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## **Supporting Information**

## Palladium-Catalyzed Asymmetric Allenylic Alkylation: Construction of Multiple Chiral Thiochromanone Derivatives

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#### 1. General and Materials

General: All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Solvents were treated prior to use according to the standard methods. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded at room temperature in CDCl<sub>3</sub> on 400 MHz and 700 MHz instrument with TMS as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

**Materials:** Commercially available reagents and solvents were used throughout without further purification.

#### 2. Synthesis of Substrates

#### 2.1. The Synthesis of Thiochromanone Derivatives

The thiochromanone derivatives **1a-c** and **1e-1p** were synthesized from (substituted) 2-mercaptobenzaldehydes and  $\alpha,\beta$ -unsaturated ester through two steps according to the known procedure, all of which are the new compounds. Firstly, the known 2-mercaptobenzaldehydes **S1** underwent the organocatalytic domino sulfa-Michael-aldol reactions with  $\alpha,\beta$ -unsaturated ester **S2** to provide the intermediate alcohols. Then, the desired thiochromanone derivatives **1** could be synthesized through the oxidation with PCC.

Besides, thiochromanone derivative with amide group **1d** was synthesized through exchange from the thiochromanone **1c** and piperidine according to the known procedure.<sup>2</sup>

**General Procedure**: To a solution of (substituted) 2-mercaptobenzaldehydes **S1** (7.0 mmol) in dichloromethane (60 mL) was added organocatalyst (1.4 mmol, 20 mol%) and  $\alpha,\beta$ -unsaturated esters **S2** (9.1 mmol) sequentially under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about 48-120 h. The reaction was complete as monitored by TLC. Then the reaction mixture was concentrated under the reduced pressure to obtain the crude residue. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to give the intermediate alcohol compounds.

To a solution of pyridinium chlorochromate (PCC, 2.5 equiv.) in dichloromethane (0.1 M) was added celite (equal in quality to PCC) and the obtained alcohol compounds at ambient temperature. TLC analysis indicated completion of the reactions after about 5-8 h. After filtration through celite, the volatiles were removed under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable thiochromanone derivatives 1.

#### 3-Nitro-2-phenylthiochroman-4-one (1a):

0.243 g, 30% yield (two steps), orange solid, mp 173-174 °C, new compound,  $R_f = 0.05$  (hexanes/

ethyl acetate 3/1), keto. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (d, J = 7.6 Hz, 1H), 7.56-7.45 (m, 3H), 7.42-7.34 (m, 3H), 7.34-7.26 (m, 2H), 6.13 (d, J =13.1 Hz, 1H), 5.27 (d, J = 13.1 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  184.0, 140.6, 135.2, 133.0, 130.7, 129.9, 129.4, 128.9, 128.0, 126.9, 126.2, 95.1, 48.3.

HRMS Calculated for C<sub>15</sub>H<sub>12</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 286.0532, found: 286.0533.

#### 1-(4-Hydroxy-2-phenyl-2*H*-thiochromen-3-yl)ethan-1-one (1b):

0.324 g, 41% yield (two steps), yellow viscous liquid, new compound,  $R_f = 0.79$  (hexanes/ethyl acetate 3/1), enol. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, J = 7.8, 1.5 Hz, 1H), 7.29-7.25 (m, 1H), 7.25-7.15 (m, 6H), 7.15-7.08 (m, 1H), 4.99 (s, 1H), Ме 2.18 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.2, 173.9, 142.0, 134.5, 132.3, 129.3, 128.7, 128.0, 127.7, 127.5, 126.8, 125.9, 106.0, 42.0, 25.2. HRMS Cal-

culated for  $C_{17}H_{15}O_2S$   $[M+H]^+$  283.0787, found: 283.0788.

#### Methyl 4-hydroxy-2-phenyl-2*H*-thiochromene-3-carboxylate (1c):

1.126 g, 39% yield (two steps), pale yellow viscous liquid, new compound,  $R_{\rm f} = 0.47$  (hexanes/ ethyl acetate 20/1), enol/keto = 14.3/1. The enol isomer: <sup>1</sup>H NMR (400 MHz, OMe CDCl<sub>3</sub>) δ 13.04 (s, 1H), 8.01-7.92 (m, 1H), 7.25-7.12 (m, 8H), 5.12 (s, 1H), 3.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.8, 166.1, 142.7, 134.2, 131.4, 128.5, 127.8, 127.4, 126.6, 126.5, 125.6, 96.9, 52.3, 39.6. HRMS Calculated for  $C_{17}H_{15}O_3S$  [M+H]<sup>+</sup> 299.0736, found: 299.0742.

#### Methyl 4-hydroxy-2-(o-tolyl)-2H-thiochromene-3-carboxylate (1e):

0.701 g, 32% yield (two steps), pale yellow solid, mp 115-116  $^{\circ}$ C, new compound,  $R_f = 0.62$ OH O (hexanes/ethyl acetate 20/1), enol/keto = 12.5/1. The enol isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.08 (s, 1H), 8.06-7.95 (m, 1H), 7.24-7.19 (m, 2H), 7.17-7.14 (m, 1H), 7.12-7.04 (m, 2H), 6.98-6.89 (m, 2H), 5.32 (s, 1H), 3.71 (s, 3H), 2.49 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.8, 166.6, 139.8, 134.3, 133.9, 131.4, 130.8, 128.6, 128.1, 127.4, 126.5, 126.2, 126.1, 125.7, 96.5, 52.4, 35.7, 19.7. HRMS Calculated for  $C_{18}H_{17}O_3S$   $[M+H]^+$  313.0893, found: 313.0890.

#### Methyl 4-hydroxy-2-(*m*-tolyl)-2*H*-thiochromene-3-carboxylate (1f):

0.575 g, 26% yield (two steps), pale yellow viscous liquid, new compound,  $R_{\rm f} = 0.62$  (hexanes/ ethyl acetate 20/1), enol/keto = 14.3/1. The enol isomer: <sup>1</sup>H NMR (400 ОН ОМе MHz, CDCl<sub>3</sub>) δ 13.05 (s, 1H), 8.03-7.87 (m, 1H), 7.25-7.14 (m, 3H), 7.11-6.94 (m, 4H), 5.09 (s, 1H), 3.75 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 166.1, 142.6, 138.1, 134.2, 131.4, 128.5, 128.3, 128.3, 127.8, 127.4, 126.5, 125.6, 123.7, 96.8, 52.3, 39.6, 21.5. HRMS Calculated for C<sub>18</sub>H<sub>17</sub>O<sub>3</sub>S

[M+H]<sup>+</sup> 313.0893, found: 313.0889.

#### Methyl 4-hydroxy-2-(p-tolyl)-2H-thiochromene-3-carboxylate (1g):

0.362 g, 17% yield (two steps), pale yellow viscous liquid, new compound,  $R_f = 0.62$  (hexanes/oth O ethyl acetate 20/1), enol/keto = 14.3/1. The enol isomer:  $^1$ H NMR (400

OMe MHz, CDCl<sub>3</sub>)  $\delta$  13.03 (s, 1H), 8.01-7.92 (m, 1H), 7.24-7.14 (m, 3H), 7.08 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 5.10 (s, 1H), 3.76 (s, 3H), 2.24 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 166.0, 139.8, 137.2,

134.2, 131.4, 129.2, 128.5, 127.8, 126.5, 126.5, 125.6, 97.0, 52.3, 39.4, 21.1. HRMS Calculated for  $C_{18}H_{17}O_{3}S$  [M+H]<sup>+</sup> 313.0893, found: 313.0891.

#### Methyl 2-(4-fluorophenyl)-4-hydroxy-2*H*-thiochromene-3-carboxylate (1h):

0.582 g, 26% yield (two steps), pale yellow viscous liquid, new compound,  $R_f = 0.50$  (hexanes/

ethyl acetate 20/1), enol/keto = 20.0/1. The enol isomer: 
$$^{1}$$
H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.02 (s, 1H), 8.00-7.93 (m, 1H), 7.30-7.14 (m, 5H), 6.90-6.83 (m, 2H), 5.10 (s, 1H), 3.77 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 166.1, 162.1 (d,  $^{1}J_{F-C}$  = 246.0 Hz), 138.5 (d,  $^{4}J_{F-C}$  = 3.0 Hz), 133.9, 131.5, 128.4, 128.2 (d,  $^{3}J_{F-C}$  = 8.3 Hz), 127.9, 126.5, 125.8, 115.3 (d,  $^{2}J_{F-C}$  = 21.7 Hz), 97.0, 52.4,

131.5, 128.4, 128.2 (d,  ${}^{3}J_{F-C} = 8.3 \text{ Hz}$ ), 127.9, 126.5, 125.8, 115.3 (d,  ${}^{2}J_{F-C} = 21.7 \text{ Hz}$ ), 97.0, 52.4, 39.0.  ${}^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.11. HRMS Calculated for  $C_{17}H_{14}FO_{3}S$  [M+H]<sup>+</sup> 317.0642, found: 317.0643.

## Methyl 2-(4-chlorophenyl)-4-hydroxy-2*H*-thiochromene-3-carboxylate (1i):

0.895 g, 38% yield (two steps), pale yellow viscous liquid, new compound,  $R_{\rm f} = 0.50$  (hexanes/

ethyl acetate 20/1), enol/keto = 14.3/1. The enol isomer: 
$$^{1}$$
H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.02 (s, 1H), 7.98-7.93 (m, 1H), 7.29-7.20 (m, 2H), 7.18-7.09 (m, 5H), 5.08 (s, 1H), 3.77 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 166.2, 141.2, 133.7, 133.2, 131.6, 128.6, 128.3, 128.0, 127.9, 126.6,

125.8, 96.7, 52.4, 39.0. HRMS Calculated for  $C_{17}H_{14}ClO_3S$  [M+H]<sup>+</sup> 333.0347 ( $^{35}Cl$ ) and 335.0321 ( $^{37}Cl$ ), found: 333.0350 ( $^{35}Cl$ ) and 335.0324 ( $^{37}Cl$ ).

#### Methyl 2-(4-bromophenyl)-4-hydroxy-2*H*-thiochromene-3-carboxylate (1j):

1.272 g, 48% yield (two steps), pale yellow viscous liquid, new compound,  $R_{\rm f} = 0.50$  (hexanes/

121.4, 96.6, 52.4, 39.1. HRMS Calculated for  $C_{17}H_{14}BrO_3S$  [M+H]<sup>+</sup> 376.9842 (<sup>79</sup>Br) and 378.9822 (<sup>81</sup>Br), found: 376.9844 (<sup>79</sup>Br) and 378.9832 (<sup>81</sup>Br).

#### Methyl 4-hydroxy-2-(4-methoxyphenyl)-2H-thiochromene-3-carboxylate (1k):

0.555 g, 34% yield (two steps, 1.0 equivalent amount of organocatalyst was used), light yellow liquid, new compound,  $R_f = 0.42$  (hexanes/ethyl acetate 20/1), enol/keto = 11.1/1. The enol isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$   $\rho_{MP}$  13.01 (s, 1H), 7.96 (dd, J = 7.7, 1.5 Hz, 1H), 7.26-7.16 (m, 3H), 7.14-7.07 (m, 2H), 6.76-6.68 (m,

2H), 5.09 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 165.9, 158.9, 134.9, 134.2, 131.4, 128.5, 127.9, 127.7, 126.4, 125.6, 113.8, 97.2, 55.2, 52.3, 39.1. HRMS Calculated for  $C_{18}H_{16}NaO_4S$  [M+Na] $^+$  351.0662, found: 351.0665.

#### Methyl 4-hydroxy-2-methyl-2*H*-thiochromene-3-carboxylate (11):

0.488 g, 42% yield (two steps), pale yellow viscous liquid, new compound,  $R_f = 0.67$  (hexanes/oH O ethyl acetate 20/1), enol/keto = 11.1/1. The enol isomer:  $^1$ H NMR (400 MHz, OMe CDCl<sub>3</sub>)  $\delta$  12.67 (s, 1H), 7.95-7.81 (m, 1H), 7.34-7.26 (m, 2H), 7.24-7.19 (m, 1H), 4.02 (q, J = 6.9 Hz, 1H), 3.86 (s, 3H), 1.35 (d, J = 6.9 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 164.5, 134.6, 131.1, 128.2, 128.0, 126.5, 125.4, 100.0, 52.1, 31.9, 23.1. HRMS Calculated for  $C_{12}H_{16}NO_3S$  [M+NH<sub>4</sub>] $^+$  254.0845, found: 254.0846.

#### Methyl 4-hydroxy-6-nitro-2-phenyl-2*H*-thiochromene-3-carboxylate (1m):

0.296 g, 12% yield (two steps), pale yellow solid, mp 182-183 °C, new compound,  $R_f = 0.34$  OH O (hexanes/ethyl acetate 20/1), enol. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.04 (s, 1H), 8.82 (d, J = 2.5 Hz, 1H), 8.08 (dd, J = 8.7, 2.5 Hz, 1H), 7.30 (d, J = 8.7 Hz, 1H), 7.25-7.08 (m, 5H), 5.25 (s, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 163.8, 145.7, 143.3, 141.8, 128.8, 128.7, 128.2, 128.0, 126.5, 125.4, 121.7, 97.6, 52.7, 40.1. HRMS Calculated for  $C_{17}H_{14}NO_5S$  [M+H]<sup>+</sup> 344.0587, found: 344.0589.

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#### Methyl 4-hydroxy-6-methoxy-2-phenyl-2*H*-thiochromene-3-carboxylate (1n):

0.092 g, 9% yield (two steps), pale yellow viscous liquid, new compound,  $R_f = 0.54$  (hexanes/ethyl acetate 20/1), enol/keto = 12.5/1. The enol isomer:  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.07 (s, 1H), 7.51 (d, J=2.8 Hz, 1H), 7.23-7.10 (m, 5H), 7.06 (d, J=8.6 Hz, 1H), 6.84 (dd, J=8.6, 2.8 Hz, 1H), 5.09 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 166.1, 157.9, 142.6, 129.5, 128.9, 128.4, 127.4, 126.7, 124.8, 118.7, 110.9, 97.5, 55.5, 52.3, 39.6. HRMS Calculated for  $C_{18}H_{16}NaO_4S$  [M+Na] $^+$  351.0662, found: 351.0657.

#### Methyl 4-hydroxy-6-methyl-2-phenyl-2*H*-thiochromene-3-carboxylate (10):

0.994 g, 40% yield (two steps), pale yellow solid, mp 143-144  $^{\circ}$ C, new compound,  $R_f = 0.59$  (he-match of the compound o

#### tert-Butyl 4-hydroxy-2-phenyl-2H-thiochromene-3-carboxylate (1p):

0.250 g, 8% yield (two steps), pale yellow viscous liquid, new compound,  $R_f = 0.62$  (hexanes/ethyl acetate 20/1), enol/keto = 2.5/1. The enol and keto mixture: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.24 (s, 1H, enol), 8.15 (dd, J = 8.0, 1.2 Hz, 1H, keto), 7.95 (dd, J = 7.7, 1.5 Hz, 1H, enol),

7.45-7.16 (m, 16H, enol and keto), 5.05 (s, 1H, enol), 4.93 (d, J = 12.6 Hz, 1H, keto), 4.19 (d, J = 12.6 Hz, 1H, keto), 4.10 (d, J = 12.6 Hz, 1H, ke

27.6. HRMS Calculated for  $C_{20}H_{21}O_3S$  [M+H]<sup>+</sup> 341.1206, found: 341.1203.

## Methyl 2-(benzofuran-2-yl)-4-hydroxy-2*H*-thiochromene-3-carboxylate (1q):

0.732 g, 23% yield (two steps), yellow solid, mp 146-147 °C, new compound,  $R_{\rm f} = 0.51$  (hexanes/

ethyl acetate 20/1), enol. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  13.03 (s, 1H), 7.98 (dd, J = 7.3, 1.8 Hz, 1H), 7.38 (dd, J = 18.4, 8.0 Hz, 2H), 7.27-7.17 (m, 4H), 7.14-7.09 (m, 1H), 6.30 (s, 1H), 5.31 (s, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.5, 166.5, 156.5, 155.1, 133.9, 131.6, 128.2, 128.1, 128.0, 126.8, 125.9, 124.3, 122.7, 120.8, 111.3, 104.8, 94.8, 52.4,

34.4. HRMS Calculated for C<sub>19</sub>H<sub>14</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup> 361.0505, found: 361.0499.

To a solution of thiochromanone derivative **1c** (2.5 mmol, 0.746 g) in toluene (25 mL) was added the piperidine (5.0 mmol, 0.426 g) and 4-dimethylaminopyridine (DMAP) (1.0 mmol, 0.122 g) sequentially. The mixture was refluxed for 24 hours. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure to afford the crude residue. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate/dichloromethane (20/1/1-3/1/1) as eluent to give the desirable thiochromanone derivative with amide **1d**.

#### 2-Phenyl-3-(piperidine-1-carbonyl)thiochroman-4-one (1d):

0.335 g, 38% yield, white solid, mp 202-203  $^{\circ}$ C, new compound,  $R_f = 0.43$  (hexanes/ethyl acetate 3/1), keto.  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 (dd, J = 8.0, 1.3 Hz, 1H), 7.51-7.40 (m, 3H), 7.38-7.26 (m, 4H), 7.25-7.18 (m, 1H), 5.27 (d, J = 12.5 Hz, 1H), 4.54 (d, J = 12.5 Hz, 1H), 3.71-3.55 (m, 1H), 3.53-3.41 (m, 1H), 3.39-3.30 (m, 1H), 3.29-3.11 (m, 1H), 1.65-1.37 (m, 4H), 1.27-1.04 (m, 2H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  192.0, 166.0, 141.5, 137.3, 133.9, 130.5, 129.9, 128.8, 128.5, 128.1, 127.2, 125.5, 58.5, 48.5, 47.5, 43.1, 26.3, 25.5, 24.5. HRMS Calculated for  $C_{21}H_{22}NO_2S$  [M+H] $^+$  352.1366, found: 352.1367.

#### 2.2. Synthesis of Allenylic Carbonates

The allenylic carbonates 2a-2m could be conveniently synthesized from the commercially available propargyl alcohol and aldehydes through two steps according to the known procedure, <sup>3,4</sup> all of which are new compounds. Firstly, the propargyl alcohol underwent copper-catalyzed reactions with aldehydes to provide the intermediate allenylic alcohols. Then, the allenylic carbonates 2 were prepared from the above allenylic alcohol intermediates according to the known literature procedure with slight modification. In addition, allenylic carbonate 2n, a new compound, could be synthesized through two steps according to the known procedure. Firstly, the propargylic dioxolanone 81 underwent copper-catalyzed 8n2 substitution with Grignard reagent to provide the intermediate  $\alpha$ -hydroxyallene. Then, the allenylic carbonate 2n was prepared from the above  $\alpha$ -hydroxyallene intermediate according to the known literature procedure with slight modification.

General Procedure: To a dried Schlenk flask were sequentially added copper dibromide (1.787 g, 8.0 mmol), diphenyl(2-pyrrolidinyl)methanol (5.067 g, 20 mmol), 1,4-dioxane (40 mL), aldehydes (30 mmol), and propargyl alcohol (1.682 g, 30 mmol) under the nitrogen atmosphere. The mixture was stirred in an oil bath preheated at 70 °C or 130 °C for 12-20 h. After cooling to room temperature, the resulting mixture was diluted with diethyl ether (60 mL), which was washed with an aqueous solution of hydrochloric acid (3.0 M, 60 mL). After separation, the aqueous layer was extracted with diethyl ether (60 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (20/1-5/1) as eluent to afford the intermediate allenylic alcohols.

A solution of the above allenylic alcohols (9.7 mmol) and pyridine (2.34 mL, 29.1 mmol) in dichloromethane (25 mL) was cooled to 0 °C. The ethyl chloroformate (1.85 mL, 19.4 mmol) (or isopropyl chloroformate) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature. When the reaction was completed as monitored by TLC, the reaction mixture was acidified with the hydrogen chloride aqueous solution (3.0 M) to pH 5-6 and extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chroma- tography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable allenylic carbonates 2.

#### Ethyl (4-phenylbuta-2,3-dien-1-yl) carbonate (2a):

0.184 g, 24% yield (two steps), yellow liquid, new compound,  $R_f = 0.49$  (hexanes/ethyl acetate 10/1).  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.28 (m, 4H), 7.25-7.14 (m, 1H), 6.37-6.28 (m, 1H), 5.84-5.68 (m, 1H), 4.78-4.67 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.7, 155.0, 133.2, 128.7, 127.4, 127.1, 96.7, 90.8, 65.1, 64.2, 14.3. HRMS Calculated for

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#### Isopropyl (4-phenylbuta-2,3-dien-1-yl) carbonate (2a"):

1.120 g, 45% yield (two steps), yellow liquid, new compound,  $R_f = 0.56$  (hexanes/ethyl acetate 20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.27 (m, 4H), 7.25-7.19 (m, 1H), 6.37-6.26 (m, 1H), 5.83-5.64 (m, 1H), 4.92-4.83 (m, 1H), 4.76-4.66 (m, 2H), 1.30 (d, J = 6.3 Hz, 3H), 1.26 (d, J = 6.3 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.6, 154.5, 133.2, 128.7, 127.4, 127.1, 96.7, 90.9, 72.2, 64.9, 21.8, 21.7. HRMS Calculated for  $C_{14}H_{16}NaO_3$  [M+Na]<sup>+</sup> 255.0992, found: 255.0993.

#### Ethyl (4-(o-tolyl)buta-2,3-dien-1-yl) carbonate (2b):

0.191 g, 4% yield (two steps), yellow liquid, new compound,  $R_f = 0.53$  (hexanes/ethyl acetate Me 20/1).  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39-7.32 (m 1H), 7.18-7.10 (m, 3H), 6.58-6.43 (m, 1H), 5.72 (q, J = 6.7 Hz, 1H), 4.77-4.69 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 155.0, 135.3, 131.4, 130.5, 127.6, 127.4, 126.2, 94.0, 89.8, 65.4, 64.2, 19.9, 14.3. HRMS Calculated for  $C_{14}H_{17}O_{3}$  [M+H] $^+$  233.1172, found: 233.1174.

#### Ethyl (4-(m-tolyl)buta-2,3-dien-1-yl) carbonate (2c):

1.212 g, 26% yield (two steps), yellow liquid, new compound,  $R_f = 0.53$  (hexanes/ethyl acetate 20/1).  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 (t, J = 7.5 Hz, 1H), 7.13-7.07 (m, 2H), 7.04 (d, J = 7.5 Hz, 1H), 6.33-6.25 (m, 1H), 5.80-5.69 (m, 1H), 4.77-4.68 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.7, 155.0, 138.3, 133.0,

128.6, 128.3, 127.7, 124.2, 96.7, 90.6, 65.3, 64.2, 21.4, 14.3. HRMS Calculated for  $C_{14}H_{16}NaO_3$   $[M+Na]^+$  255.0992, found: 255.0994.

Ethyl (4-(p-tolyl)buta-2,3-dien-1-yl) carbonate (2d):

64.2, 21.3, 14.3. HRMS Calculated for  $C_{14}H_{16}KO_3 [M+K]^+ 271.0731$ , found: 271.0732.

#### Ethyl (4-(3-fluorophenyl)buta-2,3-dien-1-yl) carbonate (2e):

1.775 g, 38% yield (two steps), yellow liquid, new compound,  $R_f = 0.44$  (hexanes/ethyl acetate 20/1).  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29-7.26 (m, 1H), 7.06 (d, J = 0.44 (hexanes/ethyl acetate 20/1).  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29-7.26 (m, 1H), 7.06 (d, J = 0.44 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 5.90-5.64 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 5.90-5.64 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 5.90-5.64 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 5.90-5.64 (m, 1H), 4.78-4.68 (m, 2H), 4.20 (q, J = 0.44 (m, 1H), 5.90-5.64 (m, 1H), 6.96-6.86 (m, 1H), 6.36-6.22 (m, 1H), 6.96-6.86 (m, 1H), 6.96-6

(376 MHz, CDCl<sub>3</sub>)  $\delta$  -113.32. The HRMS Calculated for C<sub>13</sub>H<sub>14</sub>FO<sub>3</sub> [M+H]<sup>+</sup> 237.0921, found: 237.0922.

#### 4-(3-Chlorophenyl)buta-2,3-dien-1-yl ethyl carbonate (2f):

2.096 g, 42% yield (two steps), yellow liquid, new compound,  $R_f = 0.39$  (hexanes/ethyl acetate 20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (s, 1H), 7.26-7.14 (m, 3H), 6.31-6.23 (m, 1H), 5.87-5.73 (m, 1H), 4.77-4.69 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  206.8, 154.9, 135.3, 134.6, 129.9, 127.4, 126.9, 125.2, 95.9, 91.3, 64.7, 64.3, 14.3. HRMS Calculated for  $C_{13}H_{17}CINO_3$  [M+NH<sub>4</sub>]<sup>+</sup> 270.0891 (<sup>35</sup>Cl) and 272.0866 (<sup>37</sup>Cl), found: 270.0889 (<sup>35</sup>Cl) and 272.0856 (<sup>37</sup>Cl).

#### 4-(3-Bromophenyl)buta-2,3-dien-1-yl ethyl carbonate (2g):

 $2.252~g,\,38\%$  yield (two steps), yellow liquid, new compound,  $R_{\rm f}=0.38$  (hexanes/ethyl acetate

20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (s, 1H), 7.38-7.30 (m, 1H), 7.23-7.13 (m, 2H), 6.37-6.15 (m, 1H), 5.88-5.69 (m, 1H), 4.77-4.68 (m, 2H), 4.21 (q, 
$$J = 7.1$$
 Hz, 2H), 1.30 (t,  $J = 7.1$  Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.7, 154.9, 135.5, 130.3, 130.1, 129.8, 125.7, 122.8,

95.8, 91.4, 64.7, 64.3, 14.3. HRMS Calculated for  $C_{13}H_{17}BrNO_3$  [M+NH<sub>4</sub>]<sup>+</sup> 314.0386 (<sup>79</sup>Br) and 316.0367 (<sup>81</sup>Br), found: 314.0392 (<sup>79</sup>Br) and 316.0374 (<sup>81</sup>Br).

## Ethyl (4-(3-methoxyphenyl)buta-2,3-dien-1-yl) carbonate (2h):

 $1.390 \ g, \ 28\% \ yield \ (two \ steps), \ yellow \ liquid, \ new \ compound, \ R_{\rm f} = 0.34 \ (hexanes/ethyl \ acetate$ 

MeO Complete MeO MHz, CDCl<sub>3</sub>) 
$$\delta$$
 7.22 (t,  $J$  = 7.9 Hz, 1H), 6.92-6.825 (m, 2H), 6.78 (dd,  $J$  = 8.2, 2.3 Hz, 1H), 6.33-6.22 (m, 1H), 5.83-5.65 (m, 1H), 4.77-4.68 (m, 2H), 4.19 (q,  $J$  = 7.1 Hz,

2H), 3.81 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.7, 159.9, 154.9, 134.6, 129.6, 119.7, 113.3, 112.2, 96.7, 90.9, 65.1, 64.2, 55.2, 14.3. HRMS Calculated for  $C_{14}H_{17}O_4$  [M+H]<sup>+</sup> 249.1121, found: 249.1119.

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#### 4-(3,5-Dimethylphenyl)buta-2,3-dien-1-yl ethyl carbonate (2i):

2.200 g, 45% yield (two steps), pale yellow liquid, new compound,  $R_{\rm f} = 0.45$  (hexanes/ethyl

acetate 20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.91 (s, 2H), 6.86 (s, 1H), 6.27-6.20 (m, 1H), 5.83-5.62 (m, 1H), 4.75-4.68 (m, 2H), 4.24-4.16 (m, 2H), 2.29 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.7, 155.0, 138.2, 132.9, 129.2, 124.9, 96.7,

90.5, 65.3, 64.2, 21.2, 14.3. HRMS Calculated for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub> [M+H]<sup>+</sup> 247.1329, found: 247.1328.

#### 4-([1,1'-Biphenyl]-4-yl)buta-2,3-dien-1-yl ethyl carbonate (2j):

2.123 g, 36% yield (two steps), yellow liquid, new compound,  $R_f = 0.32$  (hexanes/ethyl acetate 20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60-7.53 (m, 4H), 7.45-7.41 (m, 2H), 7.38-7.31 (m, 3H), 6.38-6.33 (m, 1H), 5.86-5.69 (m, 1H), 4.79-4.69 (m, 2H),

4.24-4.17 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.9, 155.0, 140.7, 140.3, 132.2, 128.8, 127.5, 127.4, 127.4, 127.0, 96.4, 90.9, 65.1, 64.2, 14.3. HRMS Calculated for  $C_{19}H_{19}O_3$  [M+H]<sup>+</sup> 295.1329, found: 295.1327.

### Ethyl (4-(naphthalen-2-yl)buta-2,3-dien-1-yl) carbonate (2k):

 $1.834\ g,\ 34\%\ yield\ (two\ steps),\ pale\ yellow\ liquid,\ new\ compound,\ R_{\rm f}=0.57\ (hexanes/ethyl)$ 

acetate 20/1).  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82-7.73 (m, 3H), 7.65 (s, 1H), 7.48-7.38 (m, 3H), 6.57-6.42 (m, 1H), 5.94-5.67 (m, 1H), 4.81-4.71 (m, 2H), 4.25-4.14 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.2, 155.0, 133.6, 132.9, 130.7, 128.4,

127.8, 127.8, 126.4, 126.1, 125.9, 124.7, 97.1, 91.1, 65.2, 64.2, 14.3. HRMS Calculated for  $C_{17}H_{20}NO_3$  [M+NH<sub>4</sub>]<sup>+</sup> 286.1438, found: 286.1437.

#### Ethyl (4-(thiophen-3-yl)buta-2,3-dien-1-yl) carbonate (21):

1.726 g, 38% yield (two steps), yellow liquid, new compound,  $R_f = 0.62$  (hexanes/ethyl acetate 20/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.25 (m, 1H), 7.11 (d, J = 2.8 Hz, 1H), 7.09-7.02 (m, 1H), 6.45-6.33 (m, 1H), 5.77-5.59 (m, 1H), 4.74-4.65 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.0, 154.9, 134.3, 126.4, 126.1, 121.7, 91.3, 90.0, 65.1, 64.2, 14.3. HRMS Calculated for  $C_{11}H_{12}NaO_3S$  [M+Na]<sup>+</sup> 247.0399, found: 247.0401.

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#### Ethyl penta-2,3-dien-1-yl carbonate (2m):

0.408 g, 13% yield (two steps), colorless liquid, new compound,  $R_f = 0.58$  (hexanes/ethyl acetate 20/1).  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.41-5.10 (m, 2H), 4.63-4.56 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.68 (dd, J = 5.7, 4.5 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.5, 155.0, 87.7, 85.9, 66.0, 64.0, 14.3, 13.8. HRMS Calculated for  $C_8H_{13}O_3$  [M+H]<sup>+</sup> 157.0859, found: 157.0859.

To a dried Schlenk flask were sequentially added catalyst Cu(MeCN)<sub>4</sub>BF<sub>4</sub> (0.189 g, 0.6 mmol), (*n*-BuO)<sub>3</sub>P (0.32 mL, 1.2 mmol) and dichloromethane (10 mL) under the nitrogen atmosphere. The mixture was stirred at room temperature for 1 h. After cooling to -10 °C, the methylmagnesium bromide (12 mL, 1.0 M in tetrahydrofuran, 12 mmol) was added and the reaction was stirred for 30 min at -10 °C. Then, a solution of the dioxolanone **S1** (1.129 g, 6 mmol) in dichloromethane (5.0 mL) was added and the reaction mixture was stirred at -10 °C for 22 h. Afterwards, the reaction mixture was quenched with ammonium chloride saturated solution. After separation, the aqueous layer was extracted with diethyl ether (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl

acetate (20/1-10/1) as eluent to afford the intermediate  $\alpha$ -hydroxyallene.

A solution of the above  $\alpha$ -hydroxyallene (0.343 g, 2.1 mmol) and pyridine (0.51 mL, 6.3 mmol) in dichloromethane (10 mL) was cooled to 0 °C. The ethyl chloroformate (0.40 mL, 4.2 mmol) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature. When the reaction was completed as monitored by TLC, the reaction mixture was acidified with the hydrogen chloride aqueous solution (3.0 M) to pH 5-6 and extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (50/1) as eluent to give the desirable allenylic carbonate 2n.

#### Ethyl (4-phenylpenta-2,3-dien-1-yl) carbonate (2n):

0.451 g, 33% yield (two steps), pale yellow liquid, new compound,  $R_f = 0.67$  (hexanes/ethyl acetate 20/1).  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42-7.37 (m, 2H), 7.35-7.29 (m, 2H), 7.25-7.19 (m, 1H), 5.73-5.57 (m, 1H), 4.70 (d, J = 6.8 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.12 (d, J = 2.8 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  205.8, 155.0, 136.0, 128.4, 127.1, 125.9, 102.9, 88.7, 65.7, 64.1, 16.8, 14.3. HRMS Calculated for  $C_{14}H_{20}NO_3$  [M+NH<sub>4</sub>]<sup>+</sup> 250.1438, found: 250.1443.

#### 3. Palladium-Catalyzed Asymmetric Allenylic Alkylation

The metal precursor Pd(dba)<sub>2</sub> (0.02 mmol, 11.5 mg, 10 mol%), ligand (*R*)-DTB-BIPHEP (**L4**) (0.022 mmol, 22.7 mg, 11 mol%) and tetrahydrofuran (1.5 mL) were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at 30 °C for 30 min. Then the mixture was cooled to -20 °C. Thereafter, the thiochromanone derivatives **1** (0.2 mmol), 5Å MS (50.0 mg) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (35.9 μL, 0.24 mmol) were added and the reaction was stirred at -20 °C for 10 minutes. Sequentially, the allenylic carbonates **2** (0.3 mmol) and tetrahydrofuran (0.5 mL) were added slowly. The mixture was stirred at -20 °C for 72-168 h. After the completion of the reaction, the volatiles were directly removed under the reduced pressure. The residue was quickly purified by column chromatography on silica gel (hexanes/ethyl acetate/dichloromethane 100/1/2-100/3/6) to give the desirable allenylic alkylation products **3**.

The racemates were prepared by running reactions with an achiral 1,3-bis(diphenylphosphino)-propane ligand at 30 °C. It was worth noting that the products 3 were sensitive to water or alcohol, which would lead to partial decrease of dr value.

### (-)-Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ca):

The reaction was conducted at -20  $^{\circ}$ C for 72 h. 78.5 mg, 92% yield, pale yellow viscous liquid, new compound,  $R_f = 0.28$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),  $[\alpha]_D^{20} = -209.67$  (c 0.63, CHCl<sub>3</sub>). The major diastereoisomer:  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17

(d, 
$$J = 7.9$$
 Hz, 1H), 7.43-7.31 (m, 6H), 7.27-7.22 (m, 4H), 7.20-7.10 (m, 3H), 6.22-5.96 (m, 1H), 5.66-5.43 (m, 1H), 4.98 (s, 1H), 3.65 (s, 3H), 3.22-3.02 (m, 1H), 2.73-2.51 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.4, 169.7, 141.5, 135.6, 133.9, 133.2, 130.8,

130.5, 129.2, 128.9, 128.6, 128.5, 127.3, 127.1, 126.8, 125.5, 95.5, 89.9, 62.7, 52.4, 51.1, 32.5. HPLC: Chiralpak IC column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 15.0 min (minor) and 16.0 min (major). HRMS Calculated for the  $C_{27}H_{23}O_3S$  [M+H]<sup>+</sup> 427.1362, found: 427.1372.

The mixtrue with low 2.3:1 dr: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, J = 7.9 Hz, 1H, major),

7.88 (d, 
$$J = 7.9$$
 Hz, 1H, minor),  
7.40-7.12 (m, 26H, major + minor),  
6.16-6.01 (m, 2H, major + minor),  
5.62-5.45 (m, 2H, major + minor),  
5.09 (s, 1H, minor), 4.98 (s, 1H,

major), 3.65 (s, 6H, major + minor), 3.18-3.04 (m, 2H, major + minor), 2.67-2.53 (m, 2H, major + minor).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 207.2, 192.4, 192.2, 169.7, 169.7, 141.5, 141.0, 135.7, 135.6, 133.9, 133.8, 133.2, 133.0, 130.8, 130.8, 130.5, 130.4, 129.2, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 125.5, 125.4, 95.9, 95.5, 90.0,

#### (-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(o-tolyl)thiochromane-3-carboxylate (3ea):

The reaction was conducted at -20 °C for 120 h. 71.9 mg, 82% yield, pale yellow viscous liquid, new compound,  $R_f = 0.36$  (hexanes/ethyl acetate 20/1), 24.0:1 dr, 98% ee (major diastereoisomer),

 $[\alpha]_{D}^{20} = -25.30$  (c 0.83, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (dd, J = 8.0, 1.3 Hz, 1H), 7.52 (d, J= 7.7 Hz, 1H), 7.42-7.34 (m, 1H), 7.29-7.09 (m, 10H), 6.00-5.85 (m, 1H), 5.65-5.43 (m, 1H), 5.04 (s, 1H), 3.62 (s, 3H), 3.15-3.00 (m, 1H), 2.84-2.69 (m, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

207.0, 192.1, 170.1, 141.3, 136.4, 134.9, 134.1, 133.2, 130.9, 130.8, 130.5, 128.5, 128.5, 128.1, 127.1, 127.0, 126.9, 126.4, 125.4, 94.9, 89.9, 62.0, 52.5, 47.0, 32.8, 20.3. HPLC: Chiralpak ID column, 254 nm, 30 °C, n-Hexane/i-PrOH = 97/3, flow = 1.0 mL/min, retention time 13.9 min (major) and 16.6 min. HRMS Calculated for  $C_{28}H_{24}NaO_3S$  [M+Na]<sup>+</sup> 463.1338, found: 463.1341.

#### (-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(m-tolyl)thiochromane-3-carboxylate(3fa):

The reaction was conducted at -20 °C for 120 h. 78.1 mg, 89% yield, pale yellow viscous liquid, new compound,  $R_f = 0.36$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),

 $[\alpha]_{D}^{20} = -241.32$  (c 0.90, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24-8.10 (m, 1H), 7.42-7.37 (m, 1H), 7.27-7.13 (m, 10H), 6.19-6.00 (m, 1H), 5.60-5.41 (m, 1H), 4.97 (s, 1H), 3.65 (s, 3H), 3.22-3.03 (m, 1H), 2.69-2.52 (m, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.5, 192.5, 169.7, 141.7, 138.1,

135.3, 134.0, 133.2, 130.8, 130.5, 130.1, 129.7, 128.6, 128.4, 127.3, 127.1, 126.8, 126.1, 125.5, 95.5, 90.0, 62.7, 52.3, 51.1, 32.4, 21.5. HPLC: Chiralcel OD-3 column, 254 nm, 30 °C, n-Hexane/ i-PrOH = 95/5, flow = 0.8 mL/min, retention time 10.2 min and 23.6 min (major). HRMS Calculated for C<sub>28</sub>H<sub>24</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup> 463.1338, found: 463.1342.

#### (-)-Methyl 4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)-2-(p-tolyl)thiochromane-3-carboxylate(3ga):

The reaction was conducted at -20 °C for 120 h. 79.3 mg, 90% yield, pale yellow viscous liquid, new compound,  $R_f = 0.36$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),

 $[\alpha]_{D}^{20} = -226.76$  (c 0.93, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31-8.04 (m, 1H), 7.43-7.37 (m, 1H), 7.27-7.22 (m, 6H), 7.20-7.11 (m, 5H), 6.21-6.00 (m, 1H), 5.61-5.41 (m, 1H), 4.96 (s, 1H), 3.65 (s, 3H), 3.16-3.03 (m, 1H), 2.64-2.55 (m, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.4, 192.6,

169.8, 141.7, 138.8, 134.0, 133.2, 132.4, 130.9, 130.5, 129.2, 129.0, 128.6, 127.3, 127.0, 126.9, 125.5, 95.5, 89.9, 62.8, 52.4, 50.9, 32.4, 21.2. HPLC: Chiralpak IA, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/ min, retention time 13.6 min and 17.4 min (major). HRMS Calculated for C<sub>28</sub>H<sub>24</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup> 463.1338, found: 463.1340.

(-)-Methyl 2-(4-fluorophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxy-

late (3ha): The reaction was conducted at -20 °C for 120 hours. 83.4 mg, 94% yield, pale yellow

viscous liquid, new compound,  $R_f = 0.40$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major diastereoisomer),  $[\alpha]_D^{20} = -215.33$  (c 0.73, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (dd, J = 8.0, 1.2 Hz, 1H), 7.44-7.34 (m, 3H), 7.27-7.22 (m, 4H), 7.20-7.12 (m, 3H), 7.07-6.96 (m, 2H), 6.18-5.97 (m, 1H), 5.63-5.41 (m, 1H), 4.95 (s, 1H), 3.65 (s, 3H), 3.17- 3.04 (m, 1H), 2.63-2.50 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.1, 169.7, 162.8 (d,  $^{1}J_{F-C}$  = 248.6 Hz), 141.2, 133.8, 133.3, 131.4 (d,

 $^4J_{\text{F-C}}$  = 3.4 Hz), 131.0, 131.0, 130.8, 130.5, 128.6, 127.2 (d,  $^3J_{\text{F-C}}$  = 8.9 Hz), 126.8, 125.7, 115.5 (d,  $^2J_{\text{F-C}}$  = 21.6 Hz), 95.6, 89.8, 62.6, 52.4, 50.3, 32.4.  $^{19}\text{F}$  NMR (376 MHz, CDCl<sub>3</sub>) δ -112.38. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.6 min and 15.7 min (major). HRMS Calculated for  $C_{27}H_{21}\text{FNaO}_3\text{S}$  [M+Na]<sup>+</sup> 467.1088, found: 467.1087.

#### (-)-Methyl 2-(4-chlorophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxy-

late (3ia): The reaction was conducted at -20  $^{\circ}$ C for 120 hours. 88.3 mg, 96% yield, pale yellow viscous liquid, new compound,  $R_f = 0.40$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major

diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -200.57$  (c 1.03, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, J = 7.9 Hz, 1H), 7.44-7.38 (m, 1H), 7.35-7.28 (m, 4H), 7.27-7.21 (m, 4H), 7.19-7.13 (m, 3H), 6.19-5.99 (m, 1H), 5.60-5.40 (m, 1H), 4.93 (s, 1H), 3.64 (s, 3H), 3.17-3.04 (m, 1H), 2.64-2.53 (m, 1H).  $^{13}$ C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  207.4, 192.0, 169.6, 141.0, 134.8, 134.1, 133.8, 133.4, 130.8, 130.6, 130.5, 128.7, 128.6, 127.3, 127.2, 126.9, 125.7, 95.6, 89.8, 62.5, 52.5, 50.5, 32.5. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 10.2 min and 16.5 min (major). HRMS Calculated for  $C_{27}H_{21}ClNaO_3S$  [M+Na]<sup>+</sup> 483.0792 ( $^{35}Cl$ ) and 485.0773 ( $^{37}Cl$ ), found: 483.0793 ( $^{35}Cl$ ) and 485.0792 ( $^{37}Cl$ ).

(-)-Methyl 2-(4-bromophenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxy-

late (3ja): The reaction was conducted at -20  $^{\circ}$ C for 120 hours. 94.5 mg, 93% yield, pale yellow viscous liquid, new compound,  $R_f = 0.40$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major

CO<sub>2</sub>Me

diastereoisomer),  $\left[\alpha\right]_{D}^{20} = -186.71$  (*c* 1.10, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (dd, J = 8.0, 1.2 Hz, 1H), 7.51-7.35 (m, 3H), 7.28-7.21 (m, 6H), 7.19-7.13 (m, 3H), 6.14-6.00 (m, 1H), 5.57-5.44 (m, 1H), 4.91 (s, 1H), 3.64 (s, 3H), 3.17-3.04 (m, 1H), 2.62-2.52 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

207.4, 192.0, 169.6, 141.0, 134.6, 133.8, 133.4, 131.7, 130.9, 130.7, 130.5, 128.6, 127.3, 127.2, 126.9, 125.7, 123.0, 95.6, 89.8, 62.5, 52.5, 50.5, 32.5. HPLC: Chiralcel OD-H column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 11.1 min (minor) and 17.2 min (major). HRMS Calculated for  $C_{27}H_{21}BrNaO_3S$  [M+Na] $^+$  527.0287 ( $^{79}Br$ ) and 529.0270 ( $^{81}Br$ ), found: 527.0292 ( $^{79}Br$ ) and 529.0275 ( $^{81}Br$ ).

(-)-Methyl 2-(4-methoxyphenyl)-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carbo-xylate (3ka): The reaction was conducted at -20  $^{\circ}$ C for 72 h. 76.9 mg, 84% yield, pale yellow viscous liquid, new compound,  $R_f = 0.23$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major

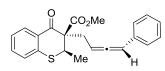
diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -208.12$  (c 1.07, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21-8.09 (m, 1H), 7.43-7.34 (m, 1H), 7.33-7.27 (m, 2H), 7.26-7.20 (m, 4H),

7.19-7.13 (m, 3H), 6.89-6.81 (m, 2H), 6.15-6.00 (m, 1H), 5.59-5.43 (m, 1H), 4.93 (s, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 3.15-3.01 (m, 1H), 2.65-2.52 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.4, 192.6, 169.8, 159.8, 141.8, 134.0, 133.2, 130.8, 130.5, 130.4, 128.6, 127.4, 127.2, 127.0, 126.9, 125.5, 113.8, 95.4, 89.9, 62.8, 55.3, 52.4, 50.5,

32.4. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 94/6, flow = 1.0 mL/min, retention time 13.3 min (minor) and 26.0 min (major). HRMS Calculated for  $C_{28}H_{24}NaO_4S$  [M+Na]<sup>+</sup> 479.1288, found: 479.1291.

#### (-)-Methyl 2-methyl-4-oxo-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3la):

The reaction was conducted at -20  $^{\circ}$ C for 72 h. 68.2 mg, 94% yield, pale yellow viscous liquid, new compound,  $R_f = 0.45$  (hexanes/ethyl acetate 20/1), 9.0:1 dr, 99% ee (major diastereoisomer),



 $[\alpha]^{20}_{D} = -87.47$  (*c* 0.95, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, J = 7.6 Hz, 1H), 7.41-7.34 (m, 1H), 7.30-7.14 (m, 7H), 6.29-5.97 (m, 1H), 5.65-5.35 (m, 1H), 3.84 (q, J = 6.9 Hz, 1H), 3.63 (s, 3H), 3.39-3.24 (m, 1H), 2.92-2.77 (m,

1H), 1.61 (d, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.1, 191.7, 170.2, 141.3, 134.0, 133.0, 130.7, 130.4, 128.6, 127.2, 127.1, 126.9, 125.3, 95.0, 89.3, 61.7, 52.4, 41.8, 31.1, 15.6. HPLC: Chiralpak IC column, 254 nm, 30 °C, n-Hexane/i-PrOH = 99/1, flow = 1.0 mL/min, retention time 19.7 min (major) and 22.0 min. HRMS Calculated for  $C_{22}H_{21}O_3S$  [M+H]<sup>+</sup> 365.1206, found: 365.1209.

(-)-Methyl 6-nitro-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3ma): The reaction was conducted at -20  $^{\circ}$ C for 120 h. 86.1 mg, 91% yield, pale yellow viscous liquid, new compound,  $R_f = 0.18$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major

O<sub>2</sub>N CO<sub>2</sub>Me

diastereoisomer),  $[\alpha]_D^{20} = -207.17$  (*c* 1.10, CHCl<sub>3</sub>). The major diastereoisomer:  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 (d, J = 2.5 Hz, 1H), 8.16 (dd, J = 8.7, 2.6 Hz, 1H), 7.40-7.32 (m, 6H), 7.24-7.19 (m, 2H), 7.18-7.08 (m, 3H), 6.15-5.99 (m, 1H), 5.62-

5.48 (m, 1H), 5.07 (s, 1H), 3.66 (s, 3H), 3.22-3.07 (m, 1H), 2.63-2.52 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.5, 190.5, 168.9, 149.7, 145.6, 134.2, 133.6, 130.9, 129.4, 129.2, 128.8, 128.6, 128.1, 127.2, 126.7, 126.7, 125.7, 96.2, 89.3, 62.1, 52.6, 51.0, 32.0. HPLC: Chiralpak IB column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 85/15, flow = 1.0 mL/min, retention time 11.4 min and 18.6 min (major). HRMS Calculated for  $C_{27}H_{22}NO_5S$  [M+H] $^+$  472.1213, found: 472.1218.

(-)-Methyl 6-methoxy-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate (3na): The reaction was conducted at -20 °C for 120 h. 78.8 mg, 86% yield, yellow viscous liquid, new compound,  $R_f = 0.21$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),  $[\alpha]_D^{20} = -234.07$  (c 0.93, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, J = 2.9 Hz, 1H), 7.39-7.29 (m, 5H), 7.25- 7.21 (m, 2H), 7.19-7.09 (m, 4H), 7.05-6.98 (m, 1H), 6.15-6.04 (m, 1H), 5.59-5.43 (m, 1H), 4.96 (s, 1H), 3.84 (s, 3H), 3.65 (s, 3H), 3.19-3.06 (m, 1H), 2.66-2.54 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.5, 169.8,

157.8, 135.7, 133.9, 133.0, 131.6, 129.1, 128.8, 128.6, 128.6, 128.5, 127.1, 126.9, 122.3, 112.6, 95.5, 89.9, 62.8, 55.6, 52.4, 51.5, 32.5. HPLC: Chiral- pak AD-3, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 90/10, flow = 0.8 mL/min, retention time 18.2 min and 19.4 min (major). HRMS Calculated for

 $C_{28}H_{25}O_4S$  [M+ H]<sup>+</sup> 457.1468, found: 457.1466.

