Lewis Base-catalyzed Reactions of Cyclopropenones: Novel Synthesis of Mono- or Multi-substituted Allenic Esters

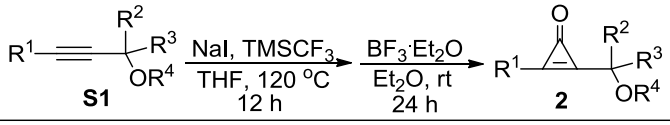
Yuan-Liang Yang, Zhen Zhang, Xiao-Nan Zhang, Dei Wang, Yin Wei,* Min Shi*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.
weiyin@mail.sioc.ac.cn; mshi@mail.sioc.ac.cn. Fax: 86-21-64166128.

CONTENTS

General Remarks: ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, IC-H columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

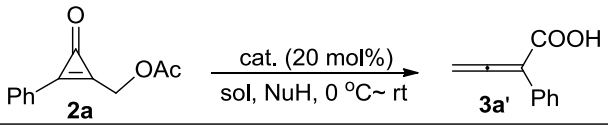
Table S. Preparation of various substrates **2**.



Entry	$R^1/R^2/R^3/R^4$	yield (two steps%)[a]
1	C_6H_5/H/H/Ac (**S1a**)	50 (**2a**)
2	4-$MeOC_6H_4$/H/H/Ac (**S1b**)	47 (**2b**)
3	4-$NO_2C_6H_4$/H/H/Ac (**S1c**)	52 (**2c**)
4	4-$^tBuC_6H_4$/H/H/Ac (**S1d**)	10 (**2d**)
5	4-ClC_6H_4/H/H/Ac (**S1e**)	55 (**2e**)
6	4-BrC_6H_4/H/H/Ac (**S1f**)	57 (**2f**)
7	3-FC_6H_4/H/H/Ac (**S1g**)	55 (**2g**)
8	3-BrC_6H_4/H/H/Ac (**S1h**)	52 (**2h**)
9	3-MeC_6H_4/H/H/Ac (**S1i**)	54 (**2i**)
10	2-CNC_6H_4/H/H/Ac (**S1j**)	45 (**2j**)
11	2-$CO_2MeC_6H_4$/H/H/Ac (**S1k**)	60 (**2k**)
12	2-$MeOC_6H_4$/H/H/Ac (**S1l**)	36 (**2l**)
13	1-naphthyl/H/H/Ac (**S1m**)	55 (**2m**)
14	$CH_2C_6H_5$/H/H/Ac (**S1n**)	15 (**2n**)
15	2-thienyl/H/H/Ac (**S1o**)	45 (**2o**)
16	C_6H_5/C_6H_5/H/Ac (**S1p**)	59 (**2p**)
17	C_6H_5/4-ClC_6H_4/H/Ac (**S1q**)	56 (**2q**)
18	C_6H_5/2-naphthyl/H/Ac (**S1r**)	52 (**2r**)
19	C_6H_5/1-naphthyl/H/Ac (**S1s**)	40 (**2s**)
20	C_6H_5/9-phenanthryl/H/Ac (**S1t**)	46 (**2t**)
21	C_6H_5/3-MeC_6H_4/H/Ac (**S1u**)	46 (**2u**)
22	C_6H_5/2-BrC_6H_4/H/Ac (**S1v**)	51 (**2v**)
23	C_6H_5/2,4-$Cl_2C_6H_3$/H/Ac (**S1w**)	58 (**2w**)
24	4-ClC_6H_4/Me/H/Ac (**S1x**)	53 (**2x**)
25	$C_6H_5/(CH_2)_5$/Ac (**S1y**)	80 (**2y**)
26	C_6H_5/CH_3/4-ClC_6H_4/Ac (**S1z**)	45 (**2z**)
27	4-BrC_6H_4/2-naphthyl/H/Ac (**S1aa**)	38 (**2aa**)
28	4-MeC_6H_4/2-naphthyl/H/Ac (**S1bb**)	39 (**2bb**)
29	3-MeC_6H_4/2-naphthyl/H/Ac (**S1cc**)	30 (**2cc**)
30	C_6H_5/H/H/Ms (**S1dd**)	60 (**2dd**)

[a]Isolated yield.

Table S1. Optimization of the reaction conditions.

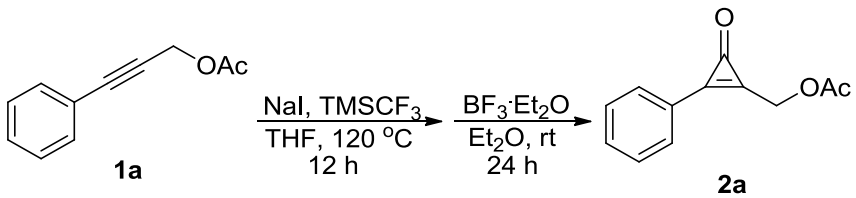


entry	catalyst	solvent	NuH (equiv)	yield[a]
1	DABCO	toluene	H_2O (1.0)	N.R
2	DABCO	MeCN	H_2O (1.0)	N.R
3	DABCO	DCM	H_2O (1.0)	N.R
4	DABCO	DMF	H_2O (1.0)	N.D
5	DABCO	Et_2O	H_2O (1.0)	N.R
6	DABCO	THF	H_2O (2.0)	38 (**3a'**)
7	DABCO	THF	H_2O (5.0)	38 (**3a'**)
8	DABCO	THF	H_2O (10.0)	31 (**3a'**)
9	-	THF	H_2O (1.0)	N.R
10	DABCO	THF	H_2O (0.5)	trace

[a]Isolated yield. Unless otherwise specified, to a mixture of **2a** (0.10 mmol) and catalyst (0.02 mmol) in solvent (1.0 mL) under Ar atmosphere at 0 °C was added NuH, then the resulting reaction mixtures were stirred at room temperature for 3 days.

We found that these solvents were not suitable for the reaction and the corresponding product **3a'** could not be obtained (Table S1, entries 1-5). The employed amount of H_2O ranging from 0.50 to 10.0 equiv with respect to **2a** was also investigated and we found that the yield decreased along with the employed amount of H_2O increasing (Table S1, entries 6-8). When the employed amount of H_2O was reduced to 0.50 equiv, only trace amount of product was obtained (Table S1, entry 10). The control experiment indicated that the reaction did not take place in the absence of DABCO (Table S1, entry 9).

General Procedure for the Preparation of Substrates 2 using 2a as an Example.

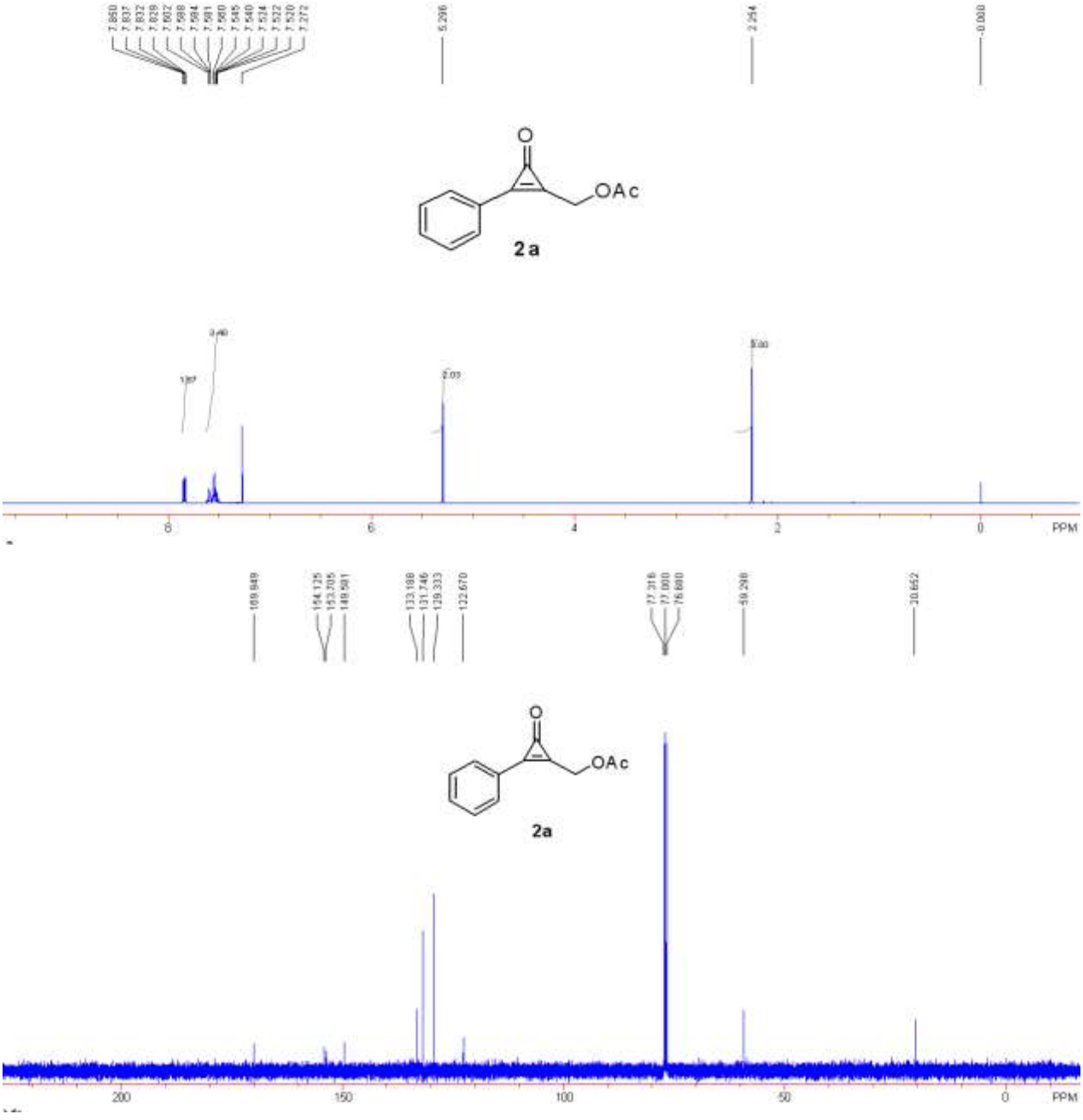


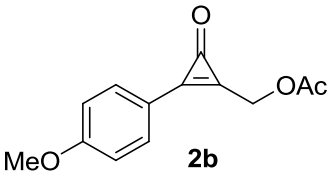
Following the previous literature,[1][2] **1a** (10.0 mmol), NaI (22.0 mmol), $TMSCF_3$ (20 mmol) and 20.0 mL THF were added to a pressure tube under Ar atmosphere, and the resulting mixture was conducted at 120 °C for 12 hours. On cooling to room temperature, the reaction solution was filtered by a celite and the filtrate was concentrated under reduced pressure for next step without further purification. Above intermediate was dissolved in 20.0 mL Et_2O and 1.5 mL $BF_3{\cdot}Et_2O$ was added in

one portion, the resulting mixture was stirred at room temperature and monitored by TLC. After the intermediate was consumed, the reaction was quenched by addition of saturated $NaHCO_3$ solution, extracted with Et_2O, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/2~2/1 as eluent) to furnish product **2a** as a yellow solid (1.02 g, 50% yield).

(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2a:

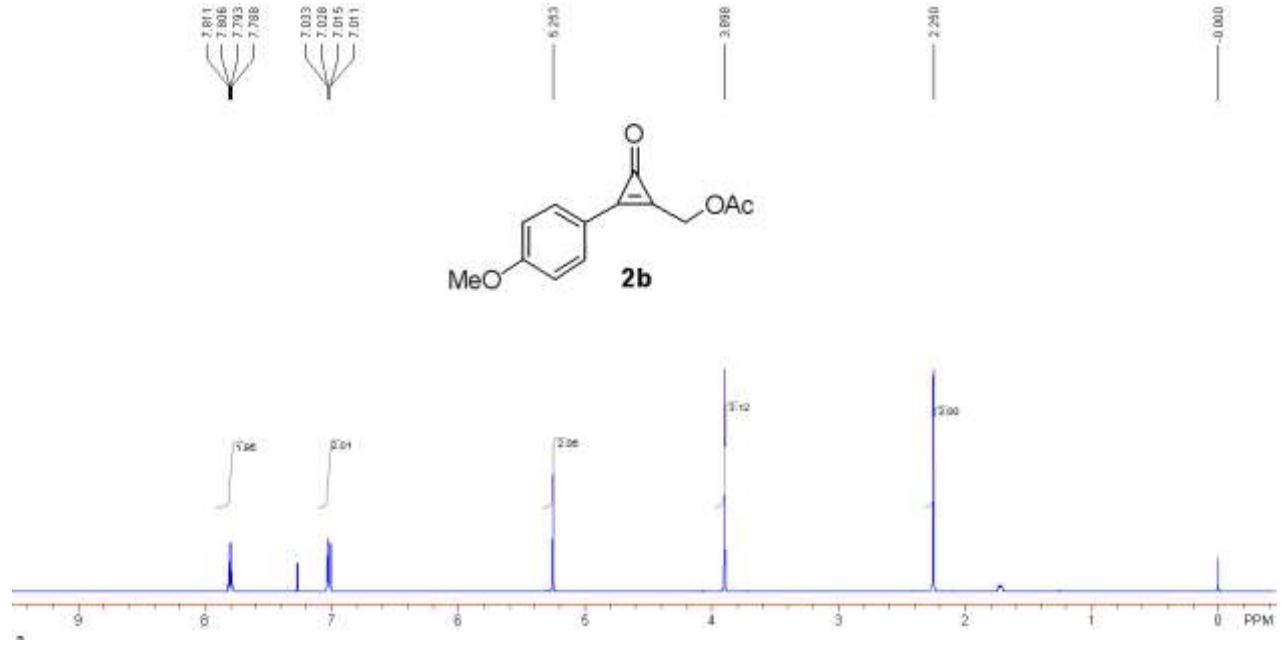
This is a known compound.[2] A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.85-7.83 (2H, m), 7.60-7.52 (3H, m), 5.30 (2H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 154.1, 153.7, 149.6, 133.2, 131.7, 129.3, 122.7, 59.3, 20.7.

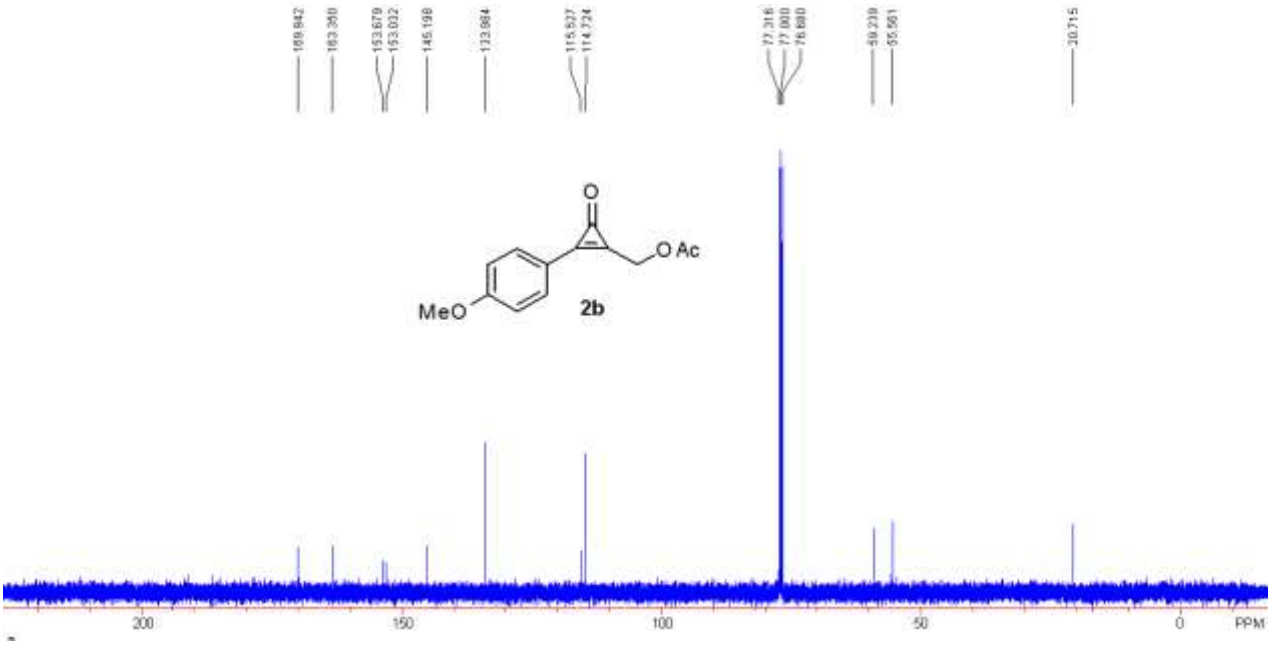


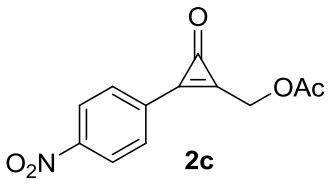


2b

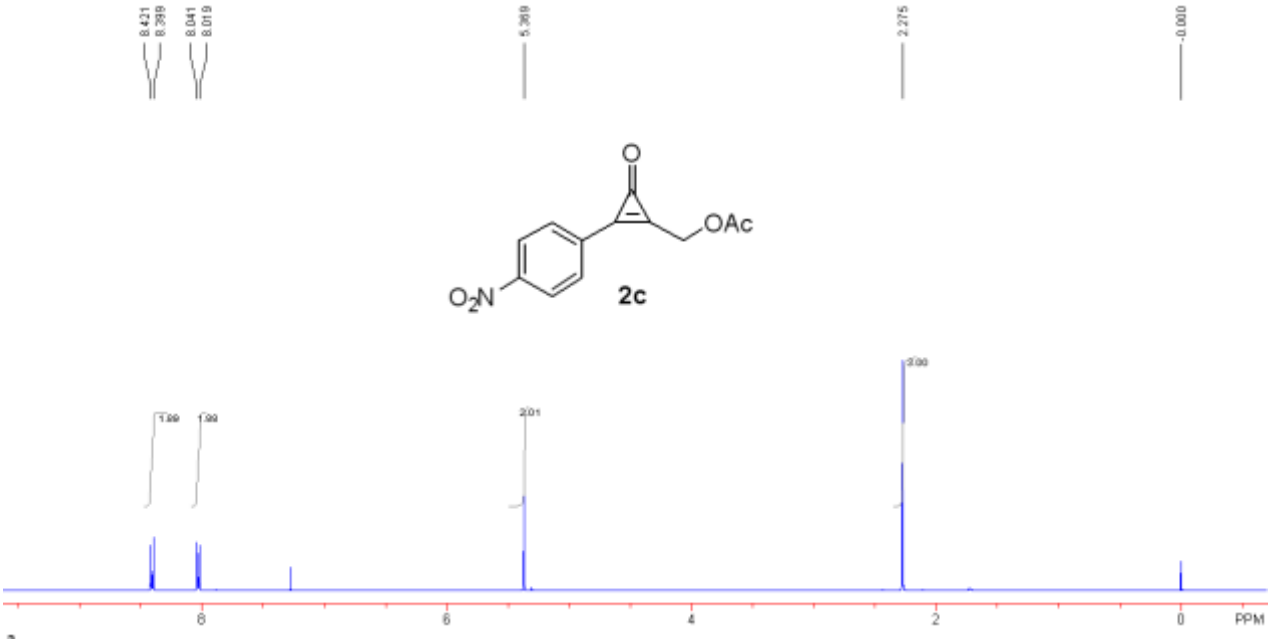
(2-(4-methoxyphenyl)-3-oxocycloprop-1-enyl)methyl acetate 2b: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2b** (47% yield). A yellow solid. m.p. for **2b** = 115-116 ^{o}C; IR (CH_2Cl_2): ν 3051, 2922, 2842, 1856, 1743, 1630, 1600, 1571, 1507, 1467, 1370, 1307, 1257, 1218, 1171, 1113, 1024, 910, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80 (2H, dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz), 7.02 (2H, dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz), 5.25 (2H, s), 3.90 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 163.3, 153.7, 153.0, 145.2, 134.0, 115.5, 114.7, 59.2, 55.6, 20.7; MS (ESI) m/e 233.1 (M^++H); HRMS (ESI) for $C_{13}H_{12}O_4$ (M^+): 232.0736, Found: 232.0747.

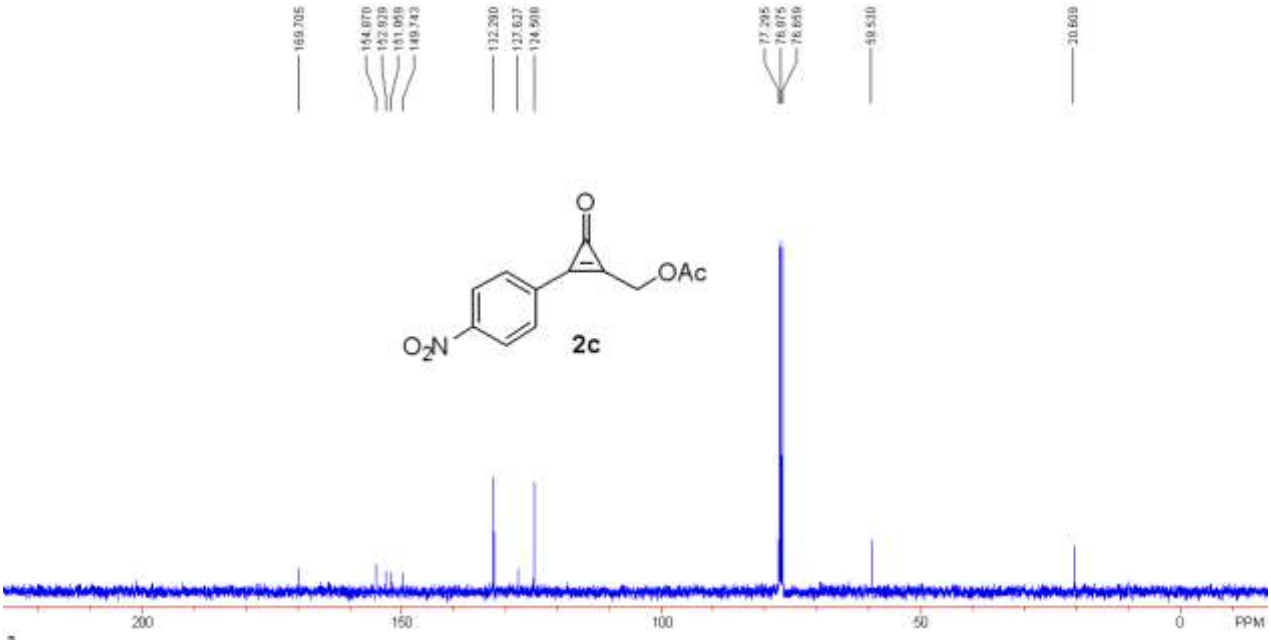


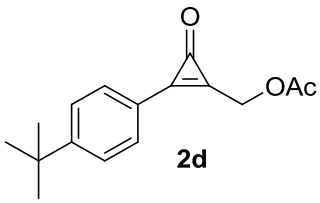




(2-(4-nitrophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2c: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2c** (52% yield). A yellow solid. m.p. for **2c** = 139-140 ^{o}C; IR (CH_2Cl_2): ν 3104, 2924, 2853, 1861, 1746, 1647, 1600, 1519, 1432, 1380, 1343, 1316, 1281, 1219, 1090, 1043, 990, 867, 855 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.41 (2H, d, *J* = 8.8 Hz), 8.03 (2H, d, *J* = 8.8 Hz), 5.37 (2H, s), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 154.9, 152.9, 152.0, 149.7, 132.3, 127.6, 124.5, 59.5, 20.6; MS (ESI) m/e 248.1 (M^++H); HRMS (ESI) for $C_{12}H_9NO_5$ (M^+): 247.0481, Found: 247.0486.

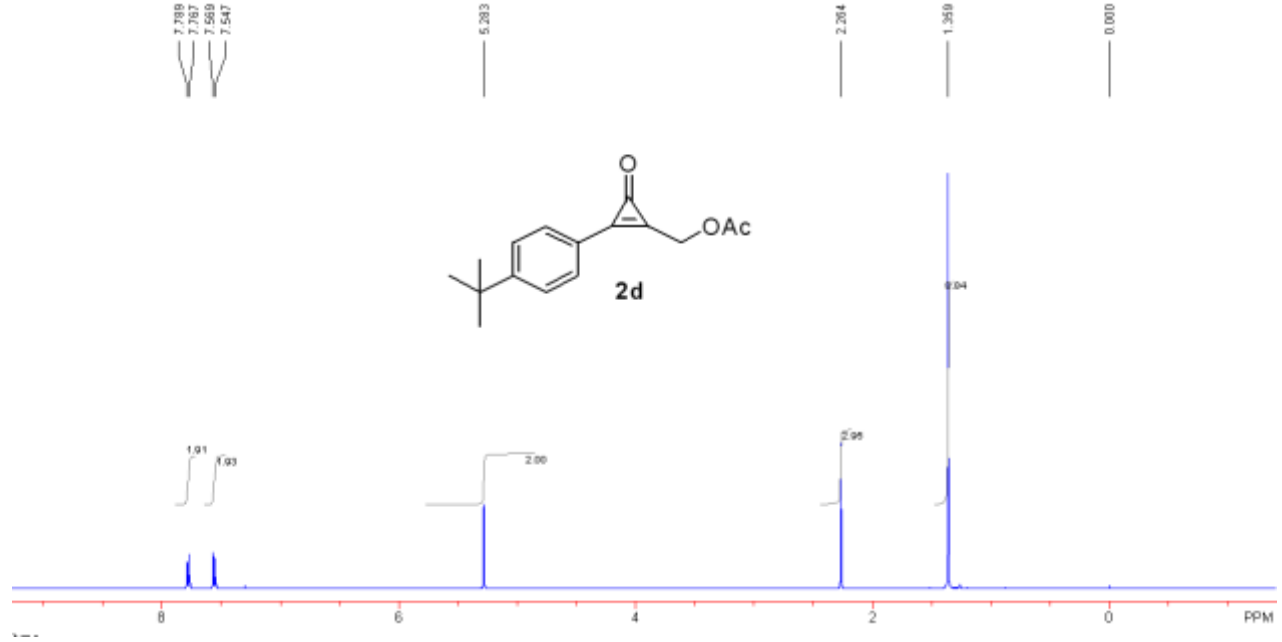


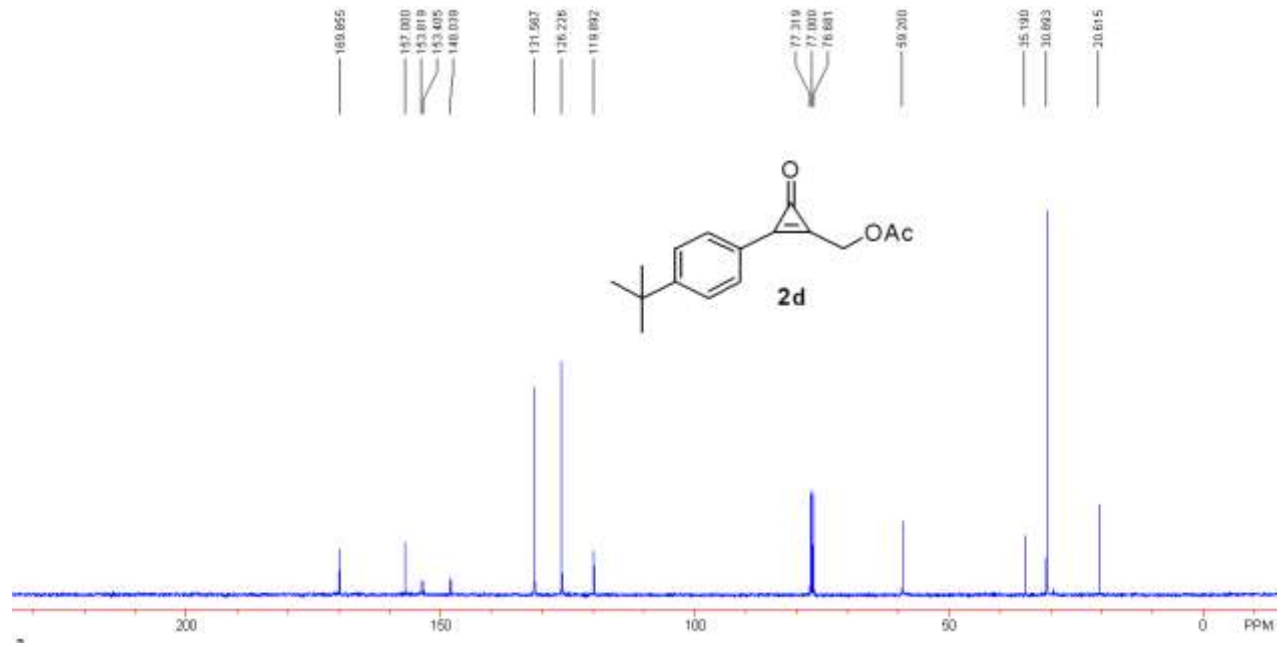


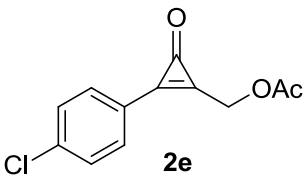


(2-(4-tert-butylphenyl)-3-oxocycloprop-1-enyl)methyl acetate 2d: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2d** (10% yield). A yellow solid. m.p. for **2d** = 116-117 ^{o}C; IR (CH_2Cl_2): ν 2961, 2926, 1854, 1748, 1638, 1504, 1412, 1364, 1259, 1218, 1088, 1037, 1016, 841, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.78 (2H, d, *J* = 8.8 Hz), 7.56 (2H, d, *J* = 8.8 Hz), 5.28 (2H, s), 2.26 (3H, s), 1.36

(9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 157.0, 153.8, 153.4, 148.0, 131.6, 126.2, 119.9, 59.2, 35.2, 30.9, 20.6; MS (ESI) m/e 259.1 (M^++H); HRMS (ESI) for $C_{16}H_{18}O_3$ (M^+): 258.1256, Found: 258.1257.

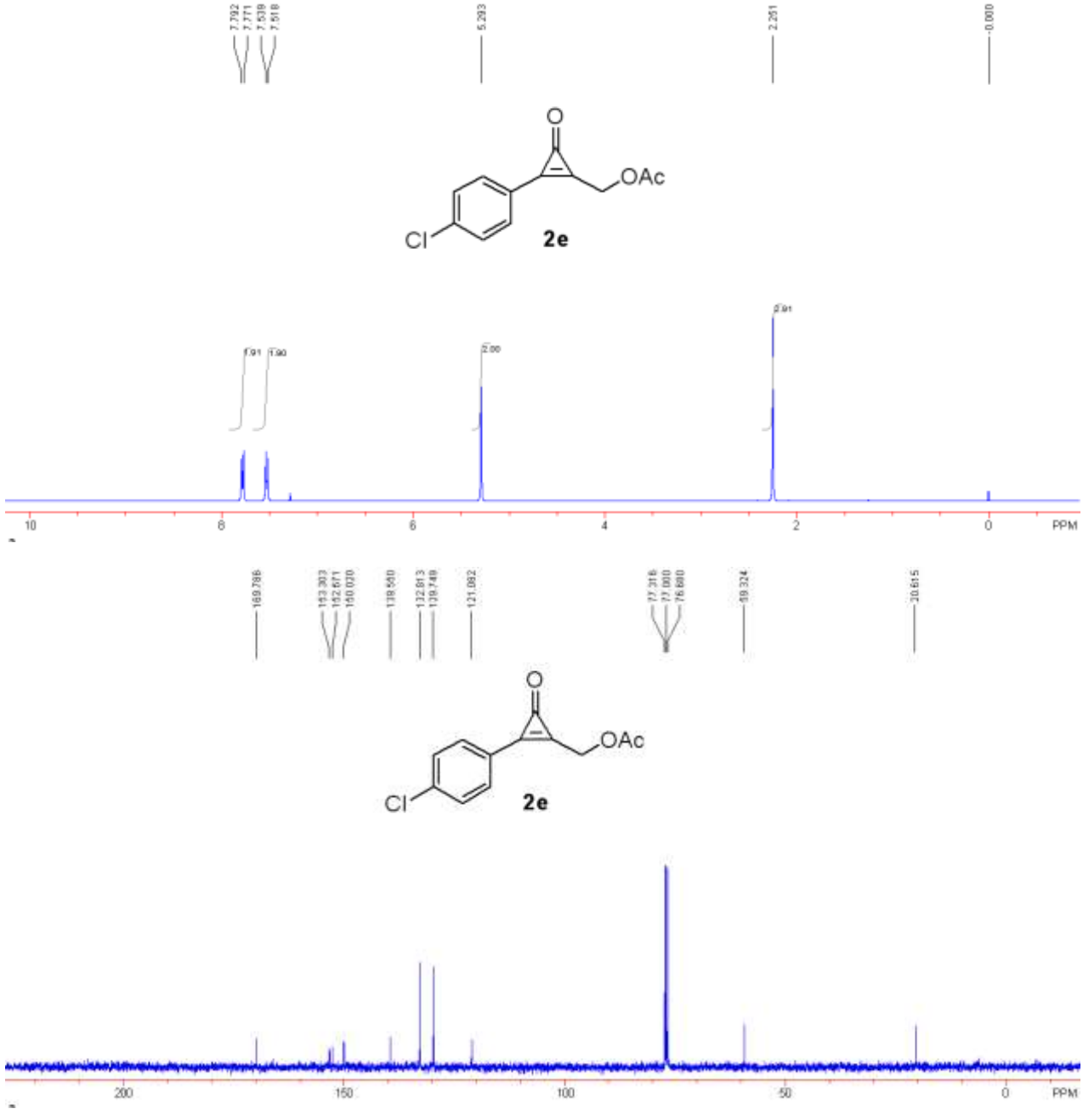


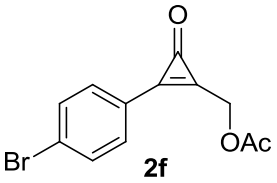




(2-(4-chlorophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2e: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2e**

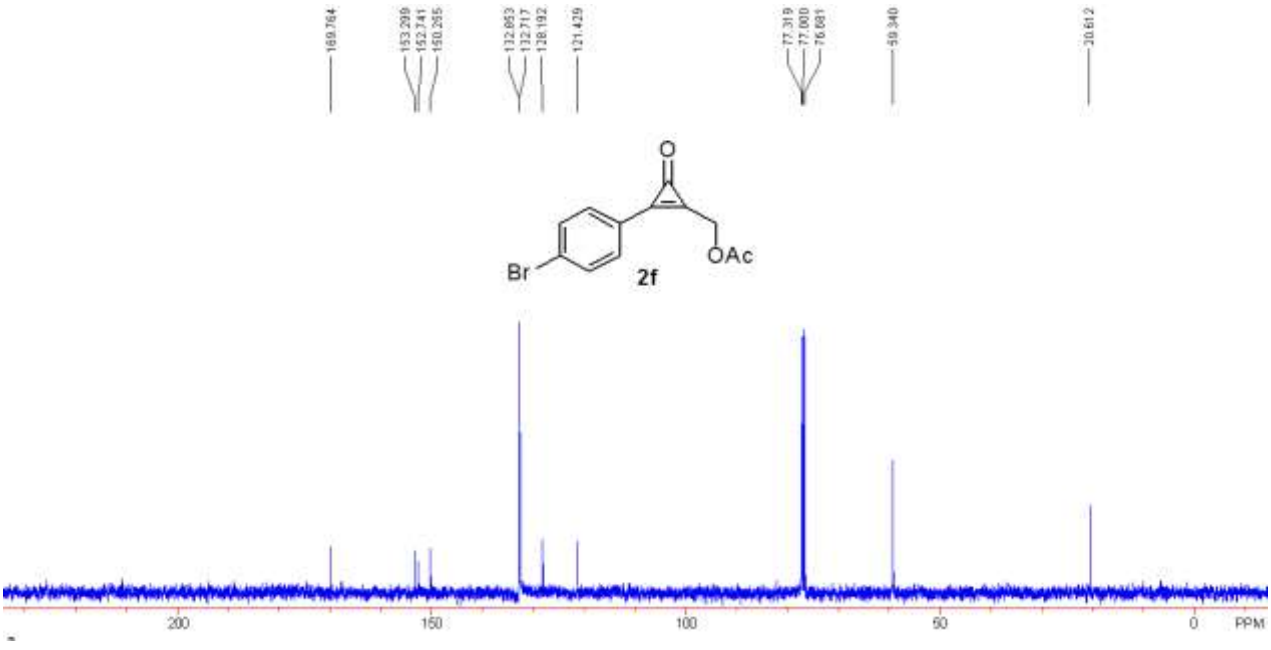
(55% yield). A yellow solid. m.p. for **2e** = 126-127 ^{o}C; IR (CH_2Cl_2): ν 3087, 2929, 1934, 1859, 1807, 1741, 1634, 1587, 1566, 1482, 1440, 1402, 1368, 1276, 1224, 1173, 1095, 1044, 1011, 990, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.78 (2H, d, *J* = 8.4 Hz), 7.53 (2H, d, *J* = 8.4 Hz), 5.29 (2H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 153.3, 152.7, 150.0, 139.6, 132.8, 129.7, 121.1, 59.3, 20.6; MS (ESI) m/e 237.0 (M^{+}+H); HRMS (ESI) for $C_{12}H_9ClO_3$ (M^{+}): 236.0240, Found: 236.0249.

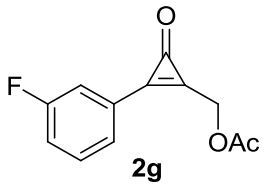




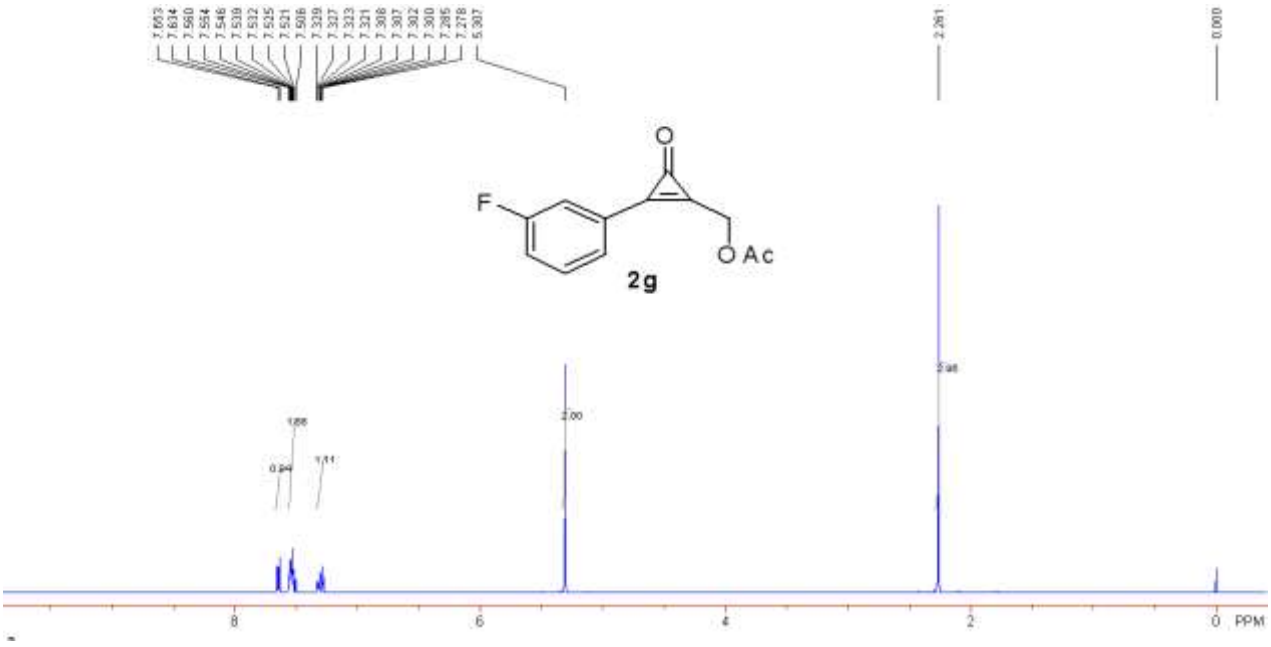
2f

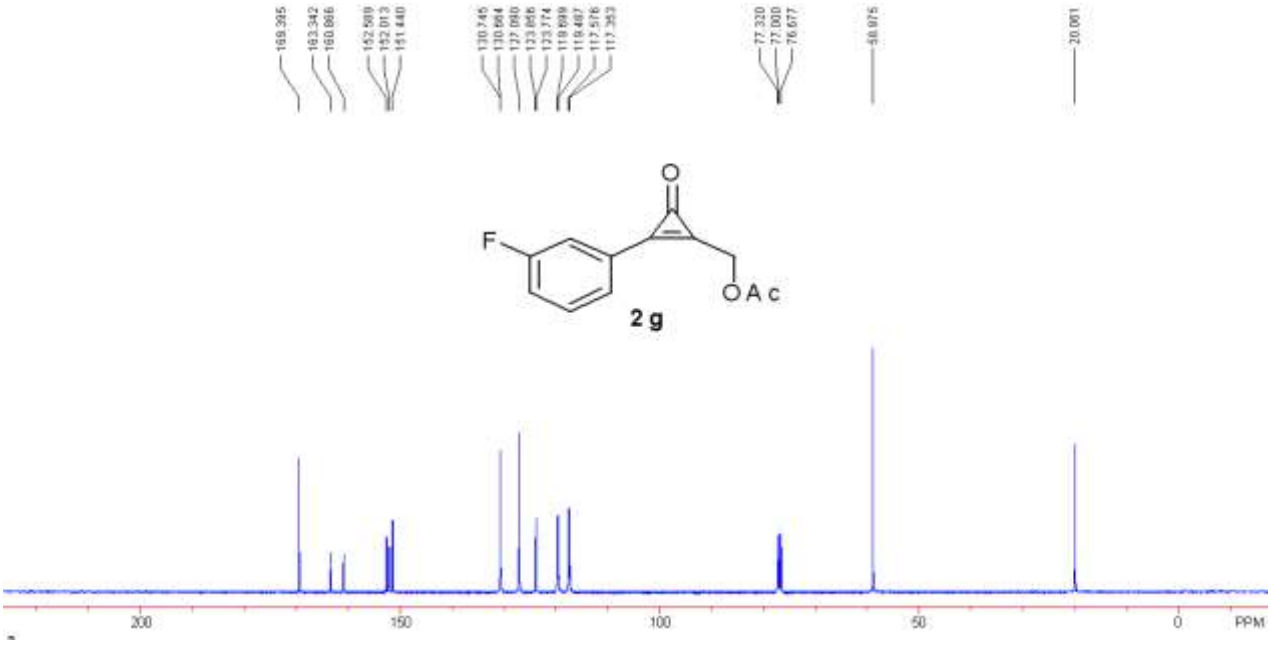
(2-(4-bromophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2f: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2f** (57% yield). A yellow solid. m.p. for **2f** = 153-155 ^{o}C; IR (CH_2Cl_2): ν 2962, 1860, 1746, 1634, 1582, 1400, 1259, 1236, 1090, 1064, 1017, 797 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70-7.69 (4H, m), 5.28 (2H, s), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 153.3, 152.7, 150.3, 132.9, 132.7, 128.2, 121.4, 59.3, 20.6; MS (ESI) m/e 281.0 (M^{+}+H); HRMS (ESI) for $C_{12}H_9BrO_3$ (M^{+}): 279.9735, Found: 279.9747.





(2-(3-fluorophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2g: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2g** (55% yield). A yellow solid. m.p. for **2g** = 90-92 ^{o}C; IR (CH_2Cl_2): ν 3054, 1854, 1749, 1646, 1607, 1584, 1483, 1442, 1377, 1265, 1217, 1040, 878, 793 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.64 (1H, d, J = 7.6 Hz), 7.56-7.51 (2H, m), 7.33-7.28 (1H, m), 5.31 (2H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 163.3, 160.9, 152.6, 152.0, 151.4, 130.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.1, 123.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 119.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 117.5 (d, $J_{C\text{-}F}$ = 22.3 Hz), 59.0, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -110.9; MS (ESI) m/e 221.0 (M^++H); HRMS (ESI) for $C_{12}H_9FO_3$ (M^+): 220.0536, Found: 220.0544.


