Supporting Information

Amine-catalyzed Formal (3+3) Annulations of 2-(Acetoxymethyl)buta-2,3-dienoates with Sulfur Ylide: Synthesis of 4H-Pyran Bearing Vinyl Sulfide Group

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Contents

I. General information

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

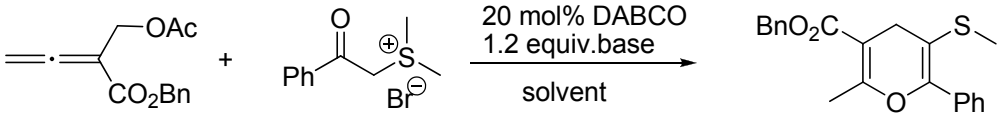
NMR spectrum: ^{1}H and ^{13}C spectra were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR. For ^{1}H NMR, chemical shifts were reported downfield from $CDCl_3$ (δ: 7.27 ppm). For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference.

Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

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**[a]



1a **2a** **3aa**

Entry	1a/2a	Base	Solvent	T (°C)	Yield (%)[b]
1	1 : 1.2	K_2CO_3	benzene	r.t.	70
2	1 : 2.1	K_2CO_3	benzene	r.t.	53
3	1 : 1.2	Cs_2CO_3	benzene	r.t.	59
4	1 : 1.2	K_2CO_3	PhMe	r.t.	27
5	1 : 1.2	K_2CO_3	CH_2Cl_2	r.t.	88
6	1 : 1.2	K_2CO_3	MeCN	r.t.	62
7	1 : 1.2	K_2CO_3	DMF	r.t.	47
8	**1 : 1.2**	**K_2CO_3**	**Acetone**	**r.t.**	**96**
9	1 : 1.2	K_2CO_3	Acetone	reflux	70
10	1 : 1.2	Na_2CO_3	Acetone	r.t.	88

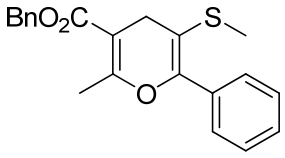
[a]Reaction conditions: to the solution of **2a** (31.3 mg, 0.12 mmol, 1.2 equiv.), base (0.12 mmol, 1.2 equiv.), DABCO (2.3 mg, 0.02 mmol, 20 mol%) in acetone (1.3 mL), was slowly added the solution of **1a** (24.6 mg, 0.10 mmol) in acetone (1.3 mL) over 20 minutes. [b]Isolated yield.

Optimization was conducted with the model reaction between **1a** and **2a** in the presence of 20 mol% DABCO (Table S1). When 1.2 equivalents of K_2CO_3 were used as the base, compound **3aa** could be isolated in 70% yield (entry 1, Table S1). This transformation seemed to be strongly dependent on the solvent (entries 4-8, Table S1) and solvent Acetone was found out to be the optimal one. To our delight, the yield reached as high as 96% when K_2CO_3 was used (entry 8, Table S1).

□. The Procedure for (3+3) Annulations

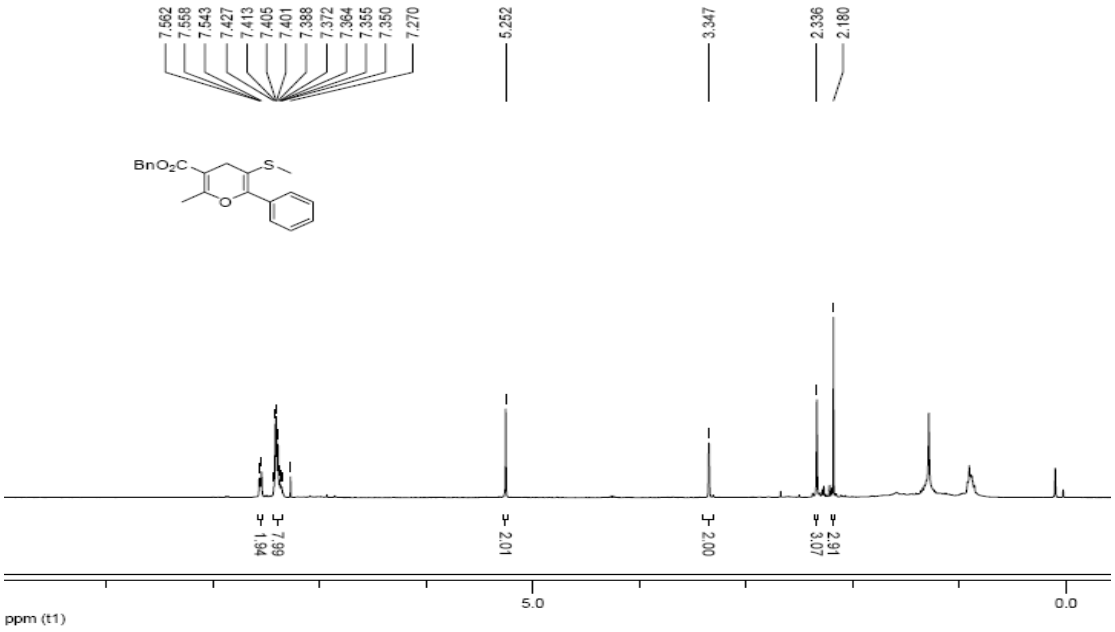
In a 25 mL Schlenk tube, the mixture of **2** (0.12 mmol, 1.2 equiv.), DABCO (2.3 mg, 20 mol %) and K_2CO_3 (16.6 mg, 0.12 mmol, 1.2 equiv.) was introduced with acetone (1.3 mL). The mixture was stirred at room temperature. To this reaction mixture the solution of **1** (0.10 mmol) in acetone (1.3 mL) was slowly added over 20 minutes. The reaction mixture was monitored by TLC. When the reaction was finished, the mixture was directly subjected to silica gel column chromatography (petroleum ether: EtOAc 20:1) to give the product **3**.

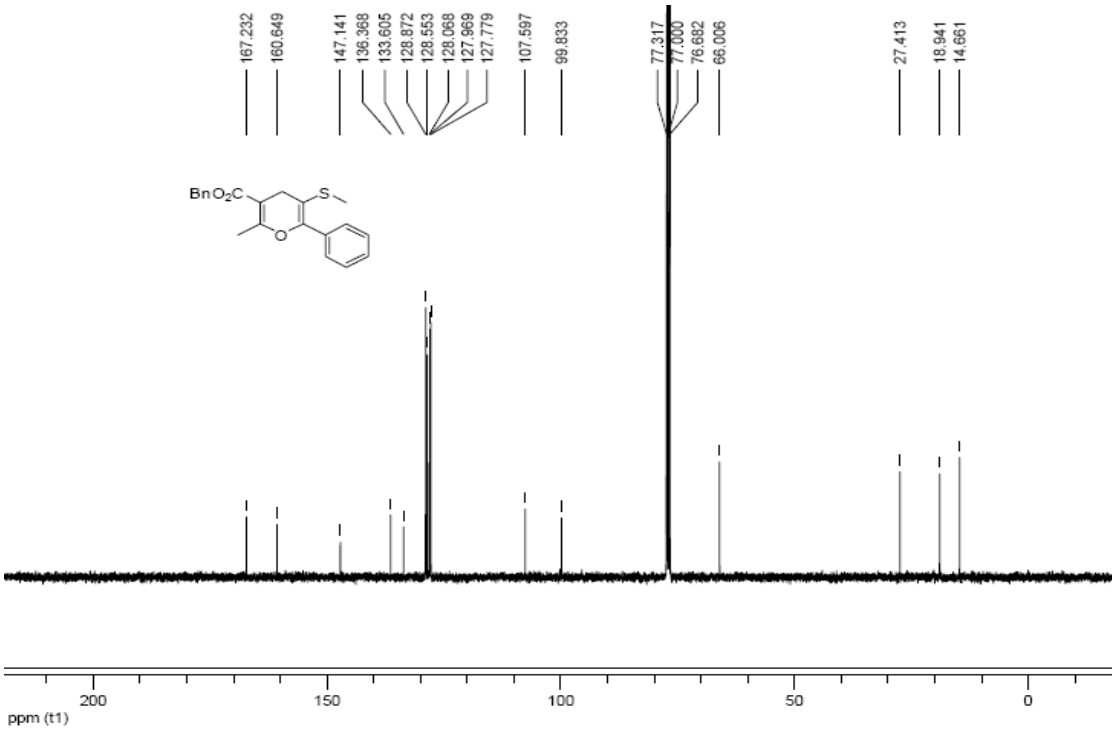
IV. Data for the Compounds 3

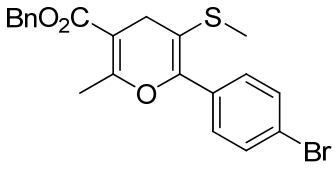


3aa Yield = 96%, 33.9 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 2.18(s, 3H), 2.34(s, 3H), 3.35(s, 2H), 5.25(s, 2H), 7.35-7.43(m, 8H), 7.54-7.57(m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.7, 18.9, 27.4, 66.0, 99.8, 107.6, 127.8, 128.0, 128.1, 128.6, 128.9, 133.6, 136.4, 147.1, 160.6, 167.2. HRMS (EI) Calcd for $C_{21}H_{20}O_3S$ 352.1133, found 352.1128.

