**Supplementary information for:**

# Highly stereoselective synthesis of indanes with four stereogenic centers via sequential Michael reaction and [3+2] cycloaddition

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**General Information**:

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.0, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.23, triplet).

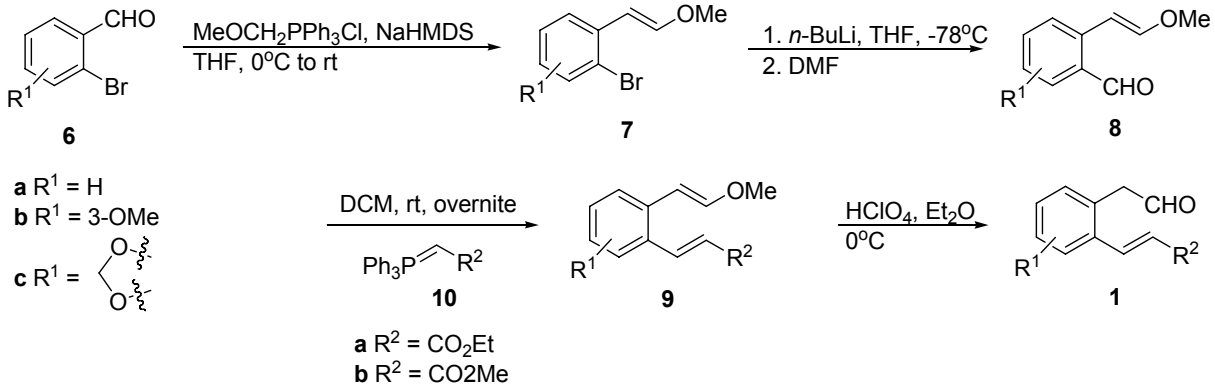
Enantioselectivities were determined by High Performance Liquid Chromatography (HPLC) analysis employing a Daicel Chirapak AD-H (0.46cm x 25 cm), Chirapak AS-H (0.46cm x 25 cm), Chiracel OD-H (0.46cm x 25 cm) column.

Optical rotations were measured in $CHCl_3$ on a *Schmidt + Haensdch* polarimeter (Polartronic MH8) with a 1 cm cell (*c* given in g/100 mL).

High resolution mass spectrometry (HRMS) was recorded on Finnigan MAT 95 × P spectrometer.

The enantiomers used to determine the *ee* values were synthesized with DL-proline as catalyst. All other reagents were available from commercial sources and used without further purification.

**Typical procedures for the preparation of aldehydes 1:**




(Adapted from K. Uchida, S. Yokoshima, T. Kan, T. Fukuyama. *Org. Lett.*, **2006**, *8*, 5311–5313)
2.0 M sodium bis(trimethylsilyl)amide in tetrahydrofuran (6 mL, 12 mmol,1.2 equiv.) was added dropwise to a stirred solution of (methoxymethyl)triphenylphosphonium chloride (3.77 g, 11 mmol, 1.1 equiv.) in 20 mL of anhydrous tetrahydrofuran at 0 °C under nitrogen atmosphere for 2 hours. A solution of the corresponding bromobenzaldehyde **6** (10 mmol) was then added dropwise to the reaction mixture. After stirring at 0 °C for 10 minutes, the reaction mixture was allowed to warm to room temperature (22 °C) and stirred for another 2 hours. The yellow solution was quenched with saturated aqueous ammonium chloride (5 mL) and the solvent was evaporated under reduced pressure. Diethyl ether was added to the residue and the mixture was filtered. The filtrate was washed with sodium bicarbonate, water and then finally with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:dichloromethane = 9:1) to give compound **7**. The product was the mixture of *E* and *Z* isomers.

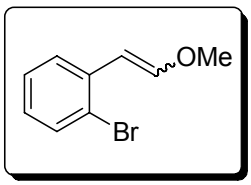
(Adapted from M.-Y. Lin, A. Das, R.-S. Liu. *J. Am. Chem. Soc.*, **2006**, *128*, 9340–9341)
2.0 M *n*-butyllithium in cyclohexane (4 mL, 9.6 mmol, 1.2 equiv.) was added dropwise to a stirring solution compound **7** (8 mmol) in 20 mL anhydrous tetrahydrofuran at -78 °C under nitrogen atmosphere. After stirring at -78 °C for 2 hours, anhydrous N,N-dimethylformamide (0.92 mL, 12 mmol, 1.5 equiv.) was added to form a light yellow solution. After 30 min, 25 mL water was added to reaction mixture, extracted with diethyl ether and the combined organic layers were concentrated under reduce pressure. The crude product was eluted through a silica column (hexane:EtOAc = 19:1) to afford compound **8.** The product was the mixture of *E* and *Z* isomers.

(Adapted from B. Tan, D. Zhu, L. Zhang, P. J. Chua, X. Zeng, G. Zhong, *Chem. Eur. J.* **2010**, *16*, 3842-3845)
Corresponding ylide **10** (1.1 equiv) was added potion wise to a stirring solution of compound **8** (6 mmol) in 10 mL of dichloromethane at 23 °C and the reaction was stirred overnight. Diethyl ether was added to the residue and the mixture was filtered. The filtrate was washed with sodium bicarbonate, water and then finally with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:dichloromethane = 9:1) to give compound **9**. The product was the mixture of *E* and *Z* isomers.

(Adapted from F. Richter, M. Bauer, C. Perez, C. Maichle-Mössmer, M. E. Maier. *J. Org. Chem.* **2002**, *67,* 2474-2480)
70% perchloric acid in water (7 mL) was added dropwise to a stirring solution of compound **8** (5 mmol) in diethyl ether 10 mL at 0 ºC. After 10 minutes, the cooling bath was removed and stirring continued until the reaction proceeds to completion (reaction monitored by TLC). The mixture was diluted with water (10 mL) and extracted with ethyl acetate. The combined organic layers were washed with saturated sodium bicarbonate, brine, dried with sodium sulfate, filtered and concentrated *in vacuo* to afford compound **1**.

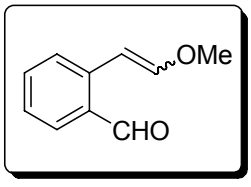
**Experimental data of Compounds 7a-9d and 1a-e.**

1-bromo-2-(2-methoxyvinyl)benzene (**7a**)




Compound **7a** was prepared according to the general procedure from 2-bromobenzaldehyde **6a** (1.85 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.97 g, 92% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1.6)
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.03 (1H, d, *J* = 8 Hz), 7.53 (2.6H, d, *J* = 8 Hz), 7.34 (1.6H, d, *J* = 8 Hz), 7.26-7.18 (2.6H, m), 7.02-6.96 (4.2H, m), 6.25 (1H, d, *J* = 7.2 Hz), 6.09 (1.6H, d, *J* = 12.8 Hz), 5.60 (1H, d, *J* = 7.2 Hz), 3.78, 3.73 (7.8H, s).
$^{13}$C NMR (100 MHz, $CDCl_3$): 150.7, 149.4, 136.5, 135.3, 133.1, 132.7, 130.5, 127.7, 127.3, 127.3, 127.3, 125.9, 123.2, 122.9, 104.6, 104.0, 61.1, 56.8.

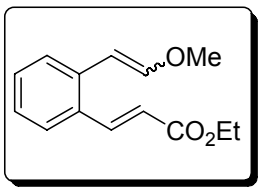
2-(2-methoxyvinyl)benzaldehyde (**8a**) (new compound)




Compound **8a** was prepared according to the general procedure from 1-bromo-2-(2-methoxyvinyl)benzene (**7a**) (1.70 g, 8 mmol) to provide the title compound as a pale yellow liquid (1.26g, 97% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1).

$^1$H NMR (400 MHz, $CDCl_3$): δ 10.21 (2H, d, *J* = 15.6 Hz), 7.88 (1H, d, *J* = 7.6 Hz), 7.79 (2H, t, *J* = 7.6 Hz), 7.53-7.47 (2H, m), 7.42 (1H, d, *J* = 7.6 Hz), 7.34-7.29 (2H, m), 7.02 (1H, d, *J* = 12.8 Hz), 6.75 (1H, d, *J* = 12.8 Hz), 6.32 (1H, d, *J* = 7.2 Hz), 6.11 (1H, d, *J* = 7.2 Hz), 3.77, 3.76 (6H, s).
$^{13}$C NMR (100 MHz, $CDCl_3$): 192.8, 152.3, 150.2, 138.9, 137.6, 133.7, 133.3, 132.5, 132.1, 131.9, 131.2, 130.2, 126.3, 126.1, 126.0, 101.2, 100.6, 60.7, 56.7.
HRMS (ESI) calcd for $C_{10}H_{11}O_2$, m/z 163.0759 [M+H], found 163.0751.

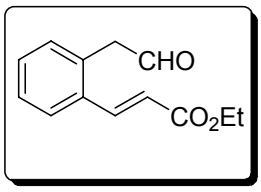
((2*E*)-ethyl 3-(2-(2-methoxyvinyl)phenyl)acrylate (**9a**) (new compound)




Compound **9a** was prepared according to the general procedure from 2-(2-methoxyvinyl)benzaldehyde (**8a**) (0.97 g, 6 mmol) and ylide **10a** (2.30g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (1.27g, 91% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1).

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.01 (2H, dd, J = 15.8, 5.2 Hz), 7.83 (1H, d, J = 7.9 Hz), 7.50 (2H, d, *J* = 7.8Hz), 7.32-7.26 (3H, m), 7.23-7.13 (2H, m), 6.82 (1H, d, *J* = 10.6 Hz), 6.33 (2H, dd, *J* = 15.9, 8.3 Hz), 6.22 (1H, d, *J* = 7.1 Hz), 6.04 (1H, d, *J* = 12.7 Hz), 5.46 (1H, d, *J* = 7.1 Hz), 4.26 (4H, dq, *J* = 7.2, 2.3 Hz), 3.71, 3.70 (6H, s), 1.33 (6H, t, *J* = 7.2 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 167.2, 167.1, 151.2, 149.0, 143.1, 142.8, 136.5, 135.2, 132.0, 132.0, 130.1, 130.0, 129.7, 127.1, 126.8, 126.7, 126.4, 119.5, 119.4, 102.2, 101.9, 60.7, 60.5, 60.5, 56.8, 14.4.
HRMS (ESI) calcd for $C_{14}H_{17}O_3$, m/z 233.1178 [M+H], found 233.1181.

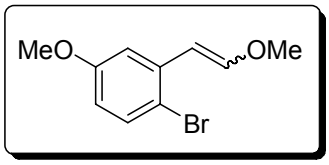
(*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate (**1a**) (new compound)




Compound **1a** was prepared according to the general procedure from ((2*E*)-ethyl 3-(2-(2-methoxyvinyl)phenyl)acrylate **9a** (1.16 g, 5 mmol) to provide the title compound as a pale yellow liquid (1.06g, 98% yield) after concentration *in vacuo*.

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.75 (1H, s), 7.83 (1H, d, *J* = 15.7 Hz), 7.64 (1H, d, *J* = 7.5 Hz), 7.41-7.33 (2H, m), 7.22 (1H, d, *J* = 7.3 Hz), 6.39 (1H, d, *J* = 15.7 Hz), 4.27 (2H, q, *J* = 7.1 Hz), 3.89 (2H, s), 1.34 (3H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 198.3, 166.6, 141.1, 134.3, 131.7, 131.4, 130.4, 128.2, 127.1, 121.0, 60.7, 48.1, 14.3.
HRMS (ESI) calcd for $C_{12}H_{13}O_3$, m/z 205.0865 [M+H], found 205.0866.

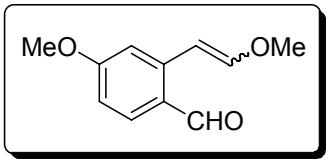
1-bromo-4-methoxy-2-(2-methoxyvinyl)benzene (**7b**)




Compound **7b** was prepared according to the general procedure from 2-bromo-5-methoxybenzaldehyde **6b** (2.31 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.87 g, 77% yield) after flash column chromatography. The product was the

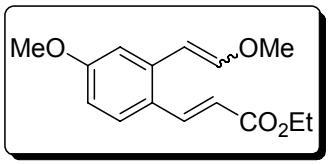
mixture of *E* and *Z* isomers (ratio 1:1.3)
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.65 (1H, d, *J* = 2.6 Hz), 7.38 (2.3H, d, *J* = 8.8 Hz), 6.96 (1.3H, d, *J* = 12.9 Hz), 6.85 (1.3H, d, *J* = 2.2 Hz), 6.57-6.56 (1.3H, m), 6.21 (1H, d, *J* = 7.2 Hz), 6.03 (1.3H, d, *J* = 12.8 Hz), 5.55 (1H, d, *J* = 7.2 Hz), 3.75-3.69 (13.8H, m).
$^{13}$C NMR (100 MHz, $CDCl_3$): 159.1, 158.7, 150.7, 149.6, 137.1, 135.8, 133.5, 132.9, 115.7, 113.8, 113.6, 113.2, 113.2, 111.1, 104.6, 103.9, 61.1, 56.7, 55.5, 55.5.

4-methoxy-2-(2-methoxyvinyl)benzaldehyde (**8b**) (new compound)



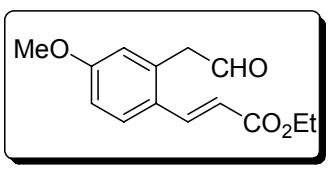

Compound **8b** was prepared according to the general procedure from 1-bromo-4-methoxy-2-(2-methoxyvinyl)benzene **7b** (1.70 g, 7 mmol) to provide the title compound as a pale yellow liquid (1.12 g, 77% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1.5).
$^1$H NMR (400 MHz, $CDCl_3$): δ 10.06 (2.5H, d, *J* = 10.2 Hz), 7.73-7.70 (2.5H, m), 7.48 (1H, d, *J* = 2.4 Hz), 7.03 (1.5H, d, *J* = 12.8 Hz), 6.86-6.75 (5.5H, m), 6.31 (1H, d, *J* = 7.4 Hz), 6.22 (1H, d, *J* = 7.1 Hz), 3.86 (7.5H, s), 3.76 (7.5H, d, *J* = 11.9 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 191.5, 191.4, 163.8, 163.6, 152.3, 150.7, 141.4, 139.7, 135.4, 134.5, 126.1, 126.1, 115.2, 120.0, 111.9, 111.0, 101.4, 100.5, 61.0, 56.7, 55.5, 55.5.
HRMS (ESI) calcd for $C_{11}H_{13}O_2$, m/z 193.0865 [M+H], found 193.0867.

(2*E*)-ethyl 3-(4-methoxy-2-(2-methoxyvinyl)phenyl)acrylate (**9b**) (new compound)




Compound **9b** was prepared according to the general procedure from 4-methoxy-2-(2-methoxyvinyl)benzaldehyde **8b** (1.04 g, 5 mmol) and ylide **10a** (1.91 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (0.76 g, 58% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1.6).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.96 (2.6H, dd, J = 15.8, 9.2 Hz), 7.50 (2.6H, d, J = 15.7 Hz), 7.46-7.40 (1.6H, m), 6.85-6.77 (2H, m), 6.71 (2.6H, d, *J* = 8.6 Hz), 6.26 (1.6H, d, *J* = 5.6 Hz), 6.22 (2.6H, d, *J* = 6.5 Hz), 6.04 (1H, d, *J* = 12.6 Hz), 5.47 (1.6H, d, *J* = 7.2 Hz), 4.24 (4H, q, *J* = 7.0 Hz), 3.78 (7.8H, s), 3.70 (7.8H, d, *J* = 7.2 Hz), 1.31 (7.8H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 167.4, 167.3, 161.0, 160.7, 151.2, 148.6, 142.8, 142.1, 138.3, 136.8, 128.4, 124.7, 119.7, 112.5, 111.3, 110.9, 102.3, 102.1, 60.7, 60.2, 60.2, 60.0, 56.7, 55.2, 55.1, 14.0.
HRMS (ESI) calcd for $C_{15}H_{19}O_4$, m/z 263.1283 [M+H], found 263.1286.

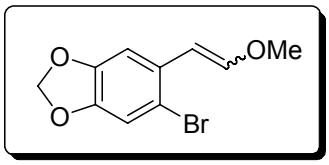
(*E*)-ethyl 3-(2-(formylmethyl)-4-methoxyphenyl)acrylate (**1b**) (new compound)




Compound **1b** was prepared according to the general procedure from (((2*E*)-ethyl 3-(4-methoxy-2-(2-methoxyvinyl)phenyl)acrylate **9b** (0.73 g, 2.8 mmol) to provide the title compound as a pale

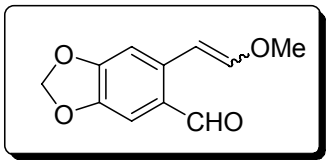
yellow liquid (0.43 g, 62% yield) after flash column chromatography (hexane:EtOAc = 9:1)
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.71 (1H, s), 7.76 (1H, d, *J* = 15.7 Hz), 7.60 (1H, d, *J* = 8.8 Hz), 6.86 (1H, dd, *J* = 8.7, 2.5 Hz), 6.72 (1H, d, *J* = 2.5 Hz), 6.28 (1H, d, *J* = 15.7 Hz), 4.24 (2H, q, J = 7.2 Hz), 3.85 (2H, s), 3.81, (3H, s), 1.32 (3H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 198.1, 166.9, 161.2, 140.5, 133.6, 128.6, 126.6, 118.3, 116.5, 113.9, 60.4, 55.4, 48.1, 14.3.
HRMS (ESI) calcd for $C_{14}H_{17}O_4$, m/z 249.1127 [M+H], found 249.1132.

5-bromo-6-(2-methoxyvinyl)benzo[*d*][1,3]dioxole (**7c**)



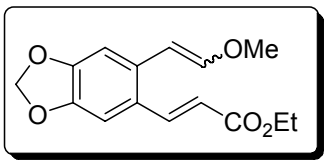

Compound **7c** was prepared according to the general procedure from 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde **6c** (2.29 g, 10 mmol) to provide the title compound as a pale yellow liquid (2.21 g, 86% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:3)
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, s), 7.00, 6.99 (4H, s), 6.86 (3H, d, *J* = 12.8 Hz), 6.82 (3H, s), 6.15 (1H, d, *J* = 7.2 Hz), 6.02 (3H, d, *J* = 12.9 Hz), 5.94 (8H, s), 5.51 (1H, d, *J* = 7.2 Hz), 3.76, 3.70 (12H, s).
$^{13}$C NMR (100 MHz, $CDCl_3$): 149.3, 147.8, 147.3, 146.7, 146.3, 145.9, 129.2, 128.4, 113.0, 112.9, 112.3, 112.0, 109.4, 104.8, 104.3, 103.6, 101.5, 101.4, 60.4, 56.2.

6-(2-methoxyvinyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (**8c**) (new compound)




Compound **8b** was prepared according to the general procedure from 5-bromo-6-(2-methoxyvinyl)benzo[*d*][1,3]dioxole **7c** (2.05 g, 8 mmol) and 1.7 M *tert*-butyllithium in tetrahydrofuran (5.7 mL, 9.6 mmol, 1.2 equiv.) to provide the title compound as a pale yellow liquid (1.44 g, 87% yield) after concentration *in vacuo*. The crude product was used directly for the next step without purification.
HRMS (ESI) calcd for $C_{11}H_{11}O_4$, m/z 207.0657 [M+H], found 207.0652.

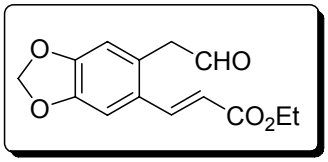
(*E*)-ethyl 3-(6-(2-methoxyvinyl)benzo[*d*][1,3]dioxol-5-yl)acrylate (**9c**) (new compound)




Compound **9c** was prepared according to the general procedure from 6-(2-methoxyvinyl)benzo[*d*][1,3]dioxole-5-carbaldehyde **8c** (1.24 g, 6 mmol) and ylide **10a** (2.30 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (0.66 g, 40% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1.6).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (2.6H, dd, J = 15.7, 8.0 Hz), 7.38, (1H, s), 7.01, (2.6H, s), 6.75 (1.6H, s), 6.72 (1H, s), 6.22-6.17 (3.2H, m), 6.03 (1.6H, d, *J* = 12.7 Hz), 5.97 (5.2H, s), 5.94 (1H, s), 5.45 (1H, d, *J* = 7.2 Hz), 4.25 (5.2H, q, *J* = 7.1 Hz), 3.75, 3.72 (7.8H, s), 1.33 (7.8H, t, *J* = 7.1 Hz).

$^{13}$C NMR (100 MHz, $CDCl_3$): 167.5, 167.5, 150.8, 149.8, 149.3, 148.4, 146.8, 146.5, 142.4, 142.2, 132.3, 131.0, 126.0, 125.7, 117.2, 117.1, 109.7, 106.7, 106.0, 105.8, 102.2, 101.8, 101.6, 101.5, 60.8, 60.6, 60.5, 57.0,14.5.
HRMS (ESI) calcd for $C_{15}H_{17}O_5$, m/z 277.1076 [M+H], found 277.1078.

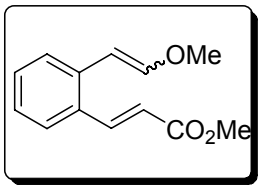
(*E*)-ethyl 3-(6-(2-oxoethyl)benzo[*d*][1,3]dioxol-5-yl)acrylate (**1c**) (new compound)




Compound **1c** was prepared according to the general procedure from (*E*)-ethyl 3-(6-(2-methoxyvinyl)benzo[*d*][1,3]dioxol-5-yl) acrylate **9c** (0.55 g, 2 mmol) to provide the title compound as a pale yellow liquid (0.47 g, 90% yield) after flash column chromatography (hexane:EtOAc = 9:1)

$^1$H NMR (400 MHz, $CDCl_3$): δ 10.3 (1H, s), 8.42 (1H, d, *J* = 15.7 Hz), 7.35 (1H, s), 7.06 (1H, s), 6.31 (1H, d, *J* = 15.7 Hz), 6.11 (1H, s), 4.29 (2H, q, J = 7.2 Hz), 1.35 (3H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 188.9, 166.4, 152.8, 149.8, 139.5, 134.1, 129.8, 122.6, 109.1, 107.0, 102.7, 61.0, 29.9, 14.5.
HRMS (ESI) calcd for $C_{14}H_{15}O_5$, m/z 263.0919 [M+H], found 263.0921.

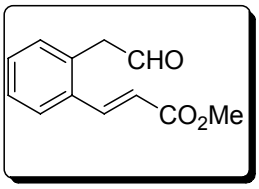
((2*E*)-methyl 3-(2-(2-methoxyvinyl)phenyl)acrylate (**9d**) (new compound)




Compound **9d** was prepared according to the general procedure from 2-(2-methoxyvinyl)benzaldehyde (**8a**) (0.97 g, 6 mmol) and ylide **10b** (2.20g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (1.18g, 90% yield) after flash column chromatography. The product was the mixture of *E* and *Z* isomers (ratio 1:1.5).

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.01 (2.5H, dd, J = 15.9, 4.8 Hz), 7.52 (1H, d, J = 7.8 Hz), 7.33 (2.5H, d, J = 7.7 Hz), 7.30 (4H, d, *J* = 4.2 Hz), 7.22-7.18 (2.5H, m), 6.83 (1.5H, d, *J* = 12.7 Hz), 6.34 (2.5H, dd, *J* = 15.9, 9.4 Hz), 6.25 (1H, d, *J* = 7.1 Hz), 6.04 (1.5H, d, *J* = 12.7 Hz), 5.47 (1H, d, *J* = 7.1 Hz), 3.81, 3.74 (15H, m).
$^{13}$C NMR (100 MHz, $CDCl_3$): 167.5, 167.4, 151.2, 149.0, 143.3, 143.0, 136.5, 135.3, 131.9, 131.9, 130.1, 129.9, 129.7, 127.1, 126.7, 126.7, 126.3, 119.0, 118.9, 102.1, 101.8, 60.6, 56.8, 51.7, 51.6.
HRMS (ESI) calcd for $C_{13}H_{15}O_3$, m/z 219.1021 [M+H], found 219.1017.

(*E*)-methyl 3-(2-(formylmethyl)phenyl)acrylate (**1d**) (new compound)

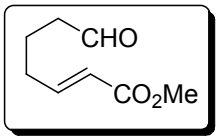



Compound **1d** was prepared according to the general procedure from ((2*E*)-methyl 3-(2-(2-methoxyvinyl)phenyl)acrylate **9d** (1.10 g, 5 mmol) to provide the title compound as a pale yellow liquid (0.91g, 95% yield) after concentration *in vacuo*.

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.74 (1H, s), 7.83 (1H, d, *J* = 15.7 Hz), 7.63 (1H, d, *J* = 7.4 Hz), 7.41-7.33 (2H, m), 7.22 (1H, d, *J* = 7.3 Hz), 6.39 (1H, d, J = 15.7 Hz), 3.88 (2H, s), 3.81 (3H, s).

$^{13}$C NMR (100 MHz, $CDCl_3$): 198.4, 167.2, 141.5, 134.4, 131.8, 131.5, 130.6, 128.4, 127.3, 120.8, 52.0, 48.3.
HRMS (ESI) calcd for $C_{12}H_{13}O_3$, m/z 205.0865 [M+H], found 205.0868.

(E)-methyl 6-formylhex-2-enoate (**1e**)



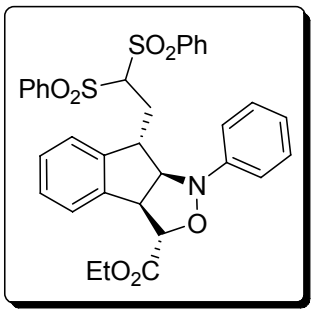

Compound **1e** was prepared according to the procedure[1] from 5,5-dimethoxy- pentanal (1.46 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.29 g, 83% yield).
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.78 (1H, s), 6.97-6.89 (1H, m), 5.85 (1H, d, $J$ = 15.6 Hz), 3.73 (3H, s), 2.49 (2H, t, $J$ = 7.2 Hz), 2.29-2.23 (2H, m), 1.85-1.78 (2H, m).
$^{13}$C NMR (100 MHz, $CDCl_3$): 201.8, 167.1, 148.1, 122.1, 51.7, 43.2, 31.5, 20.5.

**General experimental procedure for the synthesis of indanes with 3 stereogenic centers via tandem Michael-[3+2] cycloaddition reaction:**

Corresponding aldehydes **1** (0.15 mmol, 1.5 equiv.) was added to a 5 mL drum vial containing a stirring mixture of 2-[diphenyl[(trimethylsilyl)oxy]methyl]-(2S)-pyrrolidine **I** (1.6 mg, 0.005 mmol, 20 mol %), 1,1-bis(phenylsulfonyl)ethylene **2** (30.8 mg, 0.1 mmol) and toluene (0.6 ml, 0.17 M) at -20 °C. The reaction was stirred at this temperature for 24 hours (reaction monitored by TLC). Respective hydroxyamines **3** (0.15 mmol, 1.5 equiv.) was then added to the reaction mixture and stirred at room temperature for 3 hours, unless otherwise stated. The reaction mixture was purified by flash column chromatography (Hexane:EtOAc = 85:15) yielding pure indanes **4**.

**Experimental data of Compounds 4a-4k**

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-phenyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4a**) (new compound)

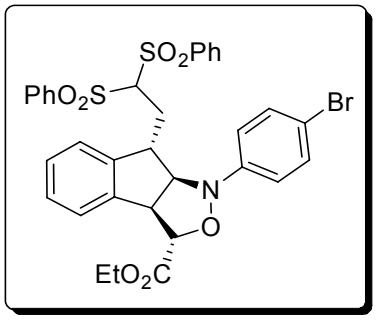



Indane **4a** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine **3a** (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.5 mg, 98% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.79-7.11 (19H, m), 4.79-4.77 (1H, m), 4.51-4.48 (3H, m), 4.19-4.11 (2H, m), 4.68-3.66 (1H, m), 2.73-2.66 (1H, m), 2.57-2.50 (1H, m), 1.25 (3H, t, $J$ = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.3, 149.2, 142.9, 141.5, 138.3, 137.2, 134.9, 134.6, 130.1, 129.3, 129.3, 129.1, 128.7, 128.6, 125.1, 124.6, 124.4, 118.3, 83.4, 80.0, 76.5, 61.9, 56.0, 47.0, 31.1, 29.8, 14.2.

[1] Kumpulainen, E. T. T.; Koskinen, A. M. P.; Rissanen, K. *Org. Lett.*, **2007**, *9*, 5043.

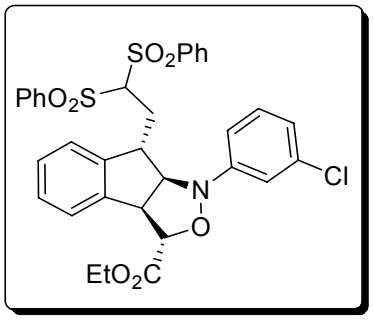
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 13.0 min, $t_R$ (minor) = 39.8 min; 98% ee.
$[\alpha]_D^{22}$ = - 74.7 (*c* = 1.5, $CHCl_3$).
HRMS (ESI) calcd for $C_{33}H_{32}NO_7S_2$, m/z 618.1620 [M+H], found 618.1612.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-(4-bromophenyl)-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4b**) (new compound)




Indane **4b** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-(4-bromophenyl)hydroxylamine **3b** (28.2 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (64.1 mg, 92% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.82-7.21 (18H, m), 4.78-4.75 (1H, m), 4.51-4.43 (3H, m), 4.24-4.14 (2H, m), 3.74-3.70 (1H, m), 2.72-2.65 (1H, m), 2.58-2.51 (1H, m), 1.27 (3H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.2, 148.6, 142.7, 141.2, 138.2, 137.1, 135.0, 134.6, 132.1, 130.1, 129.4, 129.3, 129.0, 128.7, 125.1, 124.7, 119.4, 116.8, 83.4, 80.2, 68.2, 62.0, 56.0, 47.0, 29.7, 25.8, 14.3.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 81.3 min, $t_R$ (major) = 114.0 min; 96% ee.
$[\alpha]_D^{22}$ = - 88.7 (*c* = 1.5, $CHCl_3$).
HRMS (ESI) calcd for $C_{33}H_{31}NO_7S_2Br$, m/z 696.0725 [M+H], found 696.0716.

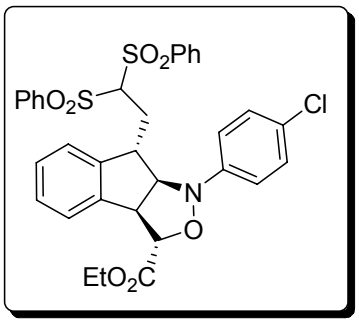
(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-(3-chlorophenyl)-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4c**) (new compound)




Indane **4c** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-(3-chlorophenyl)hydroxylamine **3c** (21.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (63.2 mg, 97% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.87-7.28 (13H, m), 7.24-7.03 (5H, m), 4.81 (1H, dd, *J* = 7.1, 3.2 Hz), 4.56-4.46 (3H, m), 4.21-4.12 (2H, m), 3.70-3.66 (1H, m), 2.71-2.66 (1H, m), 2.62-2.59 (1H, m), 1.28 (3H, t, *J* = 7.2 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.2, 150.8, 142.6, 141.0, 138.2, 137.1, 135.1, 135.1, 135.0, 134.6, 130.3, 130.1, 129.4, 129.3, 129.0, 128.7, 125.0, 124.6, 123.5, 117.2, 114.6, 83.6, 80.2, 76.4, 62.1, 60.6, 55.6, 47.2, 29.8, 14.2.
HPLC: Chiralpak OD-H (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 40.4 min, $t_R$ (minor) = 47.2 min; 98% ee.

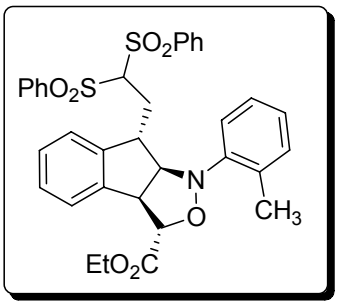
$[\alpha]_D^{22}$ = - 102.8 (*c* = 1.5, $CHCl_3$).
HRMS (ESI) calcd for $C_{33}H_{31}NO_7S_2Cl$, m/z 652.1230 [M+H], found 652.1234.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-(4-chlorophenyl)-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4d**) (new compound)




Indane **4d** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-(4-chlorophenyl)hydroxylamine **3d** (21.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.1 mg, 92% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.21 (18H, m), 4.75 (1H, dd, *J* = 7.1, 2.9 Hz), 4.51-4.43 (3H, m), 4.22-4.11 (2H, m), 3.73-3.70 (1H, m), 2.72-2.65 (1H, m), 2.57-2.50 (1H, m), 1.28 (3H, t, *J* = 7.2 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.2, 148.0, 142.7, 141.2, 138.2, 137.1, 135.0, 134.6, 130.1, 129.4, 129.3, 129.2, 129.0, 128.7, 125.1, 124.7, 119.3, 83.4, 80.2, 62.0, 60.6, 56.0, 47.0, 29.8, 21.2, 14.4, 14.3.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH, 80/20, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 29.6 min, $t_R$ (major) = 39.5 min; 98% ee.
$[\alpha]_D^{22}$ = - 96.3 (*c* = 1.3, $CHCl_3$).
HRMS (ESI) calcd for $C_{33}H_{31}NO_7S_2Cl$, m/z 652.1230 [M+H], found 652.1237.