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# (-)-Methyl 6-methyl-4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxy-late (3oa): The reaction was conducted at -20 $^{\circ}$ C for 120 hours. 82.9 mg, 94% yield, pale yellow viscous liquid, new compound, $R_f = 0.31$ (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major

Me CO<sub>2</sub>Me

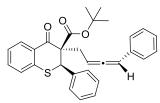
diastereoisomer),  $[\alpha]^{20}_{D} = -225.21$  (c 0.88, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00-7.94 (m, 1H), 7.39-7.30 (m, 5H), 7.26-7.21 (m, 3H), 7.20-7.11 (m, 4H), 6.15-6.02 (m, 1H), 5.59-5.45 (m, 1H), 4.96 (s, 1H), 3.64 (s, 3H), 3.17-3.06 (m, 1H), 2.64-2.55 (m, 1H), 2.36 (s, 3H).  $^{13}$ C NMR

(100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.7, 169.8, 138.2, 135.7, 135.5, 134.4, 134.0, 130.6, 129.1, 128.8, 128.5, 128.5, 127.2, 127.0, 126.9, 95.4 89.9, 62.8, 52.3, 51.3, 32.5, 21.0. HPLC: Chiralpak AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 96/4, flow = 1.0 mL/min, retention time 22.0 min and 25.0 min (major). HRMS Calculated for  $C_{28}H_{25}O_{3}S$  [M+H]<sup>+</sup> 441.1519, found: 441.1516.

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## $(\textbf{-})\textbf{-}t\textbf{-}\textbf{Butyl} \ \ \textbf{4}\textbf{-}\textbf{oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)} thio chromane-3-carboxylate \ \ (\textbf{3pa}):$

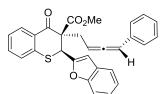
The reaction was conducted at -20  $^{\circ}$ C for 120 h. 88.7 mg, 95% yield, pale yellow viscous liquid, new compound,  $R_f = 0.40$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),



 $\left[\alpha\right]^{20}_{D} = -182.51$  (*c* 1.03, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (dd, J = 8.2, 1.5 Hz, 1H), 7.50-7.43 (m, 2H), 7.40-7.31 (m, 4H), 7.26-7.13 (m, 7H), 6.17-6.01 (m, 1H), 5.56-5.41 (m, 1H), 4.92 (s, 1H), 3.19-3.03 (m, 1H), 2.62-2.41 (m, 1H), 1.32 (s, 9H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.4,

168.1, 141.7, 135.5, 134.2, 132.8, 131.2, 130.3, 129.6, 128.8, 128.5, 128.4, 126.9, 126.9, 126.8, 125.2, 95.2, 90.1, 83.2, 62.2, 51.3, 32.0, 27.7. HPLC: Chiralpak AD-3 column, 254 nm, 30 °C, n-Hexane/i-PrOH = 96/4, flow = 0.8 mL/min, the retention time 11.2 min and 13.5 min (major). HRMS Calculated for  $C_{30}H_{28}NaO_{3}S$  [M+Na]<sup>+</sup> 491.1651, found: 491.1656.

# (+)-Methyl 2-(benzofuran-2-yl)-4-oxo-3-(-4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carbo-xylate (3qa): The reaction was conducted at -20 $^{\circ}$ C for 72 h. 79.1 mg, 85% yield, pale yellow viscous liquid, new compound, $R_f = 0.32$ (hexanes/ethyl acetate 20/1), 5.7:1 dr, 97% ee (major



diastereoisomer),  $\left[\alpha\right]^{20}_{D} = +33.29$  (c 0.82, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (dd, J = 8.0, 1.1 Hz, 1H), 7.53-7.47 (m, 1H), 7.43-7.37 (m, 2H), 7.28-7.16 (m, 9H), 6.75 (s, 1H), 6.14-6.01 (m, 1H), 5.65-5.52 (m, 1H), 5.14 (s, 1H), 3.65 (s, 3H), 3.28-3.16 (m, 1H), 2.97-2.85 (m, 1H).  $^{13}$ C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  207.7, 190.9, 169.5, 154.3, 152.6, 139.9, 133.8, 133.5, 130.5, 130.4, 128.6, 128.0, 127.3, 127.1, 126.9, 125.8, 124.7, 123.0, 121.3, 111.2, 106.1, 95.3, 89.2, 61.3, 52.7, 44.6, 32.9. HPLC: Chiralpak AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 93/7, flow = 1.0 mL/min, the

retention time 19.8 min and 22.3 min (major). HRMS Calculated for  $C_{29}H_{23}O_4S$  [M+H]<sup>+</sup> 467.1312, found: 467.1320.

#### (+)-3-Acetyl-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochroman-4-one (3ba):

The reaction was conducted at 30  $^{\circ}$ C for 48 hours with commercially available (1*R*,1'*R*,2*S*,2'*S*)-DuanPhos as the chiral ligand. 49.8 mg, 61% yield, pale yellow viscous liquid, new compound, R<sub>f</sub>

= 0.35 (hexanes/ethyl acetate 20/1), 24.0:1 dr, 74% ee (major isomer),  $[\alpha]^{20}_{D}$  = +0.69 (c 0.58, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (dd, J = 8.0, 1.2 Hz, 1H), 7.46- 7.41 (m, 1H), 7.30-7.23 (m, 9H), 7.21-7.14 (m, 3H), 6.18-6.03 (m, 1H), 5.48-5.37 (m, 1H), 4.86 (s, 1H), 3.24-3.13 (m, 1H), 2.80-2.70 (m,

1H), 2.11 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 205.2, 194.4, 140.8, 137.1, 133.9, 133.8, 130.9, 130.2, 128.8, 128.7, 128.6, 128.5, 127.4, 127.1, 126.8, 125.7, 95.5, 89.6, 67.1, 51.2, 33.7, 31.5. HPLC: Chiralcel OD-H column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.4 min and 11.5 min (major). HRMS Calculated for  $C_{27}H_{23}O_{2}S$  [M+ H]<sup>+</sup> 411.1413, found: 411.1415. Notably, the absolute and relative configurations of this allenylic alkylation product were not further assigned.

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#### 2-Phenyl-3-(4-phenylbuta-2,3-dien-1-yl)-3-(piperidine-1-carbonyl)thiochroman-4-one (3da):

The reaction was conducted at -20  $^{\circ}$ C for 168 h and the *rac*-**3da** was prepared with *rac*-BINAP at -20  $^{\circ}$ C. 32.3 mg, 34% yield, pale yellow viscous liquid, new compound,  $R_f = 0.52$  (hexanes/ethyl

acetate 5/1), 24.0:1 dr, >99% ee (major diastereoisomer),  $\left[\alpha\right]^{20}_{D}$  = -49.90 (c 1.08, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (dd, J = 7.9, 1.2 Hz, 1H), 7.51-7.43 (m, 1H), 7.37-7.33 (m, 1H), 7.33-7.28 (m, 3H), 7.27-7.21 (m, 7H), 7.19-7.14 (m, 1H), 6.22-6.02 (m, 1H), 5.71-5.55 (m, 1H), 4.87 (s, 1H), 4.04-

3.14 (m, 2H), 3.14-2.13 (m, 4H), 1.50-1.37 (m, 4H), 1.37-1.10 (m, 2H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.7, 192.6, 167.3, 140.5, 137.9, 134.3, 133.7, 131.8, 130.1, 129.1, 128.6, 128.5, 128.3, 127.8, 126.9, 126.9, 126.1, 94.6, 91.0, 63.0, 52.1, 38.5, 24.9, 24.3. HPLC: Chiralpak IB column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 94/6, flow = 1.0 mL/min, retention time 13.1 min and 20.6 min (major). HRMS Calculated for  $C_{31}H_{30}NO_{2}S$  [M+H] $^{+}$  480.1992, found: 480.2000.

(-)-Methyl (2R,3S)-3-((R)-4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-6-nitro-4-oxo-2-phenylthio-chromane-3-carboxylate (3mk): The reaction was conducted at -20 °C for 168 h. 91.3 mg, 88% yield, pale yellow solid, mp 197-198 °C, new compound,  $R_f = 0.12$  (hexanes/ethyl acetate 20/1),

32.3:1 dr, >99% ee (major diastereoisomer),  $\left[\alpha\right]^{20}_{D} =$  -223.76 (*c* 1.14, CHCl<sub>3</sub>). The major diaster reoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.92 (d, J = 2.5 Hz, 1H), 8.03 (dd, J = 8.7, 2.5 Hz, 1H), 7.75-7.65 (m, 3H), 7.47 (s, 1H), 7.45-7.35 (m, 7H), 7.31 (dd, J = 8.5, 1.4 Hz, 1H), 7.24-7.21

(m, 1H), 6.33-6.18 (m, 1H), 5.70-5.55 (m, 1H), 5.11 (s, 1H), 3.65 (s, 3H), 3.28-3.11 (m, 1H), 2.66-2.50 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  208.1, 190.5, 168.9, 149.6, 145.5, 134.2, 133.5, 132.6, 131.1, 130.8, 129.5, 129.2, 128.8, 128.3, 128.1, 127.7, 127.7, 126.5, 126.4, 125.9, 125.7, 125.6, 124.5, 96.6, 89.6, 62.2, 52.7, 51.0, 32.0. HPLC: Chiralpak IB column, 254 nm, 30 °C,

n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 12.7 min (minor) and 22.5 min (major). HRMS Calculated for  $C_{31}H_{24}NO_5S$  [M+H]<sup>+</sup> 522.1370, found: 522.1377.

#### Methyl 4-oxo-2-phenyl-3-(4-(o-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cb):

The reaction was conducted at -20  $^{\circ}$ C for 72 h. 81.7 mg, 93% yield, pale yellow viscous liquid, new compound,  $R_f = 0.43$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),

 $[\alpha]^{20}_{D} = -193.32$  (*c* 0.96, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (dd, J = 8.2, 1.4 Hz, 1H), 7.48-7.21 (m, 9H), 7.20-7.03 (m, 3H), 6.47-6.18 (m, 1H), 5.61-5.38 (m, 1H), 4.99 (s, 1H), 3.64 (s, 3H), 3.23-3.01 (m, 1H), 2.68-2.53 (m, 1H),

2.24 (s, 3H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  208.0, 192.4, 169.7, 141.6, 135.6, 135.0, 133.3, 132.2, 130.8, 130.5, 130.4, 129.2, 128.9, 128.5, 127.5, 127.3, 127.0, 126.1, 125.6, 92.8, 88.9, 62.7, 52.4, 51.2, 32.5, 19.8. HPLC: Chiralcel OD-H column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 10.1 min and 25.1 min (major). HRMS Calculated for  $C_{28}H_{24}NaO_3S$  [M+Na] $^+$  463.1338, found: 463.1342.

#### (-)-Methyl -oxo-2-phenyl-3-(4-(*m*-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate(3cc):

The reaction was conducted at -20  $^{\circ}$ C for 72 h. 86.1 mg, 98% yield, pale yellow viscous liquid, new compound,  $R_f = 0.43$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major diastereoisomer),

[ $\alpha$ ]<sup>20</sup><sub>D</sub> = -213.13 (c 0.70, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23-8.11 (m, 1H), 7.44-7.31 (m, 6H), 7.26-7.22 (m, 2H), 7.16-7.10 (m, 1H), 7.01-6.95 (m, 3H), 6.16-5.97 (m, 1H), 5.59-5.42 (m, 1H), 4.99 (s, 1H), 3.65 (s, 3H), 3.19-3.07 (m, 1H), 2.65-2.55 (m, 1H), 2.28 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

207.4, 192.4, 169.7, 141.5, 138.1, 135.6, 133.8, 133.2, 130.9, 130.5, 129.1, 128.9, 128.5, 128.5, 127.9, 127.5, 127.3, 125.5, 124.0, 95.6, 89.7, 62.7, 52.3, 51.1, 32.5, 21.3. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.7 min and 21.8 min (major). HRMS Calculated for  $C_{28}H_{24}NaO_3S$  [M+Na] $^+$  463.1338, found: 463.1341.

#### (-)-Methyl 4-oxo-2-phenyl-3-(4-(p-tolyl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cd):

The reaction was conducted at -20  $^{\circ}$ C for 72 h. 84.5 mg, 96% yield, pale yellow viscous liquid, new compound,  $R_f = 0.43$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major diastereoisomer),

 $\left[\alpha\right]^{20}_{D} = -193.85 \ (c\ 0.57,\ CHCl_{3}).$  The major diastereoisomer:  $^{1}H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.22-8.11 (m, 1H), 7.43-7.31 (m, 6H), 7.26-7.22 (m, 2H), 7.12-7.01 (m, 4H), 6.19-5.94 (m, 1H), 5.59-5.40 (m, 1H), 4.99 (s, 1H), 3.65 (s, 3H), 3.19-3.04 (m, 1H), 2.66-2.54 (m, 1H), 2.30 (s, 3H).  $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.2,

192.5, 169.7, 141.5, 136.8, 135.6, 133.2, 130.9, 130.9, 130.5, 129.3, 129.1, 128.9, 128.5, 127.3, 126.7, 125.5, 95.4, 89.7, 62.7, 52.3, 51.1, 32.6, 21.2. HPLC: Chiralcel OD-H column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 9.6 min and 18.8 min (major). HRMS Calculated for  $C_{28}H_{24}NaO_3S$  [M+Na] $^+$  463.1338, found: 463.1342.

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(-)-Methyl 3-(4-(3-fluorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxy-late (3ce): The reaction was conducted at -20  $^{\circ}$ C for 120 hours. 83.7 mg, 94% yield, pale yellow viscous liquid, new compound,  $R_f = 0.38$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major

diastereoisomer),  $[\alpha]_D^{20} = -179.28$  (c 0.85, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20-8.13 (m, 1H), 7.43-7.32 (m, 6H), 7.27-7.17 (m, 3H), 6.98-6.92 (m, 1H), 6.91-6.80 (m, 2H), 6.16-5.95 (m, 1H), 5.69-5.48 (m, 1H), 4.94 (s,

1H), 3.65 (s, 3H), 3.20-3.02 (m, 1H), 2.69-2.47 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.6, 192.3, 169.6, 163.1 (d,  $^{1}J_{F-C} = 245.2$  Hz), 141.5, 136.5 (d,  $^{3}J_{F-C} = 7.7$  Hz), 135.5, 133.3, 130.8, 130.5, 129.9 (d,  $^{3}J_{F-C} = 8.3$  Hz), 129.2, 128.9, 128.5, 127.2, 125.6, 122.6 (d,  $^{4}J_{F-C} = 2.7$  Hz), 113.9 (d,  $^{2}J_{F-C} = 21.3$  Hz), 113.4 (d,  $^{2}J_{F-C} = 22.4$  Hz), 94.8 (d,  $^{4}J_{F-C} = 2.5$  Hz), 90.4, 62.6, 52.4, 51.3, 32.4.  $^{19}$ F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -113.49. HPLC: Chiralcel OD-3 column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 0.8 mL/min, retention time 12.3 min and 35.0 min (major). HRMS Calculated for  $C_{27}H_{21}$ FNaO<sub>3</sub>S [M+Na]<sup>+</sup> 467.1088, found: 467.1084.

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(-)-Methyl 3-(4-(3-chlorophenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3cf): The reaction was conducted at -20 °C for 120 hours 83.1 mg 90% yield pale yellow

late (3cf): The reaction was conducted at -20  $^{\circ}$ C for 120 hours. 83.1 mg, 90% yield, pale yellow viscous liquid, new compound,  $R_f = 0.38$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major

diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -188.92$  (c 0.84, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21-8.14 (m, 1H), 7.44- 7.32 (m, 6H), 7.27-7.23 (m, 2H), 7.20-7.10 (m, 3H), 7.08-7.01 (m, 1H), 6.16-5.92 (m, 1H), 5.67-5.51 (m, 1H), 4.93 (s, 1H), 3.65 (s, 3H), 3.17-3.06 (m, 1H), 2.65-2.55 (m, 1H).

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.6, 192.3, 169.6, 141.5, 136.1, 135.5, 134.5, 133.3, 130.8, 130.5, 129.7, 129.2, 129.0, 128.5, 127.2, 127.0, 126.7, 125.6, 125.0, 94.6, 90.4, 62.6, 52.4, 51.3, 32.4. HPLC: Chiralcel OD-3 column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 95/5, flow = 0.8 mL/min, retention time 12.7 min (minor) and 37.3 min (major). HRMS Calculated for C<sub>27</sub>H<sub>22</sub>ClO<sub>3</sub>S [M+H]<sup>+</sup> 461.0973 (<sup>35</sup>Cl) and 463.0953 (<sup>37</sup>Cl), found: 461.0969 (<sup>35</sup>Cl) and 463.0938 (<sup>37</sup>Cl).

 $(\hbox{--})\hbox{--}Methyl \hbox{--}3\hbox{--}(4\hbox{--}(3\hbox{--}bromophenyl) but a-2,} \hbox{--}3\hbox{--}dien-1\hbox{--}yl)\hbox{--}4\hbox{--}oxo-2\hbox{--}phenyl thiochromane-3-carboxy-1-2.}$ 

late (3cg): The reaction was conducted at -20  $^{\circ}$ C for 120 hours. 94.4 mg, 93% yield, pale yellow viscous liquid, new compound,  $R_f = 0.38$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 98% ee (major

diastereoisomer),  $[\alpha]_D^{20} = -173.55$  (*c* 0.87, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (dd, J = 7.8, 1.0 Hz, 1H), 7.43-7.23 (m, 10H), 7.15-7.05 (m, 2H), 6.15-5.93 (m, 1H), 5.73-5.50 (m, 1H), 4.93 (s, 1H), 3.65 (s, 3H), 3.23-3.01

(m, 1H), 2.72-2.48 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.6, 192.3, 169.6, 141.5, 136.3, 135.5, 133.3, 130.8, 130.5, 130.0, 129.9, 129.6, 129.2, 129.0, 128.6, 127.3, 125.6, 125.4, 122.8, 94.5, 90.5, 62.6, 52.4, 51.3, 32.4. HPLC: Chiralcel OD-3 column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-Pr-OH = 95/5, flow = 0.8 mL/min, retention time 13.1 min and 39.9 min (major). HRMS Calculated for  $C_{27}H_{22}BrO_3S$  [M+H] $^+$  505.0468 ( $^{79}Br$ ) and 507.0450 ( $^{81}Br$ ), found: 505.0471 ( $^{79}Br$ ) and 507.0454 ( $^{81}Br$ ).

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(-)-Methyl 3-(4-(3-methoxyphenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carbo-xylate (3ch): The reaction was conducted at -20  $^{\circ}$ C for 72 hours. 84.6 mg, 93% yield, pale yellow viscous liquid, new compound,  $R_f = 0.20$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 99% ee (major

diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -192.34$  (c 1.02, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.27-8.04 (m, 1H), 7.42-7.29 (m, 6H), 7.25-7.21 (m, 2H), 7.17-7.12 (m, 1H), 6.80-6.67 (m, 3H), 6.11-5.99 (m, 1H), 5.61-5.42 (m, 1H), 4.98 (s, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.17- 3.05 (m, 1H),

2.65-2.54 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 192.4, 169.7, 159.9, 141.5, 135.6, 135.4, 133.2, 130.8, 130.5, 129.5, 129.2, 128.9, 128.5, 127.3, 125.5, 119.5, 113.1, 111.9, 95.6, 90.0, 62.7, 55.2, 52.3, 51.2, 32.4. HPLC: Chiralcel OD-3 column, 254 nm, 30 °C, n-Hexane/i-PrOH = 94/6, flow = 0.8 mL/ min, retention time 14.7 min and 32.0 min (major). HRMS Calculated for  $C_{28}H_{25}O_4S$  [M+H] $^+$  457.1468, found: 457.1473.

(-)-Methyl 3-(4-(3,5-dimethylphenyl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-car-

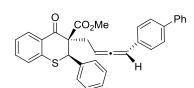
**boxylate** (3ci): The reaction was conducted at -20  $^{\circ}$ C for 120 h. 89.1 mg, 98% yield, pale yellow viscous liquid, new compound,  $R_f = 0.33$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major

diastereoisomer),  $\left[\alpha\right]_{D}^{20} = -195.93$  (c 0.74, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25-8.08 (m, 1H), 7.43-7.29 (m, 6H), 7.26-7.22 (m, 2H), 6.87-6.72 (m, 3H), 6.13-5.92 (m, 1H), 5.57-5.39 (m, 1H), 5.00 (s, 1H), 3.65 (s, 3H), 3.25-3.06 (m, 1H), 2.66-2.53 (m, 1H), 2.24 (s, 6H).  $^{13}$ C NMR

(100 MHz, CDCl<sub>3</sub>)  $\delta$  207.5, 192.4, 169.8, 141.5, 138.0, 135.6, 133.7, 133.2, 130.9, 130.5, 129.1, 128.8, 128.5, 127.3, 125.5, 124.7, 95.7, 89.5, 62.7, 52.3, 51.0, 32.5, 21.2. HPLC: Chiralcel OD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 96/4, flow = 1.0 mL/min, retention time 9.3 min and 20.1 min (major). HRMS Calculated for  $C_{29}H_{27}O_3S$  [M+H]<sup>+</sup> 455.1675, found: 455.1682.

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(-)-Methyl 3-(4-([1,1'-biphenyl]-4-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-car-boxylate (3cj): The reaction was conducted at -20  $^{\circ}$ C for 120 h. 96.2 mg, 96% yield, pale yellow viscous liquid, new compound,  $R_f = 0.31$  (hexanes/ethyl acetate 20/1), 49.0:1 dr, 99% ee (major



diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -186.99$  (*c* 1.10, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.22-8.12 (m, 1H), 7.58-7.53 (m, 2H), 7.50-7.45 (m, 2H), 7.43-7.30 (m, 9H), 7.26-7.22 (m, 4H), 6.22-6.04 (m, 1H), 5.66-5.48 (m, 1H), 5.00 (s, 1H), 3.65 (s, 3H), 3.21-3.03 (m, 1H), 2.69-2.56 (m, 1H).

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.6, 192.4, 169.7, 141.5, 140.8, 139.9, 135.6, 133.3, 133.0, 130.8, 130.5, 129.2, 128.9, 128.8, 128.5, 127.3, 126.9, 125.6, 95.2, 90.0, 62.7, 52.4, 51.2, 32.5. HPLC: Chiralpak ID + IC column, 254 nm, 30 °C, *n*-Hexane/*i*-PrOH = 94/6, flow = 1.0 mL/min, retention time 43.1 min (major) and 47.4 min (minor). HRMS Calculated for  $C_{33}H_{27}O_{3}S$  [M+H]<sup>+</sup> 503.1675, found: 503.1673.

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(-)-Methyl 3-(4-(naphthalen-2-yl)buta-2,3-dien-1-yl)-4-oxo-2-phenylthiochromane-3-carboxylate (3ck): The reaction was conducted at -20 °C for 120 h. 90.4 mg, 95% yield, pale yellow viscous liquid, new compound, R<sub>f</sub> = 0.30 (hexanes/ethyl acetate 20/1), 24.0:1 dr, 99% ee (major

diastereoisomer),  $\left[\alpha\right]_{D}^{20} = -160.81$  (c 1.10, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (dd, J = 7.9, 1.1 Hz, 1H), 7.76-7.67 (m, 3H), 7.55-7.52 (m, 1H), 7.45-7.31 (m, 9H), 7.24-7.19 (m, 2H), 6.35-6.16 (m, 1H), 5.69-5.50 (m, 1H), 5.01 (s, 1H), 3.64 (s, 3H), 3.23-3.07 (m, 1H), 2.70-

2.59 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.0, 192.4, 169.7, 141.5, 135.6, 133.6, 133.2, 132.7, 131.5, 130.8, 130.5, 129.2, 128.9, 128.5, 128.2, 127.7, 127.7, 127.3, 126.2, 125.7, 125.6, 124.8, 95.9, 90.2, 62.8, 52.4, 51.2, 32.6. HPLC: Chiralpak IC column, 254 nm, 30 °C, n-Hexane/ i-PrOH = 94/6, flow = 1.0 mL/min, retention time 20.5 min (minor) and 22.8 min (major). HRMS Calculated for  $C_{31}H_{28}NO_3S$  [M+NH<sub>4</sub>]<sup>+</sup> 494.1784, found: 494.1777.

(-)-Methyl 4-oxo-2-phenyl-3-(4-(thiophen-3-yl)buta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cl): The reaction was conducted at -20 °C for 120 h. 78.2 mg, 90% yield, pale yellow viscous liquid, new compound,  $R_f = 0.32$  (hexanes/ethyl acetate 20/1), 32.3:1 dr, 98% ee (major diaste-

reoisomer),  $\left[\alpha\right]_{D}^{20} = -187.60$  (c 0.92, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22-8.13 (m, 1H), 7.42-7.32 (m, 6H), 7.25-7.18 (m, 3H), 6.99-6.91 (m, 2H), 6.31-5.97 (m, 1H), 5.52-5.41 (m, 1H), 4.97 (s, 1H), 3.64 (s, 3H), 3.15-3.05 (m, 1H), 2.63-2.54 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.6, 192.4,

169.7, 141.5, 135.6, 135.1, 133.2, 130.8, 130.5, 129.2, 128.9, 128.5, 127.3, 126.3, 125.9, 125.5, 121.0, 90.1, 89.1, 62.7, 52.3, 51.1, 32.6. HPLC: Chiralcel OD-3 column, 254 nm, 30 °C, n-Hexane /i-PrOH = 93/7, flow = 0.8 mL/min, retention time 11.9 min (minor) and 25.4 min (major). HRMS Calculated for  $C_{25}H_{24}NO_3S_2$  [M+NH<sub>4</sub>]<sup>+</sup> 450.1192, found: 450.1182.

#### (-)-Methyl 4-oxo-3-(penta-2,3-dien-1-yl)-2-phenylthiochromane-3-carboxylate (3cm):

The reaction was conducted at -20 °C for 120 h. 39.3 mg, 54% yield, pale yellow viscous liquid, new compound,  $R_f = 0.39$  (hexanes/ethyl acetate 20/1), 7.3:1 dr, 97% ee (major diastereoisomer),

 $\left[\alpha\right]^{20}_{D} = -173.75$  (c 0.85, CHCl<sub>3</sub>). The major diastereoisomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29-8.02 (m, 1H), 7.44-7.31 (m, 6H), 7.28-7.22 (m, 2H), 5.08-4.92 (m, 3H), 3.66 (s, 3H), 3.06-2.95 (m, 1H), 2.52-2.40 (m, 1H), 1.55-1.48 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.0, 192.6, 169.8, 141.4, 135.7, 133.1, 131.0, 130.4, 129.1, 128.8, 128.4,

127.3, 125.5, 86.8, 85.2, 63.0, 52.3, 50.7, 32.6, 14.1. HPLC: Chiralpak AD-3 column, 254 nm, 30 °C, n-Hexane/i-PrOH = 97/3, flow = 0.8 mL/min, retention time 18.8 min and 19.8 min (major). HRMS Calculated for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 365.1206, found: 365.1208.

(-)-Methyl 4-oxo-2-phenyl-3-(4-phenylpenta-2,3-dien-1-yl)thiochromane-3-carboxylate (3cn):

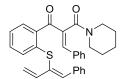
The reaction was conducted at 30 °C for 120 h. 63.7 mg, 72% yield, pale yellow viscous liquid, new compound,  $R_f = 0.41$  (hexanes/ethyl acetate 20/1), 6.7:1 dr, 90% ee (major diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -109.42 \ (c\ 0.88,\ CHCl_{3}).$  The major diastereoisomer:  $^{1}H\ NMR\ (400\ MHz,\ CDCl_{3})\ \delta\ 8.17$  (dd,  $J=7.9,\ 1.1\ Hz,\ 1H),\ 7.41-7.37\ (m,\ 1H),\ 7.36-7.29\ (m,\ 5H),\ 7.28-7.12\ (m,\ 7H),\ 5.45-5.32\ (m,\ 7H)$ 

1H), 5.01 (s, 1H), 3.62 (s, 3H), 3.22-3.10 (m, 1H), 2.65-2.50 (m, 1H), 1.99 (d, J = 2.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.8, 192.3, 169.8, 141.4, 136.7, 135.9, 133.2, 130.7, 130.4, 128.9, 128.8, 128.5, 128.3, 127.3, 126.9, 125.8, 125.4, 101.9, 87.7, 62.7, 52.3, 50.4, 32.7, 16.9. HPLC: Chiralpak AD-H column, 254 nm, 30 °C,

n-Hexane/i-Pr- OH = 96/4, flow = 1.0 mL/min, retention time 14.0 min and 17.1 min (major). HRMS Calculated for  $C_{28}H_{24}NaO_3S$  [M+Na] $^+$  463.1338, found: 463.1346.

#### The Chemo- or Regioselective Isomers with the Different EWG

**2-Benzylidene-1-(2-((1-phenylbuta-1,3-dien-2-yl)thio)phenyl)-3-(piperidin-1-yl)propane-1,3-dione (4'da):** 46.1 mg, 48% yield, yellow viscous liquid, new compound,  $R_f = 0.18$  (hexanes/ethyl acetate 5/1), 16.7/1 (Z/E or E/Z). The major diastereoisomer:  $^1H$  NMR (400 MHz, CDCl $_3$   $\delta$  7.56-



7.42 (m, 4H), 7.41-7.26 (m, 10H), 7.09 (s, 1H), 7.00 (s, 1H), 6.83 (dd, J = 16.8, 10.5 Hz, 1H), 5.74 (d, J = 16.8 Hz, 1H), 5.28 (d, J = 10.6 Hz, 1H), 3.89-3.62 (m, 2H), 3.57-3.26 (m, 2H), 1.77-1.45 (m, 5H), 1.20-0.96 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  194.7, 165.5, 143.8, 139.2, 137.2, 136.1,

134.4, 133.4, 133.2, 131.7, 131.2, 130.8, 130.6, 130.0, 129.4, 129.0, 128.9, 128.4, 127.9, 126.3, 120.1, 47.8, 42.4, 26.1, 25.3, 24.6. HRMS Calculated for  $C_{31}H_{30}NO_2S$  [M+H]<sup>+</sup> 480.1992, found: 480.2001. (The Z/E configuration of carbon-carbon double bond is not further assigned)

#### (-)-2-Nitro-3-phenyl-1-(2-((4-phenylbuta-2,3-dien-1-yl)thio)phenyl)prop-2-en-1-one (4aa):

The reaction was conducted at 30 °C for 24 h with L1. 59.3 mg, 72% yield, pale yellow viscous

liquid, new compound,  $R_f=0.26$  (hexanes/ethyl acetate 20/1), 84% ee, single isomer,  $\left[\alpha\right]^{20}_{D}=$  -178.56 (c 0.63, CHCl<sub>3</sub>).  $^{1}H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.67-8.48 (m, 1H), 7.61-7.50 (m, 3H), 7.48-7.18 (m, 10H), 7.18-7.12 (m, 1H), 6.15-6.01 (m, 1H), 5.90-5.75 (m, 1H), 3.47-3.32 (m, 2H).  $^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  205.8, 179.7, 149.9, 137.5, 136.3, 134.6, 132.8, 131.3, 130.5, 129.5,

129.2, 128.7, 128.6, 128.5, 127.4, 126.8, 126.7, 125.6, 95.6, 93.5, 28.6. HPLC: Chiralpak IA column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 94/6, flow = 1.0 mL/min, retention time 15.2 min and 16.2 min (major). HRMS Calculated for  $C_{25}H_{19}KNO_3S$  [M+K] $^+$  452.0717, found: 452.0731. (The absolute configuration of allene moiety is not further assigned)

S21

#### 4. Scale-up Synthesis

The metal precursor Pd(dba)<sub>2</sub> (0.26 mmol, 0.150 g), the chiral ligand (*R*)-DTB-BIPHEP (**L4**) (0.286 mmol, 0.295 g) and tetrahydrofuran (23 mL) were placed in a dried Schlenk tube under nitrogen atmosphere. The mixture was stirred at 30 °C for 30 min. Then, the mixture was cooled to -20 °C. Then, the substrate thiochromanone **1c** (2.6 mmol, 0.776 g), 5Å MS (0.650 g) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 3.12 mmol, 0.47 mL) were added, and the reaction was stirred at -20 °C for 10 minutes. Sequentially, allenylic carbonate **2a** (3.9 mmol, 0.851 g) and tetrahydrofuran (3.0 mL) were added slowly. The mixture was stirred at -20 °C for 168 hours. After the completion of the reaction, the volatiles were directly removed under the reduced pressure. The crude residue was quickly purified by column chromatography on silica gel (hexanes/ethyl acetate /dichloromethane 100/1/2-100/3/6) to give the chiral allenylic alkylation product **3ca** 0.987 g, 89% isolated yield, 24.0:1 dr and 99% ee for the major diastereoisomer.

The racemate was prepared by running reaction with an achiral 1,3-bis(diphenylphosphino)-propane ligand at 30 °C. Notably, the product **3ca** was a little sensitive to water or alcohol, which would lead to slight decrease of dr value.

#### 5. Product Elaborations

#### 5.1. The Oxidation of Sulfide

At -78 °C, to a solution of (-)-3ca (85.3 mg, 0.2 mmol, 99% ee) in dichloromethane (3.0 mL) was added 3-chloroperoxybenzoic acid (*m*-CPBA) (60.9 mg, 0.3 mmol, 85%) in dichloromethane (2.0 mL). The mixture was stirred at -78 °C for 48 hours. Then, to the reaction mixture was added a solution of *m*-CPBA (60.9 mg, 0.3 mmol, 85%) in dichloromethane (10 mL). The mixture was stirred at -78 °C for another 48 hours. After that, it was quenched with aqueous sodium bicarbonate and warmed to room temperature. The aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (5/1-3/1) as eluent to give the oxidative product sulfoxide 5.

**Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 1-oxide** (**5**): 71.7 mg, 81% yield, colorless viscous liquid, new compound,  $R_f = 0.23$  (hexanes/ethyl acetate 3/1), 19.0:1 dr, 99% ee (major diastereoisomer),  $[α]_D^{20} = -357.57$  (c 1.00, CHCl<sub>3</sub>). The major diastereoisomer:  ${}^1$ H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.45-7.34 (m, 5H), 7.25-7.06 (m, 5H), 6.17-6.01 (m, 1H), 5.38-5.26 (m, 1H), 4.82 (s, 1H), 3.76 (s, 3H), 3.44-3.29 (m, 1H), 2.51-2.37 (m, 1H).  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.5, 190.8, 169.0, 147.6, 135.0, 133.3, 131.2, 129.9, 129.6, 129.6, 129.4, 129.1, 128.6, 127.3, 126.9, 96.1, 88.4, 70.5, 63.6, 53.1, 32.5. HPLC: Chiralpak AD-3 column, 254 nm, 30  ${}^{\circ}$ C, n-Hexane/i-PrOH = 70/30, flow = 0.7 mL/min, retention time 27.6 min (major) and 32.7 min. HRMS Calculated for  $C_{27}H_{22}NaO_4S$  [M+Na] $^+$  465.1131, found: 465.1139.

At room temperature, to a solution of (-)-3ca (85.3 mg, 0.2 mmol, 99% ee) in dichloromethane (3.0 mL) was added m-CPBA (121.8 mg, 0.6 mmol, 85%) in dichloromethane (2.0 mL). The mixture was stirred for 24 hours. Then, the reaction mixture was quenched with saturated sodium bicarbonate aqueous solution, and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate (5/1) as eluent to give the oxidative product sulfone 6.

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(-)-Methyl 4-oxo-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 1,1-dioxide (6): 60.9 mg, 66% yield, colorless viscous liquid, new compound,  $R_f = 0.51$  (hexanes/ ethyl acetate 3/1), 11.5:1 dr, 99% ee (major diastereoisomer),  $[\alpha]^{20}_{D} = -135.23$  (c 1.05, CHCl<sub>3</sub>). The major diastereoisomer:  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33-8.20 (m, 1H), 8.03-7.96 (m, 1H), 7.84-7.72 (m, 2H), 7.64-7.53 (m, 2H), 7.49-7.38 (m, 3H), 7.25-7.10 (m, 3H), 7.12-7.05 (m, 2H), 6.08-5.93 (m, 1H), 5.49-5.38 (m, 1H), 5.11 (s, 1H), 3.69 (s, 3H), 3.31-3.17 (m, 1H), 2.64-2.50 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.4, 189.6, 169.0, 141.6, 134.7, 133.4, 133.2, 131.8, 130.7, 130.2, 129.4, 128.7, 128.7, 127.4, 126.8, 125.7, 123.9, 96.5, 88.8, 68.3, 63.1, 53.3, 33.9. HPLC: Chiralpak IC column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 65/35, flow = 0.8 mL/min, retention time 22.8 min and 40.9 min (major). HRMS Calculated for  $C_{27}H_{22}NaO_5S$  [M+Na] $^+$  481.1080, found: 481.1078.

#### 5.2. The Hydrogenation of Allenyl Functional Group

To a solution of the chiral allenylic alkylation product (-)-3ca (42.7 mg, 0.1 mmol, 99% ee) in ethyl acetate (1.0 mL) was added 10% Pd/C (5.3 mg, 0.005 mmol). The resulting mixture was degassed and stirred under hydrogen gas balloon pressure for about 13 hours at 25  $^{\circ}$ C. After the completion of hydrogenation, the volatiles were removed under the reduced pressure. The crude residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate (30/1-20/1) as eluent to give the desirable allene hydrogenation product (2*R*,3*S*)-(+)-7.

#### (2R,3S)-(+)-Methyl 4-oxo-2-phenyl-3-(4-phenylbutyl)thiochromane-3-carboxylate (7):

40.8 mg, 95% yield, colorless liquid, new compound,  $R_f = 0.28$  (hexanes/ethyl acetate 20/1), 97% ee,  $[\alpha]^{20}_D = +14.31$  (c 1.02, CHCl<sub>3</sub>).  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (dd, J = 8.2, 1.3 Hz, 1H), 7.43-7.37 (m, 1H), 7.33-7.22 (m, 9H), 7.18-7.09 (m, 3H), 4.68 (s, 1H), 3.61 (s, 3H), 2.62-2.44 (m, 2H), 2.17-2.05 (m, 1H), 1.93-1.80 (m, 1H), 1.63-1.48 (m, 3H), 1.27-1.17 (m, 1H).  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.7, 170.4, 142.4, 141.3, 136.1, 133.1, 130.9, 130.4, 129.0, 128.7, 128.5, 128.4, 128.3, 127.2, 125.7, 125.5, 62.6, 52.2, 51.9, 35.5, 32.8, 31.8, 24.2. HPLC: Chiralpak AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 95/5, flow = 1.0 mL/min, retention time 11.7 min and 14.4 min (major). HRMS Calculated for  $C_{27}H_{26}NaO_3S$  [M+Na] +453.1495, found: 453.1503.

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#### 5.3. The Reduction of Carbonyl Functional Group

To a solution of lithium aluminium tetrahydride (15.2 mg, 0.4 mmol) in diethyl ether (7.0 mL) at -78 °C, the chiral compound (-)-3ca (85.3 mg, 0.2 mmol, 99% ee) and diethyl ether (1.0 mL) were added. The mixture was stirred at -78 °C for 5 hours. The reaction was quenched with 0.5 M potassium sodium tartrate aqueous solution (1.0 mL) and warmed to room temperature. After filtration through the celite, the combined organic layer was dried over sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate (20/1-10/1) as eluent to afford the desirable ketone carbonyl reductive product (-)-8.

The relative configuration of the hydroxyl group of the reductive product  $\bf 8$  was assigned as S by NOE.

(-)-Methyl 4-hydroxy-2-phenyl-3-(4-phenylbuta-2,3-dien-1-yl)thiochromane-3-carboxylate 8: 58.8 mg, 69% yield, colorless liquid, new compound,  $R_f = 0.48$  (hexanes/ethyl acetate 5/1), 13.3:1 dr, 99% ee (major diastereoisomer),  $\left[\alpha\right]^{20}_{D} = -33.73$  (c 0.83, CHCl<sub>3</sub>). The major diastereoisomer:  $^{1}$ H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, J = 7.5 Hz, 1H), 7.49-7.42 (m, 2H), 7.29-7.17 (m, 11H), 6.15-6.08 (m, 1H), 5.56-5.53 (m, 1H), 5.17 (d, J = 6.3 Hz, 1H), 4.58 (s, 1H), 3.55 (s, 3H), 3.43 (d, J = 6.4 Hz, 1H), 2.87-2.82 (m, 1H), 2.52-2.48 (m, 1H).  $^{13}$ C NMR (175 MHz, CDCl<sub>3</sub>)  $\delta$  207.0, 173.6, 138.6, 133.9, 133.9, 132.7, 130.4, 130.2, 128.6, 128.3, 127.9, 127.7, 127.1, 126.9, 125.8, 125.2, 94.8, 89.4, 72.3, 55.4, 52.0, 50.1, 36.4. HPLC: Chiralpak IA + AS-H column, 254 nm, 30  $^{\circ}$ C, n-Hexane/i-PrOH = 95/5, flow = 0.8 mL/min, retention time 62.0 min and 72.2 min (major). HRMS Calculated for  $C_{27}H_{24}$  NaO<sub>3</sub>S [M+Na]<sup>+</sup> 451.1338, found: 451.1335.

## The NOE Result of Carbonyl Reduction (-)-8

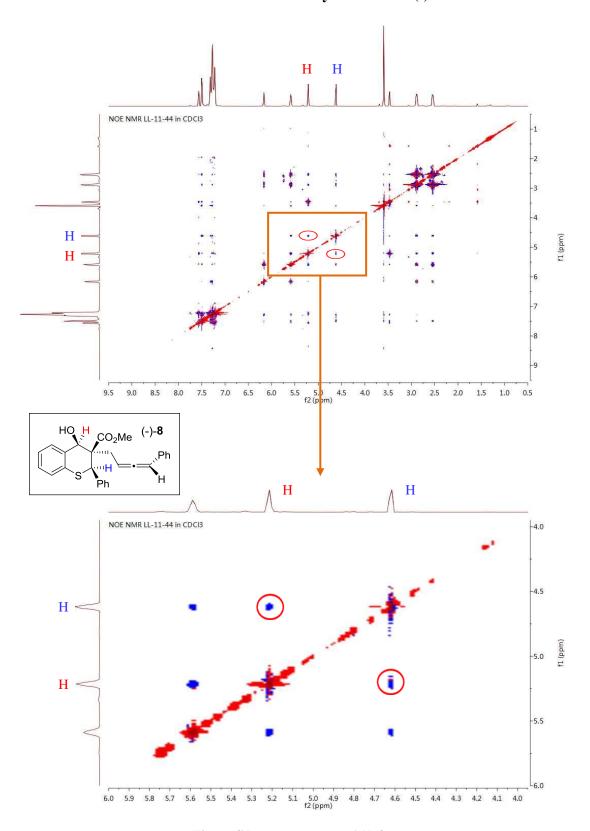


Figure S1. NOE spectrum of (-)-8

#### 6. Determination of Absolute Configuration

To determine the absolute configuration of (-)-methyl 3-(4-(naphthalen-2-yl)buta-2,3 -dien-1-yl) -6-nitro-4-oxo-2-phenylthiochromane-3-carboxylate (3mk, 32.3:1 dr, >99% ee): (-)-3mk was completely dissolved in dichloromethane (2.0 mL), and n-hexane (2.0 mL) was added slowly at room temperature. The solvent diffused slowly, and the single crystal was obtained after about 36 hours. The structure in **Figure S2** showed the absolute configuration is (2R,3S,R<sub>a</sub>). The CCDC number is 2214958. These details can be obtained free of charge via www.ccdc.com.ac.uk/data\_request/cif from the Cambridge Crystallographic Data Centre.

Figure S2. X-Ray Structure of (-)- $(2R,3S,R_a)$ -3mk

#### Crystal Data and Structure Refinement for mo\_d8v22443\_0m for (-)-(2R,3S,Ra)-3mk

Identification code mo\_d8v22443\_0m

Empirical formula C<sub>31</sub>H<sub>23</sub>NO<sub>5</sub>S

Formula weight 521.56Temperature 213(2) KWavelength 0.71073 Å

Crystal system Orthorhombic

Space group P 21 21 21

Unit cell dimensions a = 6.8379(3) Å  $\alpha = 90^{\circ}$ 

b = 16.3952(5) Å  $\beta$  = 90 ° c = 22.7541(8) Å  $\gamma$  = 90 °

Volume 2550.93(16) Å<sup>3</sup>

Z

Density (calculated) 1.358 Mg/m<sup>3</sup>
Absorption coefficient 0.170 mm<sup>-1</sup>

F(000) 1088

Crystal size  $0.200 \times 0.150 \times 0.120 \text{ mm}^3$ 

Theta range for data collection 2.641 to 25.997 °.