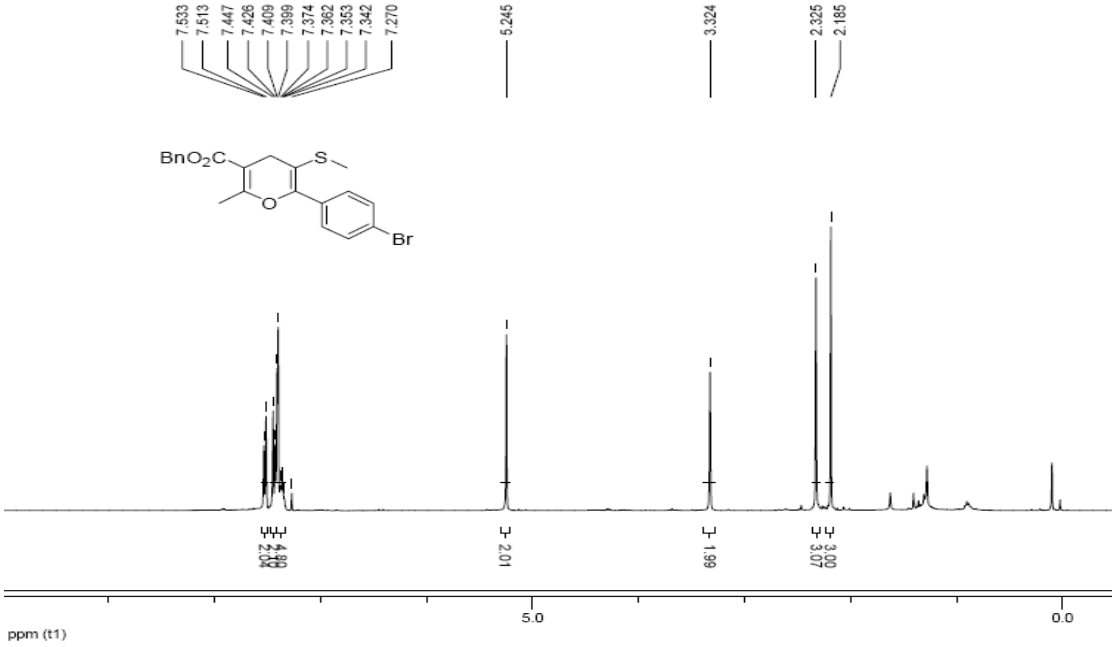


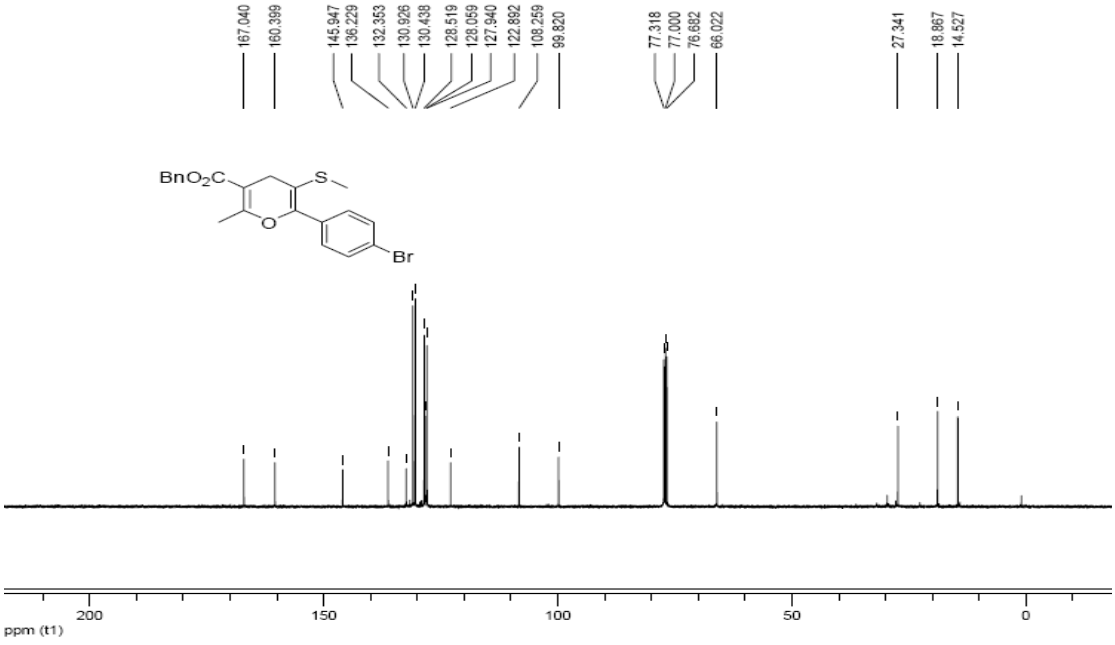


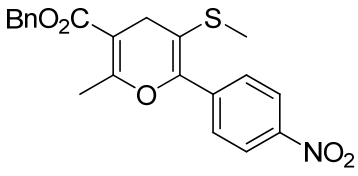


3ab Yield = 86%, 37.0 mg, slight yellow solid, M.p: 85-91°C (recrystallization from petroleum ether and ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19(s, 3H), 2.33(s, 3H), 3.32(s, 2H), 5.25(s, 2H), 7.34-7.41(m, 5H), 7.44(d, *J* = 8.4 Hz, 2H), 7.52(d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 18.9, 27.3, 66.0, 99.8, 108.3, 122.9, 127.9, 128.1, 128.5, 130.4, 130.9, 132.4, 136.2, 145.9, 160.4, 167.0. HRMS (EI, Br^{79}) Calcd for $C_{21}H_{19}BrO_3S$ 430.0238, found 430.0241.

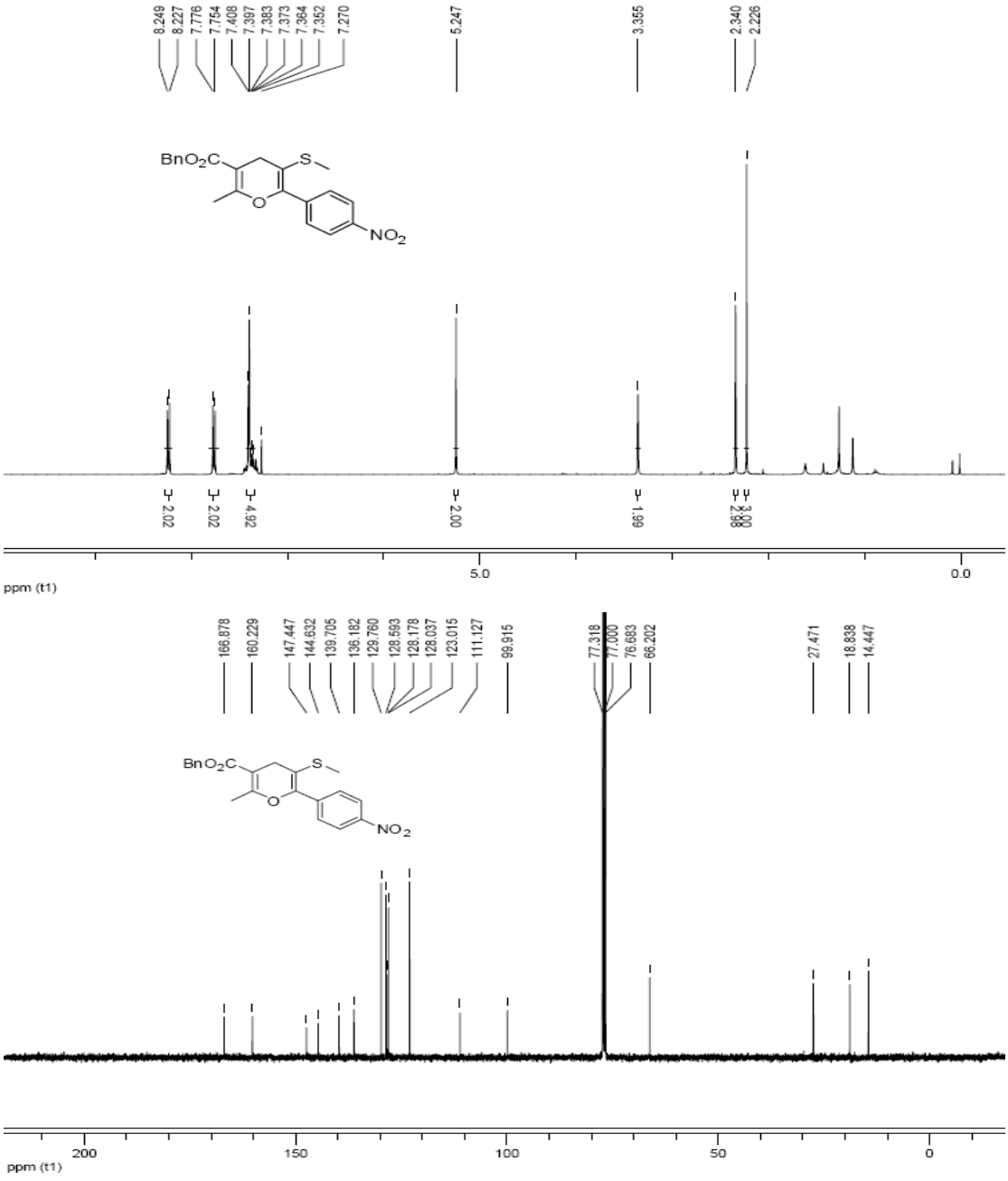


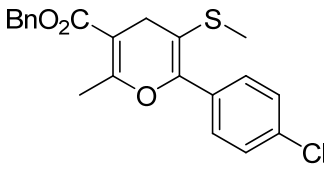




3ac Yield = 75%, 29.8 mg, yellow solid, M.p: 57-61°C (recrystallization from petroleum ether and ethyl acetate).

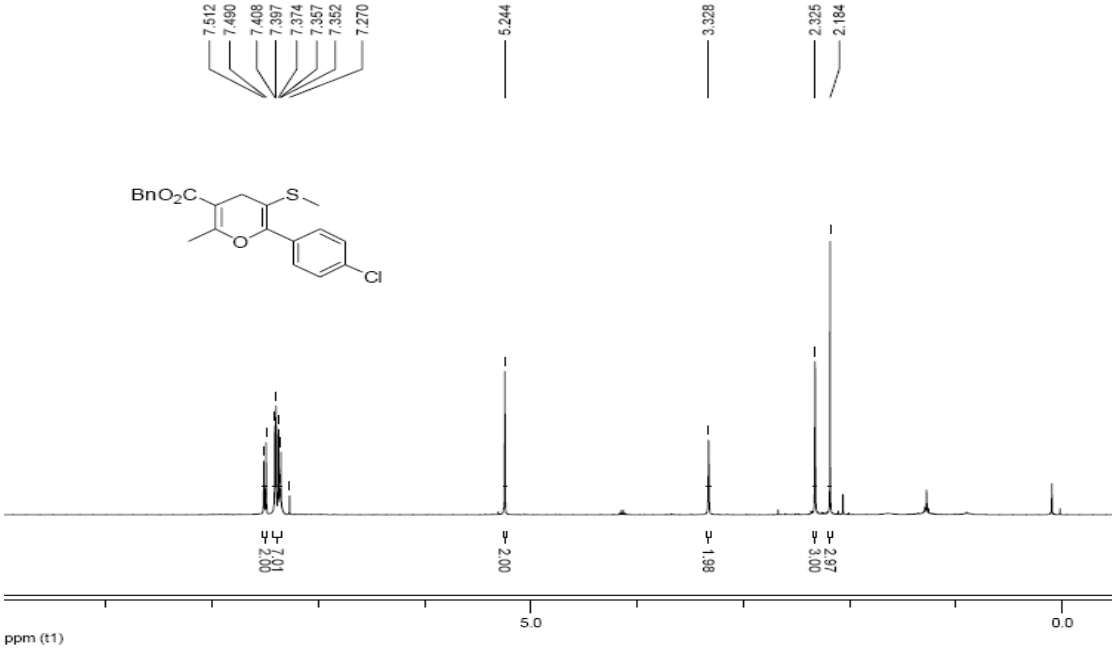
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23(s, 3H), 2.34(s, 3H), 3.36(s, 2H), 5.25(s, 2H), 7.35-7.41(m, 5H), 7.77(d, *J* =8.8 Hz, 2H), 8.24(d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 18.8, 27.5, 66.2, 99.9, 111.1, 123.0, 128.0, 128.2, 128.6, 129.8, 136.2, 139.7, 144.6, 147.4, 160.2, 166.9. HRMS (EI) Calcd for $C_{21}H_{19}NO_5S$ 397.0984, found 397.0986.

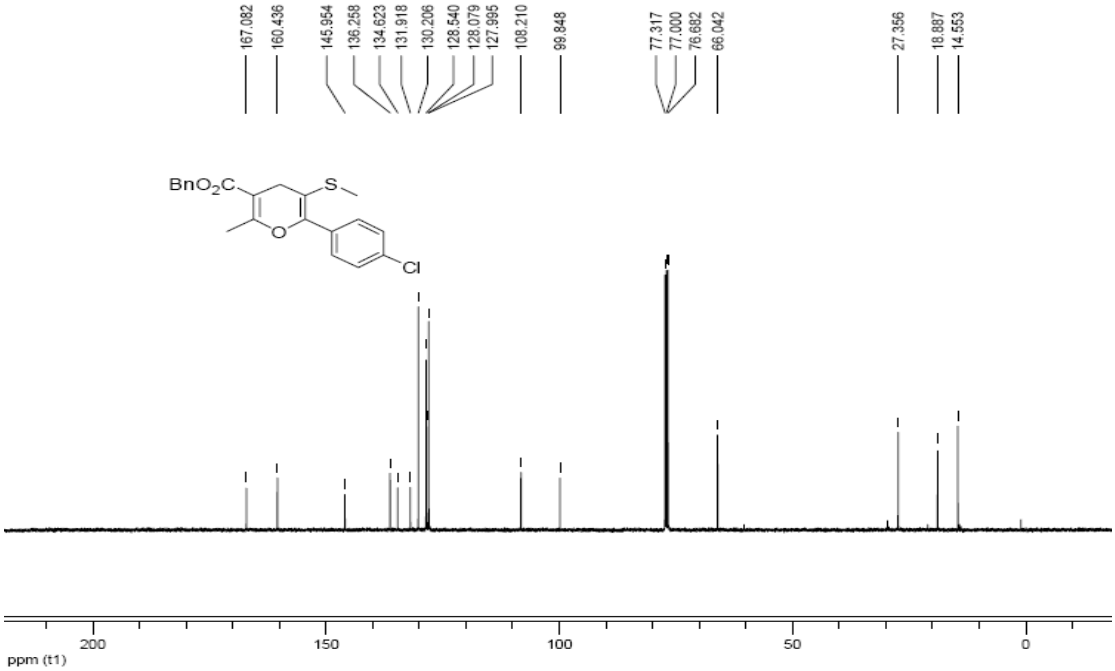


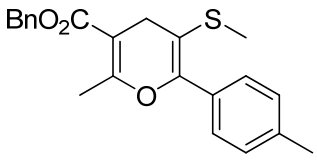


3ad Yield = 84%, 32.5 mg, yellow solid, M.p: 77-82 ^{o}C (recrystallization from petroleum ether and ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18(s, 3H), 2.33(s, 3H), 3.33(s, 2H), 5.24(s, 2H), 7.35-7.41(m, 7H), 7.50(d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 18.9, 27.4, 66.0, 99.8, 108.2, 128.0, 128.1, 128.5, 130.2, 131.9, 134.6, 136.3, 146.0, 160.4, 167.1. HRMS (EI) Calcd for $C_{21}H_{19}ClO_3S$ 386.0743, found 386.0746.