F
OAc
2g
PPM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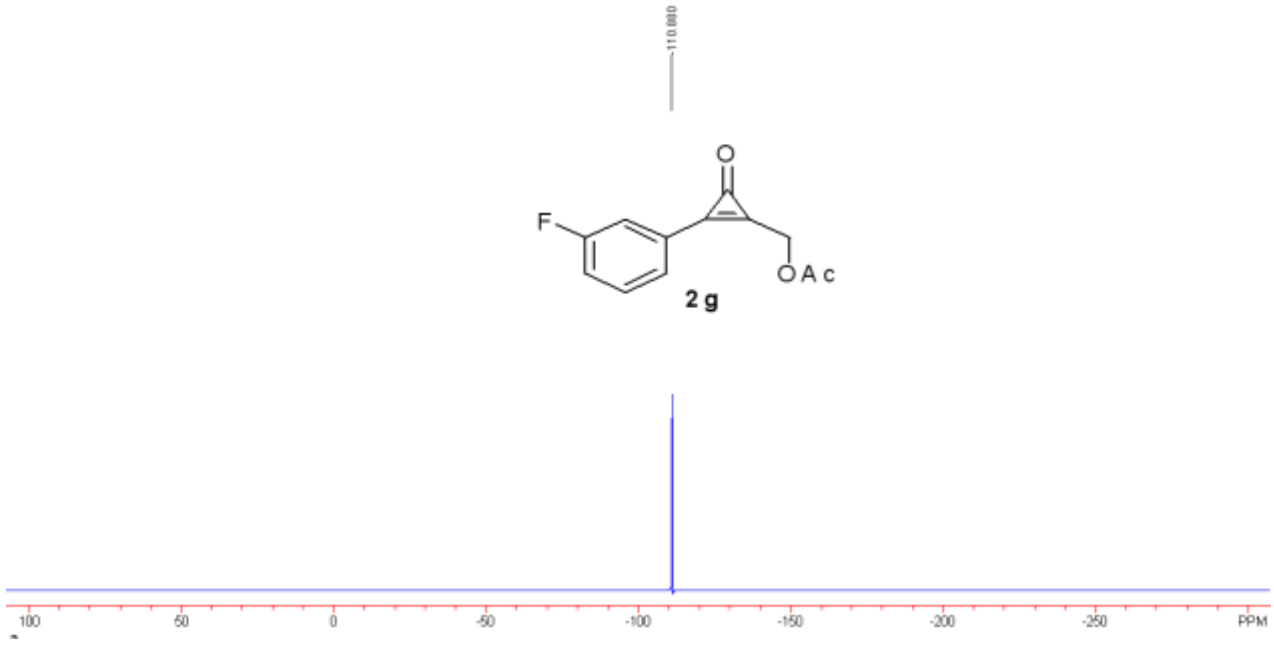
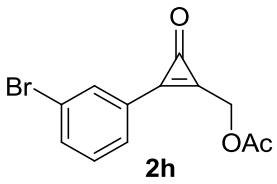
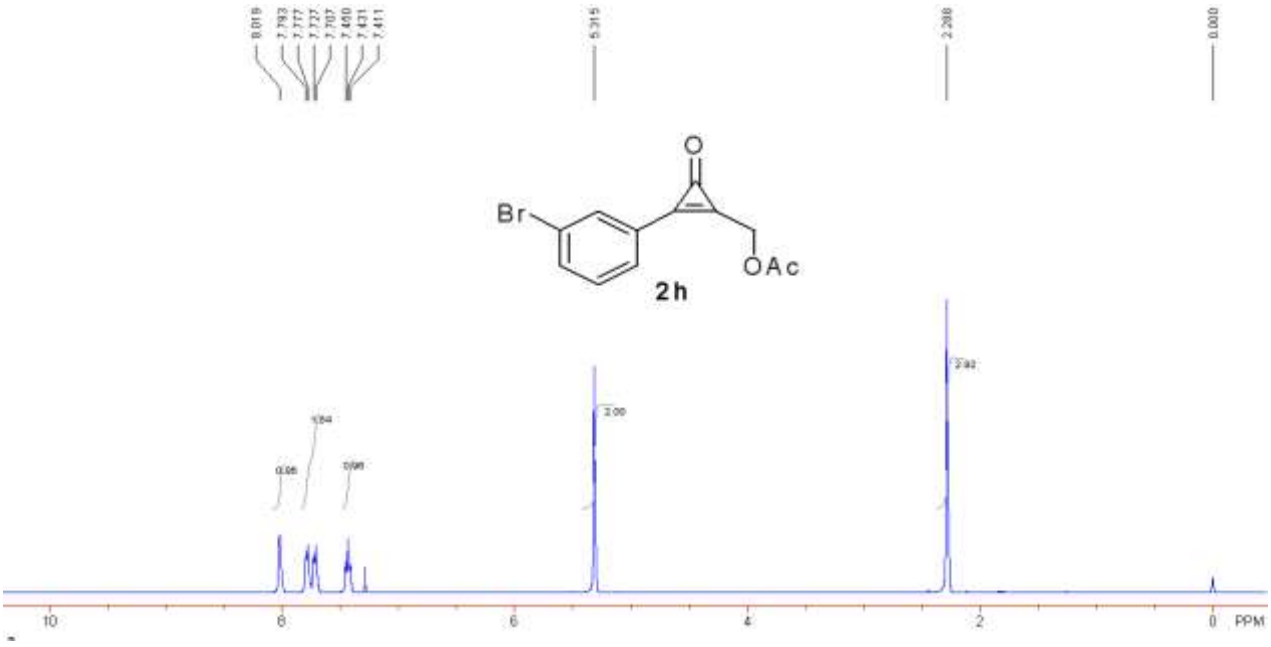
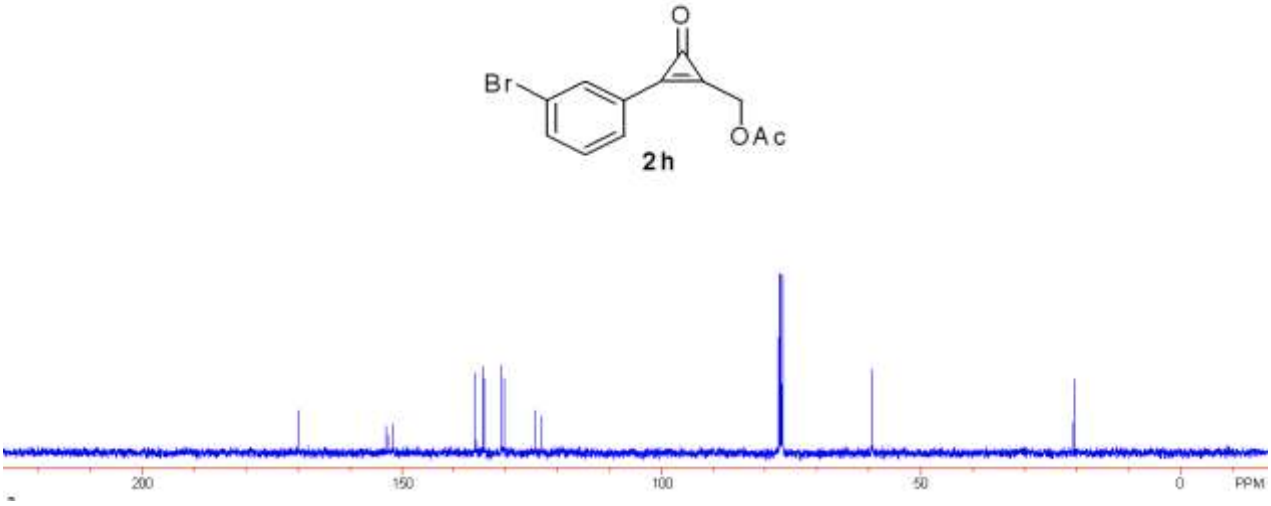
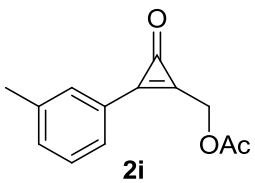




(2-(3-bromophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2h: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2h** (52% yield). A yellow solid. m.p. for **2h** = 107-109 ^{o}C; IR (CH_2Cl_2): ν 3094, 3052, 2926, 1934, 1859, 1745, 1638, 1589, 1558, 1472, 1422, 1379, 1264, 1221, 1071, 1044, 937, 894 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.02 (1H, s), 7.79 (1H, d, *J* = 6.4 Hz), 7.72 (1H, d, *J* = 8.0 Hz), 7.43 (1H, t, *J* = 8.0 Hz), 5.32 (2H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 153.1, 152.6, 151.7, 135.8, 134.2, 130.8, 130.3, 124.3, 123.1, 59.5, 20.7; MS (ESI) m/e 281.0 (M^++H); HRMS (ESI) for $C_{12}H_9BrO_3$ (M^+): 279.9735, Found: 279.9742.

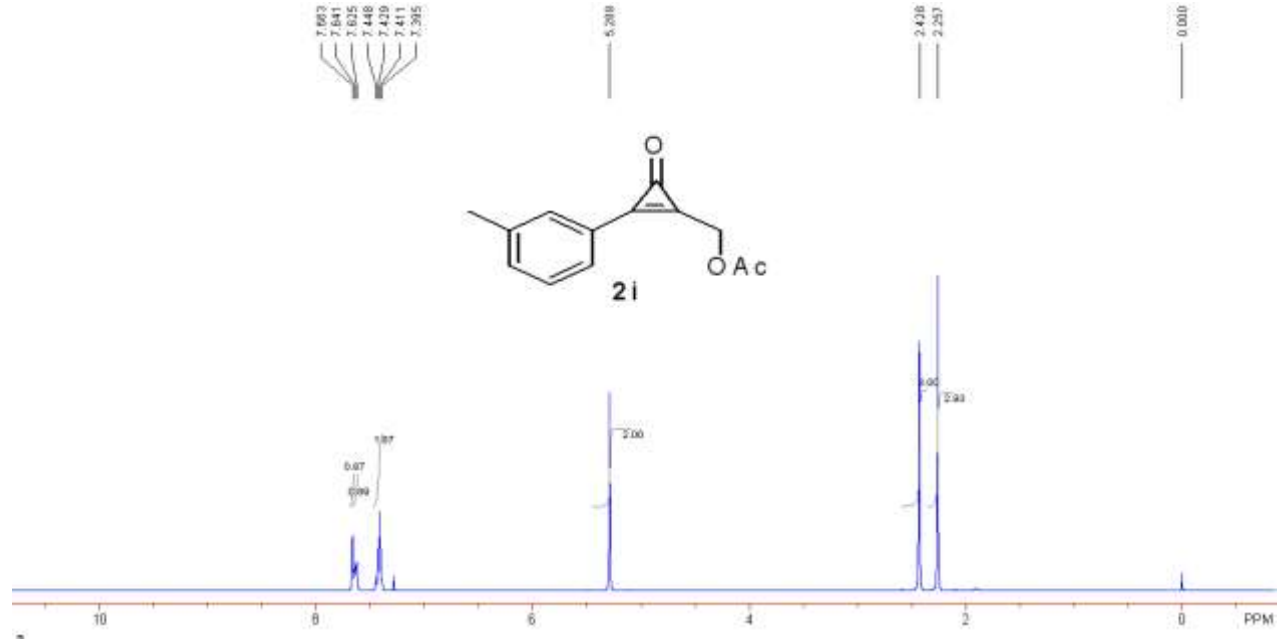


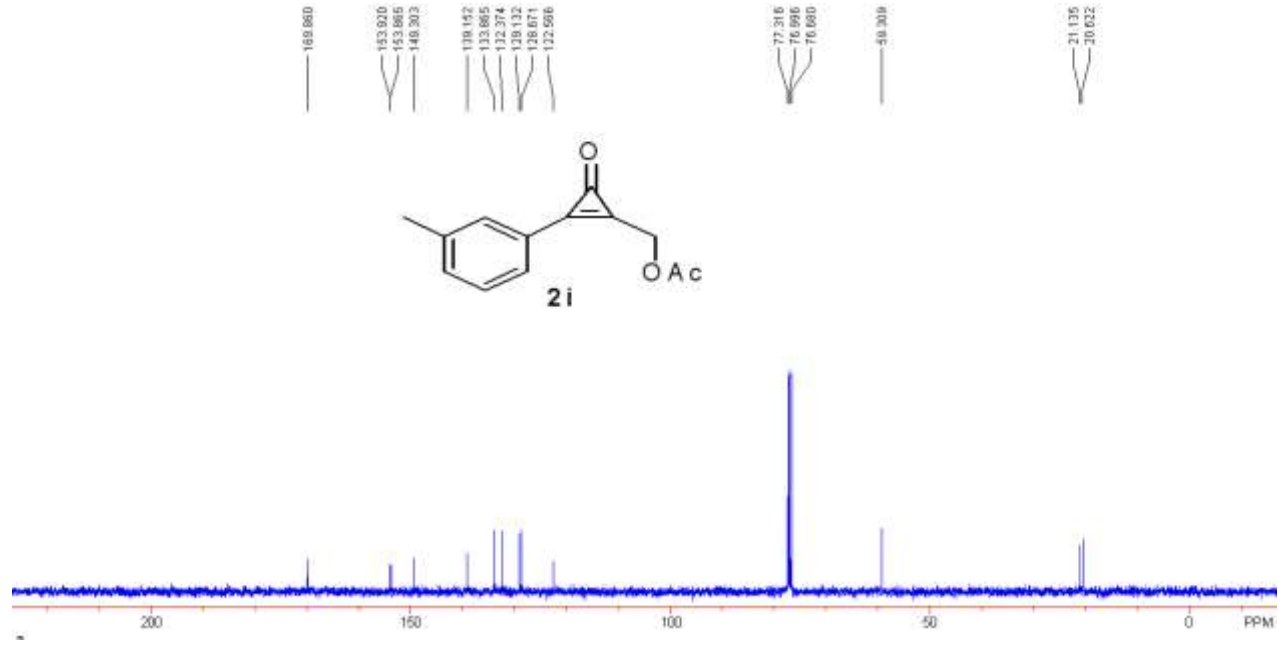


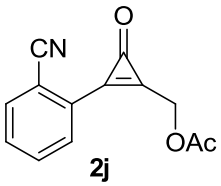


(3-oxo-2-m-tolylcycloprop-1-enyl)methyl acetate 2i: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2i** (54% yield). A yellow solid. m.p. for **2i** = 67-69 ^{o}C; IR (CH_2Cl_2): ν 2925, 1851, 1745, 1637, 1483, 1423, 1375, 1215, 1090, 1039, 922, 888 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.66 (1H, s), 7.63 (1H, d, *J* = 6.4 Hz), 7.45-7.40 (2H, m), 5.29 (2H, s), 2.43 (3H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ

169.9, 153.9, 153.86, 149.3, 139.2, 133.9, 132.4, 129.1, 128.7, 122.6, 59.3, 21.1, 20.6; MS (ESI) m/e 217.1 (M^++H); HRMS (ESI) for $C_{13}H_{12}O_3$ (M^+): 216.0786, Found: 216.0794.

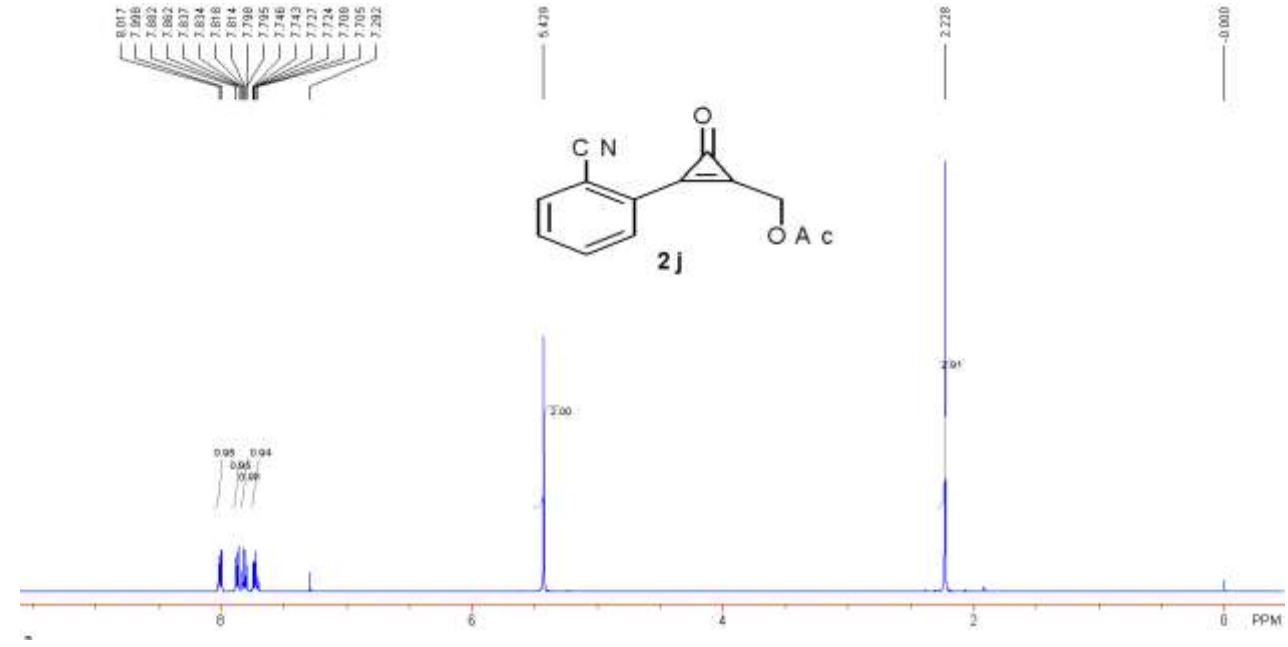


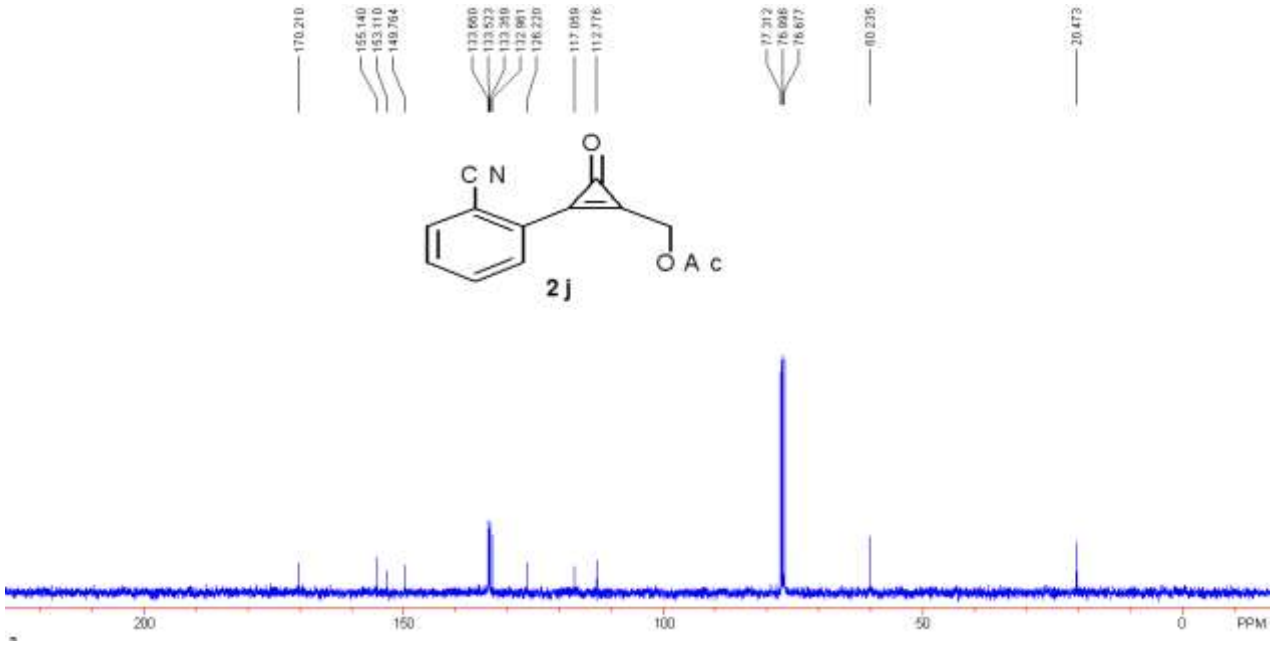


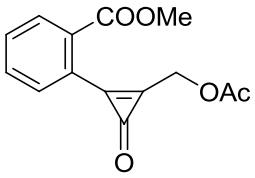


(2-(2-cyanophenyl)-3-oxocycloprop-1-enyl)methyl acetate 2j: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2j** (45% yield). A yellow solid. m.p. for **2j** = 152-154 ^oC; IR (CH_2Cl_2): ν 2961, 2928, 2231, 1859, 1753,

1644, 1480, 1427, 1379, 1259, 1218, 1089, 1035, 928, 865 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.00 (1H, d, J = 7.6 Hz), 7.87 (1H, d, J = 8.0 Hz), 7.82 (1H, dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.72 (1H, dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 5.43 (2H, s), 2.23 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 155.1, 153.1, 149.8, 133.7, 133.5, 133.4, 133.0, 126.2, 117.1, 112.8, 60.2, 20.5; MS (ESI) m/e 228.1 (M^++H); HRMS (ESI) for $C_{13}H_9NO_3$ (M^+): 227.0582, Found: 227.0591.

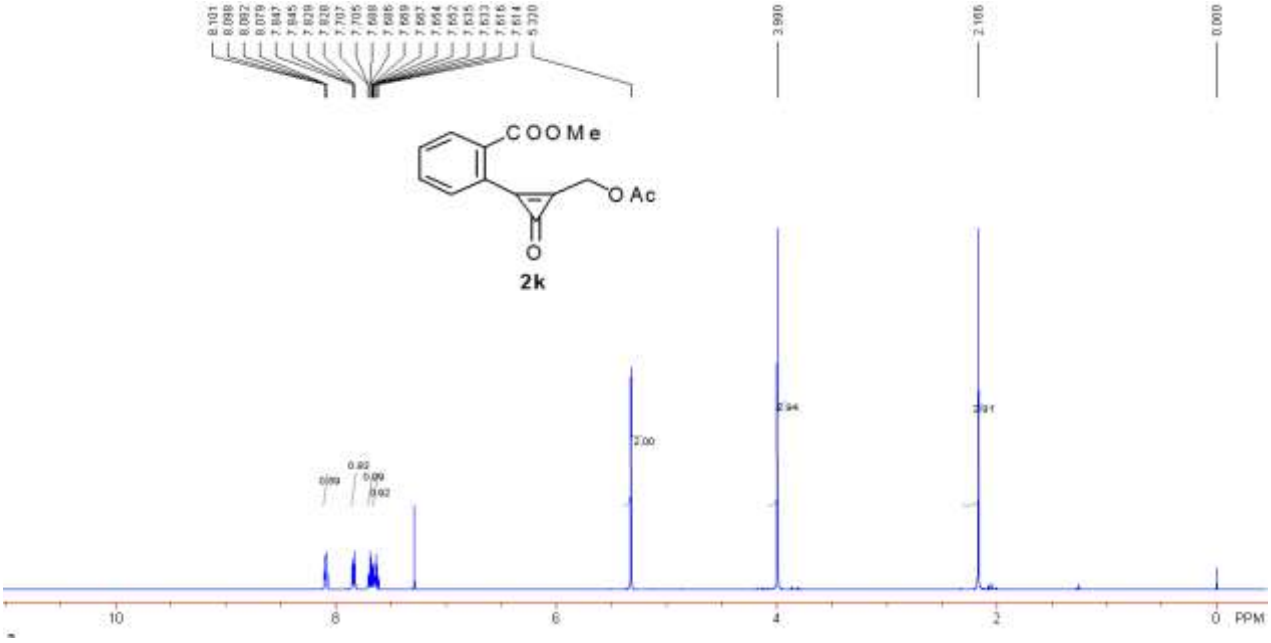


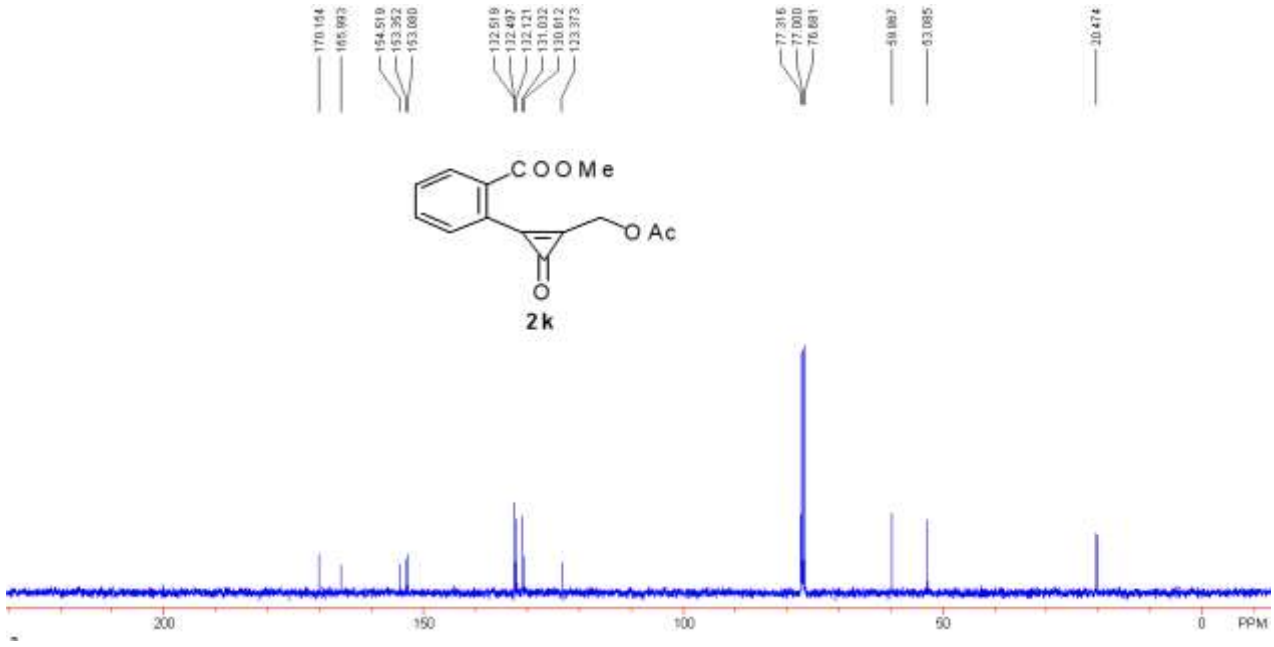


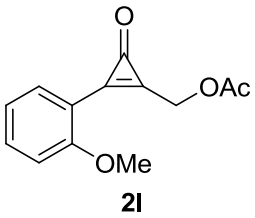


2k

methyl 2-(2-(acetoxymethyl)-3-oxocycloprop-1-enyl)benzoate 2k: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2k** (60% yield). A white solid. m.p. for **2k** = 66-67 ^{o}C; IR (CH_2Cl_2): ν 2953, 1857, 1744, 1719, 1641, 1594, 1573, 1432, 1374, 1271, 1217, 1130, 1082, 1043, 960, 865 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.09 (1H, dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.84 (1H, dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.69 (1H, dt, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.63 (1H, dt, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 5.32 (2H, s), 3.99 (3H, s), 2.17 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 166.0, 154.5, 153.4, 153.1, 132.52, 132.50, 132.1, 131.0, 130.6, 123.4, 59.9, 53.1, 20.5; MS (ESI) m/e 261.1 (M^++H); HRMS (ESI) for $C_{14}H_{12}O_5$ (M^+): 260.0685, Found: 260.0692.

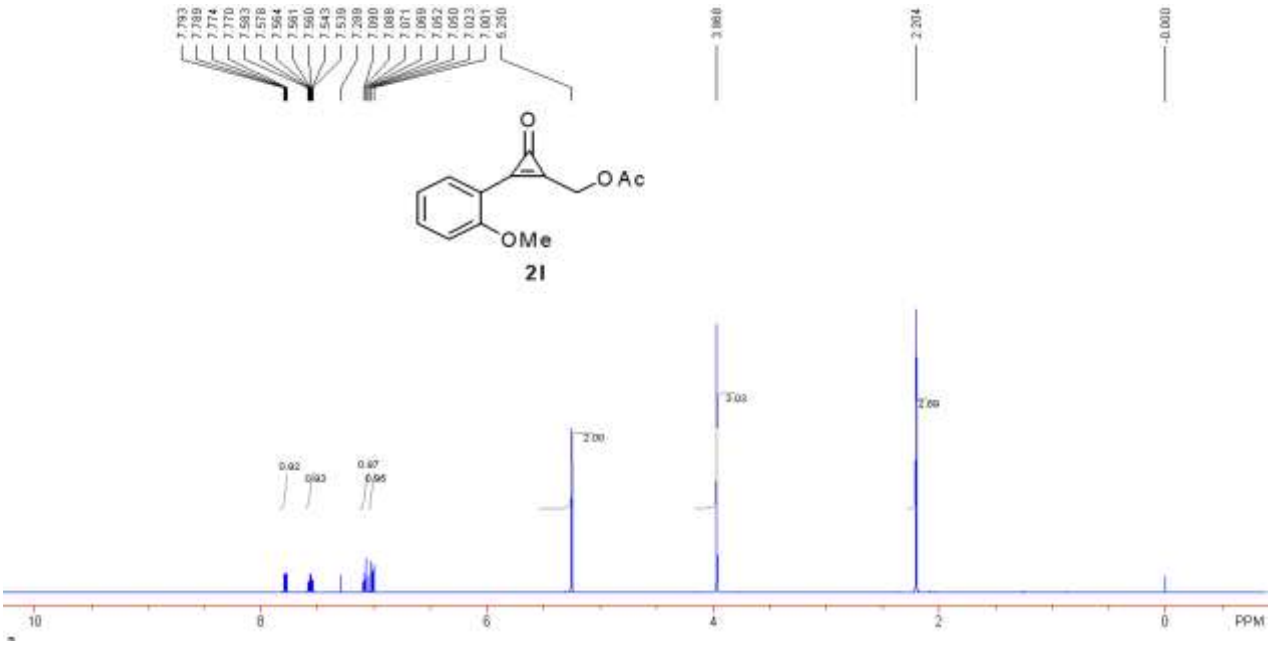


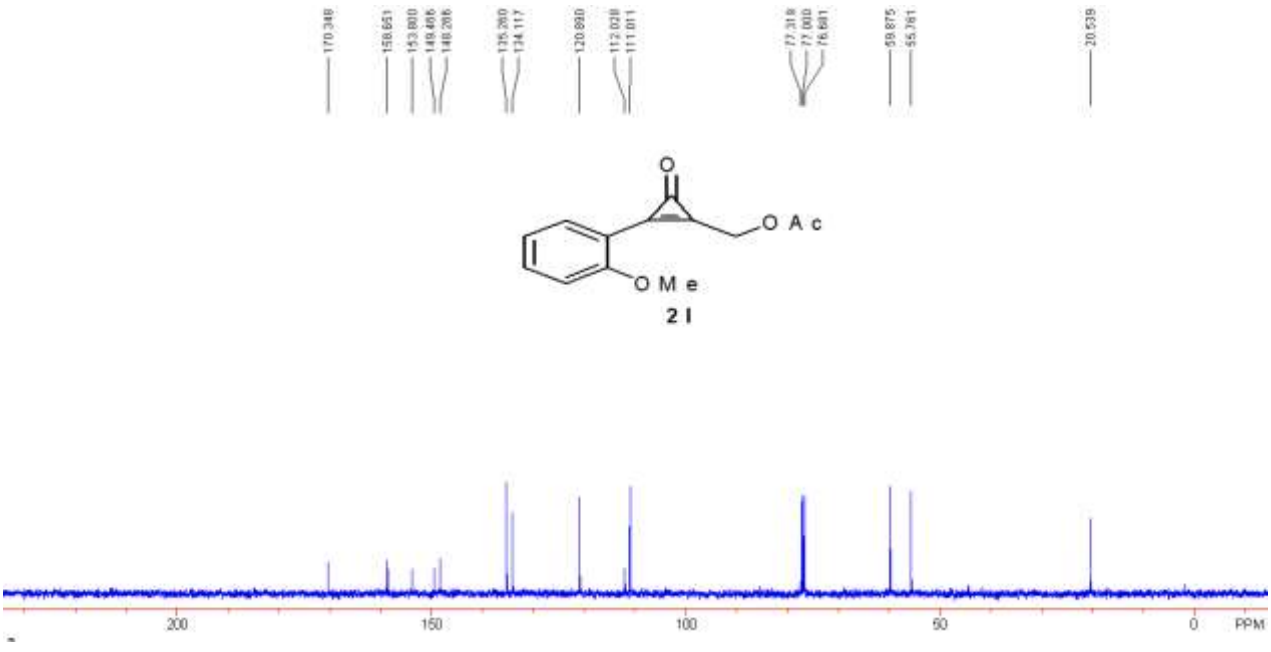


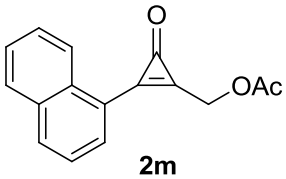


2l

(2-(2-methoxyphenyl)-3-oxocycloprop-1-enyl)methyl acetate 2l: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2l** (36% yield). A yellow solid. m.p. for **2l** = 98-100 ^{o}C; IR (CH_2Cl_2): ν 2938, 1848, 1744, 1636, 1596, 1577, 1488, 1465, 1436, 1372, 1279, 1219, 1163, 1043, 1020, 865 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.78 (1H, dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.58-7.54 (1H, m), 7.07 (1H, dt, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.01 (1H, d, J = 8.8 Hz), 5.25 (2H, s), 3.97 (3H, s), 2.20 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3, 158.7, 153.8, 149.5, 148.3, 135.3, 134.1, 120.9, 112.0, 111.0, 59.9, 55.8, 20.5; MS (ESI) m/e 233.1 (M^++H); HRMS (ESI) for $C_{13}H_{12}O_4$ (M^+): 232.0736, Found: 232.0745.

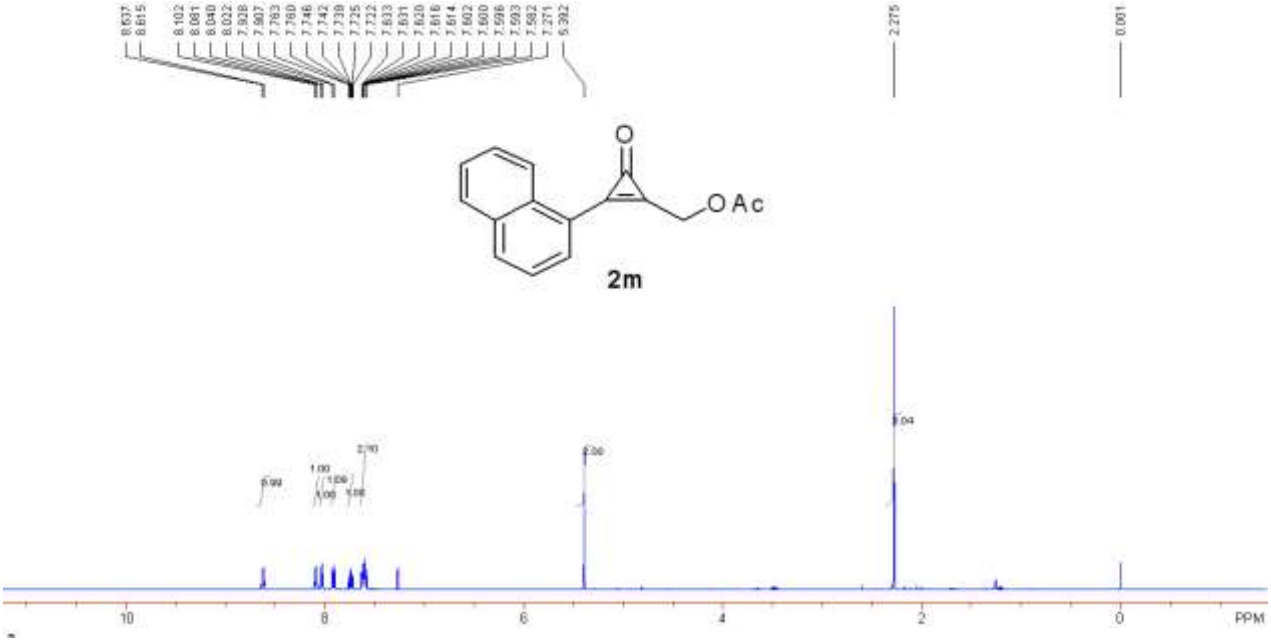


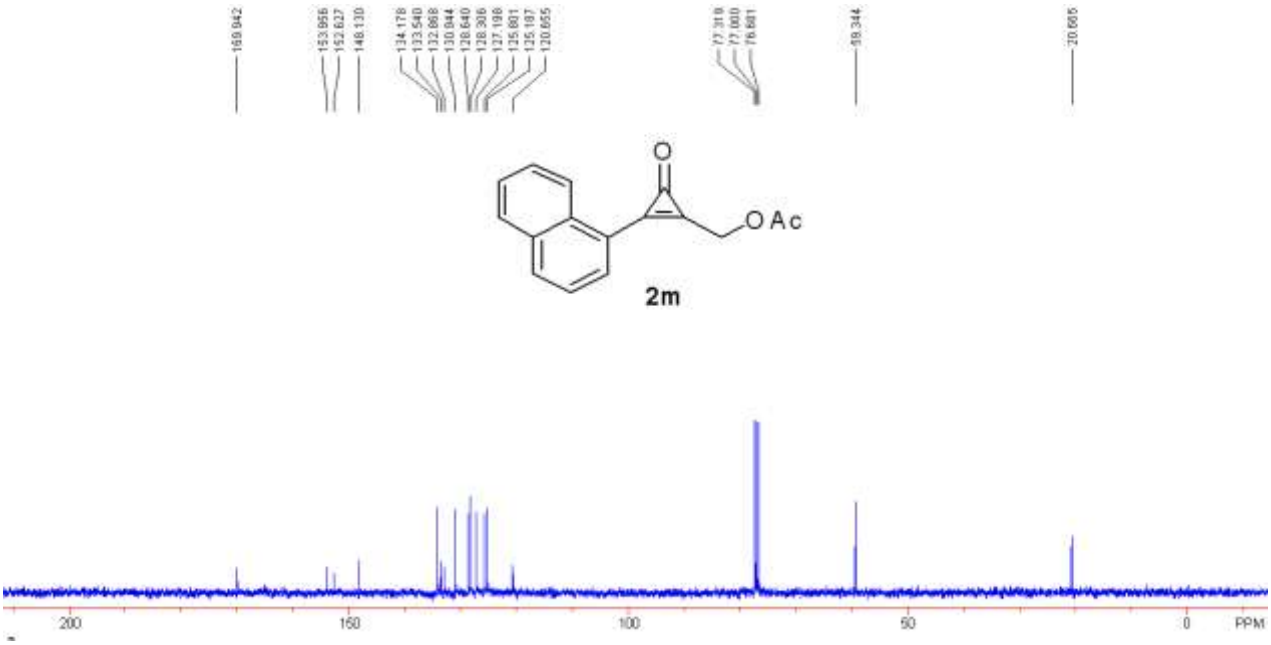




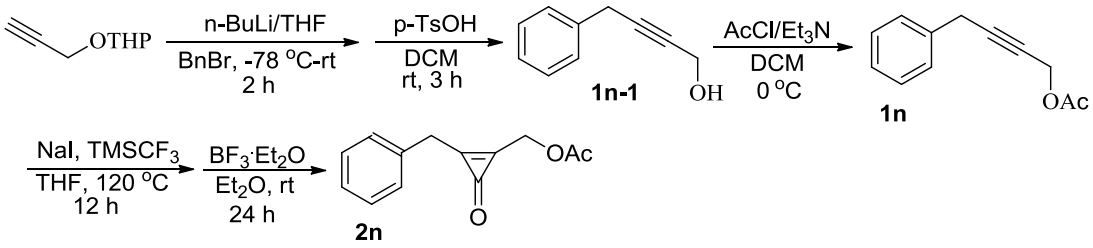
(2-(naphthalen-1-yl)-3-oxocycloprop-1-enyl)methyl acetate 2m: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2m** (55% yield). A yellow solid. m.p. for **2m** = 111-113 ^{o}C; IR (CH_2Cl_2): ν 2962, 1845, 1749, 1630, 1374, 1259, 1221, 1087, 1015, 864, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.63 (1H, d, *J* = 8.8 Hz), 8.09 (1H, d, *J* = 8.4 Hz), 8.03 (1H, d, *J* = 6.4 Hz), 7.92 (1H, d, *J* = 8.4 Hz), 7.76-7.72 (1H,

m), 7.63-7.58 (2H, m), 5.39 (2H, s), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 154.0, 152.7, 148.1, 134.2, 133.5, 132.9, 130.9, 128.6, 128.3, 127.2, 125.8, 125.2, 120.7, 59.3, 20.7; MS (ESI) m/e 253.1 (M^++H); HRMS (ESI) for $C_{16}H_{12}O_3$ (M^+): 252.0786, Found: 252.0792.



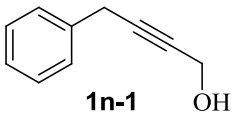


Typical procedure for preparation of **2n**:

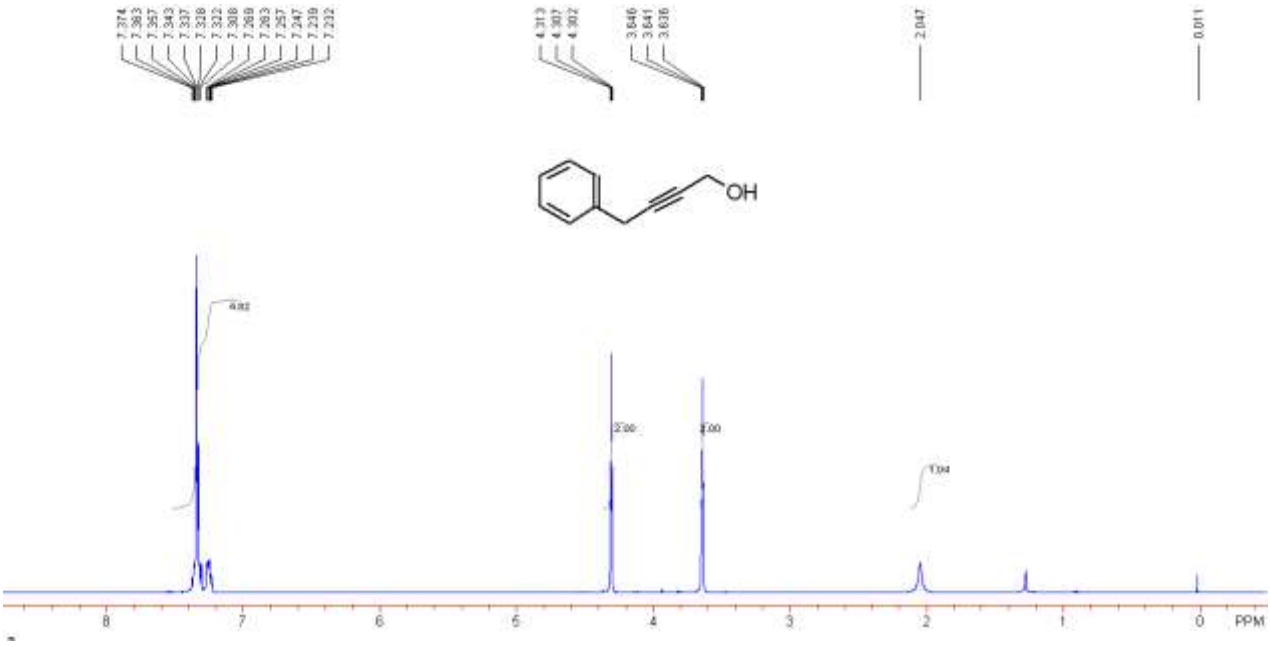


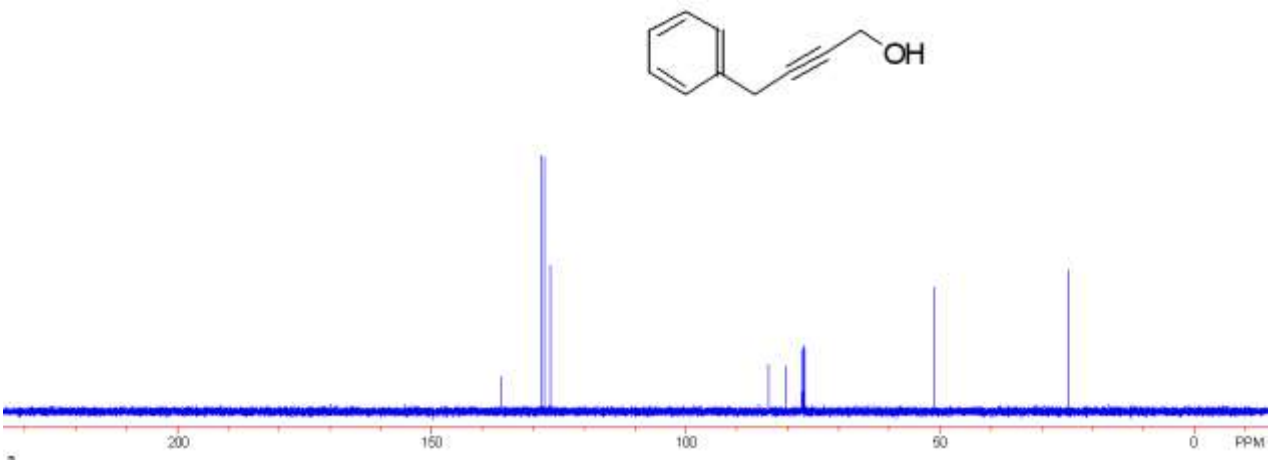
To a solution of 2-(prop-2-ynyloxy)tetrahydro-2H-pyran (10.0 mmol) in 10.0 mL THF at -78 °C was added n-BuLi (2.50 M ,4.40 mL) under Ar atmosphere, the resulting mixture was stirred for 1 hour at this temperature and BnBr (11.0 mmol) was added, then the reaction was allowed to warm to room temperature for 2 hours. After the reaction completed, the reaction was quenched by addition of saturated NH_4Cl solution, extracted with Et_2O, dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/20) to give the target product **1n-1**.

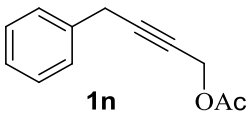
Above **1n-1** (470 mg, 3.2 mmol) was dissolved in 10 mL of CH_2Cl_2 mixed with 0.51 mL (3.86 mmol) Et_3N and 0.28 mL (3.86 mmol) of AcCl was added at 0 °C, the resulting mixture was stirred at this temperature for 1 hour. The reaction was quenched by addition of saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/8 as eluent) to furnish product **1n** as colorless oil (300 mg, 50% yield).



4-phenylbut-2-yn-1-ol 1n-1: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1n-1** (29% yield). A colorless oil. IR (CH_2Cl_2): ν 3338, 3061, 3029, 2924, 1719, 1600, 1494, 1452, 1397, 1263, 1176, 1129, 1073, 1018, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.37-7.23 (5H, m), 4.31 (2H, t, *J* = 2.0 Hz), 3.64 (2H, t, *J* = 2.0 Hz), 2.05 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4, 128.5, 127.83, 127.82, 126.6, 83.8, 80.4, 51.2, 25.0; MS (%) m/e 146 (53), 131 (14), 128 (82), 115 (100), 102 (11), 91 (35), 77 (16), 63 (14); HRMS (EI) for $C_{10}H_{10}O$: 146.0732; Found: 146.0729.

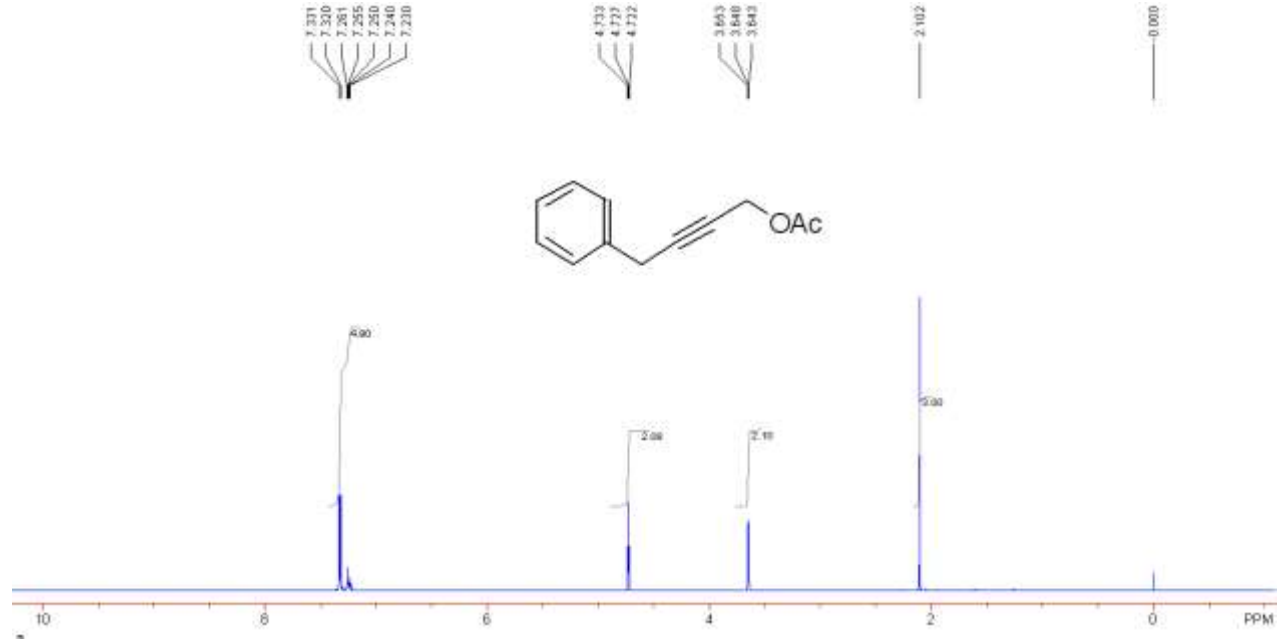


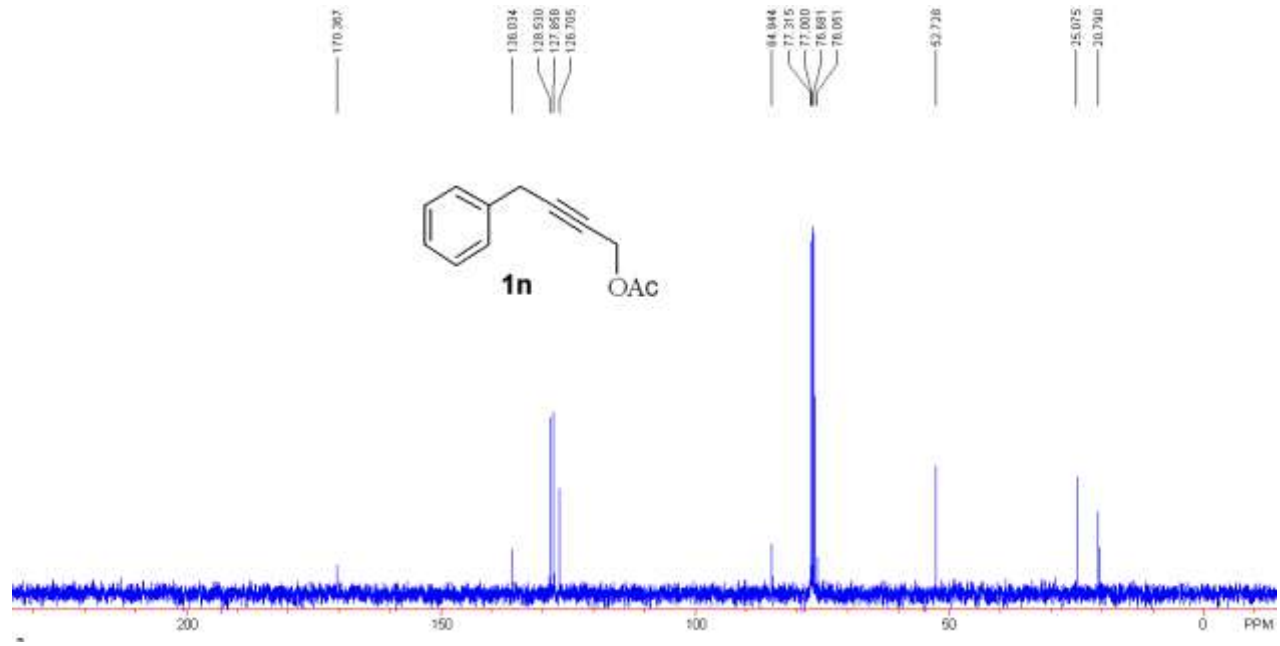


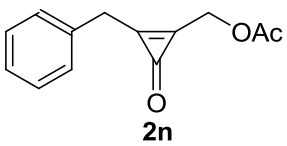


4-phenylbut-2-ynyl acetate 1n: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1n** (50% yield). A colorless oil. IR (CH_2Cl_2): ν 2954, 2923, 2852, 1850, 1745, 1643, 1602, 1496, 1454, 1375, 1219, 1145, 1044, 832, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.33-7.23 (5H, m), 4.73 (2H, t, *J* = 2.0 Hz), 3.65 (2H, t, *J* = 2.0 Hz), 2.10 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 136.0, 128.5, 127.9, 126.7, 84.9, 76.1, 52.7, 25.1, 20.8; MS (%) m/e 188 (2), 146 (48), 128 (100), 115 (25), 102 (21), 91 (12), 77

(14), 63 (11); HRMS (EI) for $C_{12}H_{12}O_2$: 188.0837; Found: 188.0833.



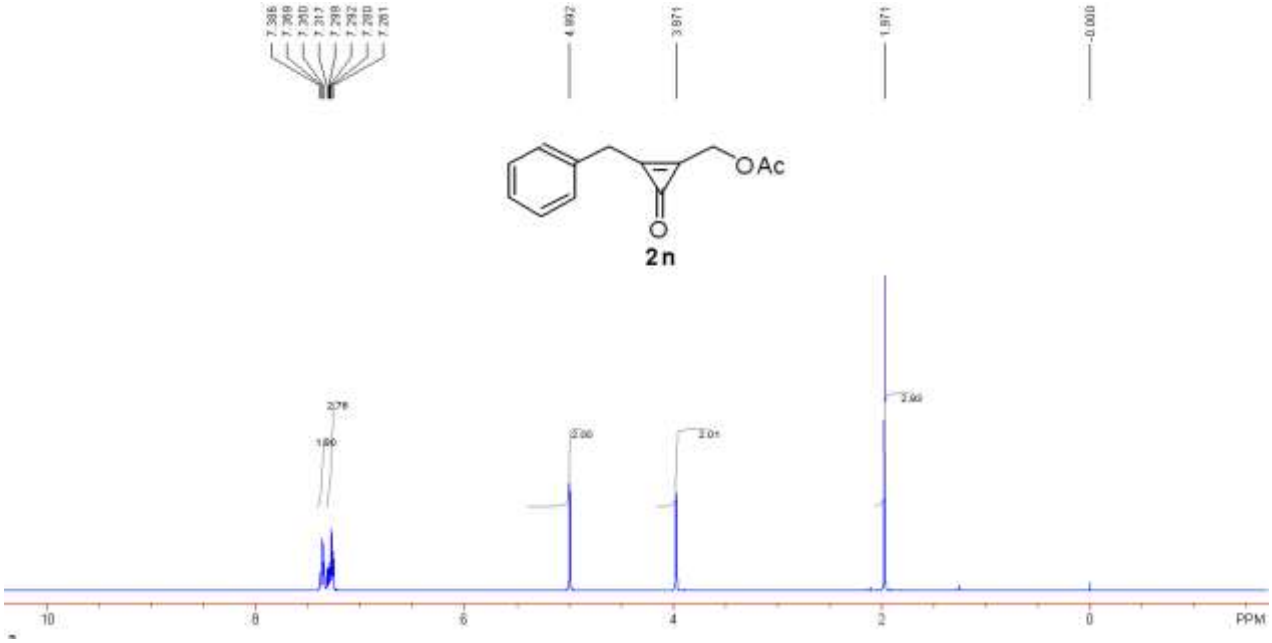


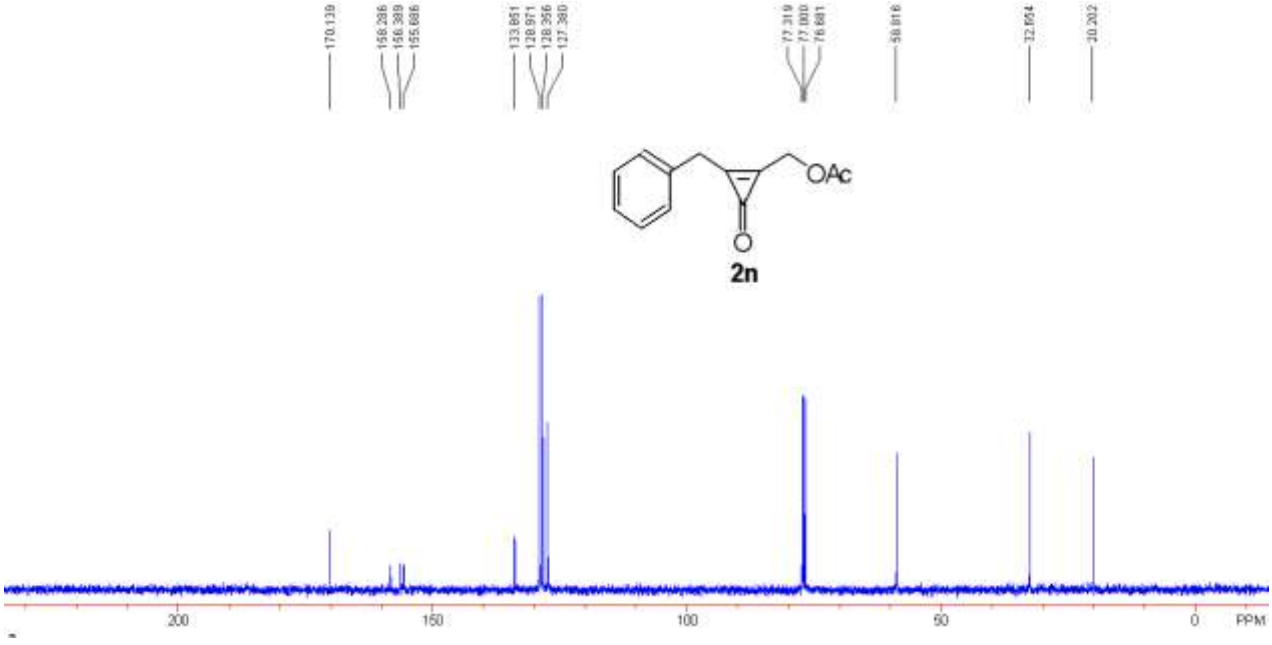


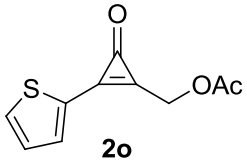
2n

(2-benzyl-3-oxocycloprop-1-enyl)methyl acetate 2n: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2n** (30% yield). A colorless oil. IR (CH_2Cl_2): ν 2962, 1850, 1744, 1641, 1496, 1454, 1414, 1258, 1219, 1016, 863, 795, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.38 (2H, d, *J* = 7.2 Hz), 7.35-7.26 (3H, m), 4.99 (2H, s), 3.97 (2H, s), 1.97 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1, 158.3, 156.4, 155.7, 133.9,

129.0, 128.4, 127.4, 58.8, 32.7, 20.2; MS (ESI) m/e 217.1 (M^++H); HRMS (ESI) for $C_{13}H_{12}O_3$ (M^+): 216.0786, Found: 216.0790.

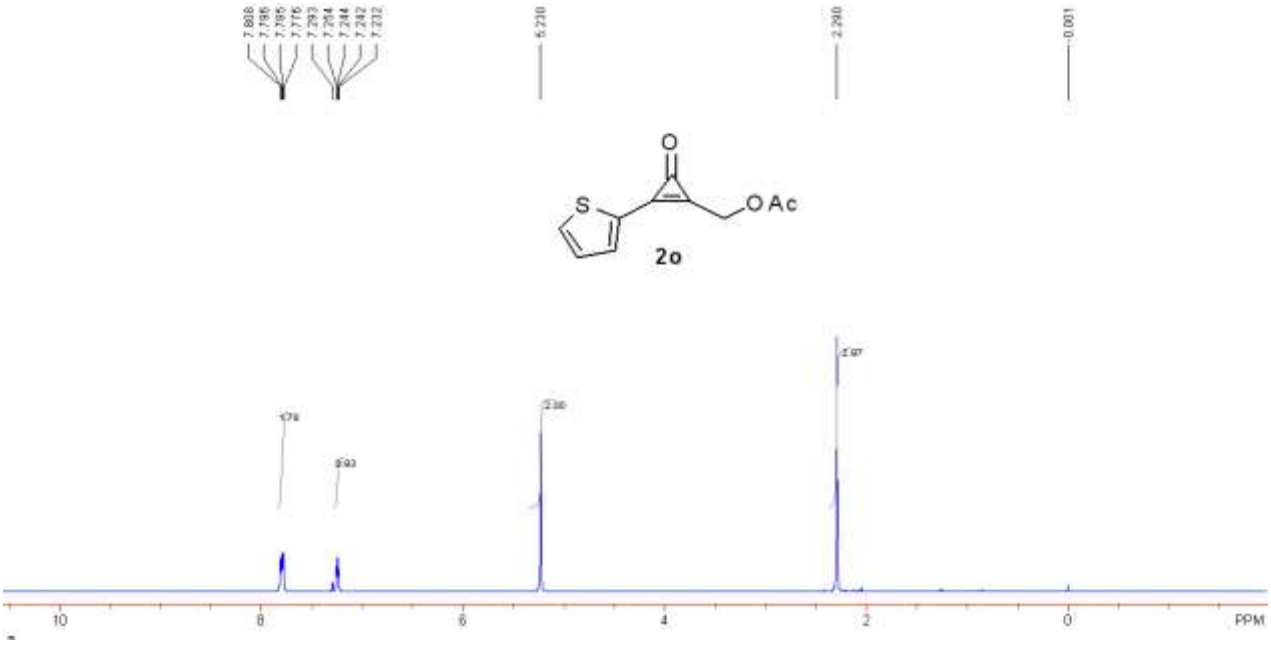


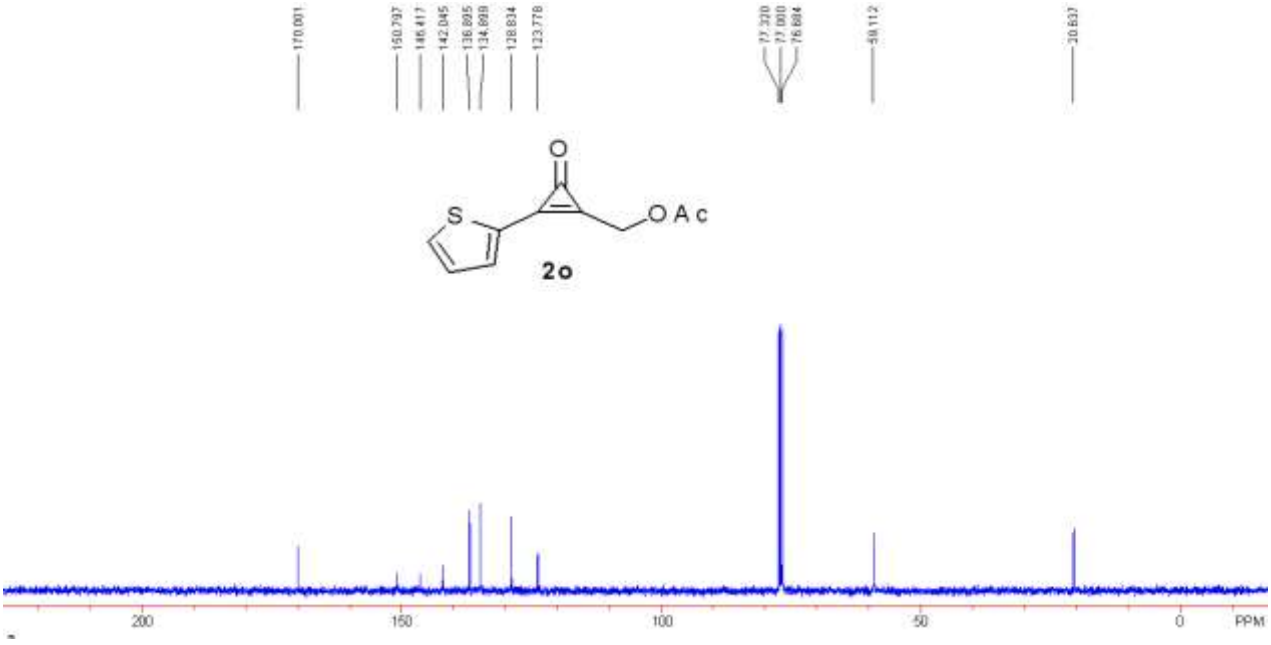


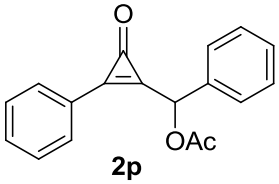


(3-oxo-2-(thiophen-2-yl)cycloprop-1-enyl)methyl acetate 2o: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2o** (45% yield). A yellow solid. m.p. for **2o** = 109-111 ^oC; IR (CH_2Cl_2): ν 3088, 2928, 1850, 1743, 1627, 1409,

1378, 1365, 1215, 1037, 928, 853 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.79 (2H, dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz), 7.25 (1H, dd, J_1 = 4.8 Hz, J_2 = 4.0 Hz), 5.23 (2H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 150.8, 146.4, 142.0, 136.9, 134.9, 128.8, 123.8, 59.1, 20.6; MS (ESI) m/e 209.0 (M^++H); HRMS (ESI) for $C_{10}H_8O_3S$ (M^+): 208.0194, Found: 208.0203.

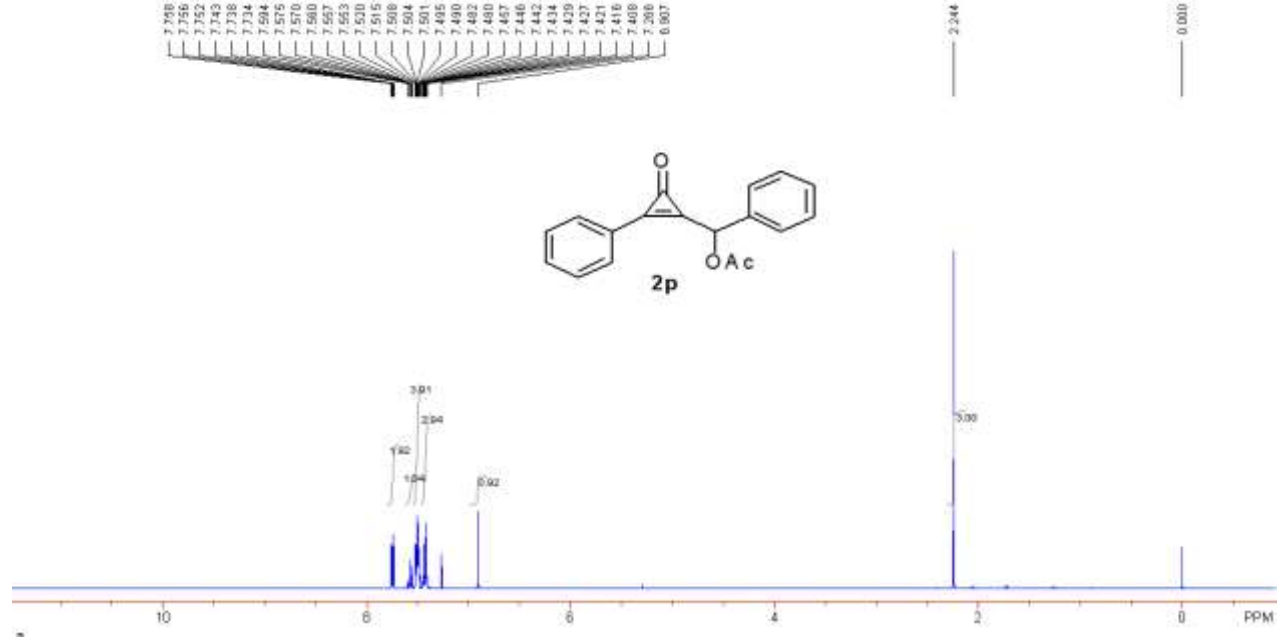


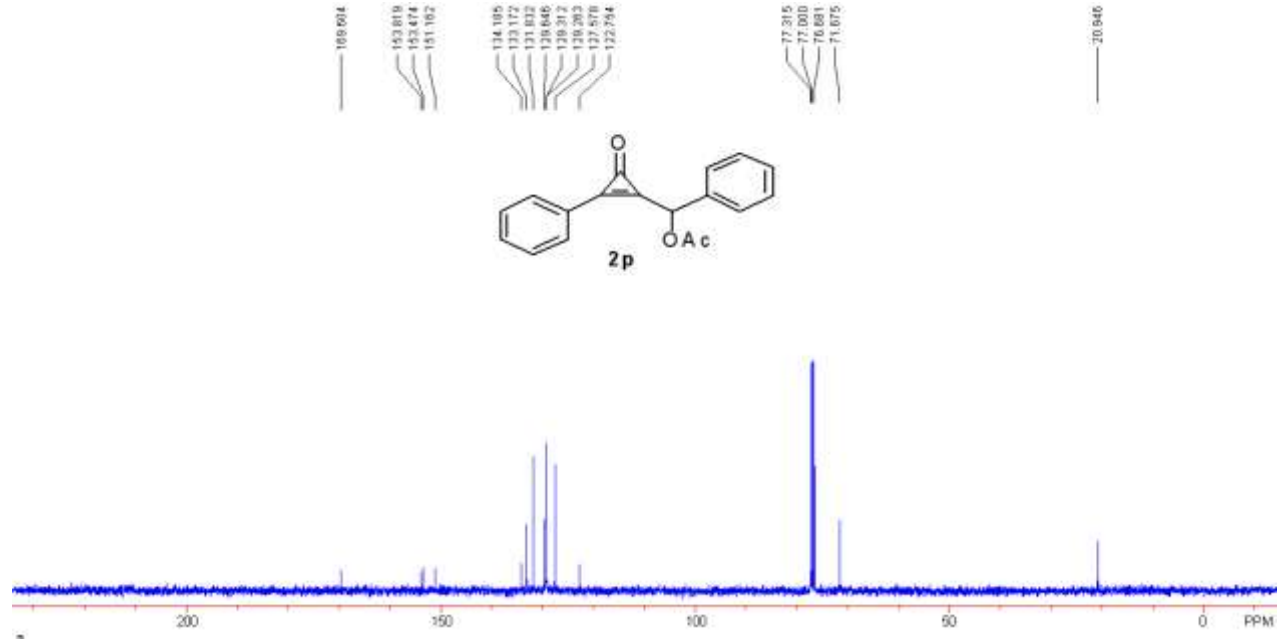


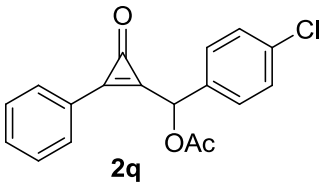


(3-oxo-2-phenylcycloprop-1-enyl)(phenyl)methyl acetate 2p: This is a known compound.[2] A

yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.76-7.73 (2H, m), 7.58-7.55 (1H, m), 7.52-7.48 (4H, m), 7.46-7.41 (3H, m), 6.91 (1H, s), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 153.8, 153.5, 151.2, 134.2, 133.2, 131.8, 129.6, 129.3, 129.26, 127.6, 122.8, 71.7, 20.9.

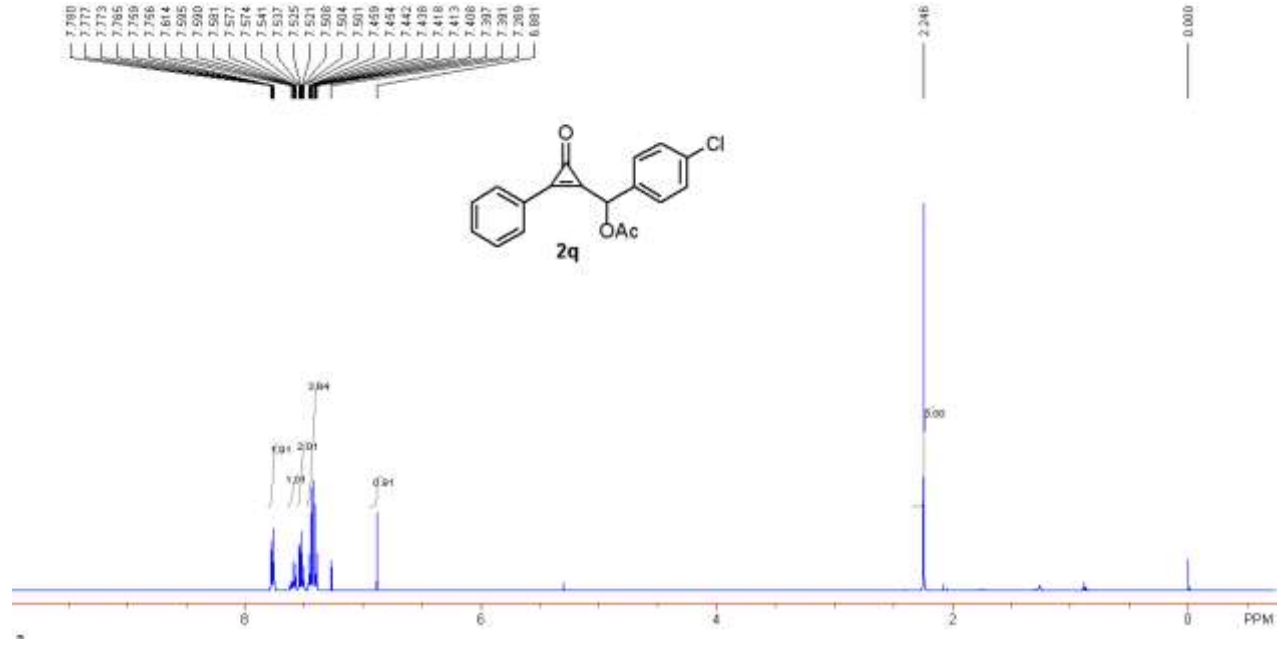


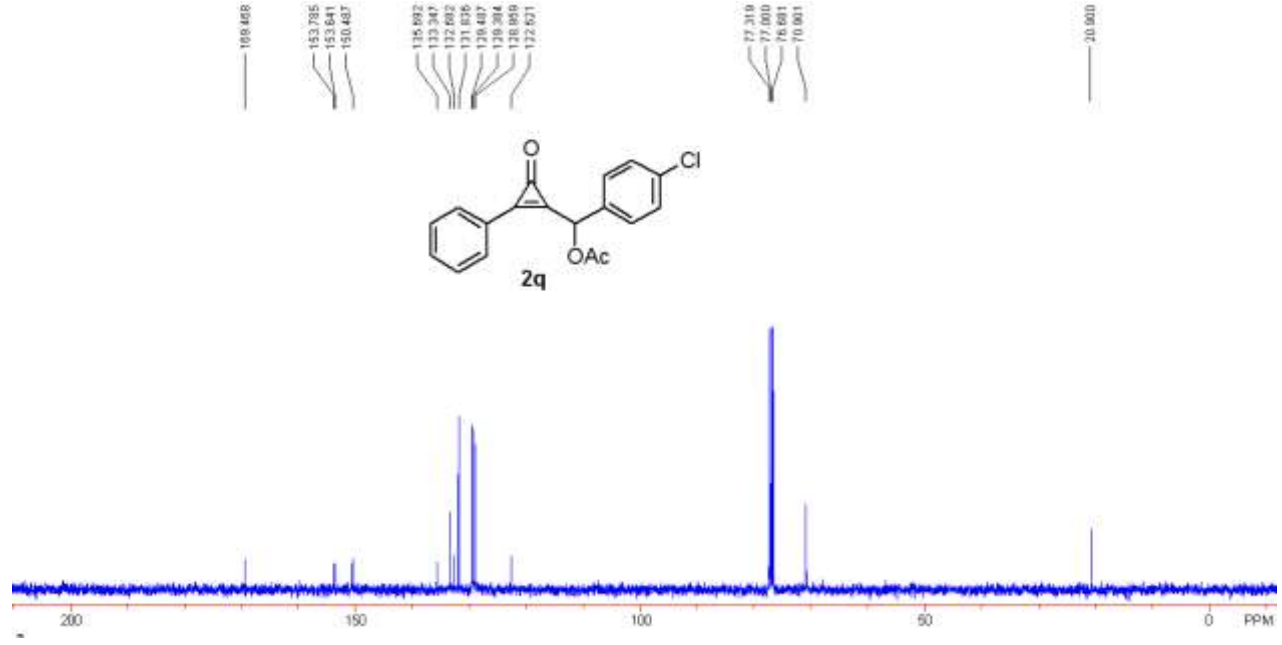


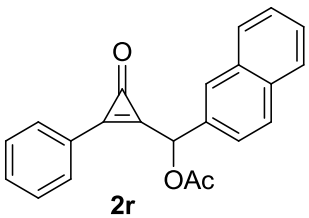


(4-chlorophenyl)(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2q: This is a known compound.[2] A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.78-7.76 (2H, m), 7.61-7.57 (1H,

m), 7.54-7.50 (2H, m), 7.46-7.39 (4H, m), 6.88 (1H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 153.8, 153.6, 150.5, 135.7, 133.3, 132.7, 131.8, 129.5, 129.4, 129.0, 122.6, 70.9, 20.9.

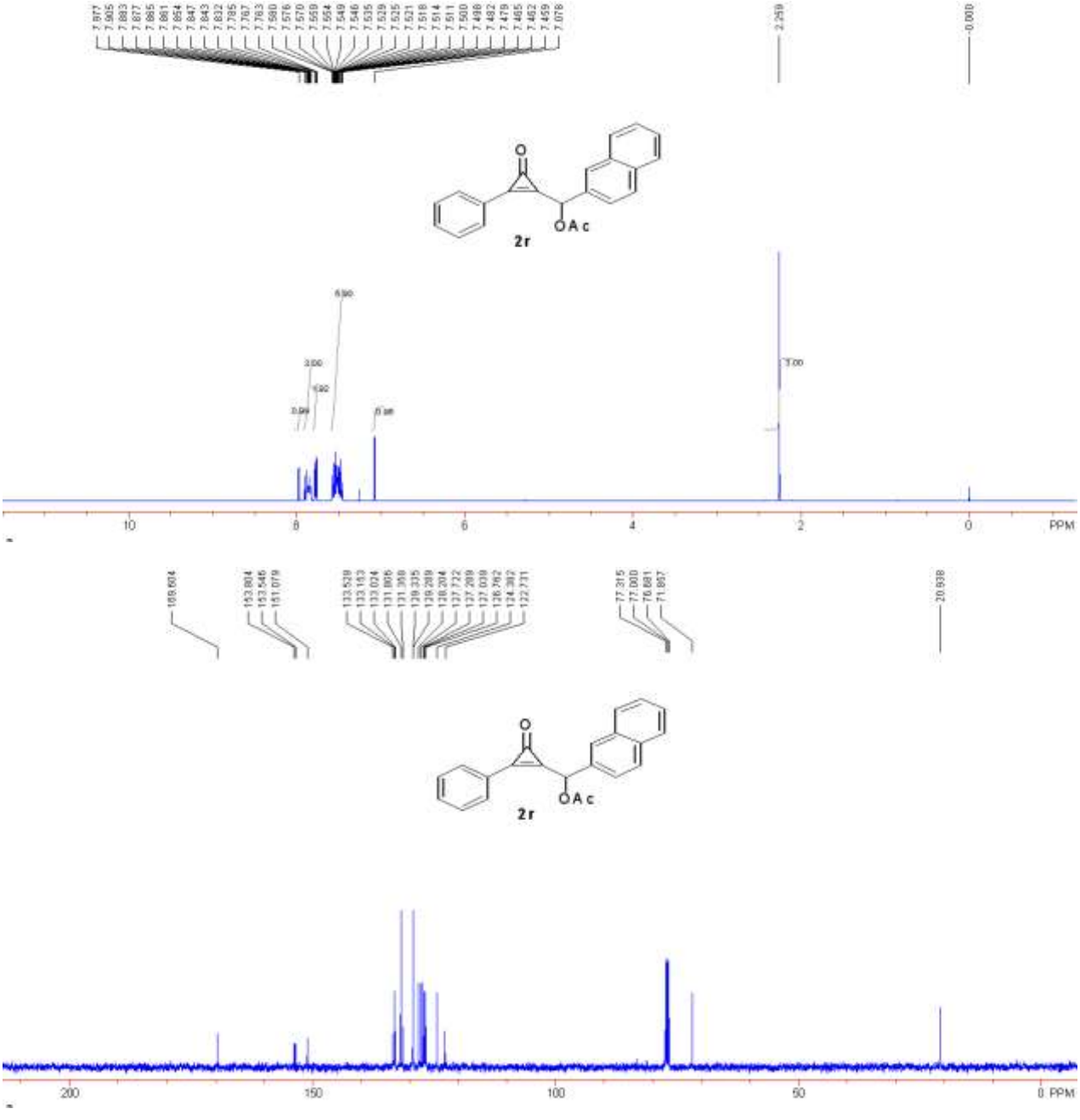


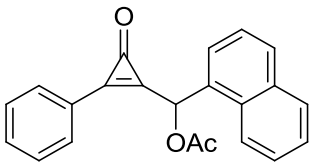




naphthalen-2-yl(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2r: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target

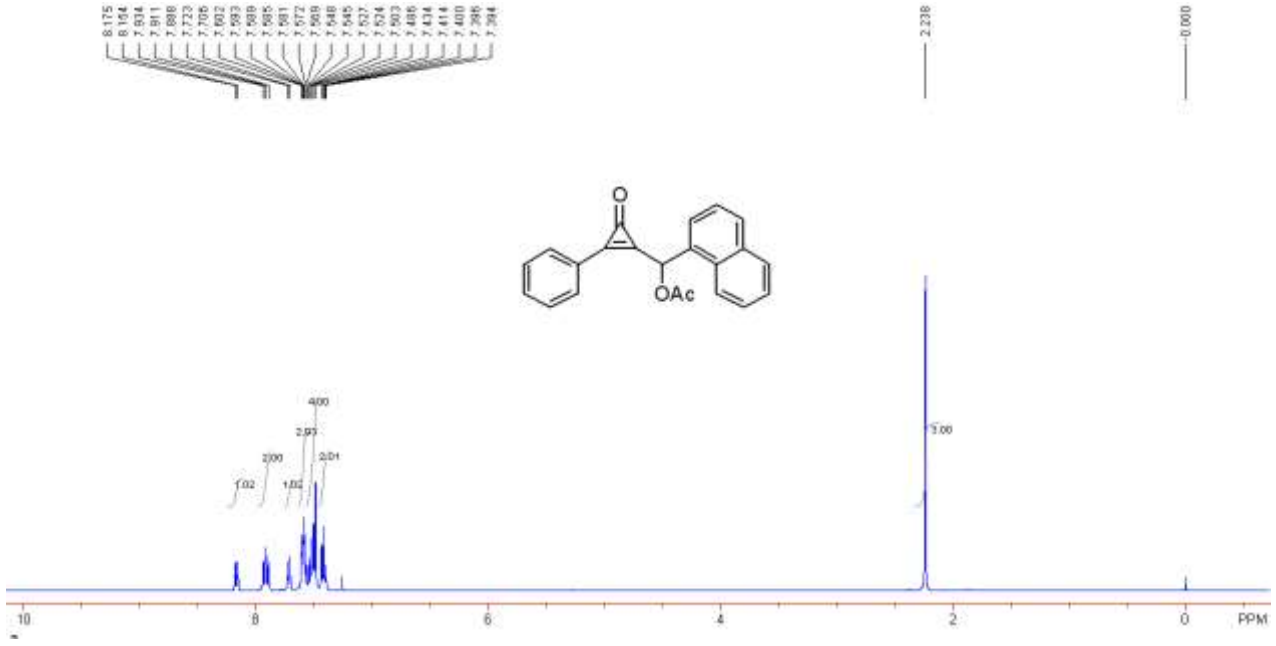
product **2r** (52% yield). A yellow solid. m.p. for **2r** = 161-162 ^{o}C; IR (CH_2Cl_2): ν 3057, 2961, 1854, 1744, 1637, 1508, 1488, 1448, 1369, 1218, 1168, 1125, 1022, 934, 816, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (1H, s), 7.91-7.83 (3H, m), 7.79-7.63 (2H, m), 7.58-7.46 (6H, m), 7.08 (1H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 153.8, 153.5, 151.1, 133.5, 133.2, 133.0, 131.8, 131.4, 129.3, 129.29, 128.2, 127.7, 127.3, 127.0, 126.8, 124.4, 122.7, 71.9, 20.9; MS (ESI) m/e 679.2 ($2M^{+}$+Na); HRMS (ESI) for $C_{22}H_{16}O_3Na$ (M^{+}+Na): 351.0992, Found: 351.0995.

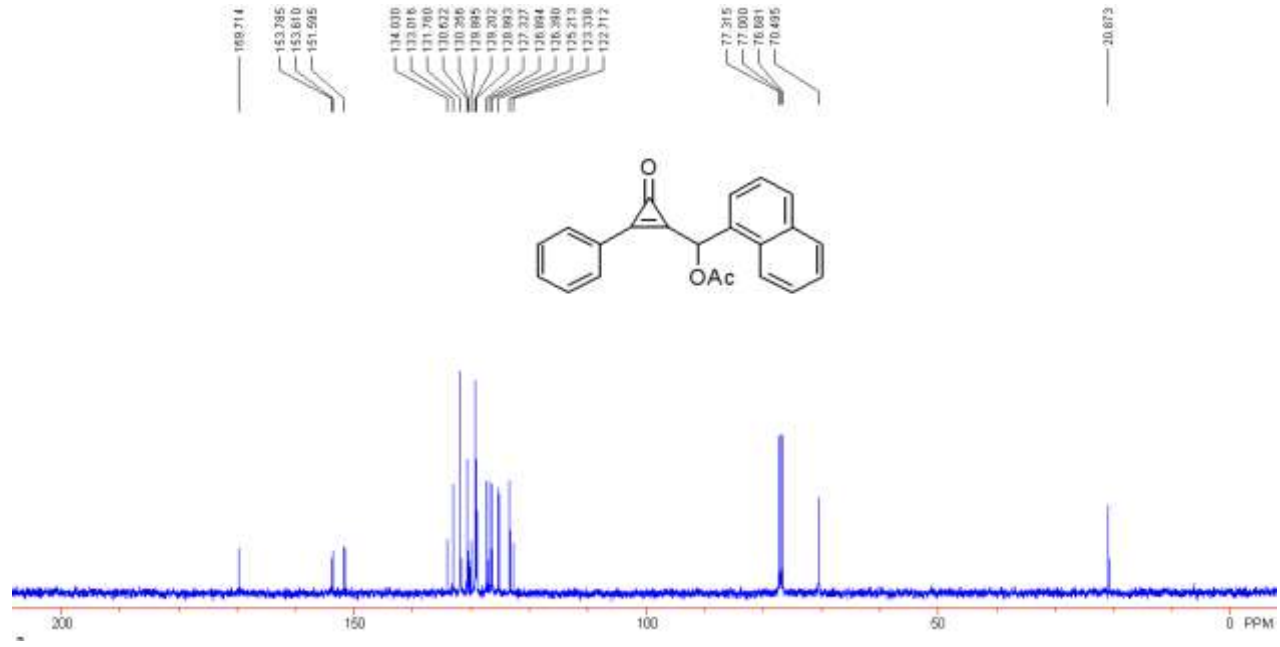


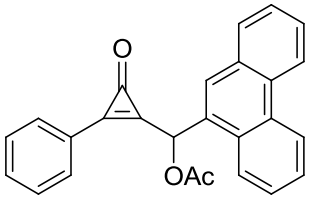


2s

naphthalen-1-yl(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2s: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2s** (40% yield). A yellow solid. m.p. for **2s** = 118-120 ^{o}C; IR (CH_2Cl_2): ν 3062, 1853, 1731, 1640, 1508, 1488, 1446, 1366, 1285, 1218, 1168, 1123, 1077, 1015, 934, 858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.16 (1H, d, *J* = 8.1 Hz), 7.91 (2H, t, *J* = 9.2 Hz), 7.71 (1H, d, *J* = 6.8 Hz), 7.60-7.57 (3H, m), 7.55-7.49 (4H, m), 7.43-7.39 (2H, m), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 153.8, 153.6, 151.6, 134.0, 133.0, 131.8, 130.6, 130.4, 130.0, 129.2, 129.0, 127.3, 126.9, 126.4, 125.2, 123.3, 122.7, 70.5, 20.9; MS (ESI) m/e 329.1 (M^{+}+H); HRMS (ESI) for $C_{22}H_{17}O_3$ (M^{+}+H): 329.1172, Found: 329.1169.

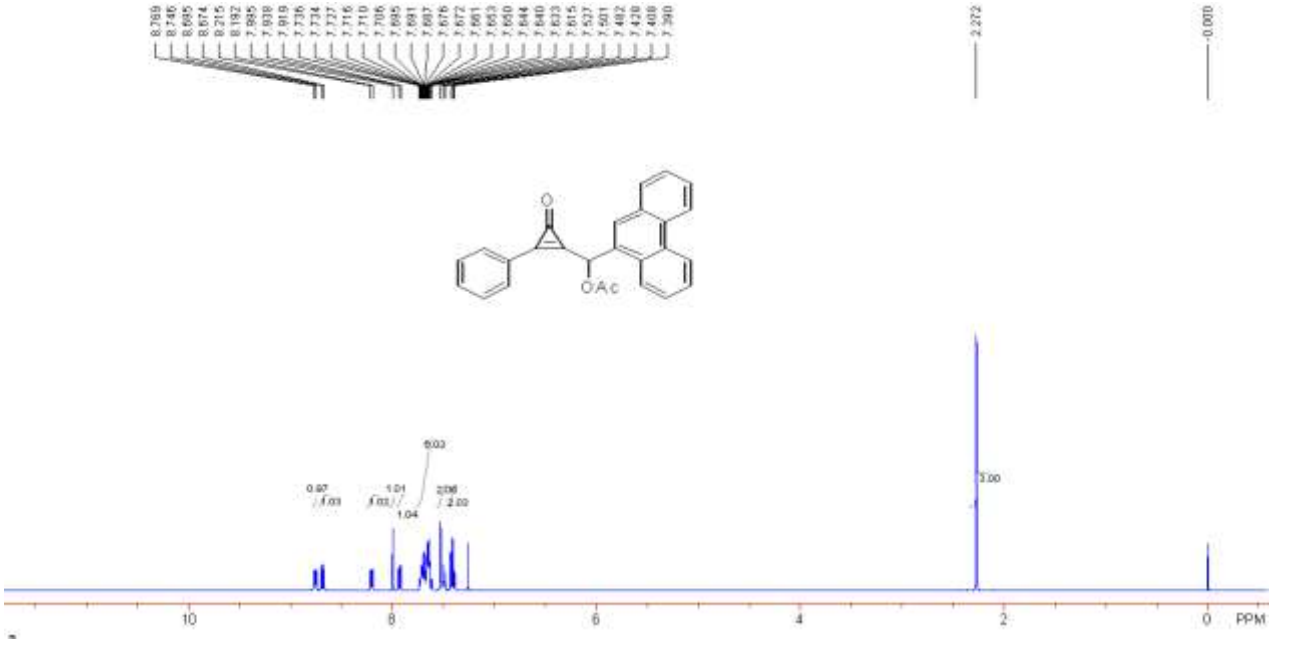


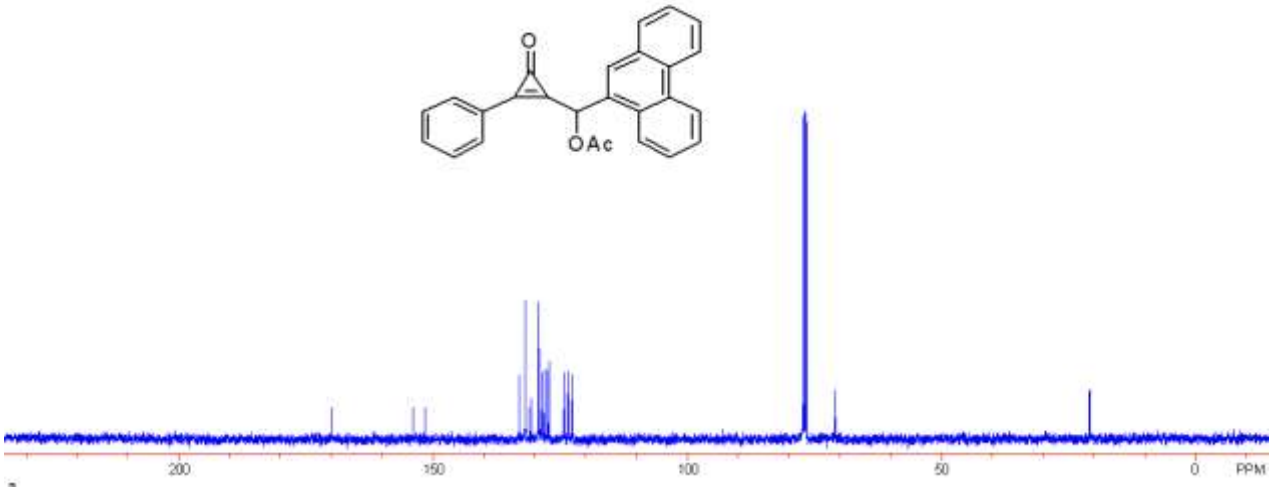


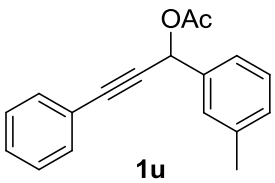


2t

(3-oxo-2-phenylcycloprop-1-enyl)(phenanthren-9-yl)methyl acetate 2t: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2t** (46% yield). A white solid. m.p. for **2t** = 177-179 ^{o}C; IR (CH_2Cl_2): ν 2924, 2853, 1854, 1746, 1636, 1530, 1488, 1448, 1370, 1260, 1217, 1175, 1094, 1019, 974, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.76 (1H, d, *J* = 9.2 Hz), 8.68 (1H, d, *J* = 8.4 Hz), 8.20 (1H, d, *J* = 9.2 Hz), 8.00 (1H, s), 7.30 (1H, d, *J* = 7.2 Hz), 7.74-7.62 (6H, m), 7.53-7.48 (2H, m), 7.43-7.39 (2H, m), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 154.0, 151.6, 133.1, 131.9, 131.1, 131.0, 130.7, 129.3, 129.2, 128.8, 128.6, 128.5, 128.0, 127.5, 127.2, 127.1, 124.3, 123.5, 122.8, 122.6, 71.0, 21.0; MS (ESI) m/e 319.1 (M-OAc); HRMS (ESI) for $C_{24}H_{15}O$ (M-OAc): 319.1117, Found: 319.1120.



