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Electronic Supplementary Information

Electron Donor-free Photoredox Catalysis via Electron Transfer Cascade by Cooperative Organic Photocatalysts

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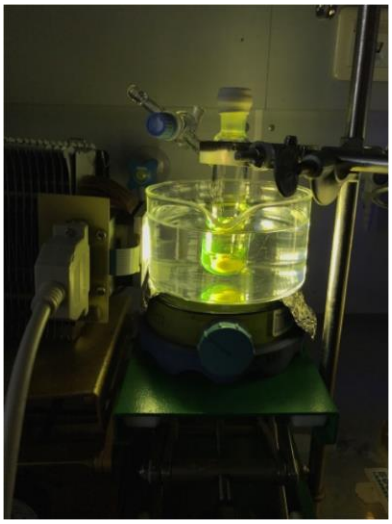
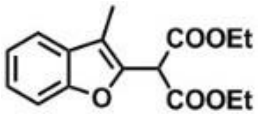
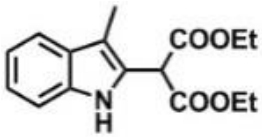
Photograph of the setup for the sacrificial reagent free and photocatalytic C-C bond formation reactions using cooperative photocatalyst systems



Products NMR data:

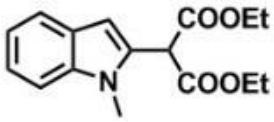


Diethyl 2-(3-methyl-1H-2,3-benzofuran-2-yl)malonate *(table 1, entry 5).* Follow the general procedure, Hexane/CH_2Cl_2 = 1/1 was used as eluent to give the product as a yellow oil (99 mg, 90%). ^{1}H NMR (300 MHz, DMSO) δ : 7.63 - 7.60 (m, 1 H), 7.56 - 7.54 (m, 1 H), 7.37 - 7.26 (m, 2 H), 5.49 (s, 1 H), 4.26 - 4.14 (m, 4 H), 2.22 (s, 3 H), 1.22 (t, *J* = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, DMSO) δ : 165.93, 153.47, 144.29, 129.10, 124.67, 122.58, 119.66, 114.25, 110.92, 61.67, 50.00, 13.85, 7.42. Molecular weight $C_{16}H_{18}O_5$: calculated 290.12, found 290.20.

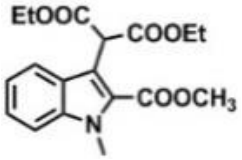


Diethyl 2-(1,3-dimethyl-1H-indole-2-yl)malonate *(table 1, entry 6)*. Follow the general procedure, Hexane/CH_2Cl_2 = 2/1 was used as eluent to give the product as a yellow solid (97 mg, 88%). ^{1}H NMR (300 MHz, CDCl3) δ : 8.93 (br, 1 H), 7.58 - 7.55 (m, 1 H), 7.39 - 7.36 (m,

1 H), 7.24 - 7.15 (m, 1 H), 7.19 - 7.10 (m, 1 H), 5.00 (s, 1 H), 4.34 - 4.18 (m, 4 H), 2.34 (s, 3 H), 1.31 (t, *J* = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl3) δ : 167.38, 135.83, 128.26, 124.53, 122.36, 119.22, 118.78, 111.09, 110.60, 62.29, 49.31, 14.03, 8.51. Molecular weight $C_{16}H_{19}NO_4$: calculated 289.13, found 289.00.



Diethyl 2-(1-methyl-1H-indole-2-yl)malonate *(table 1, entry 7)*. Follow the general procedure, Hexane/CH_2Cl_2 = 1/1 was used as eluent to give the product as a yellow solid (86 mg, 78%). ^{1}H NMR (300 MHz, CDCl3) δ : 7.61 (d, J = 7.81 Hz, 1 H), 7.33 (d, J = 7.72 Hz, 1 H), 7.25 - 7.21 (m, 1 H), 7.13 - 7.08 (m, 1 H), 6.50 (s, 1 H), 4.93 (s, 1 H), 4.34 - 4.20 (m, 4 H), 3.73 (s, 3 H), 1.30 (t, *J* = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl3) δ : 166.99, 137.93, 130.90, 127.27, 121.97, 120.79, 119.71, 109.30, 103.01, 62.23, 51.32, 30.31, 14.05. Molecular weight $C_{16}H_{19}NO_4$: calculated 289.13, found 289.00.



Diethyl 2-(2-(methoxycarbonyl)-1-methyl-1H-indole-3-yl)malonate *(table 1, entry 7)*. Follow the general procedure, Hexane/CH_2Cl_2 = 1/2 was used as eluent to give the product as a green-yellow solid (115 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.77 (d, *J* = 8.21 Hz, 1 H), 7.41 - 7.34 (m, 2 H), 7.21 - 7.15 (m, 1 H), 5.79 (s, 1 H), 4.28 - 4.21 (m, 4 H), 4.03 (s, 3 H), 3.96 (s, 3 H), 1.27 (t, *J* = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 168.55, 162.51, 138.68, 126.15, 125.65, 125.36, 121.99, 120.77, 114.50, 110.35, 61.69, 51.77, 49.96, 32.28, 14.09. Molecular weight $C_{18}H_{21}NO_6$: calculated 347.14, found 346.95.

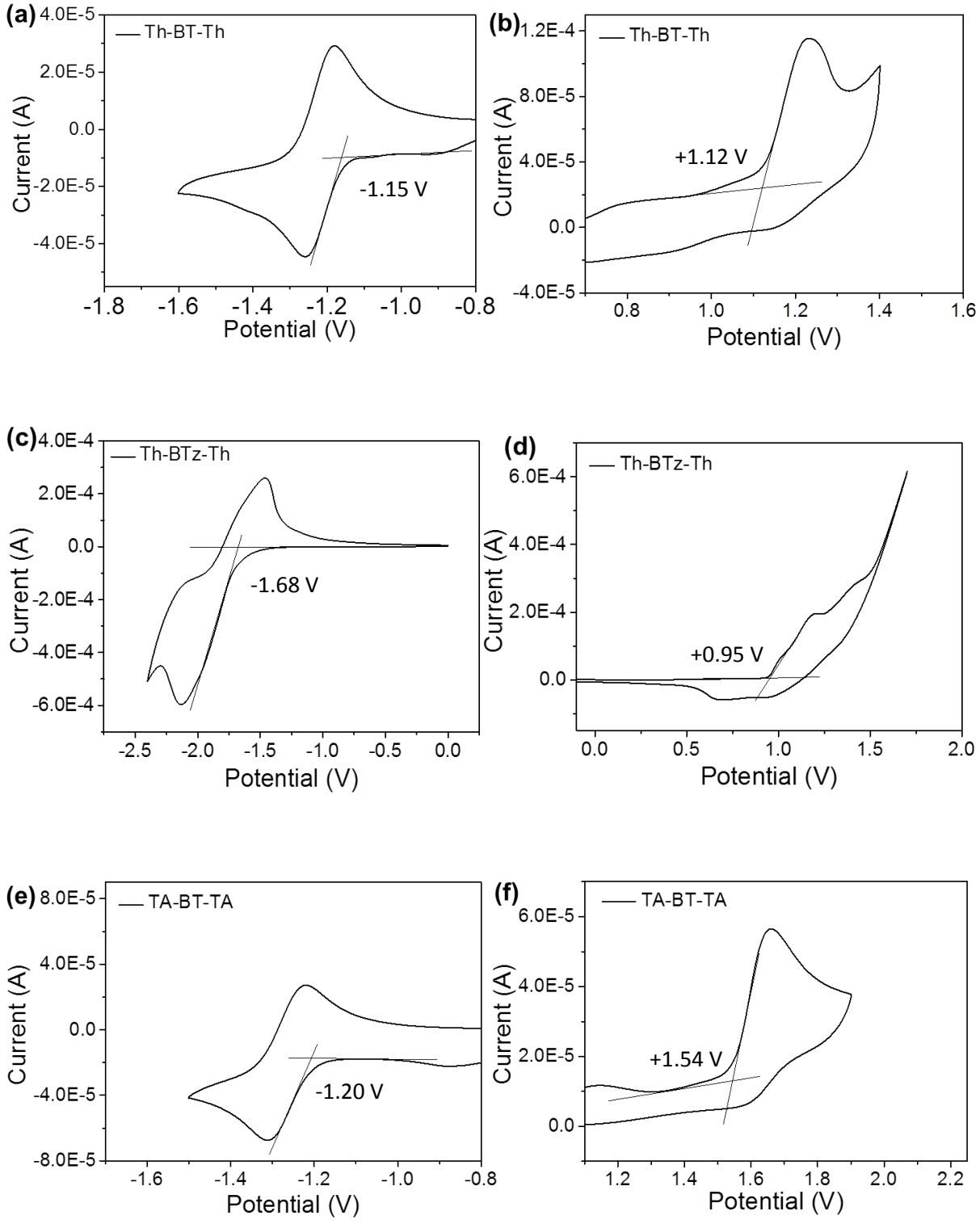


Fig. S1. Reductive potentials of (a) **Th-BT-Th**, (c) **Th-BTz-Th** and (e) **TA-BT-TA** and oxidative potential of (b) **Th-BT-Th**, (d) **Th-BTz-Th** and (f) **TA-BT-TA** determined via cyclic voltammetry (vs. SCE)

Table S1. Redox potentials of the molecular photocatalysts.

Entry	Photocatalysts	Ground state (V vs. SCE)[a]		$E_{0,0}$[b]	Excited state (V vs. SCE)[c]	
		HOMO	LUMO		HOMO	LUMO
1	Th-BT-Th	+1.12	-1.15	2.13	+1.16	-1.01
2	Th-BTz-Th	+0.95	-1.68	2.30	+0.62	-1.35
3	TA-BT-TA	+1.54	-1.20	2.34	+1.14	-0.80

[a]Ground state redox potentials were determined by cyclic voltammetry;

[b]$E_{0,0}$ was obtained from the maximum emission;

[c]Excited state redox potential were calculated with the method described in previous report (reference 42 in the manuscript).

For one of the reaction system (Table 1, entry 5), both apparent quantum yield and catalytic turnover number were calculated as below:

Apparent Quantum Yield Φ_{AQY}:

$$\Phi_{AQY} = \frac{moles\ of\ product\ evolved}{moles\ of\ incident\ photons} = \frac{N_e}{N_p} \times 100\% = \frac{\frac{M \times N_A}{S \times P \times t}}{\hbar \times \frac{c}{\lambda}} \times 100\%$$

$$= \frac{M \times N_A \times \hbar \times c}{S \times P \times t \times \lambda} \times 100\%$$

$$= \frac{0.038 * 10^{-3} mol \times 0.93 \times 6.023 * 10^{23} mol^{-1} \times 6.63 * 10^{-34} m^2 kg/s \times 3 * 10^8 m/s}{(3.3 * 3.1/3.14) cm^2 \times 0.1 w/cm^2 \times 24 * 3600 s \times 460 nm} \times 100\%$$

$$= 0.04\%$$

Catalytic turnover number TON:

$$TON = \frac{the\ mole\ of\ product}{the\ mole\ of\ photocatalyst} == \frac{0.38\ mmol * 87\%}{0.038\ mmol} = 8.7$$

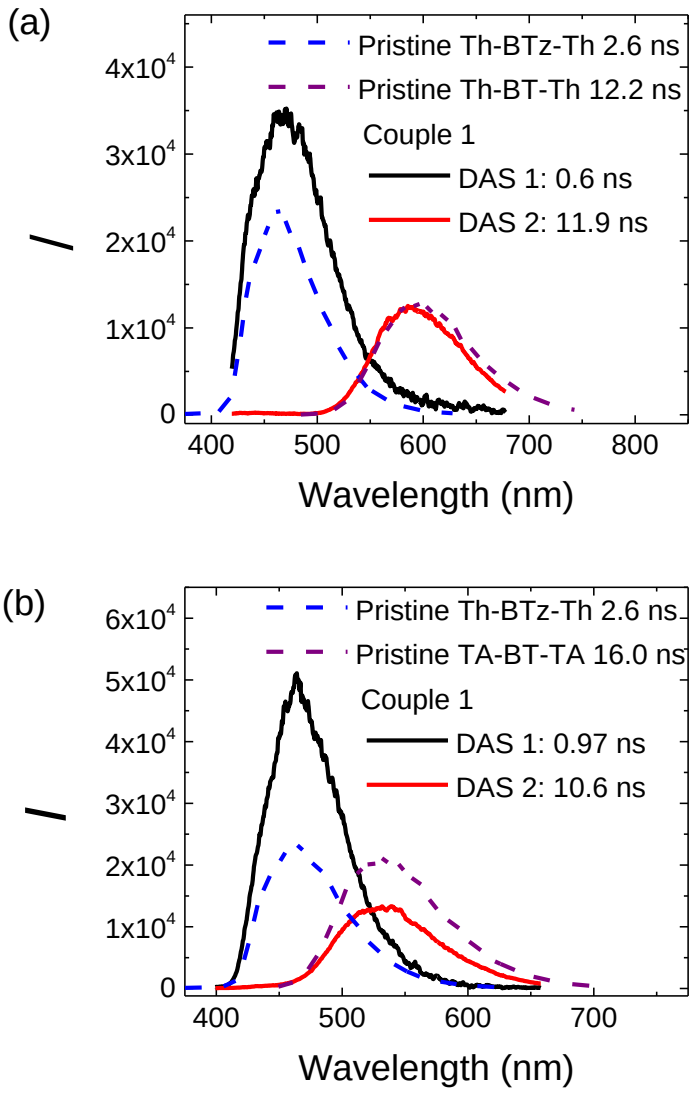


Fig. S2. Decay associated spectra (DAS) derived by a global fitting analysis of the TRPL data. (a) Couple 1 and (b) couple 2.

