Supporting Information for

A practical route to azo compounds by metal-free aerobic oxidation of arylhydrazides using NO_x system

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1. General Considerations

All commercially available compounds and solvents were purchased and used as received, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid stain followed by heating. Flash chromatography was performed using silica gel (particle size 40−63 μm, 230−400 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 400 MHz NMR (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F). Chemical shift values are given in parts per million relative to internal TMS (0.00 ppm for ^{1}H) or $CDCl_3$ (77.06 ppm for ^{13}C). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d

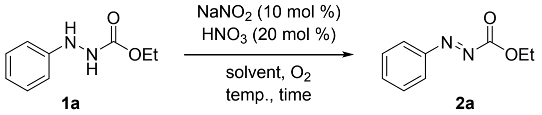
= doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. Coupling constants, J, were reported in hertz unit (Hz). High-resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using FAB method and magnetic sector mass analyzer.

2. Preparation of hydrazides

All hydrazides were prepared according to the known procedures: **1a–f**,[1] **1g**,[2] **1h–n**,[1] **1o**,[3] **3a–l**,[4] **5a–b**,[5] and **5c**.[6]

3. Optimization of metal-free aerobic oxidation of hydrazides

A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with ethyl 2-phenylhydrazinecarboxylate (0.5 mmol) and $NaNO_2$ (10 mol %, 0.05 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.5 mL of solvent was added, HNO_3 (20 mol %, 0.1 mmol) and solvent (0.5 mL) were added in sequence. After the time tested, the reaction was diluted by adding CH_2Cl_2 and washed with a saturated aqueous solution of Na_2CO_3. Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated on rotary evaporator. The ^{1}H NMR yield of the desired product was determined by integration using an internal standard (1,1,2,2-tetrachloroethane).



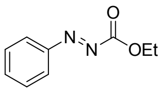
entry	solvent	atmosphere	Temp. (℃)	Time (h)	Yield(%)
1	AcOH	O_2	50	15	98
2	CH_2Cl_2	O_2	50	15	79
3	1,4-dioxane	O_2	50	15	65
4	CH_3CN	O_2	50	15	97
5	toluene	O_2	50	15	99
6	CH_3CN	O_2	50	3	15
7	toluene	O_2	50	3	99
8	toluene	O_2	50	1	99
9	toluene	O_2	50	0.5	70
10	toluene	O_2	rt	3	18
11	toluene	O_2	rt	15	96
12	CH_3CN	O_2	rt	15	54

13	CH_3CN	air	50	15	38
14	toluene	air	50	3	46
15	toluene	air	50	15	82
16	toluene	air	50	24	84
17	toluene	air	50	48	84
18	toluene	N_2	50	3	9
19[a]	toluene	O_2	50	3	4
20[a]	CH_3CN	O_2	50	3	7
21[b]	toluene	O_2	50	3	5
22[b]	CH_3CN	O_2	50	3	7
23[c]	toluene	O_2	50	3	16
24[d]	toluene	O_2	50	3	50
25[e]	toluene	O_2	50	3	76

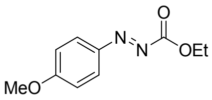
[a]No $NaNO_2$. [b]No HNO_3. [c]The use of AcOH instead of HNO_3. [d]The use of H_2SO_4 instead of HNO_3. [e]The use of TsOH instead of HNO_3.

4. General procedure for NO_x-catalyzed aerobic oxidation of hydrazides

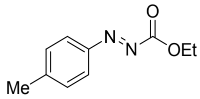
A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with hydrazines (0.5 mmol) and $NaNO_2$ (10 mol %, 0.05 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.5 mL of toluene was added, HNO_3 (20 mol %, 0.1 mmol) and toluene (0.5 mL) were added in sequence. The reaction mixture was stirred under an O_2 balloon at 50 °C for 3 h, and then cooled to room temperature. The reaction was diluted by adding CH_2Cl_2 and washed with a saturated aqueous solution of Na_2CO_3. Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated on rotary evaporator. The crude NMR of residue was pure, but, we purified the product by column chromatography for publication.



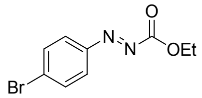
Ethyl 2-phenylazocarboxylate[3] **(2a)**; 99% (88.2 mg), orange oil, EA/hexane = 1:5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J=8.3 Hz, 2H), δ 7.59-7.50 (m, 3H), δ 4.51 (q, J=7.2 Hz, 2H), δ 1.46 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 151.6, 133.8, 129.3, 123.7, 64.5, 14.2.



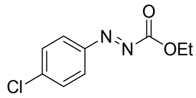
Ethyl 2-(4-methoxyphenyl)azocarboxylate[3] **(2b)**; 97% (101.0 mg), red oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J=9.1 Hz, 2H), δ 7.00 (d, J=9.1 Hz, 2H), δ 4.50 (q, J=7.1 Hz, 2H), δ 3.90 (s, 3H), δ 1.46 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.6, 162.1, 146.1, 126.4, 114.4, 64.1, 55.7, 14.2.



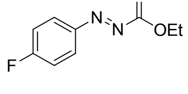
Ethyl 2-(4-methylphenyl)azocarboxylate[3] **(2c)**; 99% (95.1 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J=8.3 Hz, 2H), δ 7.32 (d, J=8.0 Hz, 2H), δ 4.51 (q, J=7.1 Hz, 2H), δ 2.44 (s, 3H), δ 1.47 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.2, 149.8, 145.1, 130.0, 123.9, 64.3, 21.7, 14.2.



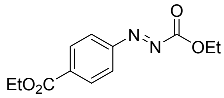
Ethyl 2-(4-bromophenyl)azocarboxylate[3] **(2d)**; 98% (126.0 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J=8.8 Hz, 2H), δ 7.72 (d, J=8.7 Hz, 2H), δ 4.57 (q, J=7.1 Hz, 2H), δ 1.52 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.9, 150.2, 132.7, 128.8, 125.1, 64.6, 14.1.



Ethyl 2-(4-chlorophenyl)azocarboxylate[3] **(2e)**; 99% (105.3 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J=8.8 Hz, 2H), δ 7.50 (d, J=8.8 Hz, 2H), δ 4.52 (q, J=7.1 Hz, 2H), δ 1.47 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.9, 149.9, 140.1, 129.6, 125.0, 64.6, 14.1.

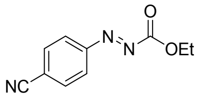


Ethyl 2-(4-fluorophenyl)azocarboxylate[3] **(2f)**; 98% (96.1 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01-7.94 (m, 2H), δ 7.21 (t, J=8.5 Hz, 2H), δ 4.52 (q, J=7.1 Hz, 2H), δ 1.47 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.0 (d, J= 256.6 Hz), 161.9, 148.1 (d, J= 3.0 Hz), 126.1 (d, J=9.6 Hz), 116.4 (d, J=23.2 Hz), 64.5, 14.1; ^{19}F NMR (376MHz, CDCl$_3$) δ -104.2.

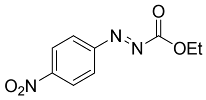


Ethyl 2-[4-(ethoxycarbonyl)phenyl]azocarboxylate[2] **(2g)**; 99% (123.9 mg), orange oil, EA/hexane

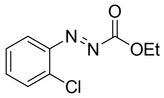
= 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J=8.5 Hz, 2H), δ 7.96 (d, J=8.5 Hz, 2H), δ 4.54 (q, J=7.1 Hz, 2H), δ 4.42 (q, J=7.1 Hz, 2H), δ 1.48 (t, J=7.1 Hz, 3H), δ 1.42 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 161.9, 153.8, 134.6, 130.6, 123.4, 64.7, 61.5, 14.3, 14.2.



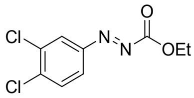
Ethyl 2-(4-cyanophenyl)azocarboxylate[3] **(2h)**; 99% (100.6 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J=8.4 Hz, 2H), δ 7.84 (d, J=8.3 Hz, 2H), δ 4.54 (q, J=7.1 Hz, 2H), δ 1.48 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 153.1, 133.4, 123.9, 117.7, 116.7, 64.9, 14.1.



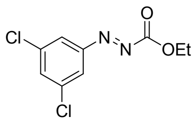
Ethyl 2-(4-nitrophenyl)azocarboxylate[3] **(2i)**; 97% (108.2 mg), red solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J=9.1 Hz, 2H), δ 8.06 (d, J=9.1 Hz, 2H), δ 4.56 (q, J=7.1 Hz, 2H), δ 1.49 (t, J=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.2, 150.3, 124.8, 124.2, 65.0, 14.1.



Ethyl 2-(2-chlorophenyl)azocarboxylate[3] **(2j)**; 75% (79.7 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.55 (m, 2H), δ 7.49 (t, J=7.0 Hz, 1H), δ 7.33 (t, J=7.1 Hz, 1H), δ 4.52 (q, J=7.1 Hz, 2H), δ 1.46 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 147.9, 137.3, 134.4, 131.1, 127.3, 117.2, 64.6, 14.1.

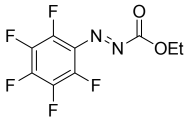


Ethyl 2-(3,4-dichlorophenyl)azocarboxylate[3] **(2k)**; 99% (122.3 mg), red solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), δ 7.80 (d, J=8.5 Hz, 1H), δ 7.63 (d, J=8.5 Hz, 1H), δ 4.53 (q, J=7.1 Hz, 2H), δ 1.47 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 150.3, 138.1, 134.0, 131.2, 124.6, 123.5, 64.8, 14.2.

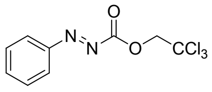


Ethyl 2-(3,5-dichlorophenyl)azocarboxylate[3] **(2l)**; 98% (121.1 mg), orange oil, EA/hexane = 1:5,

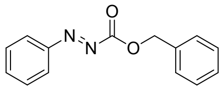
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), δ 7.56 (s, 1H), δ 4.53 (q, J=7.1 Hz, 2H), δ 1.47 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 152.4, 136.0, 132.9, 122.1, 64.8, 14.1.



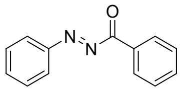
Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate[3] **(2m)**; 92% (123.3 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (q, J=7.1 Hz, 2H), δ 1.48 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 144.8-144.6 (m), 144.3-143.0 (m), 142.4-142.0 (m), 140.7-140.3 (m), 139.5-139.0 (m), 136.9-136.5 (m), 126.9-126.7 (m), 65.2, 14.0; ^{19}F NMR (376MHz, $CDCl_3$) δ -146.5, -160.9.



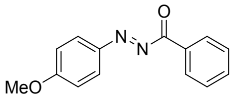
2,2,2-Trichloroethyl 2-phenylazocarboxylate[3] **(2n)**; 99% (139.4 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=7.7 Hz, 2H), δ 7.64 (t, J=7.3 Hz, 1H), δ 7.56 (t, J=7.5 Hz, 2H), δ 5.07 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 151.7, 134.6, 129.4, 124.2, 94.0, 76.5.



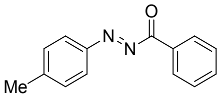
Benzyl 2-phenylazocarboxylate[3] **(2o)**; 97% (116.5 mg), orange oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J=7.6 Hz, 2H), δ 7.60-7.56 (m, 1H), δ 7.54-7.45 (m, 4H), δ 7.43-7.36 (m, 3H), δ 5.47 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 151.6, 134.4, 133.9, 129.3, 128.9, 128.8, 128.7, 123.8, 69.9.



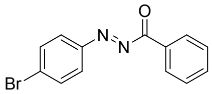
Benzoylazobenzene[3] **(4a)**; 99% (104.1 mg), red oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J=8.1 Hz, 2H), δ 8.00 (d, J=7.9 Hz, 2H), δ 7.66 (t, J=7.4 Hz, 1H), δ 7.62-7.49 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 152.0, 134.6, 133.4, 130.8, 130.5, 129.4, 128.9, 123.6.



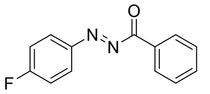
Benzoyl-2-(4-methoxyphenyl)diazene[7] **(4b)**; 98% (117.7 mg), dark red oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=7.5 Hz, 2H), δ 8.01 (d, J=8.9 Hz, 2H), δ 7.64 (t, J=7.4 Hz, 1H), δ 7.51 (t, J=7.7 Hz, 2H), δ 7.03 (d, J=8.9 Hz, 2H), δ 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 164.2, 146.8, 134.3, 131.7, 130.6, 128.8, 126.2, 114.5, 55.8.



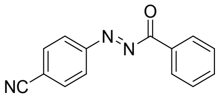
Benzoyl-2-(4-methylphenyl)diazene[7] **(4c)**; 99% (111.0 mg), orange solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=7.8 Hz, 2H), δ 7.90 (d, J=8.2 Hz, 2H), δ 7.63 (t, J=7.4 Hz, 1H), δ 7.49 (t, J=7.7 Hz, 2H), δ 7.34 (d, J=8.1 Hz, 2H), δ 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.9, 150.4, 144.6, 134.4, 131.1, 130.5, 130.0, 128.8, 123.7, 21.7.



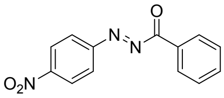
Benzoyl-2-(4-bromophenyl)diazene[7] **(4d)**; 99% (143.1 mg), orange solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=8.3 Hz, 2H), δ 7.87 (d, J=8.6 Hz, 2H), δ 7.73-7.65 (m, 3H), δ 7.53 (t, J=7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 150.7, 134.7, 132.7, 130.7, 130.5, 128.9, 128.4, 125.0.



Benzoyl-2-(4-fluorophenyl)diazene[8] **(4e)**; 97% (110.7 mg), red solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-7.98 (m, 4H), δ 7.66 (t, J=7.4 Hz, 1H), δ 7.52 (t, J=7.7 Hz, 2H), δ 7.24 (t, J=8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.6, 165.8 (d, J=255.9 Hz), 148.6 (d, J=2.8 Hz), 134.6, 130.8, 129.7 (d, J=165.5 Hz), 123.0 (J=9.5 Hz), 116.5(J=23.2 Hz); ^{19}F NMR (376MHz, $CDCl_3$) δ -104.2.

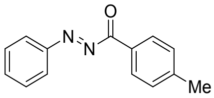


Benzoyl-2-(4-cyanophenyl)diazene[8] **(4f)**; 99% (116.4 mg), light brown solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=8.4 Hz, 2H), δ 8.02 (d, J=8.2 Hz, 2H), δ 7.88 (d, J=8.4 Hz, 2H), δ 7.70 (t, J=7.4 Hz, 1H), δ 7.55 (t, J=7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 153.5, 135.0, 133.5, 130.5, 130.1, 129.1, 123.9, 117.9, 116.4.

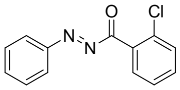


Benzoyl-2-(4-nitroophenyl)diazene[7] **(4g)**; 98% (125.1 mg), orange solid, EA/hexane = 1:5, ^{1}H

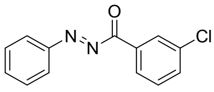
NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J=8.9 Hz, 2H), δ 8.12 (d, J=8.9 Hz, 2H), δ 8.03 (d, J= 7.3Hz, 2H), δ 7.71 (t, J=7.4 Hz, 1H), δ 7.56 (t, J=7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 154.5, 150.1, 135.0, 130.5, 130.0, 129.1, 124.9, 124.1.



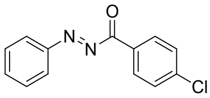
(4-Methylbenzoyl)-2-phenyldiazene[8] **(4h)**; 99% (111.0 mg), orange solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.92 (m, 4H), δ 7.61-7.52 (m, 3H), δ 7.30 (d, J=8.2 Hz, 2H), δ 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.9, 152.1, 145.7, 133.3, 130.6, 129.6, 129.3, 128.2, 123.5, 21.9.



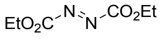
(2-Chlorobenzoyl)-2-phenyldiazene (4i); 99% (121.1 mg), red oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.94 (m, 3H), δ 7.62-7.46 (m, 5H), δ 7.44-7.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 152.1, 134.7, 134.1, 133.6, 132.9, 131.5, 130.9, 129.4, 126.9, 123.8; HRMS (FAB) m/z calcd. for $C_{13}H_{10}ClN_2O_1$ $[M + H]^+$: 245.0482, found 245.0484.



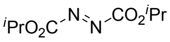
(3-Chlorobenzoyl)-2-phenyldiazene (4j); 97% (118.7 mg), red solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), δ 8.01 (d, J=6.8 Hz, 2H), δ 7.96 (d, J=7.4 Hz, 1H), δ 7.66-7.55 (m, 4H), δ 7.48 (t, J=7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 152.0, 135.1, 134.4, 133.8, 132.6, 130.4, 130.2, 129.4, 128.6, 123.7; HRMS (FAB) m/z calcd. for $C_{13}H_{10}ClN_2O_1$ $[M + H]^+$: 245.0482, found 245.0485.



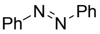
(4-Chlorobenzoyl)-2-phenyldiazene[8] **(4k)**; 98% (119.9 mg), red solid, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 4H), δ 7.64-7.54 (m, 3H), δ 7.50 (d, J=8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 152.0, 141.2, 133.7, 131.9, 129.4(2C), 129.3, 123.7.



Diethyl azodicarboxylate[5] **(6a)**; crude yield: 76% (66.2 mg), EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (q, J=7.1 Hz, 4H), δ 1.45 (t, J=7.1 Hz, 6H).



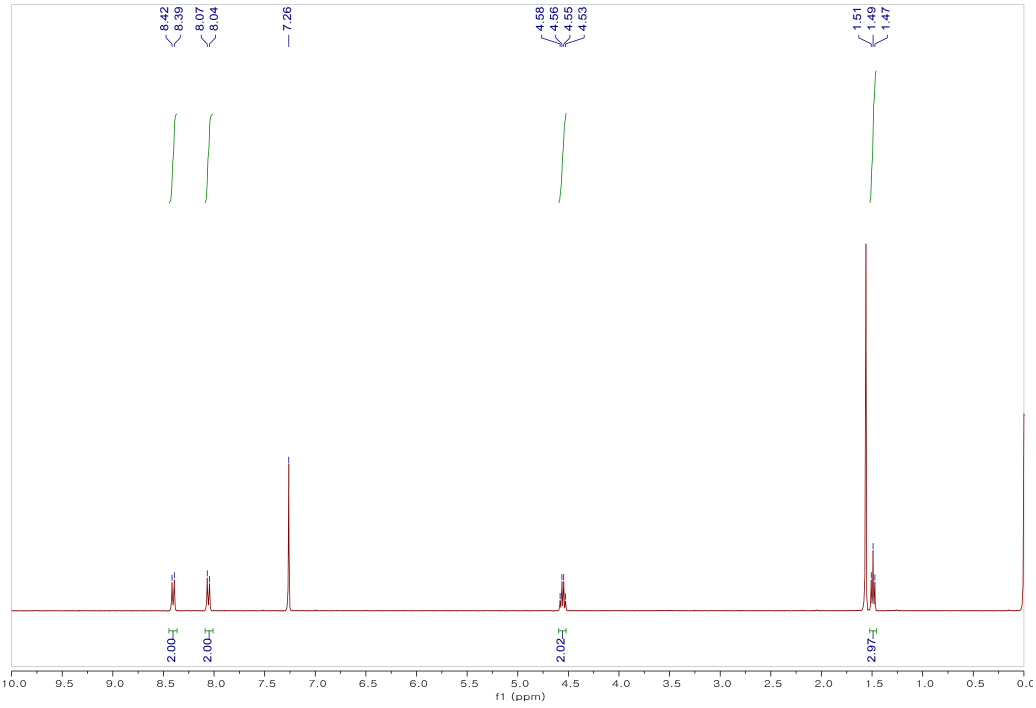
Diisopropyl azodicarboxylate[5] **(6b)**; 77% (77.9 mg), yellow oil, EA/hexane = 1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29-5.19 (m, 2H), δ 1.43 (d, J=6.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 74.4, 21.6.



Diazobenzene[6] **(6c)**; 99% (90.2 mg), orange solid, EA/hexane = 1:20, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J=7.0 Hz, 4H), δ 7.55-7.44 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 131.0, 129.1, 122.9.

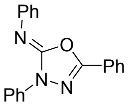
5. Procedure for NO_x-catalyzed aerobic oxidation of hydrazide on large scale

A 250 mL round-bottom flask, which was equipped with a magnetic stir bar and charged with ethyl 2-(4-nitrophenyl)hydrazinecarboxylate (40 mmol) and $NaNO_2$ (10 mol %, 4 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 50 mL of toluene was added, HNO_3 (20 mol %, 8 mmol) and toluene (50 mL) were added in sequence. The reaction mixture was stirred under an O_2 balloon at 50 °C for 4 h, and then cooled to room temperature. The reaction was diluted by adding CH_2Cl_2 and washed with a saturated aqueous solution of Na_2CO_3. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated on rotary evaporator. The residue was pure without further purification. The crude NMR was attached below.



6. Procedure for the one-pot annulation reaction

A 15 mm flame-dried test tube, which was equipped with a magnetic stir bar and charged with 1-benzoyl-2-phenylhydrazine (0.75 mmol) and $NaNO_2$ (10 mol %, 0.075 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.75 mL of CH_3CN was added, HNO_3 (20 mol %, 0.15 mmol) and CH_3CN (0.75 mL) were added in sequence. The reaction mixture was stirred under an O_2 balloon at 50 ℃. After 3 h, the reaction mixture was added to 100 mL two neck round bottom flask, which was equipped with a magnetic stir bar, K_2CO_3 (3 mmol, 414.6 mg), CH_3CN (2.5 mL), and reflux system under N_2. Then, the test tube was washed with the additional CH_3CN (1 mL) and the solution was added to the round bottom flask. After the addition of PhNCS (0.5 mmol, 62 μL) to the round bottom flask, the reaction mixture was refluxed. After 2 h, the reaction mixture was cooled, quenched with 5% $Na_2S_2O_3$ (5 mL), diluted with brine (10 mL), and then extracted with EtOAc (15 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated on rotary evaporator. The residue was purified by column chromatography to give annulation product (EtOAc/PE=1:60).



(*Z*)-*N*,3,5-Triphenyl-1,3,4-oxadiazol-2(3*H*)-imine[9] **(7a)**; 83% (130.0 mg), white solid, EA/PE = 1:60, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J=7.8 Hz, 2H), δ 7.89 (d, J=7.9 Hz, 2H), δ 7.52-7.42 (m, 5H), δ 7.40-7.29 (m, 4H), δ 7.21 (t, J=7.4 Hz, 1H), δ 7.10 (t, J=7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 145.5, 144.4, 137.6, 131.5, 129.0, 128.9(2C), 125.9, 124.9, 123.6, 123.3, 123.2, 118.5.

