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Supporting Information

Cut and Sew: Benzofuran-Ring-Opening Enabled Cyclopentenone Ring Formation

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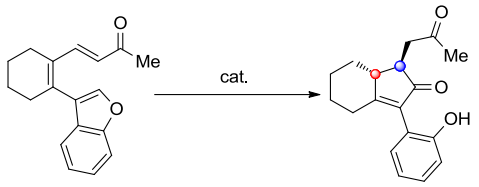
1. General remarks

All reactions were carried out in oven-dried glassware. All the reactions were monitored by thin-layer chromatography (TLC). Purification of products was carried out by silica gel column chromatography.

$^{1}H/^{13}C$ NMR spectra were recorded on Bruker Avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Data for ^{1}H NMR spectra were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.00 ppm). HRMS (ESI) spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE).

All reagents and solvents were obtained from commercial sources and used without further purification. Raw materials ethyl 2-oxocyclohexane-1-carboxylate (**M2**) and benzofuran-3-ylboronic acid (**M4**) were purchased from commercial sources and used without further purification. Materials **M1** (including **M1-1a** ~ **M1-1k**) were synthesized according to known methods.[1-3]

2. Optimization of the Reaction Conditions



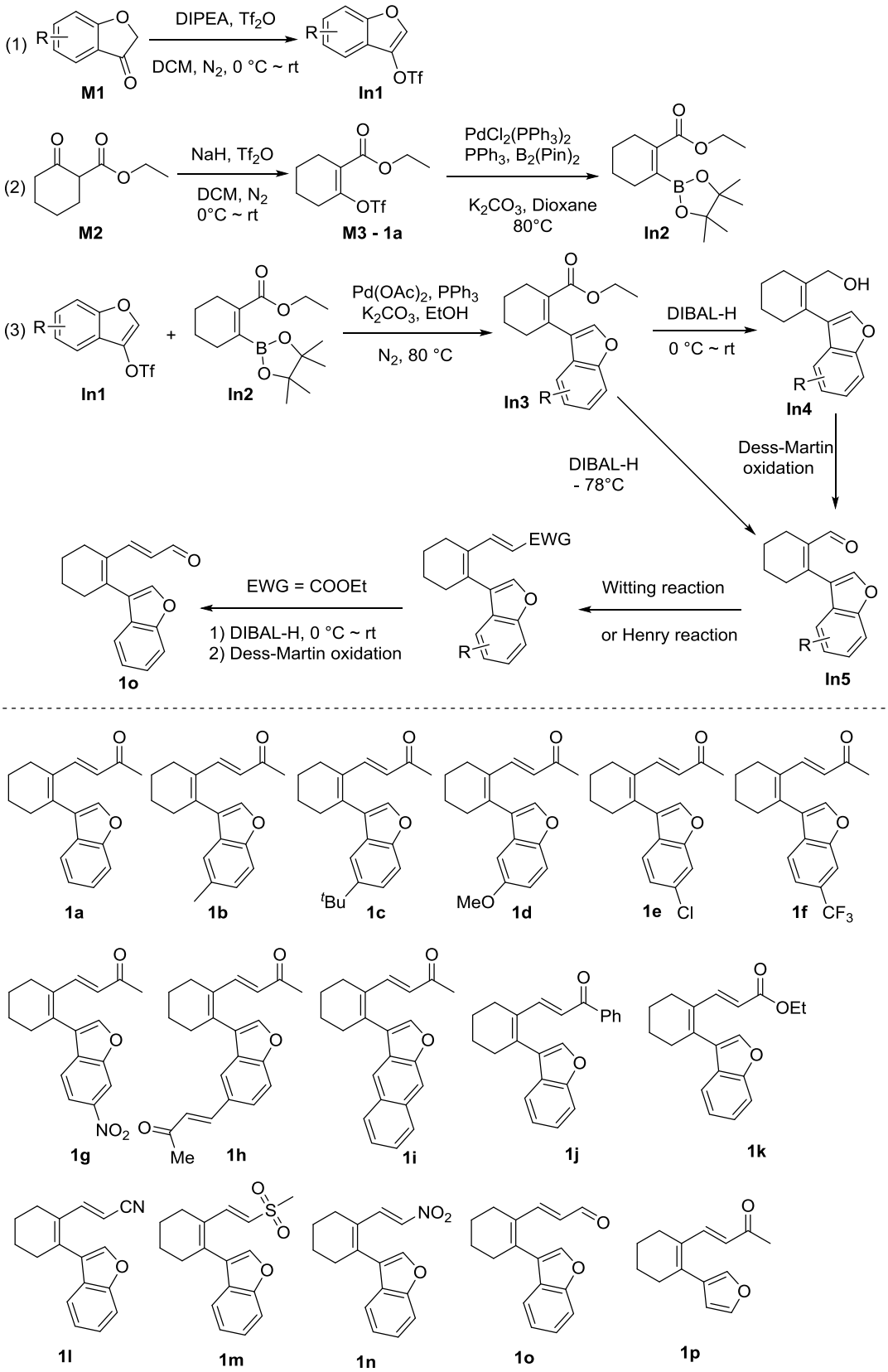
1a **2a**

Entry	catalyst	solvent	time	yield (%)[b]
1	$Fe(OTf)_3$	CH_3NO_2	6 h	80 (68)
2	$FeCl_3$	CH_3NO_2	2 h	trace
3	$Zn(OTf)_2$	CH_3NO_2	16 h	ND
4	$In(OTf)_3$	CH_3NO_2	12 h	51
5	$Cu(OTf)_2$	CH_3NO_2	48 h	55
6	$Sc(OTf)_3$	CH_3NO_2	9 h	54
7	AgOTf	CH_3NO_2	36 h	52
8	**TMSOTf**	**CH_3NO_2**	**4.5 h**	**86 (75)**
9	TfOH	CH_3NO_2	7.5 h	78
10	PTSA·H_2O	CH_3NO_2	72 h	65
11	TMSOTf	$CHCl_3$	1.5 h	83
12	TMSOTf	THF	48 h	53
13	TMSOTf	DCM	4.5 h	58
14	TMSOTf	toluene	2 h	54
15[c]	TMSOTf	CH_3NO_2	37 h	84

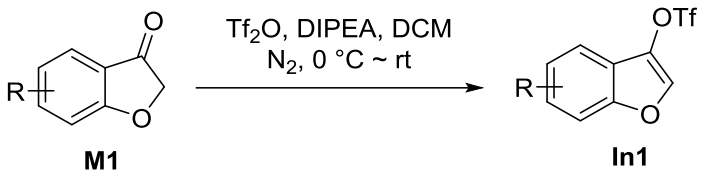
Table 1 Optimization of the Reaction Conditions[a] .[a]Recation conditions: 0.1 mmol of **1a**, 20 mol% catalyst in solvent at room temperature. [b]NMR yield using CH_2Br_2 as internal standard. Isolated yields shown in parentheses. [c]10 mol% of catalyst was used.

3. Synthesis route overview of substrates 1a ~ 1p

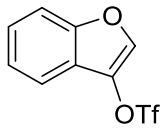
Synthesis route overview:



3.1. General procedures for the synthesis of fragment In1



DIPEA (1.1 mL, 6.5 mmol) was added dropwise via syringe to a stirred solution of material **M1** (5 mmol) in dry CH_2Cl_2 under nitrogen at 0 ℃. After the mixture was stirred for 10 min, trifluoromethanesulfonic anhydride (1.3 mL, 7.5 mmol) was then added and the mixture was continued to stir at rt. The reaction was monitored by TLC. After the material was completed, the reaction was quenched by water (15 mL) and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude extracts were purified by silica gel column chromatography to afford the product **In1** in corresponding yields.



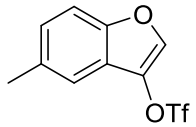
Benzofuran-3-yl trifluoromethanesulfonate (In1-1a)

Yellow liquid; 1.1836 g; 89% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 150/1), R_f = 0.60 (petroleum ether/ethyl acetate = 50/1).

IR (KBr) $\tilde{\nu}$ 3132.0, 1580.6, 1454.6, 1433.9, 1217.1, 1137.9, 854.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 135.4, 134.2, 126.2, 120.4, 120.2, 118.8 (q, *J* = 320.0 Hz), 118.1, 112.4.



5-Methylbenzofuran-3-yl trifluoromethanesulfonate (In1-1b)

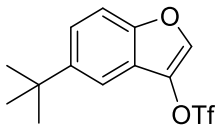
Yellow liquid; 1.2040 g; 86% yield; purified by silica gel chromatography (pure petroleum ether), R_f = 0.60 (pure petroleum ether).

IR (KBr) $\tilde{\nu}$ 2927.1, 1579.5, 1433.1, 1214.6, 1139.0, 856.1, 603.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 – 7.32 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 135.4, 134.0, 133.9, 127.6, 120.3, 118.8 (q, *J* = 321.4 Hz), 117.6, 111.9, 21.3.

HRMS (ESI) m/z calcd. for $C_{10}H_8F_3O_4S$ $[M+H]^+$: 281.0090, found: 281.0090.



5-(*tert*-Butyl)benzofuran-3-yl trifluoromethanesulfonate (In1-1c)

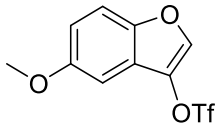
Yellow liquid; 1.4184 g; 92% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 50/1), R_f = 0.80 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 2965.9, 1577.5, 1433.5, 1216.7, 1141.8, 856.6, 720.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.57 (s, 1H), 7.49 – 7.39 (m, 2H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.5, 135.3, 134.4, 124.4, 119.8, 118.8 (q, *J* = 321.4 Hz), 114.0, 111.8, 34.9, 31.6.

HRMS (ESI) m/z calcd. for $C_{13}H_{14}F_3O_4S$ $[M+H]^+$: 323.0559, found: 323.0559.



5-Methoxy-3-((trifluoromethyl)sulfonyl)benzofuran (In1-1d)

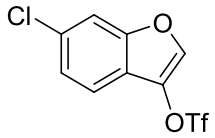
Yellow liquid; 1.2284 g; 83% yield; purified by silica gel chromatography (pure petroleum ether), R_f = 0.40 (petroleum ether/ethyl acetate = 200/1).

IR (KBr) $\tilde{\nu}$ 2838.9, 1624.3, 1488.6, 1431.7, 1228.2, 1136.1, 853.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.39 (d, *J* = 9.8 Hz, 1H), 7.03 – 6.97 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 148.2, 136.0, 134.1, 120.7, 118.79 (q, *J* = 321.7 Hz), 115.7, 113.2, 99.7, 55.9.

HRMS (ESI) m/z calcd. for $C_{10}H_8F_3O_5S$ $[M+H]^+$: 297.0039, found: 297.0040.



6-Chlorobenzofuran-3-yl trifluoromethanesulfonate (In1-1e)

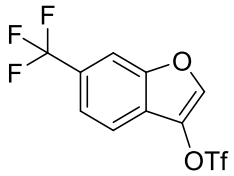
Yellow solid; 1.2748 g; 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 200/1), R_f = 0.61 (petroleum ether/ethyl acetate = 50/1).

IR (KBr) $\tilde{\nu}$ 2926.7, 1598.8, 1433.9, 1216.4, 1139.9, 1070.3, 852.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.55 – 7.49 (m, 2H), 7.34 (dd, *J* = 8.4, 1.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 136.0, 133.9, 132.5, 125.1, 118.9, 118.8, 118.8 (q, *J* = 320.0 Hz), 113.0.

HRMS (ESI) m/z calcd. for $C_9H_5ClF_3O_4S$ $[M+H]^+$: 300.9544, found: 300.9542.



6-(Trifluoromethyl)benzofuran-3-yl trifluoromethanesulfonate (In1-1f)

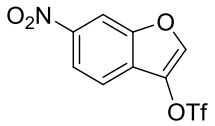
Yellow liquid; 1.3860 g; 83% yield; purified by silica gel chromatography (petroleum ether), R_f = 0.41 (petroleum ether).

IR (KBr) $\tilde{\nu}$ 3127.2, 1578.0, 1502.3, 1433.7, 1337.6, 1073.9, 705.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.82 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 137.9, 133.8, 128.9 (q, *J* = 33.0 Hz), 123.1, 123.9 (q, *J* = 272.3 Hz), 121.2 (q, *J* = 3.6 Hz), 119.0, 118.8 (q, *J* = 321.5 Hz), 110.25 (q, *J* = 4.3 Hz).

HRMS (ESI) m/z calcd. for $C_{10}H_5F_6O_4S$ $[M+H]^+$: 334.9807, found: 334.9803.



6-Nitrobenzofuran-3-yl trifluoromethanesulfonate (In1-1g)

Yellow solid; 1.3372 g; 86% yield; purified by silica gel chromatography (petroleum

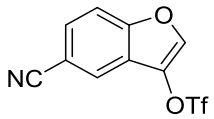
ether/ethyl acetate = 30/1), R_f = 0.61 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{v}$ 3114.9, 1576.3, 1530.1, 1434.6, 1349.7, 1216.1, 852.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.8 Hz, 1H), 8.31 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.11 (s, 1H), 7.78 (d, *J* = 8.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 146.5, 140.3, 133.8, 125.5, 119.8, 118.7 (q, *J* = 321.6 Hz), 118.8, 109.2.

HRMS (ESI) m/z calcd. for $C_9H_5F_3NO_6S$ $[M+H]^+$: 311.9784, found: 311.9778.



5-Cyanobenzofuran-3-yl trifluoromethanesulfonate (In1-1h)

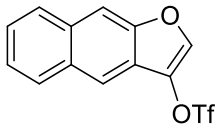
Yellow solid; 1.1930 g; 82% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.61 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{v}$ 3124.7, 2235.1, 1434.4, 1217.2, 1138.1, 852.4, 636.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.71 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 137.7, 133.5, 129.7, 123.6, 121.0, 118.2, 118.7 (q, *J* = 321.5 Hz), 113.9, 108.7.

HRMS (ESI) m/z calcd. for $C_{10}H_4F_3NNaO_4S$ $[M+Na]^+$: 313.9705, found: 313.9710.



Naphtho[2,3-*b*]furan-3-yl trifluoromethanesulfonate (In1-1i)

Yellow liquid; 1.3746 g; 87% yield; purified by silica gel chromatography (petroleum ether), R_f = 0.40 (petroleum ether).

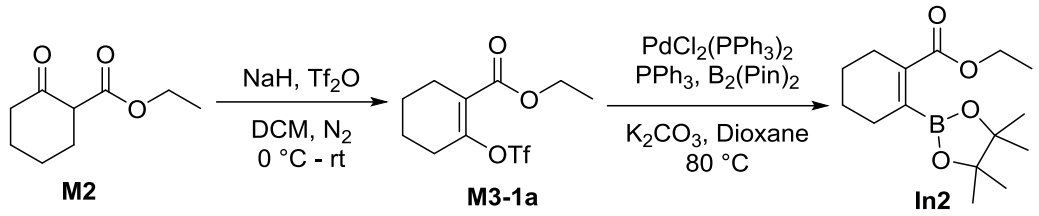
IR (KBr) $\tilde{v}$ 3186.9, 3134.6, 3056.6, 1739.4, 1422.9, 1214.7, 863.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.00 – 7.95 (m, 1H), 7.94 – 7.86 (m, 3H), 7.53 – 7.44 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 137.6, 133.9, 132.0, 130.6, 128.3, 128.0, 126.1, 125.2, 120.8, 118.85 (q, *J* = 321.4 Hz), 116.5, 108.4.

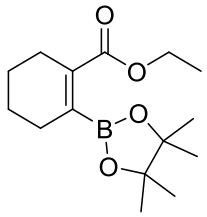
HRMS (ESI) m/z calcd. for $C_{13}H_8F_3O_4S$ $[M+H]^+$: 317.0090, found: 317.0086.

3.2. Procedures for the synthesis of fragment In2



To a solution of ethyl 2-oxocyclohexane-1-carboxylate **M2 (**15 mmol) in CH_2Cl_2 (40 mL) was slowly added NaH (60% w/w dispersion in mineral oil, 780 mg, 19.5 mmol) at 0 ℃. After stirring for 30 min, trifluoromethanesulfonic anhydride (3.8 mL, 22.5 mmol) was added dropwise to the reaction. The resulting mixture was then warmed to room temperature. After stirring overnight, the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic phases were washed with saturated brine, dried over anhydrous Na_2SO_4, concentrated under vacuum. The resulting crude product was purified by flash column chromatography over silica gel to afford the product **M3-1a**.

In a Schlenk flask, a mixture of **M3-1a** (3.0204 g, 10 mmol), $B_2(pin)_2$ (2.7933 g, 11 mmol), PPh_3 (157.4 mg, 0.6 mmol), $PdCl_2(PPh_3)_2$ (210.6 mg, 0.3 mmol), K_2CO_3 (2.0700 g, 15 mmol), and anhydrous 1,4-dioxane (30 mL) was vigorously stirred together at 80 ℃ for 6 h under N_2. After the reaction was complete, solvent 1,4-dioxane was removed through rotary evaporator, and then the mixture was added to saturated aqueous NH_4Cl solution, extracted with ethyl acetate three times. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude extracts were purified by silica gel column chromatography to afford the coupling product **In2**.



Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-1-carboxylate (In2)

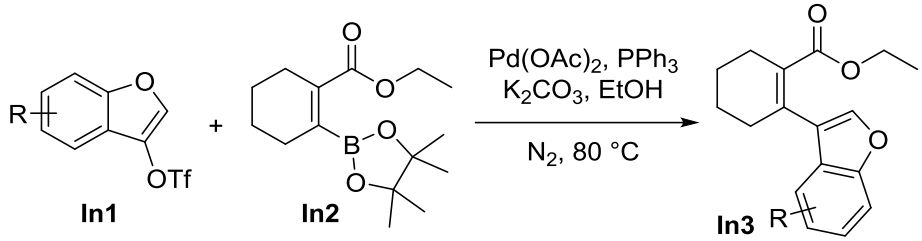
Pale yellow liquid; 1.9753 g; 47% (two steps) yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.21 (petroleum ether/ethyl acetate = 30/1).

IR (KBr) $\tilde{v}$ 2977.5, 1704.7, 1635.4, 1463.7, 1371.5, 1249.6, 850.5cm^{-1}

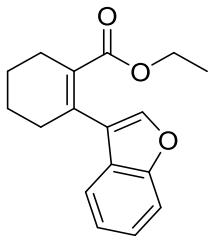
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (q, *J* = 7.1 Hz, 2H), 2.25 – 2.19 (m, 4H), 1.65 – 1.57 (m, 4H), 1.33 (s, 12H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 134.3, 83.4, 60.7, 28.0, 24.8, 24.2, 21.9, 21.5, 14.3.

3.3. General procedures for the synthesis of intermediates In3



Under N_2, a Schlenk flask was charged with anhydrous EtOH (30 mL) and a mixture of **In1** (4 mmol), **In2** (1.6811 g, 6 mmol), PPh_3 (209.8 mg, 0.8 mmol), $Pd(OAc)_2$ (89.8 mg, 0.4 mmol), K_2CO_3 (1.1057 g, 8 mmol). The reaction was stirred at 80 ℃ overnight. After the reaction was complete, most of ethanol was removed through rotary evaporator. The reaction was quenched by saturated aqueous NH_4Cl solution and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the coupling product **In3**.



Ethyl 2-(benzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1a)

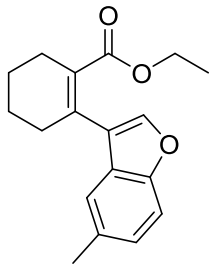
White solid; 907.6 mg; 84% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2934.2, 1704.7, 1683.7, 1452.1, 1370.9, 1253.7, 757.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.48 – 7.41 (m, 2H), 7.30 – 7.23 (m, 1H) ,7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 2.50 (dq, *J* = 6.2, 3.4 Hz, 2H), 2.45 (dt, *J* = 6.4, 3.5 Hz, 2H), 1.78 (p, *J* = 3.1 Hz, 4H), 0.72 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 154.9, 141.2, 134.8, 130.2, 127.2, 124.2, 123.1, 122.5, 120.2, 111.4, 60.3, 32.6, 26.8, 22.4, 21.9, 13.3.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1329, found: 271.1327.



Ethyl 2-(5-methylbenzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1b)

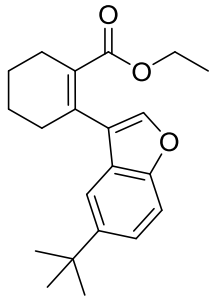
Pale liquid; 738.8 mg; 65% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 35/1), R_f = 0.22 (petroleum ether/ethyl acetate = 30/1).

IR (KBr) $\tilde{\nu}$ 2935.1, 1704.7, 1473.4, 1371.1, 1276.6, 1048.8, 796.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.21 (s, 1H), 7.07 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.52 – 2.46 (m, 2H), 2.44 (q, *J* = 3.0 Hz, 2H), 2.41 (s, 3H), 1.77 (p, *J* = 3.1 Hz, 4H), 0.75 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 153.3, 141.3, 134.9, 132.0, 130.1, 127.2, 125.5, 122.8, 120.0, 111.0, 60.3, 32.5, 26.8, 22.4, 21.9, 21.3, 13.4.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found: 285.1484.



Ethyl 2-(5-(*tert*-butyl)benzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1c)

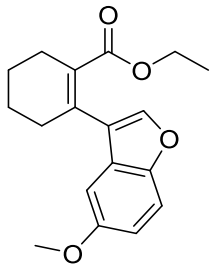
Pale yellow liquid; 887.2 mg; 68% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1),R_f = 0.60 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 2936.9, 1712.5, 1479.1, 1274.7, 1245.8, 1085.7, 746.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.39 – 7.36 (m, 2H), 7.33 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 2.54 – 2.50 (m, 2H), 2.45 (td, *J* = 5.6, 2.5 Hz, 2H), 1.79 (p, *J* = 2.9 Hz, 4H), 1.36 (s, 9H), 0.67 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 153.1, 145.7, 141.5, 134.9, 129.9, 126.7, 123.3, 122.2, 116.4, 110.7, 60.3, 34.7, 32.7, 31.9, 26.9, 22.4, 21.9, 13.2.

HRMS (ESI) m/z calcd. for $C_{21}H_{27}O_3$ $[M+H]^+$: 327.1955, found: 327.1953.



Ethyl 2-(5-methoxybenzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1d)

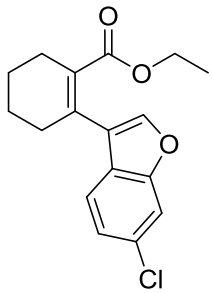
Pale yellow liquid; 672.3 mg; 56% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.61 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2937.1, 1714.7, 1616.1, 1475.3, 1373.0, 1047.7, 802.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 6.89 – 6.85 (m, 2H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.53 – 2.47 (m, 2H), 2.47 – 2.41 (m, 2H), 1.78 (p, *J* = 3.1 Hz, 4H), 0.75 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 155.9, 149.8, 142.1, 134.7, 130.2, 127.7, 123.2, 113.3, 111.9, 102.6, 60.3, 56.0, 32.5, 26.8, 22.4, 21.9, 13.3.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1434, found: 301.1434.



Ethyl 2-(6-chlorobenzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1e)

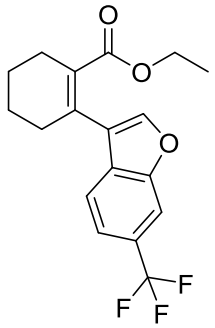
Pale yellow liquid; 1.1069 g; 91% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.61 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2935.7, 1697.1, 1471.4, 1255.4, 1135.4, 1088.3, 862.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.19 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.49 (dt, *J* = 6.5, 4.0 Hz, 2H), 2.44 – 2.39 (m, 2H), 1.77 (p, *J* = 3.2 Hz, 4H), 0.79 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 154.9, 141.8, 134.2, 130.7, 130.2, 125.9, 123.3, 123.0, 120.8, 112.0, 60.4, 32.6, 26.8, 22.3, 21.8, 13.5.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}ClO_3$ $[M+H]^+$: 305.0939, found: 305.0939.



Ethyl 2-(6-(trifluoromethyl)benzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1f)

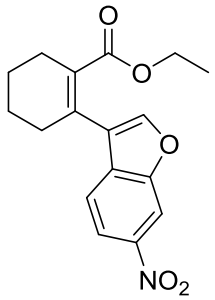
Pale yellow liquid; 811.5 mg; 60% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.42 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2939.2, 1712.5, 1437.7, 1330.8, 1047.4, 902.5, 679.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.63 (s, 1H), 7.57 – 7.43 (m, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.55 – 2.47 (m, 2H), 2.47 – 2.40 (m, 2H), 1.79 (p, *J* = 3.1 Hz, 4H), 0.78 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 153.9, 143.6, 134.0, 131.1, 130.3, 126.7 (q, *J* = 32.7 Hz), 124.5 (q, *J* = 271.8 Hz), 123.2, 120.8, 119.5 (q, *J* = 3.4 Hz), 109.1 (q, *J* = 4.2 Hz), 60.4, 32.7, 26.7, 22.3, 21.8, 13.4.

HRMS (ESI) m/z calcd. for $C_{18}H_{18}F_3O_3$ $[M+H]^+$: 339.1203, found: 339.1204.



Ethyl 2-(6-nitrobenzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1g)

Pale yellow liquid; 642.8 mg; 51% yield; purified by silica gel chromatography

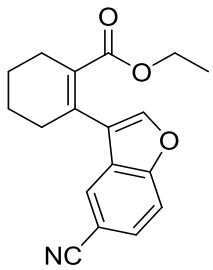
(petroleum ether/ethyl acetate = 20/1), R_f = 0.41 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2937.0, 1712.7, 1519.6, 1346.0, 1234.4, 1049.1, 823.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.75 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 2.55 – 2.48 (m, 2H), 2.43 (dt, *J* = 7.8, 4.1 Hz, 2H), 1.80 (p, *J* = 3.3 Hz, 4H), 0.82 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 153.5, 146.1, 145.1, 133.6, 133.1, 131.7, 123.6, 120.3, 118.3, 108.1, 60.4, 32.8, 26.7, 22.2, 21.8, 13.6.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NO_5$ $[M+H]^+$: 316.1179, found: 316.1180.



Ethyl 2-(5-cyanobenzofuran-3-yl)cyclohex-1-ene-1-carboxylate (In3-1h)

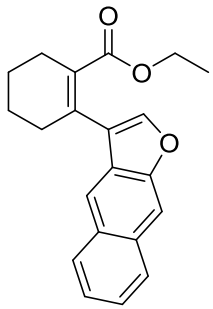
Pale yellow liquid; 661.1 mg; 56% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.58 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 2937.0, 2227.4, 1715.1, 1463.7, 1236.1, 1047.1, 813.9cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.61 (s, 1H), 7.55 (s, 2H), 3.90 (q, *J* = 7.1 Hz, 2H), 2.51 (dt, *J* = 6.3, 4.0 Hz, 2H), 2.42 (dt, *J* = 8.1, 4.1 Hz, 2H), 1.80 (p, *J* = 3.1 Hz, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 156.5, 143.1, 133.5, 131.7, 128.0, 127.9, 125.5, 123.1, 119.3, 112.8, 106.6, 60.4, 32.8, 26.7, 22.2, 21.8, 13.6.

HRMS (ESI) m/z calcd. for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1281, found: 296.1281.



Ethyl 2-(naphtho[2,3-*b*]furan-3-yl)cyclohex-1-ene-1-carboxylate (In3-1i)

Yellow liquid; 998.8 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.18 (petroleum ether/ethyl acetate = 30/1).

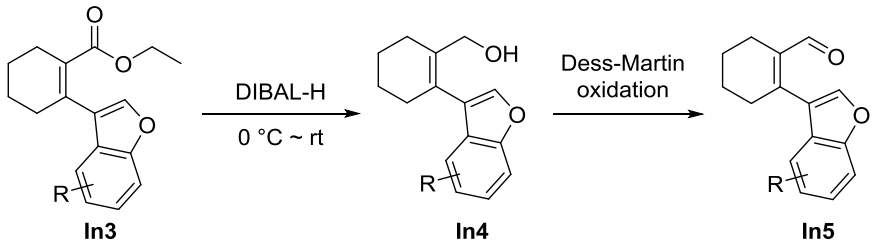
IR (KBr) $\tilde{\nu}$ 2933.6, 1704.8, 1442.5, 1373.1, 1254.1, 1093.3, 862.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.4, 2.6 Hz, 2H), 7.88 (d, *J* = 9.7 Hz, 2H), 7.60 (s, 1H), 7.46 – 7.36 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.48 (m, 4H), 1.82 (p, *J* = 3.1 Hz, 4H), 0.68 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 153.9, 143.4, 134.5, 131.4, 130.7, 130.3, 128.3, 128.2, 127.8, 125.0, 124.1, 122.6, 118.1, 107.0, 60.3, 32.5, 26.8, 22.4, 22.0, 13.4.

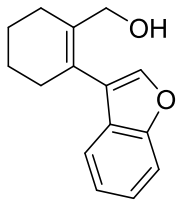
HRMS (ESI) m/z calcd. for $C_{21}H_{21}O_3$ $[M+H]^+$: 321.1485, found: 321.1484.

3.4. General procedures for the synthesis of intermediates In4 and In5



A solution of **In3 (**2 mmol**)** in dry DCM (30 mL) was added to an oven-dried Schlenk flask under N_2 and stirred at 0 ℃ for 5 min. DIBAL-H (1 M in hexanes, 5 mL, 5 mmol) was then slowly added and the reaction was warmed to room temperature. After completion, the reaction was diluted with saturated aqueous NH_4Cl solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the products **In4-1a**, **In4-1b**, **In4-1c**, **In4-1e**, **In4-1f**, **In4-1h**, and **In4-1i**.

To a solution of **In4** (1.5 mmol) in DCM (30 mL) was added Dess-Martin periodinane (DMP) (954.3 mg, 2.25 mmol) slowly at 0 ℃. Then the solution was warmed to room temperature and stirred for 10-20 min. After completion, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ solution and $NaHCO_3$ solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to obtain the aldehyde product **In5-1a**, **In5-1b**, **In5-1c**, **In5-1e**, **In5-1f**, **In5-1h**, and **In5-1i**.



(2-(Benzofuran-3-yl)cyclohex-1-en-1-yl)methanol (In4-1a)

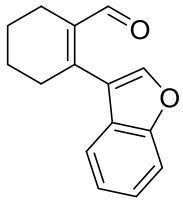
Pale liquid; 342.2 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3364.2, 2929.3, 1663.4, 1452.1, 1211.1, 1008.6, 746.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 3H), 7.31 – 7.26 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.02 (s, 2H), 2.36 – 2.30 (m, 4H), 1.80 – 1.74 (m, 4H), 1.45 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.4, 135.9, 127.7, 125.8, 124.3, 122.6, 121.7, 120.3, 111.5, 64.1, 31.6, 27.2, 23.0, 22.7.

HRMS (ESI) m/z calcd. for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1223, found: 229.1225.



2-(Benzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1a)

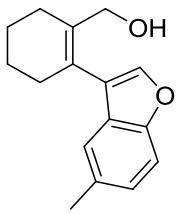
Yellow liquid; 264.5 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2933.4, 2858.3, 1712.4, 1668.0, 1452.1, 1220.7, 1110.6, 747.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.58 (s, 1H), 7.54 – 7.49 (m, 2H), 7.37 – 7.31 (m, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.41 (td, *J* = 6.0, 2.7 Hz, 2H), 1.85 – 1.73 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 155.3, 148.3, 143.4, 138.0, 127.2, 125.1, 123.3, 120.3, 119.5, 111.9, 33.1, 22.6, 22.3, 21.5.

HRMS (ESI) m/z calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found: 227.1066.



(2-(5-Methylbenzofuran-3-yl)cyclohex-1-en-1-yl)methanol (In4-1b)

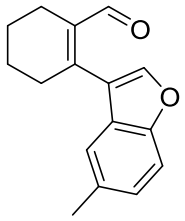
Pale yellow liquid; 377.7 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1), R_f = 0.18 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3347.2, 2927.8, 1666.7, 1471.4, 1216.9, 1097.3, 985.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 2H), 2.42 (s, 3H), 2.34 – 2.27 (m, 4H), 1.75 (p, *J* = 3.1 Hz, 4H), 1.64 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.6, 135.8, 132.1, 127.8, 125.9, 125.6, 121.5, 120.1, 111.1, 64.1, 31.6, 27.2, 23.0, 22.7, 21.4.

HRMS (ESI) m/z calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1384.



2-(5-Methylbenzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1b)

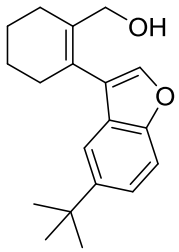
Yellow liquid; 288.1 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2935.1, 2859.1, 1711.1, 1668.0, 1473.3, 1222.5, 1110.6, 798.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.53 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 2.65 – 2.57 (m, 2H), 2.44 (s, 3H), 2.42 – 2.38 (m, 2H), 1.85 – 1.73 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 153.7, 148.6, 143.5, 137.9, 132.9, 127.3, 126.4, 120.0, 119.3, 111.4, 33.1, 22.6, 22.4, 21.5, 21.4.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found: 241.1223.



(2-(5-(*tert*-Butyl)benzofuran-3-yl)cyclohex-1-en-1-yl)methanol (In4-1c)

Pale yellow liquid; 449.0 mg; 79% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1), R_f = 0.80 (petroleum ether/ethyl acetate = 10/1)

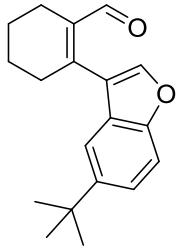
IR (KBr) $\tilde{\nu}$ 3383.0, 2932.0, 2862.3, 1661.9, 1479.1, 1363.3, 1110.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.0 Hz, 2H), 7.37 (qd, *J* = 8.8, 1.4 Hz, 2H),

4.04 (s, 2H), 2.35 (dtt, J = 9.9, 6.7, 3.1 Hz, 4H), 1.78 (p, J = 3.0 Hz, 4H), 1.44 (br s, 1H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 145.7, 141.7, 135.7, 127.3, 125.9, 122.3, 121.9, 116.4, 110.8, 64.2, 34.8, 31.9, 31.6, 27.3, 23.0, 22.7.

HRMS (ESI) m/z calcd. for $C_{19}H_{24}NaO_2$ $[M+Na]^+$: 307.1669, found: 307.1663.



2-(5-(*tert*-Butyl)benzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1c)

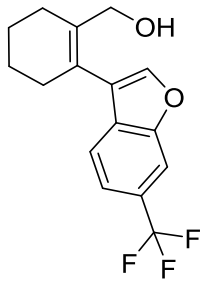
Yellow liquid; 359.8 mg; 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 25/1), R_f = 0.58 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 2952.6, 2861.4, 1714.9, 1673.5, 1469.7, 1361.6, 1268.4, 805.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.54 (s, 1H), 7.47 – 7.39 (m, 3H), 2.64 (td, J = 5.8, 2.9 Hz, 2H), 2.42 (ddt, J = 5.8, 4.2, 2.3 Hz, 2H), 1.87 – 1.74 (m, 4H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 153.6, 148.5, 146.6, 143.6, 137.9, 126.8, 123.1, 119.7, 116.2, 111.2, 34.8, 33.0, 31.8, 22.7, 22.4, 21.5.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_2$ $[M+H]^+$: 283.1693, found: 283.1688.



(2-(6-(Trifluoromethyl)benzofuran-3-yl)cyclohex-1-en-1-yl)methanol (In4-1f)

Pale yellow liquid; 450.0 mg; 76% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1), R_f = 0.18 (petroleum ether/ethyl acetate = 10/1).

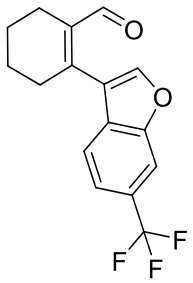
IR (KBr) $\tilde{\nu}$ 3362.5, 2931.4, 2860.6, 1627.6, 1434.7, 1331.5, 1122.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.62 (s, 1H), 7.59 (d, J = 8.2 Hz, 1H),

7.48 (d, J = 8.2 Hz, 1H), 3.99 (s, 2H), 2.32 (q, J = 3.4 Hz, 4H), 1.77 (p, J = 3.1 Hz, 4H), 1.61 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 144.0, 136.6, 130.7, 126.7 (q, J = 32.8 Hz), 125.0, 124.5 (q, J = 271.8 Hz), 121.8, 120.9, 119.6 (q, J = 3.7 Hz), 109.2 (q, J = 4.2 Hz), 63.9, 31.6, 27.2, 22.9, 22.5.

HRMS (ESI) m/z calcd. for $C_{16}H_{16}F_3O_2$ $[M+H]^+$: 297.1097, found: 297.1099.



2-(6-(Trifluoromethyl)benzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1f)

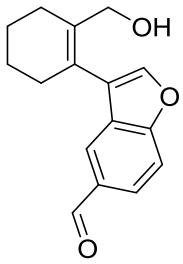
Yellow liquid; 366.1 mg; 83% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 2941.6, 2866.6, 1714.9, 1640.1, 1434.8, 1244.8, 1126.3, 943.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.82 (s, 1H), 7.73 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 2.62 (tt, J = 5.8, 2.4 Hz, 2H), 2.43 (td, J = 6.0, 2.8 Hz, 2H), 1.86 – 1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 154.3, 147.1, 145.6, 138.7, 130.2, 127.6 (q, J = 32.8 Hz), 124.2 (q, J = 272.0 Hz), 120.8, 120.3 (q, J = 3.7 Hz), 119.6, 109.6 (q, J = 4.1 Hz), 33.1, 22.6, 22.2, 21.3.

HRMS (ESI) m/z calcd. for $C_{16}H_{14}F_3O_2$ $[M+H]^+$: 295.0940, found: 295.0936.



3-(2-(Hydroxymethyl)cyclohex-1-en-1-yl)benzofuran-5-carbaldehyde (In4-1h)

After the hydrogenation by DIBAL-H (1 M in hexanes, 10 mL, 10 mmol), the CN group on intermediate **In3-1h** was also transferred to the formyl group.

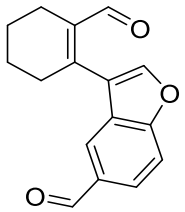
Yellow solid; 399.5 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1), R_f = 0.21 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3422.7, 2930.7, 2857.7, 1697.1, 1584.9, 1442.5, 1216.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.07 (d, *J* = 1.6 Hz, 1H), 7.86 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.61 – 7.57 (m, 2H), 4.02 (s, 2H), 2.35 (dp, *J* = 8.1, 2.9 Hz, 4H), 1.79 (p, *J* = 3.1 Hz, 4H), 1.71 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.5, 143.3, 136.8, 132.1, 128.4, 126.1, 124.8, 123.7, 122.5, 112.3, 63.9, 31.6, 27.3, 22.9, 22.5.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1172, found: 257.1172.



3-(2-Formylcyclohex-1-en-1-yl)benzofuran-5-carbaldehyde (In5-1h)

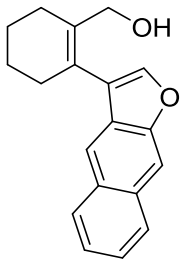
Yellow solid; 316.3 mg; 83% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1), R_f = 0.40 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 2935.0, 2859.7, 1703.3, 1695.1, 1668.1, 1442.5, 1224.6, 1058.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.71 (s, 1H), 8.09 (s, 1H), 7.93 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.71 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 2.66 (tt, *J* = 5.9, 2.3 Hz, 2H), 2.43 (td, *J* = 6.0, 2.9 Hz, 2H), 1.90 – 1.75 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 191.3, 158.5, 147.0, 144.9, 138.9, 132.7, 127.9, 126.7, 123.3, 120.1, 112.7, 33.1, 22.6, 22.2, 21.3.

HRMS (ESI) m/z calcd. for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1016, found: 255.1014.



(2-(Naphtho[2,3-*b*]furan-3-yl)cyclohex-1-en-1-yl)methanol (In4-1i)

Pale yellow liquid; 417.2 mg; 75% yield; purified by silica gel chromatography

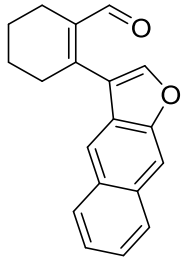
(petroleum ether/ethyl acetate = 8/1), R_f = 0.61 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{v}$ 3390.2, 2932.2, 1640.9, 1440.3, 1264.3, 1087.7, 983.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 3H), 7.87 (s, 1H), 7.56 (s, 1H), 7.47 – 7.35 (m, 2H), 4.04 (s, 2H), 2.44 – 2.38 (m, 2H), 2.35 (dt, *J* = 6.5, 3.7 Hz, 2H), 1.80 (p, *J* = 3.0 Hz, 4H), 1.49 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.7, 136.3, 131.4, 130.3, 128.9, 128.1, 127.8, 125.6, 125.0, 124.1, 121.3, 118.2, 107.1, 64.1, 31.5, 27.3, 23.0, 22.7.

HRMS (ESI) m/z calcd. for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380, found: 279.1377.



2-(Naphtho[2,3-*b*]furan-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1i)

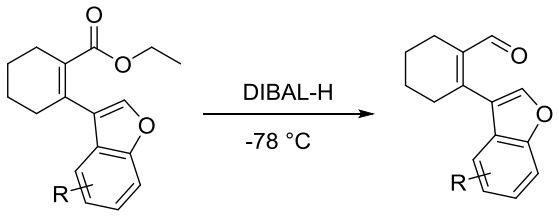
Yellow liquid; 339.6 mg; 82% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.61 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{v}$ 2935.0, 2859.4, 1715.7, 1668.1, 1440.7, 1268.9, 863.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.96 (s, 1H), 7.95 – 7.89 (m, 3H), 7.66 (s, 1H), 7.50 – 7.40 (m, 2H), 2.70 (td, *J* = 6.0, 3.1 Hz, 2H), 2.45 (tt, *J* = 5.8, 2.4 Hz, 2H), 1.90 – 1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.0, 148.1, 145.6, 138.4, 131.6, 130.5, 128.2, 128.2, 127.8, 125.5, 124.5, 119.1, 118.4, 107.6, 33.0, 22.7, 22.4, 21.5.

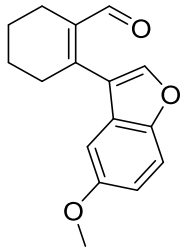
HRMS (ESI) m/z calcd. for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found: 277.1223.



In3 **In5**

A solution of **In3** (2 mmol) in dry DCM (10 mL) was added to an oven-dried Schlenk flask under N_2 and stirred at -78 ℃ for 5 min, DIBAL-H (1 M in hexanes,

2.4 mL, 2.4 mmol) was then slowly added and the reaction stirred at -78 ℃. After completion, the reaction was diluted with saturated aqueous NH_4Cl solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to obtain the product **In5-1d**, **In5-1e**, and **In5-1g**.



2-(5-Methoxybenzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1d)

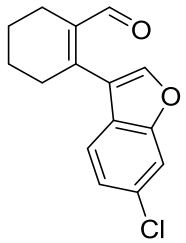
Yellow liquid; 358.6 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.36 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2934.0, 2857.9, 1711.5, 1668.1, 1475.1, 1365.3, 1217.7, 1028.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.55 (s, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 6.95 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 2.65 – 2.59 (m, 2H), 2.41 (ddt, *J* = 5.9, 4.4, 2.3 Hz, 2H), 1.86 – 1.73 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.4, 150.2, 148.4, 144.2, 137.9, 127.7, 119.7, 113.9, 112.4, 102.7, 56.0, 33.0, 22.6, 22.3, 21.4.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1172, found: 257.1171.



2-(6-Chlorobenzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1e)

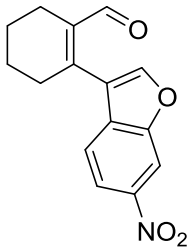
Yellow liquid; 374.5 mg; 72% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.42 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2934.8, 2859.5, 1712.7, 1668.1, 1467.5, 1220.7, 1116.5, 892.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.58 (s, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.26 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.60 (td, *J* = 5.9, 3.0 Hz, 2H), 2.41 (td, *J* = 6.0, 2.8 Hz, 2H), 1.86 – 1.72 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 155.3, 147.5, 143.9, 138.4, 131.1, 125.9, 124.1, 120.8, 119.5, 112.4, 33.1, 22.6, 22.3, 21.4.

HRMS (ESI) m/z calcd. for $C_{15}H_{14}ClO_2$ $[M+H]^+$: 261.0677, found: 261.0678.



2-(6-Nitrobenzofuran-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1g)

Yellow solid; 379.5 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

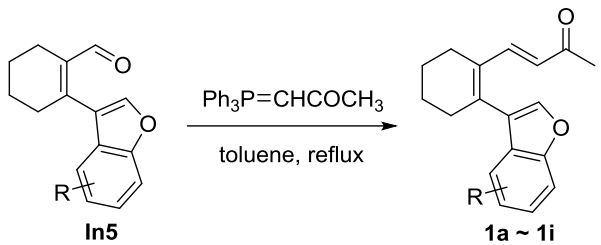
IR (KBr) $\tilde{\nu}$ 2940.3, 2864.2, 1715.3, 1650.2, 1521.7, 1442.3, 1340.1, 1231.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.45 (d, *J* = 2.0 Hz, 1H), 8.21 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.87 (s, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 2.63 (tt, *J* = 6.0, 2.4 Hz, 2H), 2.43 (tt, *J* = 5.6, 2.3 Hz, 2H), 1.88 – 1.78 (m, 4H).

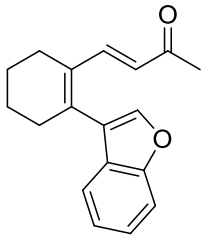
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 154.0, 147.9, 146.3, 145.6, 139.1, 132.8, 120.4, 120.0, 119.0, 108.5, 33.2, 22.6, 22.2, 21.3.

HRMS (ESI) m/z calcd. for $C_{15}H_{14}NO_4$ $[M+H]^+$: 272.0917, found: 272.0916.

3.5. General procedures for the synthesis of substrates 1a ~ 1l



To a solution of **In5** (1 mmol) in toluene (5 mL) was added Wittig reagent $Ph_3P{=}CHCOCH_3$ (3 mmol) slowly at room temperature. Then the solution was warmed to 120 ℃ and reflux for overnight. After the reaction was complete, most of toluene was removed. The crude extracts were purified by silica gel column chromatography to afford the products **1a – 1i**



(*E*)-4-(2-(Benzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1a)

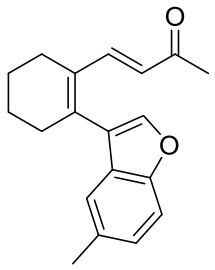
Yellow liquid; 239.5 mg; 90% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{v}$ 2940.7, 2867.1, 1720.6, 1640.1, 1463.0, 1230.8, 757.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 4H), 7.33 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.25 (td, *J* = 7.5, 1.0 Hz, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 2.57 (dt, *J* = 6.9, 3.5 Hz, 2H), 2.38 (td, *J* = 5.9, 2.7 Hz, 2H), 2.05 (s, 3H), 1.86 – 1.78 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 155.2, 143.6, 142.8, 137.9, 132.2, 127.3, 125.7, 124.7, 122.9, 121.6, 120.7, 111.8, 33.1, 26.6, 25.5, 22.6, 22.2.

HRMS (ESI) m/z calcd. for $C_{18}H_{18}KO_2$ $[M+K]^+$: 305.0938, found: 305.0936.



(*E*)-4-(2-(5-Methylbenzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1b)

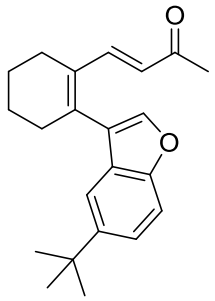
Yellow liquid; 246.5 mg; 88% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 18/1), R_f = 0.38 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2933.4, 2863.7, 1716.3, 1636.0, 1486.9, 1234.7, 982.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.14 (d, *J* = 16.2 Hz, 1H), 2.60 – 2.52 (m, 2H), 2.43 (s, 3H), 2.37 (td, *J* = 6.0, 2.7 Hz, 2H), 2.06 (s, 3H), 1.88 – 1.77 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 153.7, 143.7, 143.0, 138.1, 132.5, 132.1, 127.3, 126.0, 125.6, 121.3, 120.5, 111.3, 33.0, 26.5, 25.5, 22.6, 22.2, 21.4.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1536, found: 281.1536.



(*E*)-4-(2-(5-(*tert*-Butyl)benzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1c)

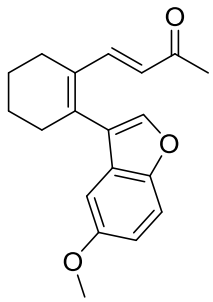
Yellow liquid; 273.9 mg; 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 15/1), R_f = 0.30 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2959.0, 2868.7, 1715.6, 1640.0, 1488.7, 1264.4, 1087.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.38 (m, 2H), 6.15 (d, *J* = 16.2 Hz, 1H), 2.61 – 2.54 (m, 2H), 2.42 – 2.36 (m, 2H), 2.03 (s, 3H), 1.86 – 1.80 (m, 4H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 153.5, 146.2, 144.1, 143.1, 138.1, 131.9, 126.8, 125.6, 122.7, 121.8, 116.8, 111.0, 34.8, 33.2, 31.9, 26.4, 25.5, 22.6, 22.2.

HRMS (ESI) m/z calcd. for $C_{22}H_{27}O_2$ $[M+H]^+$: 323.2006, found: 323.2003.



(*E*)-4-(2-(5-Methoxybenzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1d)

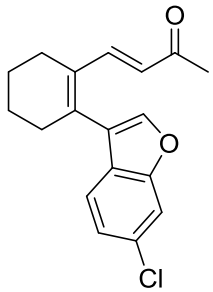
Yellow liquid; 245.8 mg; 83% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2935.1, 2860.8, 1715.1, 1668.0, 1475.3, 1263.1, 1030.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.47 (d, *J* = 16.2 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 6.93 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 2.55 (dt, *J* = 6.7, 3.4 Hz, 2H), 2.38 (td, *J* = 5.8, 2.6 Hz, 2H), 2.06 (s, 3H), 1.87 – 1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 156.2, 150.2, 143.7, 143.6, 137.9, 132.1, 127.8, 125.6, 121.8, 113.5, 112.2, 103.2, 56.0, 33.0, 26.6, 25.5, 22.6, 22.2.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1483.