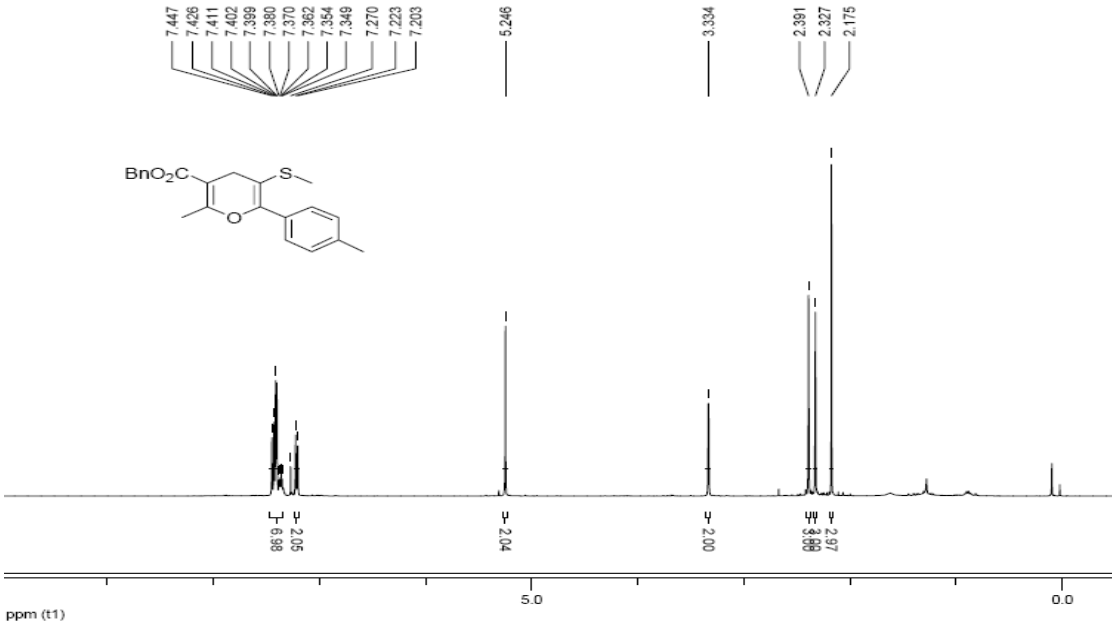


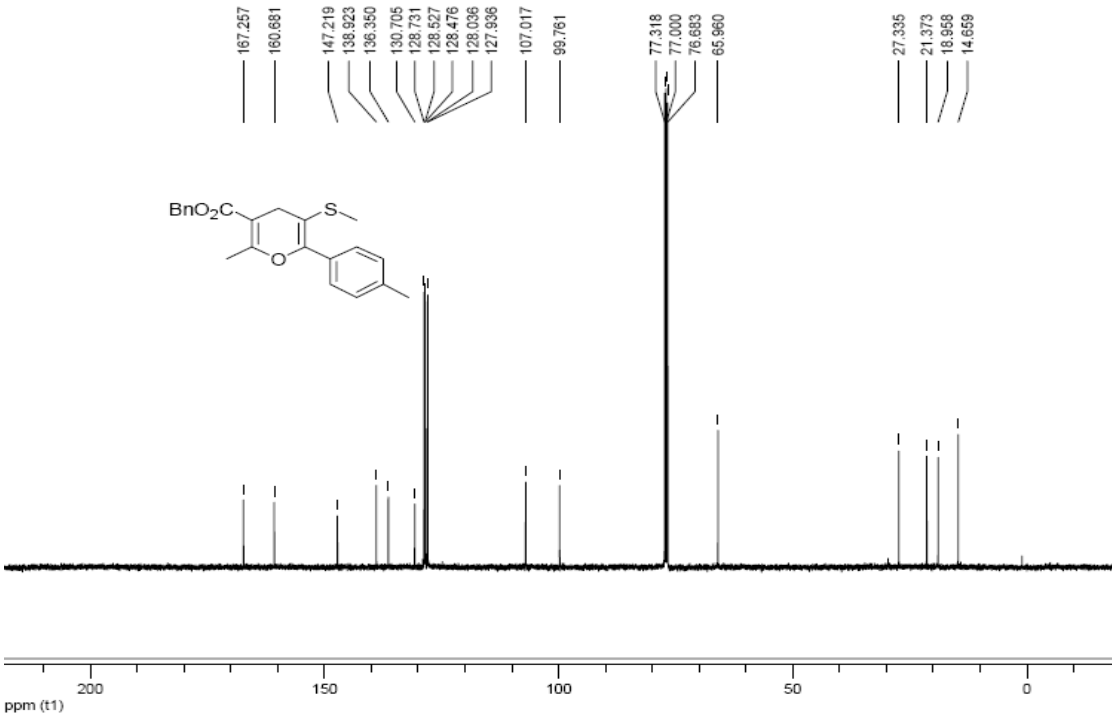


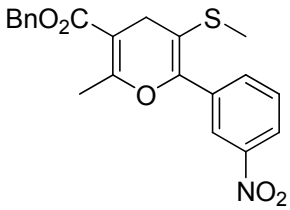


3ae Yield = 84%, 30.6 mg, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18(s, 3H), 2.33(s, 3H), 2.39(s, 3H), 3.33(s, 2H), 5.25(s, 2H), 7.21(d, J = 8.0 Hz, 2H), 7.34-7.45(m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 19.0, 21.4, 27.3, 66.0, 99.8, 107.0, 127.9, 128.0, 128.5, 128.5, 128.7, 130.7, 136.4, 138.9, 147.2, 160.7, 167.3. HRMS (EI) Calcd for $C_{22}H_{22}O_3S$ 366.1290, found 366.1292.

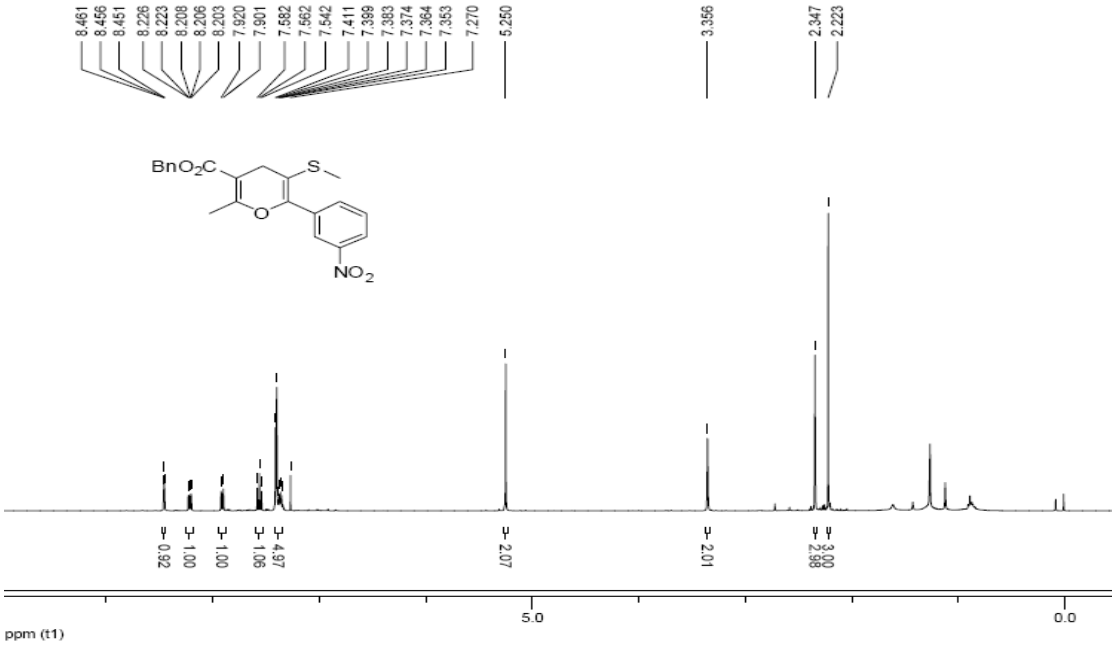


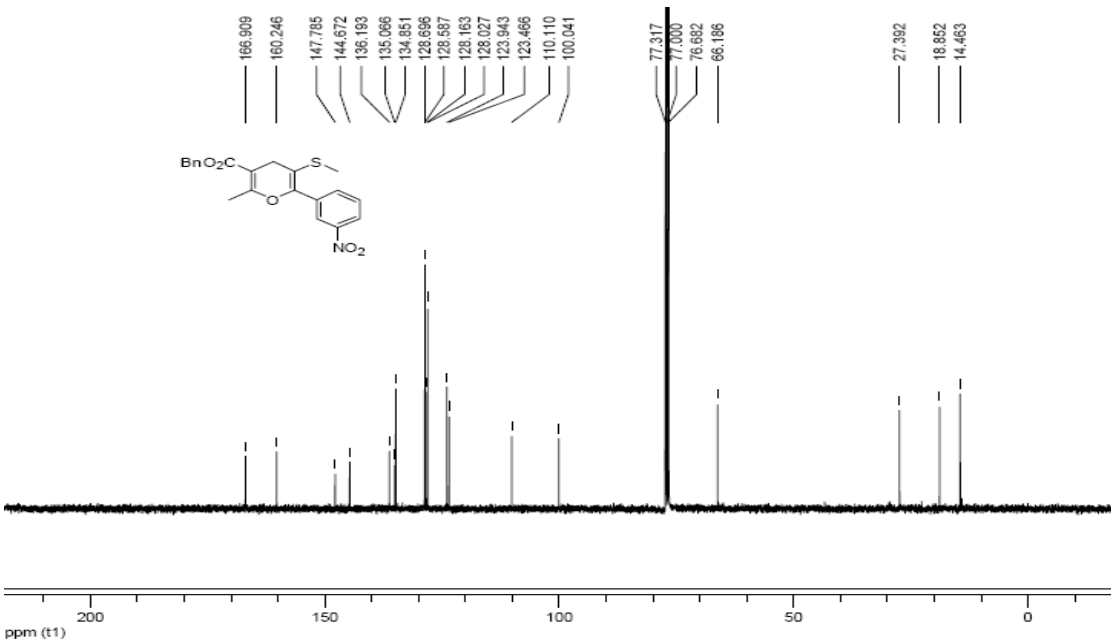


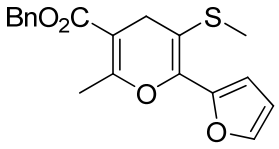


3af Yield = 83%, 33.0 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 2.22(s, 3H), 2.35(s, 3H), 3.36(s, 2H), 5.25(s, 2H), 7.35-7.42(m, 5H), 7.56(t, J = 8.0 Hz, 1H), 7.90-7.92(m, 1H), 8.20-8.23(m, 1H), 8.46(t, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 18.9, 27.4, 66.2, 100.0, 110.1, 123.5, 123.9, 128.0, 128.2, 128.6, 128.7, 134.9, 135.1, 136.2, 144.7, 147.8, 160.2, 166.9. HRMS (EI) Calcd for $C_{21}H_{19}NO_5S$ 397.0984, found 397.0987.

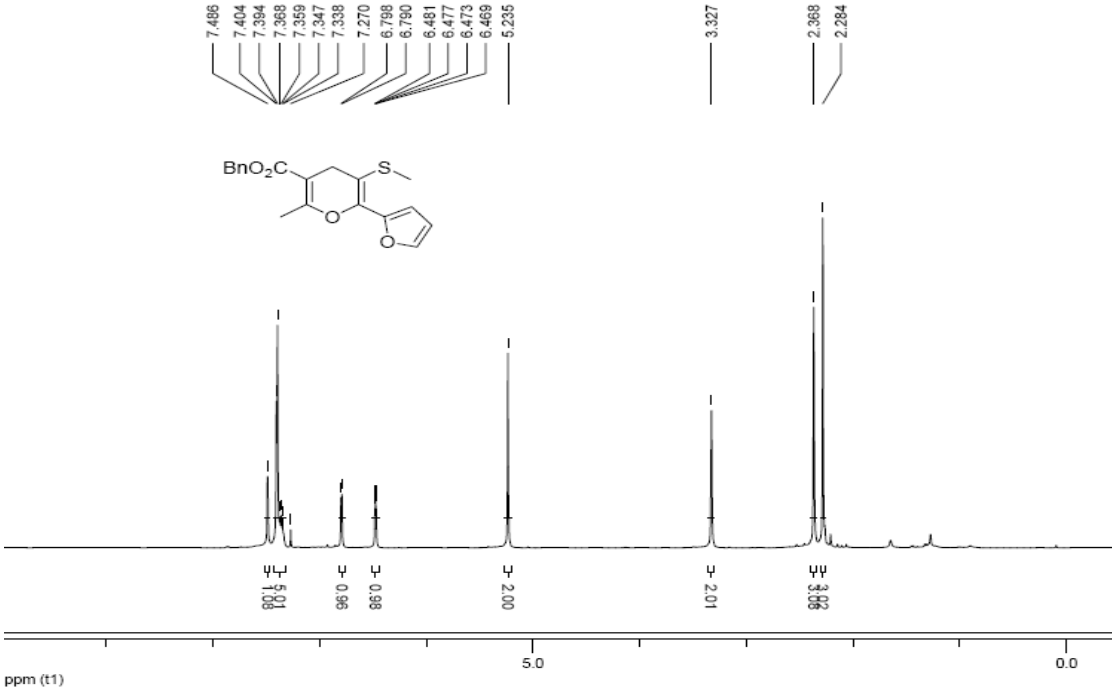


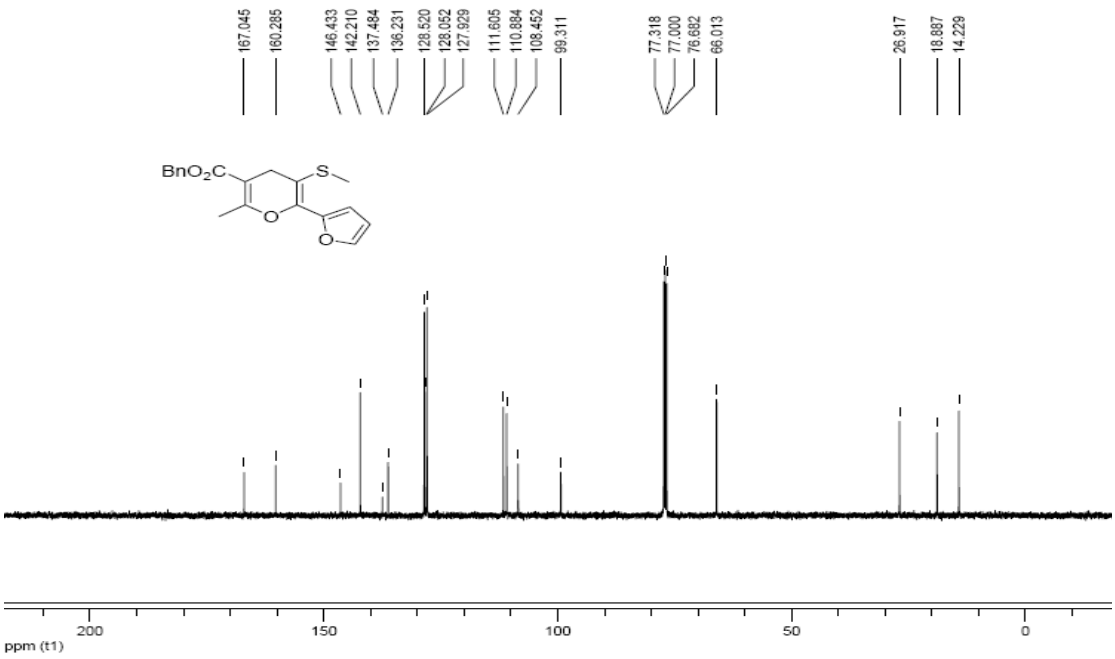


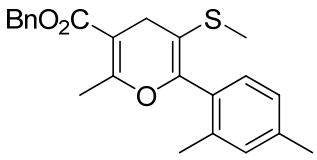


3ag Yield = 88%, 30.2 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 2.28(s, 3H), 2.37(s, 3H), 3.33(s, 2H), 5.24(s, 2H), 6.48(dd, *J* = 1.6 Hz, *J* = 3.2 Hz, 1H), 6.79(d, *J* = 3.2 Hz, 1H), 7.33-7.41(m, 5H), 7.49(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 18.9, 27.0, 66.1, 99.4, 108.5, 110.9, 111.6, 128.0, 128.1, 128.6, 136.3, 137.6, 142.2, 146.5, 160.3, 167.1. HRMS (EI) Calcd for $C_{19}H_{18}O_4S$ 342.0926, found 342.0920.

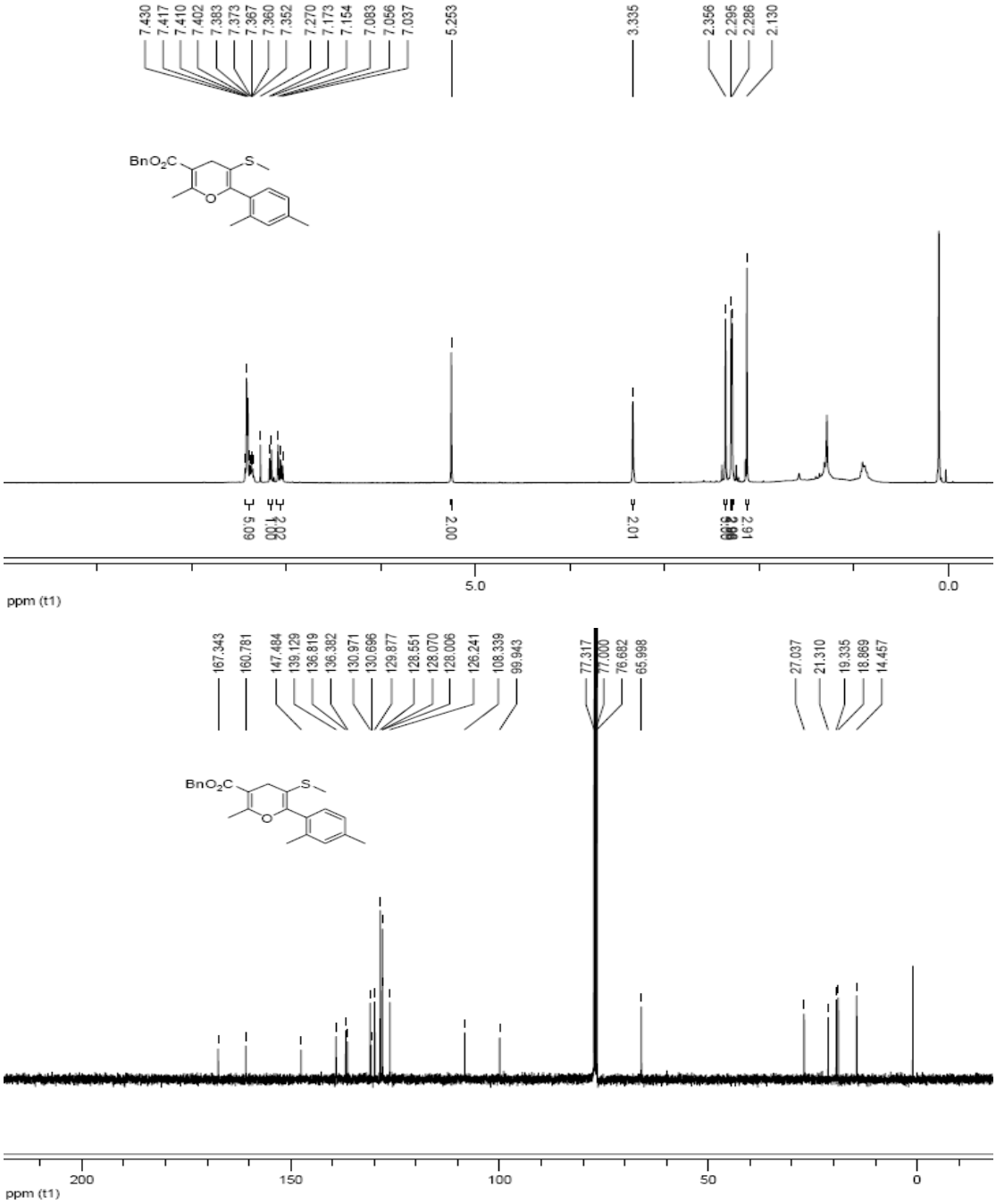


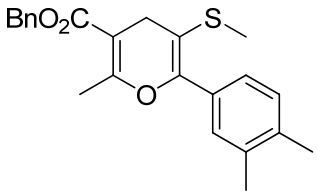




3ah Yield = 80%, 30.4 mg, slight yellow oil.

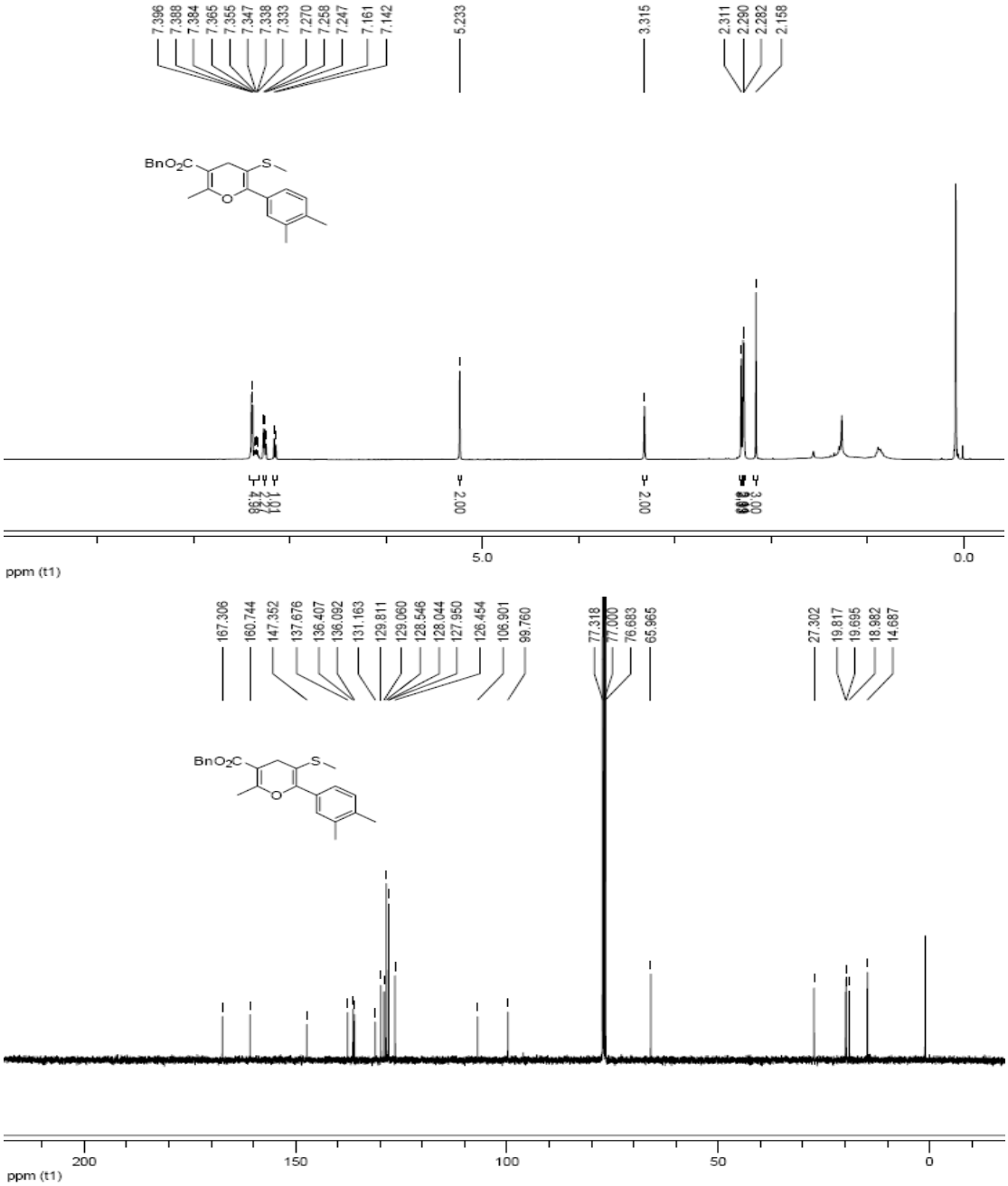
^{1}H NMR(400 MHz, $CDCl_3$): δ 2.13(s, 3H), 2.29(s, 3H), 2.30(s, 3H), 2.36(s, 3H), 3.34(s, 2H), 5.25(s, 2H), 7.03-7.09(m, 2H), 7.15-7.18(m, 1H), 7.35-7.43(m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 18.9, 19.3, 21.3, 27.0, 66.0, 99.9, 108.3, 126.2, 128.0, 128.1, 128.6, 129.9, 130.7, 131.0, 136.4, 136.8, 139.1, 147.5, 160.8, 167.3. HRMS (EI) Calcd for $C_{23}H_{24}O_3S$ 380.1446, found 380.1440.

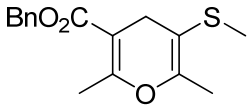




3ai Yield = 91%, 34.4 mg, slight yellow oil.

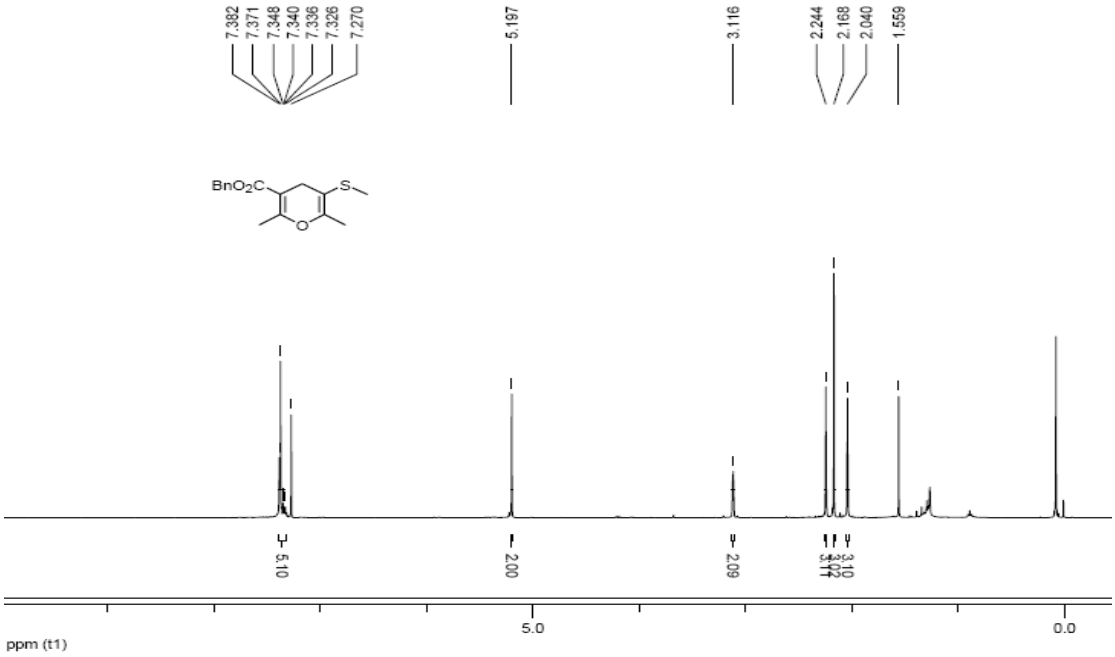
^{1}H NMR(400 MHz, $CDCl_3$): δ 2.16(s, 3H), 2.28(s, 3H), 2.29(s, 3H), 2.31(s, 3H), 3.32(s, 2H), 5.23(s, 2H), 7.14-7.17(m, 1H), 7.24-7.27(m, 2H), 7.33-7.40(m, 5H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.7, 19.0, 19.7, 19.8, 27.3, 66.0, 99.8, 106.9, 126.5, 127.95, 128.04, 128.5, 129.1, 129.8, 131.2, 136.1, 136.4, 137.7, 147.4, 160.7, 167.3. HRMS (EI) Calcd for $C_{23}H_{24}O_3S$ 380.1446, found 380.1448.

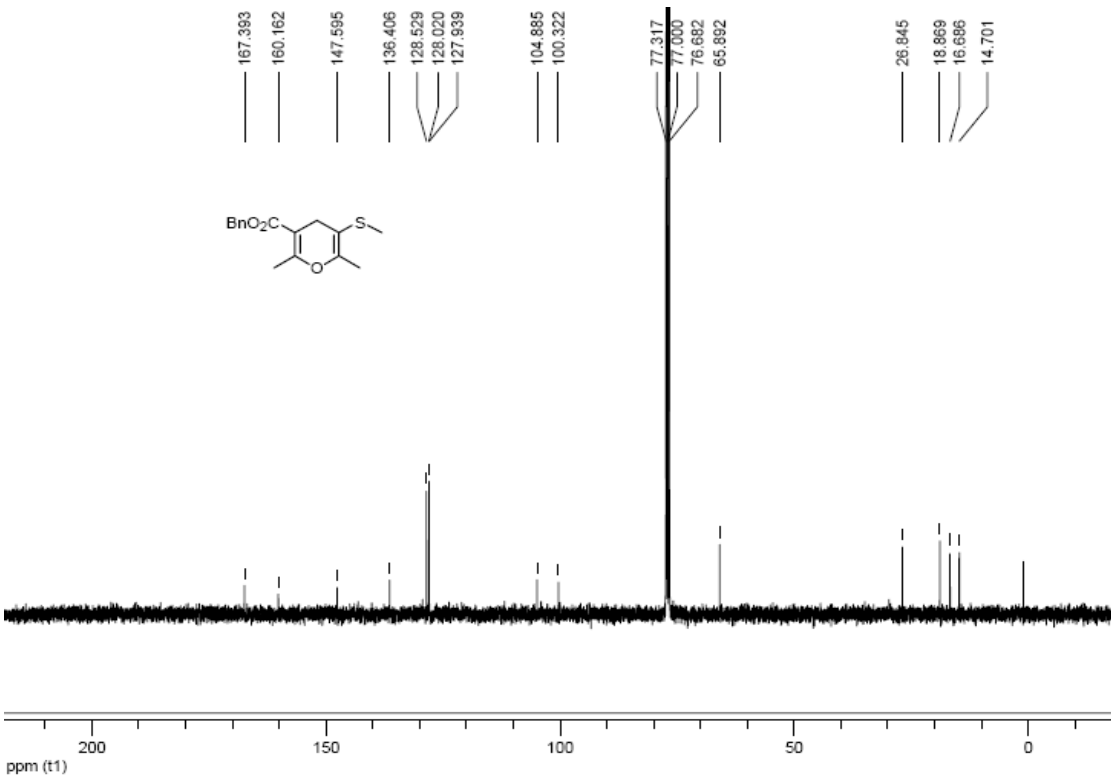


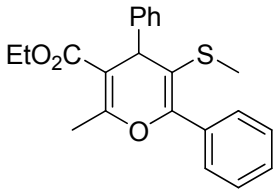


3aj Yield = 17%, 5.0 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 2.04(s, 3H), 2.17(s, 3H), 2.24(s, 3H), 3.12(s, 2H), 5.20(s, 2H), 7.32-7.39(m, 5H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.7, 16.7, 18.9, 26.8, 65.9, 100.3, 104.9, 127.9, 128.0, 128.5, 136.4, 147.6, 160.2, 167.4. HRMS (EI) Calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0969.

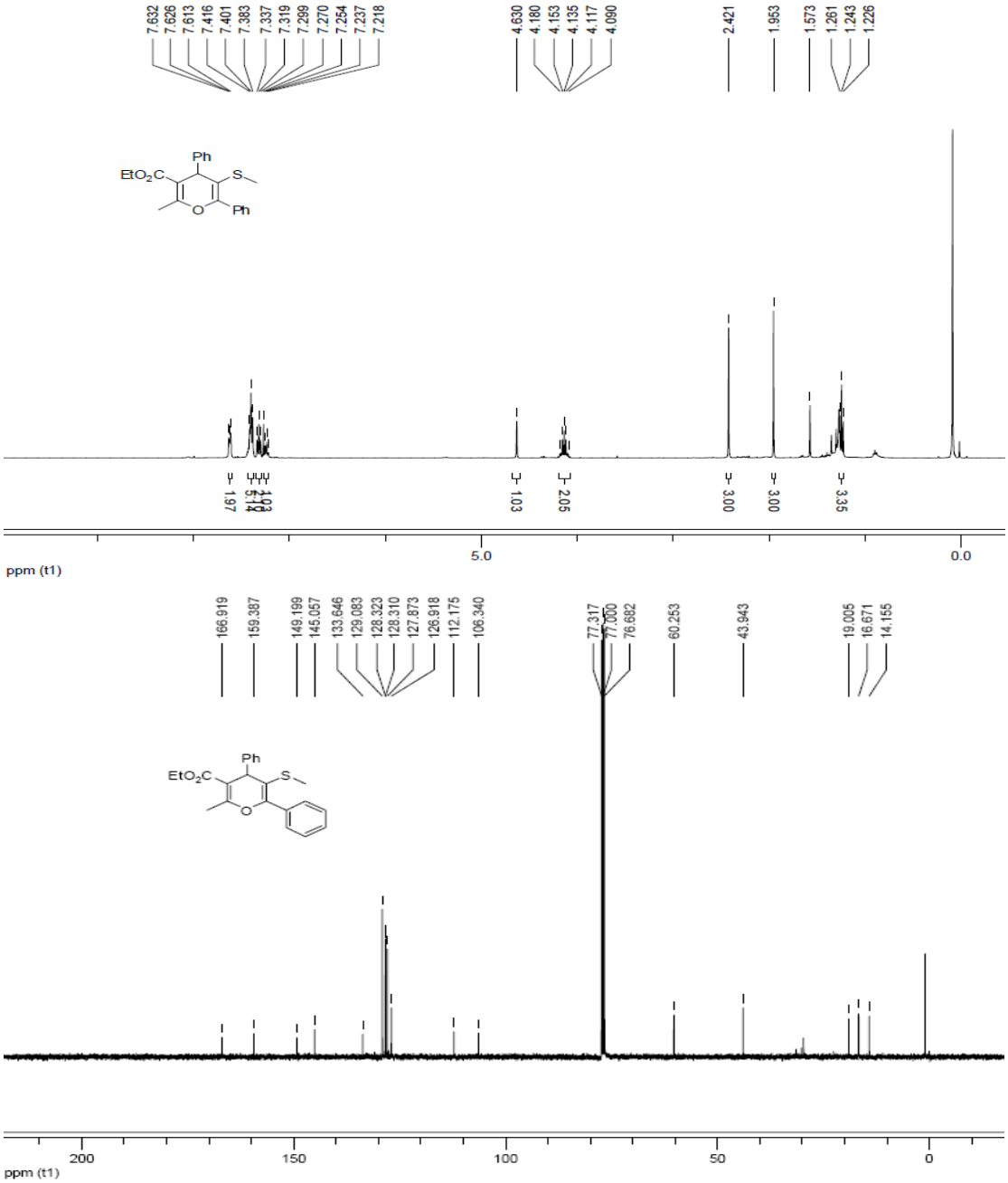


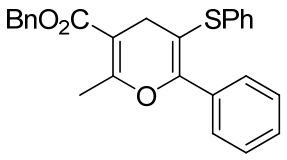




3ba Yield = 29%, 10.7 mg, slight yellow oil.

