complex***, the reaction mixture was transferred to the 10 mL vial and additional 0.2 mL of methylene chloride-d_2 was used to rinse the vial. Then, the solvent was reduced to a minimal volume. Crystals suitable for X-ray analysis were grown by layering pentane on top of a concentrated solution of the metal species in methylene chloride-d_2 at -30 °C.



Yellow solid; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.05 (m, 3H), 6.81 (s, 1H), 2.80 (s, 3H), 2.28 (s, 3H), 1.56 (s, 15H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 176.3, 161.9 (q, *J* = 35.8 Hz) 142.5, 141.9, 140.1, 132.5, 132.3, 129.2 (2C), 128.4 (2C), 125.7, 123.2, 120.7, 116.6 (q, *J* = 291.0 Hz), 114.5, 99.0, 85.4 (5C), 28.0, 21.6, 9.9 (5C); **^{19}F NMR** (564 MHz, CD_2Cl_2) δ –74.6; **High Resolution MS** (EI): Calculated for $C_{27}H_{30}IrN_2O_3S$ $[M\text{-}CO_2CF_3]^+$: 655.1601, Found: 655.1608.

3. Catalytic C–H Amidation Reaction using Iridacycle



To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *N*-acetylindole (**1**, 23 μL, 0.20 mmol), *p*-toluenesulfonyl azide (**2**, 31 μL, 0.20 mmol), ***Iridacycle*** (**5**, 12 mg, 0.020 mmol, 10 mol %), $NaNTf_2$ (6.1 mg, 0.020 mmol, 10 mol %) and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 40 °C for 16 h. The reaction mixture was filtered through a pad of celite with EtOAc (10 mL x 3) and concentrated under reduced pressure. The crude yield of **4** (60%) and **3** (<5%) were measured by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

4. Deuterium Labeling Test: Intermolecular Competition Test

To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *p*-toluenesulfonyl azide (31 μL, 0.20 mmol), IrCp*(OTFA)$_2$ (4.4 mg, 0.0080 mmol, 4 mol %), NaNTf$_2$ (2.4 mg, 0.0080 mmol, 4 mol %), and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a preheated oil bath at 40 °C for 10 min and then *N*-acetyl-3-methylindole (17 mg, 0.10 mmol) and *N*-acetyl-3-methylindole-d_n[S2] (18 mg, 0.10 mmol) were added. After the mixture was further stirred in an oil bath at 40 °C for 7 min, it was cooled to -78 °C for 5 min, filtered through a plug of silica and then washed with cold ethyl acetate. Organic solvents were removed under reduced pressure and the crude mixture was further purified by silica gel column chromatography with n-hexane/EtOAc as an eluent to recover the starting material and the desired amidated product. KIE value (P_H/P_D = 3.69) was determined by the ratio of desired product.

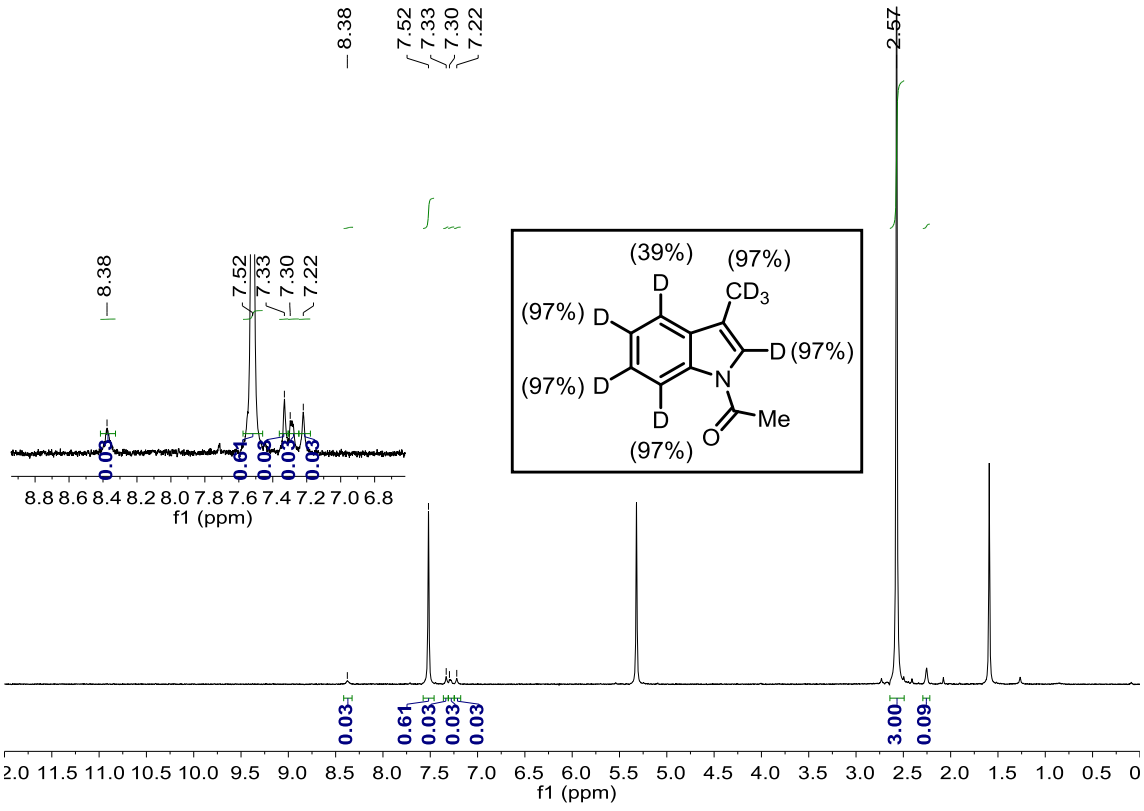


Figure S4. [1]H NMR of starting material: Deuterated *N*-acetyl-3-methylindole (Scheme 3)

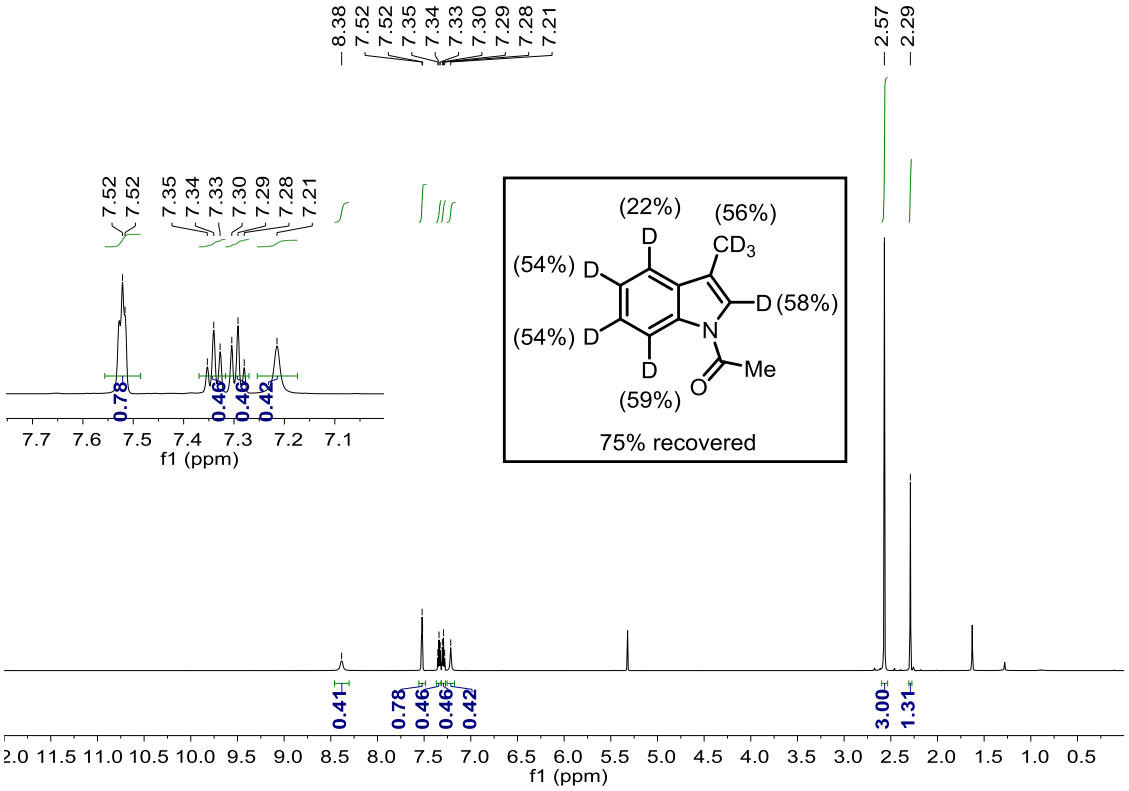


Figure S5. [1]H NMR of intermolecular competition test: recovering starting material (Scheme 3)

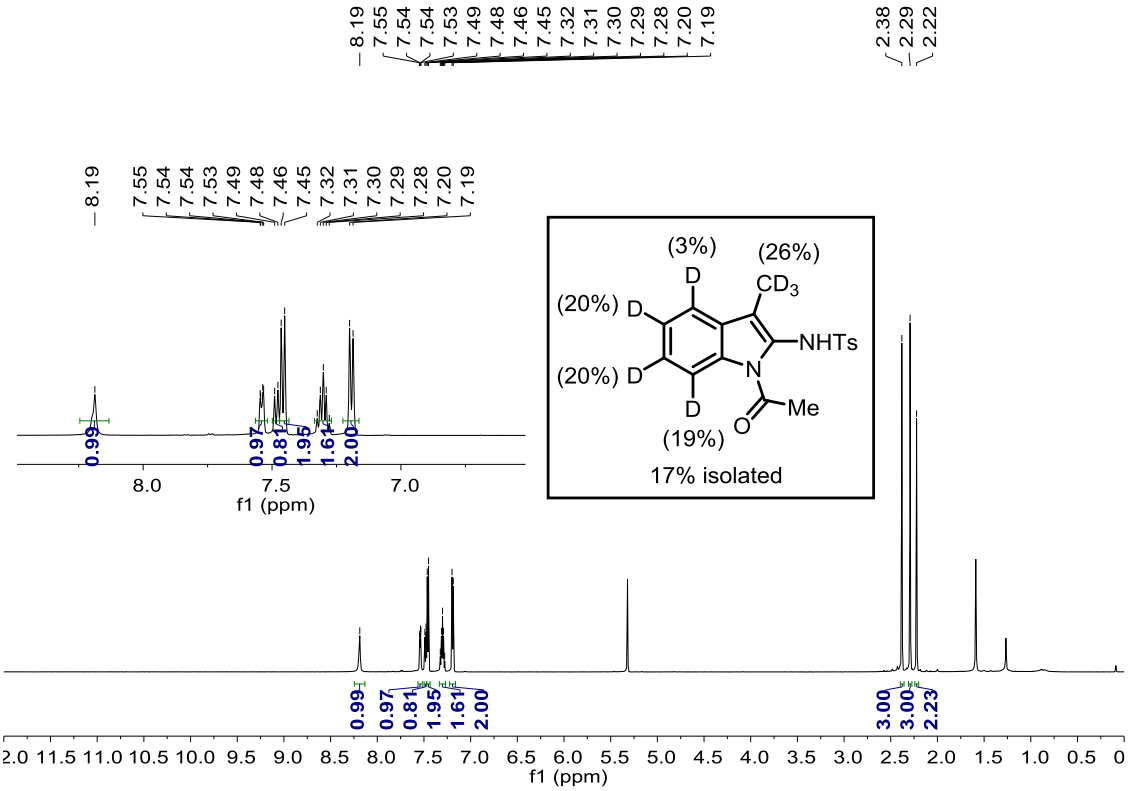
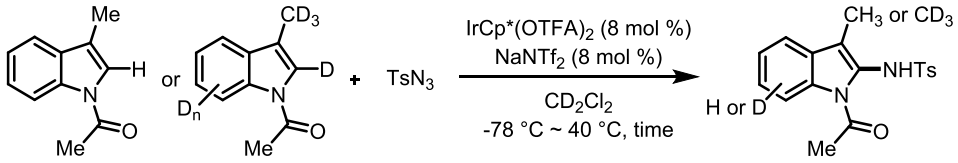


Figure S6. [1]H NMR of intermolecular competition test: amidated product (Scheme 3)

5. Deuterium Kinetic Isotope Effect: Initial Rate Comparison Test



To a J-Young NMR tube were added *N*-acetyl-3-methylindole (17 mg, 0.10 mmol) or *N*-acetyl-3-methylindole-d_n (18 mg, 0.10 mmol), IrCp*(OTFA)$_2$ (4.4 mg, 0.0080 mmol, 4 mol %), $NaNTf_2$ (2.4 mg, 0.0080 mmol, 4 mol %), 1,2-dibromethane as an internal standard (14 μL, 0.20 mmol) and methylene chloride-d_2 (0.5 mL) under argon atmosphere. The NMR tube was gently shaken and allowed to cool at -78 °C for 15 min. *p*-toluenesulfonyl azide (31 μL, 0.20 mmol) was added, and the NMR tube was again shaken to insure through mixing of the reagents and started to measure its conversion over 10 min with a 1 min interval at the 40 °C (NMR probe temperature). KIE value (k_H/k_D =1.8) was determined by comparing the relative initial rates.

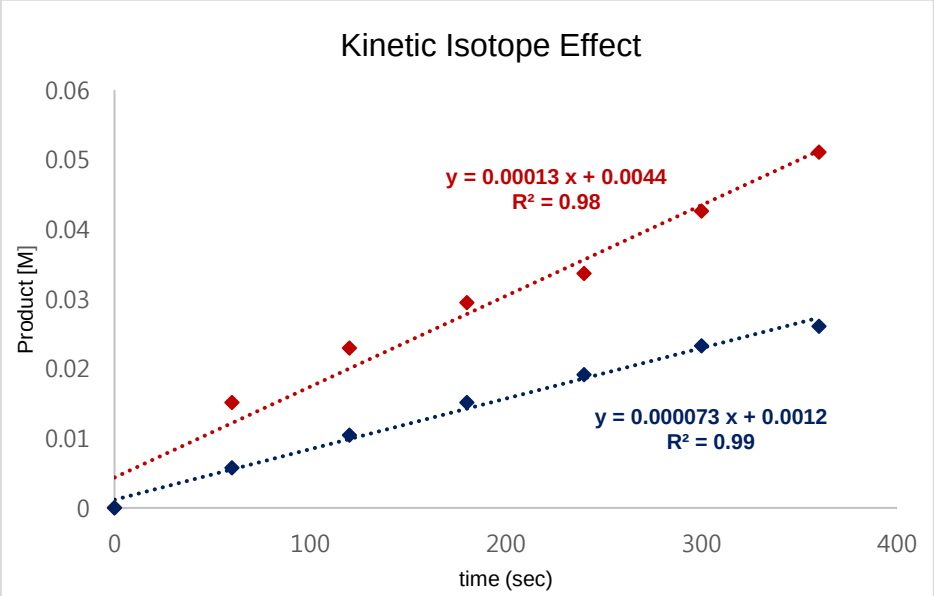


Figure S7. Initial rate of *N*-acetyl-3-methylindole (red diamond) and *N*-acetyl-3-methylindole-d_n (blue diamond)

6. Reversibility Test and Initial Rate Comparison Test with *N*-Acetylindole

Reversibility Test

To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *p*-toluenesulfonyl azide (31 μL, 0.20 mmol), IrCp*(OTFA)$_2$ (4.4 mg, 0.0080 mmol, 4 mol %), NaNTf$_2$ (2.4 mg, 0.0080 mmol, 4 mol %), and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a preheated oil bath at 40 °C for 10 min and then *N*-acetylindole (16 mg, 0.10 mmol) and *N*-acetyl-2-deutrio-indole (16 mg, 0.10 mmol) were added. After the mixture was further stirred in an oil bath at 40 °C for 5 min, it was cooled to -78 °C for 5 min, filtered through a plug of silica and then washed with cold ethyl acetate. Organic solvents were removed under reduced pressure and the crude mixture was further purified by silica gel column chromatography with n-hexane/EtOAc as an eluent to recover the starting material and the amidated product.

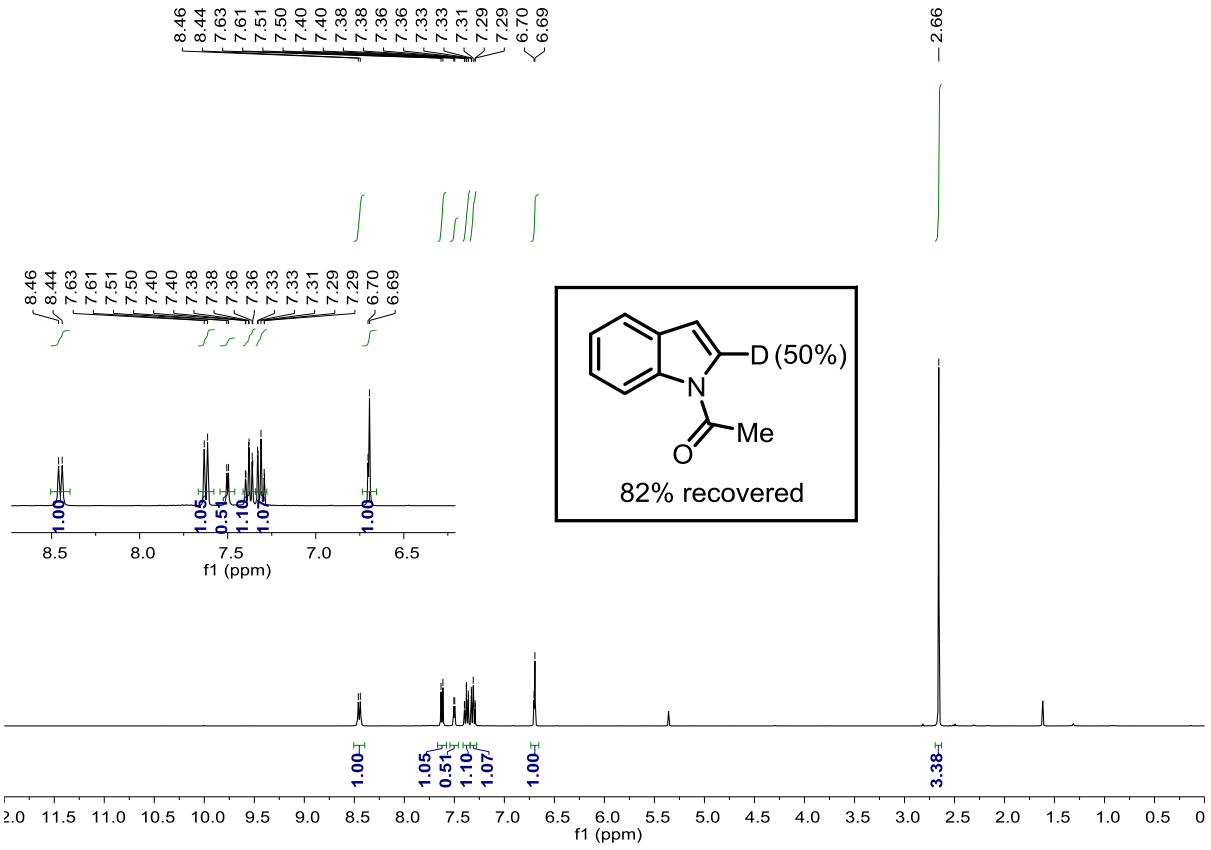


Figure S8. ^{1}H NMR of intermolecular competition test: recovering starting material.

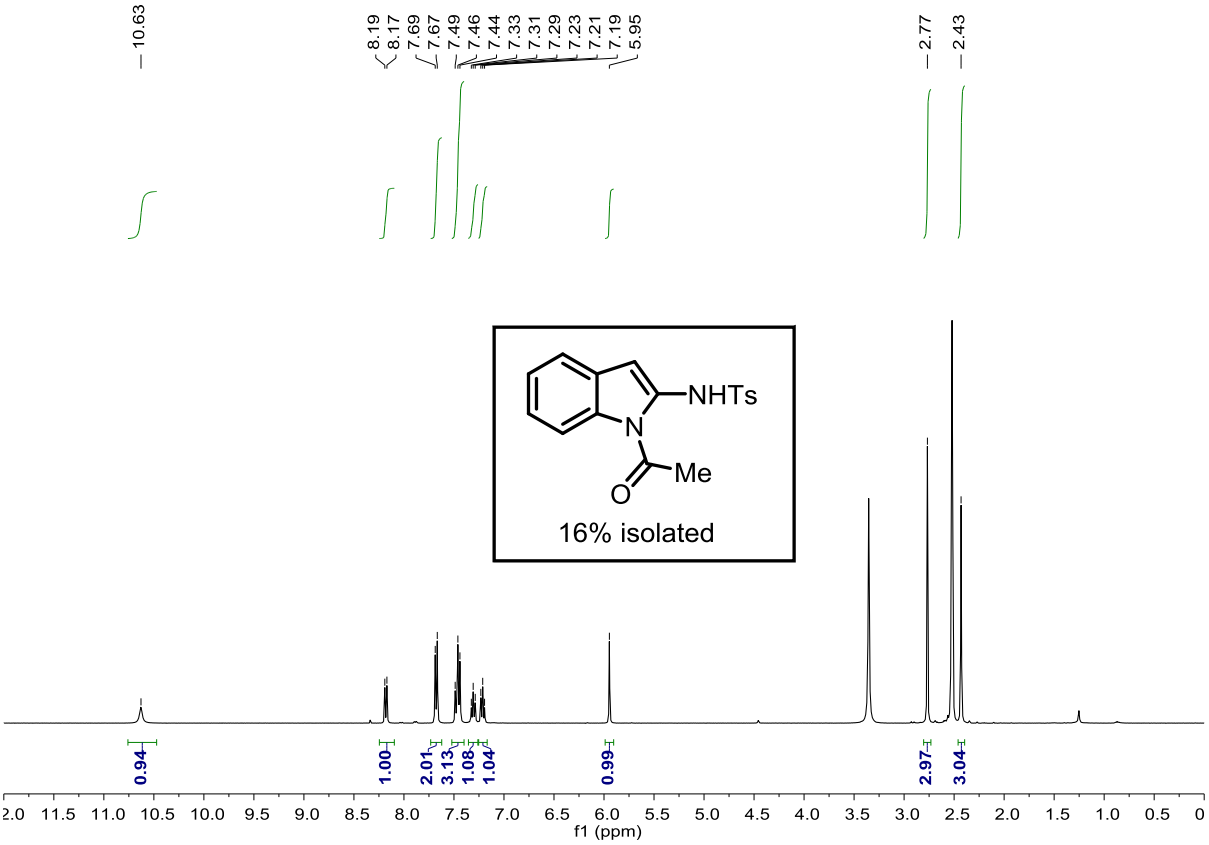
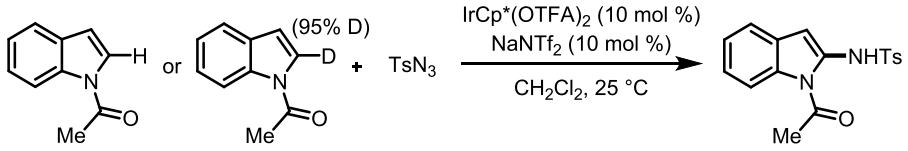


Figure S9. ^{1}H NMR of intermolecular competition test: amidated product

Initial Rate Comparison Test



To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *N*-acetylindole (32 mg, 0.20 mmol) or *N*-acetyl-2-deutrio-indole[S3] (32 mg, 0.20 mmol), *p*-toluenesulfonyl azide (31 μL, 0.20 mmol), IrCp*(OTFA)$_2$ (11 mg, 0.020 mmol, 10 mol %), $NaNTf_2$ (6.1 mg, 0.020 mmol, 10 mol %), 1,2-dibromethane as an internal standard (14 μL, 0.20 mmol) and methylene chloride (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a preheated oil bath at 25 °C. For each 20 min, 10 μL of the reaction mixture was transferred to NMR tube and diluted with DMSO-d_6, analyzed by ^{1}H NMR spectroscopy. The initial reaction rate was obtained by plotting the six points to obtain KIE value to be 1.5.

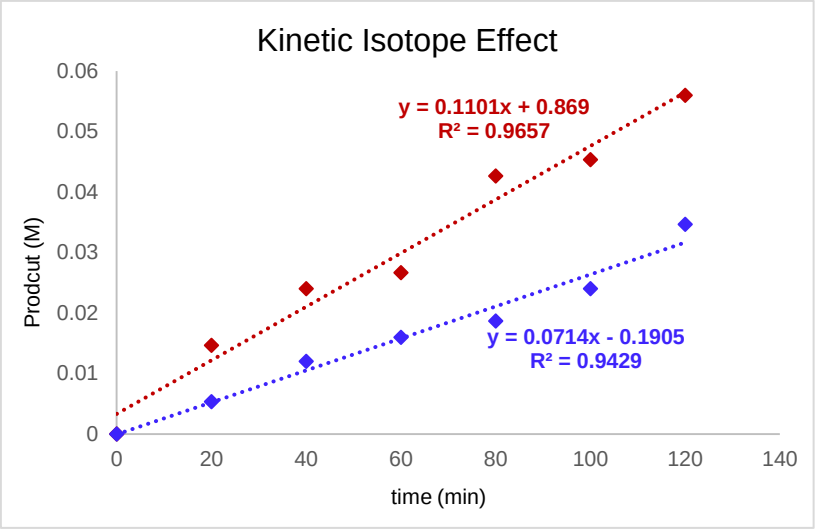
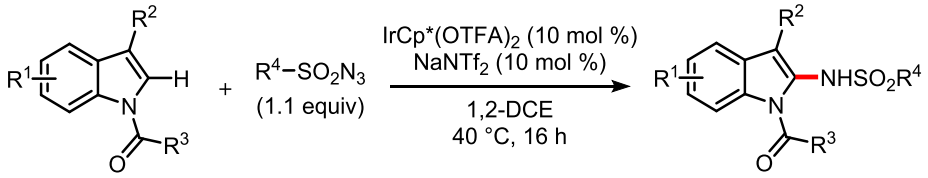


Figure S10. Initial rate of *N*-acetylindole (red diamond) and *N*-acetyl-2-deuterio-indole (blue diamond)

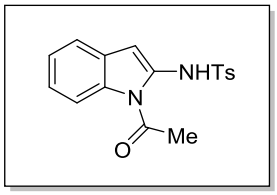
V. Procedure for the Ir-Catalyzed C–H Amination with Azides



To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added indole (0.20 mmol), azide (0.22 mmol), $IrCp^*(OTFA)_2$ (11 mg, 0.020 mmol, 10 mol %), and $NaNTf_2$ (6.1 mg, 0.020 mmol, 10 mol %) in 1,2-dichloroethane (0.5 mL) under atmospheric conditions. The reaction mixture was stirred at the indicated temperature for 16 h, filtered through a pad of celite and then washed with EtOAc (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product.

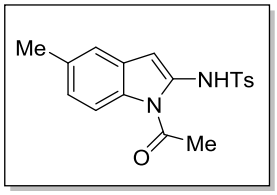
***N*-(1-Acetyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2–4 and Figure 2–3, **4**)

[Separation condition (HPLC): Chiral-pak IA-3, Hx/THF=4:1, 0.8 mL/min, 254 nm]



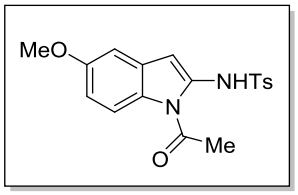
White solid (56 mg, 85%); **m.p.** 170 – 172 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 7.9 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 5.93 (s, 1H), 2.76 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.6, 143.8, 136.0, 134.3, 130.7, 129.8 (2C), 127.1 (2C), 126.8, 124.9, 123.3, 120.6, 115.6, 105.0, 27.1, 21.1; **IR** (cm^{-1}) 3140, 2917, 1719, 1629, 1596, 1313, 1252, 1146, 1087, 765, 685, 595, 546; **High Resolution MS** (EI): Calculated for $C_{17}H_{16}N_2O_3S$ $[M]^+$: 328.0882, Found: 328.0883.

***N*-(1-Acetyl-5-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **7**)



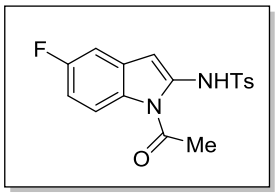
Yellow solid (58 mg, 84%); **m.p.** 189 – 191 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.54 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.23 (s, 1H), 7.10 (d, J = 8.3 Hz, 1H), 5.85 (s, 1H), 2.73 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.3, 143.8, 135.9, 132.5, 132.4, 130.7, 129.8 (2C), 127.1 (2C), 127.0, 126.1, 120.3, 115.4, 105.0, 26.9, 21.1, 20.8; **IR** (cm^{-1}) 3048, 2919, 1702, 1624, 1311, 1151, 1086, 779, 574, 547; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_3S$ $[M]^+$: 342.1038, Found: 342.1040.

***N*-(1-Acetyl-5-methoxy-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **8**)



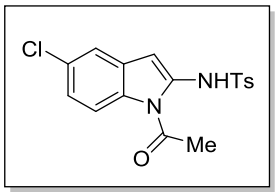
Yellow solid (57 mg, 80%); **m.p.** 176 – 178 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.57 (s, 1H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.00 (s, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 5.88 (s, 1H), 3.73 (s, 3H), 2.73 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.1, 155.7, 143.8, 136.1, 131.1, 129.8 (2C), 128.9, 127.8, 127.0 (2C), 116.7, 113.4, 105.1, 103.1, 55.2, 26.8, 21.1; **IR** (cm^{-1}) 3133, 2916, 2845, 1710, 1613, 1304, 1147, 1085, 1021, 780, 542; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_4S$ $[M]^+$: 358.0987, Found: 358.0990.

***N*-(1-Acetyl-5-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **9**)



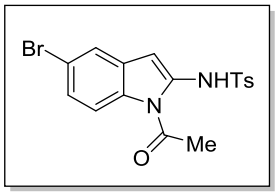
Yellow solid (33 mg, 48%); **m.p.** 144 – 146 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 8.17 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.13 (td, *J* = 9.3, 2.8 Hz, 1H), 5.95 (s, 1H), 2.75 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.6, 159.8 (d, *J* = 237.7 Hz), 144.0, 135.9, 132.4, 130.9, 130.0 (2C), 128.1 (d, *J* = 10.4 Hz), 127.1 (2C), 117.3 (d, *J* = 8.9 Hz), 112.6 (d, *J* = 24.7 Hz), 106.3 (d, *J* = 24.2 Hz), 104.7 (d, *J* = 3.7 Hz), 27.0, 21.2; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -119.2; **IR** (cm^{-1}) 3136, 2920, 1705, 1634, 1604, 1478, 1293, 1145, 1086, 779, 572, 545; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}FN_2O_3S$ $[M]^+$: 346.0787, Found: 346.0785.

***N*-(1-Acetyl-5-chloro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **10**)



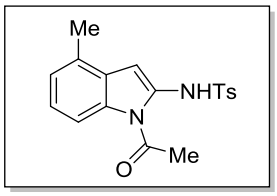
Brown solid (36 mg, 50%); **m.p.** 167 – 169 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.70 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.57 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 1H), 5.93 (s, 1H), 2.75 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.5, 143.9, 135.7, 132.7, 132.2, 129.8 (2C), 128.3, 127.6, 127.0 (2C), 124.6, 119.9, 117.1, 104.0, 26.9, 21.1; **IR** (cm^{-1}) 2929, 2849, 1710, 1624, 1293, 1147, 1087, 778, 541, 523; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}ClN_2O_3S$ $[M]^+$: 362.0492, Found: 362.0489.

***N*-(1-Acetyl-5-bromo-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **11**)



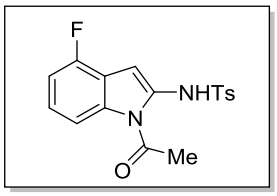
Brown solid (37 mg, 46%); **m.p.** 192 – 194 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.70 (s, 1H), 8.09 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 2.1 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.45 – 7.40 (m, 3H), 5.93 (s, 1H), 2.75 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.6, 143.9, 135.7, 133.0, 132.0, 129.8 (2C), 128.8, 127.3, 127.0 (2C), 122.9, 117.5, 115.7, 103.9, 27.0, 21.1; **IR** (cm^{-1}) 3054, 2920, 1712, 1625, 1292, 1146, 1087, 778, 701, 541; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}BrN_2O_3S$ $[M]^+$: 405.9987, Found: 405.9989.

***N*-(1-Acetyl-4-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **12**)



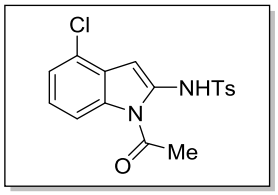
Yellow solid (58 mg, 80%); **m.p.** 192 – 194 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.55 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.24 – 7.12 (m, 1H), 7.01 (d, J = 7.4 Hz, 1H), 5.91 (s, 1H), 2.72 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.5, 143.8, 135.9, 134.1, 130.2, 129.7 (2C), 129.3, 127.1 (2C), 126.3, 124.9, 123.7, 113.2, 103.6, 27.0, 21.0, 17.9; **IR** (cm^{-1}) 3142, 2913, 1712, 1633, 1591, 1312, 1233, 1148, 1082, 867, 747, 550; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_3S$ $[M]^+$: 342.1038, Found: 342.1040.

***N*-(1-Acetyl-4-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **13**)



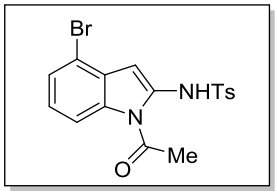
Yellow solid (31 mg, 45%); **m.p.** 161 – 163 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.75 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 – 7.23 (m, 1H), 7.04 (dd, J = 9.9, 8.1 Hz, 1H), 5.89 (s, 1H), 2.76 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.8, 155.2 (d, J = 245.6 Hz), 144.0, 136.2 (d, J = 9.2 Hz), 135.7, 131.5, 129.9 (2C), 127.1 (2C), 125.9 (d, J = 7.1 Hz), 115.5 (d, J = 22.0 Hz), 112.2 (d, J = 3.5 Hz), 108.7 (d, J = 17.9 Hz), 99.4, 27.0, 21.1; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -122.5; **IR** (cm^{-1}) 3111, 2921, 1592, 1463, 1237, 1147, 1089, 752, 656, 544; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}FN_2O_3S$ $[M]^+$: 346.0787, Found: 346.0784.

***N*-(1-Acetyl-4-chloro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **14**)



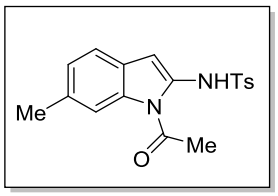
Yellow solid (46 mg, 64%); **m.p.** 140 – 142 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.20 – 8.05 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 5.87 (s, 1H), 2.76 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.7, 144.0, 135.6, 134.8, 132.1, 129.8 (2C), 127.1 (2C), 125.8, 125.3, 124.1, 123.0, 114.5, 101.5, 27.0, 21.1; **IR** (cm^{-1}) 3147, 2912, 1720, 1631, 1444, 1315, 1244, 1142, 1086, 822, 785, 716, 548; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}ClN_2O_3S$ $[M]^+$: 362.0492, Found: 362.0493.

***N*-(1-Acetyl-4-bromo-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **15**)



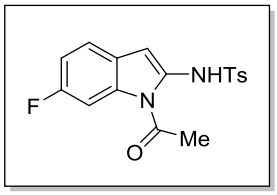
Brown solid (35 mg, 43%); **m.p.** 130 – 132 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.78 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.36 (m, 3H), 7.23 (t, *J* = 8.1 Hz, 1H), 5.78 (s, 1H), 2.76 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.7, 144.0, 135.5, 134.4, 132.1, 129.8 (2C), 127.2, 127.1 (2C), 126.1, 126.0, 114.9, 113.1, 103.3, 27.0, 21.0; **IR** (cm^{-1}) 3090, 2940, 1723, 1596, 1578, 1267, 1137, 1087, 776, 546; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}BrN_2O_3S$ $[M]^+$: 405.9987, Found: 405.9985.

***N*-(1-Acetyl-6-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **16**)



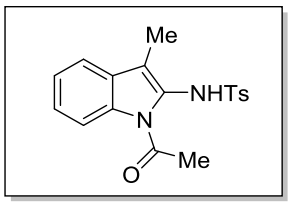
Brown solid (34 mg, 50%); **m.p.** 168 – 170 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.01 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.87 (s, 1H), 2.73 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.5, 143.7, 136.0, 134.7, 134.4, 123.0, 129.8 (2C), 127.0 (2C), 124.6, 124.5, 120.2, 115.7, 105.3, 27.0, 21.7, 21.1; **IR** (cm^{-1}) 3061, 2921, 1712, 1632, 1599, 1322, 1144, 1084, 756, 541; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_3S$ $[M]^+$: 342.1038, Found: 342.1040.

***N*-(1-Acetyl-6-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **17**)



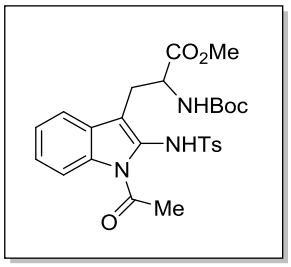
White solid (42 mg, 61%); **m.p.** 165 – 167 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.62 (s, 1H), 7.95 (d, *J* = 11.0 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.02 (m, 1H), 5.95 (s, 1H), 2.76 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 170.6, 160.4 (d, *J* = 238.1 Hz), 143.8, 135.9, 134.3 (d, *J* = 13.1 Hz), 131.0 (d, *J* = 3.8 Hz), 129.8 (2C), 127.0 (2C), 123.3, 121.9 (d, *J* = 9.9 Hz), 111.4 (d, *J* = 23.8 Hz), 105.3, 102.7 (d, *J* = 29.0 Hz), 26.88, 21.05; **^{19}F NMR** (564 MHz, DMSO-d_6) δ -116.2 (td, *J* = 10.1, 5.7 Hz); **IR** (cm^{-1}) 3142, 2919, 1718, 1640, 1597, 1279, 1151, 1106, 883, 810, 761, 683, 548; **High Resolution MS** (EI): Calculated for $C_{17}H_{15}FN_2O_3S$ $[M]^+$: 346.0787, Found: 346.0789.

***N*-(1-Acetyl-3-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **18**)



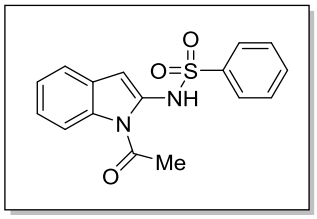
White solid (58 mg, 85%); **m.p.** 166 – 168 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 8.19 (s, 1H), 7.54 (d, *J* = 6.7 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.25 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 170.9, 144.4, 135.8, 133.1, 129.4 (2C), 129.2, 128.0, 127.4 (2C), 125.1, 123.2, 119.8, 117.0, 113.7, 26.4, 21.2, 8.5; **IR** (cm^{-1}) 3239, 2919, 1638, 1451, 1368, 1302, 1162, 814, 732, 673, 554; **High Resolution MS** (EI): Calculated for $C_{18}H_{18}N_2O_3S$ $[M]^+$: 342.1038, Found: 342.1036.

Methyl 3-[1-acetyl-2-{(4-methylphenyl)sulfonamido}-1*H*-indol-3-yl]-2-{(*tert*-butoxycarbonyl)amino}propanoate (Scheme 4, **19**)



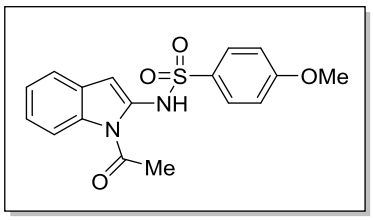
White solid (38 mg, 36%); **m.p.** 165 – 167 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 8.32 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 5.35 (s, 1H), 4.55 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.00 (m, 2H), 2.48 – 2.29 (m, 6H), 1.37 (s, 9H); **^{13}C NMR** (150 MHz, CD_2Cl_2) 173.0, 171.7, 155.8, 145.3, 135.9, 134.1, 130.2 (2C), 129.8, 128.6, 128.1 (2C), 125.9, 123.9, 120.3, 115.8, 114.8, 80.5, 78.1, 53.0, 28.5 (3C), 27.2, 26.7, 21.9; **IR** (cm^{-1}) 3371, 3256, 2971, 2920, 1688, 1521, 1343, 1163, 680, 532; **High Resolution MS** (EI): Calculated for $C_{26}H_{31}N_3O_7S$ $[M]^+$: 529.1883, Found: 529.1881.

***N*-(1-Acetyl-1*H*-indol-2-yl)-benzenesulfonamide** (Scheme 4, **20**)



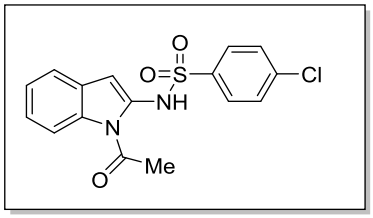
Yellow solid (53 mg, 84%); **m.p.** 138 – 140 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.69 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 2H), 7.74 – 7.70 (m, 1H), 7.67 – 7.60 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.14 (m, 1H), 5.91 (s, 1H), 2.75 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.5, 138.8, 134.3, 133.4, 130.5, 129.4 (2C), 127.0 (2C), 126.8, 125.0, 123.3, 120.6, 115.6, 105.2, 27.0; **IR** (cm^{-1}) 3126, 2919, 1706, 1625, 1310, 1251, 1144, 1084, 759, 570, 543; **High Resolution MS** (EI): Calculated for $C_{16}H_{14}N_2O_3S$ $[M]^+$: 314.0725, Found: 314.0723.

***N*-(1-Acetyl-1*H*-indol-2-yl)-4-methoxybenzenesulfonamide** (Scheme 4, **21**)



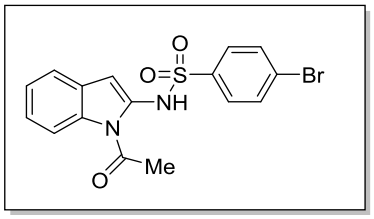
Brown solid (52 mg, 75%); **m.p.** 160 – 162 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.53 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.22 – 7.17 (m, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 5.93 (s, 1H), 3.85 (s, 3H), 2.76 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.7, 162.9, 134.4, 131.0, 130.3, 129.4 (2C), 126.9, 125.0, 123.4, 120.7, 115.7, 114.6 (2C), 105.1, 55.8, 27.2; **IR** (cm^{-1}) 3219, 3002, 1677, 1574, 1450, 1367, 1306, 1243, 1148, 1024, 771, 667, 547; **High Resolution MS** (EI): Calculated for $C_{17}H_{16}N_2O_4S$ $[M]^+$: 344.0831, Found: 344.0829.

***N*-(1-Acetyl-1*H*-indol-2-yl)-4-chlorobenzenesulfonamide** (Scheme 4, **22**)



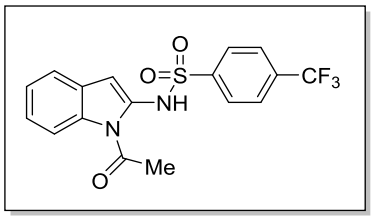
White solid (59 mg, 85%); **m.p.** 164 – 166 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.81 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.16 (m, 1H), 5.99 (s, 1H), 2.76 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.5, 138.3, 137.6, 134.4, 130.3, 129.6 (2C), 129.0 (2C), 126.8, 125.1, 123.4, 120.7, 115.7, 105.5, 27.1; **IR** (cm^{-1}) 3089, 2956, 1711, 1624, 1594, 1465, 1314, 1277, 1172, 1148, 1083, 787, 753, 543; **High Resolution MS** (EI): Calculated for $C_{16}H_{13}ClN_2O_3S$ $[M]^+$: 348.0335, Found: 348.0332.

***N*-(1-Acetyl-1*H*-indol-2-yl)-4-bromobenzenesulfonamide** (Scheme 4, **23**)



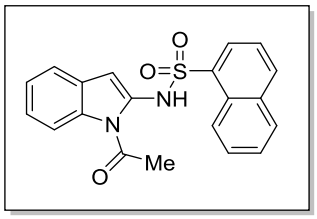
Brown solid (66 mg, 84%); **m.p.** 165 – 167 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.21 – 7.18 (m, 1H), 6.00 (s, 1H), 2.76 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.4, 138.0, 134.4, 132.5 (2C), 130.2, 129.0 (2C), 127.4, 126.8, 125.1, 123.4, 120.7, 115.6, 105.5, 27.1; **IR** (cm^{-1}) 3087, 1704, 1625, 1594, 1465, 1315, 1146, 1082, 783, 584, 543; **High Resolution MS** (EI): Calculated for $C_{16}H_{13}BrN_2O_3S$ $[M]^+$: 391.9830, Found: 391.9829.

***N*-(1-Acetyl-1*H*-indol-2-yl)-4-(trifluoromethyl)benzenesulfonamide** (Scheme 4, **24**)



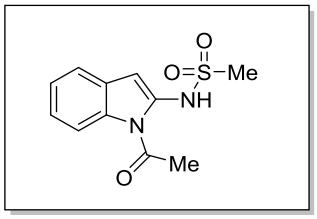
White solid (66 mg, 86%); **m.p.** 155 – 157 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.99 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.23 – 7.18 (m, 1H), 6.02 (s, 1H), 2.76 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.3, 142.7, 134.4, 133.0 (q, *J* = 32.3 Hz), 130.0, 128.0 (2C), 126.7, 126.7 (q, *J* = 3.3 Hz, 2C), 125.1, 124.3 (q, *J* = 273.0 Hz), 123.4, 120.7, 115.6, 105.6, 27.0; **^{19}F NMR** (564 MHz, DMSO-d_6) δ -61.69; **IR** (cm^{-1}) 3127, 1718, 1620, 1592, 1319, 1148, 1061, 760, 583, 539; **High Resolution MS** (EI): Calculated for $C_{17}H_{13}F_3N_2O_3S$ $[M]^+$: 382.0599, Found: 382.0601.

***N*-(1-Acetyl-1*H*-indol-2-yl)naphthalene-1-sulfonamide** (Scheme 4, **25**)



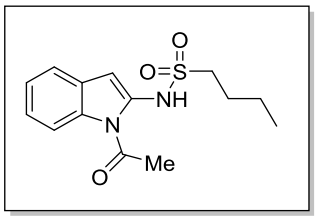
White solid (64 mg, 88%); **m.p.** 150 – 152 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.92 (s, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.66 – 7.58 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 – 7.12 (m, 1H), 5.66 (s, 1H), 2.75 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.4, 134.8, 134.3, 133.9, 133.8, 130.0, 129.9, 129.3, 128.3, 127.3, 127.2, 126.7, 125.1, 124.6, 124.2, 123.4, 120.6, 115.6, 106.0, 27.0; **IR** (cm^{-1}) 3055, 2931, 1640, 1460, 1311, 1171, 1102, 853, 756, 686, 581, 501; **High Resolution MS** (EI): Calculated for $C_{20}H_{16}N_2O_3S$ $[M]^+$: 364.0882, Found: 364.0883.

***N*-(1-Acetyl-1*H*-indol-2-yl)methanesulfonamide** (Scheme 4, **26**)



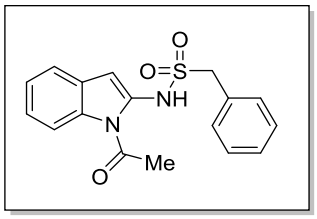
Brown solid (43 mg, 86%); **m.p.** 138 – 140 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.30 – 7.24 (m, 1H), 6.77 (s, 1H), 3.19 (s, 3H), 2.75 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.7, 134.5, 131.4, 127.2, 124.9, 123.5, 120.6, 115.8, 105.4, 39.4, 27.2; **IR** (cm^{-1}) 3015, 2934, 1704, 1638, 1281, 1130, 970, 776, 581, 502; **High Resolution MS** (EI): Calculated for $C_{11}H_{12}N_2O_3S$ $[M]^+$: 252.0569, Found: 252.0569.

***N*-(1-Acetyl-1*H*-indol-2-yl)butane-1-sulfonamide** (Scheme 4, **27**)



White solid (48 mg, 82%); **m.p.** 107 – 109 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.29 – 7.22 (m, 1H), 6.72 (s, 1H), 3.31 – 3.23 (m, 2H), 2.76 (s, 3H), 1.80 – 1.72 (m, 2H), 1.53 – 1.35 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 170.8, 134.4, 131.1, 127.2, 124.9, 123.5, 120.6, 115.8, 105.6, 50.5, 27.2, 25.1, 20.8, 13.6; **IR** (cm^{-1}) 2958, 2874, 1713, 1639, 1598, 1464, 1319, 1133, 853, 755, 507; **High Resolution MS** (EI): Calculated for $C_{14}H_{18}N_2O_3S$ $[M]^+$: 294.1038, Found: 294.1041.

***N*-(1-Acetyl-1*H*-indol-2-yl)-1-phenylmethanesulfonamide** (Scheme 4, **28**)



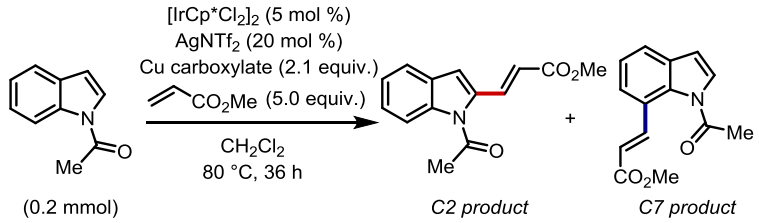
White solid (51 mg, 78%); **m.p.** 154 – 156 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 1H), 7.29 – 7.25 (m, 1H), 6.76 (s, 1H), 4.65 (s, 2H), 2.71 (s, 3H); **^{13}C NMR** (150 MHz, DMSO-d_6) δ 170.8, 134.3, 131.1, 131.1 (2C), 129.2, 128.5 (2C), 128.4, 127.3, 124.9, 123.5, 120.6, 115.8, 105.4, 57.2, 27.0; **IR** (cm^{-1}) 2959, 2918, 1697, 1630, 1594, 1311, 1145, 1123, 808, 764, 696, 540, 499; **High Resolution MS** (EI): Calculated for $C_{17}H_{16}N_2O_3S$ $[M]^+$: 328.0882, Found: 328.0883.

VI. Procedure for the Ir-Catalyzed C–H Olefination with Acrylates

1. Procedure for Reaction Optimization

To a seal tube with a oval-shaped Teflon spinbar were added *N*-acetylindole (32 mg, 0.20 mmol), methyl acrylate (91 μL, 1.0 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5 mol %), $AgNTf_2$ (15.5 mg, 0.040 mmol, 20 mol %) and copper carboxylate (0.42 mmol) in methylene chloride (1.5 mL) under Ar-purged conditions. The reaction mixture was stirred in a pre-heated oil bath or a heating block at the 80 °C for 36 h. The reaction mixture was cooled to room temperature, filtered through a plug of celite and 3M aqueous NH_3 solution was added. The two layers were seperated, and the aqueous layer was extracted with methylene chloride (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude yield and regiomeric ratios were measured by ^1H NMR using dibromomethane as an internal standard.

Table S3. Copper Carboxylates Screen

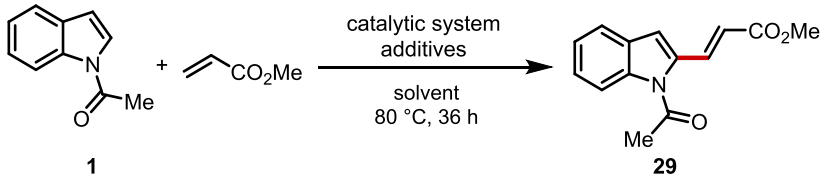


entry	Cu carboxylate	yield (%) (*C2-product*)	yield (%) (*C7-product*)	ratio (C2:C7)
1	$Cu(OAc)_2$	23	28	1:1.2
2	$Cu(OPiv)_2$	22	42	1:1.9
3	$Cu(OTFA)_2$	66	5	13.2:1

2. Further Optimizations for Improved Catalytic Reaction

To afford high yields of **29**, further studies were conducted according to the above general procedure. The crude yield was measured by ^{1}H NMR using dibromomethane as an internal standard.

