Electronic Supplementary Material (ESI) for ChemComm.

Organocatalytic asymmetric strategies to carbocyclic structures by γ-alkylation-annulation sequences

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Contents

1. General methods

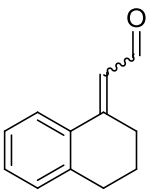
NMR spectra were acquired on a Bruker AVANCE III HD spectrometer running at 400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F and 162 MHz for ^{31}P, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). For ^{19}F NMR and ^{31}P NMR internal standards of $CFCl_3$ and 85% H_3PO_4 were used, respectively. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; bs, broad signal. ^{13}C NMR spectra were acquired in broad band decoupled mode. Mass spectra were recorded on a Bruker MicroTOF-Q High Performance LC-MS system. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet radiation or $KMnO_4$ stain. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka) was used. Optical rotations were measured on a Bellingham+Stanley ADP440+ polarimeter, α values are given in $deg \cdot cm^3 \cdot g^{-1} \cdot dm^{-1}$; concentration c in $g \cdot (100\ ml)^{-1}$. The enantiomeric excess (ee) of the products was determined by chiral stationary phase Waters ACQUITY UPC^2 (Daicel Chiralpak) or HPLC (Daicel Chiralcel IA column). Unless otherwise noted, gradient runs were performed with 100% supercritical CO_2 for 30 s, then going from 99% CO_2 to 60:40 CO_2/solvent over 4 min. Reference samples for UPC^2 analysis were prepared using a mixture of product obtained from reactions with **3** and *ent*-**3**. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification.

2. Synthesis of starting materials

Enals **1** were synthesized from their corresponding ketones, which were commercially available *via* a Horner-Wadsworth-Emmons and DIBAL-H reduction sequence according to the procedures previously reported.[1] Electrophiles **2** were synthesized according to procedures previously reported.[2] Catalyst **3a** was purchased from commercial sources. Catalyst **3b** was synthesized in accordance to literature procedures.[3] Nitrostyrenes **6** were purchased from commercial sources.

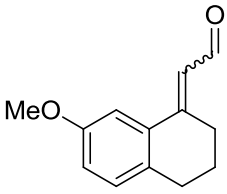
For characterization of *E*/*Z* mixtures, * denotes minor isomer, + denotes overlap of signals from both isomers, while no signs denotes signals of major isomer. For compounds **1** ^{13}C NMR signals are only given for the major isomer. A majority of the enals **1** have already been described in previous publications,[4] however, for the benefit of the reader, characterization data for all enals **1** are provided.

2.1. Characterization data for enals **1**



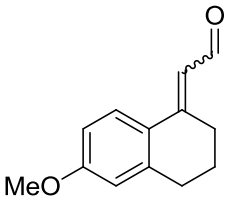
1a

Orange oil obtained as a 5.8:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, *J* = 7.8 Hz, 1H), 9.84* (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.43–7.13^{+} (m, 7H), 6.54 (dt, *J* = 7.9, 1.7 Hz, 1H), 6.07* (dt, *J* = 8.0, 1.4 Hz, 1H), 3.17-3.07 (m, 2H), 2.91^{+} (t, *J* = 6.3 Hz, 4H), 2.67* (td, *J* = 6.5, 1.4 Hz, 2H), 2.24-1.86^{+} (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 157.4, 140.3, 133.4, 130.7, 129.7, 126.7, 125.6, 122.8, 30.2, 27.2, 23.1. HRMS (ESI+) *m*/*z* calcd. for $C_{12}H_{12}O$ $[M+H]^{+}$: 173.0961; found: 173.0958.



1b

Orange solid obtained as a 4.2:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, *J* = 7.8 Hz, 1H), 9.92* (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.13–7.07^{+} (m, 2H), 6.94^{+} (td, *J* = 8.6, 2.7 Hz, 2H), 6.86* (d, *J* = 2.7 Hz, 1H), 6.51 (dt, *J* = 7.9, 1.7 Hz, 1H), 6.06* (dt, *J* = 8.1, 1.4 Hz, 1H), 3.81 (s, 3H), 3.80* (s, 3H), 3.09 (ddd, *J* = 7.8, 4.9, 1.7 Hz, 2H), 2.83^{+} (t, *J* = 6.3 Hz, 4H), 2.64* (td, *J* = 6.5, 1.3 Hz, 2H), 1.97^{+} (dq, *J* = 12.5, 6.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 158.2, 157.5, 134.1, 132.8, 130.6, 122.8, 118.1, 109.1, 55.5, 29.4, 27.1, 23.4. HRMS (ESI+) *m*/*z* calcd. for $C_{13}H_{14}O_2$ $[M+H]^{+}$: 203.1067; found: 203.1065.



1c

Orange solid obtained as a 5.6:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (d, *J* = 7.9 Hz, 1H), 9.81* (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.30* (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.76–6.74* (m, 2H), 6.68 (d, *J* = 2.7 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 6.00* (d, *J* = 8.0 Hz, 1H), 3.84^{+} (s, 6H), 3.10 (td, *J* = 6.4, 1.6 Hz, 2H), 2.87^{+} (t, *J* = 6.2 Hz, 4H), 2.64* (t, *J* = 6.3 Hz, 2H), 1.96^{+} (p, *J* = 6.3 Hz, 4H). ^{13}C NMR (100 MHz,

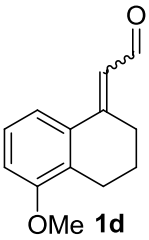
[1] H. Jiang, K. S. Halskov, T. K. Johansen and K. A. Jørgensen, *Chem.–Eur. J.*, 2011, **17**, 3842.

[2] Diethyl (3-oxo-3-phenylprop-1-en-2-yl)phosphonate (**2a**): C. De Fusco, T. Fuoco, A. Lattanzi and G. Croce, *Org. Lett.*, 2012, **14**, 4078; ethyl 2-(diethoxyphosphoryl)acrylate (**2b**): A. T. Biju, M. Padmanaban, N. E. Wurz and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 8412; tetraethyl ethene-1,1-diylbis(phosphonate) (**2c**) was purchased from commercial sources; diethyl (1-(phenylsulfonyl)vinyl)phosphonate (**2d**): W. Flitsch and W. Lubisch, *Chem. Ber.*, 1984, **117**, 1424.

[3] Ł. Albrecht, G. Dickmeiss, F. C. Acosta, C. Rodríguez-Escrich, R. L. Davis and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2012, **134**, 2543.

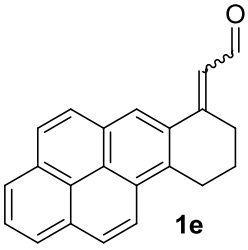
[4] K. S. Halskov, B. S. Donslund, S. Barfüsser and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2014, **53**, 4137.

$CDCl_3$) δ 191.1, 161.6, 157.3, 142.5, 127.5, 126.0, 121.0, 113.8, 113.4, 55.5, 30.7, 27.2, 23.1. HRMS (ESI+) *m*/*z* calcd. for $C_{13}H_{14}O_2$ $[M+H]^+$: 203.1067; found: 203.1067.



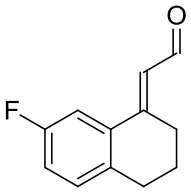
1d

Orange solid obtained as a 3.3:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (d, *J* = 7.9 Hz, 1H), 9.89* (d, *J* = 7.9 Hz, 1H), 7.29$^+$ (d, *J* = 8.1 Hz, 3H). 7.21$^+$ (t, *J* = 8.1 Hz, 3H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.05* (d, *J* = 8.1 Hz, 1H), 3.86* (s, 3H), 3.85 (s, 3H), 3.08 (m, 2H), 2.85-2.78$^+$ (m, 4H), 2.61-2.55* (m, 2H), 2.06* (k, *J* = 6.4 Hz, 2H), 1.98 (k, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5*, 191.2, 161.5*, 158.1, 157.2, 157.1*, 134.5, 134.0*, 128.9, 128.2*, 126.6, 126.0*, 125.9*, 123.3*, 123.1, 117.4, 111.7*, 111.4, 55.5, 55.4*, 34.7*, 26.5, 23.6*, 23.2, 22.9*, 22.5*. HRMS (ESI+) *m*/*z* calcd. for $C_{13}H_{14}O_2$ $[M+H]^+$: 203.1067; found: 203.1068.



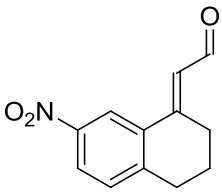
1e

Orange solid obtained as a 5.7:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (d, *J* = 7.8 Hz, 1H), 10.00* (d, *J* = 8.1 Hz, 1H), 8.46 (s, 1H), 8.33-7.95$^+$ (m, 15H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.29* (d, *J* = 8.1 Hz, 1H), 3.64-3.58$^+$ (m, 4H), 3.33-3.26 (m, 2H), 2.88–2.82* (m, 2H), 2.39-2.24$^+$ (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 159.1, 133.3, 131.7, 131.3, 131.2, 129.7, 129.1, 128.1, 127.8, 127.4, 126.7, 125.9, 125.4, 125.3, 124.4, 124.0, 123.0, 122.0, 26.9, 26.6, 23.3. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{16}O$ $[M+H]^+$: 297.1274; found: 297.1275.



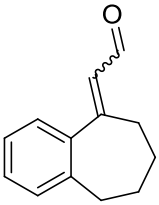
1f

Yellow solid obtained as a single isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (d, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 10.5, 2.7 Hz, 1H), 7.13 (dd, *J* = 8.3, 5.8 Hz, 1H), 7.01 (dt, *J* = 8.3, 2.7 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 3.08 (t, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 1.95 (k, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 161.3 (d, *J* = 244.1 Hz), 155.7 (d, *J* = 3.3 Hz), 135.8 (d, *J* = 2.8 Hz), 134.7 (d, *J* = 7.0 Hz), 130.9 (d, *J* = 8.1 Hz), 123.0, 117.6 (d, *J* = 21.6 Hz), 111.4 (d, *J* = 22.0 Hz), 29.3, 26.6, 22.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.68-(-115.78) (m). HRMS (ESI+) *m*/*z* calcd. for $C_{12}H_{11}FO$ $[M+H]^+$: 191.0867; found: 191.0868.



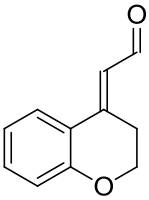
1g

Yellow solid obtained as a single isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (d, *J* = 7.3 Hz, 1H), 8.56 (d, *J* = 2.3 Hz, 1H), 8.15 (dd, *J* = 8.5; 2.3 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 7.3 Hz, 1H), 3.16 (t, *J* = 6.3 Hz, 2H), 3.00 (t, *J* = 6.3 Hz, 2H), 2.03 (k, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 154.0, 147.1, 147.0, 134.8, 130.8, 124.5, 124.3, 120.7, 30.3, 26.7, 22.4. HRMS (ESI+) *m*/*z* calcd. for $C_{12}H_{11}NO_3$ $[M+H]^+$: 218.0812; found: 218.0812



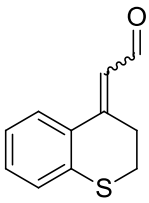
1h

Orange oil obtained as a 3.1:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (d, *J* = 7.9 Hz, 1H), 9.44* (d, *J* = 8.2 Hz, 1H), 7.30–7.10$^+$ (m, 8H), 6.18* (d, *J* = 8.3 Hz, 1H), 6.08 (d, *J* = 8.0, 1H), 2.99 (t, *J* = 6.0 Hz, 2H), 2.85–2.79 (m, 2H), 2.77* (t, *J* = 6.0 Hz, 2H), 2.00–1.72$^+$ (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 166.9, 139.8, 129.7, 129.2, 129.1, 128.2, 127.5, 126.7, 34.6, 30.1, 27.6, 26.6. HRMS (ESI+) *m*/*z* calcd. for $C_{13}H_{14}O$ $[M+H]^+$: 187.1117; found: 187.1118.



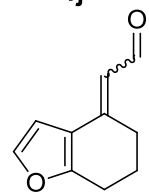
1i

Yellow solid obtained as a single isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.0, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 7.6, 1H), 4.31 (t, *J* = 6.0 Hz, 2H), 3.25 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 156.8, 150.1, 132.8, 125.3, 121.3, 119.9, 119.8, 118.2, 65.3, 26.0. HRMS (ESI+) *m*/*z* calcd. for $C_{11}H_{10}O_2$ $[M+H]^+$: 175.0754; found: 175.0754.



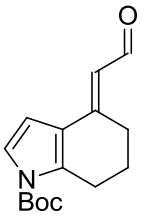
1j

Orange solid obtained as a 5.6:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (d, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28–7.22 (m, 1H), 7.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.09–7.13 (m, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 3.47–3.42 (m, 2H), 3.15–3.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 154.2, 136.8, 132.0, 130.7, 127.9, 127.6, 125.1, 124.5, 27.1, 26.6. HRMS (ESI+) *m*/*z* calcd. for $C_{11}H_{10}OS$ $[M+H]^+$: 191.0525; found: 191.0527.



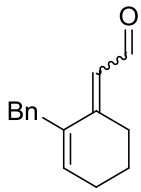
1k

Brown solid obtained as a 2.1:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26* (d, *J* = 8.5 Hz, 1H), 10.08 (d, *J* = 8.2 Hz, 1H), 7.36* (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 6.64* (d, *J* = 2.1 Hz, 1H), 6.51 (d, *J* = 2.1 Hz, 1H), 6.09 (d, *J* = 8.2 Hz, 1H), 5.82* (d, *J* = 8.5 Hz, 1H), 3.00–2.94 (m, 2H), 2.80$^+$ (t, *J* = 6.2 Hz, 4H), 2.56–2.53* (m, 2H), 2.05$^+$ (p, *J* = 6.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 158.5, 152.9, 142.7, 120.8, 119.5, 106.4, 25.4, 23.7, 23.1. HRMS (ESI+) *m*/*z* calcd. for $C_{10}H_{10}O_2$ $[M+H]^+$: 163.0759; found: 163.0754.



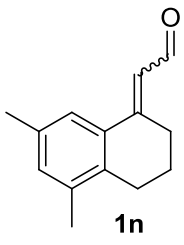
1l

Orange solid obtained as a single isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 6.37 (d, *J* = 3.6 Hz, 1H), 6.16 (d, *J* = 8.3 Hz, 1H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.97–2.92 (m, 2H), 2.00 (p, *J* = 6.2 Hz, 2H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 154.3, 149.0, 137.6, 122.9, 122.0, 120.2, 107.0, 84.7, 28.2 (3C), 25.4, 25.0, 23.4. HRMS (ESI+) *m*/*z* calcd. for $C_{15}H_{19}NO_3$ $[M+H]^+$: 262.1443; found: 262.1439.



1m

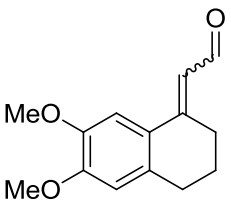
For synthesis, see previous reports.[5] The compound was obtained as a 9:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.10 (d, *J* = 7.9 Hz, 1H), 10.04* (d, *J* = 8.4 Hz, 1H), 7.32–7.11$^+$ (m, 10H), 6.11 (t, *J* = 4.5 Hz, 1H), 6.01* (t, *J* = 4.5 Hz, 1H) 5.96 (d, *J* = 7.9 Hz, 1H), 5.73* (d, *J* = 8.4 Hz, 1H), 3.83* (s, 2H), 3.56 (s, 2H), 2.96–2.90 (m, 2H) 2.65–2.58*, (m, 1H), 2.46–2.41* (m, 2H), 2.36-2.28$^+$ (m, 3H), 1.88–1.78$^+$ (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.4, 156.0, 139.7, 139.1, 136.0, 128.5 (2C), 128.4 (2C), 126.2, 123.2, 39.1, 26.5, 26.1, 22.2. HRMS (ESI+) *m*/*z* calcd. for $[C_{15}H_{16}O+Na]^+$: 235.1093; found 235.1093.



1n

Yellow solid obtained as a 11.7:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (d, *J* = 8.0 Hz, 1H), 9.85* (d, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.10* (s, 1H), 7.07 (s, 1H), 6.99* (s, 1H), 6.51 (d, *J* = 8.0, 1H), 6.04* (d, *J* = 8.0 Hz, 1H), 3.07–3.01 (m, 2H), 2.75$^+$ (t, *J* = 6.4 Hz, 4H), 2.61–2.56* (m, 2H), 2.32$^+$ (s, 6H), 2.24$^+$ (s, 6H), 2.12-2.05* (m, 2H), 2.06–1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 159.0, 136.8, 135.4, 135.3, 133.5, 133.3, 123.8, 122.6, 26.6, 26.5, 23.1, 21.0, 19.5. HRMS (ESI+) *m*/*z* calcd. for $C_{14}H_{16}O$ $[M+H]^+$: 201.1274; found: 201.1276.

[5] K. S. Halskov, T. K. Johansen, R. L. Davis, M. Steurer, F. Jensen and K. A. Jørgensen, *J. Am. Chem. Soc*., 2012, **134**, 12943.



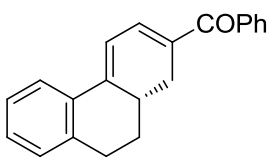
1o

Orange solid obtained as a 5:1 *E*/*Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 6.63 (s, 1H), 6.45 (dt, *J* = 8.0, 1.6 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.08 (ddd, *J* = 8.0, 4.9, 1.7 Hz, 2H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.00–1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 157.1, 151.5, 147.7, 134.4, 125.1, 120.8, 111.3, 107.3, 55.9, 55.9 , 29.8, 26.8, 23.1. HRMS (ESI+) *m*/*z* calcd. for $C_{14}H_{16}O_3$ $[M+H]^+$: 233.1178; found: 201.1177.

3. General procedures for the organocatalytic reactions

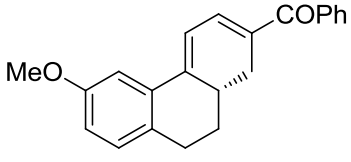
3.1. Asymmetric formation of chiral carbocycles **5**

A glass vial equipped with a magnetic stirring bar was charged with enal **1** (0.10 mmol, 1.0 eq), catalyst **3a** (0.005 mmol, 0.05 eq), $PhCO_2H$ (0.005 mmol, 0.05 eq) and $CHCl_3$ (0.3 mL). Electrophile **2** (0.12 mmol, 1.2 eq) was then added and the mixture was stirred for 24 h at ambient temperature. The mixture was then diluted with 0.6 mL $CHCl_3$ and 1.5 eq Cs_2CO_3 was added. The mixture was stirred for 2 h at ambient temperature and subsequently subjected directly to FC on silica gel to yield product **5**.
For the following compounds altered conditions were applied: Compounds **5c**,**h** were synthesized with 10 mol% of **3a** and 10 mol% $PhCO_2H$. Compound **5e** was synthesized with a reaction time of 4 h for the second step. Compounds **5j**,**l** were synthesized with a reaction time of 48 h for the first step. Compound **5m** was synthesized with 20 mol% of **3a** and in the absence of $PhCO_2H$.



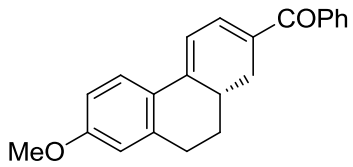
5a

Isolated as a yellow oil by FC on silica gel using Et_2O/pentane 3:97 to 1:19 as eluent. $[\alpha]_D^{22}$ = −488.2 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (m, 1H), 7.71–7.66 (m, 2H), 7.55–7.49 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.25–7.14 (m, 3H), 6.86 (dd, *J* = 6.0, 2.7 Hz, 1H), 6.77 (dd, *J* = 6.2, 2.7 Hz, 1H), 3.04 (dd, *J* = 16.6, 7.1 Hz, 1H), 2.94–2.81 (m, 2H), 2.81–2.68 (m, 1H), 2.31–2.14 (m, 2H), 1.65 (qd, *J* = 12.2, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 144.2, 139.4, 139.0, 138.7, 135.4, 132.1, 131.2, 129.5, 129.0 (2C), 128.6, 128.1 (2C), 126.4, 124.1, 116.2, 36.6, 30.5, 29.8, 29.8. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{18}O$ $[M+H]^+$: 287.1430; found: 287.1429. UPC^2: IB, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{minor} = 4.03 min; t_{major} = 4.19 min.



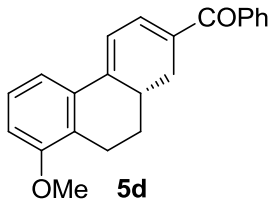
5b

Isolated as a yellow oil by FC on silica gel using Et_2O/pentane 1:14 as eluent. $[\alpha]_D^{22}$ = −318.7 (c 0.2 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.56–7.50 (m, 1H), 7.48–7.42 (m, 2H), 7.28–7.24 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.88–6.81 (m, 2H), 6.73 (dd, *J* = 6.2, 2.7 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, *J* = 16.6, 7.1 Hz, 1H), 2.89–2.64 (m, 3H), 2.30–2.13 (m, 2H), 1.68–1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 158.3, 144.3, 139.0, 138.8, 135.7, 133.1, 132.2, 131.4, 130.5, 129.1 (2C), 128.2 (2C), 116.6, 115.5, 108.5, 55.5, 36.6, 30.3, 30.0, 29.8. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{20}O_2$ $[M+H]^+$: 317.1536; found: 317.1537. UPC^2: IB, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.39 min; t_{minor} = 4.17 min.



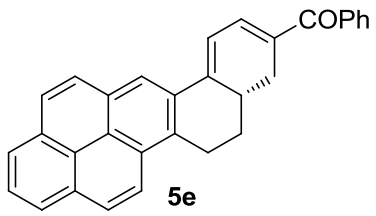
5c

Isolated as a yellow oil by FC on silica gel using Et_2O/pentane 1:9 as eluent. $[\alpha]_D^{22}$ = −697.4 (*c* 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 1H), 7.69–7.63 (m, 2H), 7.54–7.48 (m, 1H), 7.47–7.40 (m, 2H), 6.85 (dd, *J* = 6.2, 2.7 Hz, 1H), 6.78 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 6.62 (dd, *J* = 6.2, 2.6 Hz, 1H), 3.83 (s, 3H), 3.03 (dd, *J* = 16.5, 7.1 Hz, 1H), 2.85 (dd, *J* = 8.7, 3.5 Hz, 2H), 2.77–2.63 (m, 1H), 2.28–2.12 (m, 2H), 1.71–1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 160.0, 144.5, 141.2, 139.7, 138.9, 134.2, 131.0, 128.9 (2C), 128.0 (2C), 125.9, 125.1, 114.2, 113.4, 113.3, 55.3, 36.5, 30.8, 30.0, 29.7. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{20}O_2$ $[M+H]^+$: 317.1536; found: 317.1541. UPC^2: IA, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{minor} = 5.81 min; t_{major} = 6.14 min.



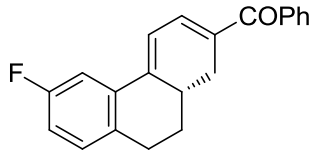
5d

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 1:20 as eluent. $[\alpha]_D^{22}$ = −280.0 (*c* 1.2 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.67 (s, 1H), 7.55–7.49 (m, 1H), 7.47–7.37 (m, 3H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.84 (dd, *J* = 6.2, 2.8 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.75 (dd, *J* = 6.2 Hz, 2.3 Hz, 1H), 3.85 (s, 3H), 3.17 (ddd, *J* = 17.0, 4.1, 2.6 Hz, 1H), 3.04 (dd, *J* = 16.6, 7.3 Hz, 1H), 2.80–2.63 (m, 1H), 2.45 (ddd, *J* = 17.0, 12.9, 4.2 Hz, 1H) 2.32 (m, 2H), 1.64–1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 157.2, 144.4, 139.0, 138.8, 135.3, 133.2, 131.2, 129.0 (2C), 128.5, 128.1 (2C), 126.5, 116.8, 116.3, 109.7, 55.5, 36.0, 29.9, 29.3, 22.8. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{20}O_2$ $[M+H]^+$: 317.1536; found: 317.1537. UPC^2: ID, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 5.07 min; t_{minor} = 5.21 min



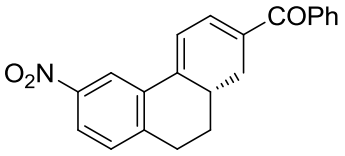
5e

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 1:10 as eluent. $[\alpha]_D^{22}$ = −120.2 (*c* 2.0 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.32 (d, *J* = 9.2 Hz, 1H), 8.19–8.10 (m, 3H), 8.01–7.96 (m, 3H), 7.76–7.71 (m, 2H), 7.59–7.45 (m, 3H), 7.14 (dd, *J* = 6.1, 2.6 Hz, 1H), 6.98 (dd, *J* = 6.1, 2.6 Hz, 1H), 3.90 (dt, *J* = 16.6, 3.4 Hz, 1H), 3.77 (ddd, *J* = 17.0, 13.0, 4.7 Hz, 1H), 3.18 (dd, *J* = 17.0, 7.3 Hz, 1H), 3.04–2.89 (m, 1H), 2.54–2.33 (m, 2H), 1.84 (dq, *J* = 13.0, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 145.0, 139.0, 138.8, 135.4, 133.9, 133.3, 131.6, 131.3, 131.1, 129.9, 129.7, 129.1 (2C), 128.2 (2C), 128.0, 127.8, 127.2, 126.3, 125.2, 125.1, 124.9, 124.7, 123.2, 120.7, 117.6, 36.1, 30.0, 29.8, 26.4. HRMS (ESI+) *m*/*z* calcd. for $C_{31}H_{22}O$ $[M+H]^+$: 411.1743; found: 411.1743. HPLC: IA, 95:5 hexane/*i*-PrOH, 1.0 mL·min^{-1}; t_{major} = 23.68 min; t_{minor} = 22.45 min.



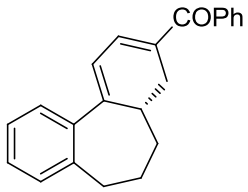
5f

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 1:10 as eluent. $[\alpha]_D^{22}$ = −260.6 (*c* 1.3 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.56–7.50 (m, 1H), 7.48–7.37 (m, 3H), 7.11 (dd, *J* = 8.4, 7.0 Hz, 1H), 6.93 (dt, *J* = 8.4, 2.7 Hz, 1H), 6.84 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.69 (dd, *J* = 6.1, 2.7 Hz, 1H), 3.04 (dd, *J* = 16.6, 7.0 Hz, 1H), 2.92–2.64 (m, 3H), 2.31–2.13 (m, 2H), 1.61 (dq, *J* = 12.8, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 161.6 (d, *J* = 244.4 Hz), 143.1 (d, *J* = 3.0 Hz), 138.5, 138.3, 136.0, 134.9 (d, *J* = 2.8 Hz), 133.9 (d, *J* = 7.1 Hz), 131.4, 130.8 (d, *J* = 7.8 Hz), 129.0 (2C), 128.2 (2C), 117.3, 115.8 (d, *J* = 22.1 Hz), 110.1 (d, *J* = 21.9 Hz), 36.2, 29.84, 29.79, 29.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.35–(−116.46) (m). HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{17}FO$ $[M+H]^+$: 305.1336; found: 305.1340. UPC^2: IB, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.79 min; t_{minor} = 3.68 min.



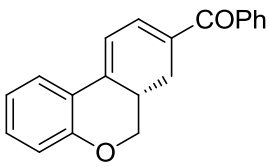
5g

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 1:9 to 3:17 as eluent. $[\alpha]_D^{22}$ = –369.8 (*c* 0.53 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.3 Hz, 1H), 8.03 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.72–7.66 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.43 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.90 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.86 (dd, *J* = 6.1, 2.7 Hz, 1H), 3.11–2.71 (m, 4H), 2.33–2.18 (m, 2H), 1.65 (qd, *J* = 12.8, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 146.9, 145.8, 141.3, 138.2, 137.6, 136.8, 133.6, 131.6, 130.4, 129.0 (2C), 128.2 (2C), 122.4, 119.2, 118.7, 35.9, 30.6, 29.6, 28.9. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{17}NO_3$ $[M+H]^+$: 332.1281, found: 332.1284. UPC^2: IB, CO_2/MeOH gradient, 3.0 mL·min^{-1}, t_{major} = 4.94 min, t_{minor} = 4.78 min.



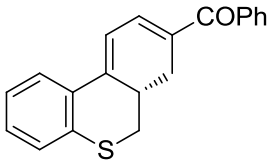
5h

Isolated as a pale yellow oil by FC on silica gel using Et_2O/pentane 3:97 to 1:19 as eluent. $[\alpha]_D^{22}$ = –181.0 (*c* 0.4 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.66 (m, 2H), 7.56–7.49 (m, 1H), 7.48–7.41 (m, 2H), 7.33–7.28 (m, 1H), 7.25–7.19 (m, 2H), 7.17–7.11 (m, 1H), 6.79 (d, *J* = 5.8 Hz, 1H), 6.18 (d, *J* = 5.7 Hz, 1H), 2.91–2.71 (m, 4H), 2.69–2.56 (m, 1H), 1.90–1.75 (m, 3H), 1.71–1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 153.1, 140.9, 139.7, 138.7, 137.8, 134.3, 131.3, 129.4, 129.0 (2C), 128.1, 128.1 (2C), 127.4, 126.3, 120.9, 36.1, 33.6, 30.2, 29.0, 25.3. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{20}O$ $[M+H]^+$: 301.1587; found: 301.1591. UPC^2: IA, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{minor} = 3.60 min; t_{major} = 3.67 min.



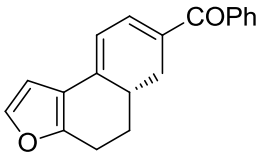
5i

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 3:22 to 1:9 as eluent. $[\alpha]_D^{22}$ = –476.5 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.64 (m, 2H), 7.61 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.55–7.50 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.21 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 6.94 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 6.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.81 (dd, *J* = 6.1, 2.8 Hz, 1H), 6.57 (dd, *J* = 6.2, 2.6 Hz, 1H), 4.43 (dd, *J* = 10.6, 5.3 Hz, 1H), 4.00 (dd, *J* = 12.2, 10.6 Hz, 1H), 3.49–3.35 (m, 1H), 2.92 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.23 (ddd, *J* = 19.2, 16.7, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 156.5, 139.0, 138.4, 138.2, 133.4, 131.4, 130.8, 128.9 (2C), 128.1 (2C), 124.2, 121.6, 120.0, 118.2, 113.7, 70.5, 35.7, 23.9. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{16}O_2$ $[M+H]^+$: 289.1223; found: 289.1224. UPC^2: IA, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{minor} = 5.26 min; t_{major} = 5.48 min.



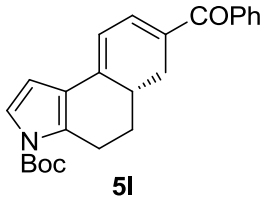
5j

Isolated as an yellow oil by FC on silica gel using CH_2Cl_2/pentane 1:1 to 3:1 as eluent. $[\alpha]_D^{22}$ = –365.0 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.64 (m, 3H), 7.56–7.50 (m, 1H), 7.48–7.42 (m, 2H), 7.24 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.16 (td, *J* = 7.5, 1.7 Hz, 1H), 7.11 (td, *J* = 7.5, 1.7 Hz, 1H), 6.81 (dd, *J* = 6.0, 2.6 Hz, 1H), 6.63 (dd, *J* = 6.1, 2.7 Hz, 1H), 3.38–3.23 (m, 1H), 3.05–2.84 (m, 3H), 2.56–2.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 142.0, 138.3, 138.3, 135.8, 135.5, 132.4, 131.5, 129.0, 128.9 (2C), 128.5, 128.2 (2C), 125.9, 125.6, 119.0, 40.6, 32.2, 29.2. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{16}OS$ $[M+H]^+$: 305.0995; found: 305.0997. UPC^2: ID, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{major} = 5.73 min; t_{minor} = 6.19 min.



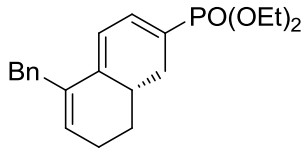
5k

Isolated as a yellow oil by FC on silica gel using Et_2O/ pentane 1:9 as eluent. $[\alpha]_D^{22}$ = −108.0 (c 0.2 in CH_2Cl_2). H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 2H), 7.52–7.47 (m, 1H), 7.46–7.39 (m, 2H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 6.11 (dd, *J* = 6.1, 2.3 Hz, 1H), 3.11 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.93–2.87 (m, 1H), 2.84–2.75 (m, 1H), 2.73–2.62 (m, 1H), 2.33–2.25 (m, 1H), 2.22–2.13 (m, 1H), 1.75 (qd, *J* = 12.6, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 156.6, 142.6, 140.8, 139.7, 139.1, 133.1, 131.2, 129.1 (2C), 128.2 (2C), 118.3, 114.0, 106.2, 35.0, 30.9, 29.3, 23.6. HRMS (ESI+) *m/z* calcd. for $C_{19}H_{16}O_2$ $[M+H]^+$: 277.1223; found: 277.1221. UPC^2: IA, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.25 min; t_{minor} = 4.06 min.



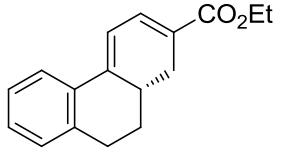
5l

Isolated as a yellow solid by FC on silica gel using Et_2O/pentane 1:1 as eluent. $[\alpha]_D^{22}$ = −196.9 (*c* 0.6 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.59 (m, 2H), 7.52–7.45 (m, 1H), 7.45–7.39 (m, 2H), 7.20 (d, *J* = 3.5 Hz, 1H), 6.81 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.36 (d, *J* = 3.6 Hz, 1H), 6.16 (dd, *J* = 6.2, 2.4 Hz, 1H), 3.35 (dd, *J* = 18.0, 3.8 Hz, 1H), 3.09 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.86 (ddd, *J* = 18.0, 12.7, 5.3 Hz, 1H), 2.75–2.61 (m, 1H), 2.29–2.10 (m, 2H), 1.77–1.62 (m, 1H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 149.1, 142.0, 140.1, 139.1, 135.1, 132.7, 130.9, 128.9 (2C), 128.0 (2C), 122.0, 121.9, 113.4, 106.4, 84.1, 34.7, 30.9, 29.2, 28.0 (3C), 24.6. HRMS (ESI+) *m/z* calcd. for $C_{24}H_{25}NO_3$ $[M+H]^+$: 376.1907; found: 376.1914. UPC^2: ID, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{minor} = 4.90 min; t_{major} = 5.67 min.



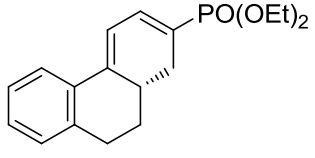
5m

Isolated as a yellow oil by FC on silica gel using EtOAc/pentane 1:1 as eluent. $[\alpha]_D^{22}$ = –8.4 (*c* 1.3 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.13 (m, 5H), 6.78 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.96 (d, J = 4.5 Hz, 1H), 5.82 (t, *J* = 4.2 Hz, 1H), 4.13–3.97 (m, 4H), 3.54 (s, 2H), 2.65–2.49 (m, 1H), 2.48 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.33–2.23 (m, 2H), 2.17-1.89 (m, 2H), 1.48 (dq, *J* = 11.9, 6.2 Hz, 1H), 1.32 (q, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (d, *J* = 4.4 Hz), 140.0, 138.1 (d, *J* = 9.9 Hz), 134.8 (d, *J* = 1.7 Hz), 134.1, 128.6 (2C), 128.0 (2C), 126.0, 123.2 (d, *J* = 188.7 Hz), 116.3, (d, *J* = 18.8 Hz), 61.6 (d, 4.7 Hz), 61.5 (d, 4.9 Hz), 38.6, 35.2 (d, *J* = 8.2 Hz), 30.2 (d, *J* = 8.9 Hz), 29.8, 25.9, 16.5 (d, *J* = 6.4 Hz), 16.4 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.9. HRMS (ESI+) *m/z* calcd. for $C_{21}H_{27}O_3P$ $[M+H]^+$: 359.1771; found: 359.1774. UPC^2: IA, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.24 min; t_{minor} = 3.07 min.



5n

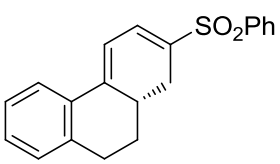
Isolated as a pale yellow oil by FC on silica gel using Et_2O/pentane 1:30 as eluent. $[\alpha]_D^{22}$ = –329.8 (*c* 0.6 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 1H), 7.23–7.17 (m, 3H), 7.16–7.11 (m, 1H), 6.74 (dd, *J* = 5.9, 2.7 Hz, 1H), 4.25 (q, *J* = 7.3 Hz, 2H), 2.91–2.76 (m, 3H), 2.73–2.59 (m, 1H), 2.18–2.05 (m, 2H), 1.58 (dq, *J* = 12.5, 5.5 Hz, 1H), 1.33 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 142.6, 139.0, 134.3, 132.4, 129.4, 128.3, 127.5, 126.4, 123.9, 116.1, 60.4, 36.5, 30.5, 29.8, 29.6, 14.4. HRMS (ESI+) *m/z* calcd. for $C_{17}H_{18}O_2$ $[M+H]^+$: 255.1380; found: 255.1380. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.78 min; t_{minor} = 3.86 min.



5o

Isolated as a yellow oil by FC on silica gel using EtOAc/pentane 1:1 as eluent. $[\alpha]_D^{22}$ = –228.6 (*c* 0.7 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 5.7, 4.2 Hz, 1H), 7.22–7.16 (m, 2H), 7.15-7.10 (m, 1H), 6.97 (dd, *J* = 5.7, 2.9 Hz, 1H), 6.71 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.18–4.01 (m, 4H), 2.93-2.72 (m, 2H), 2.71–2.58

(m, 1H), 2.54 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.15–2.01 (m, 2H), 1.55 (dq, *J* = 12.3, 5.2 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 (d, *J* = 4.5 Hz), 138.8, 138.0 (d, *J* = 10.0 Hz), 132.2 (d, *J* = 1.7 Hz), 129.3, 128.3, 126.4, 124.1 (d, *J* = 189.0 Hz), 123.8, 115.5 (d, *J* = 20.0 Hz), 61.7 (d, *J* = 5.1 Hz), 61.6 (d, *J* = 5.1 Hz), 35.9 (d, *J* = 8.2 Hz), 30.4, 30.0 (d, *J* = 8.0 Hz), 29.7, 16.5 (d, *J* = 6.7 Hz), 16.4 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.0 HRMS (ESI+) *m*/*z* calcd. for $C_{18}H_{23}O_3P$ $[M+H]^+$: 319.1458; found: 319.1460. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 5.49 min; t_{minor} = 5.23 min.

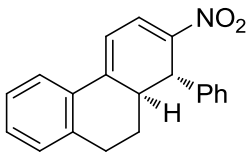


5p

Isolated as a pale yellow solid by FC on silica gel using CH_2Cl_2/pentane 3:2 to 4:1 as eluent. $[\alpha]_D^{22}$ = –142.2 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.89 (m, 2H), 7.76–7.70 (m, 1H), 7.64–7.58 (m, 1H), 7.57–7.50 (m, 2H), 7.24–7.16 (m, 3H), 7.14–7.09 (m, 1H), 6.74 (dd, *J* = 6.3, 2.6 Hz, 1H), 2.87–2.57 (m, 4H), 2.13–1.98 (m, 2H), 1.50 (qd, *J* = 12.3, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.1, 139.0, 135.3, 133.3, 133.1, 131.5, 129.4, 129.2 (2C), 128.9, 127.8 (2C), 126.5, 124.1, 114.5, 36.7, 30.2, 29.6, 28.6. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{18}O_2S$ $[M+H]^+$: 323.1100; found: 323.1102. UPC^2: IA, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{major} = 5.02 min; t_{minor} = 5.23 min.

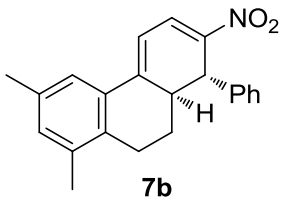
3.2. Asymmetric formation of chiral carbocycles **7**

A glass vial equipped with a magnetic stirring bar was charged with enal **1** (0.20 mmol, 2.0 eq), catalyst **3b** (0.02 mmol, 0.2 eq), nitro olefin **6** (0.10 mmol, 1.0 eq), *i*-PrNEt$_2$ (0.50 mmol, 0.5 eq) and MeCN (0.3 mL). The mixture was stirred for 22-65 h at 40 °C (individual reaction times specified below). The solvent was evaporated *in vacuo* and the mixture was then subjected to FC (loaded with CH_2Cl_2) on silica gel to yield product **7**. For compound **7b** DABCO (0.50 mmol, 0.5 eq) was employed instead of *i*-PrNEt$_2$. Compound **7i** was synthesized using 0.10 mmol (1.0 eq) of enal **1** and 0.20 mmol of nitro olefin **6** (2.0 eq).