(*E*)-4-(2-(6-Chlorobenzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1e)

Yellow liquid; 255.1 mg; 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

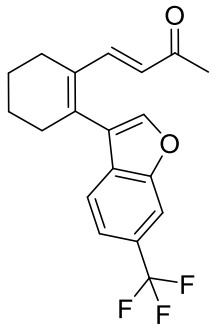
IR (KBr) $\tilde{\nu}$ 2932.3, 2859.9, 1715.6, 1666.3, 1467.5, 1261.6, 892.9 cm^{-1}

^{1}H NMR (400 MHz, CDCl3) δ 7.53 (d, *J* = 4.5 Hz, 2H), 7.40 (d, *J* = 16.1 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.16 (d, *J* = 16.1 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.43 – 2.33 (m, 2H), 2.07 (s, 3H), 1.85 – 1.77 (m, 4H).

^{13}C NMR (100 MHz, CDCl3) δ 199.1, 155.3, 143.4, 143.0, 137.1, 132.7, 130.7, 126.0,

125.8, 123.7, 121.6, 121.2, 112.3, 33.1, 26.9, 25.5, 22.5, 22.1.

HRMS (ESI) m/z calcd. for $C_{18}H_{18}ClO_2$ $[M+H]^+$: 301.0990, found: 301.0984.



(*E*)-4-(2-(6-(Trifluoromethyl)benzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1f)

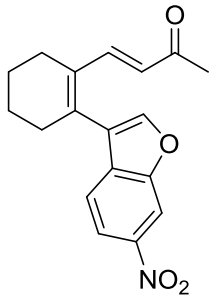
Yellow liquid; 284.0 mg; 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.21(petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2946.4, 2872.3, 1700.9, 1630.5, 1432.8, 1171.2, 1126.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 16.1 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 2.57 – 2.50 (m, 2H), 2.43 – 2.35 (m, 2H), 2.07 (s, 3H), 1.86 – 1.79 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 154.3, 145.2, 142.8, 136.8, 133.0, 130.3, 127.1 (q, *J* = 33.0 Hz), 125.9, 124.4 (q, *J* = 272.1 Hz), 121.7, 121.2, 119.9 (q, *J* = 3.5 Hz), 109.5 (q, *J* = 4.2 Hz), 33.1, 27.0, 25.5, 22.5, 22.1.

HRMS (ESI) m/z calcd. for $C_{19}H_{17}F_3NaO_2$ $[M+Na]^+$: 357.1073, found: 357.1069.



(*E*)-4-(2-(6-Nitrobenzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1g)

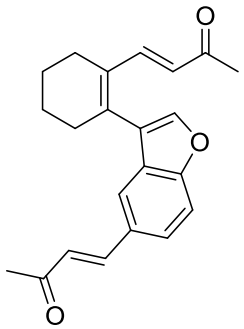
Yellow solid; 252.0 mg; 81% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.42 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 2932.9, 2861.5, 1668.0, 1520.1, 1440.7, 1354.1, 1259.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.9 Hz, 1H), 8.18 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.80 (s, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 16.0 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 2.58 – 2.49 (m, 2H), 2.44 – 2.35 (m, 2H), 2.08 (s, 3H), 1.89 – 1.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 153.9, 147.6, 145.4, 142.0, 135.8, 133.6, 133.0, 126.1, 122.1, 120.7, 118.6, 108.4, 33.2, 27.4, 25.6, 22.5, 22.1.

HRMS (ESI) m/z calcd. for $C_{18}H_{18}NO_4$ $[M+H]^+$: 312.1230, found: 312.1229.



(*E*)-4-(2-(5-((*E*)-3-Oxobut-1-en-1-yl)benzofuran-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1h)

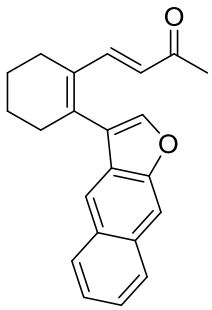
Yellow solid; 297.4 mg; 89% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1), R_f = 0.20 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{v}$ 2932.4, 2860.0, 1714.7, 1666.6, 1603.7, 1359.6, 1260.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 5H), 7.42 (d, *J* = 16.1 Hz, 1H), 6.70 (d, *J* = 16.2 Hz, 1H), 6.20 (d, *J* = 16.1 Hz, 1H), 2.60 – 2.52 (m, 2H), 2.39 (d, *J* = 7.5 Hz, 5H), 2.07 (s, 3H), 1.84 (p, *J* = 6.1 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 198.2, 156.4, 143.8, 143.6, 142.8, 137.0, 132.9, 129.8, 128.1, 126.6, 125.8, 124.9, 121.8, 121.2, 112.5, 33.1, 27.4, 27.1, 25.6, 22.5, 22.1.

HRMS (ESI) m/z calcd. for $C_{22}H_{23}O_3$ $[M+H]^+$: 335.1642, found: 335.1641.



(*E*)-4-(2-(Naphtho[2,3-*b*]furan-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1i)

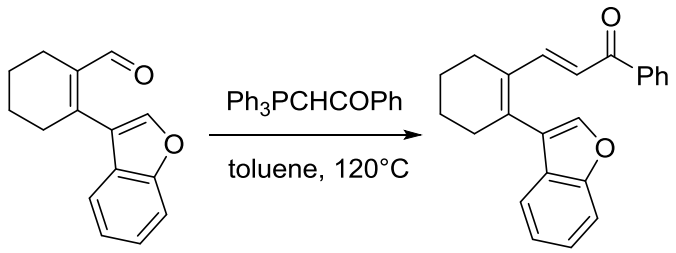
Yellow liquid; 278.2 mg; 88% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.22 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2933.1, 2858.7, 1715.7, 1665.7, 1441.3, 1263.0, 863.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 4H), 7.62 (s, 1H), 7.51 (d, *J* = 16.2 Hz, 1H), 7.48 – 7.38 (m, 2H), 6.18 (d, *J* = 16.2 Hz, 1H), 2.66 – 2.60 (m, 2H), 2.45 – 2.39 (m, 2H), 2.00 (s, 3H), 1.91 – 1.82 (m, 4H).

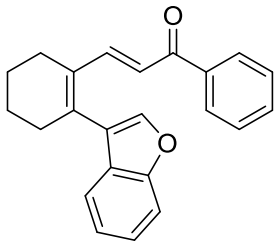
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 154.0, 145.1, 143.3, 137.6, 132.7, 131.5, 130.4, 128.3, 128.1, 127.8, 125.9, 125.3, 124.4, 121.1, 118.8, 107.4, 33.0, 26.7, 25.6, 22.6, 22.2.

HRMS (ESI) m/z calcd. for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536, found: 317.1533.



In5-1a **1j**

To a solution of **In5-1a** (226.1 mg, 1 mmol) in toluene (5 mL) was added Wittig reagent Ph_3P=CHCOPh (1.0513 g, 3 mmol) slowly at room temperature. Then the solution was warmed to 120 ℃ and reflux for overnight. After the reaction was complete, most of toluene was removed. The crude extracts were purified by silica gel column chromatography to afford the product **1j**



(*E*)-3-(2-(benzofuran-3-yl)cyclohex-1-en-1-yl)-1-phenylprop-2-en-1-one (1j)

Yellow liquid; 213.3 mg; 65% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.4 (petroleum ether/ethyl acetate = 10/1).

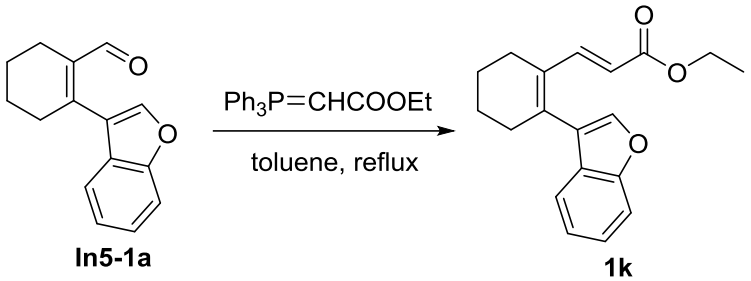
IR (KBr) $\tilde{\nu}$ 2931.9, 2859.4, 1735.6, 1657.4, 1583.3, 1450.9, 1285.1, 1018.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.84 – 7.81 (m, 1H), 7.73 (d, *J* =

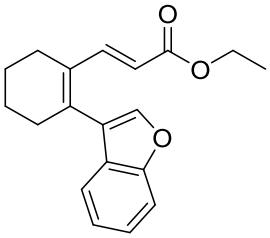
15.5 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.40 – 7.34 (m, 2H), 7.31 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.94 (d, *J* = 15.6 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.53 – 2.47 (m, 2H), 1.91 – 1.79 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 155.3, 144.6, 142.8, 138.8, 138.5, 132.7, 132.3, 128.4, 128.3, 127.3, 124.6, 122.9, 121.5, 120.6, 120.4, 111.7, 33.0, 25.8, 22.6, 22.3.

HRMS (ESI) m/z calcd. for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1536, found: 329.1538.



To a solution of **In5-1a** (1 mmol) in toluene (5 mL) was added carbethoxy-methylene triphenylphosphorane (1.0354 g, 3 mmol) slowly at room temperature. Then the solution was warmed to 120 ℃ and reflux for overnight. After the reaction was complete, most of toluene was removed. The crude extracts were purified by silica gel column chromatography to afford the product **1k**.



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Ethyl (*E*)-3-(2-(benzofuran-3-yl)cyclohex-1-en-1-yl)acrylate (1k)

White solid; 266.5 mg; 90% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.52 (petroleum ether/ethyl acetate = 10/1).

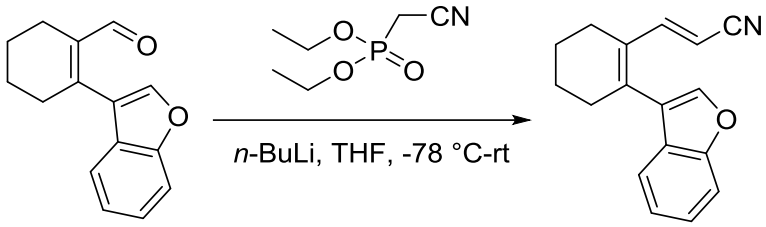
IR (KBr) $\tilde{\nu}$ 2932.1, 2859.0, 1709.3, 1615.6, 1452.1, 1302.7, 1172.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.8 Hz, 1H), 7.54 – 7.38 (m, 3H), 7.30 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.26 – 7.20 (m, 1H), 5.89 (d, *J* = 15.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.55 (td, *J* = 5.9, 2.4 Hz, 2H), 2.36 (td, *J* = 6.0, 2.7 Hz, 2H), 1.84 – 1.76 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 155.3, 144.1, 142.8, 136.9, 132.0, 127.3, 124.5,

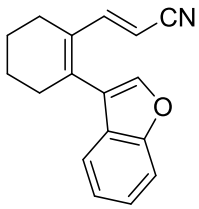
122.8, 121.4, 120.7, 116.1, 111.7, 60.1, 32.7, 25.6, 22.6, 22.3, 14.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485, found: 297.1485.



In5-1a **1l**

n-Butyl lithium (2.5 M in hexanes, 0.8 mL, 2 mmol) was added dropwise to a stirred, cooled (-78 ℃) solution of diethyl (1-cyanomethyl)phosphonate (0.32 mL, 354 mg, 2 mmol) in THF (4 mL) under an N_2 atmosphere. After stirring for 20 min at this temperature, a solution of **In5-1a** (1 mmol) in THF (1 mL) was added dropwise at -78 ℃. The mixture was allowed to warm to room temperature and stirred for 1 h before the reaction was quenched with NH_4Cl solution. EA (5 mL) was added to aid phase separation and the mixture was partitioned. The aqueous phase was extracted with EA three times and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude extracts were purified by silica gel column chromatography to afford the product **1l**



(*E*)-3-(2-(Benzofuran-3-yl)cyclohex-1-en-1-yl)acrylonitrile (1l)

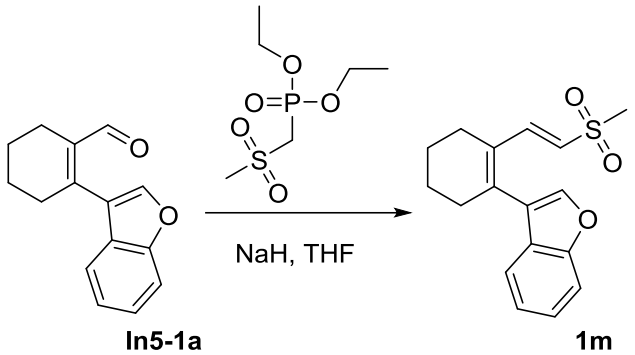
White solid; 132.0 mg; 53% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.60 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 2932.4, 2858.0, 2238.1, 1640.1, 1443.3, 1270.1, 796.5 cm^{-1}

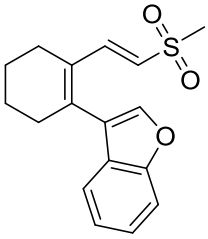
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 7.41 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.25 (td, *J* = 7.5, 1.1 Hz, 1H), 5.29 (d, *J* = 16.4 Hz, 1H), 2.55 (td, *J* = 6.1, 2.4 Hz, 2H), 2.28 (td, *J* = 6.0, 2.4 Hz, 2H), 1.86 – 1.75 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.9, 142.8, 138.5, 131.7, 127.0, 124.9, 123.2, 121.0, 120.4, 119.1, 111.9, 93.5, 32.9, 24.7, 22.4, 21.9.

HRMS (ESI) m/z calcd. for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1126, found: 250.1123.



To a solution of Diethyl(methylsulfonylmethyl)phosphonate **(**1.2 mmol) in THF(5 mL) was slowly added NaH (60% w/w dispersion in mineral oil, 52 mg, 1.3 mmol) at 0 ℃ under N_2. After stirring for 30 min, **In5-1a** (226.1 mg, 1 mmol) was added dropwise to the reaction. The resulting mixture was then warmed to room temperature. After completion, the reaction was diluted with saturated aqueous NH_4Cl solution, extracted with EA three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the product **1m**



(*E*)-3-(2-(2-(methylsulfonyl)vinyl)cyclohex-1-en-1-yl)benzofuran (1m)

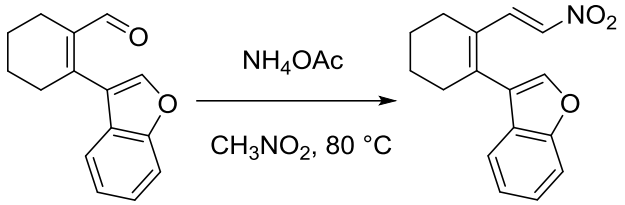
Yellow liquid; 211.4 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1), R_f = 0.2 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 2930.8, 2860.7, 1611.1, 1452.1, 1299.8, 1233.7, 1131.4, 969.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.3 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.29 (m, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 15.2 Hz, 1H), 2.86 (s, 3H), 2.59 (dt, *J* = 7.2, 3.5 Hz, 2H), 2.38 – 2.28 (m, 2H), 1.87 – 1.77 (m, 4H).

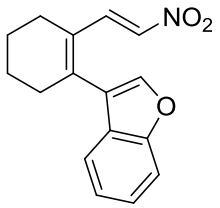
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.2, 142.9, 140.4, 130.0, 126.9, 124.9, 124.3, 123.0, 120.8, 120.4, 111.9, 43.4, 32.8, 25.7, 22.4, 22.0.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}O_3S$ $[M+H]^+$: 303.1049, found: 303.1051.



In5-1a **1n**

To a solution of **In5-1a** (1 mmol) in nitromethane (1 mL) was added NH_4OAc (154.2 mg, 2 mmol) slowly at room temperature. Then the solution was warmed to 80 ℃ for 1 h, the reaction was complete, The crude extracts were purified by silica gel column chromatography to afford the product **1n**



(*E*)-3-(2-(2-nitrovinyl)cyclohex-1-en-1-yl)benzofuran (1n)

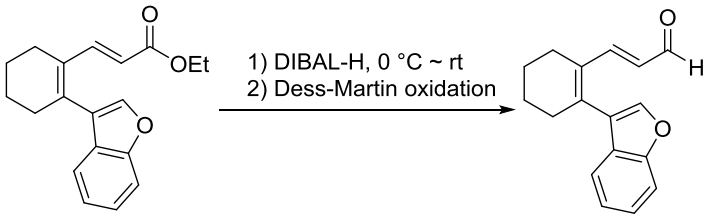
Yellow liquid; 177.6 mg, 66% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.4 (petroleum ether/ethyl acetate =10/1).

IR (KBr) $\tilde{v}$ 2928.7, 2856.5, 1714.8, 1612.5, 1506.1, 1451.9, 1335.8, 748.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 13.4 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.29 – 7.26 (m, 1H), 7.12 (d, *J* = 13.3 Hz, 1H), 2.67 – 2.59 (m, 2H), 2.39 – 2.31 (m, 2H), 1.88 – 1.81 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 143.6, 143.1, 138.5, 135.8, 128.7, 126.8, 125.1, 123.2, 121.0, 120.4, 112.0, 33.1, 25.8, 22.2, 21.9.

HRMS (ESI) m/z calcd. for $C_{16}H_{16}NO_3$ $[M+H]^+$: 270.1125, found: 270.1130.

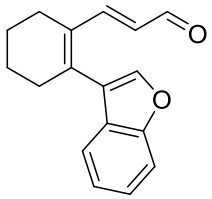


1k **1o**

The **1k (**2 mmol**)** was dissolved in dry DCM (30 mL) under N_2 in an oven-dried Schlenk flask and stirred at 0 ℃ for 5 min. DIBAL-H (1 M in hexanes, 5 mL, 5 mmol) was then slowly added and the reaction was warmed to room temperature. After

completion, the reaction was diluted with saturated aqueous NH_4Cl solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the corresponding **alcohol**.

To a solution of **alcohol** (1.5 mmol) in DCM (30 mL) was added Dess-Martin periodinane (DMP) (954.3 mg, 2.25 mmol) slowly at 0 ℃. Then the solution was warmed to room temperature and stirred for 5-10 min. After the reaction was complete, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ solution and $NaHCO_3$ solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the aldehyde product **1o**.



(*E*)-3-(2-(Benzofuran-3-yl)cyclohex-1-en-1-yl)acrylaldehyde (1o)

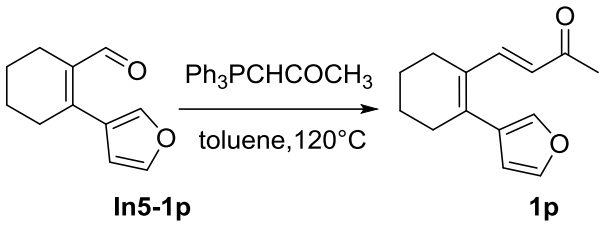
Yellow liquid; 267.2 mg; 53% (two steps) yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 15/1), R_f = 0.30 (petroleum ether/ethyl acetate = 10/1).

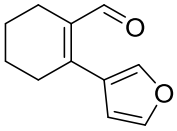
IR (KBr) $\tilde{\nu}$ 2932.5, 2860.0, 1675.9, 1606.6, 1452.1, 1131.9, 748.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.48 – 7.39 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.18 (dd, *J* = 15.7, 7.9 Hz, 1H), 2.59 (dt, *J* = 7.1, 3.6 Hz, 2H), 2.44 – 2.35 (m, 2H), 1.89 – 1.76 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 155.3, 152.2, 142.9, 139.5, 132.6, 127.1, 126.9, 124.9, 123.1, 121.4, 120.6, 111.8, 33.2, 25.6, 22.5, 22.1.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found: 253.1221.





2-(furan-3-yl)cyclohex-1-ene-1-carbaldehyde (In5-1p)

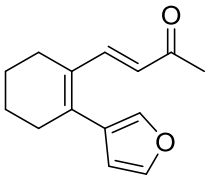
Yellow liquid; 198.1 mg, 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.6 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2928.8, 2856.5, 1732.9, 1716.1, 1663.6, 1614.9, 1245.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.49 – 7.44 (m, 1H), 7.43 (s, 1H), 6.44 (d, *J* = 1.7 Hz, 1H), 2.49 (tt, *J* = 5.7, 2.2 Hz, 2H), 2.39 – 2.29 (m, 2H), 1.79 – 1.72 (m, 2H), 1.72 – 1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 149.0, 143.5, 141.7, 136.6, 123.6, 111.0, 32.7, 22.7, 22.2, 21.4.

HRMS (ESI) m/z calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0908.



(*E*)-4-(2-(furan-3-yl)cyclohex-1-en-1-yl)but-3-en-2-one (1p)

Yellow liquid, 183.7 mg, 85% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.4 (petroleum ether/ethyl acetate =20/1).

IR (KBr) $\tilde{\nu}$ 2936.4, 2863.9, 1760.5, 1714.9, 1665.6, 1603.8, 1264.7cm^{-1}

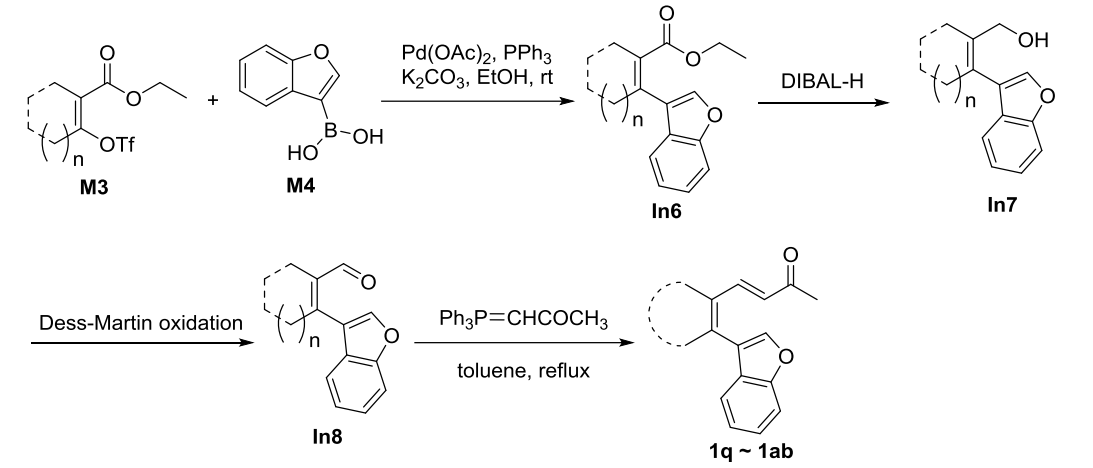
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.3 Hz, 1H), 7.45 (t, *J* = 1.8 Hz, 1H), 7.38 (s, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 6.15 (d, *J* = 16.1 Hz, 1H), 2.49 – 2.41 (m, 2H), 2.33 – 2.26 (m, 2H), 2.23 (s, 3H), 1.74 (p, *J* = 3.1 Hz, 4H).

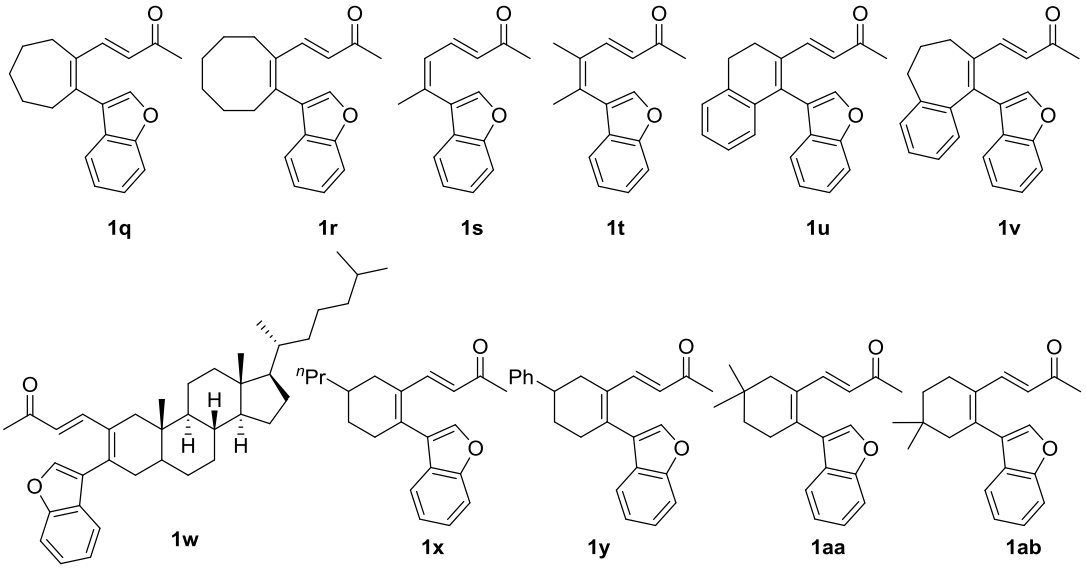
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 143.7, 143.0, 140.9, 138.7, 130.5, 125.7, 125.5, 111.0, 32.5, 27.0, 25.7, 22.4, 22.1.

HRMS (ESI) m/z calcd. for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found: 217.1223.

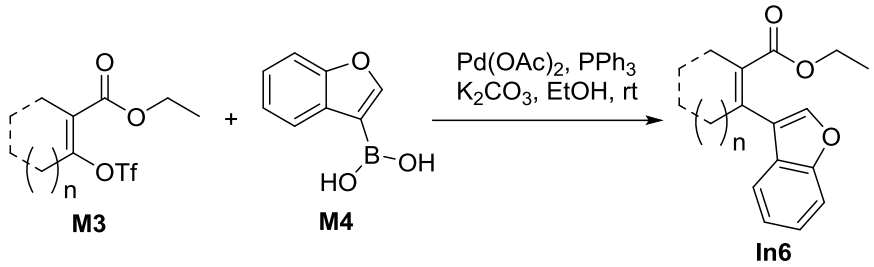
4. Synthesis route overview of substrates 1q ~ 1ab

Synthesis route overview:



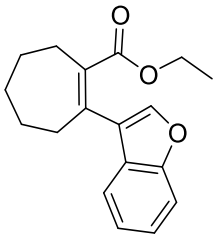


4.1. General procedures for the synthesis of intermediates In6



Materials **M3** were prepared according to the above procedures 2.2.

Under N_2, a Schlenk flask was charged with anhydrous EtOH (30 mL) and a mixture of **M3** (4 mmol), Benzofuran-3-boronic acid **M4** (712.6 mg, 4.4 mmol), PPh_3 (209.8 mg, 0.8 mmol), $Pd(OAc)_2$ (89.8 mg, 0.4 mmol), K_2CO_3(1.1057 g, 8 mmol). The reaction was stirred at rt overnight. After the reaction was complete, most of ethanol was removed through rotary evaporator. The reaction was quenched by saturated aqueous NH_4Cl solution, extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the coupling products **In6**.



Ethyl 2-(benzofuran-3-yl)cyclohept-1-ene-1-carboxylate (In6-1q)

Colourless liquid; 852.4 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.63 (petroleum ether/ethyl acetate = 10/1).

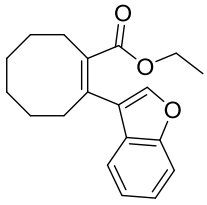
IR (KBr) $\tilde{\nu}$ 2923.5, 2852.2, 1704.7, 1452.3, 1371.1, 1260.2, 746.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 3H), 7.31 – 7.25 (m, 1H), 7.22 (td, *J* = 7.5, 1.1 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.64 (m, 2H), 2.64 – 2.60 (m, 2H), 1.92 – 1.84 (m, 2H), 1.70 (qt, *J* = 8.3, 4.2 Hz, 4H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 155.0, 140.9, 139.6, 136.2, 127.2, 124.3, 123.9,

122.6, 120.4, 111.5, 60.3, 36.1, 32.4, 31.0, 26.6, 25.8, 13.4.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found: 285.1481.



Ethyl (*Z*)-2-(benzofuran-3-yl)cyclooct-1-ene-1-carboxylate (In6-1r)

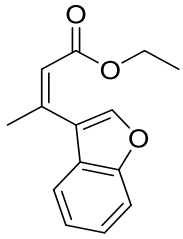
Colourless liquid; 894.5 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.67 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2926.9, 2853.4, 1713.9, 1452.8, 1369.9, 1220.1, 746.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.46 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.21 (td, *J* = 7.3, 1.2 Hz, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.56 (m, 4H), 1.89 – 1.80 (m, 2H), 1.65 – 1.57 (m, 6H), 0.71 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 154.9, 141.1, 137.6, 133.1, 127.5, 124.2, 122.9, 122.6, 120.2, 111.4, 60.1, 33.9, 30.4, 29.3, 28.7, 26.5, 26.5, 13.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found: 299.1639.



Ethyl (*Z*)-3-(benzofuran-3-yl)but-2-enoate (In6-1s)

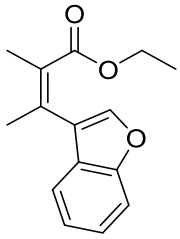
Yellow liquid; 717.9 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.67 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2981.9, 2932.0, 1713.3, 1453.2, 1276.0, 1156.1, 858.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.28 (tt, *J* = 8.3, 1.5 Hz, 1H), 7.25 – 7.18 (m, 1H), 6.06 (p, *J* = 1.4 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.26 (d, *J* = 3.2 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 155.0, 143.9, 143.2, 126.5, 124.4, 122.7, 120.7, 120.5, 119.6, 111.7, 60.0, 26.6, 13.9.

HRMS (ESI) m/z calcd. for $C_{14}H_{15}O_3$ $[M+H]^+$: 231.1016, found: 231.1012.



Ethyl (*Z*)-3-(benzofuran-3-yl)-2-methylbut-2-enoate (In6-1t)

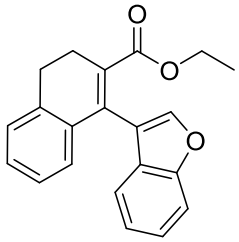
Yellow liquid; 732.3 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.67 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2981.4, 2931.7, 1712.3, 1454.1, 1303.6, 1214.9, 748.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.47 – 7.42 (m, 2H), 7.30 – 7.25 (m, 1H), 7.21 (td, *J* = 7.4, 1.1 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.15 (q, *J* = 1.1 Hz, 3H), 2.08 (q, *J* = 1.1 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.9, 141.2, 131.8, 128.5, 127.2, 124.3, 123.6, 122.6, 120.3, 111.5, 60.4, 21.2, 16.3, 13.4.

HRMS (ESI) m/z calcd. for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1172, found: 245.1167.



Ethyl 1-(benzofuran-3-yl)-3,4-dihydronaphthalene-2-carboxylate (In6-1u)

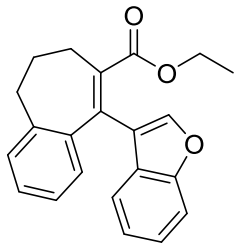
Colourless liquid; 827.1 mg; 65% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3064.1, 2937.1, 2837.1, 1710.6, 1452.5, 1272.2, 745.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 7.10 – 6.99 (m, 2H), 3.89 (d, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 8.0 Hz, 2H), 2.77 (dd, *J* = 9.3, 6.7 Hz, 2H), 0.76 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 155.0, 142.7, 136.8, 134.4, 133.2, 131.1, 128.9, 128.5, 127.5, 127.3, 126.7, 124.4, 122.8, 120.5, 118.7, 111.5, 60.4, 27.9, 25.6, 13.4.

HRMS (ESI) m/z calcd. for $C_{21}H_{19}O_3$ $[M+H]^+$: 319.1329, found: 319.1322.



Ethyl 9-(benzofuran-3-yl)-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (In6-1v)

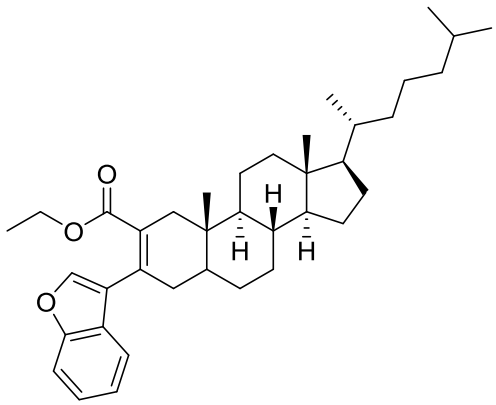
Colourless liquid; 1.0628 g; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3062.4, 2935.3, 2858.2, 1708.1, 1452.1, 1275.3,747.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.21 (m, 3H), 7.10 (dt, *J* = 15.1, 7.2 Hz, 2H), 7.03 – 6.95 (m, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.84 (td, *J* = 7.0, 2.2 Hz, 2H), 2.40 – 2.32 (m, 2H), 2.32 – 2.23 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 155.0, 143.9, 141.3, 139.8, 136.6, 132.8, 129.6, 128.8, 128.5, 127.9, 126.4, 124.3, 122.7, 121.4, 120.6, 111.4, 60.7, 35.1, 31.9, 28.0, 13.5.

HRMS (ESI) m/z calcd. for $C_{22}H_{21}O_3$ $[M+H]^+$: 333.1485, found: 333.1483.



Ethyl (8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(benzofuran-3-yl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-2-carboxylate (In6-1w)

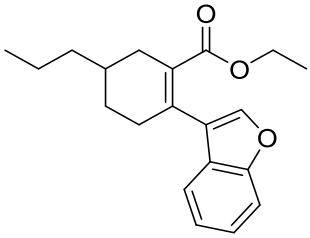
White solid; 1.1168 g; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.50 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2931.8, 2867.3, 1704.7, 1452.6, 1263.0, 1037.9, 744.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.43 (dd, *J* = 18.9, 7.9 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 3.81 (qd, *J* = 7.0, 4.5 Hz, 2H), 2.60 (d, *J* = 17.5 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.20 – 2.09 (m, 1H), 2.08 – 1.98 (m, 2H), 1.89 – 1.76 (m, 1H), 1.75 – 1.66 (m, 1H), 1.62 – 1.47 (m, 7H), 1.40 – 1.30 (m, 5H), 1.24 – 1.02 (m, 10H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 – 0.86 (m, 9H), 0.71 – 0.67 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 154.8, 141.0, 133.5, 129.2, 127.3, 124.2, 122.7, 122.5, 120.2, 111.4, 60.3, 56.5, 56.3, 53.8, 42.5, 41.3, 41.2, 39.9, 39.5, 37.6, 36.2, 35.8, 35.6, 34.2, 31.6, 28.2, 28.0, 24.2, 23.9, 22.8, 22.6, 21.2, 18.7, 13.3, 12.0, 11.7.

HRMS (ESI) m/z calcd. for $C_{38}H_{55}O_3$ $[M+H]^+$: 559.4146, found: 559.4146.



Ethyl 2-(benzofuran-3-yl)-5-propylcyclohex-1-ene-1-carboxylate (In6-1x)

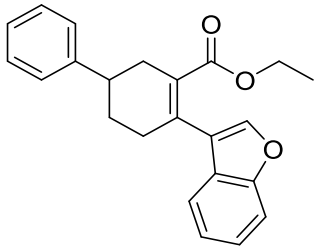
Colourless liquid; 936.5 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2926.6, 2871.5, 1704.9, 1454.1, 1251.7, 1085.5, 747.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.48 – 7.39 (m, 2H), 7.29 – 7.23 (m, 1H), 7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 3.82 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.75 – 2.65 (m, 1H), 2.54 – 2.43 (m, 2H), 2.09 – 1.97 (m, 1H), 1.92 – 1.83 (m, 1H), 1.75 – 1.64 (m, 1H), 1.46 – 1.33 (m, 5H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 154.9, 141.2, 134.6, 129.8, 127.2, 124.2, 122.9, 122.5, 120.3, 111.4, 60.3, 38.4, 33.4, 32.8, 32.8, 28.7, 20.0, 14.3, 13.3.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found: 313.1798.



Ethyl 4-(benzofuran-3-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (In6-1y)

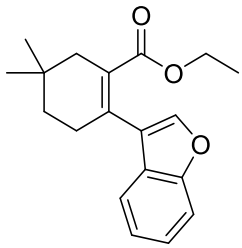
Yellow liquid; 830.8 mg; 60% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.63(petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3035.4, 2987.2, 2891.8, 1695.4, 1454.2, 1256.7, 750.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.50 – 7.44 (m, 2H), 7.38 – 7.27 (m, 5H), 7.26 – 7.19 (m, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.87 (m, 2H), 2.68 – 2.60 (m, 2H), 2.59 – 2.48 (m, 1H), 2.14 – 2.05 (m, 1H), 2.02 – 1.89 (m, 1H), 0.75 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 154.9, 145.7, 141.4, 134.7, 129.8, 128.6, 127.1, 126.9, 126.4, 124.4, 122.7, 122.6, 120.3, 111.6, 60.5, 39.4, 34.7, 33.3, 29.4, 13.4.

HRMS (ESI) m/z calcd. for $C_{23}H_{23}O_3$ $[M+H]^+$: 347.1642, found: 347.1636.



Ethyl 2-(benzofuran-3-yl)-5,5-dimethylcyclohex-1-ene-1-carboxylate (In6-1aa)

Colourless liquid; 918.3 mg; 77% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

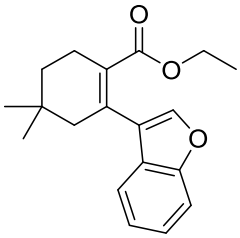
IR (KBr) $\tilde{\nu}$ 2924.6, 2869.6, 1712.7, 1454.1, 1259.3, 1056.3, 747.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 2.48 (tt, *J* = 6.5, 2.5 Hz, 2H), 2.29 (t, *J* = 2.5 Hz, 2H), 1.53 (t, *J* = 6.4 Hz, 2H), 1.05 (s, 6H),

0.71 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 154.8, 141.1, 133.7, 129.2, 127.3, 124.2, 122.8, 122.6, 120.2, 111.5, 60.3, 40.3, 35.1, 30.7, 28.5, 27.9, 13.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found: 299.1637.



Ethyl 2-(benzofuran-3-yl)-4,4-dimethylcyclohex-1-ene-1-carboxylate (In6-1ab)

Yellow liquid; 858.7 mg; 72% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.62 (petroleum ether/ethyl acetate = 10/1).

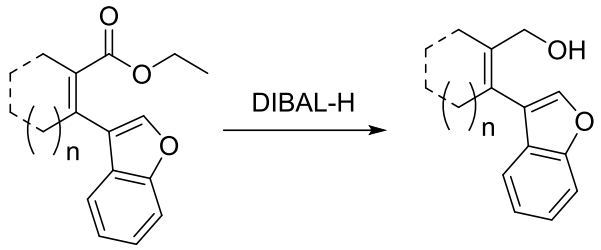
IR (KBr) $\tilde{\nu}$ 2925.8, 2868.2, 1713.1, 1453.9, 1262.9, 1052.3, 746.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.41 (dd, J = 7.9, 1.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.20 (td, J = 7.5, 1.1 Hz, 1H), 3.84 (q, J = 7.1 Hz, 2H), 2.53 (tt, J = 6.5, 2.4 Hz, 2H), 2.23 (t, J = 2.5 Hz, 2H), 1.54 (t, J = 6.5 Hz, 2H), 1.04 (s, 6H), 0.73 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 154.8, 141.0, 133.9, 129.0, 127.3, 124.2, 123.1, 122.5, 120.1, 111.5, 60.3, 46.4, 34.6, 29.2, 28.0, 24.7, 13.3.

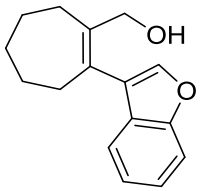
HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found: 299.1637.

4.2. General procedures for the synthesis of intermediates In7



In6 **In7**

The **In6** (3 mmol**)** in dry DCM (30 mL) was added to an oven-dried Schlenk flask under N_2 and stirred at 0 ℃ for 5 min. DIBAL-H (1 M in hexanes, 7.5 mL, 7.5 mmol) was then slowly added and the reaction was warmed to room temperature. After completion, the reaction was diluted with saturated aqueous NH_4Cl solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the products **In7**.



(2-(Benzofuran-3-yl)cyclohept-1-en-1-yl)methanol (In7-1q)

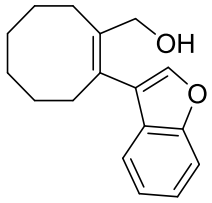
Colourless liquid; 581.1 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3355.6, 2920.6, 2848.3, 1565.0, 1452.9, 1084.9, 748.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.43 (s, 1H), 7.32 – 7.26 (m, 1H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 4.06 (s, 2H), 2.59 – 2.53 (m, 2H), 2.51 – 2.46 (m, 2H), 1.87 (p, *J* = 5.9 Hz, 2H), 1.70 – 1.60 (m, 4H), 1.41 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.1, 141.0, 132.1, 127.7, 124.3, 122.8, 122.6, 120.5, 111.6, 65.2, 35.0, 32.7, 31.7, 27.0, 26.8.

HRMS (ESI) m/z calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380, found: 243.1388.



(*Z*)-(2-(Benzofuran-3-yl)cyclooct-1-en-1-yl)methanol (In7-1r)

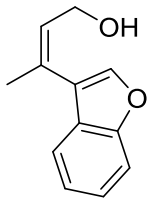
Colourless liquid; 537.9 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3356.2, 2922.1, 2848.4, 1566.7, 1452.3, 1085.7, 748.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J*= 8.3 Hz, 2H), 7.42 (s, 1H), 7.34 – 7.24 (m, 1H), 7.27 – 7.18 (m, 1H), 4.05 (s, 2H), 2.58 – 2.49 (m, 4H), 1.71 (ddt, *J* = 9.1, 6.4, 2.9 Hz, 2H), 1.65 – 1.49 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.4, 139.2, 128.5, 127.9, 124.3, 122.7, 121.6, 120.4, 111.5, 63.5, 32.4, 29.9, 28.8, 28.7, 26.9, 26.5.

HRMS (ESI) m/z calcd. for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1536, found: 257.1530.



(*Z*)-3-(Benzofuran-3-yl)but-2-en-1-ol (In7-1s)

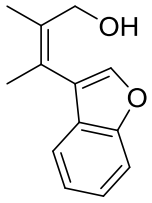
Colourless liquid; 395.0 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.25 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3348.4, 2922.4, 2866.6, 1568.0, 1452.2, 1088.2, 747.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 3H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.84 (td, *J* = 7.1, 1.6 Hz, 1H), 4.09 (d, *J* = 7.0 Hz, 2H), 2.14 (d, *J* = 1.5 Hz, 3H), 1.84 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.0, 129.9, 128.6, 127.1, 124.5, 122.8, 120.6, 120.2, 111.7, 60.1, 24.7.

HRMS (ESI) m/z calcd. for $C_{12}H_{13}O_2$ $[M+H]^+$: 189.0910, found: 189.0905.



(*Z*)-3-(Benzofuran-3-yl)-2-methylbut-2-en-1-ol (In7-1t)

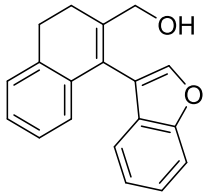
Colourless liquid; 485.0 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 3347.3, 2922.7, 2865.7, 1567.9, 1452.8, 1087.6, 747.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.51 – 7.43 (m, 3H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 4.04 (s, 2H), 2.05 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.3, 134.0, 127.7, 124.3, 123.6, 122.6, 122.5, 120.4, 111.6, 64.8, 20.2, 16.3.

HRMS (ESI) m/z calcd. for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1067, found: 203.1063.



(1-(Benzofuran-3-yl)-3,4-dihydronaphthalen-2-yl)methanol (In7-1u)

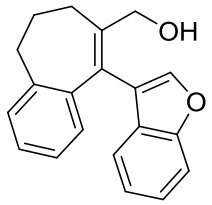
Colourless liquid; 662.7 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3356.7, 2934.9, 2883.7, 1562.0, 1452.1, 1263.1, 748.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 14.1 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.10 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.17 (d, *J* = 27.6 Hz, 2H), 2.95 (dt, *J* = 9.7, 5.5 Hz, 2H), 2.69 – 2.55 (m, 2H), 1.66 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.3, 139.7, 135.7, 135.0, 128.5, 127.4, 127.3, 126.5, 125.9, 125.1, 124.6, 122.9, 120.6, 117.4, 111.6, 63.7, 28.3, 25.6.

HRMS (ESI) m/z calcd. for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found: 277.1225.



(9-(Benzofuran-3-yl)-6,7-dihydro-5*H*-benzo[7]annulen-8-yl)methanol (In7-1v)

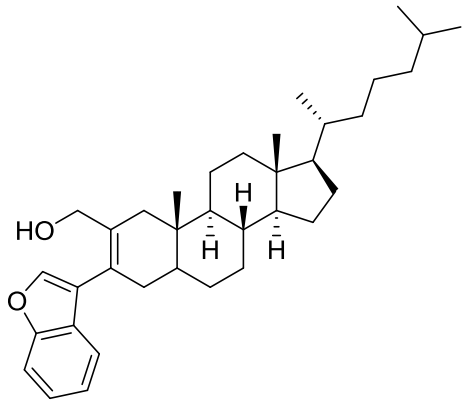
Colourless liquid; 522.2 mg; 60% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.20 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3359.0, 2935.1, 2856.1, 1560.4, 1451.6, 1265.0, 748.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.05 (m, 2H), 7.03 – 6.90 (m, 2H), 6.85 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.27 (s, 2H), 2.72 (t, *J* = 6.9 Hz, 2H), 2.22 – 2.13 (m, 2H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.64 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.4, 140.8, 140.6, 140.3, 129.1, 129.0, 128.7, 128.0, 127.3, 126.2, 124.3, 122.7, 120.9, 119.9, 111.4, 64.2, 35.2, 32.3, 28.3.

HRMS (ESI) m/z calcd. for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found: 291.1380.



((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(Benzofuran-3-yl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-2-yl)methanol (In7-1w)

White solid; 1.0844 g; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.23 (petroleum ether/ethyl acetate = 10/1).

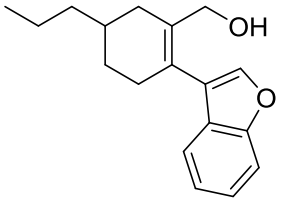
IR (KBr) $\tilde{\nu}$ 3398.8, 2931.3, 2867.6, 1713.0, 1452.1, 1382.7, 744.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 3H), 7.31 – 7.25 (m, 1H), 7.23 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.00 (s, 2H), 2.30 (d, *J* = 17.2 Hz, 1H), 2.21 (ddd, *J* = 18.1, 5.5, 2.1

Hz, 1H), 2.15 – 1.94 (m, 3H), 1.83 (ddt, *J* = 13.2, 9.4, 7.4 Hz, 1H), 1.70 (dq, *J* = 12.8, 3.4 Hz, 1H), 1.65 – 1.27 (m, 12H), 1.28 – 1.07 (m, 7H), 1.07 – 0.97 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.91 – 0.84 (m, 9H), 0.80 (ddd, *J* = 12.2, 10.5, 4.3 Hz, 1H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.4, 134.7, 127.8, 124.5, 124.3, 122.6, 121.3, 120.3, 111.6, 64.3, 56.5, 56.3, 54.1, 42.6, 42.0, 41.8, 40.0, 39.6, 36.7, 36.2, 35.8, 35.7, 34.6, 31.7, 28.3, 28.2, 28.0, 24.3, 23.9, 22.8, 22.6, 21.2, 18.8, 12.1, 12.0.

HRMS (ESI) m/z calcd. for $C_{36}H_{53}O_2$ $[M+H]^+$: 517.4040, found: 517.4030.



(2-(Benzofuran-3-yl)-5-propylcyclohex-1-en-1-yl)methanol (In7-1x)

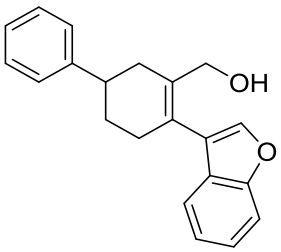
Colourless liquid; 567.3 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.24 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3348.1, 2923.4, 2870.7, 1663.2, 1452.1, 1101.9, 745.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.19 (m, 1H), 4.02 (dd, *J* = 14.6, 3.2 Hz, 2H), 2.51 – 2.35 (m, 3H), 1.90 (ddt, *J* = 30.4, 13.3, 3.4 Hz, 2H), 1.77 – 1.62 (m, 1H), 1.48 – 1.31 (m, 6H), 0.94 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.5, 135.4, 127.7, 125.7, 124.3, 122.6, 121.5, 120.3, 111.6, 64.1, 38.9, 34.1, 33.4, 31.8, 29.3, 20.1, 14.4.

HRMS (ESI) m/z calcd. for $C_{18}H_{23}O_2$ $[M+H]^+$: 271.1693, found: 271.1696.



(4-(Benzofuran-3-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)methanol (In7-1y)

Colourless liquid; 711.7 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.21 (petroleum ether/ethyl acetate =

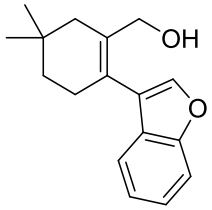
10/1).

IR (KBr) $\tilde{\nu}$ 3361.9, 2924.6, 2834.7, 1660.6, 1452.1, 1099.2, 748.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 3H), 7.37 – 7.27 (m, 5H), 7.27 – 7.20 (m, 2H), 4.11 – 4.03 (m, 2H), 2.98 (tdd, *J* = 11.1, 5.2, 2.9 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.60 – 2.50 (m, 2H), 2.44 (ddt, *J* = 17.0, 10.7, 2.9 Hz, 1H), 2.07 (dddd, *J* = 12.8, 6.4, 4.1, 2.4 Hz, 1H), 1.94 (tdd, *J* = 12.4, 9.6, 6.7 Hz, 1H), 1.55 – 1.42 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 146.5, 141.6, 135.5, 128.5, 127.7, 126.9, 126.2, 125.7, 124.4, 122.7, 121.3, 120.4, 111.6, 63.9, 40.1, 35.5, 32.2, 30.0.