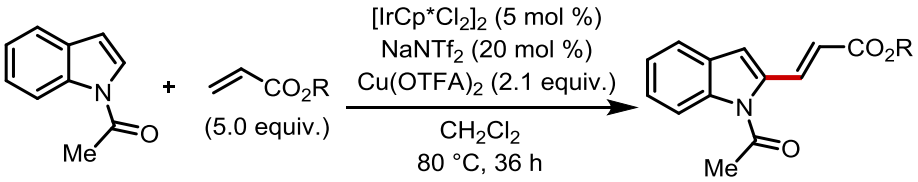
Table S4. Optimization of the Reaction Condition[a]



entry	catalytic system (mol %)	additives (mol %)	solvent	yield (%)
1	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	-	CH_2Cl_2	n.d
2	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (10)	AgOTFA (20)	CH_2Cl_2	18
3	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	$Cu(OTFA)_2$ (210)	CH_2Cl_2	66
4	$[IrCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	$Cu(OTFA)_2$ (210)	1,2-DCE	46
5	**$[IrCp^*Cl_2]_2$ (5) / $NaNTf_2$ (20)**	**$Cu(OTFA)_2$ (210)**	**CH_2Cl_2**	**82**
6	$[IrCp^*Cl_2]_2$ (5) / $NaNTf_2$ (20)	-	CH_2Cl_2	n.d
7	-	$Cu(OTFA)_2$ (210)	CH_2Cl_2	n.d

[a]Standard reaction conditions: *N*-acetylindole (23 μL, 0.20 mmol), methyl acrylate (91 μL, 1.0 mmol, 5.0 equiv.), catalyst, and additives in solvent (1.5 mL) at 80 °C for 36 h.

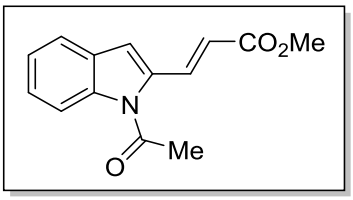
3. General Procedure for the Ir-Catalyzed C–H Olefination with Acrylates



To a seal tube with a oval-shaped spinbar were added *N*-acetylindole (32 mg, 0.20 mmol), acrylate (1.0 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.010 mmol, 5 mol %), $NaNTf_2$ (12.1 mg, 0.040 mmol, 20 mol %) and copper trifluoroacetate (121.6 mg, 0.42 mmol) in methylene chloride (1.5 mL) under Ar-purged conditions. The reaction mixture was stirred in a pre-heated oil bath at the 80 °C for 36 h. The reaction mixture was cooled to room temperature, filtered through a plug of celite and 3M aqueous NH_3 solution was added. The two layers were seperated, and the aqueous layer was extracted with methylene chloride (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude yield and regiomeric ratios were measured by ^{1}H NMR using dibromomethane as an internal standard, and the residue was purified by chromatography on silica gel

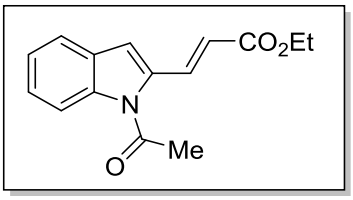
to give the desired product.

Methyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **29**)



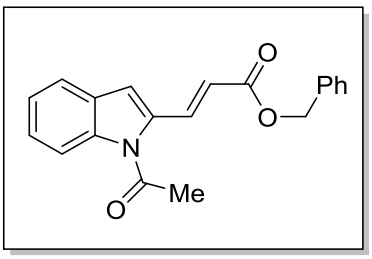
White solid (39 mg, 80%); **m.p.** 89 – 91 °C; **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.04 (d, *J* = 15.7 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 3.79 (s, 3H), 2.73 (s, 3H); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ 170.2, 166.7, 137.3, 136.3, 136.1, 129.2, 125.9, 123.7, 121.5, 119.4, 115.1, 111.7, 51.7, 27.4; **IR** (cm^{-1}) 2946, 1693, 1623, 1440, 1369, 1300, 1271, 1198, 1145, 1005, 838, 759; **High Resolution MS** (EI): Calculated for $C_{14}H_{13}NO_3$ $[M]^+$: 243.0895, Found: 243.0895.

Ethyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **30**)



Yellow solid (36 mg, 70%); **m.p.** 95 – 96 °C; **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.05 – 8.00 (m, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.32 – 7.22 (m, 1H), 6.98 (s, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.73 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ 170.6, 166.6, 137.6, 136.7, 136.1, 129.5, 126.2, 124.0, 121.8, 120.3, 115.4, 111.9, 61.0, 27.8, 14.5; **IR** (cm^{-1}) 2981, 1698, 1474, 1368, 1294, 1116, 1025, 745; **High Resolution MS** (EI): Calculated for $C_{15}H_{15}NO_3$ $[M]^+$: 257.1052, Found: 257.1051.

Benzyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **31**)



Orange oil (53 mg, 83%); **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 8.10 (d, *J* = 15.7 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.39 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.26 (s, 2H), 2.74 (s, 3H); **^{13}C NMR** (150 MHz, CD_2Cl_2) δ 170.6, 166.5, 137.7, 136.8, 136.7, 136.6, 129.6, 128.9 (2C), 128.6, 128.6 (2C), 126.3, 124.1, 122.0, 119.8, 115.5, 112.2, 66.8, 27.8; **IR** (cm^{-1}) 3054, 1702, 1456, 1371, 1300, 1264, 1211, 1164, 1026, 731, 639; **High Resolution MS** (EI): Calculated for $C_{20}H_{17}NO_3$ $[M]^+$: 319.1208, Found: 319.1207.

VII. DFT Calculations

1. Computational Details

All DFT calculations were carried out with Gaussian09 quantum chemical package.[S9] For transition state analysis, geometry optimizations were performed with M06 functional and the 6-31G** basis set. The iridium atom was represented using the Los Alamos LANL2DZ basis set,[S10] which includes relativistic effective core potentials. For those structures having various conformations, the most stable conformer was searched and utilized. Vibrational frequency calculations were carried out at the same level of theory as the geometry optimizations. The single-point calculations of the optimized geometries were performed with M06 functional and triple-zeta quality of basis set including Stuttgart/Dresden basis set (SDD) for iridium and 6-311+G** basis set for other atoms. We obtained solvation energies using the optimized gas phase structures with SMD model.[S11] Solvation calculations were carried out with the same level of single-point calculations employing the dielectric constants of $\varepsilon = 10.125$ for dichloroethane. Graphical structures are visualized with CYLview.[S12]

To interrogate stereoelectronic properties of acid additives for multivariate analysis, geometries of carboxylic acids were fully optimized with M06-2X functional[S13] and a triple zeta potential basis set (jun-cc-pVTZ),[S14] which was chosen based on the evaluation of the M06-2X functional for organic molecules with triple zeta quality basis sets resulting in quantitative correlations.[S15] Natural bond orbital (NBO) charge was calculated from the same level of theory utilizing version 3.0 embedded in Gaussian09.[S16] Sterimol values were collected using Molecular Modeling Pro®.[S17] Interrogated parameters are listed in Table S5 and Table S6.

Table S5. Physical organic parameters for carboxylic acids

entry	R	NBO Charge				IR Frequency		Sterimol Values		
		$NBO_{=O}$	NBO_{OH}	NBO_{C}	NBO_{OAvg}	$\nu_{C=O}$	$I_{C=O}$	L	B_1	B_5
1	^{t}Bu	-0.61	-0.72	0.83	-0.66	1859.18	330.32	4.27	2.93	3.34
2	^{i}Pr	-0.61	-0.71	0.82	-0.66	1862.15	318.39	4.31	2.07	3.35
3	Et	-0.61	-0.71	0.82	-0.66	1867.49	317.65	4.34	1.74	3.32
4	Me	-0.60	-0.71	0.81	-0.65	1874.00	369.93	3.03	1.70	2.20
5	CH_2Ph	-0.60	-0.71	0.83	-0.65	1864.76	348.53	4.31	1.70	6.10
6	$CH(Ph)_2$	-0.61	-0.70	0.85	-0.65	1861.20	237.87	5.71	2.16	6.02
7	$C(Ph)_3$	-0.60	-0.70	0.86	-0.65	1848.38	299.13	5.42	4.26	6.19

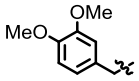
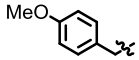
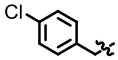
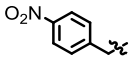
8		-0.60	-0.71	0.83	-0.66	1867.58	371.54	5.60	1.70	8.24
9		-0.61	-0.71	0.83	-0.66	1867.16	352.55	5.28	1.70	8.32
10		-0.60	-0.70	0.83	-0.65	1867.07	343.55	5.18	1.70	7.49
11		-0.60	-0.70	0.83	-0.65	1869.49	340.87	5.30	1.70	7.67
12	CH_2Cl	-0.57	-0.70	0.79	-0.64	1903.41	289.21	3.91	1.70	3.36
13	CH_2F	-0.57	-0.71	0.77	-0.64	1910.93	348.88	3.45	1.70	2.75
14	$CHCl_2$	-0.57	-0.68	0.51	-0.62	1882.14	351.07	3.91	2.01	3.44
15	CHF_2	-0.57	-0.67	0.74	-0.62	1895.15	310.65	3.45	1.85	2.74
16	CF_3	-0.54	-0.67	0.72	-0.61	1928.09	318.82	3.48	2.09	2.72
17	C_2F_5	-0.54	-0.67	0.75	-0.61	1909.44	308.58	4.95	2.12	3.82
18	$(4\text{-}CF_3)C_6H_4$	-0.59	-0.70	0.80	-0.65	1855.60	373.18	7.72	2.27	3.23
19	$(4\text{-}NO_2)C_6H_4$	-0.59	-0.70	0.80	-0.64	1858.08	367.43	7.81	1.77	3.23
20	$(4\text{-}F)C_6H_4$	-0.60	-0.70	0.80	-0.65	1848.49	398.23	7.03	1.77	3.23
21	$(4\text{-}Cl)C_6H_4$	-0.60	-0.70	0.80	-0.65	1850.18	413.28	7.74	1.77	3.23
22	Ph	-0.60	-0.70	0.80	-0.65	1855.25	387.94	6.33	1.77	3.23
23	$(4\text{-}Br)C_6F_4$	-0.56	-0.68	0.80	-0.62	1872.27	444.07	8.08	1.77	3.89

Table S6. Sterimol values for substituents on directing groups

R	L	B_1	B_5
Me	3.031	1.700	2.197
Et	4.339	1.744	3.315
Pr	5.211	1.746	3.532
^{i}Pr	4.305	2.068	3.348
Cy	6.363	2.071	3.690
^{t}Bu	4.275	2.928	3.344

VIII. Statistical Modeling

Using MATLAB student version R2014a,[S18] a script used to develop multivariate linear regression models was edited from a literature procedure.[S19] Parameters used in the model were normalized using the formula: $X_{norm} = (X - \mu)/\sigma$, where X_{norm} is the normalized parameter, X is the parameter, μ is the mean, and σ is the standard deviation. Unless otherwise noted, parameters in this section are normalized ones.

According to Curtin-Hammett principle, the relative rate of formation of competing products (X and Y) is logarithmically related to the difference in transition state energies, represented by the measured $\Delta\Delta G^{\ddagger}$ (eq S1), where R is the gas constant and T is temperature. To derive measured $\Delta\Delta G^{\ddagger}$ values, product ratios resulting from differences in selectivity were obtained experimentally. Using stepwise linear regression in Matlab®,[S18] a mathematical model was developed relating the identified steric and electronic parameters, represented by A, B, and C, to the predicted $\Delta\Delta G^{\ddagger}$ (eq S2). Thus, the predicted $\Delta\Delta G^{\ddagger}$ values can be compared with the measured $\Delta\Delta G^{\ddagger}$ values obtained from experimental results. This correlation is possible in cases where all of the compared product ratios are the result of a similar mechanism of product determination. A good correlation between the two indicates that the structural parameters included in the equation may adequately approximate the effects leading to the measured $\Delta\Delta G^{\ddagger}$.

$$\Delta\Delta G^{\ddagger} \text{ measured} = -RT \ln(\frac{X}{Y}) \qquad \text{(S1)}$$

$$\Delta\Delta G^{\ddagger} \text{ predicted} = \alpha A + \beta B + \gamma C \qquad \text{(S2)}$$

1. Univariate Regression Models of the C–H Amidation Reaction with *N*-Acylindole

Table S7. Measured $\Delta\Delta G^{\ddagger}$ and Sterimol B_1^{DG} values for directing group variations[a]

$\Delta\Delta G^{\ddagger} = -0.95 + 0.74\boldsymbol{B_1^{DG}}$

DG	**C7**:**C2**	ΔΔG‡ measured[b]	B_1^{DG}[c]
Me	1.36	0.190	1.700
Et	1.89	0.397	1.744
*i*Pr	2.57	0.588	2.068
Cy	2.43	0.552	2.071
*n*Pr	1.93	0.410	1.746

[a]ΔΔG‡ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{\ddagger} = -RT \ln([\mathbf{C2}]/[\mathbf{C7}])$ at 40 °C. [c]Parameter is not normalized, since only a single variable was used.

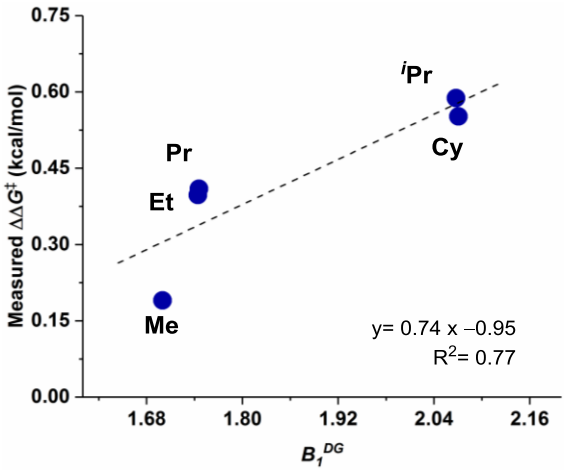
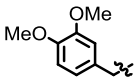
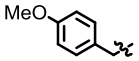
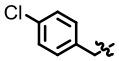
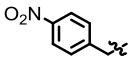


Figure S11. Univariate Regression Model with Directing Group B_1^{DG} values

2. Univariate Regression Models of the C–H Amidation Reaction with *N*-Acetylindole

Table S8. Measured $\Delta\Delta G^{\ddagger}$ and Sterimol B_5 values for carboxylate variations (data for Figure 2, left).[a]

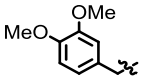
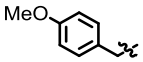
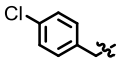
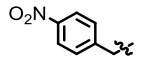
R	**3**:**4**	ΔΔG‡ measured[b]	B_5[c]
^{t}Bu	2.5:1	0.558	3.344
^{i}Pr	1.6:1	0.304	3.348
Et	1.5:1	0.258	3.315
Me	1.4:1	0.190	2.197
CH_2Ph	1:1.1	-0.066	6.099
$CH(Ph)_2$	1:1.4	-0.213	6.020
$C(Ph)_3$	1:1.4	-0.215	6.189
	1:1.0	-0.021	8.243
	1:1.1	-0.063	7.486
	1:1.2	-0.101	8.324
	1:1.4	-0.196	7.674
CH_2Cl	1:2.6	-0.584	3.363
CH_2F	1:2.8	-0.640	2.747
$CHCl_2$	1:13.3	-1.611	3.437
CHF_2	1:12.3	-1.559	2.742
CF_3	1:61.9	-2.568	2.720
C_2F_5	1:73.1	-2.671	3.816
$(4\text{-}CF_3)C_6H_4$	1:1.8	-0.355	3.231
$(4\text{-}NO_2)C_6H_4$	1:1.8	-0.375	3.227
$(4\text{-}F)C_6H_4$	1:2.2	-0.489	3.226
$(4\text{-}Cl)C_6H_4$	1:2.3	-0.508	3.230
Ph	1:2.7	-0.629	3.235

(4-Br)C_6F_4	1:6.0	-1.120	3.892

[a]$\Delta\Delta G^{\ddagger}$ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{\ddagger} = -RT \ln(\mathbf{4}/\mathbf{3})$ at 40 ˚C. [c]Parameter is not normalized, since only a single variable was used.

Table S9. Measured, predicted, and leave-one-out (LOO) predicted $\Delta\Delta G^{\ddagger}$ versus NBO_{OAvg} for carboxylate variations (data for Figure 2, right).[a]

$\Delta\Delta G^{\ddagger} = -48.3 - 34.57\ \mathbf{NBO}_{OAvg}$

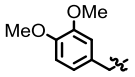
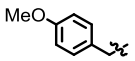
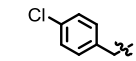
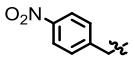
R	**3**:**4**	$\Delta\Delta G^{\ddagger}$ measured[b]	NBO_{OAvg}[c]	$\Delta\Delta G^{\ddagger}$ predicted[c]	$\Delta\Delta G^{\ddagger}$ L1O predicted
^{t}Bu	2.5:1	0.558	-0.661	0.301	0.274
^{i}Pr	1.6:1	0.304	-0.660	0.228	0.221
Et	1.5:1	0.258	-0.657	0.107	0.095
Me	1.4:1	0.190	-0.655	-0.013	-0.027
CH_2Ph	1:1.1	-0.066	-0.655	-0.013	-0.010
$CH(Ph)_2$	1:1.4	-0.213	-0.652	-0.158	-0.155
$C(Ph)_3$	1:1.4	-0.215	-0.652	-0.158	-0.155
	1:1.0	-0.021	-0.655	0.011	0.013
	1:1.1	-0.063	-0.655	0.011	0.016
	1:1.2	-0.101	-0.652	-0.134	-0.136
	1:1.4	-0.196	-0.648	-0.327	-0.334
CH_2Cl	1:2.6	-0.584	-0.637	-0.883	-0.899
CH_2F	1:2.8	-0.640	-0.638	-0.835	-0.845
$CHCl_2$	1:13.3	-1.611	-0.624	-1.487	-1.472
CHF_2	1:12.3	-1.559	-0.620	-1.680	-1.698
CF_3	1:61.9	-2.568	-0.606	-2.380	-2.308
C_2F_5	1:73.1	-2.671	-0.607	-2.332	-2.208
(4-CF_3)C_6H_4	1:1.8	-0.355	-0.647	-0.376	-0.377
(4-NO_2)C_6H_4	1:1.8	-0.375	-0.643	-0.569	-0.578
(4-F)C_6H_4	1:2.2	-0.489	-0.654	-0.062	-0.034
(4-Cl)C_6H_4	1:2.3	-0.508	-0.651	-0.182	-0.164
Ph	1:2.7	-0.629	-0.653	-0.086	-0.052
(4-Br)C_6F_4	1:6.0	-1.120	-0.621	-1.656	-1.735

[a]$\Delta\Delta G^{\ddagger}$ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{\ddagger} = -RT \ln(\mathbf{4}/\mathbf{3})$ at 40 ˚C. [c]Parameter is not normalized, since only a single variable was used.

RMS error	0.305
R^2	0.911
Adjusted R^2	0.907
F-stat	215

Table S10. Measured, predicted, and leave-one-out (LOO) predicted $\Delta\Delta G^{‡}$ versus $NBO_{=O}$ for carboxylate variations.[a]

$\Delta\Delta G^{‡} = -21.50 - 35.59\ \mathbf{NBO_{=O}}$

R	**3**:**4**	ΔΔG‡ measured[b]	$NBO_{=O}$[c]	ΔΔG‡ predicted[c]	ΔΔG‡ L1O predicted
^{t}Bu	2.5:1	0.558	-0.607	0.105	0.067
^{i}Pr	1.6:1	0.304	-0.610	0.212	0.203
Et	1.5:1	0.258	-0.607	0.105	0.092
Me	1.4:1	0.190	-0.600	-0.144	-0.164
CH_2Ph	1:1.1	-0.066	-0.603	-0.037	-0.035
$CH(Ph)_2$	1:1.4	-0.213	-0.606	0.070	0.092
$C(Ph)_3$	1:1.4	-0.215	-0.600	-0.144	-0.140
	1:1.0	-0.021	-0.601	-0.108	-0.114
	1:1.1	-0.063	-0.605	0.034	0.041
	1:1.2	-0.101	-0.602	-0.073	-0.071
	1:1.4	-0.196	-0.596	-0.286	-0.291
CH_2Cl	1:2.6	-0.584	-0.569	-0.358	-0.358
CH_2F	1:2.8	-0.640	-0.568	-0.571	-0.580
$CHCl_2$	1:13.3	-1.611	-0.568	-0.037	-0.006
CHF_2	1:12.3	-1.559	-0.566	-0.144	-0.122
CF_3	1:61.9	-2.568	-0.539	-0.073	-0.037
C_2F_5	1:73.1	-2.671	-0.543	-1.568	-1.631
$(4\text{-}CF_3)C_6H_4$	1:1.8	-0.355	-0.594	-1.247	-1.306
$(4\text{-}NO_2)C_6H_4$	1:1.8	-0.375	-0.588	-1.283	-1.343
$(4\text{-}F)C_6H_4$	1:2.2	-0.489	-0.603	-1.283	-1.252
$(4\text{-}Cl)C_6H_4$	1:2.3	-0.508	-0.600	-1.354	-1.333
Ph	1:2.7	-0.629	-0.602	-2.315	-2.215
$(4\text{-}Br)C_6F_4$	1:6.0	-1.120	-0.560	-2.173	-2.009

[a]ΔΔG‡ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{‡} = -RT \ln(\mathbf{4}/\mathbf{3})$ at 40 °C. [c]Parameter is not normalized, since only a single variable was used.

RMS error	0.423
R^2	0.829
Adjusted R^2	0.821
F-stat	102

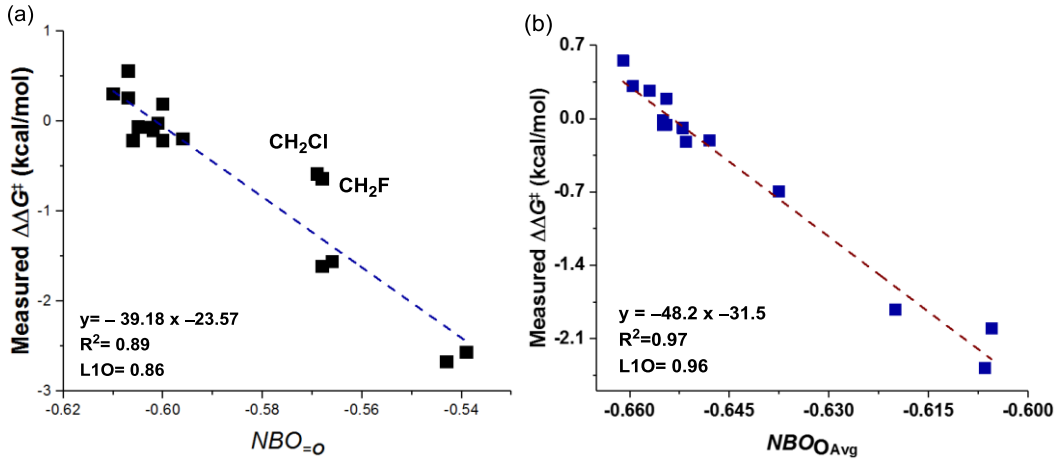


Figure S12. Univariate regression models with $NBO_{=O}$ (a) and NBO_{OAVG} (b)

As discussed in the main text, utilization of NBO charges of carbonyl oxygen ($NBO_{=O}$) also gave correlative model (in the case of acetic acid derivatives), as shown in Figure S12a. However, R^2 value (0.89) is slightly lower than that with averaged NBO charges in Figure S12b (R^2= 0.97). This lowered accuracy is attributed to overestimated carbonyl charges in the case of fluoroacetic acid and chloroacetic acid, as highlighted in Figure S13. This is because the most stable conformer was only considered to measure the charges: it may cause inaccurate results if substituent contains highly inductive group, such as halogen atoms. Indeed, as shown in Figure S13a and Figure S13b, $NBO_{=O}$ values were highly dependent on the choice of conformer. For example, $NBO_{=O}$ value was –0.568 when fluoro substituent is proximal to carbonyl oxygen, but the value significantly decreased to -0.600 when another conformer was considered.

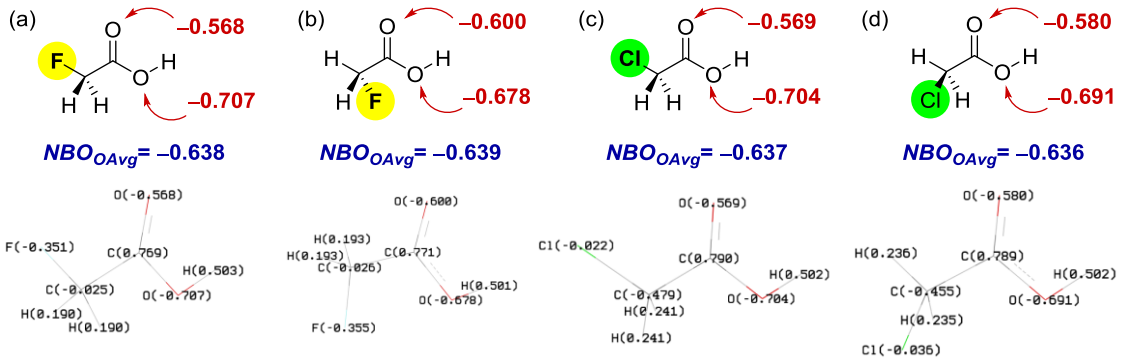


Figure S13. Calculated NBO charges of fluoroacetic acid (a, b) and chloroacetic acid conformers (c, d).

Interestingly, however, average charge values of two carboxylic oxygens were almost unchanged regardless of conformations, and more negative value was obtained (–0.64) with fluoroacetic acid. The same tendency was also observed with chloroacetic acid, as shown in Figure S13c and Figure S13d. The series of analysis enabled us to rationalize the effectiveness of NBO_{OAvg} in describing carboxylate additives.

3. Multivariate Regression Models of C–H Amidation Reactions[a]

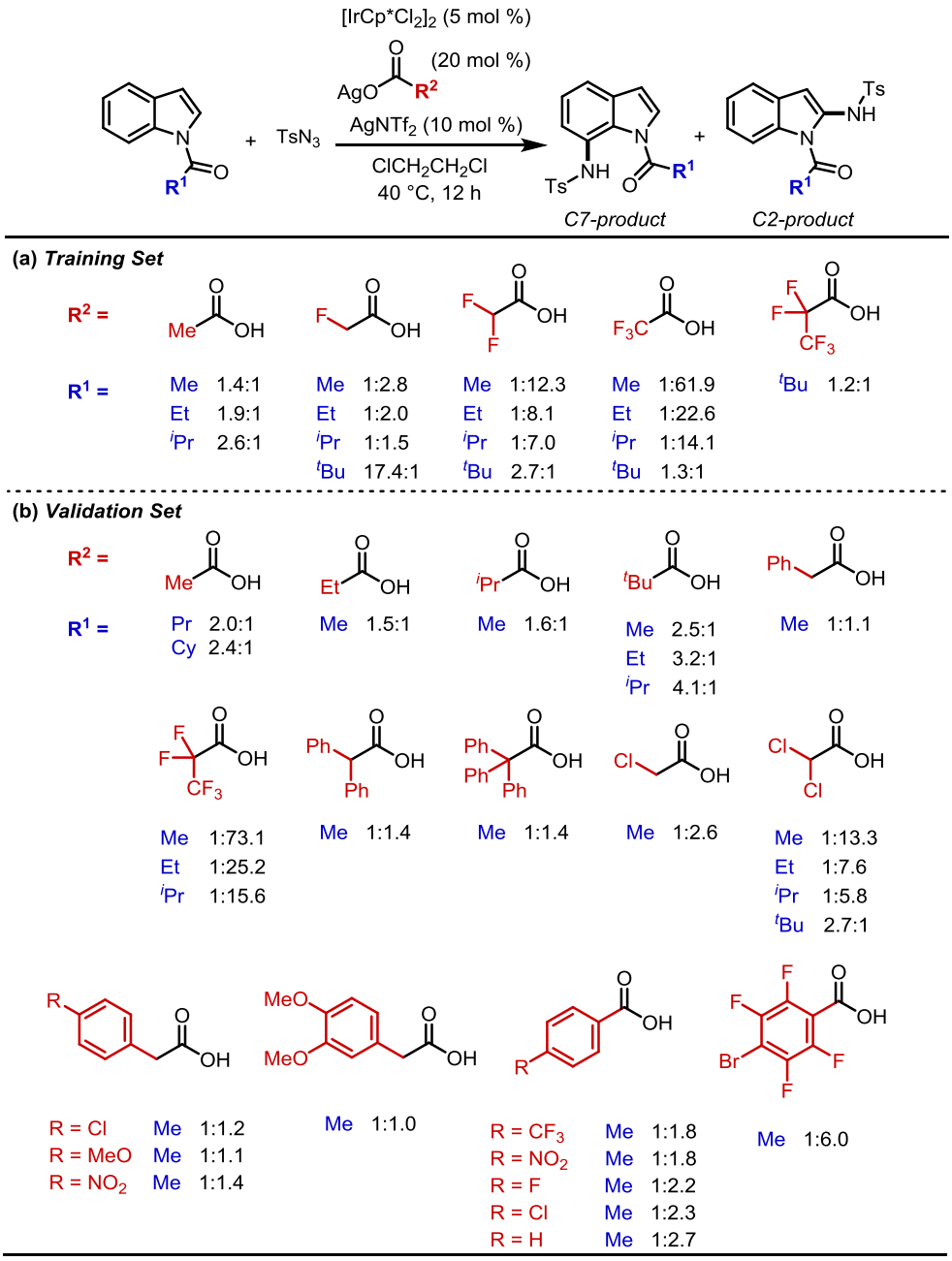


Figure S14. Full list of training and validation sets used for statistical modeling. [a]C7:C2 ratio.

Table S11. Measured and predicted $\Delta\Delta G^{\ddagger}$ for the training set (data for Figure 3).[a]

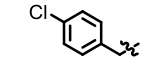
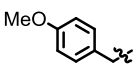
$$\Delta\Delta G^{\ddagger}_{norm} = -0.333 - 0.975\,\boldsymbol{NBO_{OAvg}} + 0.735\,\boldsymbol{B_1^{DG}}$$

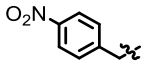
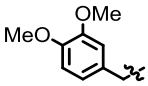
R	DG	**C7**:**C2**	ΔΔG‡ measured[b]	ΔΔG‡ predicted
CH_3	Me	1.4:1	0.190	0.146
CH_2F	Me	1:2.8	-0.640	-0.699
CHF_2	Me	1:12.3	-1.559	-1.569
CF_3	Me	1:61.9	-2.568	-2.290
CH_3	Et	1.9:1	0.397	0.229
CH_2F	Et	1:2.0	-0.426	-0.616
CHF_2	Et	1:8.1	-1.298	-1.486
CF_3	Et	1:22.6	-1.940	-2.207
CH_3	^{i}Pr	2.6:1	0.588	0.835
CH_2F	^{i}Pr	1:1.5	-0.266	-0.010
CHF_2	^{i}Pr	1:7.0	-1.211	-0.880
CF_3	^{i}Pr	1:14.1	-1.647	-1.601
CH_2F	^{t}Bu	17.4:1	1.778	1.602
CHF_2	^{t}Bu	2.7:1	0.612	0.732
CF_3	^{t}Bu	1.3:1	0.157	0.012
C_2F_5	^{t}Bu	1.2:1	0.095	0.061

[a]ΔΔG‡ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{\ddagger} = -RT\ln([\mathbf{C2}]/[\mathbf{C7}])$ at 40 °C.

RMS error	0.207
R^2	0.972
Adjusted R^2	0.967
F-stat	223

Table S12. Measured and predicted $\Delta\Delta G^{\ddagger}$ for the validation set (data for Figure 3).[a]

R	DG	**C7**:**C2**	ΔΔG‡ measured[b]	ΔΔG‡ predicted
Et	Me	1.5:1	0.258	0.270
^{i}Pr	Me	1.6:1	0.304	0.395
^{t}Bu	Me	2.5:1	0.558	0.469
CH_2Ph	Me	1:1.1	-0.066	0.146
C_2F_5	Me	1:73.1	-2.671	-2.240
$CH(Ph)_2$	Me	1:1.4	-0.213	-0.003
$C(Ph)_3$	Me	1:1.4	-0.215	-0.003
	Me	1:1.2	-0.101	0.022
	Me	1:1.1	-0.063	0.171

	Me	1:1.4	-0.196	-0.177
	Me	1:1.0	-0.021	0.171
CH_2Cl	Me	1:2.6	-0.584	-0.749
$CHCl_2$	Me	1:13.3	-1.611	-1.370
C_2F_5	Et	1:25.2	-2.008	-2.157
^{t}Bu	Et	3.2:1	0.730	0.552
^{t}Bu	^{i}Pr	4.1:1	0.878	1.158
C_2F_5	^{i}Pr	1:15.6	-1.710	-1.551
$CHCl_2$	^{i}Pr	1:5.8	-1.099	-0.681
$CHCl_2$	Et	1:7.6	-1.258	-1.287
$CHCl_2$	^{t}Bu	2.7:1	0.608	0.931
(4-CF_3)C_6H_4	Me	1:1.8	-0.355	-0.227
(4-NO_2)C_6H_4	Me	1:1.8	-0.375	-0.426
(4-F)C_6H_4	Me	1:2.2	-0.489	0.096
(4-Cl)C_6H_4	Me	1:2.3	-0.508	-0.028
Ph	Me	1:2.7	-0.629	0.072
(4-Br)C_6F_4	Me	1:6.0	-1.120	-1.544
CH_3	Cy	2.4:1	0.552	0.841
CH_3	Pr	2.0:1	0.410	0.232

[a]$\Delta\Delta G^{\ddagger}$ is reported in kcal/mol. [b]Calculated by $\Delta\Delta G^{\ddagger} = -RT \ln([\mathbf{C2}]/[\mathbf{C7}])$ at 40 °C.

IX. References

(S1) Xu, L.; Zhang, C.; He, Y.; Tan, L.; Ma, D. Rhodium-catalyzed regioselective C7-functionalization of *N*-pivaloylindoles. *Angew. Chem., Int. Ed.* **2016**, *55*, 321–325.

(S2) Schofield, J.; Derdau, V.; Atzrodt, J.; Zane, P.; Guo, Z.; Horn, R. V.; Czepczor, V.; Stoltz, A.; Pardon, M. Effect of deuteration on metabolism and clearance of Nerispirdine (HP184) and AVE5638. *Bioorg*. *Med*. *Chem*. **2015**, *23*, 3831–3842.

(S3) Sevov, C. S.; Hartwig, J. F. Iridium-catalyzed intermolecular asymmetric hydroheteroarylation of bicycloalkenes. *J. Am. Chem. Soc.* **2013**, *135*, 2116–2119.

(S4) Boltalin, A. I.; Kas'yanov, A.; Karpova, E. V.; Troyanov, S. I. Crystal structure and thermal stability of $Ag_3(CHF_2COO)_3(H_2O)_2$. *Russ*. *J. Coord*. *Chem*. **2004**, *30*, 692–697.

(S5) Endo, K.; Grubbs, R. H. Chelated ruthenium catalysts for Z-selective olefin metathesis. *J. Am. Chem. Soc*. **2011**, *133*, 8525–8527.

(S6) Feller, M.; Lux, K.; Kornath, A. Crystal structure and spectroscopic investigation of bromofluoro- and fluoroiodomethane. *Eur*. *J. Inorg*. *Chem.* **2015**, 5357–5362.

(S7) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. Rhodium-catalyzed intermolecular amidation of arenes with sulfonyl azides via chelation-assisted C–H bond activation. *J. Am. Chem. Soc.* **2012**, *134*, 9110–9113.

(S8) Kim, J.; Chang, S. Iridium- catalyzed direct C–H amidation with weakly coordinating carbonyl directing groups under mild conditions. *Angew. Chem., Int. Ed.* **2014**, *53*, 2203–2207.

(S9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Kudin, E. B. K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

(S10) Hay, P. J.; Wadt, W. R. *Ab initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys*. **1985**, *82*, 270–283.

(S11) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron

density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

(S12) CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).

(S13) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(S14) Papajak, E.; Zheng, J.; Xu, X.; Leverentz, H. R.; Truhlar, D. G. Perspectives on basis sets beautiful: Seasonal plantings of diffuse basis functions. *J. Chem. Thoery Comput.* **2011**, *7*, 3027–3034.

(S15) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835.

(S16) NBO Version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter J. E.; Weinhold, F, 1998.

(S17) Molecular Modeling Pro v. 6.36, Norgwyn Montgomery Software Inc., North Wales, PA, 2012.

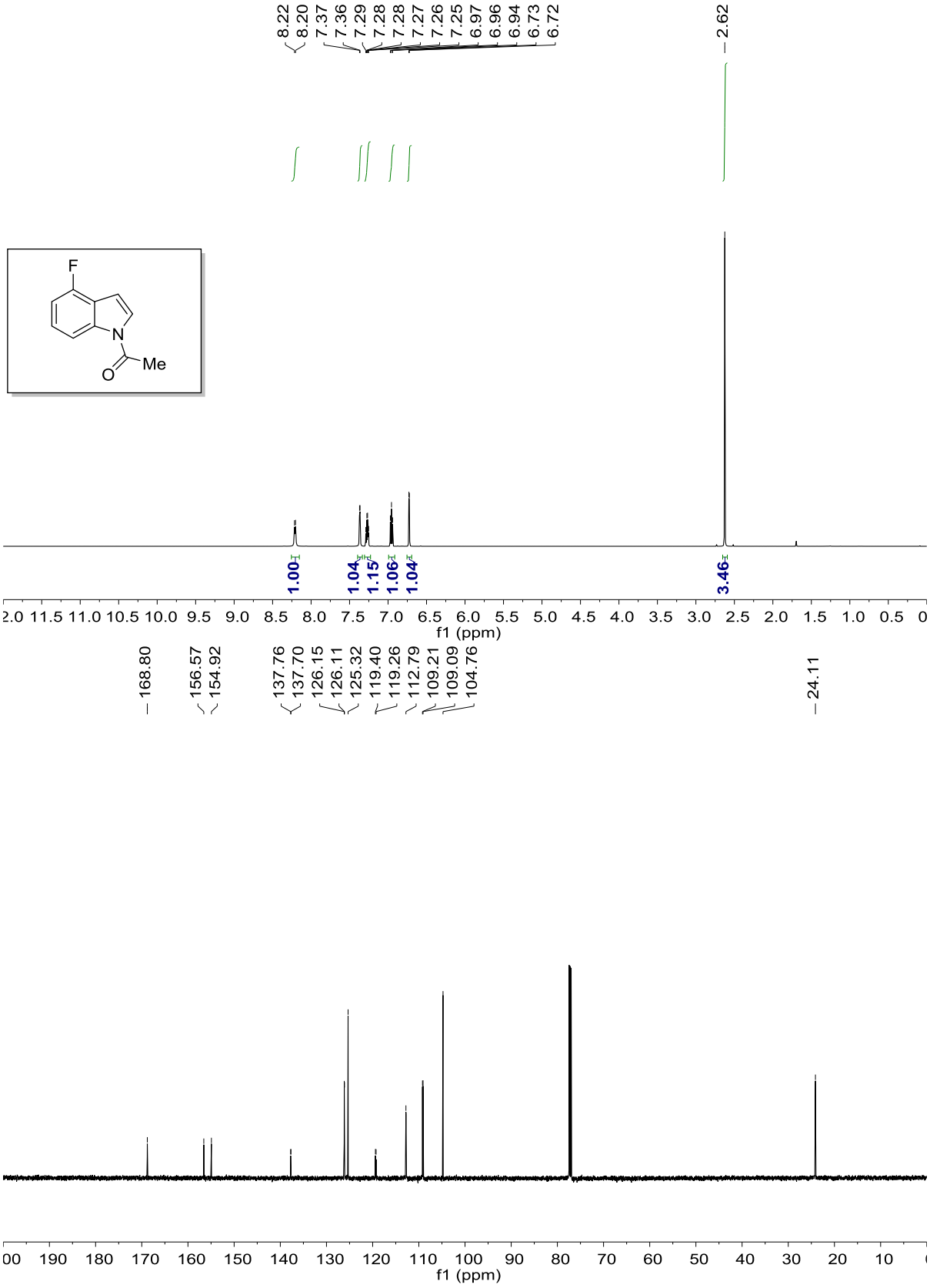
(S18) *MATLAB Student Version*, The MathWorks, Inc., Natick, MA, 2014.

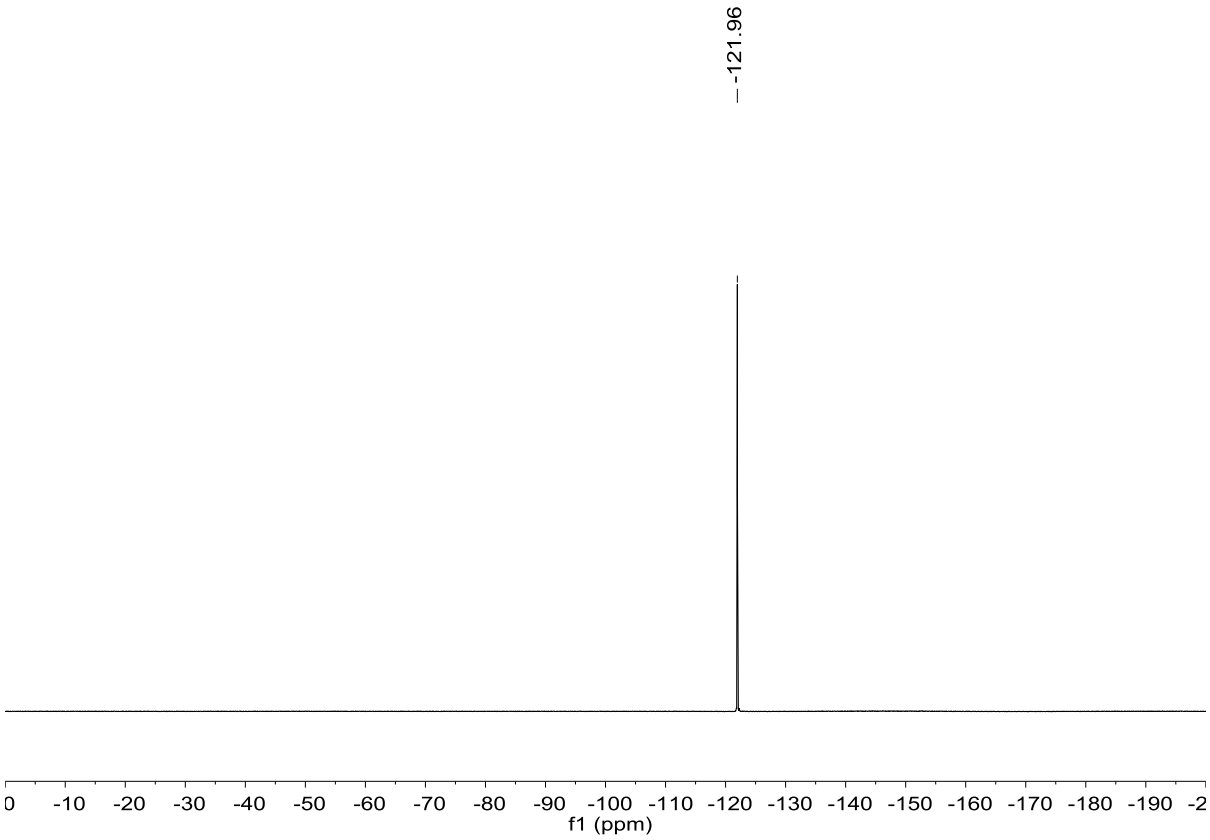
(S19) Milo, A.; Bess, E. N.; Sigman, M. S. Interrogating selectivity in catalysis using molecular vibrations. *Nature* **2014**, *507*, 210–214.

