Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper Mediated Decarboxylative Direct C─H Arylation of Heteroarenes with Benzoic Acids

Tuhin Patra, Sudip Nandi, Santosh K. Sahoo and Debabrata Maiti*

Department of Chemistry, Indian Institute of Technology Bombay
Powai, Mumbai-400076, India
dmaiti@chem.iitb.ac.in

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1. General considerations

Reagent information:

All commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Merck and Spectrochem and used without further purification. Copper catalysts were obtained from Sigma-Aldrich. All solvents were bought from Merck. Toluene was dried with sodium and distilled immediate before use and purged with molecular oxygen vigorously for 2 hours and used further. Unless otherwise mentioned all reactions were carried out under oxygen atmosphere. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254}$) visualized under UV illumination at 254 nm.

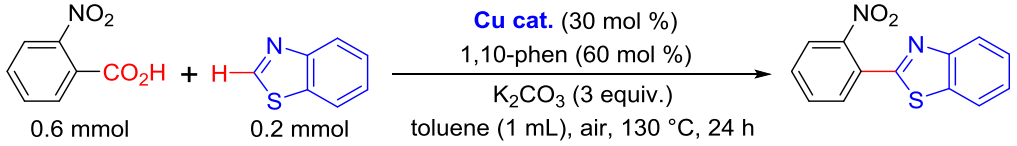
Analytical Information:

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 (400 MHz and 100 MHz respectively) and 500 (500 MHz and 125 MHz respectively) instrument. All NMR spectra were reported in parts per million (ppm) downfield of TMS and were internally referenced to TMS (0 ppm) or residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.23 ppm for ^{13}C). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, m = multiplet. Infrared spectra were recorded in chloroform solution on a Perkin-Elmer spectrum one FT-IR spectrometer in transmittance mode (%T, cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Q-TOF micromass (YA-105) and Bruker Maxis Impact system (282001.00081) mass spectrometer in positive ESI mode. Yields for optimizations were determined from gas chromatography (GC) of the crude reaction mixture using *n*-decane as internal standard. All GC analysis was done in a Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.).

2. Experimental Section

2.1 Optimization details for decarboxylative C─H arylation:

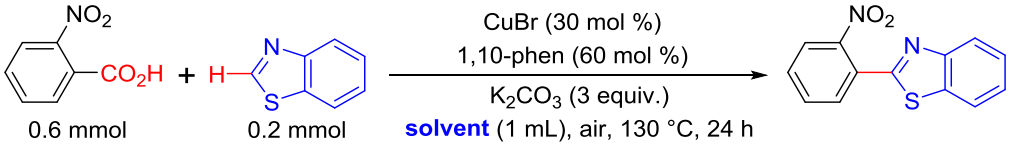
Table S1: Optimization of copper salt



Entry	Copper salt	GC yield (%)
1	$CuCl_2$	16
2	**CuBr**	**26**
3	CuCN	-
4	CuSCN	3

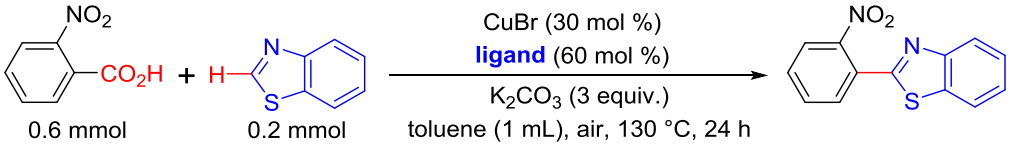
5	CuI	-
6	CuF_2	-
7	$CuBr_2$	20
8	CuCl	5
9	$Cu(acac)_2$	-
10	$Cu(OAc)_2$	-
11	$CuCO_3$	20
12	Cu_2O	22
13	$Cu(OTf)_2$	8

Table S2: Optimization of solvent



Entry	Solvent	GC yield (%)
1	DMF	11
2	**Toluene**	**27**
3	DMSO	<1
4	Cyclohexane	4
5	*m*-xylene	25
6	DCE	11
7	Dixoane	7
8	Trifluorotoluene	21
9	NMP	<1
10	N,N-dimethylaniline	-
11	Benzene	9
12	Ethylbenzene	16
13	Mesitylene	18

Table S3: Optimization of ligand



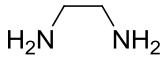
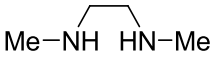
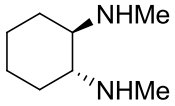
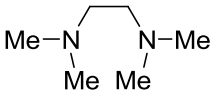
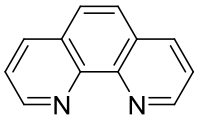
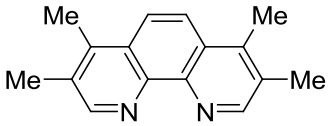
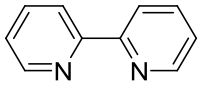
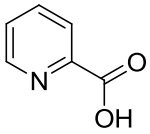
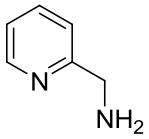
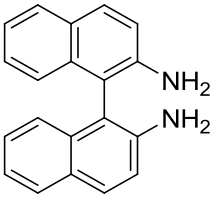
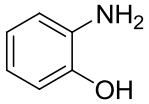
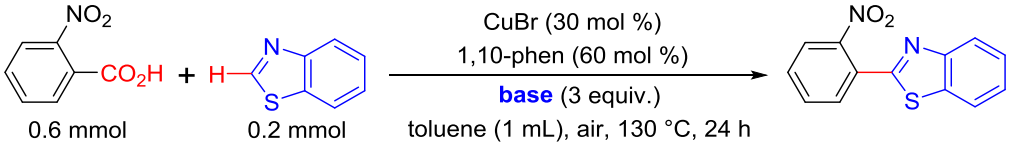
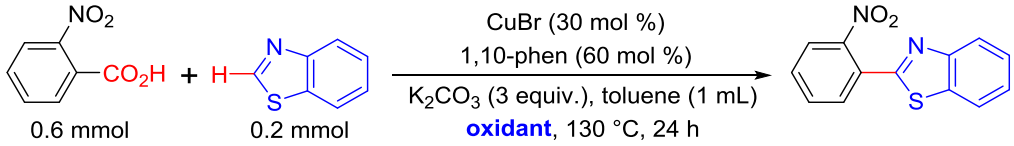
Entry	Ligand	GC yield (%)
1		-
2		12
3		6
4		14
5		**27**
6		25
7		16
8	EtNHMe	6
9		3
10		7
11		9
12		<1

Table S4: Optimization of base



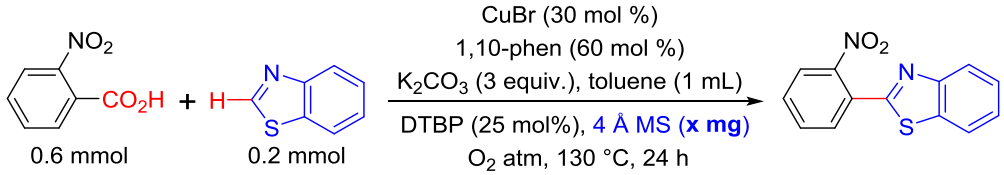
Entry	Base	GC yield (%)
1	$KHCO_3$	12
2	**K_2CO_3**	**27**
3	KF	24
4	K_3PO_4	10
5	Cs_2CO_3	-
6	$NaHCO_3$	22
7	KOH	-
8	KO^tBu	-

Table S5: Optimization of oxidant



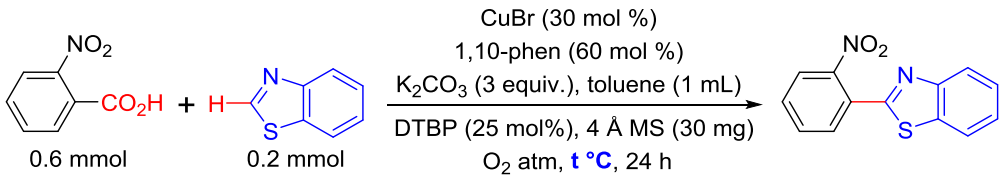
Entry	Oxidant	GC yield (%)
1	air	27
2	$K_2S_2O_8$	20
3	O_2	57
4	oxone	18
5	DTBP	28
6	TBHP	18
7	DDQ	13
8	**O_2 + DTBP (25 mol%)**	**63**

Table S6: Optimization of amount of molecular sieves



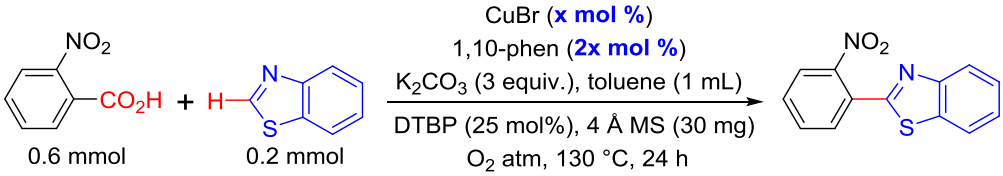
Entry	4 Å MS (mg)	GC yield (%)
1	-	63
2	15	67
3	30	72
4	60	69

Table S7: Optimization of temperature



Entry	Temperature (°C)	GC yield (%)
1	110	10
2	120	32
3	130	72
4	**140**	**76**
5	150	65
6	160	39

Table S8: Optimization of catalyst loading

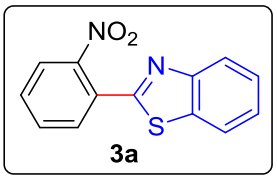


Entry	CuBr (mol%)	1,10-phen (mol%)	GC yield (%)
1	-	-	-
2	5	10	11
3	10	20	32
4	15	30	53
5	20	40	61
6	**30**	**60**	**76**
7	40	80	73
8	100	200	39
9	30	-	15
10	30	30	62

2.2 General procedure A for decarboxylative C–H arylation:

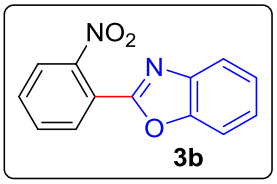
In a clean, oven–dried screw cap reaction tube containing magnetic stir–bar, benzoic acid (0.6 mmol), CuBr (0.03-0.06 mmol), 1,10-phenanthroline (0.06-0.12 mmol), K_2CO_3 (3 equiv, 0.6 mmol), 4 Å MS (30 mg) were weighed and the tube was tightly closed by screw cap fitted with rubber septum. The tube was evacuated and backfilled with molecular oxygen through standard Schlenk technique, and this sequence was repeated for three additional times. Then, under positive pressure of oxygen, heteroarene (0.2 mmol), di-tert-butyl peroxide (DTBP, 25 mol%) and toluene (1 mL) were added by syringes. Molecular oxygen was purged for 15 min through this solution in reaction tube and the reaction tube was placed in a preheated oil bath at 140 °C to stir vigorously for 24 h. Then reaction mixture was cooled to room temperature and filtered through celite with aid of ethyl acetate (10 mL). Then, this filtrate was concentrated under reduced pressure and purified by column chromatography through silica gel using petrolium ether/ethyl acetate as eluent.

