

## Diamine-Mediated Degradative Dimerisation of Morita-Baylis-Hillman Ketones

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### **SUPPORTING INFORMATION**

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## General

The aldehydes and diamine used in the study were purchased from Sigma-Aldrich. Ethylenediamine was distilled prior to use. Anhydrous ethylenediamine was prepared following a literature protocol.<sup>1</sup> Solvents were distilled for the reactions. IBX was synthesised from 2-iodobenzoic acid following a literature protocol.<sup>2</sup> Synthesis of Morita-Baylis-Hillman adducts and their oxidation were performed using reported protocols.<sup>3</sup> Silica gel (100-200 mesh) and other common reagents were procured from local suppliers. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 MHz and 400 MHz NMR spectrometer. Elemental analysis was recorded on Thermo Finnigan FLASH EA 1112. High resolution mass spectral analysis (HRMS) was performed on a XEVO G2-S QT instrument of Waters Corporation, USA.

## Experimental Section

### **General procedure for the synthesis of methylene-bridged bis-1,3-dicarbonyl compounds:**

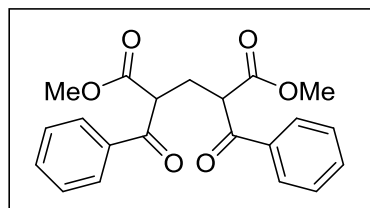
MBH ketone **1** (0.5 mmol) was dissolved in dioxane (500  $\mu$ L) followed by the addition of ethylene-1,2-diamine (**2c**, 0.6 mmol) to the reaction flask. The resulting reaction mixture was allowed to stir at room temperature for the time mentioned in **Table 2** of the manuscript for the respective adducts. The crude residue was directly subjected to the silica gel chromatography (EtOAc: petroleum ether) to obtain pure **3** (as a mixture of two diastereomers; ratio mentioned for each adduct in the tabulation section below).

### **One pot protocol for the synthesis of dimethyl 2,4-dibenzoylpentanedioate (**3a**) from Morita-Baylis-Hillman adduct **4**:**

MBH adduct **4** (96 mg, 0.5 mmol) was dissolved in CH<sub>3</sub>CN (4 mL) followed by the addition IBX (210 mg, 0.75 mmol). The resulting mixture was allowed to stir at 80 °C and the progress of the reaction was monitored using thin layer chromatography. After 5 h, upon complete consumption of **4**, the reaction mixture was cooled to room temperature followed by the addition of ethylene-1, 2-diamine (**2c**, 40  $\mu$ L, 0.6 mmol) to the reaction flask. The resulting reaction mixture was allowed to stir at room temperature for 40 min. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude residue was subjected to the silica gel chromatography (EtOAc: petroleum ether, 2:8) to obtain pure **3a** as a white solid; yield (mixture of two diastereomers): 67 mg (73%).

### Tabulated data of the synthesised products:

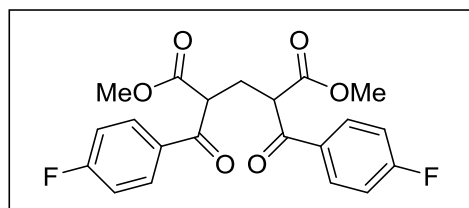
#### Dimethyl 2,4-dibenzoylpentanedioate (3a):<sup>4</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 81 mg (88%); White solid; The ratio of the two diastereomers is 1.4:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.54-2.79 (m, 2H), 3.62 (s, 2.47H), 3.74 (s, 3.54H), 4.59 (t, *J* = 7.5 Hz, 0.82H), 4.68 (t, *J* = 7.5 Hz, 1.14H), 7.44-7.53 (m, 4H), 7.55-7.63 (m, 2H), 8.02-8.09 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 27.80, 28.35, 51.03, 51.28, 52.66, 128.85, 128.88, 128.95, 133.91, 133.93, 135.30, 135.76, 169.80, 170.20, 194.70, 195.09; HRMS (ESI-TOF): *m/z* [M+Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>20</sub>O<sub>6</sub>Na: 391.1152; found 391.1285.

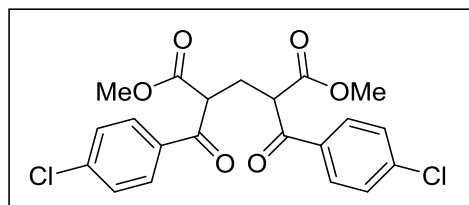
#### Dimethyl 2,4-bis(4-fluorobenzoyl)pentanedioate (3b):<sup>4</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 95 mg (94%); Light yellow semi-solid; The ratio of the two diastereomers is 2.6:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.49-2.75 (m, 2H), 3.64 (s, 1.68H), 3.75 (s, 4.32H), 4.53 (t, *J* = 7.5 Hz, 0.61H), 4.63 (t, *J* = 7.5 Hz, 1.46H), 7.11-7.21 (m, 4H), 8.05-8.14 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 27.65, 28.30, 50.96, 51.19, 52.73, 116.09 (d, *J* = 22.0 Hz), 131.64 (d, *J* = 9.0 Hz), 131.78 (d, *J* = 10.0 Hz), 132.15 (d, *J* = 3.0 Hz), 166.26 (d, *J* = 255.0 Hz), 169.61, 170.10, 193.09, 193.54.

#### Dimethyl 2,4-bis(4-chlorobenzoyl)pentanedioate (3c):<sup>4</sup>

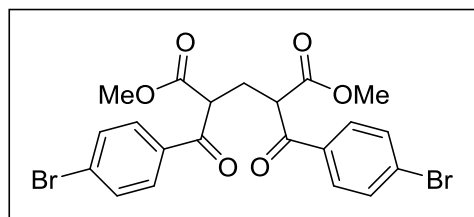


Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 93 mg (85%); White solid; The ratio of the two diastereomers is 1.7:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.49-2.74 (m, 2H), 3.64 (s, 2.19H), 3.74 (s, 3.81H), 4.51 (t, *J* = 7.5 Hz, 0.79H), 4.61 (t, *J* = 7.5 Hz, 1.30 H), 7.42-7.50 (m, 4H), 7.96-8.03 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):

27.52, 28.15, 50.94, 51.73, 52.79, 129.26, 130.26, 130.37, 133.56, 134.02, 140.57, 140.62, 169.51, 169.97, 193.47, 193.91.

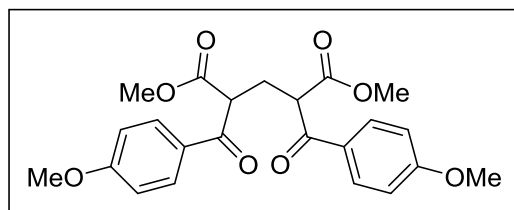
**Dimethyl 2,4-bis(4-bromobenzoyl)pentanedioate (3d):**<sup>4</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 111 mg (85%); Light yellow solid; The ratio of the two diastereomers is 1.9:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.49-2.74 (m, 2H) 3.64 (s, 2.09H), 3.74 (s, 3.91H), 4.50 (t, *J* = 7.5 Hz, 0.76H), 4.60 (t, *J* = 7.0 Hz, 1.34H), 7.61-7.66 (m, 4H), 7.87-7.94 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 27.49, 28.10, 50.93, 51.10, 52.79, 52.80, 129.38, 129.44, 130.31, 130.42, 132.26, 134.01, 134.45, 169.47, 169.90, 193.67, 194.09.

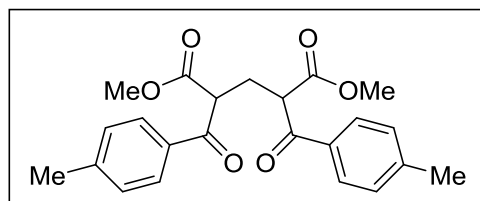
**Dimethyl 2,4-bis(4-methoxybenzoyl)pentanedioate (3e):**<sup>4</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 80 mg (74%); light yellow gum; The ratio of the two diastereomers is 1.4:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.49-2.74 (m, 2H), 3.63 (s, 2.47H), 3.74 (s, 3.52H), 3.85 (s, 3.59H), 3.87 (s, 2.51H), 4.52 (t, *J* = 7.5 Hz, 0.83H), 4.60 (t, *J* = 7.5 Hz, 1.15H), 6.93 (d, *J* = 8.5 Hz, 2.38H), 6.96 (d, *J* = 9.0 Hz, 1.75H), 8.04 (d, *J* = 8.5 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 28.06, 28.70, 50.81, 51.08, 52.52, 55.52, 55.54, 114.05, 114.06, 128.31, 128.80, 131.30, 131.40, 164.16, 170.02, 170.46, 193.18, 193.61.

**Dimethyl 2,4-bis(4-methylbenzoyl)pentanedioate (3f):**<sup>4</sup>

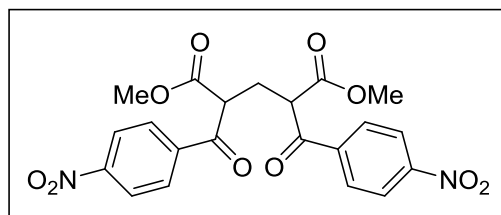


Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 82 mg (82 %); White semi-solid; The ratio of the two diastereomers is 1.6:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.40 (s, 3.74H), 2.42 (s, 2.50H), 2.52-2.76 (m, 2H), 3.63 (s, 2.31H), 3.74 (s, 3.69H), 4.55 (t, *J* = 7.5 Hz, 0.82H), 4.63 (t, *J* = 7.5 Hz, 1.26H), 7.26 (d, *J* = 8.0 Hz, 2.52H), 7.30 (d, *J*

= 8.5 Hz, 1.68H), 7.94 (d,  $J = 8.0$  Hz, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 21.70, 27.90, 28.46, 50.96, 51.22, 52.58, 129.00, 129.09, 129.56, 129.58, 132.87, 133.32, 144.91, 169.94, 170.31, 194.30, 194.70.

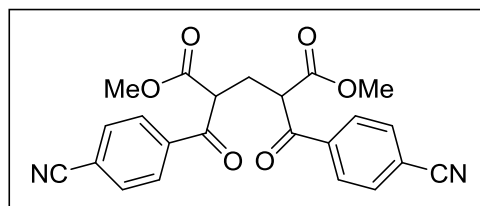
**Dimethyl 2,4-bis(4-nitrobenzoyl)pentanedioate (3g):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 42 mg (37%); yellow gum; The ratio of the two diastereomers is 1.2:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54-2.80 (m, 2H), 3.67 (s, 2.79H), 3.78 (s, 3.20H), 4.61 (t,  $J = 7.0$  Hz, 0.94H), 4.72 (t,  $J = 7.0$  Hz, 1.10H), 8.21 (d,  $J = 9.0$  Hz, 1.91H), 8.26 (d,  $J = 8.5$  Hz, 2.25H), 8.34-8.39 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 27.06, 27.66, 51.24, 51.39, 53.04, 53.05, 124.10, 129.83, 130.00, 139.70, 140.14, 150.78, 150.81, 169.02, 169.50, 193.29, 193.62.; Anal. calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_{10}$ : C, 55.03; H, 3.96; N, 6.11; found C, 55.12; H, 3.91; N, 6.18.

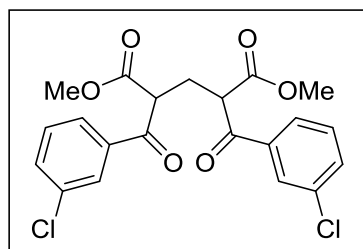
**Dimethyl 2,4-bis(4-cyanobenzoyl)pentanedioate (3h):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 30 mg (29%); white semi-solid; The ratio of the two diastereomers is 1.2:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.50-2.76 (m, 2H), 3.66 (s, 2.73H), 3.76 (s, 3.28H), 4.56 (t,  $J = 7.0$  Hz, 0.94H), 4.68 (t,  $J = 7.0$  Hz, 1.12H), 7.80-7.84 (m, 4H), 8.14 (d,  $J = 8.5$  Hz, 1.87H), 8.18 (d,  $J = 8.5$  Hz, 2.35H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 27.10, 27.73, 51.02, 51.19, 53.00, 53.02, 117.22, 117.26, 117.68, 129.17, 129.33, 132.75, 132.77, 138.18, 138.64, 169.08, 169.60, 193.46, 193.82; Anal. calculated for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_6$ : C, 66.03; H, 4.34; N, 6.70; found C, 66.12; H, 4.38; N, 6.65.