HRMS (ESI) m/z calcd. for $C_{21}H_{21}O_2$ $[M+H]^+$: 305.1536, found: 305.1541.



(2-(Benzofuran-3-yl)-5,5-dimethylcyclohex-1-en-1-yl)methanol (In7-1aa)

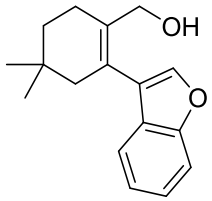
Colourless liquid; 537.9 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.23 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3348.4, 2950.1, 2919.7, 1664.0, 1452.1, 1100.7, 745.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 3H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 2.11 (t, *J* = 2.3 Hz, 2H), 1.51 (t, *J* = 6.5 Hz, 2H), 1.37 (br s, 1H),1.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 141.4, 134.8, 127.8, 124.3(2C), 122.6, 121.5, 120.3, 111.6, 64.2, 41.2, 35.6, 29.6, 28.9, 28.2.

HRMS (ESI) m/z calcd. for $C_{17}H_{20}NaO_2$ $[M+Na]^+$: 279.1356, found: 279.1351.



(2-(Benzofuran-3-yl)-4,4-dimethylcyclohex-1-en-1-yl)methanol (In7-1ab)

Yellow liquid; 614.8 mg; 80% yield; purified by silica gel chromatography (petroleum

ether/ethyl acetate = 20/1), R_f = 0.23 (petroleum ether/ethyl acetate = 10/1)

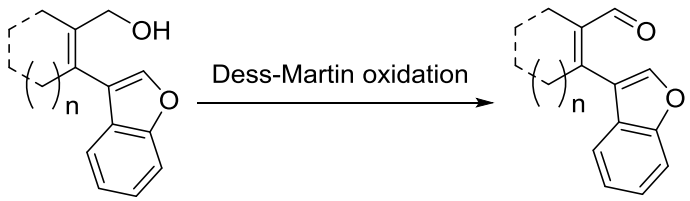
IR (KBr) $\tilde{v}$ 3349.0, 2949.0, 2868.0, 1666.2, 1453.1, 1100.4, 746.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.02 (s, 2H), 2.36 (td, *J* = 6.3, 3.1 Hz, 2H), 2.13 (d, *J* = 2.7 Hz, 2H), 1.53 (t, *J* = 6.5 Hz, 2H), 1.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 141.4, 134.6, 127.7, 124.7, 124.3, 122.6, 121.6, 120.2, 111.6, 63.7, 45.4, 35.3, 29.3, 28.1, 25.2.

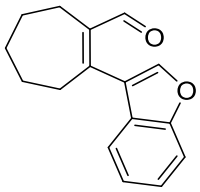
HRMS (ESI) m/z calcd. for $C_{17}H_{20}NaO_2$ $[M+Na]^+$: 279.1356, found: 279.1351.

4.3. General procedures for the synthesis of intermediates In8



In7 **In8**

To a solution of **In7** (1.5 mmol) in DCM (30 mL) was added Dess-Martin periodinane (DMP) (954.3 mg, 2.25 mmol) slowly at 0 ℃. Then the solution was warmed to room temperature and stirred for 10-20 min. After the reaction was complete, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ solution and $NaHCO_3$ solution, extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the aldehyde products **In8**.



2-(Benzofuran-3-yl)cyclohept-1-ene-1-carbaldehyde (In8-1q)

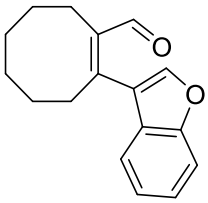
Yellow liquid; 270.1 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2923.0, 2850.7, 1725.2, 1667.2, 1452.1, 1245.7, 747.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.57 – 7.48 (m, 3H), 7.35 (td, *J* = 7.7, 1.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.2 Hz, 1H), 2.87 – 2.81 (m, 2H), 2.71 – 2.64 (m, 2H), 1.95 – 1.87 (m, 2H), 1.77 (dt, *J* = 11.9, 6.1 Hz, 2H), 1.56 (p, *J* = 5.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 155.5, 154.6, 144.6, 143.9, 126.8, 125.2, 123.4, 120.5, 120.2, 112.0, 36.6, 32.5, 26.1, 26.1, 25.1.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found: 241.1219.



(*Z*)-2-(Benzofuran-3-yl)cyclooct-1-ene-1-carbaldehyde (In8-1r)

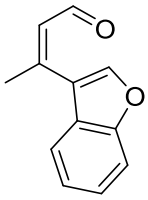
Colourless liquid; 285.9 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2924.5, 2852.3, 1727.0, 1666.5, 1452.2, 1265.6, 748.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.56 (s, 1H), 7.52 (t, *J* = 8.8 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 2.86 – 2.76 (m, 2H), 2.68 – 2.59 (m, 2H), 1.72 – 1.62 (m, 4H), 1.55 (p, *J* = 2.8 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 155.3, 151.7, 143.7, 141.7, 127.3, 125.1, 123.4, 120.3, 119.2, 111.9, 34.1, 29.9, 29.2, 26.7, 26.4, 24.1.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found: 255.1376.



(*Z*)-3-(Benzofuran-3-yl)but-2-enal (In8-1s)

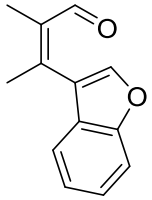
Yellow liquid; 223.3 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2927.3, 2854.1, 1724.5, 1664.3, 1452.1, 1134.2, 748.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.56 (dd, *J* = 11.4, 7.9 Hz, 2H), 7.37 (td, *J* = 8.3, 7.8, 1.4 Hz, 1H), 7.31 (td, *J* = 7.5, 1.1 Hz, 1H), 6.26 (dq, *J* = 8.1, 1.4 Hz, 1H), 2.40 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 155.5, 151.3, 144.0, 130.9, 126.4, 125.4, 123.6, 120.4, 119.3, 112.0, 25.5.

HRMS (ESI) m/z calcd. for $C_{12}H_{11}O_2$ $[M+H]^+$: 187.0754, found: 187.0753.



(*Z*)-3-(Benzofuran-3-yl)-2-methylbut-2-enal (In8-1t)

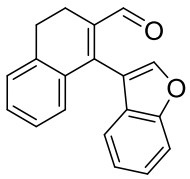
Colourless liquid; 225.1 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.6 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2924.0, 2854.1, 1721.3, 1667.7, 1453.1, 1111.4, 748.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.57 – 7.48 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.28 (td, *J* = 7.8, 1.6 Hz, 1H), 2.35 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 155.4, 146.4, 143.7, 137.2, 127.0, 125.2, 123.4, 120.4, 120.2, 111.9, 22.0, 11.4.

HRMS (ESI) m/z calcd. for $C_{13}H_{12}NaO_2$ $[M+Na]^+$: 223.0730, found: 223.0730.



1-(Benzofuran-3-yl)-3,4-dihydronaphthalene-2-carbaldehyde (In8-1u)

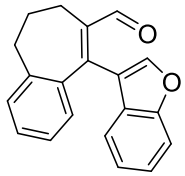
Colourless liquid; 370.0 mg; 90% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.50 (petroleum ether/ethyl acetate = 10/1)

IR (KBr) $\tilde{\nu}$ 2974.8, 2844.1, 1720.2, 1660.5, 1452.2, 1258.3, 749.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.72 (d, *J* = 1.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.36 (ddt, *J* = 8.5, 6.9, 1.7 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.22 – 7.17 (m, 1H), 7.09 (dt, *J* = 4.6, 1.6 Hz, 2H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.85 – 2.63 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 155.2, 145.1, 143.6, 138.5, 137.3, 133.7, 130.6, 128.2, 128.0, 127.9, 126.8, 125.3, 123.4, 120.7, 115.2, 111.9, 27.6, 20.8.

HRMS (ESI) m/z calcd. for $C_{19}H_{15}O_2$ $[M+H]^+$: 275.1067, found: 275.1061.



9-(Benzofuran-3-yl)-6,7-dihydro-5*H*-benzo[7]annulene-8-carbaldehyde (In8-1v)

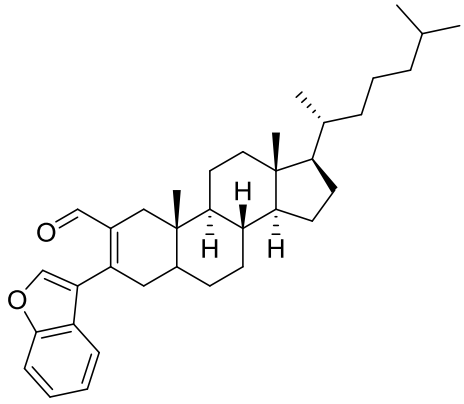
Yellow liquid; 302.5 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.50 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2934.6, 2857.9, 1735.6, 1660.7, 1450.9, 1253.1, 748.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.74 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.24 (m, 3H), 7.15 (td, *J* = 7.4, 1.8 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.23 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 155.6, 148.5, 146.6, 141.8, 141.1, 138.7, 129.7, 129.7, 129.3, 127.3, 126.6, 125.2, 123.4, 120.9, 118.1, 111.8, 34.7, 32.3, 22.7.

HRMS (ESI) m/z calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found: 289.1220.



(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(Benzofuran-3-yl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-2-carbaldehyde (In8-1w)

White solid; 555.5 mg; 72% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

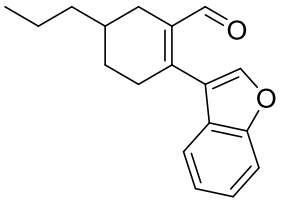
IR (KBr) $\tilde{\nu}$ 2928.2, 2862.5, 1714.3, 1668.3, 1452.2, 1261.1, 746.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.57 (s, 1H), 7.51 (t, *J* = 8.9 Hz, 2H),

7.38 – 7.31 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 2.68 (d, *J* = 17.7 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.41 – 2.25 (m, 1H), 2.07 – 2.00 (m, 1H), 1.83 (dt, *J* = 18.5, 3.2 Hz, 2H), 1.70 (ddd, *J* = 18.1, 13.6, 3.4 Hz, 3H), 1.62 – 1.50 (m, 5H), 1.39 – 1.29 (m, 6H), 1.17 – 1.07 (m, 6H), 1.05 – 0.98 (m, 3H), 0.90 – 0.84 (m, 9H), 0.81 (s, 3H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 155.2, 147.3, 143.2, 136.9, 127.3, 125.1, 123.3, 120.2, 119.1, 111.9, 56.4, 56.3, 53.9, 42.5, 41.4, 39.9, 39.5, 38.0, 36.9, 36.2, 35.8, 35.6, 34.0, 31.5, 28.2, 28.1, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.0, 11.8.

HRMS (ESI) m/z calcd. for $C_{36}H_{51}O_2$ $[M+H]^+$: 515.3884, found: 515.3888.



2-(Benzofuran-3-yl)-5-propylcyclohex-1-ene-1-carbaldehyde (In8-1x)

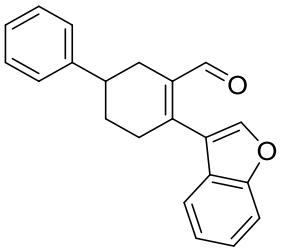
Colourless liquid; 321.8 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.51 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2925.0, 2870.8, 1728.2, 1668.0, 1452.2, 1220.8, 747.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.58 (s, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 2.78 – 2.56 (m, 3H), 1.97 – 1.81 (m, 2H), 1.42 (dtt, *J* = 16.2, 10.5, 4.8 Hz, 6H), 0.94 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 155.3, 148.3, 143.4, 137.6, 127.2, 125.1, 123.3, 120.3, 119.4, 111.9, 38.5, 33.2, 32.4, 29.2, 28.6, 20.0, 14.3.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}O_2$ $[M+H]^+$: 269.1536, found: 269.1531.



4-(Benzofuran-3-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carbaldehyde (In8-1y)

Colourless liquid; 362.6 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.61 (petroleum ether/ethyl acetate =

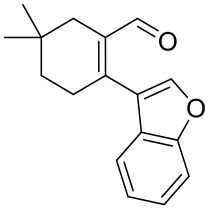
10/1).

IR (KBr) $\tilde{\nu}$ 2927.9, 2858.3, 1726.7, 1666.8, 1452.2, 1224.6, 748.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.30 (m, 4H), 7.30 – 7.27 (m, 2H), 7.24 (tt, *J* = 6.8, 1.5 Hz, 1H), 3.00 – 2.87 (m, 2H), 2.86 – 2.72 (m, 2H), 2.44 – 2.33 (m, 1H), 2.20 – 2.11 (m, 1H), 2.03 – 1.90 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 155.3, 147.9, 145.5, 143.6, 137.5, 128.6, 127.2, 126.9, 126.5, 125.2, 123.5, 120.3, 119.2, 112.0, 39.0, 33.6, 30.5, 29.5.

HRMS (ESI) m/z calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found: 303.1374.



2-(Benzofuran-3-yl)-5,5-dimethylcyclohex-1-ene-1-carbaldehyde (In8-1aa)

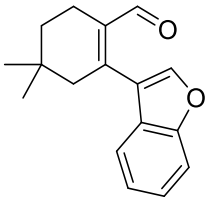
Colourless liquid; 304.9 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2923.0, 2864.6, 1726.6, 1668.1, 1452.1, 1233.3, 748.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.59 (s, 1H), 7.52 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 8.2 Hz, 1H), 2.67 (tt, *J* = 6.4, 2.3 Hz, 2H), 2.22 (t, *J* = 2.3 Hz, 2H), 1.58 (t, *J* = 6.4 Hz, 2H), 1.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 155.3, 147.3, 143.2, 136.9, 127.3, 125.1, 123.4, 120.2, 119.3, 111.9, 36.1, 35.0, 31.1, 28.3, 28.0.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_2$ $[M+Na]^+$: 277.1199, found: 277.1193.



2-(Benzofuran-3-yl)-4,4-dimethylcyclohex-1-ene-1-carbaldehyde (In8-1ab)

Yellow liquid; 308.8 mg; 81% yield; purified by silica gel chromatography (petroleum

ether/ethyl acetate = 20/1), R_f = 0.60 (petroleum ether/ethyl acetate = 10/1).

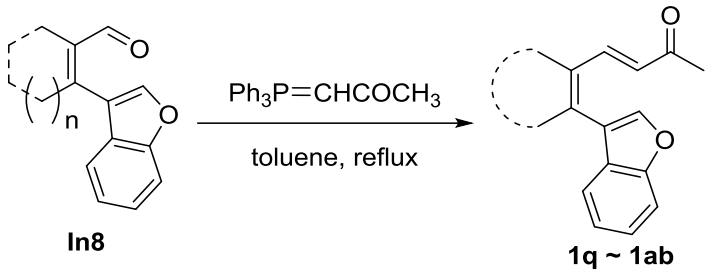
IR (KBr) $\tilde{v}$ 2927.4, 2866.7, 1720.1, 1667.0, 1452.9, 1234.0, 750.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.56 (s, 1H), 7.51 (dd, *J* = 14.7, 7.8 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 2.50 – 2.38 (m, 4H), 1.55 (t, *J* = 6.5 Hz, 2H), 1.05 (s, 6H).

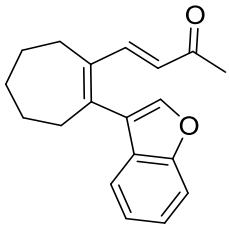
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 155.3, 147.5, 143.2, 136.9, 127.1, 125.1, 123.3, 120.2, 119.5, 111.9, 46.8, 34.2, 29.4, 28.0, 20.6.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_2$ $[M+Na]^+$: 277.1199, found: 277.1193.

4.4. General procedures for the synthesis of substrates 1q ~ 1ab



To a solution of **In8** (1 mmol) in toluene (5 mL) was added triphenylphosphoranylidene-2-propanone (955.1 mg, 3 mmol) slowly at room temperature. Then the solution was warmed to 120 ℃ and reflux for overnight. After the reaction was complete, most of toluene was removed. The crude extracts were purified by silica gel column chromatography to afford the products **1q ~ 1ab**.



(*E*)-4-(2-(Benzofuran-3-yl)cyclohept-1-en-1-yl)but-3-en-2-one (1q)

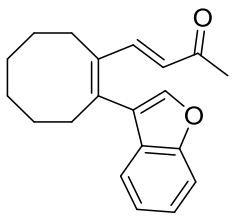
Yellow liquid; 182.1 mg; 65% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2923.0, 2850.7, 1715.1, 1650.2, 1452.7, 1245.1, 748.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 4H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.22 (d, *J* = 16.1 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.64 – 2.57 (m, 2H), 2.11 (s, 3H), 1.90 (p, *J* = 6.2 Hz, 2H), 1.70 (p, *J* = 5.8 Hz, 2H), 1.61 (p, *J* = 5.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 155.4, 143.9, 143.4, 143.1, 139.5, 127.1, 125.9, 124.8, 123.0, 122.4, 120.7, 111.8, 35.9, 32.2, 28.7, 27.0, 26.3, 25.9.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1356, found: 303.1352.



(*E*)-4-((*Z*)-2-(Benzofuran-3-yl)cyclooct-1-en-1-yl)but-3-en-2-one (1r)

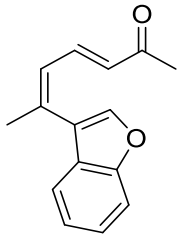
Yellow liquid; 147.1 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 30/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2924.3, 2852.2, 1712.1, 1649.1, 1452.7, 1263.4, 749.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.40 (d, *J* = 16.2 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 6.21 (d, *J* = 16.2 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.72 – 2.64 (m, 2H), 2.04 (s, 3H), 1.76 – 1.68 (m, 2H), 1.65 – 1.53 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 155.2, 143.6, 143.1, 141.3, 136.1, 127.5, 126.4, 124.7, 123.0, 121.4, 120.7, 111.8, 34.4, 29.7, 29.6, 26.9(2C), 26.7, 26.5.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found: 295.1691.



(3*E*,5*Z*)-6-(Benzofuran-3-yl)hepta-3,5-dien-2-one (1s)

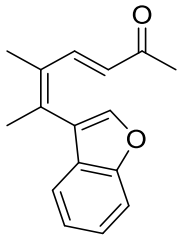
Yellow liquid; 119.8 mg; 53% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2924.5, 2854.0, 1714.2, 1665.9, 1615.0, 1452.9, 750.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.55 – 7.50 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 6.44 – 6.38 (m, 1H), 6.15 (d, *J* = 15.6 Hz, 1H), 2.30 (d, *J* = 1.8 Hz, 3H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 155.4, 143.0, 140.7, 139.1, 129.9, 127.6, 126.7, 124.9, 123.1, 120.8, 120.6, 111.9, 26.9, 25.5.

HRMS (ESI) m/z calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1067, found: 227.1065.



(3*E*,5*Z*)-6-(Benzofuran-3-yl)-5-methylhepta-3,5-dien-2-one (1t)

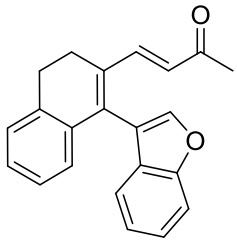
Yellow liquid; 136.9 mg; 57% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2923.7, 2851.2, 1714.3, 1668.0, 1615.8, 1453.1, 751.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.46 (ddd, *J* = 7.8, 1.4, 0.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 16.1 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 2.04 (q, *J* = 1.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 155.3, 144.1, 143.0, 135.4, 131.4, 127.2, 126.6, 124.8, 123.0, 122.4, 120.7, 111.8, 26.8, 21.8, 14.6.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223, found: 241.1219.



(*E*)-4-(1-(Benzofuran-3-yl)-3,4-dihydronaphthalen-2-yl)but-3-en-2-one (1u)

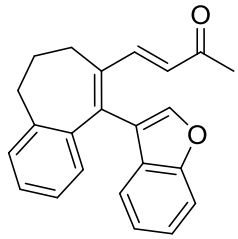
Yellow liquid; 157.1 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.30 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2927.8, 2850.5, 1712.6, 1666.6, 1607.1, 1422.4, 1215.3, 749.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 16.1 Hz, 1H), 7.35 (ddd, *J* = 8.5, 5.8, 2.9 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 3.08 – 2.93 (m, 2H), 2.78 – 2.63 (m, 2H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 155.2, 144.6, 142.6, 136.9, 134.7, 134.5, 128.7, 128.2, 127.5, 127.4, 127.2, 126.7, 124.9, 123.1, 120.9, 117.2, 111.8, 27.8, 27.1, 24.6.

HRMS (ESI) m/z calcd. for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1380, found: 315.1374.



(*E*)-4-(9-(Benzofuran-3-yl)-6,7-dihydro-5*H*-benzo[7]annulen-8-yl)but-3-en-2-one (1v)

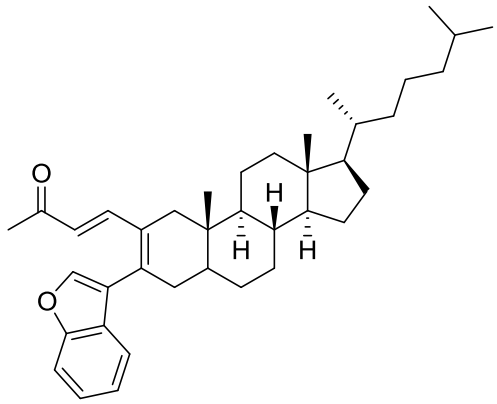
Yellow solid; 164.1 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2936.9, 2857.9, 1719.1, 1662.3, 1452.1, 1267.0, 750.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.63 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.27 (dt, *J* = 13.9, 7.2 Hz, 3H), 7.09 (dt, *J* = 19.5, 7.5 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 2.78 (t, *J* = 7.0 Hz, 2H), 2.38 (t, *J* = 6.9 Hz, 2H), 2.23 (q, *J* = 7.4 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 155.4, 145.5, 142.6, 141.0, 140.4, 139.0, 136.8, 129.8, 128.8, 128.6, 127.7, 126.8, 126.4, 124.8, 123.0, 121.1, 120.3, 111.7, 33.9, 32.1, 27.3, 26.1.

HRMS (ESI) m/z calcd. for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1536 found: 329.1533.



(*E*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(Benzofuran-3-yl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-2-yl)but-3-en-2-one (1w)

White solid; 277.2 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

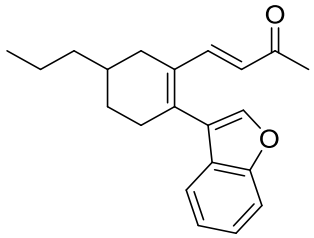
IR (KBr) $\tilde{\nu}$ 2927.3, 2865.1, 1714.4, 1664.6, 1506.2, 1275.3, 764.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 –

7.22 (m, 1H), 6.15 (d, J = 16.1 Hz, 1H), 2.48 – 2.38 (m, 2H), 2.35 – 2.24 (m, 1H), 2.04 (s, 3H), 2.00 – 1.92 (m, 1H), 1.89 – 1.79 (m, 1H), 1.76 – 1.69 (m, 1H), 1.64 – 1.48 (m, 6H), 1.42 – 1.29 (m, 6H), 1.21 – 1.04 (m, 8H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 – 0.81 (m, 12H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 155.2, 144.0, 142.7, 136.6, 131.1, 127.3, 125.7, 124.7, 122.9, 121.2, 120.7, 111.8, 56.5, 56.3, 54.1, 42.5, 41.5, 40.0, 39.9, 39.6, 37.8, 36.2, 35.8, 35.6, 34.4, 31.6, 28.2, 28.2, 28.0, 26.6, 24.2, 23.9, 22.8, 22.6, 21.2, 18.8, 12.1, 12.0.

HRMS (ESI) m/z calcd. for $C_{39}H_{55}O_2$ $[M+H]^+$: 555.4197, found: 555.4196.



(*E*)-4-(2-(Benzofuran-3-yl)-5-propylcyclohex-1-en-1-yl)but-3-en-2-one (1x)

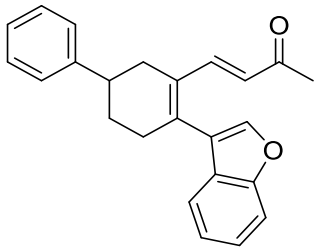
Yellow liquid; 169.5 mg; 55% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.45 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{v}$ 2983.8, 2939.9, 1732.2, 1714.7, 1600.5, 1449.6, 751.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 4H), 7.33 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 7.1 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 2.63 – 2.50 (m, 3H), 2.05 (s, 3H), 1.95 – 1.89 (m, 2H), 1.48 – 1.36 (m, 6H), 0.96 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 155.2, 143.6, 142.8, 137.8, 131.9, 127.3, 125.7, 124.7, 122.9, 121.4, 120.7, 111.8, 38.7, 33.2, 33.0, 32.3, 28.8, 26.6, 20.0, 14.3.

HRMS (ESI) m/z calcd. for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849, found: 309.1844.



(*E*)-4-(4-(Benzofuran-3-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)but-3-en-2-one (1y)

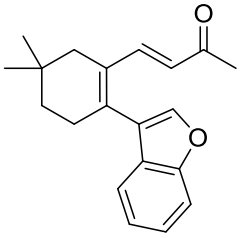
Yellow liquid; 171.1 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.42 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2926.9, 2860.1, 1711.6, 1666.7, 1494.1, 1225.1, 748.9 cm^{-1}

^{1}H NMR (400 MHz, CDCl3) δ 7.57 (s, 1H), 7.56 – 7.45 (m, 3H), 7.42 – 7.33 (m, 3H), 7.33 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 6.16 (d, *J* = 16.1 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.82 – 2.68 (m, 3H), 2.51 – 2.38 (m, 1H), 2.18 – 2.09 (m, 1H), 2.05 (s, 3H), 2.02 – 1.94 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 155.3, 145.9, 143.0, 142.8, 137.5, 131.9, 128.7, 127.2, 126.9, 126.5, 125.8, 124.9, 123.0, 121.3, 120.7, 111.9, 39.7, 33.9, 33.5, 29.5, 27.1.

HRMS (ESI) m/z calcd. for $C_{24}H_{23}O_2$ $[M+H]^+$: 343.1693, found: 343.1687.



(*E*)-4-(2-(Benzofuran-3-yl)-5,5-dimethylcyclohex-1-en-1-yl)but-3-en-2-one (1aa)

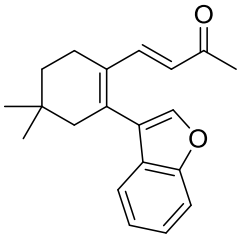
Yellow liquid; 205.9 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2955.3, 2924.6, 1713.1, 1667.2, 1452.2, 1263.7, 750.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.41 (m, 4H), 7.33 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.25 (td, *J* = 7.5, 1.1 Hz, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 2.60 (t, *J* = 6.5 Hz, 2H), 2.16 (t, *J* = 2.2 Hz, 2H), 2.05 (s, 3H), 1.57 (t, *J* = 6.5 Hz, 2H), 1.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 155.2, 143.7, 142.7, 136.5, 131.2, 127.3, 125.6, 124.8, 123.0, 121.4, 120.7, 111.8, 39.3, 35.1, 30.9, 28.8, 28.3, 26.7.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found: 295.1693.



(*E*)-4-(2-(Benzofuran-3-yl)-4,4-dimethylcyclohex-1-en-1-yl)but-3-en-2-one (1ab)

Yellow liquid; 176.5 mg; 60% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.35 (petroleum ether/ethyl acetate = 10/1).

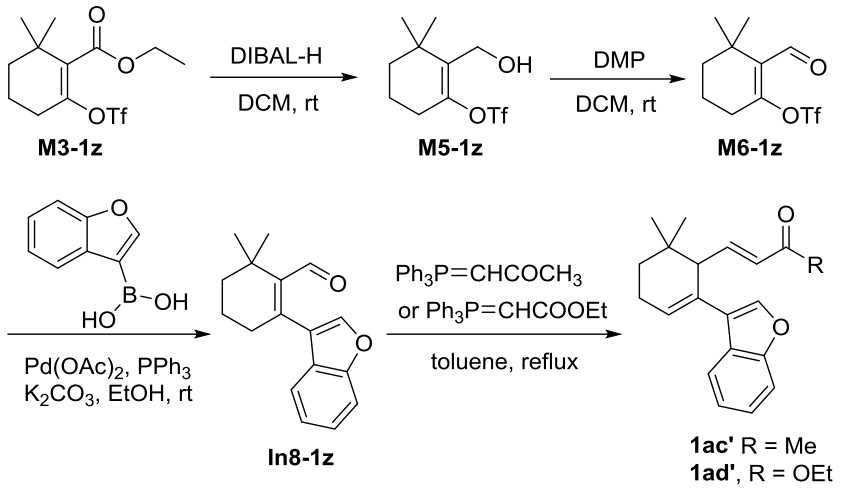
IR (KBr) $\tilde{\nu}$ 2952.8, 2921.1, 1719.0, 1667.6, 1452.1, 1257.7, 748.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.41 (m, 4H), 7.33 (td, *J* = 7.9, 1.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 2.41 (td, *J* = 6.7, 3.1 Hz, 2H), 2.35 (s, 2H), 2.07 (s, 3H), 1.61 (t, *J* = 6.6 Hz, 2H), 1.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 155.2, 143.0, 142.7, 136.9, 131.0, 127.2, 125.9, 124.7, 122.9, 121.6, 120.6, 111.8, 46.8, 34.8, 29.3, 27.9, 26.7, 23.4.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found: 295.1693.

5. Procedures for the synthesis of substrates 1ac' and 1ad'



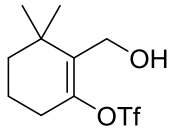
Material **M3-1z** was prepared according to the above procedures 2.2. **M3-1z** (8 mmol) was dissolved in CH_2Cl_2 (40 mL) under N_2 and placed in a dry ice/acetone bath. Once cooled, DIBAL-H (1 M, 20 mL, 20 mmol) was added and then the mixture was stirred for 10 minutes. A saturated aqueous solution of HCl (3 M) was added and then the mixture was warmed to ambient temperature. The organic phase was separated, and the aqueous phase was extracted with DCM three times. The combined organic phases were dried Na_2SO_4 and concentrated. The crude extract was purified by silica gel column chromatography to afford the product **M5-1z**.

To a solution of **M5-1z** (5 mmol) in DCM (30 mL) was added Dess-Martin periodinane (DMP) (3.18 g, 7.5 mmol,) slowly at room temperature. Then the solution stirred for 5-10 minutes at room temperature. After the solution was complete, the reaction was diluted with sequentially with a saturated aqueous $Na_2S_2O_3$ solution and $NaHCO_3$ solution. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The crude extract was purified by silica gel column chromatography to afford the aldehyde product **M6-1z**.

Under N_2, a Schlenk flask was charged with anhydrous EtOH (30 mL) and a mixture of **M6-1z** (4 mmol), Benzofuran-3-boronic acid (713 mg, 4.4 mmol), PPh_3 (209.8 mg, 0.8 mmol), $Pd(OAc)_2$ (89.8 mg, 0.4 mmol), K_2CO_3(1.1057 g, 8 mmol). The reaction was stirred at room temperature overnight. After the reaction was

complete, most of ethanol was removed through rotary evaporator. The reaction was quenched by saturated aqueous NH_4Cl solution, extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude extracts were purified by silica gel column chromatography to afford the coupling product **In8-1z**.

To a solution of **In8-1z** (1 mmol) in toluene (20 mL) was added phosphoranylidene-2-propanone (954 mg, 3 mmol) or carbethoxy-methylene triphenylphosphorane (1.0354 g, 3 mmol) slowly at room temperature. Then the solution was warmed to 120 ℃ and reflux for overnight. After the reaction was complete, most of toluene was removed through rotary evaporator. The crude extracts were purified by silica gel column chromatography to afford the products **1ac'** and **1ad'**



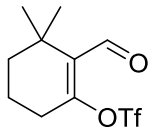
2-(Hydroxymethyl)-3,3-dimethylcyclohex-1-en-1-yl trifluoromethanesulfonate (M5-1z)

Colourless liquid; 1.5210 g; 66% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1), R_f = 0.3 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 3424.1, 2955.2, 1679.7, 1414.6, 1211.4, 1144.1, 898.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 2H), 2.37 (t, J = 6.4 Hz, 2H), 1.82 – 1.79 (m, 2H), 1.54 – 1.48 (m, 2H), 1.22 (br s, 1H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 136.8, 118.3 (q, *J* = 319.5 Hz), 56.3, 37.9, 35.4, 28.2, 27.7, 19.0.



2-Formyl-3,3-dimethylcyclohex-1-en-1-yl trifluoromethanesulfonate (M6-1z)

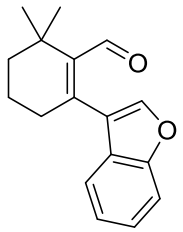
Colourless liquid; 1.2586 g; 88% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.60 (petroleum ether/ethyl acetate =

10/1).

IR (KBr) $\tilde{\nu}$ 2963.1, 1729.4, 1680.1, 1463.4, 1241.1, 1139.9, 610.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 2.57 (t, *J* = 6.2 Hz, 2H), 1.82 (dt, *J* = 11.7, 6.0 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 161.7, 136.7, 118.3 (q, *J* = 319.8 Hz), 39.0, 34.8, 29.9, 27.2, 18.5.



2-(Benzofuran-3-yl)-6,6-dimethylcyclohex-1-ene-1-carbaldehyde (In8-1z)

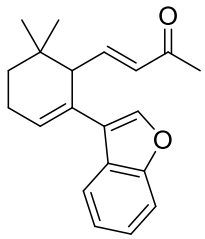
Colourless liquid; 792.9 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 40/1), R_f = 0.56 (petroleum ether/ethyl acetate = 10/1).

IR (KBr) $\tilde{\nu}$ 2921.1, 2865.0, 1728.4, 1669.1, 1452.1, 1234.1, 751.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.54 (s, 1H), 7.49 (dd, *J* = 15.1, 8.0 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 2.58 (t, *J* = 6.1 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.65 – 1.57 (m, 2H), 1.34 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 155.2, 149.0, 145.4, 143.3, 127.3, 125.1, 123.3, 120.2, 120.2, 111.8, 40.4, 34.7, 33.7, 27.8, 18.9.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_2$ $[M+Na]^+$: 277.1199, found: 277.1193.



(*E*)-4-(2-(Benzofuran-3-yl)-6,6-dimethylcyclohex-2-en-1-yl)but-3-en-2-one (1ac')

Yellow solid; 147.1 mg; 50% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.30 (petroleum ether/ethyl acetate = 10/1).

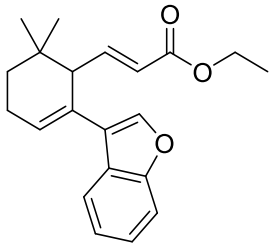
IR (KBr) $\tilde{\nu}$ 2960.7, 2871.5, 1727.0, 1713.9, 1673.6, 1463.2, 1257.4, 754.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 – 7.42 (m, 2H),

7.31 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 6.76 (dd, *J* = 15.9, 8.9 Hz, 1H), 6.35 (t, *J* = 3.8 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 2.90 (d, *J* = 8.9 Hz, 1H), 2.34 (tt, *J* = 5.9, 3.6 Hz, 2H), 2.16 (s, 3H), 1.66 – 1.56 (m, 1H), 1.39 – 1.30 (m, 1H), 1.11 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 155.5, 148.4, 141.1, 132.7, 128.2, 126.6, 126.4, 124.3, 122.7, 122.2, 120.8, 111.7, 52.0, 33.0, 30.4, 28.5, 27.1, 26.6, 23.5.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found: 295.1691.



Ethyl (*E*)-3-(2-(benzofuran-3-yl)-6,6-dimethylcyclohex-2-en-1-yl)acrylate (1ad')

Yellow liquid; 226.9 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1), R_f = 0.40 (petroleum ether/ethyl acetate = 10/1).

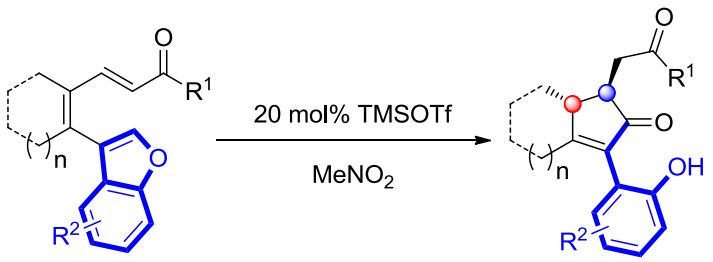
IR (KBr) $\tilde{v}$ 2960.1, 2870.4, 1737.6, 1714.1, 1643.5, 1460.1, 1266.7, 749.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (s, 1H), 7.45 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.28 – 7.19 (m, 1H), 6.96 (dd, *J* = 15.6, 8.9 Hz, 1H), 6.34 (t, *J* = 3.8 Hz, 1H), 5.77 (dd, *J* = 15.6, 0.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 8.9 Hz, 1H), 2.33 (qd, *J* = 6.3, 2.3 Hz, 2H), 1.63 (ddd, *J* = 13.6, 9.9, 7.4 Hz, 1H), 1.36 – 1.26 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 155.5, 149.4, 141.2, 128.3, 126.5, 126.5, 124.3, 123.1, 122.7, 122.2, 121.0, 111.6, 60.3, 51.7, 33.0, 30.2, 28.6, 26.6, 23.6, 14.2.

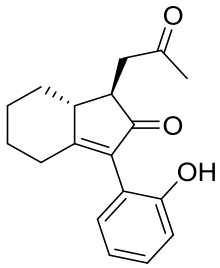
HRMS (ESI) m/z calcd. for $C_{21}H_{24}NaO_3$ $[M+Na]^+$: 347.1618, found: 347.1617.

6. General procedures for this reaction



1 **2**

To a solution of **1** (0.2 mmol) in $MeNO_2$ (1.0 mL) was added TMSOTf (7.2 μL, 0.04 mmol). Then the reaction was stirred at corresponding temperature and monitored by TLC. After the reaction was complete, the reaction mixture was purified by silica gel column chromatography to afford corresponding products **2** in corresponding yields.



***trans*-3-(2-Hydroxyphenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2a)**

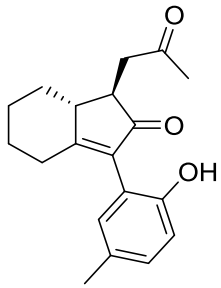
Pale yellow solid; 42.6 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3376.4, 2934.8, 2857.7, 1702.6, 1605.5, 1366.1, 756.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.26 – 7.21 (m, 1H), 7.01 (ddd, *J* = 8.1, 5.1, 1.4 Hz, 2H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 3.08 – 3.00 (m, 2H), 2.75 (dd, *J* = 18.2, 8.3 Hz, 1H), 2.48 – 2.39 (m, 3H), 2.25 – 2.14 (m, 4H), 2.02 (ddt, *J* = 13.7, 4.9, 2.4 Hz, 1H), 1.90 (dq, *J* = 12.8, 2.6 Hz, 1H), 1.60 – 1.39 (m, 2H), 1.32 (dd, *J* = 13.3, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 206.8, 180.9, 155.0, 135.4, 130.6, 129.9, 120.3, 119.2, 118.6, 49.0, 47.7, 44.1, 34.5, 30.0, 29.8, 26.9, 25.3.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found: 285.1485.



***trans*-3-(2-Hydroxy-5-methylphenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2b)**

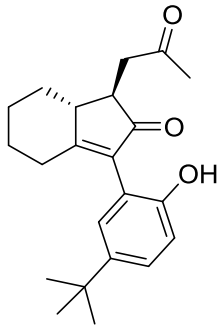
Yellow liquid; 42.3 mg; 71% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3381.1, 2930.8, 2857.9, 1711.1, 1702.1, 1605.3, 1366.8, 736.4 cm^{-1}

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.26 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 3.09 – 2.99 (m, 2H), 2.74 (dd, *J* = 18.2, 8.3 Hz, 1H), 2.48 – 2.37 (m, 3H), 2.27 (s, 3H), 2.25 – 2.20 (m, 1H), 2.19 (s, 3H), 2.08 – 1.97 (m, 1H), 1.95 – 1.85 (m, 1H), 1.61 – 1.35 (m, 2H), 1.31 (dd, *J* = 13.4, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 206.8, 180.5, 152.6, 135.4, 130.9, 130.5, 129.4, 119.0, 118.5, 49.0, 47.8, 44.1, 34.5, 30.0, 29.8, 26.9, 25.3, 20.5.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found: 299.1640.



***trans*-3-(5-(*tert*-Butyl)-2-hydroxyphenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2c)**

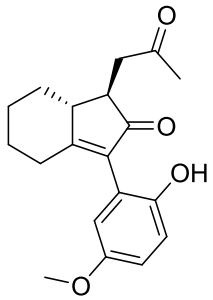
Yellow liquid; 52.4 mg; 77% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.12 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3370.7, 2948.9, 2860.2, 1714.3, 1704.7, 1668.2, 1240.9, 1046.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.27 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.00 (d, *J* = 2.6 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.10 – 3.01 (m, 2H), 2.71 (dd, *J* = 18.1, 8.6 Hz, 1H), 2.52 – 2.39 (m, 3H), 2.26 – 2.21 (m, 1H), 2.19 (s, 3H), 2.07 – 2.00 (m, 1H), 1.94 – 1.87 (m, 1H), 1.50 (dtt, *J* = 27.2, 13.0, 3.4 Hz, 2H), 1.36 – 1.31 (m, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 206.7, 180.7, 152.6, 142.8, 136.0, 127.6, 126.9, 118.4, 118.3, 49.2, 47.8, 44.1, 34.6, 34.0, 31.5, 30.0, 30.0, 27.0, 25.3.

HRMS (ESI) m/z calcd. for $C_{28}H_{29}O_3$ $[M+H]^+$: 341.2111, found: 341.2110.



***trans*-3-(2-Hydroxy-5-methoxyphenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2 *H*-inden-2-one (2d)**

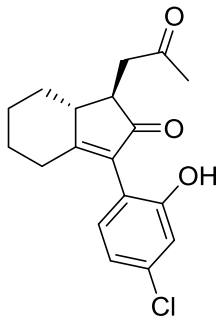
Yellow liquid; 47.1 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.08 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3365.3, 2929.2, 2854.1, 1713.3, 1702.5, 1607.9, 1494.2, 1211.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.56 (d, *J* = 3.0 Hz, 1H), 3.75 (s, 3H), 3.10 – 3.00 (m, 2H), 2.73 (dd, *J* = 18.2, 8.3 Hz, 1H), 2.48 – 2.37 (m, 3H), 2.26 – 2.20 (m, 1H), 2.18 (s, 3H), 2.06 – 1.98 (m, 1H), 1.94 – 1.85 (m, 1H), 1.59 – 1.36 (m, 2H), 1.28 (dd, *J* = 13.4, 3.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 206.7, 180.9, 153.2, 148.8, 135.2, 120.0, 119.3, 115.9, 115.1, 55.8, 49.0, 47.8, 44.0, 34.4, 29.9, 29.8, 26.9, 25.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1591, found: 315.1589.



***trans*-3-(4-Chloro-2-hydroxyphenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2e)**

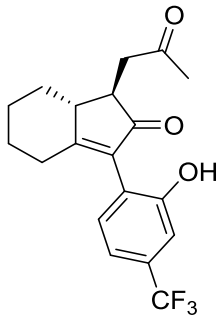
Yellow solid; 56.6 mg; 89% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1)

IR (KBr) $\tilde{\nu}$ 3305.8, 2934.6, 2857.1, 1714.5, 1704.6, 1643.1, 1410.7, 1206.6 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.95 – 6.87 (m, 2H), 3.03 (dd, *J* = 18.3, 3.5 Hz, 1H), 2.99 – 2.92 (m, 1H), 2.78 (dd, *J* = 18.3, 7.8 Hz, 1H), 2.46 – 2.35 (m, 3H), 2.21 (d, *J* = 12.0 Hz, 1H), 2.18 (s, 3H), 2.06 – 1.99 (m, 1H), 1.94 – 1.85 (m, 1H), 1.58 – 1.38 (m, 2H), 1.30 (dd, *J* = 14.5, 3.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 206.9, 181.2, 155.9, 135.0, 134.4, 131.4, 120.4, 118.7, 117.8, 48.9, 47.8, 43.9, 34.4, 30.0, 29.8, 26.9, 25.2.

HRMS (ESI) m/z calcd. for $C_{18}H_{20}ClO_3$ $[M+H]^+$: 319.1095, found: 319.1097.



***trans*-3-(2-Hydroxy-4-(trifluoromethyl)phenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2f)**

Yellow solid; 57.7 mg; 82% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1)

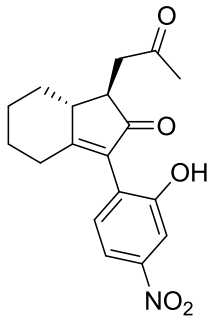
IR (KBr) $\tilde{\nu}$ 3350.4, 2926.4, 2854.1, 1700.7, 1691.7, 1611.6, 1425.2, 1122.5 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.22 (s, 1H), 7.18 – 7.10 (m, 2H), 3.04 (dd, *J* = 18.4, 3.6 Hz, 1H), 2.94 (ddt, *J* = 14.1, 4.1, 2.0 Hz, 1H), 2.83 (dd, *J* = 18.4, 7.6

Hz, 1H), 2.50 – 2.37 (m, 3H), 2.26 – 2.20 (m, 1H), 2.19 (s, 3H), 2.07 – 2.00 (m, 1H), 1.94 – 1.87 (m, 1H), 1.57 – 1.40 (m, 2H), 1.34 – 1.27 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 207.0, 181.8, 155.3, 134.3, 131.8 (q, *J* = 32.4 Hz), 131.1, 123.9 (q, *J* = 272.3 Hz), 122.8, 116.7 (q, *J* = 3.8 Hz), 115.4 (q, *J* = 3.6 Hz), 48.9, 47.9, 43.8, 34.3, 29.9, 29.7, 26.8, 25.2.

HRMS (ESI) m/z calcd. for $C_{19}H_{19}F_3NaO_3$ $[M+Na]^+$: 375.1179, found: 375.1173.



***trans*-3-(2-Hydroxy-4-nitrophenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2g)**

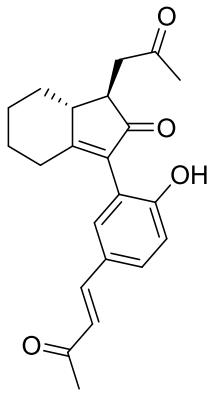
Yellow solid; 52.7 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 1/1), R_f = 0.10 (petroleum ether/ethyl acetate = 2/1)

IR (KBr) $\tilde{\nu}$ 3434.8, 2937.2, 2857.6, 2255.9, 2128.9, 1666.6, 1650.6, 1524.4, 1347.7 ,1026.4 cm^{-1}

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 7.69 (dd, *J* = 6.9, 2.3 Hz, 2H), 7.26 – 7.21 (m, 1H), 2.91 (dd, *J* = 17.8, 4.2 Hz, 1H), 2.67 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.46 – 2.25 (m, 4H), 2.21 – 2.16 (m, 1H), 2.14 (s, 3H), 1.93 – 1.85 (m, 1H), 1.82 – 1.74 (m, 1H), 1.54 – 1.24 (m, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 207.4, 206.1, 179.0, 156.1, 148.1, 132.5, 131.9, 127.1, 113.9, 110.3, 48.5, 47.5, 43.8, 34.4, 30.3, 30.0, 26.5, 25.2.

HRMS (ESI) m/z calcd. for $C_{18}H_{20}NO_5$ $[M+H]^+$: 330.1336, found: 330.1334.



***trans*-3-(2-Hydroxy-5-((*E*)-3-oxobut-1-en-1-yl)phenyl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2h)**

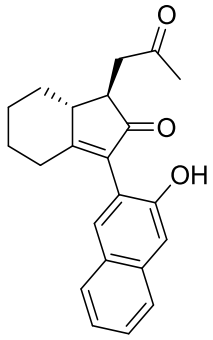
Yellow liquid; 49.3 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 1/1), R_f = 0.09 (petroleum ether/ethyl acetate = 1/1)

IR (KBr) $\tilde{v}$ 3281.9, 2930.6, 2855.5, 1714.1, 1695.2, 1650.9, 1592.9, 1257.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.50 – 7.42 (m, 2H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 3.05 (dd, *J* = 18.3, 3.6 Hz, 1H), 3.00 – 2.92 (m, 1H), 2.83 (dd, *J* = 18.3, 7.7 Hz, 1H), 2.51 – 2.38 (m, 3H), 2.35 (s, 3H), 2.29 – 2.21 (m, 1H), 2.19 (s, 3H), 2.09 – 2.00 (m, 1H), 1.95 – 1.89 (m, 1H), 1.61 – 1.41 (m, 2H), 1.35 – 1.27 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 207.0, 198.5, 181.3, 157.5, 143.3, 134.4, 131.4, 129.8, 126.6, 124.9, 119.7, 118.9, 48.8, 47.8, 43.9, 34.3, 30.0, 29.8, 27.4, 26.9, 25.2.

HRMS (ESI) m/z calcd. for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found: 353.1744.



***trans*-3-(3-Hydroxynaphthalen-2-yl)-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2i)**

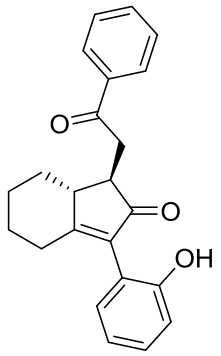
Yellow liquid; 48.1 mg; 72% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.40 (petroleum ether/ethyl acetate = 1/1)

IR (KBr) $\tilde{\nu}$ 3363.8, 2926.5, 2852.3, 1715.7, 1702.3, 1625.5, 1446.4, 1242.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 19.3, 8.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.39 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.34 (s, 1H), 7.29 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 3.09 – 2.97 (m, 2H), 2.79 (dd, *J* = 18.2, 7.9 Hz, 1H), 2.50 – 2.38 (m, 3H), 2.28 – 2.19 (m, 1H), 2.18 (s, 3H), 2.04 – 1.96 (m, 1H), 1.95 – 1.87 (m, 1H), 1.61 – 1.41 (m, 2H), 1.36 – 1.27 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 207.0, 181.3, 152.7, 135.1, 134.8, 130.3, 128.5, 127.6, 126.5, 126.3, 123.7, 121.7, 112.9, 48.9, 47.9, 44.0, 34.4, 30.0, 29.8, 26.9, 25.3.