2.3 Characterization data of arylated products:



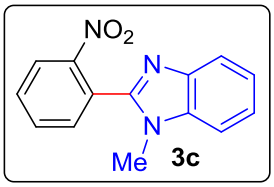
3a

2-(2-nitrophenyl)benzo[*d*]thiazole (Table 2, entry 3a): Light yellow solid. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.81 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.71 (td, *J* = 7.5, 1.2 Hz, 1H), 7.65 (td, *J* = 7.8, 1.4 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.43 (m, 1H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.55, 153.75, 136.00, 132.60, 132.01, 131.15, 131.11, 128.33, 126.79, 126.08, 124.72, 124.14, 121.79; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{13}H_9N_2O_2S$: 257.0385, found: 257.0377; **IR** (thin film) 705, 729, 759, 970, 1313, 1361, 1433, 1473, 1534, 3069 cm^{-1}.

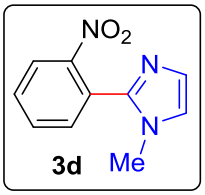


3b

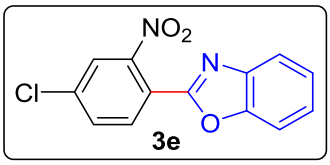
2-(2-nitrophenyl)benzo[*d*]oxazole (Table 2, entry 3b): Light yellow solid. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.73 (td, *J* = 7.6, 1.3 Hz, 1H), 7.68 (td, *J* = 7.7, 1.5 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 – 7.36 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.98, 151.20, 141.72, 132.55, 132.05, 131.59, 126.22, 125.14, 124.38, 121.65, 120.88, 111.13; HRMS (*m*/*z*): $[M + H]^+$ calcd for $C_{13}H_9N_2O_3$: 2411.0608, found: 241.0607; **IR** (thin film) 706, 745, 776, 810, 854, 1036, 1197, 1239, 1310, 1345, 1377, 1537, 1614, 2363, 2901, 3081 cm^{-1}.



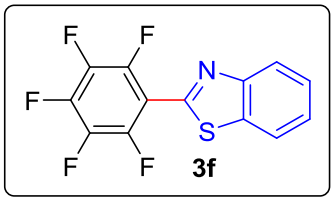
1-methyl-2-(2-nitrophenyl)-1H-benzo[*d*]imidazole (Table 2, entry 3c): Yellow solid. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.80 (td, *J* = 7.7, 1.3 Hz, 2H), 7.73 (td, *J* = 7.9, 1.6 Hz, 1H), 7.68 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.40 – 7.31 (m, 2H), 3.63 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.88, 142.88, 135.81, 133.78, 133.21, 131.37, 126.13, 125.08, 124.07, 123.55, 122.86, 120.27, 109.85, 30.84; **HRMS (*m/z*):** $[M + Na]^+$ calcd for $C_{14}H_{11}N_3O_2Na$: 276.0743, found: 276.0745; **IR** (thin film) 746, 792, 855, 1032, 1093, 1262, 1347, 1391, 1471, 1529, 1709, 2964, 3068, 3398 cm^{-1}.



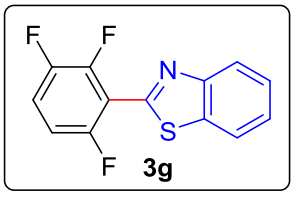
1-methyl-2-(2-nitrophenyl)-1H-imidazole (Table 2, entry 3d): White solid. Eluent: petrolium ether/ ethyl acetate (94/6 v/v). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.12 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.72 (td, *J* = 7.5, 1.3 Hz, 1H), 7.64 (td, *J* = 8.0, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.14 (s, 1H), 7.03 (s, 1H), 3.50 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.02, 143.52, 133.41, 133.21, 130.63, 129.17, 126.27, 124.90, 121.97, 33.57; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{10}H_{10}N_3O_2$: 204.0773, found: 204.0766; **IR** (thin film) 729, 764, 853, 918, 1021, 1147, 1225, 1352, 1530, 2254, 2288, 2947, 3023 cm^{-1}.



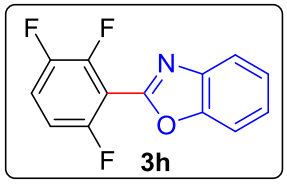
2-(4-chloro-2-nitrophenyl)benzo[*d*]oxazole (Table 2, entry 3e): Pale yellow solid. Eluent: petrolium ether/ ethyl acetate (96/4 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.71 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.43 – 7.39 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.96, 151.16, 149.59, 141.64, 138.18, 132.64, 132.47, 126.49, 125.33, 124.68, 120.98, 119.81, 111.19; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{13}H_8N_2O_3Cl$: 275.0223, found: 275.0222; **IR** (thin film) 766, 808, 837, 1035, 1091, 1198, 1238, 1371, 1542, 1692, 2363, 2947 cm^{-1}.



2-(perfluorophenyl)benzo[*d*]thiazole (Table 2, entry 3f): White solid. Eluent: petrolium ether/ ethyl acetate (97/3 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.06; 152.89, 152.88, 152.84, 152.83 (dd, *J*= 6.8, 5.2 Hz); 146.60, 146.58, 146.48, 146.46, 144.09, 143.99, 143.93, 143.88 (m); 143.84, 143.70, 143.57, 141.26, 141.13, 141.00 (m); 139.65, 139.51, 139.46, 139.38, 137.14, 137.09, 137.02, 136.98 (m); 135.82, 135.79, 135.77 (t, *J*= 2.3 Hz), 126.98, 126.61, 124.38, 121.64; 109.98, 109.88, 109.83, 109.73 (m); **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{13}H_5F_5NS$: 302.0063, found: 302.0068.

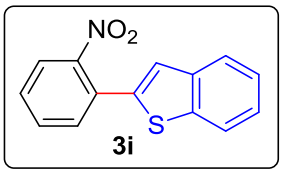


2-(2,3,6-trifluorophenyl)benzo[*d*]thiazole (Table 2, entry 3g): White solid. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.98 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.51 – 7.45 (m, 1H), 7.34 – 7.27 (m, 1H), 7.04 (tdd, *J* = 9.3, 3.8, 2.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.19, 157.16, 157.13 , 154.68, 154.65, 154.62 (dt, *J*= 253.2, 3.3 Hz); 154.95, 154.91, 154.88, 154.84 (q, *J*= 3.8 Hz); 153.15; 150.10, 150.04, 149.95, 149.89, 147.53, 147.47, 147.38, 147.31 (ddd, *J*= 259.5, 15.4, 6.3 Hz); 149.07, 149.03, 148.94, 148.90, 146.62, 146.58, 146.49, 146.45 (ddd, *J*= 247.3, 13.1, 3.8 Hz); 135.89, 135.87, 135.85 (t, *J*= 2.4 Hz); 126.71, 126.25, 124.26, 121.58; 118.98, 118.97, 118.88, 118.87, 118.79, 118.78, 118.69, 118.67 (qd, *J*= 10.2, 1.5 Hz); 114.03, 113.91, 113.85, 113.73 (dd, *J*= 18.2, 12.4 Hz); 111.97, 111.92, 111.90, 111.86, 111.72, 111.68, 111.65, 111.61 (dq, *J*= 24.7, 4.4 Hz); **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{13}H_7F_3NS$: 266.0251, found: 266.0247.

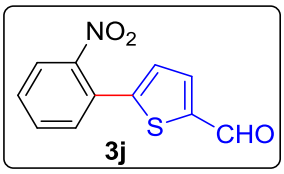


2-(2,3,6-trifluorophenyl)benzo[*d*]oxazole (Table 2, entry 3h): Light yellow solid. Eluent: petrolium ether/ ethyl acetate (98/2 v/v). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 – 7.86 (m, 1H), 7.68 – 7.64 (m, 1H), 7.43 (dq, *J* = 7.0, 6.2 Hz, 2H), 7.35 (qd, *J* = 9.0, 4.8 Hz, 1H), 7.09 – 7.03 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.86; 155.35, 155.32, 154.10 (m); 150.74; 150.65,

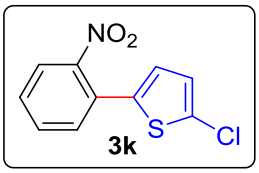
150.60, 149.00, 148.92 (m); 148.14, 148.05, 146.58, 146.46 (m); 141.45, 126.41, 125.17, 121.02; 120.05, 119.95, 119.86, 119.75 (dd, *J*= 19.3, 10.2 Hz); 112.29, 112.24, 112.19, 112.05, 112.00, 111.95 (dt, *J*= 24.5, 4.6 Hz); 111.17; 108.39, 108.27, 108.11 (m); **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{13}H_7F_3NO$: 250.0480, found: 250.0475.



2-(2-nitrophenyl)benzo[*b*]thiophene (Table 3, entry 3i): White solid. Eluent: petrolium ether/ ethyl acetate (97/3 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.76 (m, 3H), 7.66 – 7.60 (m, 2H), 7.55 – 7.49 (m, 1H), 7.42 – 7.34 (m, 2H), 7.31 (s, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.75, 140.60, 140.05, 137.64, 132.71, 132.28, 129.38, 128.82, 125.13, 124.93, 124.30, 124.25, 124.01, 122.36; **HRMS (*m/z*):** $[M + Na]^+$ calcd for $C_{14}H_9NO_2SNa$: 278.0252, found: 278.0255; **IR** (thin film) 725, 751, 844, 945, 1086, 1157, 1300, 1355, 1432, 1528, 1607, 2850, 2919, 3058, 3067 cm^{-1}.