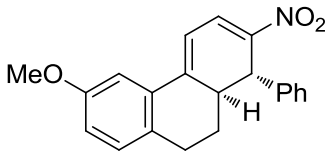
7a

Isolated after 22 h of reaction time as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 1:2 as eluent. $[\alpha]_D^{22}$ = –45.6. (*c* 0.2 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.48 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.35–7.21 (m, 7H), 7.11 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.64 (dd, *J* = 6.8, 2.5 Hz, 1H), 4.08 (dd, *J* = 13.4, 1.9 Hz, 1H), 3.08 –2.98 (m, 1H), 2.87–2.72 (m, 2H), 1.98–1.91 (m, 1H), 1.80 (qd, *J* = 12.6, 6.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 145.2 , 142.8, 138.6, 132.5, 129.5, 129.4, 129.2, 128.8 (2C), 127.6 (2C), 127.2, 126.6, 124.7, 113.1, 47.9, 46.5, 30.1, 29.8. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{17}NO_2$ $[M+H]^+$: 304.1338; found: 304.1336. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t $_{major}$ = 6.61 min; t_{minor} = 6.10 min.



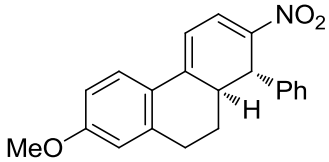
7b

Isolated after 48 h of reaction time as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 1:2 as eluent. $[\alpha]_D^{22}$ = –27.0 (*c* 0.7 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.7 Hz, 1H), 7.34 (s, 1H), 7.32–7.20 (m, 5H), 6.99 (s, 1H), 6.54 (dd, *J* = 6.8, 1.4 Hz, 1H), 4.10 (d, *J* = 10.0 Hz, 1H), 3.00-2.90 (m, 1H), 2.81 (dd, *J* = 17.2, 4.9 Hz, 1H), 2.58 (ddd, *J* = 17.2, 11.8, 5.2 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H), 2.11–2.03 (m, 1H), 1.88 (dq, *J* = 12.6, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.4, 143.5, 136.8, 135.6, 133.8, 133.3, 132.2, 129.2, 128.8 (2C), 127.4 (2C), 127.1, 123.0, 112.8, 46.9, 46.4, 31.2, 27.1, 21.0, 19.4. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{21}NO_2$ $[M+H]^+$: 332.1645; found: 332.1645. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t $_{major}$ = 6.91 min; t_{minor} = 6.20 min.



7c

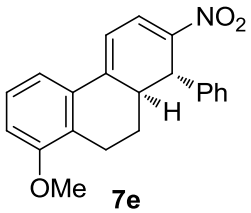
Isolated after 24 h of reaction time as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 4:6 to 6:4 as eluent. $[\alpha]_D^{22}$ = –66.0 (*c* 0.1 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.30–7.17 (m, 5H), 7.13(d, *J* = 2.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.55 (dd, *J* = 6.9, 2.5 Hz, 1H), 4.02 (dd, *J* = 13.3, 1.9 Hz, 1H), 3.78 (s, 3H), 2.95 (tdd, *J* = 13.3, 4.0, 2.5 Hz, 1H), 2.75–2.59 (m, 2H), 1.91–1.83 (m, 1H), 1.71 (qd *J* = 12.6, 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 148.7, 145.2, 142.8, 133.4, 131.1, 130.3, 129.0, 128.8 (2C), 127.6 (2C), 127.2, 116.4, 113.3, 108.8, 55.4, 47.9, 46.5, 30.19, 29.33. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.1443; found: 334.1438. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t $_{major}$ = 6.69 min; t_{minor} = 7.17 min.



7d

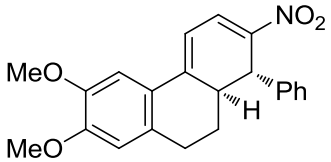
Isolated after 65 h of reaction time as an orange solid by FC on silica gel using CH_2Cl_2/pentane 4:6 to 6:4 as eluent. $[\alpha]_D^{22}$ = –25.5 (*c* 0.1 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.9 Hz, 1H), 7.42 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.30–7.18 (m, 5H), 6.74 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.47 (dd, *J* = 6.9, 2.6 Hz, 1H), 3.98 (dd, *J* = 14.3, 2.1 Hz, 1H), 3.75 (s, 3H), 2.99–2.89 (m, 1H),

2.76–2.61 (m, 2H), 1.89–1.80 (m, 1H), 1.75–1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 147.6, 145.0, 143.0, 140.7, 130.1, 128.7 (2C), 127.8 (2C), 127.1, 126.5, 125.1, 113.6, 113.2, 111.0, 55.3, 48.2, 46.5, 30.5, 29.4. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.1443; found: 334.1439. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 7.47 min; t_{minor} = 8.29 min.



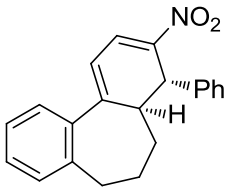
7e

Isolated after 65 h of reaction time as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 4:6 to 1:1 as eluent. $[\alpha]_D^{22}$ = –4.4 (*c* 1.0 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.28–7.24 (m, 6H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.53 (dd, *J* = 6.9, 2.3 Hz, 1H), 4.04 (dd, *J* = 11.0, 1.6 Hz, 1H), 3.76 (s, 3H), 3.01–2.88 (m, 2H), 2.42 (ddd, *J* = 18.0, 12.6, 5.6 Hz, 1H), 2.02–1.95 (m, 1H), 1.76 (qd, *J* = 12.9, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 157.2, 148.1, 146.2, 143.3, 134.2, 128.9, 128.8 (2C), 127.5 (2C), 127.4, 127.2, 126.8, 116.7, 113.4, 110.4, 55.5, 47.2, 46.2, 30.4, 23.6. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.1443; found: 334.1437. UPC^2: IB, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.95 min; t_{minor} = 4.65 min.



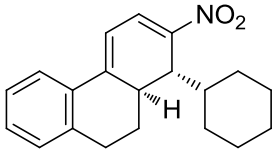
7f

Isolated after 52 h of reaction time as an orange solid by FC on silica gel using Et_2O/CH_2Cl_2/pentane 1:1:4 as eluent. $[\alpha]_D^{22}$ = –96.6 (*c* 0.3 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.30–7.24 (m, 2H), 7.23–7.17 (m, 3H), 7.10 (s, 1H), 6.50 (s, 1H), 6.44 (dd, *J* = 6.9, 2.5 Hz, 1H), 3.98 (dd, *J* = 14.3, 2.1 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 2.99–2.88 (m, 1H), 2.68–2.61 (m, 2H), 1.90–1.83 (m, 1H), 1.74–1.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 148.0 , 147.7, 145.0 , 143.0 , 132.8, 129.9, 128.8 (2C), 127.8 (2C), 127.1, 124.6 , 111.3, 111.1, 106.9 , 56.0, 55.9, 48.2, 46.4, 29.9, 29.7. HRMS (ESI+) *m*/*z* calcd. for $C_{22}H_{21}NO_4$ $[M+H]^+$: 364.1549; found: 364.1548. UPC^2: IB, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 5.25 min; t_{minor} = 5.00 min.



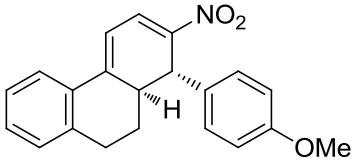
7g

Isolated after 24 h of reaction time as a yellow oil by FC on silica gel using CH_2Cl_2/pentane 1:2 as eluent. $[\alpha]_D^{22}$ = +116.6 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.6 Hz, 1H), 7.29–7.09 (m, 9H), 6.25 (d, *J* = 6.6 Hz, 1H), 4.10 (bs, 1H), 2.95 (dd, *J* = 11.9, 4.6 Hz, 1H), 2.89-2.83 (m, 2H), 2.11-2.00 (m, 1H), 1.93–1.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 146.9, 140.4 (2C), 140.1, 130.1, 128.8 (3C), 128.3, 127.5, 127.4, 126.7 (2C), 126.4, 117.4, 47.3, 44.7, 35.0, 34.5, 25.2. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{19}NO_2$ $[M+H]^+$: 318.1489; found: 318.1493. UPC^2: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.37 min; t_{minor} = 4.71 min.



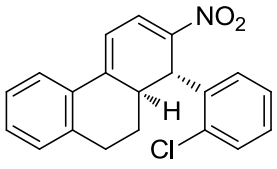
7h

Isolated after 48 h of reaction time as a yellow oil by FC on silica gel using CH_2Cl_2/pentane 1:3 as eluent. $[\alpha]_D^{22}$ = +93.0 (*c* 0.2 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.31–7.13 (m, 3H), 6.13 (dd, *J* = 6.7, 1.0 Hz, 1H), 3.16 (ddd, *J* = 18.0, 11.9, 6.4 Hz, 1H), 3.03 (t, *J* = 3.0 Hz, 1H), 2.95 (dd, *J* = 17.8, 6.1 Hz, 1H), 2.29 (d, *J* = 13.9Hz, 1H), 2.06 (dq, *J* = 12.7, 6.3 Hz, 1H), 1.84–1.55 (m, 6H), 1.31–1.18 (m, 3H), 1.18–0.98 (m, 2H), 0.97–0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 146.1, 137.5, 135.9, 129.3, 129.1, 128.5, 126.2, 124.7, 114.0, 43.7, 42.4, 39.1, 34.9, 30.1, 28.8, 27.2, 26.4, 26.3, 26.2. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{23}NO_2$ $[M+H]^+$: 310.1802; found: 310.1802. UPC^2: ID, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.33 min; t_{minor} = 3.47 min.



7i

Isolated after 48 h of reaction time as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 1:1→2:1 as eluent. $[\alpha]_D^{22}$ = –40.0 (*c* 0.2 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.44 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.28-7.19 (m, 4H), 7.11 (d, *J* = 6.9 Hz, 1H), 6.88–6.83 (m, 2H), 6.62 (dd, *J* = 6.9, 2.5 Hz, 1H), 4.02 (dd, *J* = 13.4, 1.4 Hz, 1H), 3.79 (s, 3H), 3.05-2.95 (m, 1H), 2.86–2.72 (m, 2H), 1.99–1.91 (m, 1H), 1.78 (dq, *J* = 12.6, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.8, 145.1, 138.6, 134.7, 132.6, 129.5, 129.4, 128.8, 128.7 (2C), 126.6, 124.7, 114.2 (2C), 113.1, 55.3, 47.0, 46.7, 30.2, 29.9. HRMS (ESI+) *m*/*z* calcd. for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.1438; found: 334.1441. UPC^2: IB, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.62 min; t_{minor} = 4.45 min.

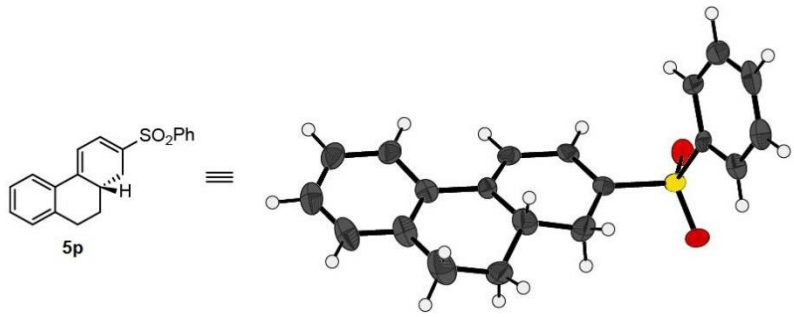


7j

Isolated after 48 h as a yellow solid by FC on silica gel using CH_2Cl_2/pentane 2:1 as eluent. $[\alpha]_D^{22}$ = –168.8 (*c* 0.5 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.66 (m, 1H), 7.57 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.44–7.40 (m, 1H), 7.34–7.29 (m, 1H), 7.29–7.17 (m, 4H), 7.15–7.09 (m, 1H), 6.63 (dd, *J* = 6.9, 2.4 Hz, 1H), 4.77 (d, *J* = 12.9 Hz, 1H), 3.07 (t, *J* = 12.9 Hz, 1H), 2.89–2.75 (m, 2H), 2.06–1.97 (m, 1H), 1.90 (qd, *J* = 12.6, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 145.6, 140.2, 138.6, 134.2, 132.6, 130.0, 129.9, 129.6, 129.4, 128.2, 127.4 (bs), 127.3, 126.6, 124.7, 113.1, 46.2 (bs), 43.5 (bs), 30.17, 29.37. HRMS (ESI+) *m*/*z* calcd. for $C_{20}H_{16}ClNO_2$ $[M+H]^+$: 338.0942; found: 338.0939. UPC^2: IB, CO_2/i-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.66 min; t_{minor} = 4.44 min.

4. X-Ray structures and crystal data

Compound **5p**

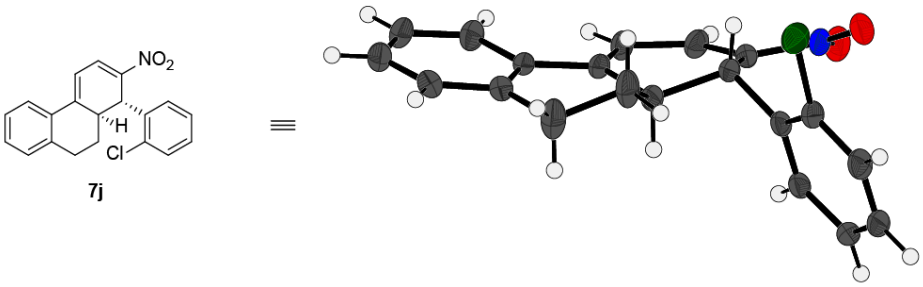


Item	Value
Molecular formula	$C_{20}H_{18}O_2S$
Formula weight	322.4
Crystal system	triclinic
Space group	P1
a (Å)	8.0288
b (Å)	9.2244
c (Å)	11.46
α (°)	103.126
β (°)	98.144
γ (°)	98.902
Volume ($Å^3$)	802.7
Z	2
T (K)	100
ρ ($g\ cm^{-1}$)	1.334
λ (Å)	0.56086
μ (mm^{-1})	0.115
# measured refl	36305
# unique refl	7505
R_{int}	0.0489
# parameters	415
$R(F^2)$, all refl	0.0798

$R_w(F^2)$, all refl	0.1354
Goodness of fit	1.057

Crystal data for [**5p**]: $C_{20}H_{18}O_2S$, *M* = 322.4, triclinic, space group P1 (no. 1), *a* = 8.0288(16) Å, *b* = 9.2244(19) Å, *c* = 11.46(3) Å, *α* = 103.126(5)°, *β* = 98.144(7)°, *γ* = 98.902(5)°, *V* = 802.7(3) $Å^3$, *T* = 100 K, *Z* = 2, d_c = 1.334 g cm^{-3}, *μ*(Mo Kα, λ = 0.56086 Å) = 0.115 mm^{-1}, 36305 reflections collected, 7505 unique [R_{int} = 0.0489], which were used in all calculations. Refinement on F^2, final R(F) = 0.0798, R_w(F2) = 0.1354. CCDC number 971515.

Compound **7j**

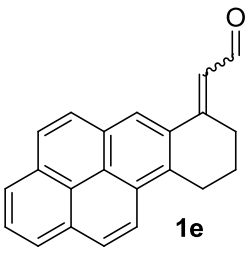


Item	Value
Molecular formula	$C_{20}H_{16}ClNO_2$
Formula weight	337.79
Crystal system	orthorhombic
Space Group	P 21 21 21
a (Å)	11.8439
b (Å)	11.8914
c (Å)	22.4284
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	3158.84
Z	8
T (K)	100
ρ (g cm^{-1})	1.421
λ (Å)	0.71073
μ (mm^{-1})	0.254
# measured refl	25699
# unique refl	10247
R_{int}	0.0636
# parameters	442
$R(F^2)$, all refl	0.0918
$R_w(F^2)$, all refl	0.1417
Goodness of fit	1.04

Crystal data for [**7j**]: $C_{20}H_{16}ClNO_2$, M = 337.79, orthorhombic, space group P 21 21 21 (no. 115), a = 11.8439(4) Å, b = 11.8914(2) Å, c = 22.4284(6) Å, V = 3158.84(14) Å^3, T = 100 K, Z = 8, d_c = 1.421 g cm^{-3}, μ(Mo Kα, λ = 0.71073 Å) = 0.254 mm^{-1}, 25699 reflections collected, 10247 unique [R_{int} = 0.0636], which were used in all calculations. Refinement on F^2, final R(F) = 0.0918, R_w(F2) = 0.1417. CCDC number 1009726.

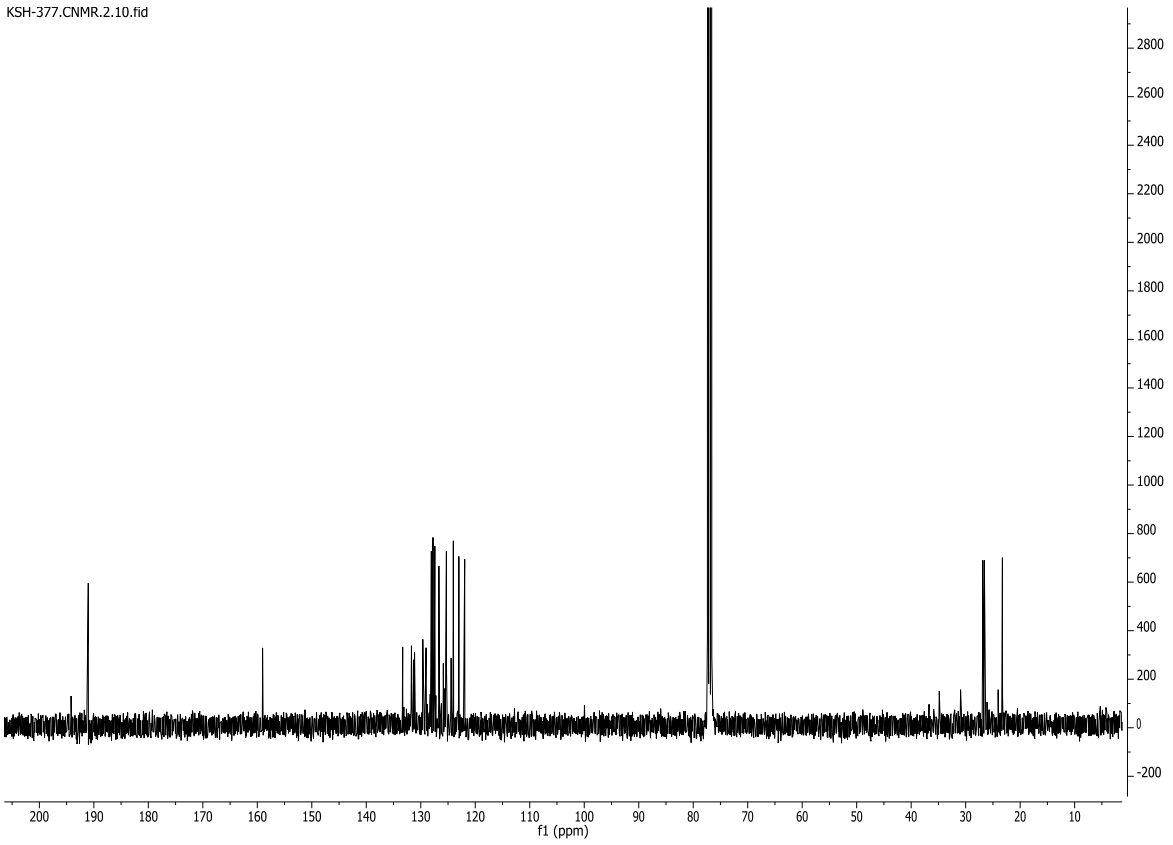
5. NMR spectra of novel compounds

KSH-377.HNMR.10.fid

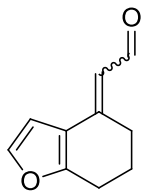


1e

KSH-377.CNMR.2.10.fid

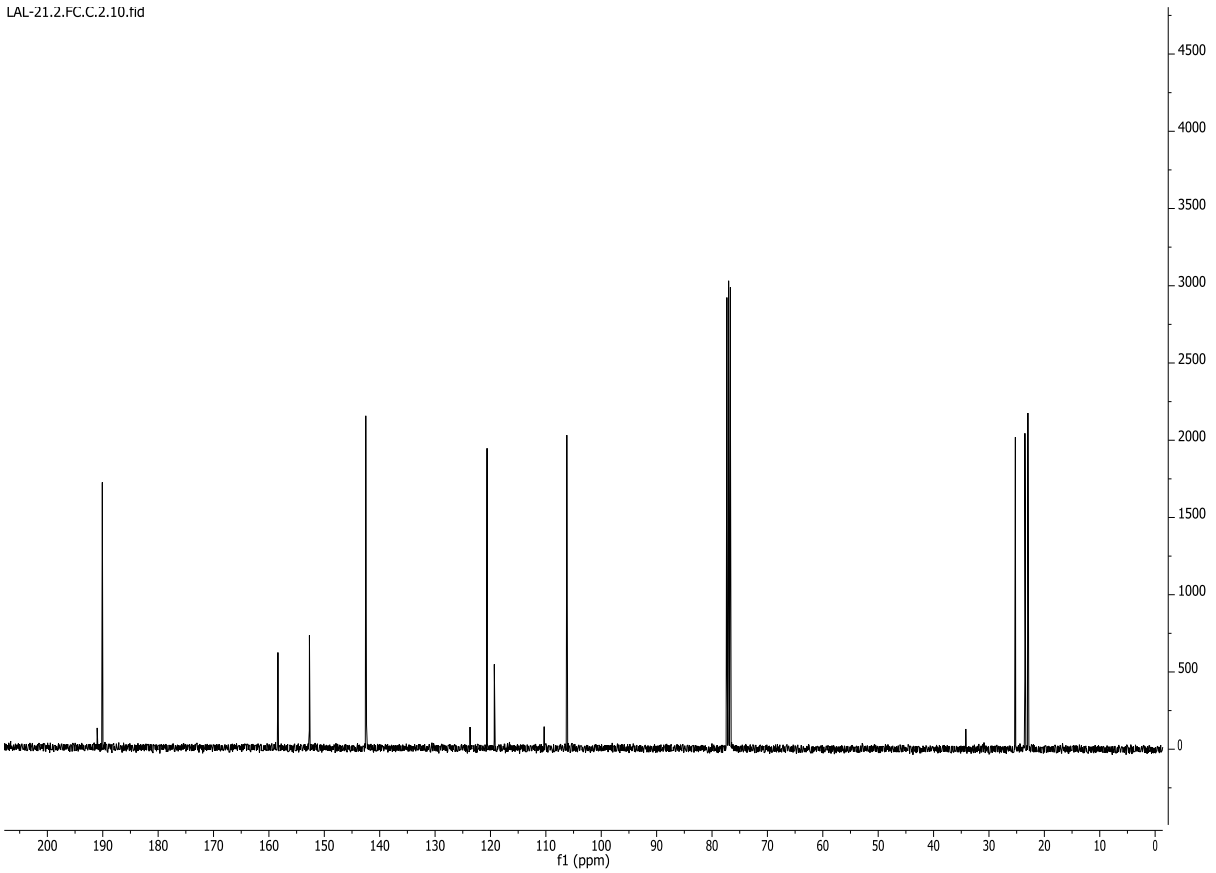


LAL-21.2.FC.H.2.10.fid

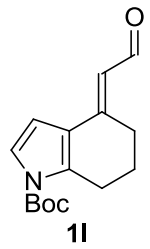


1k

LAL-21.2.FC.C.2.10.fid

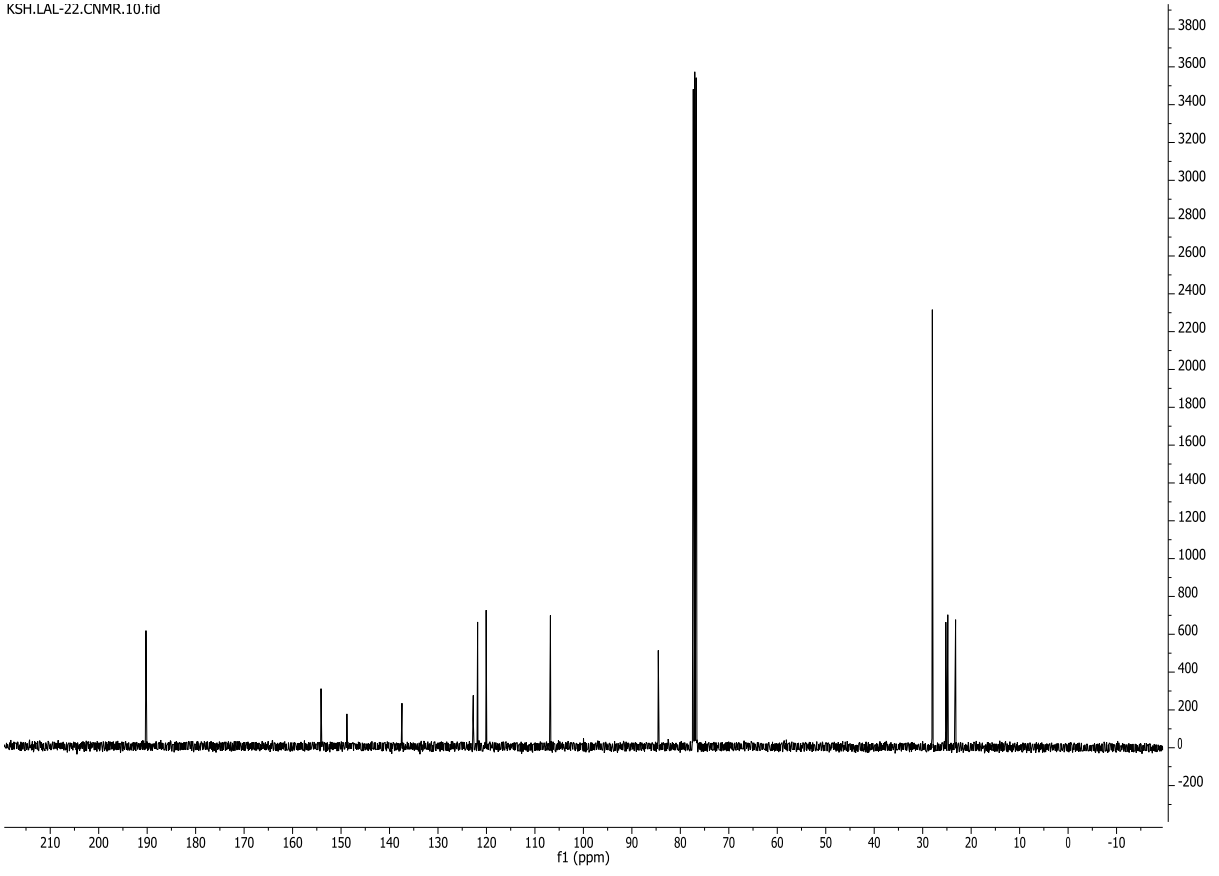


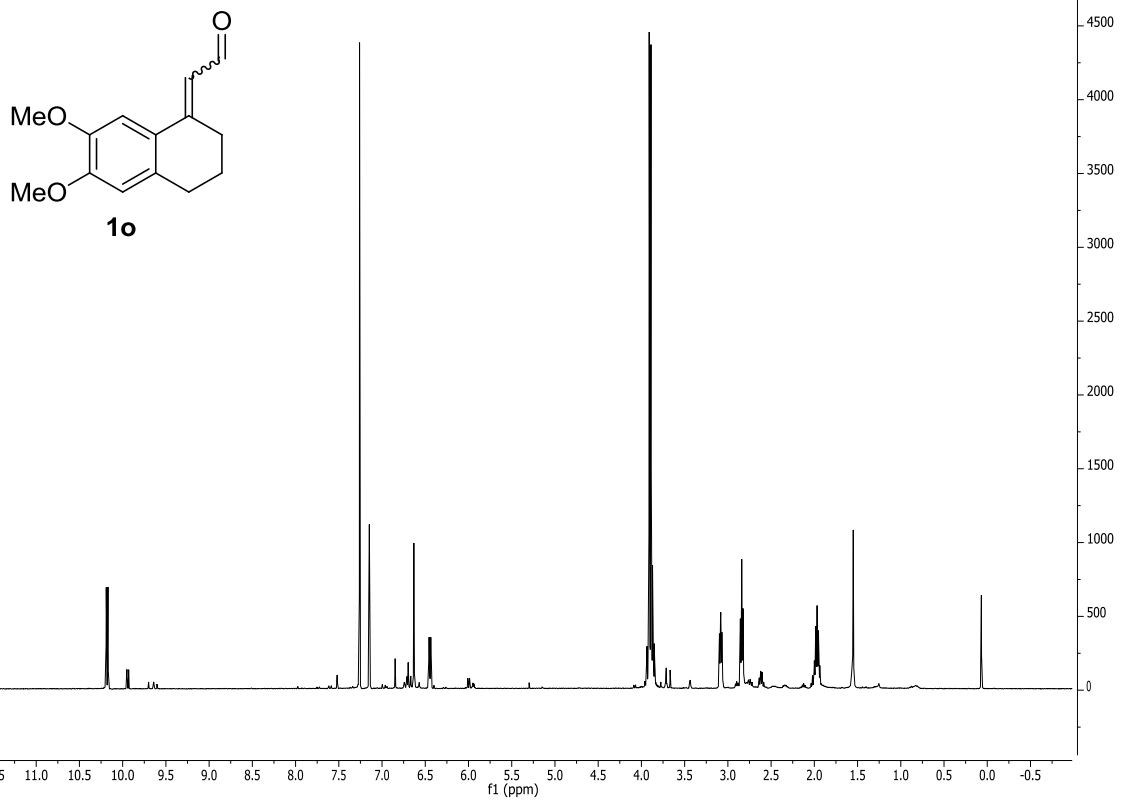
LAL-22.2.FC.H.10.fid

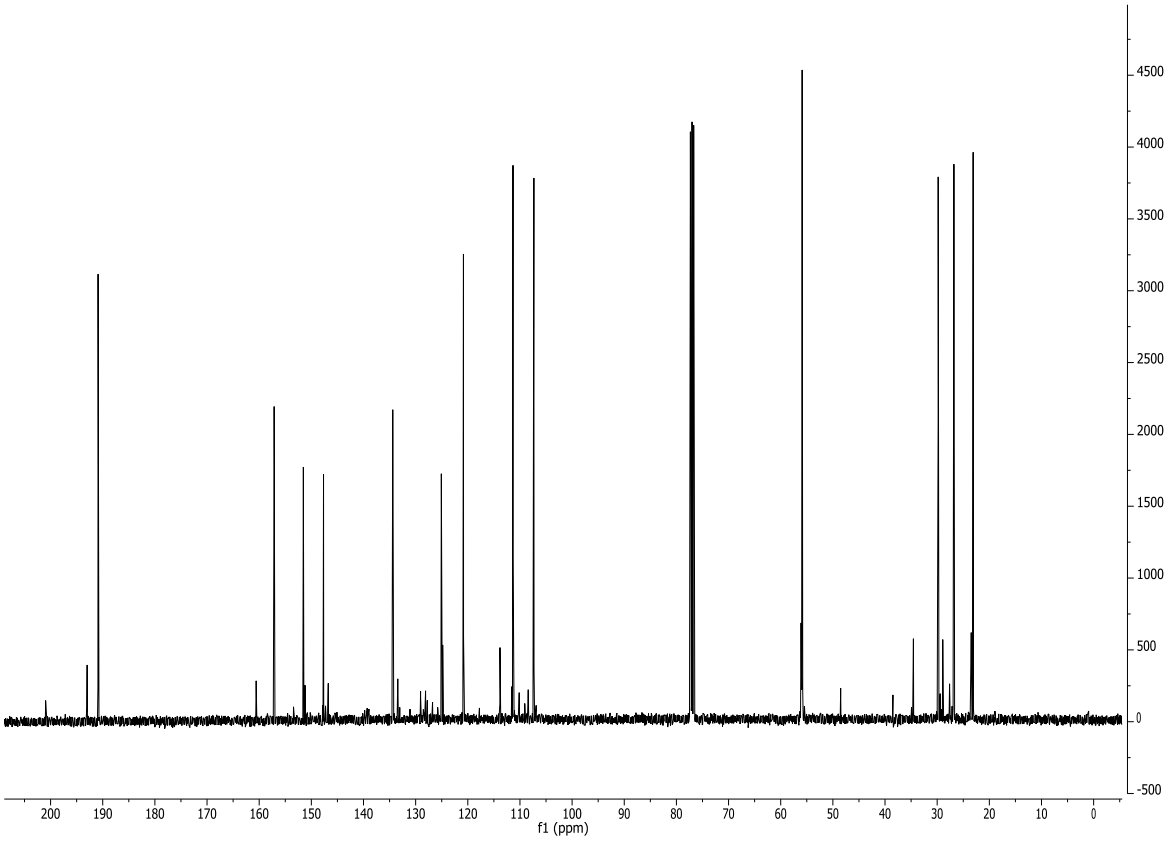


1l

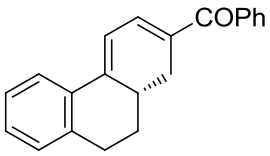
KSH.LAL-22.CNMR.10.fid




O
MeO
MeO
1o
4500
4000
3500
3000
2500
2000
1500
1000
500
0
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