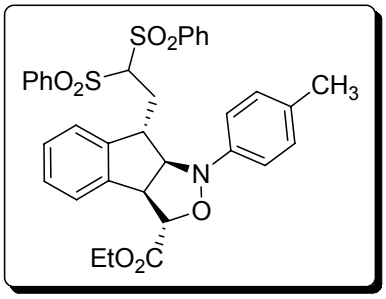
(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-*o*-tolyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4e**) (new compound)




Indane **4e** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-o-tolylhydroxylamine **3e** (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (61.0 mg, 97% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.67-7.29 (15H, m), 7.25-7.21 (3H, m), 4.62 (1H, dd, *J* = 7.4, 4.6 Hz), 4.50 (1H, dd, *J* = 7.2, 2.3 Hz), 4.40 (1H, d, *J* = 4.6 Hz), 4.34 (1H, dd, *J* = 7.4, 3.4 Hz), 4.13-4.09 (1H, m), 4.01-3.97 (1H, m), 3.39-3.36 (1H, m), 2.69-2.62 (1H, m), 2.39 (3H, s), 2.38-2.31 (1H, m), 1.17 (3H, t, *J* = 7.1 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.6, 145.1, 143.3, 142.3, 138.3, 137.3, 136.9, 134.8, 134.6, 131.3, 129.8, 129.4, 129.2, 128.6, 128.5, 127.5, 126.8, 125.2, 124.6, 121.5, 83.1, 80.0, 74.5, 61.6, 57.6, 46.9, 30.0, 18.6, 14.2.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 8.6 min, $t_R$ (minor) = 46.9 min; 95% ee.
$[\alpha]_D^{22}$ = - 57.8 (*c* = 0.9, $CHCl_3$).

HRMS (ESI) calcd for $C_{34}H_{34}NO_7S_2$, m/z 632.1777 [M+H], found 632.1764.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-*p*-tolyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4f**) (new compound)




Indane **4f** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-p-tolylhydroxylamine **3f** (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.8 mg, 96% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.76-7.16 (18H, m), 4.15-4.68 (1H, m), 4.47-4.43 (2H, m), 4.37-4.35 (1H, m), 4.22-4.14 (2H, m), 3.66-3.61 (1H, m), 2.72-2.65 (1H, m), 2.51-2.43 (1H, m), 2.35 (1H, s), 1.27 (3H, t, $J$ = 7.1 Hz).

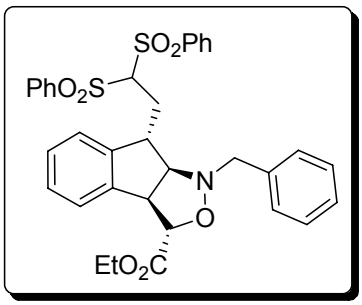
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.4, 146.5, 143.0, 141.7, 138.3, 137.2, 134.8, 134.7, 134.6, 130.1, 129.8, 129.3, 129.3, 129.2, 128.6, 128.6, 125.1, 124.7, 119.4, 83.2, 80.0, 76.9, 61.8, 56.3, 46.9, 29.8, 21.1, 14.3.

HPLC: Chiralpak AS-H (hexane/*i*-PrOH, 80/20, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 41.9 min, $t_R$ (major) = 64.9 min; 98% ee.

$[\alpha]_D^{22}$ = - 73.5 ($c$ = 1.5, $CHCl_3$).

HRMS (ESI) calcd for $C_{34}H_{34}NO_7S_2$, m/z 632.1777 [M+H], found 632.1764.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 1-benzyl-8-(2,2-bis(phenylsulfonyl)ethyl)-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4g**) (new compound)




Indane **4g** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.) and *N*-benzylhydroxylamine **3g** (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (57.7 mg, 91% yield) after flash column chromatography on silica gel.

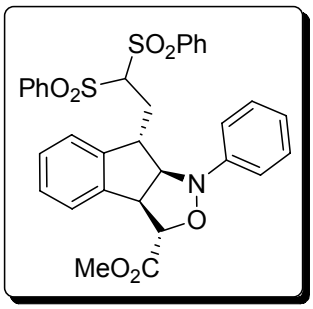
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.89 (4H, dd, $J$ = 19.0, 7.9 Hz), 7.67 (2H, t, $J$ = 7.4 Hz), 7.52-7.46 (4H, m), 7.35-7.30 (8H, m), 7.14-7.12 (1H, m), 5.27-5.25 (1H, m), 4.42-4.25 (4H, m), 4.17 (1H, d, $J$ = 13.7 Hz), 4.02-3.99 (1H, m), 3.95 (1H, d, $J$ = 13.8 Hz), 3.60-3.57 (1H, m), 2.78-2.71 (1H, m), 2.39-2.32 (1H, m), 1.34 (3H, t, $J$ = 7.1 Hz).

$^{13}$C NMR (100 MHz, $CDCl_3$): 171.9, 142.5, 141.4, 138.7, 137.1, 134.9, 134.5, 130.4, 129.4, 129.3, 129.2, 129.2, 128.7, 128.6, 128.4, 127.7, 125.1, 124.2, 83.6, 79.9, 79.4, 77.4, 62.2, 61.9, 56.3, 46.4, 29.7, 14.4.

HPLC: Chiralpak OD-H (hexane/*i*-PrOH, 70/30, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 14.9 min, $t_R$ (major) = 19.1 min; 98% ee.

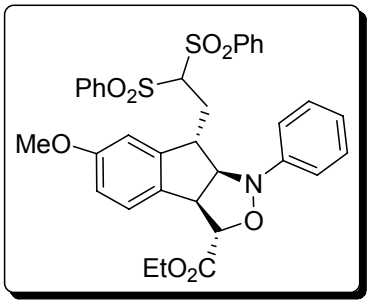
$[\alpha]_D^{22}$ = - 30.8 (*c* = 1.5, $CHCl_3$).
HRMS (ESI) calcd for $C_{34}H_{34}NO_7S_2$, m/z 632.1777 [M+H], found 632.1783.

(3*S*,3a*S*,8*S*,8a*R*)-methyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-phenyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4h**) (new compound)



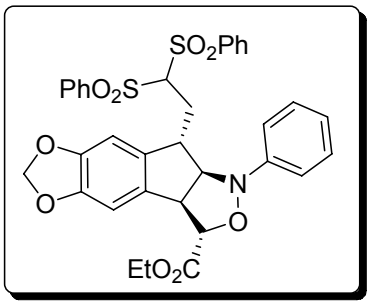

Indane **4h** was prepared according to the general procedure from (*E*)-methyl 3-(2-(formylmethyl)phenyl)acrylate **1d** (30.6 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine **3a** (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (54.2 mg, 90% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.79-7.12 (19H, m), 4.74 (1H, dd, *J* = 7.3, 2.6 Hz), 4.50 (3H, s), 3.71 (3H, s), 3.66-3.63 (1H, m), 2.71-2.64 (1H, m), 2.55-2.48 (1H, m).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.8, 148.9, 143.0, 141.5, 138.3, 137.2, 134.9, 134.6, 130.1, 129.4, 129.3, 129.3, 129.1, 128.7, 128.7, 125.1, 124.6, 124.6, 118.5, 83.3, 80.1, 76.4, 56.0, 52.7, 46.9, 30.0.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 14.9 min, $t_R$ (minor) = 27.9 min; 98% ee.
$[\alpha]_D^{22}$ = - 21.0 (*c* = 1.3, $CHCl_3$).
HRMS (ESI) calcd for $C_{32}H_{28}NO_7S_2$, m/z 602.1307 [M+H], found 602.1301.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-6-methoxy-1-phenyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4i**) (new compound)




Indane **4i** was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)-4-methoxyphenyl)acrylate **1b** (37.2 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine **3a** (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (63.4 mg, 98% yield) after flash column chromatography on silica gel.
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.79-7.10 (16H, m), 6.83 (1H, dd, *J* = 8.3, 1.8 Hz), 6.72 (1H, s), 4.80-4.78 (1H, m), 4.51-4.39 (3H, m), 4.16-4.10 (2H, m), 3.80 (3H, s), 3.67-3.64 (1H, m), 2.73-2.66 (1H, m), 2.57-2.51 (1H, m), 1.24 (3H, t, *J* = 7.2 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.4, 160.4, 149.2, 144.4, 138.3, 137.2, 134.9, 134.5, 133.4, 130.1, 129.3, 129.3, 129.2, 129.0, 125.8, 124.3, 118.2, 114.9, 109.6, 83.6, 80.0, 76.9, 61.8, 55.7, 55.3, 47.0, 29.7, 14.2.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 11.0 min, $t_R$ (minor) = 22.8 min; 92% ee.
$[\alpha]_D^{22}$ = - 33.4 (*c* = 1.0, $CHCl_3$).
HRMS (ESI) calcd for $C_{34}H_{34}NO_8S_2$, m/z 648.1726 [M+H], found 648.1721.

(3*S*,3a*S*,8*S*,8a*R*)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-5,6-dioxomethylenyl-1-phenyl-3,3a,8,8a-tetrahydro-1*H*-indeno[2,1-*c*]isoxazole-3-carboxylate (**4j**) (new compound)




Indane **4j** was prepared according to the general procedure from (*E*)-ethyl 3-(6-(2-oxoethyl)benzo[*d*][1,3]dioxol-5-yl)acrylate **1c** (39.3 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine **3a** (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (62.5 mg, 97% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.79-7.29 (14H, m), 7.13 (1H, d, *J* = 7.0 Hz), 6.76 (1H, s), 6.63 (1H, s), 5.97 (2H, d, *J* = 8.8 Hz), 4.65 (1H, dd, *J* = 7.1, 2.7 Hz), 4.41-4.34 (3H, m), 4.19-4.11 (2H, m), 3.55-3.51 (1H, m), 2.61-2.54 (1H, m), 2.49-2.42 (1H, m), 1.25 (3H, t, *J* = 10.4 Hz).

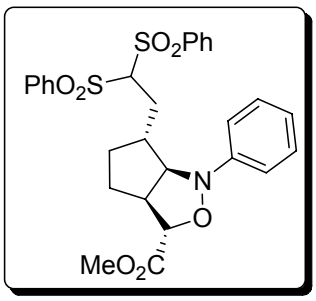
$^{13}$C NMR (100 MHz, $CDCl_3$): 170.2, 149.1, 148.4, 138.2, 137.2, 135.8, 134.9, 134.6, 134.2, 130.1, 129.4, 129.3, 129.2, 124.6, 118.5, 105.2, 105.0, 101.7, 83.3, 80.1, 76.8, 61.8, 56.0, 46.9, 30.2, 14.2.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (major) = 44.7 min, $t_R$ (minor) = 51.8 min; 99% ee.

$[\alpha]_D^{22}$ = - 57.2 (*c* = 1.1, $CHCl_3$).

HRMS (ESI) calcd for $C_{34}H_{32}NO_9S_2$, m/z 662.1519 [M+H], found 662.1515.

methyl 6-(2,2-bis(phenylsulfonyl)ethyl)-hexahydro-1-phenyl-1*H*-cyclopenta[*c*]isoxazole-3-carboxylate (**4k)** (new compound)




Compound **4k** was prepared according to the general procedure from (*E*)-methyl 6-formylhex-2-enoate **1e** (23.4 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine **3a** (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (52.2 mg, 94% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.76 (4H, dd, *J* = 13.4, 7.8 Hz), 7.63-7.58 (2H, m), 7.46 (2H, t, *J* = 7.8 Hz), 7.40 (2H, t *J* = 7.8 Hz), 7.30-7.26 (2H, m), 7.16 (2H, d, *J* = 8 Hz), 7.00 (1H, t *J* = 7.3 Hz), 4.90-4.88 (1H, m), 4.27 (1H, d, *J* = 4.6 Hz), 4.00-3.97 (1H, m), 3.57, (3H, s), 3.46-3.38 (1H, m), 2.40 (3H, s), 2.10-1.97 (2H, m), 1.76-1.68 (1H, m), 1.42-1.37 (1H, m).

$^{13}$C NMR (100 MHz, $CDCl_3$): 171.0, 149.6, 138.4, 137.4, 134.7, 134.5, 129.9, 129.3, 129.2, 129.2, 129.0, 123.1, 116.4, 84.0, 80.7, 75.6, 52.4, 49.9, 42.2, 30.9, 29.5, 28.3.

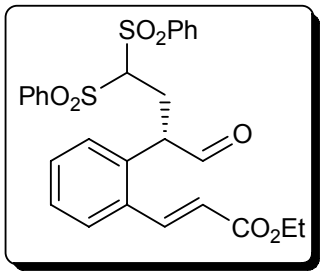
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 70/30, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 20.7 min, $t_R$ (major) = 23.0 min; 94% ee.

$[\alpha]_D^{20}$ = - 81.5 (*c* = 1.0, $CHCl_3$).

HRMS (ESI) calcd for $C_{28}H_{30}NO_7S_2$, m/z 556.1464 [M+H], found 556.1459.

**Experimental data of Compound A**

(*E*)-ethyl 3-(2-((S)-1-formyl-3,3-bis(phenylsulfonyl)propyl)phenyl)acrylate (**A**) (new compound)




Michael adduct A was prepared according to the general procedure from (*E*)-ethyl 3-(2-(formylmethyl)phenyl)acrylate **1a** (35.4 mg, 0.15 mmol, 1.5 equiv.), without the addition of hydroxyamines, to provide the title compound as a white solid (63.4 mg, 87% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.55 (1H, s), 8.12 (1H, d, *J* = 15.6 Hz), 7.96-7.94 (2H, m), 7.80-7.79 (2H, m), 7.73-7.64 (3H, m), 7.58 (2H, t, *J* = 7.6 Hz), 7.50 (2H, t, *J* = 7.6 Hz), 7.36 (1H, t, *J* = 7.2 Hz), 7.31-7.29 (1H, m), 6.85-6.84 (1H, m), 6.41 (1H, d, *J* = 15.6 Hz), 4.80-4.76 (1H, m), 4.46-4.43 (1H, m), 4.31-4.26 (2H, m), 2.94-2.86 (1H, m), 2.56-2.48 (1H, m), 1.33 (3H, t, *J* = 7.2 Hz).

$^{13}$C NMR (100 MHz, $CDCl_3$): 198.0, 166.3, 140.7, 138.0, 137.3, 135.6, 135.0, 134.9, 133.8, 131.1, 130.2, 129.9, 129.8, 129.4, 129.4, 129.2, 128.3, 123.0, 80.2, 61.1, 52.3, 26.5, 14.5.

HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 70/30, flow rate 1 mL/min, λ= 220 nm),

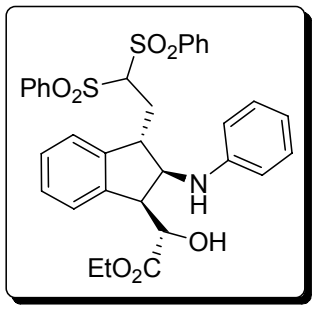
$t_R$ (major) = 31.237 min, $t_R$ (minor) = 37.617 min; 97% ee.

$[\alpha]_D^{22}$ = - 51.9 (*c* = 1.4, $CHCl_3$).

HRMS (ESI) calcd for $C_{27}H_{27}O_7S_2$, m/z 527.1198 [M+H], found 527.1211.

**Experimental procedure and data for the synthesis α-hydroxy-γ-amino acid derivative 5:**

(*S*)-ethyl 2-((1*S*,2*R*,3*S*)-3-(2,2-bis(phenylsulfonyl)ethyl)-2-(phenylamino)-2,3-dihydro-1*H*-inden-1-yl)-2-hydroxyacetate (**5**) (new compound)




10% Pd/C (30 mg) was added to a solution of indane **4a** (0.1 mmol) in methanol (5.0 mL) at room temperature under an atmosphere of hydrogen by means of a balloon. After stirring overnight, the mixture was filtered through Celite. Removal of the solvent from the filtrate under reduced pressure afforded the α-hydroxy-γ-amino acid derivative **5** as a white solid (60.5 mg, 98% yield).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.91 (2H, d, *J* = 7.6 Hz), 7.68 (1H, t, J = 7.4Hz), 7.55-7.49 (3H, m), 7.38 (2H, d, *J* = 7.6 Hz), 7.30-7.22 (7H, m), 7.04-7.03 (1H, m), 6.82 (1H, t, *J* = 7.2 Hz), 6.64 (2H, d, *J* = 7.8 Hz), 5.39 (1H, d, *J* = 9.1 Hz), 4.41 (1H, d, *J* = 9.5 Hz), 4.35 (1H, s), 4.19-4.10 (1H, m), 4.05 (1H, d, *J* = 7.8 Hz), 3.83-3.73 (2H, m), 3.19-3.11 (1H, m), 3.02 (1H, s), 2.77-2.72 (1H, m), 2.57-2.50 (1H, m), 0.98 (3H, t, *J* = 7.1 Hz).

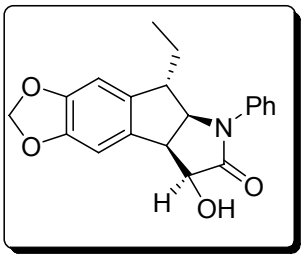
$^{13}$C NMR (100 MHz, $CDCl_3$): 174.0, 146.1, 143.7, 140.9, 138.0, 137.2, 134.8, 134.1, 129.9, 129.7, 129.3, 129.1, 129.1, 128.4, 128.0, 124.9, 123.3, 118.3, 112.9, 79.1, 73.7, 62.3, 62.1, 49.2, 47.1, 30.0, 13.9.

HPLC: Chiralpak IA (hexane/*i*-PrOH, 90/10, flow rate 1 mL/min, λ= 220 nm),

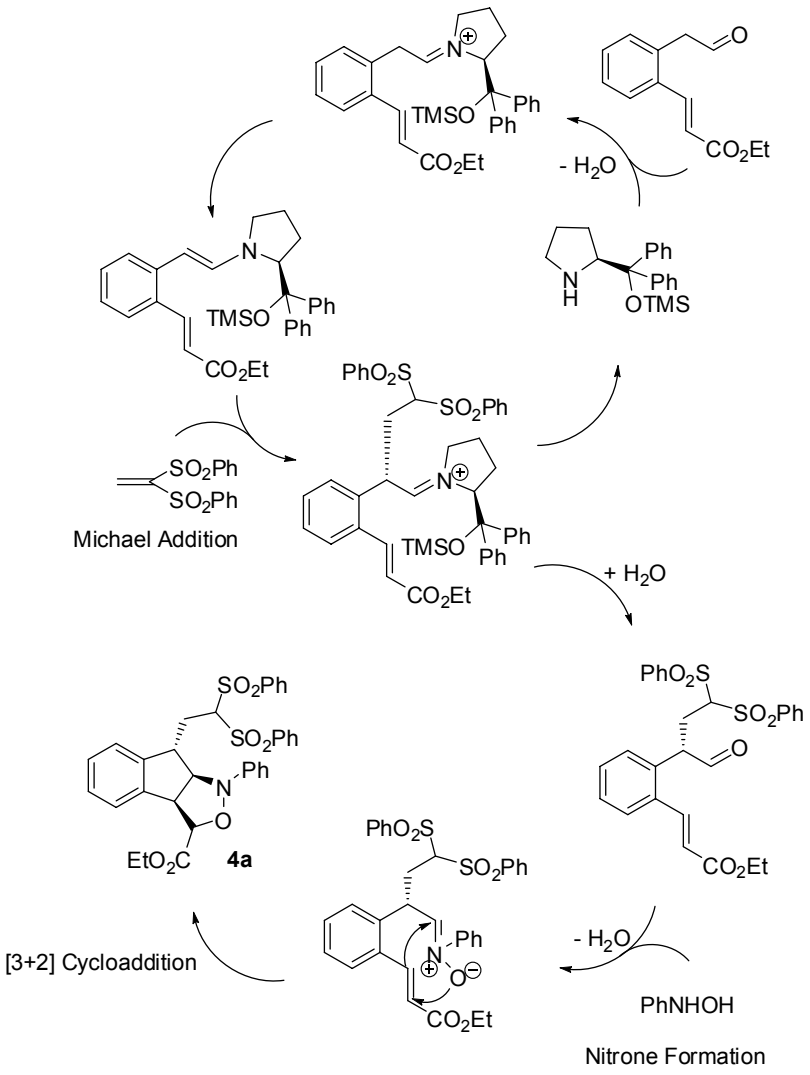
$t_R$ (minor) = 74.4 min, $t_R$ (major) = 96.0 min; 97% ee.
$[\alpha]_D^{21}$ = - 42.0 ($c$ = 1.6, $CHCl_3$).
HRMS (ESI) calcd for $C_{33}H_{34}NO_7S_2$, m/z 620.1777 [M+H], found 620.1768.

**Experimental procedure and data for the synthesis α-hydroxy-γ-lactam derivative 6:**

(3S,3aS,8S,8aR)-8-ethyl-3-hydroxy-5,6-dioxomethylenyl-1-phenyl-3,3a,8,8a-tetrahydroindeno[2,1-b]pyrrol-2(1H)-one (**6**) (new compound)

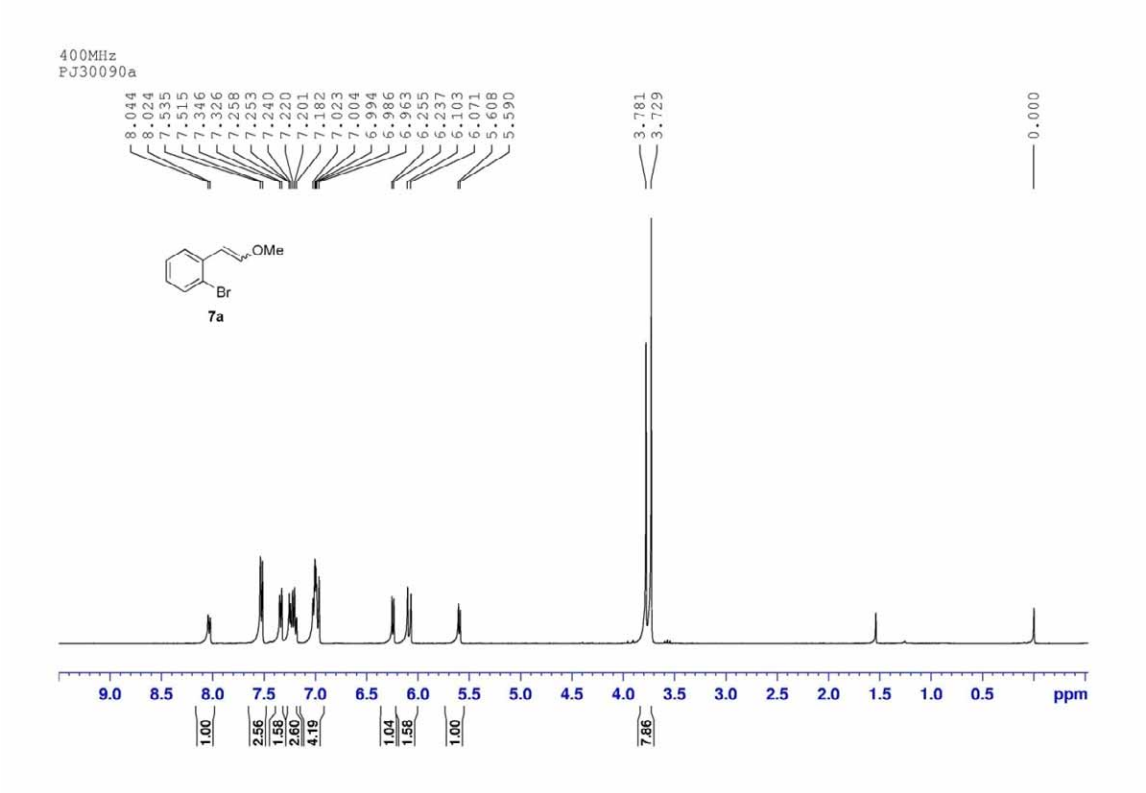


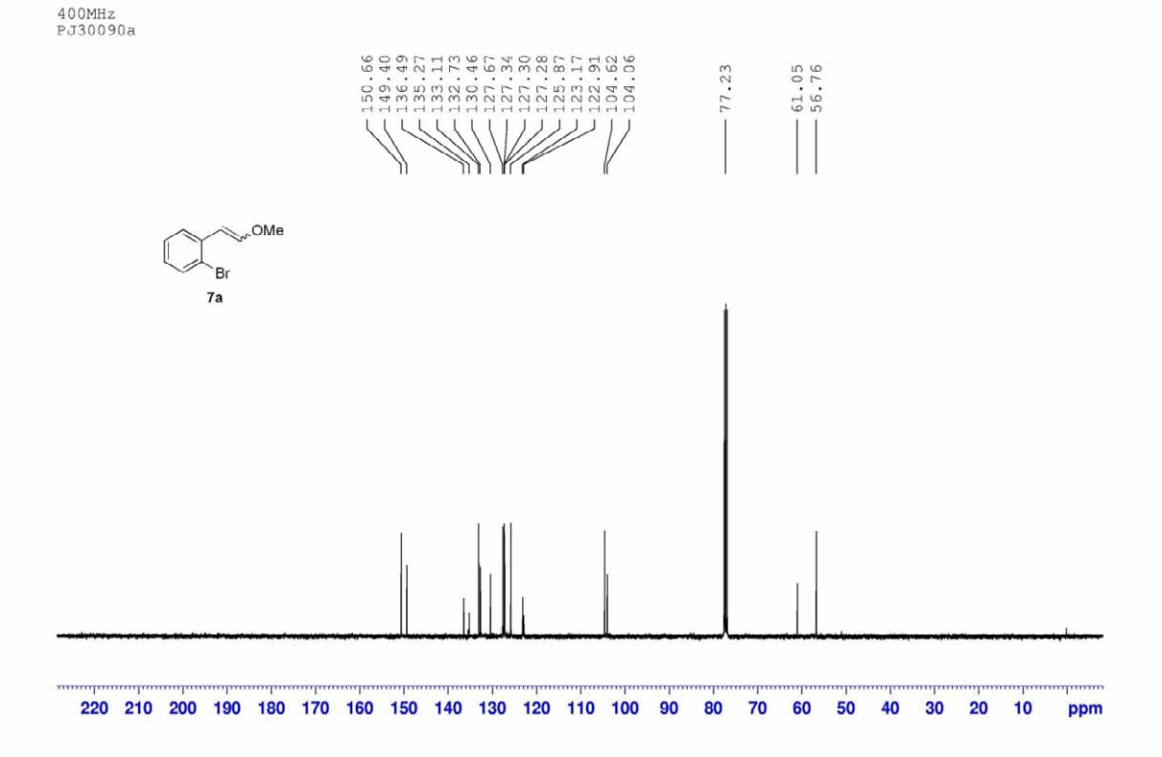

To magnesium turnings (77.8 mg, 32 equiv.), activated by TMSCL (1 drop) and 1,2-dibromoethane (1 drop), was added dropwise a solution of indane **4j** (66.0 mg, 0.1 mmol) in anhydrous methanol (10 mL) with stirring. The mixture was heated to 50 °C to initiate hydrogen generation and then to reflux for 2 hours. After cooling down to room temperature, 2N HCl solution (10 mL) was then added and extracted with ether. The organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 7:3) to afford the α-hydroxy-γ-lactam derivative **6** as a pale yellow solid (15.9 mg, 47% yield).
$^1$H NMR (400 MHz, $CDCl_3$): δ 7.41-7.24 (5H, m), 7.10 (1H, s), 6.51 (1H, s), 5.93 (1H, s), 4.74 (1H, d, $J$ = 8.6 Hz), 4.63 (1H, d, $J$ = 5.3 Hz), 4.17 (1H, t, $J$ = 6.9 Hz), 3.13 (1H, s), 2.95 (1H, t, $J$ = 6.6 Hz), 1.60-1.51 (2H, m), 0.92 (3H, t, $J$ = 7.3 Hz).
$^{13}$C NMR (100 MHz, $CDCl_3$): 172.7, 148.0, 147.3, 138.5, 137.1, 130.6, 129.3, 126.3, 123.4, 109.0, 105.2, 101.4, 72.0, 65.7, 49.6, 45.6, 27.9, 11.5.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH, 60/40, flow rate 1 mL/min, λ= 220 nm),
$t_R$ (minor) = 10.0 min, $t_R$ (major) = 13.1 min; 94% ee.
$[\alpha]_D^{21}$ = - 107.7 ($c$ = 1.0, $CHCl_3$).
HRMS (ESI) calcd for $C_{20}H_{20}NO_4$, m/z 338.1892 [M+H], found 338.1389.