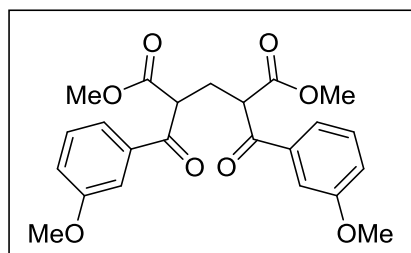
**Dimethyl 2,4-bis(3-chlorobenzoyl)pentanedioate (3i):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 73 mg (66%); transparent oil; The ratio of the two diastereomers is 1.4:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.52-2.76 (m, 2H), 3.66 (s, 2.53H), 3.76 (s, 3.46H), 4.51 (t,  $J = 7.0$  Hz, 0.87H), 4.60 (s, 1.15H), 7.40-7.49 (m, 2H), 7.58 (t,  $J = 9.5$  Hz, 2H), 7.90-7.96 (m, 2H), 8.00 (d,  $J = 10.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 27.48, 28.02, 51.00, 51.19, 52.87, 126.93, 127.06, 128.82, 128.88, 130.25, 133.89, 133.91, 135.30, 135.33, 136.84, 137.25, 169.40, 169.72, 193.45, 193.84; Anal. calculated for  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{O}_6$ : C, 57.68; H, 4.15; found C, 57.76; H, 4.19.

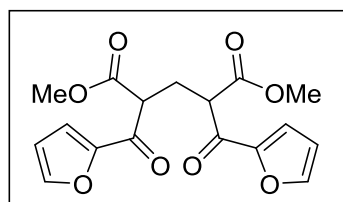
**Dimethyl 2,4-bis(3-methoxybenzoyl)pentanedioate (3j):<sup>4</sup>**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 107 mg (90%); white gum; The ratio of the two diastereomers is 1.4:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54-2.79 (m, 2H), 3.65 (s, 2.53H), 3.75 (s, 3.47H), 3.86 (s, 3.64H), 3.89 (s, 2.69H), 4.55 (t,  $J = 7.5$  Hz, 0.89H), 4.64 (t,  $J = 7.0$  Hz, 1.22H), 7.10-7.18 (m, 2H), 7.39 (dt,  $J = 8.0$  Hz, 2H), 7.55-7.59 (m, 2H), 7.62 (d,  $J = 8.0$  Hz, 0.91H), 7.65 (d,  $J = 7.5$  Hz, 1.24H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 27.96, 28.51, 51.22, 51.48, 52.62, 55.50, 112.82, 112.84, 120.68, 120.79, 121.44, 121.55, 129.86, 136.63, 137.10, 160.01, 160.03, 169.79, 170.16, 194.51, 194.93.

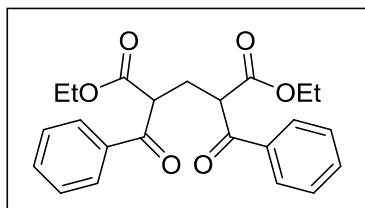
**Dimethyl 2,4-di(furan-2-carbonyl)pentanedioate (3k):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 47 mg (54%); light yellow-orange semi-solid; The ratio of the two diastereomers is 1.2:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62 (dt,  $J = 7.5$  Hz, 2H), 3.68 (s, 2.76H), 3.72 (s, 3.24H), 4.30 (t,  $J = 7.5$  Hz, 0.94H), 4.34 (t,  $J = 7.5$  Hz, 1.07H), 6.54-6.56 (m, 1.02H), 6.57-6.60 (m, 0.96H), 7.37 (d,  $J = 3.5$  Hz, 2H), 7.59 (s, 0.99H), 7.63 (s, 0.91H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 26.92, 27.39, 51.23, 51.27, 52.70, 112.74, 112.75, 119.40, 119.49, 147.52, 147.54, 151.41, 151.60, 169.33, 169.45, 182.85, 182.97; Anal. calculated for  $\text{C}_{17}\text{H}_{16}\text{O}_8$ : C, 58.62; H, 4.63; found C, 58.72; H, 4.68.

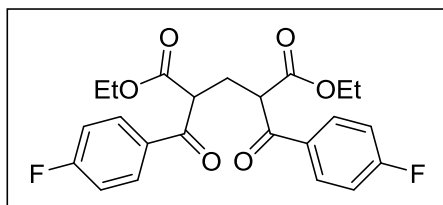
### Diethyl 2,4-dibenzoylpentanedioate (3l):<sup>4</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 74 mg (75%); white solid; The ratio of the two diastereomers is 1.7:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.10 (t, *J* = 7.0 Hz, 2.23H), 1.21 (t, *J* = 7.5 Hz, 3.77H), 2.54-2.80 (m, 2H), 4.05-4.14 (m, 1.55H), 4.15-4.29 (m, 2.52H), 4.55 (t, *J* = 7.5 Hz, 0.73H), 4.63 (t, *J* = 7.5 Hz, 1.23H), 7.44-7.52 (m, 4H), 7.55-7.62 (m, 2H), 8.05 (d, *J* = 7.5 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.88, 14.00, 27.68, 28.21, 51.35, 51.59, 61.64, 61.67, 128.80, 128.82, 128.89, 128.91, 133.77, 133.82, 135.43, 135.91, 169.34, 169.69, 194.82, 195.17.

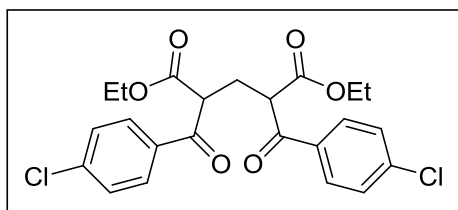
### Diethyl 2,4-bis(4-fluorobenzoyl)pentanedioate (3m):<sup>5</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 97 mg (90%); light yellow gum; The ratio of the two diastereomers is 1.1:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (t, *J* = 7.5 Hz, 2.76H), 1.22 (t, *J* = 7.5 Hz, 3.13H), 2.50-2.76 (m, 2H), 4.06-4.16 (m, 1.82 H), 4.18-4.27 (m, 2.09H), 4.49 (t, *J* = 7.5 Hz, 0.92H), 4.59 (t, *J* = 7.5 Hz, 1.02H), 7.11-7.20 (m, 4H), 8.05-8.13 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.89, 13.99, 27.52, 28.15, 51.26, 51.47, 61.76, 61.78, 116.01 (d, *J* = 22.0 Hz), 131.59 (d, *J* = 9.5 Hz), 131.73 (d, *J* = 9.0 Hz), 131.81 (d, *J* = 3.0 Hz), 132.31 (d, *J* = 3.0 Hz), 166.20 (d, *J* = 254.0 Hz), 169.14, 169.57, 193.19, 193.60.

### Diethyl 2,4-bis(4-chlorobenzoyl)pentanedioate (3n):<sup>5</sup>

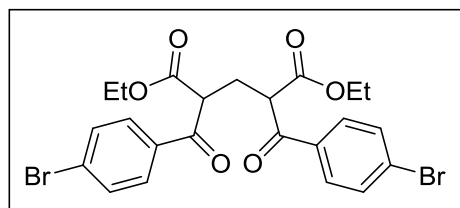


Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 85 mg (73%); white solid; The ratio of the two diastereomers is 1.3:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.13 (t, *J* = 7.5 Hz, 2.60H), 1.22 (t, *J* = 7.0 Hz, 3.60H), 2.50-2.75 (m, 2H), 4.06-4.15 (m, 1.72H), 4.15-4.28 (m, 2.28H), 4.48 (t, *J* = 7.5 Hz, 0.85H), 4.57 (t, *J* = 7.0 Hz, 1.08H), 7.45 (d, *J* = 9.0 Hz, 2.17H), 7.48 (d, *J* = 8.5 Hz, 1.63H), 7.99 (d, *J* = 9.0 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):

13.90, 13.99, 27.41, 28.00, 51.26, 51.43, 61.81, 61.83, 129.16, 129.18, 130.22, 130.33, 133.75, 134.20, 140.46, 140.48, 169.04, 169.43, 193.57, 193.96.

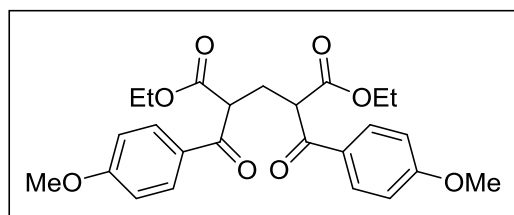
**Diethyl 2,4-bis(4-bromobenzoyl)pentanedioate (3o):**<sup>5</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 127 mg (92%); light yellow solid; The ratio of the two diastereomers is 1.2:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (t, *J* = 7.5 Hz, 2.66H), 1.21 (t, *J* = 7.0 Hz, 3.39H), 2.49-2.74 (m, 2H), 4.08-4.15 (m, 1.88 H), 4.16-4.26 (m, 2.25H), 4.47 (t, *J* = 7.5 Hz, 0.88H), 4.55 (t, *J* = 7.5 Hz, 1.09H), 7.58-7.66 (m, 4H), 7.91 (d, *J* = 8.0 Hz, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.91, 14.00, 27.38, 27.96, 51.22, 51.38, 61.84, 129.23, 129.28, 130.29, 130.39, 132.18, 134.17, 134.60, 169.00, 169.38, 193.76, 194.15.

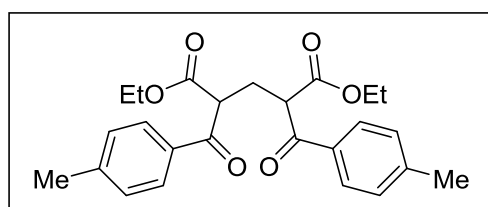
**Diethyl 2,4-bis(4-methoxybenzoyl)pentanedioate (3p):**<sup>5</sup>



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 83 mg (73%); light yellow semi-solid; The ratio of the two diastereomers is 1.1:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (t, *J* = 7.0 Hz, 2.74H), 1.22 (t, *J* = 7.5 Hz, 3.20H), 2.50-2.74 (m, 2H), 3.85 (s, 3.09H), 3.87 (s, 2.79H), 4.05-4.14 (m, 2.01H), 4.16-4.25 (m, 2.07H), 4.48 (t, *J* = 7.5 Hz, 0.90H), 4.56 (t, *J* = 7.5 Hz, 1.02H), 6.92 (d, *J* = 8.5 Hz, 2.14H), 6.96 (d, *J* = 8.5 Hz, 1.83H), 8.01-8.06 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.93, 14.03, 27.95, 28.58, 51.11, 51.36, 55.50, 55.53, 64.48, 61.51, 113.99, 128.44, 128.94, 131.27, 131.36, 164.08, 164.09, 169.56, 169.94, 193.29, 193.69.

**Diethyl 2,4-bis(4-methylbenzoyl)pentanedioate (3q):**<sup>5</sup>



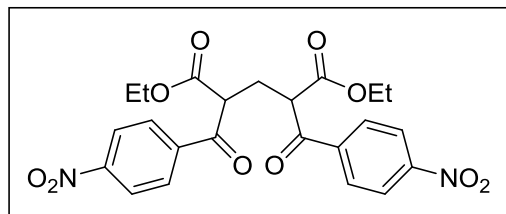
Purified by silica gel chromatography (EtOAc: petroleum ether, 1.5:8.5)

Yield: 84 mg (79%); white solid; The ratio of the two diastereomers is 1.2:1; **Two diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.12 (t, *J* = 7.0 Hz, 2.66H), 1.22 (t, *J* = 7.5 Hz, 3.35H), 2.40 (s, 3.20H), 2.42 (s, 2.70H), 2.52-2.76 (m, 2H), 4.05-4.15 (m, 1.75 H), 4.16-4.26 (m, 2.19H), 4.51 (t, *J* = 7.5 Hz, 0.87H),



4.59 (t,  $J = 7.5$  Hz, 1.05H), 7.25 (d,  $J = 8.5$  Hz, 2.21H), 7.29 (d,  $J = 8.0$  Hz, 1.74H), 7.94 (t,  $J = 8.5$  Hz, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 13.91, 14.02, 21.68, 21.70, 27.80, 28.33, 51.26, 51.52, 61.53, 61.56, 128.97, 129.05, 129.48, 129.49, 133.02, 133.47, 144.75, 169.47, 169.79, 194.41, 194.76.

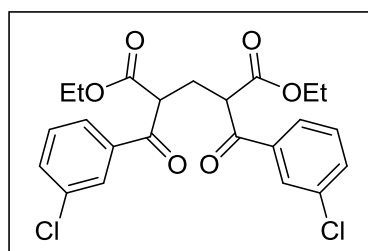
**Diethyl 2,4-bis(4-nitrobenzoyl)pentanedioate (3r):<sup>6</sup>**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 49 mg (40%); light yellow gum The ratio of the two diastereomers is 1:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.13 (t,  $J = 7.5$  Hz, 3H), 1.23 (t,  $J = 7.0$  Hz, 3H), 2.54-2.80 (m, 2H), 4.08-4.16 (m, 2H), 4.18-4.30 (m, 2H), 4.57 (t,  $J = 7.0$  Hz, 1H), 4.68 (t,  $J = 7.0$  Hz, 1H), 8.19-8.27 (m, 4H), 8.33-8.40 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 13.88, 13.96, 26.93, 27.51, 51.55, 51.68, 62.20, 124.02, 124.04, 129.79, 129.96, 139.89, 140.33, 150.72, 150.75, 168.56, 168.98, 193.40, 193.72.