HRMS (ESI) m/z calcd. for $C_{22}H_{23}O_3$ $[M+H]^+$: 335.1642, found: 335.1639.



***trans*-(1*R*,7a*R*)-3-(2-hydroxyphenyl)-1-(2-oxo-2-phenylethyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2j)**

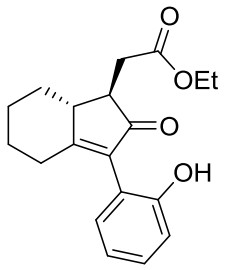
Yellow solid; 62.3 mg; 90% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.13 (petroleum ether/ethyl acetate = 2/1).

IR (KBr) $\tilde{\nu}$ 3357.6, 2932.5, 2856.1, 1683.0, 1645.5, 1598.1, 1447.6, 909.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.68 (br s, 1H), 7.61 – 7.52 (m, 1H), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.24 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.03 (ddd, *J* = 12.6, 7.9, 1.5 Hz, 2H), 6.93 (td, *J* = 7.4, 1.3 Hz, 1H), 3.65 (dd, *J* = 18.0, 3.3 Hz, 1H), 3.26 (dd, *J* = 18.0, 8.6 Hz, 1H), 3.05 (dp, *J* = 14.1, 2.0 Hz, 1H), 2.64 (dt, *J* = 9.3, 2.6 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.21 (td, *J* = 13.6, 5.6 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.95 – 1.84 (m, 1H), 1.61 – 1.39 (m, 2H), 1.37 – 1.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 198.1, 180.9, 155.0, 136.4, 135.4, 133.5, 130.7, 129.9, 128.7, 128.1, 120.3, 119.3, 118.6, 49.2, 48.0, 39.6, 34.6, 29.9, 27.0, 25.3.

HRMS (ESI) m/z calcd. for $C_{23}H_{23}O_3$ $[M+H]^+$: 347.1642, found: 347.1642.



Ethyl 2-(*trans*-3-(2-hydroxyphenyl)-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl)acetate (2k)

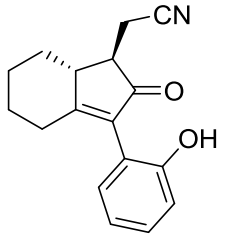
Yellow liquid; 59.1 mg; 94% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1)

IR (KBr) $\tilde{\nu}$ 3382.7, 2935.2, 2856.7, 1731.4, 1713.8, 1645.8, 1448.3, 1035.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.26 – 7.22 (m, 1H), 7.03 – 6.98 (m, 2H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.05 (ddt, *J* = 14.2, 4.1, 2.0 Hz, 1H), 2.86 (dd, *J* = 16.7, 4.2 Hz, 1H), 2.66 (dd, *J* = 16.7, 8.1 Hz, 1H), 2.56 (ddd, *J* = 12.3, 5.6, 2.6 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.41 – 2.34 (m, 1H), 2.21 (tdd, *J* = 13.0, 5.2, 1.4 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.95 – 1.87 (m, 1H), 1.57 (qt, *J* = 12.9, 3.2 Hz, 1H), 1.50 – 1.38 (m, 1H), 1.35 – 1.28 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 180.6, 171.9, 155.0, 135.5, 130.6, 129.9, 120.3, 119.1, 118.7, 60.9, 48.5, 48.3, 34.7, 34.3, 29.8, 26.8, 25.3, 14.2.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1591, found: 315.1588.



2-(*trans*-3-(2-Hydroxyphenyl)-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-inden-1-yl)acetonitrile (2l)

Yellow liquid; 28.3 mg; 53% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.10 (petroleum ether/ethyl acetate = 4/1)

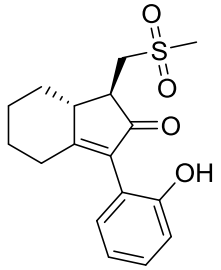
IR (KBr) $\tilde{\nu}$ 3384.7, 2936.3, 2857.9, 2249.6, 1695.3, 1638.9, 1601.9, 1449.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 2H), 7.01 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.00 – 6.89 (m, 2H), 3.02 (d, *J* = 14.3 Hz, 1H), 2.88 (ddt, *J* = 16.6, 3.5, 1.7 Hz, 1H),

2.72 – 2.63 (m, 1H), 2.47 (ddd, *J* = 26.0, 16.1, 8.1 Hz, 3H), 2.26 (td, *J* = 13.9, 5.6 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.94 (d, *J* = 13.5 Hz, 1H), 1.61 (q, *J* = 13.3 Hz, 1H), 1.51 – 1.23 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 180.5, 154.4, 134.9, 130.7, 130.1, 120.4, 118.4, 118.3, 117.9, 47.9, 47.5, 33.9, 29.8, 26.2, 24.9, 17.7.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1332.



***trans*-(1*R*,7a*R*)-3-(2-hydroxyphenyl)-1-((methylsulfonyl)methyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2m)**

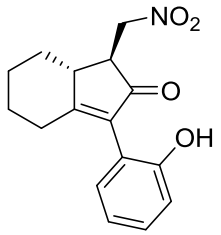
Yellow liquid; 47.4 mg; 74% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.13 (petroleum ether/ethyl acetate = 2/1).

IR (KBr) $\tilde{\nu}$ 3407.6, 2930.6, 2857.5, 1695.1, 1639.9, 1602.3, 1449.7, 1297.8, 1133.3 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.04 – 6.89 (m, 3H), 3.63 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.10 (dd, *J* = 14.0, 10.2 Hz, 1H), 3.02 (dd, *J* = 5.3, 2.9 Hz, 1H), 2.99 (s, 3H), 2.90 (ddd, *J* = 12.1, 5.6, 2.6 Hz, 1H), 2.71 (dt, *J* = 10.3, 3.1 Hz, 1H), 2.65 – 2.54 (m, 1H), 2.22 (td, *J* = 13.8, 5.8 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.94 – 1.86 (m, 1H), 1.60 (qt, *J* = 13.2, 3.4 Hz, 1H), 1.46 (tt, *J* = 13.1, 3.7 Hz, 1H), 1.30 (dd, *J* = 12.6, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 182.2, 154.5, 134.6, 130.7, 130.1, 120.5, 118.6, 118.3, 55.2, 48.0, 46.4, 42.1, 34.3, 30.0, 26.9, 25.1.

HRMS (ESI) m/z calcd. for $C_{17}H_{21}O_4S$ $[M+H]^+$: 321.1155, found:321.1157



***trans*-(1*S*,7a*R*)-3-(2-hydroxyphenyl)-1-(nitromethyl)-1,4,5,6,7,7a-hexahydro-2*H*-i**

nden-2-one (2n)

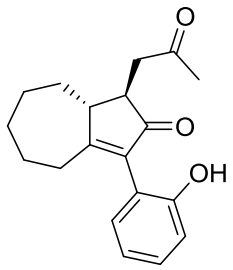
Yellow solid; 20.1 mg; 35% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1), R_f = 0.13 (petroleum ether/ethyl acetate = 2/1).

IR (KBr) $\tilde{\nu}$ 3337.6, 2931.9, 2855.2, 1681.1, 1638.6, 1600.4, 1574.6, 1367.4, 755.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 3.06 (dq, *J* = 13.8, 2.2 Hz, 1H), 2.87 – 2.72 (m, 2H), 2.28 (dd, *J* = 13.2, 5.3 Hz, 2H), 2.17 (d, *J* = 18.0 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.90 (dt, *J* = 14.5, 3.7 Hz, 1H), 1.64 – 1.51 (m, 1H), 1.41 (qt, *J* = 13.2, 3.8 Hz, 1H), 1.31 – 1.22 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 182.7, 155.1, 136.6, 130.7, 129.9, 120.3, 119.4, 119.1, 42.0(2C), 41.5, 35.2, 30.1, 27.0, 25.3.

HRMS (ESI) m/z calcd. for $C_{16}H_{18}NO_4$ $[M+H]^+$: 288.1230, found: 288.1234



***trans*-3-(2-Hydroxyphenyl)-1-(2-oxopropyl)-4,5,6,7,8,8a-hexahydroazulen-2(1*H*)-one (2q)**

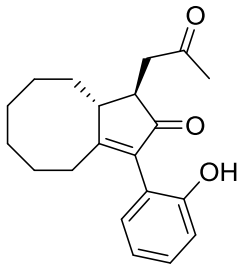
Yellow liquid; 46.5 mg; 78% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.13 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3399.2, 2927.4, 2855.9, 1717.6, 1703.8, 1598.7, 1450.7, 1242.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.04 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.1 Hz, 1H), 3.06 – 2.86 (m, 2H), 2.81 – 2.62 (m, 3H), 2.45 (dt, *J* = 7.7, 4.0 Hz, 1H), 2.21 (s, 3H), 2.12 – 2.03 (m, 1H), 1.88 (dt, *J* = 15.7, 8.1 Hz, 2H), 1.73 (ddd, *J* = 14.1, 7.1, 3.5 Hz, 1H), 1.65 – 1.42 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 207.2, 182.9, 154.6, 137.0, 130.3, 129.8, 120.1, 119.7, 118.1, 51.3, 49.2, 42.7, 32.7, 32.5, 30.9, 30.1, 29.0, 26.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1642, found: 299.1642.



***trans*-3-(2-Hydroxyphenyl)-1-(2-oxopropyl)-1,4,5,6,7,8,9,9a-octahydro-2*H*-cyclopenta[8]annulen-2-one (2r)**

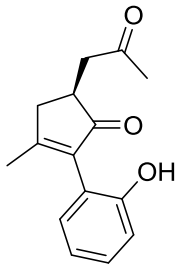
Yellow liquid; 47.4 mg; 76% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.14 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3367.3, 2927.8, 2857.0, 1695.6, 1598.4, 1450.3, 1364.3, 755.8 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (ddd, *J* = 9.6, 6.6, 1.9 Hz, 1H), 7.06 (dt, *J* = 7.5, 1.7 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.86 – 6.68 (m, 1H), 2.96 (dt, *J* = 5.7, 2.7 Hz, 2H), 2.76 (dt, *J* = 12.8, 4.7 Hz, 2H), 2.58 (q, *J* = 4.8 Hz, 1H), 2.38 – 2.30 (m, 1H), 2.28 – 2.20 (m, 1H), 2.16 (s, 3H), 1.84 – 1.65 (m, 4H), 1.63 – 1.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 207.9, 184.1, 154.2, 137.7, 130.2, 129.7, 120.1, 119.6, 117.2, 49.8, 45.4, 43.4, 30.0, 29.7, 29.4, 26.4, 26.0, 25.7, 24.4.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found: 313.1793.



2-(2-Hydroxyphenyl)-3-methyl-5-(2-oxopropyl)cyclopent-2-en-1-one (2s)

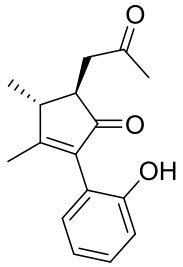
Yellow liquid; 34.2 mg; 70% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.23 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3374.7, 2911.9, 1704.4, 1682.5, 1602.5, 1451.8, 1289.1, 755.7 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.25 – 7.20 (m, 1H), 7.01 (ddd, *J* = 15.4, 7.9, 1.5 Hz, 2H), 6.92 (td, *J* = 7.5, 1.3 Hz, 1H), 3.07 (dt, *J* = 18.9, 5.4 Hz, 2H), 2.87 (ddt, *J* = 10.0, 6.5, 3.0 Hz, 1H), 2.75 (dd, *J* = 18.1, 8.3 Hz, 1H), 2.40 (ddd, *J* = 18.8, 2.8, 1.3 Hz, 1H), 2.18 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 207.0, 174.9, 154.8, 138.4, 130.6, 129.9, 120.3, 119.3, 118.3, 44.4, 40.8, 40.3, 29.9, 18.8.

HRMS (ESI) m/z calcd. for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1172, found: 245.1171.



***trans*-2-(2-Hydroxyphenyl)-3,4-dimethyl-5-(2-oxopropyl)cyclopent-2-en-1-one (2t)**

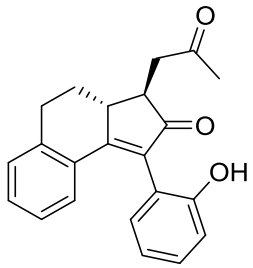
Yellow liquid; 34.1 mg; 66% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.21 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3383.3, 2969.4, 2930.2, 1712.7, 1703.7, 1602.8, 1453.4, 756.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.26 – 7.20 (m, 1H), 7.00 (ddd, *J* = 15.3, 7.9, 1.5 Hz, 2H), 6.92 (td, *J* = 7.4, 1.2 Hz, 1H), 3.03 (dd, *J* = 18.2, 3.9 Hz, 1H), 2.82 (dd, *J* = 18.3, 7.5 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.43 (dt, *J* = 7.0, 3.3 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 207.0, 178.4, 154.9, 138.0, 130.7, 129.9, 120.2, 119.4, 118.3, 49.1, 45.9, 43.8, 30.0, 18.0, 16.6.

HRMS (ESI) m/z calcd. for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found: 259.1325.



***trans*-1-(2-Hydroxyphenyl)-3-(2-oxopropyl)-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*] naphthalen-2-one (2u)**

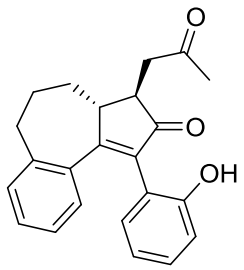
Yellow liquid; 59.8 mg; 90% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.16 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3388.4, 2924.2, 2854.6, 1692.3, 1678.5, 1591.5, 1449.8, 755.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.16 (m, 5H), 7.04 (dd, *J* = 7.8, 1.7 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 3.15 (dt, *J* = 18.6, 3.0 Hz, 1H), 3.10 – 3.03 (m, 2H), 2.97 (ddd, *J* = 18.5, 7.2, 2.1 Hz, 1H), 2.73 (dt, *J* = 13.6, 3.7 Hz, 1H), 2.55 (dt, *J* = 6.9, 3.5 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.20 (s, 3H), 1.89 – 1.76 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 206.4, 167.7, 153.5, 139.0, 131.8, 129.9, 129.3, 129.1, 129.1, 128.5, 128.0, 124.9, 119.7, 119.1, 116.9, 46.2, 45.4, 42.6, 29.0, 28.9, 28.6.

HRMS (ESI) m/z calcd. for $C_{22}H_{21}O_3$ $[M+H]^+$: 333.1485, found: 333.1479.



***trans*-1-(2-Hydroxyphenyl)-3-(2-oxopropyl)-3a,4,5,6-tetrahydrobenzo[e]azulen-2(3*H*)-one (2v)**

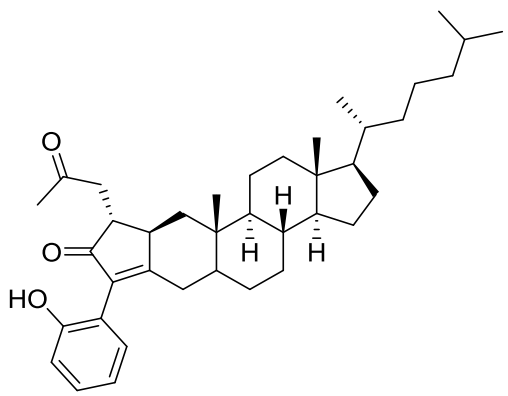
Yellow liquid; 63.7 mg; 92% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.13 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3373.7, 2925.8, 2852.7, 1698.1, 1600.2, 1450.6, 1360.8, 754.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.20 – 7.08 (m, 3H), 6.97 – 6.88 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.60 (t, *J* = 7.4 Hz, 1H), 3.10 (dd, *J* = 18.3, 3.3 Hz, 1H), 2.98 – 2.76 (m, 3H), 2.71 – 2.54 (m, 3H), 2.17 (s, 3H), 2.16 – 2.06 (m, 1H), 1.82 – 1.62 (m, 2H).

^{13}C NMR (100MHz, $CDCl_3$) δ 211.5, 206.6, 179.8, 155.3, 141.7, 138.4, 137.0, 132.0, 129.9, 129.7, 129.7, 129.2, 126.1, 120.1, 119.3, 118.4, 50.8, 49.2, 45.6, 39.5, 37.3, 29.9, 27.7.

HRMS (ESI) m/z calcd. for $C_{23}H_{22}NaO_3$ $[M+Na]^+$: 369.1461, found: 369.1456.



***trans*-(1*R*,3a*S*,3b*R*,10a*S*,10b*S*,12a*R*)-7-(2-Hydroxyphenyl)-10a,12a-dimethyl-1-((*R*)-6-methylheptan-2-yl)-9-(2-oxopropyl)-2,3,3a,3b,4,5,5a,6,9,9a,10,10a,10b,11,12,12a-hexadecahydrodicyclopenta[*a*,*h*]phenanthren-8(1*H*)-one (2w)**

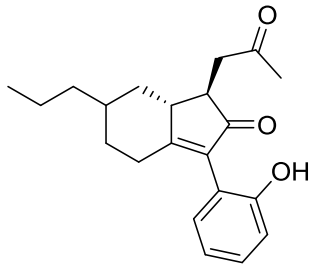
Brown solid; 91.6 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.15 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3365.6, 2932.2, 2867.6, 1714.8, 1696.5, 1600.4, 1452.2, 1364.9, 1264.2, 739.4 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 9.1 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 3.00 (dd, *J* = 18.2, 3.7 Hz, 1H), 2.74 (dd, *J* = 18.2, 7.9 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.43 – 2.34 (m, 2H), 2.29 – 2.21 (m, 1H), 2.17 (s, 3H), 1.99 (d, *J* = 12.8 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.70 – 1.64 (m, 1H), 1.60 – 1.47 (m, 4H), 1.41 – 1.21 (m, 12H), 1.16 – 1.07 (m, 6H), 0.97 (s, 3H), 0.91 (d, *J* = 6.2 Hz, 4H), 0.87 (s, 3H), 0.85 (s, 3H), 0.67 (s, 3H).

^{13}C NMR (100MHz, $CDCl_3$) δ 210.9, 206.7, 180.8, 154.9, 134.8, 130.7, 129.8, 120.1, 119.1, 118.5, 56.2, 56.2, 53.9, 48.0, 47.2, 46.1, 45.1, 43.7, 42.5, 39.8, 39.4, 36.7, 36.1, 35.7, 35.2, 32.9, 31.7, 29.9, 28.9, 28.1, 27.9, 24.1, 23.7, 22.7, 22.5, 21.2, 18.6, 12.3, 12.0.

HRMS (ESI) m/z calcd. for $C_{39}H_{57}O_3$ $[M+H]^+$: 573.4302, found: 573.4305.



***trans*-3-(2-Hydroxyphenyl)-1-(2-oxopropyl)-6-propyl-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2x)**

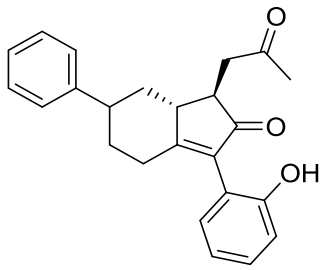
Yellow liquid; 51.5 mg; 79% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.13 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3363.4, 2927.8, 2859.8, 1713.8, 1696.7, 1547.4, 1264.1, 731.0 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 3.09 – 2.95 (m, 2H), 2.74 (dd, *J* = 18.1, 8.1 Hz, 1H), 2.51 – 2.35 (m, 3H), 2.30 – 2.20 (m, 1H), 2.18 (s, 3H), 2.00 (ddd, *J* = 13.4, 6.0, 3.0 Hz, 1H), 1.45 – 1.28 (m, 3H), 1.26 (dd, *J* = 9.0, 6.3 Hz, 2H), 1.11 (tt, *J* = 12.9, 6.5 Hz, 1H), 1.04 – 0.93 (m, 1H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 206.9, 180.9, 155.0, 135.2, 130.7, 129.9, 120.2, 119.3, 118.6, 48.7, 47.8, 44.0, 40.7, 38.5, 36.5, 33.1, 30.0, 29.4, 20.1, 14.3.

HRMS (ESI) m/z calcd for $C_{21}H_{27}O_3$ $[M+H]^+$: 327.1955,found: 327.1949.



***trans*-3-(2-Hydroxyphenyl)-1-(2-oxopropyl)-6-phenyl-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2y)**

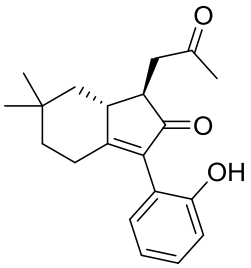
Yellow liquid; 57.6 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.15(petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3365.5, 2926.0, 2859.4, 1713.6, 1697.7, 1601.7, 1452.2, 756.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.04 (dd, *J* = 20.7, 8.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 3.18 – 3.10 (m, 1H), 3.05 (dd, *J* = 18.3, 3.6 Hz, 1H), 2.89 (tt, *J* = 12.6, 3.4 Hz, 1H), 2.78 (dd, *J* = 18.3, 8.2 Hz, 1H), 2.69 – 2.54 (m, 2H), 2.50 (dt, *J* = 7.4, 3.0 Hz, 1H), 2.42 (td, *J* = 13.8, 5.4 Hz, 1H), 2.22 – 2.10 (m, 4H), 1.68 (qd, *J* = 13.0, 3.9 Hz, 1H), 1.54 (q, *J* = 12.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 206.7, 179.0, 154.9, 144.8, 135.7, 130.6, 130.0, 128.5, 126.7, 126.5, 120.3, 119.0, 118.5, 48.7, 47.6, 43.8, 43.1, 41.2, 34.0, 29.9, 29.5.

HRMS (ESI) m/z calcd. for $C_{24}H_{25}O_3$ $[M+H]^+$: 361.1798, found: 361.1793.



***trans*-3-(2-Hydroxyphenyl)-6,6-dimethyl-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2aa)**

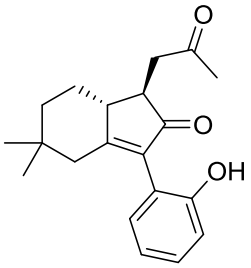
Yellow liquid; 48.1 mg; 77% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.18 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3381.4, 2958.4, 2925.1, 1703.1, 1602.1, 1450.2, 1261.9, 754. 1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.27 – 7.22 (m, 1H), 7.02 (ddd, *J* = 8.2, 4.1, 1.5 Hz, 2H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 3.04 (dd, *J* = 18.2, 3.6 Hz, 1H), 2.91 (ddd, *J* = 14.7, 4.5, 2.3 Hz, 1H), 2.75 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.47 – 2.37 (m, 2H), 2.19 (s, 3H), 2.10 (ddd, *J* = 13.0, 5.6, 2.7 Hz, 1H), 1.66 (ddt, *J* = 13.3, 5.5, 2.5 Hz, 1H), 1.39 (td, *J* = 13.4, 4.4 Hz, 2H), 1.10 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 206.7, 180.8, 155.0, 135.6, 130.6, 130.0, 120.3, 119.3, 118.8, 47.9, 46.9, 45.4, 43.9, 39.3, 31.9, 31.1, 30.0, 26.2, 23.9.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found: 313.1792.



***trans*-3-(2-Hydroxyphenyl)-5,5-dimethyl-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2ab)**

Yellow liquid; 46.8 mg; 75% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.17(petroleum ether/ethyl acetate = 4/1).

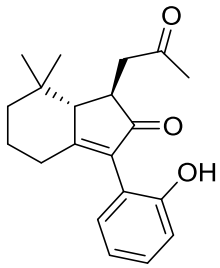
IR (KBr) $\tilde{\nu}$ 3387.2, 2955.1, 2926.7, 1704.0, 1602.1, 1452.7, 1264.0, 754.9 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.26 – 7.21 (m, 1H), 7.00 (ddd, *J* = 12.3, 7.9, 1.5 Hz, 2H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 3.04 (dd, *J* = 18.2, 3.7 Hz, 1H), 2.81

(dd, J = 18.3, 7.8 Hz, 1H), 2.69 (dd, J = 13.9, 2.0 Hz, 1H), 2.45 (dt, J = 7.6, 3.5 Hz, 1H), 2.25 – 2.21 (m, 1H), 2.25 – 2.21 (m, 1H), 2.18 (s, 3H), 2.06 (d, J = 13.9 Hz, 1H), 1.58 – 1.41 (m, 3H), 1.05 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 207.1, 179.5, 154.9, 136.9, 130.4, 129.8, 120.2, 119.1, 118.3, 48.4, 47.7, 44.0, 42.4, 38.4, 34.4, 32.3, 30.0, 29.8, 25.2.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found: 313.1792.



***trans*-3-(2-Hydroxyphenyl)-7,7-dimethyl-1-(2-oxopropyl)-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (2ac)**

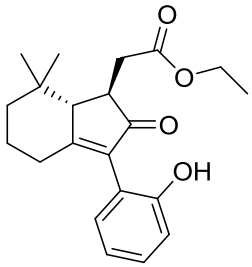
Yellow liquid; 45.0 mg; 72% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1), R_f = 0.19 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3437.9, 2960.2, 2927.6, 1714.4, 1672.9, 1615.2, 1461.8, 1260.5, 753.2 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.26 – 7.21 (m, 1H), 7.00 (ddd, J = 8.3, 4.9, 1.5 Hz, 2H), 6.91 (td, J = 7.4, 1.2 Hz, 1H), 3.02 (dd, J = 17.8, 5.5 Hz, 1H), 2.97 – 2.91 (m, 1H), 2.88 (dd, J = 17.9, 4.7 Hz, 1H), 2.56 (dt, J = 7.3, 3.3 Hz, 1H), 2.39 – 2.36 (m, 1H), 2.22 – 2.10 (m, 4H), 1.89 – 1.79 (m, 1H), 1.72 – 1.61 (m, 2H), 1.58 – 1.52 (m, 1H), 1.08 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 207.0, 179.0, 155.0, 136.3, 130.4, 129.9, 120.2, 119.2, 118.1, 57.7, 45.3, 42.3, 40.3, 36.7, 30.4, 30.2, 29.0, 22.2, 19.5.

HRMS (ESI) m/z calcd. for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found: 313.1792.



Ethyl

2-(*trans*-3-(2-hydroxyphenyl)-7,7-dimethyl-2-oxo-2,4,5,6,7,7a-hexahydro-1*H*-indeen-1-yl)acetate (2ad)

Yellow liquid; 37.7 mg; 60% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 8/1), R_f = 0.20 (petroleum ether/ethyl acetate = 4/1).

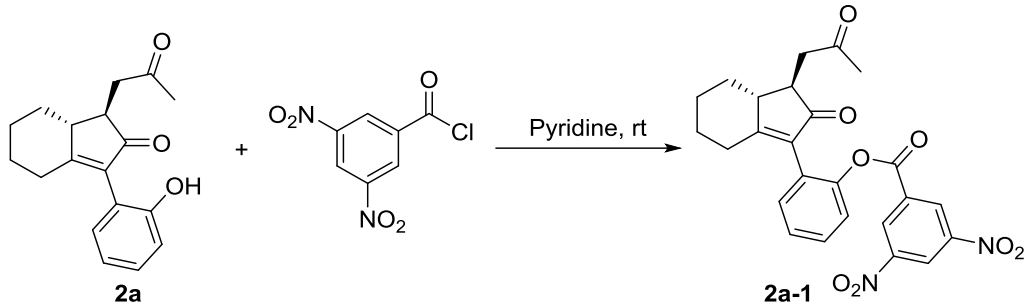
IR (KBr) $\tilde{\nu}$ 3420.1, 2959.2, 2926.3, 1730.2, 1715.1, 1645.9, 1450.2, 752.1 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H), 7.00 (td, *J* = 5.4, 2.8 Hz, 2H), 6.91 (td, *J* = 7.4, 1.2 Hz, 1H), 4.17 – 4.06 (m, 2H), 2.98 – 2.92 (m, 1H), 2.91 – 2.85 (m, 1H), 2.70 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.57 (dq, *J* = 6.8, 2.3 Hz, 1H), 2.43 (d, *J* = 2.3 Hz, 1H), 2.21 – 2.10 (m, 1H), 1.90 – 1.82 (m, 1H), 1.75 – 1.62 (m, 1H), 1.60 – 1.55 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 179.6, 171.8, 154.9, 136.3, 130.4, 129.9, 120.2, 119.1, 118.1, 61.0, 57.5, 42.6, 40.2, 36.9, 36.6, 30.3, 29.1, 22.4, 19.4, 14.1.

HRMS (ESI) m/z calcd. for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1904, found: 343.1904.

7. Procedure for the synthesis of product 2a-1 and X-ray of 2a-1



To a solution of **2a** (568 mg, 0.2 mmol) in dichloromethane (1 mL) was added 3,5-dimitrobenzoyl chloride (69.1 mg, 0.3 mmol) and pyridine (36.4 mg, 0.4 mmol). The solution was stirred at room temperature for overnight. Saturated NH_4Cl-solution (10 mL) was added and the aqueous layer was extracted with DCM (3*5 mL). The combined layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography to afford the product **2a-1**. Yellow solid; 76.5 mg; 80% yield; purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1), R_f = 0.23 (petroleum ether/ethyl acetate = 4/1).

IR (KBr) $\tilde{\nu}$ 3443.8, 2933.6, 2860.0, 1754.7, 1715.3, 1694.5, 1629.9, 1548.5, 1346.2, 762.6 cm^{-1}

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 – 9.27 (m, 1H), 9.15 – 9.09 (m, 2H), 7.74 – 7.64 (m, 2H), 7.60 (td, J = 7.3, 1.8 Hz, 1H), 7.44 (dd, J = 7.6, 1.7 Hz, 1H), 2.94 (dd, J = 17.8, 4.2 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.77 – 2.69 (m, 1H), 2.58 (dd, J = 12.0, 5.3 Hz, 1H), 2.48 – 2.30 (m, 3H), 2.23 – 2.04 (m, 4H), 1.93 (d, J = 13.7 Hz, 1H), 1.70 – 1.57 (m, 1H), 1.55 – 1.38 (m, 2H).

^{13}C NMR (100MHz, DMSO-d_6) δ 206.8, 205.9, 178.7, 161.2, 149.0, 148.6, 133.1, 132.7, 131.7, 129.6, 129.5, 126.9, 125.6, 123.4, 123.0, 48.5, 47.4, 43.4, 34.5, 29.9, 29.1, 26.8, 25.1.

HRMS (ESI) m/z calcd. for $C_{25}H_{23}N_2O_8$ $[M+H]^+$: 479.1449, found: 479.1450

X-ray Structure for compound 2a-1

The CCDC no. of compound **2a-1** is 1990467.

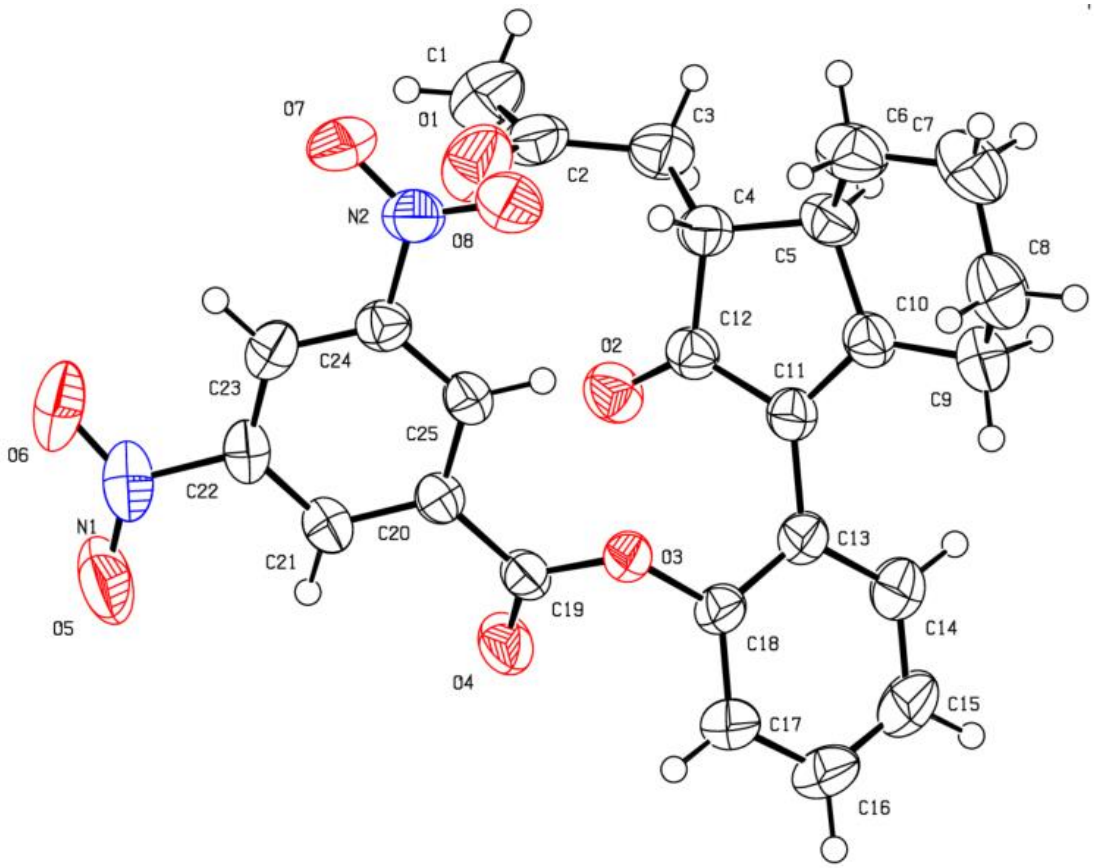


Figure 1 ORTEP representation of compound 2a-1. Thermal ellipsoids are drawn at the 50% probability level.

Bond precision:	C-C = 0.0034 A	Wavelength=0.71073	
Cell:	a=8.1947(4)	b=22.1997(8)	c=12.9203(5)
	alpha=90	beta=102.070(4)	gamma=90
Temperature:	293 K		

Calculated	Reported
Volume	2298.50(17)	2298.50(17)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn

Moiety formula	C25 H22 N2 O8	?
Sum formula	C25 H22 N2 O8	C25 H22 N2 O8
Mr	478.45	478.44
Dx,g cm-3	1.383	1.383
Z	4	4
Mu (mm-1)	0.104	0.104
F000	1000.0	1000.0
F000’	1000.57	
h,k,lmax	10,27,16	10,27,16
Nref	4702	4693
Tmin,Tmax	0.995,0.997	0.774,1.000
Tmin’	0.994	

Correction method= # Reported T Limits: Tmin=0.774 Tmax=1.000

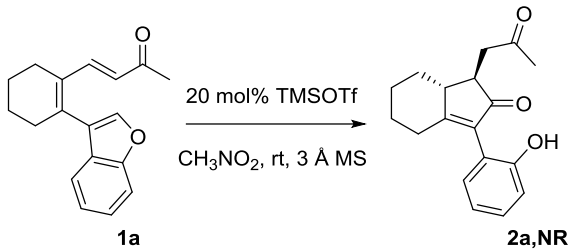
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.372

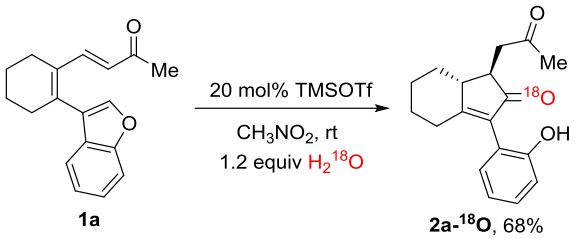
R(reflections)= 0.0531(3726) wR2(reflections)= 0.1608(4693)

S = 1.019 Npar= 317

8. Control experiment

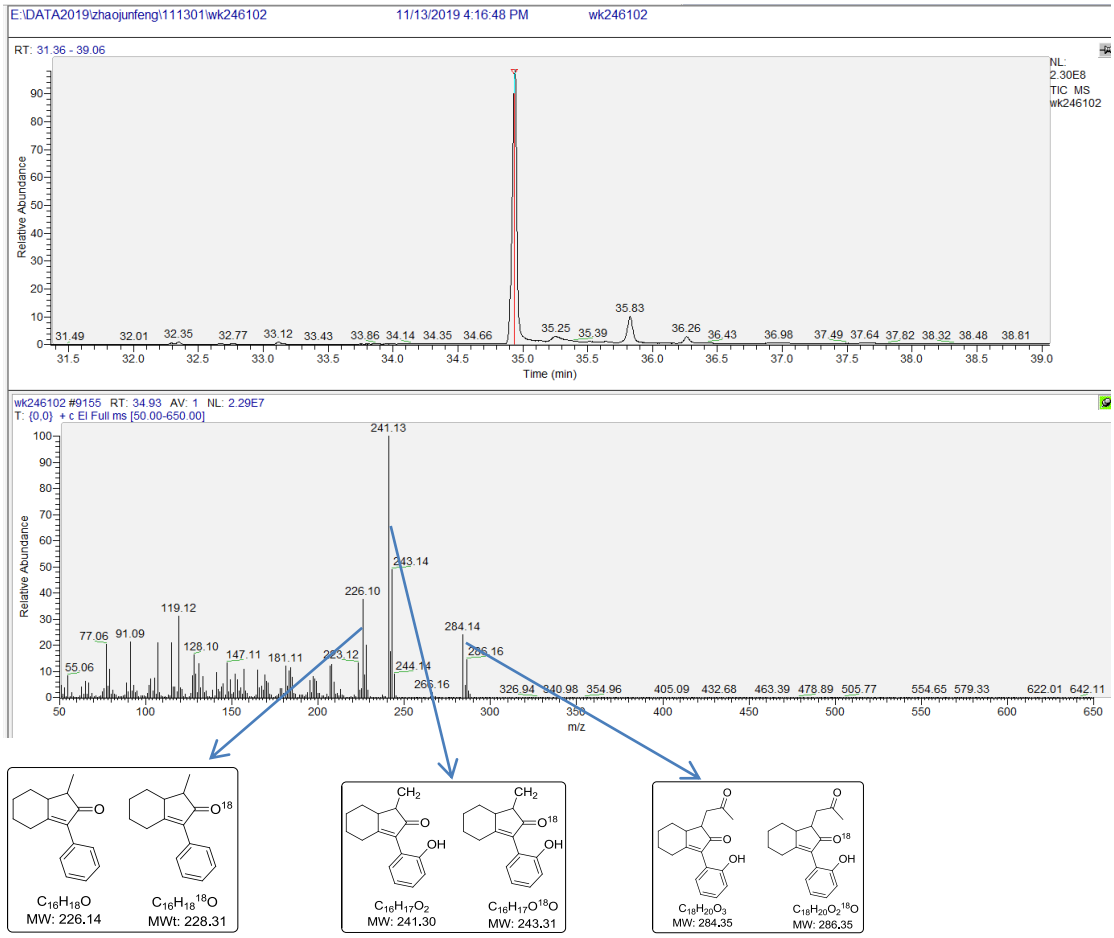


To a solution of **1a** (0.2 mmol) in $MeNO_2$ (1.0 mL) was added 3 Å MS (50 mg). The reaction was stirred for 10 min at room temperature, then TMSOTf (7.2 μL, 0.04 mmol) was added.The reaction was monitored by TLC.



To a solution of **1a** (0.2 mmol) in anhydrous $MeNO_2$ (1.0 mL) was added $H_2{}^{18}O$ (4.8 μL, 0.24 mmol).The mixture was stirred for 10 min at room temperature, and then TMSOTf (7.2 μL, 0.04 mmol) was added. The reaction was monitored by TLC. After the reaction was complete, the mixture was purified by silica gel column chromatography to afford product **2a-^{18}O** in 68% yield.

GCMS for 2a-^{18}O

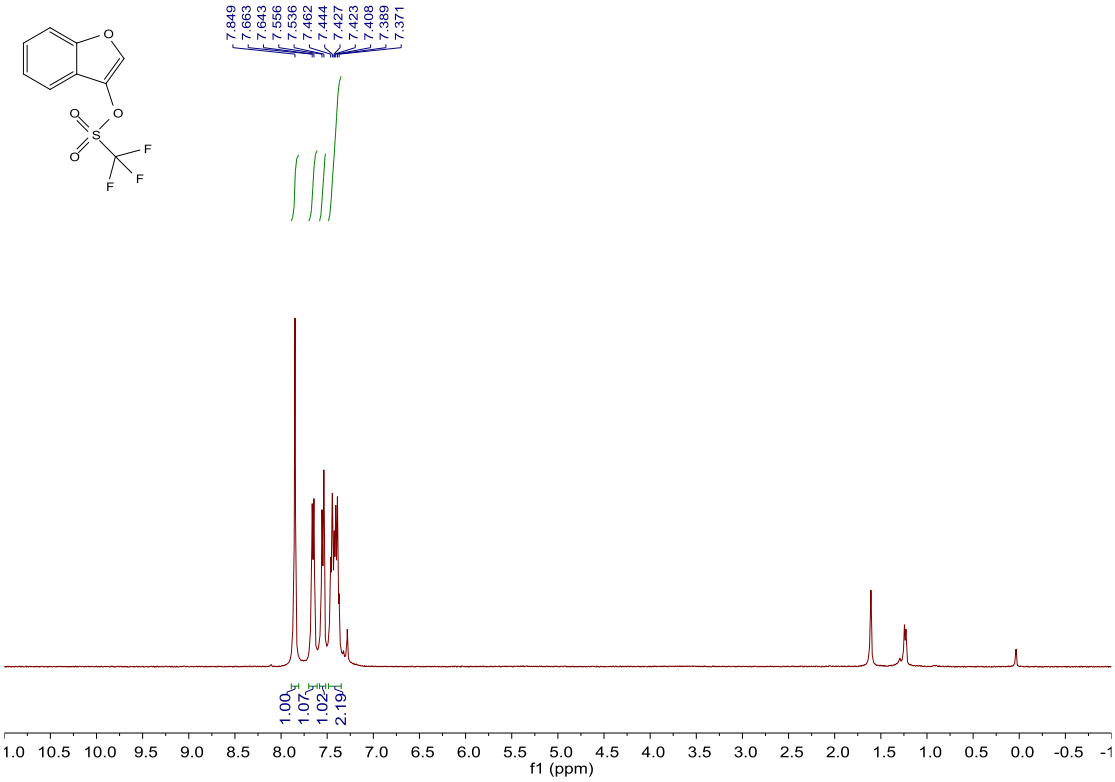


9. Reference

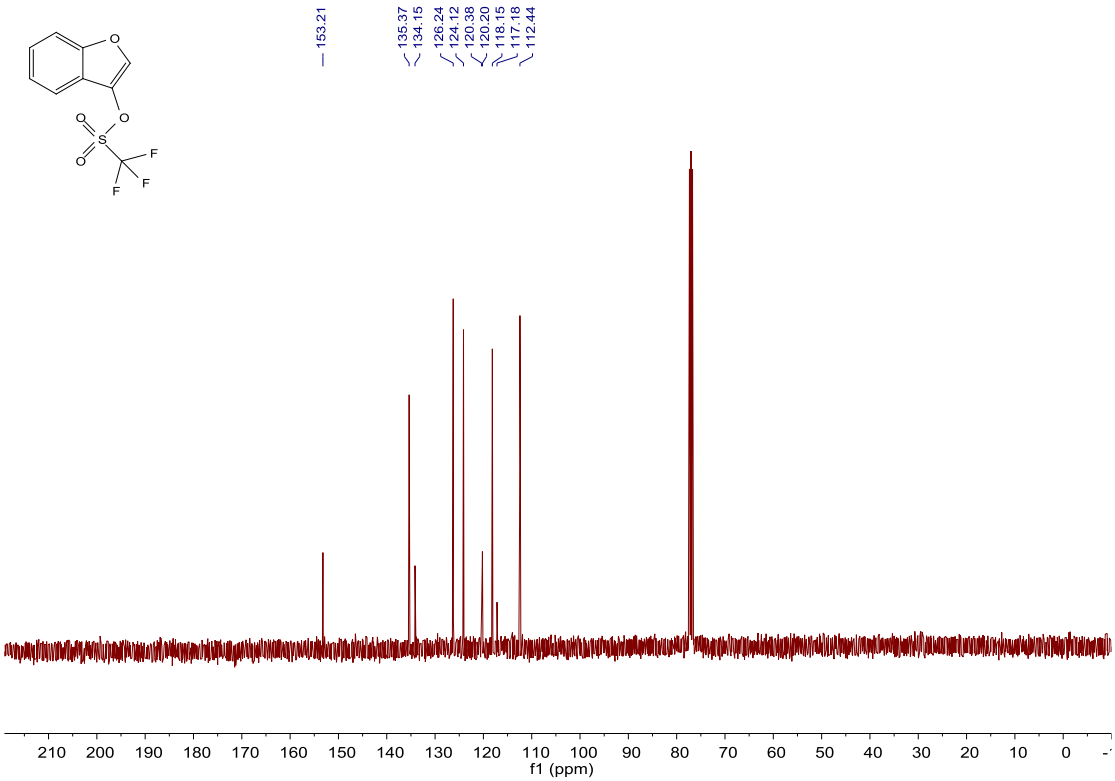
(1) N. Hadj-esfandiari, L. Navidpour, H. Shadnia, M. Amini, N. Samadi, M. A. Faramarzi and A. Shafiee, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6354-6363.
(2) A. E. Gormemis, T. S. Ha, I. Im, K. Y. Jung, J. Y. Lee, C. S. Park and Y. C. Kim, *Chembiochem*, 2005, **6**, 1745-1748.
(3) C. Shu, R. Liu, S. Liu, J. Q. Li, Y. F. Yu, Q. He, X. Lu and L. W. Ye, *Chem. Asian J.*, 2014, **9**, 1-6.

