Supplementary Information

Atomically dispersed Co catalyst for efficient oxidative fabrication of benzoheterocycles under ambient oxygen condition

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General Experimental Details

Chemicals. 2-Methylimidazole (2-MI), cobaltous nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), benzaldehyde, *o*-phenylenediamine, 2-aminophenol, 2-aminobenzenethiol and *m*-xylene were acquired from Shanghai Macklin Biochemical Co., Ltd. Methanol, petroleum ether, ethyl acetate, and zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$) were acquired from Sinopharm Chemical Reagent Co., Ltd.

Preparation of NC. In a typical experiment, 670 mg $Zn(NO_3)_2·6H_2O$ was dissolved in 30 mL methanol to form solution 1, and 1980 mg 2-methylimidazole (2-MI) was dissolved in 30 mL methanol to form solution 2. Subsequently, solution 1 was dropwise added to solution 2 under vigorously stirring for 8 h at room temperature. Afterward, the generated ZIF-8 was collected by centrifugation, washed with methanol (three times), and finally dried overnight. The dried ZIF-8 was placed in the porcelain boat and pyrolyzed under 100 mL/min N_2 flow at 800 ^oC for 2 h (3 ^oC/min).

Preparation of Co/NC catalyst. Typically, 218 mg $Zn(NO_3)_2·6H_2O$ and 520 mg $Co(NO_3)_2·6H_2O$ were dissolved in 30 mL methanol to form solution 1, and 1980 mg 2-MI was dissolved in 30 mL methanol to form solution 2. Subsequently, solution 1 was dropwise added to solution 2 under vigorously stirring for 8 h at room temperature. Afterward, the generated precursor was collected by centrifugation, washed with methanol (three times), and finally dried overnight. The dried precursor was placed in the porcelain boat and pyrolyzed under 100 mL/min N_2 flow at 800 ^oC for 2 h.

Preparation of Co/SiO_2. 25 mg $Co(NO_3)_2·6H_2O$ and 670 mg $Zn(NO_3)_2·6H_2O$ were dissolved in 50 mL methanol to form solution 1, and 195 mg fumed silica was dissolved in 50 mL methanol to form solution 2. Subsequently, solution 1 was added to solution 2 under vigorously stirring for 8 h at room temperature. Afterward, the solvent was removed by rotary evaporation, and the obtained solids were dried overnight at 80 ^{o}C. Finally, the dried solids were placed in the porcelain boat and pyrolyzed under 100 mL/min N_2 flow at 450 ^{o}C for 2 h. The resulting sample was designated as Co/SiO_2.

Characterization. Scanning electron microscopy (SEM) images were characterized by a Hitachi SU8010 field emission scanning electron microscopy. High-resolution transmission electron microscopy (HR-TEM) and energy-dispersive X-ray (EDX) mapping images were taken by a JEM-2100F electron microscope. Aberration-corrected high angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images were recorded by an FEI Themis Z. The contents of metal in samples were analyzed by an ICP-OES730 inductively coupled plasma optical emission spectrometer (ICP-OES). X-ray photoelectron spectroscopy (XPS) characterizations were carried out on the Thermo ESCALAB 250xi. Powder X-ray diffraction (XRD) patterns were obtained from a Brucker D8 advance X-ray diffractometer using Co Kα radiation. X-ray absorption fine structure (XAFS) measurements were carried out at the TableXAFS 500A. The N_2 adsorption-desorption tests were obtained from an automated gas sorption analyzer (Quantachrome, Autosorb-Iq-MP, United States). The Brunauer-Emmet-Teller (BET) was used to calculate the specific surface areas, the average pore sizes, and the total pore volumes of the catalysts.

Supplementary Figures

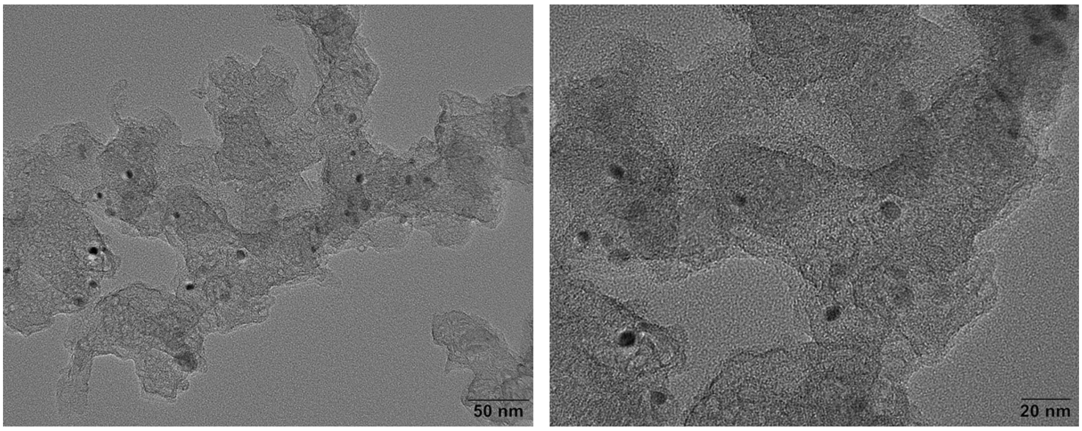


Fig. S1. TEM images of Co/NC.

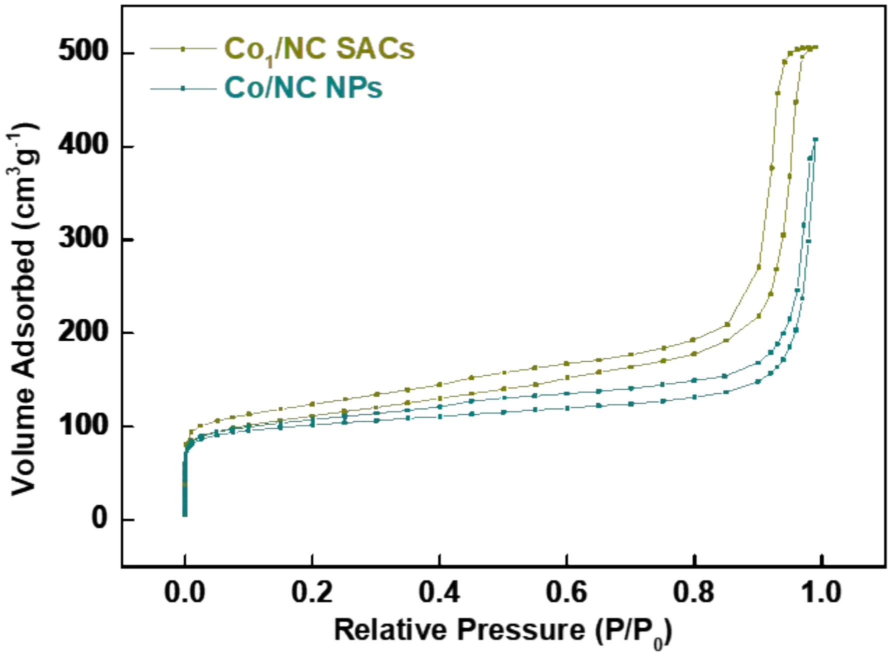


Fig. S2. N_2 adsorption−desorption isotherms of Co_1/NC and Co/NC.

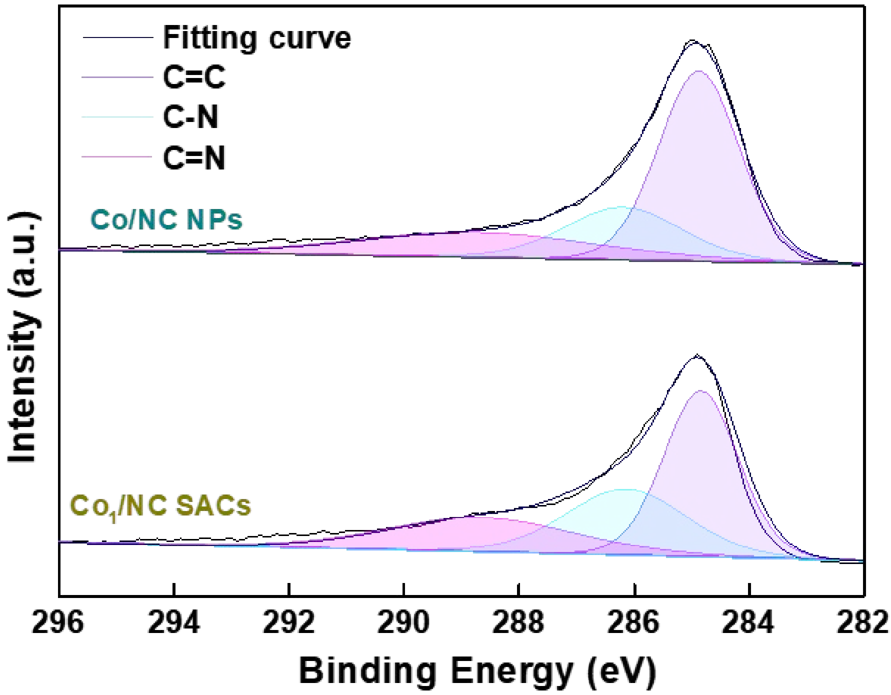


Fig. S3. XPS spectra of C 1s in Co_1/NC and Co/NC catalysts.

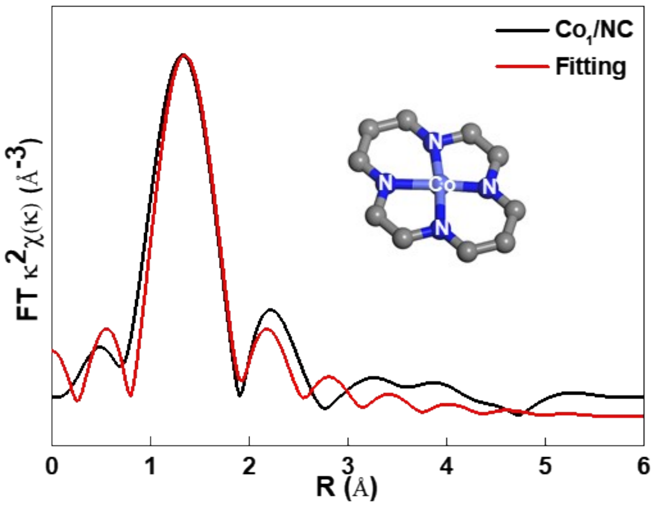


Fig. S4. The corresponding FT-EXAFS fitting curves of Co_1/NC, inset is the view of the fitted structure simulated by density of theory calculation.

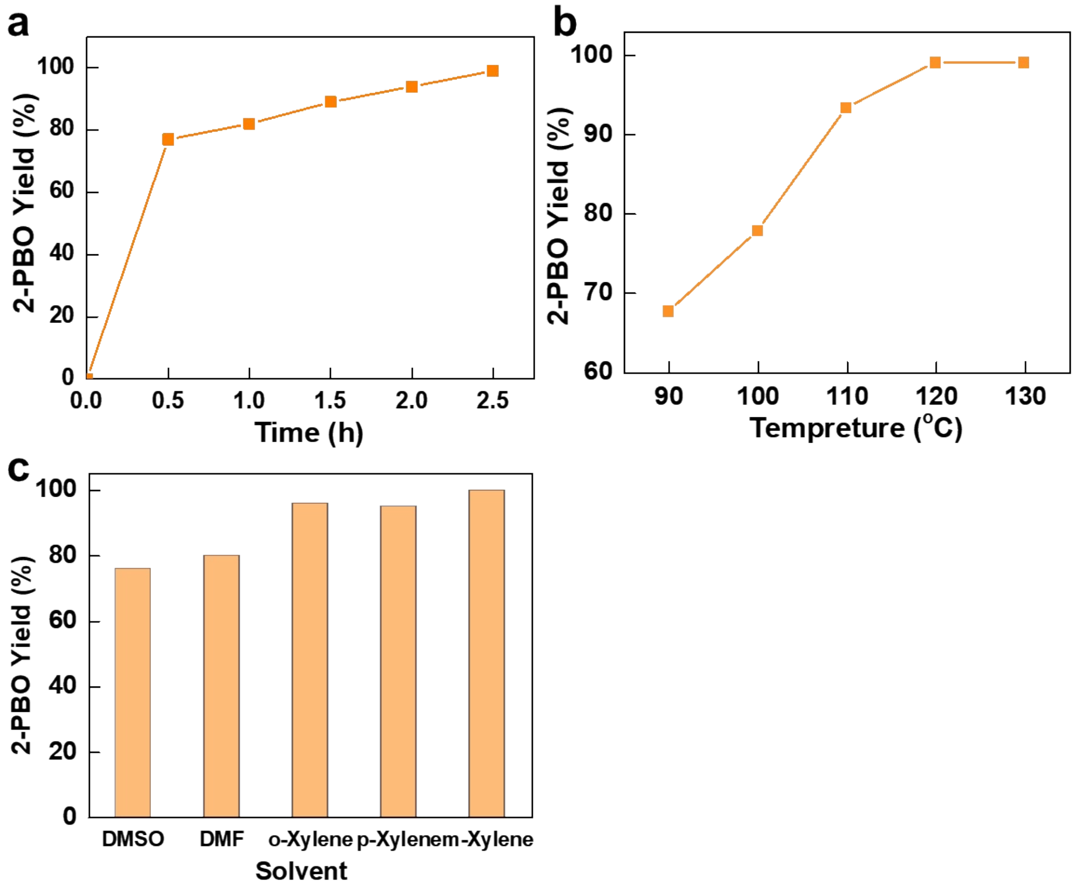


Fig. S5. Influences of (a) time, (b) temperature, and (c) solvents on the oxidative coupling of 2-aminophenol with benzaldehyde to 2-PBO over Co_1/NC catalyst, respectively. Conditions: (a) Firstly, 0.2 mmol 2-aminophenol, 0.2 mmol benzaldehyde, 3 mL *m*-xylene, 120 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 120 °C, 0.5-2.5 h. (b) Firstly, 0.2 mmol 2-aminophenol, 0.2 mmol benzaldehyde, 3 mL *m*-xylene, 90-130 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 90-130 °C, 2.5 h. (c) Firstly, 0.2 mmol 2-aminophenol, 0.2 mmol benzaldehyde, 3 mL solvent, 120 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 120 °C, 2.5 h.

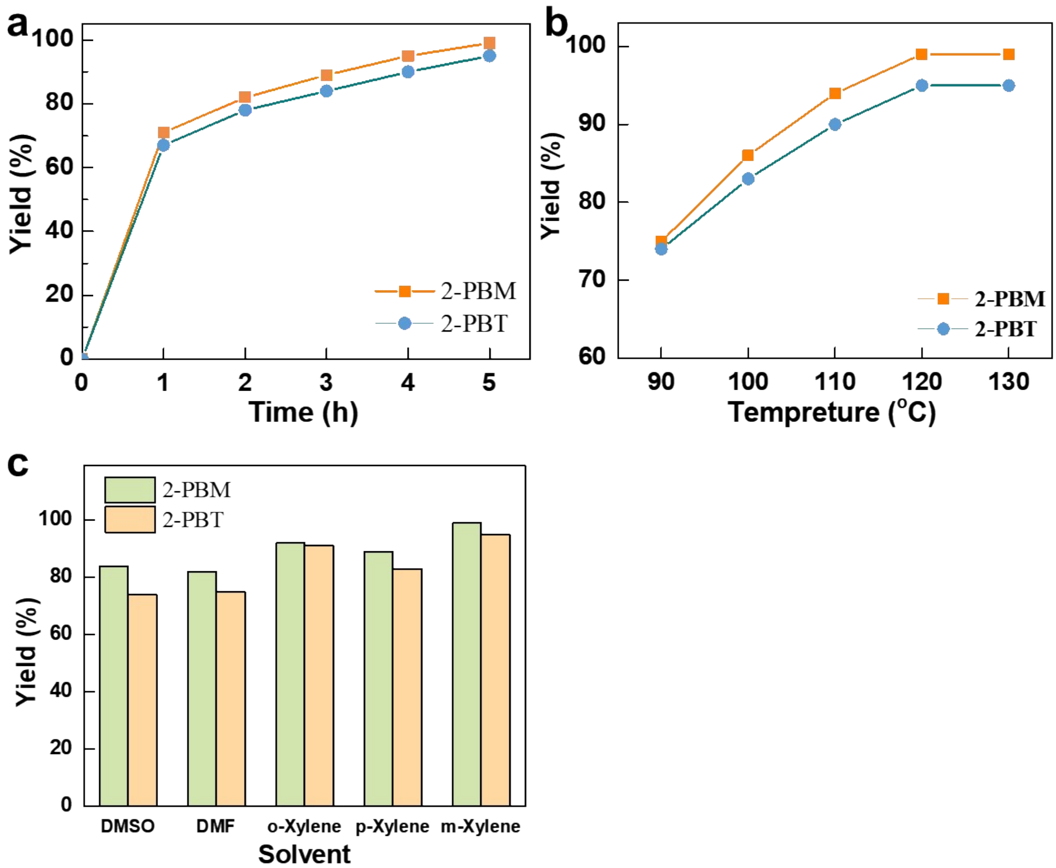


Fig. S6. Influences of (a) time, (b) temperature, and (c) solvents on the oxidative coupling of 2-aminobenzenethiol or *o*-phenylenediamine with benzaldehyde to 2-PBT and 2-PBM over Co_1/NC catalyst, respectively. Conditions: (a) Firstly, 0.2 mmol 2-aminobenzenethiol or *o*-phenylenediamine, 0.2 mmol benzaldehyde, 3 mL *m*-xylene, 120 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 120 °C, 1-5 h. (b) Firstly, 0.2 mmol 2-aminobenzenethiol or *o*-phenylenediamine, 0.2 mmol benzaldehyde, 3 mL *m*-xylene, 90-130 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 90-130 °C, 5 h. (c) Firstly, 0.2 mmol 2-aminobenzenethiol or *o*-phenylenediamine, 0.2 mmol benzaldehyde, 3 mL solvents, 120 °C, 1 h; then, 1.38 mol % Co_1/NC, 1 bar O_2, 120 °C, 5 h.

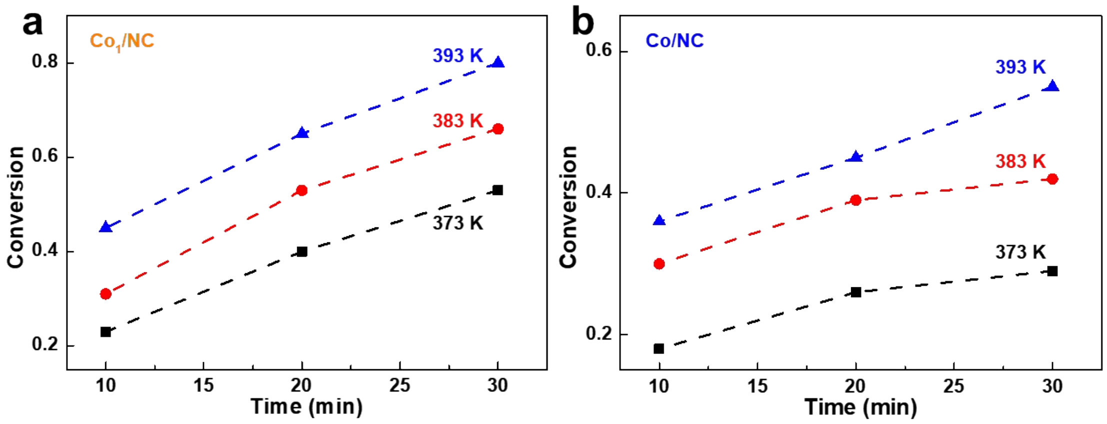


Fig. S7. Oxidation synthesis of 2-PBO over (a) Co_1/NC and (b) Co/NC catalysts under different temperatures. Condition: 0.2 mmol *(E)*-2-(benzylideneamino)phenol, 3 mL *m*-xylene, 30 mg catalysts, 1 bar O_2.

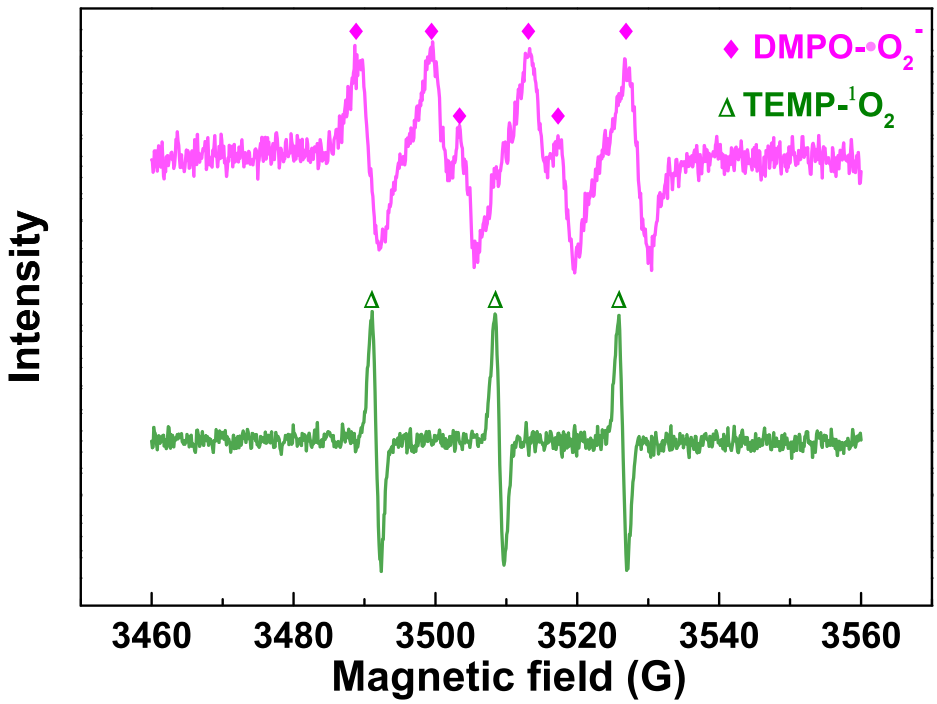


Fig. S8. EPR signals of TEMP-$^1O_2$ and DMPO-•O_2^- adduct in *m*-xylene in the presence of Co_1/NC at 120 ^oC in 30 min.