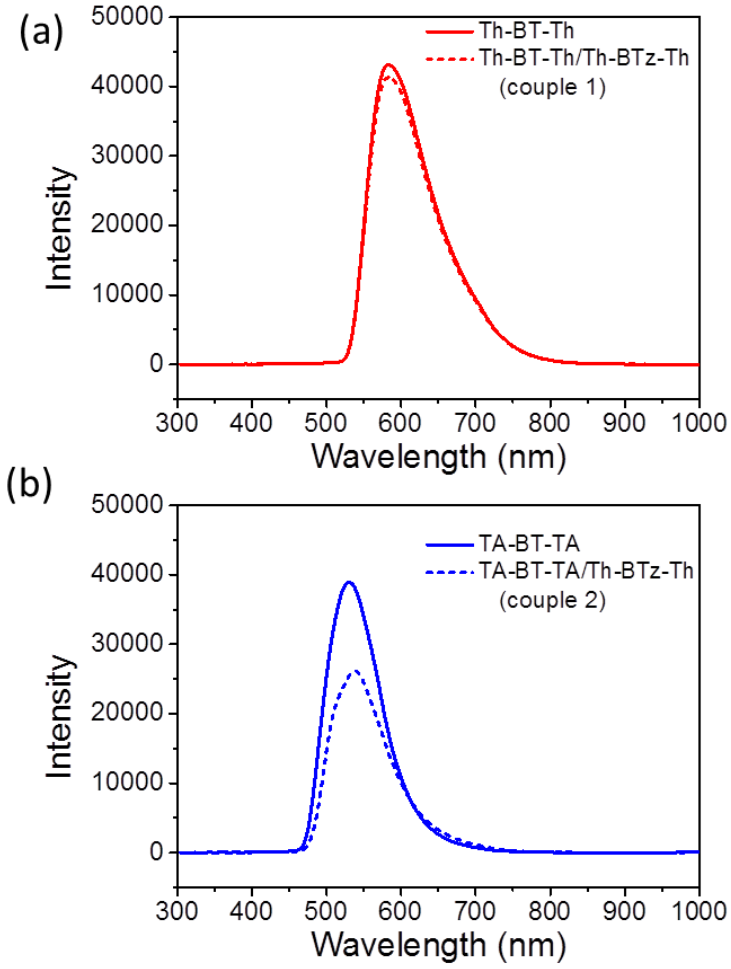


Fig. S3. Fluorescence quenching within the photocatalyst couples in solution by only exciting Th-BT-Th and TA-BT-TA. The ratios of the OSs were 1:1 for both couples. Excitation wavelength: (a) **500** nm, (b) **450** nm.

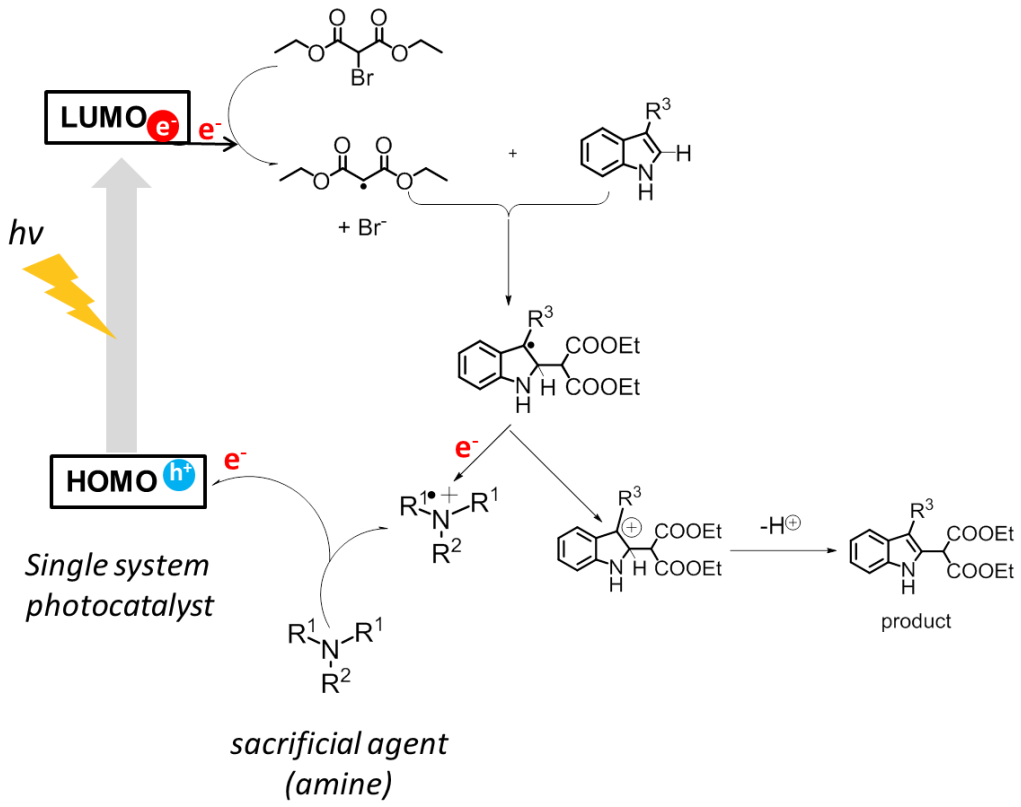


Fig. S4. Conventional reaction mechanism of the photocatalytic C-C coupling reaction between electron-rich heteroaromates and bromomalonates using a single system photocatalyst. Here, amine is used as sacrificial reagent.

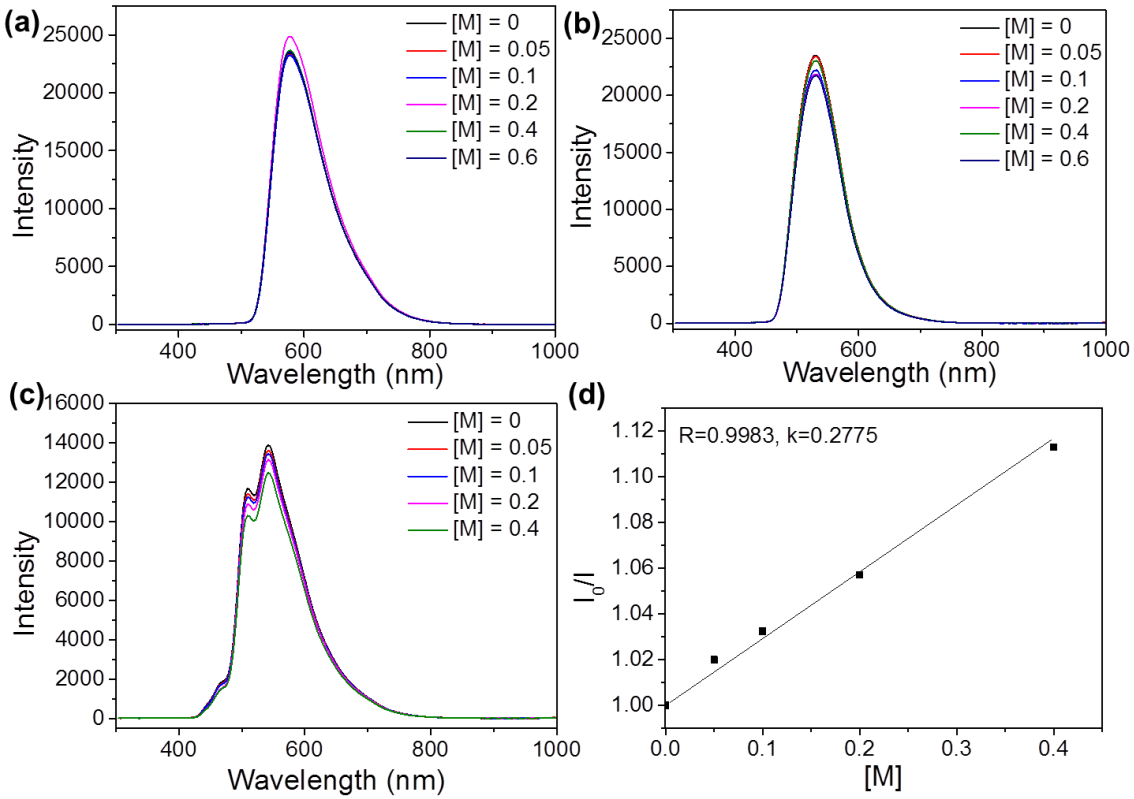


Fig. S5. Fluorescence quenching spectra of (a)**Th-BT-Th**, (b)**TA-BT-TA** (c)**Th-BTz-Th** with diethyl bromomalonate and (d) Stern-Volmer analysis of quenching rate between **Th-BTz-Th** and diethyl bromomalonate.

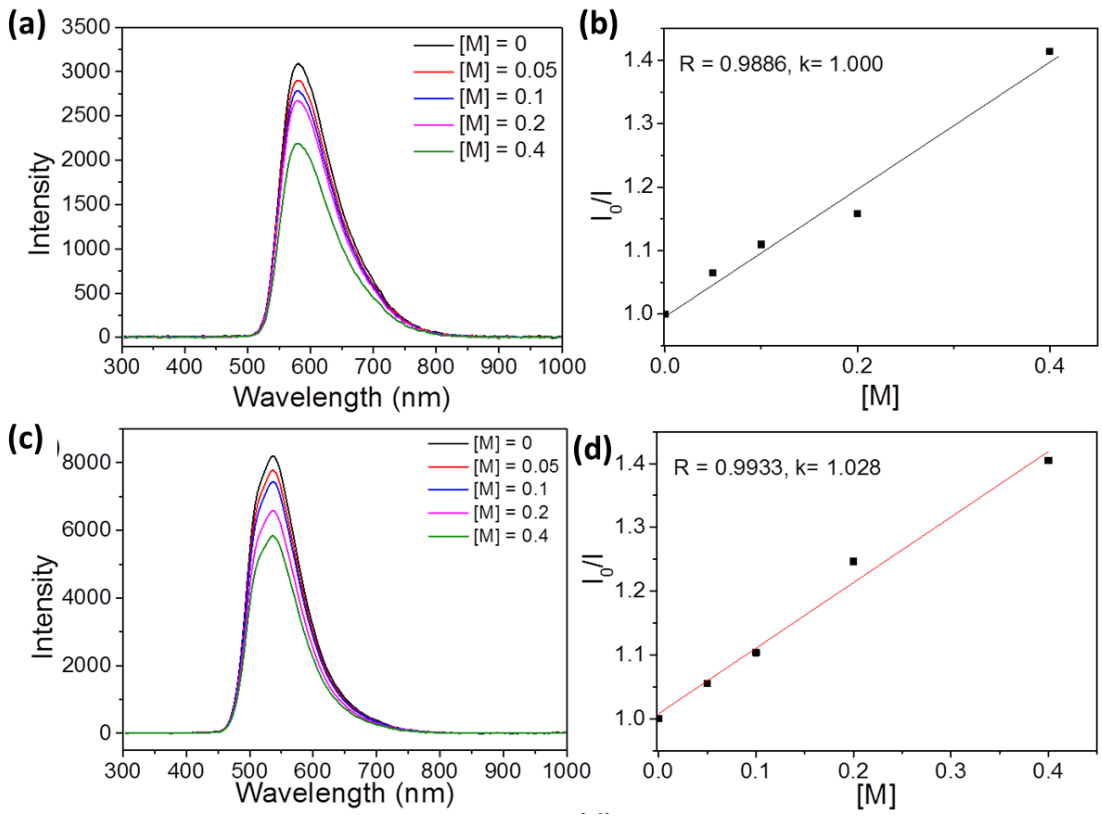


Fig. S6. Fluorescence quenching for (a) **cooperative catalyst system 1 (Th-BTz-Th** and **Th-BT-Th)** and (c) **cooperative catalyst system 2 (Th-BTz-Th** and **TA-BT-TA)** with diethyl bromomalonate and Stern-Volmer analysis of (b) cooperative **couple 1** and (d) **couple 2** with diethyl bromomalonate.

