



Selective Synthesis of Benzimidazoles from *o*-Phenylenediamine and Aldehydes Promoted by Supported Gold Nanoparticles

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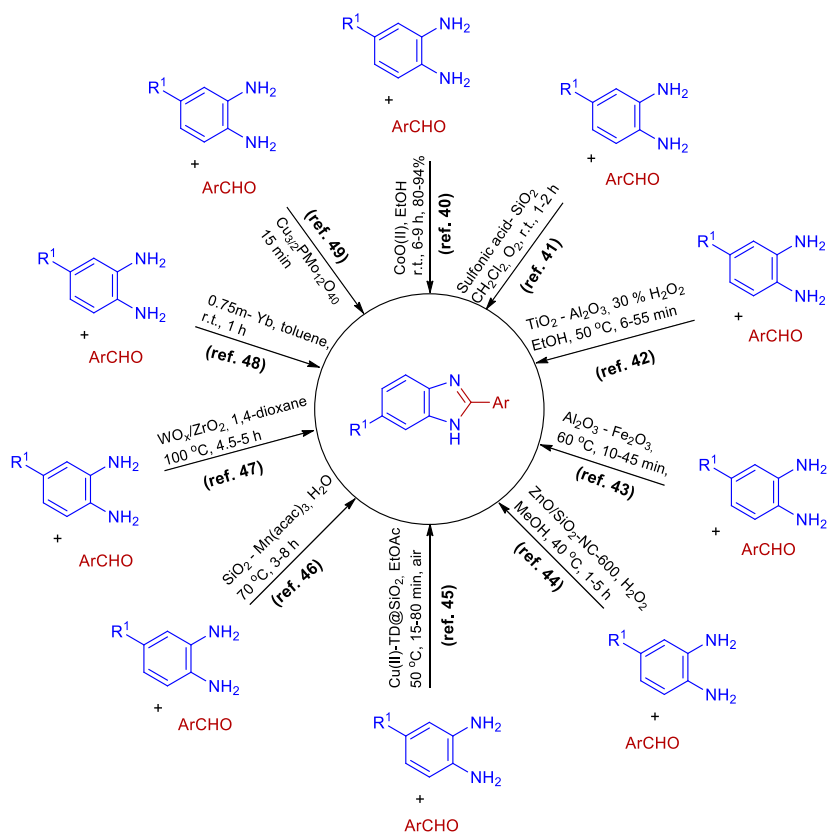
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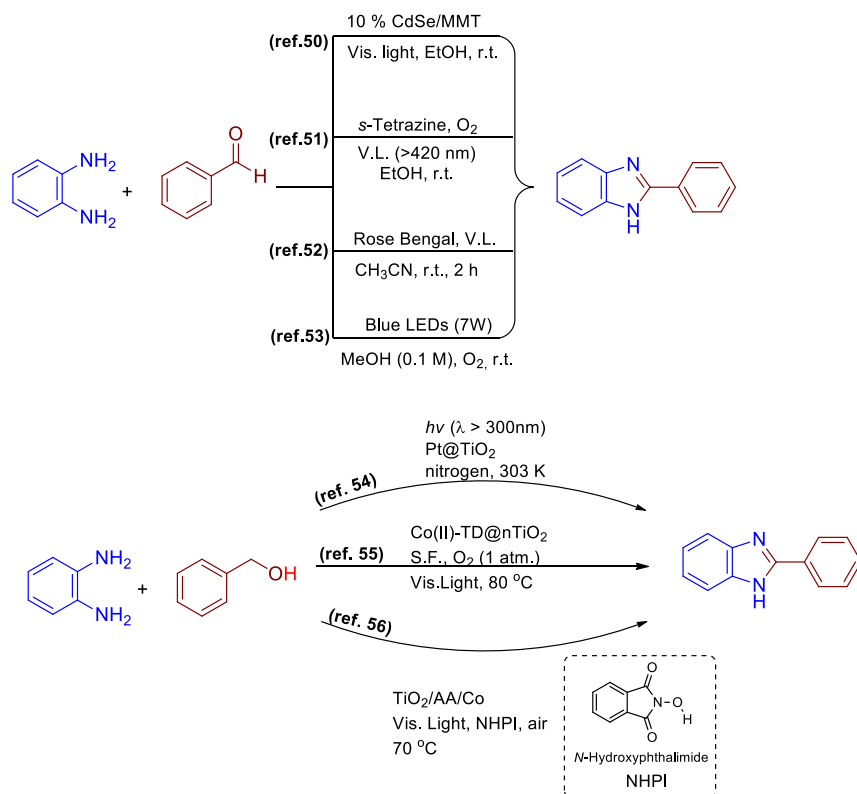
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Metal oxides as heterogeneous catalysts

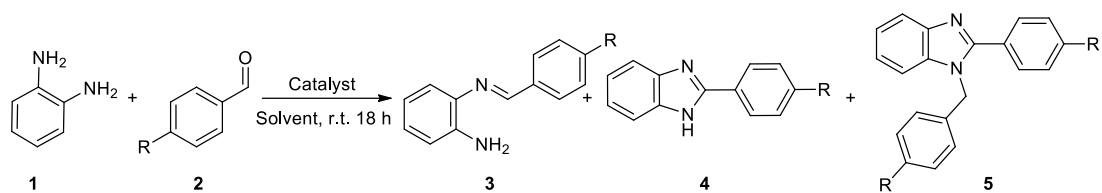


Scheme S1. Synthesis of benzimidazole derivatives using metal oxides as heterogeneous catalysts.

Visible-Light promoted synthesis

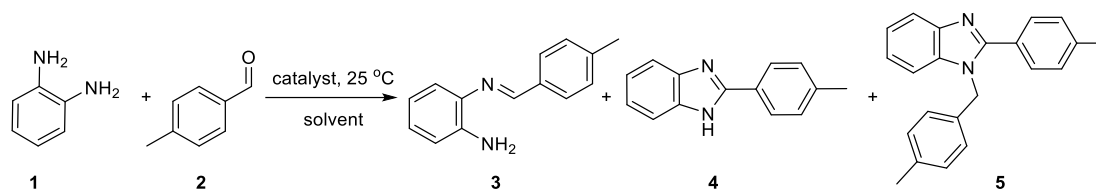


Scheme S2. Synthesis of benzimidazole derivatives under photocatalytic reactions.

Table S1. Homogeneous catalyst screening for the reaction between **1** and **2**.

Entry	Catalyst ^a	Solvent	Conversion (%) ^b	3 (%) ^c	4 (%) ^c	5 (%) ^c
1	HAuCl ₄	CH ₃ CN	100	-	32	68
2	HAuCl ₄	CH ₃ OH	68	-	14	54
3	HAuCl ₄	EtOH	100	-	66	34
4	HAuCl ₄	1,2-DCE	85	51	29	5
5	HAuCl ₄	EtOAc	71	-	57	14
6	HAuCl ₄	Toluene	95	32	45	18
7	AuCl	CH ₃ CN	82	-	58	24
8	AgNO ₃	MeOH	100	-	63	37
9	Cu(ClO ₄) ₂ •6H ₂ O	CH ₃ CN	100	-	40	60

^a Reaction conditions: *o*-phenylenediamine **1** (0.1 mmol), 4-methylbenzaldehyde **2** (0.1 mmol), catalyst (20 % mol), solvent (1 ml), at room temperature for 18 h. ^b Based on the consumption of **2** determined from the crude ¹H NMR mixture of the reaction. ^c Yields of **3**, **4**, **5** were determined by ¹H NMR from the crude reaction mixture.

Table 2. Heterogeneous M_xO_y screening for the reaction between **1** and **2**.

Entry	Catalyst	Solvent	Time (h)	2 (%) ^a	3 (%) ^a	4 (%) ^a	5 (%) ^a
1	SiO ₂	CH ₃ CN	2	0	49	33	13
2	Al ₂ O ₃	CH ₃ CN	2	0	44	38	18
3	Al ₂ O ₃	CH ₃ CN	48	0	18	46	36
4	Al ₂ O ₃	MeOH	48	0	-	40	60
5	TiO ₂ (Degussa)	MeOH	2	0	-	41	59
6	TiO ₂ (Degussa)	CH ₃ CN	2	0	-	46	54
7	TiO ₂ (Hombikat)	CH ₃ CN	2	0	-	61	39
8 ^b	hv/TiO ₂ (Hombikat)	MeOH	1	0	-	65	35

^a Reaction conditions: 0.1 mmol of **1**, 0.1 mmol of **2**, catalyst (20 mg), 1mL of solvent, at 25 °C. Yields of **2**, **3**, **4** and **5** were determined by ¹H NMR from the crude reaction mixture. ^b Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), TiO₂ (20 mg), solvent (1 ml) at Xenon Lamp for 1 h.

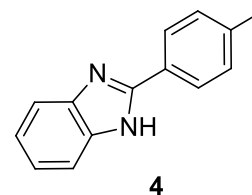
Table S3. Solvent screening for the reaction between **1** and **2** catalyzed by Au/Al₂O₃.

Entry	Solvent ^a	Temperature (°C)	2 (%) ^b	3 (%) ^b	4 (%) ^b	5 (%) ^b
1	MeOH	r.t.	-	-	100	-
2	MeOH (repeat of 1)	r.t.	-	5	90	5
3	EtOAc	r.t.	10	33	30	27
4	CH ₃ CN	r.t.	-	16	50	34
5	Toluene	r.t.	-	100	-	-
6	Toluene	130	-	-	87	13

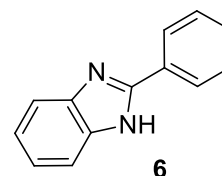
^a Reaction conditions: *o*-phenylenediamine **1** (0.1 mmol), 4-methylbenzaldehyde **2** (0.1 mmol), catalyst (20 mg, 1 mol % Au loading), solvent (1 ml) for 18 h. ^b Yields of **2**, **3**, **4**, **5** were determined by ¹H NMR from the crude reaction mixture.

^1H and ^{13}C NMR data of 2-substituted-1*H*-1,3-benzodiazoles

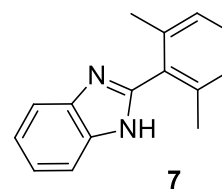
2-(4-Methylphenyl)-1*H*-1,3-benzodiazole (4)^{[1],[2]}: 62 mg, 99% yield, brown solid, m.p. 214-216 °C; ^1H NMR (500 MHz, CD_3OD) δ 7.96 (d, J = 8.0 Hz, 2H), 7.70 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 2H), 7.45 (dd, J_1 = 6.0 Hz, J_2 = 3.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 151.4, 145.2, 134.7, 131.4, 128.5, 126.6, 122.8, 115.0, 21.6; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2$: 209.1073, found: 209.1075.



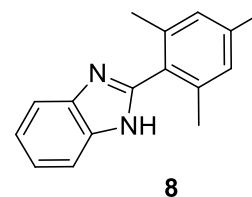
2-Phenyl-1*H*-1,3-benzodiazole (6)^{[1],[3]}: 57 mg, 98% yield, brown solid, m.p. 242-244 °C; ^1H NMR (500 MHz, CD_3OD) δ 8.11 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 2H), 7.73 (dd, J_1 = 6.5 Hz, J_2 = 3.5 Hz, 2H), 7.65 (m, 3H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 3.0 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 151.5, 135.3, 133.8, 130.8, 128.6, 126.5, 126.2, 115.2.; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{11}\text{N}_2$: 195.0916, found: 195.0913.



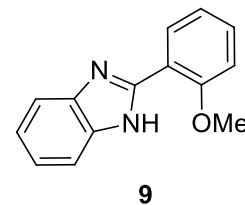
2-(2,6-Dimethylphenyl)-1*H*-1,3-benzodiazole (7)^[5]: 43 mg, 65% yield, light yellow solid, m.p. 225-227 °C; ^1H NMR (500 MHz, CD_3OD) δ 7.60 (m, 2H), 7.28 (m, 3H), 7.17 (d, J = 7.5 Hz, 2H), 2.14 (s, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 153.2, 139.1, 132.3, 130.7, 128.5, 124.3, 123.6, 114.0, 20.0; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2$: 223.1230, found: 223.1239.



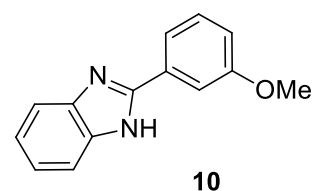
2-(2,4,6-Trimethylphenyl)-1*H*-1,3-benzodiazole (8)^{[6],[7]}: 36 mg, 51% yield, yellow solid, m.p. 258-260 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (dd, J = 5.0, 3.0 Hz, 2H), 7.18 (dd, J = 5.5, 3.0 Hz, 2H), 6.79 (s, 2H), 2.31 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.7, 139.5, 137.9, 137.6, 128.3, 128.0, 122.6, 114.9, 21.3, 19.8; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2$: 237.1386, found: 237.1397.



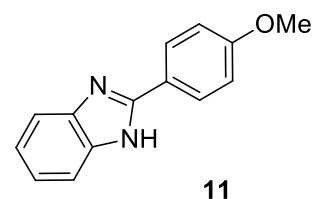
2-(2-Methoxyphenyl)-1*H*-1,3-benzodiazole (9)^[8]: 66 mg, 98% yield, brown solid, m.p. 176-178 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.59 (d, *J* = 8.0 Hz, 1H), 7.66 (br s, 2H), 7.42 (dd shown as t, *J* = 7.0 Hz, 1H), 7.26 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.5 Hz, 2H), 7.14 (dd shown as t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 4.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 156.9, 150.0, 131.4, 130.3, 122.7, 121.9, 118.0, 111.6, 56.1; HRMS (ESI) [*M* + *H*]⁺ calcd for C₁₄H₁₃N₂O : 225.1022, found : 225.1030.



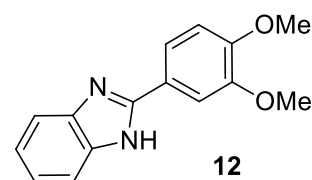
2-(3-Methoxyphenyl)-1*H*-1,3-benzodiazole (10)^[9]: 67 mg, 99% yield, brown solid, m.p. 169-171 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.18 (br s, 1H), 7.88 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.70 (dd, *J*₁ = 6.5 Hz, *J*₂ = 3.5 Hz, 2H), 7.26 (dd, *J*₁ = 6.0 Hz, *J*₂ = 4.0 Hz, 2H), 7.11 (dd shown as t, *J* = 8.0 Hz, 1H), 6.83 (dd, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 160.2, 149.9, 134.2, 130.4, 126.0, 125.1, 120.1, 119.0, 114.5, 112.5, 55.7; HRMS (ESI) [*M* + *H*]⁺ calcd for C₁₄H₁₃N₂O : 225.1022, found : 225.1034.



2-(4-Methoxyphenyl)-1*H*-1,3-benzodiazole (11)^{[1],[3]}: 67 mg, 99% yield, brown solid, m.p. 223-225 °C; ¹H NMR (500 MHz, CD₃OD) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.72 (dd, *J*₁ = 6.5 Hz, *J*₂ = 3.5 Hz, 2H), 7.49 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 165.1, 151.0, 133.9, 130.6, 126.8, 116.7, 116.3, 114.7, 56.3; HRMS (ESI) [*M* + *H*]⁺ calcd for C₁₄H₁₃N₂O : 225.1022, found : 225.1024.

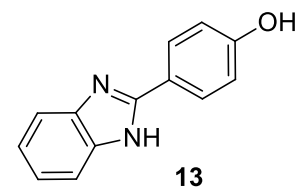


2-(3,4-Dimethoxyphenyl)-1*H*-1,3-benzodiazole (12)^[8]: 75 mg, 98% yield, brown solid, m.p. 211-213 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.68 (s, 1H), 7.66 (dd, *J*₁ = 8.5 Hz, *J*₂ = 1.5 Hz, 1H), 7.60 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0, 2H), 7.31 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 153.3, 152.8, 151.0, 138.0,

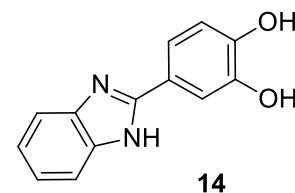


124.8, 121.5, 121.3, 115.3, 112.9, 111.2, 56.6, 56.5; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{15}N_2O_2$: 255.1128, found : 255.1126.

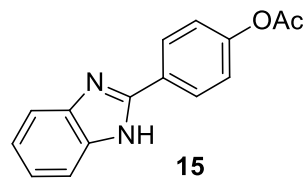
4-(1*H*-1,3-Benzodiazol-2-yl)phenol (13)^[3]: 62 mg, 98% yield, brown solid, m.p. 259-261 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.97 (d, $J = 8.5$ Hz, 2H), 7.67 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.43 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.02 (d, $J = 8.5$ Hz, 2H); ¹³C NMR (125 MHz, CD₃OD) δ 163.5, 151.8, 134.6, 130.6, 126.3, 117.6, 116.2, 114.7. HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{11}N_2O$: 211.0866, found : 211.0874.



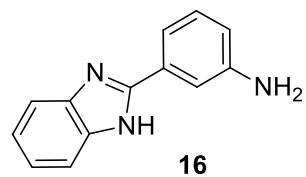
4-(1*H*-1,3-Benzodiazol-2-yl)-1,2-benzenediol (14)^[10]: 66 mg, 98% yield, brown solid, m.p. 181-183 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.65 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.54 (d, $J = 1.5$ Hz, 1H), 7.48 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz, 1H), 7.40 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 152.4, 151.4, 147.6, 135.6, 125.8, 121.2, 117.6, 117.1, 115.3, 114.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{11}N_2O_2$: 227.0815, found : 227.0824.



4-(1*H*-1,3-Benzodiazol-2-yl)-phenyl acetate (15): 69 mg, 91% yield, yellow solid, m.p. 245-247 °C; ¹H NMR (500 MHz, CD₃OD) δ 8.10 (d, $J = 8.5$ Hz, 2H), 7.60 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.25 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CD₃OD) δ 170.8, 153.8, 152.6, 129.0, 128.6, 124.0, 123.6, 116.9, 116.7, 20.9; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{13}N_2O_2$: 253.0972, found : 253.0975.

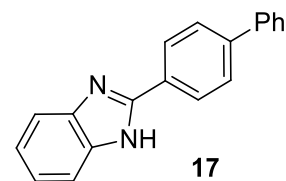


3-(1*H*-1,3-Benzodiazol-2-yl)aniline (16): 43 mg, 68% yield, brown solid, m.p. 182-184 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.5$ Hz, 2H), 7.46 (s, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.22 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.5$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 1H), 6.70 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H); ¹³C NMR

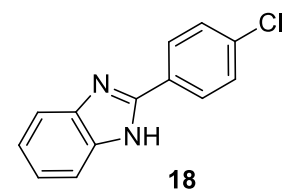


(125 MHz, CDCl₃) δ 152.2, 147.2, 130.8, 130.0, 122.9, 117.0, 116.7, 113.4; HRMS (ESI) [M + H]⁺ calcd for C₁₃H₁₂N₃ : 210.1026, found : 210.1024.

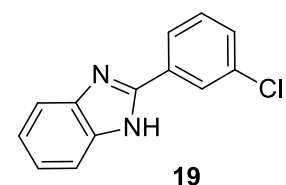
2-([1,1'-Biphenyl]-4-yl)-1H-1,3-benzodiazole (17)^[2]: 65 mg, 80% yield, brown solid, m.p. 288-290 °C; ¹H NMR (500 MHz, CD₃OD) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.75 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.40 (t, *J* = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 151.3, 146.7, 140.4, 135.2, 130.2, 129.6, 129.1, 128.1, 126.6, 124.7, 115.2; HRMS (ESI) [M + H]⁺ calcd for C₁₉H₁₅N₂ : 271.1230, found : 271.1230.



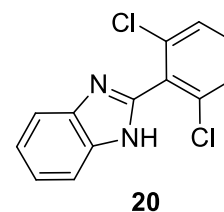
2-(4-Chlorophenyl)-1H-1,3-benzodiazole (18)^{[1],[3],[2]}: 67 mg, 98% yield, light yellow solid, m.p. 288-289 °C; ¹H NMR (500 MHz, CD₃OD) δ 8.11 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 152.2, 137.3, 132.1, 130.3, 129.7, 129.3, 129.1, 124.1; HRMS (ESI) [M + H]⁺ calcd for C₁₃H₁₀ClN₂ : 229.0527, found : 229.0528.



2-(3-Chlorophenyl)-1H-1,3-benzodiazole (19): 68 mg, 98% yield, orange semisolid; ¹H NMR (500 MHz, CD₃OD) δ 8.12 (d, *J* = 2.0 Hz, 1H), 8.02 (dt, *J*₁ = 7.0 Hz, *J*₂ = 1.5 Hz, 1H), 7.71 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.62 (m, 2H), 7.45 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H); ¹³C NMR (125 MHz, CD₃OD) δ 150.2, 136.6, 135.8, 133.3, 132.3, 128.6, 128.4, 126.8, 126.5, 115.4; HRMS (ESI) [M + H]⁺ calcd for C₁₃H₁₀ClN₂ : 229.0527, found : 229.0528.

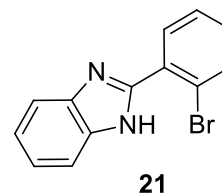


2-(2,6-Dichlorophenyl)-1H-1,3-benzodiazole (20): 77 mg, 96% yield, yellow solid, m.p. 247-249 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.66 (dd, *J*₁ = 6.5 Hz, *J*₂ = 3.5 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.34 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.5 Hz, 2H); ¹³C NMR (125 MHz, CD₃OD) δ 148.2, 138.8, 137.2, 133.6, 130.6, 129.4,

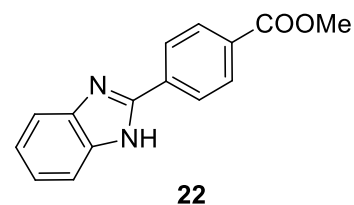


124.5, 116.2; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_9Cl_2N_2$: 263.0137, found : 263.0143.

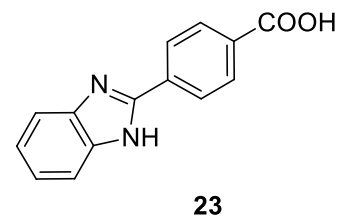
2-(2-Bromophenyl)-1H-1,3-benzodiazole (21): 73 mg, 89% yield, light yellow solid, m.p. 243-244 °C; 1H NMR (600 MHz, CD_3OD) δ 7.79 (d, $J = 7.8$ Hz, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.64 (br s, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 1H), 7.30 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H); ^{13}C NMR (150 MHz, CD_3OD) δ 152.3, 134.7, 133.5, 133.2, 132.6, 128.8, 124.0, 123.2; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{10}BrN_2$: 273.0022/275.0002, found : 273.0027/275.0007.



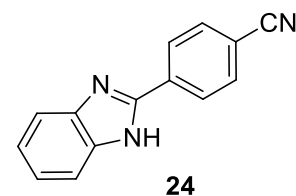
Methyl 4-(1H-1,3-benzodiazol-2-yl)benzoate (22): 67 mg, 88% yield, light yellow solid, m.p. 196-198 °C; 1H NMR (500 MHz, CD_3OD) δ 8.19 – 8.14 (m, 4H), 7.70 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.42 (dd, $J_1 = 6.5$ Hz, $J_2 = 3.5$ Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 167.3, 150.8, 137.1, 133.9, 131.9, 131.4, 128.3, 126.0, 115.7, 53.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{13}N_2O_2$: 253.0972, found : 253.0973.



4-(1H-1,3-Benzodiazol-2-yl)benzoic acid (23): 70 mg, 98% yield, light yellow solid, m.p. 295-297 °C; 1H NMR (500 MHz, DMSO) δ 8.29 (d, $J = 7.5$ Hz, 2H), 8.11 (d, $J = 8.0$ Hz, 2H), 7.63 (dd shown as s, 2H), 7.25 – 7.20 (dd shown as m, 2H). ^{13}C NMR (125 MHz, DMSO) δ 166.7, 148.7, 135.1, 133.4, 130.2, 129.9, 127.7, 124.8, 114.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{14}H_{11}N_2O_2$: 239.0815, found : 239.0813.

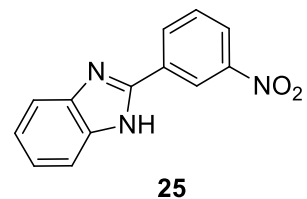


4-(1H-1,3-Benzodiazol-2-yl)benzonitrile (24)^[2]: 65 mg, 98% yield, orange solid, m.p. 264-266 °C; 1H NMR (500 MHz, CD_3OD) δ 8.26 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.75 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.47 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 150.1, 137.0,

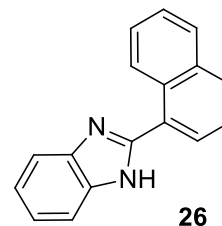


134.4, 131.9, 129.0, 126.4, 118.9, 116.1, 115.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{14}H_{10}N_3$: 220.0869, found : 220.0869.

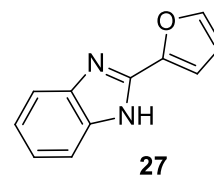
2-(3-Nitrophenyl)-1H-1,3-benzodiazole (25)^[31]: 70 mg, 97% yield, brown solid, m.p. 180-181 °C; ¹H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.19 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, 1H), 7.69 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.58 (dd shown as t, $J = 8.0$ Hz, 1H), 7.30 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H); ¹³C NMR (125 MHz, $CDCl_3$) δ 149.4, 148.7, 132.8, 131.6, 130.3, 124.6, 123.9, 121.4, 115.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{10}N_3O_2$: 240.0767, found : 240.0768.



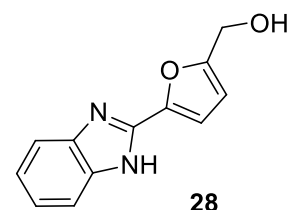
2-(Naphthalen-1-yl)-1H-1,3-benzodiazole (26)^[31]: 63 mg, 86% yield, white solid, m.p. 298-300 °C; ¹H NMR (500 MHz, CD_3OD) δ 8.46 (m, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.99 (m, 1H), 7.87 (dd, $J_1 = 7.0$ Hz, $J_2 = 1.0$ Hz, 1H), 7.68 (br, 2H), 7.63 (dd, $J_1 = 6.5$ Hz, $J_2 = 1.0$ Hz, 1H), 7.55–7.59 (m, 2H), 7.32 (m, 2H); ¹³C NMR (125 MHz, CD_3OD) δ 153.3, 135.4, 132.6, 131.6, 129.6, 129.29, 129.28, 128.2, 127.5, 126.7, 126.1, 123.9, 116.3; ¹H NMR (500 MHz, $DMSO-d_6$) δ 9.14 (d, $J = 8.5$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 8.03 (t, $J = 8.5$ Hz, 2H), 7.68 (m, 3H), 7.65–7.60 (m, 2H); ¹³C NMR (125 MHz, $DMSO-d_6$) δ 151.6, 133.6, 130.5, 130.1, 128.4, 127.9, 127.7, 127.0, 126.4, 126.3, 125.3, 122.0, 115.2; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{13}N_2$: 245.1073, found : 245.1079.



2-(Furan-2-yl)-1H-1,3-benzodiazole (27)^{[11],[31]}: 44 mg, 80% yield, dark brown solid, m.p. 221-223 °C; ¹H NMR (500 MHz, CD_3OD) δ 7.88 (dd shown as s, 1H), 7.63 (dd, $J_1 = 5.5$ Hz, $J_2 = 3.0$ Hz, 2H), 7.38 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 3H), 6.75 (dd shown as d, $J = 1.5$ Hz, 1H); ¹³C NMR (125 MHz, CD_3OD) δ 147.7, 143.6, 143.3, 136.3, 125.8, 115.3, 115.1, 113.9; HRMS (ESI) $[M + H]^+$ calcd for $C_{11}H_9N_2O$: 185.0709, found : 185.0708.

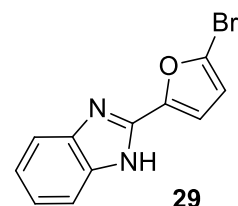


[5-(1*H*-1,3-Benzodiazol-2-yl)furan-2-yl]methanol (28)^[11]: 61 mg, 95% yield, dark brown solid, m.p. 203-205 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.60 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.5 Hz, 2H), 7.34 (dd, *J*₁ = 6.5 Hz, *J*₂ = 3.5 Hz, 2H), 7.27 (d, *J* = 3.5 Hz, 1H), 6.60 (d, *J* = 3.5 Hz, 1H), 4.66 (s, 2H); ¹³C NMR (125 MHz, CD₃OD) δ 159.9, 144.0, 143.5, 137.2, 125.3, 115.4, 115.1, 111.2, 57.4; HRMS (ESI) [M + H]⁺ calcd for C₁₂H₁₁N₂O₂ : 215.0815, found : 215.0818.



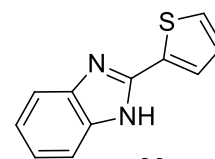
28

2-(5-Bromofuran-2-yl)-1*H*-1,3-benzodiazole (29): 74 mg, 95% yield, brown oil; ¹H NMR (600 MHz, CD₃OD) δ 7.56 (dd, *J*₁ = 4.8 Hz, *J*₂ = 3.0 Hz, 2H), 7.25 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.15 (d, *J* = 3.6 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H); ¹³C NMR (150 MHz, CD₃OD) δ 148.4, 144.1, 125.5, 124.3, 116.0, 115.3, 114.1; HRMS (ESI) [M + H]⁺ calcd for C₁₁H₈BrN₂O : 262.9815/264.9794, found : 262.9814/264.9793.



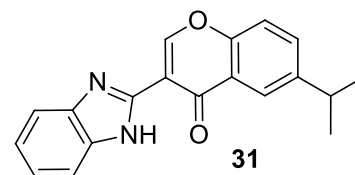
29

2-(thiophen-2-yl)-1*H*-1,3-benzodiazole (30)^{[11],[3]}: 56 mg, 95% yield, brown solid, m.p. 215-217 °C; ¹H NMR (500 MHz, CD₃OD) δ 8.04 (d, *J* = 3.5 Hz, 1H), 7.93 (d, *J* = 5.0 Hz, 1H), 7.68 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.46 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 7.34 (dd shown as t, *J* = 4 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 146.7, 134.9, 133.7, 132.61, 132.6, 130.2, 127.6, 126.6, 114.9; HRMS (ESI) [M + H]⁺ calcd for C₁₁H₉N₂S : 201.0480, found : 201.0478.



30

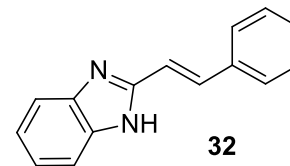
3-(1*H*-1,3-Benzodiazol-2-yl)-6-isopropyl-4*H*-chromen-4-one (31): 88 mg, 96% yield, yellow solid, m.p. 225-227 °C; ¹H NMR (500 MHz, CDCl₃) δ 11.88 (br s, 1H), 9.35 (s, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.64 (dd, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz, 3H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.28 (dd, *J*₁ = 6.0 Hz, *J*₂ = 3.0 Hz, 2H), 3.03 – 3.05 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 176.7, 157.5, 154.7, 147.4, 146.4, 133.7, 123.8, 123.0, 122.8,



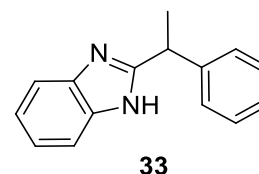
31

118.6, 113.7, 34.0, 24.0 (2C); HRMS (ESI) $[M + H]^+$ calcd for $C_{19}H_{17}N_2O_2$: 305.1284, found : 305.1281.

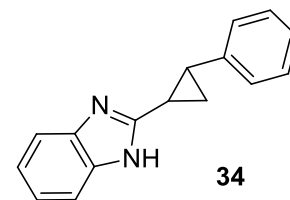
(E)-2-(2-Phenylethenyl)-1H-1,3-benzodiazole (32)^[3]: 63 mg, 96% yield, light yellow solid, m.p. 164-166 °C; ¹H NMR (500 MHz, CD₃OD) δ 7.60 – 7.56 (m, 3H), 7.53 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.5$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.31 (d, $J = 7.0$ Hz, 1H), 7.22 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.13 (d, $J = 16.5$ Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 152.5, 137.1, 136.9, 130.2, 130.1, 129.9, 128.1, 124.0, 117.2, 115.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{13}N_2$: 221.1063, found : 221.1054.



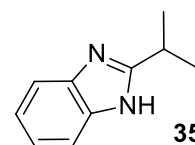
2-(1-Phenylethyl)-1H-1,3-benzodiazole (33): 65 mg, 98% yield, white solid, m.p. 208-210 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.49 (dd shown as brs, 2H), 7.30 (d, $J = 3.6$ Hz, 4H), 7.21 – 7.20 (m, 1H), 7.18 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.6$ Hz, 2H), 4.41 (dd, $J_1 = 14.4$ Hz, $J_2 = 7.2$ Hz, 1H), 1.78 (d, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.2, 144.4, 129.8, 128.3, 128.0, 123.3, 41.3, 20.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{15}N_2$: 223.1230, found : 223.1230.



2-(2-Phenylcyclopropyl)-1H-1,3-benzodiazole (34): 62 mg, 88% yield, orange semisolid; ¹H NMR (600 MHz, CDCl₃) δ 7.52 (dd shown as br s, 2H), 7.24 (t, $J = 7.2$ Hz, 2H), 7.20 – 7.17 (m, 3H), 7.03 (d, $J = 7.2$ Hz, 2H), 2.68 – 2.65 (m, 1H), 2.28 (m, 1H), 2.00 (m, 1H), 1.51 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 155.7, 140.7, 128.6, 126.4, 126.0, 122.3, 114.6, 27.6, 21.5, 17.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{16}H_{15}N_2$: 235.1230, found : 235.1233.

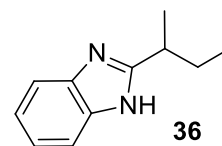


2-(Isopropyl)-1H-1,3-benzodiazole (35)^{[1],[12]}: 42 mg, 87% yield, yellow solid, m.p. 160-162 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.55 (br s, 2H), 7.20 (dd, $J_1 = 5.8$ Hz, $J_2 = 3.0$ Hz, 2H), 3.29 (m, 1H), 1.47 (d, $J = 6.6$ Hz, 6H); ¹³C NMR (150 MHz,

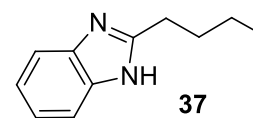


CDCl_3) δ 160.2, 122.2, 114.7, 29.2, 21.7; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2$: 161.1073, found : 161.1074.

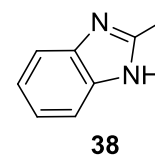
2-(*sec*-Butyl)-1*H*-1,3-benzodiazole (36)^[12]: 42 mg, 80% yield, white solid, m.p. 206-208 °C; ^1H NMR (600 MHz, CDCl_3) δ 10.2 (br s, 1H), 7.55 (dd, $J_1 = 5.4$ Hz, $J_2 = 3.0$ Hz, 2H), 7.20 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 3.13 – 3.07 (m, 1H), 1.97 – 1.93 (m, 1H), 1.79 – 1.74 (m, 1H), 1.45 (d, $J = 6.6$ Hz, 3H), 0.92 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.8, 138.4, 122.2, 114.8, 36.6, 29.5, 19.6, 12.1; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2$: 175.1230, found : 175.1231.



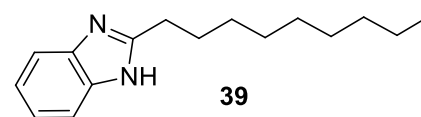
2-Butyl-1*H*-1,3-benzodiazole (37)^[12]: 49 mg, 95% yield, light brown solid, m.p. 148-151 °C; ^1H NMR (500 MHz, CDCl_3) δ 10.44 (br s, 1H), 7.54 (dd, $J_1 = 5.5$ Hz, $J_2 = 3.0$ Hz, 2H), 7.21 (dd, $J_1 = 5.5$ Hz, $J_2 = 3.0$ Hz, 2H), 2.94 (t, $J = 8.0$ Hz, 2H), 1.82 (dd, $J_1 = 15.0$ Hz, $J_2 = 7.5$ Hz, 2H), 1.36 (dd, $J_1 = 15.0$ Hz, $J_2 = 7.5$ Hz, 2H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 138.1, 122.4, 114.6, 30.5, 28.9, 22.5, 13.8; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2$: 175.1230, found : 175.1248.



2-Methyl-1*H*-1,3-benzodiazole (38)^[13]: 39 mg, 98% yield, yellow oil; ^1H NMR (500 MHz, CD_3OD) δ 7.49 (dd, $J_1 = 6$ Hz, $J_2 = 3$ Hz, 2H), 7.12 (dd, $J_1 = 6$ Hz, $J_2 = 3$ Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 151.3, 121.1, 14.6; HRMS (ESI) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_9\text{N}_2$: 133.0760, found : 133.0761.

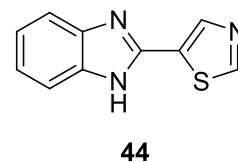


2-Nonyl-1*H*-1,3-benzodiazole (39): 68 mg, 93% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 10.20 (s, 1H), 7.54 (dd, $J = 5.8, 3.1$ Hz, 2H), 7.20 (dd, $J = 5.9, 3.0$ Hz, 2H), 2.90 (t, $J = 7.7$ Hz, 2H), 1.81 (dt, $J = 15.3, 7.7$ Hz, 2H), 1.30 (d, $J = 7.4$ Hz, 2H), 1.25 (d, $J = 6.2$ Hz, 4H), 1.18 (s, 4H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.47, 137.55, 122.62,



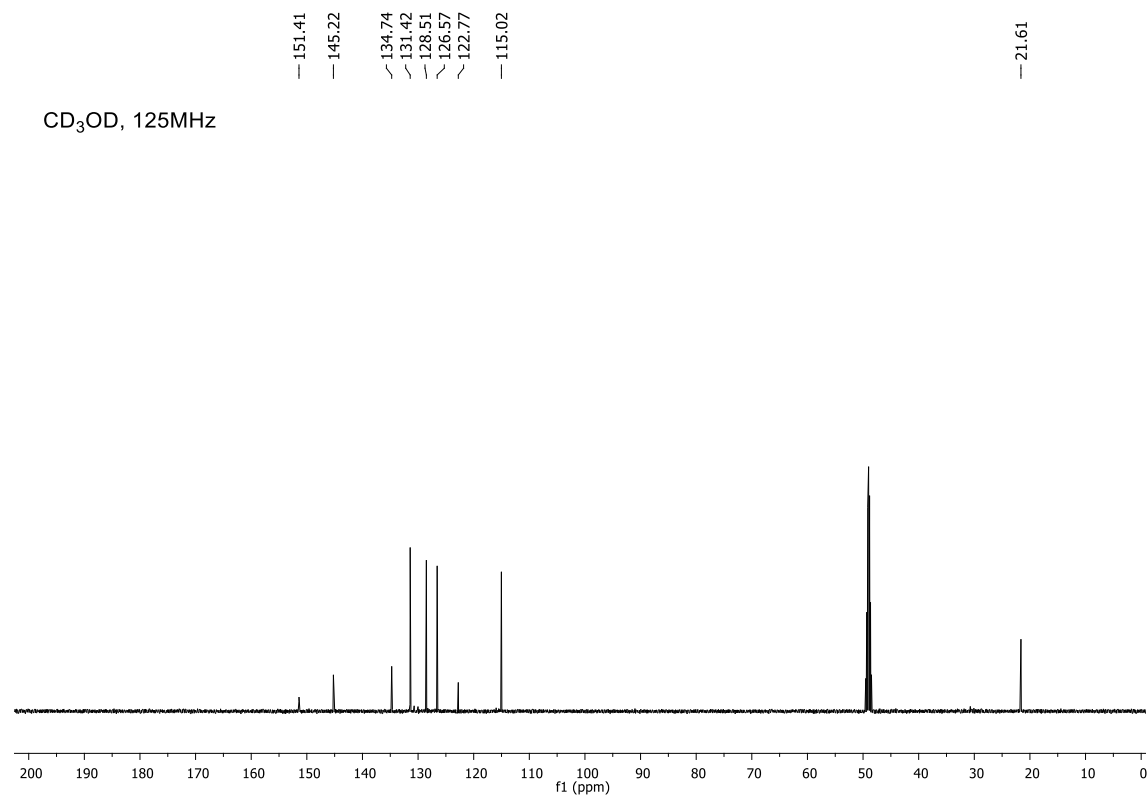
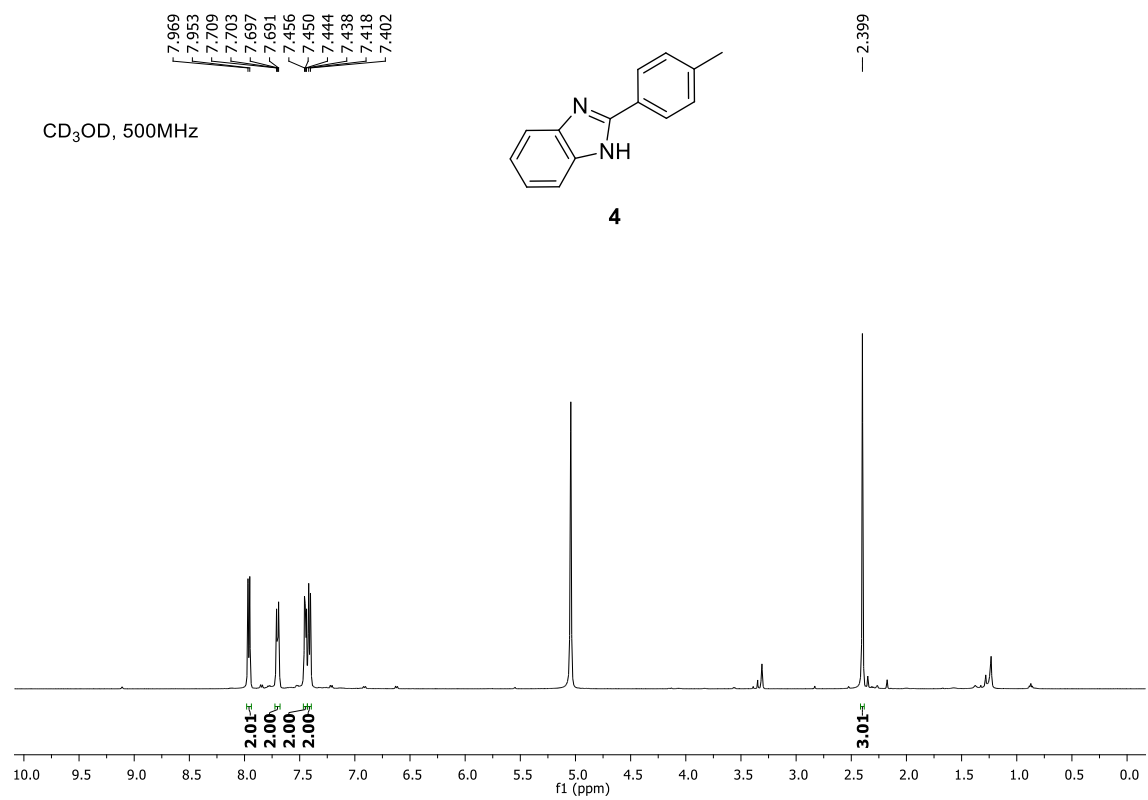
114.55, 77.37, 77.16, 76.95, 31.96, 29.57, 29.46, 29.44, 29.39, 28.97, 28.42, 22.76, 14.21; HRMS (ESI) $[M + H]^+$ calcd for $C_{16}H_{25}N_2$: 245.2012, found : 245.2017.

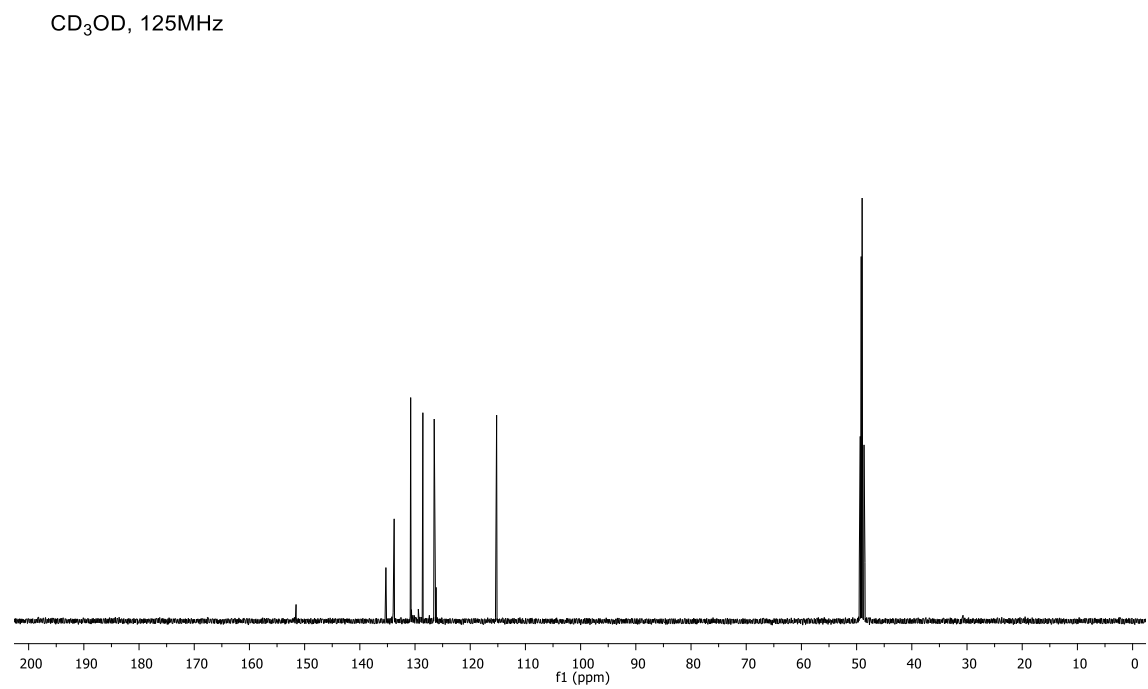
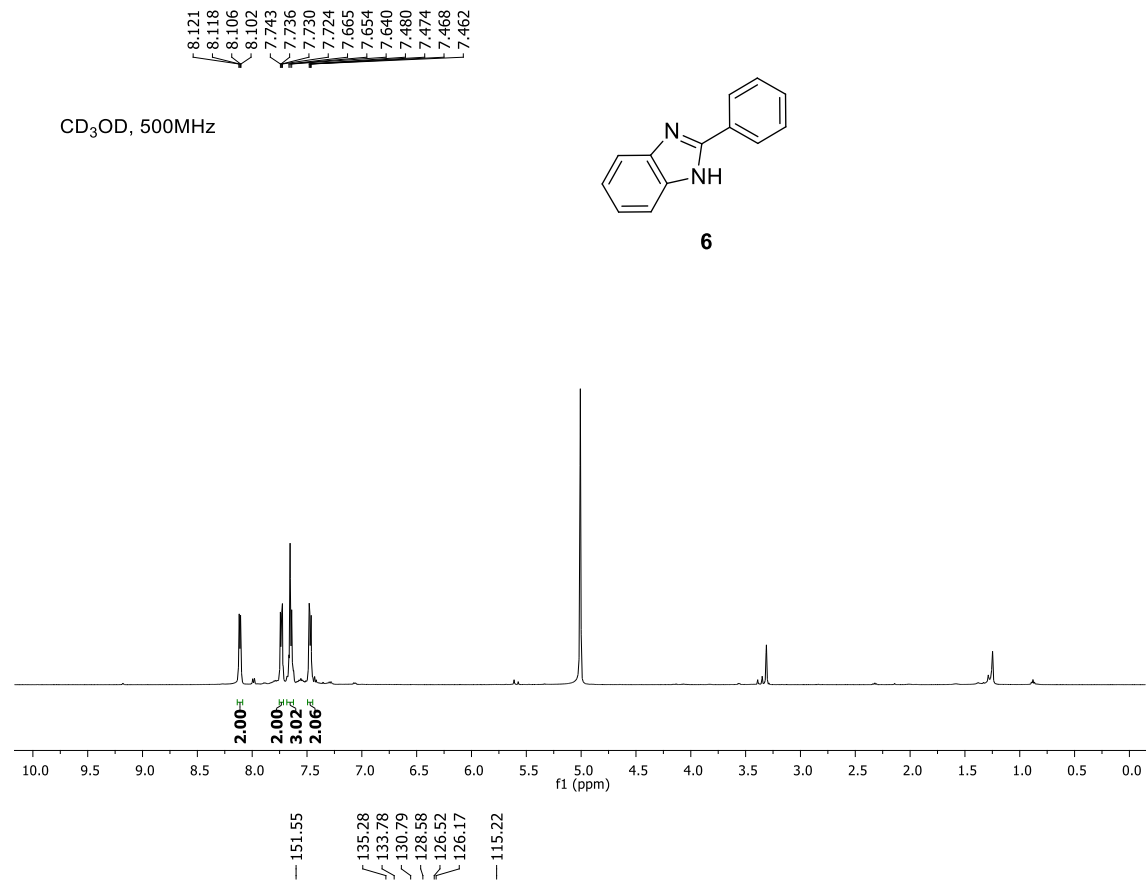
2-(1,3-Thiazol-5-yl)-1H-1,3-benzodiazole (44): 55 mg, 92% yield, yellow semi-solid; 1H NMR (600 MHz, CD_3OD) δ 9.10 (s, 1H), 8.46 (s, 1H), 7.56 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.25 (dd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 2H); ^{13}C NMR (150 MHz, CD_3OD) δ 157.3, 145.7, 143.1, 130.4, 124.5, 124.3, 116.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{10}H_7N_3S$: 202.0433, found : 202.0440

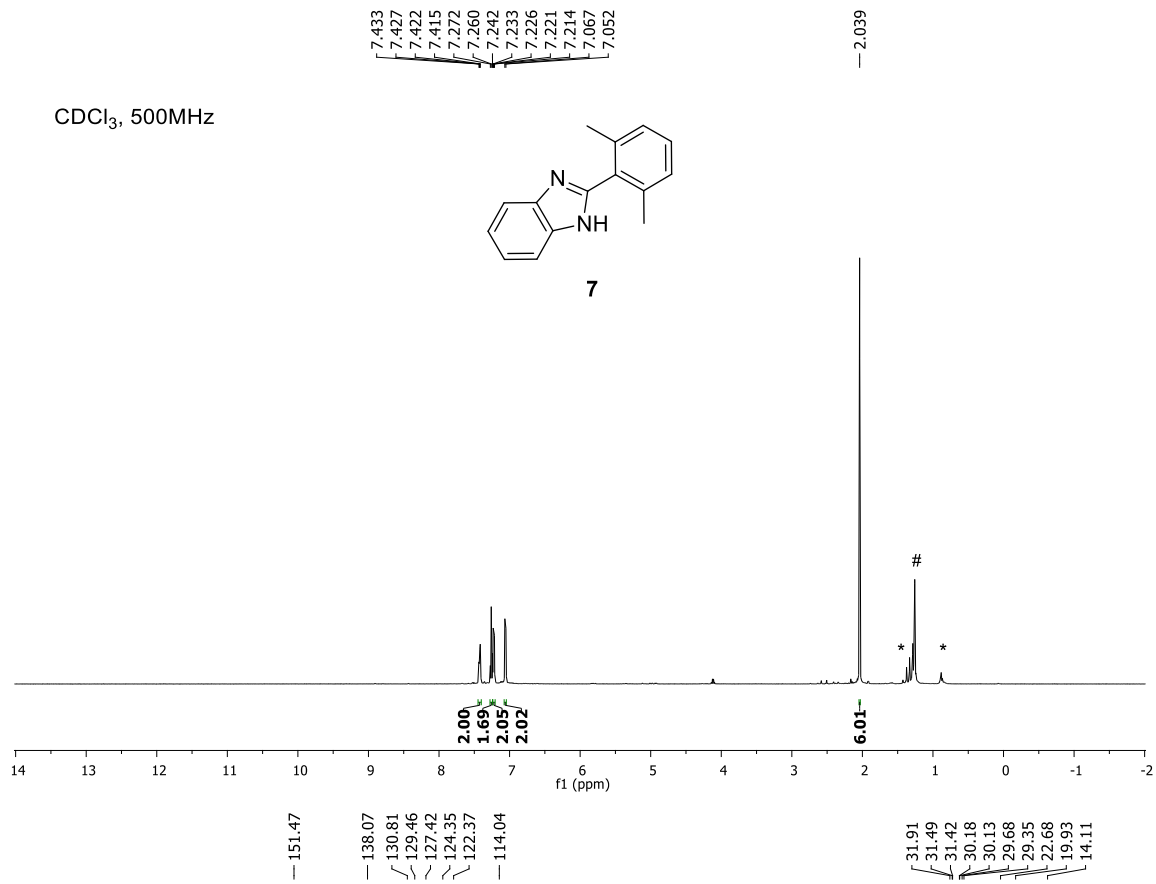


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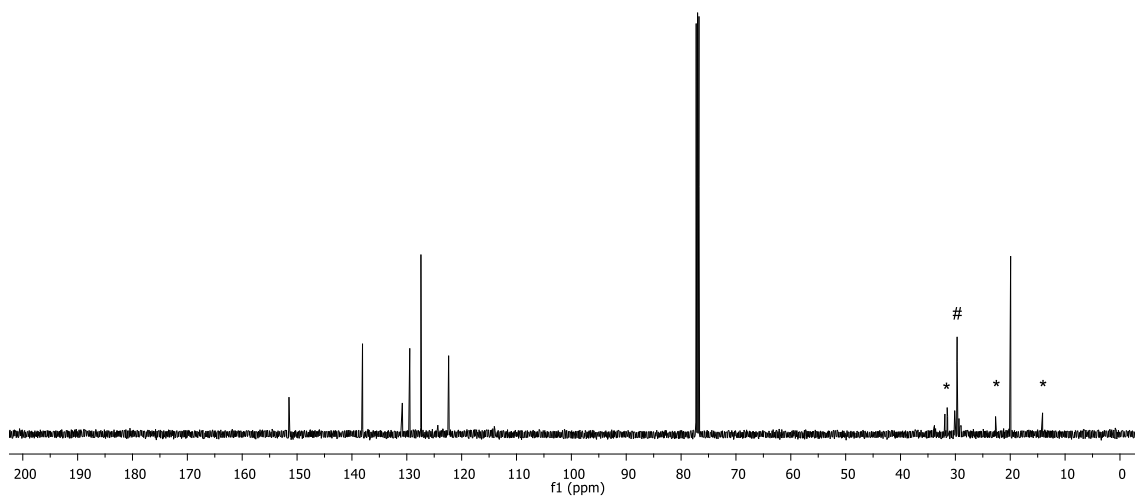
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Copies of ¹H and ¹³C NMR spectra of 2-substituted-1H-1,3- benzodiazoles

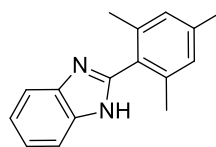




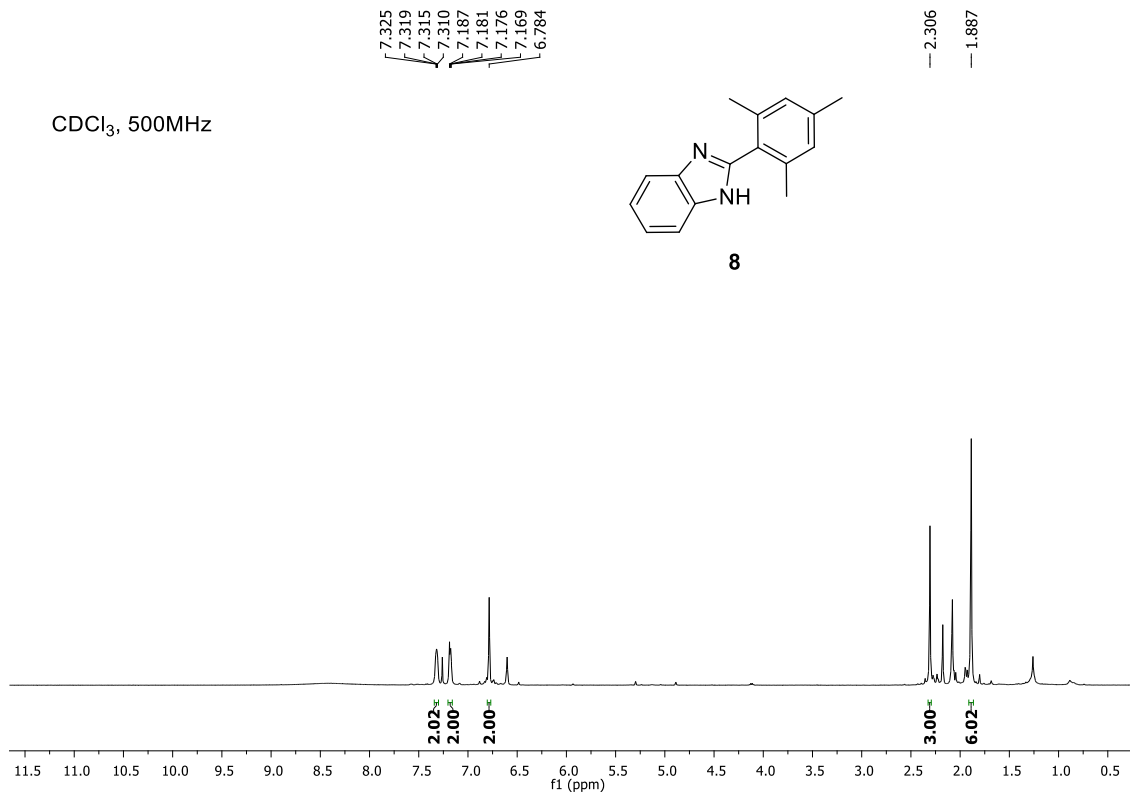
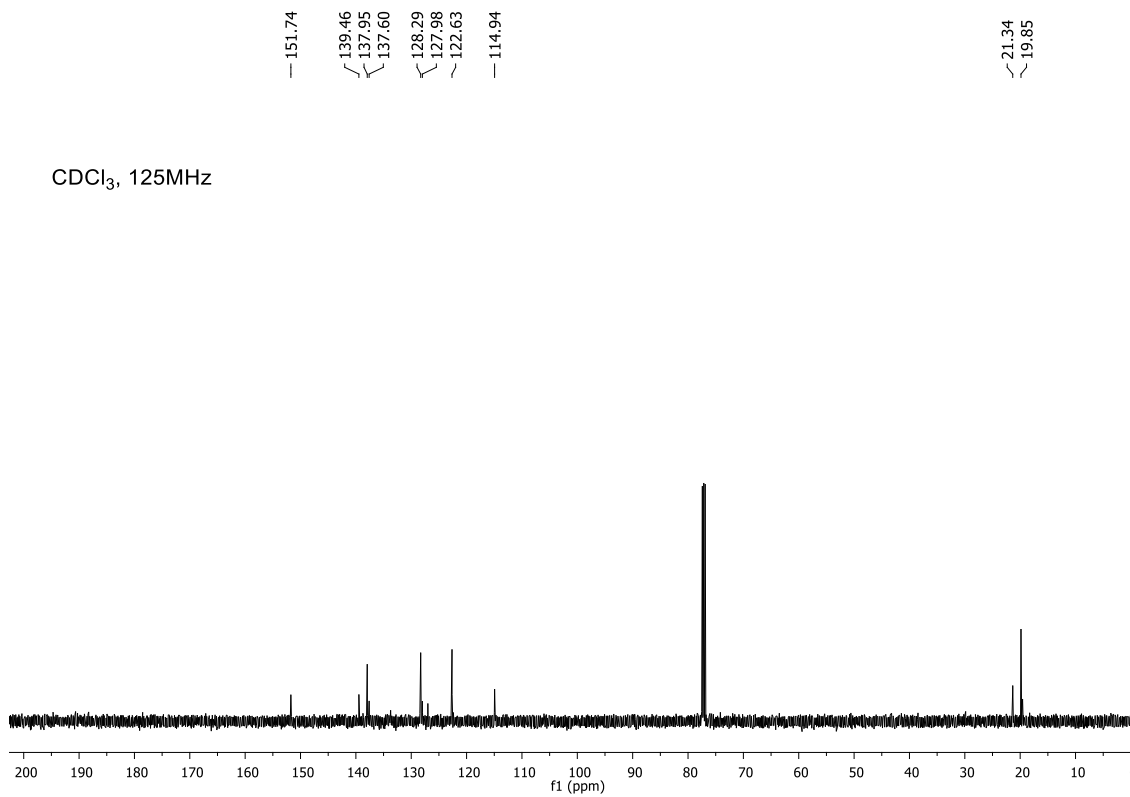
CDCl₃, 125MHz

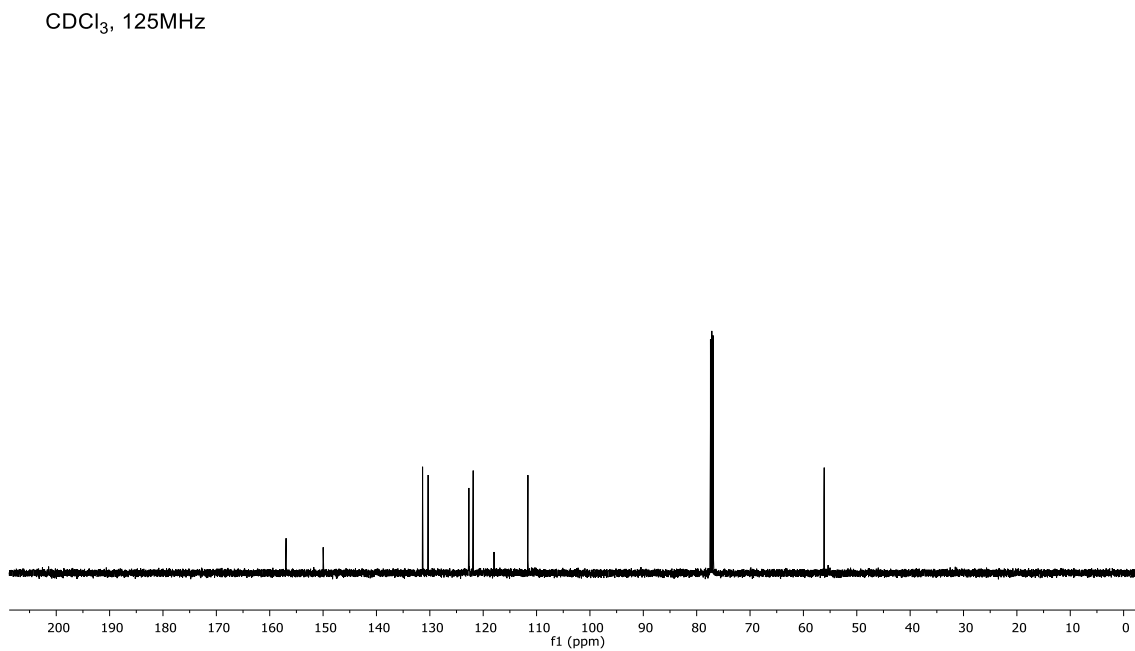
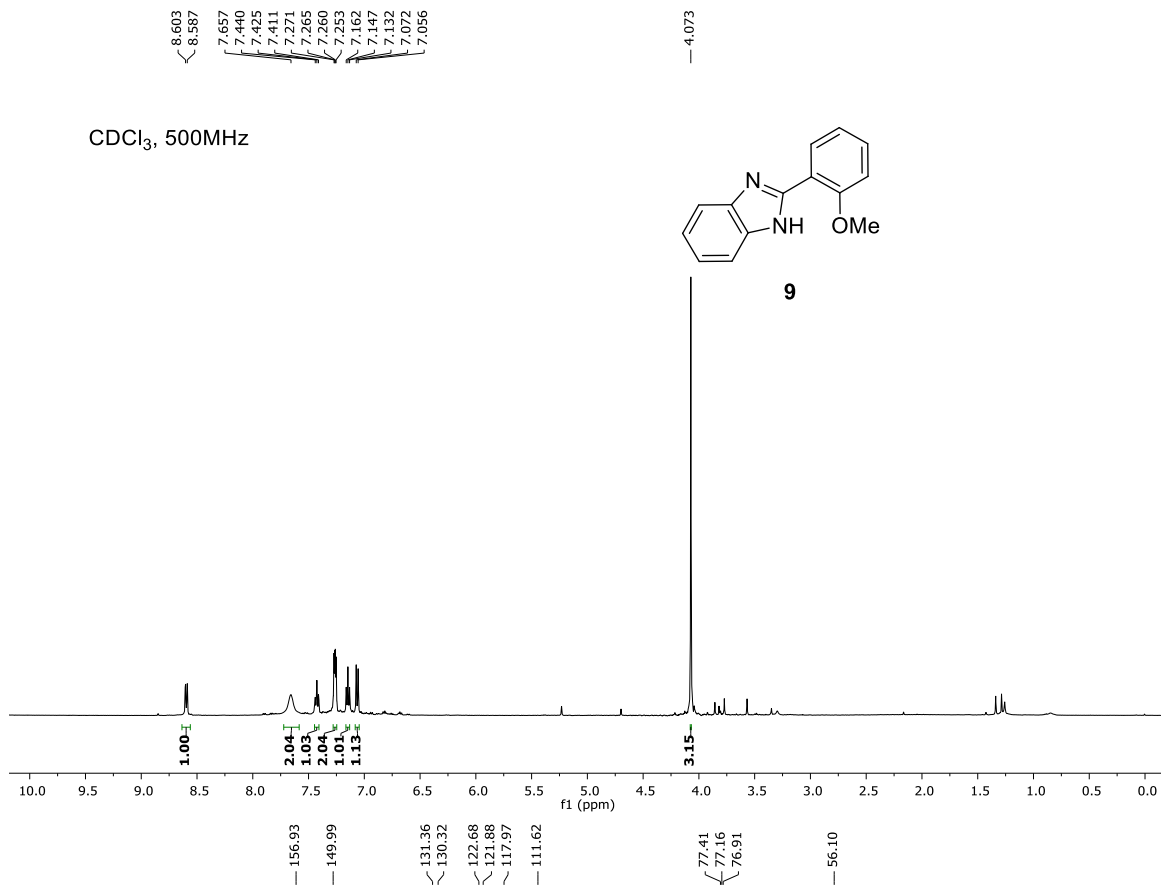


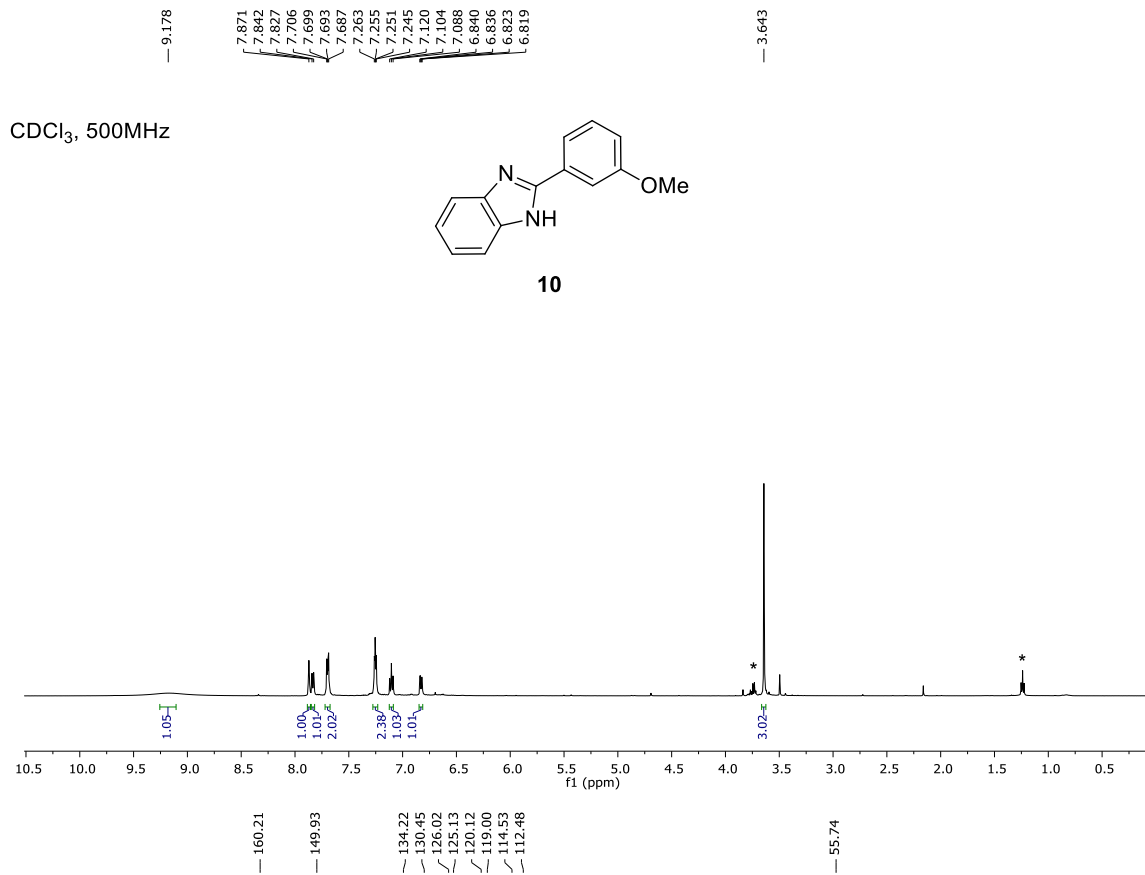
= grease, * = Hexane

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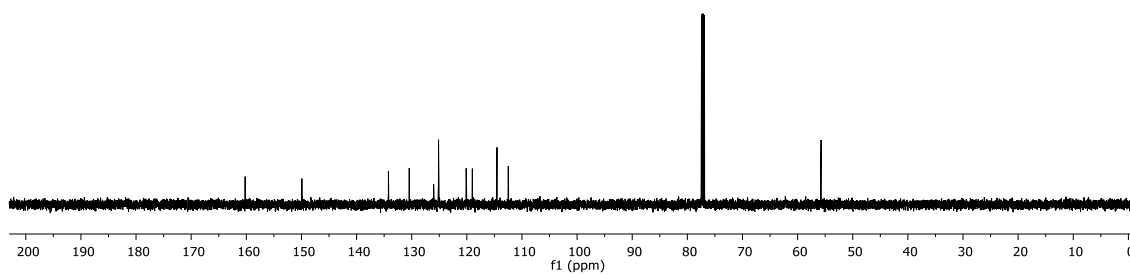
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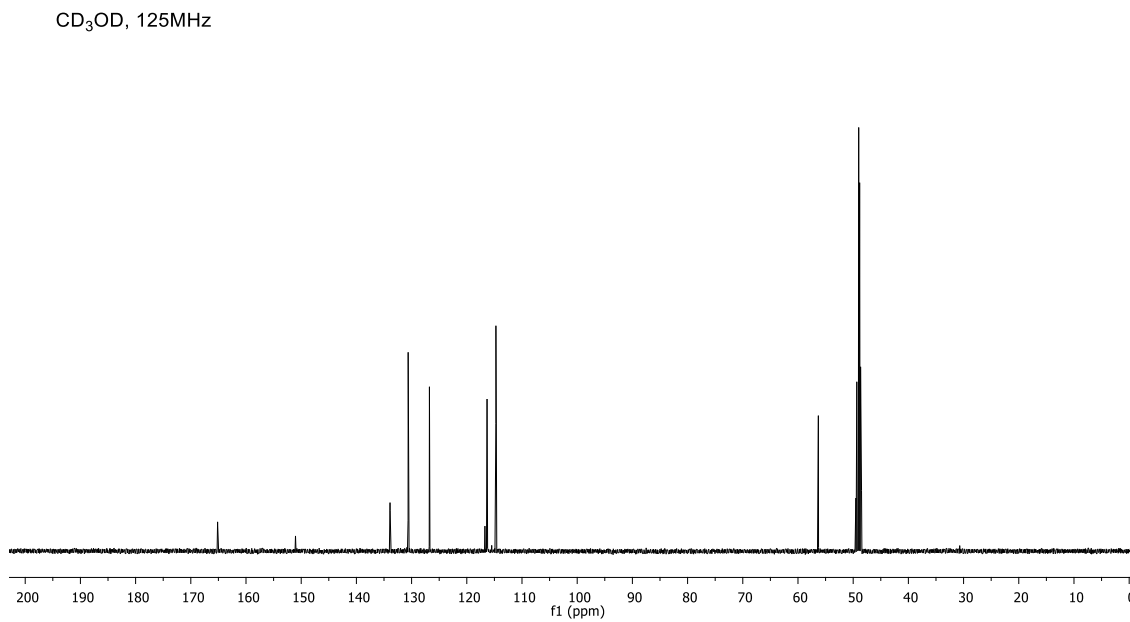
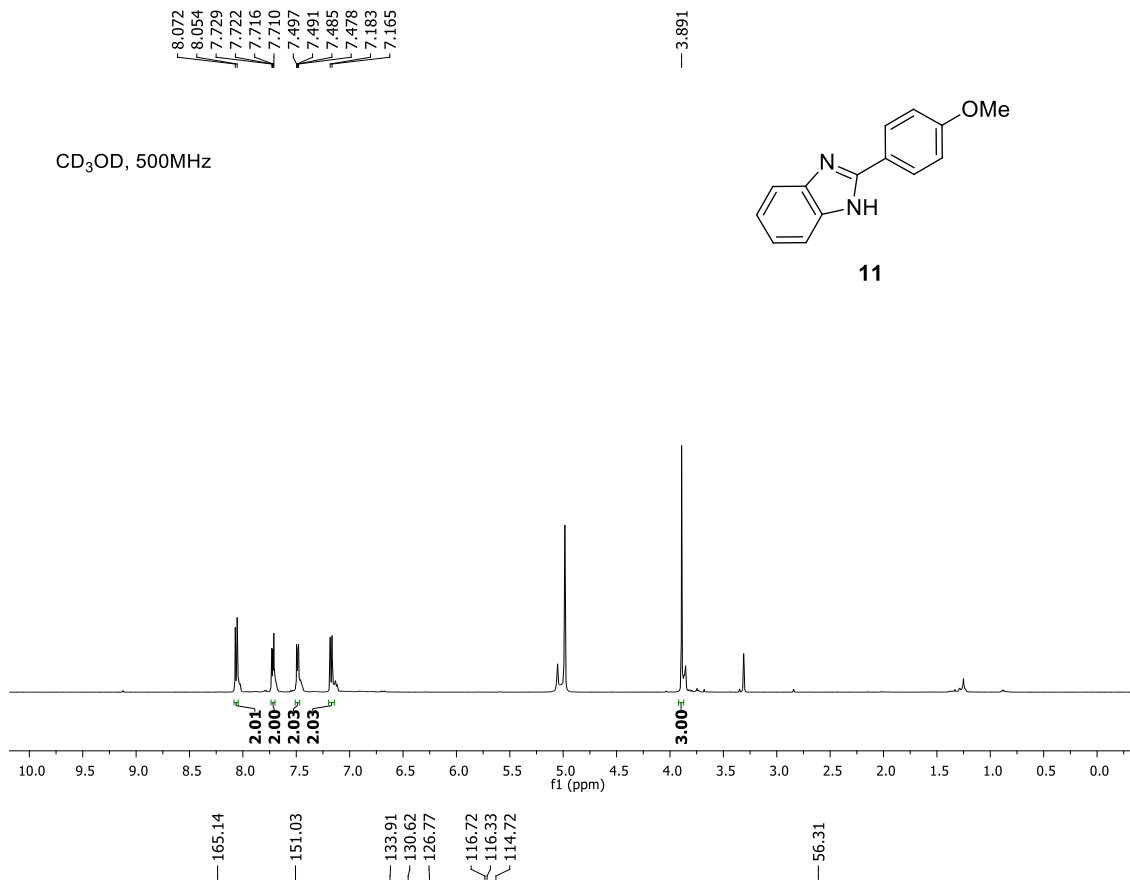


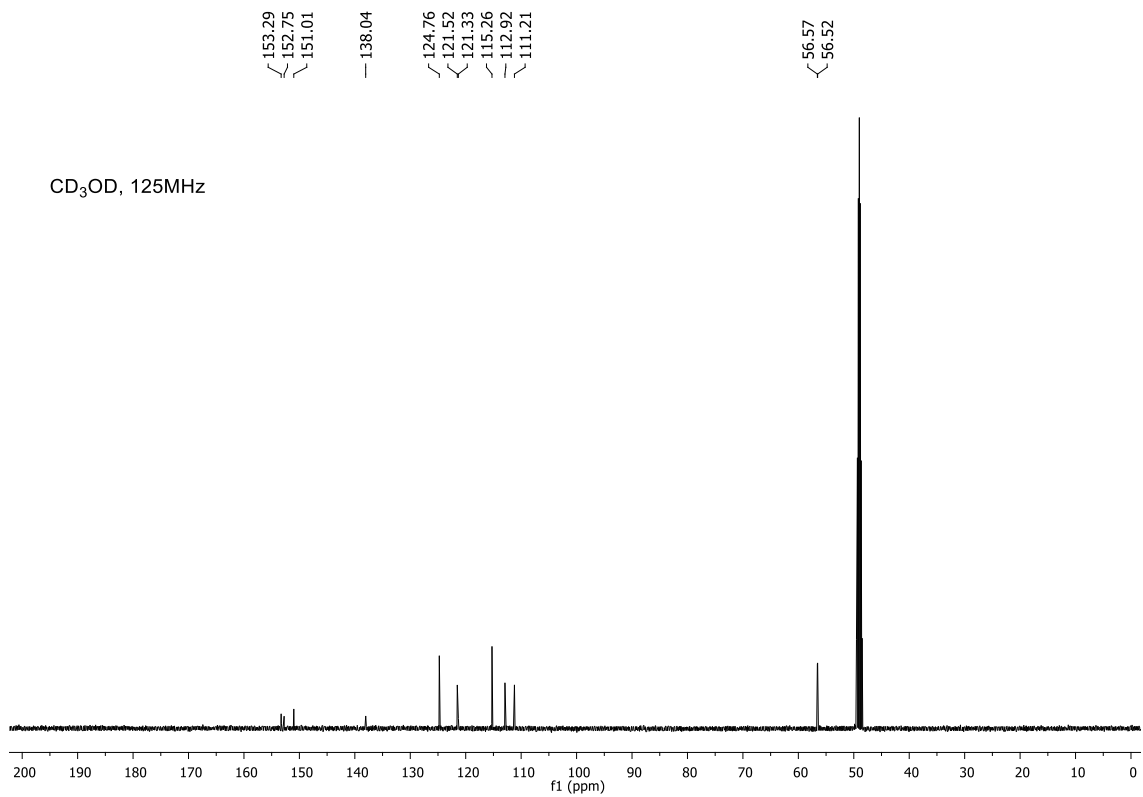
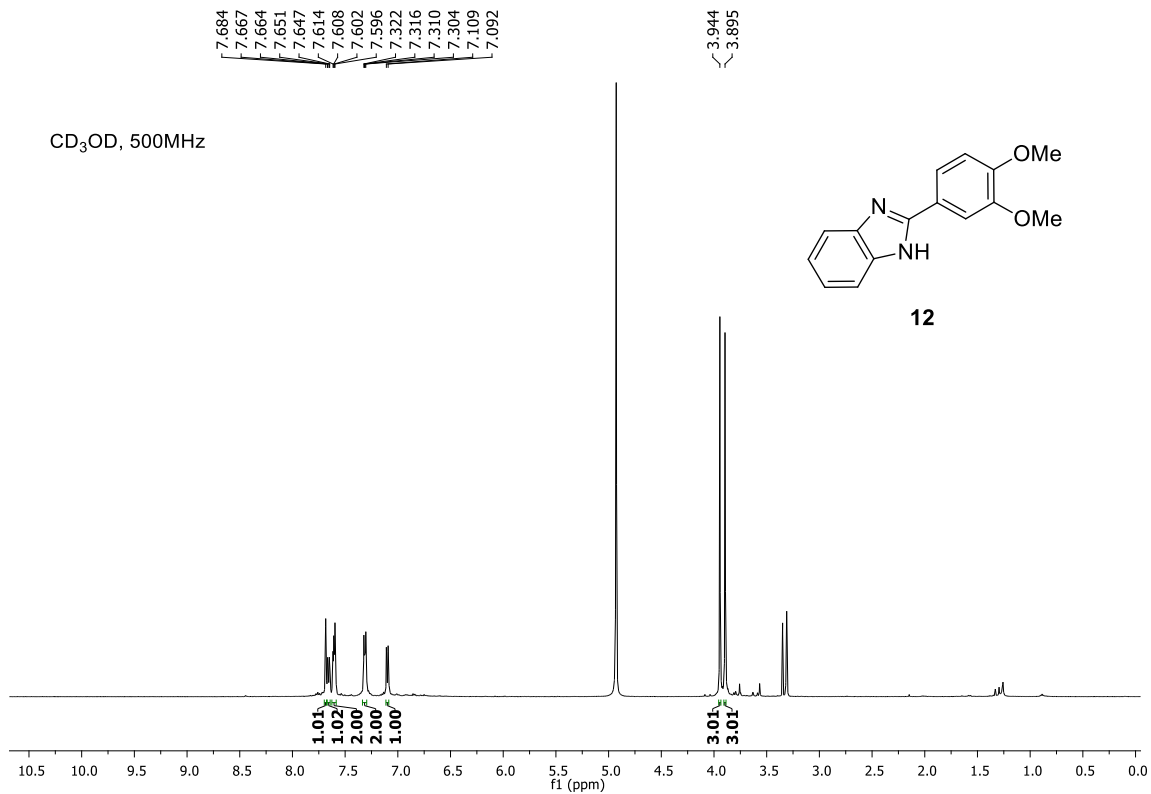


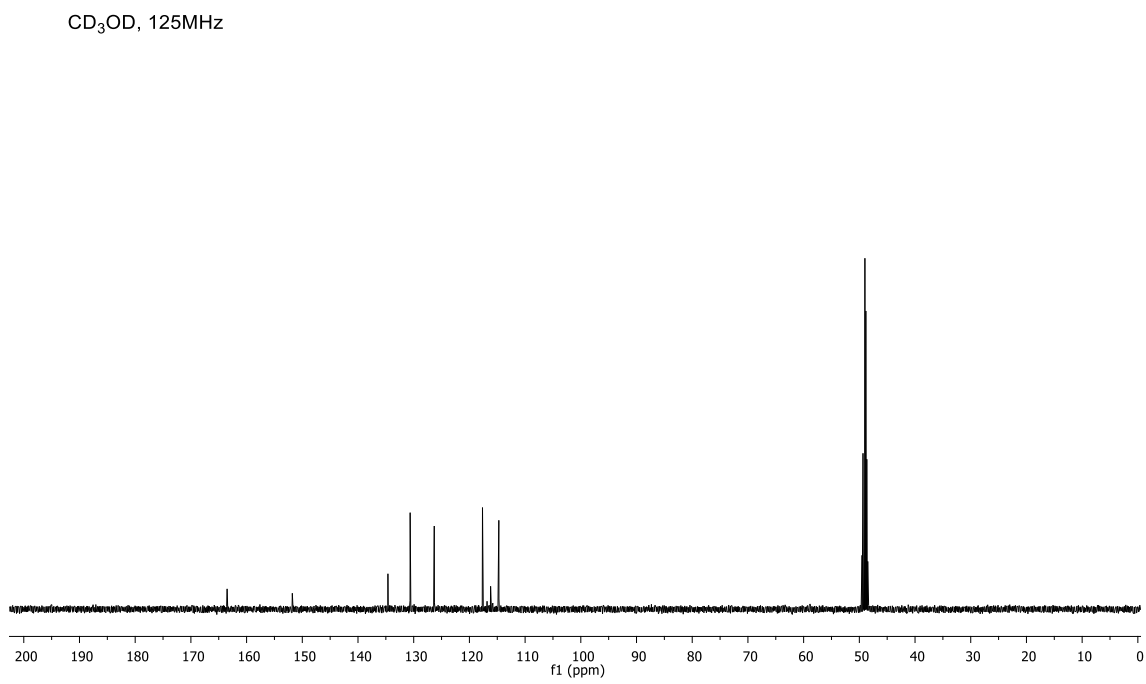
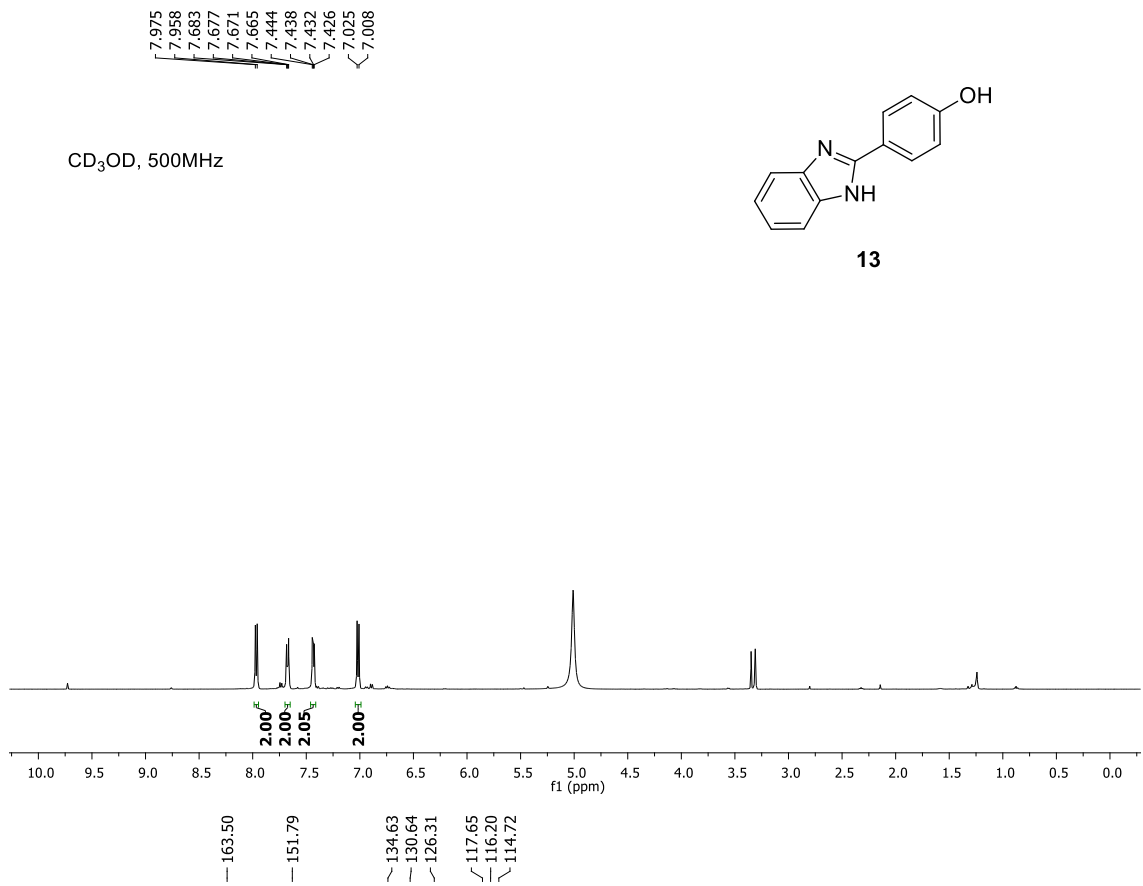
CDCl₃, 125MHz



* = Ethanol

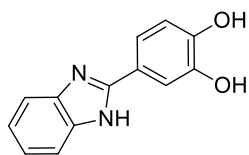




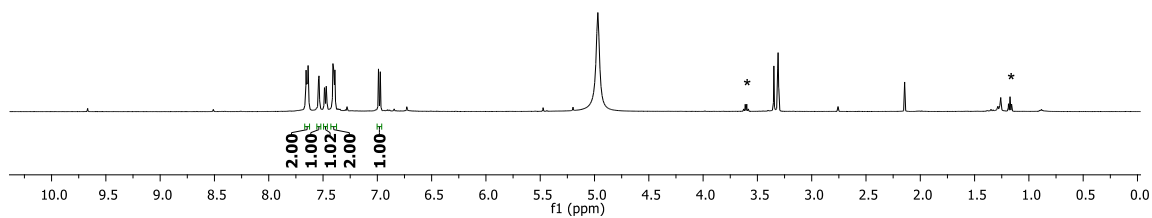


7.656
7.650
7.644
7.638
7.540
7.537
7.487
7.483
7.470
7.467
7.409
7.403
7.397
7.391
6.989
6.973

CD₃OD, 500MHz

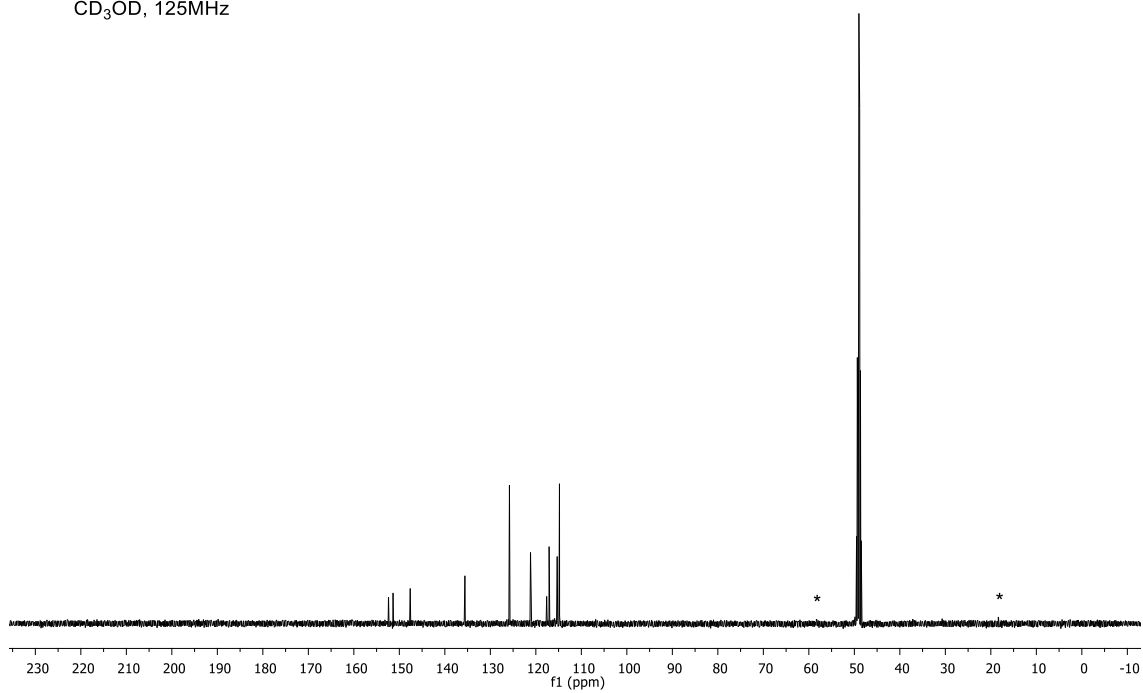


14

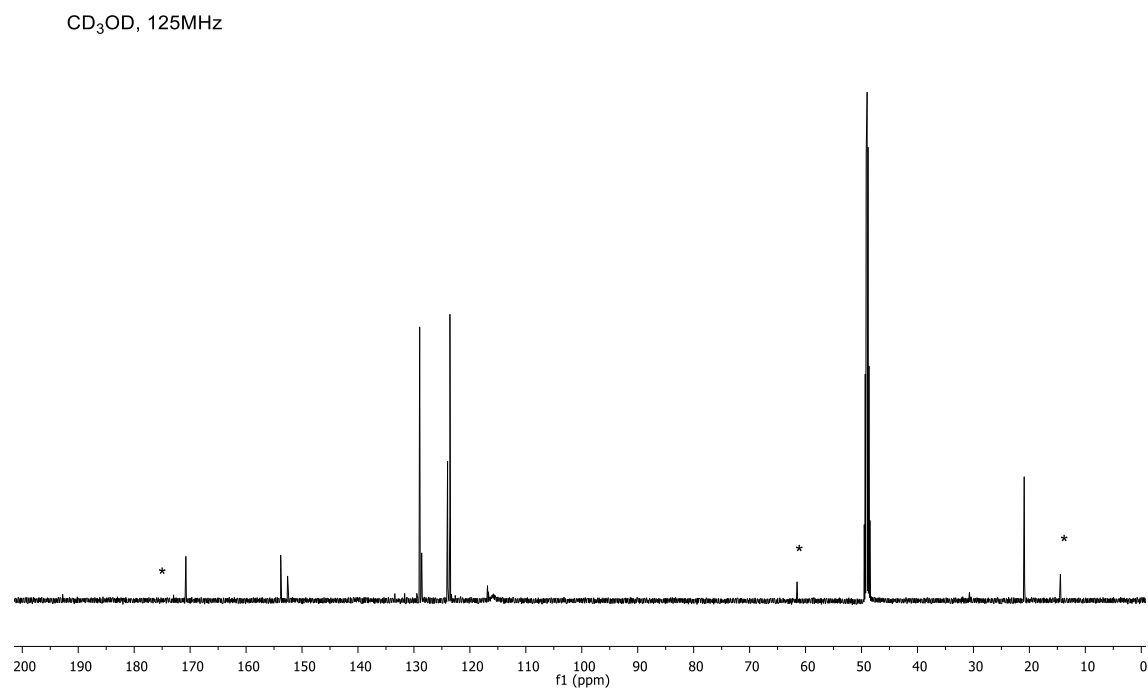
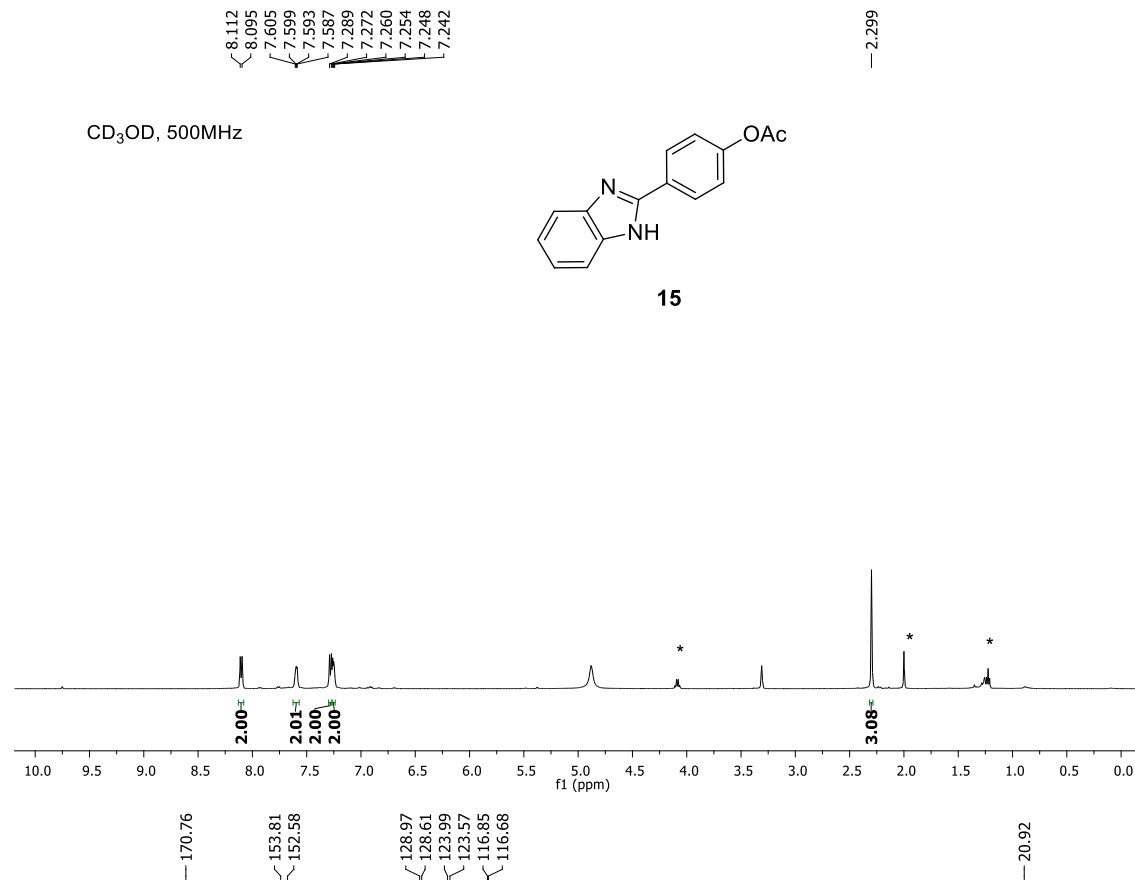


152.38
151.38
147.61
135.59
125.80
121.17
117.62
117.08
115.31
114.80

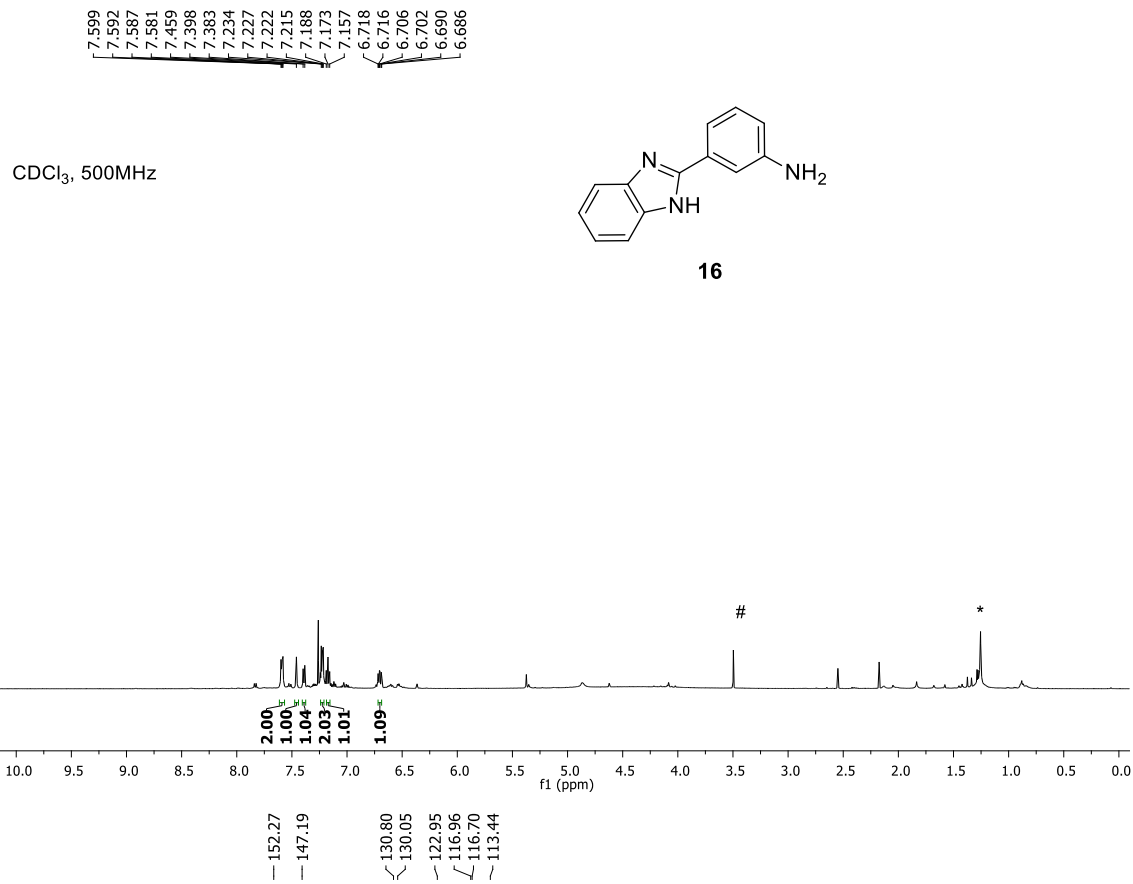
CD₃OD, 125MHz



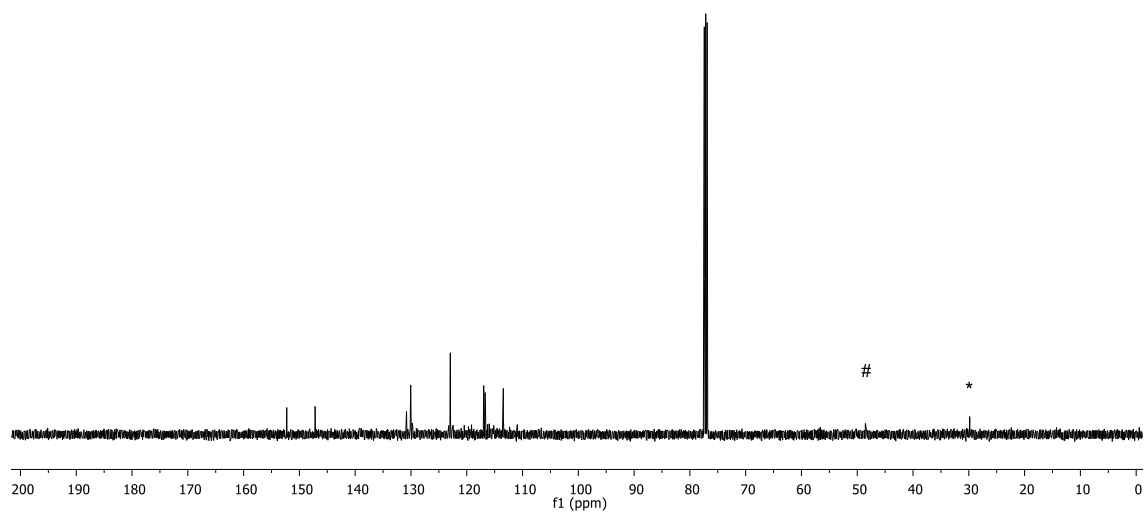
* = ethanol



* = ethyl acetate

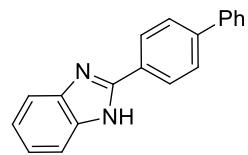


CDCl₃, 125MHz

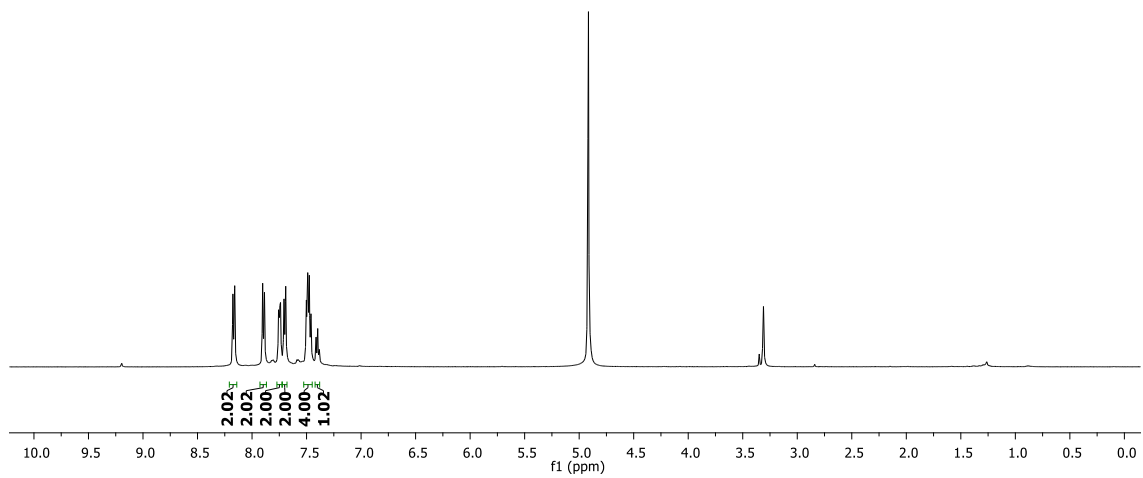


* = grease, # = methanol

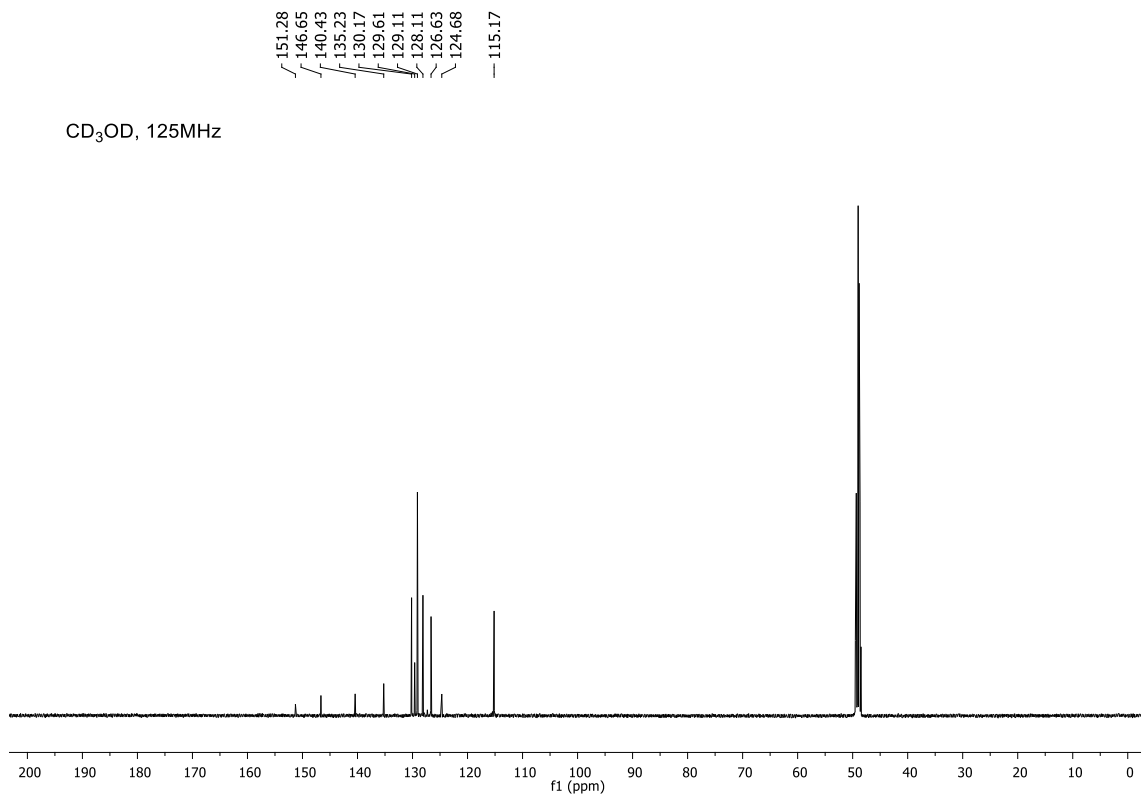
CD₃OD, 500MHz

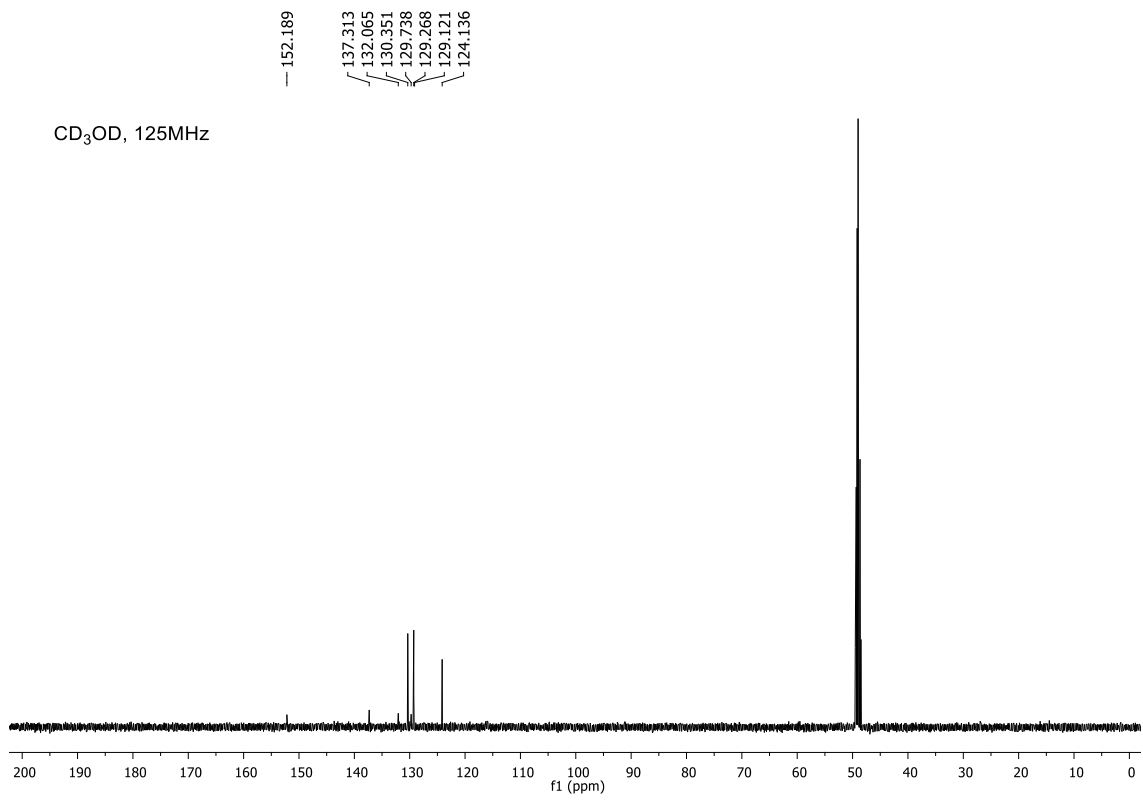
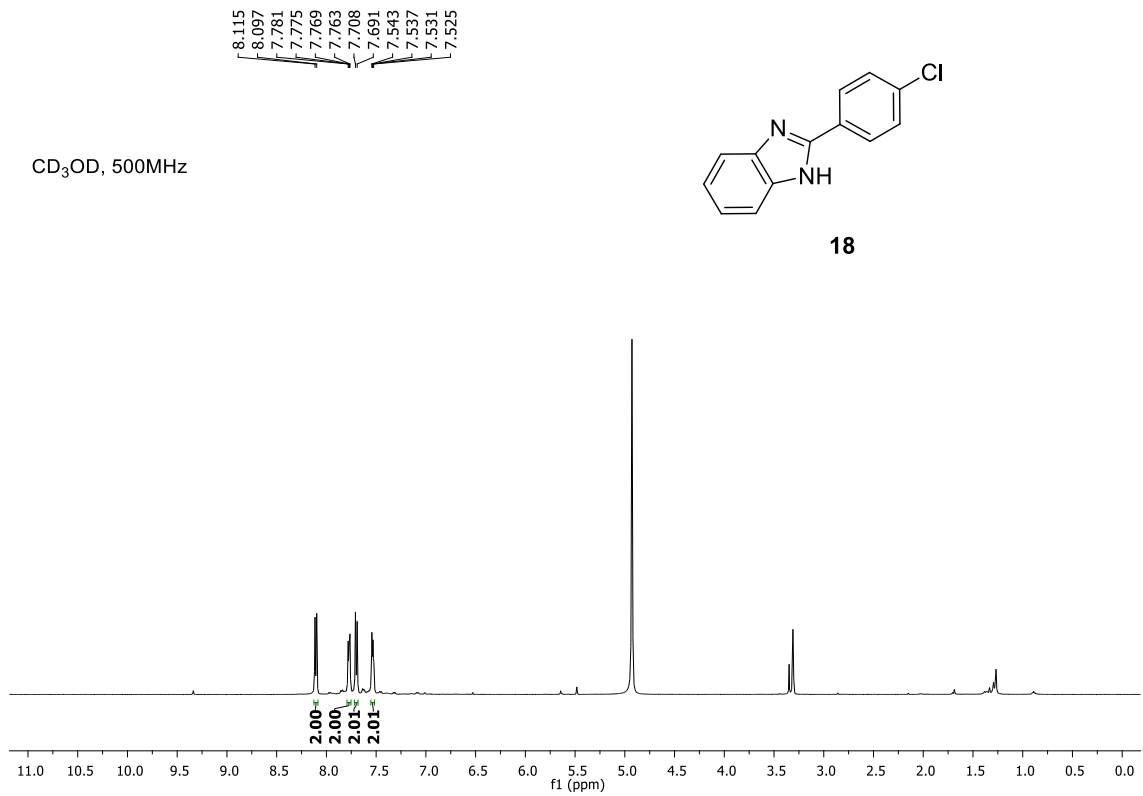


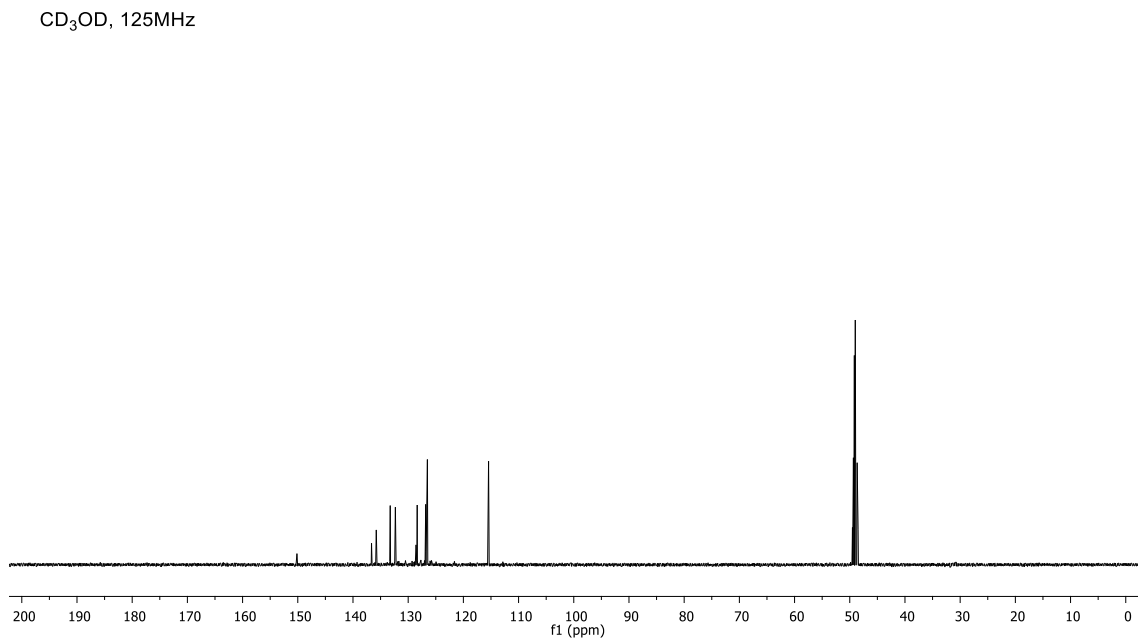
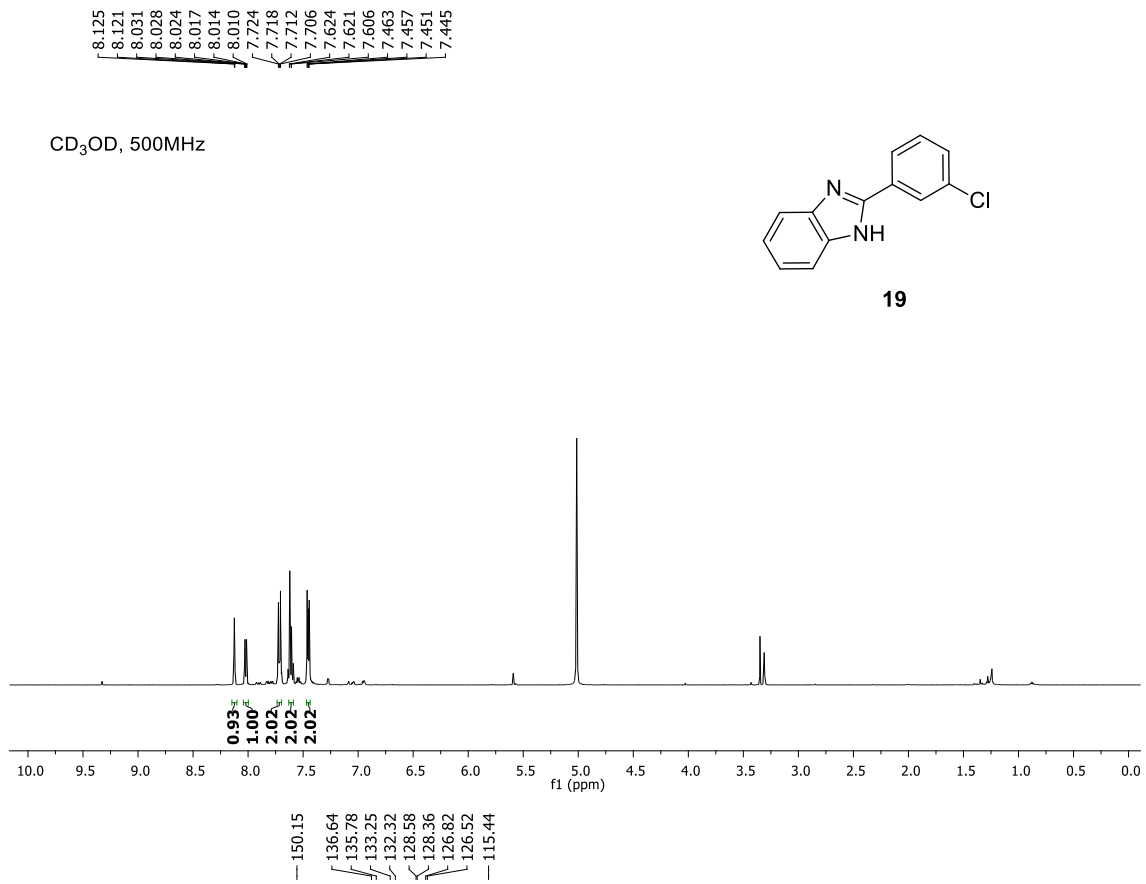
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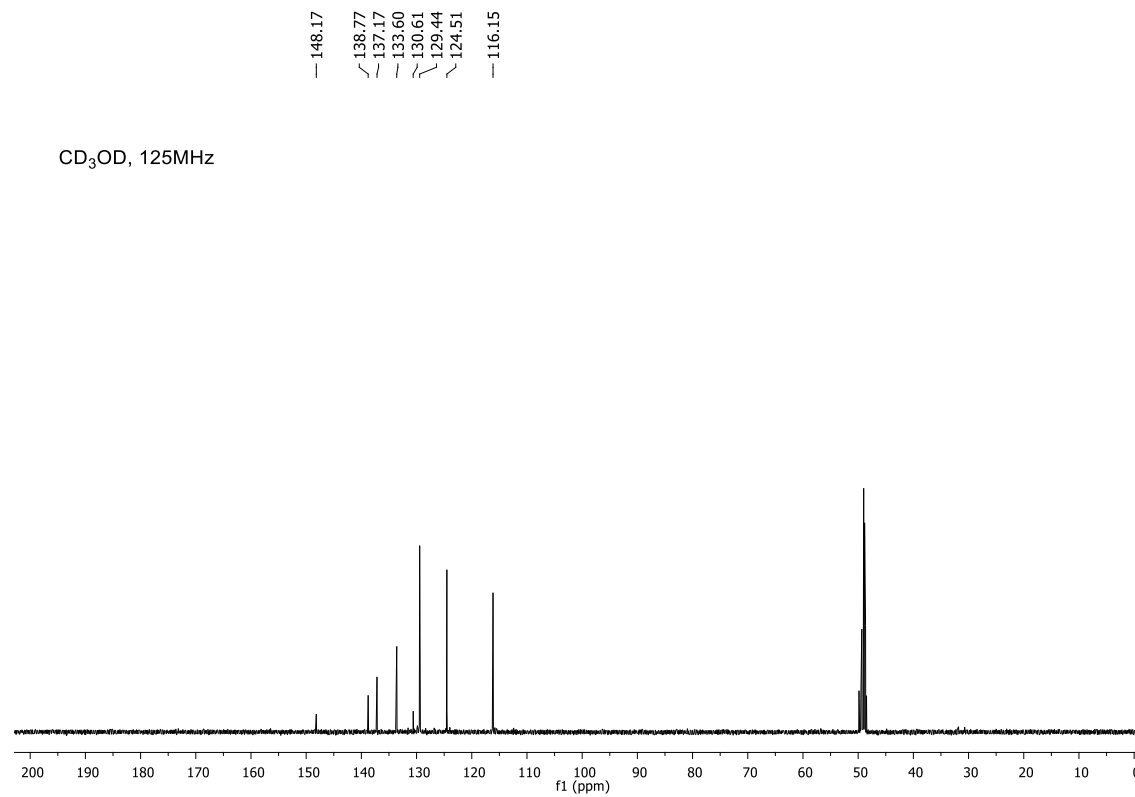
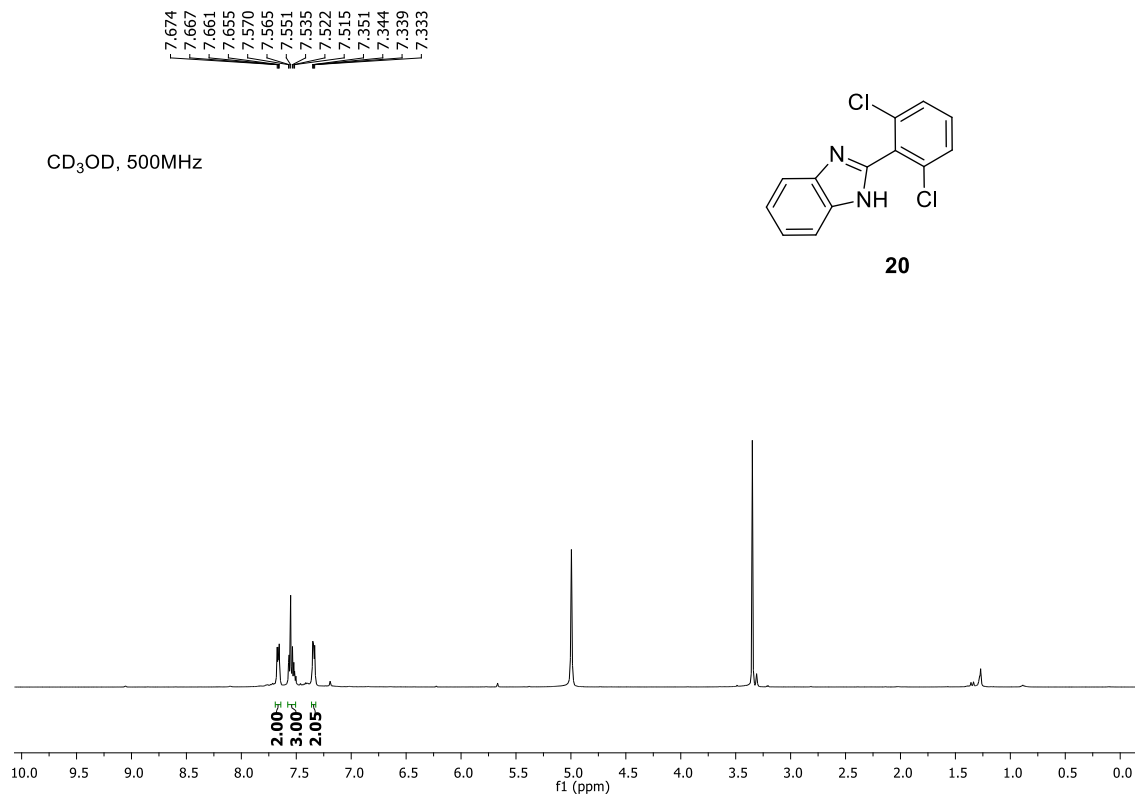


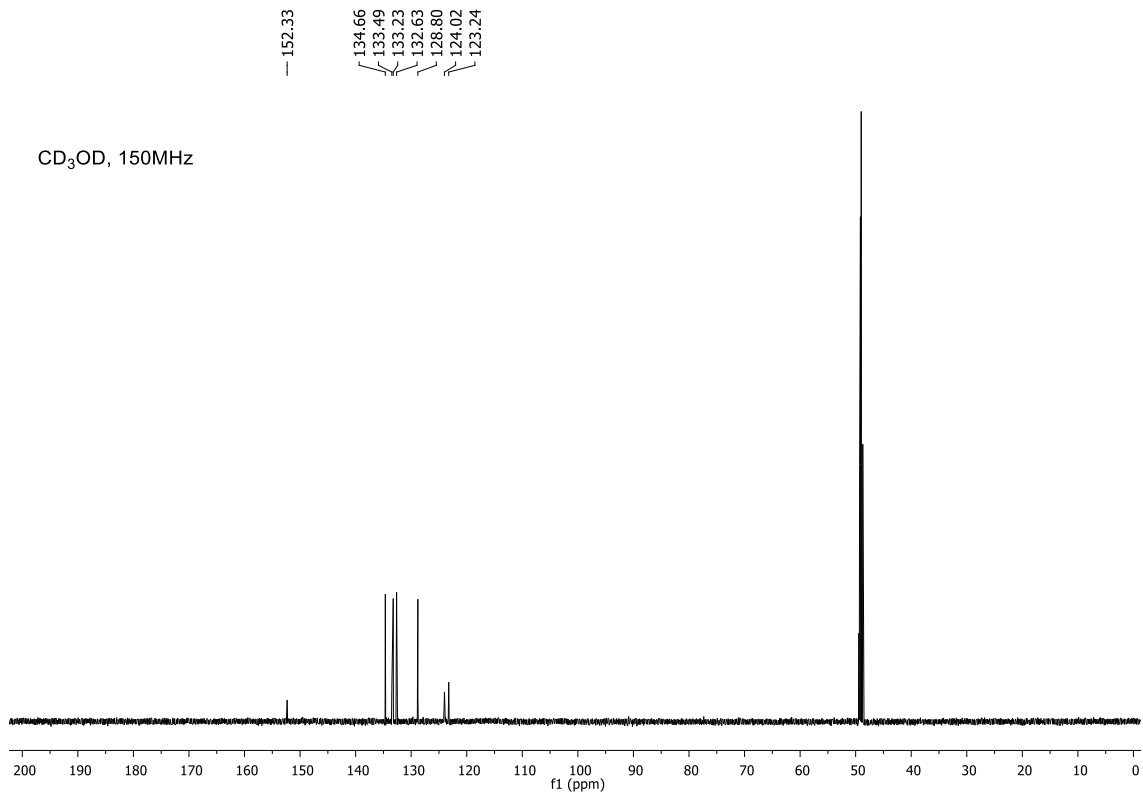
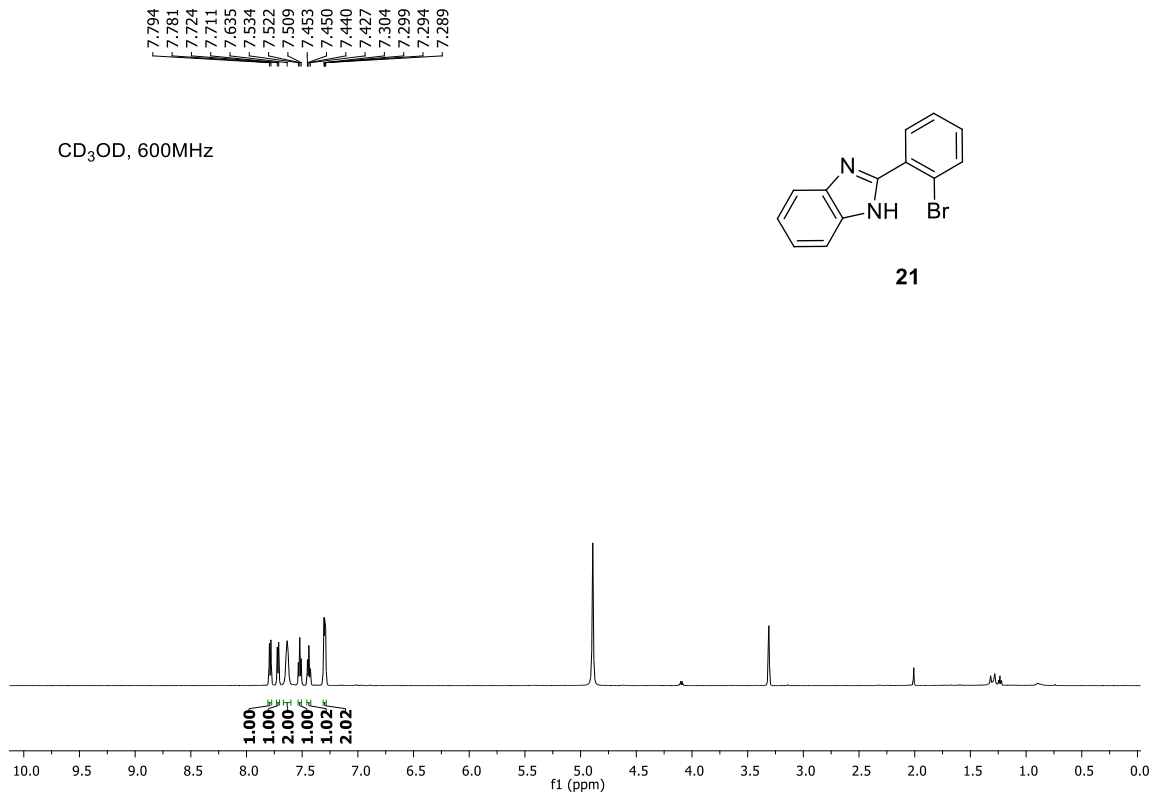
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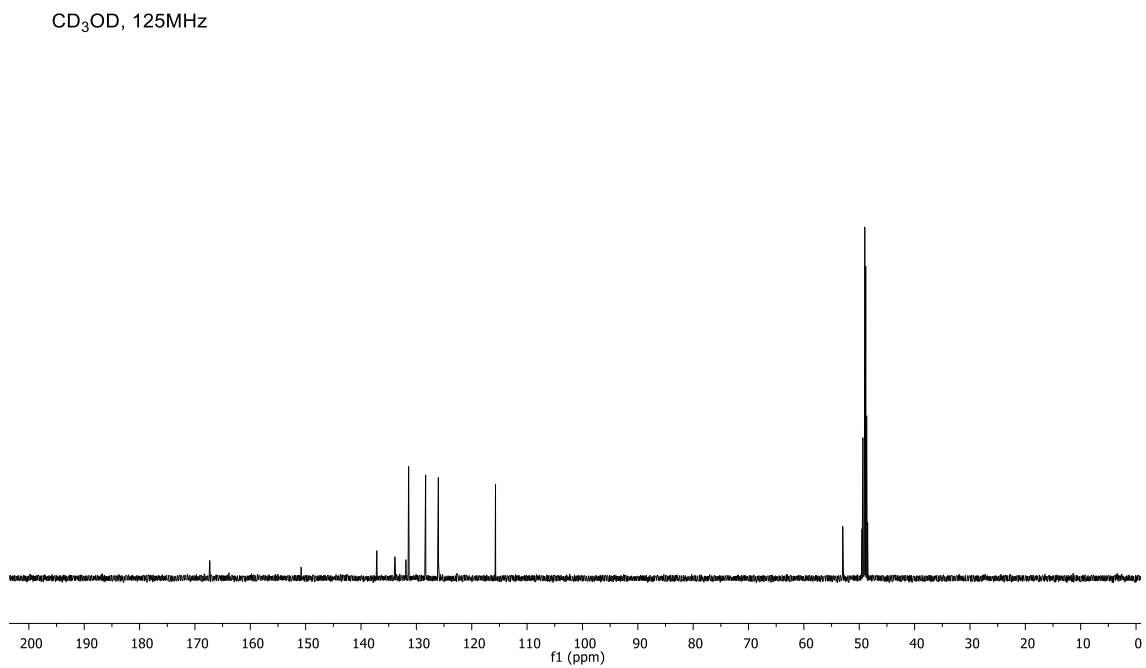
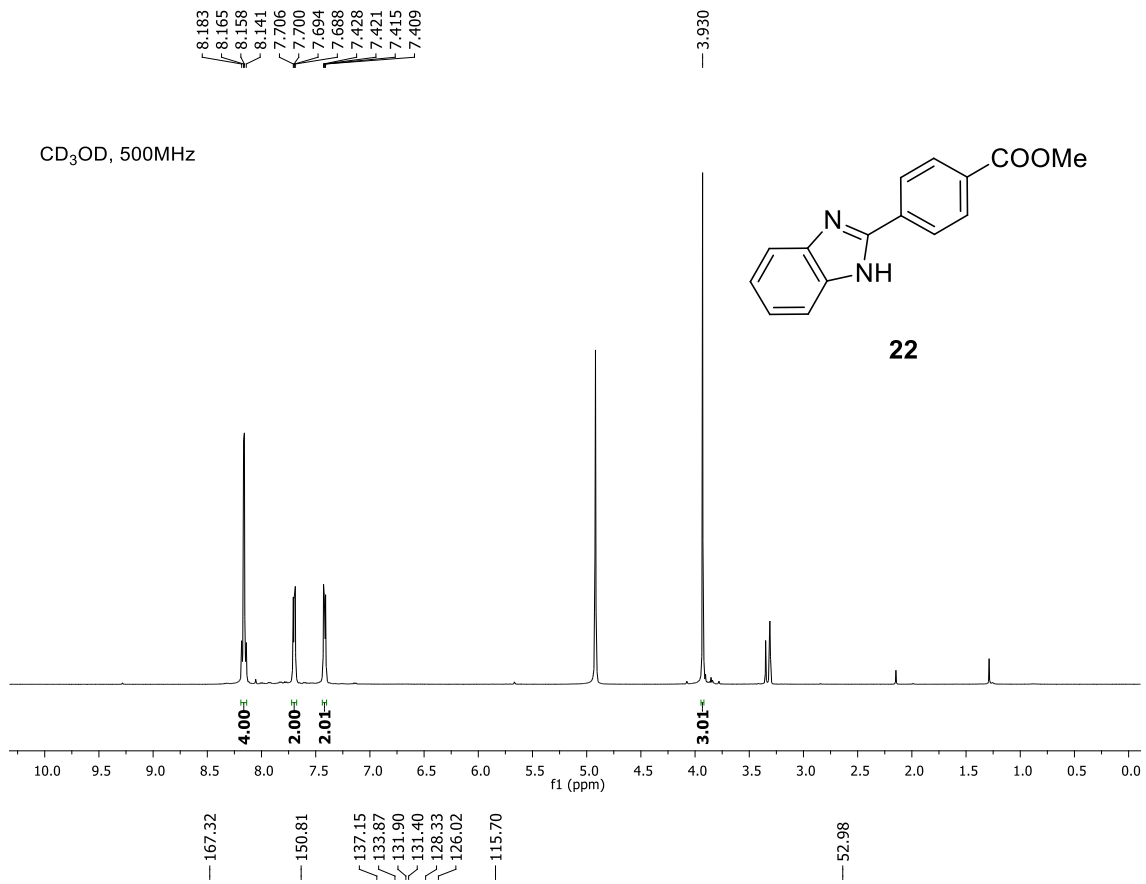


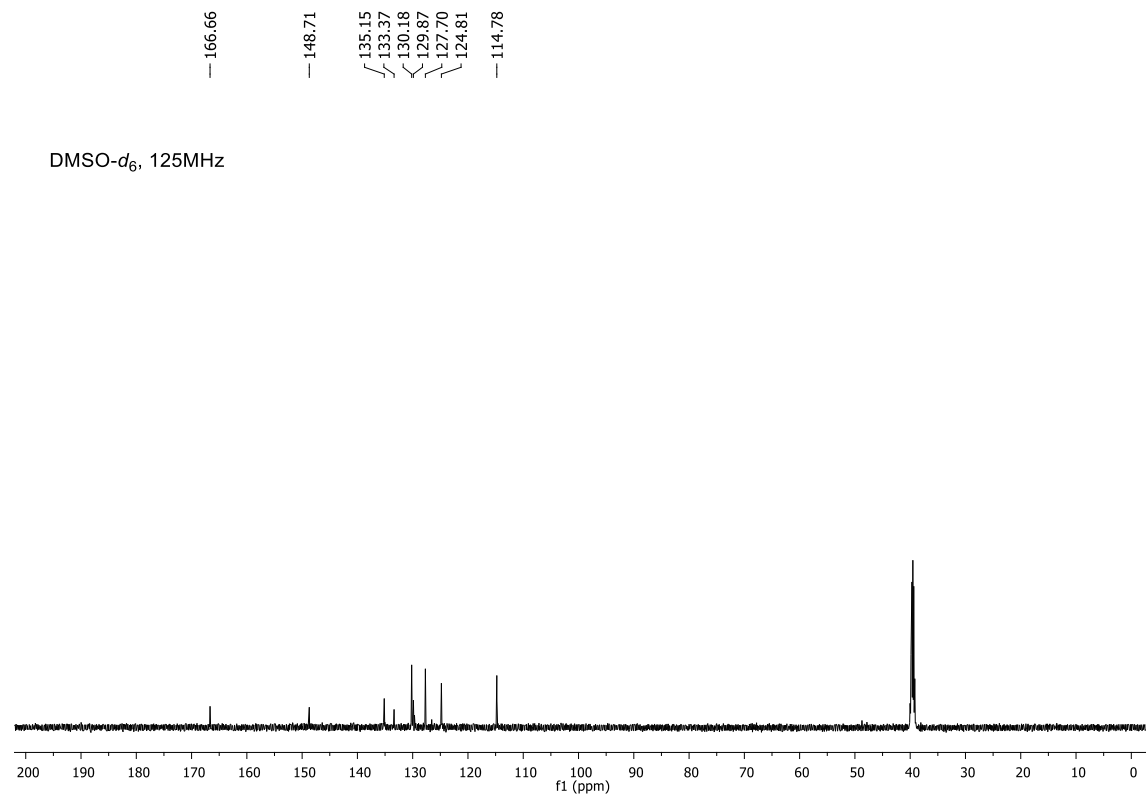
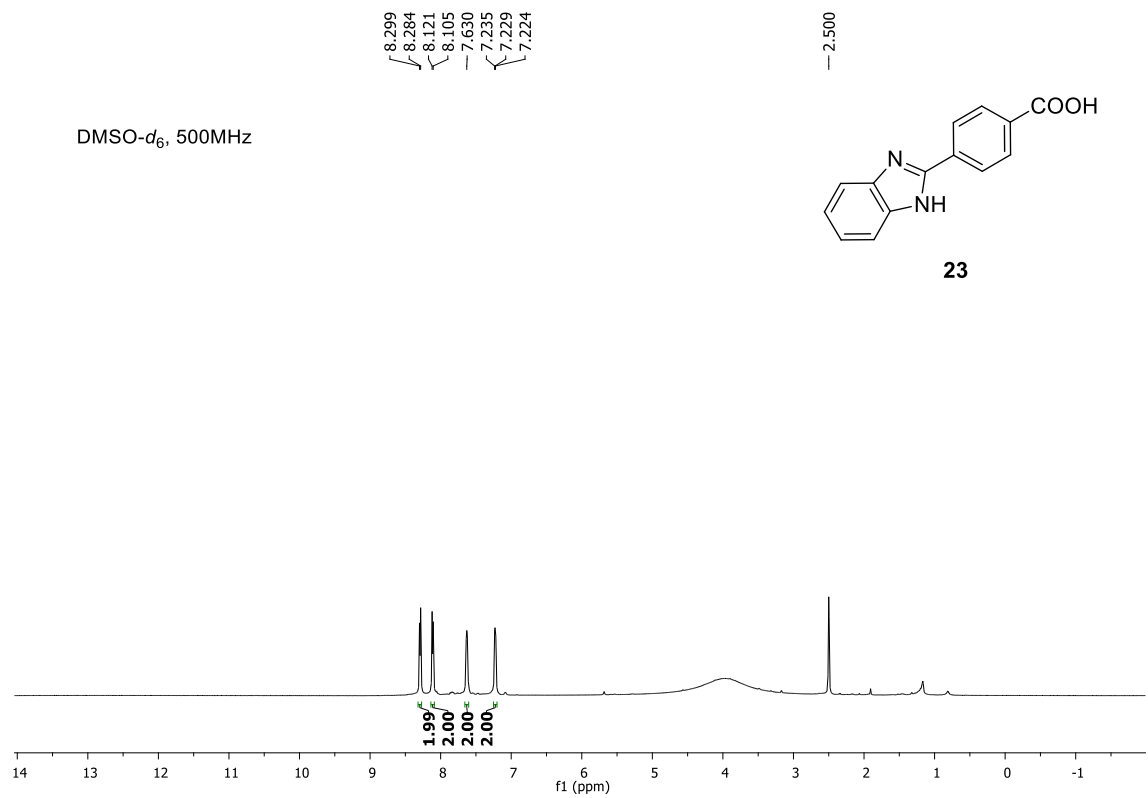


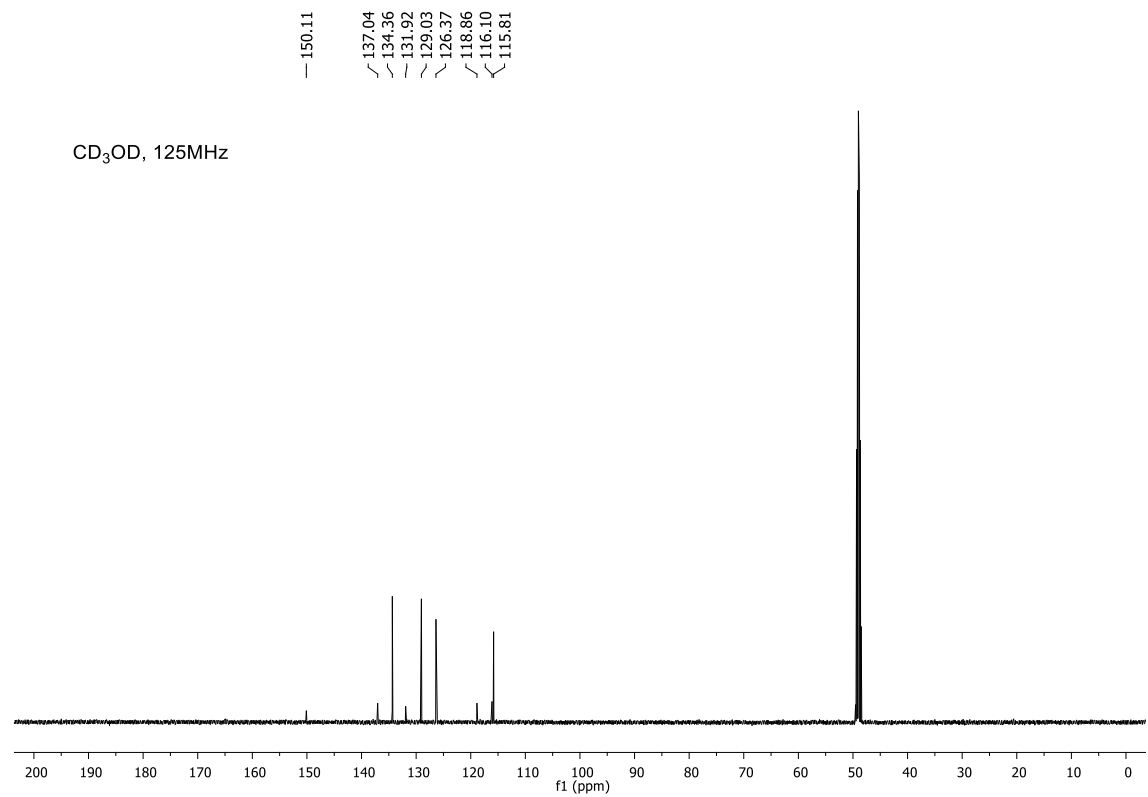
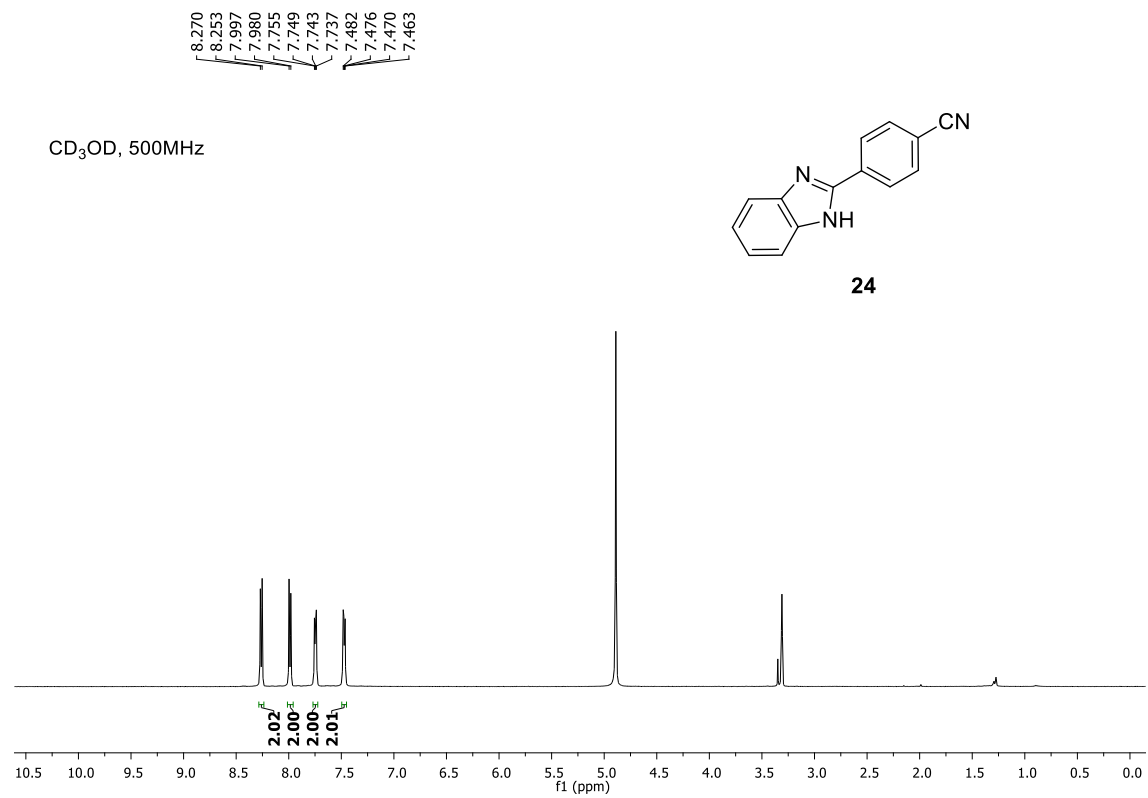


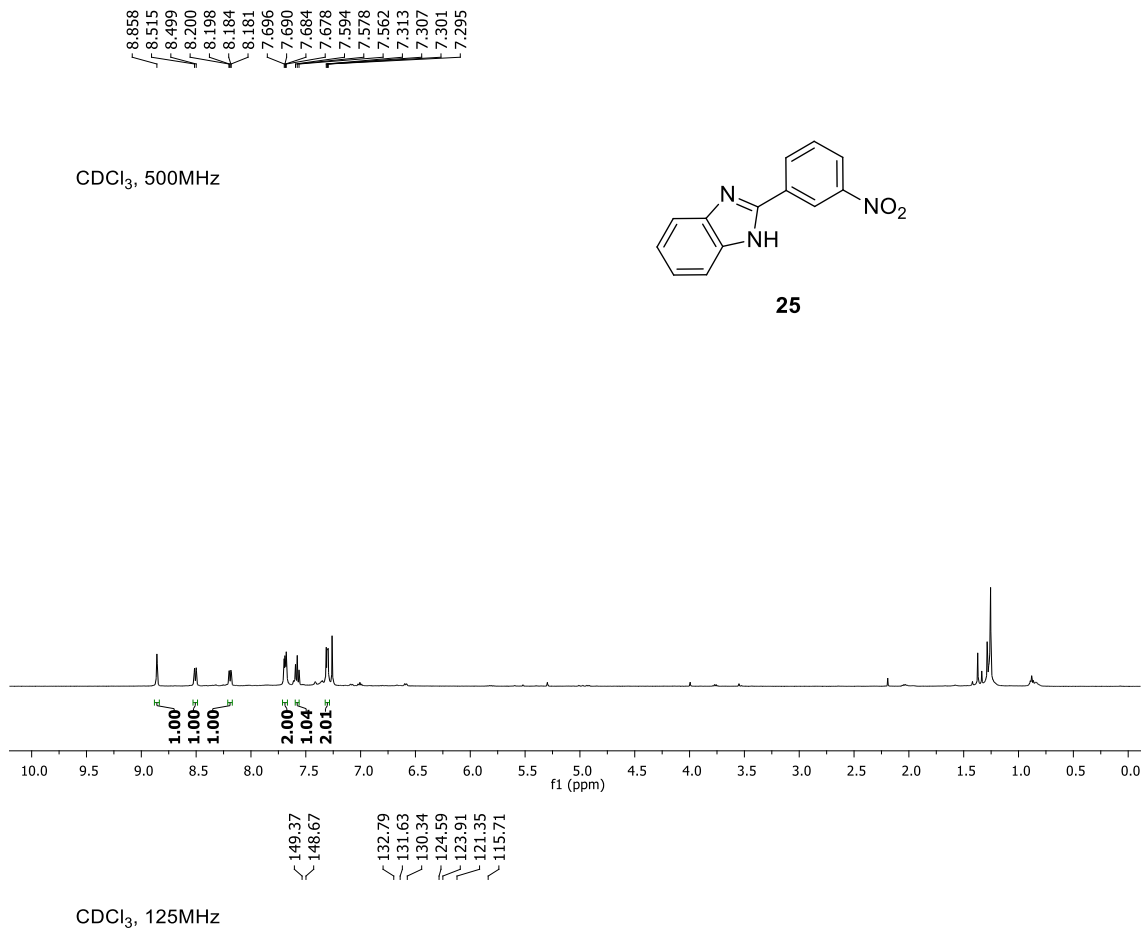




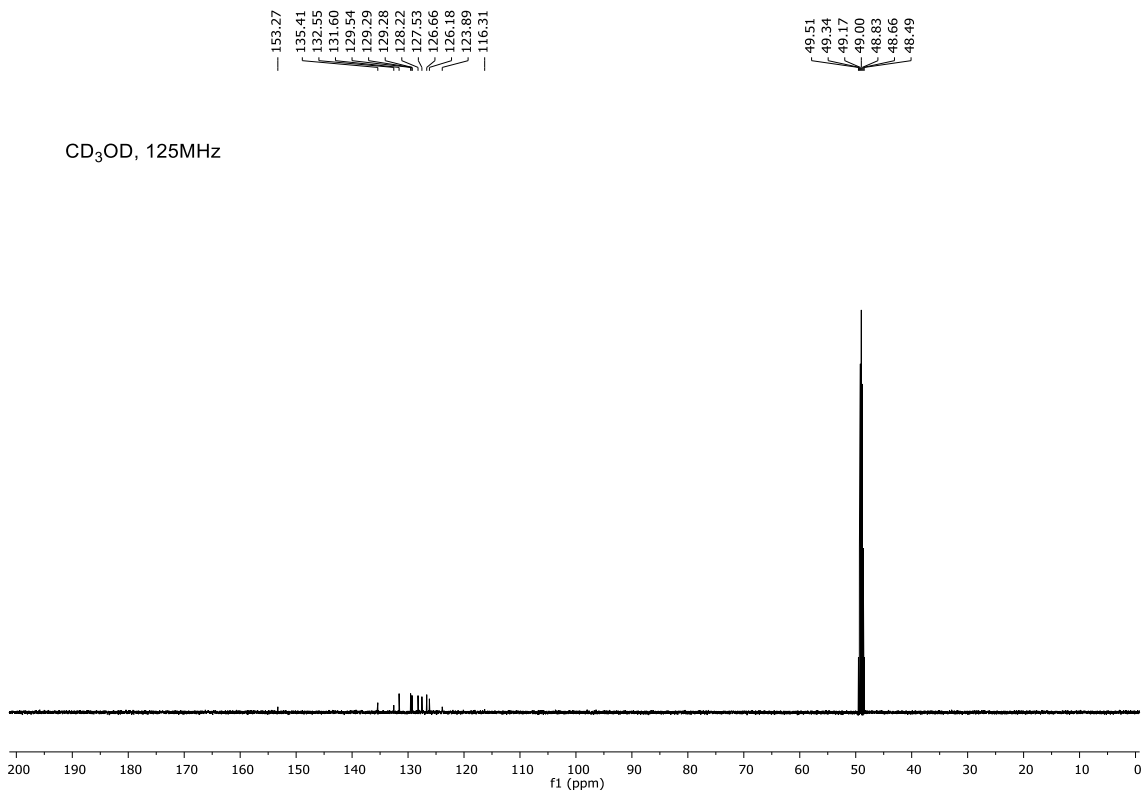
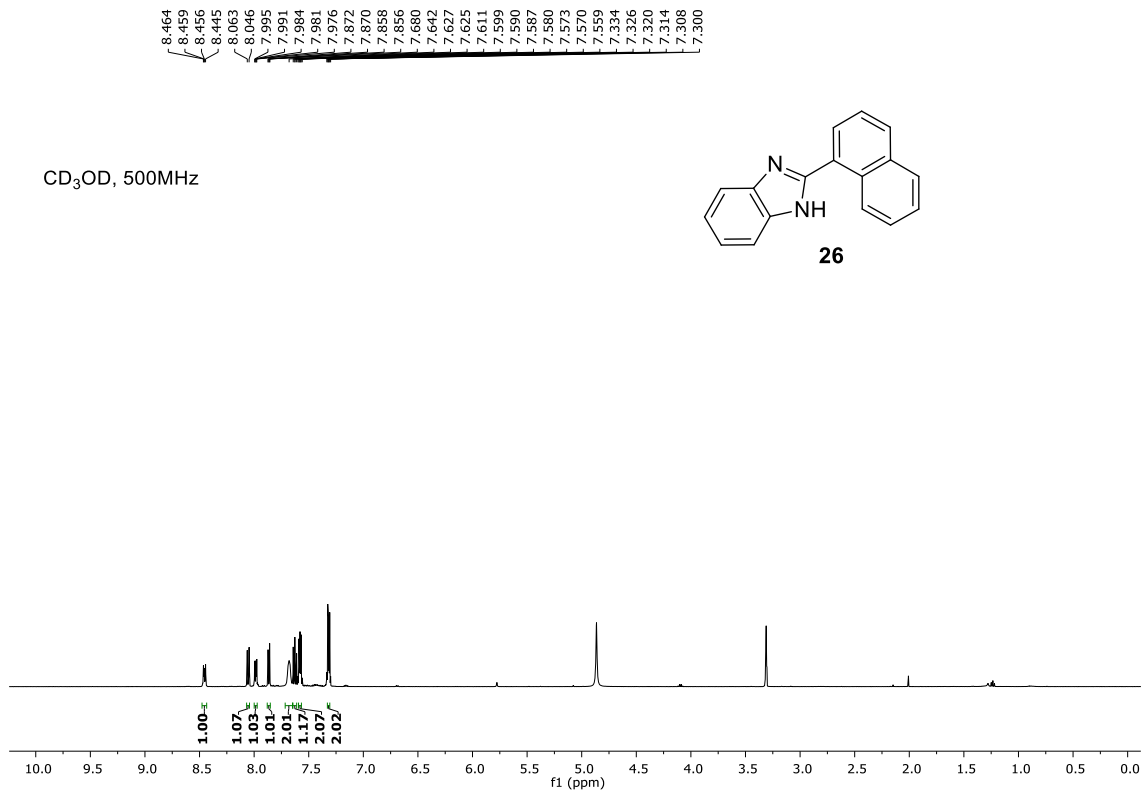


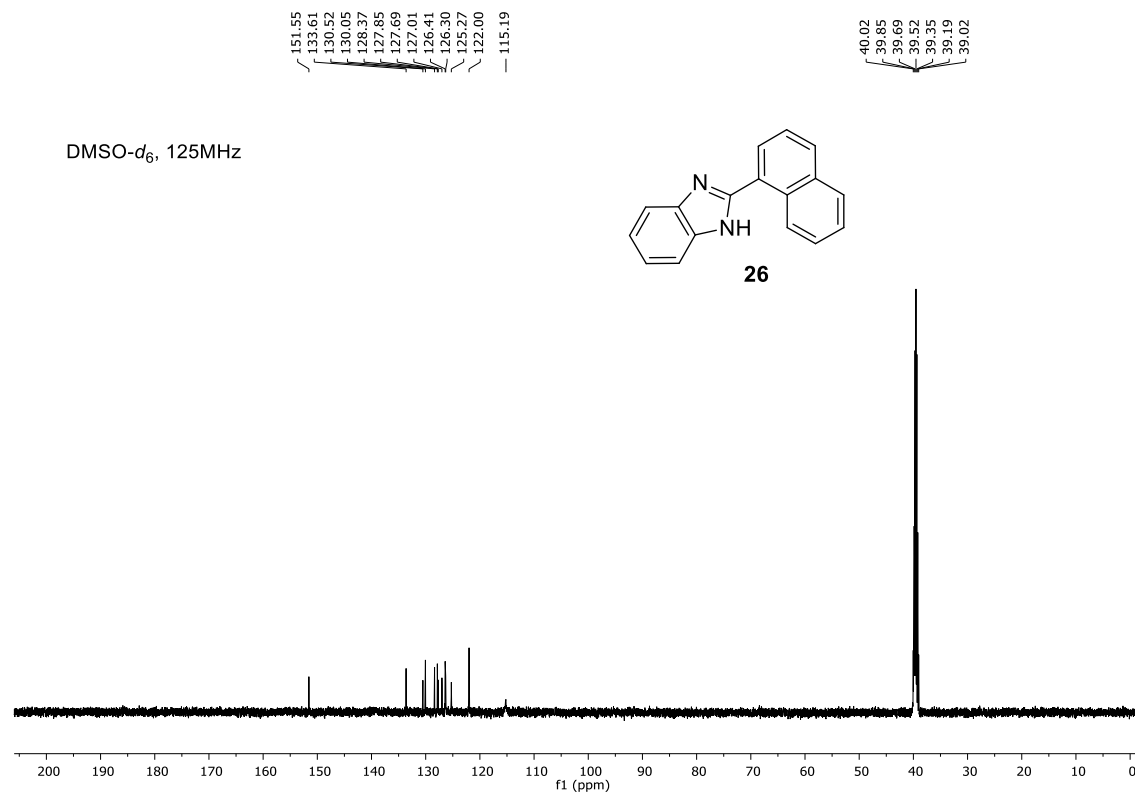
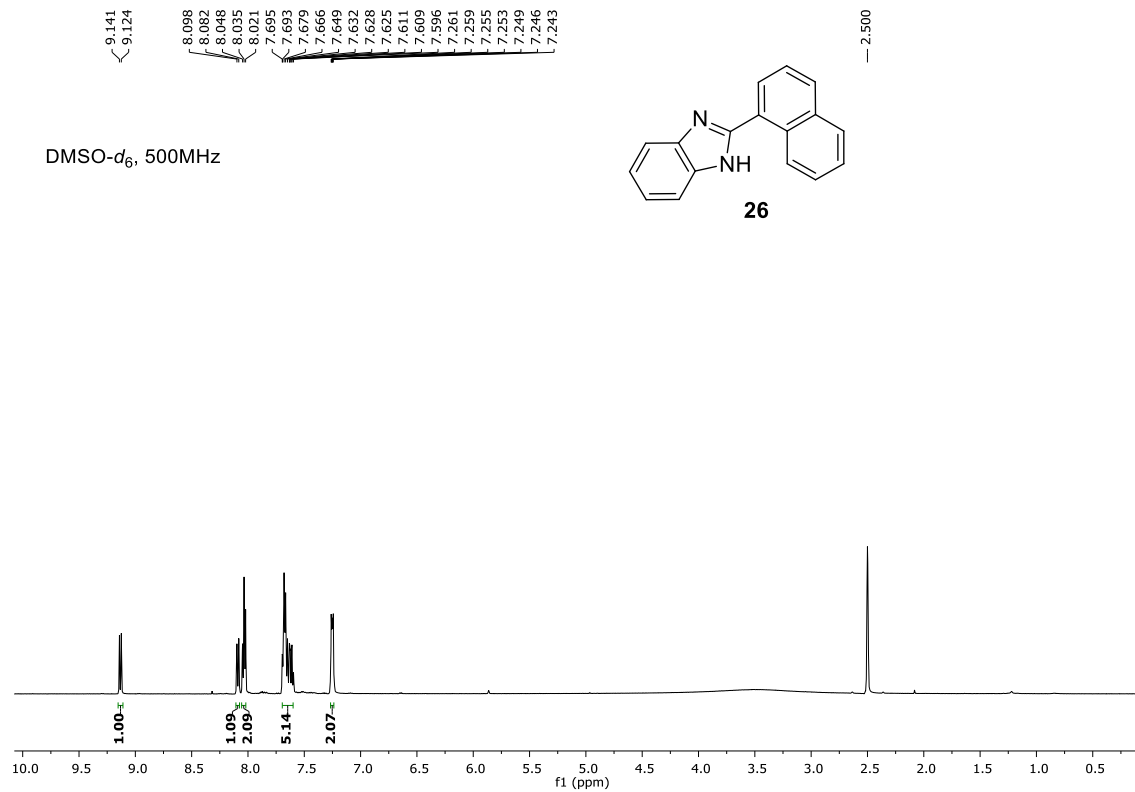


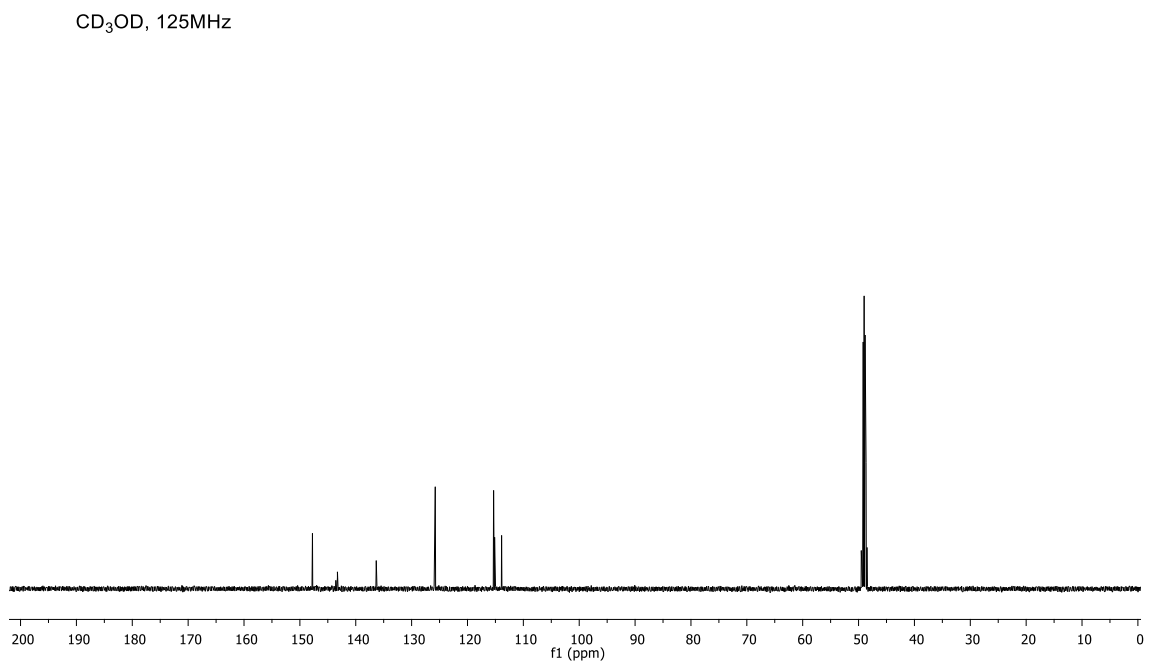
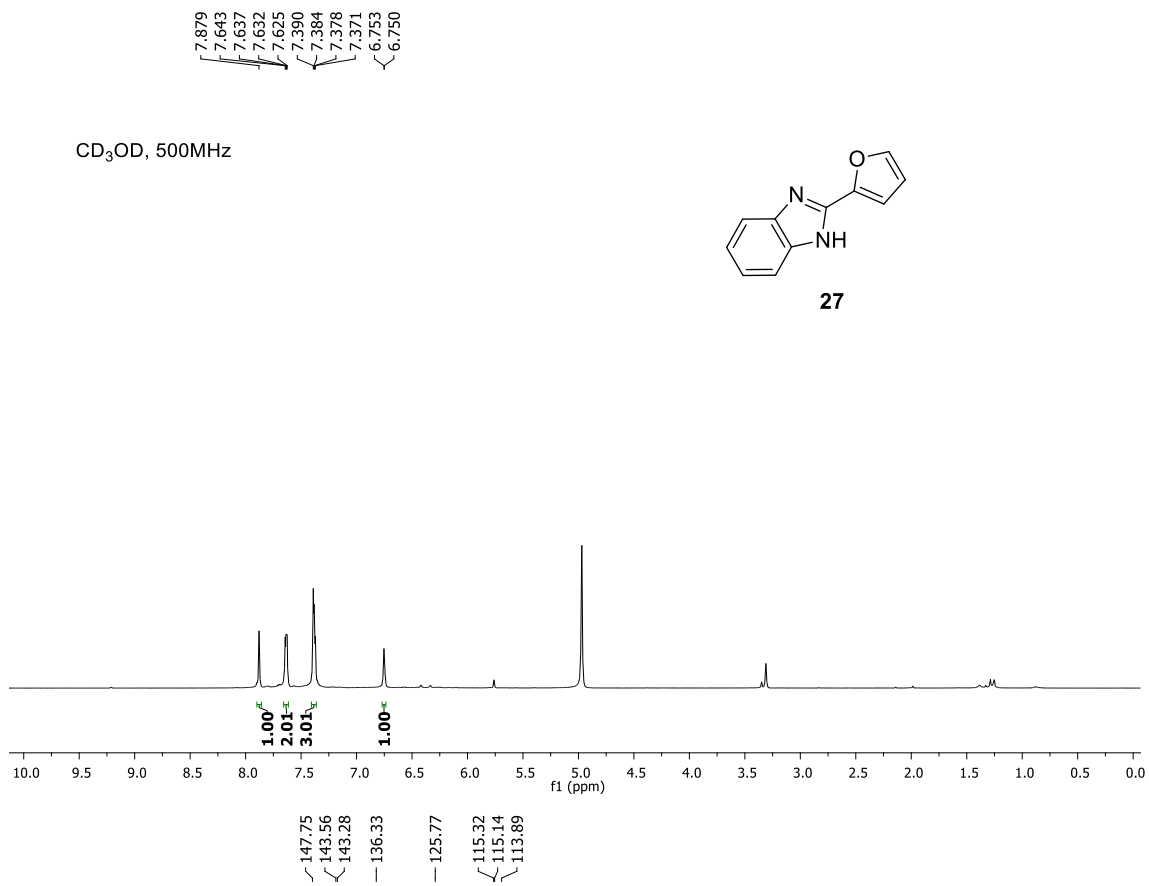


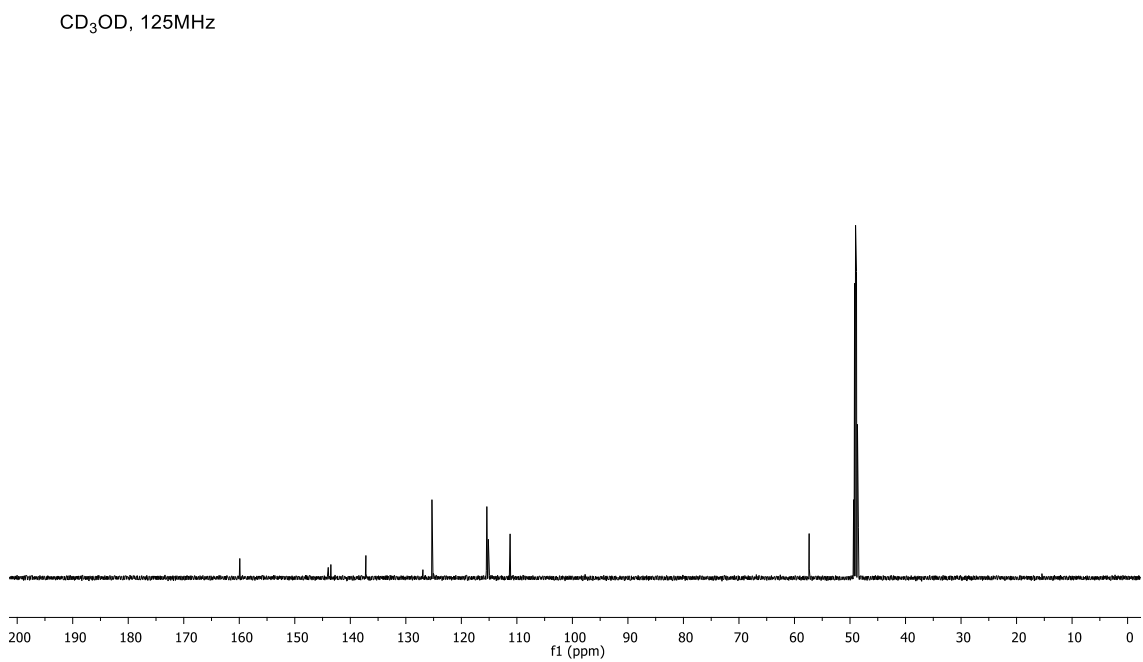
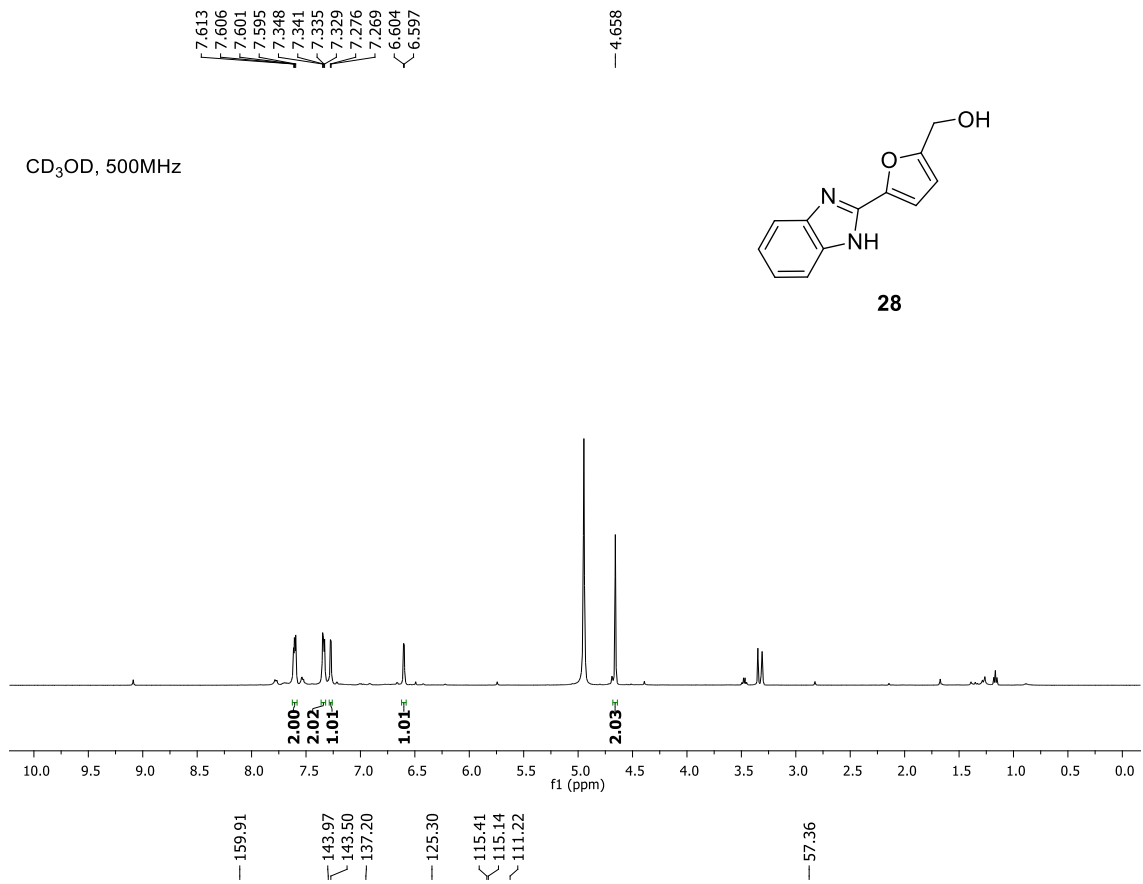


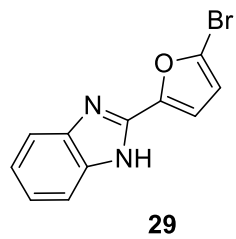
= grease, * = hexane



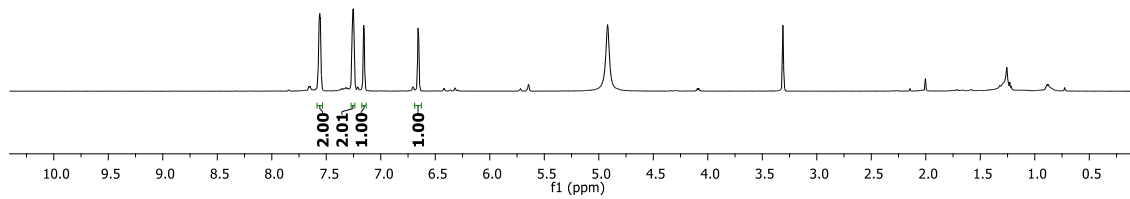




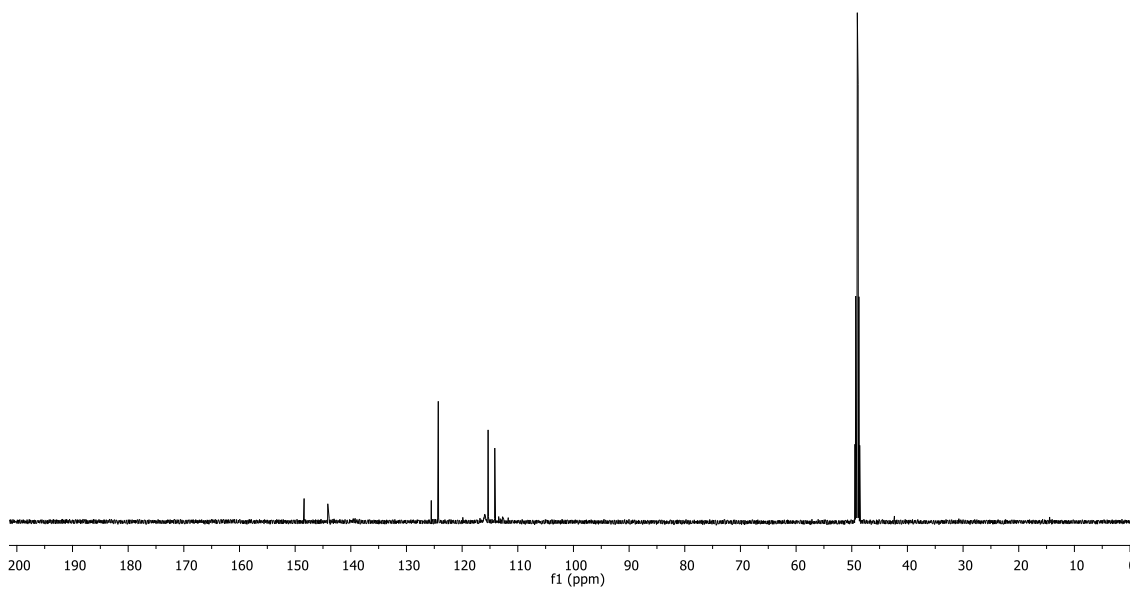


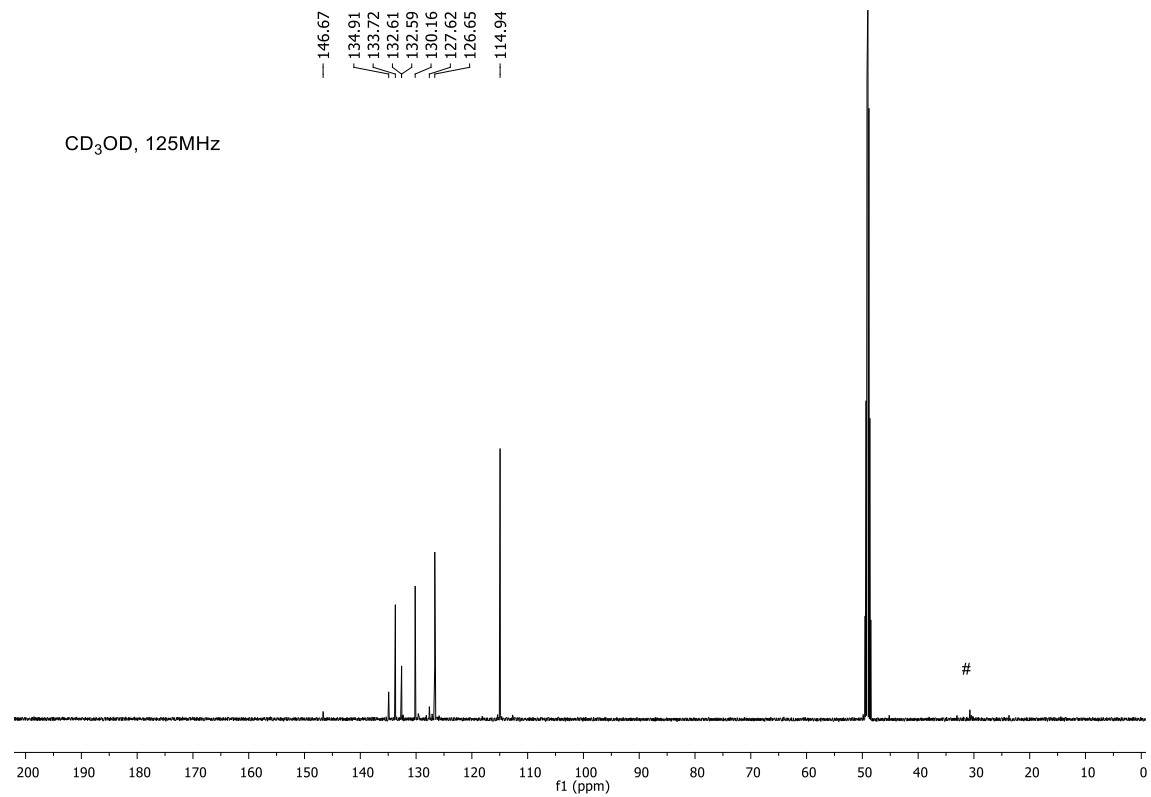
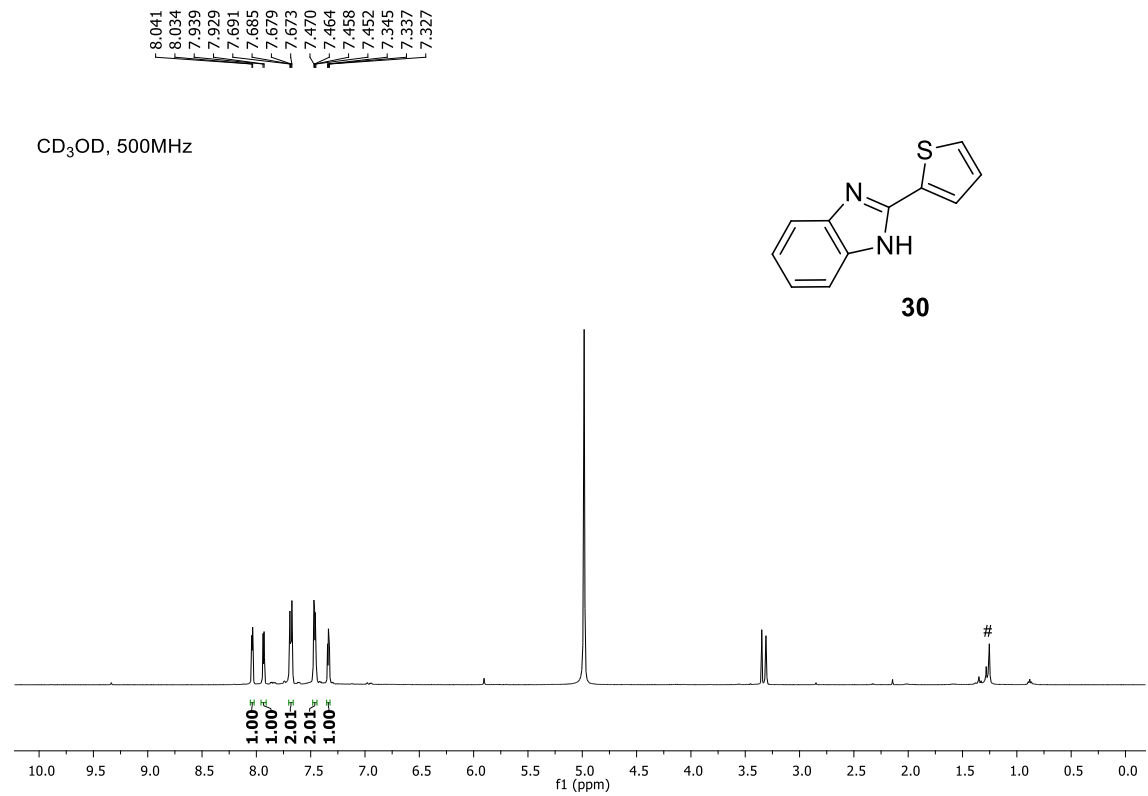
CD₃OD, 600MHz

7.568
7.563
7.560
7.555
7.261
7.256
7.251
7.246
7.158
7.152
6.659
6.653

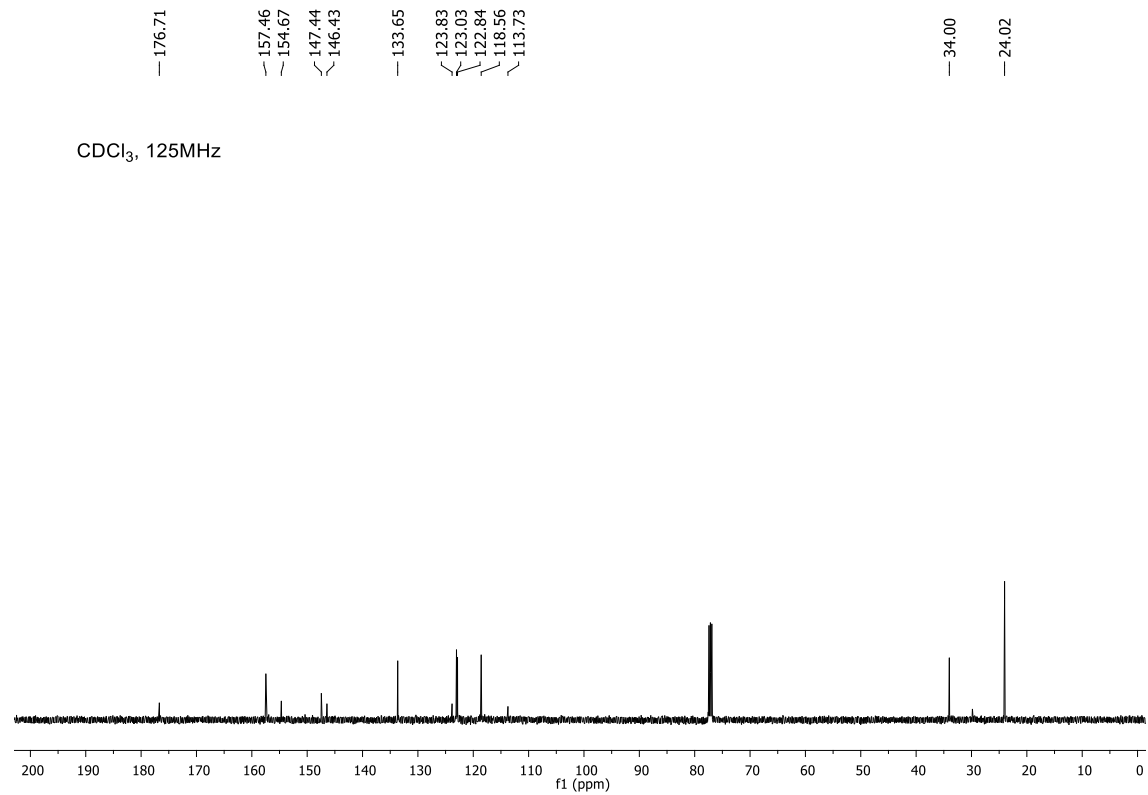
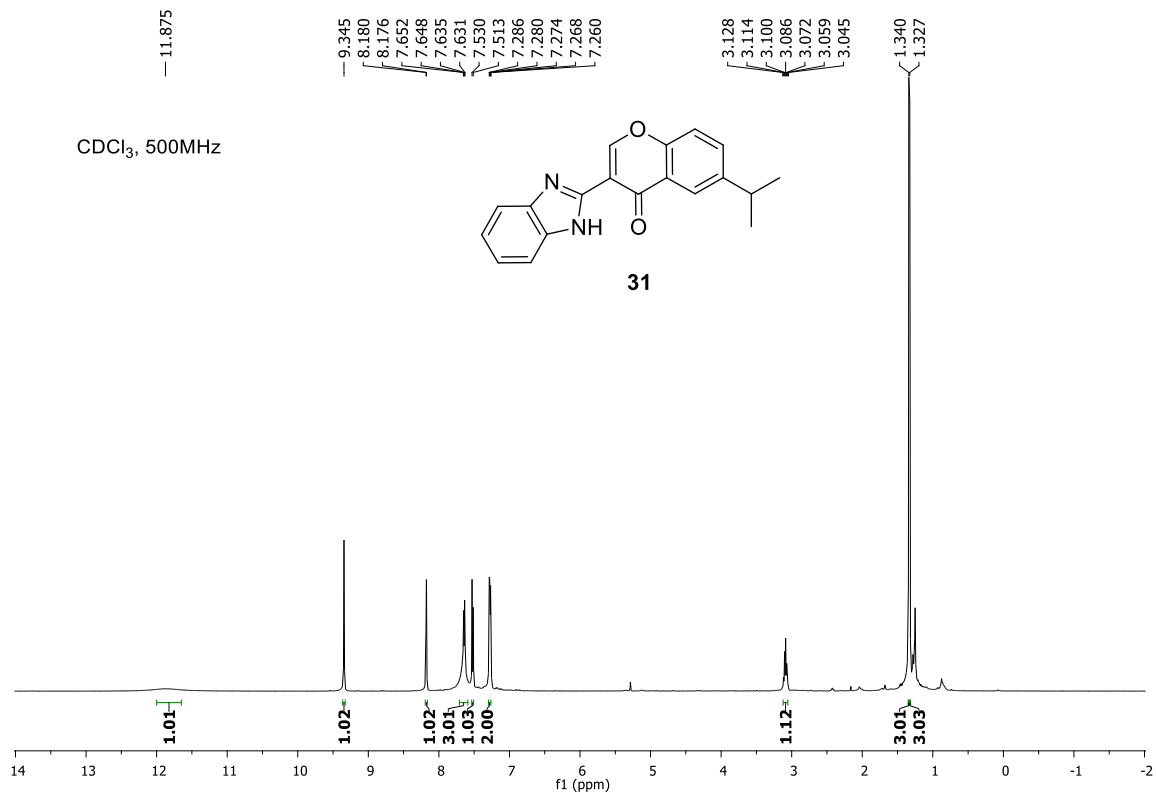


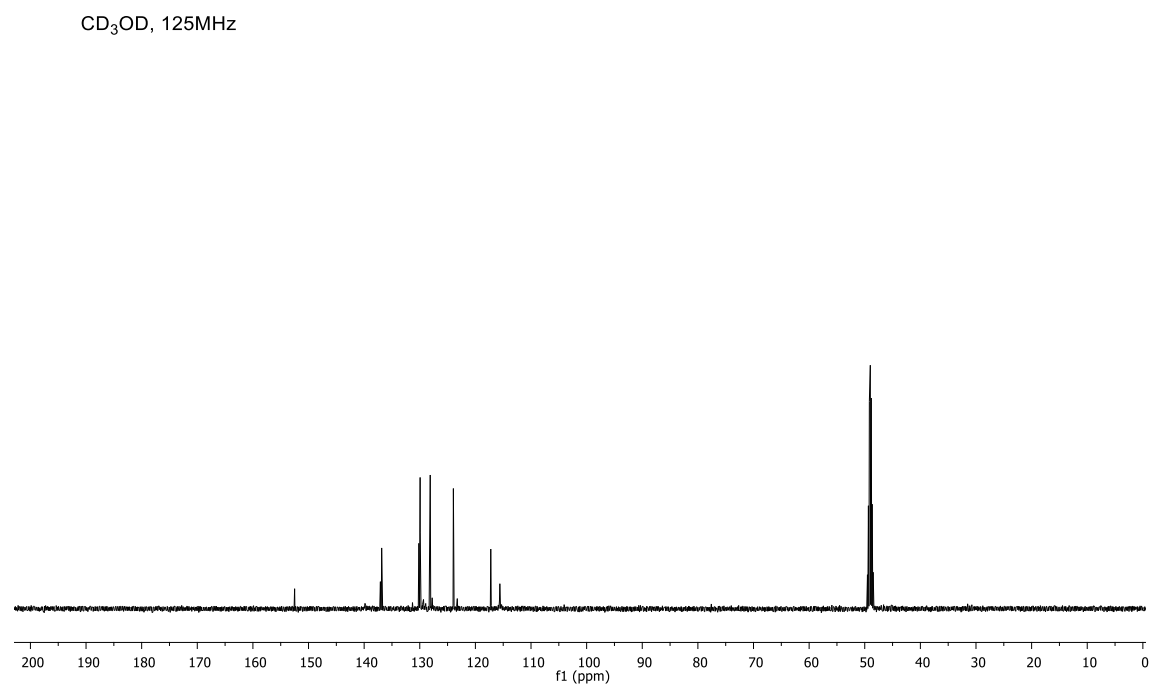
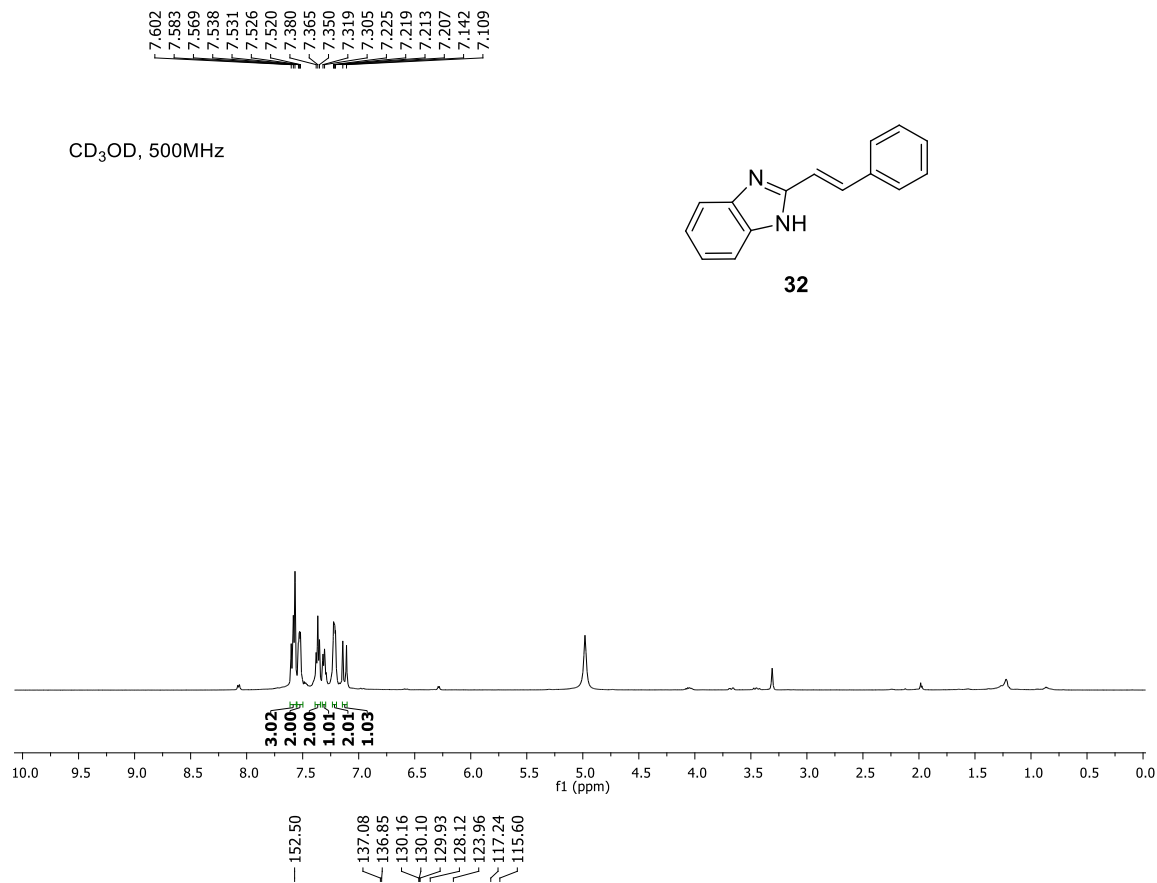
148.39
144.14
125.54
124.28
115.96
115.33
114.14

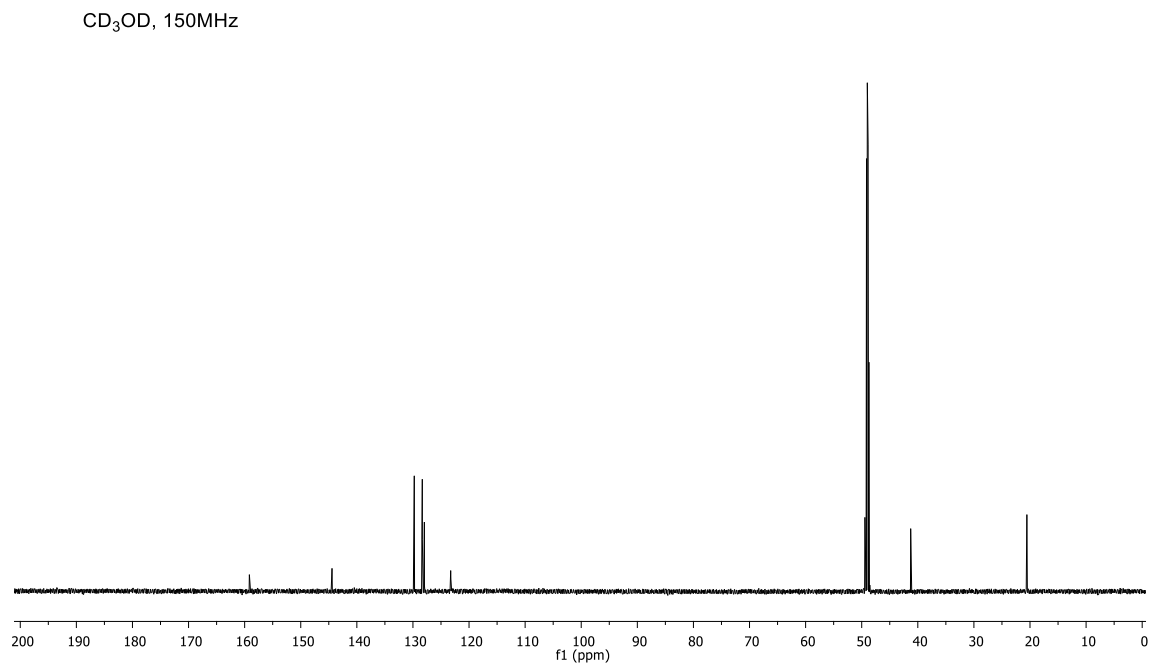
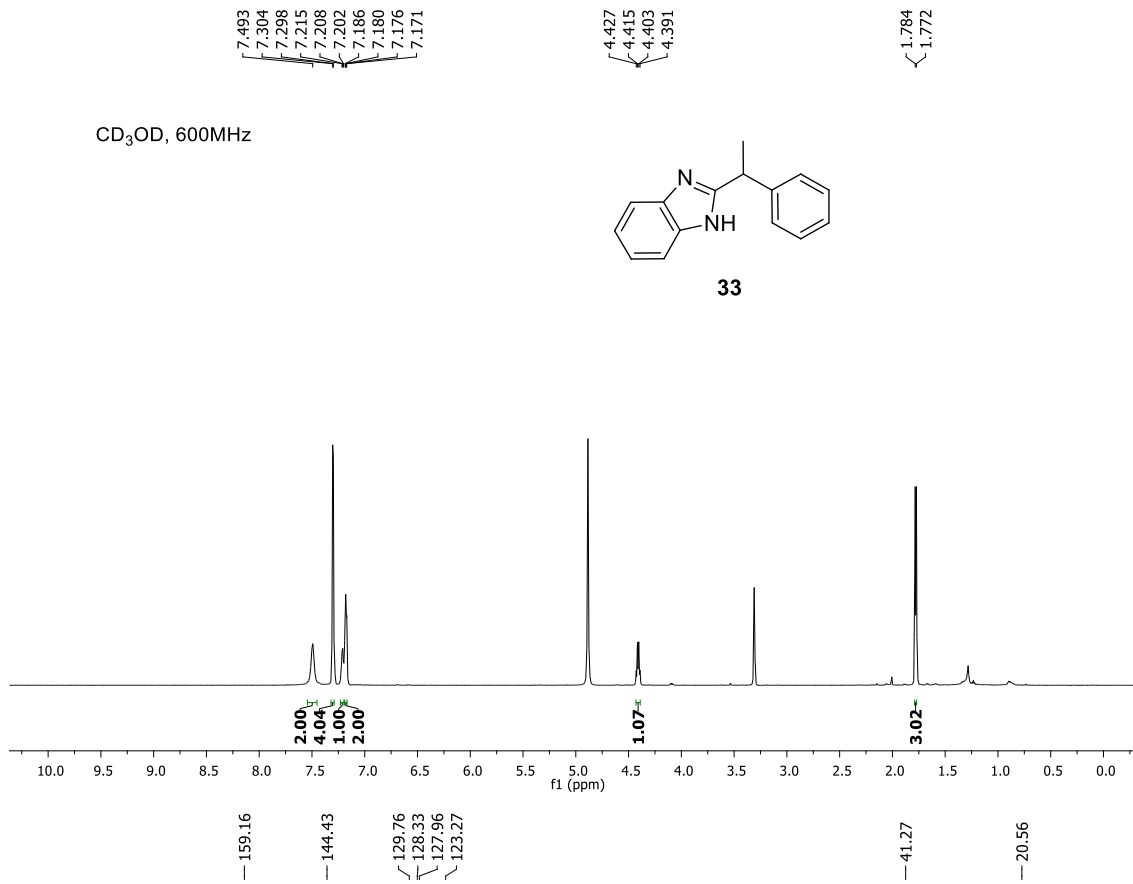
CD₃OD, 150MHz

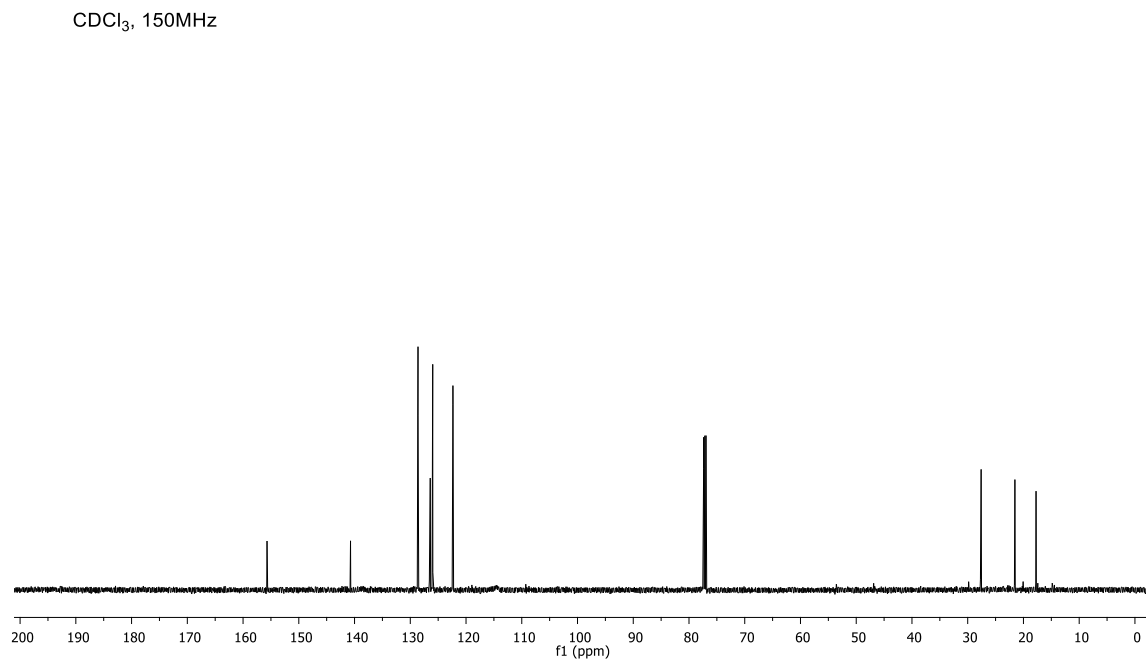
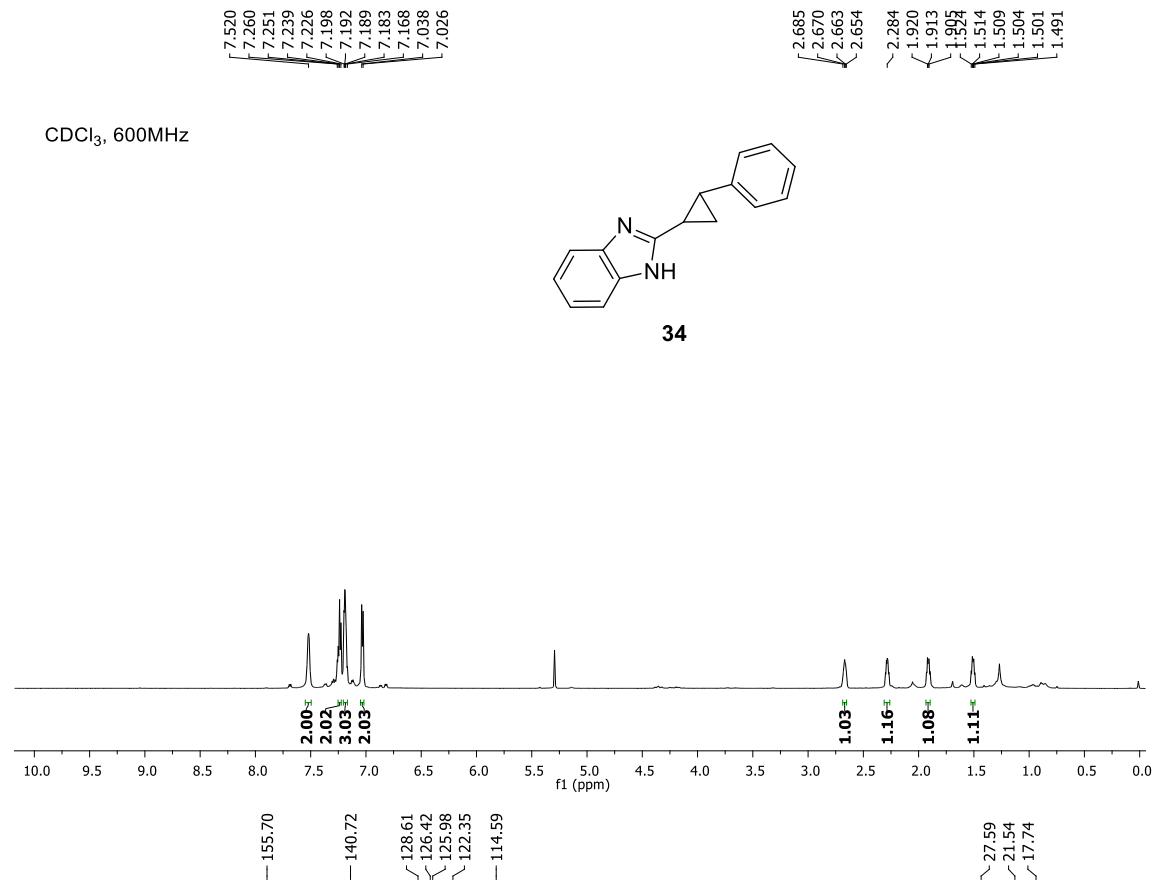


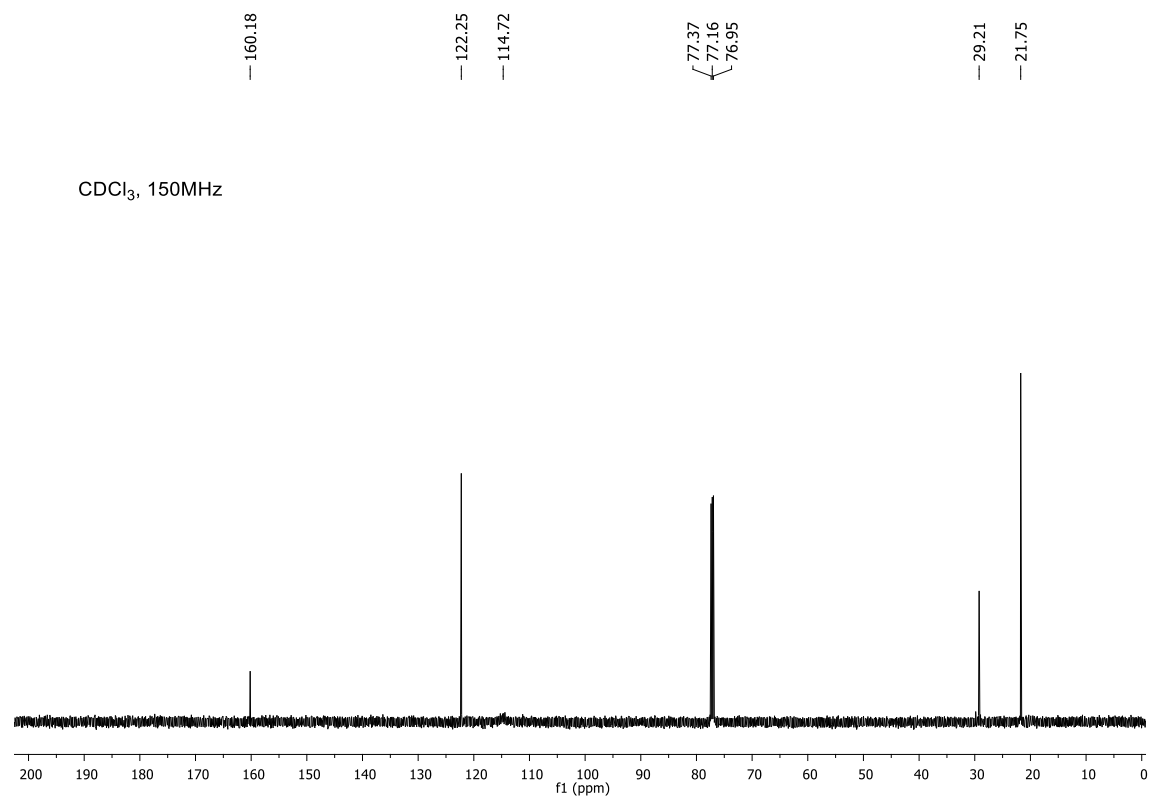
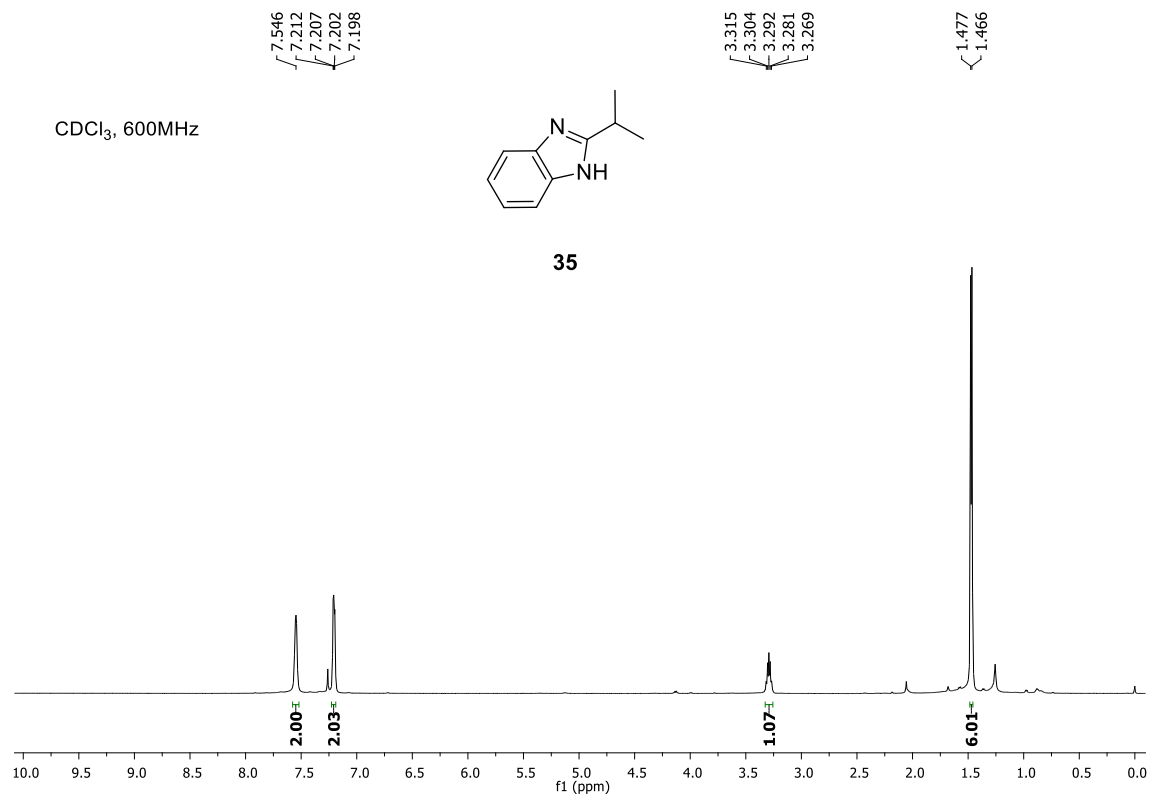
= grease

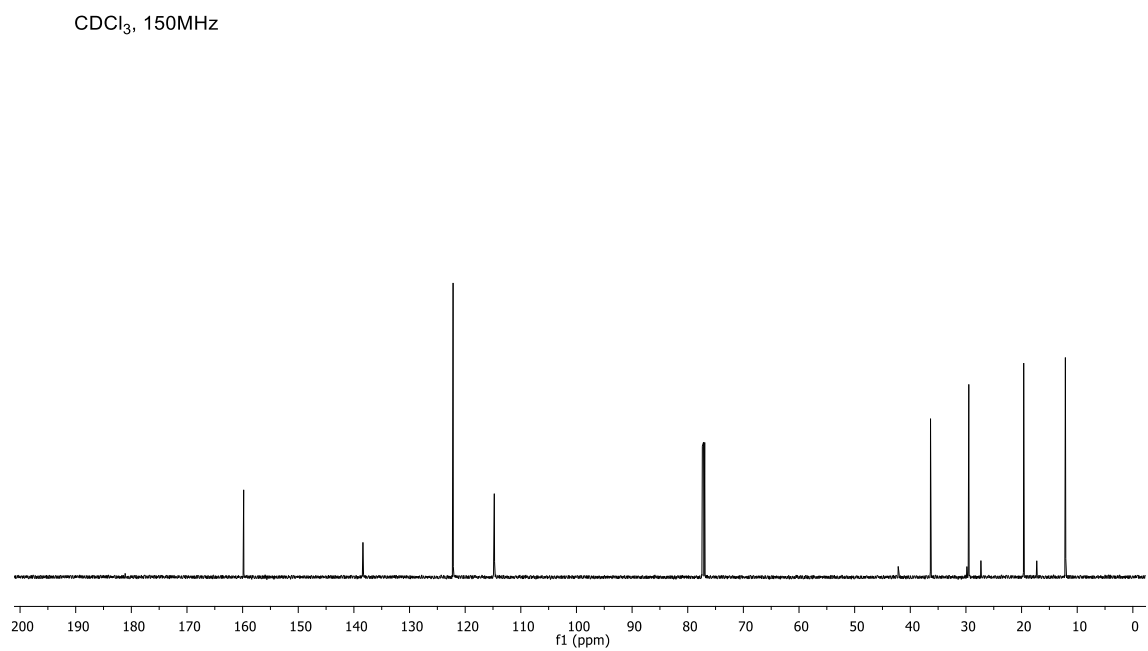
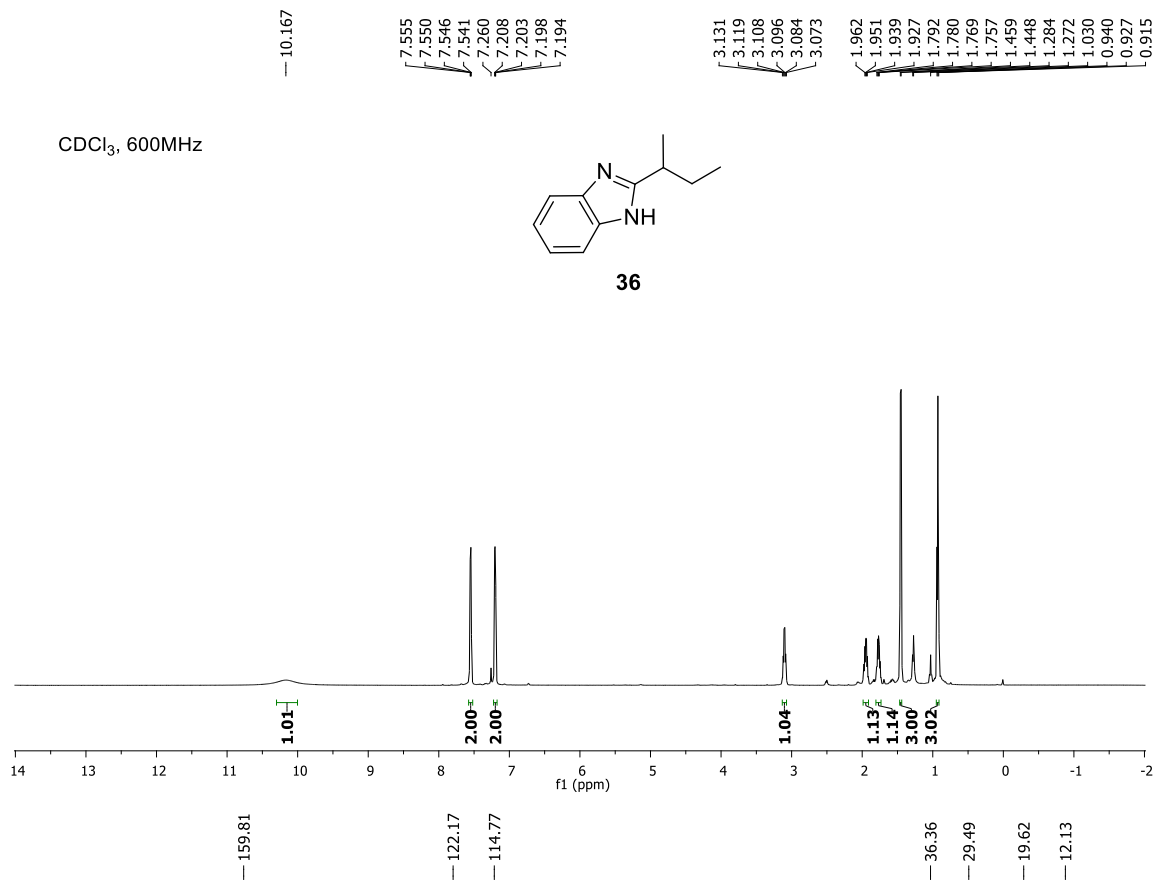


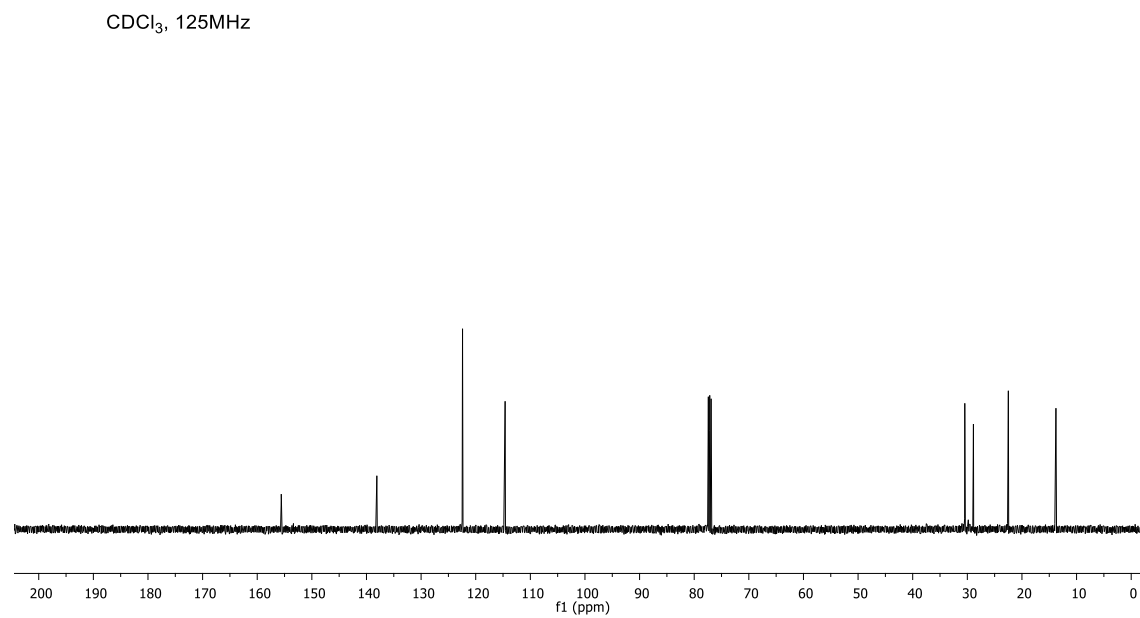
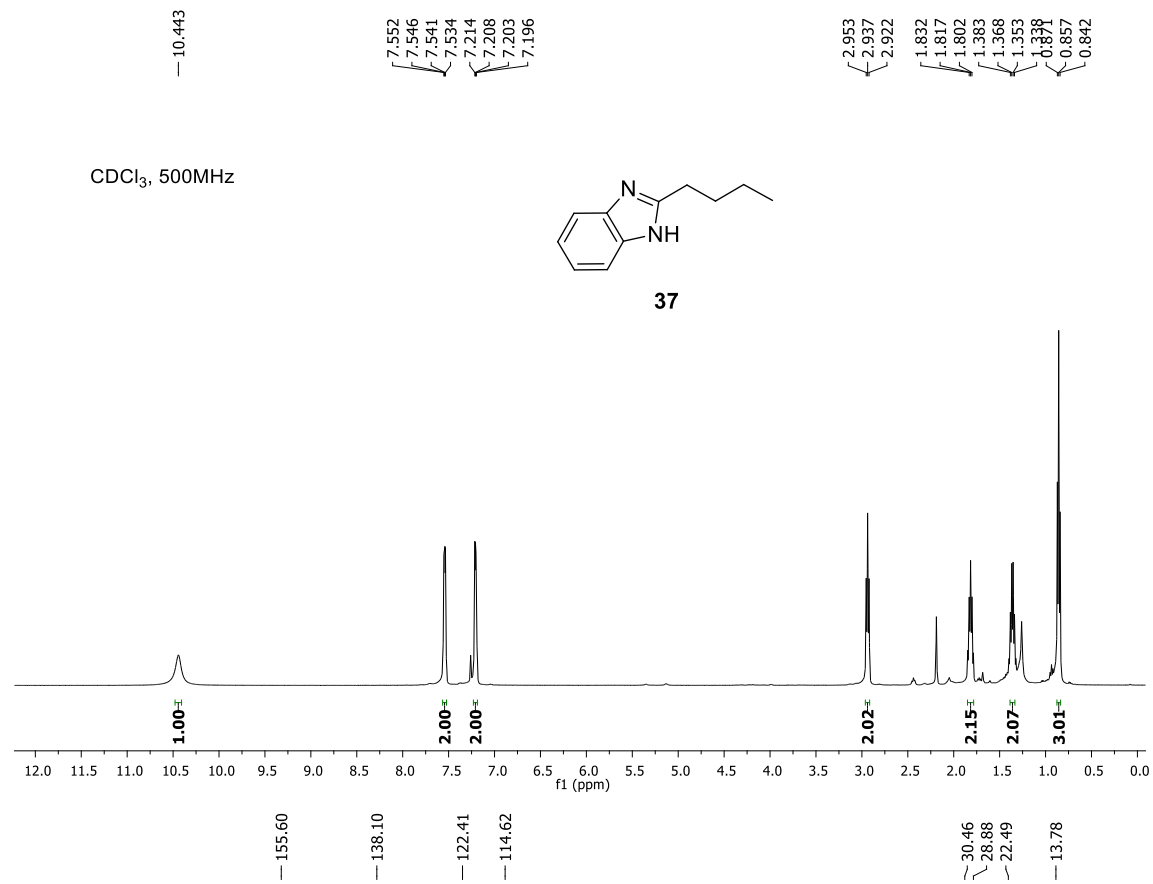


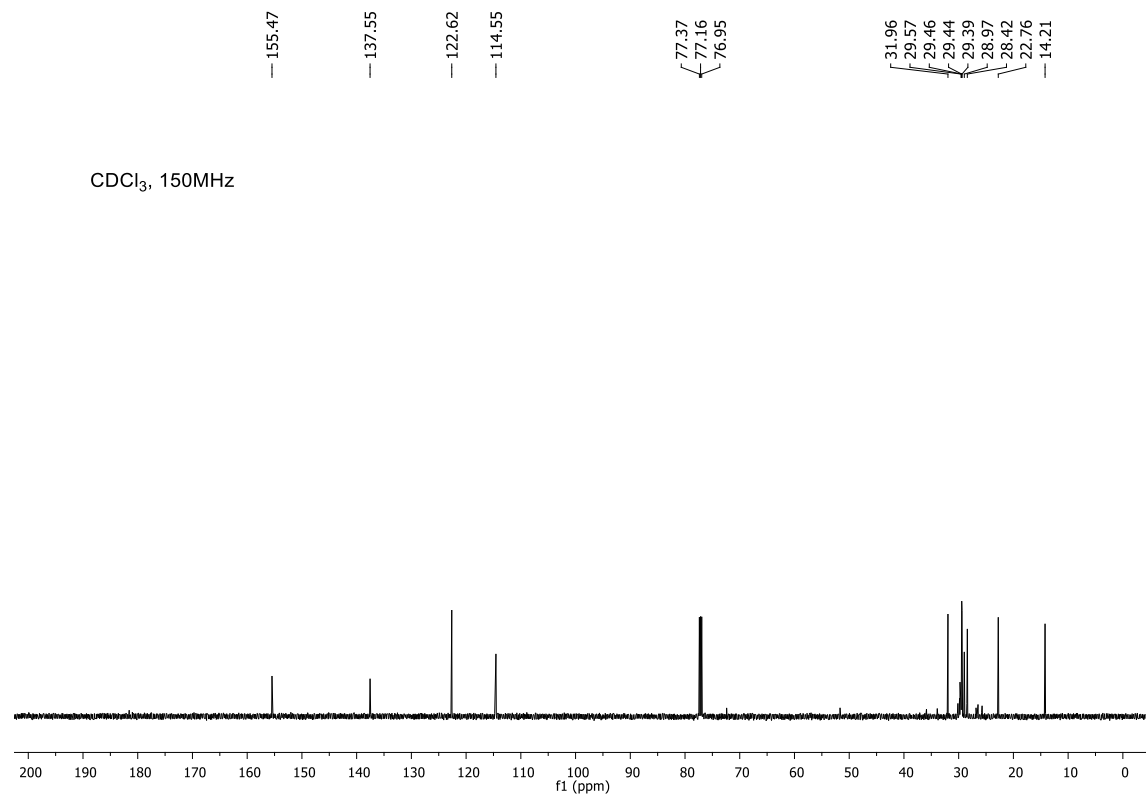
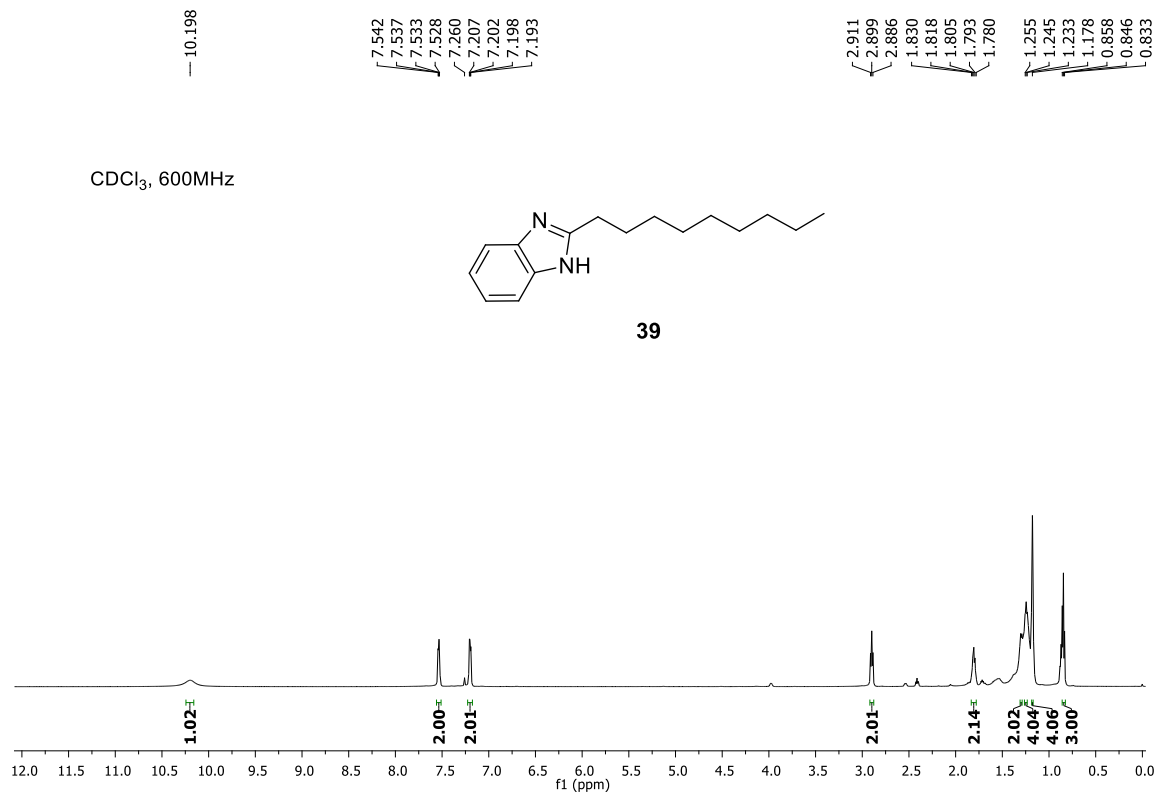










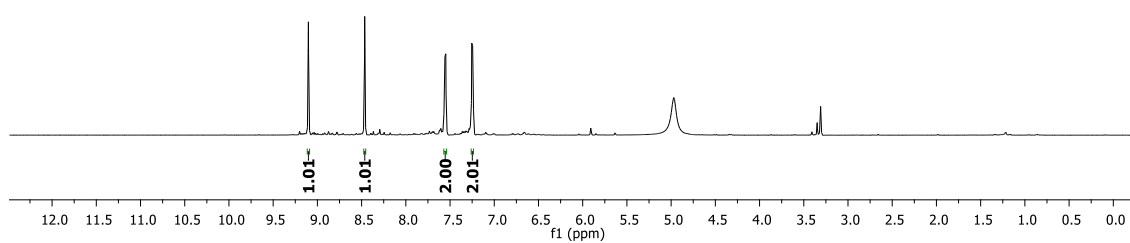


CD₃OD, 600MHz

9.102
8.465
7.563
7.558
7.553
7.548
7.255
7.250
7.245
7.240

C1=CC=C2N=C(N1)C3=CN=CS3

44



CD₃OD, 150MHz

157.26
145.71
143.05
130.35
124.45
124.26
116.02