10. Copies of ^{1}H-NMR & ^{13}C-NMR spectrum

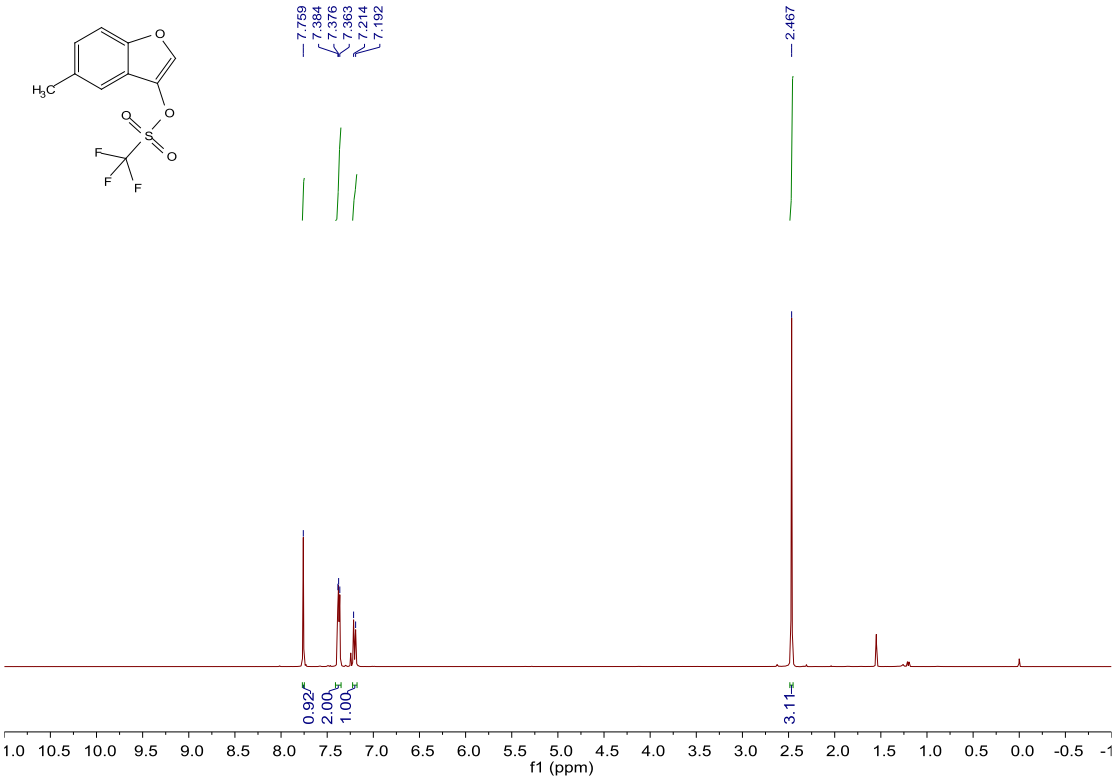
^{1}H NMR of In1-1a



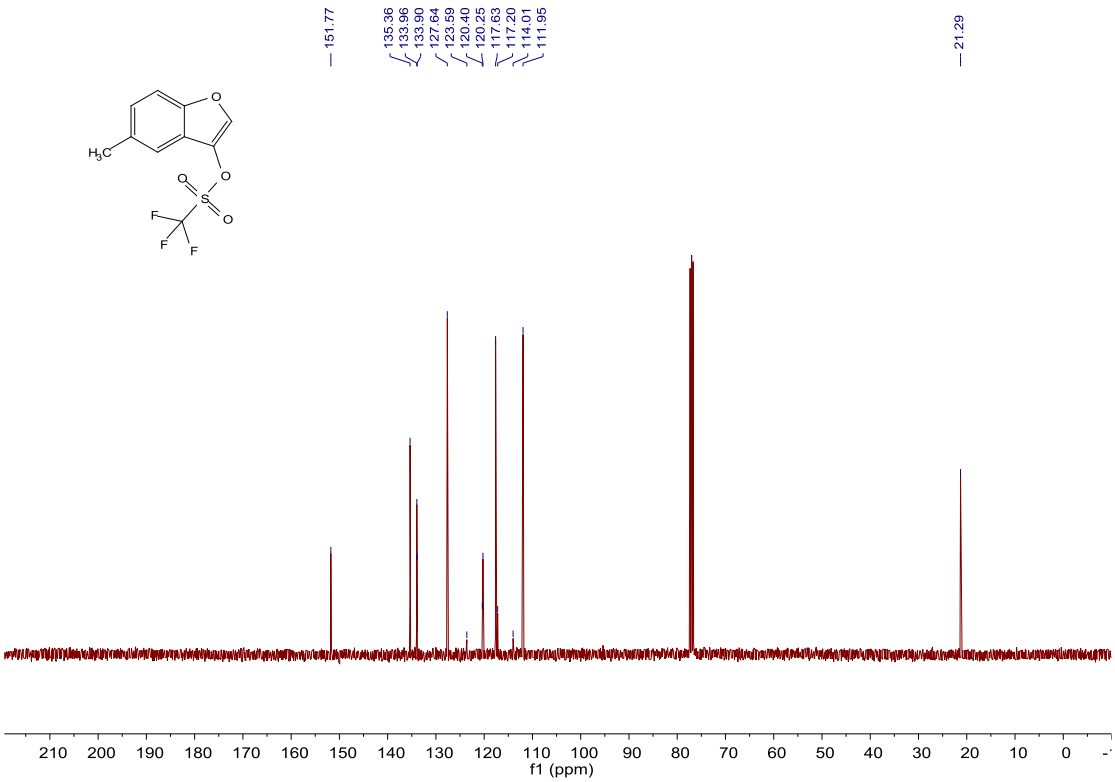
^{13}C NMR of In1-1a



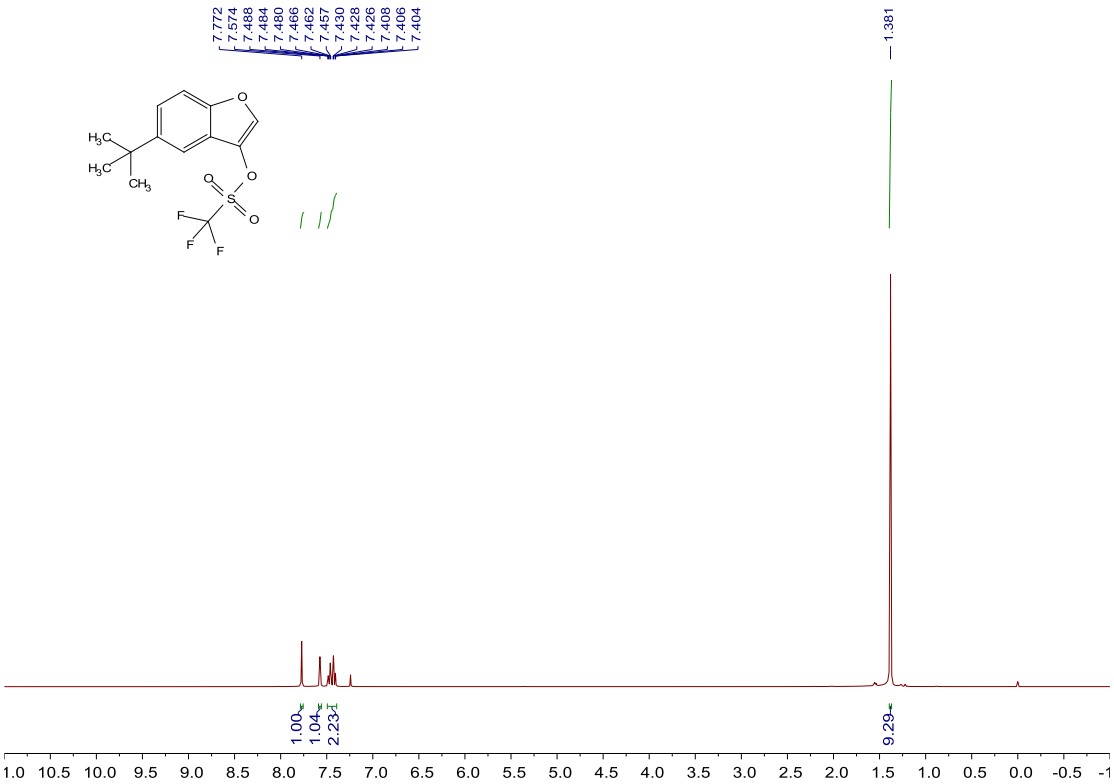
^{1}H NMR of In1-1b



^{13}C NMR of In1-1b



^{1}H NMR of In1-1c



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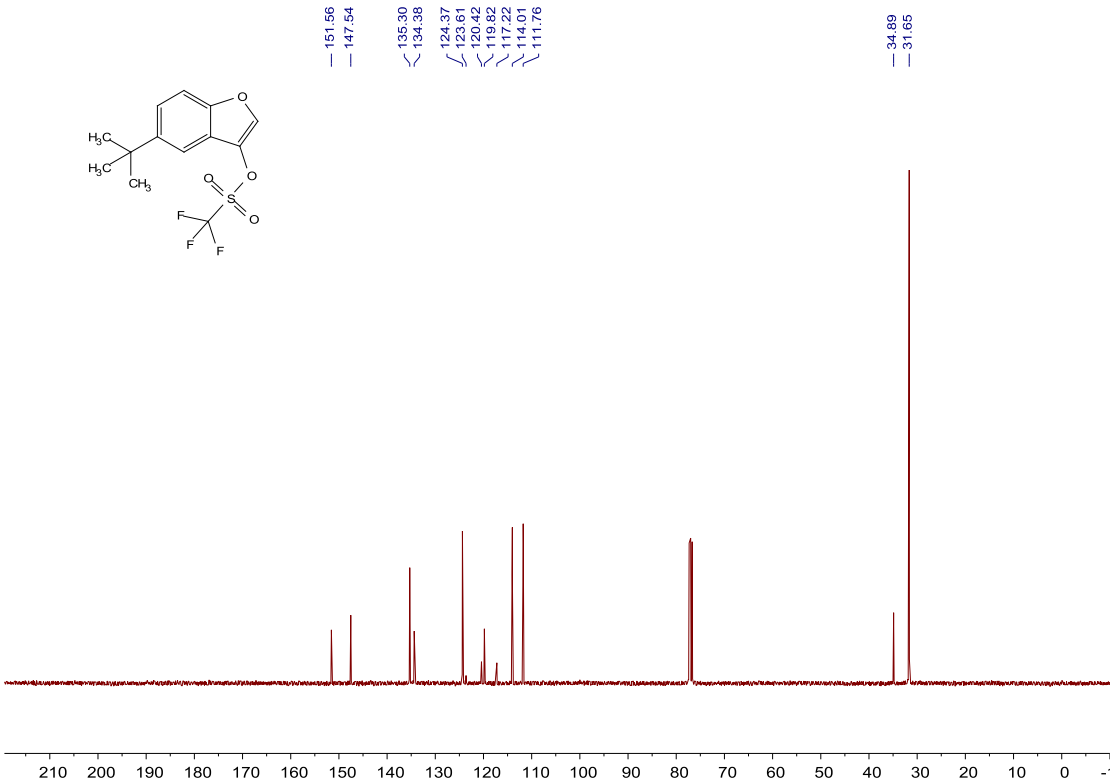
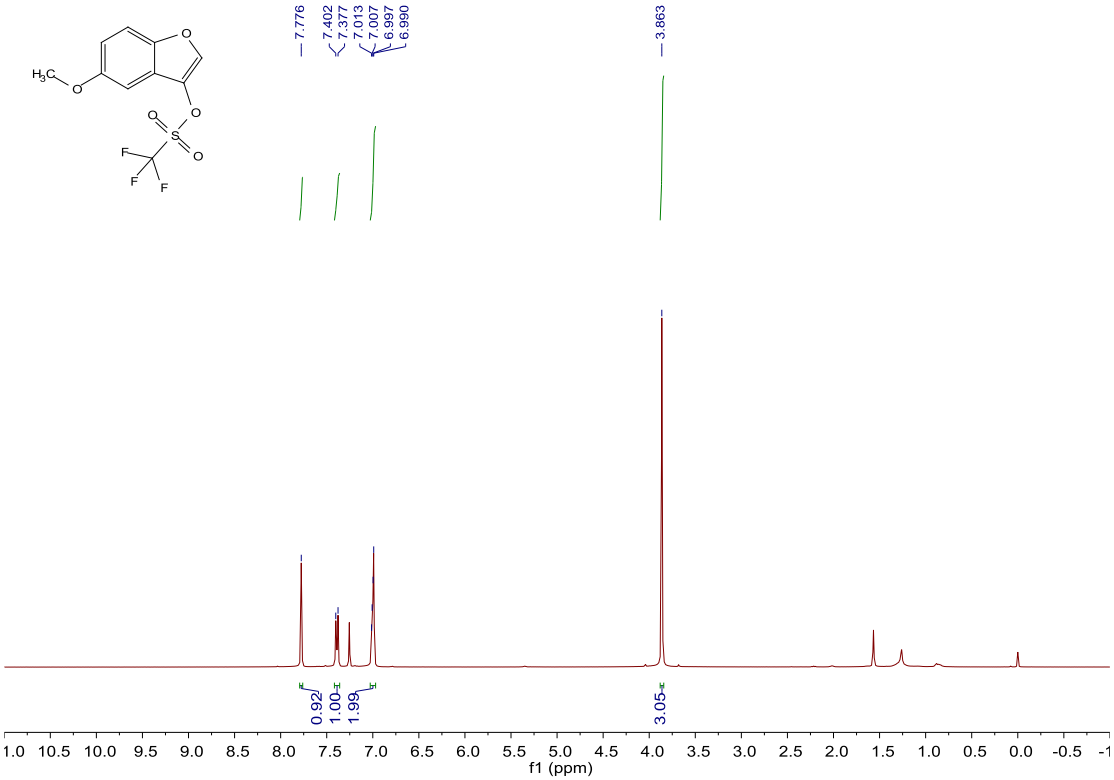
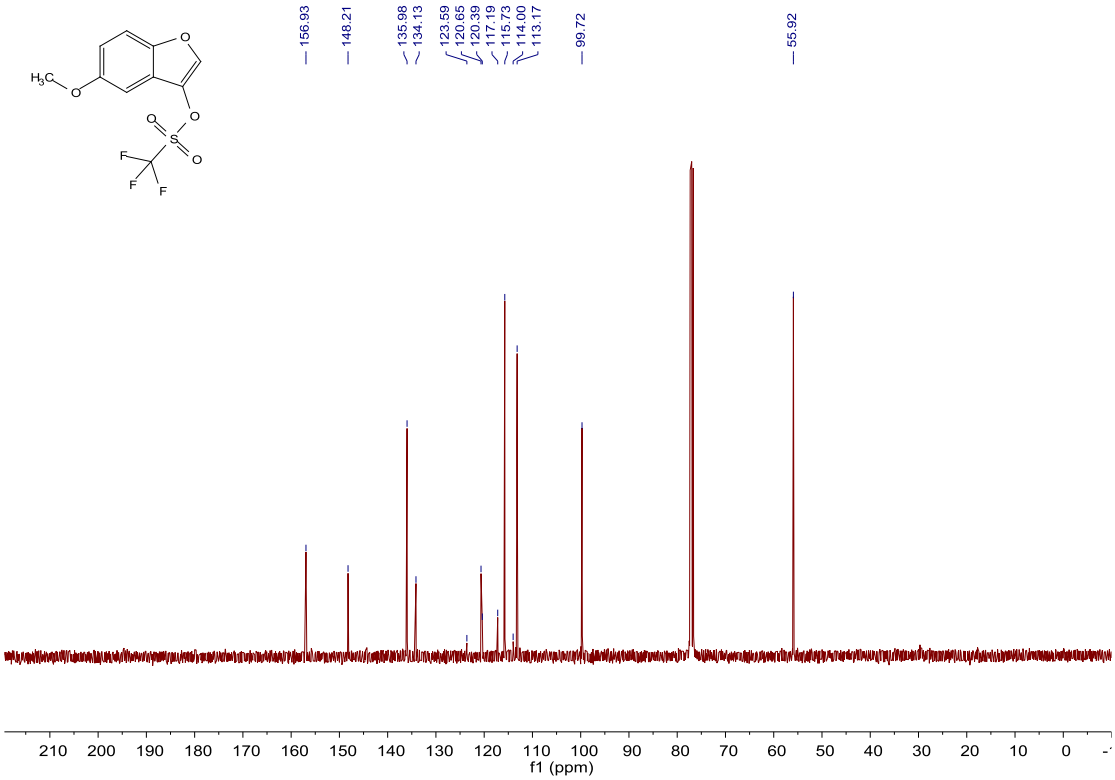


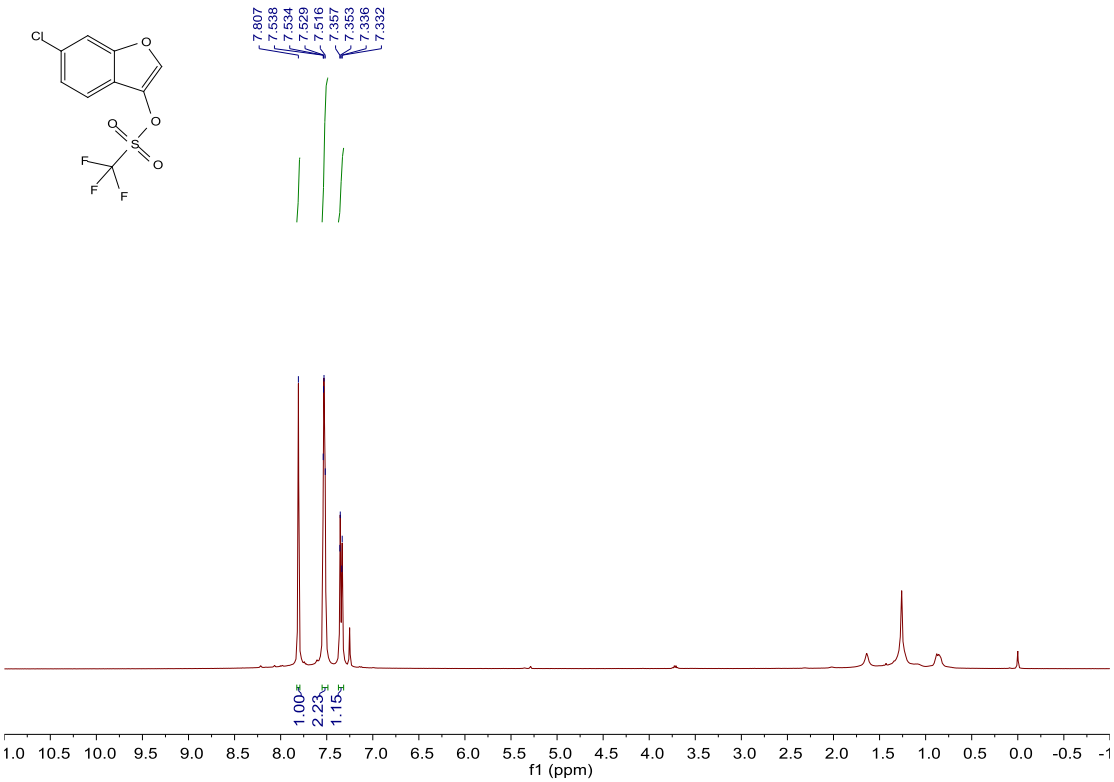
^{1}H NMR of In1-1d



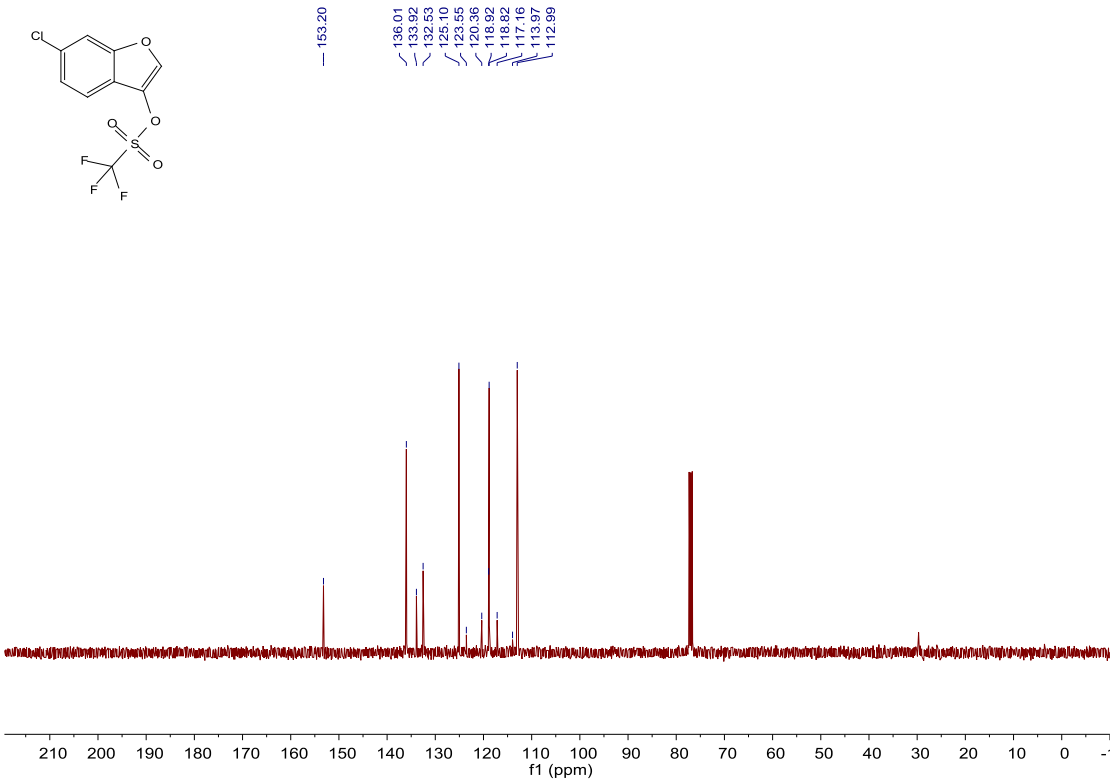
^{13}C NMR of In1-1d



^{1}H NMR of In1-1e



^{13}C NMR of In1-1e



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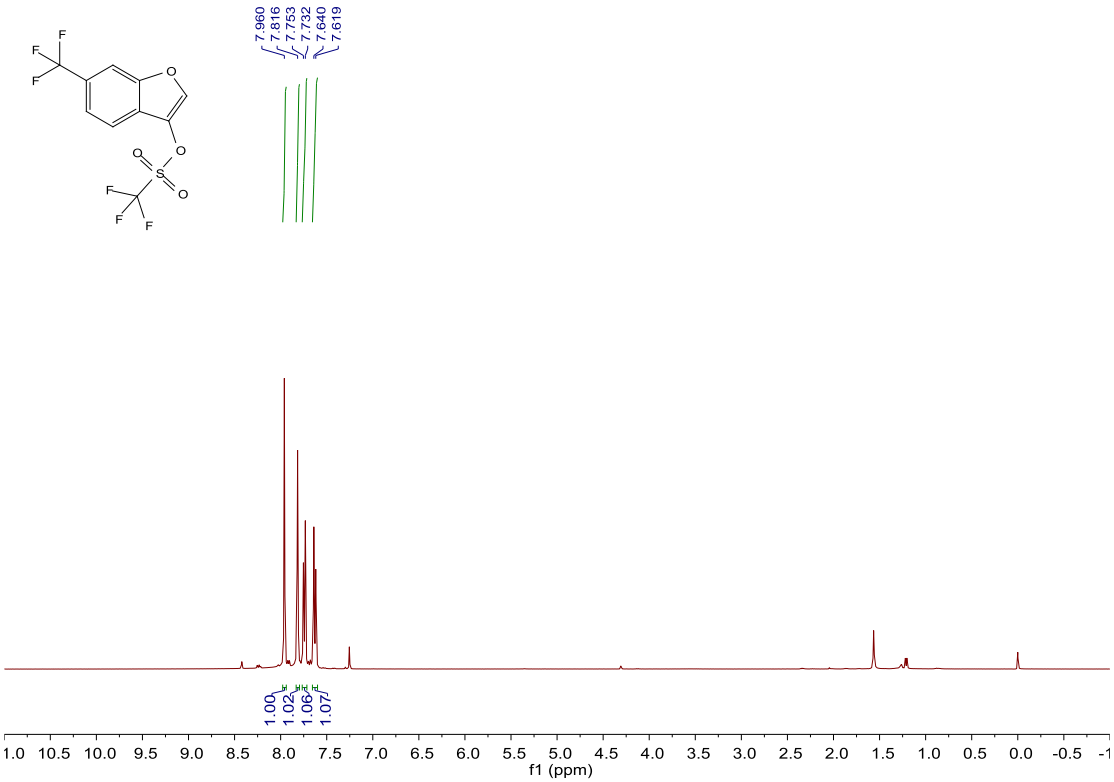

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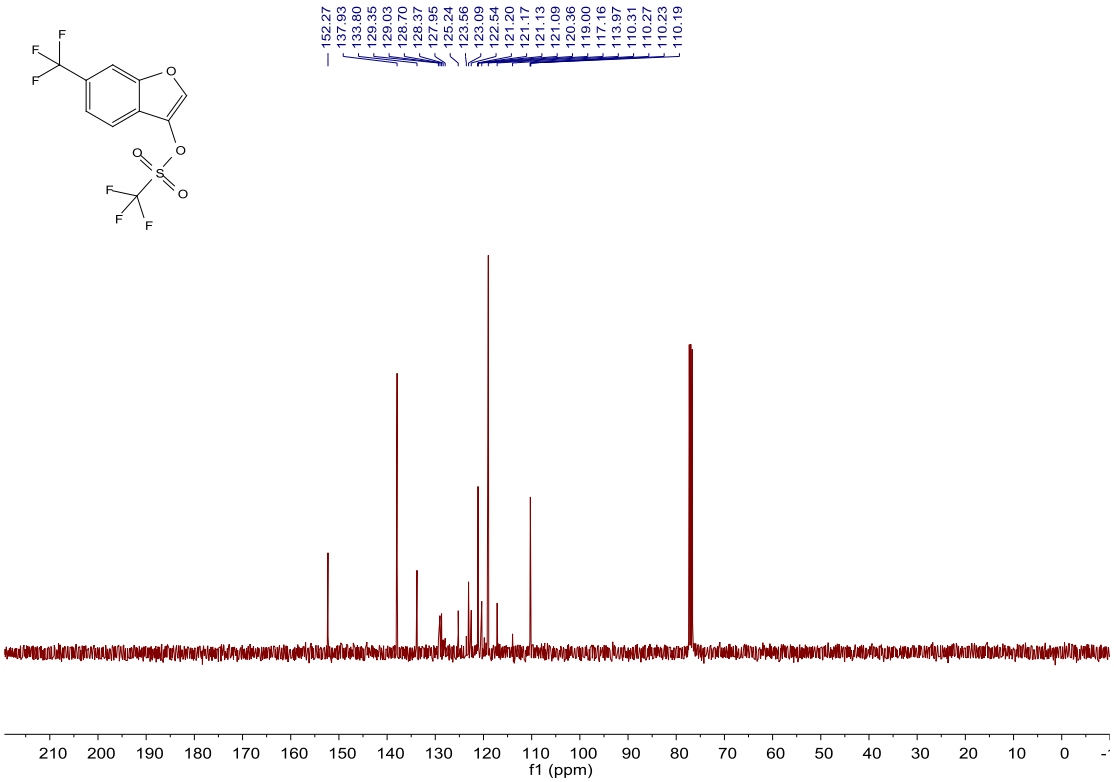

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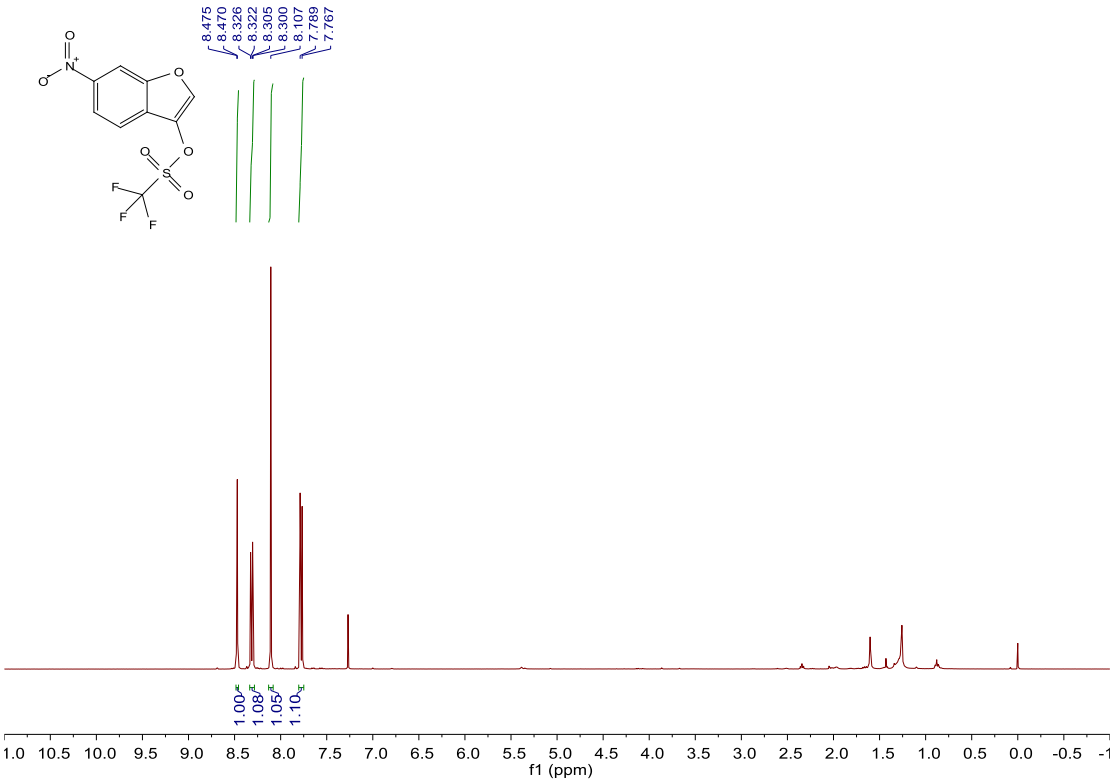

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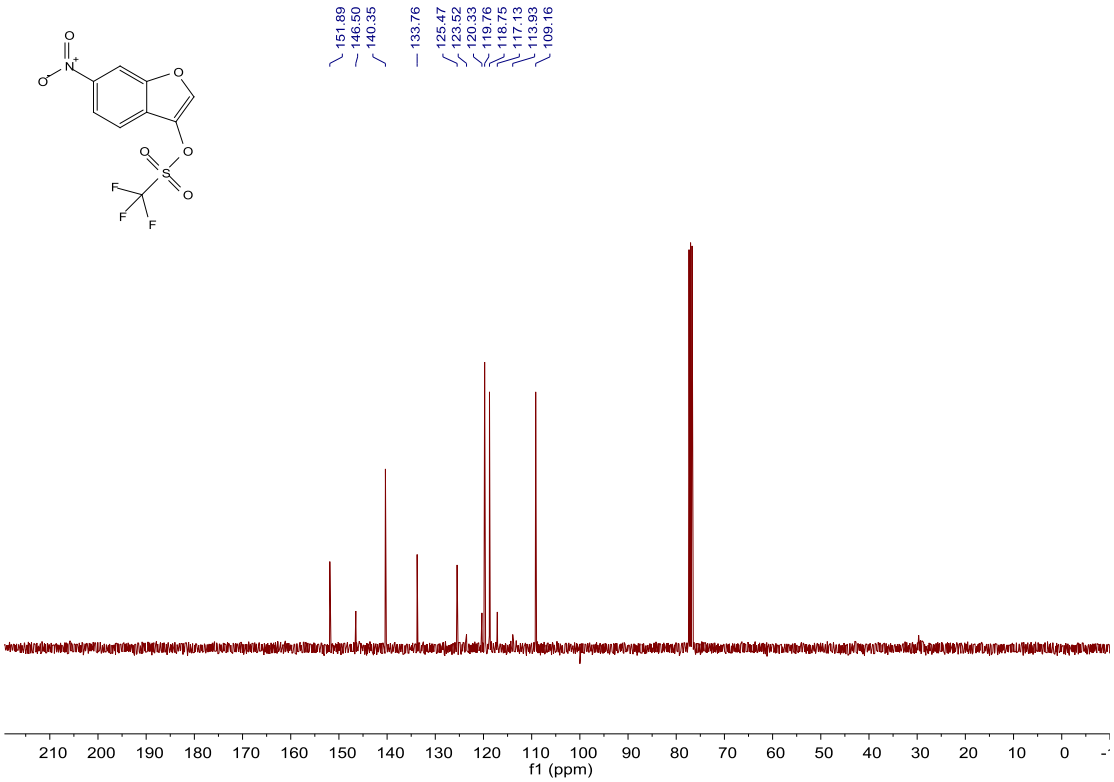
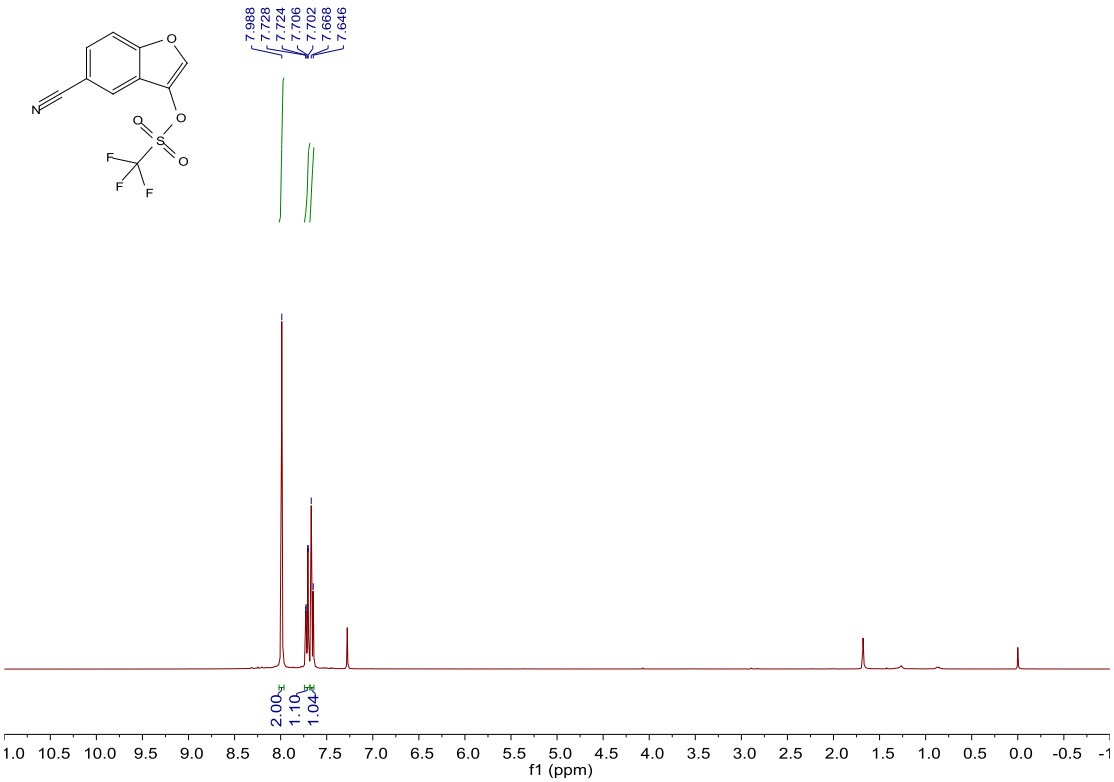


^{1}H NMR of In1-1h



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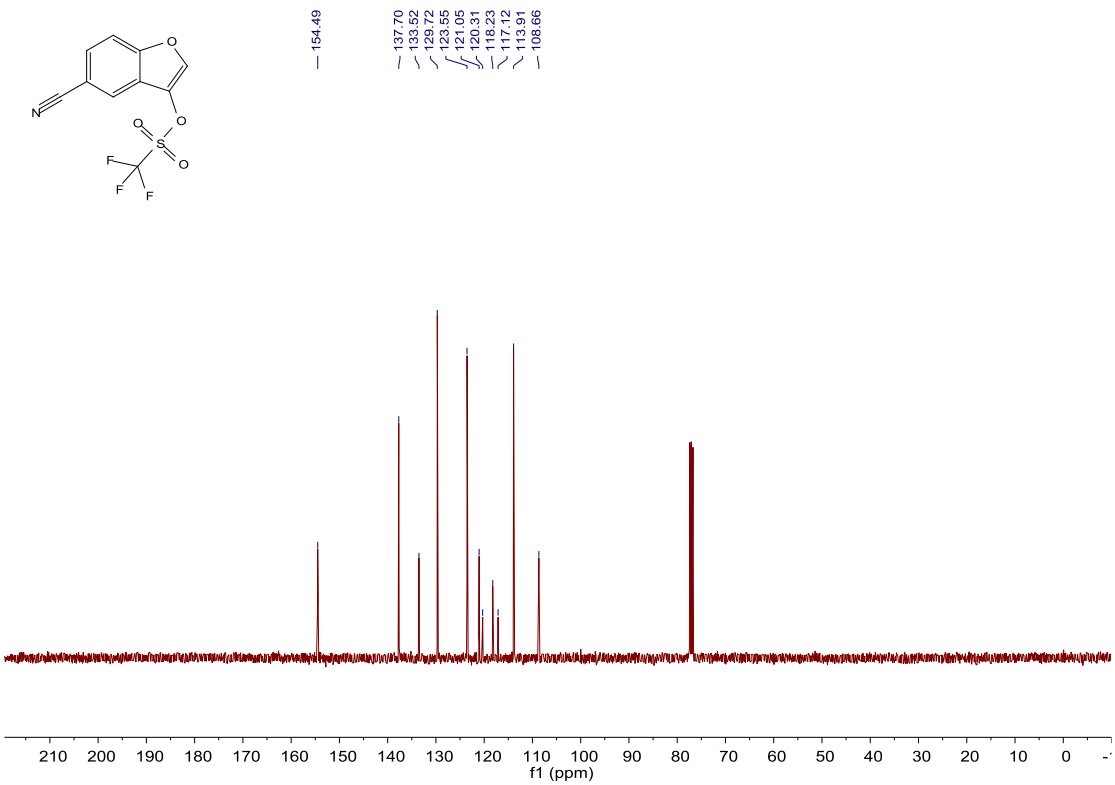
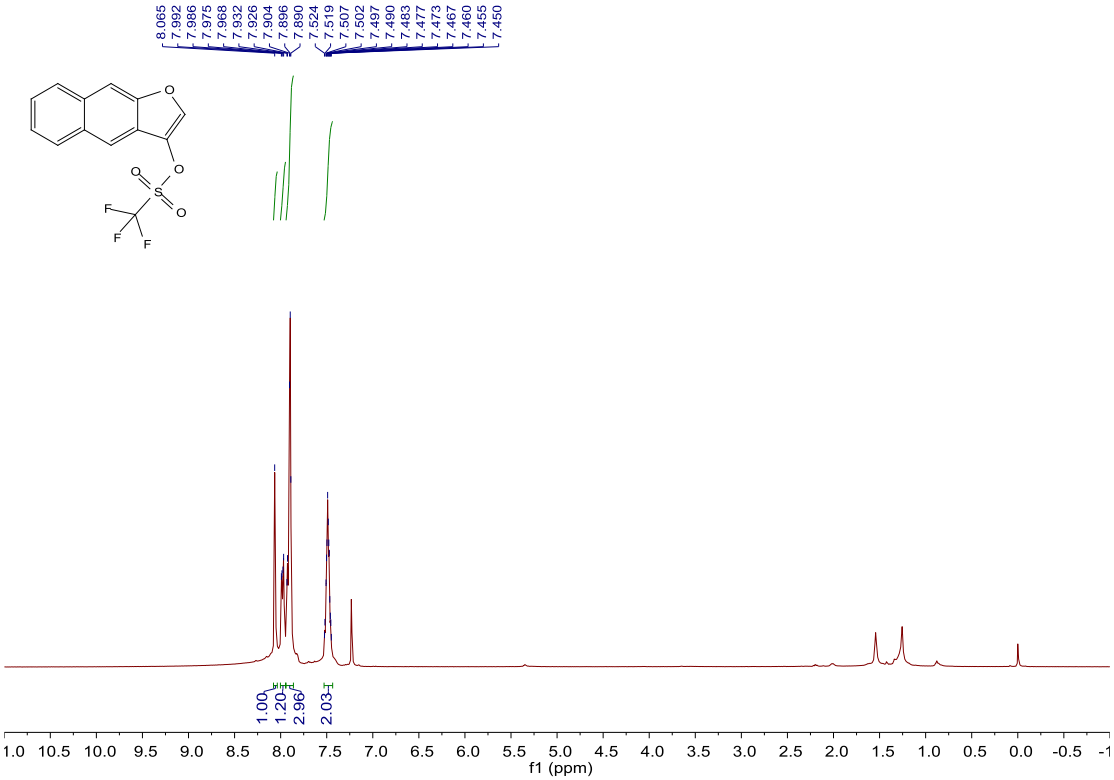


^{1}H NMR of In1-1i



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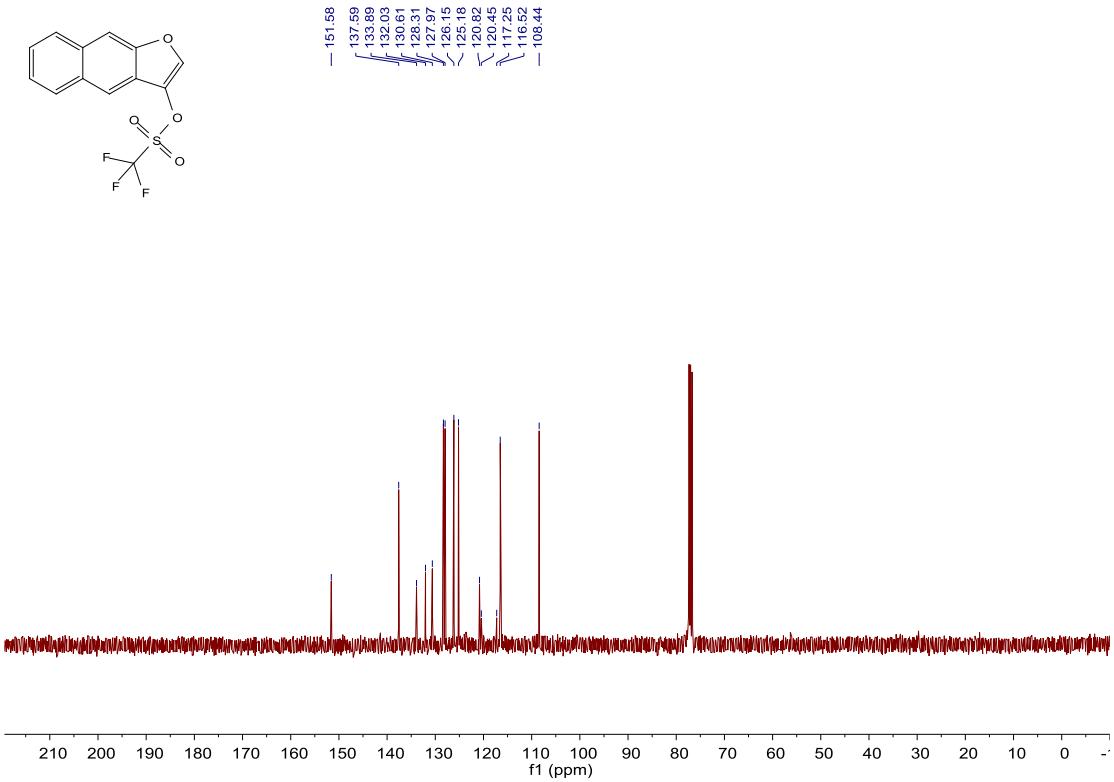
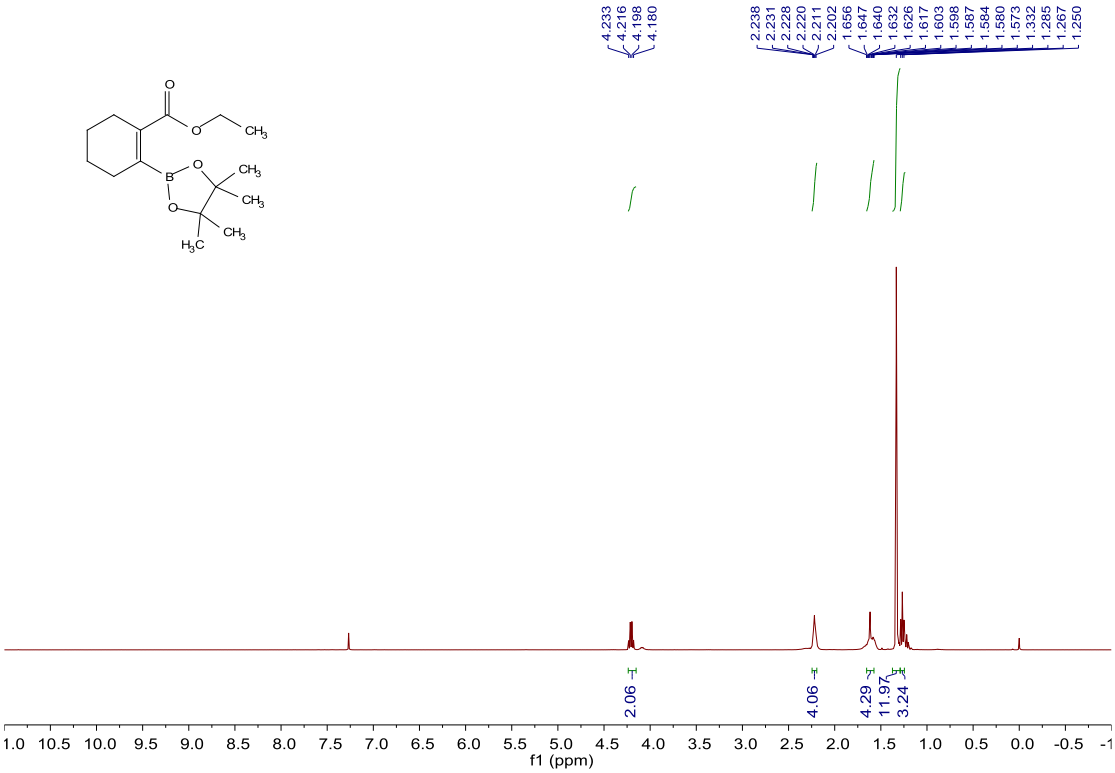


^{1}H NMR of In2



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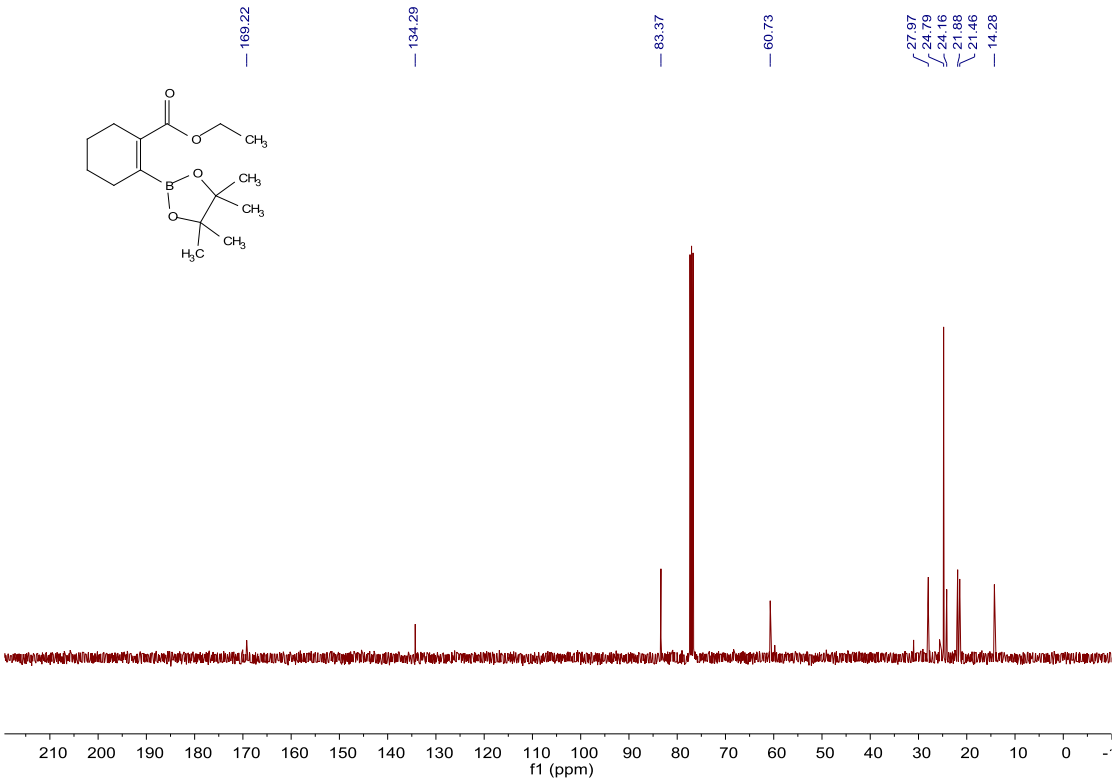
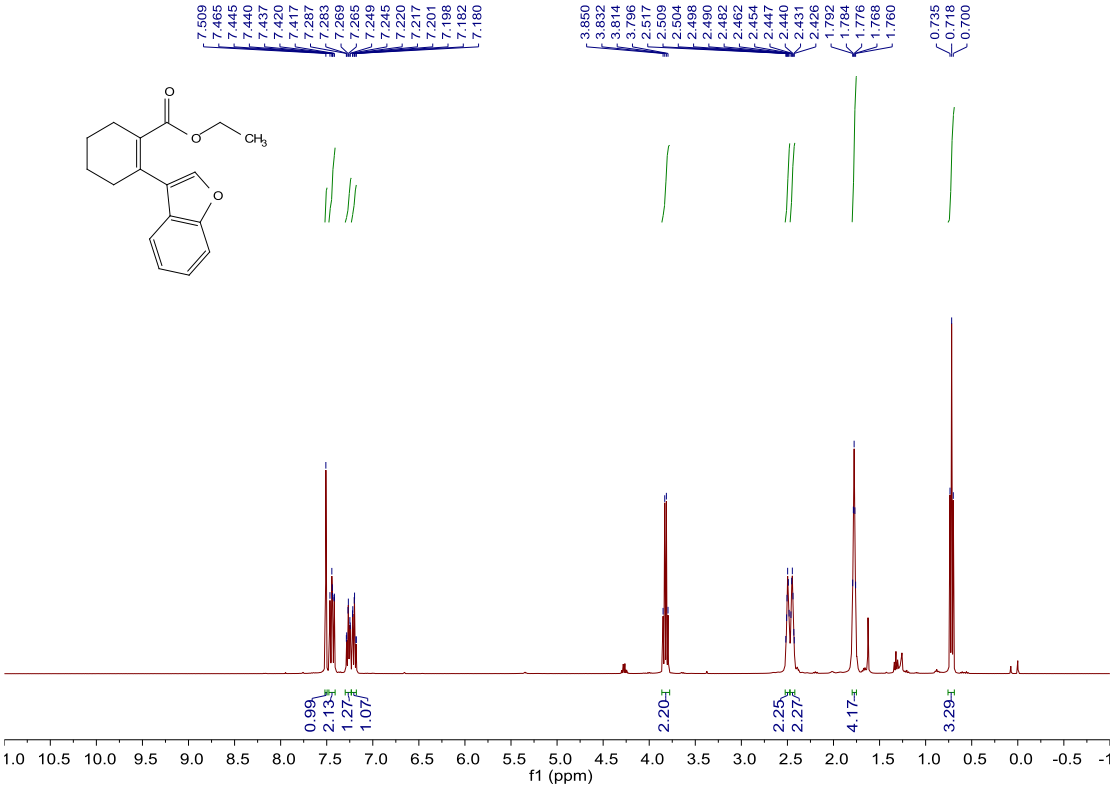


1H NMR of In3-1a



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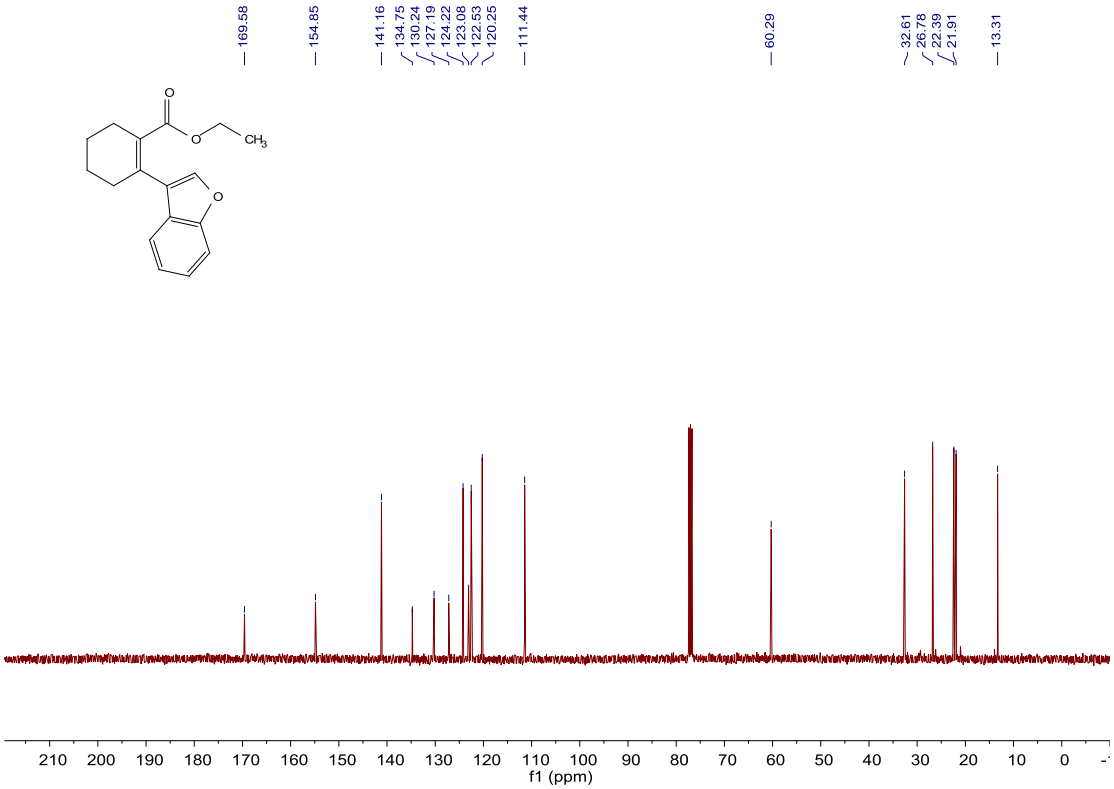