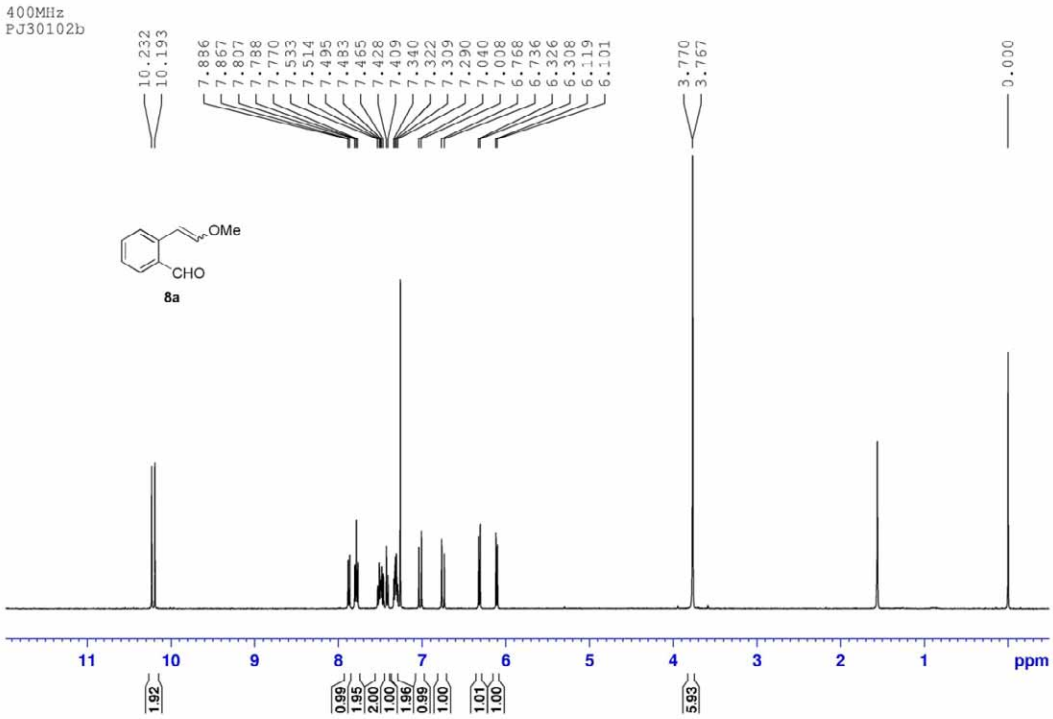



**Scheme** Proposed catalytic cycle and reaction pathway of the sequential reaction.

## $^{1}$H and $^{13}$C NMR Spectra of Compounds 7a-9d and 1a-1e

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10.193
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7.867
7.807
7.788
7.770
7.533
7.514
7.495
7.483
7.465
7.428
7.409
7.340
7.322
7.309
7.290
7.040
7.008
6.768
6.736
6.326
6.308
6.119
6.101
3.770
3.767
0.000
OMe
CHO
8a
11
10
9
8
7
6
5
4
3
2
1
ppm
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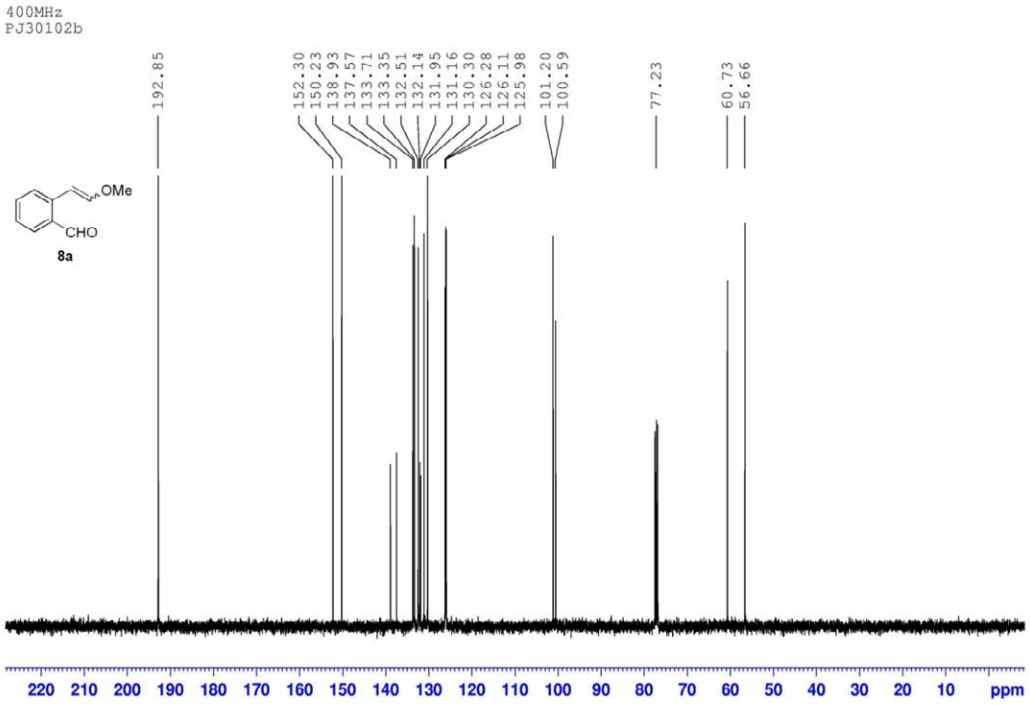
0.99
1.95
2.00
1.00
1.96
0.99
1.00
1.01
1.00
5.93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150.23
138.93
137.57
133.71
133.35
132.51
132.14
131.95
131.16
130.30
126.28
126.11
125.98
101.20
100.59
77.23
60.73
56.66
OMe
CHO
8a
220
210
200
190
180
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150
140
130
120
110
100
90
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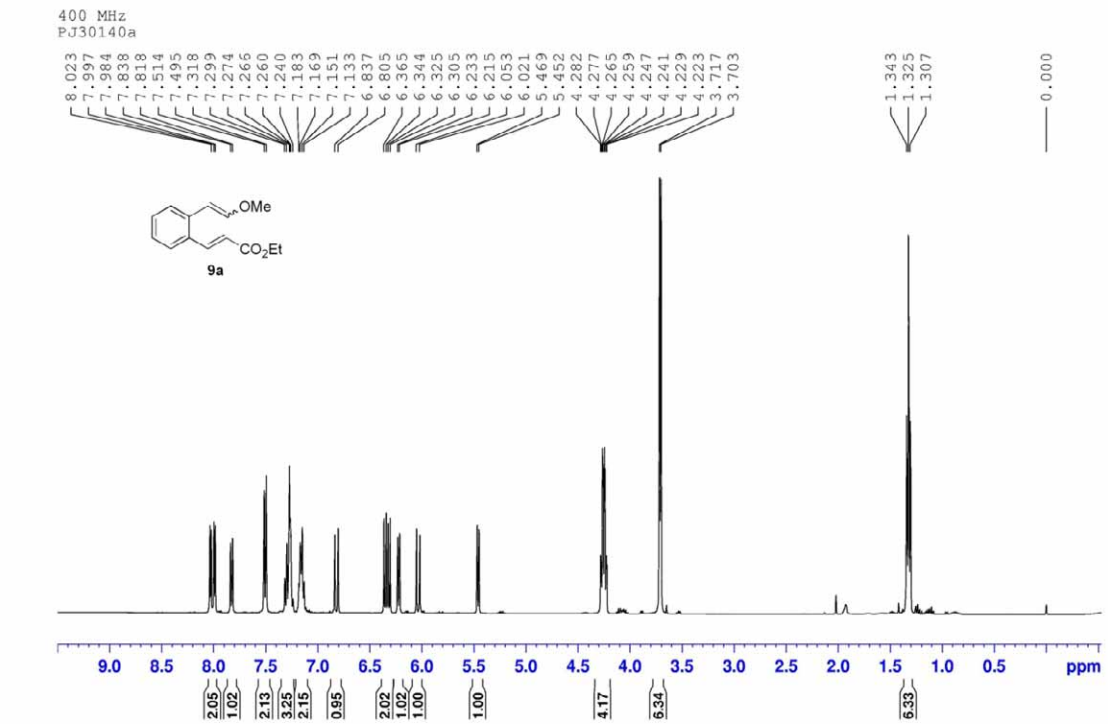
70
60
50
40
30
20
10
ppm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PJ30140a
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7.984
7.838
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7.318
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7.274
7.266
7.260
7.240
7.183
7.169
7.151
7.133
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6.805
6.365
6.344
6.325
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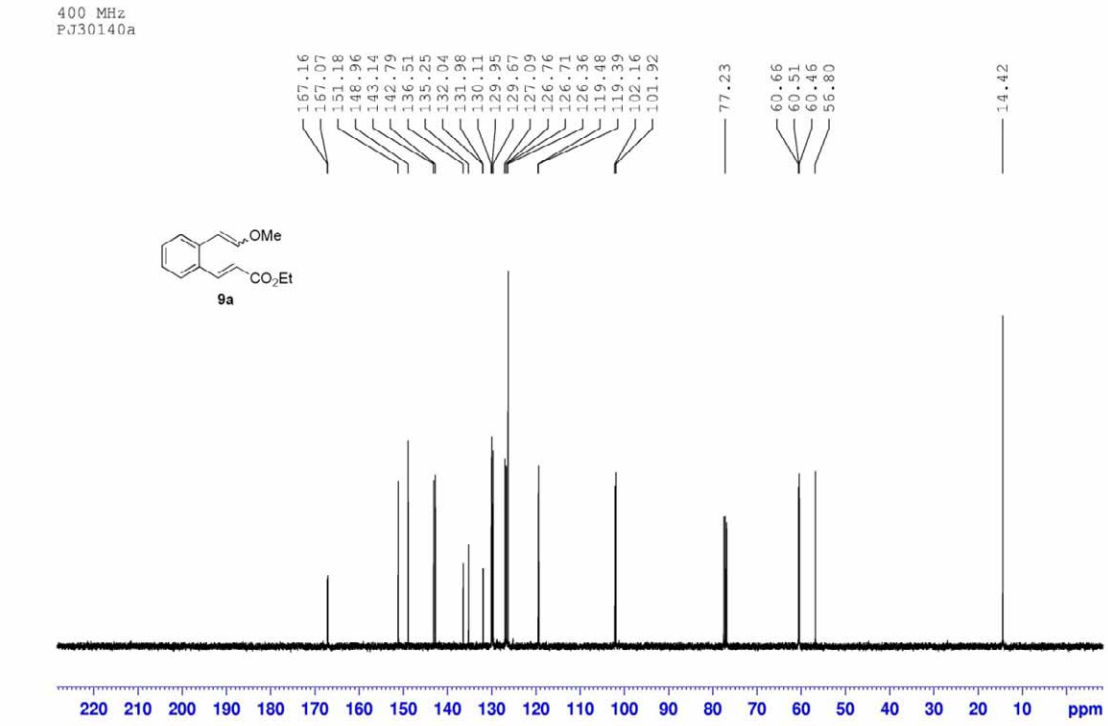
6.233
6.215
6.053
6.021
5.469
5.452
4.282
4.277
4.265
4.259
4.247
4.241
4.229
4.223
3.717
3.703
1.343
1.325
1.307
0.000
OMe
CO2Et
9a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05 1.02 2.13 3.25 2.15 0.95 2.02 1.02 1.00 1.00 4.17 6.34 6.33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167.07
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143.14
142.79
136.51
135.25
132.04
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130.11
129.95
129.67
127.09
126.76
126.71
126.36
119.48
119.39
102.16
101.92
77.23
60.66
60.51
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56.80
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CO2Et
9a
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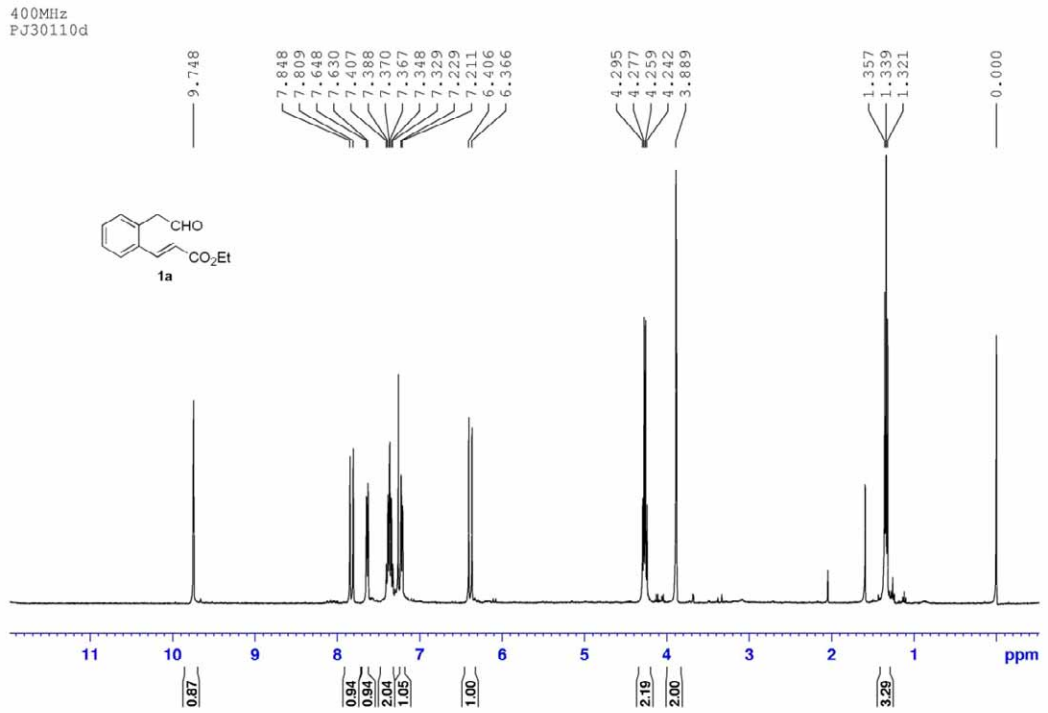
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PJ30110d
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7.809
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7.630
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7.388
7.370
7.367
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7.229
7.211
6.406
6.366
4.295
4.277
4.259
4.242
3.889
1.357
1.339
1.321
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CHO
CO2Et
1a
11
10
9
8
7
6
5
4
3
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1
ppm
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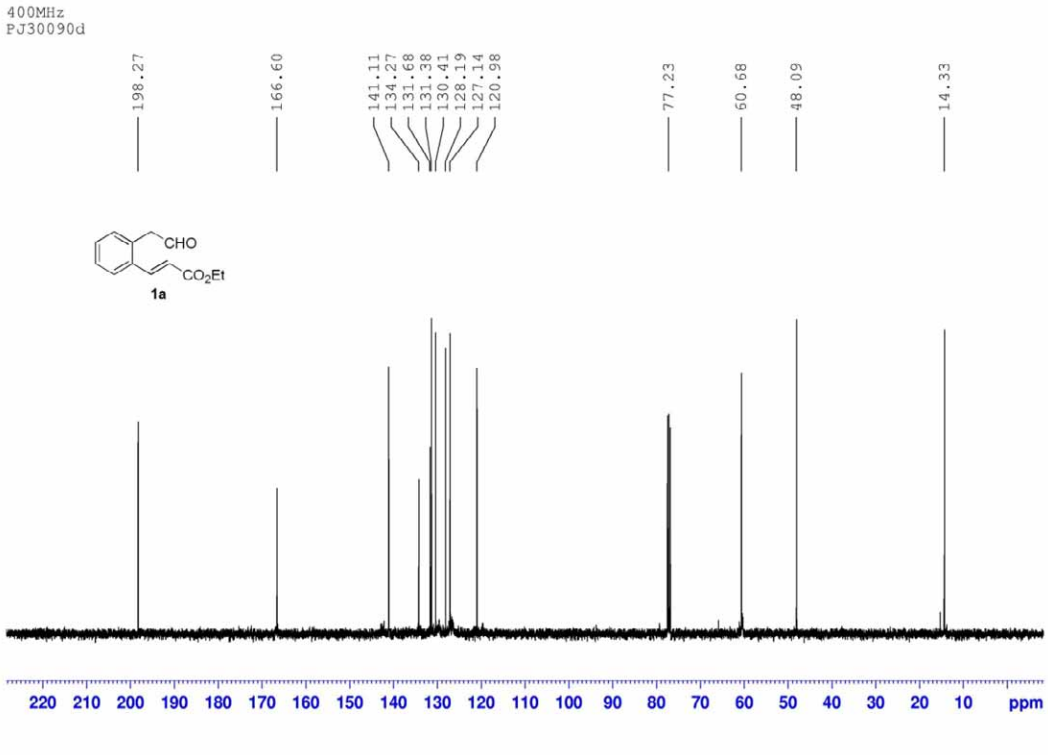
1.05
1.00
2.19
2.00
3.29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PJ30090d
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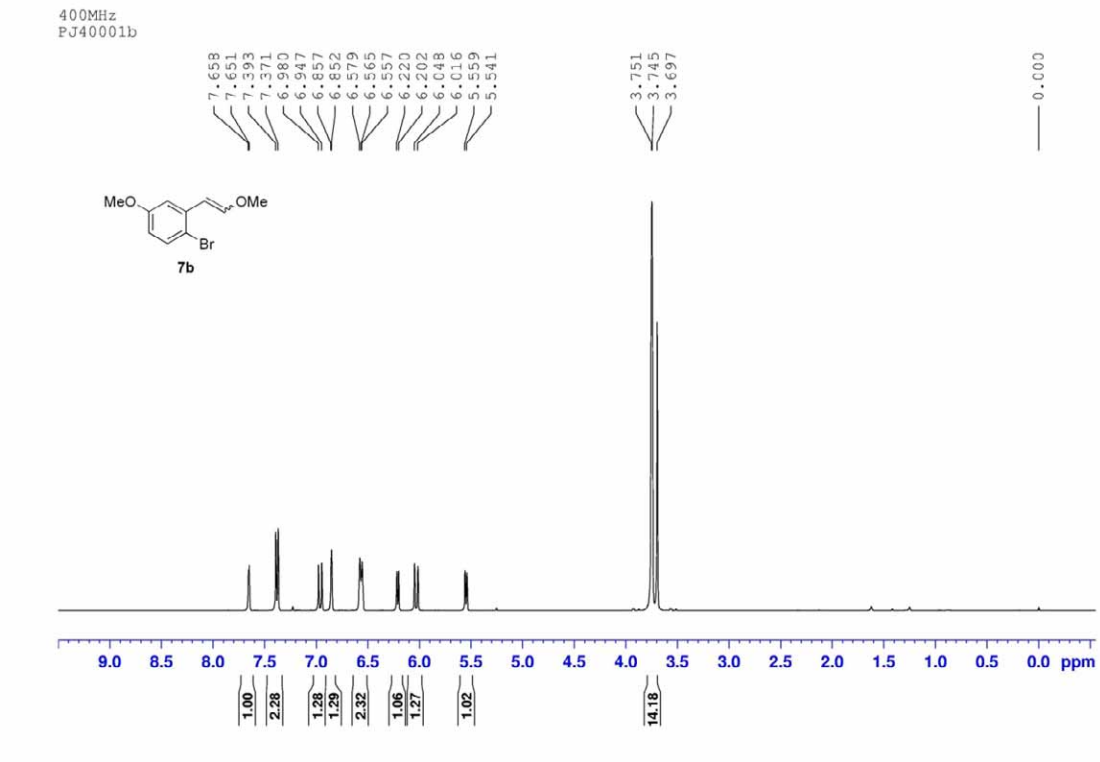
141.11
134.27
131.68
131.38
130.41
128.19
127.14
120.98
77.23
60.68
48.09
14.33
CHO
CO2Et
1a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
PJ40001b
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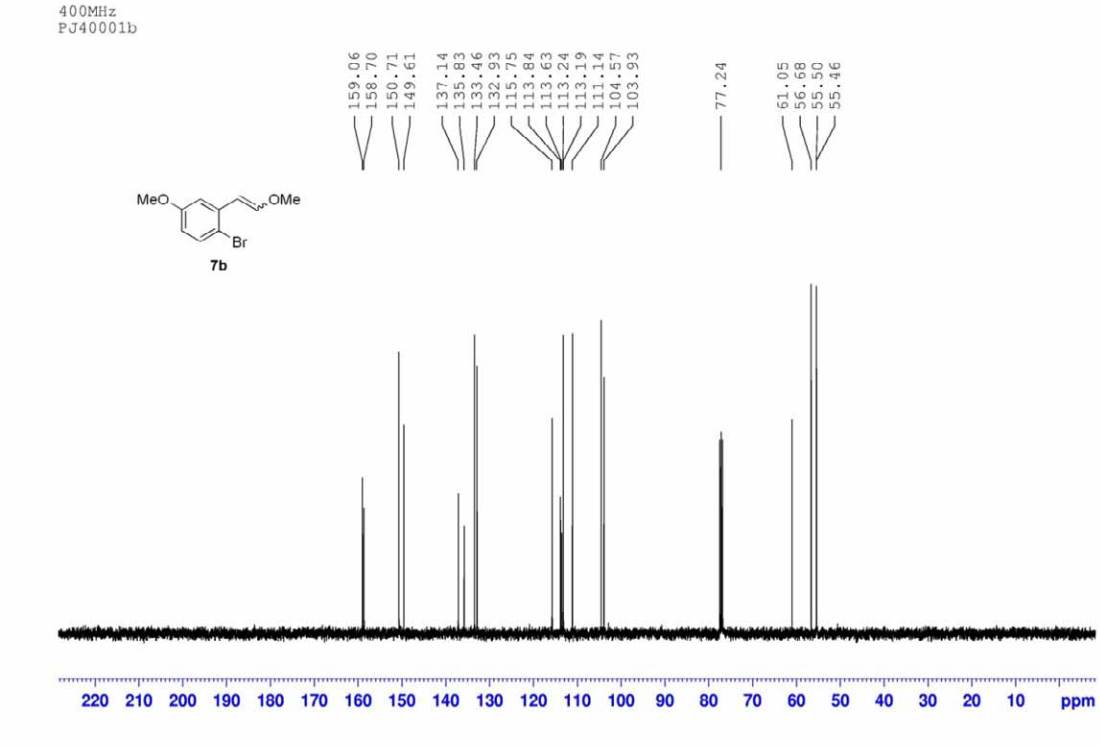
7.393
7.371
6.980
6.947
6.857
6.852
6.579
6.565
6.557
6.220
6.202
6.048
6.016
5.559
5.541
3.751
3.745
3.697
0.000
MeO
OMe
Br
7b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.28
1.28
1.29
2.32
1.06
1.27
1.02
14.18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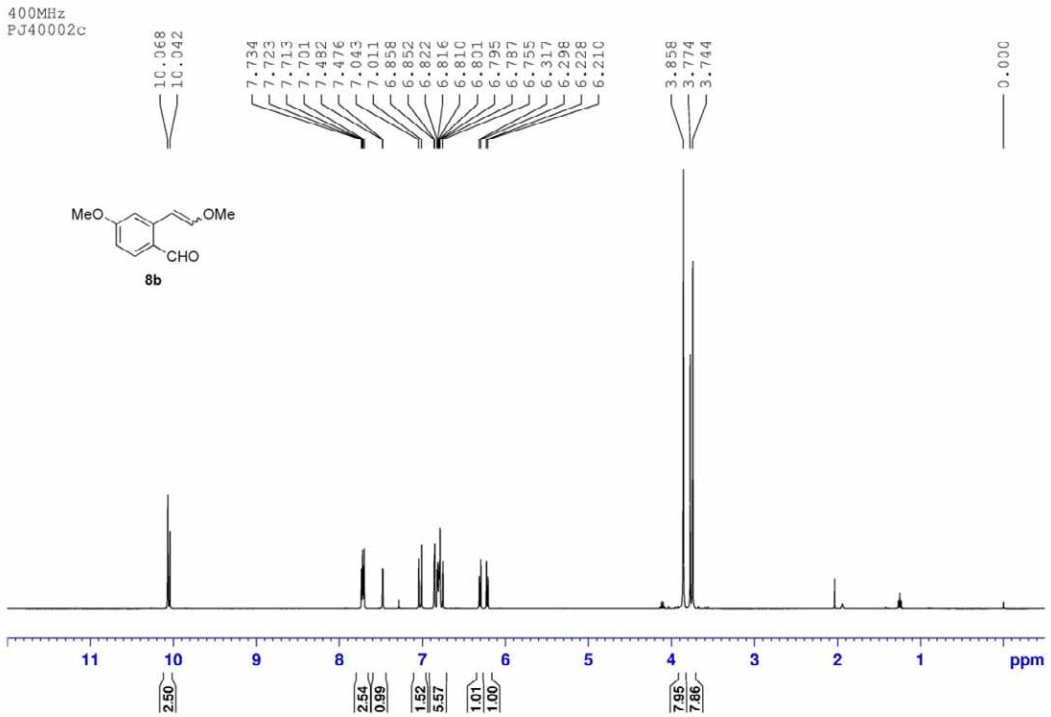
PJ40001b
159.06
158.70
150.71
149.61
137.14
135.83
133.46
132.93
115.75
113.84
113.63
113.24
113.19
111.14
104.57
103.93
77.24
61.05
56.68
55.50
55.46
MeO
OMe
Br
7b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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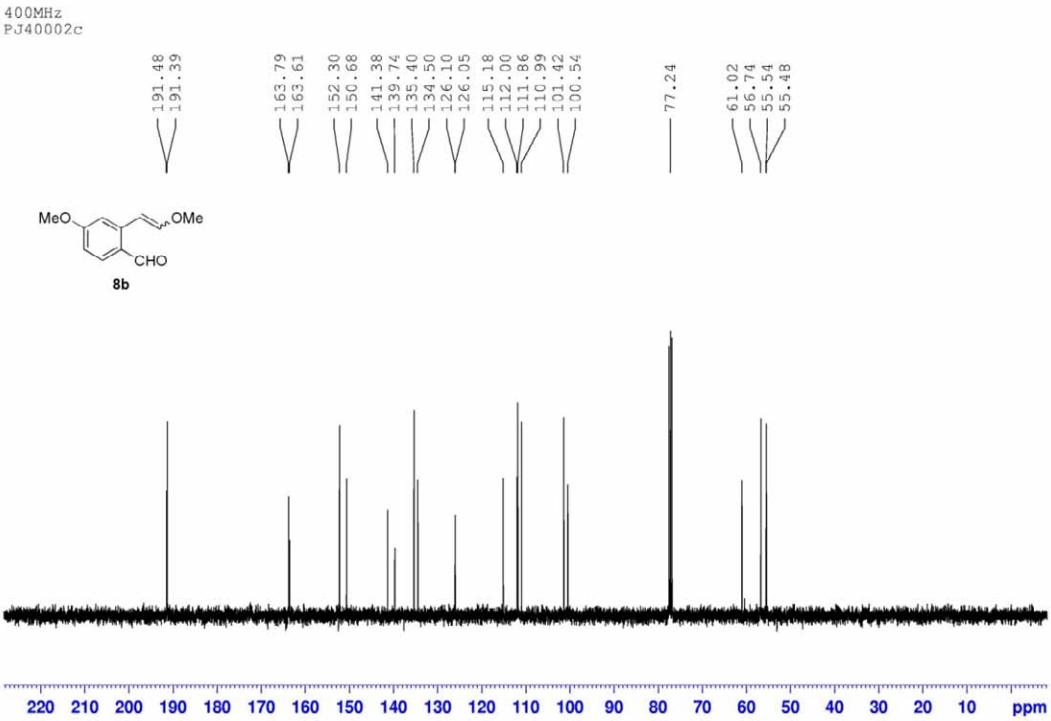
PJ40002c
10.068
10.042
7.734
7.723
7.713
7.701
7.482
7.476
7.043
7.011
6.858
6.852
6.822
6.816
6.810
6.801
6.795
6.787
6.755
6.317
6.298
6.228
6.210
3.858
3.774
3.744
0.000
MeO
OMe
CHO
8b
11
10
9
8
7
6
5
4
3
2
1
ppm
2.50
2.54
0.99
1.52
5.57
1.01
1.00
7.95
7.86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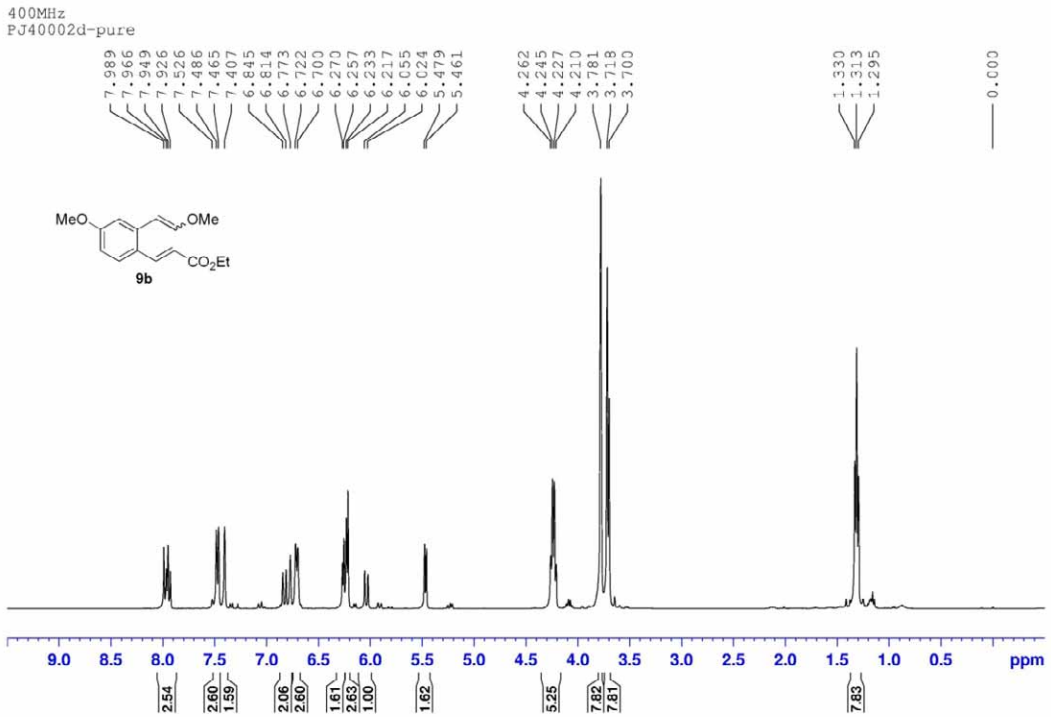
191.48
191.39
163.79
163.61
152.30
150.68
141.38
139.74
135.40
134.50
126.10
126.05
115.18
112.00
111.86
110.99
101.42
100.54
77.24
61.02
56.74
55.54
55.48
MeO
OMe
CHO
8b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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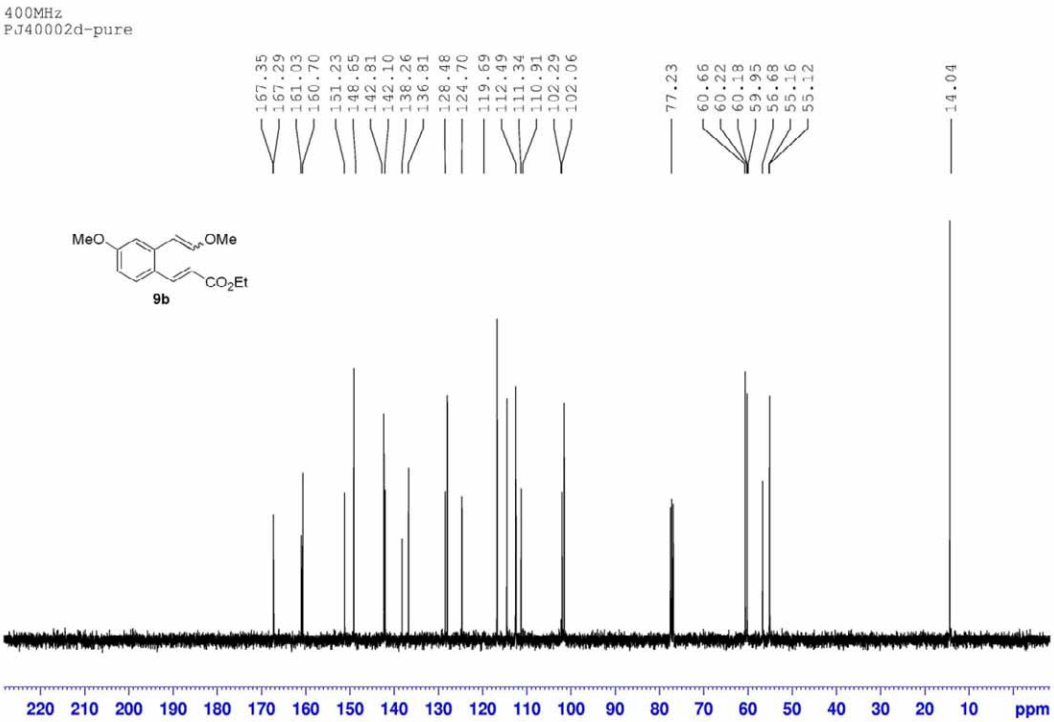
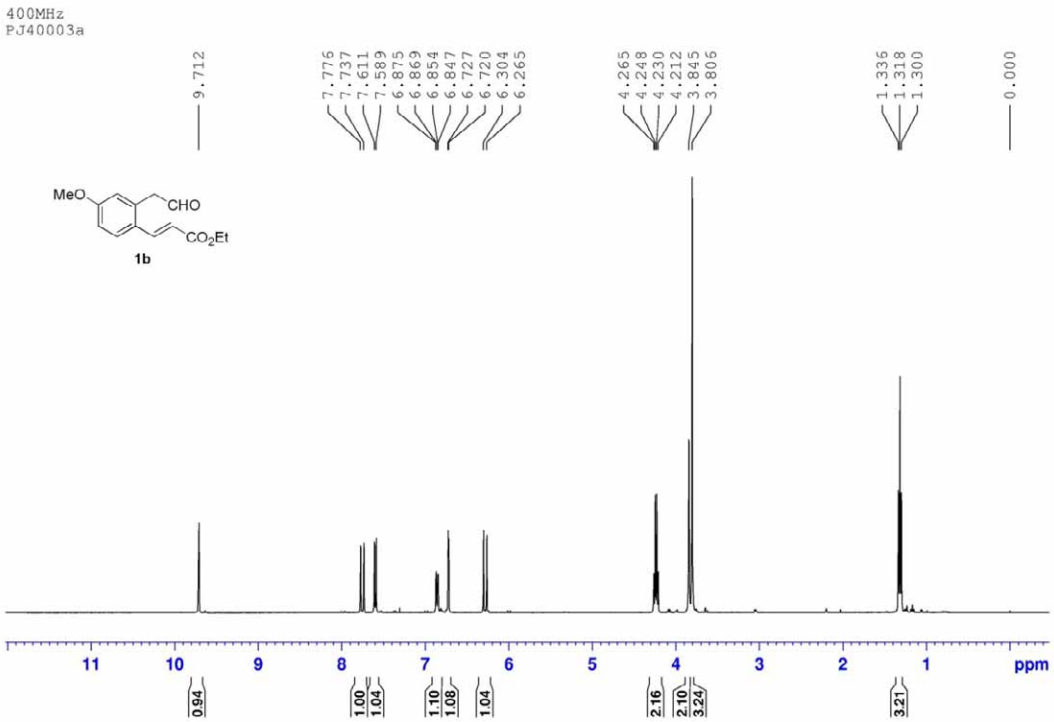
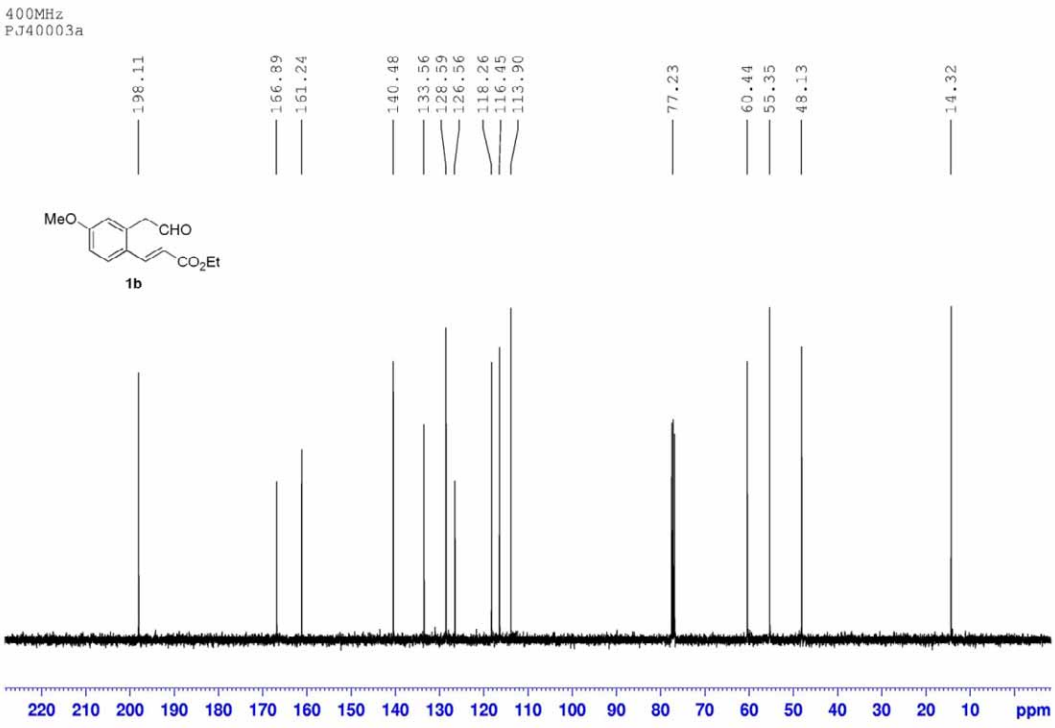
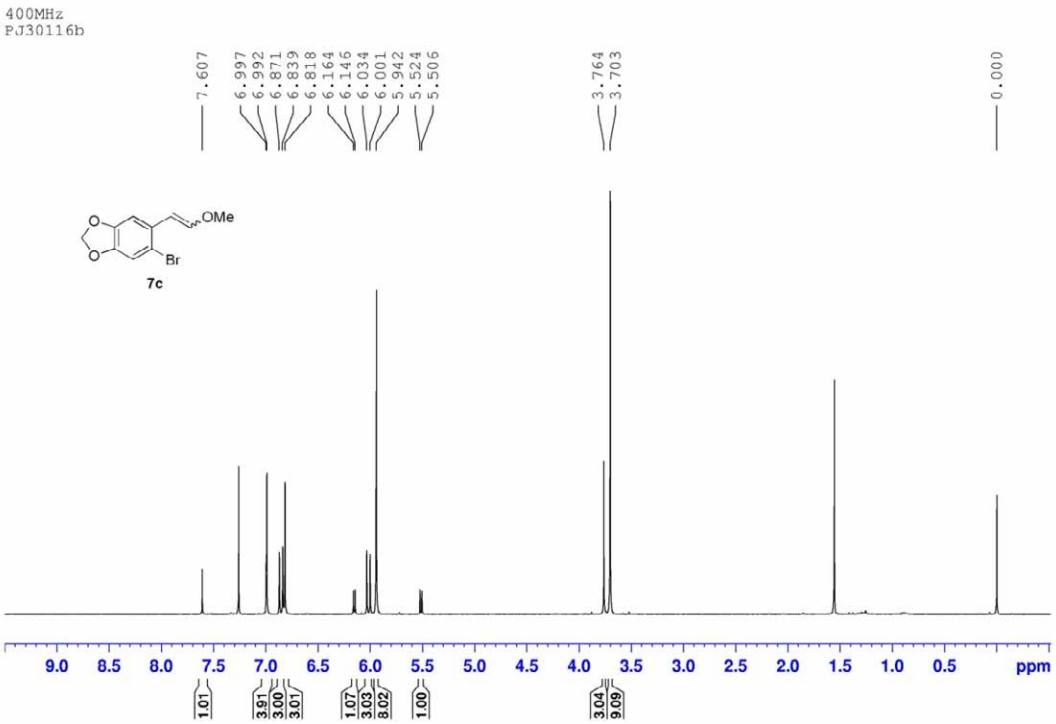
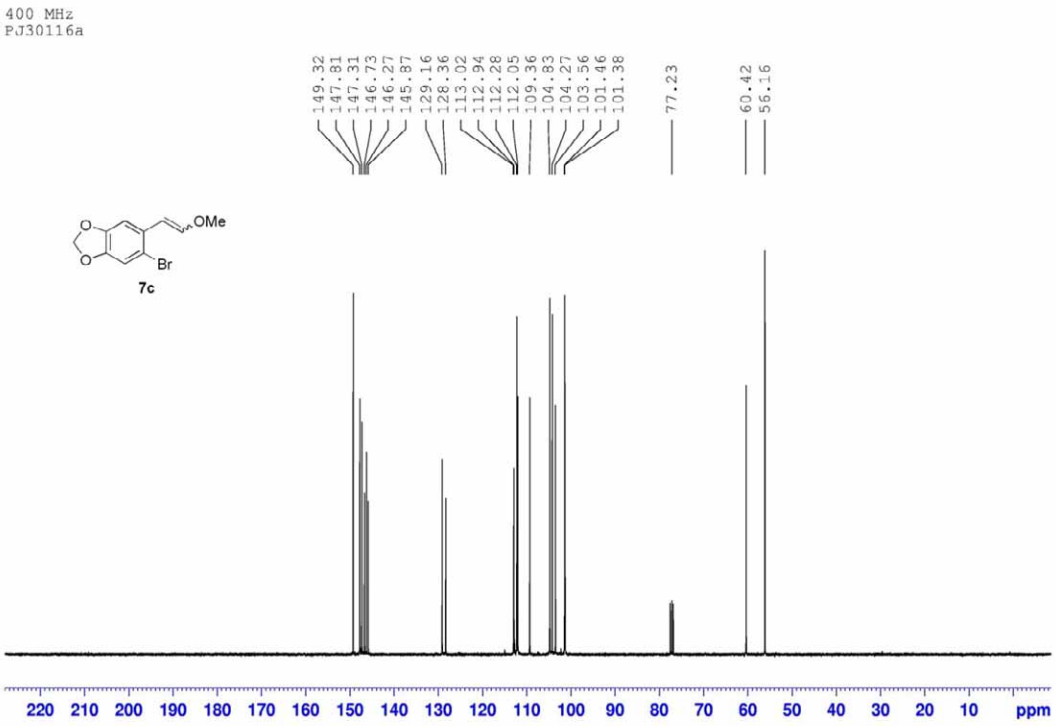
PJ40002d-pure
7.989
7.966
7.949
7.926
7.526
7.486
7.465
7.407
6.845
6.814
6.773
6.722
6.700
6.270
6.257
6.233
6.217
6.055
6.024
5.479
5.461
4.262
4.245
4.227
4.210
3.781
3.718
3.700
1.330
1.313
1.295
0.000
MeO
OMe
CO2Et
9b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.54
2.60
1.59
2.06
2.60
1.61
2.63
1.00
1.62
5.25
7.82
7.81
7.83