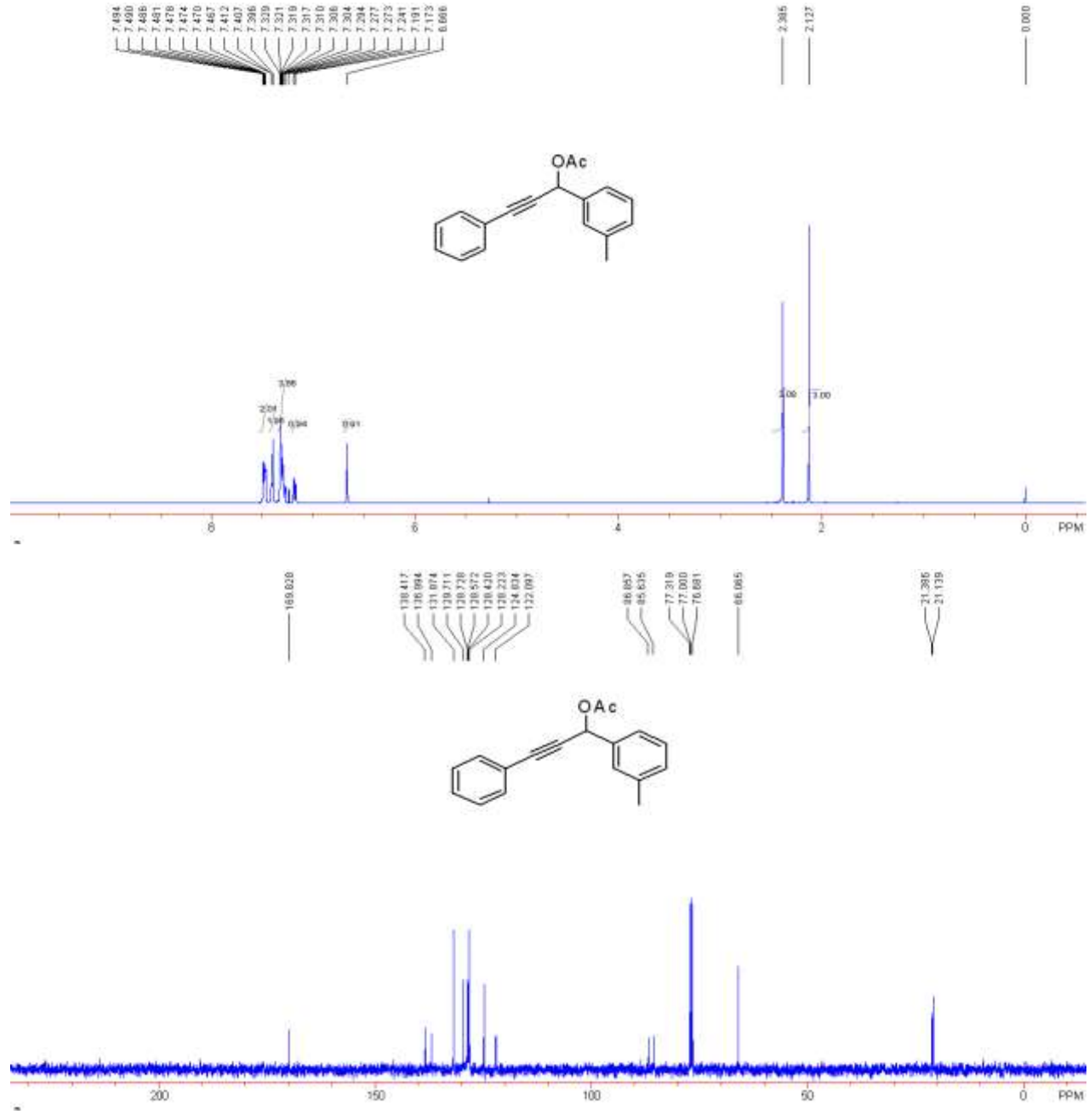


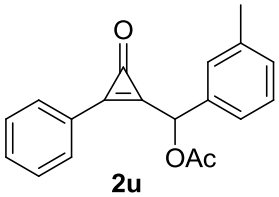


1u

3-phenyl-1-m-tolylprop-2-ynyl acetate 1u: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1u** (81% yield). A colorless oil. IR (CH_2Cl_2): ν 2923, 1739, 1608, 1490, 1443, 1368, 1332, 1259, 1218, 1153, 1012, 955, 915, 881 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.49-7.47 (2H, m), 7.41-7.40 (2H, m), 7.33-7.28 (4H, s), 7.18 (1H, d, *J* = 7.2 Hz), 6.67 (1H, s), 2.39 (3H, s), 2.13 (3H, s); ^{13}C NMR ($CDCl_3$,

100 MHz): δ 169.8, 138.4, 137.0, 131.9, 129.7, 128.7, 128.6, 128.4, 128.2, 124.8, 122.1, 86.9, 85.6, 66.1, 21.4, 21.1; MS (%) m/e 264 (60), 222 (100), 205 (72), 189 (39), 178 (37), 165 (9), 144 (11), 130 (13); HRMS (EI) for $C_{18}H_{16}O_2$: 264.1150; Found: 264.1151.

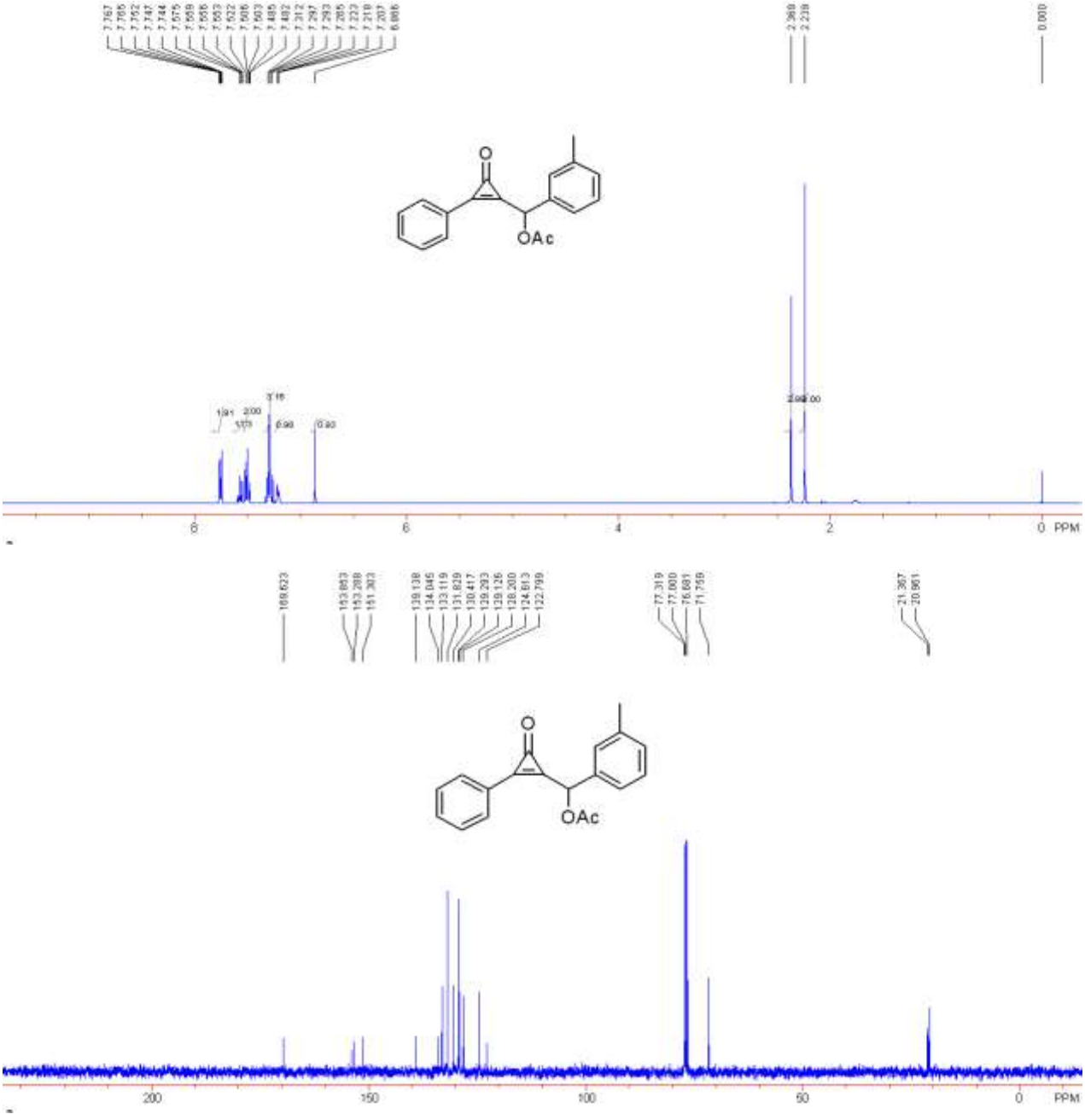


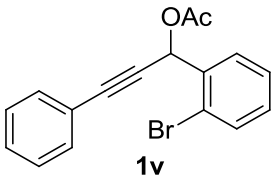


2u

(3-oxo-2-phenylcycloprop-1-enyl)(m-tolyl)methyl acetate 2u: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2u**

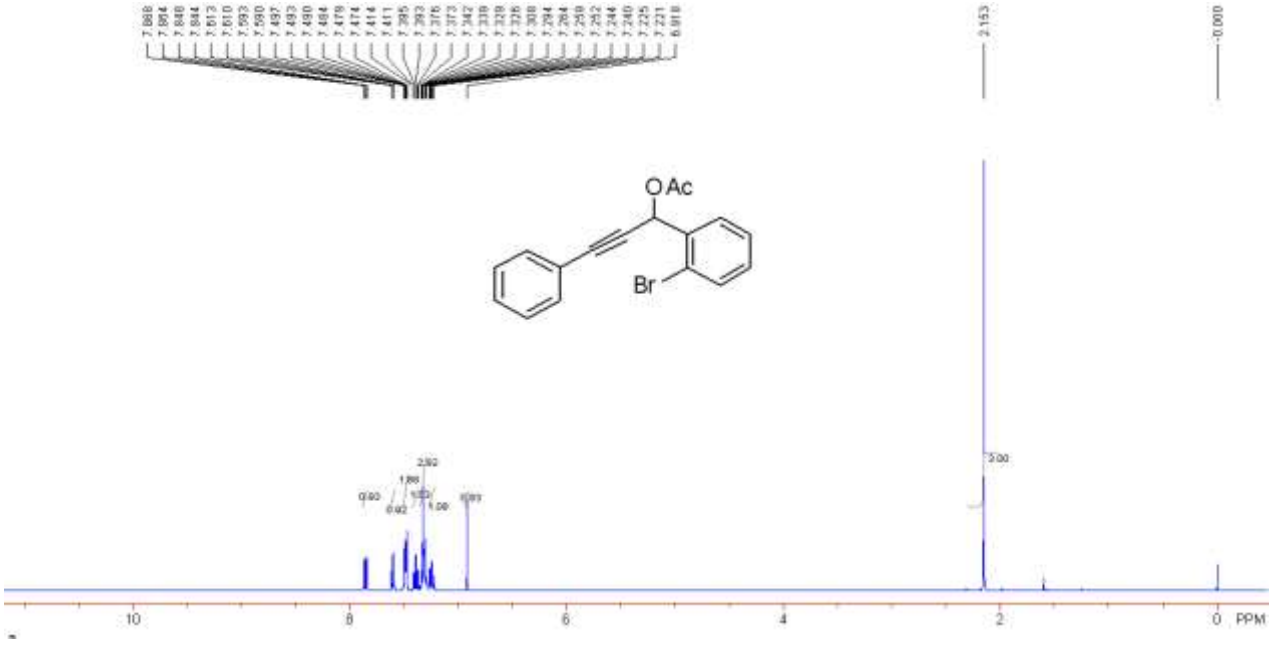
(46% yield). A yellow solid. m.p. for **2u** = 59-61 ^{o}C; IR (CH_2Cl_2): ν 2923, 1851, 1743, 1636, 1488, 1448, 1370, 1175, 1156, 974, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77-7.74 (2H, m), 7.59-7.55 (1H, m), 7.52-7.48 (2H, m), 7.33-7.21 (4H, m), 6.87 (1H, s), 2.37 (3H, s), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 153.9, 153.3, 151.3, 139.1, 134.0, 133.1, 131.8, 130.4, 129.3, 129.1, 128.2, 124.6, 122.8, 71.8, 21.4, 21.0; MS (ESI) m/e 293.1 (M^{+}+H); HRMS (ESI) for $C_{19}H_{16}O_3$ (M^{+}): 292.1099, Found: 292.1108.

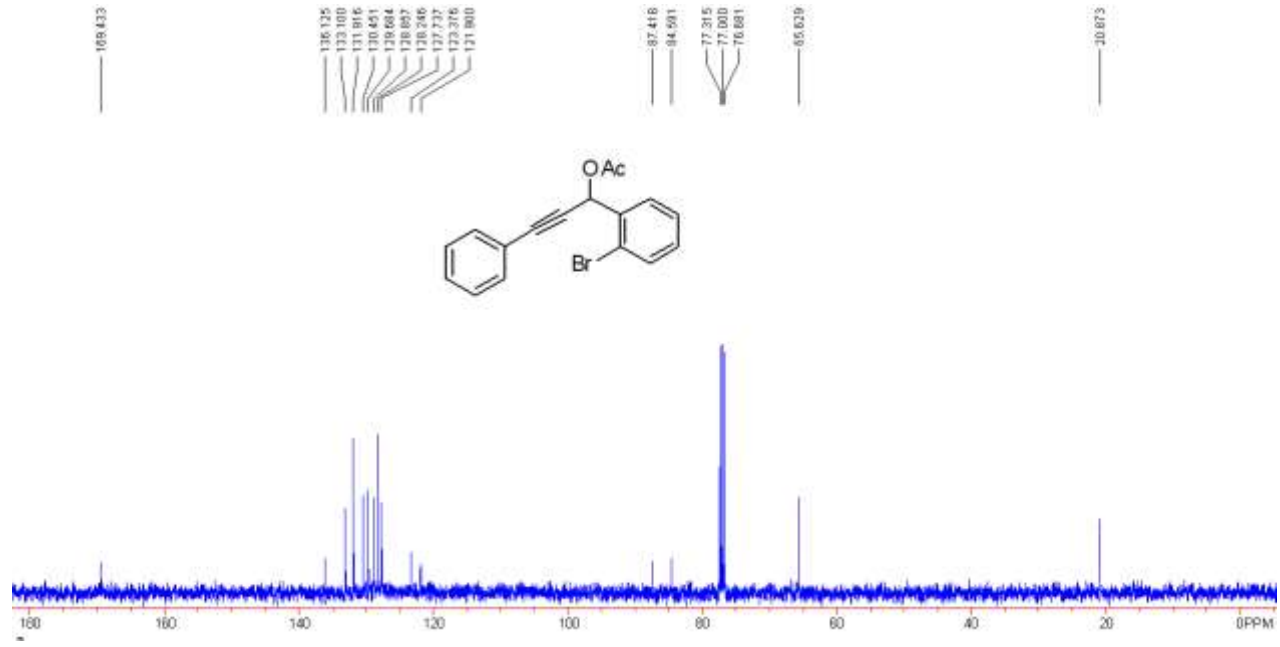


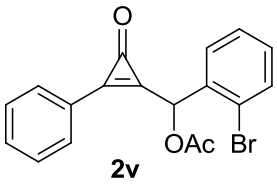


1v

1-(2-bromophenyl)-3-phenylprop-2-ynyl acetate 1v: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1v** (80% yield). A colorless oil. IR (CH_2Cl_2): ν 3061, 2228, 1741, 1570, 1490, 1470, 1441, 1368, 1334, 1213, 1120, 1070, 1014, 954, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.86 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.60 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.50-7.47 (2H, m), 7.41-7.37 (1H, m), 7.34-7.29 (3H, m), 7.26-7.22 (1H, m), 6.92 (1H, s), 2.15 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 136.1, 133.1, 131.9, 130.5, 129.7, 128.9, 128.2, 127.7, 123.4, 121.9, 87.4, 84.6, 65.6, 20.9; MS (%) m/e 328 (31), 288 (40), 269 (27), 259 (10), 207 (89), 189 (100), 178 (61); HRMS (EI) for $C_{17}H_{13}O_2Br$: 328.0099; Found: 328.0102.

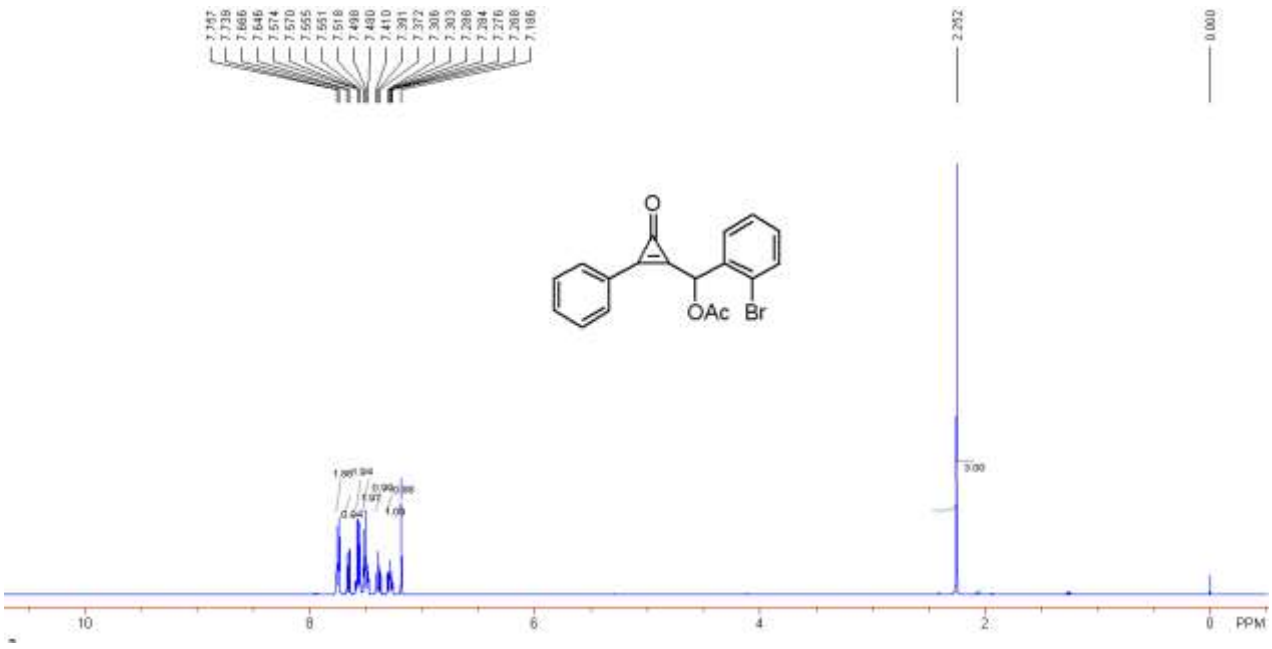


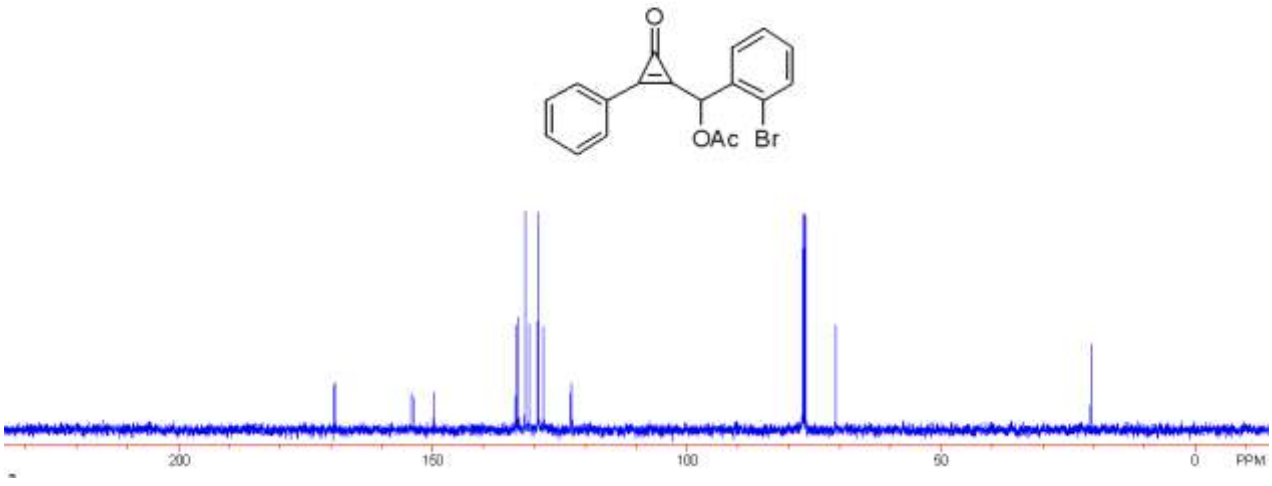


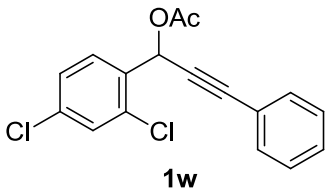


2v

(2-bromophenyl)(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2v: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2v** (51% yield). A yellow solid. m.p. for **2v** = 102-104 ^{o}C; IR (CH_2Cl_2): ν 3058, 1854, 1746, 1636, 1488, 1448, 1370, 1265, 1213, 1122, 1022, 927 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.75 (2H, d, *J* = 7.2 Hz), 7.66 (1H, d, *J* = 7.2 Hz), 7.59-7.55 (2H, m), 7.50 (2H, t, *J* = 7.2 Hz), 7.39 (1H, t, *J* = 7.2 Hz), 7.31-7.27 (1H, m), 7.19 (1H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 154.2, 153.7, 149.8, 133.7, 133.5, 133.2, 131.8, 131.0, 129.4, 129.3, 128.2, 123.0, 122.7, 70.8, 20.7; MS (ESI) m/e 357.0 (M^++H); HRMS (ESI) for $C_{18}H_{13}O_3Br$ (M^+): 356.0048, Found: 356.0055.



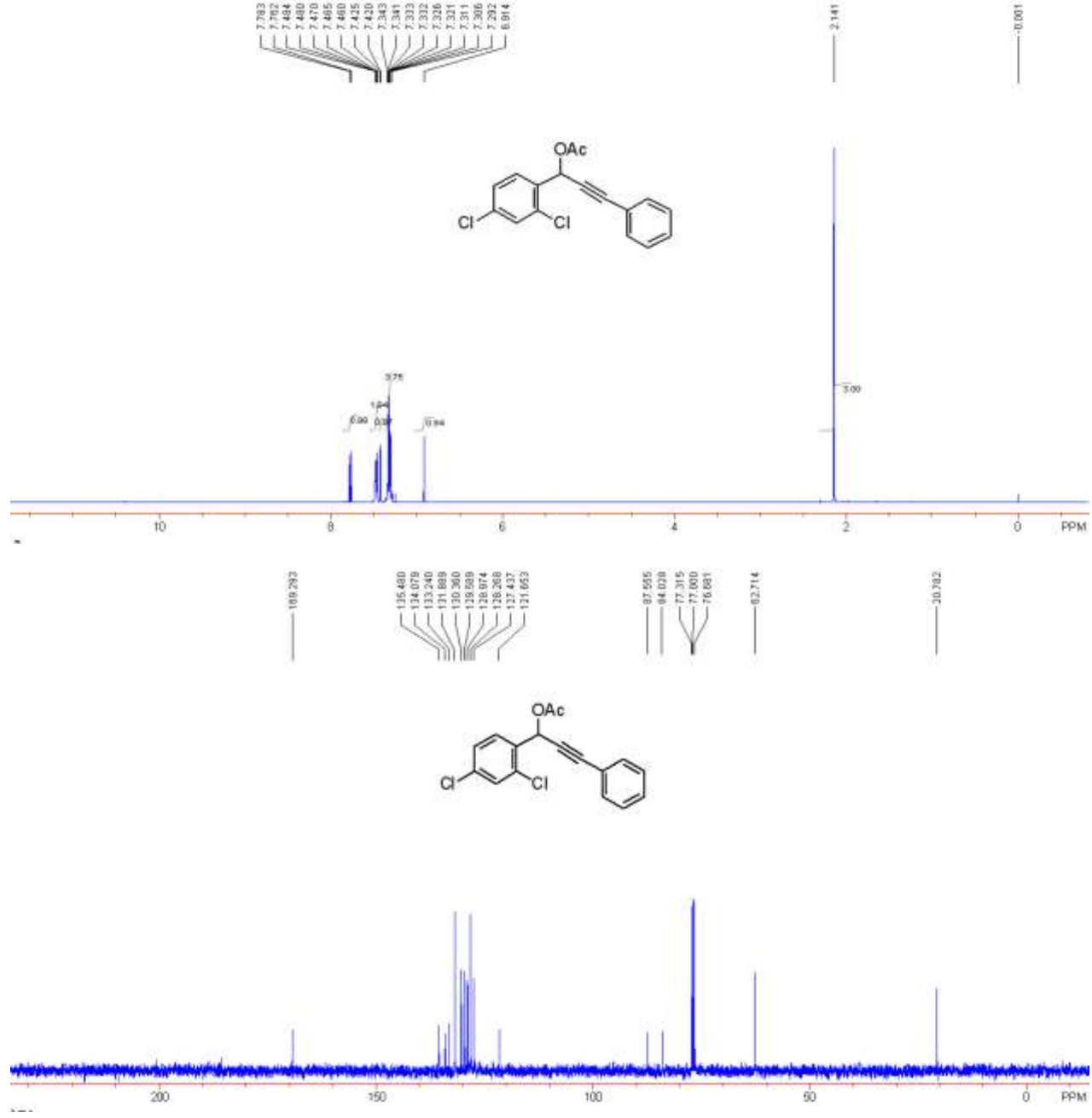


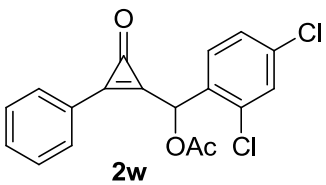


1w

1-(2,4-dichlorophenyl)-3-phenylprop-2-ynyl acetate 1w: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1w** (95% yield). A yellow oil. IR (CH_2Cl_2): ν 2962, 2230, 1746, 1589, 1563, 1490, 1471, 1368, 1216, 1139, 1102, 1057, 954, 913 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (1H, d, J = 8.4 Hz), 7.47 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.42 (1H, d, J = 2.0 Hz), 7.34-7.29 (4H, m), 6.92 (1H, s), 2.14 (3H, s);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 135.3, 134.1, 133.2, 131.9, 130.4, 129.6, 129.0, 128.3, 127.4, 121.7, 87.6, 84.0, 62.7, 20.8; MS (%) m/e 318 (65), 276 (66), 259 (79), 247 (30), 241 (100), 223 (55), 212 (36), 189 (50); HRMS (EI) for $C_{17}H_{12}O_2Cl_2$: 318.0214; Found: 318.0218.

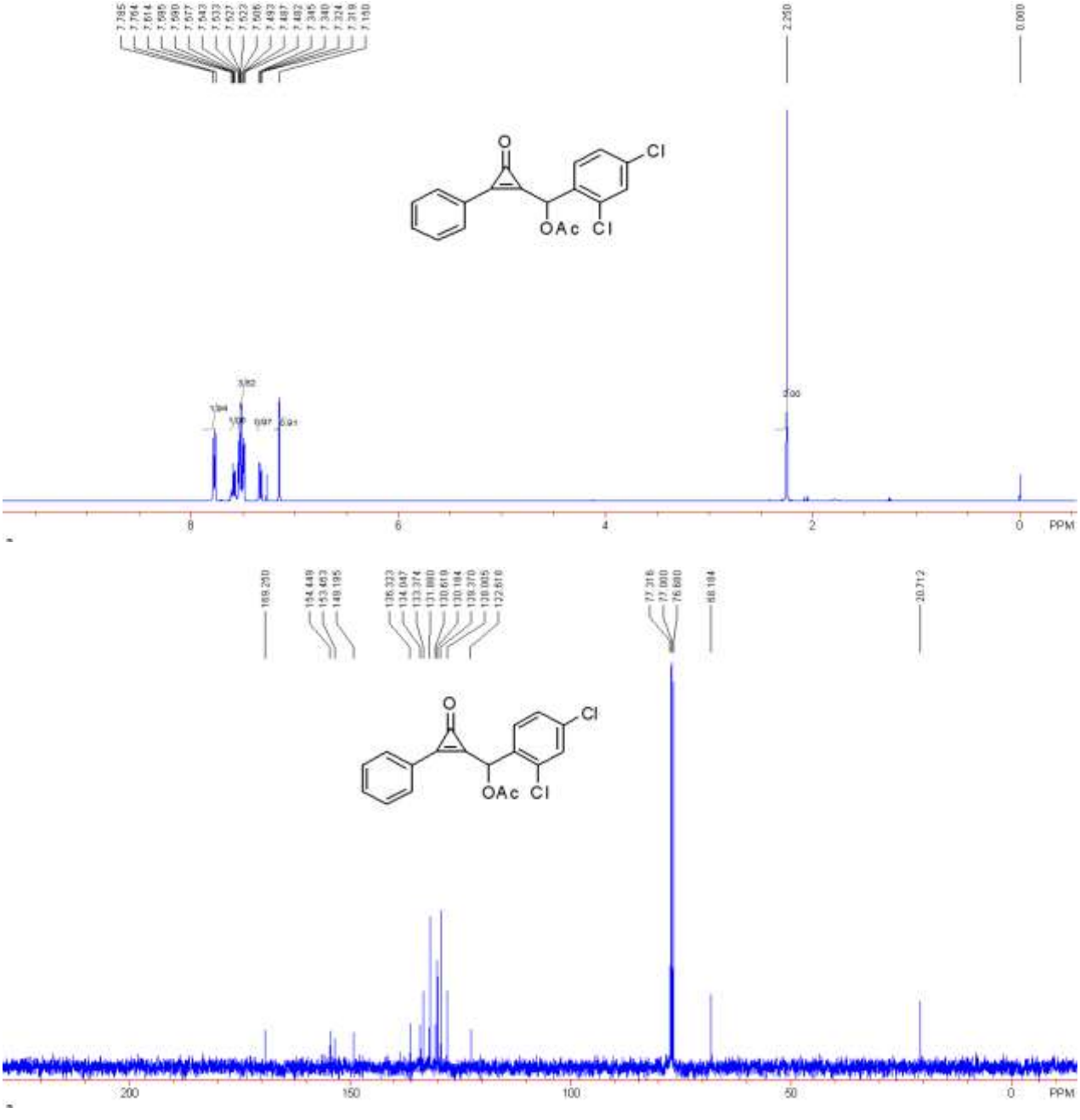


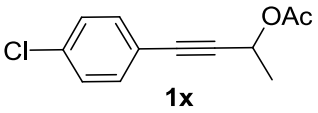


2w

(2,4-dichlorophenyl)(3-oxo-2-phenylcycloprop-1-enyl)methyl acetate 2w: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target

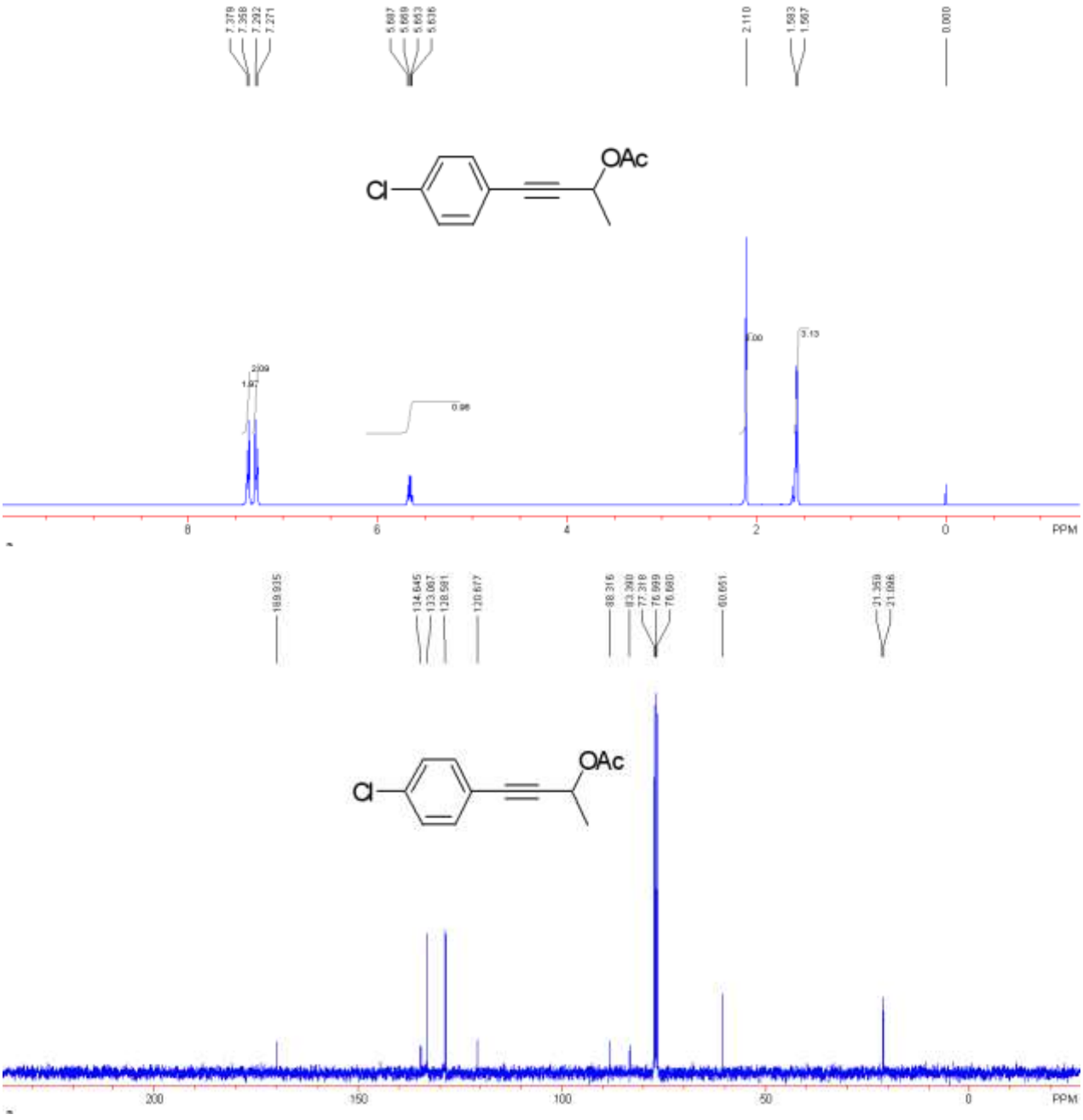
product **2w** (58% yield). A yellow solid. m.p. for **2w** = 85-86 ^{o}C; IR (CH_2Cl_2): ν 2962, 1854, 1746, 1637, 1588, 1473, 1448, 1370, 1259, 1212, 1089, 1020, 866 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (2H, d, J = 8.4 Hz), 7.61-7.58 (1H, m), 7.54-7.48 (4H, m), 7.33 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.15 (1H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 154.4, 153.5, 149.2, 136.3, 134.0, 133.4, 131.9, 130.6, 130.2, 129.4, 128.0, 122.6, 68.2, 20.7; MS (ESI) m/e 347.0 (M^++H); HRMS (ESI) for $C_{18}H_{12}O_3Cl_2$ (M^+): 346.0163, Found: 346.0169.

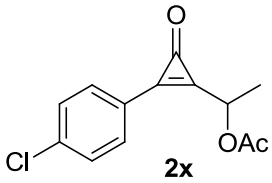




1x

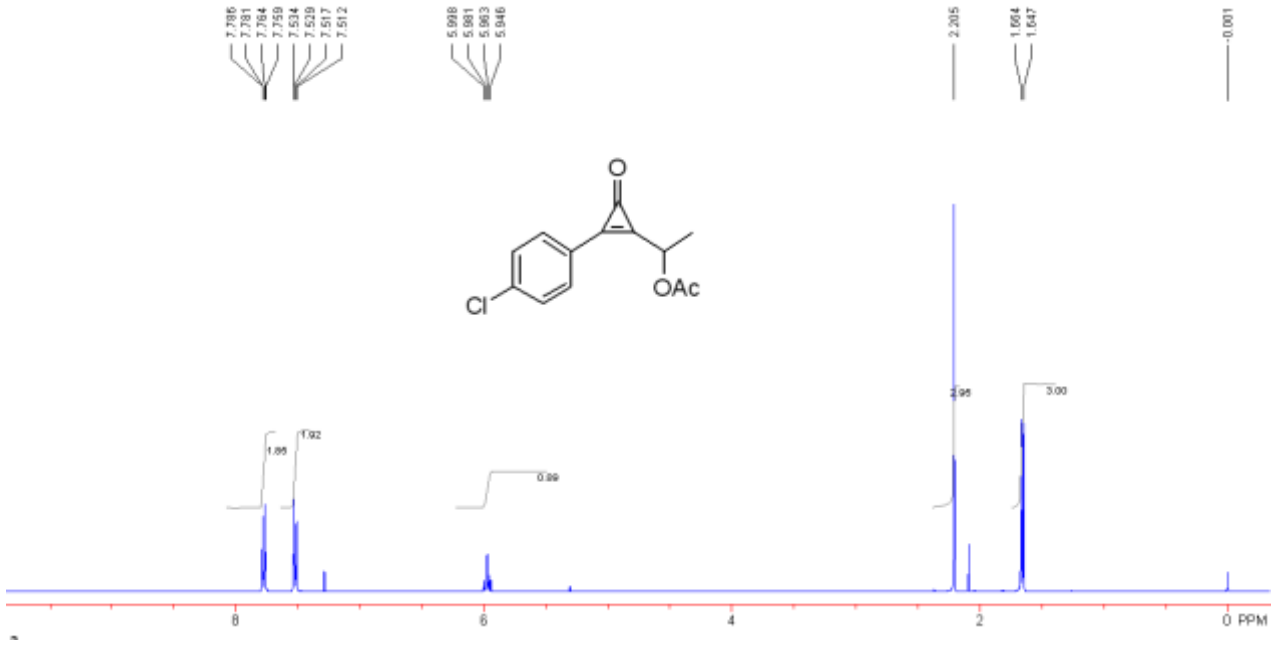
4-(4-chlorophenyl)but-3-yn-2-yl acetate 1x: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **1x** (87% yield). A yellow oil. IR (CH_2Cl_2): ν 2962, 1743, 1488, 1448, 1370, 1339, 1259, 1225, 1083, 1030, 1014, 952 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.37 (2H, d, *J* = 8.4 Hz), 7.28 (2H, d, *J* = 8.4 Hz), 5.66 (1H, q, *J* = 2.8 Hz), 2.11 (3H, s), 1.58 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 134.6, 133.1, 128.6, 120.7, 88.3, 83.4, 60.7, 21.4, 21.1; MS (%) m/e 222 (18), 207 (45), 180 (45), 162 (100), 145 (63), 136 (19), 127 (91), 115 (24), 101 (24); HRMS (EI) for $C_{12}H_{11}O_2Cl$: 222.0448; Found: 222.0447.

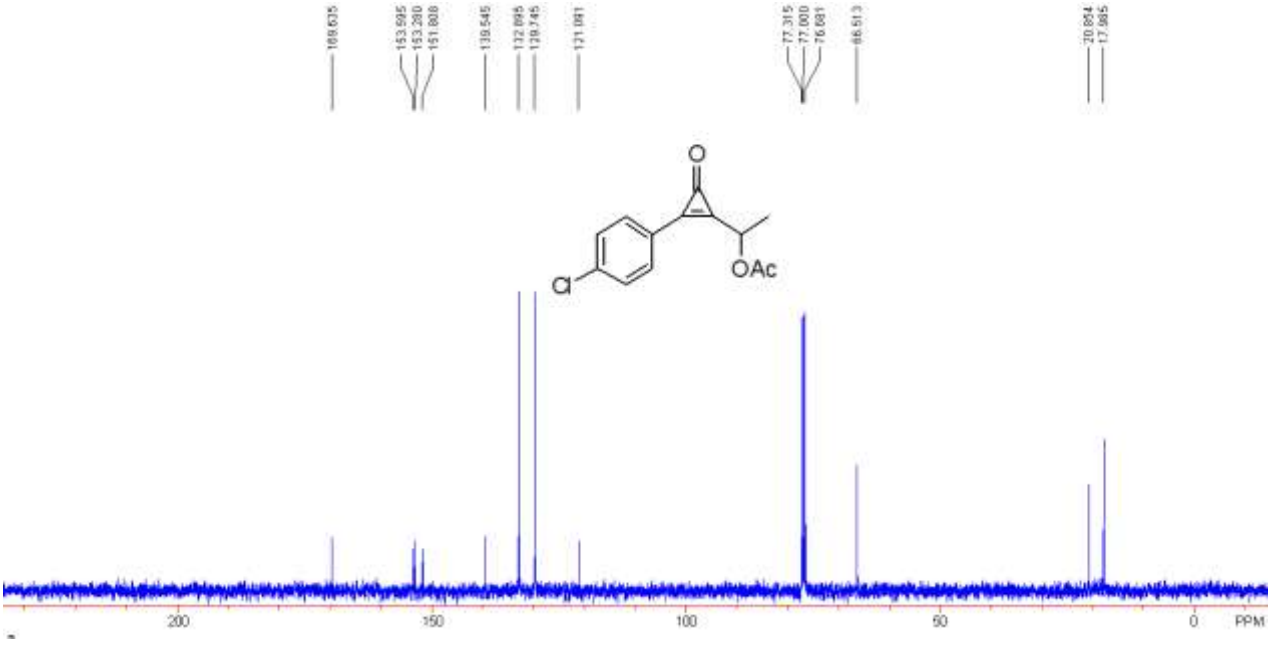


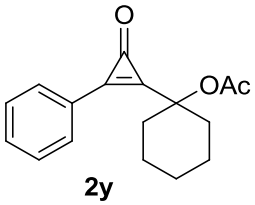


2x

1-(2-(4-chlorophenyl)-3-oxocycloprop-1-enyl)ethyl acetate 2x: Following the general procedure, the mixture was purified by column chomatography using silica gel to give the target product **2x** (53% yield). A yellow solid. m.p. for **2x** = 50-52 ^{o}C; IR (CH_2Cl_2): ν 2936, 1850, 1741, 1639, 1589, 1485, 1444, 1402, 1371, 1222, 1033, 1014, 948 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (2H, dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 7.52 (2H, dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 5.97 (1H, q, J = 6.8 Hz), 2.21 (3H, s), 1.66 (3H, d, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 153.6, 153.3, 151.8, 139.5, 132.9, 129.7, 121.1, 66.5, 20.9, 18.0; MS (ESI) m/e 251.0 (M^{+}+H); HRMS (ESI) for $C_{13}H_{11}O_3Cl$ (M^{+}): 250.0397, Found: 250.0404.

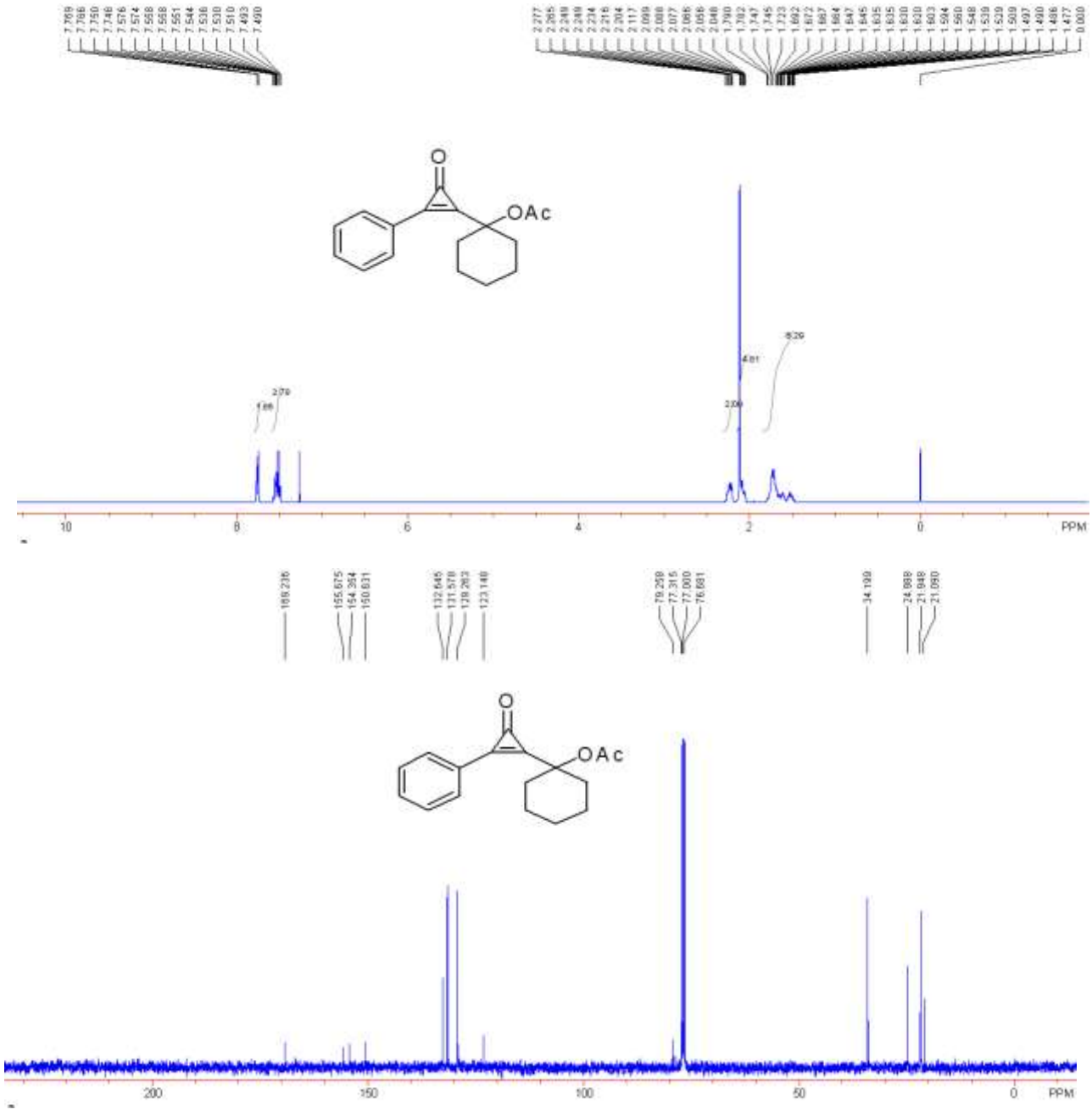


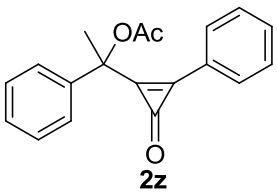




2y

1-(3-oxo-2-phenylcycloprop-1-enyl)cyclohexyl acetate 2y: Following the general procedure, the mixture was purified by column chomatography using silica gel to give the target product **2y** (80% yield). A yellow solid. m.p. for **2y** = 83-85 ^{o}C; IR (CH_2Cl_2): ν 2939, 2862, 1854, 1739, 1633, 1489, 1448, 1369, 1259, 1228, 1089, 1013, 970, 929, 796, 770, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.76 (2H, dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.56-7.49 (3H, m), 2.28-2.21 (2H, m), 2.12-2.06 (5H, m), 1.77-1.53 (6H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.2, 155.7, 154.4, 150.6, 132.6, 131.6, 129.3, 123.1, 79.3, 34.2, 25.0, 21.9, 21.1; MS (ESI) m/e 271.1 (M^++H); HRMS (ESI) for $C_{17}H_{18}O_3$ (M^+): 270.1256, Found: 270.1251.

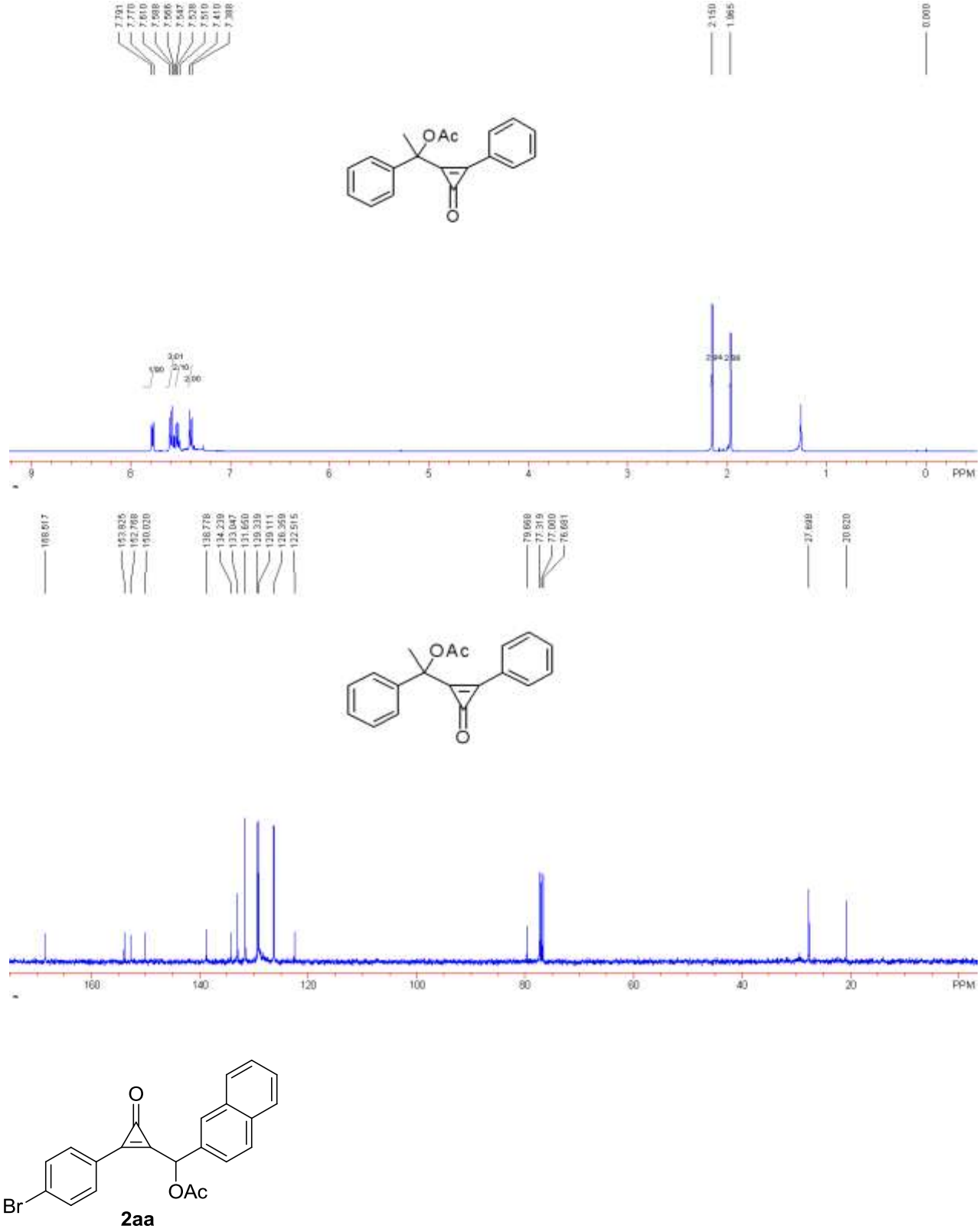




2z

1-(3-oxo-2-phenylcycloprop-1-enyl)-1-phenylethyl acetate 2z: Following the general procedure, the mixture was purified by column chomatography using silica gel to give the target product **2z** (45% yield). A yellow oil; IR (CH_2Cl_2): ν 2962, 2849, 1857, 1742, 1635, 1490, 1447, 1403, 1369, 1261, 1225, 1093, 1012, 940, 799, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80 (2H, d, *J* = 8.4 Hz), 7.60 (2H, d, *J* = 8.4 Hz), 7.57-7.51 (3H, m), 7.40 (2H, d, *J* = 8.8 Hz), 2.15 (3H, s), 1.97 (3H,

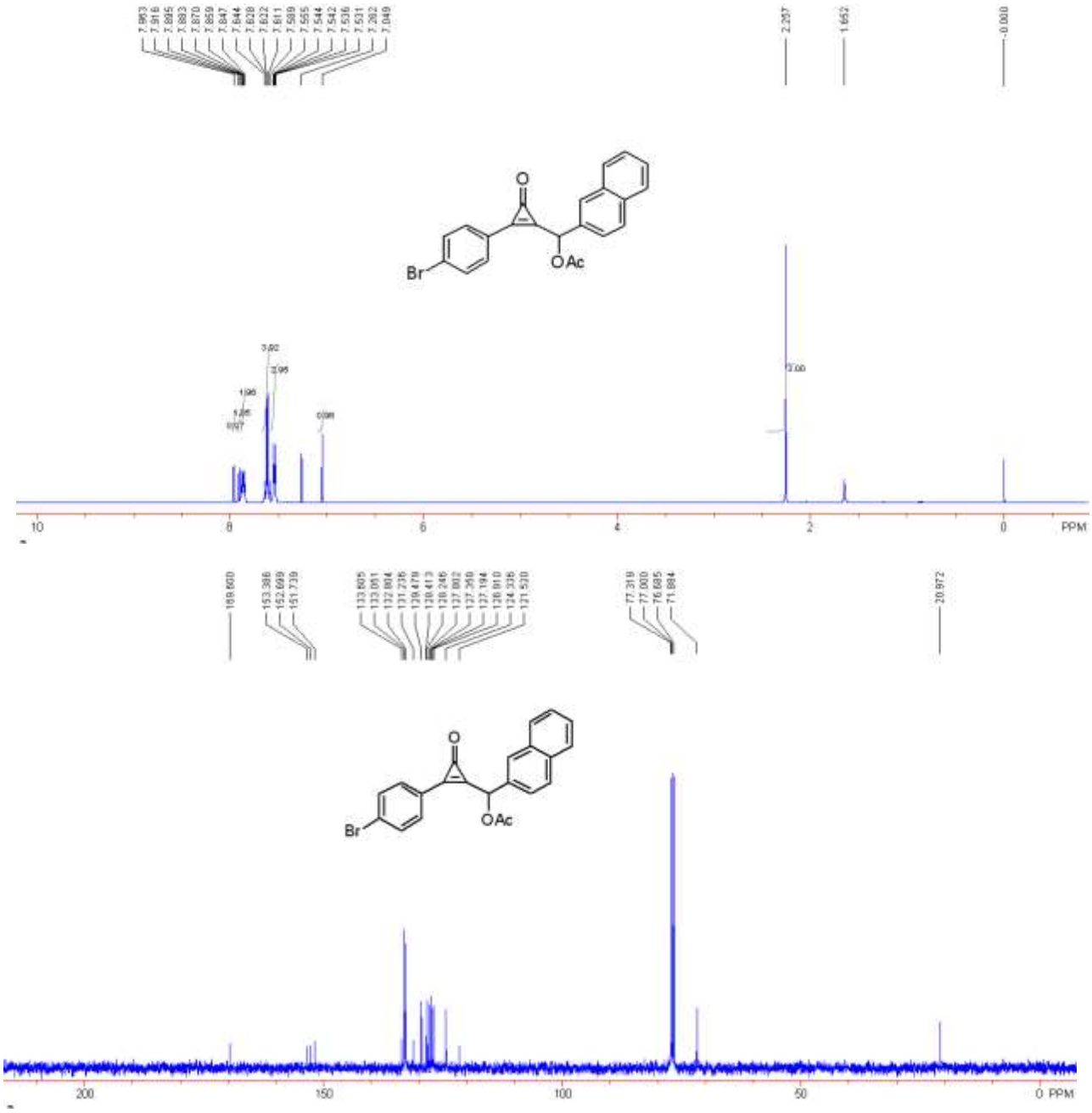
s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.6, 153.9, 152.8, 150.0, 138.8, 134.2, 133.0, 131.7, 129.3, 129.1, 126.4, 122.5, 79.7, 27.7, 20.8; MS (ESI) m/e 239.1 (M-OAc-CO); HRMS (ESI) for $C_{16}H_{12}Cl$ (M-OAc-CO): 239.0622, Found: 239.0626.

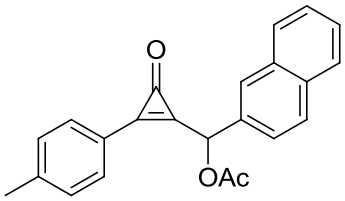


2aa

(2-(4-bromophenyl)-3-oxocycloprop-1-enyl)(naphthalen-2-yl)methyl acetate 2aa: Following the

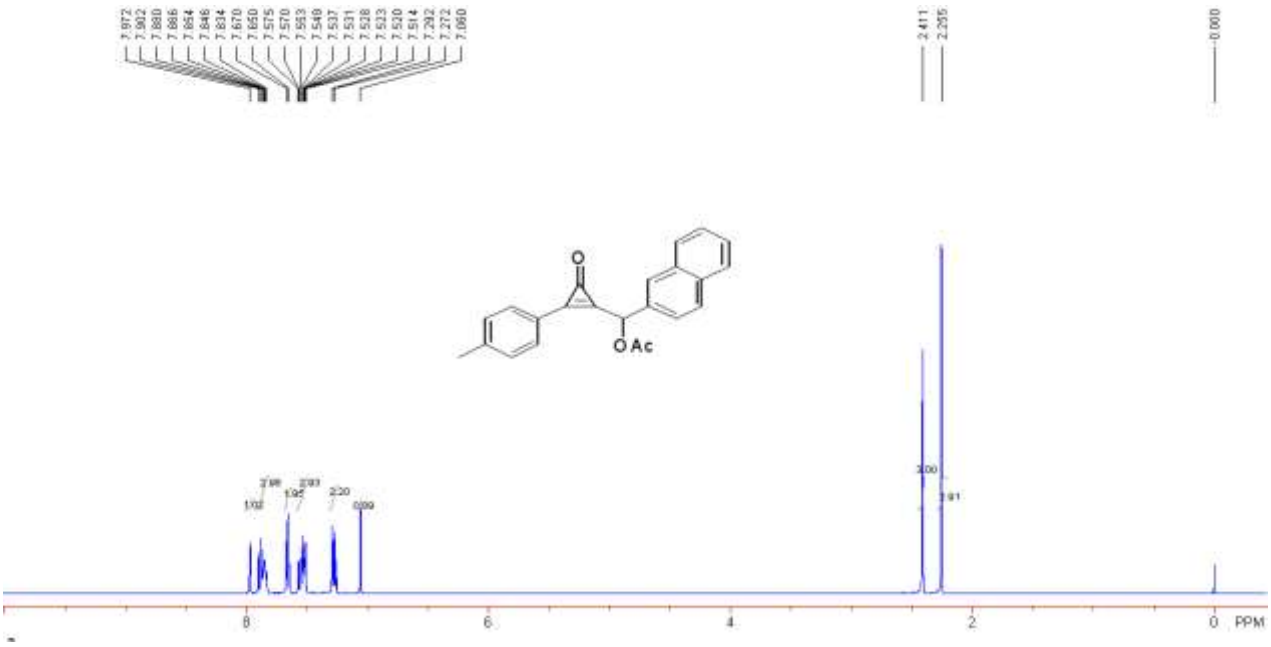
general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2aa** (38% yield). A yellow solid. m.p. for **2aa** = 165-168 ^{o}C; IR (CH_2Cl_2): ν 3062, 1850, 1736, 1637, 1583, 1478, 1397, 1366, 1215, 1207, 1103, 1016, 948, 829 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.96 (1H, s), 7.91 (1H, d, *J* = 8.4 Hz), 7.88-7.85 (2H, m), 7.64-7.59 (4H, m), 7.56-7.53 (3H, m), 7.05 (1H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 153.4, 152.7, 151.7, 133.6, 133.0, 132.8, 131.2, 129.5, 128.4, 128.2, 127.8, 127.4, 127.2, 126.9, 124.3, 121.5, 71.9, 21.0; MS (ESI) m/e 429.9 (M^{+}+Na); HRMS (ESI) for $C_{22}H_{15}O_3BrNa$ (M^{+}+Na): 429.0107, Found: 429.0097.

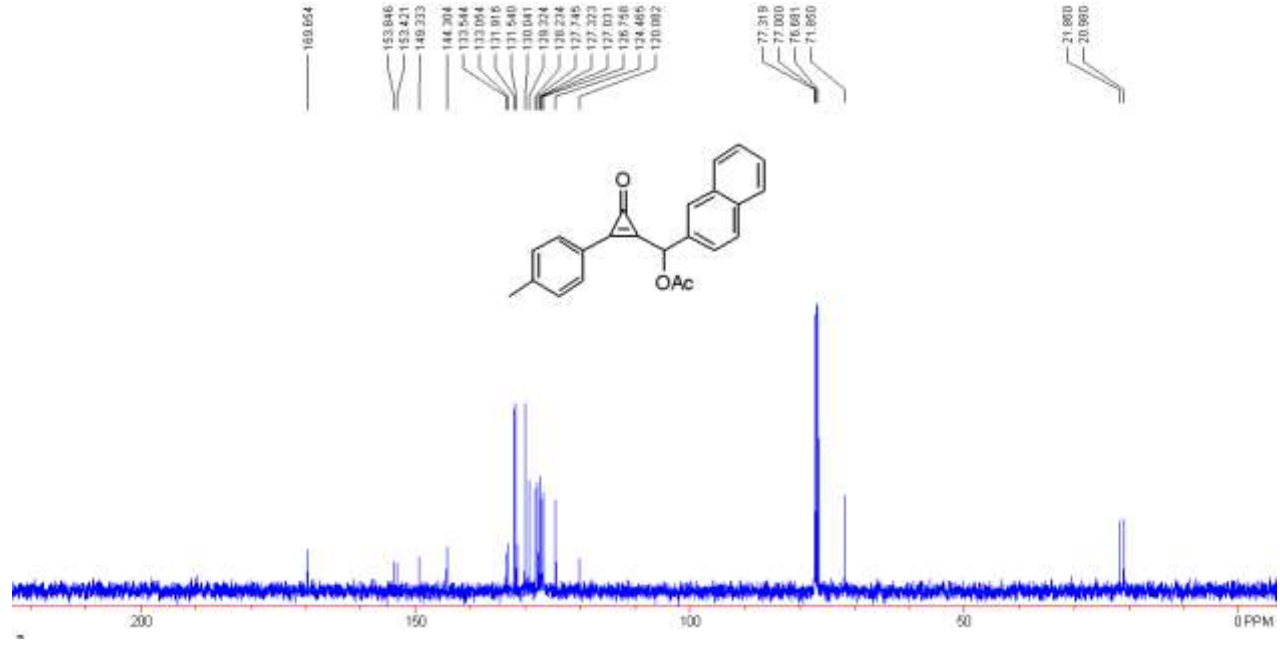


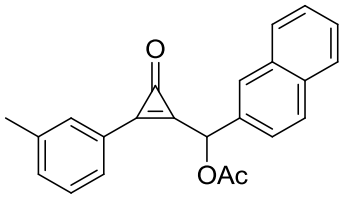


2bb

naphthalen-2-yl(3-oxo-2-p-tolylcycloprop-1-enyl)methyl acetate 2bb: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2bb** (39% yield). A yellow solid. m.p. for **2bb** = 180-182 ^{o}C; IR (CH_2Cl_2): ν 3060, 1850, 1789, 1735, 1631, 1504, 1426, 1366, 1306, 1219, 1207, 1172, 1123, 970, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (1H, s), 7.90-7.83 (3H, m), 7.66 (2H, d, *J* = 8.0 Hz), 7.58-7.51 (3H, m), 7.28 (2H, d, *J* = 8.0 Hz), 7.06 (1H, s), 2.41 (3H, s), 2.26 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 153.8, 153.4, 149.3, 144.3, 133.5, 133.0, 131.9, 131.5, 130.0, 129.3, 128.2, 127.7, 127.3, 127.0, 126.8, 124.5, 120.1, 71.9, 21.9, 21.0; MS (%) m/e 342 (25), 300 (100), 281 (4), 253 (6), 239 (12), 228 (10), 207 (2), 43 (11); HRMS (EI) for $C_{23}H_{18}O_3$: 342.1256; Found: 342.1258.

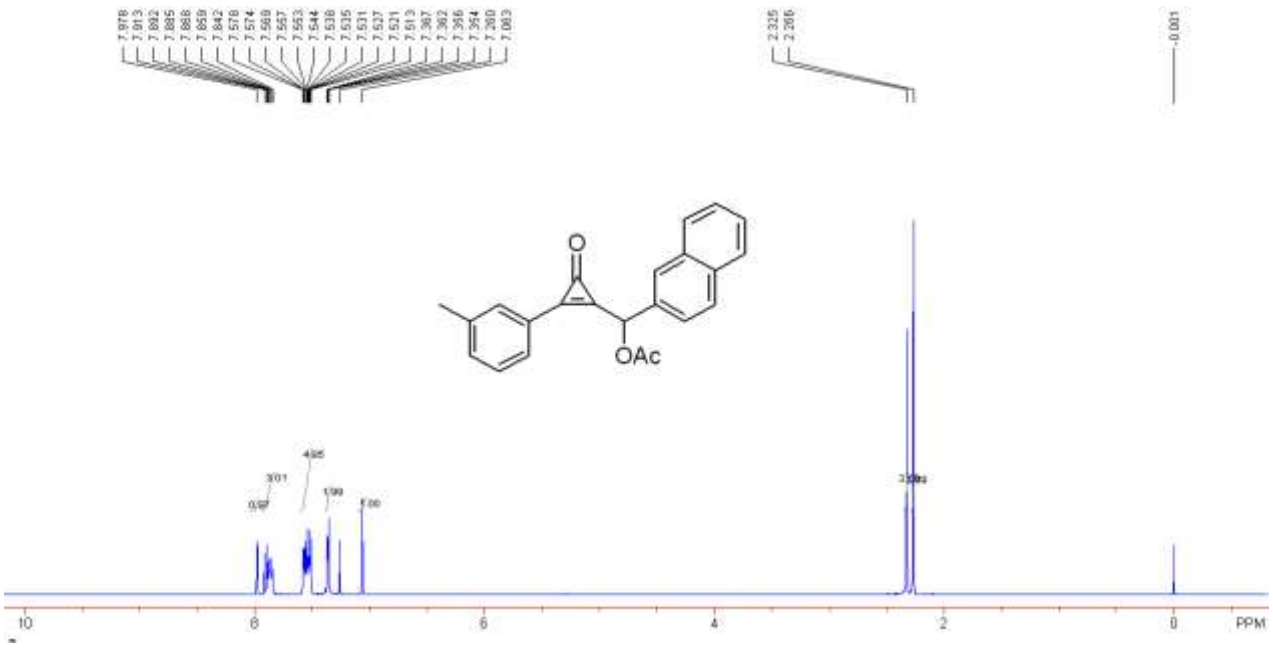


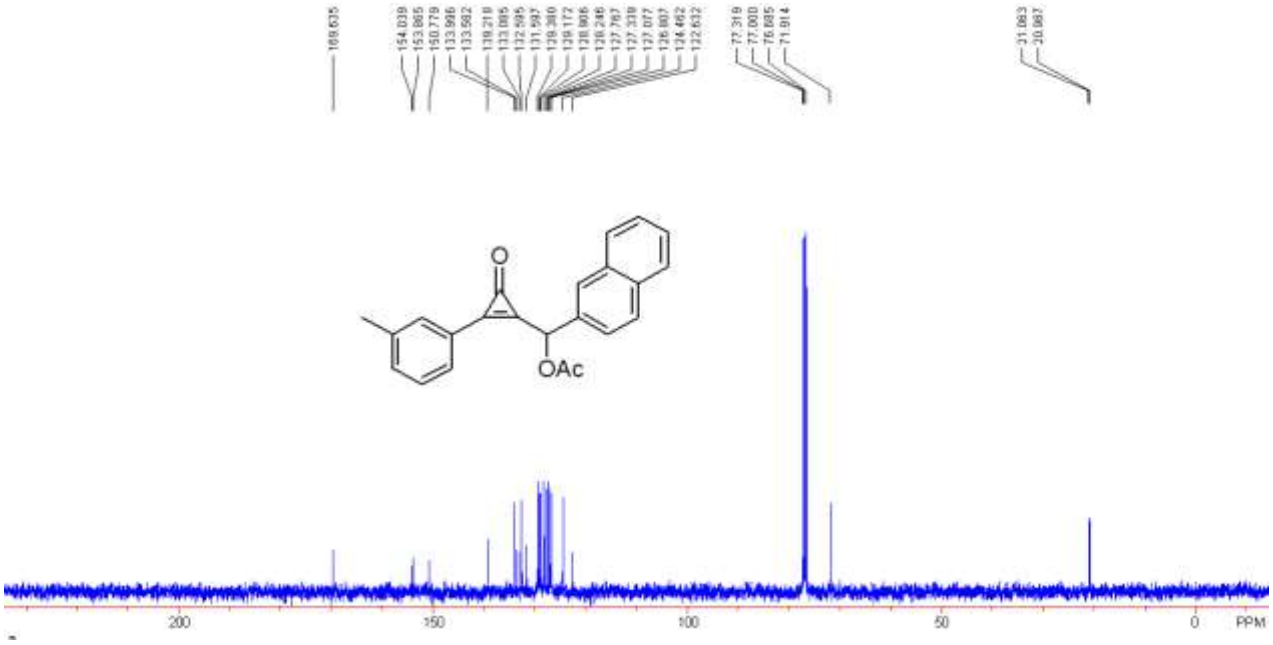


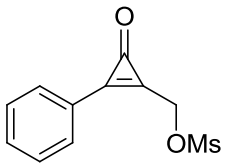


2cc

naphthalen-2-yl(3-oxo-2-m-tolylcycloprop-1-enyl)methyl acetate 2cc: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2cc** (30% yield). A yellow solid. m.p. for **2cc** = 126-128 ^{o}C; IR (CH_2Cl_2): ν 3025, 1848, 1736, 1636, 1599, 1365, 1218, 1207, 1195, 1016, 971, 867 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98 (1H, s), 7.91-7.84 (3H, m), 7.58-7.51 (5H, m), 7.37-7.36 (2H, m), 7.06 (1H, s), 2.33 (3H, s), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 154.0, 153.9, 150.8, 139.2, 134.0, 133.6, 133.1, 132.6, 131.6, 129.4, 129.2, 128.9, 128.2, 127.8, 127.3, 127.1, 126.8, 124.5, 122.6, 71.9, 21.1, 21.0; MS (ESI) m/e 685.1 ($2M^{+}$+H); HRMS (ESI) for $C_{23}H_{18}O_3Na$ (M^{+}+Na): 365.1150, Found: 365.1148.



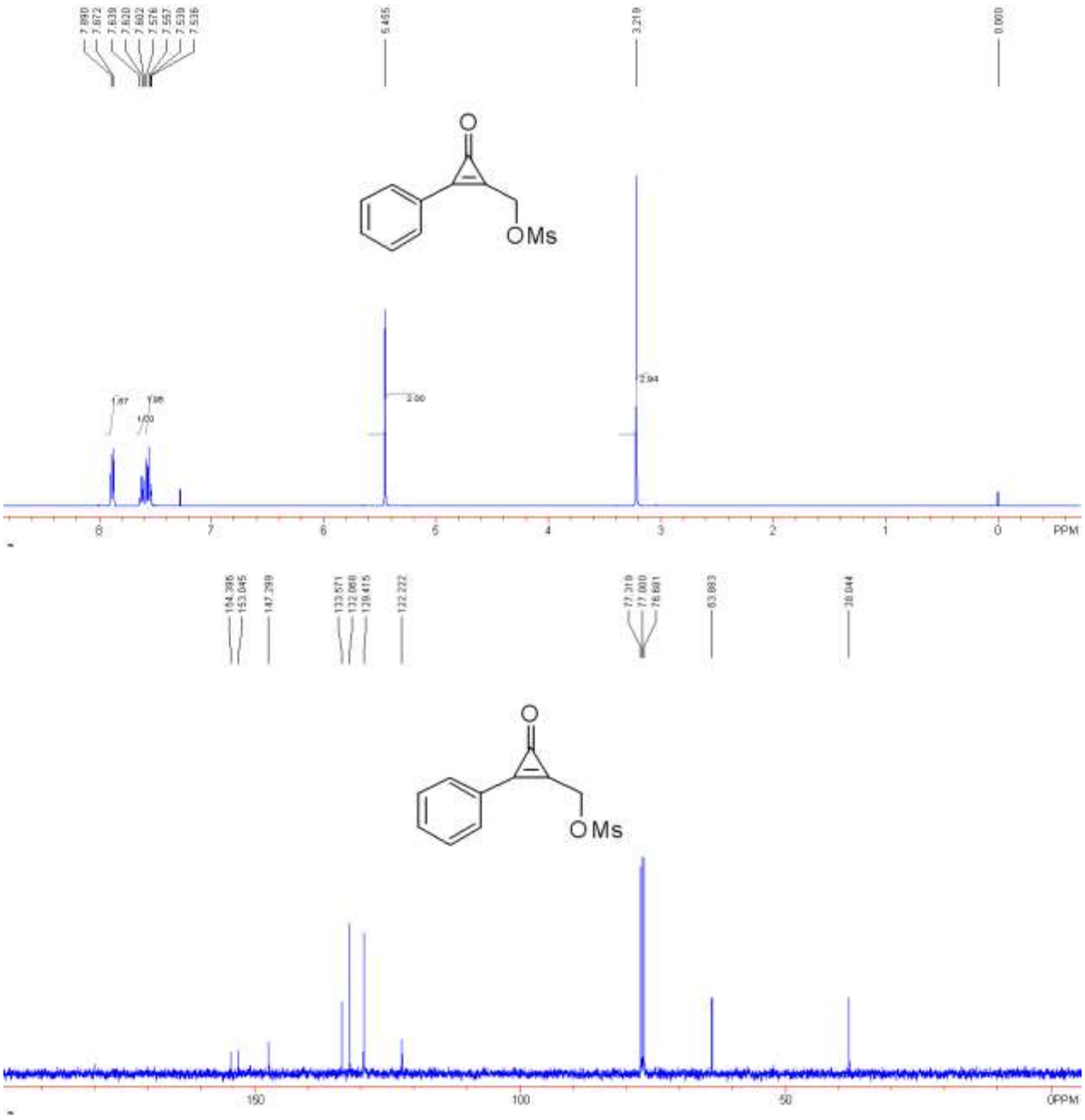




2dd

(3-oxo-2-phenylcycloprop-1-enyl)methyl methanesulfonate 2ab: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **2ab** (59% yield). A white solid. m.p. for **2ab** = 122-124 ^{o}C; IR (CH_2Cl_2): ν 2961, 2922, 1861, 1841, 1630, 1449, 1356, 1260, 1167, 1094, 982, 893 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (2H, d, *J* =

7.2 Hz), 7.62 (1H, t, *J* = 7.2 Hz), 7.58-7.54 (2H, m), 5.46 (2H, s), 3.22 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.4, 153.0, 147.3, 133.6, 132.1, 129.4, 122.2, 63.9, 38.0; MS (ESI) m/e 239.0 (M^++H); HRMS (ESI) for $C_{11}H_{11}O_4S$ (M^++H): 239.0373, Found: 239.0378.



Reference:

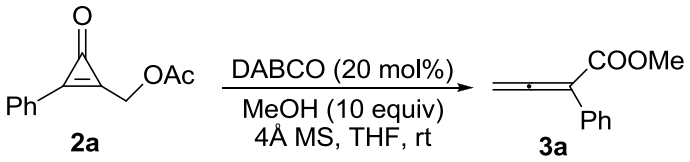
[1] Wang, F.; Luo, T.; Hu, J. B.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. K. S. Olah, G. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7153-7157.

[2] Cheng, Z.-L.; Chen, Q.-Y. *Chin. J. Chem.* **2006**, *24*, 1219-1224.

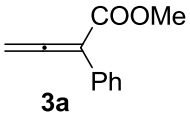
[3] Peng, C.; Wang, Y.; Wang, J. D. *J. Am. Chem. Soc*. **2008**, *130*, 1566-1567.

[4] Nishikado, H.; Nakatsuji, H.; Ueno, K.; Nagase, R.; Tanabe, Y. *Synlett* **2010**, 2087-2092.
[5] Poeylaunt-Palena, A. A.; Testero, S. A.; Mata, E. G. *Chem. Commun*. **2011**, *47*, 1565-1467.

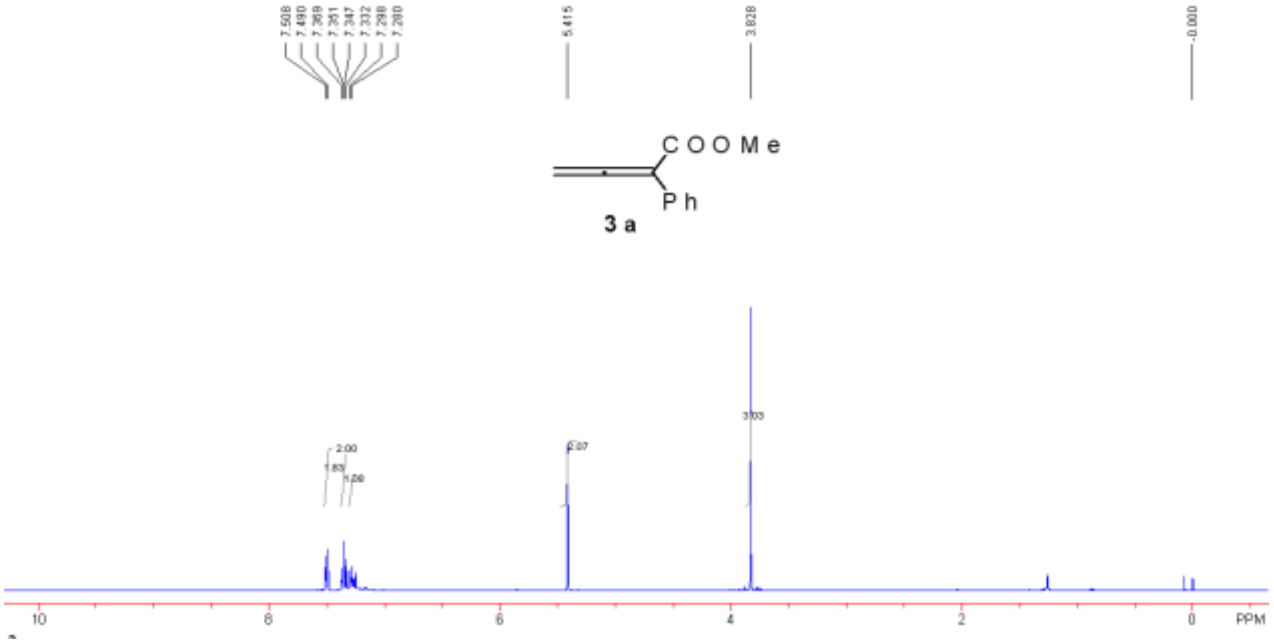
General Procedure for the Preparation of 3 from the Reaction of 2a with MeOH Using 3a as an Example in the Presence of DABCO

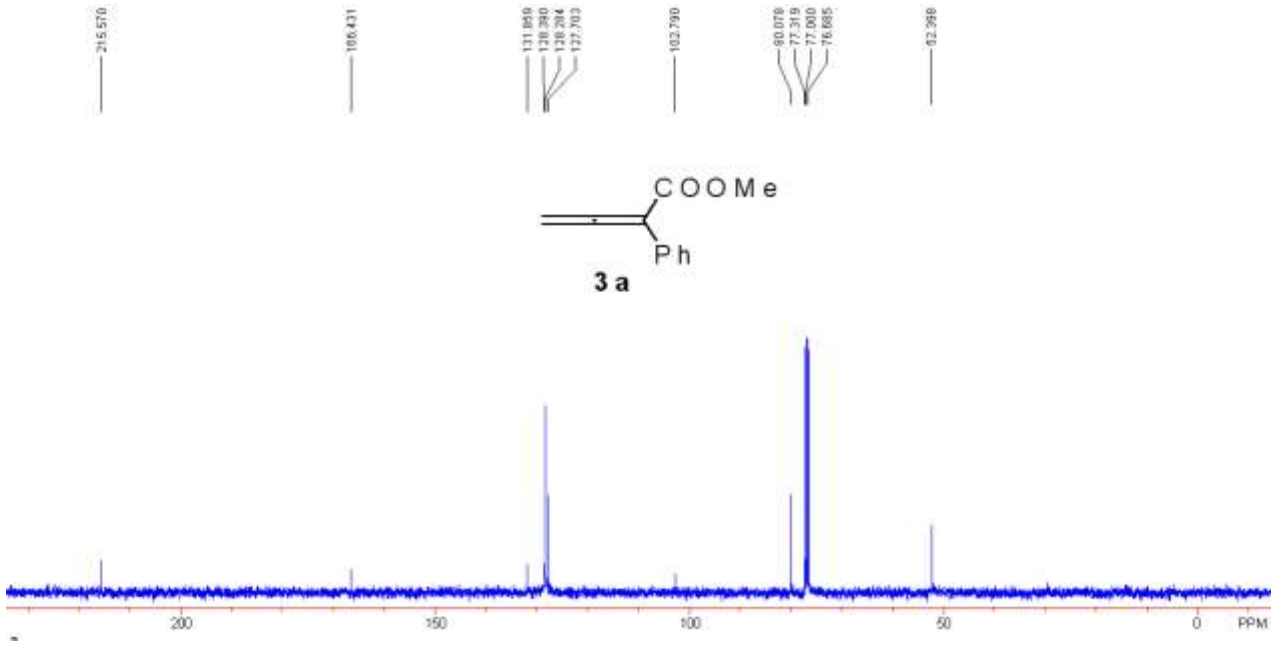


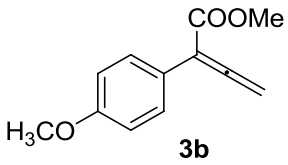
To a mixture of **2a (**0.20 mmol, 46 mg**)**, MeOH (10.0 mmol), DABCO (0.04 mmol, 5.0 mg) and 50 mg 4Å MS was added 2.0 mL of THF at room temperature (25 ^{o}C) under argon. The reaction solution was monitored by TLC. After the reaction was completed, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/16) to give the target product **3a**.



methyl 2-phenylbuta-2,3-dienoate 3a: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3a** (33 mg, 95% yield). A yellow oil. This is a known compound.[2] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.50 (2H, d, *J* = 7.2 Hz), 7.37-7.33 (2H, m), 7.29 (1H, d, *J* = 7.2 Hz), 5.42 (2H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.6, 166.4, 131.9, 128.4, 128.3, 127.7, 102.8, 80.1, 52.4.

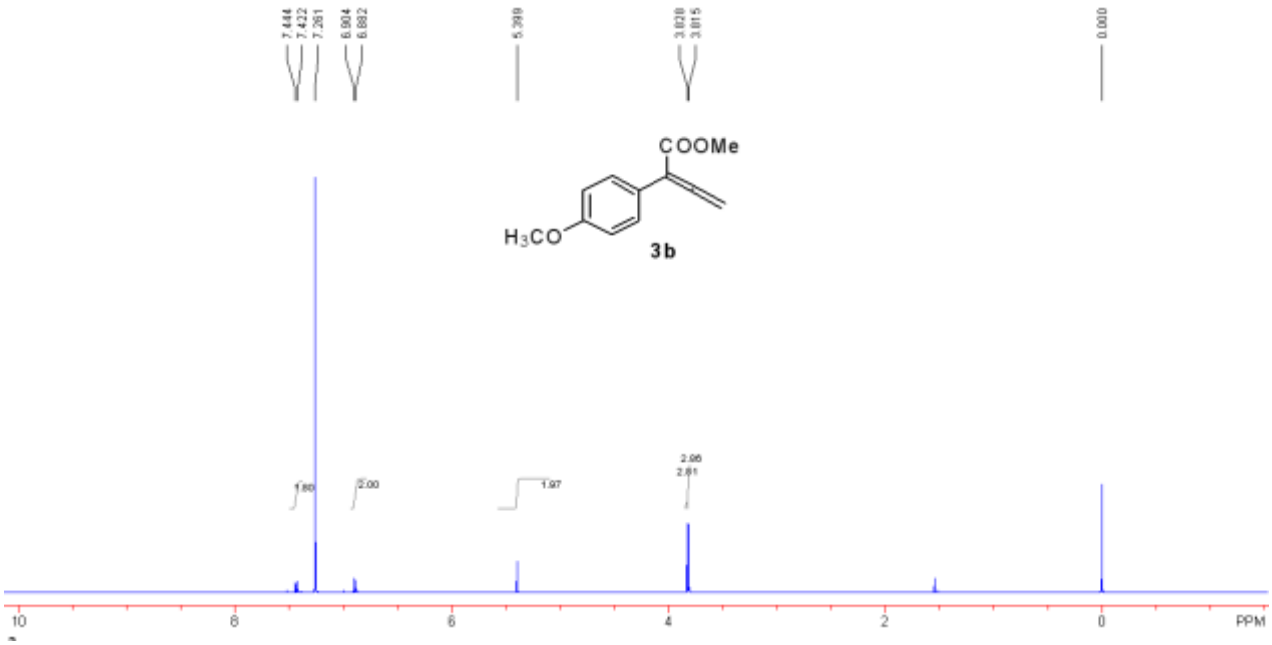


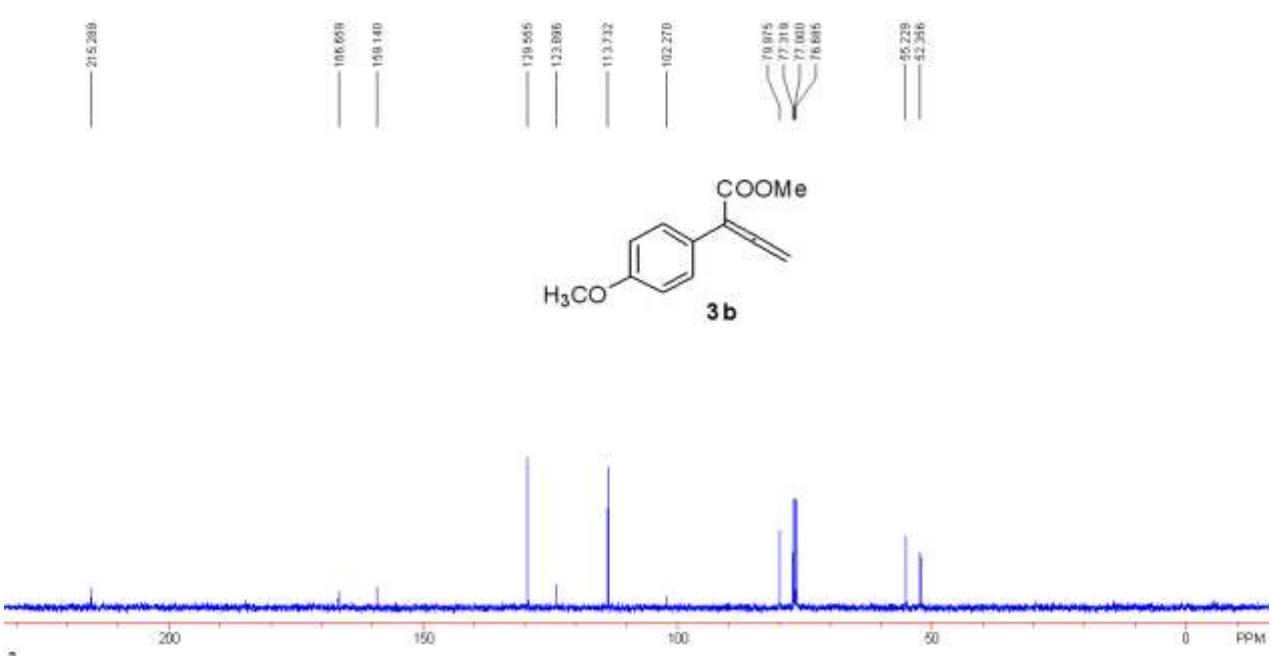


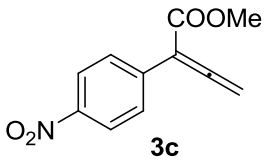


3b

methyl 2-(4-methoxyphenyl)buta-2,3-dienoate 3b: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3b** (38 mg, 93% yield). A white solid. m.p. for **3b** = 72-73 ^{o}C; IR (CH_2Cl_2): ν 2962, 1717, 1607, 1511, 1257, 1085, 1011, 859, 792 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.43 (2H, d, *J* = 8.8 Hz), 6.89 (2H, d, *J* = 8.8 Hz), 5.40 (2H, s), 3.83 (3H, s), 3.82 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.3, 166.7, 159.1, 129.6, 123.9, 113.7, 102.3, 80.0, 55.2, 52.4; MS (%) m/e 204 (96), 189 (4), 175 (9), 145 (92), 133 (100), 102 (47), 76 (19), 63 (8); HRMS (EI) for $C_{12}H_{12}O_3$: 204.0786; Found: 204.0787.

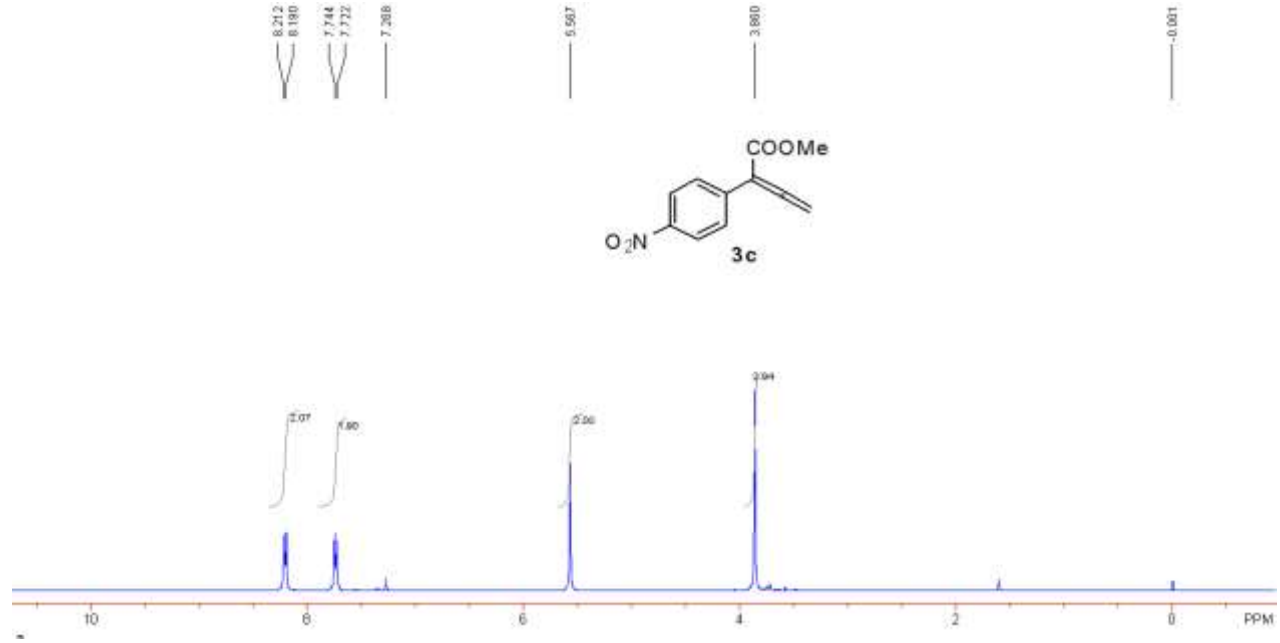


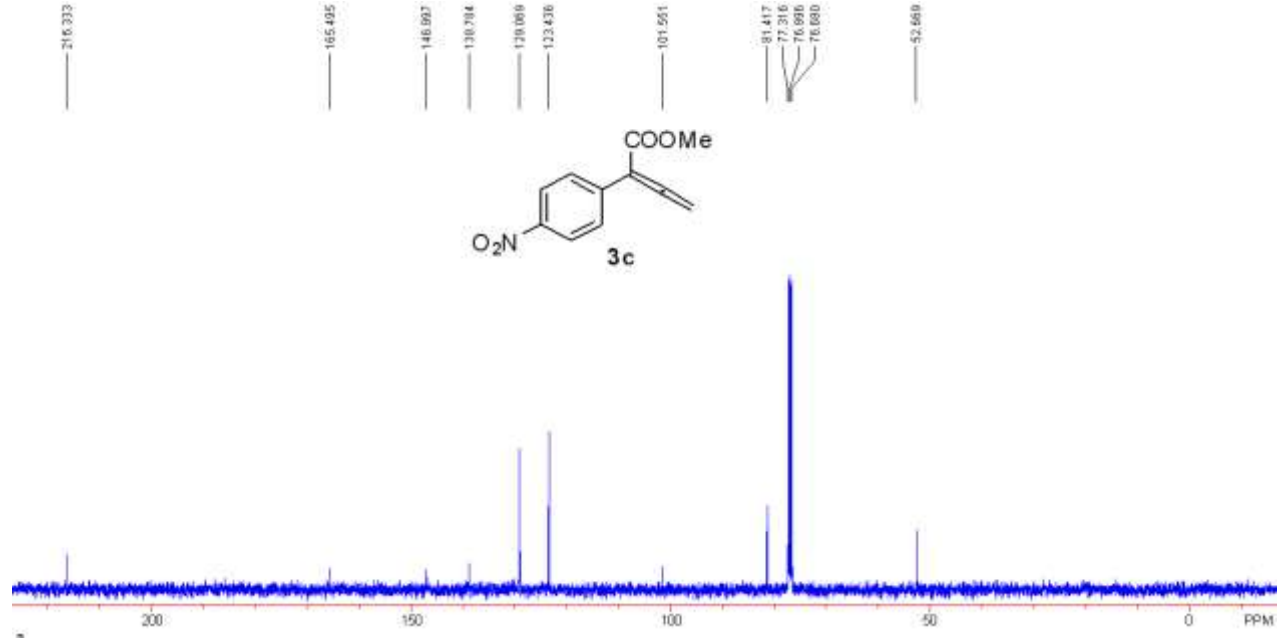


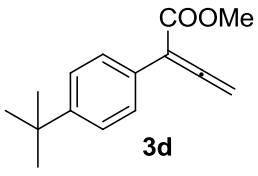


methyl 2-(4-nitrophenyl)buta-2,3-dienoate 3c: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3c** (41 mg, 94% yield). A yellow solid. m.p. for **3c** = 92-93 ^{o}C; IR (CH_2Cl_2): ν 2960, 2925, 1953, 1721, 1594, 1515, 1343, 1294, 1093, 1023, 854, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.20 (2H, d, *J* = 8.8 Hz), 7.73 (2H, d, *J* = 8.8 Hz), 5.57 (2H, s), 3.86 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.3, 165.5, 147.0, 138.8, 129.1, 123.4, 101.6, 81.4, 52.7; MS (%) m/e 219 (100), 202 (10), 189 (11), 160 (22),

148 (20), 114 (60), 102 (57), 88 (30); HRMS (EI) for $C_{11}H_9NO_4$: 219.0532; Found: 219.0529.

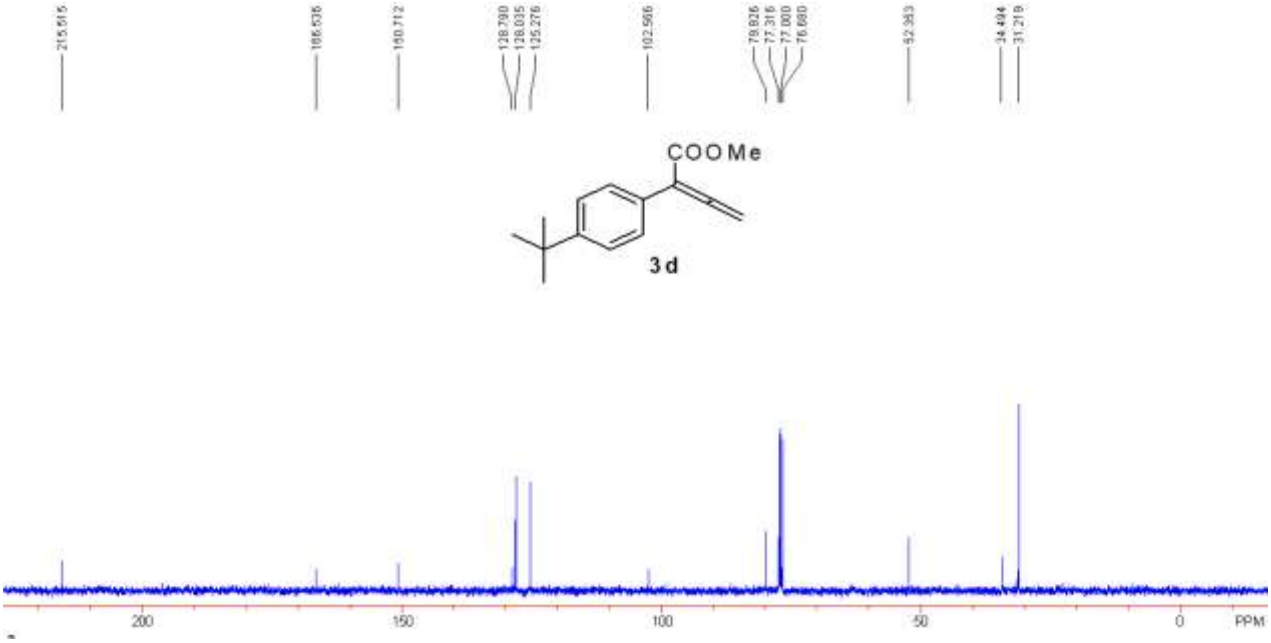


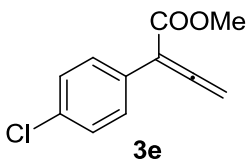




methyl 2-(4-tert-butylphenyl)buta-2,3-dienoate 3d: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3d** (42 mg, 91% yield). A yellow oil. IR (CH_2Cl_2): ν 2962, 2868, 1720, 1512, 1434, 1363, 1263, 1149, 1108, 1014, 906, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.43 (2H, d, *J* = 8.8 Hz), 7.38 (2H, d, *J* = 8.8

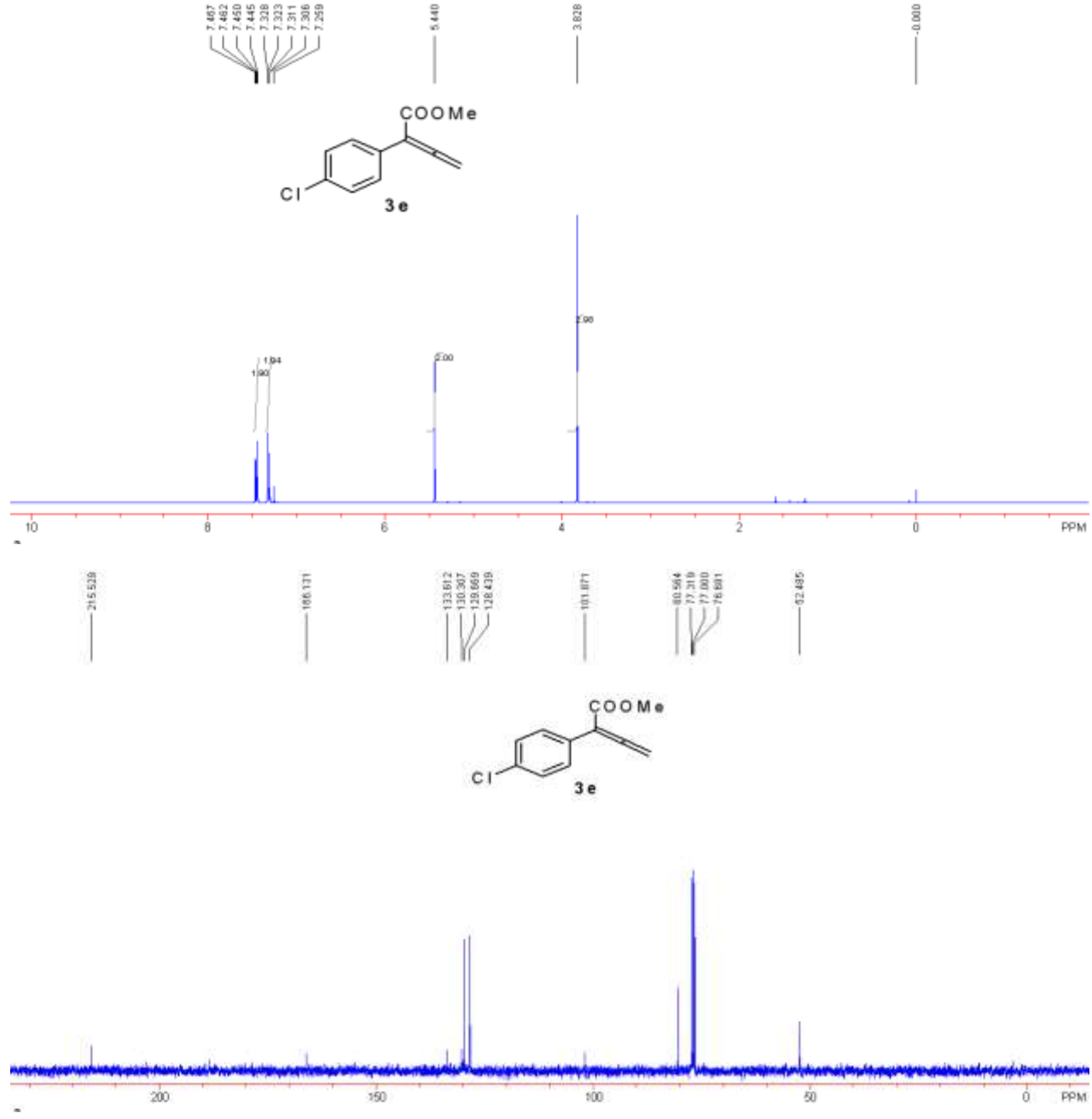
Hz), 5.39 (2H, s), 3.82 (3H, s), 1.32 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.5, 166.5, 150.7, 128.8, 128.0, 125.3, 102.6, 79.9, 52.4, 34.5, 31.2; MS (%) m/e 230 (41), 215 (100), 183 (11), 173 (14), 155 (21), 141 (19), 128 (16), 115 (21); HRMS (EI) for $C_{15}H_{18}O_2$: 230.1307; Found: 230.1311.

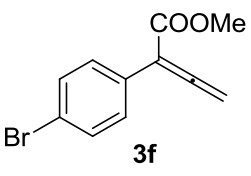




methyl 2-(4-chlorophenyl)buta-2,3-dienoate 3e: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3e** (40 mg, 96% yield). A yellow oil. IR (CH_2Cl_2): ν 2951, 1954, 1924, 1717, 1490, 1434, 1398, 1240, 1140, 1093, 1027,

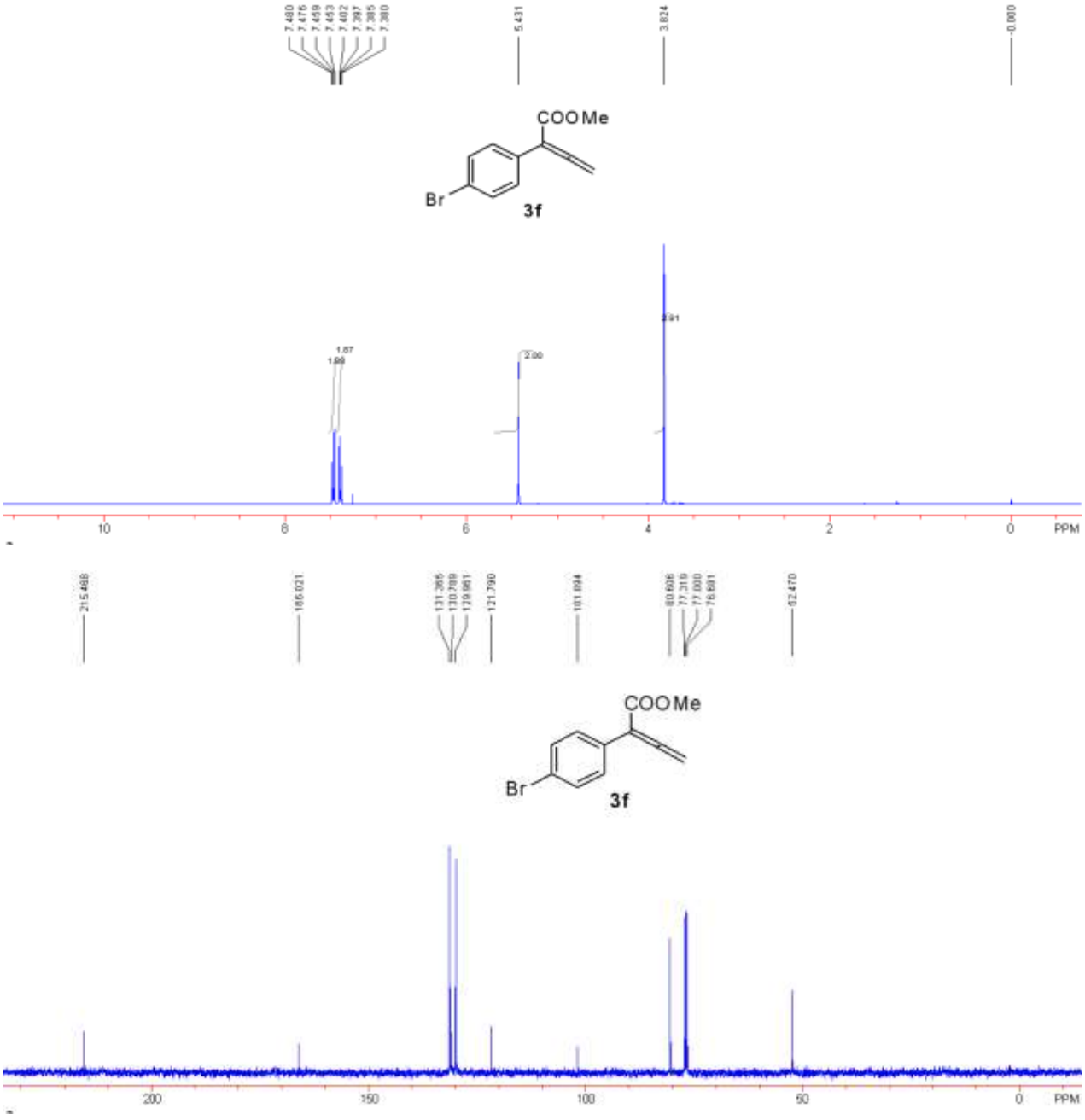
1012, 904, 852, 830, 780 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.46 (2H, dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 7.32 (2H, dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 5.44 (2H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.5, 166.1, 133.6, 130.3, 129.7, 128.4, 101.9, 80.6, 52.5; MS (%) m/e 208 (78), 179 (7), 165 (8), 149 (100), 145 (7), 137 (54), 114 (43), 102 (9); HRMS (EI) for $C_{11}H_9O_2Cl$: 208.0291; Found: 208.0296.

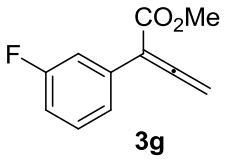




methyl 2-(4-bromophenyl)buta-2,3-dienoate 3f: Following the general procedure, the mixture was

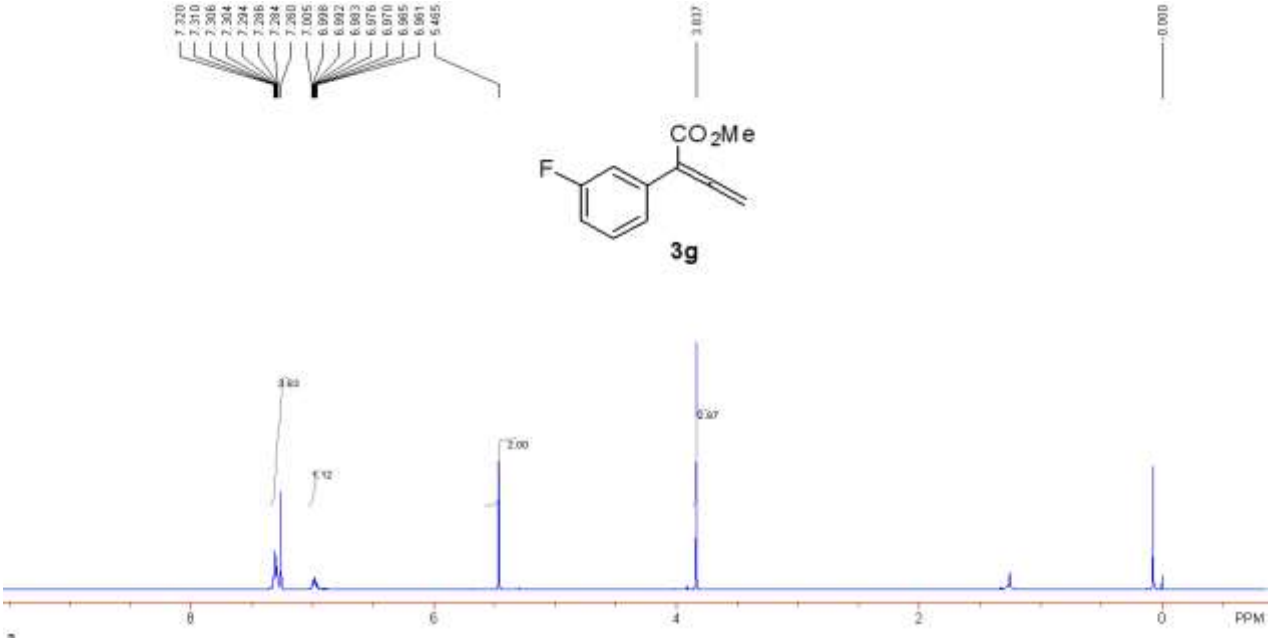
purified by column chromatography using silica gel to give the target product **3f** (42 mg, 83% yield). A yellow oil. IR (CH_2Cl_2): ν 2961, 2854, 1957, 1921, 1720, 1487, 1434, 1398, 1260, 1145, 1096, 1019, 1010, 904, 797 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47 (2H, dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 7.32 (2H, dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz), 5.43 (2H, s), 3.82 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.5, 166.0, 131.4, 130.8, 130.0, 121.8, 101.9, 80.6, 52.5; MS (%) m/e 251 (16), 195 (95), 183 (67), 145 (17), 128 (20), 114 (100), 102 (27), 88 (41), 75 (15); HRMS (EI) for $C_{11}H_9O_2Br$: 251.9786; Found: 251.9789.

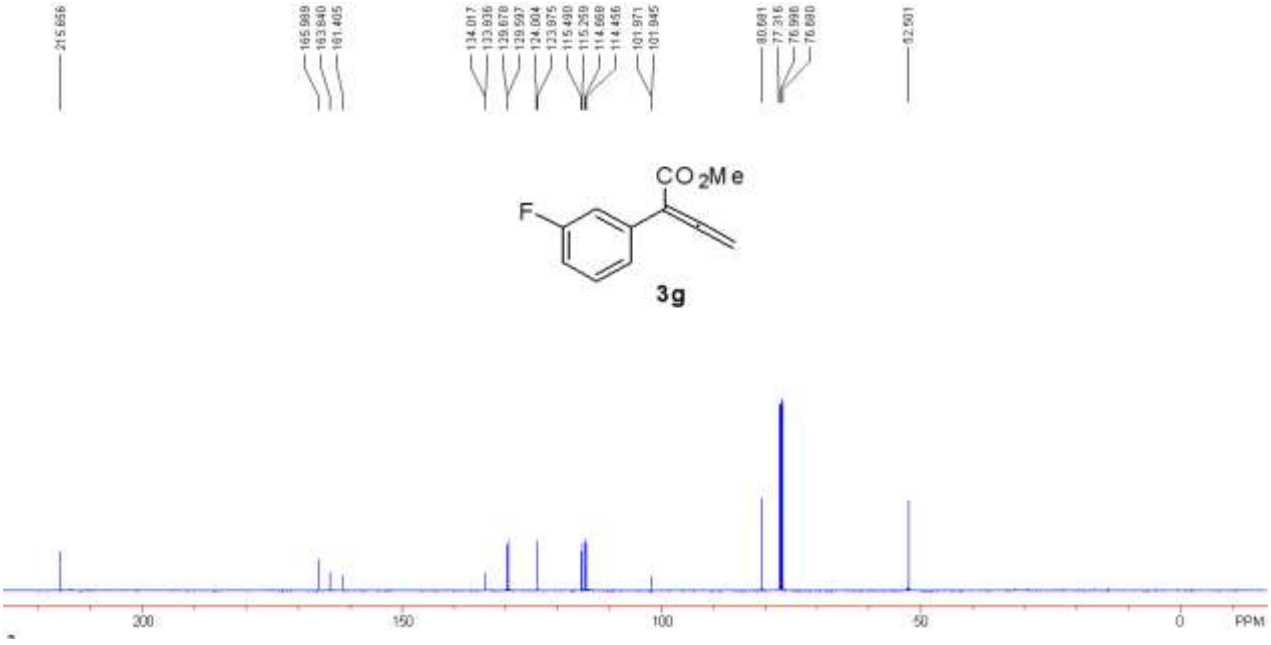


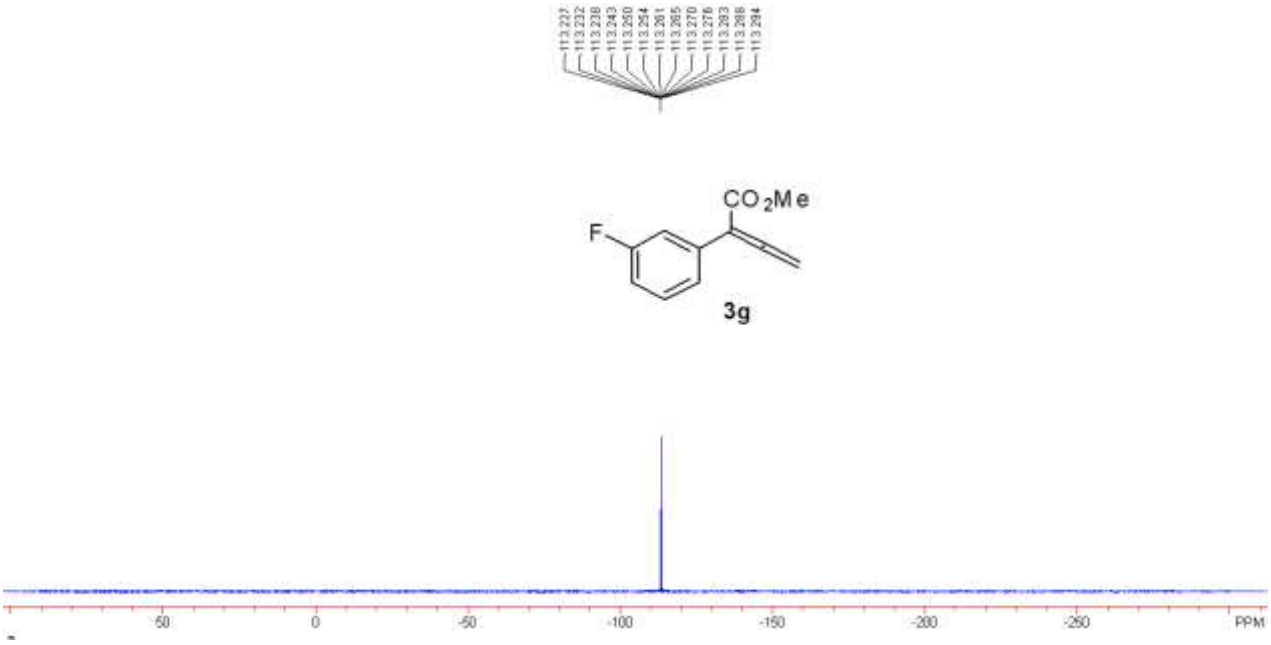


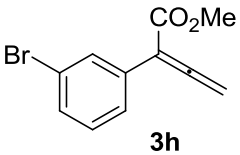
3g

methyl 2-(3-fluorophenyl)buta-2,3-dienoate 3g: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3g** (52 mg, 90% yield). A yellow oil. IR (CH_2Cl_2): ν 2953, 2256, 1955, 1717, 1613, 1585, 1486, 1435, 1277, 1248, 1130, 1036, 905, 853, 790 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32-7.26 (4H, m), 7.00-6.96 (1H, m), 5.47 (2H, s), 3.84 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.7, 166.0, 163.8, 161.4, 134.0 (d, J_{C-F} = 8.1 Hz), 129.6 (d, J_{C-F} = 8.1 Hz), 124.0 (d, J_{C-F} = 2.9 Hz), 115.4 (d, J_{C-F} = 23.1 Hz), 114.7 (d, J_{C-F} = 21.2 Hz), 102.0 (d, J_{C-F} = 2.6 Hz), 80.7, 52.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -113.2--113.3 (m); MS (%) m/e 192 (54), 177 (4), 163 (5), 146 (9), 133 (100), 121 (26), 107 (22), 83 (18), 59 (30); HRMS (EI) for $C_{11}H_9O_2F$: 192.0587; Found: 192.0585.



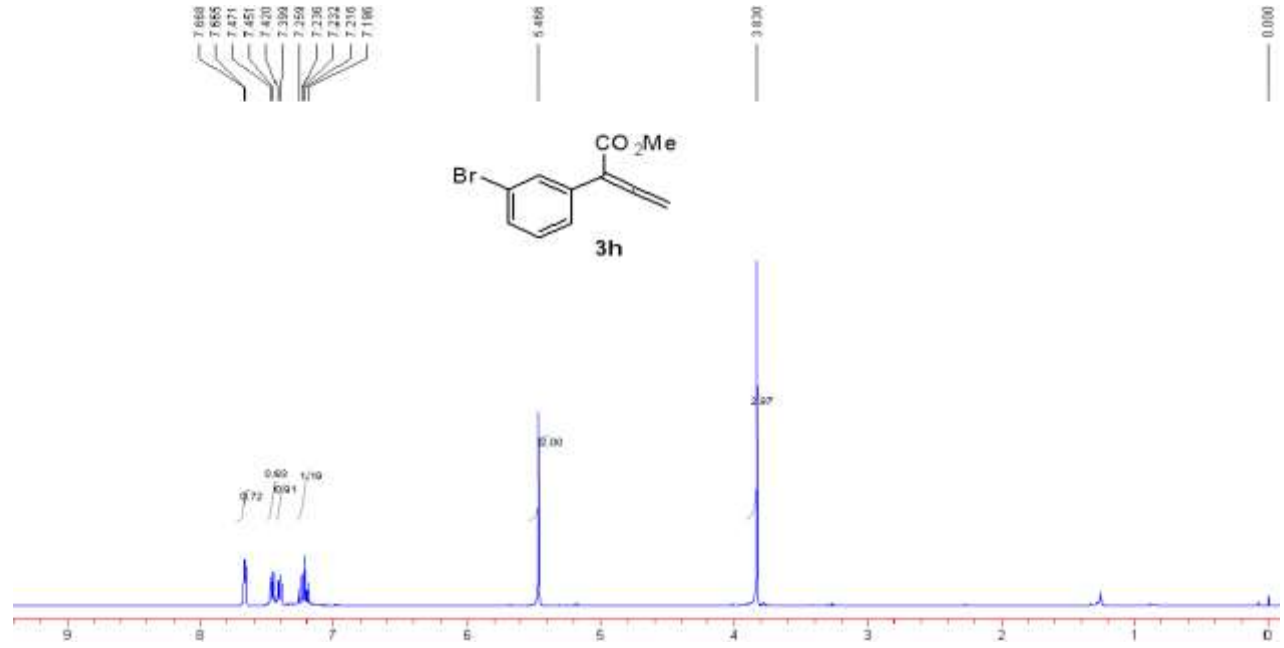


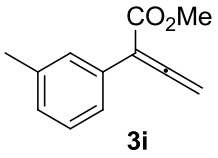




methyl 2-(3-bromophenyl)buta-2,3-dienoate 3h: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3h** (45 mg, 89% yield). A yellow oil. IR (CH_2Cl_2): ν 2952, 2924, 2853, 1954, 1923, 1719, 1591, 1560, 1473, 1433, 1261, 1146, 1075, 918, 852, 789 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.67 (1H, d, *J* = 1.2 Hz), 7.46 (1H, d, *J* = 8.0 Hz), 7.30 (1H, d, *J* = 8.4 Hz), 7.26-7.20 (1H, m), 5.47 (2H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.6, 165.9, 133.9, 131.2, 130.7, 129.7, 127.0, 122.3, 101.7, 80.7, 52.5;

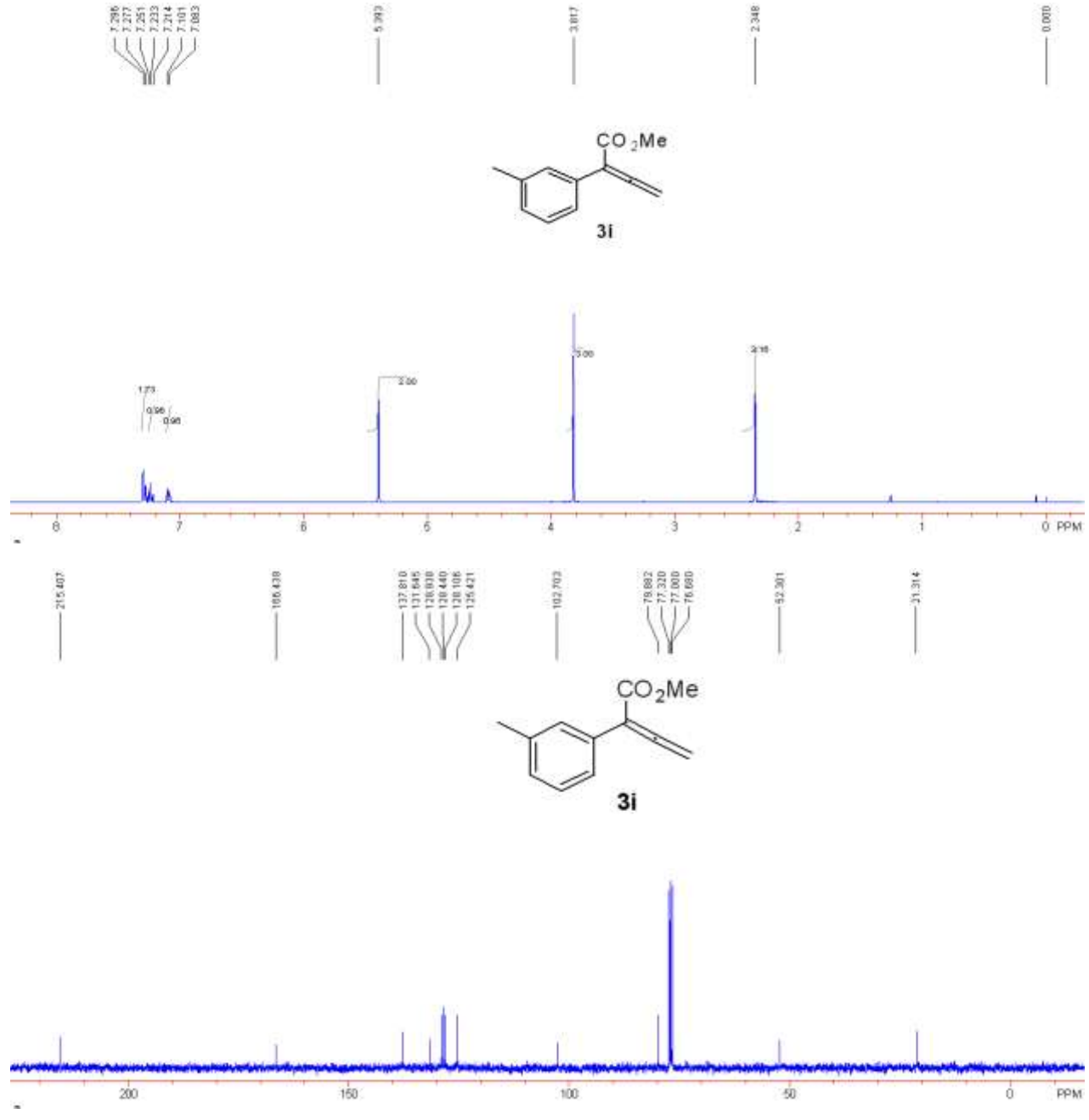
MS (%) m/e 251 (13), 195 (72), 183 (24), 153 (18), 128 (30), 117 (48), 114 (100), 102 (29), 88 (43), 43 (82); HRMS (EI) for $C_{11}H_9O_2Br$: 251.9786; Found: 251.9788.

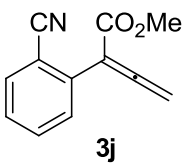




methyl 2-m-tolylbuta-2,3-dienoate 3i: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3i** (34 mg, 90% yield). A yellow oil. IR (CH_2Cl_2): ν 2961, 1953, 1924, 1720, 1605, 1487, 1434, 1258, 1137, 1090, 1017, 855, 794 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.29 (2H, d, *J* = 7.6 Hz), 7.23 (1H, t, *J* = 7.6 Hz),

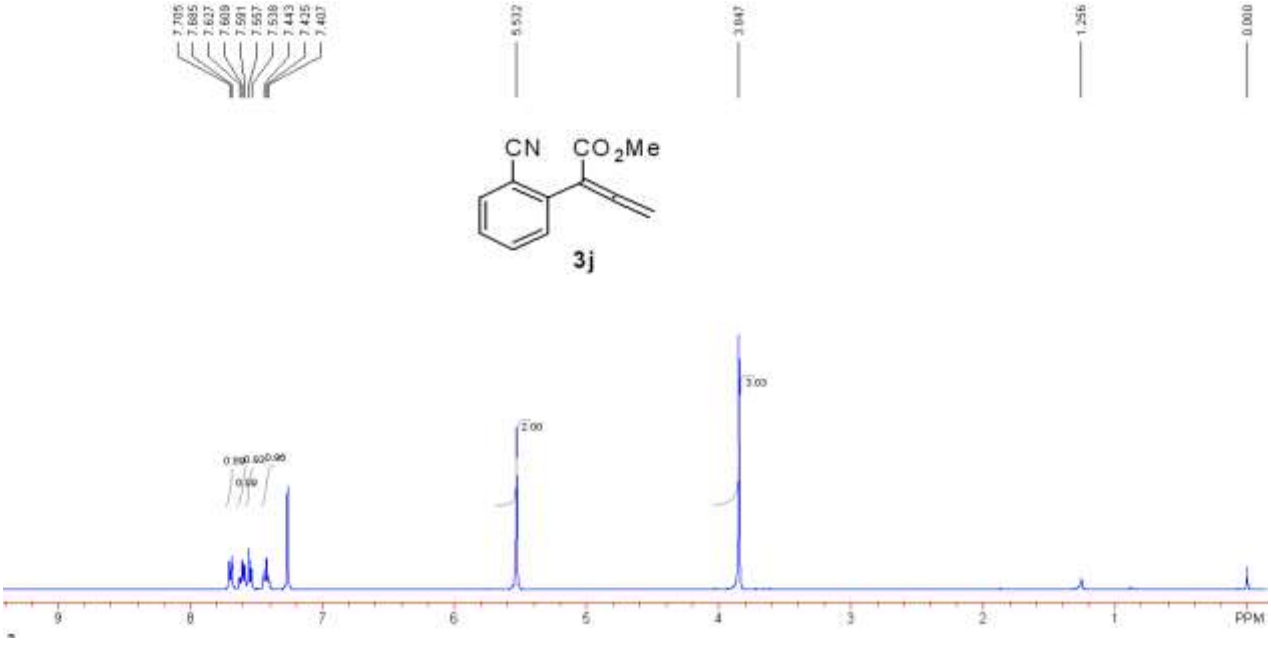
7.09 (1H, d, *J* = 7.2 Hz), 5.39 (2H, s), 3.82 (3H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.4, 166.4, 137.8, 131.6, 128.9, 128.4, 128.1, 125.4, 102.7, 80.0, 52.3, 21.3; MS (%) m/e 188 (57), 173 (11), 159 (7), 145 (11), 129 (81), 117 (41), 102 (21), 58 (32), 43 (100); HRMS (EI) for $C_{12}H_{12}O_2$: 188.0837; Found: 188.0835.

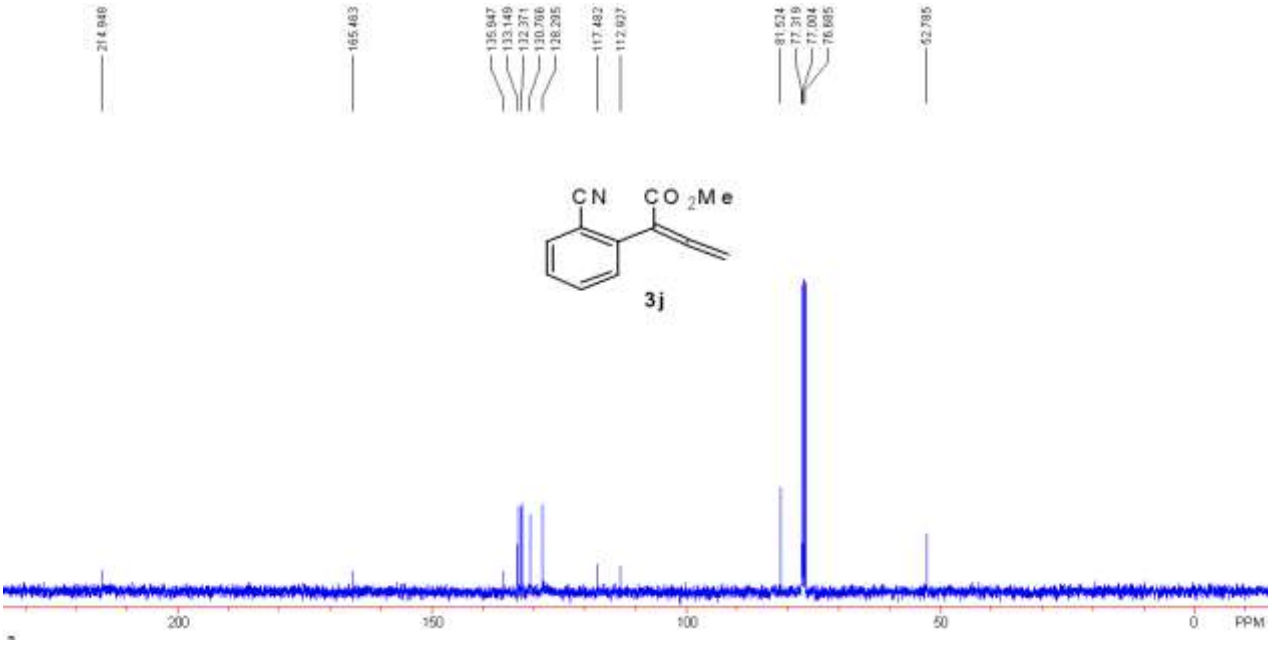


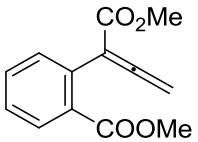


methyl 2-(2-cyanophenyl)buta-2,3-dienoate 3j: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3j** (36 mg, 90% yield).

A white solid. m.p. for **3j** = 95-96 ^{o}C. IR (CH_2Cl_2): ν 2962, 2224, 1960, 1715, 1434, 1259, 1089, 1016, 908, 863, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (1H, d, *J* = 8.0 Hz), 7.61 (1H, t, *J* = 7.2 Hz), 7.55 (1H, d, *J* = 7.6 Hz), 7.42 (1H, t, *J* = 7.2 Hz), 5.53 (2H, s), 3.85 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.9, 165.5, 136.0, 133.5, 132.4, 130.8, 128.3, 117.5, 112.9, 81.5, 52.8; MS (%) m/e 199 (55), 184 (4), 170 (12), 154 (19), 140 (100), 128 (22), 113 (44), 63 (17); HRMS (EI) for $C_{12}H_9NO_2$: 199.0633; Found: 199.0636.

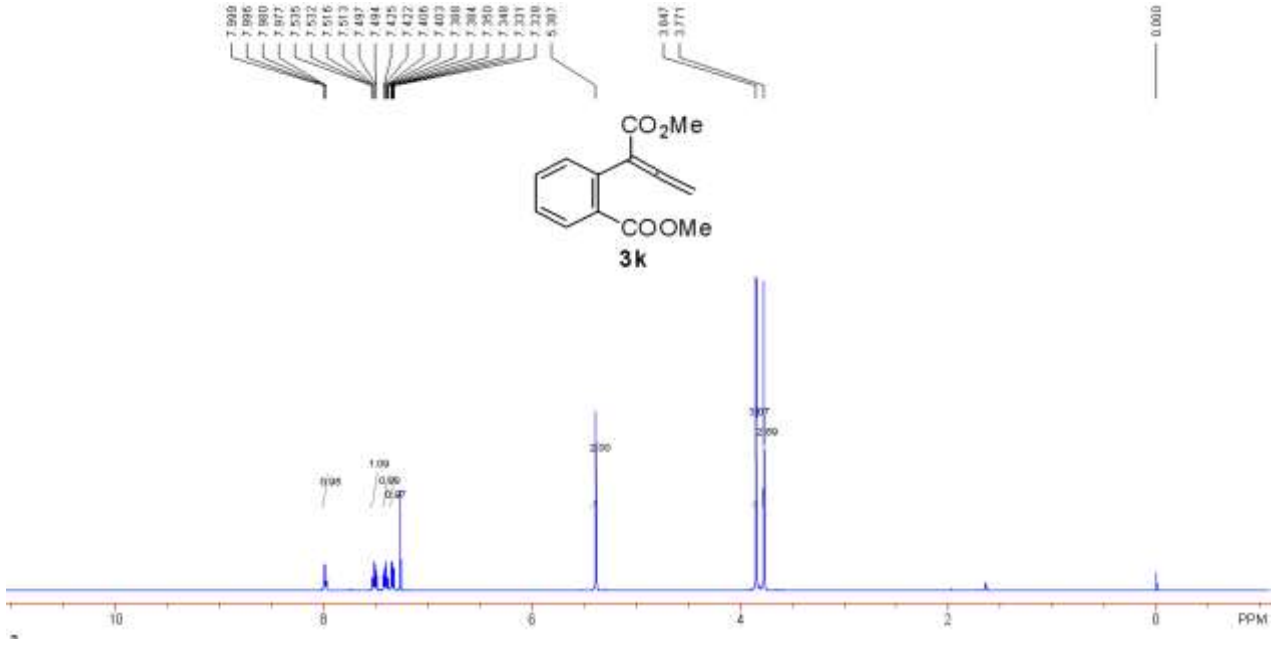


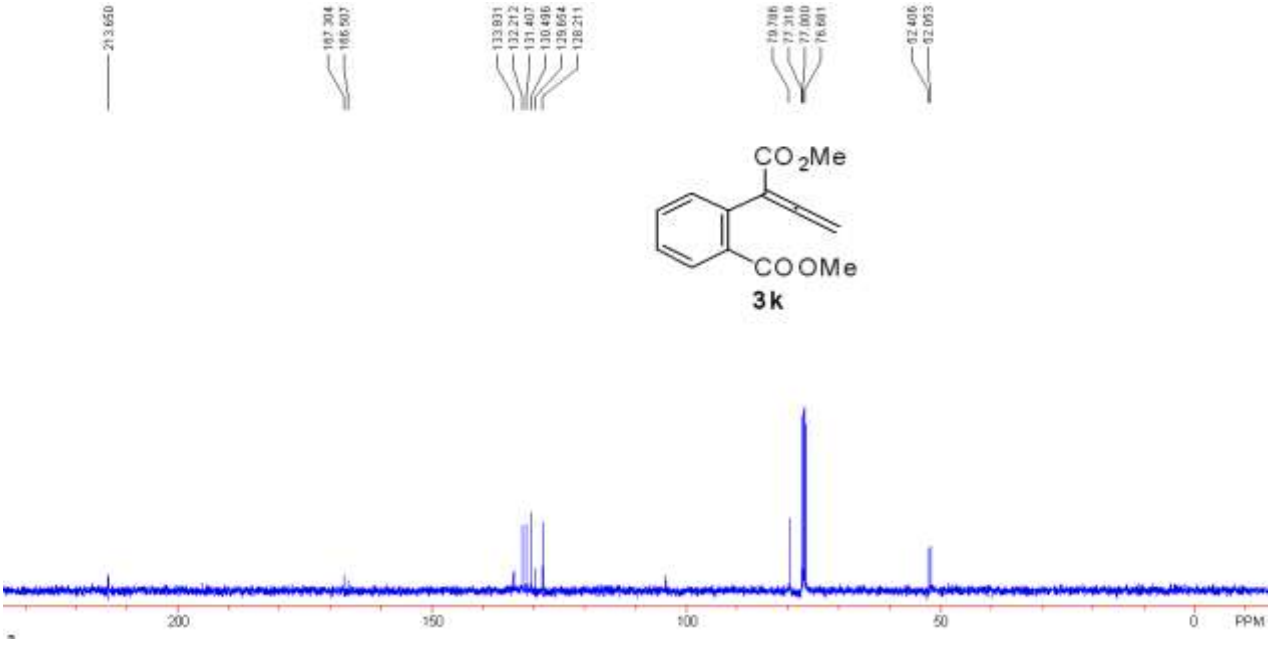


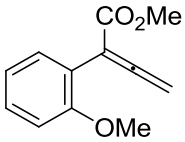


3k

methyl 2-(1-methoxy-1-oxobuta-2,3-dien-2-yl)benzoate 3k: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3k** (25 mg, 54% yield). A white solid. m.p. for **3k** = 87-88 ^{o}C. IR (CH_2Cl_2): ν 2962, 1720, 1434, 1262, 1084, 1016, 860, 796, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.99 (1H, dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.51 (1H, dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.40 (1H, dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.34 (1H, dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 5.39 (2H, s), 3.85 (3H, s), 3.77 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.7, 167.3, 166.5, 133.9, 132.2, 131.4, 130.5, 129.7, 128.2, 79.8, 52.4, 52.0; MS (%) m/e 232 (100), 217 (41), 201 (35), 173 (33), 161 (41), 143 (57), 129 (64), 115 (59), 102 (58), 88 (28); HRMS (EI) for $C_{13}H_{12}O_4$: 232.0736; Found: 232.0736.