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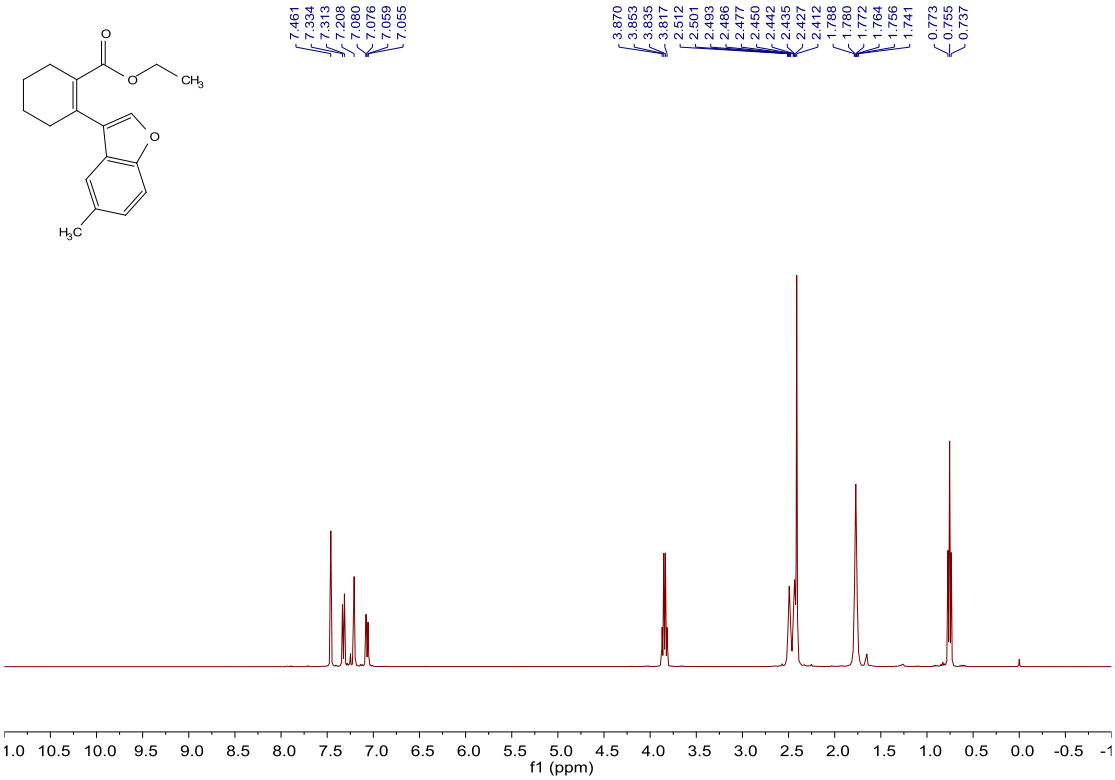

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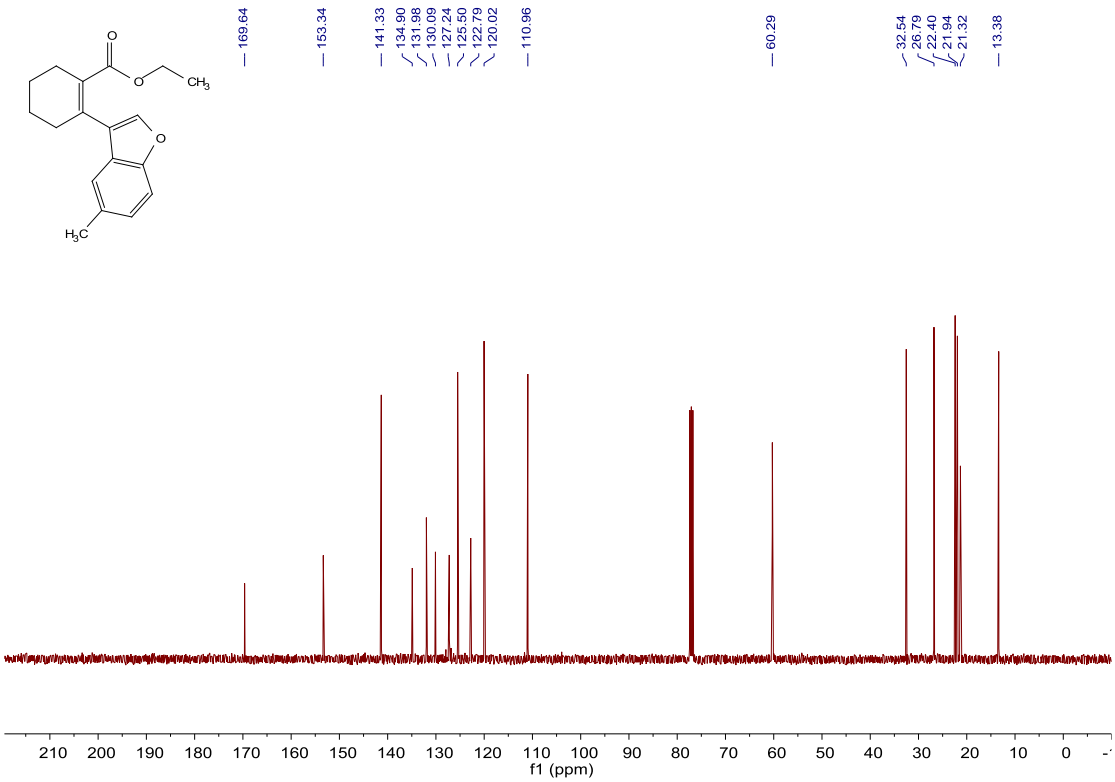

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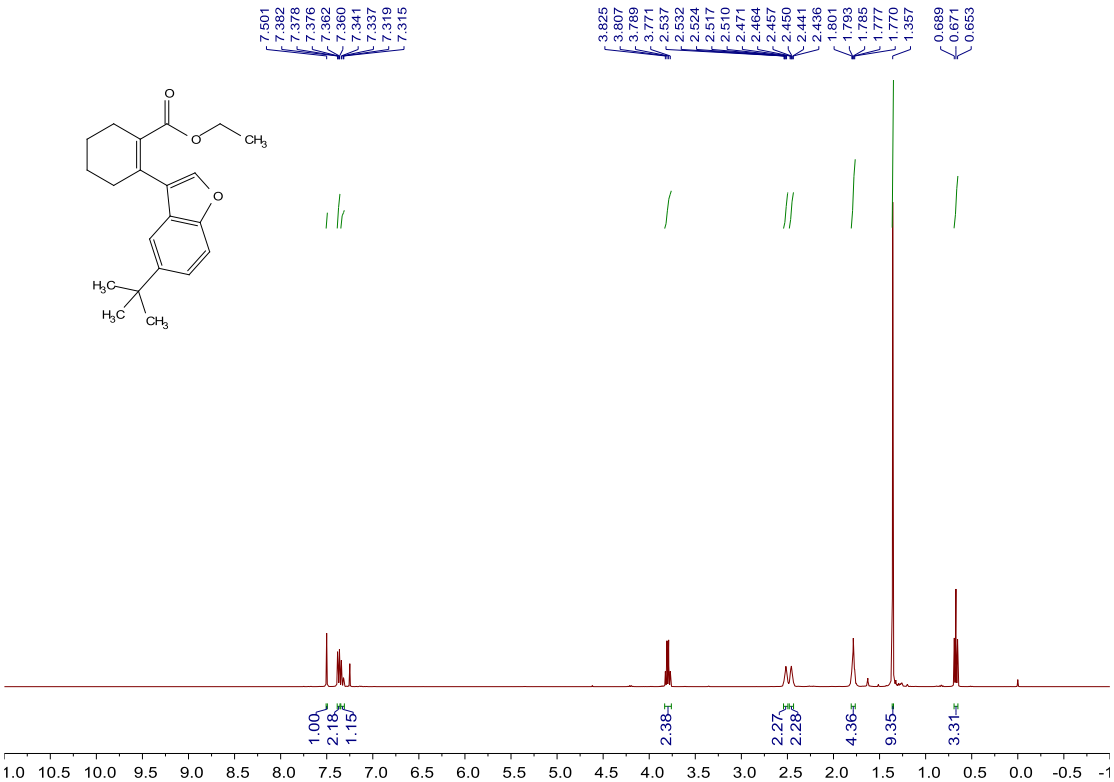

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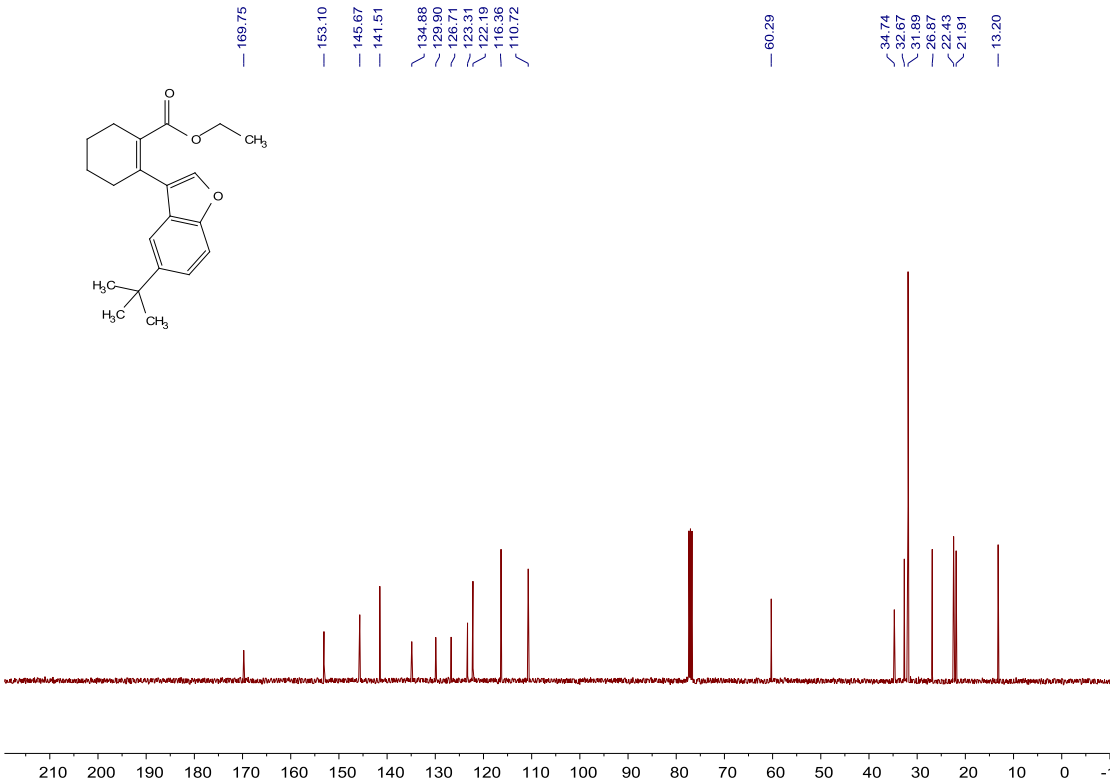

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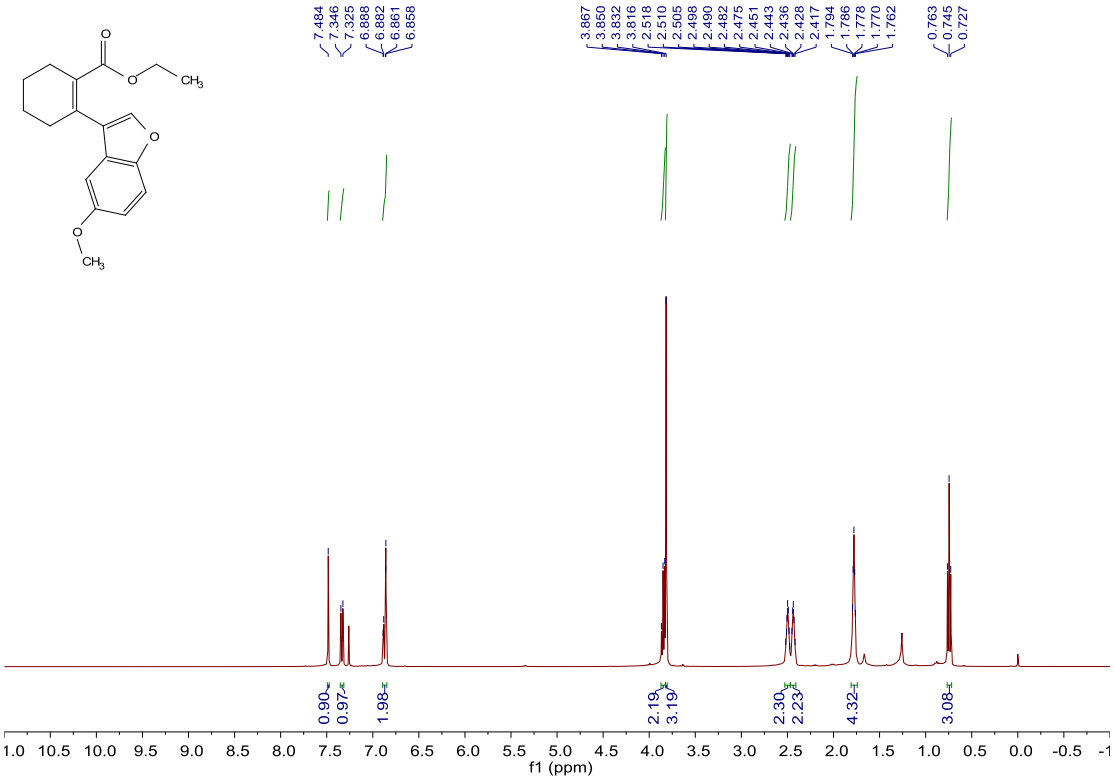

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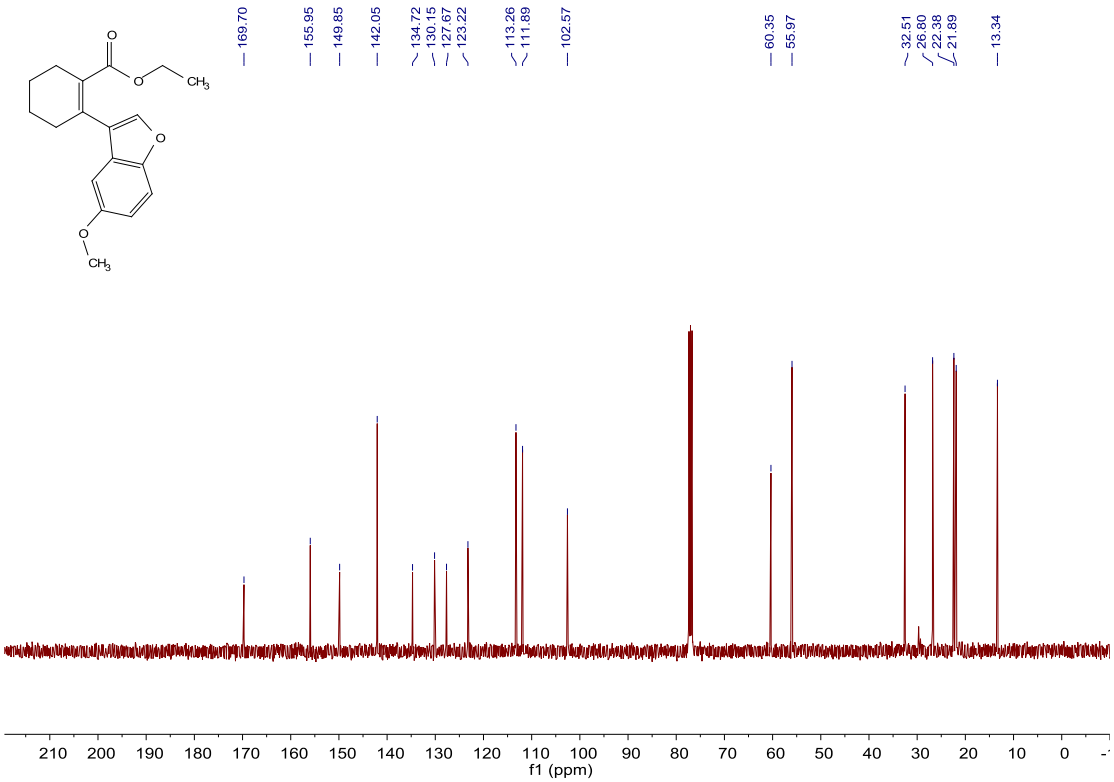

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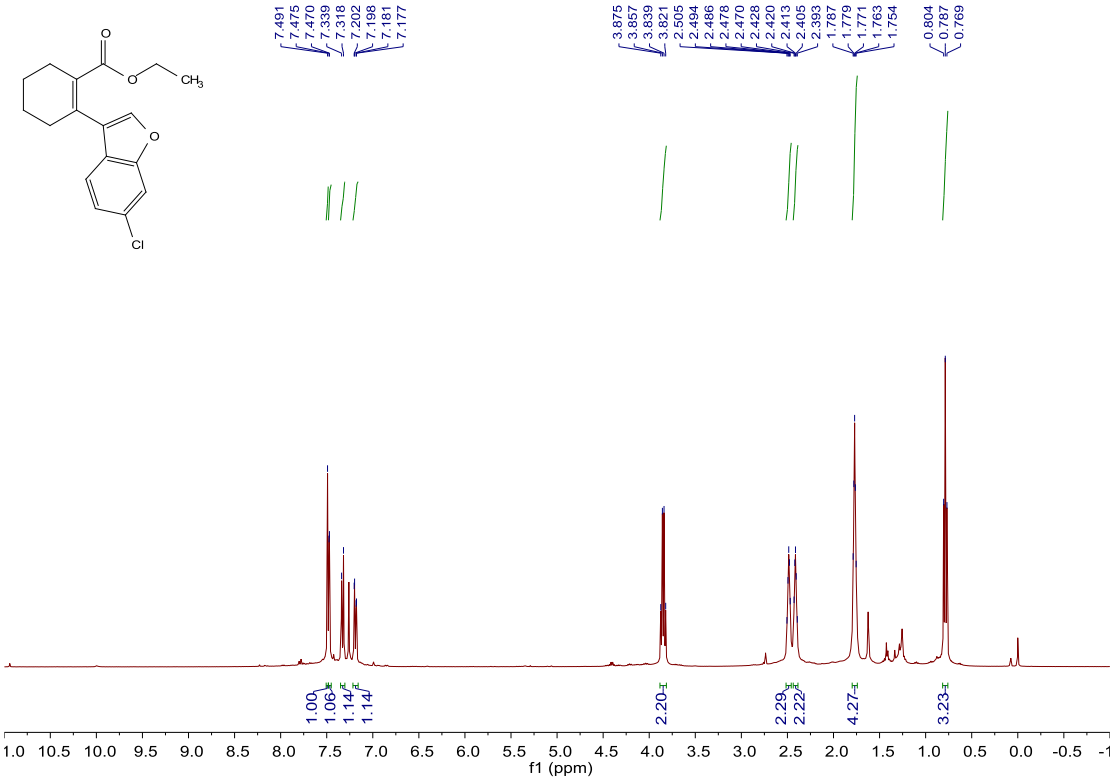

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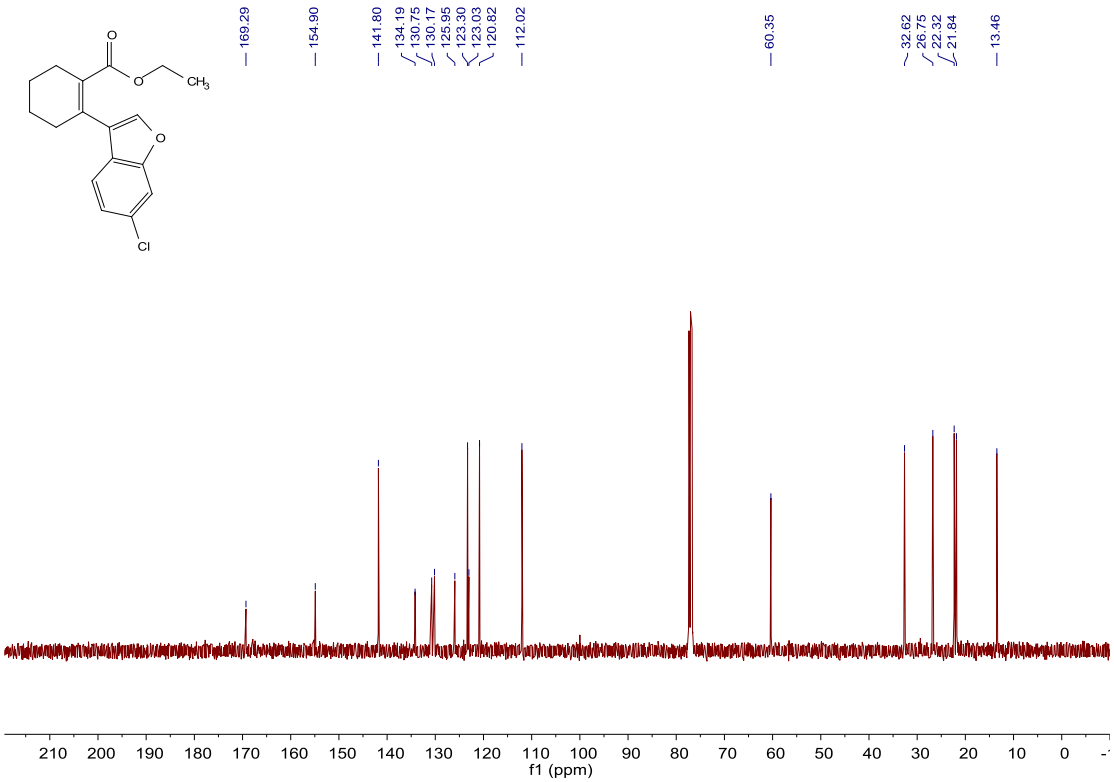

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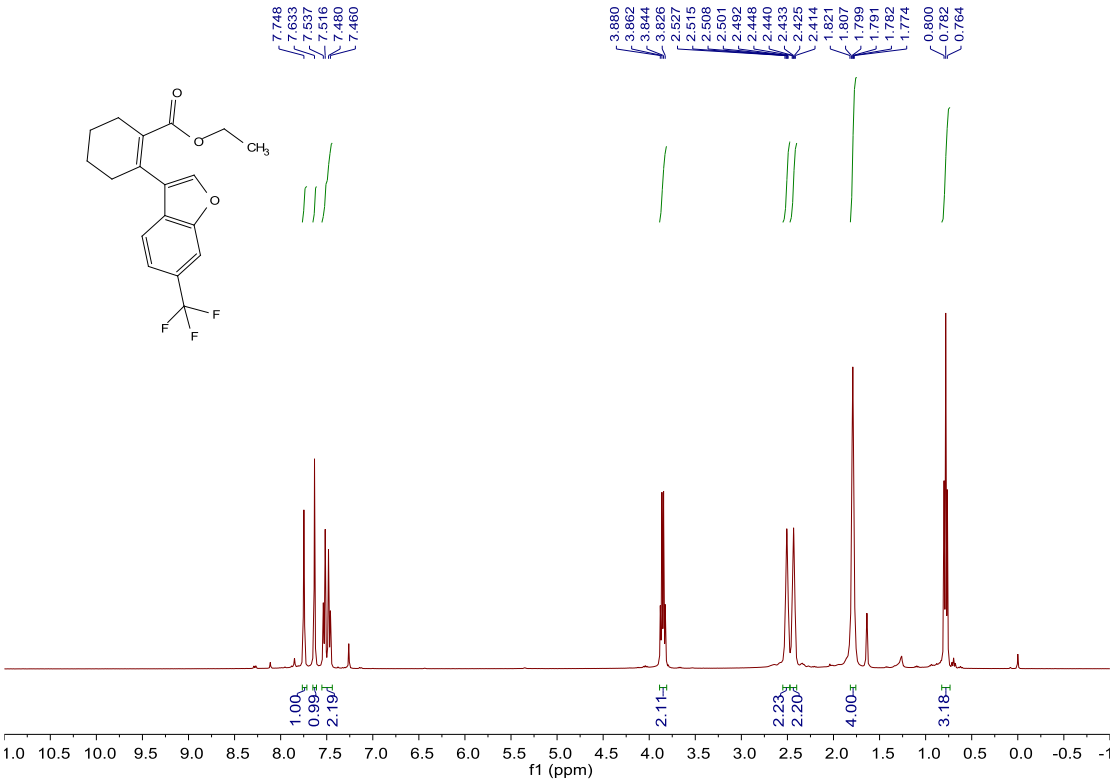

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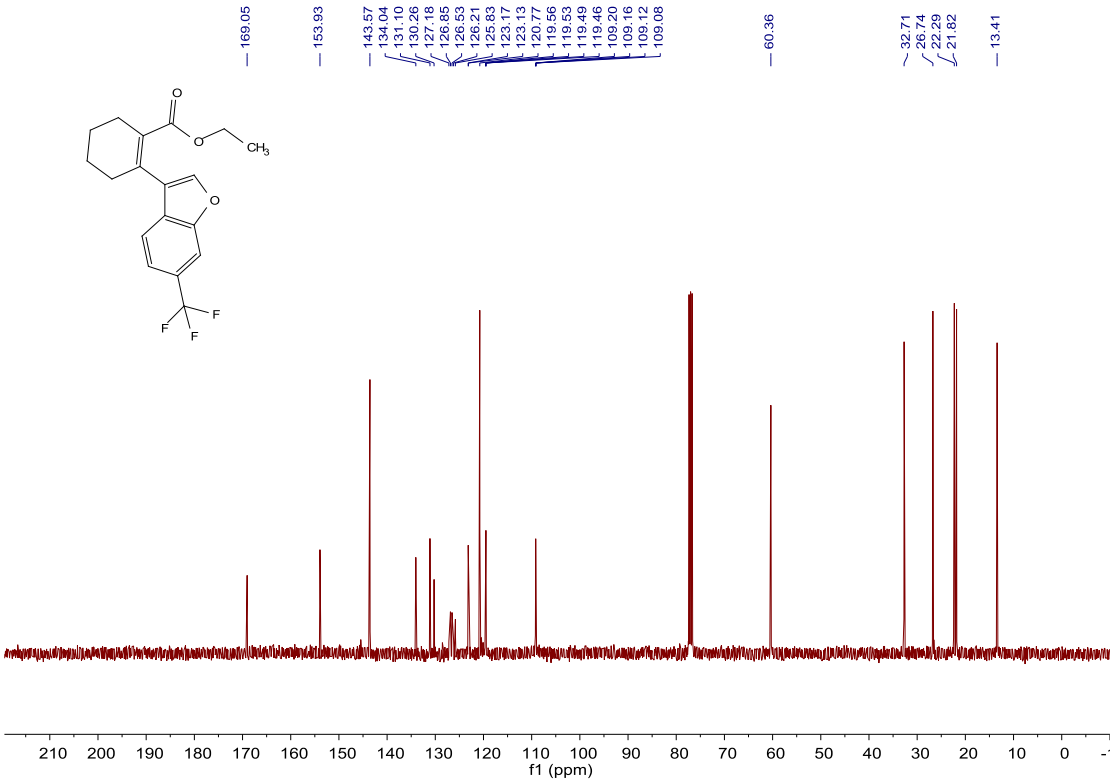

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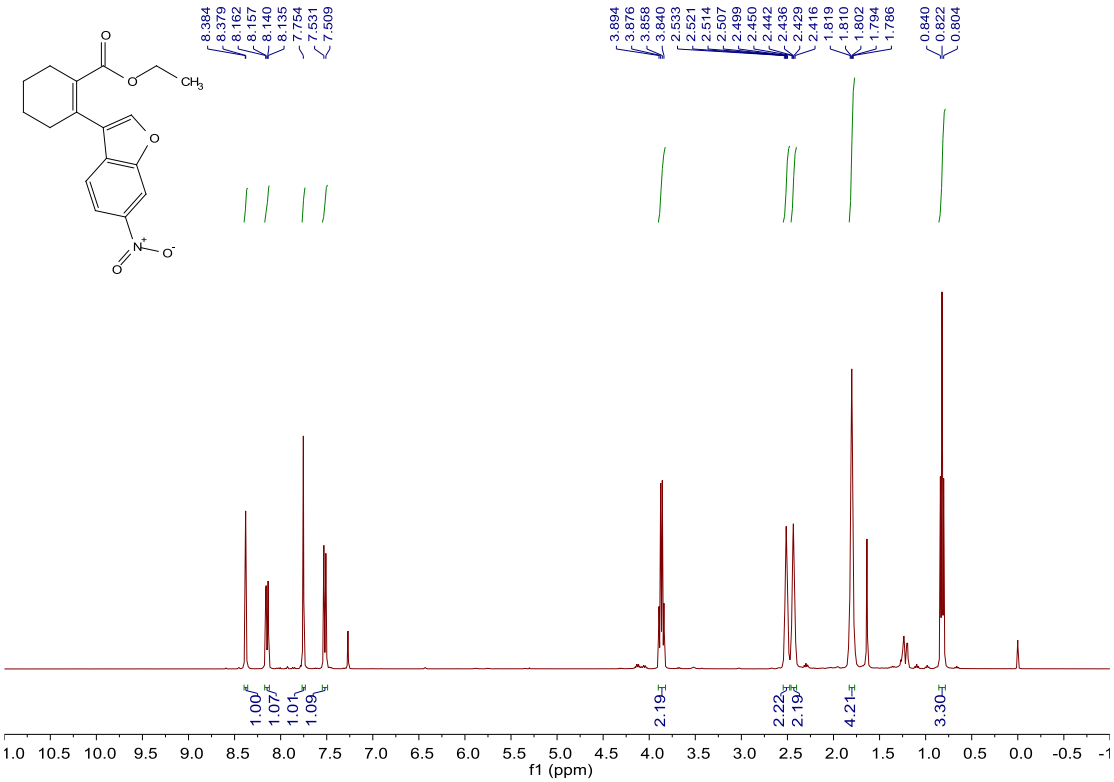

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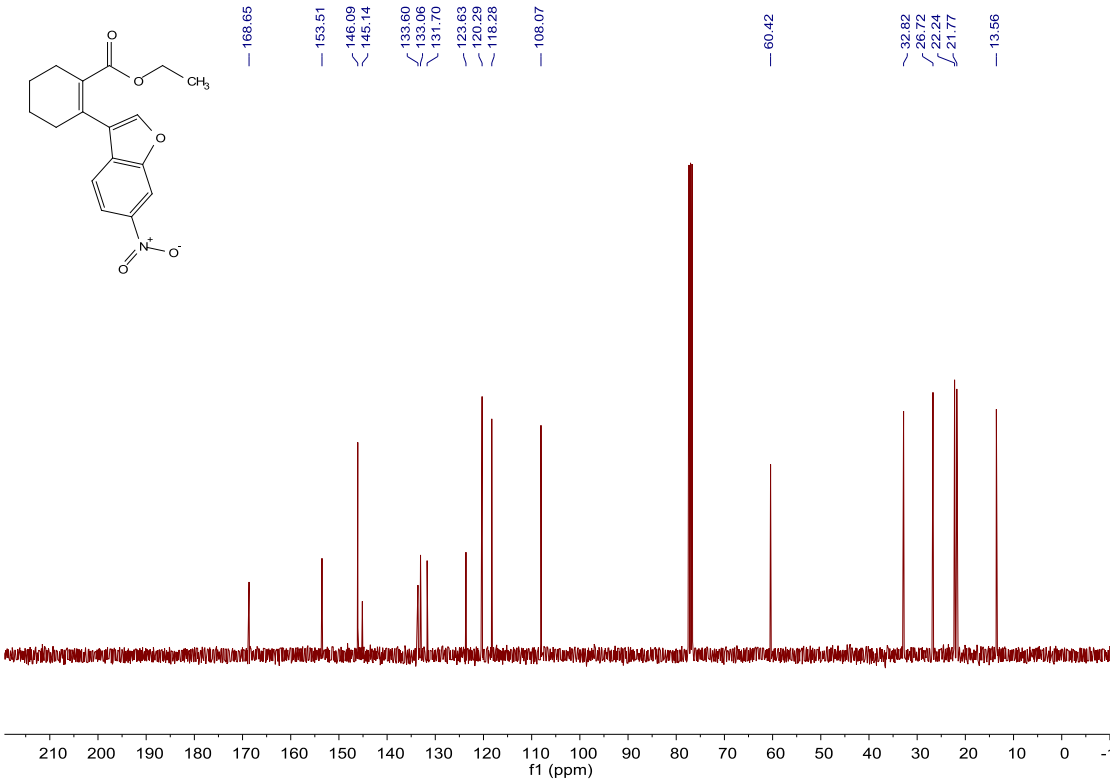

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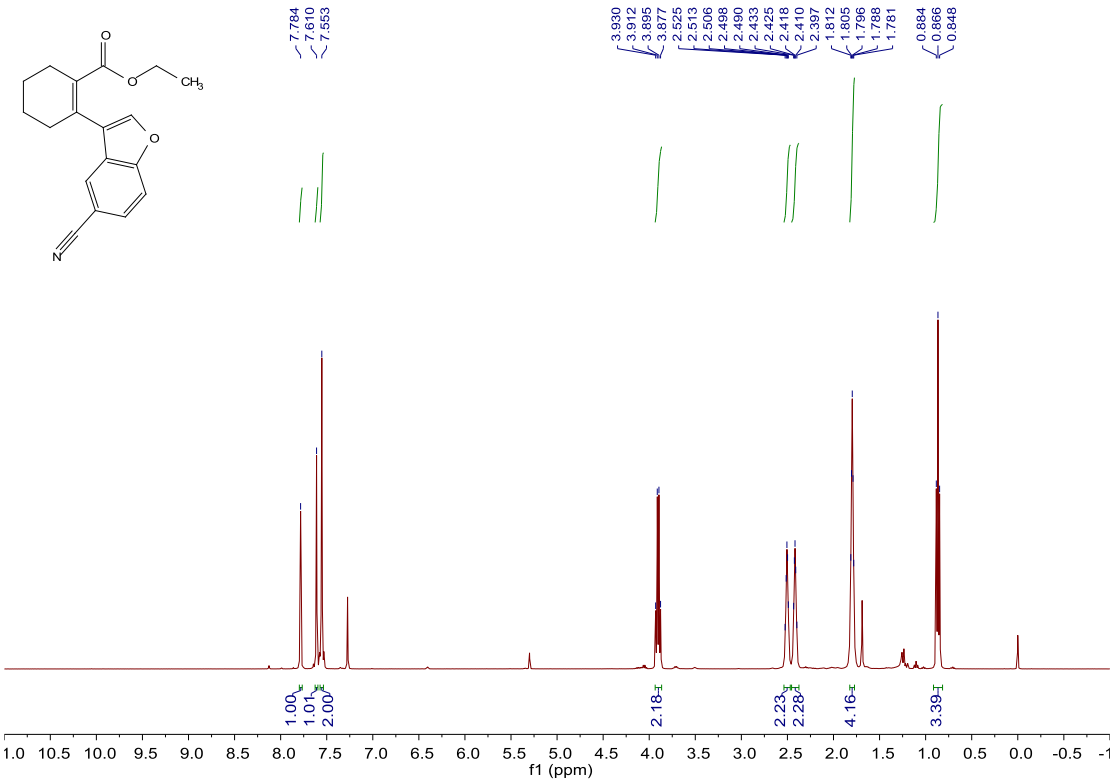

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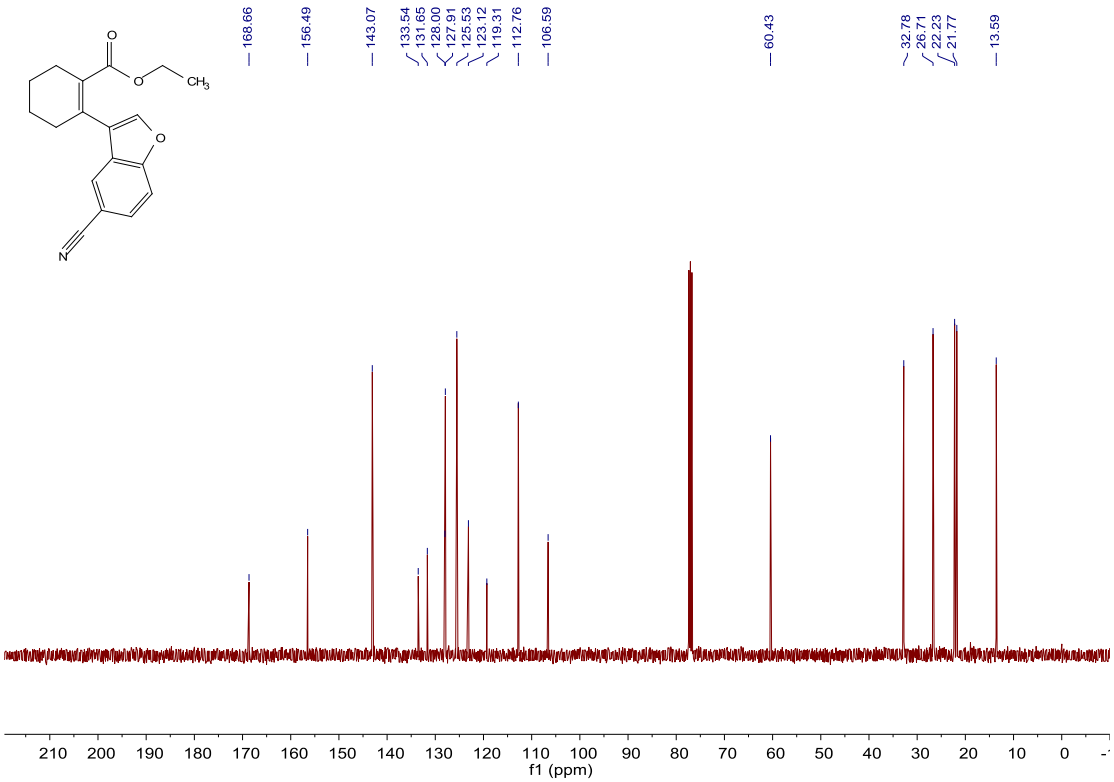

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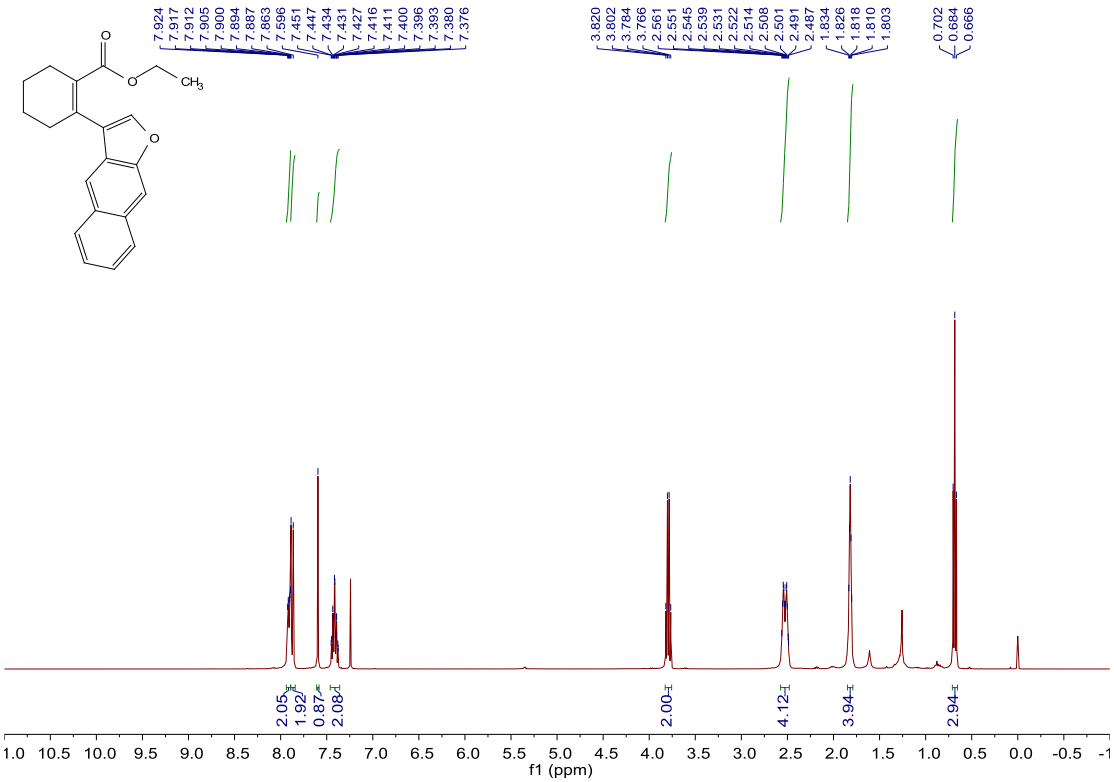

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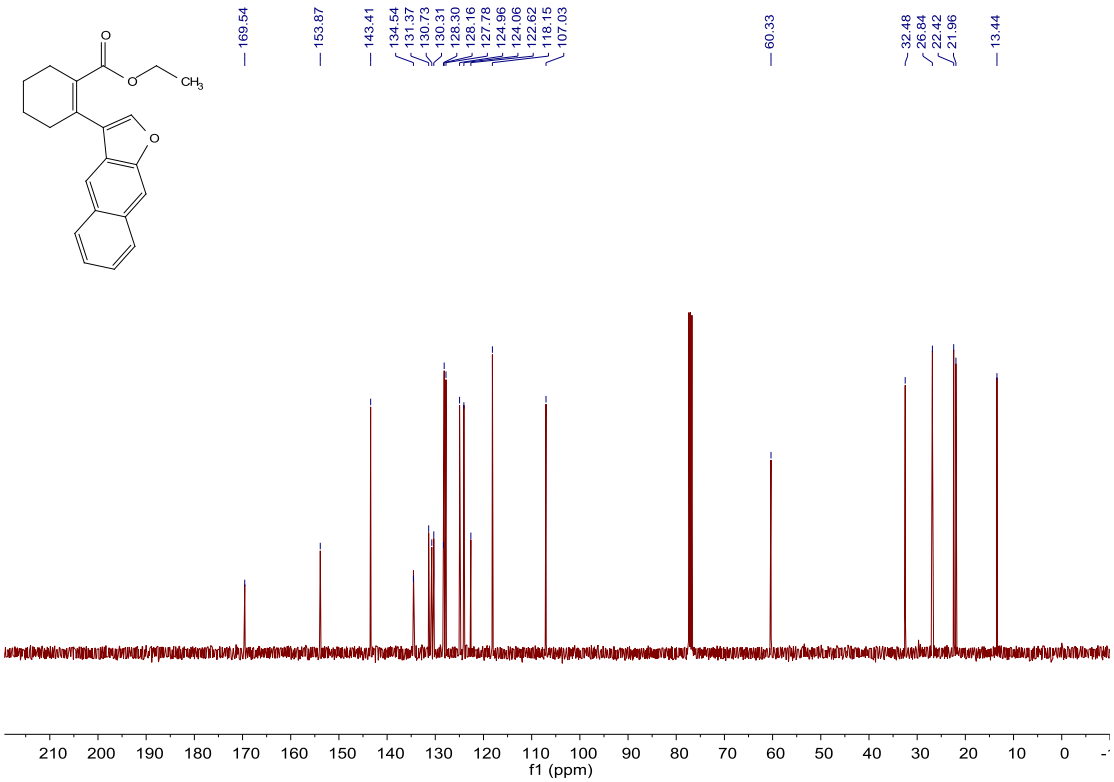
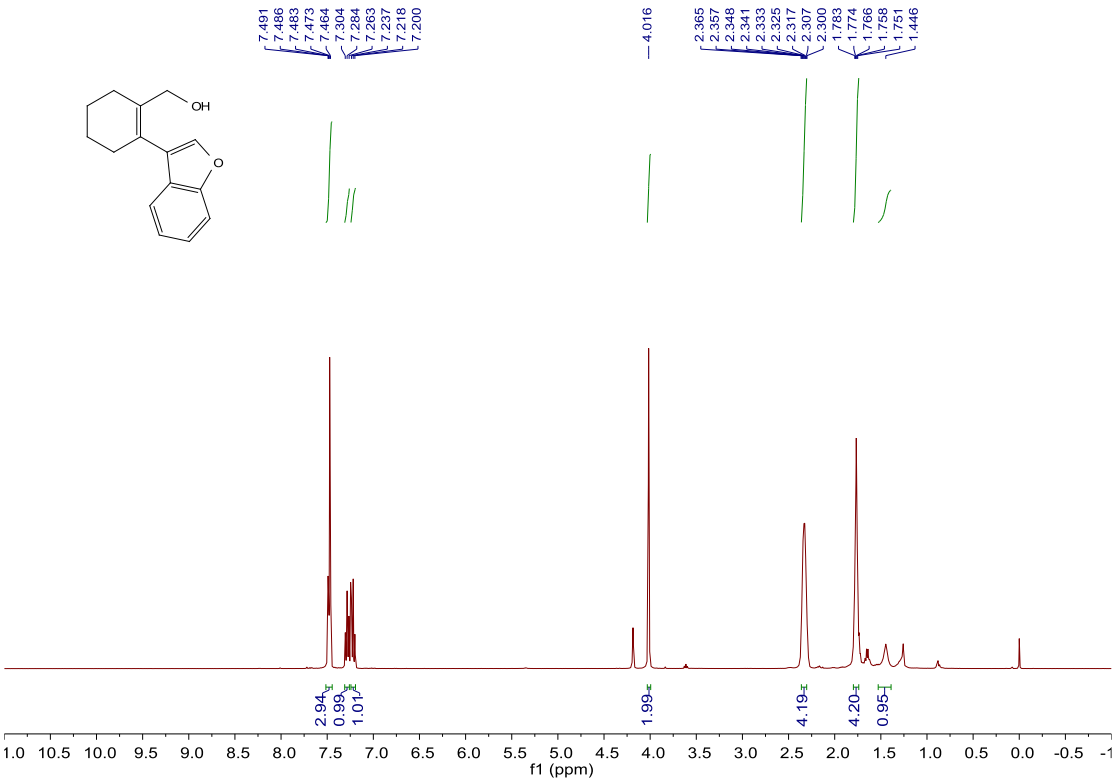


^{1}H NMR of In4-1a



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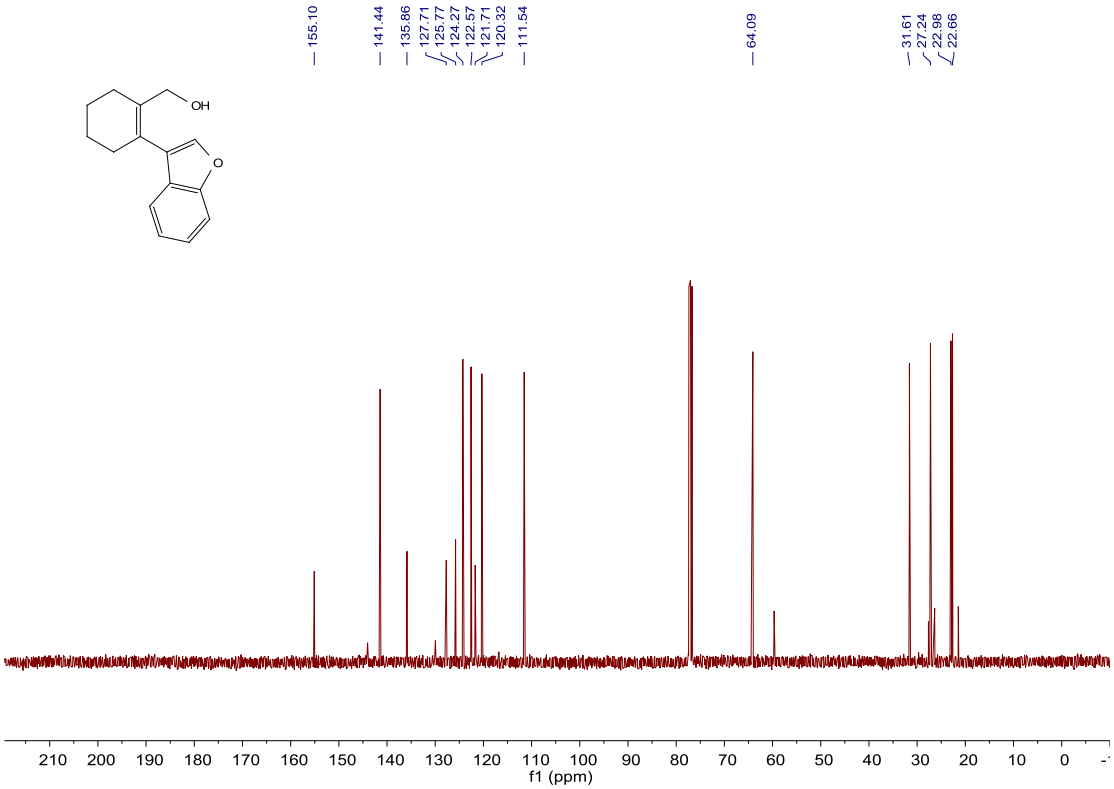
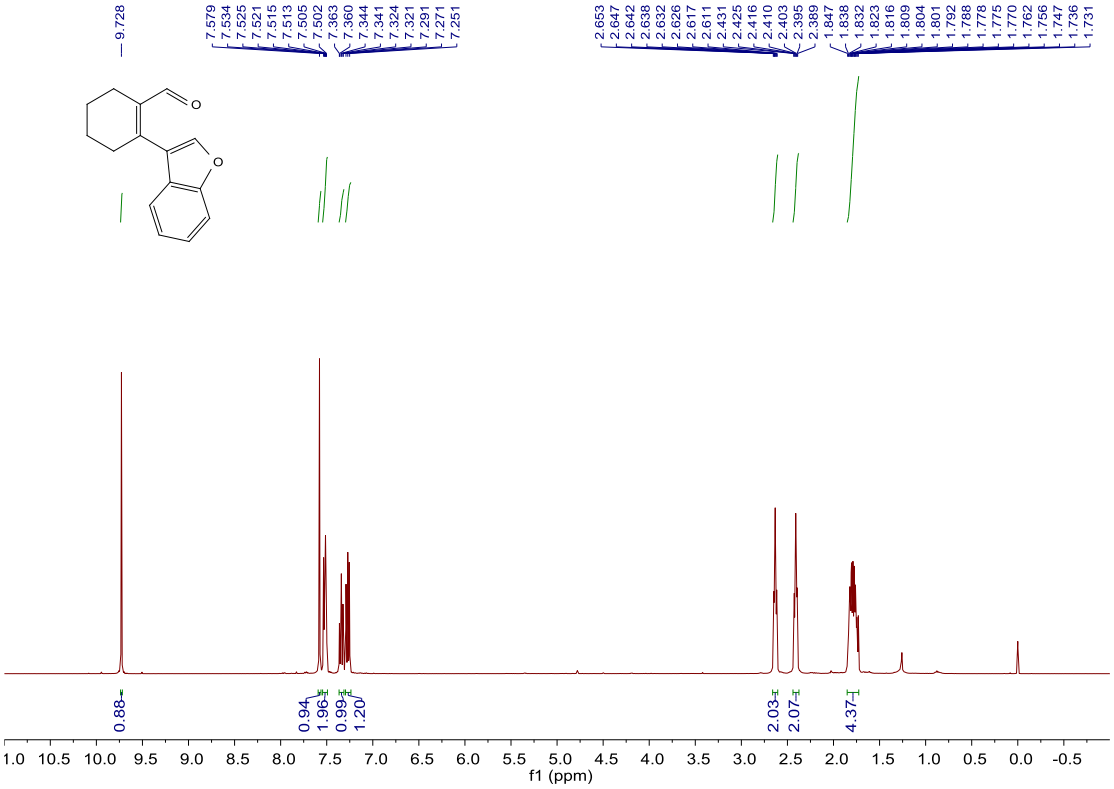


