Supporting Information

Enantioselective intramolecular Rauhut-Currier reaction catalyzed by chiral phosphinothiourea

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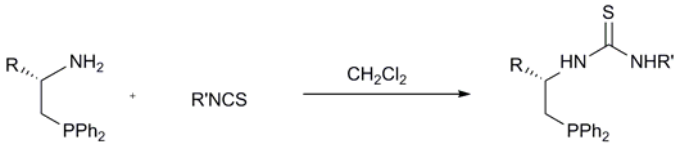
1. General Information

Melting points were taken without correction. Optical rotations were measured on a WZZ-2A digital polarimeter or a Rudolph research analytical autopol Ⅲ automatic polarimeter at the wavelength of the sodium D-line (589 nm). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 500 or 400 spectrometer. The chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0.00 ppm) using $CDCl_3$ as solvent. The chemical shifts of ^{31}P NMR spectra were referenced to an external H_3PO_4 signal (0.00 ppm). IR spectra were recorded on Nicolet Magna-I 550 or THERMO IR 200 spectrometer. High Resolution Mass spectra (HRMS) were recorded on Micromass GCT or KE465 LCT Premier/XE spectrometer. HPLC analysis was performed on Waters equipment using Daicel Chiralpak AS-H or AD-H column.

DMSO was dried over CaH_2 and distilled under reduced pressure. Toluene, THF and ether were distilled from sodium-benzophenone. Dichloromethane, chloroform and acetonitrile were distilled from CaH_2. Ethanol and *t*-BuOH was distilled from magnesium.

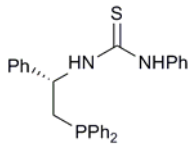
2. Synthesis of Chiral Bifunctional Organophosphine Catalysts

2.1 Synthesis of Phospinothiourea Catalysts



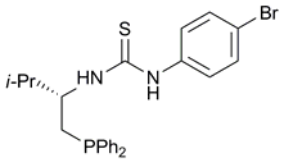
8a-d **1a-k**

To a solution of amino-phosphine compounds **8**[1] (1.0 mmol) in 2.0 mL CH_2Cl_2 was added the corresponding isothiocyanate (1.1 mmol) at room temperature, and the resulting mixture was stirred at room temperature until the reaction completed (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the chiral phosphinothiourea compounds **1a-k**. The catalysts **1b-f** and **1h-j** were described in our previous work.[2] The analytic data of compounds **1a**, **1g** and **1k** are given as follow.



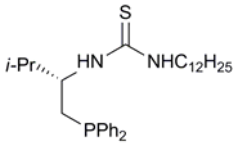
1a

Colorless oil, 65% yield, $[\alpha]_D^{30}$ -7.0 (*c* 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (br, 1H), 7.44-7.34 (m, 7H), 7.33-7.27 (m, 8H), 7.25-7.12 (m, 5H), 6.55 (d, *J* = 6.8 Hz, 1H), 5.65 (br, 1H), 2.77-2.66 (m, 1H), 2.65-2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 141.8 (d, *J* = 4.4 Hz), 138.8 (d, *J* = 12.3 Hz), 137.8 (d, *J* = 11.6 Hz), 136.6, 133.3, 133.2, 130.3, 129.1 (2), 129.0, 128.9, 128.8 (3), 128.0, 127.2, 126.7, 125.1, 57.2 (d, *J* = 17.5 Hz), 37.1 (d, *J* = 15.5 Hz); IR (KBr, cm^{-1}): ν 3373, 3239, 3052, 2923, 2853, 1596, 1522, 1494, 738, 694; ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -24.16; HRMS (ESI) calcd for $C_{27}H_{26}N_2PS$ ($[M+H]^+$) 441.1554, found: 441.1558.



1g

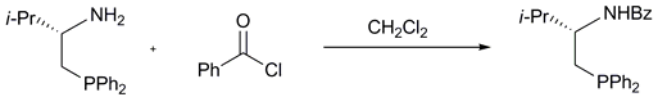
White solid, 74% yield, mp: 116.8-117.2 °C; $[\alpha]_D^{30}$ +35.0 (*c* 0.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.52 (br, 1H), 7.41-7.29 (m, 6H), 7.27-7.17 (m, 6H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.94 (br, 1H), 4.50 (br, 1H), 2.40-2.30 (m, 1H), 2.23-2.12 (m, 1H), 2.10-1.97 (m, 1H), 0.85-0.69 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.8, 138.3 (d, *J* = 11.5 Hz), 138.7 (d, *J* = 12.0 Hz), 135.4, 133.0, 132.9, 132.8, 132.7, 128.9 (2), 128.7, 128.6 (3), 126.5, 120.1, 58.5 (d, *J* = 14.1 Hz), 32.0 (d, *J* = 7.7 Hz), 31.1 (d, *J* = 14.1 Hz), 18.8, 18.4; ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -24.71; IR (KBr, cm^{-1}): ν 3218, 3030, 2959, 2867, 1529, 1487, 1338, 1300, 1008, 697; HRMS (ESI) calcd for $C_{24}H_{26}N_2BrPS$ ($[M+H]^+$) 485.0816, found: 485.0824.



1k

Colorless oil, 75% yield, $[\alpha]_D^{11}$ -4.8 (*c* 3.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.40 (m, 4H), 7.37-7.27 (m, 6H), 6.26-5.19 (br, 2H), 3.43-3.65 (br, 2H), 2.50-2.39 (m, 1H), 2.36-2.23 (m, 1H), 2.17-2.07 (m, 1H), 1.51-1.35 (m, 2H), 1.33-1.19 (m, 18H), 0.95-0.84 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.0, 138.5 (d, *J* = 12.1 Hz), 138.1 (d, *J* = 11.7 Hz), 133.0 (2), 132.8 (2), 128.9, 128.8, 128.7, 128.6 (3), 57.8, 43.7, 32.2 (d, *J* = 8.4 Hz), 31.9, 31.4 (d, *J* = 12.4 Hz), 29.7, 29.6 (2), 29.5, 29.4, 29.3, 28.8, 26.9, 22.7, 18.9, 18.2, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -24.11; IR (KBr, cm^{-1}): ν 3273, 3072, 2958, 2924, 2854, 1539, 1465, 1434, 1385, 1355, 738, 695; HRMS (ESI) calcd for $C_{30}H_{47}N_2PSNa$ ($[M+Na]^+$) 521.3095, found: 521.3099.

2.2 Synthesis of *L*-Valine-derived Phosphine-amide 2



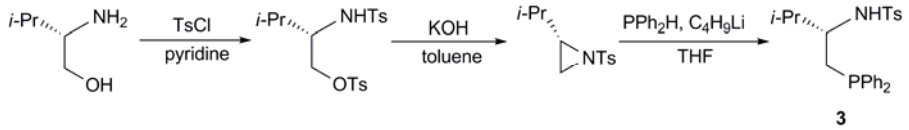
8d **2**

To a solution of aminophosphine compound **8d** (1.0 mmol) in 2.0 mL CH_2Cl_2 was added benzoyl chloride (1.1 mmol), and the resulting mixture was stirred at room temperature overnight (monitoring by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford the *L*-valine-derived phosphine-amide **2** in 65% yield.

White solid, mp: 144.9-146.8 °C; $[\alpha]_D^{25}$ +2.2 (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.27 (m, 15H), 5.88 (d, *J* = 9.2 Hz, 1H), 4.27-4.15 (m, 1H), 2.47-2.31 (m, 2H), 2.17-2.05 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 138.5 (d, *J* = 8.6 Hz), 138.4 (d, *J* = 9.4 Hz), 134.8, 133.0, 132.9, 132.8, 132.7, 131.2, 128.8, 128.7 (2), 128.6 (3), 128.4, 126.8, 53.0 (d, *J* = 13.6 Hz), 32.6 (d, *J* = 8.5 Hz), 31.6 (d, *J* = 14.5 Hz), 18.9, 18.2; ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -23.69; IR (KBr, cm^{-1}): ν 3325, 2963, 1638, 1538, 1488, 741, 696; HRMS (ESI) calcd for $C_{24}H_{27}NPO$

([M+H]$^+$) 376.1830, found: 376.1814.

2.3 Synthesis of *L*-Valine-derived Phosphine-sulfonamide 3

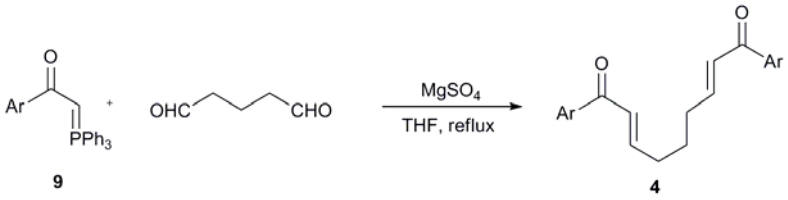


The compound **3** was synthesized from L-valinol according to the literature procedure.[3]

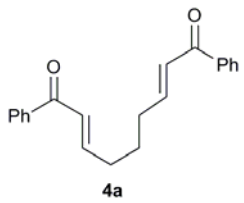
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.33-7.13 (m, 12H), 5.37 (d, *J* = 8.0 Hz, 1H), 3.17-3.06 (m, 1H), 2.35 (s, 3H), 2.17-2.07 (m, 3H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H).

3. Synthesis of the Substrates[4]

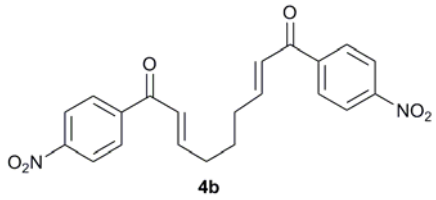
3.1 Synthesis of Symmetrical Bis(enones) 4a-o



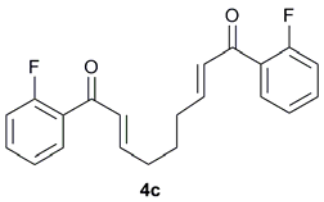
To a solution of stabilized ylide **9** (3.0 mmol) in 10 mL THF was added aqueous glutaric dialdehyde solution (25%, 0.45 mL, 1.2 mmol) and $MgSO_4$ (ca. 1.4 g). The mixture was stirred under reflux and monitored by TLC. After removing the precipitate and the solvent, the residue was purified by column chromatography to afford the bis(enones) **4a-o**. Bis(enones) **4a**, **4b**, **4g**, **4j**, **4l**, **4m**, **4n** and **4o** are known compounds.[5-7]



Colorless oil, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 4H), 7.54-7.45 (t, *J* = 7.2 Hz, 2H), 7.44-7.34 (t, *J* = 7.2 Hz, 4H), 7.05-6.93 (m, 2H), 6.85 (d, *J* = 15.6 Hz, 2H), 2.39-2.27 (m, 4H), 1.78-1.65 (m, 2H).

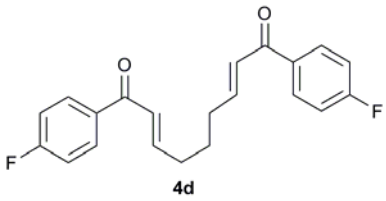


Yellow solid, 25% yield, mp: 83.7-84.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.0 Hz, 4H), 8.06 (d, *J* = 8.0 Hz, 4H), 7.18-7.08 (m, 2H), 6.93 (s, 1H), 6.89 (s, 1H), 2.50-2.40 (m, 4H), 1.88-1.76 (m, 2H).



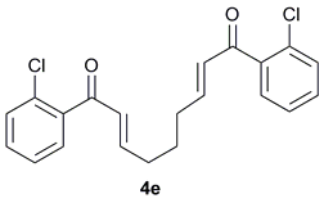
4c

Colorless oil, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.68 (m, 2H), 7.53-7.45 (m, 2H), 7.26-7.19 (m, 2H), 7.15-7.08 (m, 2H), 7.04-6.92 (m, 2H), 6.79-6.76 (m, 1H), 6.75-6.71 (m, 1H), 2.42-2.31 (m, 4H), 1.80-1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4 (2), 161.0 (d, *J* = 251.5Hz), 149.0, 133.8 (d, *J* = 8.7Hz), 130.8 (d, *J* = 2.8Hz), 130.1 (d, *J* = 5.8Hz), 126.9 (d, *J* = 13.3Hz), 124.4 (d, *J* = 3.4Hz), 116.4 (d, *J* = 22.8Hz), 31.9, 26.4; IR (KBr, cm^{-1}): ν 2934, 2864, 1672, 1612, 1480, 1452, 1301, 1211, 1153, 1102, 977, 763; HRMS (ESI) calcd for $C_{21}H_{19}F_2O_2$ ($[M+H]^+$) 341.1353, found: 341.1348.



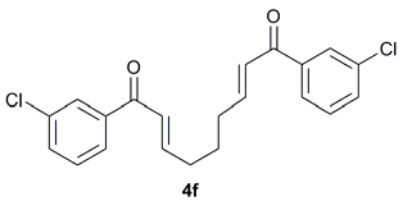
4d

Yellow solid, 79% yield, mp: 77.2-78.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 4.4 Hz, 4H), 7.10-6.92 (m, 6H), 6.81 (d, *J* = 15.2 Hz, 2H), 2.37-2.25 (m, 4H), 1.77-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 165.6 (d, *J* = 252.8 Hz), 148.7, 134.1 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 9.1 Hz), 126.0, 115.7 (d, *J* = 21.7 Hz), 32.2, 26.7; IR (KBr, cm^{-1}): ν 2944, 1668, 1620, 1593, 1504, 1407, 1334, 1301, 1265, 1231, 1201, 1158, 995, 824, 602; HRMS (ESI) calcd for $C_{21}H_{18}F_2O_2K$ ($[M+K]^+$) 379.0912, found: 379.0914.



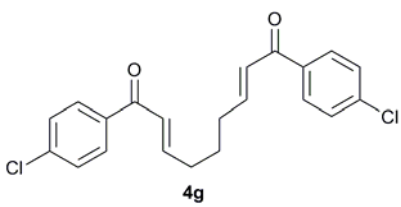
4e

Colorless oil, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.28 (m, 8H), 6.73-6.64 (m, 2H), 6.51-6.48 (m, 1H), 6.47-6.44 (m, 1H), 2.36-2.27 (m, 4H), 1.73-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 150.9, 138.9, 131.3, 131.0, 130.9, 130.2, 129.1, 126.8, 32.0, 26.1; IR (KBr, cm^{-1}): ν 2932, 2860, 1658, 1618, 1590, 1467, 1432, 1295, 1253, 1215, 1040, 974, 762; HRMS (ESI) calcd for $C_{21}H_{19}Cl_2O_2$ ($[M+H]^+$) 373.0762, found: 373.0759.



4f

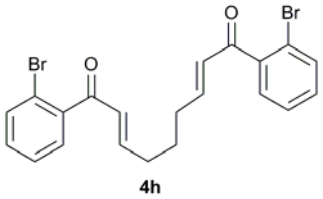
Colorless oil, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (d, *J* = 2.0 Hz, 2H), 7.82-7.77 (m, 2H), 7.54-7.49 (m, 2H), 7.43-7.37 (d, *J* = 8.0 Hz, 2H), 7.13-7.04 (m, 2H), 6.88 (d, *J* = 15.2 Hz, 2H), 2.45-2.35 (m, 4H), 1.83-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 149.5, 139.4, 134.8, 132.7, 129.9, 128.6, 126.6, 126.0, 32.2, 26.6; IR (KBr, cm^{-1}): ν 2931, 2859, 1671, 1651, 1618, 1568, 1423, 1296, 1214, 1075, 976, 789, 720; HRMS (ESI) calcd for $C_{21}H_{19}Cl_2O_2$ ($[M+H]^+$) 373.0762, found: 373.0759.



4g

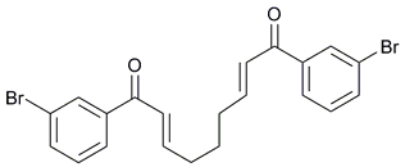
Yellow solid, 58% yield, mp: 65.6-67.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.8 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.05-6.95 (m, 2H), 6.81 (d, *J* = 15.6 Hz, 2H), 2.38-2.28 (m, 4H),

1.77-1.66 (m, 2H).



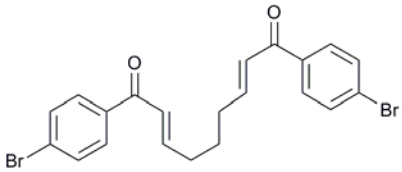
4h

Colorless oil, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.33-7.27 (t, *J* = 6.4 Hz, 2H), 7.26-7.20 (m, 4H), 6.63-6.53 (m, 2H), 6.38 (d, *J* = 15.6 Hz, 2H), 2.30-2.21 (m, 4H), 1.68-1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 151.2, 141.0, 133.3, 131.2, 130.8, 128.9, 127.3, 119.3, 32.0, 26.1; IR (KBr, cm^{-1}): ν 2925, 2854, 1659, 1633, 1589, 1467, 1429, 1292, 1025, 977, 761, 734; HRMS (ESI) calcd for $C_{21}H_{19}Br_2O_2$ ($[M+H]^+$) 460.9752, found: 460.9778.



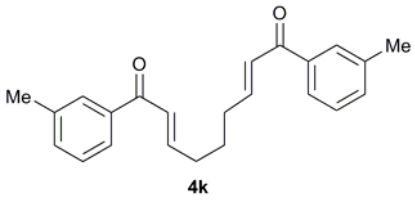
4i

Colorless oil, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.92 (t, *J* = 1.6 Hz, 2H), 7.77-7.71 (m, 2H), 7.60-7.53 (m, 2H), 7.28-7.20 (t, *J* = 8.0 Hz, 2H), 7.03-6.92 (m, 2H), 6.77 (d, *J* = 15.6 Hz, 2H), 2.35-2.25 (m, 4H), 1.73-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0, 149.5, 139.6, 135.6, 131.5, 130.2, 127.0, 126.0, 122.9, 32.2, 26.6; IR (KBr, cm^{-1}): ν 2929, 2856, 1671, 1619, 1565, 1421, 1297, 1216, 1068, 971, 788, 700; HRMS (ESI) calcd for $C_{21}H_{18}Br_2O_2Na$ ($[M+Na]^+$) 482.9571, found: 482.9581.



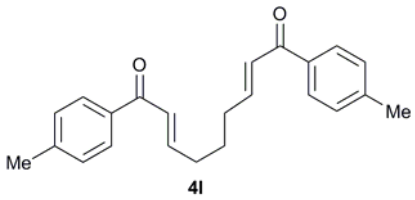
4j

Colorless oil, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H), 7.05-6.94 (m, 2H), 6.80 (d, *J* = 15.6 Hz, 2H), 2.37-2.27 (m, 4H), 1.76-1.66 (m, 2H).



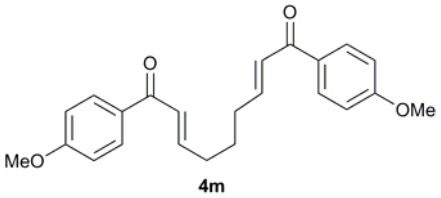
4k

Colorless oil, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.66 (m, 4H), 7.34-7.26 (m, 4H), 7.07-6.97 (m, 2H), 6.89 (d, *J* = 15.6 Hz, 2H), 2.39-2.28 (m, 10H), 1.77-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 148.3, 138.3, 137.9, 133.5, 129.0, 128.4, 126.5, 125.7, 32.1, 26.7, 21.3; IR (KBr, cm^{-1}): ν 2926, 2857, 1669, 1621, 1602, 1585, 1432, 1296, 1167, 978, 784; HRMS (ESI) calcd for $C_{23}H_{24}O_2Na$ ($[M+Na]^+$) 355.1674, found: 355.1682.



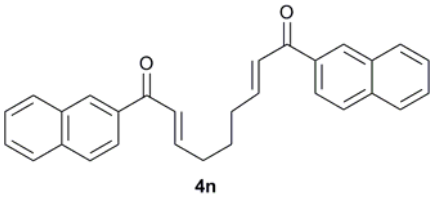
4l

Colorless oil, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.00-6.90 (m, 2H), 6.83 (d, *J* = 15.6 Hz, 2H), 2.35-2.24 (m, 10H), 1.73-1.61 (m, 2H).



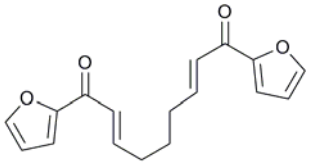
4m

White solid, 44% yield, mp: 78.4-80.1 °C (lit.[8] 77-78 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.95 (m, 2H), 7.95-7.92 (m, 2H), 7.09-7.00 (m, 2H), 6.97-6.90 (m, 6H), 3.86 (s, 6H), 2.42-2.34 (m, 4H), 1.82-1.72 (m, 2H).



4n

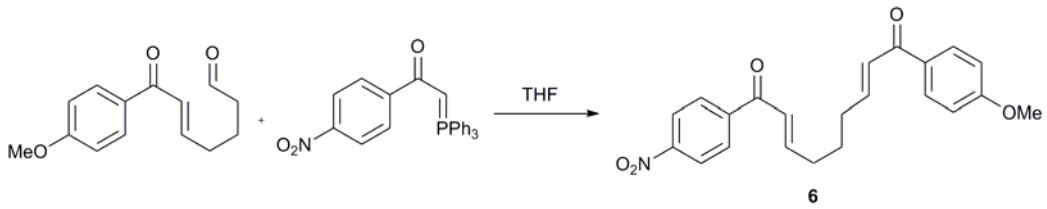
Colorless oil, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 2H), 8.06-8.00 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H), 7.97-7.83 (m, 6H), 7.63-7.49 (m, 4H), 7.20-7.06 (m, 4H), 2.52-2.42 (m, 4H), 1.90-1.80 (m, 2H).



4o

Colorless oil, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 1.2 Hz, 2H), 7.17 (d, *J* = 3.6 Hz, 2H), 7.12-7.01 (m, 2H), 6.80-6.72 (d, *J* = 15.6 Hz, 2H), 6.51-6.45 (m, 2H), 2.35-2.25 (m, 4H), 1.74-1.63 (m, 2H).

3.2 Synthesis of Unsymmetrical Bis(enone) 6



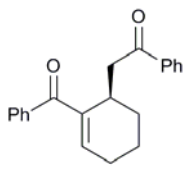
6

The compound **6** was synthesized according to the literature procedure[4] and the analytic data of compound **6** were referred to literature [9].

Yellow solid, 70% yield, mp: 99.5-99.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33-8.28 (m, 2H), 8.07-8.02 (m, 2H), 7.97-7.92 (m, 2H), 7.17-7.08 (m, 1H), 7.08-6.99 (m, 1H), 6.98-6.85 (m, 4H), 3.88 (s, 3H), 2.47-2.37 (m, 4H), 1.85-1.75 (m, 2H).

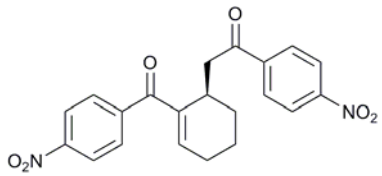
4. Asymmetric Intramolecular Rauhut-Currier Reaction (Table 3)

General procedure: To a solution of the chiral phosphinothiourea (0.04 mmol) in CH_2Cl_2 (1.0 mL) was added the bis(enones) (0.2 mmol) at -30 °C. The reaction mixture was stirred at -30 °C until the reaction completed (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the desired cyclic products. The ee values were determined by HPLC analysis with Chiralcel AD-H or AS-H column. Products **5a**, **5b**, **5g**, **5j**, **5m**, **5n**, **5o, 7a** and **7b** are known compounds.[5, 6, 9]



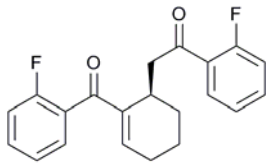
5a

80% yield, 99.4% ee, $[\alpha]_D^{25}$ +30.0 (*c* 0.35, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-8.05 (m, 2H), 7.70-7.65 (m, 2H), 7.57-7.40 (m, 6H), 6.65-6.61 (m, 1H), 3.54-3.46 (m, 1H), 3.45-3.38 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.86-2.76 (m, 1H), 2.40-2.29 (m, 1H), 2.26-2.15 (m, 1H), 1.82-1.59 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 10.5 min (minor), 13.7 min (major).



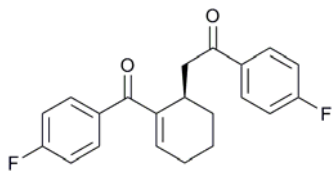
5b

92% yield, 81% ee, $[\alpha]_D^{25}$ -17.5 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.39-8.28 (m, 4H), 8.24 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 6.73-6.66 (m, 1H), 3.51-3.37 (m, 2H), 3.04-2.94 (m, 1H), 2.42 (d, *J* = 19.6 Hz, 1H), 2.28 (d, *J* = 19.6 Hz, 1H), 1.83-1.65 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 70/30, flow rate: 1.0 mL/min): t_R = 29.3 min (major), 31.6 min (minor).



5c

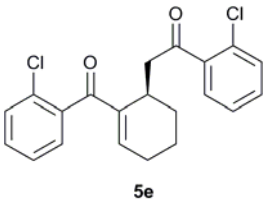
99% yield, 98% ee, $[\alpha]_D^{25}$ -14.0 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.84-7.77 (m, 1H), 7.45-7.26 (m, 3H), 7.17-6.95 (m, 4H), 6.59-6.53 (m, 1H), 3.51-3.43 (m, 1H), 3.25-3.16 (dt, *J* = 17.2 Hz, 2.8 Hz, 1H), 3.03-2.92 (m, 1H), 2.28-2.05 (m, 2H), 1.77-1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6 (d, *J* = 3.7 Hz), 194.4, 162.9 (d, *J* = 223.1 Hz), 159.4 (d, *J* = 218.5 Hz), 147.3, 142.7, 134.2 (d, *J* = 8.9 Hz), 131.9 (d, *J* = 8.0 Hz), 130.7 (d, *J* = 2.7 Hz), 130.0 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 15.7 Hz), 126.1 (d, *J* = 12.5 Hz), 124.4 (d, *J* = 3.5 Hz), 124.0 (d, *J* = 3.5 Hz), 116.7 (d, *J* = 23.5 Hz), 116.0 (d, *J* = 21.6 Hz), 46.8 (d, *J* = 6.5 Hz), 28.3, 26.7, 26.4, 17.7; IR (KBr, cm^{-1}): ν 2935, 2865, 1685, 1652, 1609, 1480, 1450, 1286, 1213, 1100, 757; HRMS (ESI) calcd for $C_{21}H_{19}F_2O_2$ ($[M+H]^+$) 341.1353, found: 341.1346. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 11.9 min (minor), 15.1 min (major).



5d

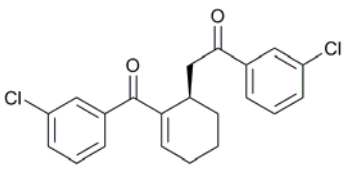
93% yield, 96% ee, $[\alpha]_D^{25}$ +21.0 (*c* 0.31, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05-7.98 (m, 2H), 7.68-7.60 (m, 2H), 7.09-6.99 (m, 4H), 6.55-6.49 (t, *J* = 3.6 Hz, 1H), 3.42-3.32 (m, 1H), 3.31-3.23 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.76-2.66 (m, 1H), 2.35-2.21 (m, 1H), 2.20-2.06 (m, 1H), 1.78-1.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 196.6, 166.6 (d, *J* = 78.7 Hz), 164.1 (d, *J* = 77.2 Hz), 144.7, 141.3, 134.8 (d, *J* = 3.0 Hz), 133.2 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 8.9 Hz), 131.1 (d, *J* = 9.1 Hz), 115.7 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.5 Hz), 42.42, 30.58, 26.57, 26.12, 18.15; IR (KBr, cm^{-1}): ν 2921, 2859, 1681, 1596, 1506, 1409, 1234, 1157, 850, 757; HRMS (ESI) calcd for $C_{21}H_{18}F_2O_2Na$ ($[M+Na]^+$) 363.1173, found: 363.1170. HPLC (AD-H

column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 12.7 min (minor), 16.6 min (major).



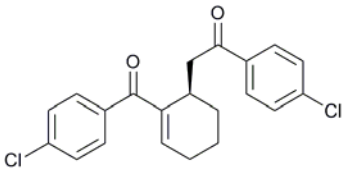
5e

99% yield, 93% ee, $[\alpha]_D^{25}$ +6.4 (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 1H), 7.44-7.22 (m, 7H), 6.58-6.54 (t, *J* = 4.0 Hz, 1H), 3.52-3.44 (m, 1H), 3.42-3.35 (dd, *J* = 16.8 Hz, 2.8 Hz, 1H), 3.04-2.93 (m, 1H), 2.34-2.12 (m, 2H), 1.89-1.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 196.2, 148.9, 141.8, 139.2, 139.1, 131.5, 131.0 (2), 130.6, 130.5, 129.8, 129.2, 128.7, 126.9, 126.5, 46.1, 28.5, 26.5, 26.3, 17.5; IR (KBr, cm^{-1}): ν 2921, 2856, 1696, 1655, 1630, 1589, 1469, 1434, 1284, 1245, 1049, 757; HRMS (ESI) calcd for $C_{21}H_{19}Cl_2O_2$ ($[M+H]^+$) 373.0762, found: 373.0763. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 14.7 min (minor), 17.8 min (major).



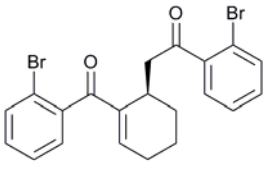
5f

93% yield, 95% ee, $[\alpha]_D^{25}$ +17.3 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.00 (t, *J* = 1.6 Hz, 1H), 7.99-7.94 (m, 1H), 7.64-7.61 (t, *J* = 1.6 Hz, 1H), 7.56-7.46 (m, 3H), 7.45-7.35 (m, 2H), 6.69-6.64 (m, 1H), 3.50-3.42 (m, 1H), 3.37-3.29 (dd, *J* = 15.2 Hz, 3.2 Hz, 1H), 2.90-2.81 (m, 1H), 2.43-2.32 (m, 1H), 2.29-2.18 (m, 1H), 1.78-1.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 196.4, 146.3, 141.1, 140.4, 138.3, 135.0, 134.3, 133.0, 131.6, 130.0, 129.5, 129.1, 128.5, 127.3, 126.6, 42.5, 30.1, 26.5, 26.3, 18.0; IR (KBr, cm^{-1}): ν 2931, 2864, 1682, 1642, 1566, 1419, 1249, 1075, 996, 774; HRMS (ESI) calcd for $C_{21}H_{19}Cl_2O_2$ ($[M+H]^+$) 373.0762, found: 373.0753. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 9.0 min (minor), 9.8 min (major).