Index ranges -8<=h<=8, -20<=k<=18, -28<=l<=28

Reflections collected 22409

Independent reflections 5005 [R(int) = 0.0593]

Completeness to theta =  $25.242^{\circ}$  99.4 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.5174

Refinement method Full-matrix least-squares on F<sup>2</sup>

Data / restraints / parameters 5005 / 0 / 344

Goodness-of-fit on F2 1.025

Final R indices [I>2sigma(I)] R1 = 0.0366, wR2 = 0.0887 R indices (all data) R1 = 0.0415, wR2 = 0.0925

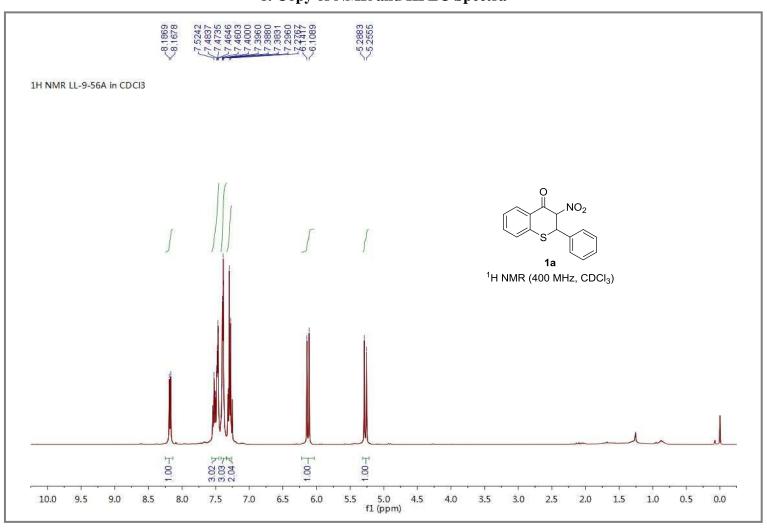
Absolute structure parameter 0.02(4)
Extinction coefficient n/a

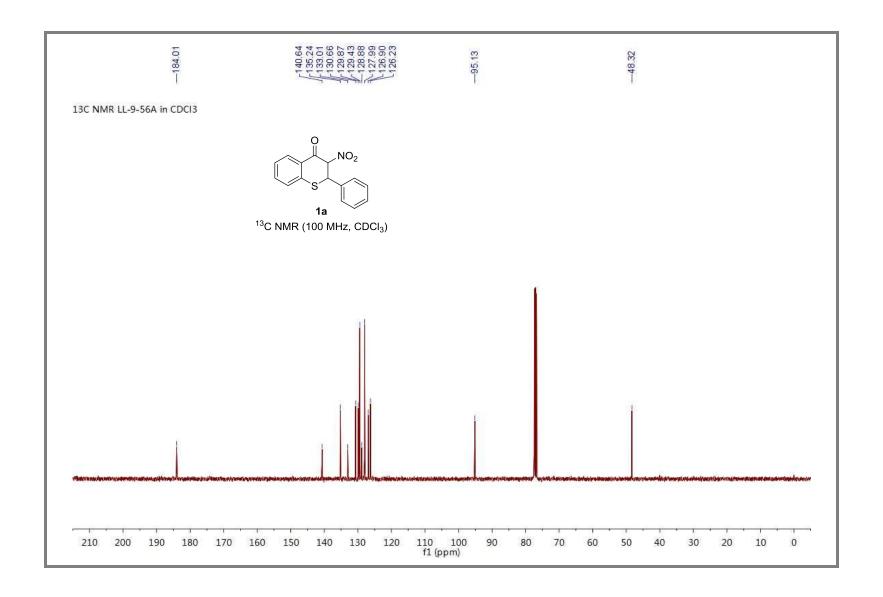
Largest diff. peak and hole 0.187 and -0.168 e.Å<sup>-3</sup>

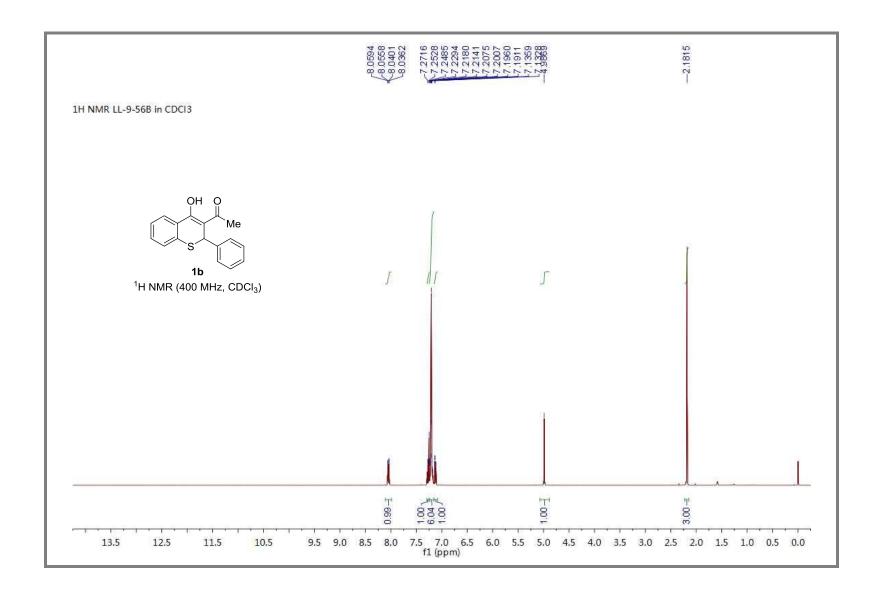
#### 7. References

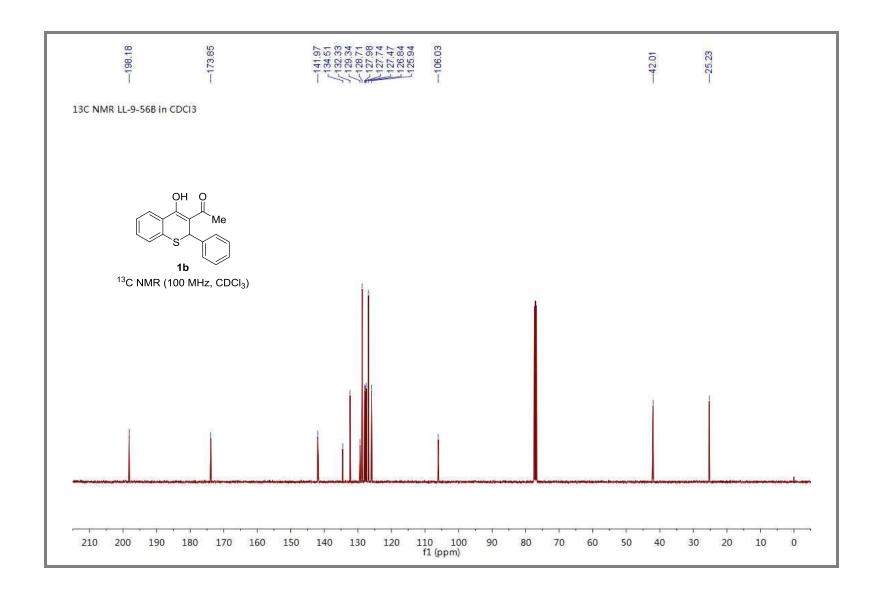
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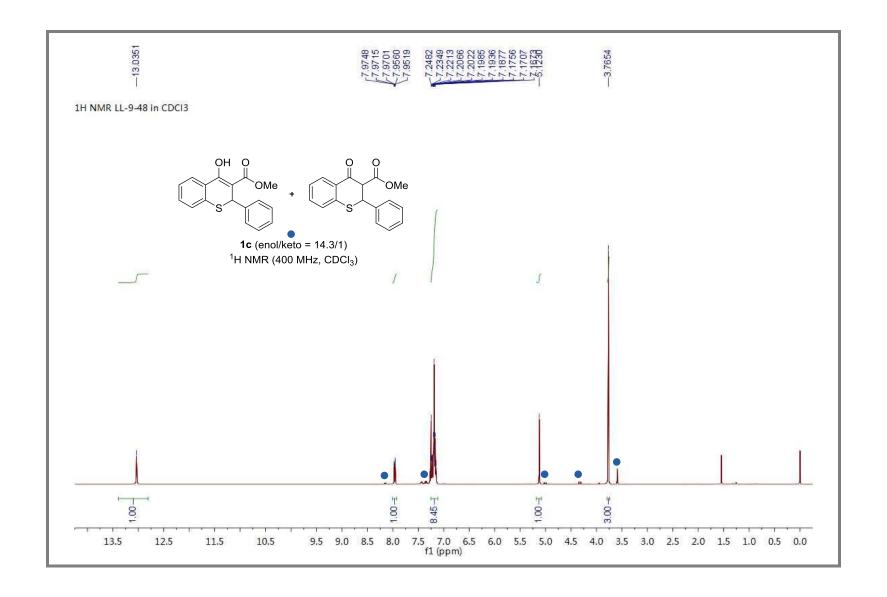
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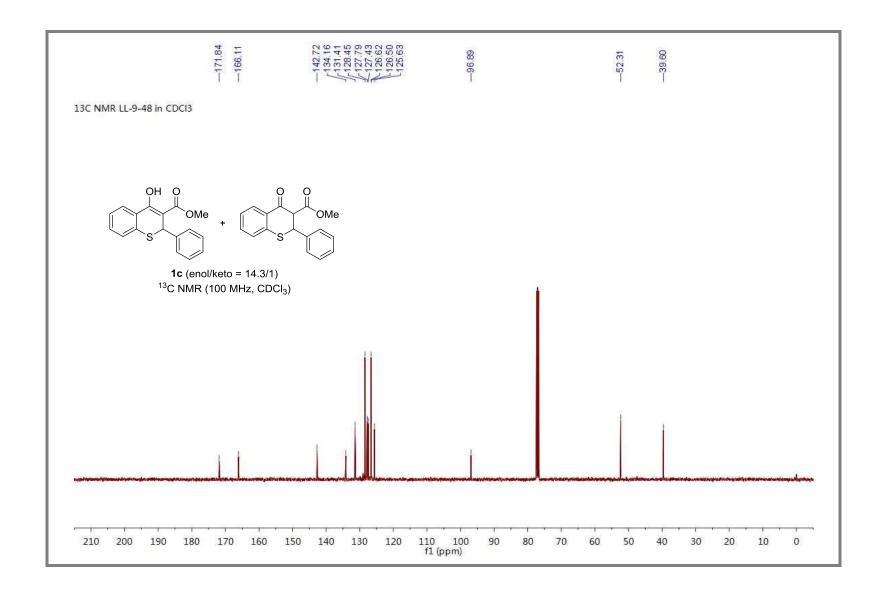