^{1}H NMR of In5-1a



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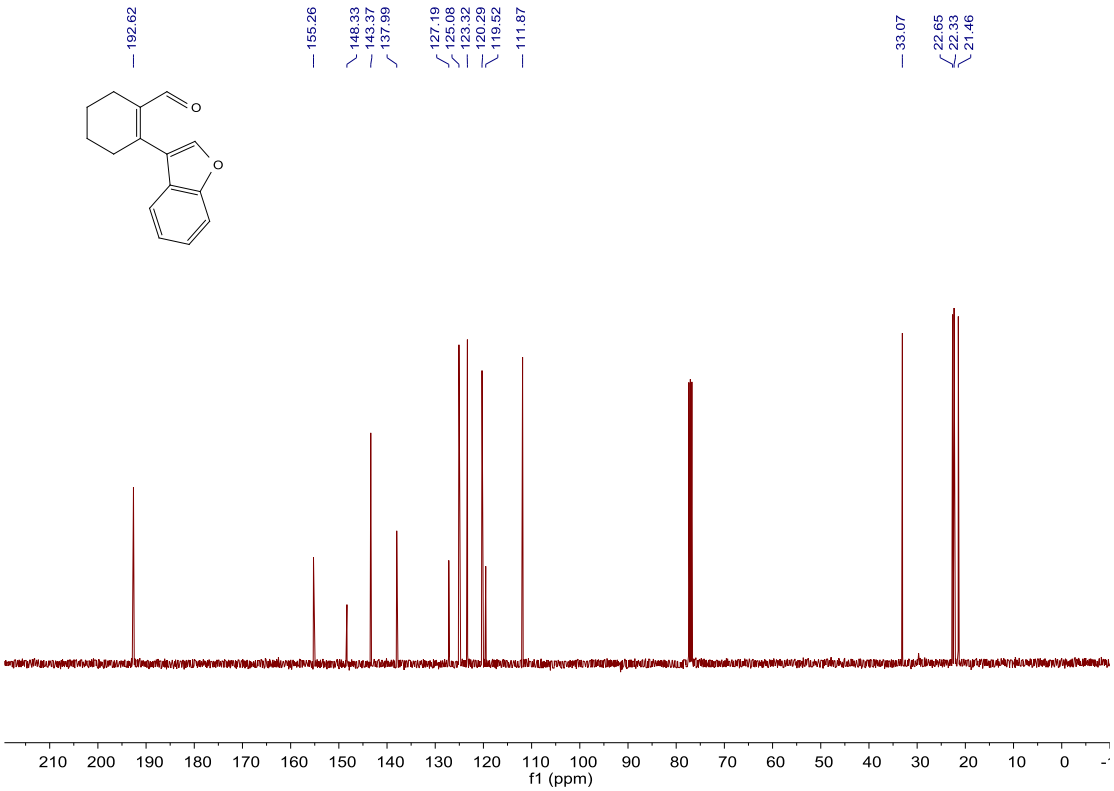

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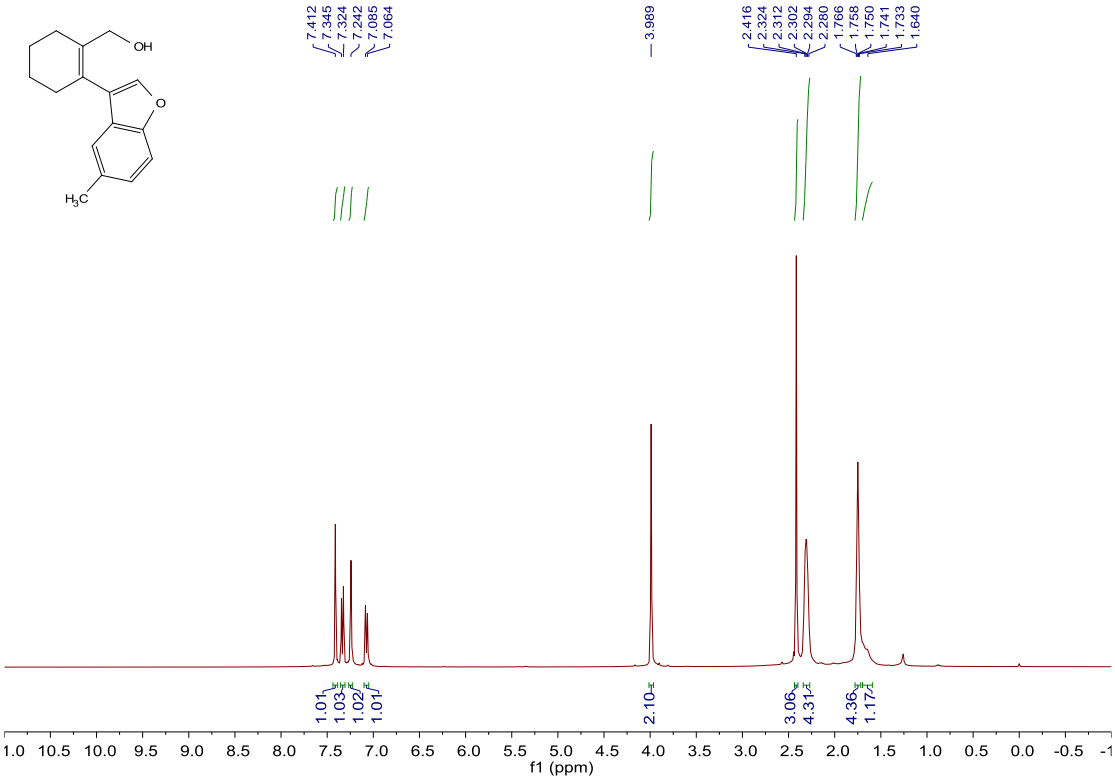

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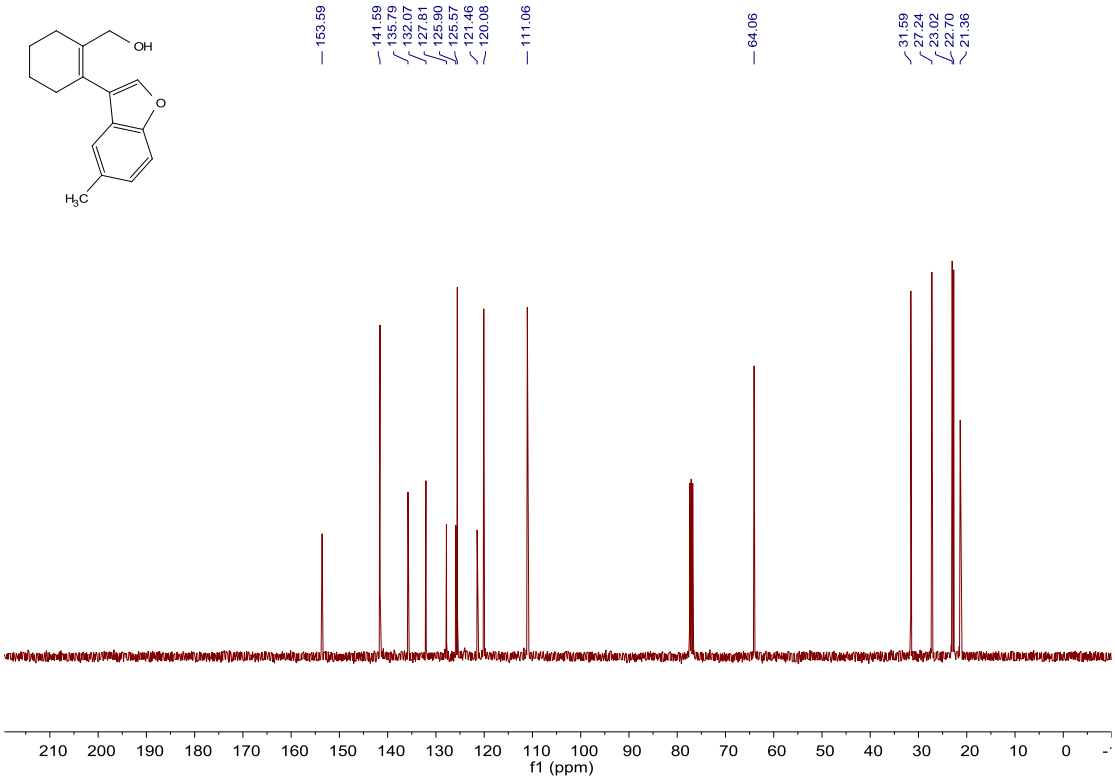

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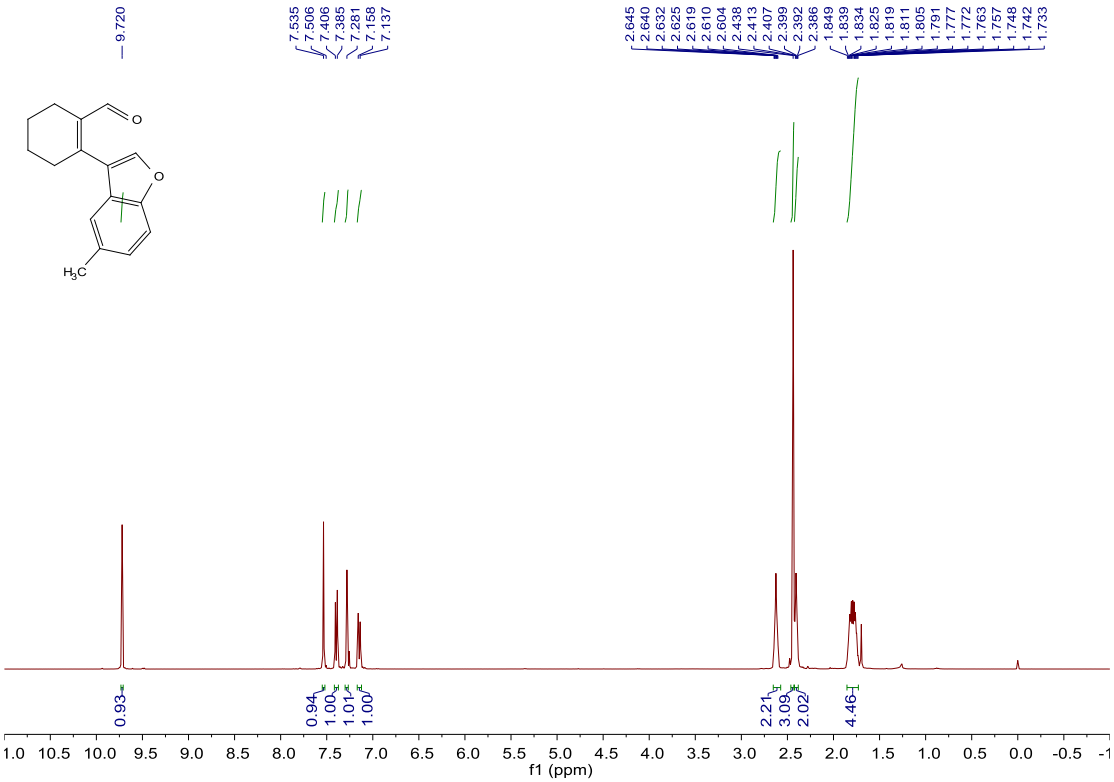

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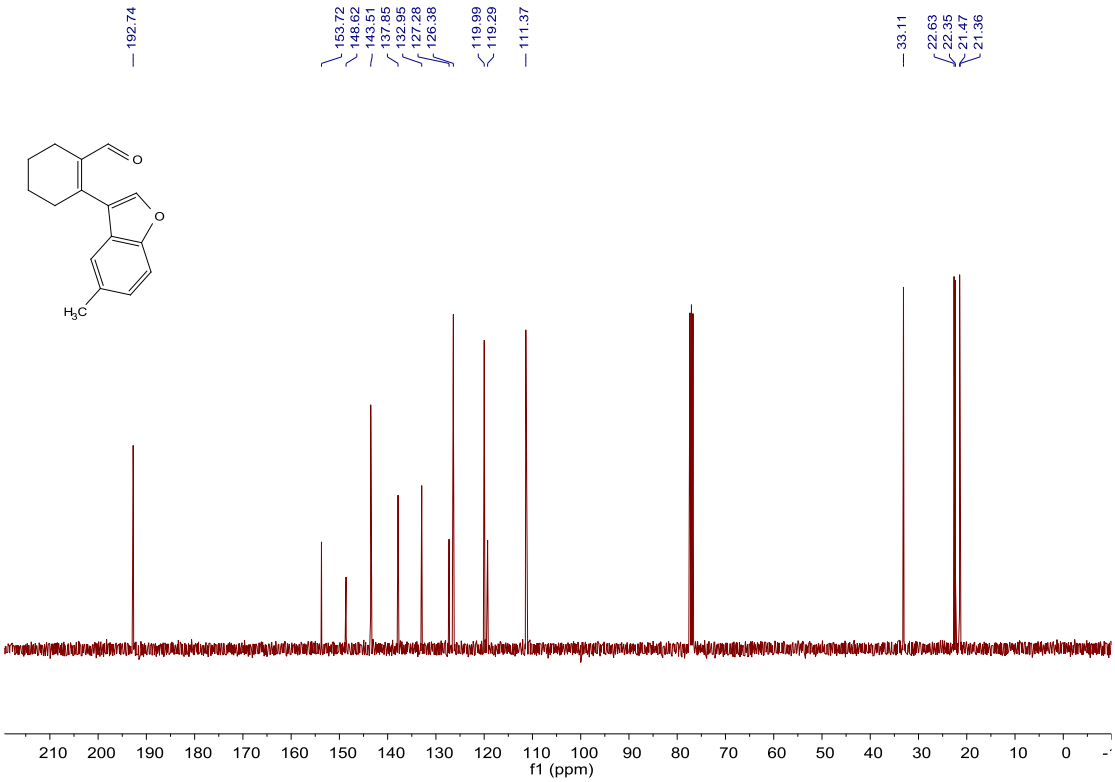
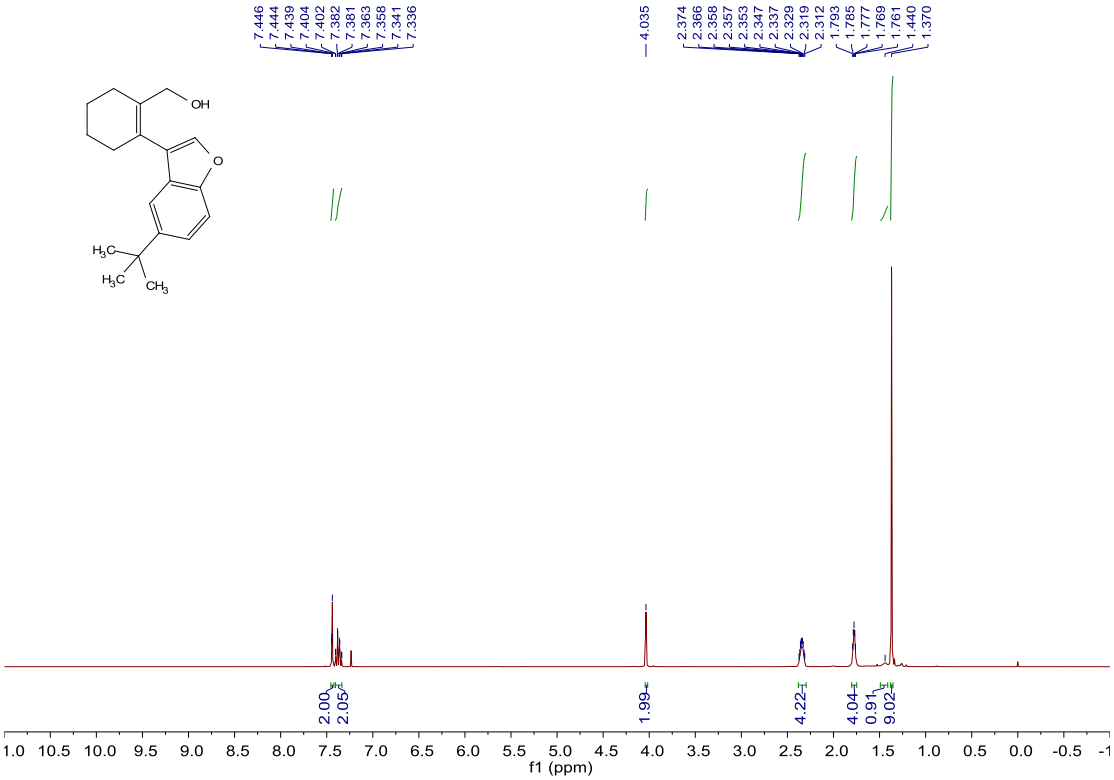
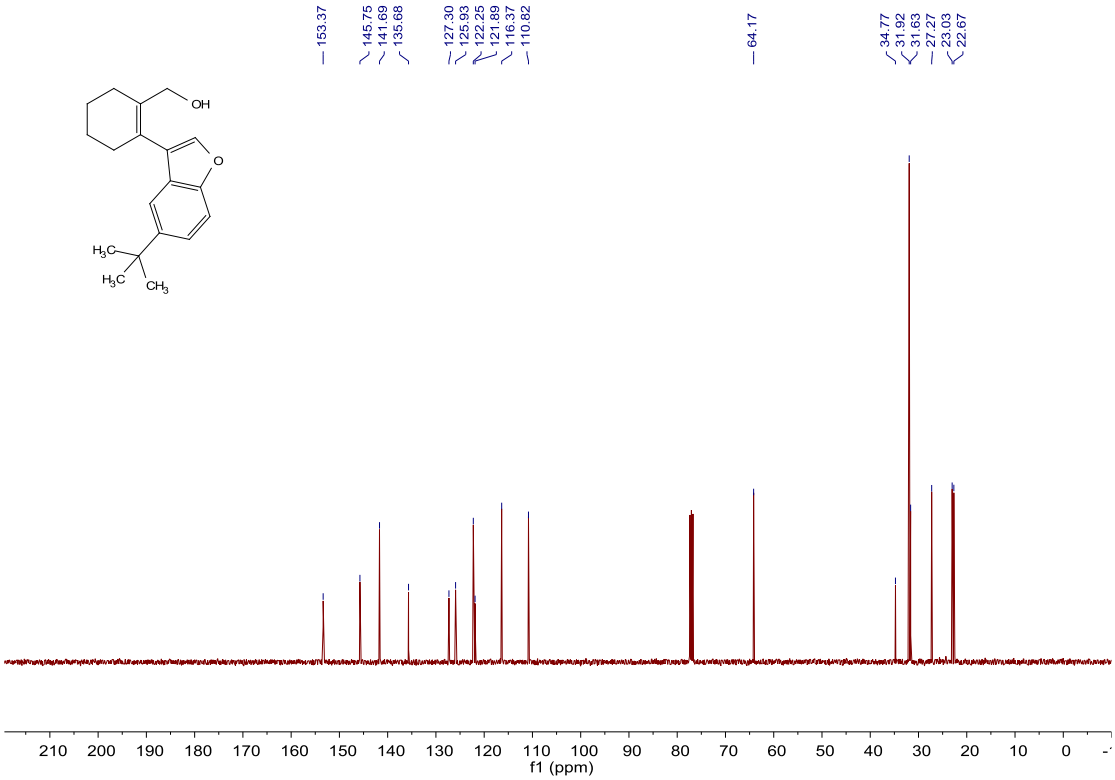


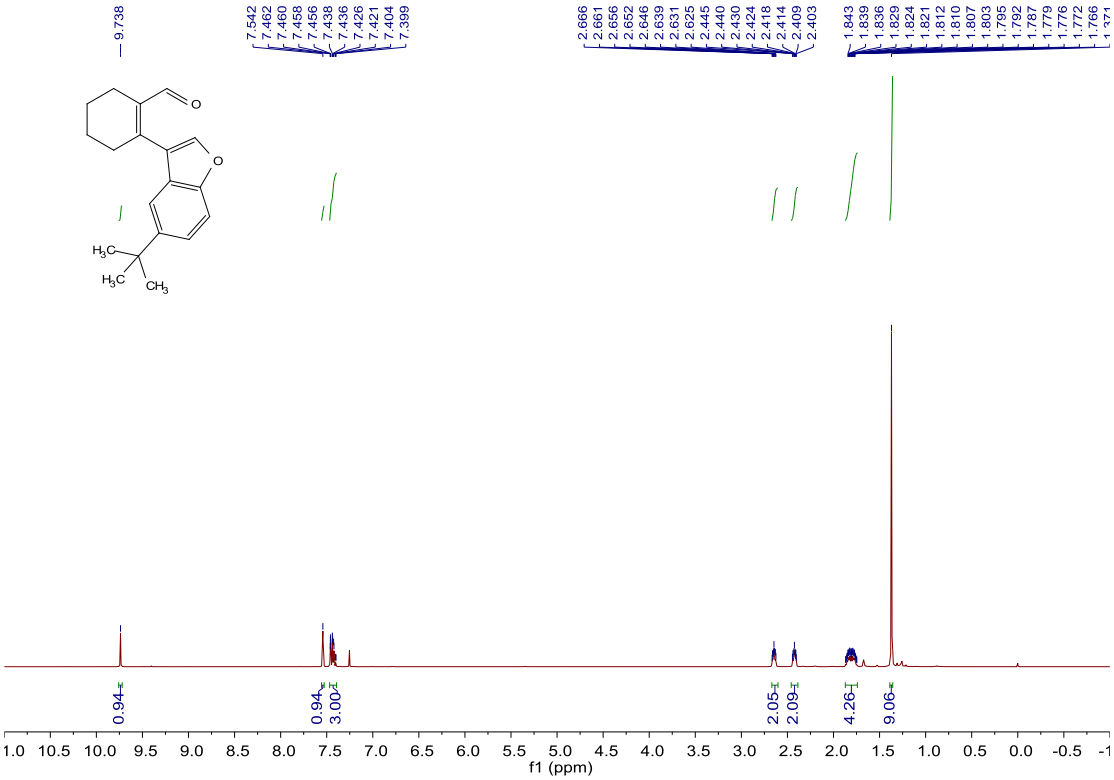
^{1}H NMR of In4-1c



^{13}C NMR of In4-1c



^{1}H NMR of In5-1c



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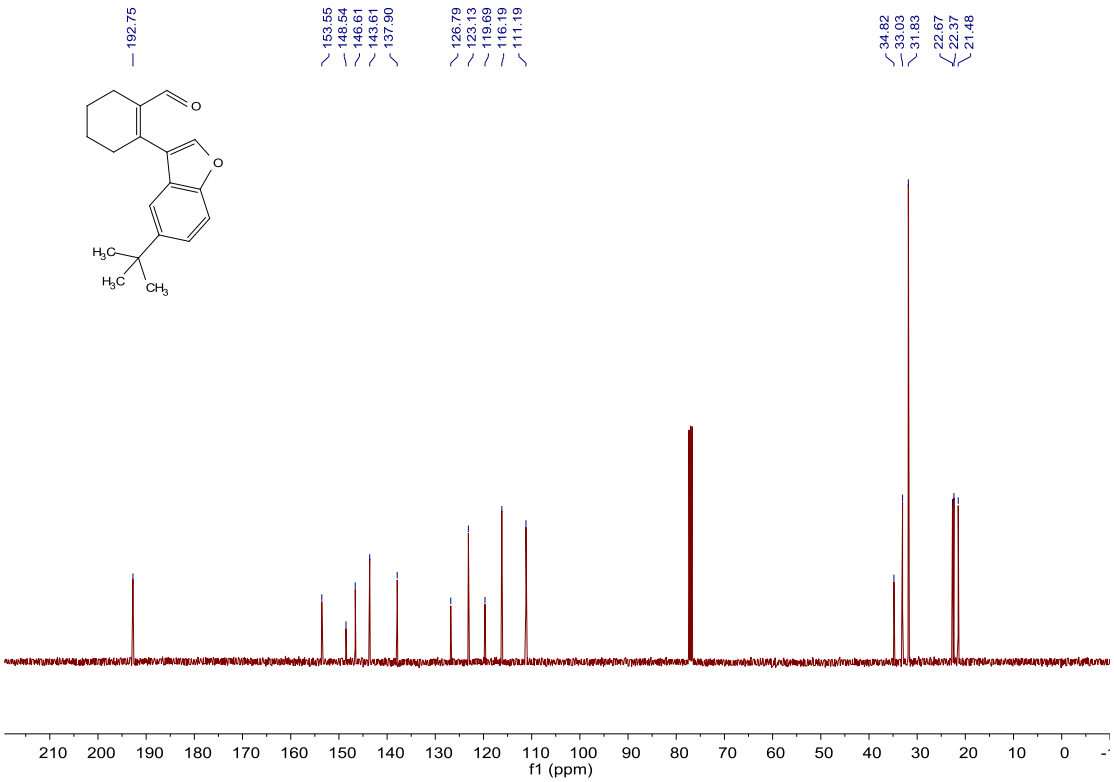

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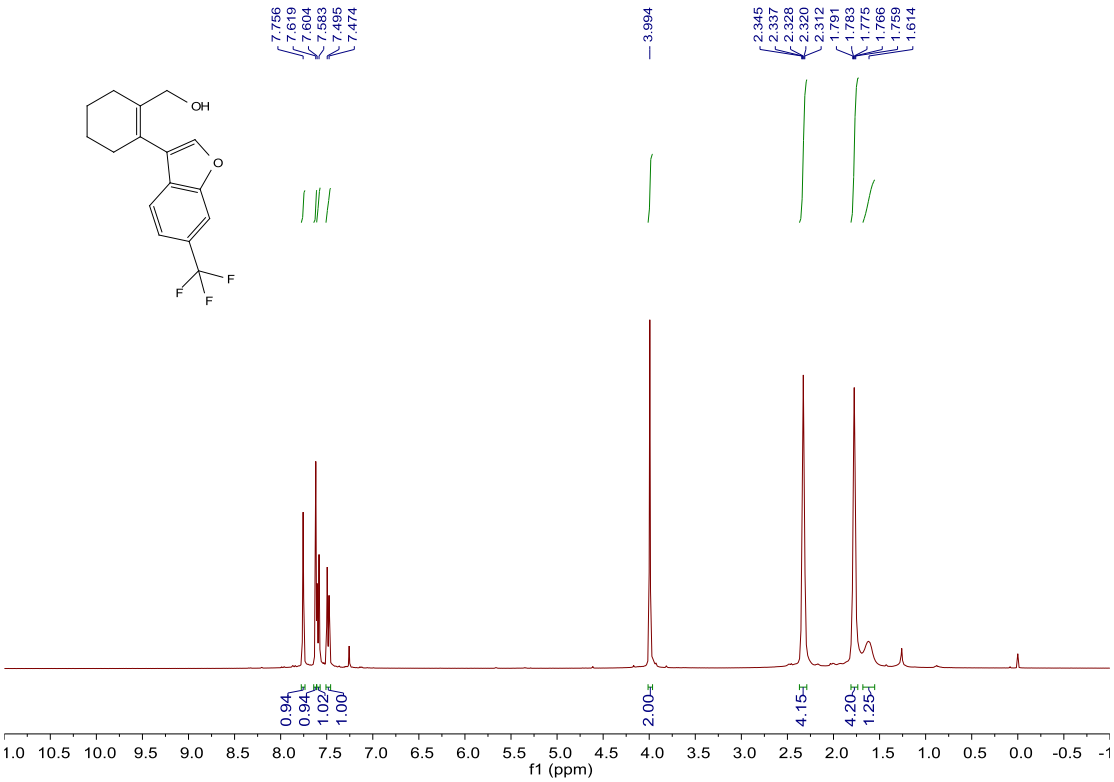

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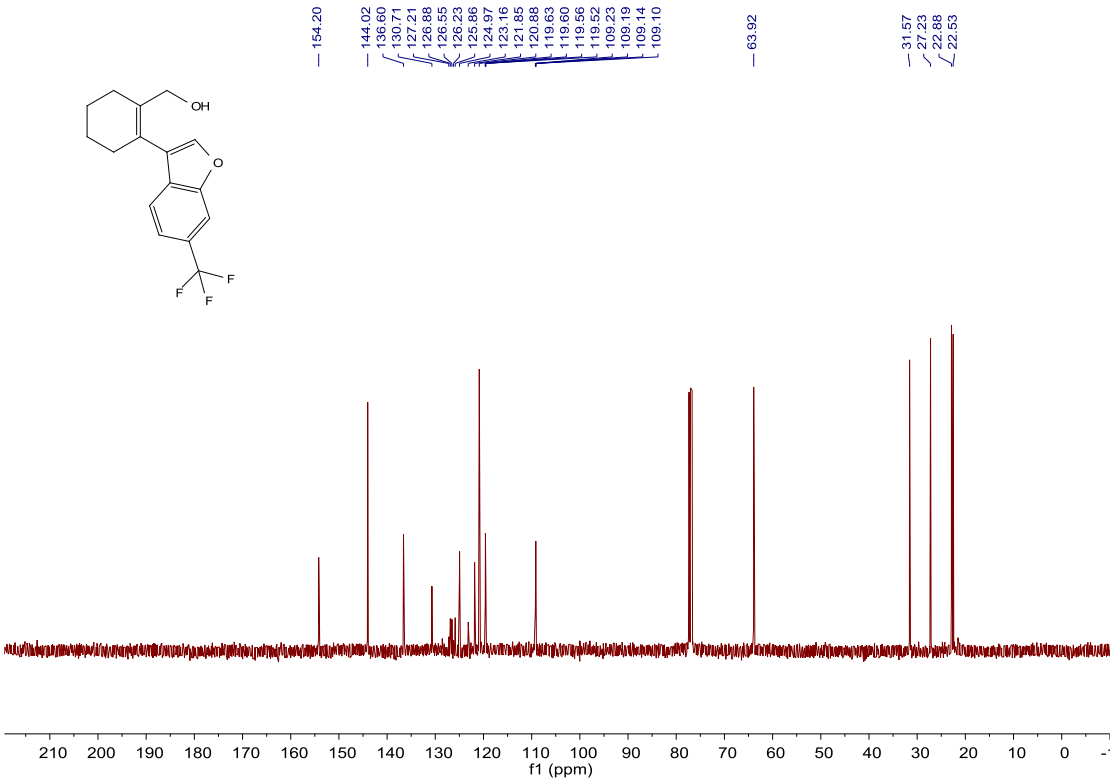

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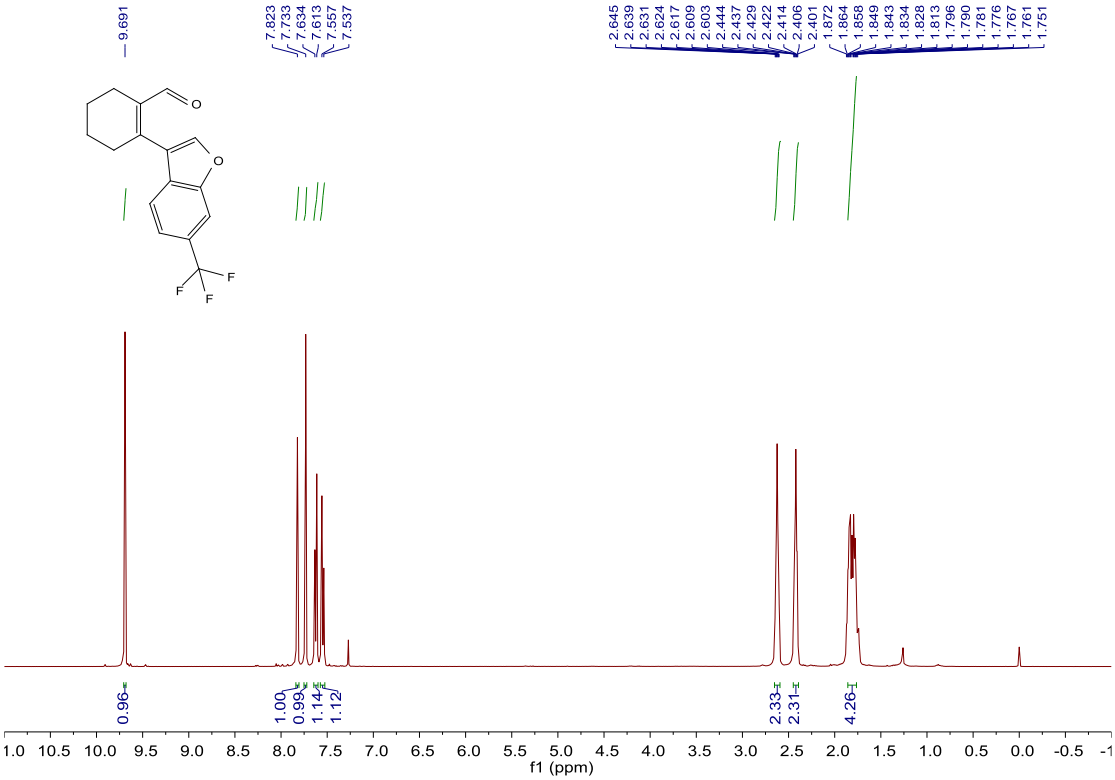

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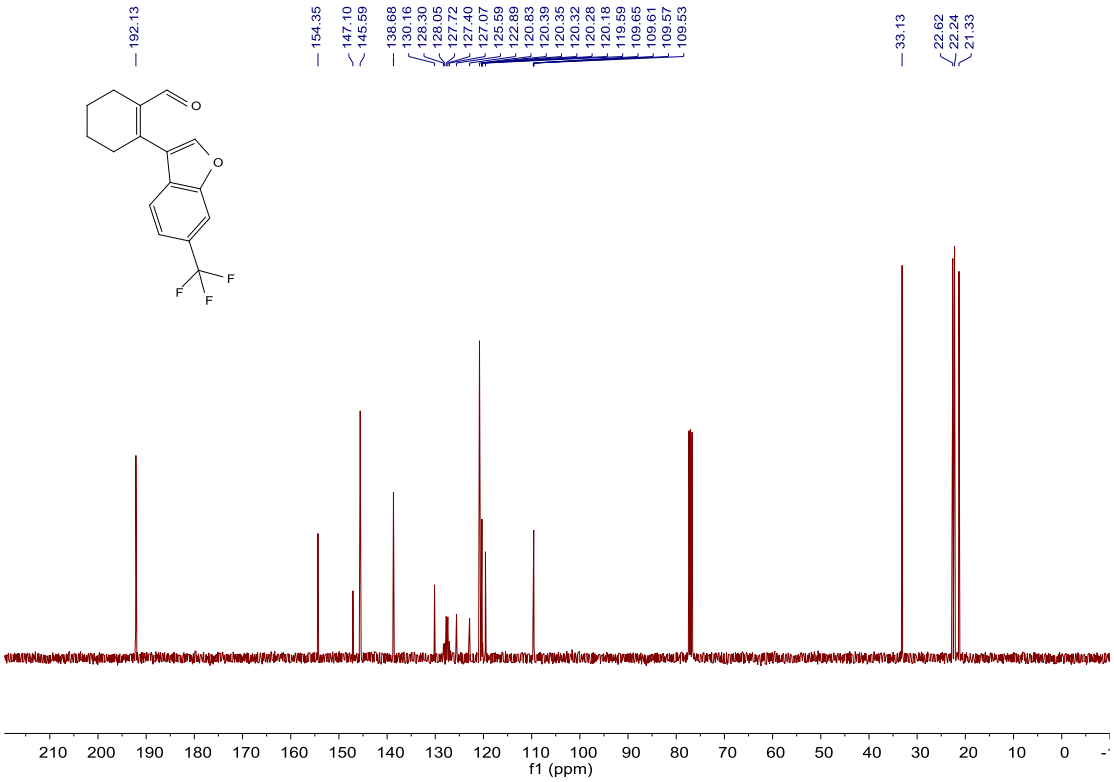
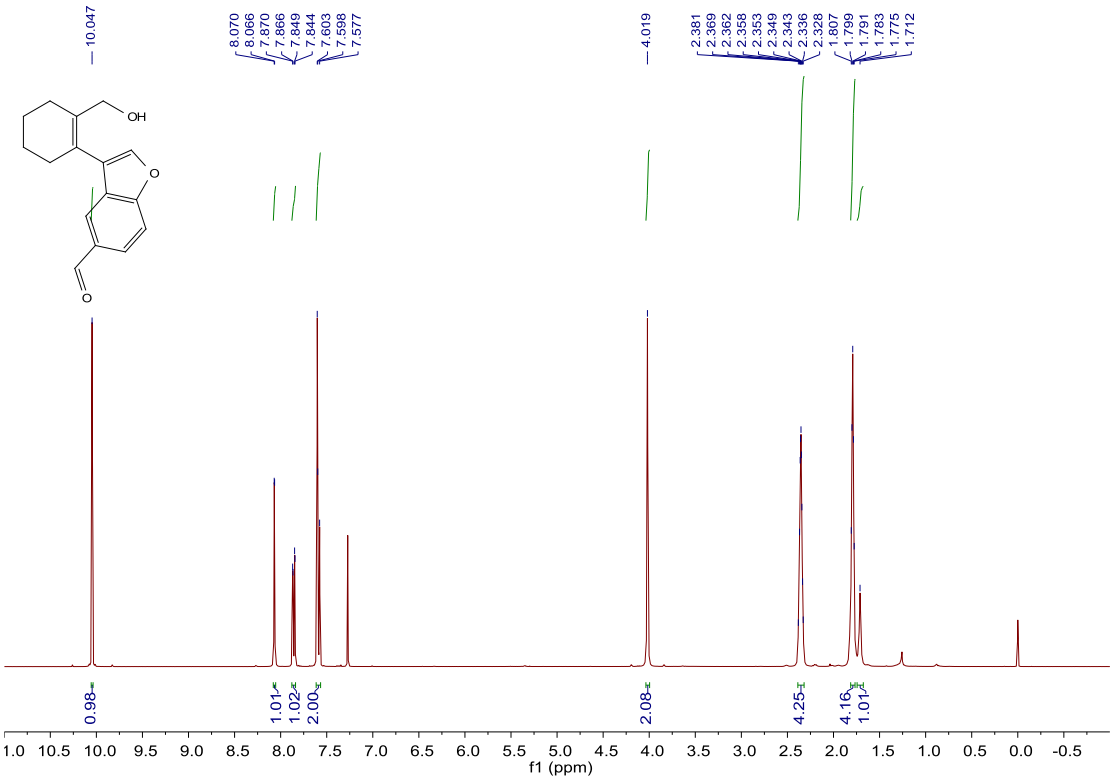
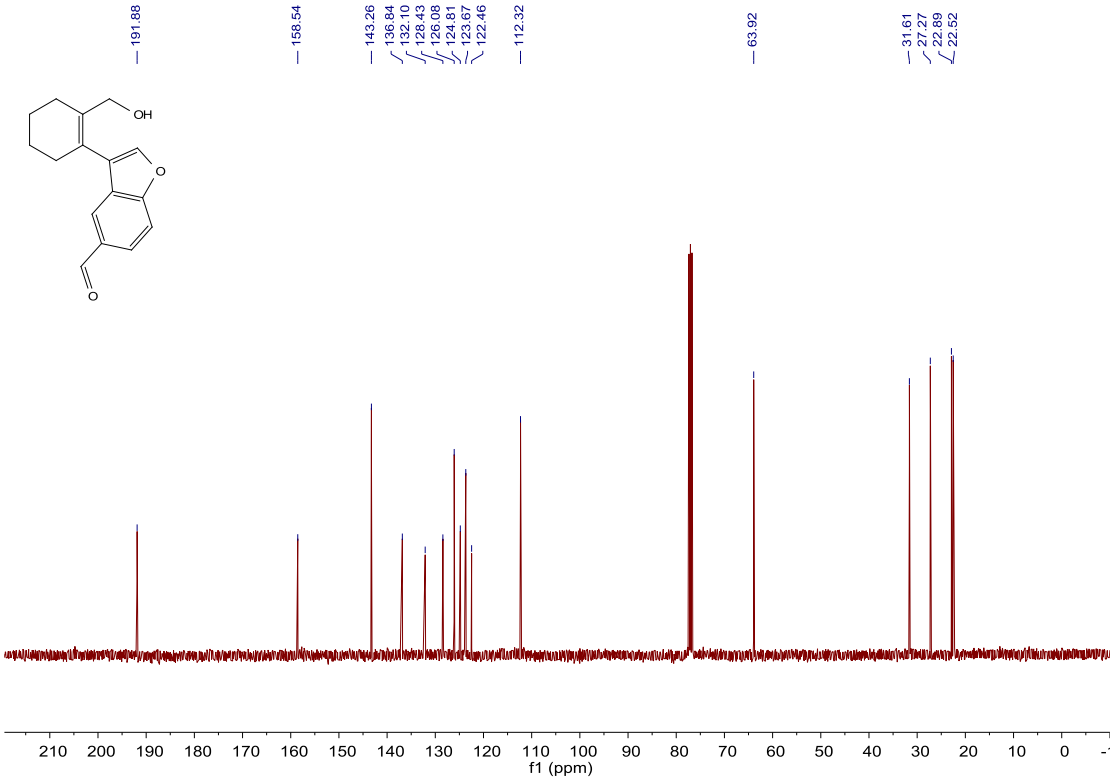


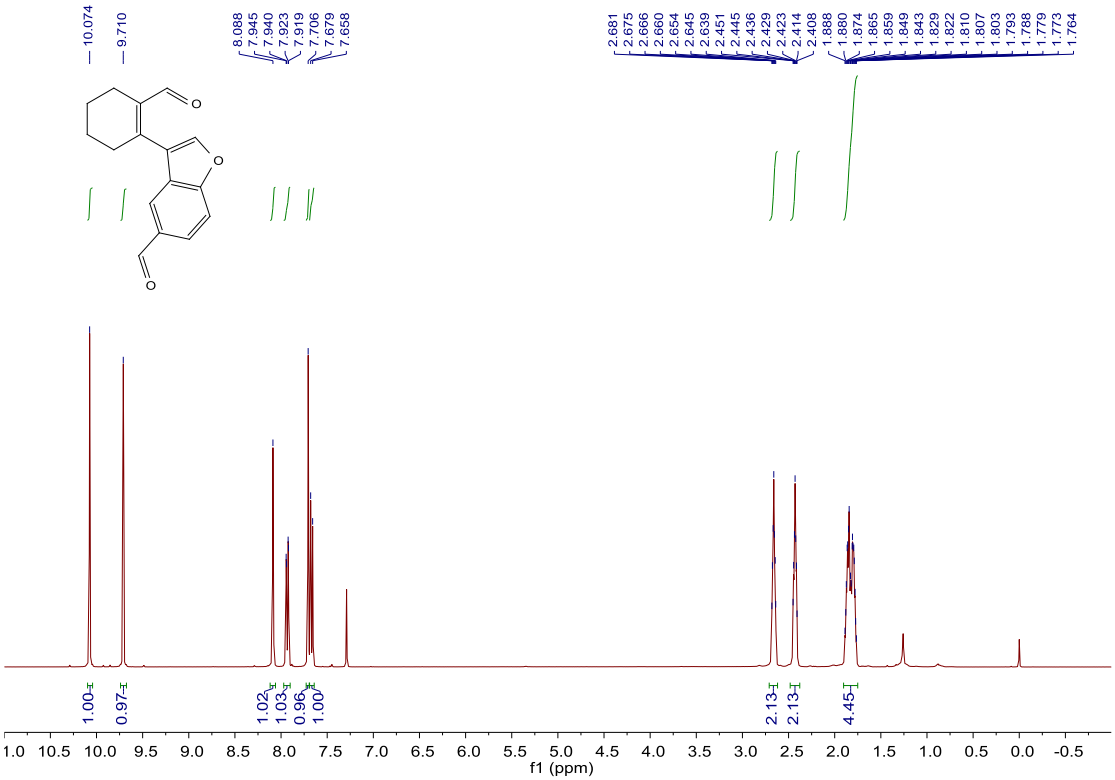
^{1}H NMR of In4-1h



^{13}C NMR of In4-1h



^{1}H NMR of In5-1h



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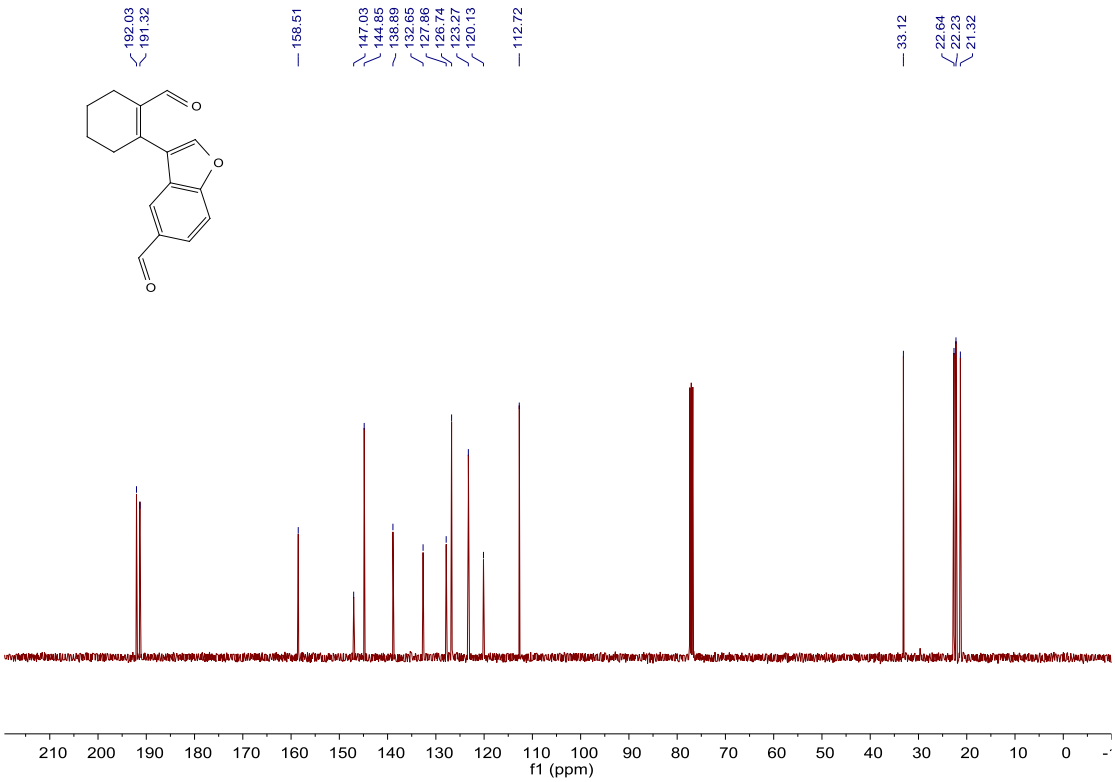

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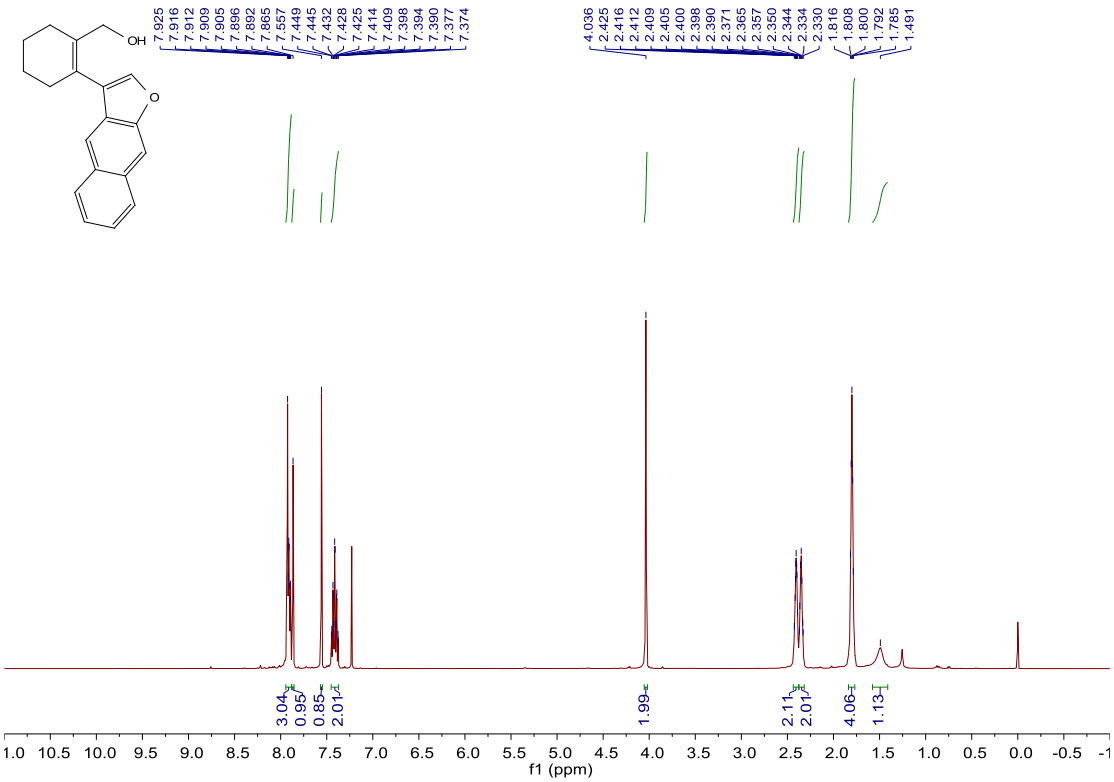