5g

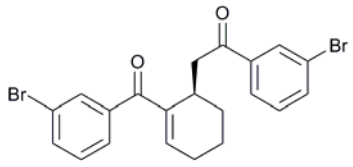
98% yield, 93% ee, $[\alpha]_D^{30}$ +14.2 (*c* 2.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.90 (dt, *J* = 8.8 Hz, 2.0 Hz, 2H), 7.59-7.52 (dt, *J* = 8.4 Hz, 2.4 Hz, 2H), 7.40-7.31 (m, 4H), 6.57-6.51 (t, *J* = 3.6 Hz, 1H), 3.42-3.31 (m, 1H), 3.31-3.21 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.78-2.67 (m, 1H), 2.36-2.22 (m, 1H), 2.22-2.08 (m, 1H), 1.74-1.51 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 16.3 min (minor), 20.7 min (major).



5h

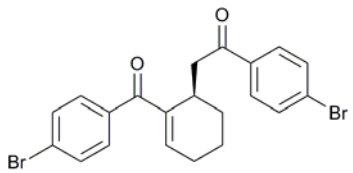
95% yield, 90% ee, $[\alpha]_D^{12}$ +10.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.44 (m, 3H), 7.36-7.11 (m, 5H), 6.51-6.45 (t, *J* = 3.6 Hz, 1H), 3.45-3.29 (m, 2H), 2.94-2.84 (m, 1H), 2.27-2.04 (m, 2H), 1.86-1.55 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 196.8, 149.3, 141.4, 141.2, 141.1, 133.8, 132.9, 131.5, 130.6, 128.9, 128.6, 127.5, 127.0, 119.5, 118.9, 45.8, 28.4, 26.6, 26.3, 17.5; IR (KBr, cm^{-1}): ν 2931, 2861, 1697, 1653, 1631, 1429, 1285, 1245, 1072, 1026, 757; HRMS (ESI) calcd for $C_{21}H_{18}Br_2O_2Na$ ($[M+Na]^+$) 482.9571, found: 482.9567. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 20.3 min (minor), 24.6 min (major).



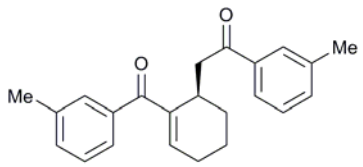
5i

90% yield, 93% ee, $[\alpha]_D^{25}$ +11.1 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.63-7.53 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.32-7.20 (m, 2H), 6.61-6.55 (t, *J* = 3.6 Hz, 1H), 3.43-3.32 (d, *J* = 6.0 Hz, 1H), 3.29-3.19 (dd, *J* = 15.2 Hz, 3.2 Hz, 1H), 2.83-2.71 (m, 1H), 2.36-2.21 (m, 1H), 2.21-2.08 (m, 1H), 1.74-1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 196.2, 146.3, 141.1, 140.6, 138.5, 135.9, 134.5, 132.0, 131.4, 130.3, 129.8, 127.8, 127.1, 123.0, 122.4, 42.4, 30.1, 26.6, 26.3, 18.0; IR (KBr, cm^{-1}): ν 2933, 2871, 1681, 1633, 1565, 1403, 1247, 1070, 997; HRMS (ESI) calcd for $C_{21}H_{18}Br_2O_2Na$ ($[M+Na]^+$) 482.9571, found: 482.9577. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 9.8 min (minor), 11.0 min (major).



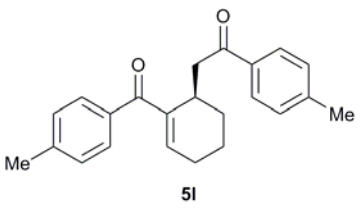
5j

91% yield, 90% ee, $[\alpha]_D^{11}$ -9.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.57-7.43 (m, 6H), 6.57-6.51 (t, *J* = 3.6 Hz, 1H), 3.40-3.31 (m, 1H), 3.29-3.21 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.78-2.67 (m, 1H), 2.34-2.21 (m, 1H), 2.20-2.07 (m, 1H), 1.74-1.51 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 17.9 min (minor), 22.6 min (major).



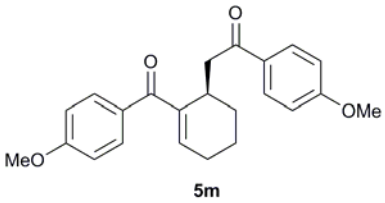
5k

72% yield, 99% ee, $[\alpha]_D^{25}$ +28.6 (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.75 (m, 2H), 7.43-7.34 (m, 2H), 7.30-7.19 (m, 4H), 6.56-6.50 (t, *J* = 3.6 Hz, 1H), 3.46-3.36 (m, 1H), 3.34-3.26 (dd, *J* = 15.2 Hz, 3.2 Hz, 1H), 2.76-2.66 (m, 1H), 2.32 (s, 6H), 2.30-2.20 (m, 1H), 2.18-2.05 (m, 1H), 1.76-1.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 198.3, 144.7, 141.7, 138.9, 138.3, 138.0, 136.8, 133.7, 132.4, 129.6, 128.9, 128.5, 127.9, 126.5, 125.8, 42.6, 30.4, 26.5, 26.1, 21.4, 18.2; IR (KBr, cm^{-1}): ν 2933, 2865, 1668, 1633, 1402, 1276, 1186, 786, 752, 692; HRMS (ESI) calcd for $C_{23}H_{24}O_2Na$ ($[M+Na]^+$) 355.1674, found: 355.1668. HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 10.8 min (minor), 12.9 min (major).



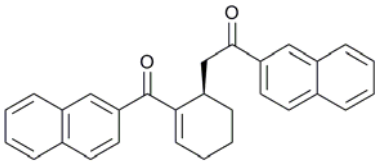
5l

(Table 3, entry 13) 85% yield, 99% ee, $[\alpha]_D^{25}$ +10.0 (*c* 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.22-7.12 (m, 4H), 6.54-6.47 (t, *J* = 3.6 Hz, 1H), 3.46-3.36 (m, 1H), 3.36-3.25 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.73-2.62 (m, 1H), 2.33 (s, 3H), 2.32(s, 3H), 2.29-2.19 (m, 1H), 2.18-2.05 (m, 1H), 1.77-1.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 197.9, 143.8, 143.7, 142.4, 141.6, 136.0, 134.3, 129.5, 129.3, 128.8, 128.6, 42.5, 30.7, 26.6, 26.1, 21.7, 21.6, 18.2; IR (KBr, cm^{-1}): ν 2926, 2864, 1679, 1643, 1605, 1448, 1407, 1270, 1180, 808, 750; HRMS (ESI) calcd for $C_{23}H_{24}O_2Na$ ($[M+Na]^+$) 355.1674, found: 355.1678. HPLC (AS-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 9.8 min (minor), 10.6 min (major).



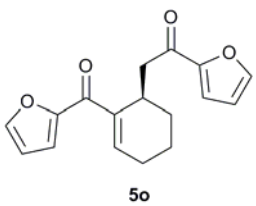
5m

64% yield, 99% ee, $[\alpha]_D^{30}$ -5.6 (*c* 1.59, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07-8.02 (m, 2H), 7.76-7.71 (m, 2H), 6.97-6.91 (m, 4H), 6.55-6.51 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.50-3.42 (m, 1H), 3.37-3.30 (dd, *J* = 14.4 Hz, 3.2 Hz, 1H), 2.73-2.65 (m, 1H), 2.39-2.27 (m, 1H), 2.25-2.13 (m, 1H), 1.82-1.57 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 41.8 min (minor), 59.6 min (major).



5n

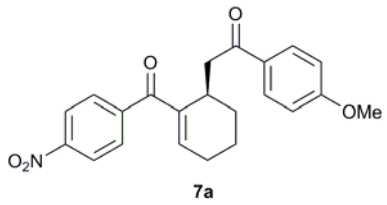
91% yield, 96% ee, $[\alpha]_D^{25}$ -25.5 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.19 (s, 1H), 8.13-8.08 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.91-7.80 (m, 5H), 7.61-7.48 (m, 4H), 6.73-6.67 (t, *J* = 3.6 Hz, 1H), 3.70-3.56 (m, 2H), 3.03-2.93 (m, 1H), 2.45-2.32 (m, 1H), 2.29-2.15 (m, 1H), 1.90-1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 198.1, 144.9, 141.8, 136.1, 135.6, 134.9, 134.1, 132.7, 132.3, 130.5, 130.3, 129.8, 129.2, 128.4 (2), 128.2, 127.9, 127.8, 127.7, 126.7, 126.6, 125.7, 124.2, 42.8, 30.9, 26.7, 26.3, 18.3; HRMS (ESI) calcd for $C_{29}H_{24}O_2Na$ ($[M+Na]^+$) 427.1674, found: 427.1665. HPLC (AS-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 13.5 min (major), 18.3 min (minor).



5o

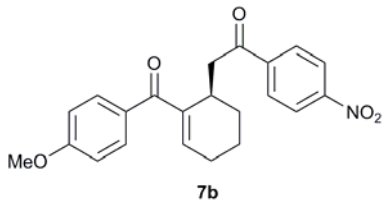
74% yield, 96% ee, $[\alpha]_D^{25}$ -9.5 (*c* 0.37, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.49 (s, 1H), 7.32 (s, 1H), 7.04 (s, 1H), 6.92 (s, 1H), 6.45 (s, 2H), 3.38 (m, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.67-2.53 (m, 1H), 2.37-2.10 (m, 2H), 1.76-1.47 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 90/10, flow rate: 1.0 mL/min): t_R = 22.7 min (minor),

34.2 min (major).



7a

71% ee, $[\alpha]_D^{30}$ -3.3 (*c* 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.34-8.29 (m, 2H), 8.25-8.20 (m, 2H), 7.74-7.69 (m, 2H), 6.97-6.92 (m, 2H), 6.64-6.54 (m, 1H), 3.88 (s, 3H), 3.48-3.40 (m, 2H), 2.87-2.78 (m, 1H), 2.42-2.30 (m, 1H), 2.28-2.18 (m, 1H), 1.81-1.62 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 85/15, flow rate: 0.9 mL/min): t_R = 43.1 min (minor), 54.5 min (major).



7b

87% ee, $[\alpha]_D^{28}$ -4.1 (*c* 0.26, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.31-8.26 (m, 2H), 8.07-8.02 (m, 2H), 7.83-7.78 (m, 2H), 6.98-6.92 (m, 2H), 6.63-6.58 (t, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), 3.51-3.42 (m, 1H), 3.35-3.28 (dd, *J* = 14.8 Hz, 3.6 Hz, 1H), 2.92-2.83 (m, 1H), 2.45-2.32 (m, 1H), 2.30-2.17 (m, 1H), 1.84-1.60 (m, 4H). HPLC (AD-H column, λ = 254 nm, eluent: hexane/2-propanol = 85/15, flow rate: 0.9 mL/min): t_R = 59.7 min (minor), 63.8 min (major).

5. References

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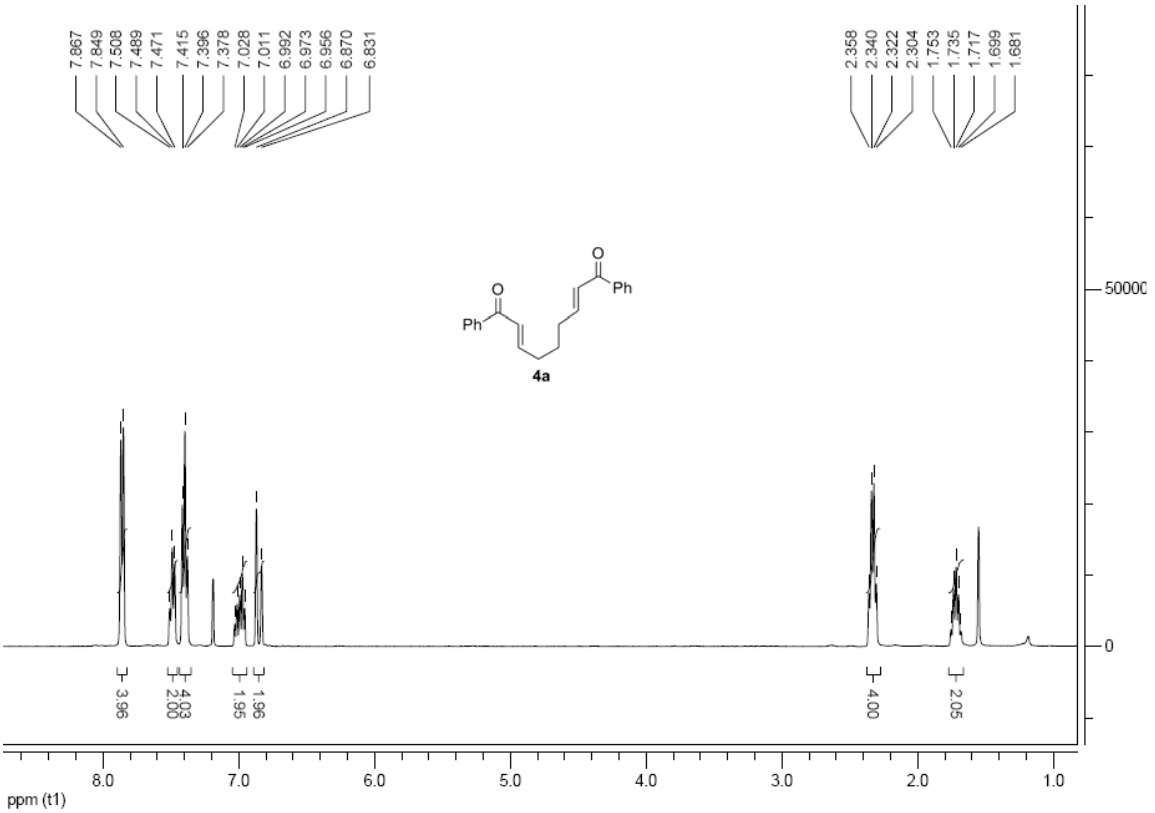
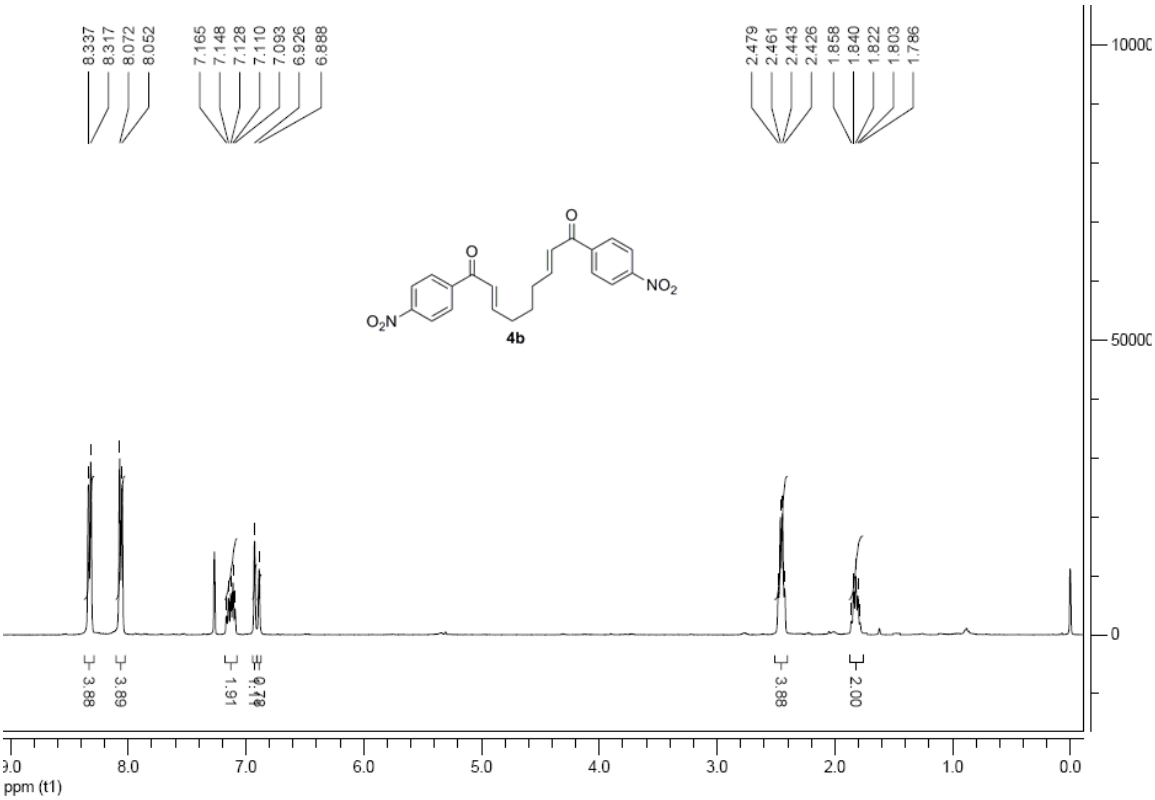
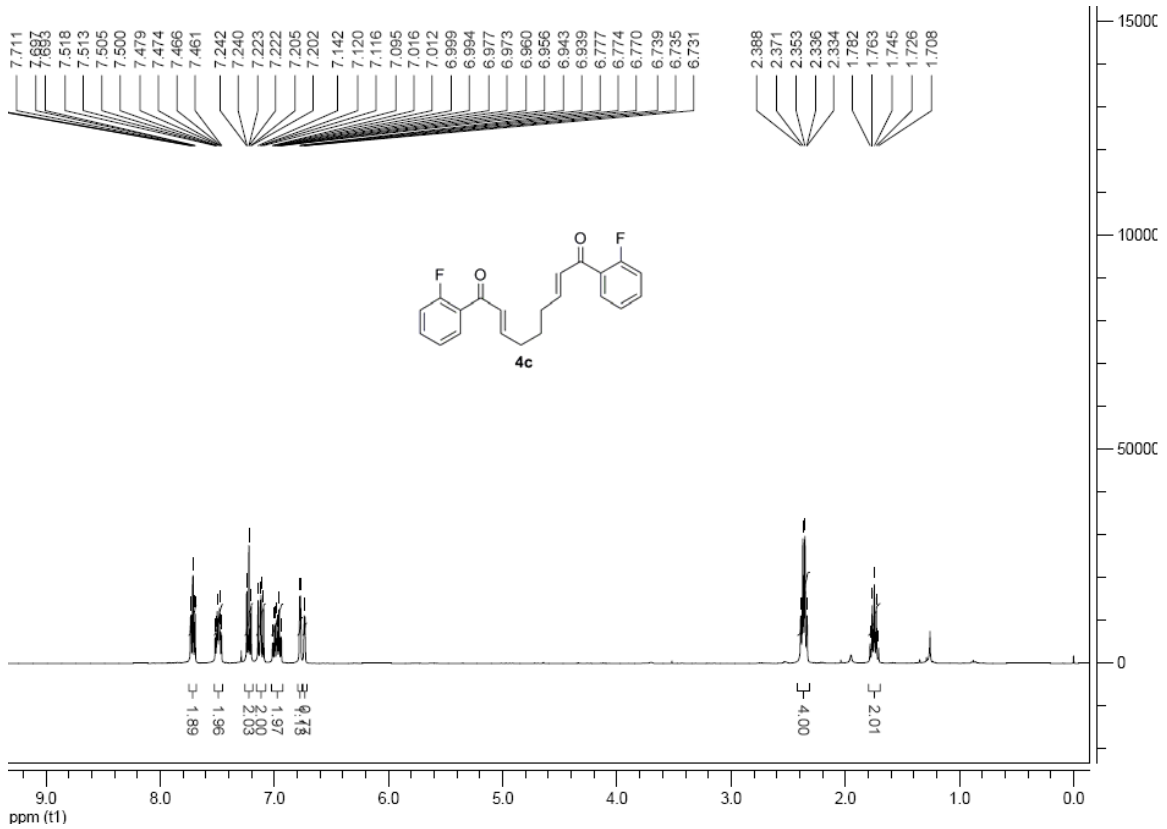
6. ^{1}H NMR and ^{13}C NMR Spectra of the Substrates and the RC Products