Appendix I

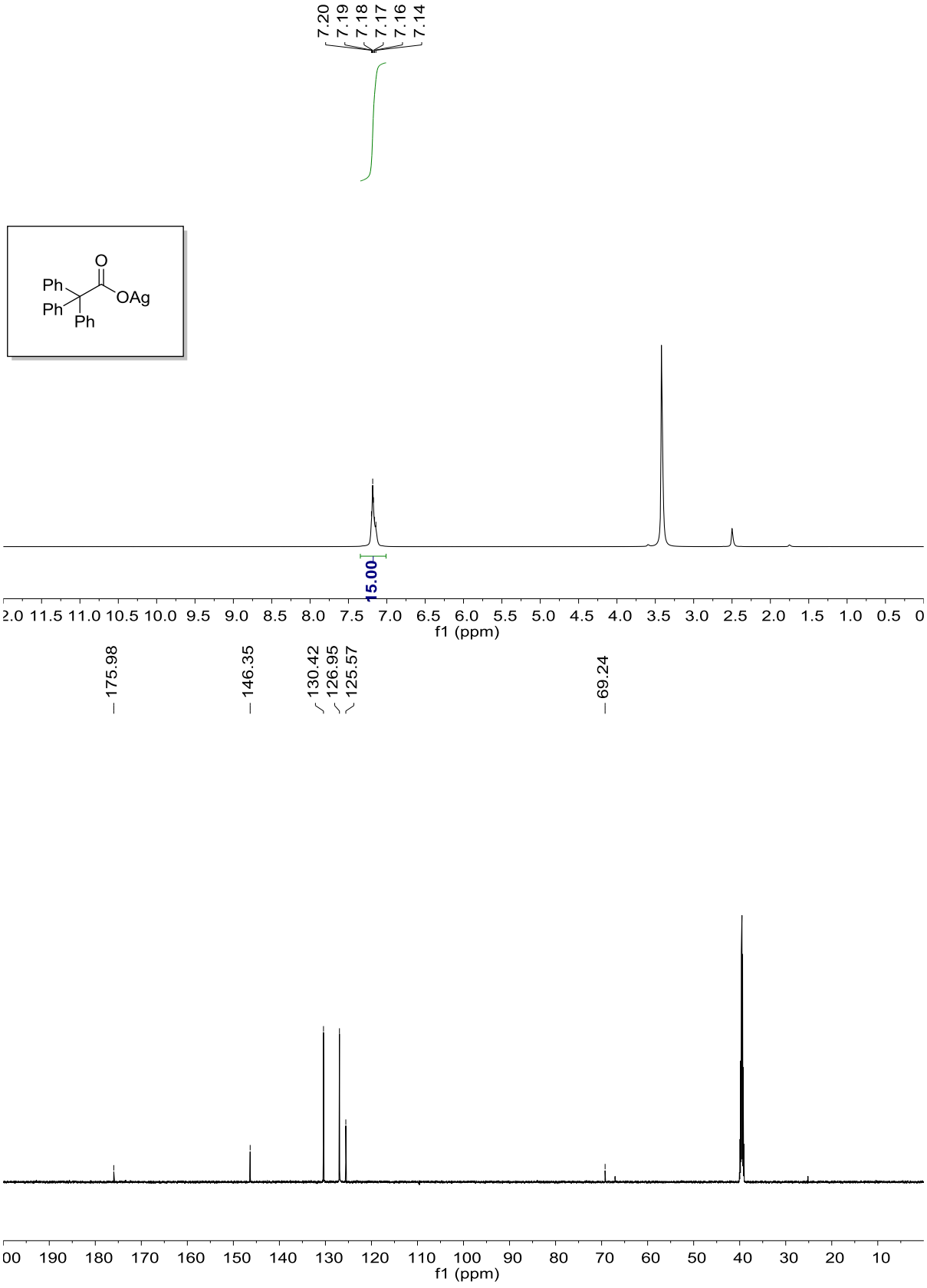
Spectral Copies of ^{1}H, ^{13}C and ^{19}F NMR of Compounds Obtained in this Study

1-Acetyl-4-fluoroindole

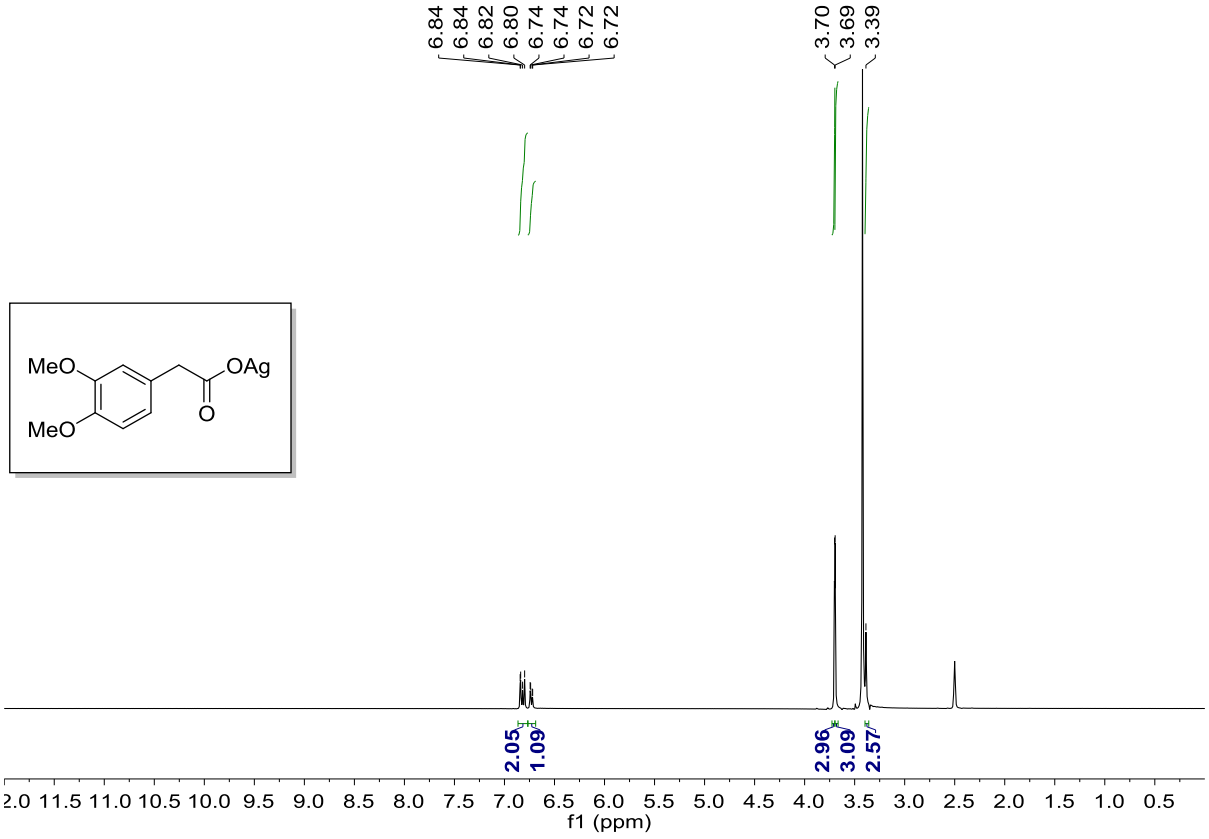


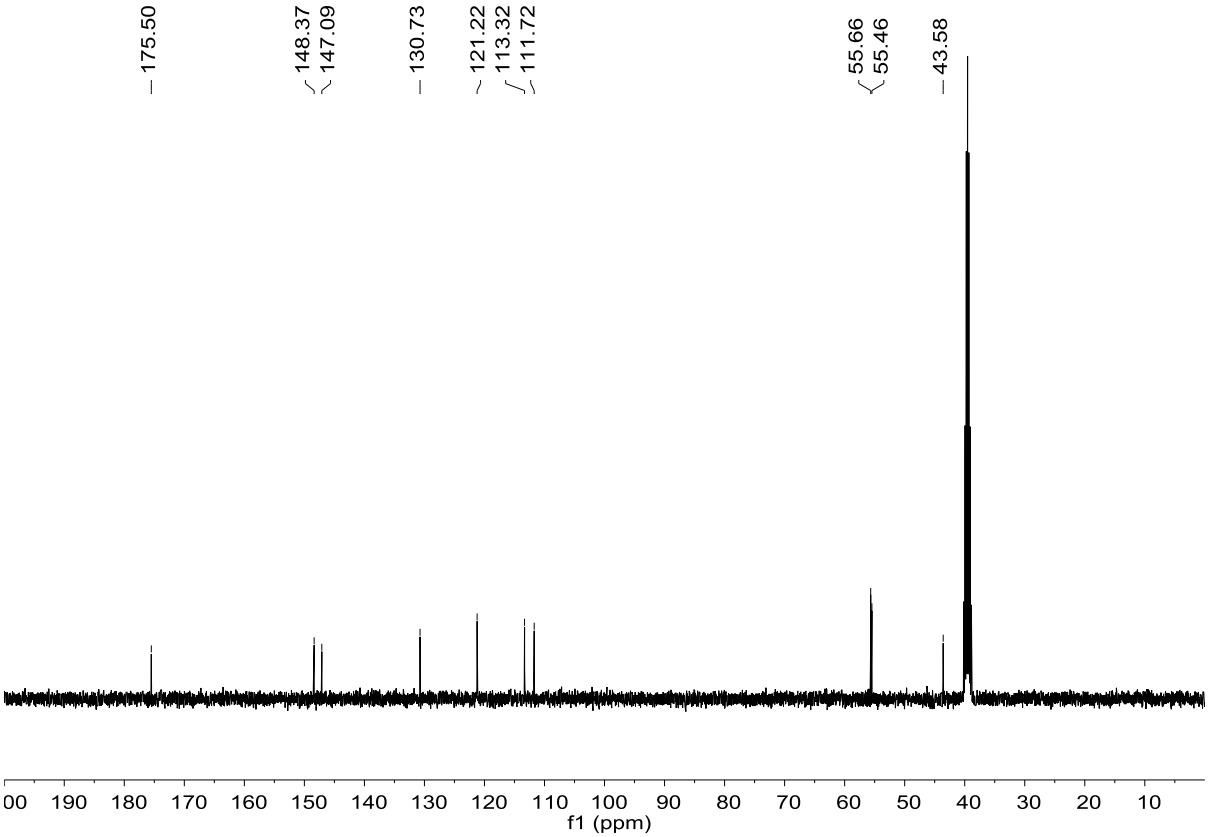

-121.96
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

Silver (2,2,2-triphenyl)acetate

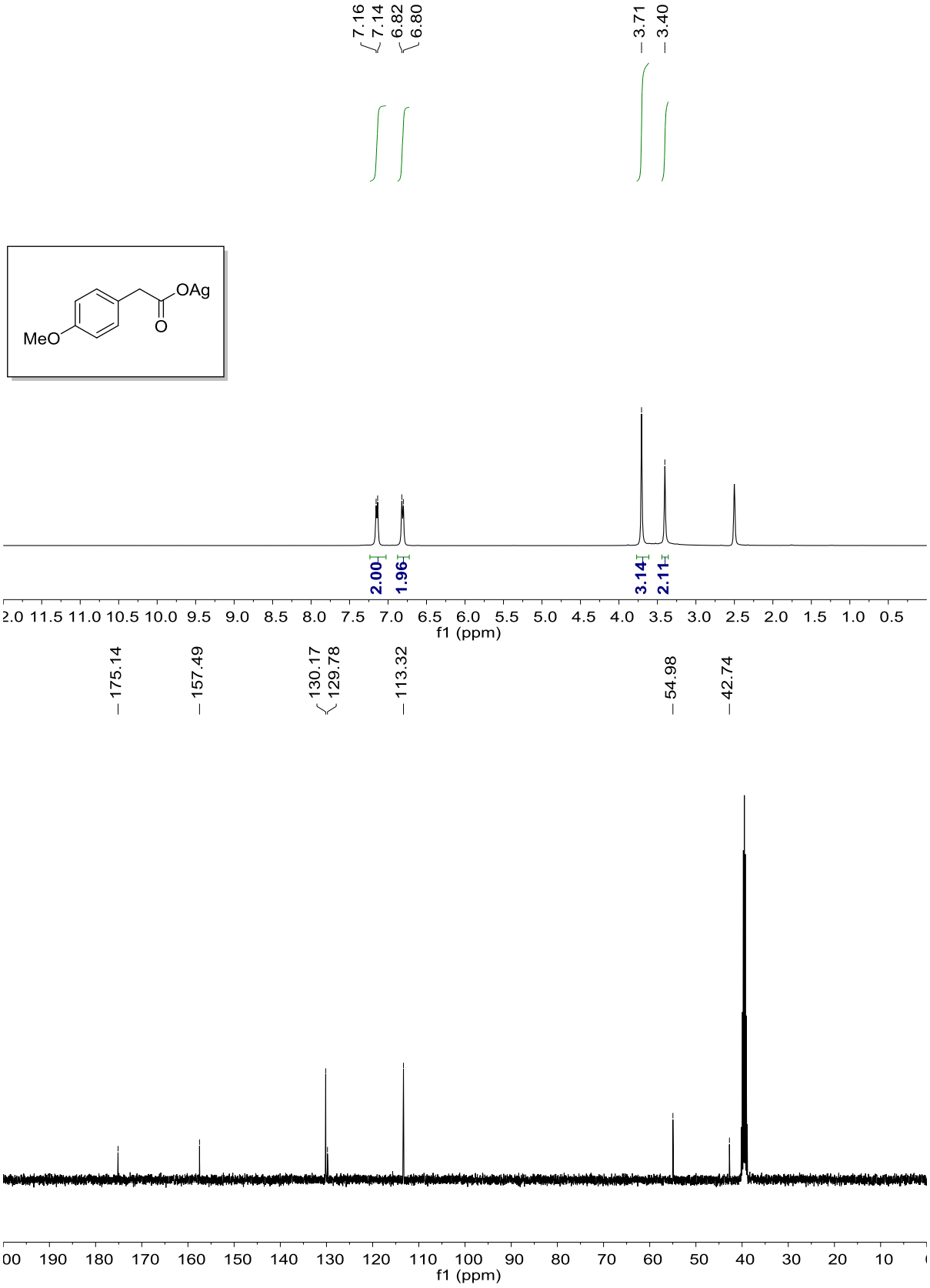


Silver 2-(3,4-dimethoxyphenyl)acetate

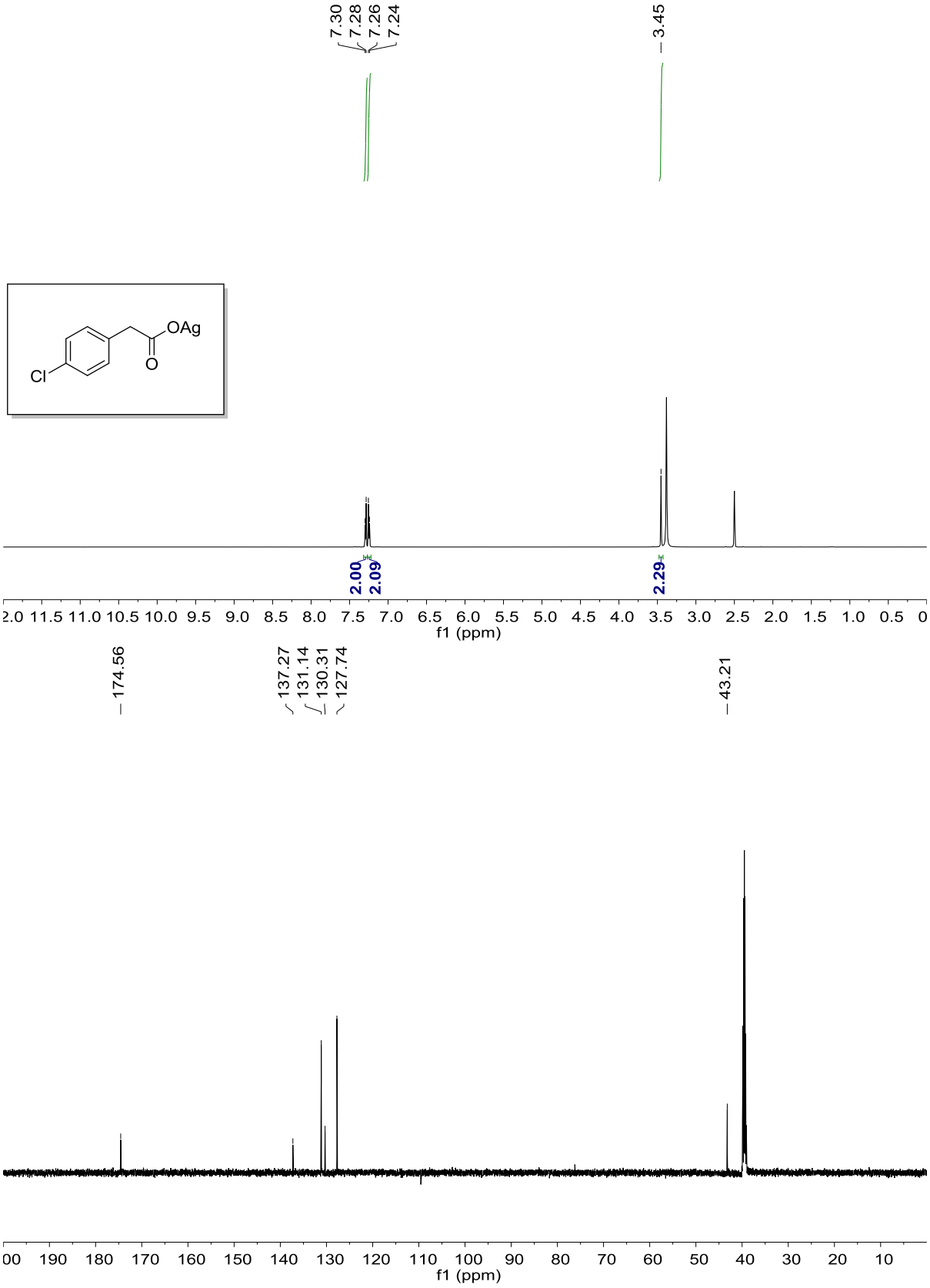




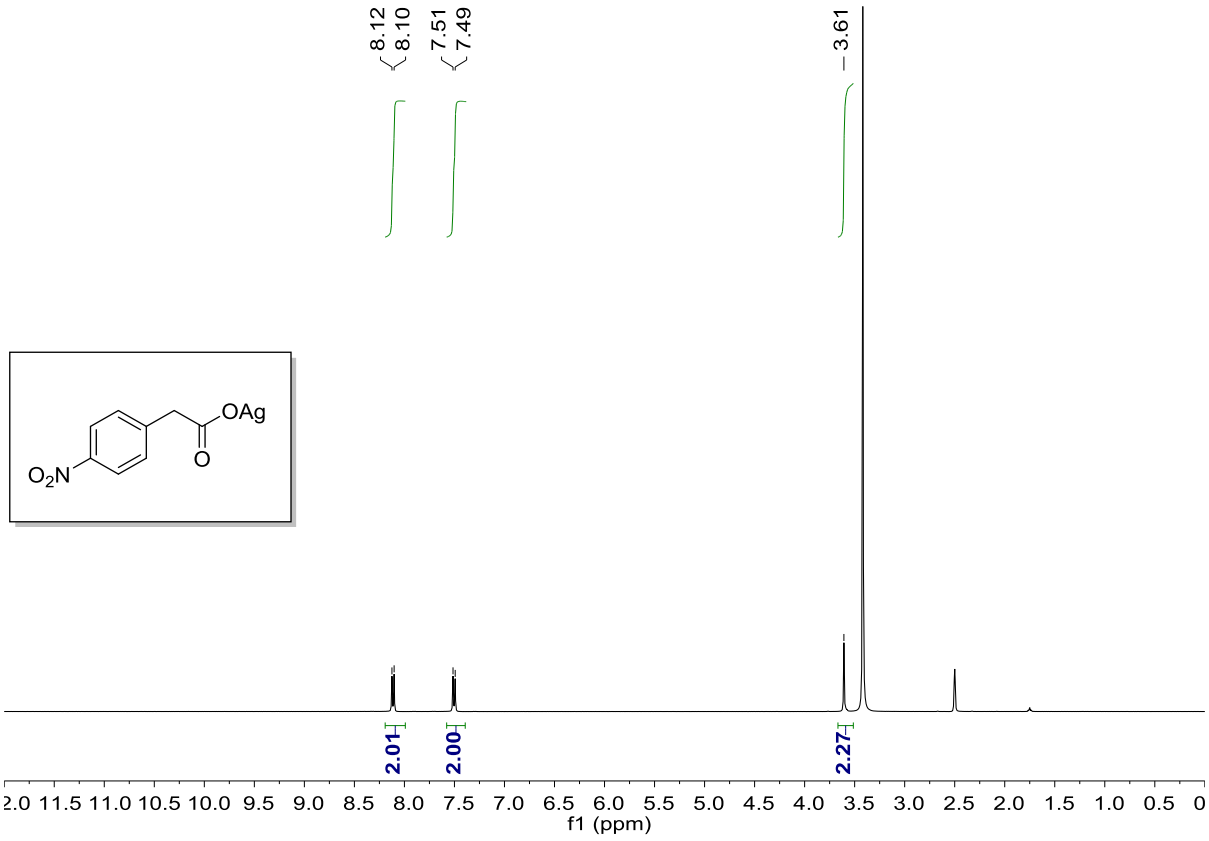
Silver 2-(4-methoxyphenyl)acetate

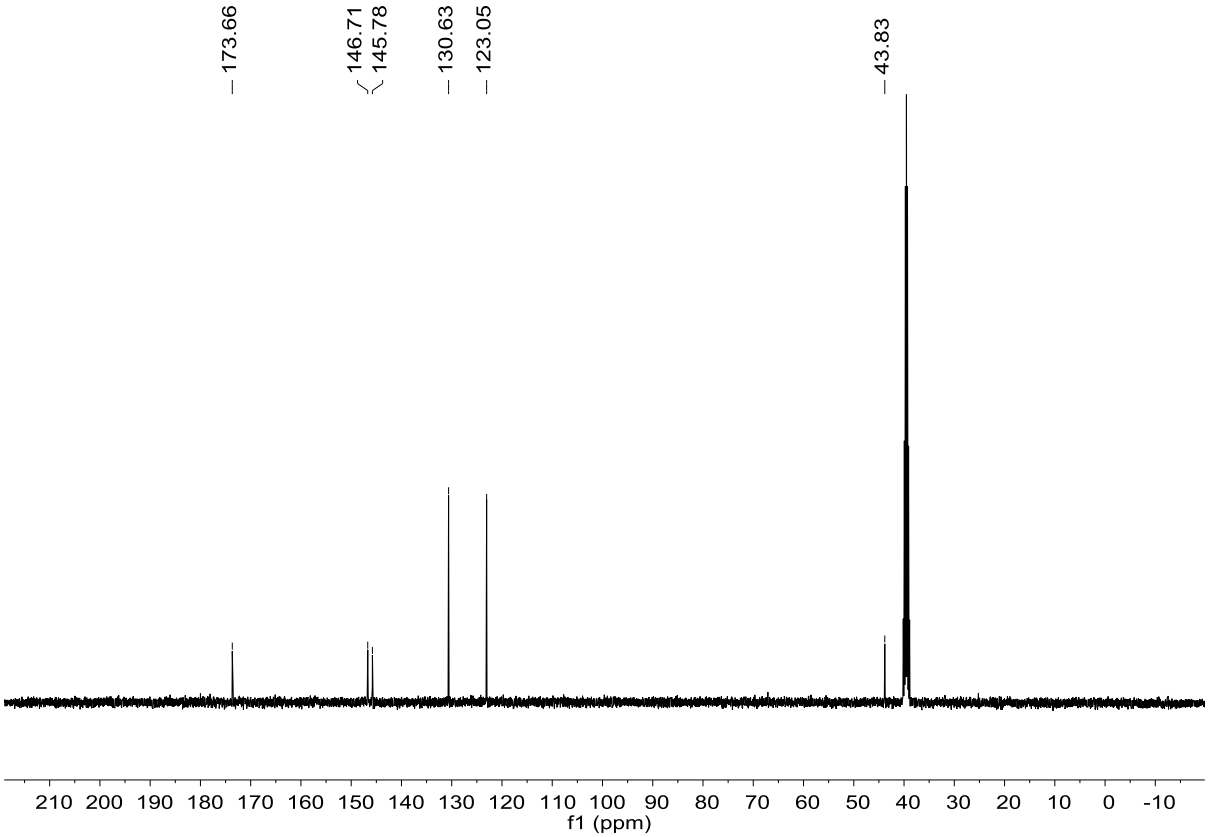


Silver 2-(4-chlorophenyl)acetate

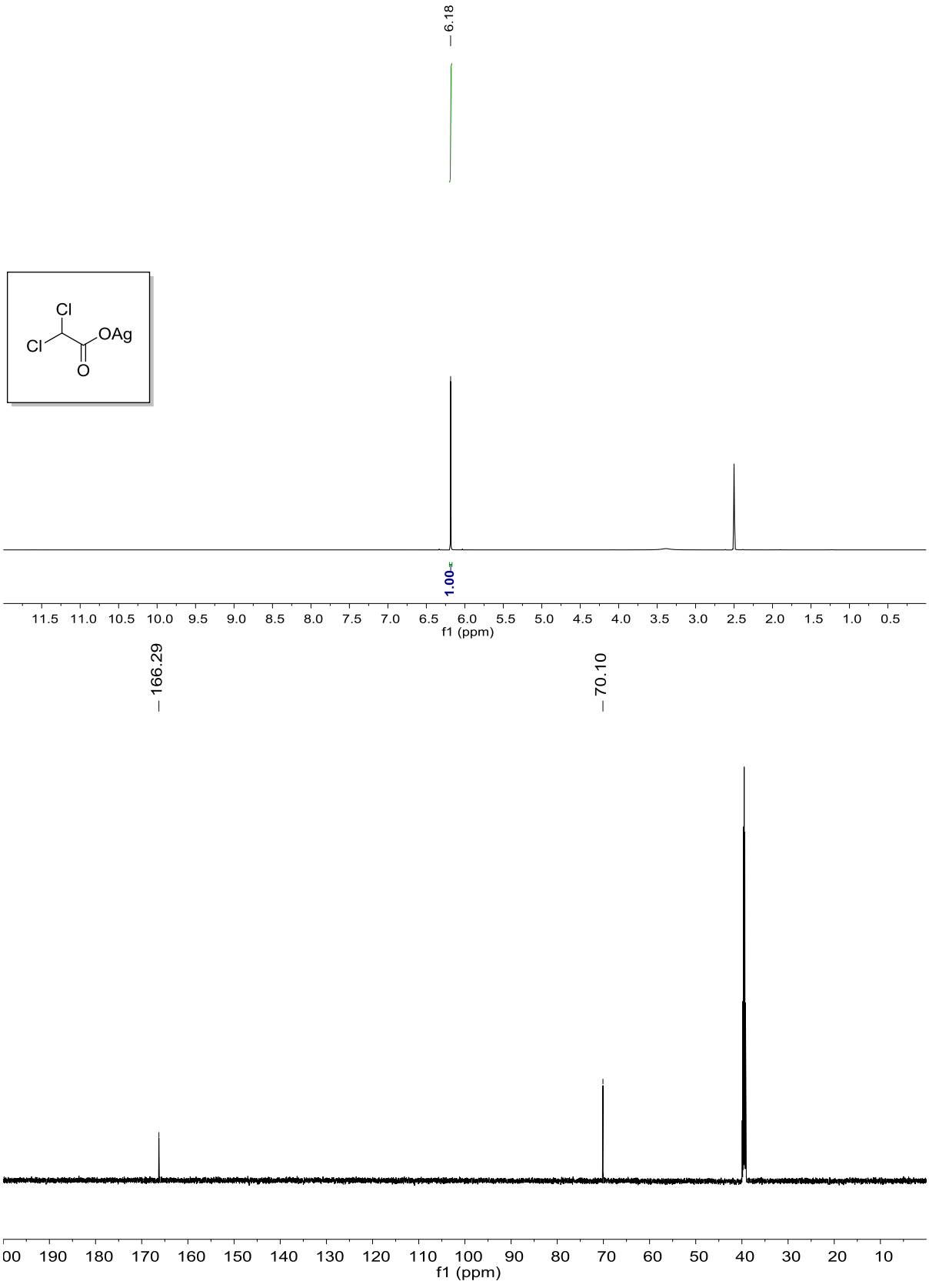


Silver 2-(4-nitrophenyl)acetate

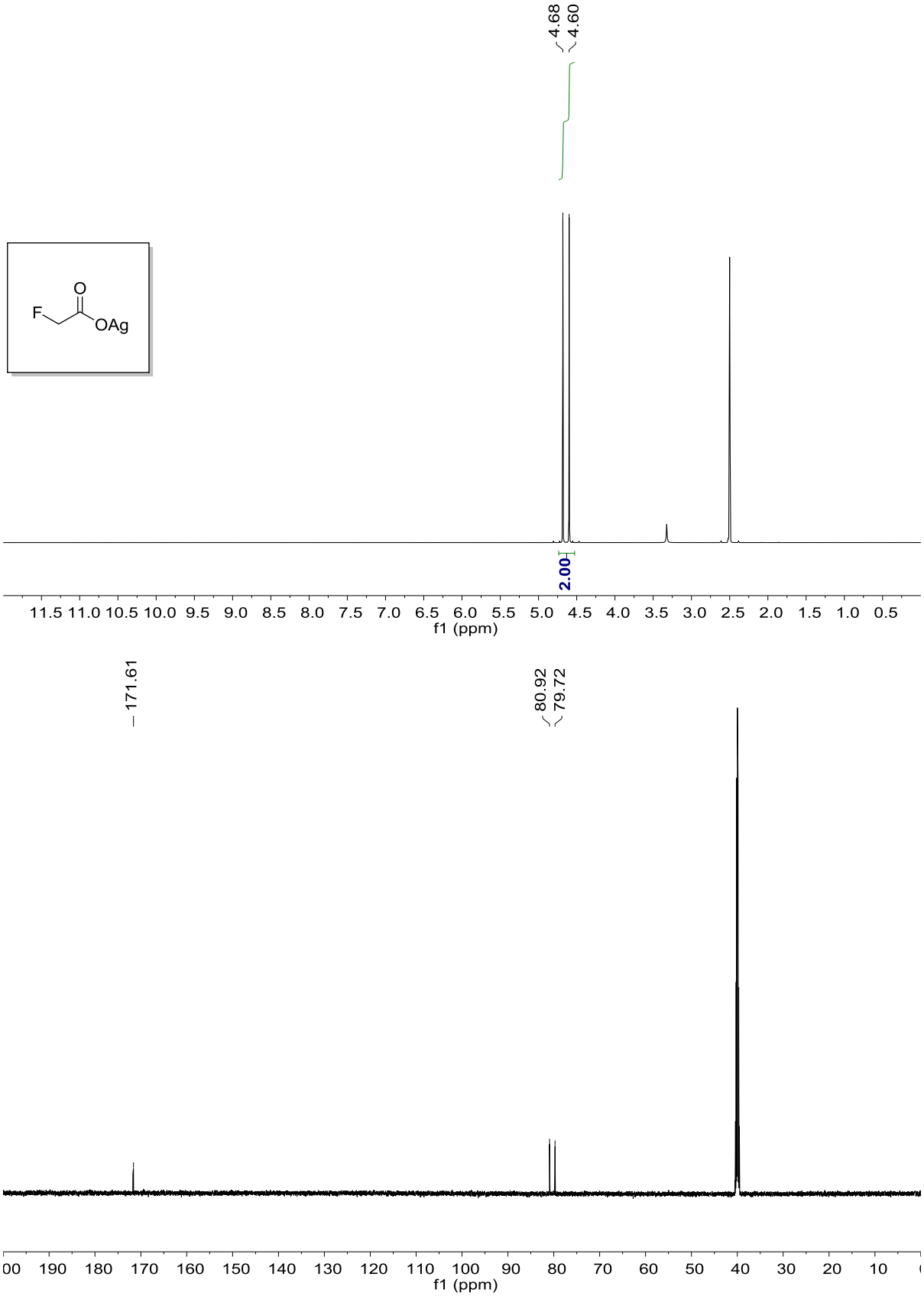


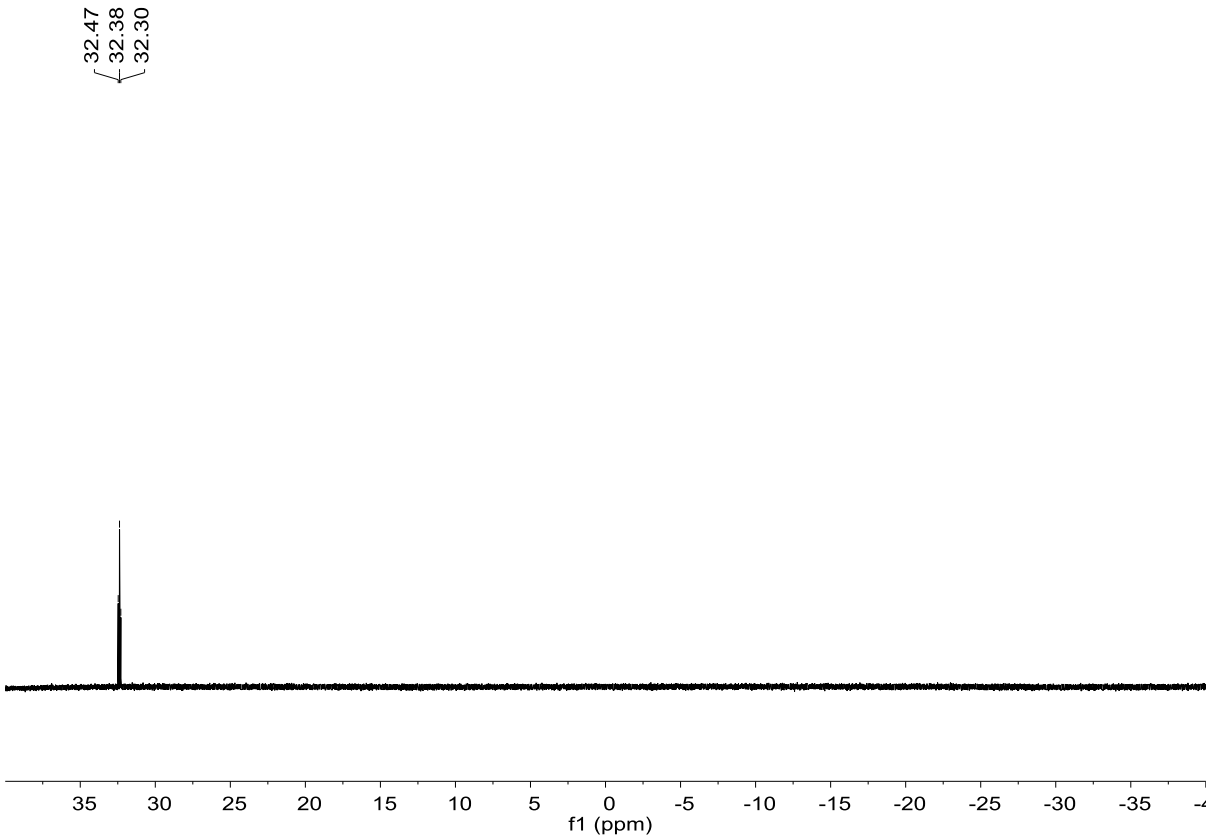


Silver 2,2-dichloroacetate

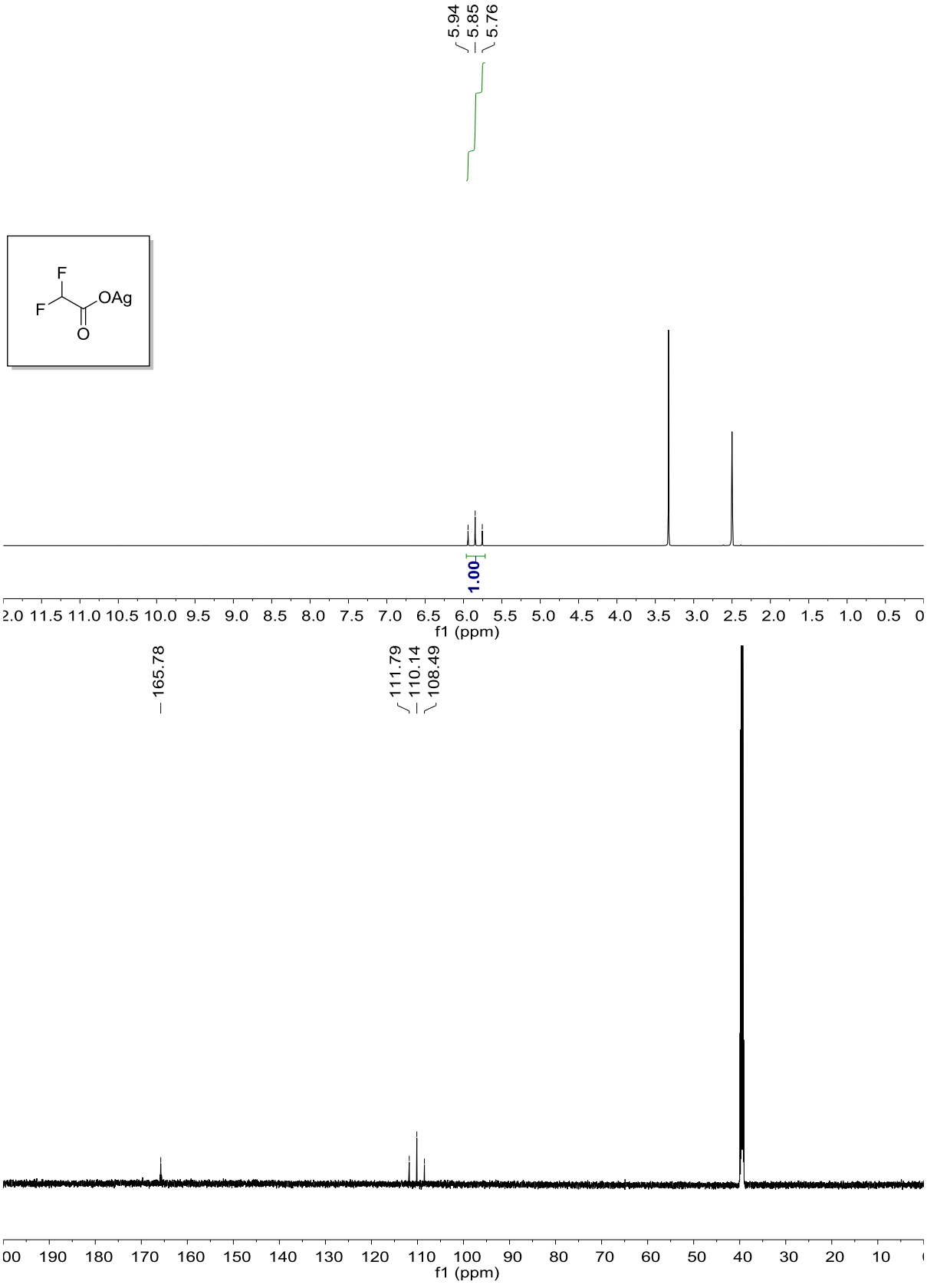


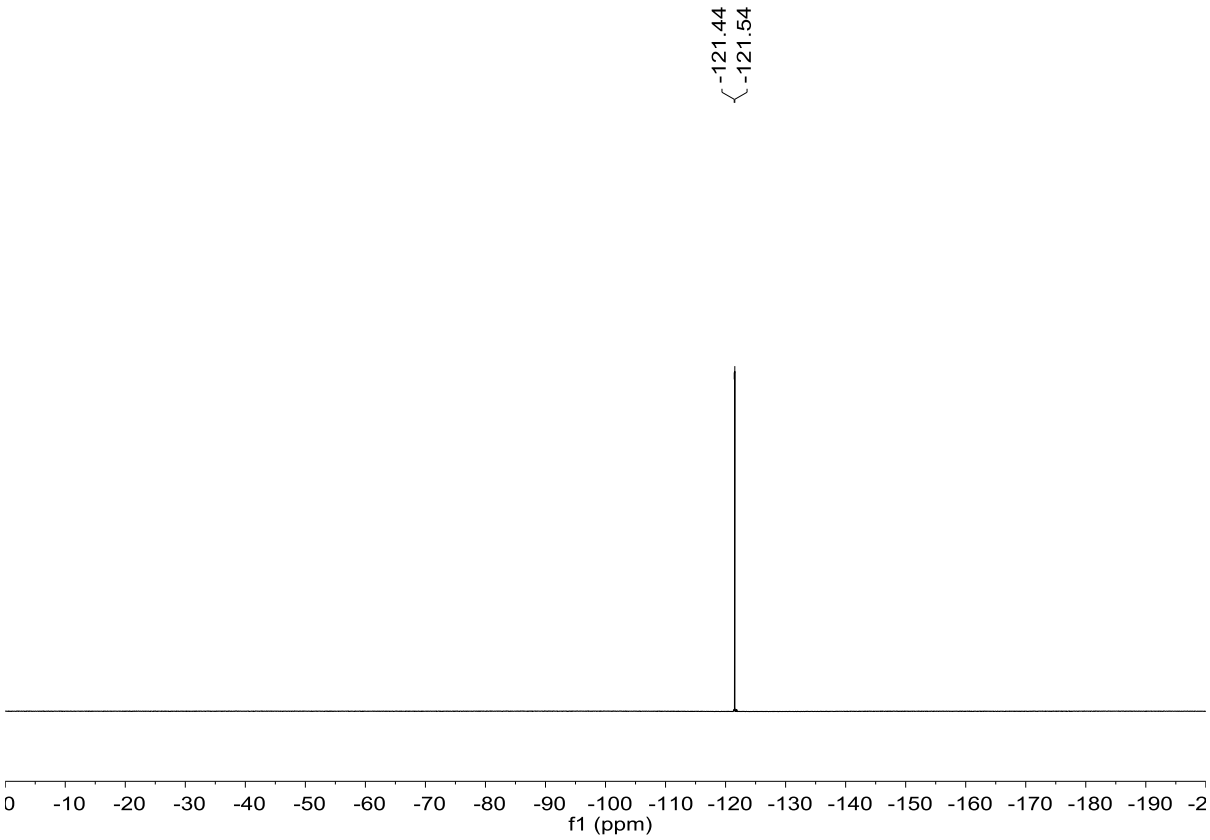
Silver fluoroacetate



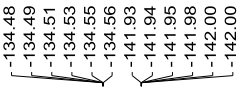

32.47
32.38
32.30
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
f1 (ppm)

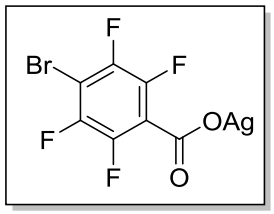
Silver 2,2-fluoroacetate

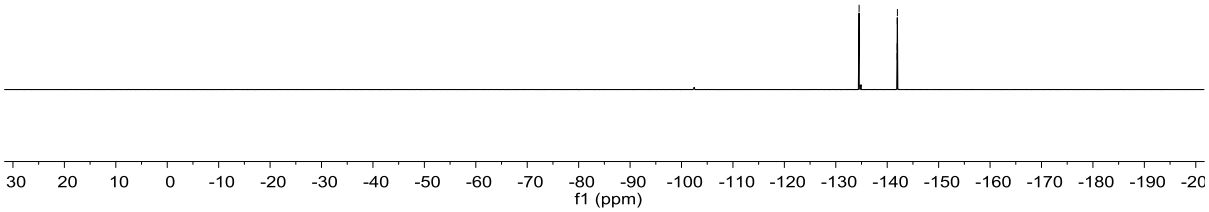


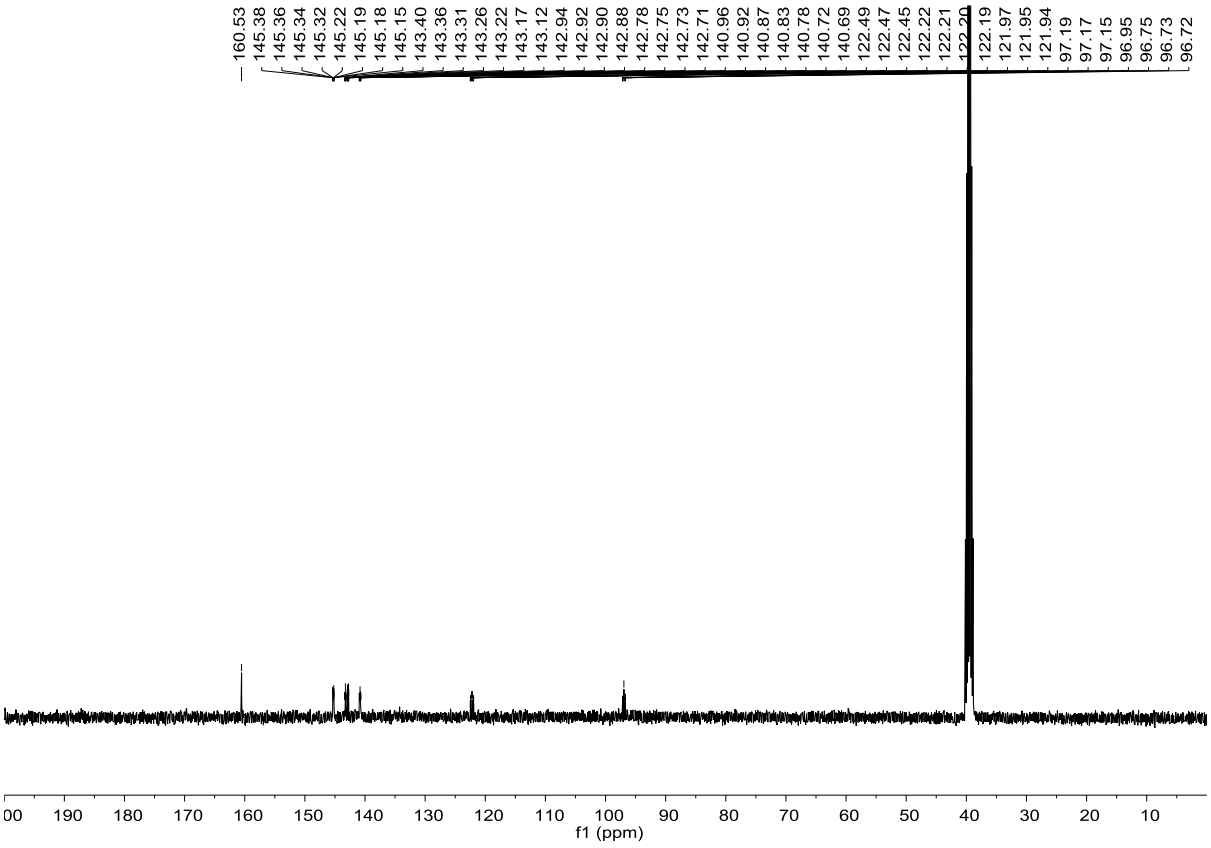

-121.44
-121.54
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

Silver 4-bromo-2,3,5,6-tetrafluorobenzoate

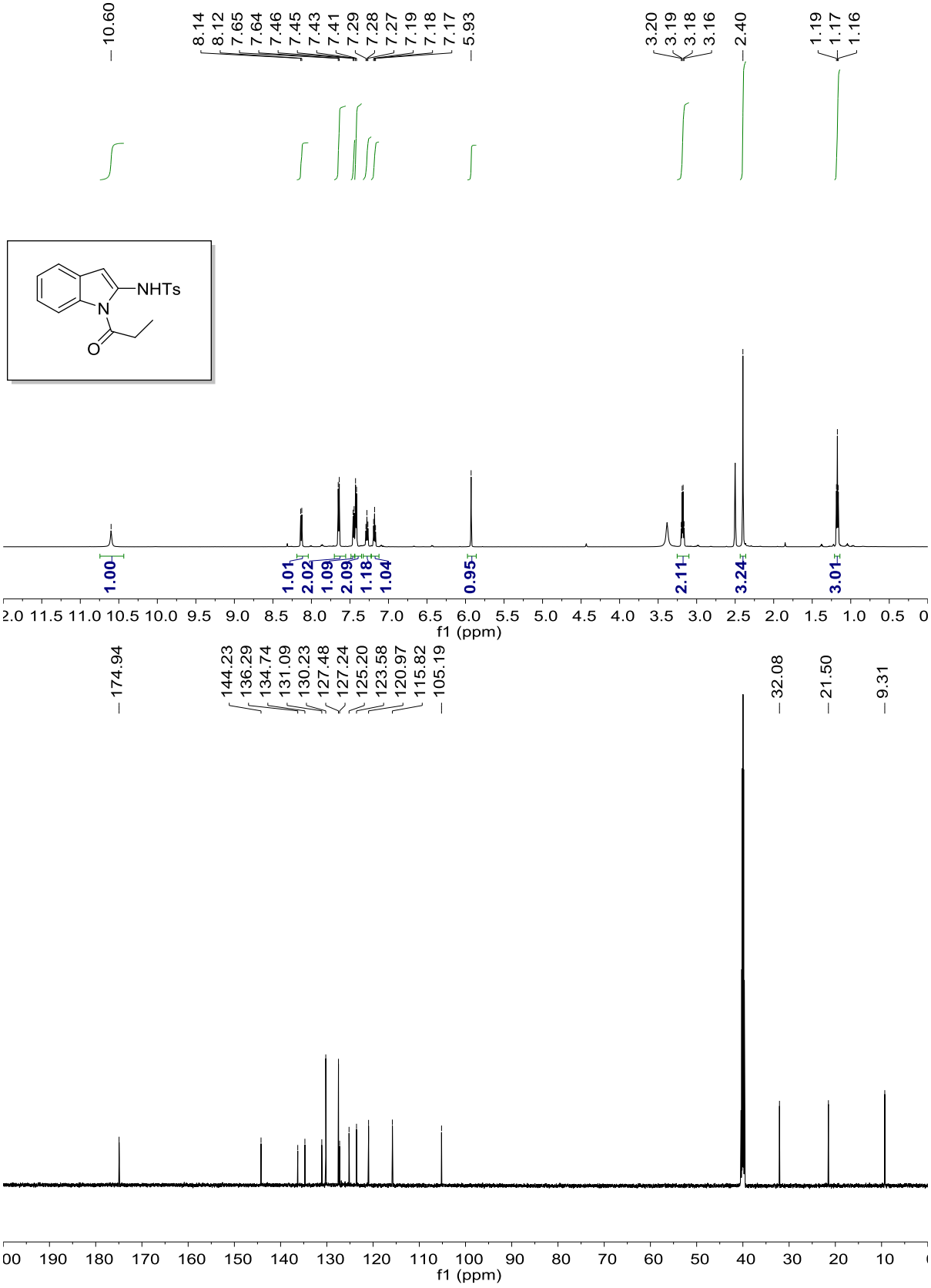




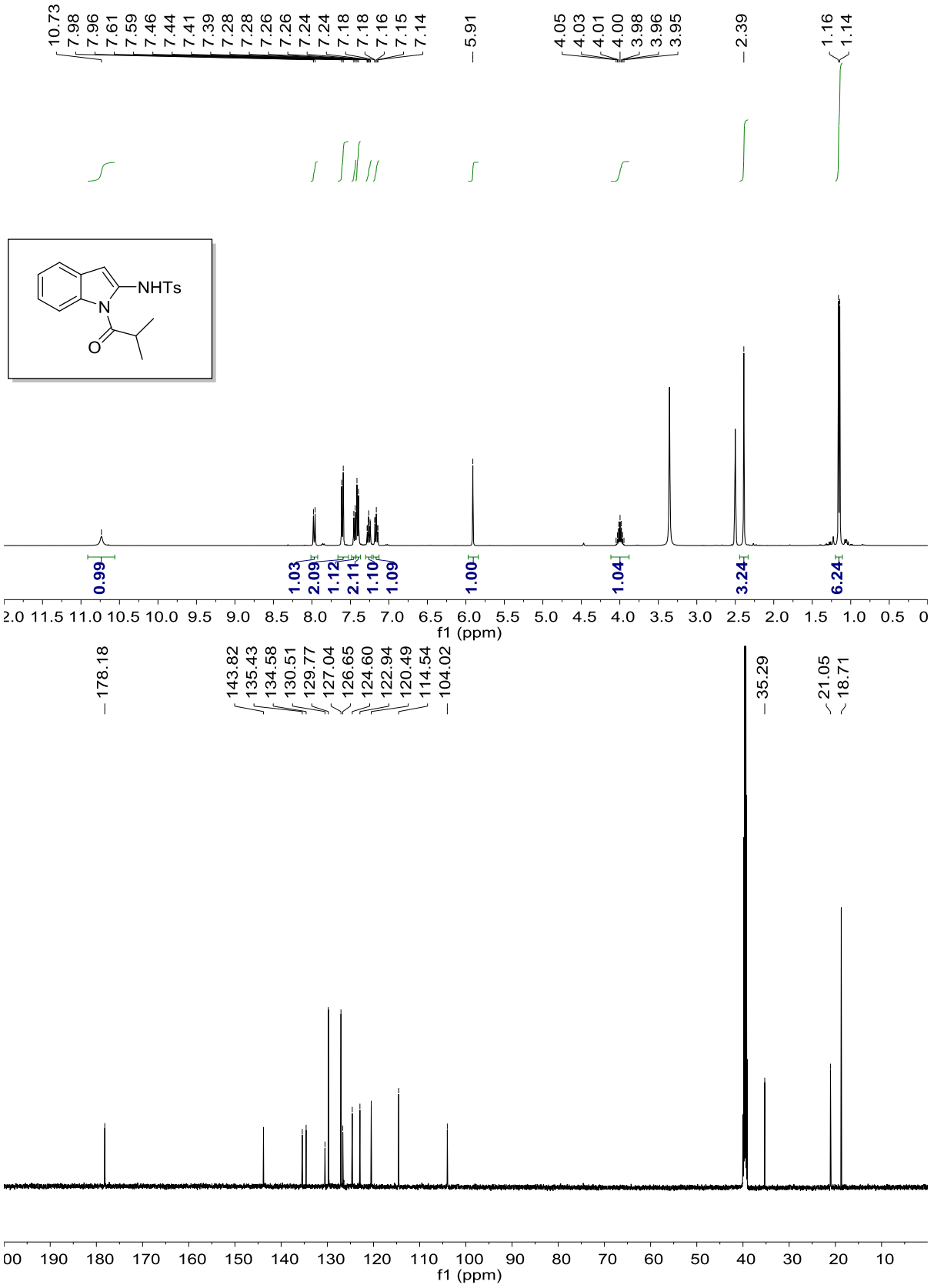




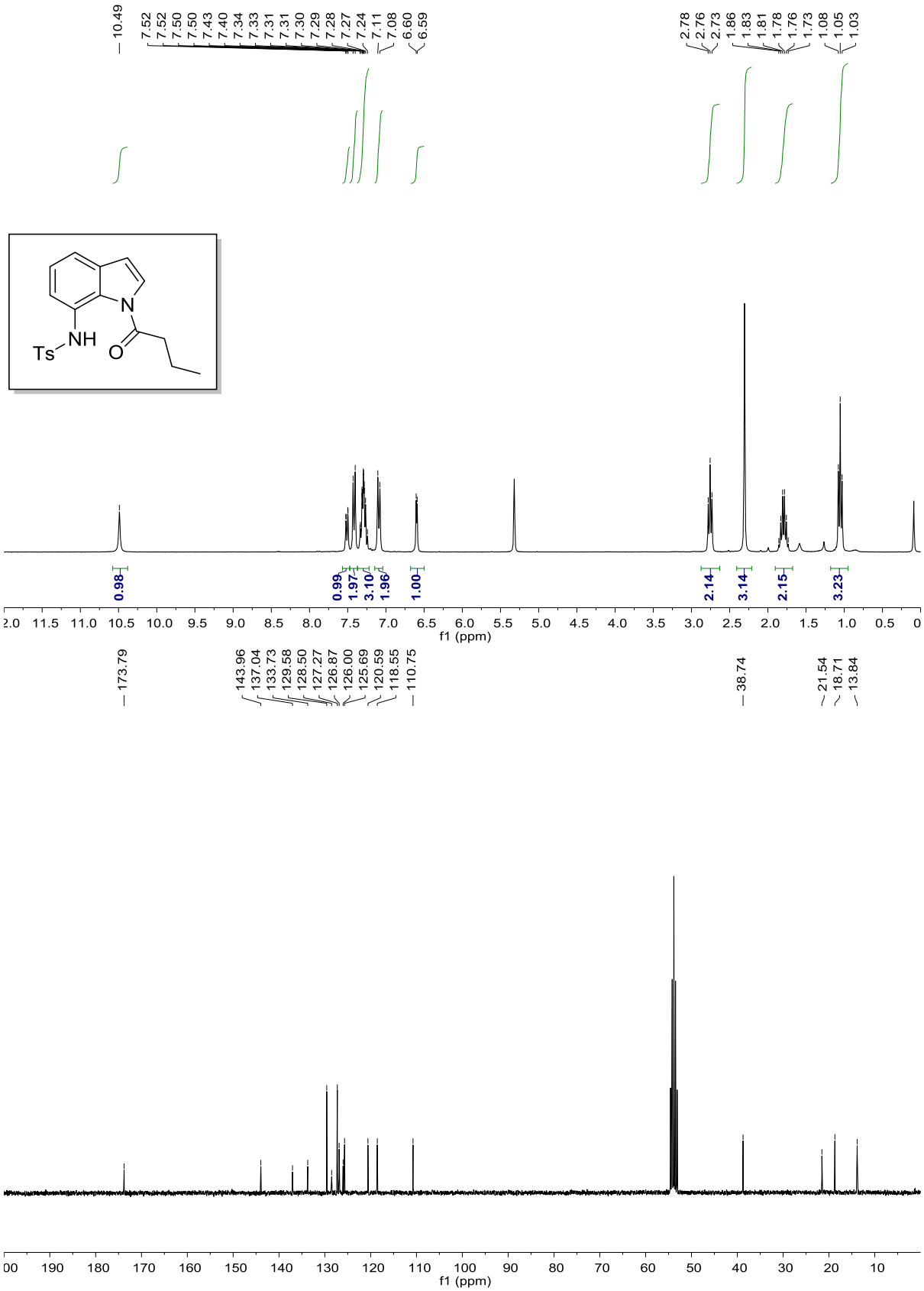
***N*-(1-Propionyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2 and Figure 3)