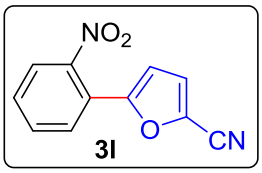


5-(2-nitrophenyl)thiophene-2-carbaldehyde (Table 3, entry 3j): Light yellow solid. Eluent: petrolium ether/ ethyl acetate (95/5 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 7.88 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.73 (d, *J* = 3.9 Hz, 1H), 7.66 (td, *J* = 7.6, 1.4 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.15 (d, *J* = 3.9 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 183.00, 149.30, 147.33, 144.88, 136.57, 132.70, 132.41, 130.30, 128.38, 127.71, 124.64; **HRMS (*m/z*):** $[M + H]^+$ calcd for $C_{11}H_8NO_3S$: 234.0219, found: 234.0218; **IR** (thin film) 744, 783, 998, 1169, 1189, 1231, 1288, 1359, 1388, 1517, 1675, 2810, 3075, 3318, 3721 cm^{-1}.

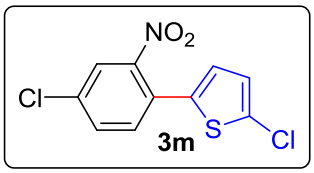


2-chloro-5-(2-nitrophenyl)thiophene (Table 3, entry 3k): Colorless solid. Eluent: petrolium ether/ ethyl acetate (96/4 v/v). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 6.88 (dd, *J* = 14.7, 3.9 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.52, 135.85, 132.40, 132.32, 131.91, 129.27, 127.74, 127.00, 126.87, 124.27, 77.55, 77.23, 76.91; **HRMS (*m/z*):** $[M + K]^+$ calcd for $C_{10}H_6NO_2SClK$: 277.9445, found:

277.9451; **IR** (thin film) 748, 779, 1037, 1086, 1205, 1359, 1498, 1518, 1547, 1737, 3037, 3057, 3179, 3322 cm^{-1}.

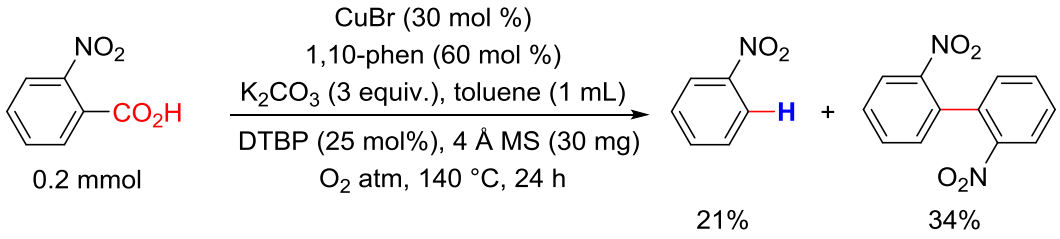


5-(2-nitrophenyl)furan-2-carbonitrile (Table 3, entry 3l): Yellow solid. Eluent: petrolium ether/ ethyl acetate (97/3 v/v). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.58 (td, *J* = 7.6, 1.0 Hz, 1H), 7.19 (d, *J* = 3.7 Hz, 1H), 6.72 (d, *J* = 3.7 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.26, 148.10, 132.78, 130.69, 130.25, 126.95, 124.69, 123.77, 122.73, 111.31, 110.93; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{11}H_6N_2O_3Na$: 273.0271, found: 273.0272; **IR** (thin film) 706, 746, 819, 854, 1036, 1283, 1353, 1462, 1526, 2234, 3115, 3121 cm^{-1}.

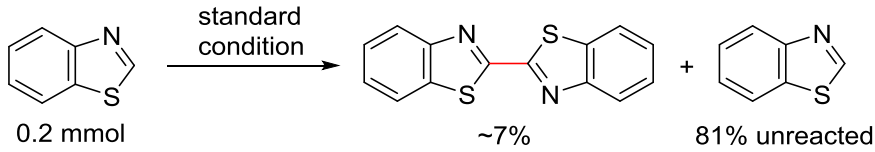


2-chloro-5-(4-chloro-2-nitrophenyl)thiophene (Table 3, entry 3m): Light yellow oil. Eluent: petrolium ether/ ethyl acetate (97/3 v/v). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 6.88 (dd, *J* = 23.3, 3.9 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.56, 135.12, 134.59, 133.37, 132.48, 132.45, 127.25, 127.14, 126.24, 124.49, 77.48, 77.23, 76.98; **HRMS (*m*/*z*):** $[M + H]^+$ calcd for $C_{10}H_6NO_2SCl_2$: 273.9496, found: 273.9497; **IR** (thin film) 792, 838, 879, 1153, 1205, 1232, 1352, 1435, 1478, 1524, 3050, 3064, 3086 cm^{-1}.

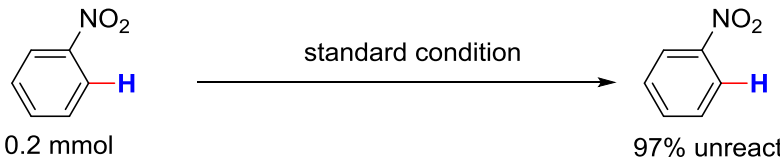
2.1 Control Experiment for mechanistic understanding:



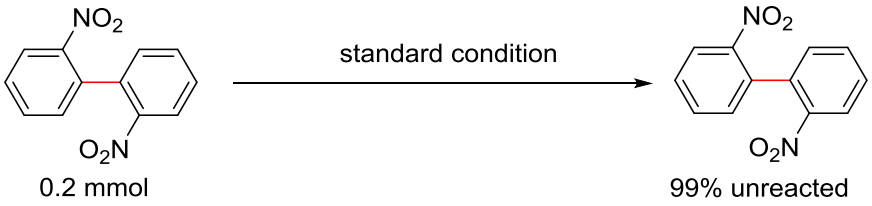
General procedure A was followed without addition of heteroarenes. After stirring at 140 °C for 24 h the reaction tube was cooled. 0.2 mmol *n*-decane (39 µL) and 2 mL of ethyl acetate was added and the solution was made homogenous by stirring and kept to settle down. 0.5 mL of aliquot was taken from this solution and used to determine the yields from GC analysis.



General procedure A was followed using benzothiazole without addition of 2-nitrobenzoic acid. GC analysis showed ~81% unreacted benzothiazole with ~7% homo-coupled product.

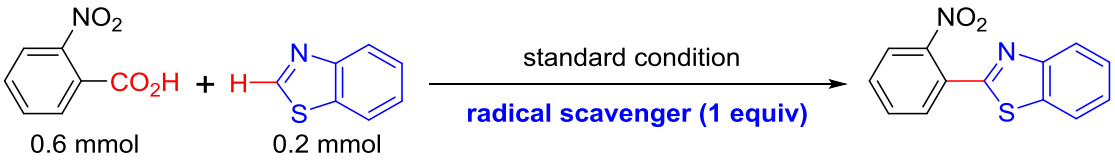


General procedure A was followed using 2-nitrobenzoic acid. GC analysis showed ~97% unreacted 2-nitrobenzoic acid.



General procedure A was followed using 2,2'-dinitro-1,1'-biphenyl. GC analysis showed ~99% recovery of starting material.

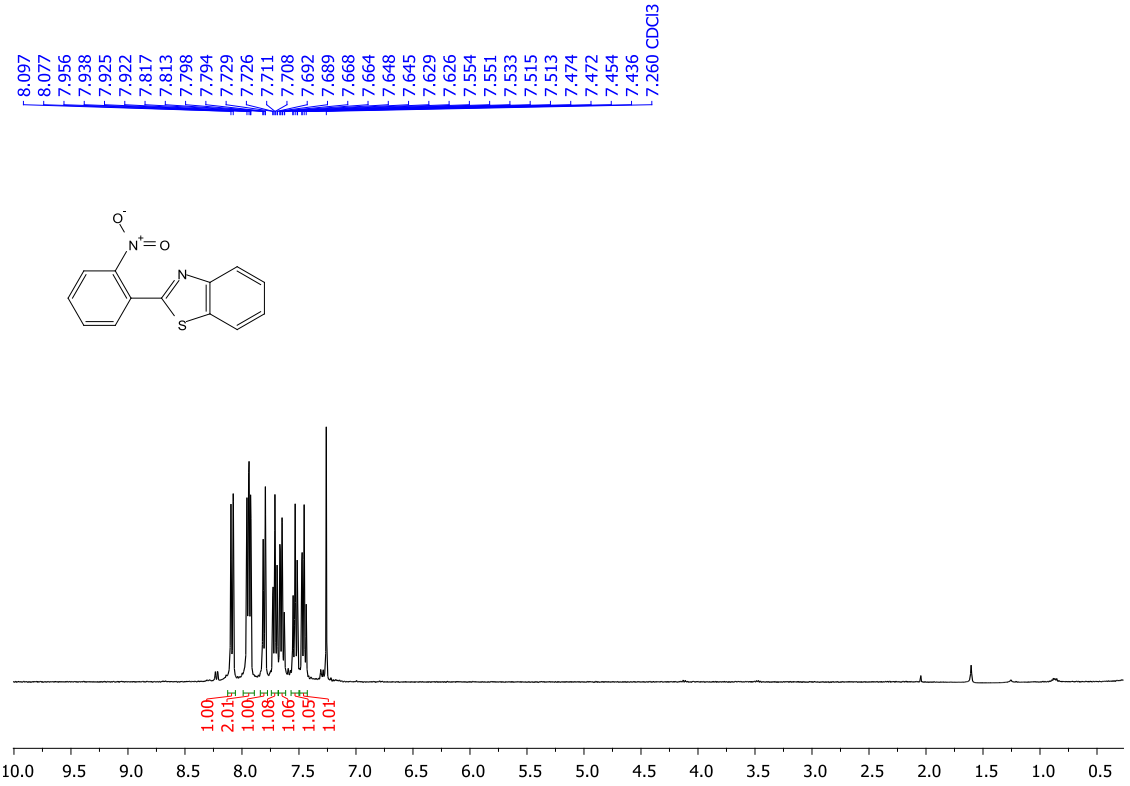
Table S9: Experiment involving radical scavenger



Entry	Radical scavenger	GC yield (%)
1	2,4,6-tri-*tert*-butylphenol	63
2	HOBt	71
3	TEMPO	73
4	AIBN	69
5	DDQ	66
6	--	76

NMR Data

Table 2, Entry 3a:



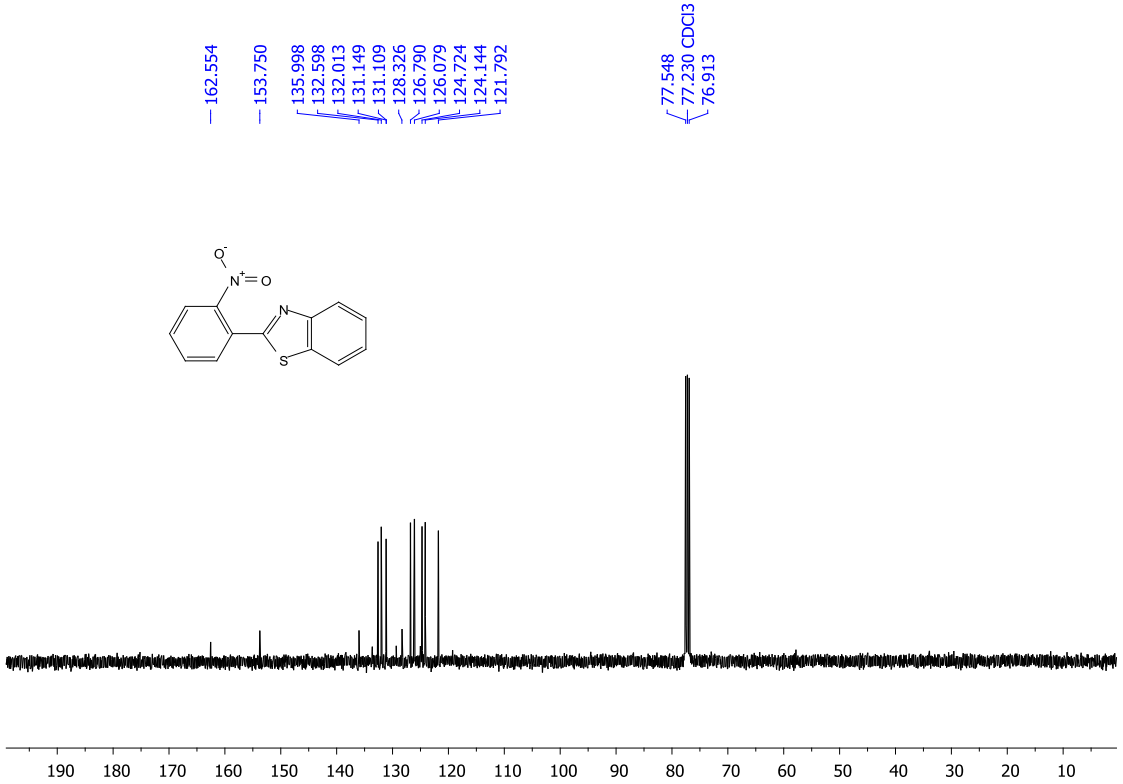


Table 2, Entry 3b:

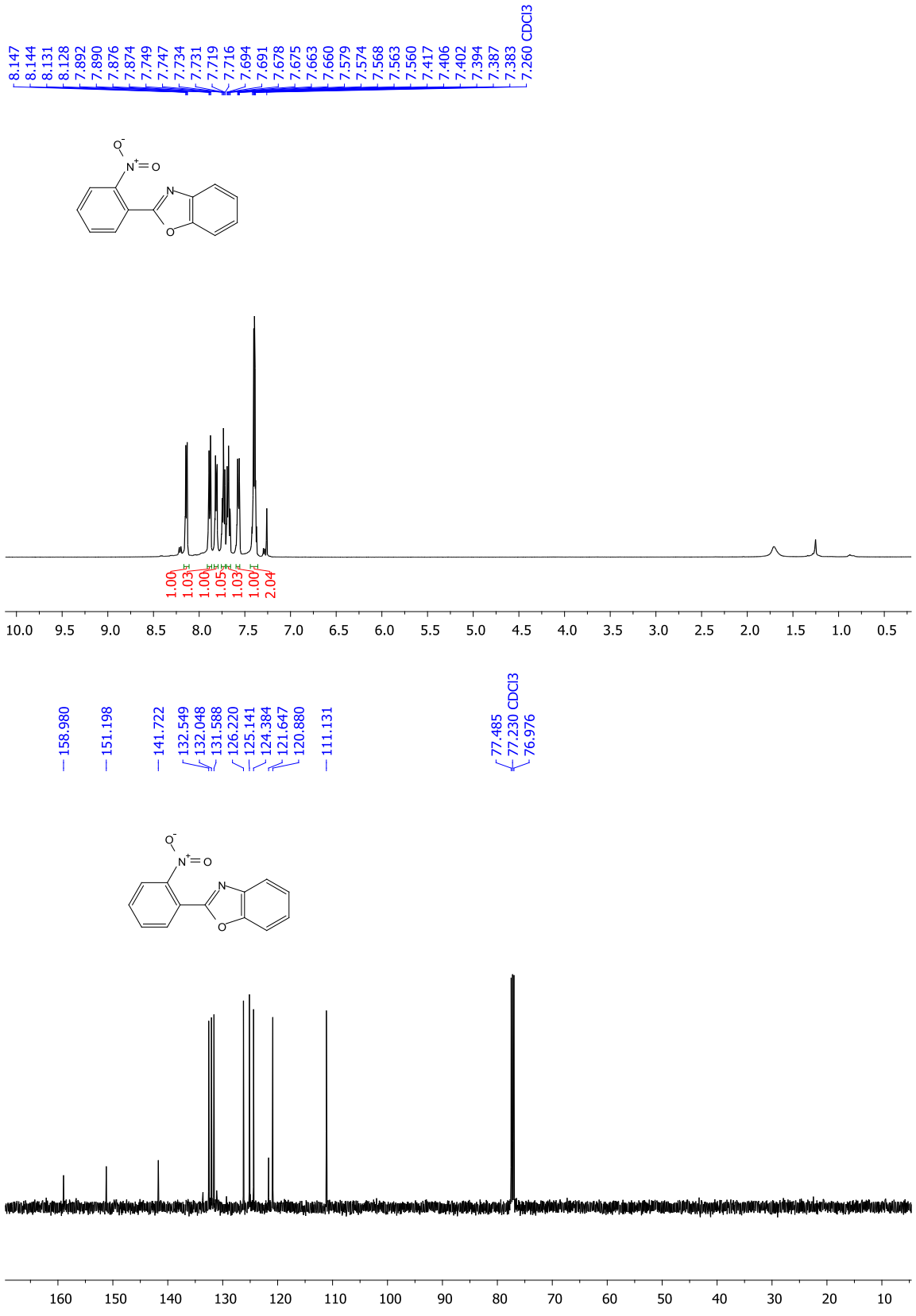
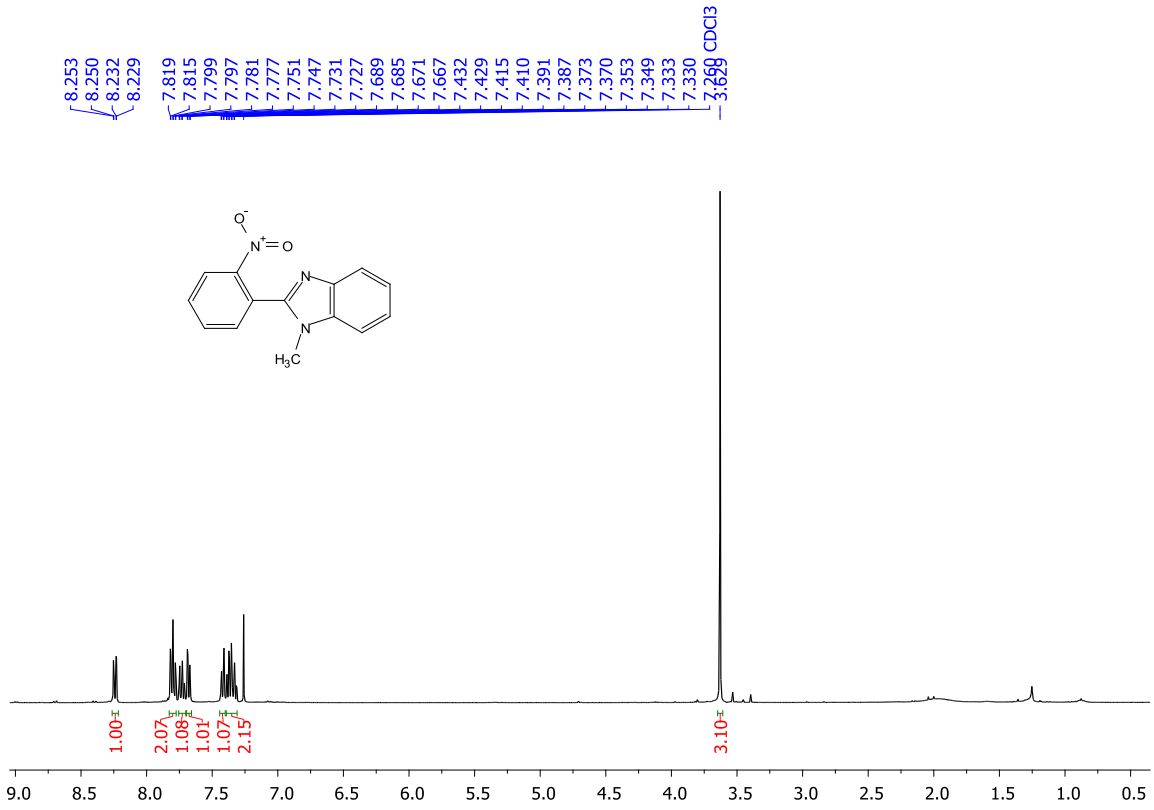


Table 2, Entry 3c:



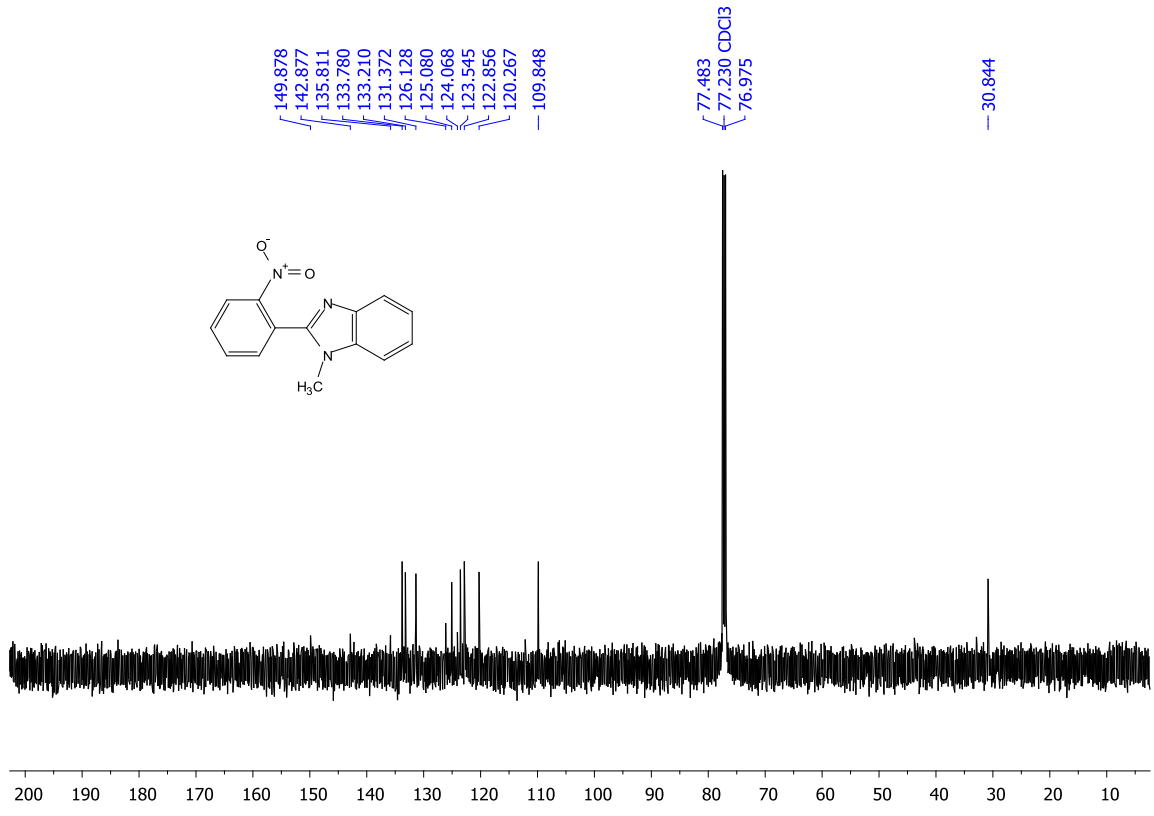
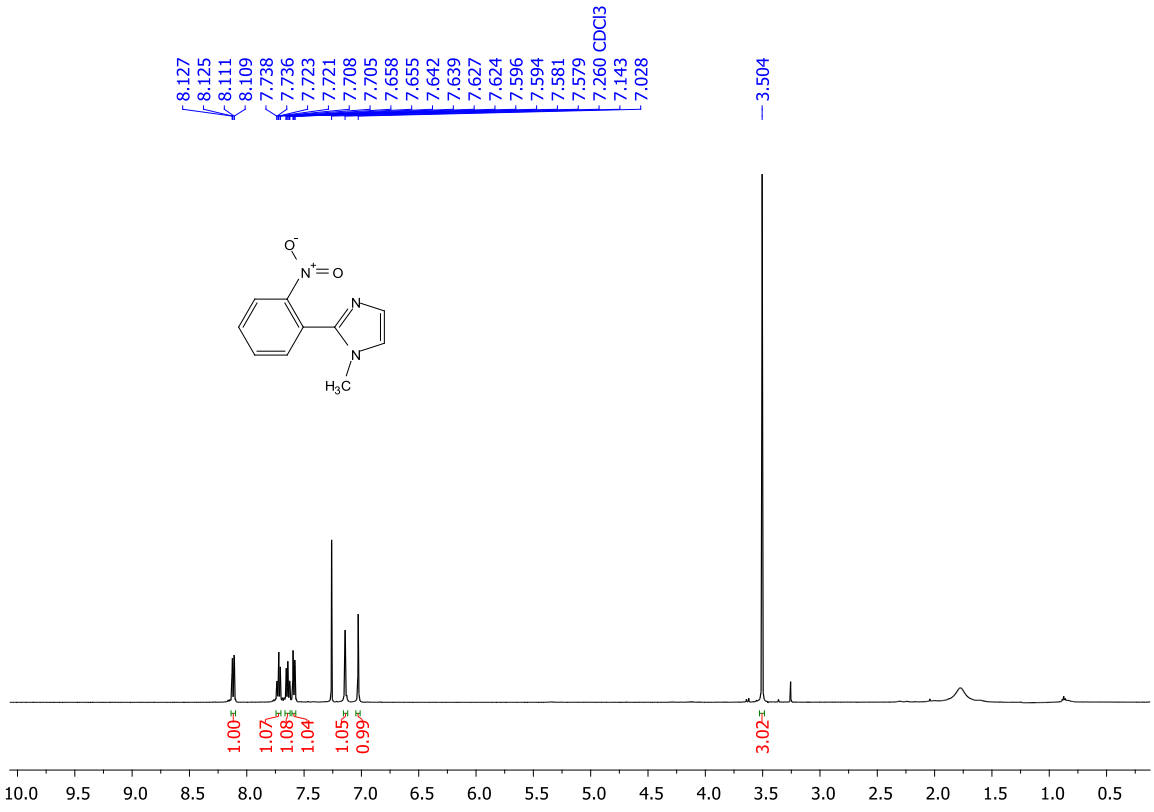


Table 2, Entry 3d:



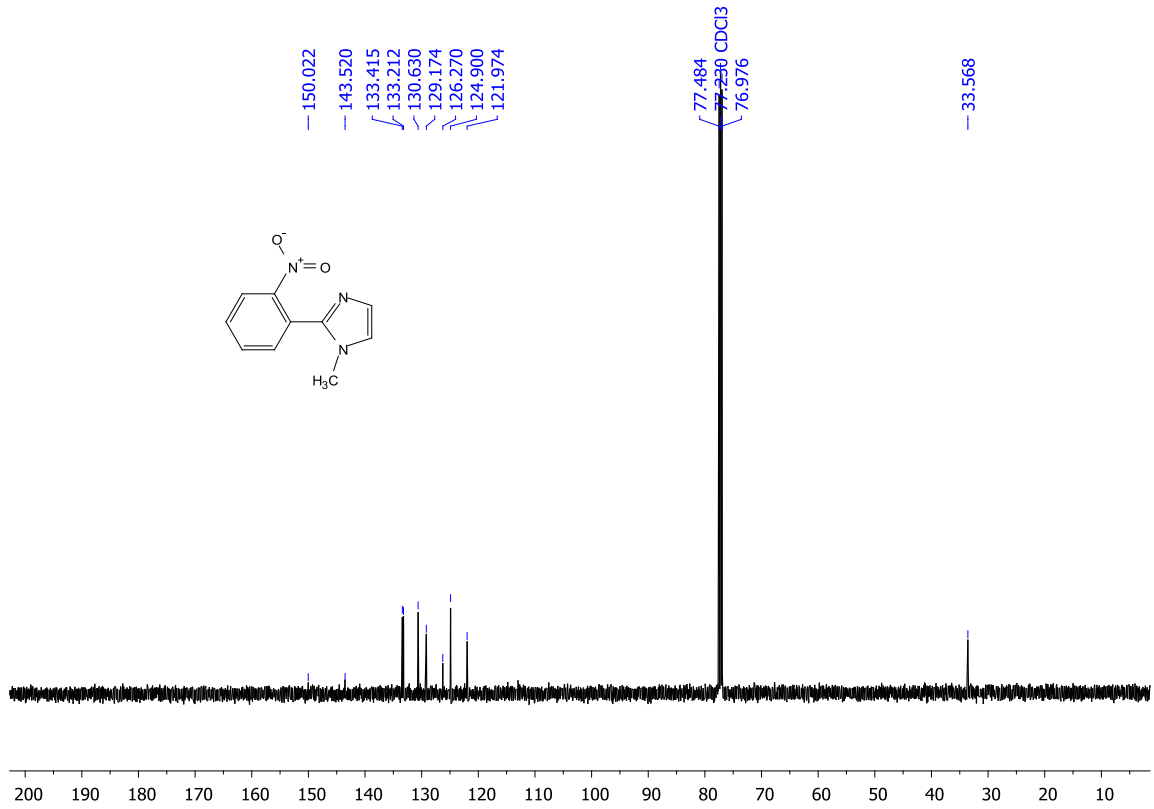


Table 2, Entry 3e:

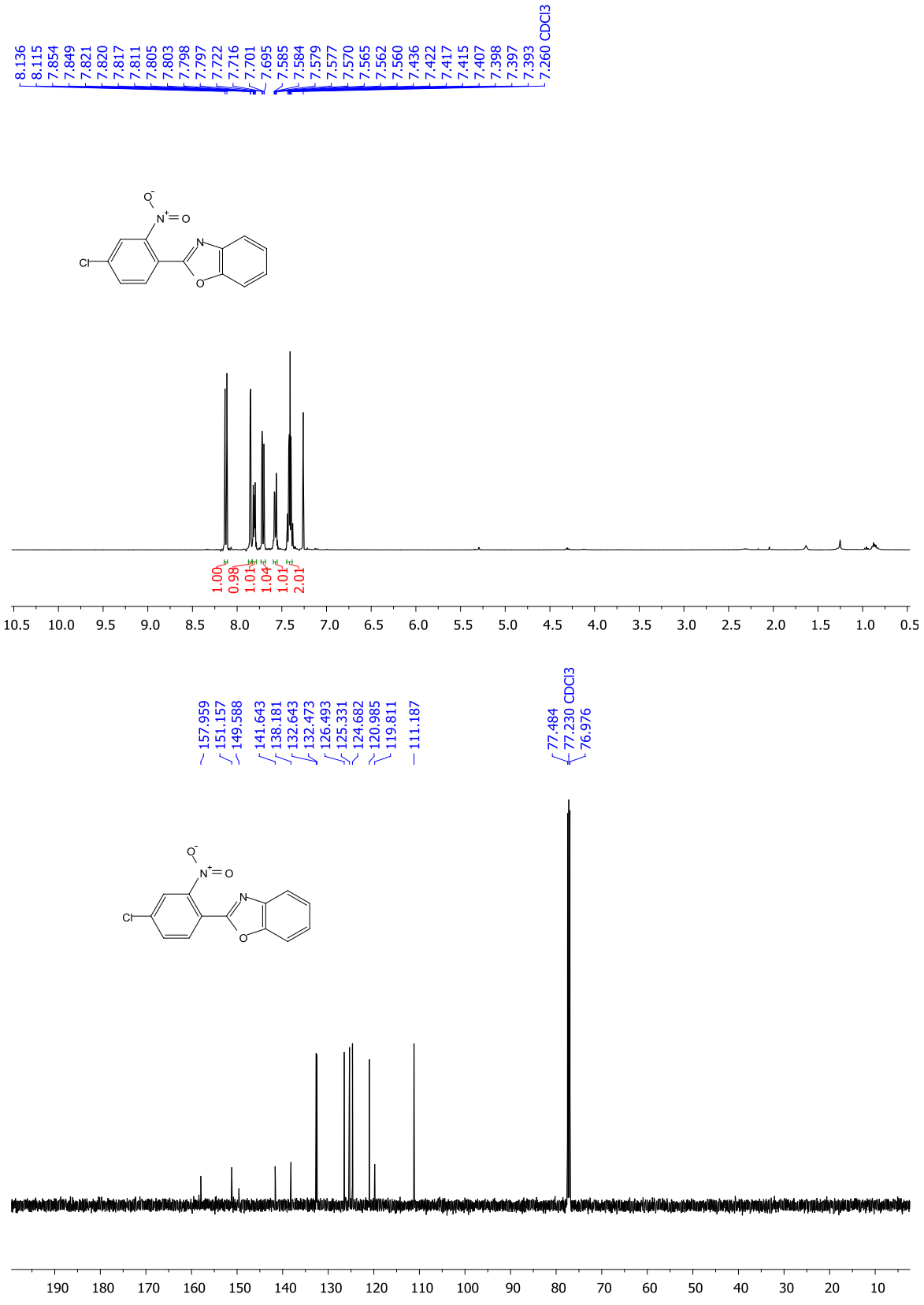
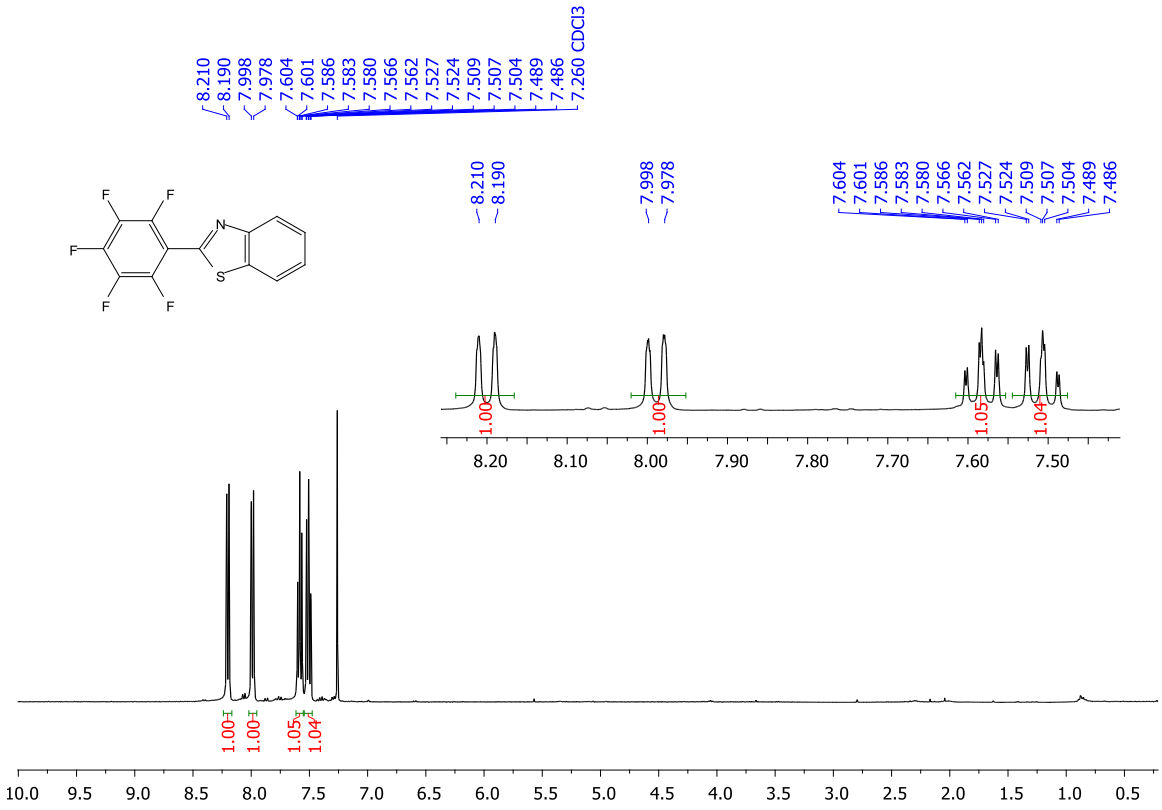


Table 2, Entry 3f:



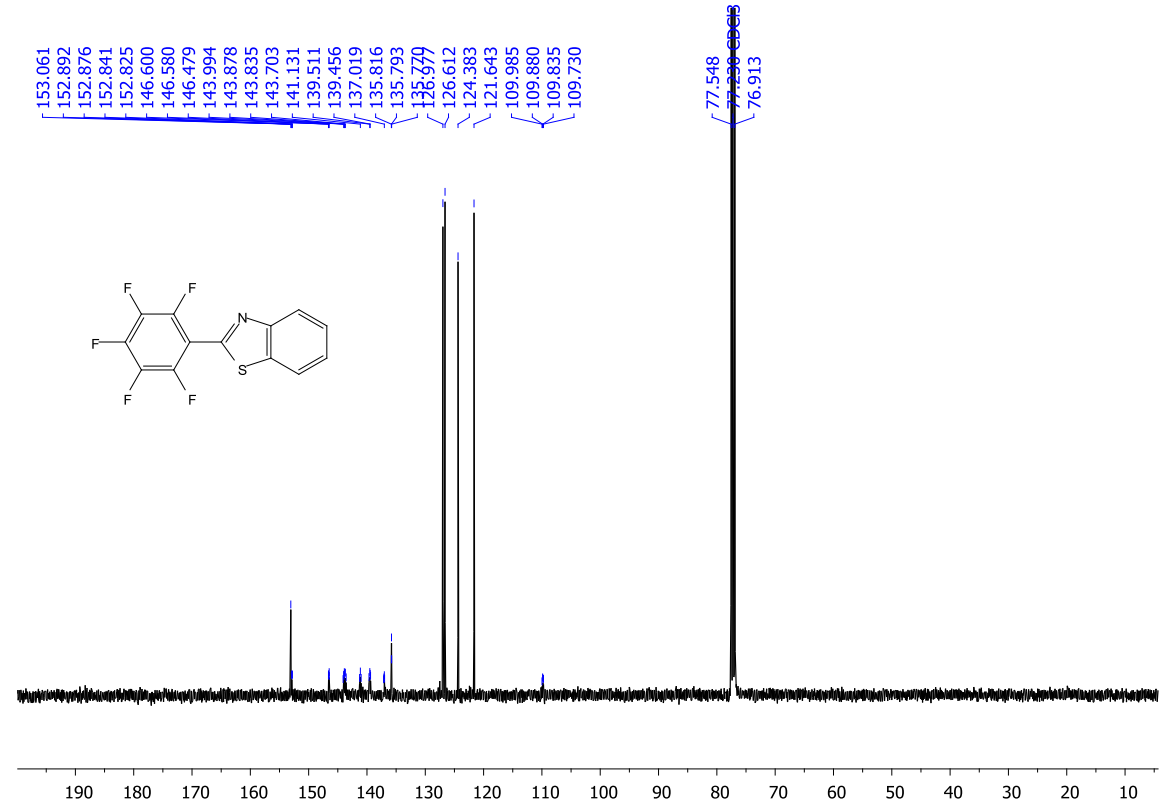


Table 2, Entry 3g:

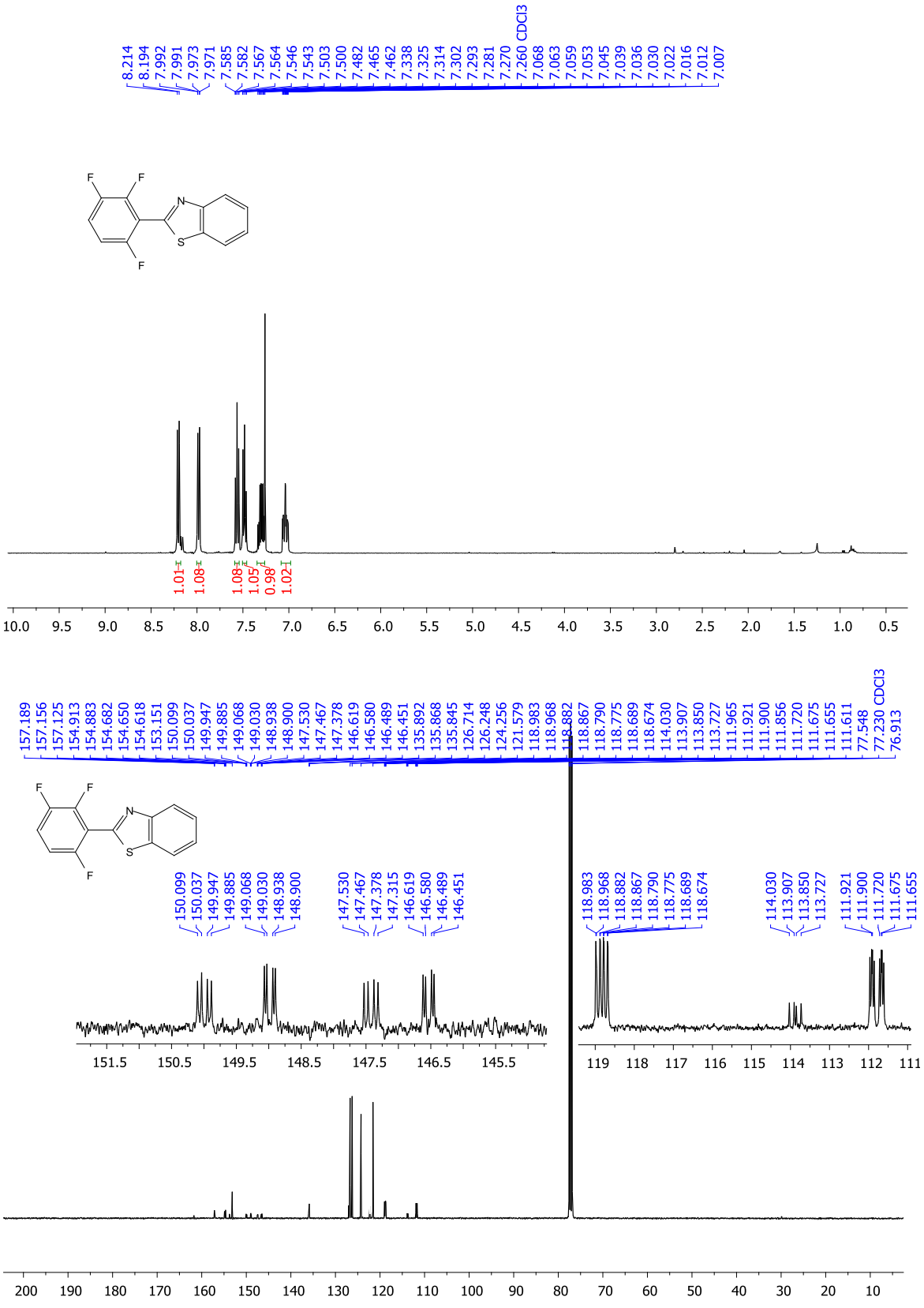


Table 2, Entry 3h:

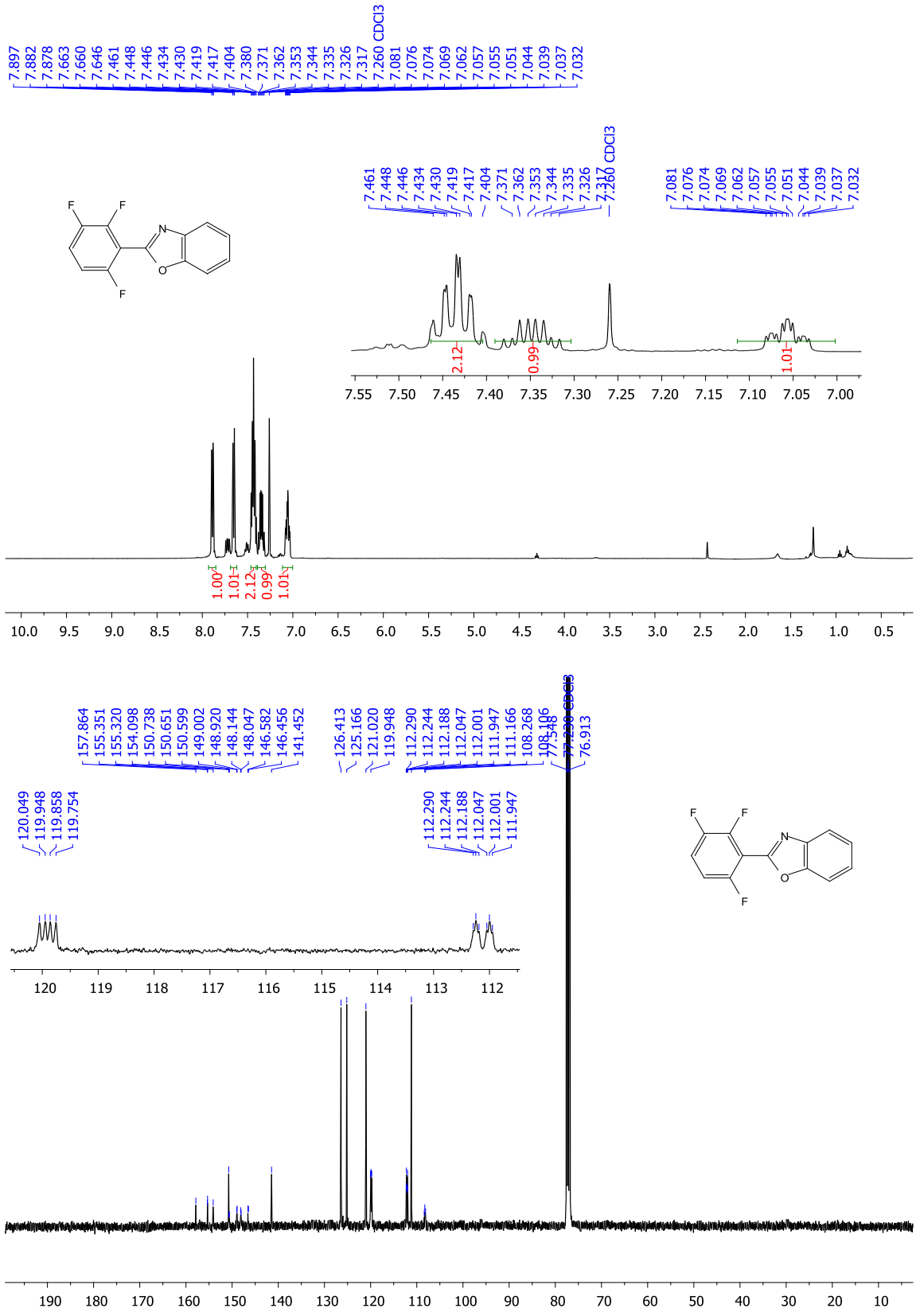


Table 3, Entry 3i:

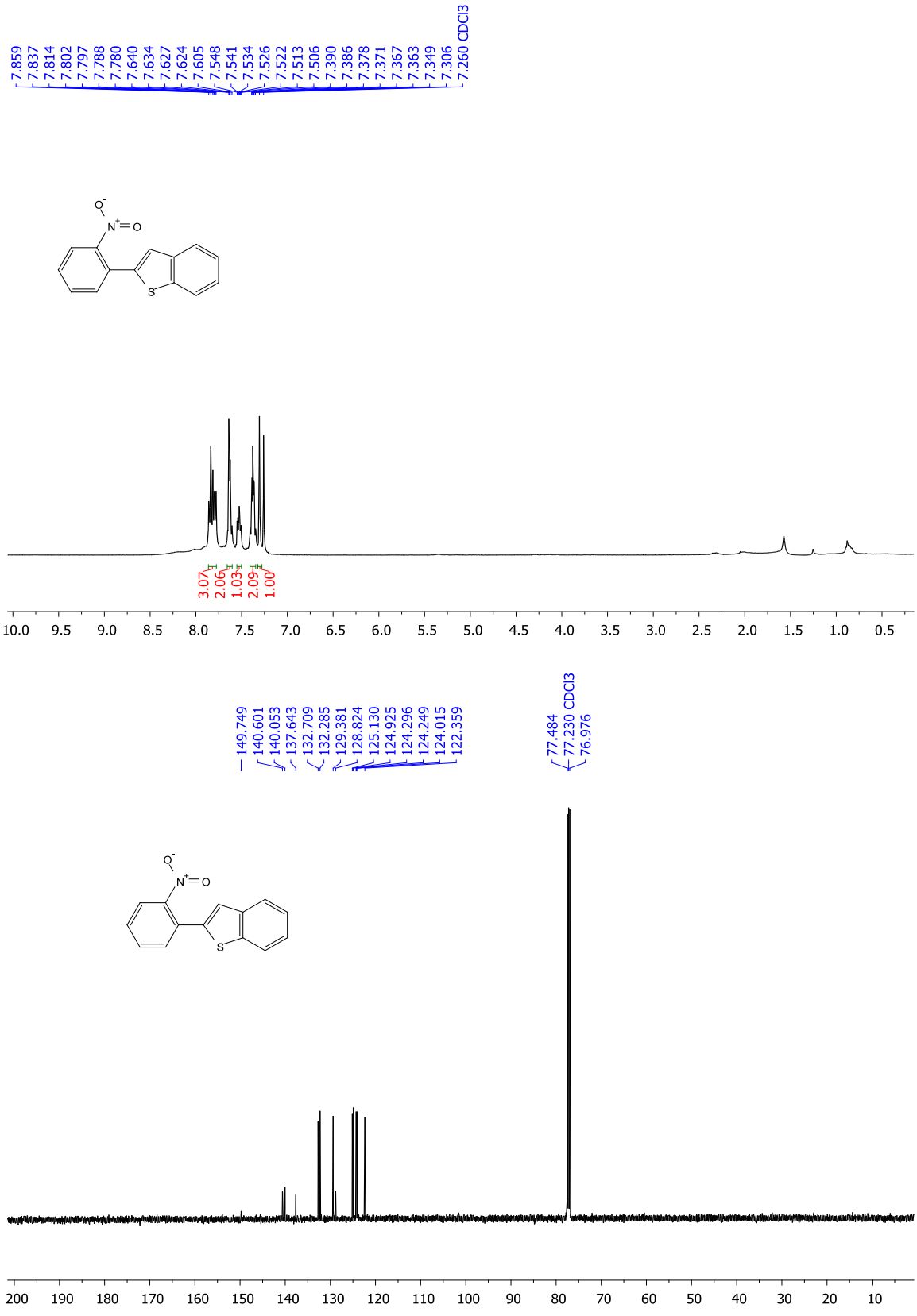


Table 3, Entry 3j:

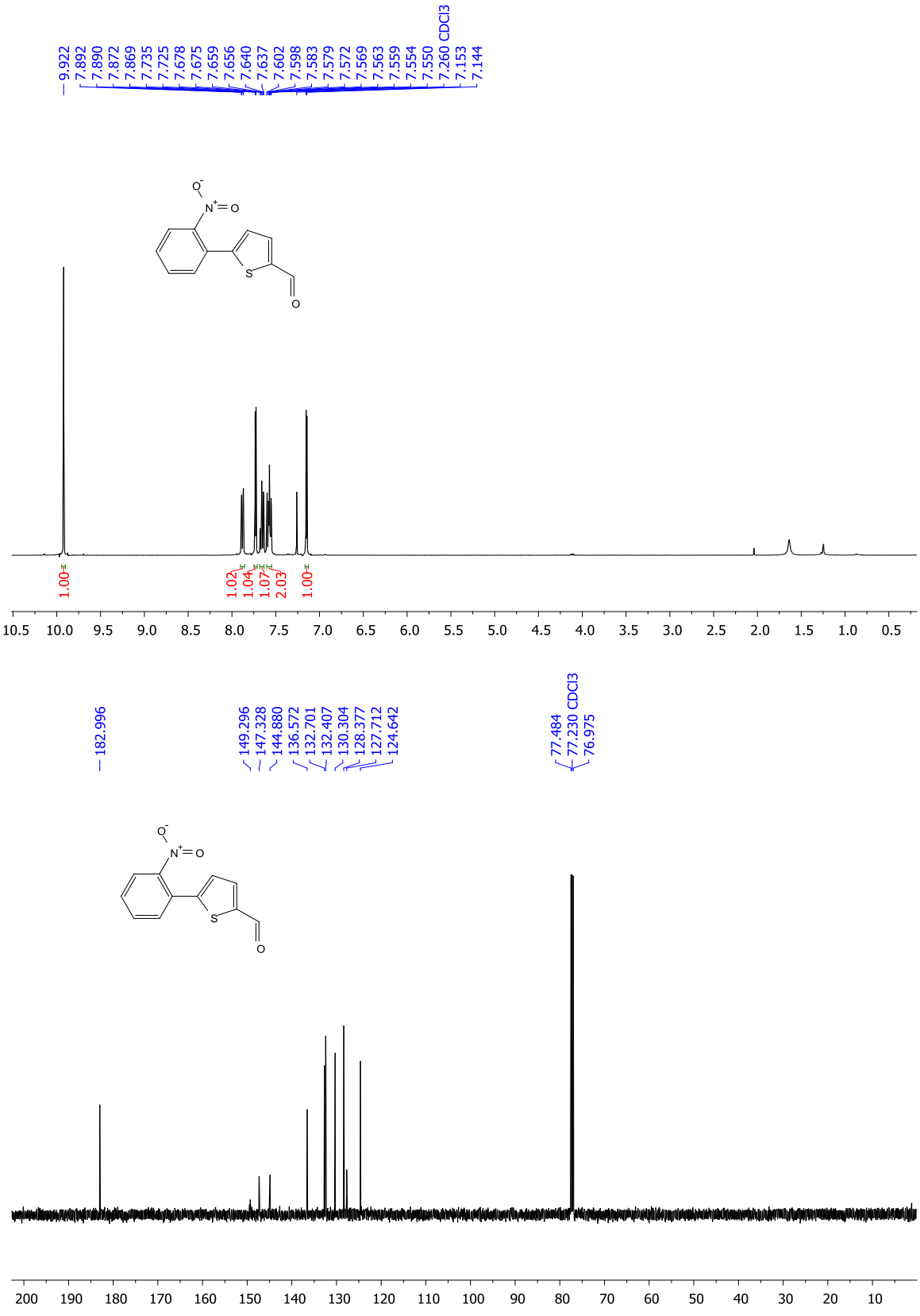


Table 3, Entry 3k:

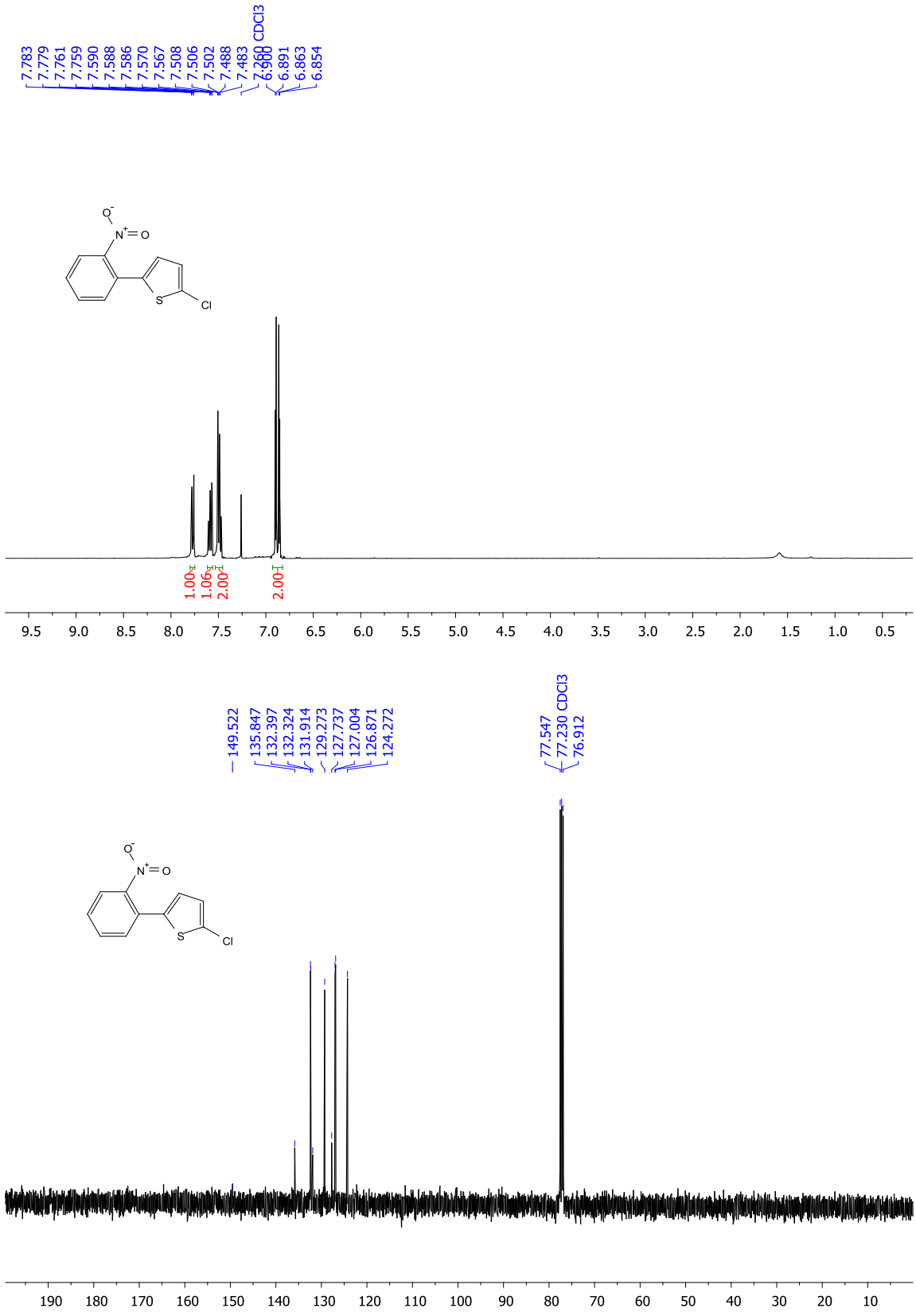


Table 3, Entry 3l:

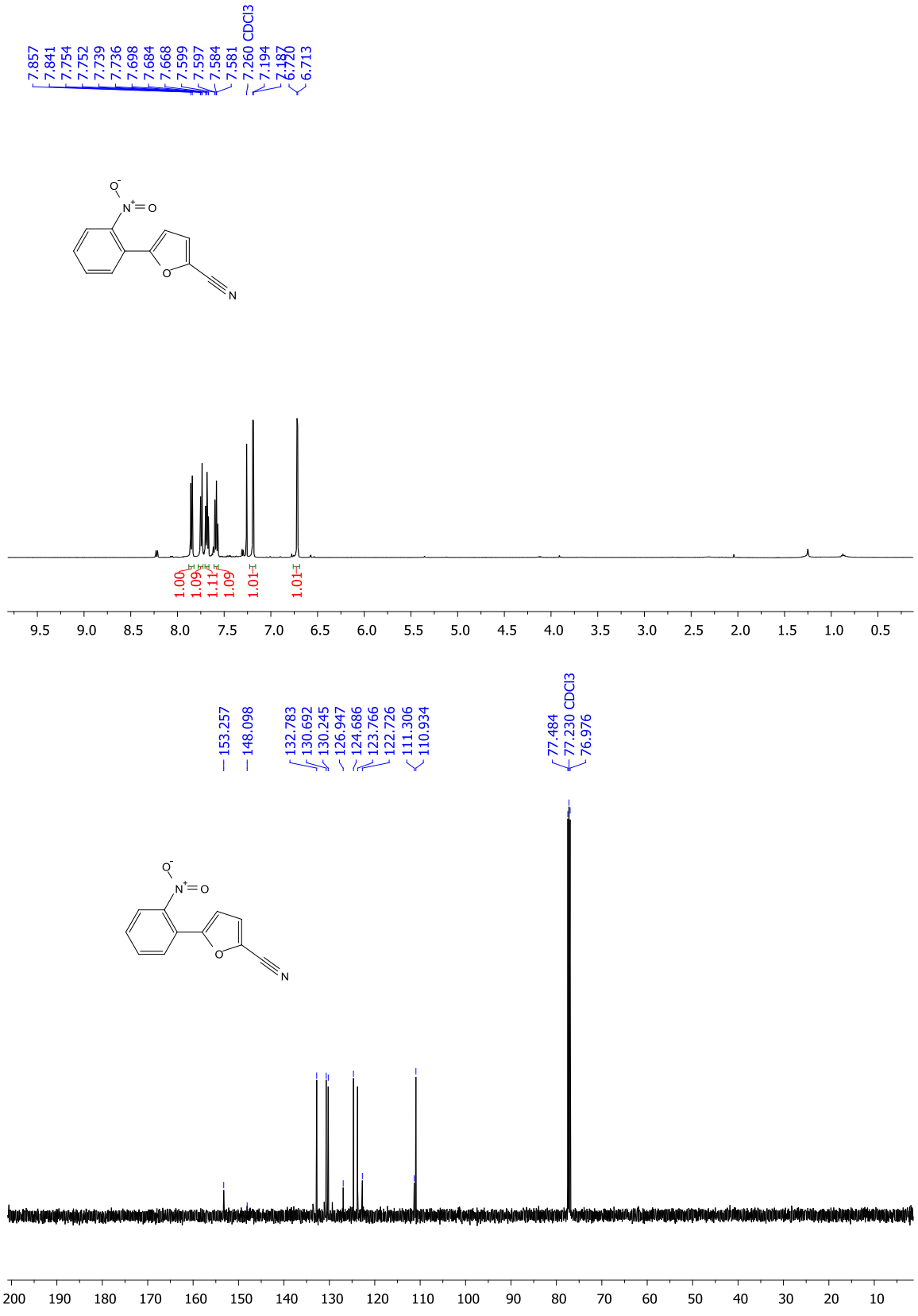


Table 3, Entry 3m: