

## Supporting Information

### Amine-Catalyzed (3+n) Annulations of 2-(Acetoxymethyl)buta-2,3-dienoates with 1,n-Bisnucleophiles (n = 3-5)

Chaolong Li, Qiongmei Zhang and Xiaofeng Tong\*  
Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China  
University of Science and Technology, Shanghai 200237, China  
[tongxf@ecust.edu.cn](mailto:tongxf@ecust.edu.cn)

### Contents

<b>I.</b>	<b>General Information</b>	.....	S2
<b>II.</b>	<b>Optimization for DABCO-Catalyzed (3+n) Annulations</b>	.....	S3
<b>III.</b>	<b>The procedure for (3+n) annulations and the data for compounds 3 and 5</b>	.....	S4
<b>IV.</b>	<b>Data for the Compounds 3, 5 and 6</b>	.....	S4

## I. General information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

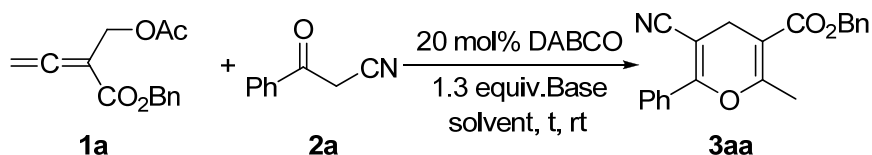
**NMR spectrum:**  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR. For  $^1\text{H}$  NMR, chemical shifts were reported downfield from  $\text{CDCl}_3$  ( $\delta$ : 7.27 ppm). For  $^{13}\text{C}$  NMR, chemical shifts were reported in the scale relative to the solvent of  $\text{CDCl}_3$  ( $\delta$ : 77.0 ppm) used as an internal reference.

**Mass spectroscopy:** Mass spectra were in general recorded on Micromass GCT.

**Chromatography:** Column chromatography was performed with silica gel (200-300 mesh ASTM).

## II. Optimization for DABCO-catalyzed (3+3) Annulations

**Table S1:** Optimization for DABCO-catalyzed (3+3) Annulations of **1a** and **2a**<sup>a</sup>



Entry	Base	Solvent	t (h)	Yield (%) <sup>b</sup>
1	Cs <sub>2</sub> CO <sub>3</sub>	benzene	18	34
2	Cs <sub>2</sub> CO <sub>3</sub>	toluene	18	96
3	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	68
4	Cs <sub>2</sub> CO <sub>3</sub>	acetone	12	96
5	Cs <sub>2</sub> CO <sub>3</sub>	THF	8	84
6	Cs <sub>2</sub> CO <sub>3</sub>	MeCN	4	97
7	Cs <sub>2</sub> CO <sub>3</sub>	DMF	0.5	94
<b>8</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>DMF</b>	<b>0.5</b>	<b>99</b>
9	Na <sub>2</sub> CO <sub>3</sub>	DMF	1	95
10 <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	DMF	0.5	91

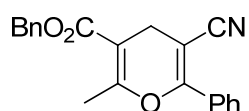
<sup>a</sup>Reaction conditions: to the solution of **2a** (26.1 mg, 0.18 mmol, 1.2 equiv.), base (0.195 mmol, 1.3 equiv.), DABCO (0.03 mmol, 20 mol%) in DMF (2 mL), was slowly added the solution of **1a** (36.9 mg, 0.15 mmol) in DMF (2 mL) over 20 minutes. <sup>b</sup>Isolated yield. <sup>c</sup>10% catalyst was used.

Optimization was conducted with the model reaction between **1a** and **2a** in the presence of 20 mol% DABCO (Table S1). When 1.3 equivalents of Cs<sub>2</sub>CO<sub>3</sub> were used as the base, compound **3aa** could be isolated in 34% yield (entry 1, Table S1). This transformation seemed to be strongly dependent on the solvent (entries 1-7, Table S1) and solvent DMF was found out to be the optimal one. To our delight, the yield reached as high as 99% when K<sub>2</sub>CO<sub>3</sub> was used and the reaction time could be shortened to 0.5 h (entry 8, Table S1).

### III. The procedure for (3+n) annulations and the data for compounds 3 and 5

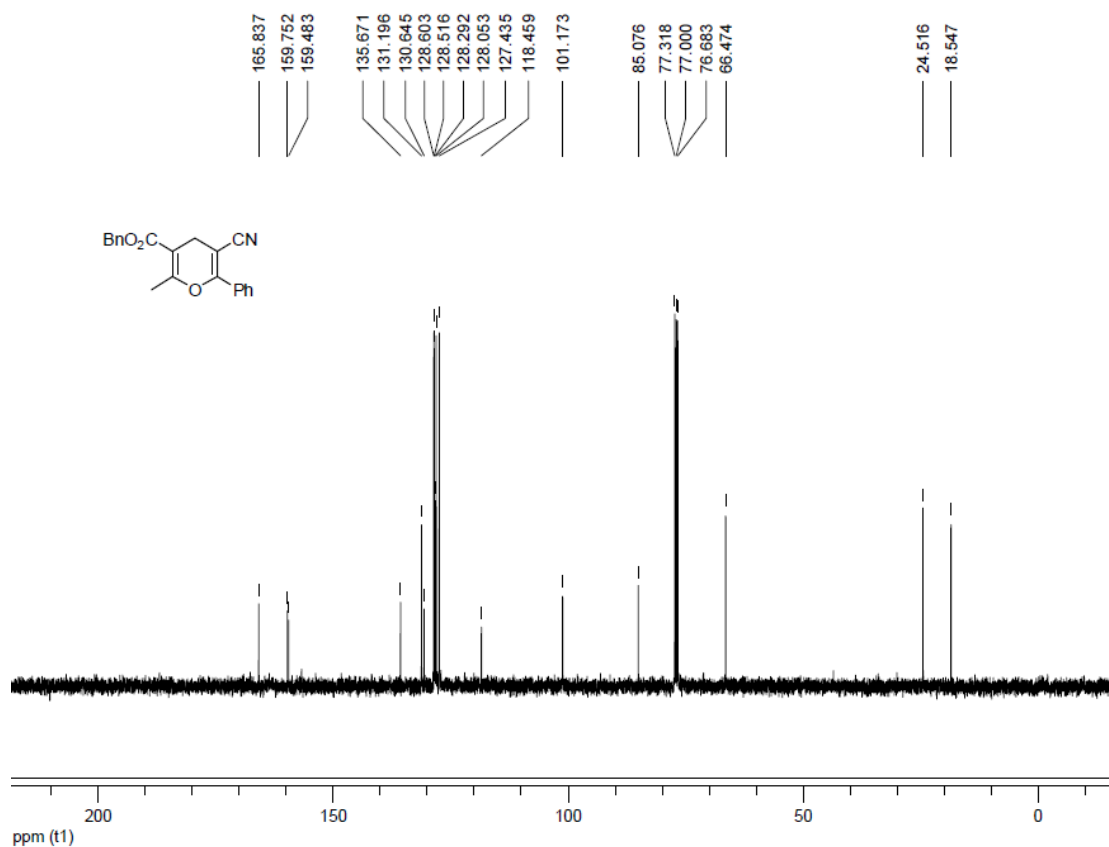
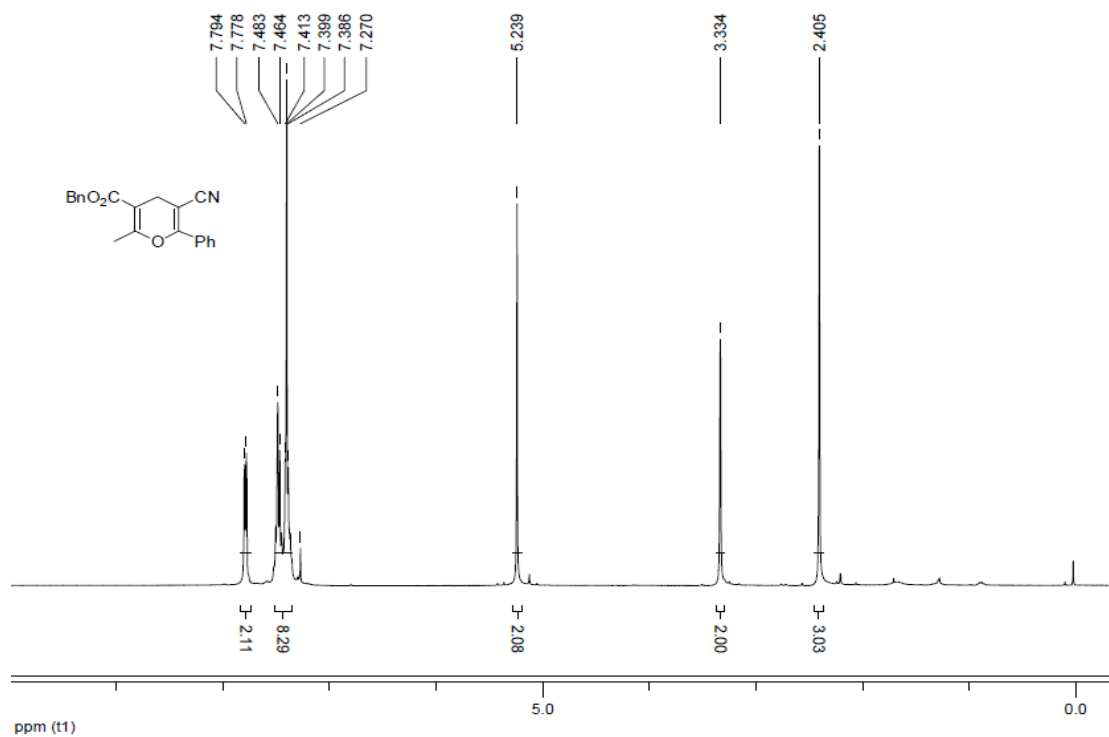
In a 25 mL Schlenk tube, the mixture of **2** (0.18 mmol, 1.2 equiv.), DABCO (3.4 mg, 20 mol %) and K<sub>2</sub>CO<sub>3</sub> (26.9 mg, 0.195 mmol, 1.3 equiv.) was introduced with DMF (2 mL). The mixture was stirred at room temperature. To this reaction mixture the solution of **1** (0.15 mmol) in DMF (2 mL) was slowly added over 20 minutes. The reaction mixture was monitored by TLC. When the reaction was finished, water (20 mL) was added to quench the reaction. The resulted mixture was extracted with EtOAc (3x20 mL), and then the organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>. After remove of organic solvent, the residue was subjected to silica gel column chromatography (petroleum ether: EtOAc 30:1 to 10:1 gradient) to give the product.