***N*-(1-Isobutyryl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2 and Figure 3)



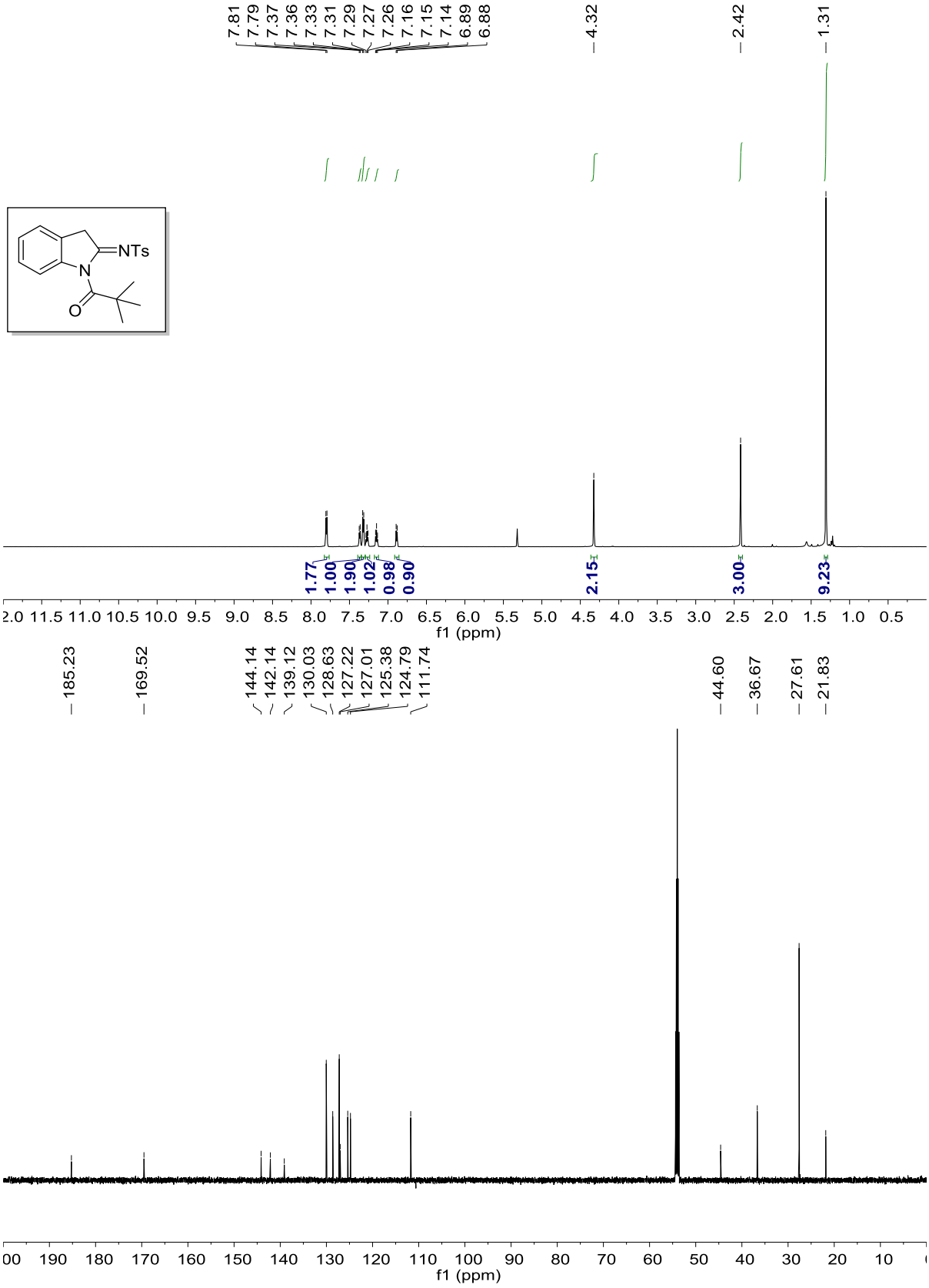
***N*-(1-Butyryl-1*H*-indol-7-yl)-4-methylbenzenesulfonamide** (Figure 3)



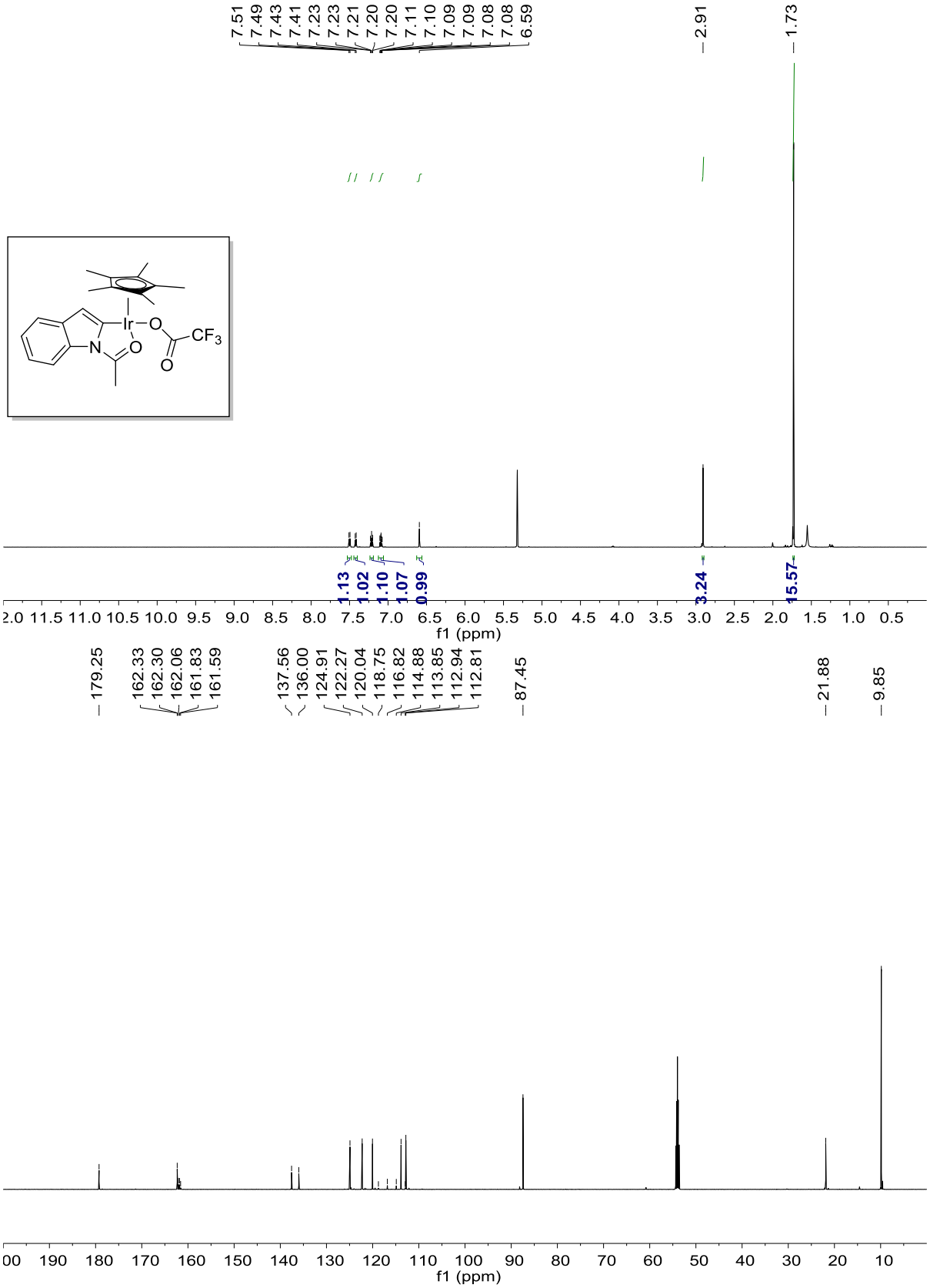
***N*-(1-Butyryl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Figure 3)

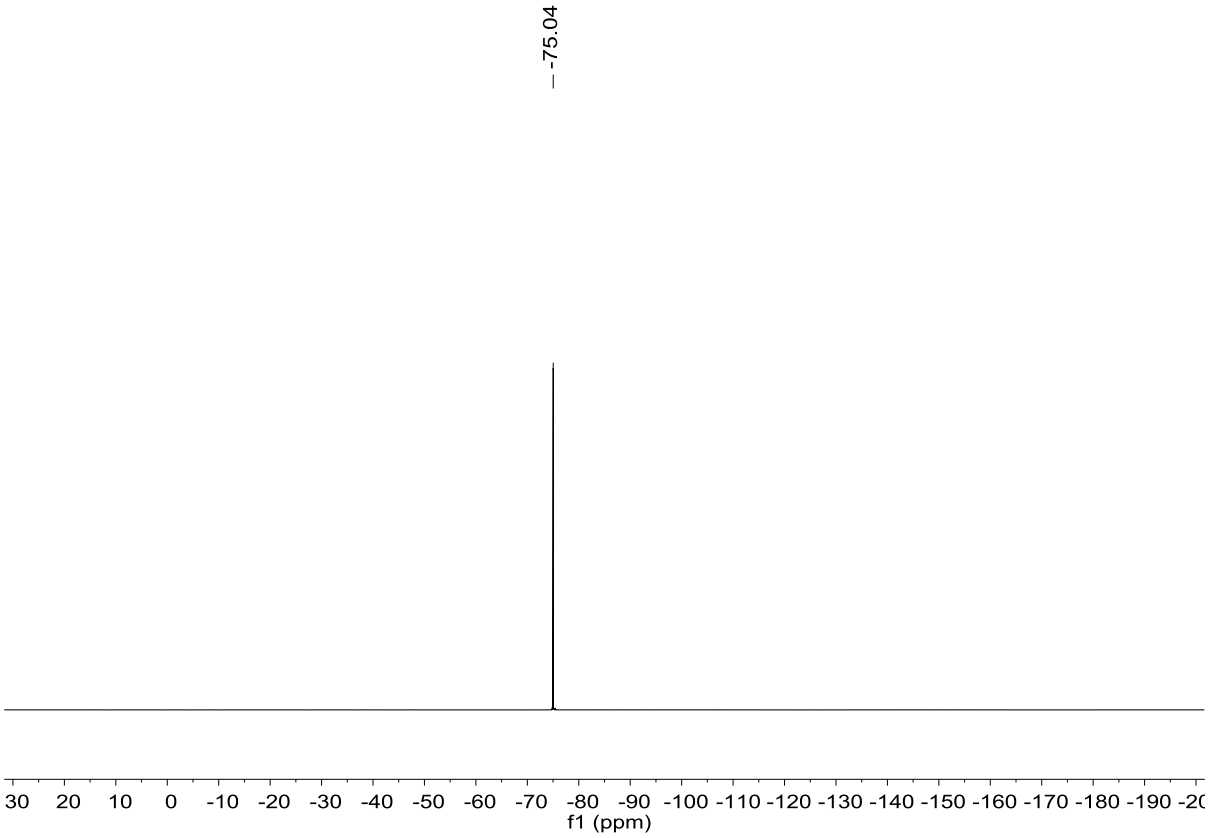
***N*-(1-Cyclohexanecarbonyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Figure 3)

***N*-(1-Pivaloylindolin-2-ylidene)-4-methylbenzenesulfonamide** (Figure 3)

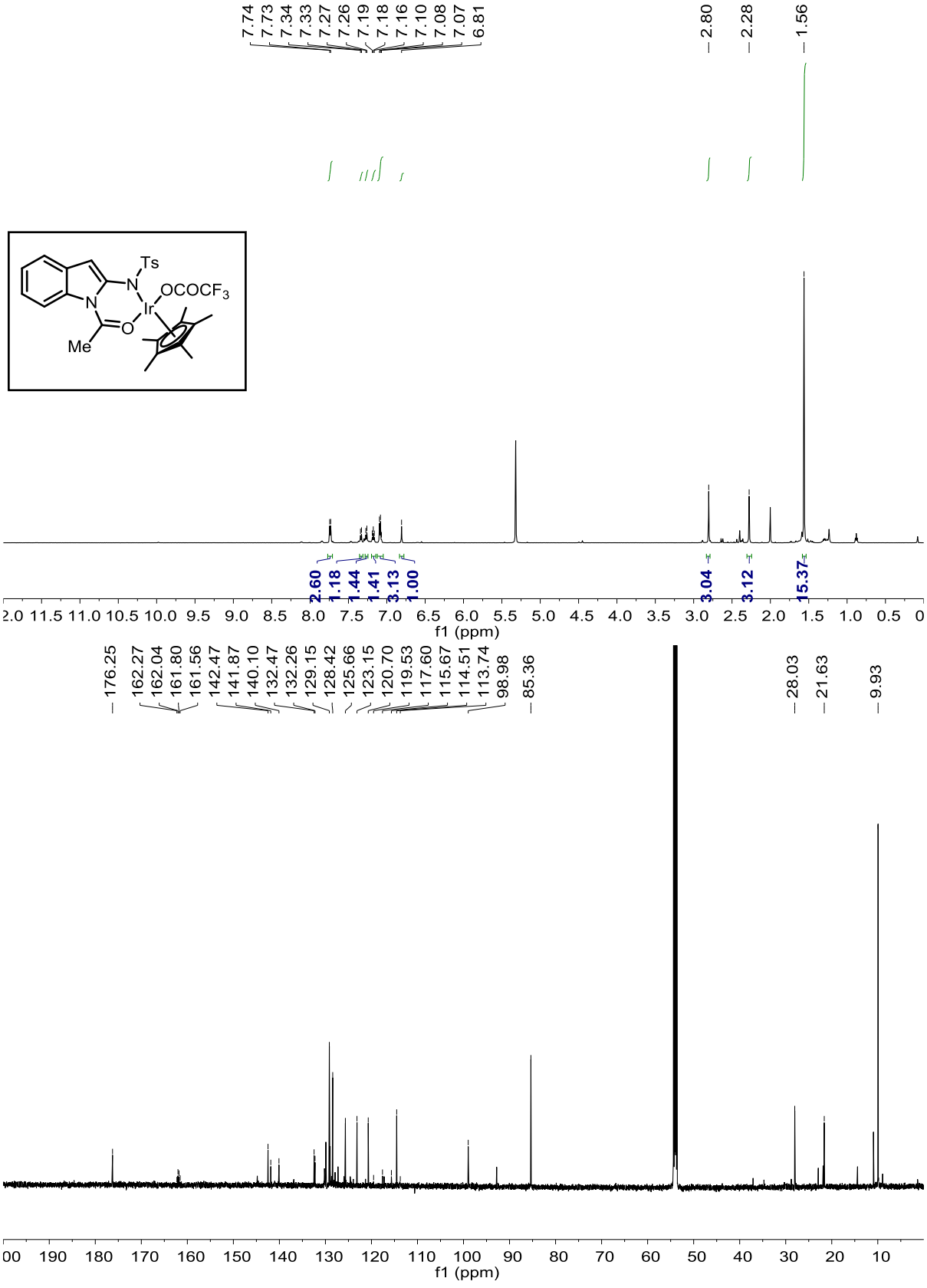


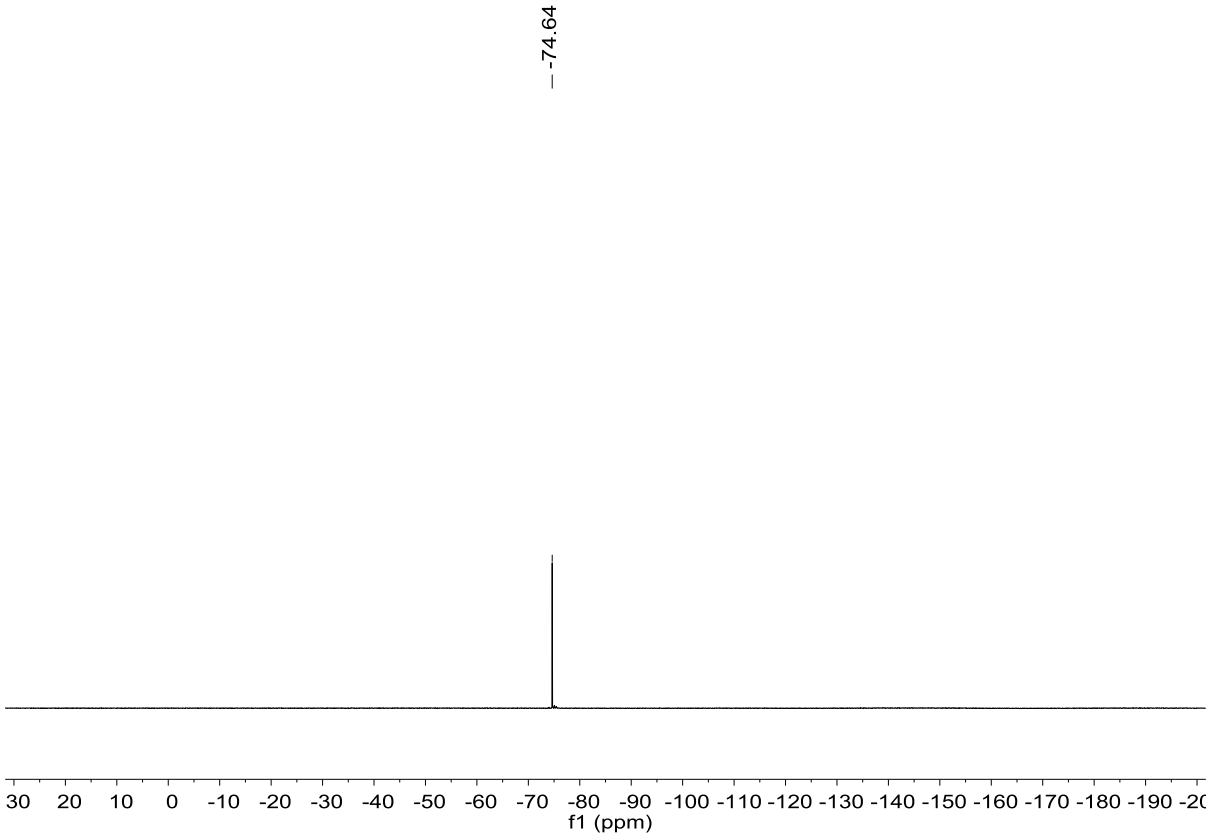
Iridacycle (Scheme 3, **5**)



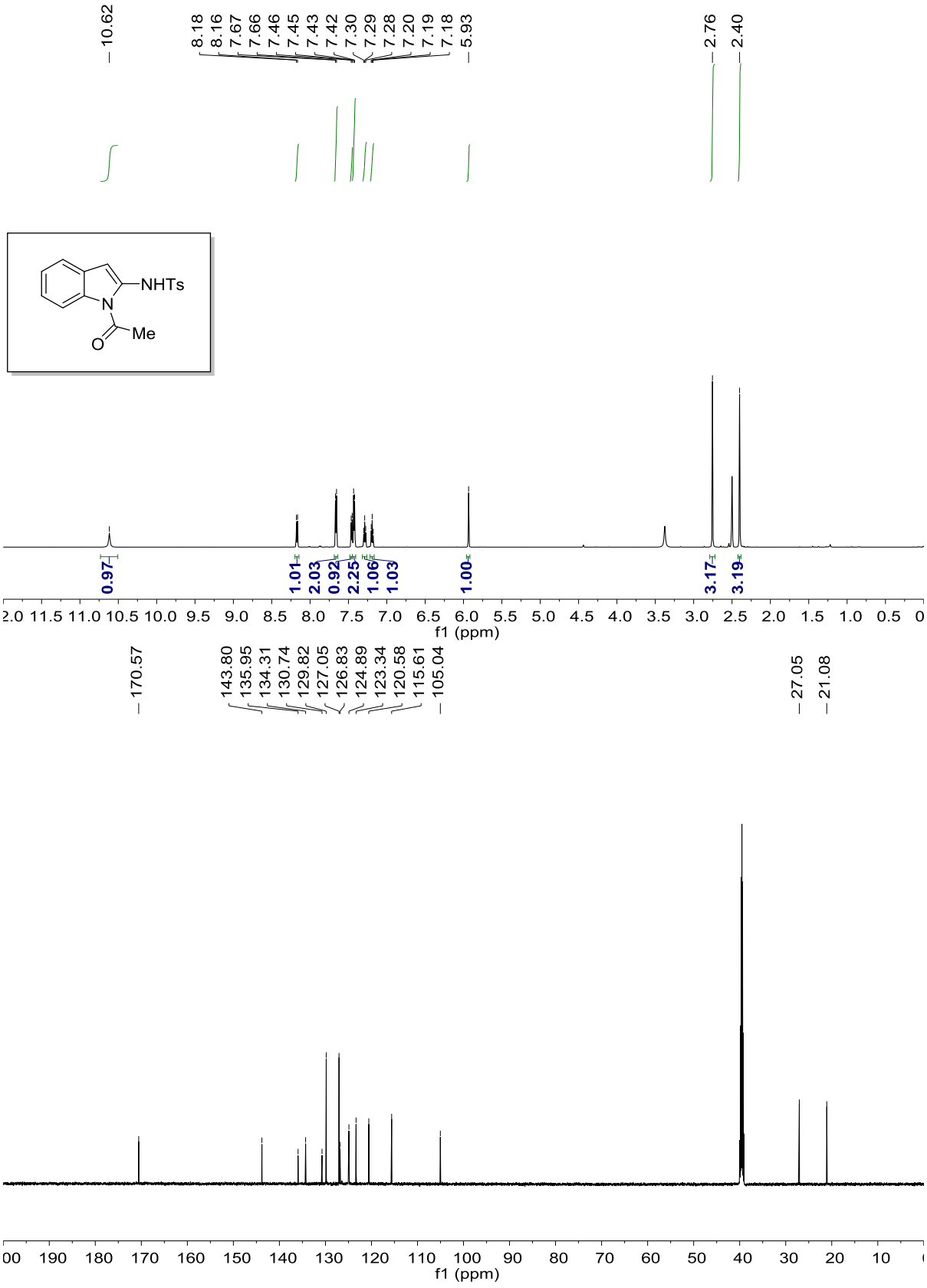

-75.04
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

Ir-Amido Complex (Scheme 3**, 6**)

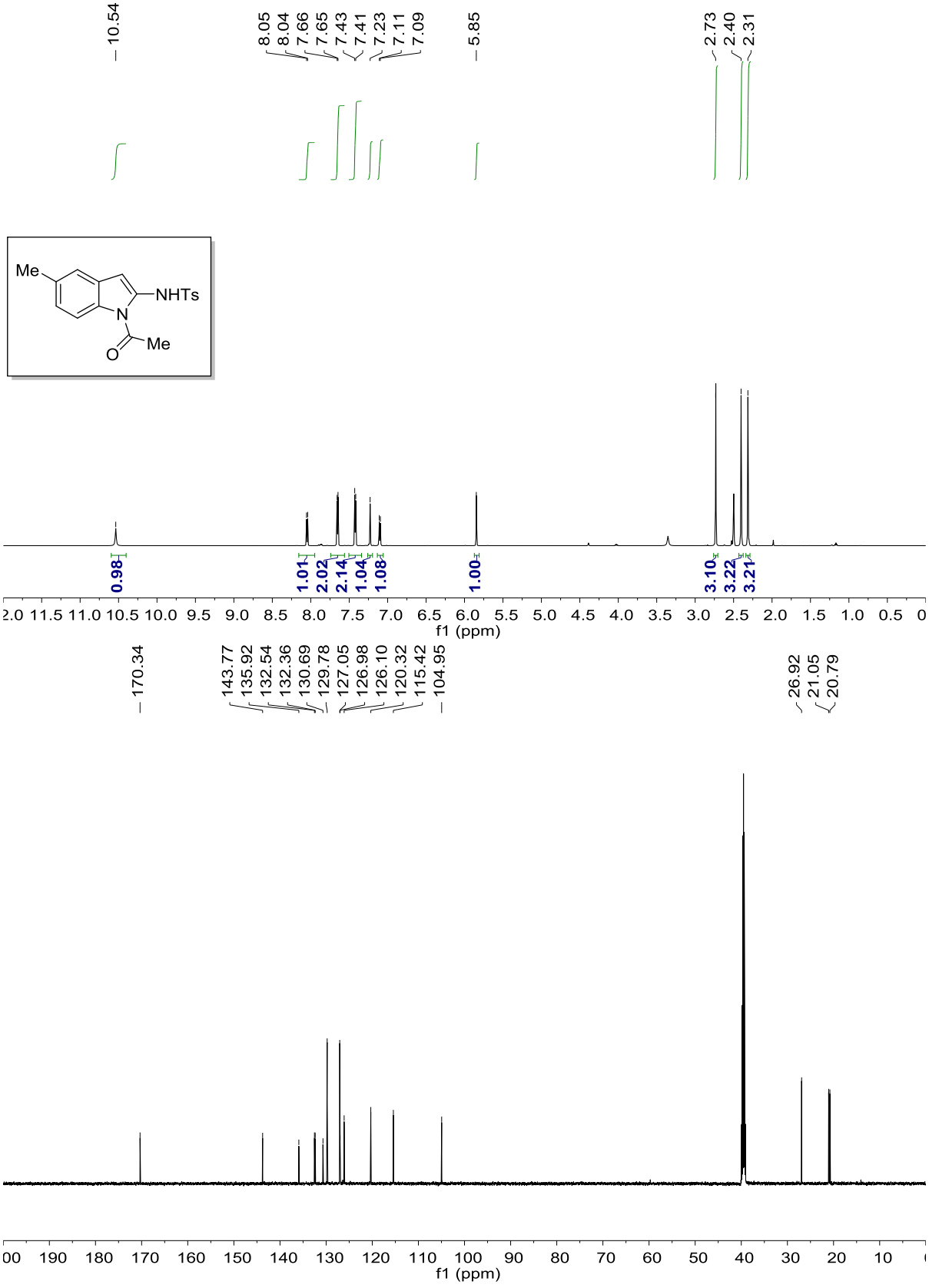



-74.64
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

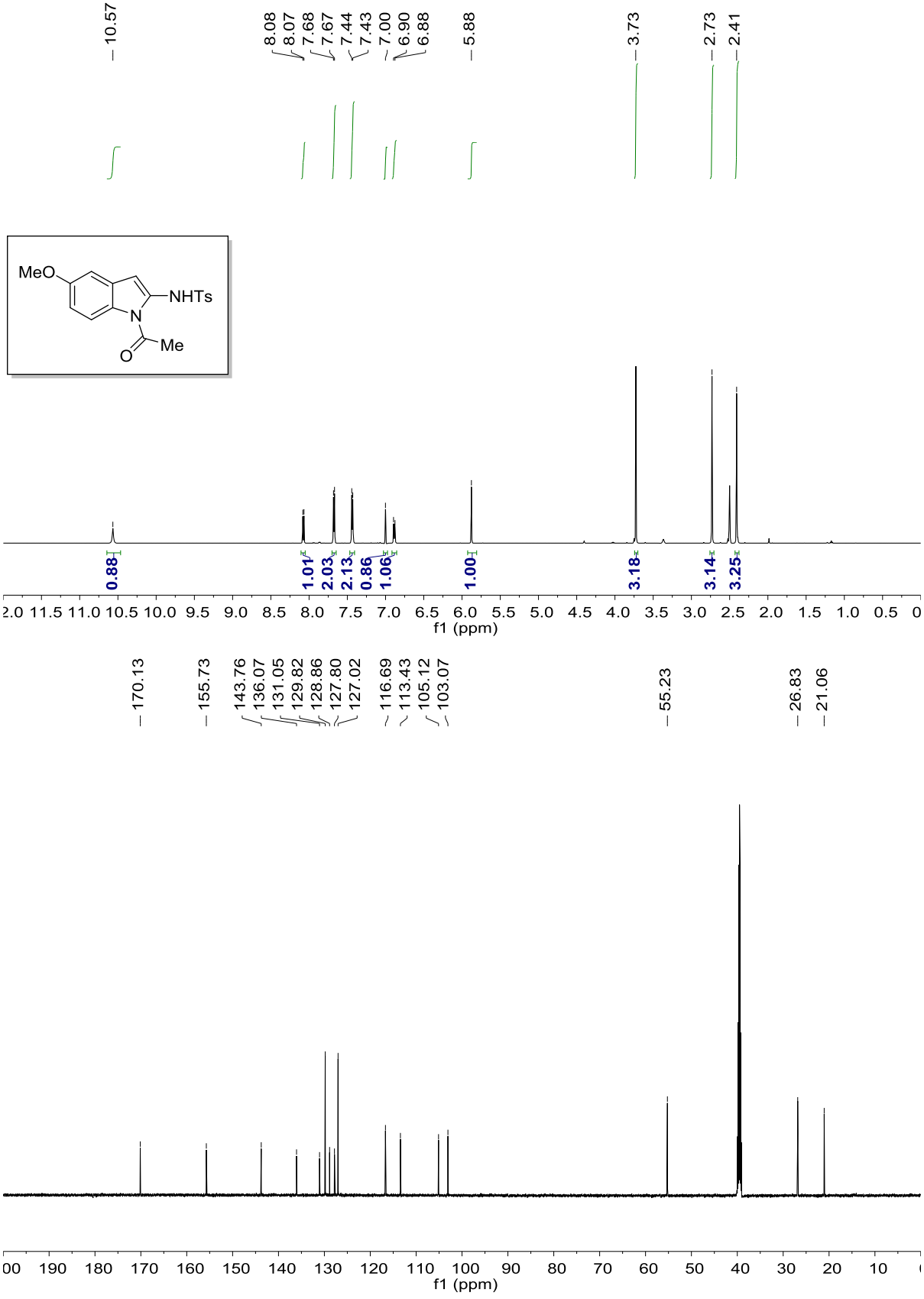
***N*-(1-Acetyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 2–4 and Figure 2–3, **4**)



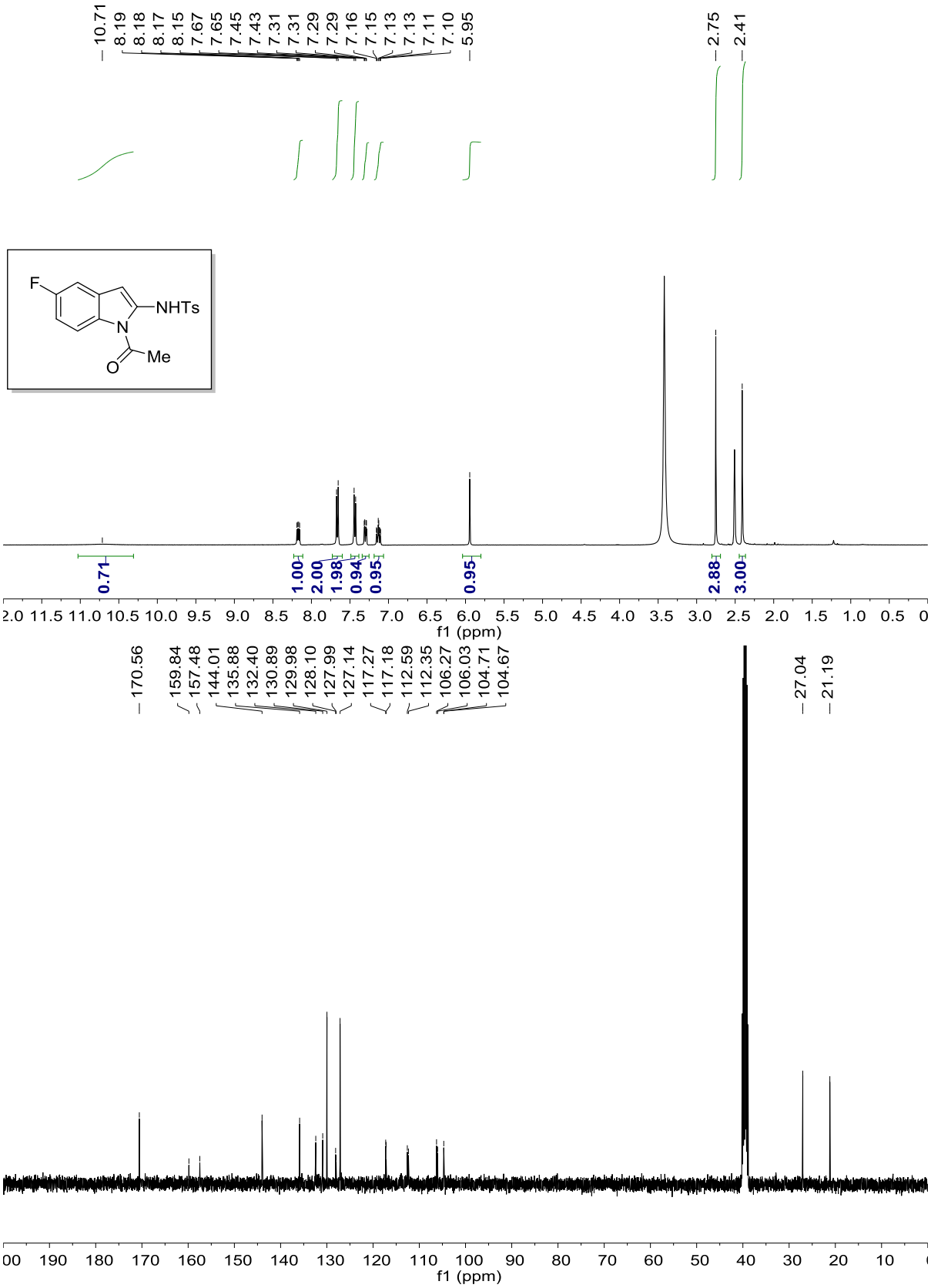
***N*-(1-Acetyl-5-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **7**)

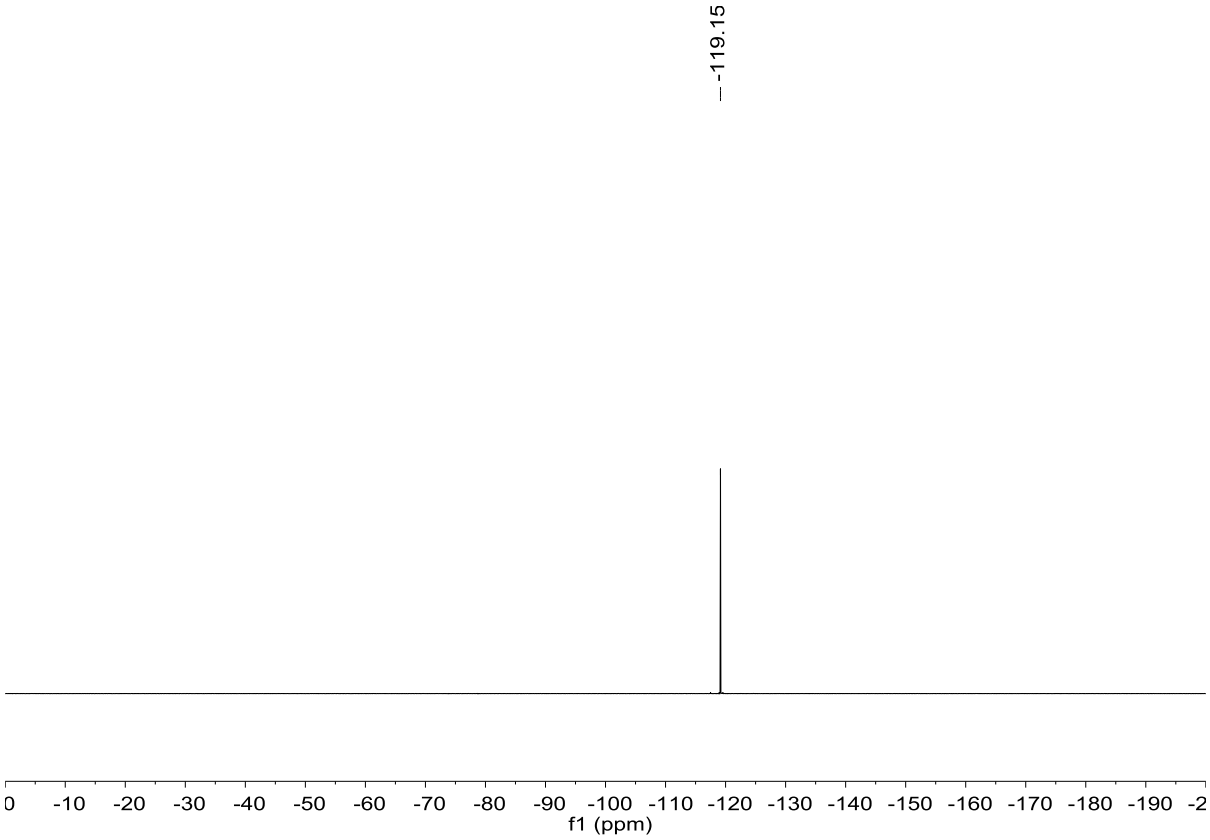


***N*-(1-Acetyl-5-methoxy-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **8**)

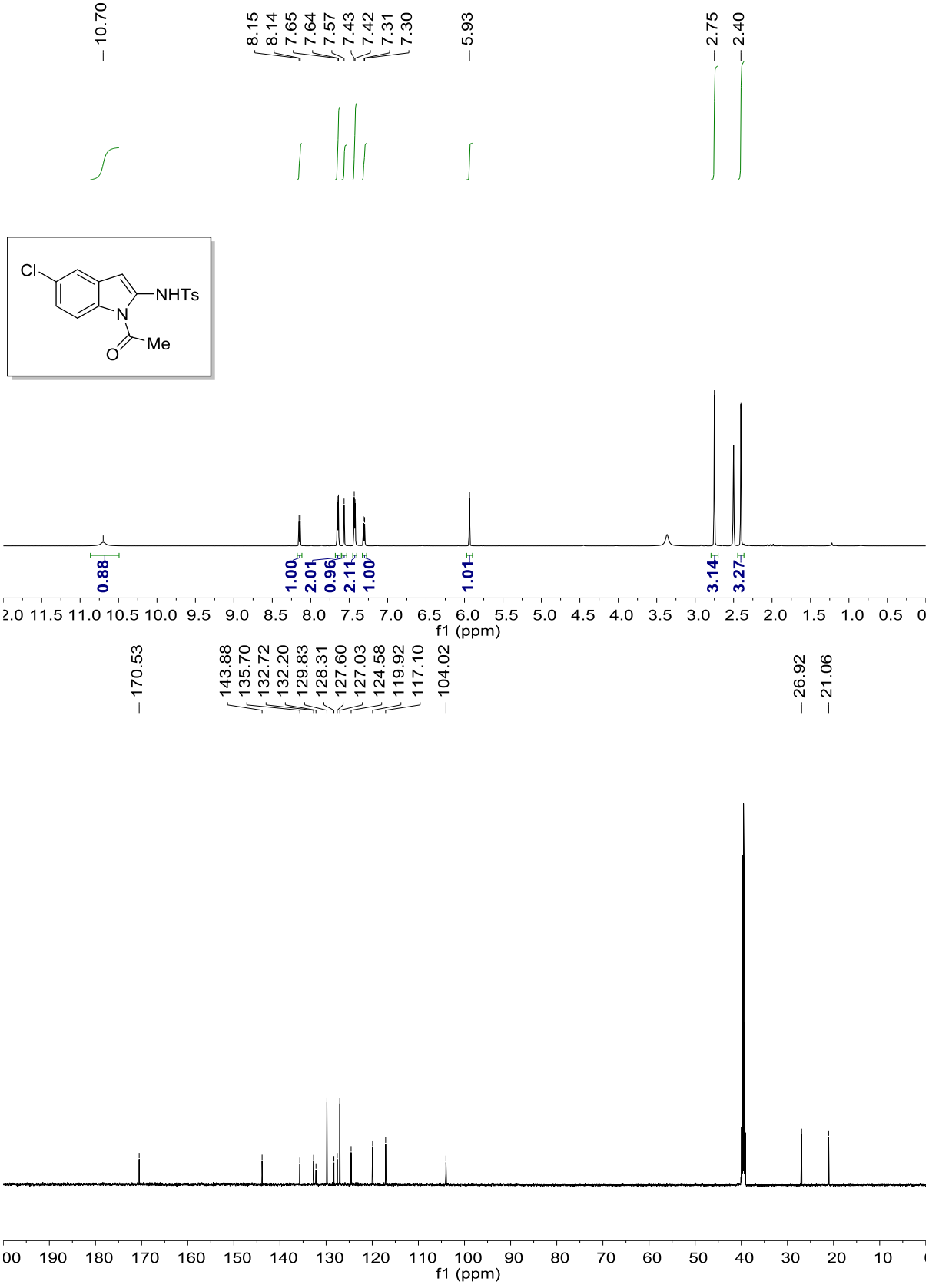


***N*-(1-Acetyl-5-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **9**)

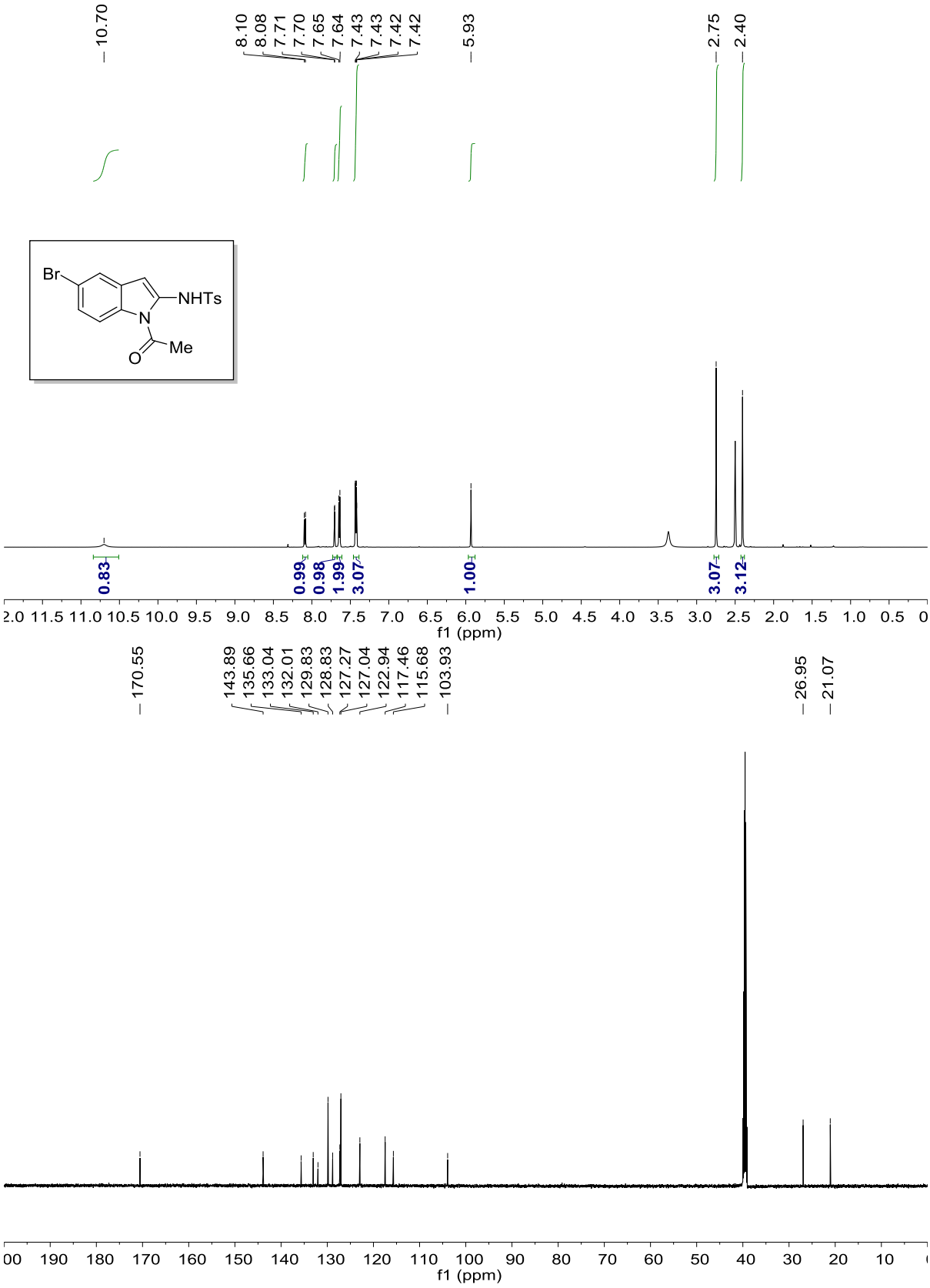



-119.15
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

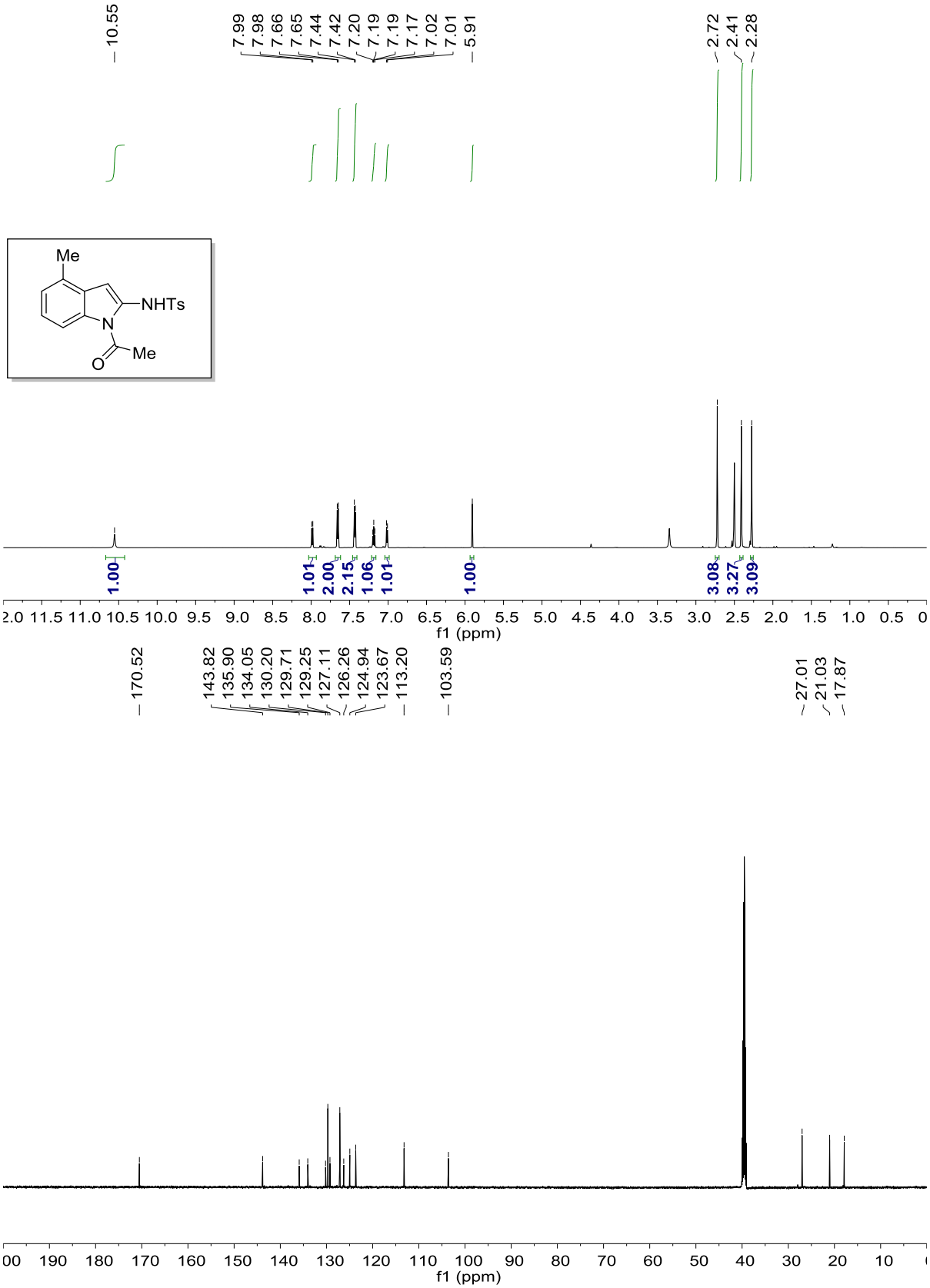
***N*-(1-Acetyl-5-chloro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **10**)



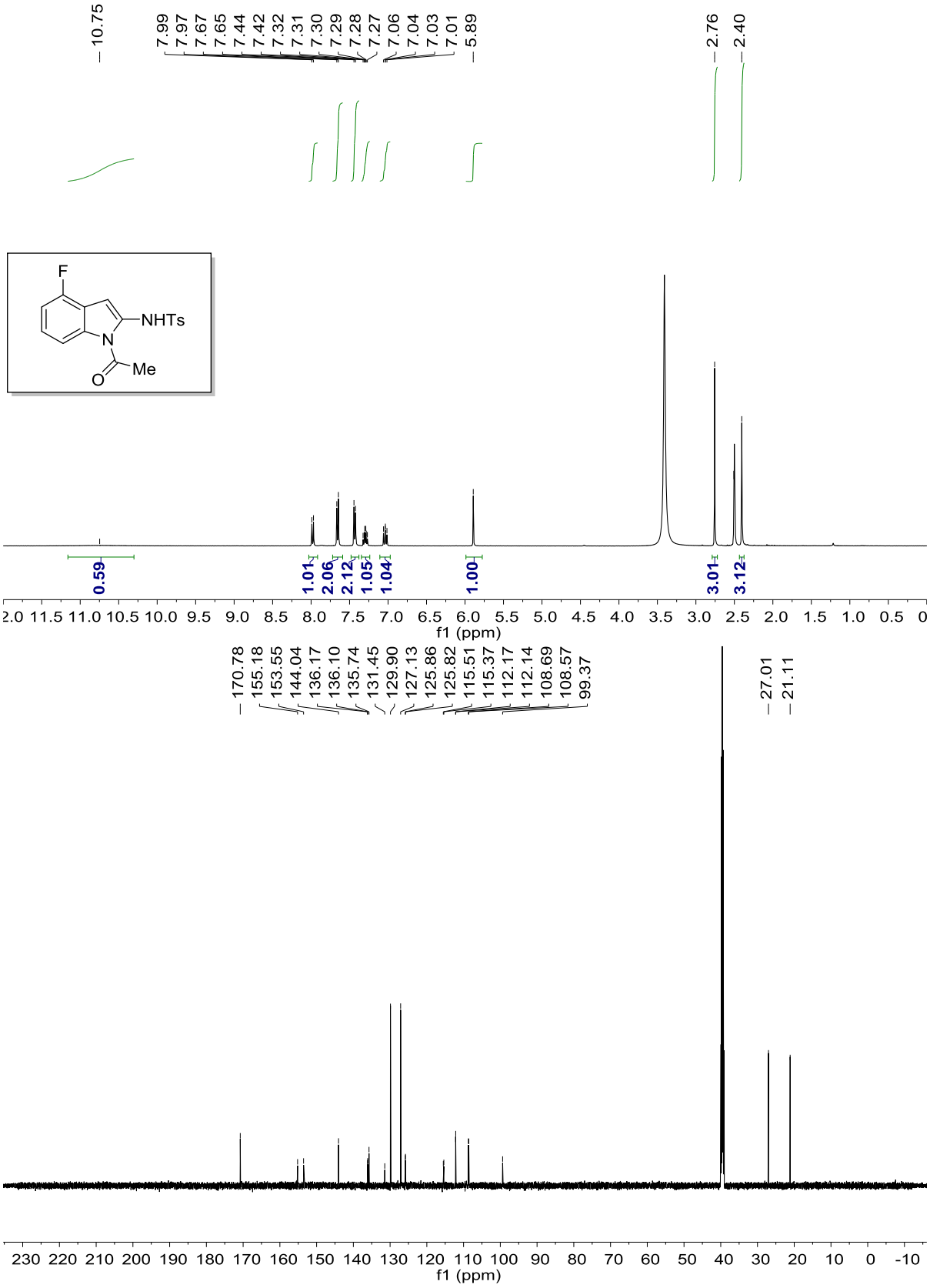
***N*-(1-Acetyl-5-bromo-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **11**)