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7.461
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7.240
7.223
7.222
7.205
7.202
7.142
7.120
7.116
7.095
7.016
7.012
6.999
6.994
6.977
6.973
6.960
6.956
6.943
6.939
6.777
6.774
6.770
6.739
6.735
6.731
2.388
2.371
2.353
2.336
2.334
1.782
1.763
1.745
1.726
1.708
F
O
O
F
4c
1.89
1.96
2.00
1.97
9.73
4.00
2.01
9.0
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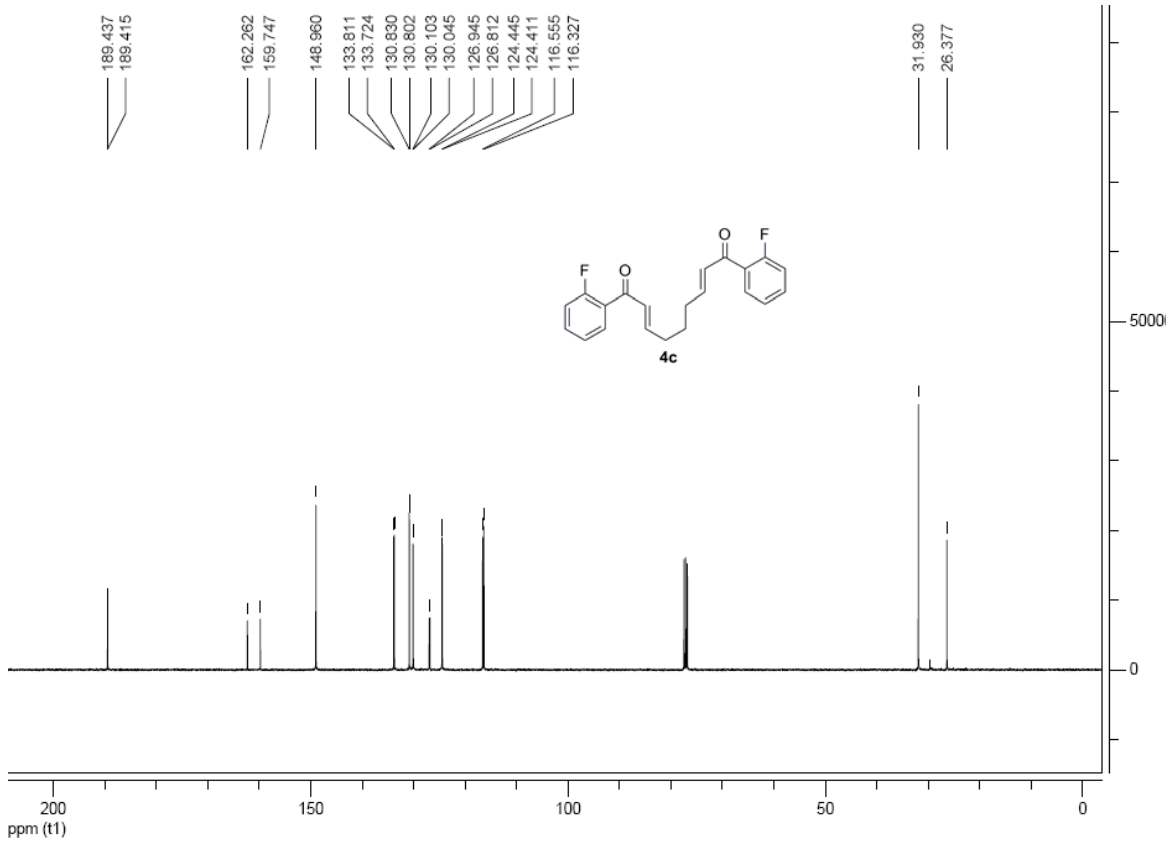
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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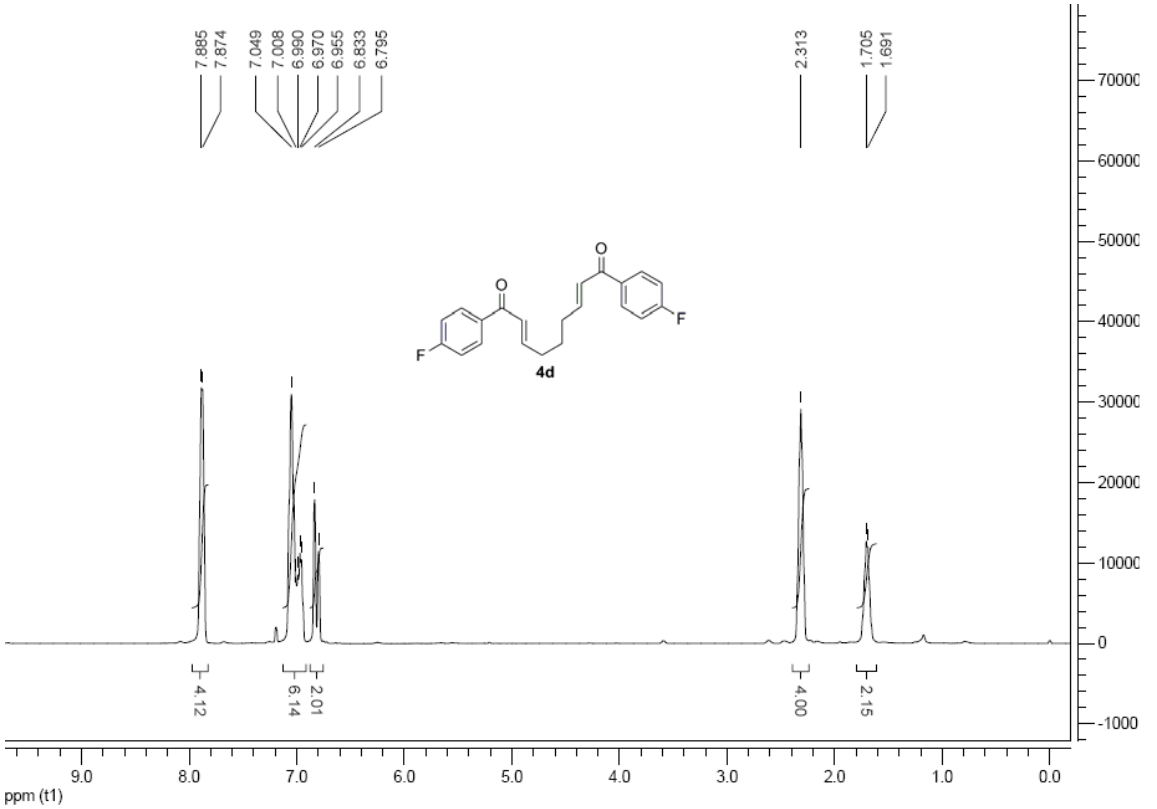
159.747
148.960
133.811
133.724
130.830
130.802
130.103
130.045
126.945
126.812
124.445
124.411
116.555
116.327
31.930
26.377
F
O
O
F
4c
200
150
100
50
0
ppm (t1)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7.874
7.049
7.008
6.990
6.970
6.955
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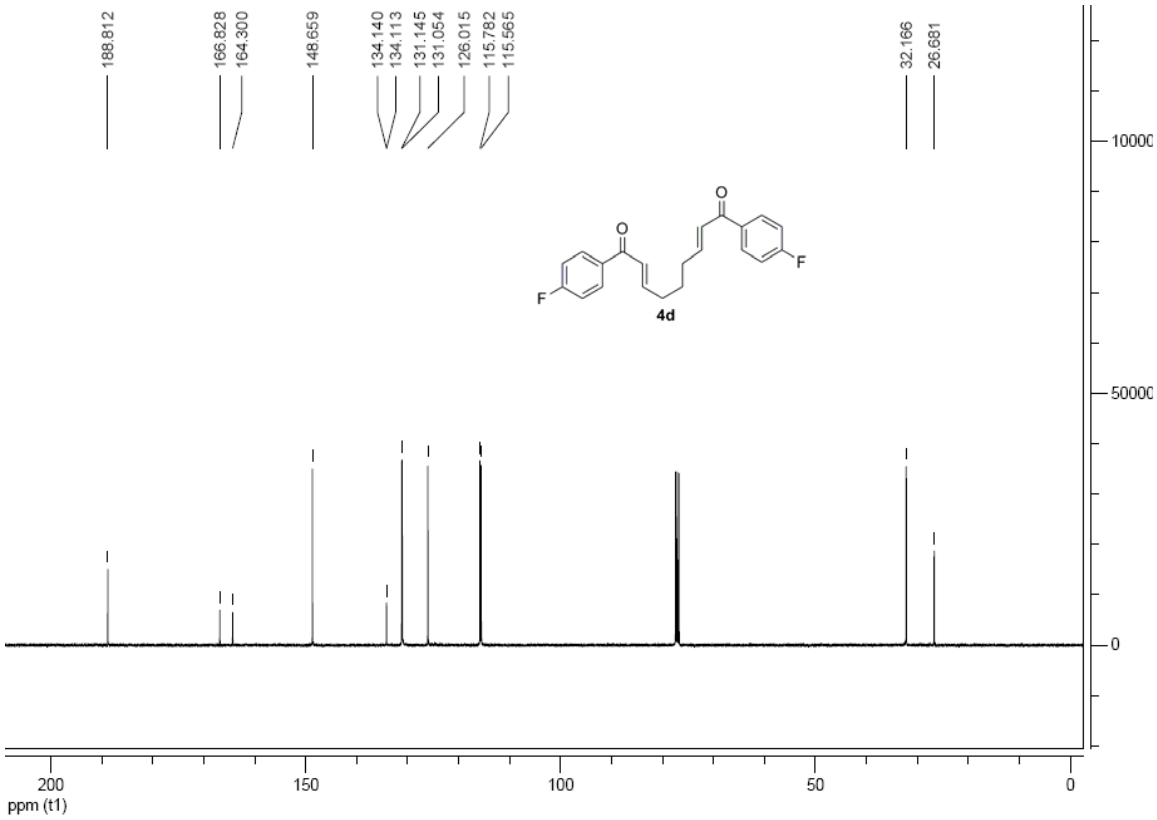
1.705
1.691
4d
4.12
9.14
2.01
4.00
2.15
ppm (t1)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166.828
164.300
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134.140
134.113
131.145
131.054
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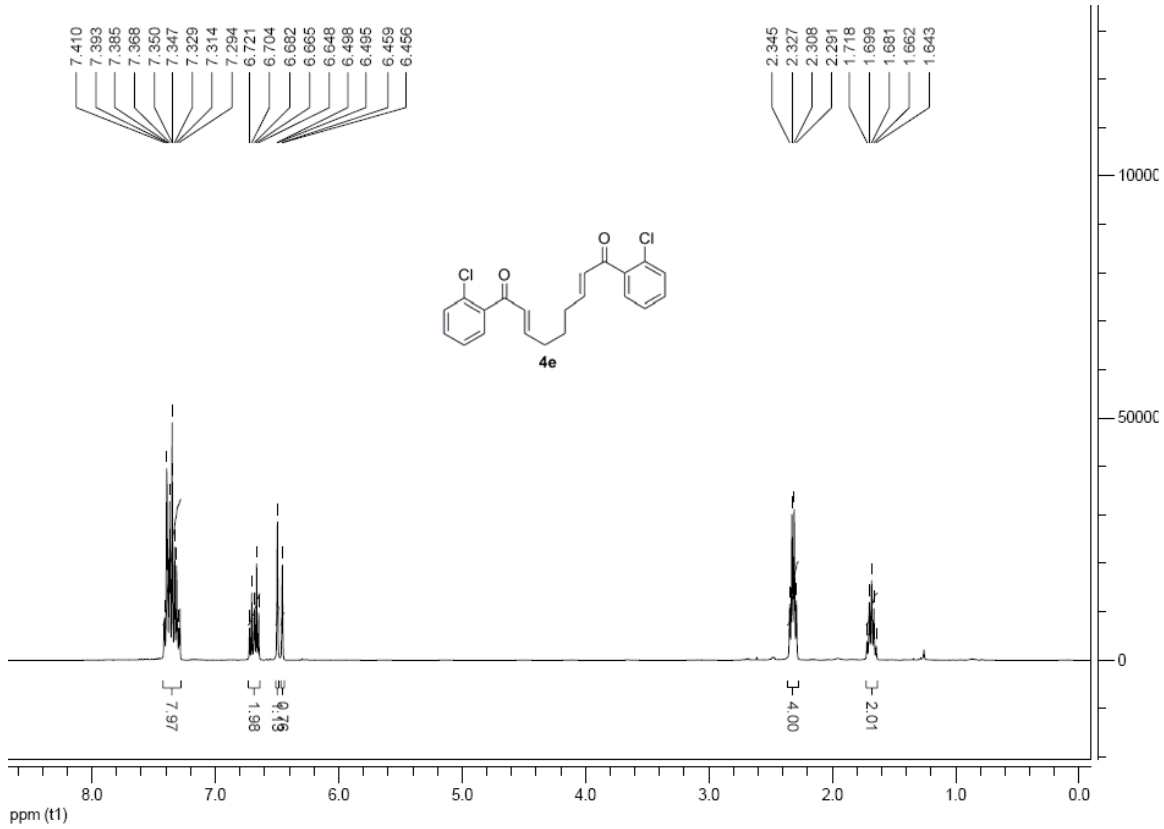
115.782
115.565
32.166
26.681
4d
ppm (t1)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7.329
7.314
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6.704
6.682
6.665
6.648
6.498
6.495
6.459
6.456
2.345
2.327
2.308
2.291
1.718
1.699
1.681
1.662
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Cl
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O
Cl
4e
7.97
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0.76
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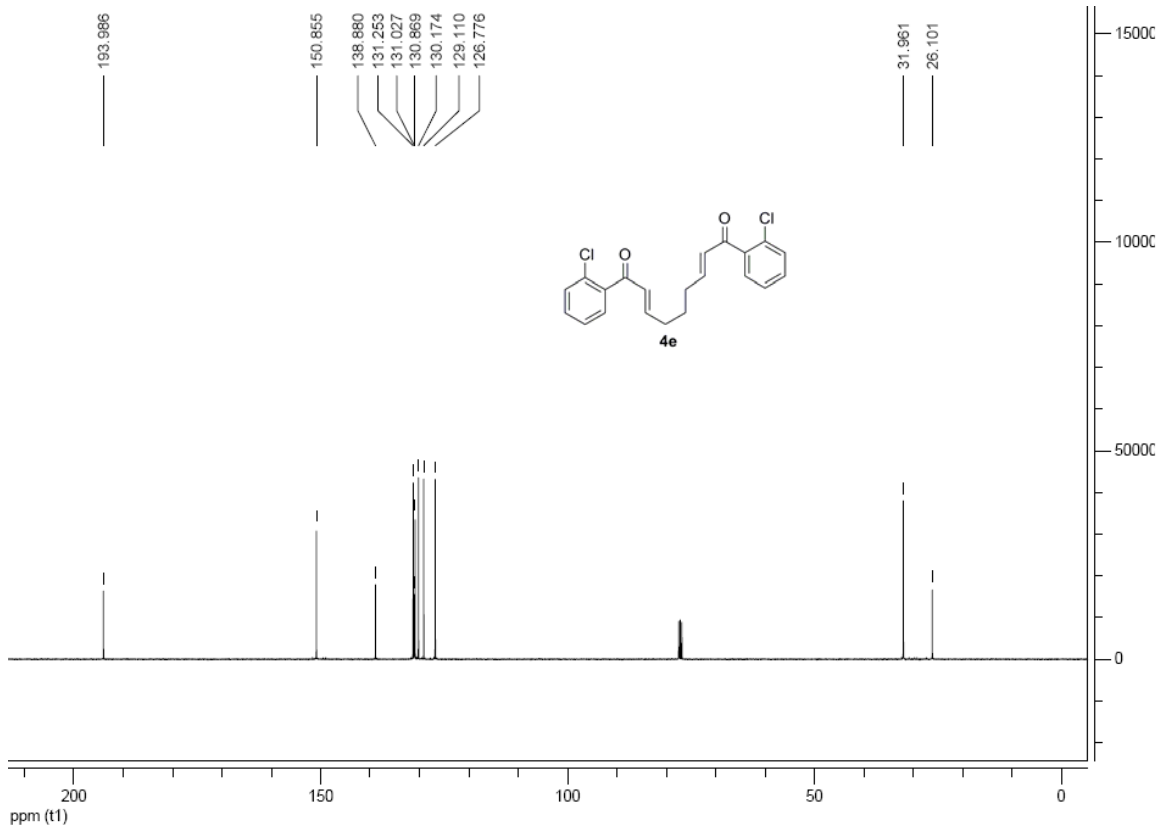
2.01
ppm (t1)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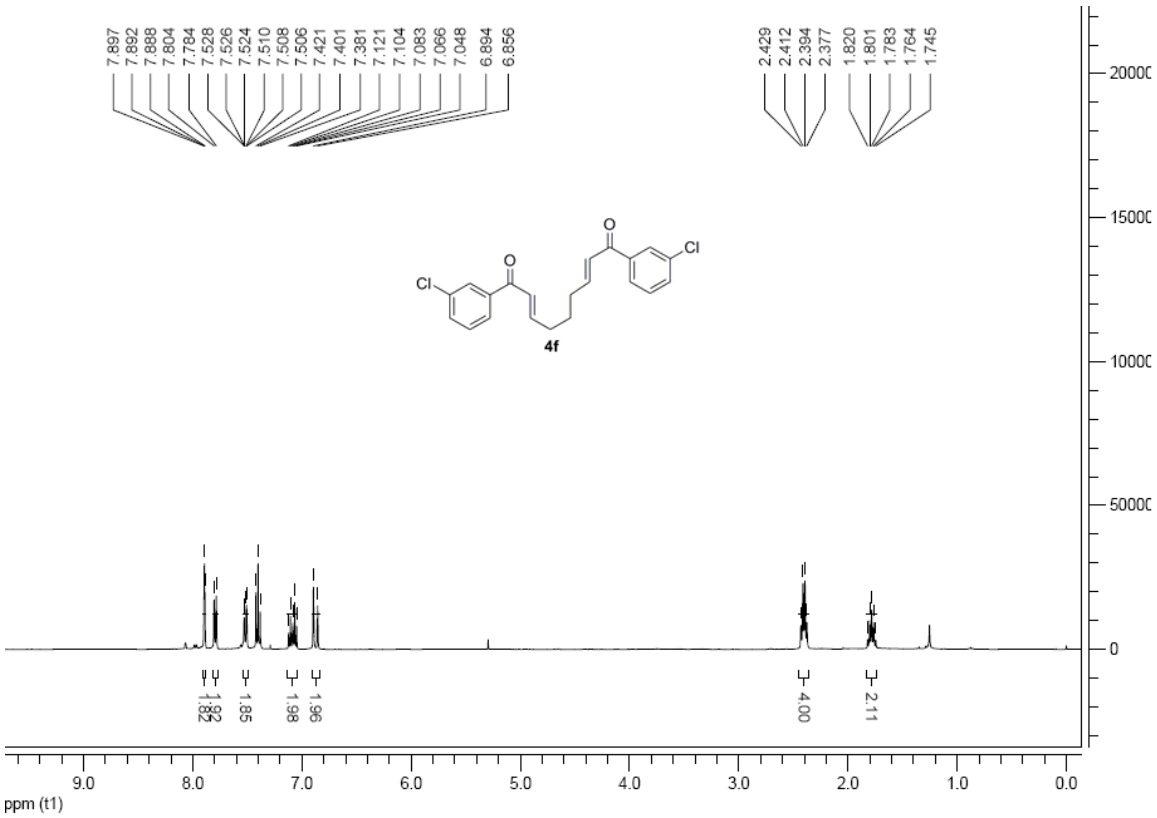
Cl
4e
ppm (t1)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7.892
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7.526
7.524
7.510
7.508
7.506
7.421
7.401
7.381
7.121
7.104
7.083
7.066
7.048
6.894
6.856
2.429
2.412
2.394
2.377
1.820
1.801
1.783
1.764
1.745
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O
Cl
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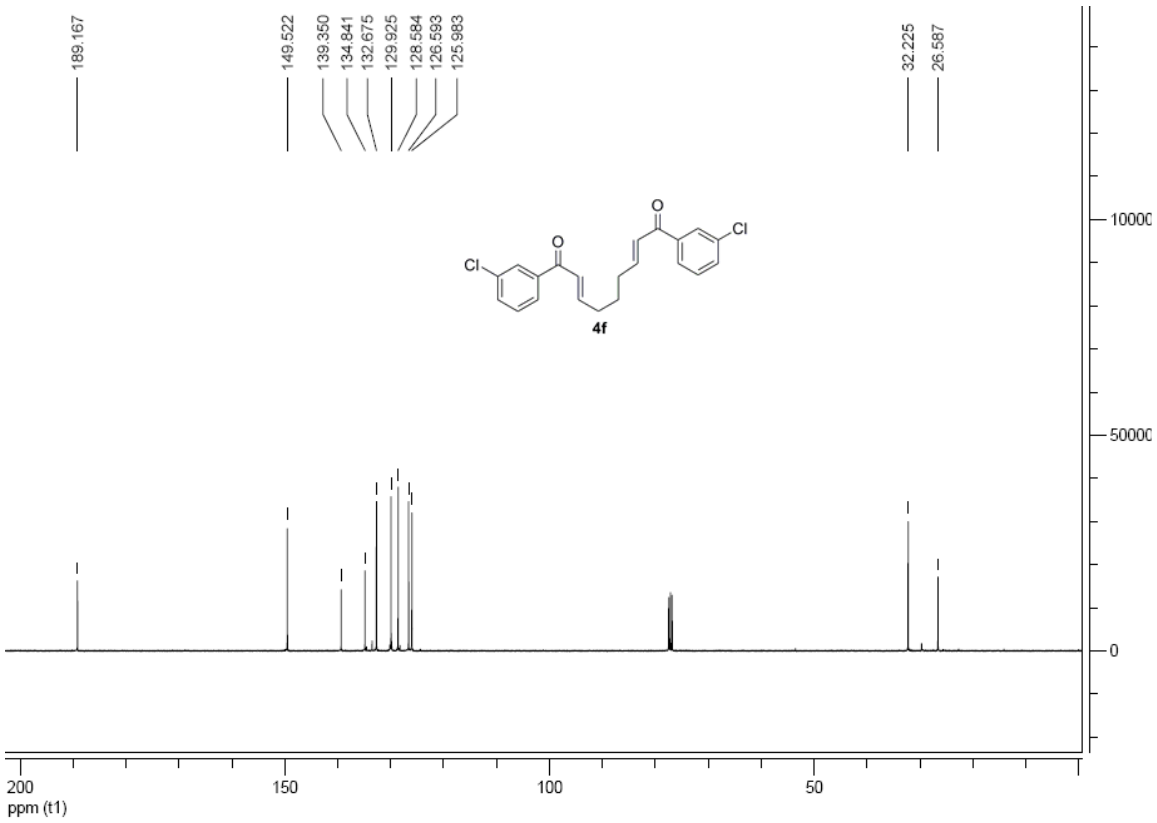
4.00
2.11
ppm (t1)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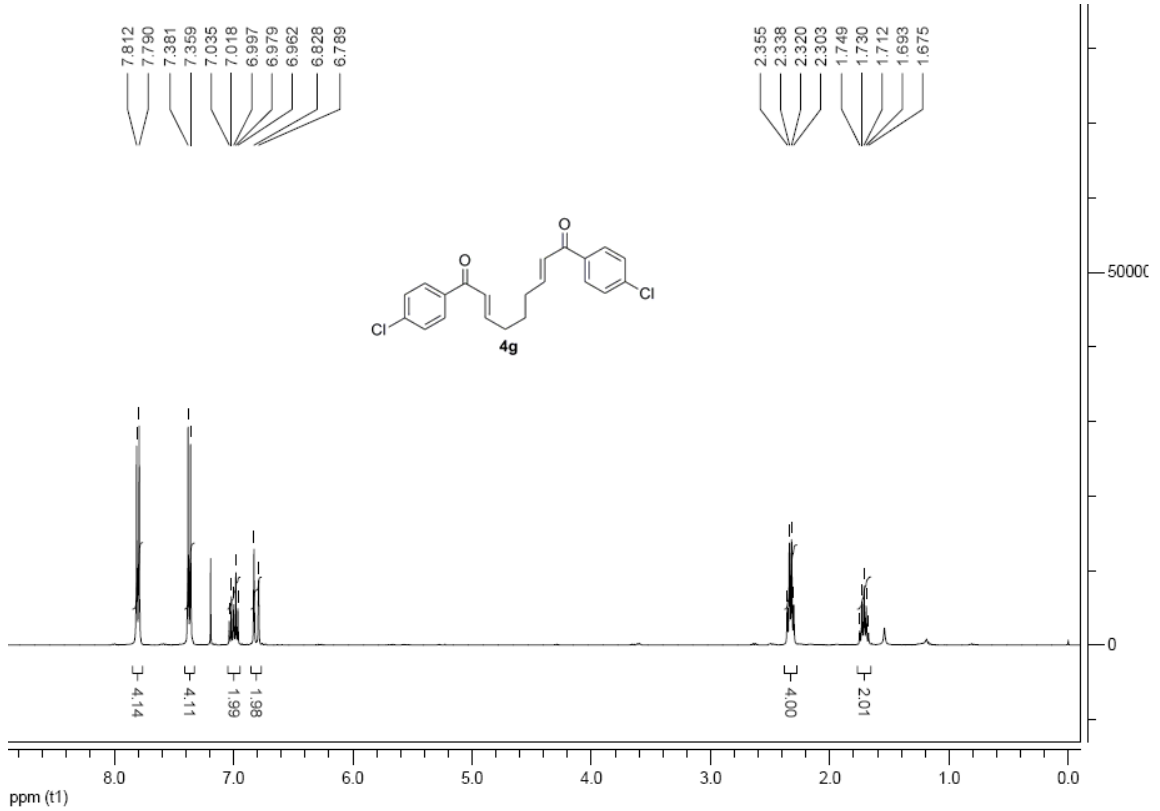
Cl
4f
ppm (t1)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6.789
2.355
2.338
2.320
2.303
1.749
1.730
1.712
1.693
1.675
Cl
Cl
4g
50000
0
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4.11
1.99
1.98
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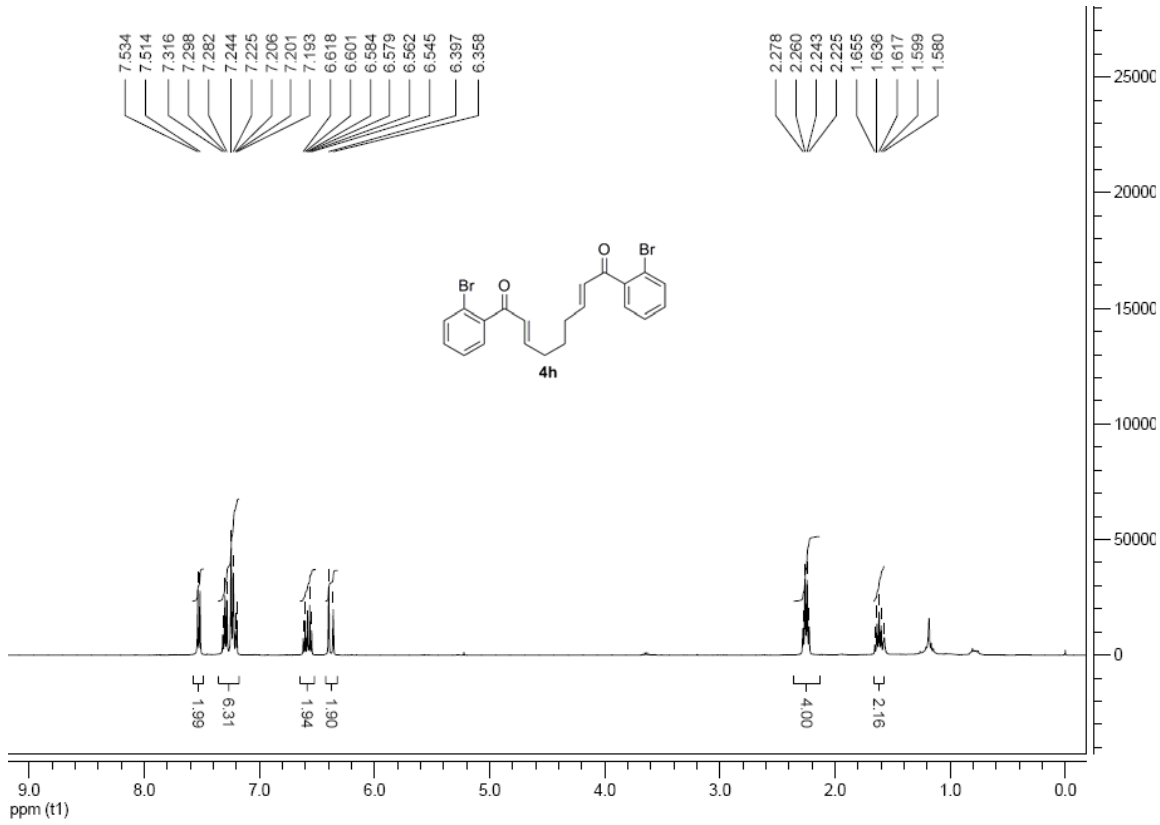
ppm (t1)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6.584
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6.562
6.545
6.397
6.358
2.278
2.260
2.243
2.225
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1.636
1.617
1.599
1.580
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Br
4h
25000
20000
15000
10000
50000
0
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1.94
1.90
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7.0
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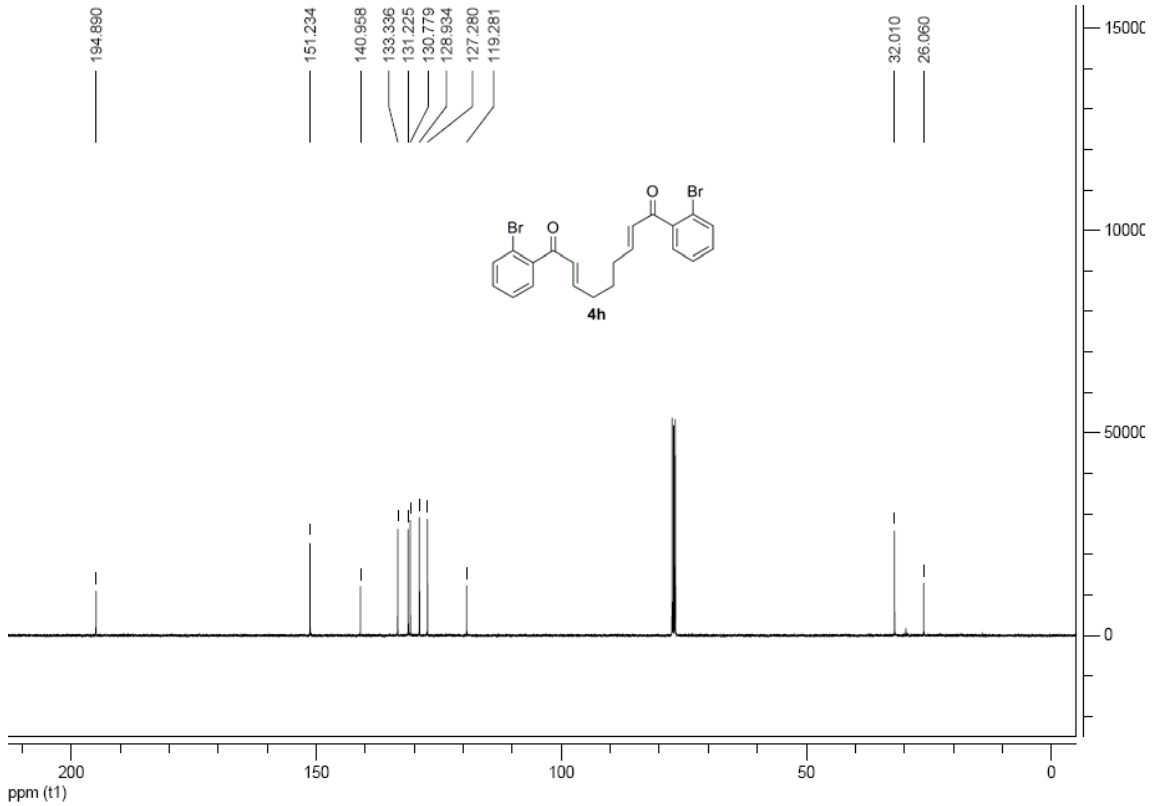
ppm (t1)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50
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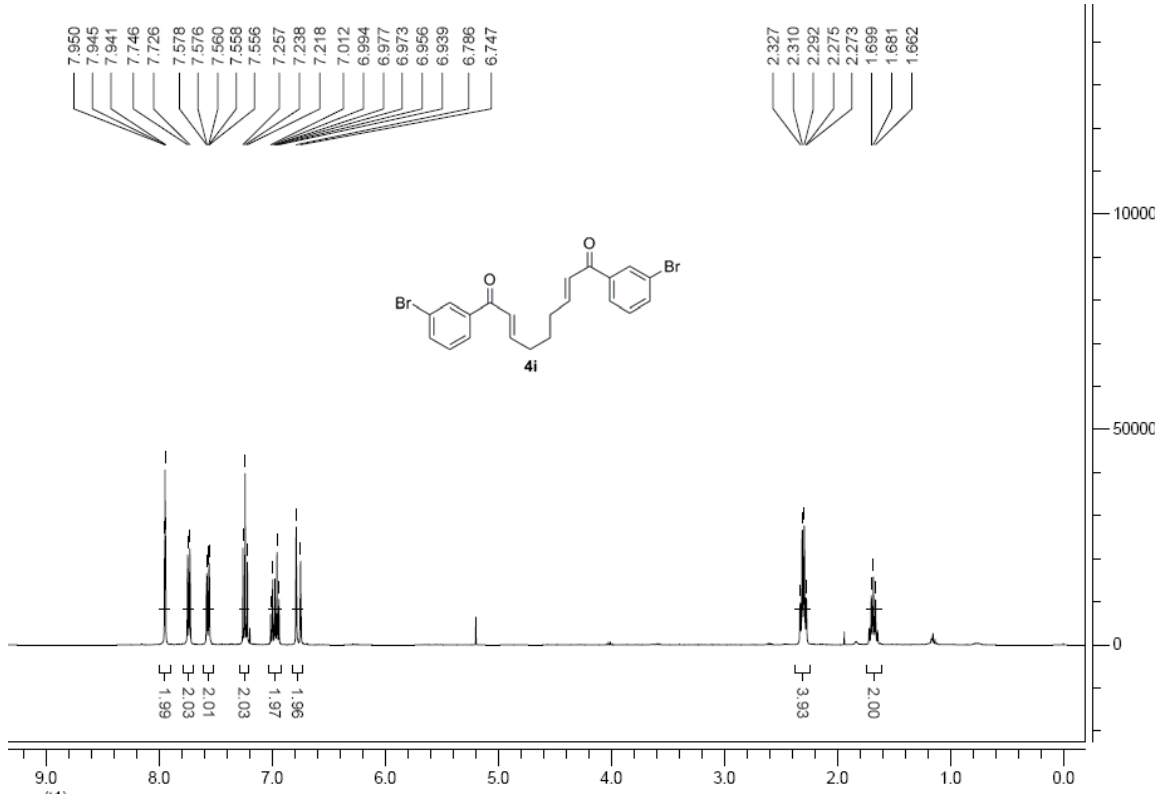
ppm (t1)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7.238
7.218
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6.977
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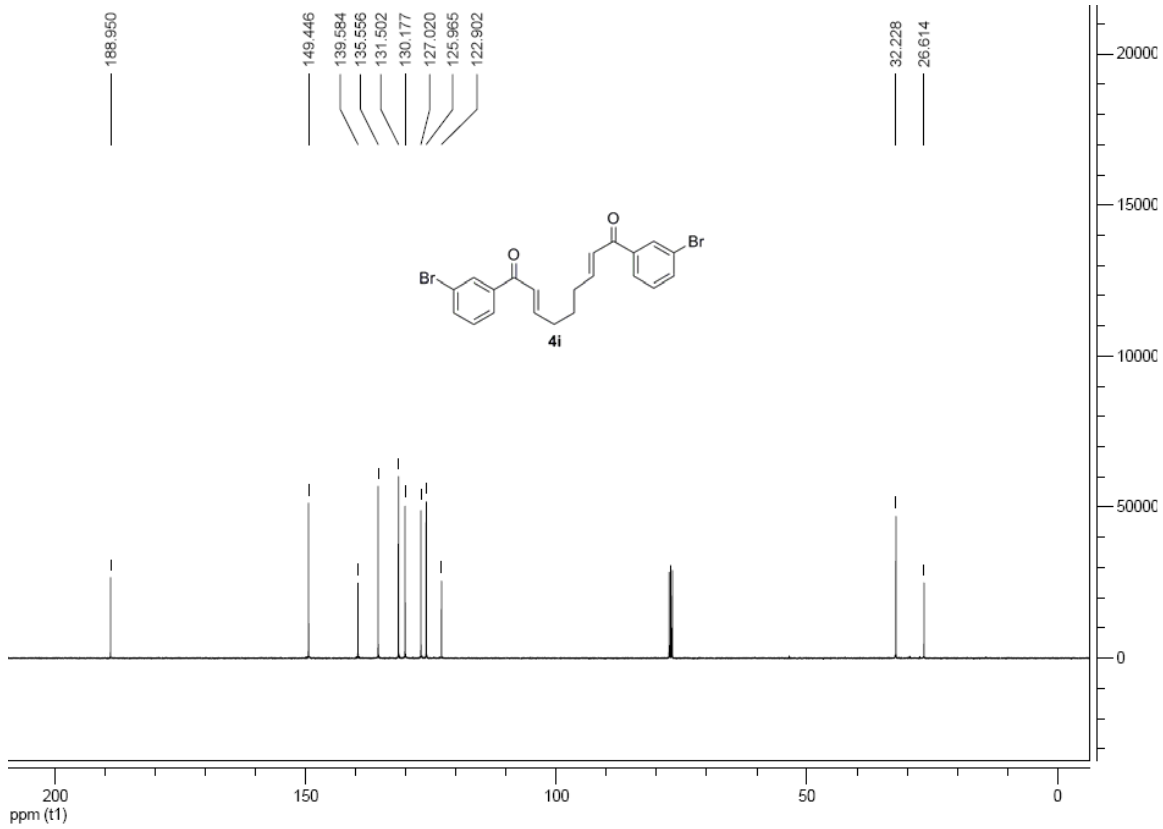
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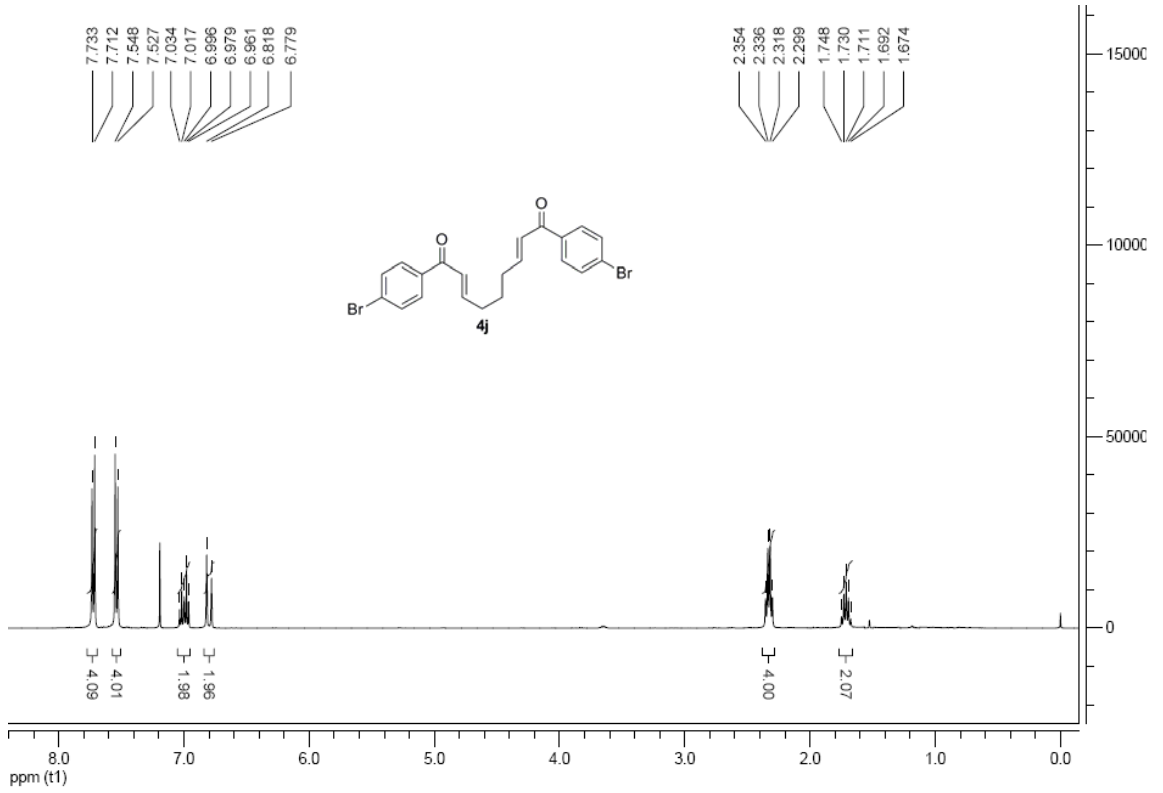
ppm (t1)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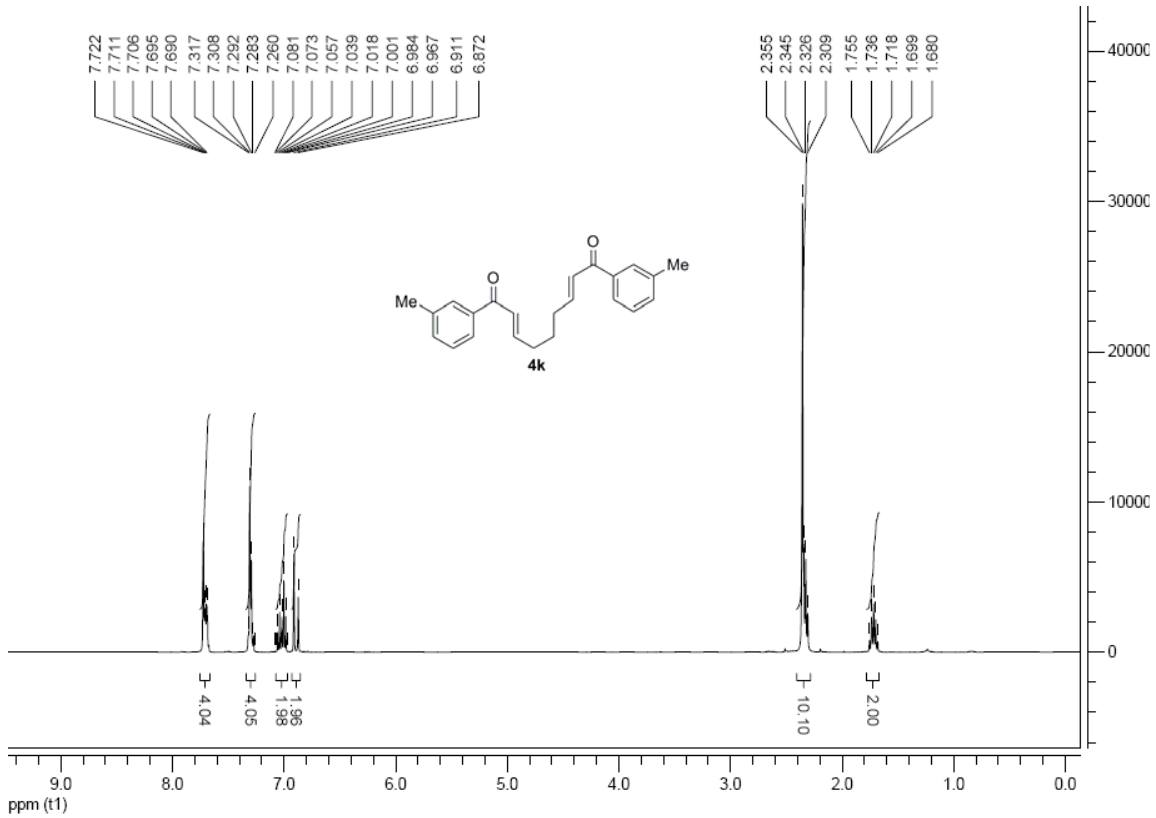
ppm (t1)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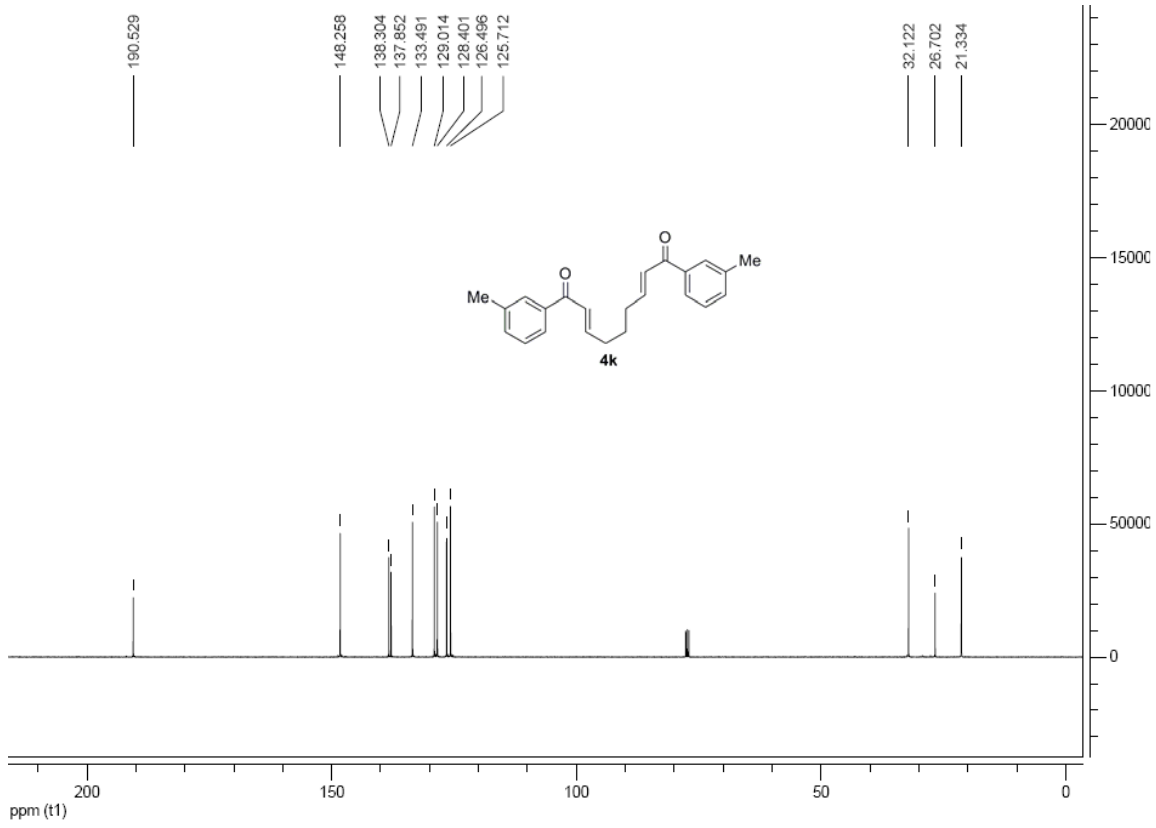
ppm (t1)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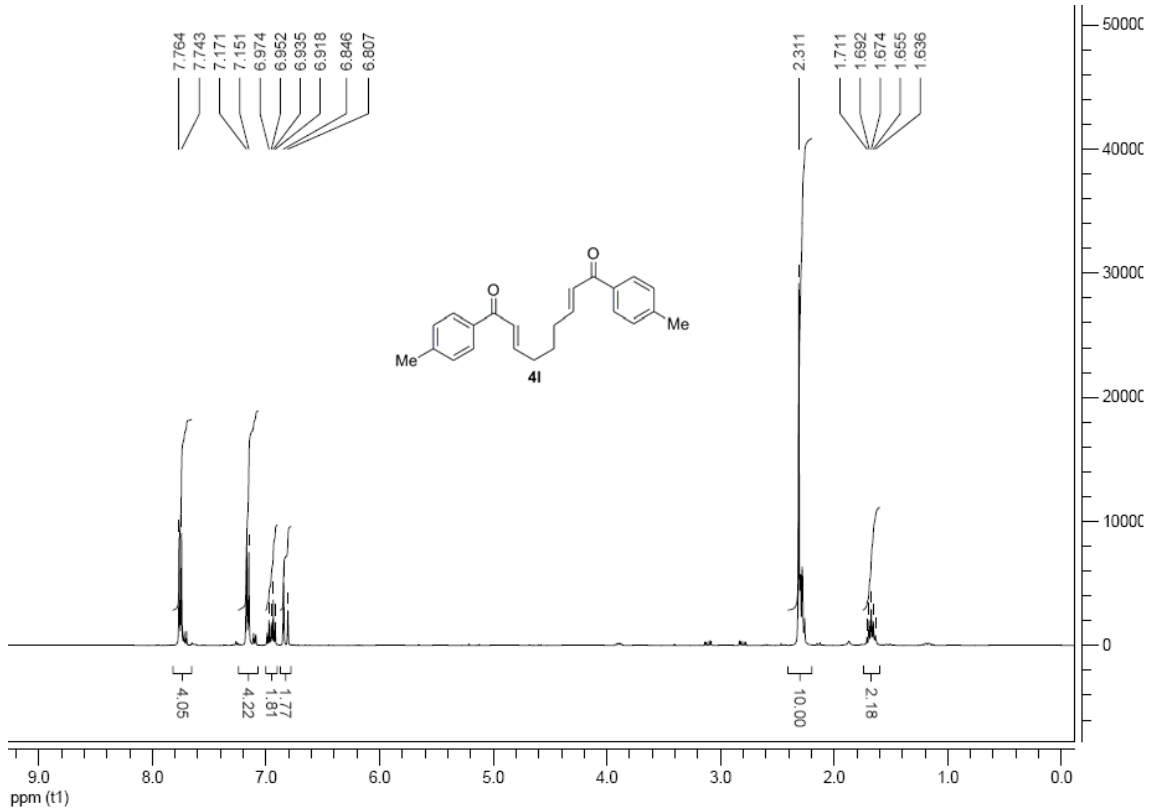
ppm (t1)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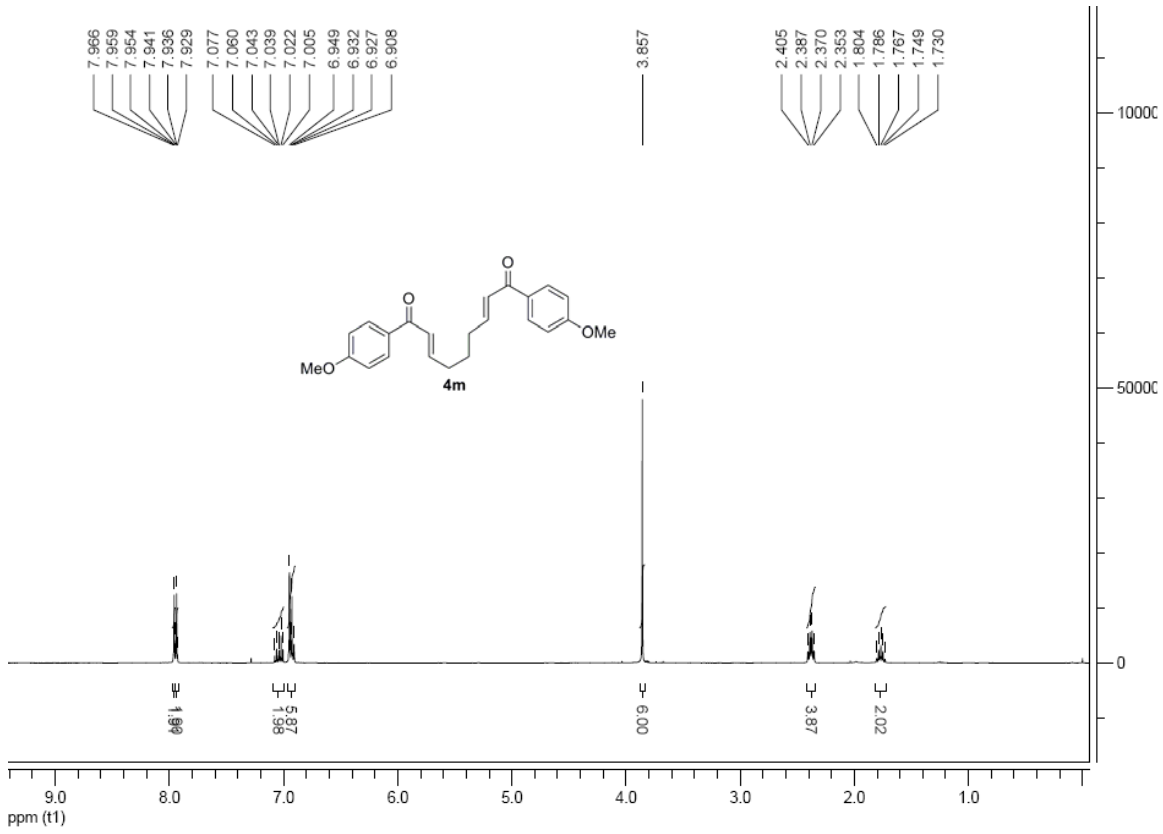
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OMe
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6.00
3.87
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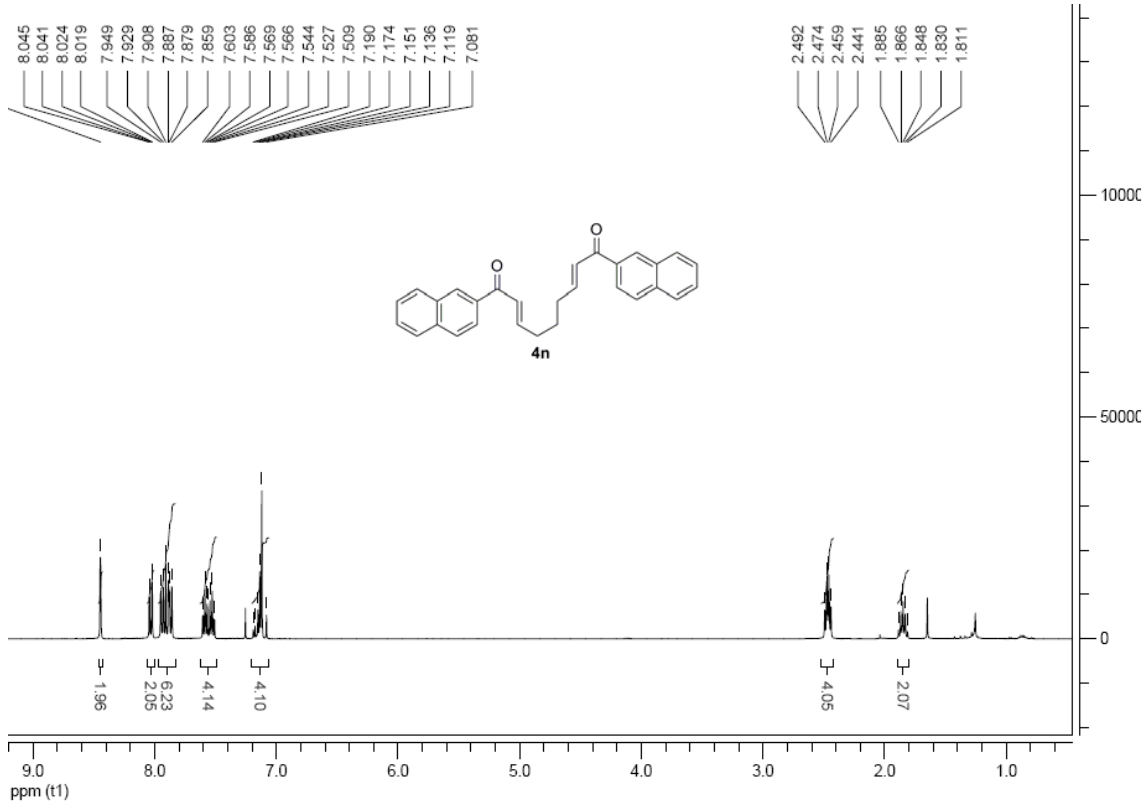
ppm (t1)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7.569
7.566
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7.527
7.509
7.190
7.174
7.151
7.136
7.119
7.081
2.492
2.474
2.459
2.441
1.885
1.866
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4n
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6.23
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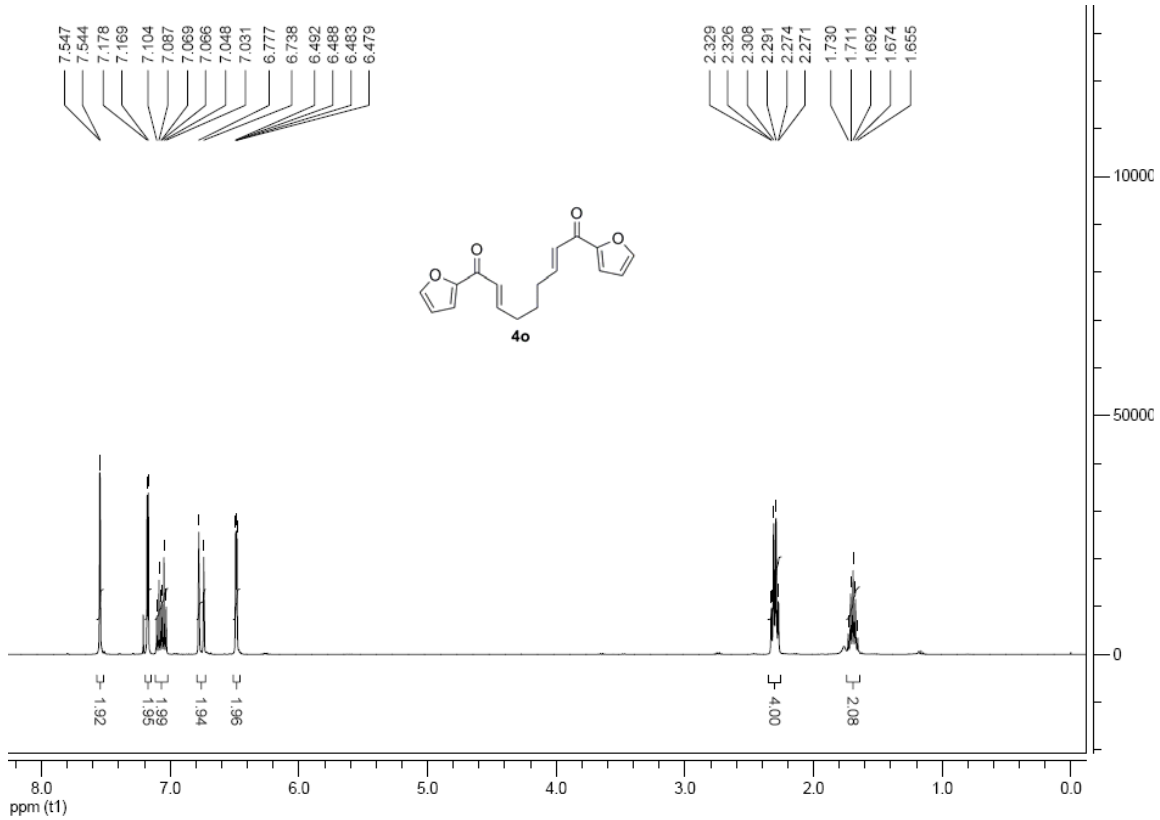
4.10
4.05
2.07
ppm (t1)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7.066
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6.492
6.488
6.483
6.479
2.329
2.326
2.308
2.291
2.274
2.271
1.730
1.711
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1.96
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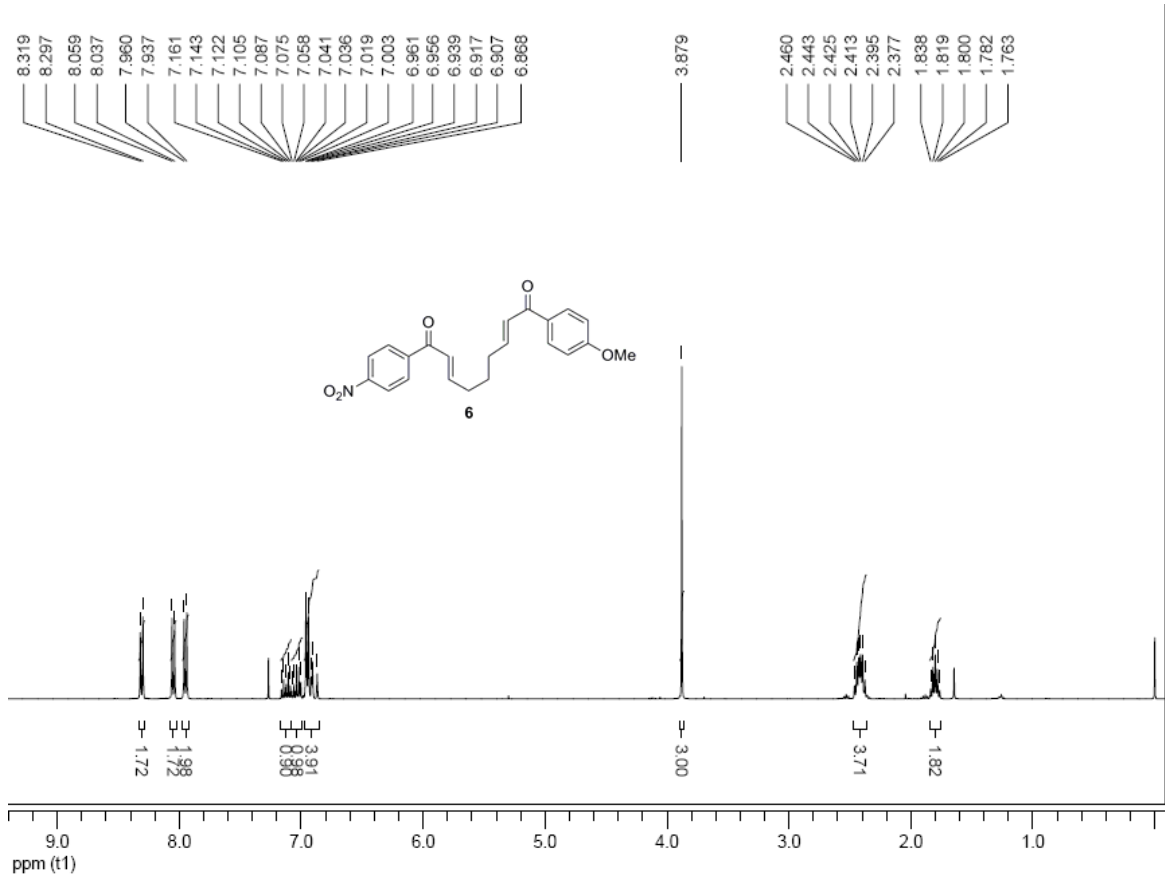
2.08
ppm (t1)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7.058
7.041
7.036
7.019
7.003
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6.956
6.939
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6.907
6.868
3.879
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2.443
2.425
2.413
2.395
2.377
1.838
1.819
1.800
1.782
1.763
O
O
OMe
O2N
6
1.72
1.98
1.72
3.91
3.00
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3.0
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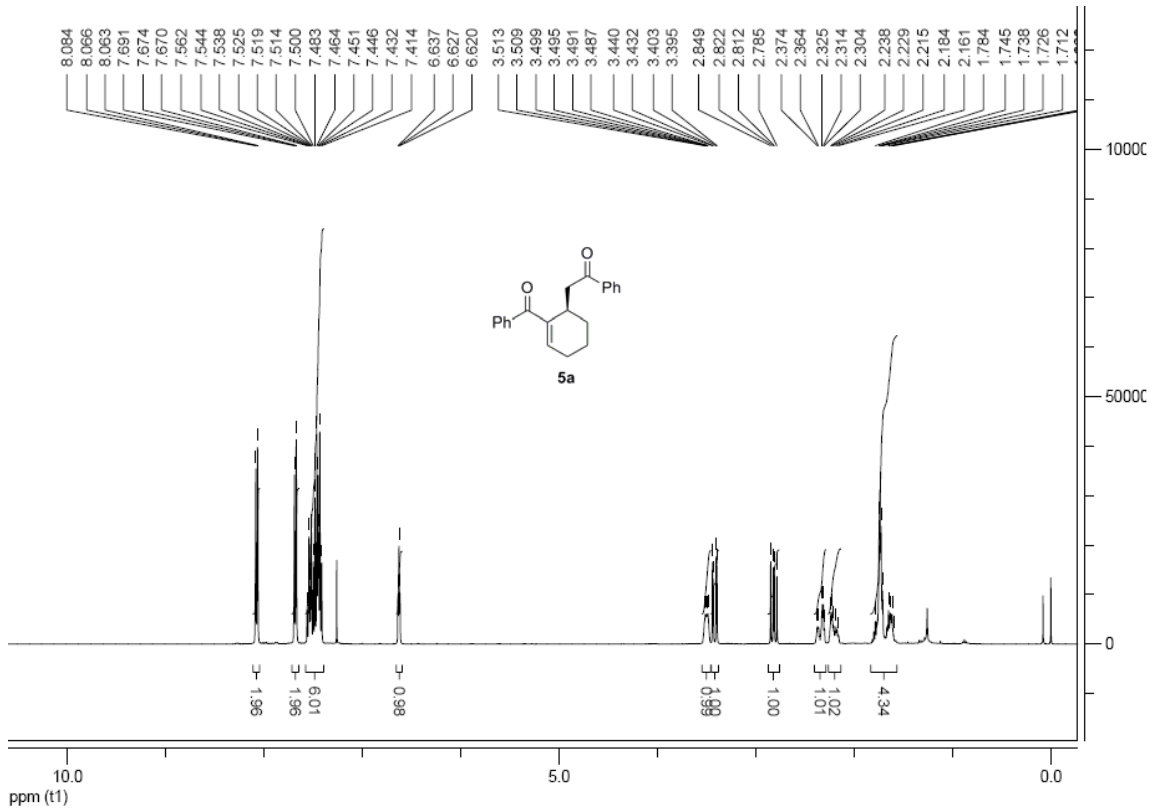
1.0
ppm (t1)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7.500
7.483
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7.451
7.446
7.432
7.414
6.637
6.627
6.620
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3.509
3.499
3.495
3.491
3.487
3.440
3.432
3.403
3.395
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2.822
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2.364
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2.314
2.304
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2.229
2.215
2.184
2.161
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1.738
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10000
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O
O
Ph
Ph
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1.96
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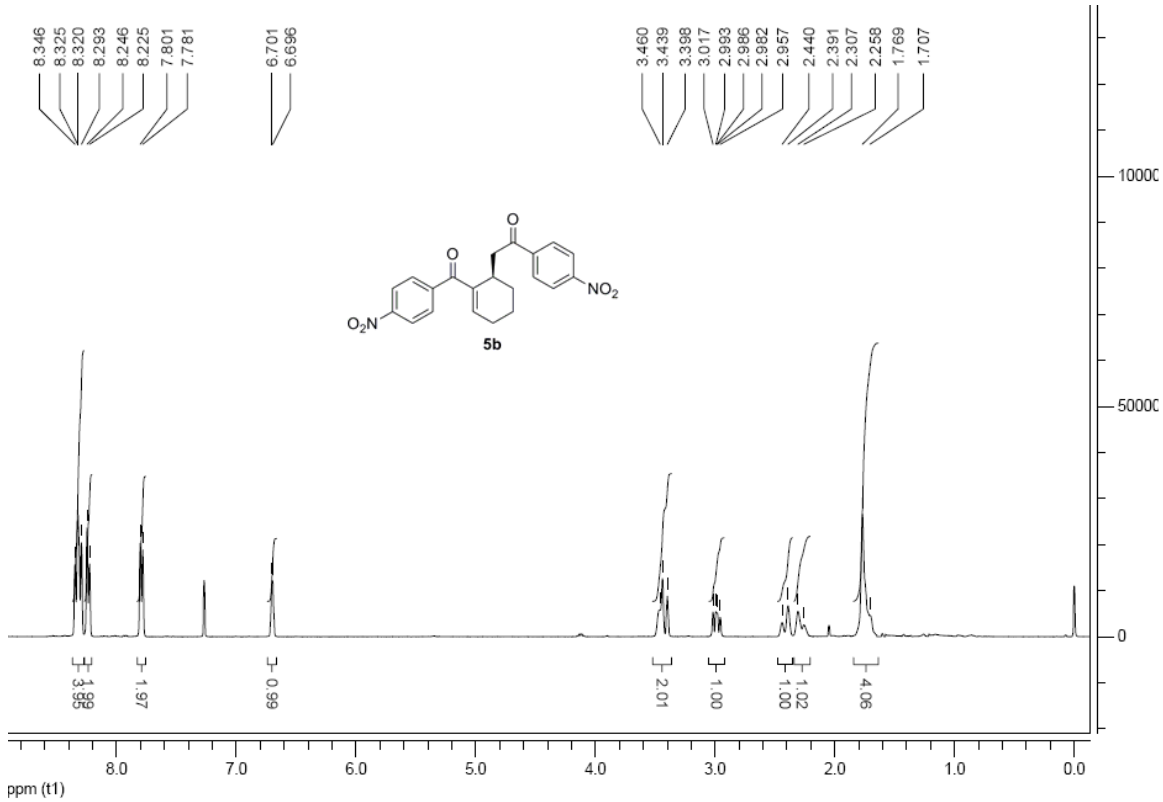
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2.986
2.982
2.957
2.440
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2.307
2.258
1.769
1.707
O
O
NO2
O2N
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2.01
1.00
1.02
4.06
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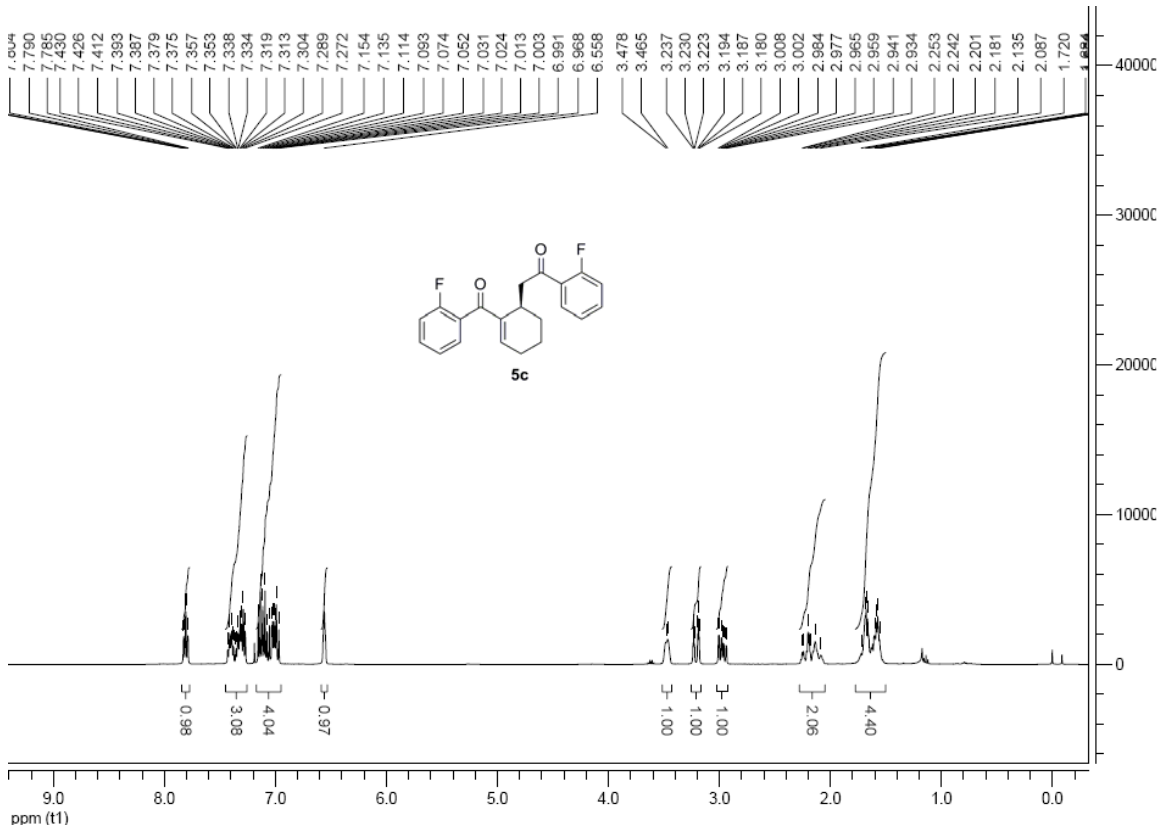
ppm (t1)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7.334
7.319
7.313
7.304
7.289
7.272
7.154
7.135
7.114
7.093
7.074
7.052
7.031
7.024
7.013
7.003
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6.968
6.558
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3.465
3.237
3.230
3.223
3.194
3.187
3.180
3.008
3.002
2.984
2.977
2.965
2.959
2.941
2.934
2.253
2.242
2.201
2.181
2.135
2.087
1.720
F
O
F
O
5c
0.98
3.08
4.04
0.97
1.00
1.00
1.00
2.06
4.40
40000
30000
20000
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2.0
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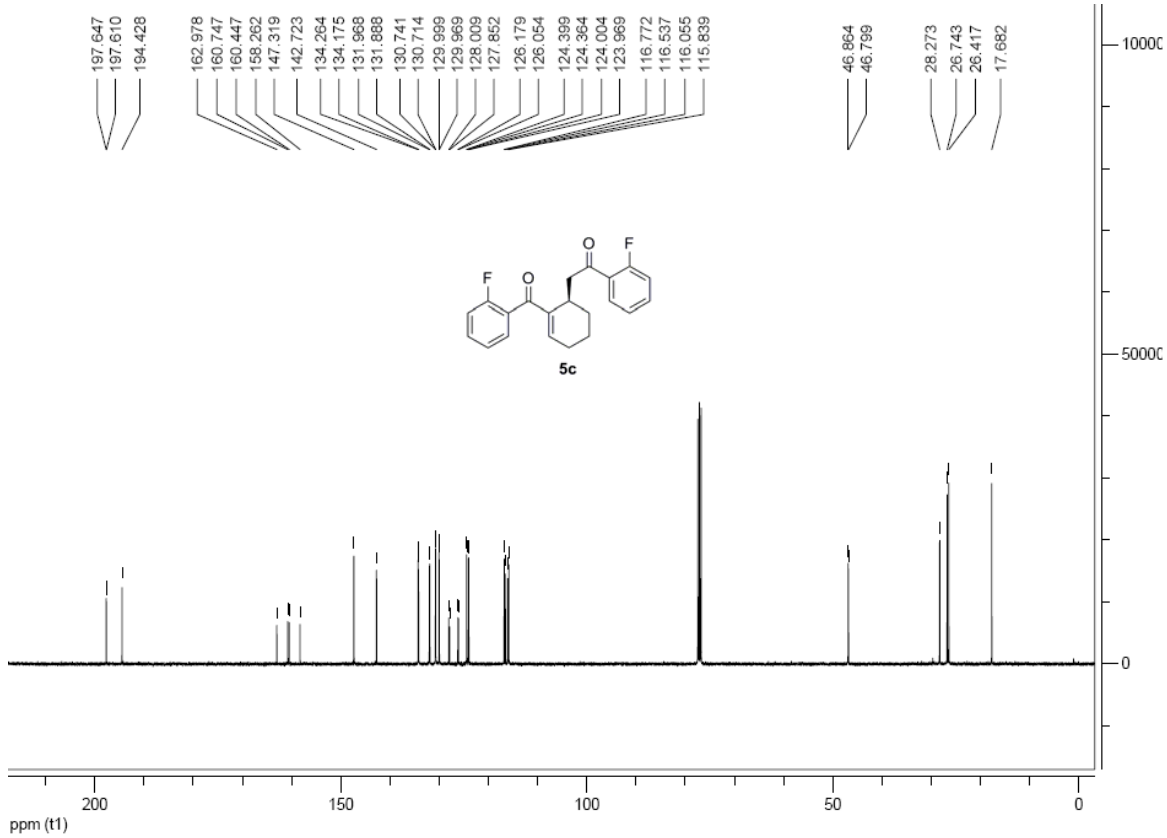
0.0
ppm (t1)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160.447
158.262
147.319
142.723
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134.175
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131.888
130.741
130.714
129.999
129.969
128.009
127.852
126.179
126.054
124.399
124.364
124.004
123.969
116.772
116.537
116.055
115.839
46.864
46.799
28.273
26.743
26.417
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O
F
F
O
5c
10000
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0
200
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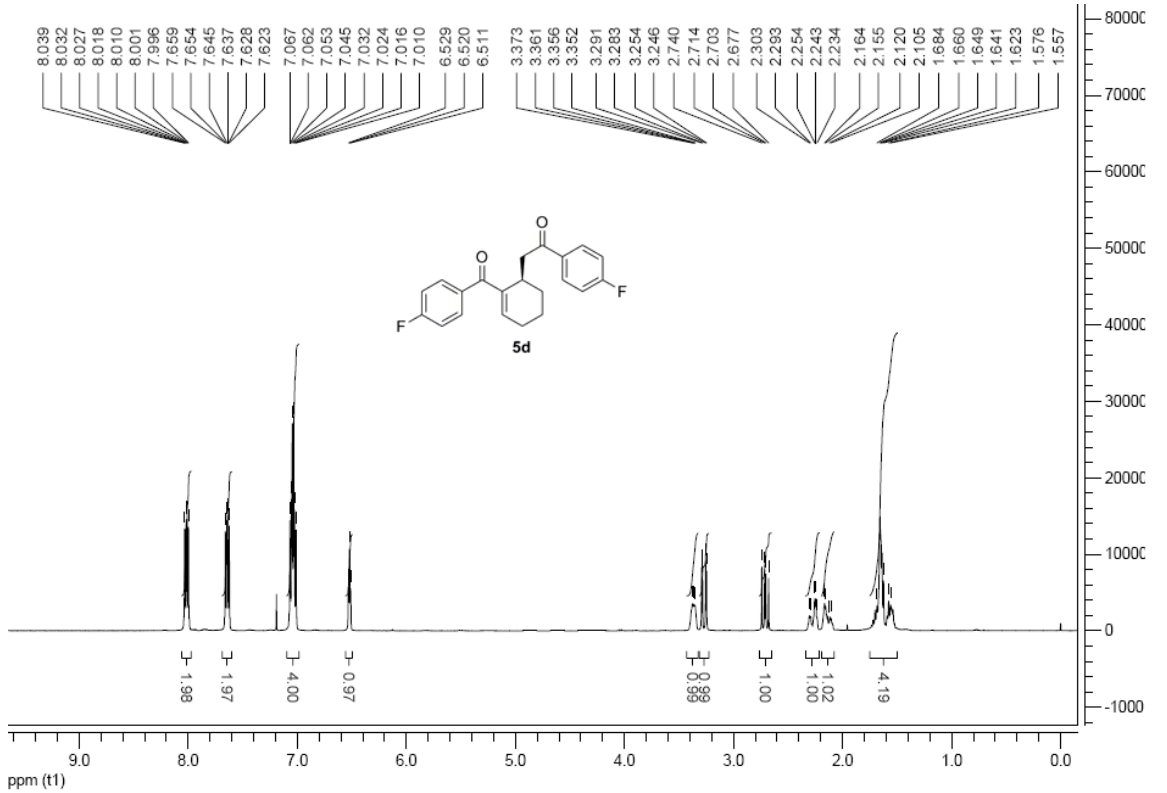
100
50
0
ppm (t1)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7.628
7.623
7.067
7.062
7.053
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7.032
7.024
7.016
7.010
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6.520
6.511
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3.361
3.356
3.352
3.291
3.283
3.254
3.246
2.740
2.714
2.703
2.677
2.303
2.293
2.254
2.243
2.234
2.164
2.155
2.120
2.105
1.684
1.660
1.649
1.641
1.623
1.576
1.557
O
O
F
F
5d
1.98
1.97
4.00
0.97
0.99
0.99
1.00
1.00
1.02
4.19
80000
70000
60000
50000
40000
30000
20000
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0
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2.0
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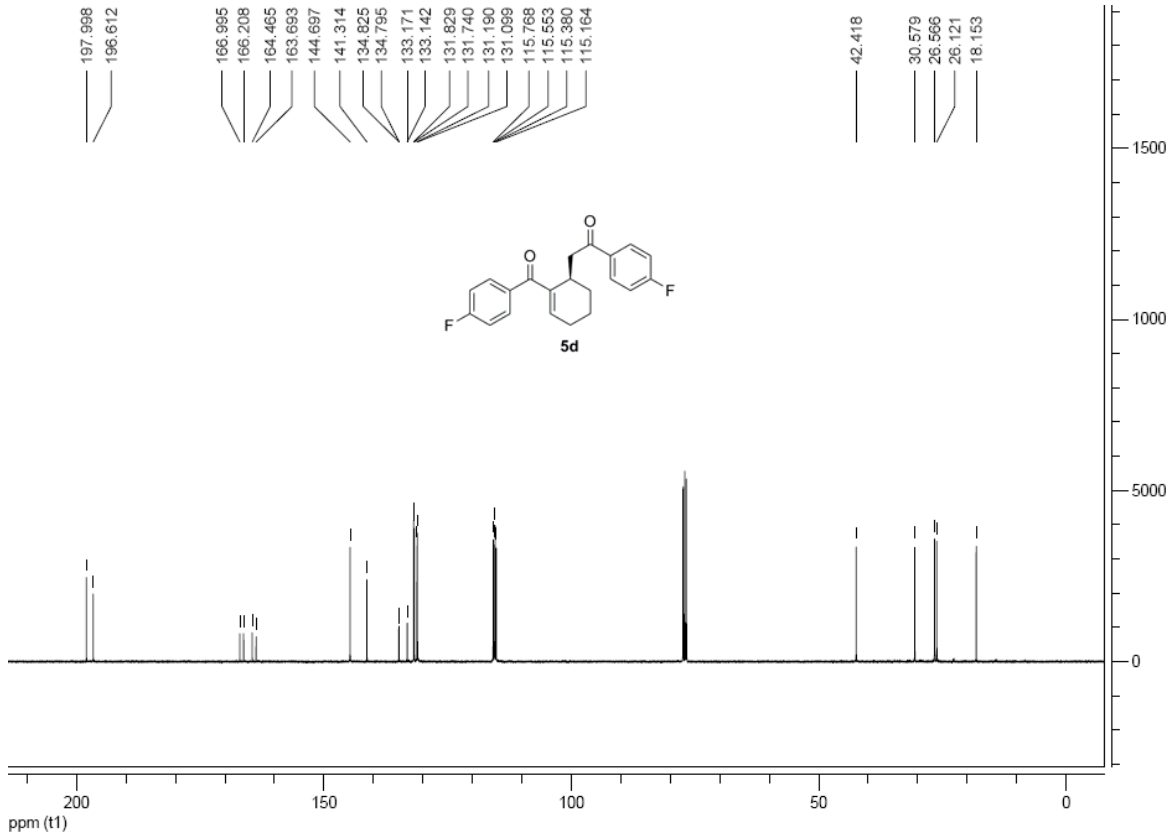
0.0
ppm (t1)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141.314
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134.795
133.171
133.142
131.829
131.740
131.190
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115.380
115.164
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30.579
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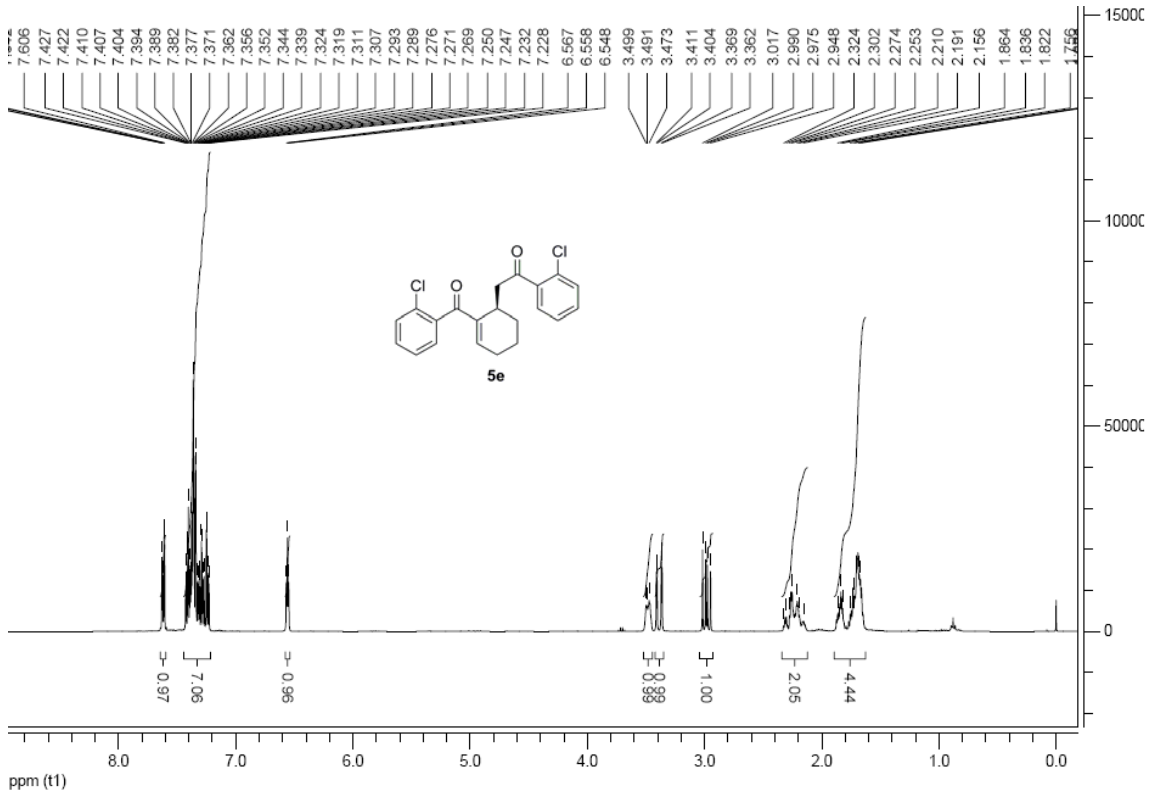
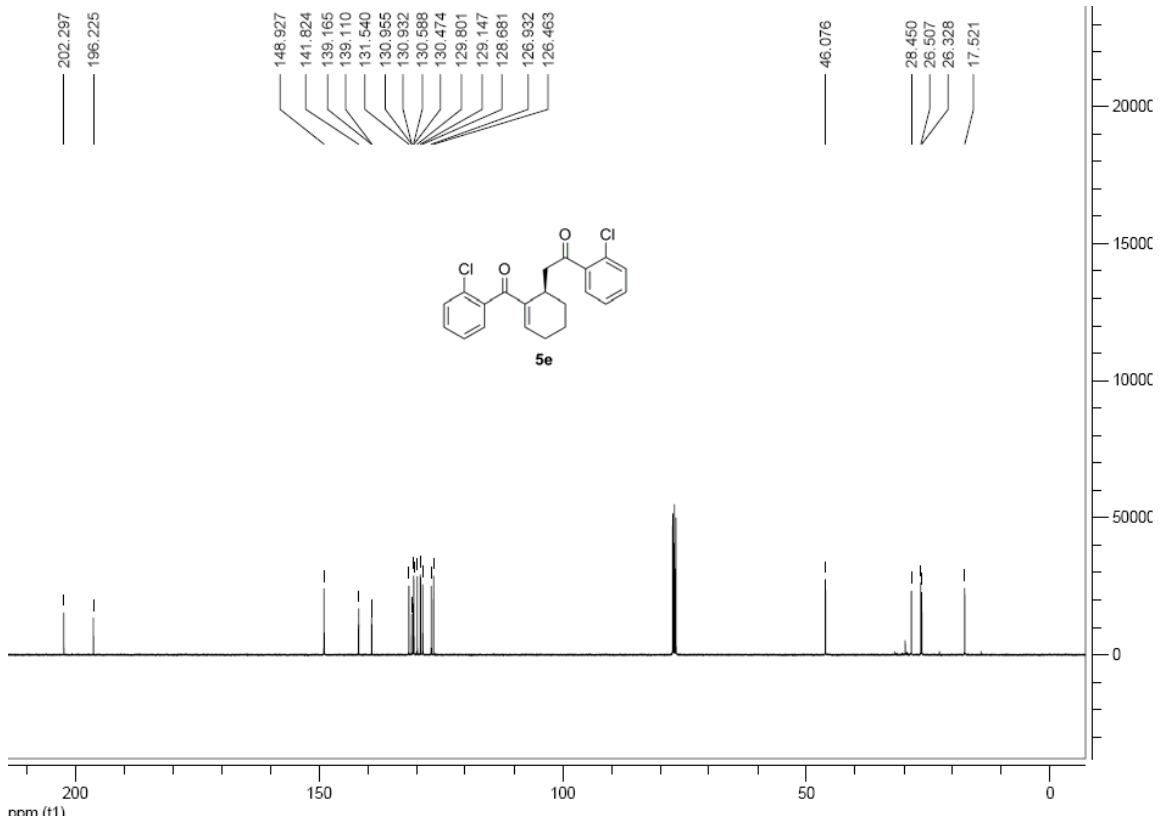
26.121
18.153
5d
ppm (t1)