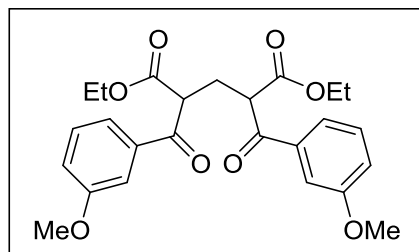
**Diethyl 2,4-bis(3-chlorobenzoyl)pentanedioate (3s):**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 57 mg (49%); light yellow gum; The ratio of the two diastereomers is 1.1:1; **Two diastereomers:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.14 (t,  $J = 7.0$  Hz, 2.71 H), 1.22 (t,  $J = 7.0$  Hz, 3.30H), 2.53-2.76 (m, 2H), 4.06-4.17 (m, 2.04H), 4.17-4.28 (m, 2.19H), 4.47 (t,  $J = 7.5$  Hz, 0.90H), 4.55 (t,  $J = 7.5$  Hz, 1.01H), 7.40-7.48 (m, 2H), 7.54-7.60 (m, 2H), 7.91-7.95 (m, 2H), 7.98-8.00 (m, 1.07H), 8.00-8.03 (m, 0.87H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 13.87, 13.97, 27.32, 27.82, 51.34, 51.49, 61.90, 126.89, 127.00, 128.80, 128.84, 130.15, 133.74, 133.76, 135.23, 135.25, 137.05, 137.43, 168.92, 169.19, 193.50, 193.84; HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{22}\text{Cl}_2\text{O}_6\text{Na}$ : 487.0686; found: 487.0688.

**Diethyl 2,4-bis(3-methoxybenzoyl)pentanedioate (3t):<sup>5</sup>**

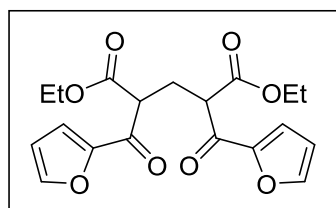


Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 89 mg (78%); light yellow gum; The ratio of the two diastereomers is 1.1:1; **Two diastereomers:**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.14 (t,  $J = 7.0$  Hz, 2.72H), 1.23 (t,  $J = 7.5$  Hz, 3.20H), 2.54-2.79 (m, 2H), 3.86 (s, 3.18H), 3.89 (s, 2.64H), 4.07-4.16 (m, 1.81H), 4.17-4.27 (m, 2.11H), 4.51 (t,  $J = 7.5$  Hz, 0.92H), 4.59 (t,  $J = 7.5$  Hz, 1.03H), 7.11-7.18 (m, 2H), 7.35-7.43 (m, 2H), 7.55-7.60 (m, 2H), 7.64 (t,  $J = 6.5$  Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.90, 14.00, 27.84, 28.37, 51.53, 51.76, 55.49, 55.50, 61.64, 112.80, 120.58, 120.69, 121.43, 121.53, 129.78, 136.80, 137.26, 159.98, 160.00, 169.33, 169.65, 194.62, 195.00.

**Diethyl 2,4-di(furan-2-carbonyl)pentanedioate (3u):<sup>5</sup>**



Purified by silica gel chromatography (EtOAc: petroleum ether, 2:8)

Yield: 78 mg (83%); Light yellow semi-solid; The ratio of the two diastereomers is 1:1; **Two**

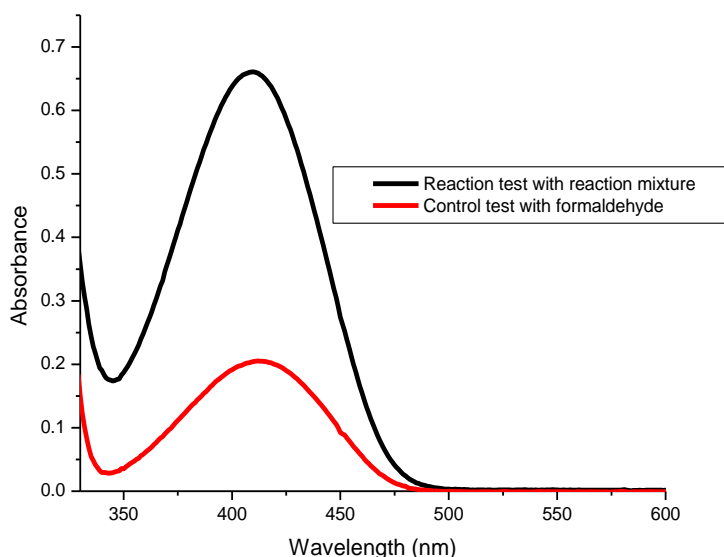
**diastereomers:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.15 (t,  $J = 7.5$  Hz, 3H), 1.20 (t,  $J = 7.0$  Hz, 3H), 2.56-2.66 (m, 2H), 4.10-4.21 (m, 4H), 4.24-4.31 (m, 2H), 6.52-6.55 (m, 1H), 6.55-6.57 (m, 1H), 7.35 (t,  $J = 3.5$  Hz, 2H), 7.58 (s, 1H), 7.61 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 13.93, 13.97, 26.78, 27.23, 51.50, 51.58, 61.66, 61.67, 112.62, 112.65, 119.18, 119.27, 147.29, 147.34, 151.48, 151.68, 168.84, 168.94, 182.97, 183.10.

## Experimental details of the Nash test

### General procedure for the Nash test:<sup>7</sup>

Formation of formaldehyde in the reaction was assessed using the Nash Test. The Nash reagent was prepared by dissolving NH<sub>4</sub>OAc (7.5 g, 95 mmol), 2,4-pentanedione (0.1 mL, 1 mmol) and acetic acid (0.15 mL, 2.5 mmol) in 50 mL of water. After obtaining a clear solution, it was stored in the dark.

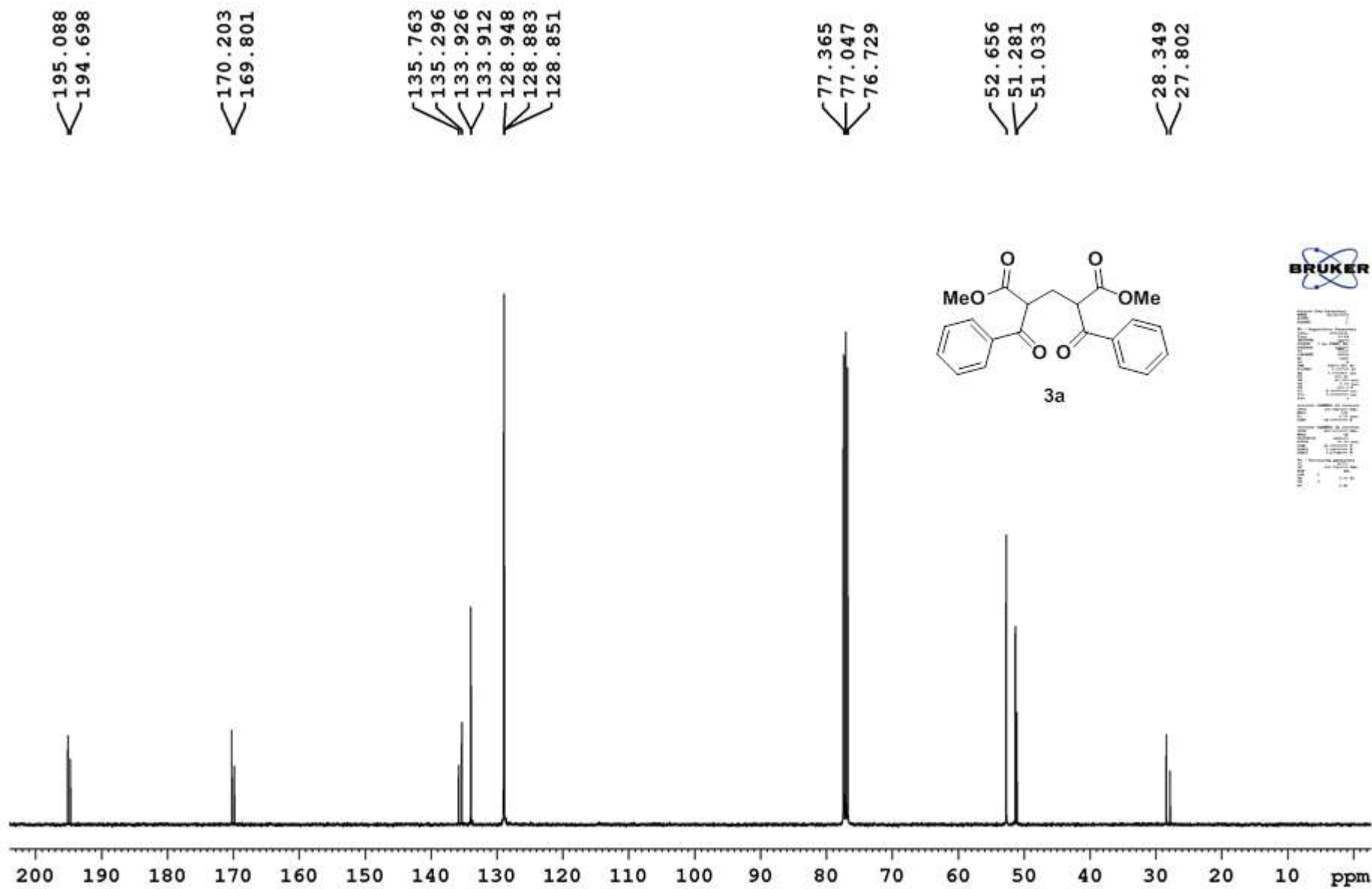
A typical reaction with the model substrate was set up under the optimised conditions; after completion of the reaction, an aliquot (50  $\mu$ L) was taken out from the reaction mixture and Nash reagent added (5 mL) was added to it. The resulting mixture was allowed to stir on a pre-heated oil-bath at 60  $^{\circ}$ C for 5 min; it was allowed to cool to room temperature. The UV spectrum of the mixture was then recorded, which showed a  $\lambda_{\text{max}}$  at 411 nm. A control test UV spectrum was similarly recorded for formaldehyde treated with the Nash reagent, and a  $\lambda_{\text{max}}$  of 412 nm was observed, to confirm the generation of formaldehyde in the reaction.



### References:

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193.537  
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131.601

116.179  
116.005

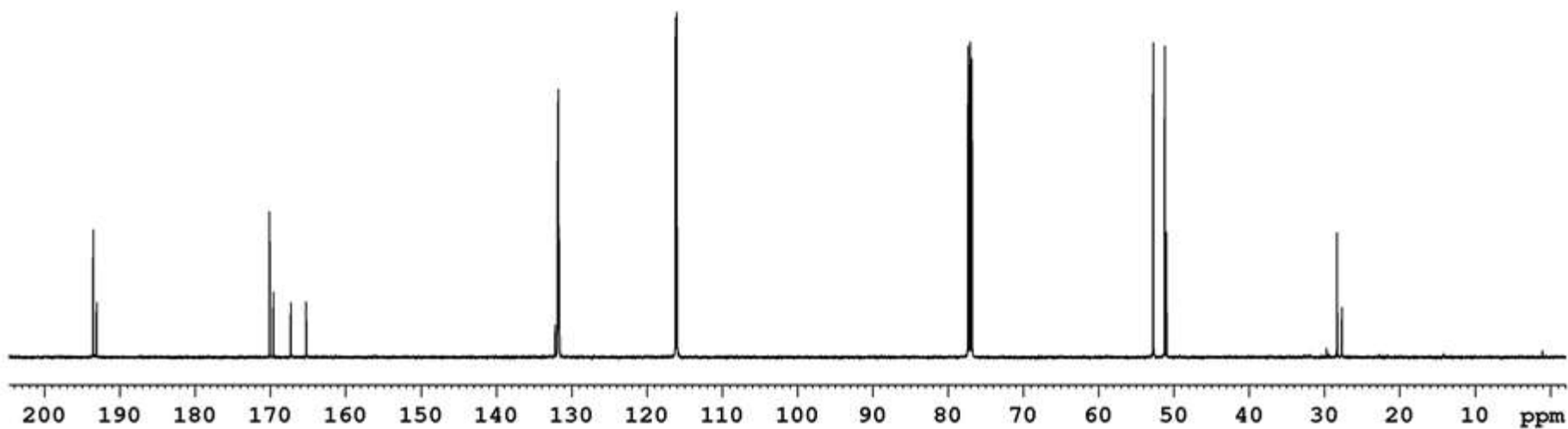
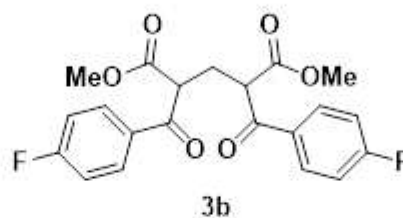
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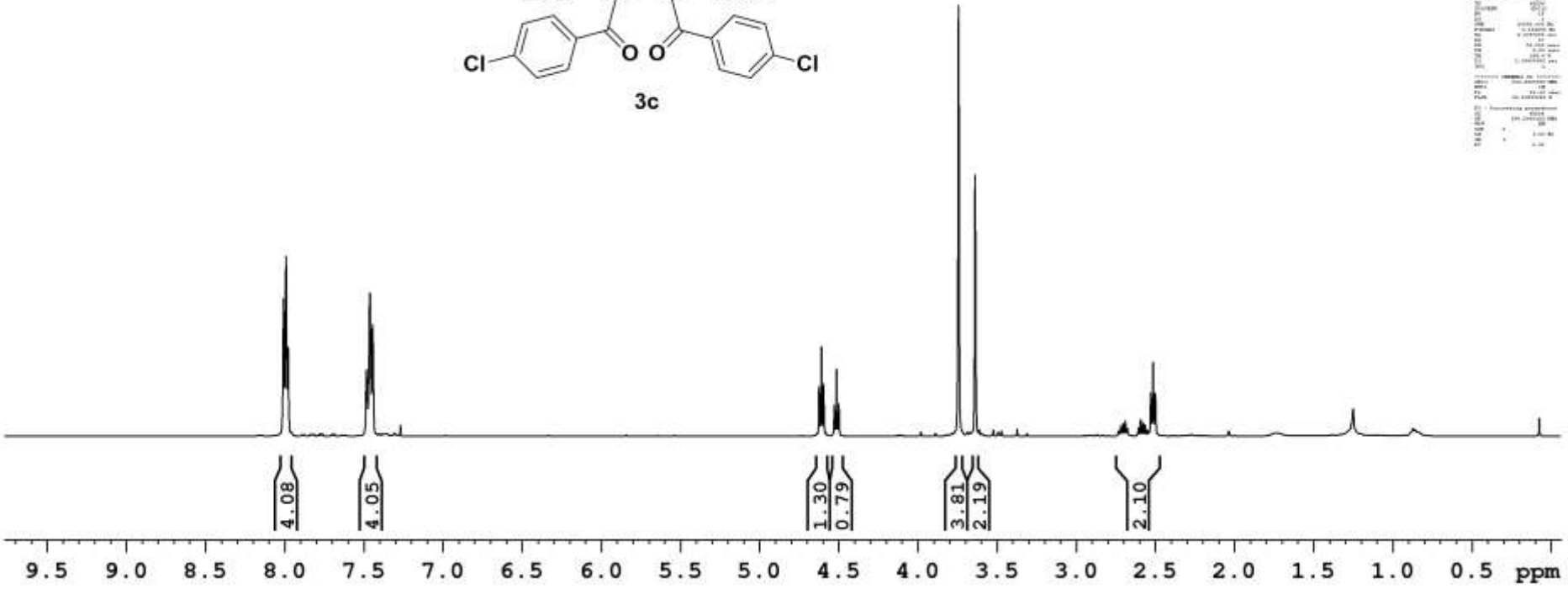
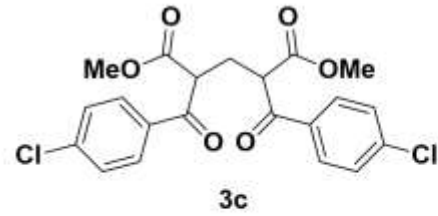


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SSB: 0  
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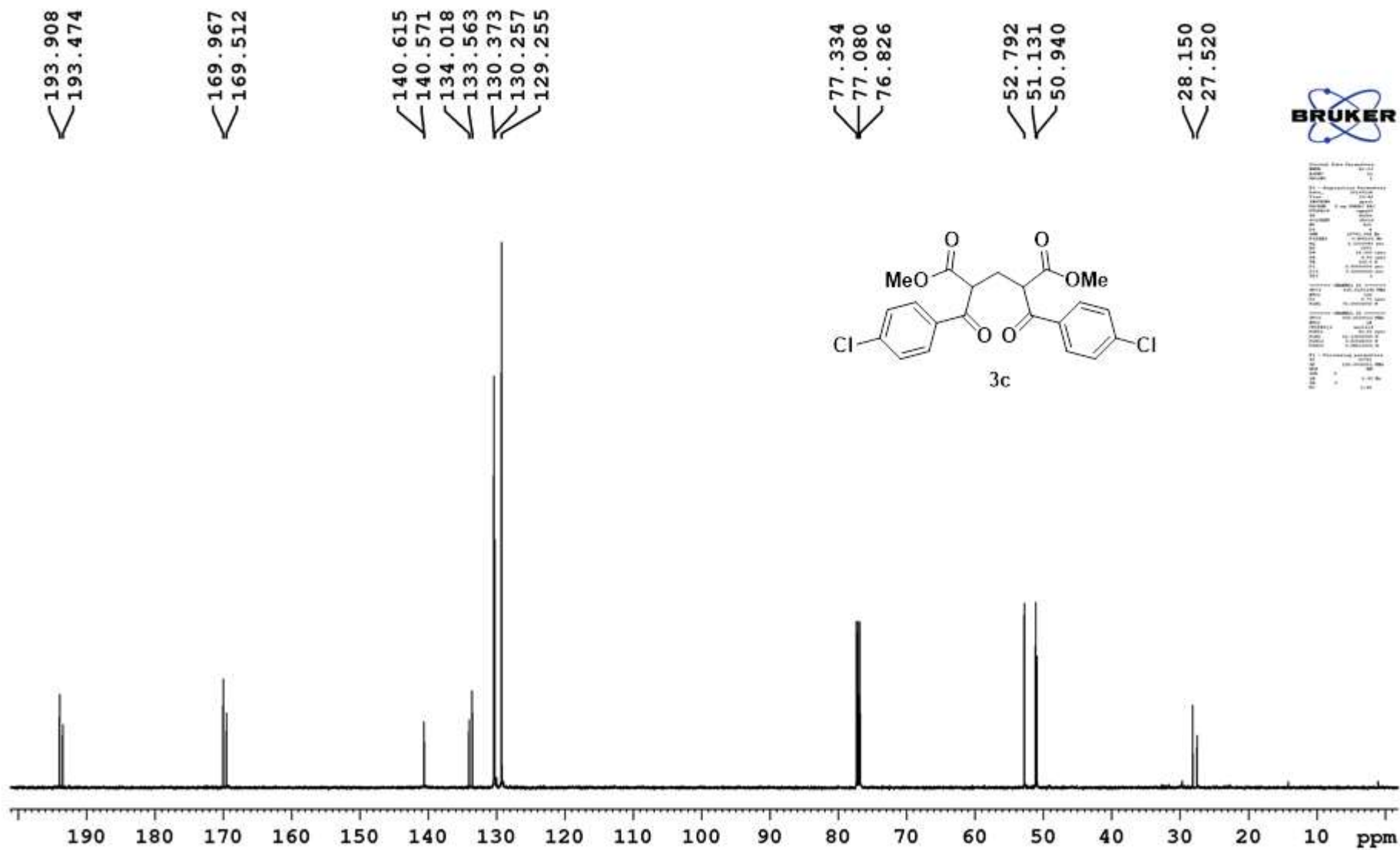


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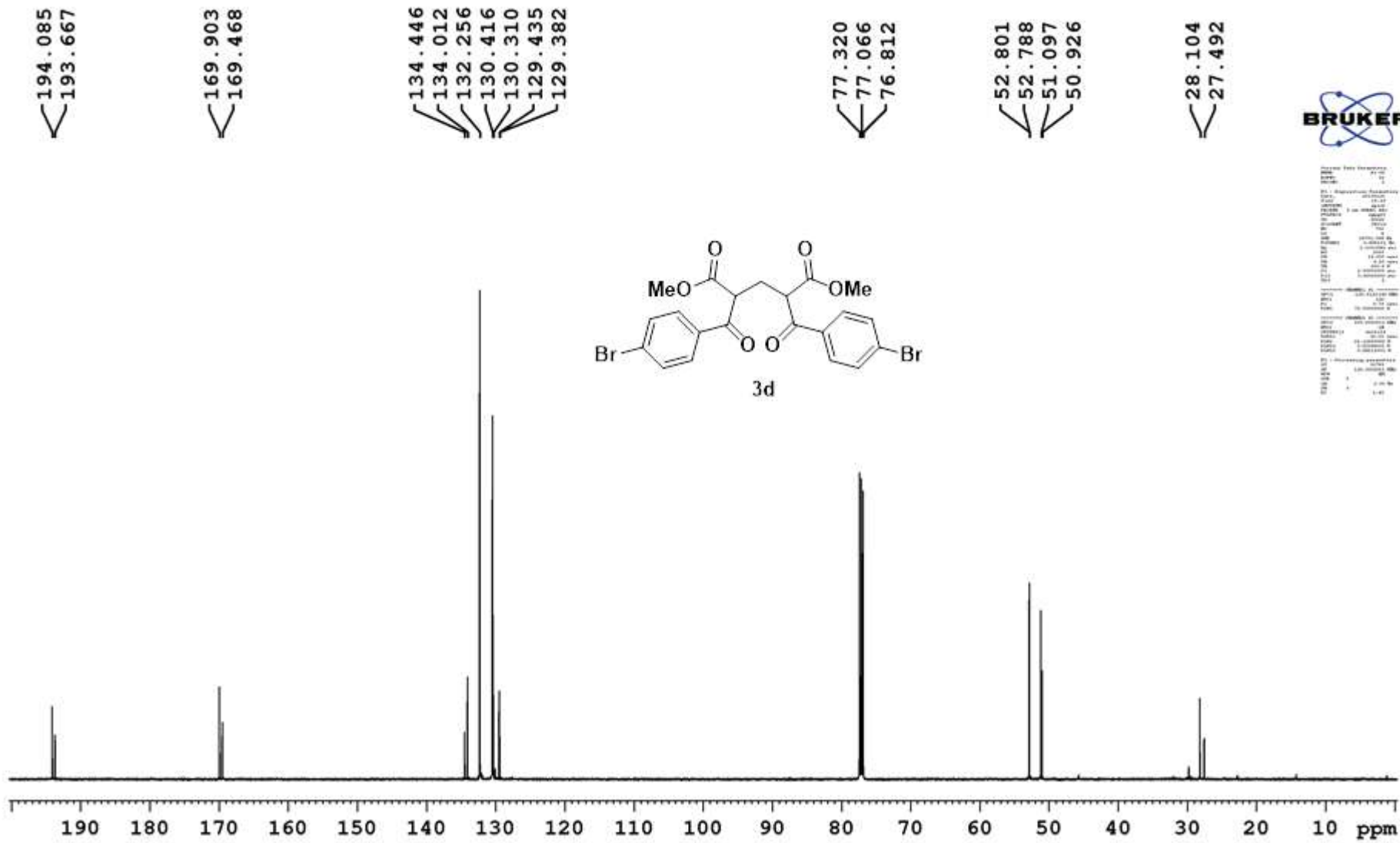
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2.526  
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2.498





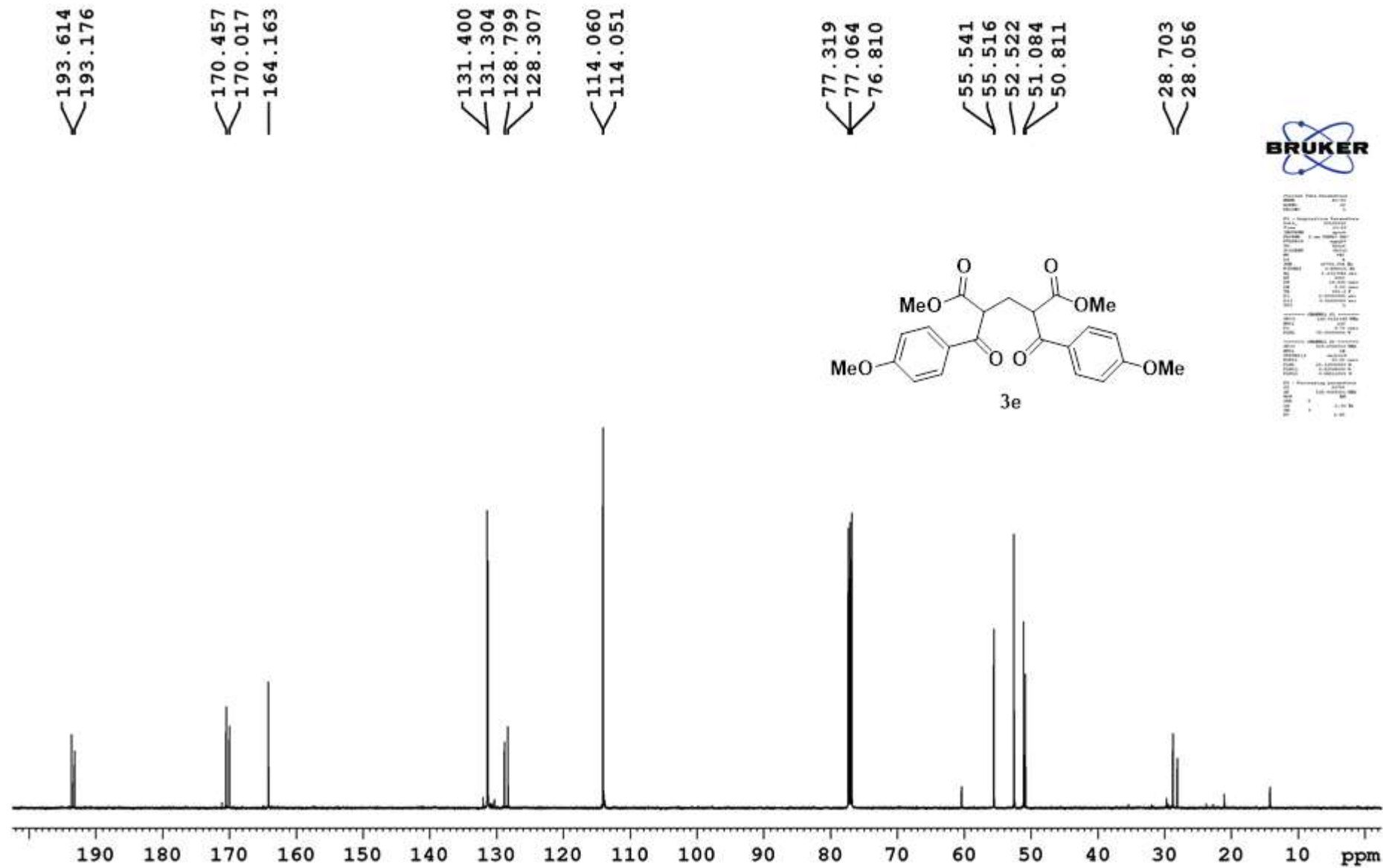






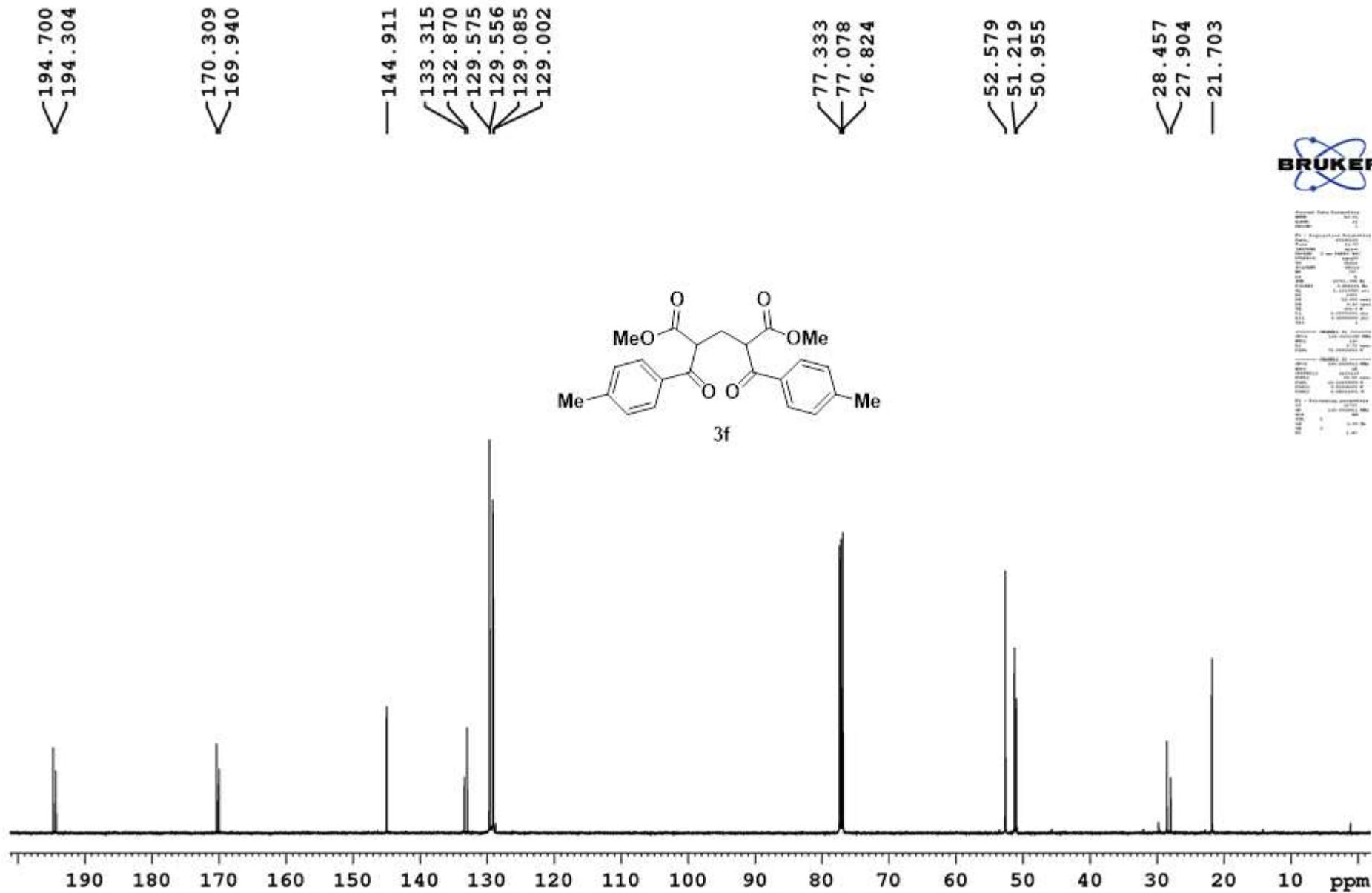
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Bruker  
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 CDCl3  
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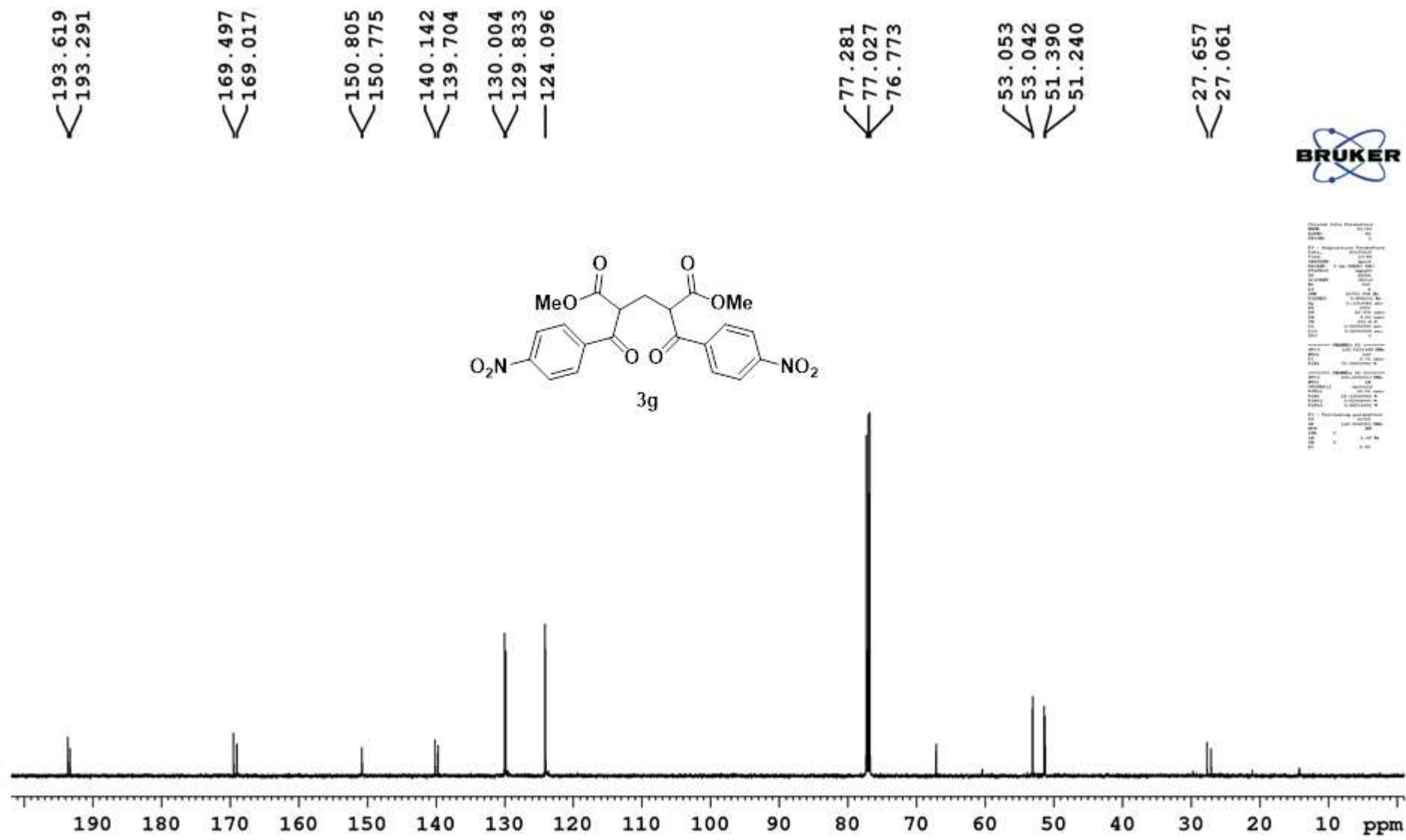




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 SFO: 101.625 MHz  
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 YA: 1.00000000  
 YB: 1.00000000  
 YC: 1.00000000  
 YD: 1.00000000  
 YE: 1.00000000  
 YF: 1.00000000  
 YG: 1.00000000  
 YH: 1.00000000  
 YI: 1.00000000  
 YJ: 1.00000000  
 YK: 1.00000000  
 YL: 1.00000000  
 YM: 1.00000000  
 YN: 1.00000000  
 YO: 1.00000000  
 YP: 1.00000000  
 YQ: 1.00000000  
 YR: 1.00000000  
 YS: 1.00000000  
 YT: 1.00000000  
 YU: 1.00000000  
 YV: 1.00000000  
 YW: 1.00000000  
 YX: 1.00000000  
 YZ: 1.00000000  
 ZA: 1.00000000  
 ZB: 1.00000000  
 ZC: 1.00000000  
 ZD: 1.00000000  
 ZE: 1.00000000  
 ZF: 1.00000000  
 ZG: 1.00000000  
 ZH: 1.00000000  
 ZI: 1.00000000  
 ZJ: 1.00000000  
 ZK: 1.00000000  
 ZL: 1.00000000  
 ZM: 1.00000000  
 ZN: 1.00000000  
 ZO: 1.00000000  
 ZP: 1.00000000  
 ZQ: 1.00000000  
 ZR: 1.00000000  
 ZS: 1.00000000  
 ZT: 1.00000000  
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 ZV: 1.00000000  
 ZW: 1.00000000  
 ZX: 1.00000000  
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 ZZ: 1.00000000

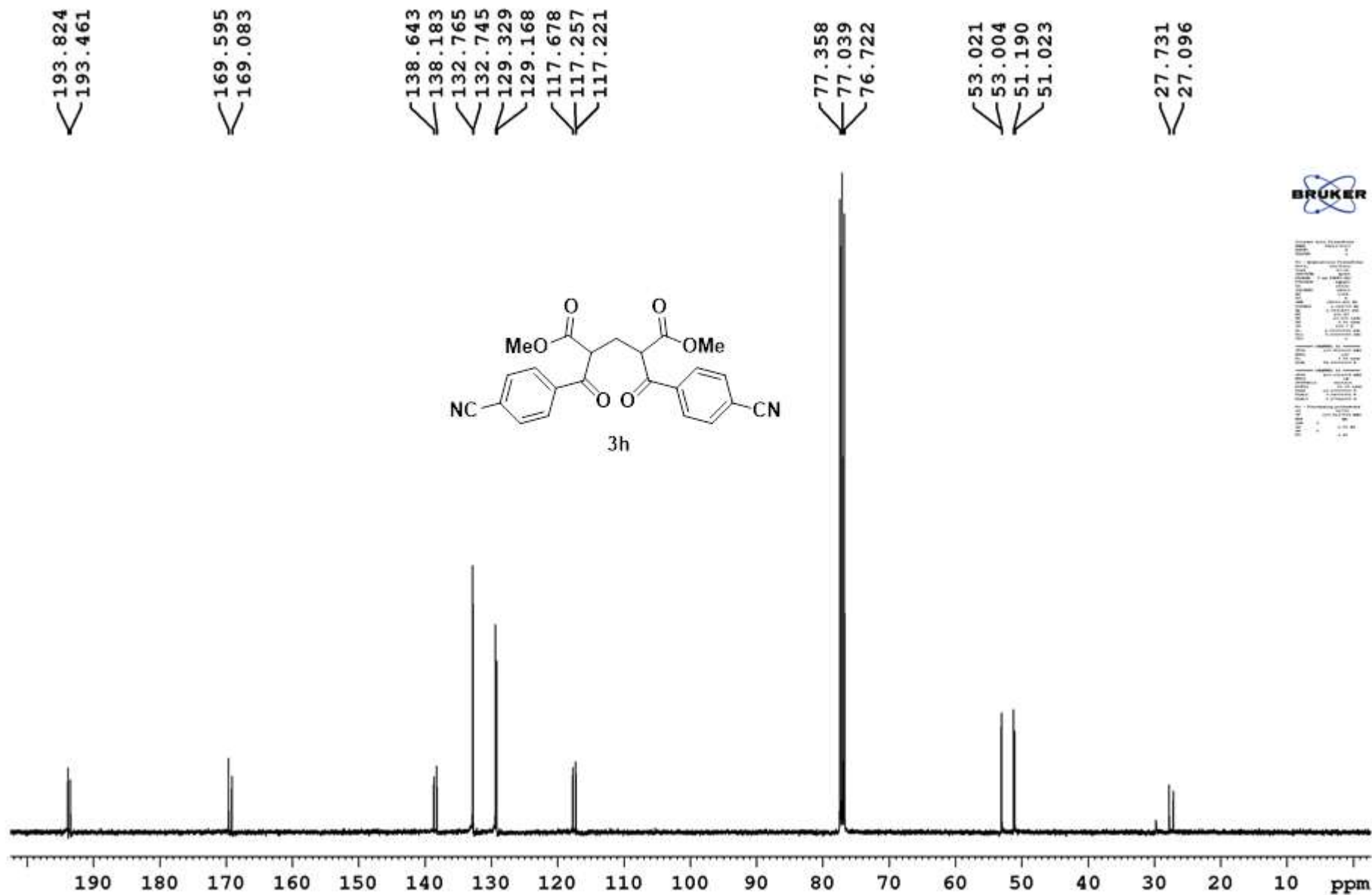




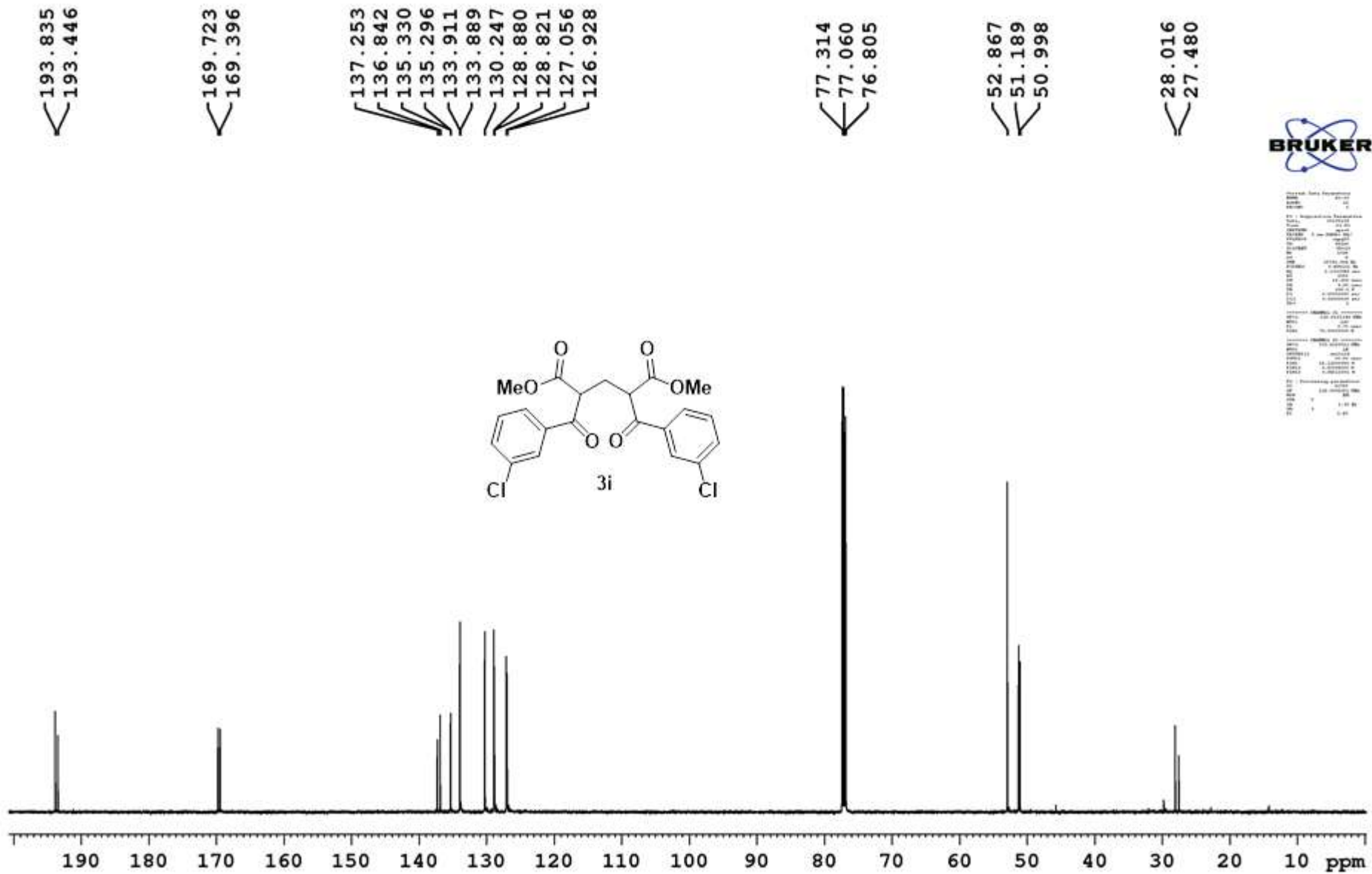


Name: 3g  
 Date: 11/11/2011  
 Time: 10:14  
 Sample: 3g  
 Solvent: CDCl3  
 Concentration: 10 mg/ml  
 Acquisition: 128 F2  
 Processing: 128 F2  
 Reference: TMS  
 Scale: 1000000  
 Gain: 1000000  
 Resolution: 0.390625  
 FWHM: 0.390625  
 S/N: 1000000  
 Integration: 1.000000  
 Baseline: 0.000000  
 Phase: 0.000000  
 Frequency: 101.625000  
 Temperature: 300.2 K  
 Pressure: 1.01325 bar  
 Humidity: 0.000000  
 Acquisition Time: 0.000000  
 Processing Time: 0.000000  
 Total Time: 0.000000