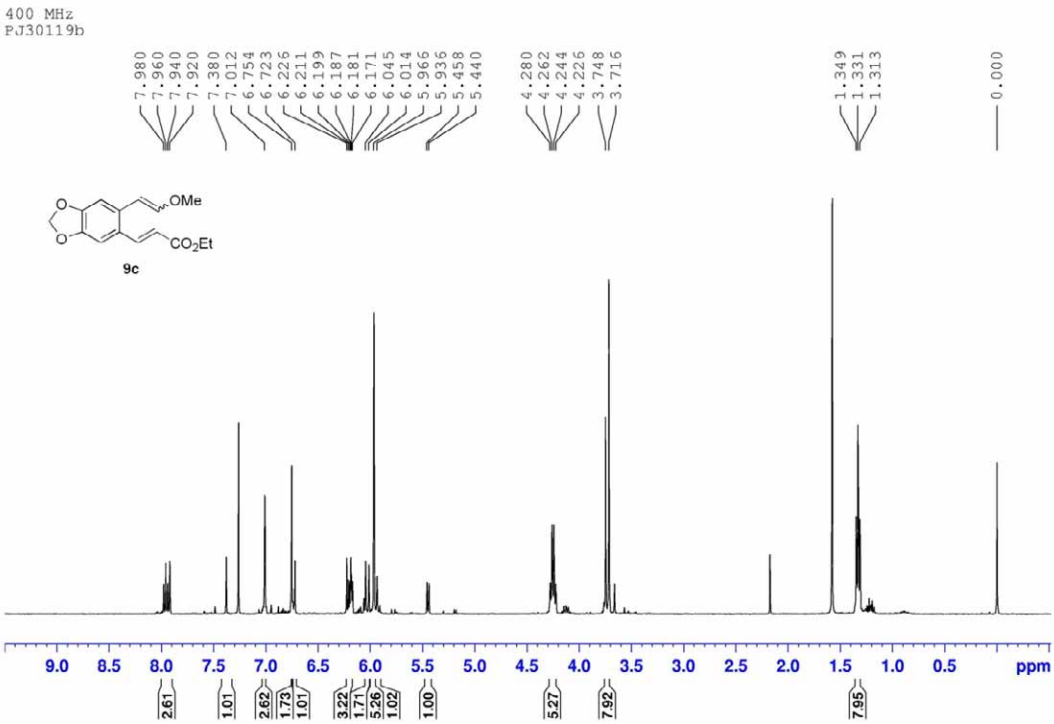

400MHz
PJ40002d-pure
167.35
167.29
161.03
160.70
151.23
148.65
142.81
142.10
138.26
136.81
128.48
124.70
119.69
112.49
111.34
110.91
102.29
102.06
77.23
60.66
60.22
60.18
59.95
56.68
55.16
55.12
14.04
MeO
OMe
CO2Et
9b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

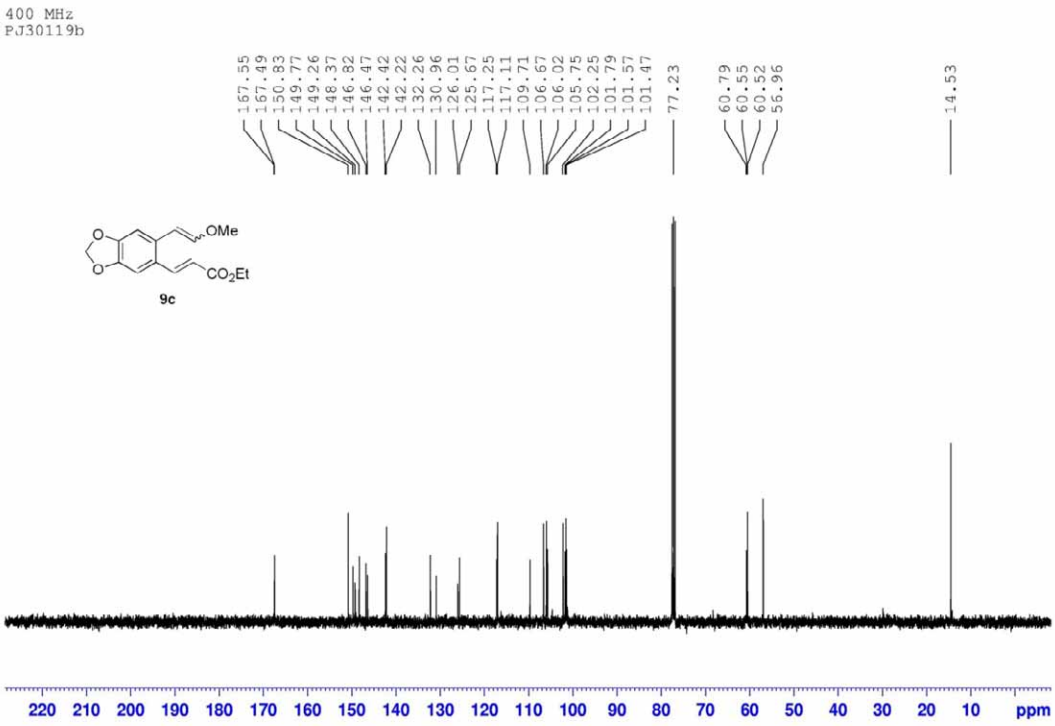

400MHz
PJ40003a
9.712
7.776
7.737
7.611
7.589
6.875
6.869
6.854
6.847
6.727
6.720
6.304
6.265
4.265
4.248
4.230
4.212
3.845
3.806
1.336
1.318
1.300
0.000
MeO
CHO
CO2Et
1b
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
1.00
1.04
1.10
1.08
1.04
2.16
2.10
3.24
3.21

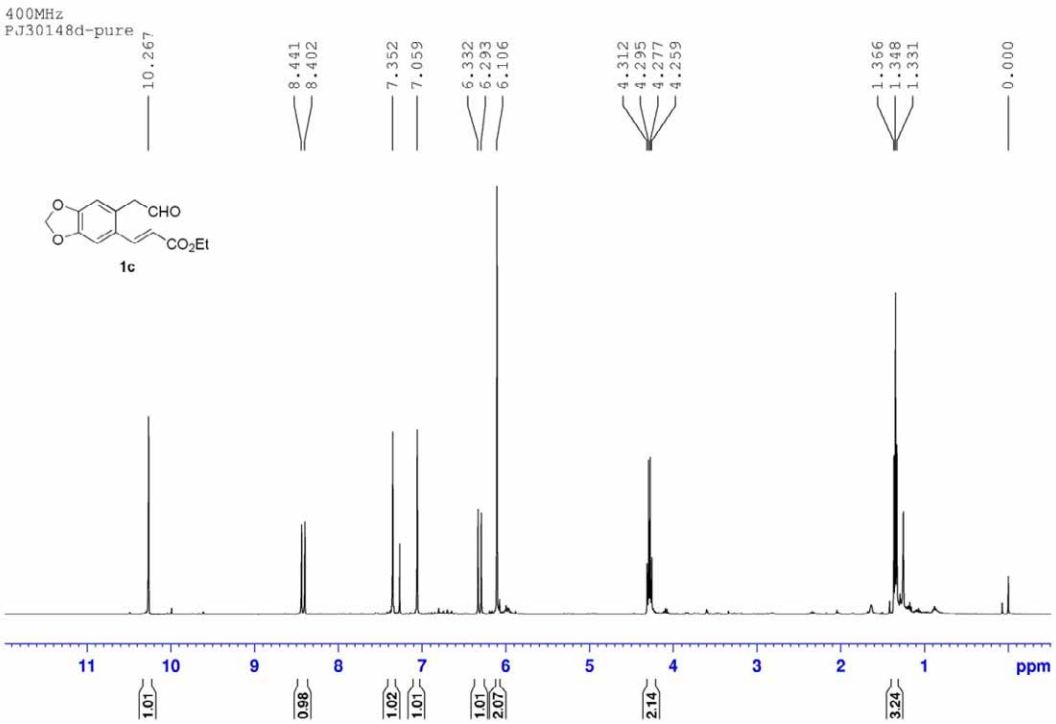

400MHz
PJ40003a
198.11
166.89
161.24
140.48
133.56
128.59
126.56
118.26
116.45
113.90
77.23
60.44
55.35
48.13
14.32
MeO
CHO
CO2Et
1b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

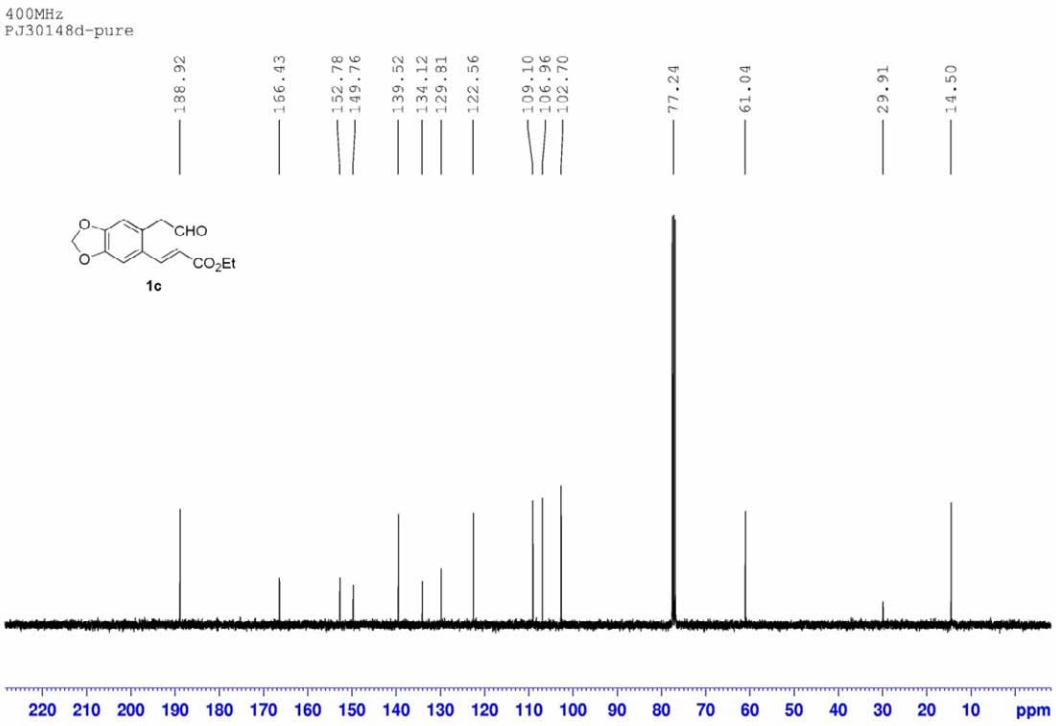

400MHz
PJ30116b
7.607
6.997
6.992
6.871
6.839
6.818
6.164
6.146
6.034
6.001
5.942
5.524
5.506
3.764
3.703
0.000
OMe
Br
7c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
3.91
3.00
3.01
1.07
3.03
8.02
1.00
3.04
9.09

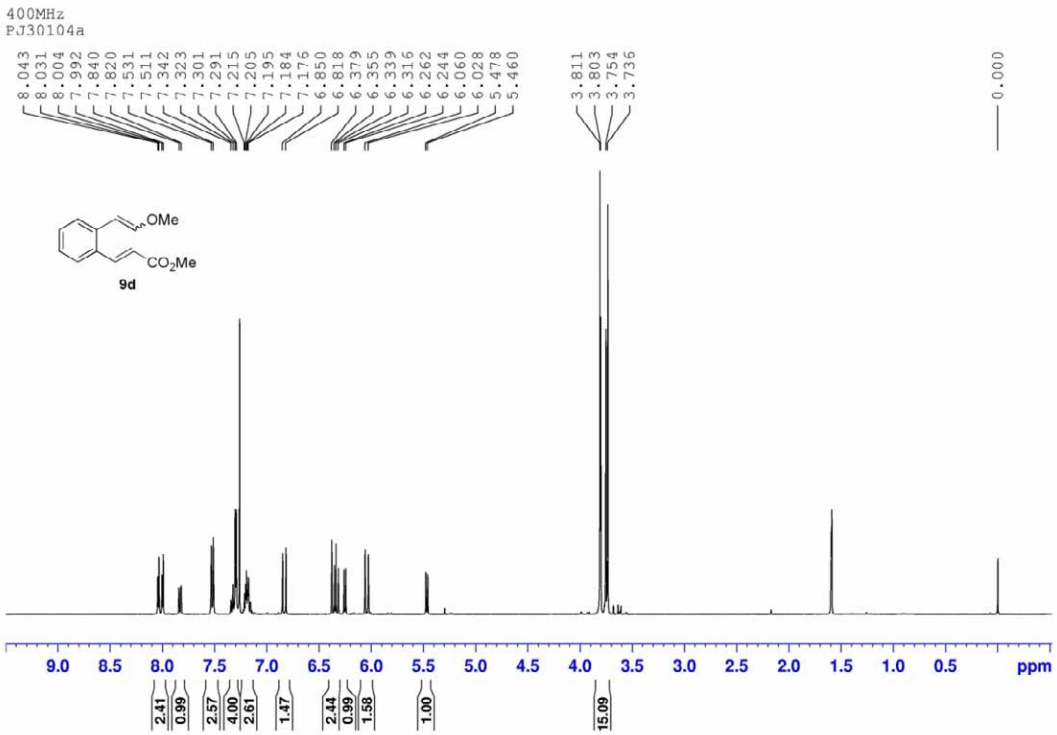

400 MHz
PJ30116a
149.32
147.81
147.31
146.73
146.27
145.87
129.16
128.36
113.02
112.94
112.28
112.05
109.36
104.83
104.27
103.56
101.46
101.38
77.23
60.42
56.16
OMe
Br
7c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

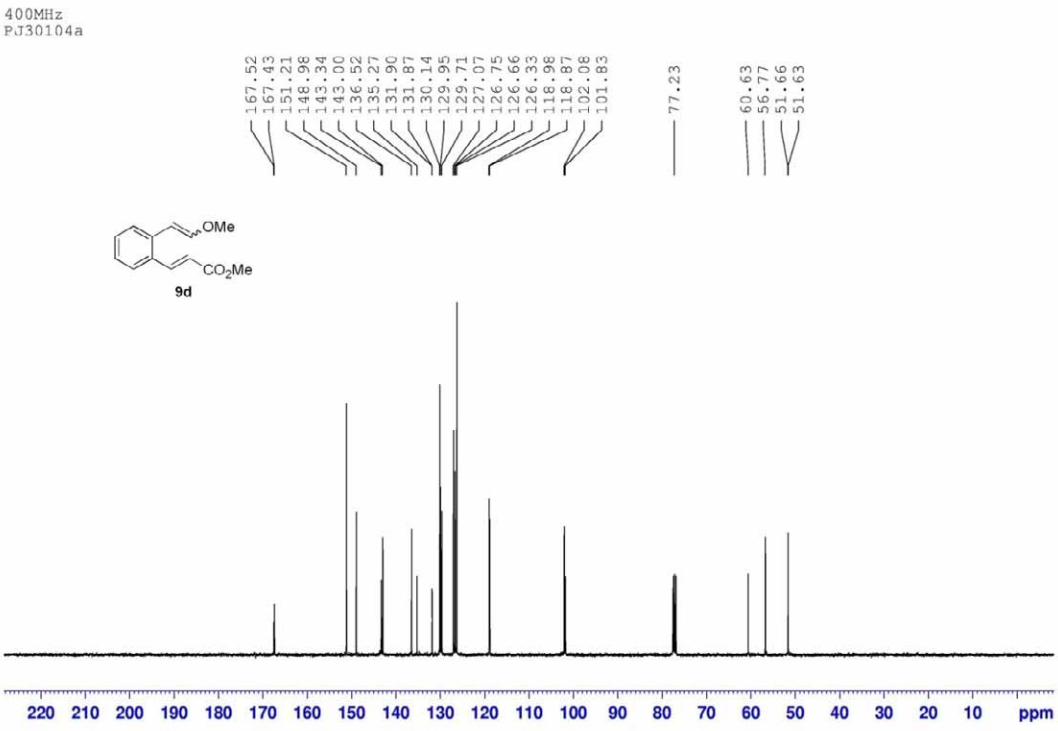

400 MHz
PJ30119b
7.980
7.960
7.940
7.920
7.380
7.012
6.754
6.723
6.226
6.211
6.199
6.187
6.181
6.171
6.045
6.014
5.966
5.936
5.458
5.440
4.280
4.262
4.244
4.226
3.748
3.716
1.349
1.331
1.313
0.000
OMe
CO2Et
9c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.61
1.01
2.62
1.73
1.01
3.22
1.71
5.26
1.02
1.00
5.27
7.92
7.95


400 MHz
PJ30119b
167.55
167.49
150.83
149.77
149.26
148.37
146.82
146.47
142.42
142.22
132.26
130.96
126.01
125.67
117.25
117.11
109.71
106.67
106.02
105.75
102.25
101.79
101.57
101.47
77.23
60.79
60.55
60.52
56.96
14.53
OMe
CO2Et
9c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
PJ30148d-pure
10.267
8.441
8.402
7.352
7.059
6.332
6.293
6.106
4.312
4.295
4.277
4.259
1.366
1.348
1.331
0.000
CHO
CO2Et
1c
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
0.98
1.02
1.01
1.01
2.07
2.14
3.24


400MHz
PJ30148d-pure
188.92
166.43
152.78
149.76
139.52
134.12
129.81
122.56
109.10
106.96
102.70
77.24
61.04
29.91
14.50
CHO
CO2Et
1c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
PJ30104a
8.043
8.031
8.004
7.992
7.840
7.820
7.531
7.511
7.342
7.323
7.301
7.291
7.215
7.205
7.195
7.184
7.176
6.850
6.818
6.379
6.355
6.339
6.316
6.262
6.244
6.060
6.028
5.478
5.460
3.811
3.803
3.754
3.736
0.000
OMe
CO2Me
9d
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
ppm
2.41
0.99
2.57
4.00
2.61
1.47
2.44
0.99
1.58
1.00
15.09


400MHz
PJ30104a
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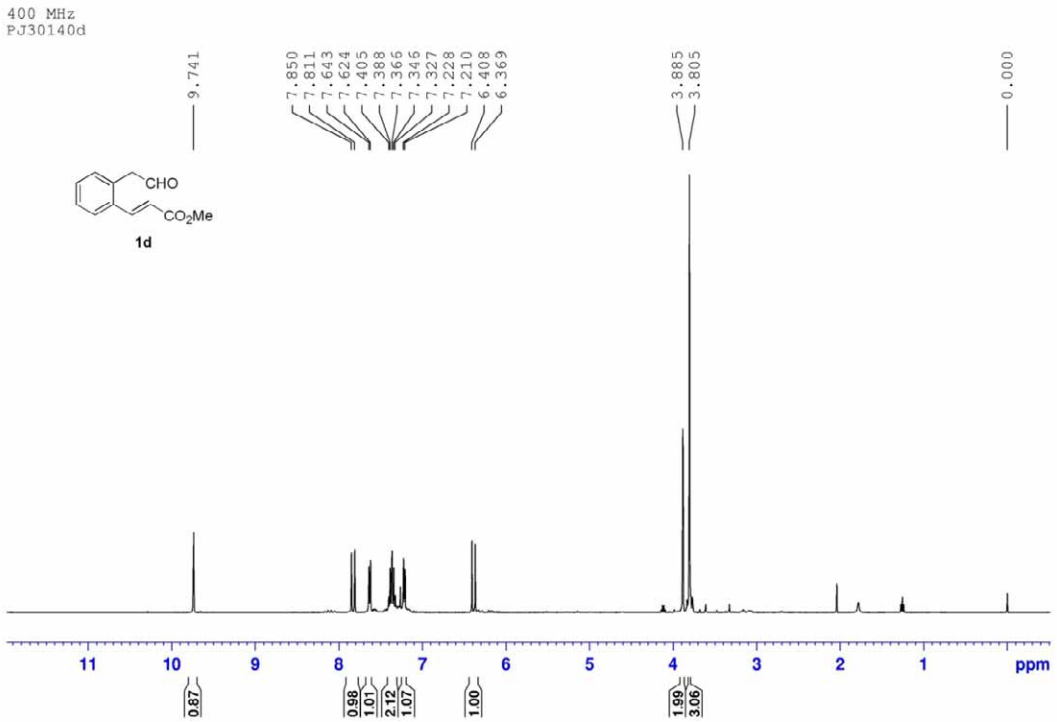
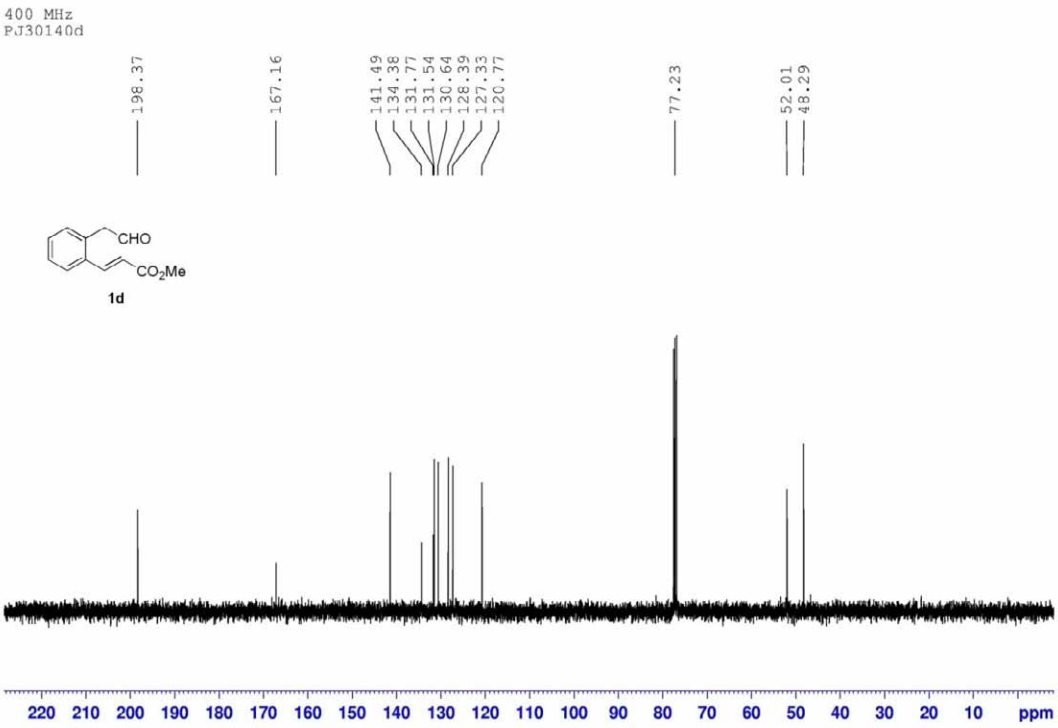
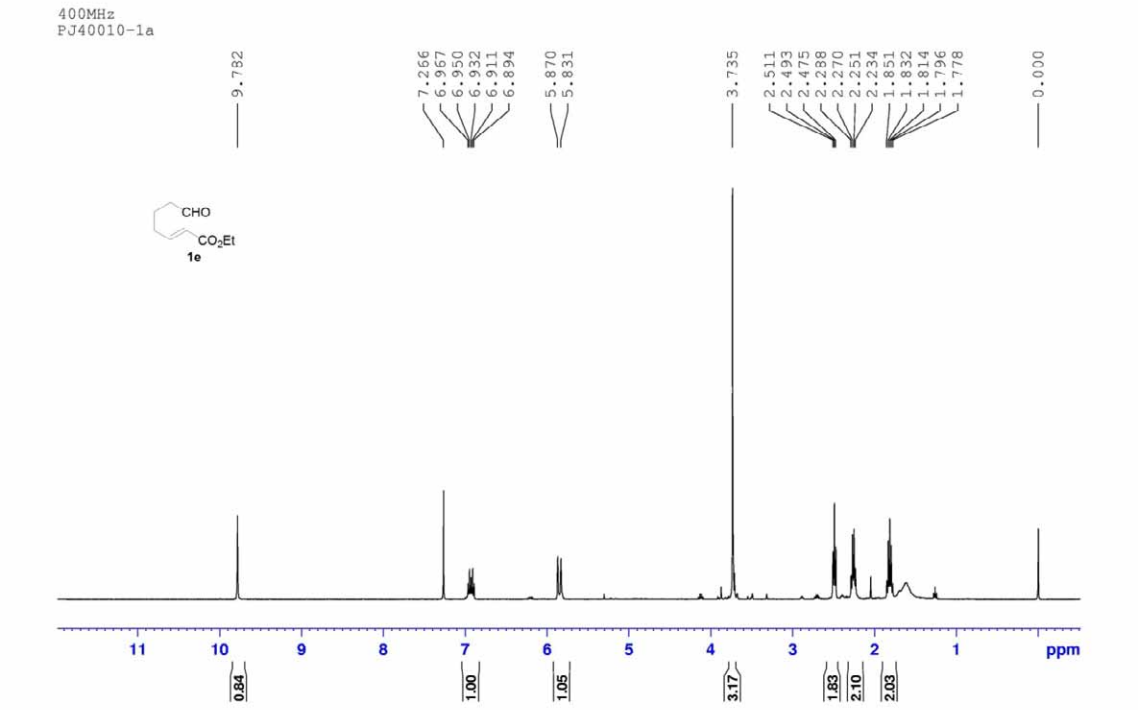
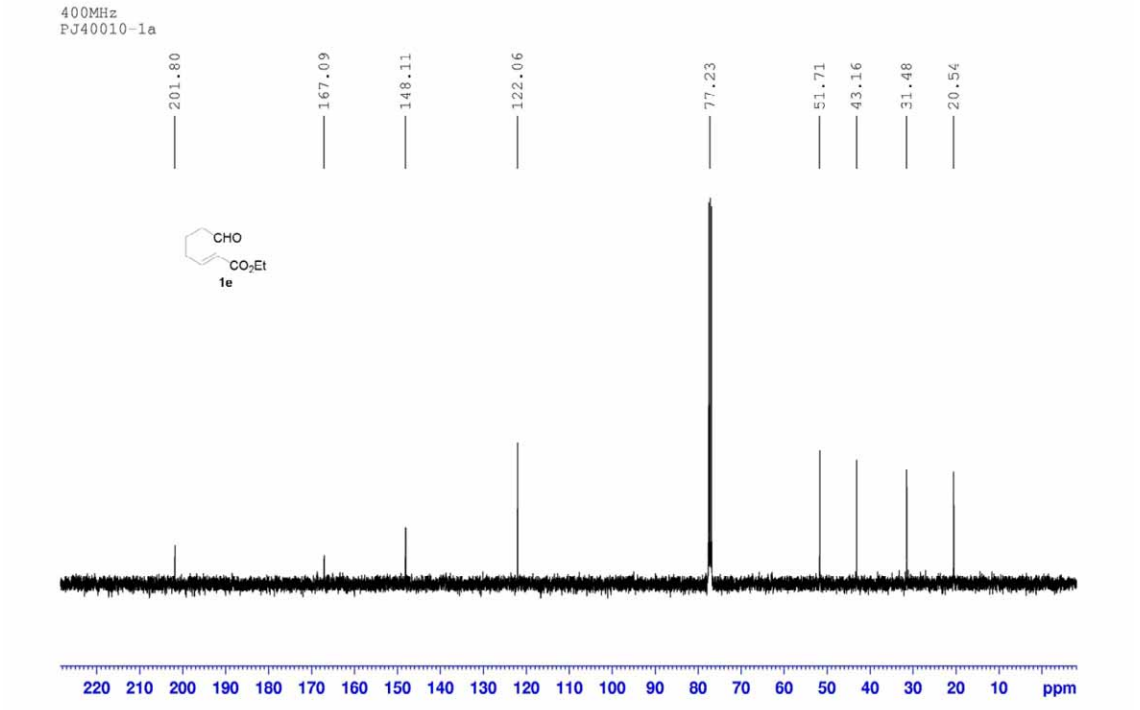
167.43
151.21
148.98
143.34
143.00
136.52
135.27
131.90
131.87
130.14
129.95
129.71
127.07
126.75
126.66
126.33
118.98
118.87
102.08
101.83
77.23
60.63
56.77
51.66
51.63
OMe
CO2Me
9d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

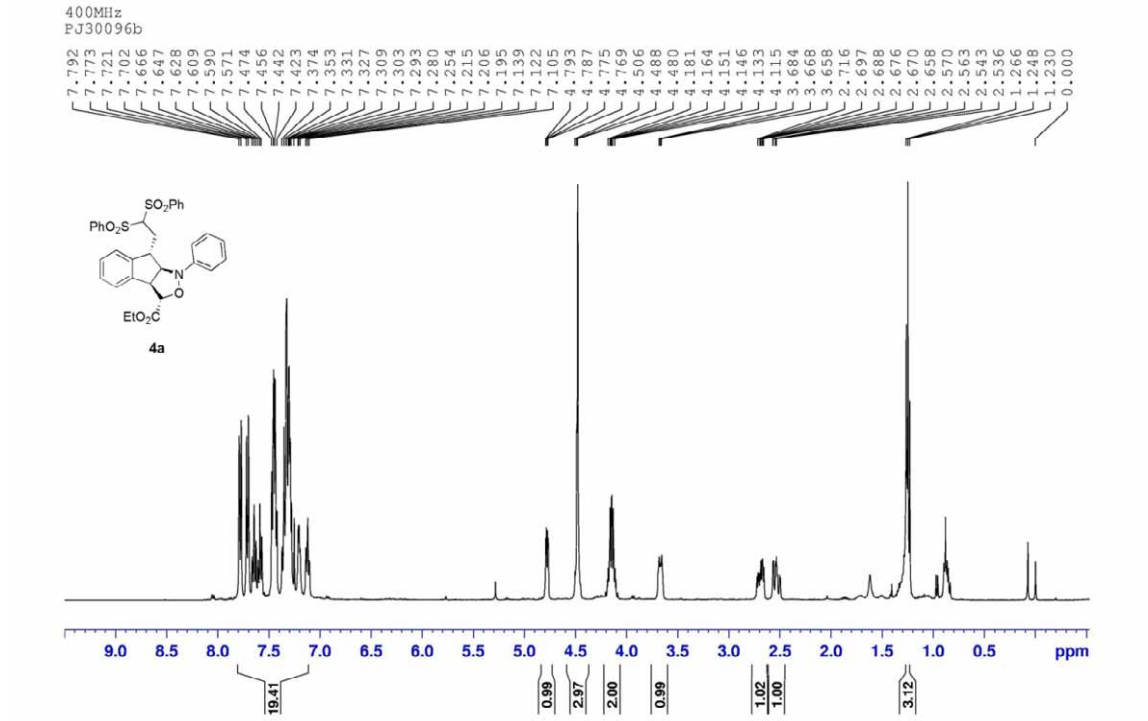

400 MHz
PJ30140d
9.741
7.850
7.811
7.643
7.624
7.405
7.388
7.366
7.346
7.327
7.228
7.210
6.408
6.369
3.885
3.805
0.000
CHO
CO2Me
1d
11
10
9
8
7
6
5
4
3
2
1
ppm
0.87
0.98
1.01
2.12
1.07
1.00
1.99
3.06