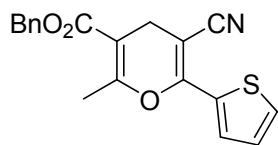
### IV. Data for the compounds 3, 5 and 6



**3aa** Light yellow solid, M.p.106-108°C (49.2 mg, 99%).

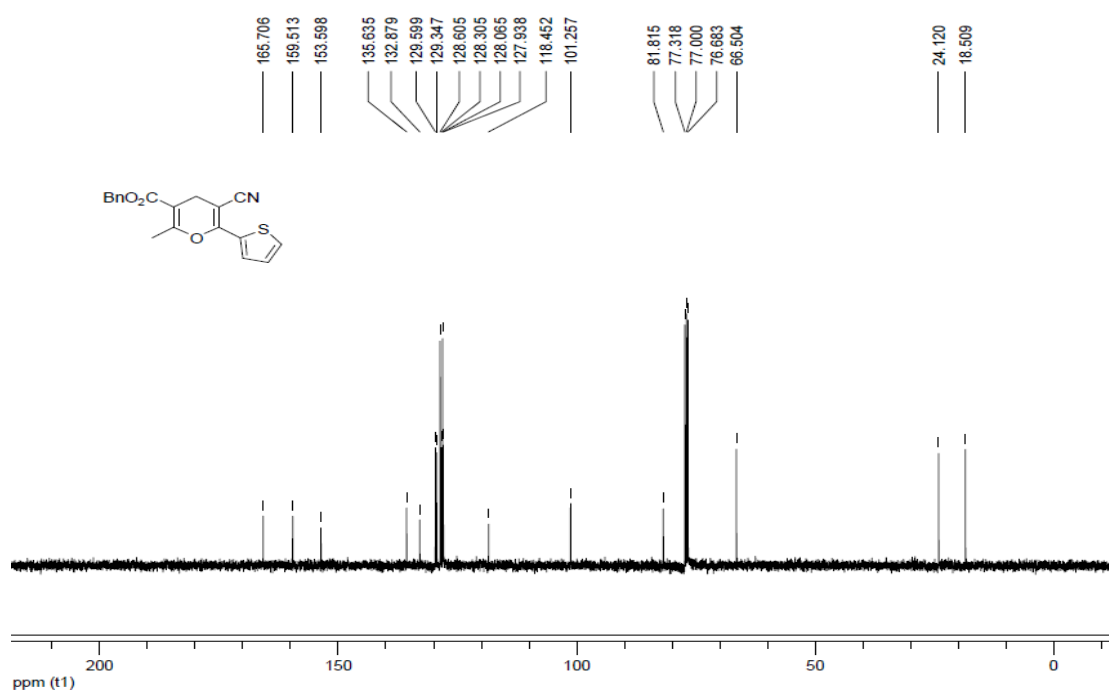
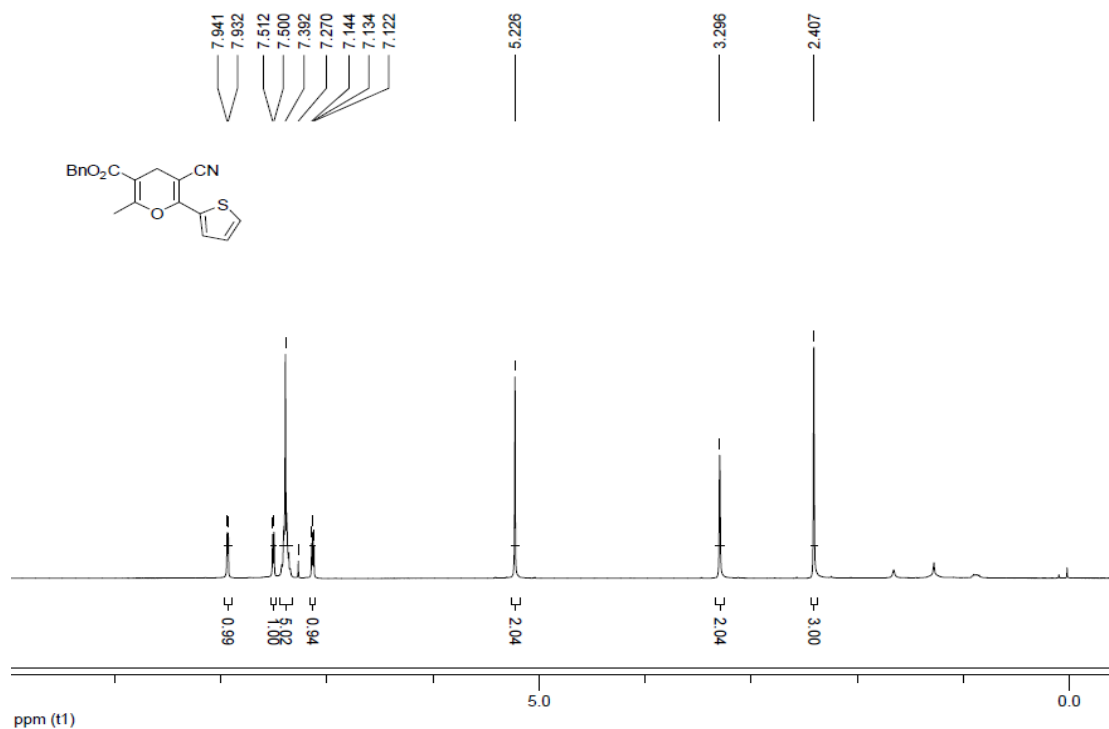
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79-7.78 (m, 2H), 7.50-7.37 (m, 8H), 5.24 (s, 2H), 3.33 (s, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.8, 159.8, 159.5, 135.7, 131.2, 130.6, 128.6, 128.5, 128.3, 128.1, 127.4, 118.5, 101.2, 85.1, 66.5, 24.5, 18.5. MS (m/z): 331; HRMS (EI<sup>+</sup>) Calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub> 331.1208, Found 331.1205.

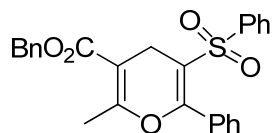




**3ab** White solid, M.p.92-94°C (47 mg, 93%).

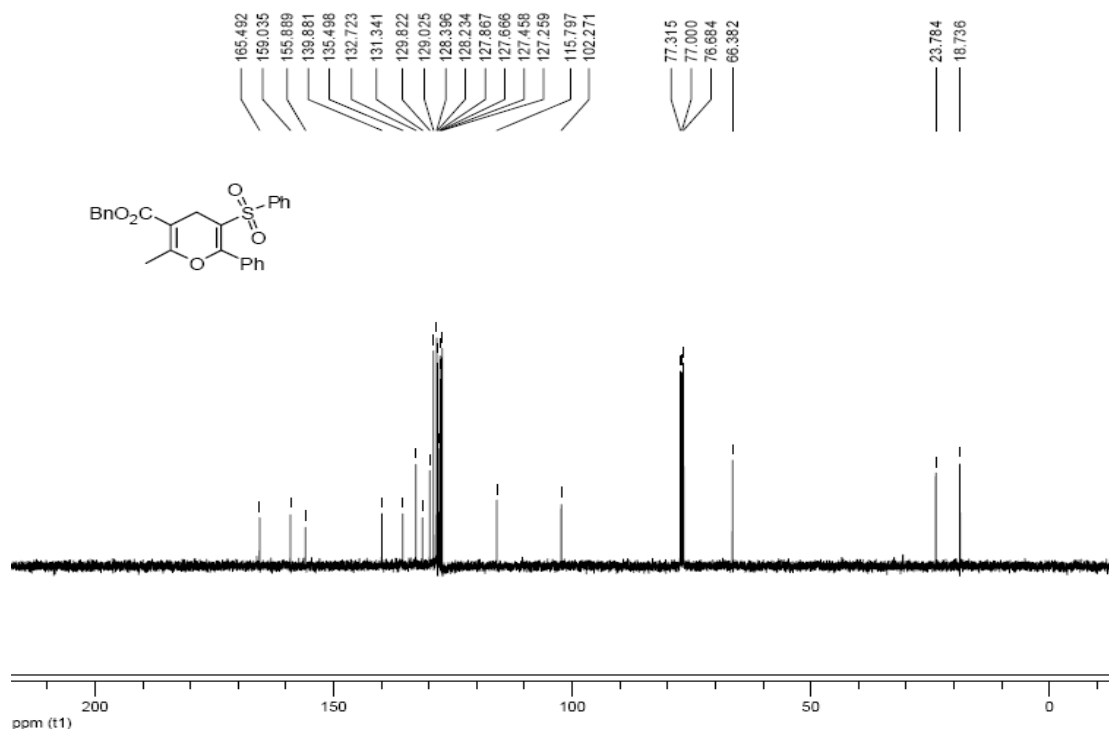
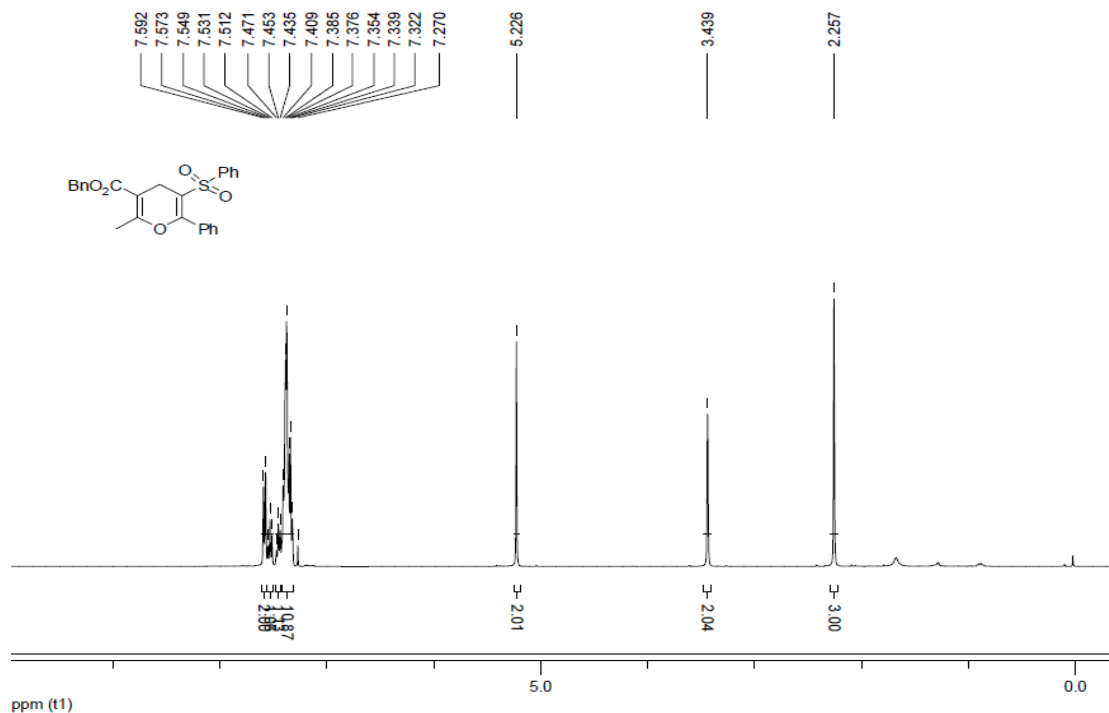
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94-7.93 (m, 1H), 7.51-7.50 (m, 1H), 7.43-7.36 (m, 5H), 7.14-7.12 (m, 1H), 5.23 (s, 2H), 3.30 (s, 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.7, 159.5, 153.6, 135.6, 132.9, 129.6, 129.3, 128.6, 128.3, 128.1, 127.9, 118.5, 101.3, 81.8, 66.5, 24.1, 18.5. MS ( $m/z$ ): 337; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{S}$  337.0773, Found 337.0776.

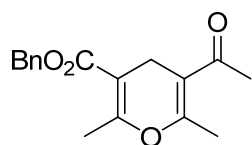




**3ac** Yellow solid, M.p. 114-116°C (55.7 mg, 83%).

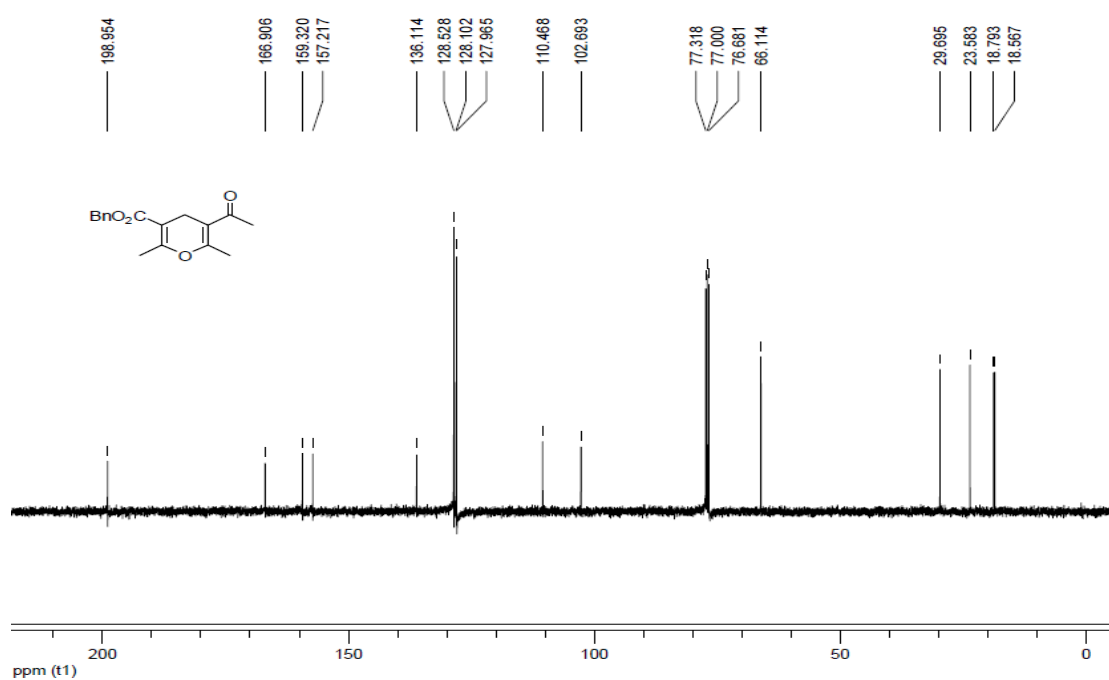
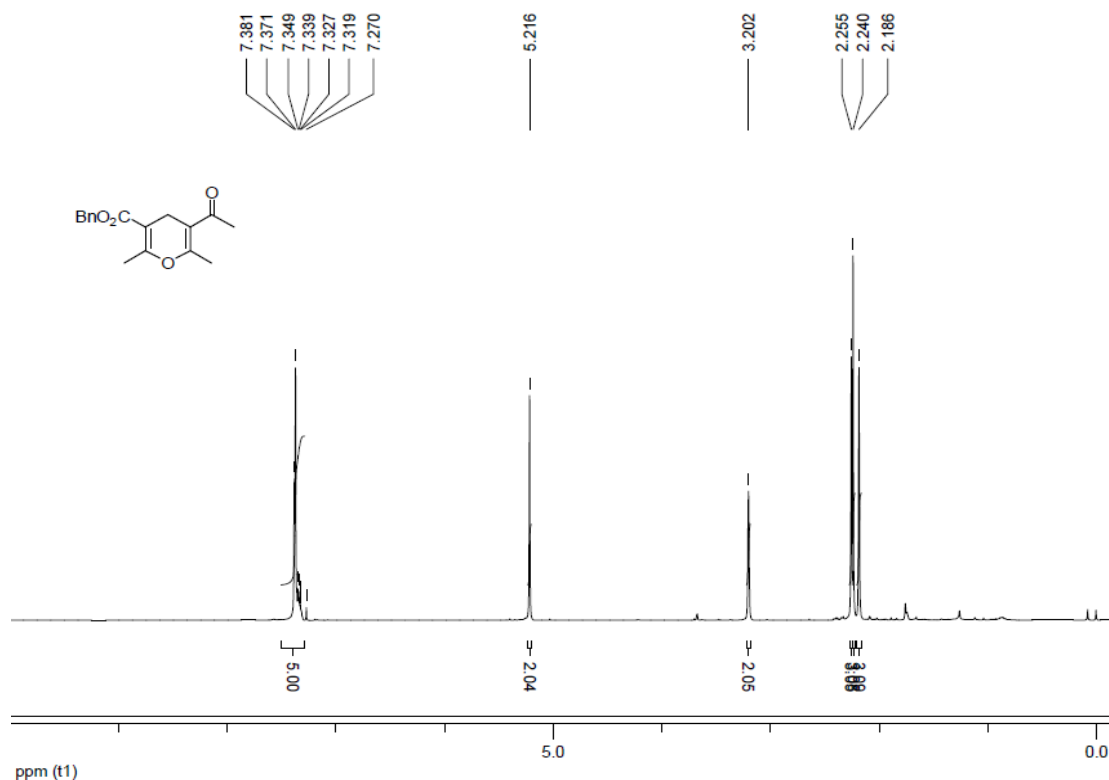
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59-7.57 (m, 2H), 7.55-7.51 (m, 1H), 7.47-7.44 (m, 1H), 7.41-7.32 (m, 11H), 5.23 (s, 2H), 3.44 (s, 2H), 2.56 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5, 159.0, 155.9, 140.0, 135.5, 132.7, 131.3, 129.8, 129.0, 128.4, 127.9, 127.7, 127.5, 127.3, 115.8, 102.3, 66.4, 23.8, 18.7. MS ( $m/z$ ): 446; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_3\text{-Bn}$  355.0640, Found 355.0637.



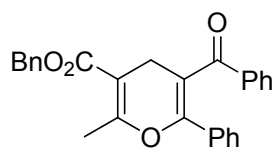


**3ad** Colourless liquid (39.2 mg, 91%)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38-7.32 (m, 5H), 5.22 (s, 2H), 3.20 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.0, 166.9, 159.3, 157.2, 136.1, 128.5, 128.1, 128.0, 110.5, 102.7, 66.1, 29.7, 23.6, 18.8, 18.6. MS ( $m/z$ ): 286; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_4\text{-CO}$  258.0892, Found 258.0894.

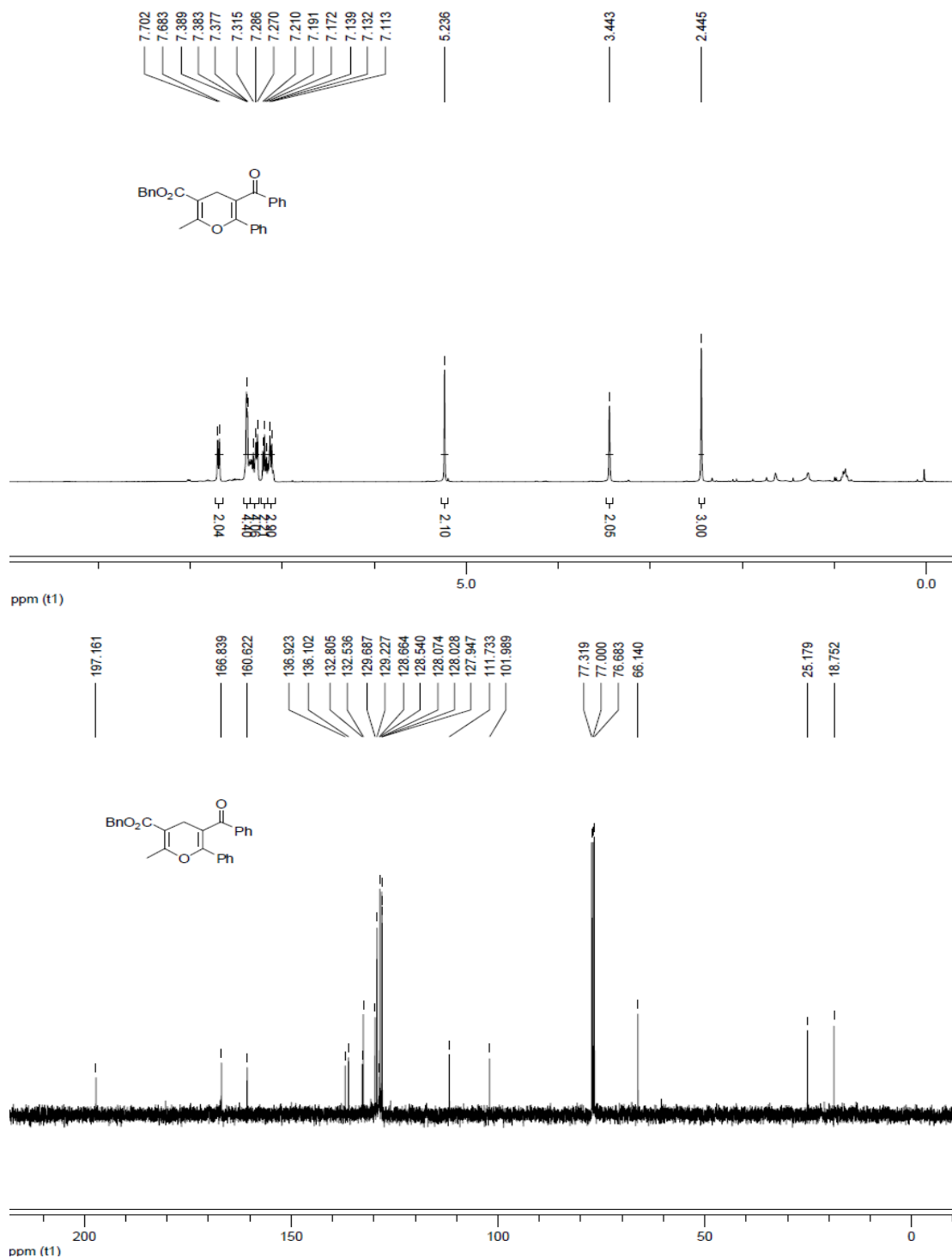


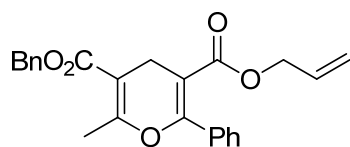




**3ae** Light yellow liquid (34.5 mg, 56%).

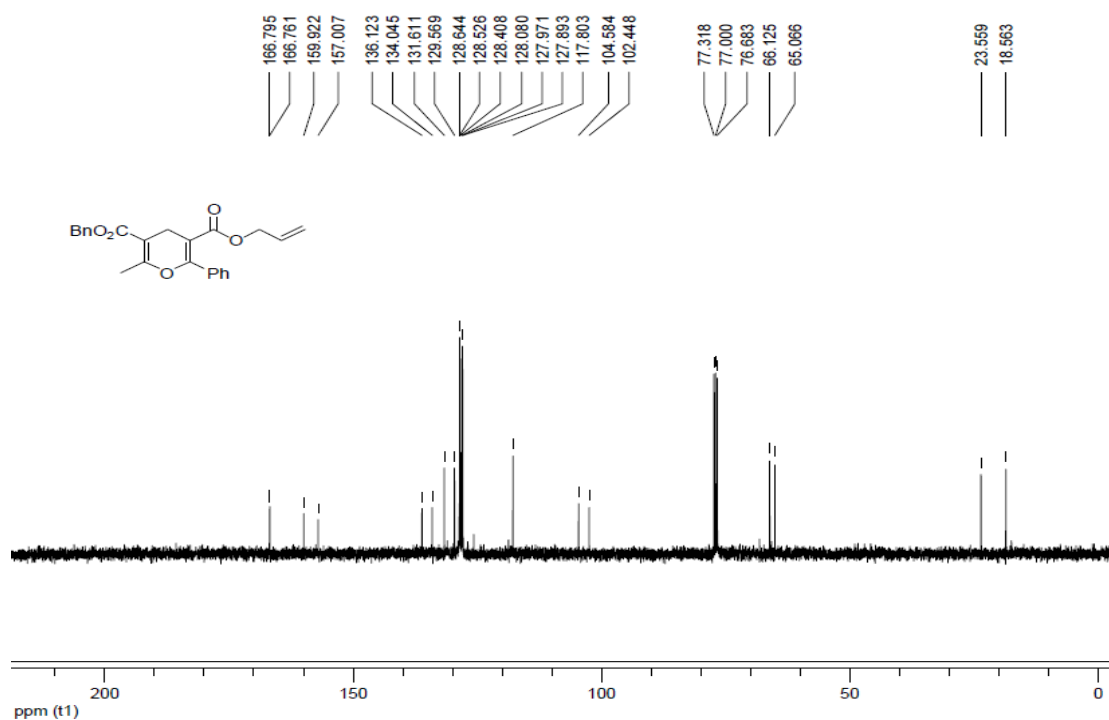
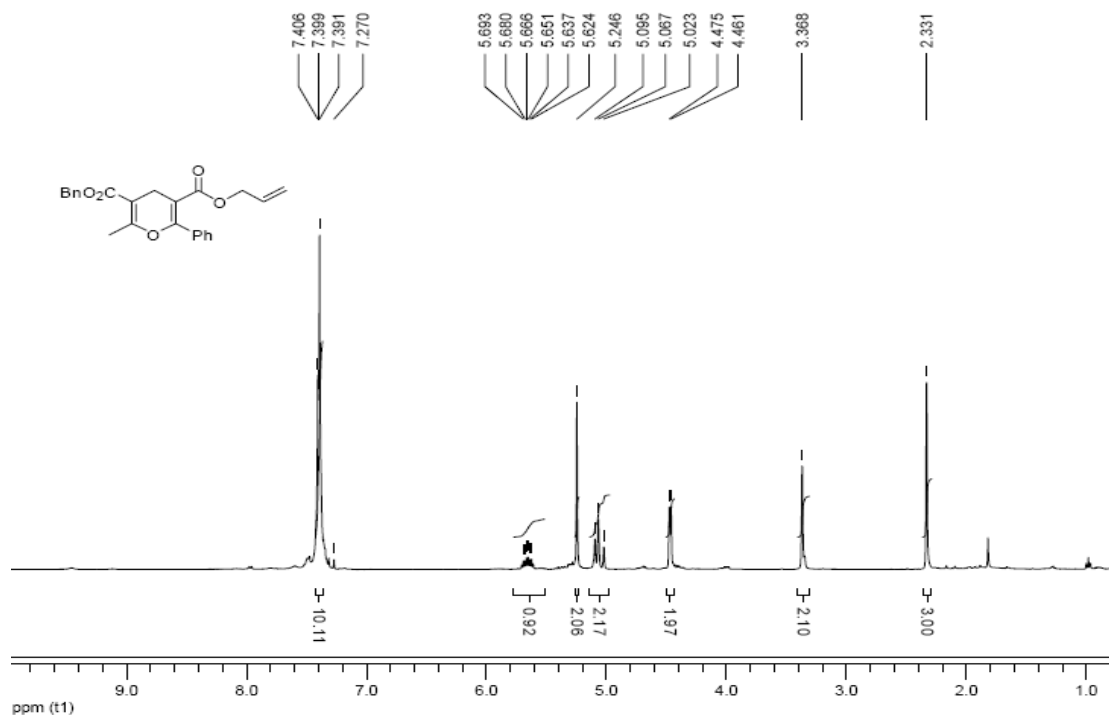
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70-7.68 (m, 2H), 7.39-7.38 (m, 4H), 7.32-7.27 (m, 4H), 7.21-7.17 (m, 2H), 7.14-7.11 (m, 3H), 5.24 (s, 2H), 3.44 (s, 2H), 2.45 (s, 3H);  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.2, 166.8, 160.6, 137.0, 136.1, 132.8, 132.5, 130.0, 129.2, 129.0, 128.5, 128.1, 128.0, 111.7, 102.0, 66.1, 25.2, 18.8. MS (m/z): 410; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{27}\text{H}_{22}\text{O}_4$  410.1518, Found 410.1516.

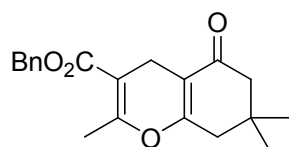




**3af** yellow liquid (47 mg, 80%).

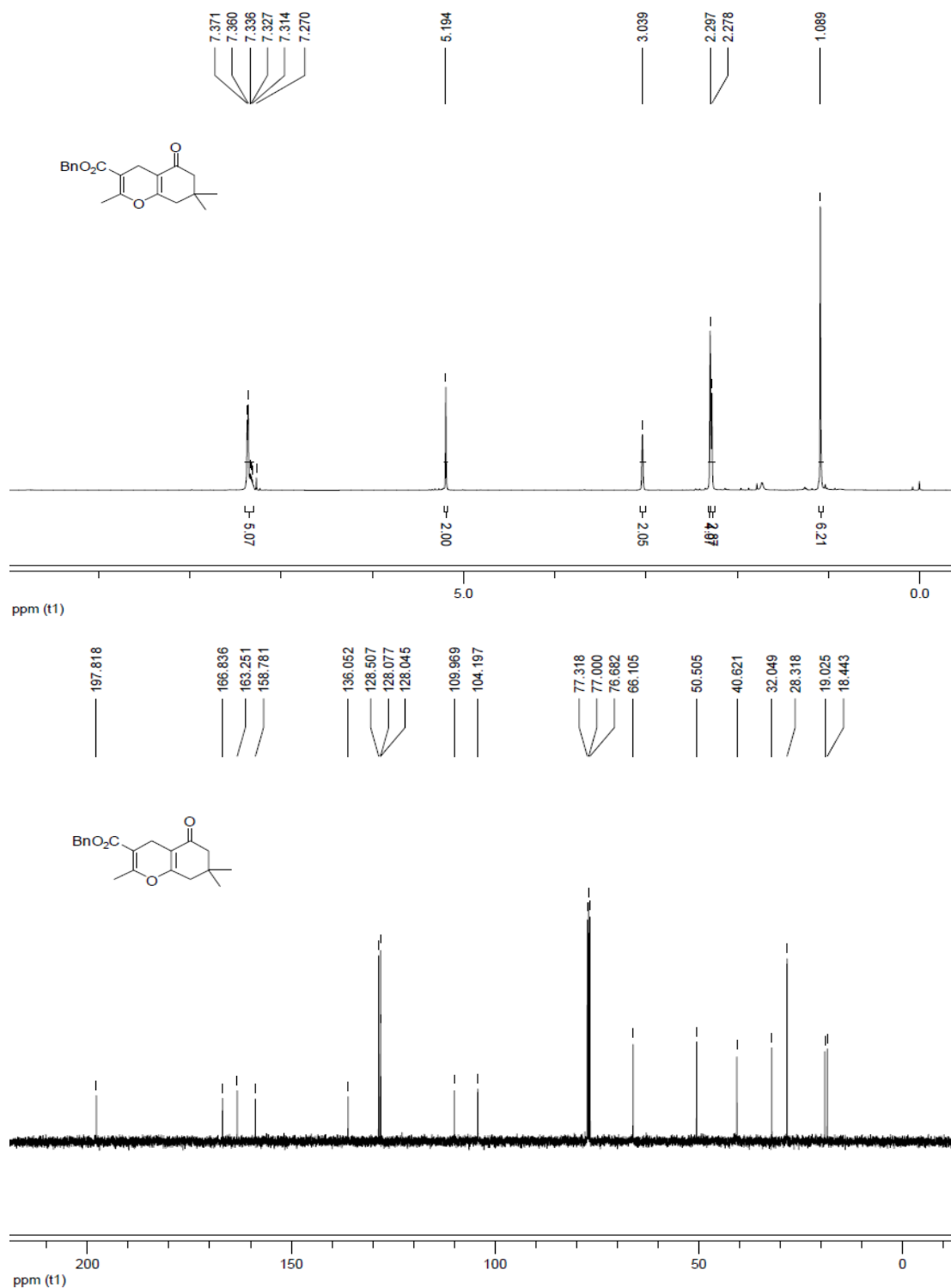
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.39 (m, 10H), 5.69-5.62 (m, 1H), 5.25 (s, 2H), 5.10-5.02 (m, 2H), 4.47 (d,  $J = 5.6$  Hz, 2H), 3.37 (s, 2H), 2.33 (s, 3H).;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.79, 166.76, 159.9, 157.0, 136.1, 134.0, 131.6, 129.6, 128.6, 128.5, 128.4, 128.0, 127.9, 117.8, 104.6, 102.4, 66.1, 65.1, 23.6, 18.6. MS ( $m/z$ ): 390; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_5$  390.1467, Found 390.1464.

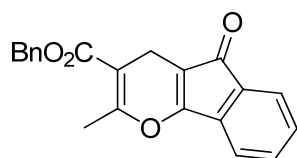




**3ag** Coloueless liquid (37.6 mg, 77%).

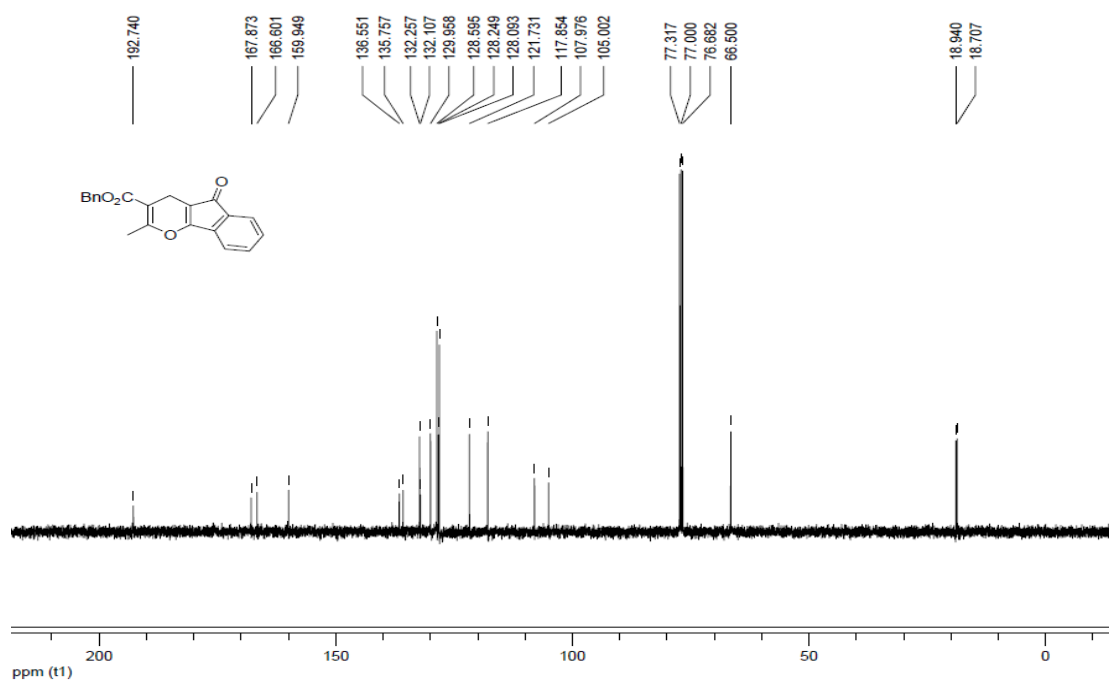
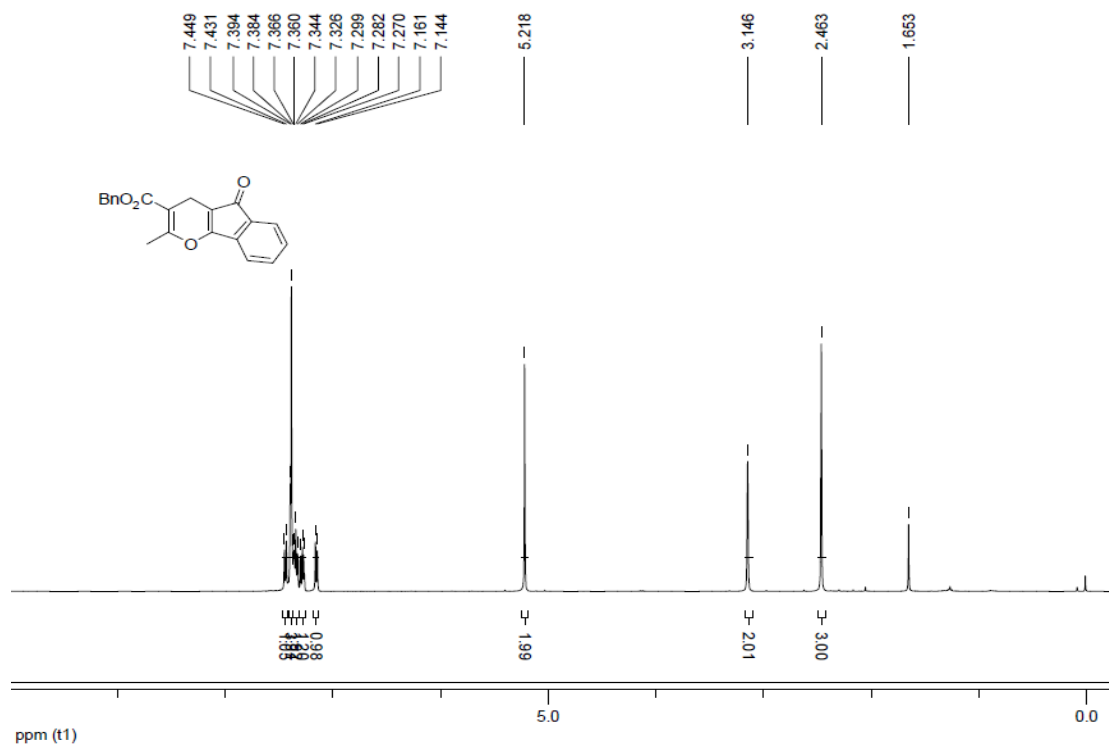
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.37-7.31 (m, 5H), 5.19 (s, 2H), 3.01 (s, 2H), 2.30 (s, 4H), 2.28 (s, 3H), 1.09 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.8, 166.8, 163.3, 158.8, 136.1, 128.5, 128.1, 128.0, 110.0, 104.2, 66.1, 50.5, 40.6, 32.0, 28.3, 19.0, 18.4. MS (m/z): 326; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{20}\text{H}_{22}\text{O}_4$  326.1518, Found 326.1516.

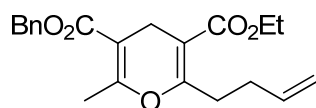




**3ah** Red solid, M.p. 133-135 °C (23.8 mg, 48%).

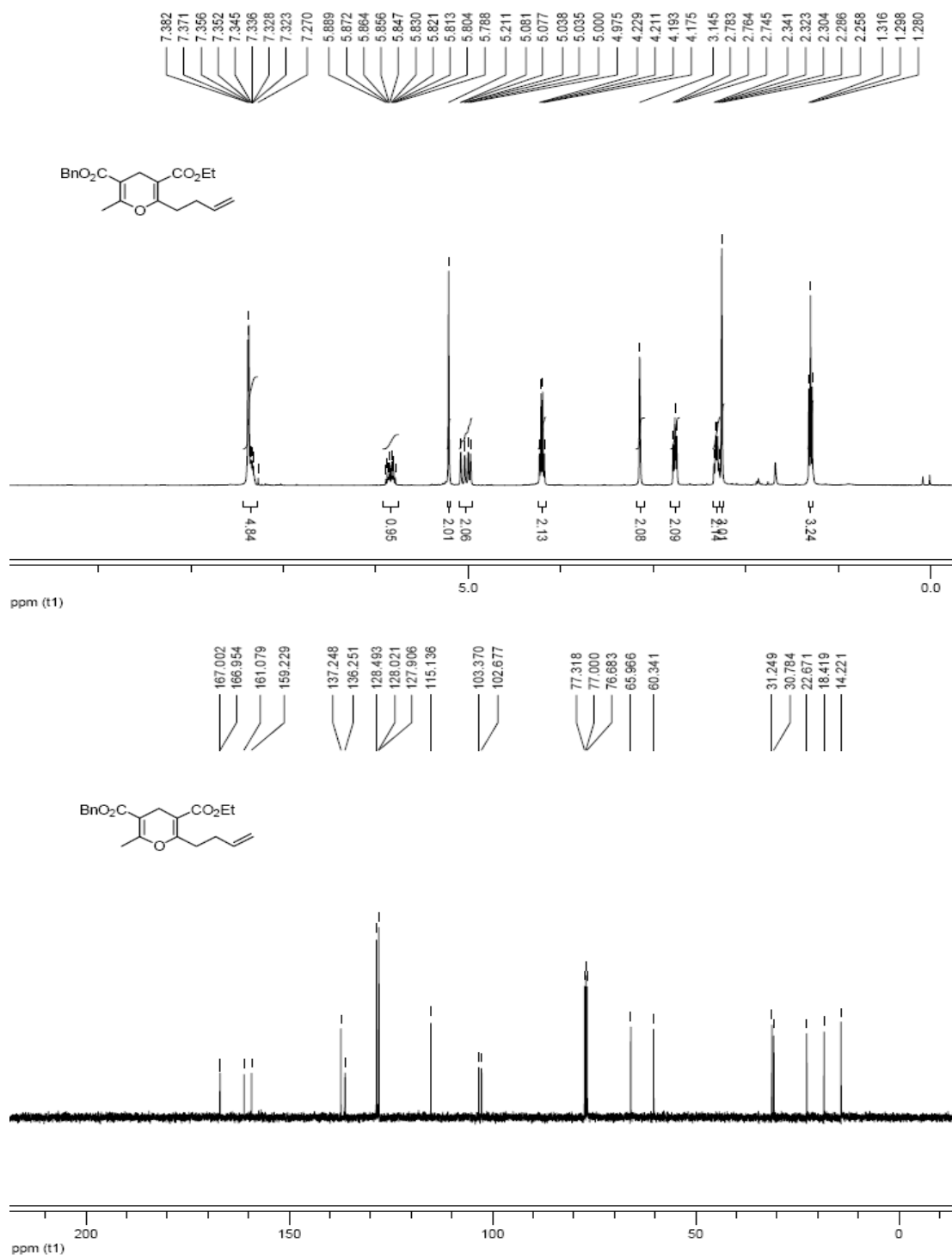
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45-7.43 (m, 1H), 7.39-7.37 (m, 4H), 7.36-7.33 (m, 2H), 7.30-7.27 (m, 1H), 7.14-7.16 (m, 1H), 5.22 (s, 2H), 3.15 (s, 2H), 2.46 (s, 3H);  
 $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.7, 167.9, 166.6, 159.9, 136.6, 135.8, 132.3, 132.1, 130.0, 128.6, 128.2, 128.1, 121.7, 117.9, 108.0, 105.0, 66.5, 18.9, 18.7. MS ( $m/z$ ): 332;  
HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_4$  332.1049, Found 332.1050.

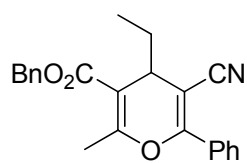




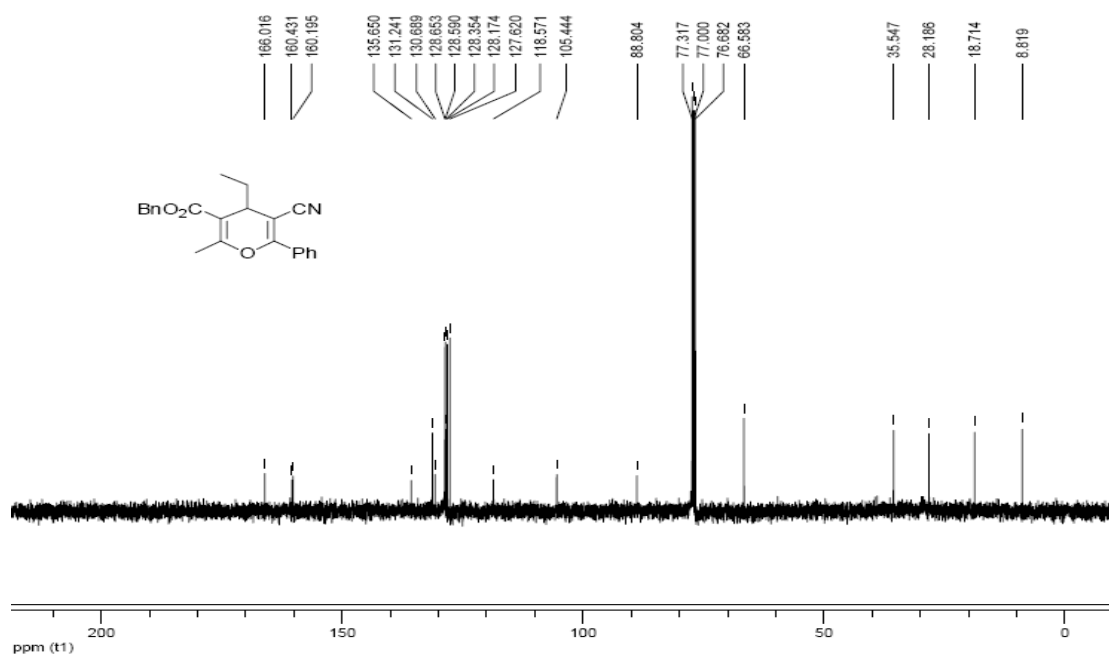
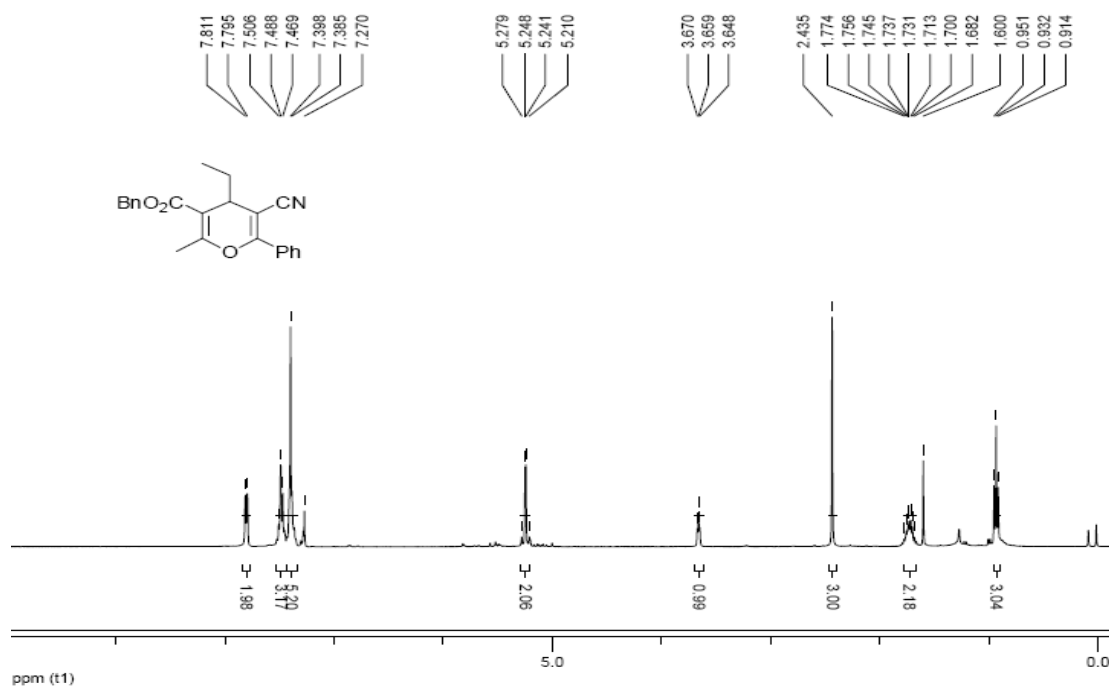
**3ai** Colouless liquid (33.5mg, 63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38-7.32 (m, 5H), 5.89-5.79 (m, 1H), 5.21 (s, 2H), 5.08-4.98 (m, 2H), 4.202 (q,  $J = 7.2$  Hz, 2H), 3.15 (s, 2H), 2.76 (t,  $J = 7.6$  Hz, 2H), 2.34-2.29 (m, 2H), 2.26 (s, 3H), 1.30 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.7, 167.9, 166.6, 159.9, 136.6, 135.8, 132.3, 132.1, 130.0, 128.6, 128.2, 128.1, 121.7, 117.9, 108.0, 105.0, 66.5, 18.9, 18.7. MS ( $m/z$ ): 356; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_4$  356.1624, Found 356.1625.

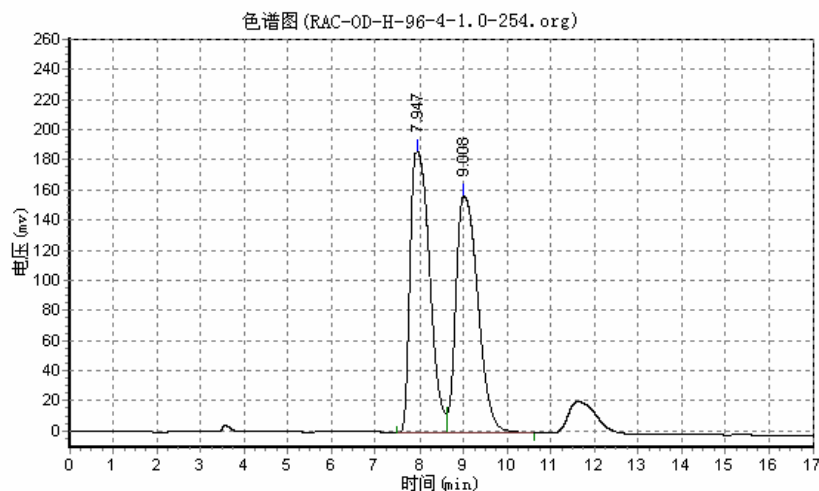




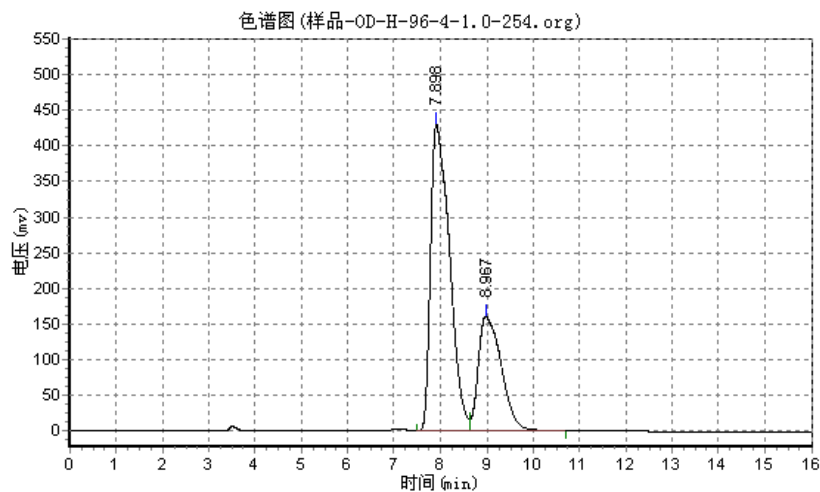
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81-7.80 (m, 2H), 7.51-7.47 (m, 3H), 7.40-7.39 (m, 5H), 5.28-5.21 (m, 2H), 3.66 (t,  $J = 4.4$  Hz, 1H), 2.44 (s, 3H), 1.77-1.68 (m, 2H), 0.93 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.0, 160.4, 160.2, 135.7, 131.2, 130.7, 128.7, 128.6, 128.4, 128.2, 127.6, 118.6, 105.4, 88.8, 66.6, 35.5, 28.2, 18.7, 8.8. MS ( $m/z$ ): 359; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{-Et}$  330.1130, Found 330.1133; HPLC: AS-H column, *n*-hexane/*i*-propanol = 96/4, Flow rate: 1.0 mL/min, UV = 254 nm,  $t_r = 7.90$  min (minor) and  $t_r = 8.97$  min (major).



HPLC (OD-H column,  $\lambda = 254$  nm, eluent: *n*-hexane/*i*-propanol = 96/4, flow rate: 1.0 mL/min)

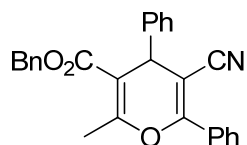


Peak 峰号	峰名	RetTime (min) 保留时间	Peak Height 峰高	Peak Area (mAu·S) 峰面积	Area (%) 含量
1		7.947	186915.516	5440910.000	49.4116
2		9.008	157549.734	5570494.500	50.5884
总计			344465.250	11011404.500	100.0000



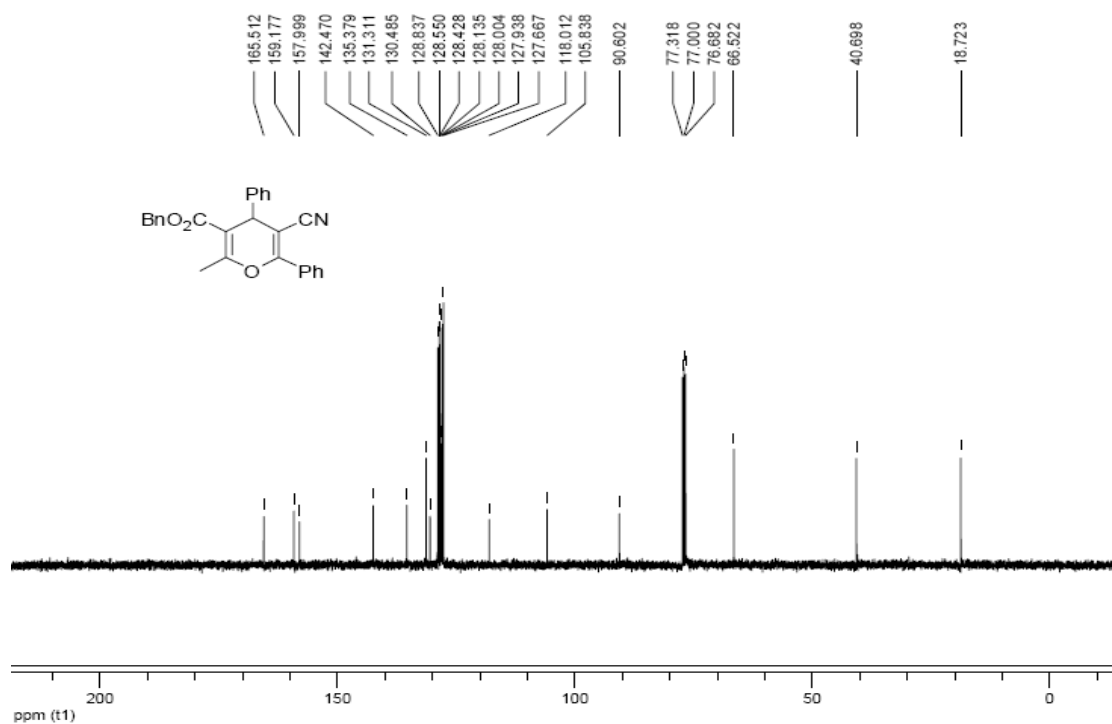
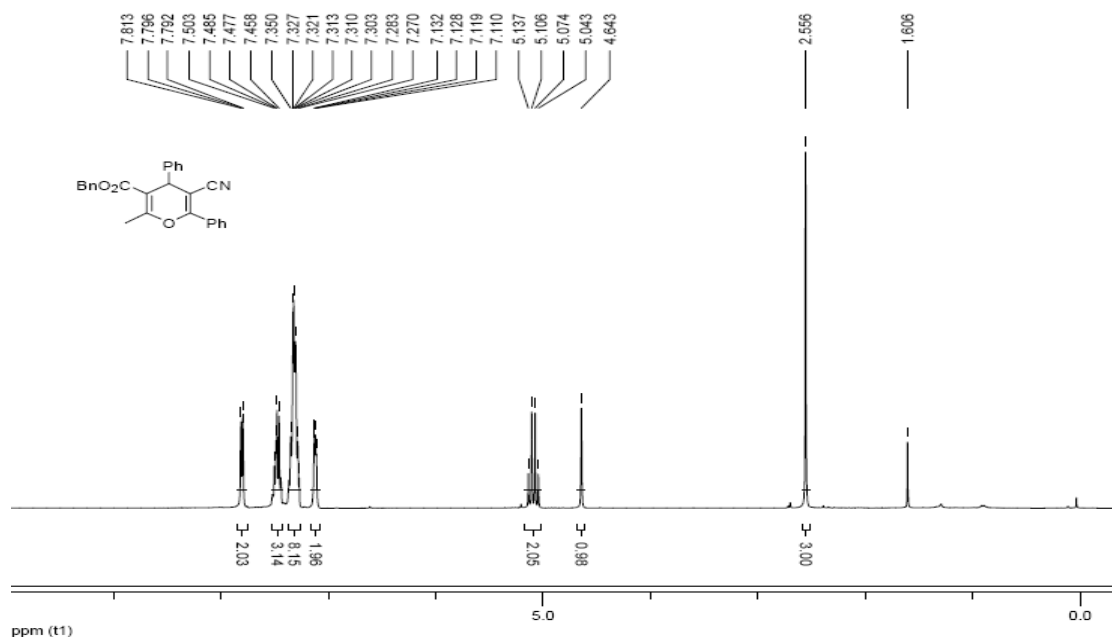
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.898	429596.656	12207069.000	68.3469
2		8.967	160829.125	5653382.000	31.6531
总计			590425.781	17860451.000	100.0000



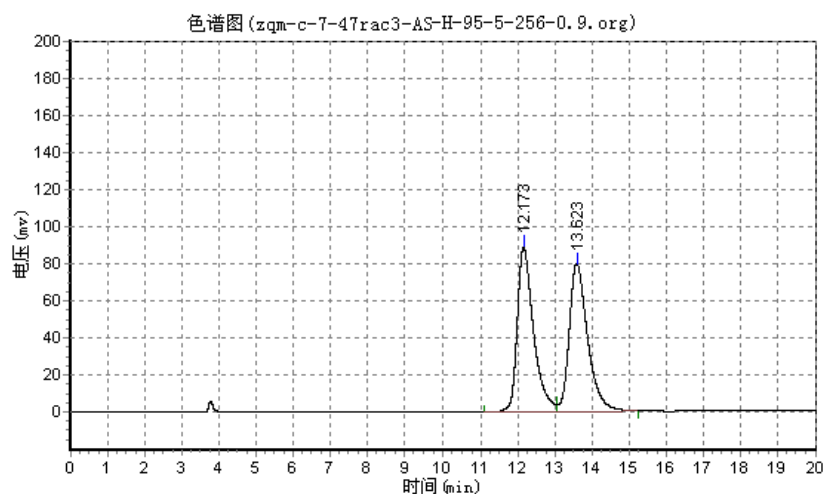
**3ca** White solid, M.p. 125-127°C (42.1 mg, 69%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81-7.79 (m, 2H), 7.50-7.46 (m, 3H), 7.35-7.27 (m, 8H), 7.13-7.11 (m, 2H), 5.14-5.04 (m, 2H), 4.64 (s, 1H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5, 159.2, 158.0, 142.5, 135.4, 131.3, 130.5, 128.8, 128.4, 128.1, 128.0, 127.9, 127.7, 118.0, 105.8, 90.6, 66.5, 40.7, 18.7. MS ( $m/z$ ): 407; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{27}\text{H}_{21}\text{NO}_3$  407.1521, Found 407.1522; HPLC: AS-H column, *n*-hexane/*i*-propanol = 95/5, Flow rate: 0.9 mL/min, UV = 254 nm,  $t_r$  = 12.07 min and  $t_r$  = 13.47 min (major).



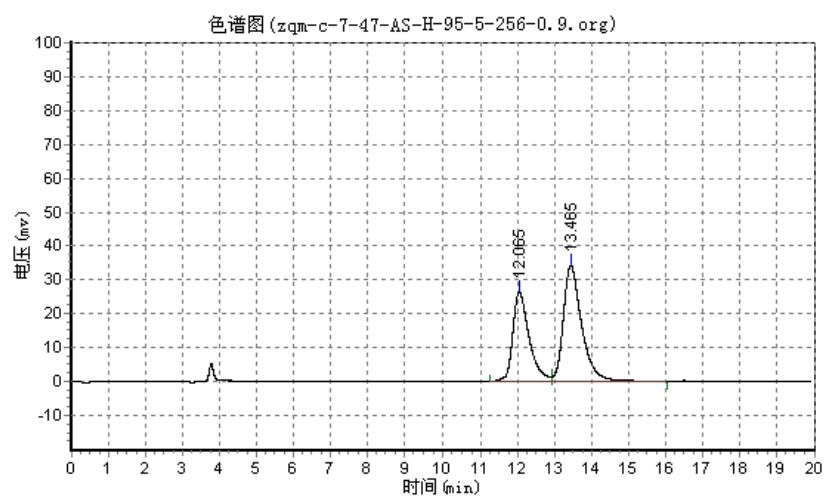


HPLC (AS-H column,  $\lambda = 254$  nm, eluent: *n*-hexane/*i*-propanol = 95/5, flow rate: 0.9 mL/min)



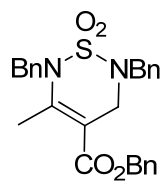
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		12.173	89019.531	2739404.250	49.4915
2		13.623	80002.461	2795697.000	50.5085
总计			169021.992	5535101.250	100.0000



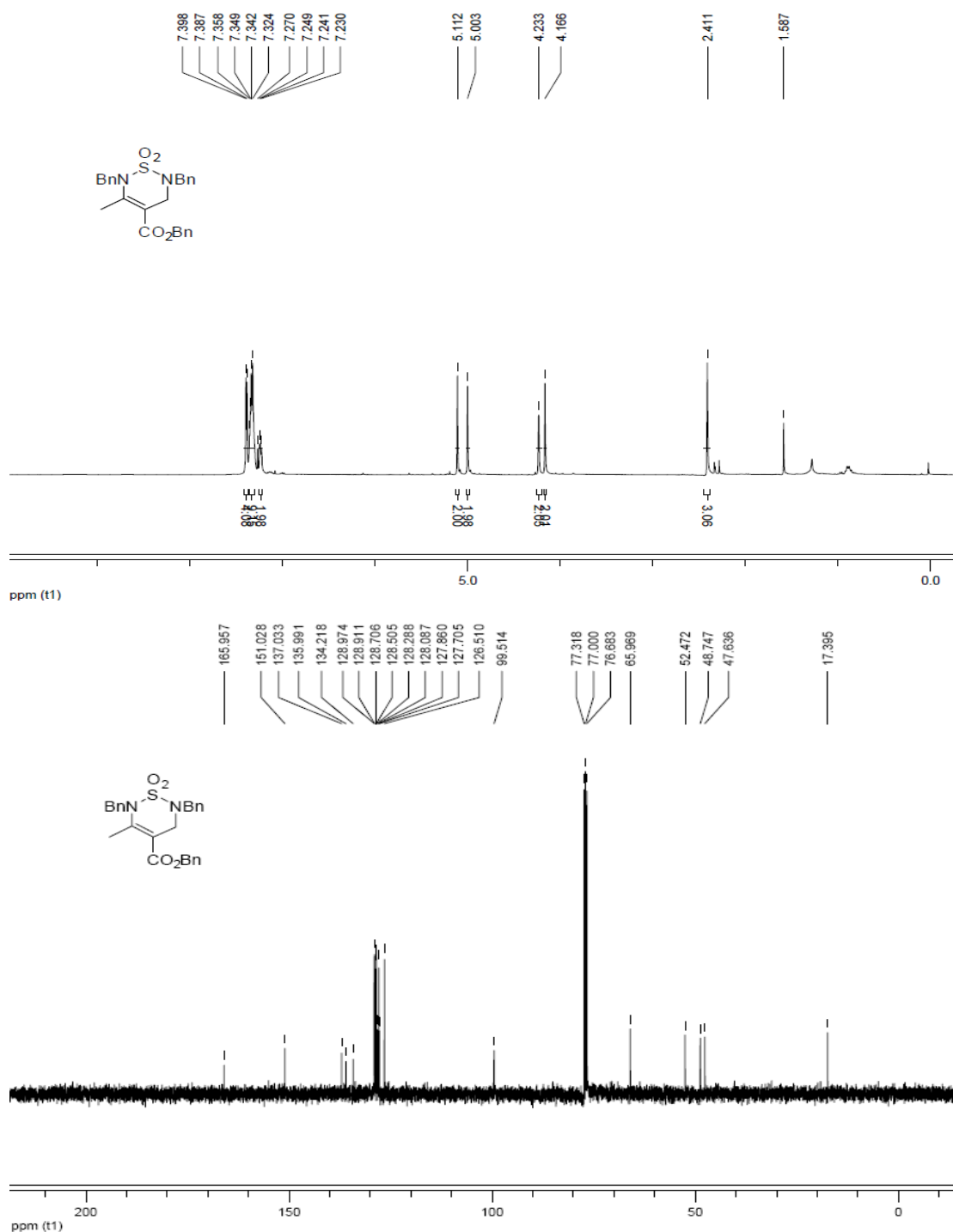
分析结果表

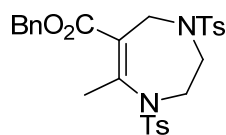
峰号	峰名	保留时间	峰高	峰面积	含量
1		12.065	26559.650	828869.688	40.7490
2		13.465	34331.723	1205214.625	59.2510
总计			60891.373	2034084.313	100.0000



