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# Supporting information

## Facile synthesis of 2,2'-dinitrosubstituted biaryls through Cu-catalyzed ligand-free decarboxylative homocoupling of *ortho*-nitrobenzonic acids

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**General considerations.** The Reagents used for experiments were commercially available and were used as received unless otherwise noted. DMSO were distilled from $CaH_2$ under reduced pressure and stored under nitrogen. All Reactions were performed under nitrogen with the strict exclusion of dioxygen and moisture using Schlenk techniques. Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded at 400, 100 and 377 MHz with $CDCl_3$ as solvent respectively, however, considering the solubility of **2g** in $CDCl_3$, its $^1H$ and $^{13}C$ NMR spectra were recorded at 400 and 100 MHz with $(CD_3)_2SO$ as solvent. All coupling constants (*J* values) were reported in Hertz (Hz). Except **2g**, all compounds' HRMS were performed by Shanghai Mass Spectrometry Centre, Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences. **2g**'s Elemental analyses were performed by Center of Analysis and Testing of Nanchang University.

**General procedure for Cu-catalyzed decarboxylative homocoupling of *ortho*-nitrobenzonic acids.** An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The tube was fitted with a rubber septum, and then it was evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (2 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under nitrogen flow. With stirring, the reaction mixtures were heated at 140 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

**4,4'-dichloro-2,2'-dinitrobiphenyl (2a).** Procedure was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 22.6 mg (72%) of the product as a yellow solid. Exhibited spectral data in accordance with previous

report.[1] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (s, 2 H), 7.68 (d, $J$ = 8.0 Hz, 2 H), 7.24 (d, $J$ = 8.0 Hz, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 147.4, 135.5, 133.7, 131.9, 131.5, 125.2.

**5,5'-dichloro-2,2'-dinitrobiphenyl (2b).** Procedure was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.9 mg (57%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[1] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.15 (d, $J$ = 8.8 Hz, 2 H), 7.52 (dd, $J$ = 8.8, 1.5 Hz, 2 H), 7.23 (d, $J$ = 1.8 Hz, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 145.1, 140.2, 134.8, 130.6, 129.6, 126.4.

**4,4'-difluoro-2,2'-dinitrobiphenyl (2c).** Procedure was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 10.1 mg (36%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[2] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.96 (dd, $J$ = 8.3, 2.6 Hz, 2 H), 7.46 - 7.41(m, 2 H), 7.31 - 7.26 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 163.2, 160.7, 132.6 (d, $J$ = 8.1 Hz), 129.1 (d, $J$ = 4.1 Hz), 121.9 (d, $J$ = 21.2 Hz), 112.8 (d, $J$ = 27.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$): $\delta$ -108.8 - -108.9 (m).

**5,5'-difluoro-2,2'-dinitrobiphenyl (2d).** Procedure was followed using 5-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.5 mg (63%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[2] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.33 - 8.29 (m, 2 H), 7.25 - 7.31 (m, 2 H), 7.01 - 6.99 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 166.0, 163.5, 136.3, 127.9 (d, $J$ = 10.1 Hz), 117.8 (d, $J$ = 24.3 Hz), 116.4 (d, $J$ = 23.2 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$): $\delta$ -105.0 - -105.1 (m). HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_6F_2N_2O_4$ 280.0296; Found 280.0301.

**4,4',5,5'-tetrafluoro-2,2'-dinitrobiphenyl (2e).** Procedure was followed using 4,5-difluoro-2-nitrobenzoic acid (40.6 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (1.5% ether in hexane) to afford 10.0 mg (32%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[2] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 - 8.17 (m, 2 H), 7.17 - 7.13 (m, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 154.4 (d, $J$ =13.1 Hz), 151.8 - 150.8 (m), 150.9 (d, $J$ = 13.1 Hz), 148.3 (d, $J$ = 13.1 Hz), 119.6 (d, $J$ = 20.2 Hz), 115.8 - 115.6 (m), 110.0. $^{19}$F NMR (377 MHz, $CDCl_3$): $\delta$ -125.4 - -125.5 (m), -131.2 - -131.3 (m). HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_4F_4N_2O_4$ 316.0107; Found 316.0102.

**2,2'-dinitro-4,4'-bis(trifluoromethyl)biphenyl (2f).** Procedure was followed using 2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (2% ether in hexane) to afford 23.7 mg (62%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[3] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.56 (s, 2 H), 8.00 (d, $J$ = 8.0 Hz, 2 H), 7.47 (d, $J$ = 8.0 Hz, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 136.6, 132.4, 131.5 - 131.4 (m), 130.4 - 130.2 (m), 123.9, 122.5 - 122.4 (m), 121.2. $^{19}$F NMR (377 MHz, $CDCl_3$): $\delta$ -63.01 (s).

**2,2'-dinitro-4,4'-bis(methylsulfonyl)biphenyl (2g).** Procedure was followed using 4-methylsulfonyl-2-nitrobenzoic acid (49.0 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (50% ether in hexane) to afford 16.6 mg (42%) of the product as a yellow solid. $^{1}$H NMR (400 MHz, $(CD_3)_2SO$): $\delta$ 8.76 (d, $J$ = 1.7 Hz, 2 H), 8.42 (dd, $J$ = 1.6 ,8.1 Hz, 2 H), 7.88 (d, $J$ = 8.0 Hz, 2 H), 3.47 (s, 6 H). $^{13}$C NMR (100 MHz, $(CD_3)_2SO$): $\delta$ 147.0, 142.7, 137.4, 133.1, 132.7, 124.0, 43.4. Anal. Calcd. for $C_{14}H_{12}N_2O_8S_2$: C, 42.00; H, 3.02. Found: C, 42.11; H, 3.08.

**2,2'-dinitrobiphenyl (2h).** Procedure was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 13.0 mg (53%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[4] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (d, $J$ = 8.0Hz, 2 H), 7.69 (t, $J$ = 8.0Hz, 2 H), 7.60 (t, $J$ = 8.0 Hz, 2 H), 7.30 (d, $J$ = 8.0 Hz, 2 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 134.2, 133.4, 130.9, 129.1, 124.8.

**4,4'-dimethyl-2,2'-dinitrobiphenyl (2i).** Procedure was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (5% ether in hexane) to afford 15.9 mg (58%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[4] Exhibited spectral data in accordance with previous report.[3] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (s, 2 H), 7.46 (d, $J$ = 8.0 Hz, 2 H), 7.15 (d, $J$ = 8.0 Hz, 2 H), 2.51 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 139.6, 134.0, 130.9, 125.1, 21.0.

**4,4'-dimethoxy-2,2'-dinitrobiphenyl (2k).** Procedure was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (8% ether in hexane) to afford 10.2 mg (34%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[4] Exhibited spectral data in accordance with previous report.[4] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.68 (s, 2 H), 7.21 - 7.16 (m, 4 H), 3.93 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.6, 148.2, 132.2, 125.7, 119.7, 109.5, 56.0.

**5,5'-dimethoxy-2,2'-dinitrobiphenyl (2l).** Procedure was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), CuI (11.4 mg, 0.06 mmol, 30 mol%) and 4 Å molecular sieves (MS). The reaction mixtures were purified by flash column chromatography on silica gel (25% ether in hexane) to

afford 19.7 mg (65%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[5] Exhibited spectral data in accordance with previous report.[5] $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.28 (d, $J$ = 8.0 Hz, 2 H), 7.02-6.99 (m, 2 H), 6.71 (d, $J$ = 2.6 Hz, 2 H), 3.90 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 163.3, 140.1, 137.4, 127.5, 115.7, 113.3, 56.1.

**References**


1. S. Tasler, J. Mies and M. Lang, Adv. Synth. Catal., 2007, 349, 2286-2300.
2. M. Protiva, J. Jílek, M. Rajšner, J. Pomykáček, M. Ryska, J. Holubek, E. Svátek and J. Metyšová, Collect. Czech. Chem. Commun., 1986, 51, 698-722.
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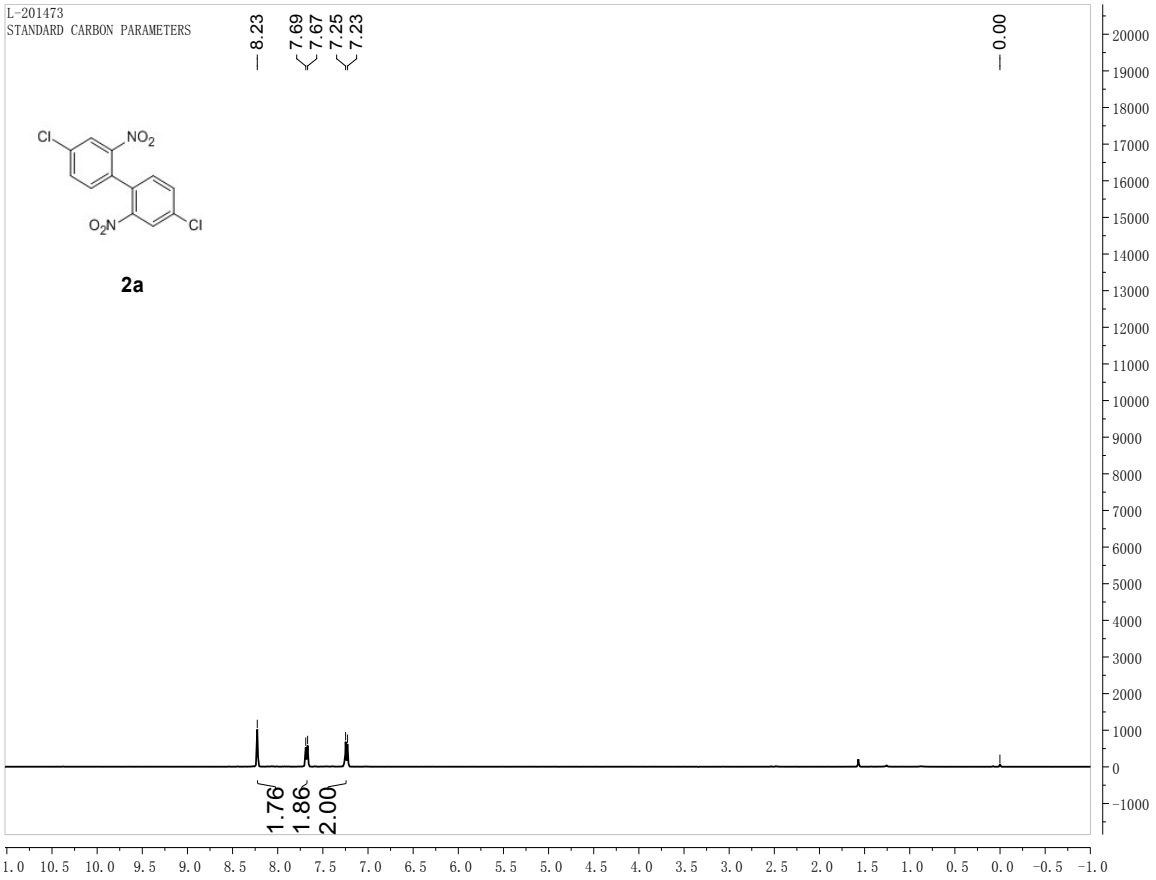
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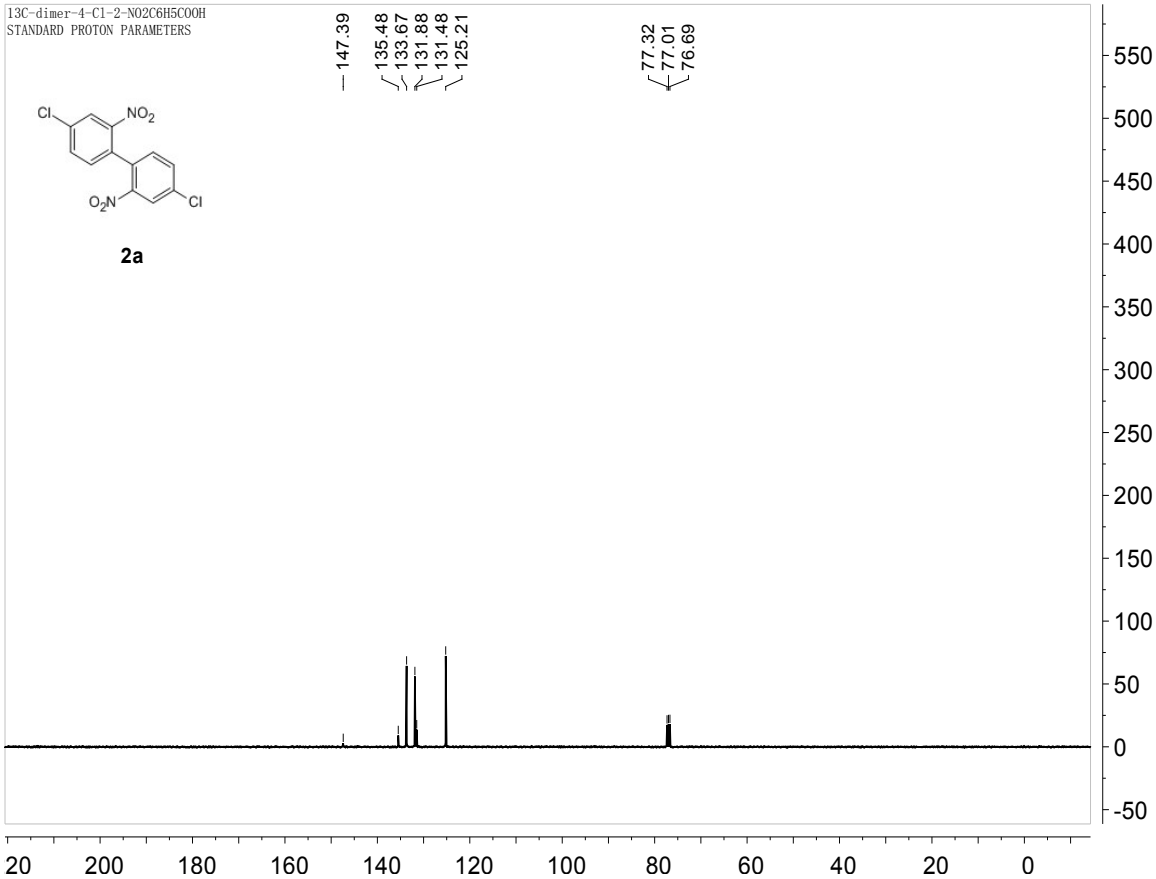
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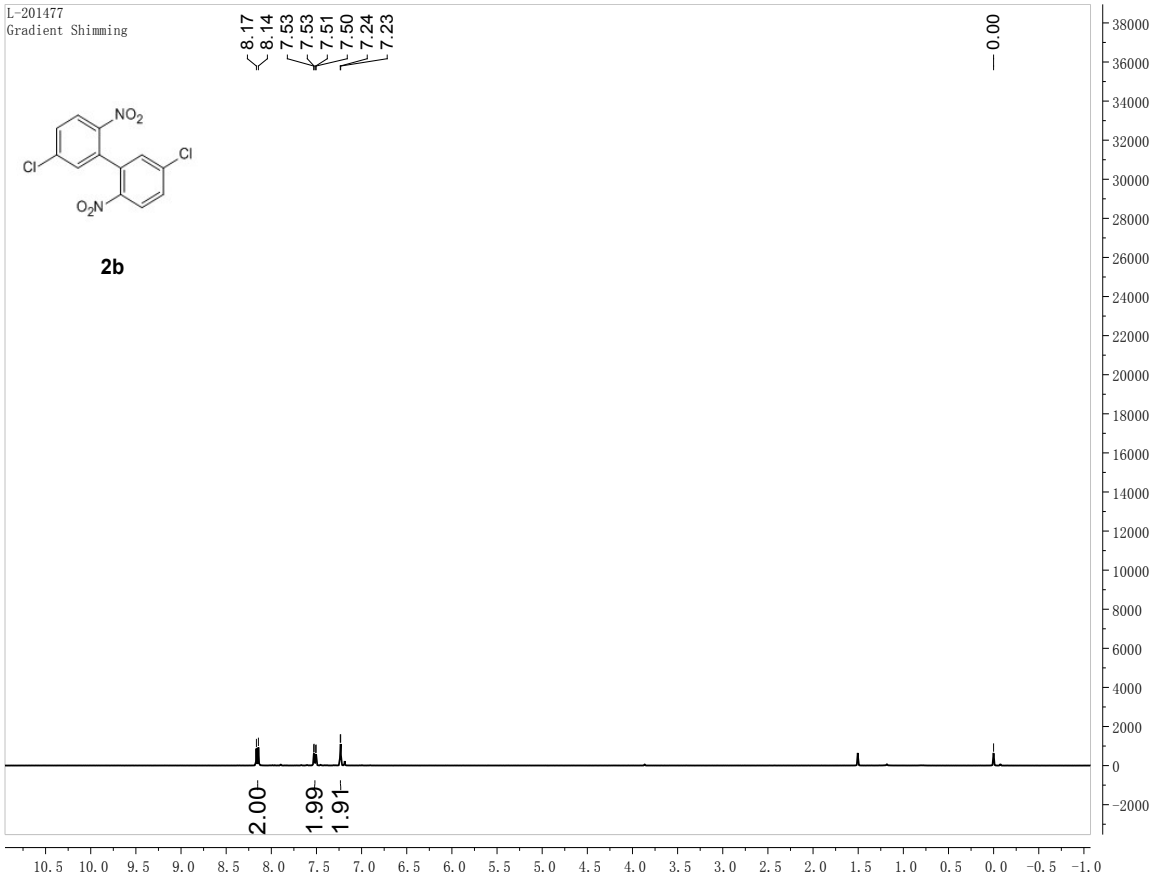
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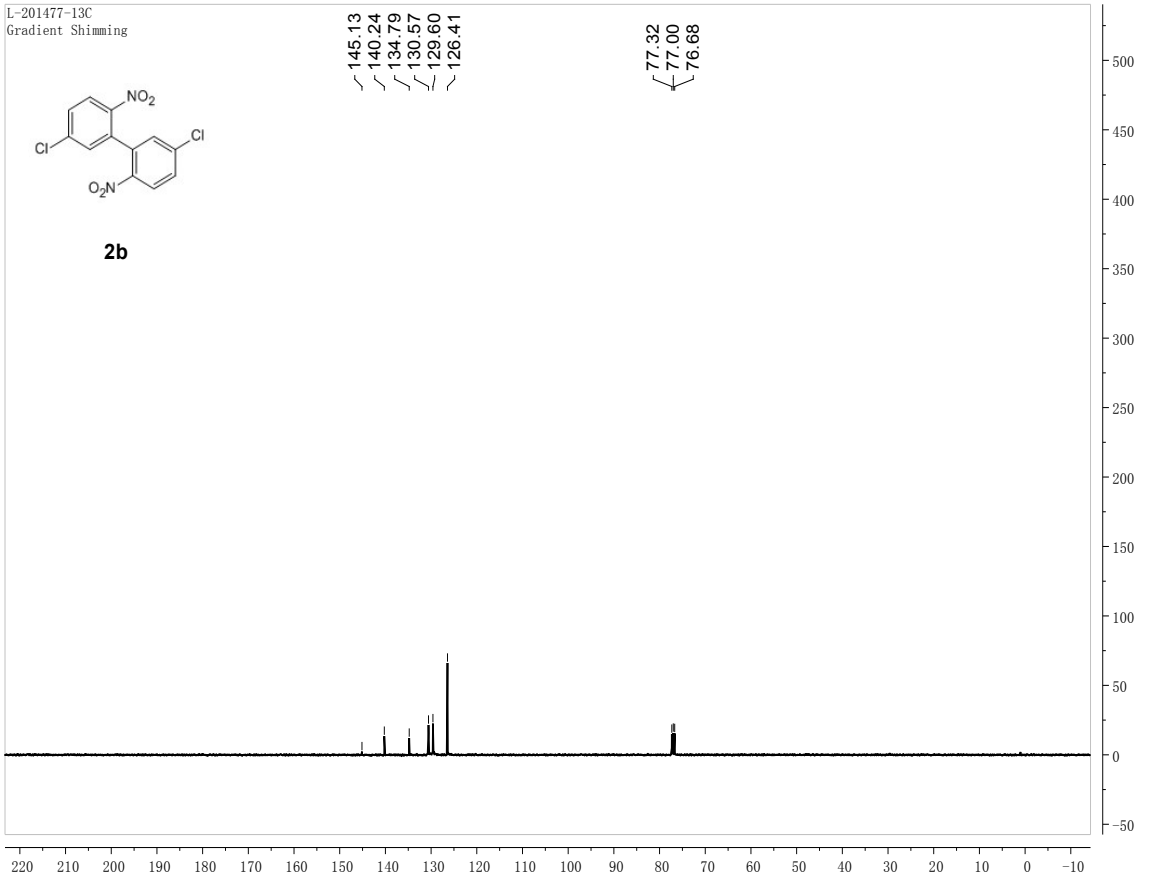
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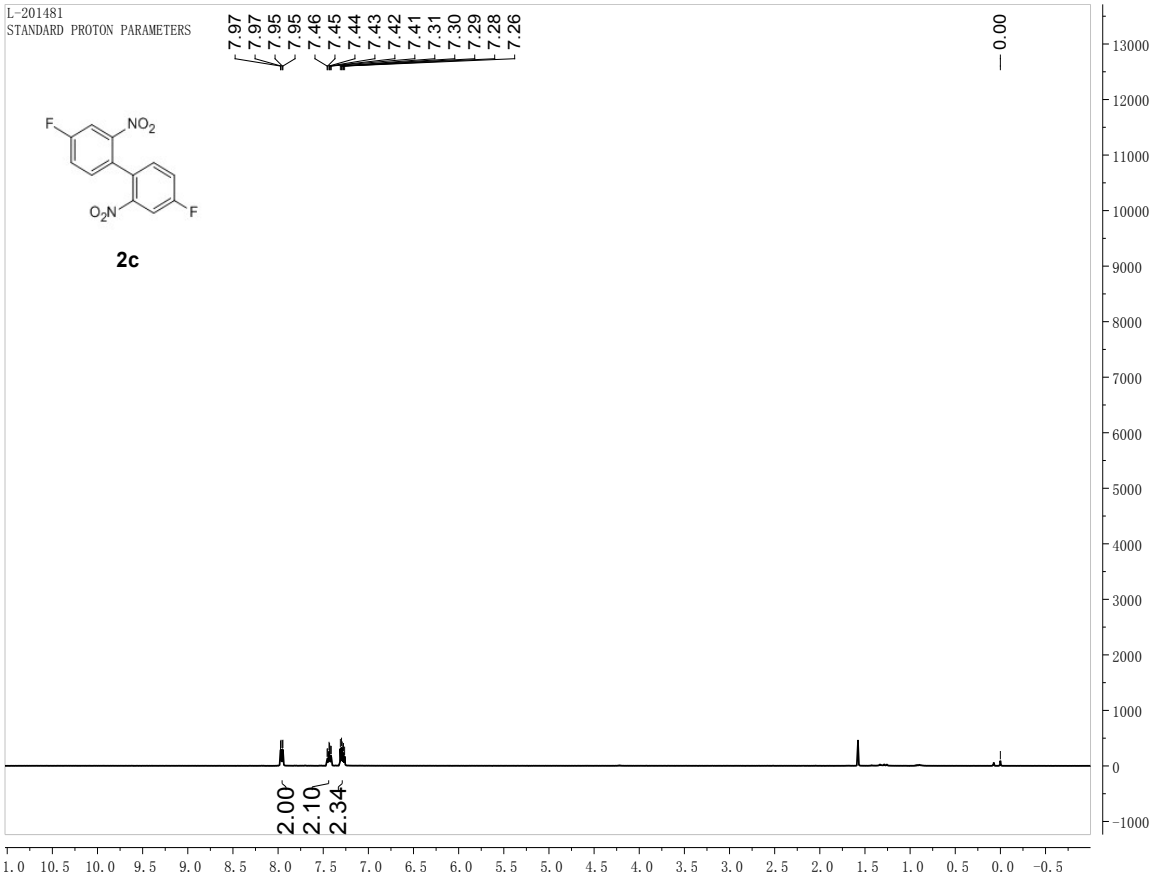
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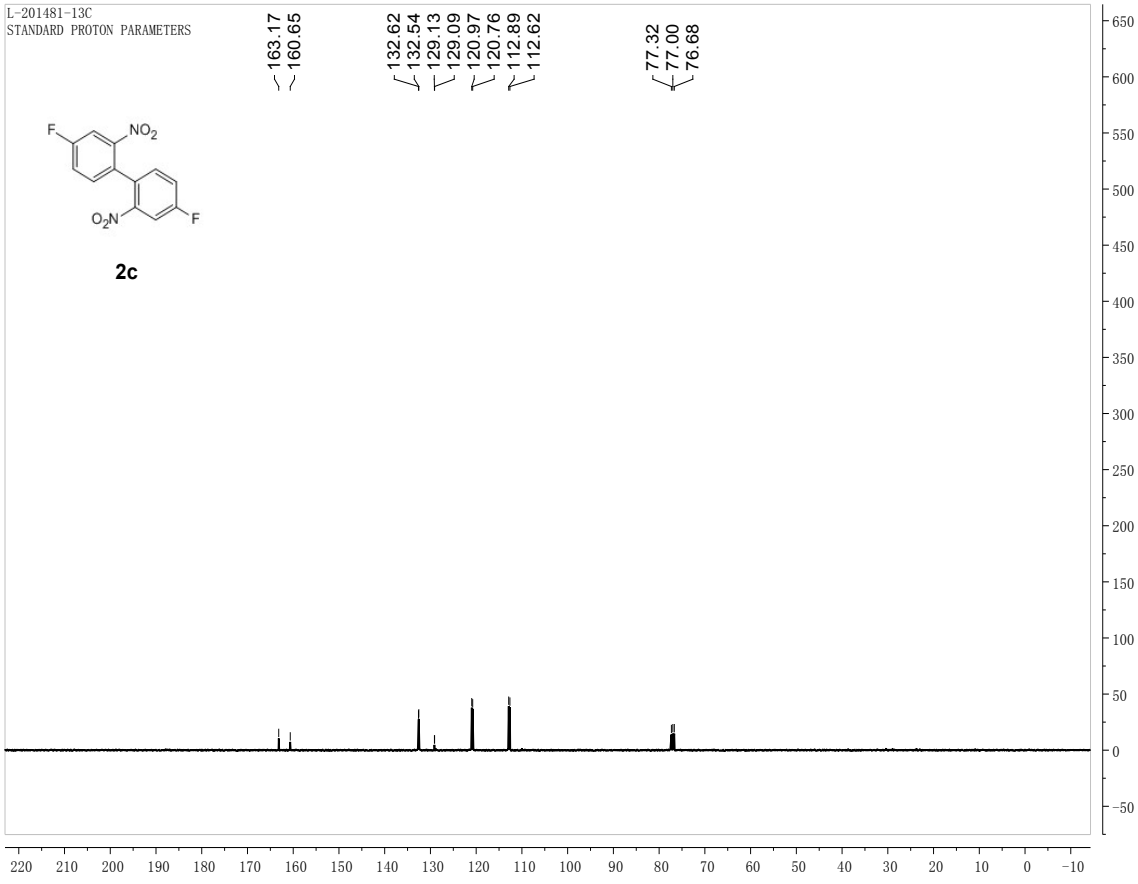
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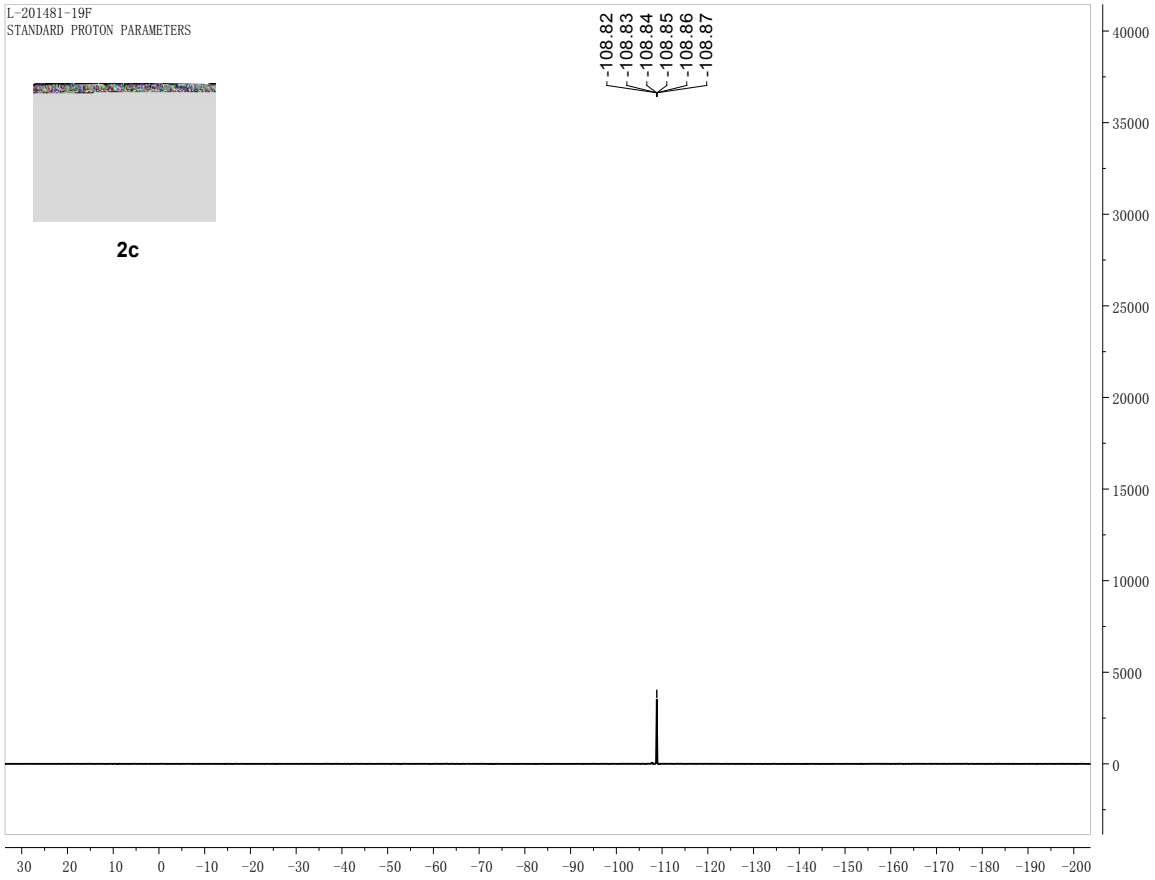
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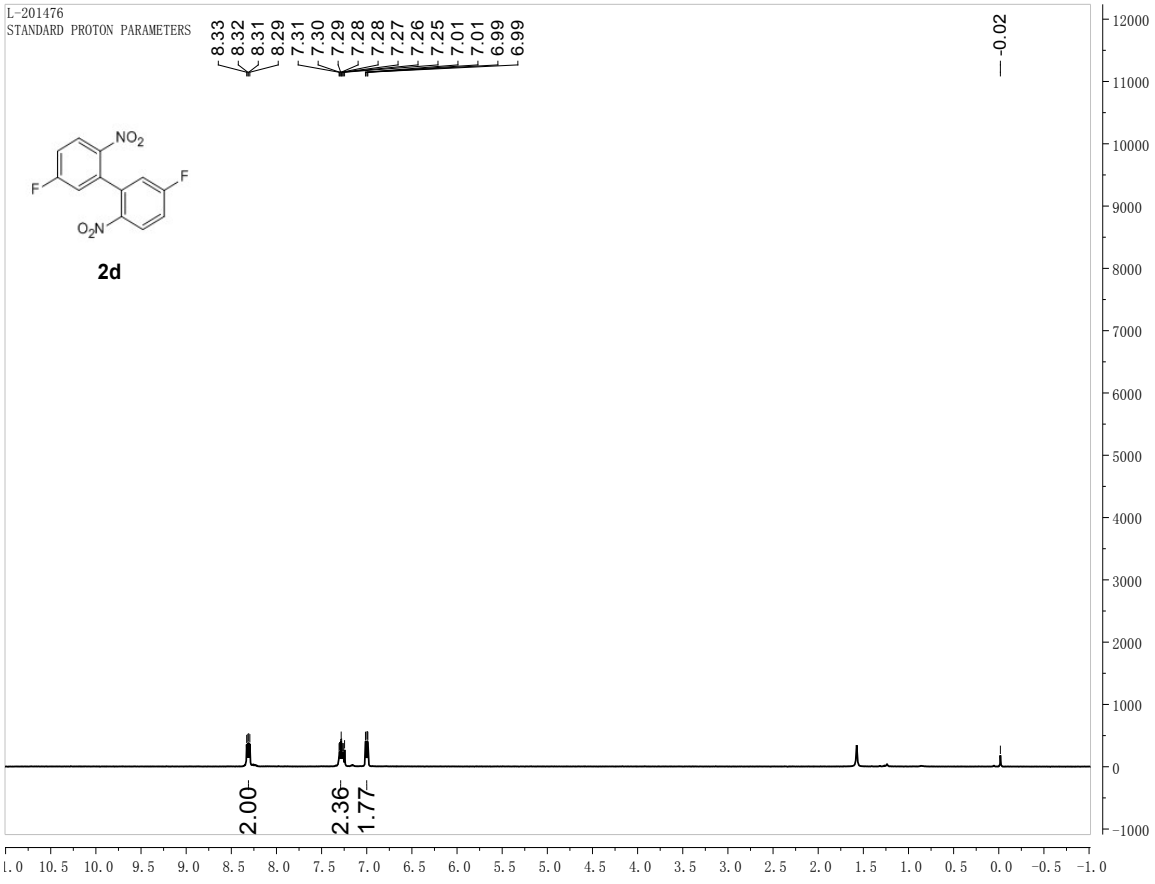
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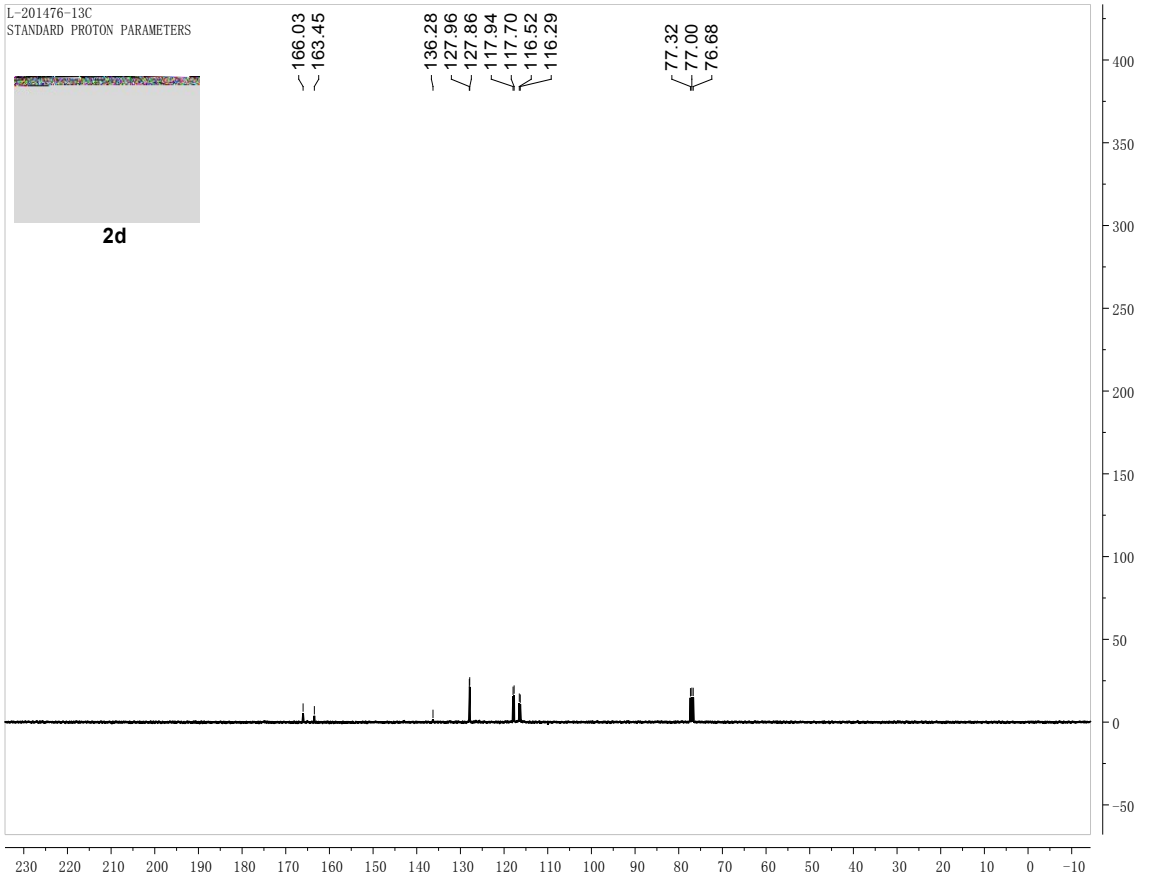
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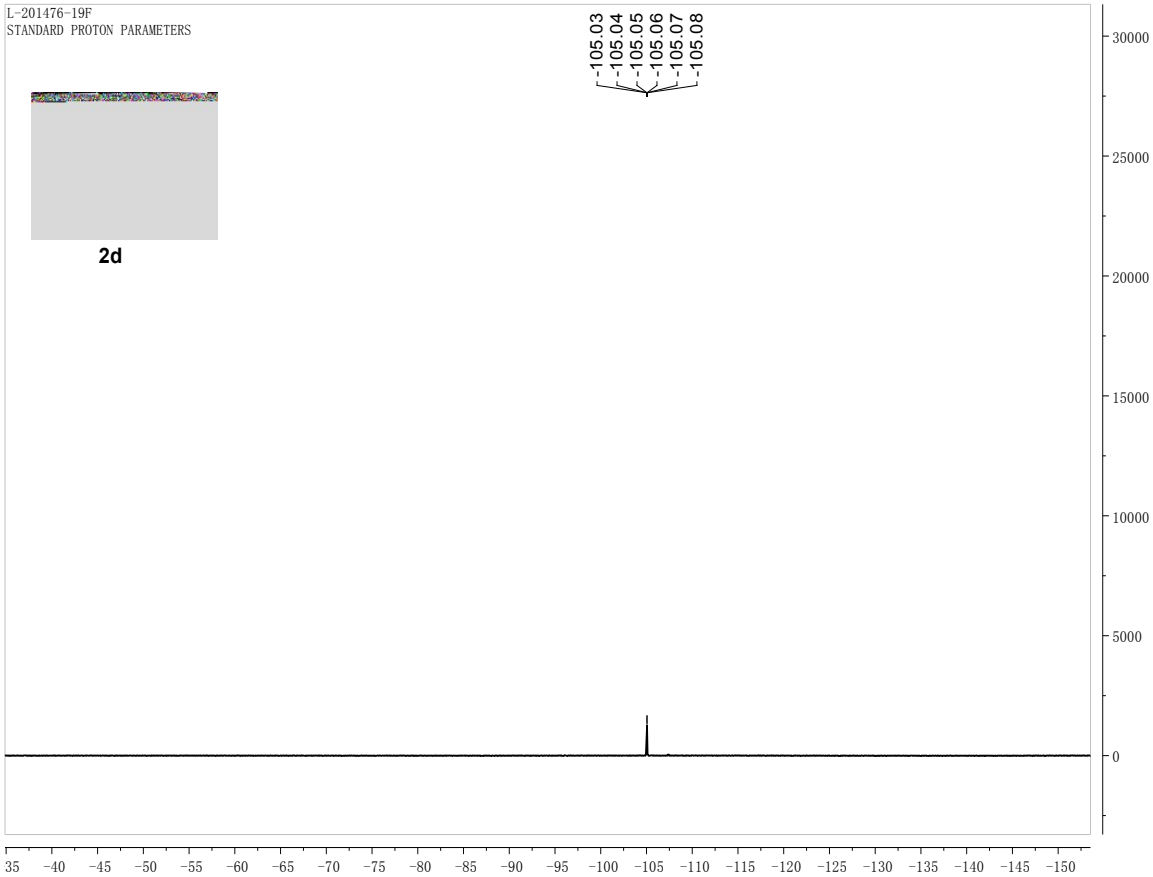
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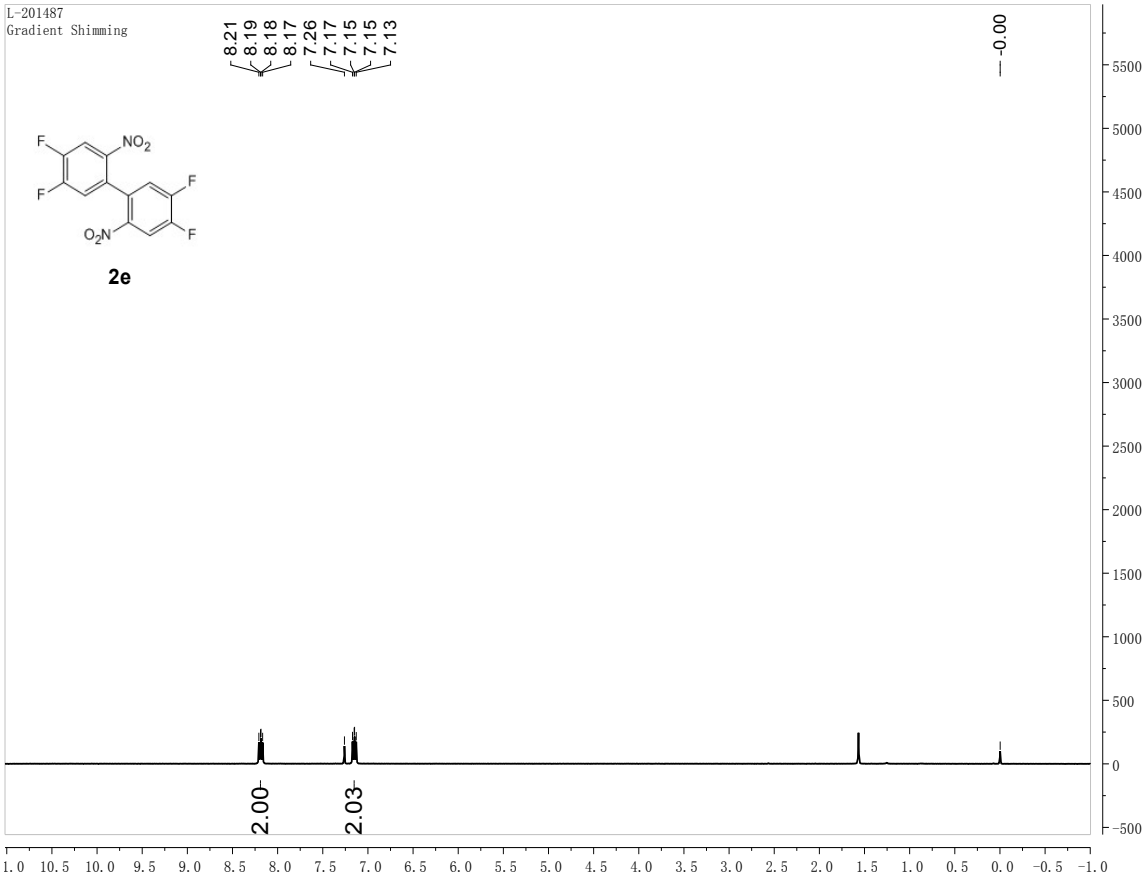
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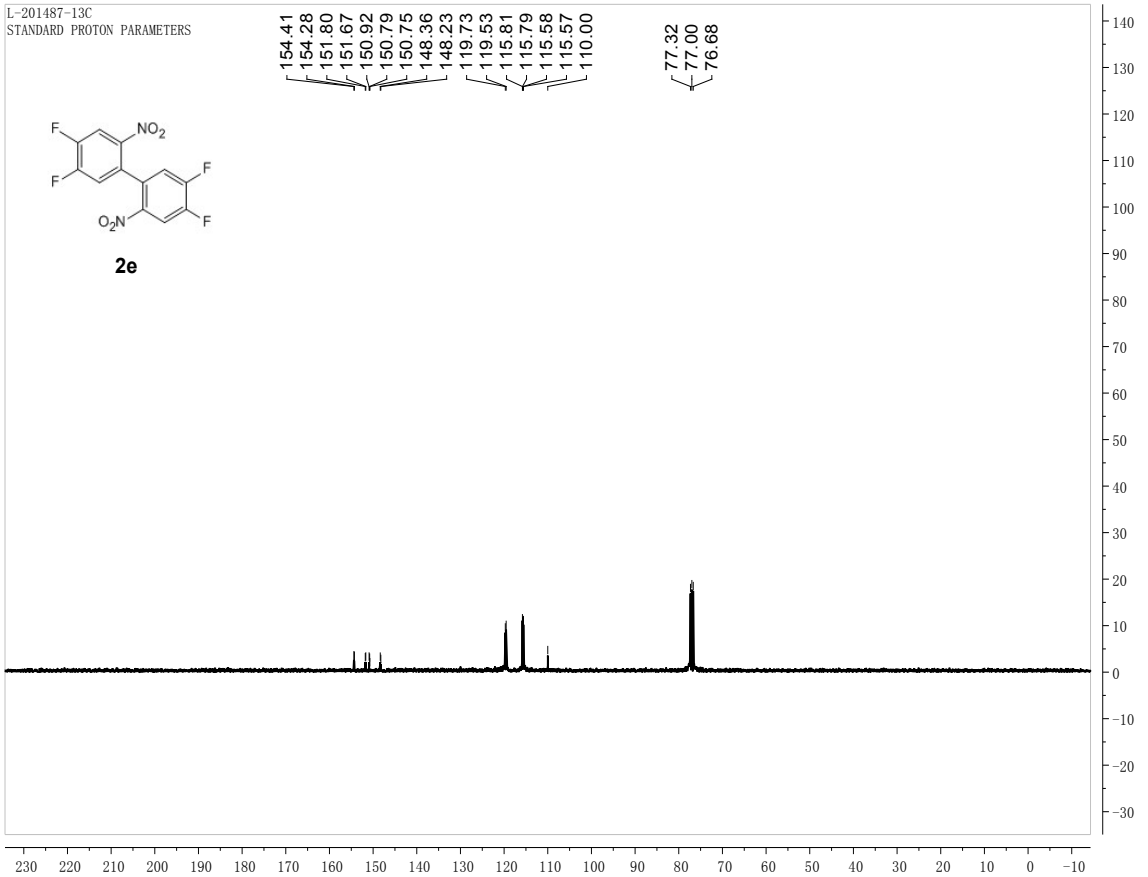
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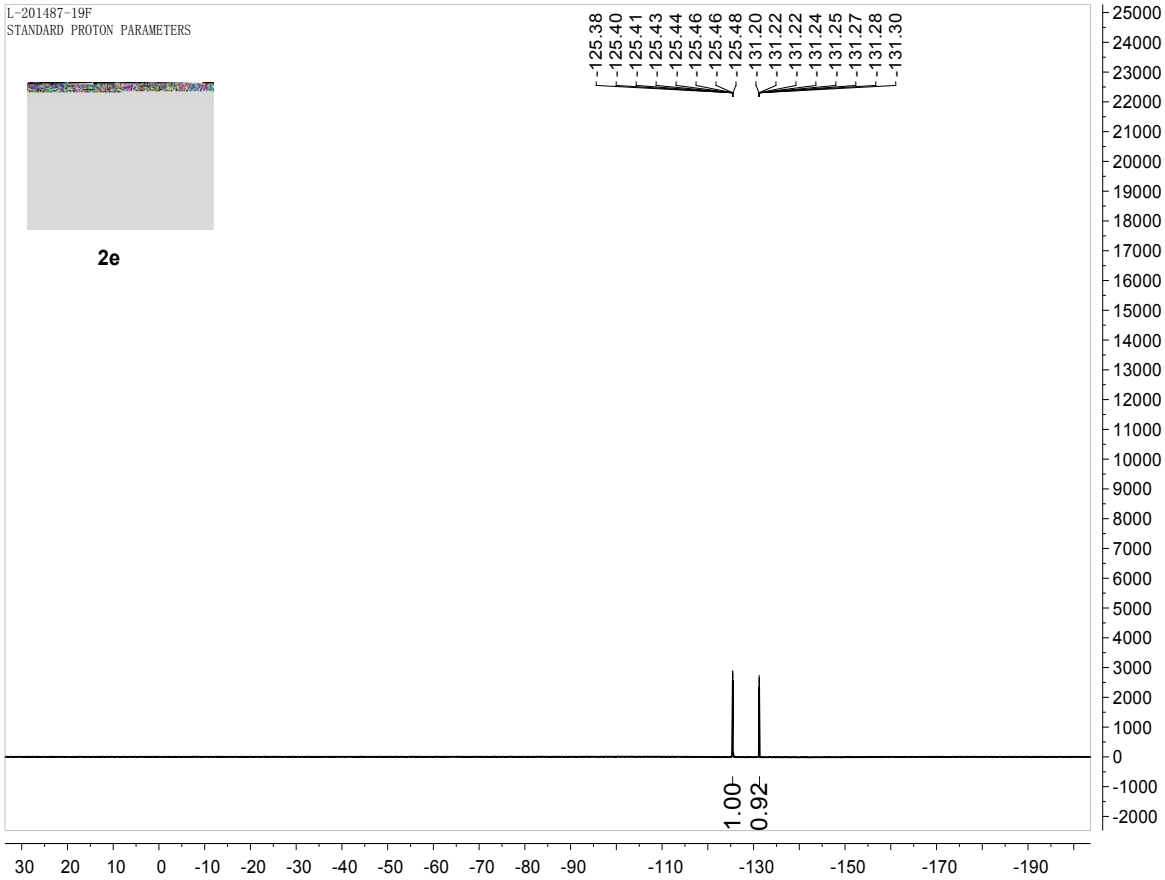
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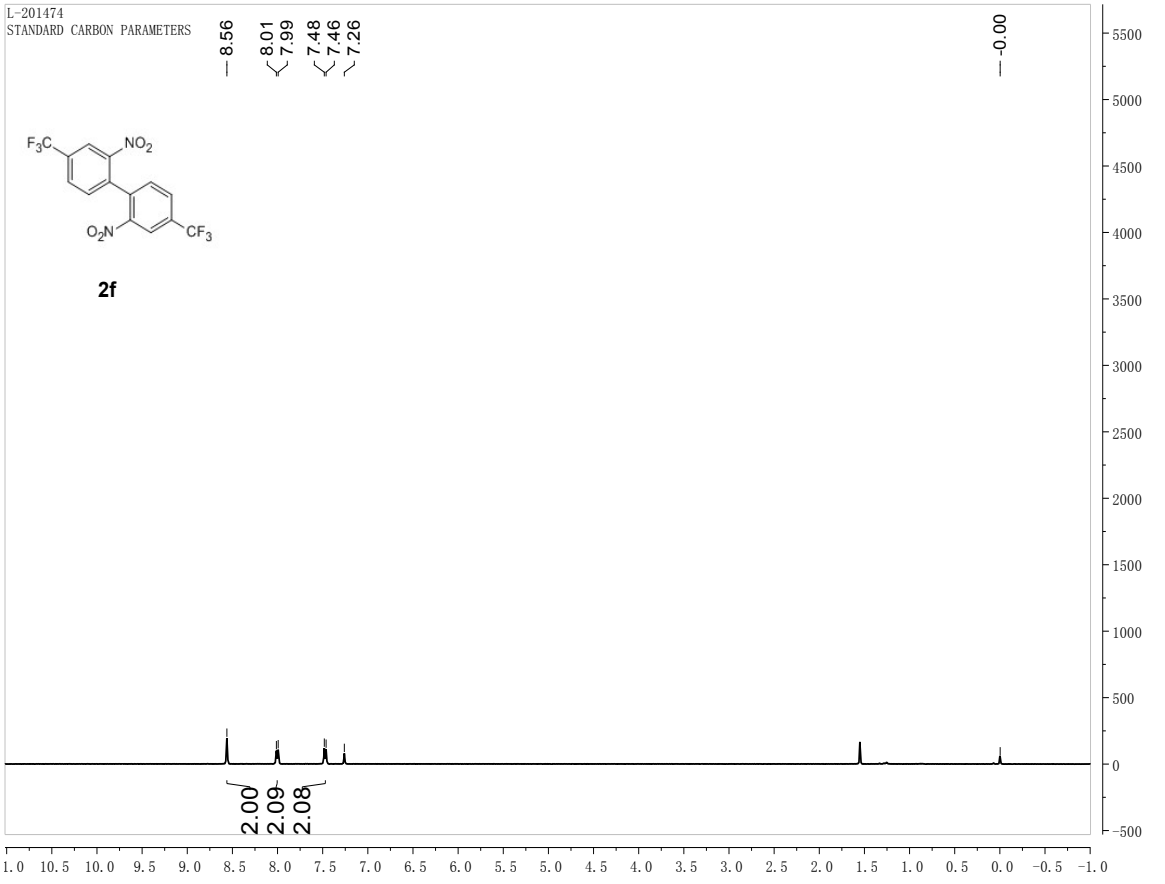
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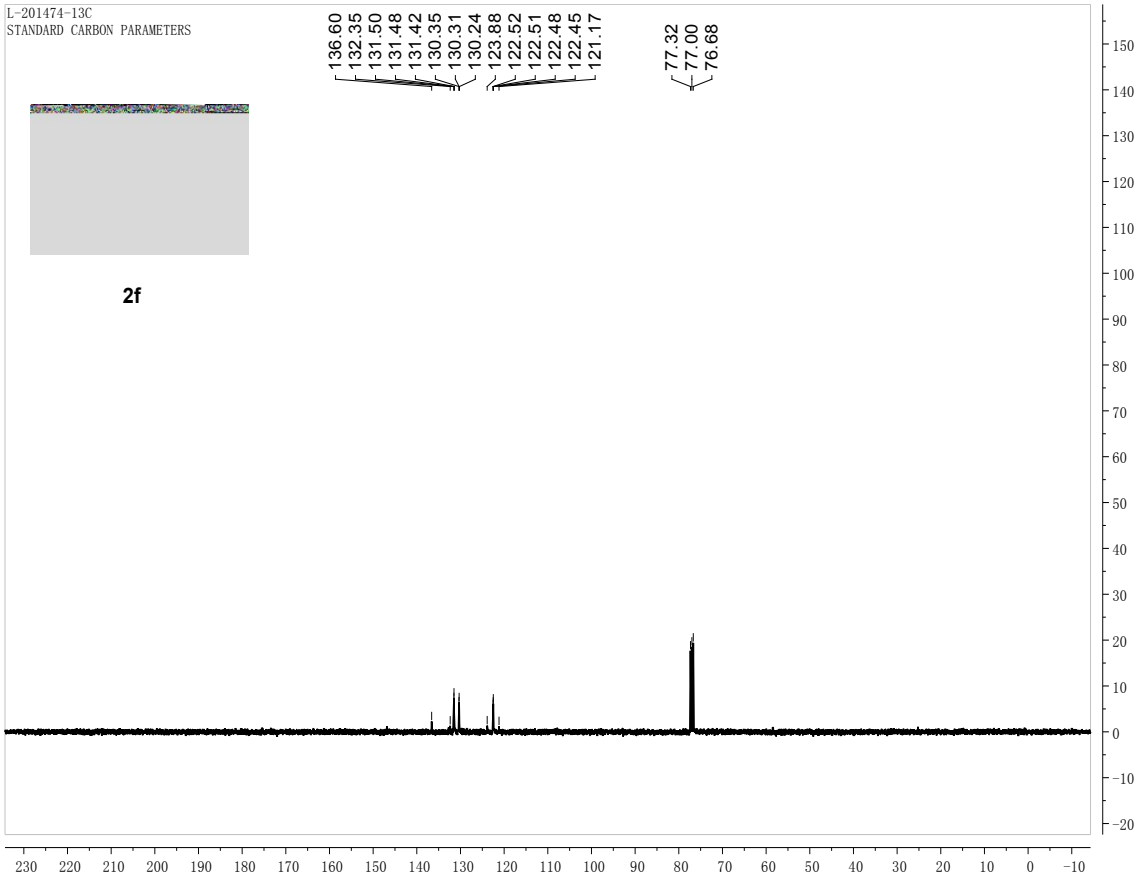
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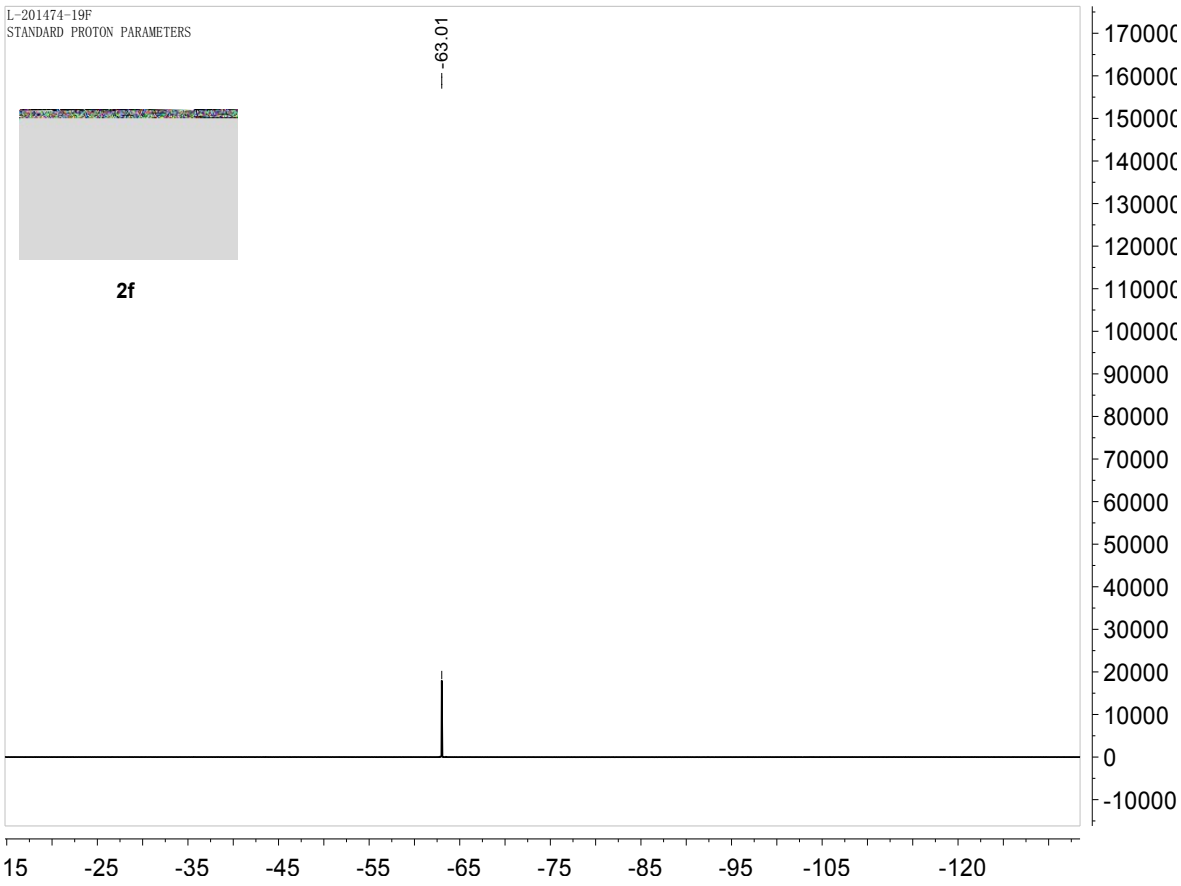
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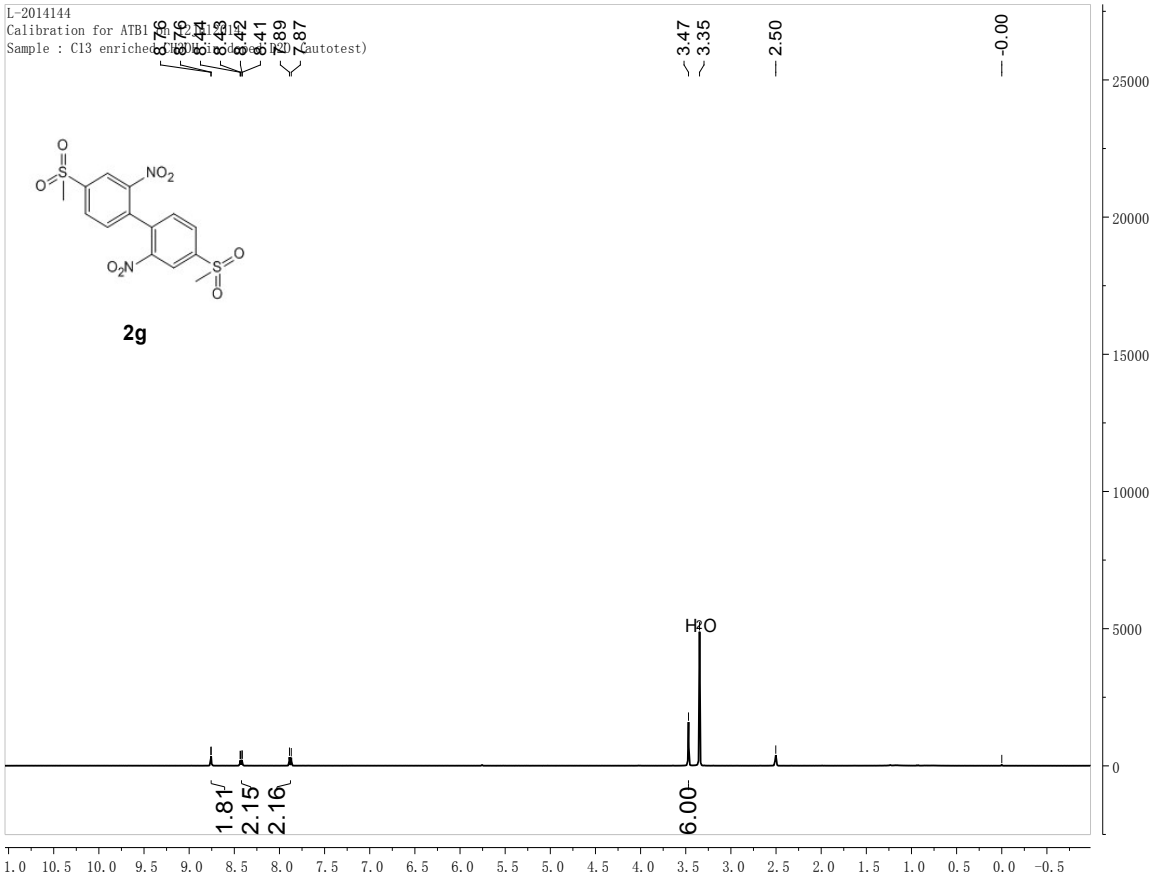
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8.42
8.41
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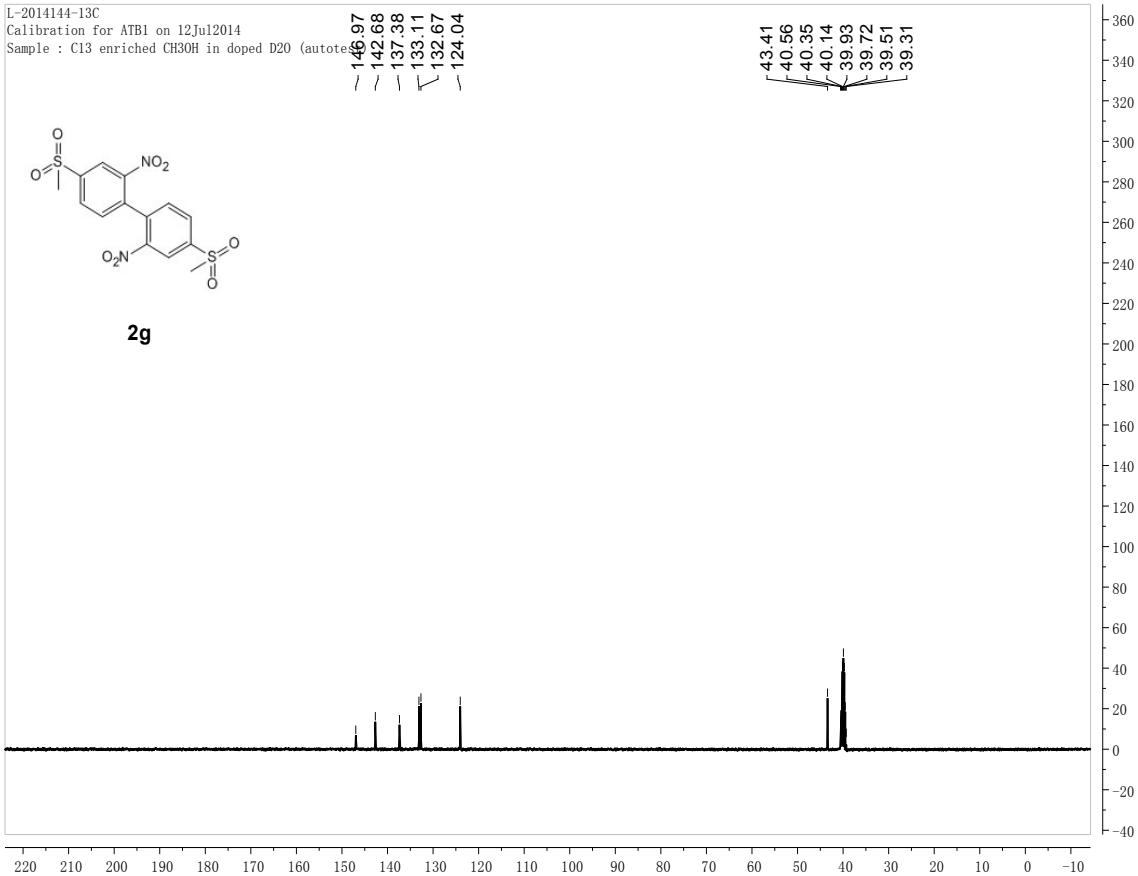
H2O
1.81
2.15
2.16
6.00



**2g**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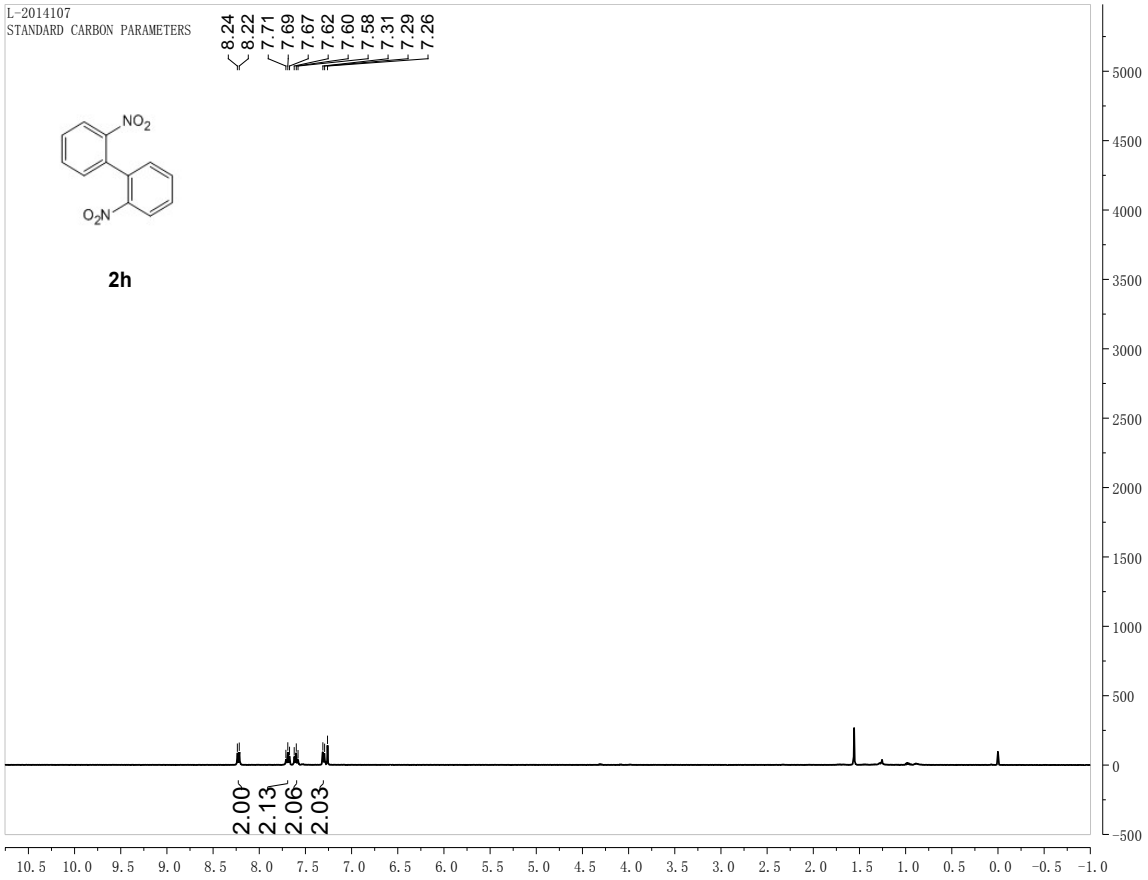
40.14
39.93
39.72
39.51
39.31