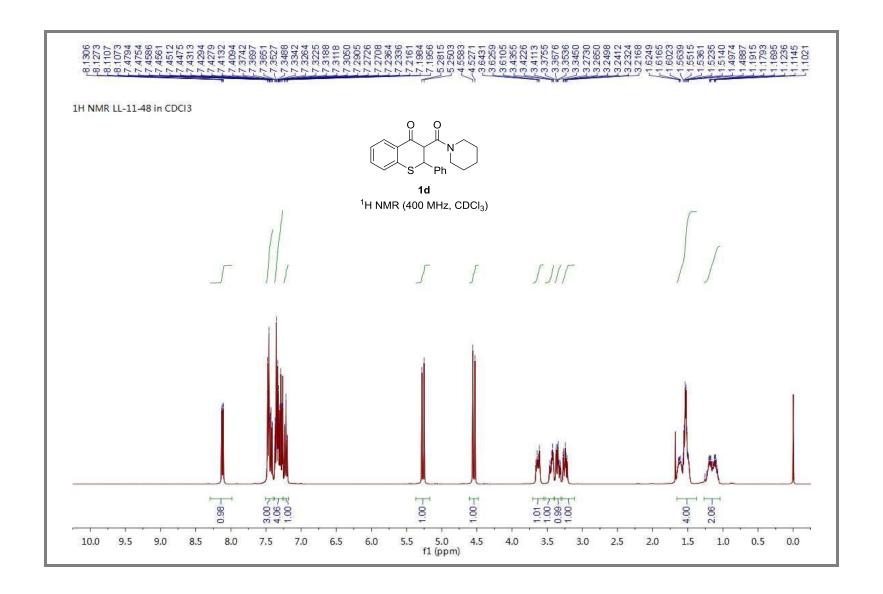


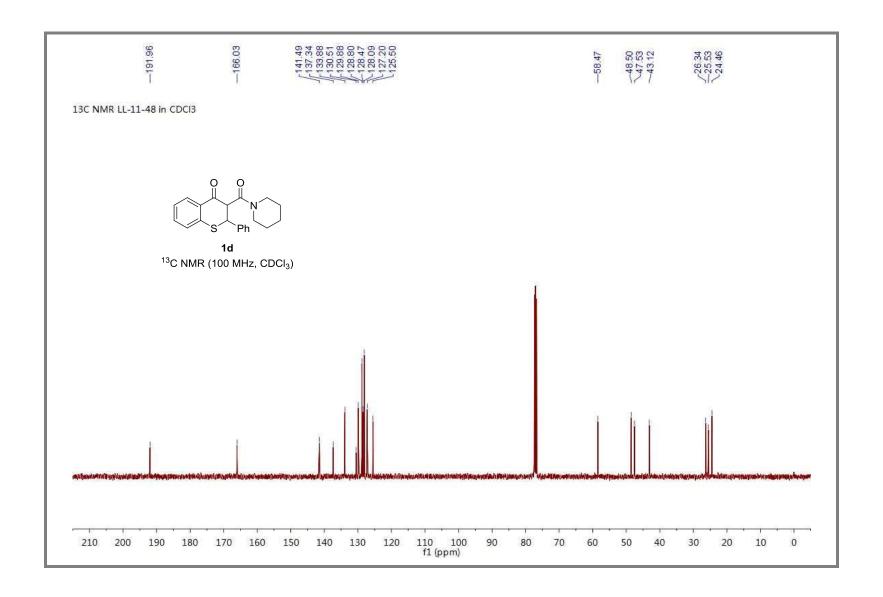


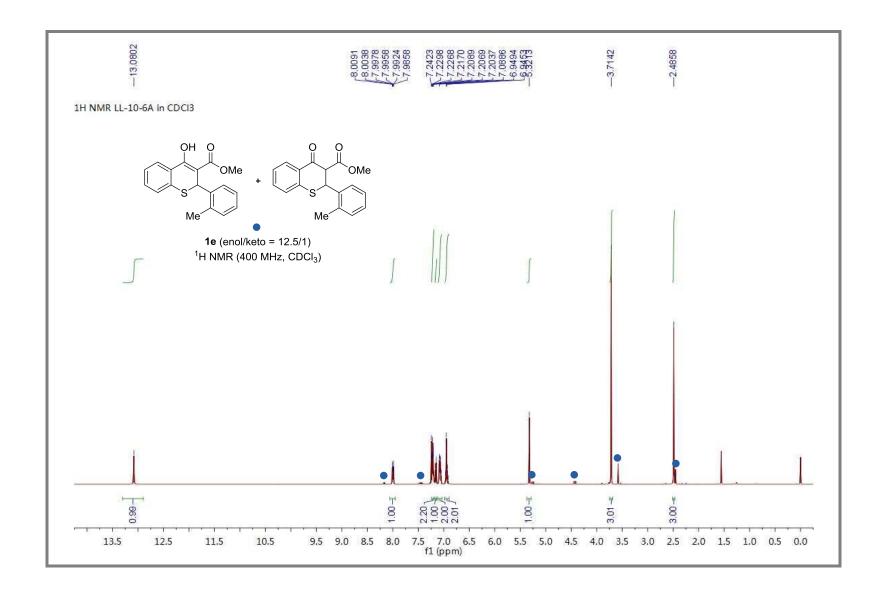


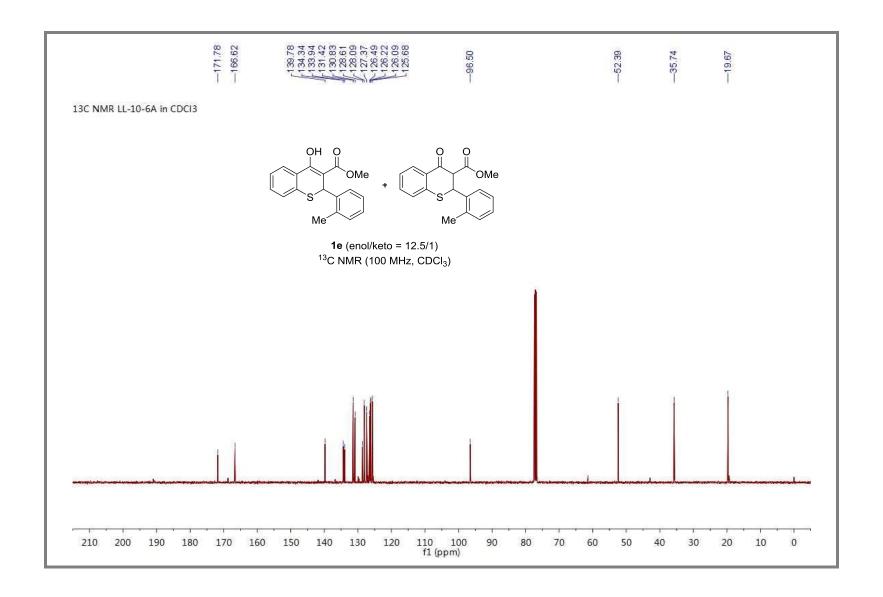


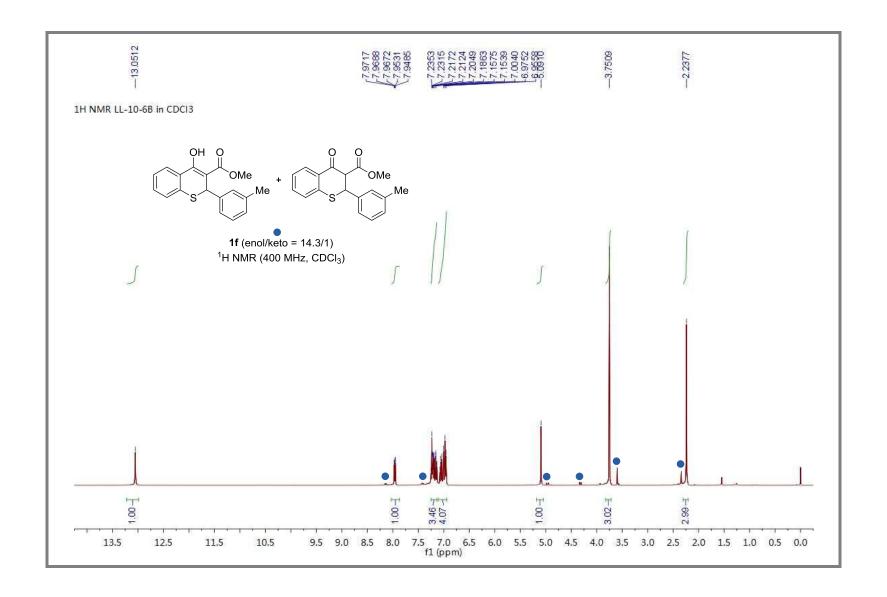


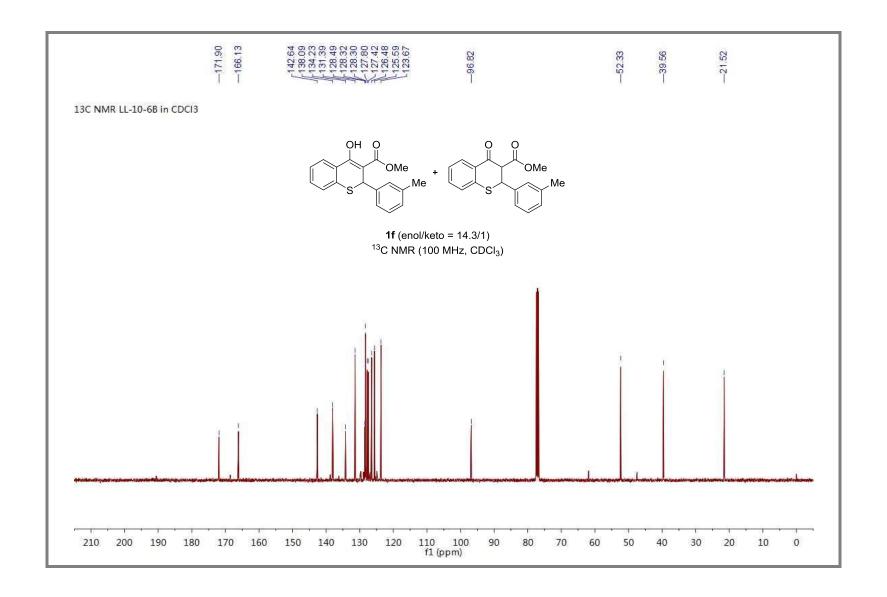


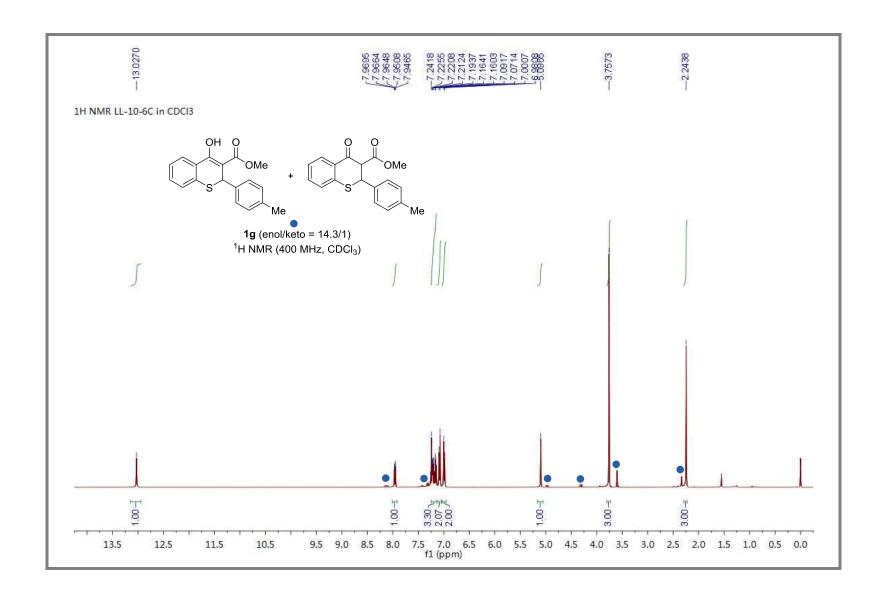


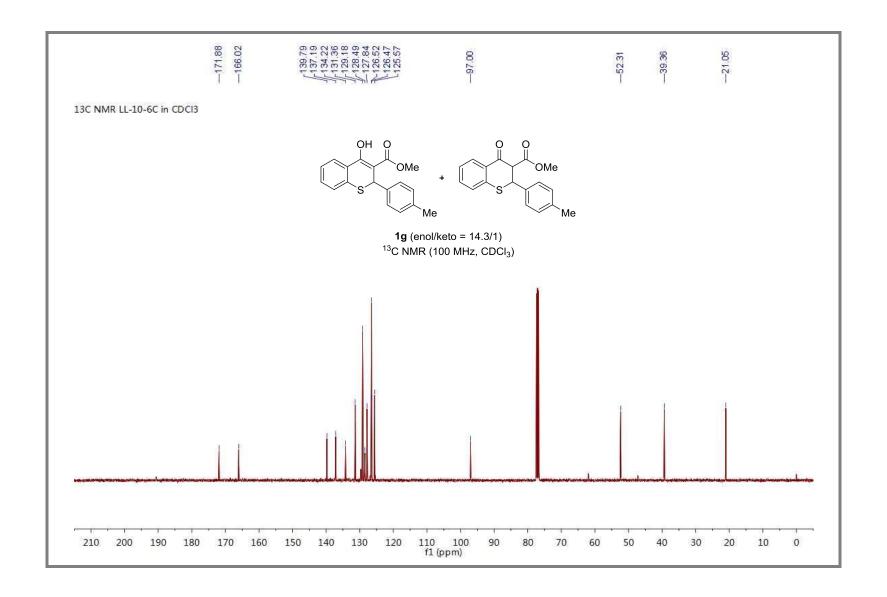


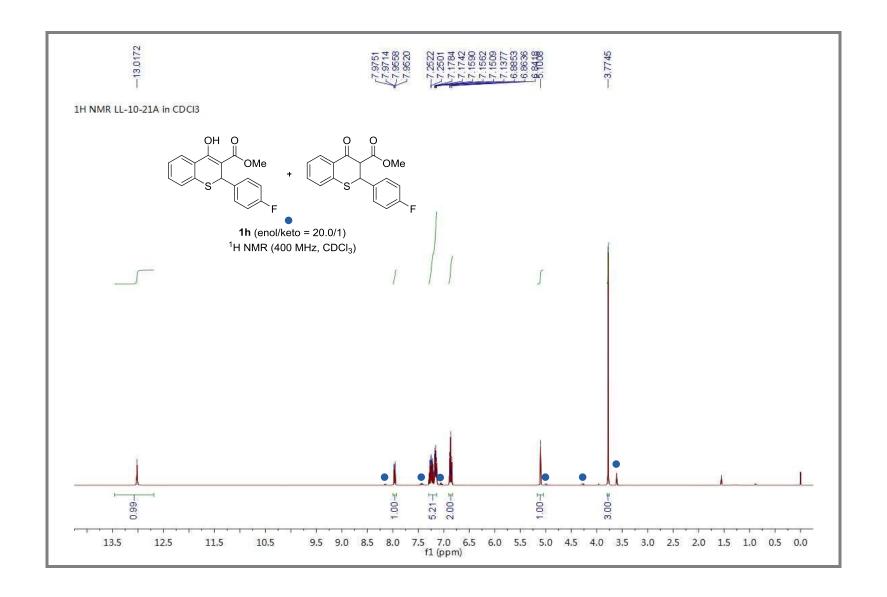


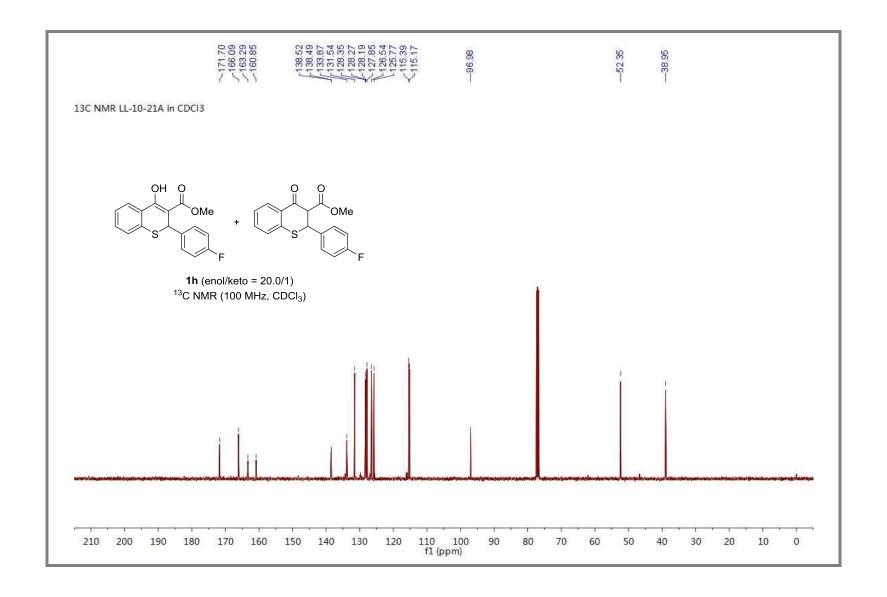


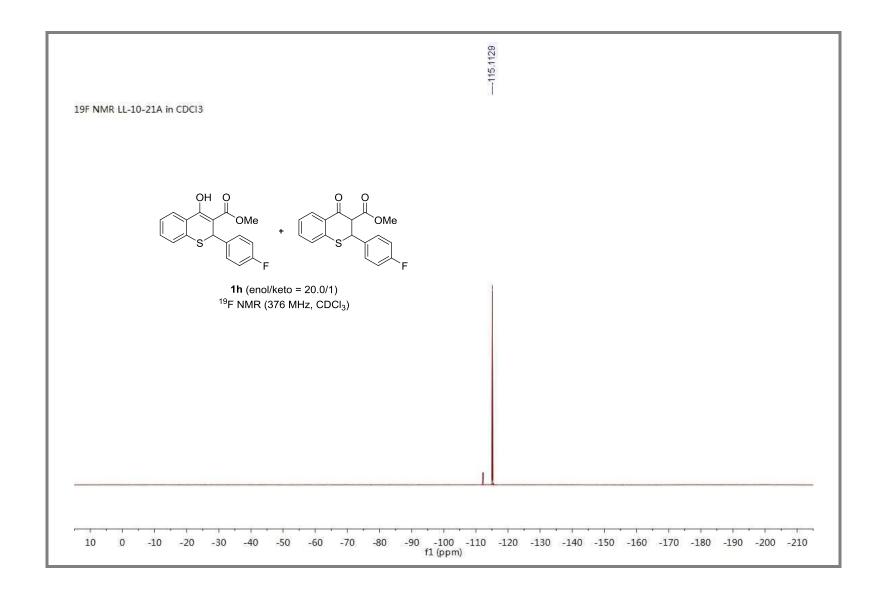


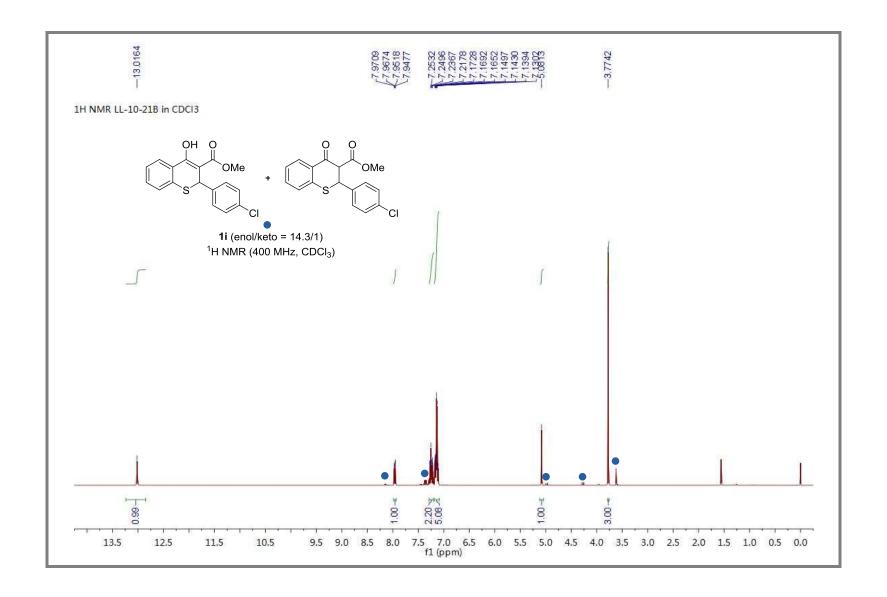


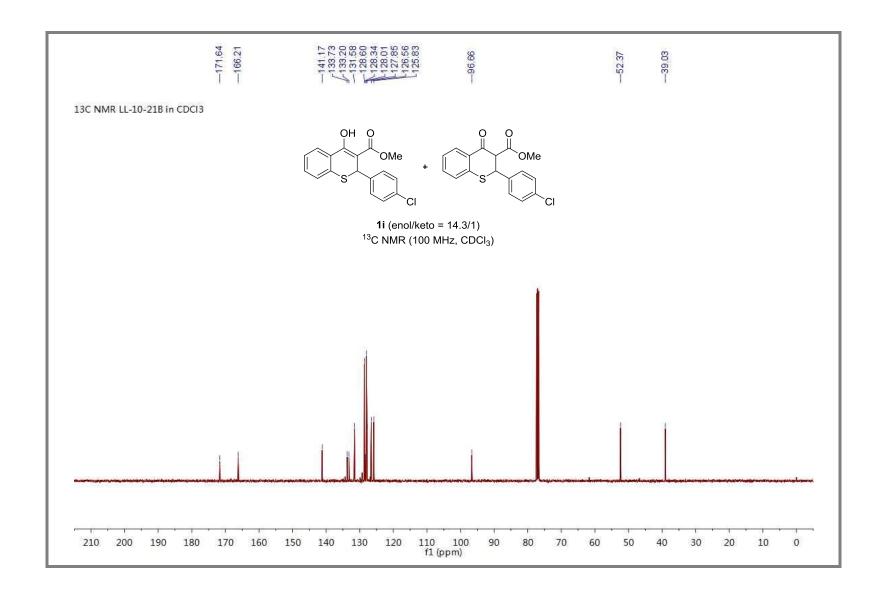


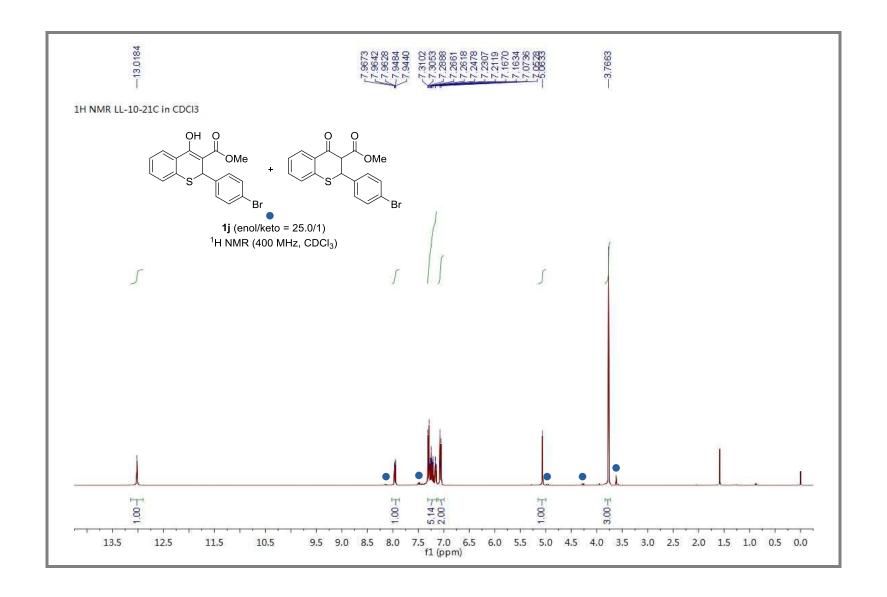


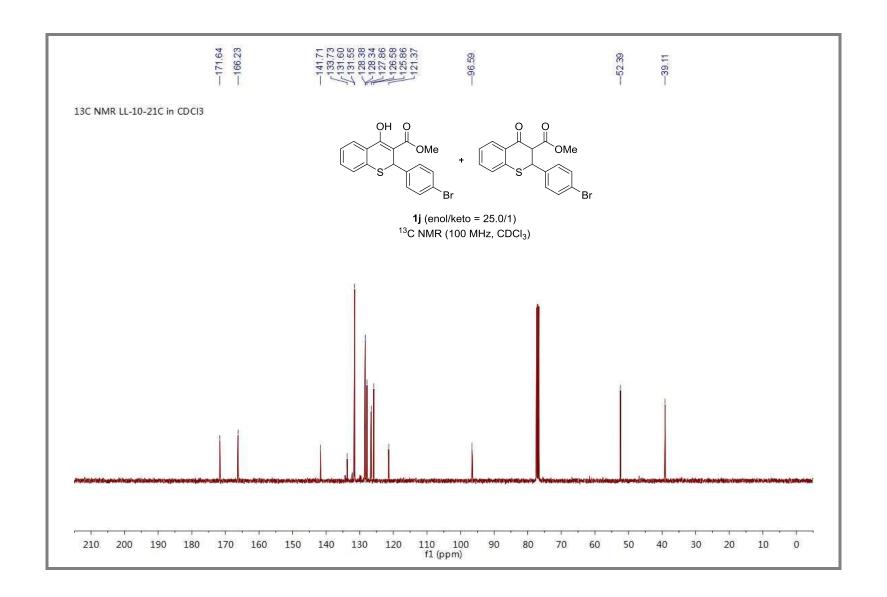


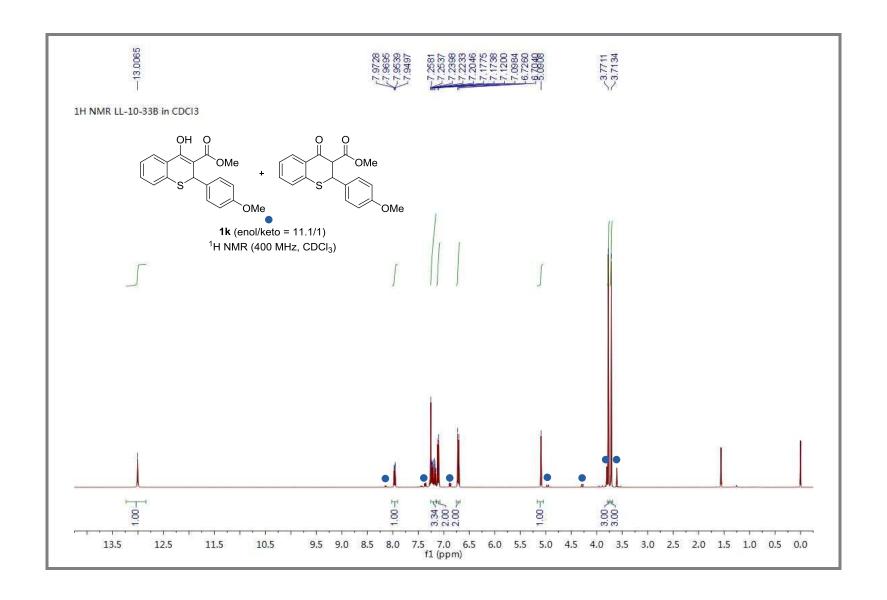


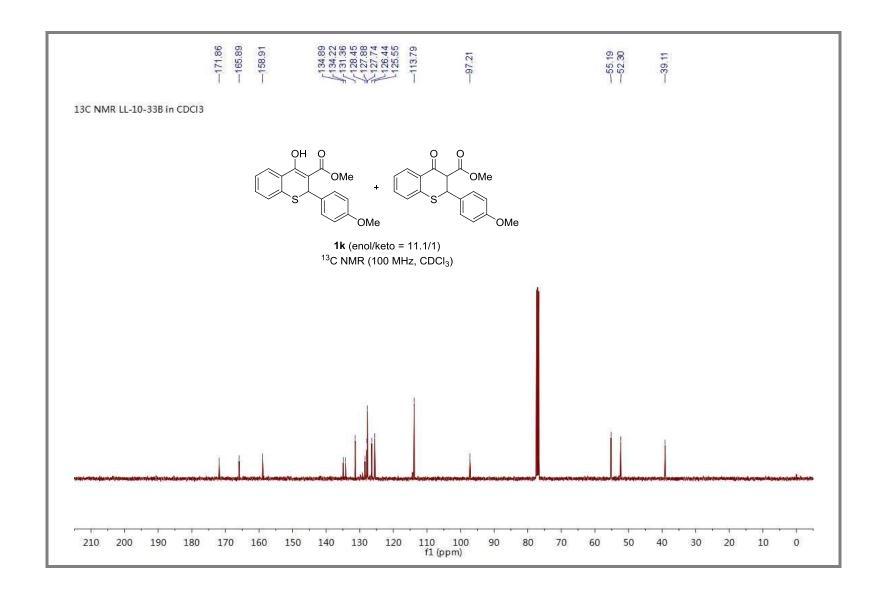


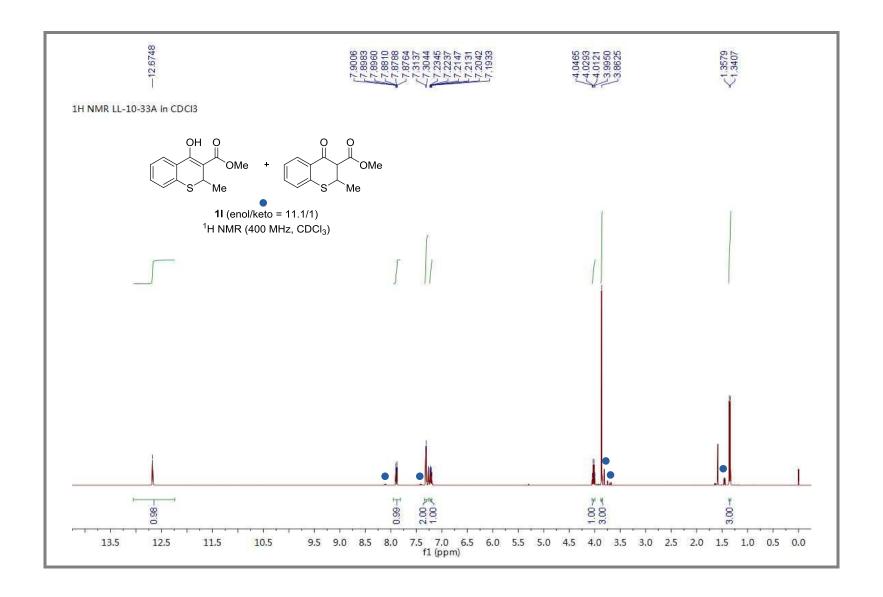


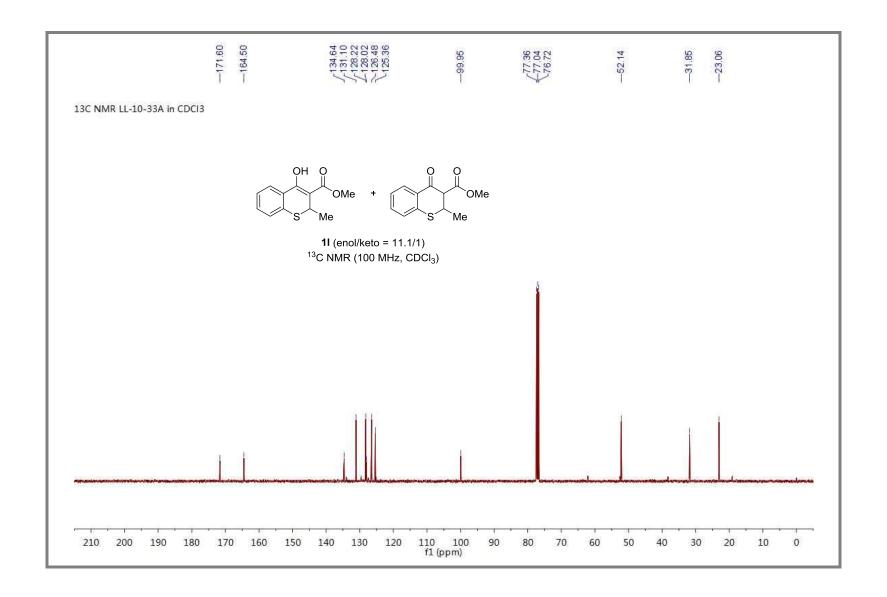


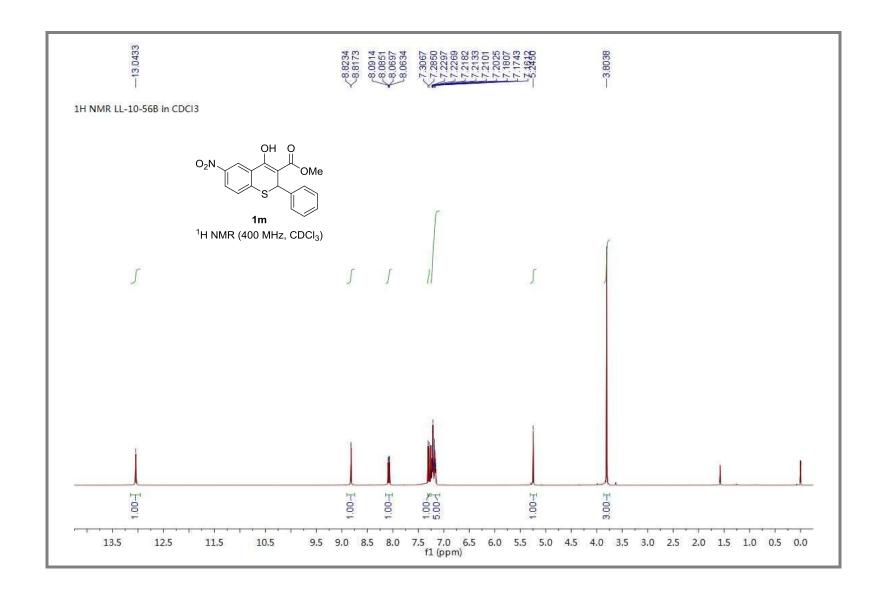


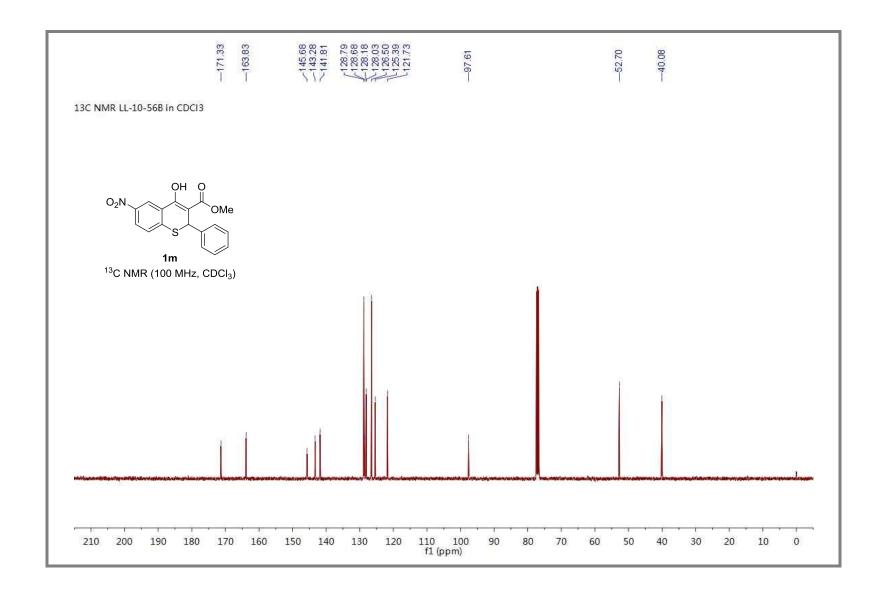


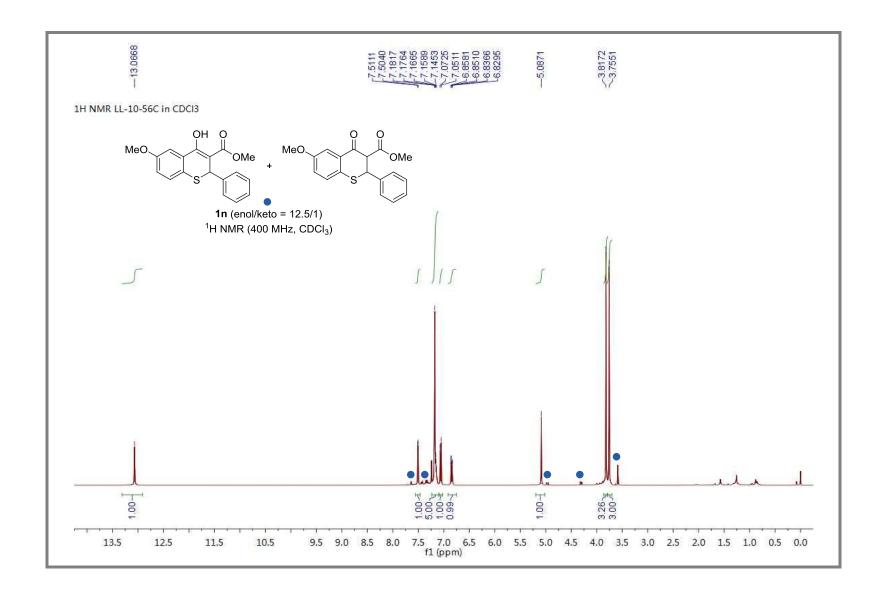


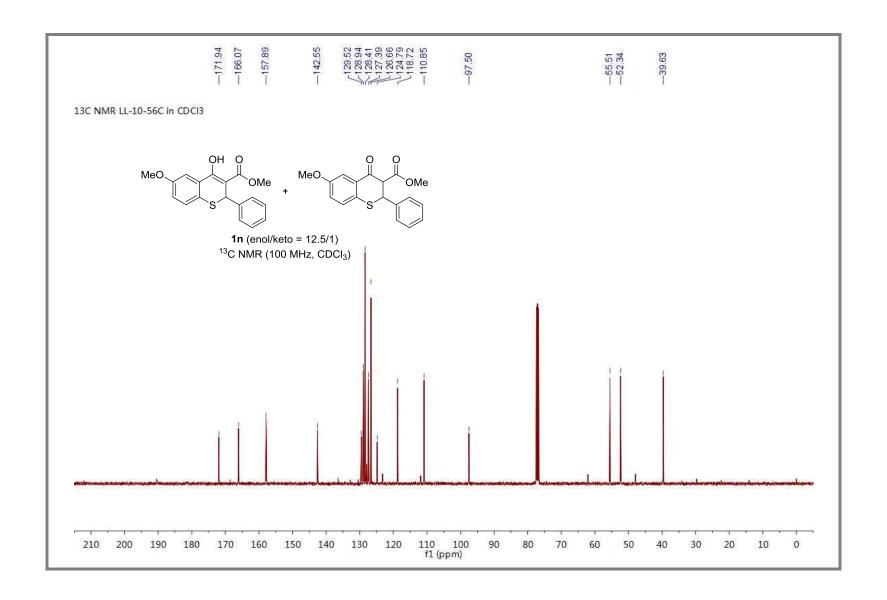


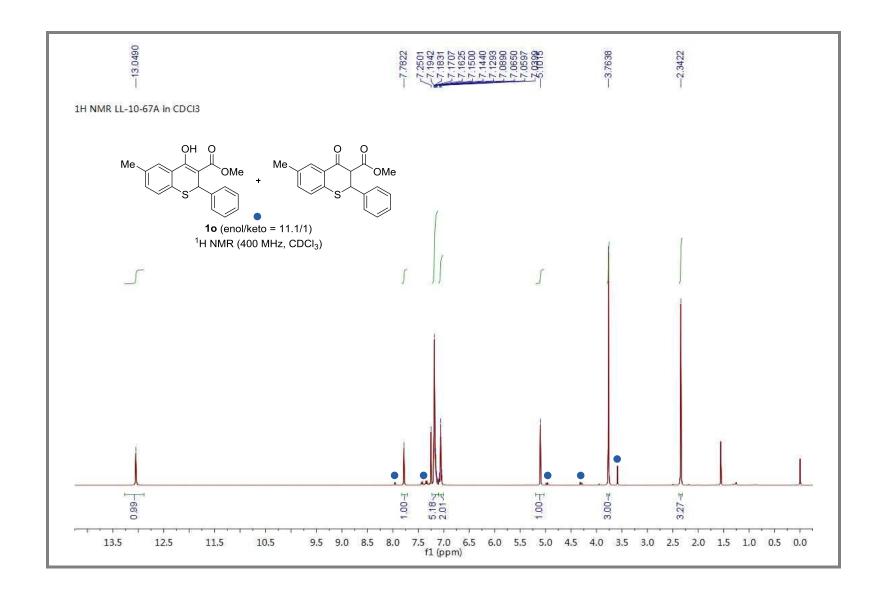


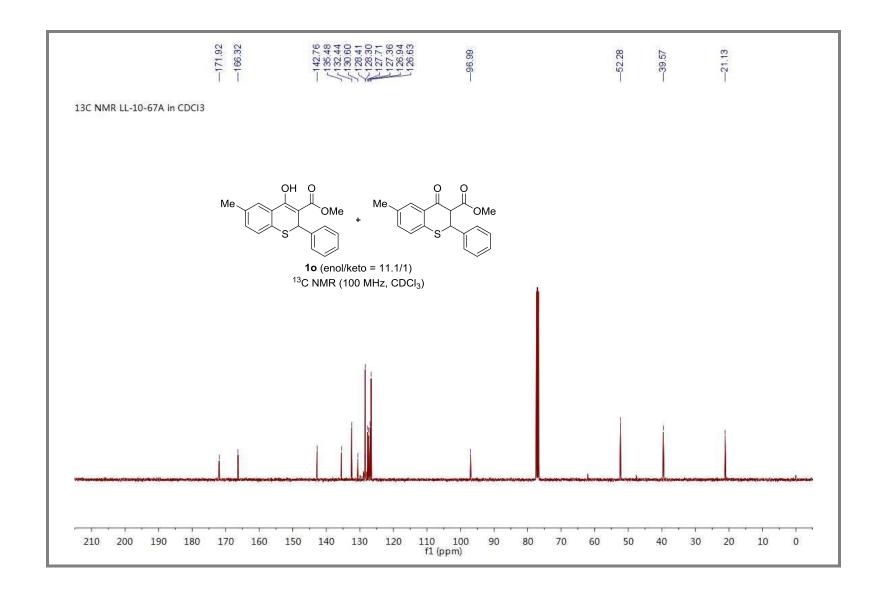


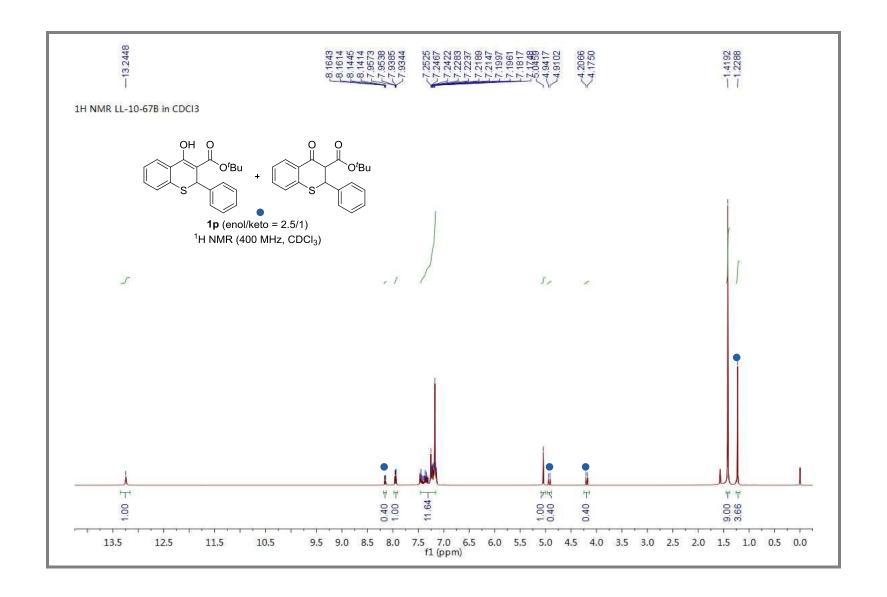


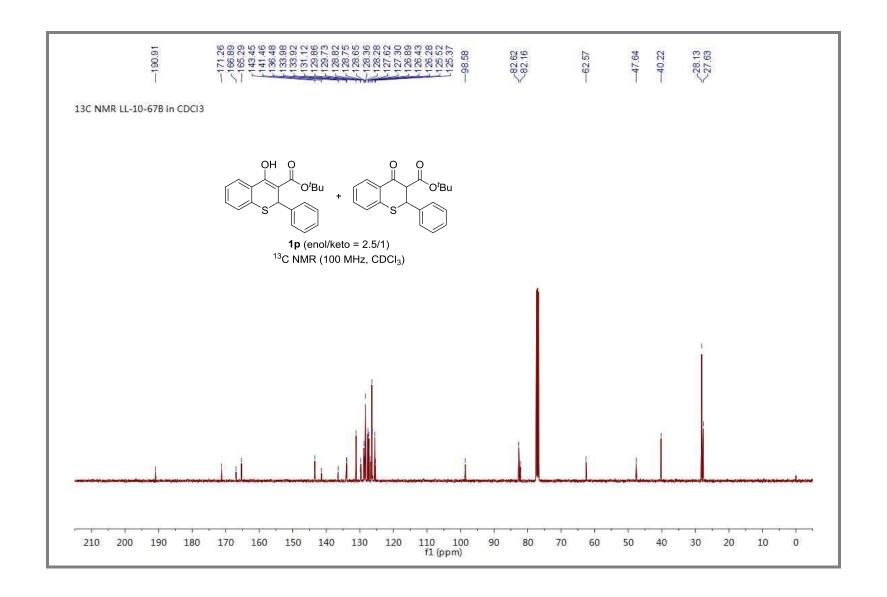


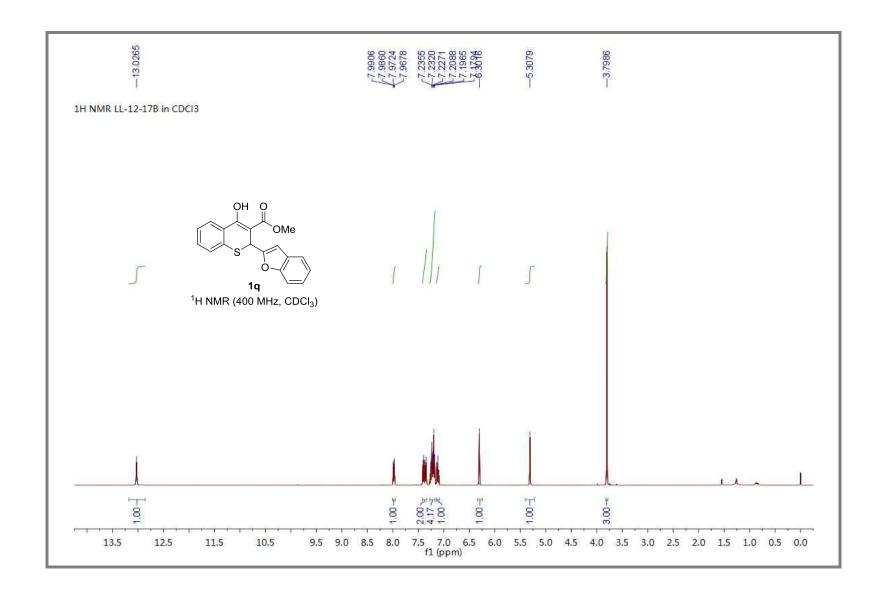


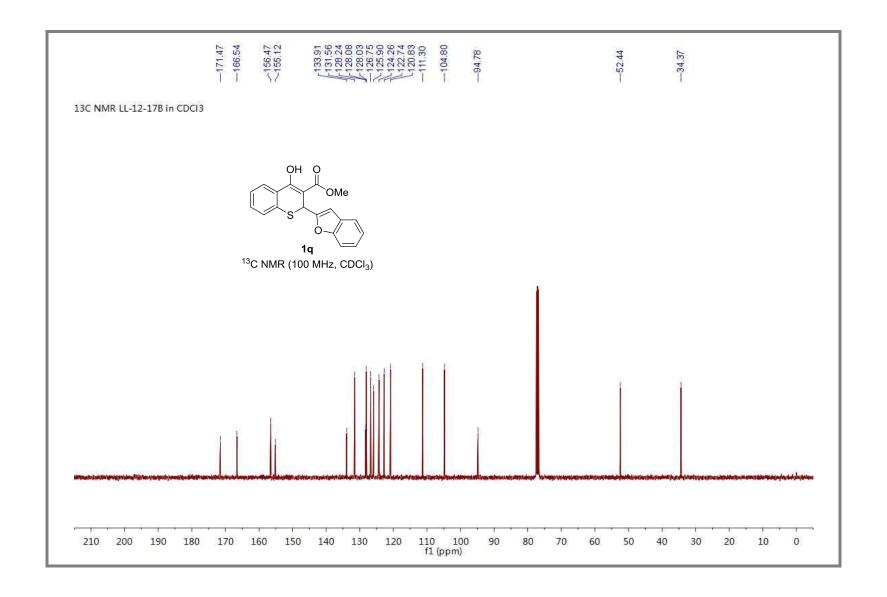


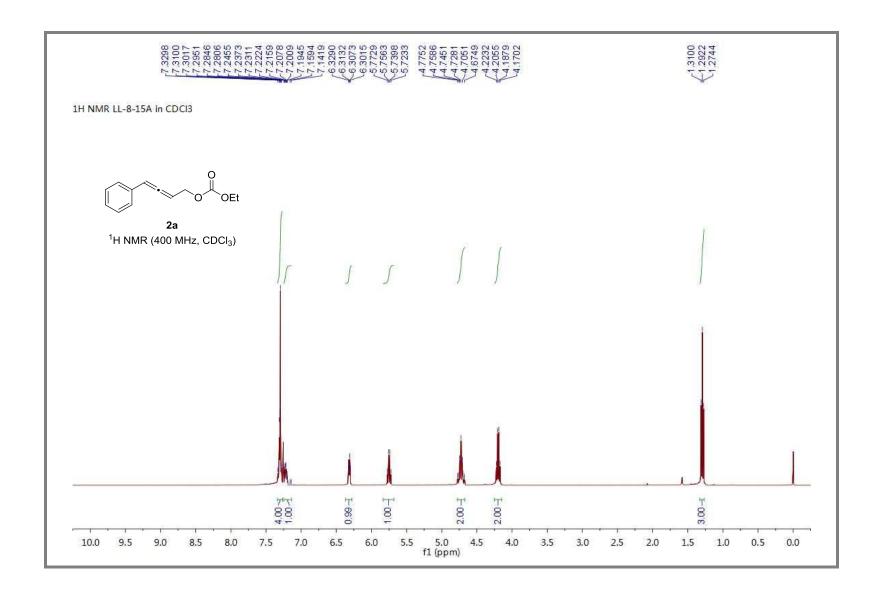


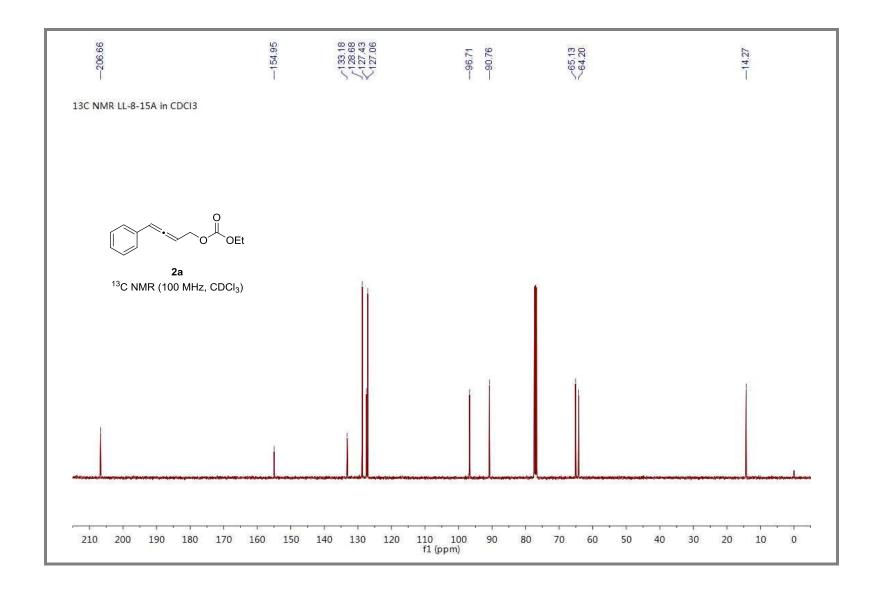


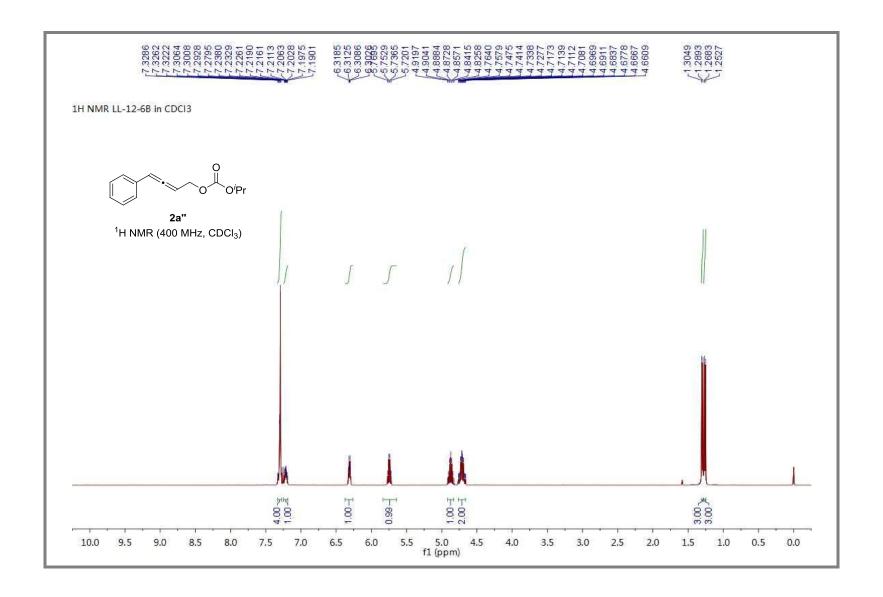


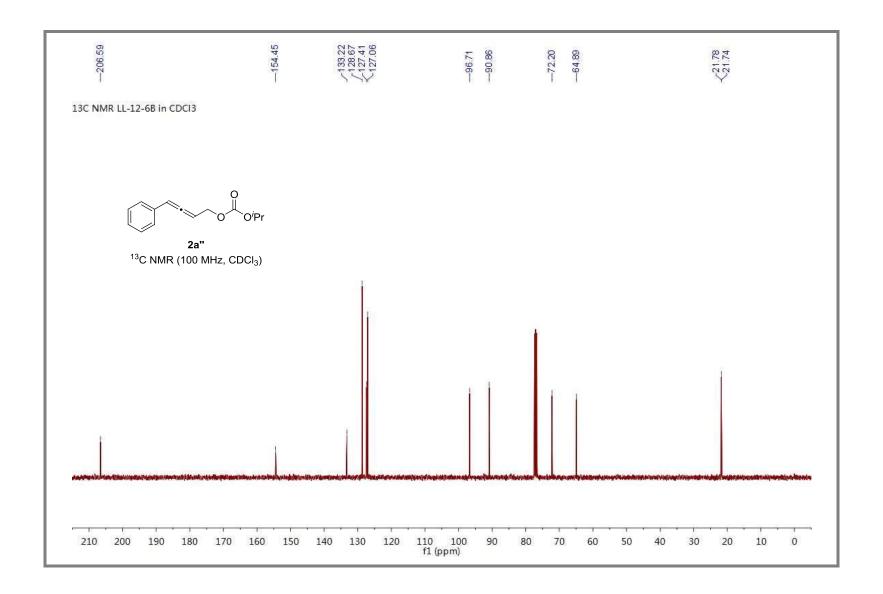


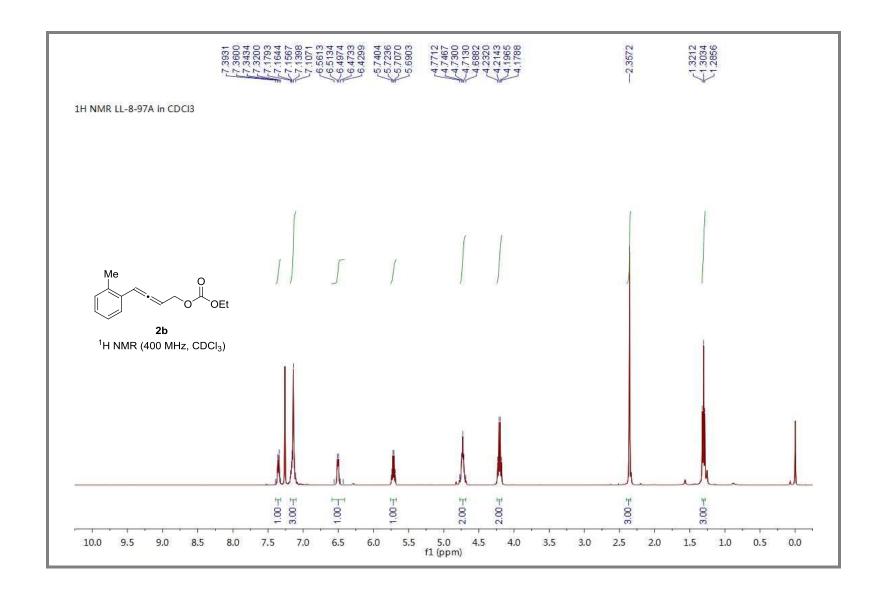


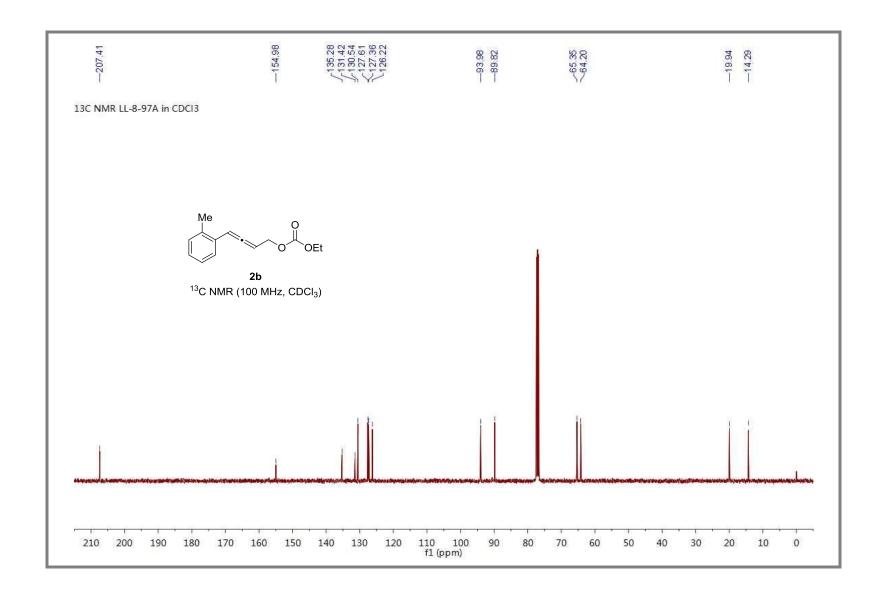


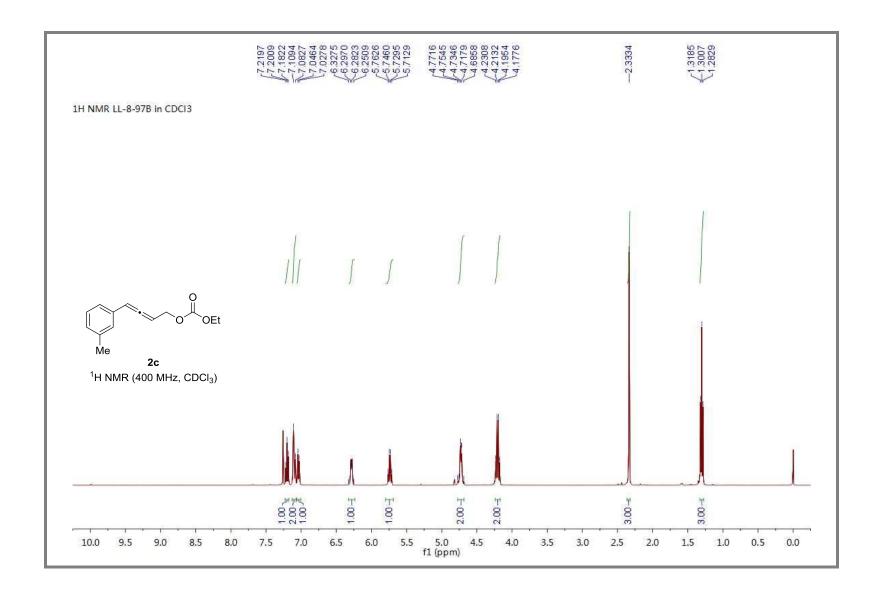


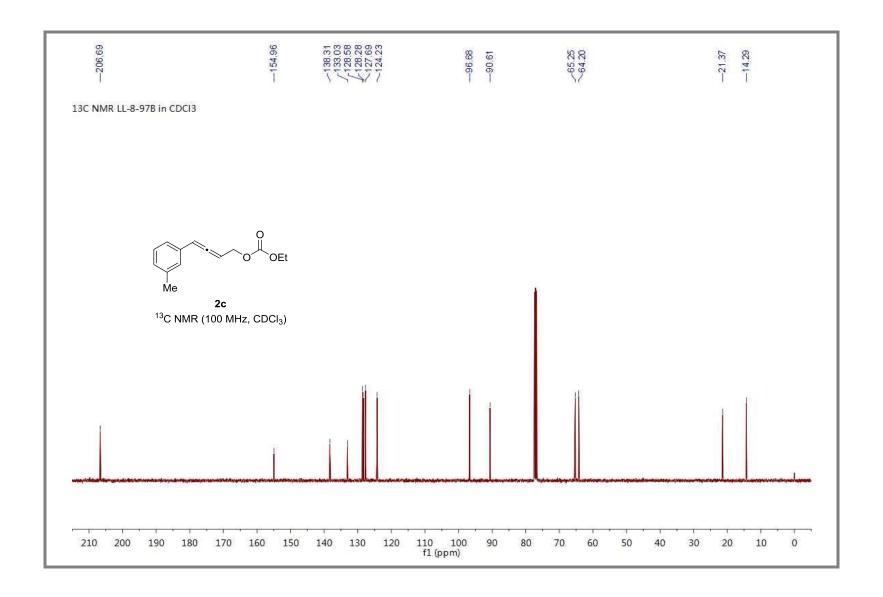


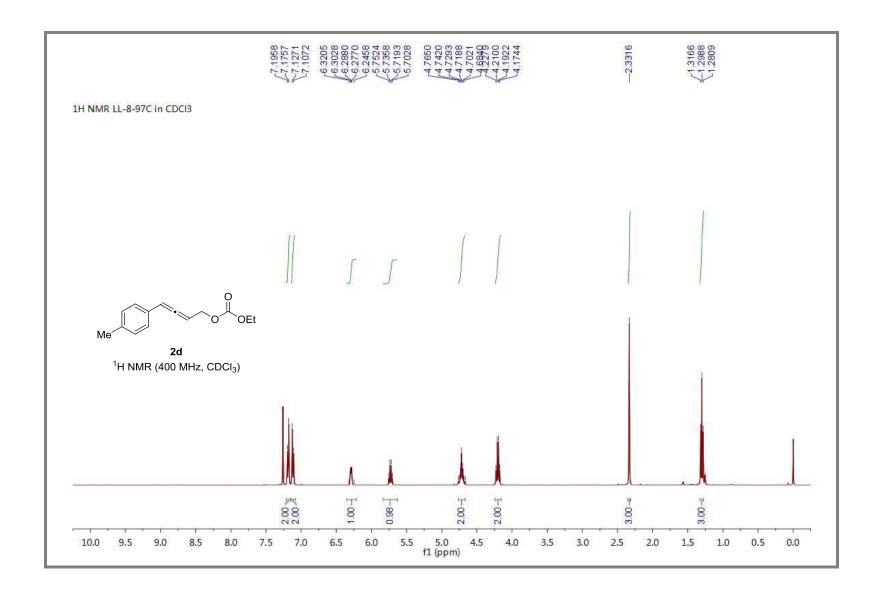


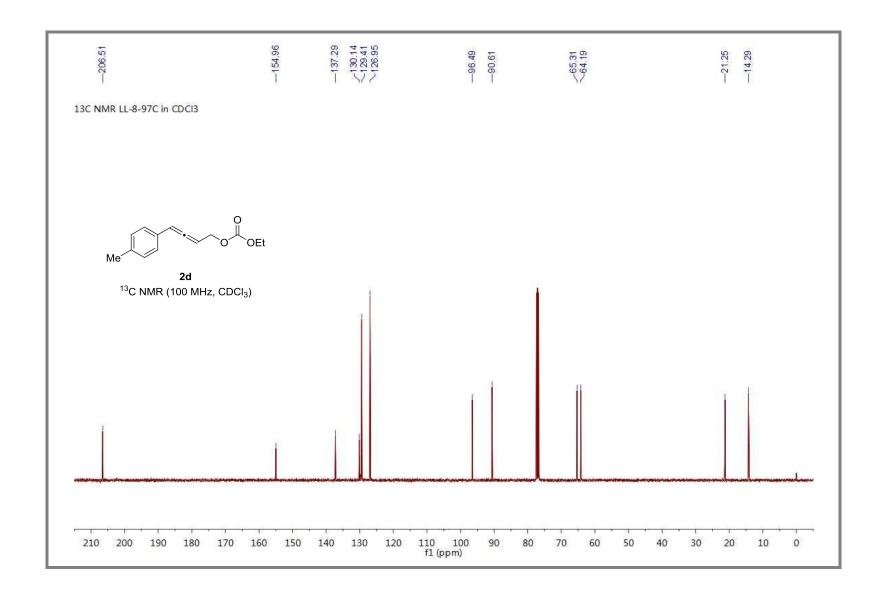


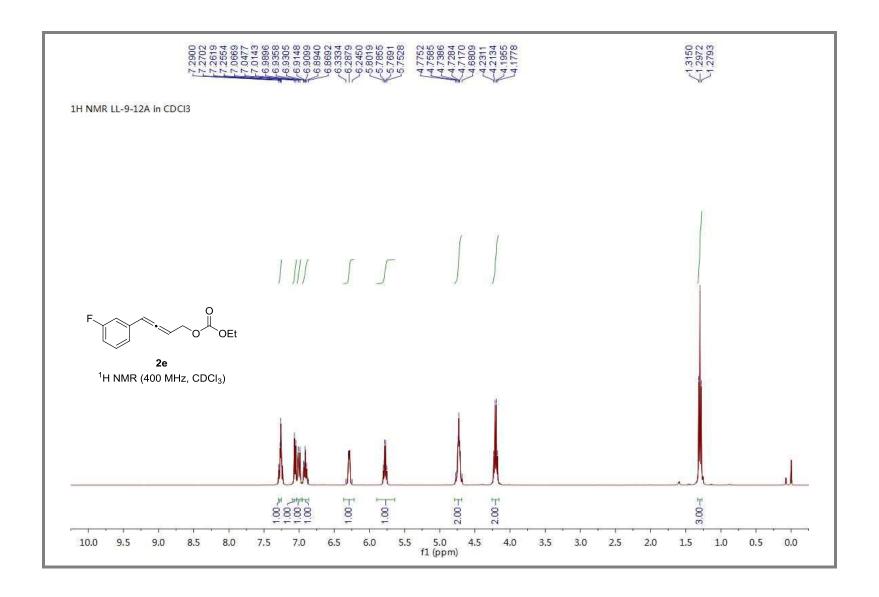


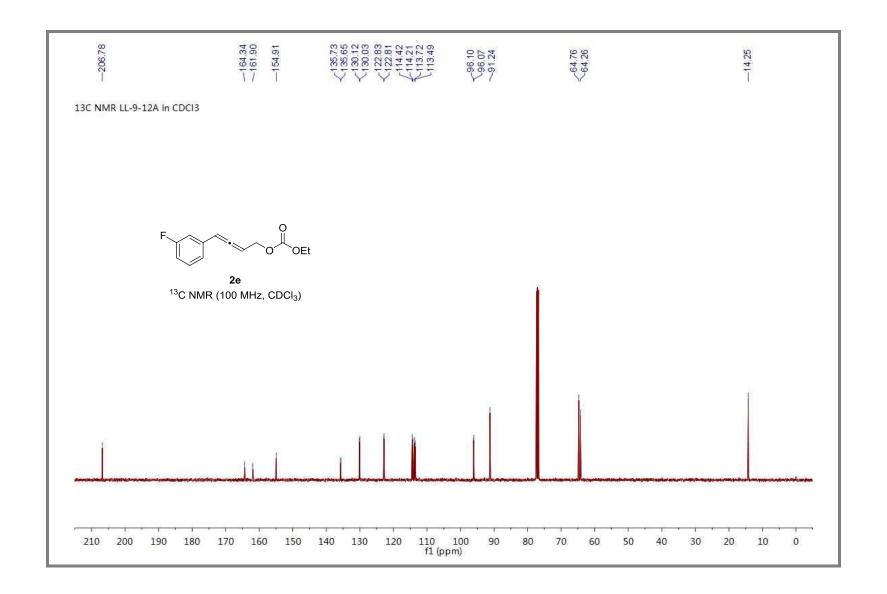


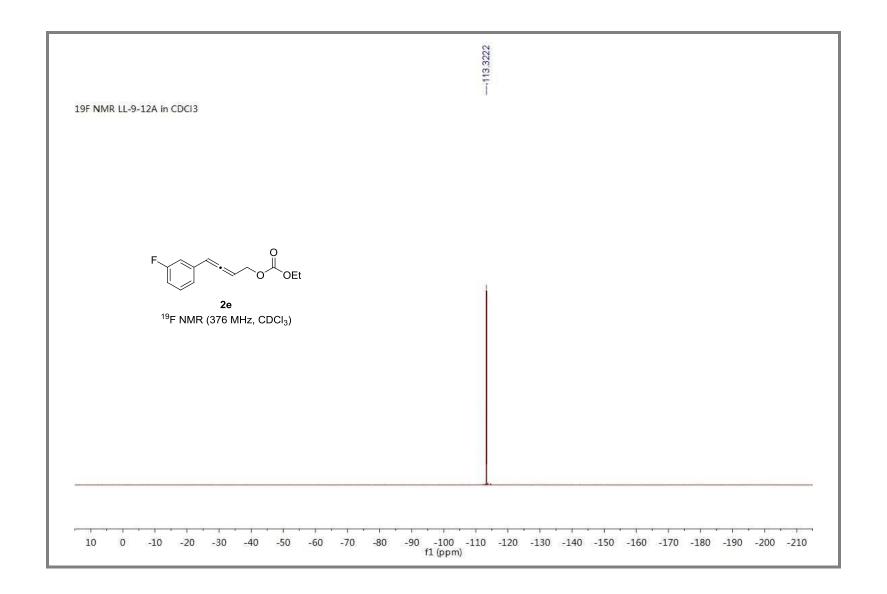


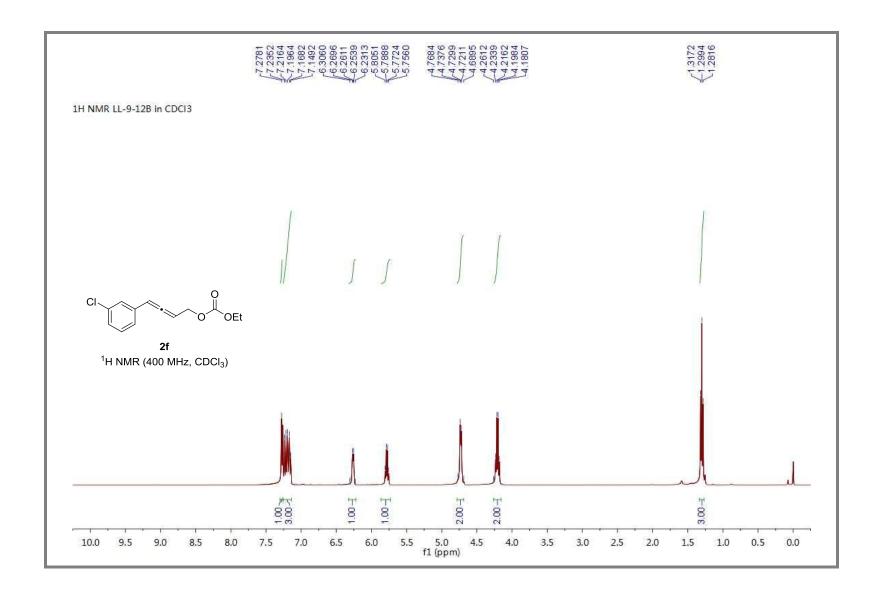


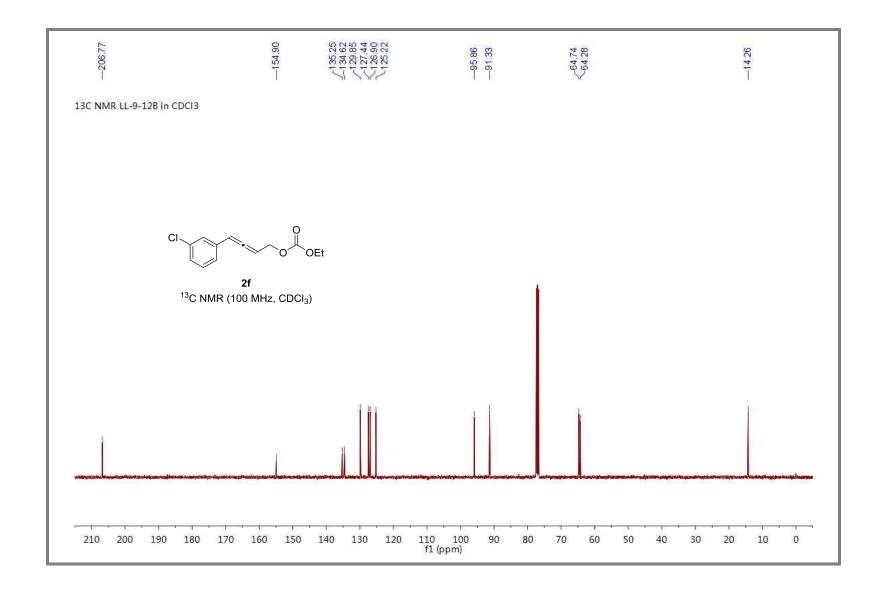


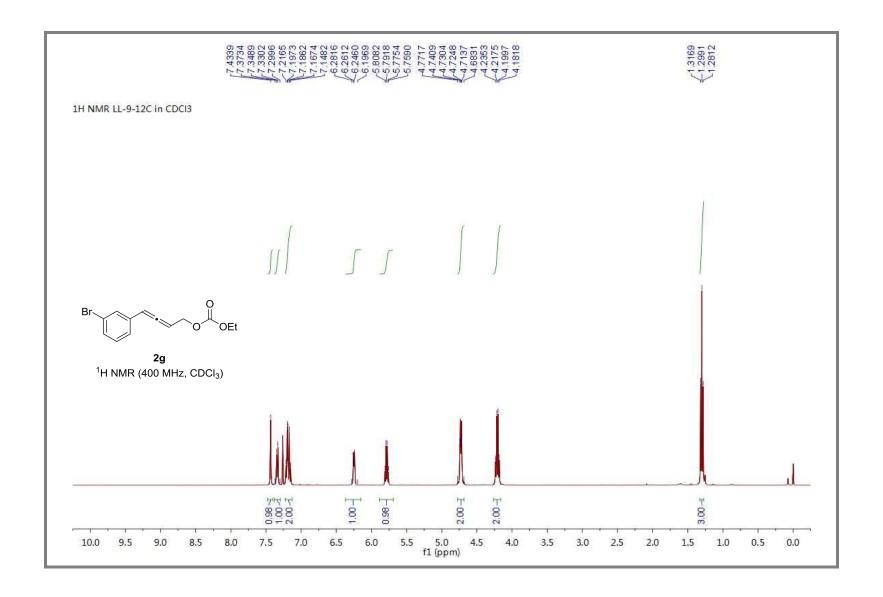


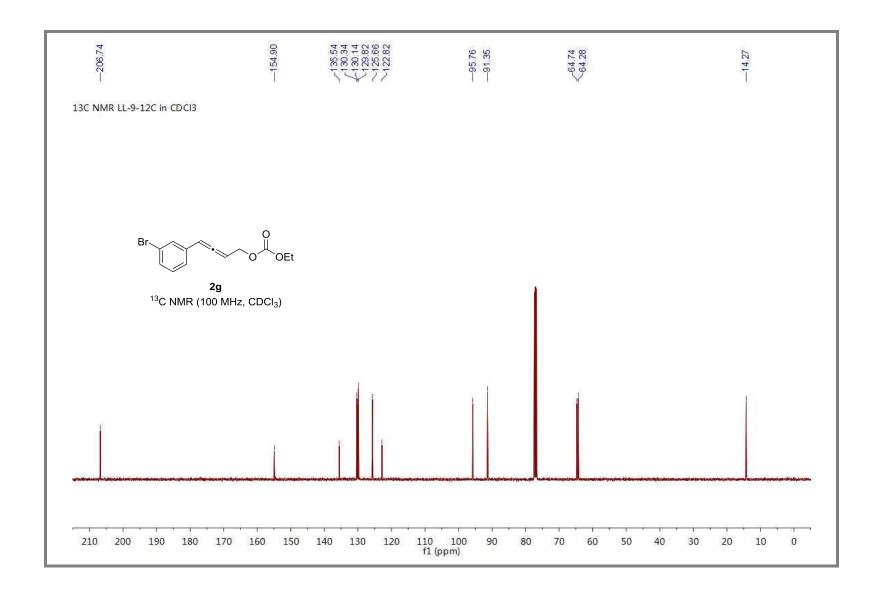


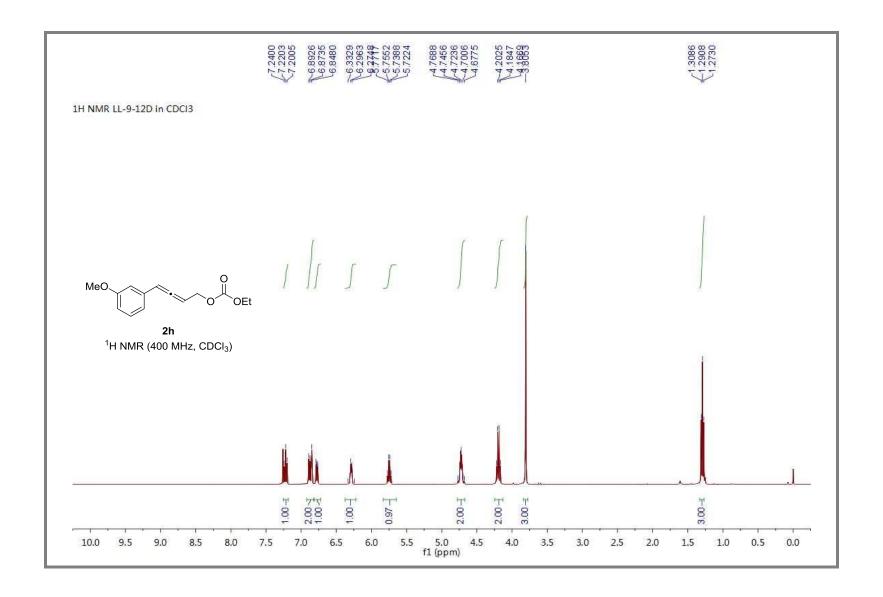


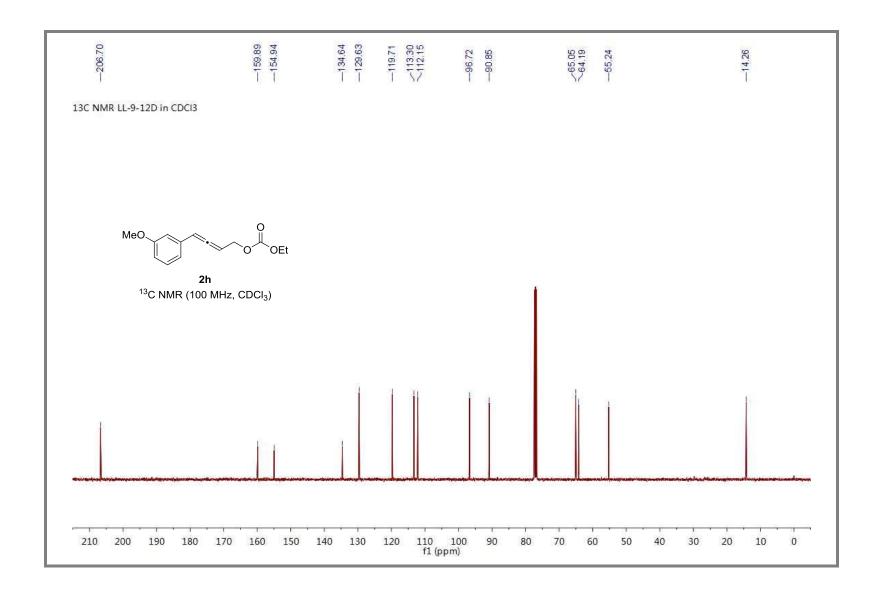


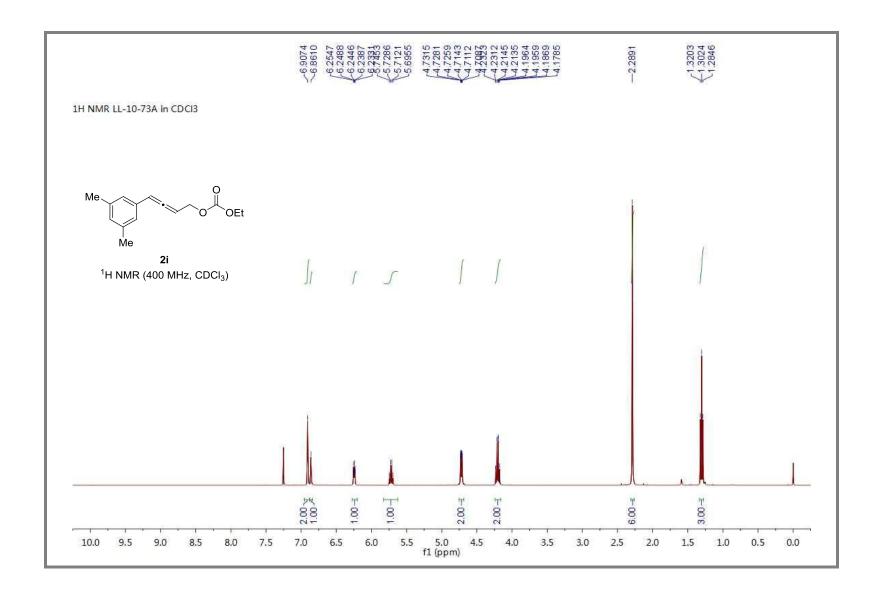


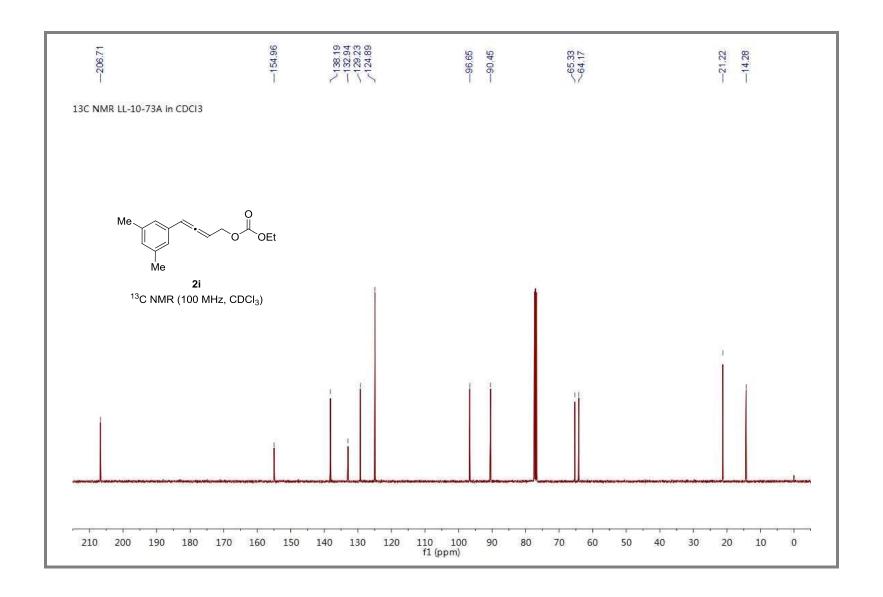


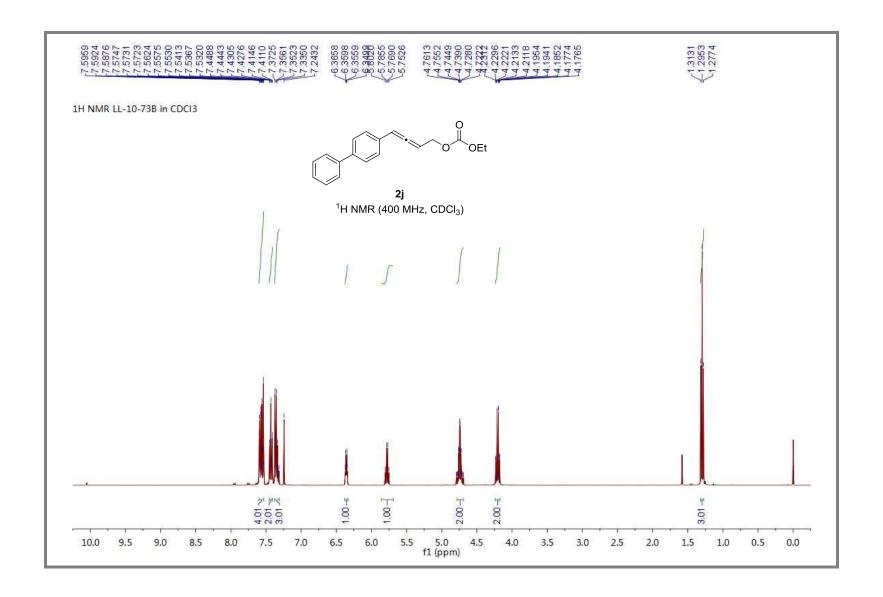


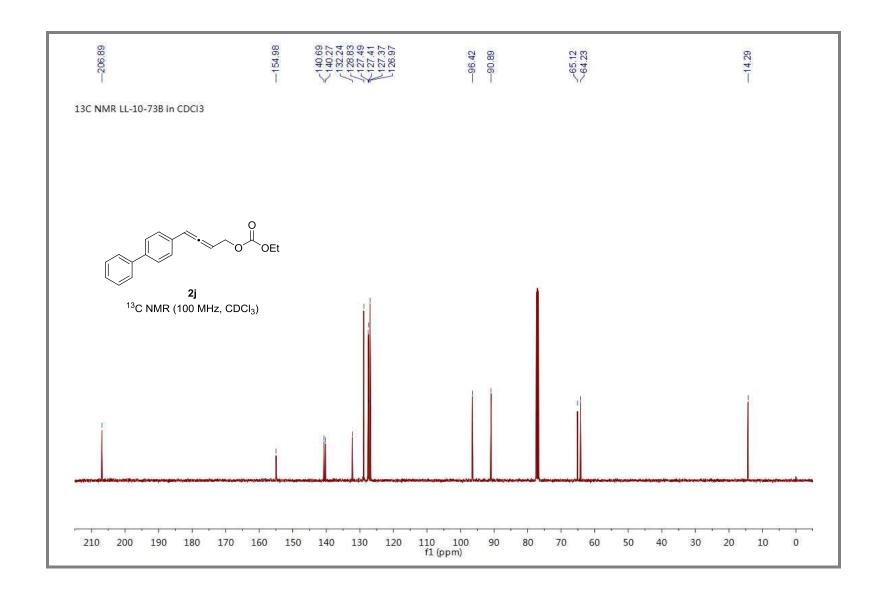


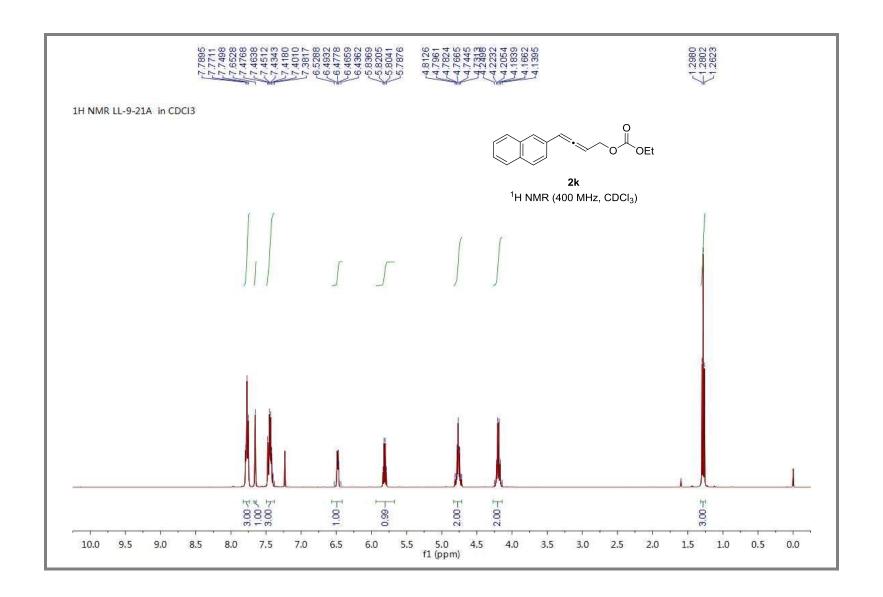


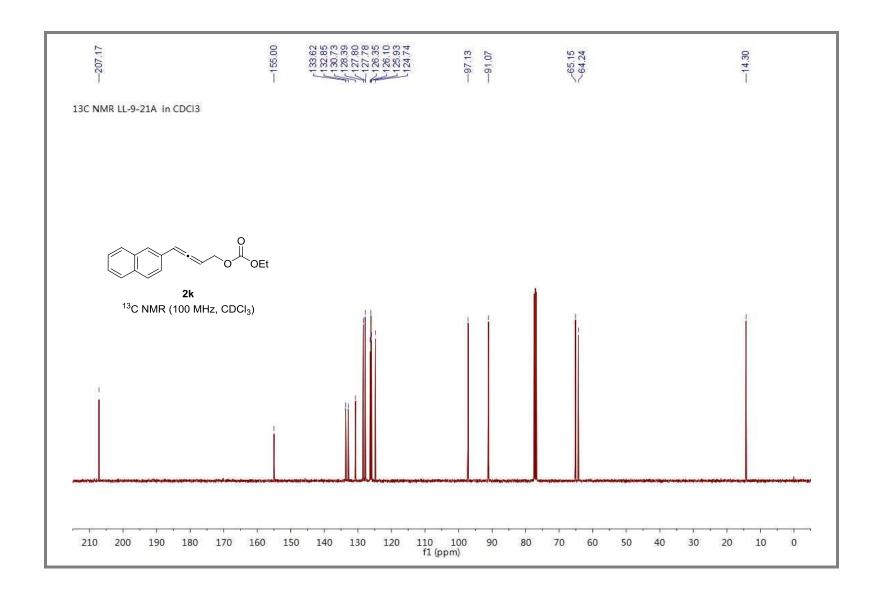


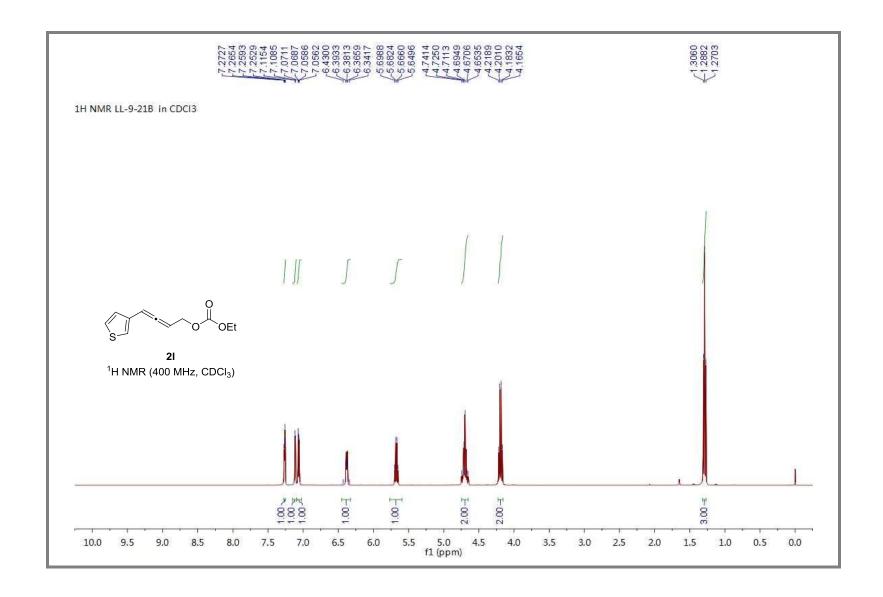


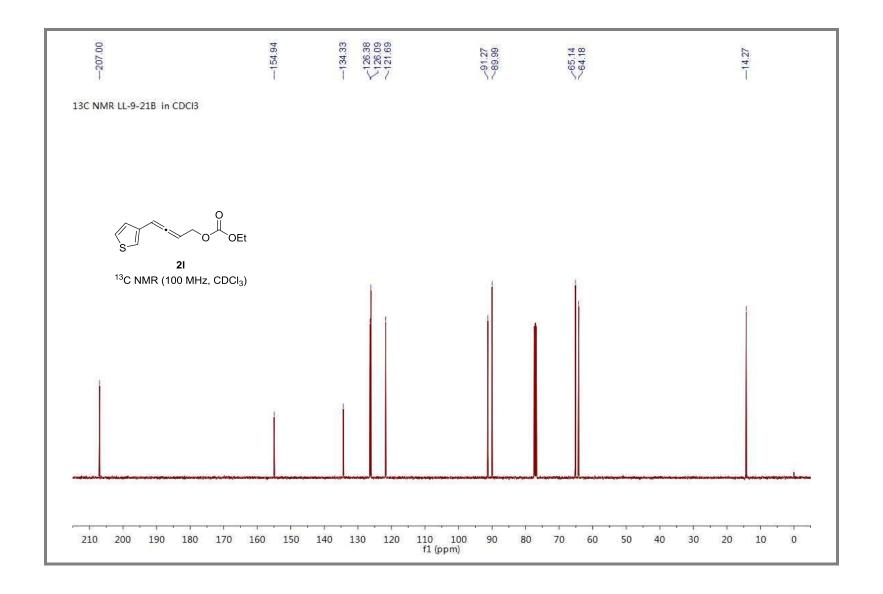


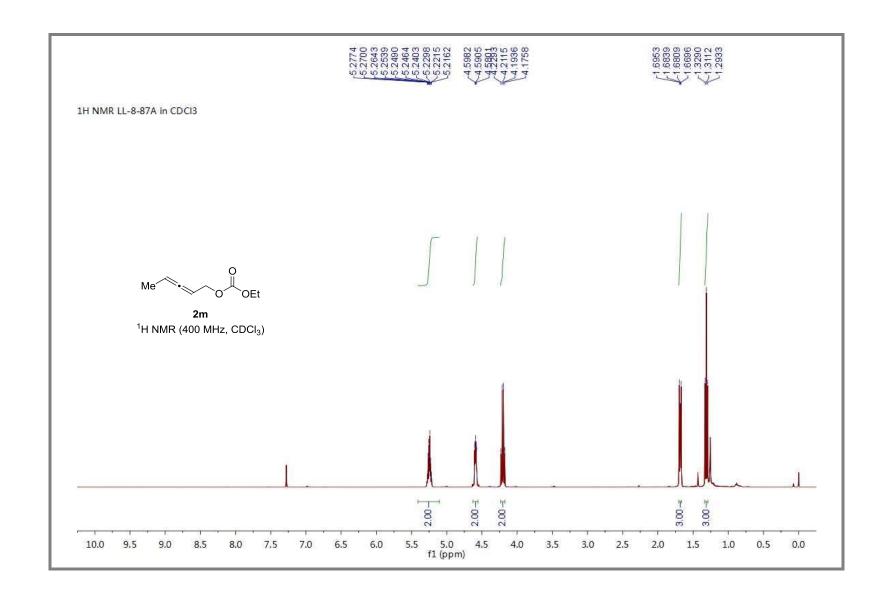


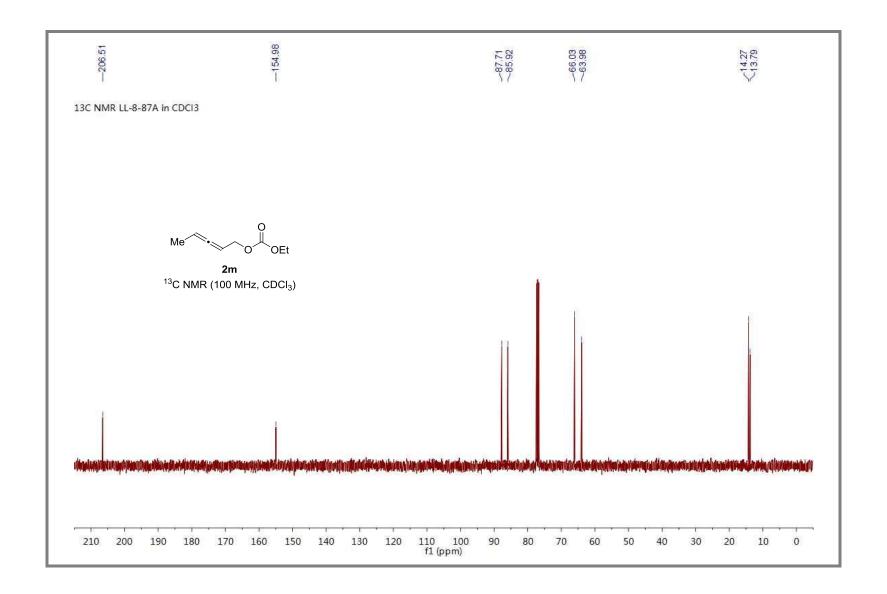


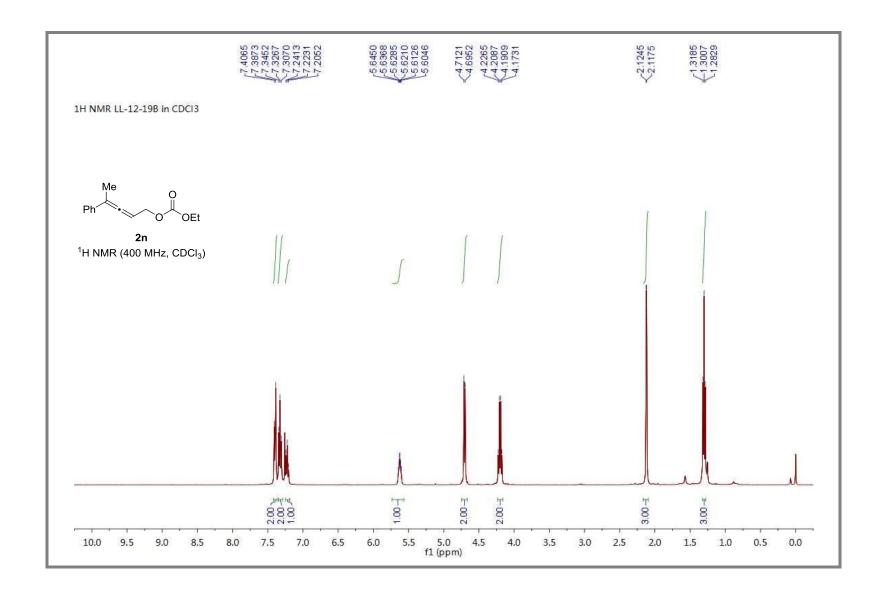


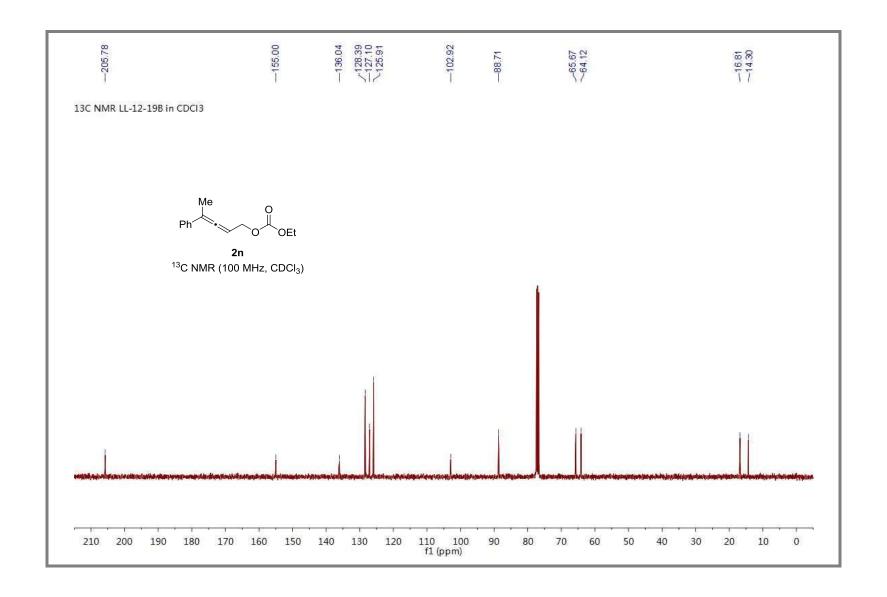


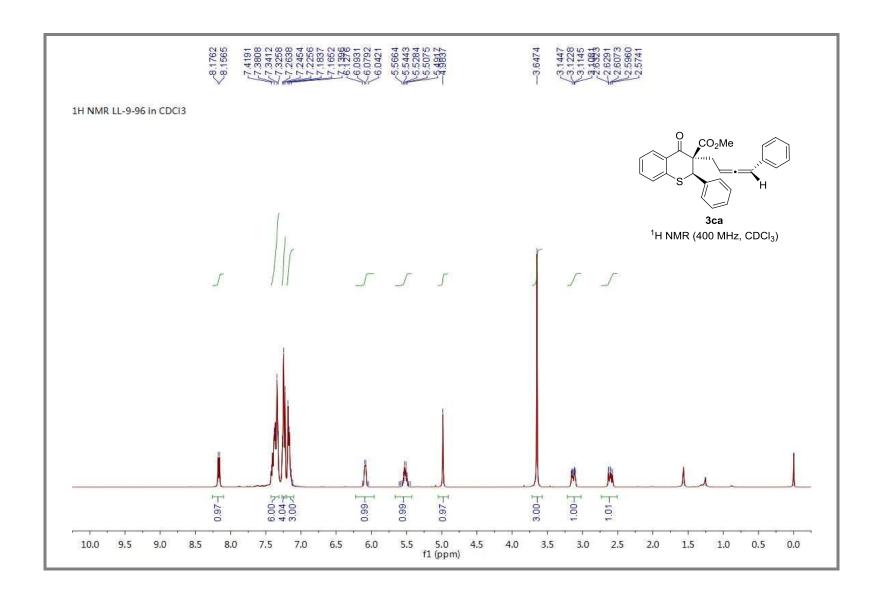


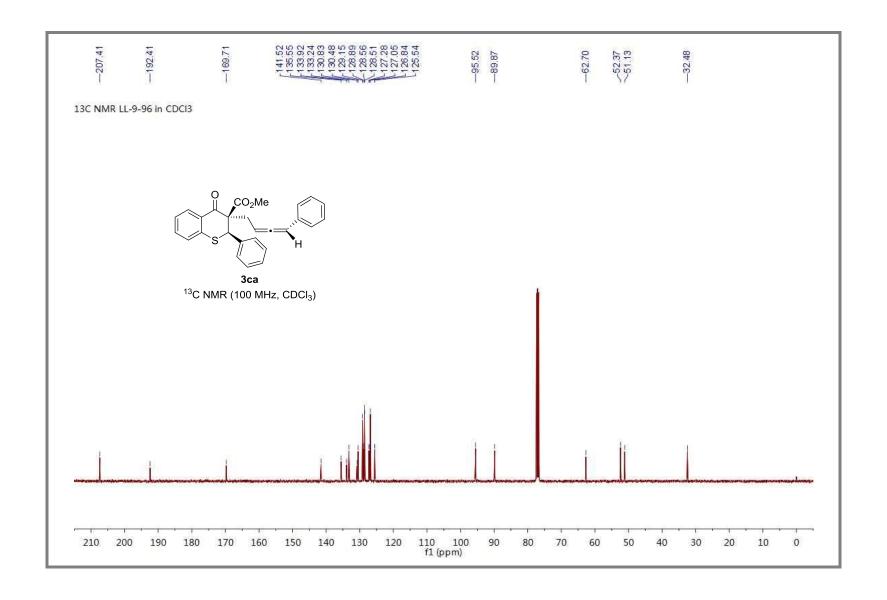


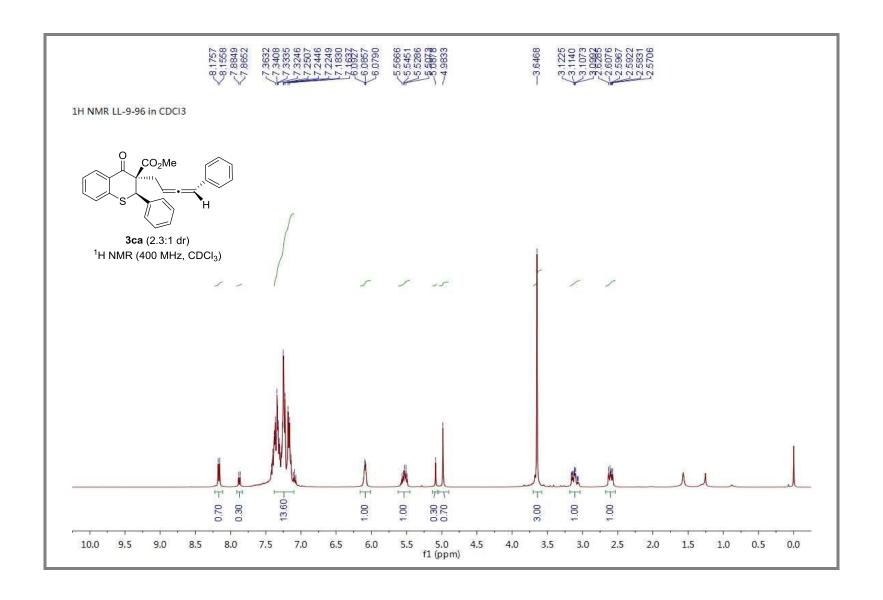


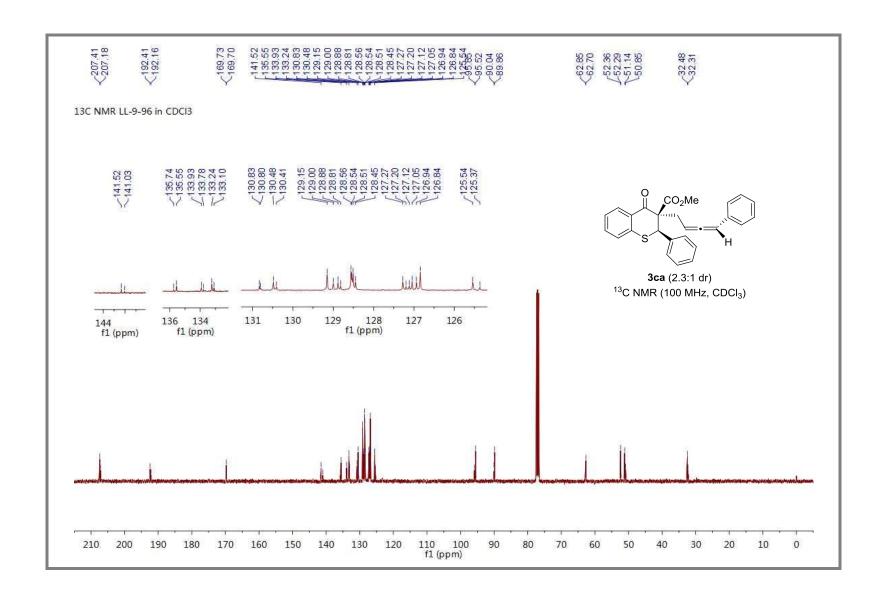


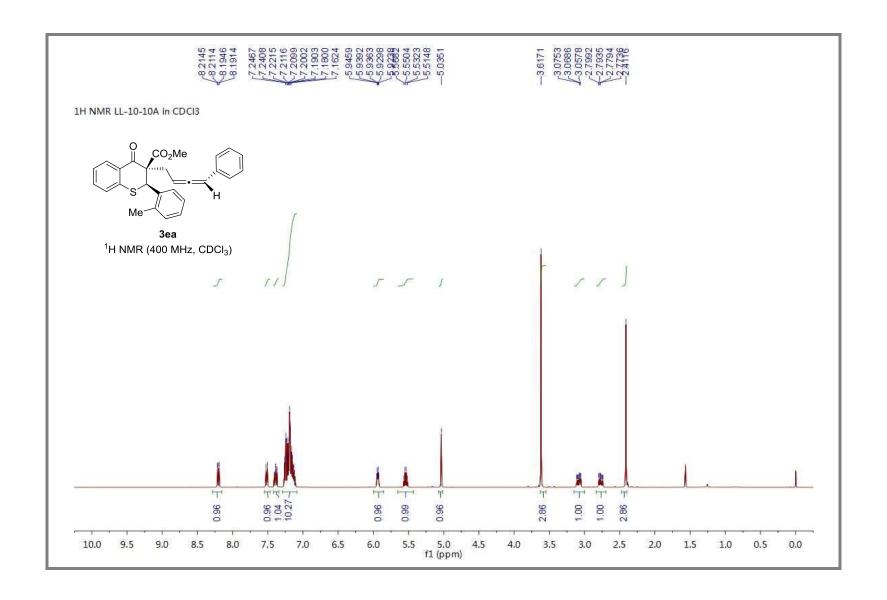


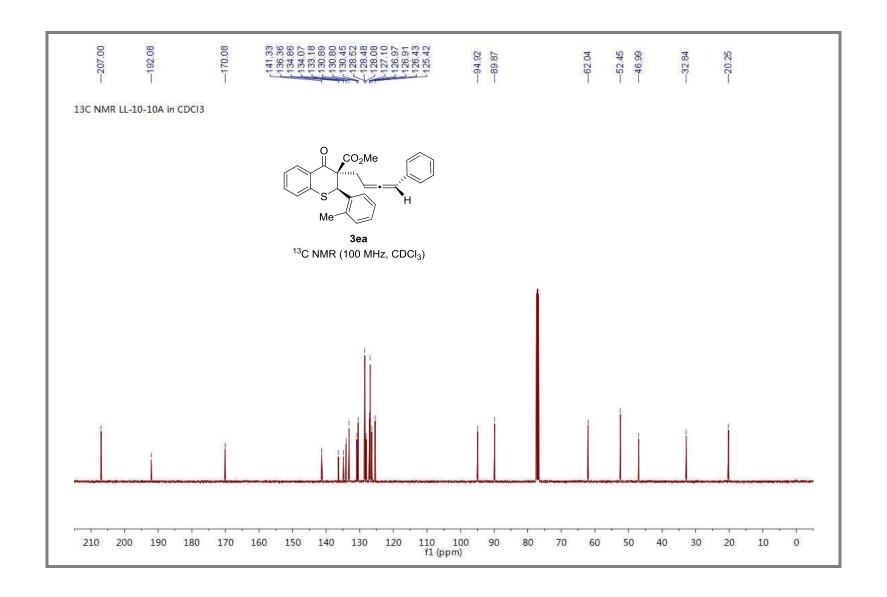


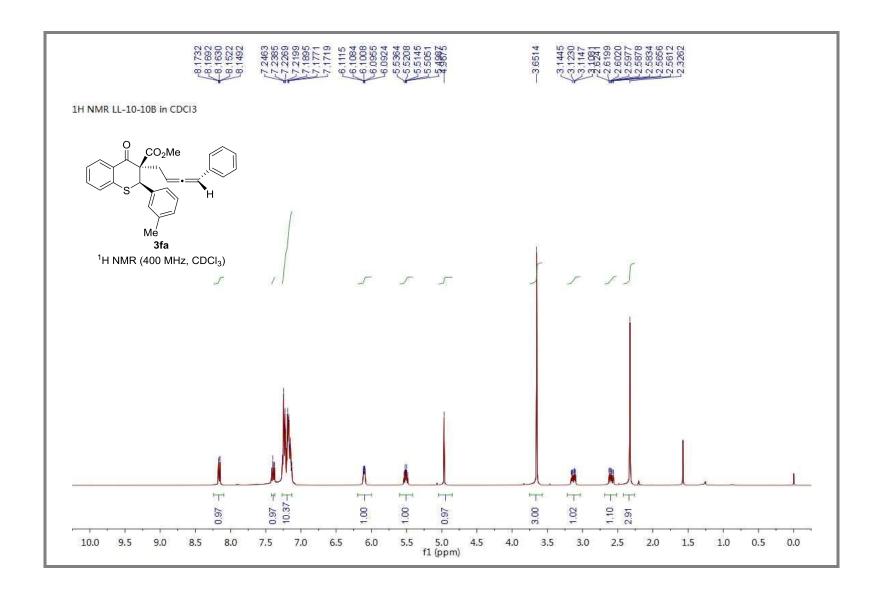


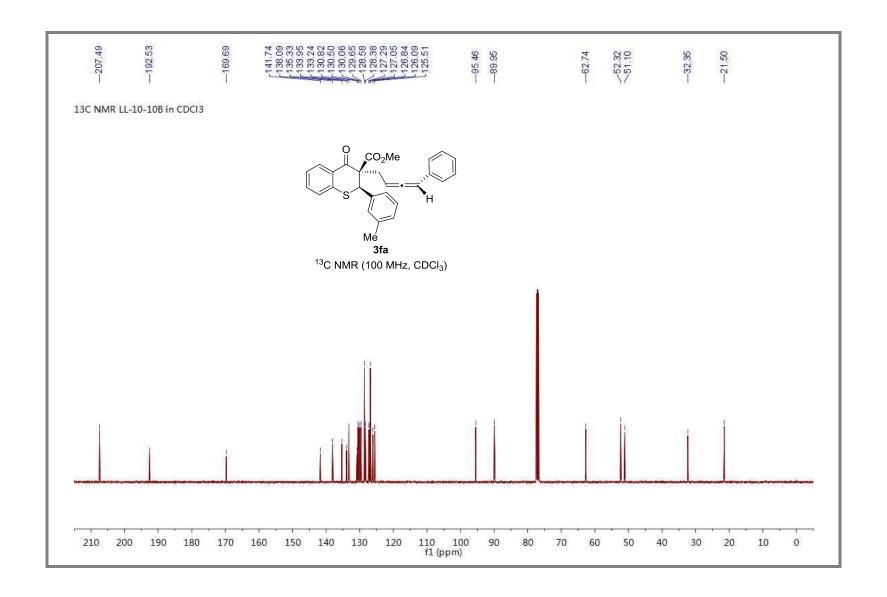


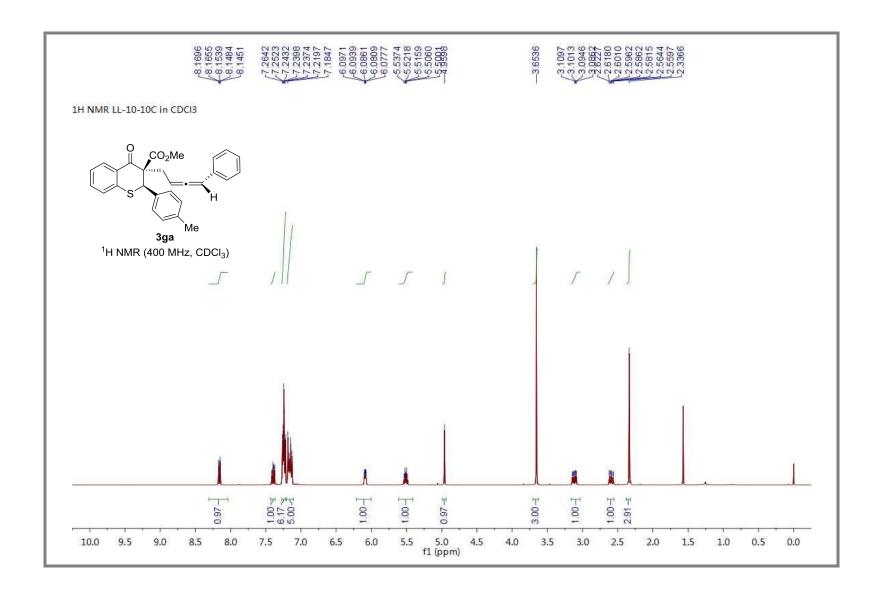


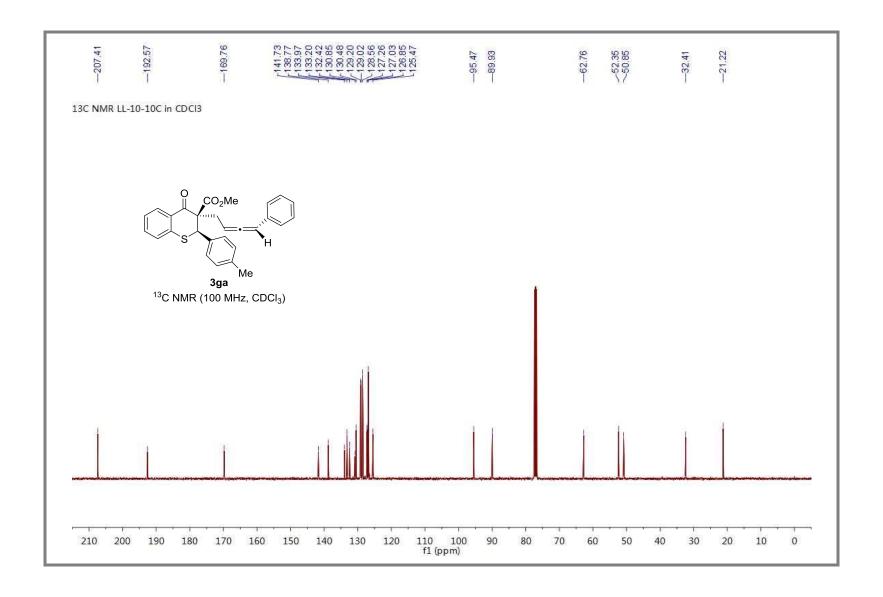


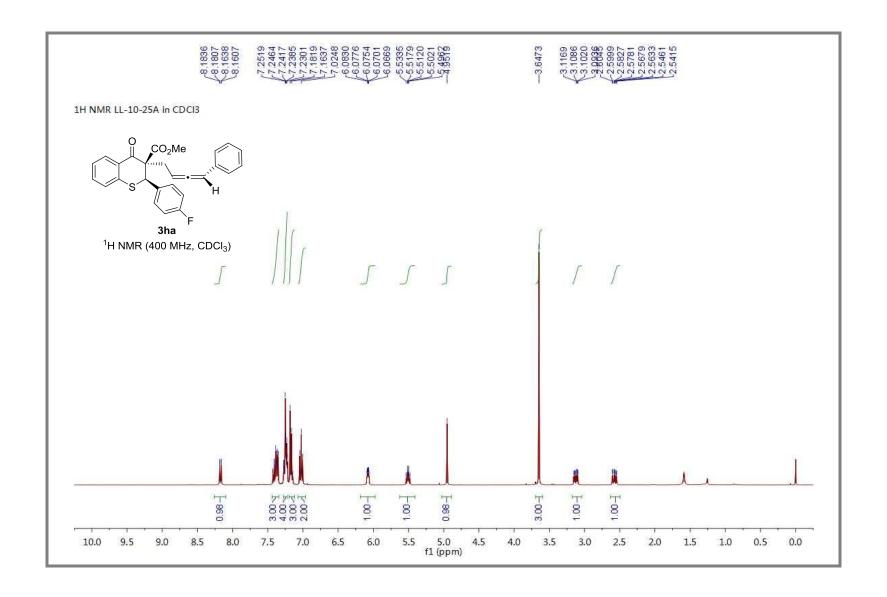


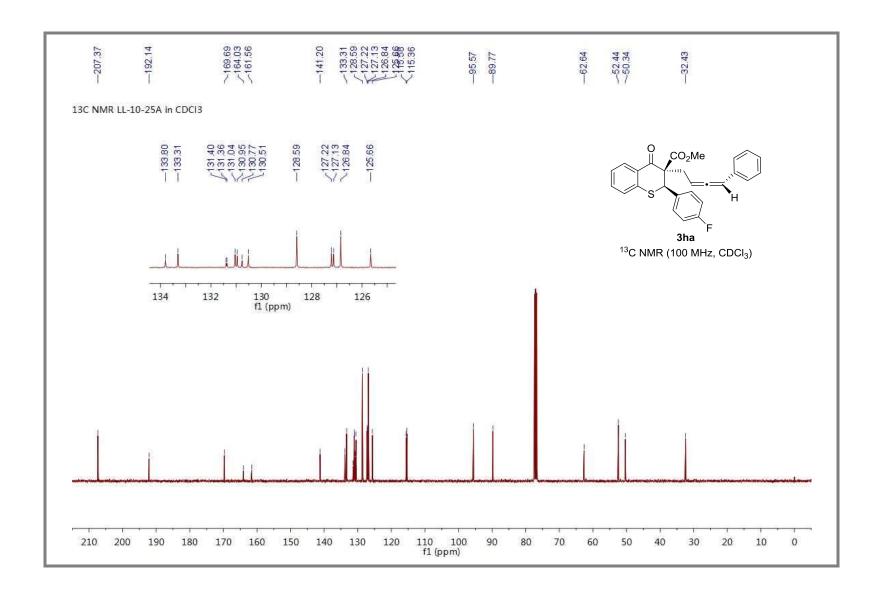


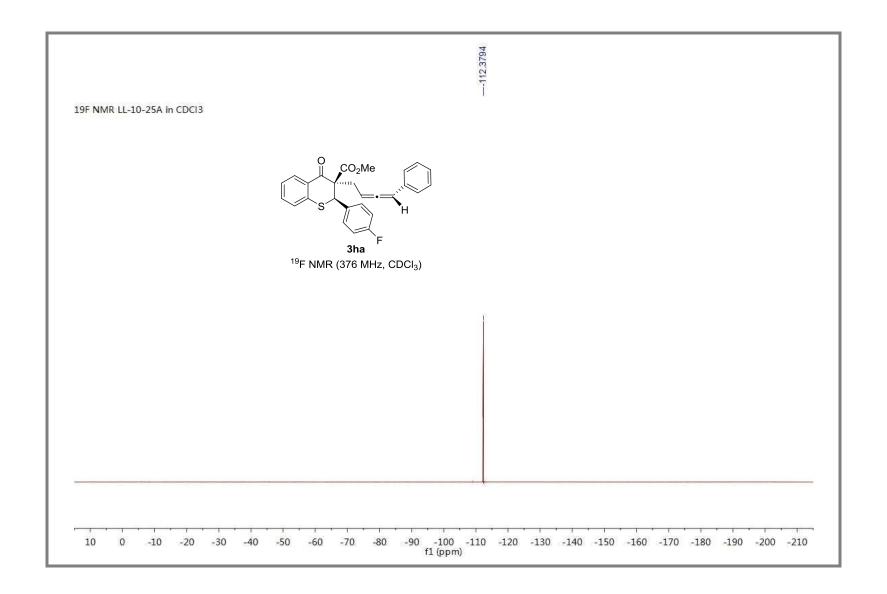


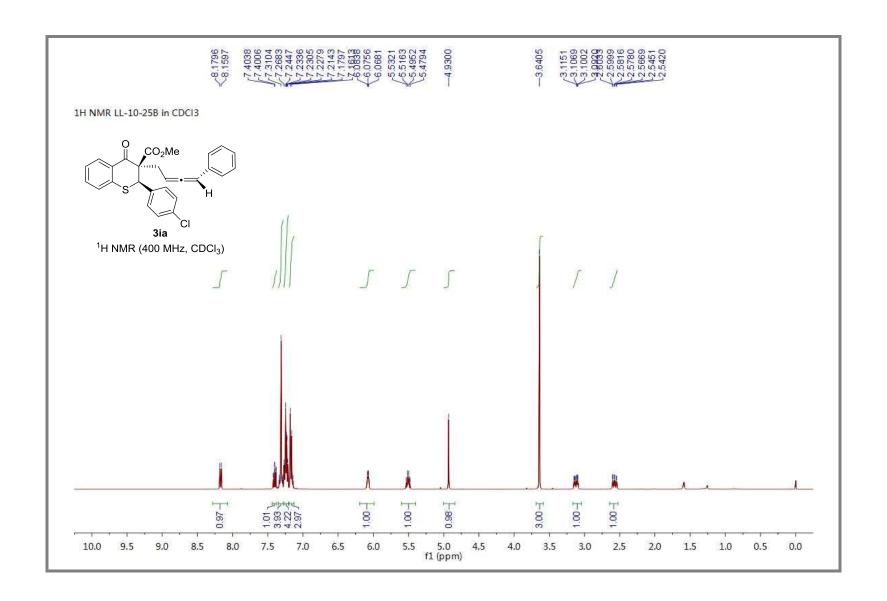


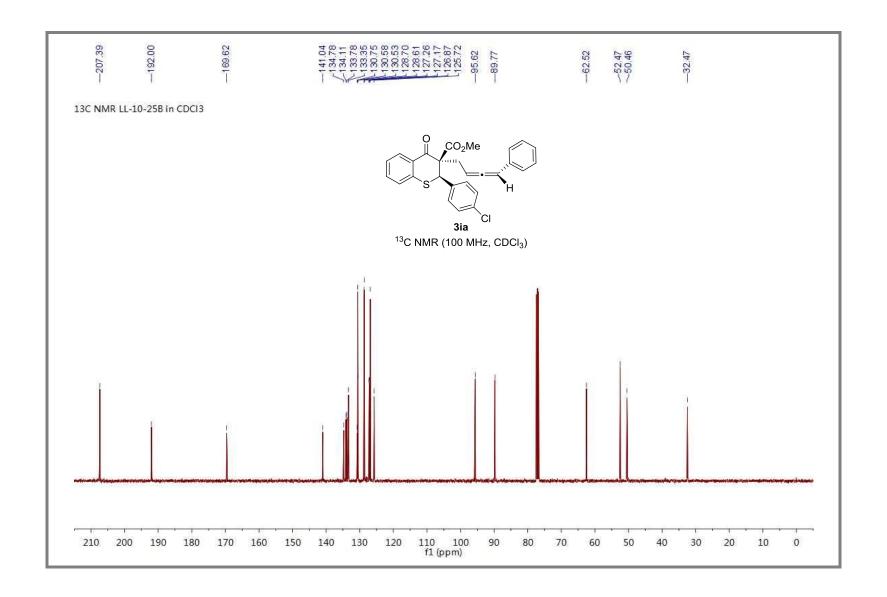


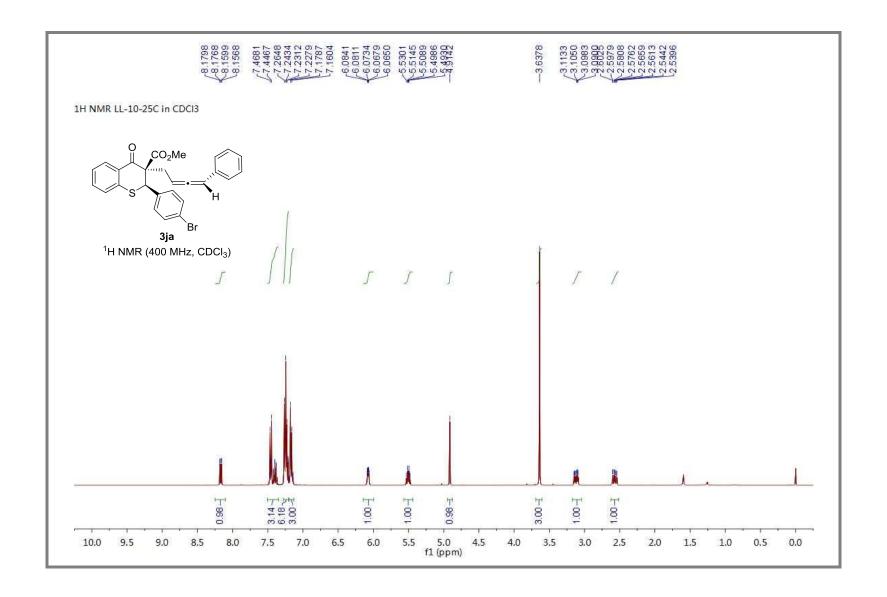


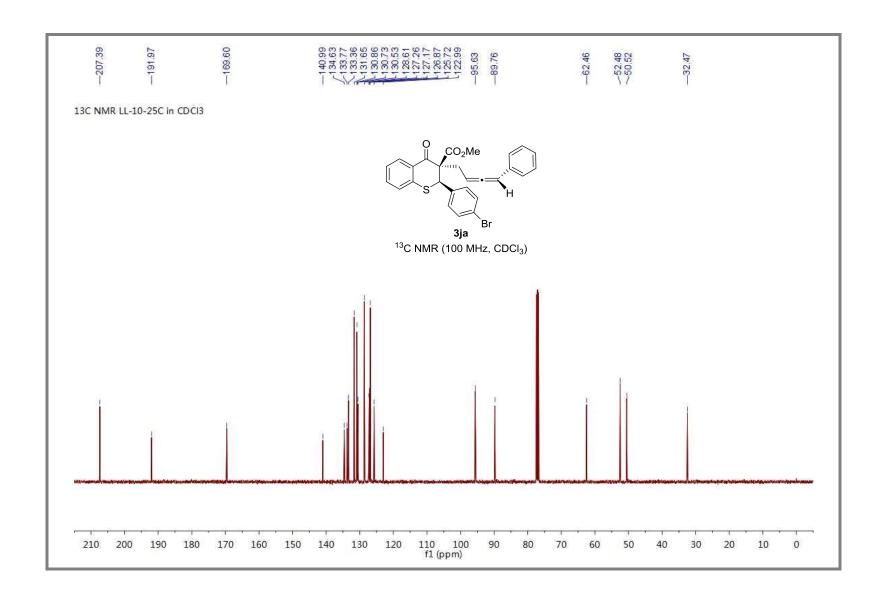


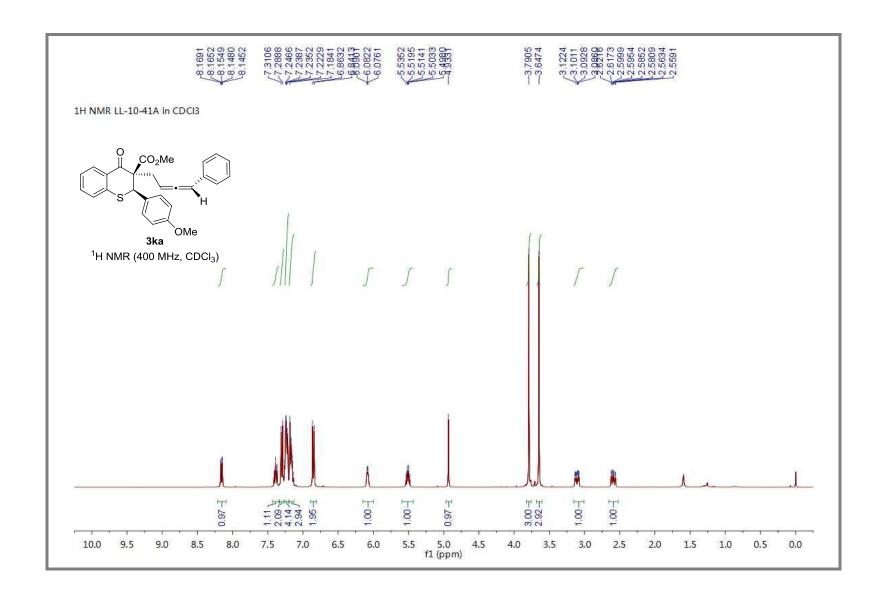


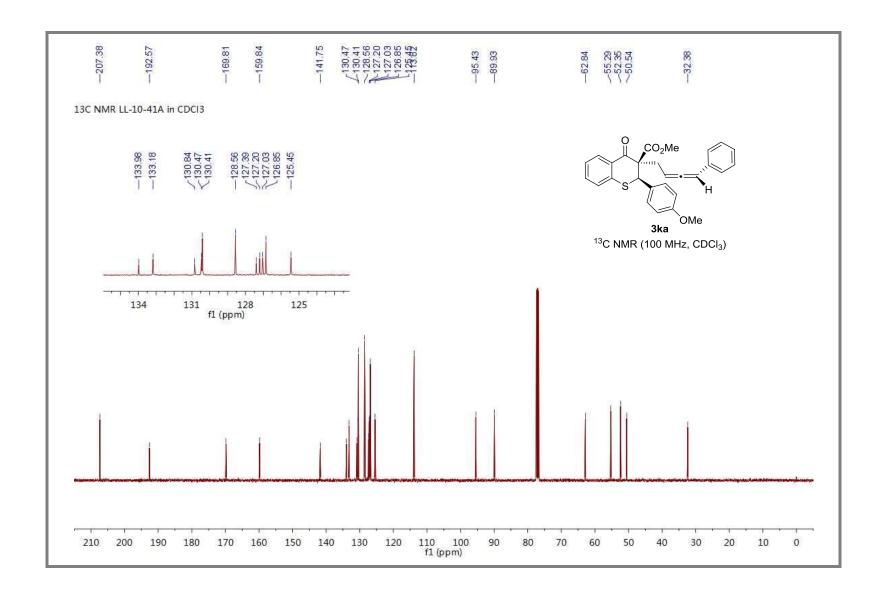


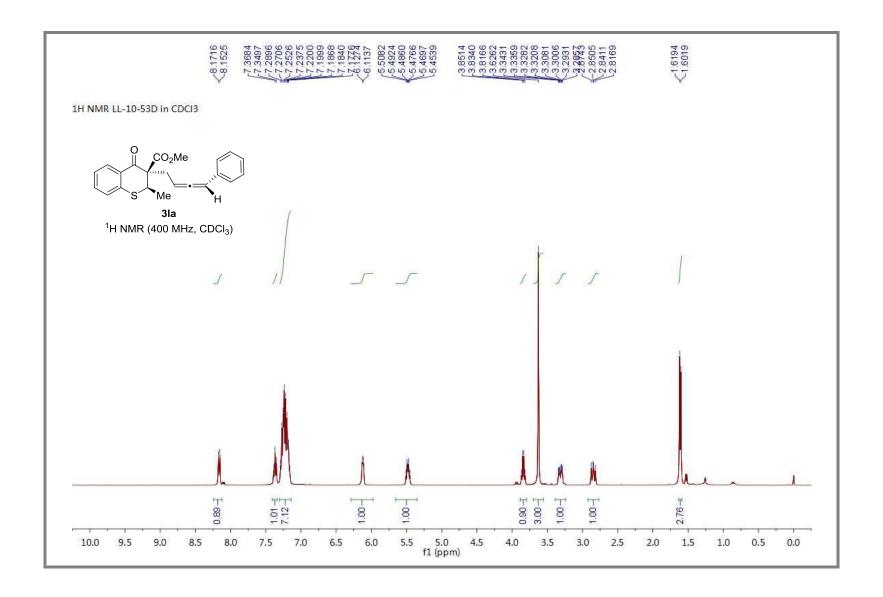


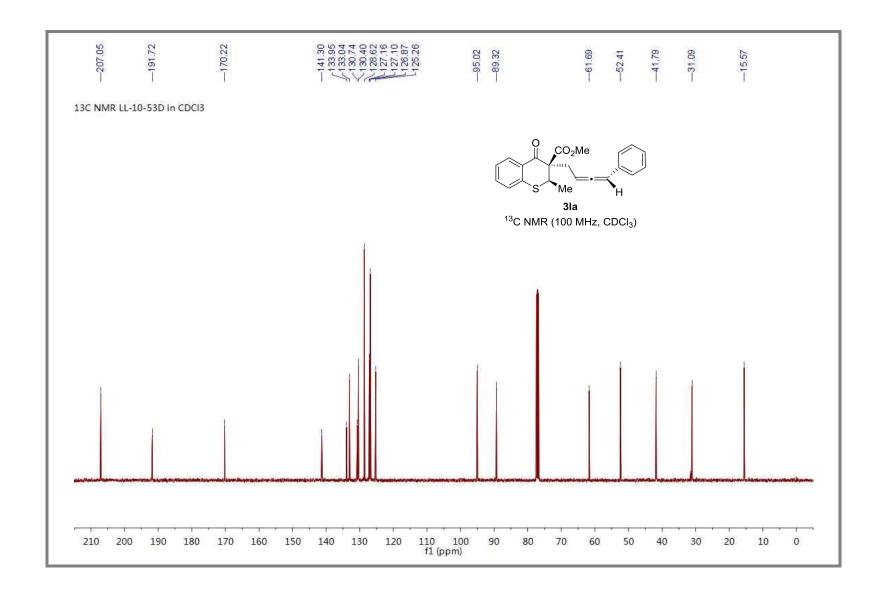


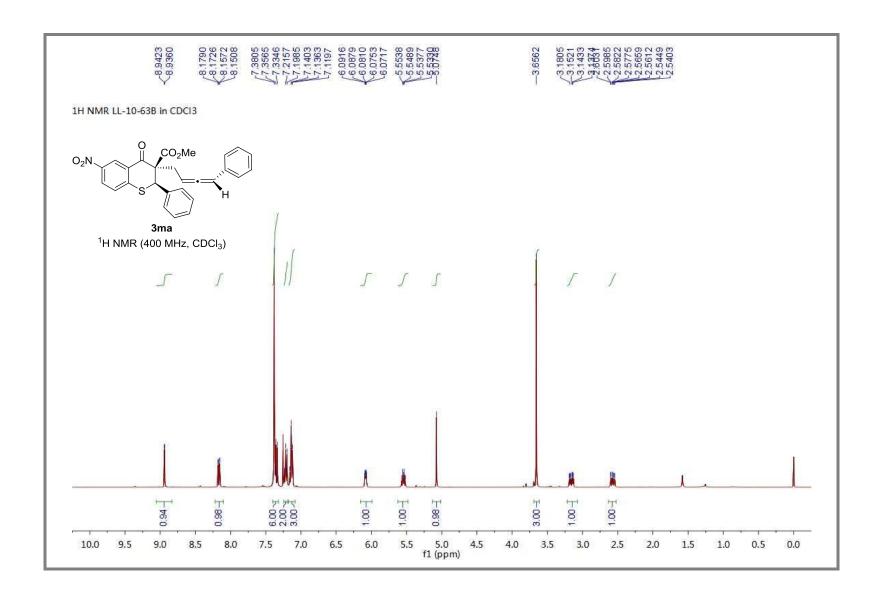


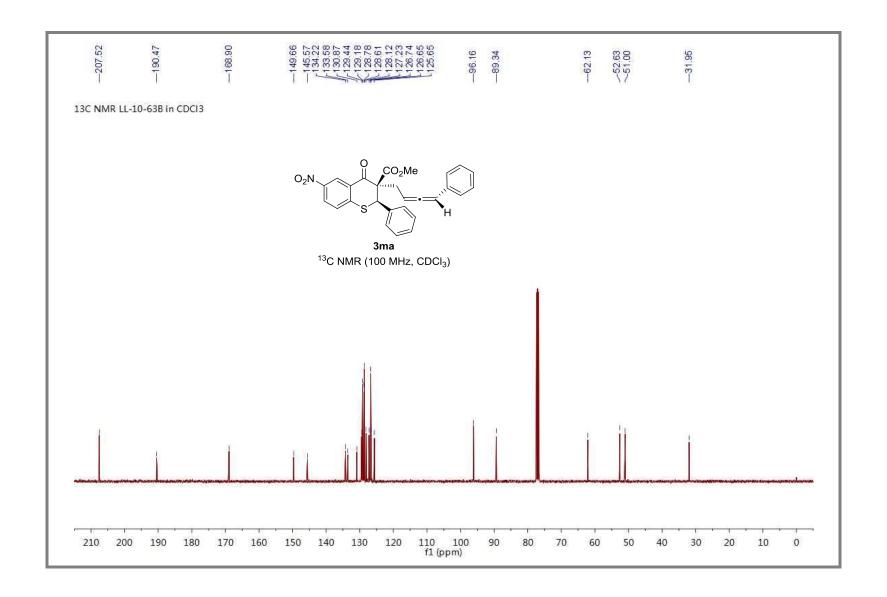


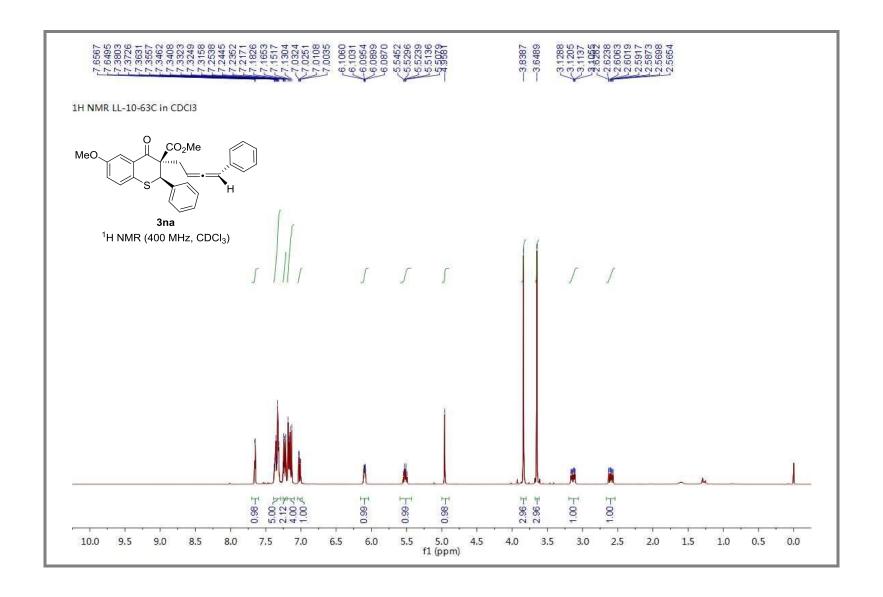


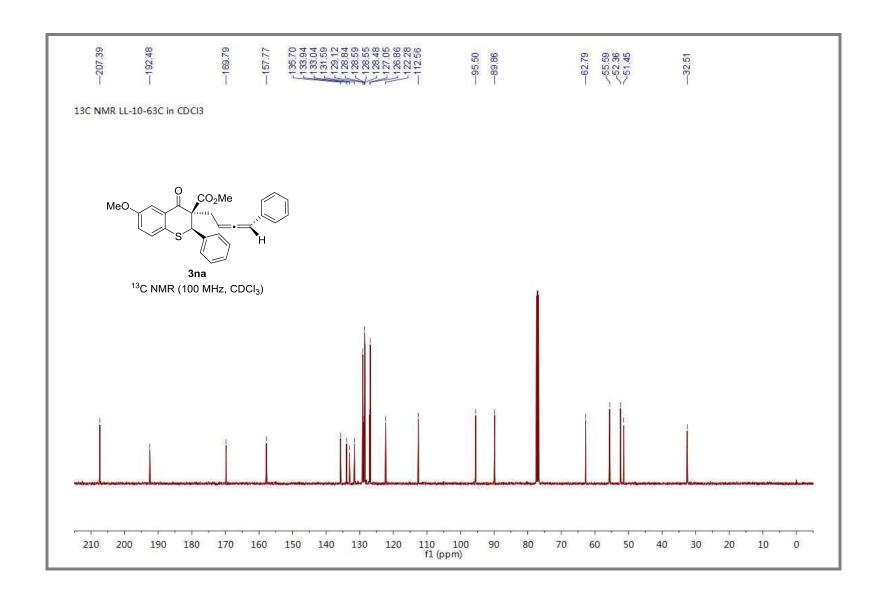


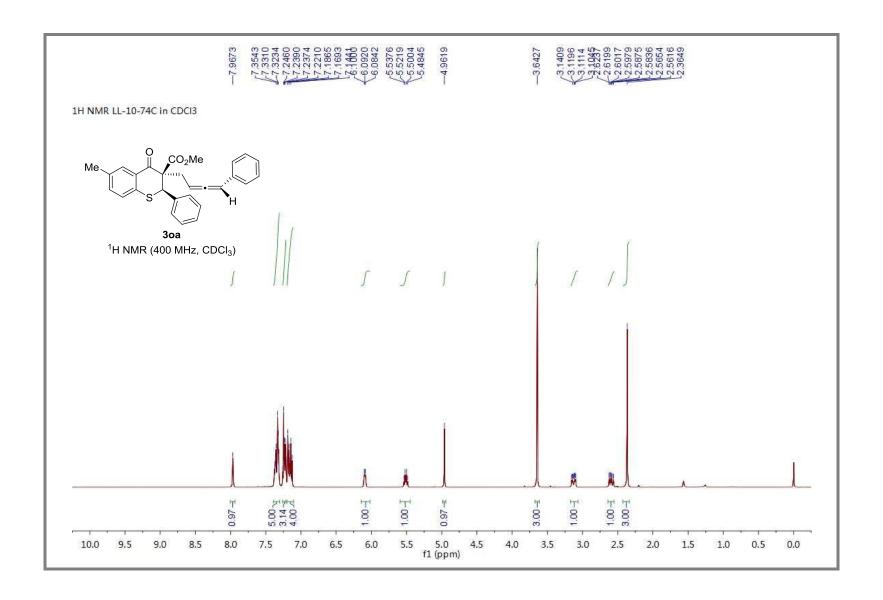


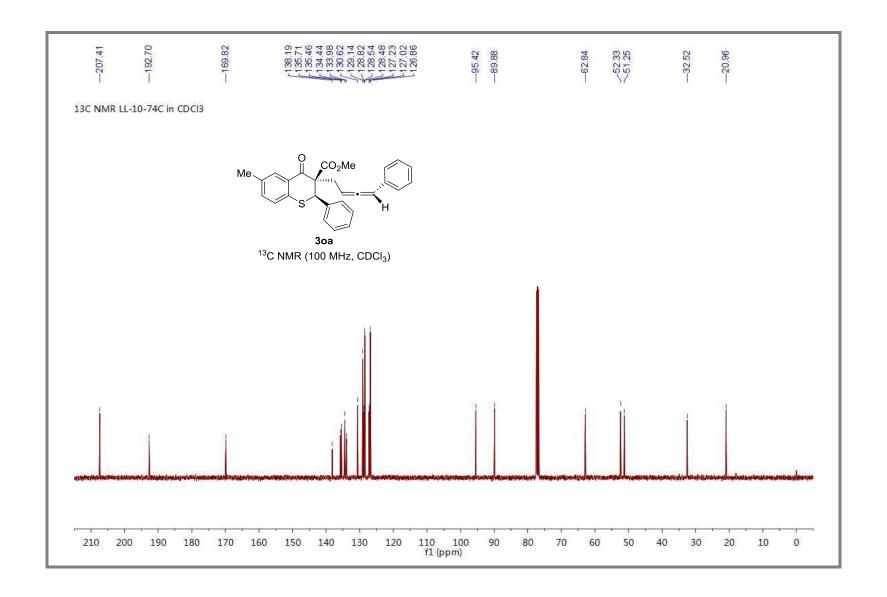


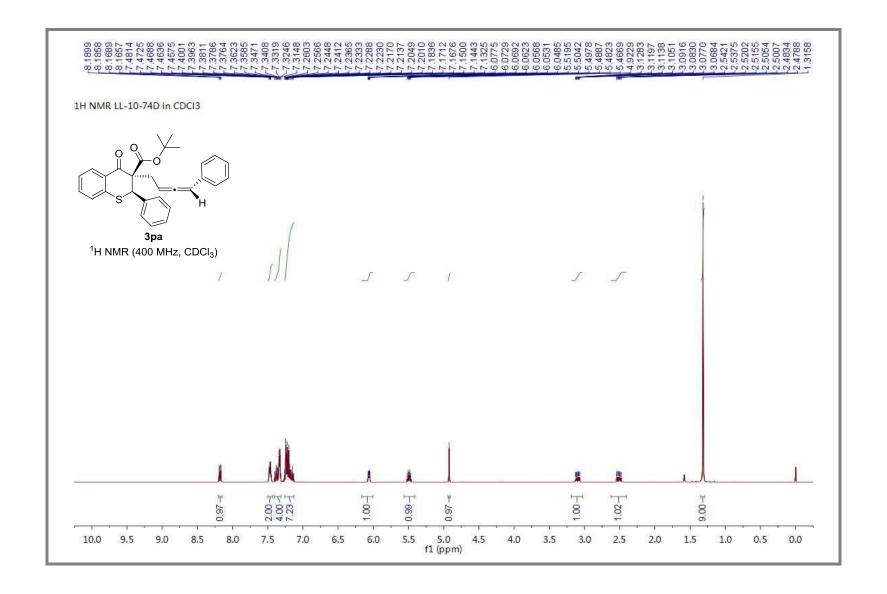


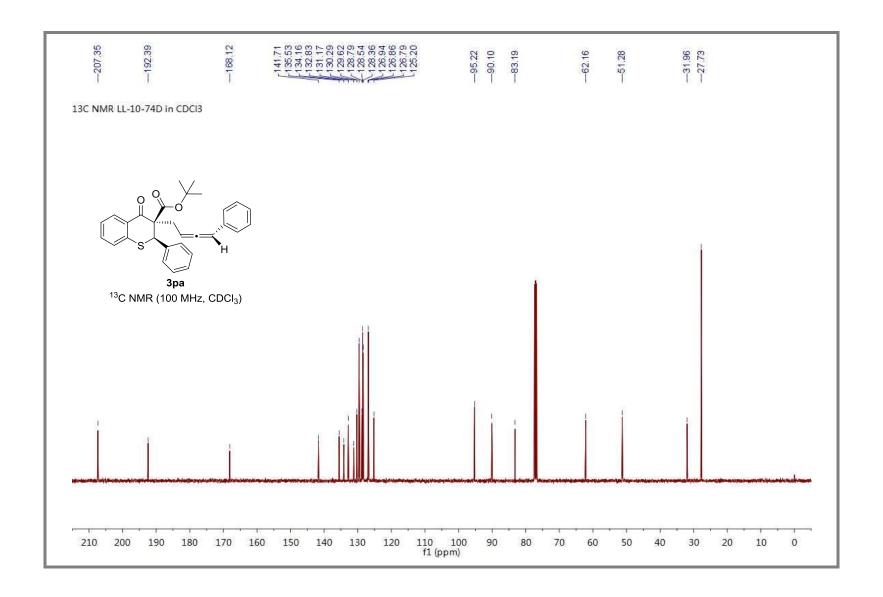


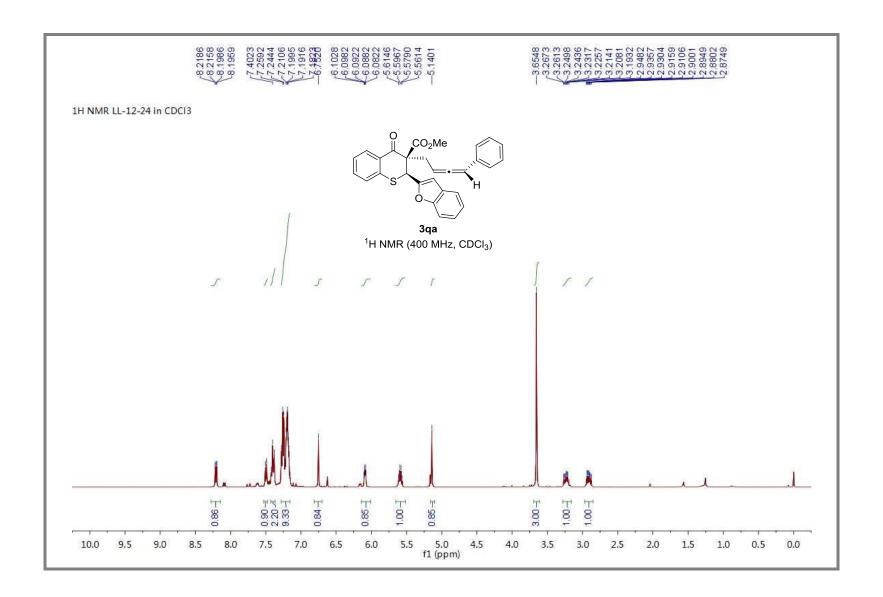


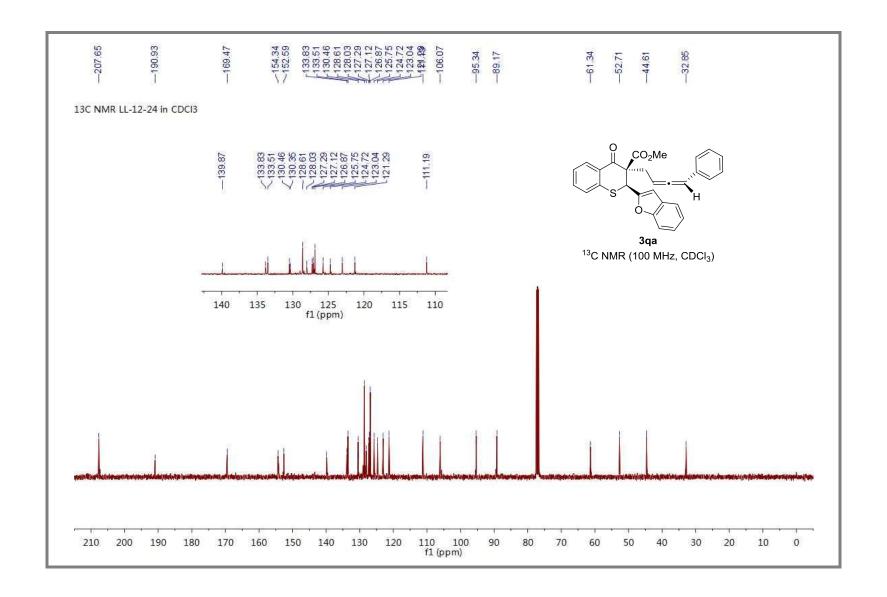


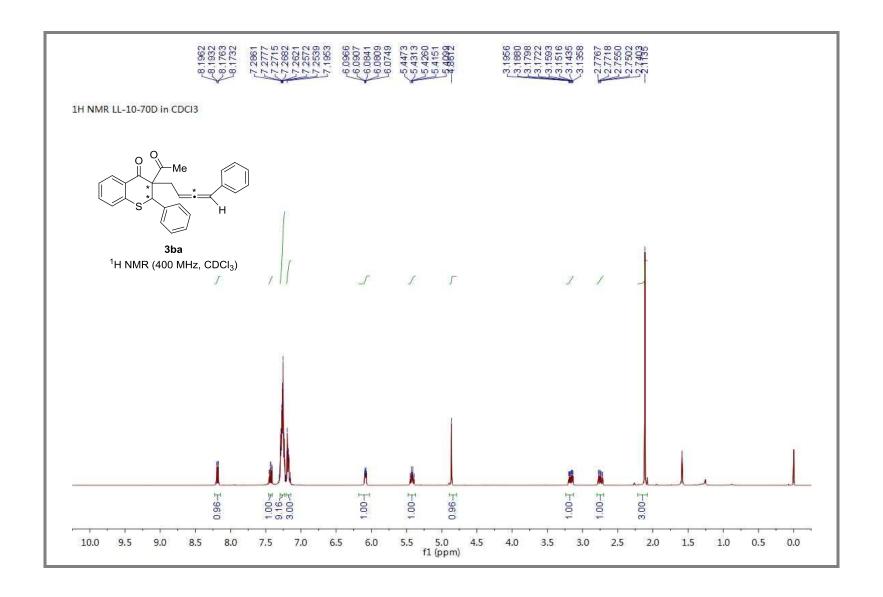


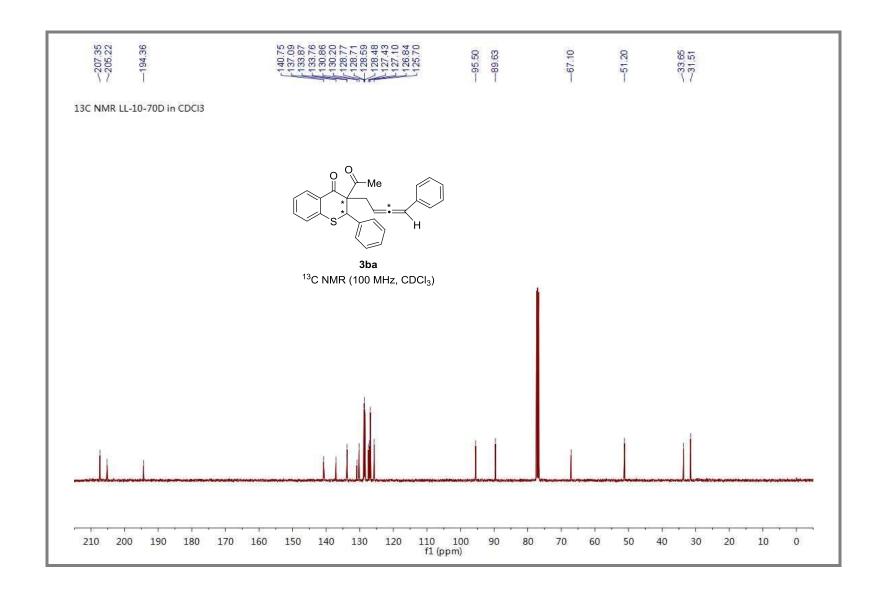


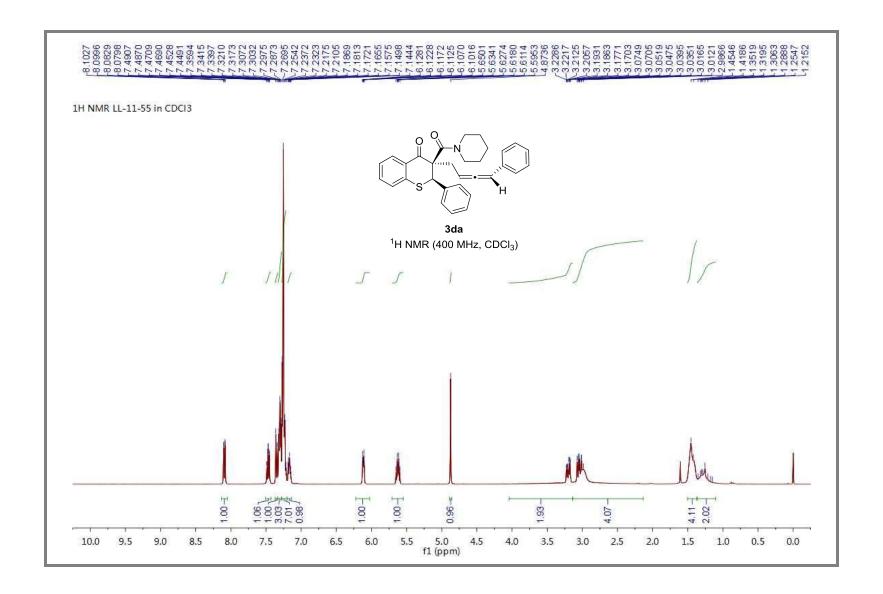


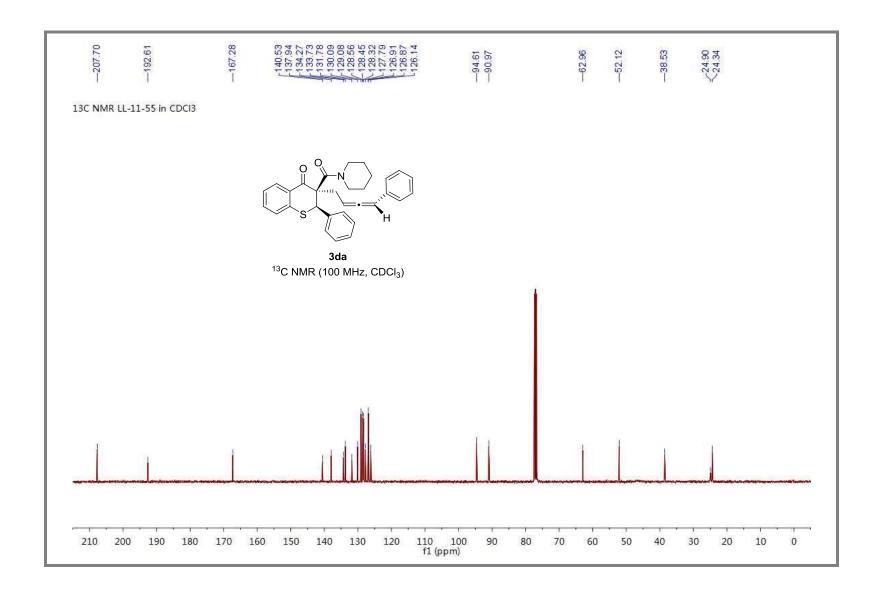


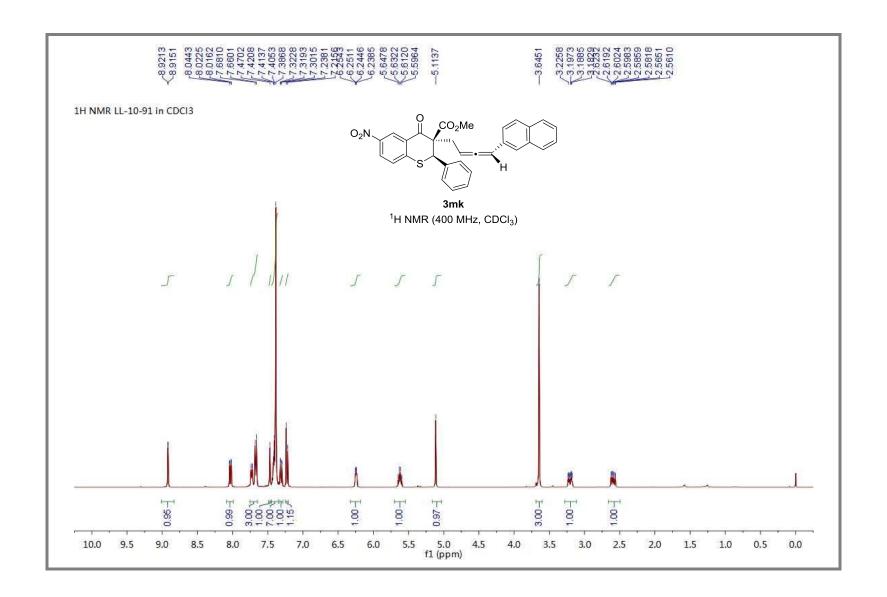


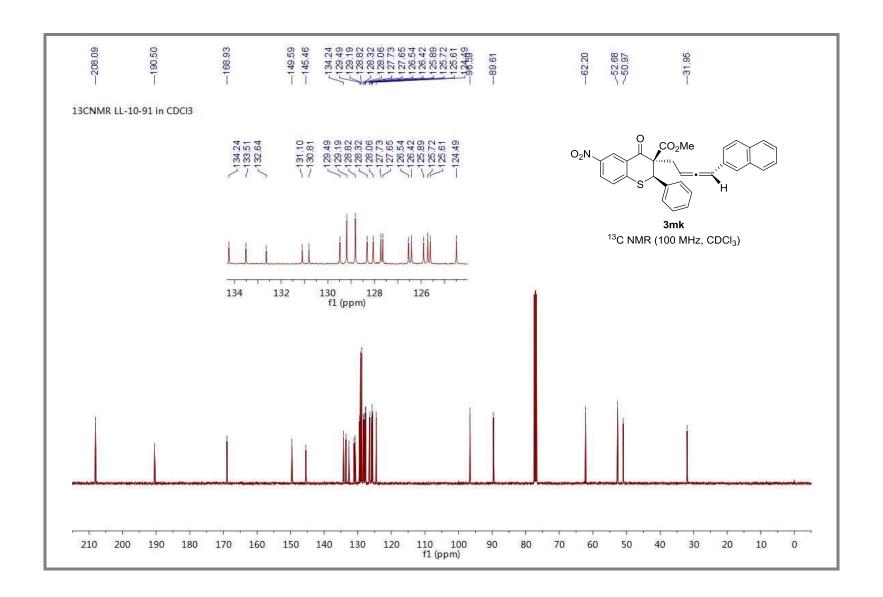


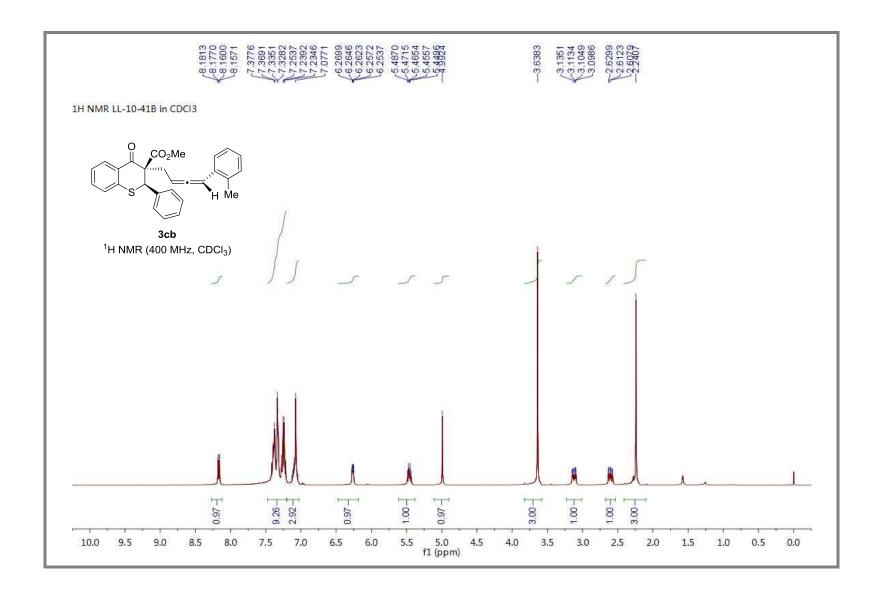


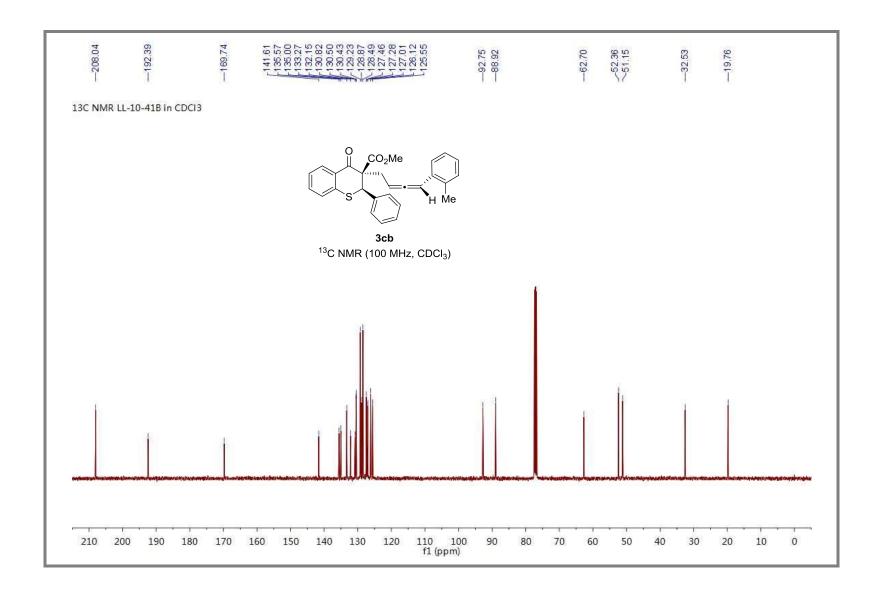


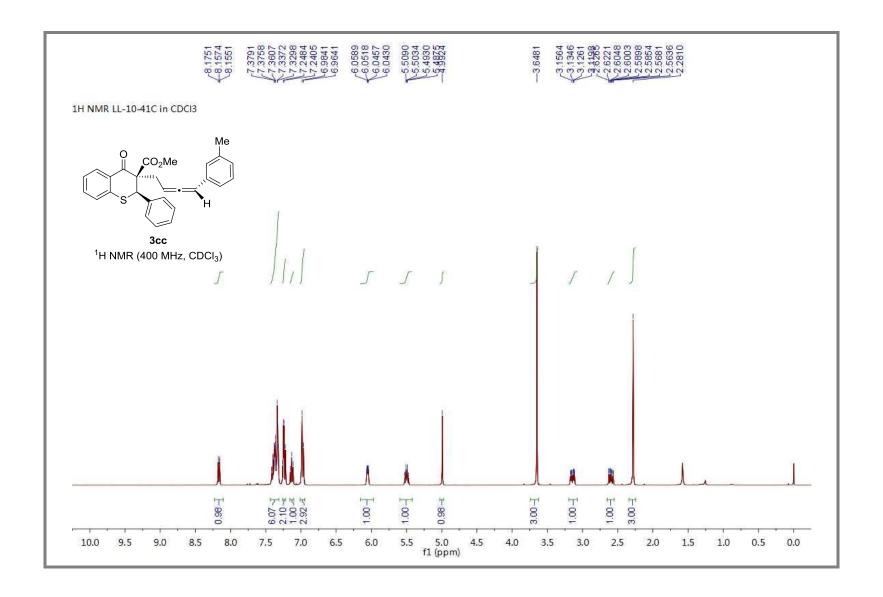


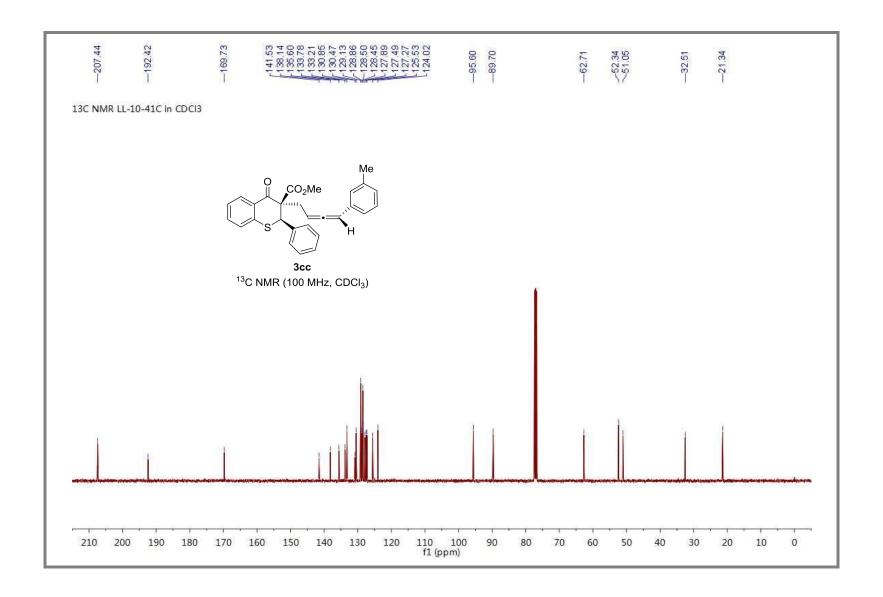


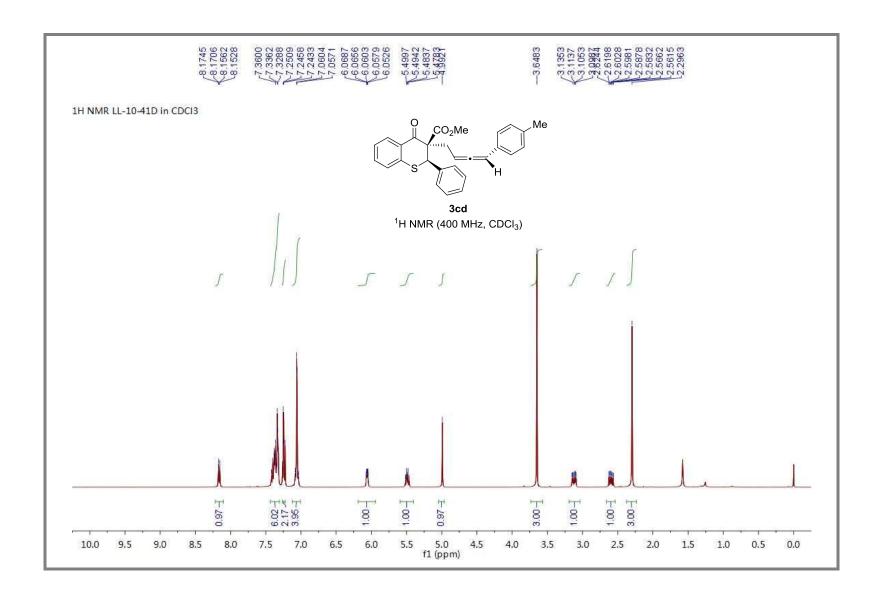


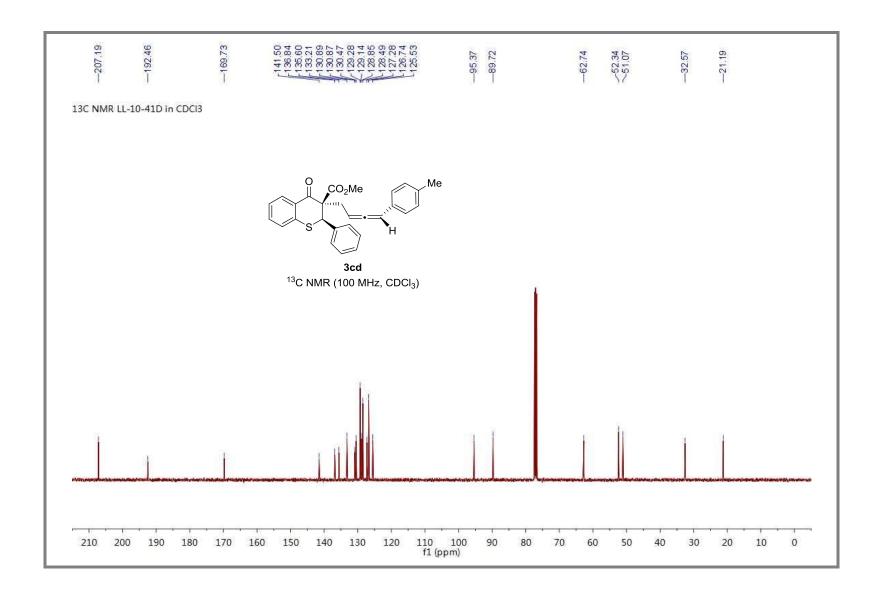


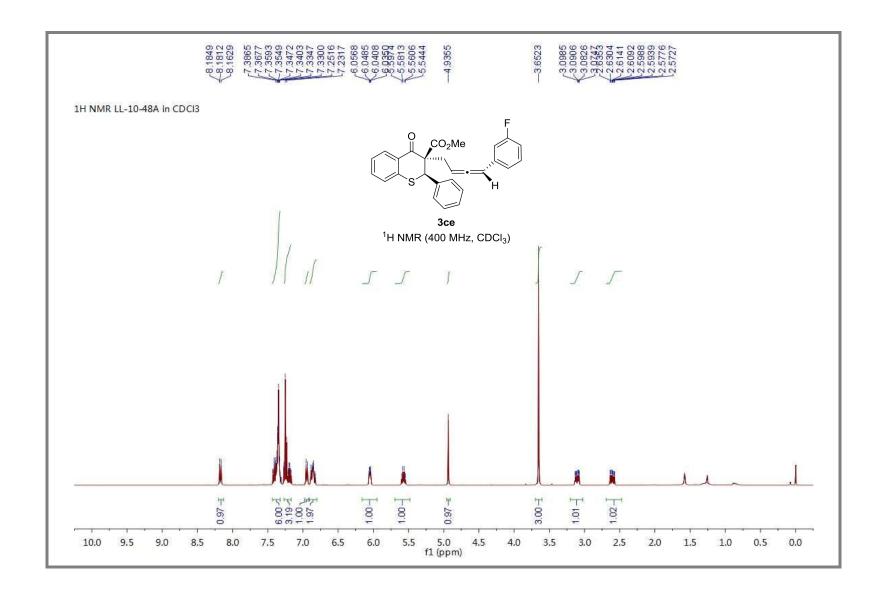


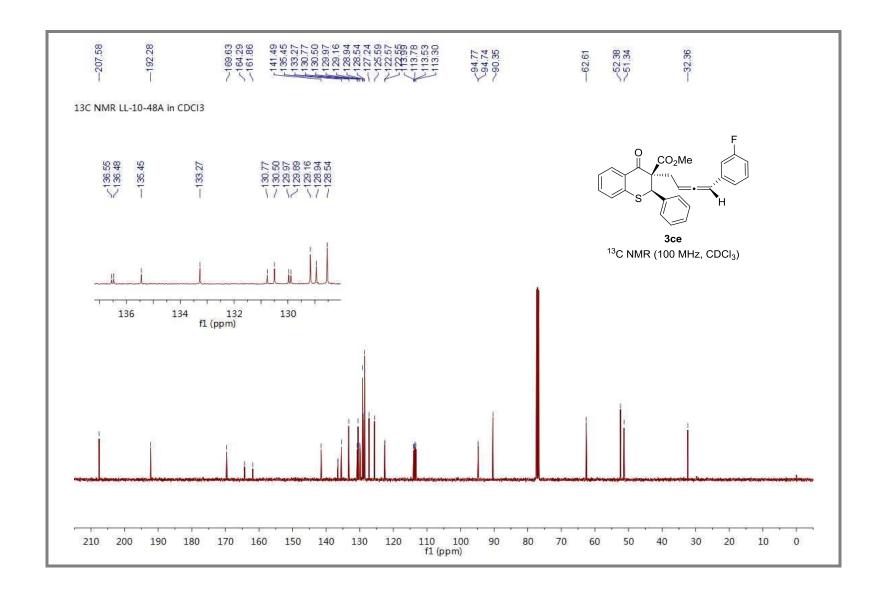


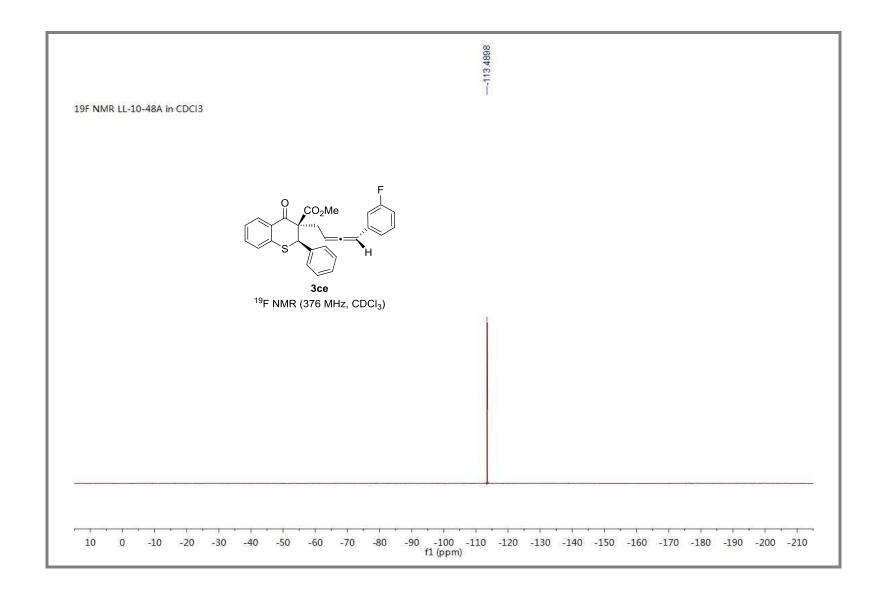


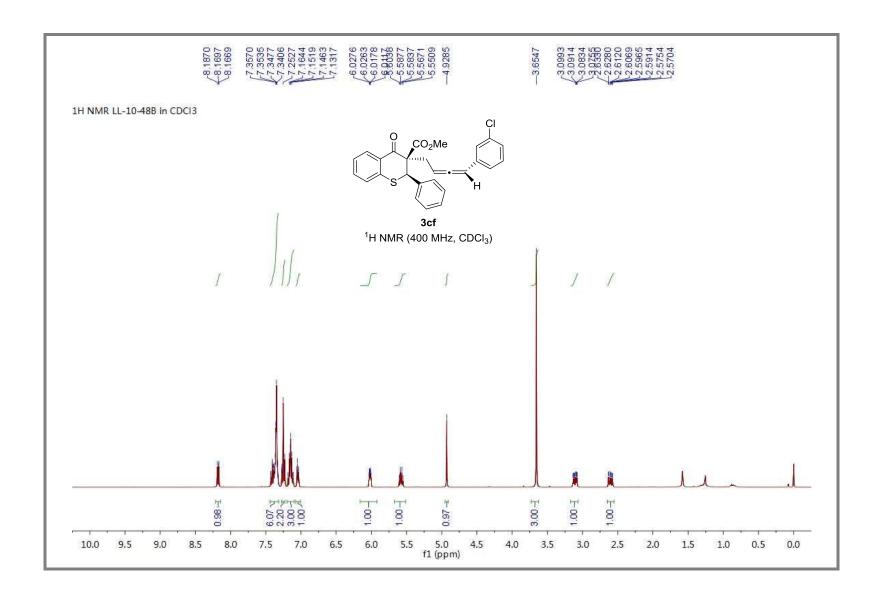


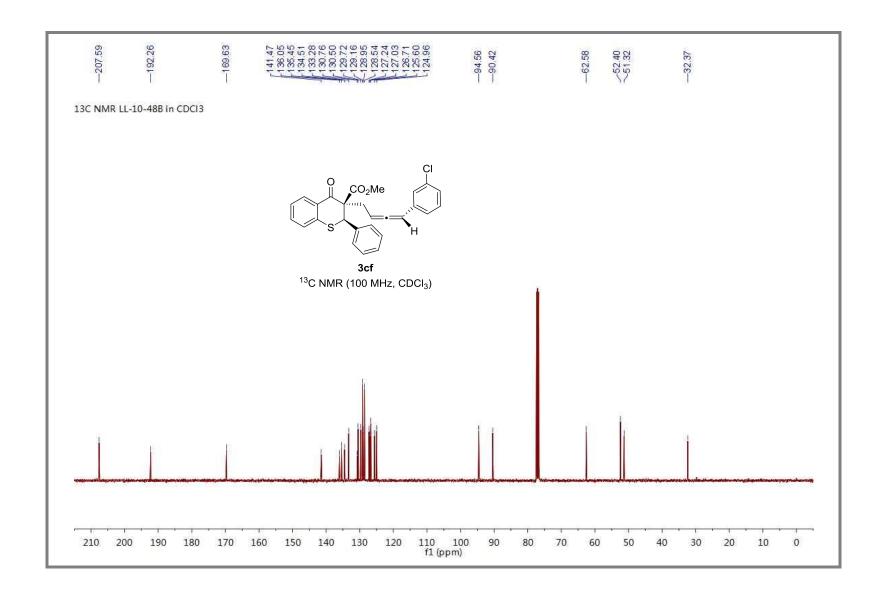


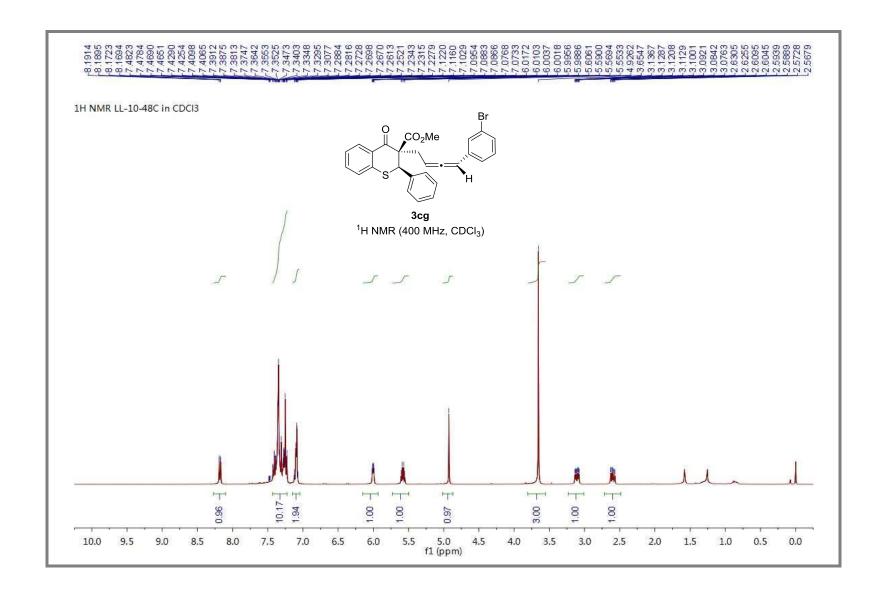


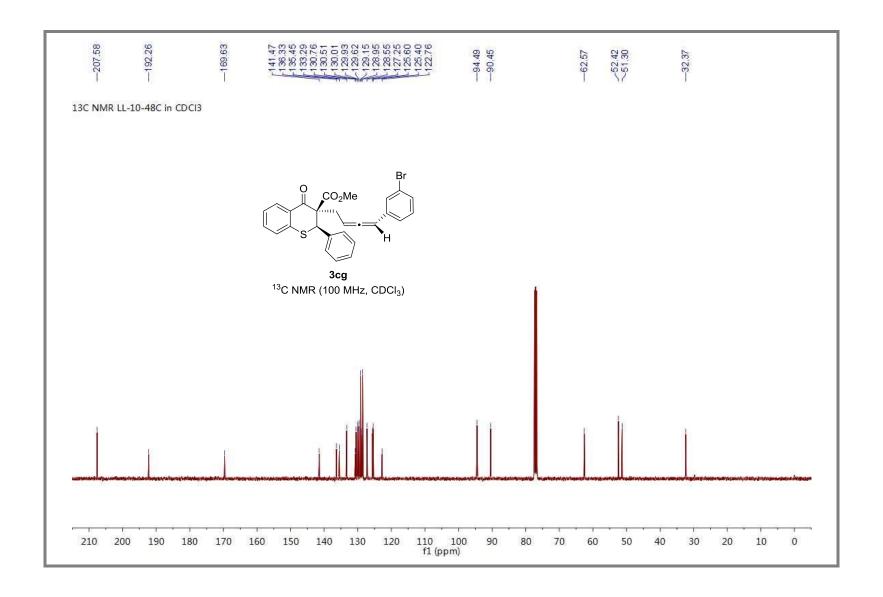


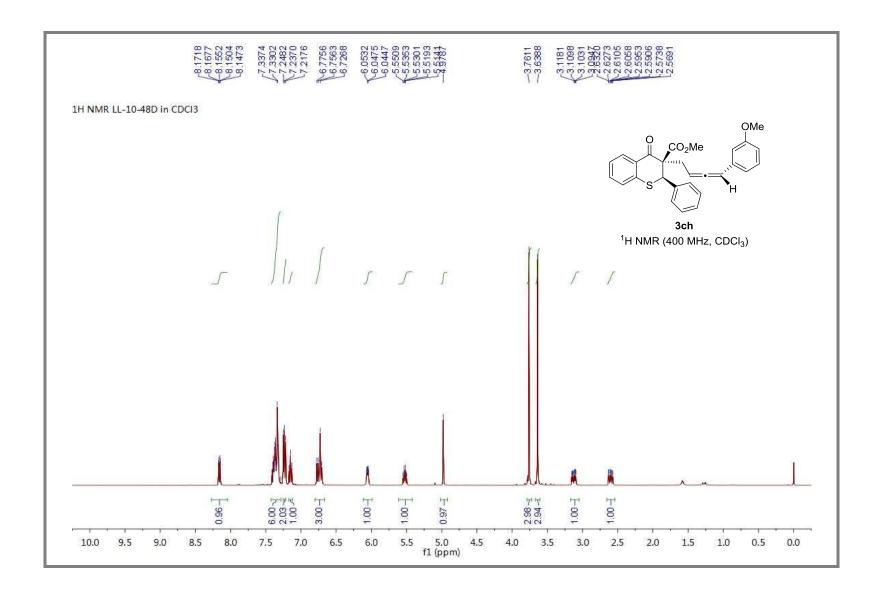


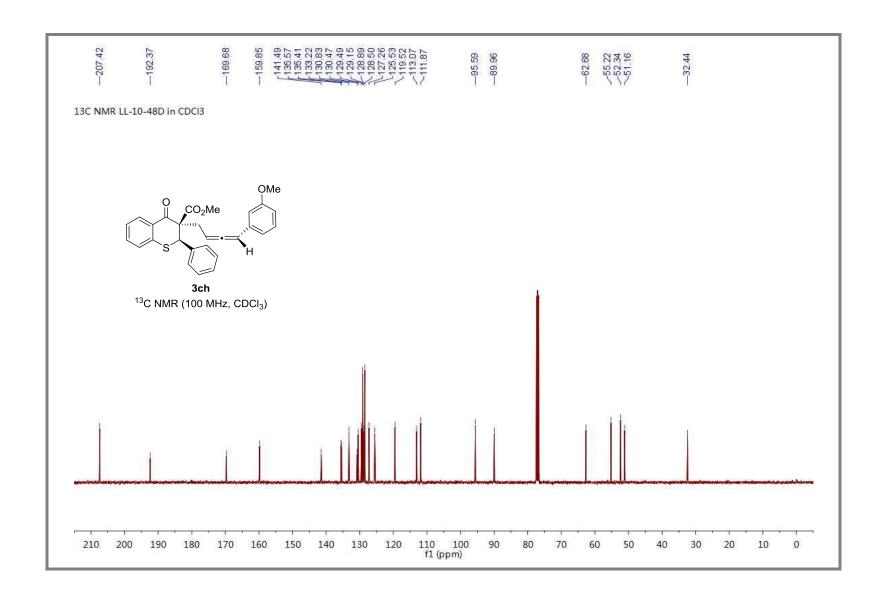


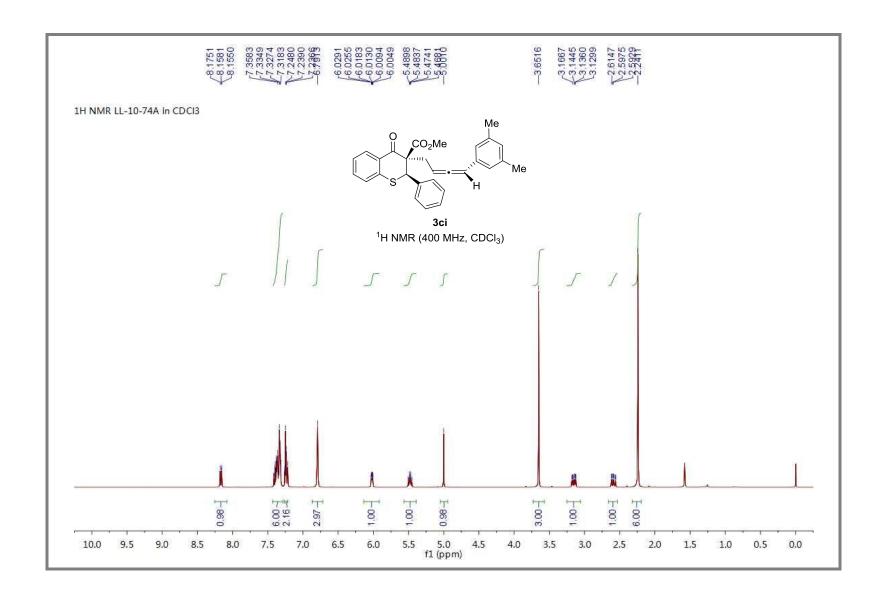


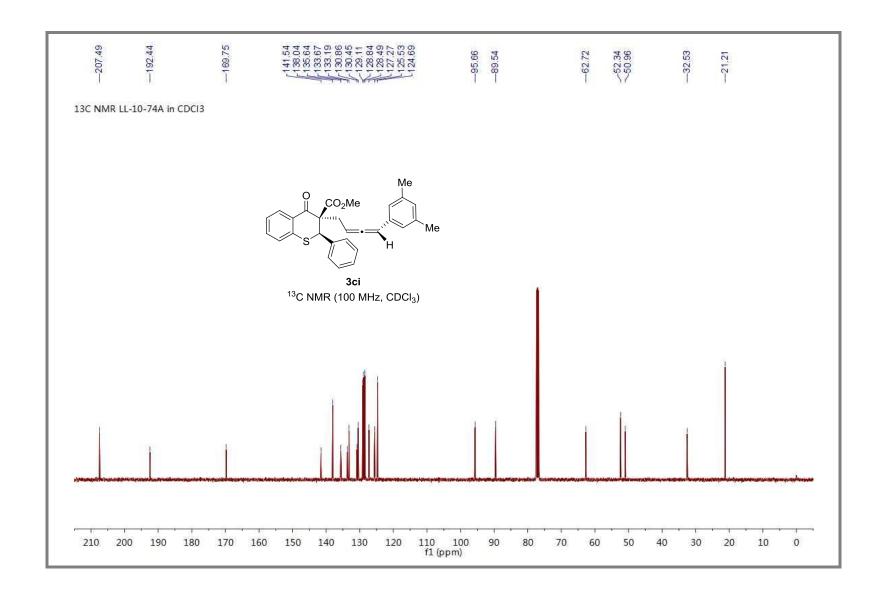


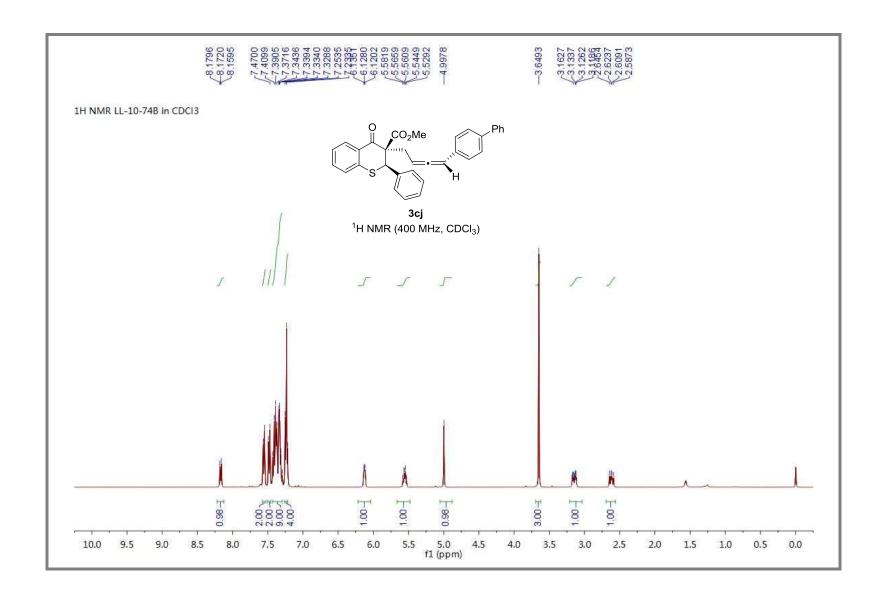


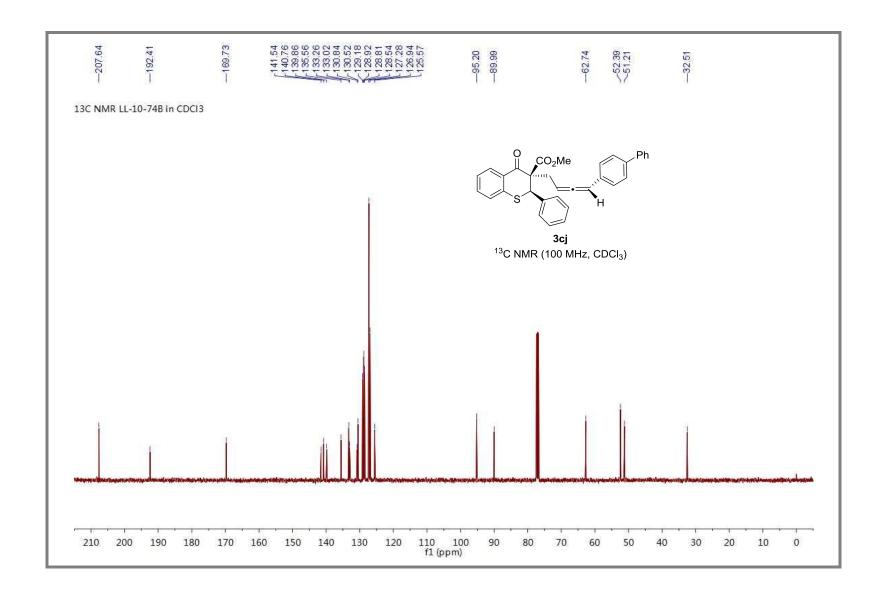


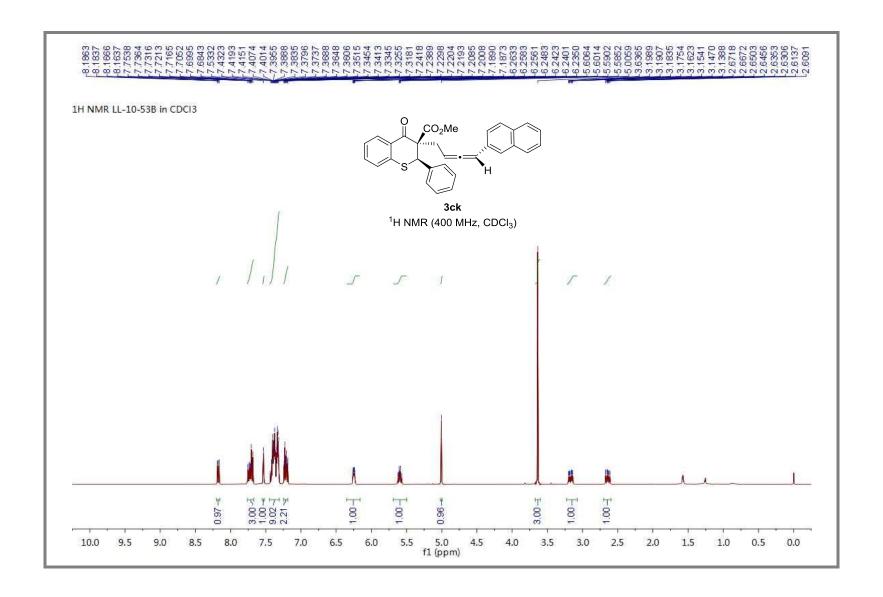


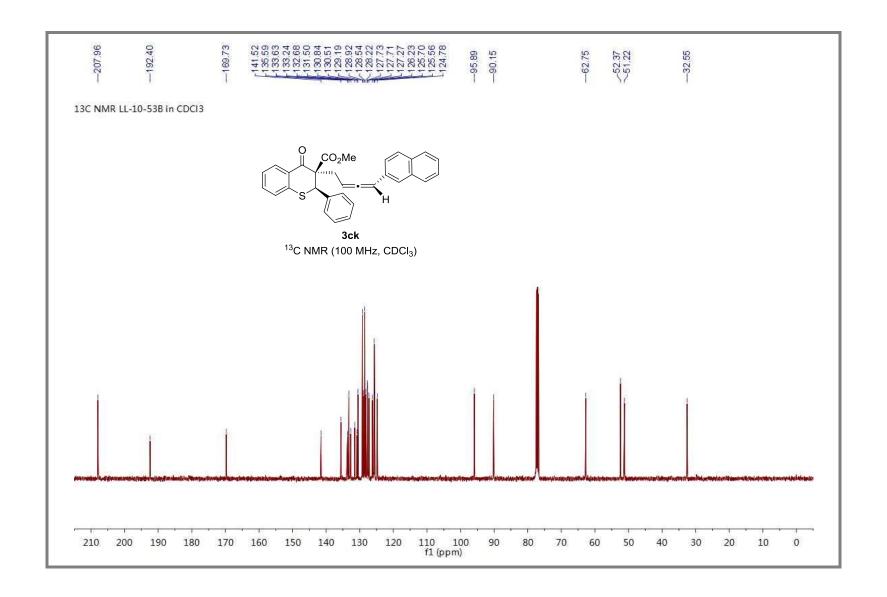


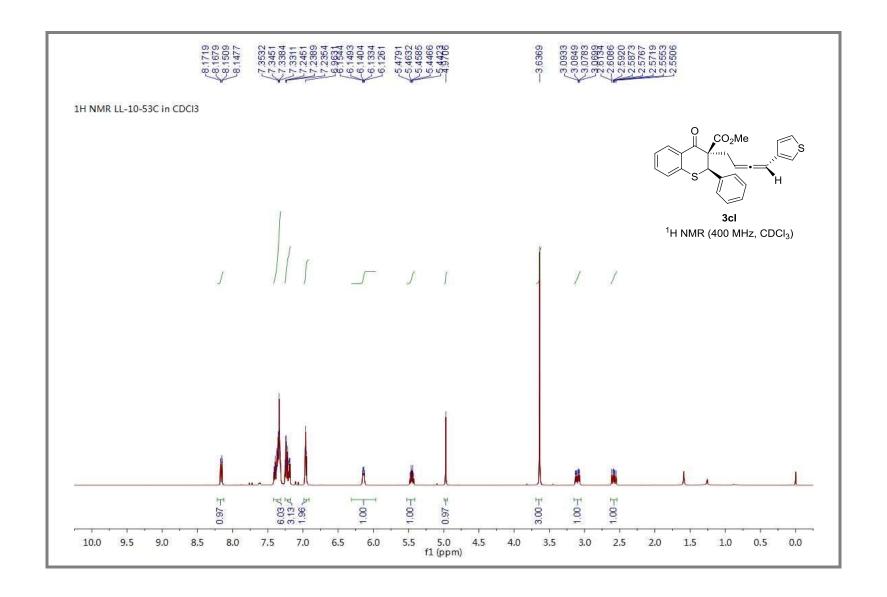


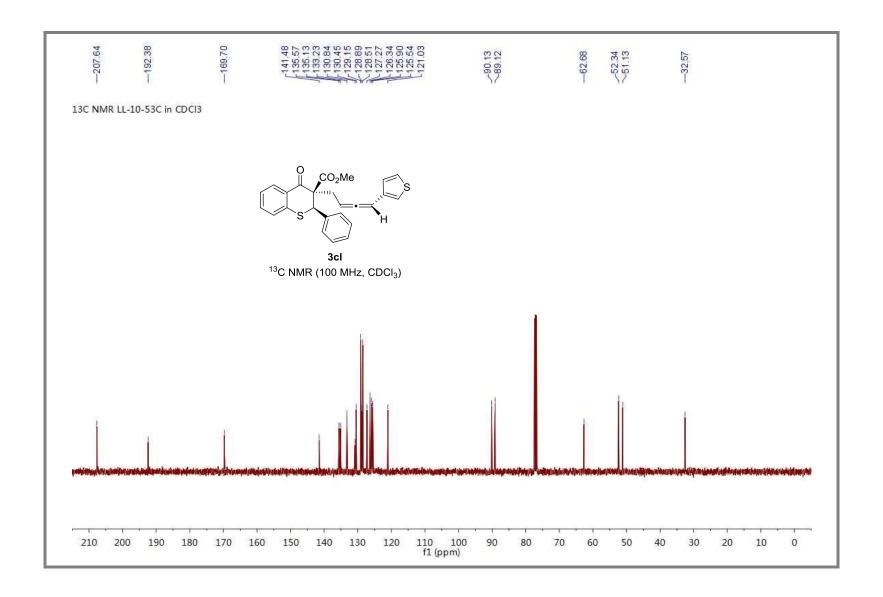


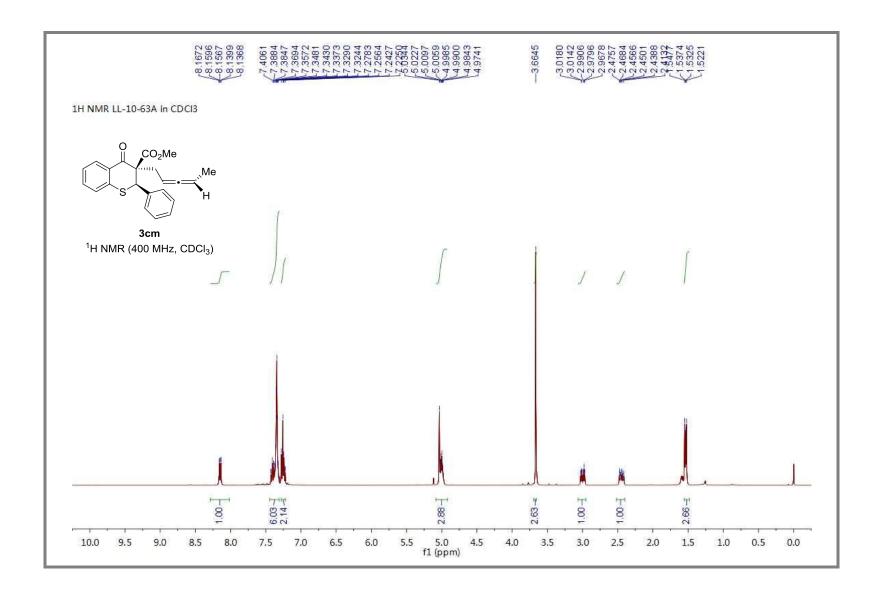


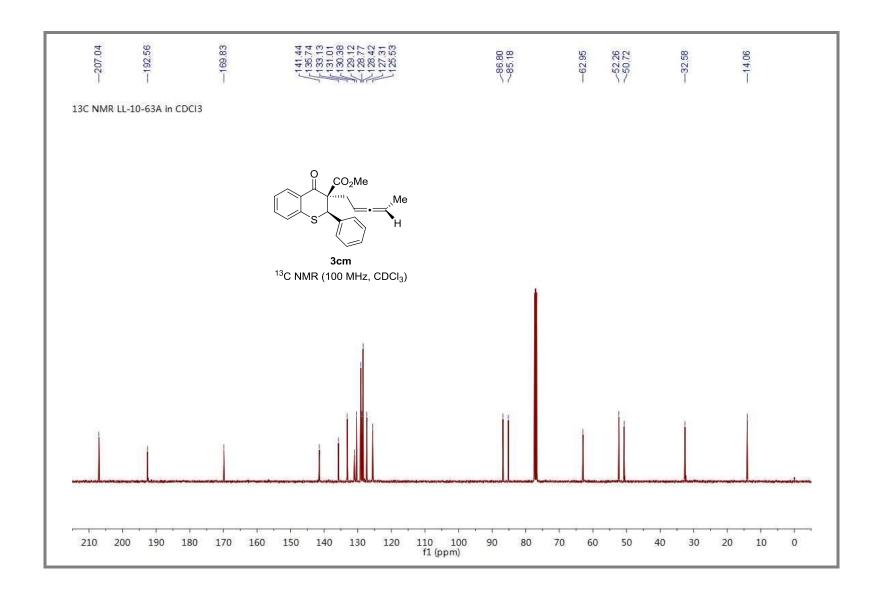


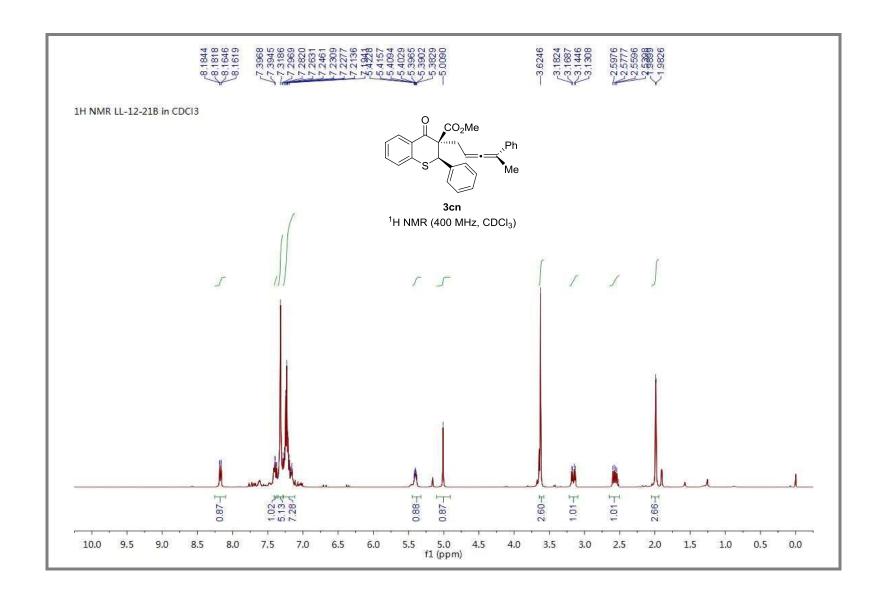


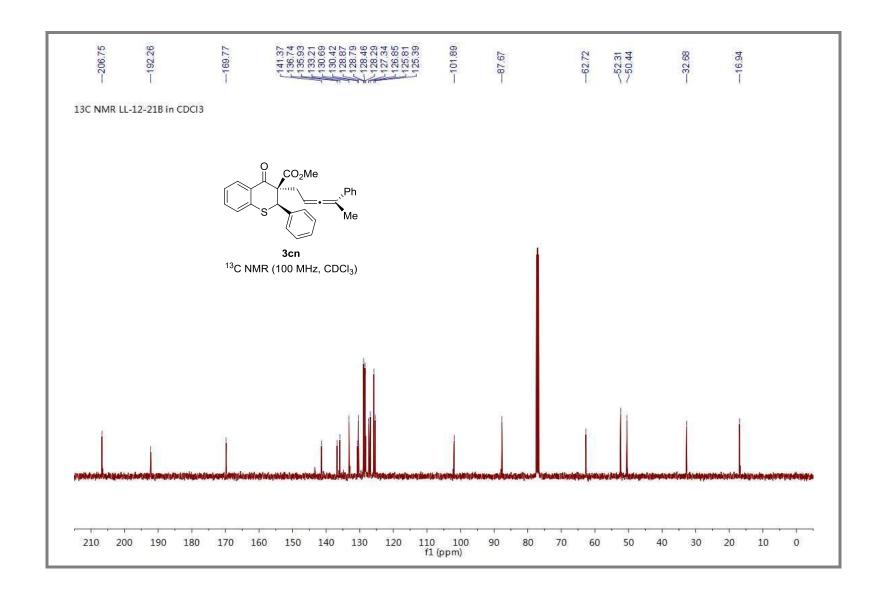


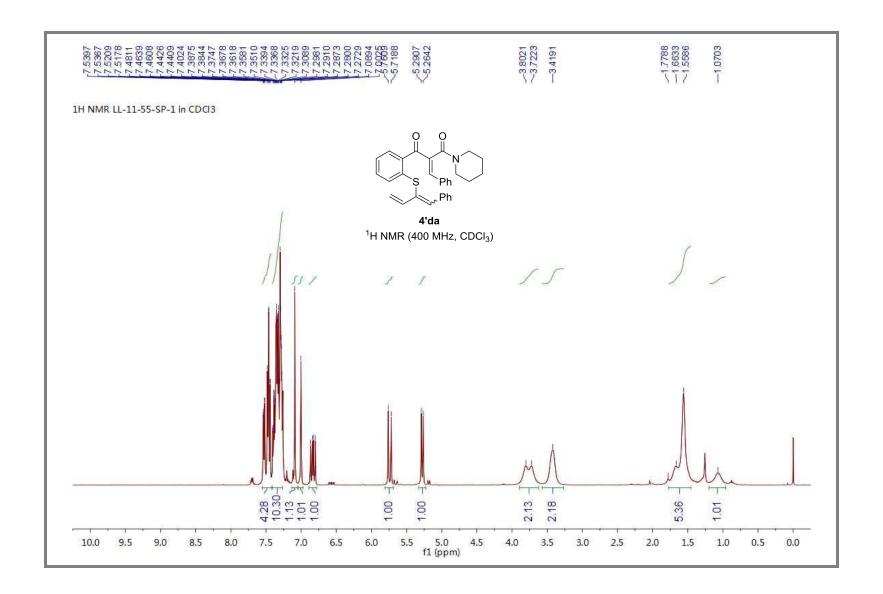


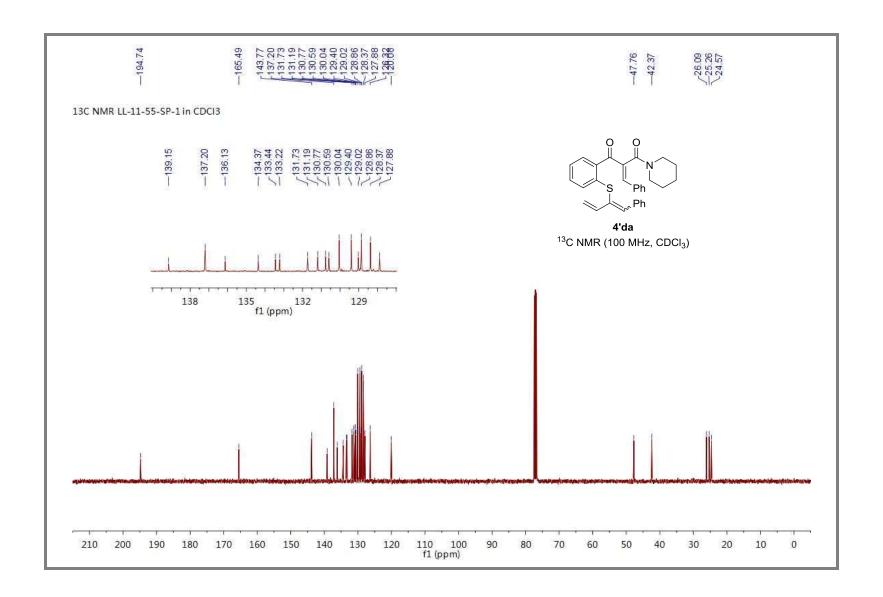


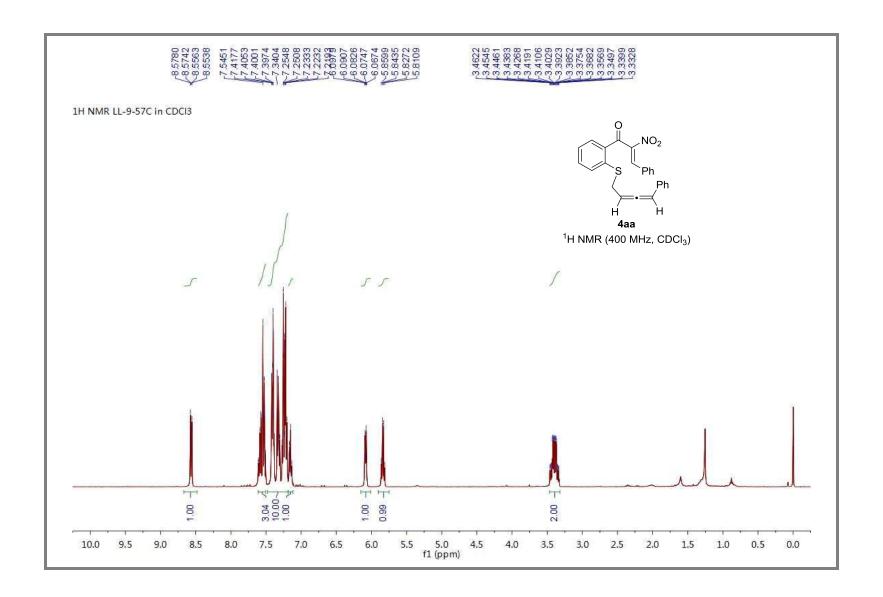


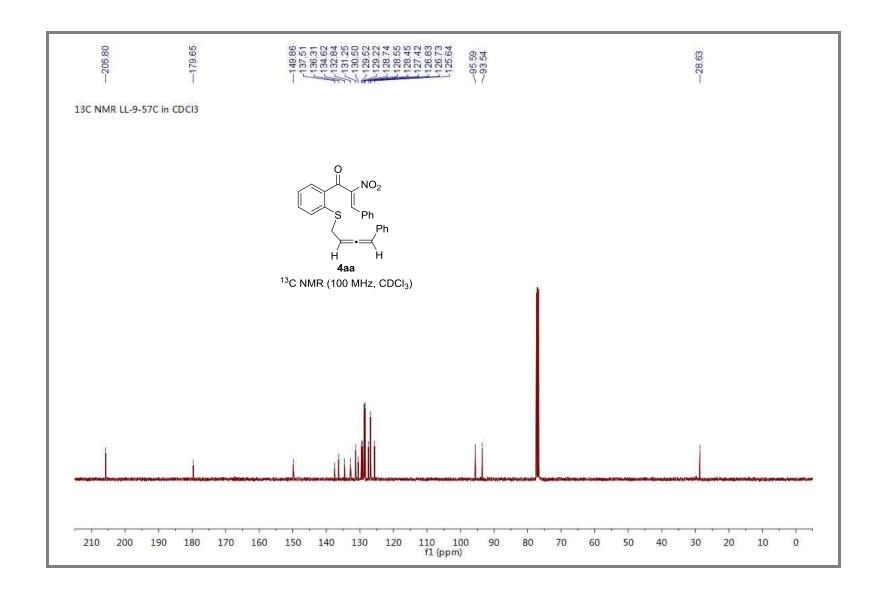


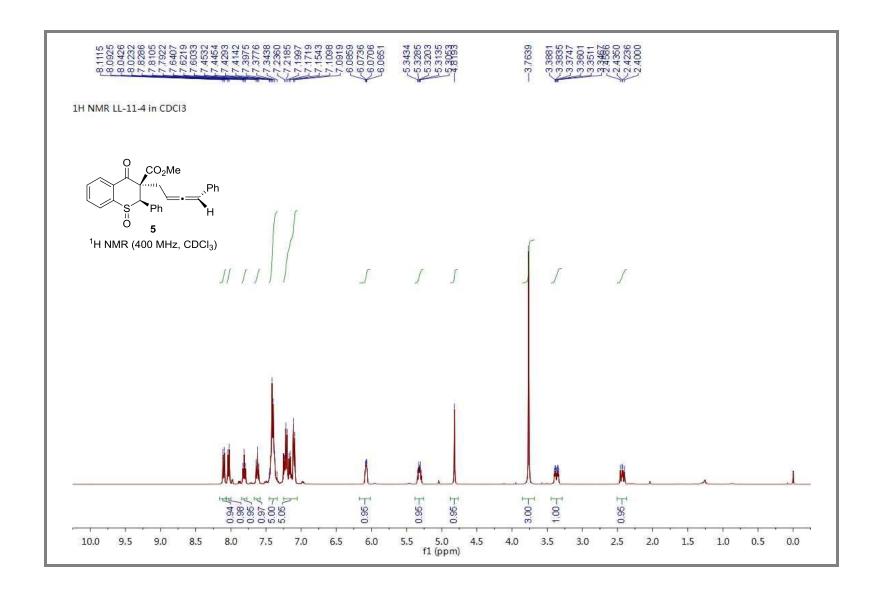


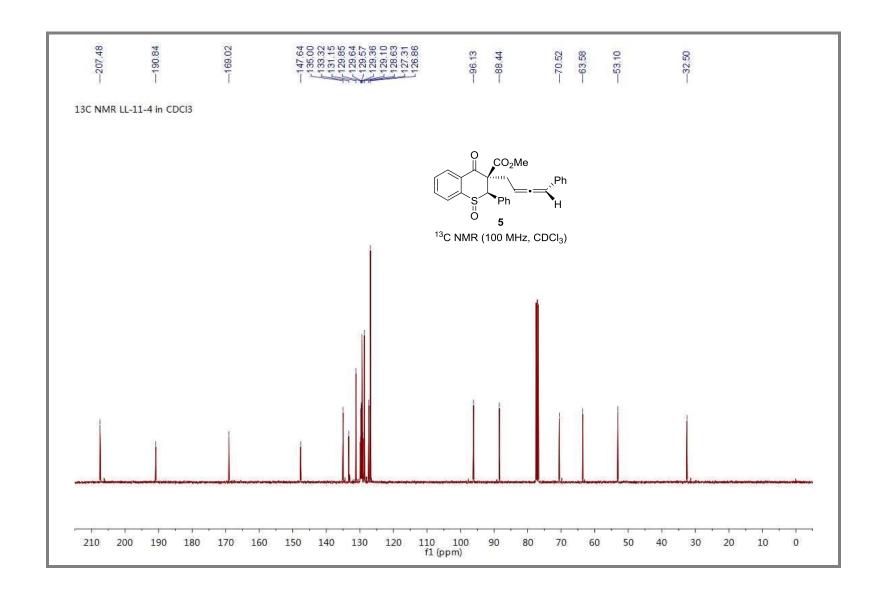


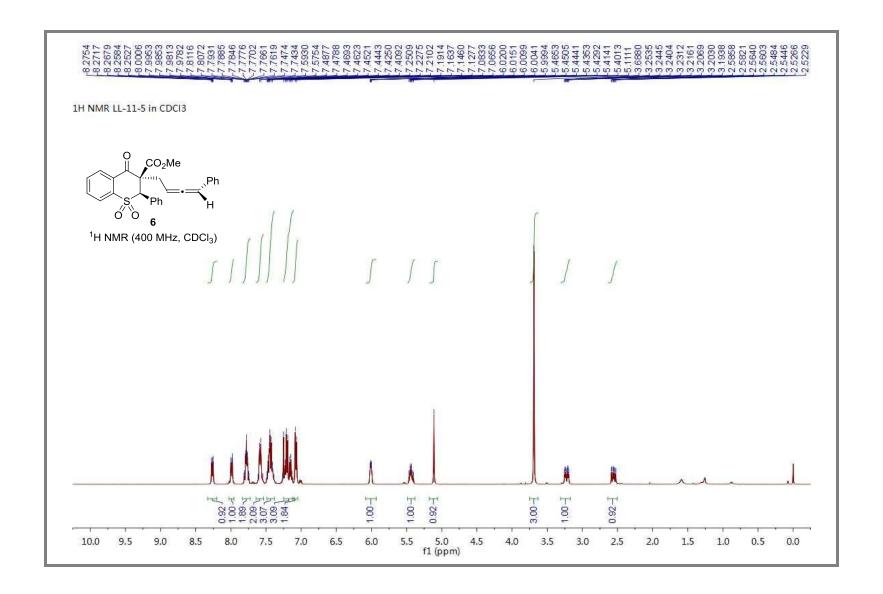


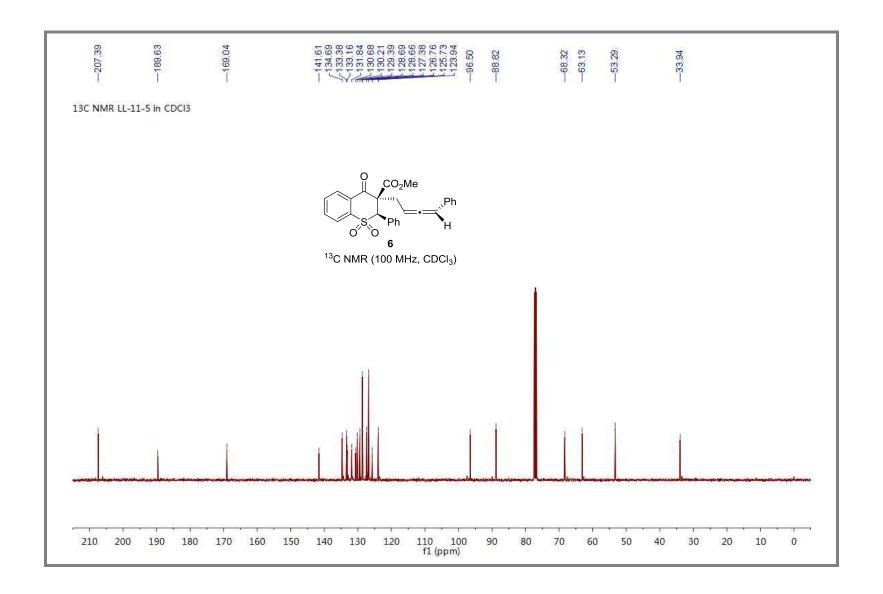


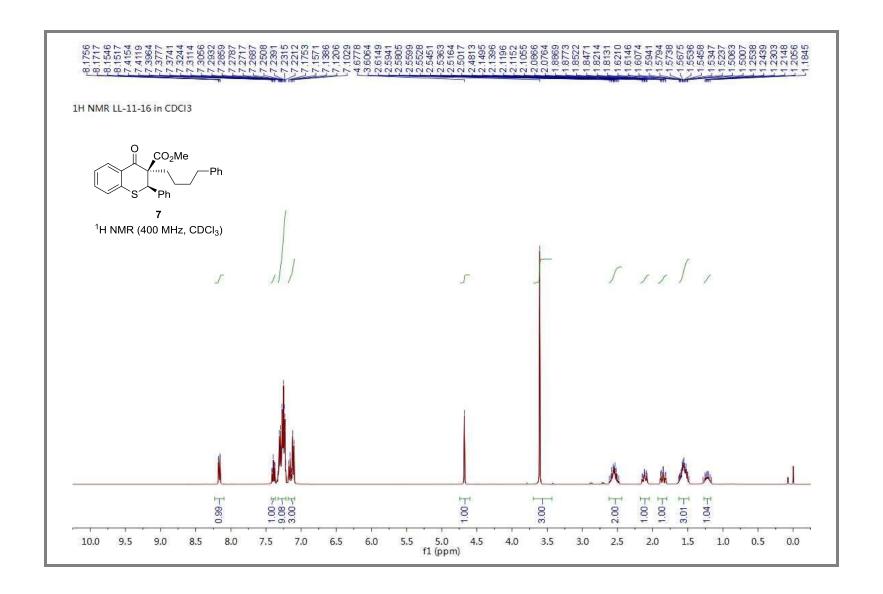


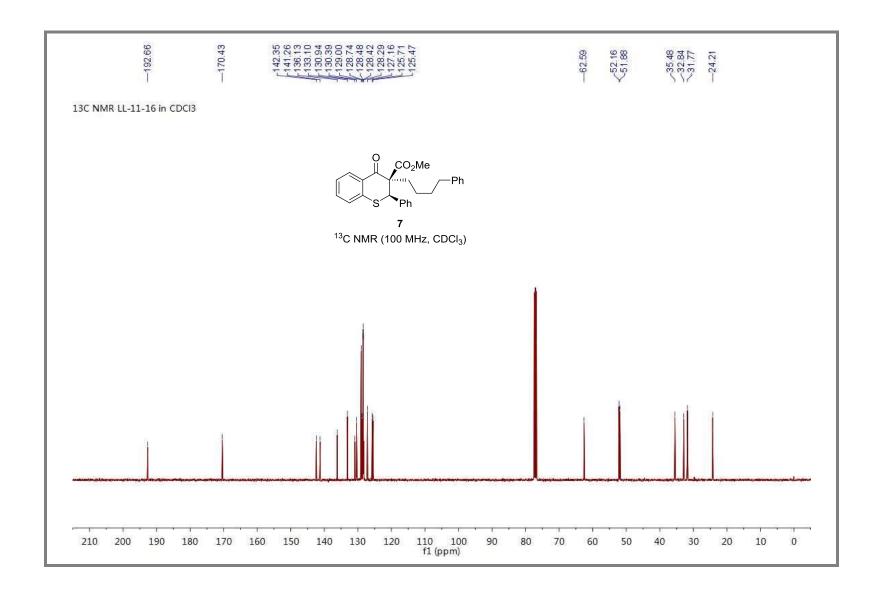


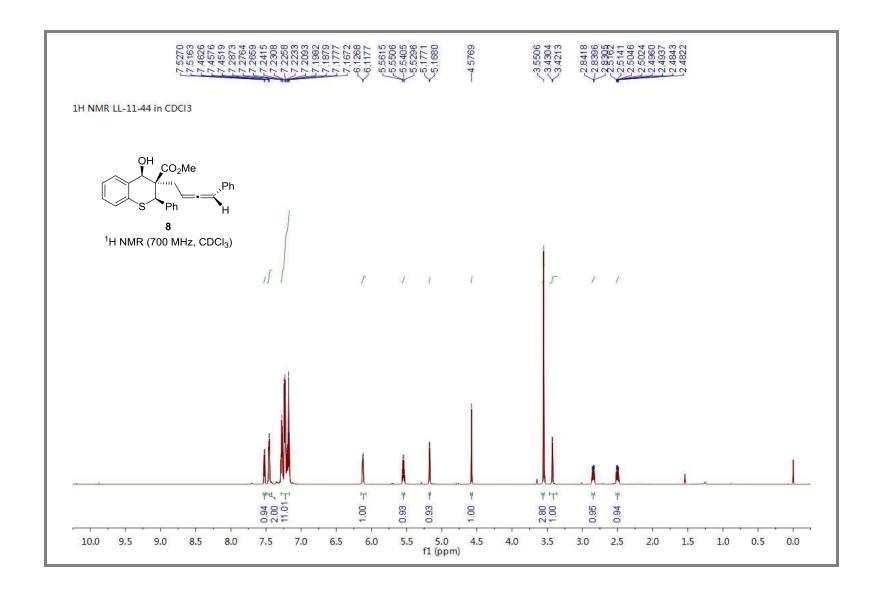


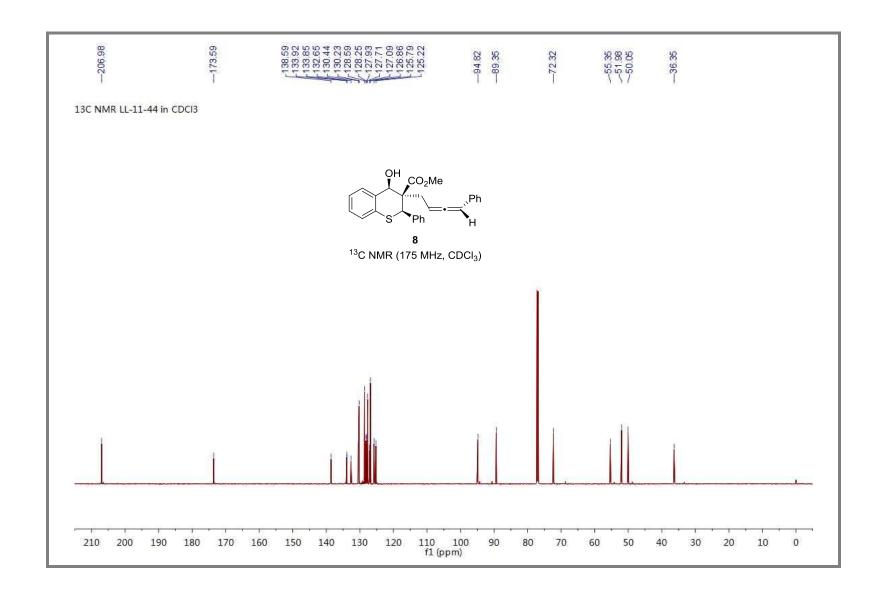




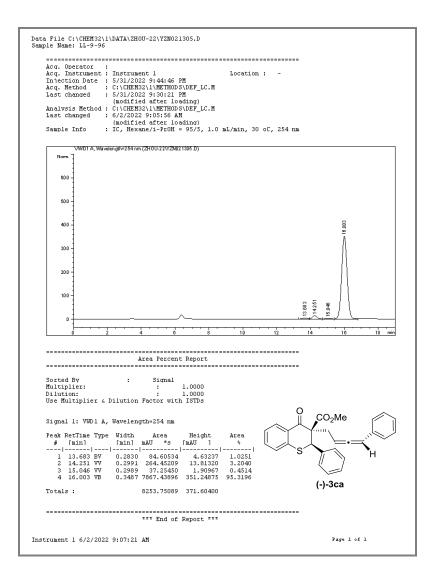


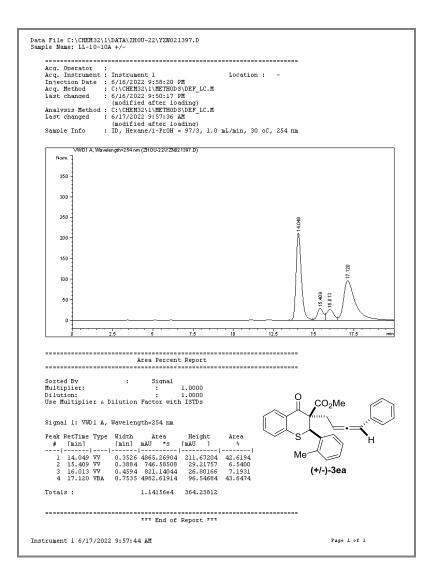


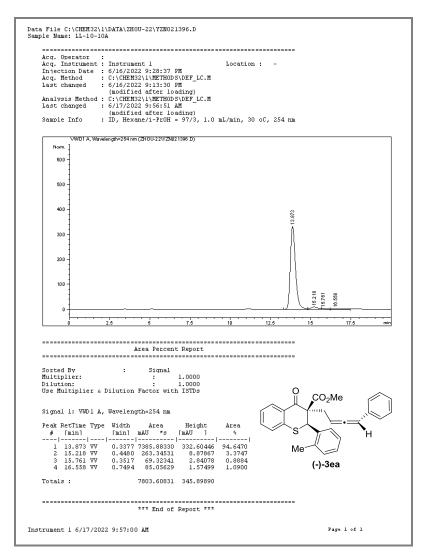


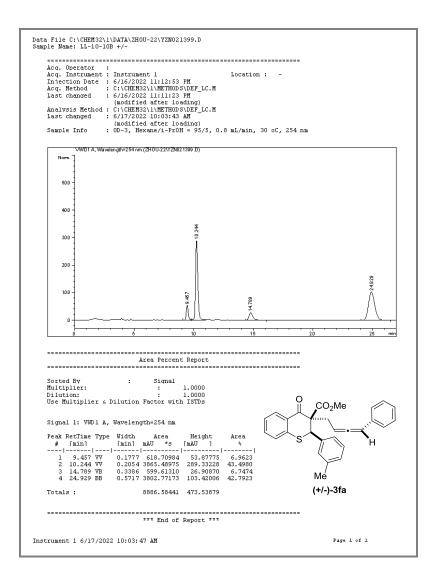


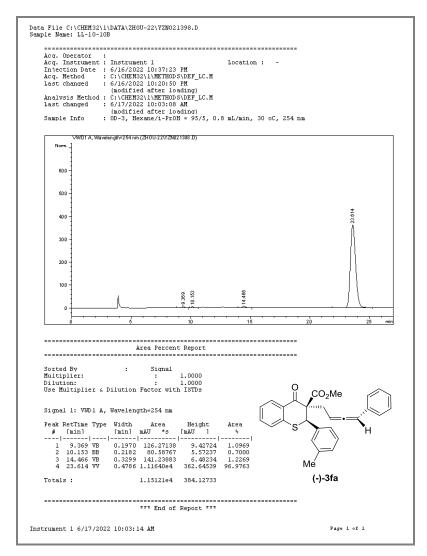
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021306.D
Sample Name: LL-9-96 +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                              Location : -
   Injection Date : 5/31/2022 10:04:59 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF LC.M
   Last changed
               : 5/31/2022 10:03:56 PM
   (modified after loading)
Analysis Method : C:\CHEM32\l\METHODS\DEF_LC.M
Last changed : 6/2/2022 9:05:02 AM
               (modified after loading)
: IC, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021306.D)
     Norm.
      400
      300 -
      200
      100
   ______
                        Area Percent Report
   .
                      : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                   CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                           Area
                                    Height
   # [min]
        [min] [min] mAU *s [mAU ]
        13.703 BV 0.2796 1181.40186
                                    65.72604
                                              9.8469
        14.266 VV 0.2934 1184.59485 62.63682
                                             9.8735
        15.054 WV
                  0.3161 4809.14453 237.68280
                                             40.0840
     4 16.009 VB
                  0.3413 4822.53174 220.28629
                                             40.1956
                                                                  (+/-)-3ca
                         1.19977e4 586.33195
   *** End of Report ***
Instrument 1 6/2/2022 9:05:10 AM
                                                                      Page 1 of 1
```

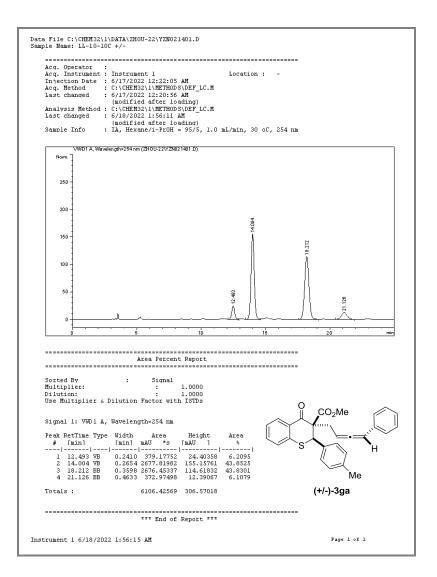


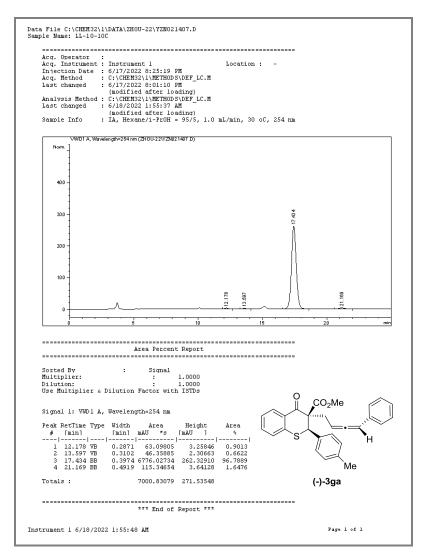




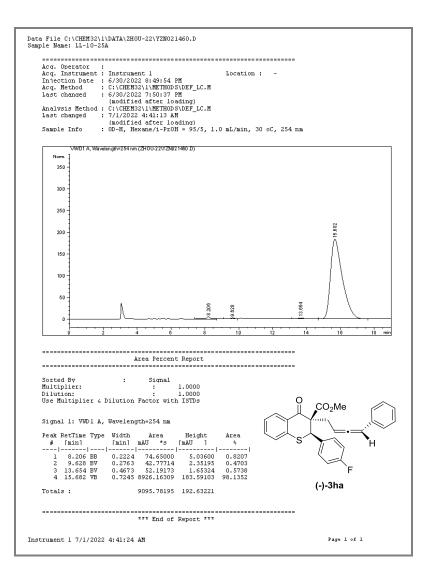


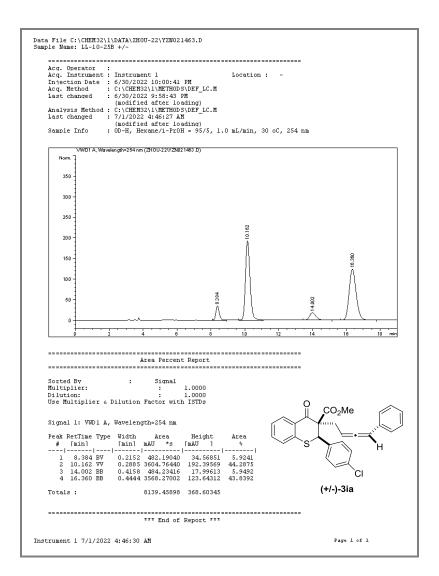


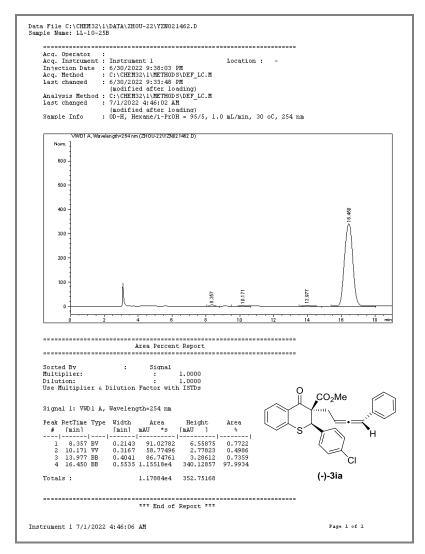




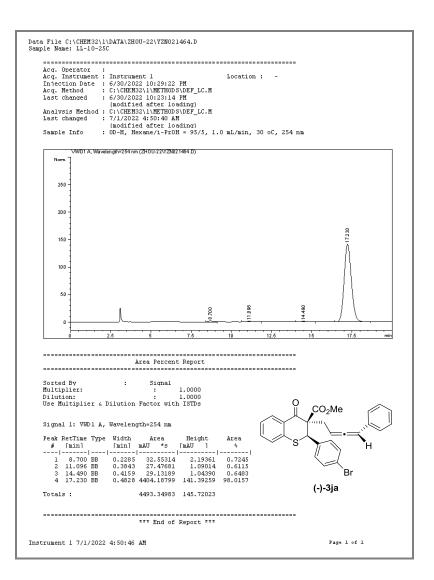
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021461.D
Sample Name: LL-10-25A +/-
   .....
  Acq. Operator :
Acq. Instrument : Instrument 1
                                             Location : -
   Injection Date : 6/30/2022 9:14:24 PM Acq. Method : C:\CHEM32\l\METHODS\DEF LC.M
   Last changed
               : 6/30/2022 9:11:25 PM
  (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 7/1/2022 4:41:13 AM
               (modified after loading)
: OD-H, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021461.D)
     Norm.
      350
      300 -
      250 -
      200 -
      150
      100
   ______
                        Area Percent Report
   .
                     : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                  CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width Area
                                   Height
   # [min]
       8.304 BV 0.2048 332.16351 24.95156
9.726 VV 0.2535 2674.45972 162.17827
                                             5.5432
                                            44.6315
5.5642
        13.714 BB
                  0.3957 333.42480
                                   12.85673
     4 15.462 BB
                 0.4010 2652.26978 102.46486
                                            44.2612
                                                                 (+/-)-3ha
                         5992.31781 302.45142
   *** End of Report ***
Instrument 1 7/1/2022 4:41:54 AM
                                                                    Page 1 of 1
```