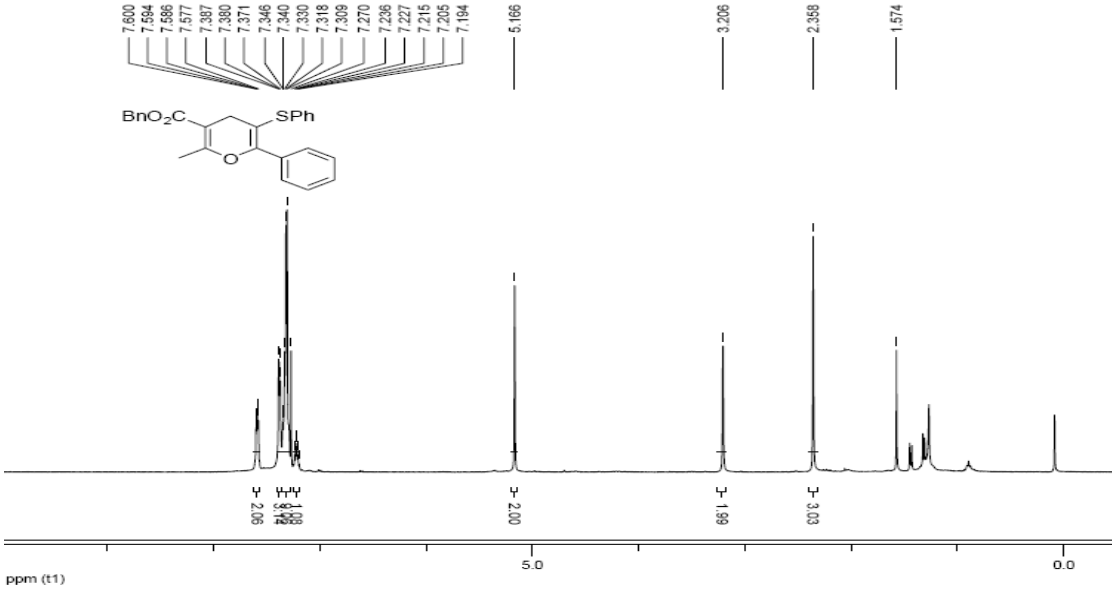
^{1}H NMR(400 MHz, $CDCl_3$): δ 1.24(t, *J* = 7.2 Hz, 3H), 1.95(s, 3H), 2.42(s, 3H), 4.09-4.18(m, 2H), 4.63(s, 1H), 7.21-7.26(m, 1H), 7.29-7.34(m, 2H), 7.38-7.42(m, 5H), 7.61-7.64(m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.2, 16.7, 19.0, 43.9, 60.3, 106.3, 112.2, 126.9, 127.9, 128.3, 128.3, 129.1, 133.6, 145.1, 149.2, 159.4, 166.9. HRMS (EI) Calcd for $C_{22}H_{22}O_3S$ 366.1290, found 366.1288.

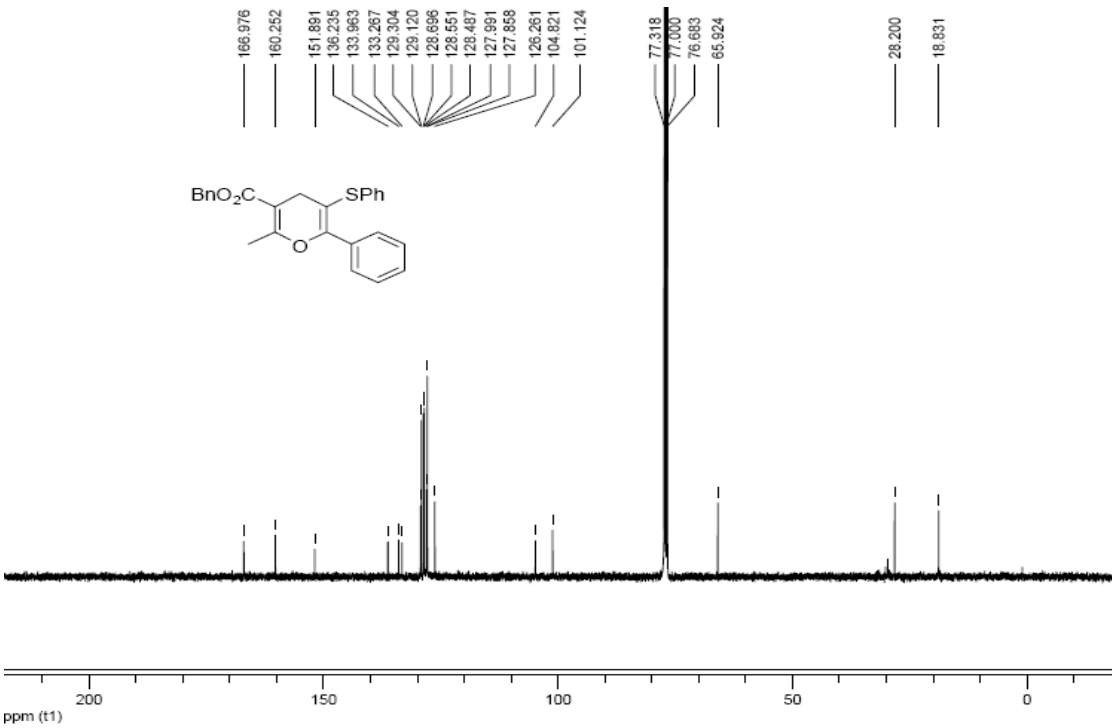


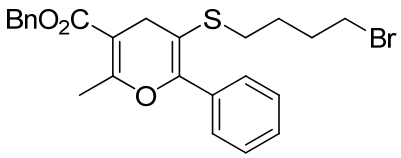


3ak Yield = 42%, 17.4 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 2.36(s, 3H), 3.12(s, 2H), 5.17(s, 2H), 7.19-7.24(m, 1H), 7.30-7.35(m, 9H), 7.37-7.39(m, 3H), 7.57-7.60(m,2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 18.8, 28.2, 65.9, 101.1, 104.8, 126.3, 127.9, 128.0, 128.5, 128.6, 128.7, 129.1, 129.3, 133.3, 134.0, 136.2, 151.9, 160.3, 167.0. HRMS (EI) Calcd for $C_{26}H_{22}O_3S$ 414.1290, found 414.1292.

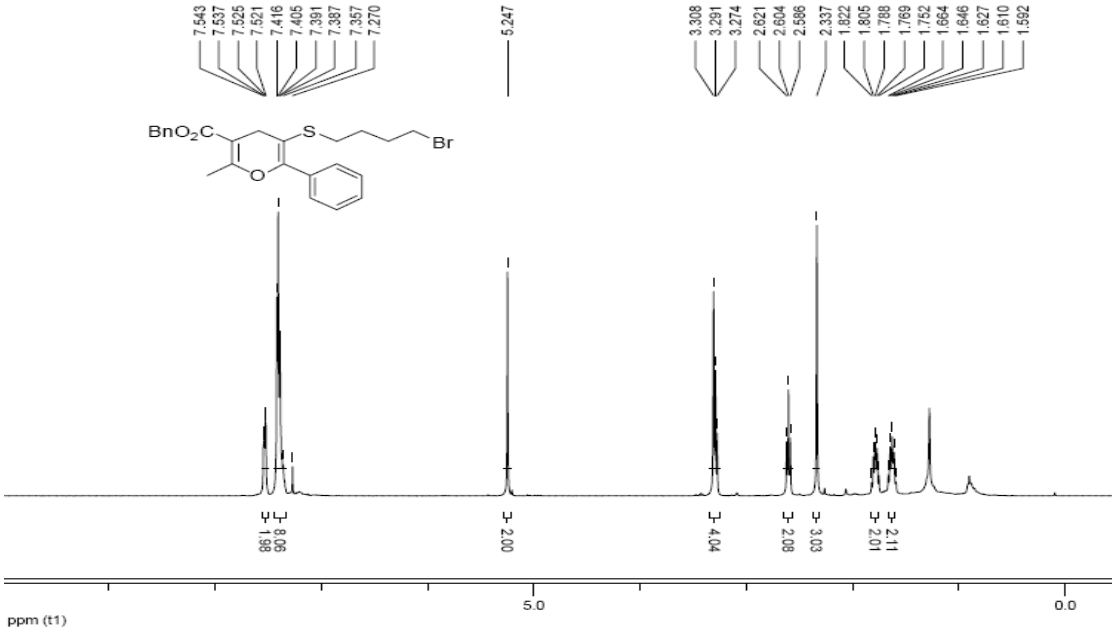


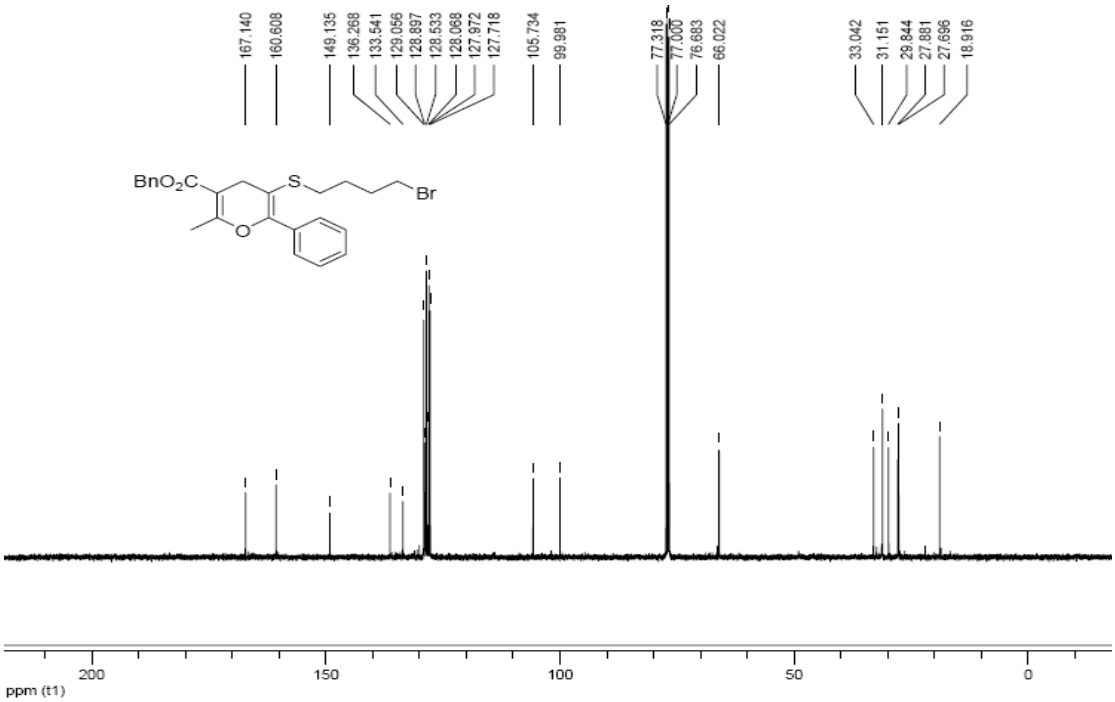


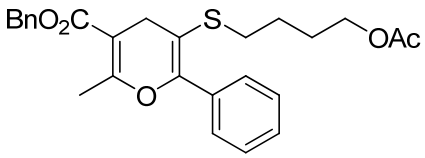


3al-1 Yield =39%, 18.3 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59-1.67(m, 2H), 1.75-1.83(m, 2H),2.34(s, 3H), 2.60(t, *J* = 7.2 Hz, 2H), 3.27-3.31(m, 4H), 5.25(s, 2H), 7.35-7.42(m, 8H), 7.52-7.55(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 27.7, 27.9, 29.8, 31.2, 33.0, 66.0, 100.0, 105.7, 127.7, 128.0, 128.1, 128.5, 128.9, 129.1, 133.5, 136.3, 149.1, 160.6, 167.1. HRMS (EI, Br^{79}) Calcd for $C_{24}H_{25}BrO_3S$ 472.0708, found 472.0712.