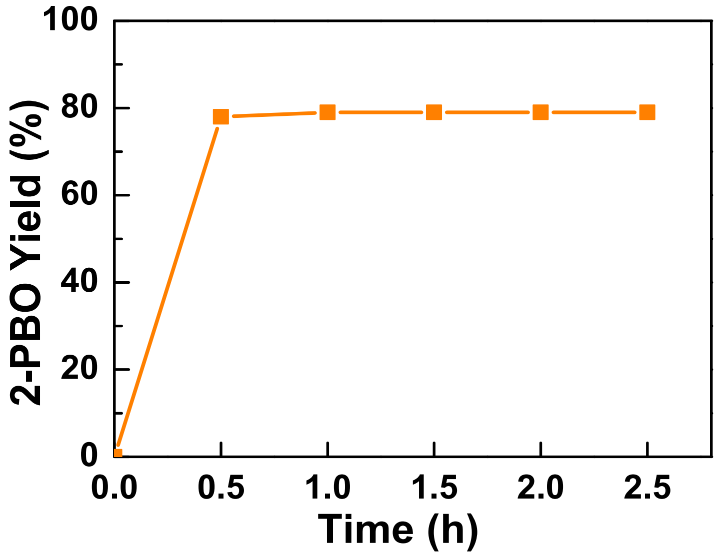


Fig. S9. The hot filtration experiment of Co_1/NC for the oxidation synthesis of 2-PBO.

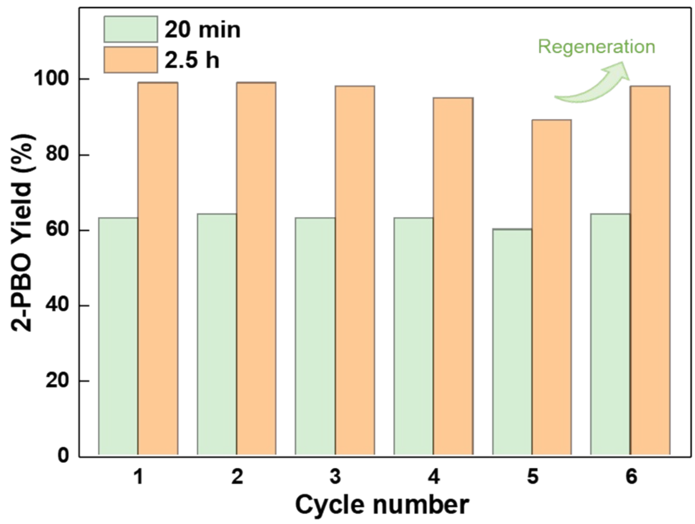


Fig. S10. The reusability of Co_1/NC in the second stage reaction time of the oxidation synthesis of 2-PBO at 20 min and 2.5h, respectively.

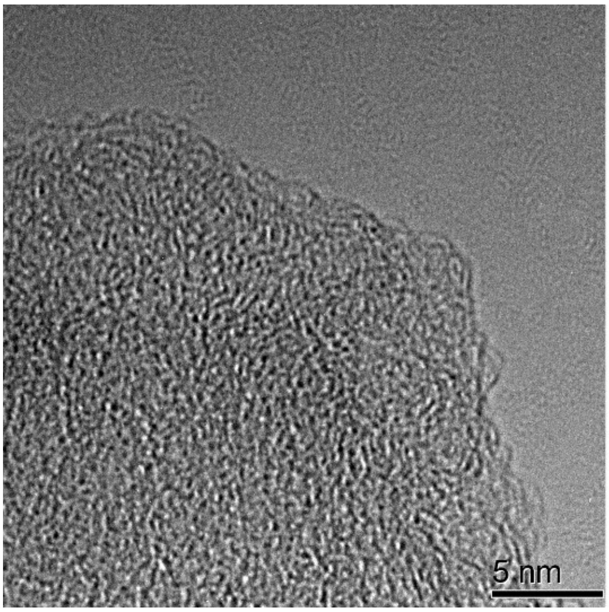


Fig. S11. TEM images of used Co_1/NC catalyst. The second stage reaction time was 2.5 h.

Supplementary Tables

Table S1. ICP-OES results of Co_1/NC and Co/NC catalysts

Sample	**Co loading (wt%)**
Co_1/NC	2.53
Co/NC	20.4
Co_1/NC-hot filtration	2.53

Table S2. Physical parameters of Co_1/NC and Co/NC catalysts

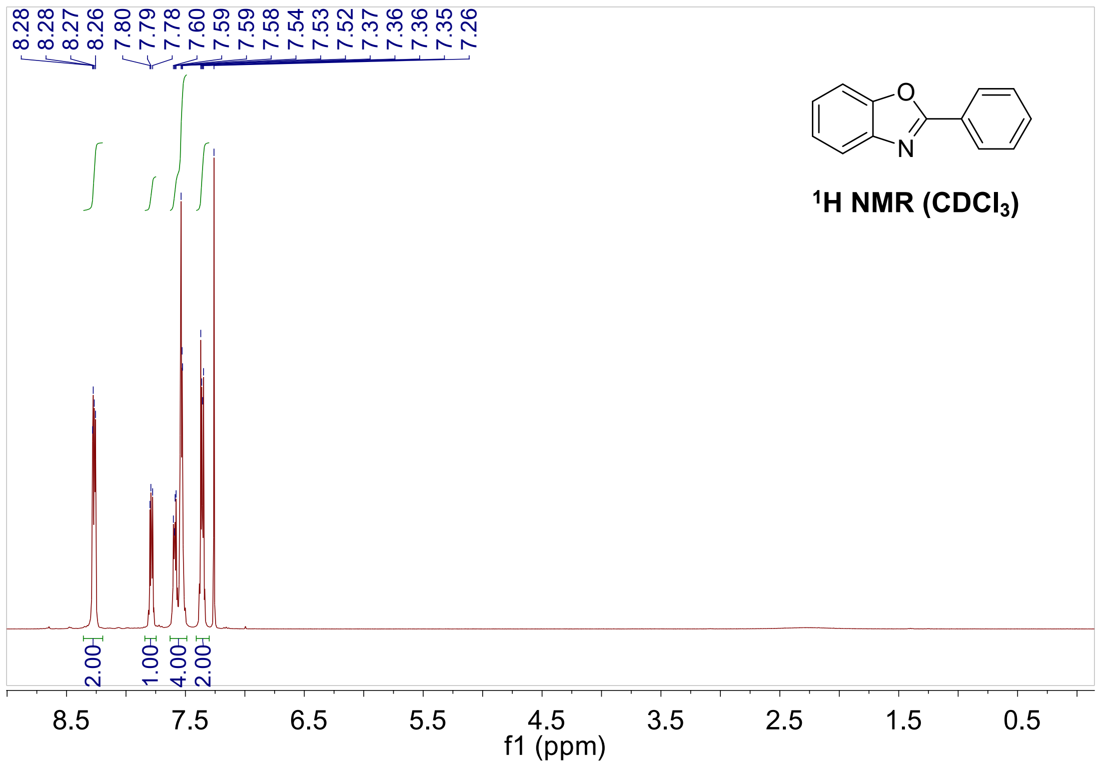
Sample	S_{BET} (m^2g^{-1})	D_{pore} (nm)	V_p (cm^3/g)
Co_1/NC	401.1	7.83	0.79
Co/NC	381.3	6.23	0.63

Table S3. The best-fitted EXAFS results of Co_1/NC catalysts [a]

Sample	Shell	*CN*	*R*(Å)	σ^2 (Å^2)	ΔE_0 (eV)	*R* factor
Co foil	Co-Co	12	2.49±0.01	0.006±0.001	7.8±0.3	0.001
Co_3O_4	Co-O	4	1.91±0.01	0.001±0.002	-7.1±1.7	0.012
	Co-Co	12	3.24±0.03	0.014±0.004	-19.4±3.2	0.020
Co_1/NC	Co-N	4.0±0.2	1.88±0.02	0.006±0.004	-4.8±4.0	0.028

[a] *CN*: coordination numbers; *R*: bond distance, σ^2: Debye-Waller factors, and ΔE_0: the inner potential correction. R factor: goodness of fit.