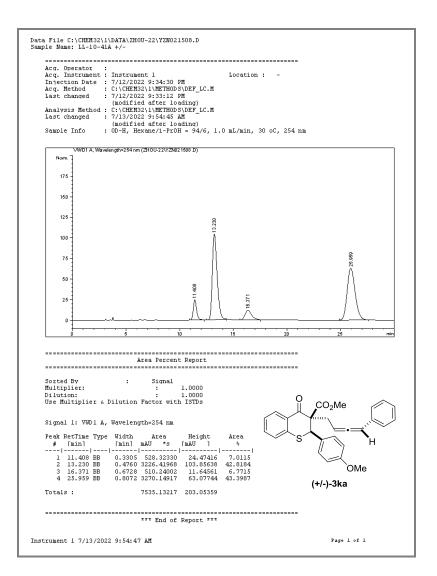


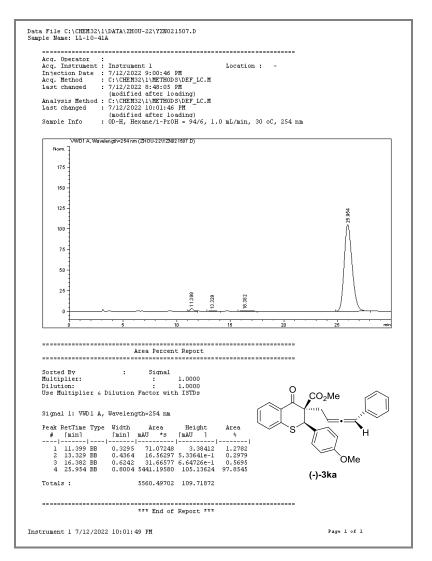




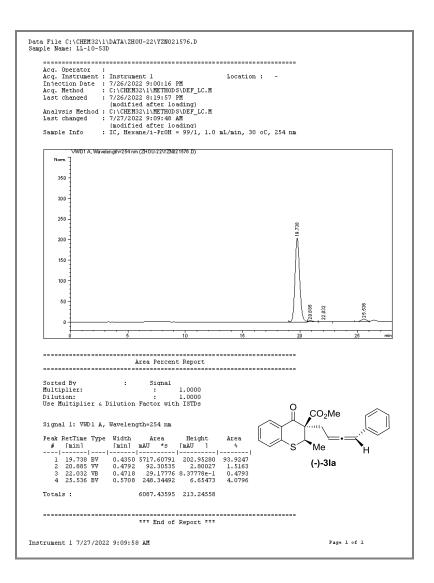
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Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021465.D
Sample Name: LL-10-25C +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                             Location : -
   Injection Date : 6/30/2022 10:53:03 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF LC.M
   Last changed
               : 6/30/2022 10:51:05 PM
   (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 7/1/2022 4:50:40 AM
               (modified after loading)
: OD-H, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021465.D)
     Norm.
      250
      200
      150
      100 -
       50
   ______
                        Area Percent Report
   .
                          : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                 CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                           Area
                                    Height
   # [min]
       8.745 VV 0.2287 625.18262 42.06327
11.077 VB 0.3851 3562.41309 142.35739
                                             7.5051
                                            42.7654
7.4812
        14.543 VB
                  0.4303 623.19031
                                   22.33843
     4 17.275 BB
                  0.5038 3519.34717 108.44839
                                            42.2484
                                                                 (+/-)-3ja
                         8330.13318 315.20749
   *** End of Report ***
Instrument 1 7/1/2022 4:51:05 AM
                                                                     Page 1 of 1
```

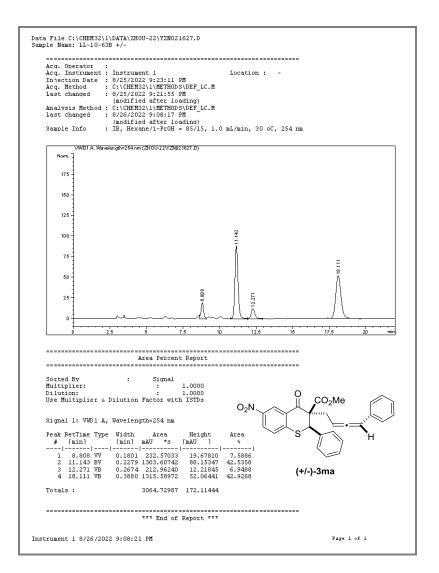


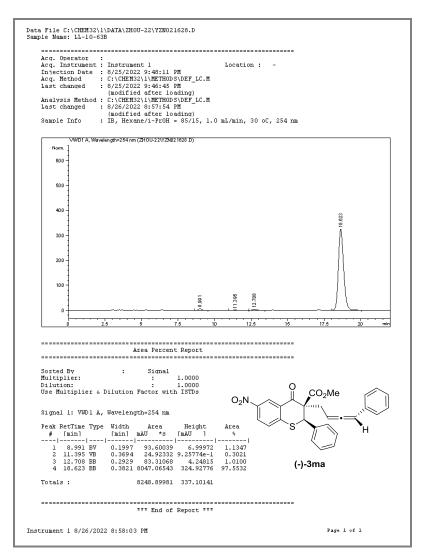




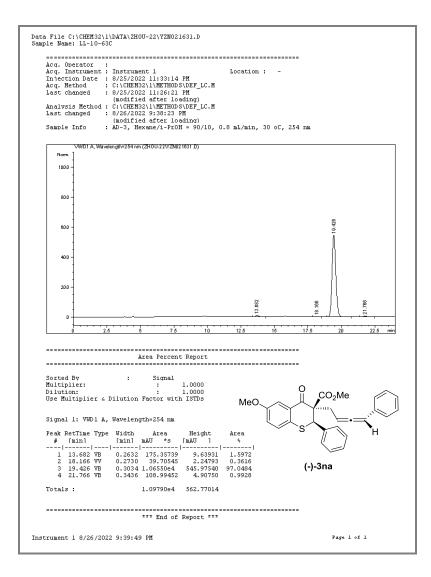
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Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21580.D
Sample Name: LL-10-53D +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                               Location : -
   Injection Date : 7/27/2022 8:40:40 AM Acq. Method : C:\CHEM32\l\METHODS\DEF LC.M
   Last changed
                : 7/27/2022 8:37:30 AM
   (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 7/27/2022 9:14:13 AM
                (modified after loading)
: IC, Hexane/i-PrOH = 99/1, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021580.D)
     Norm. 1
      300
      250 -
      200
      150
      100
   ______
                         Area Percent Report
   .
                      : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                    CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width Area
                                     Height
   # [min]
        Me
       19.109 BV 0.4115 4856.06885 183.02740 40.6086
20.037 VV 0.4314 1103.95667 39.26189 9.2318
21.074 VB 0.4557 4915.48437 166.89432 41.1054
                                                                    (+/-)-3la
     4 24.315 BV
                  0.5321 1082.72046 31.49474
                         1.19582e4 420.67836
   *** End of Report ***
Instrument 1 7/27/2022 9:14:58 AM
                                                                       Page 1 of 1
```

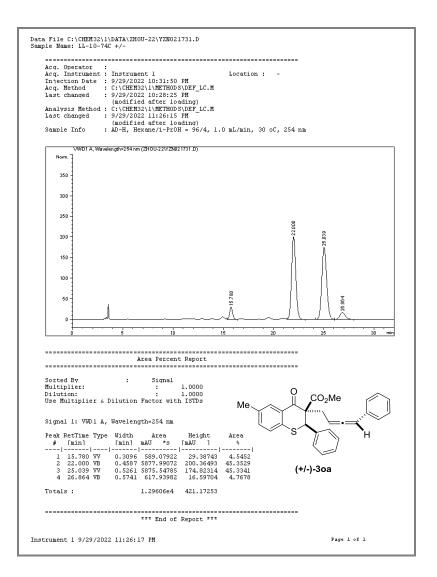


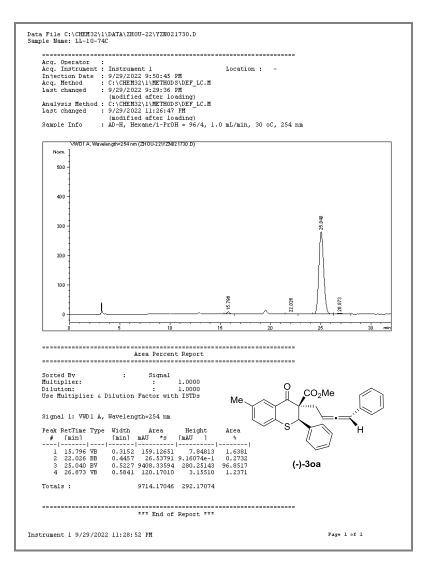


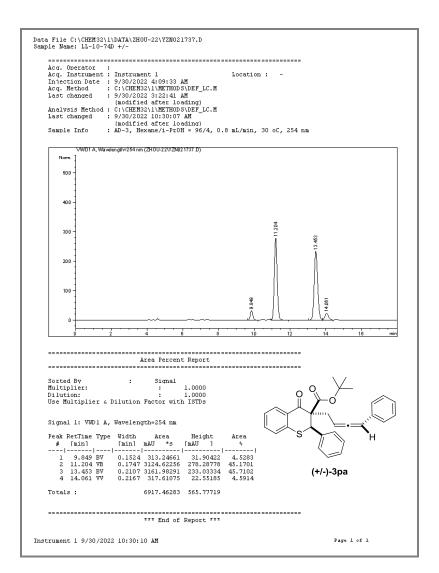


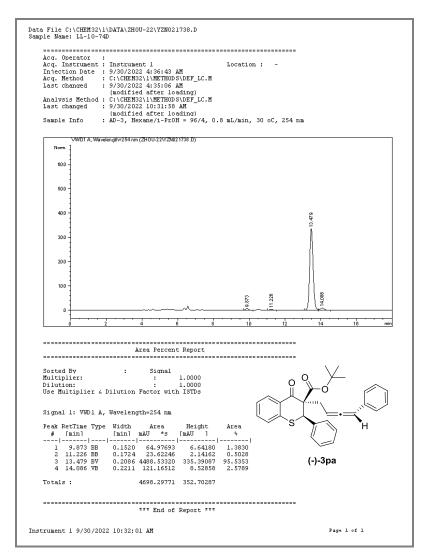
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Data File C:\CHEM32\1\DATA\ZHOU-22\YZN021616.D
Sample Name: LL-10-63C +/-
   .....
  Acq. Operator :
Acq. Instrument : Instrument 1
                                            Location : -
   Injection Date : 8/23/2022 2:03:58 AM Acq. Method : C:\CHEM32\l\METHODS\DEF LC.M
   Last changed
               : 8/23/2022 1:49:44 AM
  (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 8/26/2022 9:41:43 PM
               (modified after loading)
: AD-3, Hexane/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021616.D)
     Norm.
      100
      80
       60
       20
                                                                            22.5 min
   ______
                       Area Percent Report
   .
                     : 1.0000
: 1.0000
   Multiplier:
   Dilution:
                                                                 CO<sub>2</sub>Me
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                                   Height
                                            Area
   # [min]
       [min] [min] mAU *s [mAU ]
       13.466 BB
                 0.2546 218.44931
                                   13.07639
                                            7.2224
       17.791 BV
                 0.3474 1303.31104
                                   57.82098
                                            43.0903
                                                             (+/-)-3na
                                   52.01914
7.19370
        18.982 VB
                  0.3782 1296.90649
                                            42.8785
     4 21.201 BB
                  0.4330 205.93846
                                            6.8088
                        3024.60530 130.11022
   *** End of Report ***
Instrument 1 8/26/2022 9:41:47 PM
                                                                    Page 1 of 1
```

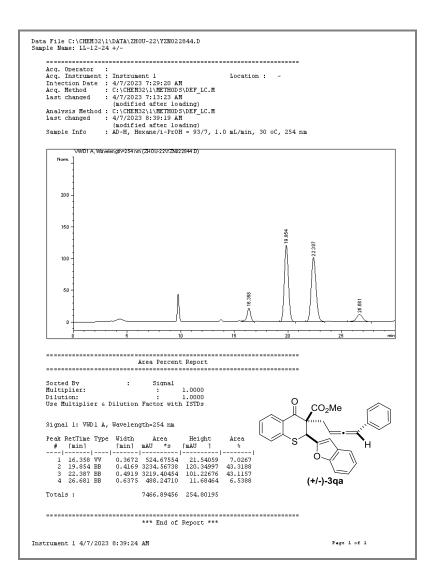


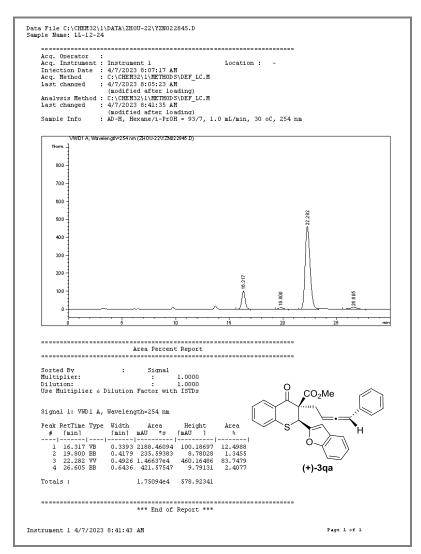




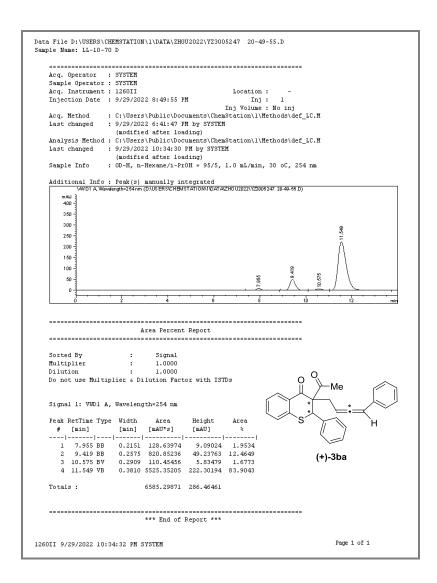


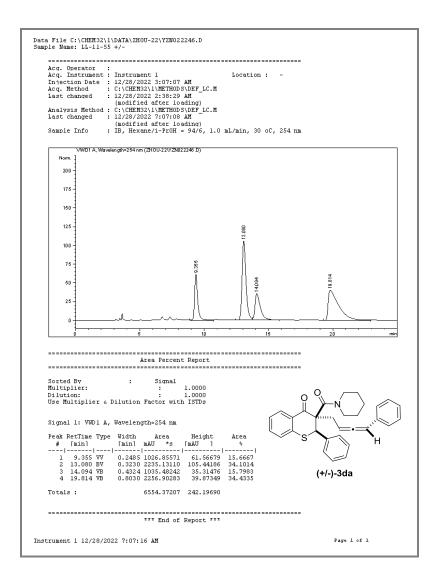


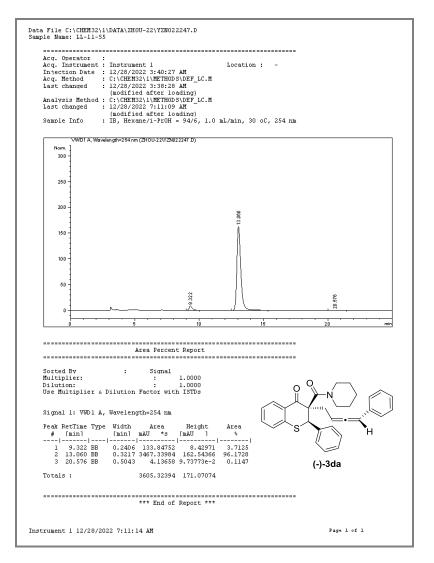


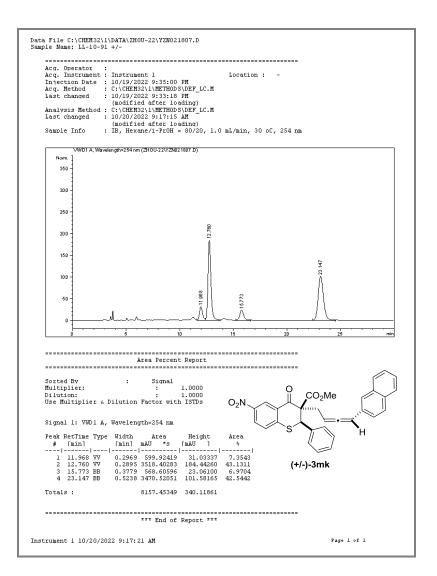


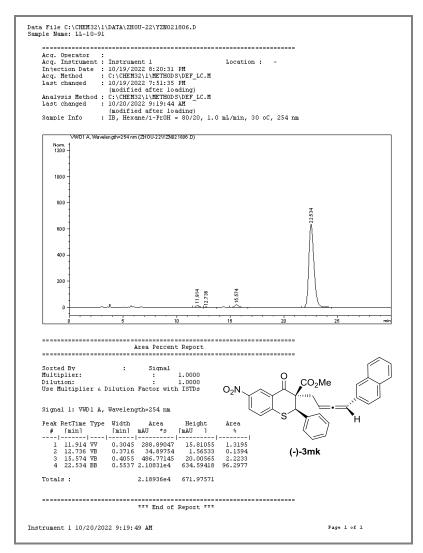
```
Data File D:\USERS\CHEMSTATION\1\DATA\ZHOU2022\YZ3005246 20-34-08.D
Sample Name: LL-10-70 D +/-
   _____
   Acg. Operator : SYSTEM
   Sample Operator : SYSTEM
   Acq. Instrument: 1260II
                                           Location : -
   Injection Date : 9/29/2022 8:34:08 PM
                                               Inj: 1
                                          Inj Volume : No inj
   Acq. Method : C:\Users\Public\Documents\ChemStation\l\Methods\def_LC.M
   Last changed : 9/29/2022 6:41:47 PM by SYSTEM
                  (modified after loading)
   Analysis Method : C:\Users\Public\Documents\ChemStation\l\Methods\def_LC.M
   Last changed : 9/29/2022 10:32:32 PM by SYSTEM
                  (modified after loading)
              : OD-H, n-Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
         VW D1 A, Wavelength=254 nm (D:\US ERS\CHEMSTATION\1\DATA\ZHO U2022\YZ3005246 20-34-08.D)
      250 -
      200 -
      150 -
      100 -
                       Area Percent Report
   -----
   Sorted By
                          Signal
                          1.0000
   Multiplier
                         1.0000
  Dilution
   Do not use Multiplier & Dilution Factor with ISTDs
  Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                          Area
                                  Height
                                           Area
                 [min] [mAU*s]
                                  [mAU]
    # [min]
   ----|------|-----|------|------|
    1 7.968 BB 0.3140 95.62804 4.22667 1.6388
     2 9.417 BB 0.2554 2837.91357 171.22769 48.6328
     3 10.586 BB 0.2802 42.20076 2.32035 0.7232
                                                              (+/-)-3ba
     4 11.610 BB 0.3819 2859.64502 115.07438 49.0052
                        5835.38739 292.84909
   Totals:
   *** End of Report ***
                                                                  Page 1 of 1
1260II 9/29/2022 10:32:34 PM SYSTEM
```



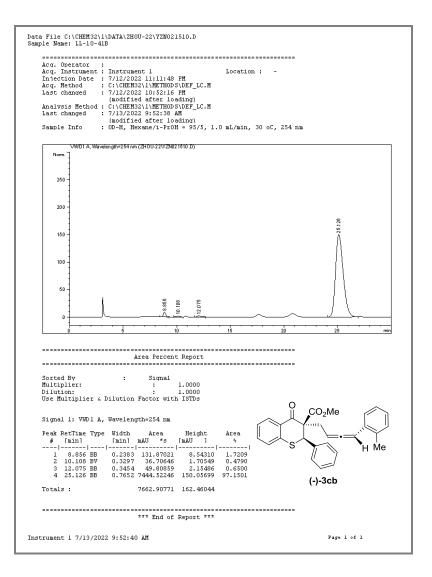


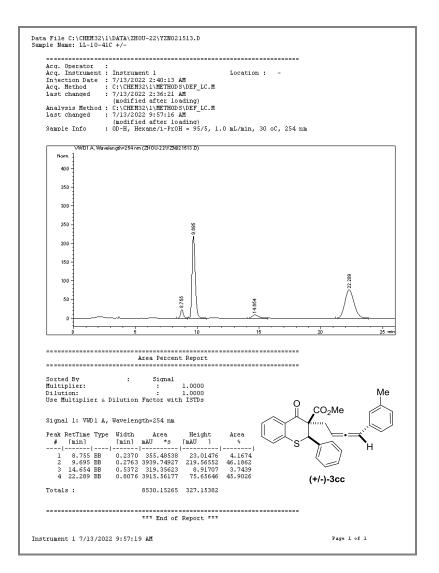


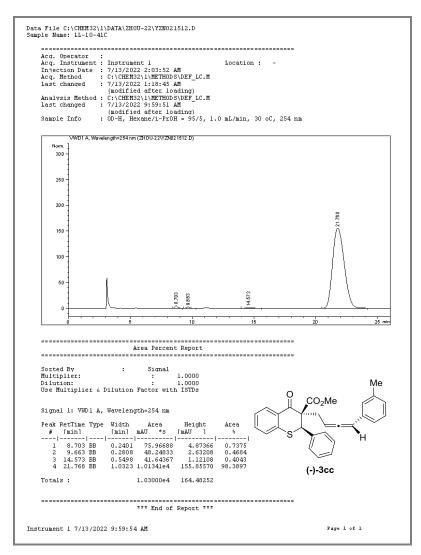




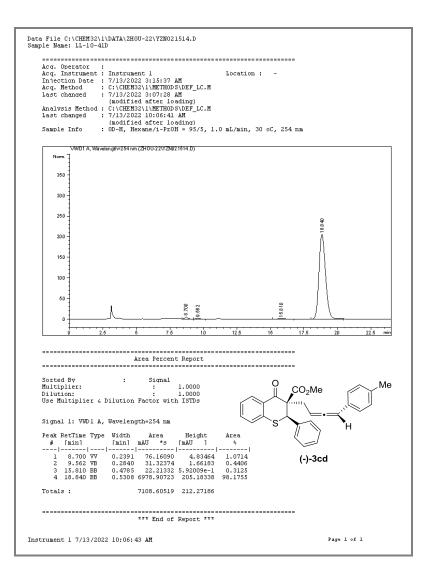
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Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21511.D
Sample Name: LL-10-41B +/-
   .....
  Acq. Operator :
Acq. Instrument : Instrument 1
                                           Location : -
  Injection Date : 7/12/2022 11:43:50 PM
Acc. Method : C:\CHEM32\1\METHODS\DEF_LC.M
   Last changed
                : 7/12/2022 11:42:35 PM
  (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
              : 7/13/2022 9:48:22 AM
               (modified after loading)
: OD-H, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021511.D)
     Norm. 1
      600
      500
      400
      300
      200
      100
   ______
                       Area Percent Report
   .
                         : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                               CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                                  Height
   # [min]
       8.851 BV
                  0.2473 609.97455
                                  37.34377
                                           3.8930
        10.053 VB 0.3069 7261.25586 361.86163 46.3432
        12.056 BB
                  0.3781 604.73486
                                  24.14730
                                           3.8596
     4 25.110 BB
                 0.7700 7192.47559
                                 144.86612
                                           45.9042
                                                              (+/-)-3cb
                        1.56684e4 568.21882
   *** End of Report ***
Instrument 1 7/13/2022 9:51:09 AM
                                                                  Page 1 of 1
```

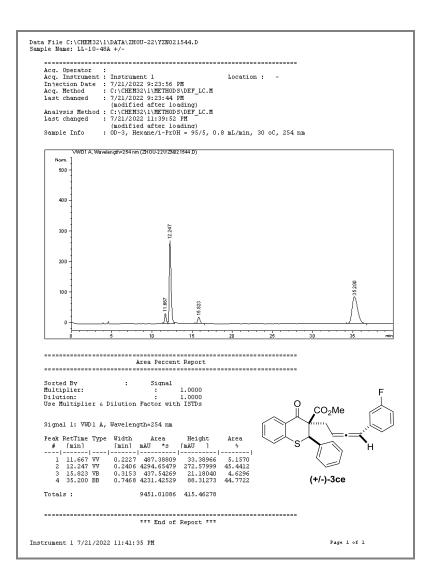


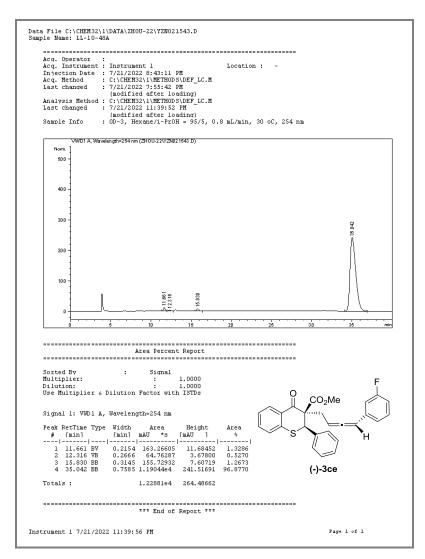




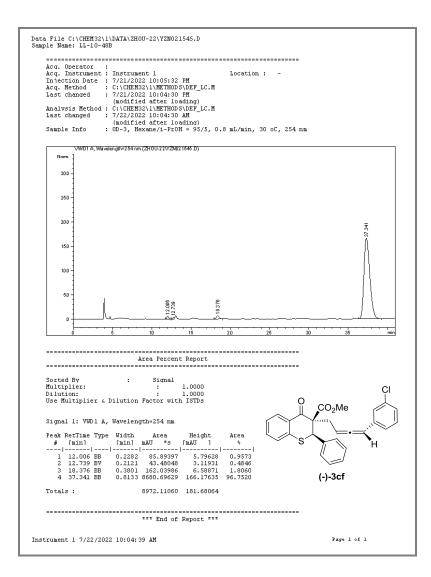
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21515.D
Sample Name: LL-10-41D +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                              Location : -
   Injection Date : 7/13/2022 3:44:48 AM Acq. Method : C:\CHEM32\l\METHODS\DEF LC.M
   Last changed
                : 7/13/2022 3:43:33 AM
   (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
Last changed: 7/13/2022 10:04:33 AM
                (modified after loading)
: OD-H, Hexane/i-PrOH = 95/5, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021515.D)
     Norm.
      300 -
      200
      100
                                                                               22.5 min
   ______
                        Area Percent Report
   .
                      : 1.0000
: 1.0000
                                                              CO<sub>2</sub>Me
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                           Area
                                    Height
                                              Area
   # [min]
        8.694 VV 0.2425 427.73480 26.45411
9.524 VV 0.2810 4403.81104 238.46748
                                              4.5443
                                                               (+/-)-3cd
                                             46.7862
        15.766 BB
                   0.5838 353.51495
                                     8.99354
     4 18.873 BB
                  0.5337 4227.57227 122.49112
                                             44.9138
                         9412.63306 396.40625
   *** End of Report ***
Instrument 1 7/13/2022 10:04:37 AM
                                                                      Page 1 of 1
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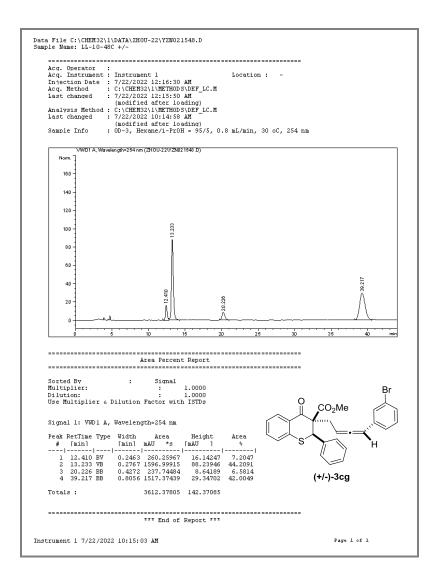


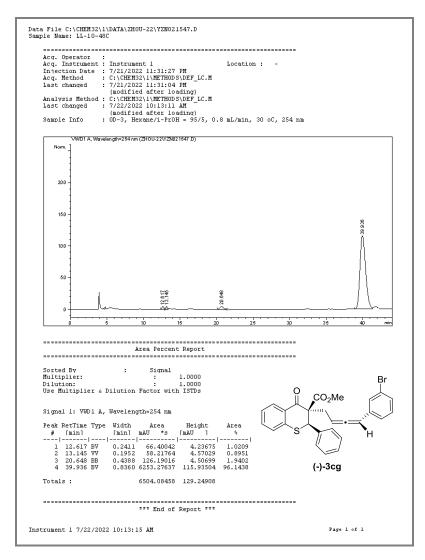


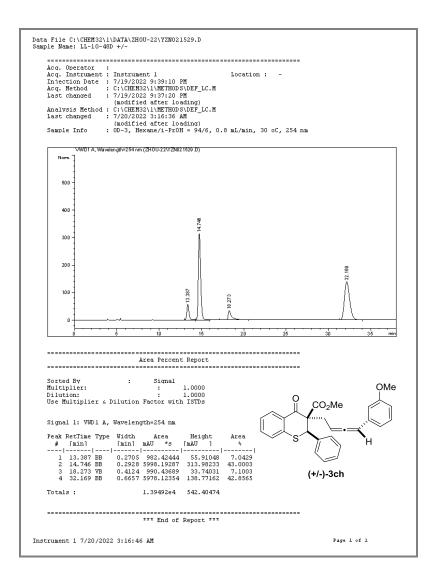


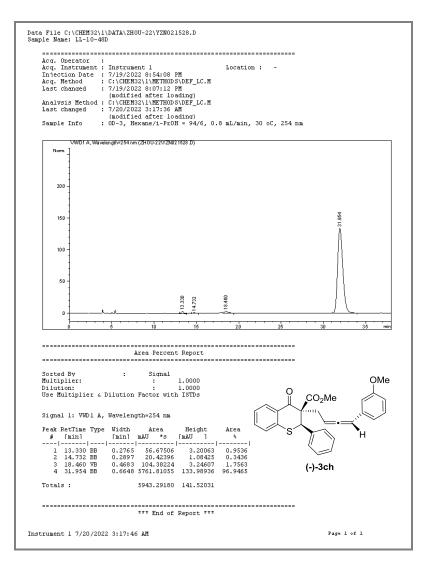
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21546.D
Sample Name: LL-10-48B +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                               Location : -
   Injection Date : 7/21/2022 10:48:39 PM Acq. Method : C:\CHEM32\l\METHOD$\DEF LC.M
   Last changed
                : 7/21/2022 10:48:12 PM
   (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 7/22/2022 10:06:38 AM
                (modified after loading)
: OD-3, Hexane/i-PrOH = 95/5, 0.8 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021546.D)
     Norm
      400
      350
      300
      250 -
      200 -
      150
      100
       50
   ______
                         Area Percent Report
   .
                      : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                    CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                           Area
                                     Height
   # [min]
        [min] [min] mAU *s [mAU ]
        12.112 VV 0.2295 1082.02344 72.47380 12.807 VB 0.2594 3699.03784 217.69196
                                              11.4343
                                              39.0898
                                    41.12384
70.56090
        18.700 BB
                   0.3912 1055.68799
                                              11.1560
                                                                   (+/-)-3cf
     4 38.060 BB
                  0.7947 3626.18237
                                              38.3199
                          9462.93164 401.85050
   *** End of Report ***
Instrument 1 7/22/2022 10:07:05 AM
                                                                       Page 1 of 1
```

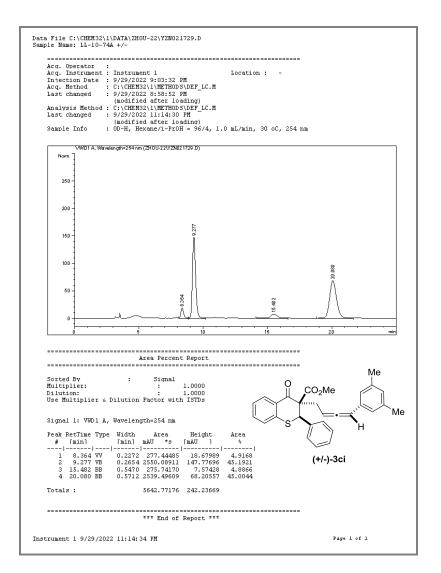


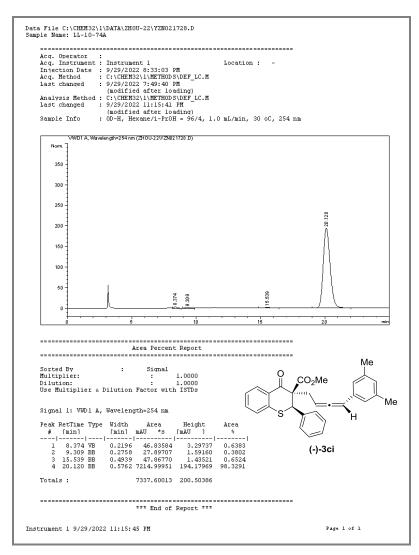




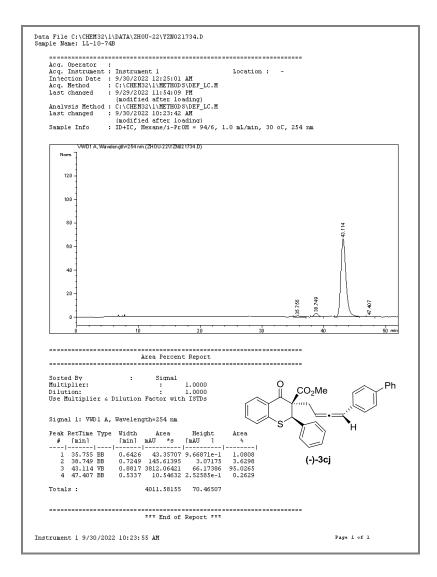


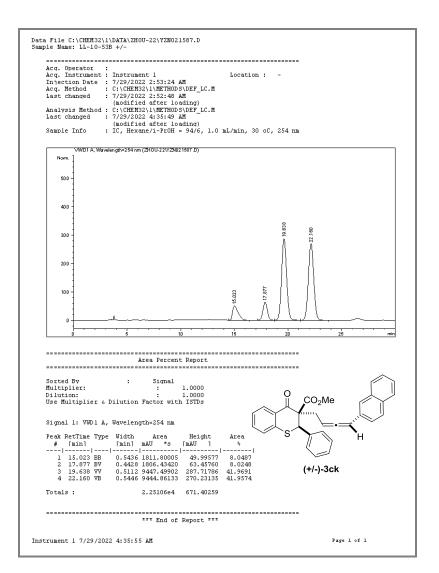


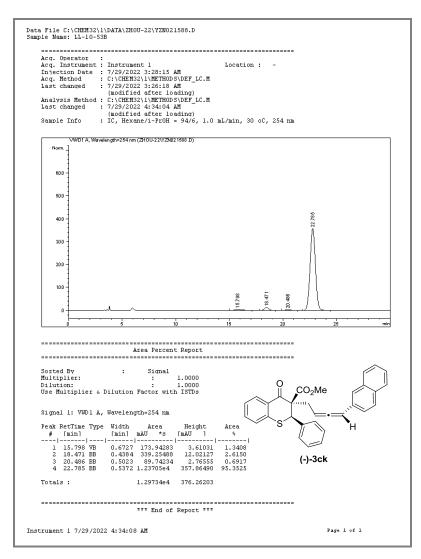




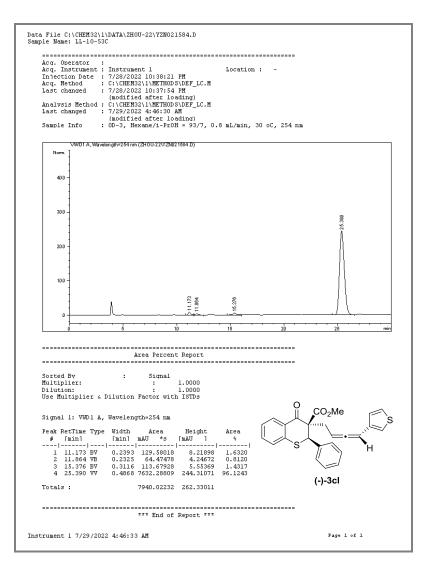
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21715.D
Sample Name: LL-10-74B +/-
   .....
   Acq. Operator :
Acq. Instrument : Instrument 1
                                              Location : -
   Injection Date : 9/28/2022 9:40:16 PM
Acq. Method : C:\CHEM32\l\METHOD$\DEF LC.M
   Last changed
               : 9/28/2022 8:27:29 PM
   (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 9/30/2022 10:27:10 AM
                (modified after loading)
: ID+IC, Hexane/i-PrOH = 94/6, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021715.D)
     Norm.
      160
      140
      120 -
      100
       80
   ______
                        Area Percent Report
   .
                          : 1.0000
: 1.0000
   Multiplier:
                                                             CO<sub>2</sub>Me
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                                    Height
   # [min]
        [min] [min] mAU *s [mAU ]
        35.527 BB
                  0.6267 544.41461
0.7234 538.08063
                                    13.44718
                                              4.8149
                                                              (+/-)-3cj
        38.502 BB
                                    11.44043
88.40113
                                             4.7589
        42.831 VB
                   0.8775 5104.59961
                                             45.1458
     4 46.831 BV
                  0.8589 5119.81348
                                    91.58820
                                             45.2804
                         1.13069e4 204.87693
   *** End of Report ***
Instrument 1 9/30/2022 10:27:12 AM
                                                                     Page 1 of 1
```

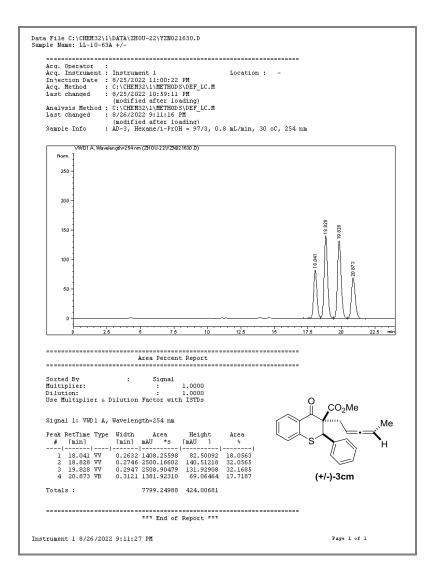


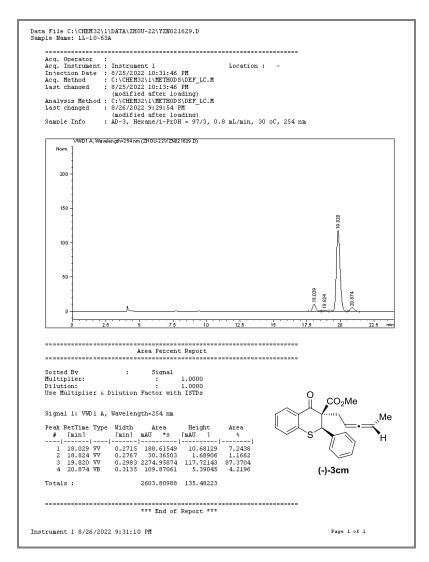




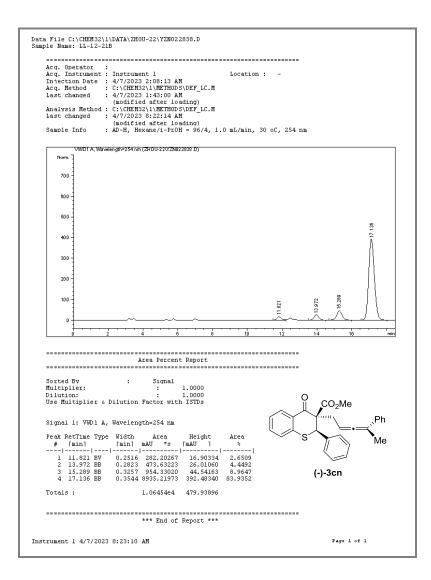
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21585.D
Sample Name: LL-10-53C +/-
   .....
  Acq. Operator :
Acq. Instrument : Instrument 1
                                            Location : -
   Injection Date : 7/28/2022 11:13:46 PM
Acc. Method : C:\CHEM32\1\METHODS\DEF_LC.M
   Last changed
               : 7/28/2022 11:11:35 PM
  (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
   Last changed
               : 7/29/2022 4:48:25 AM
               (modified after loading)
: OD-3, Hexane/i-PrOH = 93/7, 0.8 mL/min, 30 oC, 254 nm
   Sample Info
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021585.D)
     Narm.
      700
      600
      500
      400
      30.0
      200
   ______
                       Area Percent Report
   .
                         : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                 CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width
                          Area
                                   Height
                                            Area
   # [min]
       [min] [min] mAU *s [mAU ]
       10.983 VV
                  0.1991 658.74353
                                   50.87207
       11.635 VB 0.2163 5523.64844 393.20840
                                            44.6868
        15.134 VV
                  0.2871 649.02606
                                   34.62311
                                            5.2507
     4 24.908 VB
                  0.4777 5529.38184 180.06413
                                            44.7332
                                                                 (+/-)-3cl
                        1.23608e4 658.76772
   *** End of Report ***
Instrument 1 7/29/2022 4:48:29 AM
                                                                    Page 1 of 1
```



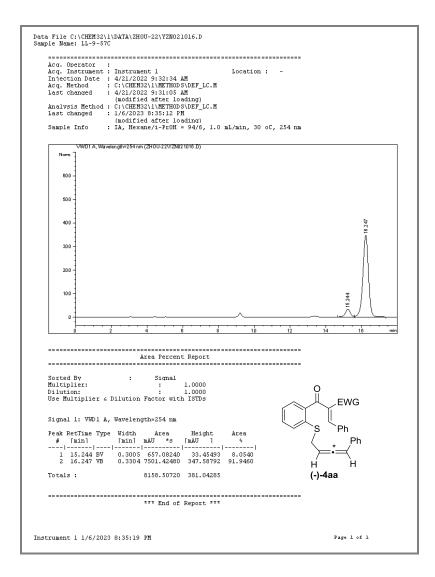


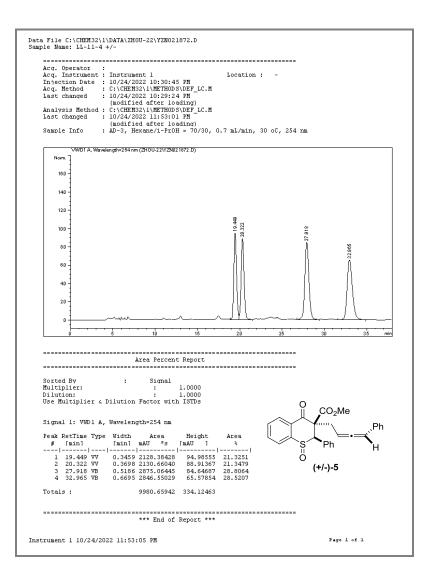


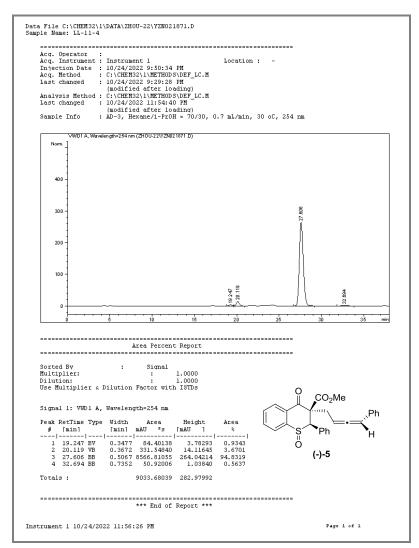
```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZN022804.D
Sample Name: LL-12-21B +/-
   Acg. Operator :
   Acq. Instrument : Instrument 1
   Injection Date : 4/2/2023 4:16:47 AM Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
                : 4/2/2023 3:58:06 AM
                   (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
   Last changed : 4/7/2023 8:20:59 AM
                   (modified after loading)
   Sample Info
                : AD-H, Hexane/i-PrOH = 96/4, 1.0 mL/min, 30 oC, 254 nm
          VWD1 A, Wavelength=254 nm (ZHOU-22\YZN022804.D)
      Norm.
       350
       300 -
       250 -
       200 -
       150
       100
   _____
                         Area Percent Report
   .
                       : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                     CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width Area
                                    Height
                                               Area
   # [min]
        [min] [min] mAU *s [mAU ]
     1 11.762 VV 0.2461 884.03217 55.33675 10.0786
2 13.897 BB 0.2779 3541.40186 197.28014 40.3747
3 15.213 BB 0.2984 885.45581 45.20324 10.0949
4 17.045 BB 0.3474 3460.45874 154.38235 39.4518
                                                                   (+/-)-3cn
   Totals:
                          8771.34857 452.20248
   .....
                          *** End of Report ***
Instrument 1 4/7/2023 8:21:08 AM
                                                                        Page 1 of 1
```

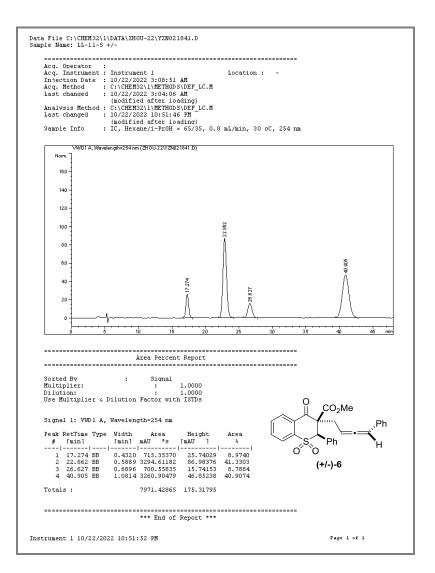


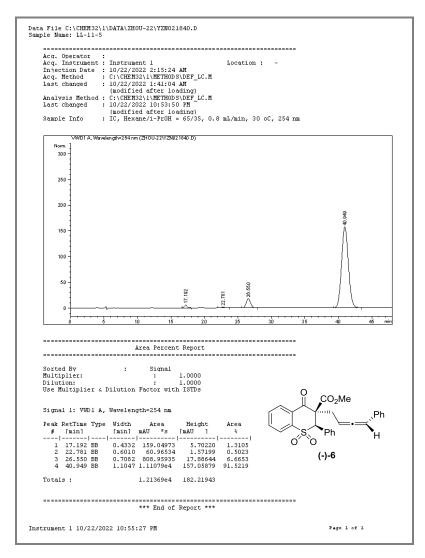
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Data File C:\CHEM32\1\DATA\ZHOU-22\YZNO21015.D
Sample Name: LL-9-57C +/-
   .....
  Acq. Operator :
Acq. Instrument : Instrument 1
                                          Location : -
  Injection Date : 4/21/2022 9:12:58 AM Acq. Method : C:\CHEM32\1\METHODS\DEF LC.M
   Last changed
              : 4/21/2022 9:06:36 AM
  (modified after loading)
Analysis Method: C:\CHEM32\l\METHODS\DEF_LC.M
Last changed: 1/6/2023 8:34:42 PM
              (modified after loading)
: IA, Hexane/i-PrOH = 94/6, 1.0 mL/min, 30 oC, 254 nm
   Sample Info
         VWD1 A, Wavelength=254 nm (ZHOU-22\YZN021015.D)
     Narm.
      60 -
      20
   ______
                      Area Percent Report
   .
                    : 1.0000
: 1.0000
   Multiplier:
   Dilution:
   Use Multiplier & Dilution Factor with ISTDs
                                                                 EWG
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width Area
                                 Height
  (+/-)-4aa
  Totals:
                       1952.23309 93.65277
   *** End of Report ***
Instrument 1 1/6/2023 8:34:47 PM
                                                                Page 1 of 1
```

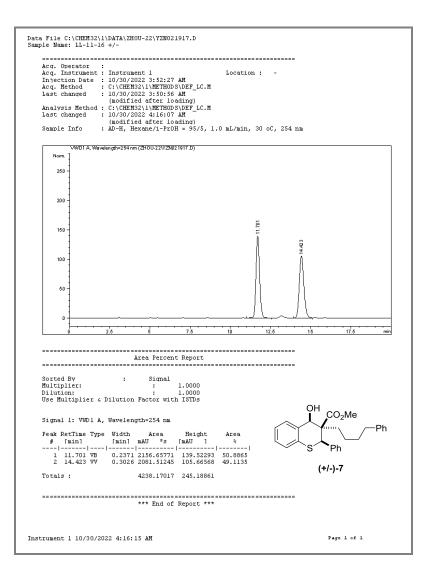


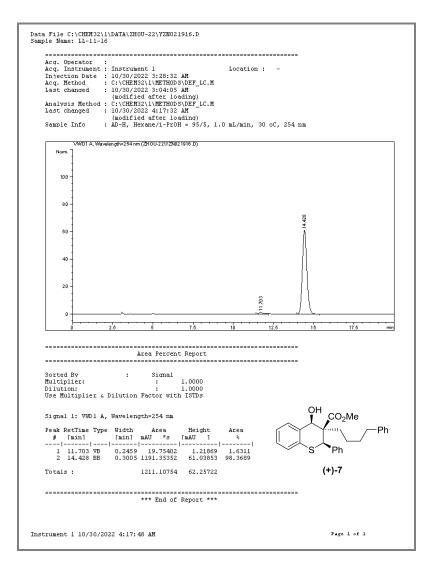












```
Data File C:\CHEM32\1\DATA\ZHOU-22\YZN022147.D
Sample Name: LL-11-44 +/-
   Acq. Operator :
Acq. Instrument : Instrument 1
                                                Location : -
   Injection Date : 11/30/2022 11:30:47 PM
   Acq. Method : C:\CHEM32\1\METHOD$\DEF_LC.M
                    (modified after loading)
   Analysis Method : C:\CHEM32\l\METHODS\DEF_LC.M
Last changed : 12/1/2022 2:31:03 AM
                (modified after loading): IA+AS-H, Hexane/i-PrOH = 95/5, 0.8 mL/min, 30 oC, 254 n
   Sample Info
           VWD1 A, Wavelength=254 nm (ZH0U-22\YZN022147.D)
      Norm.
       500
       400 -
       300
       200 -
       100
                         Area Percent Report
   -----
   Sorted By
                             Signal
                      : 1.0000
   Multiplier:
   Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs
                                                                         CO<sub>2</sub>Me
   Signal 1: VWD1 A, Wavelength=254 nm
   Peak RetTime Type Width Area
                                      Height
                                                 Area
    # [min]
                    [min] mAU *s [mAU ]
     1 46.478 BB
                   0.8766 4460.64746 77.35817
                                                8.8316
      2 62.054 BV 1.1644 2.06928e4 272.83978 40.9695
                   1.1556 4356.79199 58.02239
      3 64.322 VB
                                                8.6260
                                                                       (+/-)-8
      4 72.605 BB 1.3270 2.09975e4 244.75700 41.5729
   Totals :
                          5.05077e4 652.97735
   _____
                          *** End of Report ***
Instrument 1 12/1/2022 2:31:11 AM
                                                                          Page 1 of 1
```