5e
ppm (t1)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129.147
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26.328
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200
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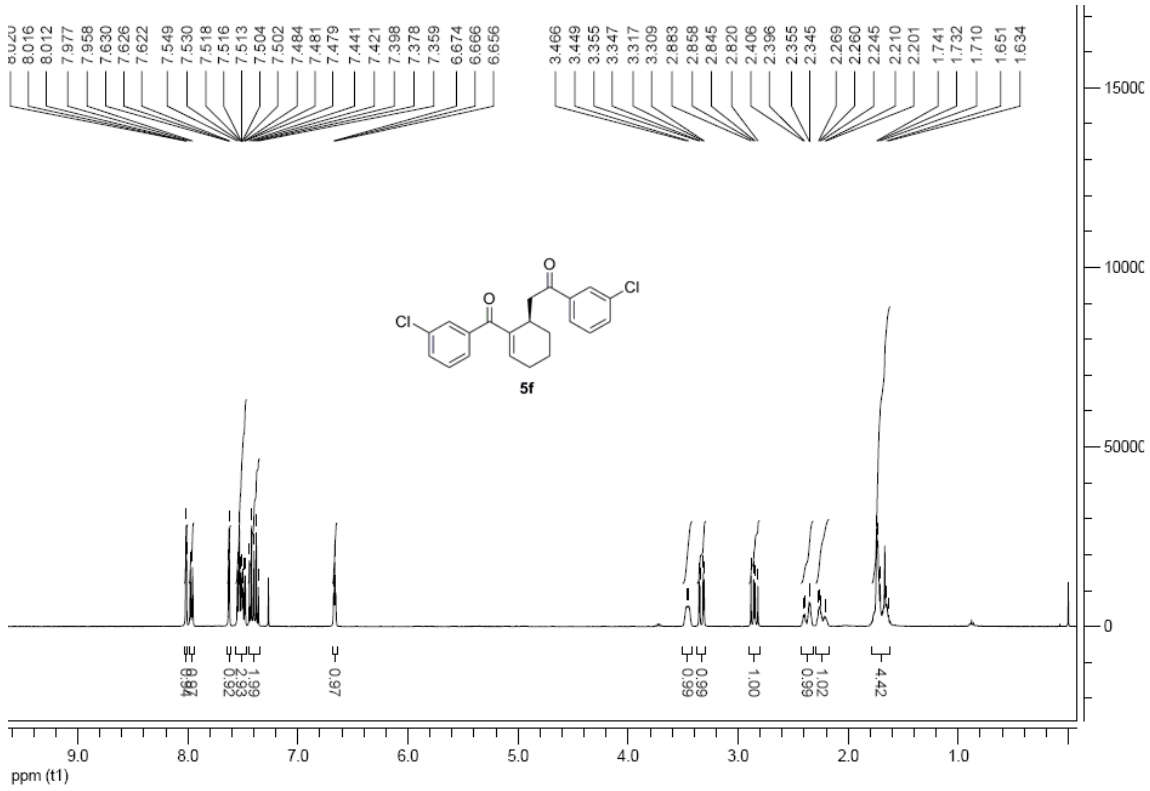
100
50
0
ppm (t1)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7.622
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7.530
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7.516
7.513
7.504
7.502
7.484
7.481
7.479
7.441
7.421
7.398
7.378
7.359
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6.666
6.656
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3.355
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3.317
3.309
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2.269
2.260
2.245
2.210
2.201
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1.732
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1.634
5f
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0.97
0.99
0.99
1.00
0.99
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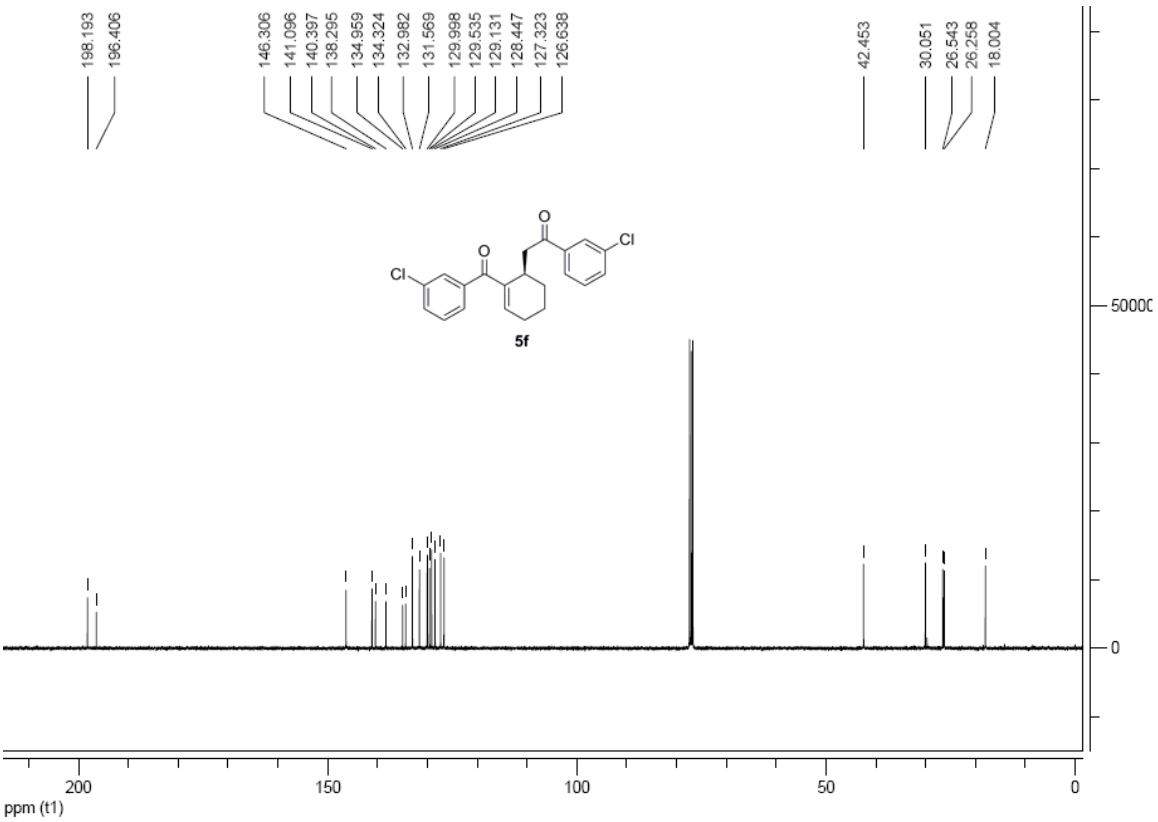
ppm (t1)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127.323
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26.258
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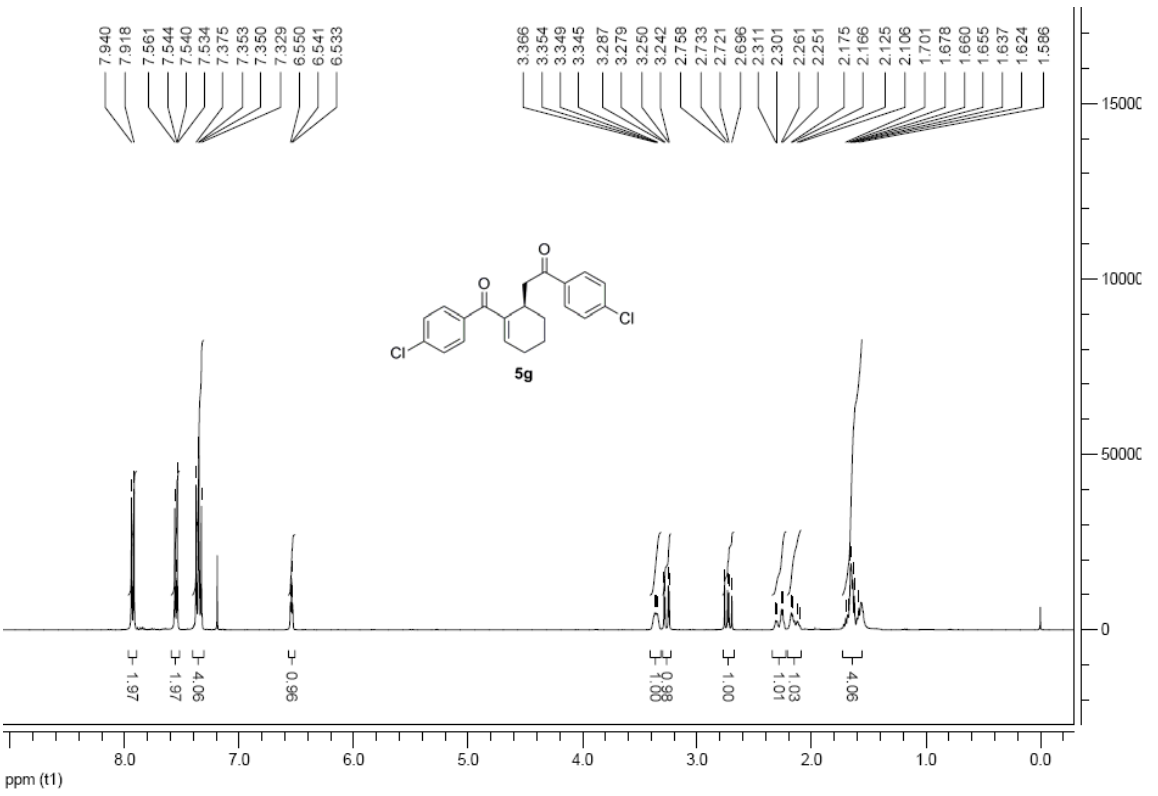
50
0
ppm (t1)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2.721
2.696
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2.251
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2.166
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1.660
1.655
1.637
1.624
1.586
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4.06
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1.00
1.01
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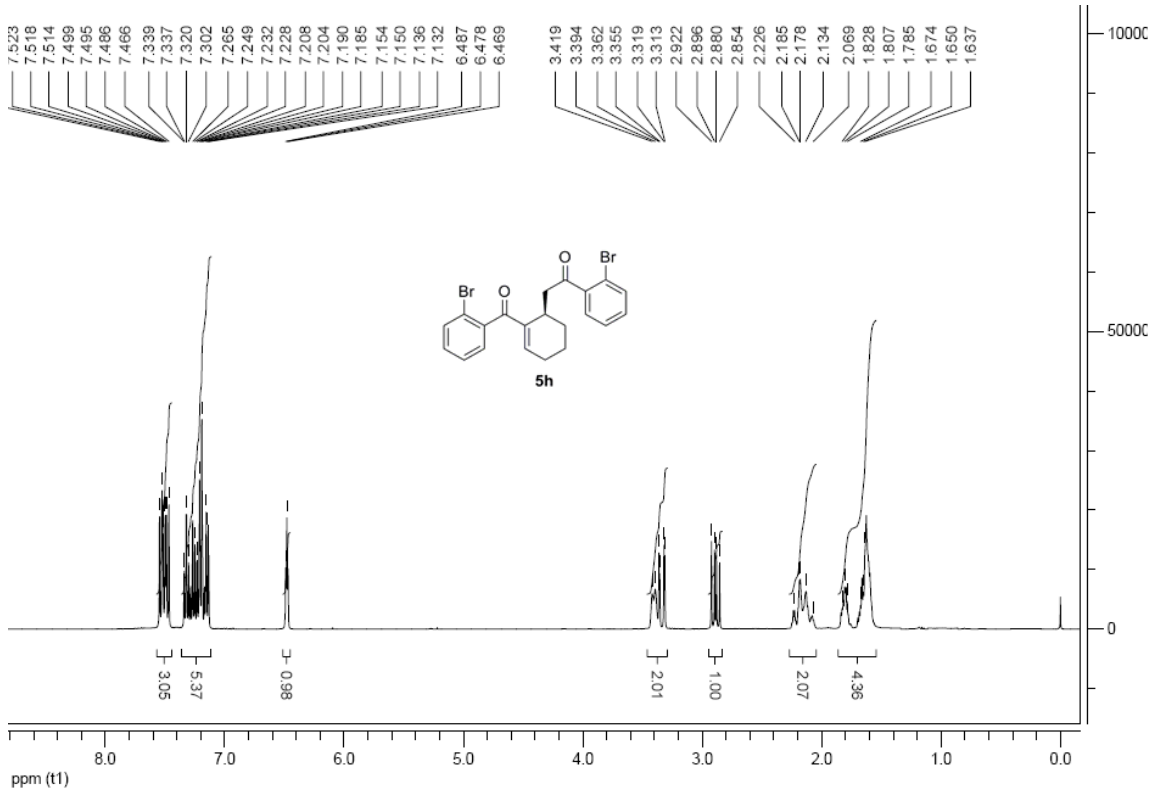
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7.228
7.208
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7.185
7.154
7.150
7.136
7.132
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6.469
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3.362
3.355
3.319
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2.226
2.185
2.178
2.134
2.069
1.828
1.807
1.785
1.674
1.650
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O
Br
5h
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5.37
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1.00
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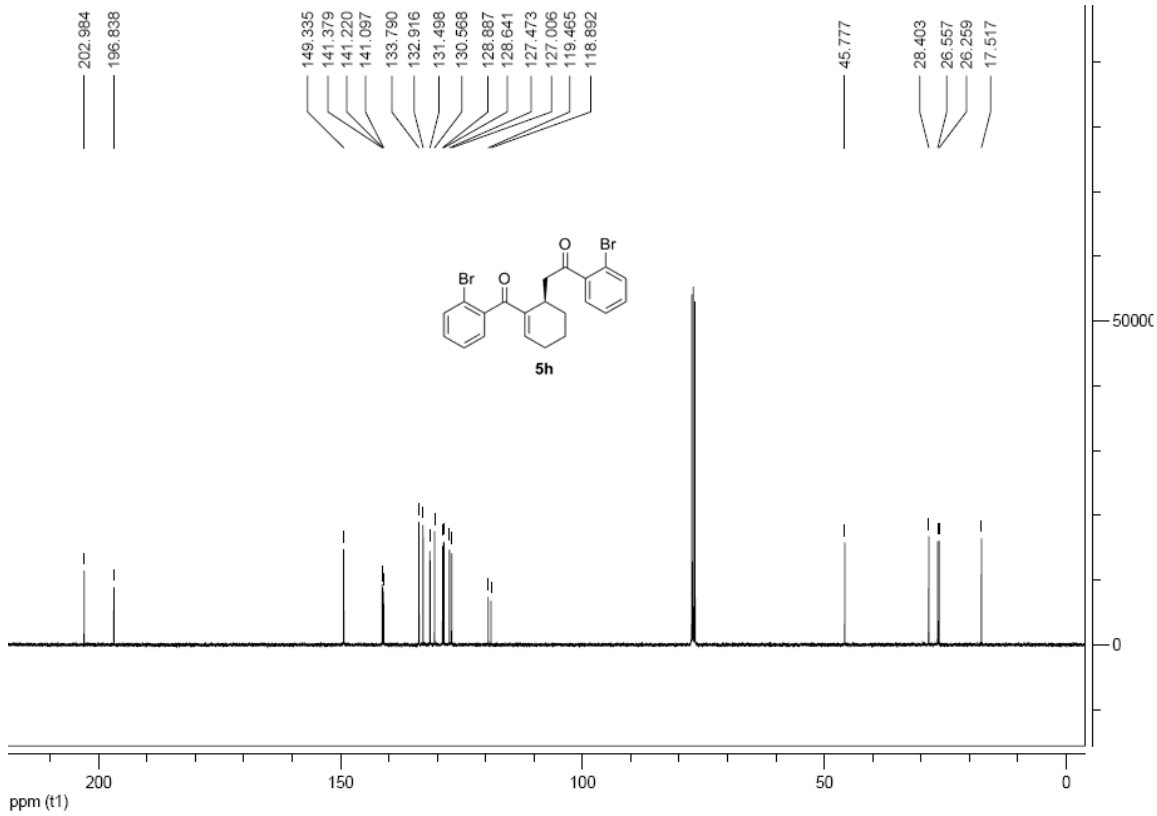
4.36
ppm (t1)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127.473
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45.777
28.403
26.557
26.259
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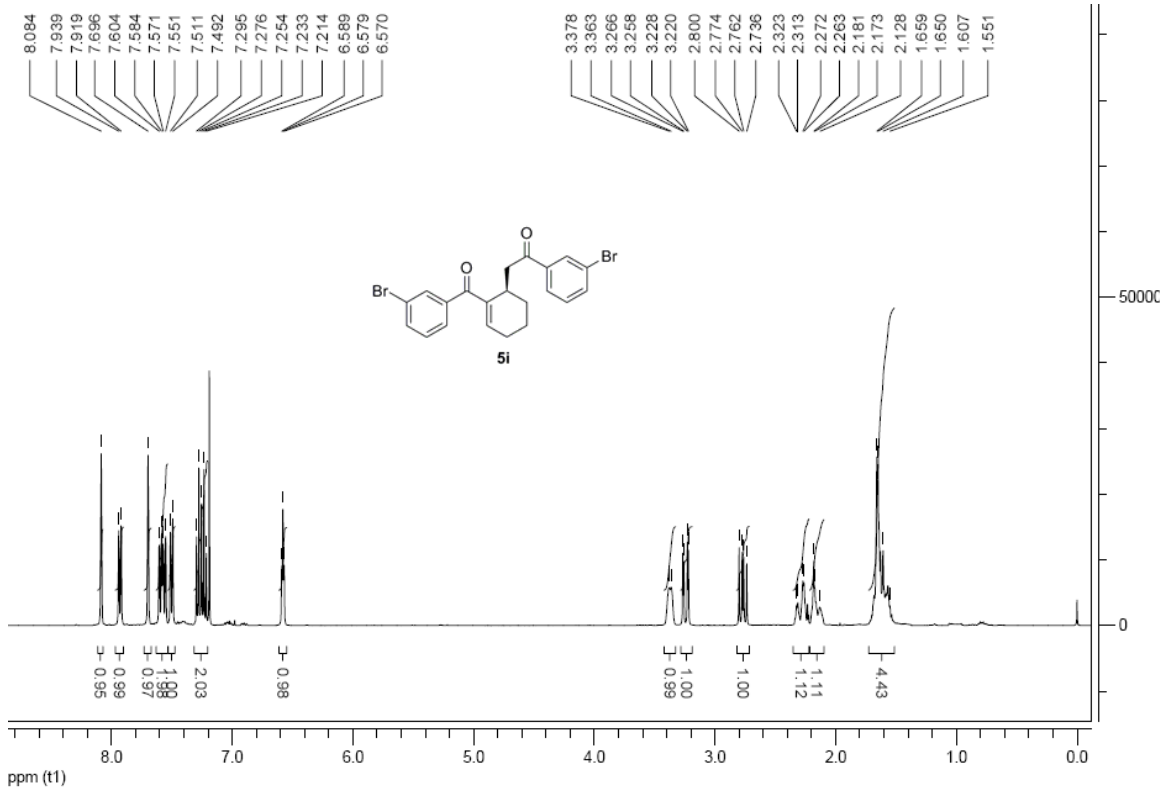
Br
O
O
Br
5h
ppm (t1)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7.254
7.233
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6.579
6.570
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3.266
3.258
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2.774
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2.736
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2.313
2.272
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2.173
2.128
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1.650
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Br
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O
Br
5i
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1.00
1.00
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1.00
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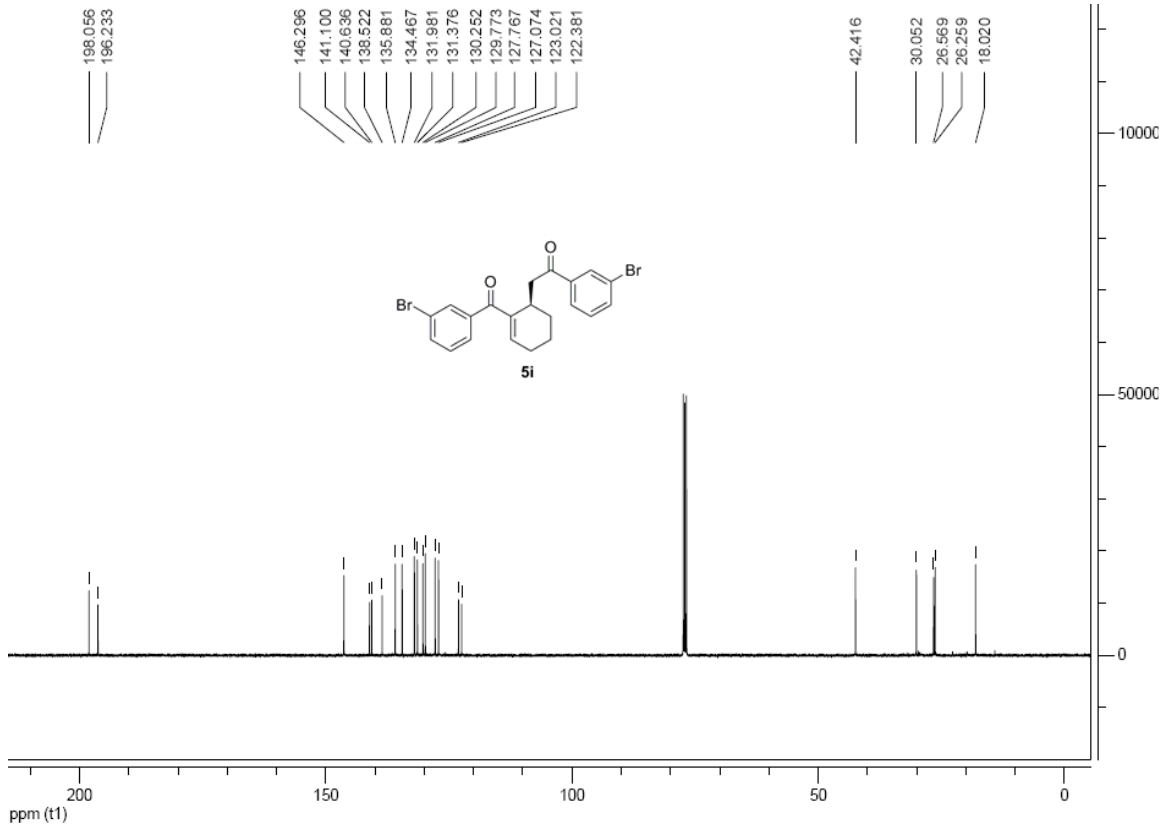
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130.252
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127.074
123.021
122.381
42.416
30.052
26.569
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O
O
Br
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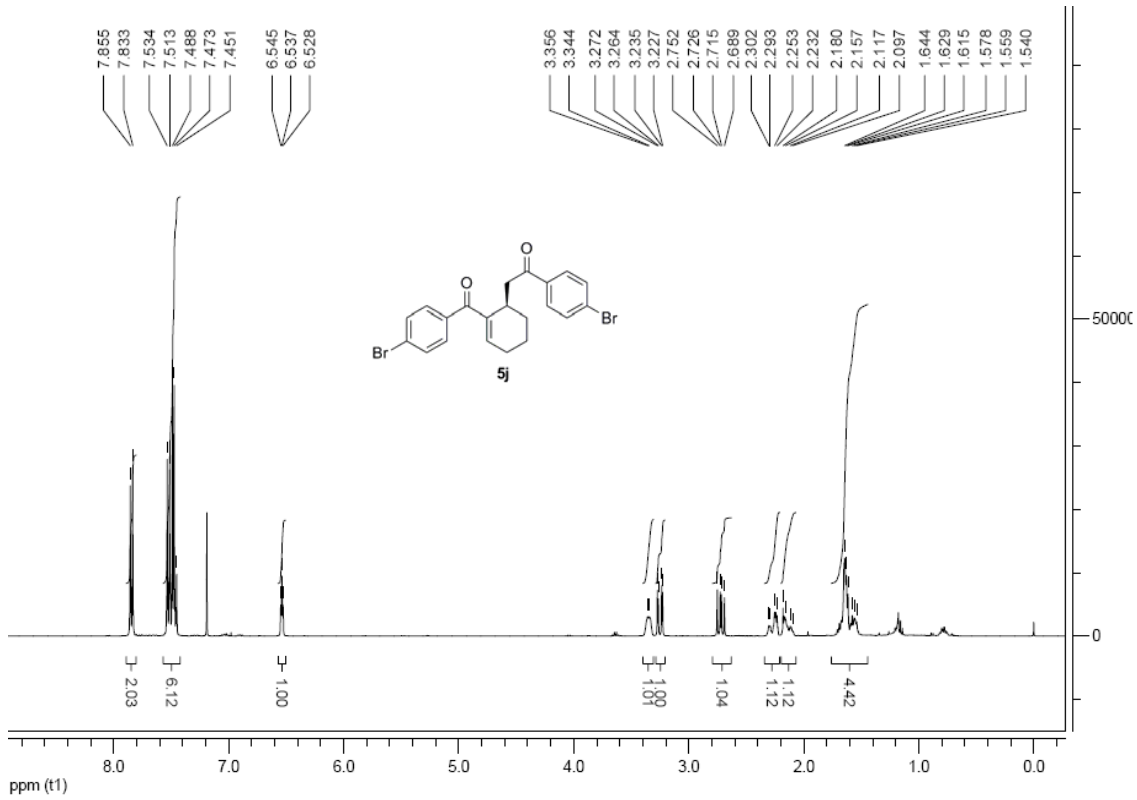
50
0
ppm (t1)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3.235
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2.752
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2.293
2.253
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2.180
2.157
2.117
2.097
1.644
1.629
1.615
1.578
1.559
1.540
Br
Br
5j
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6.12
1.00
1.00
1.01
1.04
1.12
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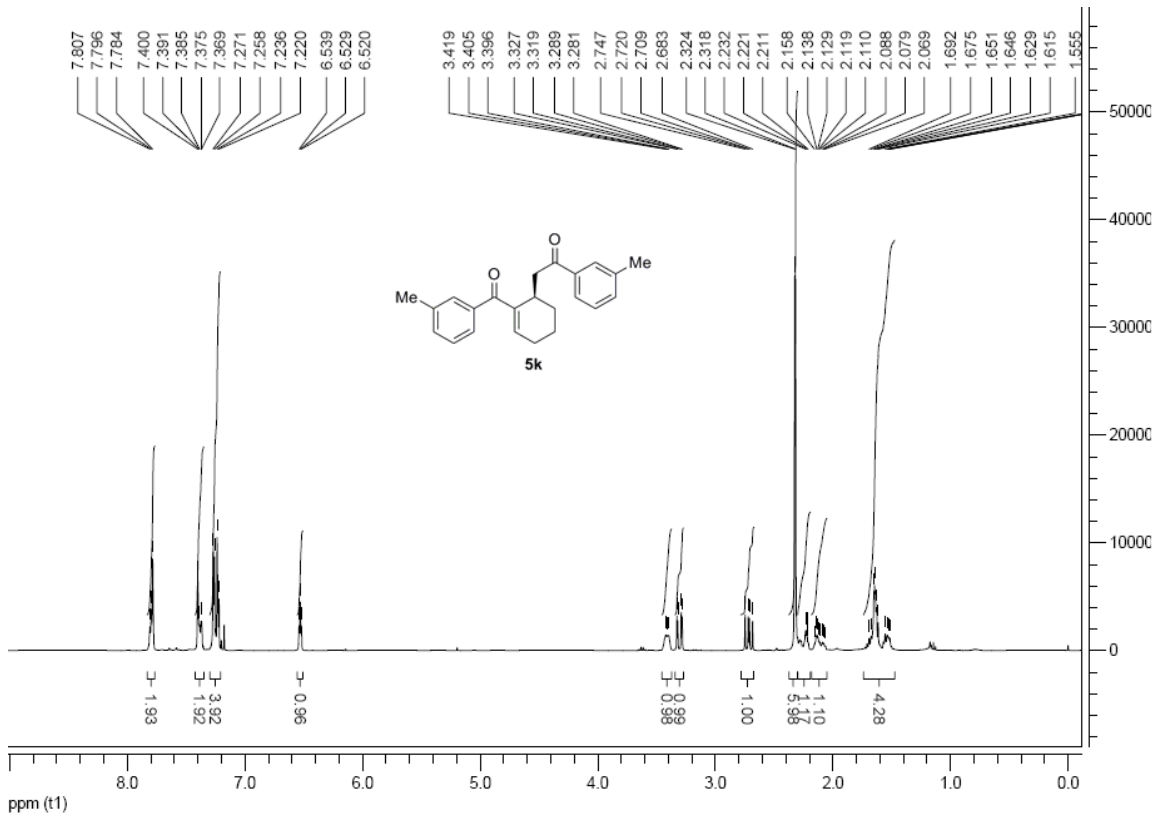
ppm (t1)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6.539
6.529
6.520
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3.396
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3.281
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2.232
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2.211
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2.138
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1.629
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1.555
Me
Me
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40000
30000
20000
10000
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1.92
3.92
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0.98
0.98
1.00
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1.10
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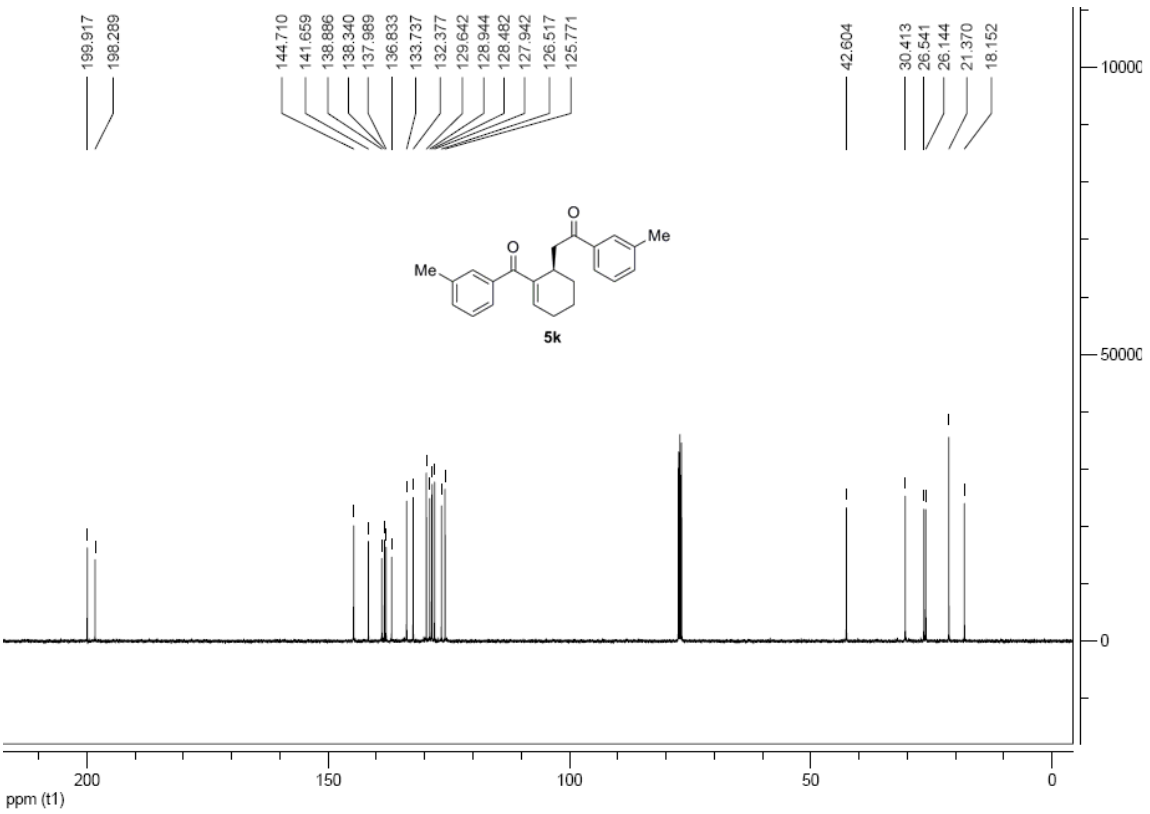
ppm (t1)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128.482
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126.517
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42.604
30.413
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18.152
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100
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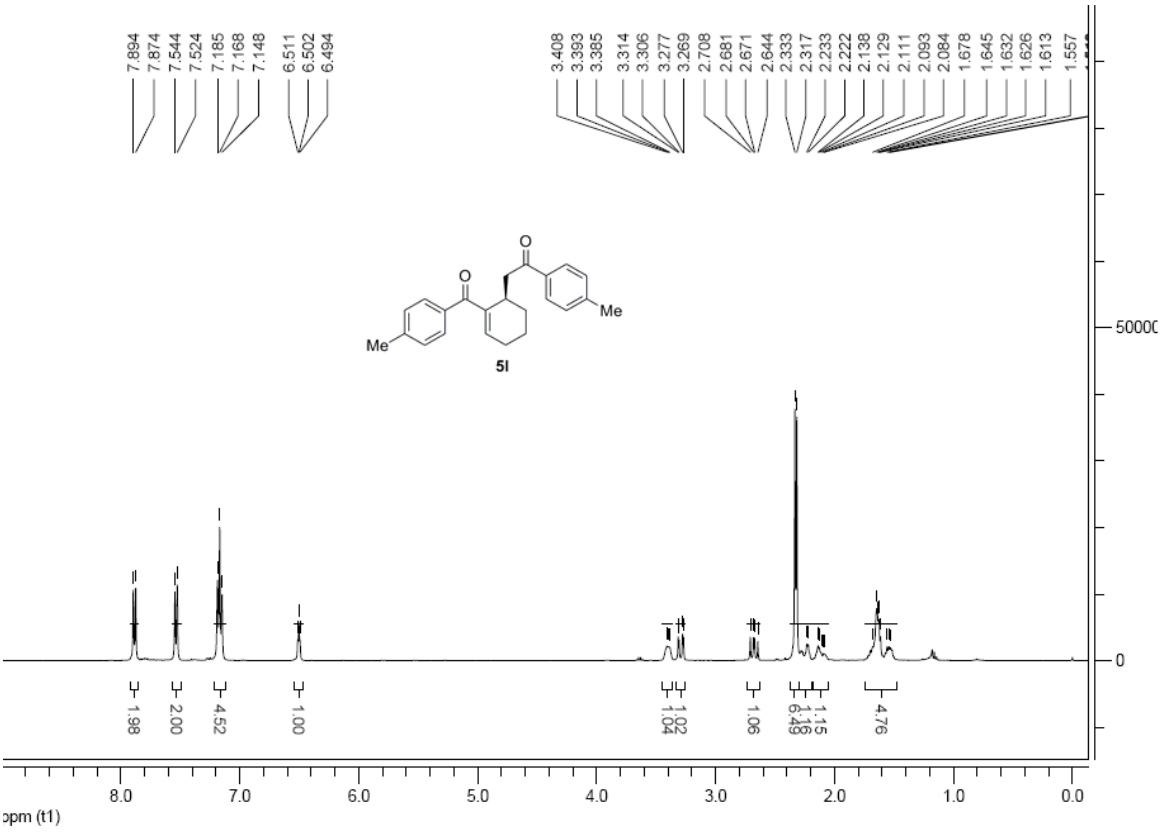
ppm (t1)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1.00
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6.49
1.16
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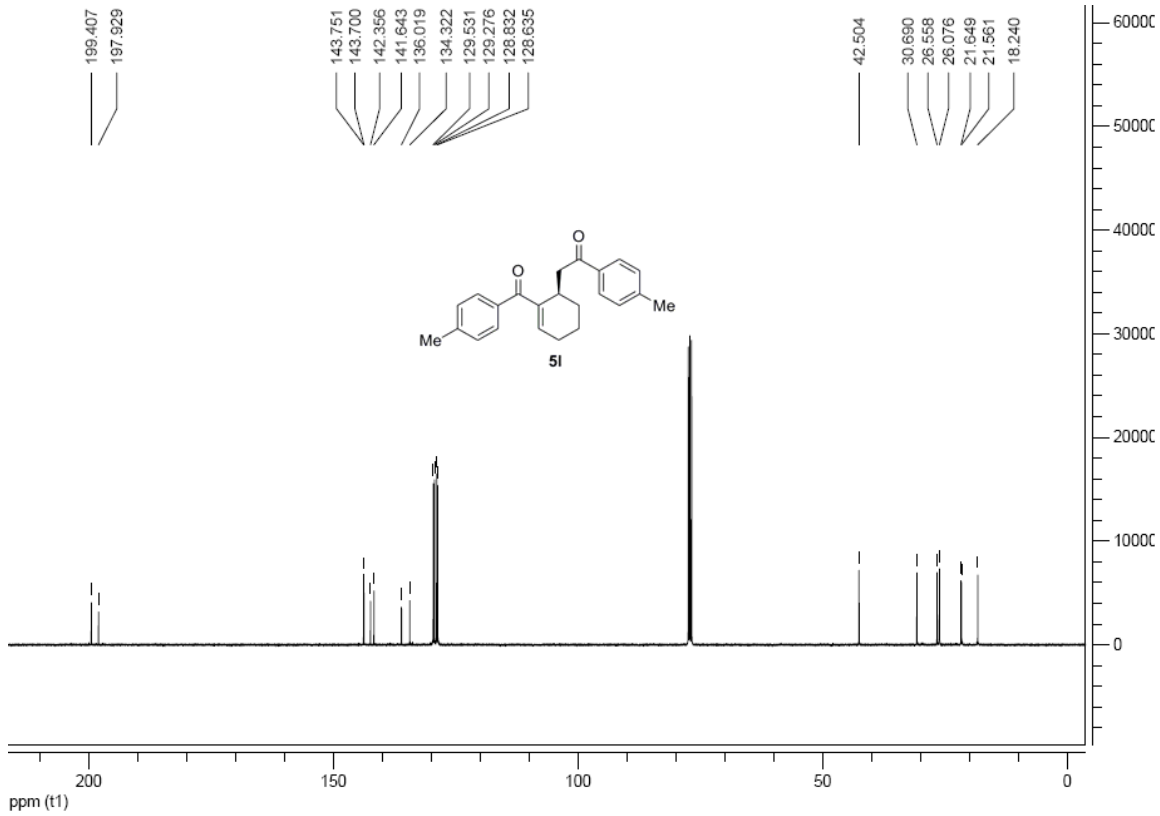
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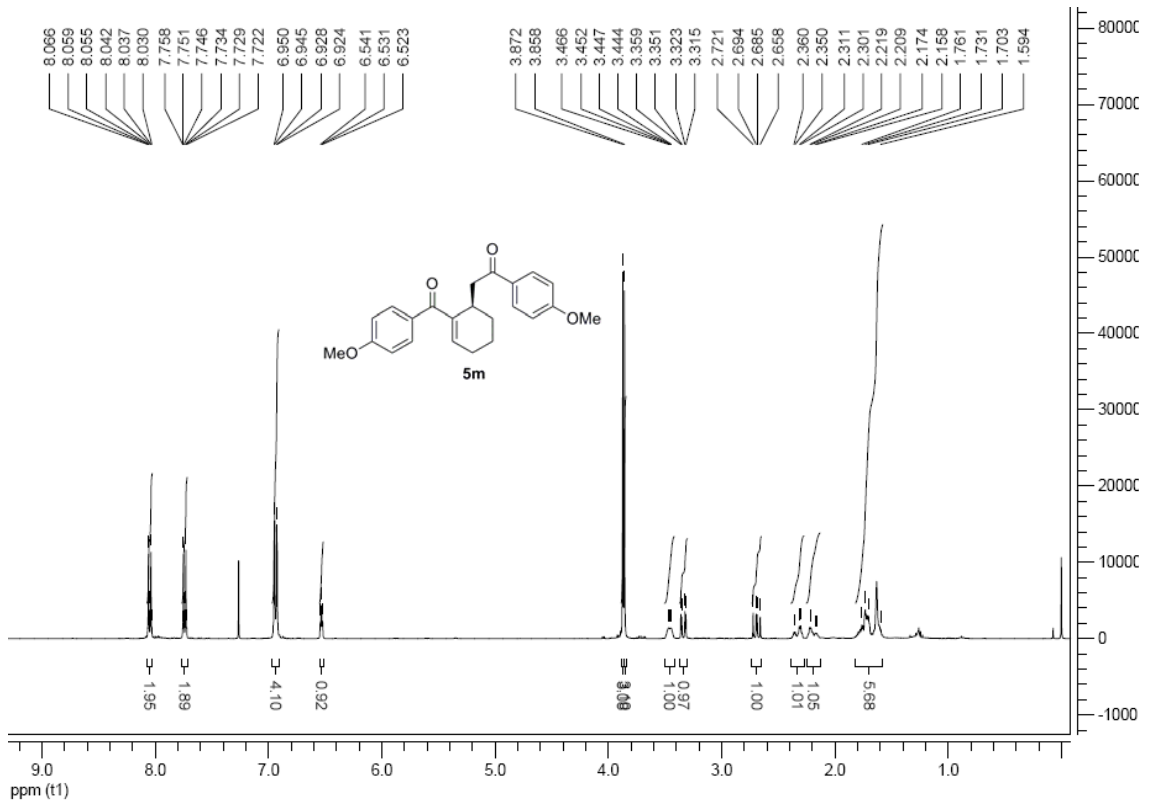
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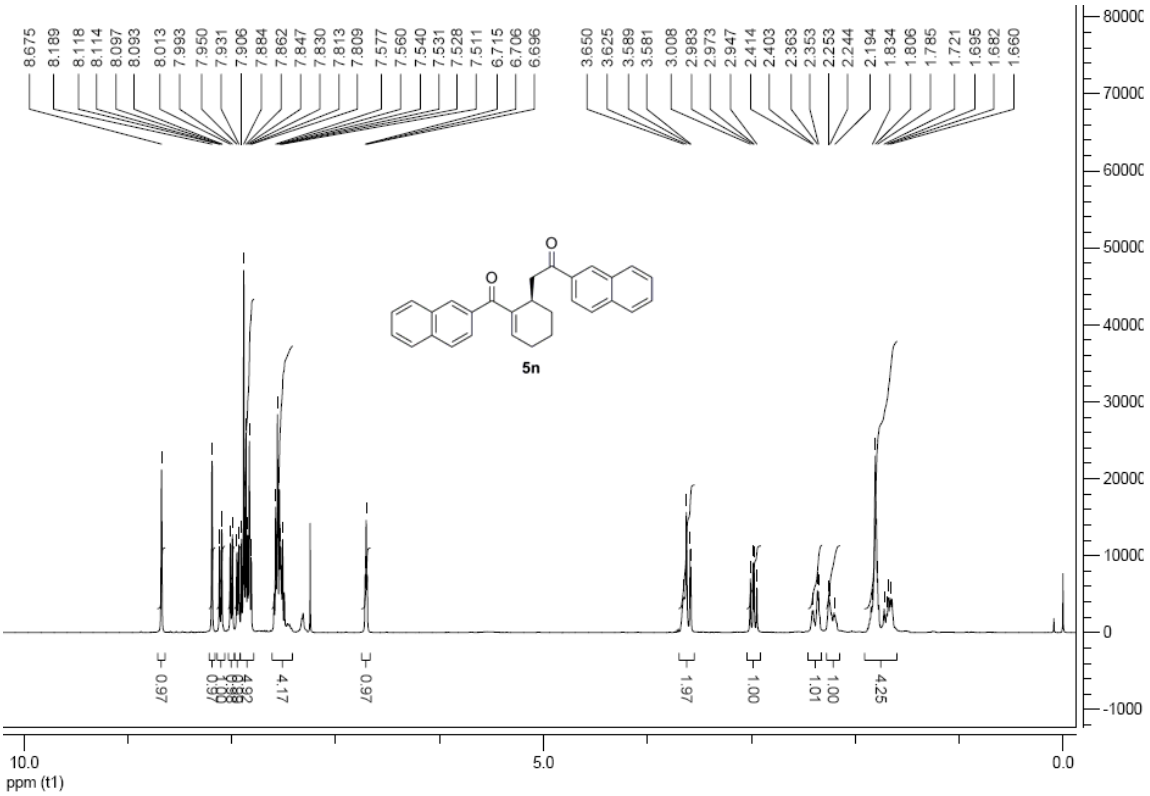
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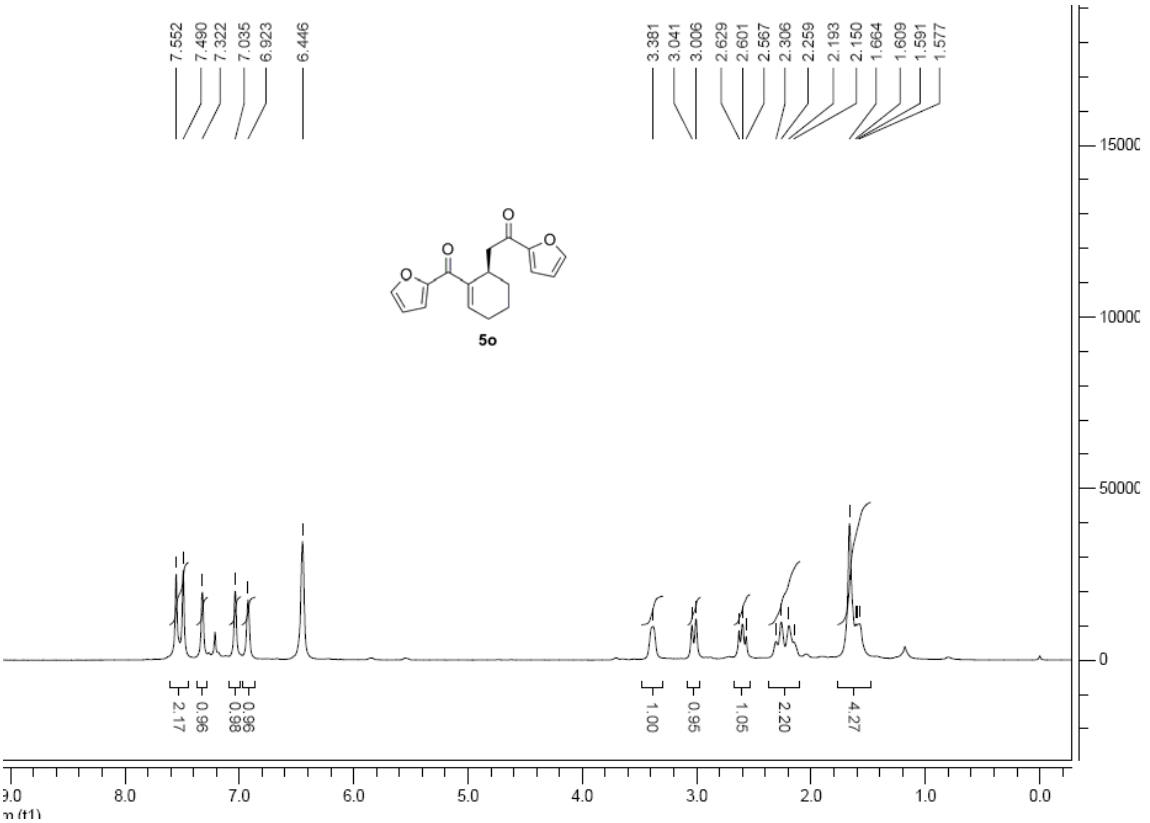
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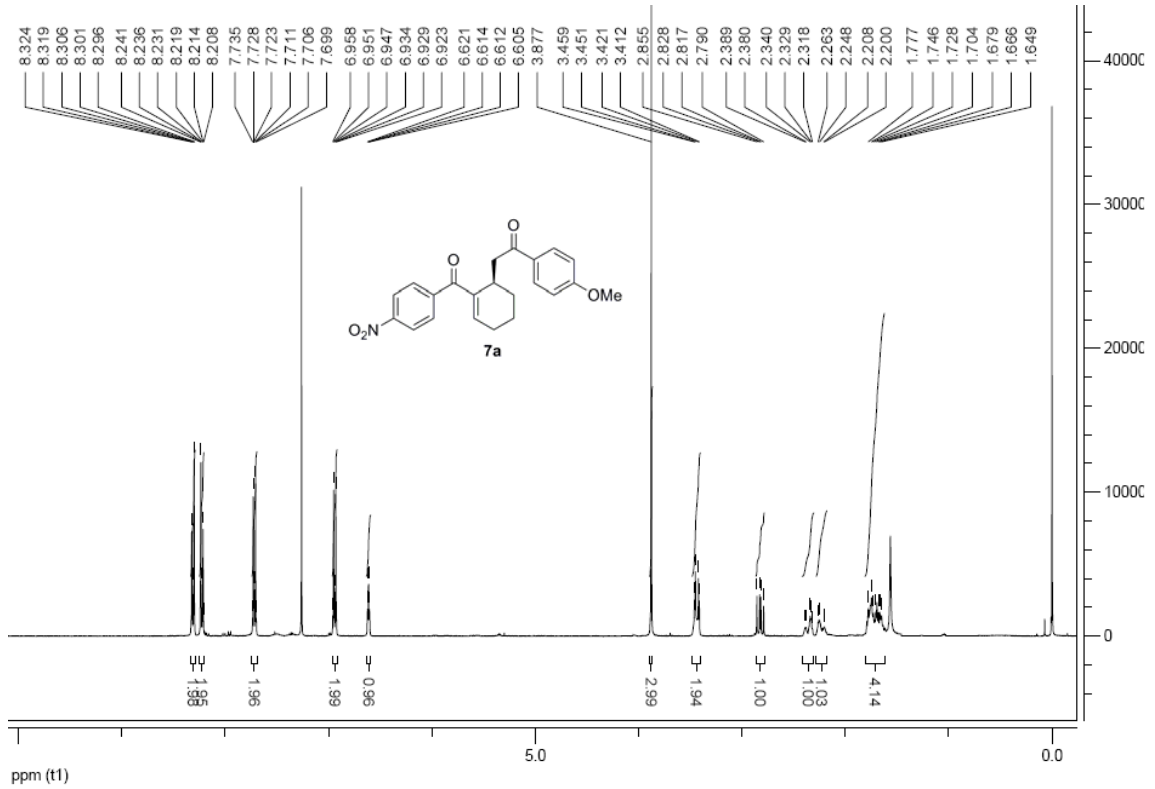
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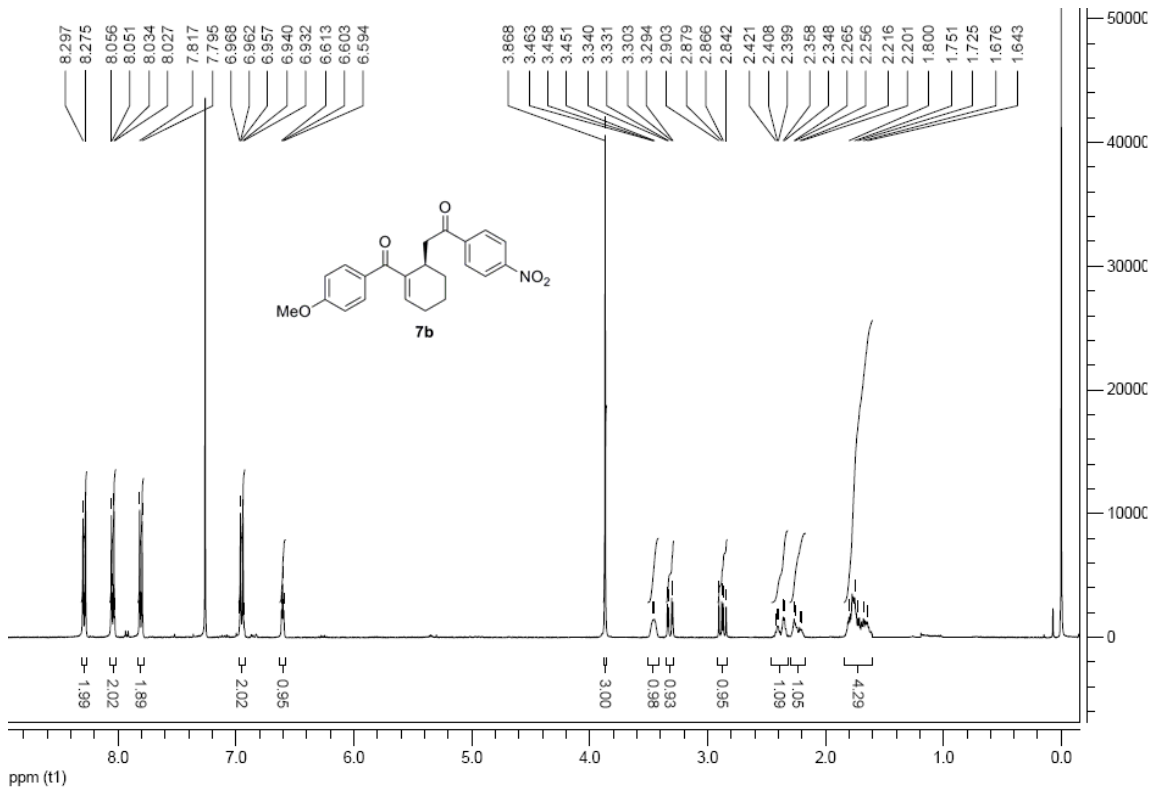
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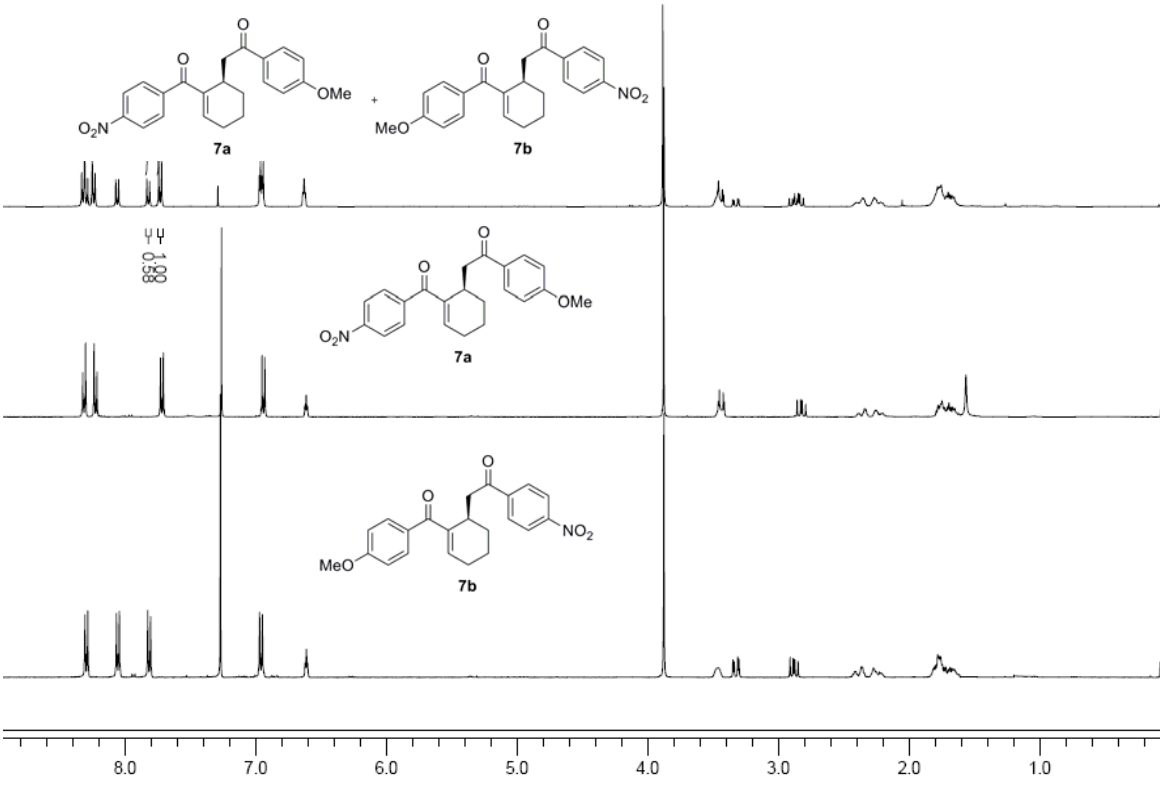
ppm (t1)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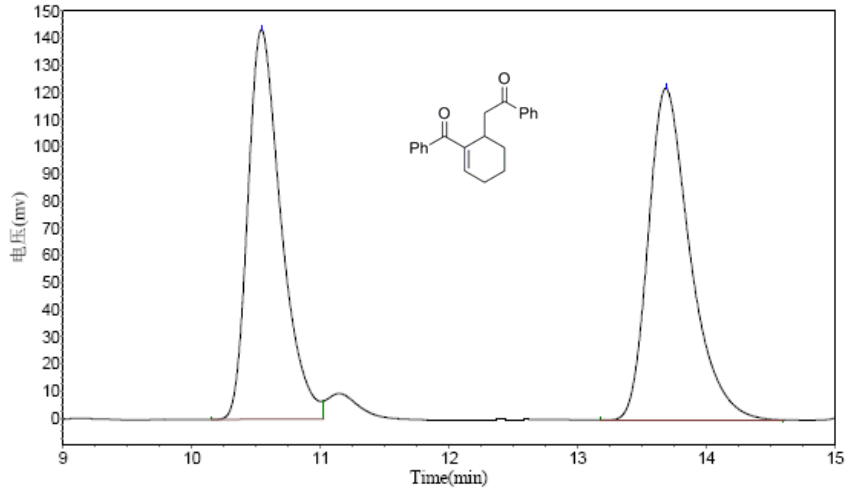
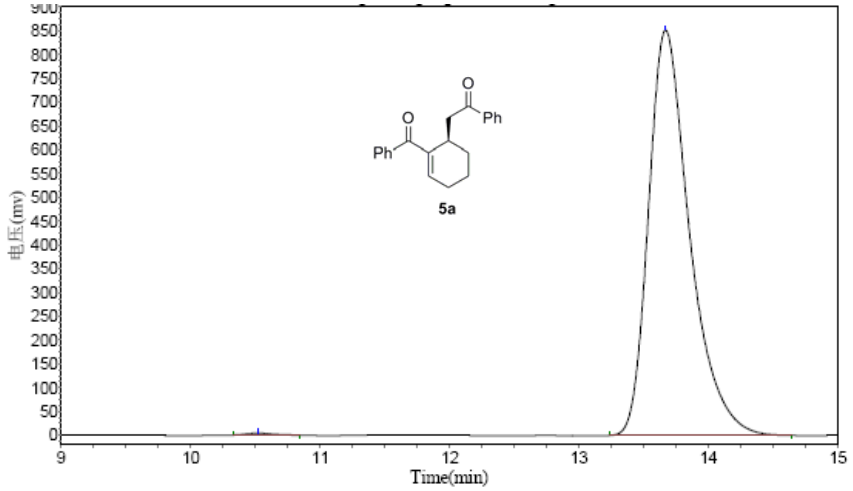
7. HPLC Spectra for the RC Products