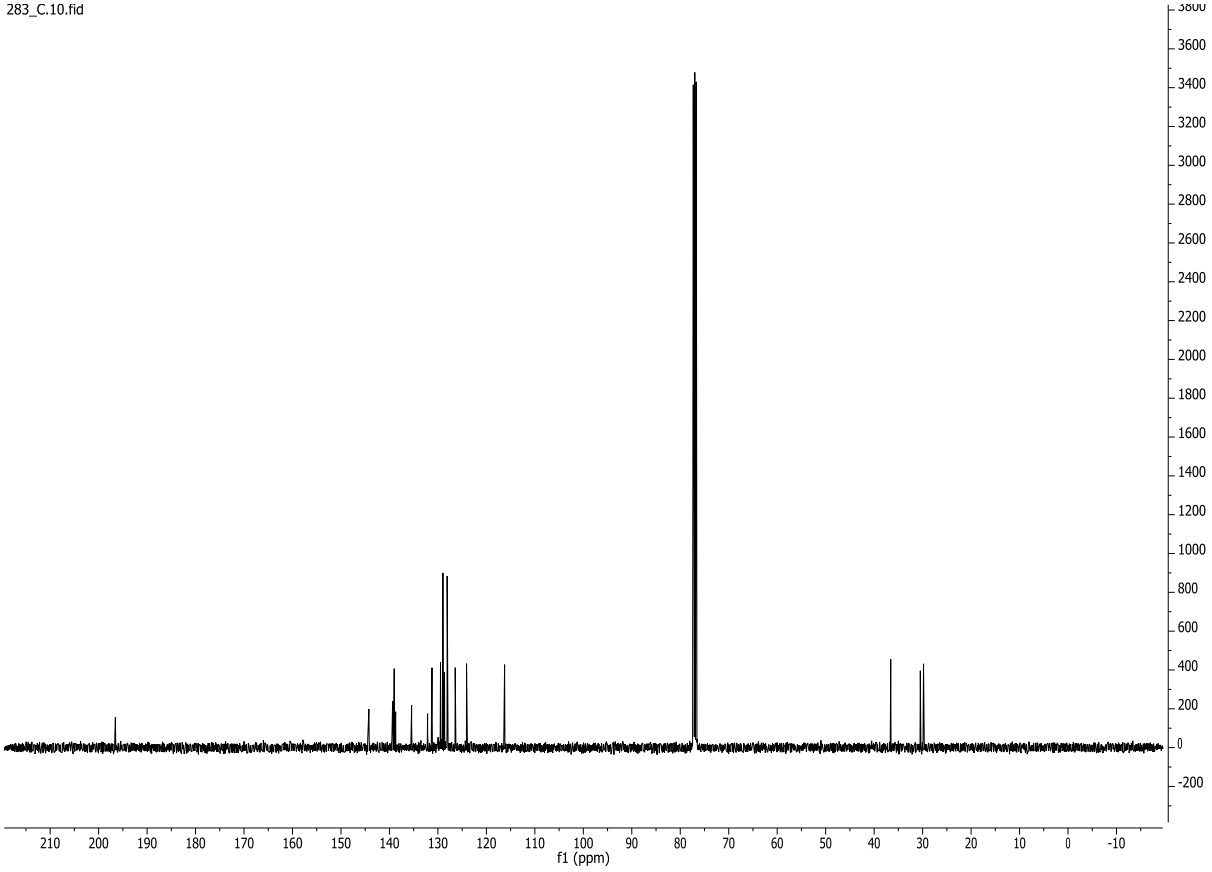

4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

300A_H.10.fid

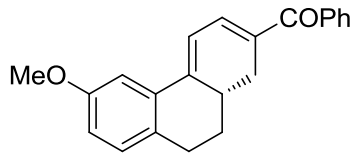


5a

283_C.10.fid

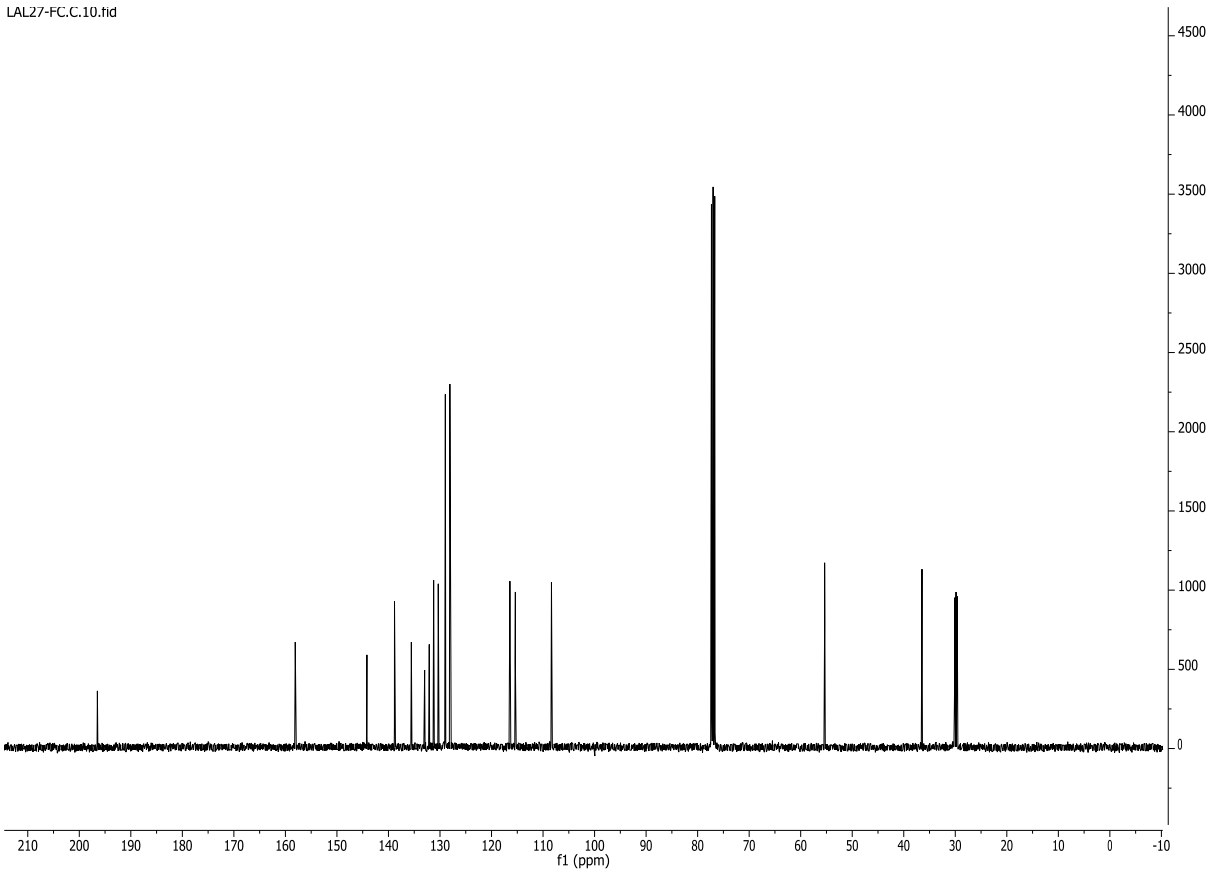


LAL27-FC.H.10.fid

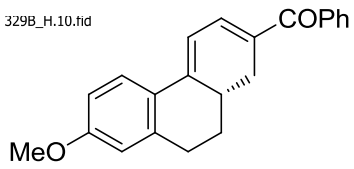


5b

LAL27-FC.C.10.fid

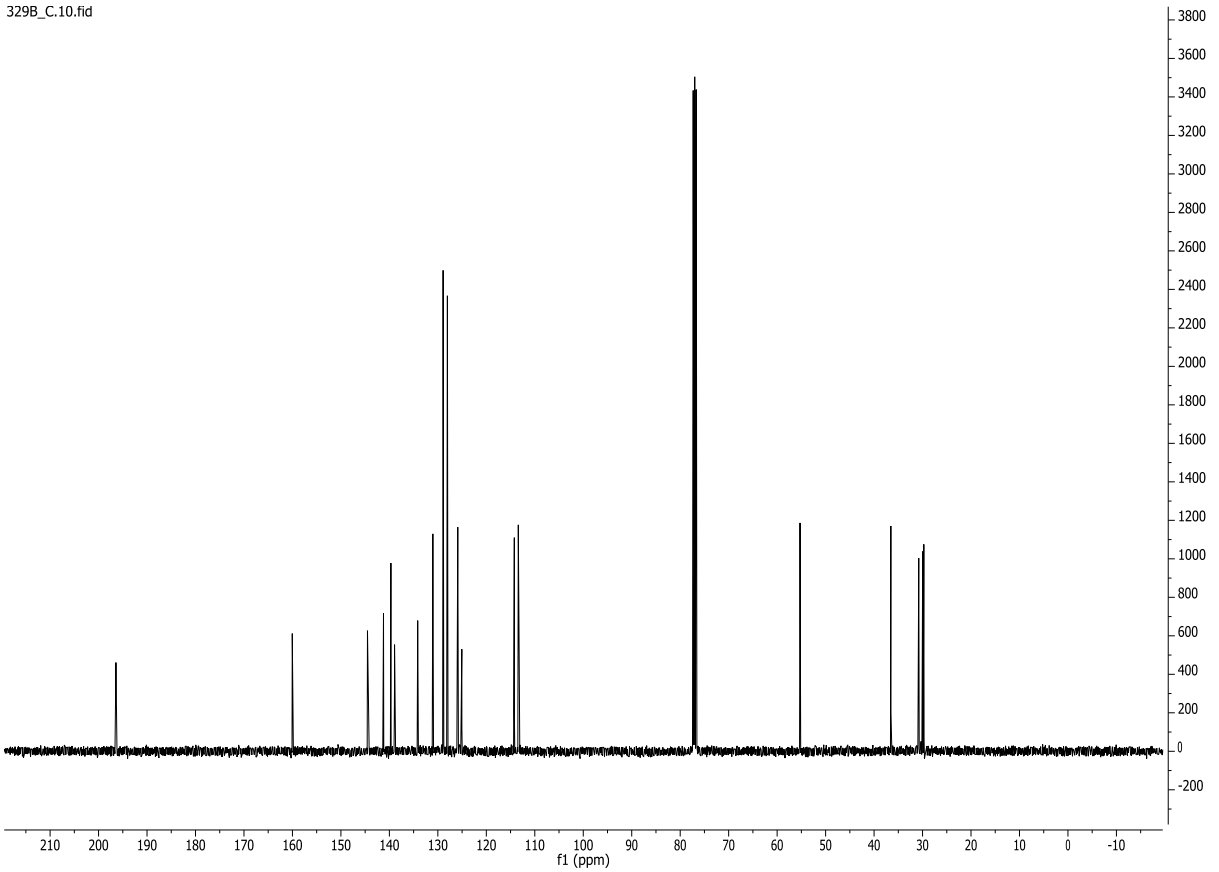


329B_H.10.fid

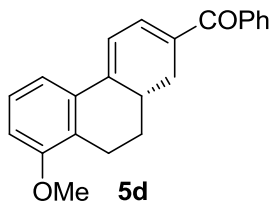


5c

329B_C.10.fid

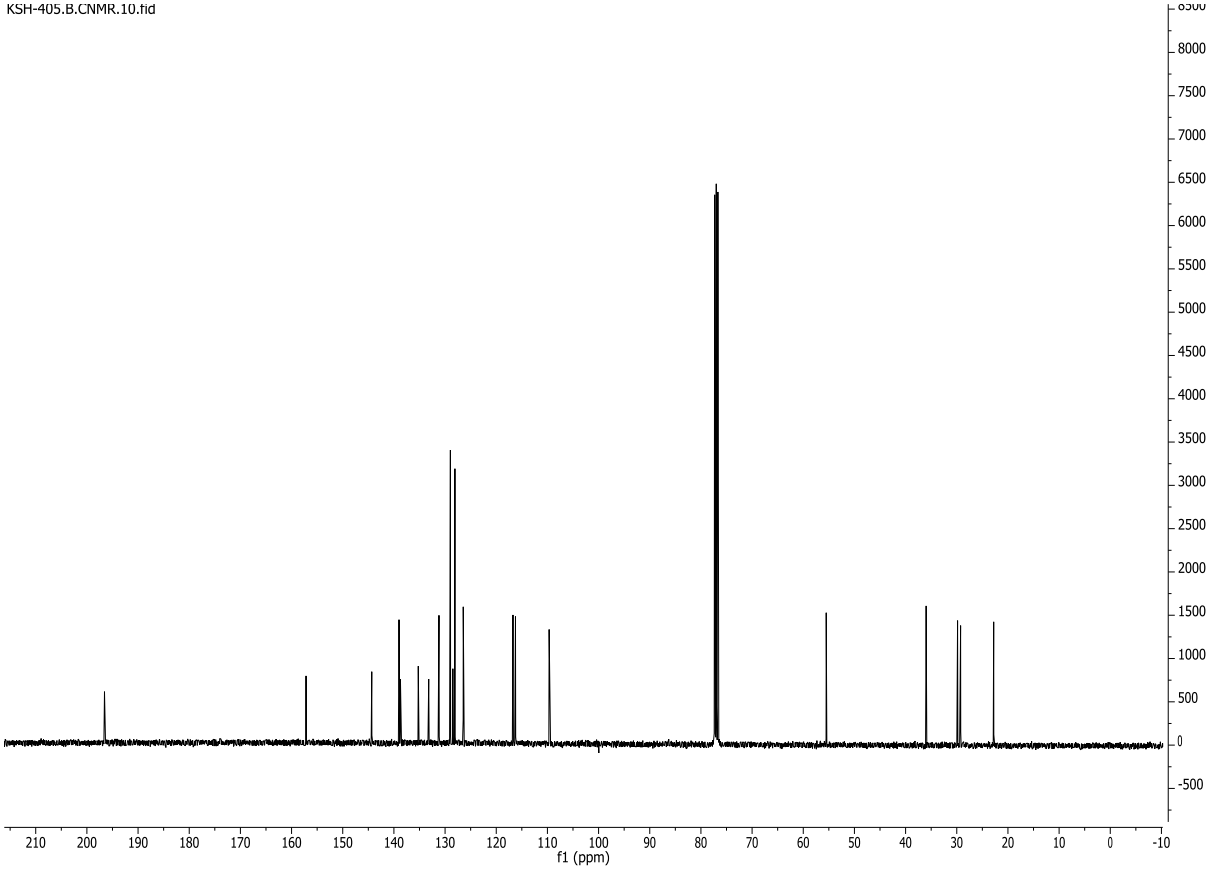


KSH-405.B.HNMR.10.fid

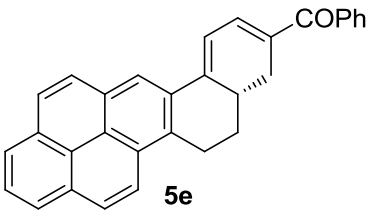


5d

KSH-405.B.CNMR.10.fid

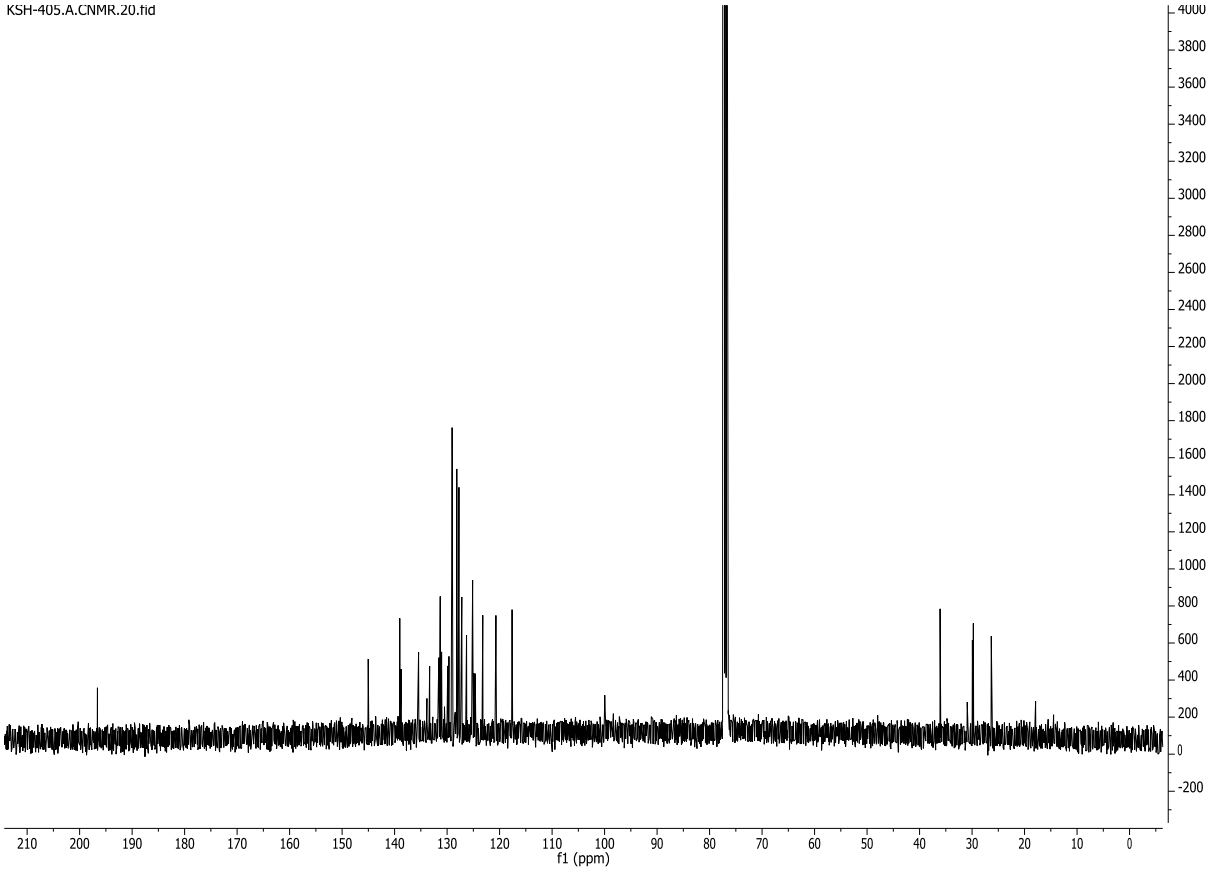


KSH-405.A.HNMR.10.fid

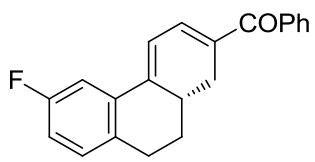


5e

KSH-405.A.CNMR.20.fid

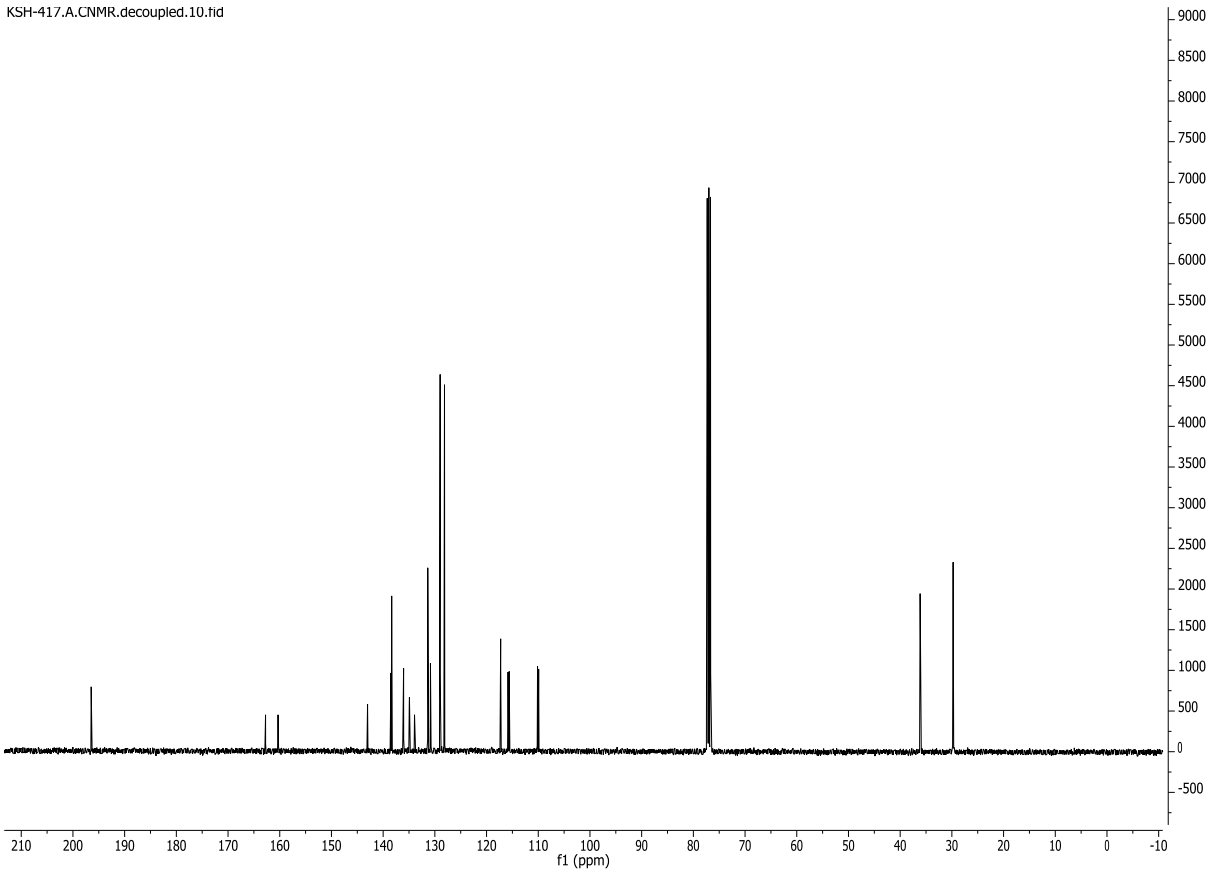


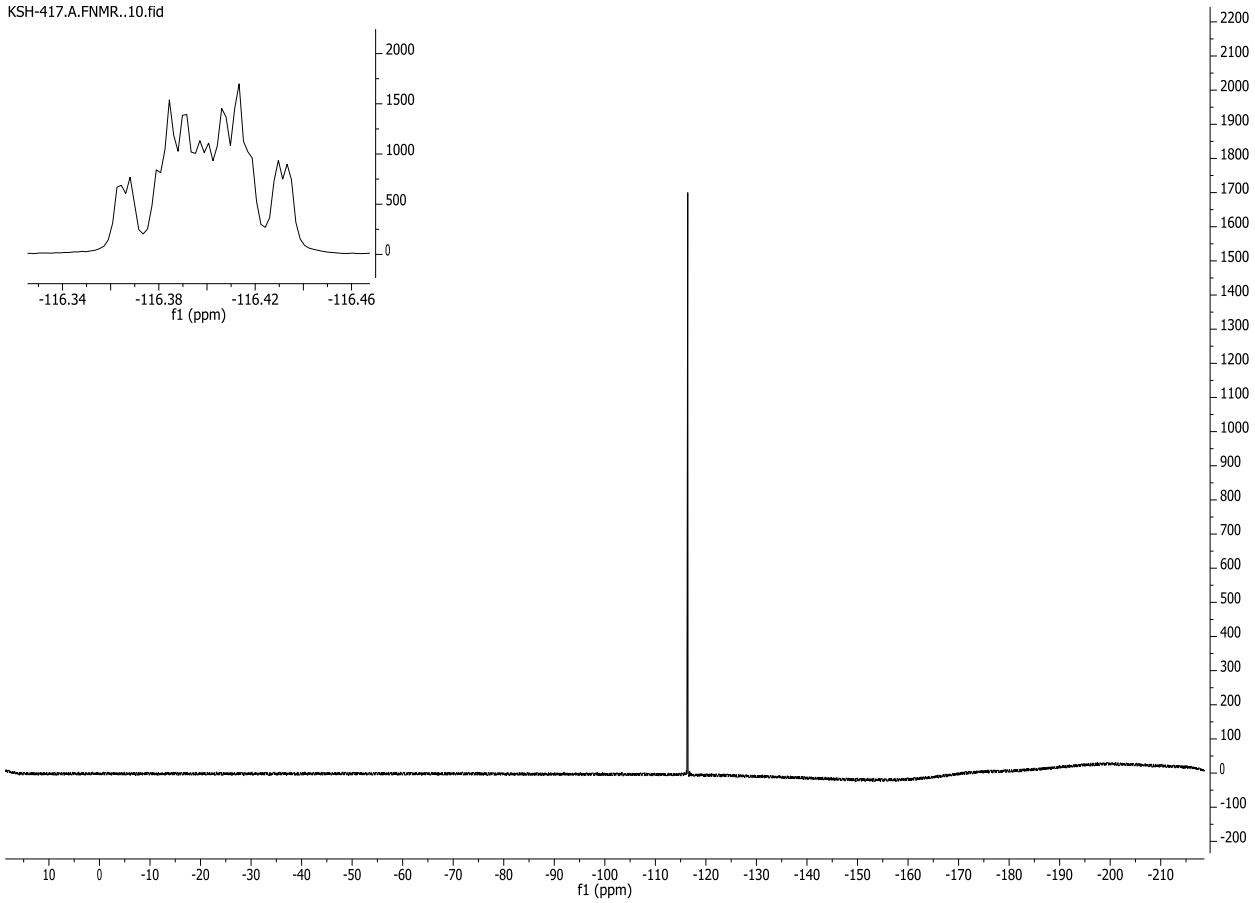
KSH-417.A.HNMR.10.fid



5f

KSH-417.A.CNMR.decoupled.10.fid




KSH-417.A.FNMR..10.fid
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1000
500
0
-116.34
-116.38
-116.42
-116.46
f1 (ppm)
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1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-100
-110
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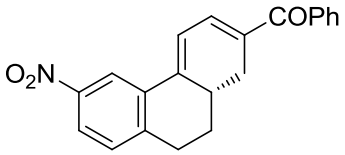
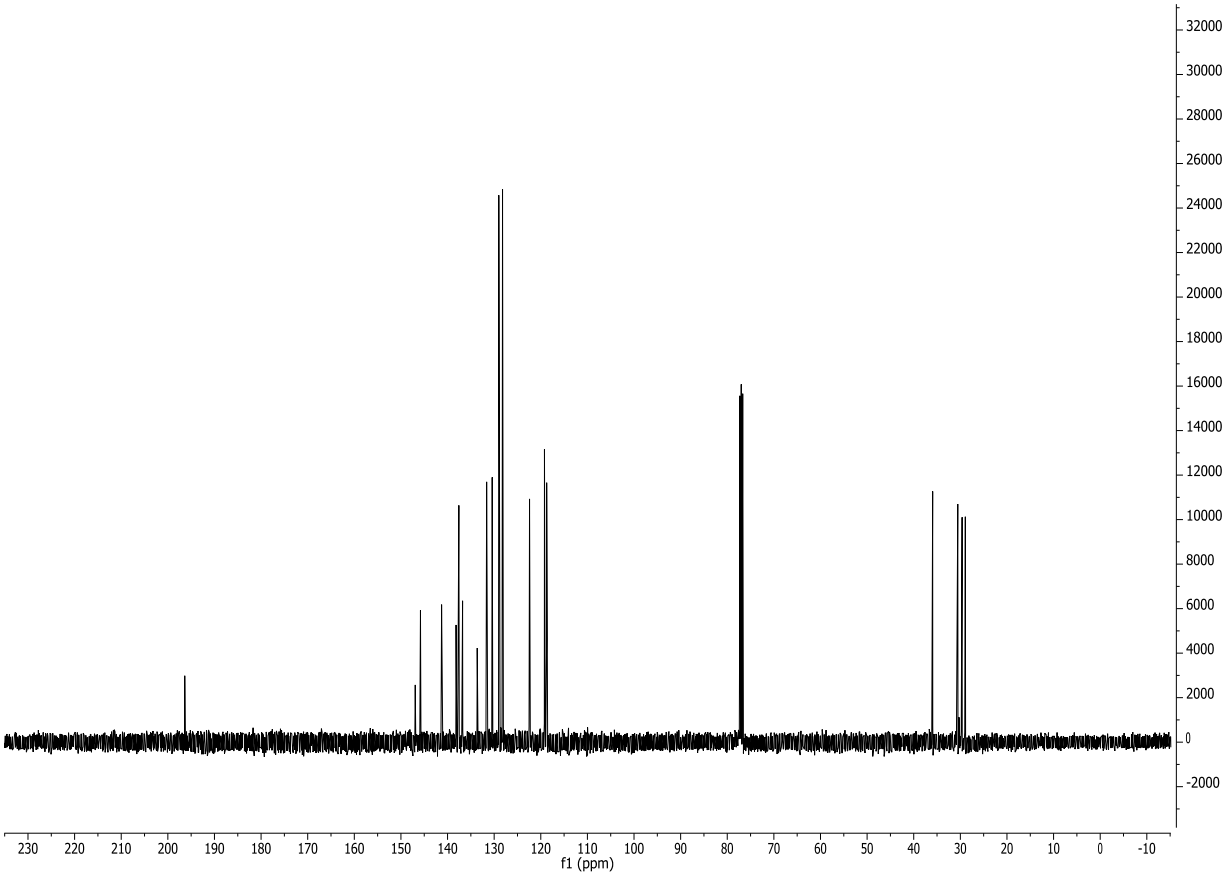
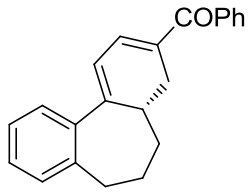
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