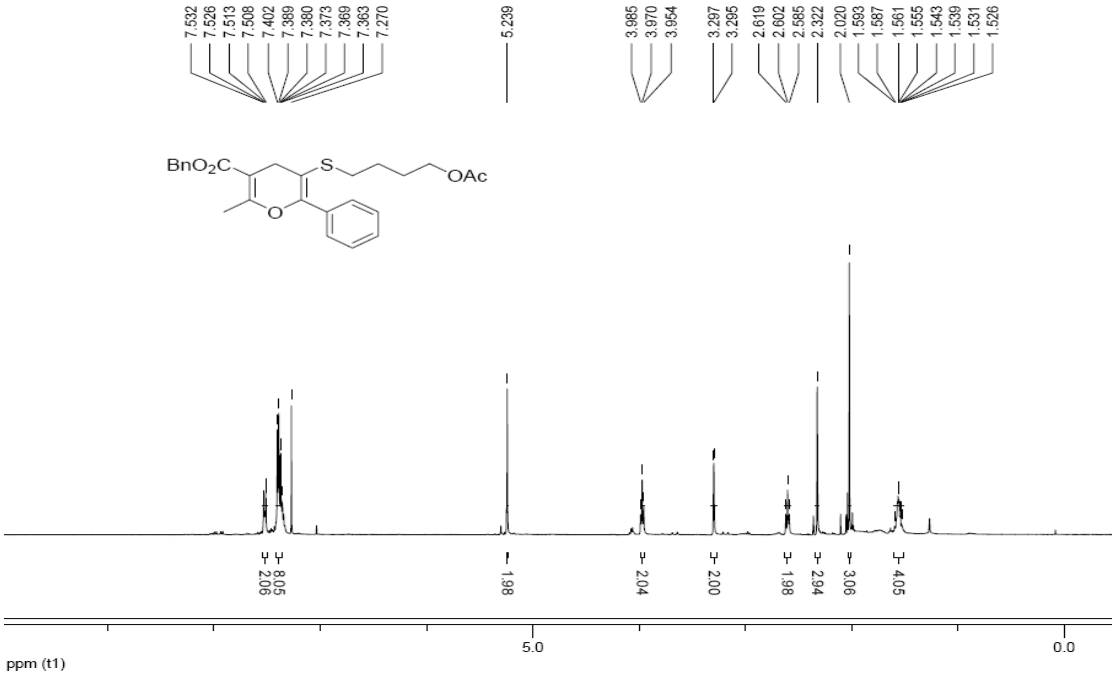


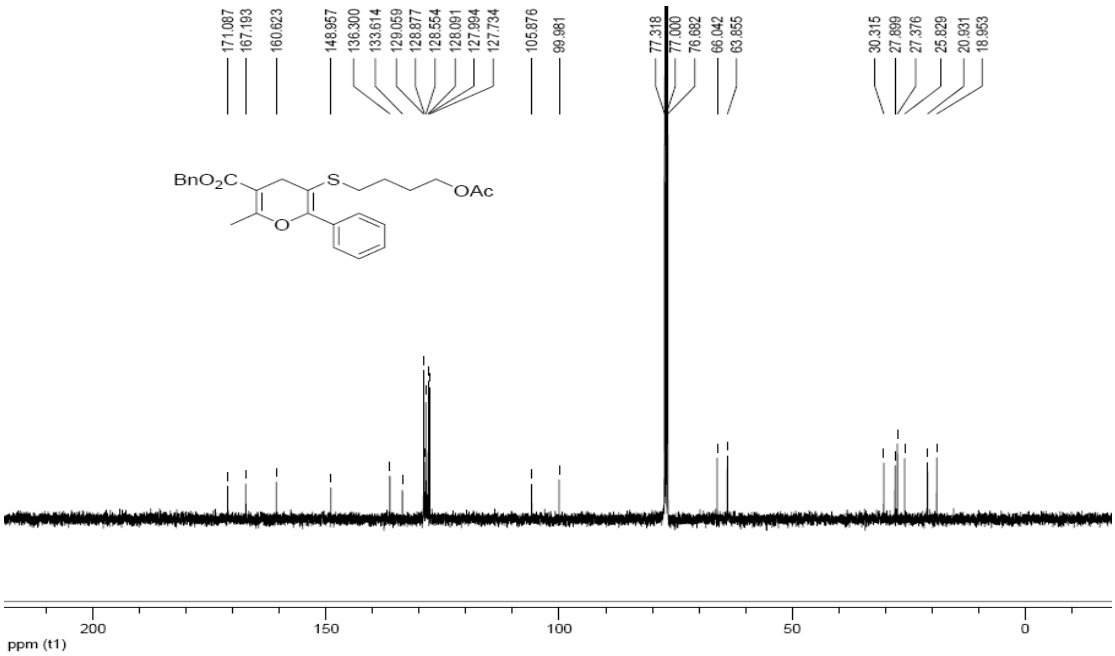


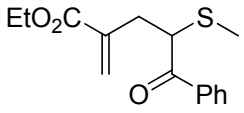


3al-2 Yield =22%, 9.8 mg, slight yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52-1.60(m, 4H), 2.02(s, 3H), 2.32(s, 3H), 2.60(t, J = 6.8 Hz, 2H), 3.30(s, 2H), 3.97(t, J = 6.4 Hz, 2H), 5.24(s, 2H), 7.36-7.41(m, 8H), 7.50-7.54(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 20.9, 25.8, 27.4, 27.9, 30.3, 63.9, 66.0, 100.0, 105.9, 127.7, 128.0, 128.1, 128.6, 128.9, 129.1, 133.6, 136.3, 149.0, 160.6, 167.2, 171.1. HRMS (EI) Calcd for $C_{26}H_{28}O_5S$ 452.1657, found 452.1661.

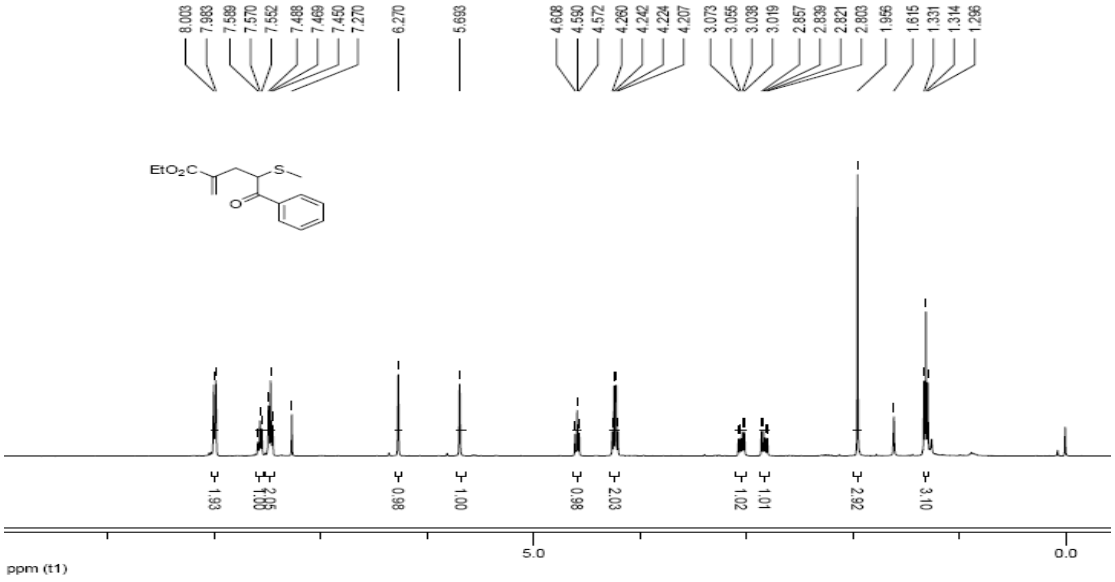


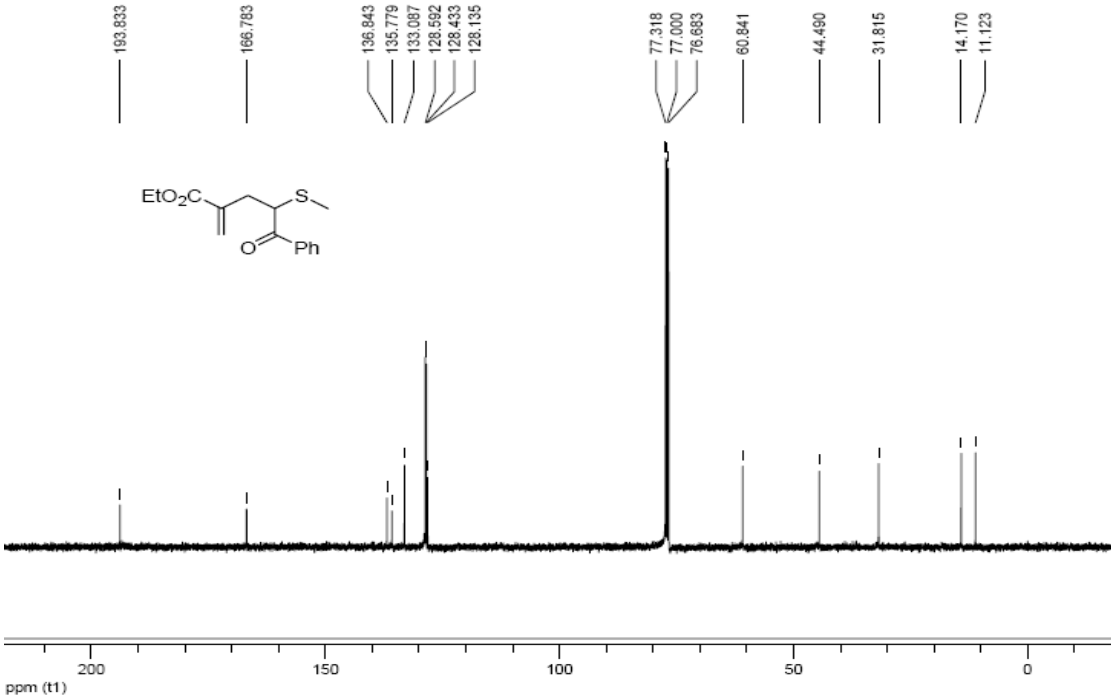




3ca Yield = 20%, 5.6 mg, slight yellow oil.

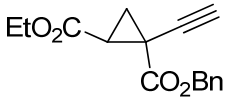
^{1}H NMR(400 MHz, $CDCl_3$): δ 1.31(t, *J* = 6.8 Hz, 3H), 1.96(s, 3H), 2.83(dd, *J* = 7.2 Hz, *J* = 14.4 Hz, 1H), 3.05(dd, *J* = 7.2 Hz, *J* = 14.0 Hz, 1H), 4.23(q, *J* = 7.2 Hz, 2H), 4.59(t, *J* = 7.2 Hz, 1H), 5.69(s, 1H), 6.27(s, 1H), 7.45-7.49(m, 2H), 7.55-7.59(m, 1H), 7.98-8.01(m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 11.1, 14.2, 31.8, 44.5, 60.8, 128.1, 128.4, 128.6, 133.1, 135.8, 136.8, 166.8, 193.8. HRMS (EI) Calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0975.