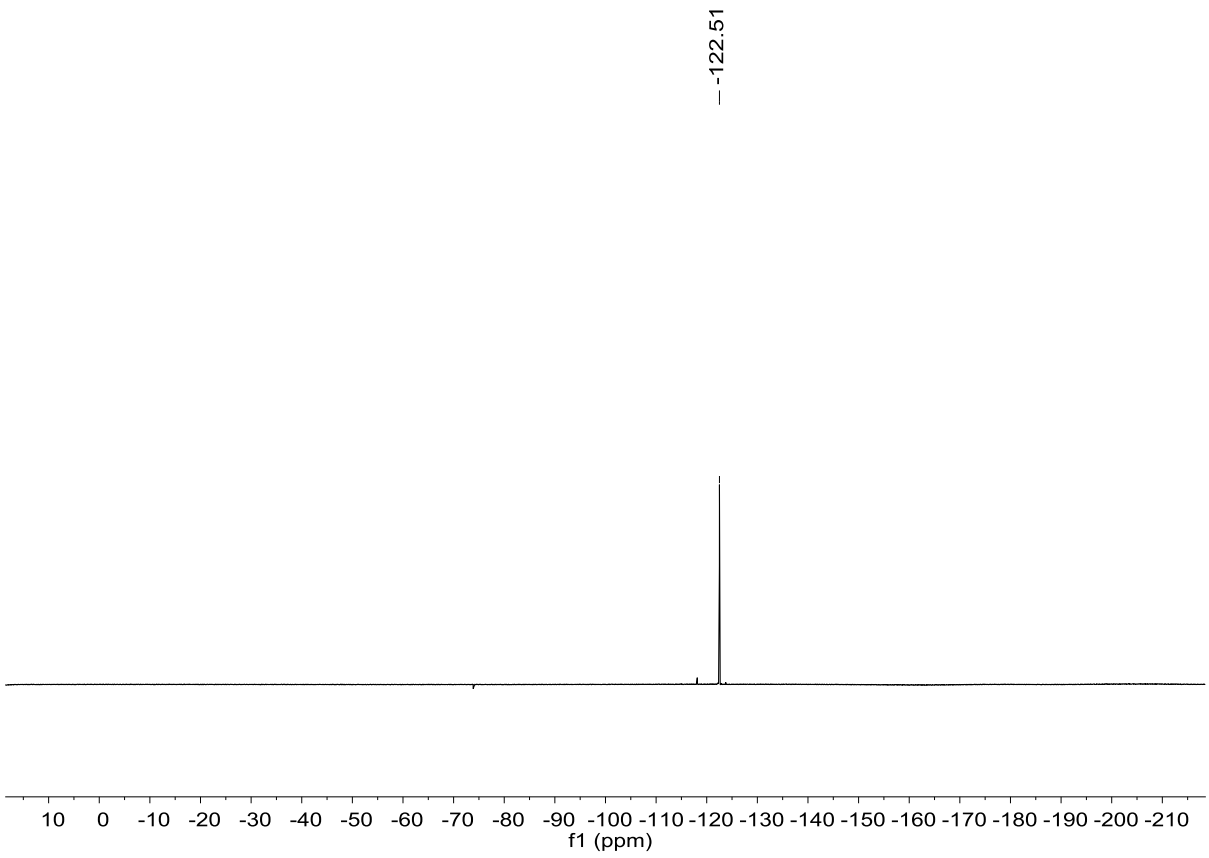


***N*-(1-Acetyl-4-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **12**)

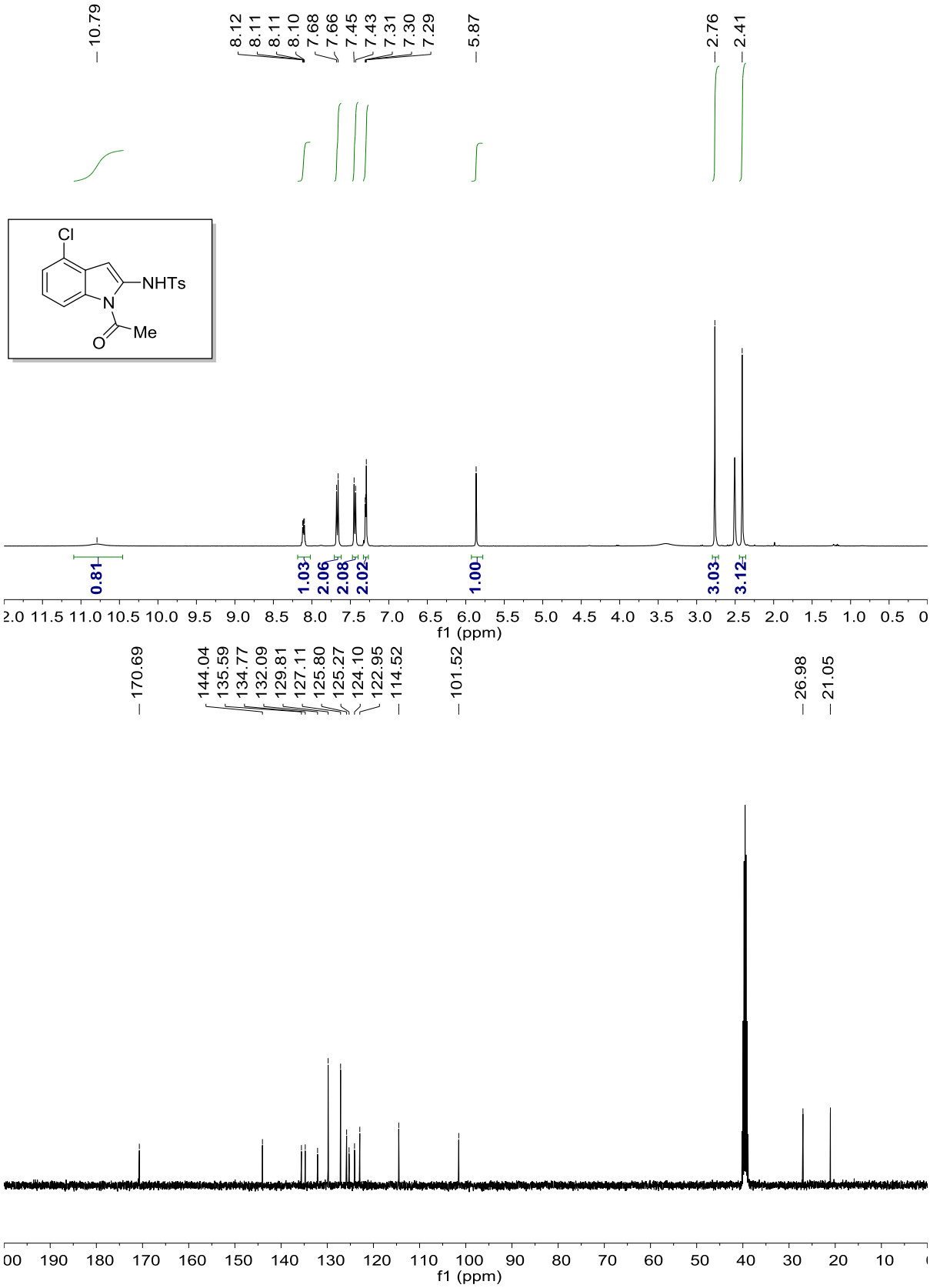


***N*-(1-Acetyl-4-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **13**)

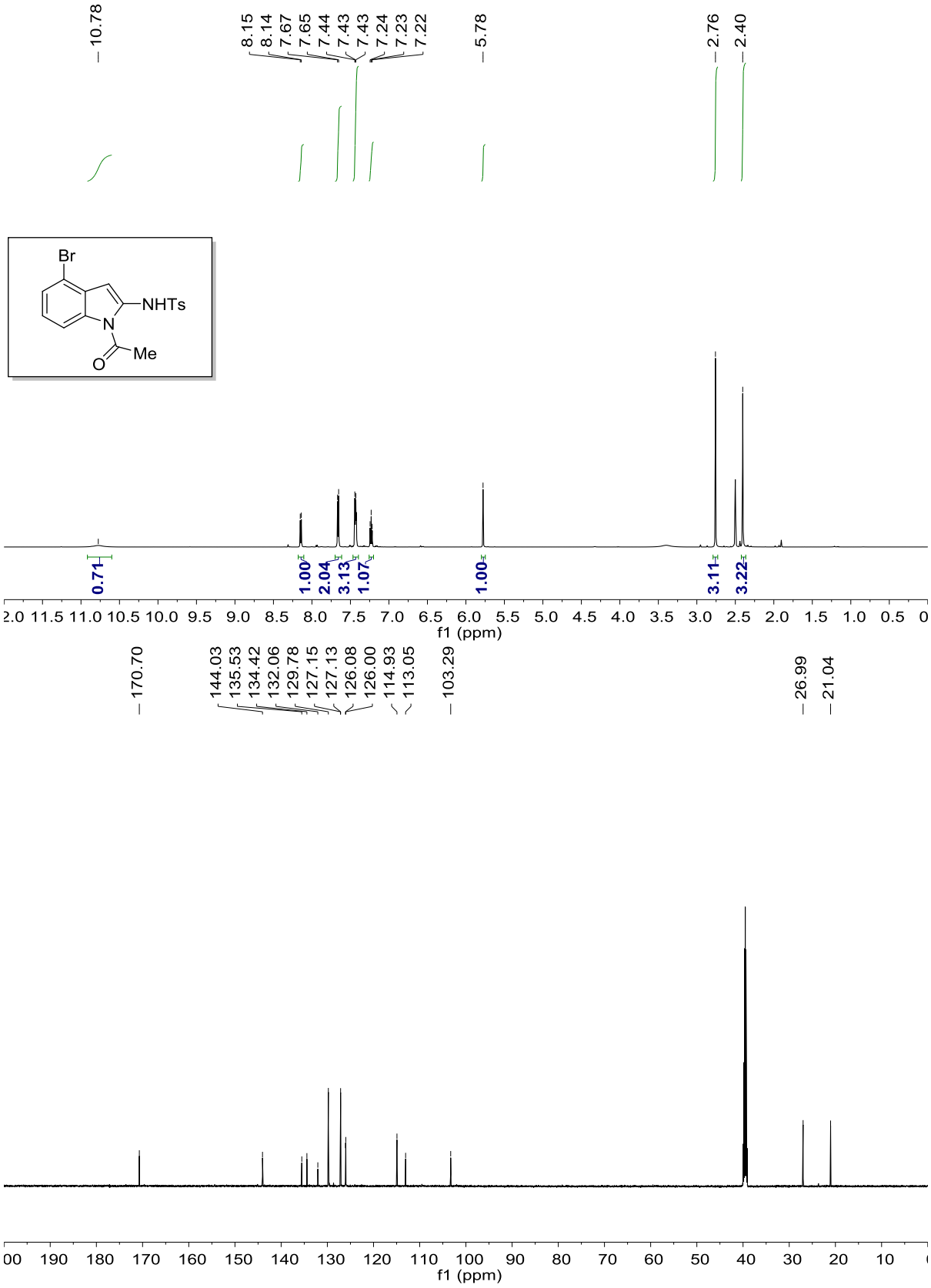



-122.51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

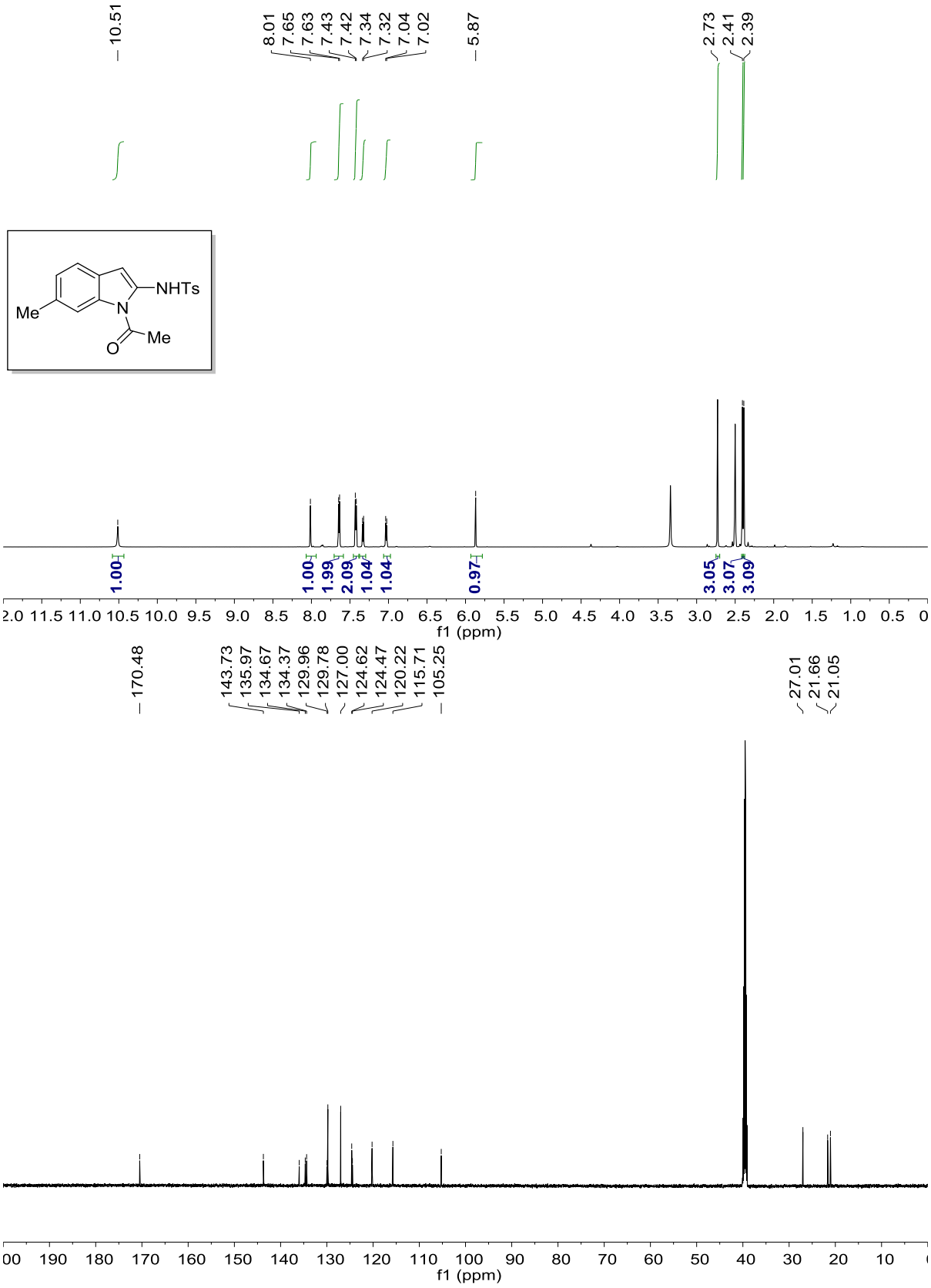
***N*-(1-Acetyl-4-chloro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **14**)



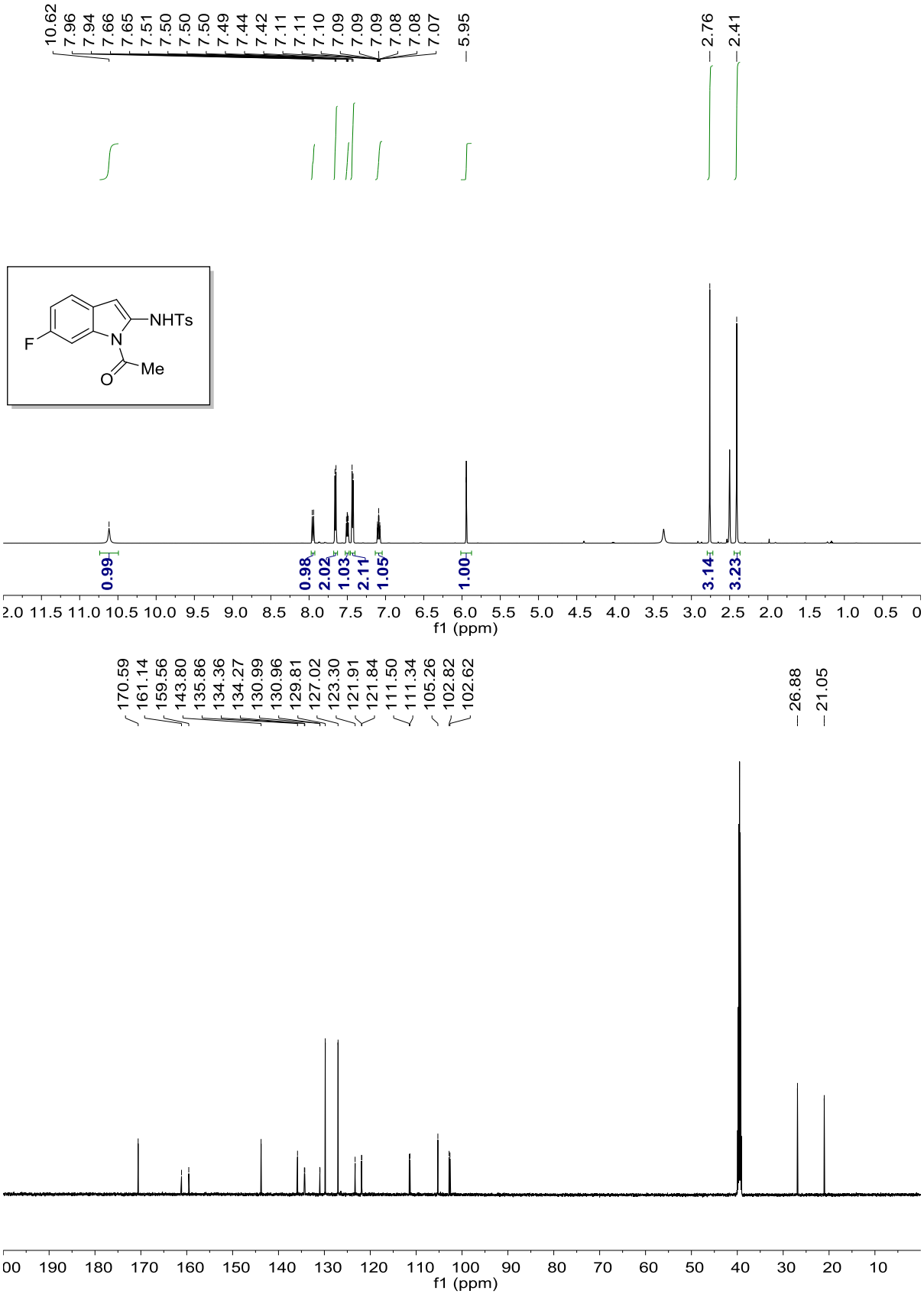
***N*-(1-Acetyl-4-bromo-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **15**)

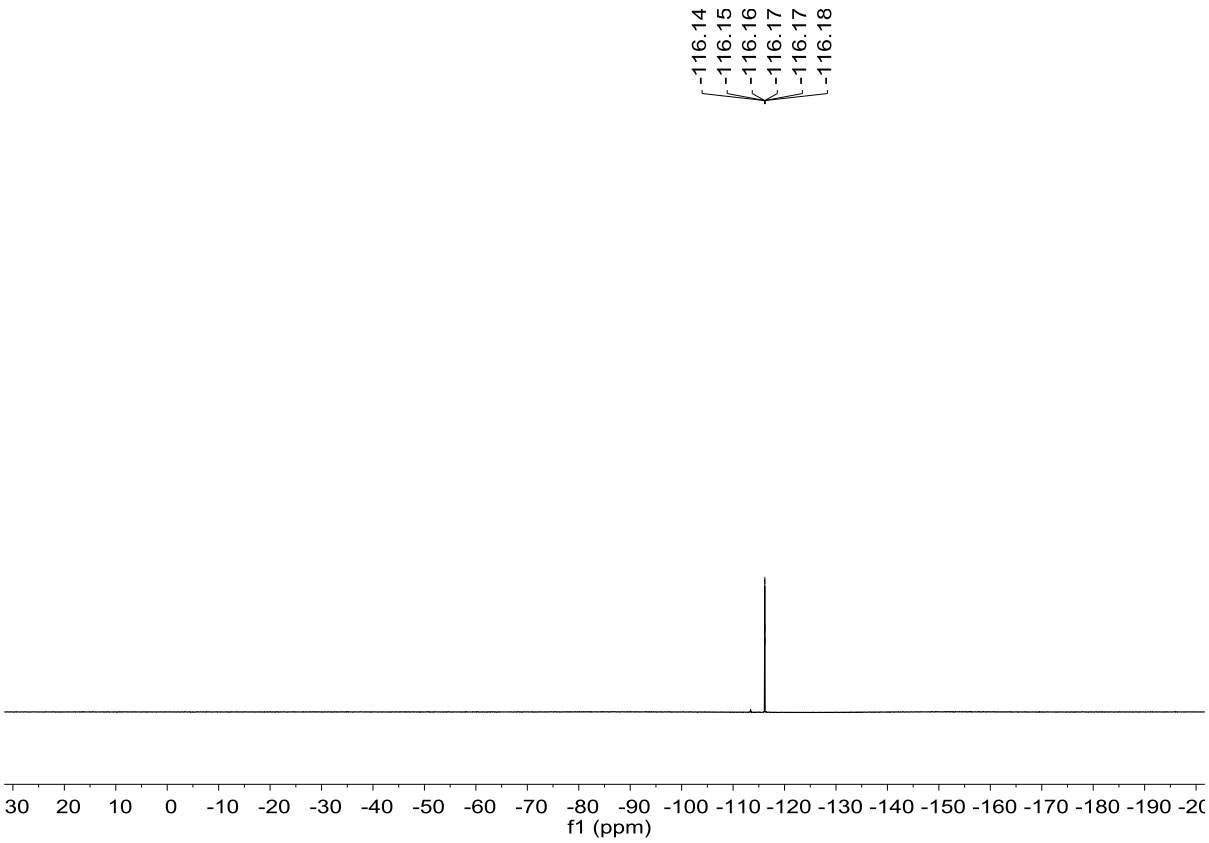


***N*-(1-Acetyl-6-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **16**)

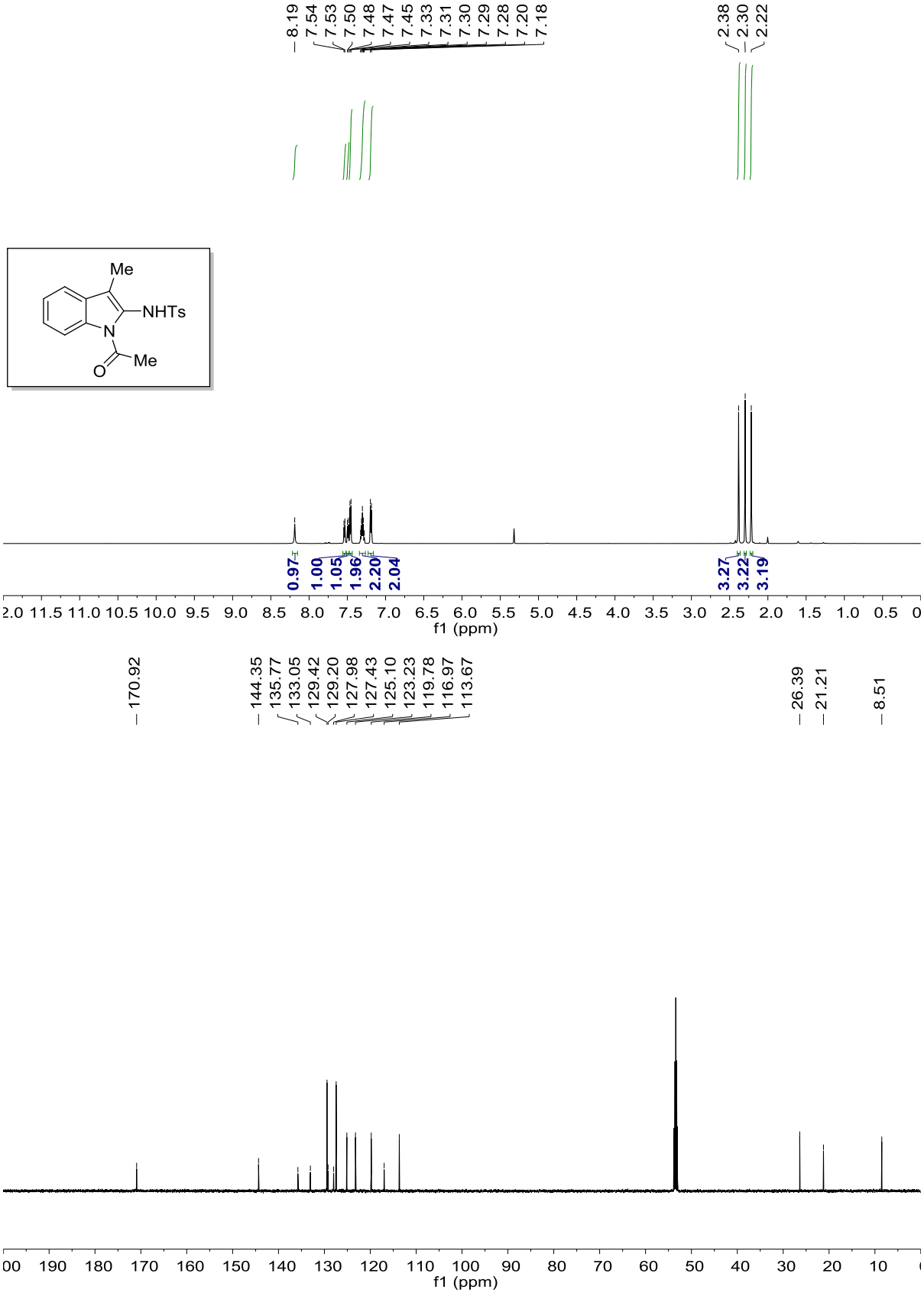


***N*-(1-Acetyl-6-fluoro-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **17**)

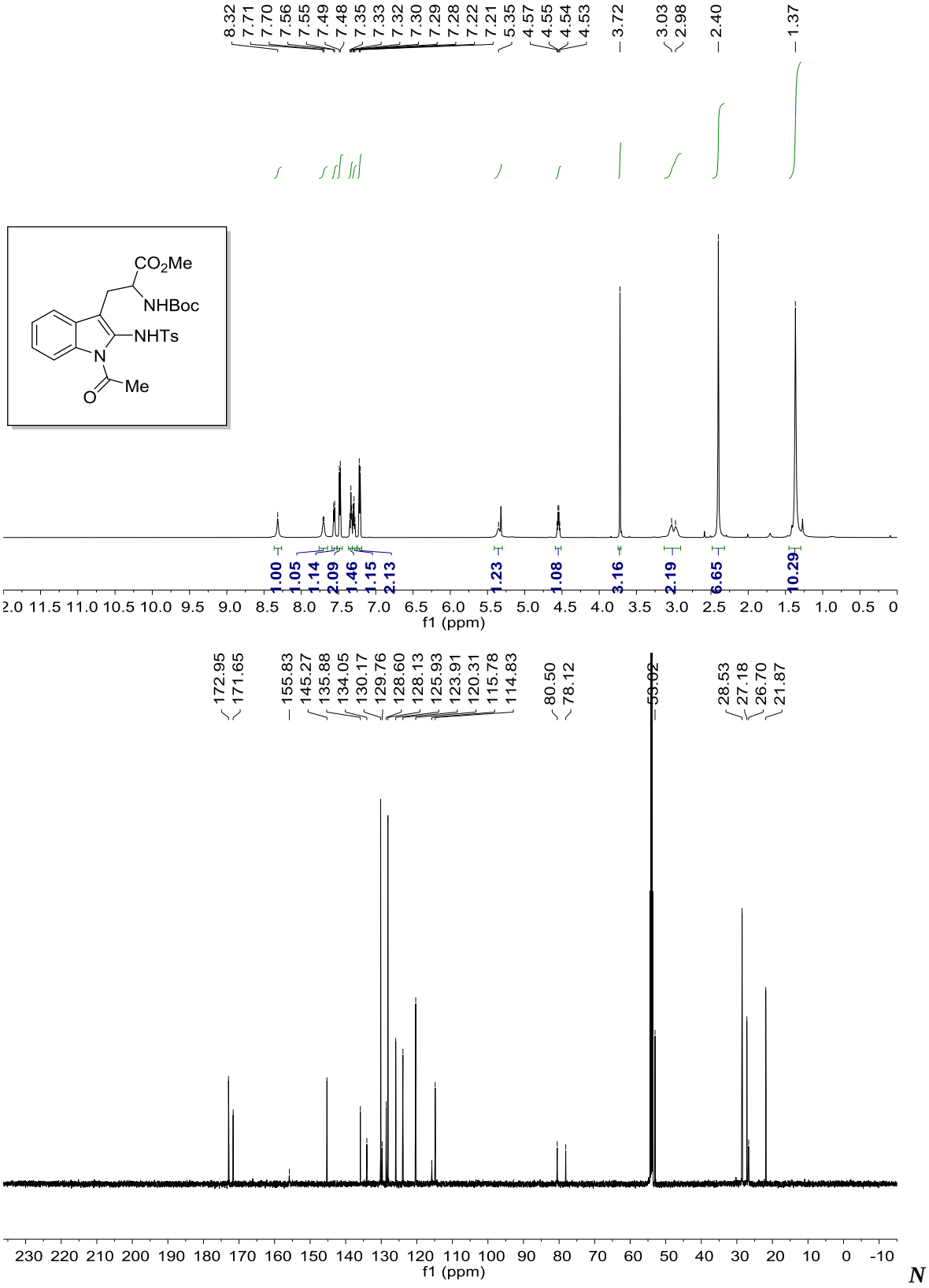



-116.14
-116.15
-116.16
-116.17
-116.17
-116.18
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

***N*-(1-Acetyl-3-methyl-1*H*-indol-2-yl)-4-methylbenzenesulfonamide** (Scheme 4, **18**)

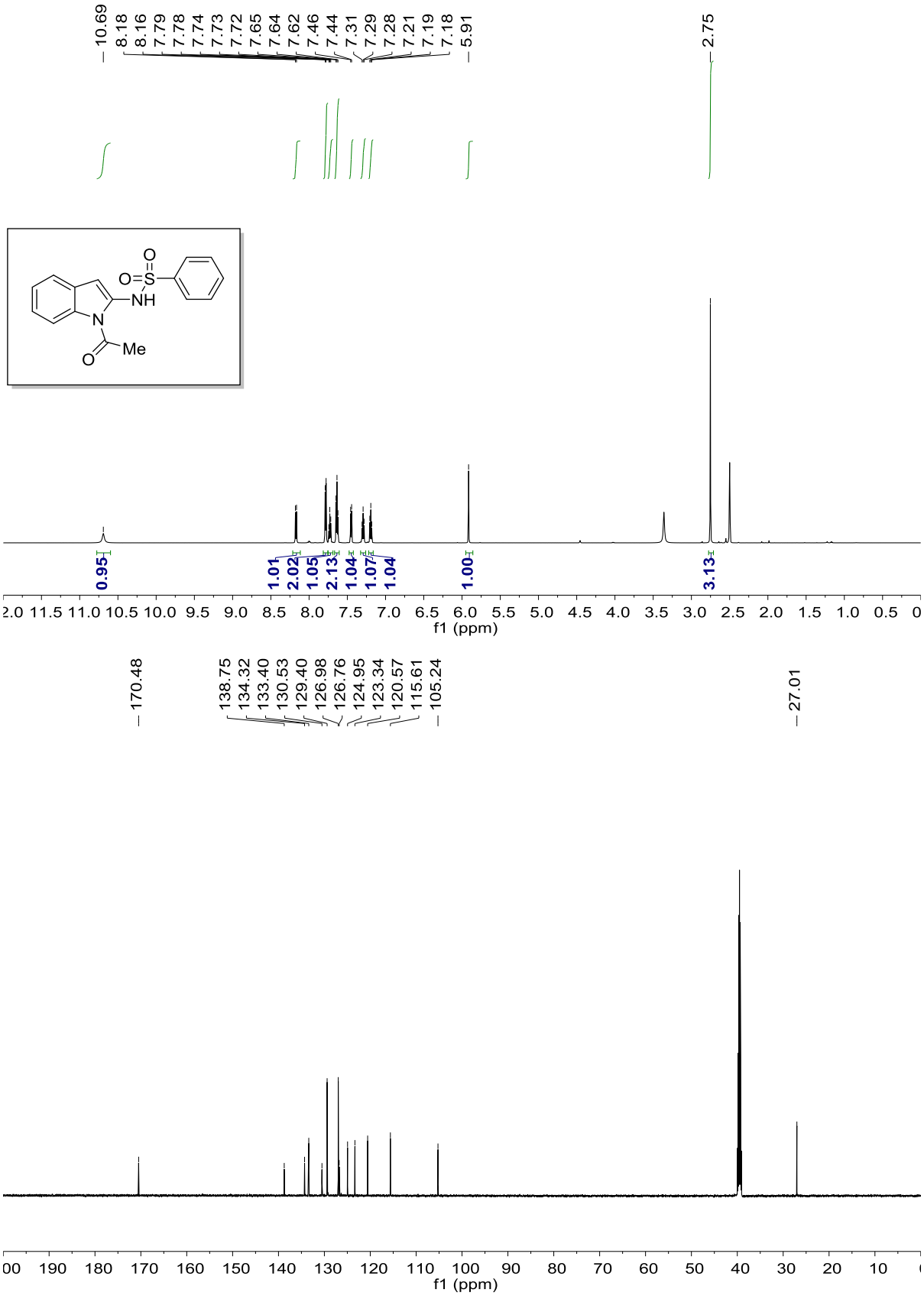


Methyl 3-(1-acetyl-2-((4-methylphenyl)sulfonamido)-1*H*-indol-3-yl)-2-((*tert*-butoxycarbonyl)amino)propanoate (Scheme 4, **19**)

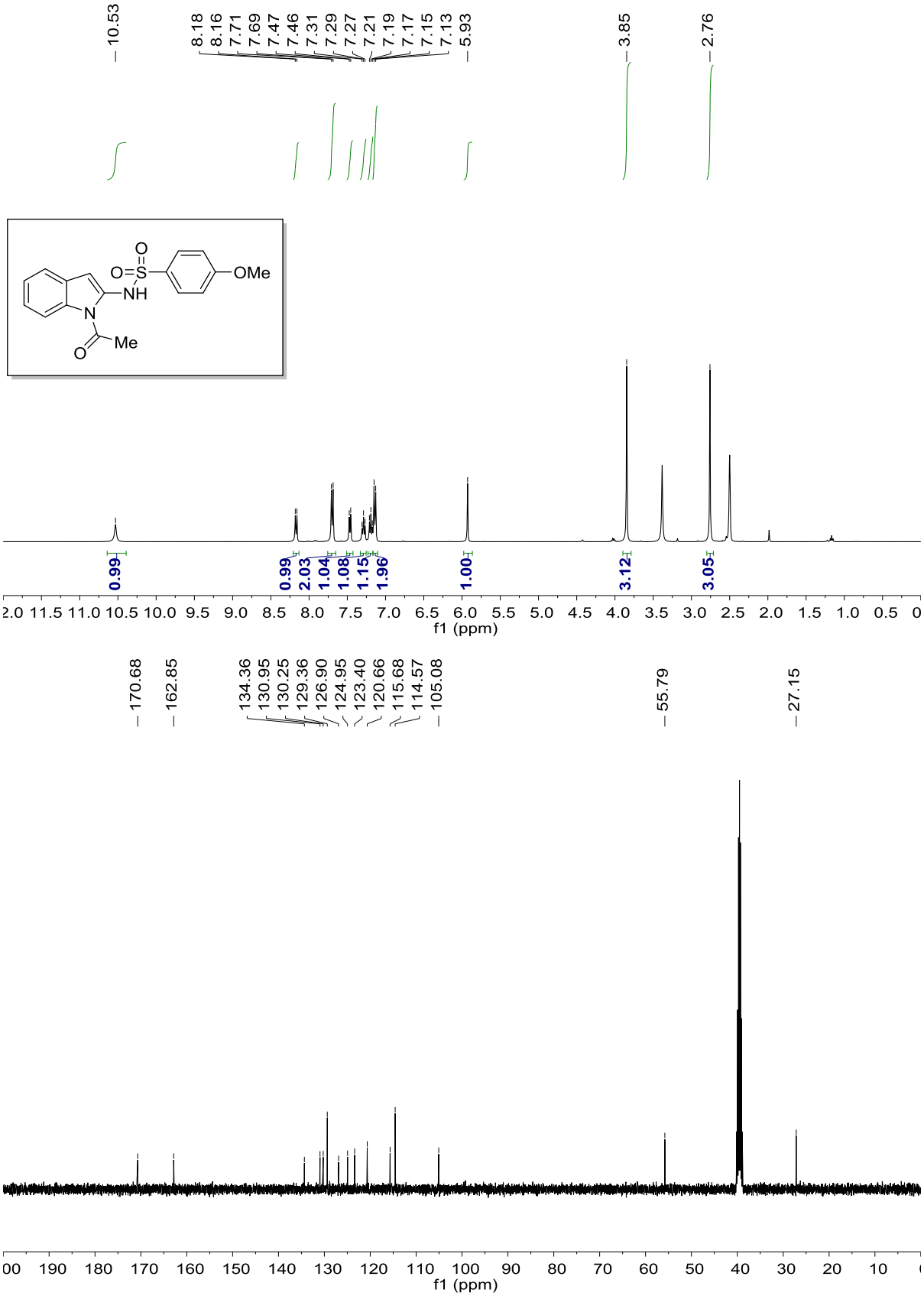


N

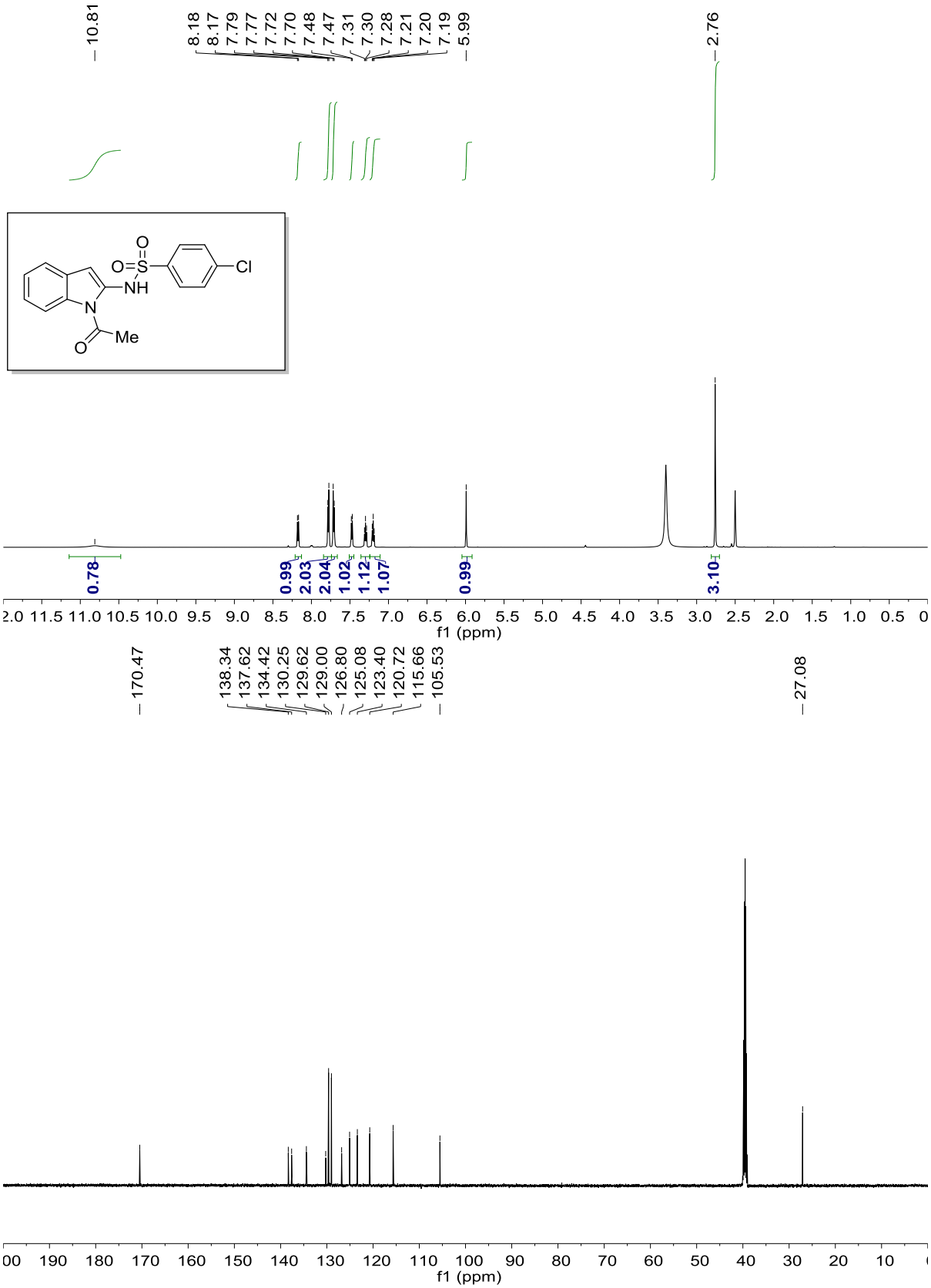
***N*-(1-Acetyl-1*H*-indol-2-yl)-benzenesulfonamide** (Scheme 4, **20**)



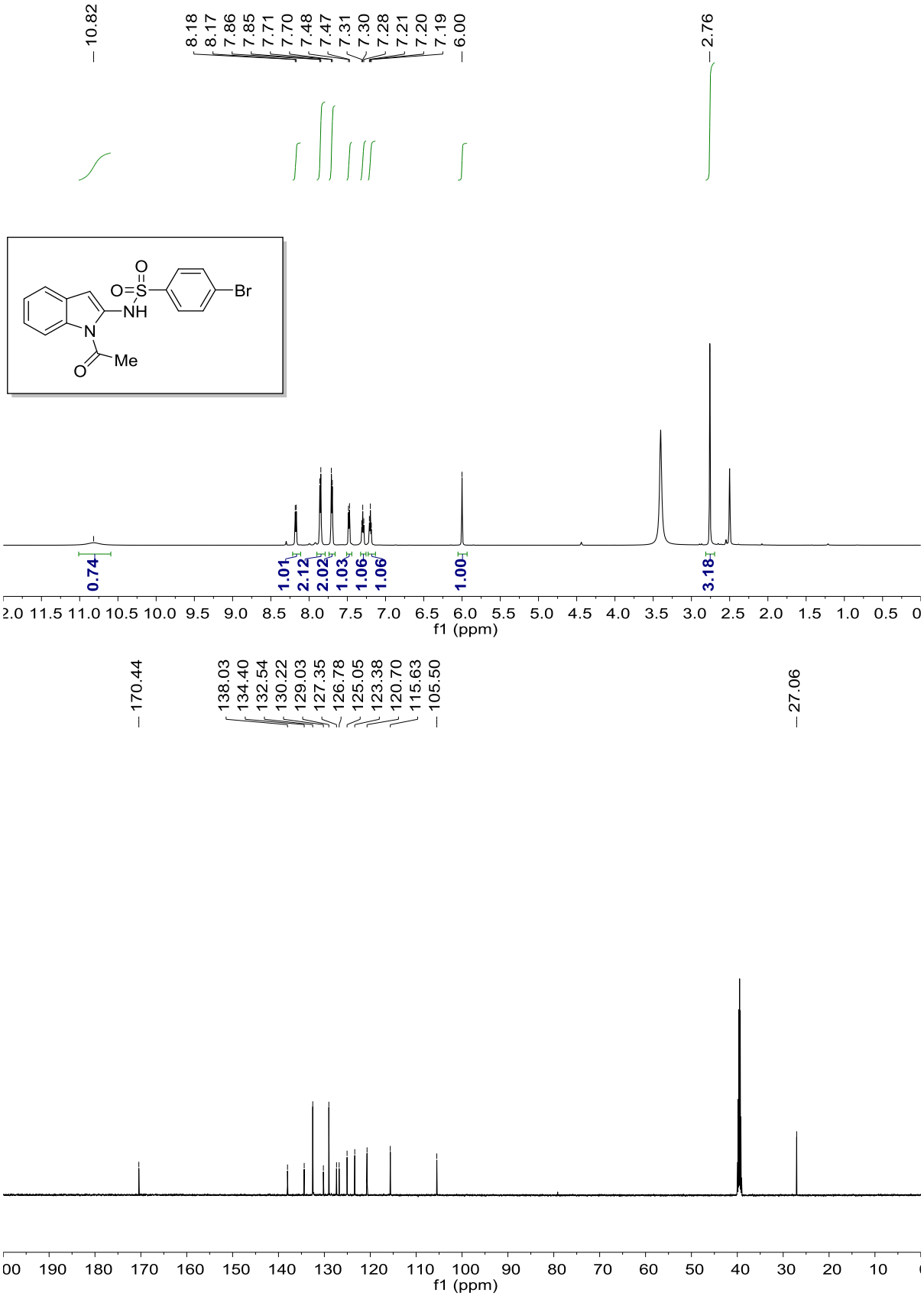
***N*-(1-Acetyl-1*H*-indol-2-yl)-4-methoxybenzenesulfonamide** (Scheme 4, **21**)



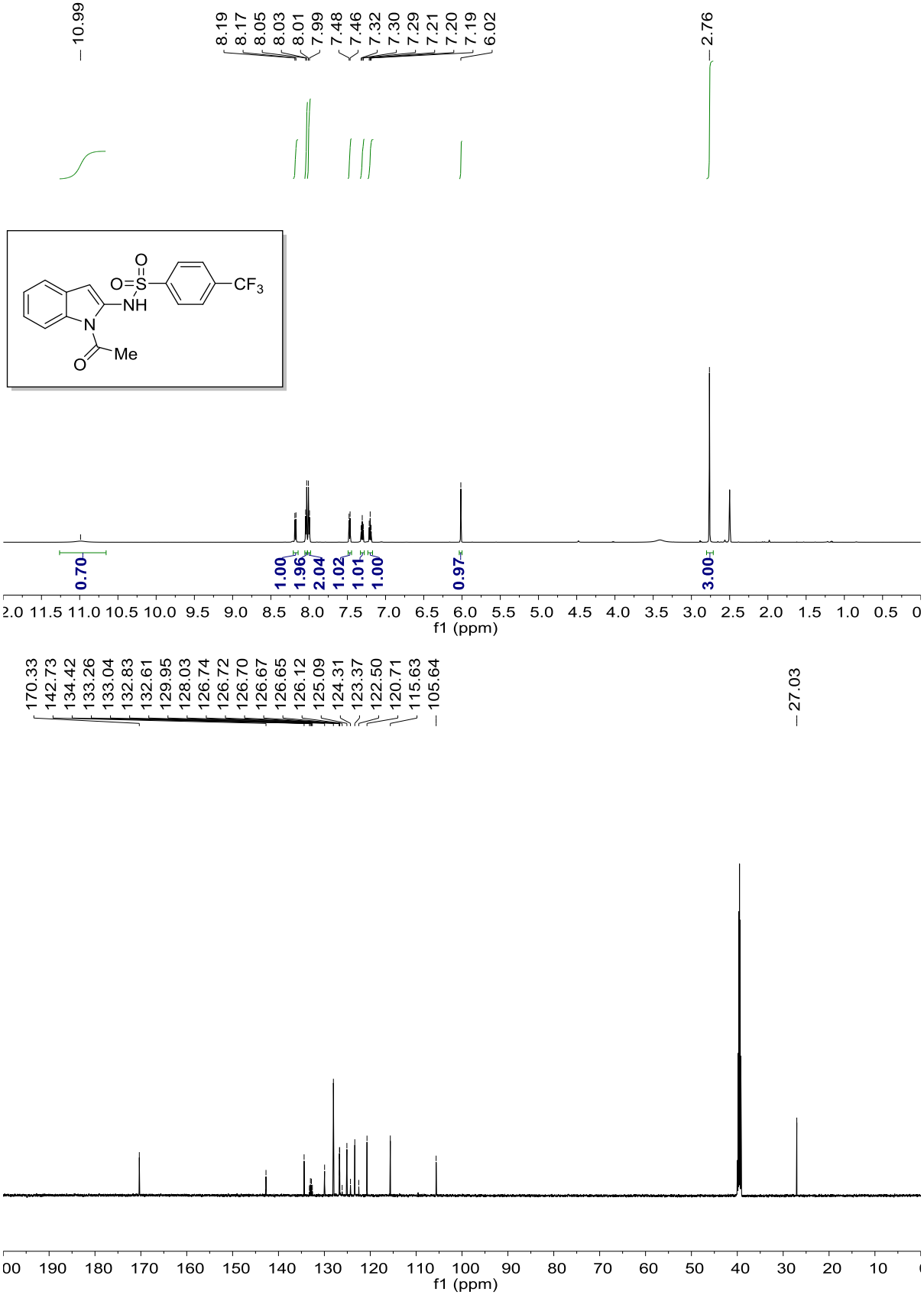
***N*-(1-Acetyl-1*H*-indol-2-yl)-4-chlorobenzenesulfonamide** (Scheme 4, **22**)