5g

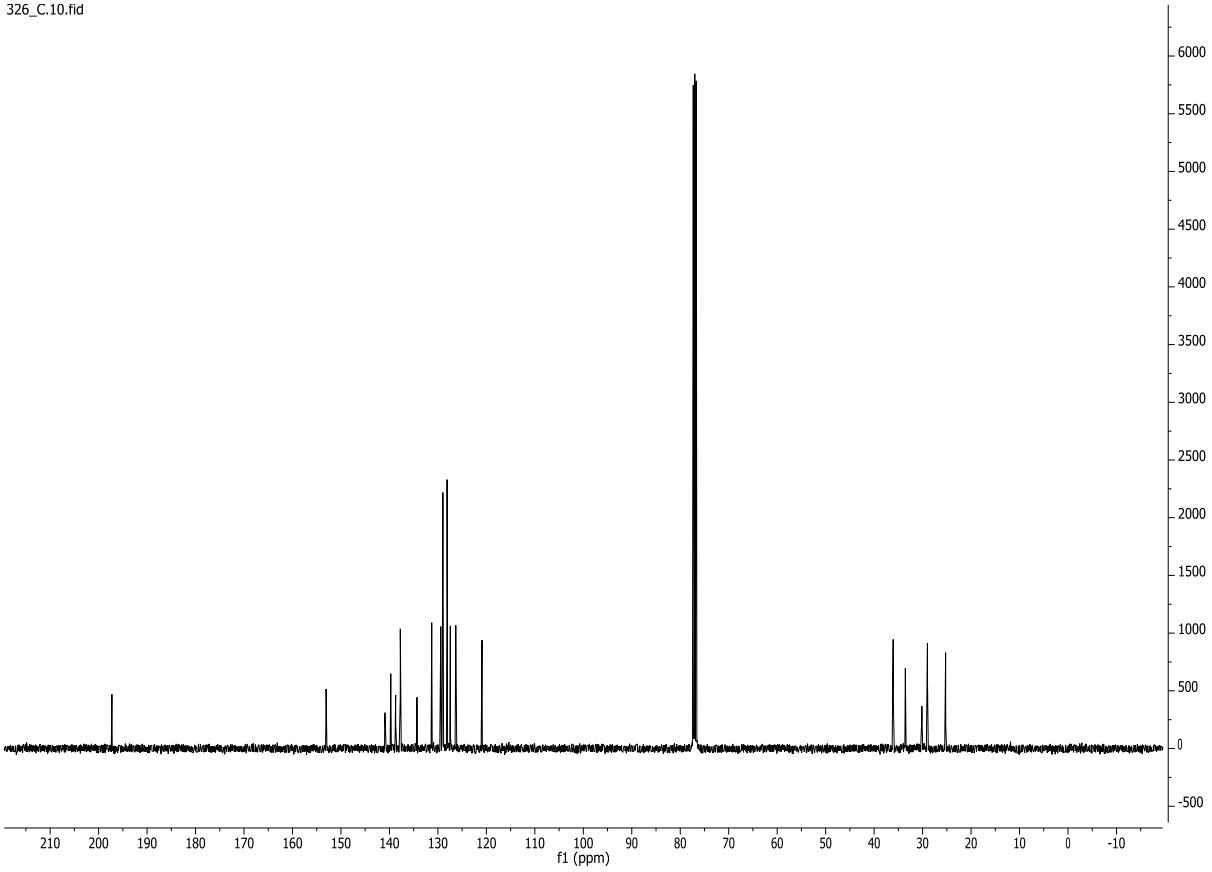


326_H.10.fid

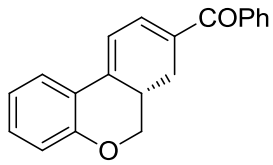


5h

326_C.10.fid

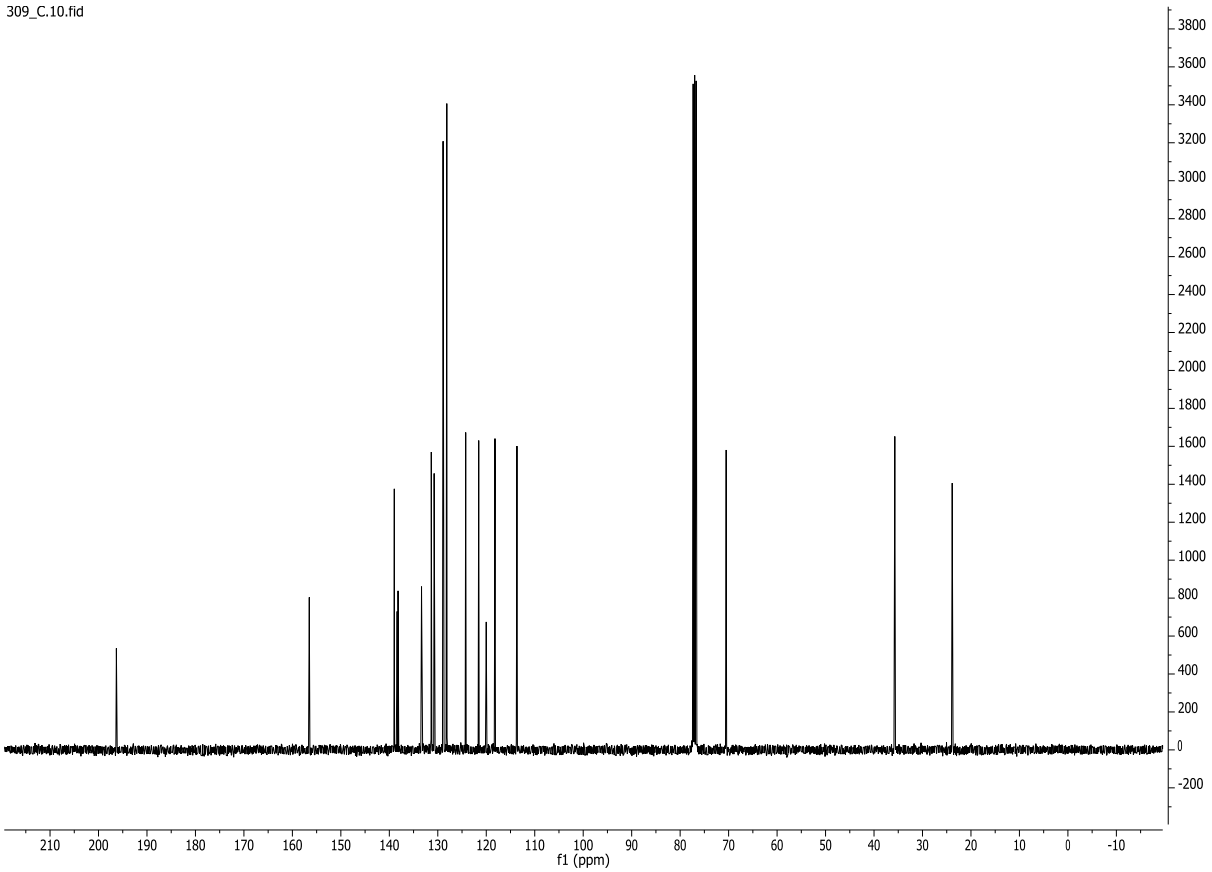


309_H.10.fid

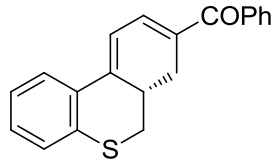


5i

309_C.10.fid

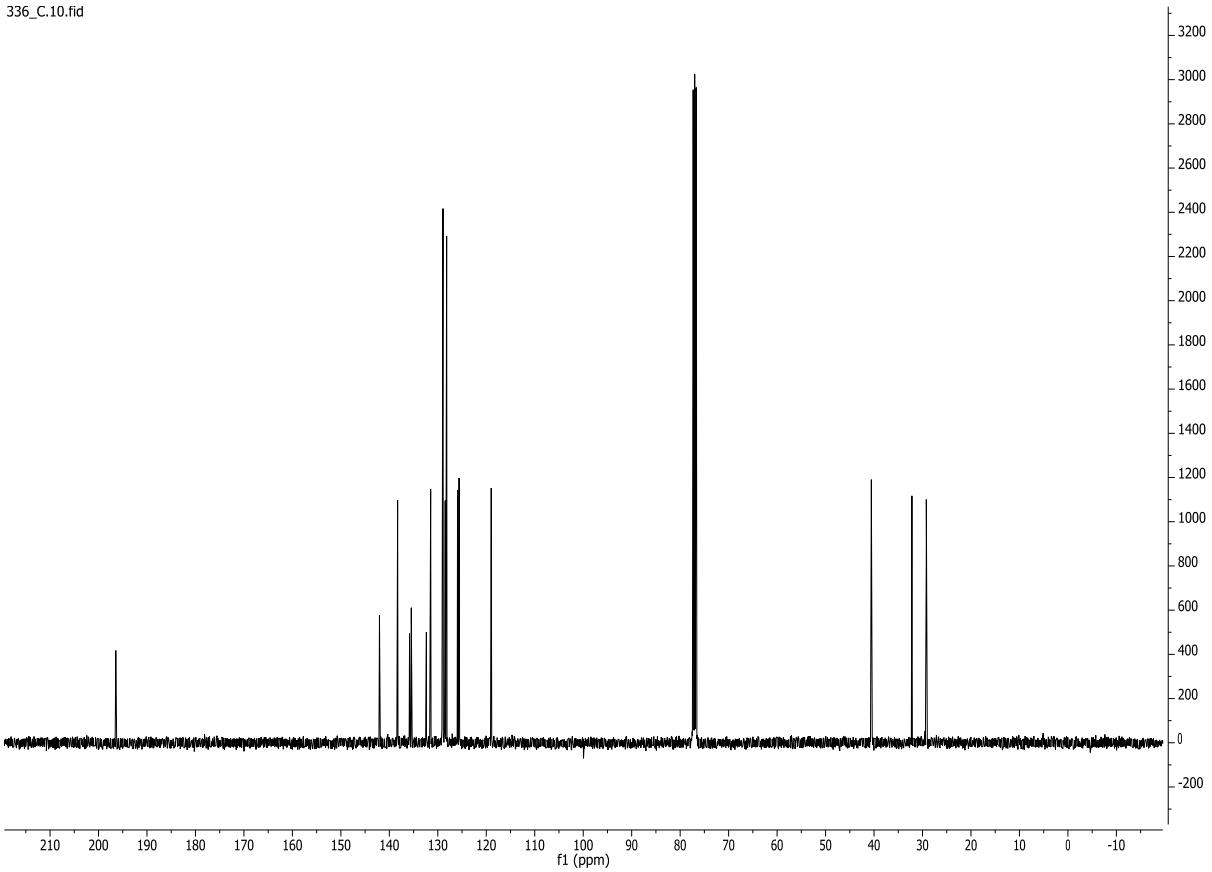


336_co.10.fid

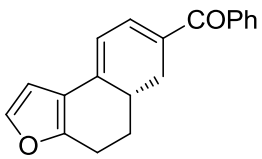


5j

336_C.10.fid

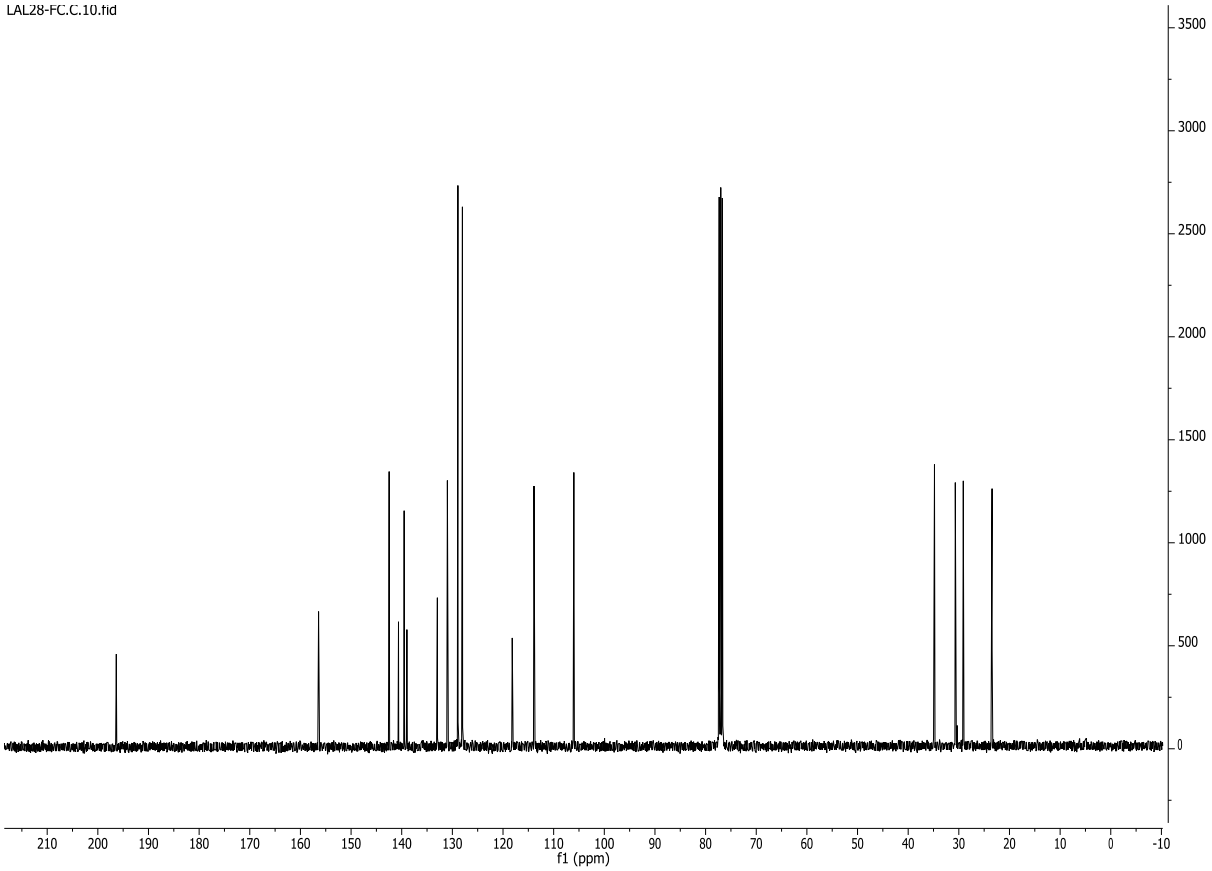


LAL28-FC.H.10.fid

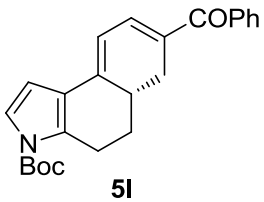


5k

LAL28-FC.C.10.fid

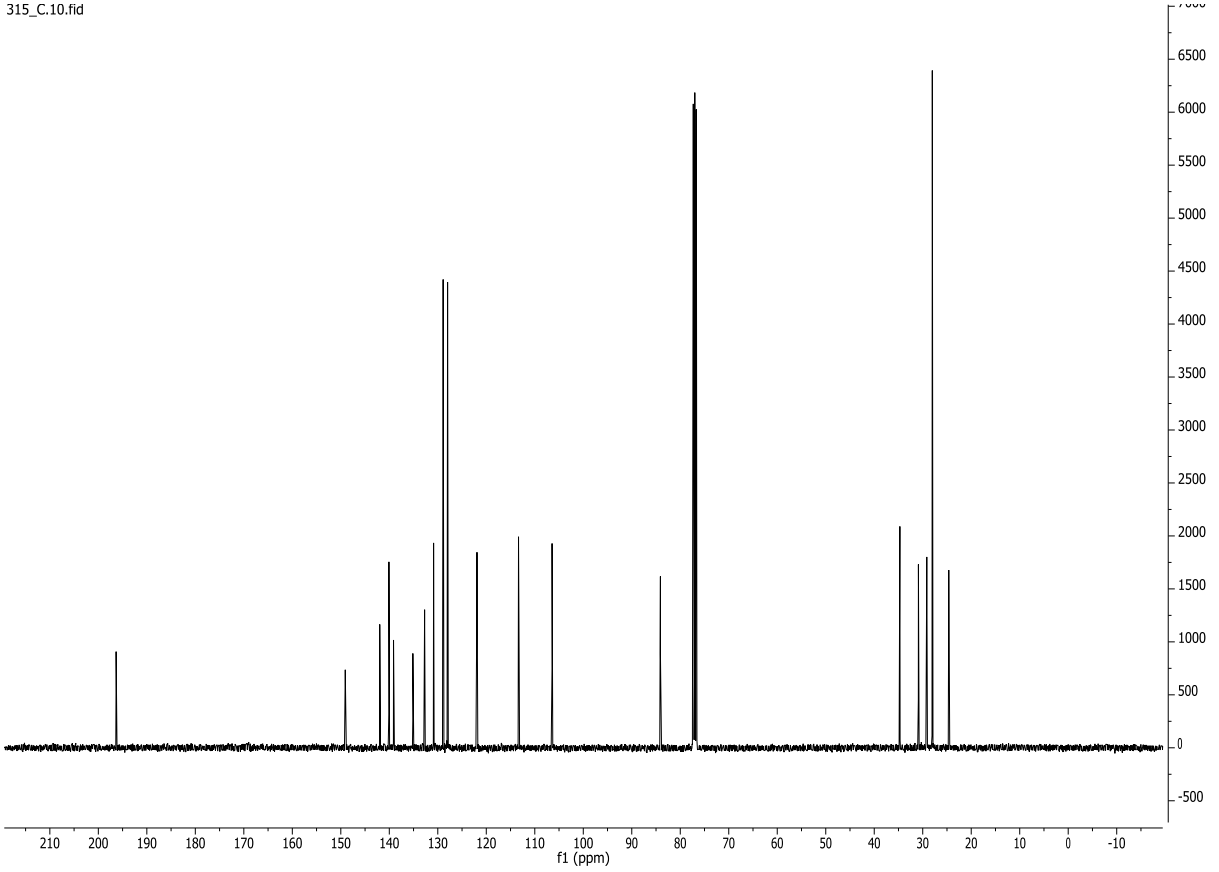


315_H.10.fid

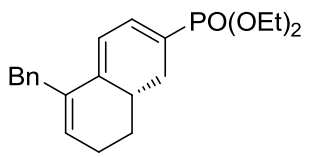


5l

315_C.10.fid

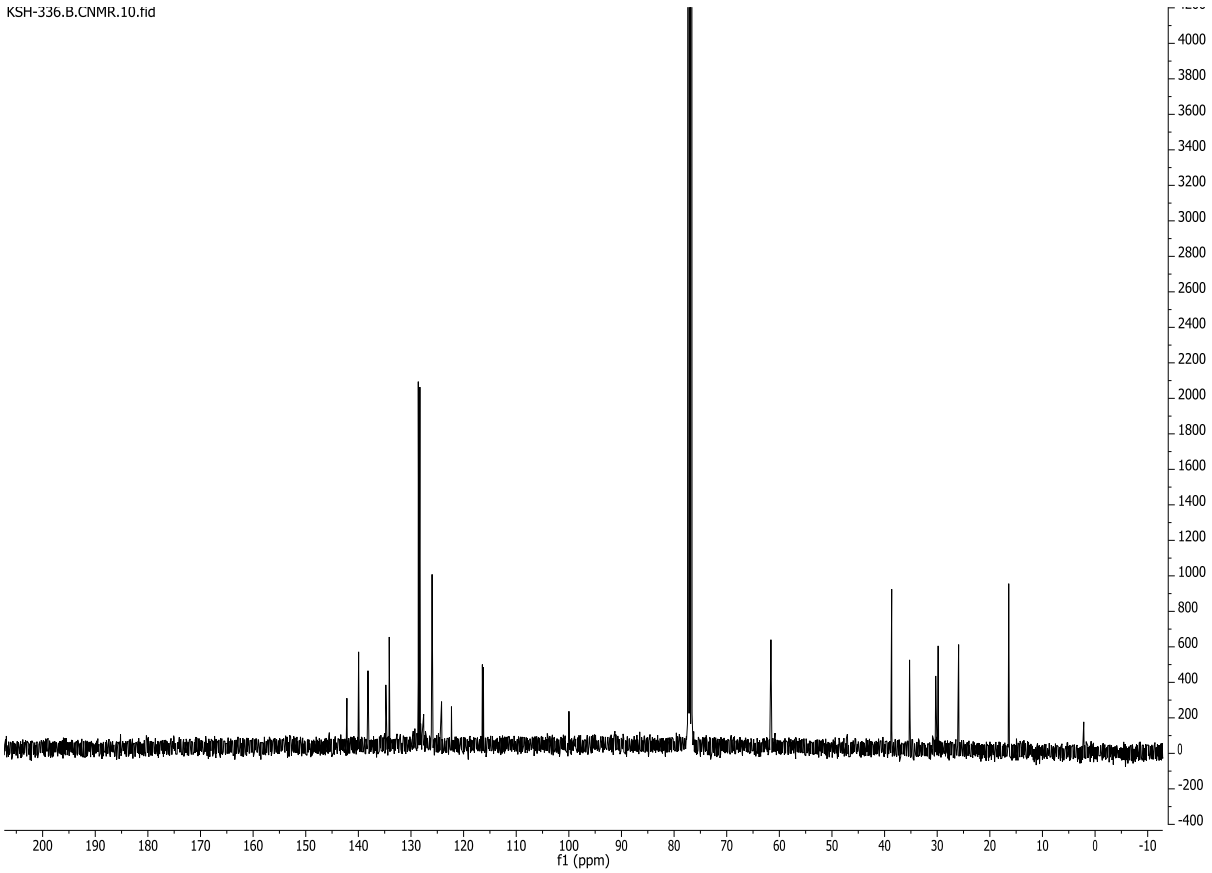


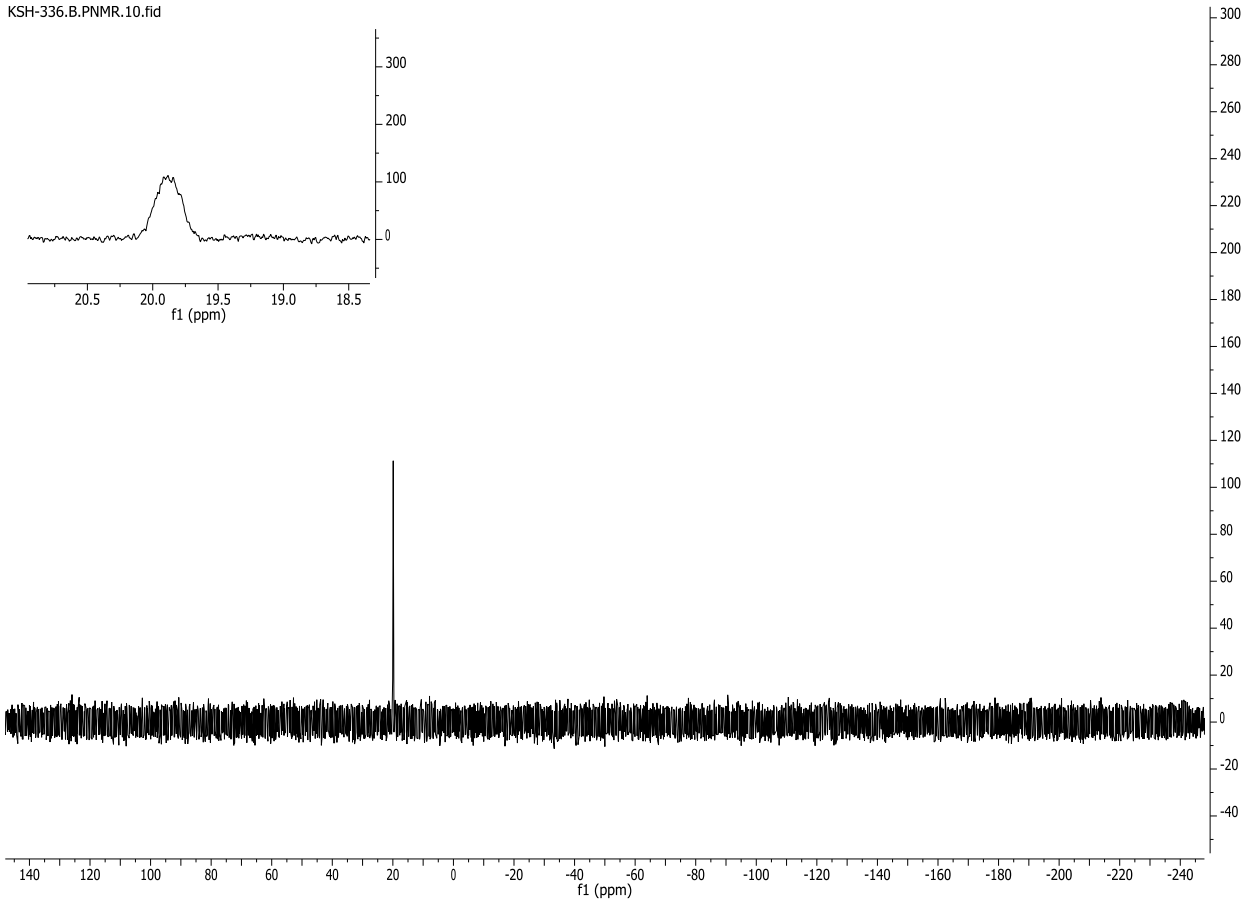
KSH-336.B.HNMR.10.fid



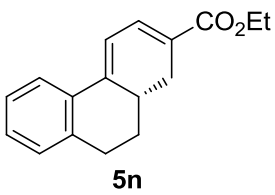
5m

KSH-336.B.CNMR.10.fid



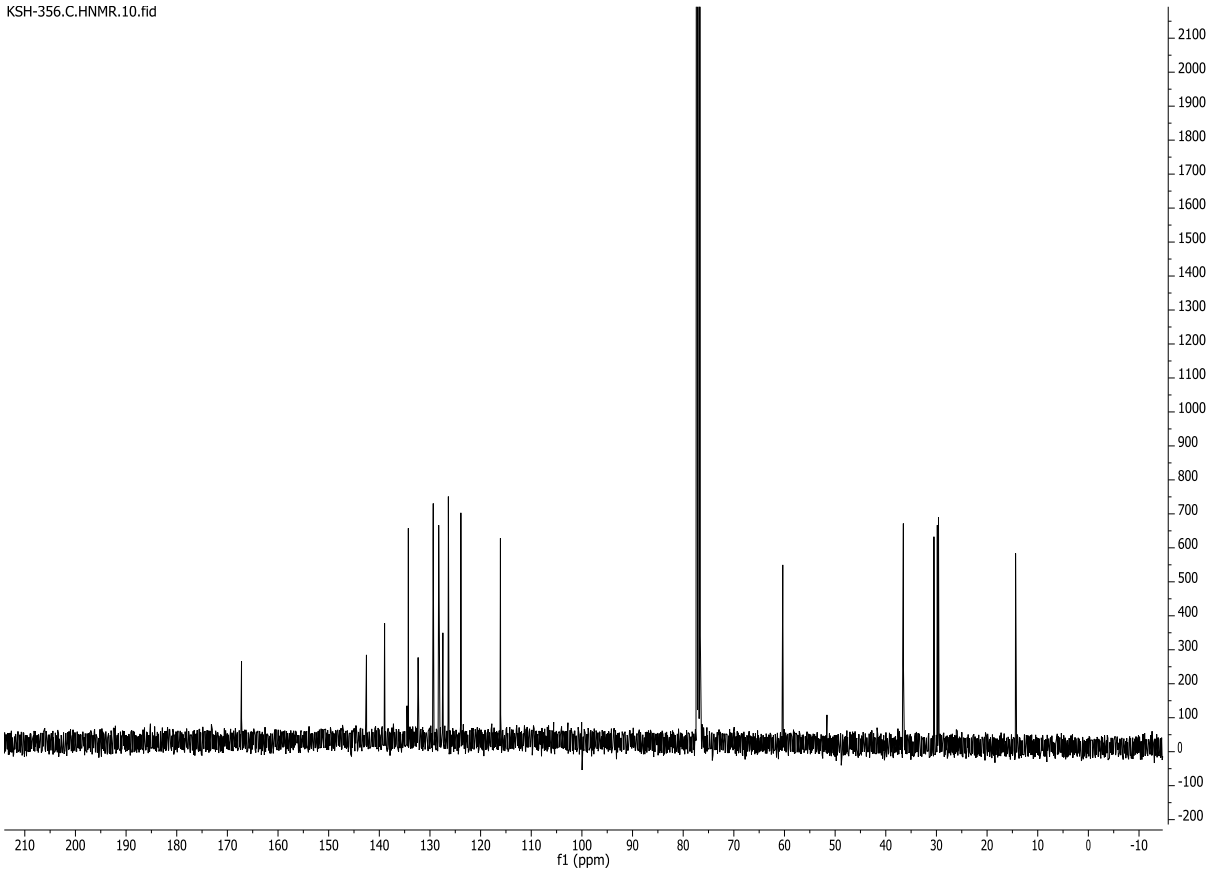

KSH-336.B.PNMR.10.fid
300
200
100
0
20.5
20.0
19.5
19.0
18.5
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

KSH-356.B.HNMR.10.fid

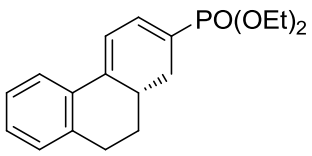


5n

KSH-356.C.HNMR.10.fid

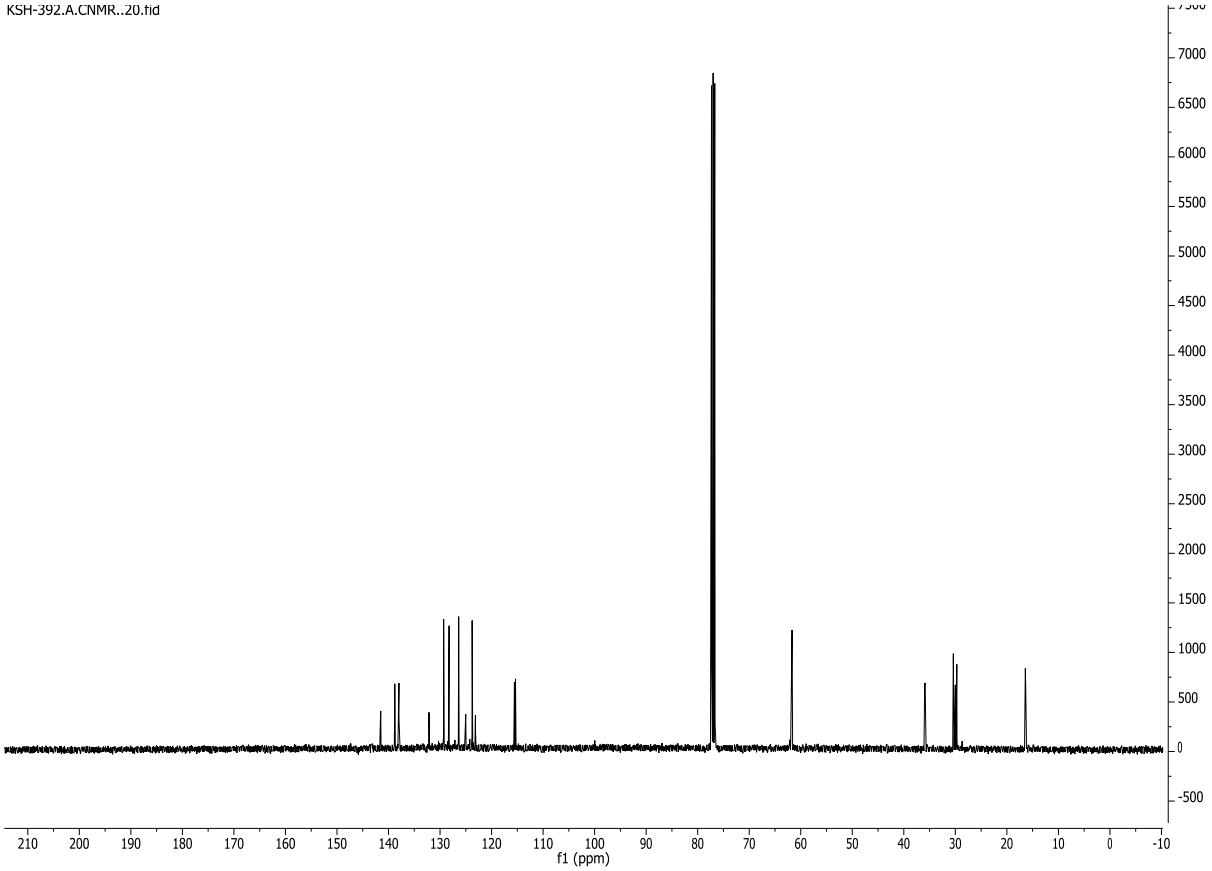


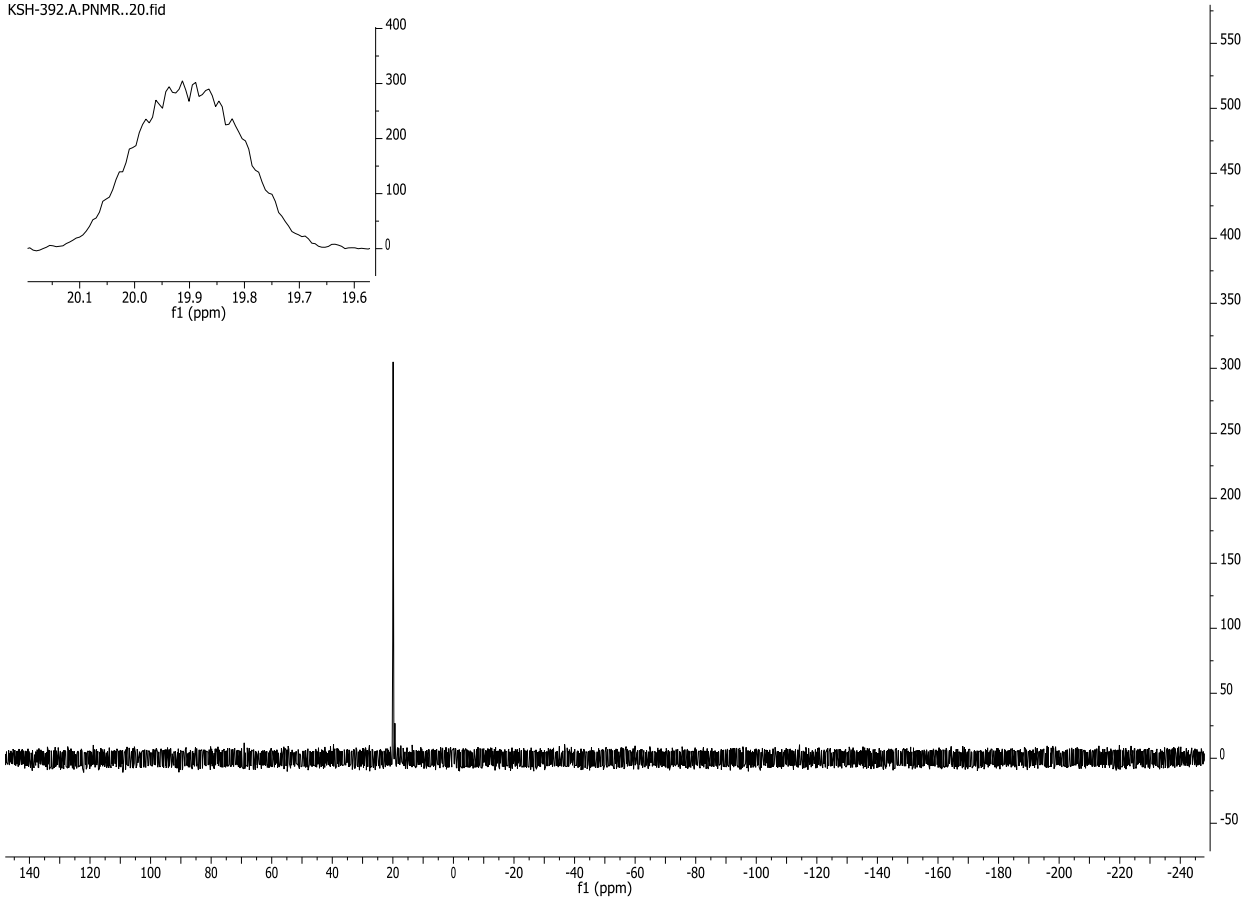
KSH-392.A.HNMR.20.fid



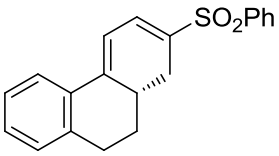
5o

KSH-392.A.CNMR..20.fid



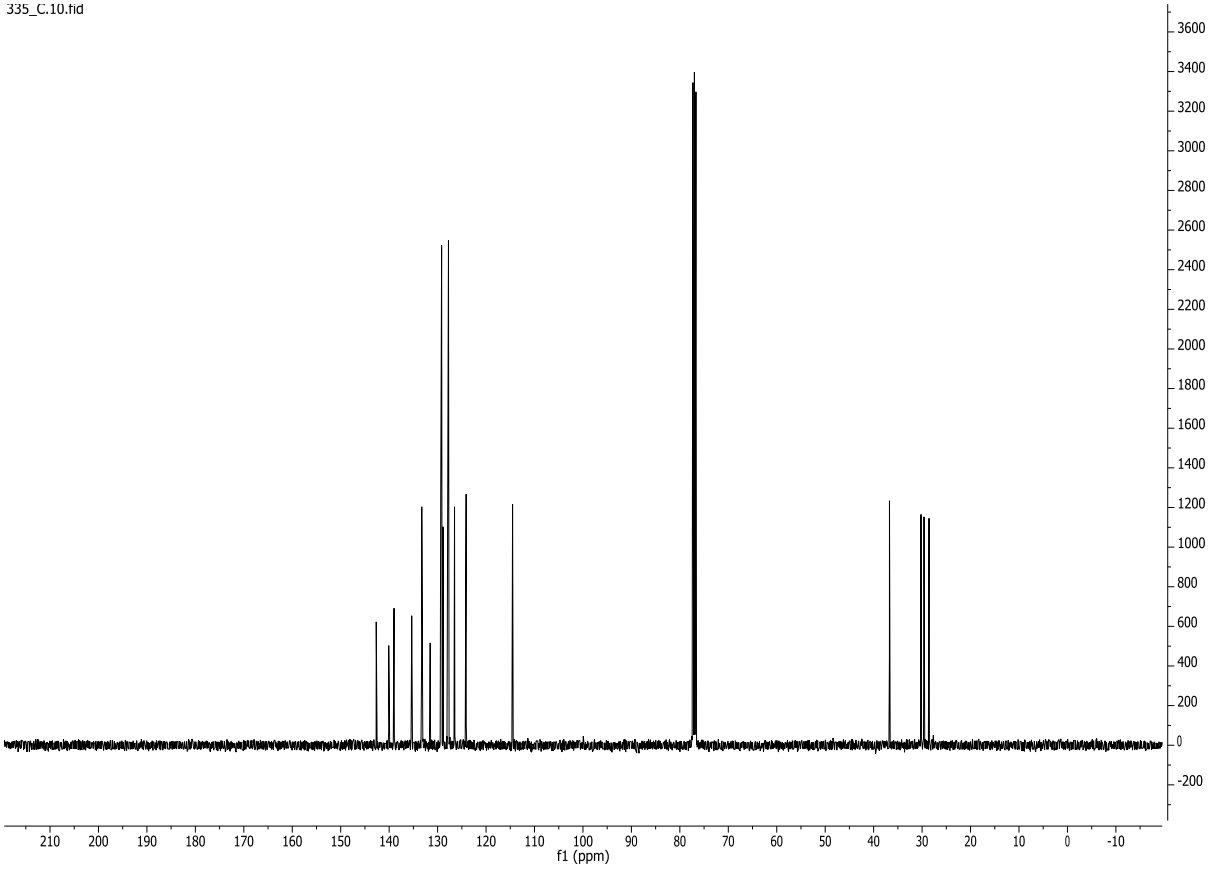

KSH-392.A.PNMR..20.fid
400
300
200
100
0
20.1
20.0
19.9
19.8
19.7
19.6
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

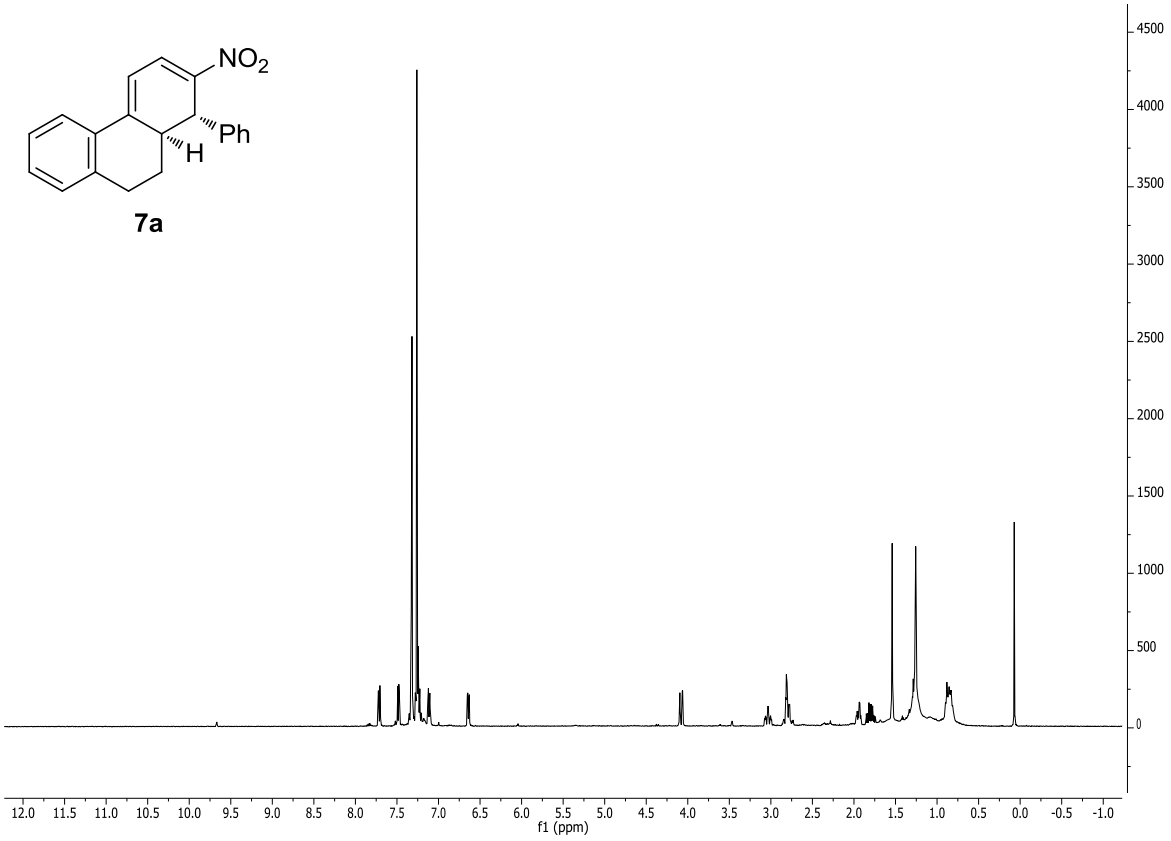
335_co.10.fid



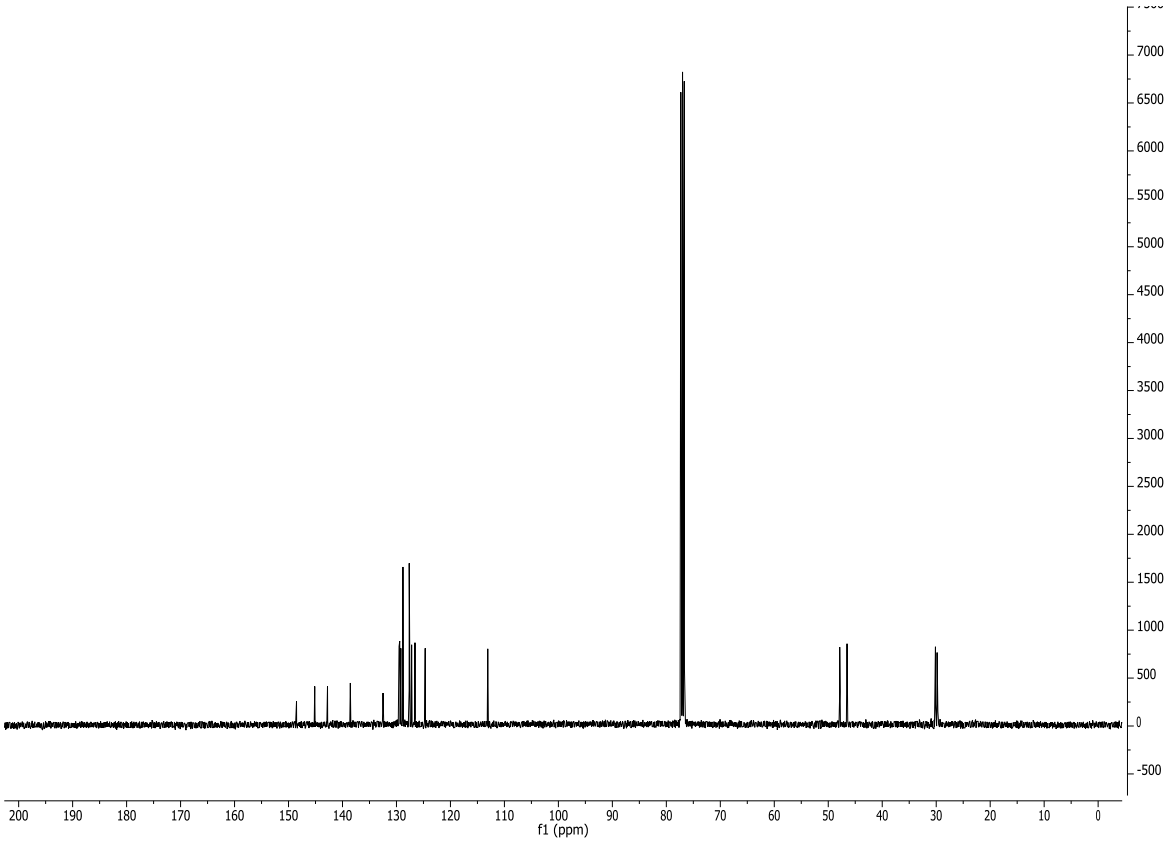
5p

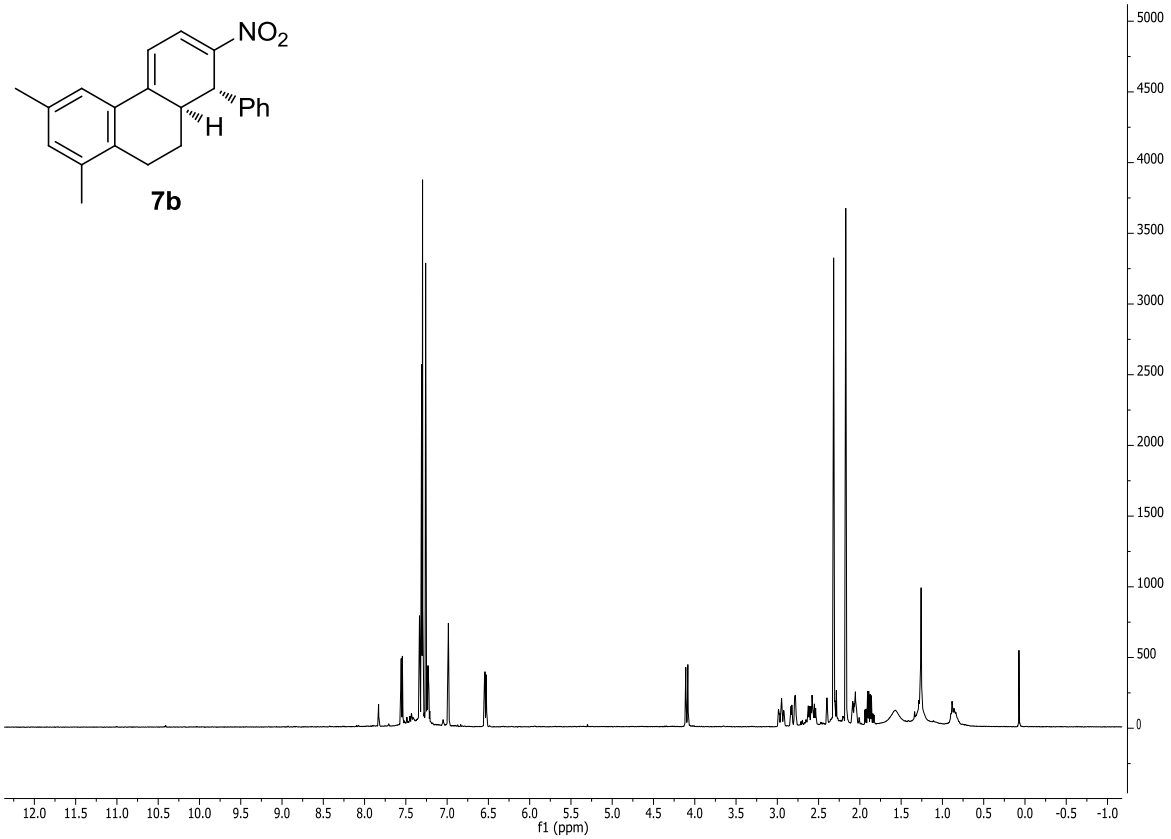
335_C.10.fid

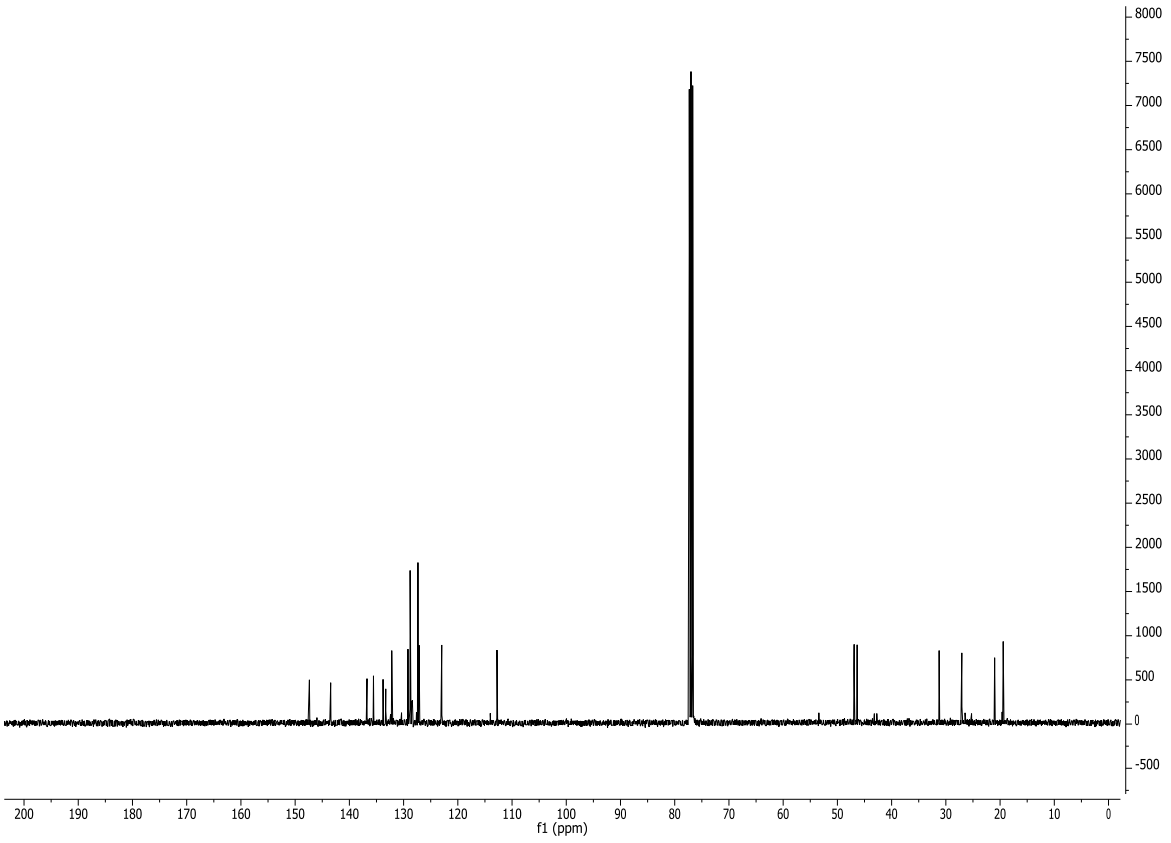


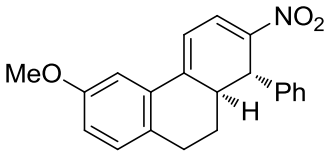


7a

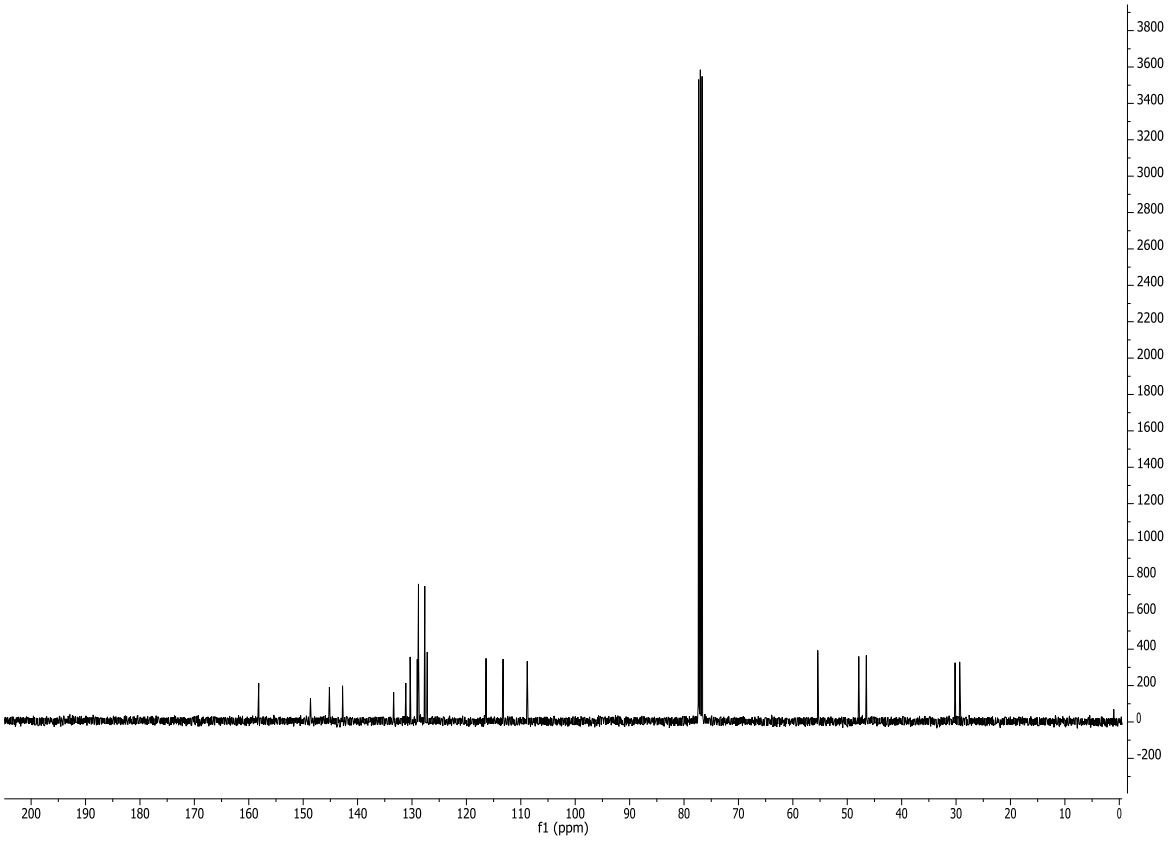


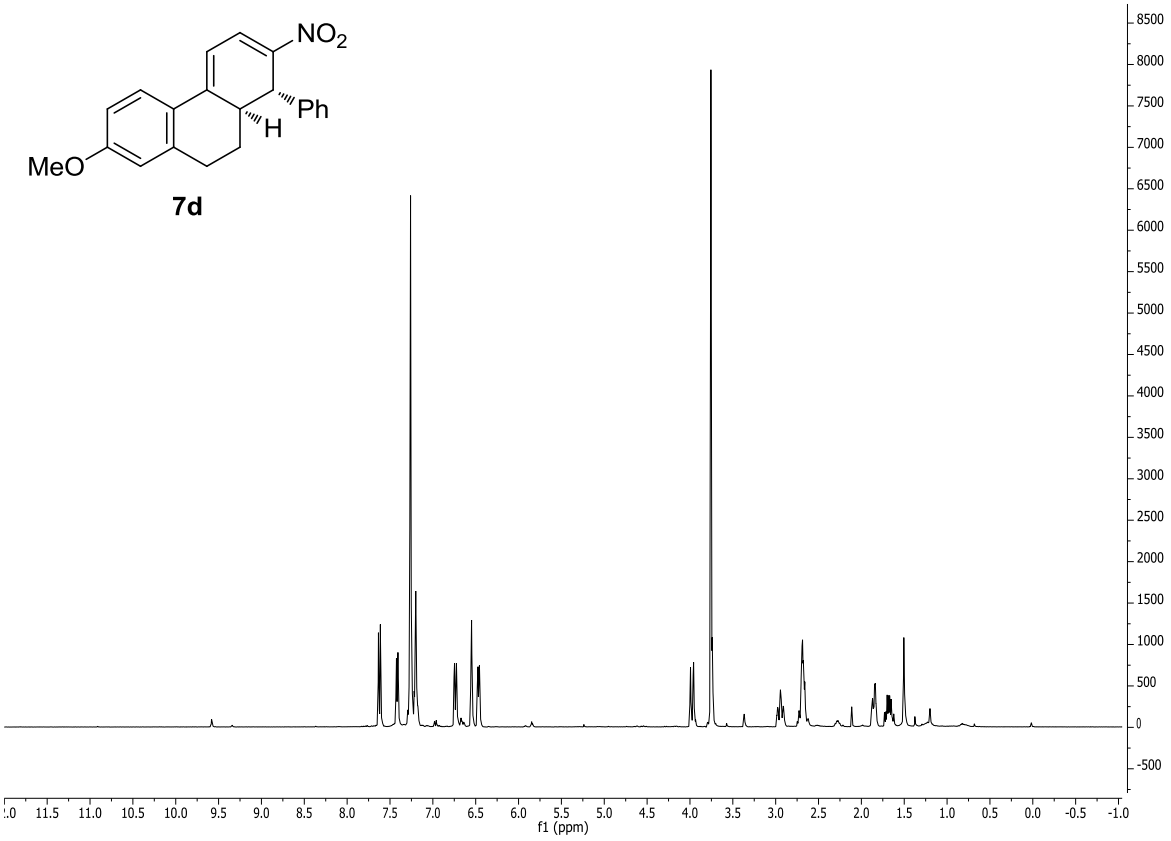

NO2
Ph
H
7b
f1 (ppm)

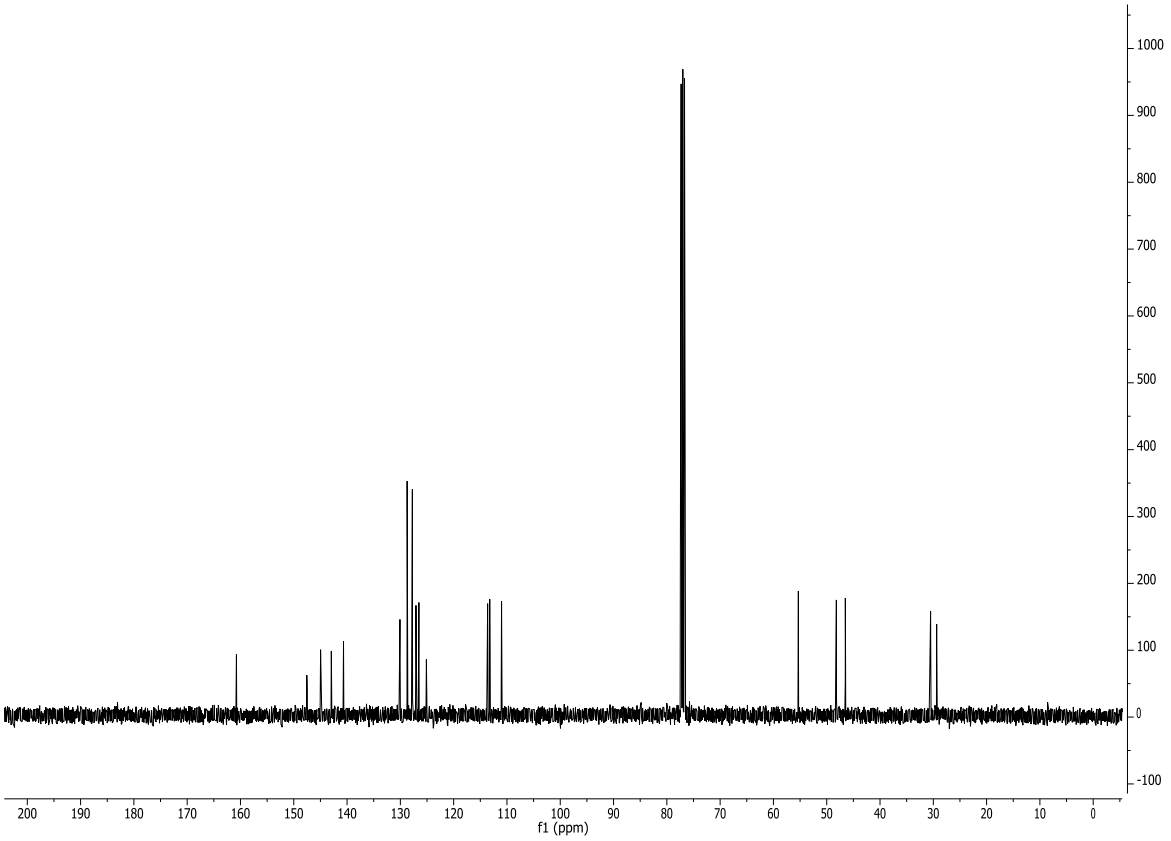

f1 (ppm)