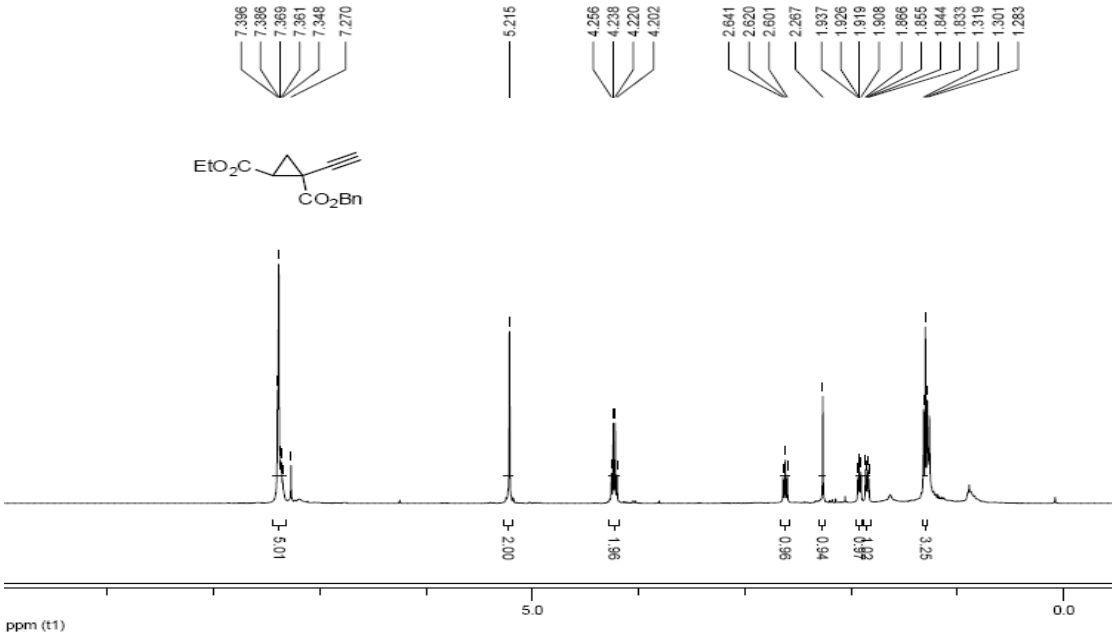
V. The Procedure for synthesis 4 and 6:

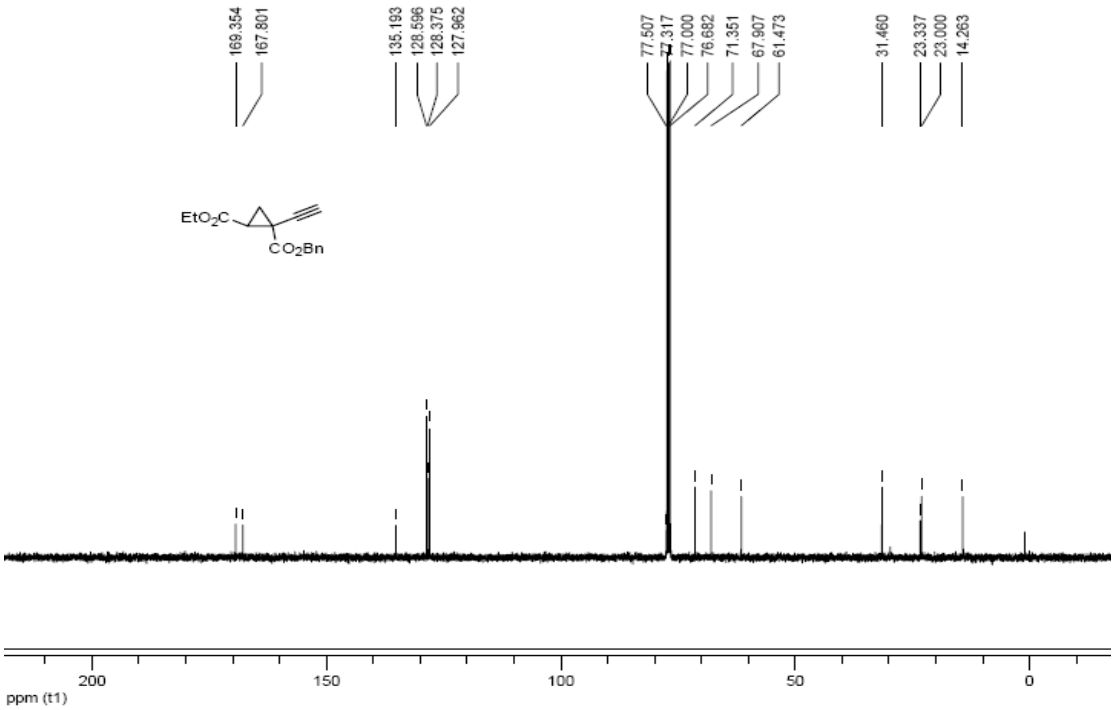
In a 25 mL Schlenk tube, the mixture of **2m** or **2a** (0.12 mmol, 1.2 equiv.) and K_2CO_3 (16.6 mg, 0.12 mmol, 1.2 equiv.) was introduced with acetone (1.3 mL). The mixture was stirred at room temperature. To this reaction mixture the solution of **5** (0.10 mmol) in acetone (1.3 mL) was slowly added over 20 minutes. The reaction mixture was monitored by TLC. When the reaction was finished, the mixture was directly subjected to silica gel column chromatography (petroleum ether: EtOAc 20:1) to give the product **4** or **6**.

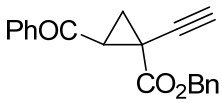


4 Yield = 53%, 14.3 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 1.30(t, *J* = 7.2 Hz, 3H), 1.85(dd, *J* = 4.4 Hz, *J* = 8.8 Hz, 1H), 1.92(dd, *J* = 4.4 Hz, *J* = 7.2 Hz, 1H), 2.27(s, 1H), 2.62(t, *J* = 8.4 Hz, 1H), 4.23(q, *J* = 7.2 Hz, 2H), 5.22(s, 2H), 7.34-7.40(m, 5H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 14.3, 23.0, 23.3, 31.5, 61.5, 67.9, 71.4, 77.5, 128.0, 128.4, 128.6, 135.2, 167.8, 169.4. HRMS (EI) Calcd for $C_{16}H_{16}O_4$ 272.1049, found 272.1057.

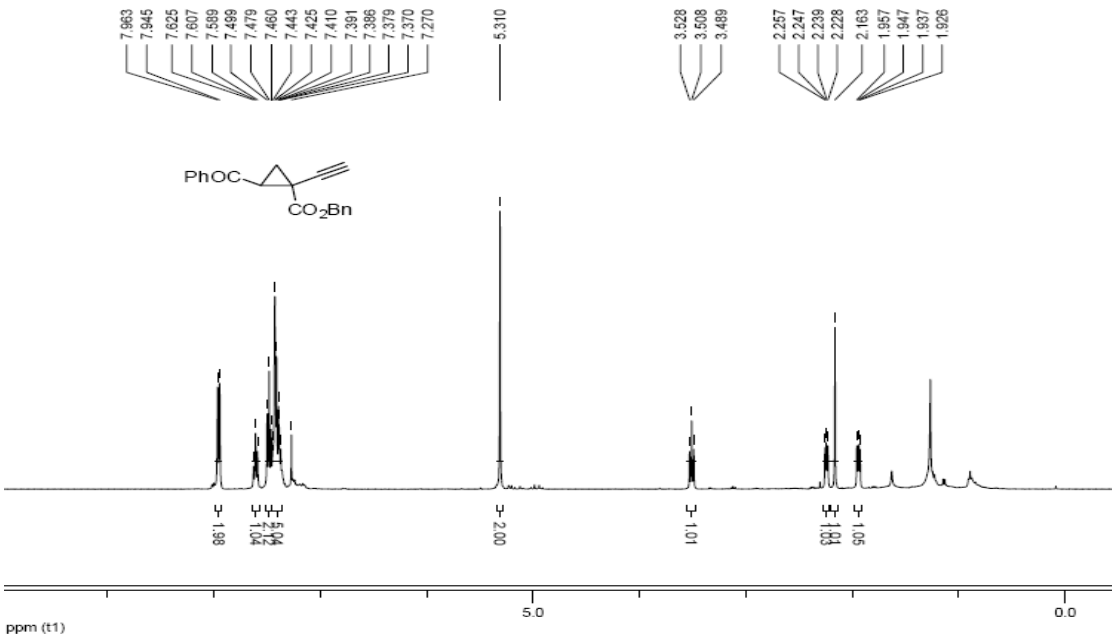


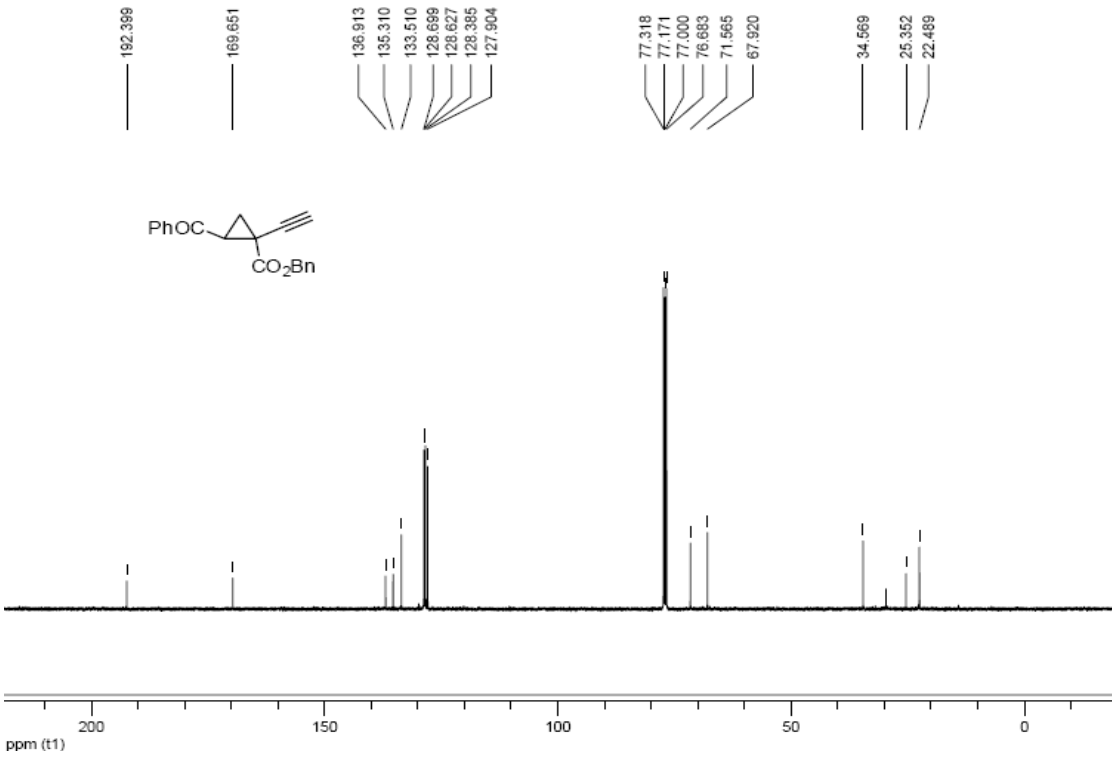




6 Yield = 68%, 20.7 mg, slight yellow oil.

^{1}H NMR(400 MHz, $CDCl_3$): δ 1.94(dd, J = 4.0 Hz, J = 8.0Hz, 1H), 2.16(s, 1H), 2.24(dd, J = 4.0 Hz, J = 7.2 Hz, 1H), 3.51(t, J = 8.0 Hz, 1H), 5.31(s, 2H), 7.37-7.45(m, 5H), 7.46-7.50(m, 2H), 7.58-7.63(m, 1H), 7.94-7.97(m, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 22.5, 25.4, 34.6, 67.9, 71.6, 77.2, 127.9, 128.4, 128.6, 128.7, 133.5, 135.3, 136.9, 169.7, 192.4. HRMS (EI) Calcd for $C_{20}H_{16}O_3$ 304.1099, found 304.1098.

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ppm (t1)