NMR spectra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1H NMR (CDCl3)
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N
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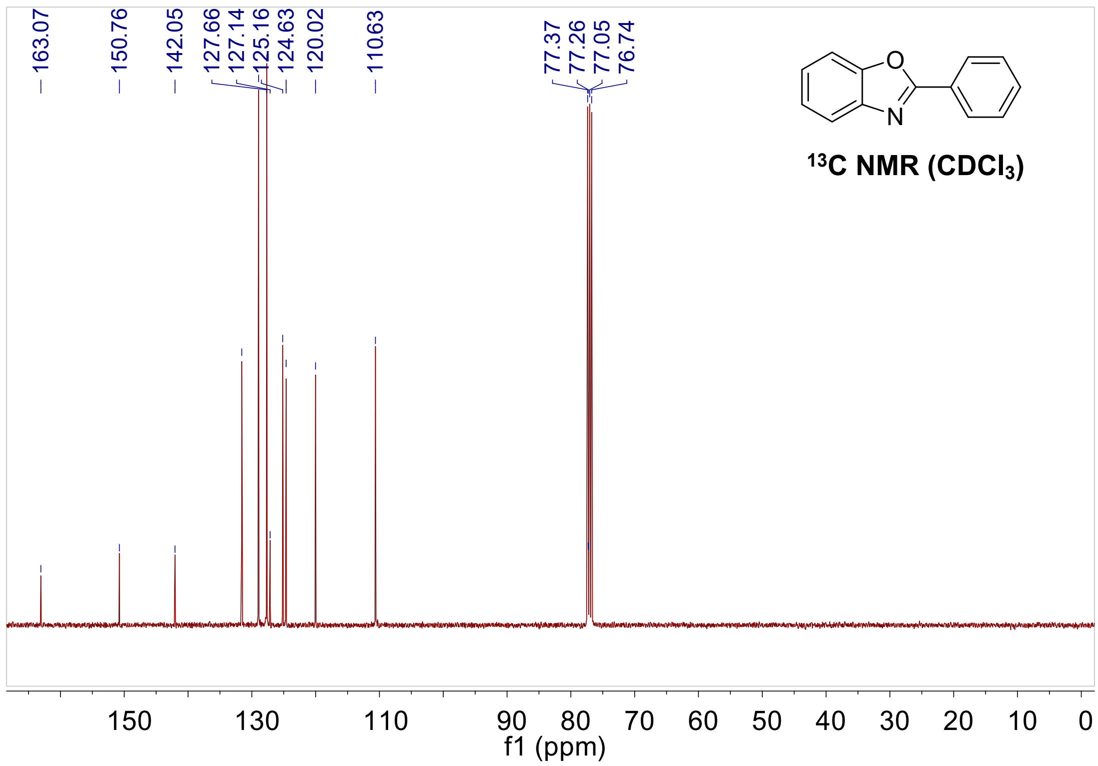
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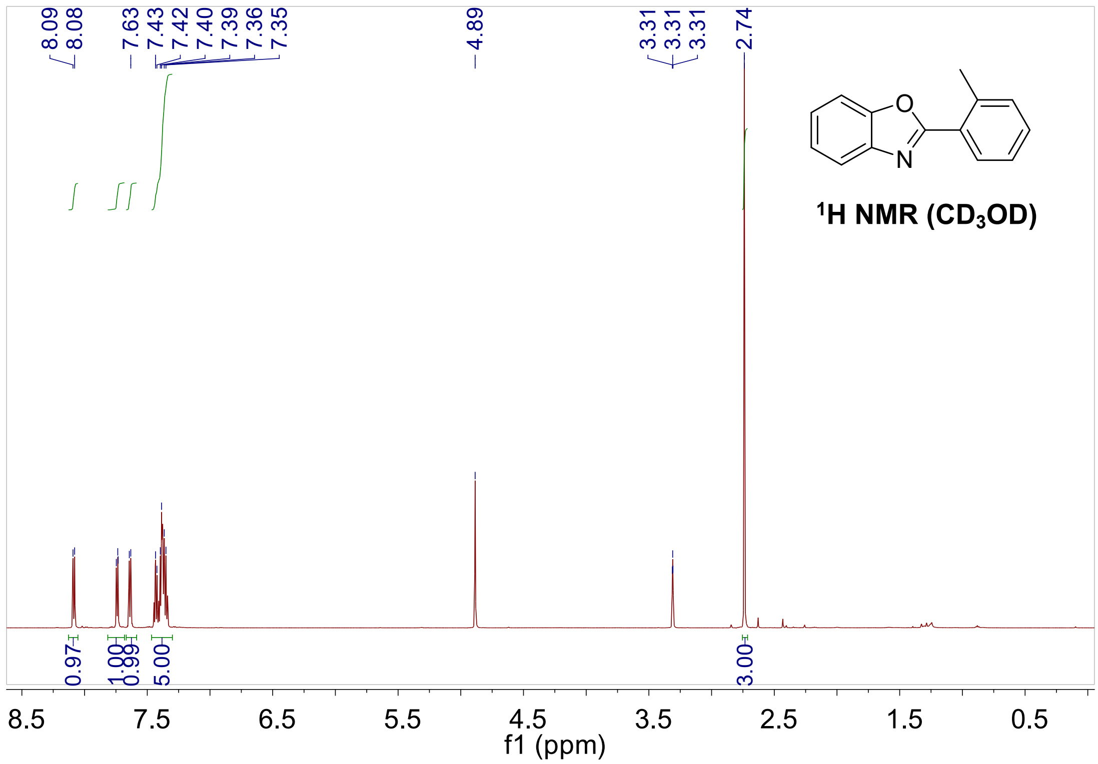
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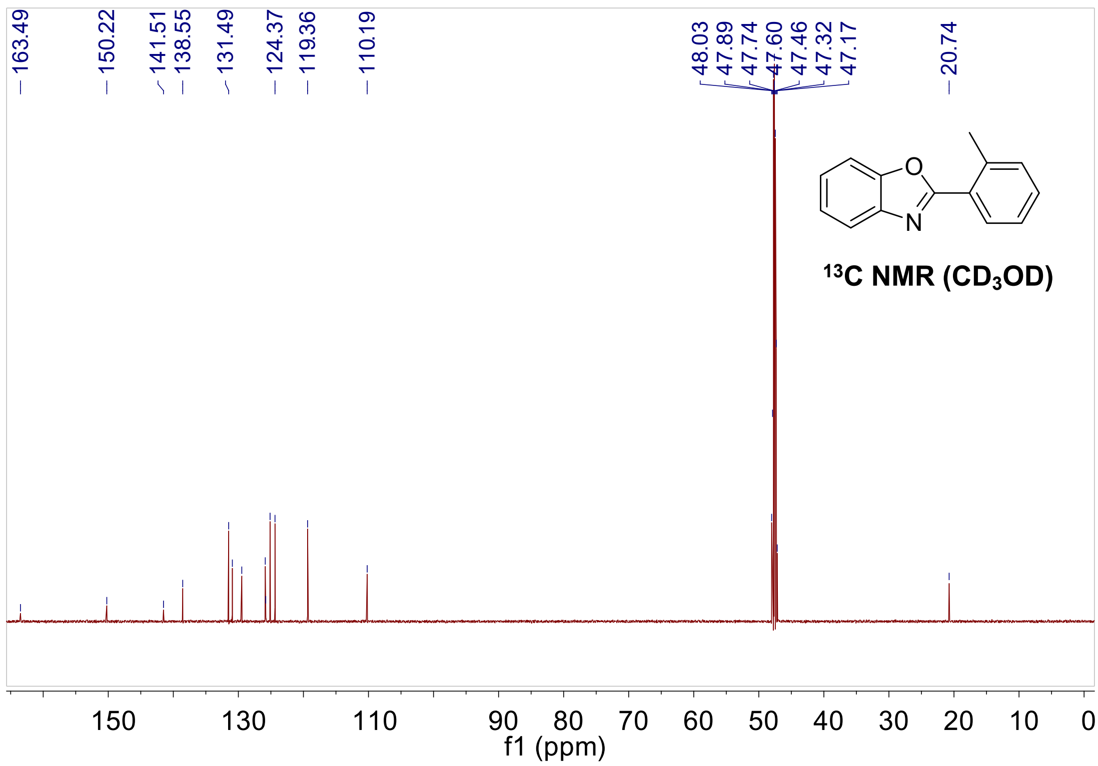
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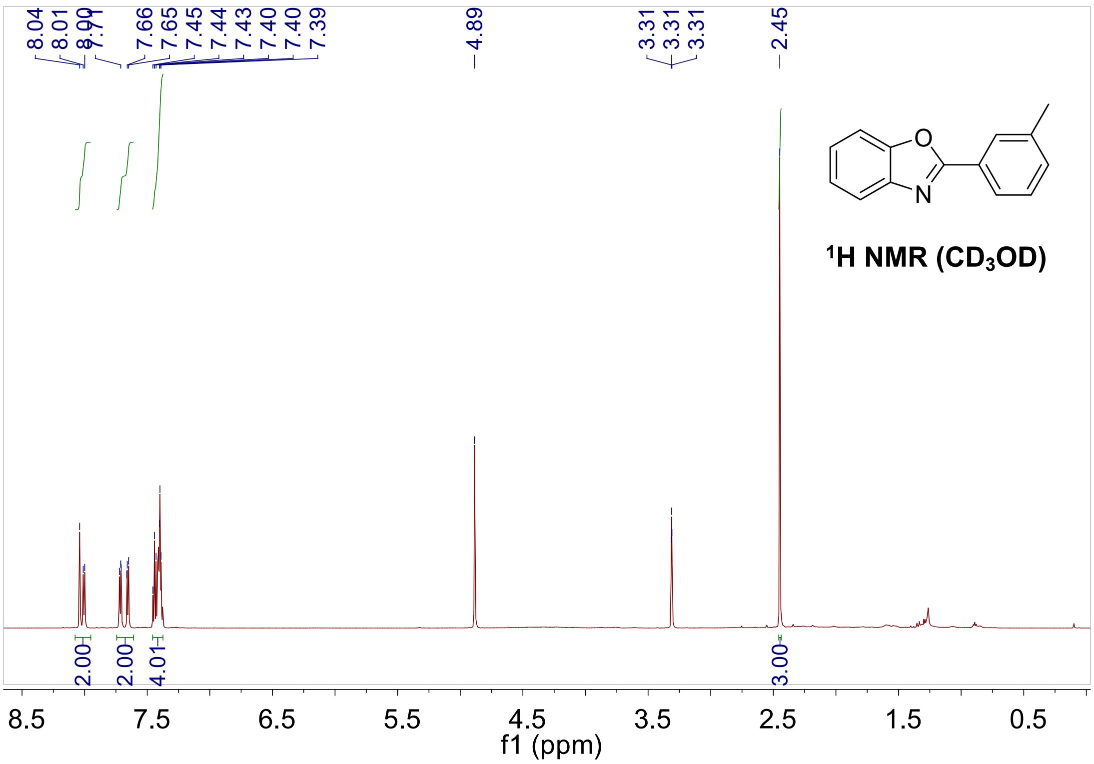
f1 (ppm)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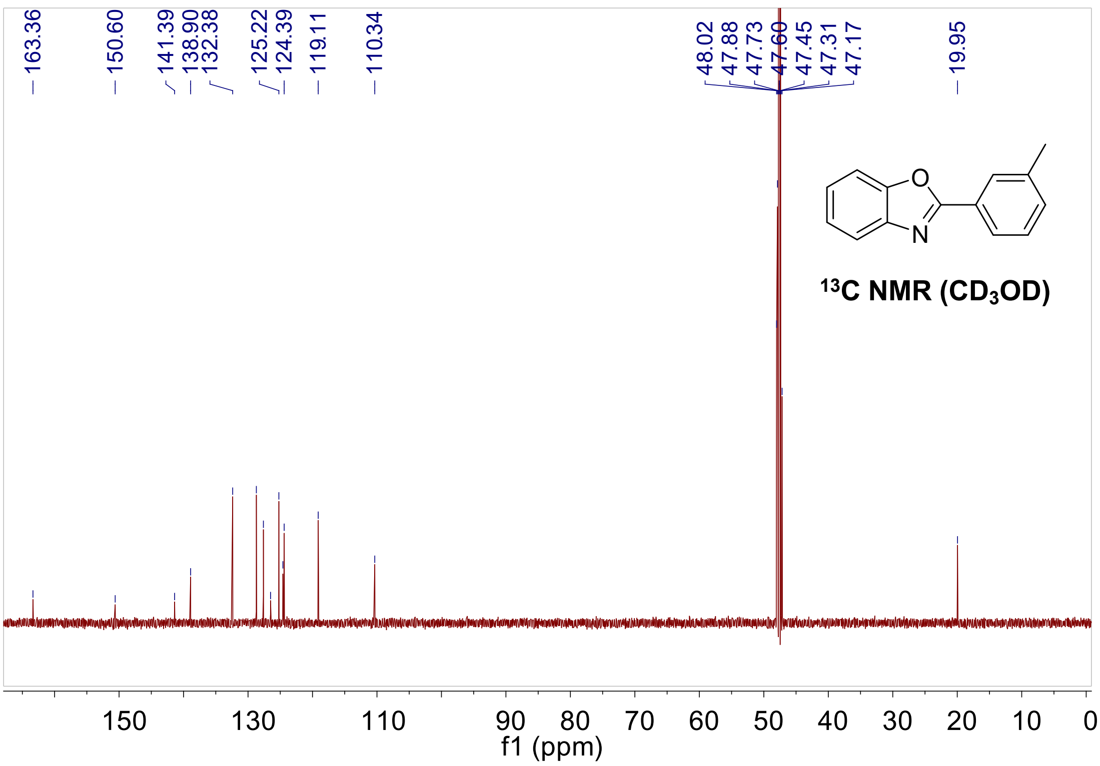
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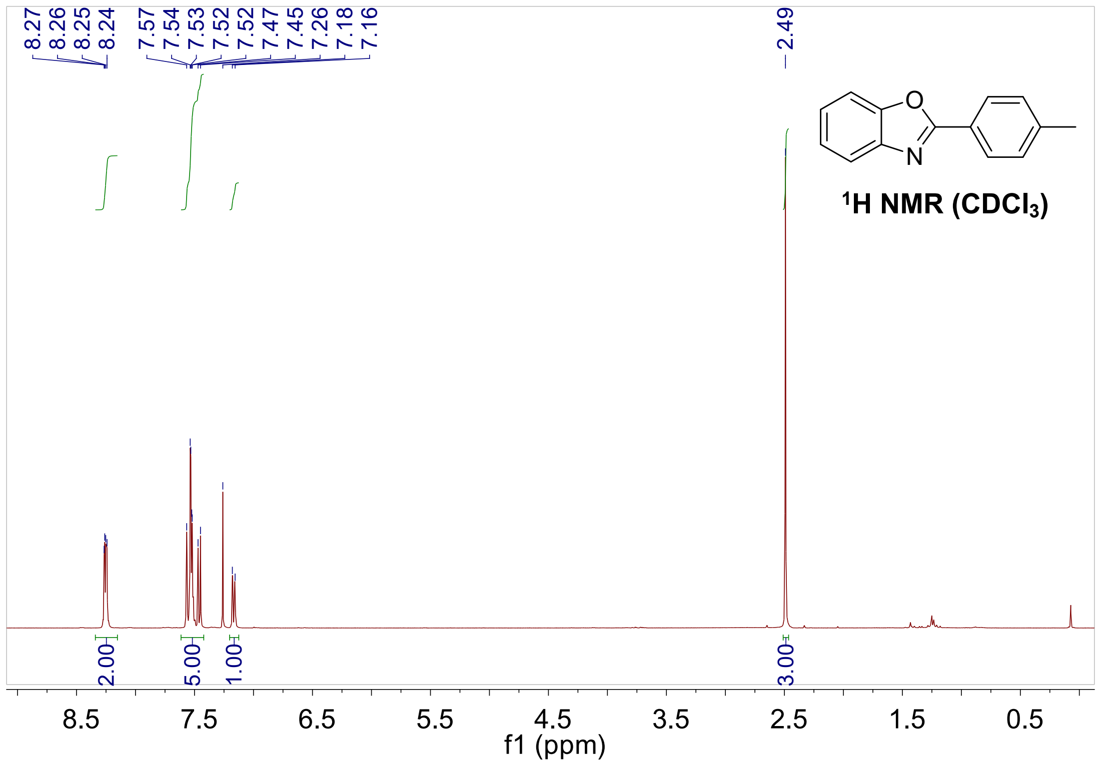
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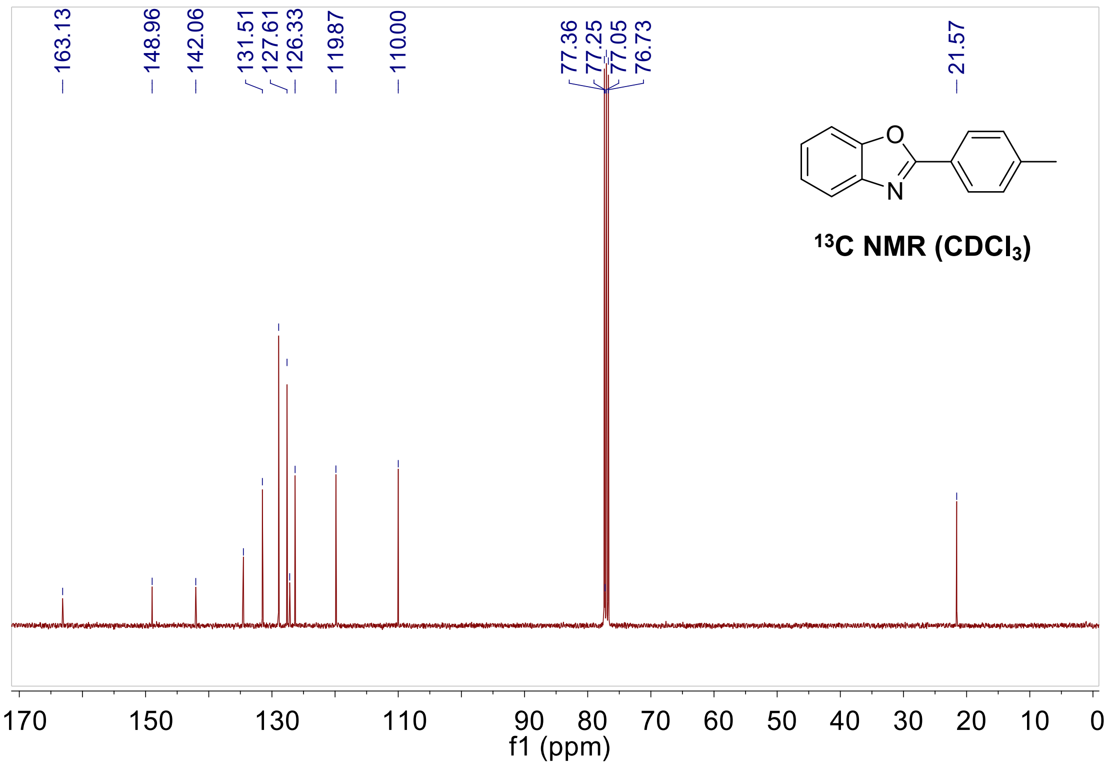
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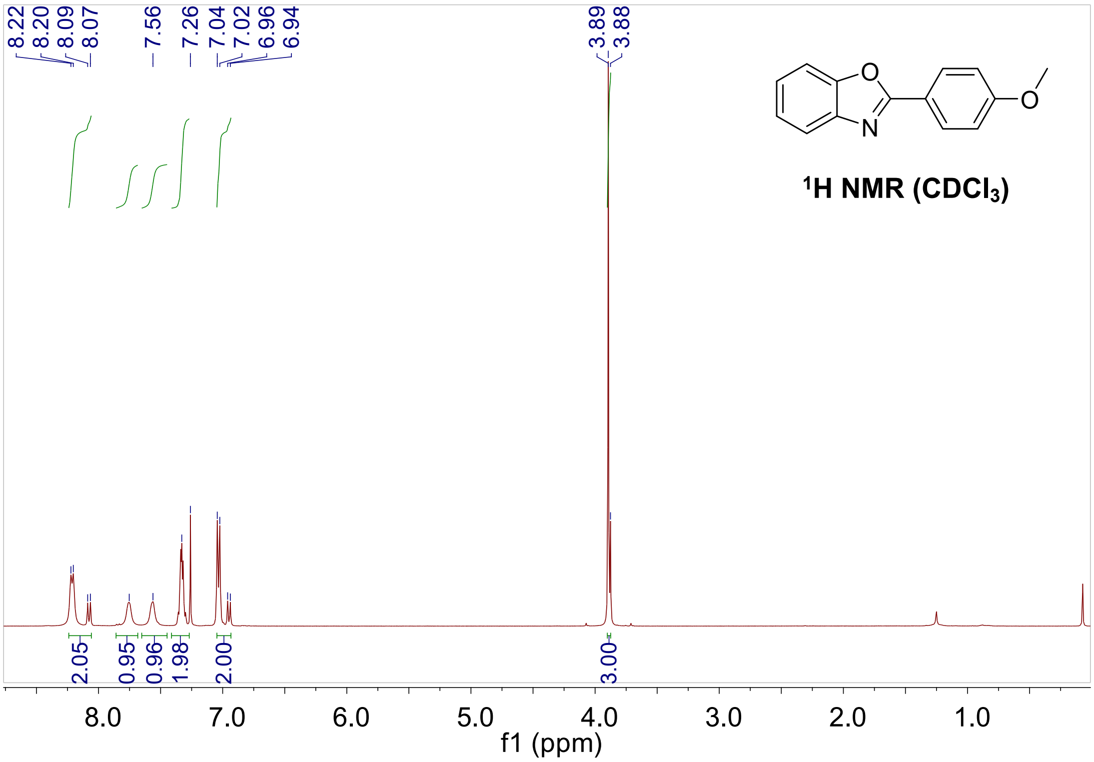
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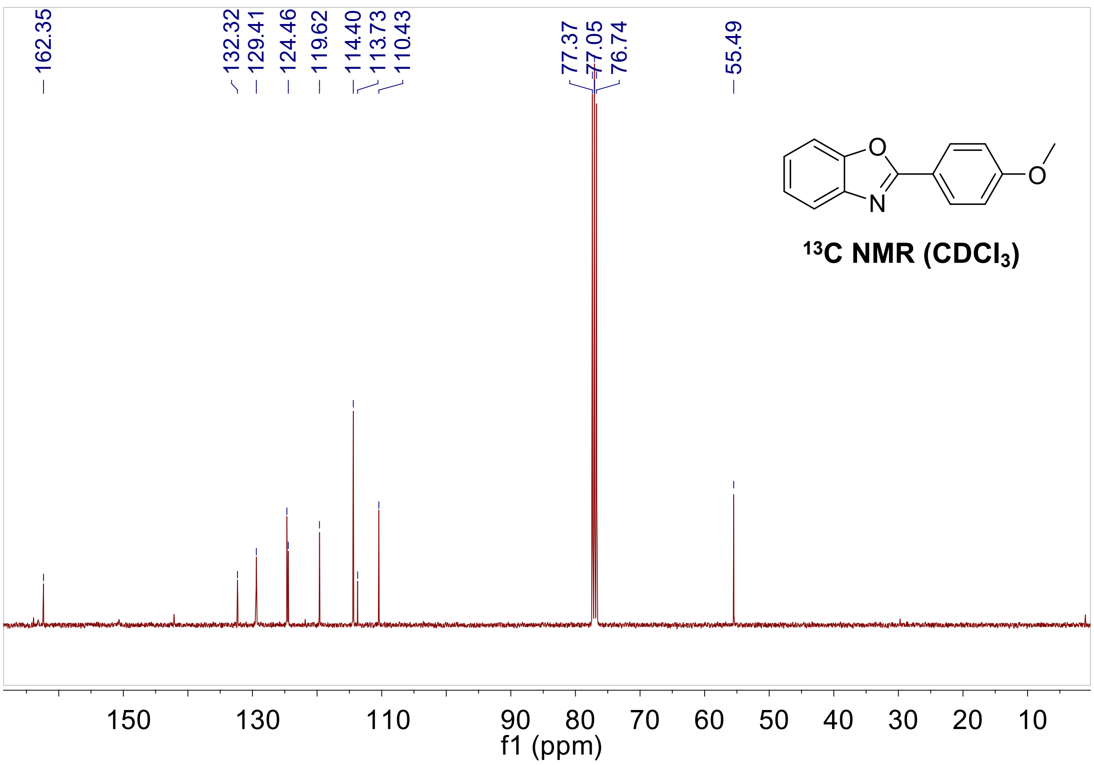
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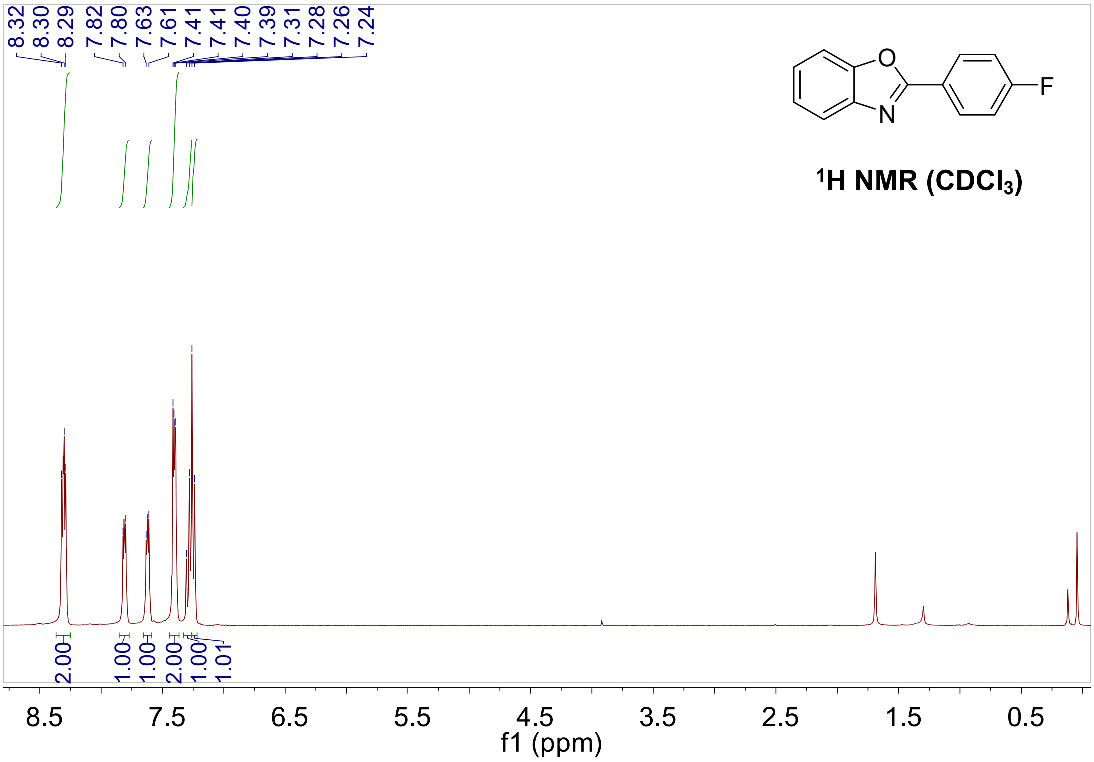
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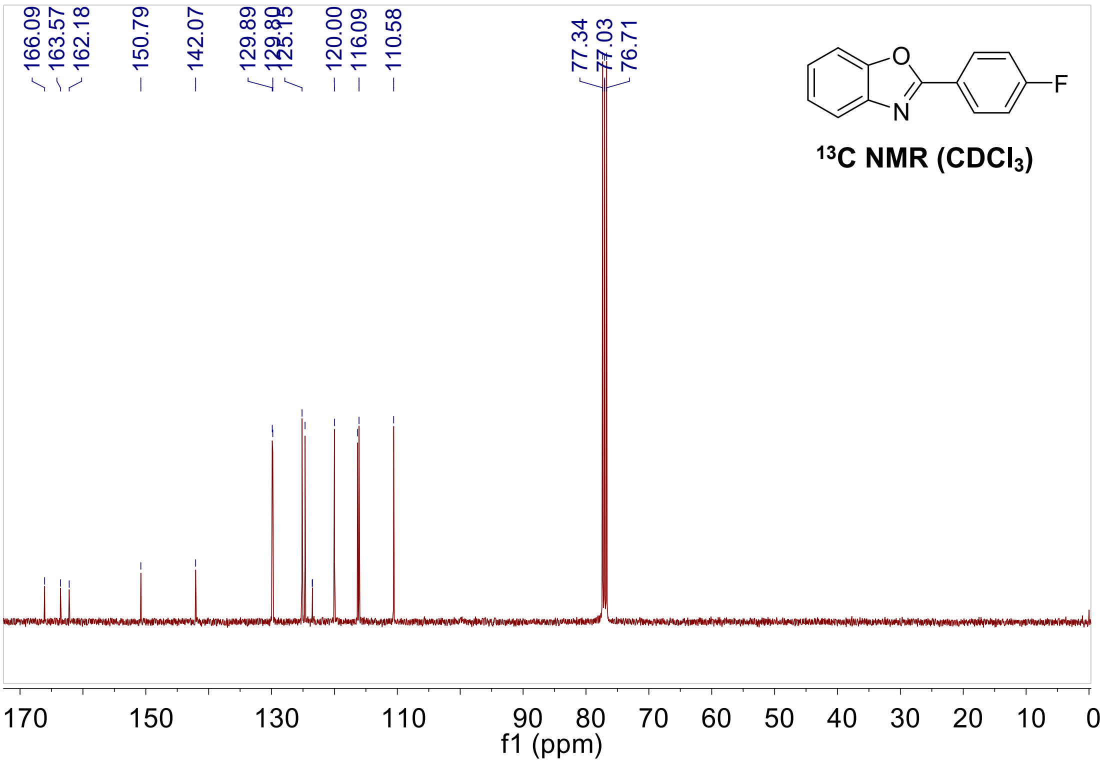
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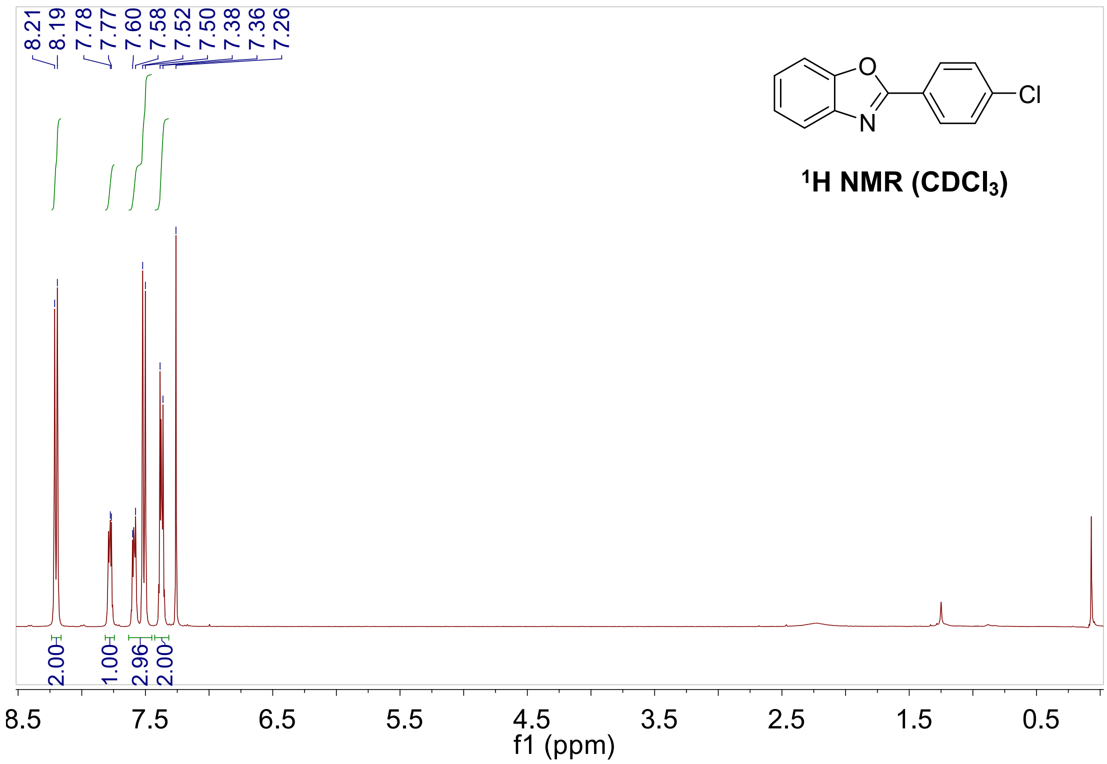
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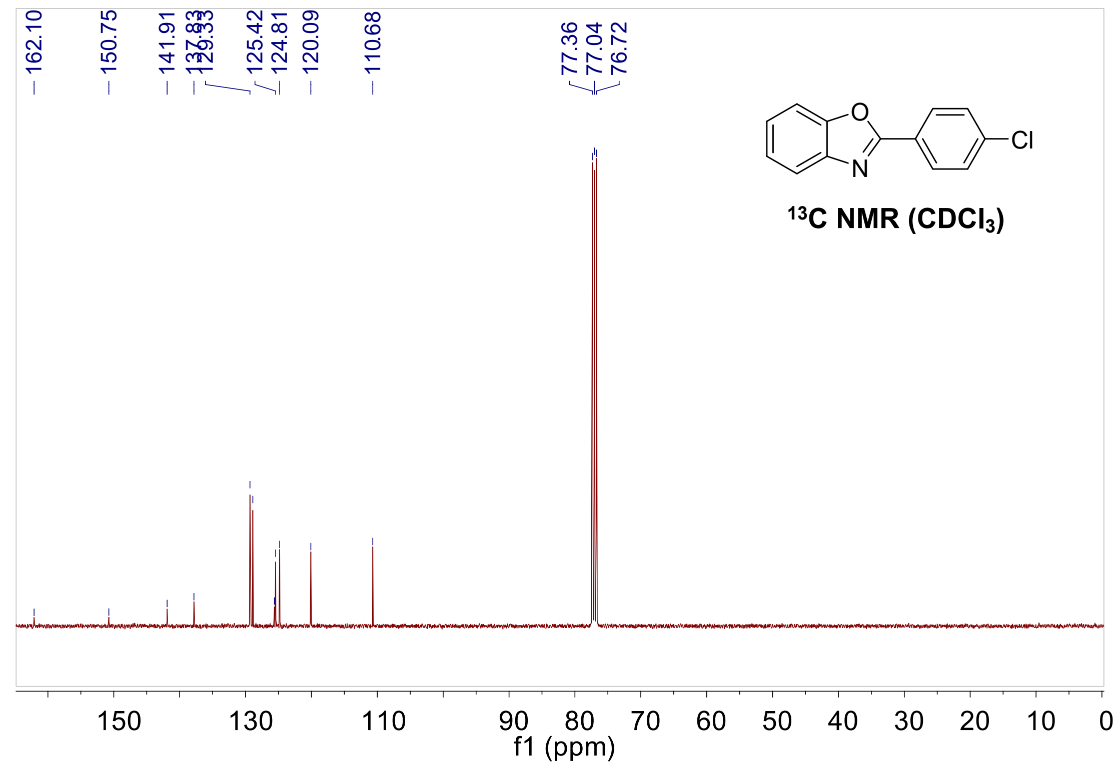
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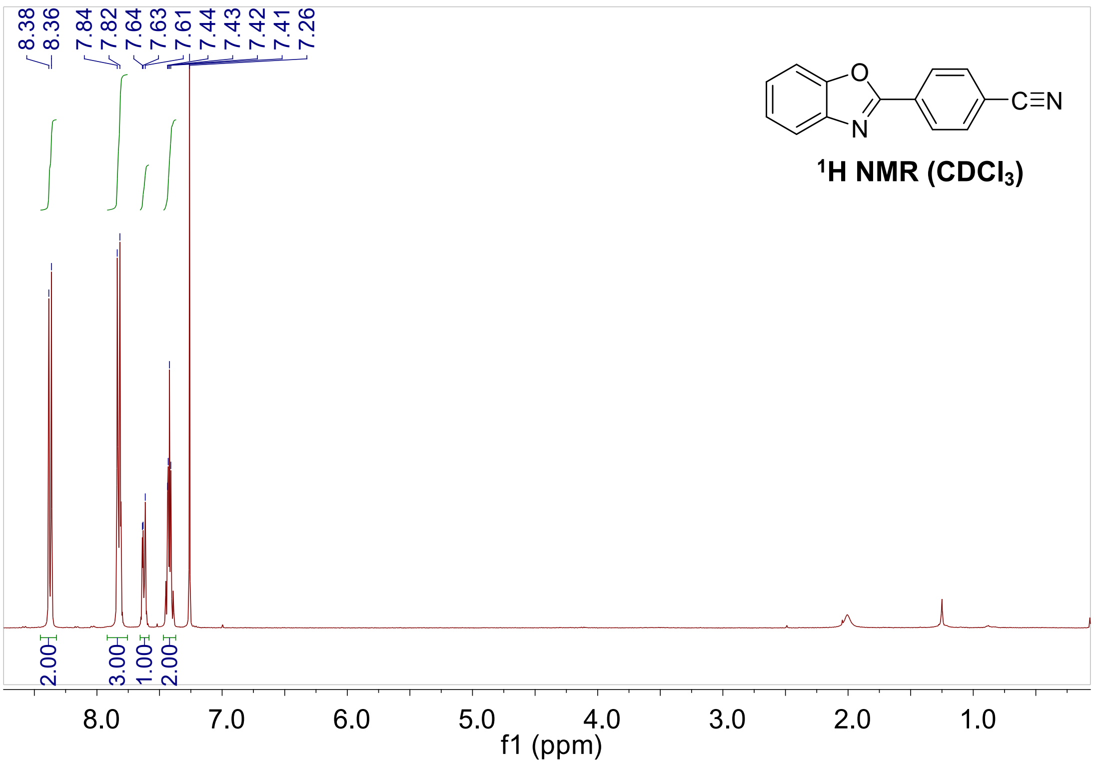
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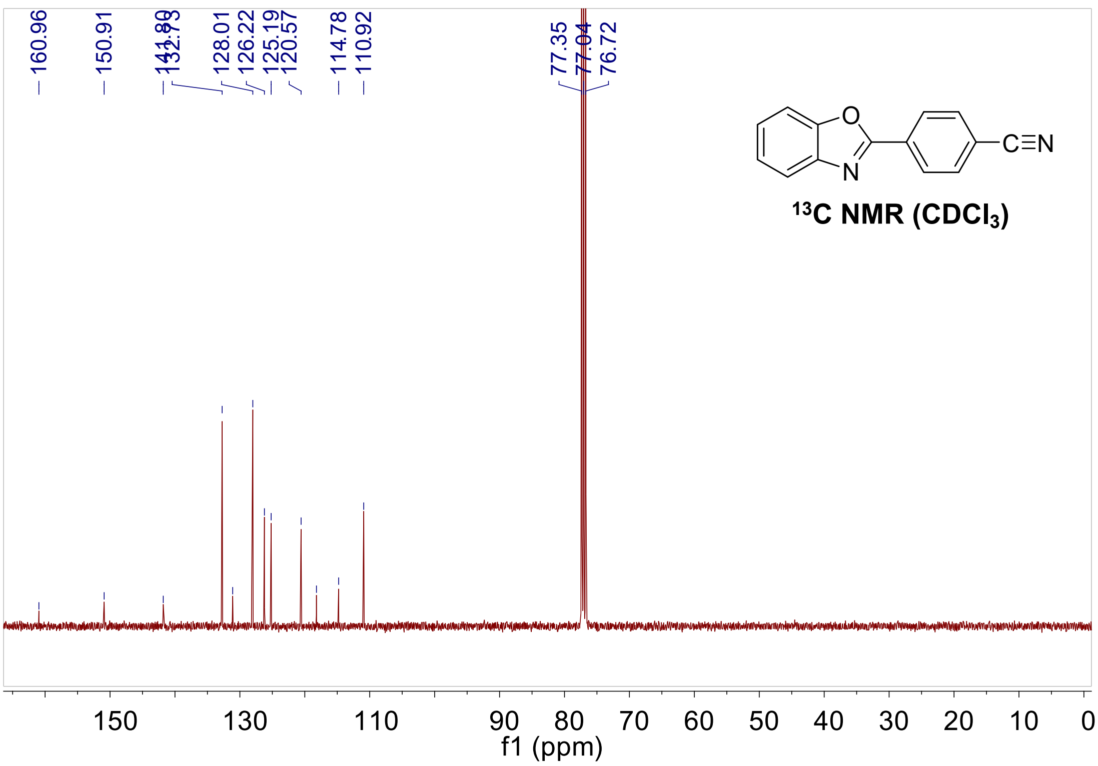
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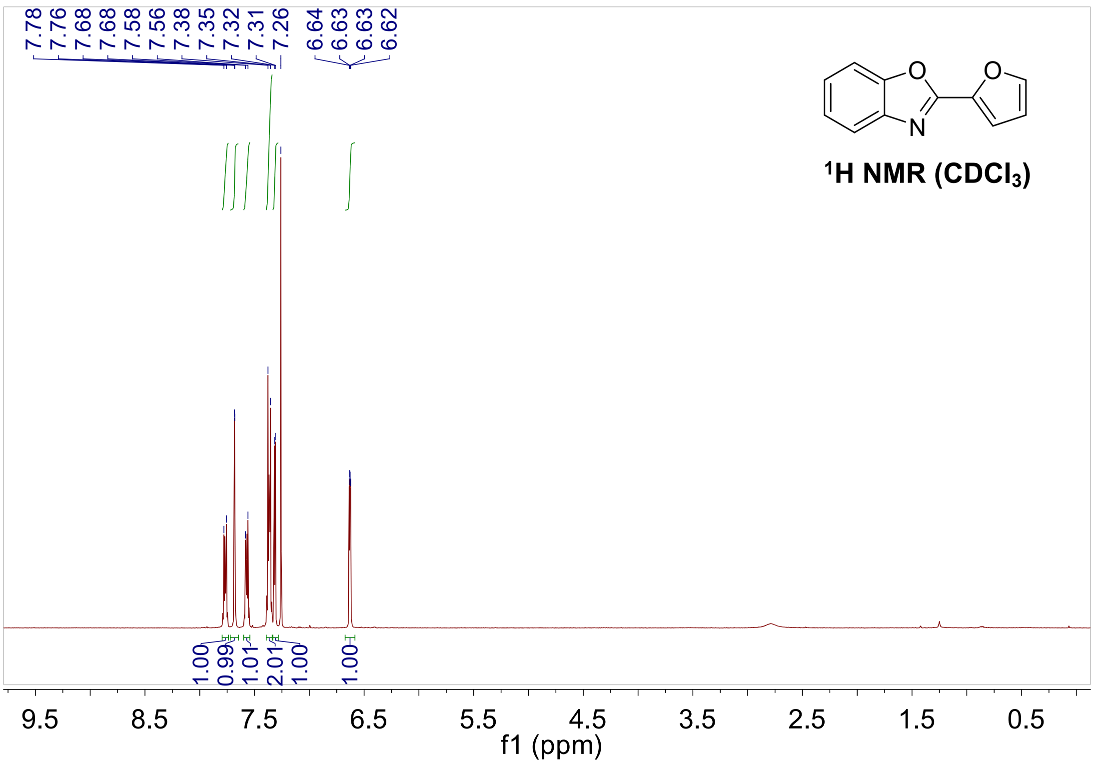
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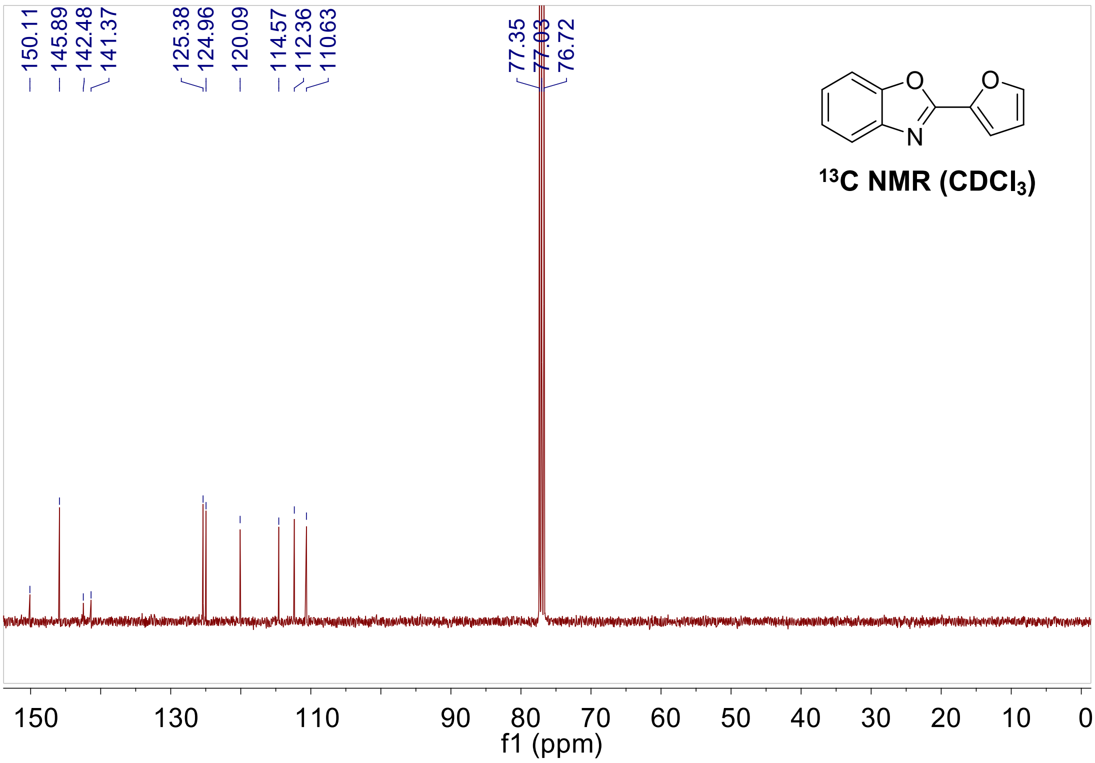
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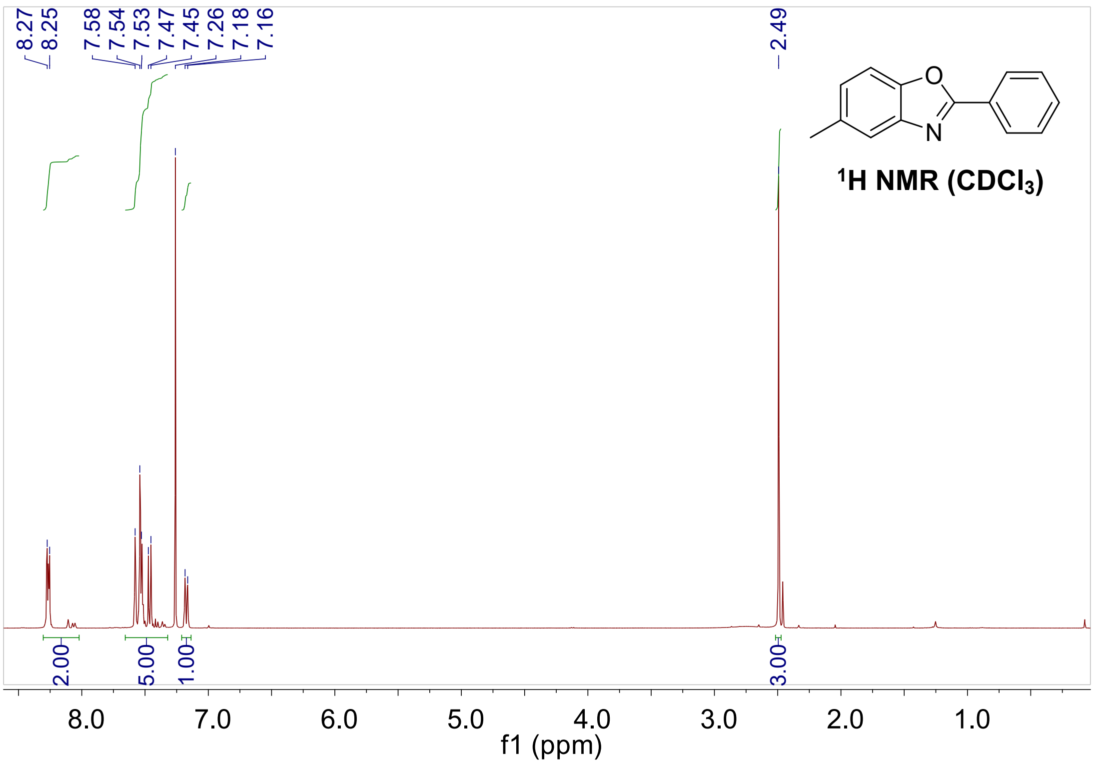