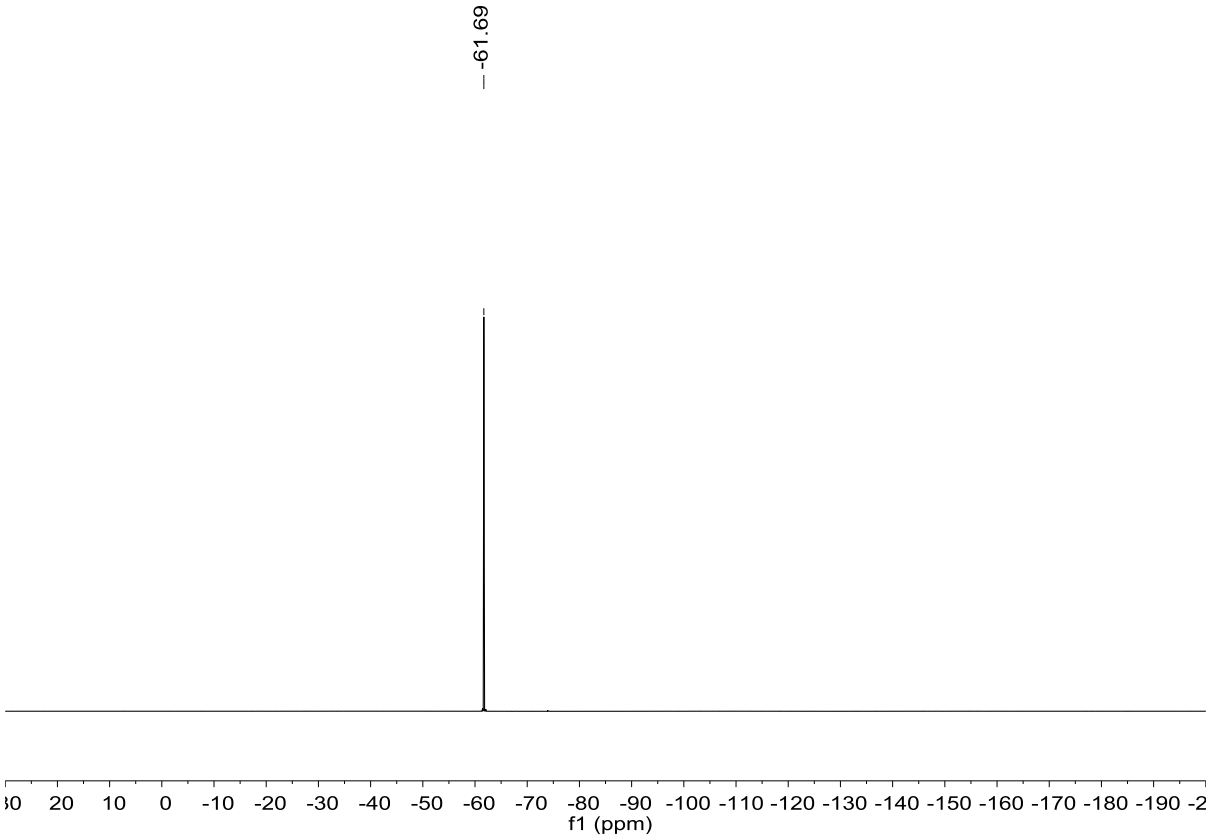


***N*-(1-Acetyl-1*H*-indol-2-yl)-4-bromobenzenesulfonamide** (Scheme 4, **23**)

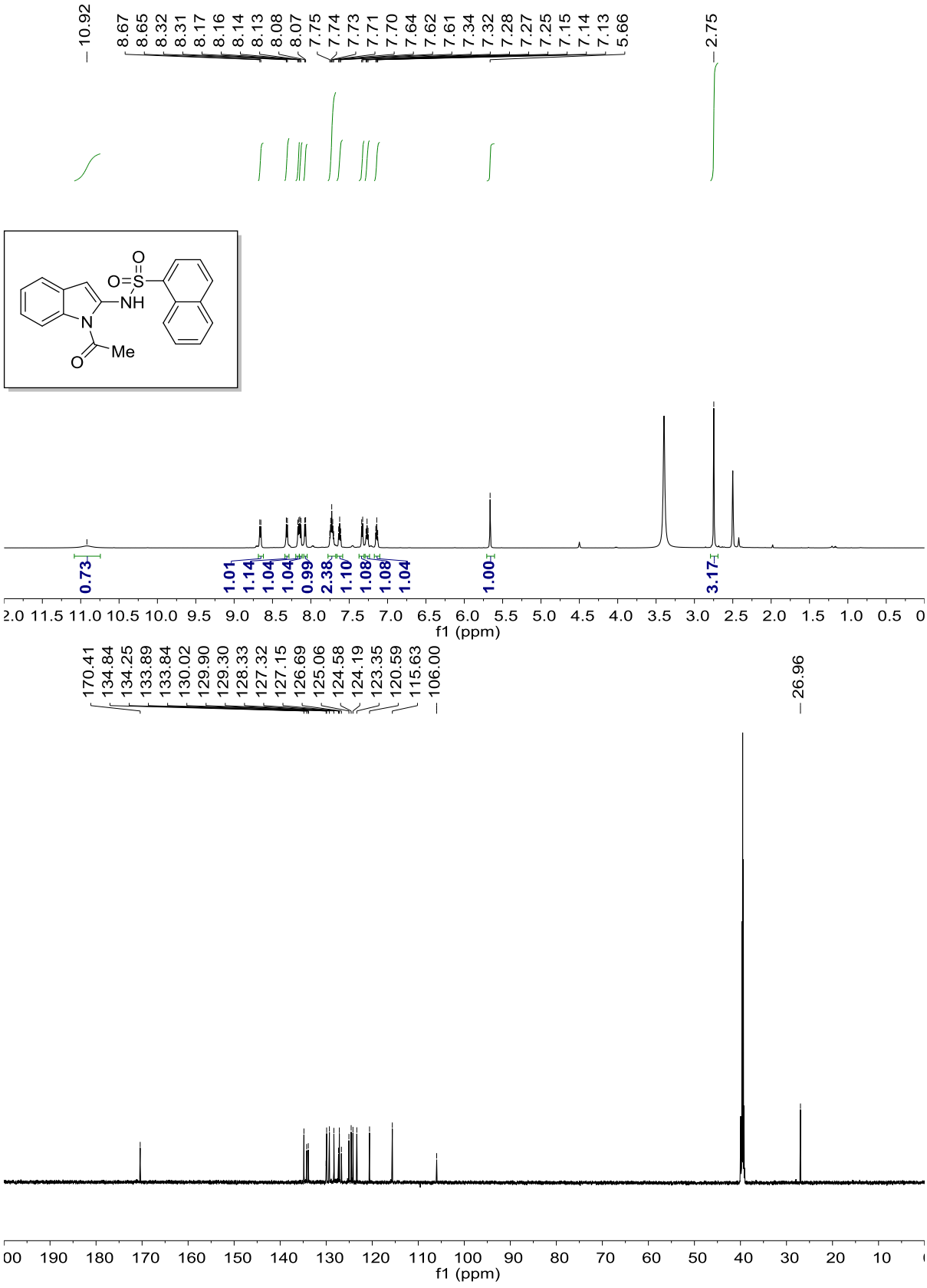


***N*-(1-Acetyl-1*H*-indol-2-yl)-4-(trifluoromethyl)benzenesulfonamide** (Scheme 4, **24**)

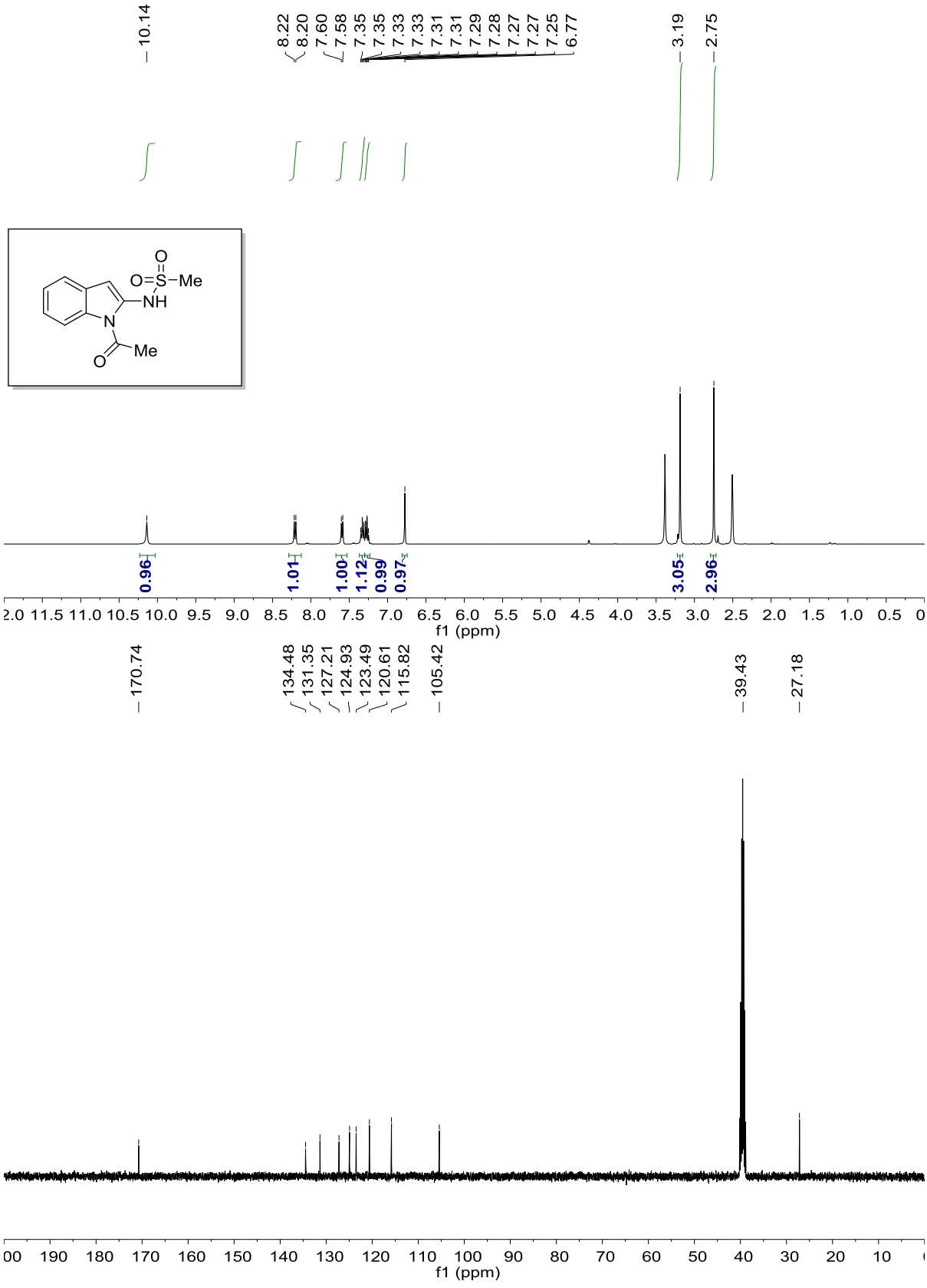



-61.69
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

***N*-(1-Acetyl-1*H*-indol-2-yl)naphthalene-1-sulfonamide** (Scheme 4, **25**)

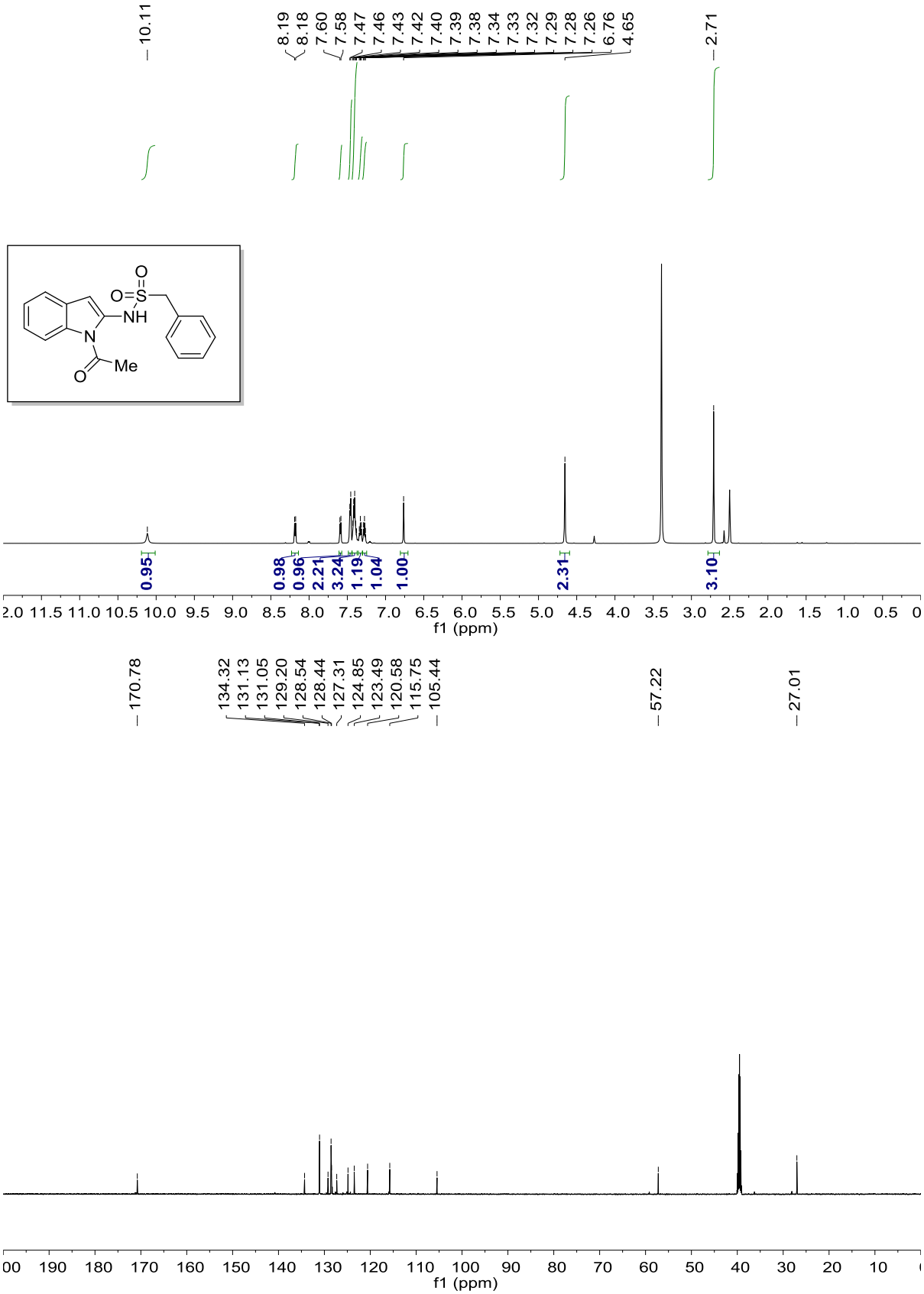


***N*-(1-Acetyl-1*H*-indol-2-yl)methanesulfonamide** (Scheme 4, **26**)

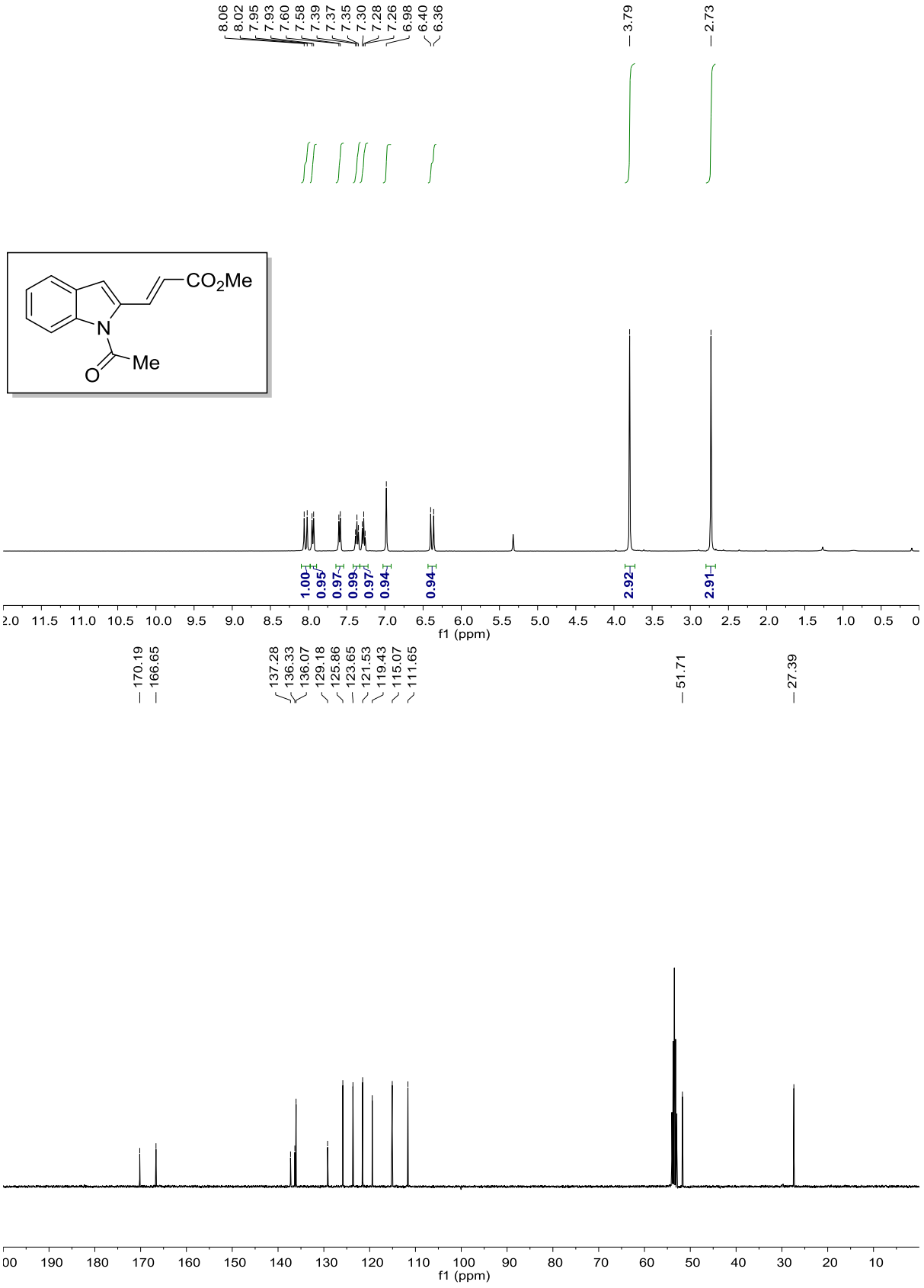


***N*-(1-Acetyl-1*H*-indol-2-yl)butane-1-sulfonamide** (Scheme 4, **27**)

***N*-(1-Acetyl-1*H*-indol-2-yl)-1-phenylmethanesulfonamide** (Scheme 4, **28**)

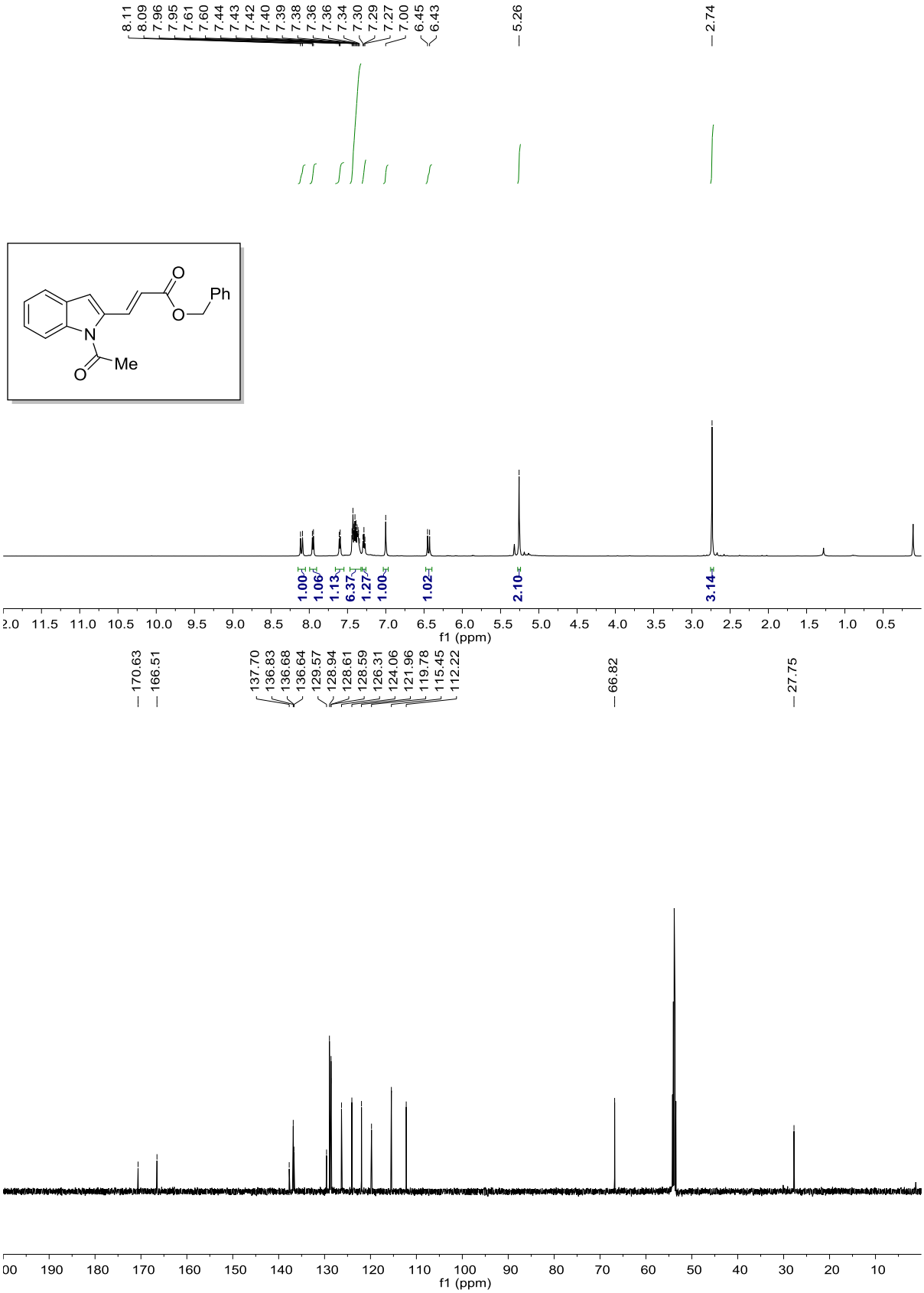


Methyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **29**)



Ethyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **30**)

Benzyl (*E*)-3-(1-acetyl-1*H*-indol-2-yl)acrylate (Scheme 5, **31**)



Appendix II

Crystallographic Data for 5, 6 and 18

Crystallographic data of 5 (Scheme 3)

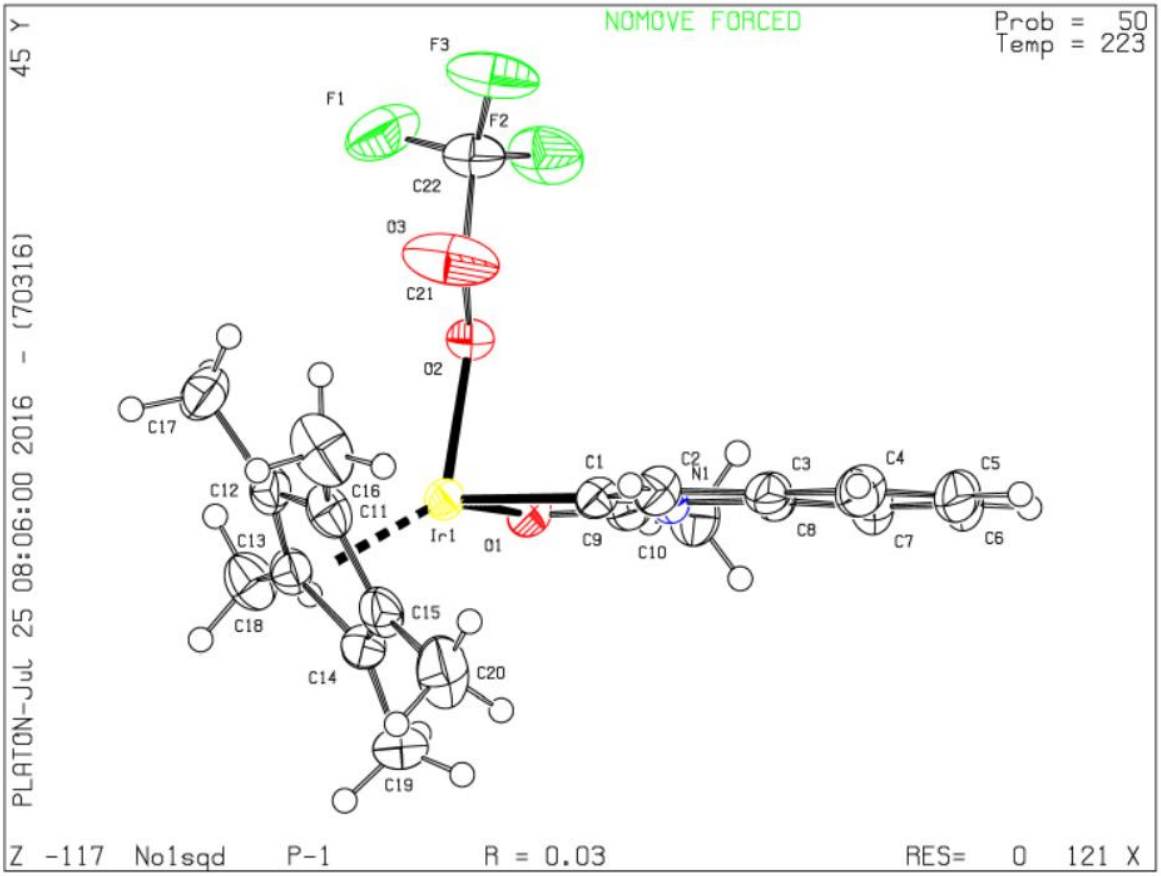


Table S13. Crystal data and structure refinement for **5**.

Identification code	No1sqd	
Empirical formula	C_{22} H_{23} F_3 Ir N O_3	
Formula weight	598.61	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2770(3) Å	α= 101.755(2)°.
	b = 9.4109(4) Å	β= 103.438(2)°.
	c = 15.3550(7) Å	γ = 106.361(2)°.
Volume	1197.89(8) $Å^3$	
Z	2	
Density (calculated)	1.660 Mg/m^3	
Absorption coefficient	5.616 mm^{-1}	
F(000)	580	
Crystal size	0.21 x 0.18 x 0.12 mm^3	
Theta range for data collection	2.36 to 28.38°.	
Index ranges	-12<=h<=12, -12<=k<=12, -20<=l<=20	
Reflections collected	35085	
Independent reflections	5981 [R(int) = 0.0736]	
Completeness to theta = 28.38°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5522 and 0.3851	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5981 / 0 / 277	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0264, wR2 = 0.0533	
R indices (all data)	R1 = 0.0352, wR2 = 0.0554	
Largest diff. peak and hole	1.221 and -0.795 $e.Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	9607(1)	7147(1)	3229(1)	28(1)
C(1)	8681(3)	6459(4)	1823(2)	29(1)
C(2)	8770(4)	5566(4)	1046(2)	36(1)
C(3)	7718(4)	5654(4)	219(2)	38(1)
C(4)	7334(4)	4943(5)	-734(2)	49(1)
C(5)	6225(5)	5277(5)	-1354(3)	57(1)
C(6)	5489(5)	6278(5)	-1049(3)	56(1)
C(7)	5835(4)	6993(5)	-109(3)	47(1)
C(8)	6963(4)	6672(4)	518(2)	34(1)
N(1)	7565(3)	7190(3)	1506(2)	29(1)
C(9)	7254(3)	8134(4)	2159(2)	31(1)
C(10)	6132(4)	8955(5)	1929(3)	46(1)
O(1)	7950(2)	8324(2)	3002(2)	31(1)
C(11)	11061(4)	5958(4)	3800(3)	39(1)
C(12)	11230(4)	7237(4)	4573(2)	35(1)
C(13)	9738(4)	7080(4)	4683(2)	33(1)
C(14)	8591(4)	5691(4)	3979(2)	38(1)
C(15)	9417(4)	4962(4)	3473(2)	41(1)
C(16)	12365(5)	5587(6)	3496(3)	63(1)
C(17)	12739(4)	8528(5)	5114(3)	52(1)
C(18)	9334(5)	8150(5)	5374(3)	47(1)
C(19)	6878(4)	5110(5)	3899(3)	59(1)
C(20)	8718(6)	3425(4)	2743(3)	65(1)
O(2)	10981(2)	9208(2)	3053(2)	32(1)
C(21)	12247(4)	9393(4)	2856(3)	39(1)
O(3)	12909(4)	8497(4)	2664(3)	81(1)
C(22)	13056(4)	11086(4)	2896(3)	47(1)
F(1)	13768(3)	11962(3)	3795(2)	79(1)
F(2)	12071(3)	11746(3)	2545(2)	71(1)
F(3)	14171(3)	11266(3)	2490(2)	81(1)

Table S15. Bond lengths [Å] and angles [°] for **5**.

Ir(1)-C(1)	2.017(3)
Ir(1)-O(2)	2.108(2)
Ir(1)-C(14)	2.124(3)
Ir(1)-C(15)	2.131(3)
Ir(1)-C(11)	2.132(3)
Ir(1)-O(1)	2.140(2)
Ir(1)-C(13)	2.223(3)
Ir(1)-C(12)	2.224(3)
C(1)-C(2)	1.347(4)
C(1)-N(1)	1.444(4)
C(2)-C(3)	1.443(5)
C(2)-H(2)	0.9400
C(3)-C(4)	1.394(5)
C(3)-C(8)	1.403(5)
C(4)-C(5)	1.383(6)
C(4)-H(4)	0.9400
C(5)-C(6)	1.380(6)
C(5)-H(5)	0.9400
C(6)-C(7)	1.382(5)
C(6)-H(6)	0.9400
C(7)-C(8)	1.393(5)
C(7)-H(7)	0.9400
C(8)-N(1)	1.415(4)
N(1)-C(9)	1.341(4)
C(9)-O(1)	1.255(4)
C(9)-C(10)	1.482(4)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-H(10C)	0.9700
C(11)-C(15)	1.451(5)
C(11)-C(12)	1.451(5)
C(11)-C(16)	1.496(5)
C(12)-C(13)	1.404(5)
C(12)-C(17)	1.489(5)

C(13)-C(14)	1.455(4)
C(13)-C(18)	1.497(5)
C(14)-C(15)	1.421(5)
C(14)-C(19)	1.494(5)
C(15)-C(20)	1.497(5)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(16)-H(16C)	0.9700
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(20)-H(20C)	0.9700
O(2)-C(21)	1.254(4)
C(21)-O(3)	1.204(4)
C(21)-C(22)	1.539(5)
C(22)-F(3)	1.315(4)
C(22)-F(2)	1.318(4)
C(22)-F(1)	1.352(5)
C(1)-Ir(1)-O(2)	85.47(11)
C(1)-Ir(1)-C(14)	117.59(13)
O(2)-Ir(1)-C(14)	156.16(12)
C(1)-Ir(1)-C(15)	99.67(13)
O(2)-Ir(1)-C(15)	149.35(12)
C(14)-Ir(1)-C(15)	39.01(14)
C(1)-Ir(1)-C(11)	115.88(13)
O(2)-Ir(1)-C(11)	110.96(12)
C(14)-Ir(1)-C(11)	66.11(14)
C(15)-Ir(1)-C(11)	39.80(14)

C(1)-Ir(1)-O(1)	77.40(10)
O(2)-Ir(1)-O(1)	78.10(8)
C(14)-Ir(1)-O(1)	100.01(11)
C(15)-Ir(1)-O(1)	132.56(12)
C(11)-Ir(1)-O(1)	163.77(11)
C(1)-Ir(1)-C(13)	156.16(13)
O(2)-Ir(1)-C(13)	117.39(10)
C(14)-Ir(1)-C(13)	39.02(12)
C(15)-Ir(1)-C(13)	64.59(12)
C(11)-Ir(1)-C(13)	64.34(13)
O(1)-Ir(1)-C(13)	99.68(10)
C(1)-Ir(1)-C(12)	153.93(13)
O(2)-Ir(1)-C(12)	98.03(11)
C(14)-Ir(1)-C(12)	64.28(13)
C(15)-Ir(1)-C(12)	64.75(12)
C(11)-Ir(1)-C(12)	38.86(13)
O(1)-Ir(1)-C(12)	128.65(10)
C(13)-Ir(1)-C(12)	36.80(12)
C(2)-C(1)-N(1)	106.0(3)
C(2)-C(1)-Ir(1)	141.9(3)
N(1)-C(1)-Ir(1)	112.1(2)
C(1)-C(2)-C(3)	110.7(3)
C(1)-C(2)-H(2)	124.6
C(3)-C(2)-H(2)	124.6
C(4)-C(3)-C(8)	119.1(3)
C(4)-C(3)-C(2)	133.7(3)
C(8)-C(3)-C(2)	107.2(3)
C(5)-C(4)-C(3)	118.6(4)
C(5)-C(4)-H(4)	120.7
C(3)-C(4)-H(4)	120.7
C(6)-C(5)-C(4)	121.6(4)
C(6)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
C(5)-C(6)-C(7)	121.3(4)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4

C(6)-C(7)-C(8)	117.3(4)
C(6)-C(7)-H(7)	121.3
C(8)-C(7)-H(7)	121.3
C(7)-C(8)-C(3)	122.1(3)
C(7)-C(8)-N(1)	131.4(3)
C(3)-C(8)-N(1)	106.4(3)
C(9)-N(1)-C(8)	132.9(3)
C(9)-N(1)-C(1)	117.5(3)
C(8)-N(1)-C(1)	109.6(2)
O(1)-C(9)-N(1)	118.0(3)
O(1)-C(9)-C(10)	119.1(3)
N(1)-C(9)-C(10)	123.0(3)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-O(1)-Ir(1)	114.98(19)
C(15)-C(11)-C(12)	107.0(3)
C(15)-C(11)-C(16)	125.6(4)
C(12)-C(11)-C(16)	126.7(4)
C(15)-C(11)-Ir(1)	70.07(18)
C(12)-C(11)-Ir(1)	74.00(19)
C(16)-C(11)-Ir(1)	128.4(3)
C(13)-C(12)-C(11)	108.7(3)
C(13)-C(12)-C(17)	126.7(3)
C(11)-C(12)-C(17)	124.6(3)
C(13)-C(12)-Ir(1)	71.56(18)
C(11)-C(12)-Ir(1)	67.14(18)
C(17)-C(12)-Ir(1)	124.8(2)
C(12)-C(13)-C(14)	108.1(3)
C(12)-C(13)-C(18)	127.5(3)
C(14)-C(13)-C(18)	124.3(3)
C(12)-C(13)-Ir(1)	71.64(19)
C(14)-C(13)-Ir(1)	66.81(18)

C(18)-C(13)-Ir(1)	125.6(2)
C(15)-C(14)-C(13)	108.1(3)
C(15)-C(14)-C(19)	127.9(3)
C(13)-C(14)-C(19)	123.7(4)
C(15)-C(14)-Ir(1)	70.8(2)
C(13)-C(14)-Ir(1)	74.17(19)
C(19)-C(14)-Ir(1)	125.5(3)
C(14)-C(15)-C(11)	107.8(3)
C(14)-C(15)-C(20)	126.0(4)
C(11)-C(15)-C(20)	126.1(4)
C(14)-C(15)-Ir(1)	70.22(19)
C(11)-C(15)-Ir(1)	70.13(18)
C(20)-C(15)-Ir(1)	126.0(3)
C(11)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(11)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5

H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(21)-O(2)-Ir(1)	124.7(2)
O(3)-C(21)-O(2)	131.2(4)
O(3)-C(21)-C(22)	117.3(3)
O(2)-C(21)-C(22)	111.5(3)
F(3)-C(22)-F(2)	108.4(3)
F(3)-C(22)-F(1)	106.0(3)
F(2)-C(22)-F(1)	104.5(3)
F(3)-C(22)-C(21)	113.3(3)
F(2)-C(22)-C(21)	113.9(3)
F(1)-C(22)-C(21)	110.1(3)

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	29(1)	25(1)	25(1)	4(1)	6(1)	7(1)
C(1)	26(2)	29(2)	29(2)	5(1)	7(1)	7(1)
C(2)	35(2)	39(2)	33(2)	3(1)	12(1)	14(2)
C(3)	31(2)	44(2)	30(2)	6(2)	11(1)	3(2)
C(4)	43(2)	63(3)	29(2)	0(2)	15(2)	5(2)
C(5)	47(2)	78(3)	25(2)	6(2)	9(2)	-3(2)
C(6)	46(2)	75(3)	33(2)	21(2)	2(2)	5(2)
C(7)	45(2)	58(2)	36(2)	18(2)	7(2)	18(2)
C(8)	31(2)	37(2)	26(2)	7(1)	8(1)	2(1)
N(1)	29(1)	31(1)	25(1)	8(1)	8(1)	9(1)
C(9)	25(2)	31(2)	33(2)	7(1)	9(1)	4(1)
C(10)	45(2)	51(2)	45(2)	13(2)	11(2)	25(2)
O(1)	27(1)	32(1)	30(1)	3(1)	9(1)	10(1)
C(11)	48(2)	44(2)	38(2)	20(2)	16(2)	26(2)
C(12)	37(2)	35(2)	32(2)	12(1)	3(1)	13(2)
C(13)	39(2)	30(2)	28(2)	9(1)	6(1)	11(1)
C(14)	39(2)	33(2)	37(2)	14(2)	6(2)	4(2)
C(15)	58(2)	26(2)	32(2)	10(1)	7(2)	10(2)
C(16)	80(3)	79(3)	67(3)	35(3)	39(2)	59(3)
C(17)	37(2)	51(2)	51(2)	14(2)	-3(2)	7(2)
C(18)	63(2)	49(2)	38(2)	13(2)	23(2)	25(2)
C(19)	44(2)	59(3)	58(3)	26(2)	9(2)	-6(2)
C(20)	104(4)	30(2)	41(2)	2(2)	2(2)	19(2)
O(2)	31(1)	30(1)	37(1)	10(1)	14(1)	10(1)
C(21)	34(2)	36(2)	51(2)	16(2)	15(2)	15(2)
O(3)	77(2)	58(2)	158(4)	56(2)	81(2)	43(2)
C(22)	41(2)	42(2)	64(3)	19(2)	25(2)	12(2)
F(1)	56(2)	61(2)	86(2)	1(2)	13(1)	-8(1)
F(2)	72(2)	52(2)	108(2)	44(2)	33(2)	30(1)
F(3)	78(2)	63(2)	133(3)	44(2)	76(2)	23(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5**.

	x	y	z	U(eq)
H(2)	9428	4967	1043	44
H(4)	7819	4252	-951	59
H(5)	5965	4810	-1999	69
H(6)	4739	6478	-1490	67
H(7)	5329	7669	100	56
H(10A)	6090	9581	2502	68
H(10B)	5090	8205	1580	68
H(10C)	6482	9615	1555	68
H(16A)	13150	6533	3512	95
H(16B)	11939	4895	2864	95
H(16C)	12853	5090	3914	95
H(17A)	12526	9481	5287	78
H(17B)	13442	8640	4734	78
H(17C)	13232	8305	5675	78
H(18A)	9043	7649	5832	71
H(18B)	8455	8405	5050	71
H(18C)	10242	9089	5688	71
H(19A)	6291	4370	3289	89
H(19B)	6492	5970	3972	89
H(19C)	6738	4612	4382	89
H(20A)	8696	2609	3043	97
H(20B)	9354	3384	2325	97
H(20C)	7650	3285	2389	97

Table S18. Torsion angles [°] for **5**.

O(2)-Ir(1)-C(1)-C(2)	101.1(4)
C(14)-Ir(1)-C(1)-C(2)	-85.2(4)
C(15)-Ir(1)-C(1)-C(2)	-48.4(4)
C(11)-Ir(1)-C(1)-C(2)	-10.0(5)
O(1)-Ir(1)-C(1)-C(2)	179.9(4)
C(13)-Ir(1)-C(1)-C(2)	-94.6(5)
C(12)-Ir(1)-C(1)-C(2)	2.1(6)
O(2)-Ir(1)-C(1)-N(1)	-75.9(2)
C(14)-Ir(1)-C(1)-N(1)	97.7(2)
C(15)-Ir(1)-C(1)-N(1)	134.6(2)
C(11)-Ir(1)-C(1)-N(1)	173.0(2)
O(1)-Ir(1)-C(1)-N(1)	2.9(2)
C(13)-Ir(1)-C(1)-N(1)	88.3(3)
C(12)-Ir(1)-C(1)-N(1)	-174.9(2)
N(1)-C(1)-C(2)-C(3)	-1.3(4)
Ir(1)-C(1)-C(2)-C(3)	-178.4(3)
C(1)-C(2)-C(3)-C(4)	-177.9(4)
C(1)-C(2)-C(3)-C(8)	0.6(4)
C(8)-C(3)-C(4)-C(5)	0.4(5)
C(2)-C(3)-C(4)-C(5)	178.8(4)
C(3)-C(4)-C(5)-C(6)	-0.6(6)
C(4)-C(5)-C(6)-C(7)	0.1(6)
C(5)-C(6)-C(7)-C(8)	0.5(6)
C(6)-C(7)-C(8)-C(3)	-0.7(5)
C(6)-C(7)-C(8)-N(1)	-179.3(3)
C(4)-C(3)-C(8)-C(7)	0.2(5)
C(2)-C(3)-C(8)-C(7)	-178.5(3)
C(4)-C(3)-C(8)-N(1)	179.2(3)
C(2)-C(3)-C(8)-N(1)	0.4(4)
C(7)-C(8)-N(1)-C(9)	0.5(6)
C(3)-C(8)-N(1)-C(9)	-178.3(3)
C(7)-C(8)-N(1)-C(1)	177.6(4)
C(3)-C(8)-N(1)-C(1)	-1.2(4)
C(2)-C(1)-N(1)-C(9)	179.1(3)

Ir(1)-C(1)-N(1)-C(9)	-2.7(3)
C(2)-C(1)-N(1)-C(8)	1.6(4)
Ir(1)-C(1)-N(1)-C(8)	179.7(2)
C(8)-N(1)-C(9)-O(1)	177.0(3)
C(1)-N(1)-C(9)-O(1)	0.1(4)
C(8)-N(1)-C(9)-C(10)	-3.0(6)
C(1)-N(1)-C(9)-C(10)	-179.9(3)
N(1)-C(9)-O(1)-Ir(1)	2.5(4)
C(10)-C(9)-O(1)-Ir(1)	-177.5(2)
C(1)-Ir(1)-O(1)-C(9)	-3.1(2)
O(2)-Ir(1)-O(1)-C(9)	84.9(2)
C(14)-Ir(1)-O(1)-C(9)	-119.4(2)
C(15)-Ir(1)-O(1)-C(9)	-94.7(2)
C(11)-Ir(1)-O(1)-C(9)	-149.4(4)
C(13)-Ir(1)-O(1)-C(9)	-159.0(2)
C(12)-Ir(1)-O(1)-C(9)	175.7(2)
C(1)-Ir(1)-C(11)-C(15)	-73.1(2)
O(2)-Ir(1)-C(11)-C(15)	-168.37(18)
C(14)-Ir(1)-C(11)-C(15)	37.3(2)
O(1)-Ir(1)-C(11)-C(15)	69.9(5)
C(13)-Ir(1)-C(11)-C(15)	80.4(2)
C(12)-Ir(1)-C(11)-C(15)	115.3(3)
C(1)-Ir(1)-C(11)-C(12)	171.56(19)
O(2)-Ir(1)-C(11)-C(12)	76.3(2)
C(14)-Ir(1)-C(11)-C(12)	-78.1(2)
C(15)-Ir(1)-C(11)-C(12)	-115.3(3)
O(1)-Ir(1)-C(11)-C(12)	-45.4(5)
C(13)-Ir(1)-C(11)-C(12)	-34.95(19)
C(1)-Ir(1)-C(11)-C(16)	47.0(4)
O(2)-Ir(1)-C(11)-C(16)	-48.2(4)
C(14)-Ir(1)-C(11)-C(16)	157.4(4)
C(15)-Ir(1)-C(11)-C(16)	120.2(5)
O(1)-Ir(1)-C(11)-C(16)	-169.9(3)
C(13)-Ir(1)-C(11)-C(16)	-159.5(4)
C(12)-Ir(1)-C(11)-C(16)	-124.5(5)
C(15)-C(11)-C(12)-C(13)	-3.0(4)

C(16)-C(11)-C(12)-C(13)	-174.0(3)
Ir(1)-C(11)-C(12)-C(13)	59.7(2)
C(15)-C(11)-C(12)-C(17)	179.8(3)
C(16)-C(11)-C(12)-C(17)	8.8(6)
Ir(1)-C(11)-C(12)-C(17)	-117.5(3)
C(15)-C(11)-C(12)-Ir(1)	-62.7(2)
C(16)-C(11)-C(12)-Ir(1)	126.4(4)
C(1)-Ir(1)-C(12)-C(13)	-137.9(3)
O(2)-Ir(1)-C(12)-C(13)	125.93(18)
C(14)-Ir(1)-C(12)-C(13)	-37.27(19)
C(15)-Ir(1)-C(12)-C(13)	-80.7(2)
C(11)-Ir(1)-C(12)-C(13)	-120.5(3)
O(1)-Ir(1)-C(12)-C(13)	44.8(2)
C(1)-Ir(1)-C(12)-C(11)	-17.5(4)
O(2)-Ir(1)-C(12)-C(11)	-113.6(2)
C(14)-Ir(1)-C(12)-C(11)	83.2(2)
C(15)-Ir(1)-C(12)-C(11)	39.8(2)
O(1)-Ir(1)-C(12)-C(11)	165.24(18)
C(13)-Ir(1)-C(12)-C(11)	120.5(3)
C(1)-Ir(1)-C(12)-C(17)	99.7(4)
O(2)-Ir(1)-C(12)-C(17)	3.6(3)
C(14)-Ir(1)-C(12)-C(17)	-159.6(3)
C(15)-Ir(1)-C(12)-C(17)	156.9(4)
C(11)-Ir(1)-C(12)-C(17)	117.2(4)
O(1)-Ir(1)-C(12)-C(17)	-77.6(3)
C(13)-Ir(1)-C(12)-C(17)	-122.4(4)
C(11)-C(12)-C(13)-C(14)	0.0(4)
C(17)-C(12)-C(13)-C(14)	177.1(3)
Ir(1)-C(12)-C(13)-C(14)	57.0(2)
C(11)-C(12)-C(13)-C(18)	-178.3(3)
C(17)-C(12)-C(13)-C(18)	-1.1(6)
Ir(1)-C(12)-C(13)-C(18)	-121.3(3)
C(11)-C(12)-C(13)-Ir(1)	-57.0(2)
C(17)-C(12)-C(13)-Ir(1)	120.1(3)
C(1)-Ir(1)-C(13)-C(12)	133.2(3)
O(2)-Ir(1)-C(13)-C(12)	-64.6(2)

C(14)-Ir(1)-C(13)-C(12)	119.9(3)
C(15)-Ir(1)-C(13)-C(12)	81.2(2)
C(11)-Ir(1)-C(13)-C(12)	36.9(2)
O(1)-Ir(1)-C(13)-C(12)	-146.08(18)
C(1)-Ir(1)-C(13)-C(14)	13.3(4)
O(2)-Ir(1)-C(13)-C(14)	175.52(17)
C(15)-Ir(1)-C(13)-C(14)	-38.7(2)
C(11)-Ir(1)-C(13)-C(14)	-83.1(2)
O(1)-Ir(1)-C(13)-C(14)	94.00(19)
C(12)-Ir(1)-C(13)-C(14)	-119.9(3)
C(1)-Ir(1)-C(13)-C(18)	-103.3(4)
O(2)-Ir(1)-C(13)-C(18)	58.9(3)
C(14)-Ir(1)-C(13)-C(18)	-116.6(4)
C(15)-Ir(1)-C(13)-C(18)	-155.3(3)
C(11)-Ir(1)-C(13)-C(18)	160.3(3)
O(1)-Ir(1)-C(13)-C(18)	-22.6(3)
C(12)-Ir(1)-C(13)-C(18)	123.5(4)
C(12)-C(13)-C(14)-C(15)	3.1(4)
C(18)-C(13)-C(14)-C(15)	-178.6(3)
Ir(1)-C(13)-C(14)-C(15)	63.1(2)
C(12)-C(13)-C(14)-C(19)	177.7(3)
C(18)-C(13)-C(14)-C(19)	-4.0(5)
Ir(1)-C(13)-C(14)-C(19)	-122.4(4)
C(12)-C(13)-C(14)-Ir(1)	-59.9(2)
C(18)-C(13)-C(14)-Ir(1)	118.4(3)
C(1)-Ir(1)-C(14)-C(15)	69.9(2)
O(2)-Ir(1)-C(14)-C(15)	-126.0(3)
C(11)-Ir(1)-C(14)-C(15)	-38.0(2)
O(1)-Ir(1)-C(14)-C(15)	150.82(19)
C(13)-Ir(1)-C(14)-C(15)	-116.1(3)
C(12)-Ir(1)-C(14)-C(15)	-80.9(2)
C(1)-Ir(1)-C(14)-C(13)	-173.98(17)
O(2)-Ir(1)-C(14)-C(13)	-9.9(4)
C(15)-Ir(1)-C(14)-C(13)	116.1(3)
C(11)-Ir(1)-C(14)-C(13)	78.1(2)
O(1)-Ir(1)-C(14)-C(13)	-93.05(18)

C(12)-Ir(1)-C(14)-C(13)	35.19(18)
C(1)-Ir(1)-C(14)-C(19)	-53.5(4)
O(2)-Ir(1)-C(14)-C(19)	110.6(4)
C(15)-Ir(1)-C(14)-C(19)	-123.4(4)
C(11)-Ir(1)-C(14)-C(19)	-161.4(4)
O(1)-Ir(1)-C(14)-C(19)	27.4(4)
C(13)-Ir(1)-C(14)-C(19)	120.5(4)
C(12)-Ir(1)-C(14)-C(19)	155.7(4)
C(13)-C(14)-C(15)-C(11)	-5.0(4)
C(19)-C(14)-C(15)-C(11)	-179.2(3)
Ir(1)-C(14)-C(15)-C(11)	60.3(2)
C(13)-C(14)-C(15)-C(20)	174.0(3)
C(19)-C(14)-C(15)-C(20)	-0.2(6)
Ir(1)-C(14)-C(15)-C(20)	-120.7(4)
C(13)-C(14)-C(15)-Ir(1)	-65.3(2)
C(19)-C(14)-C(15)-Ir(1)	120.5(4)
C(12)-C(11)-C(15)-C(14)	5.0(4)
C(16)-C(11)-C(15)-C(14)	176.0(3)
Ir(1)-C(11)-C(15)-C(14)	-60.4(2)
C(12)-C(11)-C(15)-C(20)	-174.1(3)
C(16)-C(11)-C(15)-C(20)	-3.0(6)
Ir(1)-C(11)-C(15)-C(20)	120.6(4)
C(12)-C(11)-C(15)-Ir(1)	65.3(2)
C(16)-C(11)-C(15)-Ir(1)	-123.6(4)
C(1)-Ir(1)-C(15)-C(14)	-122.4(2)
O(2)-Ir(1)-C(15)-C(14)	140.1(2)
C(11)-Ir(1)-C(15)-C(14)	118.4(3)
O(1)-Ir(1)-C(15)-C(14)	-40.7(2)
C(13)-Ir(1)-C(15)-C(14)	38.74(19)
C(12)-Ir(1)-C(15)-C(14)	79.6(2)
C(1)-Ir(1)-C(15)-C(11)	119.1(2)
O(2)-Ir(1)-C(15)-C(11)	21.7(3)
C(14)-Ir(1)-C(15)-C(11)	-118.4(3)
O(1)-Ir(1)-C(15)-C(11)	-159.13(17)
C(13)-Ir(1)-C(15)-C(11)	-79.7(2)
C(12)-Ir(1)-C(15)-C(11)	-38.8(2)

C(1)-Ir(1)-C(15)-C(20)	-1.7(4)
O(2)-Ir(1)-C(15)-C(20)	-99.2(4)
C(14)-Ir(1)-C(15)-C(20)	120.7(4)
C(11)-Ir(1)-C(15)-C(20)	-120.8(5)
O(1)-Ir(1)-C(15)-C(20)	80.1(4)
C(13)-Ir(1)-C(15)-C(20)	159.5(4)
C(12)-Ir(1)-C(15)-C(20)	-159.6(4)
C(1)-Ir(1)-O(2)-C(21)	-83.4(3)
C(14)-Ir(1)-O(2)-C(21)	110.7(4)
C(15)-Ir(1)-O(2)-C(21)	18.0(4)
C(11)-Ir(1)-O(2)-C(21)	32.6(3)
O(1)-Ir(1)-O(2)-C(21)	-161.4(3)
C(13)-Ir(1)-O(2)-C(21)	103.7(3)
C(12)-Ir(1)-O(2)-C(21)	70.6(3)
Ir(1)-O(2)-C(21)-O(3)	5.6(6)
Ir(1)-O(2)-C(21)-C(22)	-173.0(2)
O(3)-C(21)-C(22)-F(3)	16.1(6)
O(2)-C(21)-C(22)-F(3)	-165.1(3)
O(3)-C(21)-C(22)-F(2)	140.6(4)
O(2)-C(21)-C(22)-F(2)	-40.6(5)
O(3)-C(21)-C(22)-F(1)	-102.4(4)
O(2)-C(21)-C(22)-F(1)	76.5(4)

Symmetry transformations used to generate equivalent atoms:

Crystallographic data of 6 (Scheme 3)

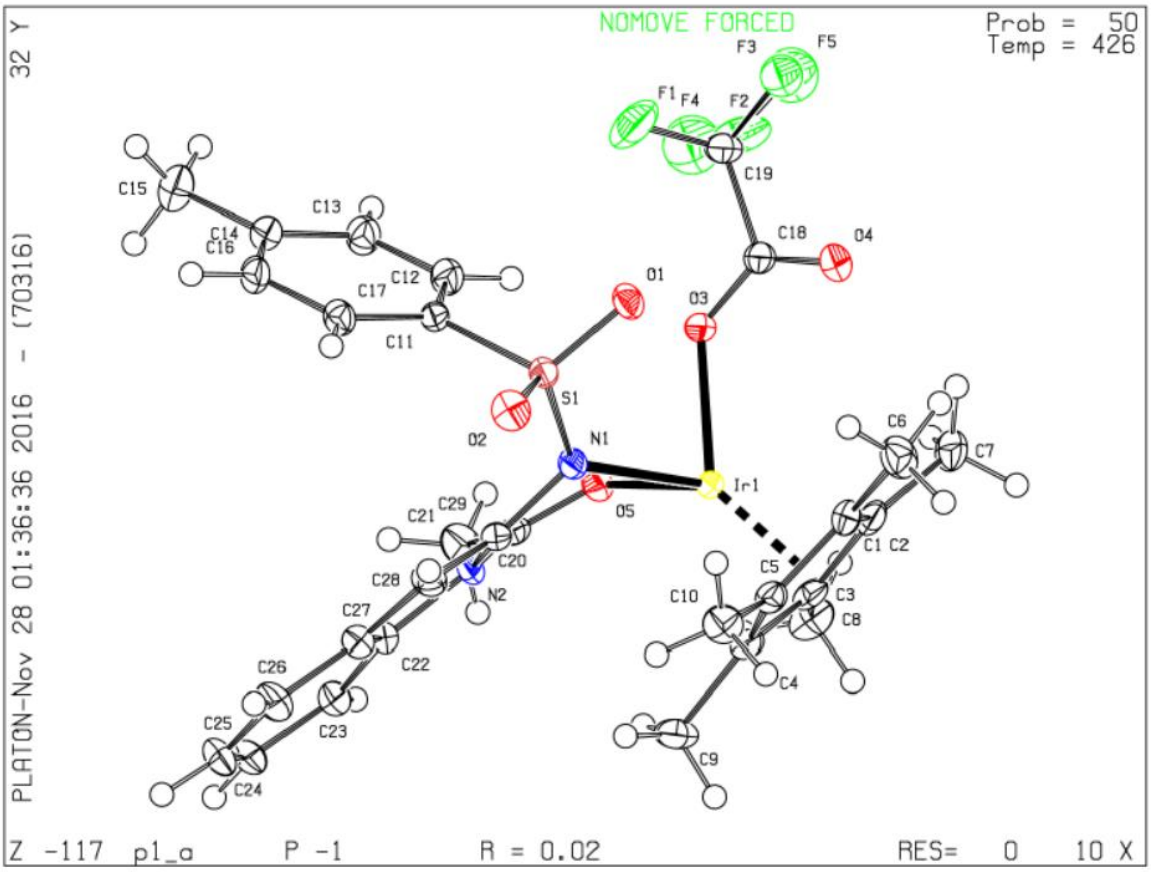


Table S19. Crystal data and structure refinement for **6**.