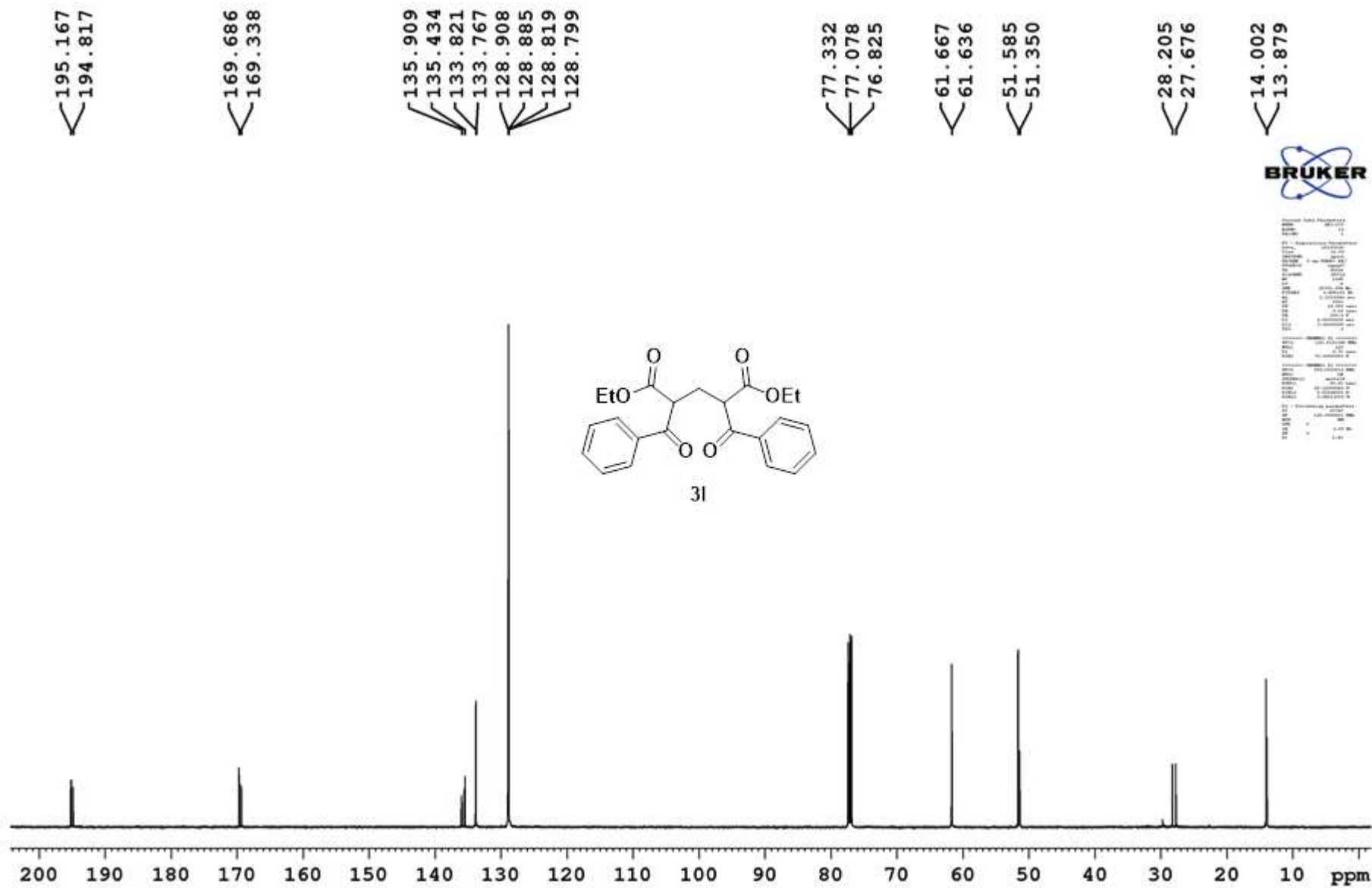








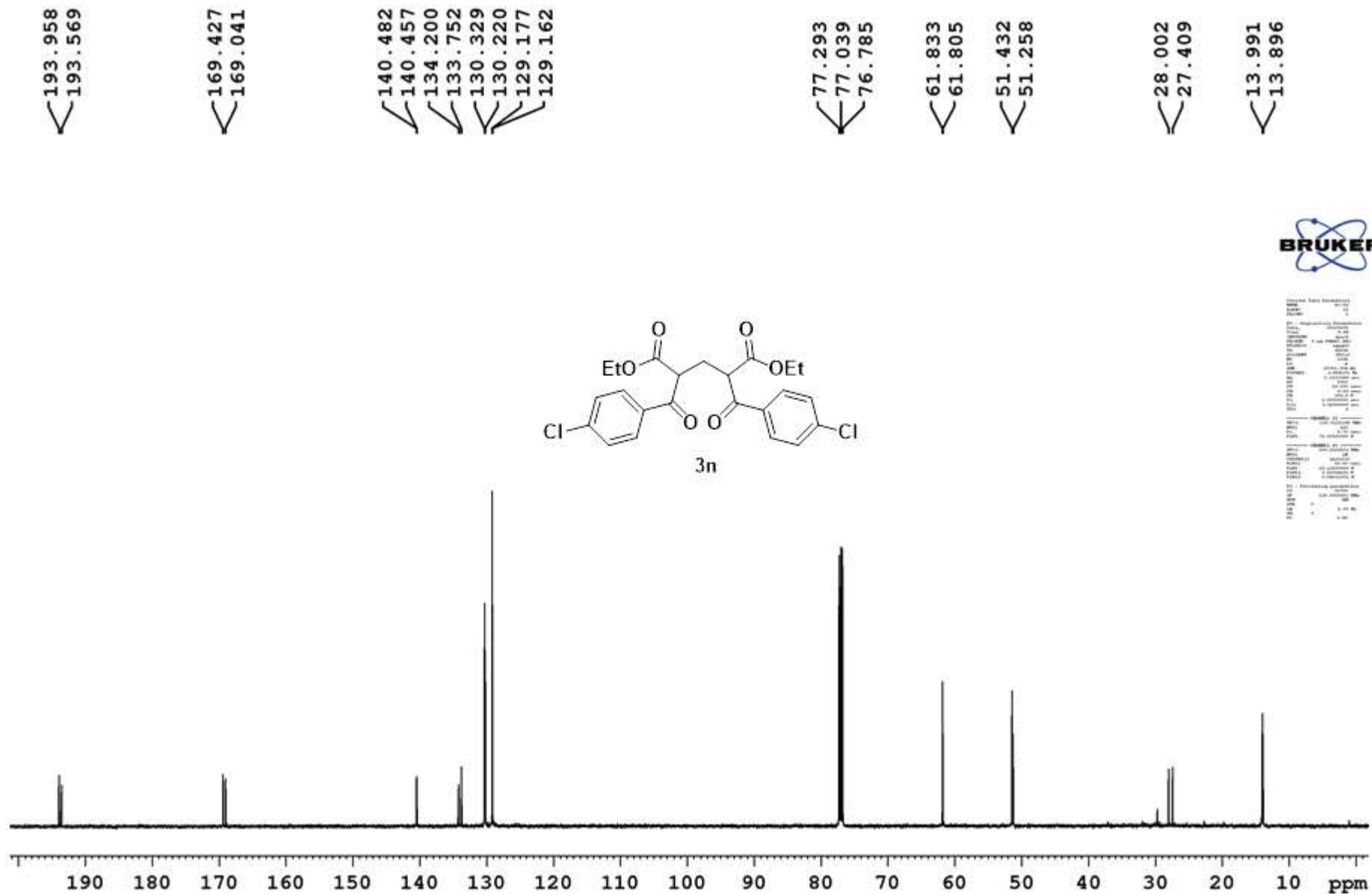






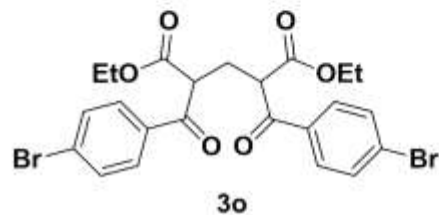




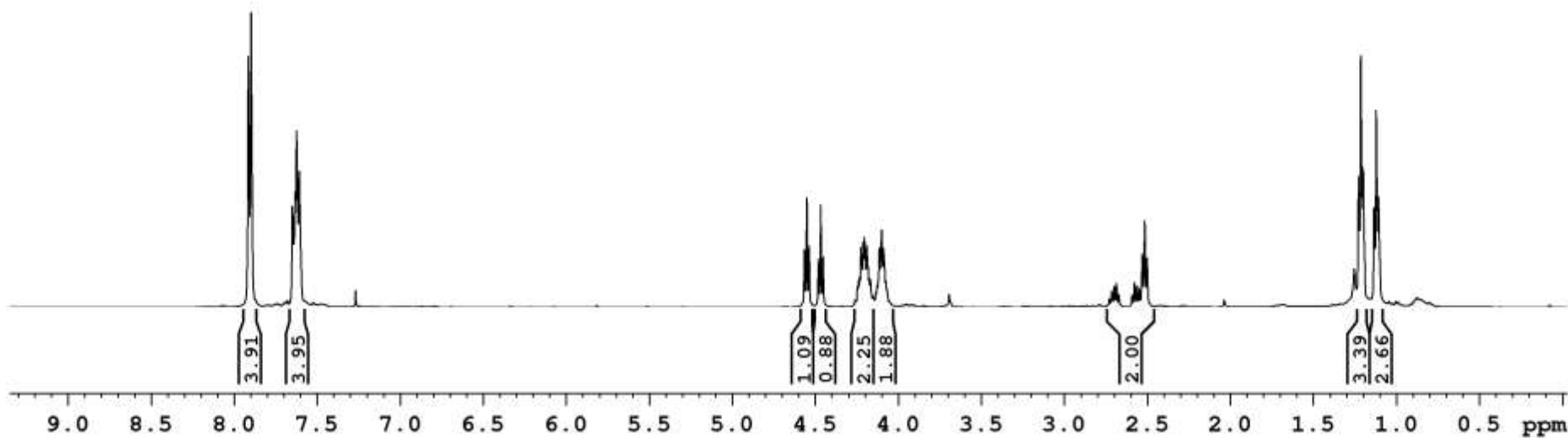


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7.633  
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7.269

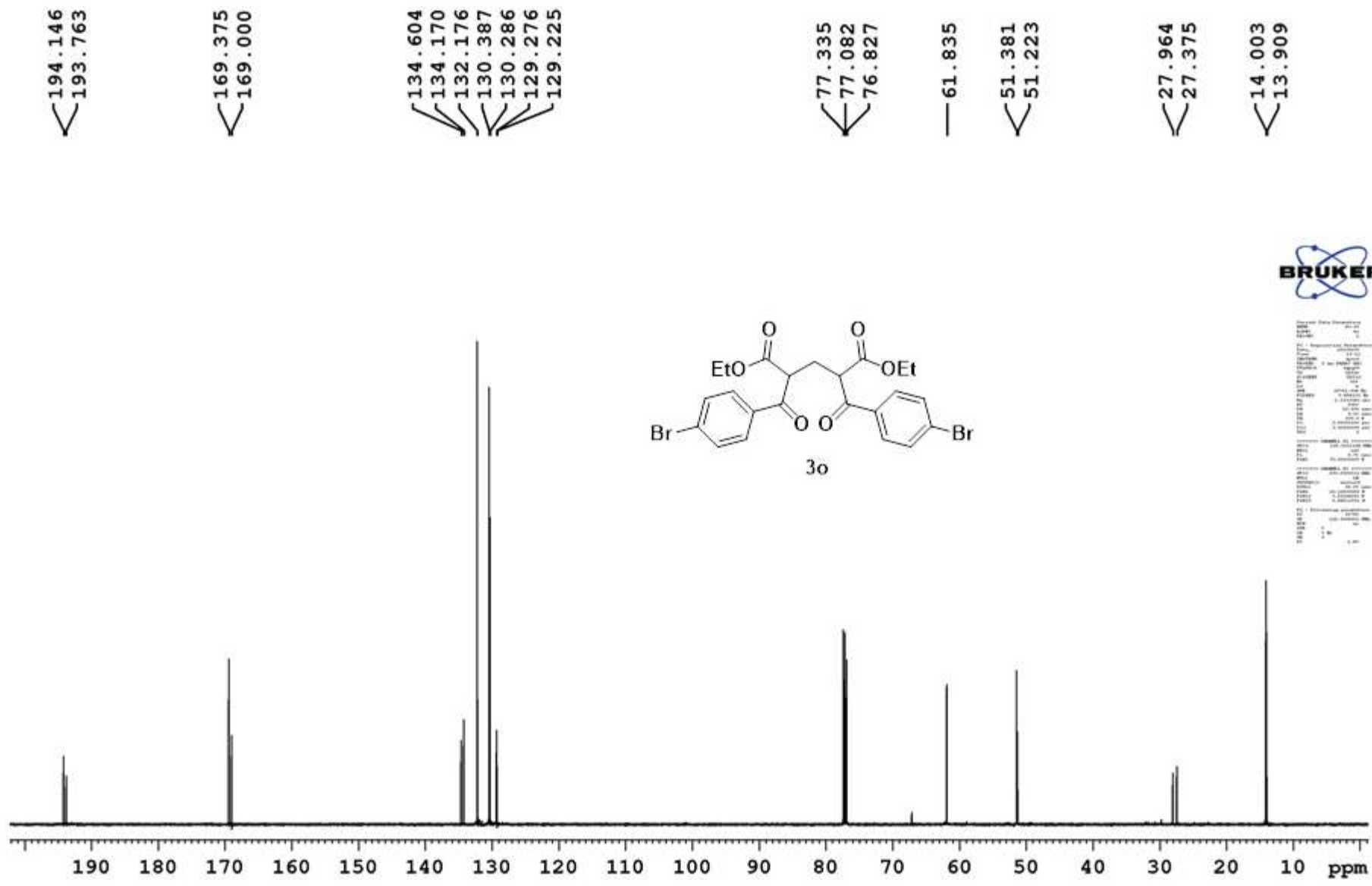
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4.453  
4.247  
4.225  
4.211  
4.204  
4.189  
4.168  
4.114  
4.100  
4.089  
2.729  
2.714  
2.700  
2.686  
2.672  
2.592  
2.577  
2.563  
2.549  
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2.516  
2.502  
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1.200  
1.136  
1.121  
1.107

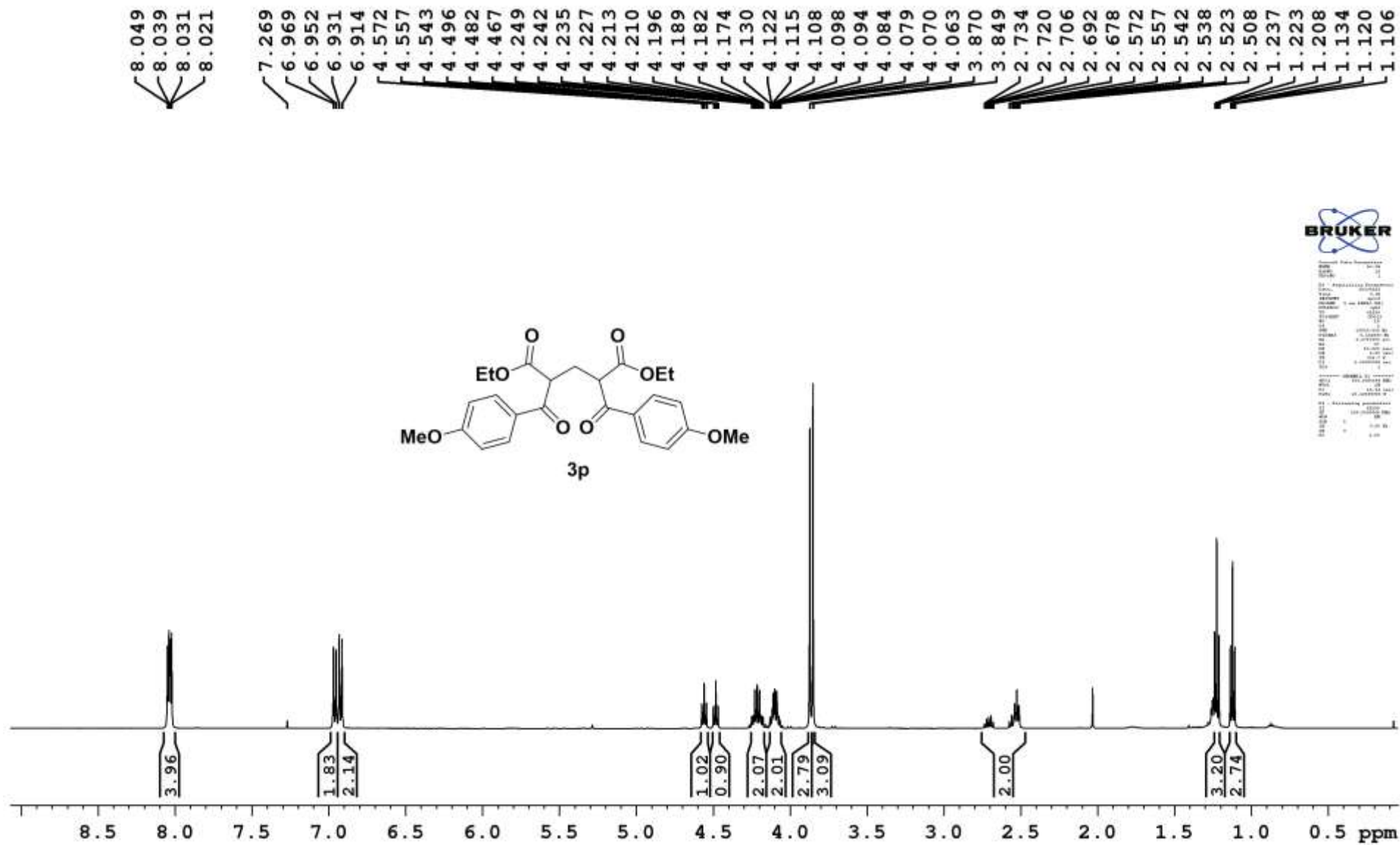


BRUKER  
 Name: 3o  
 Date: 2017-07-17  
 Time: 10:10:10  
 File: 3o\_170717\_101010.f2  
 F2 - Acquisition Parameters  
 Name: 3o\_170717\_101010  
 Date\_Time: 20170717 10:10:10  
 File: 3o\_170717\_101010.f2  
 F2 - Processing parameters  
 Name: 3o\_170717\_101010  
 Date\_Time: 20170717 10:10:10  
 File: 3o\_170717\_101010.f2  
 F2 - Reference parameters  
 Name: 3o\_170717\_101010  
 Date\_Time: 20170717 10:10:10  
 File: 3o\_170717\_101010.f2