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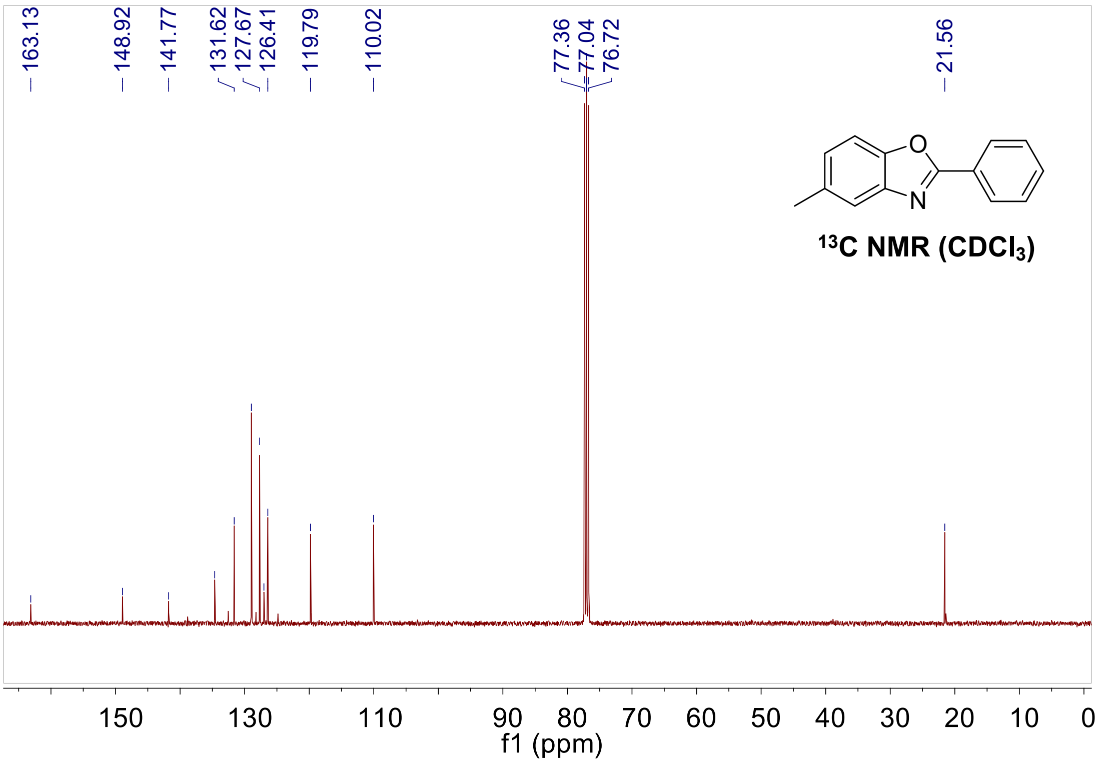
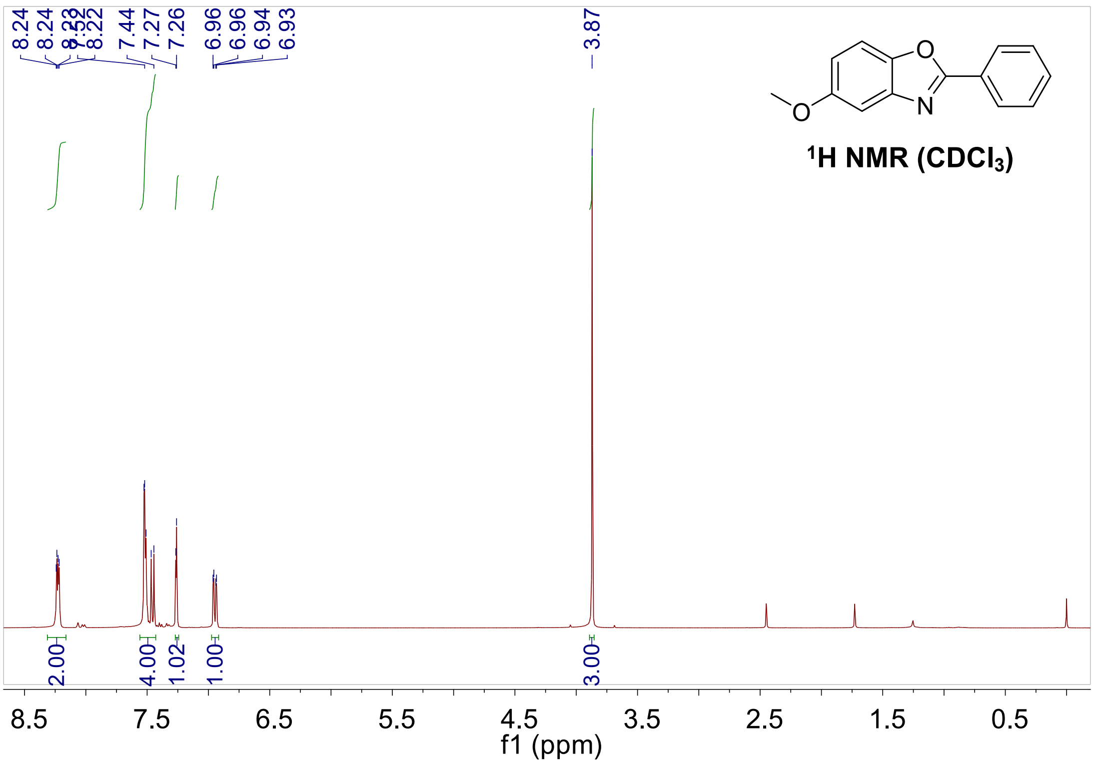
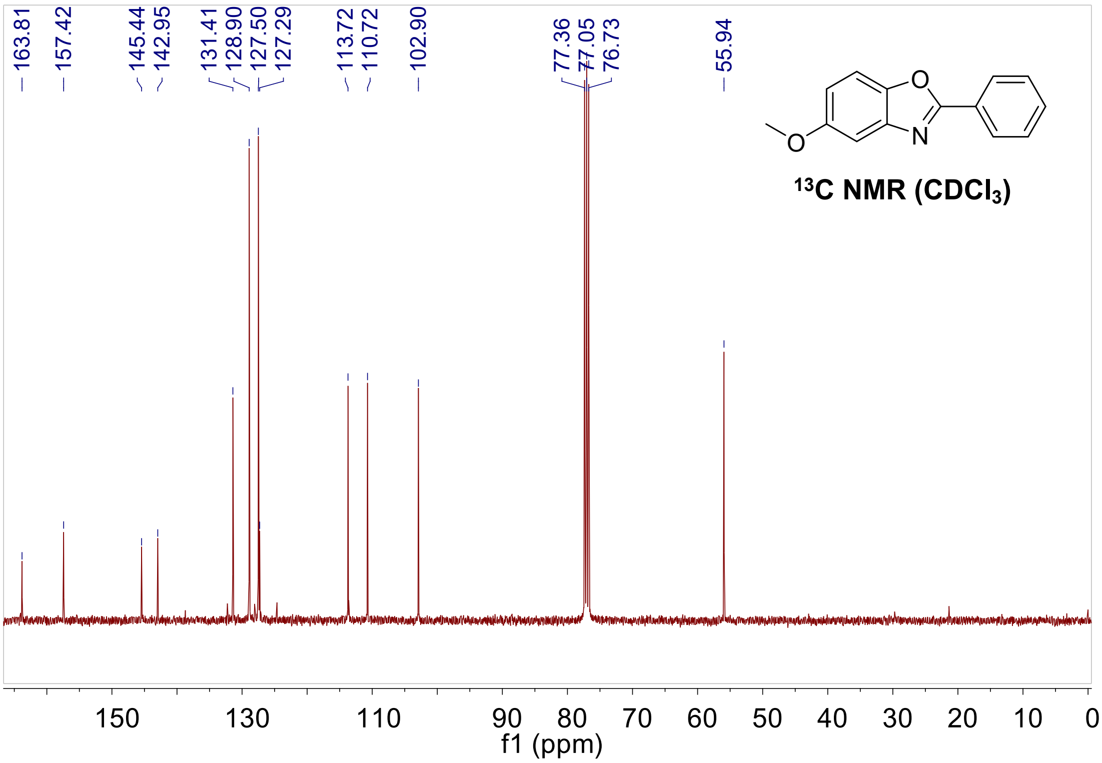
7.53
7.47
7.45
7.26
7.18
7.16
2.49
O
N
1H NMR (CDCl3)
2.00
5.00
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)