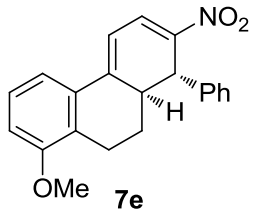


7c



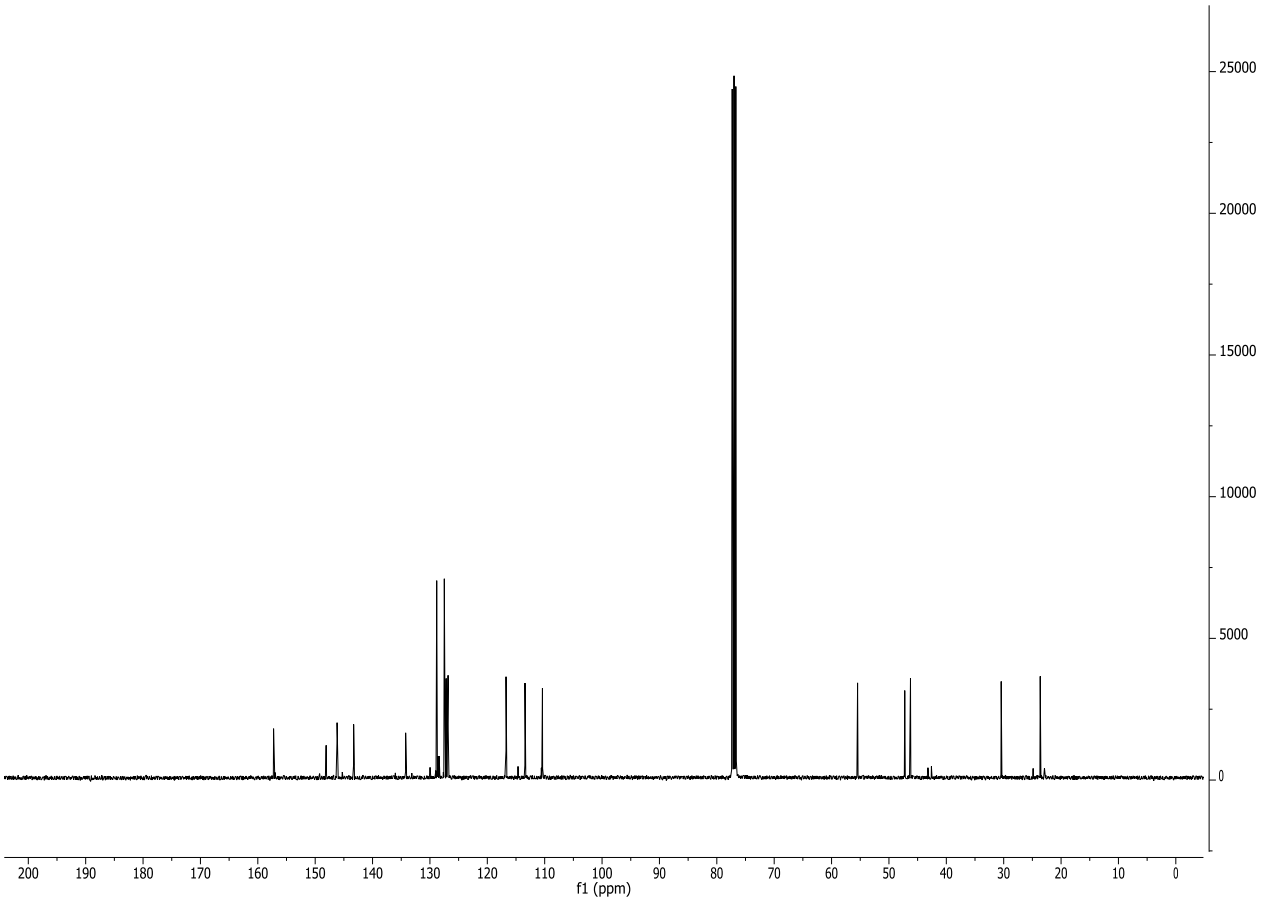

NO2
Ph
H
MeO
7d
f1 (ppm)

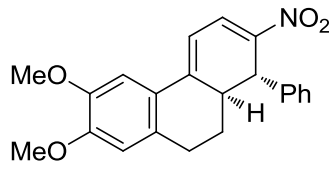

f1 (ppm)


NO2
Ph
H
OMe

7e

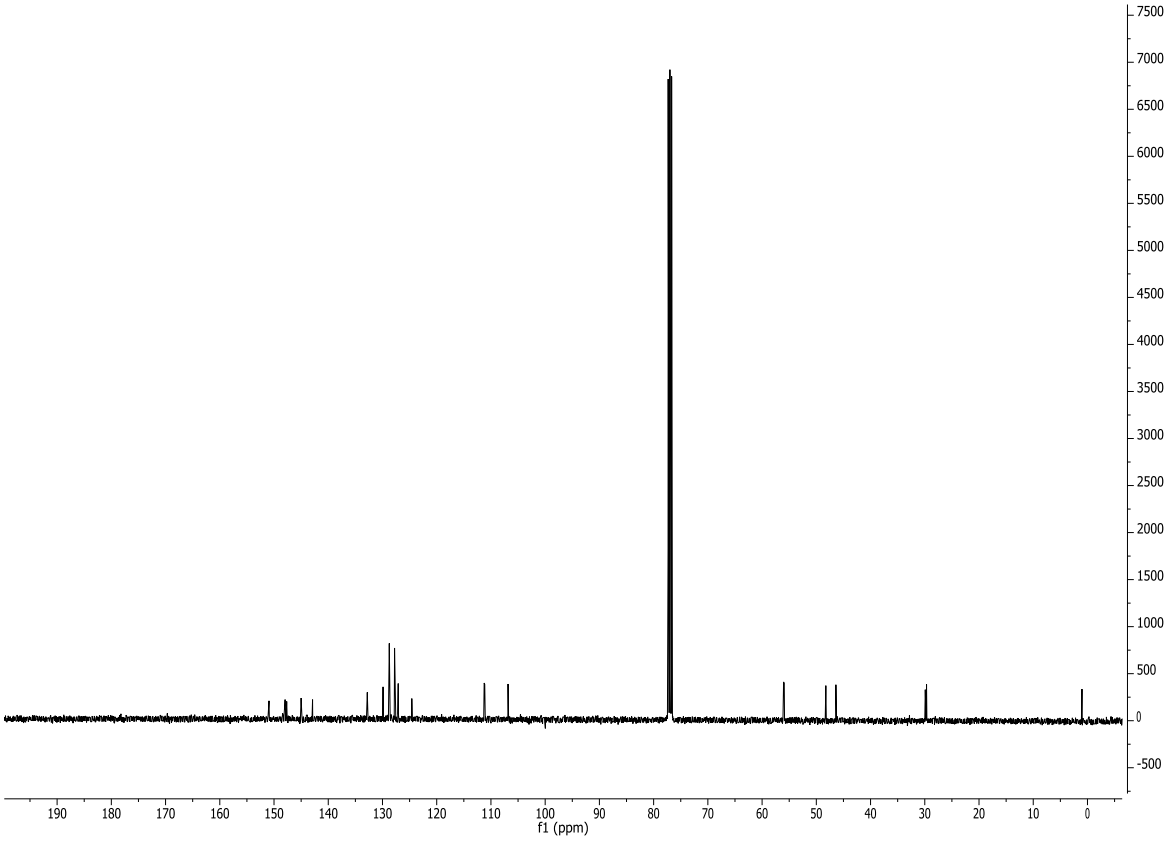
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

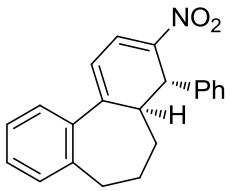

25000
20000
15000
10000
5000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NO2
MeO
Ph
H
MeO

7f

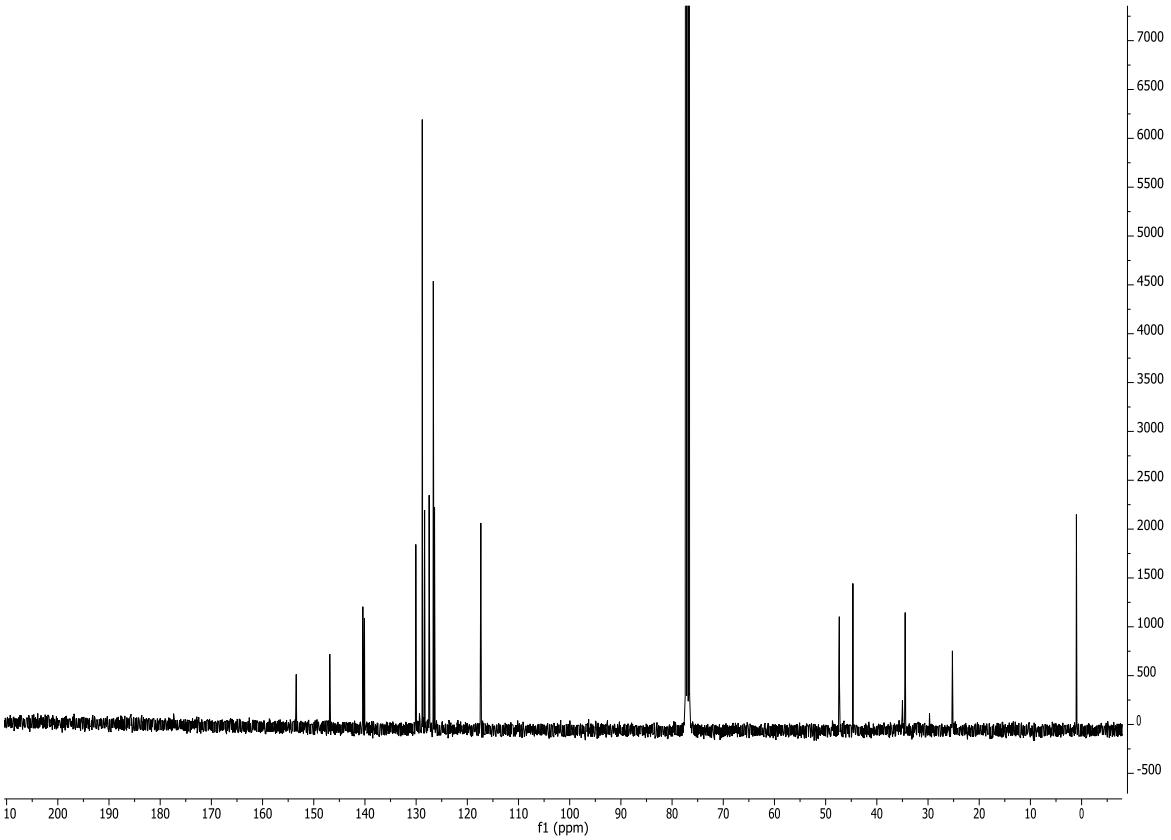
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

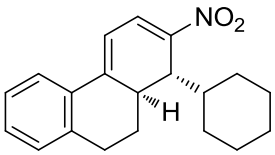

7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NO2
Ph
H

7g

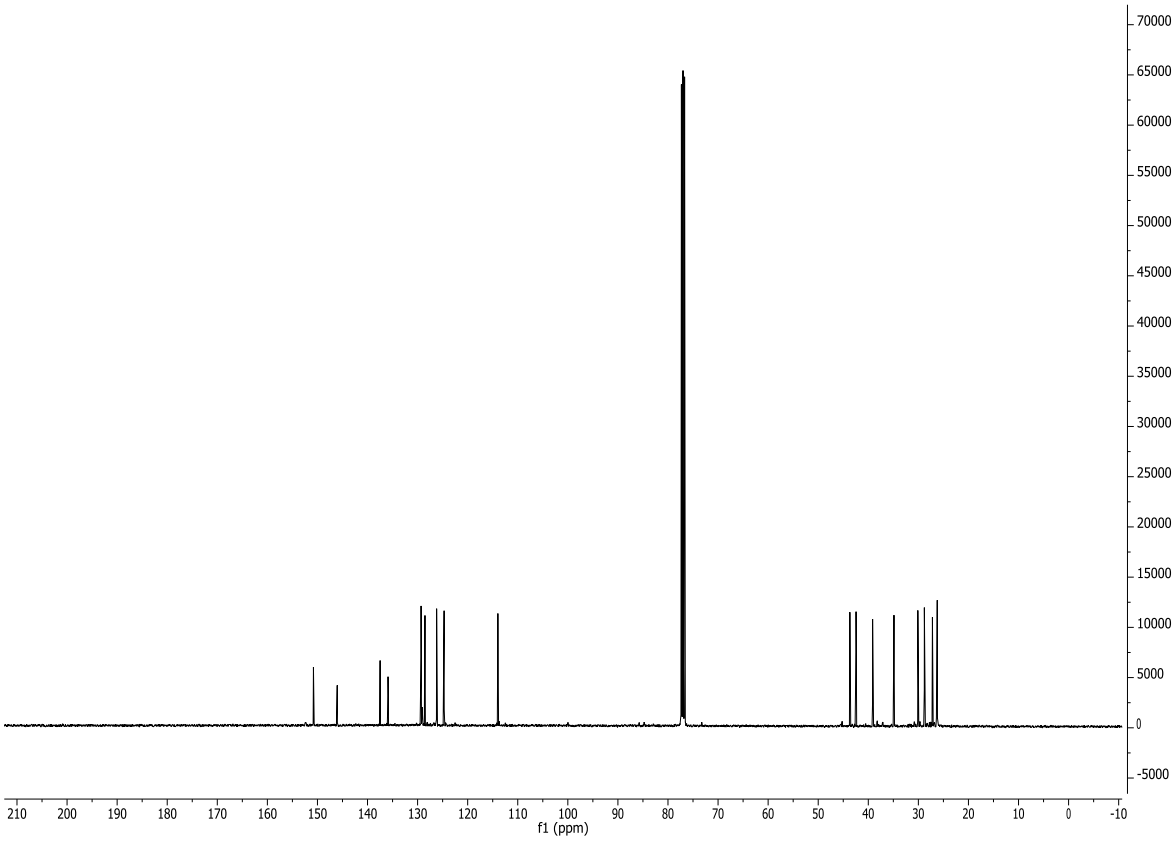
4000
3500
3000
2500
2000
1500
1000
500
0
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

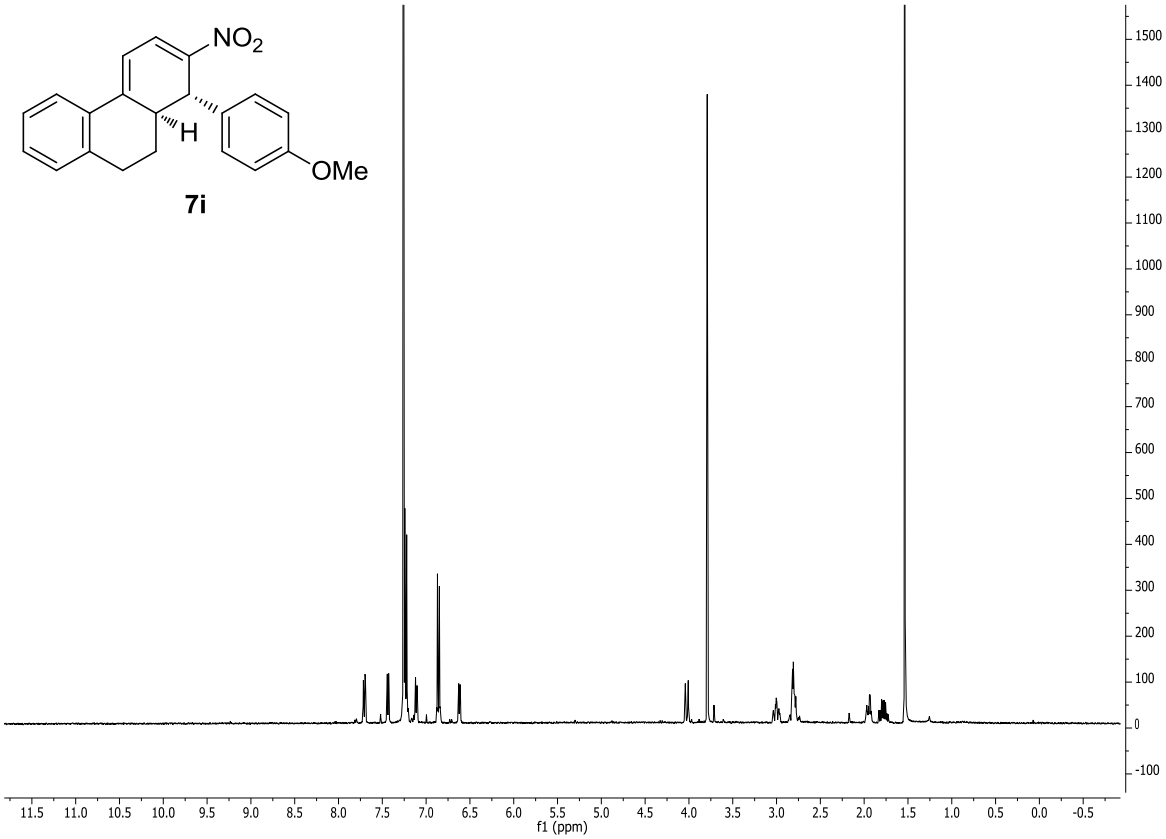

7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

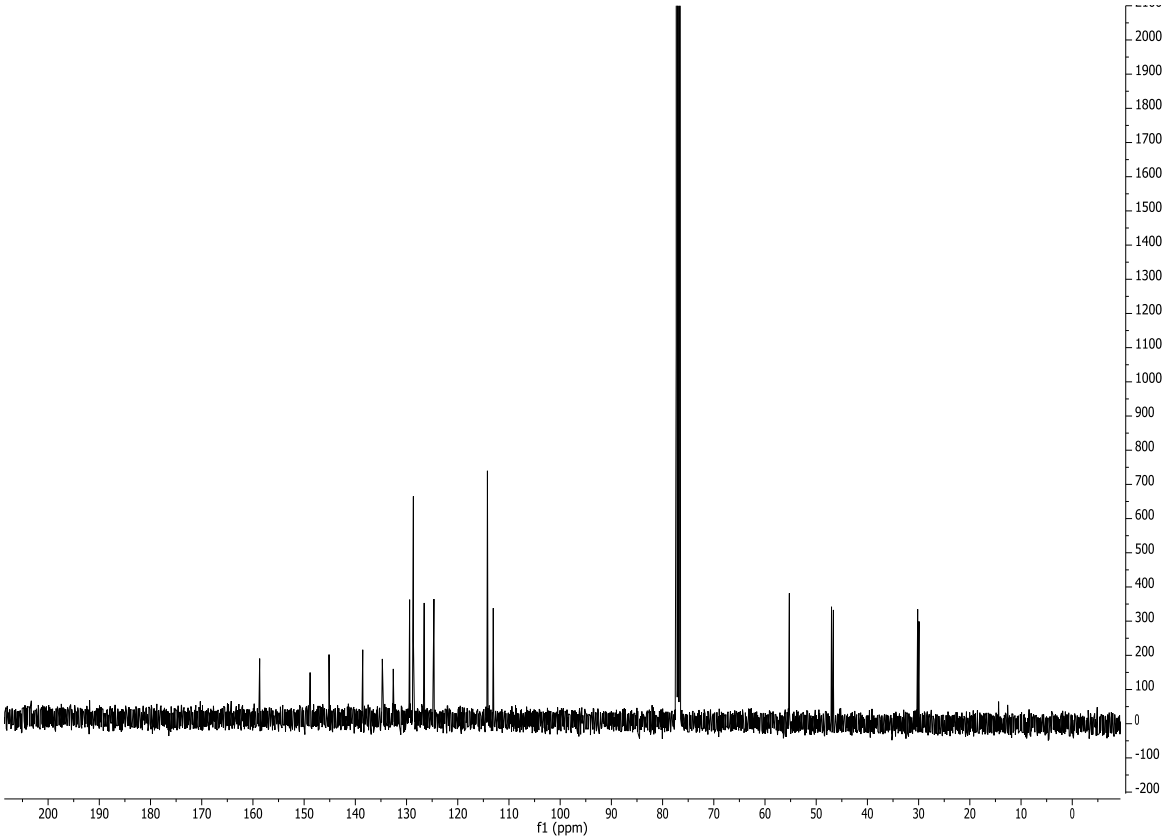

NO2
H

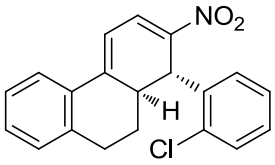
7h

7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

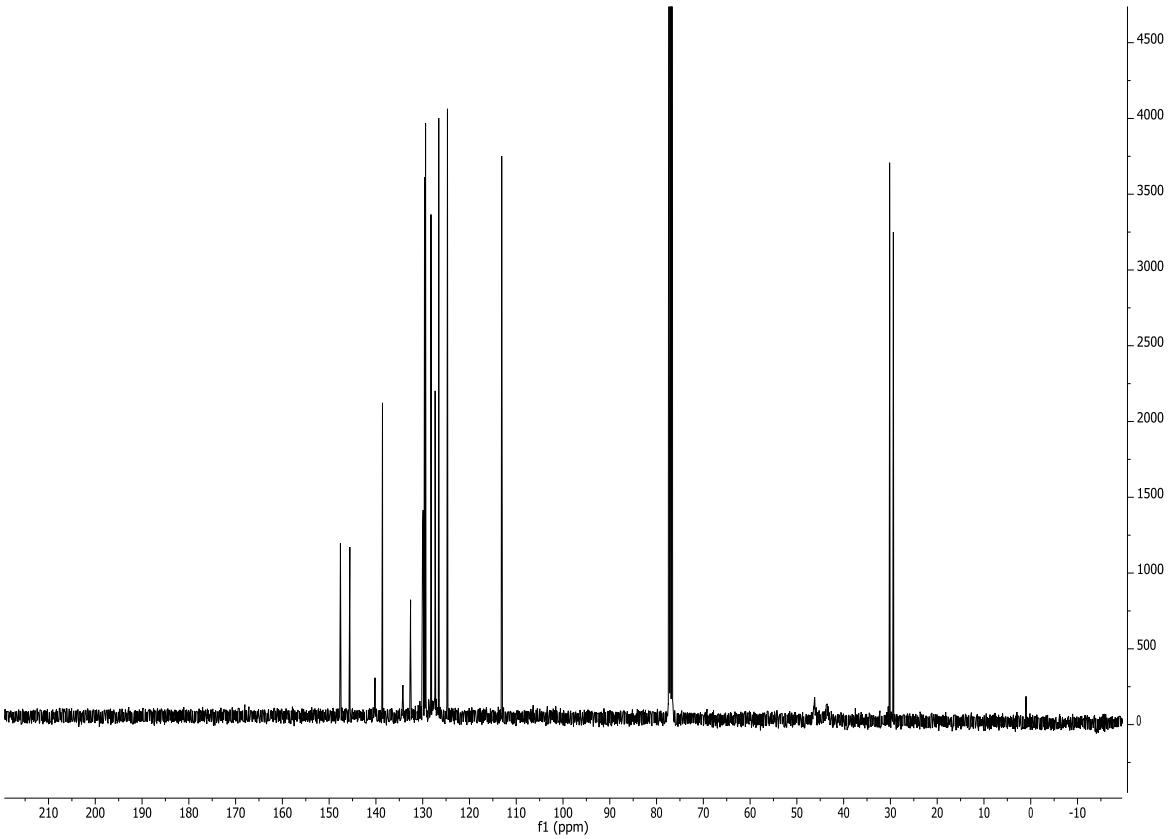

NO2
H
OMe
7i
f1 (ppm)


f1 (ppm)

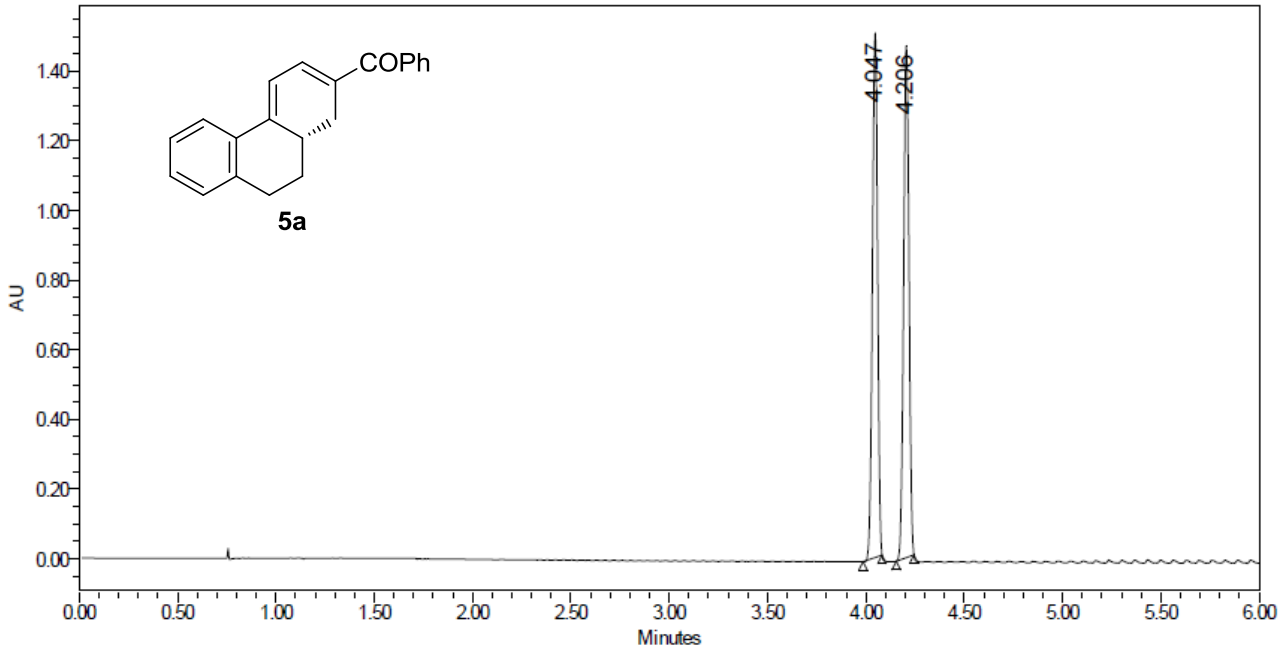

NO2
H
Cl

7j

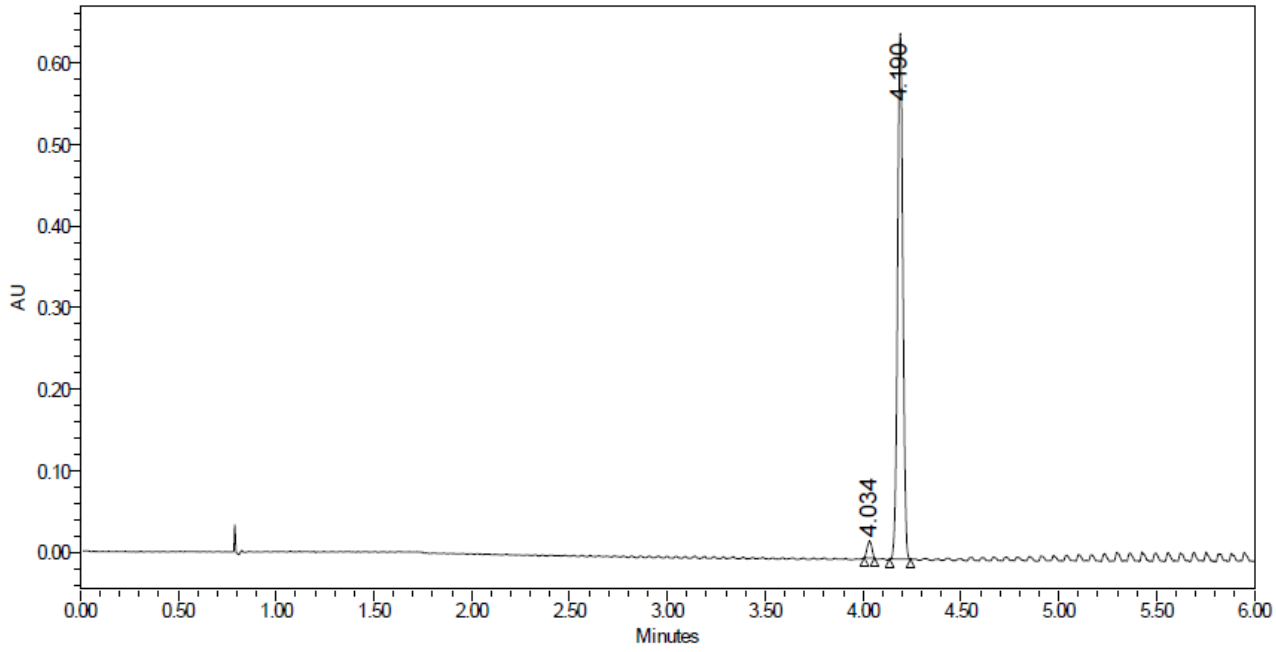
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

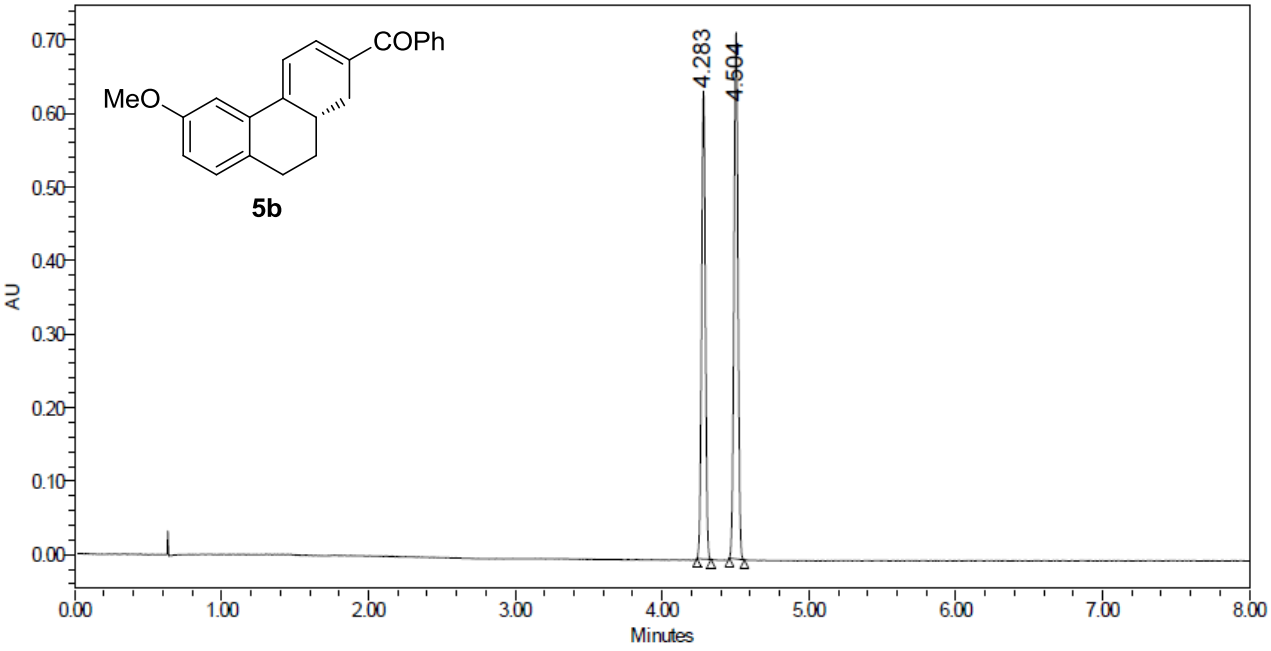
6. UPC^2 traces



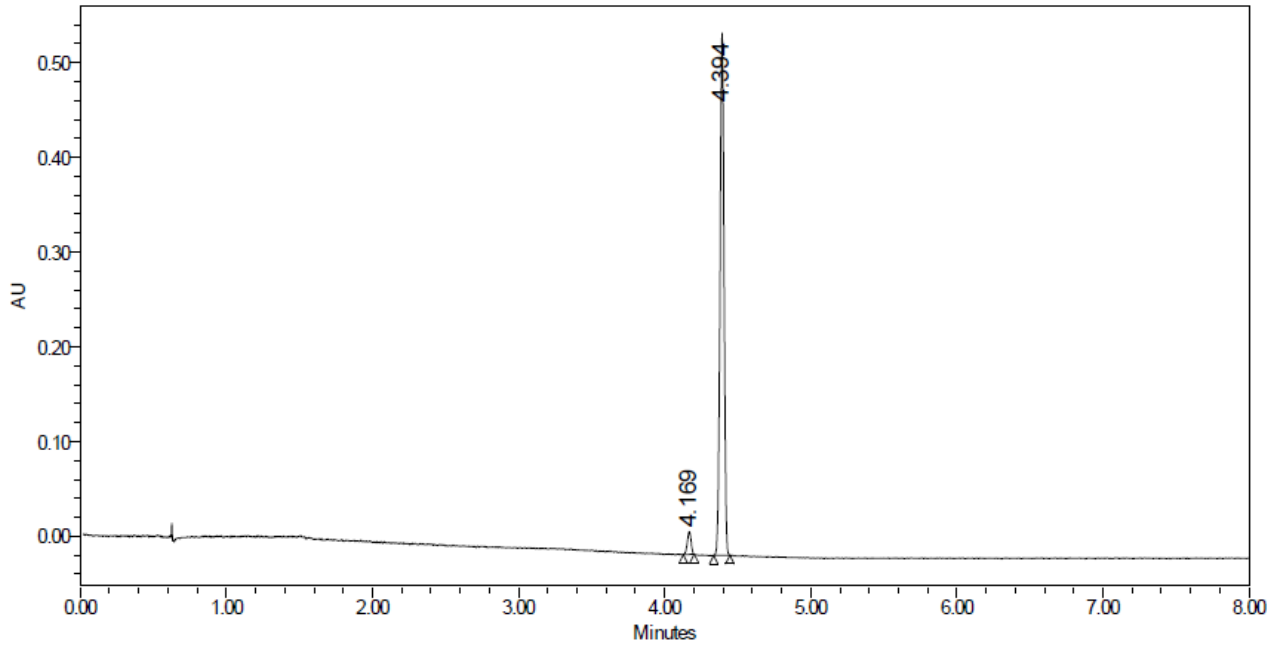
	Retention Time (min)	% Area
1	4.206	50.36
2	4.047	49.64



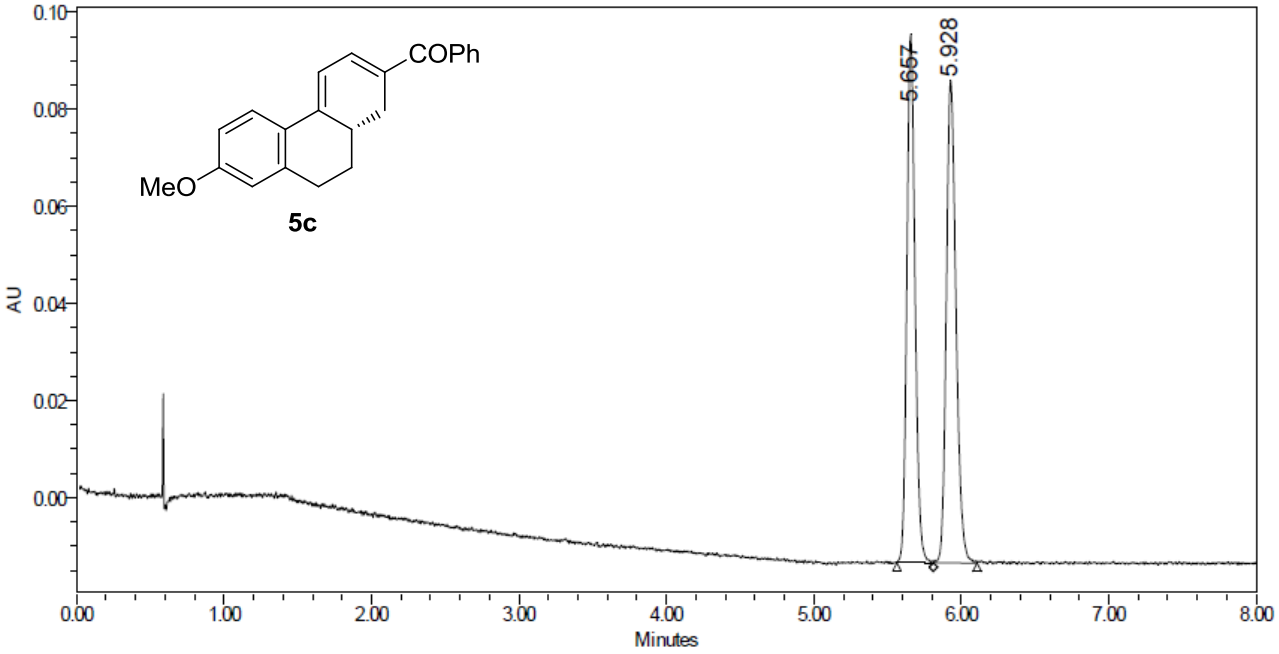
	Retention Time (min)	% Area
1	4.034	2.69
2	4.190	97.31



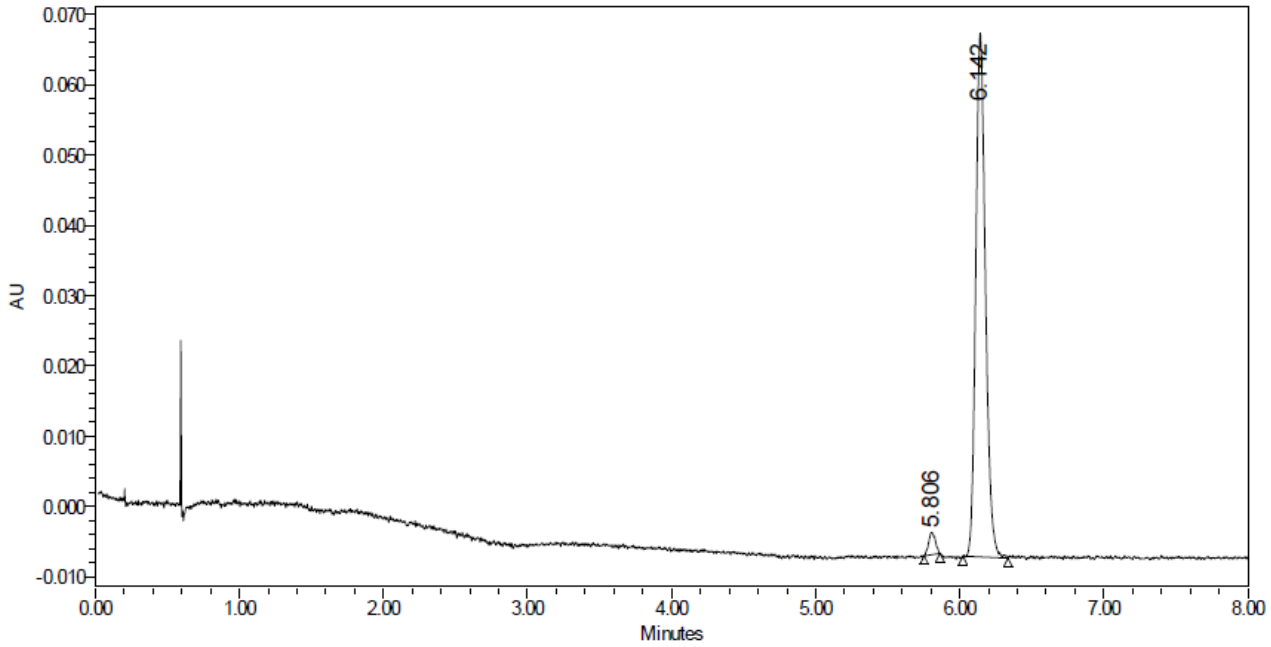
	Retention Time (min)	% Area
1	4.283	46.01
2	4.504	53.99