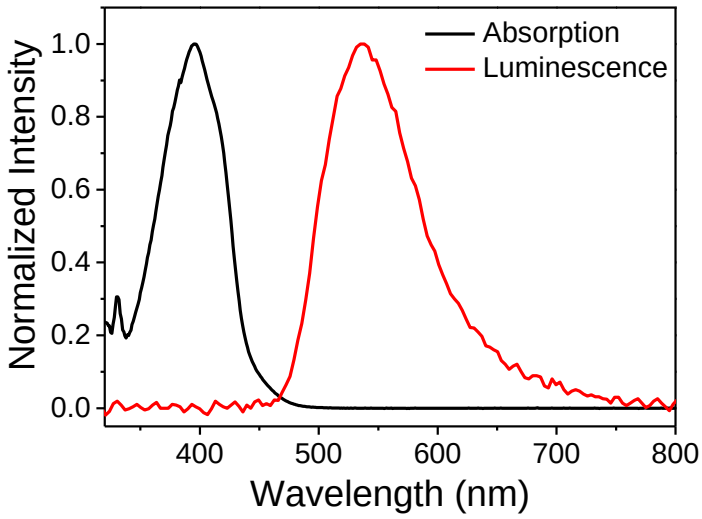


Fig. S7. UV/vis absorption and fluorescence spectra of the connected photocatalyst system **TA-BT-TA@Th-BTz-Th**.

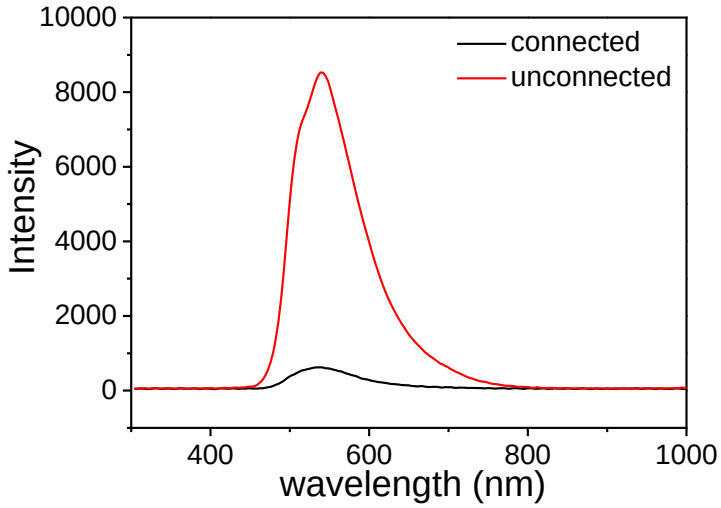


Fig. S8. Fluorescence spectra of C6-connected **Th-BTz-Th@TA-BT-TA** and unconnected photocatalyst **couple 2** containing Th-BTz-Th and TA-BT-TA under same molar ratio and concentration.

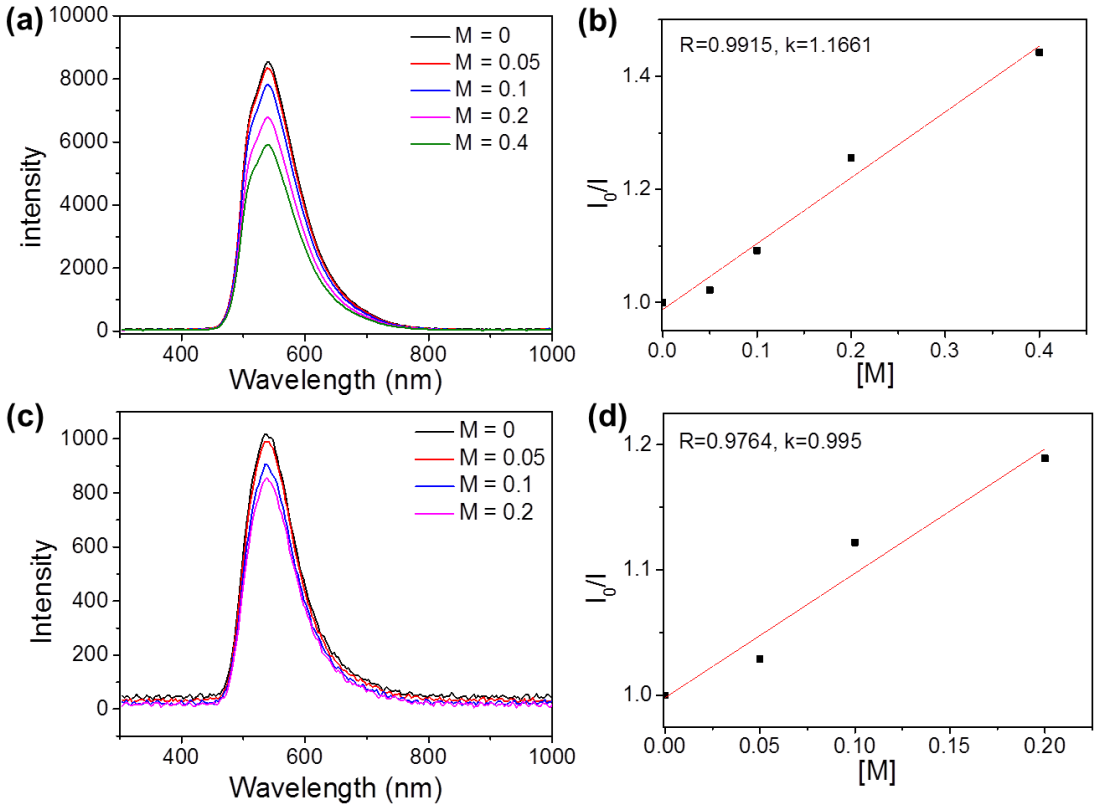


Fig. S9. Fluorescence quenching of (a) **unconnected and (c) connected Th-BTz-Th/TA-BT-TA** with diethyl bromomalonate and Stern-Volmer analysis of (b) **unconnected and (d) connected Th-BTz-Th/TA-BT-TA** with diethyl bromomalonate.

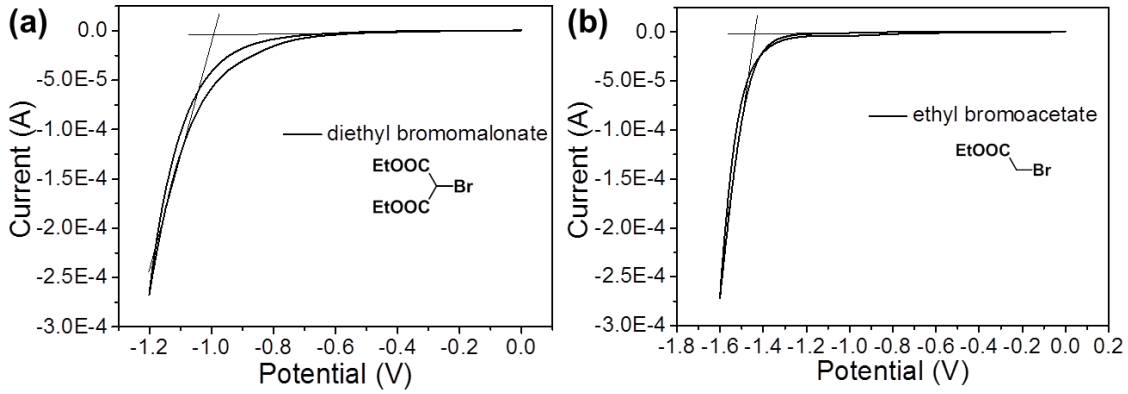


Fig. S10. Reductive potentials of (a) diethyl bromomalonate and (b) ethyl bromoacetate (potentials given vs. SCE)

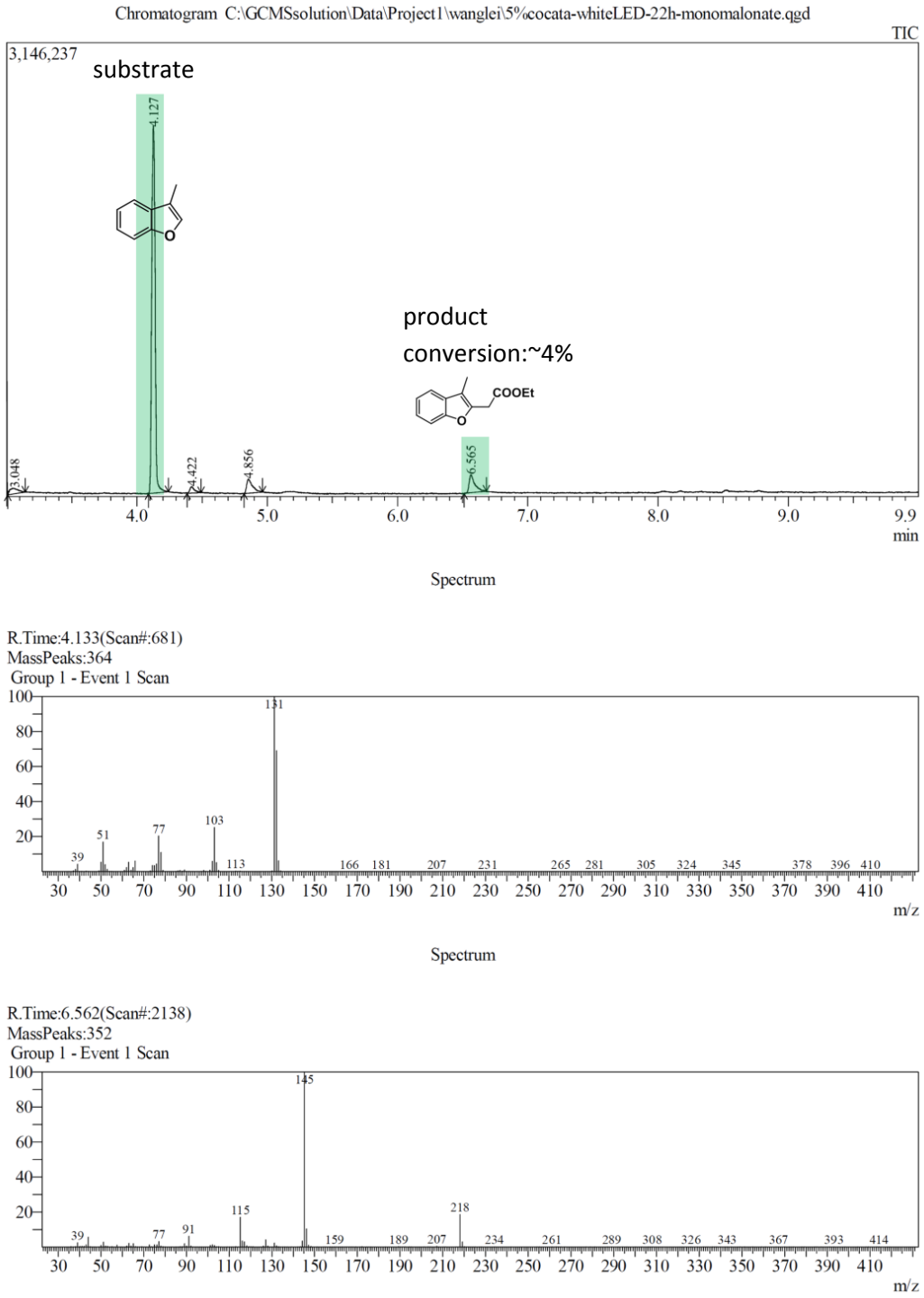


Fig. S11. C-C coupling between 3-methylbenzofuran and ethyl bromoacetate using **couple 2** (**Th-BTz-Th/TA-BT-TA)** as cocatalyst, Conversion: ~ 4%.