163.13
148.92
141.77
131.62
127.67
126.41
119.79
110.02
77.36
77.04
76.72
21.56
O
N
13C NMR (CDCl3)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.24
8.24
8.23
8.22
8.22
7.52
7.44
7.27
7.26
6.96
6.96
6.94
6.93
3.87
¹H NMR (CDCl₃)
2.00
4.00
1.02
1.00
3.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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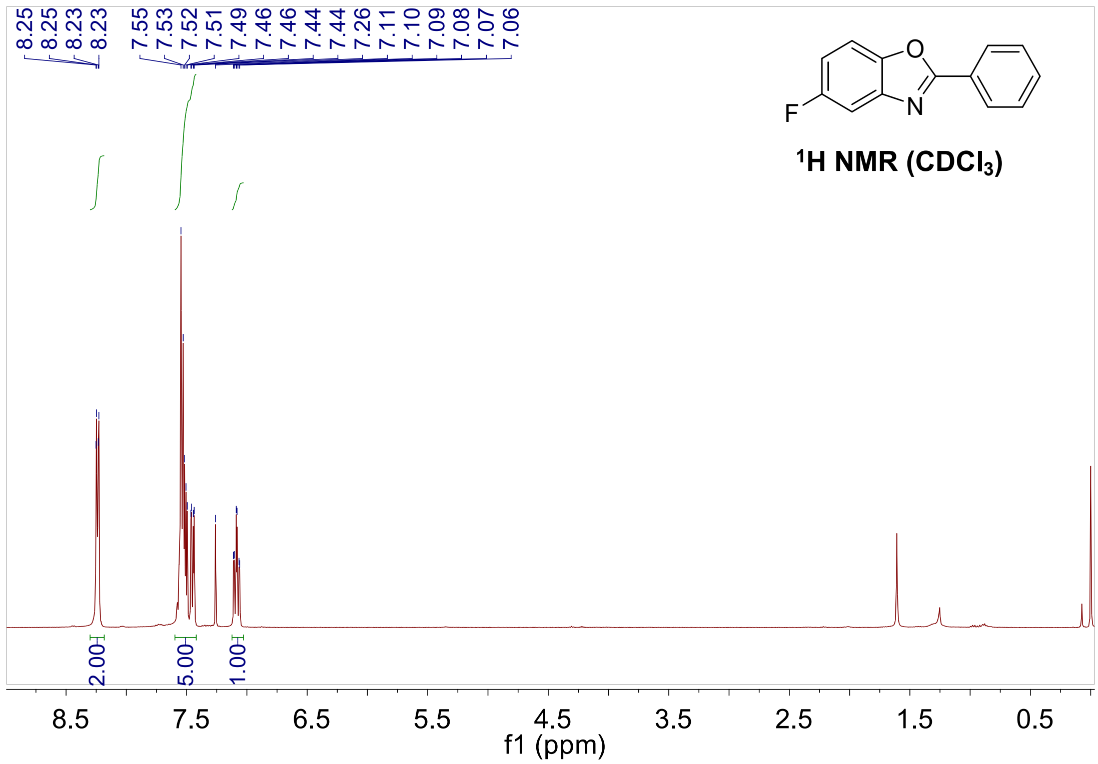
157.42
145.44
142.95
131.41
128.90
127.50
127.29
113.72
110.72
102.90
77.36
77.05
76.73
55.94
¹³C NMR (CDCl₃)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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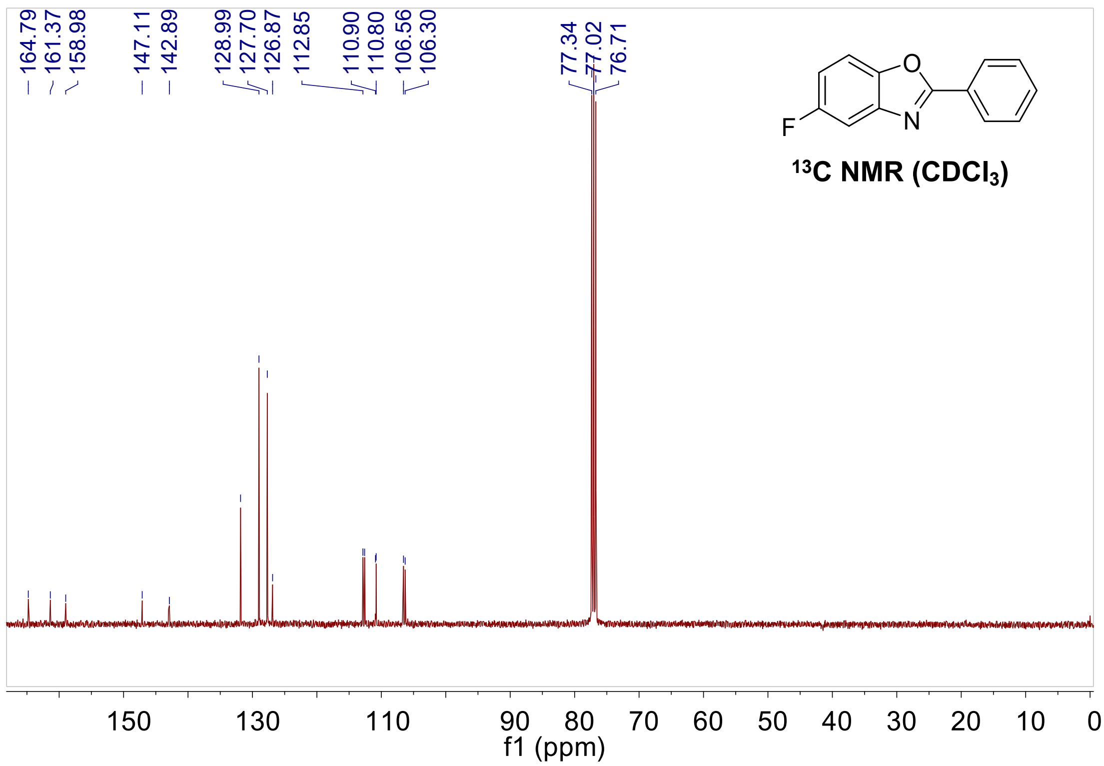
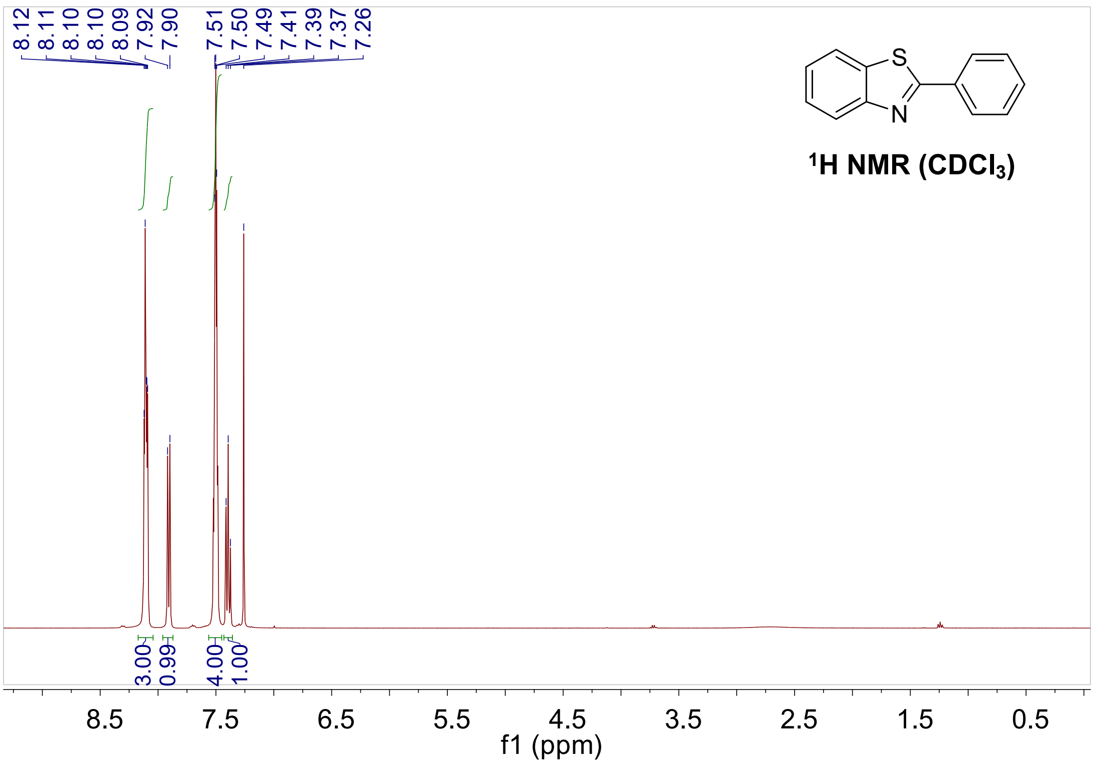
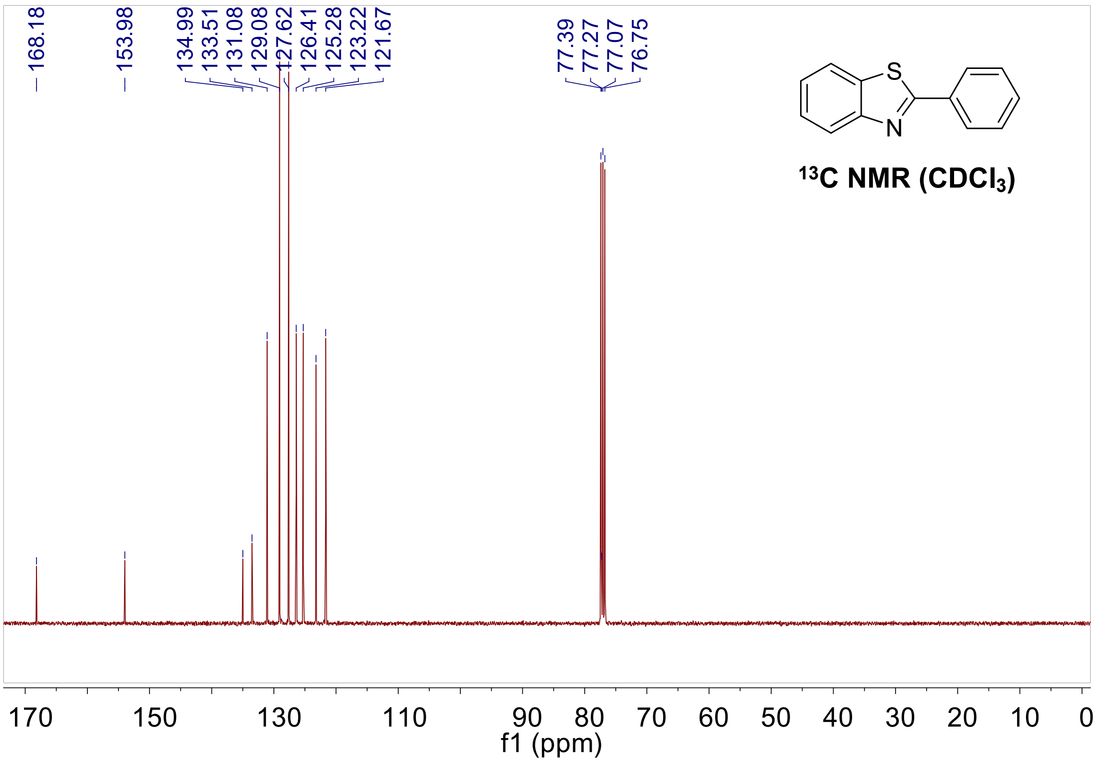
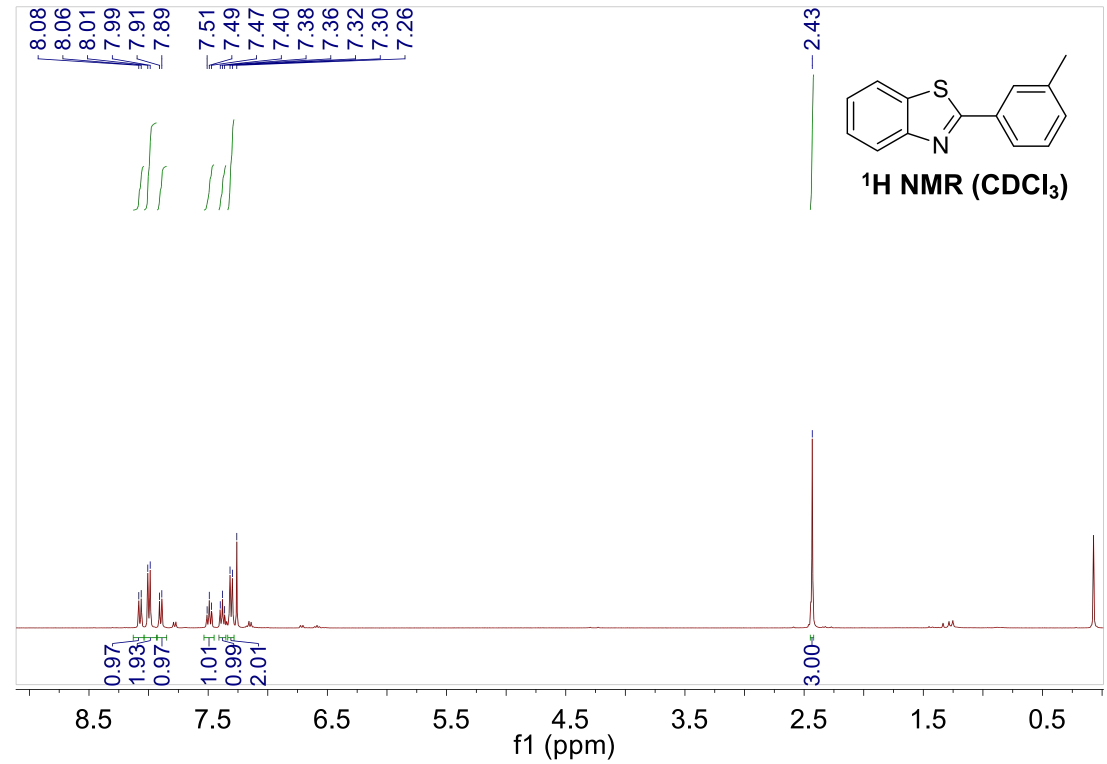
8.25
8.23
8.23
7.55
7.53
7.52
7.51
7.49
7.46
7.46
7.44
7.44
7.26
7.11
7.10
7.09
7.08
7.07
7.06
F
O
N
1H NMR (CDCl3)
2.00
5.00
1.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

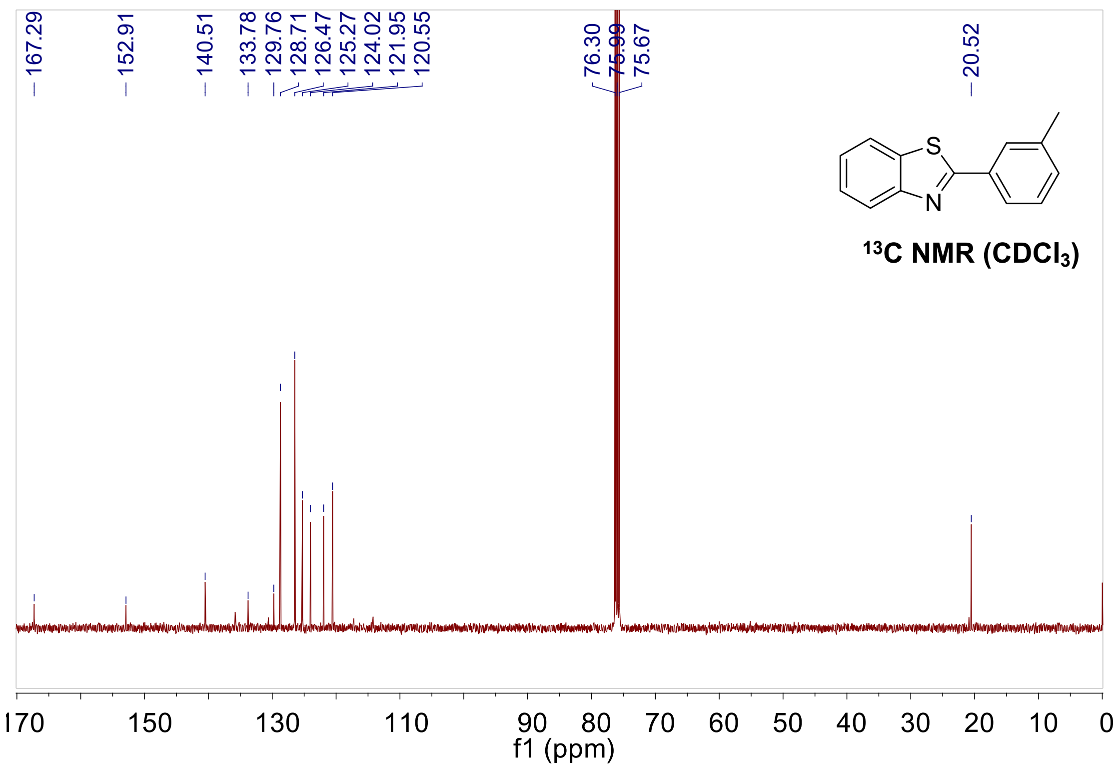

164.79
161.37
158.98
147.11
142.89
128.99
127.70
126.87
112.85
110.90
110.80
106.56
106.30
77.34
77.02
76.71
F
O
N
13C NMR (CDCl3)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.12
8.11
8.10
8.10
8.09
7.92
7.90
7.51
7.50
7.49
7.41
7.39
7.37
7.26
S
N
^{1}H NMR ($CDCl_3$)
3.00
0.99
4.00
1.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

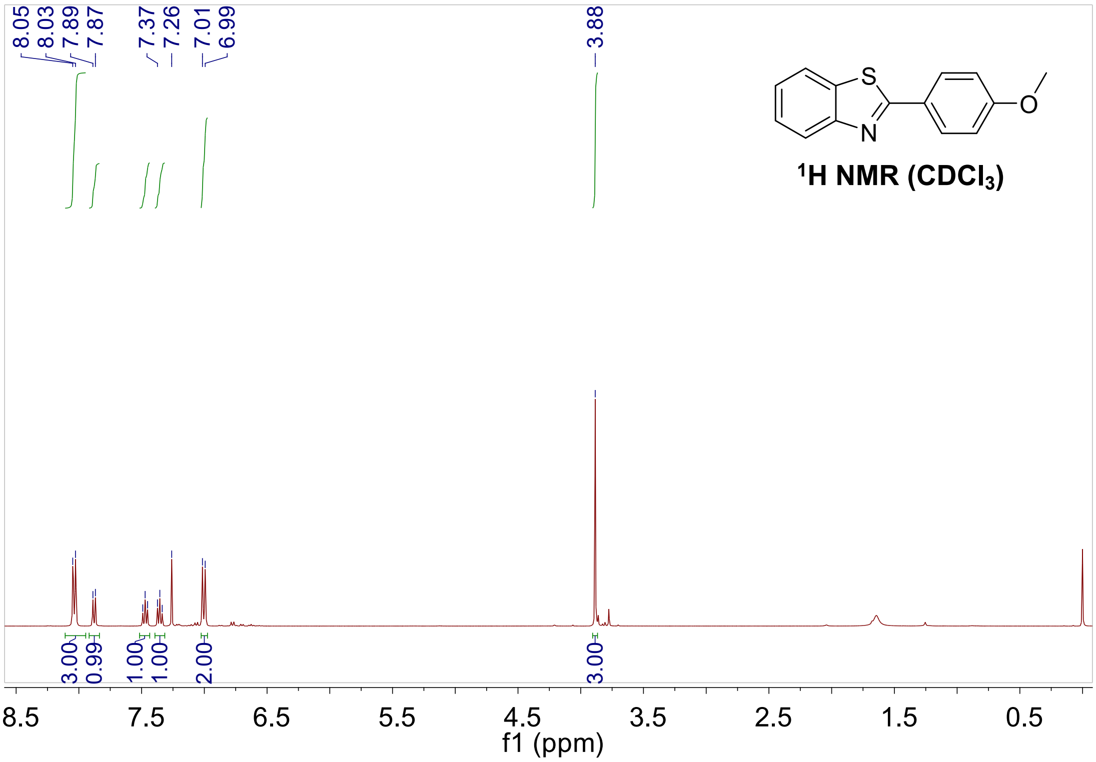

168.18
153.98
134.99
133.51
131.08
129.08
127.62
126.41
125.28
123.22
121.67
77.39
77.27
77.07
76.75
S
N
^{13}C NMR ($CDCl_3$)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

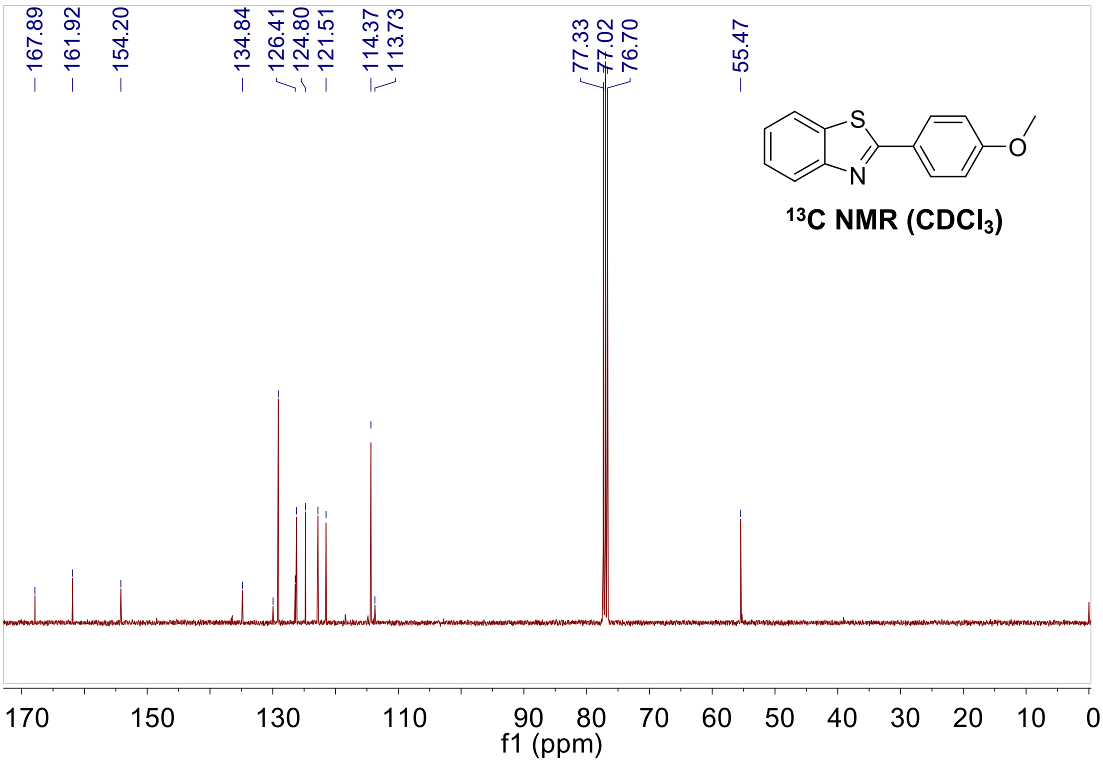


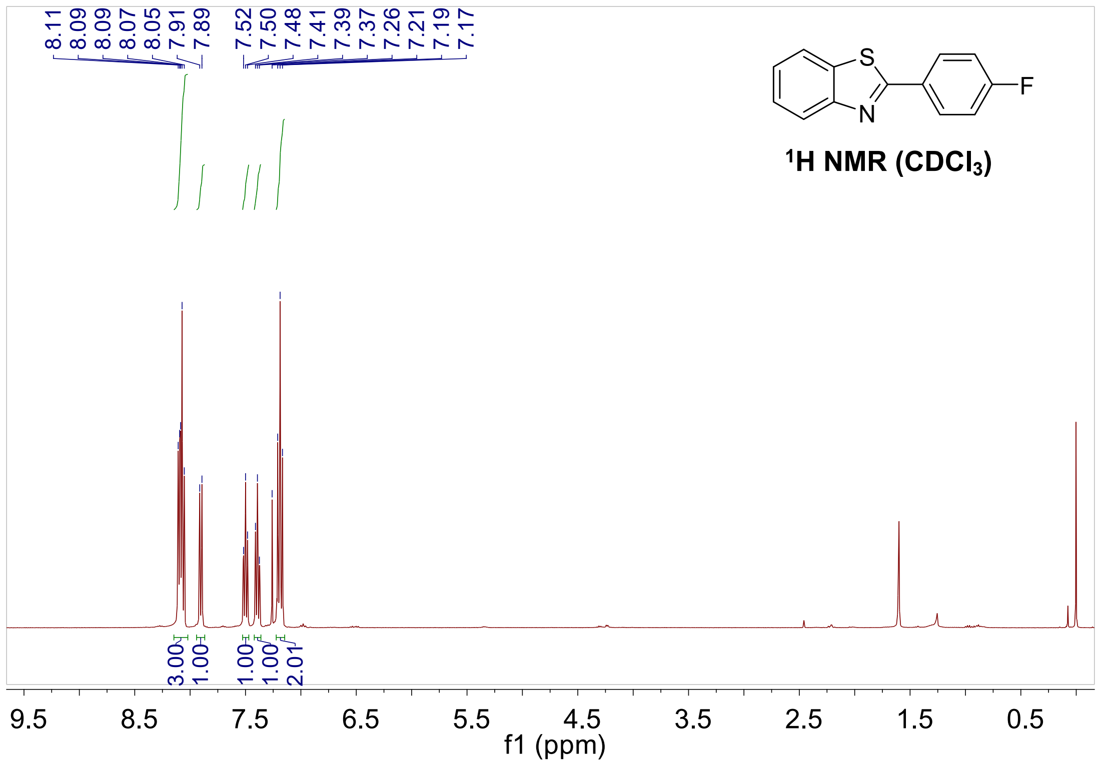
8.08
8.06
8.01
7.99
7.91
7.89
7.51
7.49
7.47
7.40
7.38
7.36
7.32
7.30
7.26
2.43
S
N
¹H NMR (CDCl₃)
0.97
1.93
0.97
1.01
0.99
2.01
3.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