Identification code	p1_a	
Empirical formula	C29 H30 F3 Ir N2 O5 S	
Formula weight	767.81	
Temperature	426(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6211(3) Å	α= 81.373(2)°.
	b = 10.9933(4) Å	β= 79.858(2)°.
	c = 14.5750(4) Å	γ = 67.962(2)°.
Volume	1400.64(8) $Å^3$	
Z	2	
Density (calculated)	1.821 Mg/m^3	
Absorption coefficient	4.904 mm^{-1}	
F(000)	756	
Crystal size	0.210 x 0.160 x 0.110 mm^3	
Theta range for data collection	2.852 to 27.971°.	
Index ranges	-12<=h<=12, -14<=k<=14, -19<=l<=19	
Reflections collected	128466	
Independent reflections	6734 [R(int) = 0.0487]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5084	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6734 / 0 / 380	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0574	
R indices (all data)	R1 = 0.0263, wR2 = 0.0597	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.039 and -1.022 $e.Å^{-3}$	

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	3066(1)	2600(1)	7630(1)	14(1)
C(1)	3112(4)	879(3)	8540(2)	20(1)
C(2)	2407(4)	892(3)	7734(2)	20(1)
C(3)	1109(3)	2074(3)	7698(2)	21(1)
C(4)	974(3)	2797(3)	8481(2)	20(1)
C(5)	2194(3)	2043(3)	9006(2)	19(1)
C(6)	4411(4)	-226(3)	8904(3)	28(1)
C(7)	2935(4)	-158(3)	7072(3)	26(1)
C(8)	69(4)	2487(4)	6979(3)	33(1)
C(9)	-282(4)	4048(4)	8727(2)	27(1)
C(10)	2506(4)	2425(4)	9873(2)	25(1)
C(11)	6069(3)	4861(3)	7392(2)	17(1)
C(12)	5959(4)	4843(3)	6453(2)	23(1)
C(13)	6222(4)	5813(3)	5801(2)	25(1)
C(14)	6588(4)	6808(3)	6073(2)	23(1)
C(15)	6854(5)	7858(4)	5356(3)	32(1)
C(16)	6668(4)	6821(3)	7015(2)	23(1)
C(17)	6397(4)	5856(3)	7683(2)	21(1)
C(18)	6009(4)	1112(3)	6503(2)	21(1)
C(19)	7252(4)	1194(4)	5681(3)	27(1)
C(20)	1763(3)	5456(3)	6799(2)	18(1)
C(21)	947(4)	6427(4)	6059(2)	30(1)
C(22)	1017(3)	7134(3)	7957(2)	19(1)
C(23)	-211(4)	8183(3)	7660(2)	23(1)
C(24)	-738(4)	9315(3)	8143(3)	28(1)
C(25)	-75(4)	9378(3)	8891(3)	30(1)
C(26)	1104(4)	8300(4)	9217(3)	29(1)
C(27)	1643(4)	7162(3)	8747(2)	22(1)
C(28)	2794(4)	5905(3)	8930(2)	22(1)
C(29)	2915(3)	5128(3)	8262(2)	16(1)
F(1)	7846(4)	2048(3)	5776(2)	58(1)

N(1)	3940(3)	3884(2)	8071(2)	17(1)
N(2)	1830(3)	5865(2)	7622(2)	16(1)
O(1)	6572(2)	2346(2)	7913(2)	22(1)
O(2)	5802(3)	3881(2)	9120(2)	24(1)
O(3)	4888(2)	2199(2)	6540(2)	19(1)
O(4)	6249(3)	77(2)	6984(2)	29(1)
O(5)	2346(2)	4282(2)	6629(2)	18(1)
S(1)	5662(1)	3629(1)	8204(1)	16(1)
F(3)	8524(5)	60(5)	5760(3)	31(1)
F(2)	6818(6)	1210(7)	4901(3)	38(1)
F(4)	6661(9)	1851(8)	4863(6)	61(2)
F(5)	8227(7)	84(6)	5403(5)	53(1)

Table S21. Bond lengths [Å] and angles [°] for **6**.

Ir(1)-O(3)	2.108(2)
Ir(1)-N(1)	2.114(2)
Ir(1)-C(4)	2.124(3)
Ir(1)-C(5)	2.128(3)
Ir(1)-C(1)	2.132(3)
Ir(1)-O(5)	2.148(2)
Ir(1)-C(3)	2.149(3)
Ir(1)-C(2)	2.172(3)
C(1)-C(5)	1.443(4)
C(1)-C(2)	1.451(4)
C(1)-C(6)	1.490(4)
C(2)-C(3)	1.427(5)
C(2)-C(7)	1.498(4)
C(3)-C(4)	1.447(5)
C(3)-C(8)	1.481(5)
C(4)-C(5)	1.431(4)
C(4)-C(9)	1.493(4)
C(5)-C(10)	1.499(4)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(17)	1.386(4)

C(11)-C(12)	1.394(4)
C(11)-S(1)	1.773(3)
C(12)-C(13)	1.385(5)
C(12)-H(12)	0.9300
C(13)-C(14)	1.395(5)
C(13)-H(13)	0.9300
C(14)-C(16)	1.391(5)
C(14)-C(15)	1.502(5)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(17)	1.397(5)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(18)-O(4)	1.208(4)
C(18)-O(3)	1.275(4)
C(18)-C(19)	1.555(4)
C(19)-F(5)	1.299(7)
C(19)-F(2)	1.274(6)
C(19)-F(1)	1.302(4)
C(19)-F(3)	1.388(6)
C(19)-F(4)	1.393(9)
C(20)-O(5)	1.242(4)
C(20)-N(2)	1.361(4)
C(20)-C(21)	1.499(4)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-C(23)	1.386(4)
C(22)-C(27)	1.399(5)
C(22)-N(2)	1.431(4)
C(23)-C(24)	1.401(5)
C(23)-H(23)	0.9300
C(24)-C(25)	1.380(6)
C(24)-H(24)	0.9300
C(25)-C(26)	1.388(5)

C(25)-H(25)	0.9300
C(26)-C(27)	1.396(4)
C(26)-H(26)	0.9300
C(27)-C(28)	1.432(4)
C(28)-C(29)	1.351(4)
C(28)-H(28)	0.9300
C(29)-N(1)	1.388(4)
C(29)-N(2)	1.449(4)
N(1)-S(1)	1.615(3)
O(1)-S(1)	1.435(2)
O(2)-S(1)	1.442(2)
O(3)-Ir(1)-N(1)	87.38(9)
O(3)-Ir(1)-C(4)	164.23(11)
N(1)-Ir(1)-C(4)	107.45(11)
O(3)-Ir(1)-C(5)	147.57(10)
N(1)-Ir(1)-C(5)	94.43(11)
C(4)-Ir(1)-C(5)	39.32(12)
O(3)-Ir(1)-C(1)	112.04(10)
N(1)-Ir(1)-C(1)	117.10(11)
C(4)-Ir(1)-C(1)	66.46(12)
C(5)-Ir(1)-C(1)	39.61(12)
O(3)-Ir(1)-O(5)	77.01(8)
N(1)-Ir(1)-O(5)	78.80(9)
C(4)-Ir(1)-O(5)	100.17(10)
C(5)-Ir(1)-O(5)	135.13(10)
C(1)-Ir(1)-O(5)	161.15(11)
O(3)-Ir(1)-C(3)	124.78(11)
N(1)-Ir(1)-C(3)	145.57(11)
C(4)-Ir(1)-C(3)	39.57(12)
C(5)-Ir(1)-C(3)	65.68(12)
C(1)-Ir(1)-C(3)	65.70(12)
O(5)-Ir(1)-C(3)	95.49(11)
O(3)-Ir(1)-C(2)	102.53(10)
N(1)-Ir(1)-C(2)	156.45(11)
C(4)-Ir(1)-C(2)	65.88(12)
C(5)-Ir(1)-C(2)	65.78(12)

C(1)-Ir(1)-C(2)	39.38(12)
O(5)-Ir(1)-C(2)	124.02(10)
C(3)-Ir(1)-C(2)	38.55(12)
C(5)-C(1)-C(2)	107.6(3)
C(5)-C(1)-C(6)	125.5(3)
C(2)-C(1)-C(6)	126.3(3)
C(5)-C(1)-Ir(1)	70.03(17)
C(2)-C(1)-Ir(1)	71.81(17)
C(6)-C(1)-Ir(1)	130.3(2)
C(3)-C(2)-C(1)	107.6(3)
C(3)-C(2)-C(7)	126.3(3)
C(1)-C(2)-C(7)	126.1(3)
C(3)-C(2)-Ir(1)	69.84(17)
C(1)-C(2)-Ir(1)	68.81(17)
C(7)-C(2)-Ir(1)	127.5(2)
C(2)-C(3)-C(4)	108.8(3)
C(2)-C(3)-C(8)	125.5(3)
C(4)-C(3)-C(8)	125.7(3)
C(2)-C(3)-Ir(1)	71.61(17)
C(4)-C(3)-Ir(1)	69.28(17)
C(8)-C(3)-Ir(1)	125.4(2)
C(5)-C(4)-C(3)	107.4(3)
C(5)-C(4)-C(9)	126.8(3)
C(3)-C(4)-C(9)	125.7(3)
C(5)-C(4)-Ir(1)	70.48(17)
C(3)-C(4)-Ir(1)	71.15(17)
C(9)-C(4)-Ir(1)	127.1(2)
C(4)-C(5)-C(1)	108.5(3)
C(4)-C(5)-C(10)	125.8(3)
C(1)-C(5)-C(10)	125.7(3)
C(4)-C(5)-Ir(1)	70.20(17)
C(1)-C(5)-Ir(1)	70.36(17)
C(10)-C(5)-Ir(1)	123.4(2)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5

C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(17)-C(11)-C(12)	120.9(3)
C(17)-C(11)-S(1)	121.4(2)
C(12)-C(11)-S(1)	117.7(2)
C(13)-C(12)-C(11)	119.5(3)
C(13)-C(12)-H(12)	120.3
C(11)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	120.8(3)
C(12)-C(13)-H(13)	119.6
C(14)-C(13)-H(13)	119.6

C(16)-C(14)-C(13)	118.9(3)
C(16)-C(14)-C(15)	121.2(3)
C(13)-C(14)-C(15)	119.9(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-C(17)	121.1(3)
C(14)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(11)-C(17)-C(16)	118.9(3)
C(11)-C(17)-H(17)	120.6
C(16)-C(17)-H(17)	120.6
O(4)-C(18)-O(3)	131.5(3)
O(4)-C(18)-C(19)	117.1(3)
O(3)-C(18)-C(19)	111.4(3)
F(5)-C(19)-F(2)	79.8(5)
F(5)-C(19)-F(1)	114.4(4)
F(2)-C(19)-F(1)	119.1(4)
F(5)-C(19)-F(3)	26.8(3)
F(2)-C(19)-F(3)	106.5(4)
F(1)-C(19)-F(3)	98.3(3)
F(5)-C(19)-F(4)	102.7(5)
F(2)-C(19)-F(4)	28.2(4)
F(1)-C(19)-F(4)	94.5(4)
F(3)-C(19)-F(4)	127.2(5)
F(5)-C(19)-C(18)	116.8(4)
F(2)-C(19)-C(18)	110.3(3)
F(1)-C(19)-C(18)	112.8(3)
F(3)-C(19)-C(18)	108.5(3)
F(4)-C(19)-C(18)	112.9(4)
O(5)-C(20)-N(2)	122.6(3)
O(5)-C(20)-C(21)	117.1(3)
N(2)-C(20)-C(21)	120.3(3)

C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(27)	121.6(3)
C(23)-C(22)-N(2)	131.6(3)
C(27)-C(22)-N(2)	106.8(3)
C(22)-C(23)-C(24)	117.3(3)
C(22)-C(23)-H(23)	121.3
C(24)-C(23)-H(23)	121.3
C(25)-C(24)-C(23)	121.4(3)
C(25)-C(24)-H(24)	119.3
C(23)-C(24)-H(24)	119.3
C(24)-C(25)-C(26)	121.0(3)
C(24)-C(25)-H(25)	119.5
C(26)-C(25)-H(25)	119.5
C(25)-C(26)-C(27)	118.4(3)
C(25)-C(26)-H(26)	120.8
C(27)-C(26)-H(26)	120.8
C(26)-C(27)-C(22)	120.1(3)
C(26)-C(27)-C(28)	131.1(3)
C(22)-C(27)-C(28)	108.8(3)
C(29)-C(28)-C(27)	108.6(3)
C(29)-C(28)-H(28)	125.7
C(27)-C(28)-H(28)	125.7
C(28)-C(29)-N(1)	131.4(3)
C(28)-C(29)-N(2)	108.6(3)
N(1)-C(29)-N(2)	119.7(3)
C(29)-N(1)-S(1)	114.6(2)
C(29)-N(1)-Ir(1)	116.50(19)
S(1)-N(1)-Ir(1)	128.87(14)
C(20)-N(2)-C(22)	127.6(3)
C(20)-N(2)-C(29)	124.8(2)
C(22)-N(2)-C(29)	107.1(2)

C(18)-O(3)-Ir(1)	124.1(2)
C(20)-O(5)-Ir(1)	126.5(2)
O(1)-S(1)-O(2)	116.54(14)
O(1)-S(1)-N(1)	107.00(13)
O(2)-S(1)-N(1)	112.95(14)
O(1)-S(1)-C(11)	110.10(14)
O(2)-S(1)-C(11)	107.23(15)
N(1)-S(1)-C(11)	102.07(14)

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	13(1)	14(1)	16(1)	-2(1)	-1(1)	-6(1)
C(1)	23(2)	16(1)	21(1)	2(1)	-2(1)	-9(1)
C(2)	22(2)	21(2)	23(2)	-1(1)	-1(1)	-14(1)
C(3)	16(1)	27(2)	24(2)	-2(1)	0(1)	-14(1)
C(4)	17(1)	21(2)	22(1)	1(1)	2(1)	-8(1)
C(5)	19(1)	19(1)	19(1)	1(1)	0(1)	-8(1)
C(6)	30(2)	19(2)	29(2)	2(1)	-6(1)	-4(1)
C(7)	30(2)	26(2)	31(2)	-8(1)	-2(1)	-17(1)
C(8)	33(2)	43(2)	28(2)	-2(2)	-1(1)	-22(2)
C(9)	18(2)	29(2)	26(2)	-2(1)	3(1)	-2(1)
C(10)	30(2)	28(2)	18(1)	-2(1)	-3(1)	-10(1)
C(11)	13(1)	14(1)	24(1)	-2(1)	-2(1)	-5(1)
C(12)	26(2)	22(2)	23(2)	-6(1)	-1(1)	-11(1)
C(13)	31(2)	24(2)	22(2)	-4(1)	-1(1)	-13(1)
C(14)	21(2)	20(2)	30(2)	-3(1)	0(1)	-9(1)
C(15)	39(2)	28(2)	33(2)	2(1)	-5(2)	-19(2)
C(16)	22(2)	18(2)	32(2)	-4(1)	-4(1)	-10(1)
C(17)	19(1)	19(1)	27(2)	-5(1)	-6(1)	-6(1)
C(18)	19(1)	23(2)	26(2)	-11(1)	2(1)	-12(1)
C(19)	20(2)	28(2)	34(2)	-13(1)	7(1)	-10(1)
C(20)	15(1)	20(1)	18(1)	-1(1)	1(1)	-7(1)
C(21)	37(2)	25(2)	22(2)	1(1)	-6(1)	-3(2)
C(22)	19(1)	14(1)	25(2)	-4(1)	2(1)	-7(1)
C(23)	20(2)	18(2)	29(2)	-2(1)	-1(1)	-5(1)
C(24)	23(2)	15(2)	38(2)	-3(1)	4(1)	-2(1)
C(25)	33(2)	17(2)	35(2)	-11(1)	6(2)	-6(1)
C(26)	31(2)	24(2)	31(2)	-13(1)	2(1)	-9(1)
C(27)	21(2)	20(2)	25(2)	-6(1)	2(1)	-8(1)
C(28)	20(2)	22(2)	23(2)	-7(1)	-2(1)	-7(1)
C(29)	13(1)	16(1)	20(1)	-2(1)	-1(1)	-5(1)
F(1)	69(2)	74(2)	54(2)	-31(2)	28(1)	-60(2)

N(1)	14(1)	16(1)	22(1)	-5(1)	-2(1)	-6(1)
N(2)	15(1)	12(1)	22(1)	-3(1)	-2(1)	-3(1)
O(1)	18(1)	15(1)	33(1)	-4(1)	-6(1)	-3(1)
O(2)	25(1)	26(1)	22(1)	-3(1)	-10(1)	-9(1)
O(3)	17(1)	19(1)	21(1)	-6(1)	2(1)	-7(1)
O(4)	26(1)	17(1)	41(1)	-6(1)	1(1)	-7(1)
O(5)	21(1)	16(1)	18(1)	-3(1)	-3(1)	-6(1)
S(1)	14(1)	15(1)	20(1)	-3(1)	-4(1)	-4(1)
F(2)	39(3)	76(4)	11(2)	-18(2)	9(2)	-33(3)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6**.

	x	y	z	U(eq)
H(6A)	4048	-678	9453	41
H(6B)	5112	117	9060	41
H(6C)	4908	-830	8434	41
H(7A)	2458	-792	7293	40
H(7B)	4013	-588	7037	40
H(7C)	2673	234	6462	40
H(8A)	567	2030	6433	49
H(8B)	-218	3420	6816	49
H(8C)	-818	2279	7223	49
H(9A)	-1131	3851	9069	41
H(9B)	-574	4598	8164	41
H(9C)	53	4501	9106	41
H(10A)	2066	3365	9883	38
H(10B)	3578	2141	9874	38
H(10C)	2072	2013	10415	38
H(12)	5711	4186	6267	27
H(13)	6153	5801	5174	30
H(15A)	5980	8653	5397	48
H(15B)	7036	7569	4742	48
H(15C)	7718	8024	5470	48
H(16)	6905	7484	7203	28
H(17)	6436	5880	8313	25
H(21A)	1319	6077	5461	45
H(21B)	1114	7238	6041	45
H(21C)	-117	6588	6200	45
H(23)	-667	8137	7160	28
H(24)	-1553	10039	7954	34
H(25)	-422	10155	9182	36
H(26)	1524	8336	9736	35
H(28)	3363	5665	9425	26

Table S24. Torsion angles [°] for **6**.

C(5)-C(1)-C(2)-C(3)	1.9(3)
C(6)-C(1)-C(2)-C(3)	173.6(3)
Ir(1)-C(1)-C(2)-C(3)	-59.3(2)
C(5)-C(1)-C(2)-C(7)	-177.1(3)
C(6)-C(1)-C(2)-C(7)	-5.4(5)
Ir(1)-C(1)-C(2)-C(7)	121.7(3)
C(5)-C(1)-C(2)-Ir(1)	61.2(2)
C(6)-C(1)-C(2)-Ir(1)	-127.1(3)
C(1)-C(2)-C(3)-C(4)	-0.9(3)
C(7)-C(2)-C(3)-C(4)	178.1(3)
Ir(1)-C(2)-C(3)-C(4)	-59.5(2)
C(1)-C(2)-C(3)-C(8)	179.4(3)
C(7)-C(2)-C(3)-C(8)	-1.6(5)
Ir(1)-C(2)-C(3)-C(8)	120.8(3)
C(1)-C(2)-C(3)-Ir(1)	58.6(2)
C(7)-C(2)-C(3)-Ir(1)	-122.4(3)
C(2)-C(3)-C(4)-C(5)	-0.5(3)
C(8)-C(3)-C(4)-C(5)	179.2(3)
Ir(1)-C(3)-C(4)-C(5)	-61.5(2)
C(2)-C(3)-C(4)-C(9)	-176.3(3)
C(8)-C(3)-C(4)-C(9)	3.3(5)
Ir(1)-C(3)-C(4)-C(9)	122.7(3)
C(2)-C(3)-C(4)-Ir(1)	61.0(2)
C(8)-C(3)-C(4)-Ir(1)	-119.3(3)
C(3)-C(4)-C(5)-C(1)	1.7(3)
C(9)-C(4)-C(5)-C(1)	177.5(3)
Ir(1)-C(4)-C(5)-C(1)	-60.2(2)
C(3)-C(4)-C(5)-C(10)	179.4(3)
C(9)-C(4)-C(5)-C(10)	-4.9(5)
Ir(1)-C(4)-C(5)-C(10)	117.5(3)
C(3)-C(4)-C(5)-Ir(1)	61.9(2)
C(9)-C(4)-C(5)-Ir(1)	-122.3(3)
C(2)-C(1)-C(5)-C(4)	-2.3(3)
C(6)-C(1)-C(5)-C(4)	-174.0(3)

Ir(1)-C(1)-C(5)-C(4)	60.1(2)
C(2)-C(1)-C(5)-C(10)	-179.9(3)
C(6)-C(1)-C(5)-C(10)	8.3(5)
Ir(1)-C(1)-C(5)-C(10)	-117.6(3)
C(2)-C(1)-C(5)-Ir(1)	-62.4(2)
C(6)-C(1)-C(5)-Ir(1)	125.9(3)
C(17)-C(11)-C(12)-C(13)	1.8(5)
S(1)-C(11)-C(12)-C(13)	178.0(3)
C(11)-C(12)-C(13)-C(14)	-0.3(5)
C(12)-C(13)-C(14)-C(16)	-0.8(5)
C(12)-C(13)-C(14)-C(15)	-179.4(3)
C(13)-C(14)-C(16)-C(17)	0.4(5)
C(15)-C(14)-C(16)-C(17)	179.0(3)
C(12)-C(11)-C(17)-C(16)	-2.1(5)
S(1)-C(11)-C(17)-C(16)	-178.2(2)
C(14)-C(16)-C(17)-C(11)	1.0(5)
O(4)-C(18)-C(19)-F(5)	19.1(6)
O(3)-C(18)-C(19)-F(5)	-160.9(4)
O(4)-C(18)-C(19)-F(2)	107.7(5)
O(3)-C(18)-C(19)-F(2)	-72.3(5)
O(4)-C(18)-C(19)-F(1)	-116.4(4)
O(3)-C(18)-C(19)-F(1)	63.6(4)
O(4)-C(18)-C(19)-F(3)	-8.6(5)
O(3)-C(18)-C(19)-F(3)	171.4(3)
O(4)-C(18)-C(19)-F(4)	137.9(5)
O(3)-C(18)-C(19)-F(4)	-42.1(5)
C(27)-C(22)-C(23)-C(24)	4.4(5)
N(2)-C(22)-C(23)-C(24)	-179.3(3)
C(22)-C(23)-C(24)-C(25)	-0.8(5)
C(23)-C(24)-C(25)-C(26)	-2.6(6)
C(24)-C(25)-C(26)-C(27)	2.4(5)
C(25)-C(26)-C(27)-C(22)	1.2(5)
C(25)-C(26)-C(27)-C(28)	-178.0(3)
C(23)-C(22)-C(27)-C(26)	-4.6(5)
N(2)-C(22)-C(27)-C(26)	178.2(3)
C(23)-C(22)-C(27)-C(28)	174.7(3)

N(2)-C(22)-C(27)-C(28)	-2.4(3)
C(26)-C(27)-C(28)-C(29)	-179.1(4)
C(22)-C(27)-C(28)-C(29)	1.7(4)
C(27)-C(28)-C(29)-N(1)	173.1(3)
C(27)-C(28)-C(29)-N(2)	-0.2(3)
C(28)-C(29)-N(1)-S(1)	-38.6(4)
N(2)-C(29)-N(1)-S(1)	134.1(2)
C(28)-C(29)-N(1)-Ir(1)	142.4(3)
N(2)-C(29)-N(1)-Ir(1)	-44.9(3)
O(5)-C(20)-N(2)-C(22)	-169.4(3)
C(21)-C(20)-N(2)-C(22)	9.7(5)
O(5)-C(20)-N(2)-C(29)	19.6(5)
C(21)-C(20)-N(2)-C(29)	-161.2(3)
C(23)-C(22)-N(2)-C(20)	13.3(5)
C(27)-C(22)-N(2)-C(20)	-170.0(3)
C(23)-C(22)-N(2)-C(29)	-174.5(3)
C(27)-C(22)-N(2)-C(29)	2.3(3)
C(28)-C(29)-N(2)-C(20)	171.2(3)
N(1)-C(29)-N(2)-C(20)	-3.0(4)
C(28)-C(29)-N(2)-C(22)	-1.3(3)
N(1)-C(29)-N(2)-C(22)	-175.5(3)
O(4)-C(18)-O(3)-Ir(1)	7.3(5)
C(19)-C(18)-O(3)-Ir(1)	-172.74(19)
N(2)-C(20)-O(5)-Ir(1)	16.5(4)
C(21)-C(20)-O(5)-Ir(1)	-162.7(2)
C(29)-N(1)-S(1)-O(1)	-175.8(2)
Ir(1)-N(1)-S(1)-O(1)	3.1(2)
C(29)-N(1)-S(1)-O(2)	54.7(3)
Ir(1)-N(1)-S(1)-O(2)	-126.47(18)
C(29)-N(1)-S(1)-C(11)	-60.1(2)
Ir(1)-N(1)-S(1)-C(11)	118.74(19)
C(17)-C(11)-S(1)-O(1)	-129.6(3)
C(12)-C(11)-S(1)-O(1)	54.2(3)
C(17)-C(11)-S(1)-O(2)	-1.9(3)
C(12)-C(11)-S(1)-O(2)	-178.1(2)
C(17)-C(11)-S(1)-N(1)	117.1(3)

C(12)-C(11)-S(1)-N(1)	-59.1(3)

Symmetry transformations used to generate equivalent atoms:

Table S25. Hydrogen bonds for **6.** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(28)-H(28)...O(2)#1	0.93	2.57	3.428(4)	153.5
C(28)-H(28)...O(2)	0.93	2.45	2.944(4)	113.5
C(12)-H(12)...O(3)	0.93	2.55	3.409(4)	154.5
C(12)-H(12)...F(1)	0.93	2.57	3.132(4)	119.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Crystallographic data of 18 (Scheme 4)

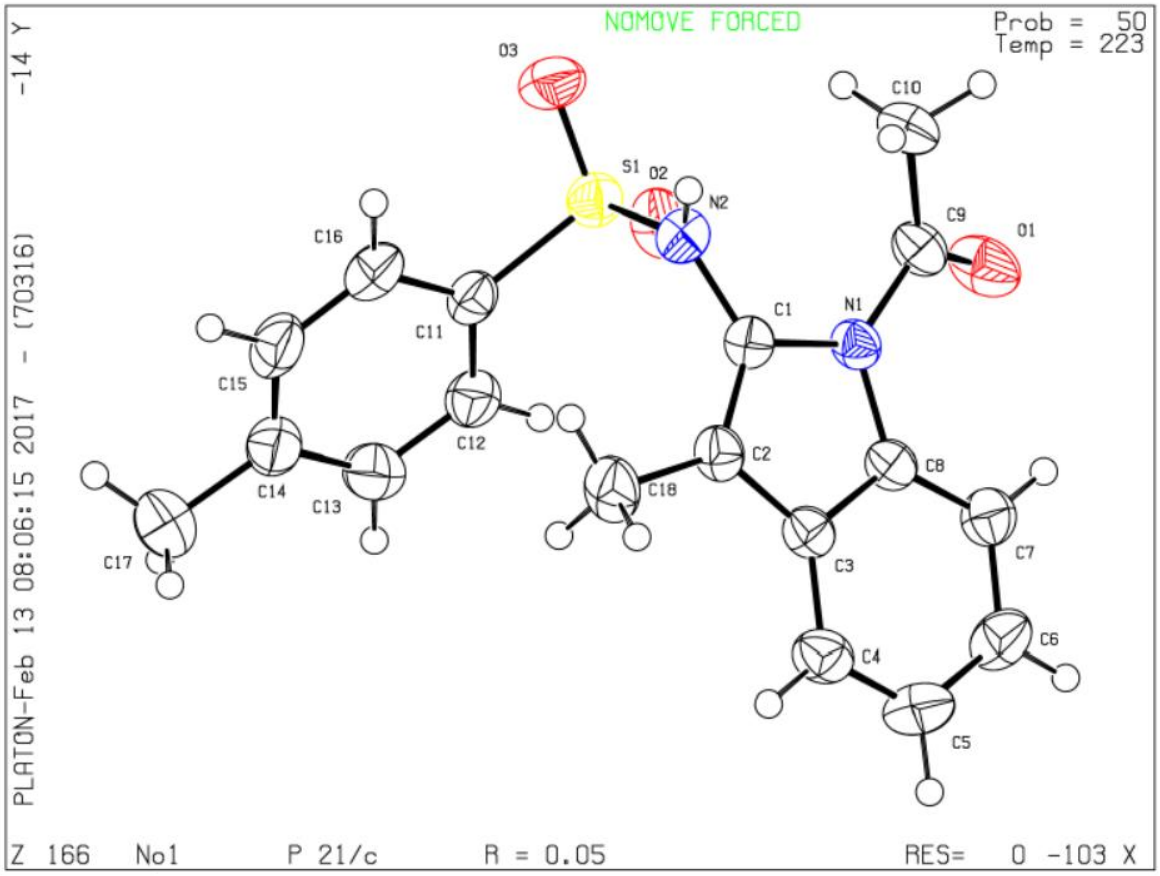


Table S26. Crystal data and structure refinement for **18**

Identification code	No1	
Empirical formula	$C_{18}\ H_{18}\ N_2\ O_3\ S$	
Formula weight	342.40	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.1548(8) Å	α= 90°.
	b = 5.2806(2) Å	β= 97.2991(19)°.
	c = 18.3203(8) Å	γ = 90°.
Volume	1646.14(12) $Å^3$	
Z	4	
Density (calculated)	1.382 Mg/m^3	
Absorption coefficient	0.216 mm^{-1}	
F(000)	720	
Crystal size	0.210 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.242 to 28.355°.	
Index ranges	-22<=h<=22, -7<=k<=7, -24<=l<=24	
Reflections collected	71612	
Independent reflections	4095 [R(int) = 0.0654]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Bruker SADABS	
Max. and min. transmission	0.7457 and 0.7134	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4095 / 0 / 220	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1096	
R indices (all data)	R1 = 0.0693, wR2 = 0.1230	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.368 and -0.364 e.$Å^{-3}$	

Table S27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **18**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1335(1)	5357(3)	1071(1)	33(1)
C(1)	1889(1)	7355(3)	1114(1)	32(1)
C(2)	2099(1)	7867(3)	443(1)	35(1)
C(3)	1669(1)	6157(3)	-64(1)	34(1)
C(4)	1654(1)	5815(4)	-823(1)	44(1)
C(5)	1188(1)	3931(4)	-1161(1)	51(1)
C(6)	734(1)	2397(4)	-763(1)	49(1)
C(7)	740(1)	2689(4)	-13(1)	42(1)
C(8)	1217(1)	4575(3)	330(1)	33(1)
C(9)	950(1)	4324(3)	1634(1)	37(1)
C(10)	832(1)	5957(4)	2278(1)	44(1)
O(1)	704(1)	2183(3)	1571(1)	55(1)
N(2)	2215(1)	8304(3)	1805(1)	37(1)
S(1)	2941(1)	6747(1)	2268(1)	39(1)
O(2)	2738(1)	4118(3)	2202(1)	49(1)
O(3)	3077(1)	7916(3)	2973(1)	56(1)
C(11)	3781(1)	7191(3)	1825(1)	37(1)
C(12)	3977(1)	5431(4)	1321(1)	46(1)
C(13)	4661(1)	5740(5)	1004(1)	54(1)
C(14)	5152(1)	7792(5)	1177(1)	52(1)
C(15)	4935(1)	9546(4)	1672(1)	51(1)
C(16)	4260(1)	9281(4)	1998(1)	46(1)
C(17)	5908(2)	8068(7)	851(2)	82(1)
C(18)	2676(1)	9797(4)	258(1)	49(1)

Table S28. Bond lengths [Å] and angles [°] for **18**.

N(1)-C(9)	1.404(2)
N(1)-C(8)	1.409(2)
N(1)-C(1)	1.416(2)
C(1)-C(2)	1.351(2)
C(1)-N(2)	1.411(2)
C(2)-C(3)	1.431(3)
C(2)-C(18)	1.489(3)
C(3)-C(4)	1.399(3)
C(3)-C(8)	1.401(2)
C(4)-C(5)	1.374(3)
C(4)-H(4)	0.9400
C(5)-C(6)	1.393(3)
C(5)-H(5)	0.9400
C(6)-C(7)	1.380(3)
C(6)-H(6)	0.9400
C(7)-C(8)	1.387(3)
C(7)-H(7)	0.9400
C(9)-O(1)	1.208(2)
C(9)-C(10)	1.495(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-H(10C)	0.9700
N(2)-S(1)	1.6359(16)
N(2)-H(2N)	0.8700
S(1)-O(3)	1.4239(15)
S(1)-O(2)	1.4324(15)
S(1)-C(11)	1.757(2)
C(11)-C(12)	1.381(3)
C(11)-C(16)	1.389(3)
C(12)-C(13)	1.383(3)
C(12)-H(12)	0.9400
C(13)-C(14)	1.384(3)
C(13)-H(13)	0.9400
C(14)-C(15)	1.380(3)

C(14)-C(17)	1.502(3)
C(15)-C(16)	1.376(3)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700

C(9)-N(1)-C(8)	124.78(15)
C(9)-N(1)-C(1)	128.61(15)
C(8)-N(1)-C(1)	106.59(14)
C(2)-C(1)-N(2)	128.69(16)
C(2)-C(1)-N(1)	110.68(15)
N(2)-C(1)-N(1)	120.09(15)
C(1)-C(2)-C(3)	106.81(15)
C(1)-C(2)-C(18)	127.27(18)
C(3)-C(2)-C(18)	125.92(17)
C(4)-C(3)-C(8)	119.57(17)
C(4)-C(3)-C(2)	132.00(17)
C(8)-C(3)-C(2)	108.39(15)
C(5)-C(4)-C(3)	118.54(18)
C(5)-C(4)-H(4)	120.7
C(3)-C(4)-H(4)	120.7
C(4)-C(5)-C(6)	121.11(19)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(7)-C(6)-C(5)	121.50(19)
C(7)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2
C(6)-C(7)-C(8)	117.41(18)
C(6)-C(7)-H(7)	121.3
C(8)-C(7)-H(7)	121.3
C(7)-C(8)-C(3)	121.86(17)

C(7)-C(8)-N(1)	130.65(16)
C(3)-C(8)-N(1)	107.46(15)
O(1)-C(9)-N(1)	119.02(17)
O(1)-C(9)-C(10)	122.34(17)
N(1)-C(9)-C(10)	118.60(16)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(1)-N(2)-S(1)	118.42(12)
C(1)-N(2)-H(2N)	120.8
S(1)-N(2)-H(2N)	120.8
O(3)-S(1)-O(2)	120.42(10)
O(3)-S(1)-N(2)	106.17(9)
O(2)-S(1)-N(2)	106.43(8)
O(3)-S(1)-C(11)	108.18(9)
O(2)-S(1)-C(11)	107.16(9)
N(2)-S(1)-C(11)	107.95(8)
C(12)-C(11)-C(16)	120.04(18)
C(12)-C(11)-S(1)	120.19(14)
C(16)-C(11)-S(1)	119.75(15)
C(11)-C(12)-C(13)	119.49(19)
C(11)-C(12)-H(12)	120.3
C(13)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	121.4(2)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(15)-C(14)-C(13)	117.9(2)
C(15)-C(14)-C(17)	121.0(2)
C(13)-C(14)-C(17)	121.1(2)
C(16)-C(15)-C(14)	122.01(19)
C(16)-C(15)-H(15)	119.0
C(14)-C(15)-H(15)	119.0
C(15)-C(16)-C(11)	119.2(2)

C(15)-C(16)-H(16)	120.4
C(11)-C(16)-H(16)	120.4
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(2)-C(18)-H(18A)	109.5
C(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S29. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **18**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	35(1)	31(1)	34(1)	3(1)	8(1)	-4(1)
C(1)	33(1)	28(1)	35(1)	3(1)	3(1)	0(1)
C(2)	34(1)	33(1)	38(1)	8(1)	4(1)	-2(1)
C(3)	36(1)	33(1)	35(1)	5(1)	6(1)	2(1)
C(4)	50(1)	47(1)	36(1)	9(1)	9(1)	0(1)
C(5)	69(1)	52(1)	33(1)	-1(1)	4(1)	1(1)
C(6)	57(1)	44(1)	44(1)	-4(1)	-2(1)	-7(1)
C(7)	45(1)	38(1)	44(1)	1(1)	6(1)	-7(1)
C(8)	35(1)	31(1)	34(1)	3(1)	7(1)	1(1)
C(9)	39(1)	34(1)	41(1)	6(1)	12(1)	1(1)
C(10)	49(1)	46(1)	39(1)	4(1)	16(1)	1(1)
O(1)	76(1)	37(1)	57(1)	4(1)	29(1)	-12(1)
N(2)	39(1)	33(1)	38(1)	-1(1)	2(1)	2(1)
S(1)	40(1)	42(1)	35(1)	5(1)	2(1)	0(1)
O(2)	46(1)	41(1)	60(1)	15(1)	7(1)	-1(1)
O(3)	57(1)	74(1)	34(1)	-2(1)	1(1)	4(1)
C(11)	36(1)	38(1)	34(1)	3(1)	-3(1)	-4(1)
C(12)	49(1)	43(1)	44(1)	-6(1)	5(1)	-13(1)
C(13)	58(1)	60(1)	46(1)	-8(1)	14(1)	-10(1)
C(14)	46(1)	68(1)	40(1)	6(1)	2(1)	-16(1)
C(15)	49(1)	53(1)	48(1)	3(1)	-6(1)	-19(1)
C(16)	52(1)	42(1)	41(1)	-4(1)	-5(1)	-6(1)
C(17)	64(2)	119(3)	66(2)	-6(2)	22(1)	-34(2)
C(18)	46(1)	49(1)	53(1)	16(1)	5(1)	-13(1)

Table S30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **18**.

	x	y	z	U(eq)
H(4)	1956	6851	-1096	53
H(5)	1175	3673	-1670	62
H(6)	416	1134	-1009	59
H(7)	433	1651	254	51
H(10A)	354	5454	2470	66
H(10B)	791	7714	2123	66
H(10C)	1276	5763	2658	66
H(2N)	2035	9684	1982	44
H(12)	3648	4034	1194	55
H(13)	4795	4532	665	65
H(15)	5257	10965	1789	62
H(16)	4125	10499	2335	55
H(17A)	5815	9037	399	123
H(17B)	6107	6404	747	123
H(17C)	6292	8939	1198	123
H(18A)	2834	10848	685	74
H(18B)	2436	10847	-144	74
H(18C)	3133	8953	111	74

Table S31. Torsion angles [°] for **18**.

C(9)-N(1)-C(1)-C(2)	-177.34(17)
C(8)-N(1)-C(1)-C(2)	1.38(19)
C(9)-N(1)-C(1)-N(2)	10.3(3)
C(8)-N(1)-C(1)-N(2)	-170.94(15)
N(2)-C(1)-C(2)-C(3)	171.64(17)
N(1)-C(1)-C(2)-C(3)	0.2(2)
N(2)-C(1)-C(2)-C(18)	-7.3(3)
N(1)-C(1)-C(2)-C(18)	-178.83(18)
C(1)-C(2)-C(3)-C(4)	-179.5(2)
C(18)-C(2)-C(3)-C(4)	-0.5(3)
C(1)-C(2)-C(3)-C(8)	-1.7(2)
C(18)-C(2)-C(3)-C(8)	177.34(18)
C(8)-C(3)-C(4)-C(5)	0.4(3)
C(2)-C(3)-C(4)-C(5)	178.1(2)
C(3)-C(4)-C(5)-C(6)	0.4(3)
C(4)-C(5)-C(6)-C(7)	-0.6(3)
C(5)-C(6)-C(7)-C(8)	0.0(3)
C(6)-C(7)-C(8)-C(3)	0.9(3)
C(6)-C(7)-C(8)-N(1)	178.60(19)
C(4)-C(3)-C(8)-C(7)	-1.1(3)
C(2)-C(3)-C(8)-C(7)	-179.30(17)
C(4)-C(3)-C(8)-N(1)	-179.30(16)
C(2)-C(3)-C(8)-N(1)	2.5(2)
C(9)-N(1)-C(8)-C(7)	-1.6(3)
C(1)-N(1)-C(8)-C(7)	179.65(19)
C(9)-N(1)-C(8)-C(3)	176.41(16)
C(1)-N(1)-C(8)-C(3)	-2.37(19)
C(8)-N(1)-C(9)-O(1)	25.4(3)
C(1)-N(1)-C(9)-O(1)	-156.14(18)
C(8)-N(1)-C(9)-C(10)	-152.32(17)
C(1)-N(1)-C(9)-C(10)	26.2(3)
C(2)-C(1)-N(2)-S(1)	-90.1(2)
N(1)-C(1)-N(2)-S(1)	80.69(19)
C(1)-N(2)-S(1)-O(3)	-172.27(14)

C(1)-N(2)-S(1)-O(2)	-42.84(16)
C(1)-N(2)-S(1)-C(11)	71.92(15)
O(3)-S(1)-C(11)-C(12)	150.59(16)
O(2)-S(1)-C(11)-C(12)	19.36(18)
N(2)-S(1)-C(11)-C(12)	-94.92(17)
O(3)-S(1)-C(11)-C(16)	-27.57(18)
O(2)-S(1)-C(11)-C(16)	-158.80(15)
N(2)-S(1)-C(11)-C(16)	86.92(16)
C(16)-C(11)-C(12)-C(13)	1.4(3)
S(1)-C(11)-C(12)-C(13)	-176.72(16)
C(11)-C(12)-C(13)-C(14)	-0.6(3)
C(12)-C(13)-C(14)-C(15)	-0.7(3)
C(12)-C(13)-C(14)-C(17)	177.9(2)
C(13)-C(14)-C(15)-C(16)	1.0(3)
C(17)-C(14)-C(15)-C(16)	-177.5(2)
C(14)-C(15)-C(16)-C(11)	-0.2(3)
C(12)-C(11)-C(16)-C(15)	-1.1(3)
S(1)-C(11)-C(16)-C(15)	177.10(15)

Symmetry transformations used to generate equivalent atoms:

Appendix III

Cartesian Coordinates of DFT-Optimized Structures

I

E(RM06) = -1356.66174110
# of negative frequency = 0

C	2.11003	-2.98362	0.93845
C	2.37342	-4.31947	1.29140
C	2.95058	-5.18144	0.36093
C	3.24324	-4.69134	-0.90435
C	2.96358	-3.36357	-1.24060
C	2.39309	-2.48150	-0.32725
C	1.40315	-3.34990	3.08830
C	1.92117	-4.51313	2.64923
H	3.15967	-6.21567	0.62252
H	3.69141	-5.34789	-1.64523
H	3.19699	-3.00617	-2.24011
H	0.96570	-3.09961	4.04385
H	1.98151	-5.43031	3.22089
N	1.49844	-2.37323	2.06583
C	0.98646	-1.12059	2.12282
O	1.16589	-0.35836	1.15080
Ir	-0.11862	1.24903	0.46023
C	1.25135	2.87442	0.09161
C	-0.74789	3.14813	1.27078
C	-1.07030	3.05209	-0.14208
C	0.17895	2.92819	-0.86529
C	0.67525	3.02326	1.41794
C	-2.42828	3.15019	-0.73990
C	-1.75686	3.26625	2.35519
C	1.46079	3.06978	2.68004
C	2.70253	2.72189	-0.19466
C	0.29128	2.77618	-2.33793
H	-0.46451	2.08162	-2.71978
H	1.27317	2.39796	-2.63381
H	0.13819	3.74539	-2.82833
H	3.18314	2.07249	0.54461
H	3.20825	3.69498	-0.16680
H	2.87447	2.28071	-1.18054
H	2.25400	2.31390	2.68131
H	0.83310	2.90360	3.56046
H	1.93921	4.05034	2.79488
H	-1.31705	3.10423	3.34314
H	-2.56162	2.53486	2.21869
H	-2.20701	4.26643	2.34759
H	-2.67611	4.19048	-0.98445
H	-3.18894	2.77529	-0.04781
H	-2.49564	2.56073	-1.65979
C	0.23522	-0.71729	3.34958
H	2.17084	-1.45646	-0.59933
C	-1.54787	-0.81956	-0.03548
O	-1.64253	-0.18992	1.07261
O	-0.74757	-0.33175	-0.89585
C	-2.27108	-2.12086	-0.26887
H	-0.04718	0.33434	3.26675
H	-0.68267	-1.30891	3.44295
H	0.83864	-0.86444	4.25112
C	-3.56403	-2.16222	0.53997
H	-4.05639	-3.13026	0.39177
H	-3.37389	-2.03302	1.61054
H	-4.26140	-1.37835	0.22214
C	-1.31252	-3.22106	0.21453
H	-1.10283	-3.12629	1.28965
H	-1.77177	-4.20280	0.05000
H	-0.36184	-3.18997	-0.33350
C	-2.55498	-2.30474	-1.75744
H	-1.63299	-2.29229	-2.34659
H	-3.05302	-3.26815	-1.91612
H	-3.21622	-1.51794	-2.13893

II

E(RM06) = -1356.63655649
# of negative frequency = 0

C	-3.07261	-1.22365	0.50145
C	-2.71704	-1.68445	-0.79154
C	-3.69760	-1.82937	-1.78305
C	-5.00365	-1.50124	-1.47132
C	-5.33561	-1.03384	-0.18974
C	-4.38560	-0.88077	0.81250
C	-0.80268	-1.53517	0.42348
C	-1.30909	-1.90219	-0.80375
H	-3.42792	-2.19595	-2.77078
H	-5.78551	-1.61035	-2.21718
H	-6.37197	-0.79269	0.03205
H	0.08656	-1.93207	0.90809
H	-0.70365	-2.32523	-1.59830
N	-1.89375	-1.14315	1.25656
C	-1.58997	-0.28437	2.30147
O	-0.48672	0.26984	2.29111
Ir	0.33277	0.51654	0.10467
C	-2.58468	-0.05268	3.38066
H	-3.26776	0.75091	3.07356
H	-3.17368	-0.94742	3.59737
H	-2.06021	0.28549	4.27653
H	-4.68179	-0.53401	1.79732
C	2.38434	-1.50062	-0.17858
O	1.83765	-1.69780	-1.26422
O	1.93538	-0.64815	0.70855
C	3.64993	-2.23361	0.26144
H	-1.06328	0.07109	-3.19796
H	0.65665	-0.37389	-3.10500
H	0.15177	1.07508	-4.00454
C	-0.04586	0.46630	-3.11314
H	-2.66537	0.84093	-1.82734
C	0.12309	1.28829	-1.88757
C	-2.39722	1.77928	-1.33032
H	2.74497	0.35082	-2.31420
H	-2.72753	2.60287	-1.97528
C	-0.93490	1.87167	-1.07131
C	2.73035	1.36536	-1.90434
H	2.98373	2.07091	-2.70559
H	-2.97576	1.83415	-0.40096
C	1.39596	1.69779	-1.34460
H	3.50901	1.43358	-1.13815
C	-0.30527	2.59496	-0.01151
C	1.14003	2.48179	-0.15709
H	-2.03102	3.01134	1.19586
C	-0.98383	3.31452	1.09721
C	2.16833	3.10127	0.71834
H	3.03242	2.43859	0.83453
H	-0.96604	4.39598	0.91444
H	-0.48353	3.12838	2.05354
H	2.52107	4.04962	0.29388
H	1.77209	3.30581	1.71728
C	4.76109	-1.19894	0.46042
H	5.68390	-1.69992	0.77742
H	4.98029	-0.67016	-0.47740
H	4.48947	-0.46274	1.22512
C	3.36877	-2.95213	1.58321
H	4.25878	-3.50885	1.90091
H	3.10350	-2.24396	2.37485
H	2.54973	-3.67620	1.47375
C	4.06341	-3.23926	-0.80476
H	4.25853	-2.74605	-1.76317
H	4.97716	-3.75776	-0.49017
H	3.28231	-3.98878	-0.97177