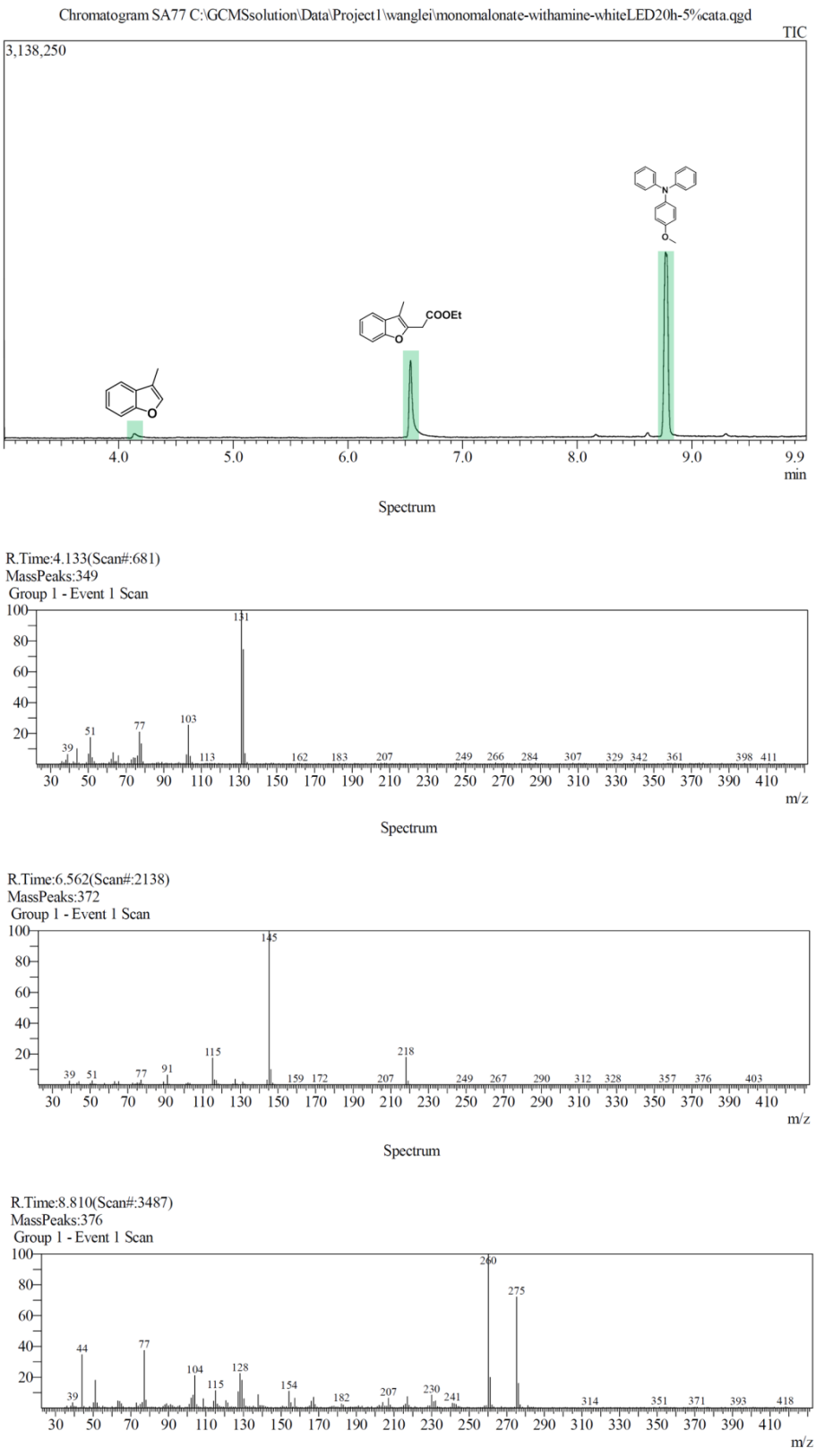
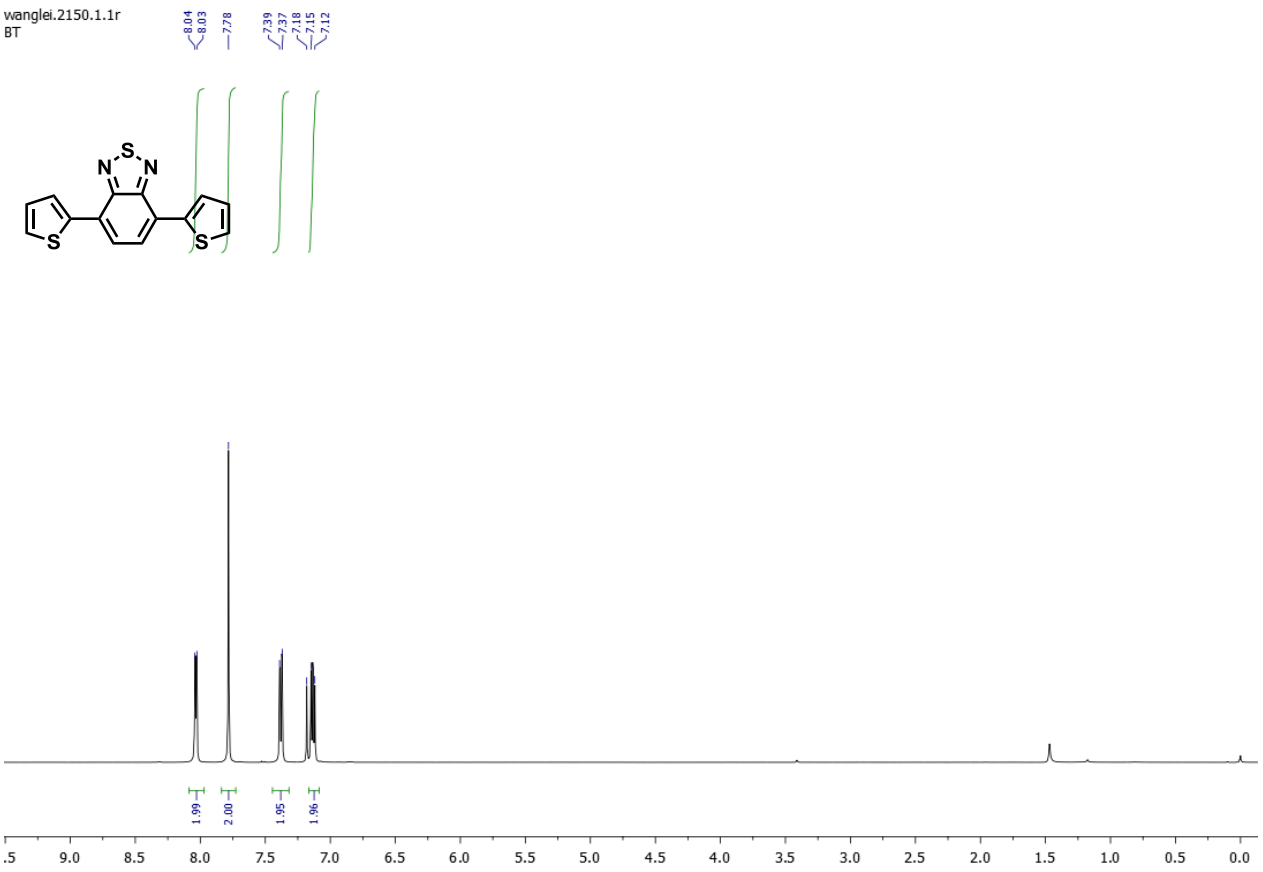