**2g**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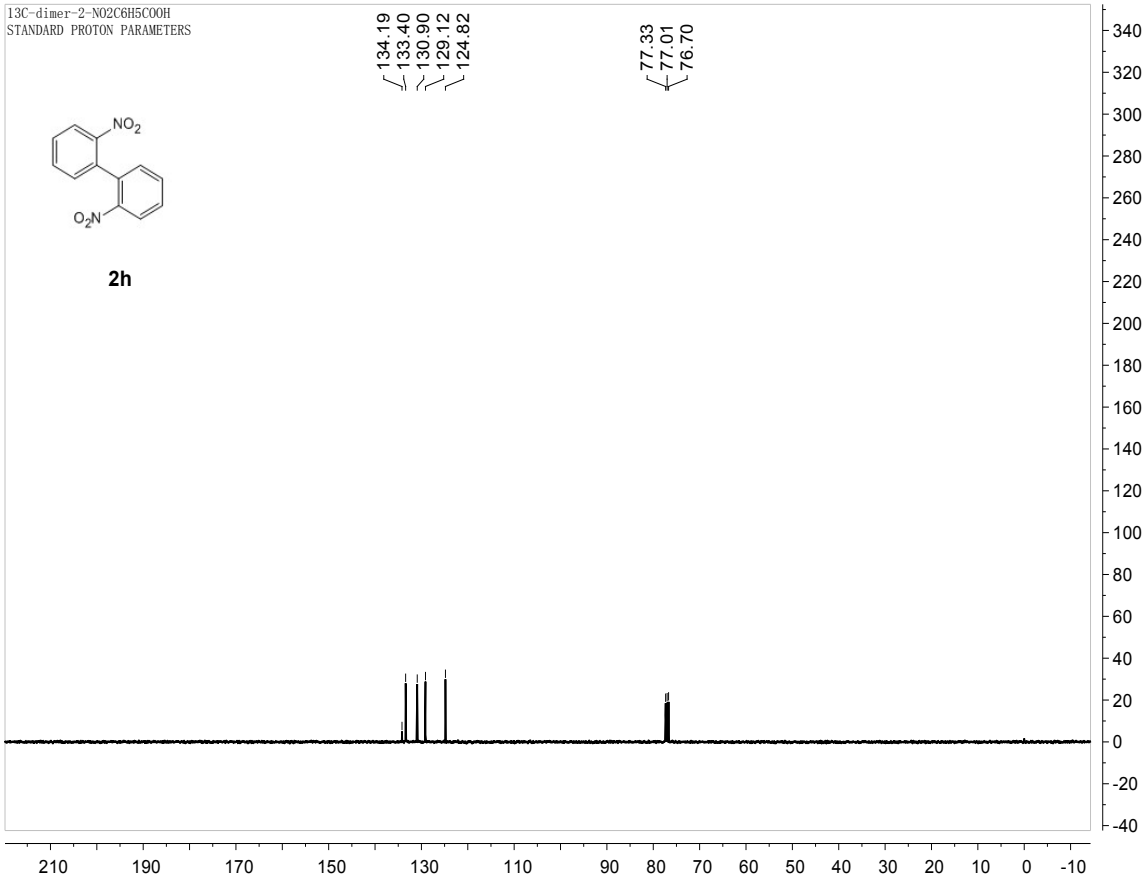
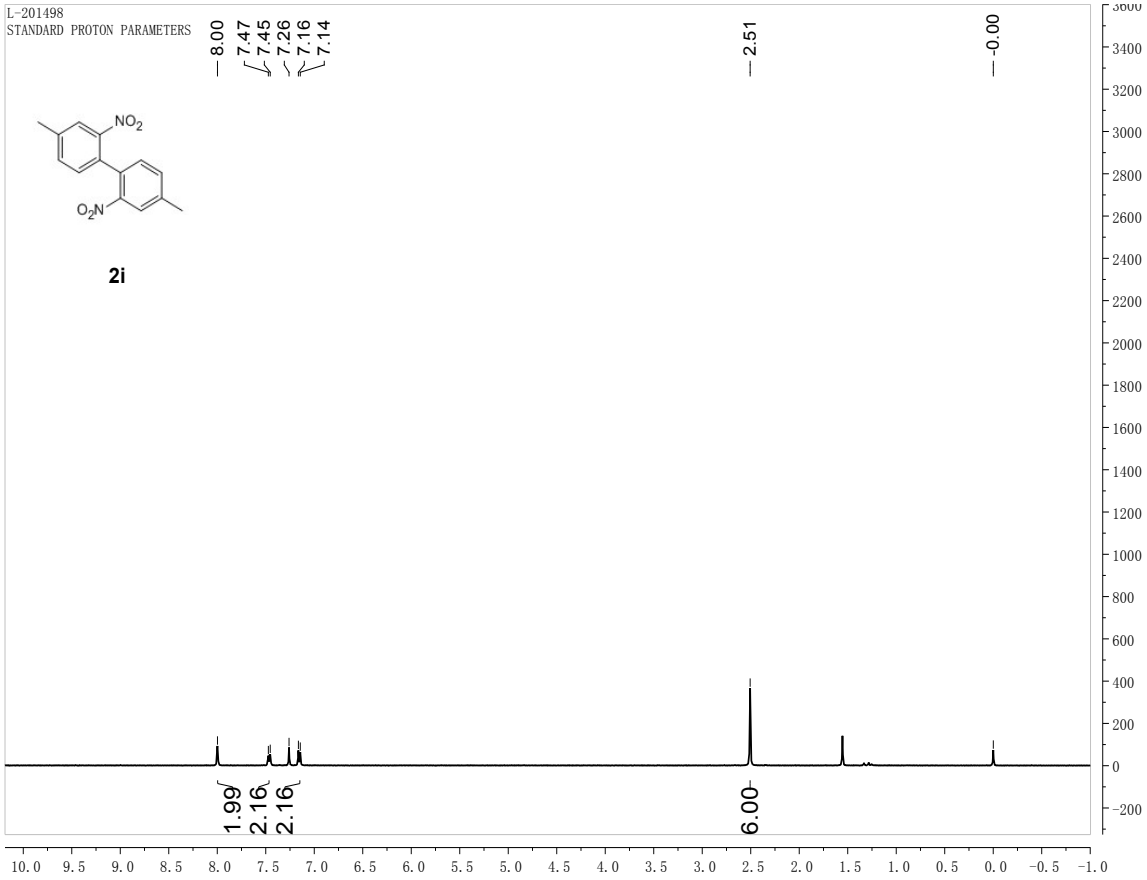
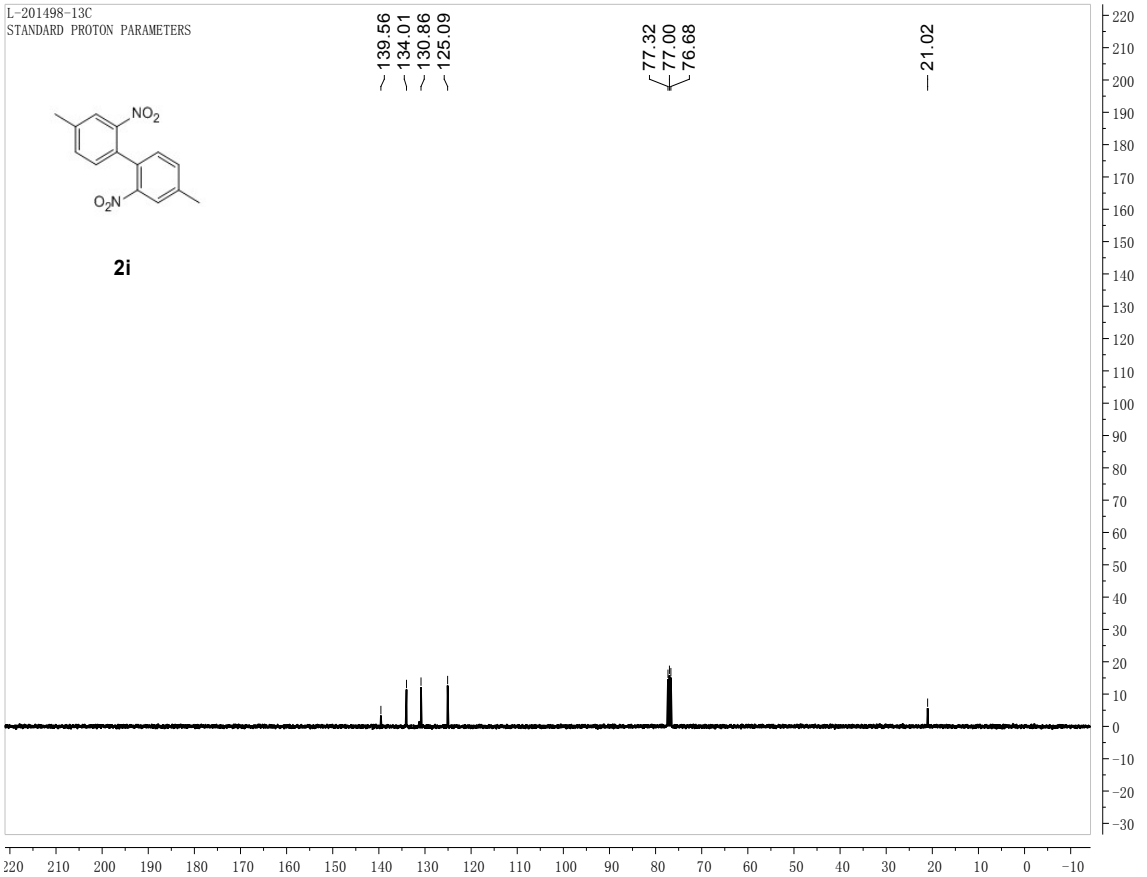
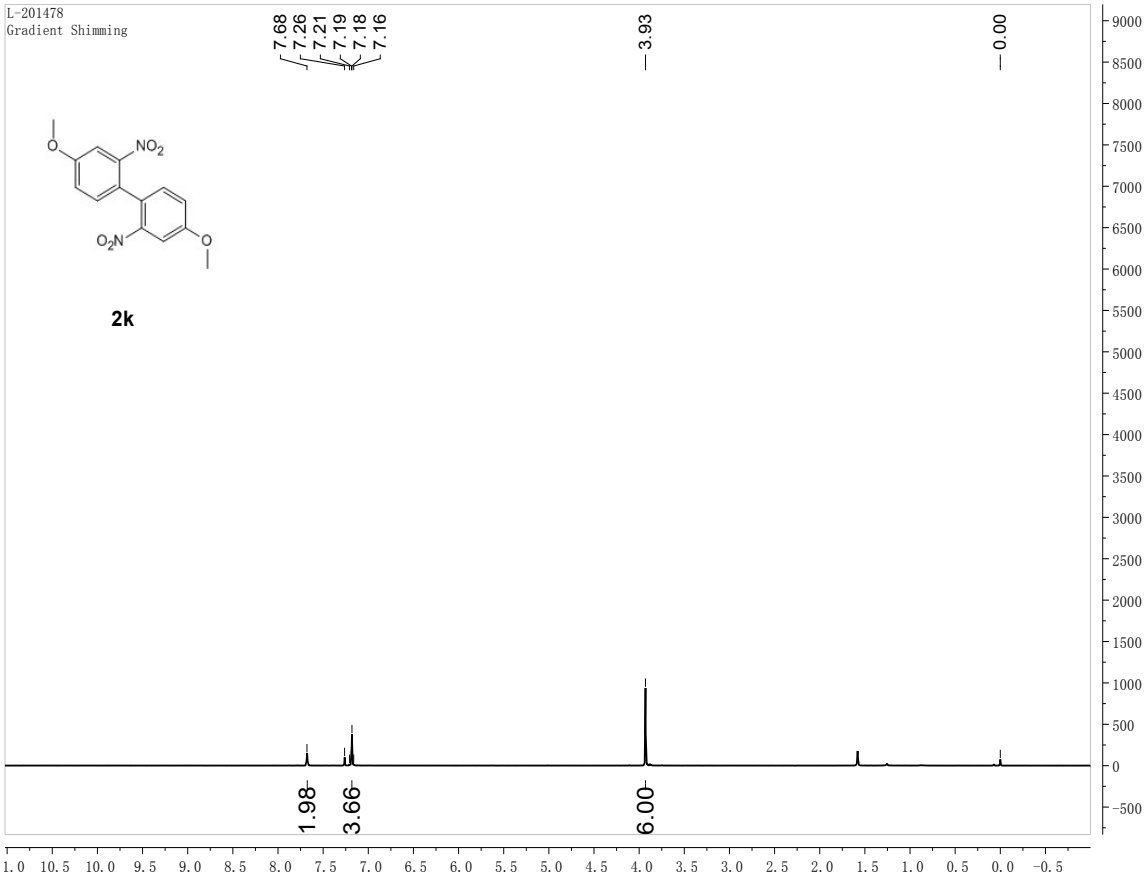
7.29
7.26
NO2
O2N
2h
2.00
2.13
2.06
2.03