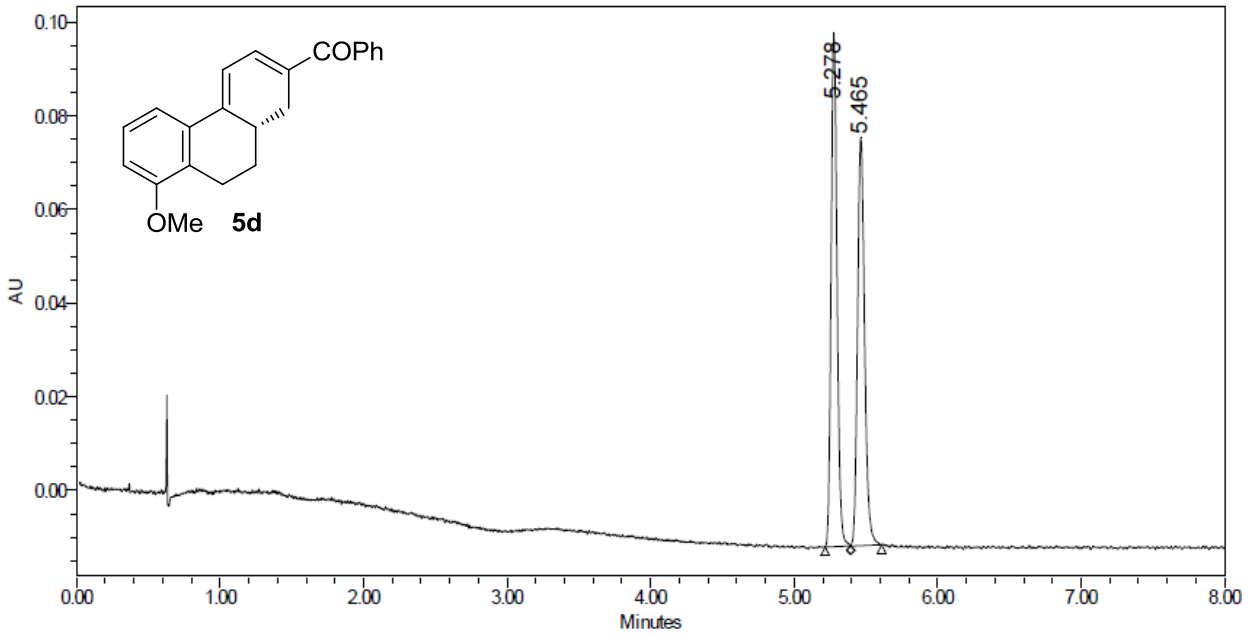
	Retention Time (min)	% Area
1	4.169	3.93
2	4.394	96.07



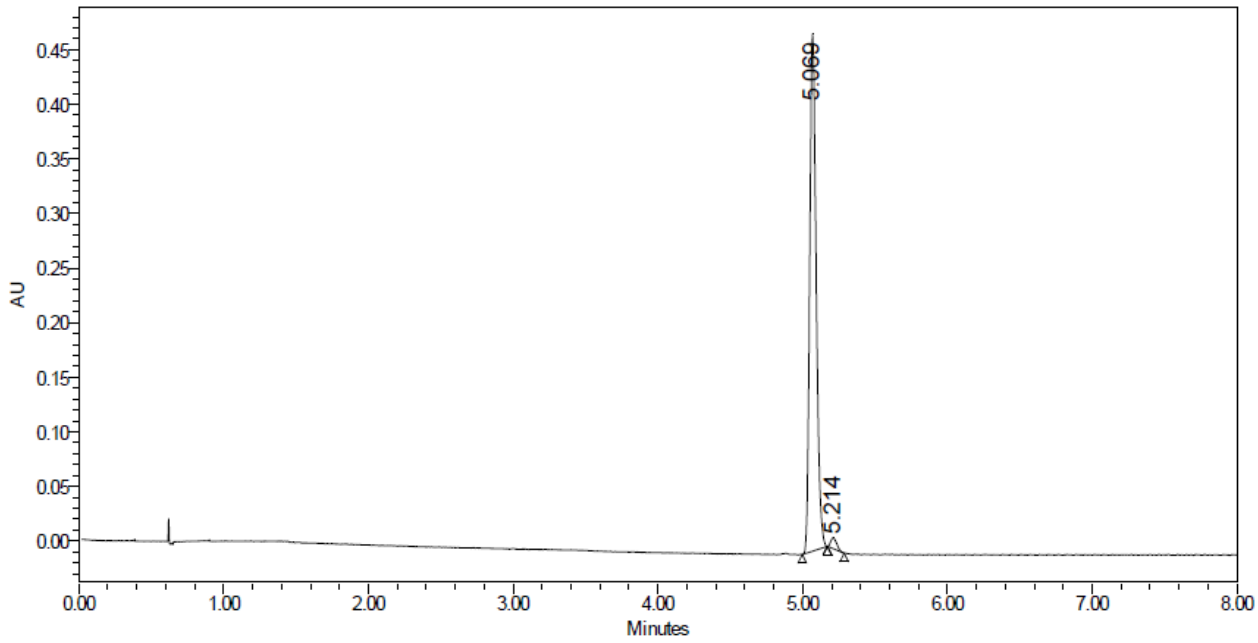
	Retention Time (min)	% Area
1	5.657	48.05
2	5.928	51.95



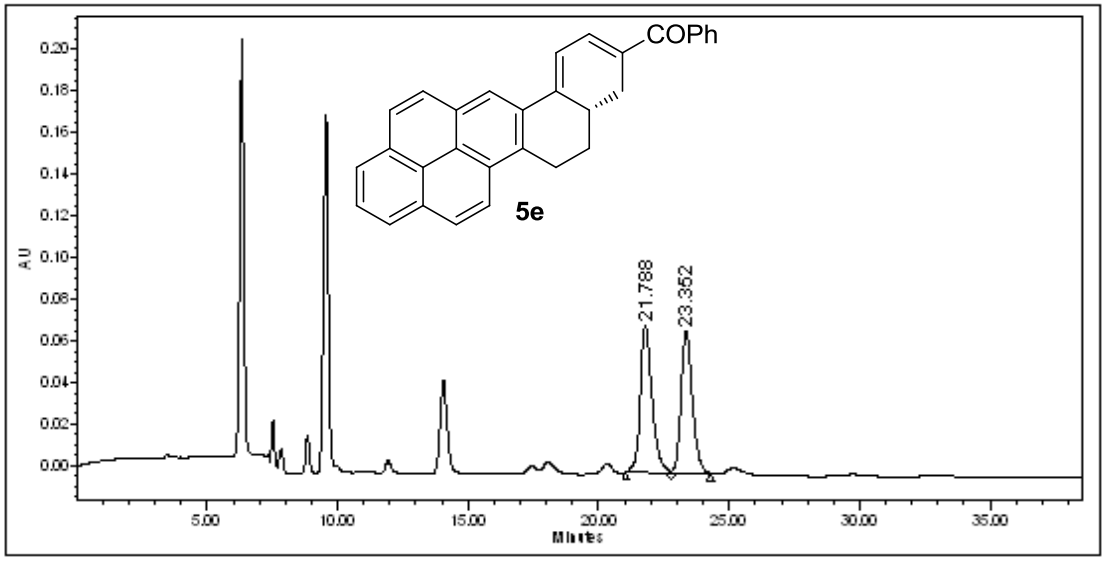
	Retention Time (min)	% Area
1	5.806	2.88
2	6.142	97.12



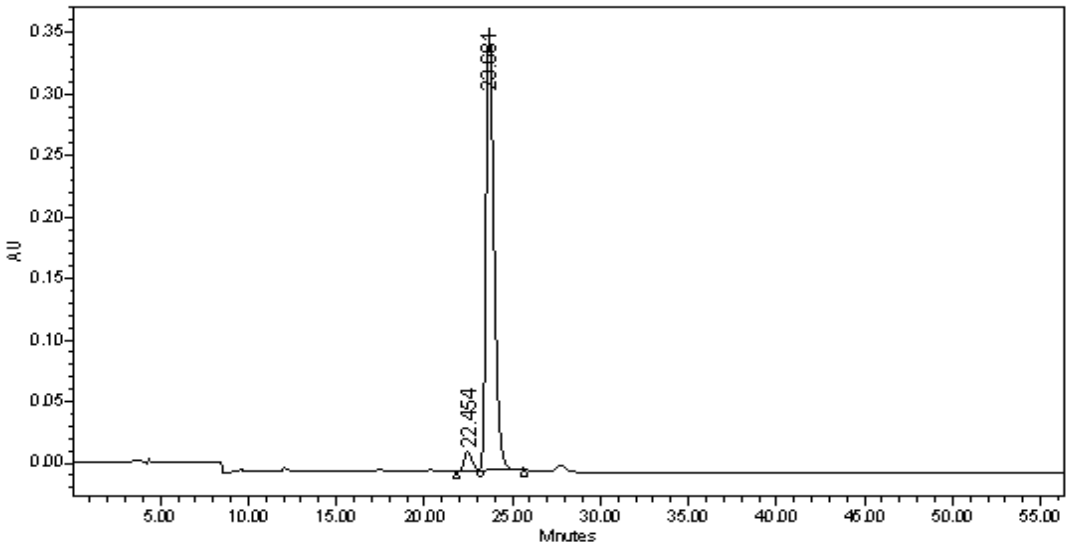
	Retention Time (min)	% Area
1	5.278	51.54
2	5.465	48.46



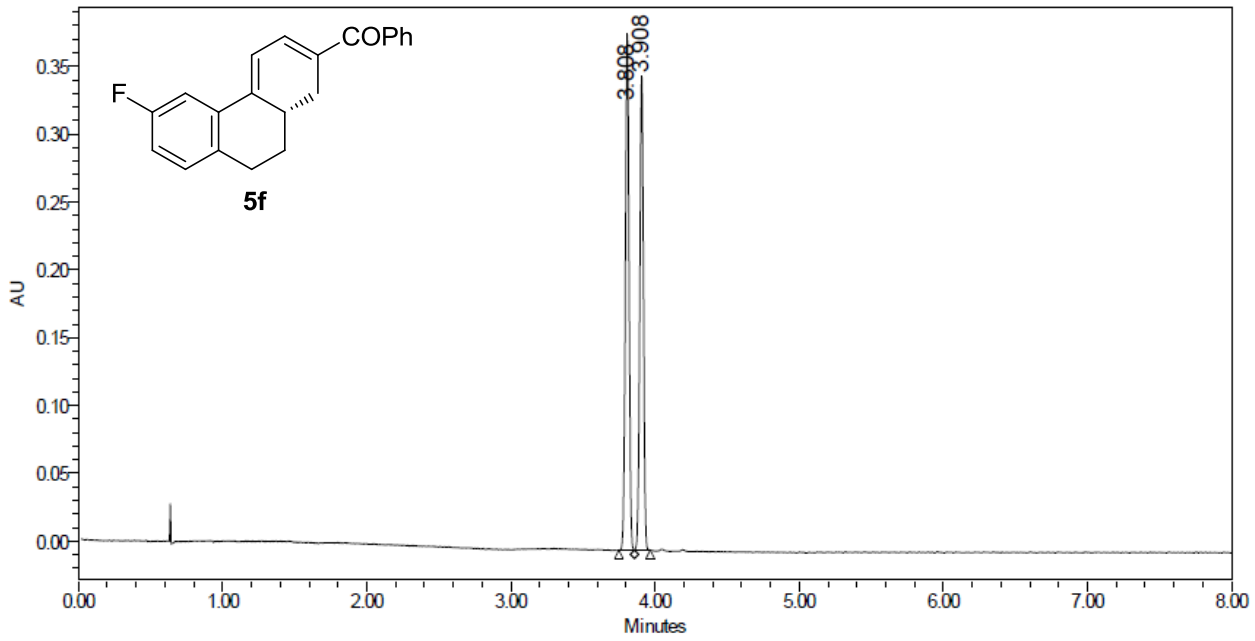
	Retention Time (min)	% Area
1	5.069	98.10
2	5.214	1.90



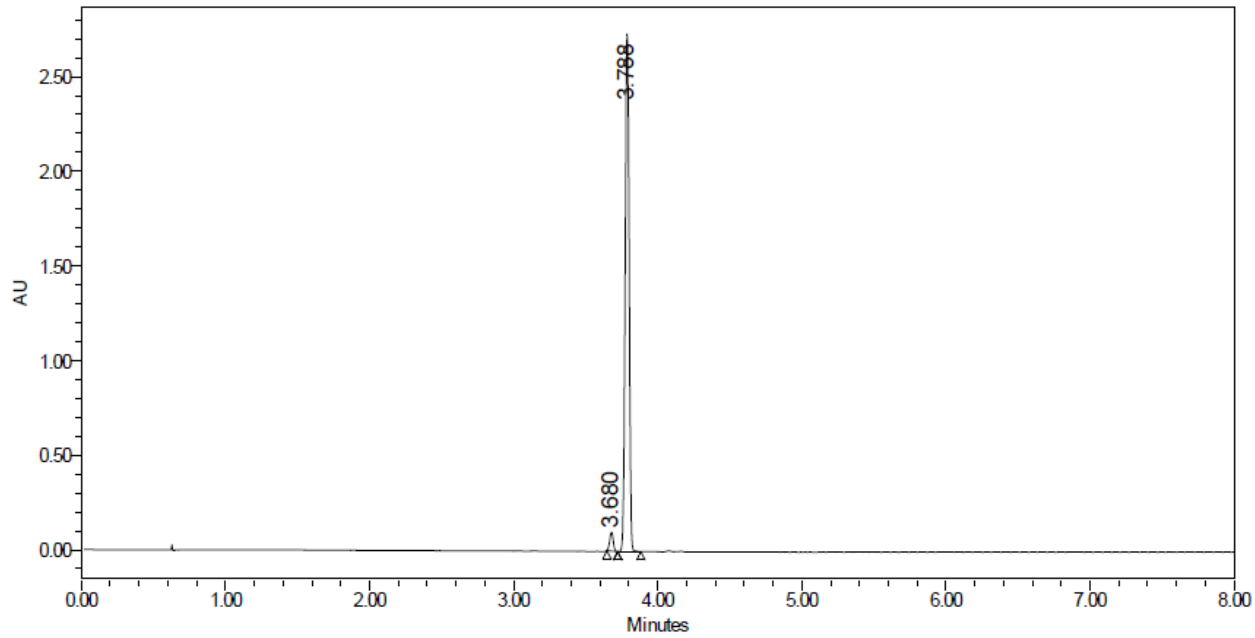
	RT	Area	% Area	Height
1	21.788	2198747	51.77	70316
2	23.352	2048623	48.23	67847



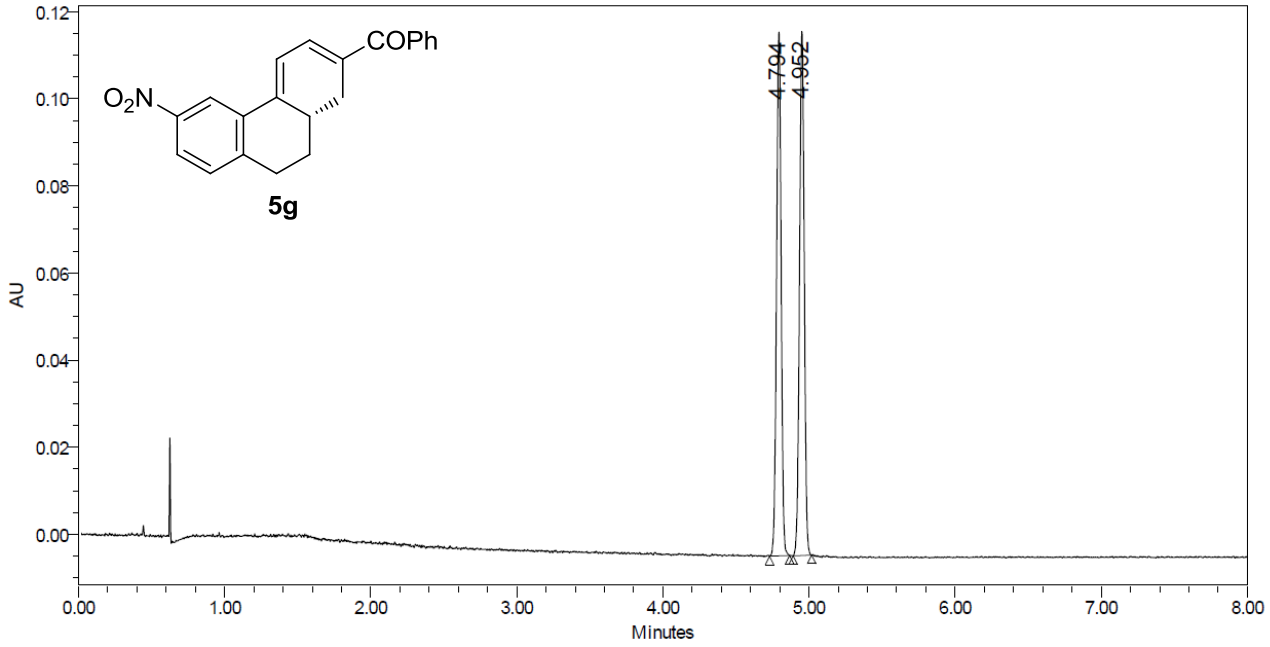
	RT	Area	% Area	Height
1	22.454	488053	4.14	16207
2	23.681	11297024	95.86	358442



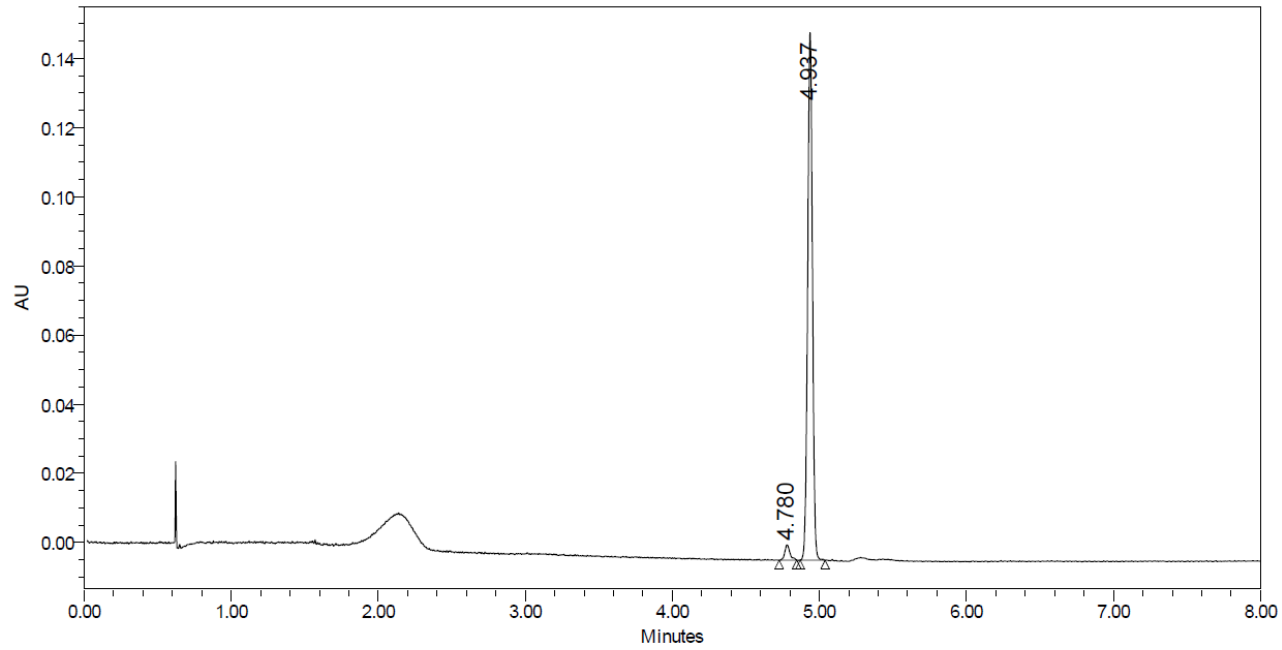
	Retention Time (min)	% Area
1	3.808	52.01
2	3.908	47.99



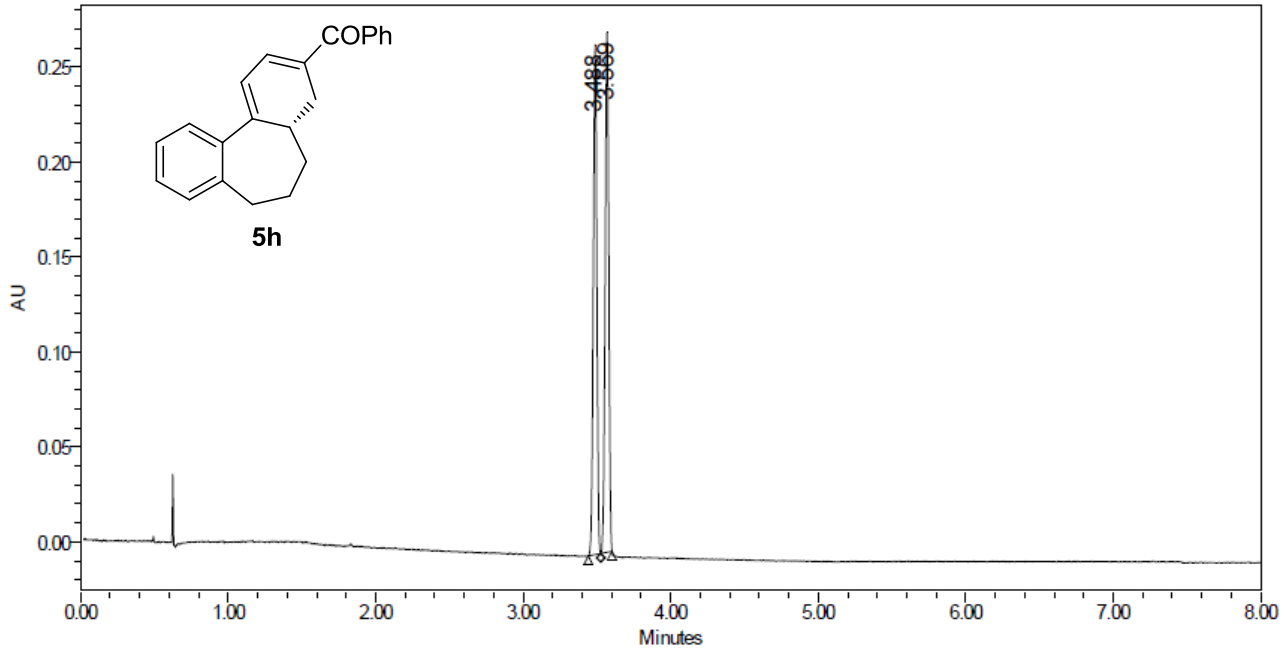
	Retention Time (min)	% Area
1	3.680	3.12
2	3.788	96.88



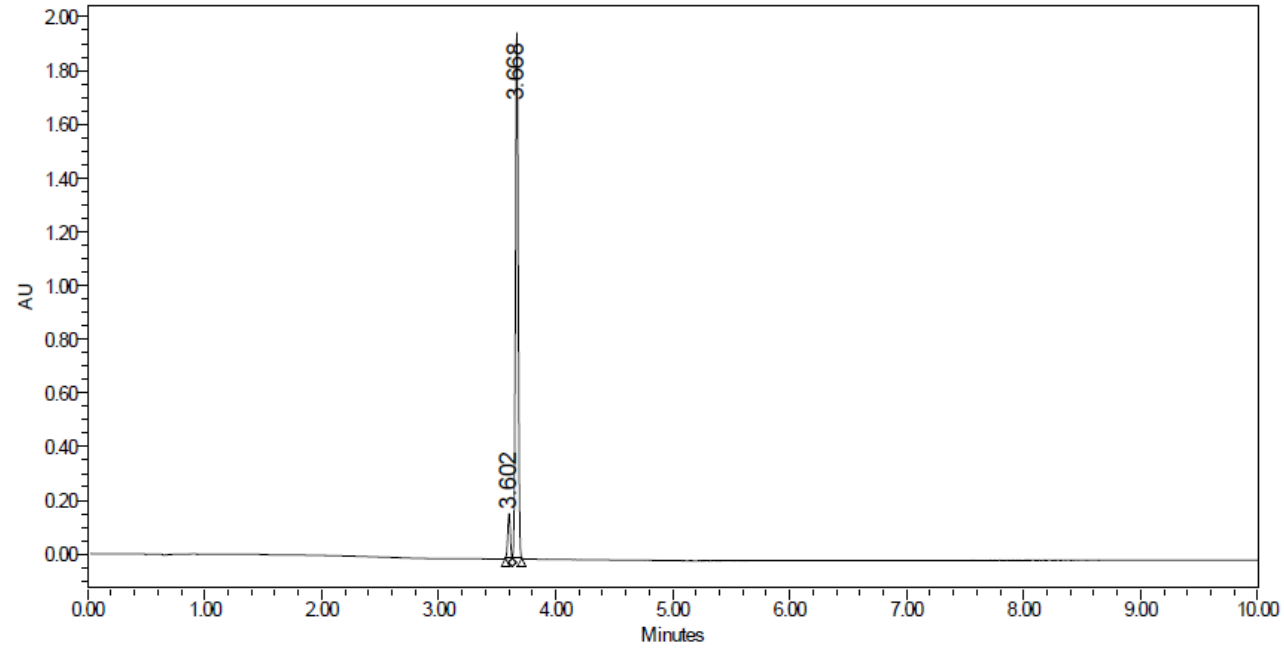
	Retention Time (min)	% Area
1	4.794	49.14
2	4.952	50.86



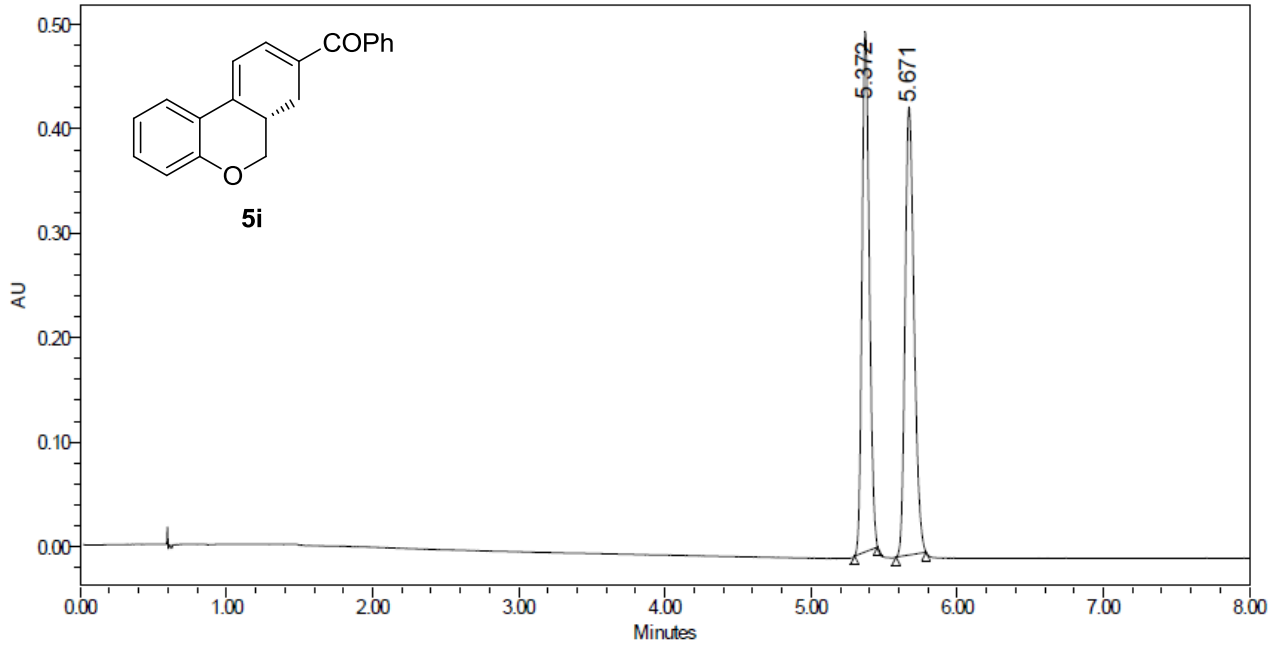
	Retention Time (min)	% Area
1	4.780	3.04
2	4.937	96.96



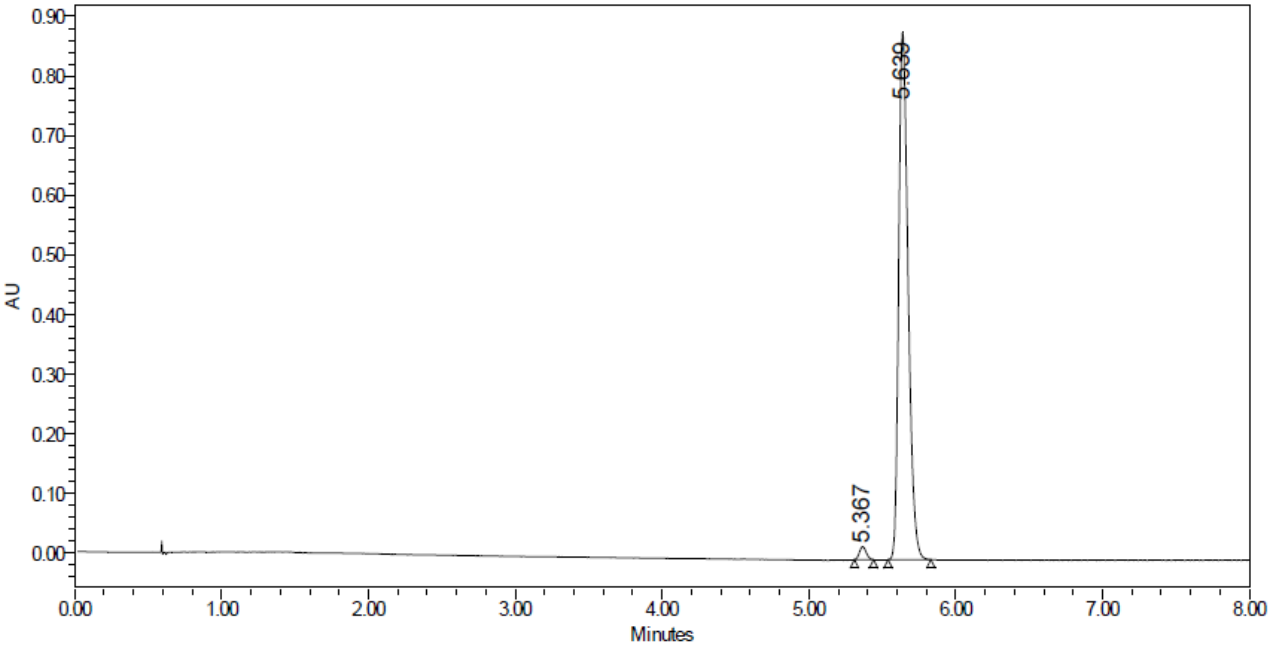
	Retention Time (min)	% Area
1	3.488	49.02
2	3.569	50.98



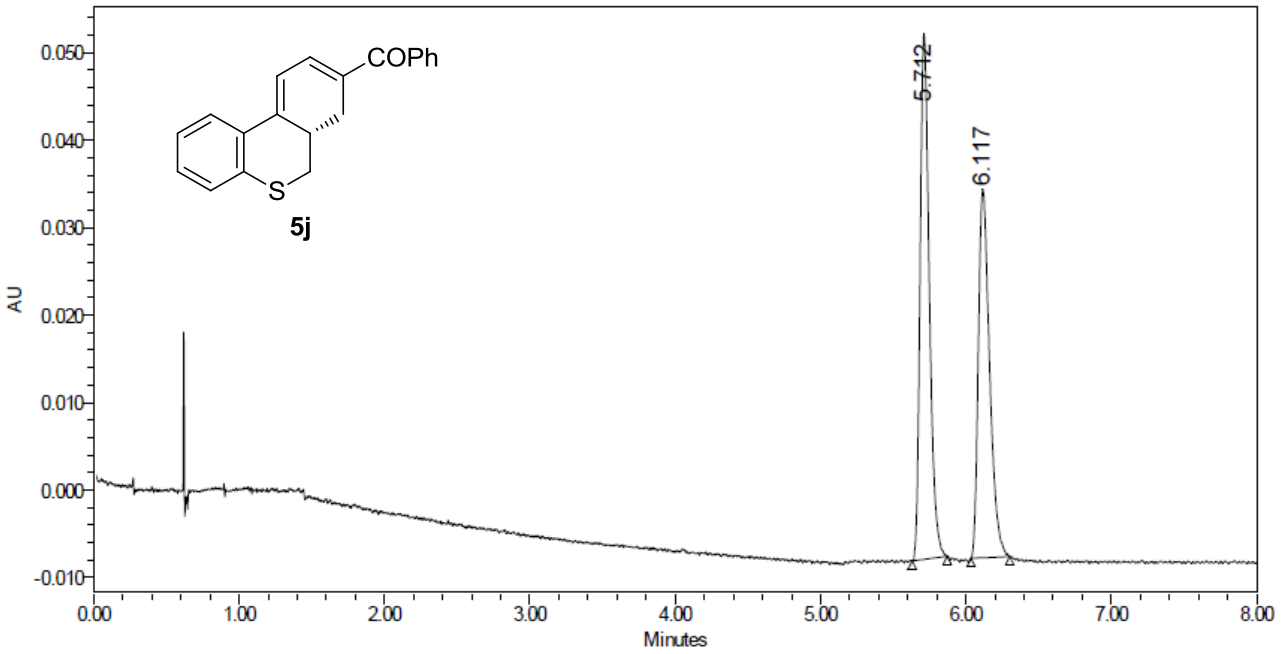
	Retention Time (min)	% Area
1	3.602	7.05
2	3.668	92.95



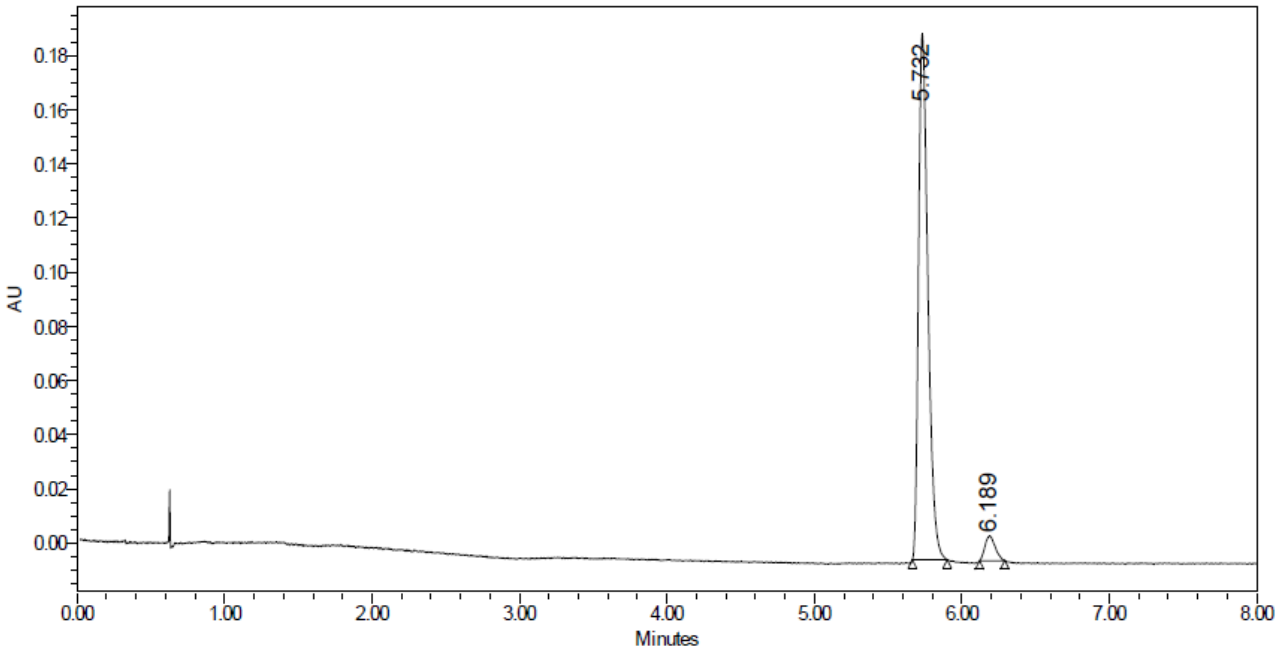
	Retention Time (min)	% Area
1	5.372	48.49
2	5.671	51.51



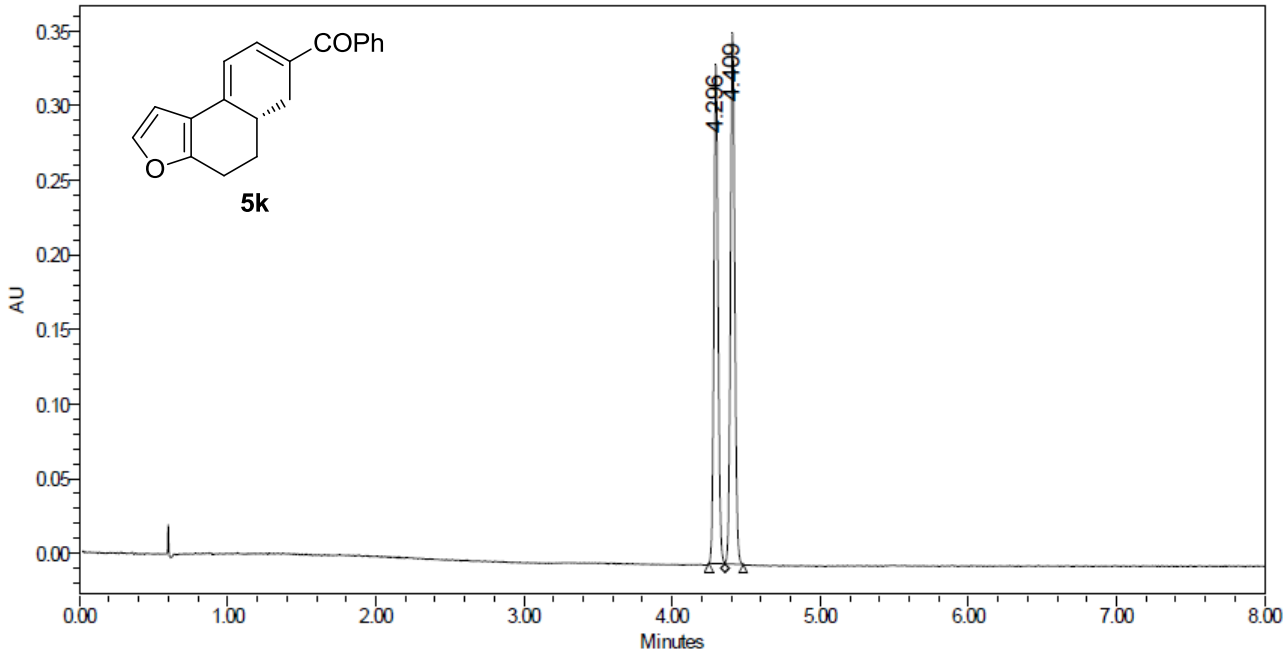
	Retention Time (min)	% Area
1	5.367	1.77
2	5.639	98.23



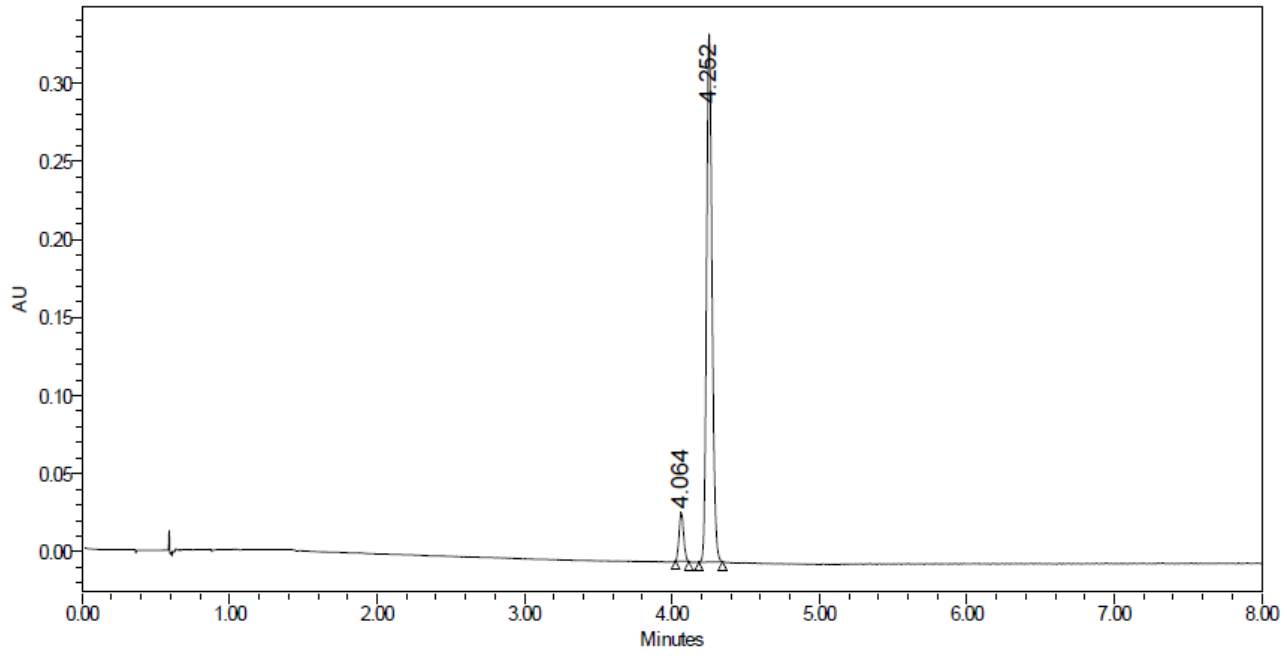
	Retention Time (min)	% Area
1	5.712	53.83
2	6.117	46.17