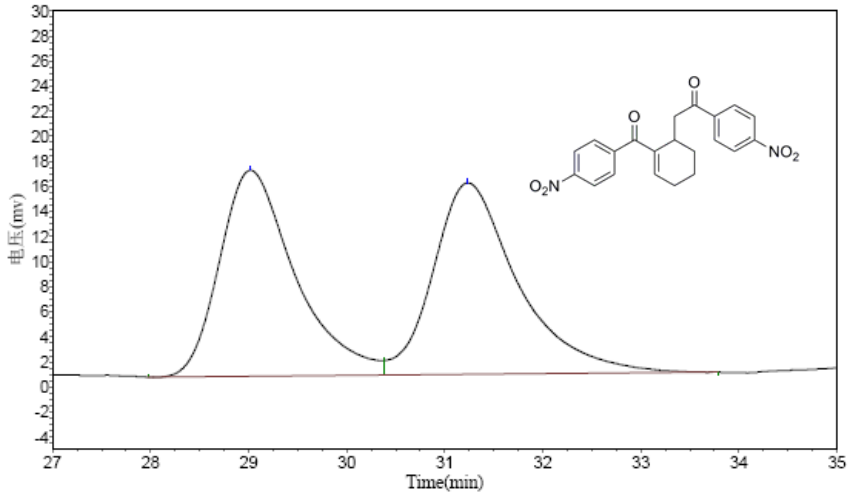
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.542	143482.984	2574735.750	48.2513
2		13.685	122174.625	2761364.250	51.7487
Total			265657.609	5336100.000	100.0000