< 193.691  
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< 169.944  
< 169.562  
< 164.089  
< 164.075

< 131.362  
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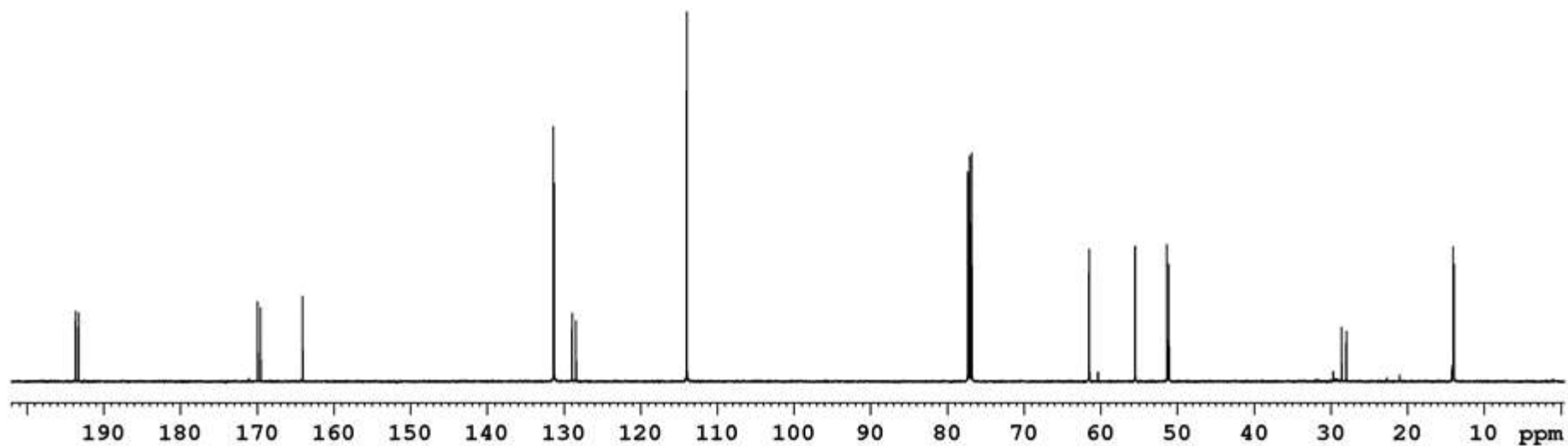
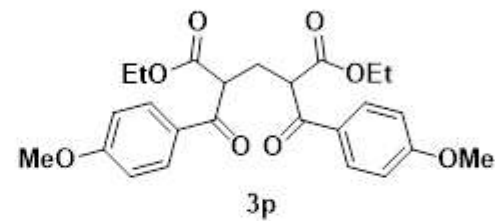
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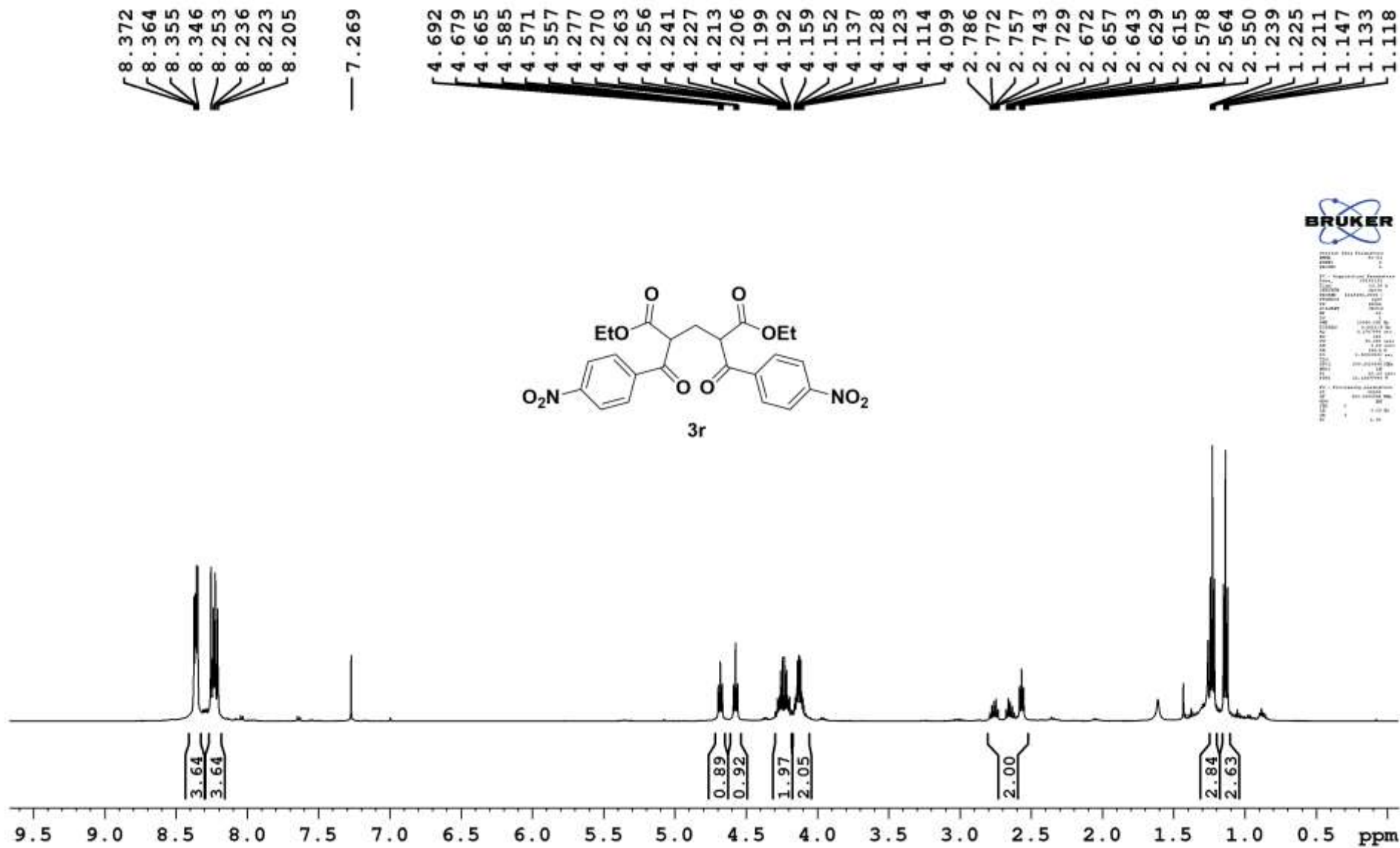
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< 13.927





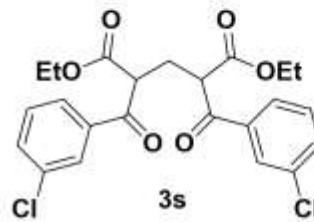






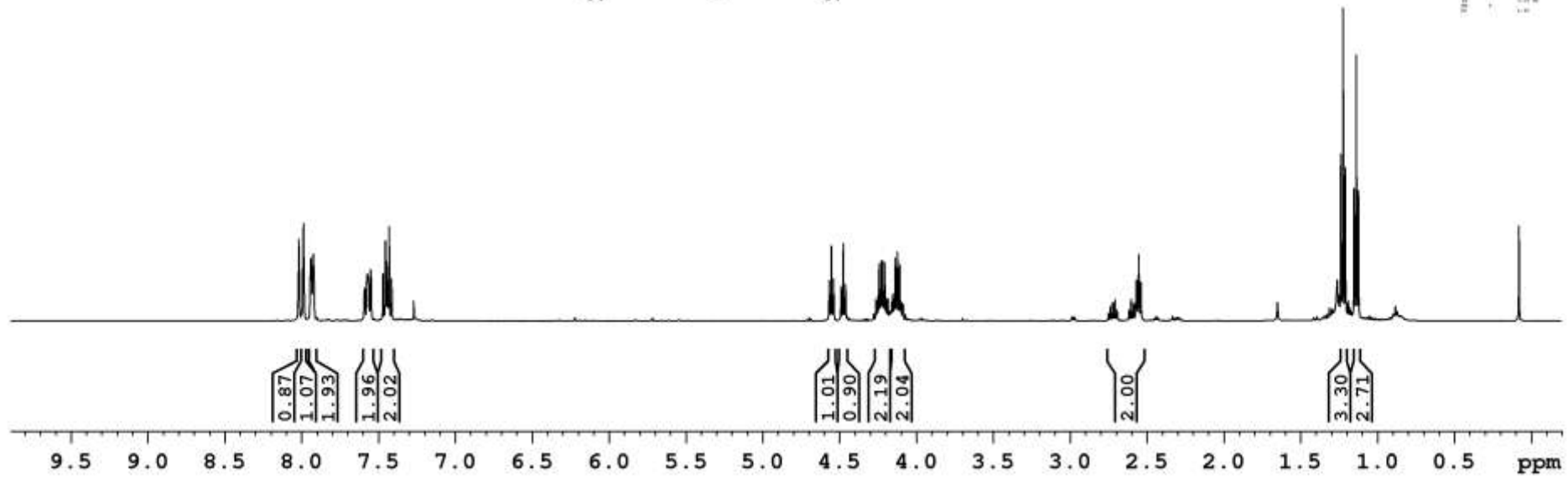


8.020  
8.017  
8.013  
7.990  
7.986  
7.983  
7.941  
7.938  
7.922  
7.920  
7.590  
7.572  
7.566  
7.550  
7.547  
7.469  
7.453  
7.444  
7.437  
7.429  
7.413  
7.269  
4.565  
4.551  
4.536  
4.488  
4.473  
4.459  
4.261  
4.254  
4.240  
4.225  
4.218  
4.204  
4.190  
4.182  
4.158  
4.150  
4.136  
4.122  
4.105  
4.084  
2.748  
2.734  
2.720  
2.705  
2.691  
2.614  
2.600  
2.585  
2.566  
2.551  
2.537  
1.235  
1.221  
1.207  
1.149  
1.135  
1.121



**BRUKER**

NAME: 3s  
EXPNO: 1  
PROCNO: 1  
PROCPS: 1  
F2 - Acquisition Parameters  
Date\_ 20110114  
Time 12.14  
INSTRUM spect  
PROBHD 5mm QNP 1H/13  
PULPROG zgpg30  
TD 65536  
SFO 400.1464000  
AQ 0.50000000  
RG 327.5  
SF 100.6260125  
FIDRES 0.18000000  
AQRES 0.39000000  
SOLVENT CDCl<sub>3</sub>  
NS 4096  
DS 4  
SWH 13172.000  
F2 - Processing parameters  
SI 32768  
SF 400.1464000  
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SSB 0  
LB 3.0000000  
GB 0  
PC 16384  
MC 0  
MD 0  
HM 0  
HT 0  
B0 12.5760000  
B1 0.0000000  
B2 0.0000000  
B3 0.0000000  
F2 - Reference chemical shifts (ppm)  
1H NMR (CDCl<sub>3</sub>)  
1.121 (t, 3H)  
1.149 (t, 3H)  
1.207 (t, 3H)  
1.221 (t, 3H)  
1.235 (t, 3H)  
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2.551 (q, 2H)  
2.566 (q, 2H)  
2.585 (q, 2H)  
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2.614 (q, 2H)  
2.691 (q, 2H)  
2.705 (q, 2H)  
2.720 (q, 2H)  
2.734 (q, 2H)  
2.748 (q, 2H)  
4.084 (q, 2H)  
4.105 (q, 2H)  
4.122 (q, 2H)  
4.136 (q, 2H)  
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4.218 (q, 2H)  
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4.565 (q, 2H)  
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7.429 (m, 4H)  
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7.572 (m, 4H)  
7.590 (m, 4H)  
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7.983 (m, 4H)  
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7.990 (m, 4H)  
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8.017 (m, 4H)  
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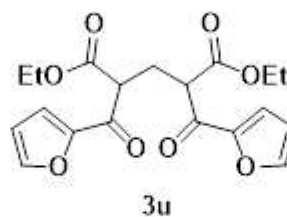












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< 168.942  
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< 151.681  
< 151.483  
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< 119.181  
< 112.653  
< 112.624

< 77.299  
< 77.045  
< 76.791

< 61.667  
< 61.657

< 51.577  
< 51.501

< 27.234  
< 26.776

< 13.969  
< 13.927