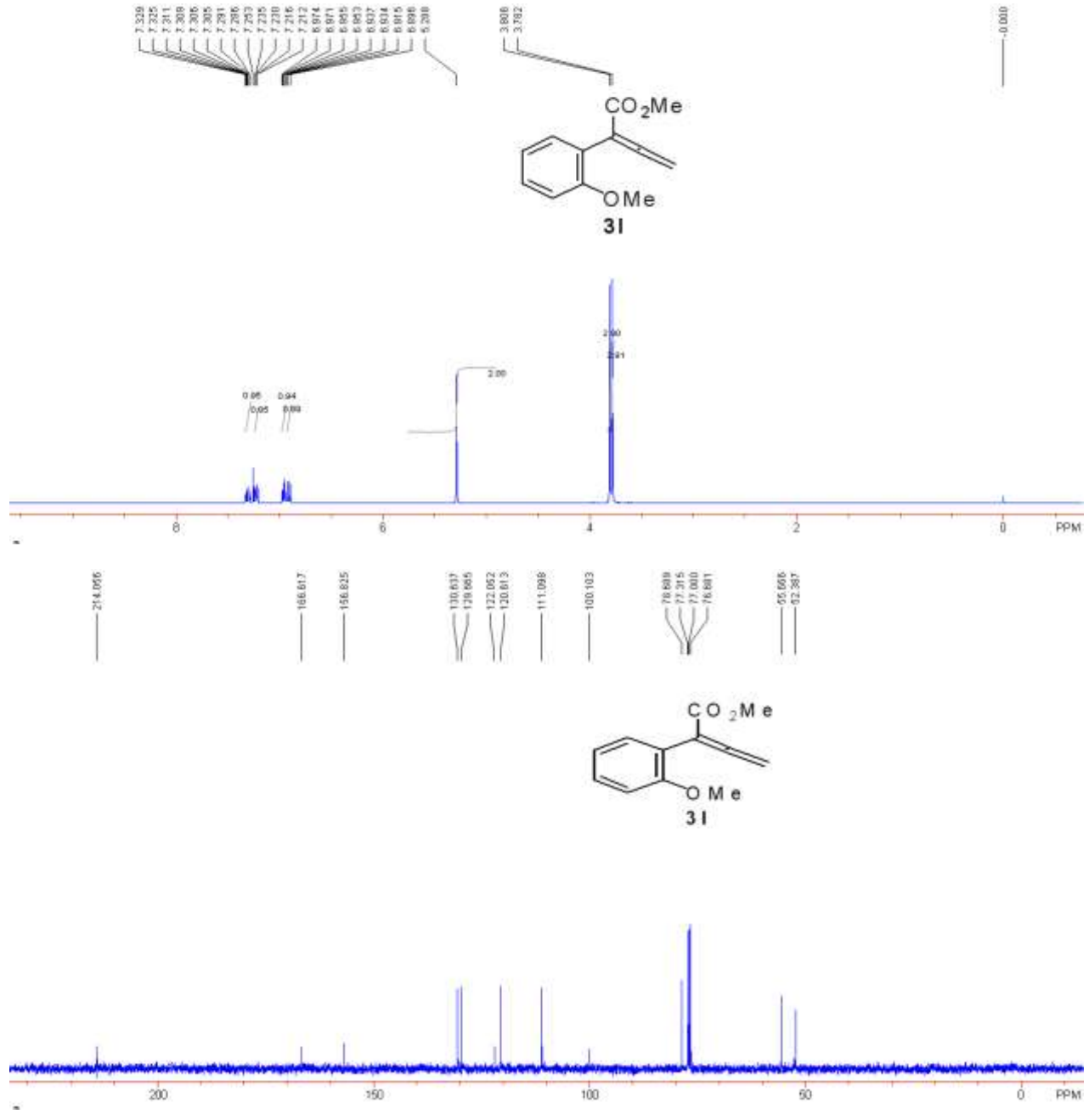


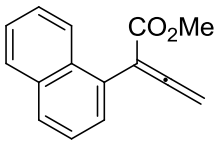




3l

methyl 2-(2-methoxyphenyl)buta-2,3-dienoate 3l: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3l** (38 mg, 93% yield). A yellow oil. IR (CH_2Cl_2): ν 2961, 1963, 1718, 1597, 1494, 1463, 1434, 1258, 1144, 1104, 1017, 905, 799, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.33-7.29 (1H, m), 7.22 (1H, dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz), 6.95 (1H, dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 6.91 (1H, d, J = 7.6 Hz), 5.29 (2H, s), 3.81 (3H, s), 3.78 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.1, 166.6, 156.8, 130.6, 129.7, 122.1, 120.6, 111.1, 100.1, 78.7, 55.7, 52.4; MS (%) m/e 204 (17), 189 (100), 172 (11), 159 (23), 145 (12), 115 (53), 102 (18), 91 (25); HRMS (EI) for $C_{12}H_{12}O_3$: 204.0786; Found: 204.0784.

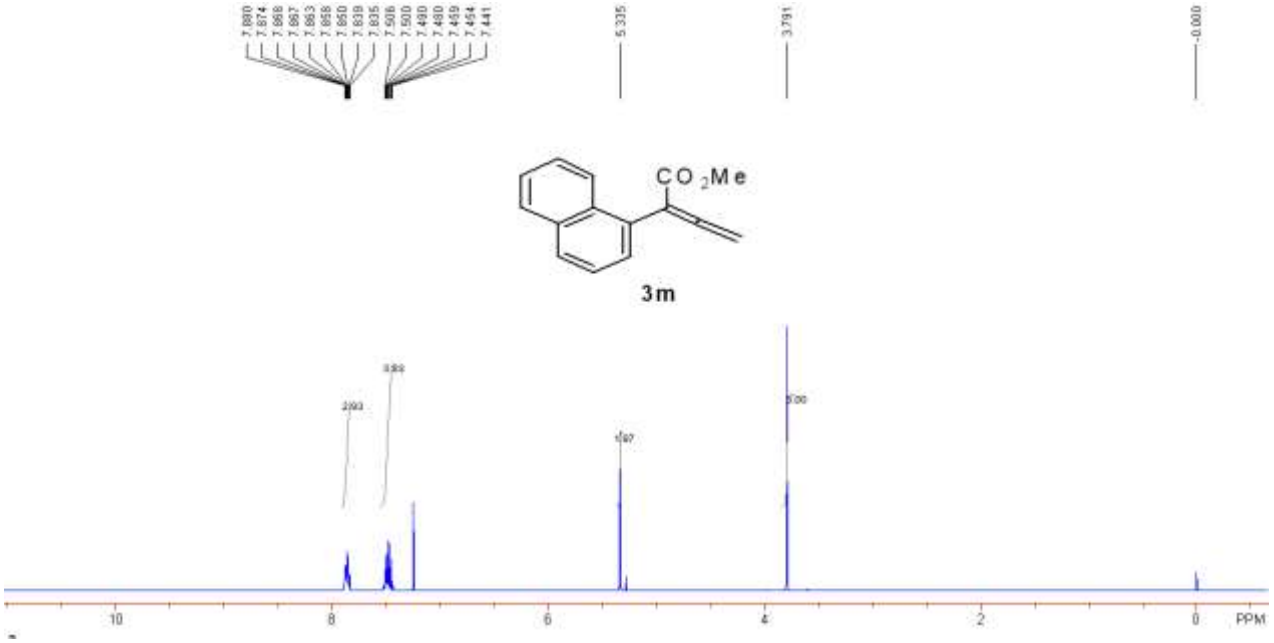


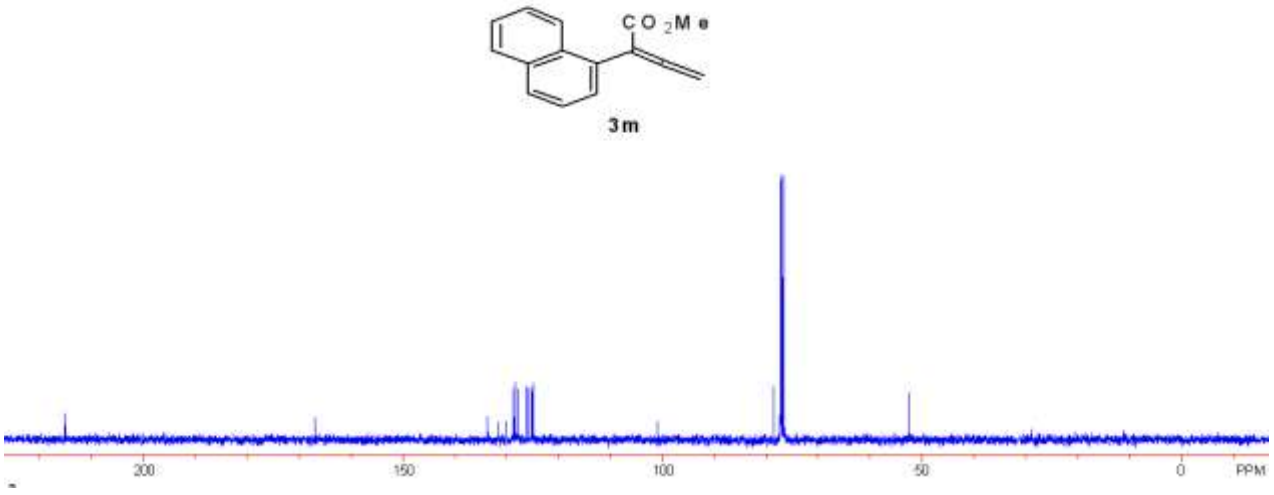


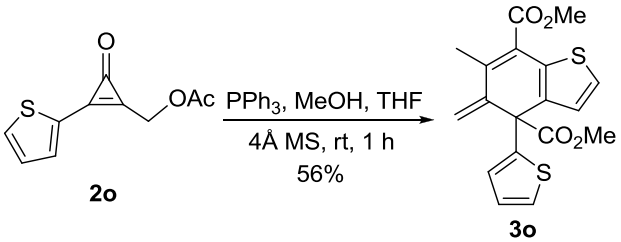
3m

methyl 2-(naphthalen-1-yl)buta-2,3-dienoate 3m: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3m** (35 mg, 78% yield). A yellow oil. IR (CH_2Cl_2): ν 2962, 1967, 1732, 1580, 1477, 1434, 1259, 1088, 1017, 864, 796 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88-7.84 (3H, m), 7.51-7.44 (4H, m), 5.34 (2H, s), 3.79 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.0, 166.8, 133.7, 131.7, 130.1, 128.8, 128.4, 127.8,

126.3, 125.8, 125.3, 125.0, 100.9, 78.6, 52.6; MS (%) m/e 224 (15), 209 (9), 192 (25), 165 (86), 163 (27), 153 (11), 139 (8), 58 (32), 43 (100); HRMS (EI) for $C_{15}H_{12}O$: 224.0837; Found: 224.0839.

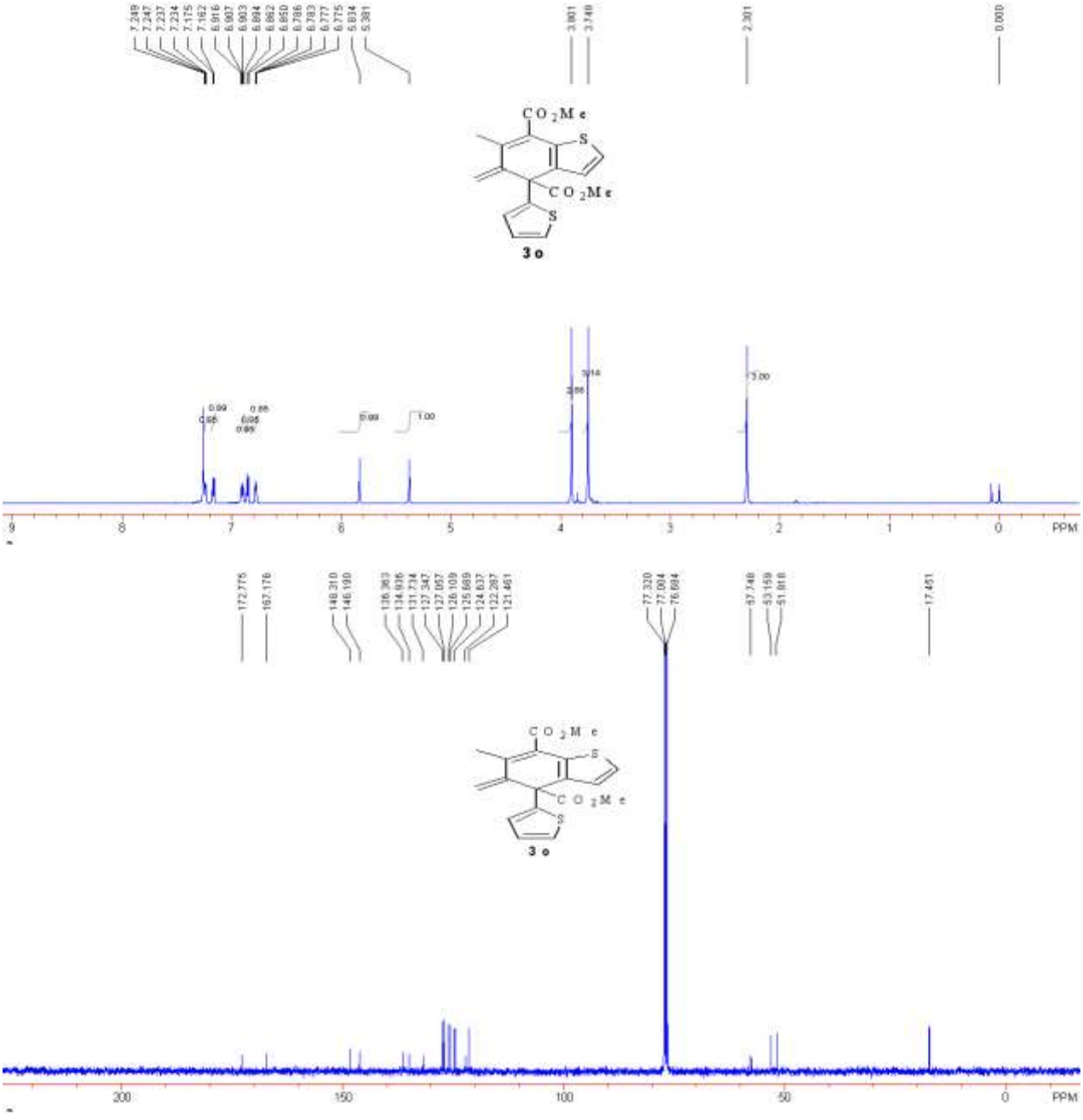




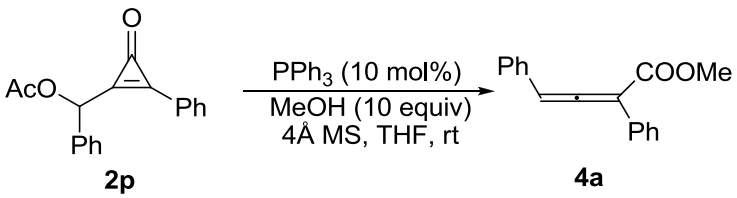


dimethyl 6-methyl-5-methylene-4-(thiophen-2-yl)-4,5-dihydrobenzo[b]thiophene-4,7-dicarboxylate 3o:

Following the general procedure, but the catalyst was switched to PPh_3. After the starting material was consumed, the resulting mixture was purified by column chromatography using silica gel to give the target product **3o** (20 mg, 56% yield). A white solid. m.p. for **3o** = 147-148 ^{o}C. IR (CH_2Cl_2): ν 2960, 1731, 1434, 1338, 1260, 1210, 1095, 1066, 1015, 839, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.24 (1H, dd, J_1 = 5.2 Hz, J_2 = 0.8 Hz), 7.17 (1H, d, J = 5.2 Hz), 6.91 (1H, dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz), 6.86 (1H, d, J = 4.8 Hz), 6.78 (1H, dd, J_1 = 3.6 Hz, J_2 = 0.8 Hz), 5.83 (1H, s), 5.38 (1H, s), 3.90 (3H, s), 3.75 (3H, s), 2.30(3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.8, 167.2, 148.3, 146.2, 136.4, 134.9, 131.7, 127.3, 127.1, 126.1, 125.7, 124.6, 122.3, 121.5, 57.7, 53.2, 51.9, 17.5; MS (ESI) m/e 378.1 (M^++NH_4); HRMS (ESI) for $C_{18}H_{20}NO_4S_2$ (M^++NH_4): 378.0828, Found: 378.0833.

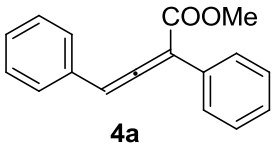


General Procedure for the Preparation of 4 from the Reaction of 2p with MeOH Using 4a as an Example in the Presence of PPh_3



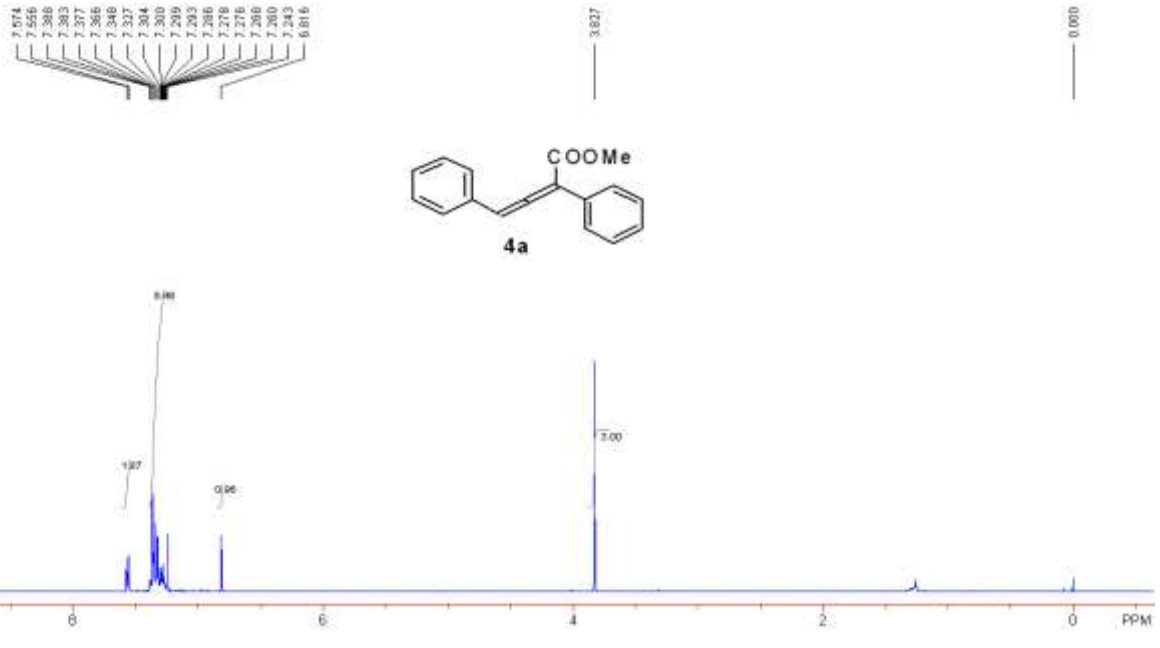
2p **4a**

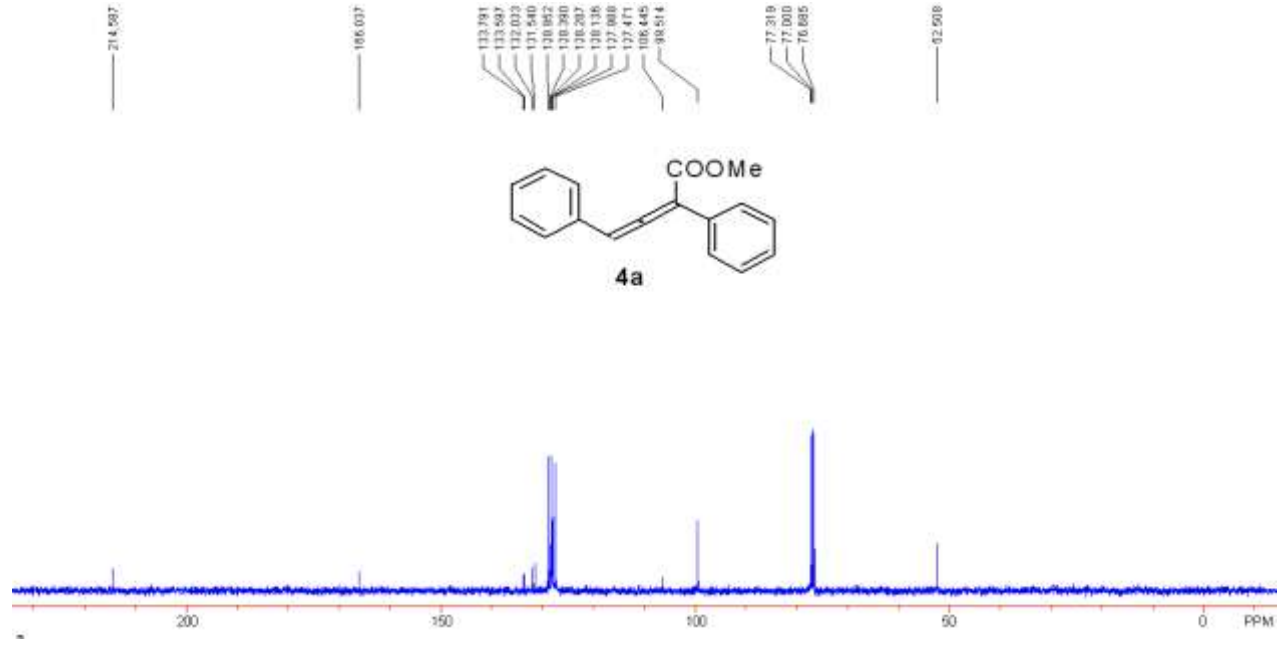
To a mixture of **2p** (0.20 mmol, 56 mg**)**, MeOH (10.0 mmol), PPh_3 (0.02 mmol, 5.2 mg) and 50 mg 4Å MS was added 2.0 mL of THF at room temperature (25 ^{o}C) under argon. The reaction solution was monitored by TLC. After the reaction was completed, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/16) to give the target product **4a**.

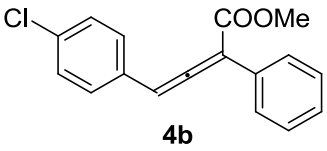


4a

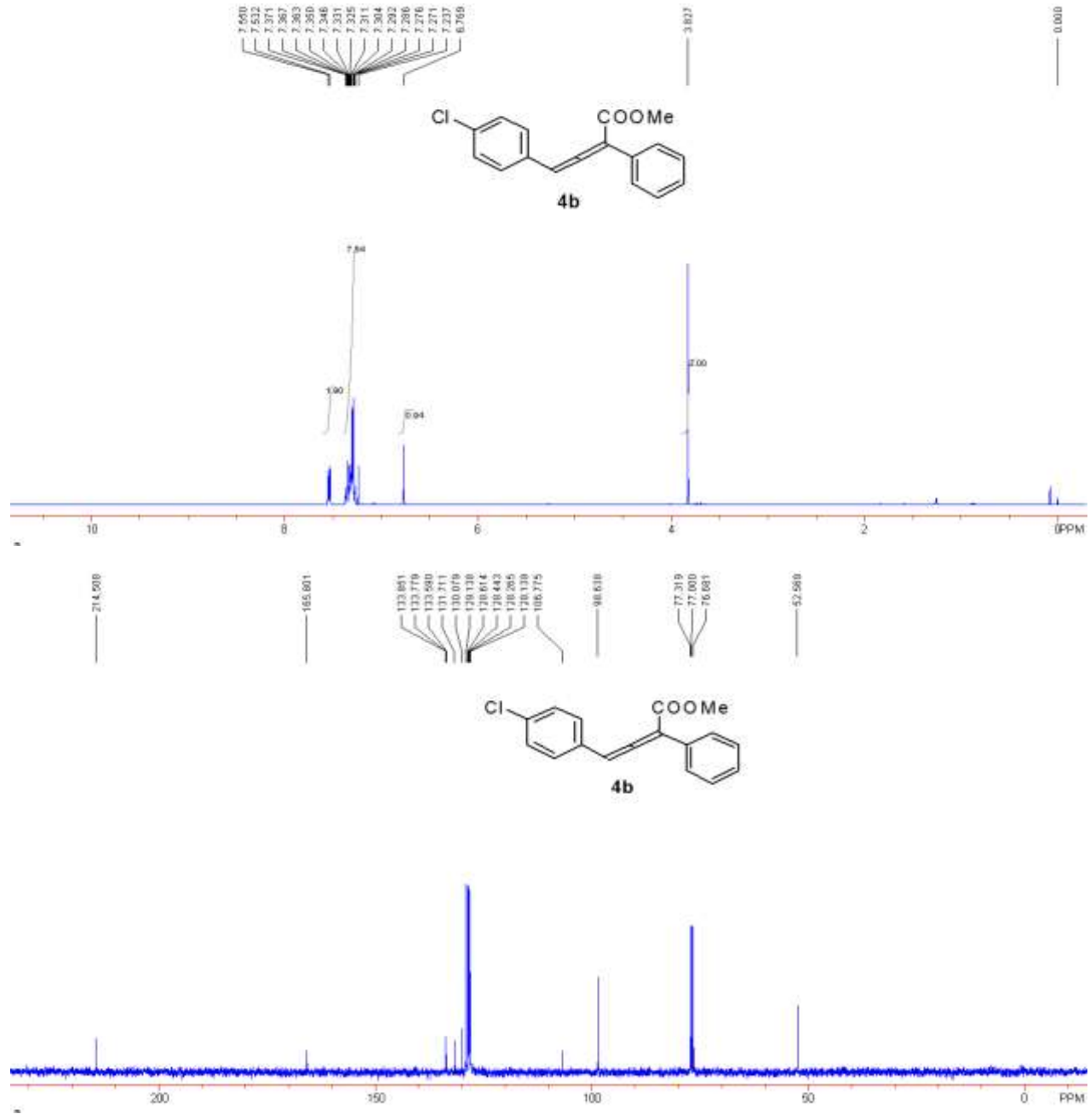
methyl 2,4-diphenylbuta-2,3-dienoate 4a: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4a** (46 mg, 92% yield). A yellow oil. IR (CH_2Cl_2): ν 2961, 2926, 1720, 1598, 1493, 1466, 1434, 1260, 1216, 1092, 1018, 998, 798 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.57 (2H, d, *J* = 7.2 Hz), 7.39-7.24 (8H, m), 6.82 (1H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.6, 166.0, 133.8, 133.6, 132.0, 131.5, 129.0, 128.4, 128.3, 128.1, 128.0, 127.5, 106.4, 99.5, 52.5; MS (%) m/e 250 (51), 235 (13), 207 (14), 191 (100), 179 (10), 165 (13), 105 (23); HRMS (EI) for $C_{17}H_{14}O_2$: 250.0994; Found: 250.0995.

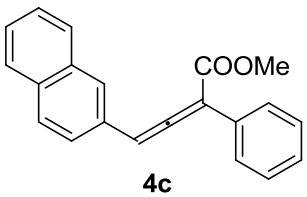






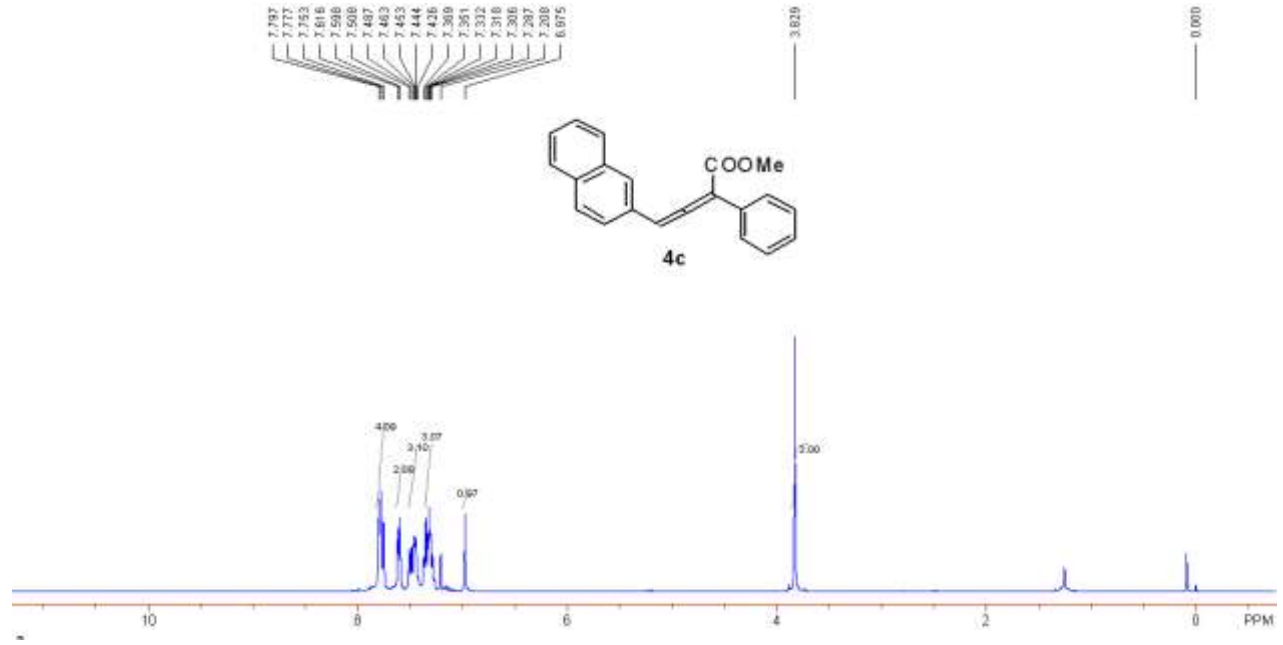
methyl 4-(4-chlorophenyl)-2-phenylbuta-2,3-dienoate 4b: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4b** (53 mg, 93% yield). A white solid. m.p. for **4b** = 120-122 ^{o}C. IR (CH_2Cl_2): ν 2961, 1930, 1720, 1489, 1433, 1259, 1214, 1088, 1013, 845, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.54 (2H, d, *J* = 7.2 Hz), 7.37-7.24 (7H, m), 6.77 (1H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.5, 165.8, 133.9, 133.8, 133.6, 131.7, 130.1, 129.1, 128.6, 128.4, 128.3, 128.1, 106.8, 98.6, 52.6; MS (%) m/e 284 (38), 269 (12), 249 (27), 241 (8), 225 (100), 189 (59), 178 (10), 163 (10), 139 (23). 94 (12); HRMS (EI) for $C_{17}H_{13}ClO_2$: 284.0604; Found: 284.0606.

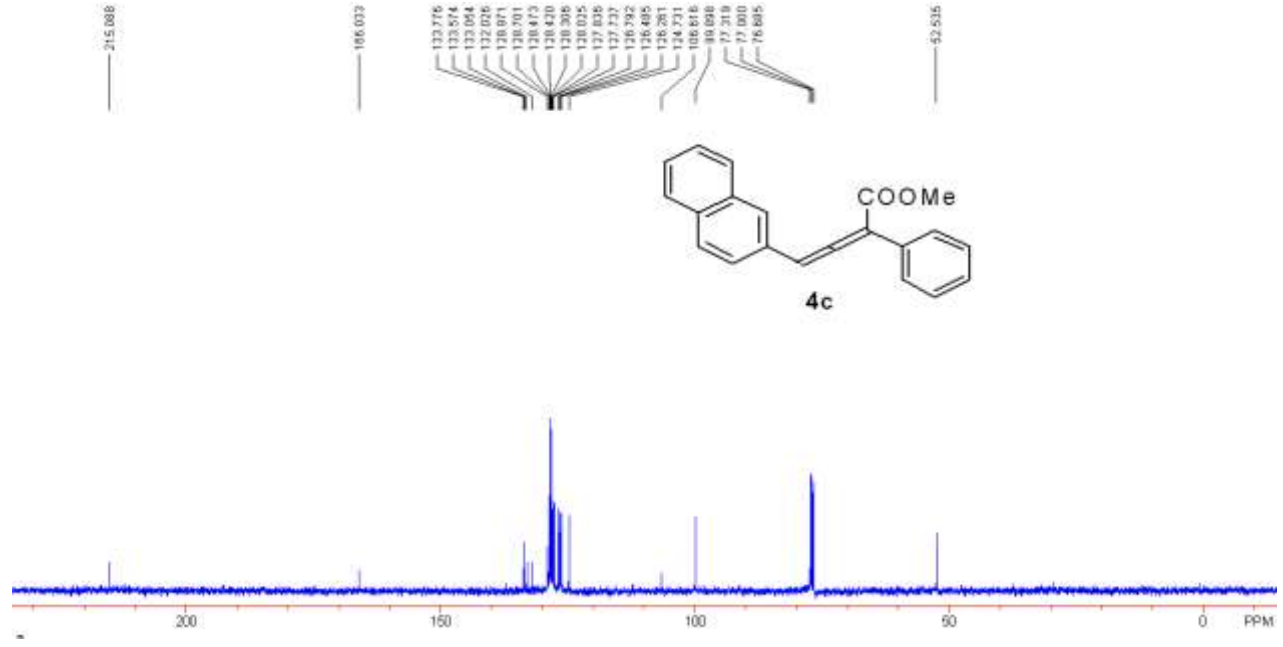


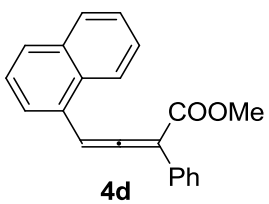


methyl 4-(naphthalen-2-yl)-2-phenylbuta-2,3-dienoate 4c: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4c** (52mg, 87% yield). A white solid. m.p. for **4c** = 93-95 ^{o}C. IR (CH_2Cl_2): ν 3056, 2963, 1932, 1719, 1493, 1434, 1217, 1134, 1118, 1018, 896, 862, 781, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80-7.53 (4H, m), 7.61 (2H, d, *J* = 7.2 Hz), 7.51-7.43 (3H, m), 7.37-7.29 (3H, m), 6.98 (1H, s), 3.83

(3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.1, 166.0, 133.8, 133.6, 133.1, 132.0, 129.0, 128.7, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 126.8, 126.5, 126.3, 124.7, 106.6, 99.9, 52.5; MS (%) m/e 300 (71), 285 (15), 262 (53), 257 (21), 241 (100), 229 (17), 183 (58), 155 (22). 115 (25); HRMS (EI) for $C_{21}H_{16}O_2$: 300.1150; Found: 300.1154.

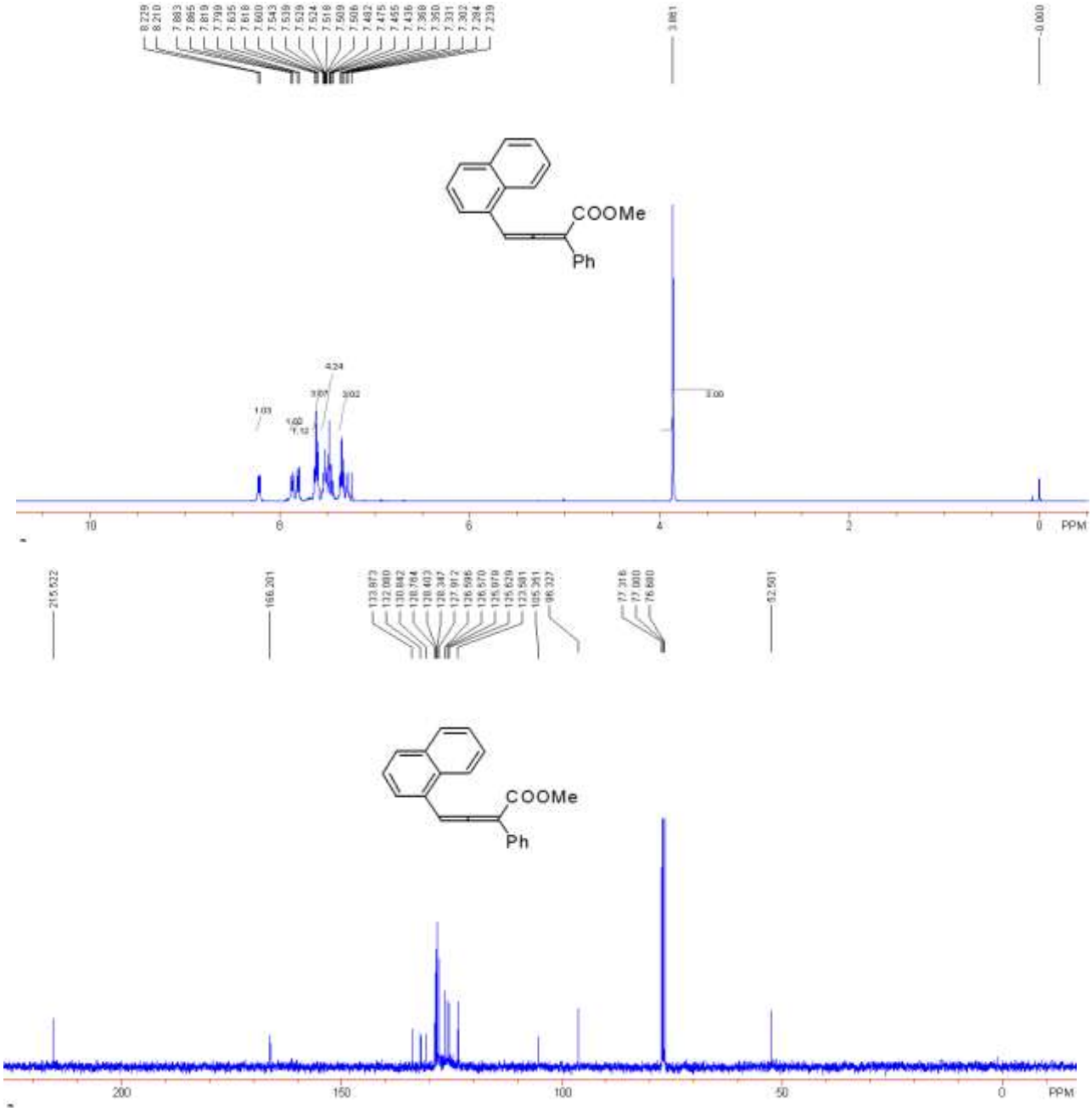


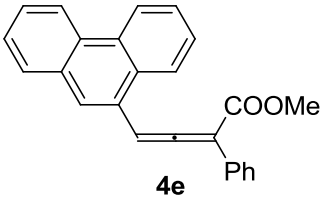




methyl 4-(naphthalen-1-yl)-2-phenylbuta-2,3-dienoate 4d: Following the general procedure, the

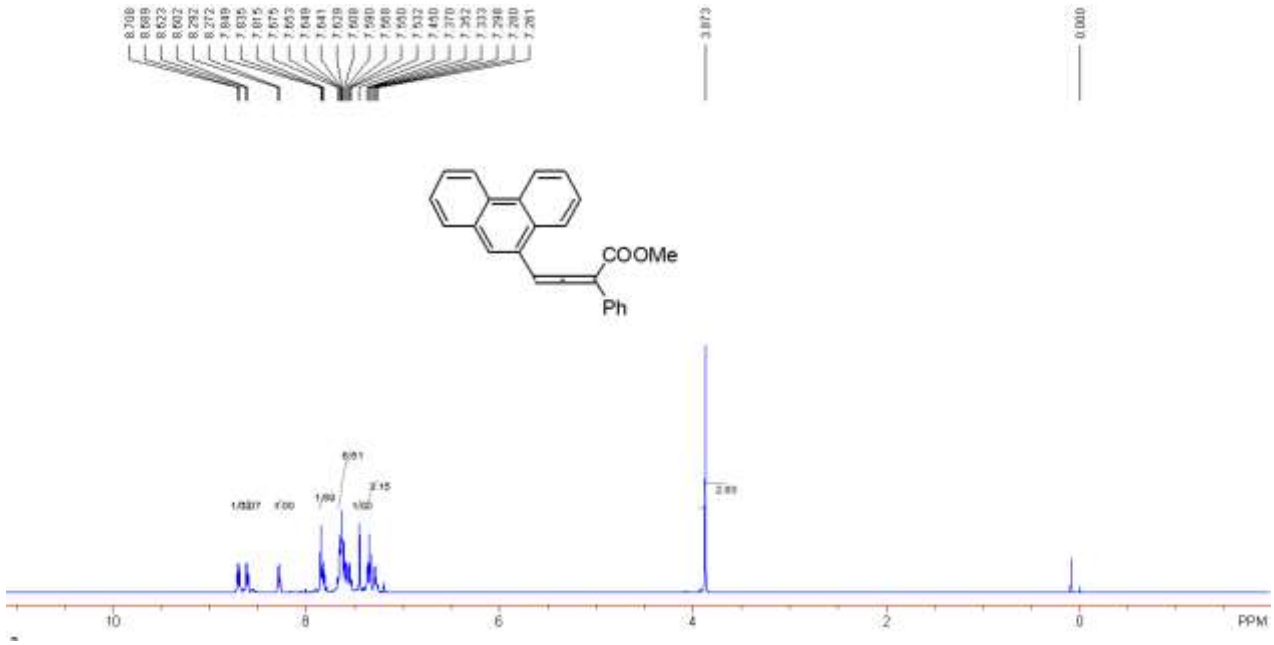
mixture was purified by column chromatography using silica gel to give the target product **4d** (48 mg, 80% yield). A yellow oil. IR (CH_2Cl_2): ν 3055, 2950, 1931, 1719, 1493, 1433, 1263, 1217, 1133, 1089, 1017, 897, 862, 799, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.22 (1H, d, *J* = 7.6 Hz), 7.87 (1H, d, *J* = 7.2 Hz), 7.81 (1H, d, *J* = 8.0 Hz), 7.62 (3H, t, *J* = 7.2 Hz), 7.54-7.44 (4H, m), 7.37-7.24 (3H, m), 3.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.5, 166.2, 134.0, 132.1, 130.8, 128.8, 128.4, 128.3, 127.9, 126.6, 126.57, 126.0, 125.6, 123.6, 105.4, 96.3, 52.5; MS (ESI) m/e 318.1 (M^++NH_4); HRMS (ESI) for $C_{21}H_{20}NO_2$ (M^++NH_4): 318.1489, Found: 318.1496.