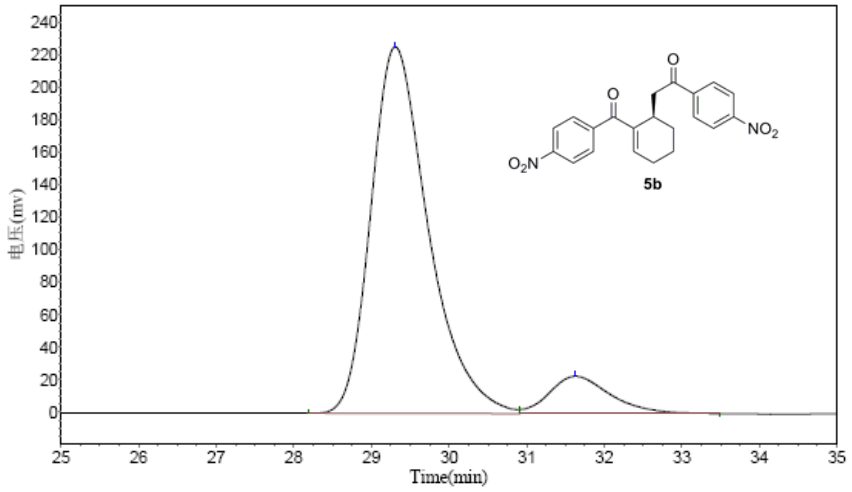
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.517	3957.247	58287.500	0.3093
2		13.668	851154.125	18783894.000	99.6907
Total			855111.372	18842181.500	100.0000