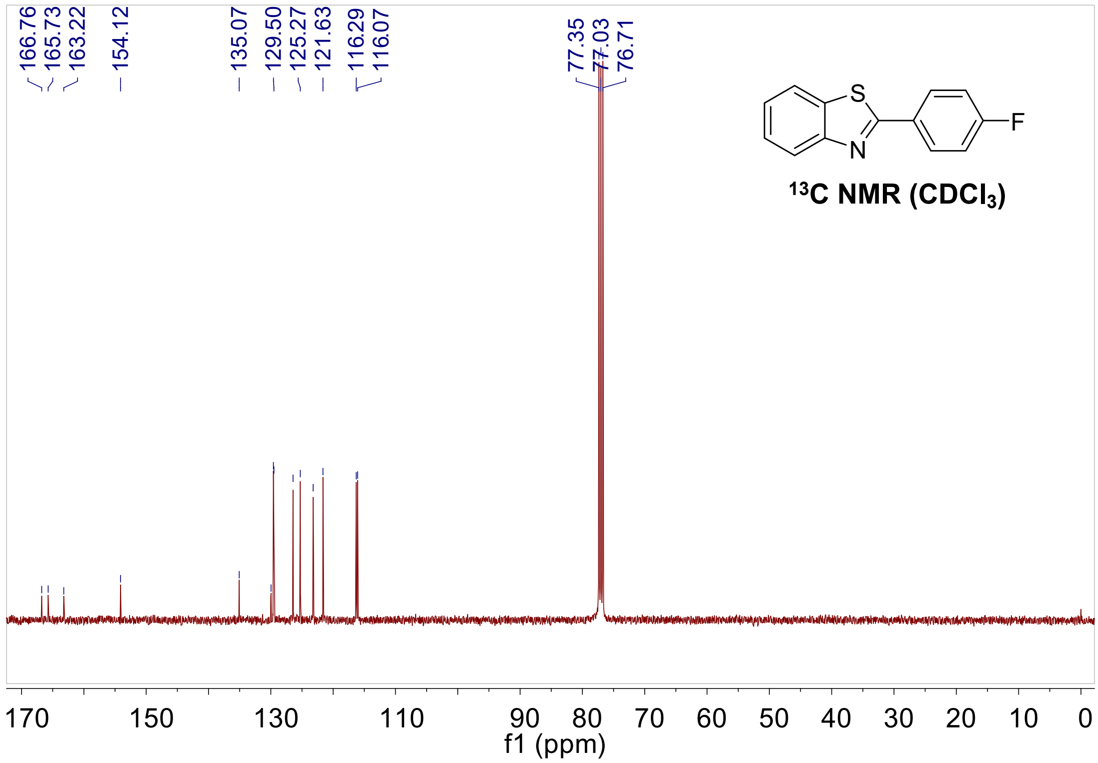


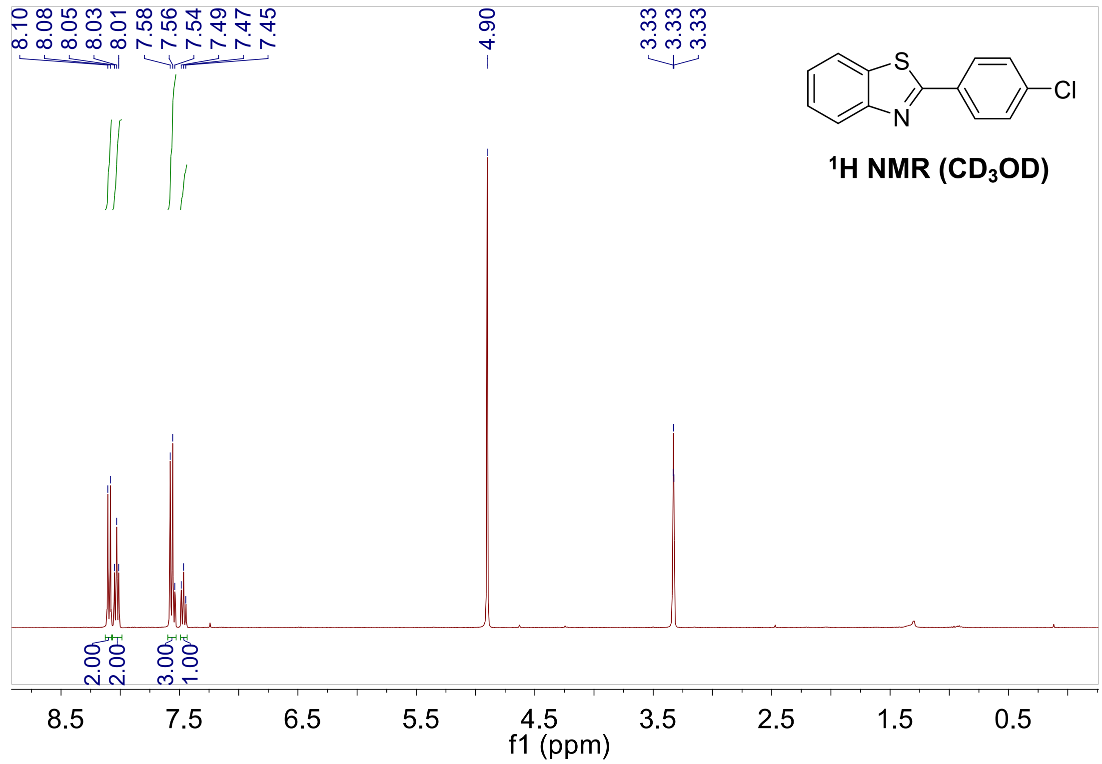
167.29
152.91
140.51
133.78
129.76
128.71
126.47
125.27
124.02
121.95
120.55
76.30
75.99
75.67
20.52
S
N
¹³C NMR (CDCl₃)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.05
8.03
7.89
7.87
7.37
7.26
7.01
6.99
3.88
S
N
O
¹H NMR (CDCl$_3$)
3.00
0.99
1.00
1.00
2.00
3.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

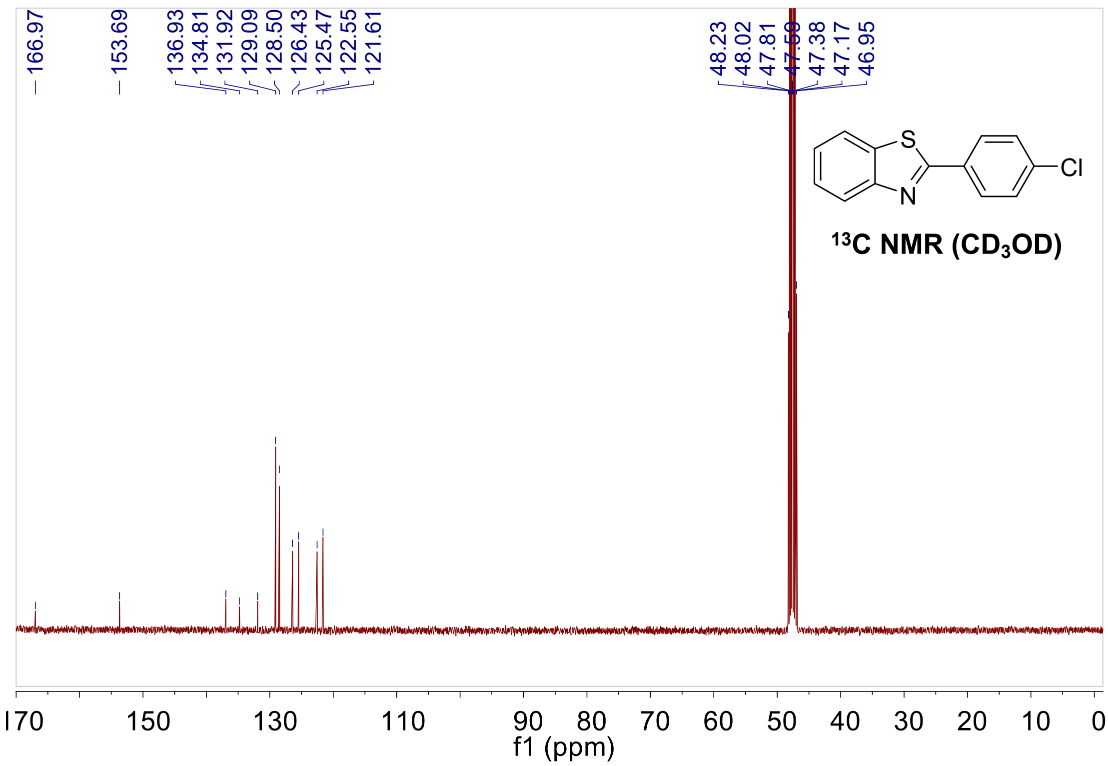

167.89
161.92
154.20
134.84
126.41
124.80
121.51
114.37
113.73
77.33
77.02
76.70
55.47
S
N
O
¹³C NMR (CDCl$_3$)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.11
8.09
8.09
8.07
8.05
7.91
7.89
7.52
7.50
7.48
7.41
7.39
7.37
7.26
7.21
7.19
7.17
S
N
F
^{1}H NMR ($CDCl_3$)
3.00
1.00
1.00
1.00
2.01
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

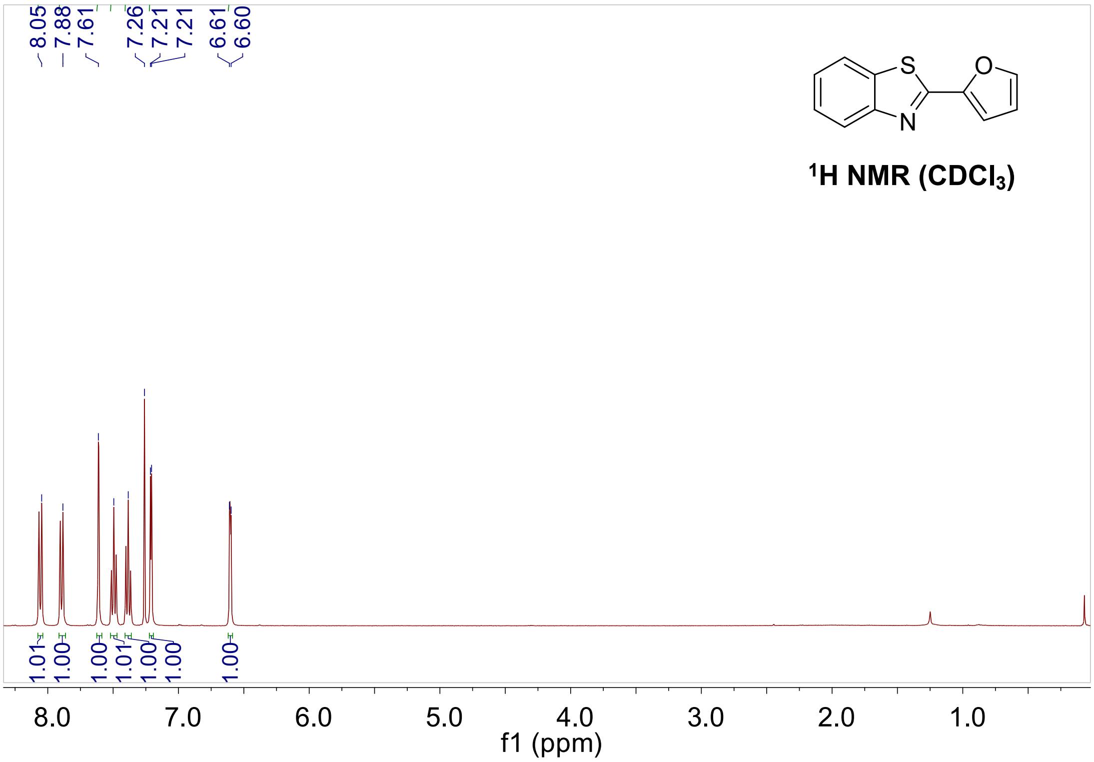

166.76
165.73
163.22
154.12
135.07
129.50
125.27
121.63
116.29
116.07
77.35
77.03
76.71
S
N
F
^{13}C NMR ($CDCl_3$)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

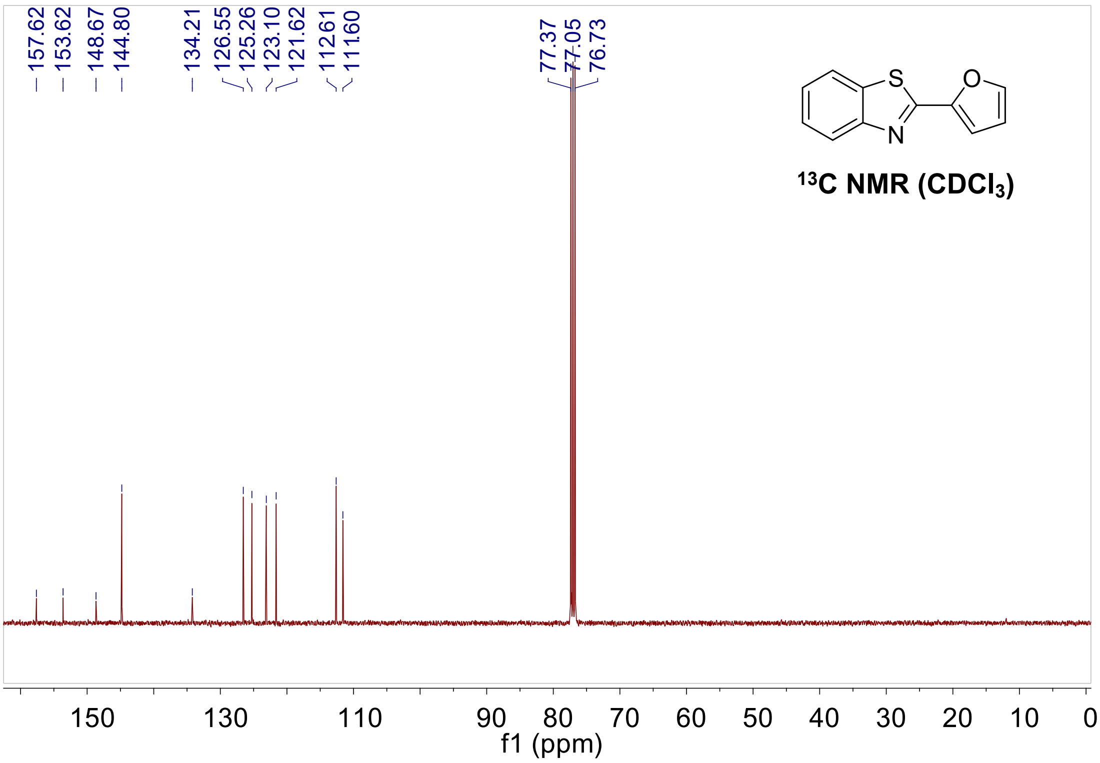


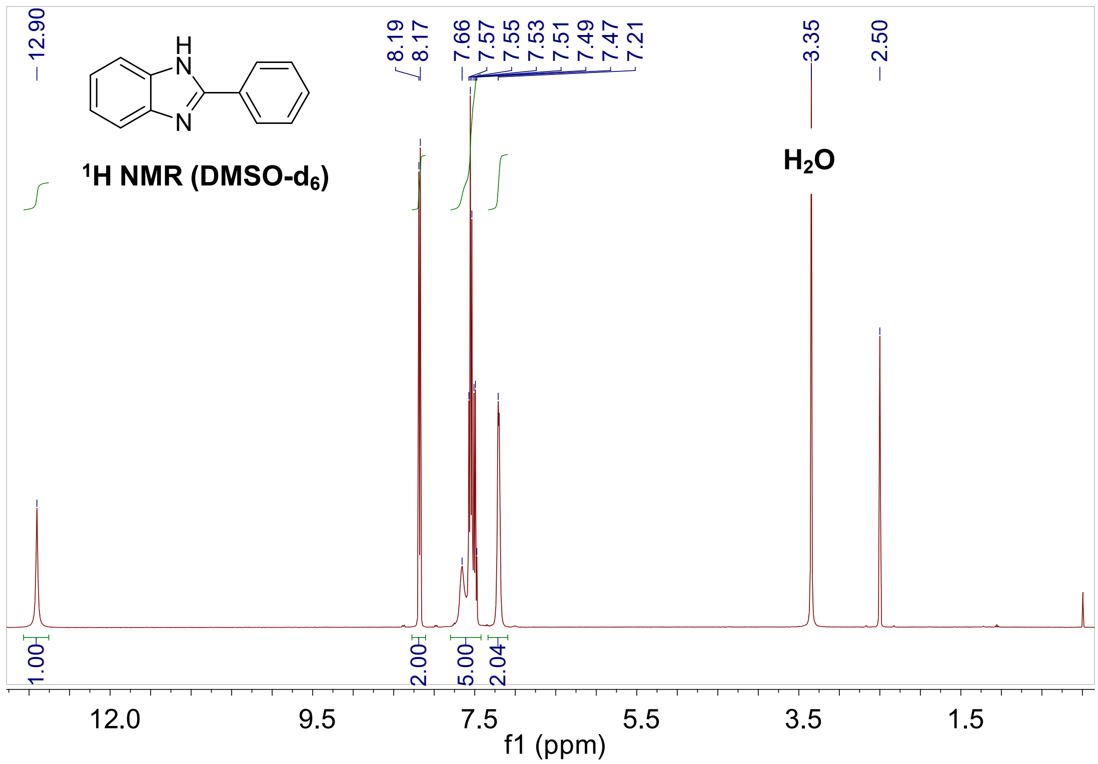
8.10
8.08
8.05
8.03
8.01
7.58
7.56
7.54
7.49
7.47
7.45
4.90
3.33
3.33
3.33
S
N
Cl
^{1}H NMR (CD_3OD)
2.00
2.00
3.00
1.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



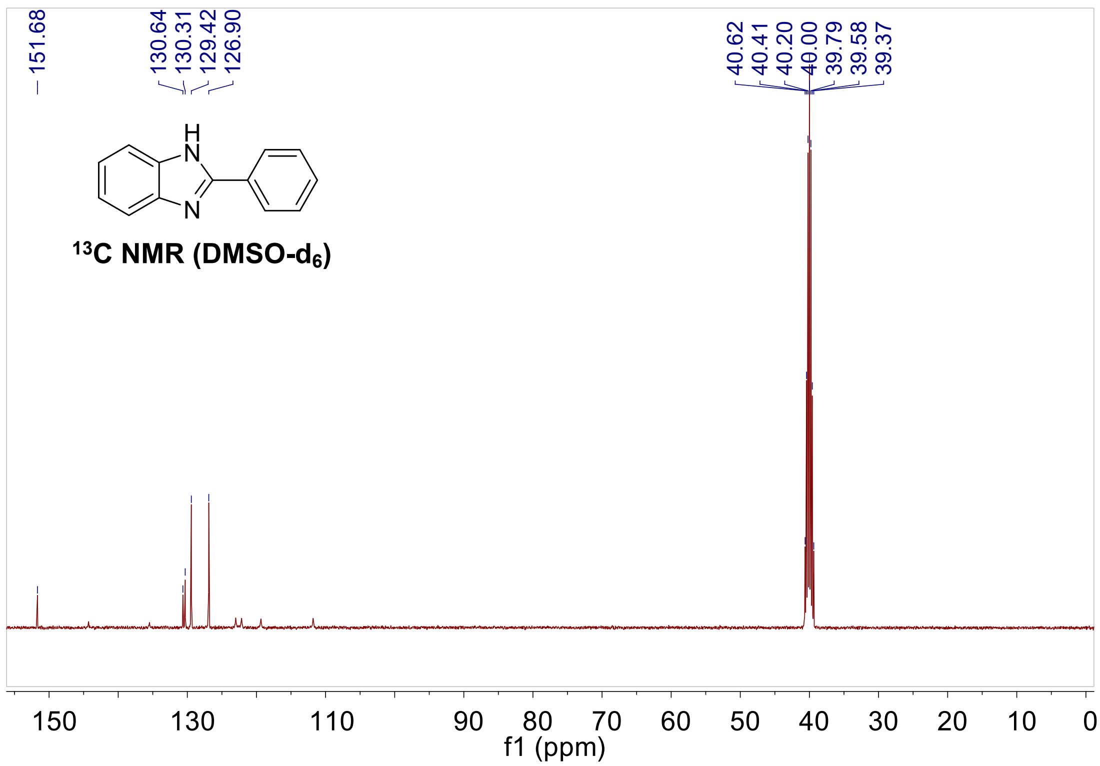
166.97
153.69
136.93
134.81
131.92
129.09
128.50
126.43
125.47
122.55
121.61
48.23
48.02
47.81
47.59
47.38
47.17
46.95
S
N
Cl
^{13}C NMR (CD_3OD)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.05
7.88
7.61
7.26
7.21
7.21
6.61
6.60
S
O
N
1H NMR (CDCl3)
1.01
1.00
1.00
1.01
1.00
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)

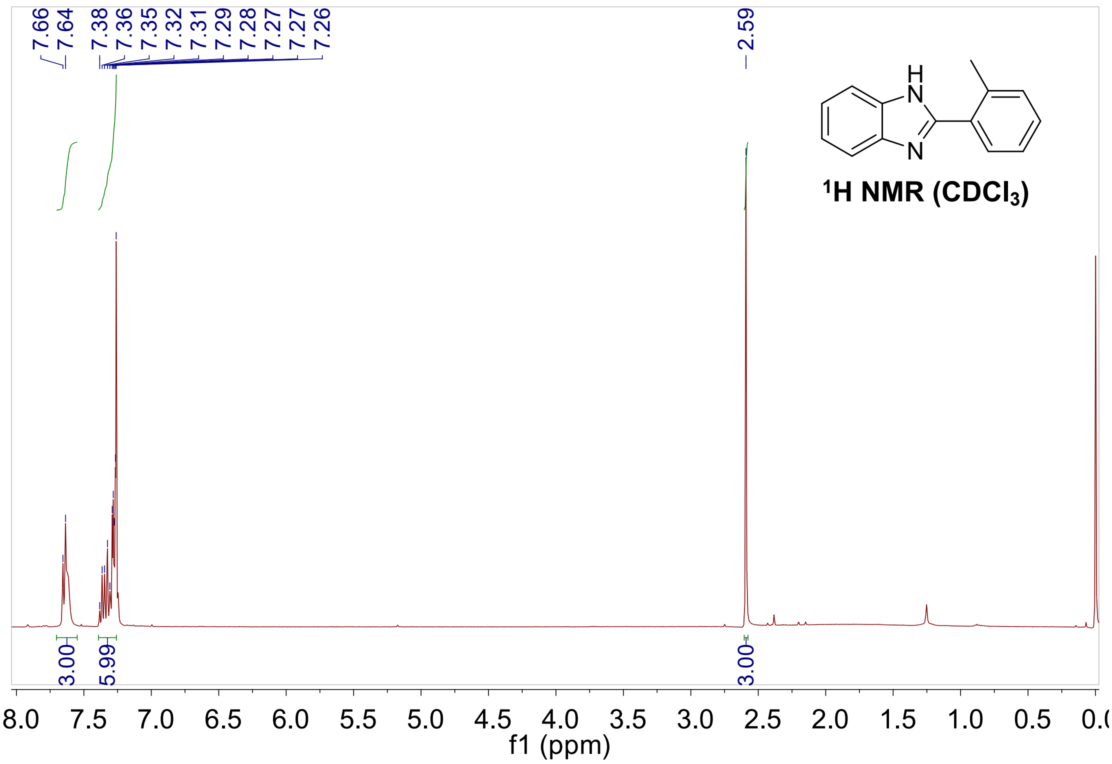

157.62
153.62
148.67
144.80
134.21
126.55
125.26
123.10
121.62
112.61
111.60
77.37
77.05
76.73
S
O
N
13C NMR (CDCl3)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