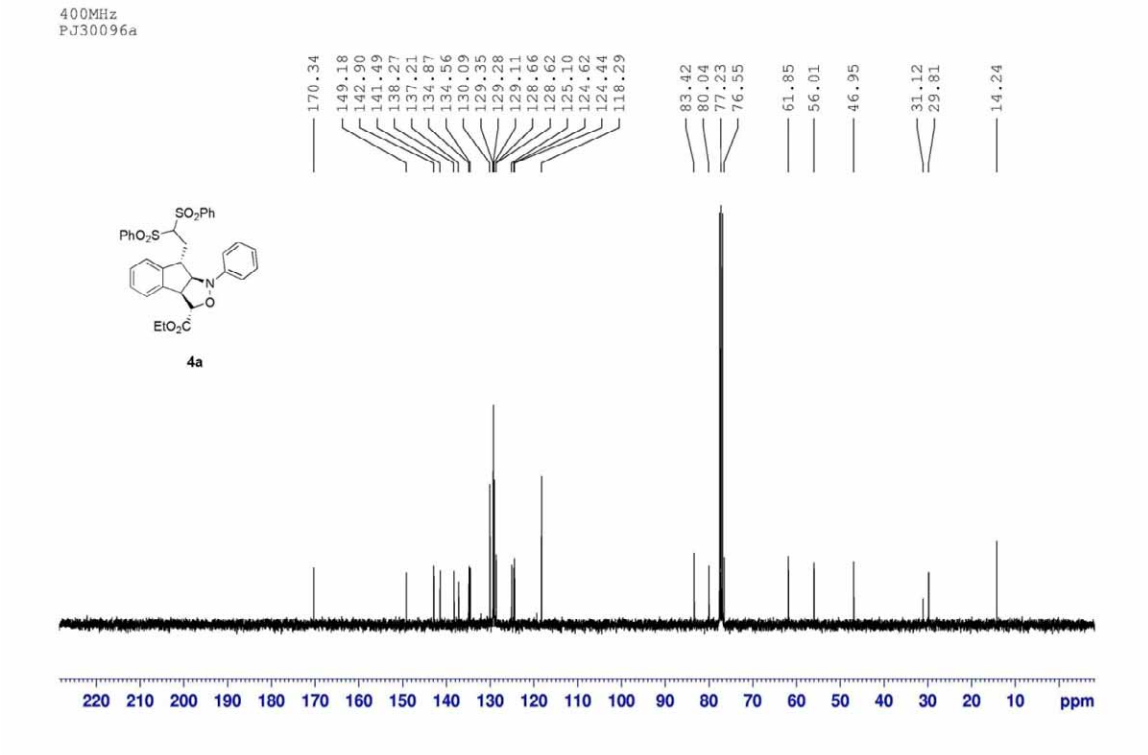

400 MHz
PJ30140d
198.37
167.16
141.49
134.38
131.77
131.54
130.64
128.39
127.33
120.77
77.23
52.01
48.29
CHO
CO2Me
1d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

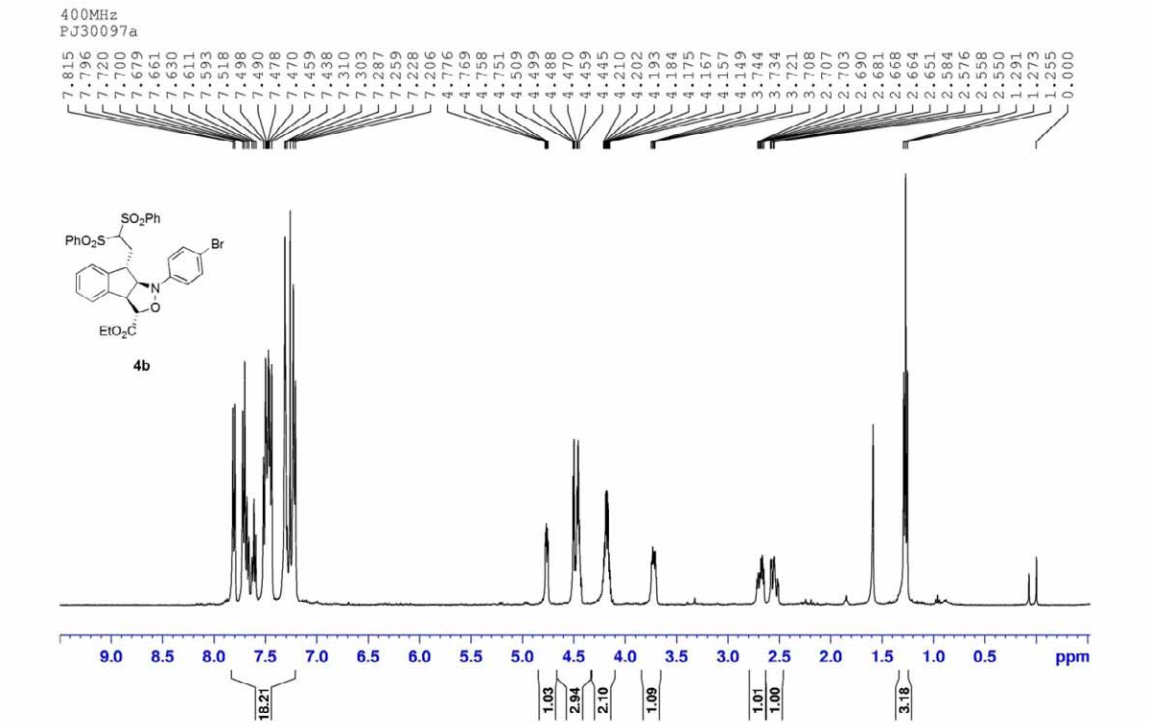

400MHz
PJ40010-1a
9.782
7.266
6.967
6.950
6.932
6.911
6.894
5.870
5.831
3.735
2.511
2.493
2.475
2.288
2.270
2.251
2.234
1.851
1.832
1.814
1.796
1.778
0.000
CHO
CO2Et
1e
11
10
9
8
7
6
5
4
3
2
1
ppm
0.84
1.00
1.05
3.17
1.83
2.10
2.03


400MHz
PJ40010-1a
201.80
167.09
148.11
122.06
77.23
51.71
43.16
31.48
20.54
CHO
CO2Et
1e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

# $^{1}$H and $^{13}$C NMR Spectra of Compounds 4a-4k




400MHz
PJ30097a
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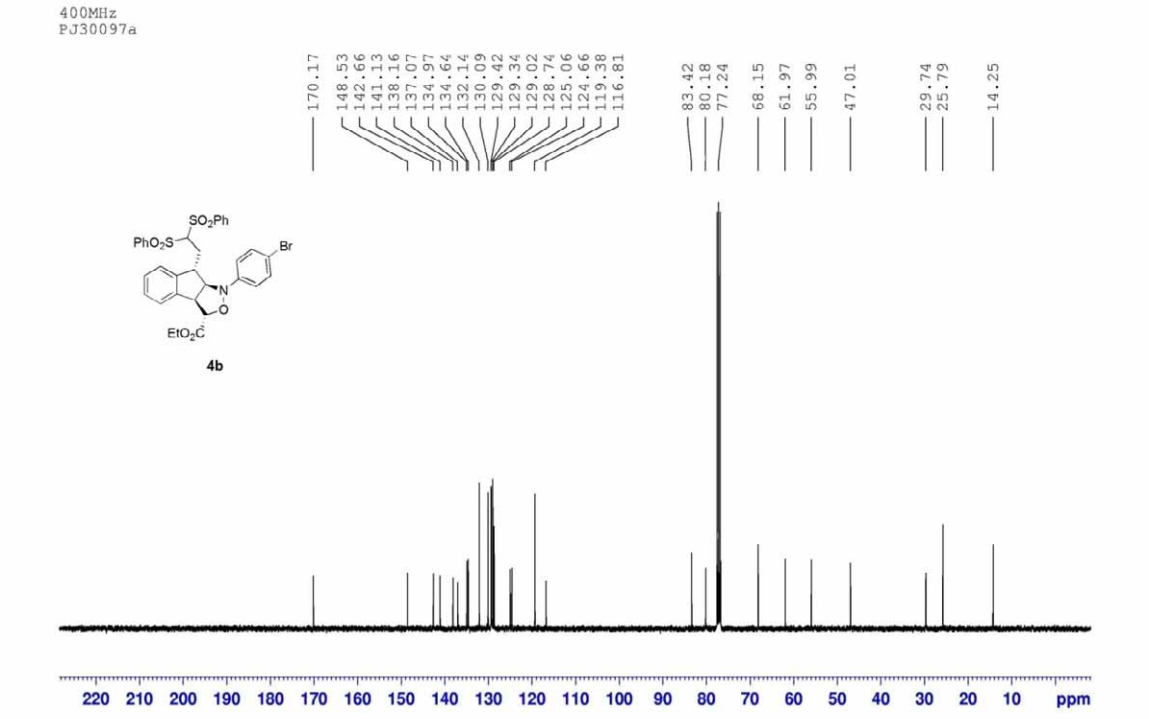
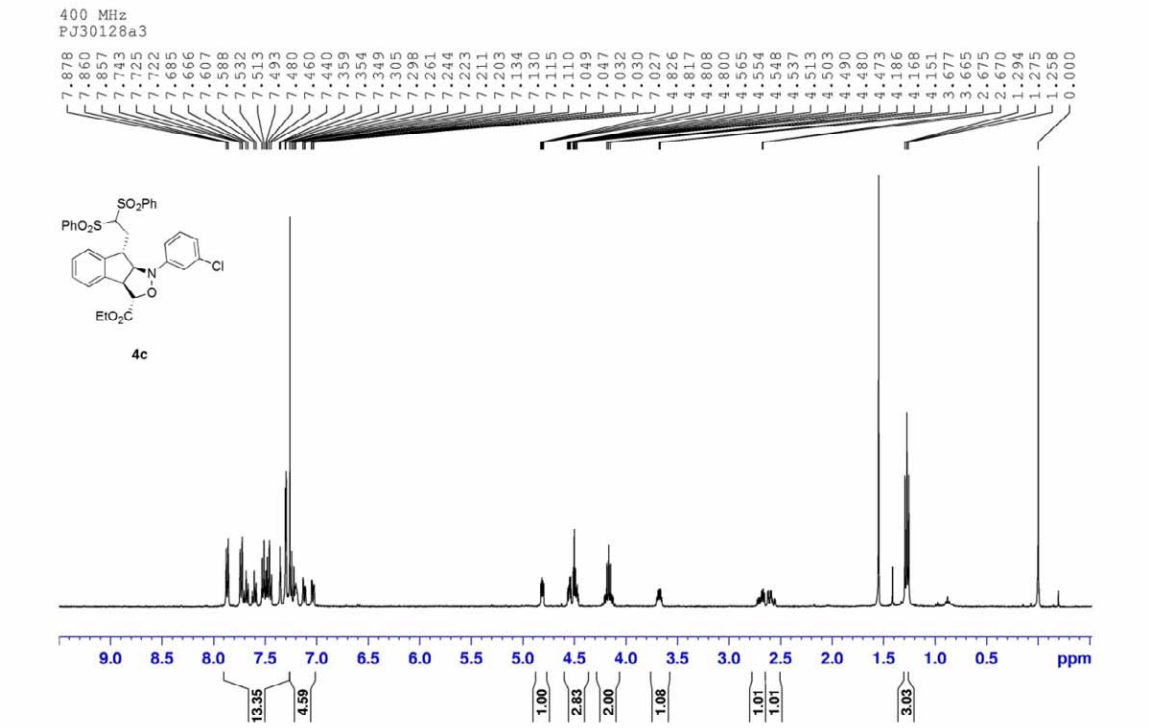
7.796
7.720
7.700
7.679
7.661
7.630
7.611
7.593
7.518
7.498
7.490
7.478
7.470
7.459
7.438
7.310
7.303
7.287
7.259
7.228
7.206
4.776
4.769
4.758
4.751
4.509
4.499
4.488
4.470
4.459
4.445
4.210
4.202
4.193
4.184
4.175
4.167
4.157
4.149
3.744
3.734
3.721
3.708
2.707
2.703
2.690
2.681
2.668
2.664
2.651
2.584
2.576
2.558
2.550
1.291
1.273
1.255
0.000
SO2Ph
PhO2S
Br
N
O
EtO2C
4b
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
ppm
18.21
1.03
2.94
2.10
1.09
1.01
1.00
3.18


400MHz
PJ30097a
170.17
148.53
142.66
141.13
138.16
137.07
134.97
134.64
132.14
130.09
129.42
129.34
129.02
128.74
125.06
124.66
119.38
116.81
83.42
80.18
77.24
68.15
61.97
55.99
47.01
29.74
25.79
14.25
SO2Ph
PhO2S
Br
N
O
EtO2C
4b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400 MHz
PJ30128a3
7.878
7.860
7.857
7.743
7.725
7.722
7.685
7.666
7.607
7.588
7.532
7.513
7.493
7.480
7.460
7.440
7.359
7.354
7.349
7.305
7.298
7.261
7.244
7.223
7.211
7.203
7.134
7.130
7.115
7.110
7.049
7.047
7.032
7.030
7.027
4.826
4.817
4.808
4.800
4.565
4.554
4.548
4.537
4.513
4.503
4.490
4.480
4.473
4.186
4.168
4.151
3.677
3.665
2.675
2.670
1.294
1.275
1.258
0.000
SO2Ph
PhO2S
Cl
N
O
EtO2C
4c
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
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ppm
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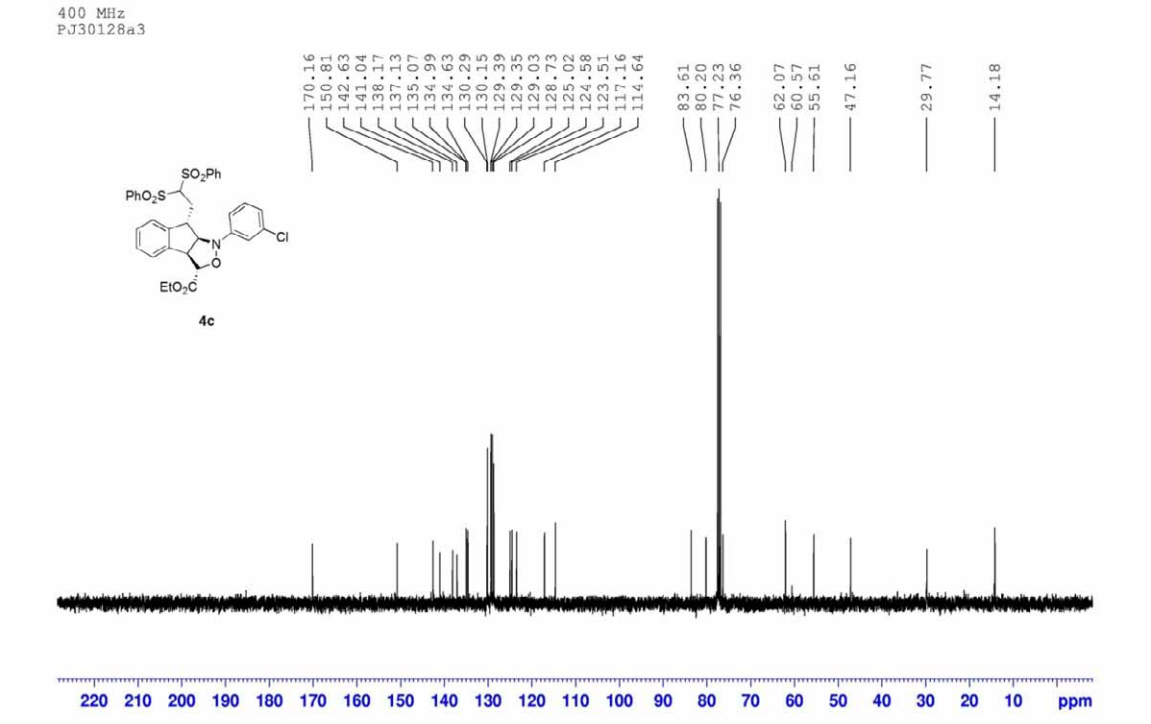
2.83
2.00
1.08
1.01
1.01
3.03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PJ30128a3
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141.04
138.17
137.13
135.07
134.99
134.63
130.29
130.15
129.39
129.35
129.03
128.73
125.02
124.58
123.51
117.16
114.64
83.61
80.20
77.23
76.36
62.07
60.57
55.61
47.16
29.77
14.18
SO2Ph
PhO2S
Cl
N
O
EtO2C
4c
220
210
200
190
180
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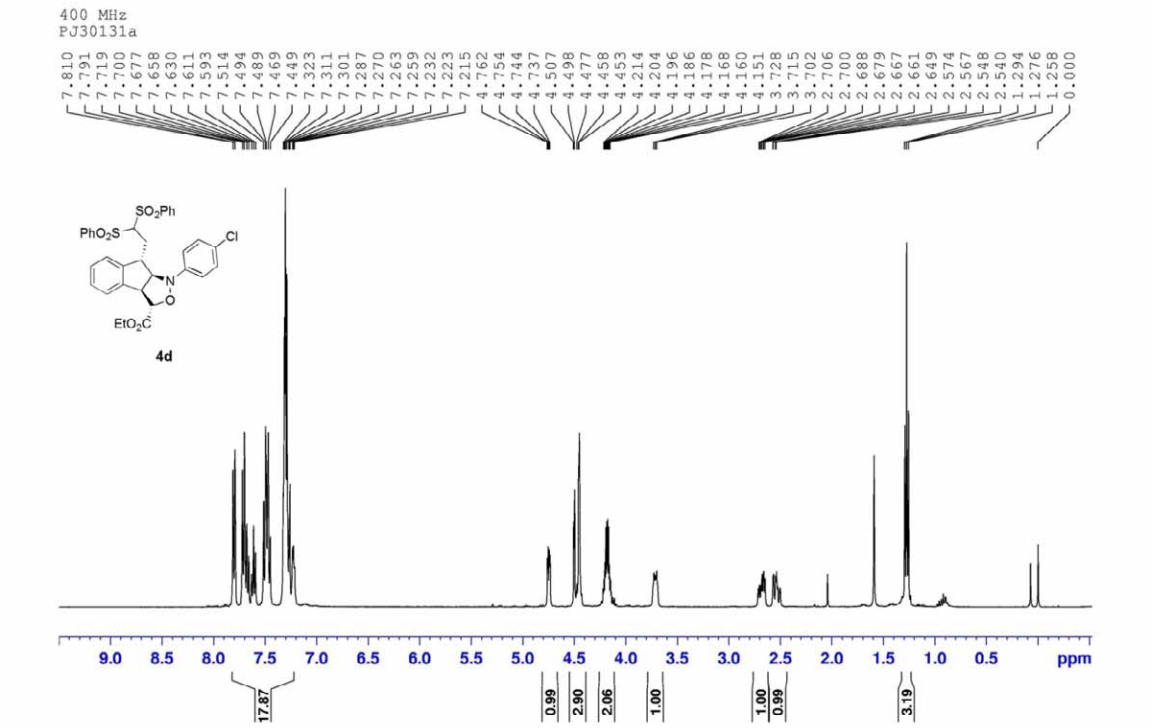
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.791
7.719
7.700
7.677
7.658
7.630
7.611
7.593
7.514
7.494
7.489
7.469
7.449
7.323
7.311
7.301
7.287
7.270
7.263
7.259
7.232
7.223
7.215
4.762
4.754
4.744
4.737
4.507
4.498
4.477
4.458
4.453
4.214
4.204
4.196
4.186
4.178
4.168
4.160
4.151
3.728
3.715
3.702
2.706
2.700
2.688
2.679
2.667
2.661
2.649
2.574
2.567
2.548
2.540
1.294
1.276
1.258
0.000
SO2Ph
PhO2S
Cl
N
O
EtO2C
4d
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
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1.0
0.5
ppm
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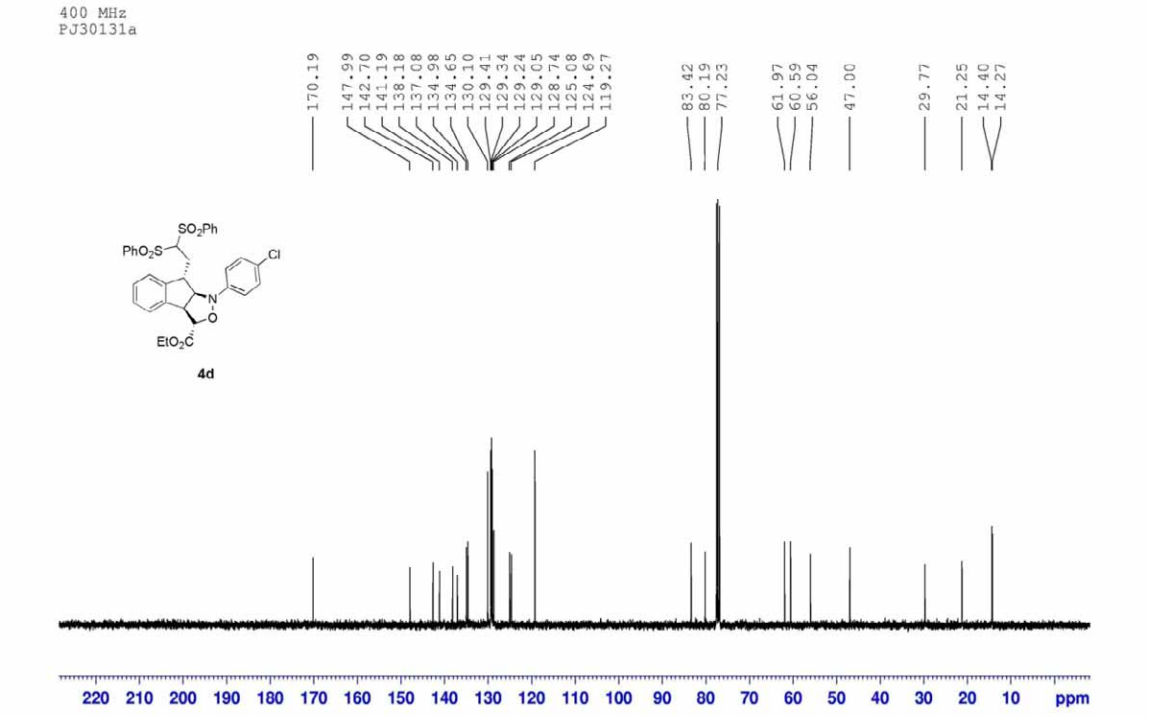
2.06
1.00
1.00
0.99
3.19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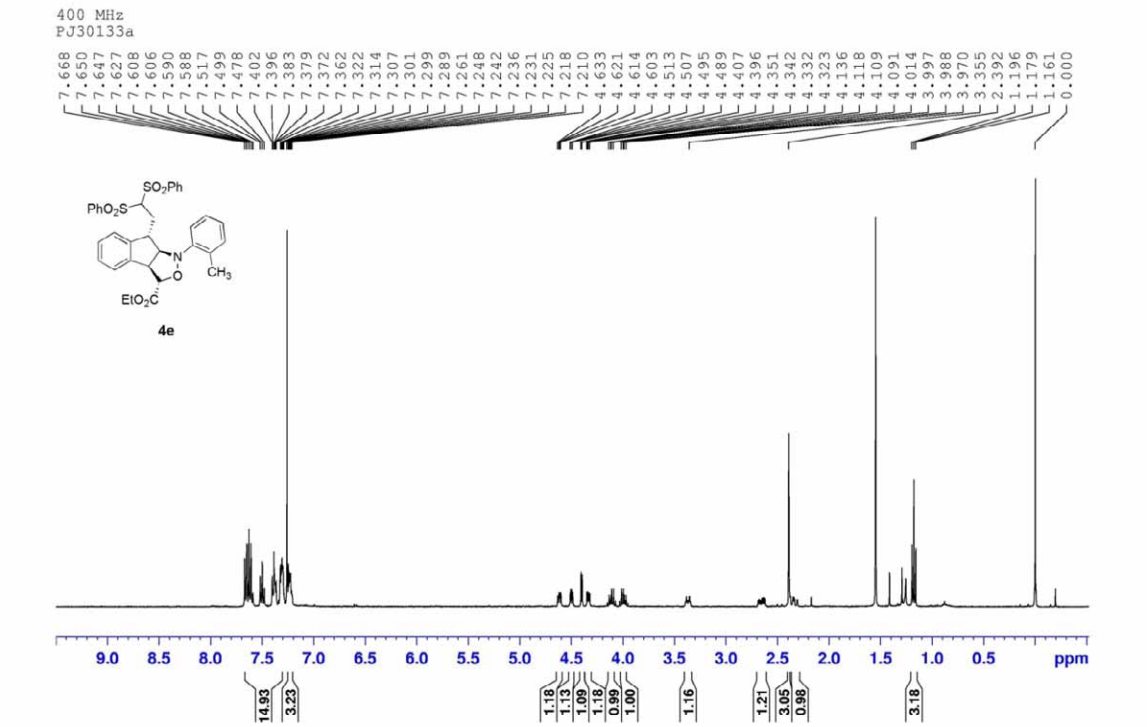
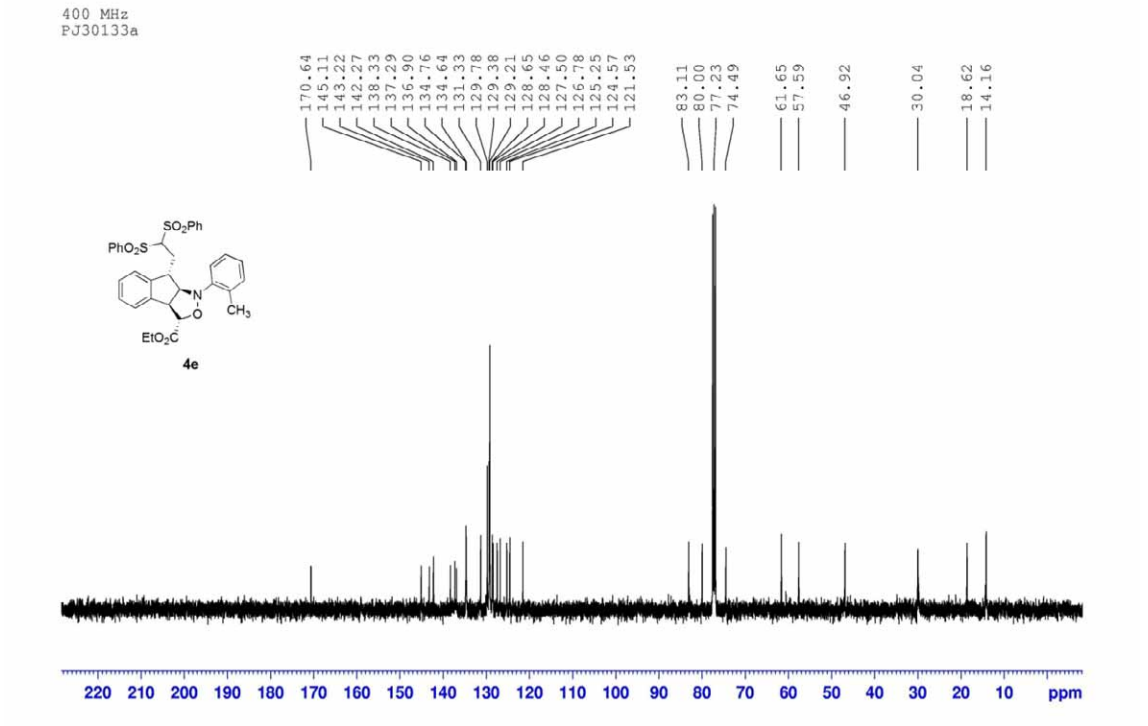
147.99
142.70
141.19
138.18
137.08
134.98
134.65
130.10
129.41
129.34
129.24
129.05
128.74
125.08
124.69
119.27
83.42
80.19
77.23
61.97
60.59
56.04
47.00
29.77
21.25
14.40
14.27
SO2Ph
PhO2S
Cl
N
O
EtO2C
4d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400 MHz
PJ30133a
7.668
7.650
7.647
7.627
7.608
7.606
7.590
7.588
7.517
7.499
7.478
7.402
7.396
7.383
7.379
7.372
7.362
7.322
7.314
7.307
7.301
7.299
7.289
7.261
7.248
7.242
7.236
7.231
7.225
7.218
7.210
4.633
4.621
4.614
4.603
4.513
4.507
4.495
4.489
4.407
4.396
4.351
4.342
4.332
4.323
4.136
4.118
4.109
4.091
4.014
3.997
3.988
3.970
3.355
2.392
1.196
1.179
1.161
0.000
SO2Ph
PhO2S
N
O
CH3
EtO2C
4e
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
ppm
14.93
3.23
1.18
1.13
1.09
1.18
0.99
1.00
1.16
1.21
3.05
0.98
3.18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145.11
143.22
142.27
138.33
137.29
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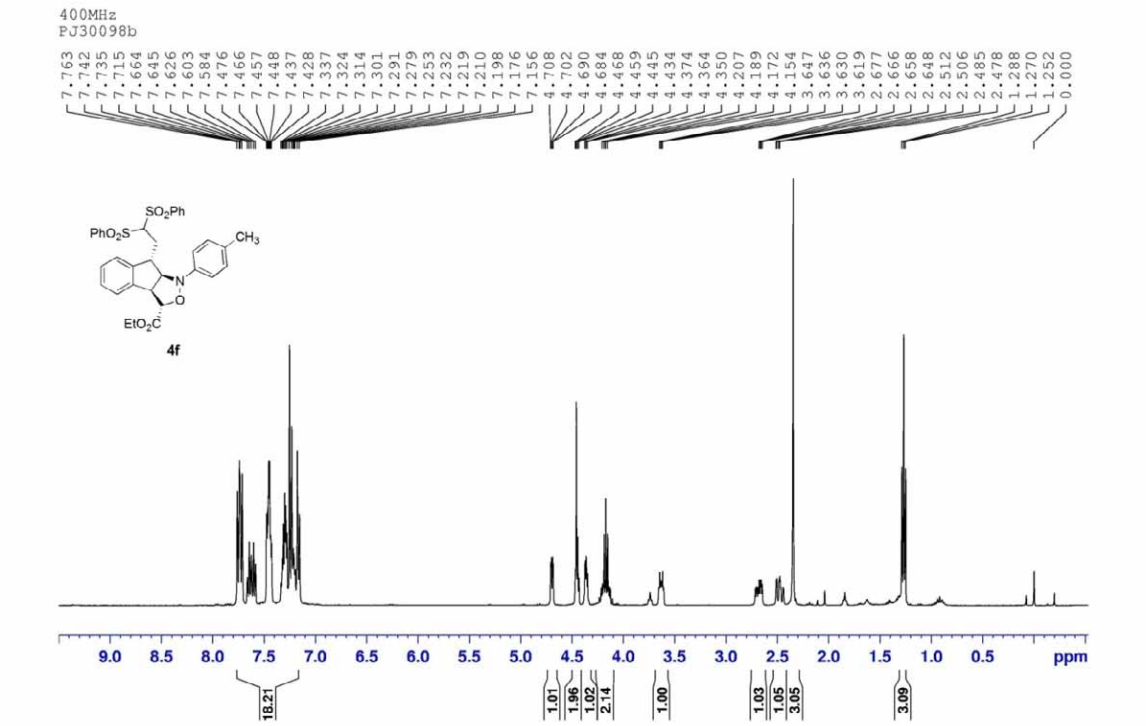
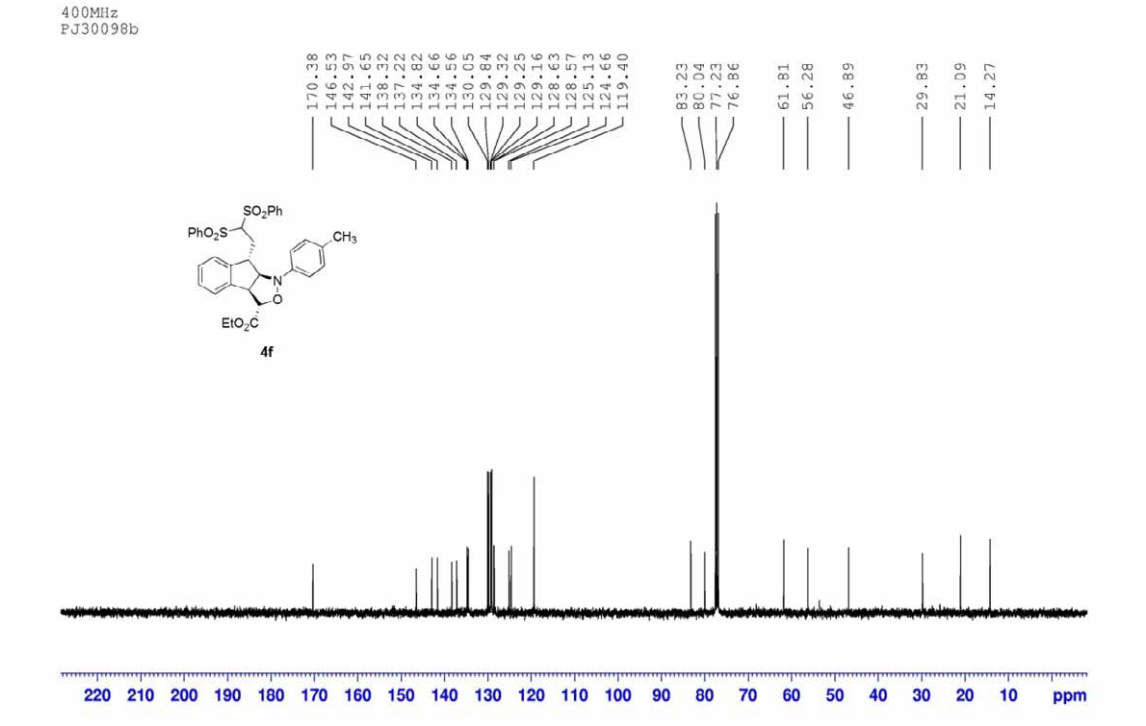
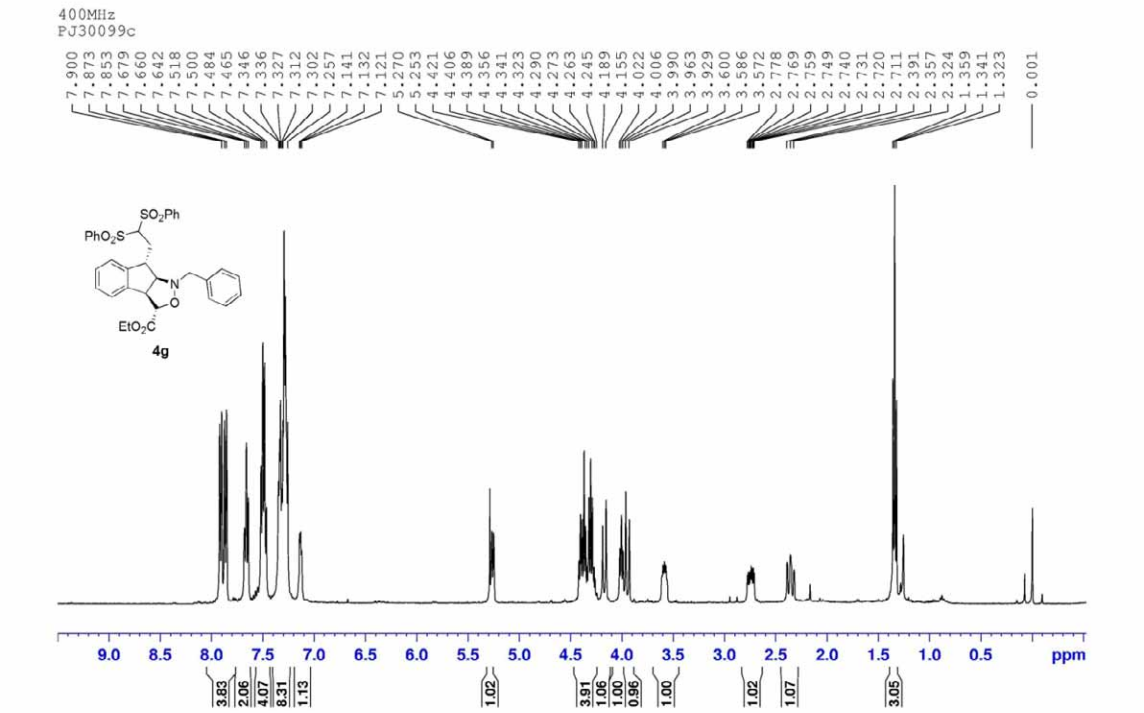
134.76
134.64
131.33
129.78
129.38
129.21
128.65
128.46
127.50
126.78
125.25
124.57
121.53
83.11
80.00
77.23
74.49
61.65
57.59
46.92
30.04
18.62
14.16
SO2Ph
PhO2S
N
O
CH3
EtO2C
4e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
PJ30098b
7.763 7.742 7.735 7.715 7.664 7.645 7.626 7.603 7.584 7.476 7.466 7.457 7.448 7.437 7.428 7.337 7.324 7.314 7.301 7.291 7.279 7.253 7.232 7.219 7.210 7.198 7.176 7.156
4.708 4.702 4.690 4.684 4.468 4.459 4.445 4.434 4.374 4.364 4.350 4.207 4.189 4.172 4.154 3.647 3.636 3.630 3.619 2.677 2.666 2.658 2.648 2.512 2.506 2.485 2.478 1.288 1.270 1.252 0.000
SO2Ph
PhO2S
CH3
N
O
EtO2C
4f
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 ppm
18.21
1.01
1.96
1.02
2.14
1.00
1.03
1.05
3.05
3.09