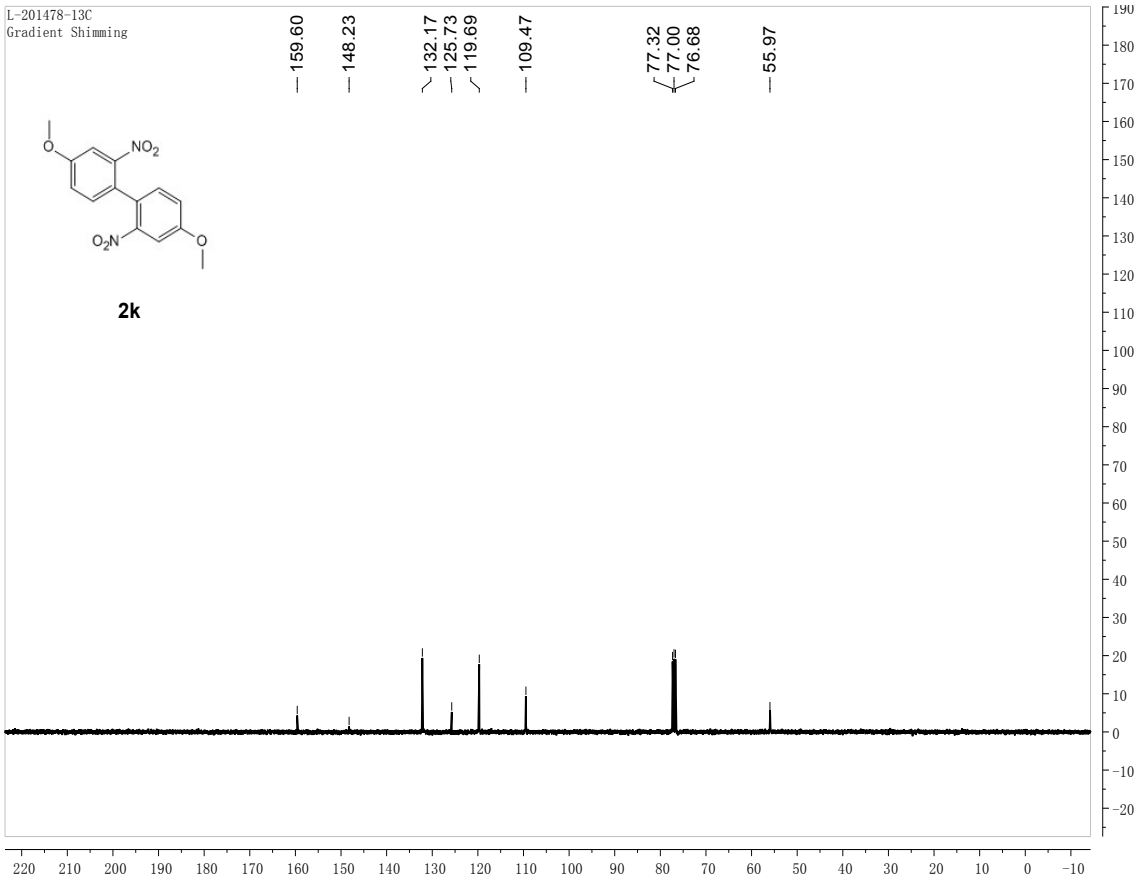

13C-dimer-2-NO2C6H5COOH
STANDARD PROTON PARAMETERS
134.19
133.40
130.90
129.12
124.82
77.33
77.01
76.70
NO2
O2N
2h


L-201498
STANDARD PROTON PARAMETERS
8.00
7.47
7.45
7.26
7.16
7.14
2.51
-0.00
NO2
O2N
2i
1.99
2.16
2.16
6.00

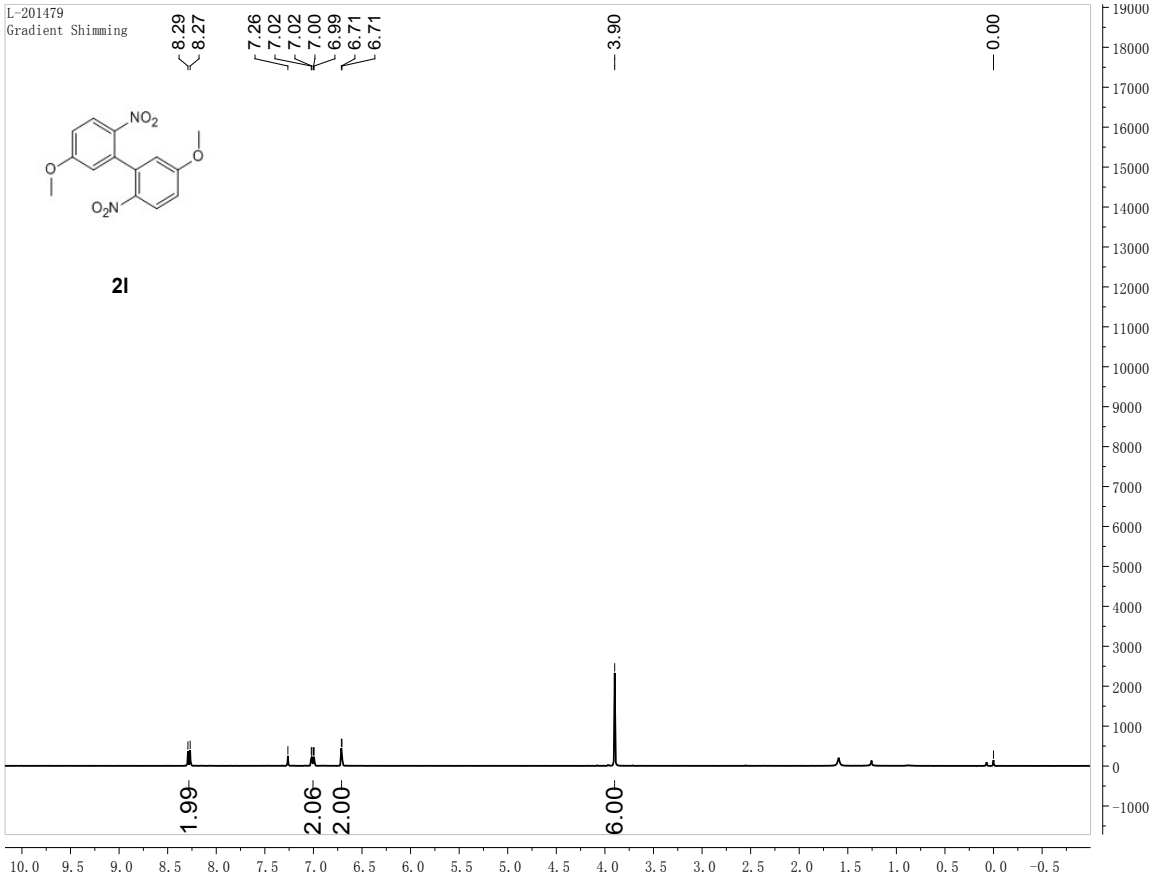

L-201498-13C
STANDARD PROTON PARAMETERS
139.56
134.01
130.86
125.09
77.32
77.00
76.68
21.02
NO2
O2N
2i


L-201478
Gradient Shimming
7.68
7.26
7.21
7.19
7.18
7.16
3.93
0.00
1.98
3.66
6.00

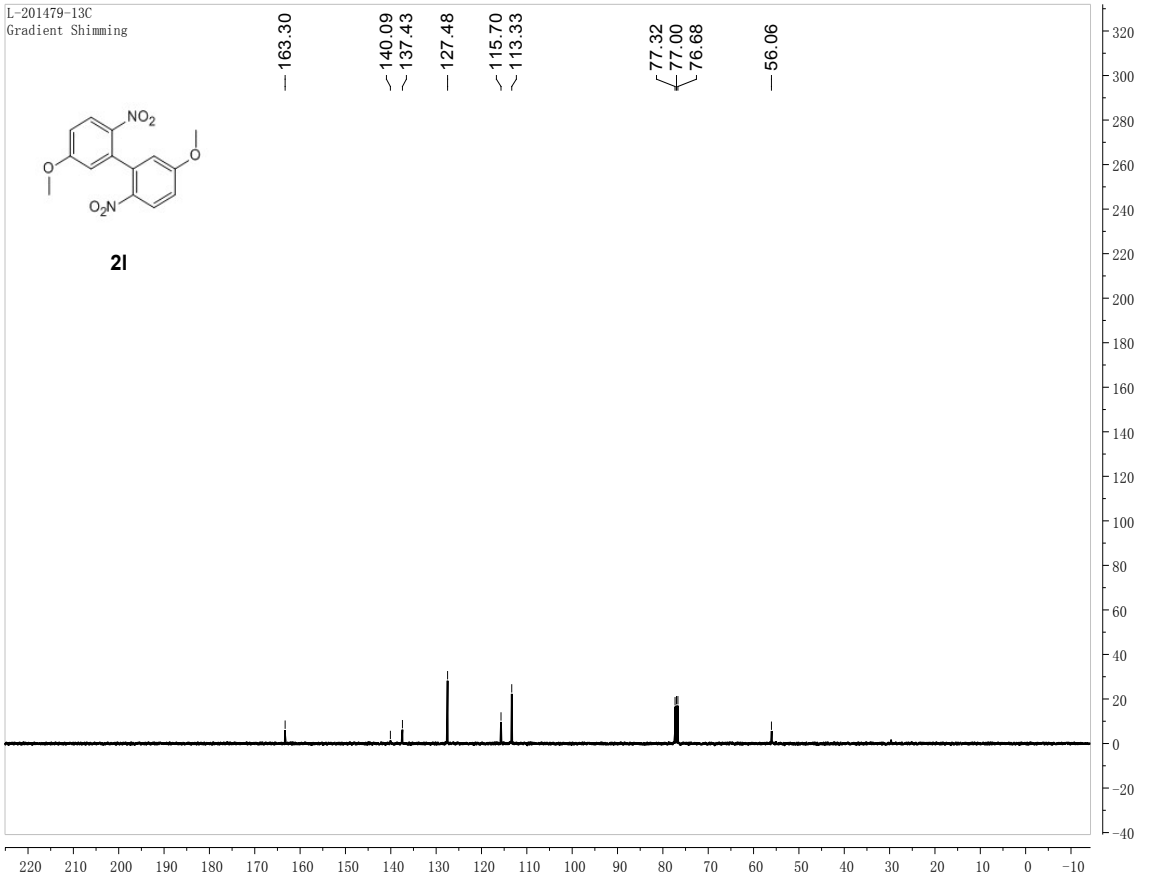
**2k**


L-201478-13C
Gradient Shimming
159.60
148.23
132.17
125.73
119.69
109.47
77.32
77.00
76.68
55.97

**2k**


L-201479
Gradient Shimming
8.29
8.27
7.26
7.02
7.02
7.00
6.99
6.71
6.71
3.90
0.00
1.99
2.06
2.00
6.00

**2l**


L-201479-13C
Gradient Shimming
163.30
140.09
137.43
127.48
115.70
113.33
77.32
77.00
76.68
56.06

**2l**