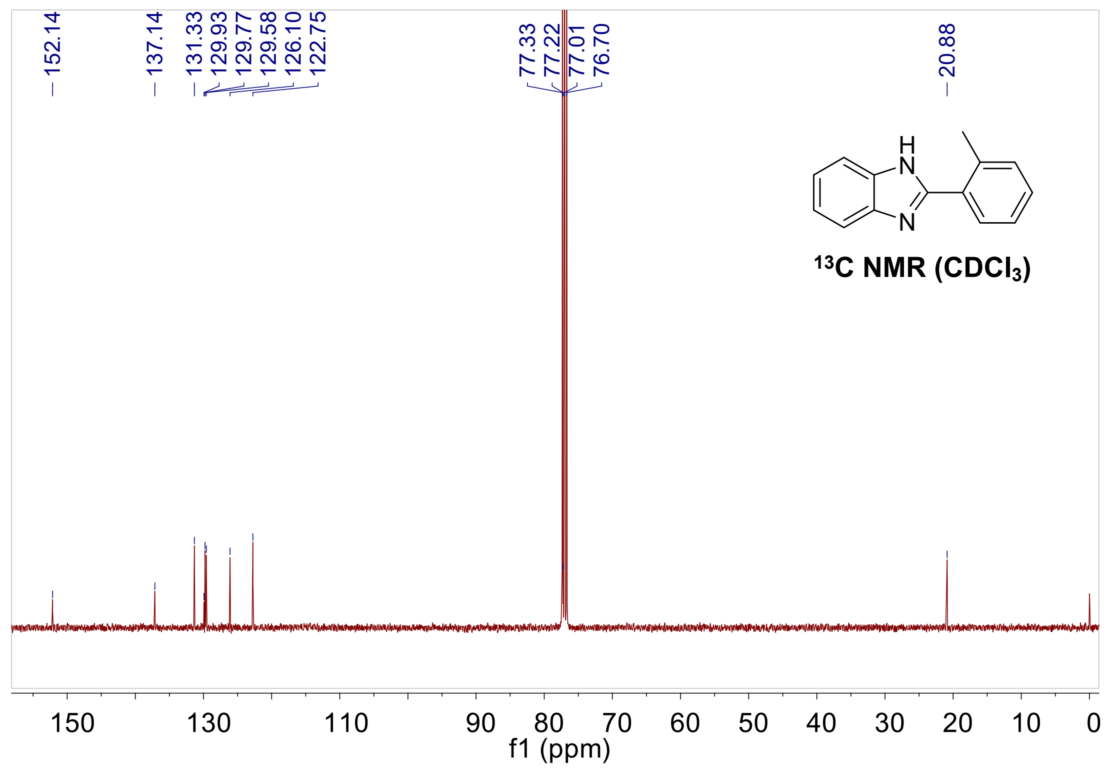


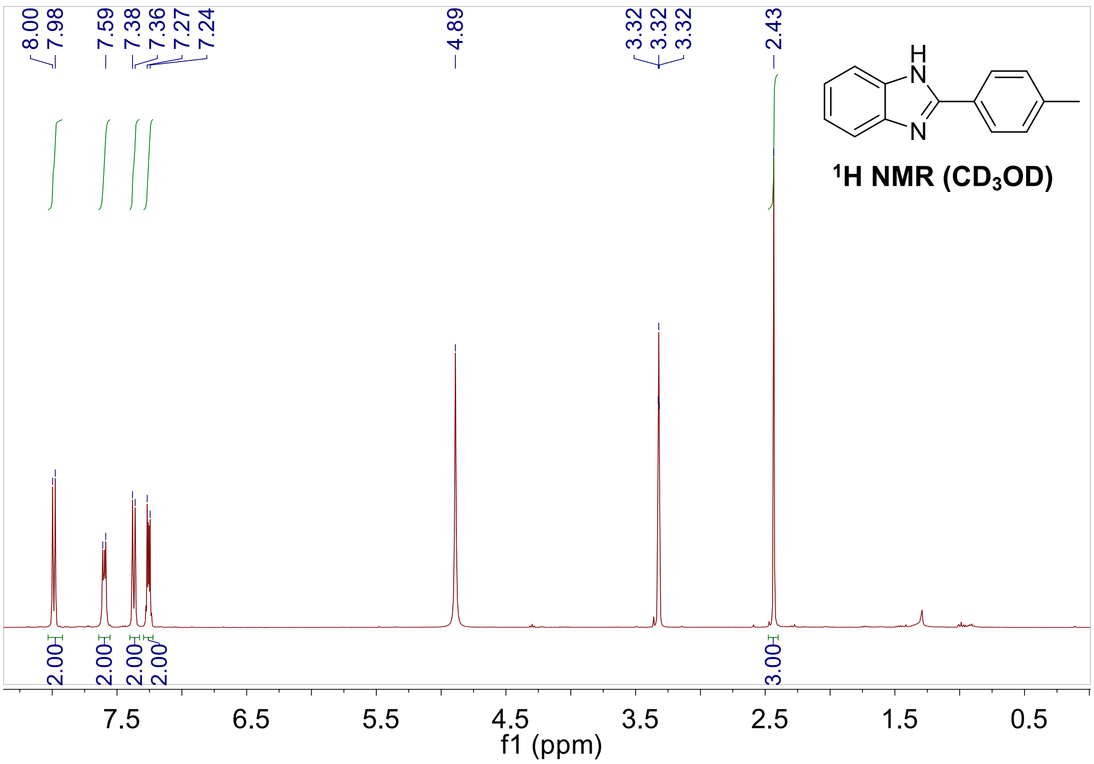
12.90
8.19
8.17
7.66
7.57
7.55
7.53
7.51
7.49
7.47
7.21
3.35
2.50
H
N
N
^{1}H NMR (DMSO-d$_6$)
H_2O
1.00
2.00
5.00
2.04
12.0
9.5
7.5
5.5
3.5
1.5
f1 (ppm)



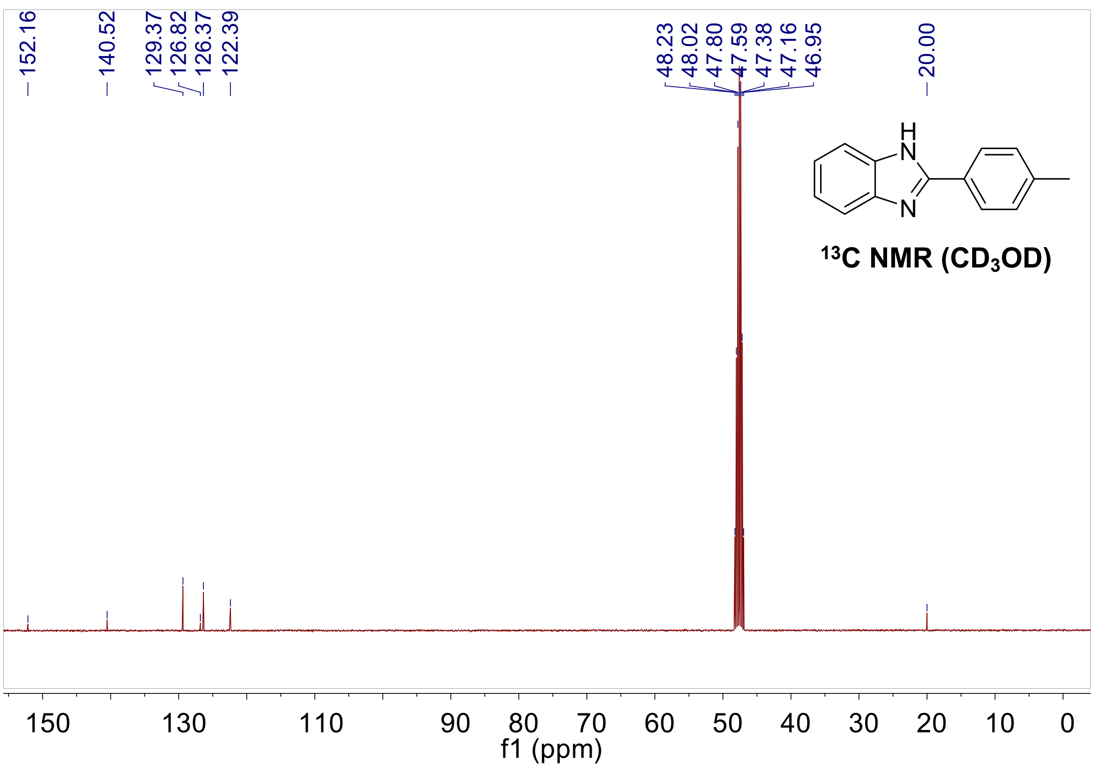
151.68
130.64
130.31
129.42
126.90
40.62
40.41
40.20
40.00
39.79
39.58
39.37
H
N
N
^{13}C NMR (DMSO-d$_6$)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.66
7.64
7.38
7.36
7.35
7.32
7.31
7.29
7.28
7.27
7.27
7.26
2.59
H
N
N
1H NMR (CDCl3)
3.00
5.99
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

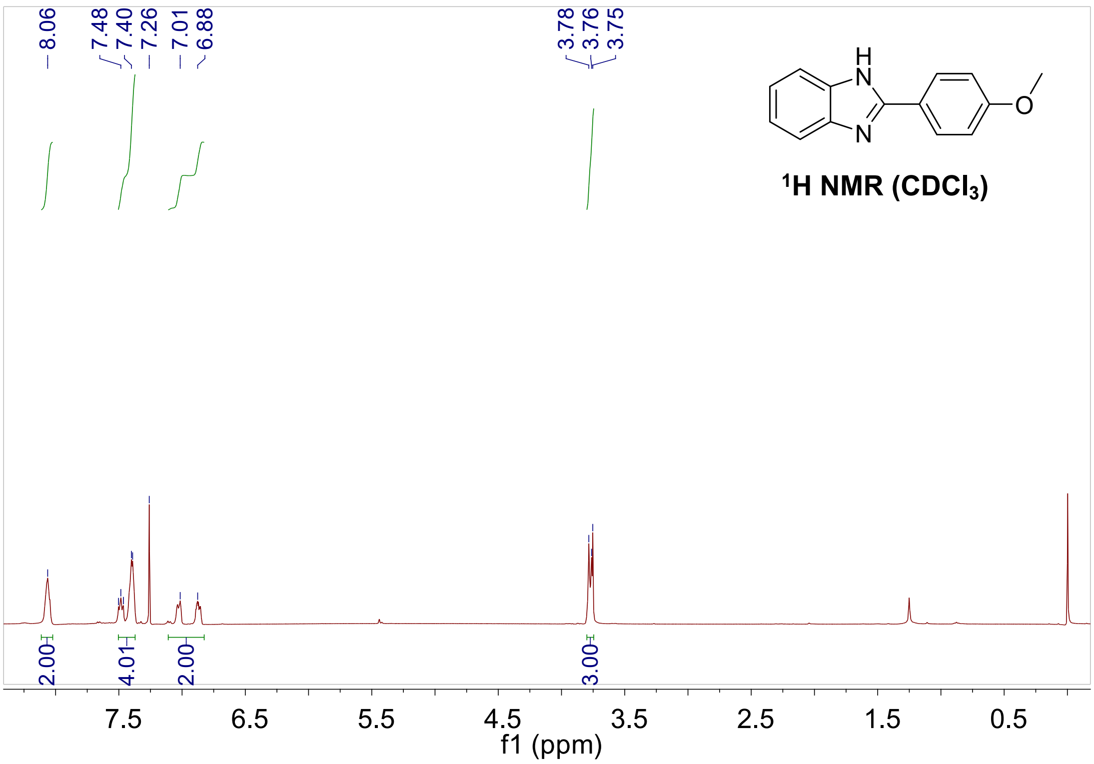

152.14
137.14
131.33
129.93
129.77
129.58
126.10
122.75
77.33
77.22
77.01
76.70
20.88
H
N
N
13C NMR (CDCl3)
150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



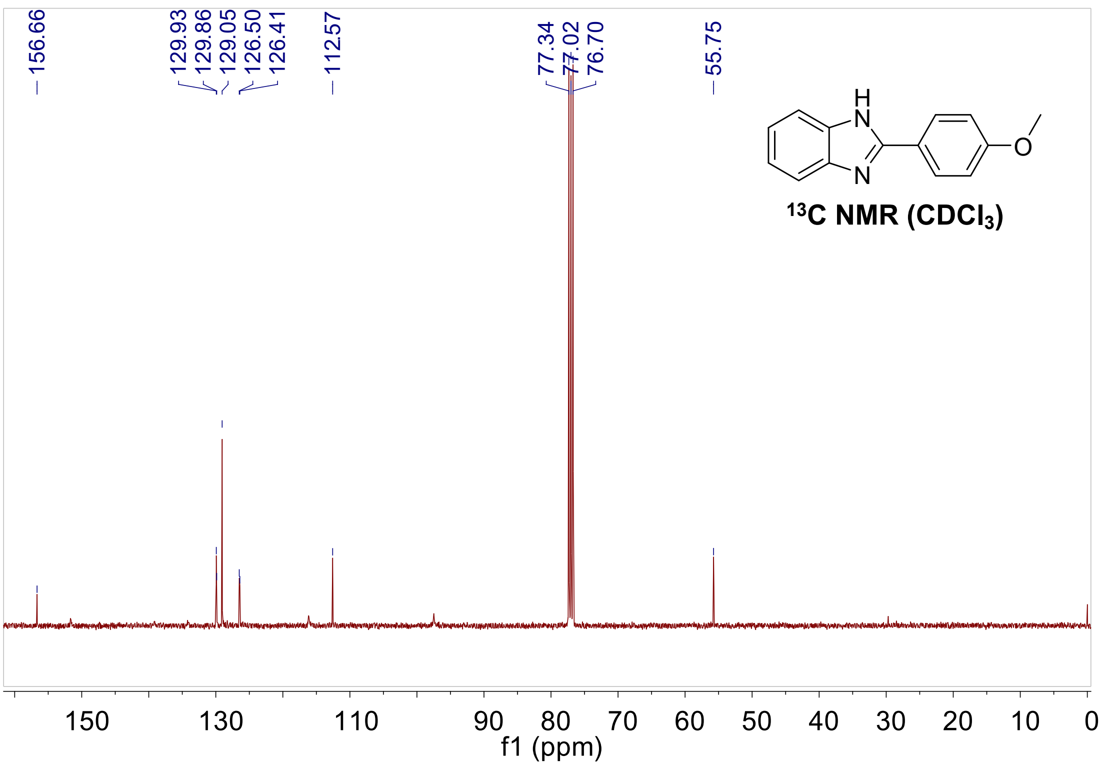
8.00
7.98
7.59
7.38
7.36
7.27
7.24
4.89
3.32
3.32
3.32
2.43
H
N
N
1H NMR (CD3OD)
2.00
2.00
2.00
2.00
3.00
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



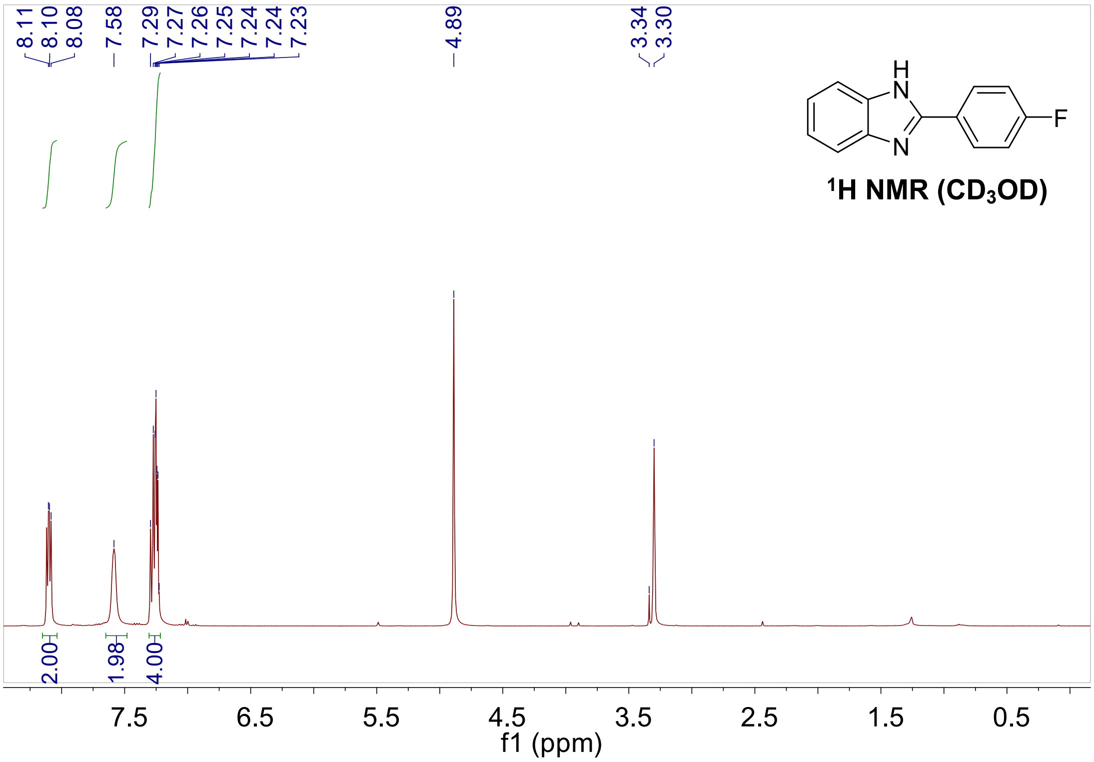
152.16
140.52
129.37
126.82
126.37
122.39
48.23
48.02
47.80
47.59
47.38
47.16
46.95
20.00
H
N
N
13C NMR (CD3OD)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

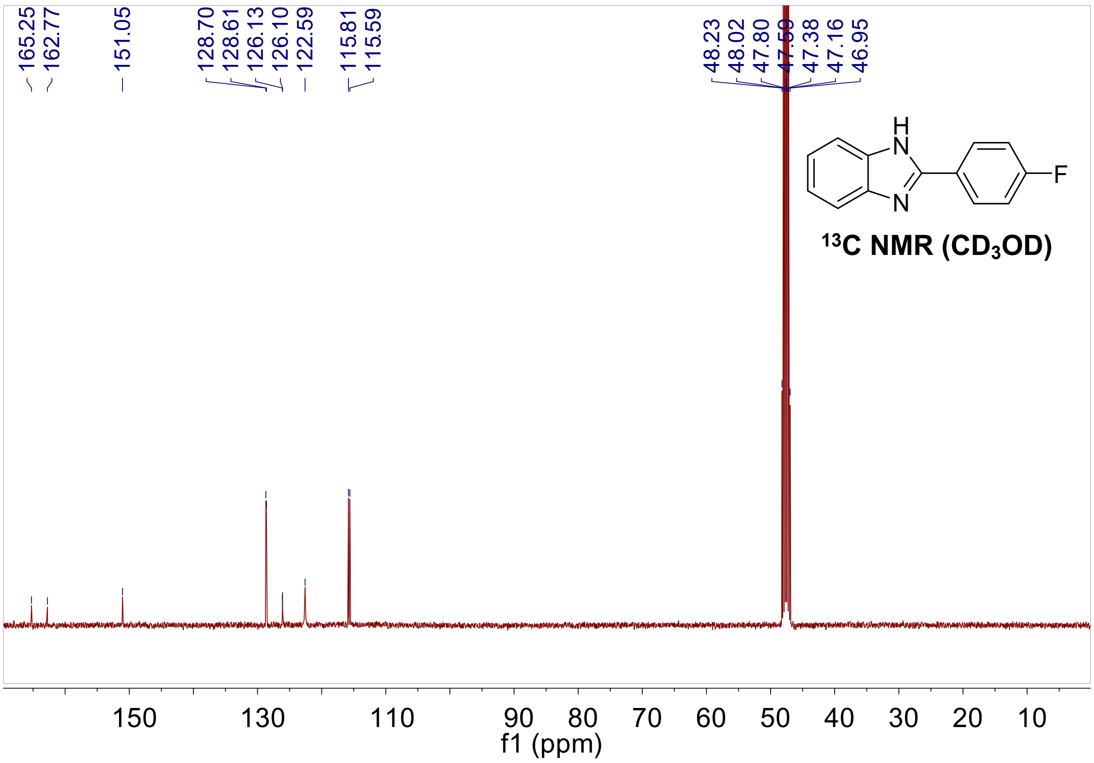


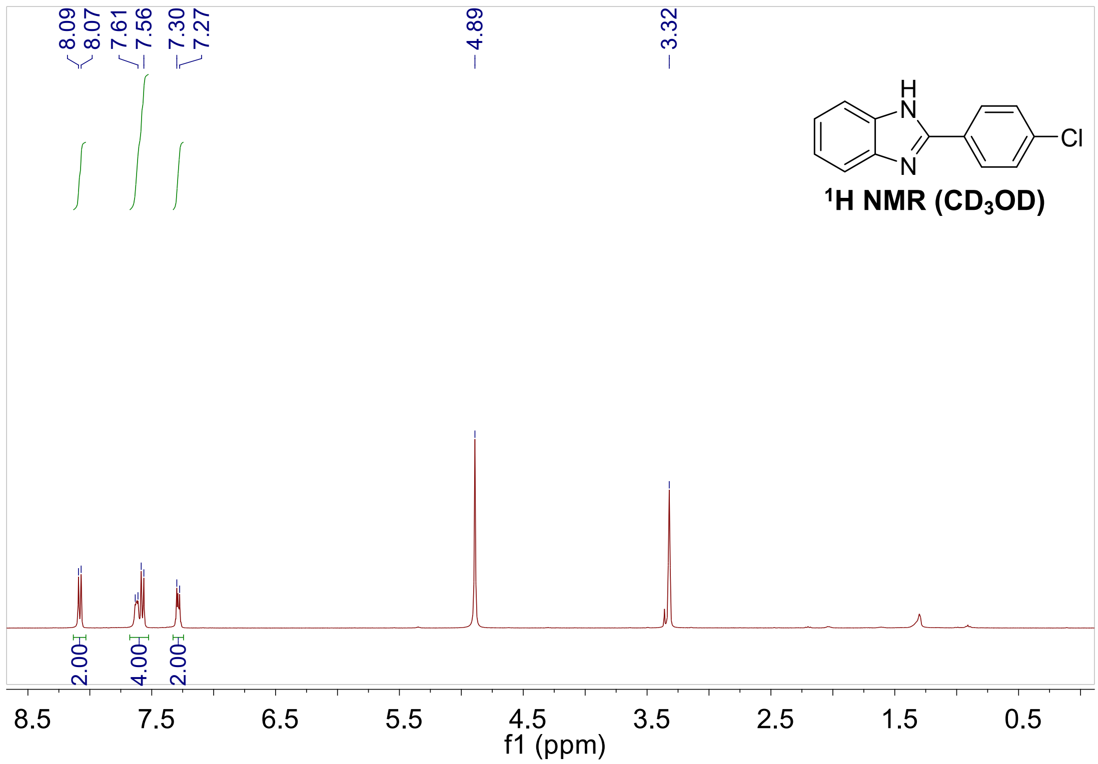
8.06
7.48
7.40
7.26
7.01
6.88
3.78
3.76
3.75
H
N
N
O
¹H NMR (CDCl3)
2.00
4.01
2.00
3.00
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