400MHz
PJ30098b
170.38 146.53 142.97 141.65 138.32 137.22 134.82 134.66 134.56 130.05 129.84 129.32 129.25 129.16 128.63 128.57 125.13 124.66 119.40
83.23 80.04 77.23 76.86
61.81 56.28 46.89 29.83 21.09 14.27
SO2Ph
PhO2S
CH3
N
O
EtO2C
4f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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PJ30099c
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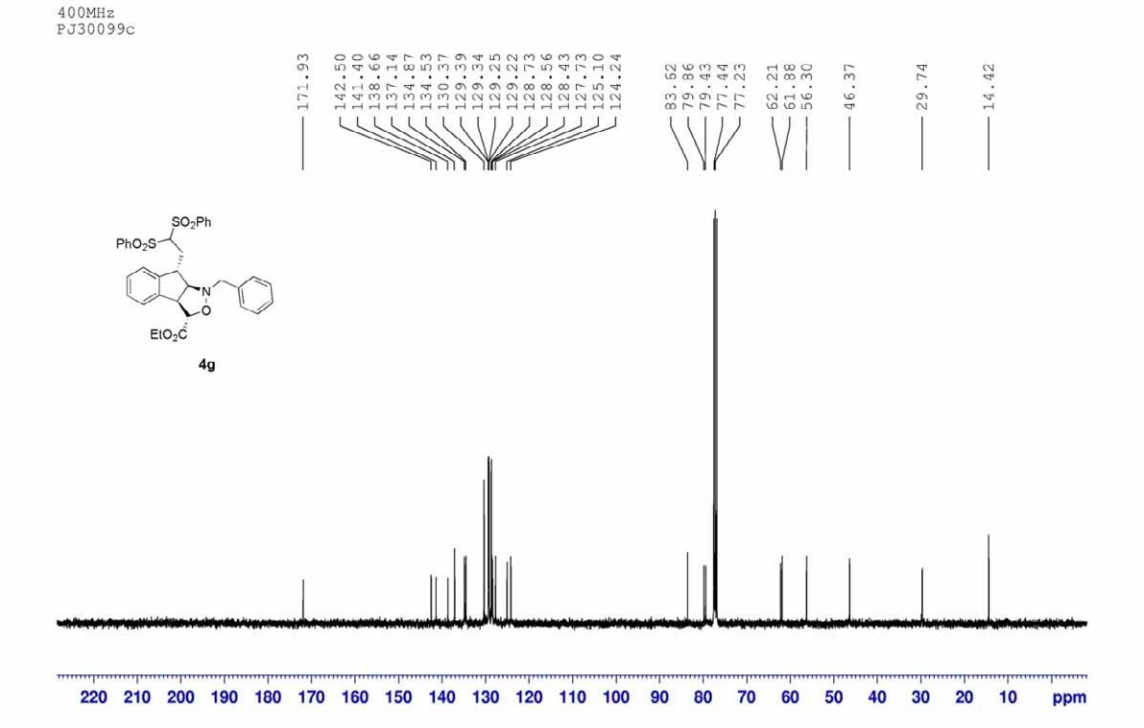
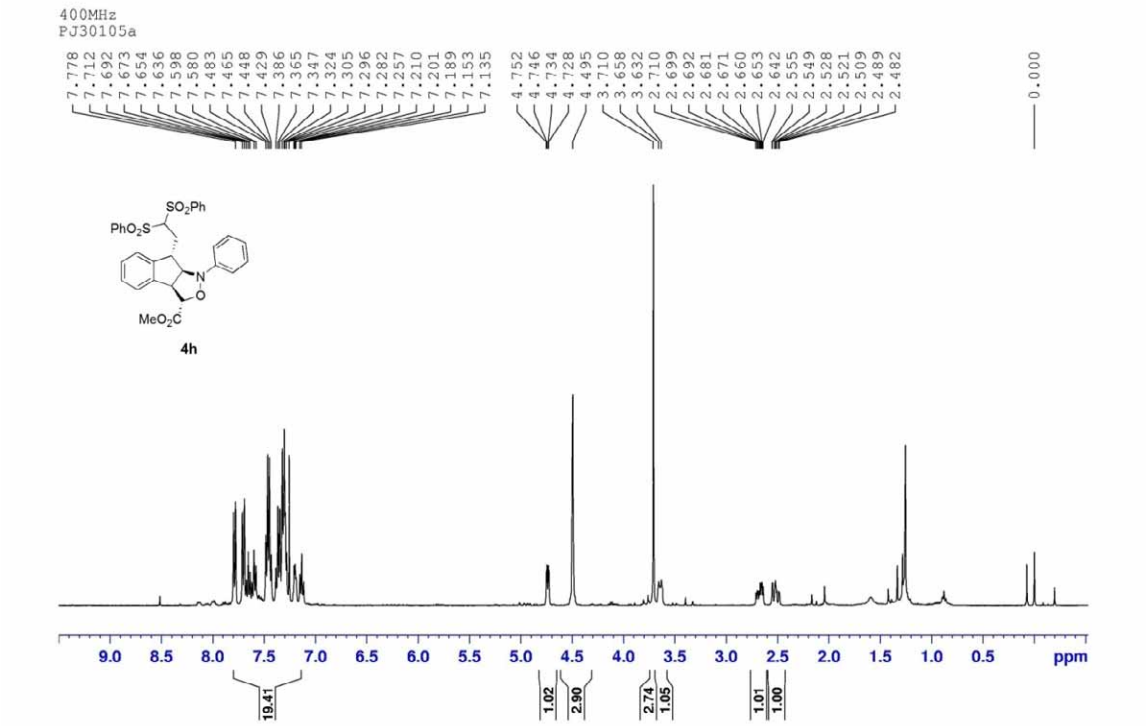
7.679
7.660
7.642
7.518
7.500
7.484
7.465
7.346
7.336
7.327
7.312
7.302
7.257
7.141
7.132
7.121
5.270
5.253
4.421
4.406
4.389
4.356
4.341
4.323
4.290
4.273
4.263
4.245
4.189
4.155
4.022
4.006
3.990
3.963
3.929
3.600
3.586
3.572
2.778
2.769
2.759
2.749
2.740
2.731
2.720
2.711
2.391
2.357
2.324
1.359
1.341
1.323
0.001
SO2Ph
PhO2S
N
O
EtO2C
4g
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
ppm
3.83
2.06
4.07
8.31
1.13
1.02
3.91
1.06
1.00
0.96
1.00
1.02
1.07
3.05


400MHz
PJ30099c
171.93
142.50
141.40
138.66
137.14
134.87
134.53
130.37
129.39
129.34
129.25
129.22
128.73
128.56
128.43
127.73
125.10
124.24
83.62
79.86
79.43
77.44
77.23
62.21
61.88
56.30
46.37
29.74
14.42
SO2Ph
PhO2S
N
O
EtO2C
4g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
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7.673
7.654
7.636
7.598
7.580
7.483
7.465
7.448
7.429
7.386
7.365
7.347
7.324
7.305
7.296
7.282
7.257
7.210
7.201
7.189
7.153
7.135
4.752
4.746
4.734
4.728
4.495
3.710
3.658
3.632
2.710
2.699
2.692
2.681
2.671
2.660
2.653
2.642
2.555
2.549
2.528
2.521
2.509
2.489
2.482
0.000
SO2Ph
PhO2S
N
O
MeO2C
4h
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
ppm
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2.90
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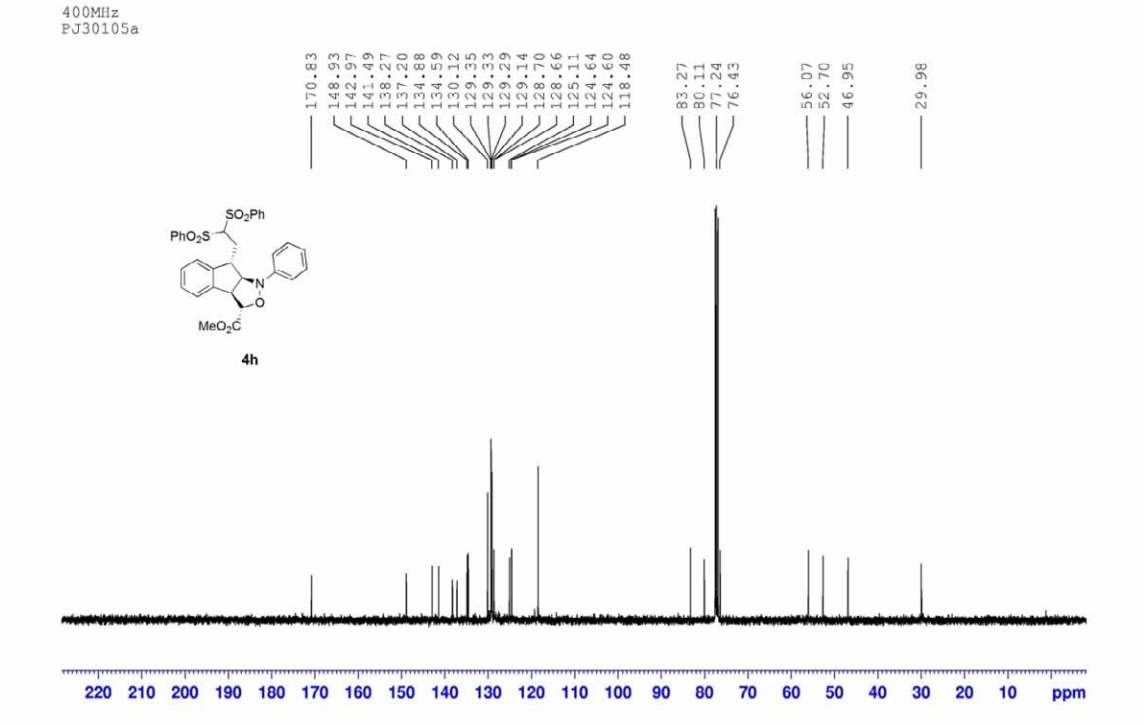
1.05
1.01
1.00


400MHz
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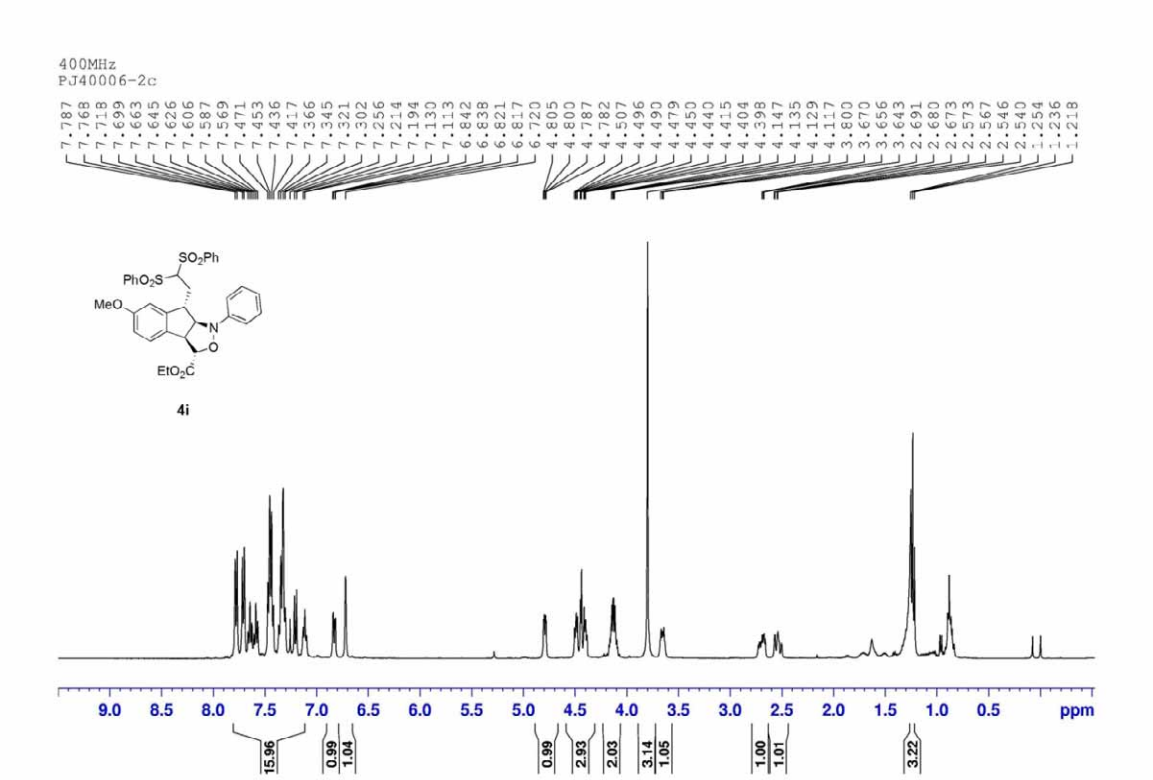
141.49
138.27
137.20
134.88
134.59
130.12
129.35
129.33
129.29
129.14
128.70
128.66
125.11
124.64
124.60
118.48
83.27
80.11
77.24
76.43
56.07
52.70
46.95
29.98
SO2Ph
PhO2S
N
O
MeO2C
4h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
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7.663
7.645
7.626
7.606
7.587
7.569
7.471
7.453
7.436
7.417
7.366
7.345
7.321
7.302
7.256
7.214
7.194
7.130
7.113
6.842
6.838
6.821
6.817
6.720
4.805
4.800
4.787
4.782
4.507
4.496
4.490
4.479
4.450
4.440
4.415
4.404
4.398
4.147
4.135
4.129
4.117
3.800
3.670
3.656
3.643
2.691
2.680
2.673
2.573
2.567
2.546
2.540
1.254
1.236
1.218
SO2Ph
PhO2S
MeO
N
O
EtO2C
4i
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
ppm
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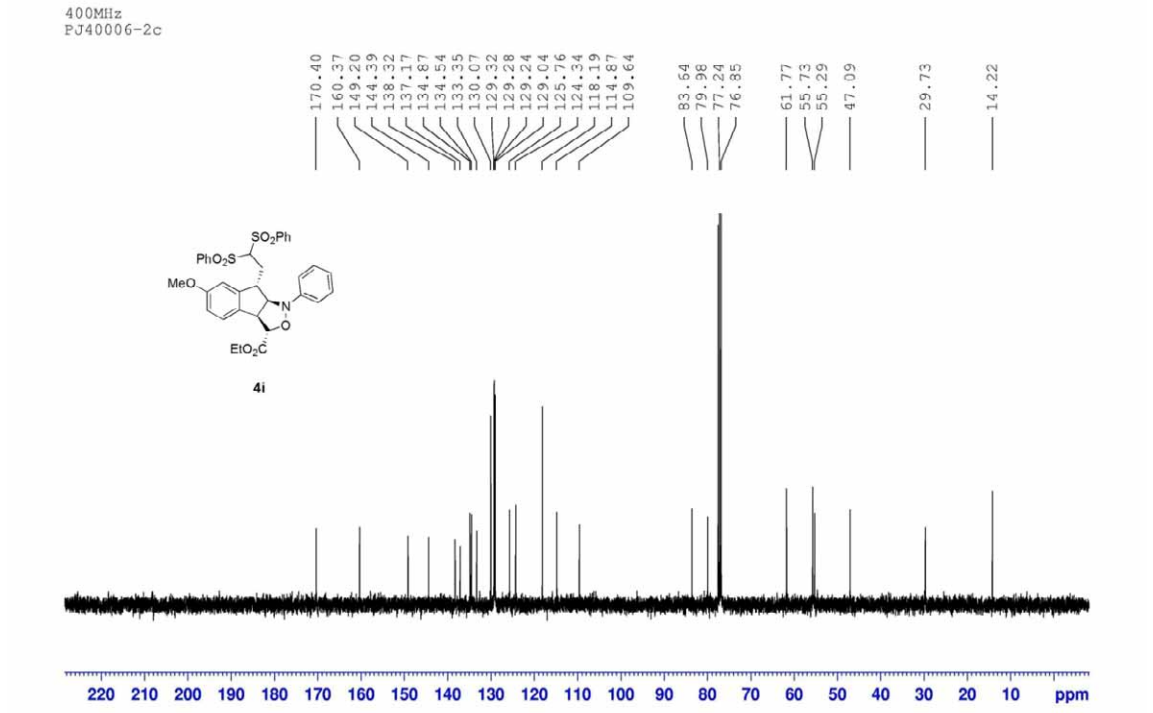
0.99
1.04
0.99
2.93
2.03
3.14
1.05
1.00
1.01
3.22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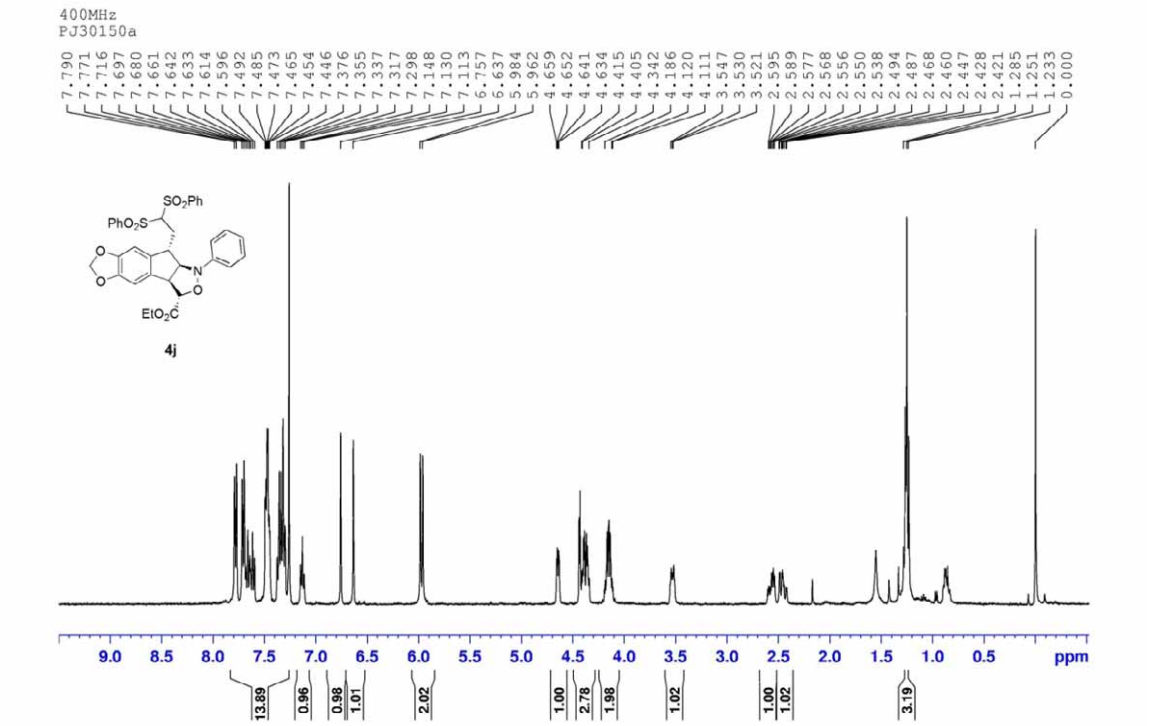
137.17
134.87
134.54
133.35
130.07
129.32
129.28
129.24
129.04
125.76
124.34
118.19
114.87
109.64
83.64
79.98
77.24
76.85
61.77
55.73
55.29
47.09
29.73
14.22
SO2Ph
PhO2S
MeO
N
O
EtO2C
4i
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


400MHz
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7.771
7.716
7.697
7.680
7.661
7.642
7.633
7.614
7.596
7.492
7.485
7.473
7.465
7.454
7.446
7.376
7.355
7.337
7.317
7.298
7.148
7.130
7.113
6.757
6.637
5.984
5.962
4.659
4.652
4.641
4.634
4.415
4.405
4.342
4.186
4.120
4.111
3.547
3.530
3.521
2.595
2.589
2.577
2.568
2.556
2.550
2.538
2.494
2.487
2.468
2.460
2.447
2.428
2.421
1.285
1.251
1.233
0.000
SO2Ph
PhO2S
N
O
EtO2C
4j
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
ppm
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0.98
1.01
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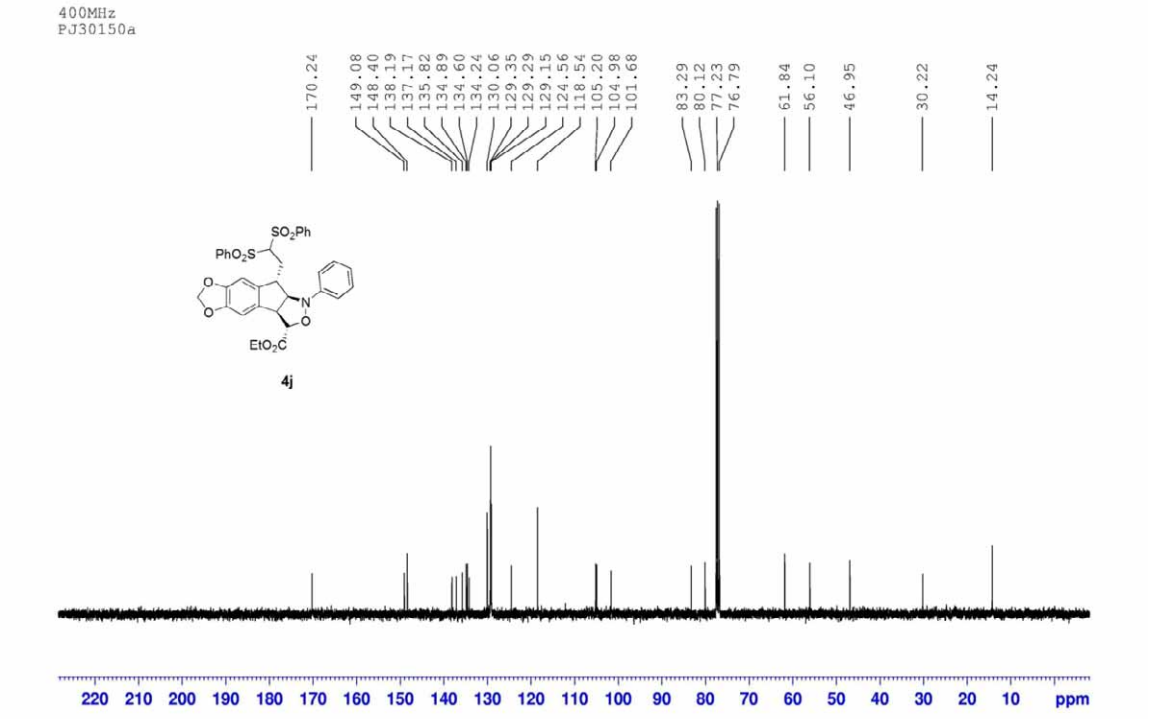
1.00
2.78
1.98
1.02
1.00
1.02
3.19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135.82
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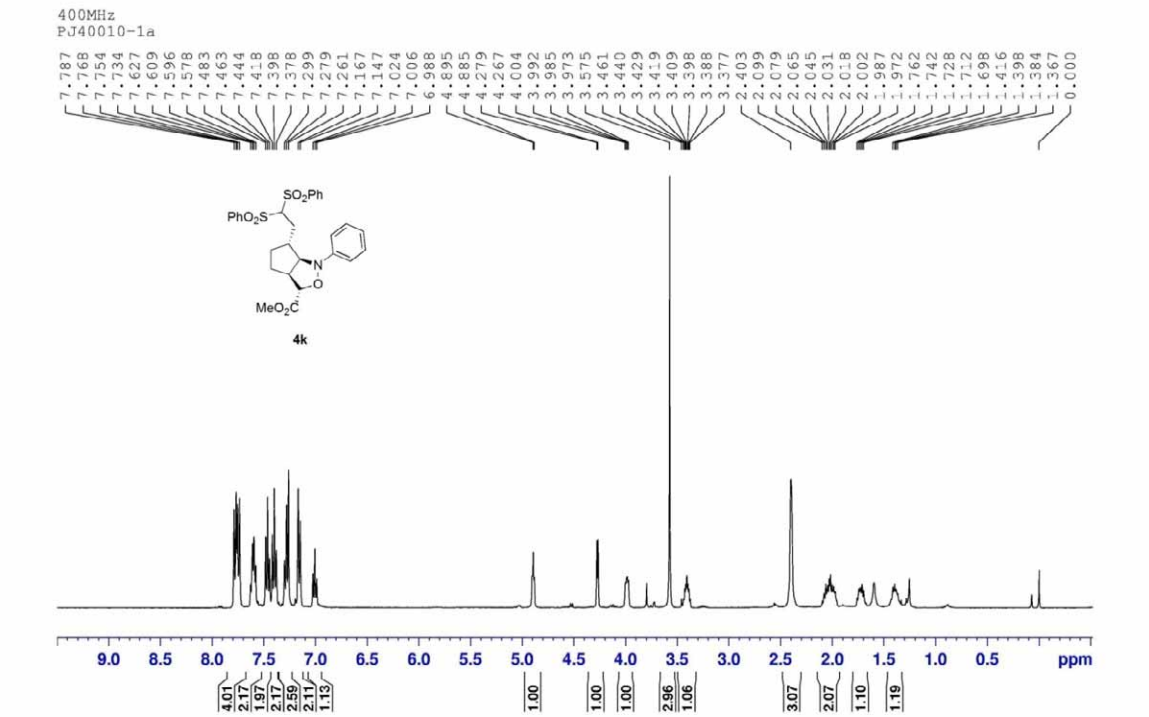
134.60
134.24
130.06
129.35
129.29
129.15
124.56
118.54
105.20
104.98
101.68
83.29
80.12
77.23
76.79
61.84
56.10
46.95
30.22
14.24
SO2Ph
PhO2S
N
O
EtO2C
4j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.596
7.578
7.483
7.463
7.444
7.418
7.398
7.378
7.299
7.279
7.261
7.167
7.147
7.024
7.006
6.988
4.895
4.885
4.279
4.267
4.004
3.992
3.985
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3.575
3.461
3.440
3.429
3.419
3.409
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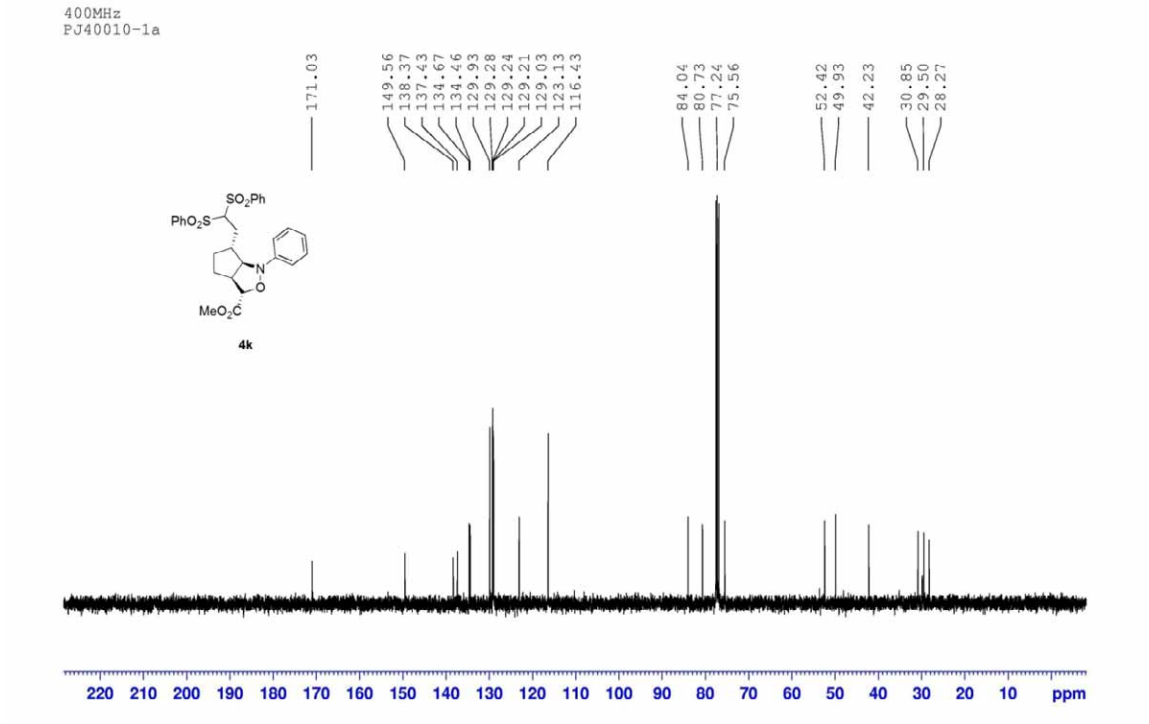
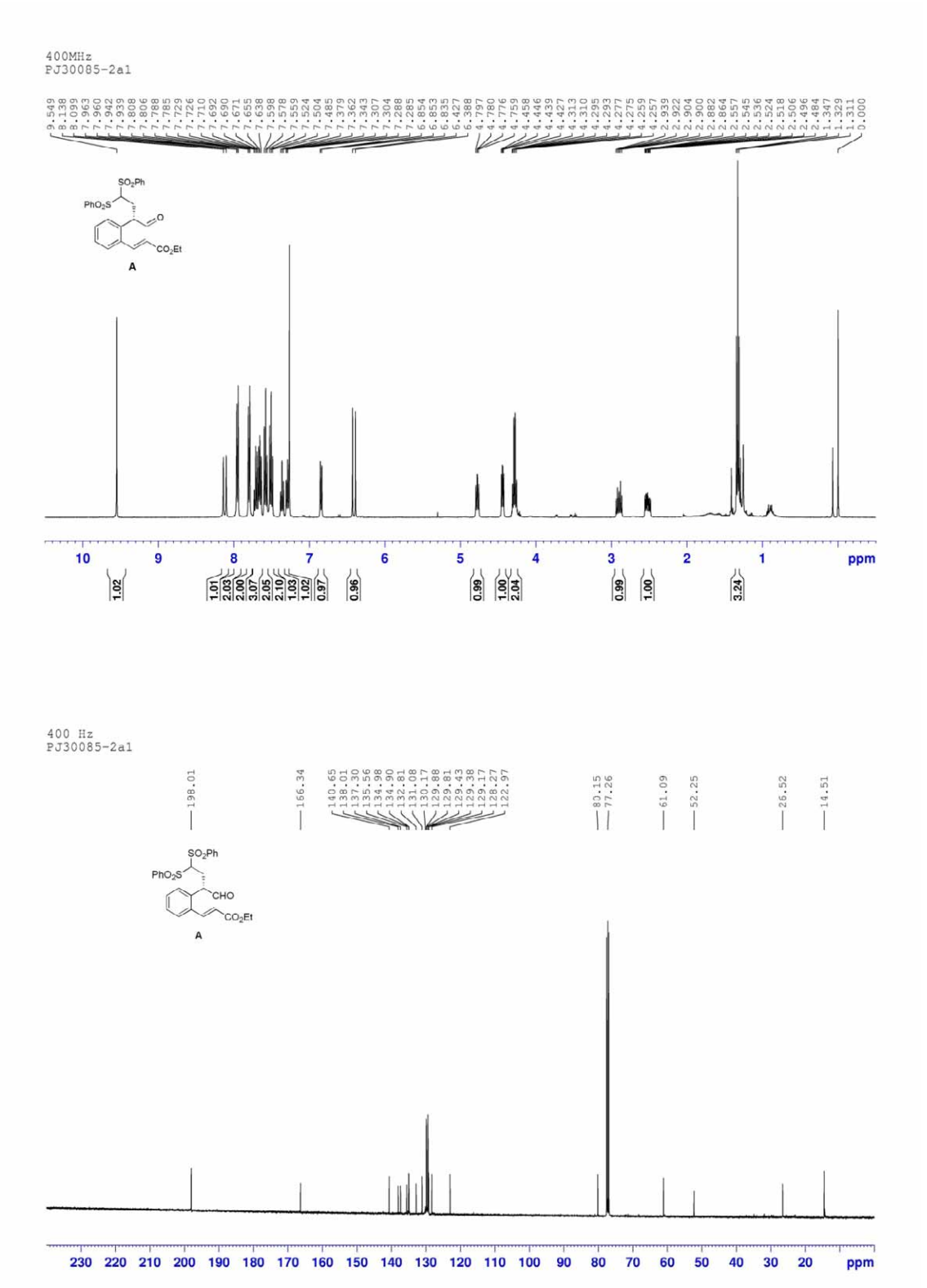
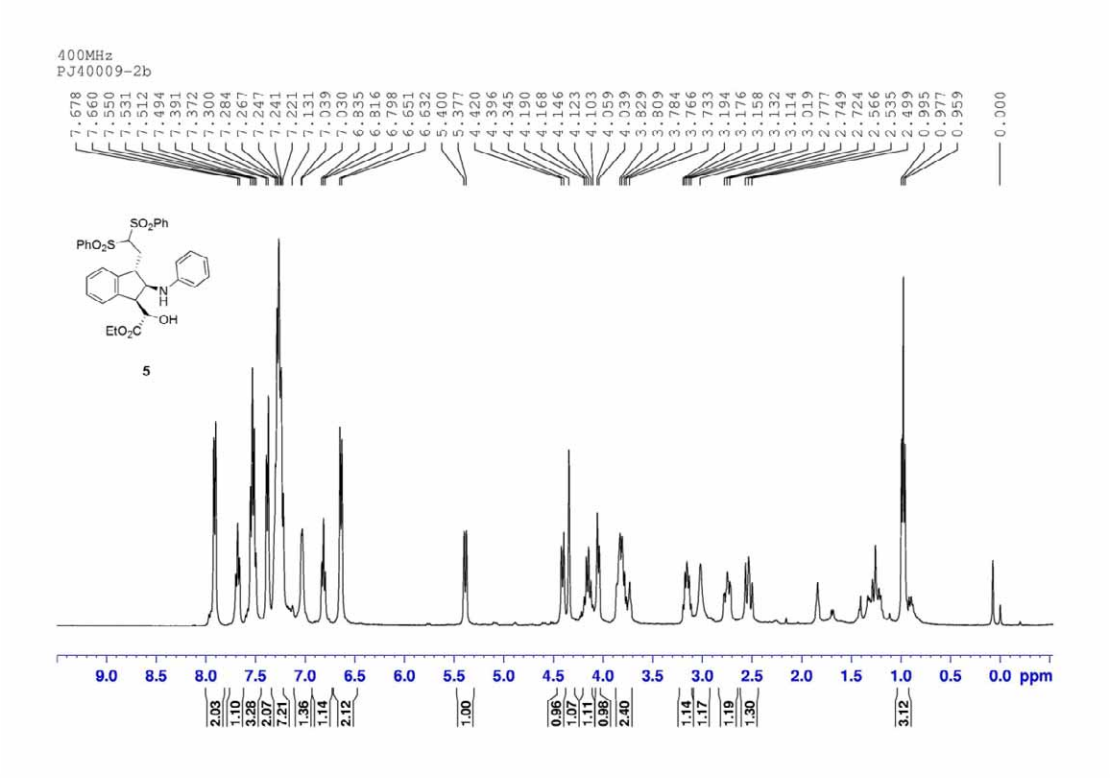
3.377
2.403
2.099
2.079
2.065
2.045
2.031
2.018
2.002
1.987
1.972
1.762
1.742
1.728
1.712
1.698
1.416
1.398
1.384
1.367
0.000
SO2Ph
PhO2S
N
O
MeO2C
4k
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.01
2.17
1.97
2.17
2.59
2.11
1.13
1.00
1.00
1.00
2.96
1.06
3.07
2.07
1.10
1.19