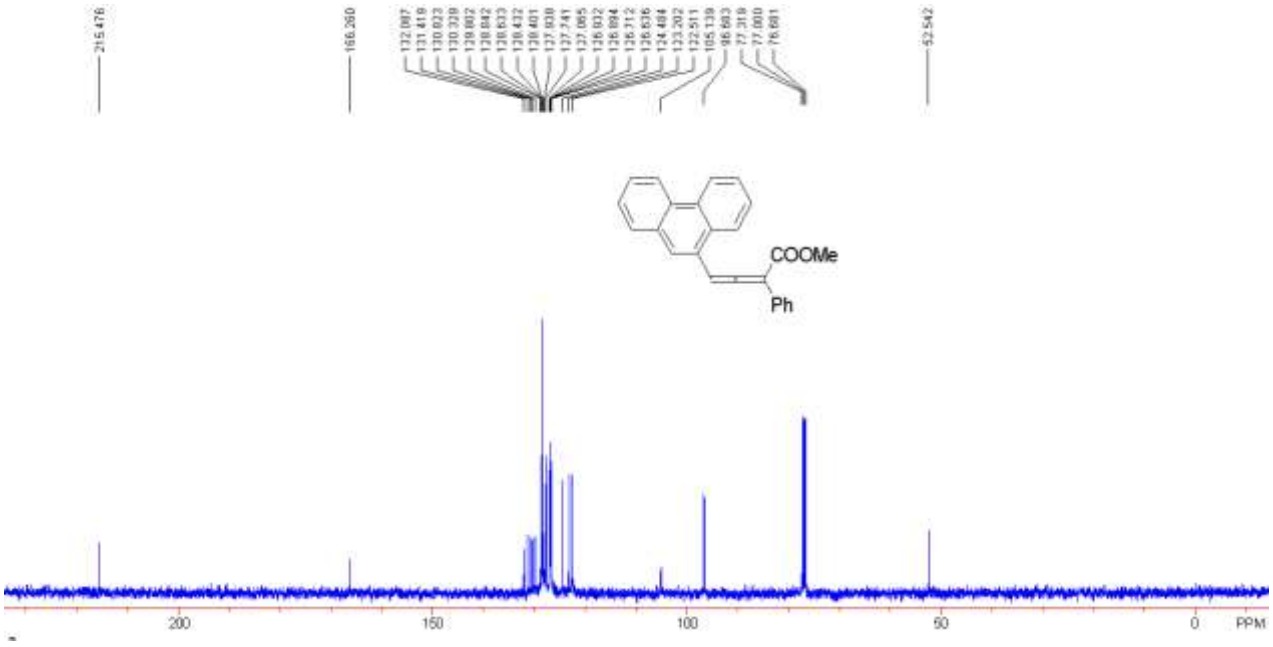


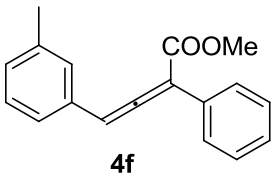


4e

methyl 4-(phenanthren-9-yl)-2-phenylbuta-2,3-dienoate 4e: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4e** (50 mg, 95% yield). A yellow solid. m.p. for **4e** = 89-92 ^{o}C. IR (CH_2Cl_2): ν 2962, 1721, 1449, 1259, 1088, 1016, 864, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.70 (1H, d, *J* = 7.6 Hz), 8.61 (1H, d, *J* = 8.4 Hz), 8.28 (1H, d, *J* = 8.0 Hz), 7.85-7.82 (2H, m), 7.68-7.55 (6H, m), 7.45 (1H, s), 7.37-7.26 (3H, m), 3.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.5, 166.3, 132.1, 131.4, 130.8, 130.3, 129.8, 128.8, 128.6, 128.43, 128.40, 127.9, 127.7, 127.1, 126.93, 126.89, 126.7, 126.6, 124.5, 123.2, 122.5, 105.1, 96.7, 52.5; MS (ESI) m/e 368.2 (M^{+}+NH_4); HRMS (ESI) for $C_{25}H_{22}NO_2$ (M^{+}+NH_4): 368.1645, Found: 368.1649.

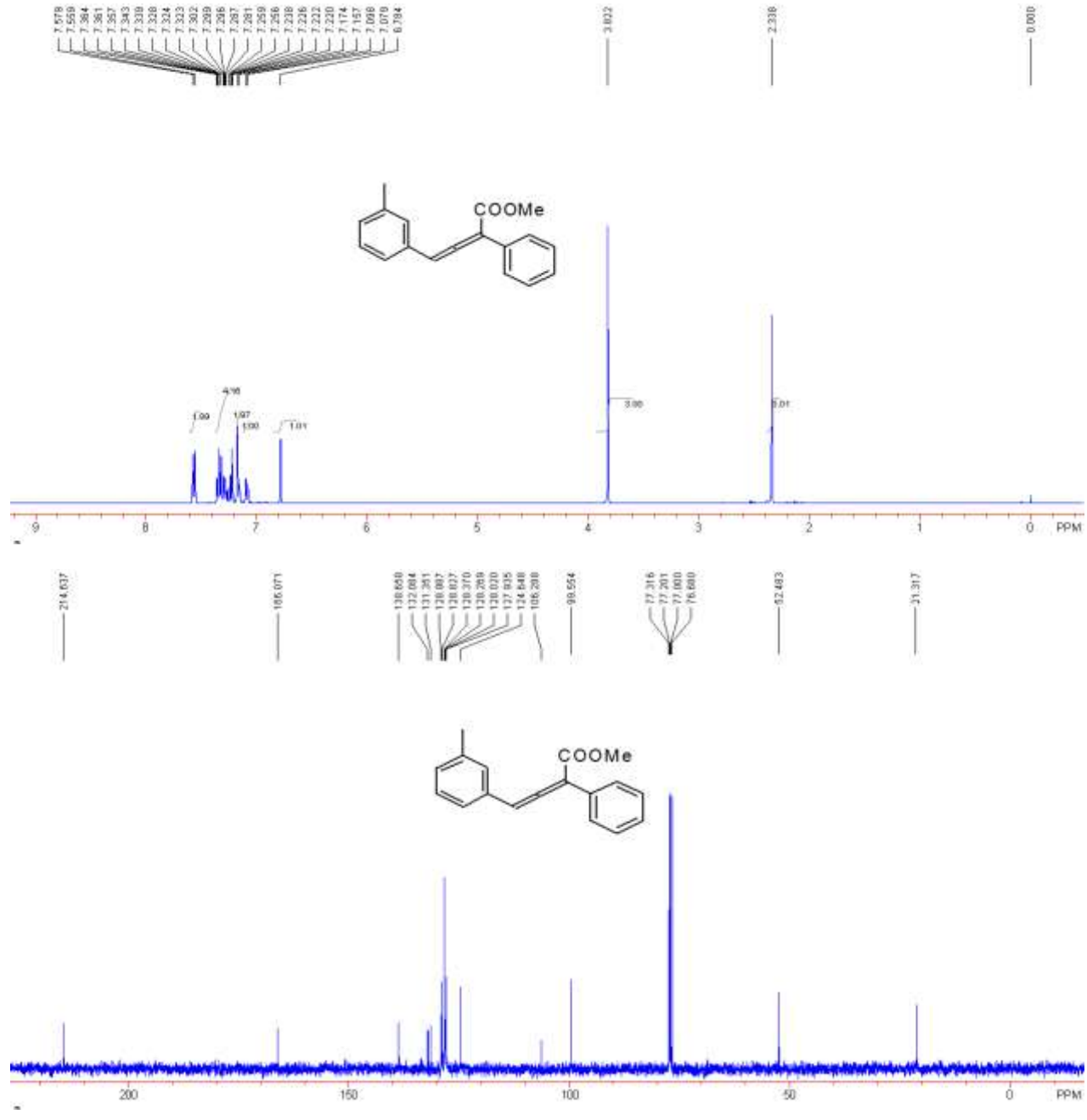


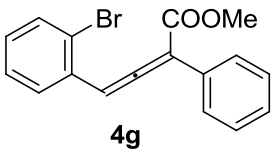




4f

methyl 2-phenyl-4-m-tolylbuta-2,3-dienoate 4f: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4f** (46 mg, 87% yield). A yellow oil. IR (CH_2Cl_2): ν 2962, 1731, 1600, 1490, 1432, 1260, 1230, 1090, 1017, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.57 (2H, d, *J* = 8.0 Hz), 7.36-7.22 (4H, m), 7.17 (2H, d, *J* = 6.4 Hz), 7.09 (1H, d, *J* = 7.6 Hz), 6.78 (1H, s), 3.82 (3H, s), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.6, 166.0, 138.7, 132.1, 131.4, 129.0, 128.8, 128.4, 128.3, 128.0, 127.9, 124.6, 106.3, 99.6, 52.5, 21.3; MS (%) m/e 264 (55), 249 (30), 221 (19), 205 (100), 189 (36), 178 (16), 165 (6), 119 (24); HRMS (EI) for $C_{18}H_{16}O_2$: 264.1150; Found: 264.1147.

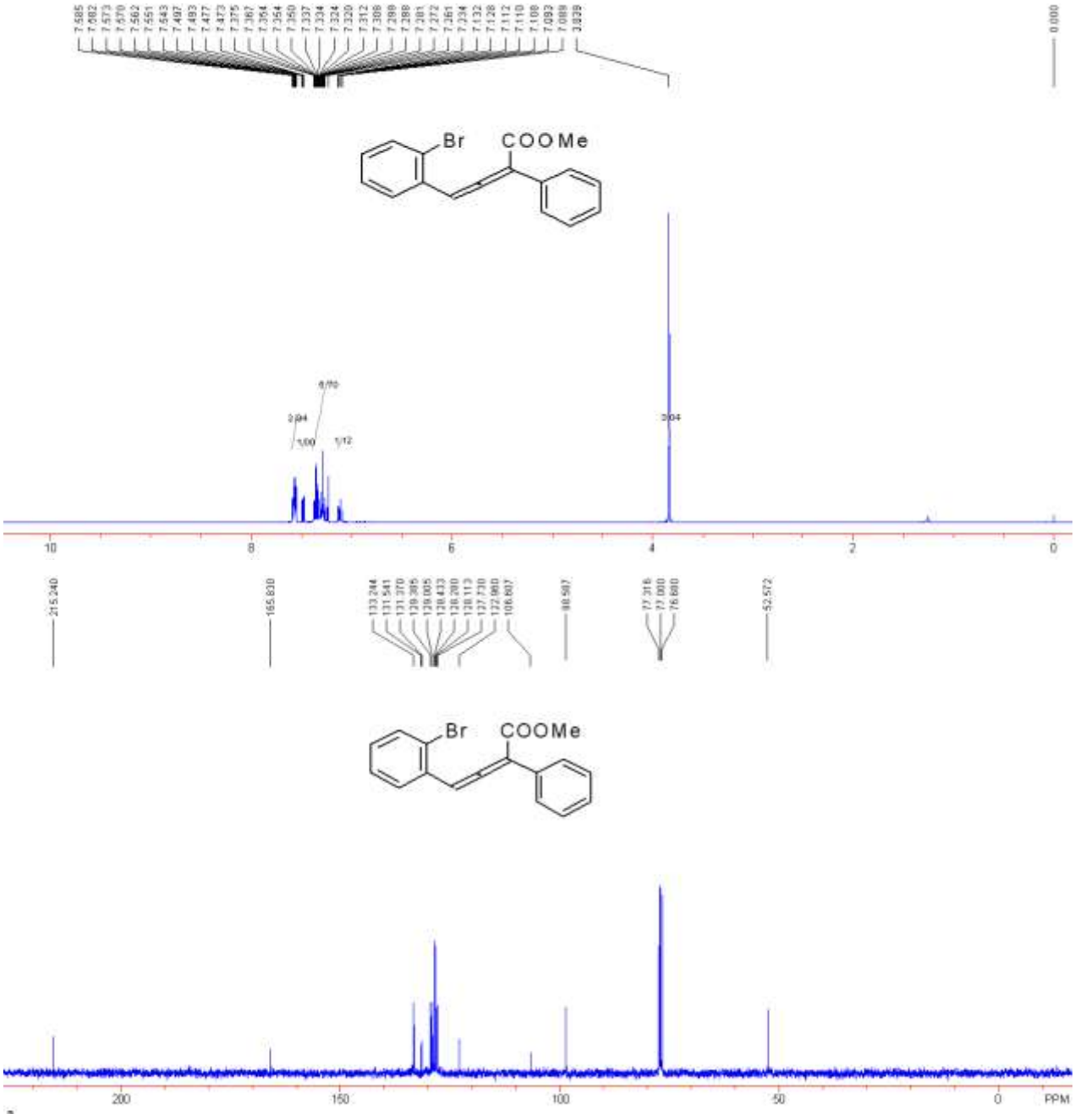


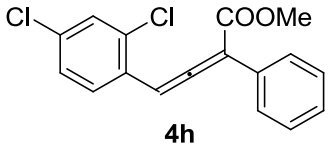


4g

methyl 4-(3-bromophenyl)-2-phenylbuta-2,3-dienoate 4g: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4g** (60 mg, 91% yield). A yellow oil. IR (CH_2Cl_2): ν 2950, 1932, 1719, 1493, 1473, 1435, 1265, 1215, 1038, 1019, 908, 797, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.59-7.54 (3H, m), 7.49 (1H, dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 7.38-7.23 (5H, m), 7.13-7.09 (1H, m), 3.84 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.2, 165.8, 133.2, 131.5, 131.4, 129.4, 129.0, 128.4, 128.3, 128.1, 127.7, 123.0, 106.6,

98.6, 52.6; MS (%) m/e 328 (11), 313 (6), 269 (41), 249 (89), 234 (22), 206 (6), 189 (100), 163 (14), 94 (14); HRMS (EI) for $C_{17}H_{13}BrO_2$: 328.0099; Found: 328.0101.

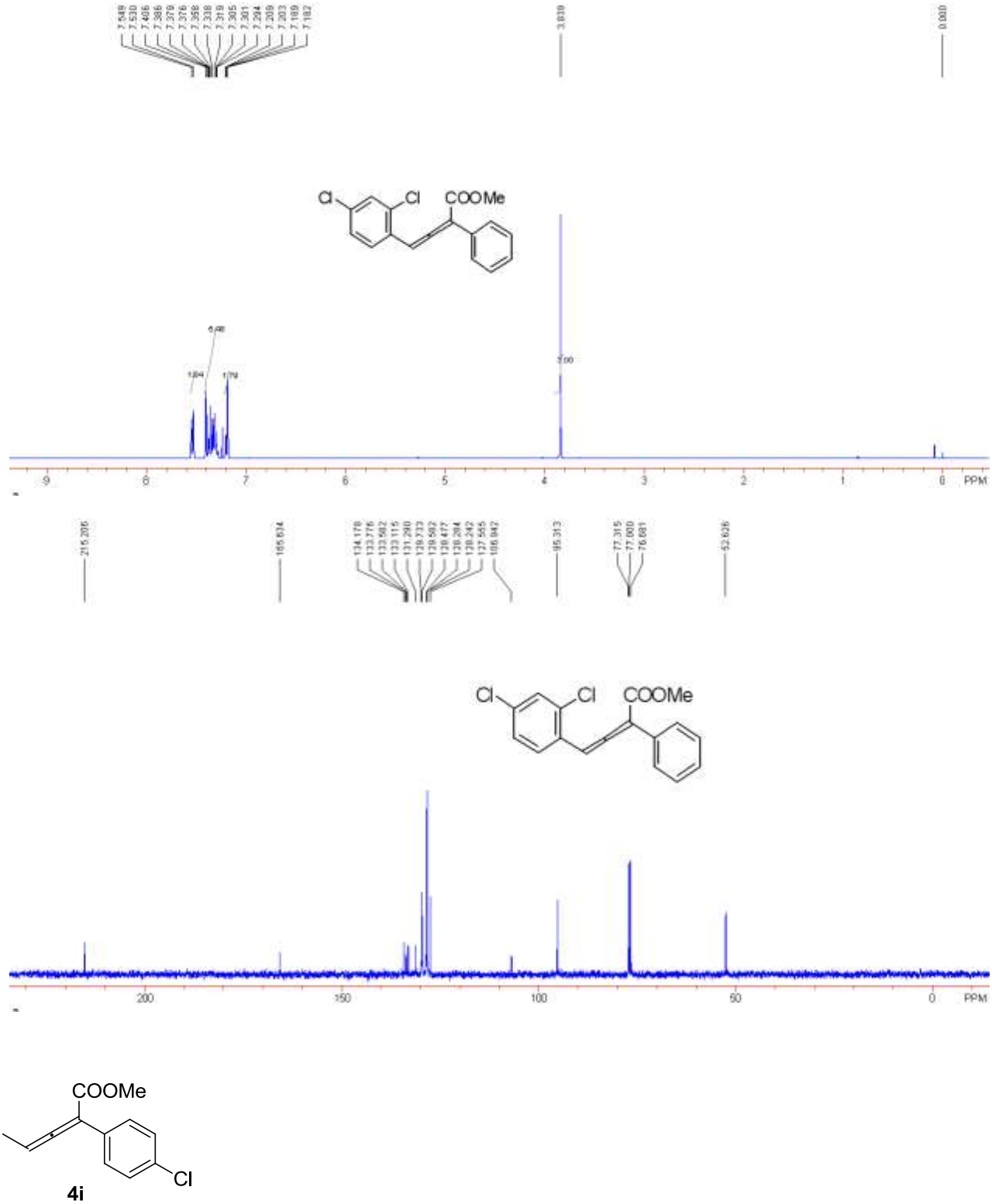




4h

methyl 4-(2,4-dichlorophenyl)-2-phenylbuta-2,3-dienoate 4h: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4h** (53mg, 83% yield). A yellow oil. IR (CH_2Cl_2): ν 2961, 1935, 1726, 1582, 1467, 1433, 1261, 1097, 1016, 864, 797, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.54 (2H, d, *J* = 7.6 Hz), 7.41-7.30

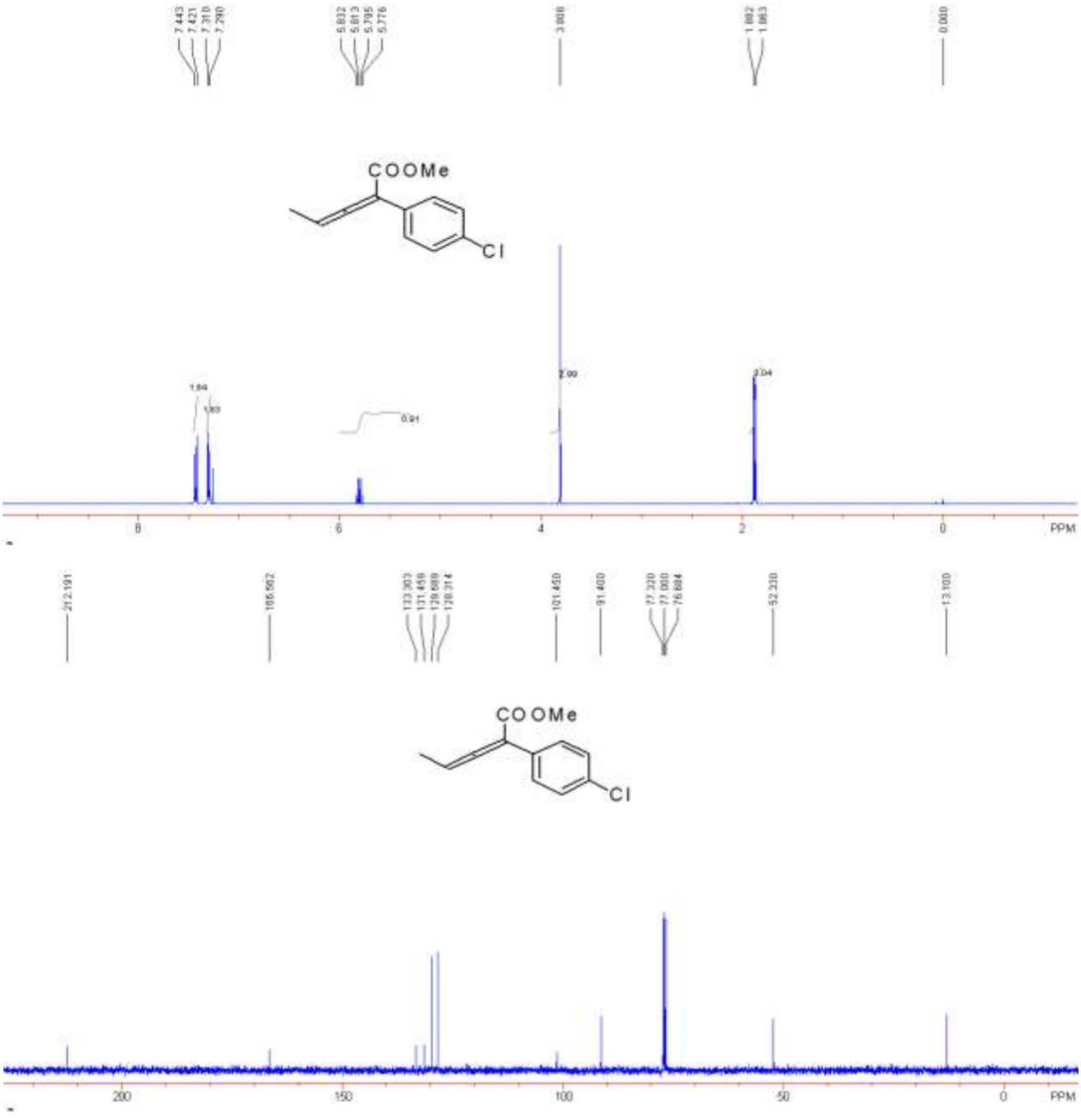
(5H, m), 7.21-7.18 (2H, m), 3.84 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 215.2, 165.6, 134.2, 133.8, 133.6, 133.1, 131.3, 129.7, 129.6, 128.5, 128.3, 128.2, 127.6, 106.9, 95.3, 52.6; MS (%) m/e 318 (40), 303 (15), 283 (53), 277 (31), 259 (100), 248 (17), 223 (22), 205 (22), 189 (64), 183 (17), 173 (25); HRMS (EI) for $C_{17}H_{12}Cl_2O_2$: 318.0214; Found: 318.0213.

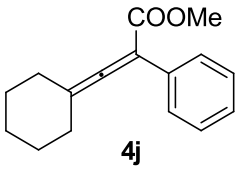


4i

methyl 2-(4-chlorophenyl)penta-2,3-dienoate 4i: Following the general procedure, the mixture

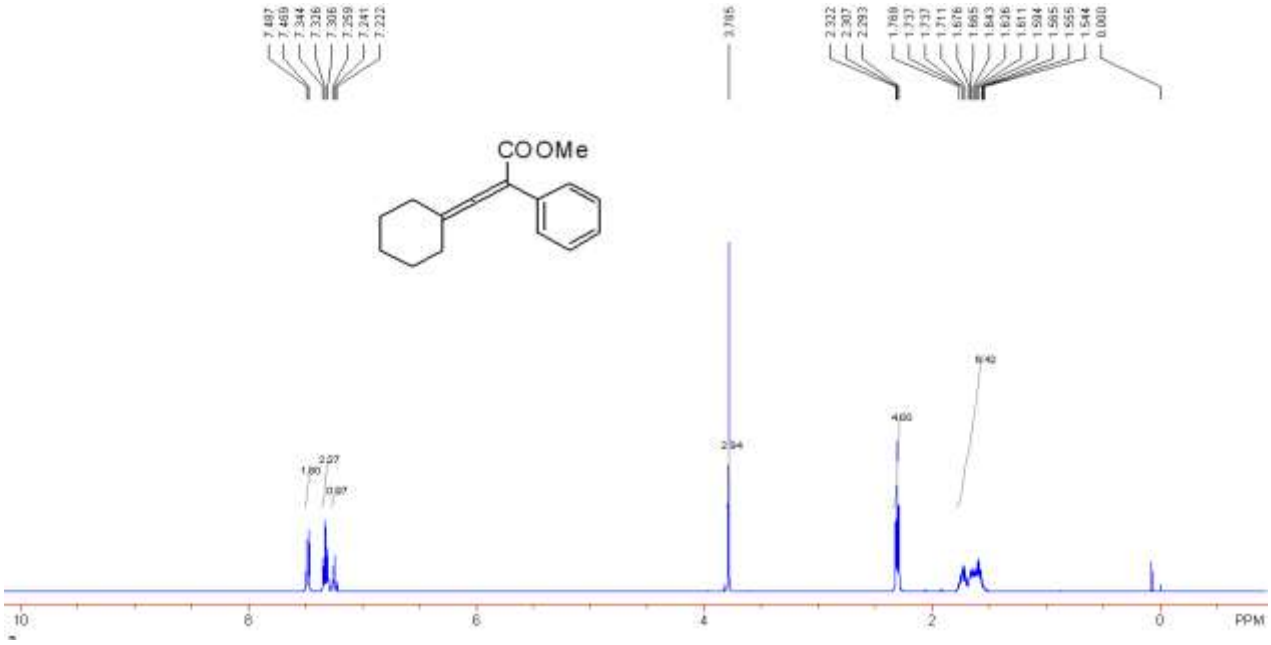
was purified by column chromatography using silica gel to give the target product **4i** (40 mg, 90% yield). A yellow solid. m.p. for **4i** = 52-54 ^{o}C. IR (CH_2Cl_2): ν 2961, 1946, 1717, 1491, 1434, 1371, 1281, 1260, 1220, 1144, 1091, 1012, 897, 863, 792, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.43 (2H, d, J = 8.8 Hz), 7.30 (2H, d, J = 8.0 Hz), 5.80 (1H, dd, J_1 = 14.8 Hz, J_2 = 7.6 Hz), 3.81 (3H, s), 1.87 (3H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.2, 166.6, 133.3, 131.5, 129.7, 128.3, 101.5, 91.4, 52.3, 13.1; MS (%) m/e 222 (51), 207 (15), 190 (23), 163 (57), 128 (100), 115 (17), 101 (19), 75 (21), 43 (44); HRMS (EI) for $C_{12}H_{11}ClO_2$: 222.0448; Found: 222.0443.

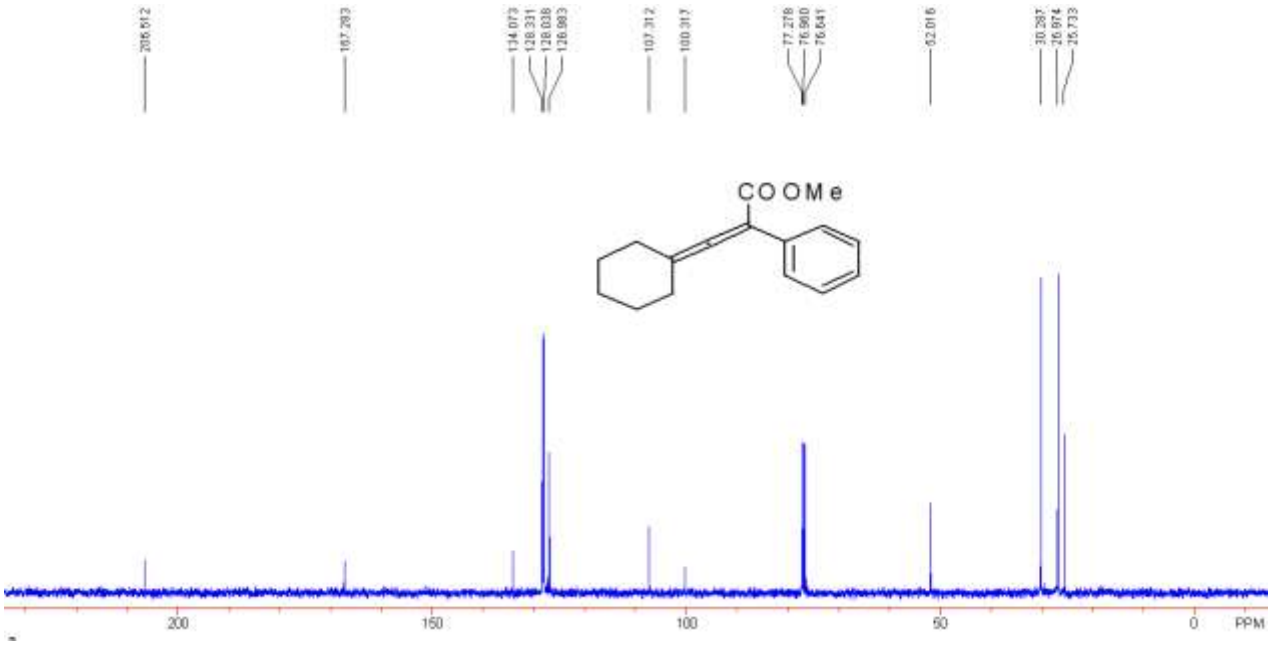


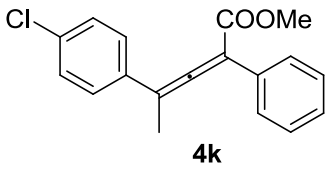


4j

methyl 3-cyclohexylidene-2-phenylacrylate 4j: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4j** (38 mg, 79% yield). A colorless oil. IR (CH_2Cl_2): ν 2931, 2854, 1949, 1713, 1492, 1434, 1264, 1224, 1192, 1165, 1092, 1040, 896, 784, 733, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.48 (2H, d, *J* = 7.2 Hz), 7.33 (2H, t, *J* = 7.2 Hz), 7.24 (1H, t, *J* = 7.2 Hz), 3.79 (3H, s), 2.31 (4H, t, *J* = 6.0 Hz), 1.77-1.54 (6H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.5, 167.3, 134.1, 128.3, 128.0, 127.0, 107.3, 100.3, 52.0, 30.3, 27.0, 25.7; MS (%) m/e 242 (85), 227 (11), 213 (90), 201 (10), 183 (54), 167 (17), 155 (49), 141 (100), 129 (30), 115 (80), 91 (35); HRMS (EI) for $C_{16}H_{18}O_2$: 242.1307; Found: 242.1303.

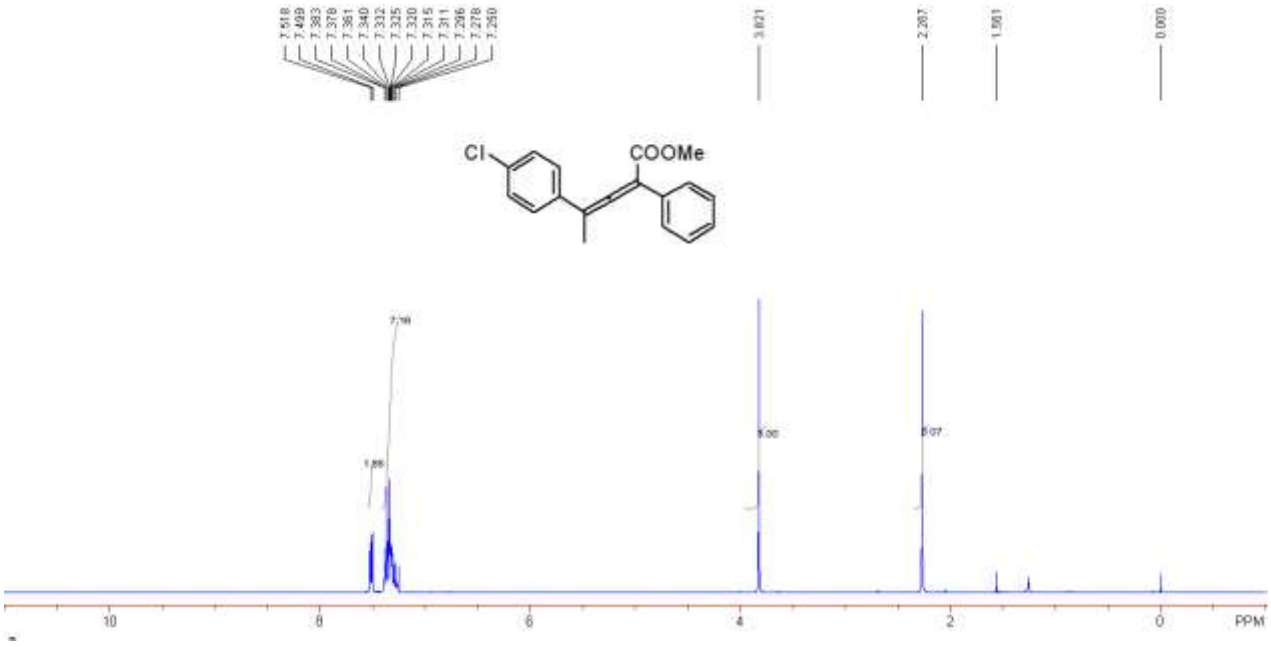


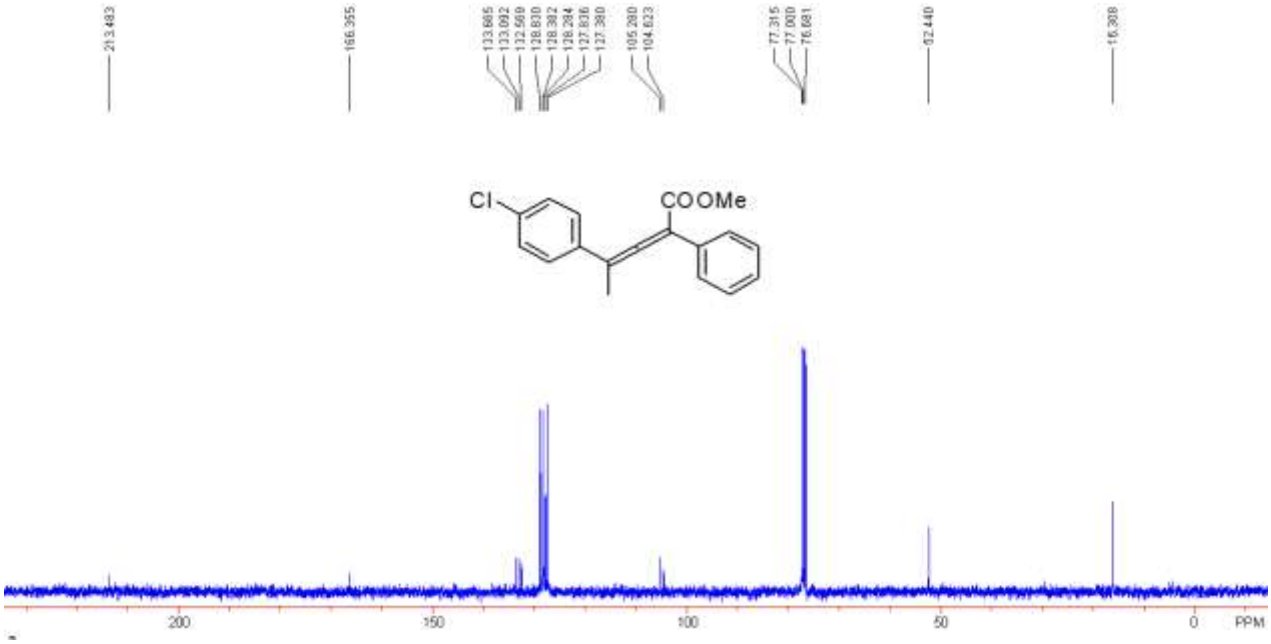




4k

methyl 4-(4-chlorophenyl)-2-phenylpenta-2,3-dienoate 4k: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4k** (17 mg, 57% yield). A white solid. m.p. for **4k** = 108-109 ^{o}C. IR (CH_2Cl_2): ν 2962, 1925, 1718, 1488, 1434, 1260, 1196, 1171, 1091, 1015, 865, 793, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.51 (2H, d, *J* = 7.6 Hz), 7.38-7.25 (7H, m), 3.82 (3H, s), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.5, 166.4, 133.7, 133.1, 132.6, 128.8, 128.4, 128.3, 127.8, 127.4, 105.3, 104.6, 52.4, 16.3; MS (%) m/e 298 (68), 283 (33), 239 (100), 202 (55), 189 (15), 127 (30), 101 (19), 77 (14); HRMS (EI) for $C_{18}H_{15}O_2Cl$: 298.0761; Found: 298.0760.





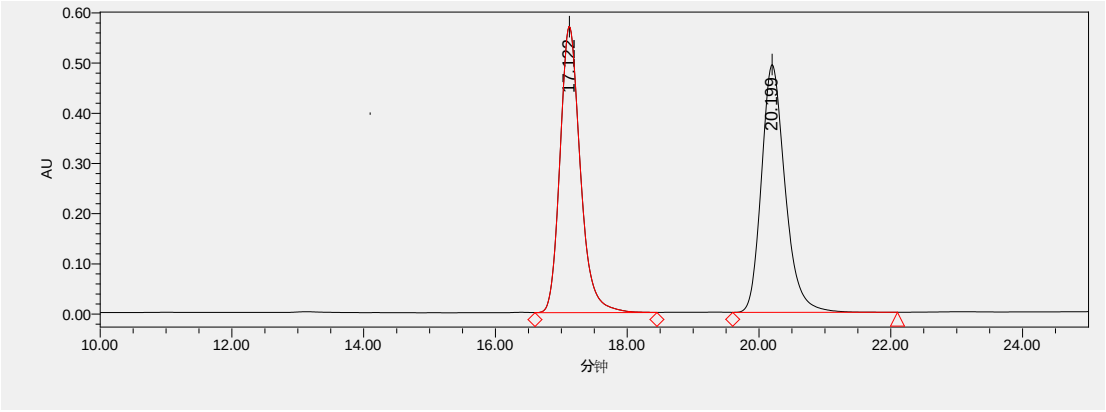
HPLC spectra:

HPLC REPORT

Sample Name: zz-21-56 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.4 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Precent	Peak Height
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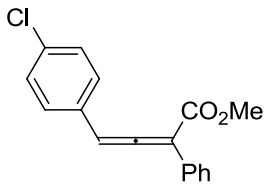
2	20.199	12313674	50.05	493742



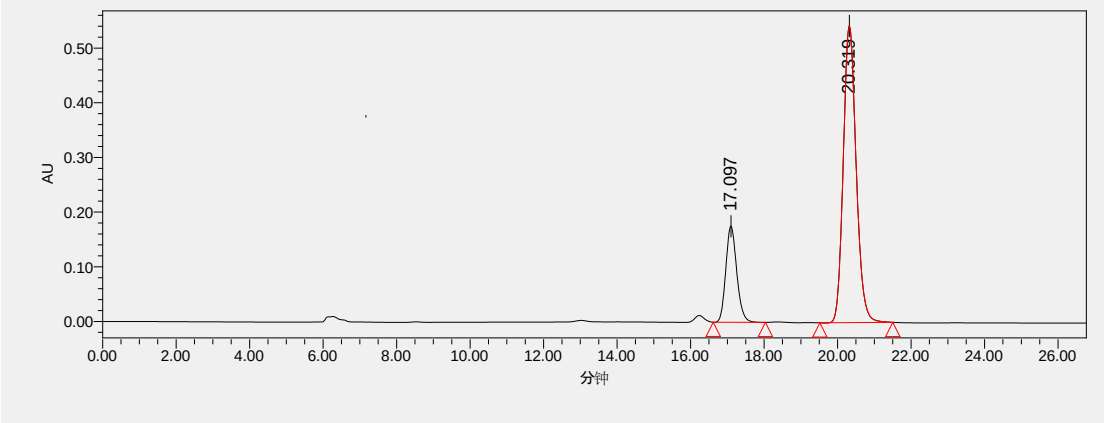
Chiral HPLC report: racemate (**4b**)

HPLC REPORT

Sample Name: zz-21-56 Date: ####

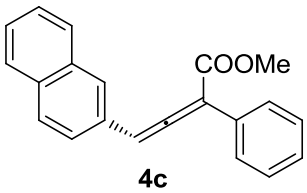
Column: AD-H Mobile Phase: hex/ipr = 95/5

Velocity (mL/min): 0.4 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Precent	Peak Height
1	17.097	3639024	21.58	175839
2	20.319	13327259	78.42	542934

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.4 mL/min; t_{minor} = 17.097 min, t_{major} = 20.319 min; ee% = 57.



4c

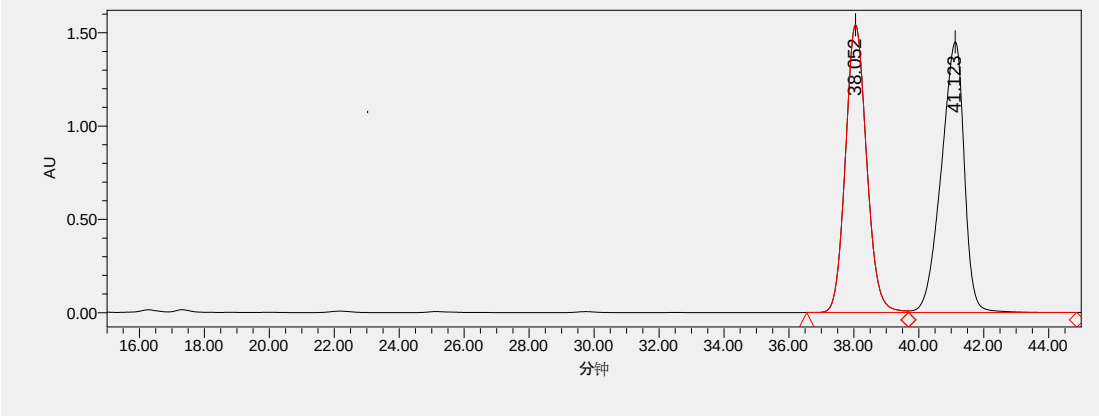
(S)-methyl 4-(naphthalen-2-yl)-2-phenylbuta-2,3-dienoate 4c: Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4c** (21 mg, 70% yield). A white solid. m.p. for **4c** = 101-103 ^{o}C. $[\alpha]^{20}_{D}$ = +42.2 (*c* 0.7, CH_2Cl_2). The ee of the product **4c** was determined to be 71% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 98:2, 0.4 mL/min, λ = 230 nm, t (major) = 37.78 min, t (minor) = 40.49 min].

HPLC REPORT

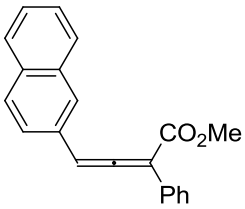
Sample Name: yyl-24-36 Date: ####

Column: AD-H Mobile Phase: hex/ipr = 98/2

Velocity (mL/min): 0.4 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Precent	Peak Height
1	38.052	69825084	49.47	1542056
2	41.123	71335140	50.53	1450728



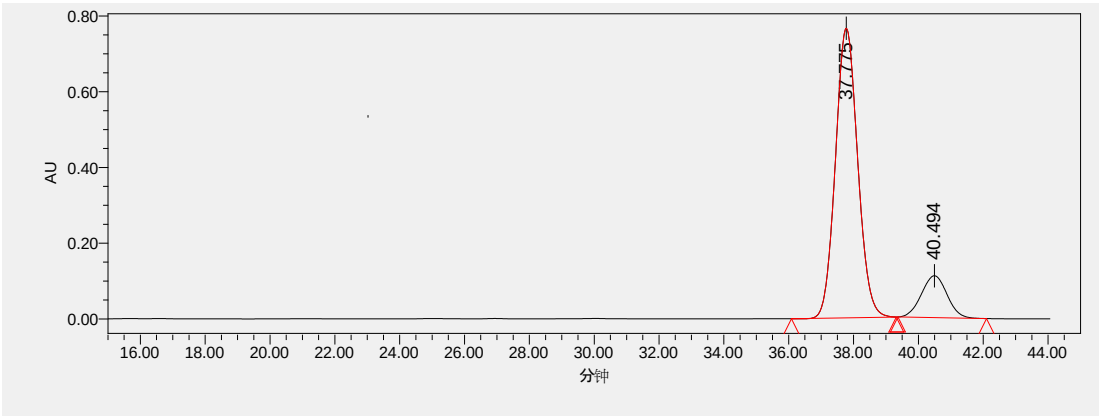
Chiral HPLC report: racemate (**4c**)

HPLC REPORT

Sample Name: yyl-24-37 Date: ####

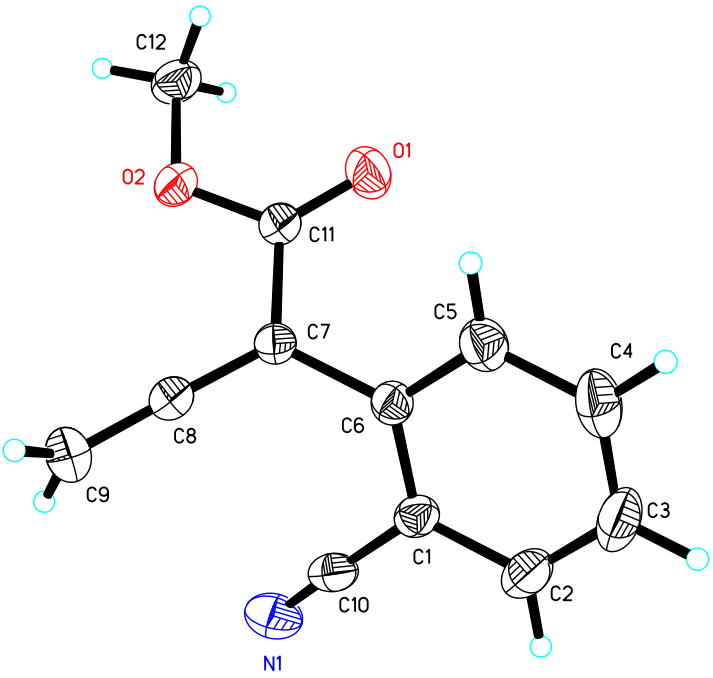
Column: AD-H Mobile Phase: hex/ipr = 98/2

Velocity (mL/min): 0.4 Detection Wavelength (nm): 230



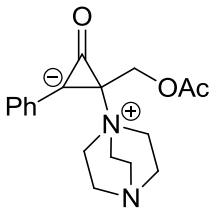
NO	R. Time	Peak Area	Precent	Peak Height
1	37.775	36447261	85.70	764551
2	40.494	6080678	14.30	110686

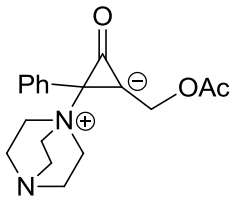
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column; λ = 230 nm; eluent: Hexane/Isopropanol = 98/2; Flow rate: 0.4 mL/min; t_{minor} = 40.494 min, t_{major} = 37.775 min; ee% = 71.

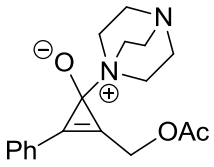


The crystal data of **3j** have been deposited in CCDC with number 917097. Empirical Formula: $C_{12}H_9NO_2$; Formula Weight: 199.20; Crystal Color, Habit: colorless; Crystal Dimensions: 0.311 x 0.186 x 0.079 mm; Crystal System: Monoclinic; Lattice Parameters: a = 8.1053(9)Å, b = 14.1123(16)Å, c = 9.2252(11)Å, $\alpha = 90^o$, $\beta = 97.664(2)^o$, $\gamma = 90^o$, V = 1045.8(2)Å^3; Space group: P2(1)/n; Z = 4; D_{calc} = 1.265 g/cm^3; F_{000} = 416; Final R indices [I>2sigma(I)] R1 = 0.0475, wR2 = 0.1163.

Calculation results







Relative energy ΔH_{298} (kcal/mol)	0.0	3.8	unstable

Calculated at mPW1K/6-31+G(d) level