II-TS

E(RM06) = -1356.63388710
# of negative frequency = 1

C	3.30426	1.00878	0.19710
C	3.31723	0.90233	-1.21580
C	4.52674	0.99343	-1.91788
C	5.69388	1.17466	-1.20088
C	5.66578	1.26651	0.19897
C	4.48156	1.18452	0.92057
C	1.12900	0.68343	-0.55544
C	1.97261	0.71764	-1.64663
H	4.53832	0.92165	-3.00237
H	6.64499	1.24920	-1.72018
H	6.59823	1.41045	0.73835
H	1.63814	0.68535	-2.67836
N	1.97216	0.87239	0.60151
C	1.37534	0.84764	1.82852
O	0.21247	0.41265	1.91005
Ir	-0.52637	-0.62594	0.06371
C	-2.01847	-2.19886	-0.28251
C	0.12717	-2.63763	0.54444
C	0.24299	-2.44143	-0.86523
C	-1.07564	-2.09632	-1.38123
C	-1.28098	-2.48602	0.90883
C	1.49174	-2.59298	-1.65667
C	1.23227	-2.98144	1.47943
C	-1.81134	-2.61104	2.29177
C	-3.47100	-1.91079	-0.38825
C	-1.43999	-1.84051	-2.80058

H	-0.59085	-1.44900	-3.36946
H	-2.24986	-1.10641	-2.86845
H	-1.77669	-2.76224	-3.29162
H	-3.92764	-1.77426	0.59557
H	-3.98682	-2.73392	-0.89730
H	-3.64326	-0.99195	-0.96016
H	-2.82810	-2.21778	2.37121
H	-1.18702	-2.05600	3.00057
H	-1.82679	-3.66192	2.60626
H	1.01408	-2.63932	2.49646
H	2.17552	-2.52186	1.16227
H	1.38657	-4.06680	1.52167
H	2.36702	-2.23138	-1.10575
H	1.44354	-2.05532	-2.60796
H	1.65581	-3.65318	-1.88645
H	4.49833	1.26508	2.00189
C	2.09748	1.32497	3.03685
H	2.84790	0.58486	3.34151
H	2.60861	2.27399	2.84898
H	1.37877	1.44128	3.84912
C	-1.83220	2.10020	-0.15129
O	-0.72020	2.61676	-0.37425
O	-2.01707	0.84164	0.03855
C	-3.09967	2.94980	-0.18280
H	0.24321	1.49543	-0.57393
C	-2.76595	4.40686	0.11774
H	-3.67868	5.01145	0.05875
H	-2.34979	4.52136	1.12550
H	-2.03806	4.80651	-0.59452
C	-3.64101	2.82405	-1.61353
H	-3.88327	1.78121	-1.85595
H	-4.55719	3.41815	-1.71421
H	-2.91331	3.19582	-2.34512
C	-4.13345	2.42543	0.81002
H	-5.03448	3.04852	0.76280
H	-4.41856	1.39171	0.58835
H	-3.75489	2.46199	1.83860

III

E(RM06) = -1356.64508704
# of negative frequency = 0

C	2.06395	-1.63332	0.10010
C	3.14692	-1.81853	-0.77248
C	2.88743	-2.13720	-2.10838
C	1.56750	-2.23977	-2.54347
C	0.50309	-2.11078	-1.64979
C	0.72401	-1.81891	-0.28823
C	3.98828	-1.34771	1.27018
C	4.35318	-1.63709	0.00163
H	3.70851	-2.30472	-2.80196
H	1.36390	-2.47594	-3.58456
H	-0.52441	-2.24734	-1.97949
H	4.59253	-1.14066	2.14288
H	5.37027	-1.72612	-0.35716
N	2.57515	-1.31805	1.35892
C	1.84611	-0.66401	2.33440
O	0.73343	-0.19765	2.08242
Ir	-0.05551	0.45056	0.01232
C	1.06094	2.32358	-0.01395
C	-1.11394	2.11456	-0.86529
C	-0.19178	1.55229	-1.82201
C	1.16177	1.72840	-1.30396
C	-0.35111	2.54912	0.28208
C	-0.56695	1.00593	-3.15148
C	-2.58680	2.19762	-1.02603
C	-0.89930	3.15613	1.52188
C	2.18881	2.64572	0.90017
C	2.41238	1.38725	-2.02883
H	2.30433	0.46292	-2.60607
H	3.25765	1.25790	-1.34497
H	2.66894	2.18962	-2.73190
H	1.88612	2.56626	1.94956
H	2.53617	3.67310	0.73518
H	3.04221	1.97772	0.73493
H	-0.28115	2.91060	2.39134
H	-1.91077	2.79012	1.72414
H	-0.94306	4.24902	1.43490
H	-3.09634	2.19955	-0.05722
H	-2.96456	1.35154	-1.60728
H	-2.84856	3.12749	-1.54658
H	-0.82965	1.82393	-3.83420
H	-1.42788	0.33679	-3.05468
H	0.25743	0.44409	-3.60057
C	2.46880	-0.51067	3.68029
H	-0.05523	-2.03509	0.44265
C	-2.58452	-1.03639	-0.11552
O	-1.71007	-0.55956	0.73384
O	-2.44146	-1.00248	-1.33627
C	-3.82884	-1.61802	0.55557
H	1.69043	-0.24738	4.39790
H	2.98070	-1.42277	3.99964
H	3.20391	0.30422	3.65879
C	-3.41900	-2.57926	1.67162
H	-4.31363	-3.01402	2.13394
H	-2.81489	-3.40835	1.27913
H	-2.84160	-2.06908	2.44894
C	-4.68171	-2.34419	-0.47663
H	-4.13820	-3.18393	-0.92410
H	-5.58650	-2.73827	0.00171
H	-4.98121	-1.67397	-1.28866
C	-4.61693	-0.44361	1.14595
H	-4.92337	0.25987	0.35959
H	-5.52841	-0.81272	1.63178
H	-4.02469	0.09808	1.89301

III-TS

E(RM06) = -1356.63245504
# of negative frequency = 1

C	1.98733	-1.48984	-0.34276
C	3.24295	-1.84792	-0.85760
C	3.52652	-1.57667	-2.19798
C	2.54570	-0.98321	-2.98832
C	1.29742	-0.66565	-2.45306
C	0.96540	-0.89600	-1.10194
C	3.19251	-2.52332	1.29390
C	3.98367	-2.49004	0.20159
H	4.48945	-1.84985	-2.62280
H	2.74577	-0.79487	-4.03998
H	0.52708	-0.25922	-3.10778
H	3.38723	-2.92197	2.27932
H	4.98807	-2.88787	0.13773
N	1.95663	-1.89903	1.00303
C	0.94454	-1.66968	1.89769
O	0.00554	-0.90137	1.65203
Ir	-0.13934	0.66403	0.05989
C	1.38499	2.21575	-0.16629
C	-0.50221	2.47522	1.20715
C	-0.91550	2.68293	-0.15400
C	0.23183	2.48411	-1.01374
C	0.92629	2.18885	1.18807
C	-2.29642	2.97550	-0.61543
C	-1.36490	2.54268	2.41679
C	1.75760	1.89200	2.38434
C	2.78982	2.05595	-0.62698
C	0.26144	2.69749	-2.48537
H	-0.66504	2.35724	-2.95908
H	1.09498	2.16479	-2.95278
H	0.37863	3.76528	-2.70953
H	3.37935	1.45847	0.07597
H	3.27284	3.03677	-0.71711
H	2.84312	1.56584	-1.60419
H	2.62449	1.27438	2.12352
H	1.17928	1.36644	3.15140
H	2.13239	2.82112	2.83114
H	-1.03627	1.82872	3.17942
H	-2.40449	2.30246	2.17348
H	-1.34326	3.54469	2.86279
H	-3.04494	2.54206	0.05399
H	-2.47567	2.56851	-1.61515
H	-2.45819	4.05958	-0.65636
C	1.01090	-2.35758	3.22130
H	1.20916	-3.42775	3.11076
H	1.81049	-1.92481	3.83501
H	0.06011	-2.21081	3.73480
H	-0.16235	-1.41065	-0.96901
C	-2.25007	-1.39786	-0.51965
O	-2.04402	-0.18535	-0.16083
O	-1.34122	-2.17331	-0.89154
C	-3.68013	-1.91038	-0.41187
C	-3.72730	-2.70710	0.89961
H	-4.74111	-3.09343	1.05887
H	-3.03668	-3.55738	0.86926
H	-3.46718	-2.07271	1.75725
C	-4.68120	-0.76188	-0.35528

H	-4.62888	-0.13825	-1.25601
H	-5.69775	-1.16636	-0.28377
H	-4.50660	-0.11902	0.51426
C	-3.98953	-2.83098	-1.59011
H	-4.99638	-3.24924	-1.47386
H	-3.96169	-2.28558	-2.54122
H	-3.27543	-3.65737	-1.65068

IV

E(RM06) = -1356.66837307
# of negative frequency = 0

C	3.44494	-0.13819	0.09106
C	3.33017	-0.06121	-1.31111
C	4.46907	0.14628	-2.08715
C	5.69687	0.27344	-1.45110
C	5.79291	0.19615	-0.06007
C	4.66893	-0.01105	0.73531
C	1.20524	-0.40030	-0.51144
C	1.93393	-0.22956	-1.64980
H	4.39336	0.20770	-3.17003
H	6.59497	0.43716	-2.04038
H	6.76334	0.30159	0.41728
H	1.53241	-0.22843	-2.65883
N	2.13323	-0.34396	0.58389
C	1.64204	-0.56849	1.82443
O	0.41304	-0.77641	1.94947
Ir	-0.71537	-0.64522	0.09010
C	-2.23174	-0.75945	-1.41119
C	-2.54297	-1.88529	0.60519
C	-1.52922	-2.59817	-0.17705
C	-1.42470	-1.95354	-1.46559
C	-2.97178	-0.77495	-0.14613
C	-0.87662	-3.86712	0.24085
C	-2.94129	-2.26852	1.98544
C	-3.91215	0.29605	0.27314
C	-2.44117	0.22479	-2.50921
C	-0.63971	-2.43927	-2.63008
H	0.24490	-3.00347	-2.32048
H	-0.30504	-1.61405	-3.26645
H	-1.26296	-3.09961	-3.24562
H	-2.63279	1.22739	-2.10856
H	-3.29973	-0.05281	-3.13354
H	-1.56100	0.29188	-3.15757
H	-3.46921	1.28403	0.09832
H	-4.16462	0.22785	1.33451
H	-4.84322	0.24414	-0.30435
H	-3.51246	-1.47912	2.48084
H	-2.05954	-2.47881	2.60127
H	-3.55864	-3.17526	1.97066
H	-0.64846	-3.85487	1.31197
H	0.06102	-4.03240	-0.29831
H	-1.53452	-4.72424	0.04922
H	4.77581	-0.06145	1.81325
C	2.52559	-0.58225	3.01874
H	3.30536	-1.34431	2.91138
H	3.01854	0.38792	3.14510
H	1.92313	-0.79888	3.90144
C	-0.50654	2.50747	0.04027
O	0.19889	2.45452	-1.06415
O	-0.76706	1.50789	0.72292
C	-1.02942	3.88340	0.38628
H	0.55534	1.54448	-1.19007
C	-2.16607	4.17102	-0.60862
H	-2.57135	5.16950	-0.40901
H	-1.81177	4.14714	-1.64510
H	-2.99178	3.45472	-0.49699
C	-1.56413	3.90239	1.81308
H	-0.77398	3.68405	2.54002
H	-1.96317	4.89819	2.03482
H	-2.36583	3.17101	1.95918
C	0.07997	4.92358	0.21471
H	-0.31618	5.91314	0.46828
H	0.92525	4.72150	0.88297
H	0.45224	4.95512	-0.81340

V

E(RM06) = -1356.66062279
# of negative frequency = 0

C	-1.39601	-1.93953	-0.43876
C	-2.24332	-2.82238	-1.13615
C	-2.37639	-2.69837	-2.51760
C	-1.66237	-1.69077	-3.15179
C	-0.80683	-0.84794	-2.43352
C	-0.61829	-0.94676	-1.04294
C	-2.38466	-3.37080	1.05138
C	-2.83710	-3.71563	-0.17054
H	-3.02945	-3.36301	-3.07681
H	-1.76201	-1.55460	-4.22591
H	-0.26423	-0.07622	-2.97951
H	-2.60804	-3.79526	2.01975
H	-3.52887	-4.52097	-0.38149
N	-1.50044	-2.27272	0.93728
C	-0.98547	-1.56187	1.97252
O	-0.28634	-0.54606	1.80337
Ir	0.76702	0.14201	0.00980
C	2.46501	-0.47798	-1.17016
C	2.80380	0.30656	1.02520
C	2.64686	1.42968	0.19619
C	2.36114	0.96053	-1.16461
C	2.61184	-0.89422	0.20406
C	2.65112	2.86482	0.58370
C	3.01482	0.27551	2.49697
C	2.75307	-2.29328	0.69204
C	2.44856	-1.37922	-2.35100
C	2.22558	1.85821	-2.34436
H	1.52817	2.67842	-2.13864
H	1.85975	1.32104	-3.22438
H	3.19420	2.30279	-2.60668
H	1.95717	-2.33084	-2.12567
H	3.47896	-1.59458	-2.66009
H	1.93019	-0.93339	-3.20450
H	2.17633	-2.98774	0.07164
H	2.39624	-2.38570	1.72428
H	3.80222	-2.61516	0.67472
H	2.20684	-0.27233	2.99751
H	3.04729	1.28089	2.92478
H	3.95879	-0.22603	2.74265
H	3.48411	3.39214	0.10237
H	2.74631	2.99712	1.66455
H	1.72208	3.35475	0.26689
C	-1.28047	-2.01729	3.36548
H	-2.09020	0.40935	-0.68398
C	-1.79026	2.09992	0.09562
O	-0.57758	1.90899	0.24427
O	-2.60388	1.19649	-0.39348
C	-2.41540	3.44258	0.40280
H	-0.76070	-1.35992	4.06302
H	-2.35533	-1.97894	3.57229
H	-0.94541	-3.04825	3.52268
C	-1.78555	4.02399	1.66693
H	-2.20172	5.02079	1.85038
H	-2.00296	3.40336	2.54419
H	-0.69927	4.11717	1.57275
C	-3.92906	3.33608	0.56010
H	-4.40698	2.95598	-0.34775
H	-4.20253	2.67596	1.39097
H	-4.33746	4.33062	0.77142
C	-2.07554	4.32914	-0.80702
H	-2.50032	3.92240	-1.73285
H	-2.50016	5.32743	-0.65187
H	-0.99087	4.43325	-0.93100

I'

E(RM06) = -1536.43273267
# of negative frequency = 0

C	3.02847	-2.23508	1.49951
C	3.94476	-2.98950	2.25422
C	5.17643	-3.33717	1.70376
C	5.46499	-2.92680	0.40911
C	4.53865	-2.18622	-0.32991
C	3.30140	-1.82648	0.19836
C	2.12355	-2.68623	3.55883
C	3.34175	-3.25900	3.53865
H	5.89145	-3.92125	2.27744
H	6.41828	-3.19159	-0.04013
H	4.78095	-1.89282	-1.34816
H	1.37233	-2.67788	4.33515
H	3.78426	-3.82619	4.34733
N	1.88688	-2.03310	2.32245
C	0.79610	-1.29252	2.01694
O	0.72358	-0.79255	0.87442
Ir	-0.33877	0.91641	0.11331
C	1.16769	2.31168	-0.48983

C	-0.39986	2.78405	1.17896
C	-1.06240	2.92148	-0.11224
C	-0.08768	2.65278	-1.13539
C	0.97049	2.42446	0.94066
C	-2.48647	3.30405	-0.29765
C	-1.07376	2.97622	2.48933
C	2.00623	2.13572	1.96687
C	2.44756	1.98497	-1.17200
C	-0.32997	2.62904	-2.59932
H	-1.39121	2.50360	-2.83040
H	0.21099	1.80655	-3.07801
H	0.00913	3.56819	-3.05354
H	3.03983	1.27098	-0.58983
H	3.05247	2.88987	-1.30912
H	2.27376	1.54641	-2.15916
H	2.66630	1.32060	1.64878
H	1.55957	1.85590	2.92624
H	2.63098	3.02080	2.13687
H	-0.47542	2.59179	3.32002
H	-2.04588	2.46980	2.50553
H	-1.25235	4.04307	2.67226
H	-2.60736	4.38889	-0.18827
H	-3.12577	2.81784	0.44668
H	-2.85634	3.02336	-1.28739
C	-0.25915	-1.10761	3.05674
H	2.57705	-1.27925	-0.39390
C	-2.01001	-0.91529	-0.49410
O	-2.15659	-0.27627	0.58455
O	-1.09979	-0.60172	-1.30182
C	-2.93524	-2.10305	-0.76365
H	-1.04627	-0.45927	2.66803
H	-0.71371	-2.07134	3.31388
H	0.16055	-0.68300	3.97534
F	-4.19868	-1.70888	-0.67798
F	-2.71808	-2.62482	-1.95521
F	-2.70977	-3.02738	0.16850

II’

E(RM06) = -1536.42055510
# of negative frequency = 0

C	-3.11401	-1.20488	0.50203
C	-2.78089	-1.68358	-0.79183
C	-3.77847	-1.83418	-1.76724
C	-5.07617	-1.49347	-1.43890
C	-5.38490	-1.00788	-0.15711
C	-4.41977	-0.84838	0.82880
C	-0.84478	-1.52262	0.39029
C	-1.37740	-1.90875	-0.82311
H	-3.52668	-2.21487	-2.75425
H	-5.87078	-1.60611	-2.17053
H	-6.41625	-0.75703	0.07694
H	0.02845	-1.95709	0.87131
H	-0.78894	-2.34950	-1.62116
N	-1.92506	-1.12055	1.23637
C	-1.60314	-0.27717	2.28678
O	-0.49690	0.27360	2.26403
Ir	0.31189	0.50388	0.10481
C	-2.57539	-0.05536	3.38695
H	-3.25440	0.76165	3.10719
H	-3.16988	-0.94780	3.59787
H	-2.03125	0.26088	4.27921
H	-4.69854	-0.48643	1.81319
C	2.35649	-1.51874	-0.16944
O	1.83567	-1.81721	-1.23288
O	1.92805	-0.67793	0.71189
C	3.70698	-2.12798	0.25026
H	-1.10089	0.04017	-3.18634
H	0.61727	-0.41379	-3.12870
H	0.10371	1.03664	-4.01577
C	-0.08031	0.43050	-3.11981
H	-2.68271	0.85090	-1.81224
C	0.11344	1.25621	-1.90010
C	-2.39537	1.78705	-1.32194
H	2.69260	0.34178	-2.46103
H	-2.71893	2.61312	-1.96703
C	-0.92948	1.85823	-1.07746
C	2.72424	1.29127	-1.92014
H	3.05711	2.07344	-2.61399
H	-2.96330	1.85557	-0.38692
C	1.39414	1.64929	-1.36644
H	3.47627	1.20572	-1.12949
C	-0.27937	2.59138	-0.03276
C	1.16025	2.45582	-0.18851
H	-1.98113	3.02198	1.20400
C	-0.94168	3.33705	1.06798
C	2.20811	3.07208	0.66487
H	3.06854	2.40385	0.77301
H	-0.94631	4.41119	0.84532
H	-0.41474	3.19520	2.01726
H	2.56269	4.01193	0.22315
H	1.83150	3.29230	1.66786
F	4.08798	-3.07937	-0.58332
F	3.63891	-2.63372	1.47821
F	4.63131	-1.16080	0.24380

II’-TS

E(RM06) = -1536.41344749
# of negative frequency = 1

C	3.34056	0.81413	0.21094
C	3.37760	0.62848	-1.19211
C	4.59925	0.66887	-1.87685
C	5.75539	0.88004	-1.14974
C	5.70313	1.05205	0.24145
C	4.50510	1.02229	0.94507
C	1.16674	0.49292	-0.56974
C	2.03768	0.43936	-1.63896
H	4.62945	0.53725	-2.95535
H	6.71617	0.91684	-1.65497
H	6.62686	1.21907	0.78905
H	1.72909	0.34997	-2.67542
N	1.99739	0.71939	0.59455
C	1.37557	0.77845	1.80304
O	0.18664	0.40681	1.87189
Ir	-0.58853	-0.61885	0.06874
C	-1.85296	-1.98164	-1.02848
C	-0.87434	-2.58334	0.99282
C	0.15820	-2.63167	-0.02518
C	-0.47219	-2.29876	-1.28819
C	-2.11016	-2.17966	0.38565
C	1.57289	-3.05532	0.16805
C	-0.66935	-2.83314	2.44221
C	-3.42556	-1.98437	1.05072
C	-2.86973	-1.56824	-2.02967
C	0.15916	-2.34236	-2.63336
H	1.25059	-2.32204	-2.57550
H	-0.16962	-1.50930	-3.26320
H	-0.12815	-3.27167	-3.14106
H	-3.55394	-0.82237	-1.61331
H	-3.46720	-2.43420	-2.34154
H	-2.40681	-1.13887	-2.92274
H	-3.90535	-1.06143	0.70889
H	-3.32633	-1.92420	2.13773
H	-4.09998	-2.81863	0.82046
H	-1.29310	-2.17537	3.05505
H	0.37272	-2.67760	2.73703
H	-0.93247	-3.87027	2.68403
H	1.91837	-2.83149	1.18303
H	2.24100	-2.53304	-0.52491
H	1.69222	-4.13341	0.00670
H	4.50411	1.16532	2.01999
C	2.08324	1.27614	3.01076
H	2.82307	0.53899	3.34581
H	2.60632	2.21516	2.80470
H	1.35337	1.42312	3.80789
C	-1.56816	2.21475	-0.24923
O	-0.42277	2.59657	-0.55189
O	-1.94237	1.03928	0.01462
C	-2.70726	3.25120	-0.22188
F	-3.53019	2.99706	-1.23831
F	-3.38902	3.14608	0.91228
F	-2.24591	4.48172	-0.33777
H	0.36016	1.44816	-0.67404

III’

E(RM06) = -1536.42992078
# of negative frequency = 0

C	2.10130	-1.62255	0.07553
C	3.19756	-1.78501	-0.78492
C	2.95821	-2.08933	-2.12778
C	1.64506	-2.20126	-2.58250
C	0.56781	-2.09833	-1.70156
C	0.76650	-1.81919	-0.33235
C	4.00787	-1.33500	1.27447

C	4.39210	-1.60179	0.00677
H	3.78934	-2.23981	-2.81319
H	1.45827	-2.42872	-3.62871
H	-0.45219	-2.25277	-2.04763
H	4.59898	-1.13149	2.15700
H	5.41442	-1.67409	-0.34064
N	2.59329	-1.32076	1.34486
C	1.84741	-0.68856	2.32199
O	0.73980	-0.21429	2.05966
Ir	-0.02573	0.42187	-0.00844
C	1.04977	2.30762	-0.02170
C	-1.12168	2.07211	-0.87018
C	-0.19459	1.53052	-1.83593
C	1.15768	1.72071	-1.31868
C	-0.36324	2.51752	0.27572
C	-0.56196	0.98964	-3.16975
C	-2.59962	2.11500	-1.00290
C	-0.91905	3.11271	1.51729
C	2.17397	2.62905	0.89643
C	2.41380	1.40459	-2.04450
H	2.30829	0.50721	-2.66258
H	3.25073	1.23977	-1.35810
H	2.68172	2.23618	-2.70811
H	1.87731	2.51538	1.94462
H	2.49954	3.66713	0.75670
H	3.03929	1.98202	0.71106
H	-0.32593	2.83442	2.39417
H	-1.94391	2.77306	1.69335
H	-0.93054	4.20777	1.45027
H	-3.09270	1.94329	-0.04038
H	-2.95986	1.35668	-1.70323
H	-2.90926	3.10195	-1.36844
H	-0.78632	1.81250	-3.86003
H	-1.44313	0.34466	-3.09688
H	0.25316	0.40144	-3.60126
C	2.44240	-0.56359	3.68208
H	-0.00967	-2.07849	0.38739
C	-2.55518	-1.04481	-0.12644
O	-1.70258	-0.58672	0.72669
O	-2.44262	-1.11501	-1.33889
C	-3.85906	-1.47405	0.57249
H	1.64503	-0.34367	4.39361
H	2.97326	-1.47093	3.98277
H	3.15412	0.27206	3.69851
F	-4.67261	-2.09850	-0.25894
F	-4.47389	-0.37331	1.02371
F	-3.61107	-2.26867	1.60998

III'-TS

E(RM06) = -1536.41152821
# of negative frequency = 1

C	2.01636	-1.43910	-0.31703
C	3.24841	-1.81231	-0.87575
C	3.45308	-1.62608	-2.24423
C	2.42087	-1.09834	-3.01616
C	1.19942	-0.76168	-2.43427
C	0.94284	-0.90816	-1.05339
C	3.33620	-2.32903	1.31771
C	4.06187	-2.36326	0.18151
H	4.39654	-1.91152	-2.70336
H	2.56046	-0.97624	-4.08704
H	0.39029	-0.40510	-3.07109
H	3.59500	-2.65123	2.31625
H	5.06925	-2.74732	0.08754
N	2.07093	-1.75022	1.05461
C	1.09976	-1.48826	1.98327
O	0.10994	-0.78833	1.72524
Ir	-0.16712	0.65572	0.05662
C	1.28658	2.22948	-0.27502
C	-0.60125	2.53349	1.09297
C	-1.02343	2.63247	-0.27771
C	0.12598	2.42349	-1.13159
C	0.82974	2.28605	1.08498
C	-2.41597	2.85264	-0.74298
C	-1.46590	2.65812	2.29653
C	1.67287	2.09454	2.29379
C	2.69503	2.07215	-0.72629
C	0.14077	2.55425	-2.61295
H	-0.76830	2.14166	-3.06243
H	0.99979	2.04151	-3.05538
H	0.20083	3.61281	-2.89554
H	3.29003	1.51116	0.00237
H	3.16551	3.05431	-0.85710
H	2.75581	1.53990	-1.68107
H	2.54712	1.47073	2.07717
H	1.10798	1.62572	3.10594
H	2.03740	3.06235	2.65949
H	-1.11776	2.01072	3.10806
H	-2.49741	2.37078	2.07205
H	-1.47559	3.68944	2.67016
H	-2.62663	3.92775	-0.79840
H	-3.14231	2.39778	-0.06348
H	-2.58058	2.42579	-1.73649
C	1.26932	-2.04937	3.35561
H	-0.15802	-1.53602	-0.84442
C	-2.16321	-1.54365	-0.34328
O	-2.06205	-0.31784	-0.06471
O	-1.24221	-2.31817	-0.66580
C	-3.60417	-2.08166	-0.29507
H	0.35239	-1.87128	3.91816
H	1.48386	-3.12192	3.32952
H	2.09962	-1.54963	3.86995
F	-4.31707	-1.47198	-1.23918
F	-3.64213	-3.38462	-0.49665
F	-4.14188	-1.80686	0.88866

IV'

E(RM06) = -1536.43857867
# of negative frequency = 0

C	3.46375	-0.23226	0.25909
C	3.40549	-0.13373	-1.14482
C	4.57999	0.03760	-1.87545
C	5.78659	0.10543	-1.19142
C	5.82611	0.00694	0.20120
C	4.66583	-0.16302	0.95172
C	1.23901	-0.41500	-0.42904
C	2.01711	-0.24966	-1.53740
H	4.54846	0.11443	-2.95940
H	6.71285	0.23779	-1.74367
H	6.78138	0.06528	0.71561
H	1.65278	-0.23217	-2.56033
N	2.12839	-0.39941	0.70022
C	1.58249	-0.60362	1.92088
O	0.34208	-0.77252	1.99428
Ir	-0.70838	-0.62730	0.10774
C	-2.28468	-0.61504	-1.35655
C	-2.50246	-1.92755	0.55181
C	-1.50296	-2.54316	-0.32701
C	-1.45874	-1.77293	-1.55475
C	-2.97557	-0.75646	-0.07132
C	-0.82588	-3.84233	-0.07155
C	-2.83993	-2.43700	1.90650
C	-3.92605	0.24990	0.47205
C	-2.53757	0.46789	-2.34580
C	-0.70854	-2.12763	-2.78711
H	0.21751	-2.66338	-2.55913
H	-0.45161	-1.24043	-3.37497
H	-1.32535	-2.77574	-3.42192
H	-2.81355	1.40446	-1.85044
H	-3.36483	0.19872	-3.01469
H	-1.65537	0.65970	-2.96662
H	-3.48668	1.25452	0.46414
H	-4.21502	0.02261	1.50117
H	-4.83812	0.28357	-0.13641
H	-3.40835	-1.70511	2.48577
H	-1.93208	-2.67599	2.47178
H	-3.43713	-3.35428	1.83502
H	-0.58510	-3.95609	0.99061
H	0.10706	-3.92417	-0.63762
H	-1.47252	-4.68091	-0.35952
H	4.72915	-0.23305	2.03205
C	2.41273	-0.63798	3.15111
H	3.16609	-1.43075	3.08508
H	2.93701	0.31415	3.28835
H	1.76553	-0.82089	4.00937
C	-0.37166	2.51717	0.00026
O	0.49994	2.48031	-0.95752
O	-0.74951	1.58720	0.70183
C	-1.02938	3.89330	0.20260
F	-2.28506	3.79182	-0.23723
F	-1.04839	4.18546	1.48985
F	-0.40999	4.84365	-0.46428
H	0.87132	1.56201	-1.04561

V'

E(RM06) = -1536.43113659
# of negative frequency = 0

C	-1.38463	-1.92430	-0.45129
C	-2.22896	-2.82269	-1.13245
C	-2.36162	-2.72224	-2.51570
C	-1.65163	-1.72243	-3.16768
C	-0.79644	-0.86538	-2.46593
C	-0.60659	-0.94194	-1.07357
C	-2.37134	-3.33023	1.06502
C	-2.81990	-3.70046	-0.15073
H	-3.01240	-3.39844	-3.06351
H	-1.75342	-1.60483	-4.24371
H	-0.25392	-0.10404	-3.02659
H	-2.59495	-3.73645	2.04110
H	-3.50696	-4.51331	-0.34757
N	-1.49213	-2.22923	0.93147
C	-1.00683	-1.47639	1.95048
O	-0.31979	-0.45558	1.75536
Ir	0.78514	0.15252	-0.03148
C	2.49312	-0.48176	-1.18970
C	2.80317	0.29575	1.01454
C	2.67625	1.42120	0.18324
C	2.41345	0.95500	-1.18356
C	2.60524	-0.90314	0.18954
C	2.70417	2.85588	0.57156
C	2.99837	0.26530	2.48806
C	2.71746	-2.30599	0.67424
C	2.48668	-1.37957	-2.37300
C	2.30199	1.85246	-2.36522
H	1.66088	2.71364	-2.14751
H	1.88476	1.33239	-3.23274
H	3.28922	2.23732	-2.65151
H	1.96802	-2.32085	-2.16636
H	3.52020	-1.61784	-2.65370
H	2.00592	-0.91646	-3.23912
H	2.14600	-2.99047	0.03807
H	2.33628	-2.39943	1.69724
H	3.76279	-2.64009	0.67871
H	2.23829	-0.35718	2.97474
H	2.93932	1.26413	2.92773
H	3.97953	-0.15725	2.73711
H	3.58558	3.35086	0.14505
H	2.73595	2.98609	1.65621
H	1.81860	3.38264	0.19796
C	-1.32090	-1.88350	3.35309
H	-2.15168	0.32621	-0.70313
C	-1.82715	2.01363	0.05397
O	-0.60872	1.93544	0.11675
O	-2.65558	1.10682	-0.36395
C	-2.49513	3.31269	0.53668
H	-0.82674	-1.19099	4.03514
H	-2.40028	-1.85733	3.53742
H	-0.97135	-2.90191	3.55486
F	-3.78790	3.32704	0.28455
F	-1.91139	4.33756	-0.06548
F	-2.29802	3.40873	1.84625

^{t}BuCO$_2$H

E(RM062X) = -347.01371424
# of negative frequency = 0

C	0.56913	-0.01437	-0.00163
C	-0.93383	0.19070	-0.00466
C	0.95171	-0.77616	1.27197
C	1.25204	1.35140	-0.02768
C	0.96201	-0.83268	-1.23431
O	-1.50174	1.24770	-0.00492
O	-1.61153	-0.97744	-0.00267
H	-2.55277	-0.75772	-0.00069
H	0.48601	-1.76005	1.29602
H	0.64911	-0.22508	2.16331
H	2.03444	-0.90160	1.30105
H	0.96351	1.94736	0.83684
H	0.97720	1.90681	-0.92329
H	2.33353	1.21443	-0.01617
H	0.48446	-1.81103	-1.22541
H	2.04337	-0.97255	-1.24029
H	0.68094	-0.31594	-2.15283

^{i}PrCO$_2$H

E(RM062X) = -307.70441646
# of negative frequency = 0

C	-0.63626	-0.17475	-0.40008
C	0.77391	0.20396	-0.01888
H	-0.59985	-0.51556	-1.43680
C	-1.56823	1.01822	-0.26287
C	-1.08382	-1.34943	0.47788
O	1.10031	1.18477	0.59057
O	1.67070	-0.72072	-0.42158
H	2.53951	-0.42735	-0.11546
H	-1.24405	1.85114	-0.88435
H	-1.58818	1.36378	0.77008
H	-2.57890	0.73577	-0.55554
H	-0.41879	-2.20406	0.36956
H	-2.09120	-1.65449	0.19762
H	-1.10021	-1.04963	1.52673

EtCO$_2$H

E(RM062X) = -268.39647015
# of negative frequency = 0

C	-0.68617	-0.74310	-0.00034
C	0.55684	0.10194	-0.00154
H	-0.63195	-1.40067	-0.86987
C	-1.95497	0.09501	0.00041
H	-0.63045	-1.39943	0.87006
O	0.59339	1.30087	0.00009
O	1.67565	-0.65157	0.00053
H	2.42852	-0.04512	0.00166
H	-1.98626	0.74255	-0.87335
H	-1.99253	0.73162	0.88196
H	-2.83389	-0.54638	-0.00652

MeCO$_2$H

E(RM062X) = -229.08855860
# of negative frequency = 0

C	-1.38891	-0.12079	-0.00007
C	0.08901	0.12645	-0.00004
H	-1.65632	-0.70938	-0.87651
H	-1.91539	0.82646	-0.00251
H	-1.65854	-0.70388	0.87942
O	0.62713	1.19748	-0.00004
O	0.78607	-1.02904	-0.00009
H	1.72409	-0.79464	0.00127

PhCH$_2$CO$_2$H

E(RM062X) = -460.12135739
# of negative frequency = 0

C	1.16922	-0.14370	1.07961
C	2.13940	0.07201	-0.05457
H	1.34818	-1.11892	1.52790
H	1.35087	0.63704	1.81452
O	2.63891	1.12145	-0.34897
O	2.36263	-1.05992	-0.74776
H	2.94239	-0.83461	-1.48828
C	-0.24628	-0.06043	0.55258
C	-0.80165	1.17886	0.24907
C	-0.99489	-1.21064	0.33573
C	-2.08958	1.26575	-0.25655
H	-0.21595	2.07614	0.40736
C	-2.28489	-1.12524	-0.16926
H	-0.56381	-2.17794	0.56109
C	-2.83498	0.11304	-0.46559
H	-2.51272	2.23434	-0.48576
H	-2.85895	-2.02739	-0.33152
H	-3.84050	0.18116	-0.85761

(Ph)$_2$CHCO$_2$H

E(RM062X) = -691.15400850
# of negative frequency = 0

C	0.02142	0.73953	0.63296
C	-0.03571	2.10059	-0.03392
H	0.03436	0.91524	1.70781
O	0.30114	2.34818	-1.15747
O	-0.56162	3.02832	0.78537
H	-0.61401	3.85581	0.28720
C	1.27982	-0.01472	0.25240
C	1.46223	-0.51212	-1.03431
C	2.27370	-0.21514	1.20237

C	2.62128	-1.19683	-1.36101
H	0.69471	-0.35957	-1.78090
C	3.43506	-0.90416	0.87745
H	2.13972	0.17125	2.20545
C	3.61073	-1.39616	-0.40606
H	2.75330	-1.57891	-2.36416
H	4.19909	-1.05443	1.62808
H	4.51258	-1.93474	-0.66327
C	-1.24595	-0.04126	0.31059
C	-1.72224	-0.95425	1.24741
C	-1.91672	0.09465	-0.89983
C	-2.84654	-1.71904	0.98079
H	-1.20312	-1.06742	2.19143
C	-3.04449	-0.67078	-1.16668
H	-1.55911	0.79931	-1.63972
C	-3.51248	-1.57862	-0.22947
H	-3.20534	-2.42293	1.71953
H	-3.55726	-0.55343	-2.11172
H	-4.39173	-2.17221	-0.43902

$(Ph)_3CCO_2H$

E(RM062X) = -922.17922721
# of negative frequency = 0

C	0.00814	-0.01045	0.47462
C	-0.06935	0.05159	2.01655
O	0.57688	0.77594	2.71952
O	-1.01340	-0.75610	2.52732
H	-1.01773	-0.60723	3.48264
C	0.10281	-1.47877	0.00484
C	1.21184	-1.96139	-0.68177
C	-0.96561	-2.35408	0.22032
C	1.26690	-3.28253	-1.11483
H	2.04557	-1.31106	-0.89793
C	-0.91110	-3.66813	-0.20967
H	-1.85573	-1.99816	0.71677
C	0.21124	-4.14332	-0.87666
H	2.14371	-3.62905	-1.64490
H	-1.75311	-4.32244	-0.02789
H	0.25362	-5.17017	-1.21337
C	1.22549	0.80022	0.01450
C	1.14979	1.68353	-1.05500
C	2.46509	0.60857	0.62683
C	2.27971	2.35998	-1.50287
H	0.20568	1.85693	-1.55105
C	3.58995	1.28225	0.18491
H	2.55330	-0.07841	1.45684
C	3.50209	2.16482	-0.88490
H	2.19416	3.04340	-2.33676
H	4.53861	1.11811	0.67779
H	4.38049	2.69315	-1.22999
C	-1.28596	0.65247	-0.03354
C	-1.79077	1.77141	0.62490
C	-1.91030	0.22936	-1.20176
C	-2.90320	2.44029	0.13860
H	-1.30031	2.14016	1.51781
C	-3.02047	0.90324	-1.69408
H	-1.52556	-0.62608	-1.73953
C	-3.52439	2.00739	-1.02432
H	-3.28084	3.30478	0.66764
H	-3.48945	0.56049	-2.60656
H	-4.39177	2.52831	-1.40609

$ClCH_2CO_2H$

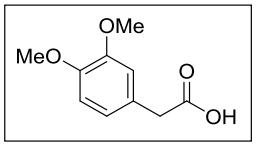
E(RM062X) = -1148.28937679
# of negative frequency = 0

C	0.25505	-0.80207	-0.00027
C	-0.93803	0.12638	-0.00142
H	0.20929	-1.43622	0.88167
Cl	1.78909	0.07345	0.00051
H	0.21045	-1.43673	-0.88191
O	-0.92404	1.31808	-0.00028
O	-2.06632	-0.60891	0.00036
H	-2.81358	0.00508	0.00112

FCH_2CO_2H

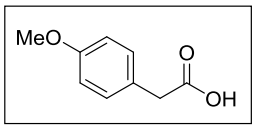
E(RM062X) =
# of negative frequency = 0

C	0.76650	-0.68056	0.00016
C	-0.51366	0.12220	-0.00022
H	0.78920	-1.31463	0.88778
F	1.84483	0.15053	-0.00005
H	0.78985	-1.31487	-0.88717
O	-0.59660	1.31118	0.00007
O	-1.56943	-0.71168	-0.00015
H	-2.37133	-0.17117	0.00085



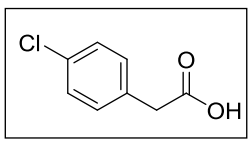
E(RM062X) = -689.16744820
# of negative frequency = 0

C	-2.42315	-0.30542	1.02171
C	-3.24251	-0.24561	-0.24279
H	-2.63390	0.57974	1.62074
H	-2.73218	-1.19381	1.56599
O	-3.80380	-1.17275	-0.75483
O	-3.25453	0.99270	-0.77638
H	-3.74676	0.94095	-1.60707
C	-0.95188	-0.37828	0.68175
C	-0.32648	-1.59790	0.53494
C	-0.21861	0.79465	0.47420
C	1.02435	-1.66506	0.19157
H	-0.88401	-2.51319	0.68306
C	1.12012	0.74254	0.13553
H	-0.71587	1.74820	0.57807
C	1.75517	-0.50936	-0.00874
H	1.49444	-2.63079	0.08428
O	1.90400	1.82482	-0.07573
O	3.06710	-0.46688	-0.33708
C	3.73527	-1.69839	-0.49305
H	4.76137	-1.45629	-0.75260
H	3.28722	-2.29168	-1.29399
H	3.72152	-2.27542	0.43485
C	1.30357	3.09299	0.04300
H	2.08503	3.81963	-0.15743
H	0.91018	3.25253	1.05011
H	0.49570	3.21617	-0.68258



E(RM062X) = -574.64686977
# of negative frequency = 0

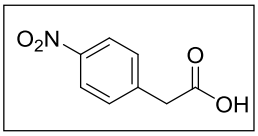
C	-2.15718	0.07278	1.02411
C	-2.94611	-0.26055	-0.21683
H	-2.50346	1.02363	1.42479
H	-2.34100	-0.71720	1.74825
O	-3.27871	-1.36244	-0.55346
O	-3.20984	0.83490	-0.95468
H	-3.65719	0.53879	-1.75910
C	-0.68721	0.15089	0.67898
C	0.07606	-1.00284	0.59080
C	-0.07713	1.37251	0.40119
C	1.42128	-0.95610	0.24483
H	-0.38575	-1.96209	0.78998
C	1.25774	1.43829	0.05658
H	-0.65975	2.28374	0.45305
C	2.01663	0.27172	-0.02452
H	1.98638	-1.87413	0.19130
H	1.73904	2.38294	-0.15473
O	3.31981	0.43046	-0.36684
C	4.12021	-0.72803	-0.45977
H	5.10930	-0.39025	-0.75488
H	3.73284	-1.41801	-1.21361
H	4.18370	-1.24273	0.50252



E(RM062X) = -919.73196897
# of negative frequency = 0

C	-2.12886	0.23580	1.00918
C	-2.94170	-0.14017	-0.20514

H	-2.39271	1.24168	1.32763
H	-2.37366	-0.47459	1.79578
O	-3.31167	-1.24905	-0.47096
O	-3.17449	0.91800	-1.00208
H	-3.64307	0.59412	-1.78370
C	-0.65845	0.15860	0.66519
C	-0.04634	-1.08208	0.51494
C	0.09353	1.30877	0.46340
C	1.29390	-1.17660	0.17904
H	-0.62823	-1.98437	0.65594
C	1.43744	1.23067	0.12762
H	-0.37286	2.27993	0.56895
C	2.02547	-0.01471	-0.01031
H	1.77190	-2.13856	0.06370
H	2.02406	2.12477	-0.02688
Cl	3.70905	-0.12448	-0.42827



E(RM062X) = -664.63402523
# of negative frequency = 0

C	-2.40680	0.24092	0.99435
C	-3.19463	-0.14539	-0.23535
H	-2.68189	1.24595	1.30491
H	-2.66027	-0.47017	1.77739
O	-3.54940	-1.25839	-0.50115
O	-3.41845	0.90879	-1.03758
H	-3.87424	0.58406	-1.82665
C	-0.93095	0.16826	0.67670
C	-0.31961	-1.07587	0.54012
C	-0.18366	1.32558	0.49027
C	1.02594	-1.16938	0.23164
H	-0.90915	-1.97422	0.67072
C	1.16538	1.25174	0.18187
H	-0.66091	2.29161	0.58797
C	1.74349	0.00203	0.06077
H	1.52230	-2.12095	0.12264
H	1.76801	2.13462	0.03599
N	3.17915	-0.08497	-0.26267
O	3.66488	-1.19029	-0.36045
O	3.78384	0.95447	-0.41037

(4-CF3)$C_6H_4CO_2H$

E(RM062X) = -757.90318600
# of negative frequency = 0

C	-3.19288	0.09664	0.00005
O	-3.83402	1.11142	0.00000
O	-3.76439	-1.12058	-0.00018
H	-4.72122	-0.98359	-0.00026
C	-1.70496	0.03984	0.00003
C	-1.01917	-1.17114	-0.00003
C	-1.01210	1.24335	0.00008
C	0.36399	-1.17254	-0.00003
H	-1.57000	-2.09986	-0.00006
C	0.37323	1.24360	0.00008
H	-1.57302	2.16720	0.00013
C	1.05108	0.03448	0.00002
H	0.91312	-2.10439	-0.00007
H	0.92423	2.17242	0.00012
C	2.55373	-0.00789	0.00001
F	3.09996	1.21058	0.00008
F	3.02427	-0.65615	-1.07474
F	3.02428	-0.65627	1.07469

(4-NO_2)$C_6H_4CO_2H$

E(RM062X) = -625.32717980
# of negative frequency = 0

C	2.82949	0.10583	-0.00017
O	3.45637	1.12877	0.00002
O	3.41199	-1.10455	0.00023
H	4.36797	-0.96077	0.00041
C	1.34013	0.03365	-0.00011
C	0.66970	-1.18431	-0.00006
C	0.63784	1.23394	-0.00010
C	-0.71542	-1.20696	-0.00002
H	1.23188	-2.10603	-0.00006
C	-0.74545	1.22488	-0.00005
H	1.19259	2.16131	-0.00013
C	-1.38960	0.00008	-0.00001
H	-1.32596	2.13389	-0.00004
N	-2.86947	-0.01852	0.00003
H	-1.27275	-2.12946	0.00002
O	-3.43892	1.04894	0.00003
O	-3.41289	-1.09965	0.00006

(4-F)$C_6H_4CO_2H$

E(RM062X) = -520.06963740
# of negative frequency = 0

C	2.12705	0.11304	0.00008
O	2.75770	1.13602	-0.00011
O	2.72140	-1.09598	0.00004
H	3.67471	-0.93796	-0.00006
C	0.64631	0.03303	0.00005
C	-0.02406	-1.18624	0.00006
C	-0.07022	1.22625	-0.00001
C	-1.40830	-1.21740	0.00003
H	0.53989	-2.10730	0.00011
C	-1.45277	1.20945	-0.00003
H	0.47510	2.15959	-0.00002
C	-2.09260	-0.01670	-0.00002
H	-2.03866	2.11705	-0.00007
F	-3.43058	-0.04165	-0.00005
H	-1.96105	-2.14547	0.00004

(4-Cl)$C_6H_4CO_2H$

E(RM062X) = -880.42767694
# of negative frequency = 0

C	2.56082	0.10724	-0.00019
O	3.19426	1.12801	-0.00035
O	3.14881	-1.10405	0.00034
H	4.10319	-0.95214	0.00034
C	1.07801	0.03380	-0.00008
C	0.40165	-1.18107	-0.00006
C	0.36649	1.22883	-0.00003
C	-0.98310	-1.20421	-0.00001
H	0.95936	-2.10602	-0.00011
C	-1.01642	1.21619	0.00004
H	0.91358	2.16119	-0.00008
C	-1.67662	-0.00400	0.00005
H	-1.58396	2.13516	0.00006
Cl	-3.41157	-0.02778	0.00010
H	-1.52507	-2.13843	-0.00002

$PhCO_2H$

E(RM062X) = -420.81706441
# of negative frequency = 0

C	1.69711	0.12279	0.00036
O	2.31762	1.15035	0.00002
O	2.30683	-1.07885	-0.00033
H	3.25870	-0.91149	-0.00054
C	0.21344	0.02897	0.00017
C	-0.44526	-1.19638	0.00016
C	-0.51086	1.21548	0.00002
C	-1.83113	-1.22929	0.00006
H	0.12606	-2.11196	0.00033
C	-1.89552	1.17791	-0.00014
H	0.02536	2.15343	0.00001
C	-2.55489	-0.04430	-0.00012
H	-2.34724	-2.17861	0.00010
H	-2.46032	2.09908	-0.00026
H	-3.63556	-0.07348	-0.00021

(4-Br)$C_6F_4CO_2H$

E(RM062X) = -3391.42636900
# of negative frequency = 0

C	-3.18482	-0.08473	-0.05466
O	-3.80540	-0.91485	-0.65033
O	-3.74469	0.89623	0.66283
H	-4.70432	0.80612	0.57476
C	-1.69193	-0.02875	-0.01481
C	-0.98684	1.16745	-0.05037
C	-0.96084	-1.21008	0.02629
C	0.39645	1.18566	-0.04946
F	-1.61919	2.32981	-0.12516
C	0.42232	-1.19788	0.04116
F	-1.57151	-2.38162	0.08883
C	1.11440	0.00184	-0.00017

```
F         1.07525      -2.34871       0.10050
Br        2.97925       0.02245       0.00805
F         1.02423       2.35119      -0.10245
```

F_2CHCO_2H

```
E(RM062X) =        -427.58077207
# of negative frequency =    0
C         0.69764       0.44409       0.02342
C        -0.79716       0.11911       0.00544
H         0.85032       1.51999       0.08170
F         1.27642      -0.03841      -1.09506
F         1.27461      -0.15609       1.08424
O        -1.64022       0.96502       0.04390
O        -1.01496      -1.19106      -0.05568
H        -1.97102      -1.34040      -0.06310
```

Cl_2CHCO_2H

```
E(RM062X) =        -328.32739466
# of negative frequency =    0
C         0.24417      -0.00381      -0.52854
C        -1.21743      -0.00080      -0.10868
Cl        1.05105       1.46843       0.05125
H         0.27586       0.00118      -1.61003
Cl        1.05184      -1.46591       0.04452
O        -2.10384       0.00941      -0.91041
O        -1.37838      -0.01063       1.21150
H        -2.32757      -0.00655       1.39658
```

CF_3CO_2H

```
E(RM062X) =        -526.84516538
# of negative frequency =    0
C        -0.59874       0.00113       0.00011
C         0.93690      -0.16219       0.00133
F        -1.18849      -1.17993      -0.00537
F        -0.98854       0.68026      -1.07701
F        -0.99169       0.67129       1.08124
O         1.48290      -1.21820      -0.00023
O         1.51858       1.03276       0.00030
H         2.47775       0.90539       0.00113
```

$C_2F_5CO_2H$

```
E(RM062X) =        -764.65696724
# of negative frequency =    0
C         0.21289      -0.51296       0.00031
C         1.41817       0.44596      -0.00060
F         0.26815      -1.29345      -1.08771
C        -1.14699       0.20860      -0.00021
F         0.26826      -1.29183       1.08953
O         1.32482       1.63359       0.00052
O         2.54530      -0.25580      -0.00071
H         3.29168       0.36044      -0.00032
F        -1.27410       0.96338      -1.08333
F        -1.27503       0.96410       1.08232
F        -2.11585      -0.70135      -0.00027
```