**5aa** Yellow liquid (35 mg, 76%).

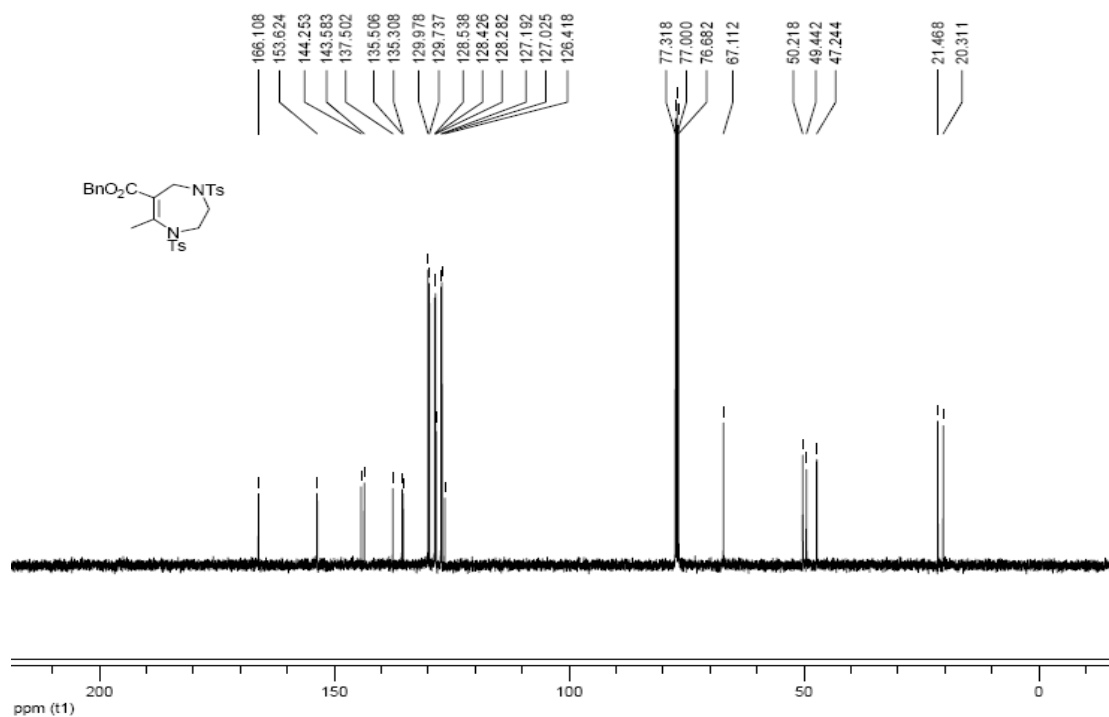
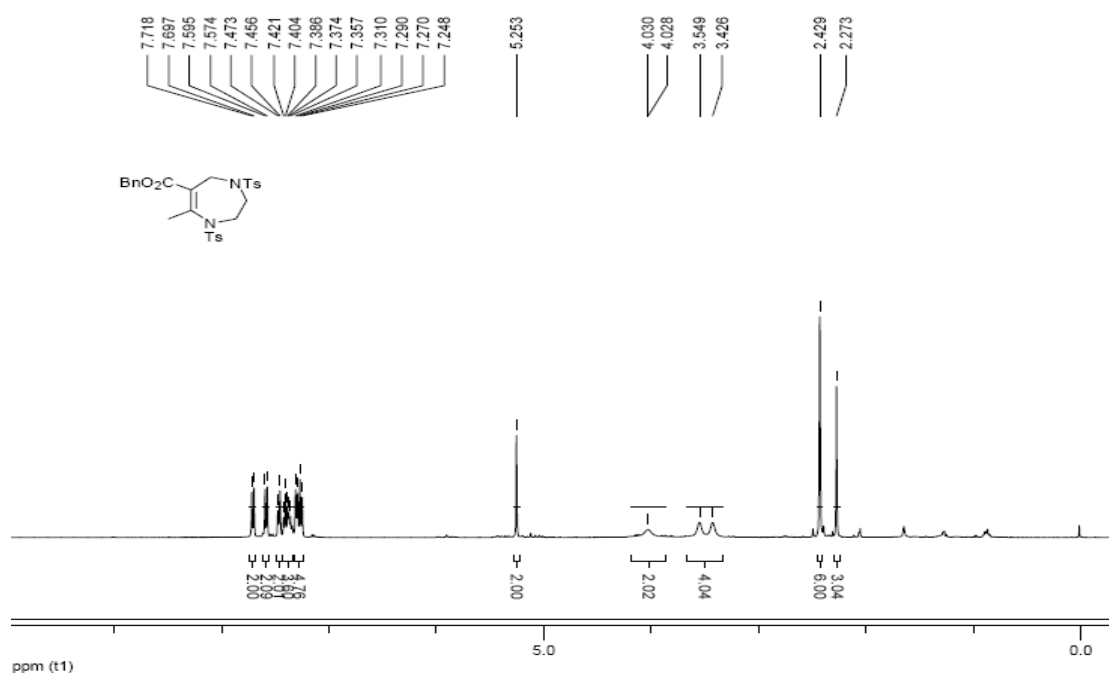
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40-7.39 (m, 4H), 7.36-7.32 (m, 9H), 7.25-7.23 (m, 2H), 5.11 (s, 2H), 5.00 (s, 2H), 4.23 (s, 2H), 4.27 (s, 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.0, 121.0, 137.0, 136.0, 134.2, 128.97, 128.91, 128.5, 128.3, 128.1, 127.9, 127.7, 126.5, 99.5, 66.0, 52.5, 48.7, 47.6, 17.4. MS (m/z): 462; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$  462.1613, Found 462.1614.

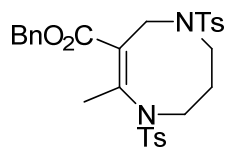




**5ab** White Solid M. p. 91-93 °C (77.8 mg, 94%).

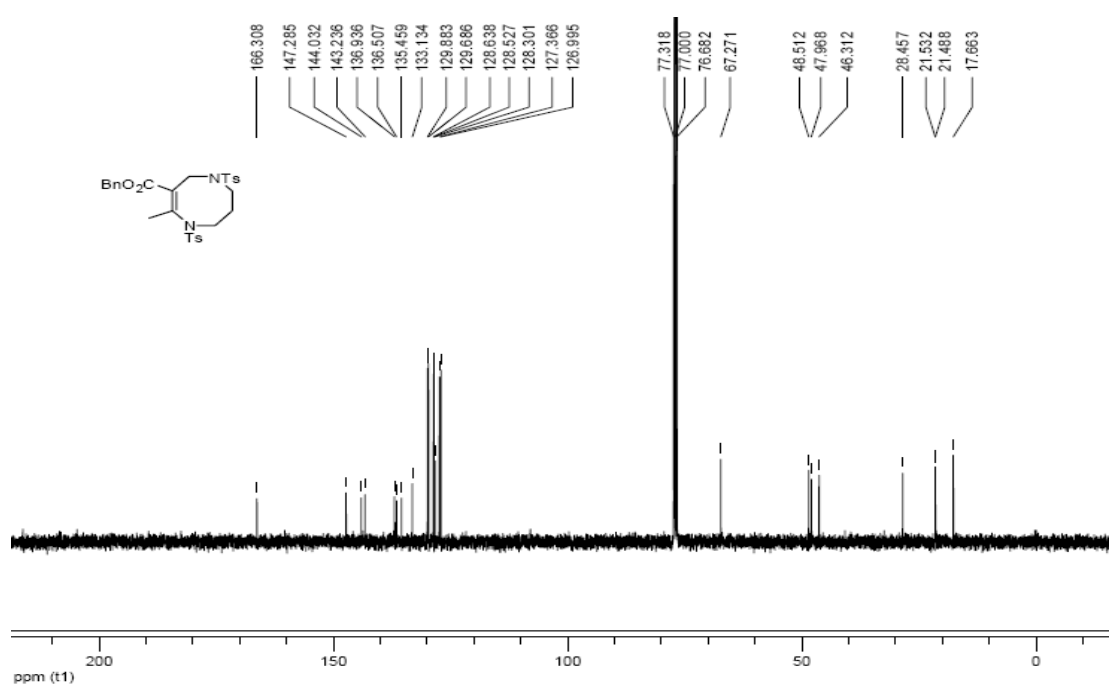
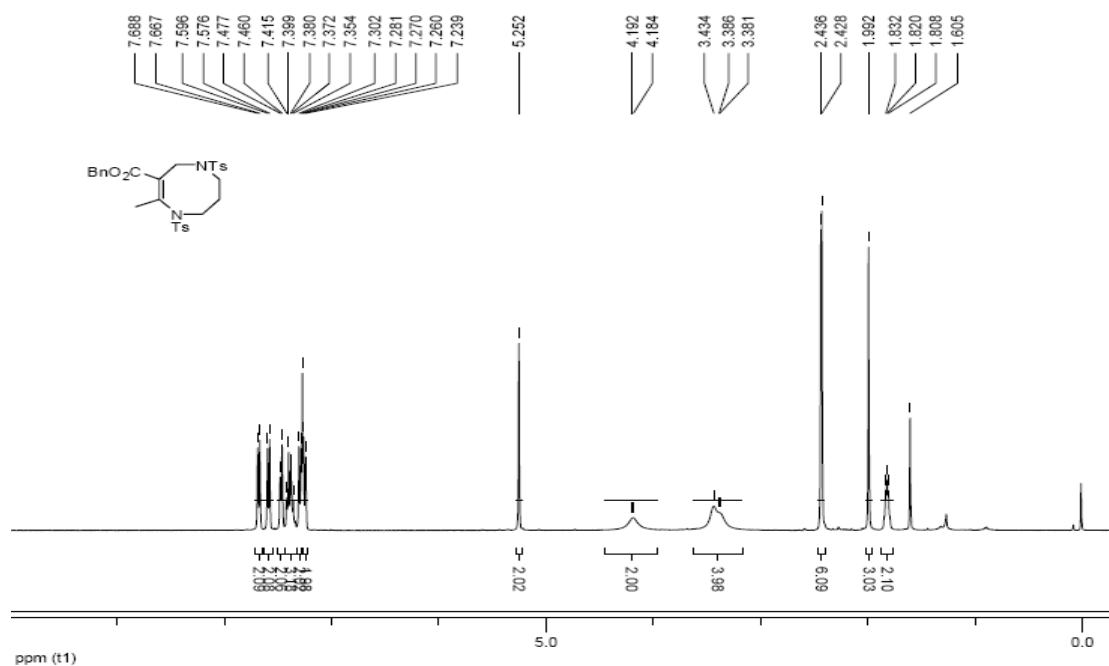
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72-7.70 (m, 2H), 7.60-7.57 (m, 2H), 7.47-7.46 (m, 2H), 7.42-7.36 (m, 4H), 7.31-7.24 (m, 4H), 5.25 (s, 2H), 4.030-4.028 (m, 2H), 3.55-3.43 (m, 4H), 2.43 (s, 6H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.1, 153.6, 144.3, 143.6, 137.5, 135.5, 135.3, 129.98, 129.73, 128.5, 128.4, 128.3, 127.2, 127.0, 126.4, 67.1, 50.2, 49.4, 47.2, 21.5, 20.3. MS (m/z): 554; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_6\text{S}_2$  554.1545, Found 554.1544.

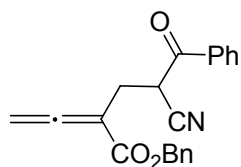




**5ac** White solid, M.p. 128-131°C (42 mg, 74%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69-7.67 (m, 2H), 7.60-7.58 (m, 2H), 7.48-7.46 (m, 2H), 7.42-7.35 (m, 3H), 7.30-7.28 (m, 2H), 7.26-7.24 (m, 2H), 5.25 (s, 2H), 4.19-4.18 (m, 2H), 3.43-3.38 (m, 4H), 2.44 (s, 3H), 2.43 (s, 3H), 1.99 (s, 3H), 1.82 (t,  $J = 4.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.3, 147.3, 144.0, 143.2, 137.0, 136.5, 135.5, 133.1, 129.88, 129.69, 128.6, 128.5, 128.3, 127.4, 127.0, 67.3, 48.5, 48.0, 46.3, 28.5, 21.53, 21.48, 17.7. MS ( $m/z$ ): 568; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2\text{-Ts}$  413.1535, Found 413.1529.





**6** Light yellow liquid (10.6 mg, 32%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72-7.70 (m, 2H), 7.47-7.40 (m, 3H), 7.34 (m, 5H), 5.25-5.17 (m, 2H), 4.980-4.975 (d,  $J = 2.0$  Hz, 1H), 4.54-4.536 (d,  $J = 2.0$  Hz, 1H), 3.65 (t,  $J = 5.6$  Hz, 1H), 2.96 (dd,  $J = 4.8$  Hz,  $J = 16.4$  Hz, 1H), 2.78 (dd,  $J = 6.0$  Hz,  $J = 16.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.4, 162.4, 150.8, 135.1, 131.6, 130.9, 128.6, 128.5, 128.4, 127.8, 119.0, 97.1, 82.2, 67.5, 40.9, 26.5. MS ( $m/z$ ): 331; HRMS ( $\text{EI}^+$ ) Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_3$  331.1208, Found 331.1212.