Fig. S12. C-C coupling between 3-methylbenzofuran and ethyl bromoacetate using **Th-BTz-Th** as catalyst and **4-methoxyltriphenylamine** as sacrificial reagent. Reaction conditions: 1 equiv. (0.38 mmol) heteroaromate, 2 equiv. ethyl bromomalonate, 0.1 equiv. photocatalyst in 2.5 mL DMF, white LED, 12 h.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7.78
7.39
7.37
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7.15
7.12
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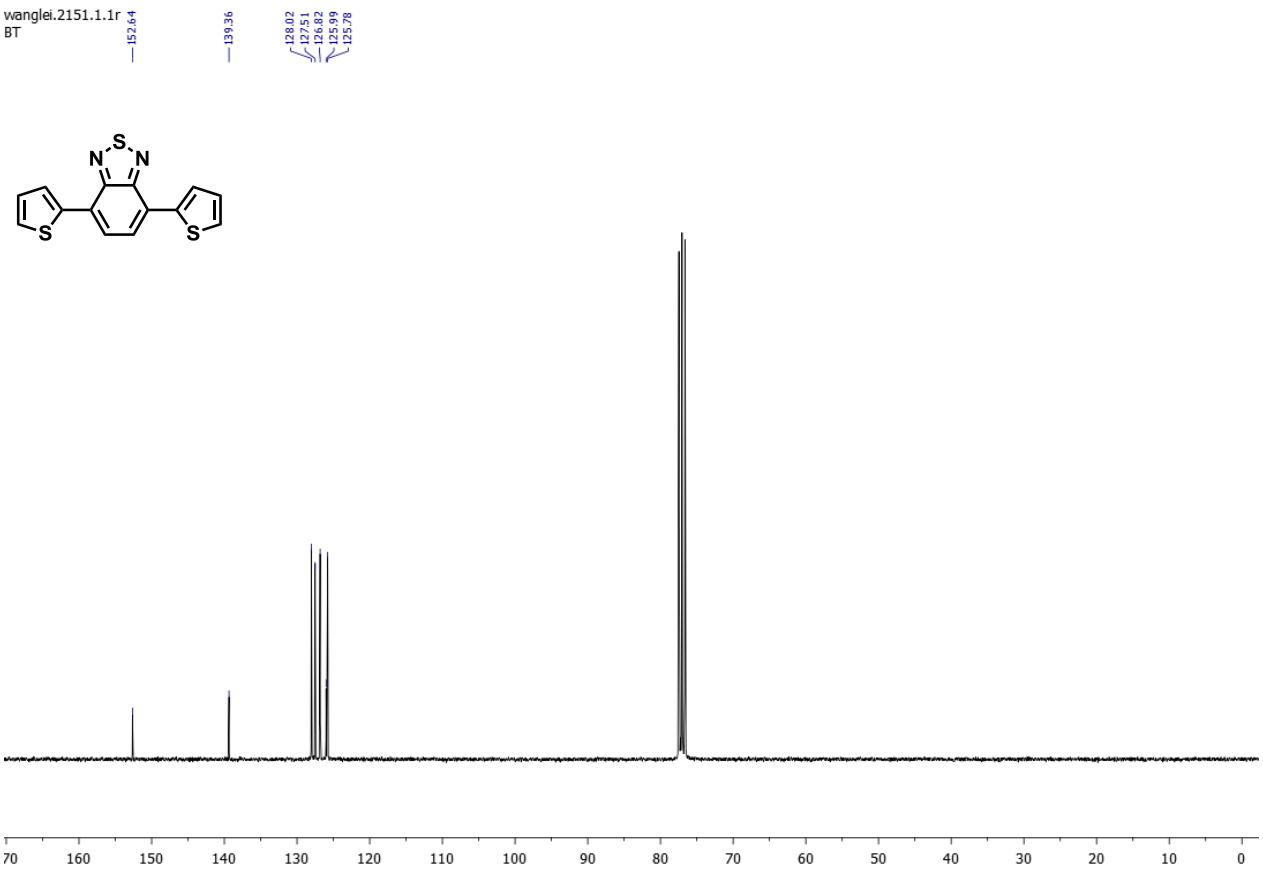
2.00
1.95
1.96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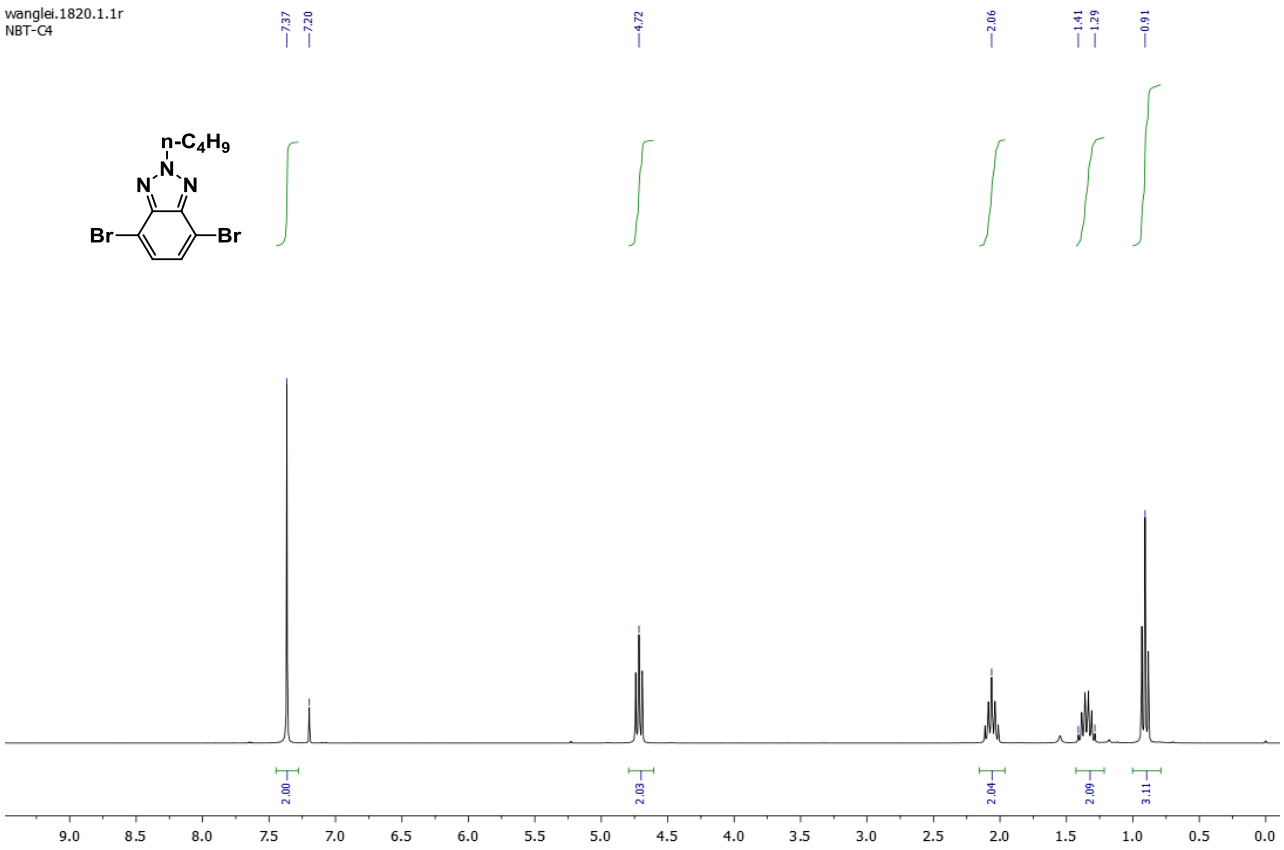
125.99
125.78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1.41
1.29
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N
N
N
Br
Br
2.00
2.03
2.04
2.09
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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1.0
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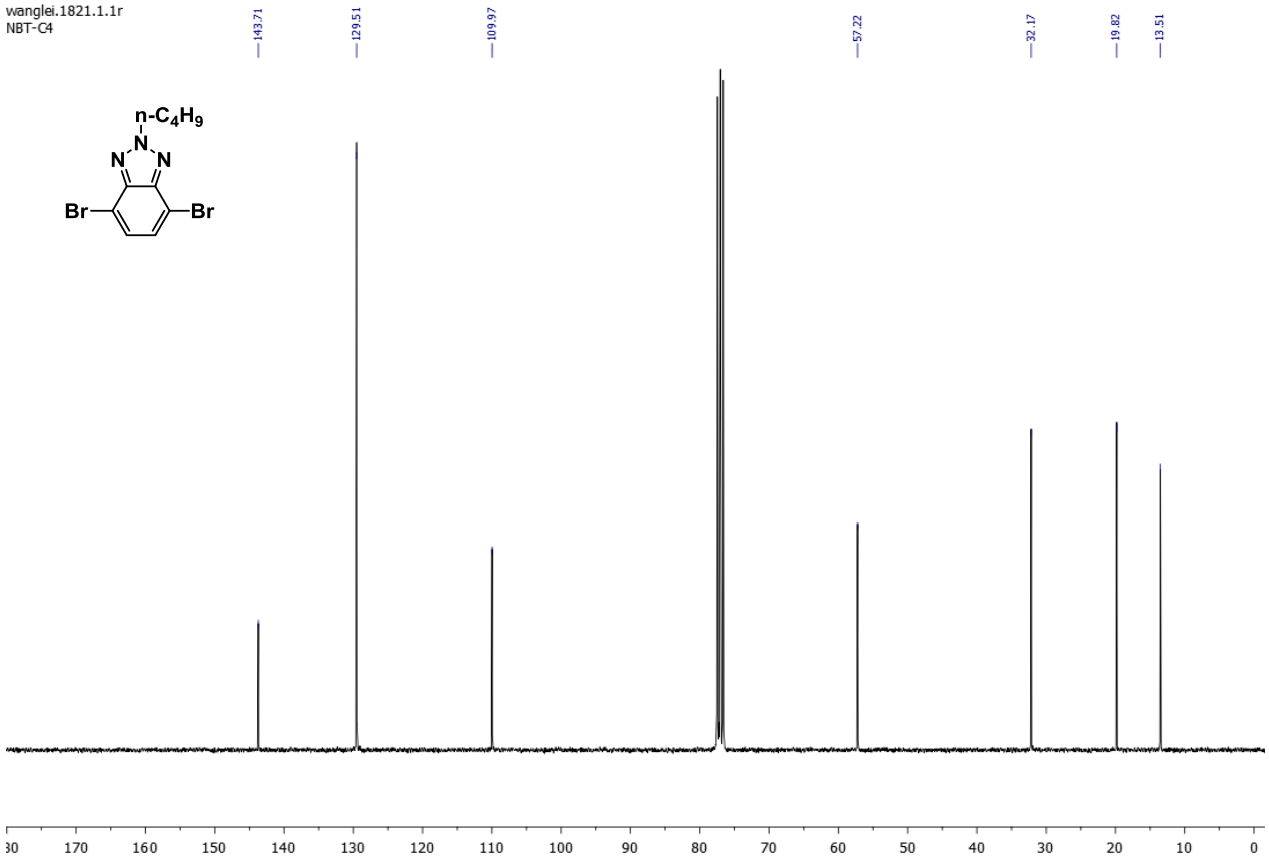
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32.17
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13.51