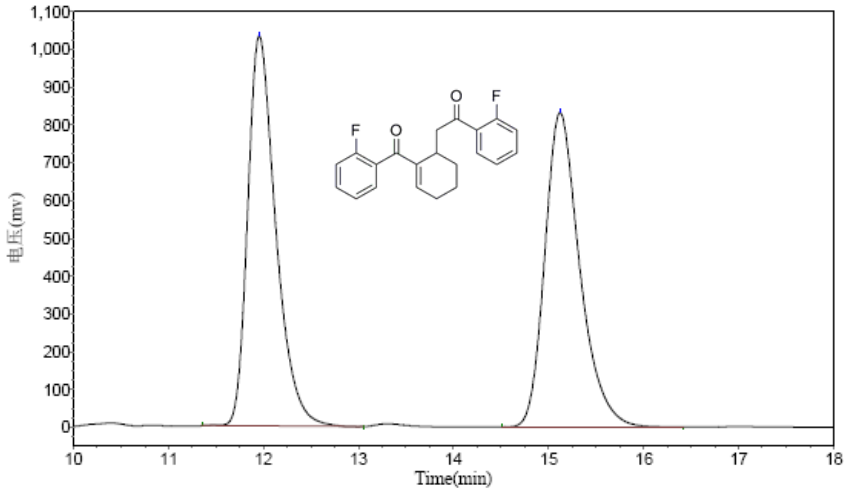
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.018	16437.477	880486.063	48.8518
2		31.237	15275.774	921875.813	51.1482
Total			31713.251	1802361.875	100.0000



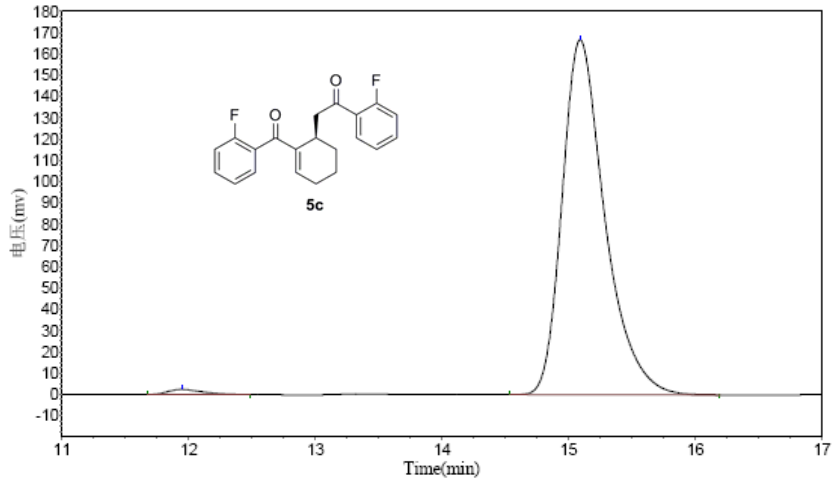
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.310	225791.406	11605697.000	90.2522
2		31.628	22942.156	1253488.875	9.7478
Total			248733.563	12859185.875	100.0000



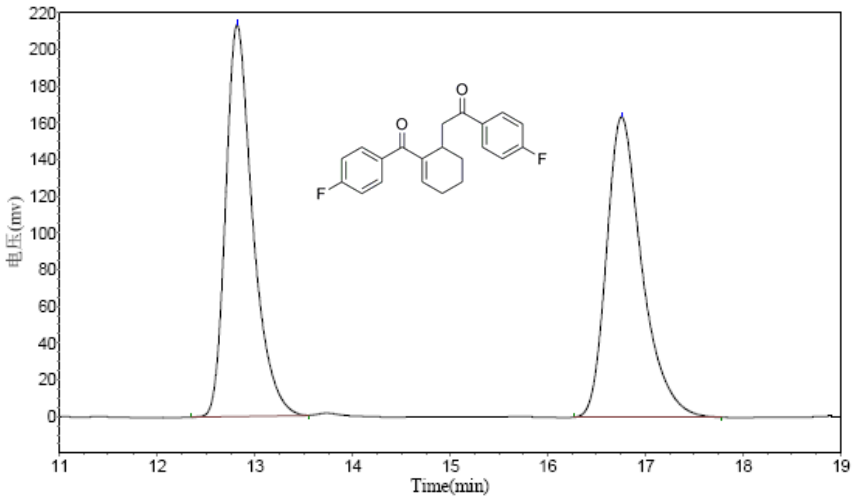
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.957	1031703.938	21211878.000	49.9113
2		15.120	831708.438	21287304.000	50.0887
Total			1863412.375	42499182.000	100.0000



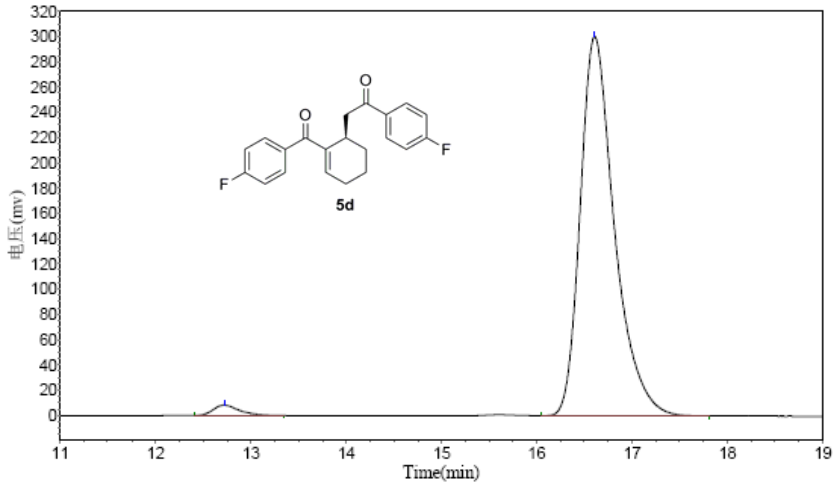
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.945	2509.320	48975.902	1.2369
2		15.092	166712.109	3910658.500	98.7631
Total			169221.429	3959634.402	100.0000



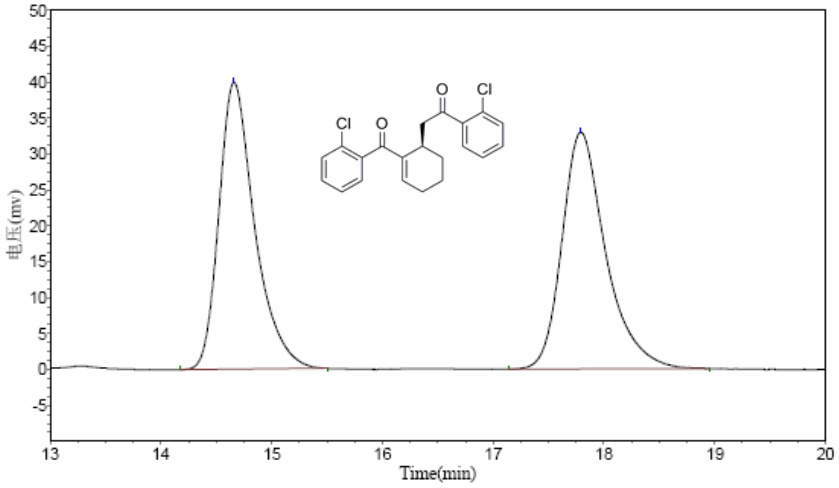
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.818	213353.906	4108998.750	49.8580
2		16.755	163706.141	4132407.750	50.1420
Total			377060.047	8241406.500	100.0000



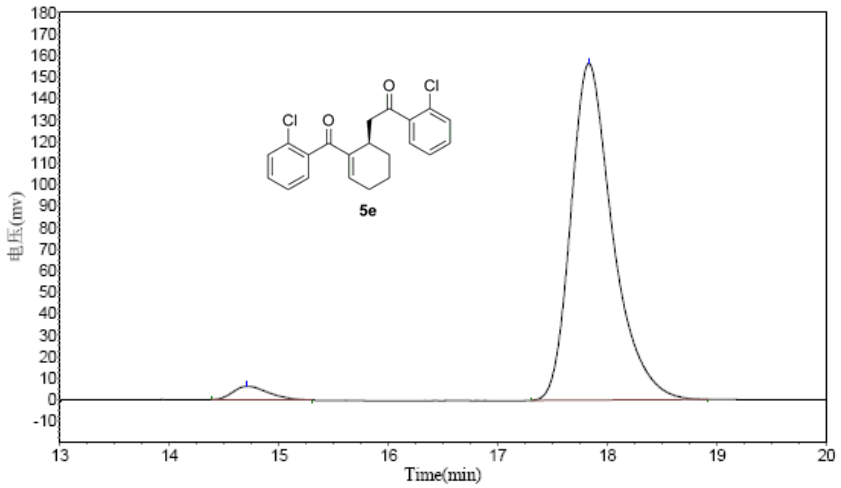
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.718	8395.831	161640.156	2.1127
2		16.607	300430.219	7489170.500	97.8873
Total			308826.050	7650810.656	100.0000



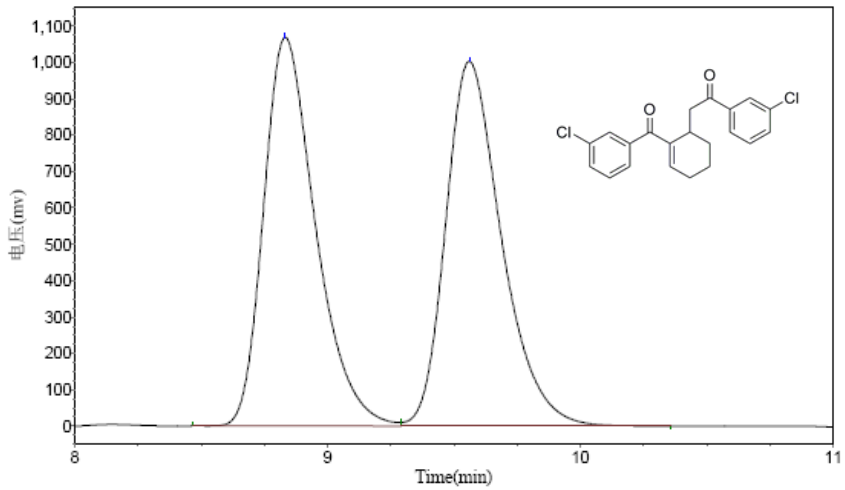
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.660	39912.090	895829.438	49.7862
2		17.792	32965.656	903523.813	50.2138
Total			72877.746	1799353.250	100.0000



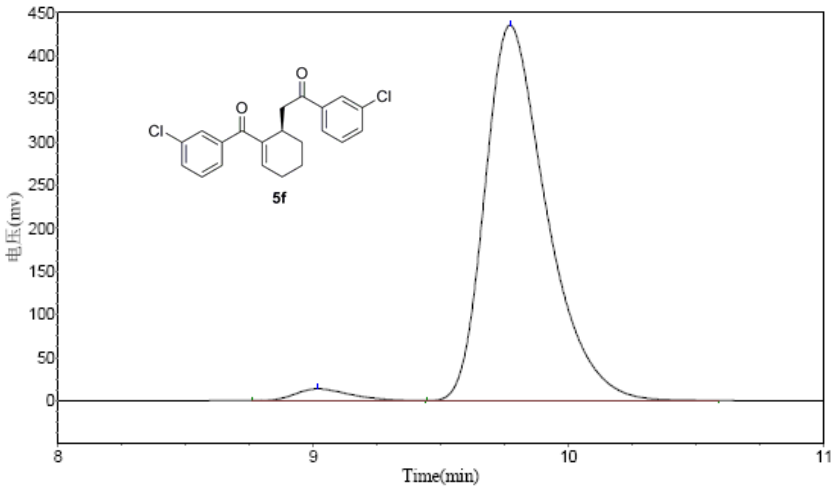
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.712	6371.322	143466.406	3.3424
2		17.830	156382.875	4148861.000	96.6576
Total			162754.197	4292327.406	100.0000



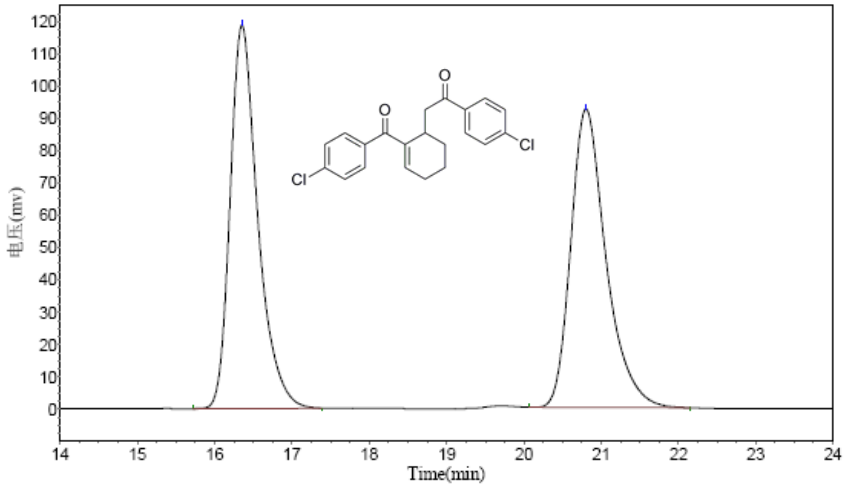
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.833	1067265.375	15230424.000	49.7560
2		9.562	1001654.313	15379817.000	50.2440
Total			2068919.688	30610241.000	100.0000



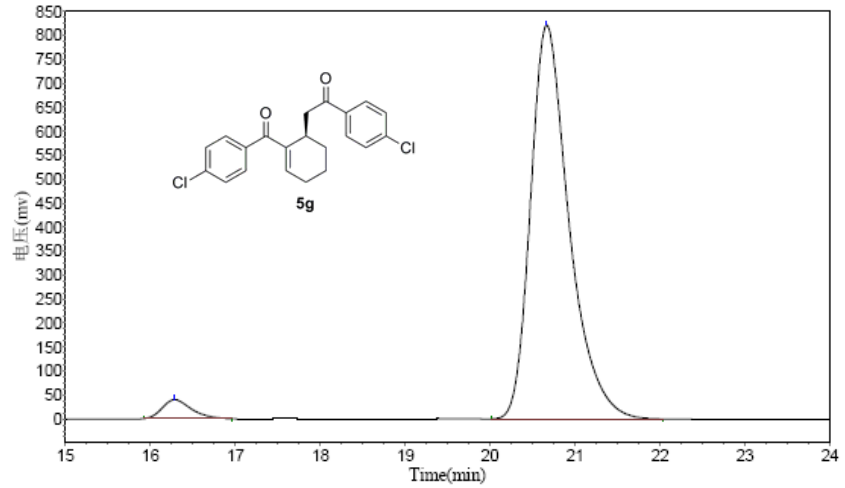
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.018	13635.750	205169.406	2.7351
2		9.772	435153.500	7296094.500	97.2649
Total			448789.250	7501263.906	100.0000