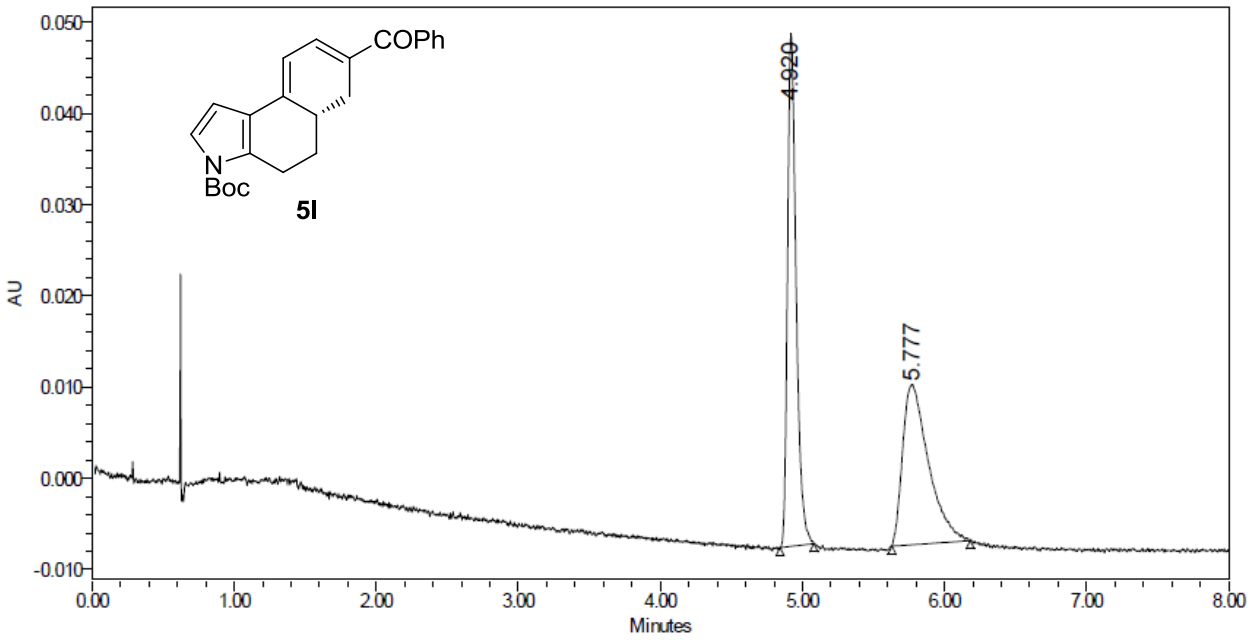
	Retention Time (min)	% Area
1	5.732	95.15
2	6.189	4.85



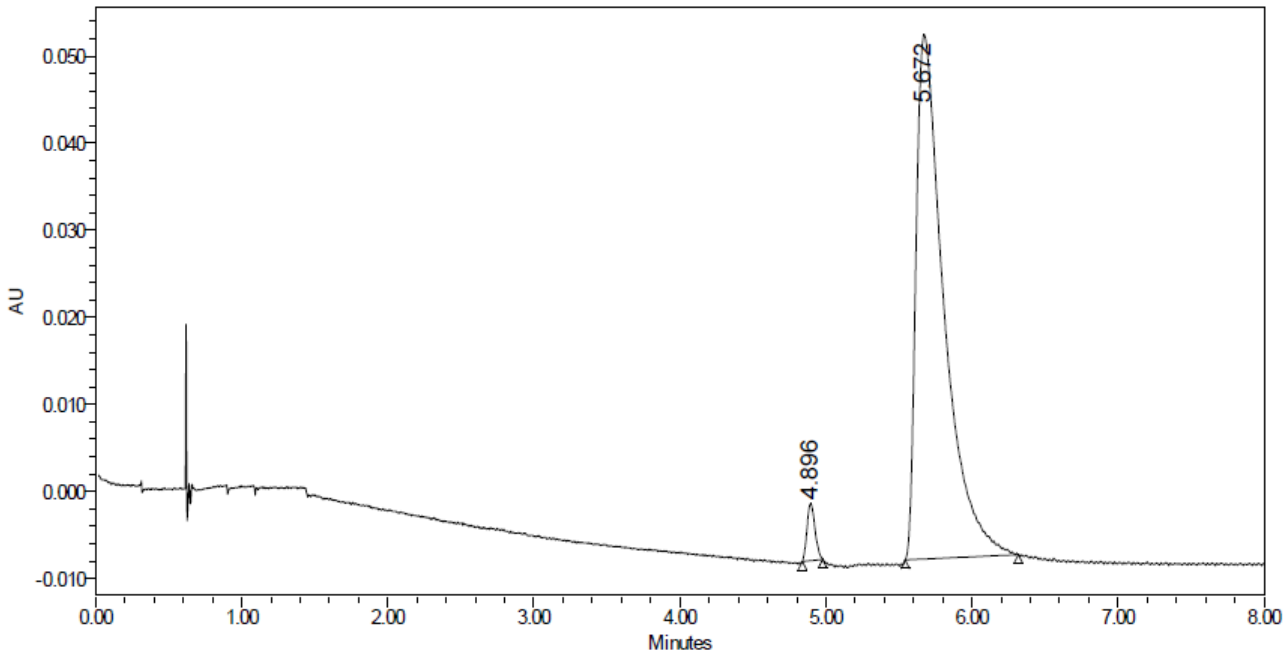
	Retention Time (min)	% Area
1	4.296	47.40
2	4.409	52.60



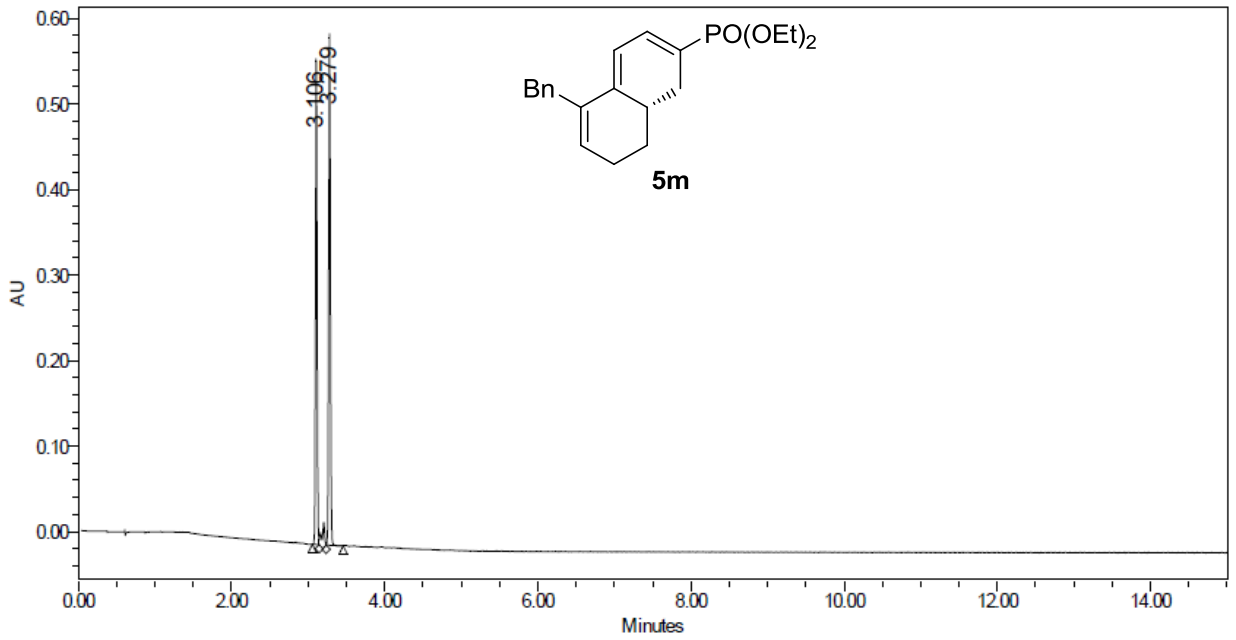
	Retention Time (min)	% Area
1	4.064	7.12
2	4.252	92.88



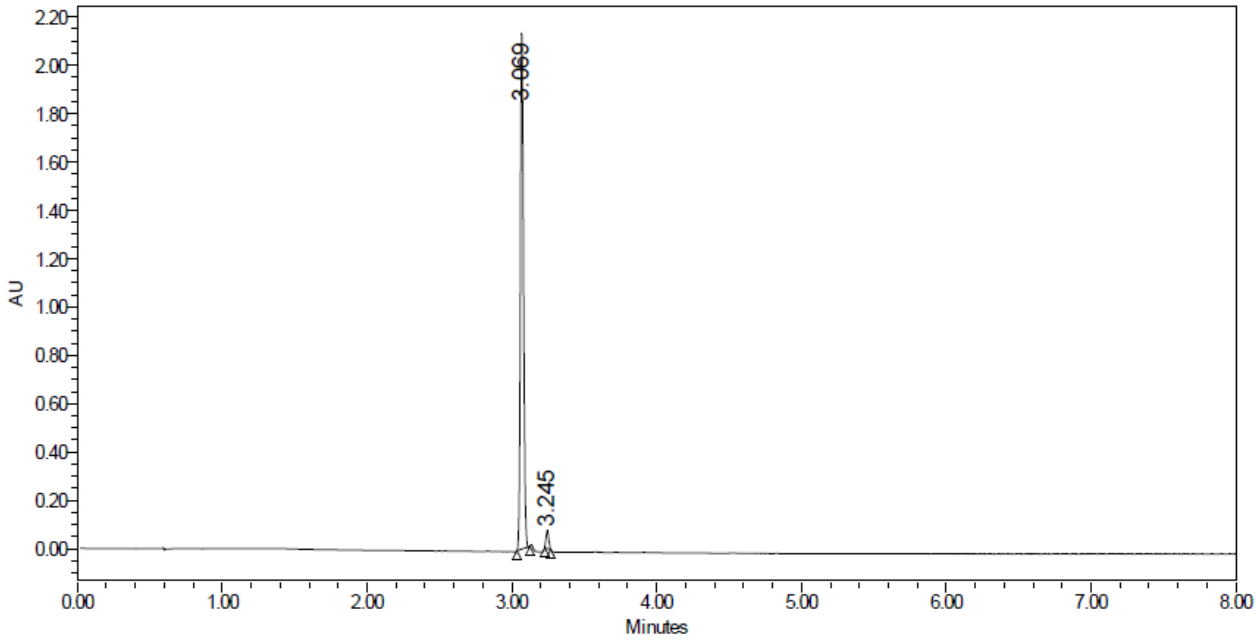
	Retention Time (min)	% Area
1	4.920	51.52
2	5.777	48.48



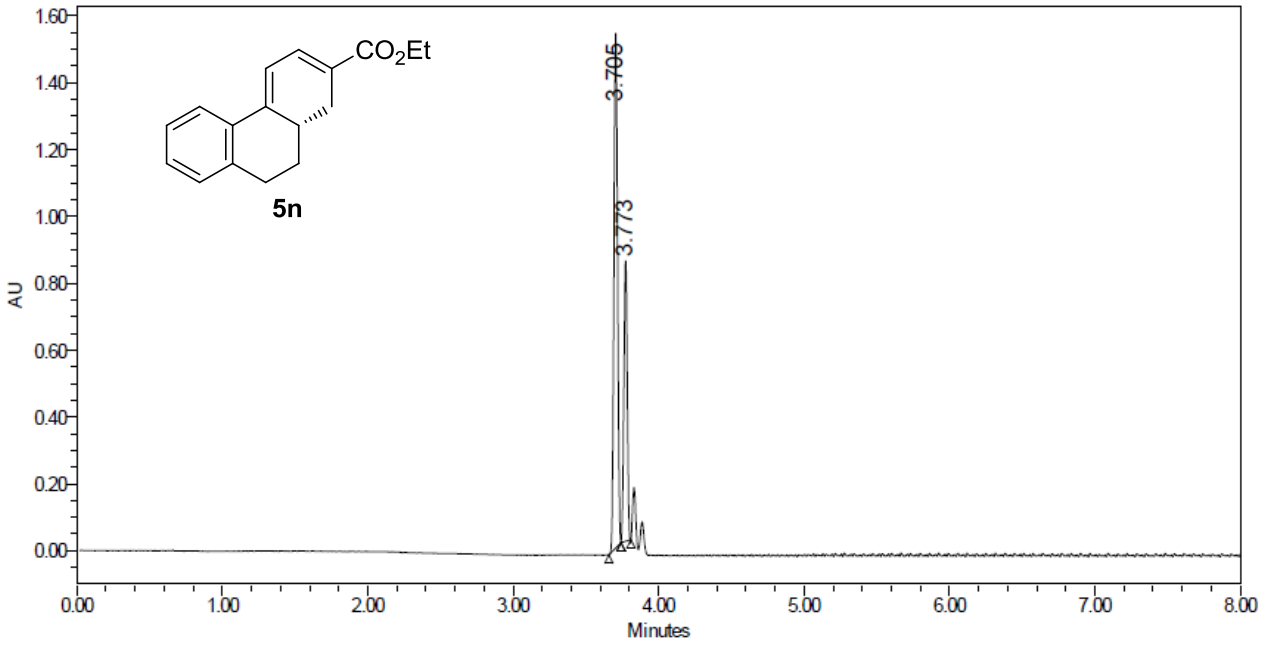
	Retention Time (min)	% Area
1	4.896	3.02
2	5.672	96.98



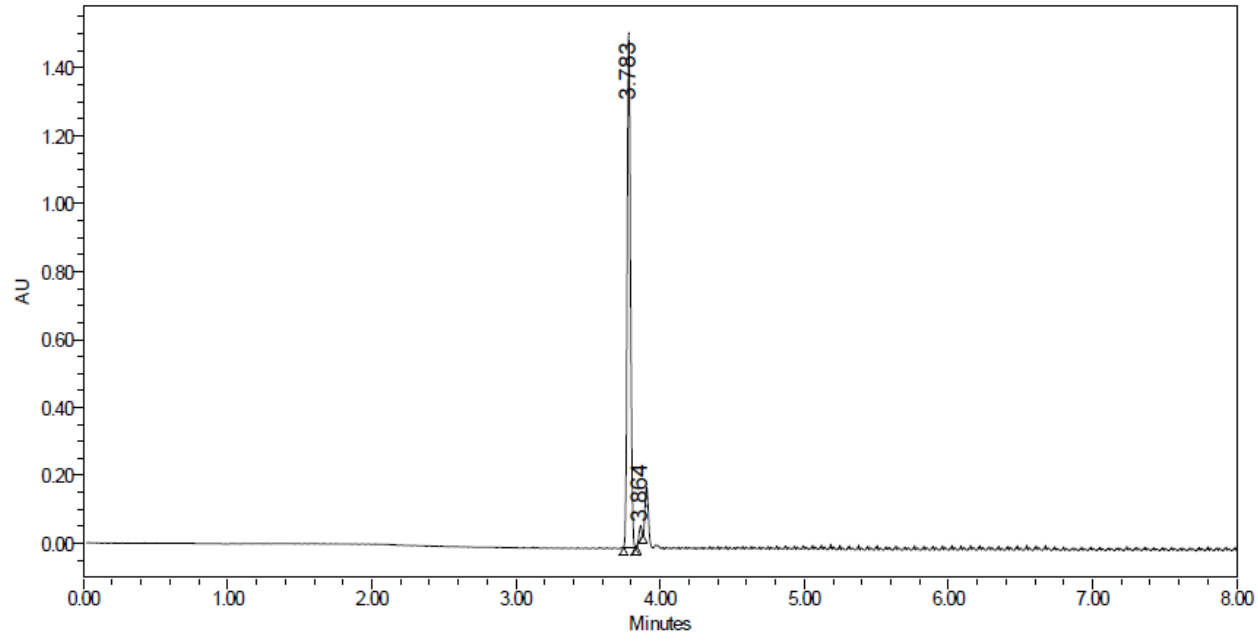
	Retention Time (min)	% Area
1	3.106	46.52
2	3.279	53.48



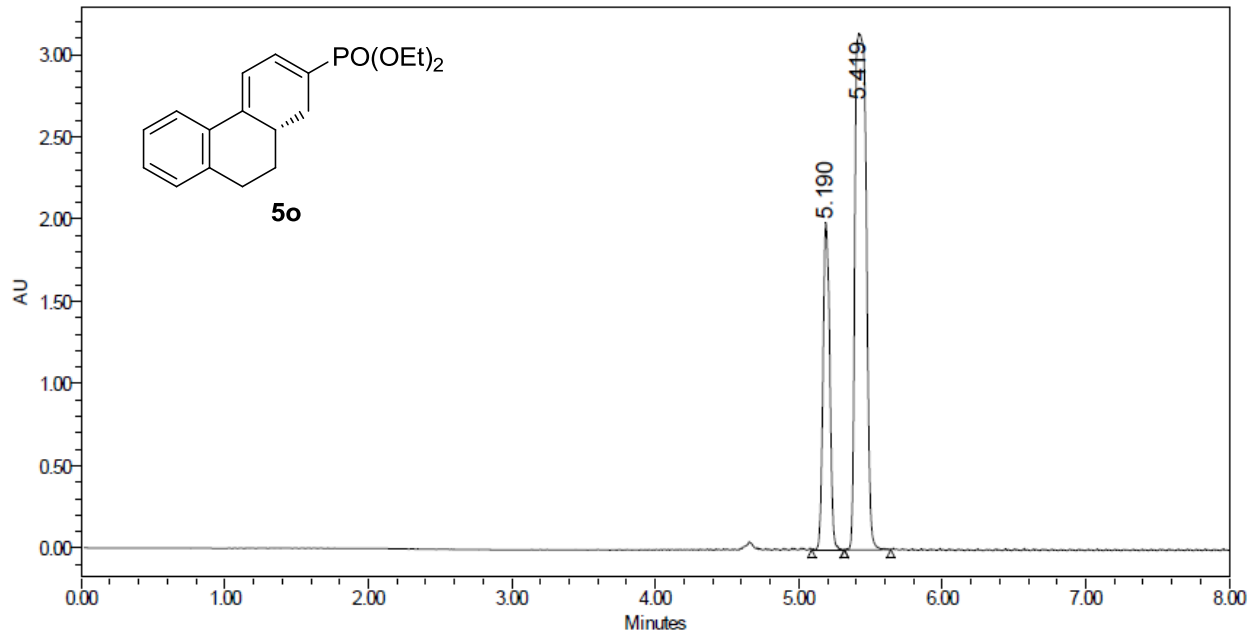
	Retention Time (min)	% Area
1	3.069	97.13
2	3.245	2.87



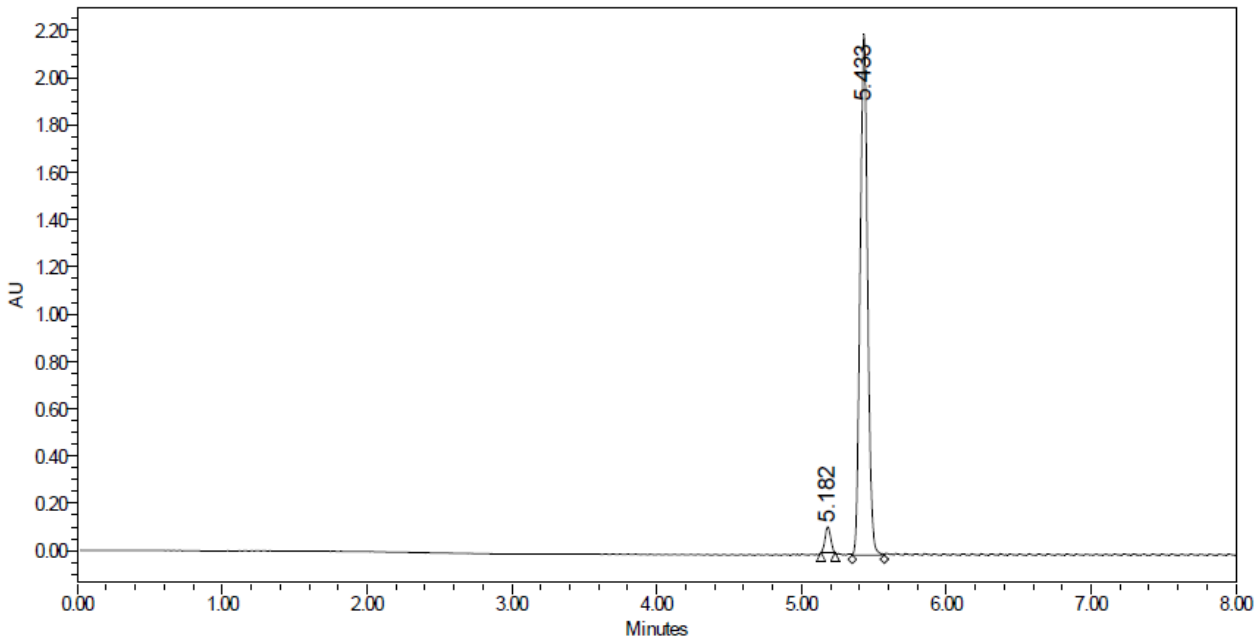
	Retention Time (min)	% Area
1	3.705	66.45
2	3.773	33.55



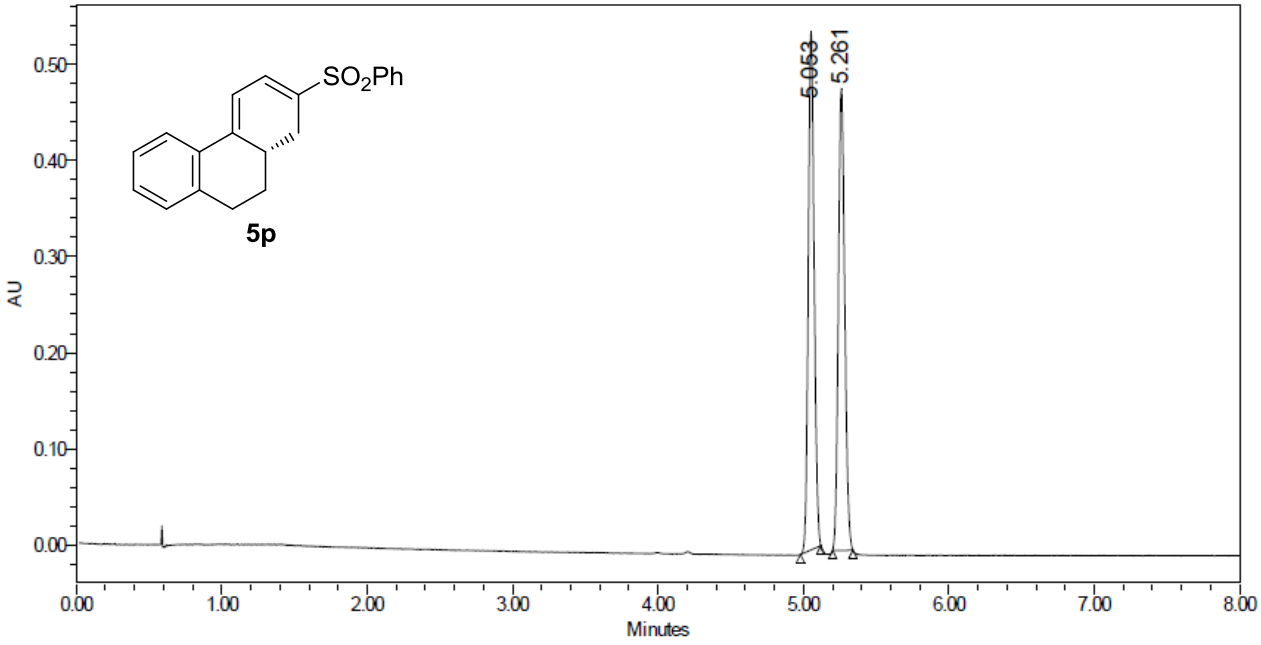
	Retention Time (min)	% Area
1	3.783	98.02
2	3.864	1.98



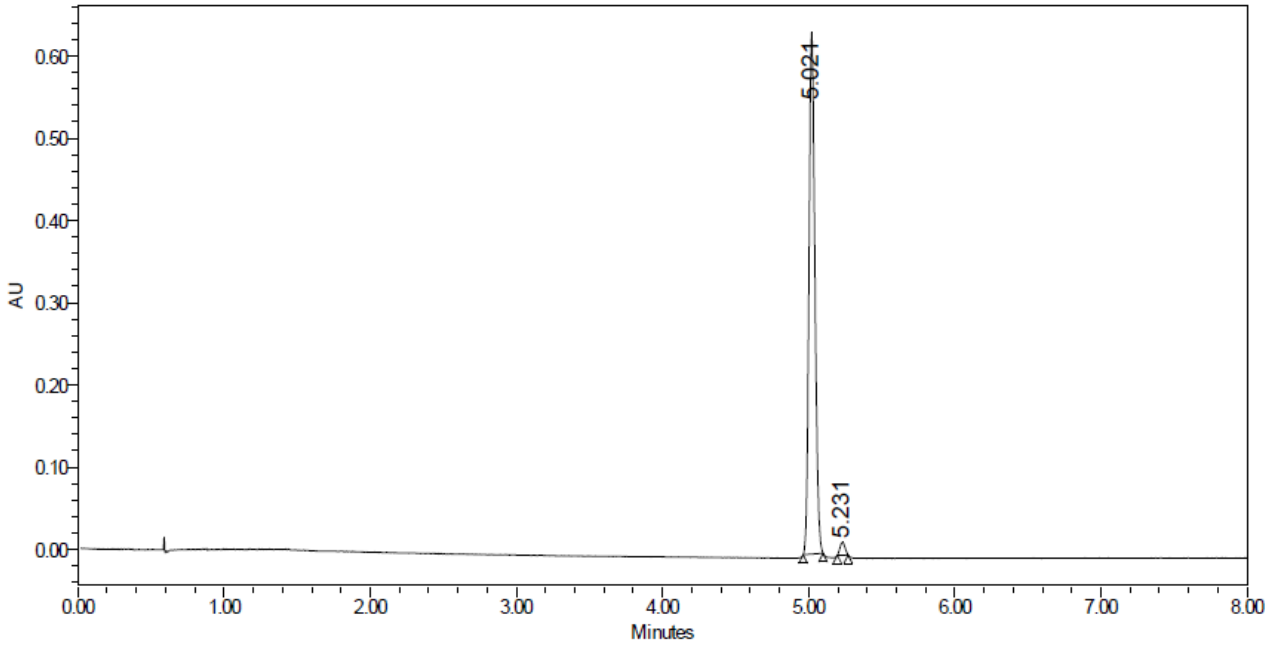
	Retention Time (min)	% Area
1	5.190	27.54
2	5.419	72.46



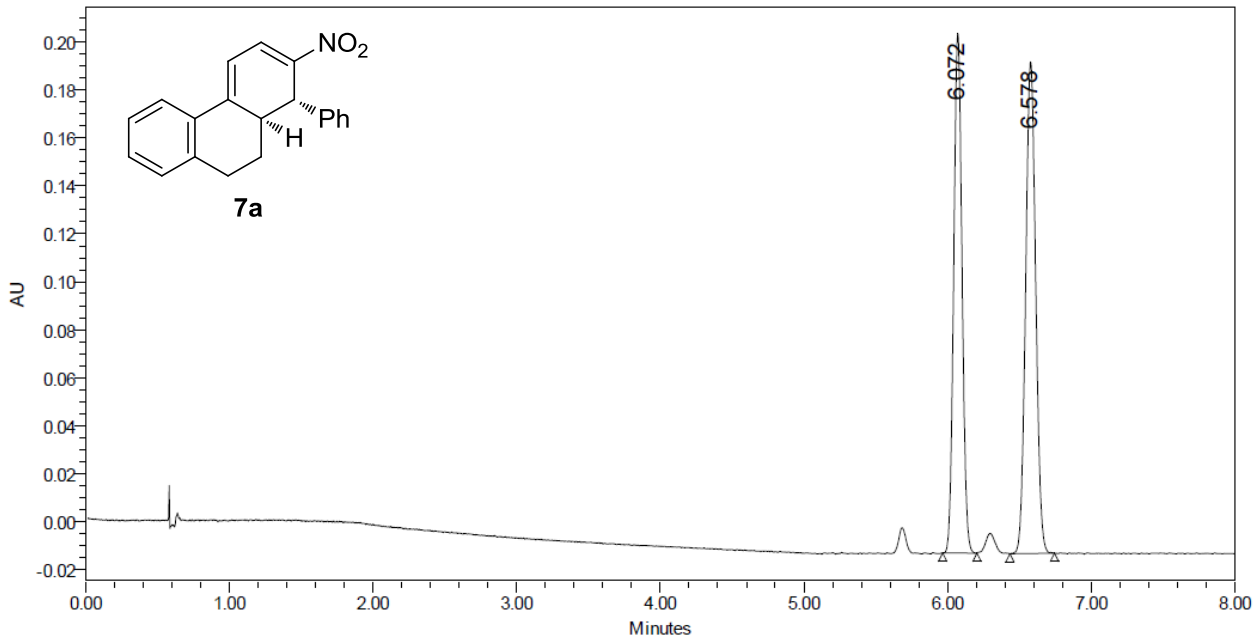
	Retention Time (min)	% Area
1	5.182	3.49
2	5.433	96.51



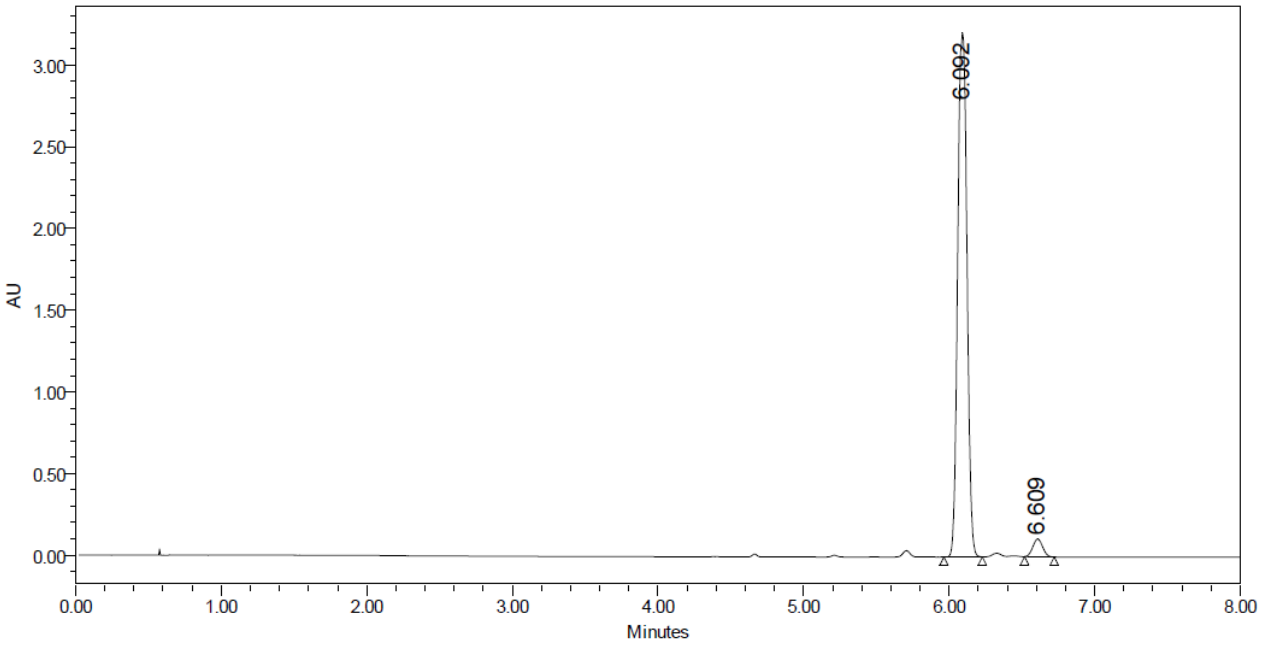
	Retention Time (min)	% Area
1	5.053	50.76
2	5.261	49.24



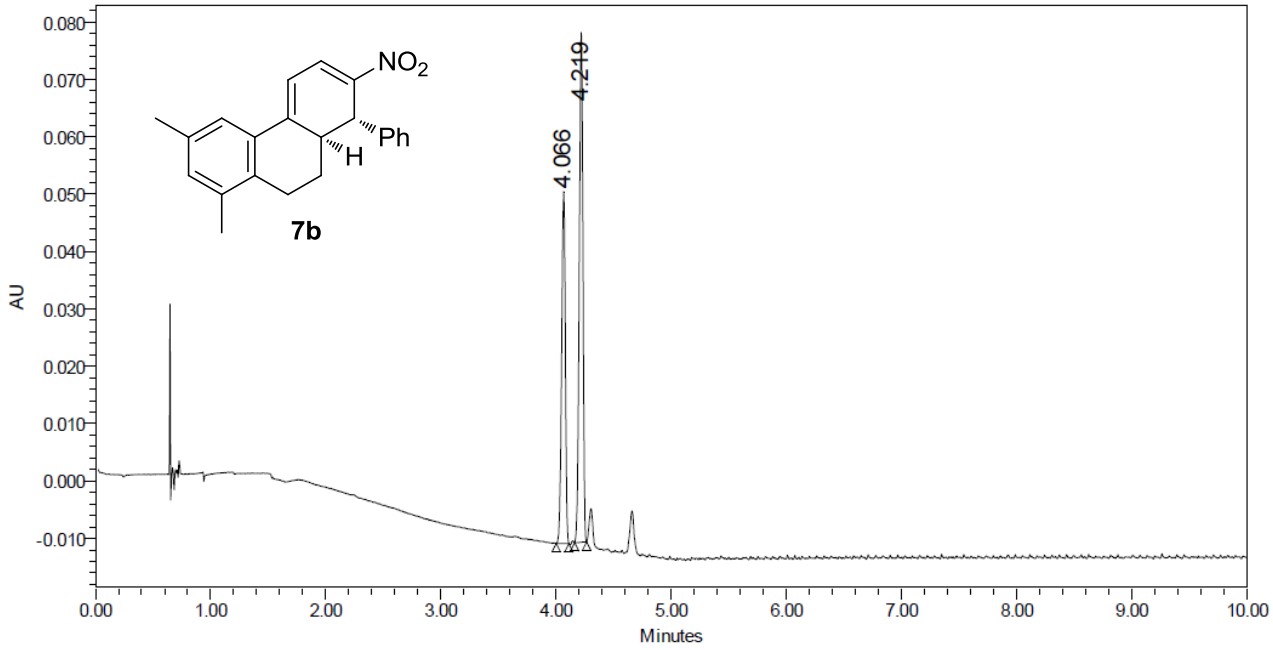
	Retention Time (min)	% Area
1	5.021	97.96
2	5.231	2.04



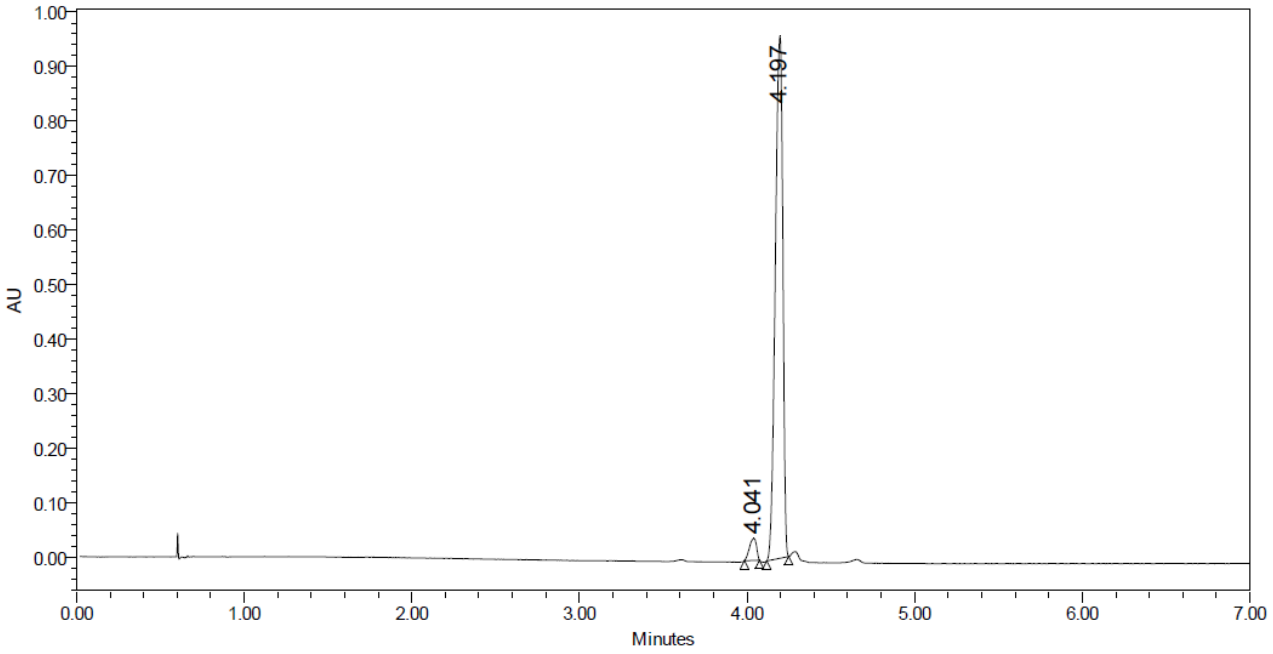
	Retention Time (min)	% Area
1	6.072	46.66
2	6.578	53.34



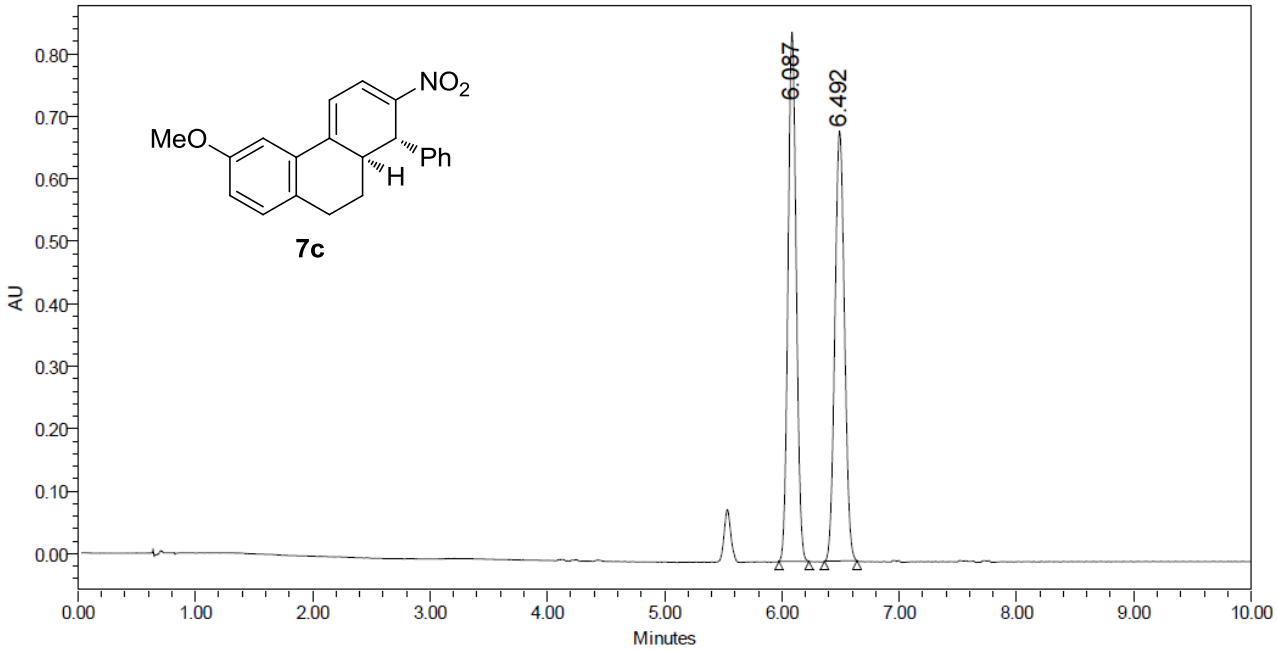
	Retention Time (min)	% Area
1	6.092	96.52
2	6.609	3.48