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N
N
N
Br
Br
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160
150
140
130
120
110
100
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70
60
50
40
30
20
10
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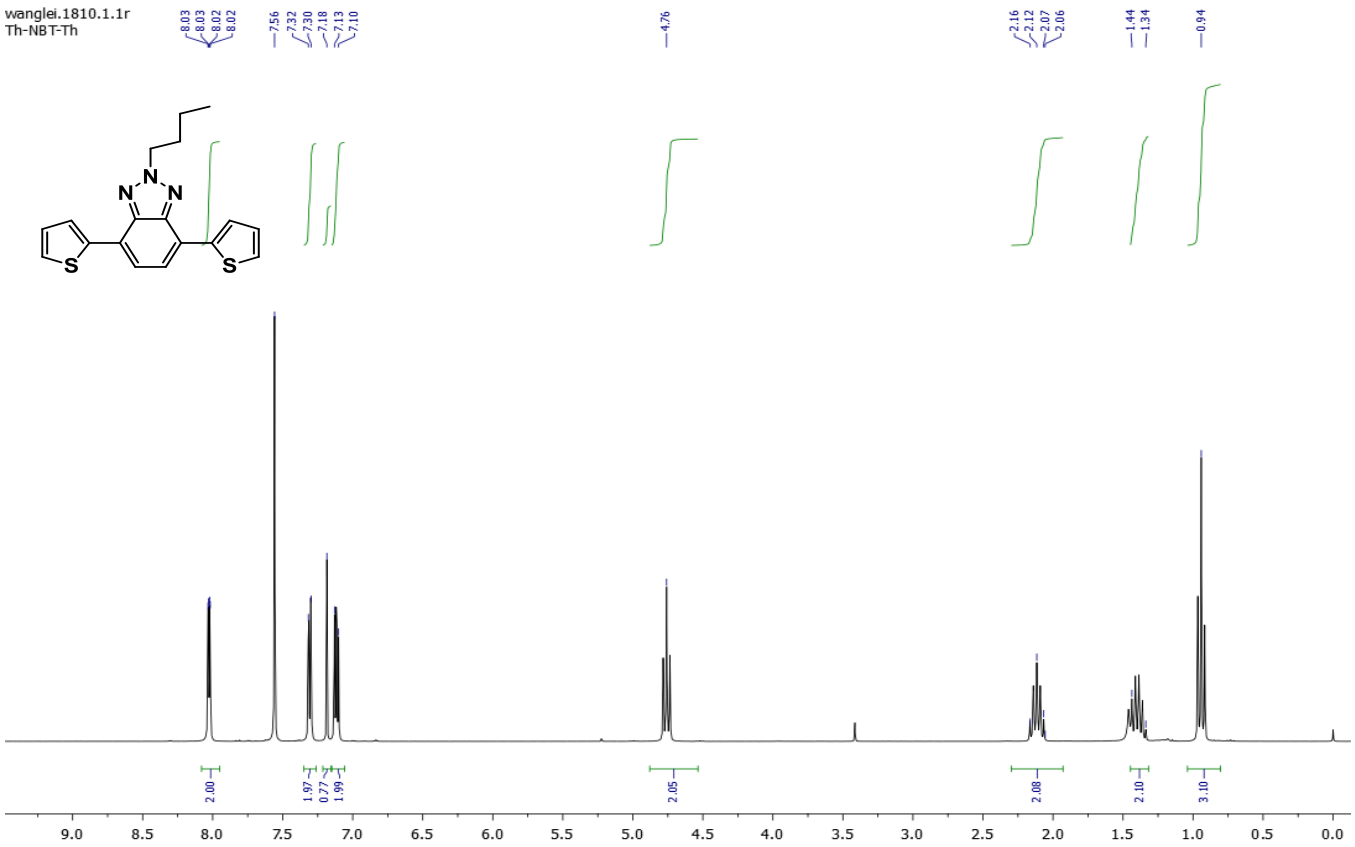
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Th-NBT-Th
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8.03
8.02
8.02
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7.32
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7.18
7.13
7.10
4.76
2.16
2.12
2.07
2.06
1.44
1.34
0.94
2.00
1.97
0.77
1.99
2.05
2.08
2.10
3.10
9.0
8.5
8.0
7.5
7.0
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6.0
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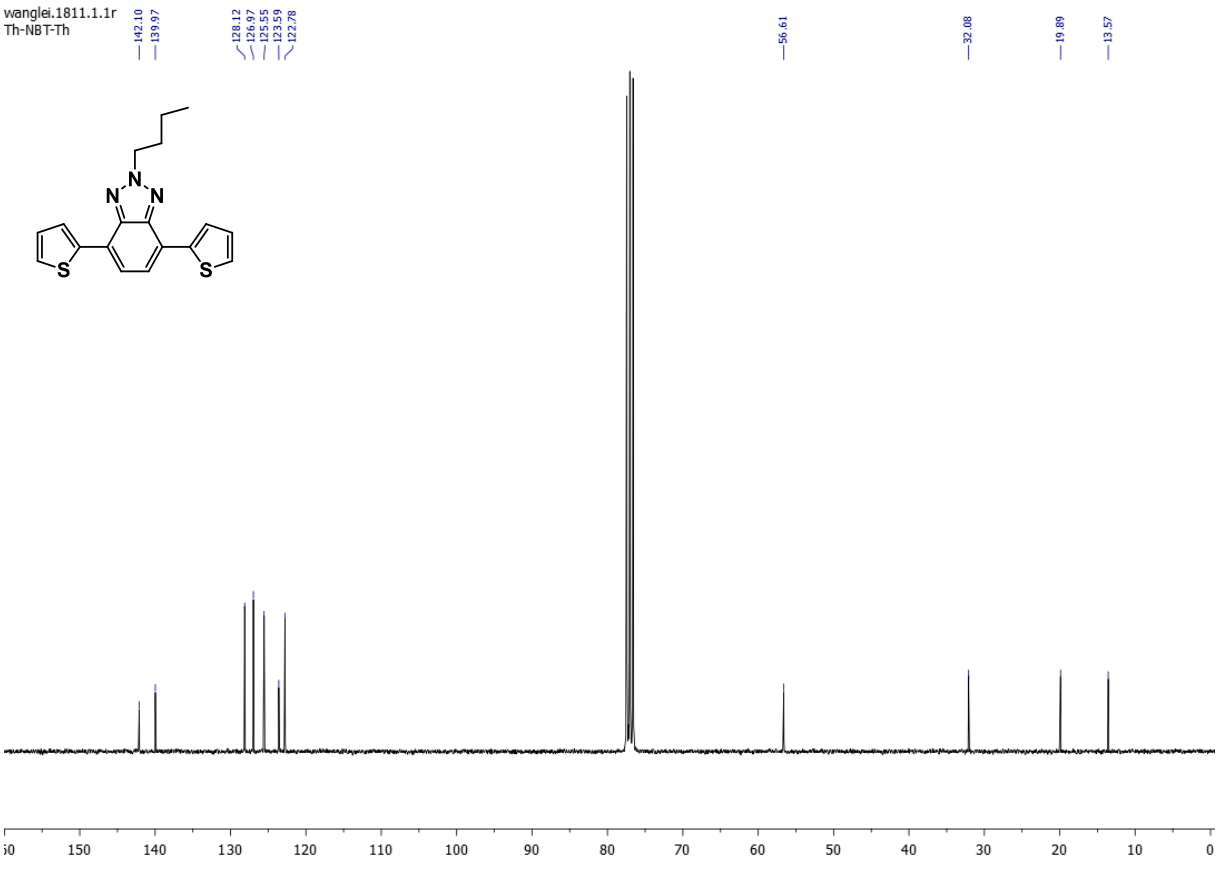
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Th-NBT-Th
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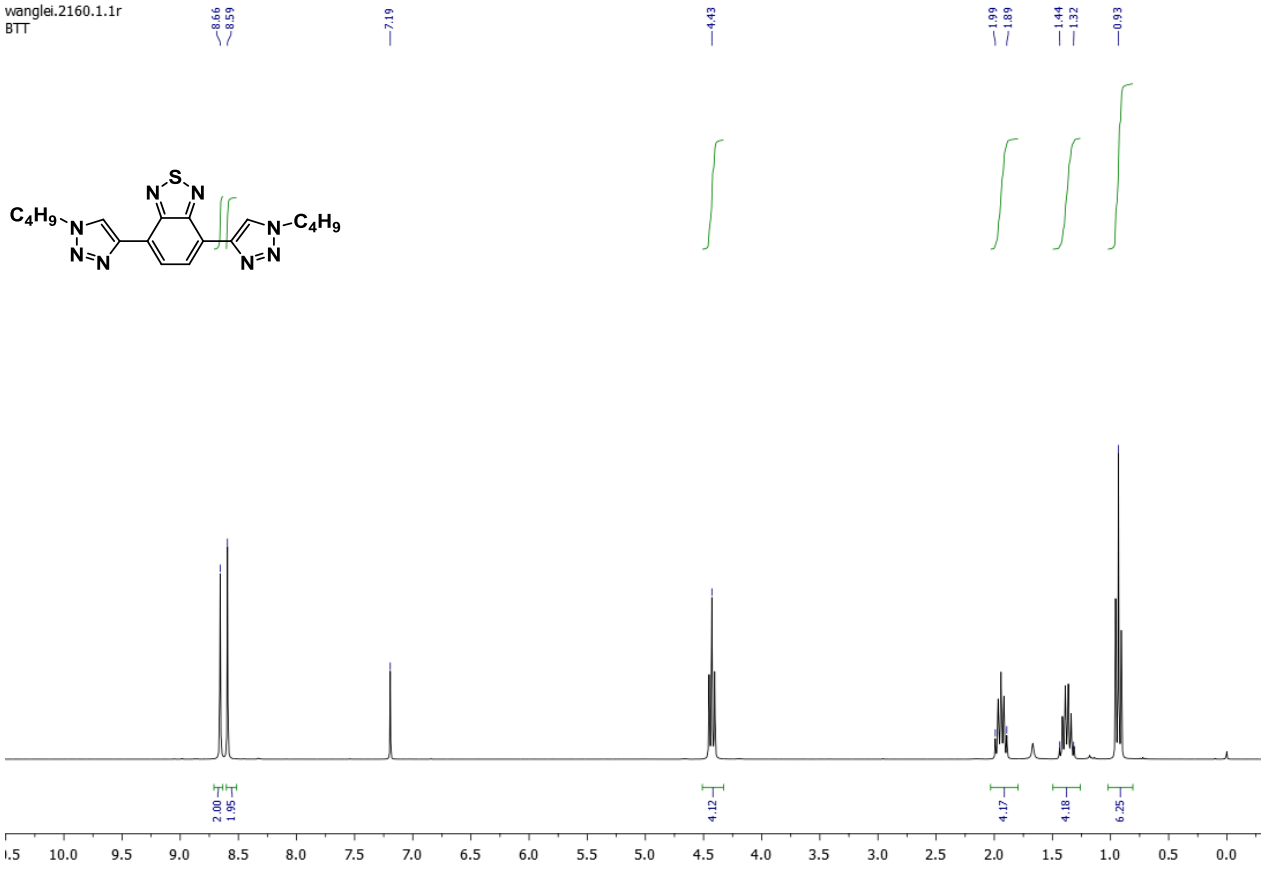
70
60
50
40
30
20
10
0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8.59
7.19