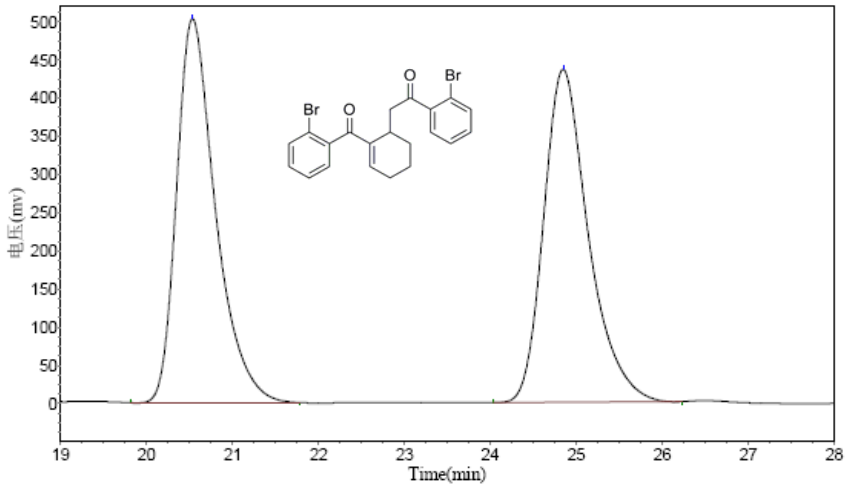
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.353	118732.156	2947821.250	50.1776
2		20.805	92428.422	2926951.250	49.8224
Total			211160.578	5874772.500	100.0000



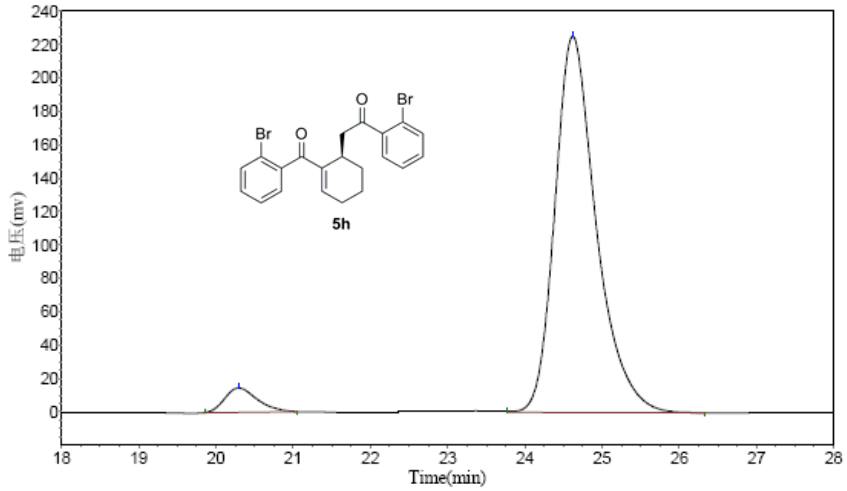
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.287	39446.340	939142.500	3.5002
2		20.667	821168.500	25891868.000	96.4998
Total			860614.840	26831010.500	100.0000



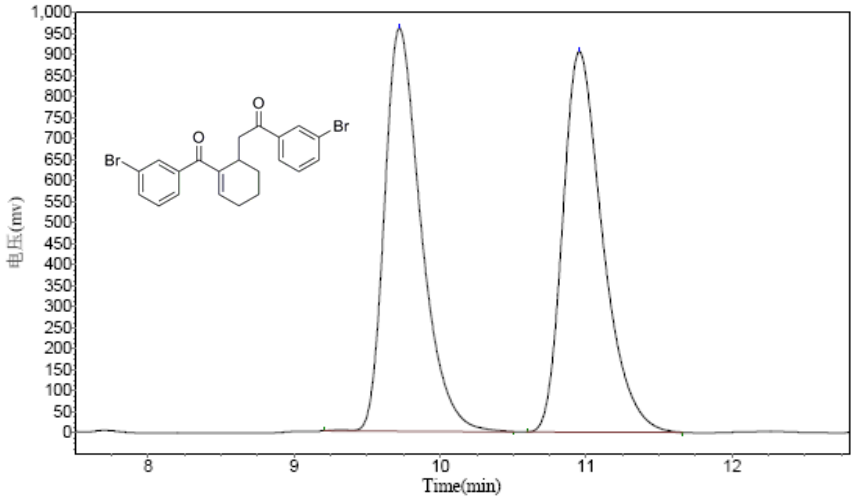
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.537	502859.469	15795092.000	50.0320
2		24.847	435850.219	15774894.000	49.9680
Total			938709.688	31569986.000	100.0000



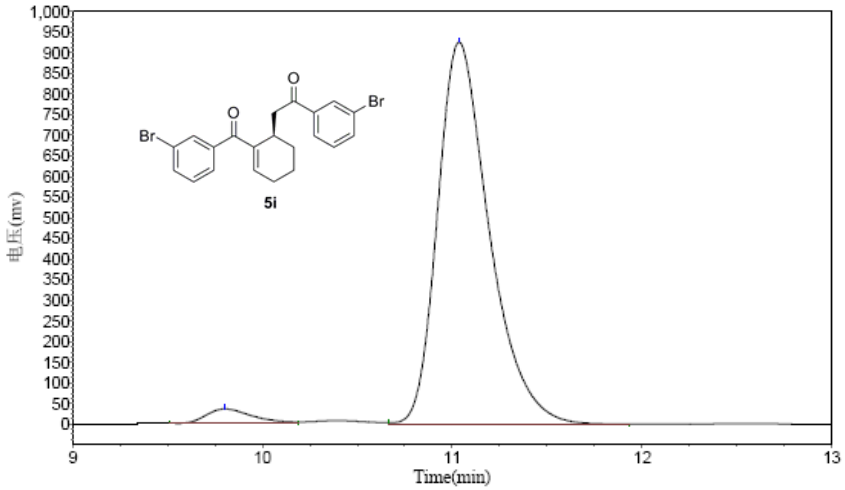
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.295	14579.244	426078.063	4.8296
2		24.622	225278.797	8396130.000	95.1704
Total			239858.041	8822208.063	100.0000



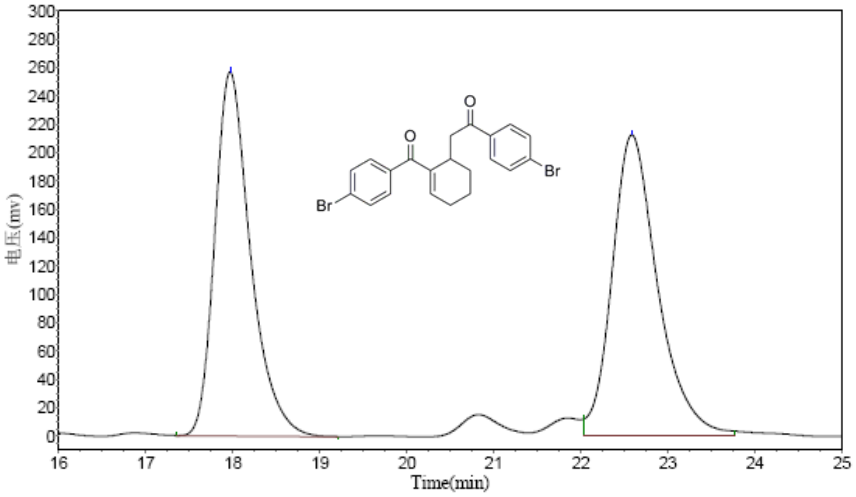
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.722	958337.000	16694626.000	49.2765
2		10.955	905099.188	17184862.000	50.7235
Total			1863436.188	33879488.000	100.0000



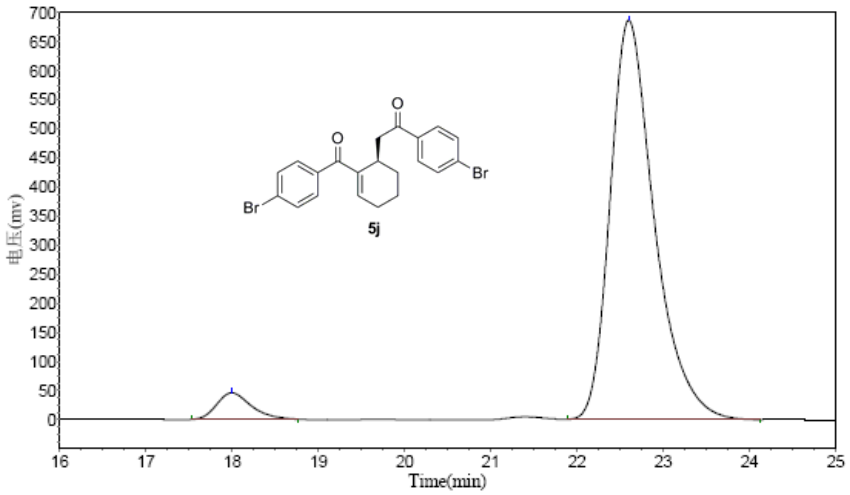
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.802	35838.309	623549.125	3.4438
2		11.037	924918.438	17482804.000	96.5562
Total			960756.746	18106353.125	100.0000



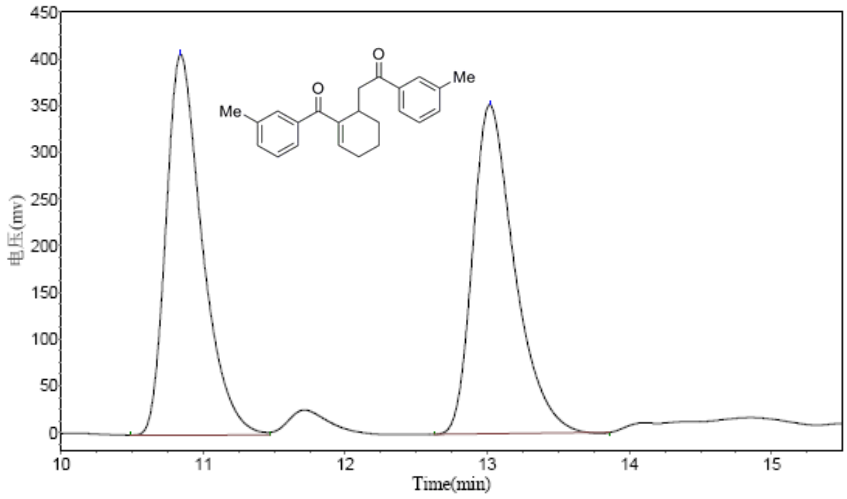
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.970	256794.438	7321348.500	48.6515
2		22.585	212396.688	7727205.500	51.3485
Total			469191.125	15048554.000	100.0000



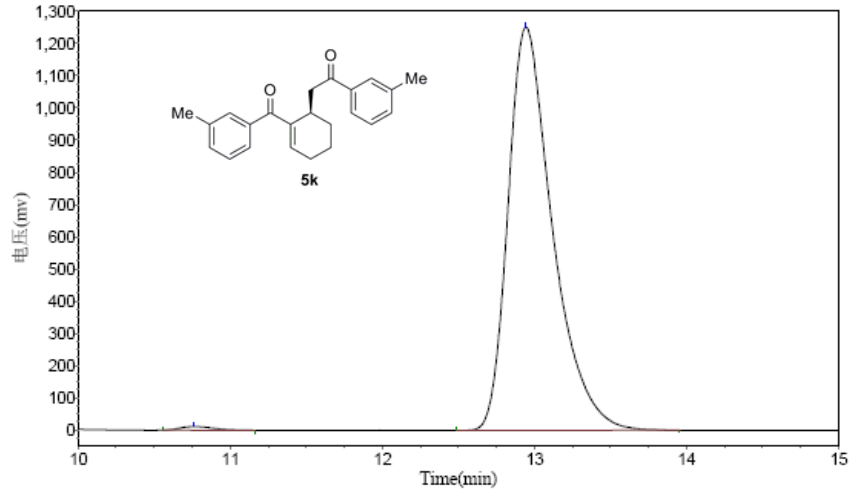
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.997	45404.969	1256551.750	4.8846
2		22.600	686619.250	24467974.000	95.1154
Total			732024.219	25724525.750	100.0000



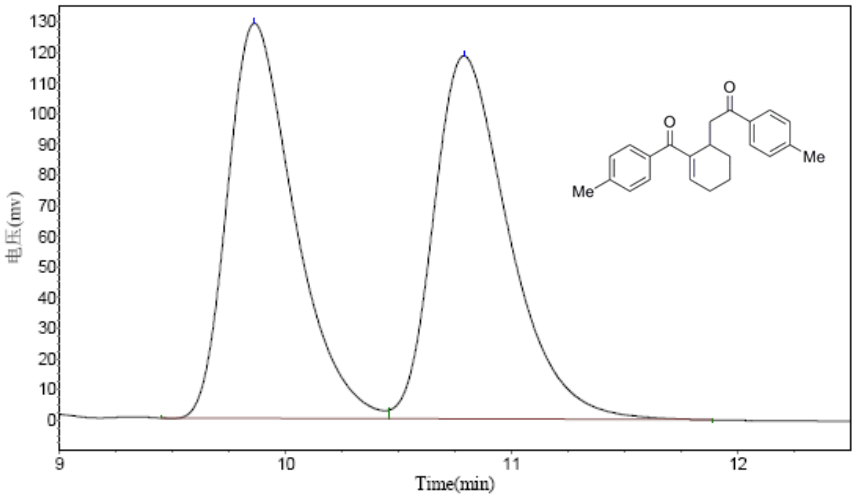
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.842	406964.031	7213235.500	50.0080
2		13.017	351966.563	7210913.500	49.9920
Total			758930.594	14424149.000	100.0000



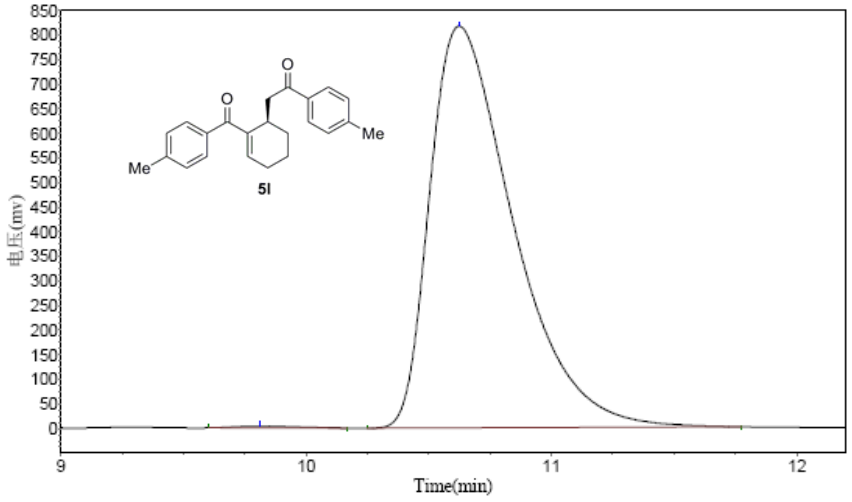
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.762	11591.408	179709.406	0.7012
2		12.943	1250660.750	25448868.000	99.2988
Total			1262252.158	25628577.406	100.0000



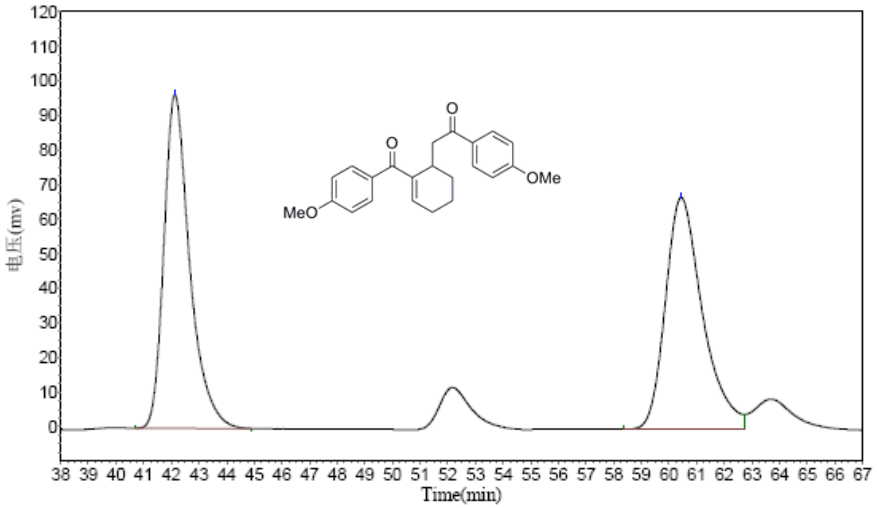
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.862	128894.945	2650824.250	49.1199
2		10.788	118471.469	2745817.750	50.8801
Total			247366.414	5396642.000	100.0000



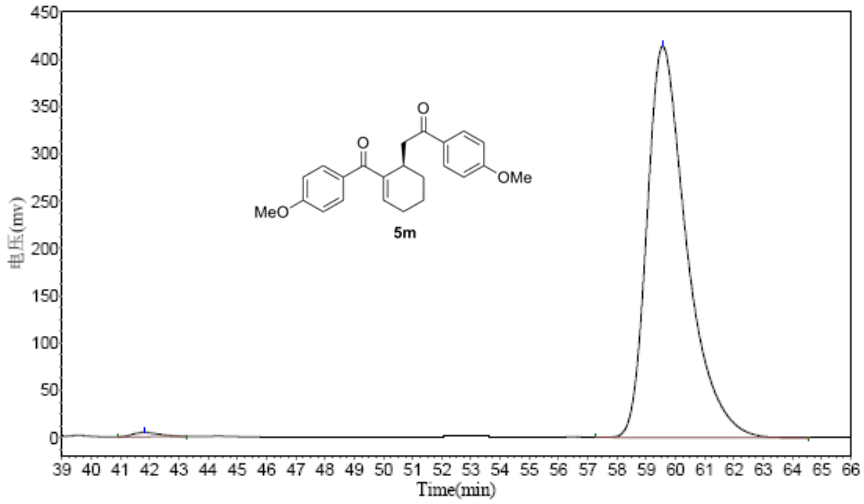
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.812	4206.788	73035.852	0.3771
2		10.623	816714.125	19296428.000	99.6229
Total			820920.913	19369463.852	100.0000



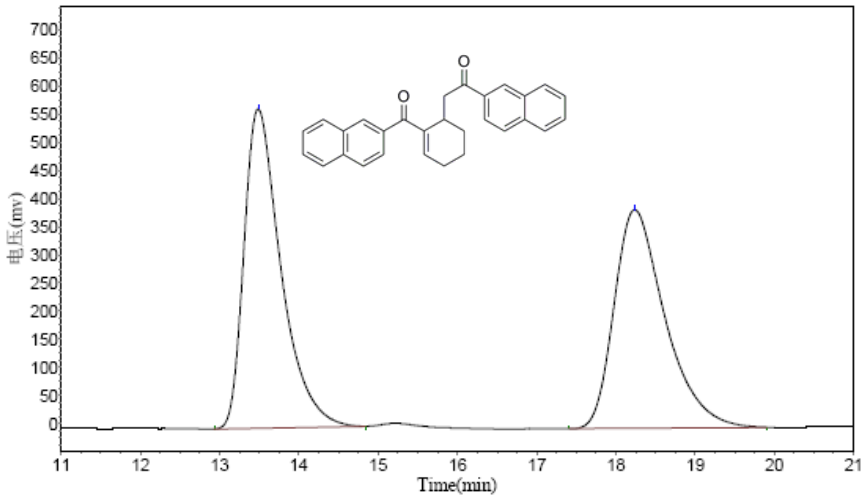
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		42.128	96395.133	6260092.000	49.9916
2		60.437	66995.758	6262185.500	50.0084
Total			163390.891	12522277.500	100.0000



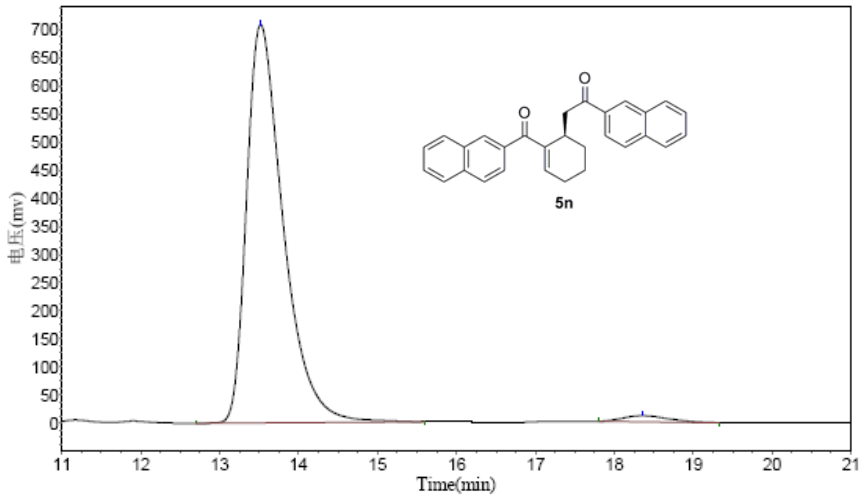
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.825	4672.614	291928.344	0.7437
2		59.560	413548.281	38960360.000	99.2563
Total			418220.895	39252288.344	100.0000



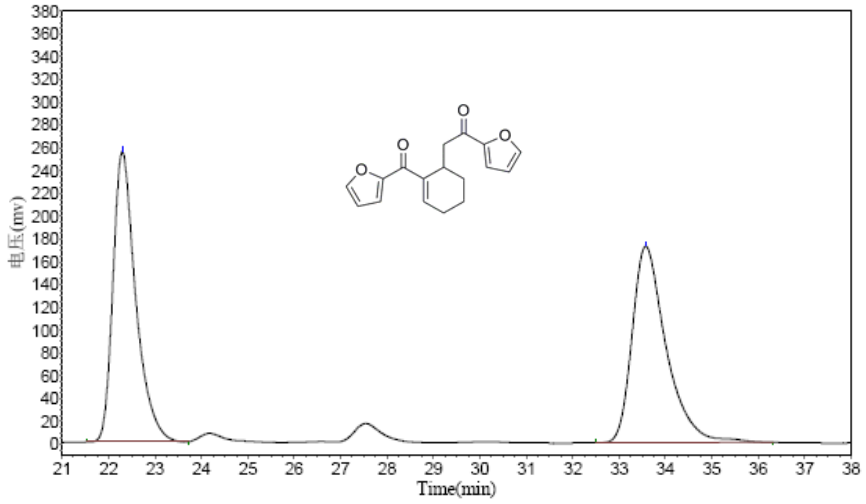
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.487	566405.500	18359796.000	51.4837
2		18.240	387981.594	17301590.000	48.5163
Total			954387.094	35661386.000	100.0000



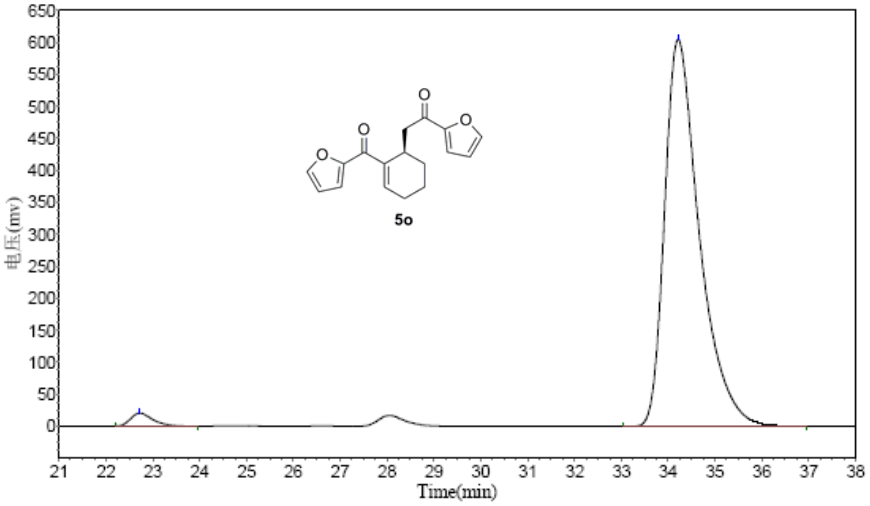
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.520	707749.500	22893766.000	98.1154
2		18.352	10850.768	439749.688	1.8846
Total			718600.268	23333515.688	100.0000



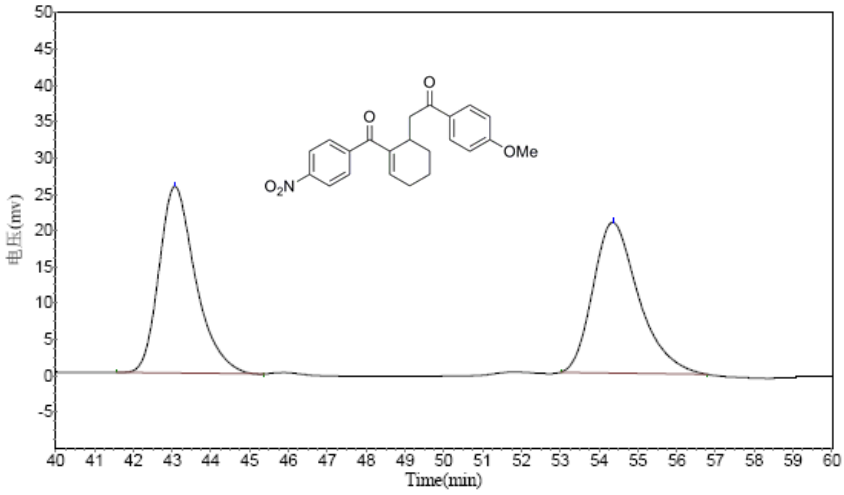
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.298	254376.953	8658969.000	49.6220
2		33.573	172314.844	8790890.000	50.3780
Total			426691.797	17449859.000	100.0000



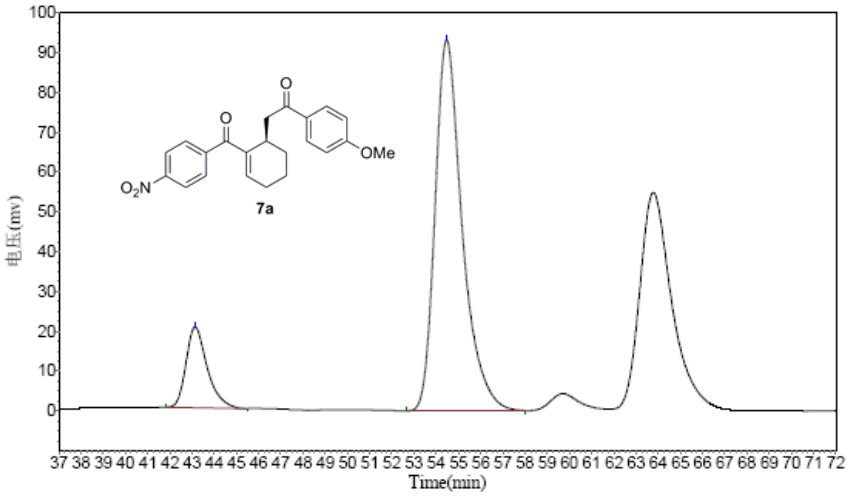
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.723	20651.174	701333.813	2.1953
2		34.212	604542.250	31245878.000	97.8047
Total			625193.424	31947211.813	100.0000



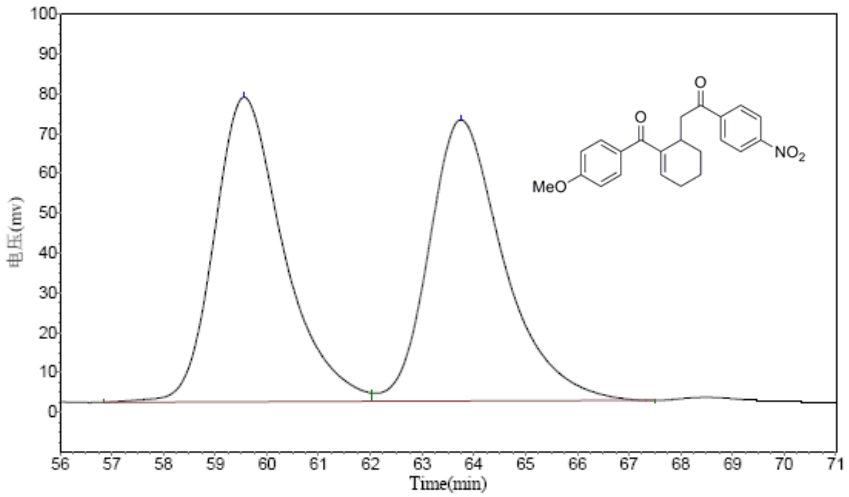
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.068	25692.404	1686344.500	49.7957
2		54.352	20720.178	1700179.875	50.2043
Total			46412.582	3386524.375	100.0000



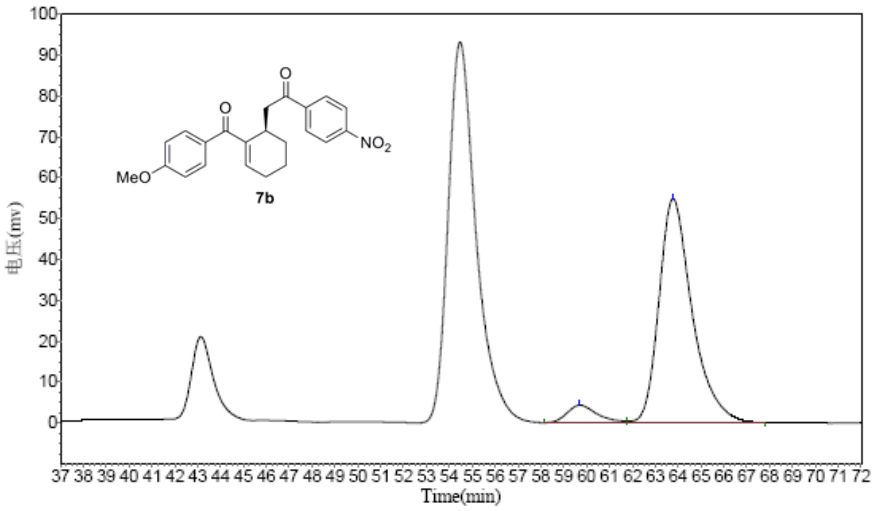
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.128	20262.498	1344219.125	14.5176
2		54.465	93173.492	7915042.500	85.4824
Total			113435.990	9259261.625	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		59.562	76536.961	7140269.500	50.0995
2		63.757	70649.539	7111903.000	49.9005
Total			147186.500	14252172.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		59.700	4268.021	390040.438	6.5849
2		63.788	54858.668	5533226.000	93.4151
Total			59126.688	5923266.438	100.0000