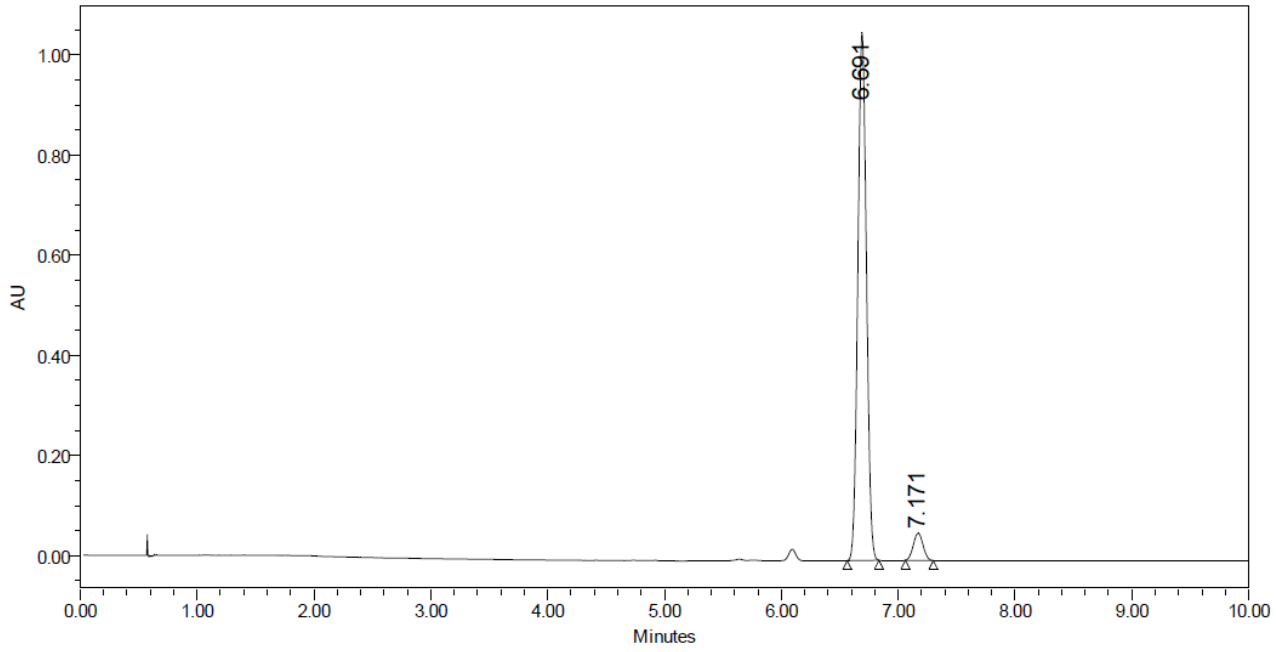
	Retention Time (min)	% Area
1	4.066	41.06
2	4.219	58.94



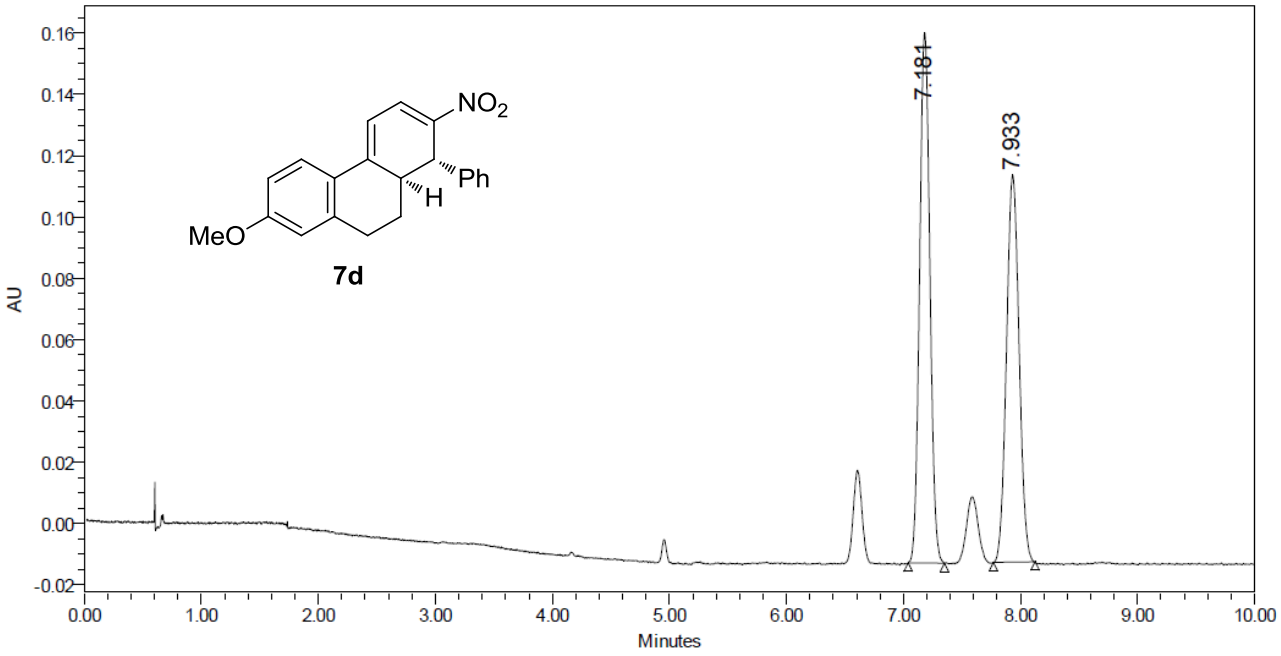
	Retention Time (min)	% Area
1	4.041	3.80
2	4.197	96.20



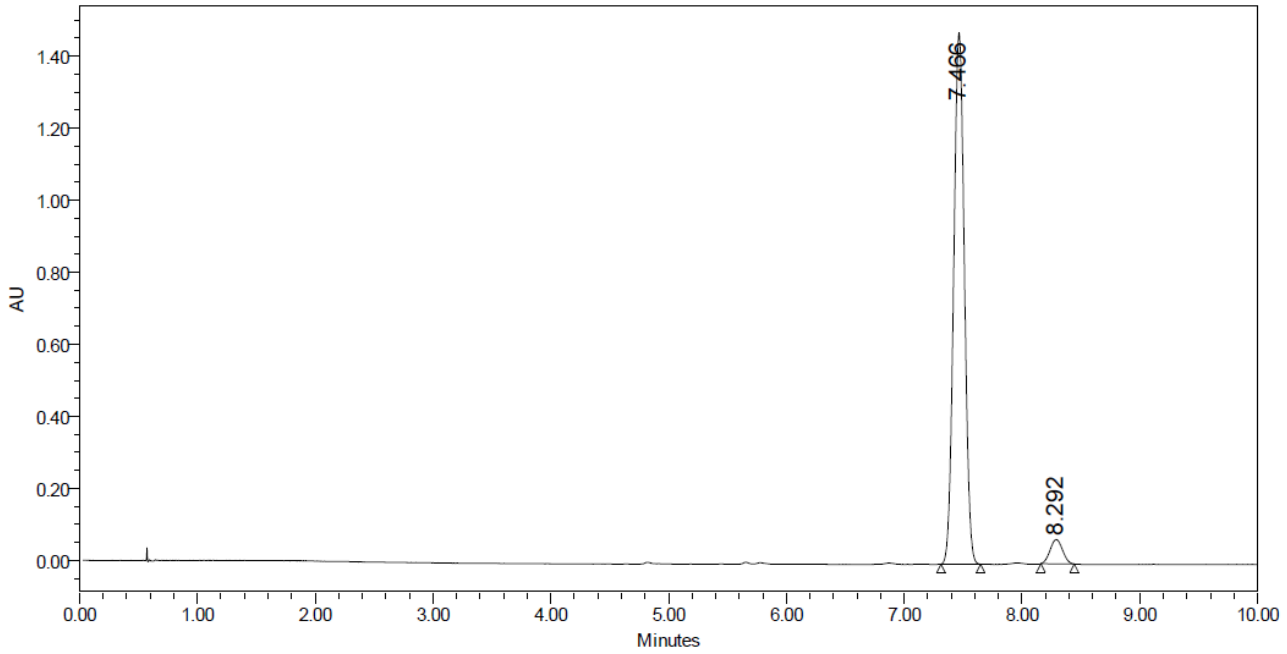
	Retention Time (min)	% Area
1	6.087	51.23
2	6.492	48.77



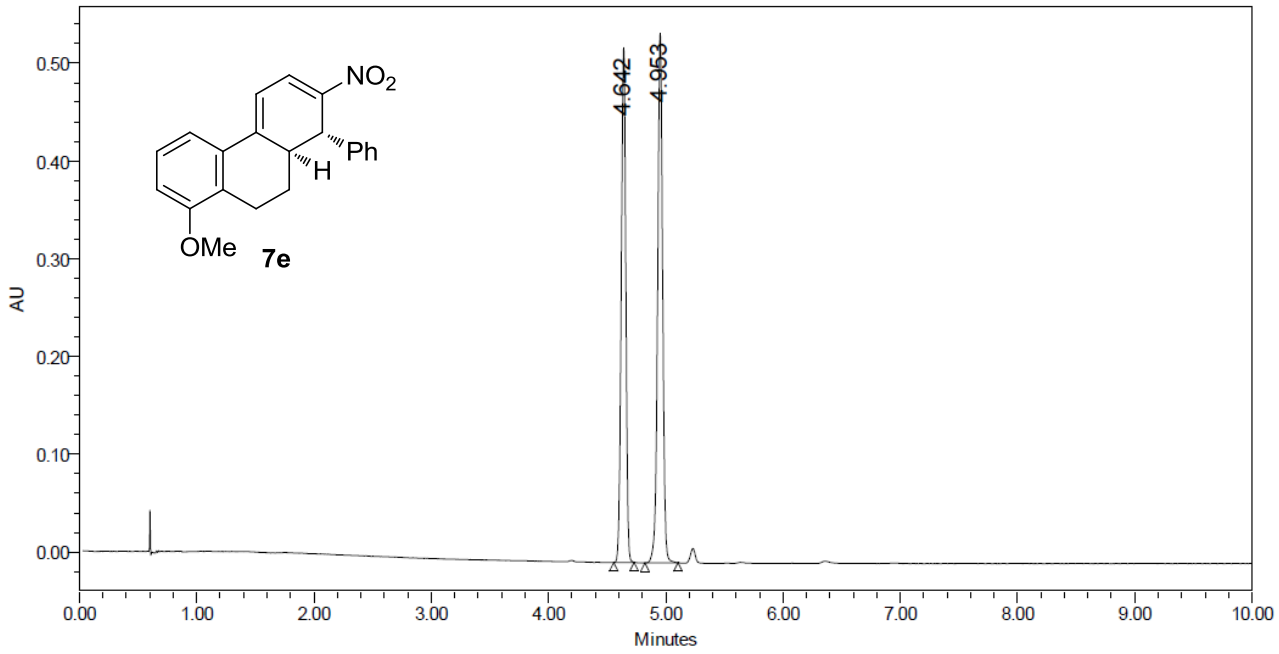
	Retention Time (min)	% Area
1	6.691	94.45
2	7.171	5.55



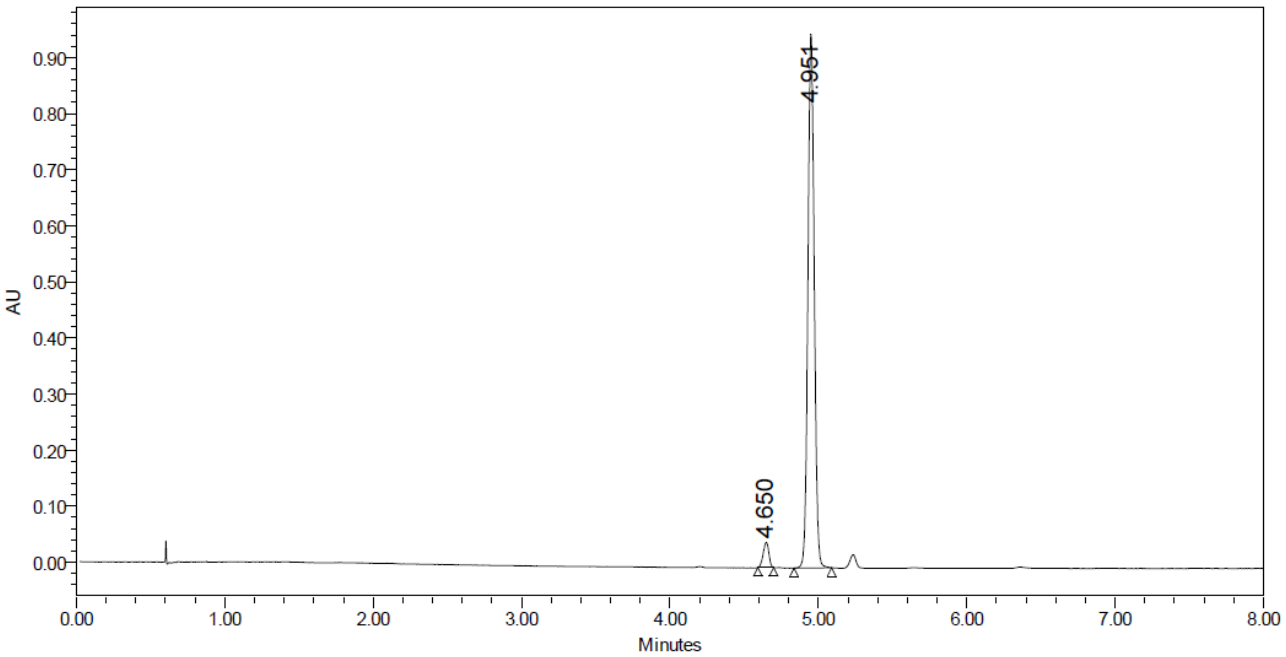
	Retention Time (min)	% Area
1	7.181	52.85
2	7.933	47.15



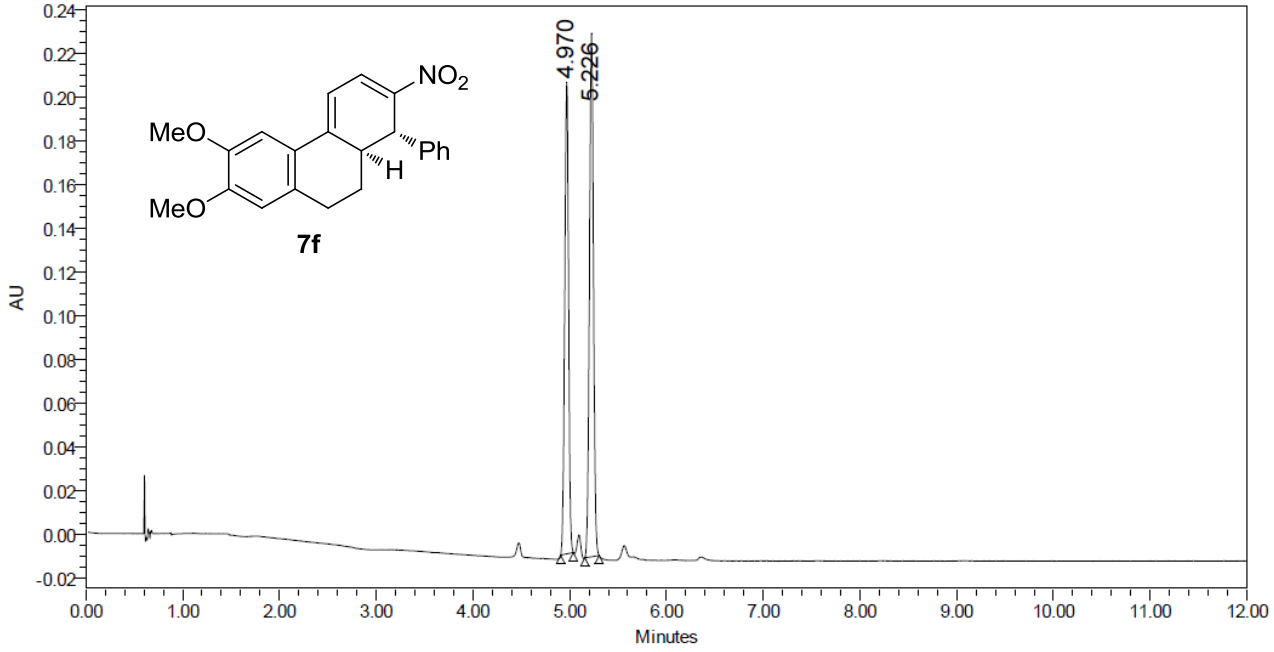
	Retention Time (min)	% Area
1	7.466	94.91
2	8.292	5.09



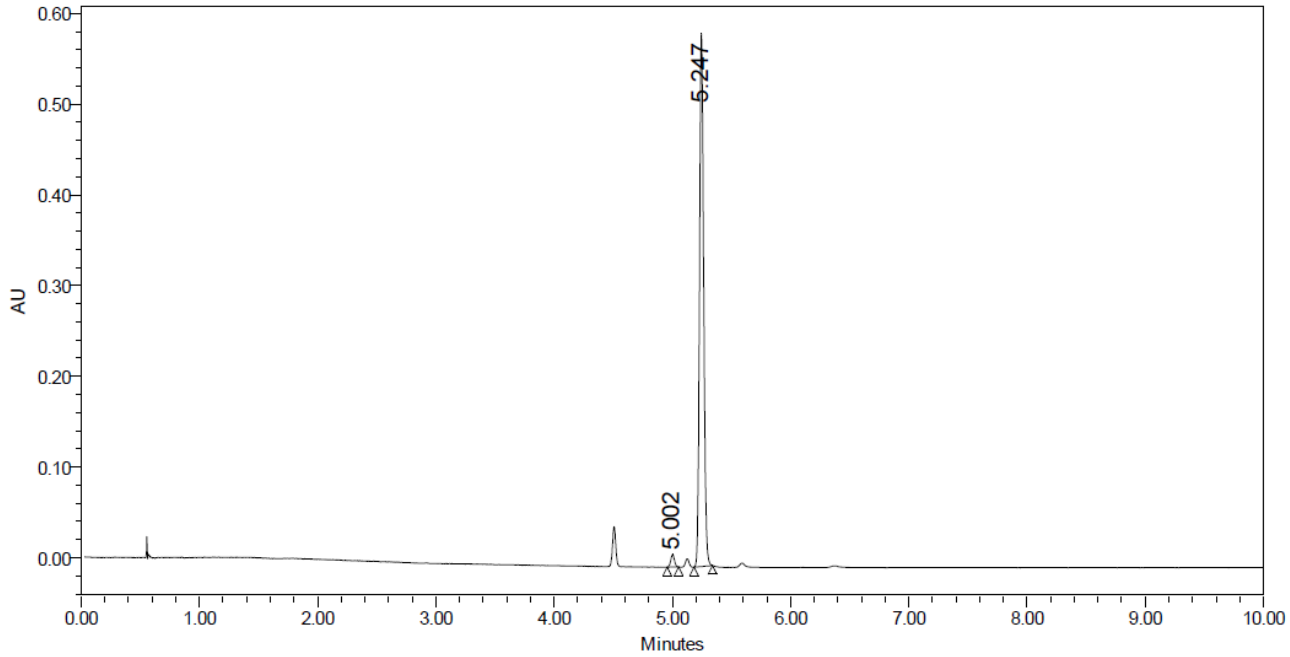
	Retention Time (min)	% Area
1	4.642	46.87
2	4.953	53.13



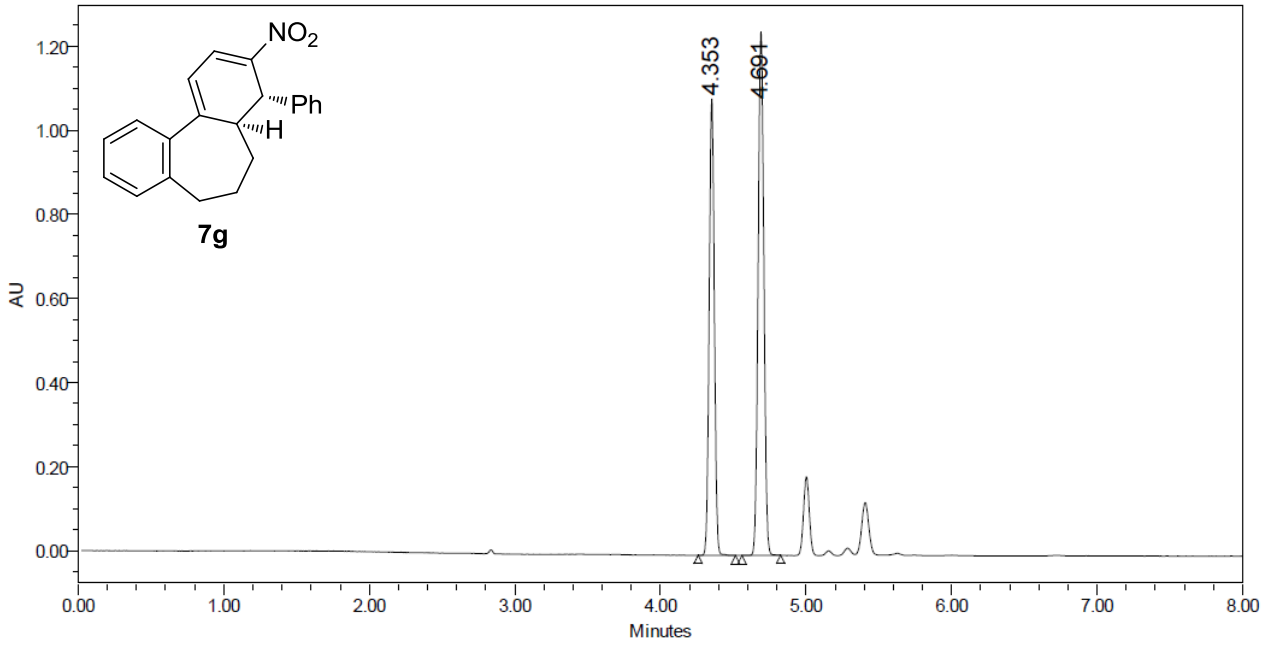
	Retention Time (min)	% Area
1	4.650	4.07
2	4.951	95.93



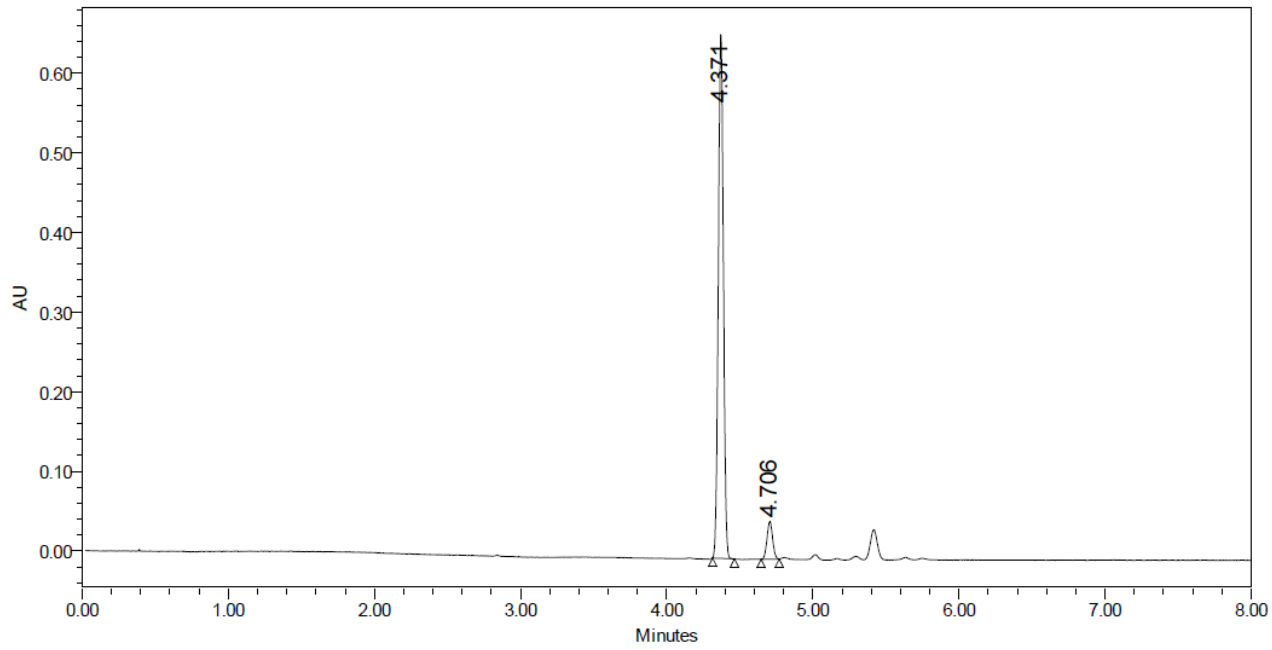
	Retention Time (min)	% Area
1	4.970	45.82
2	5.226	54.18



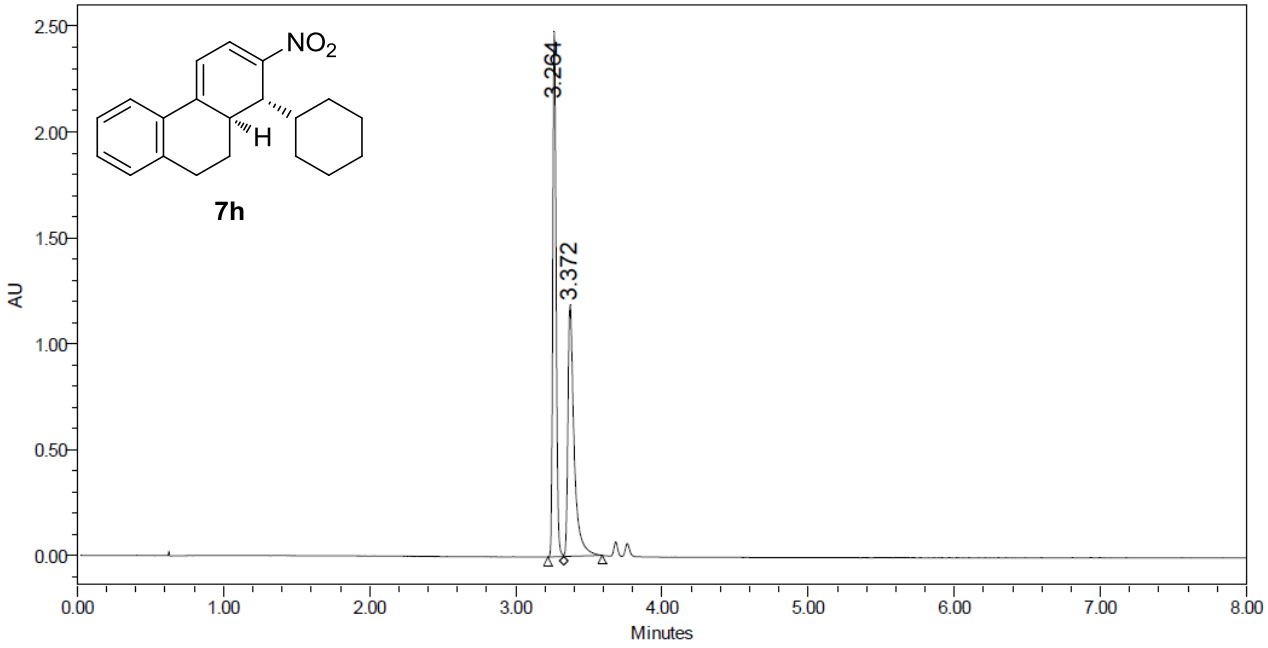
	Retention Time (min)	% Area
1	5.002	2.01
2	5.247	97.99



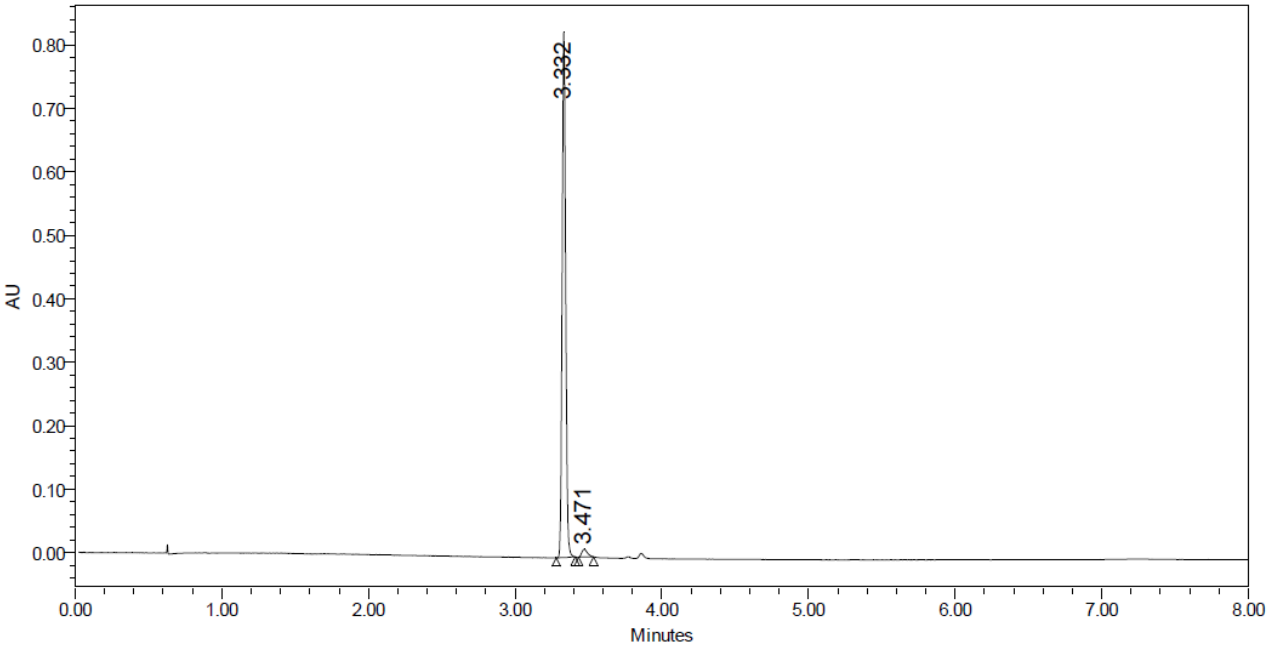
	Retention Time (min)	% Area
1	4.353	44.01
2	4.691	55.99



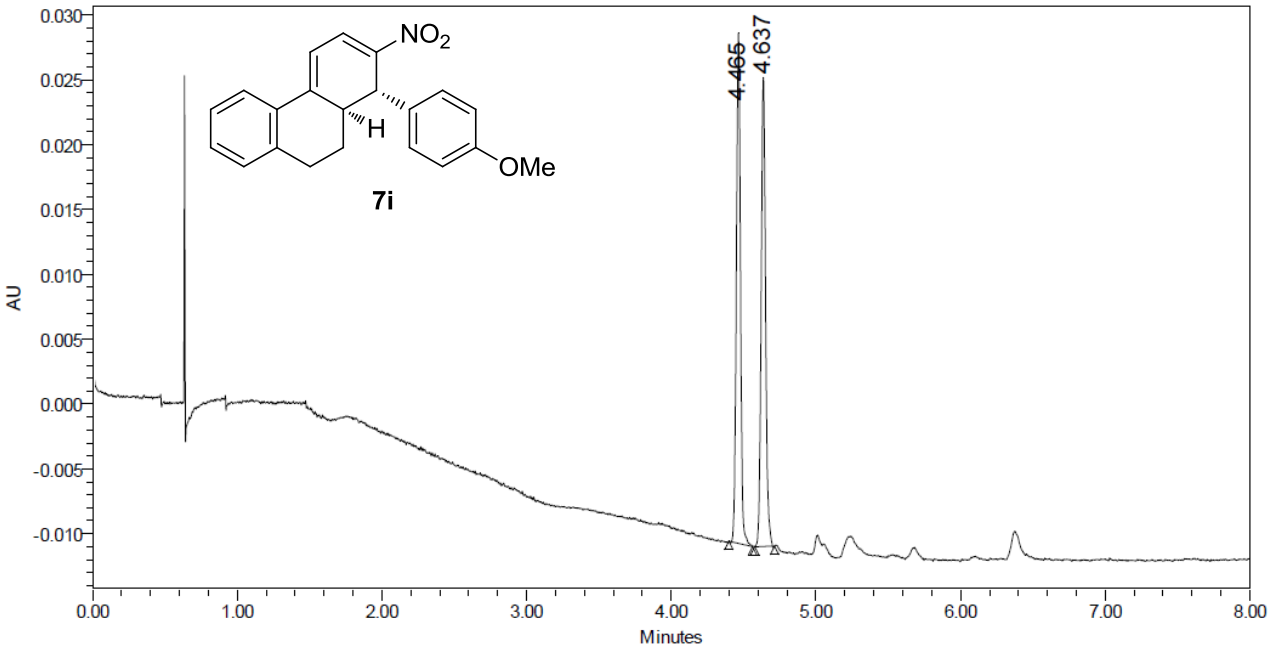
	Retention Time (min)	% Area
1	4.371	92.69
2	4.706	7.31



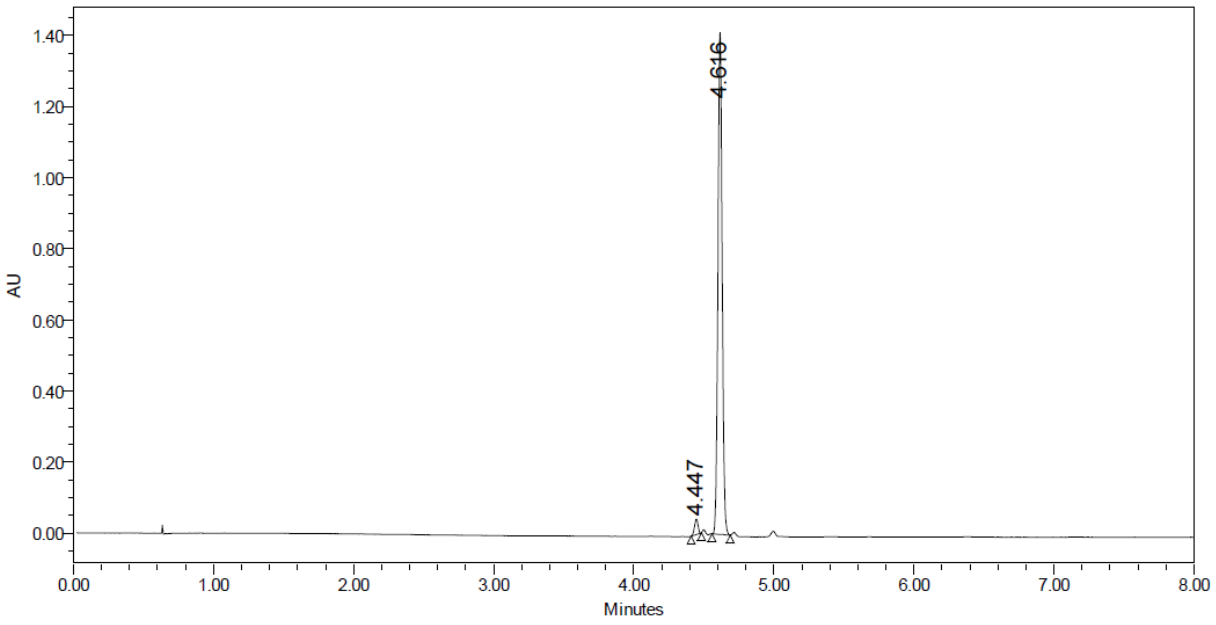
	Retention Time (min)	% Area
1	3.264	52.97
2	3.372	47.03



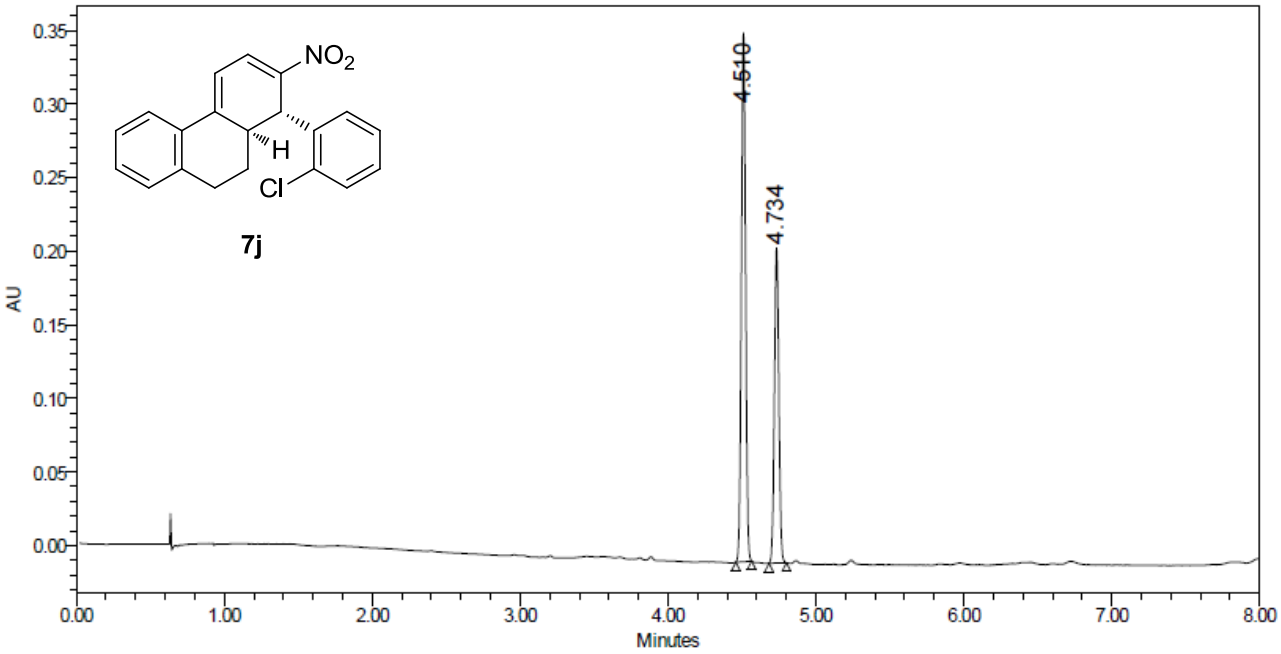
	Retention Time (min)	% Area
1	3.332	97.64
2	3.471	2.36



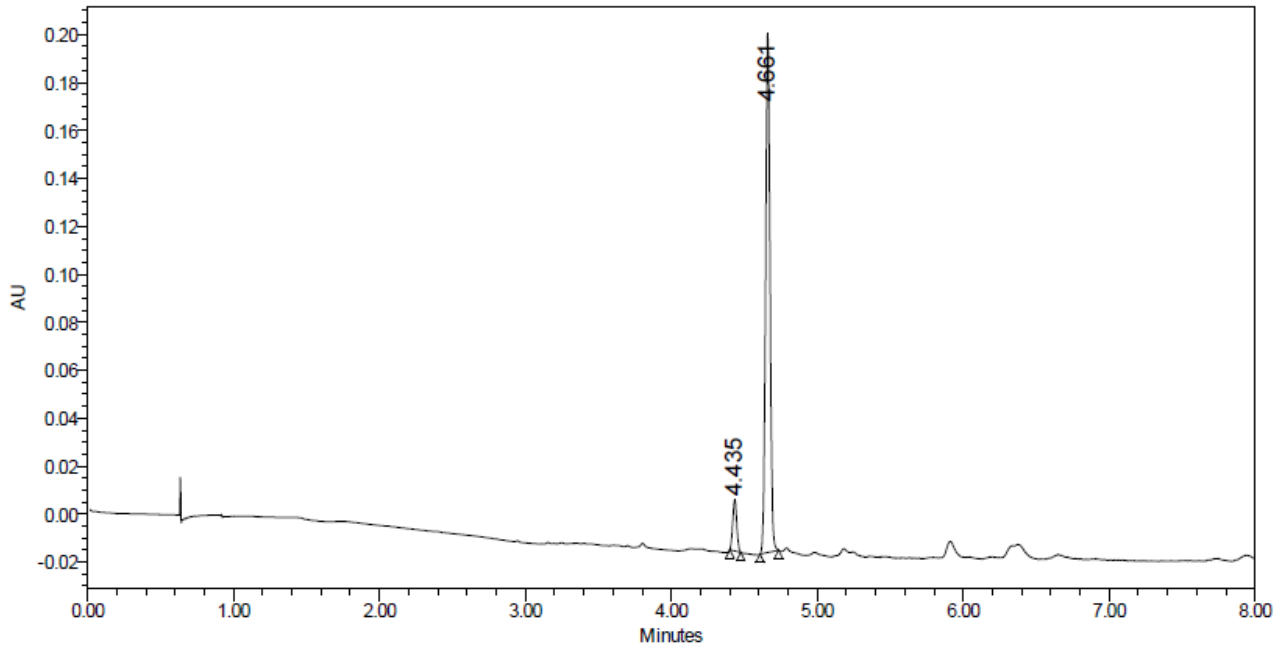
	Retention Time (min)	% Area
1	4.465	50.43
2	4.637	49.57



	Retention Time (min)	% Area
1	4.447	2.48
2	4.616	97.52



	Retention Time (min)	% Area
1	4.510	61.38
2	4.734	38.62



	Retention Time (min)	% Area
1	4.435	8.20
2	4.661	91.80