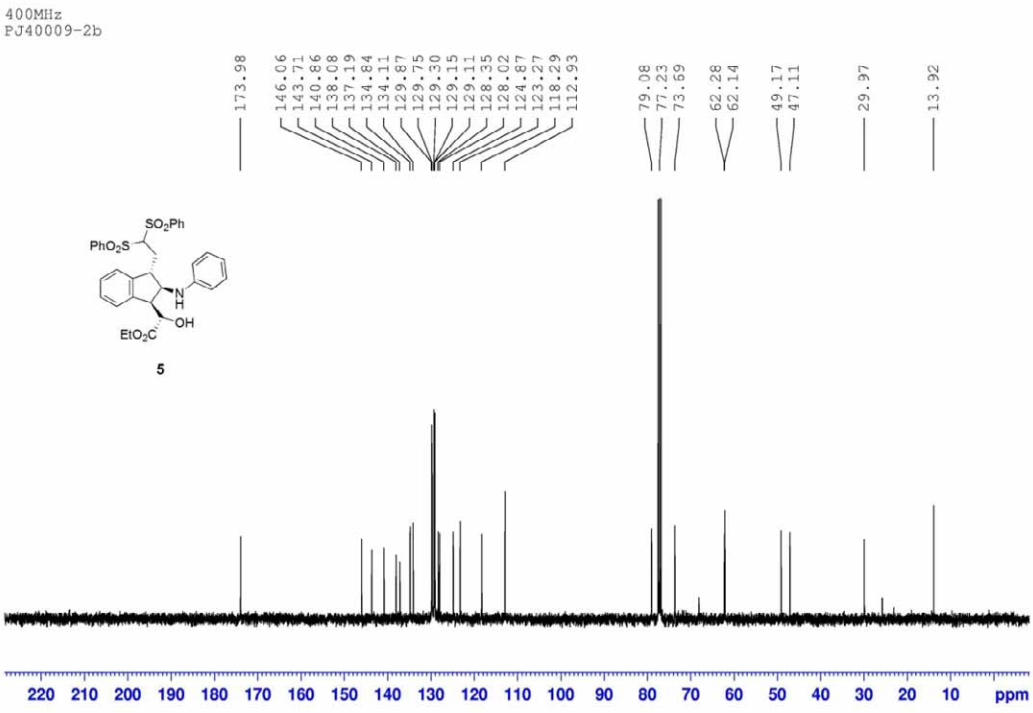

400MHz
PJ40010-1a
171.03
149.56
138.37
137.43
134.67
134.46
129.93
129.28
129.24
129.21
129.03
123.13
116.43
84.04
80.73
77.24
75.56
52.42
49.93
42.23
30.85
29.50
28.27
SO2Ph
PhO2S
N
O
MeO2C
4k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

# $^{1}$H and $^{13}$C NMR Spectra of Compound A

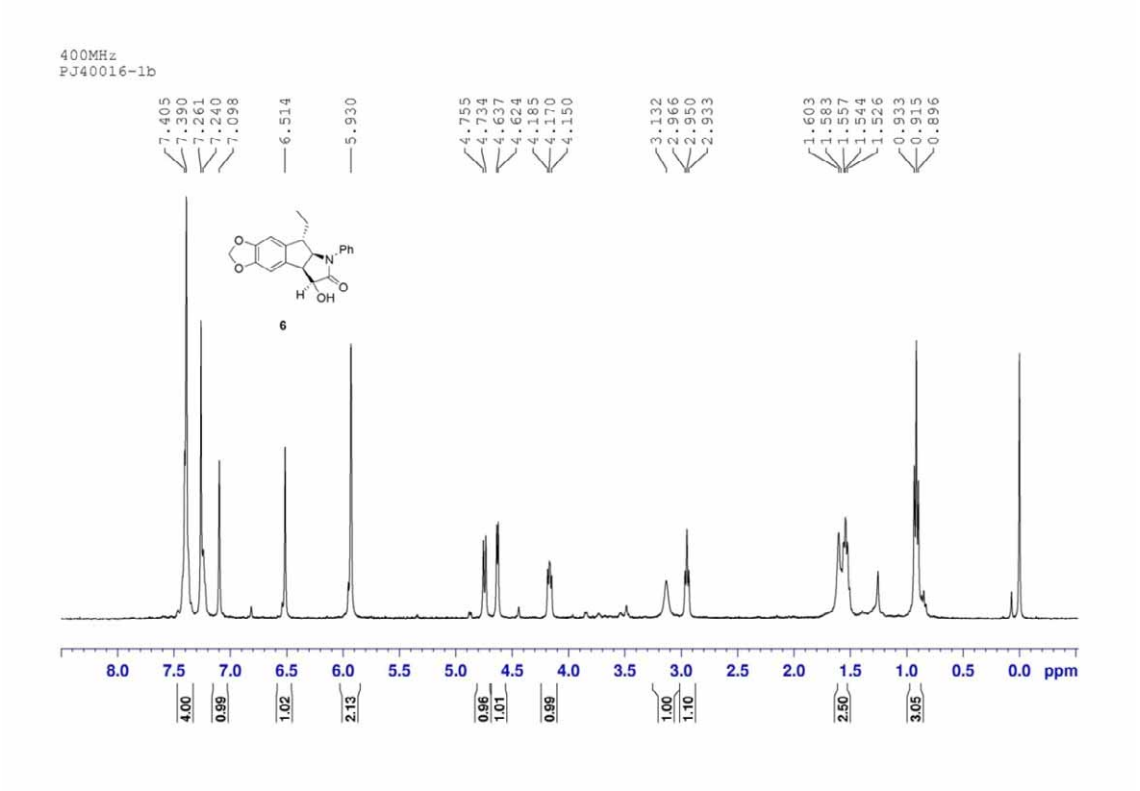


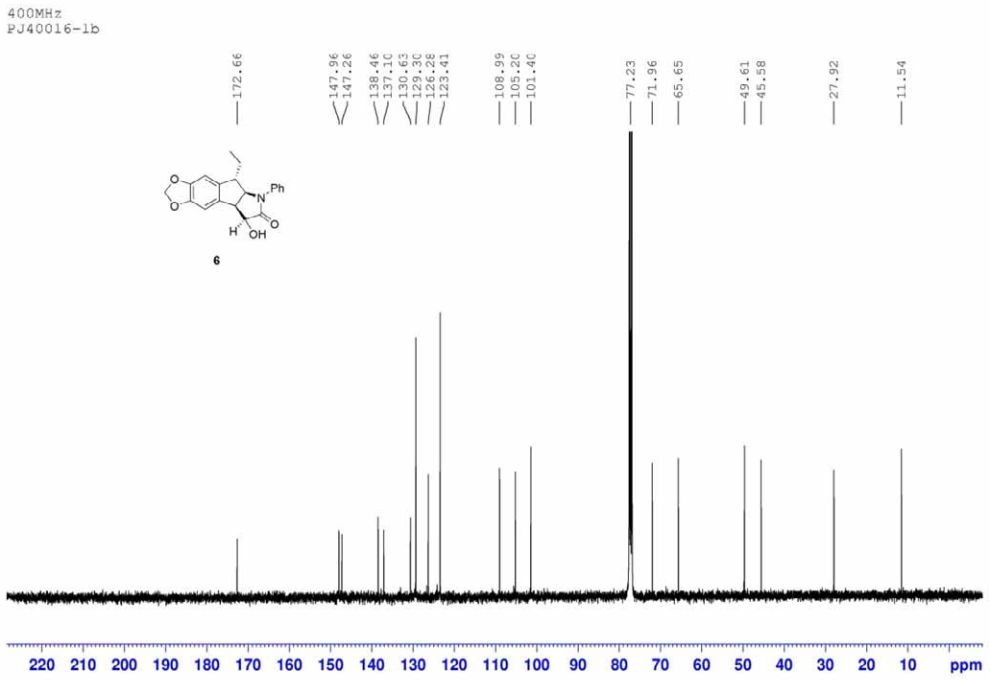
## $^{1}$H and $^{13}$C NMR Spectra of Compounds 5



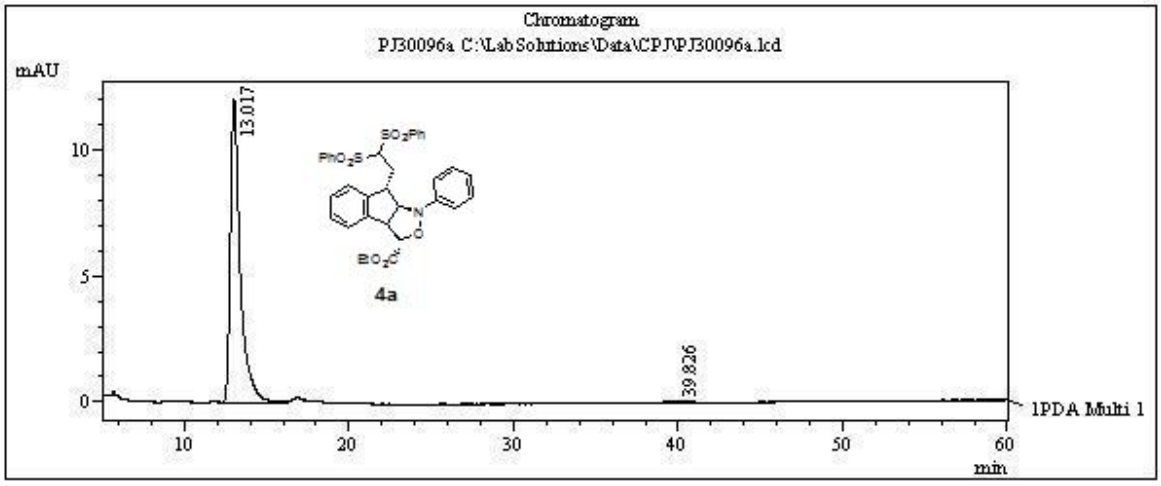



## $^{1}H$ and $^{13}C$ NMR Spectra of Compound 6



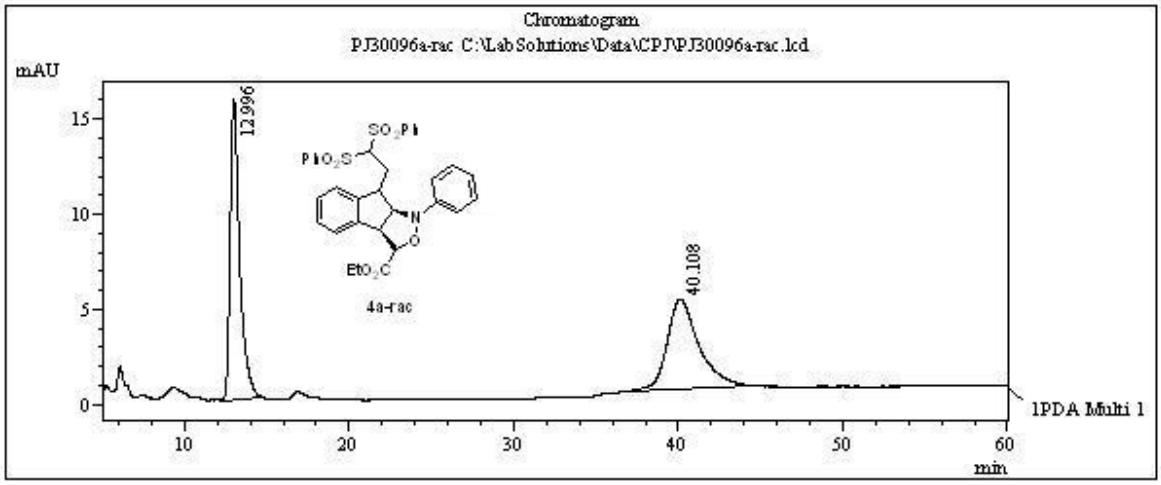



## HPLC Spectra of Compounds 4a-4k



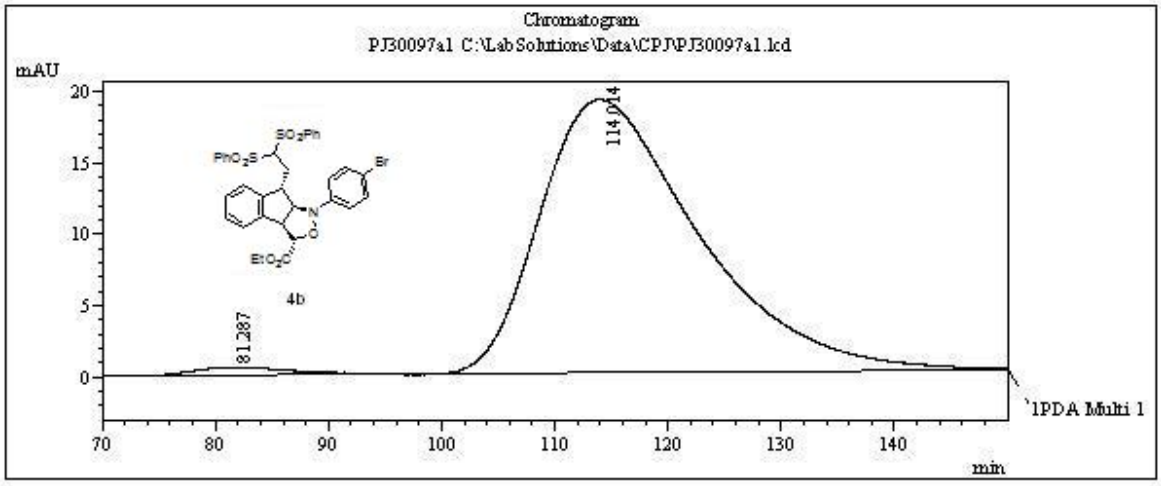

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 13.017 | 99.015 |
| 2 | 39.826 | 0.985 |
| Total | | 100.000 |



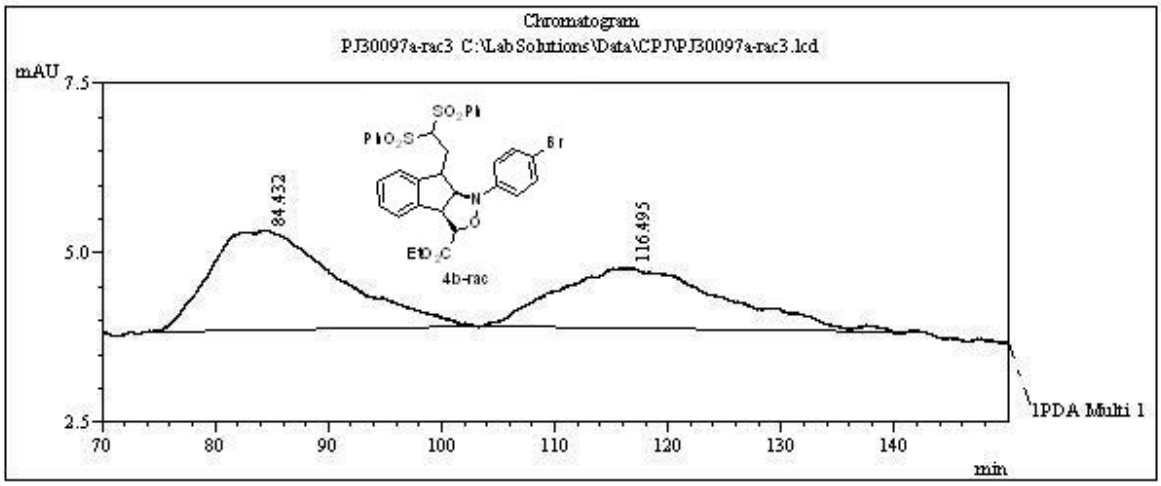

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 12.996 | 50.265 |
| 2 | 40.108 | 49.735 |
| Total | | 100.000 |



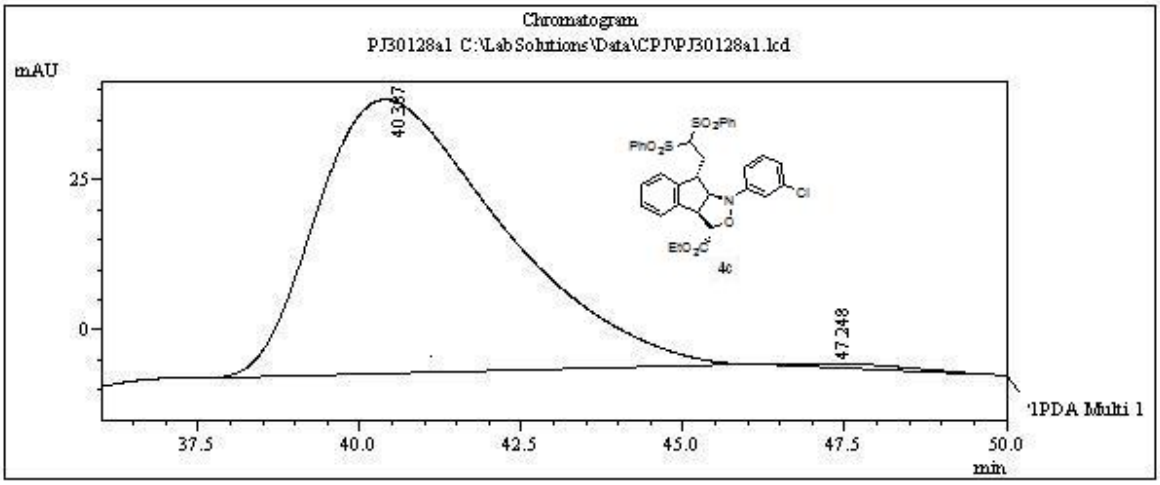

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 81.287 | 1.985 |
| 2 | 114.014 | 98.015 |
| Total | | 100.000 |



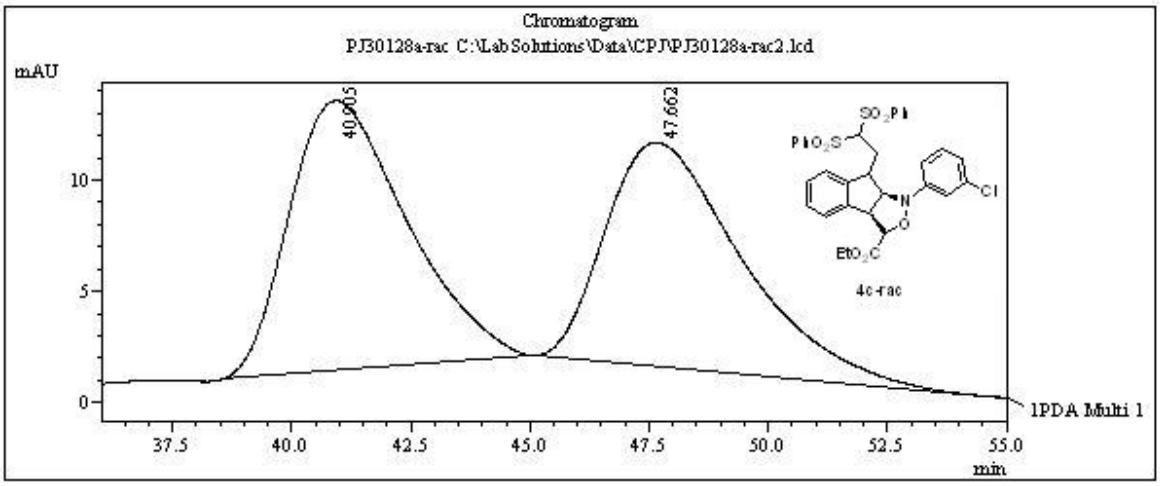

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 84.432 | 56.026 |
| 2 | 116.495 | 43.974 |
| Total | | 100.000 |



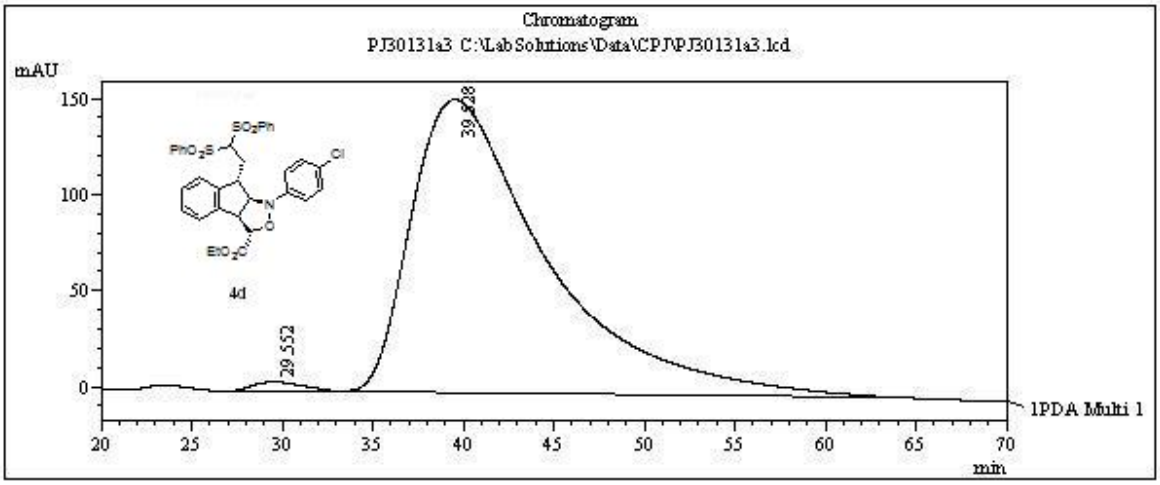

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 40.387 | 99.080 |
| 2 | 47.248 | 0.920 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

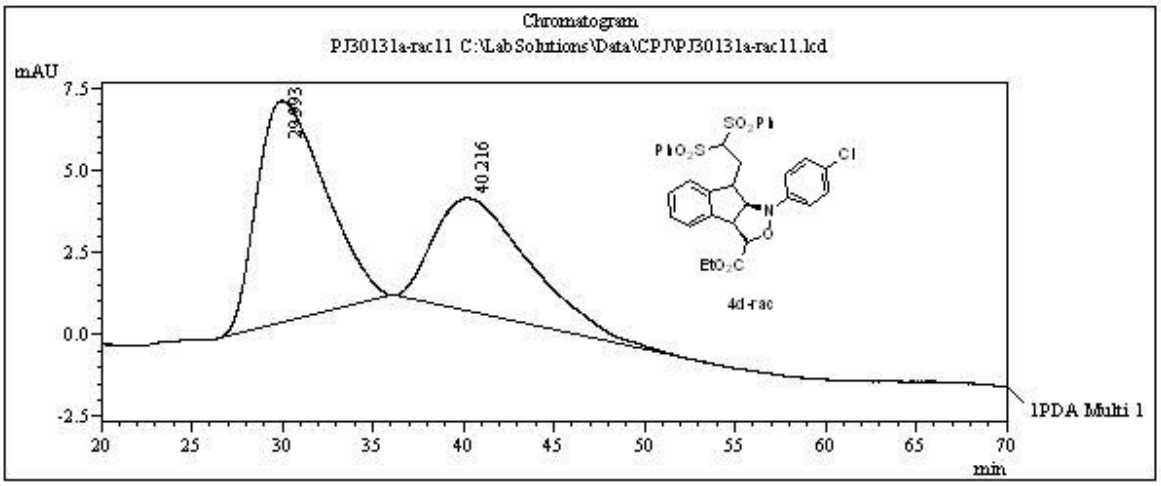
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 40.905 | 50.968 |
| 2 | 47.662 | 49.032 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

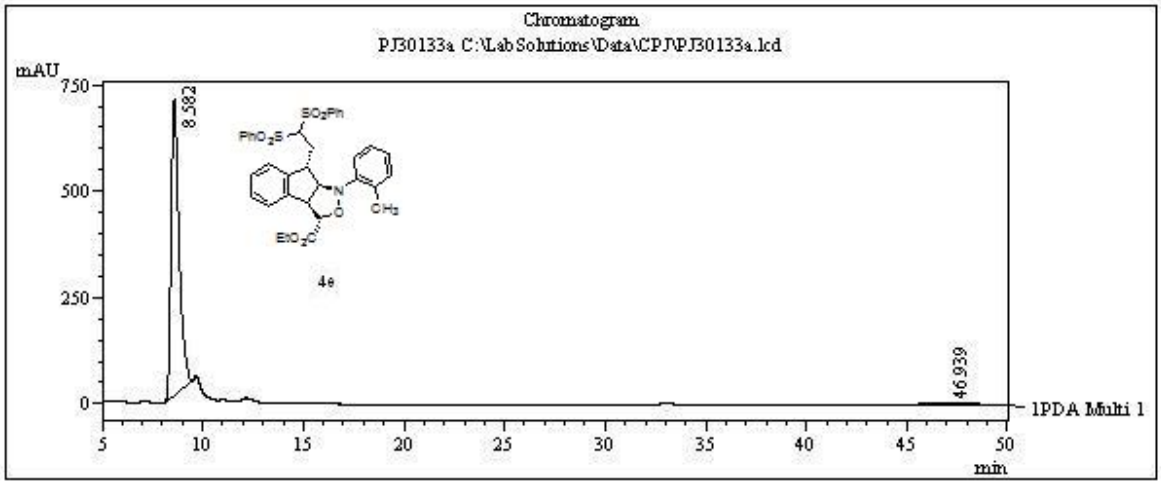
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 29.552 | 1.094 |
| 2 | 39.528 | 98.906 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

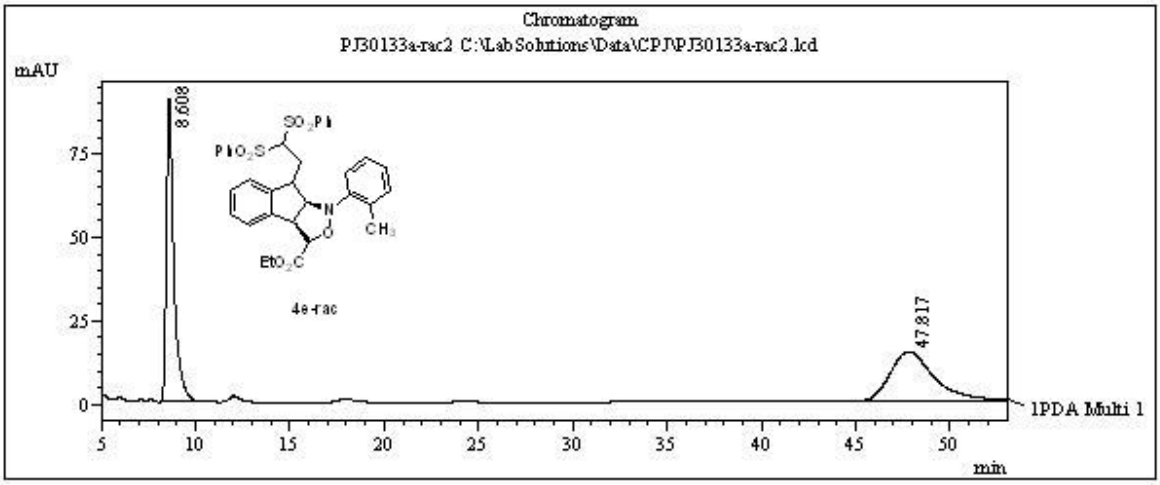
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 29.993 | 57.723 |
| 2 | 40.216 | 42.277 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

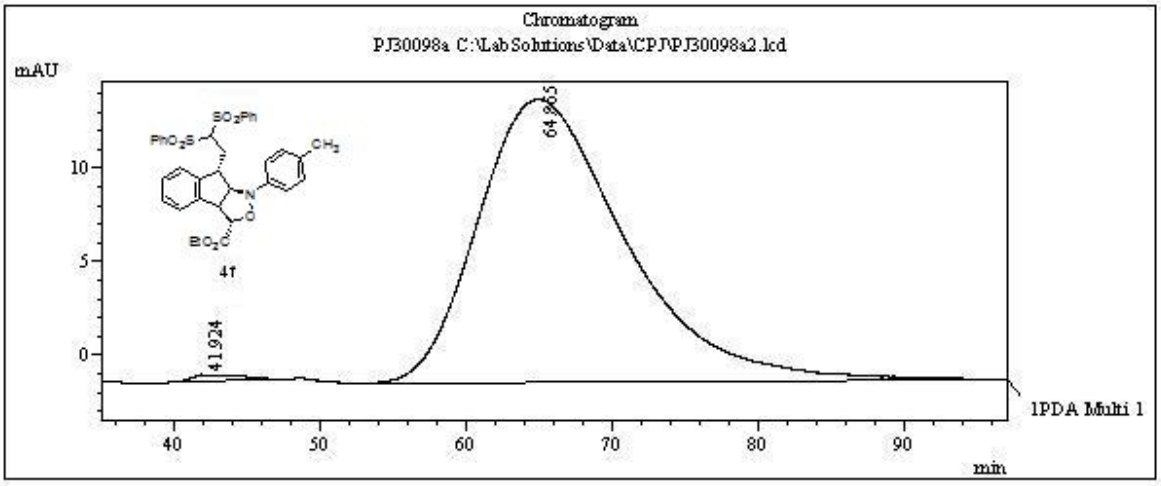
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 8.582 | 97.737 |
| 2 | 46.939 | 2.263 |
| Total | | 100.000 |