7. References

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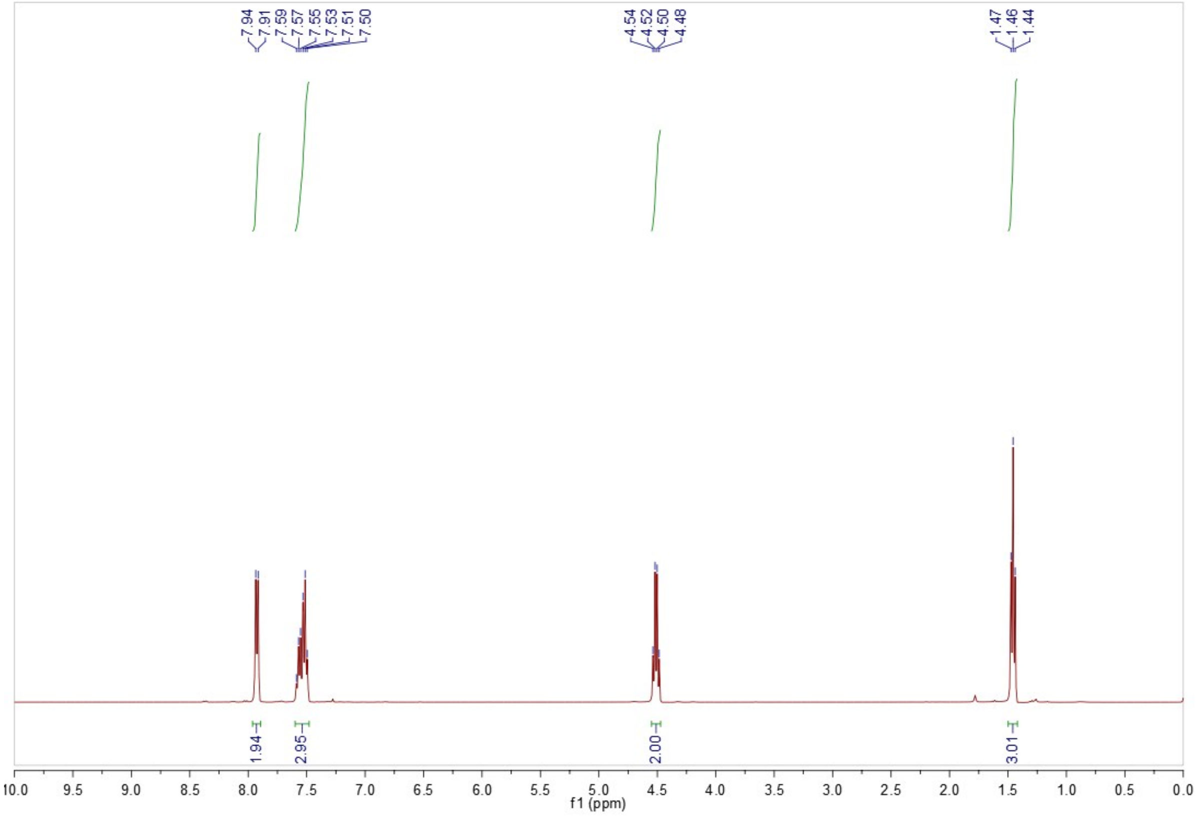
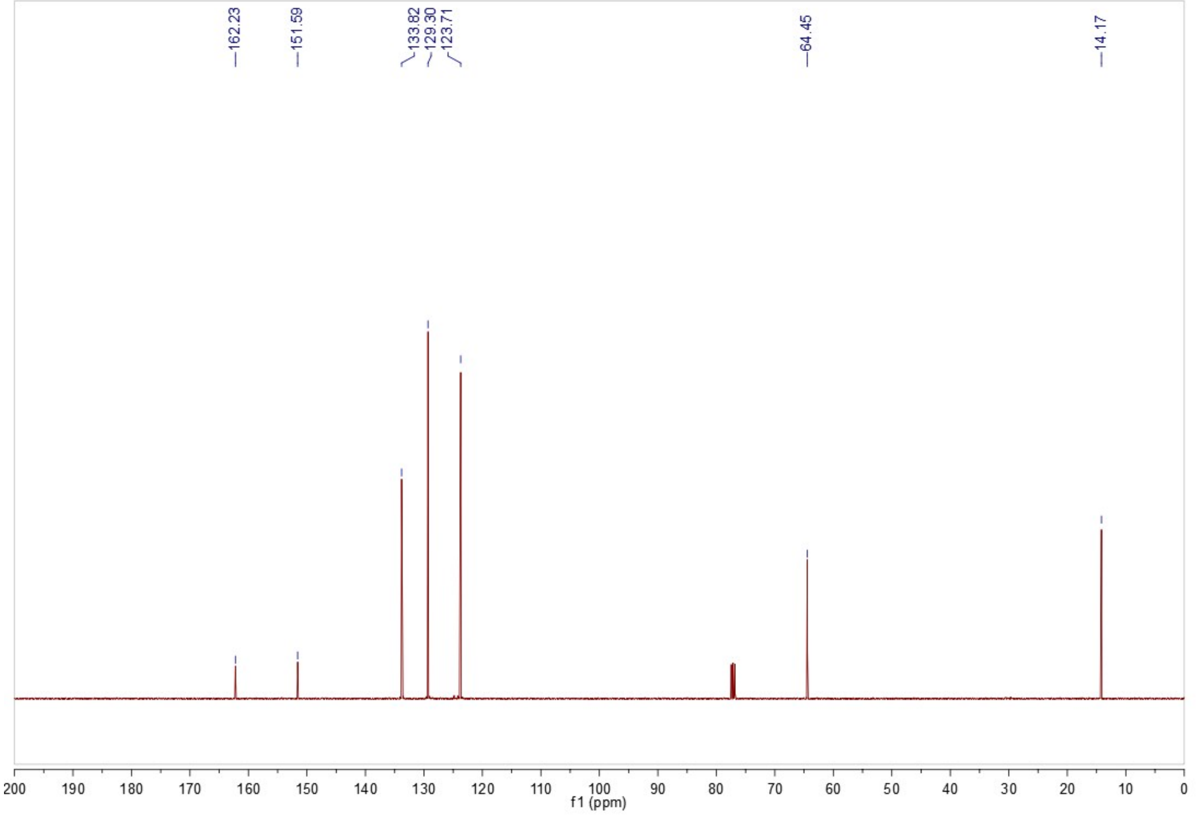
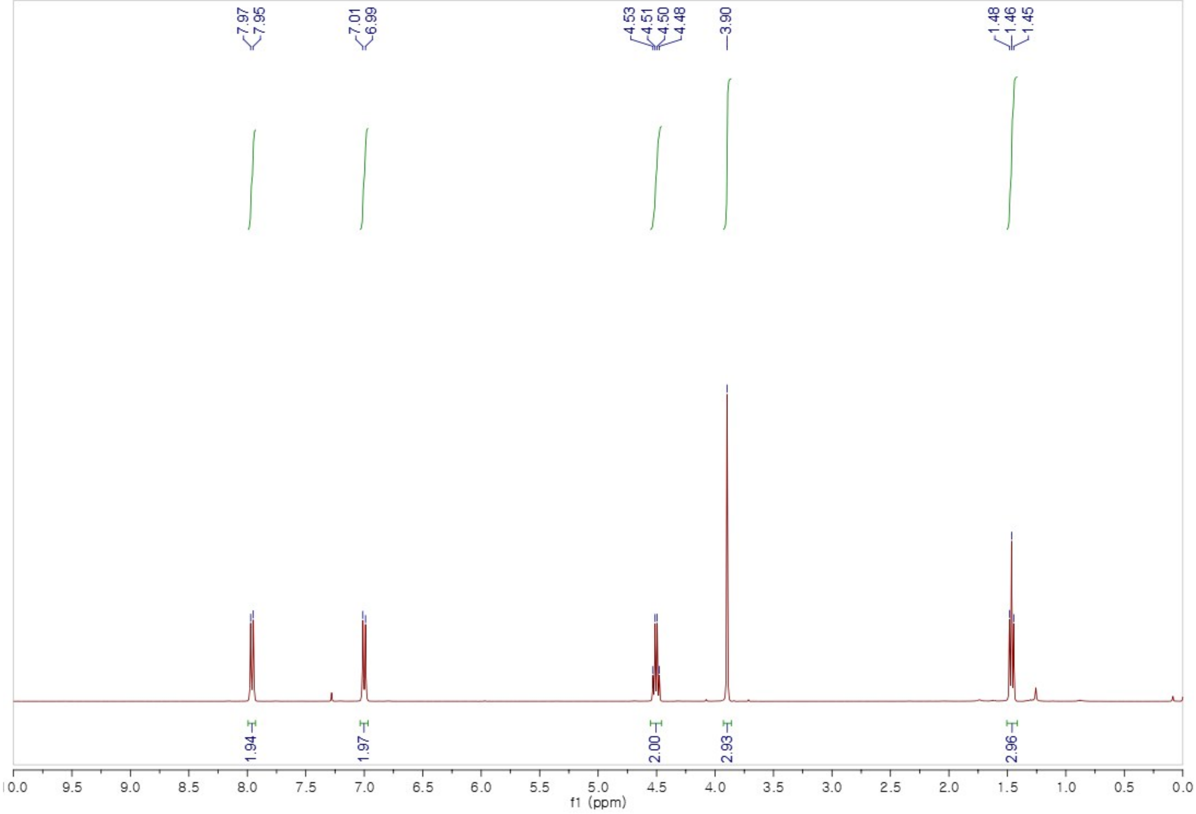
8. ^{1}H ,^{13}C and ^{19}F NMR spectra of substrates

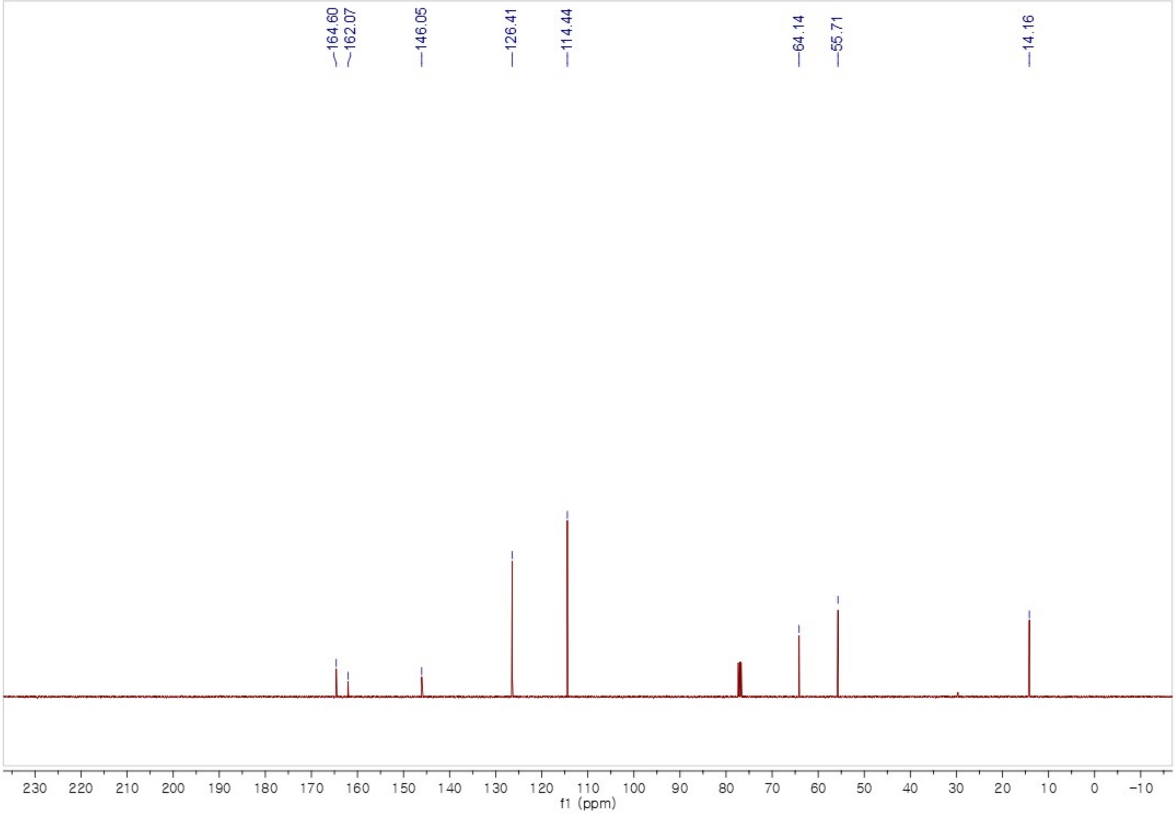
Ethyl 2-phenylazocarboxylate (2a)



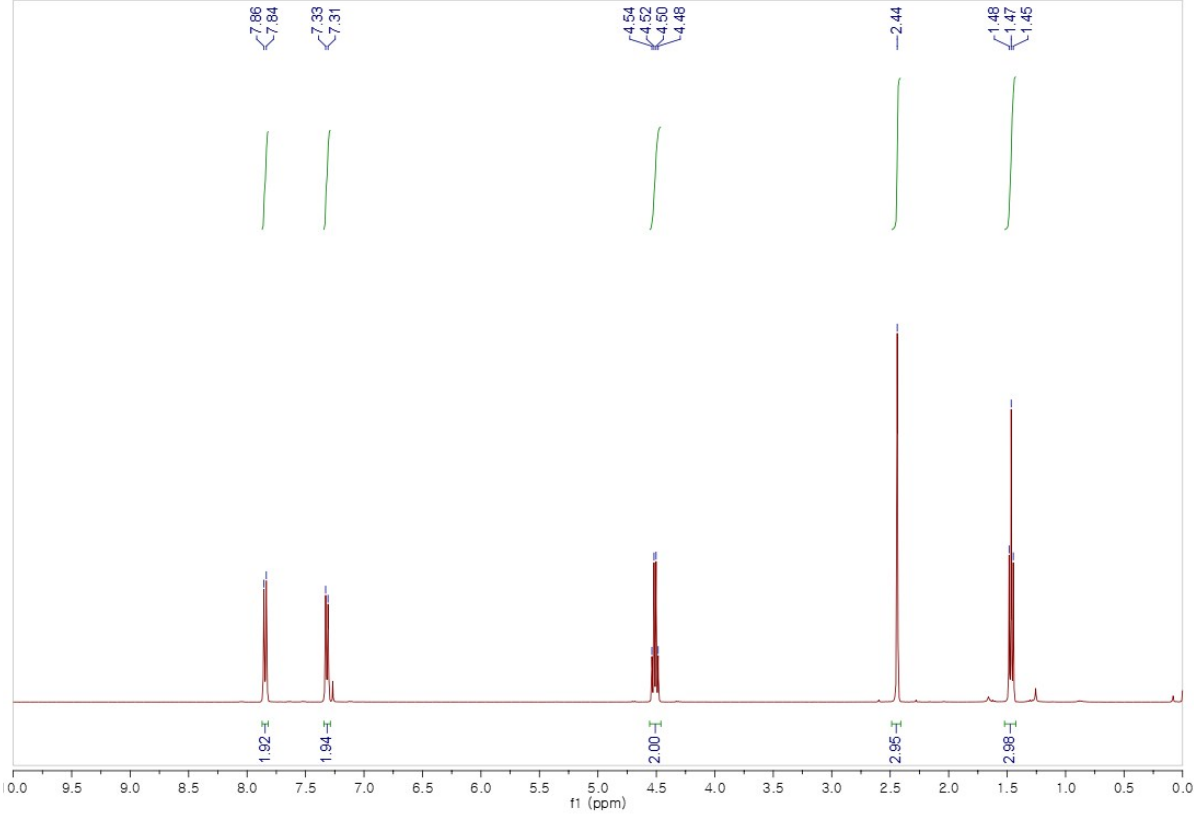


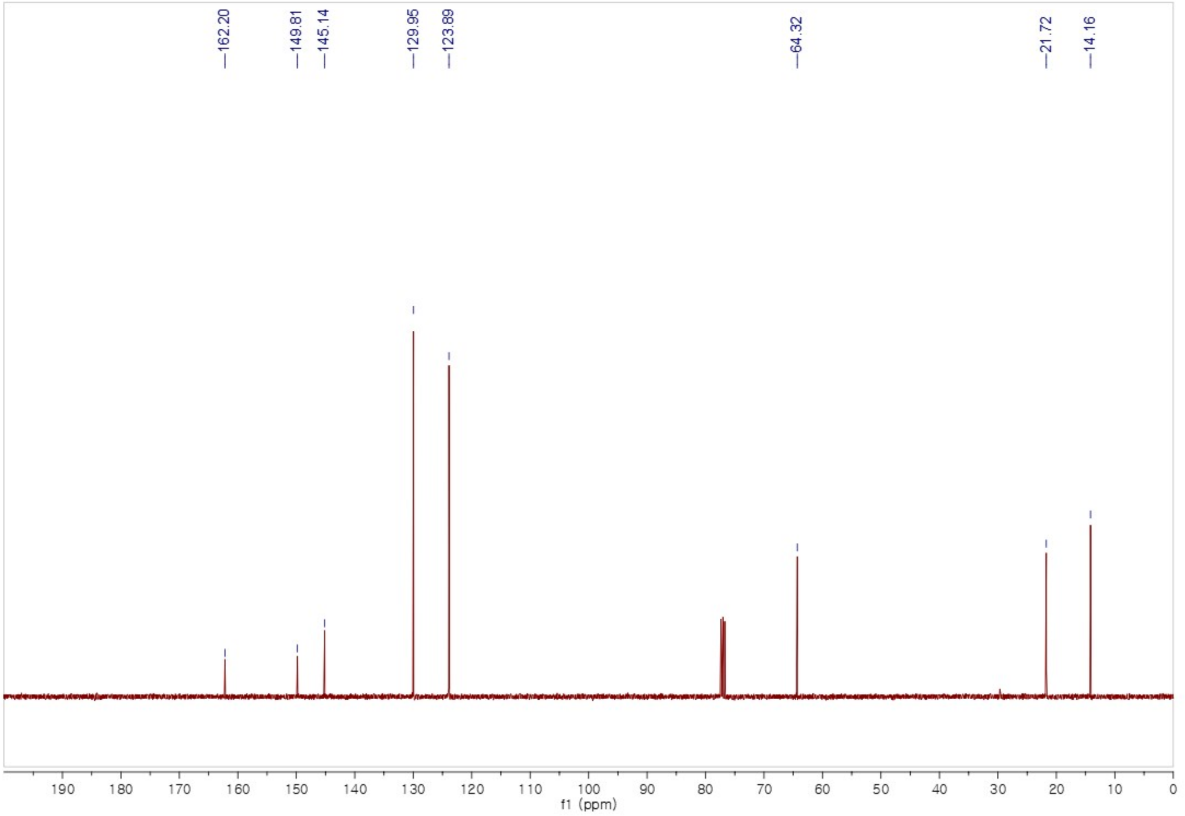
Ethyl 2-(4-methoxyphenyl)azocarboxylate (2b)



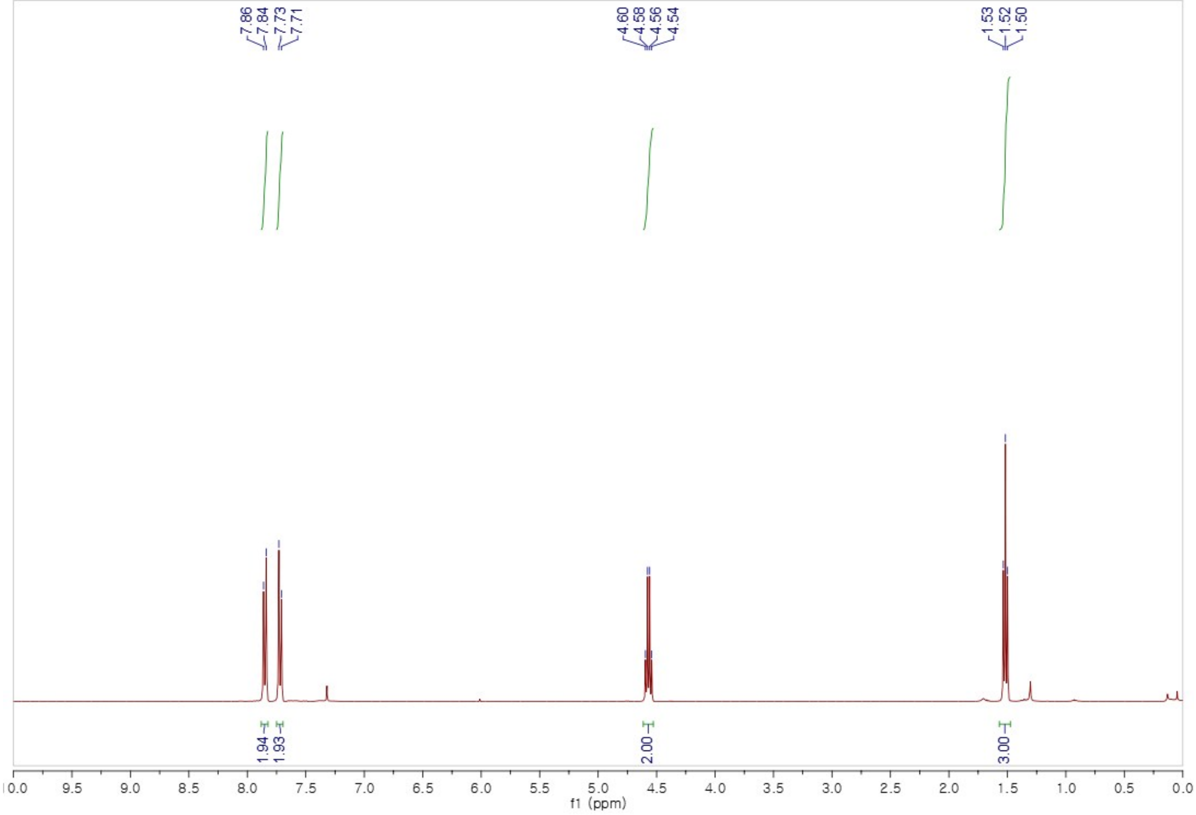


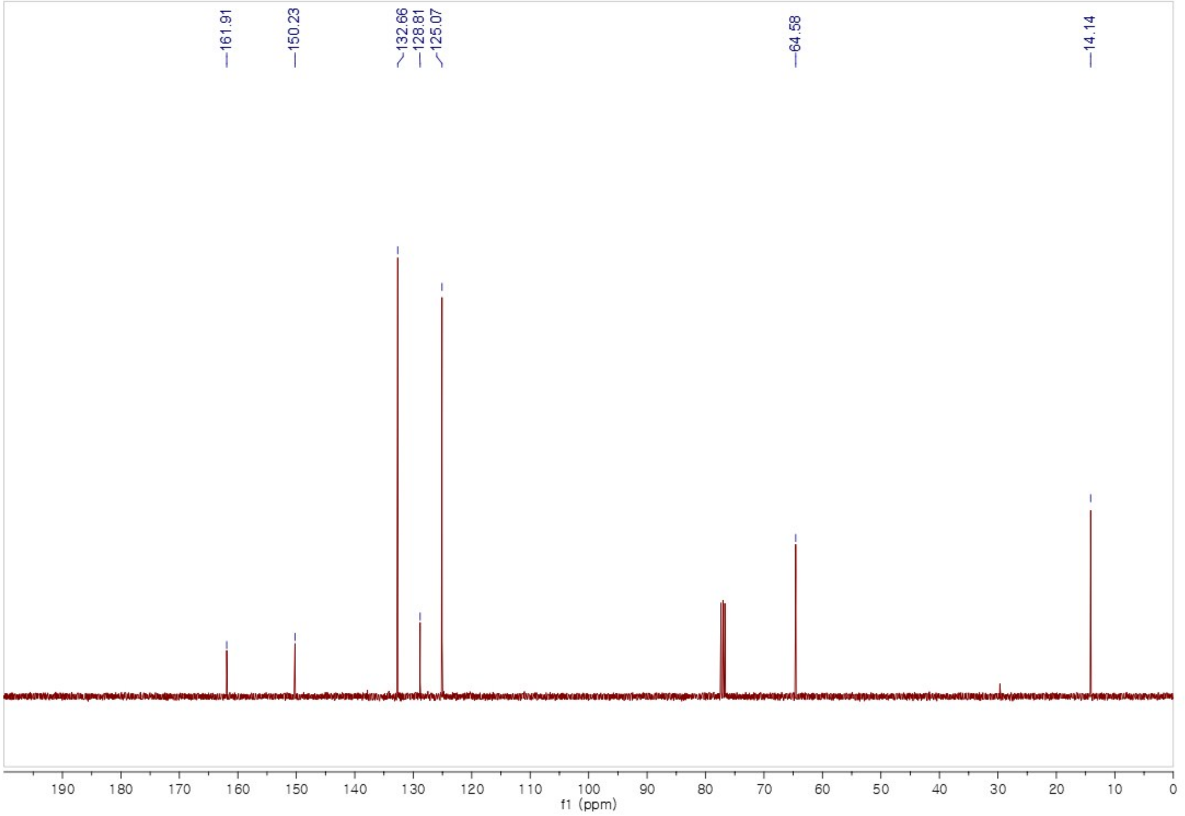
Ethyl 2-(4-methylphenyl)azocarboxylate (2c)



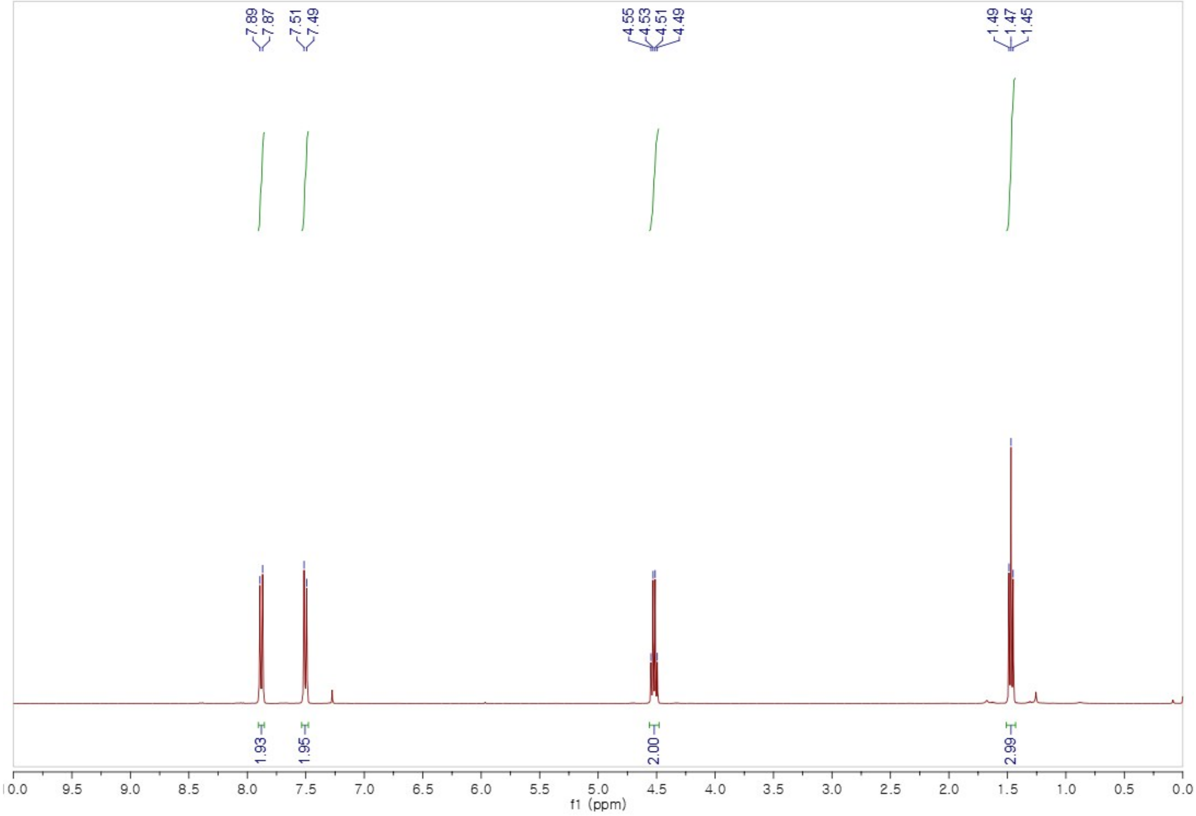


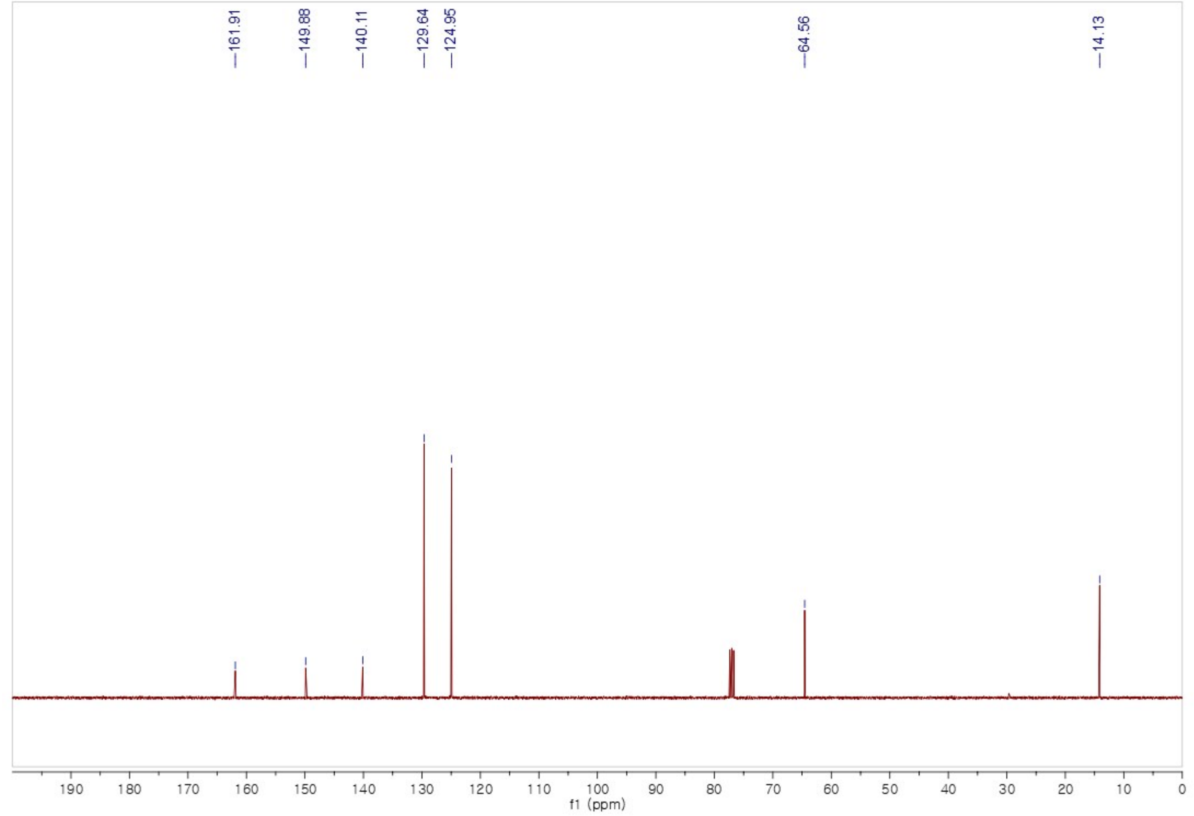
Ethyl 2-(4-bromophenyl)azocarboxylate (2d)



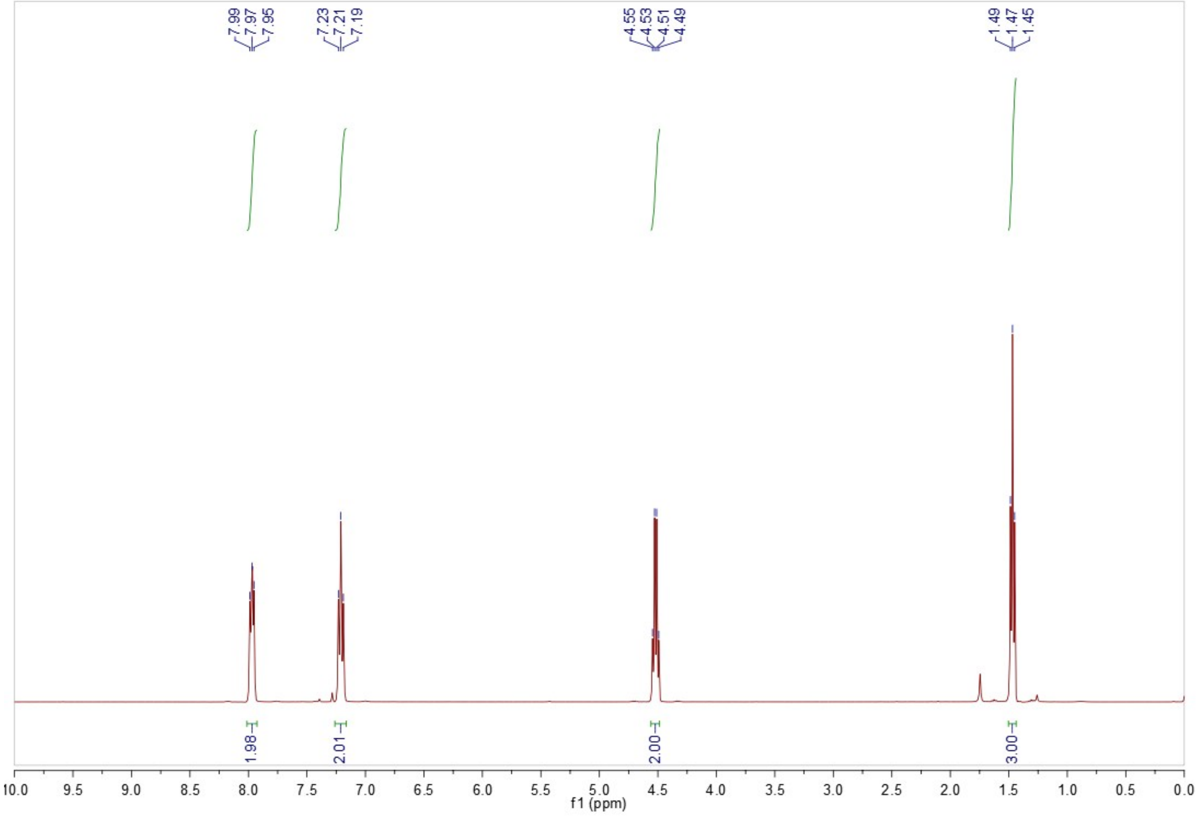


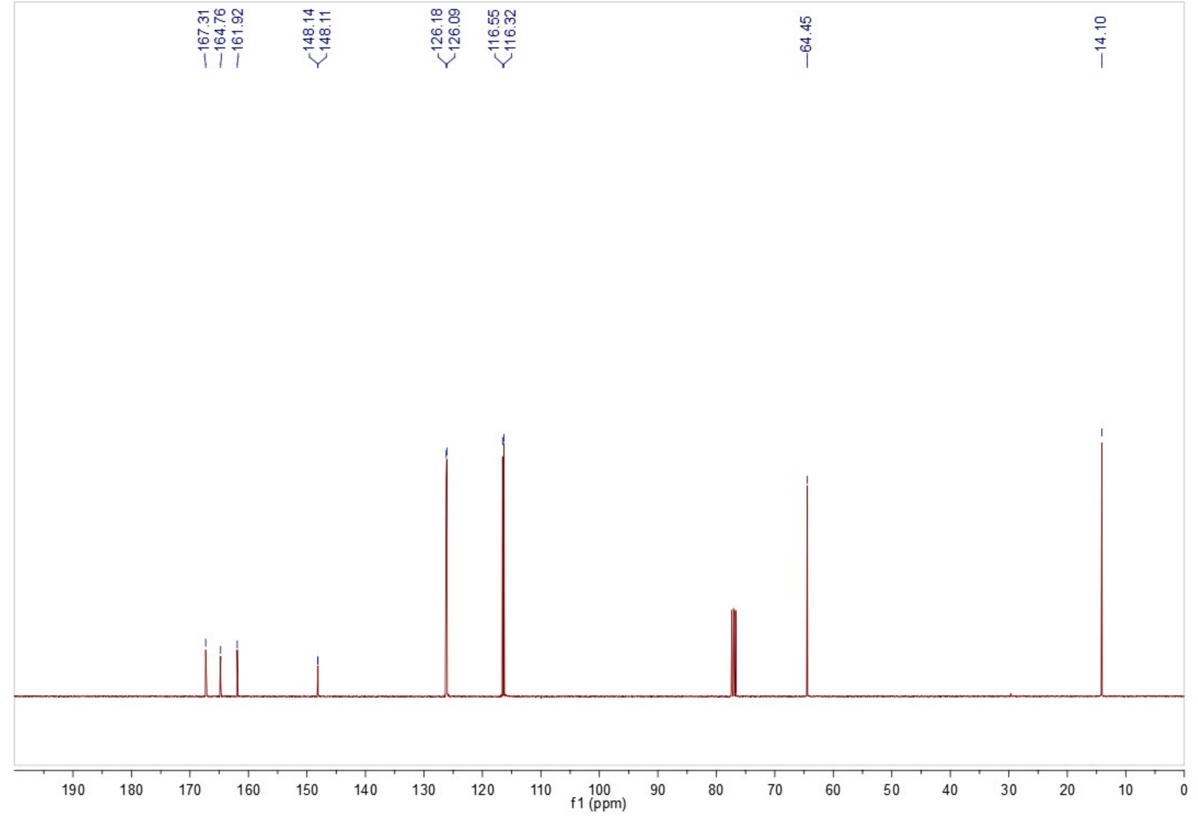
Ethyl 2-(4-chlorophenyl)azocarboxylate (2e)

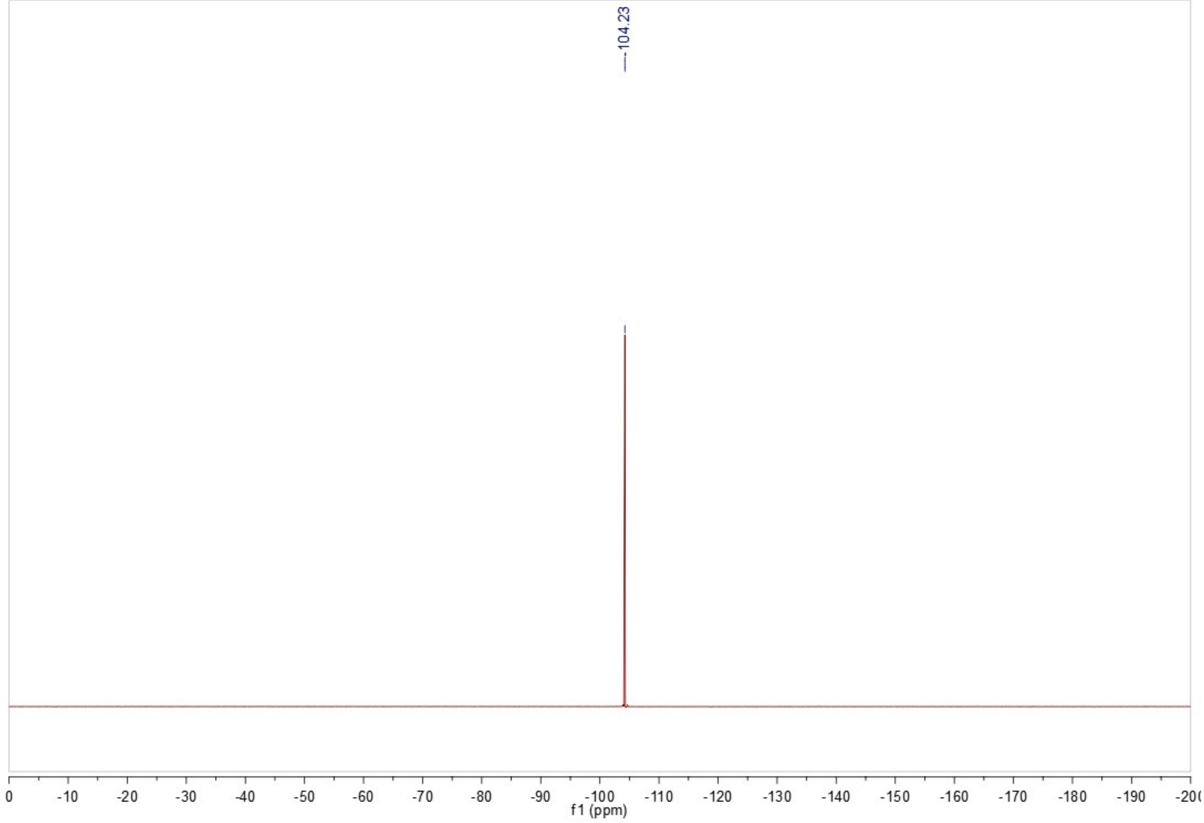




Ethyl 2-(4-fluorophenyl)azocarboxylate (2f)



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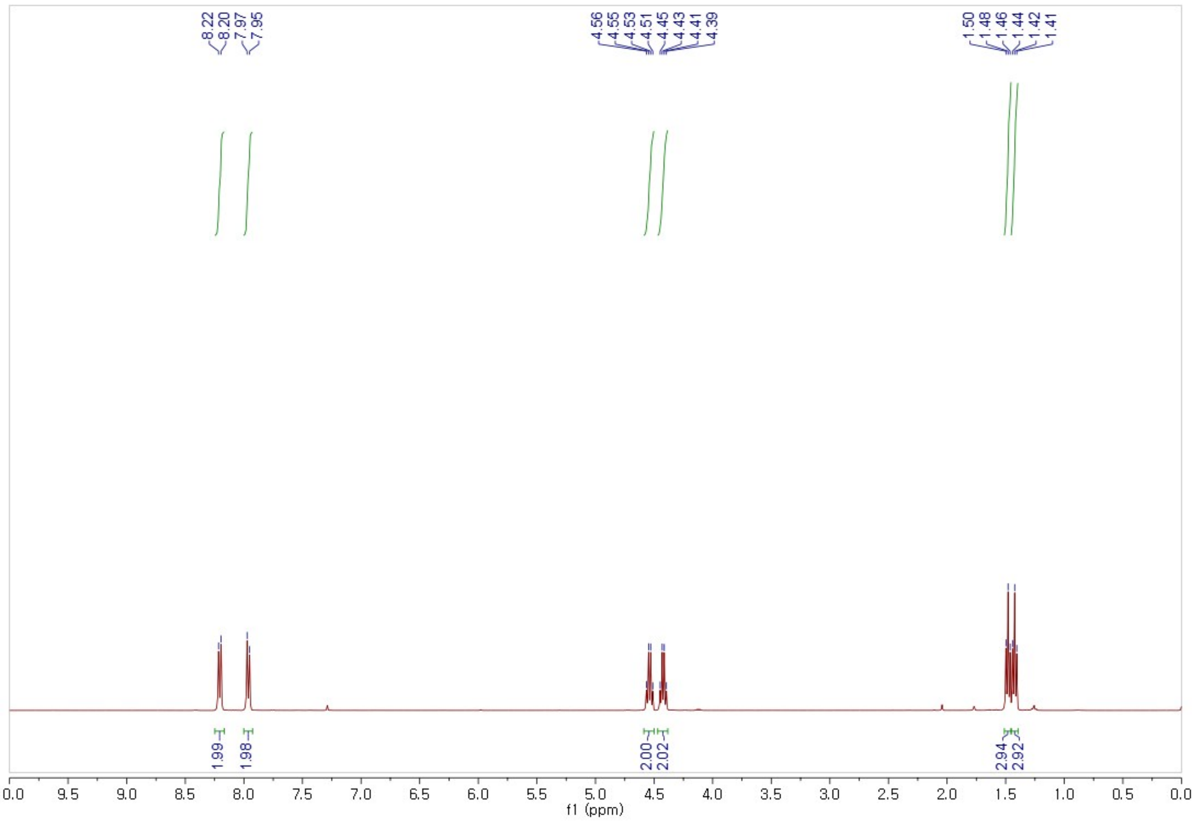
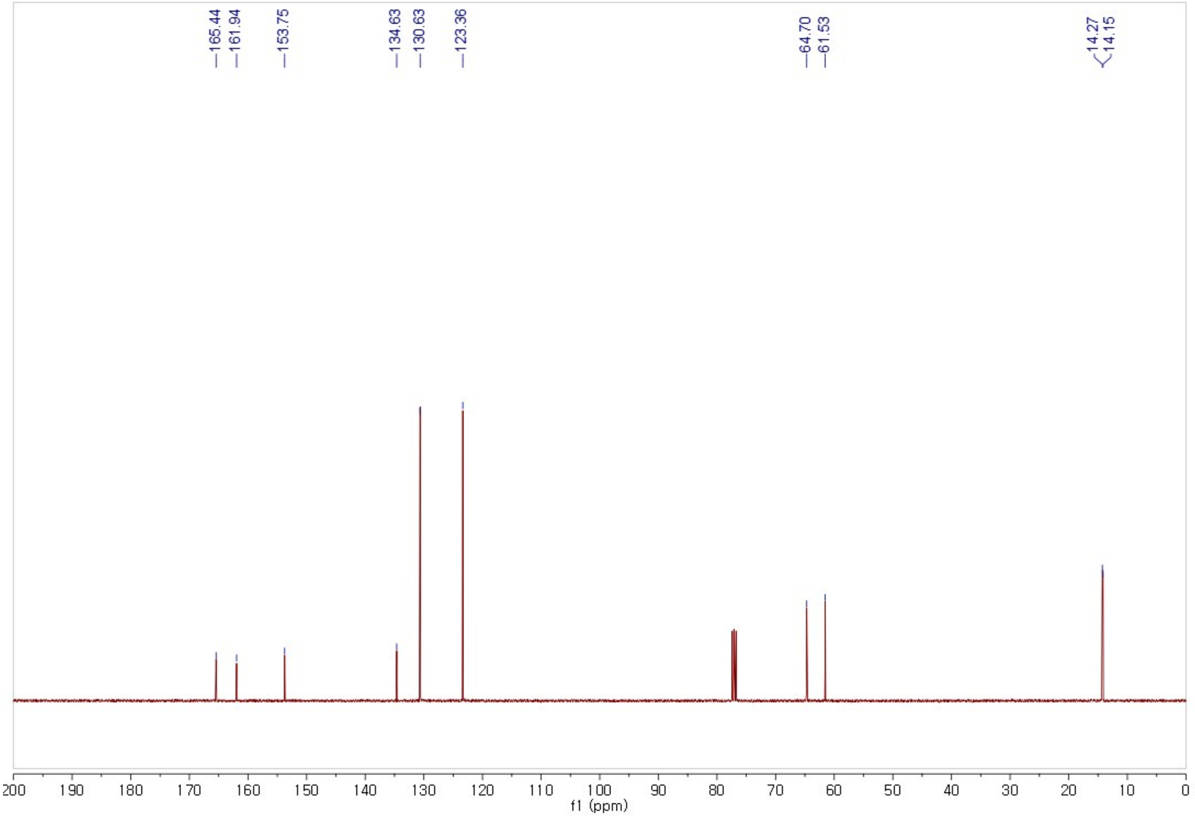
f1 (ppm)

Ethyl 2-[4-(ethoxycarbonyl)phenyl]azocarboxylate (2g)





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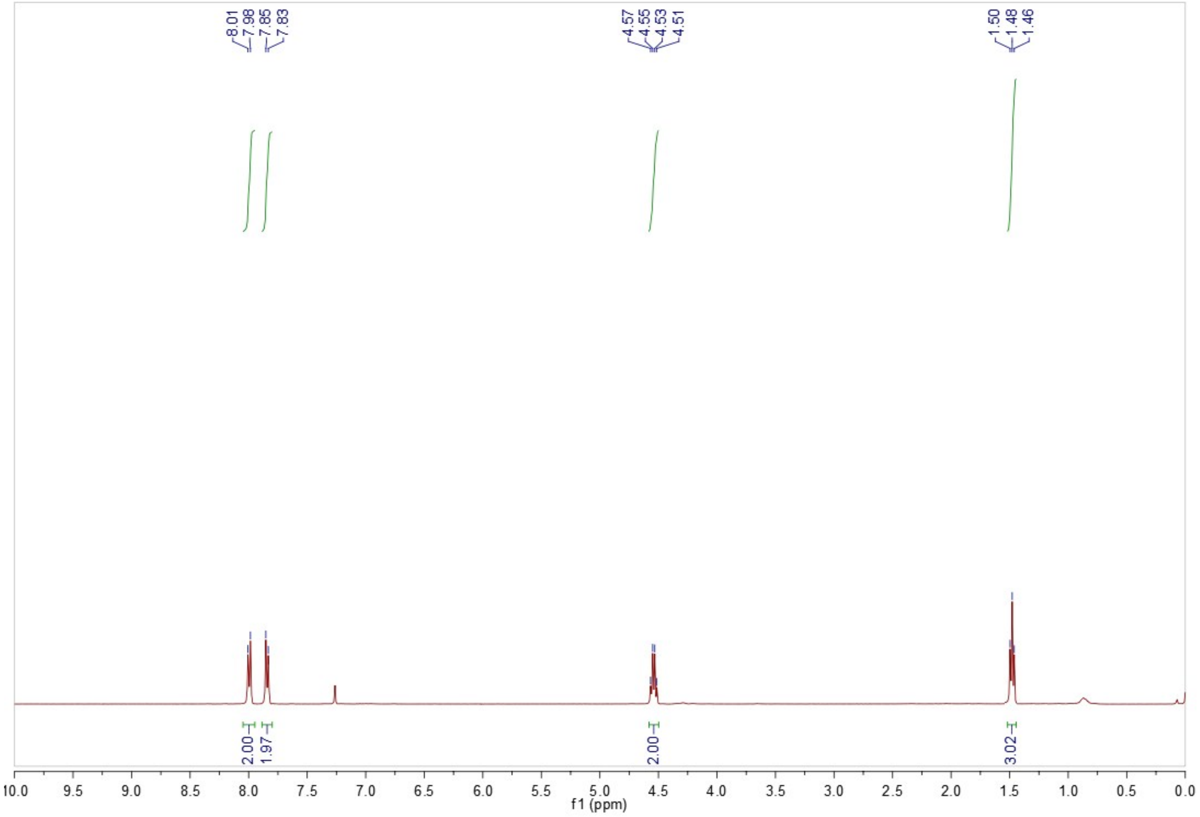

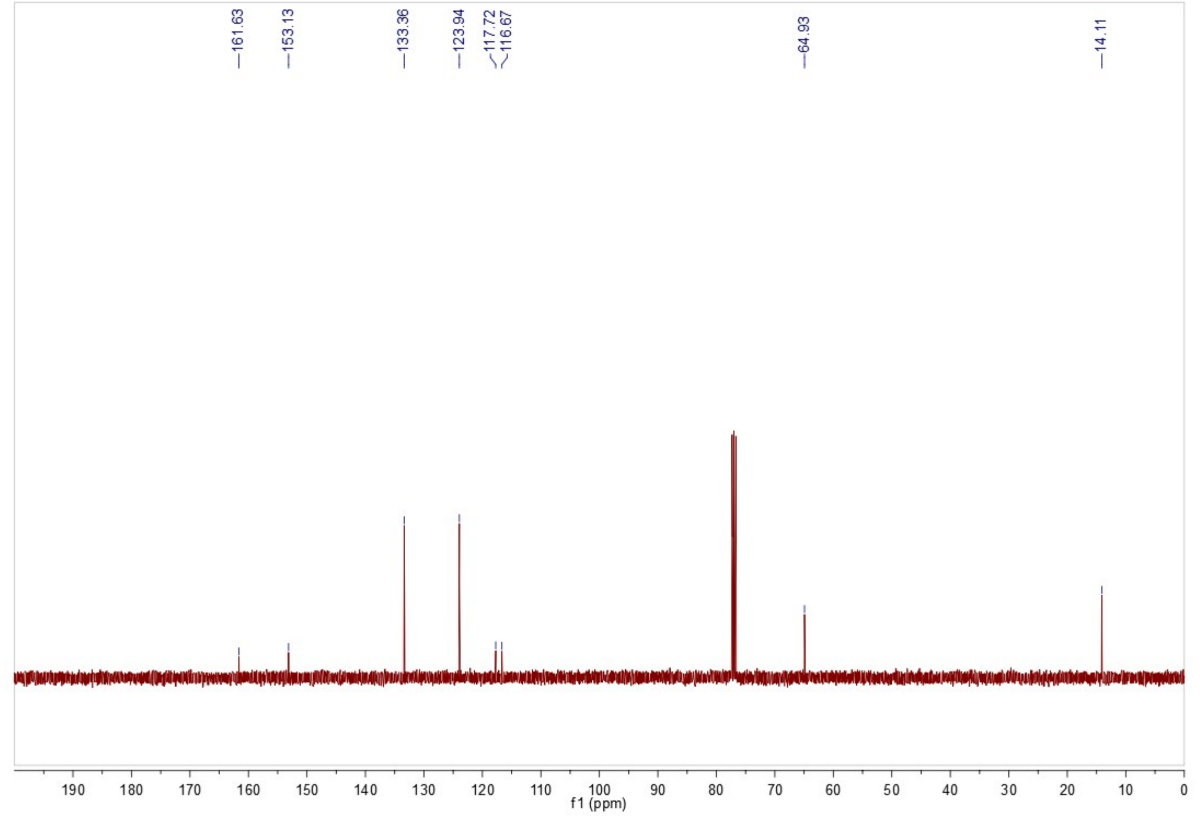

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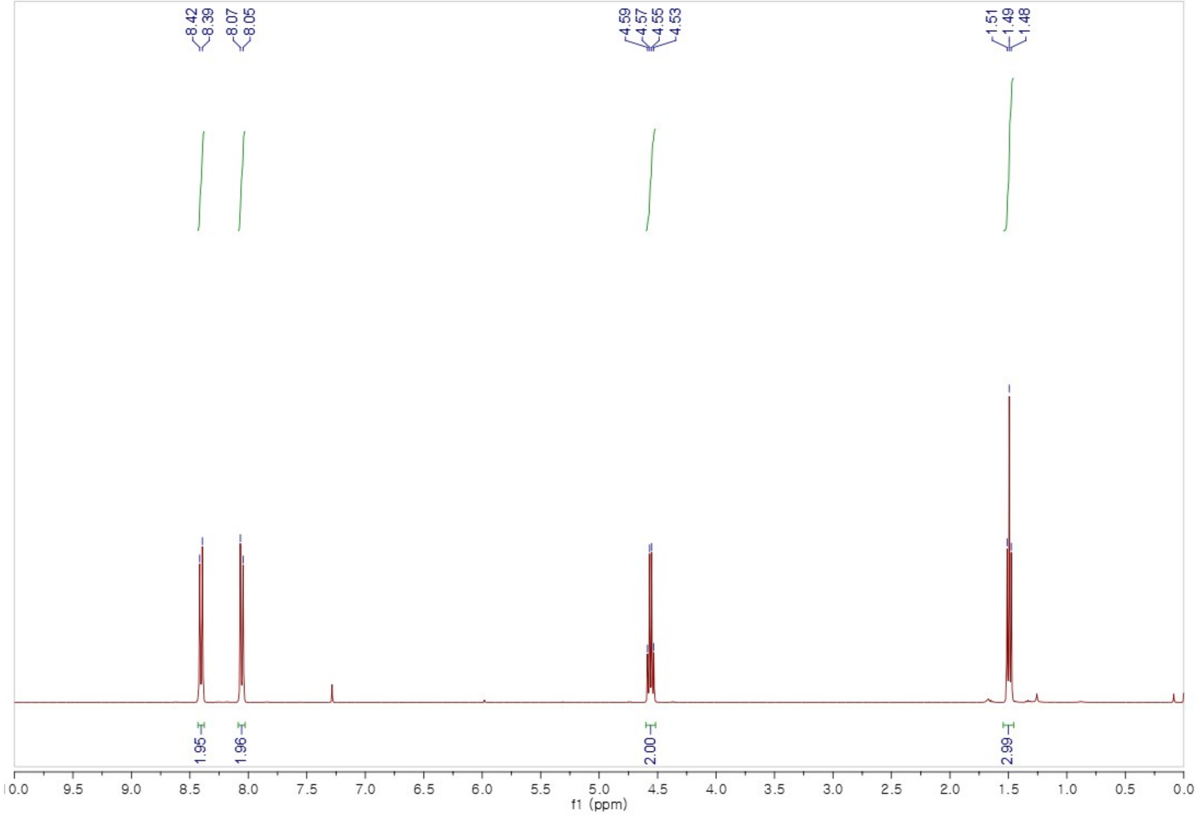
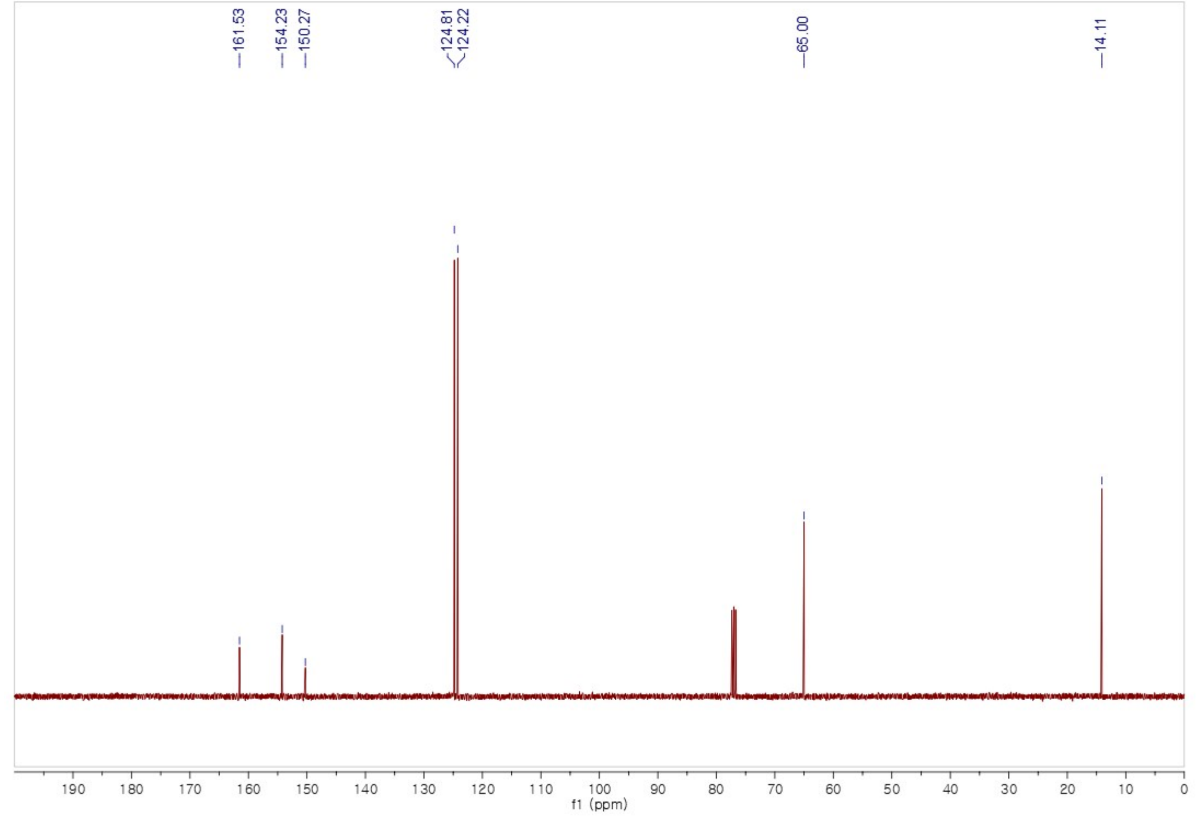
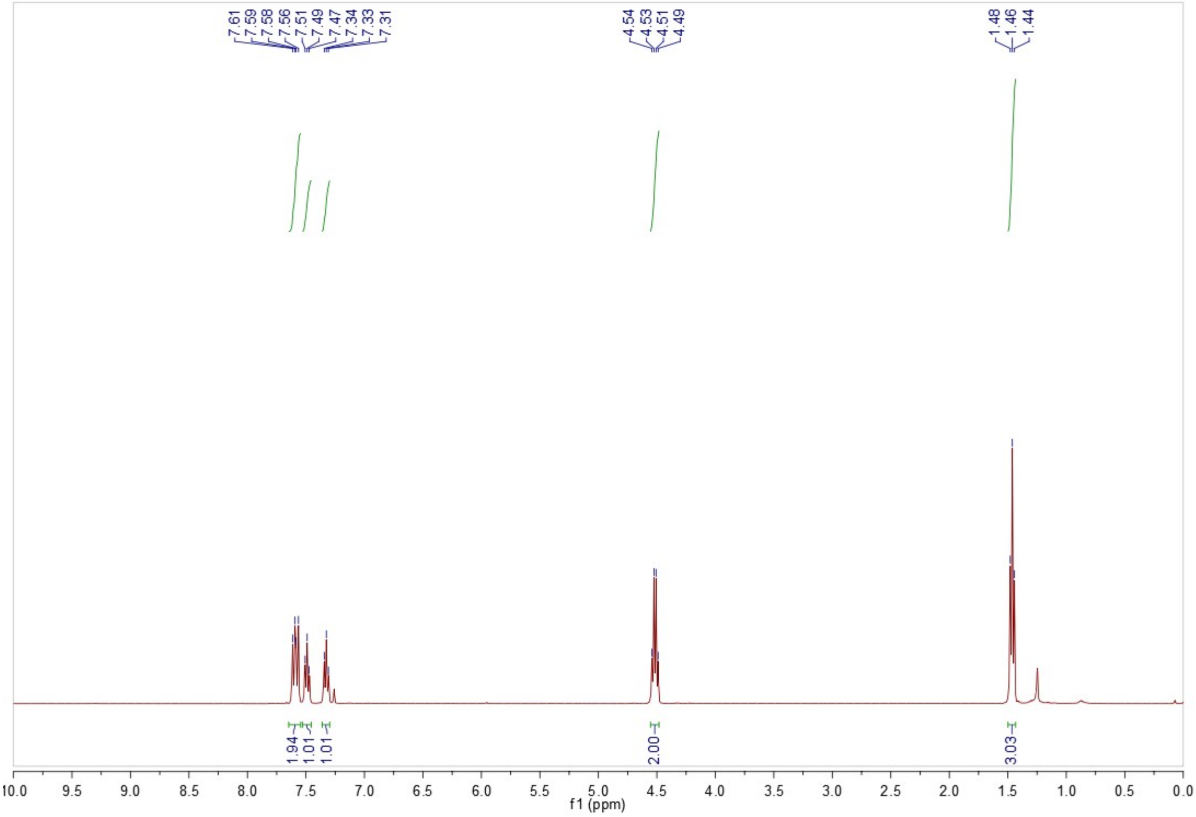
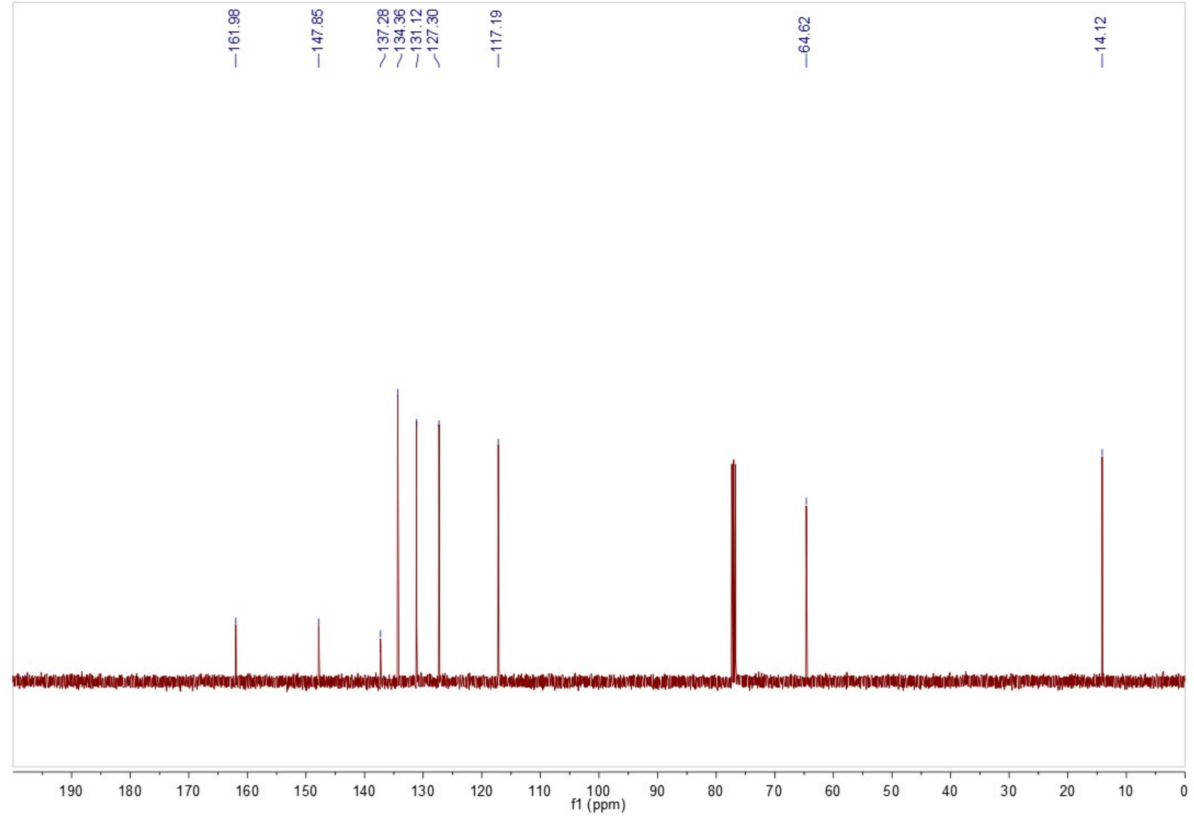


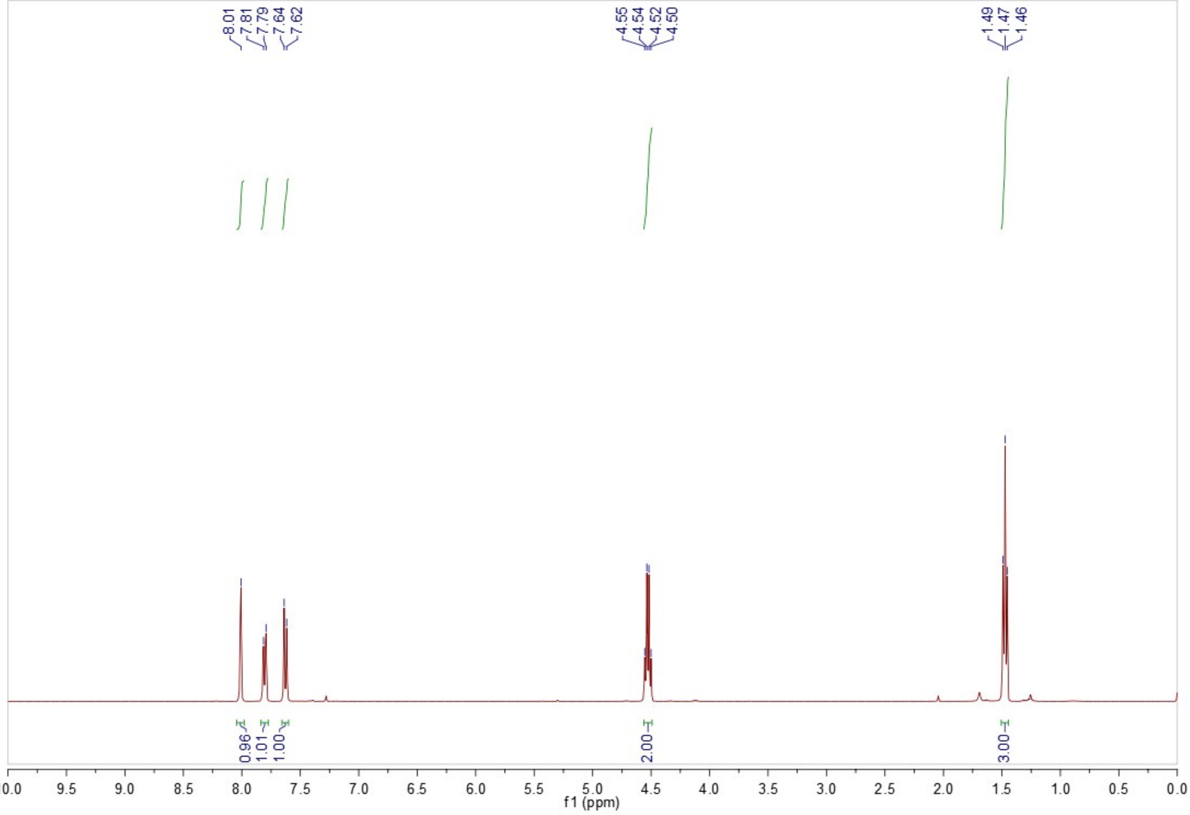


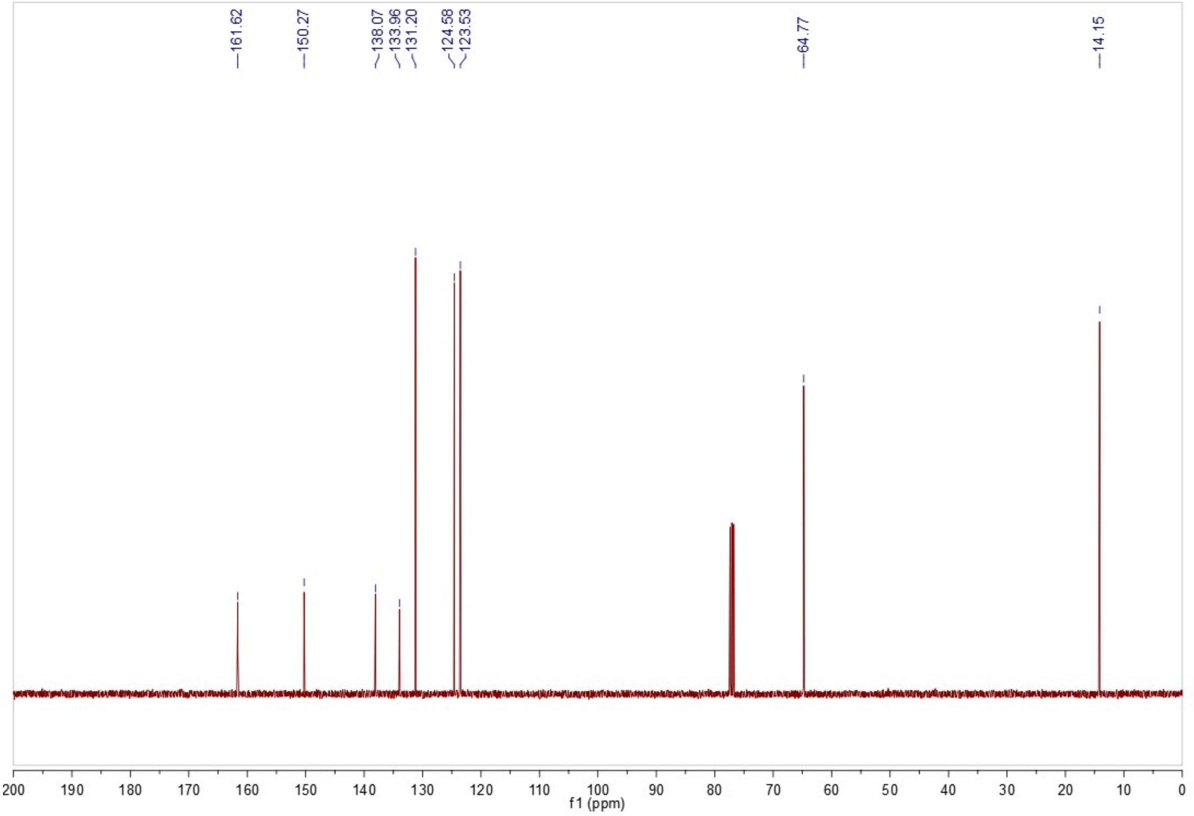
Ethyl 2-(2-chlorophenyl)azocarboxylate (2j)



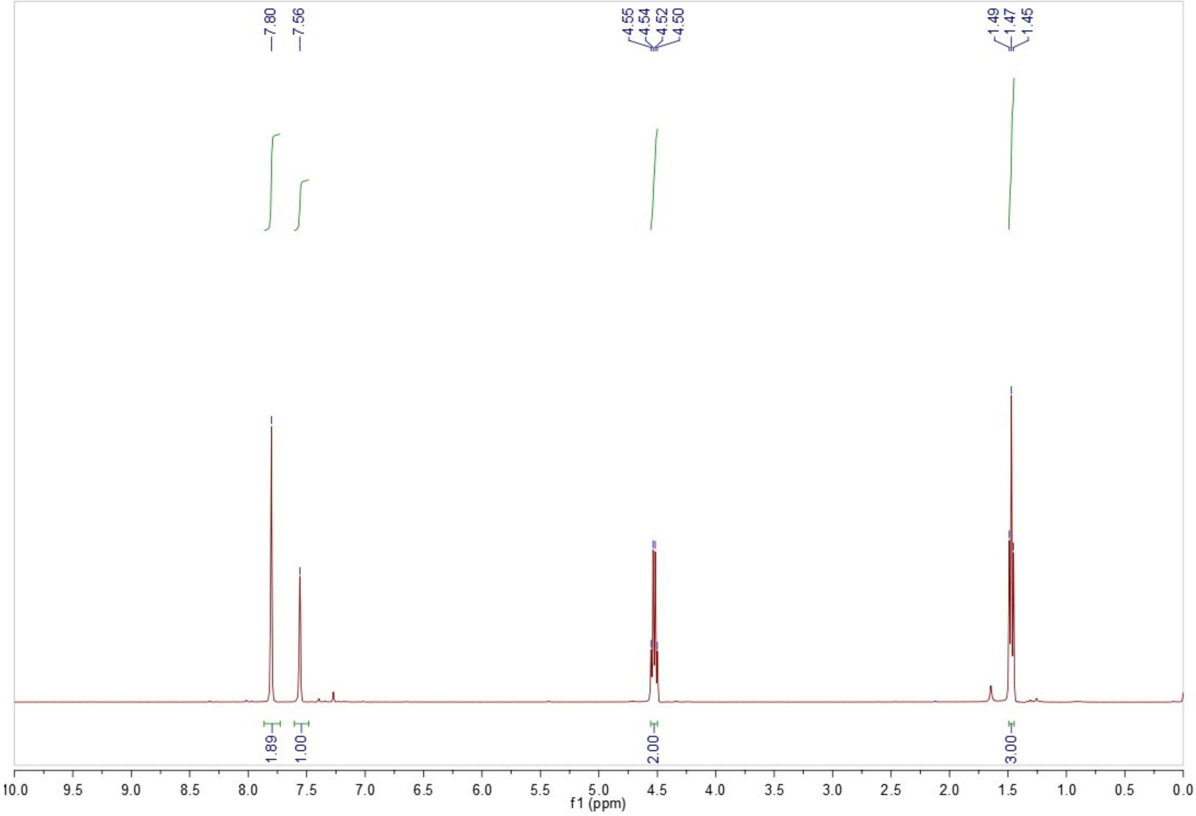


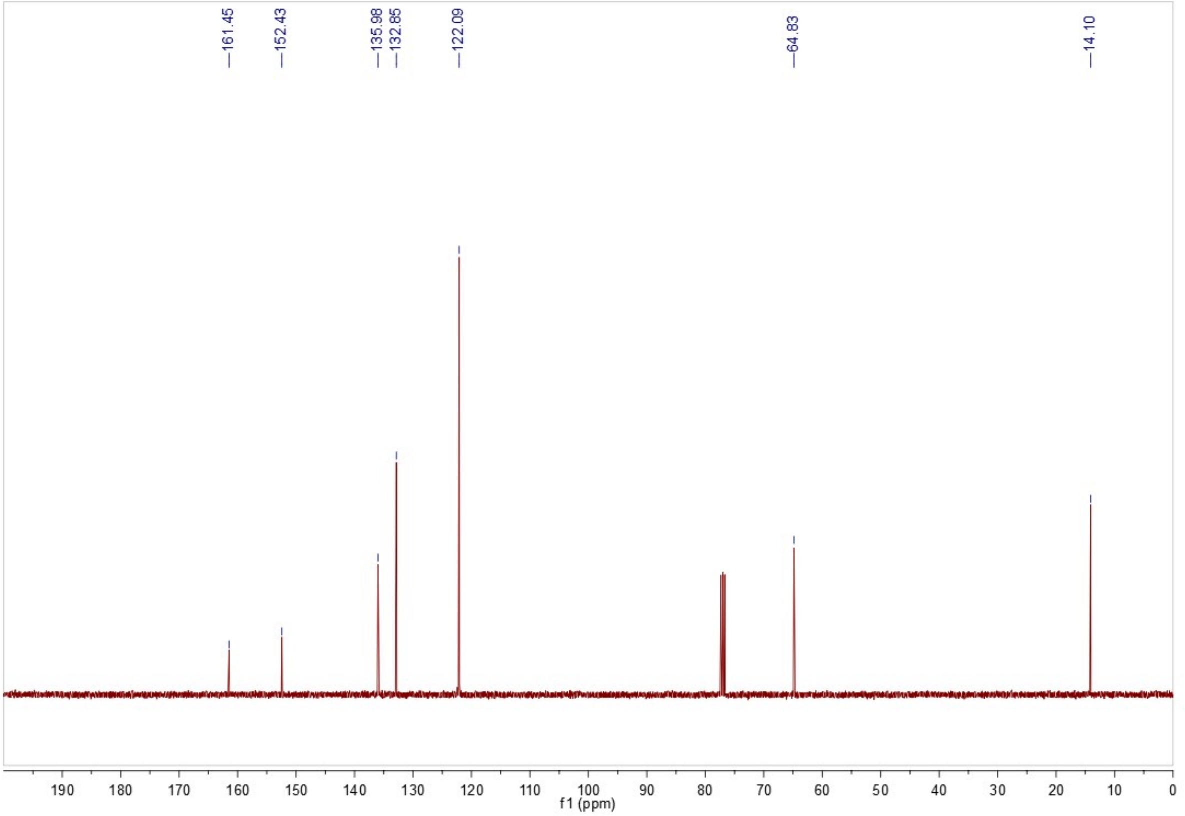
Ethyl 2-(3,4-dichlorophenyl)azocarboxylate (2k)



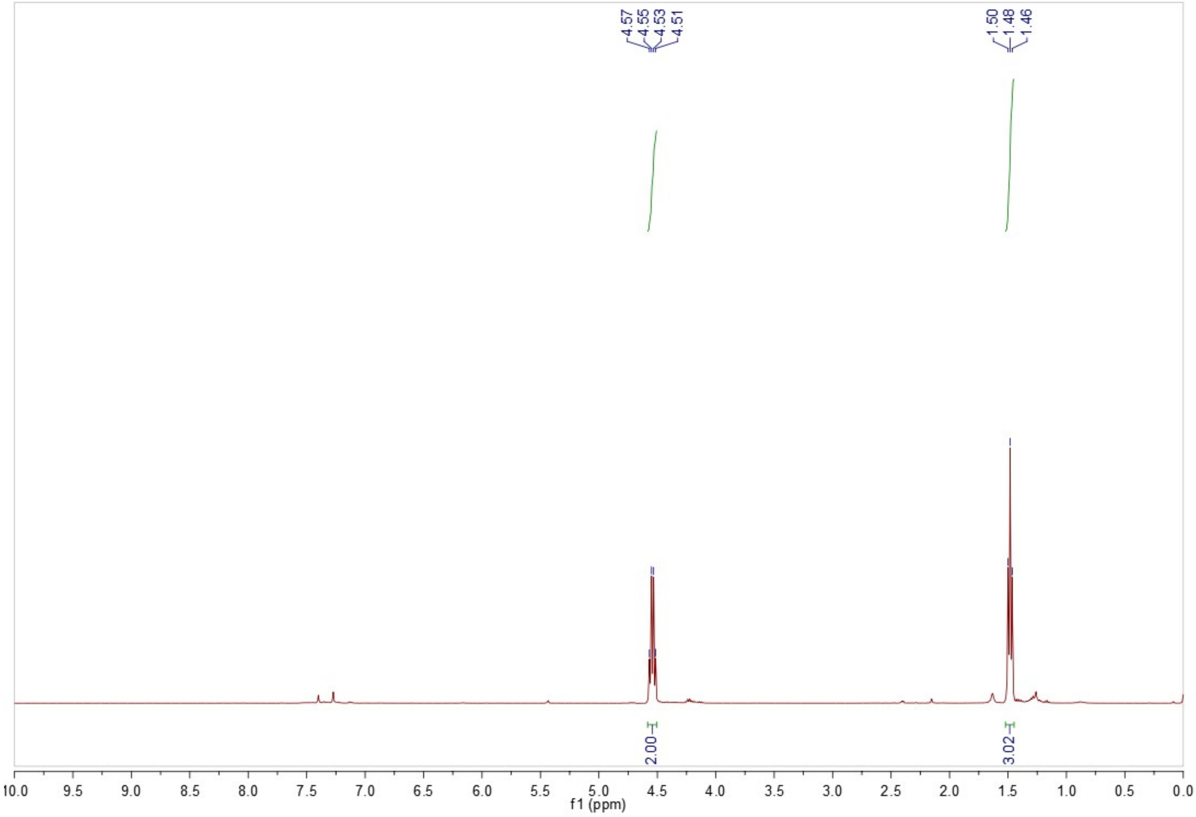


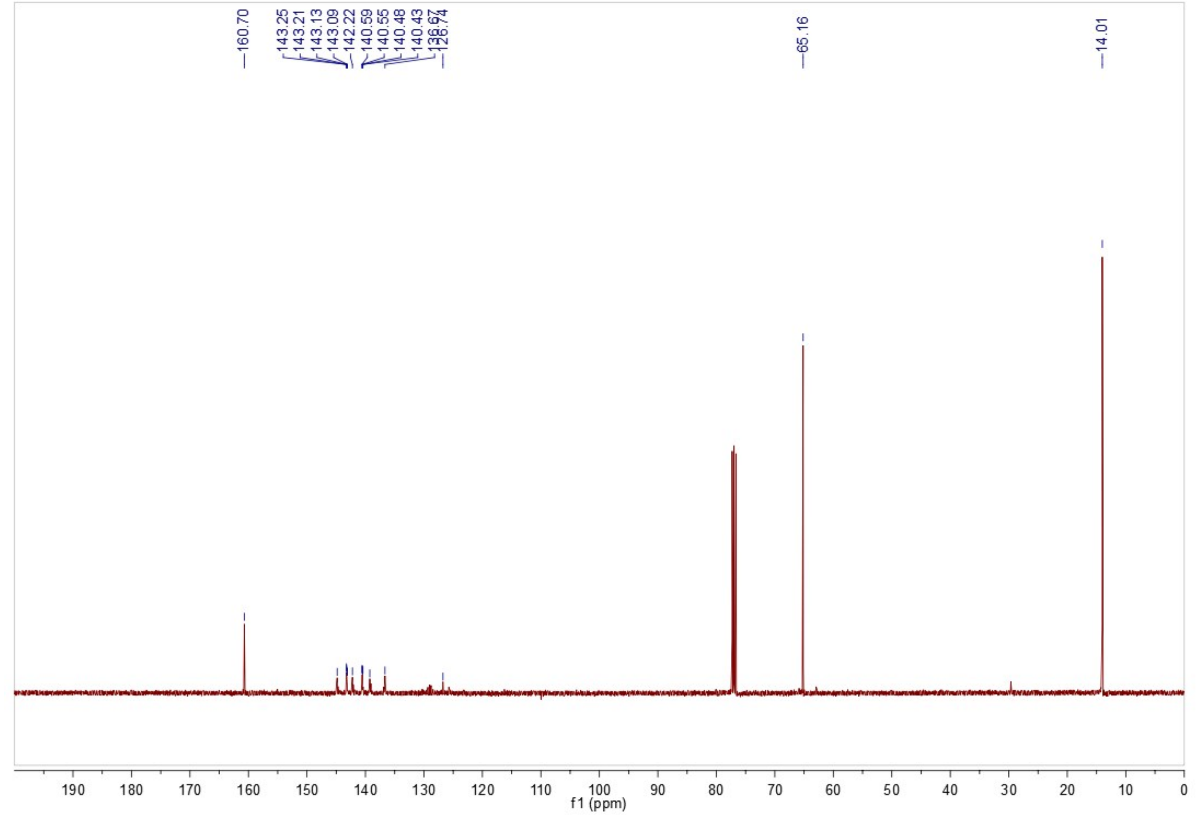
Ethyl 2-(3,5-dichlorophenyl)azocarboxylate (2l)

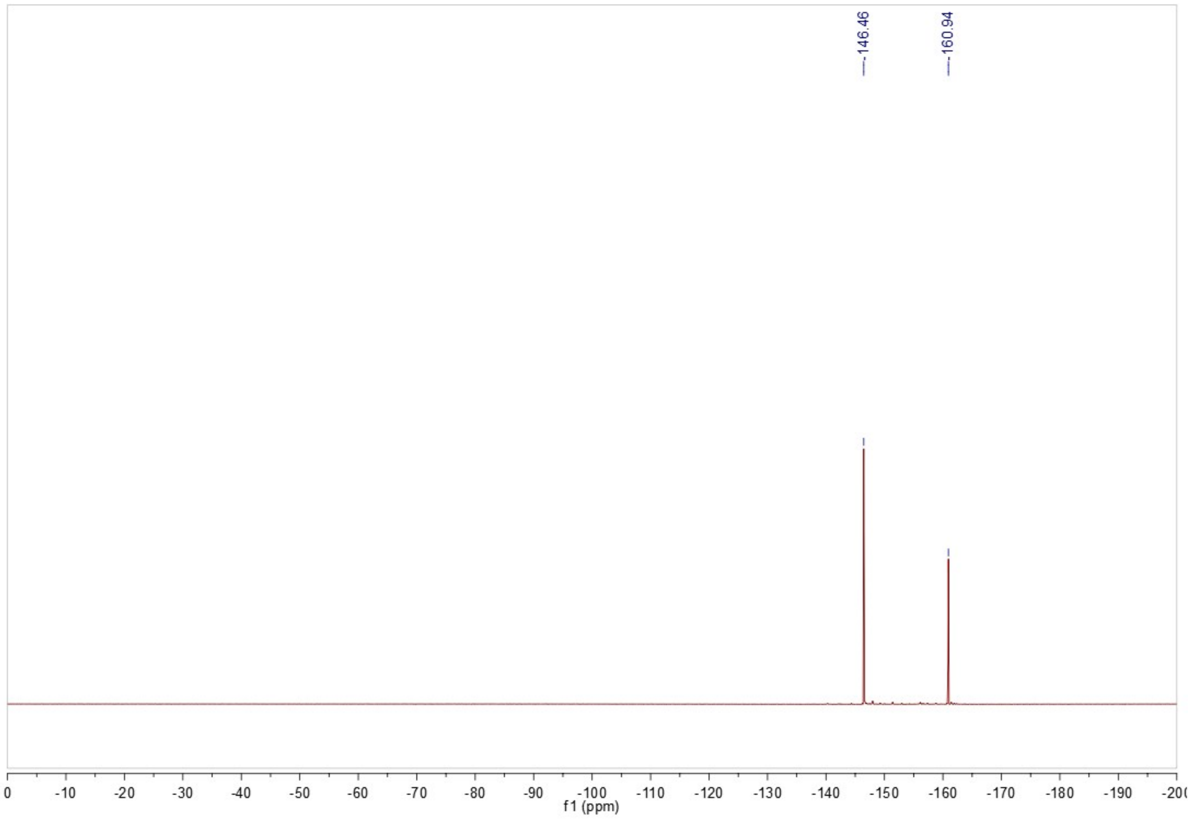




Ethyl 2-(2,3,4,5,6-pentafluorophenyl)azocarboxylate (2m)



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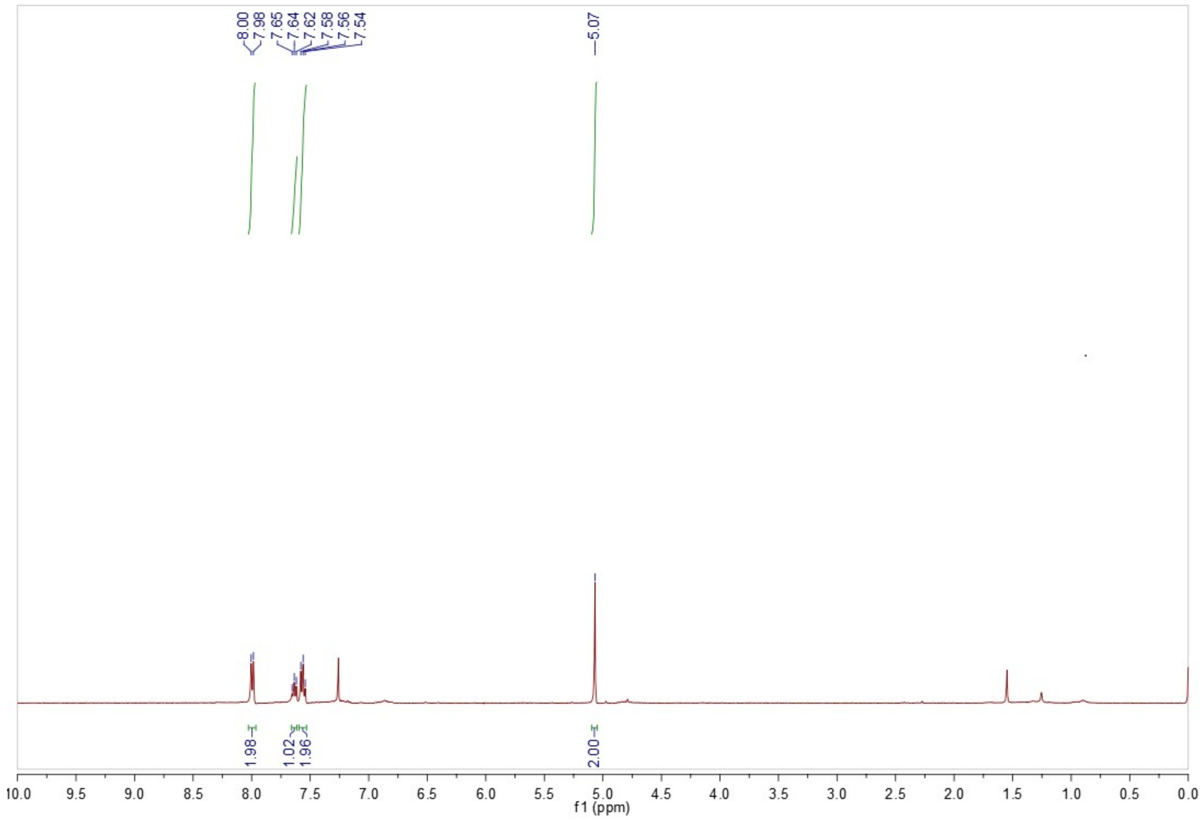
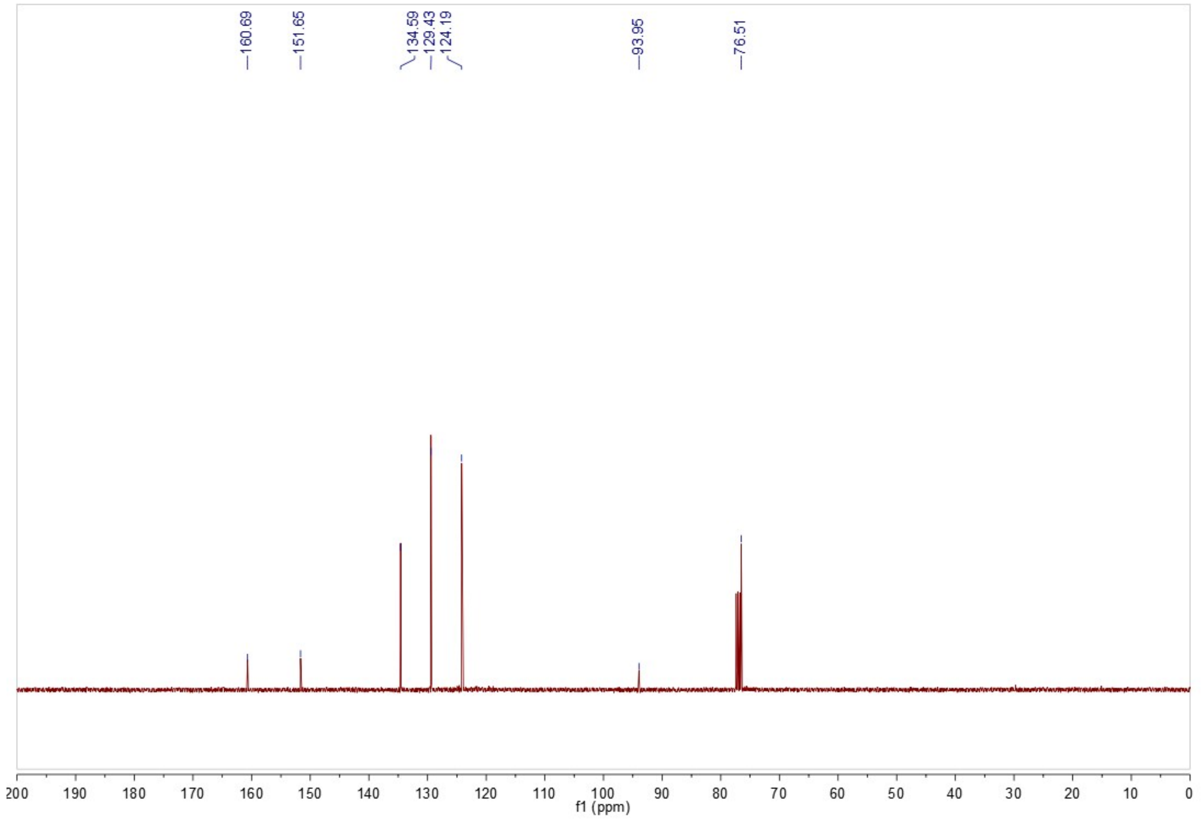
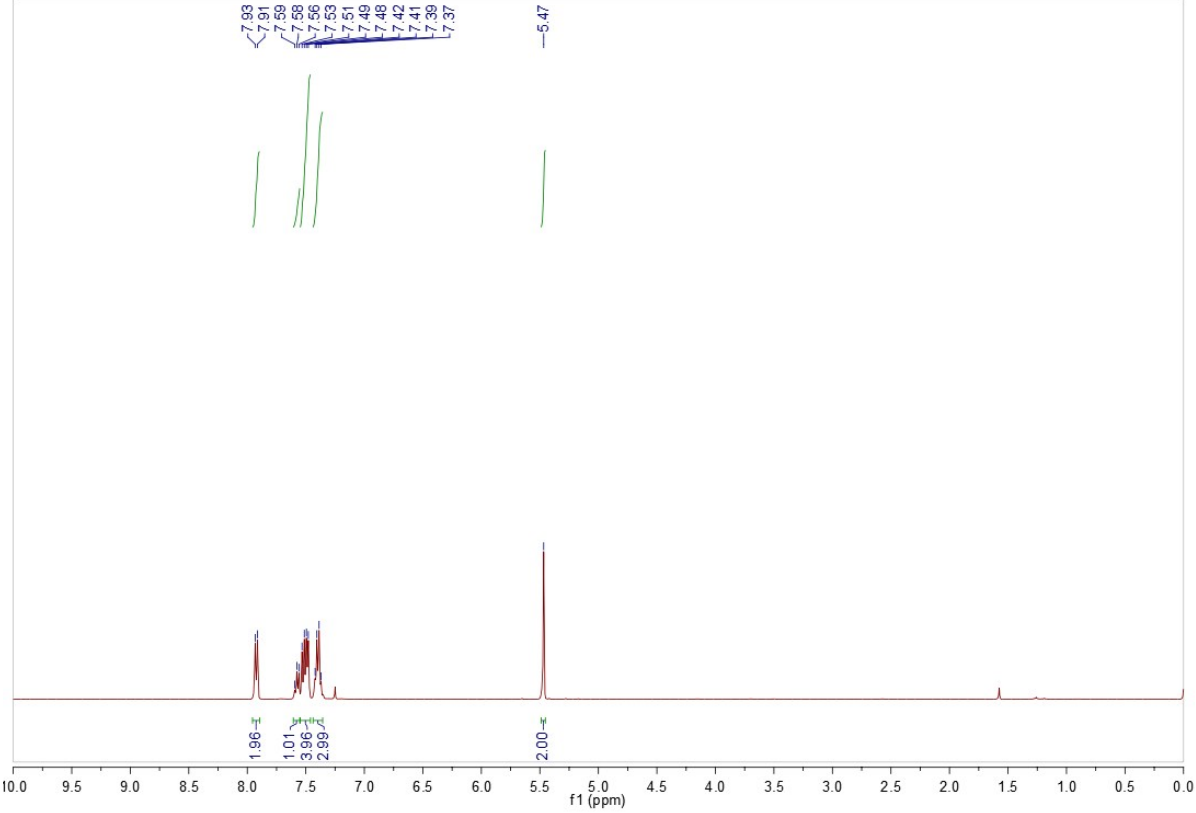
f1 (ppm)

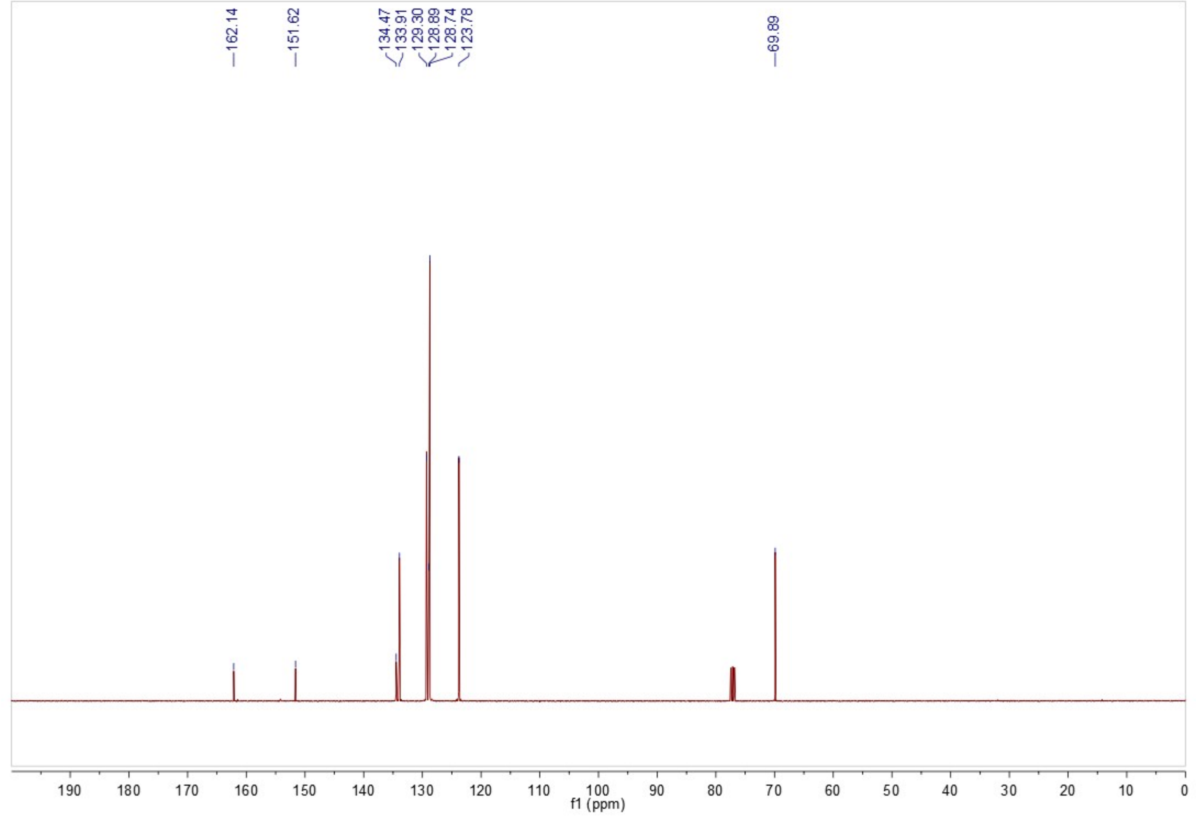
2,2,2-Trichloroethyl 2-phenylazocarboxylate (2n)



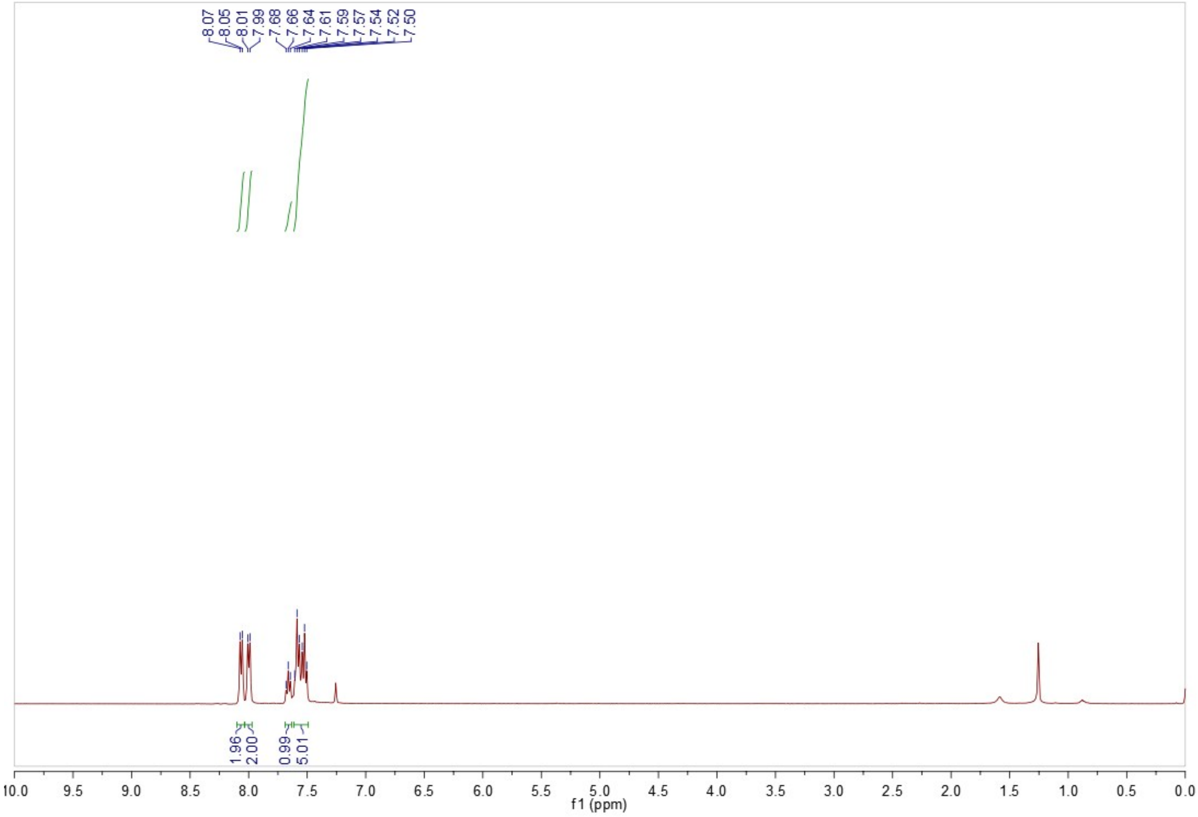


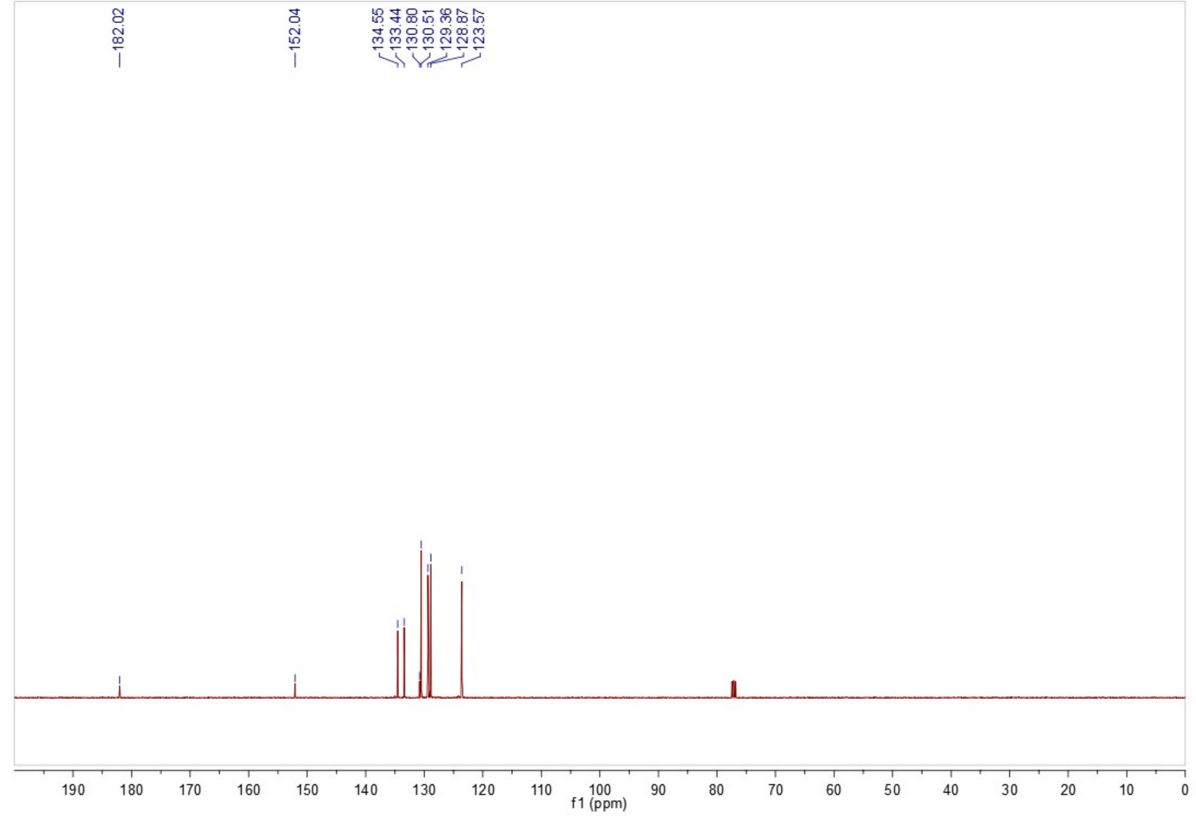
Benzyl 2-phenylazocarboxylate (2o)



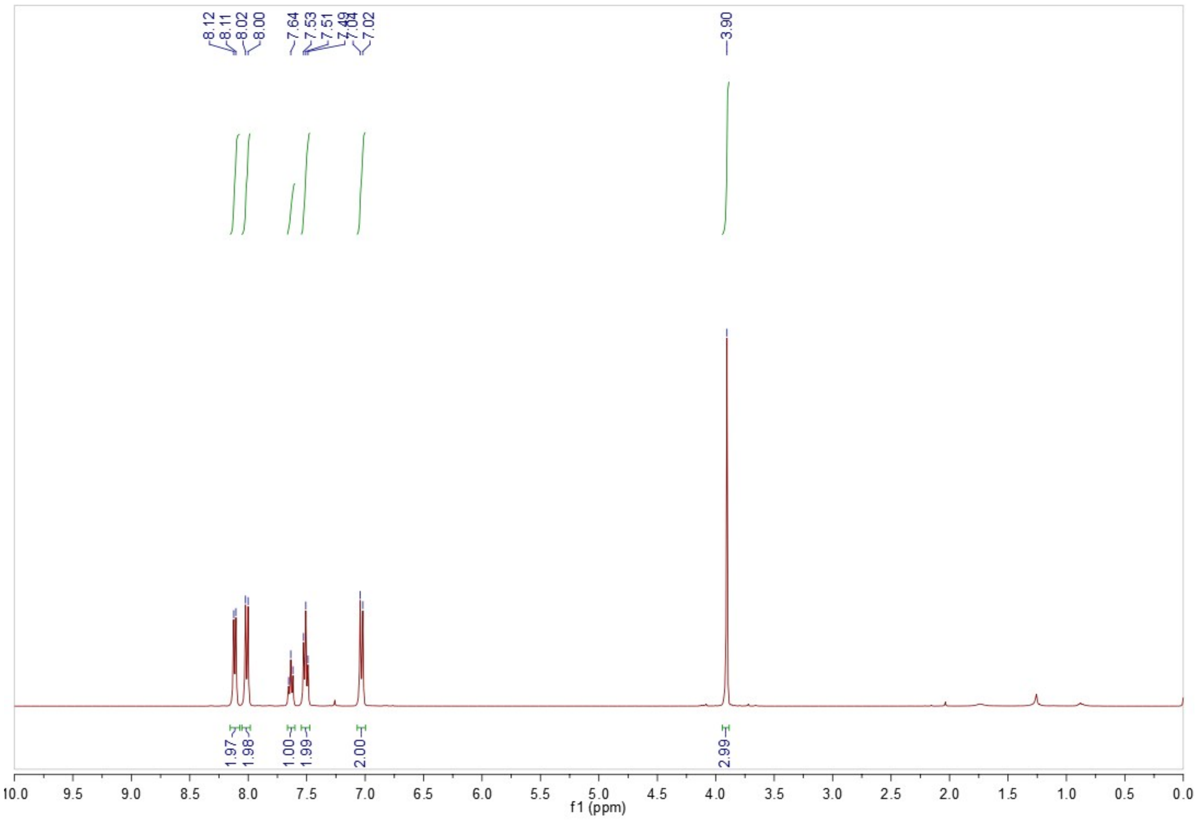


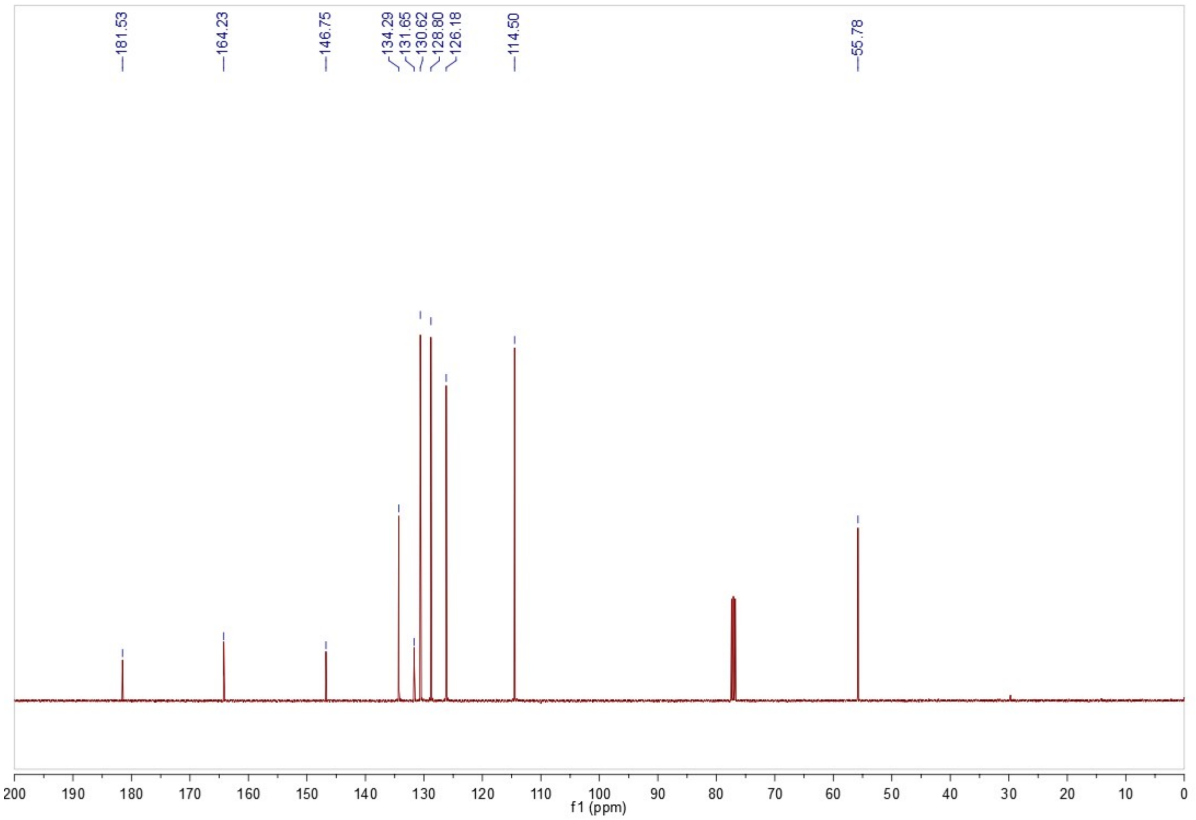
Benzoylazobenzene (4a)



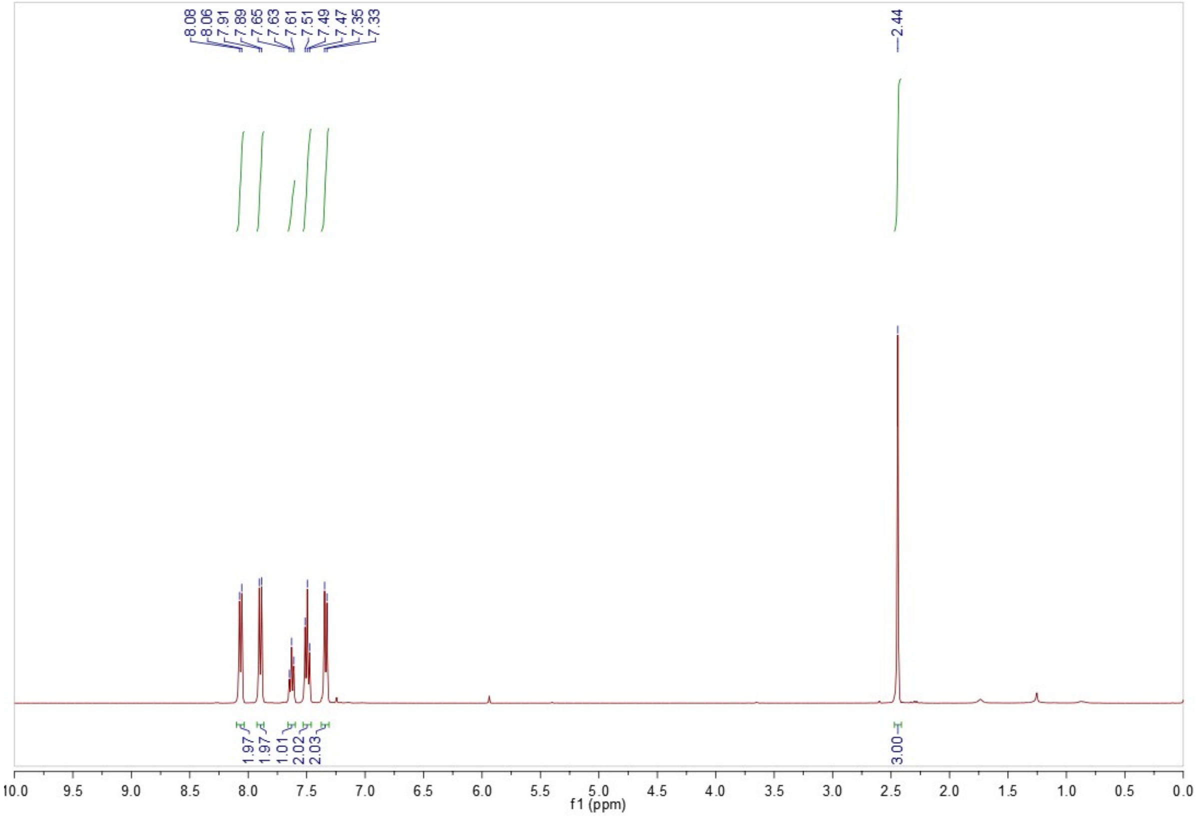


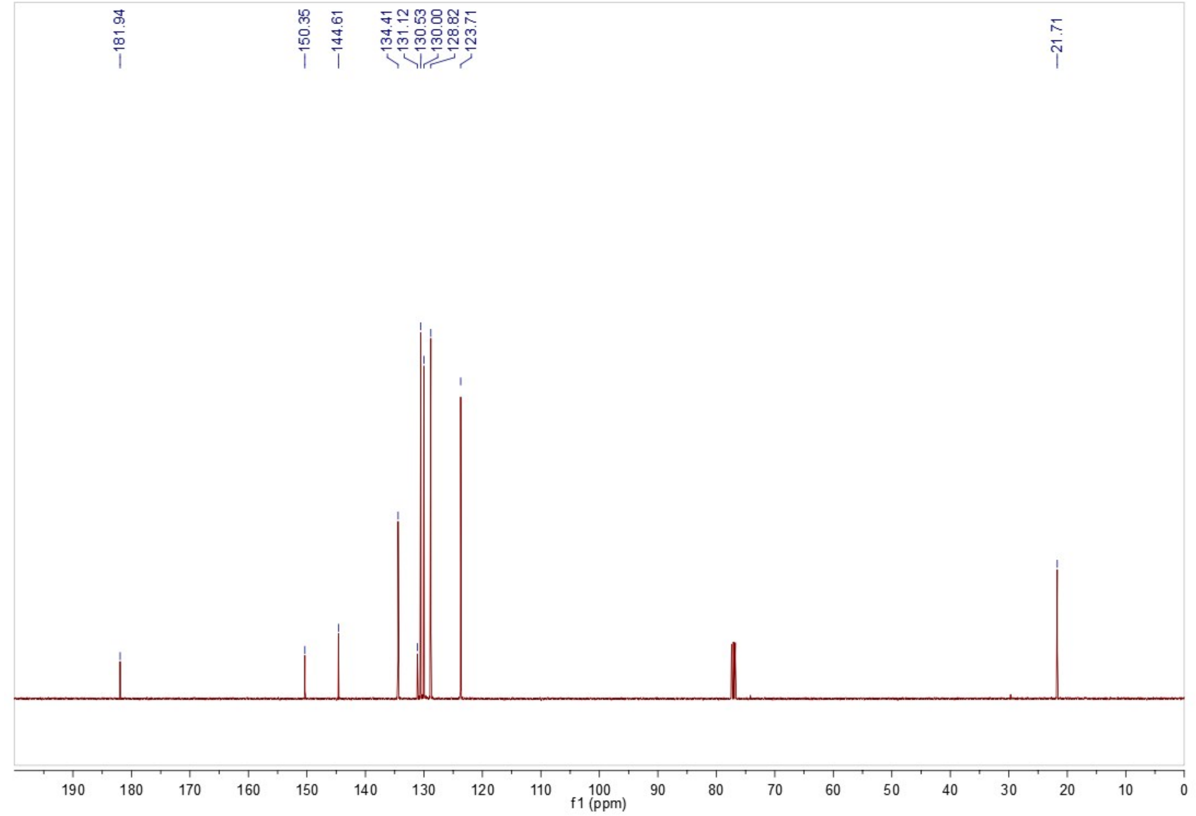
Benzoyl-2-(4-methoxyphenyl)diazene (4b)



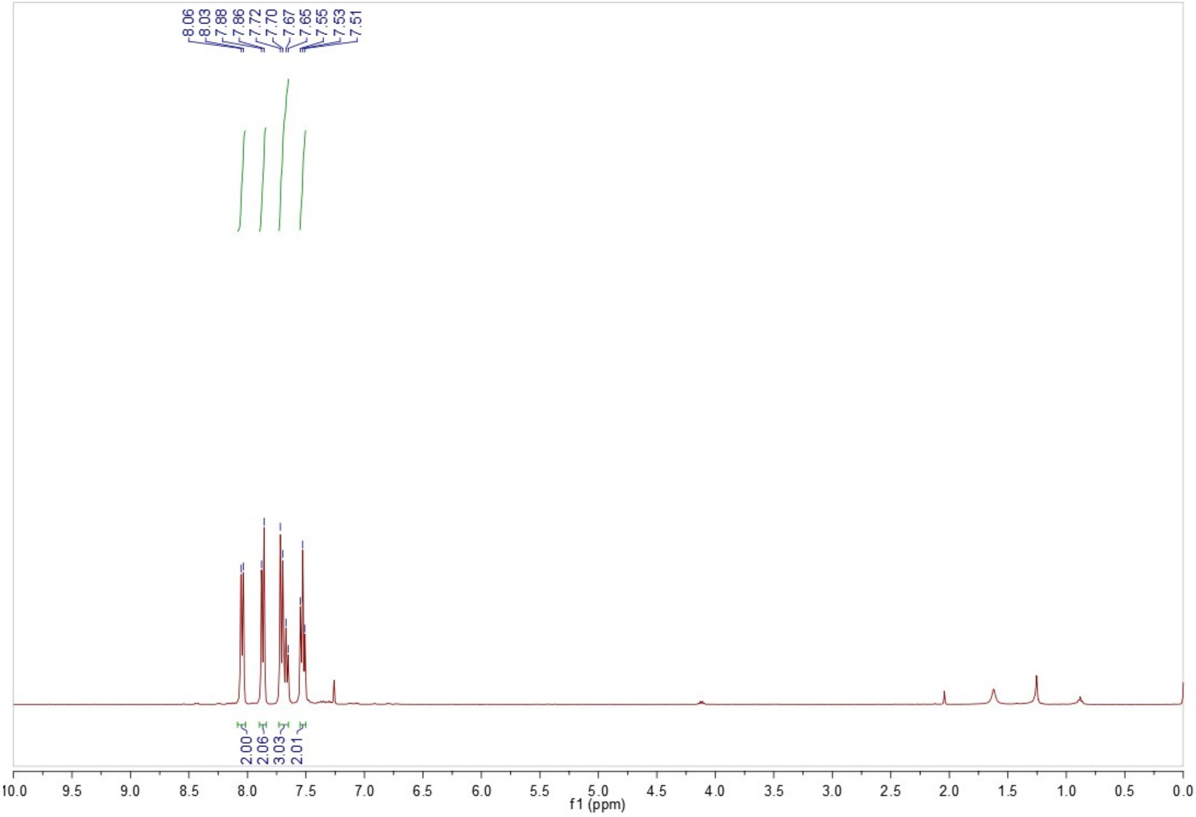


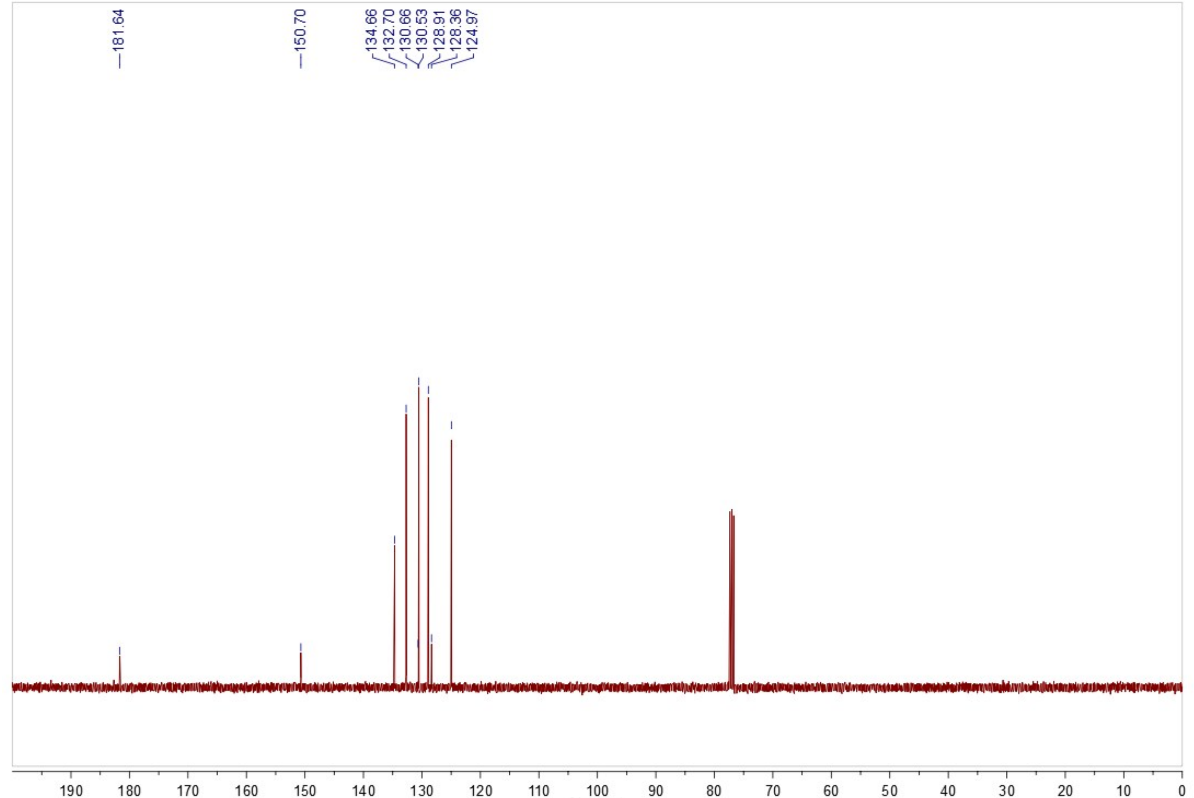
Benzoyl-2-(4-methylphenyl)diazene (4c)



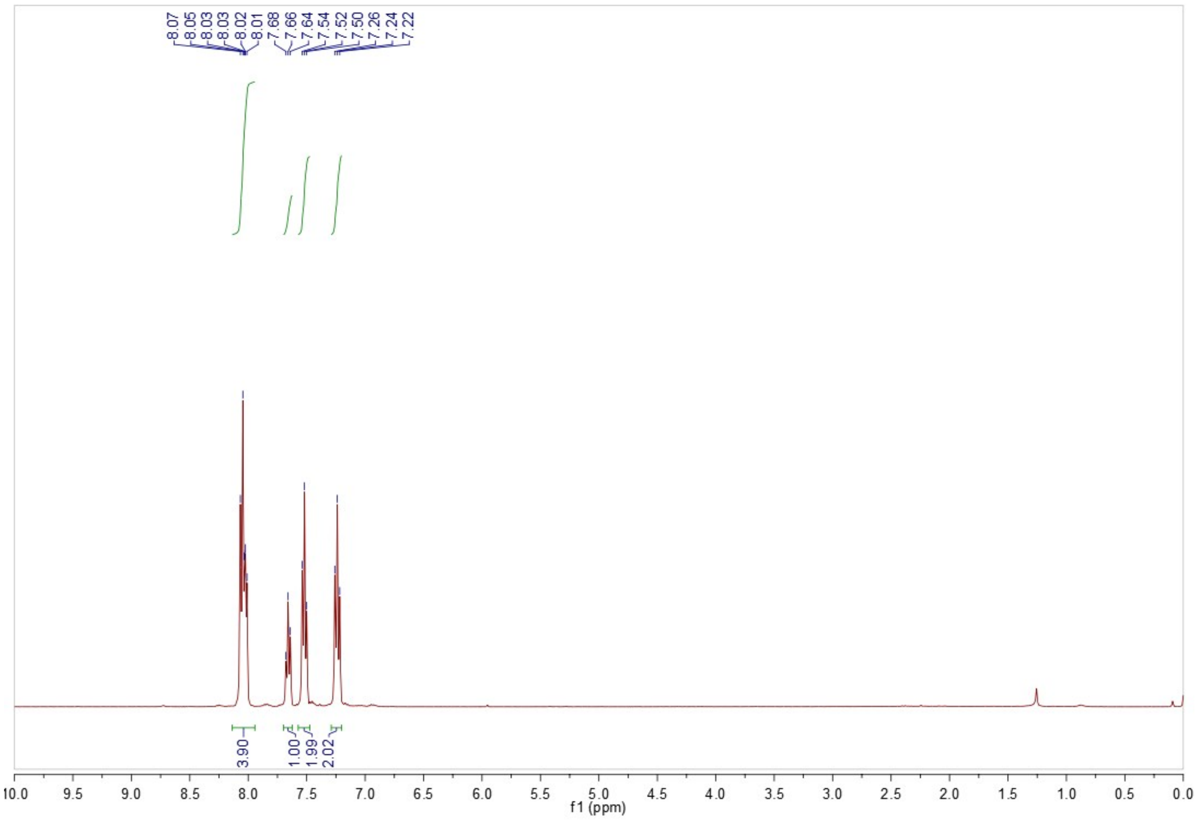


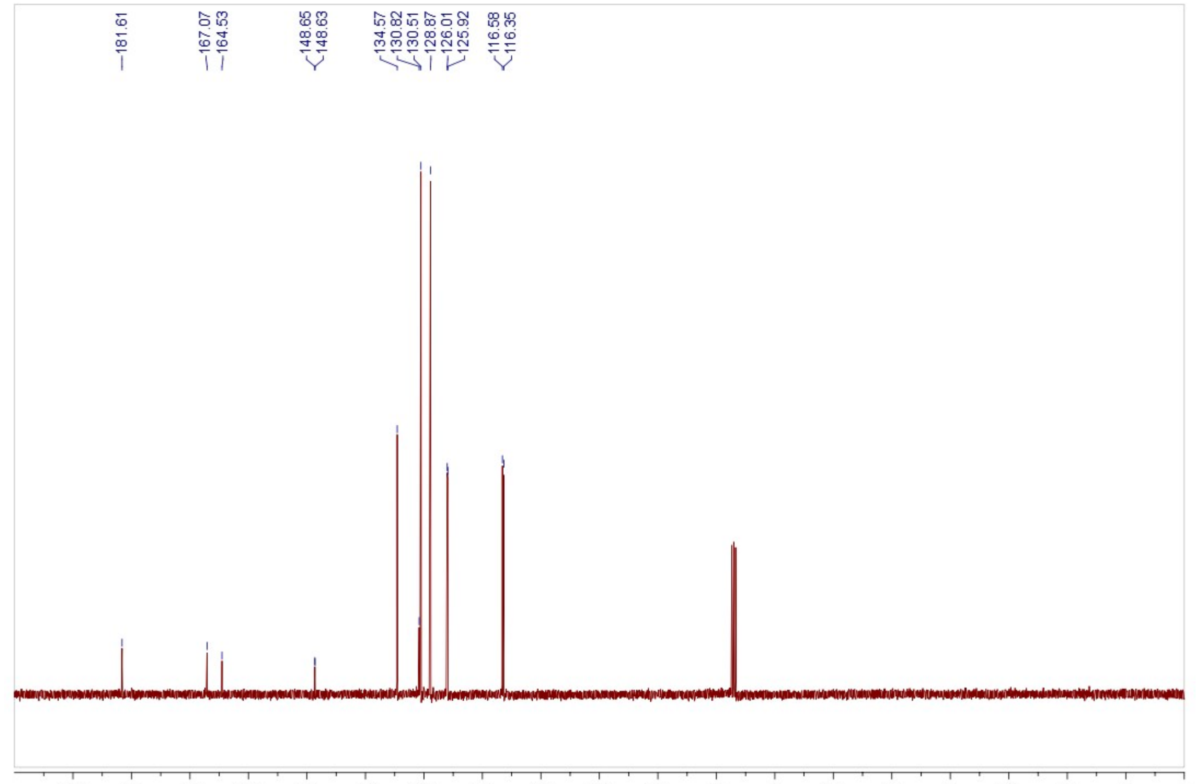
Benzoyl-2-(4-bromophenyl)diazene (4d)

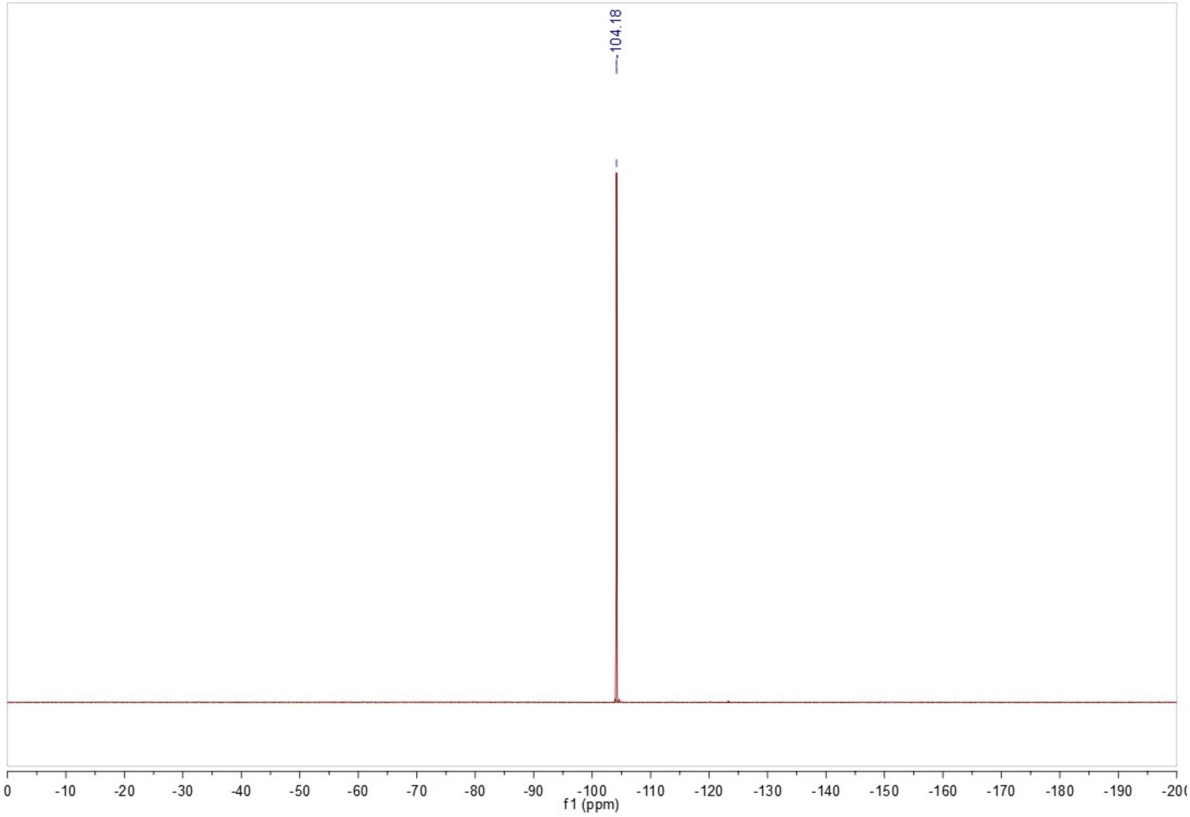




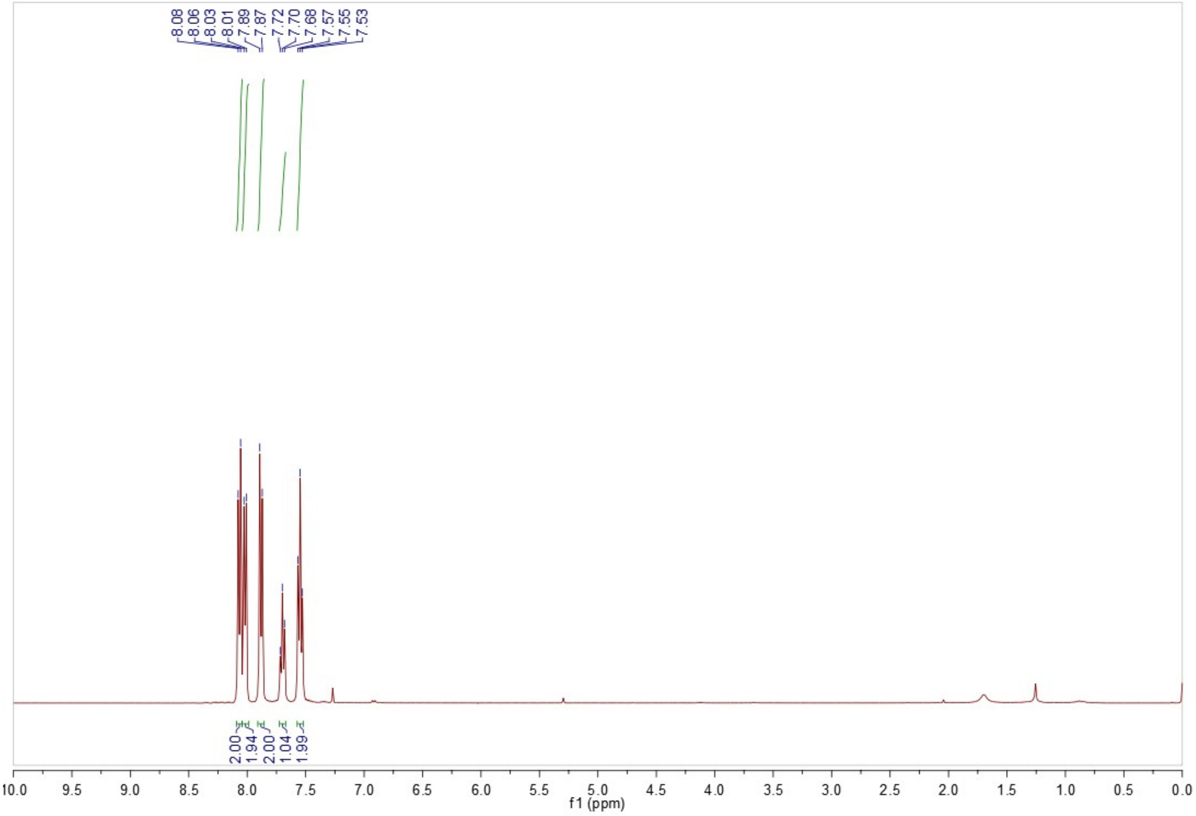
Benzoyl-2-(4-fluorophenyl)diazene (4e)

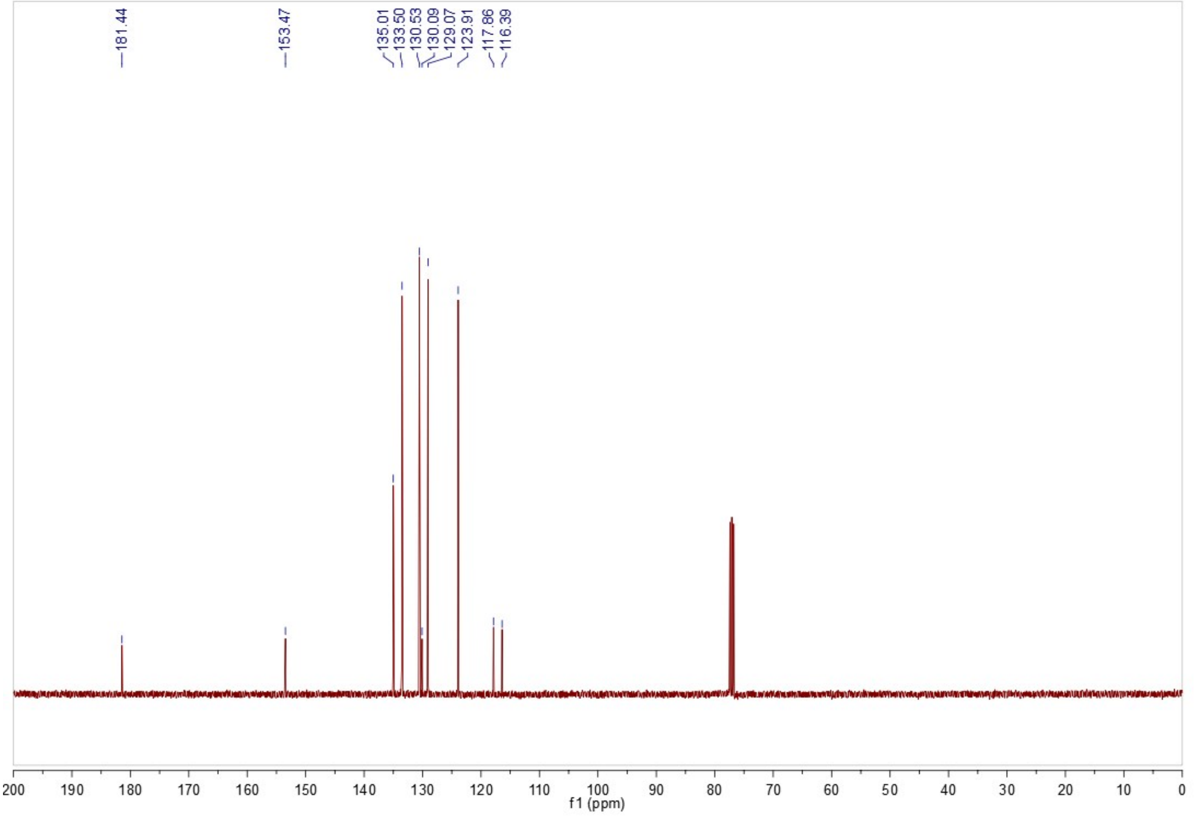




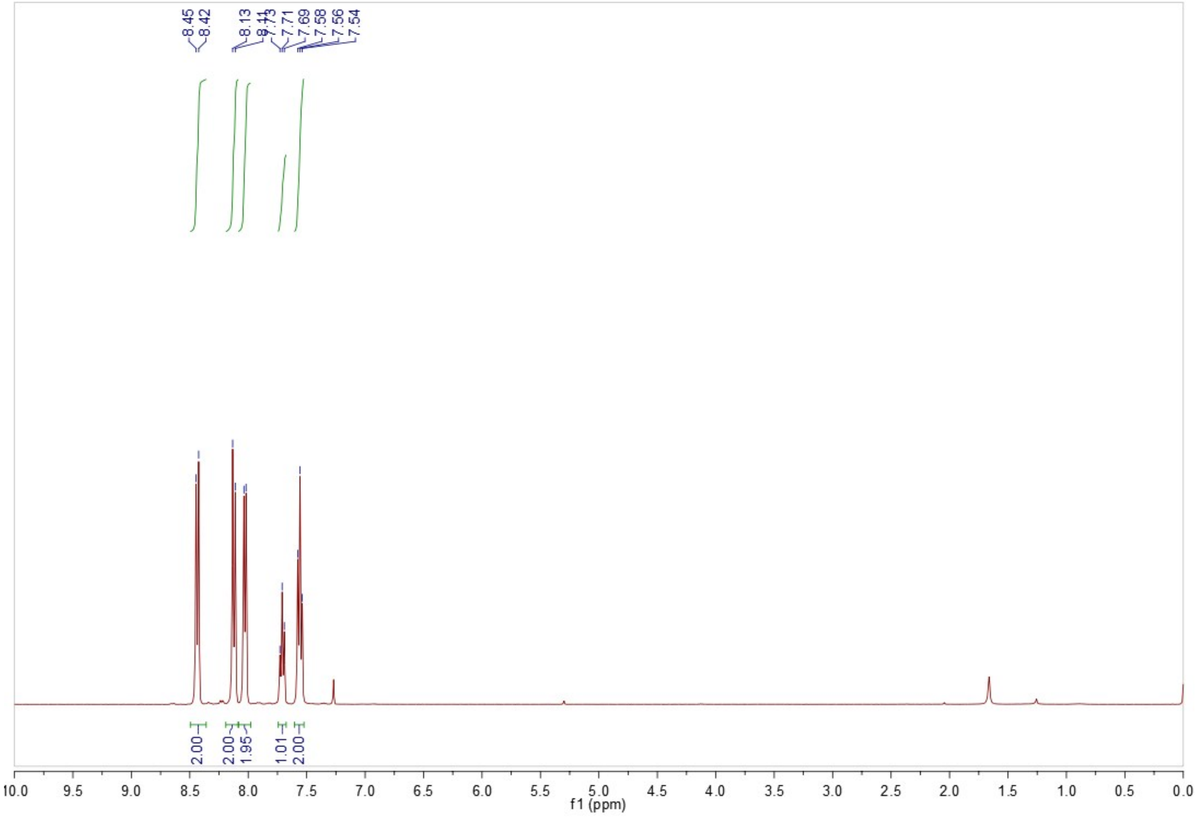

-104.18
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

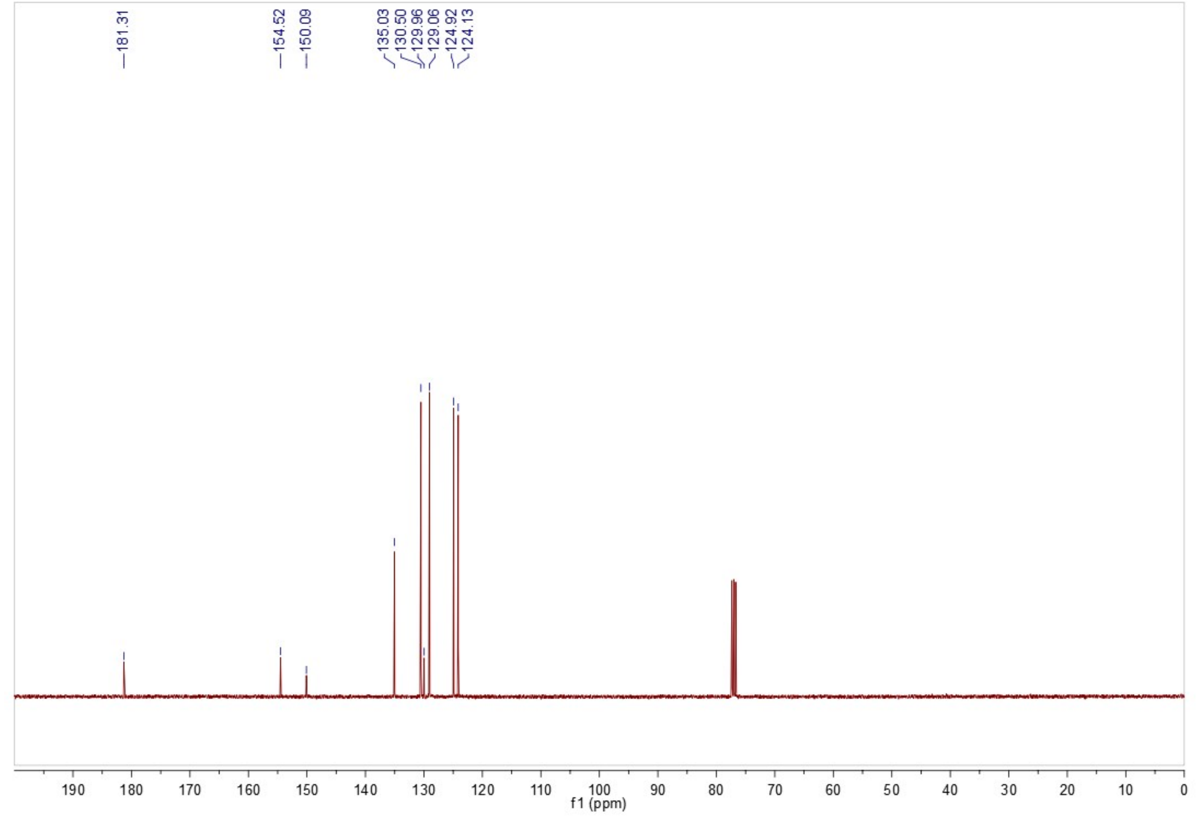
Benzoyl-2-(4-cyanophenyl)diazene (4f)



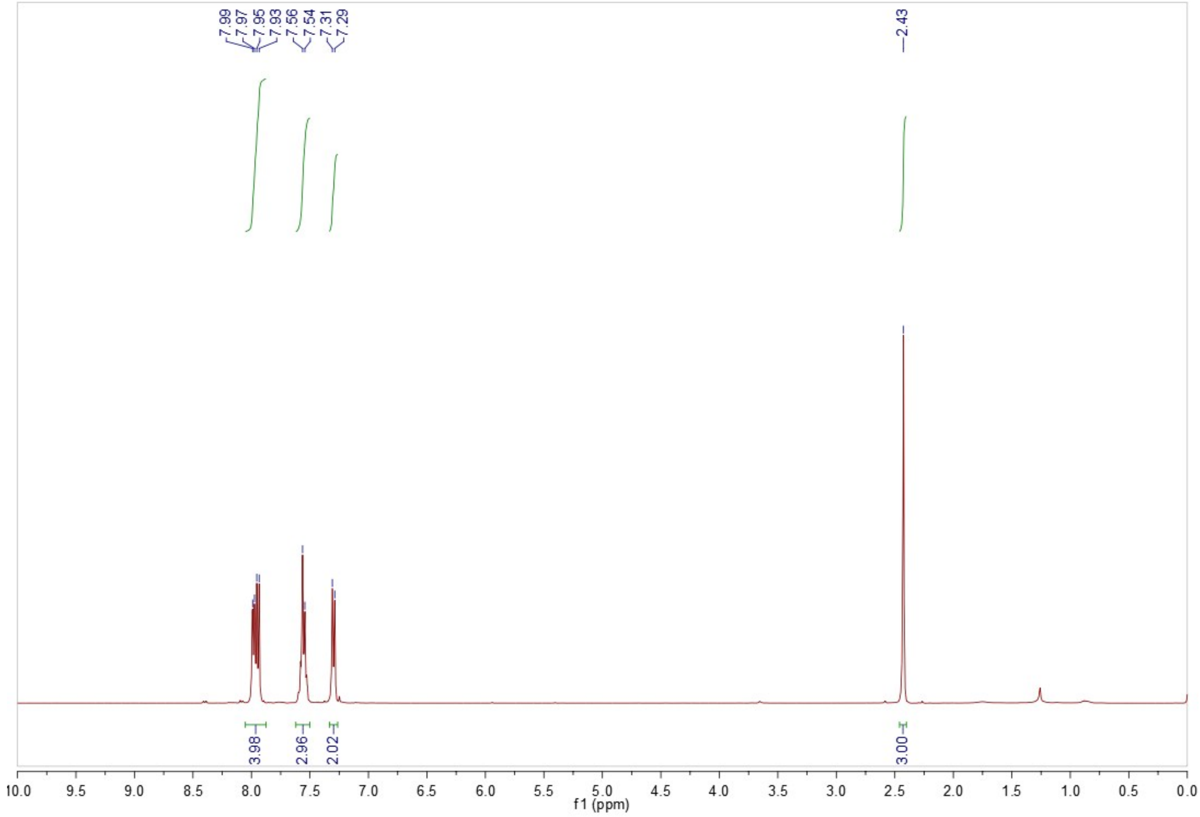


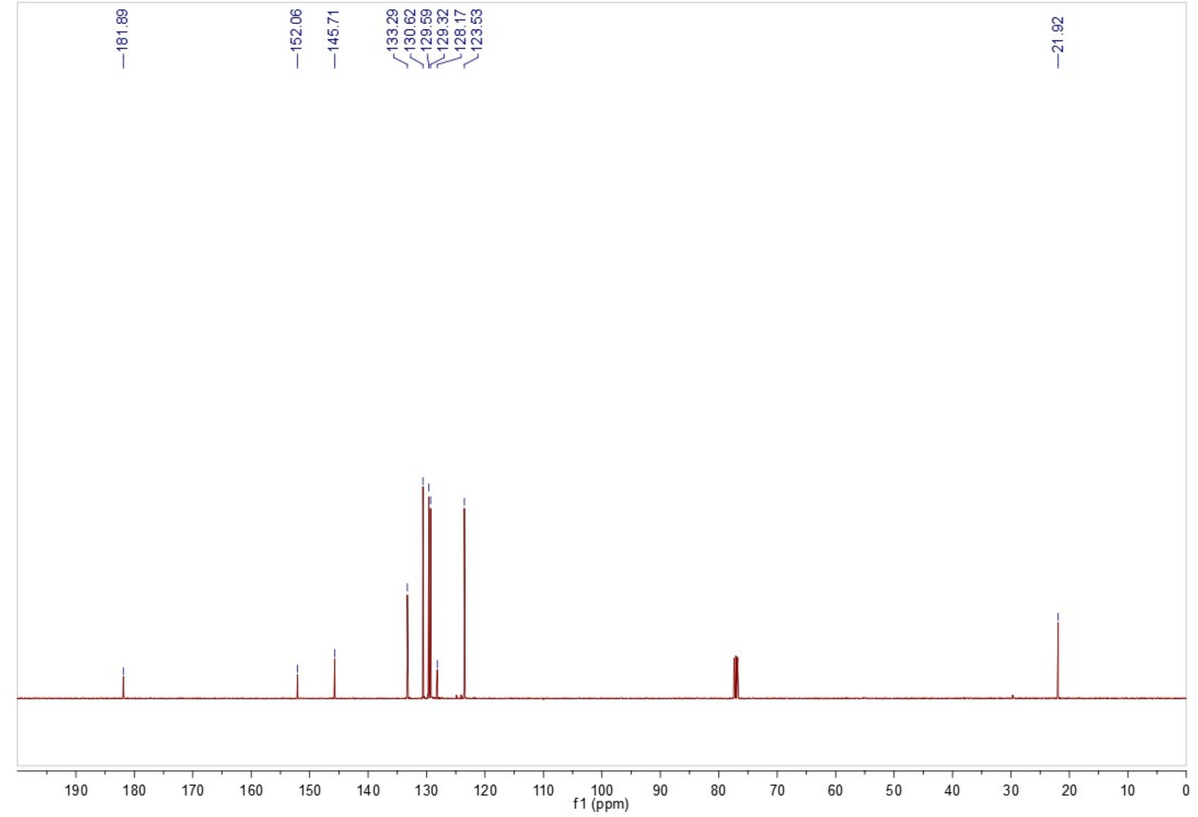
Benzoyl-2-(4-nitroophenyl)diazene (4g)



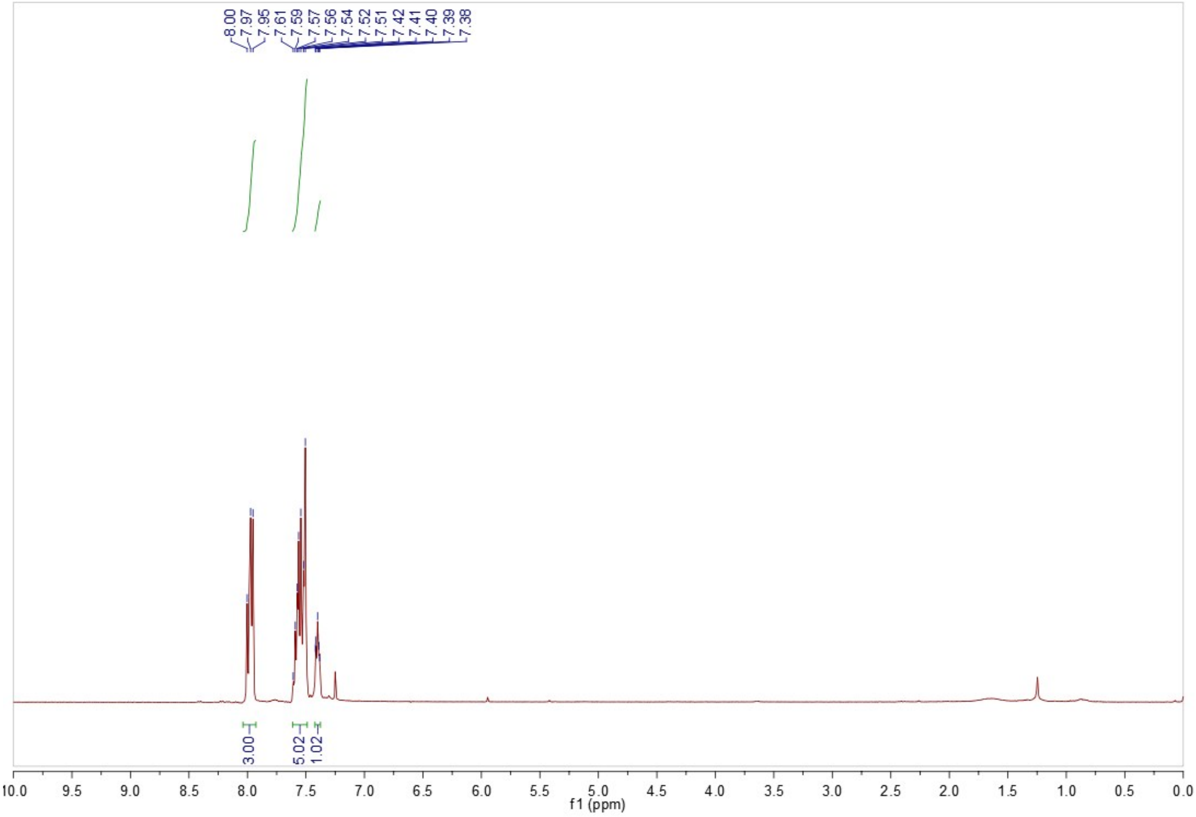


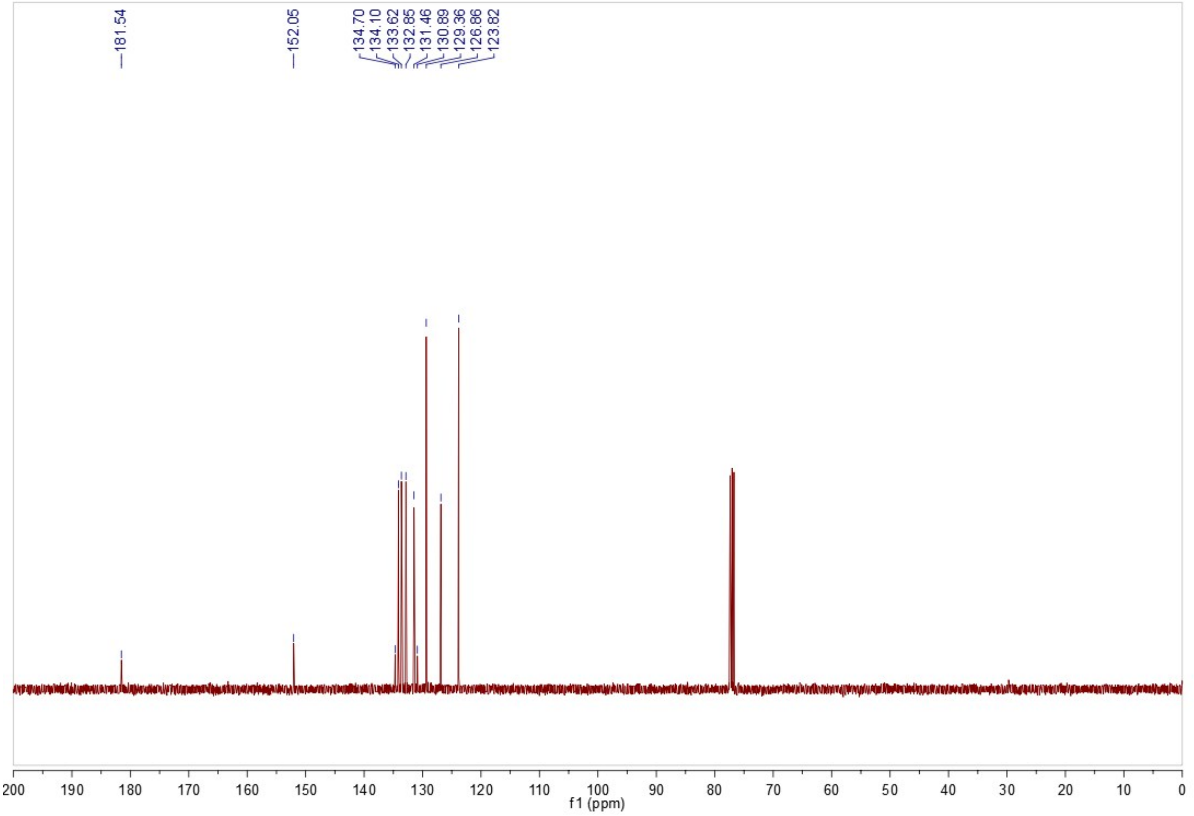
(4-Methylbenzoyl)-2-phenyldiazene (4h)



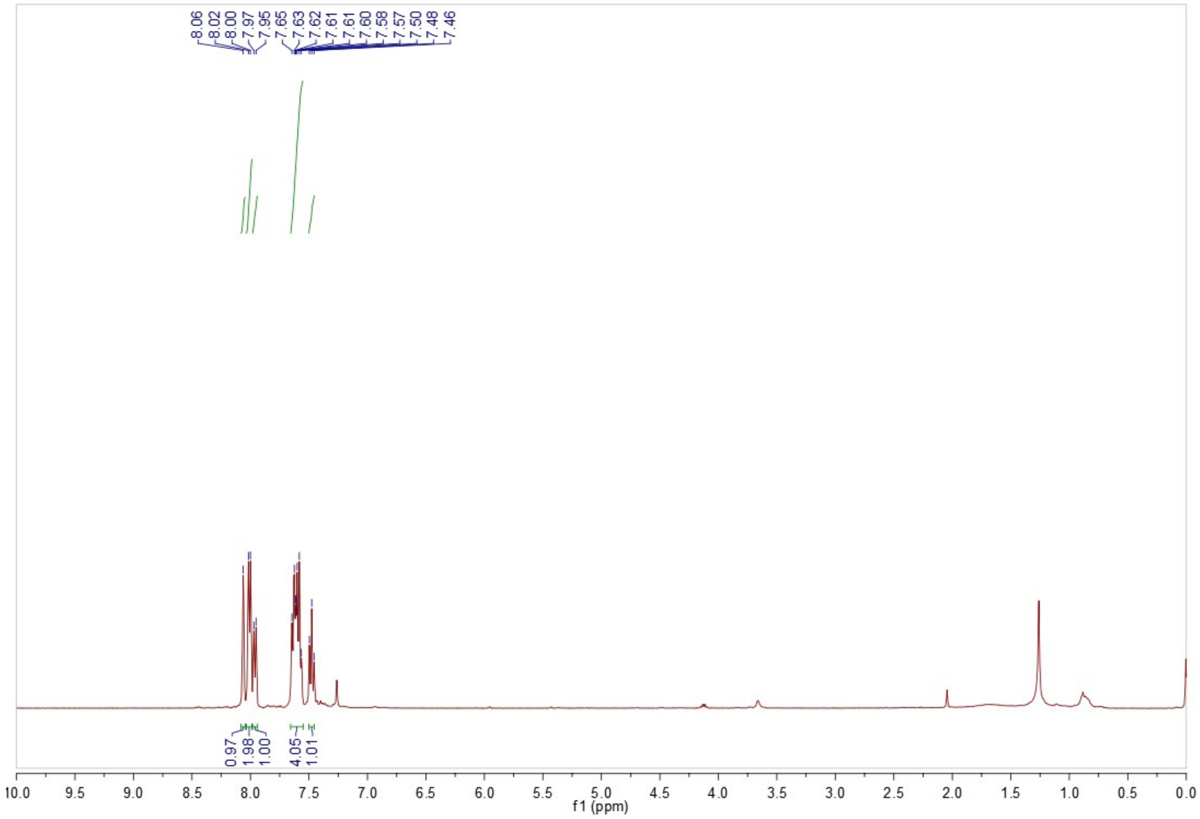


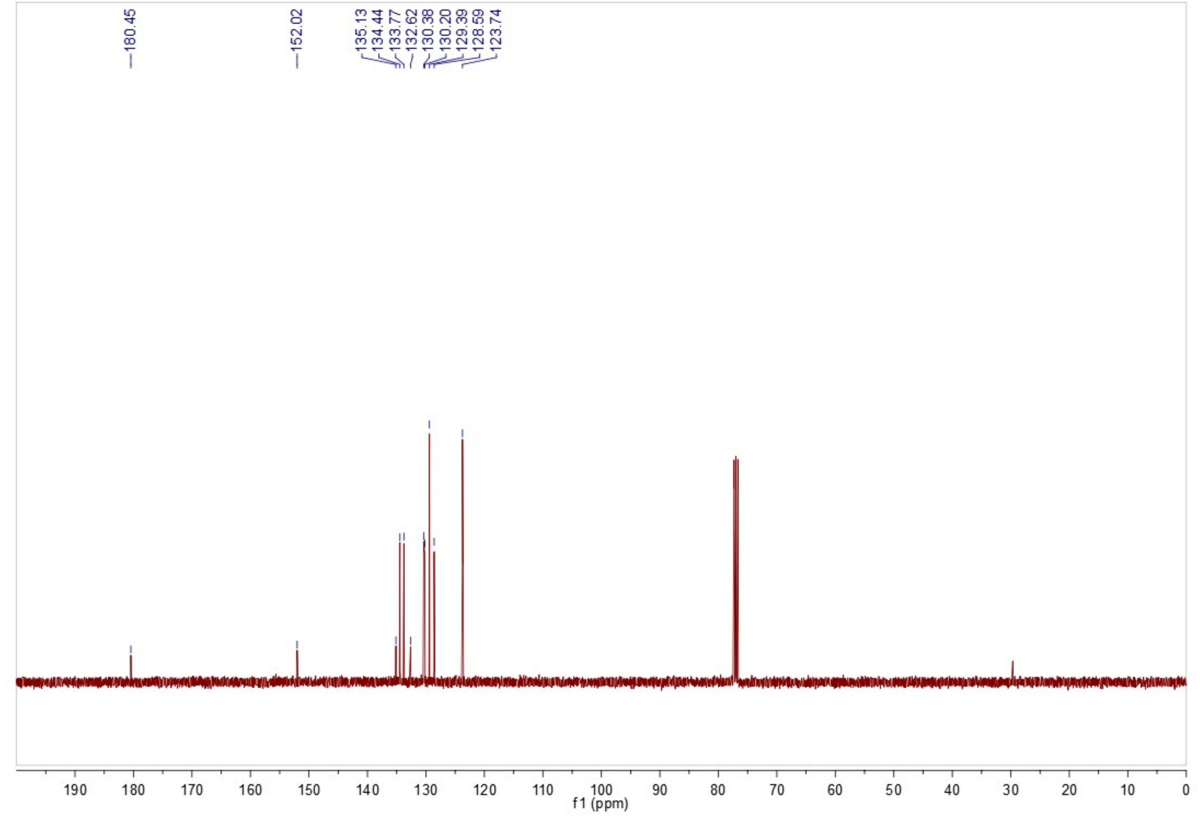
(2-Chlorobenzoyl)-2-phenyldiazene (4i)



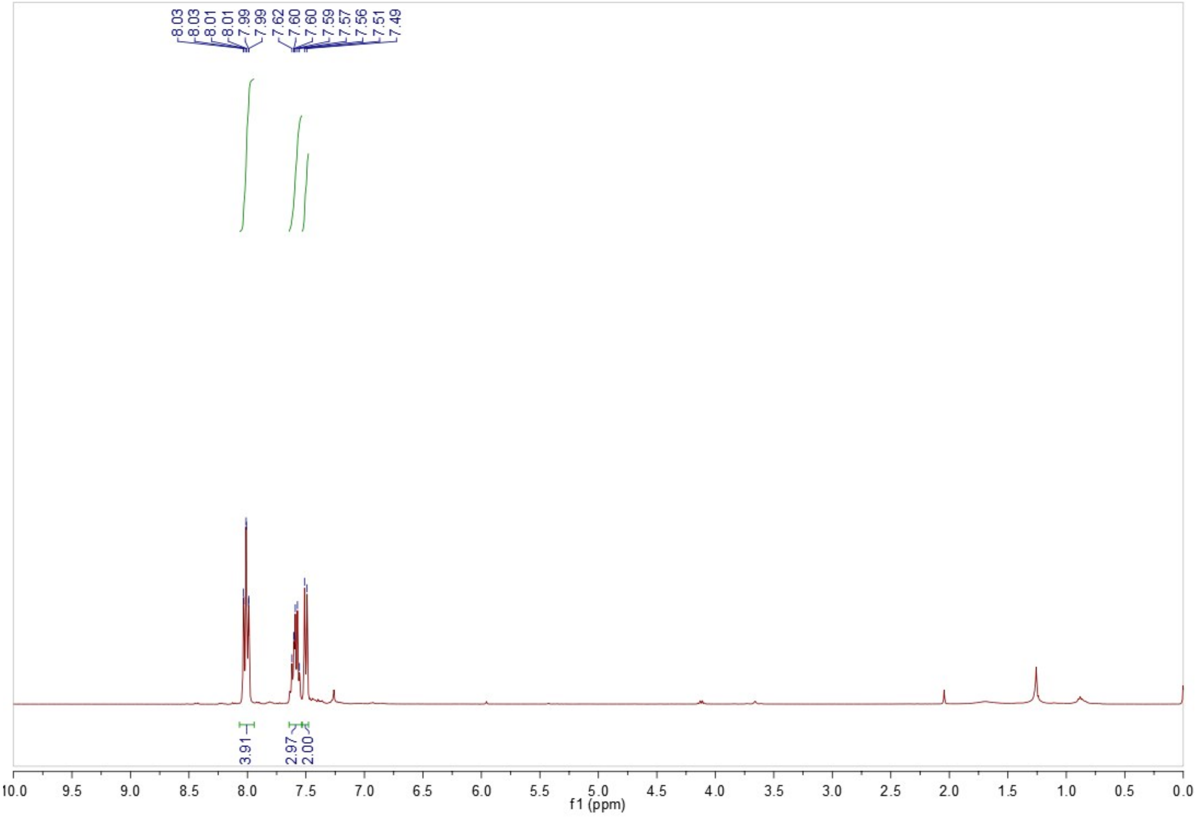


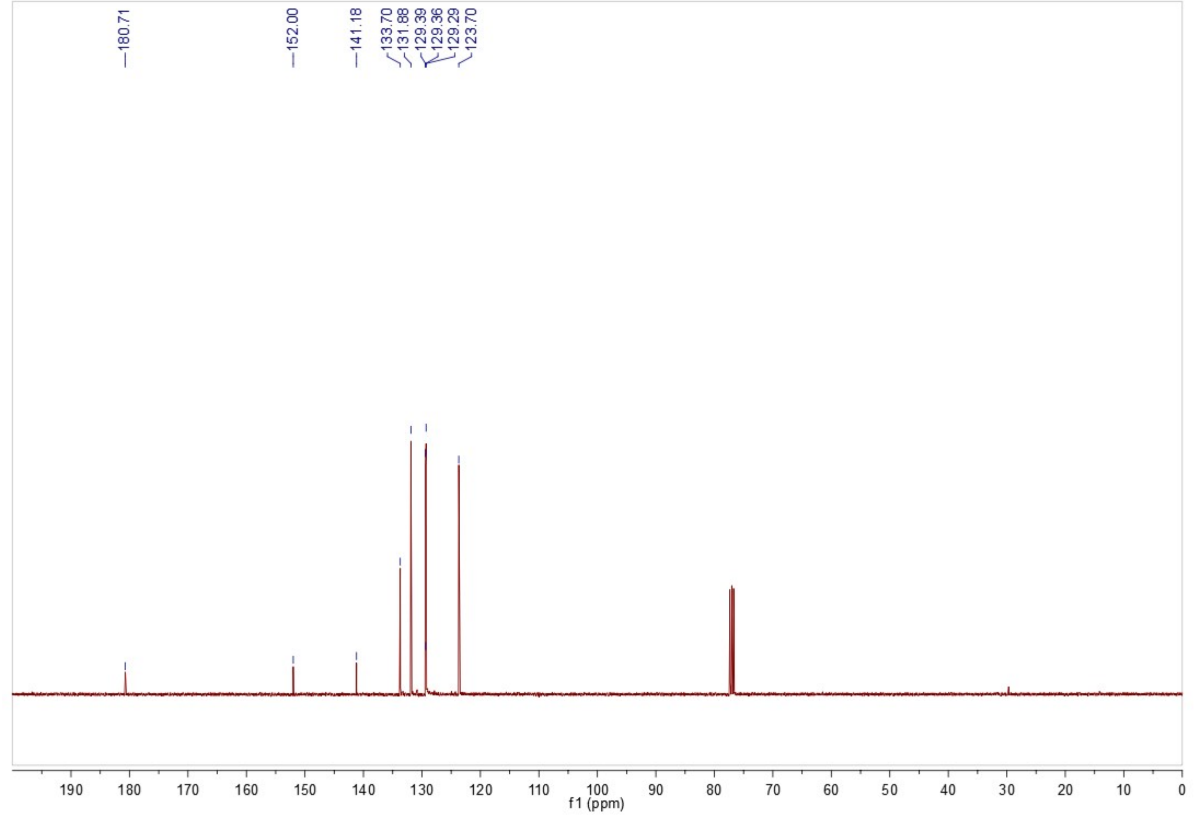
(3-Chlorobenzoyl)-2-phenyldiazene (4j)



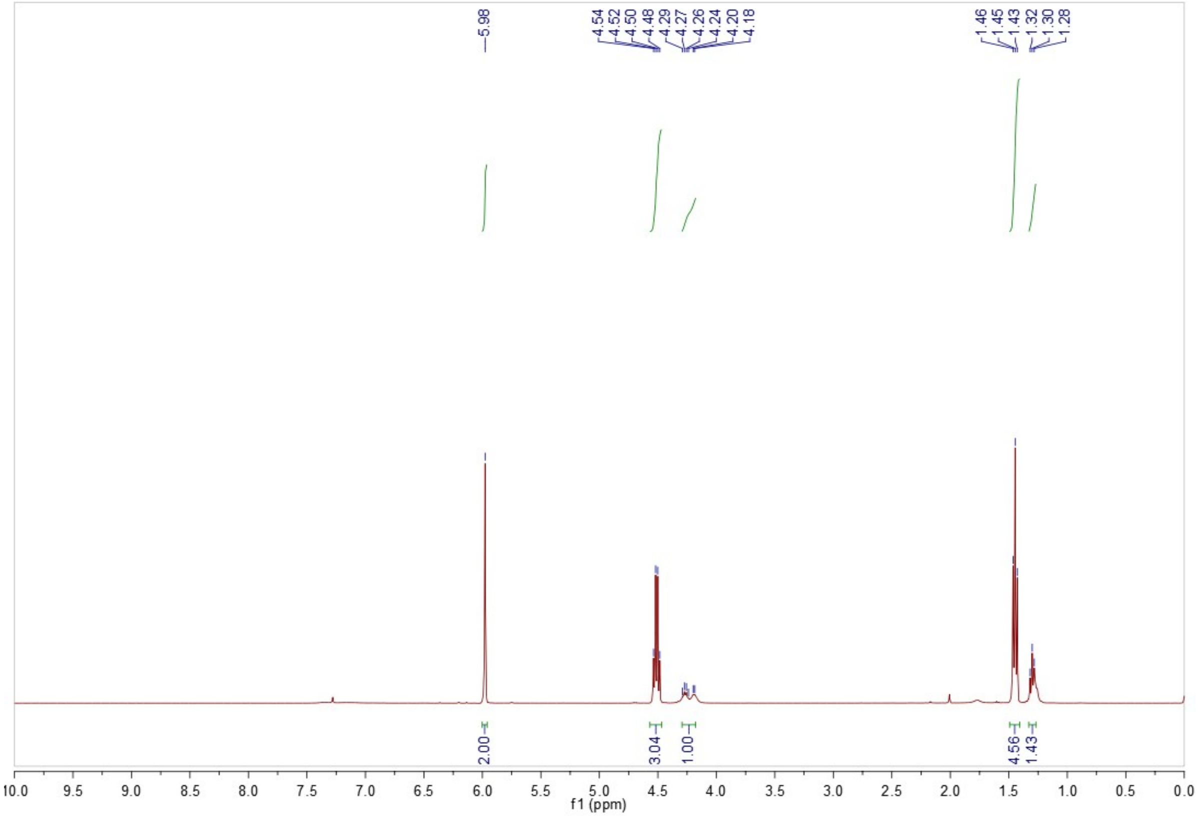


(4-Chlorobenzoyl)-2-phenyldiazene (4k)

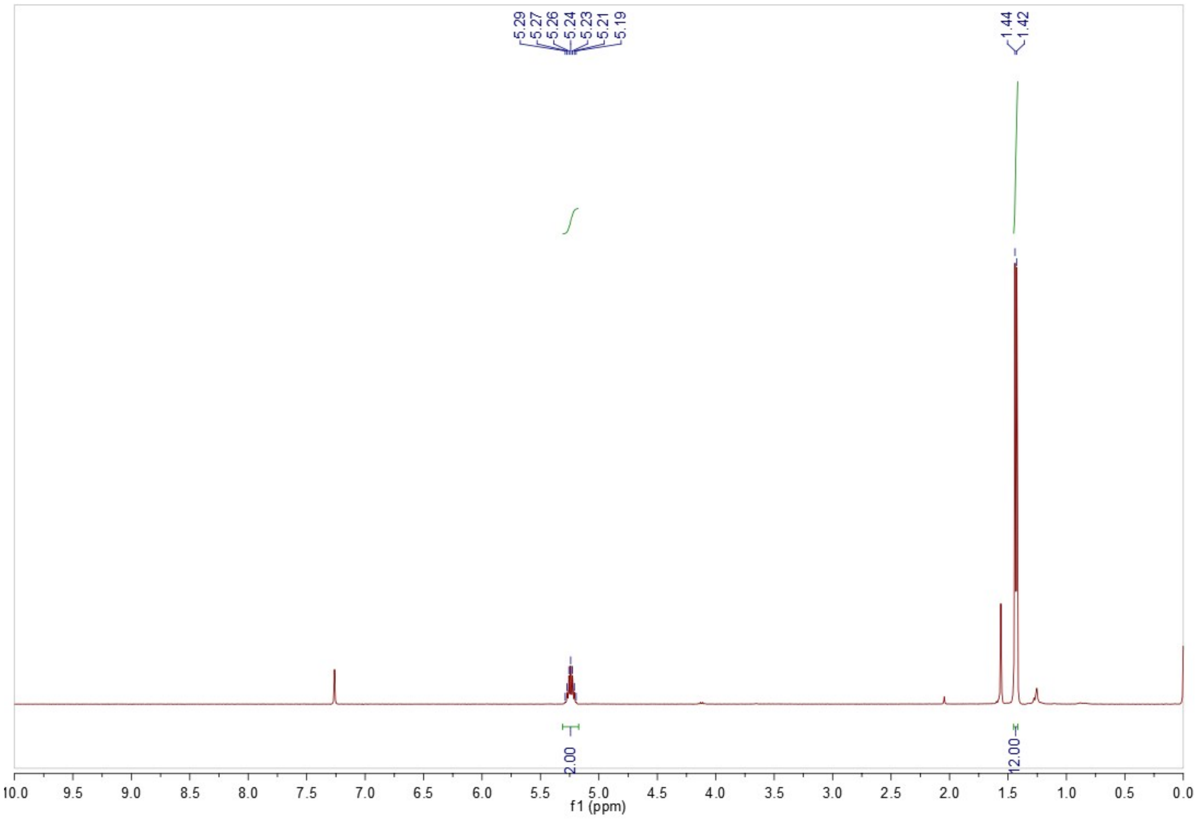


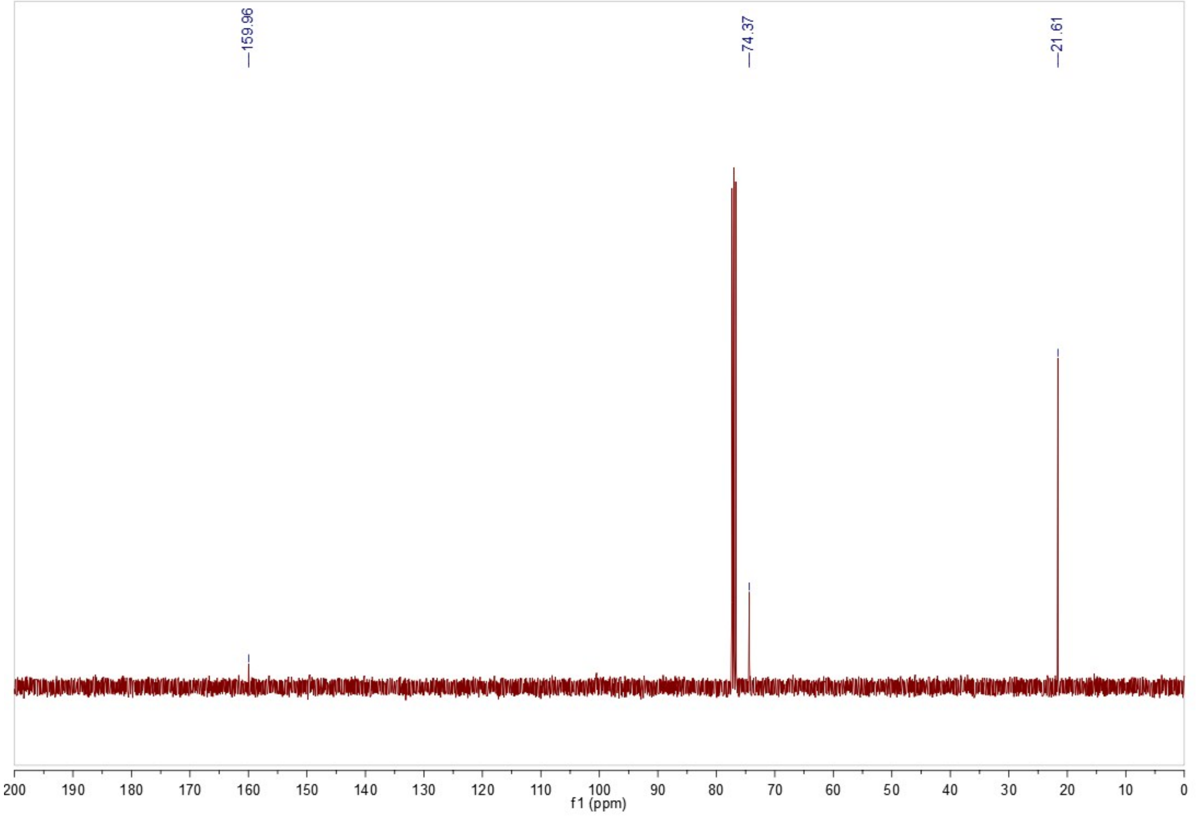


Diethyl azodicarboxylate (6a)

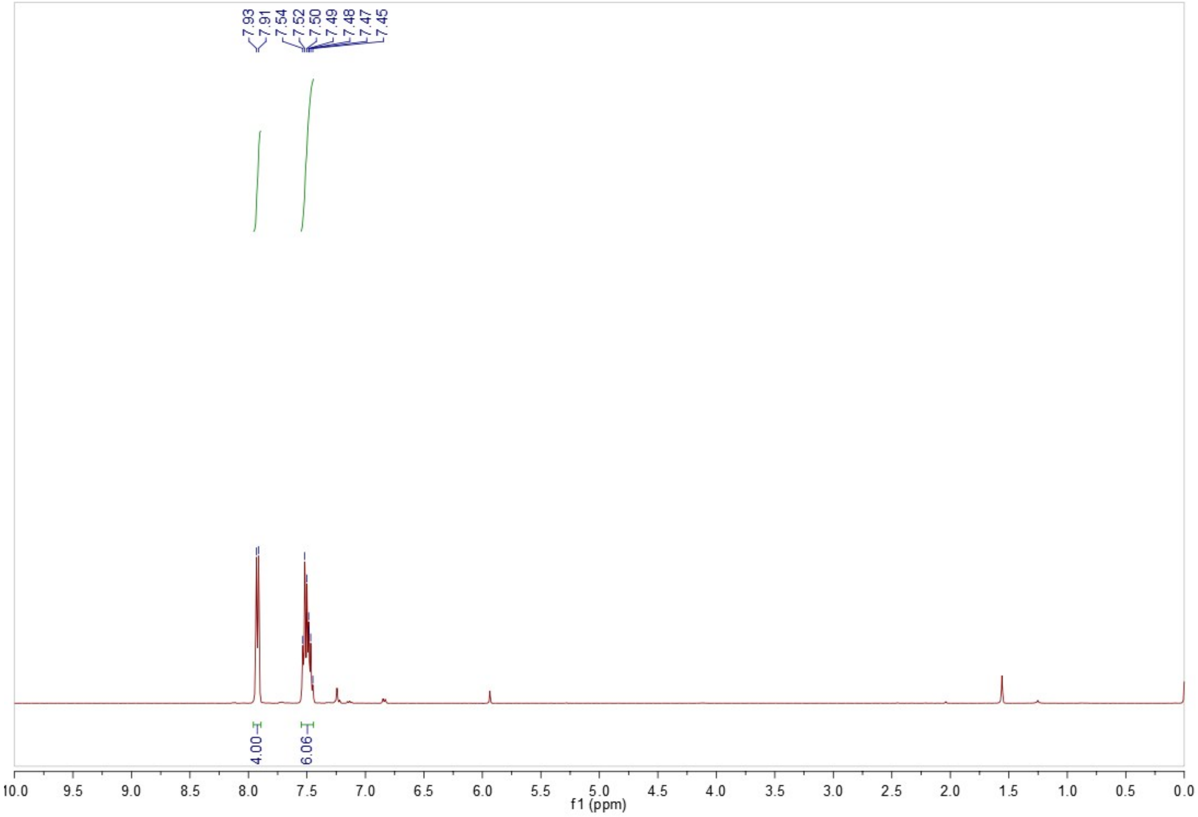


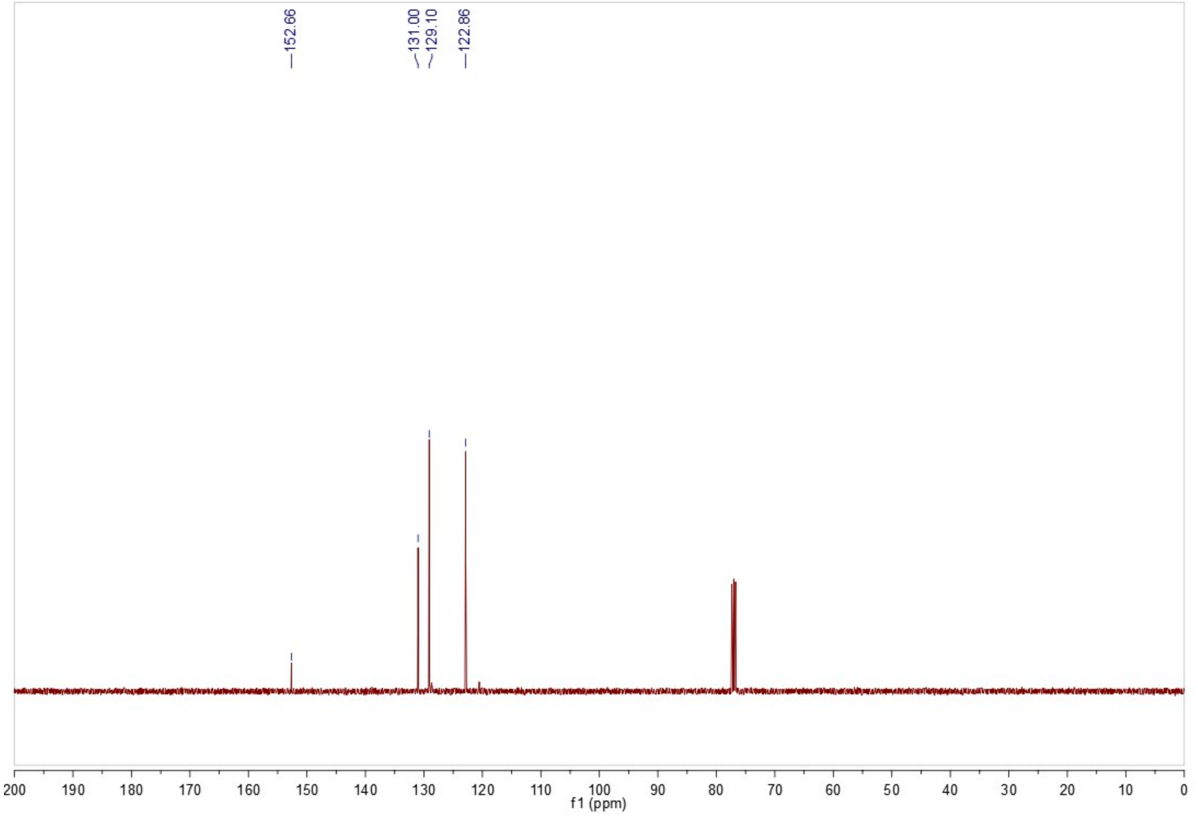
Diisopropyl azodicarboxylate (6b)





Diazobenzene (6c)





(*Z*)-*N*,3,5-Triphenyl-1,3,4-oxadiazol-2(3*H*)-imine (7a)