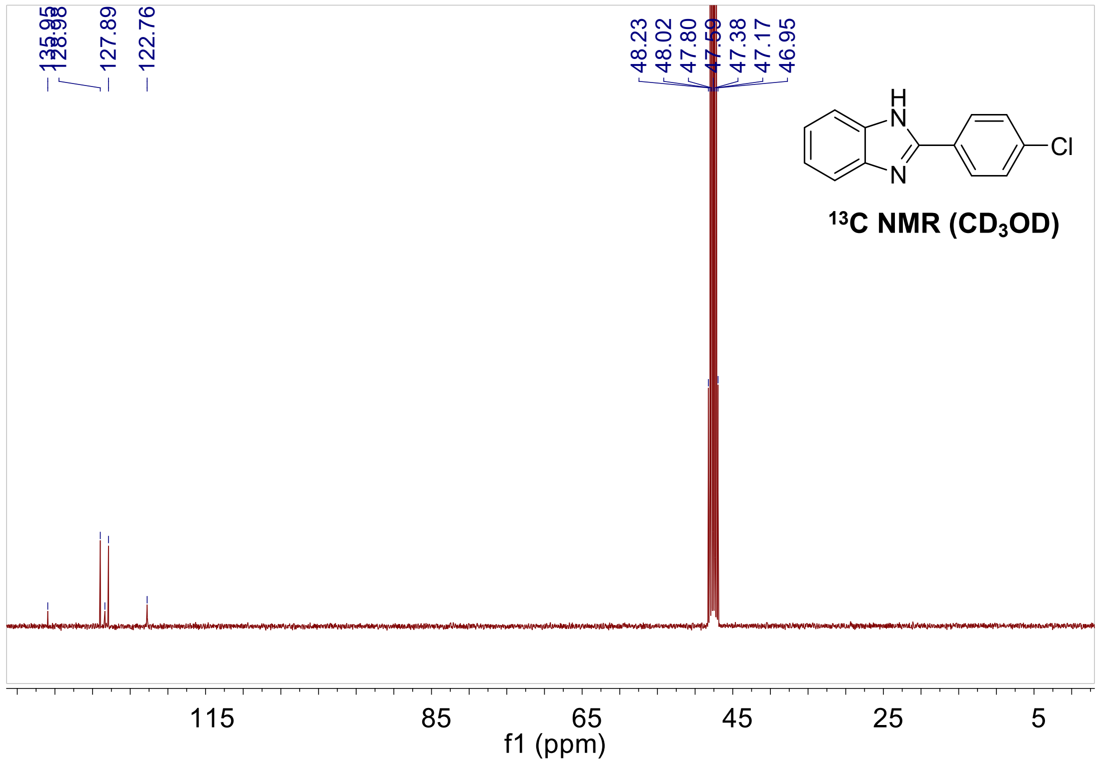
156.66
129.93
129.86
129.05
126.50
126.41
112.57
77.34
77.02
76.70
55.75
H
N
N
O
¹³C NMR (CDCl3)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.11
8.10
8.08
7.58
7.29
7.27
7.26
7.25
7.24
7.24
7.23
4.89
3.34
3.30
H
N
N
F
1H NMR (CD3OD)
2.00
1.98
4.00
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

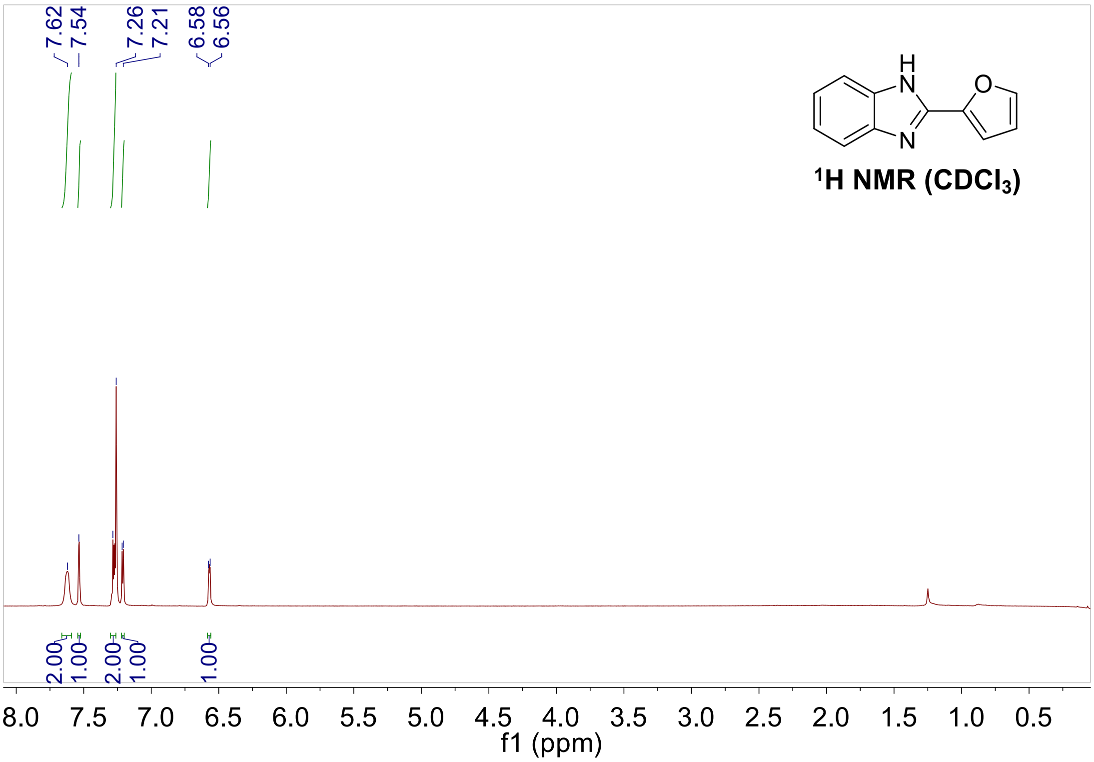

165.25
162.77
151.05
128.70
128.61
126.13
126.10
122.59
115.81
115.59
48.23
48.02
47.80
47.59
47.38
47.16
46.95
H
N
N
F
13C NMR (CD3OD)
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

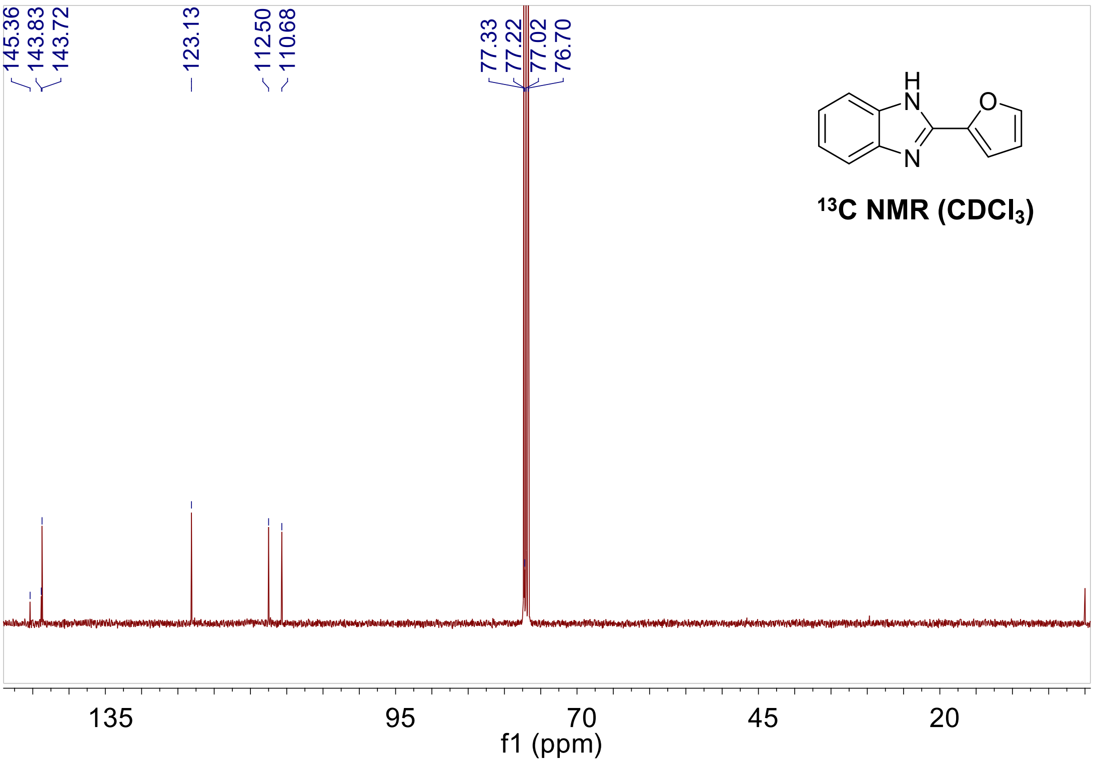


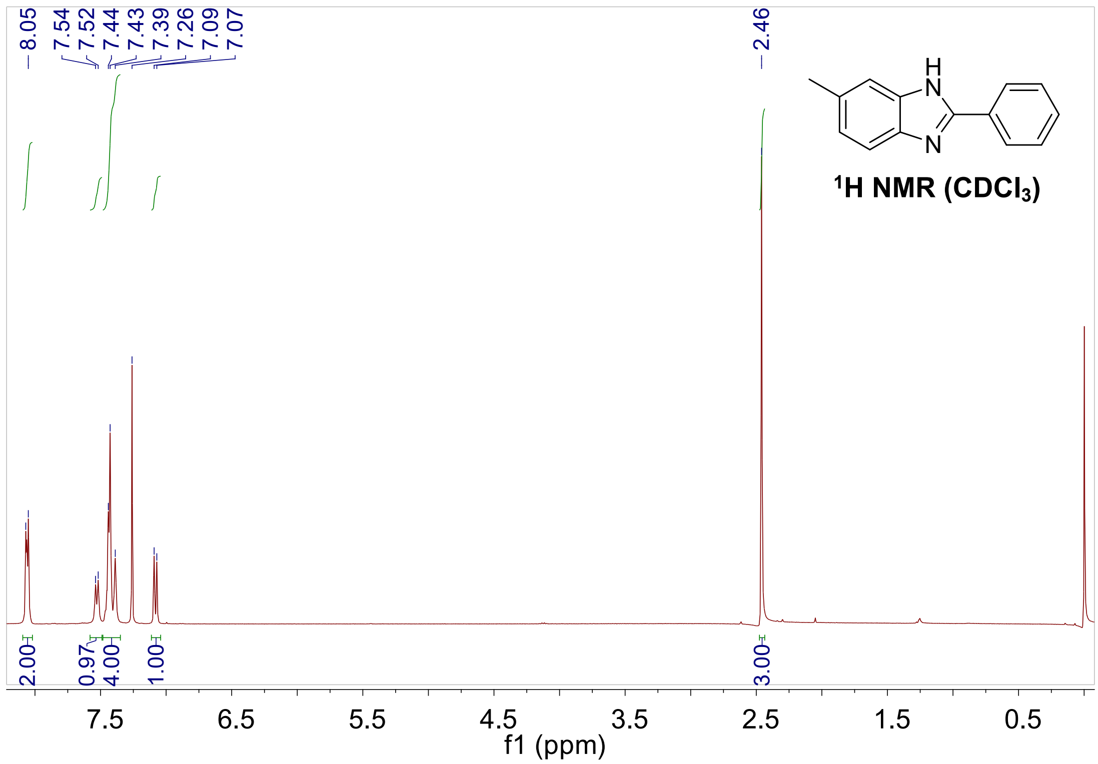
8.09
8.07
7.61
7.56
7.30
7.27
4.89
3.32
2.00
4.00
2.00
¹H NMR (CD₃OD)
Cl
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

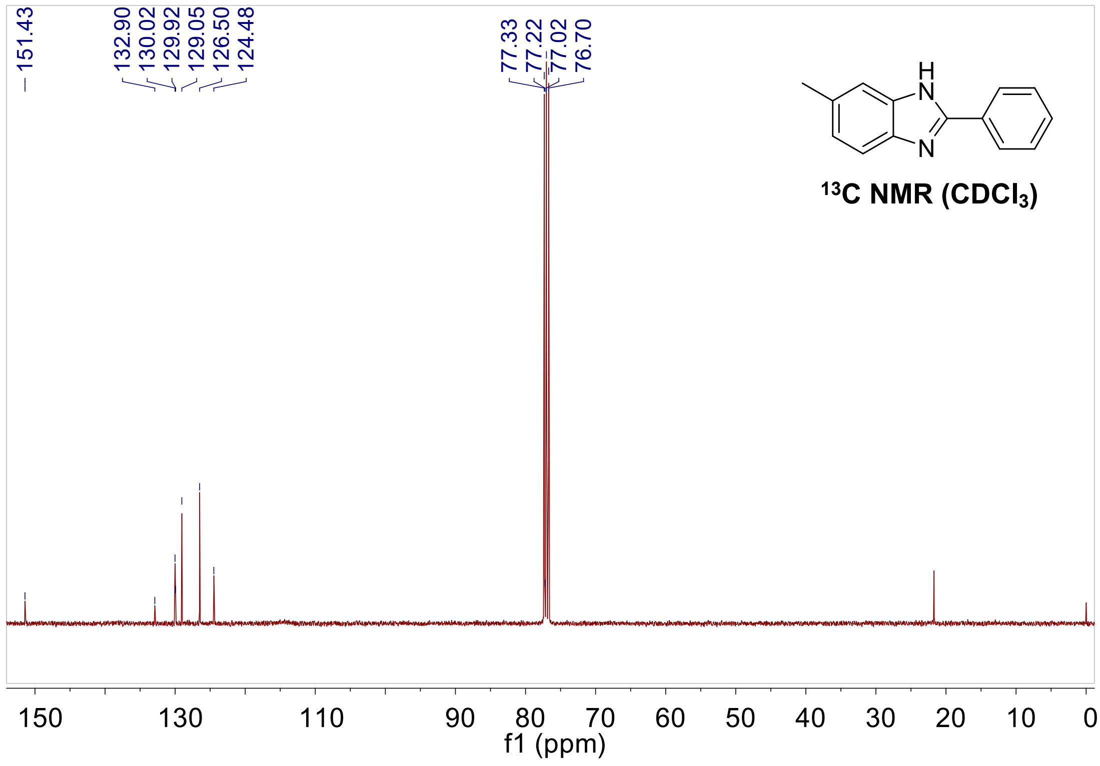


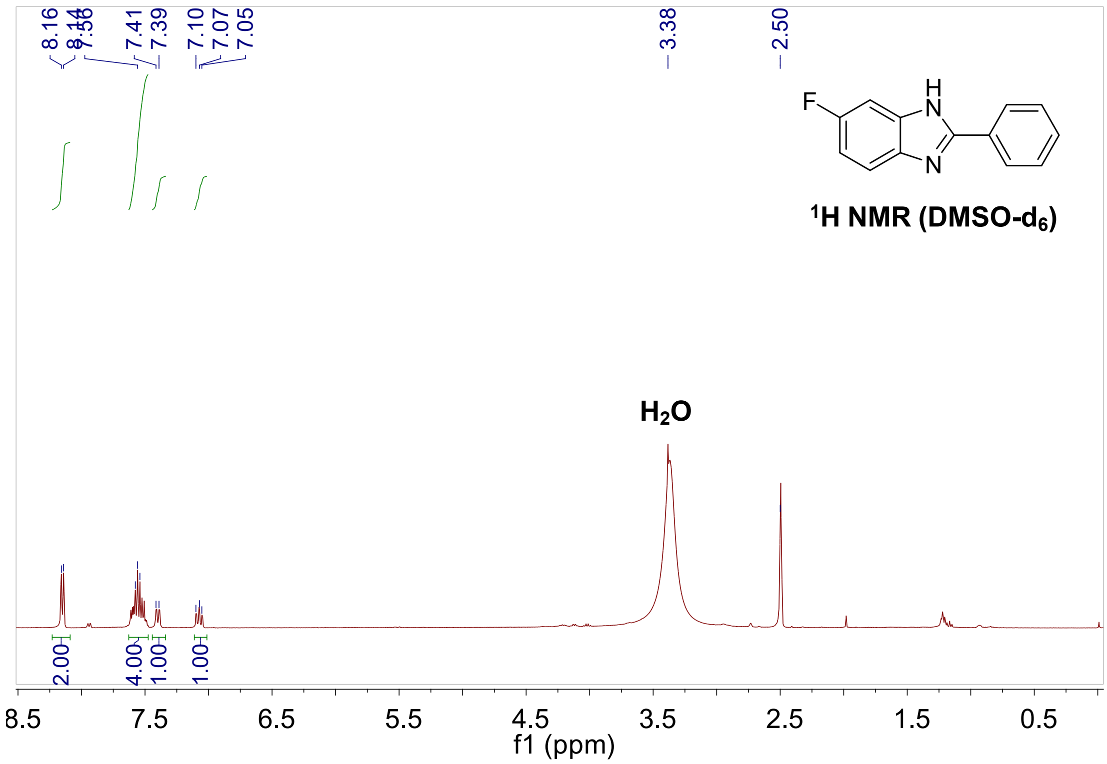
127.89
122.76
48.23
48.02
47.80
47.38
47.17
46.95
¹³C NMR (CD₃OD)
Cl
115
85
65
45
25
5
f1 (ppm)

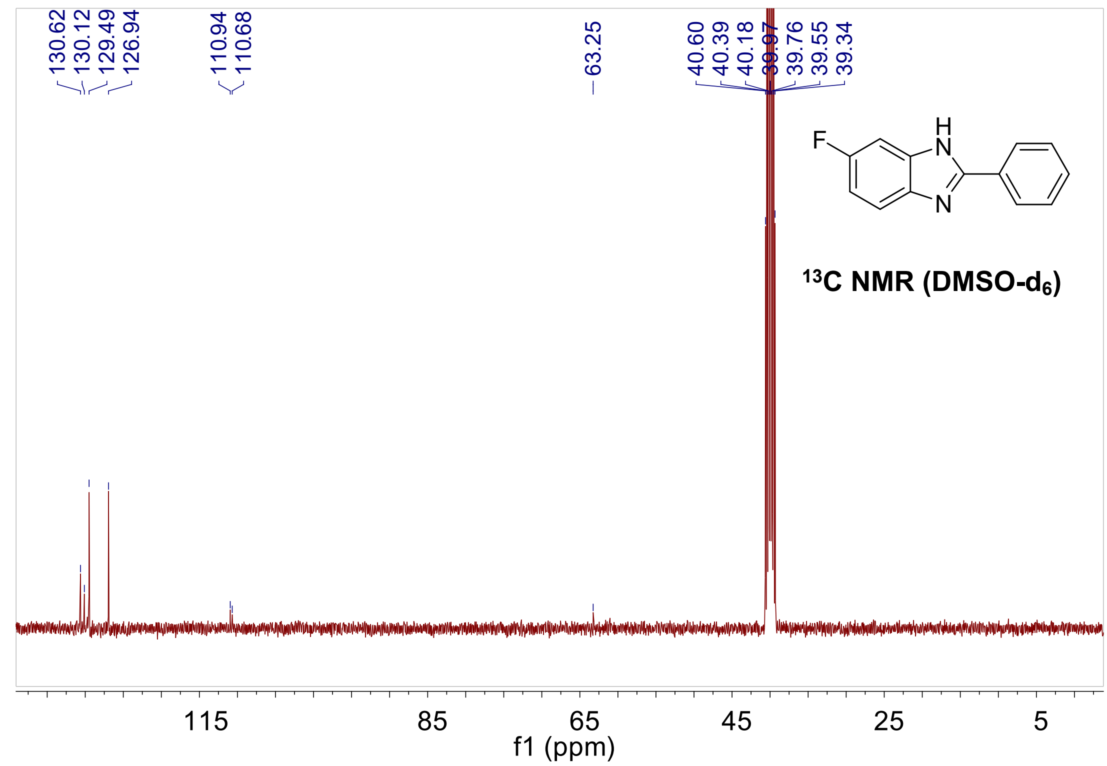

7.62
7.54
7.26
7.21
6.58
6.56
1H NMR (CDCl3)
2.00
1.00
2.00
1.00
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


145.36
143.83
143.72
123.13
112.50
110.68
77.33
77.22
77.02
76.70
13C NMR (CDCl3)
135 95 70 45 20
f1 (ppm)


8.05
7.54
7.52
7.44
7.43
7.39
7.26
7.09
7.07
2.46
H
N
N
1H NMR (CDCl3)
2.00
0.97
4.00
1.00
3.00
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


151.43
132.90
130.02
129.92
129.05
126.50
124.48
77.33
77.22
77.02
76.70
H
N
N
13C NMR (CDCl3)
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.16
8.14
7.56
7.41
7.39
7.10
7.07
7.05
3.38
2.50
F
H
N
N
1H NMR (DMSO-d6)
H2O
2.00
4.00
1.00
1.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


130.62
130.12
129.49
126.94
110.94
110.68
63.25
40.60
40.39
40.18
39.97
39.76
39.55
39.34
F
H
N
N
13C NMR (DMSO-d6)
115
85
65
45
25
5
f1 (ppm)