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1.89
1.44
1.32
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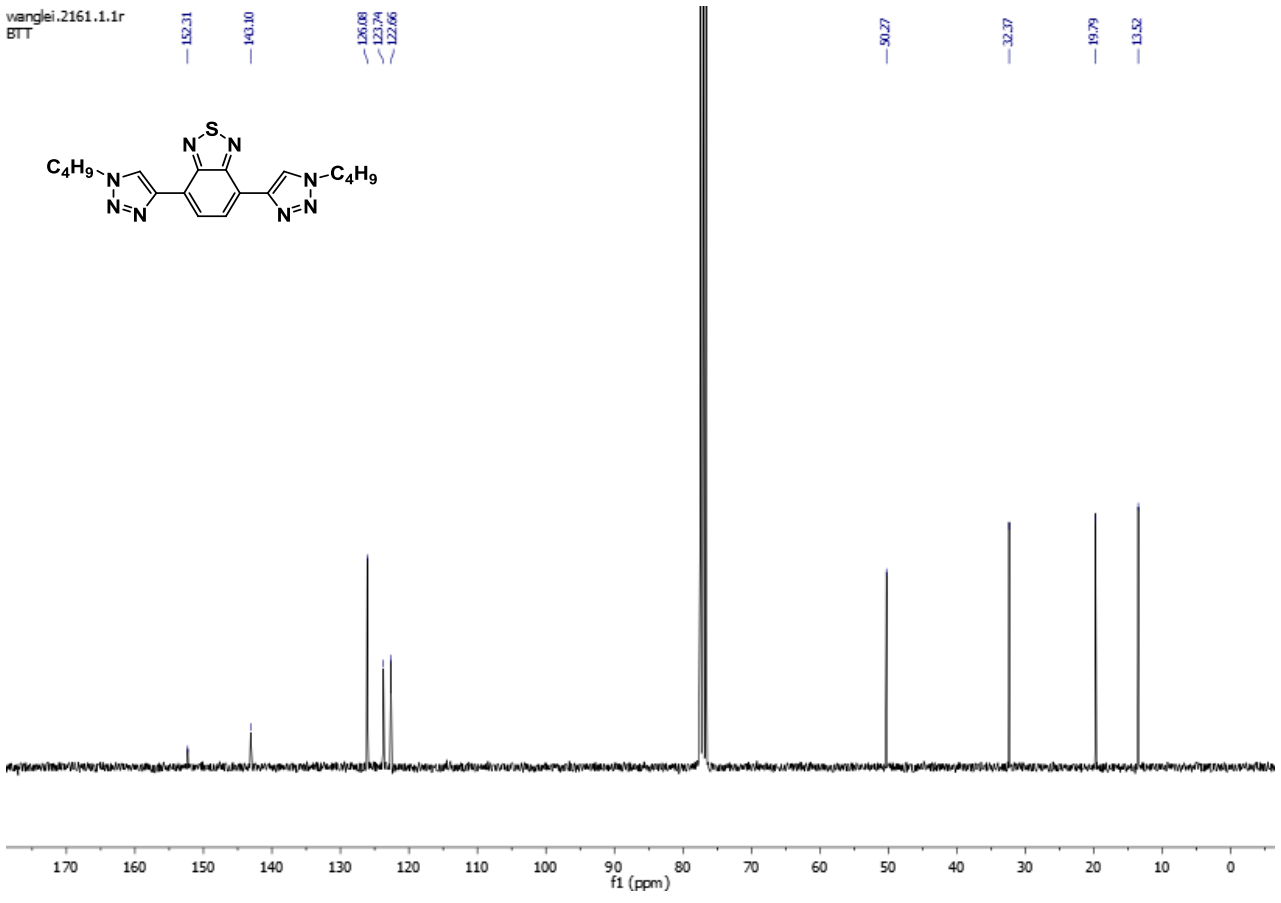
1.95
4.12
4.17
4.18
6.25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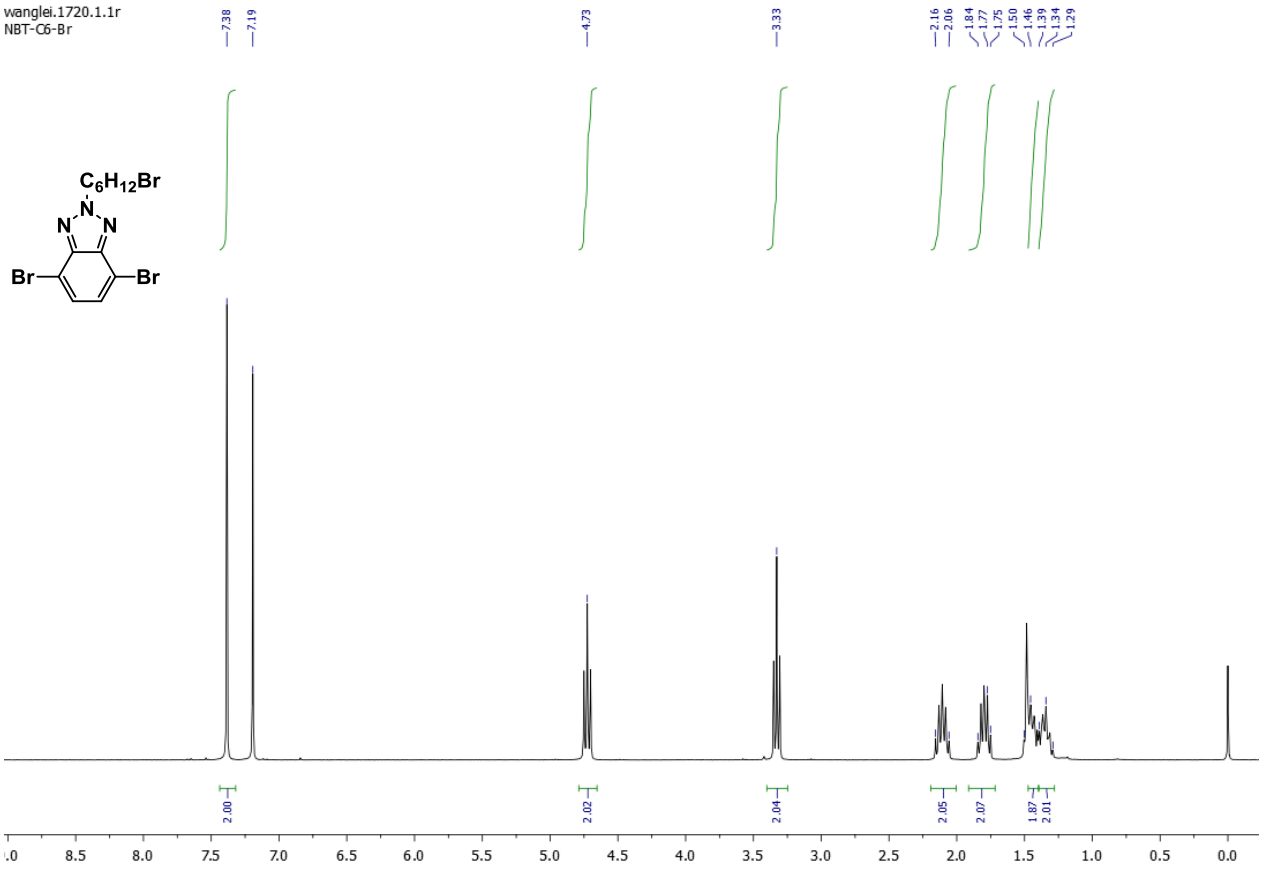
122.66
50.27
32.37
19.79
13.52
f1 (ppm)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3.33
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1.77
1.75
1.50
1.46
1.39
1.34
1.29
C6H12Br
Br
Br
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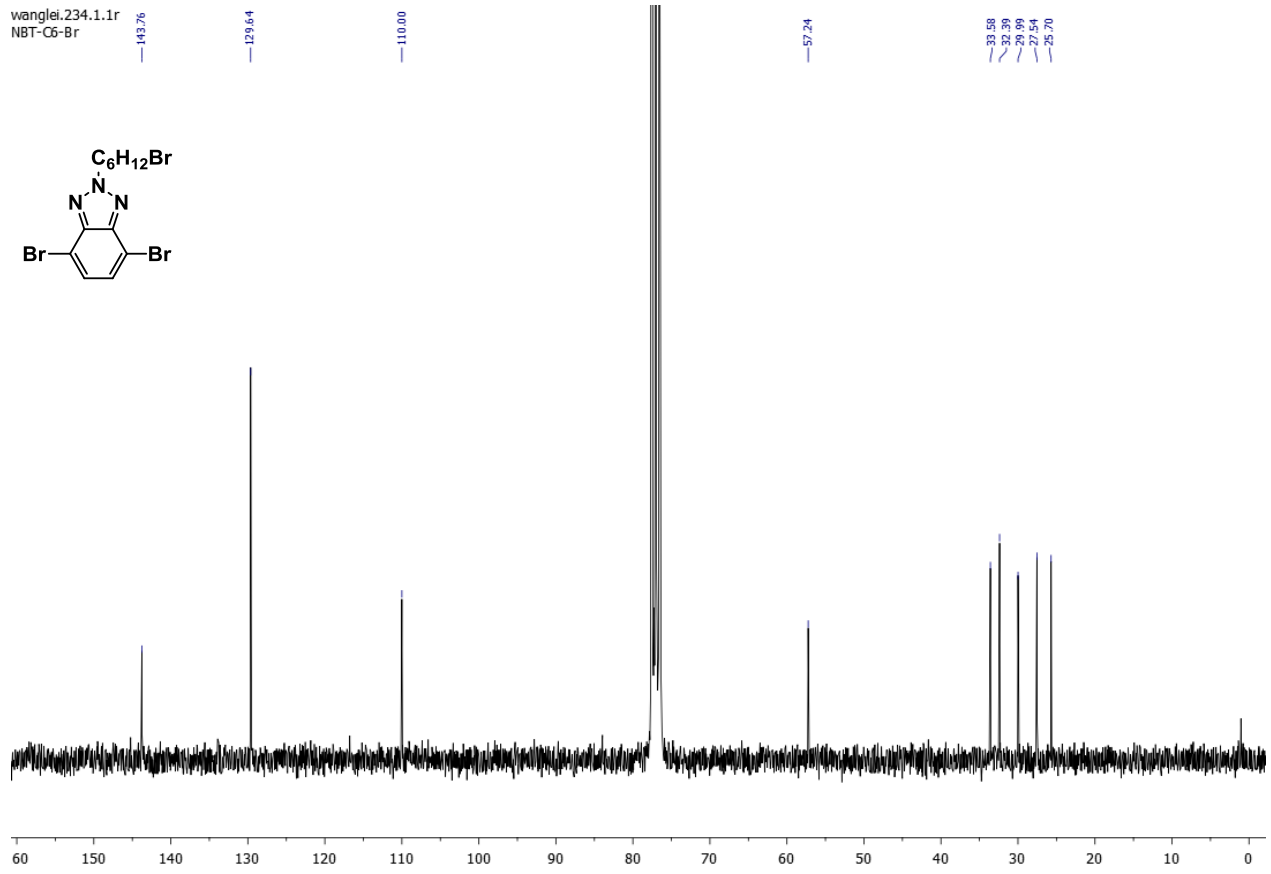
2.02
2.04
2.05
2.07
1.87
2.01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110.00
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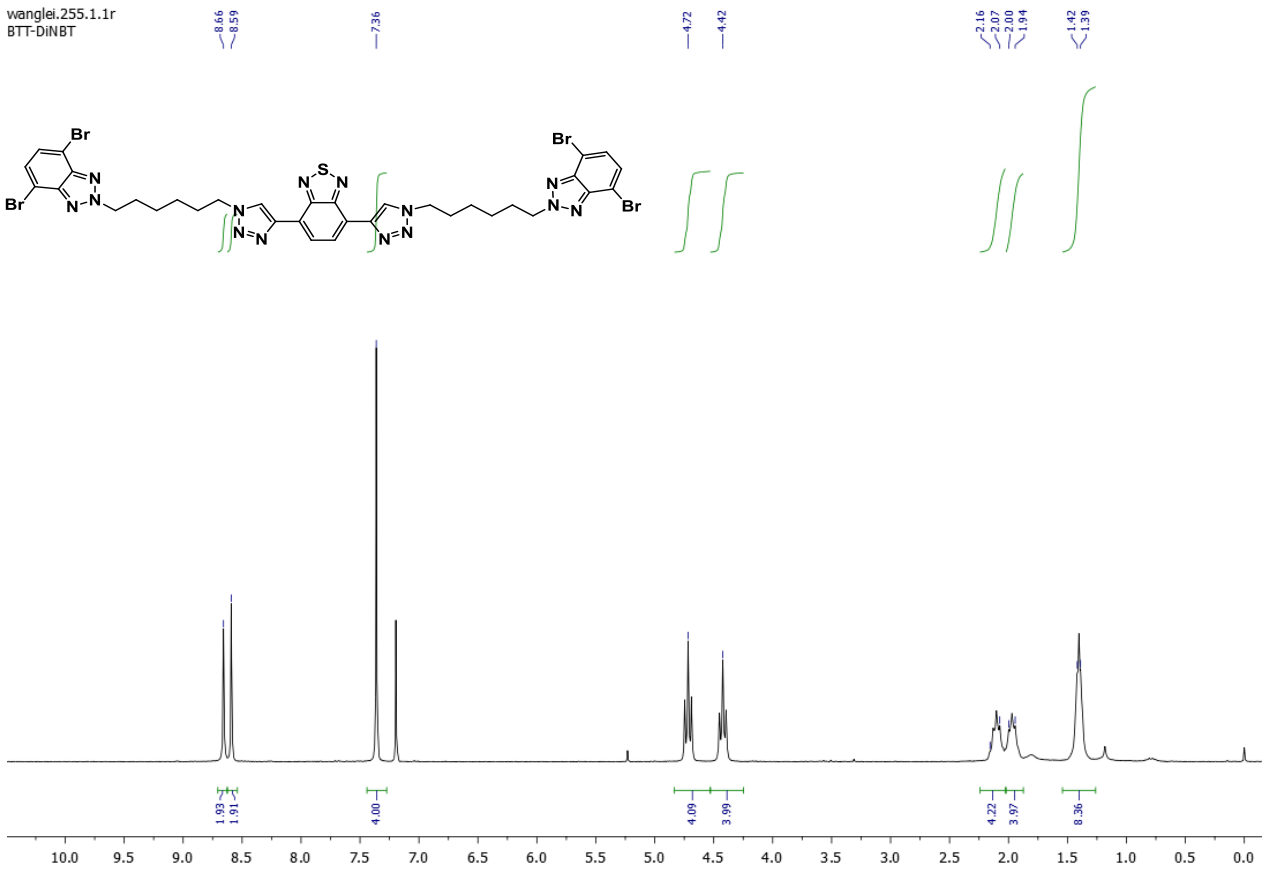
32.39
29.99
27.54
25.70
C6H12Br
Br
Br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7.36
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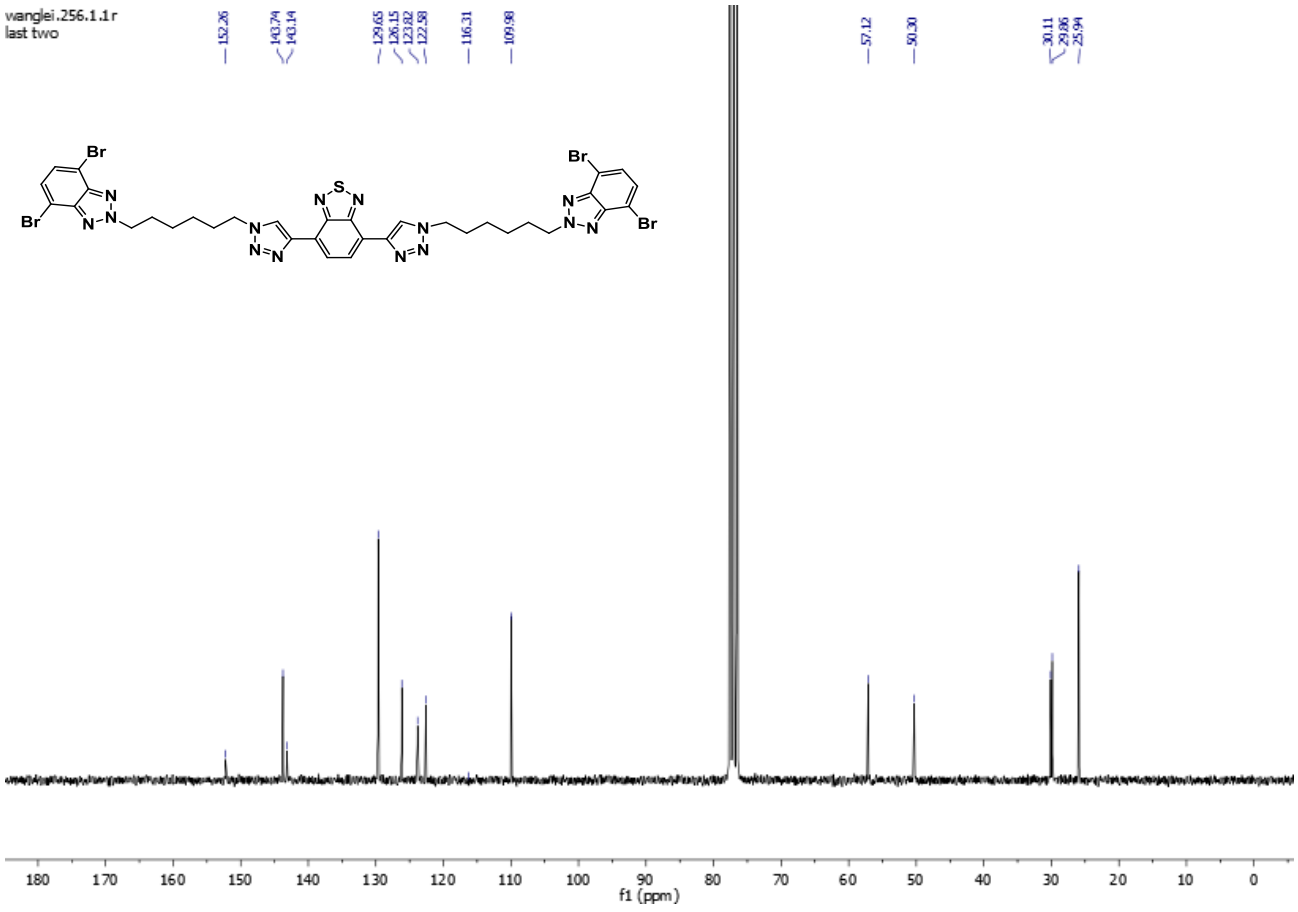
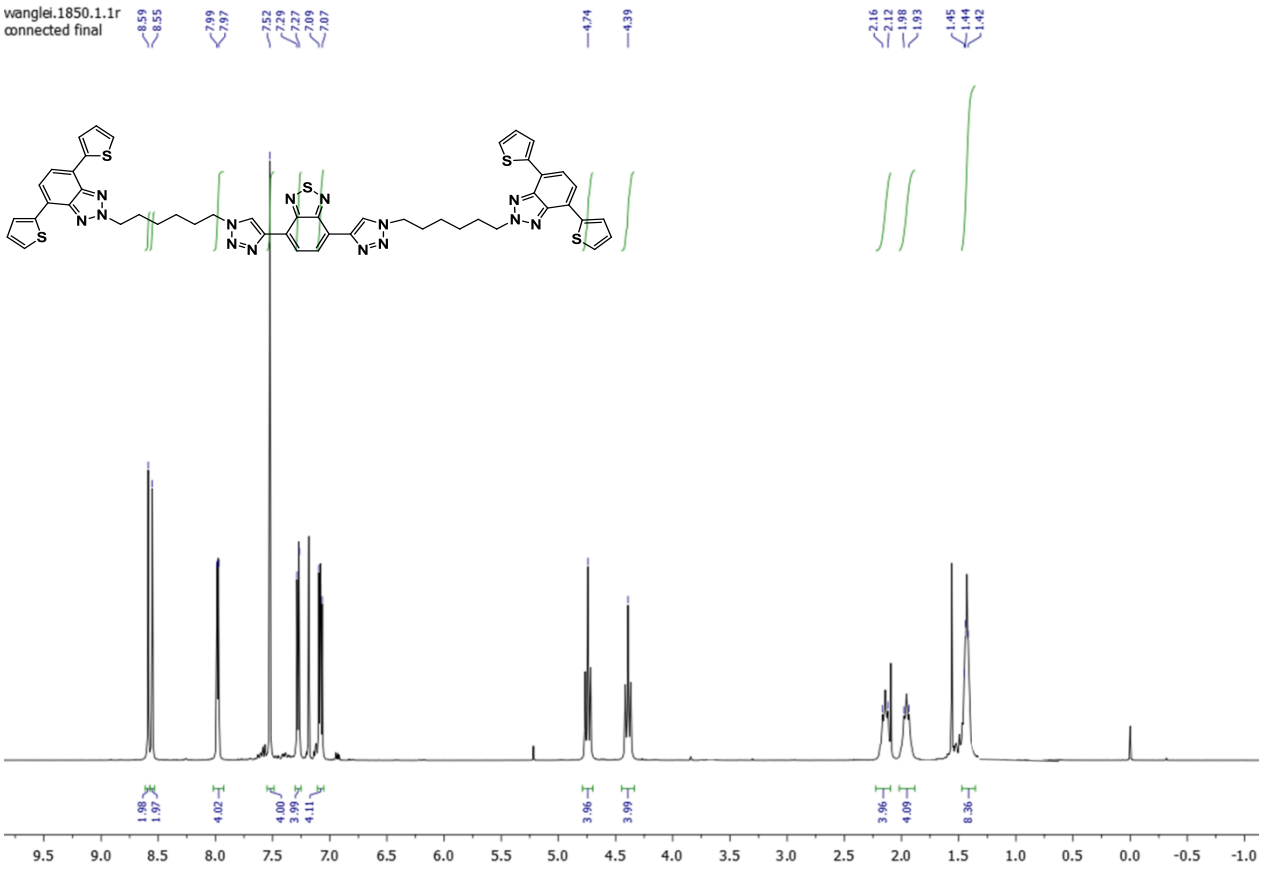
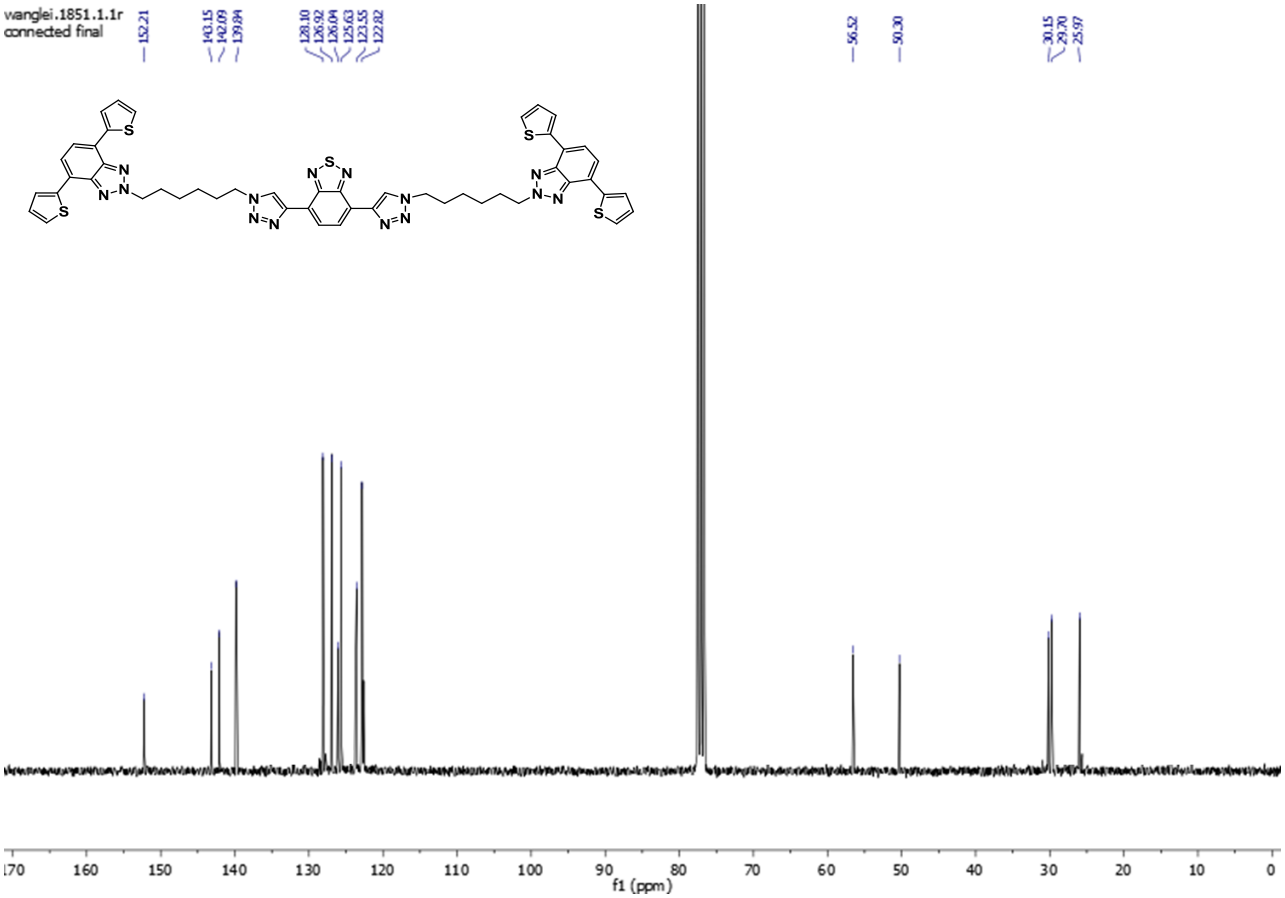
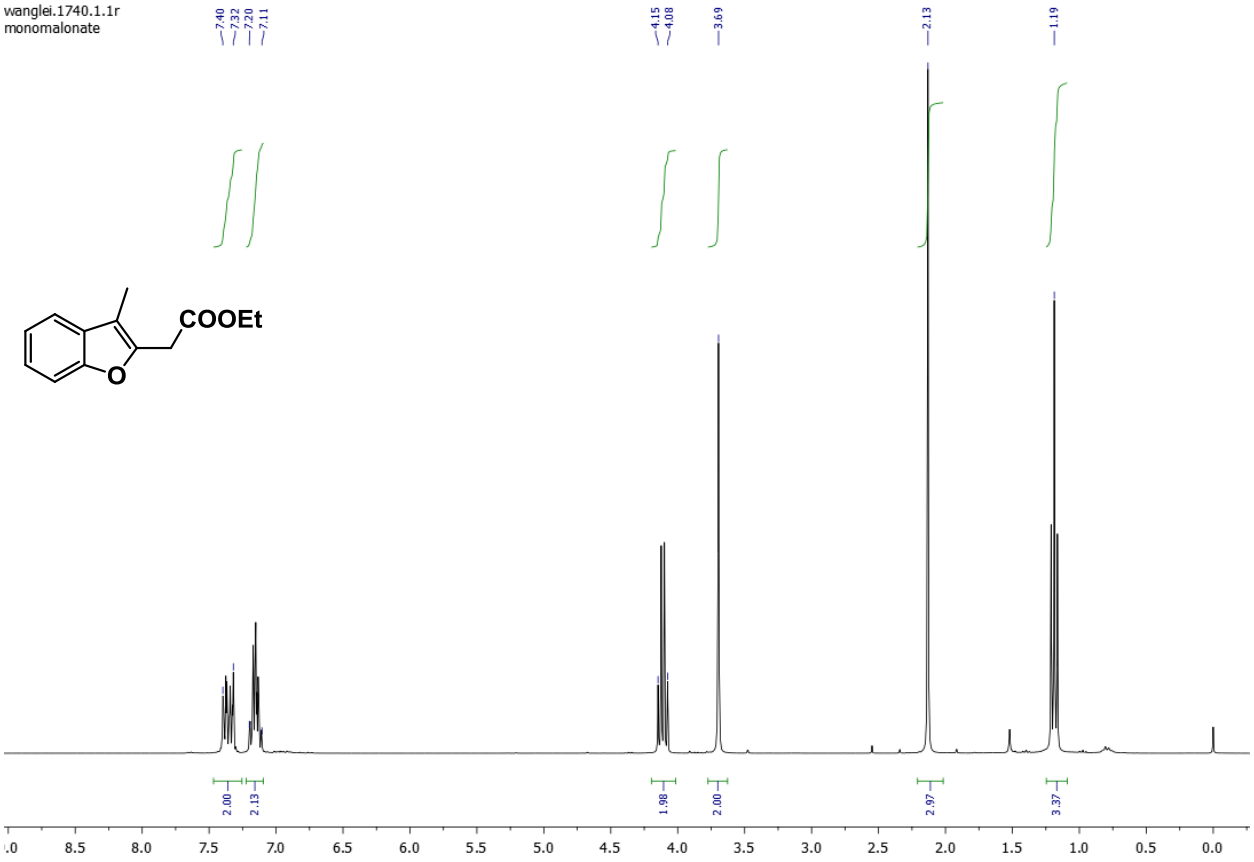
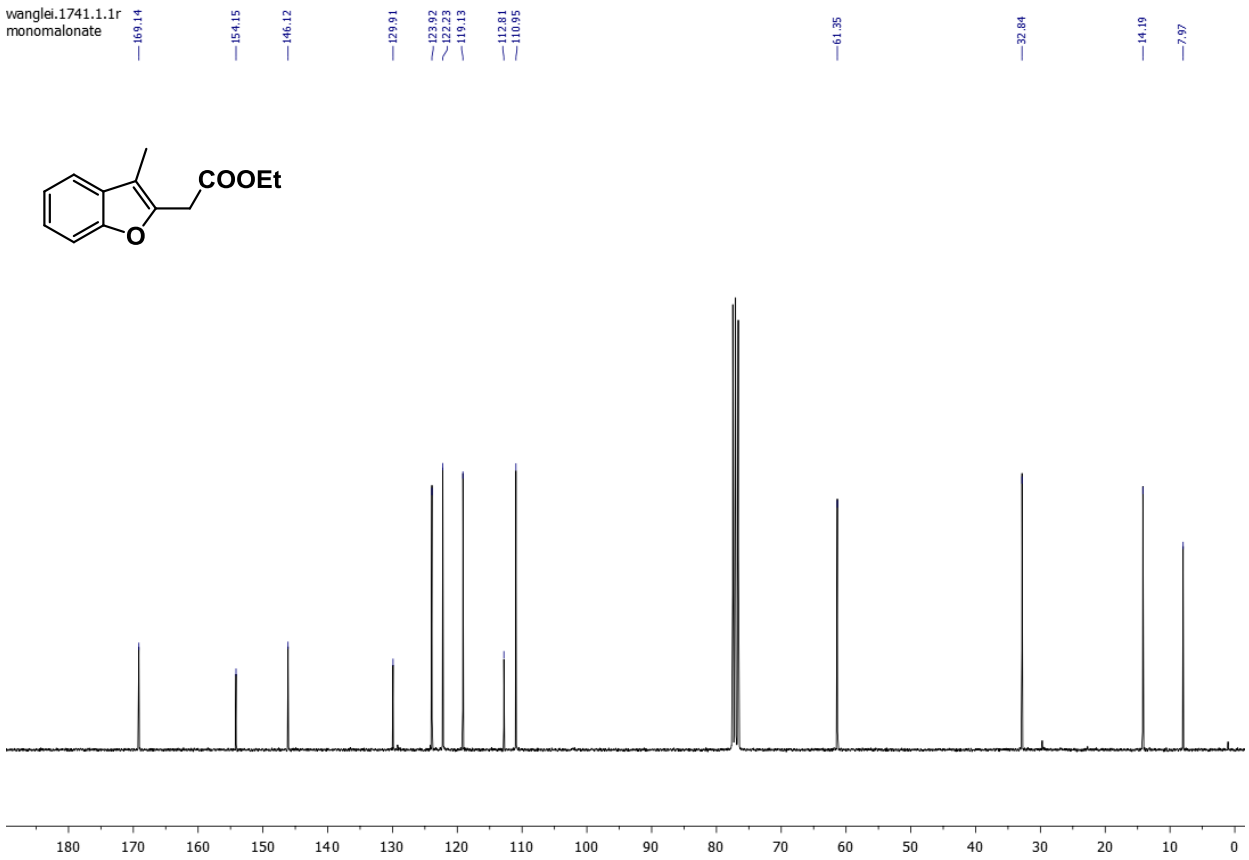
4.42
2.16
2.07
2.00
1.94