Peak Table

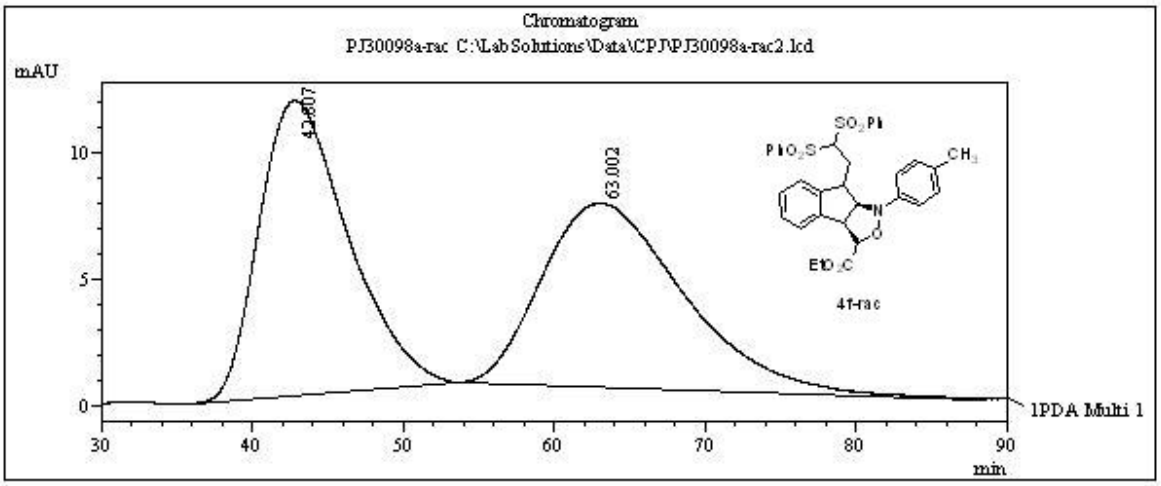
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 8.608 | 50.013 |
| 2 | 47.817 | 49.987 |
| Total | | 100.000 |



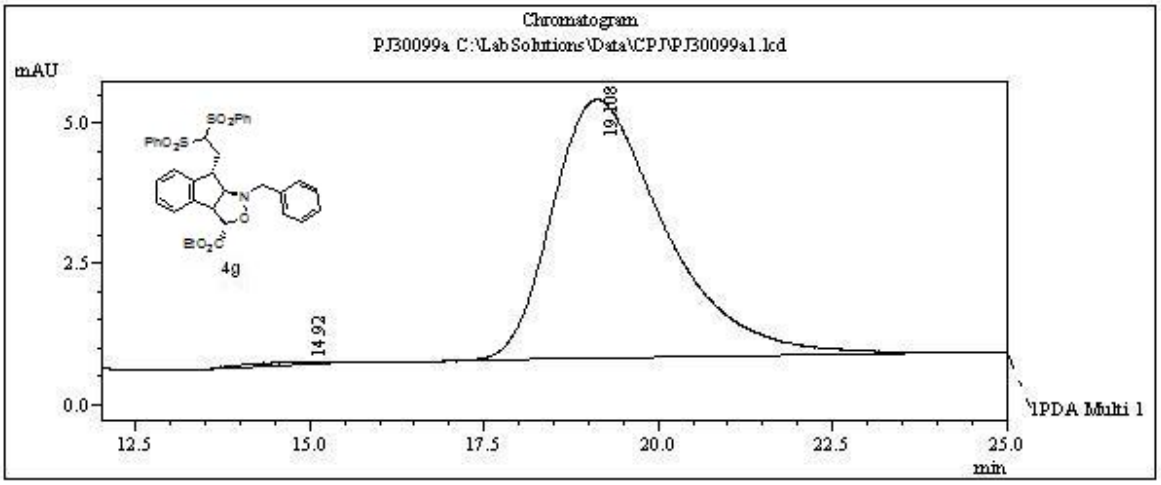

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 41.924 | 0.801 |
| 2 | 64.865 | 99.199 |
| Total | | 100.000 |



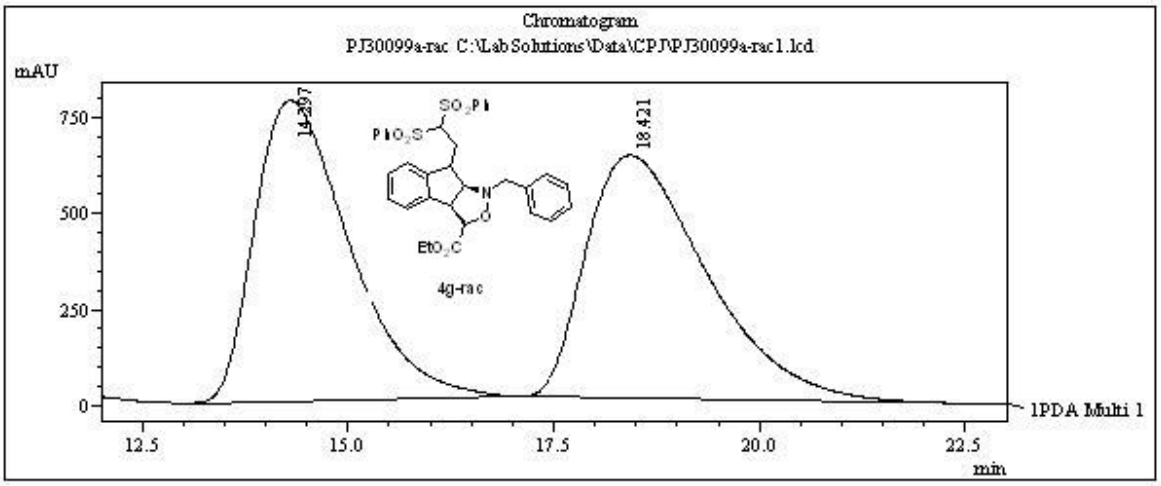

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 42.807 | 50.135 |
| 2 | 63.002 | 49.865 |
| Total | | 100.000 |



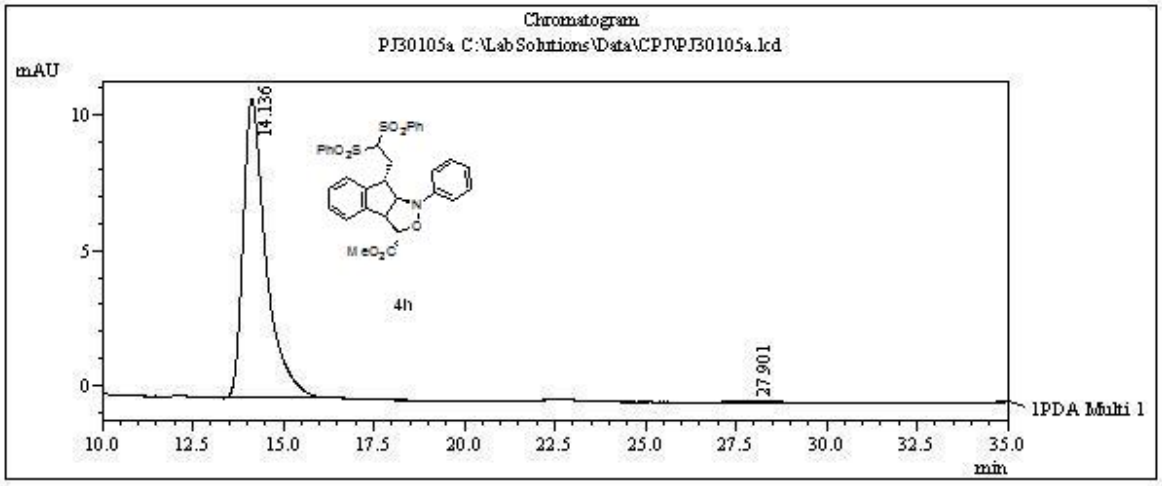

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 14.921 | 0.957 |
| 2 | 19.108 | 99.043 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

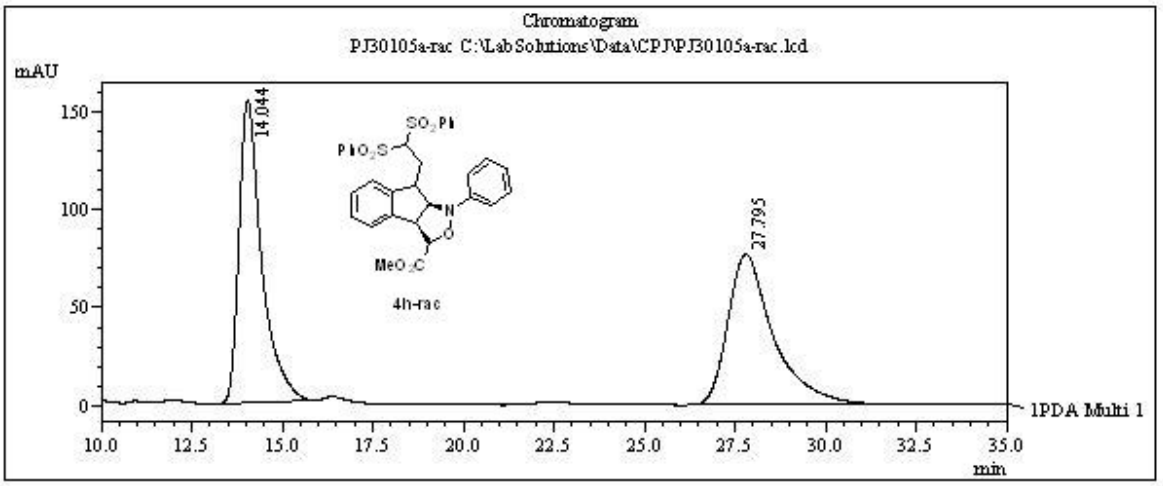
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 14.297 | 49.237 |
| 2 | 18.421 | 50.763 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

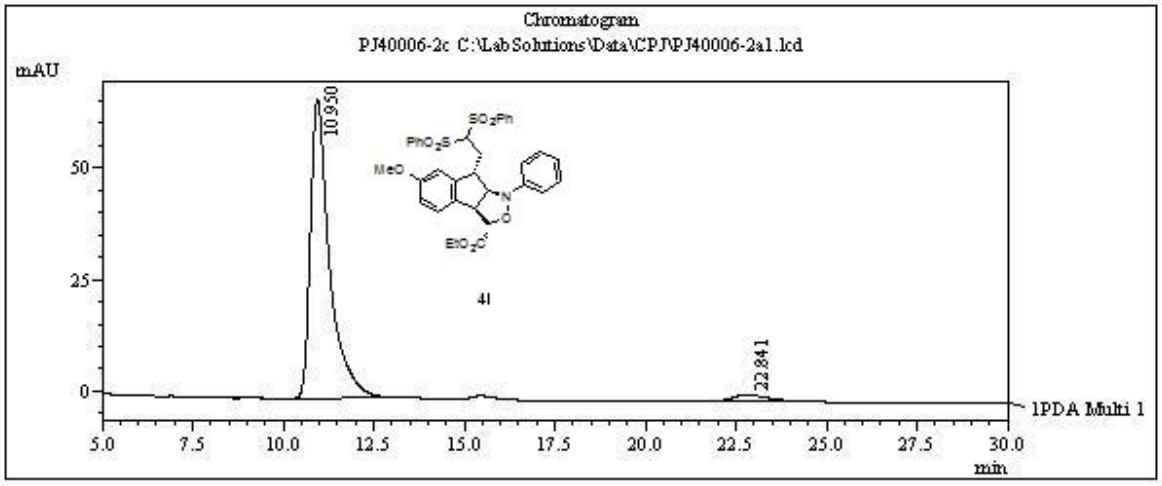
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 14.136 | 98.729 |
| 2 | 27.901 | 1.271 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

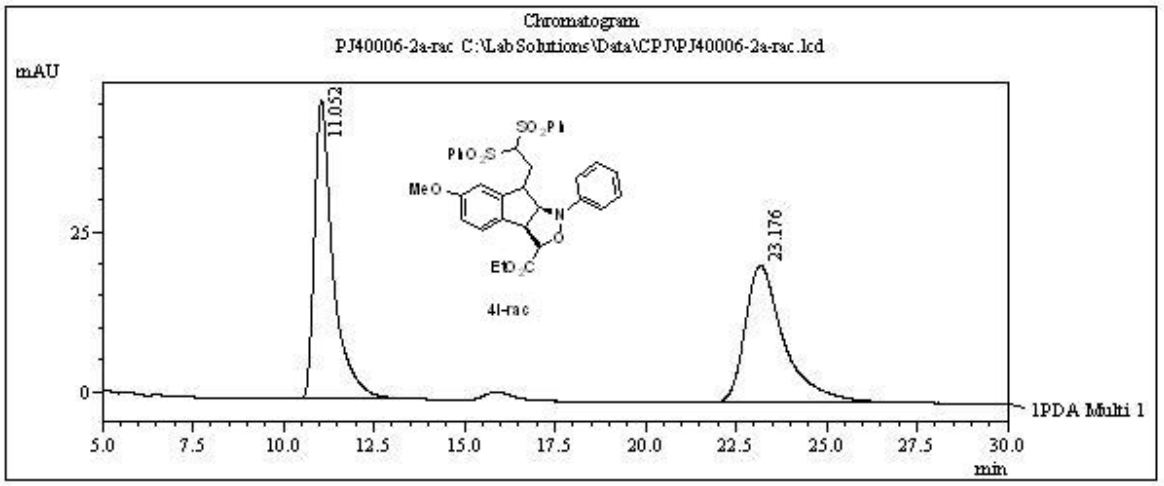
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 14.044 | 49.997 |
| 2 | 27.795 | 50.003 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

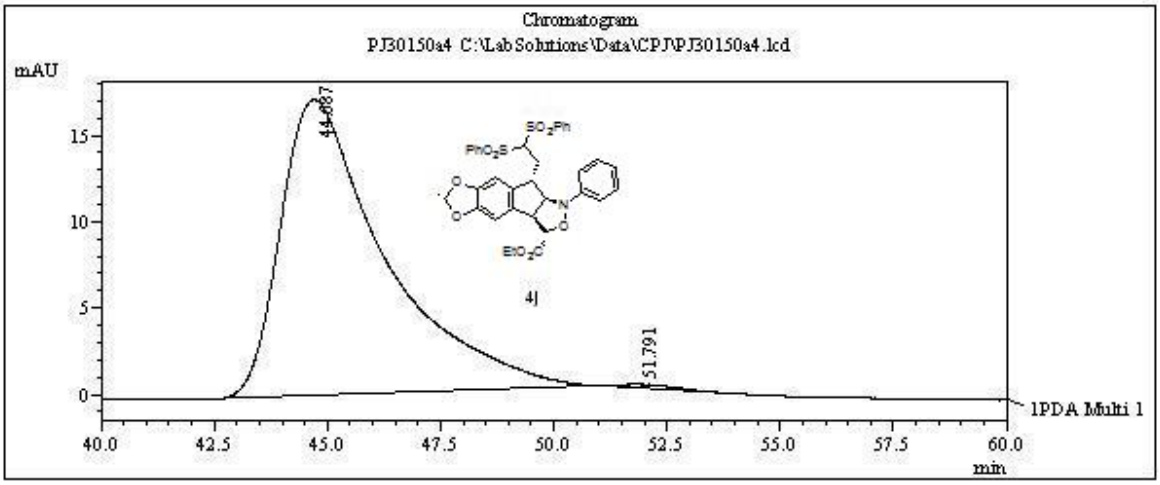
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 10.950 | 95.865 |
| 2 | 22.841 | 4.135 |
| Total | | 100.000 |




Peak Table

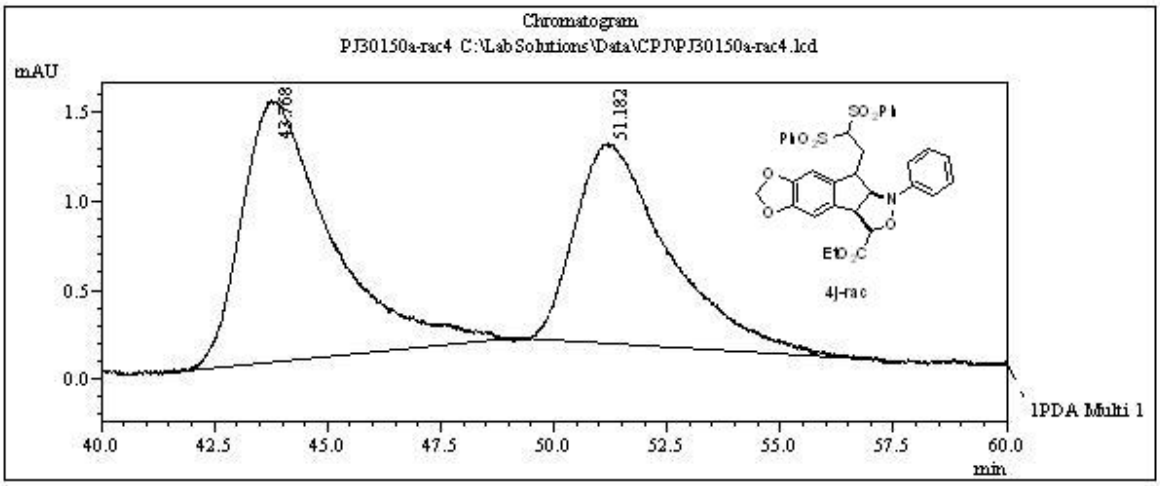
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 11.052 | 50.744 |
| 2 | 23.176 | 49.256 |
| Total | | 100.000 |



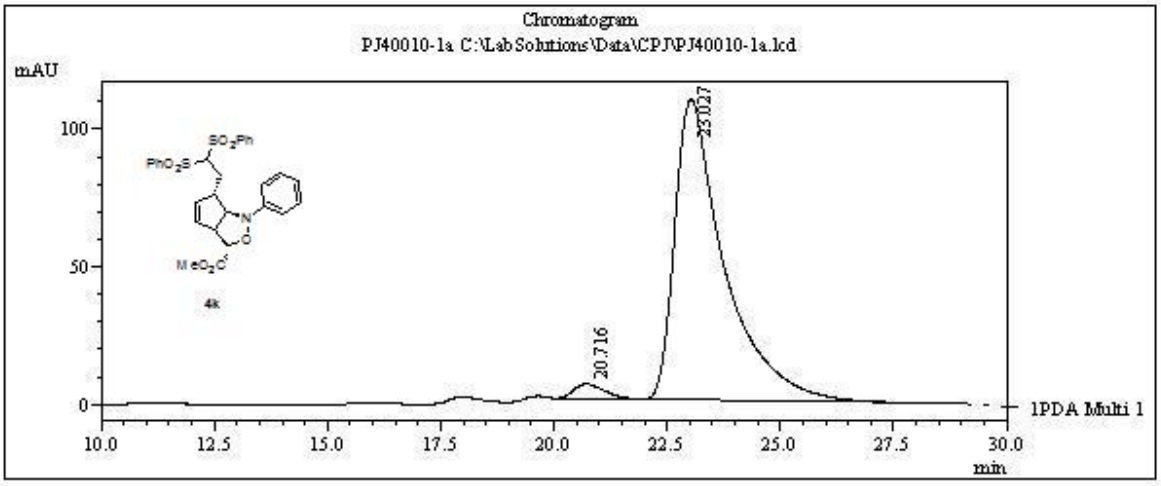

Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 44.687 | 99.353 |
| 2 | 51.791 | 0.647 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

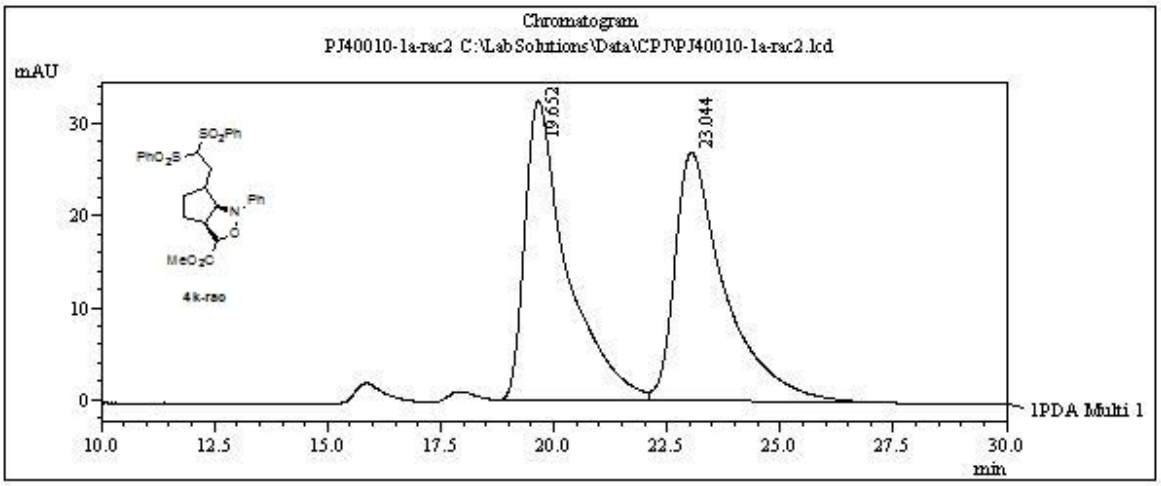
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 43.768 | 55.343 |
| 2 | 51.182 | 44.657 |
| Total | | 100.000 |




Peak Table

PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 20.716 | 3.055 |
| 2 | 23.027 | 96.945 |
| Total | | 100.000 |

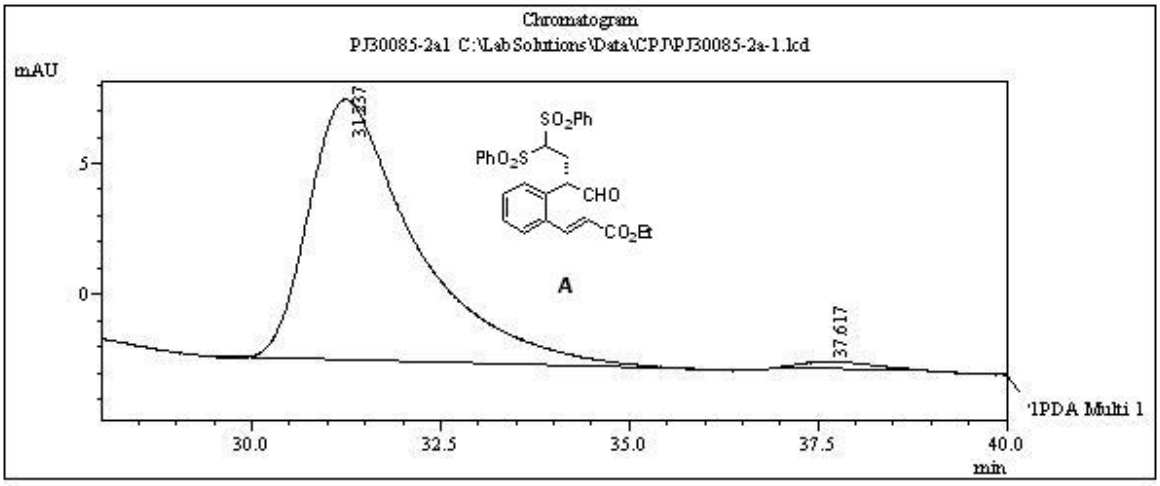



Peak Table

PDA Ch1 220nm 4nm

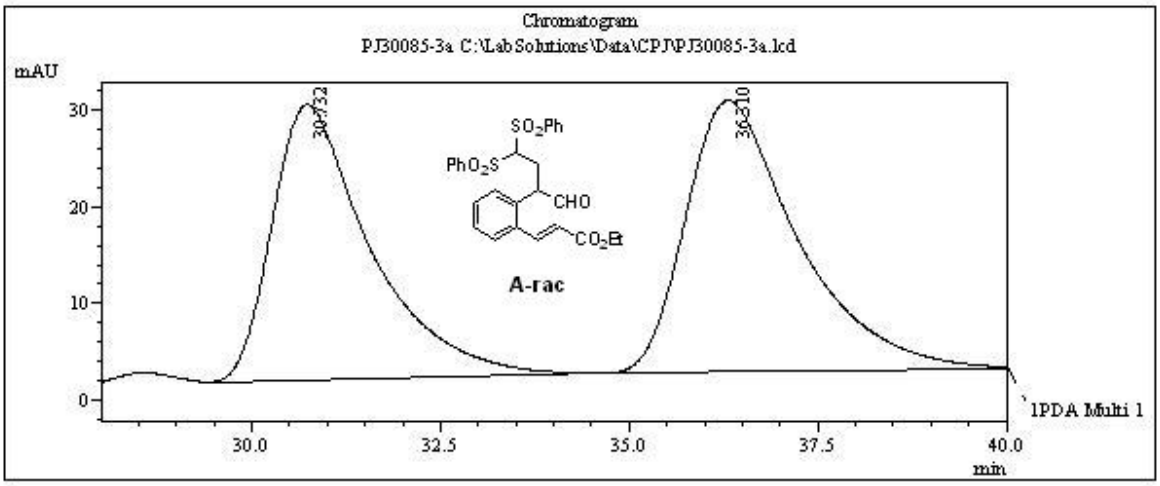
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 19.652 | 50.696 |
| 2 | 23.044 | 49.304 |
| Total | | 100.000 |

## HPLC Spectra of Compound A




Peak Table
PDA Ch1 220nm 4nm

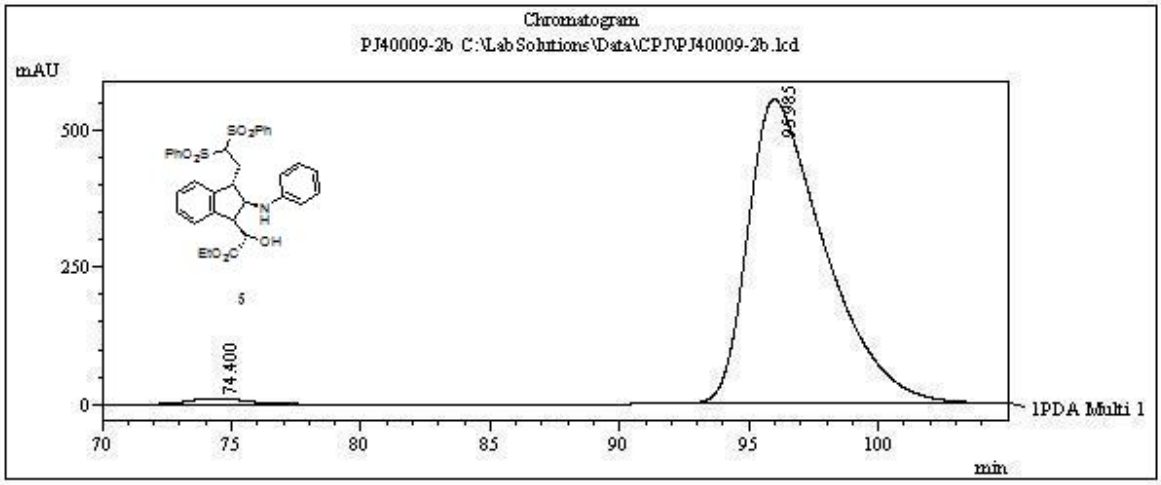
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 31.237 | 98.374 |
| 2 | 37.617 | 1.626 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

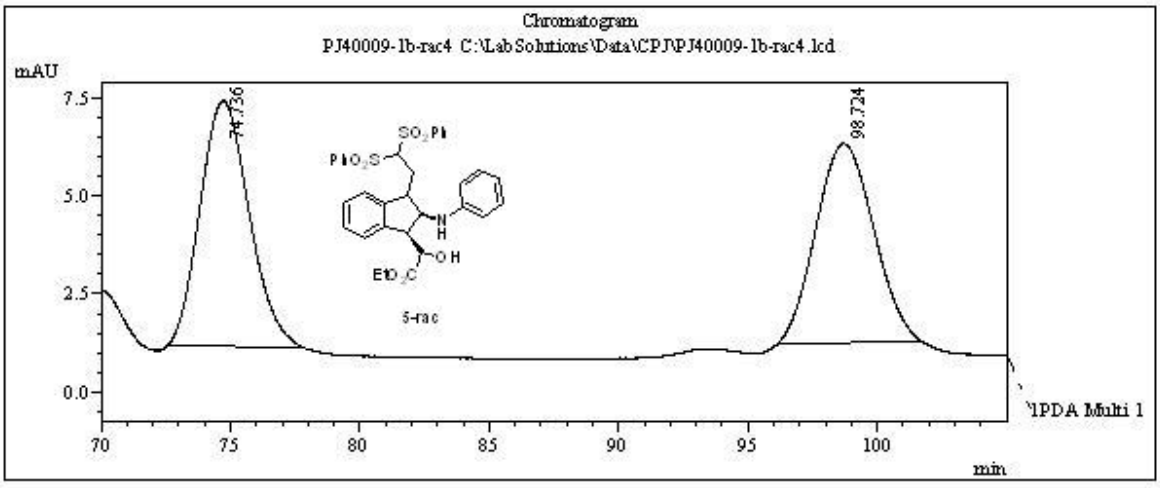
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 30.732 | 47.019 |
| 2 | 36.310 | 52.981 |
| Total | | 100.000 |

## HPLC Spectra of Compound 5




Peak Table
PDA Ch1 220nm 4nm

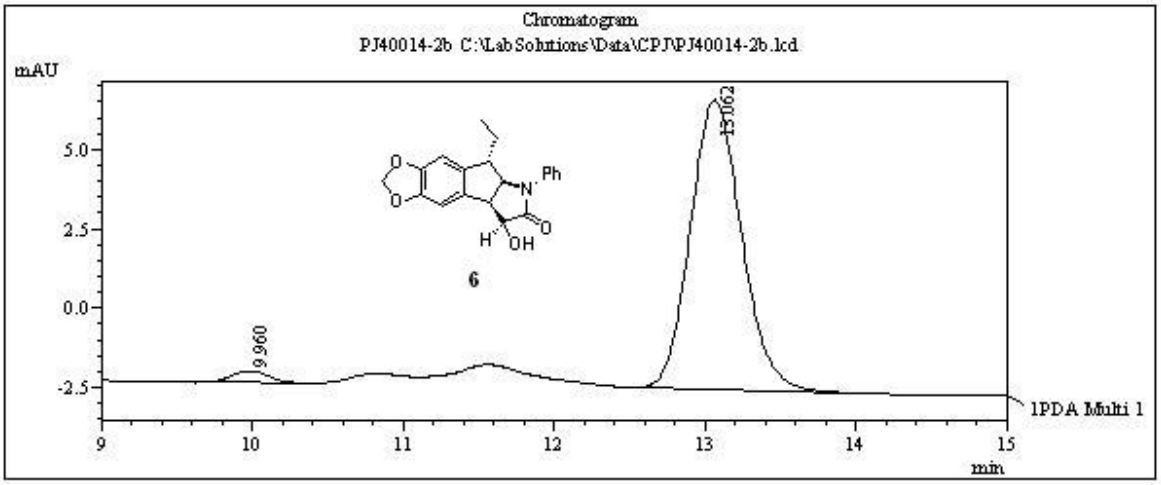
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 74.400 | 1.384 |
| 2 | 95.985 | 98.616 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

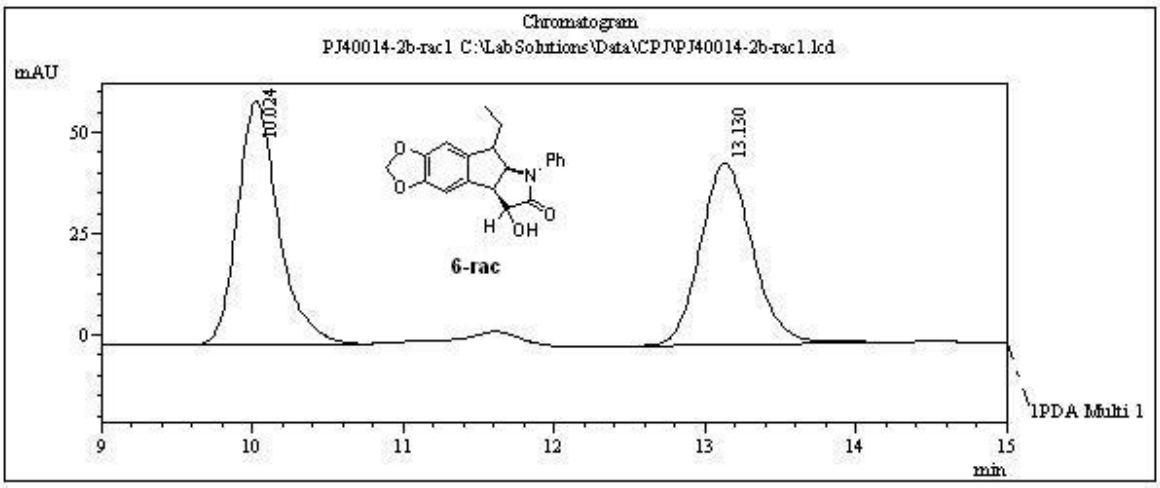
| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 74.736 | 51.054 |
| 2 | 98.724 | 48.946 |
| Total | | 100.000 |

## HPLC Spectra of Compound 6




Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 9.960 | 2.848 |
| 2 | 13.062 | 97.152 |
| Total | | 100.000 |




Peak Table
PDA Ch1 220nm 4nm

| Peak# | Ret. Time | Area % |
|---|---|---|
| 1 | 10.024 | 51.399 |
| 2 | 13.130 | 48.601 |
| Total | | 100.000 |