1.42
1.39
Br
Br
Br
Br
1.93
1.91
4.00
4.09
3.99
4.22
3.97
8.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


wanglei.256.1.1r
last two
152.26
143.74
143.14
129.65
126.15
123.82
122.58
116.31
109.98
57.12
50.20
30.11
29.86
25.94
Br
Br
Br
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


wanglei.1850.1.1r
connected final
8.59
8.55
7.99
7.97
7.52
7.29
7.27
7.09
7.07
4.74
4.39
2.16
2.12
1.98
1.93
1.45
1.44
1.42
1.98
1.97
4.02
4.00
3.99
4.11
3.96
3.99
3.96
4.09
8.36
9.5
9.0
8.5
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
0.0
-0.5
-1.0


wanglei.1851.1.1r
connected final
152.21
143.15
142.09
139.84
128.10
126.92
126.04
125.63
123.55
122.82
56.52
50.30
30.15
29.70
25.97
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


wanglei.1740.1.1r
monomalonate
7.40
7.32
7.20
7.11
4.15
4.08
3.69
2.13
1.19
COOEt
O
2.00
2.13
1.98
2.00
2.97
3.37
8.5
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
0.0


wanglei.1741.1.1r
monomalonate
169.14
154.15
146.12
129.91
123.92
122.23
119.13
112.81
110.95
61.35
32.84
14.19
7.97
COOEt
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0