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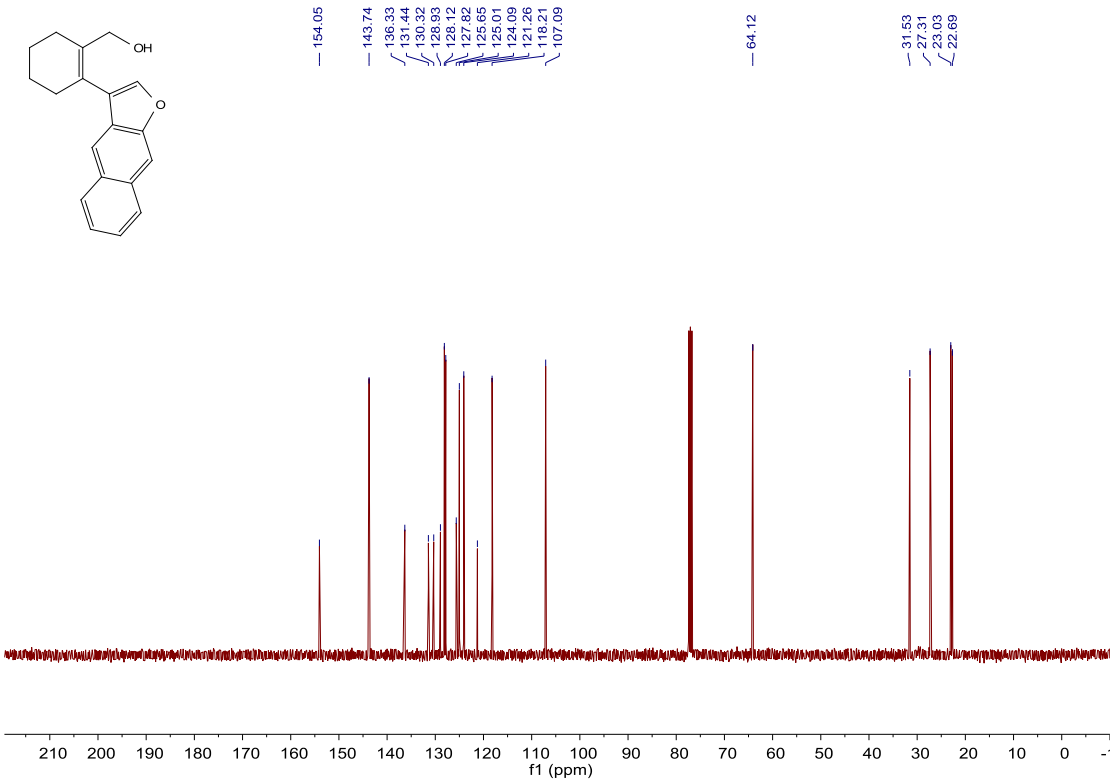

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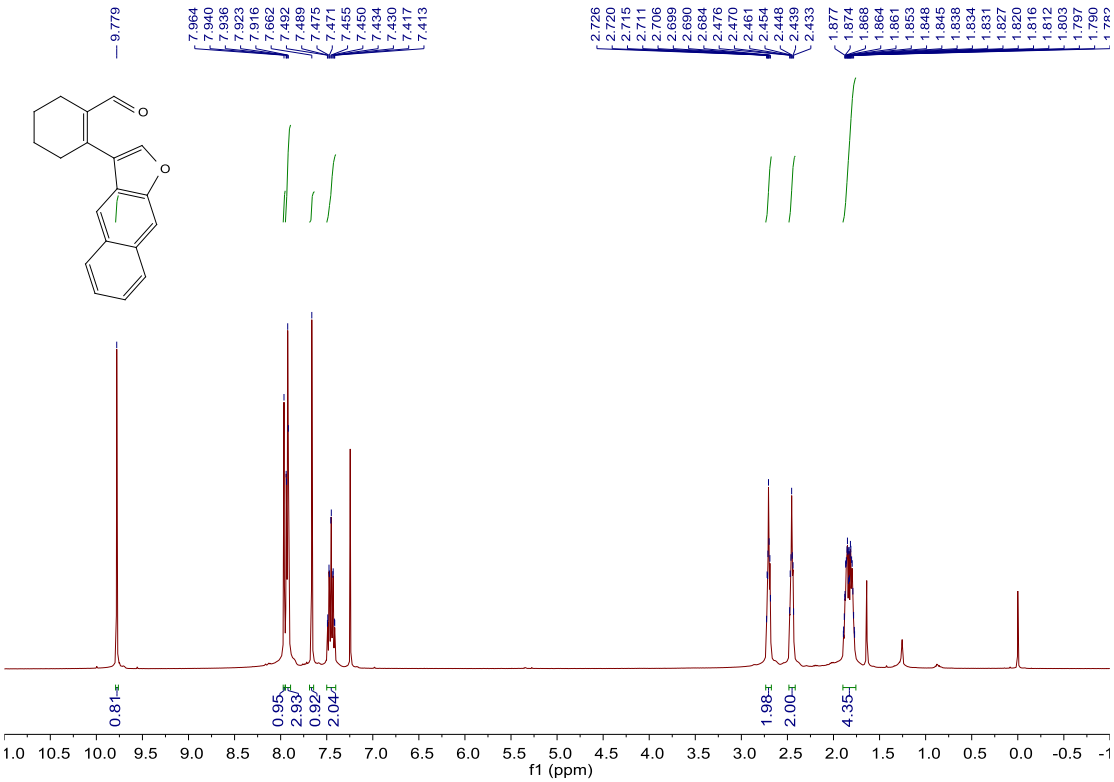
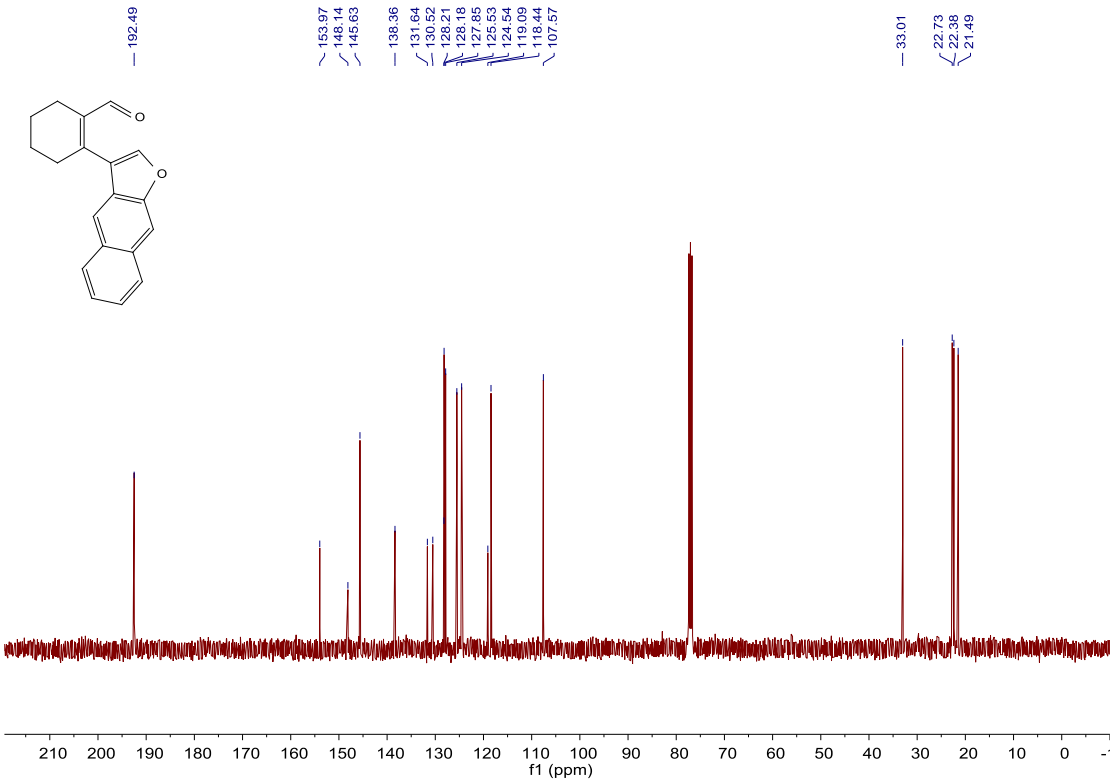


^{13}C NMR of In5-1i



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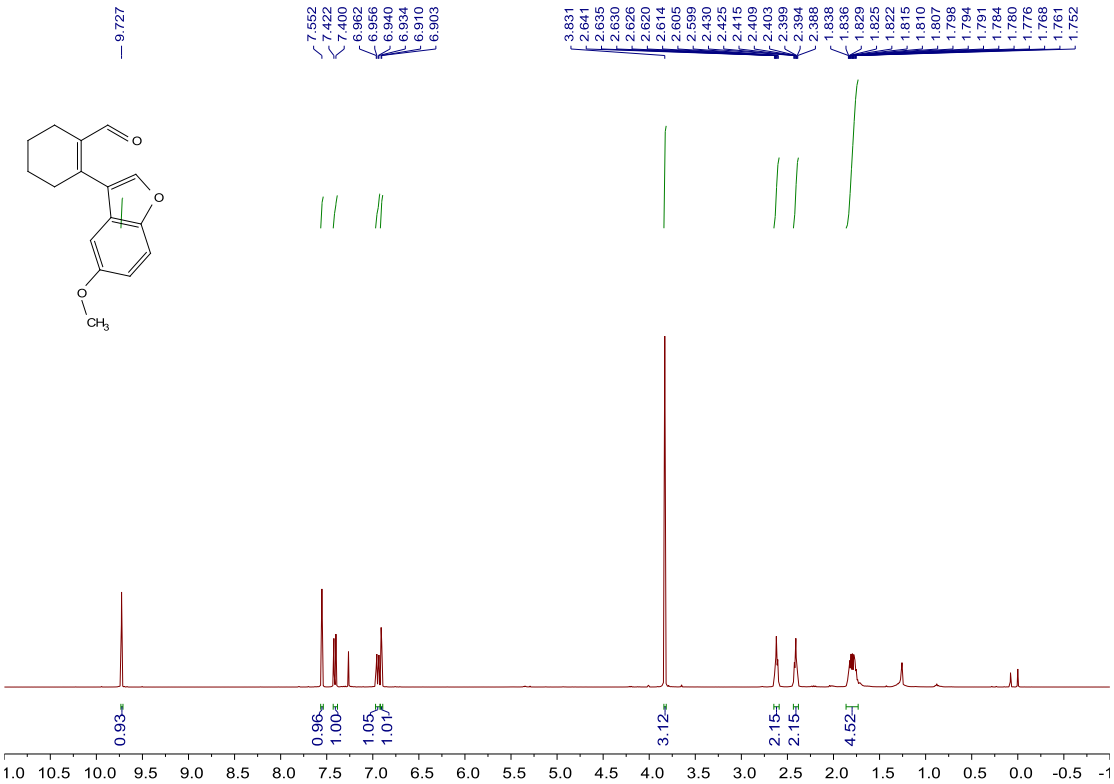

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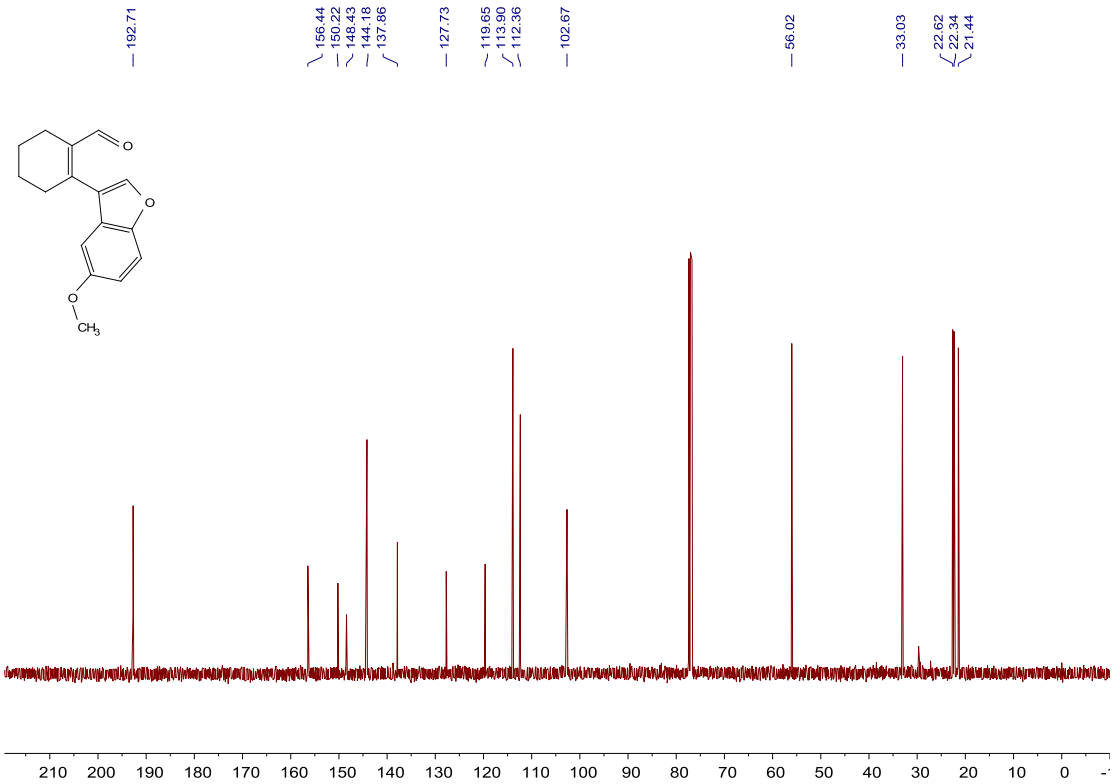

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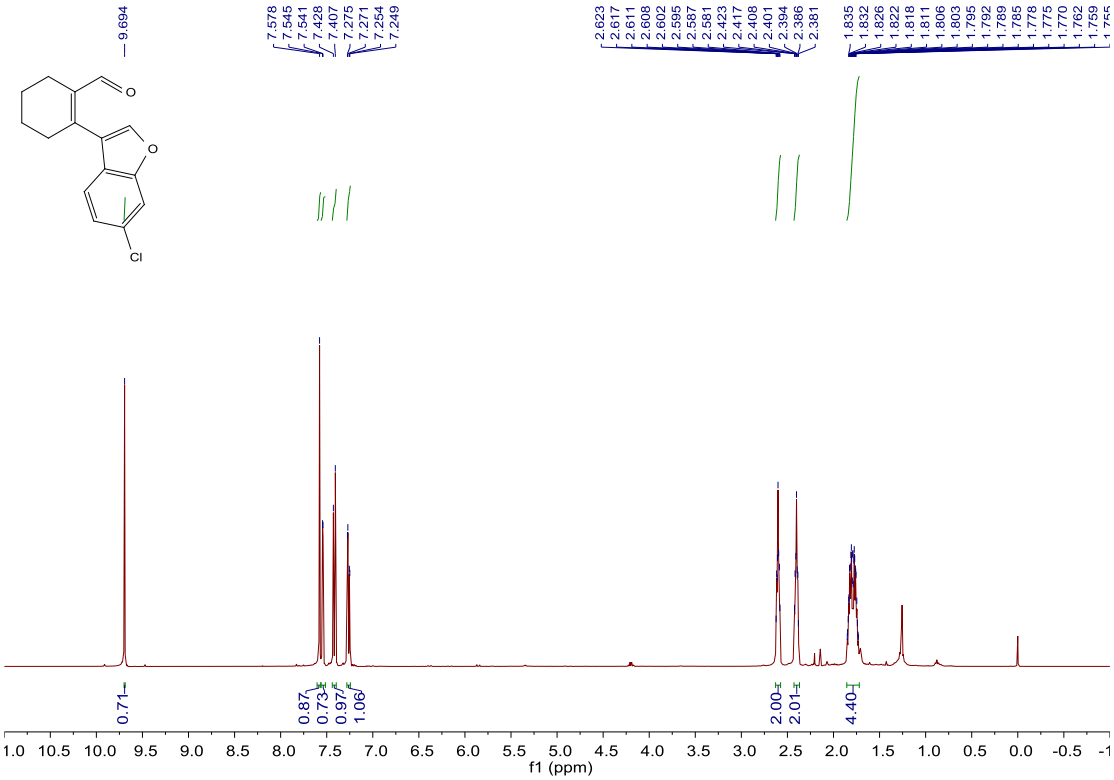

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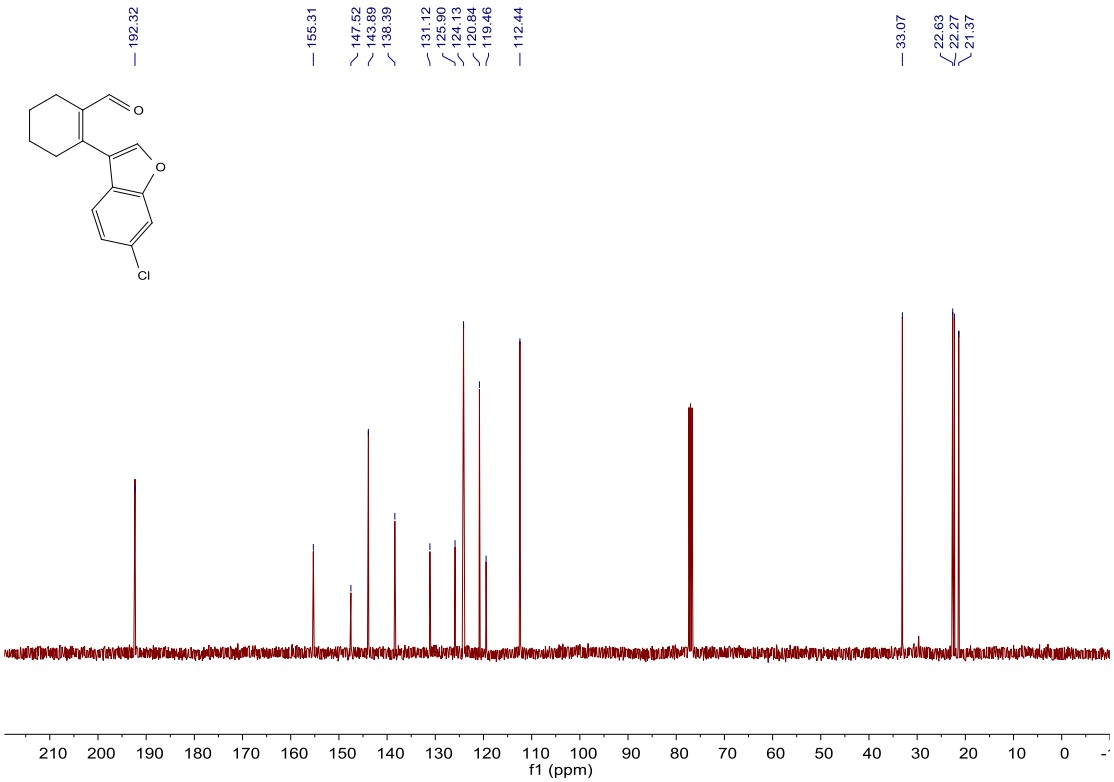

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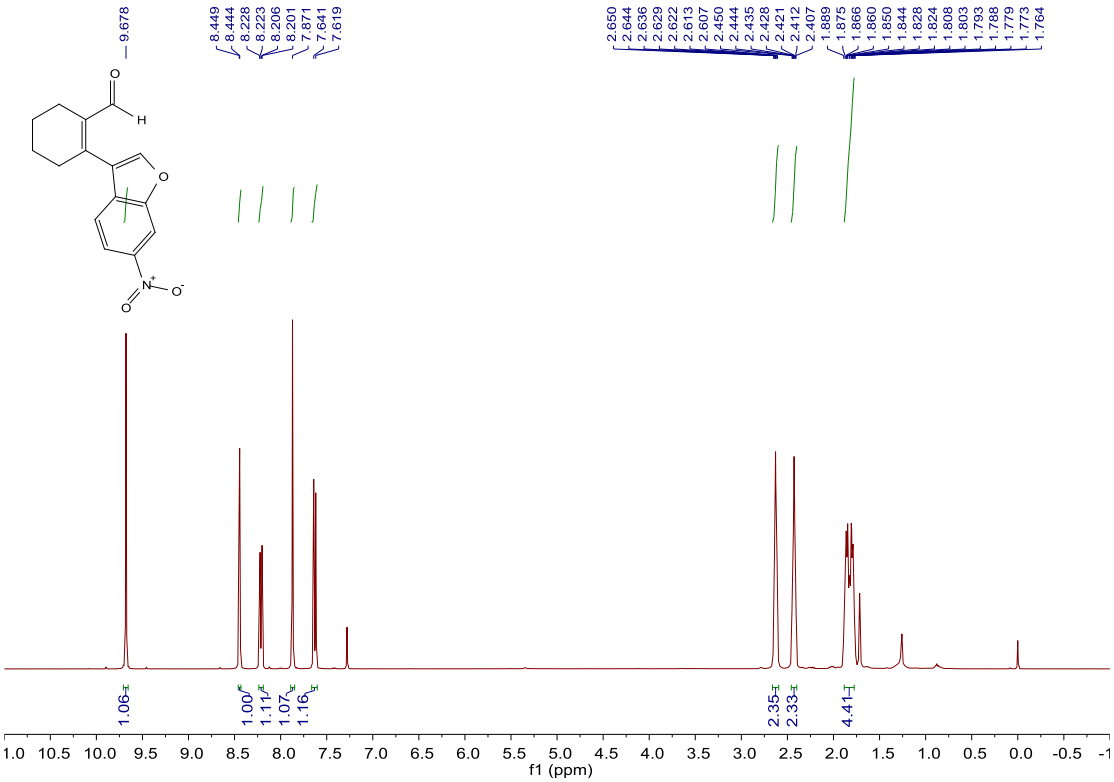

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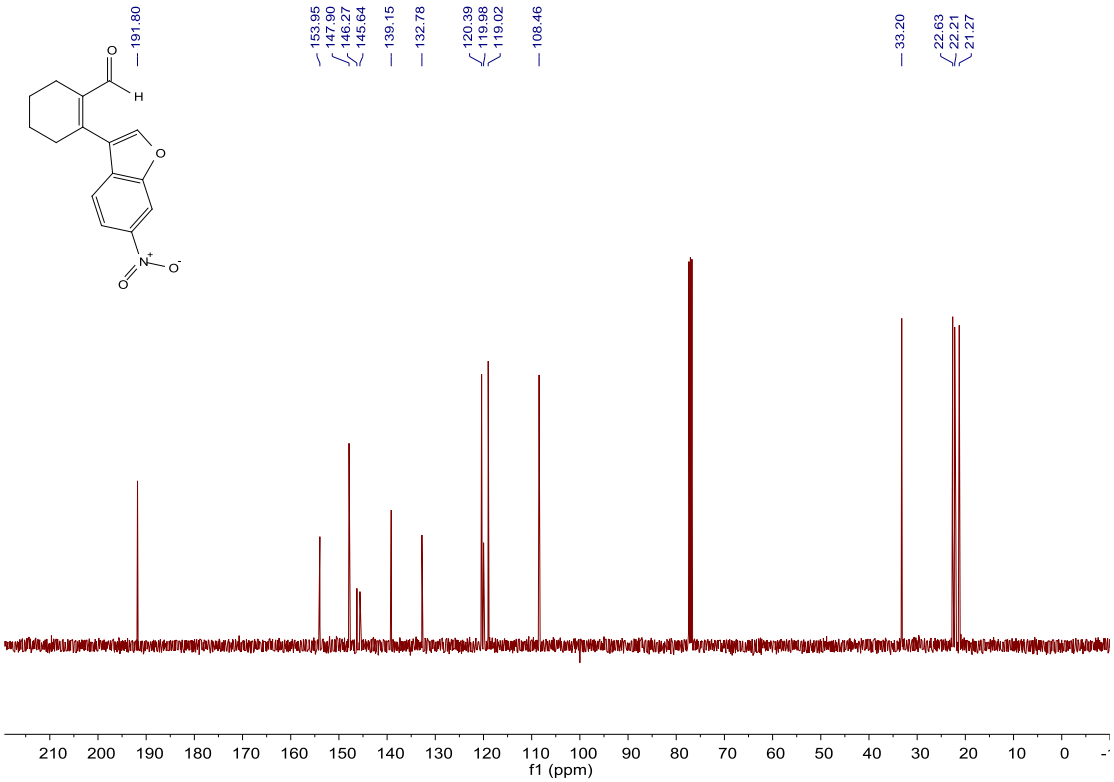
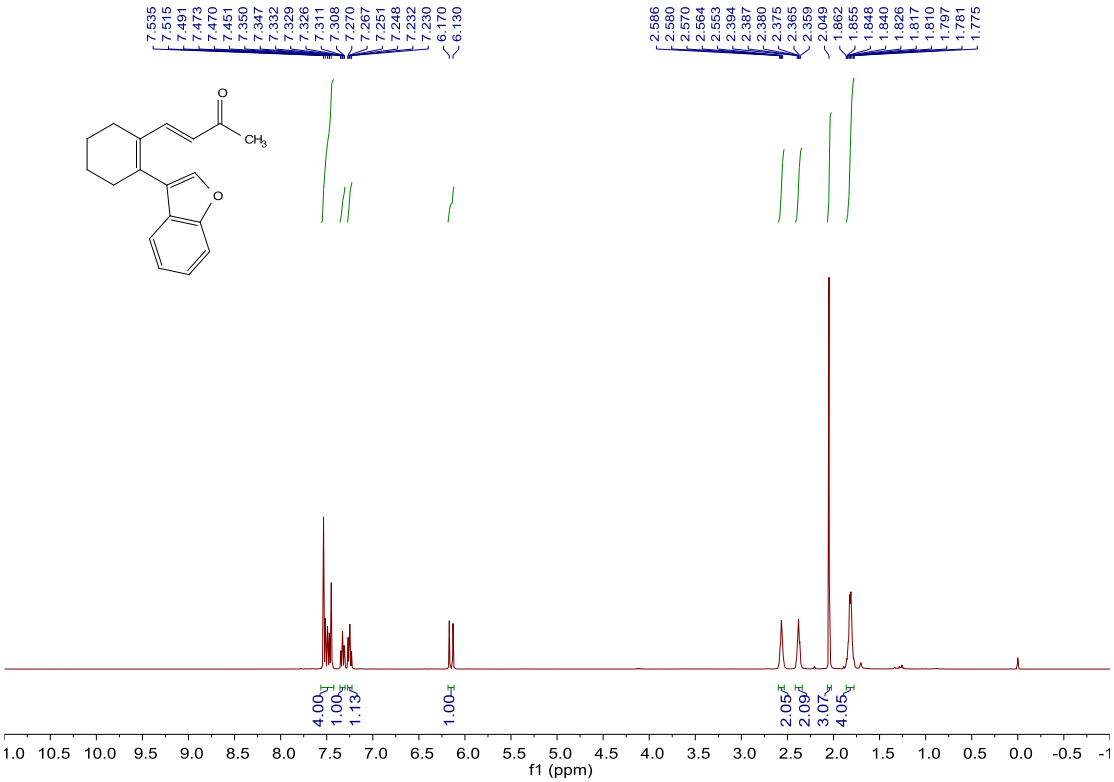
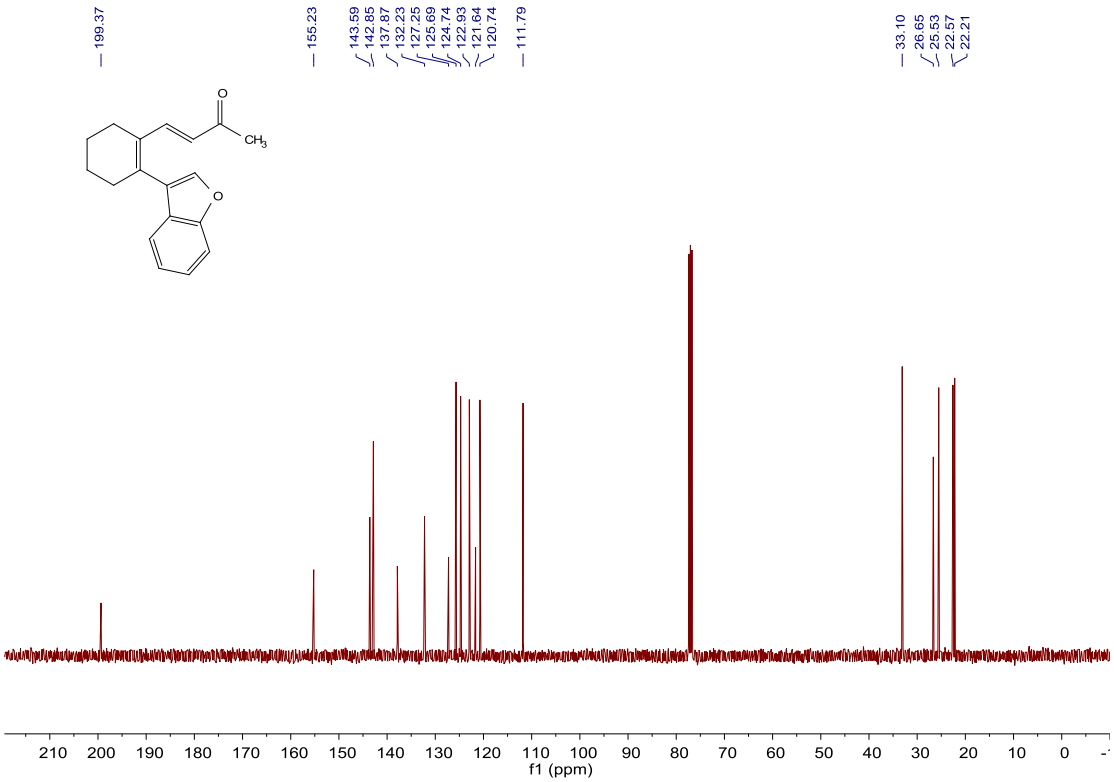


^{1}H NMR of 1a



^{13}C NMR of 1a



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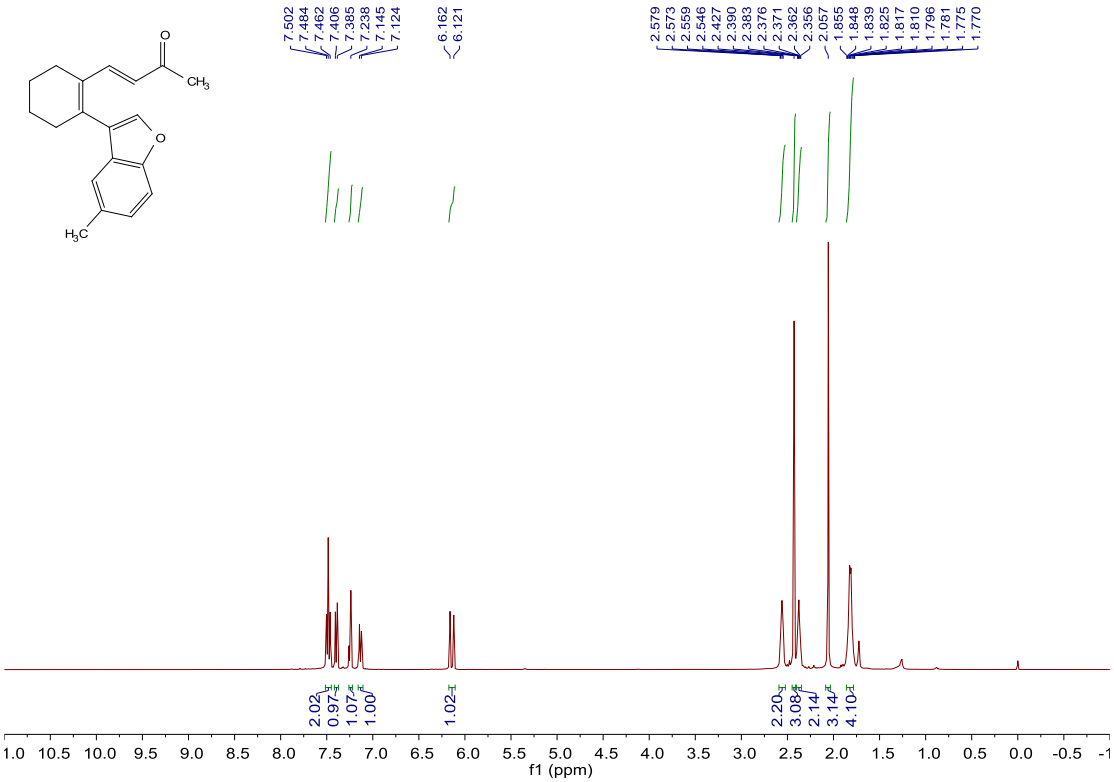

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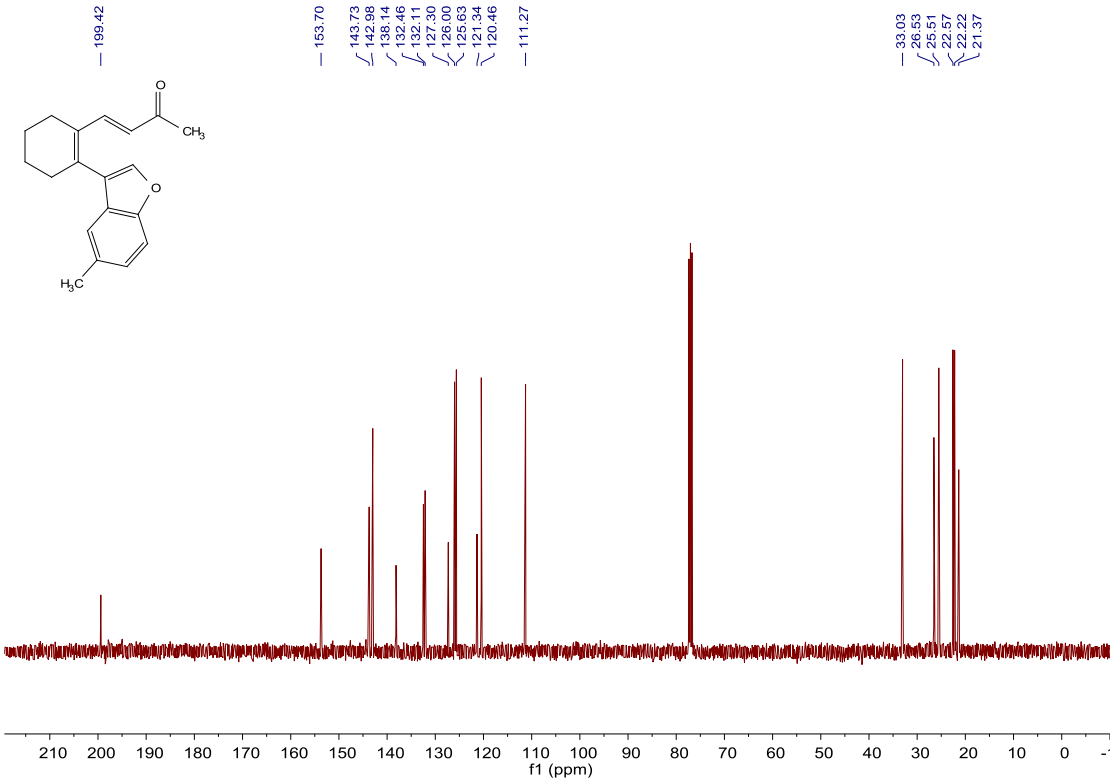

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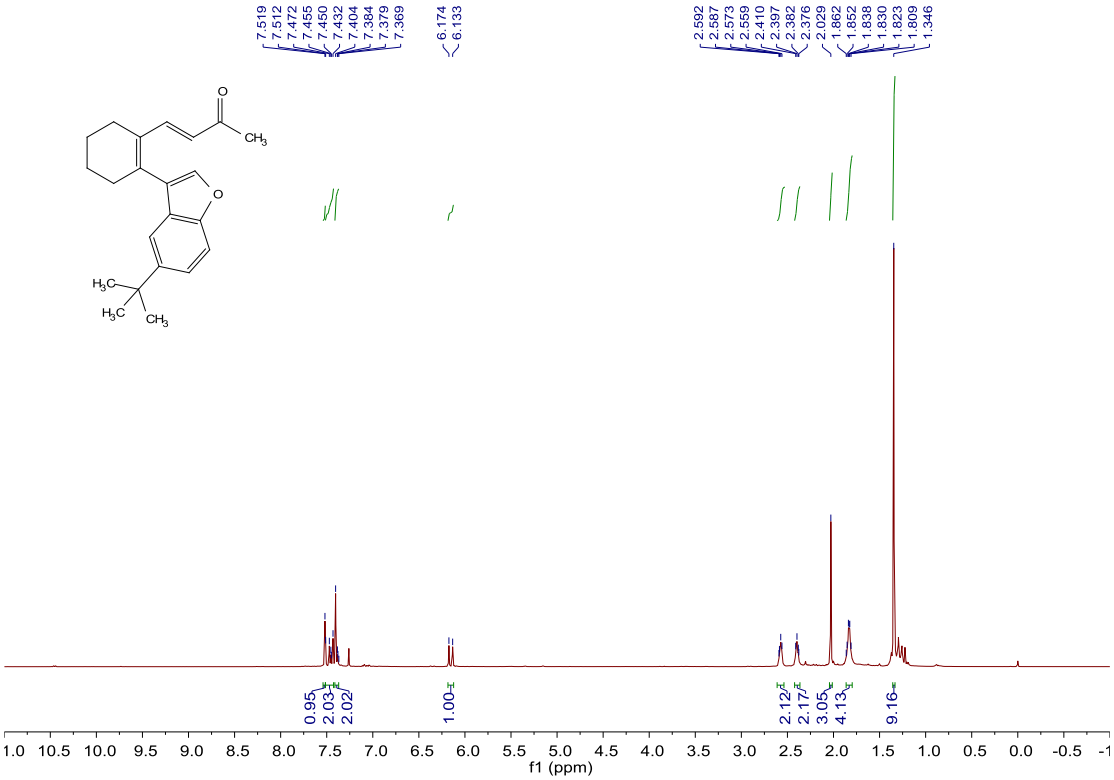

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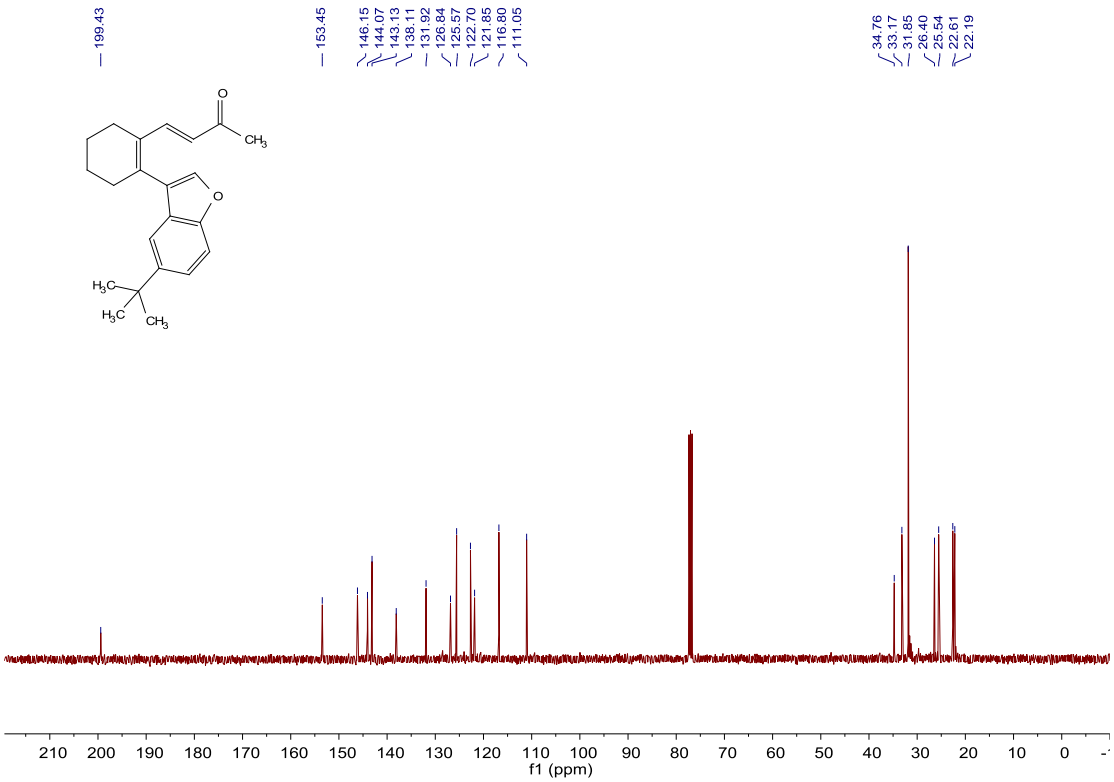

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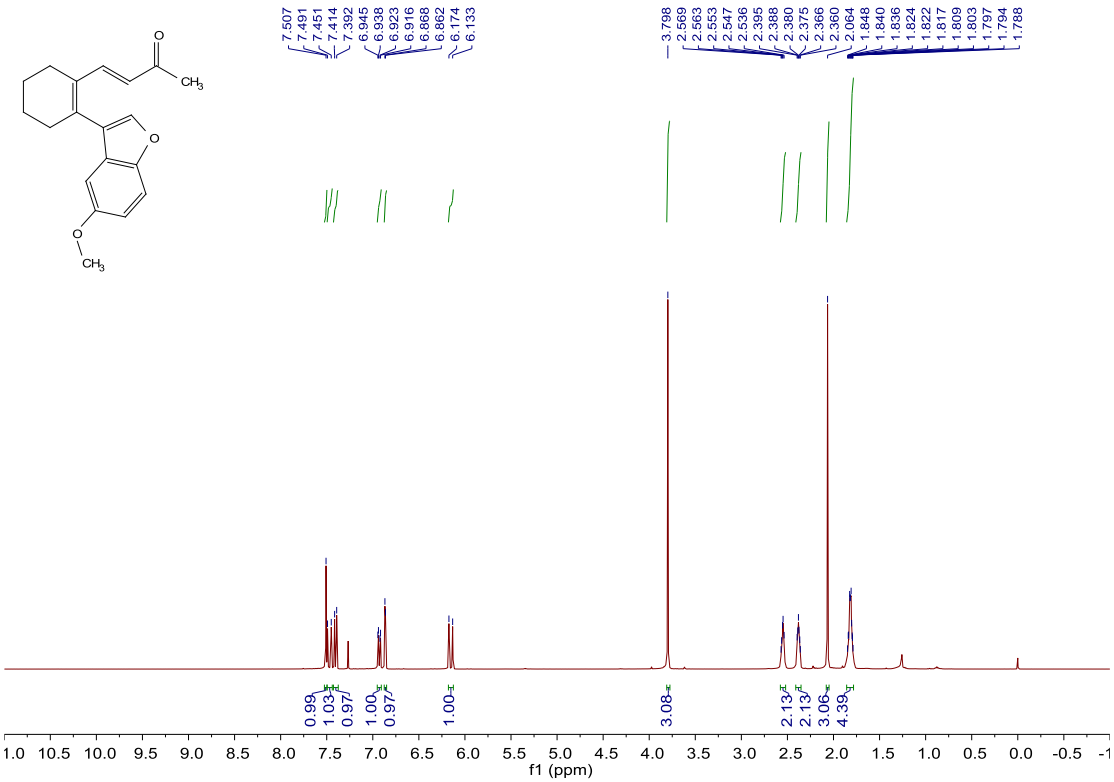

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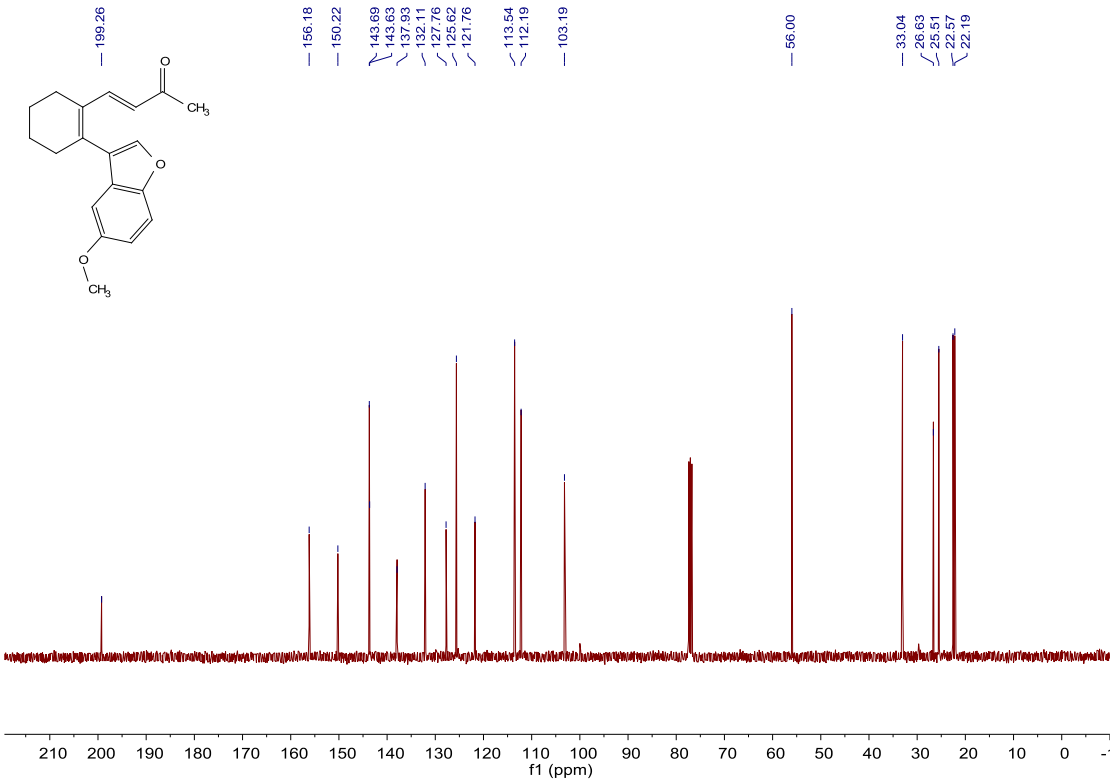

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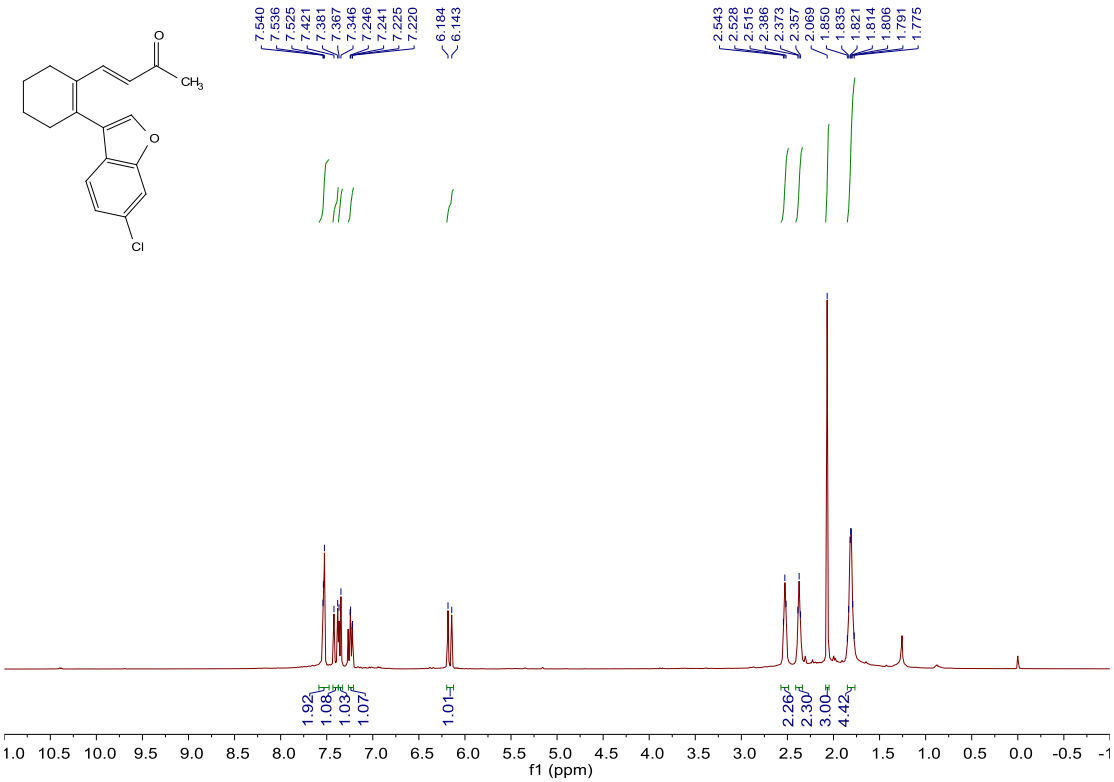

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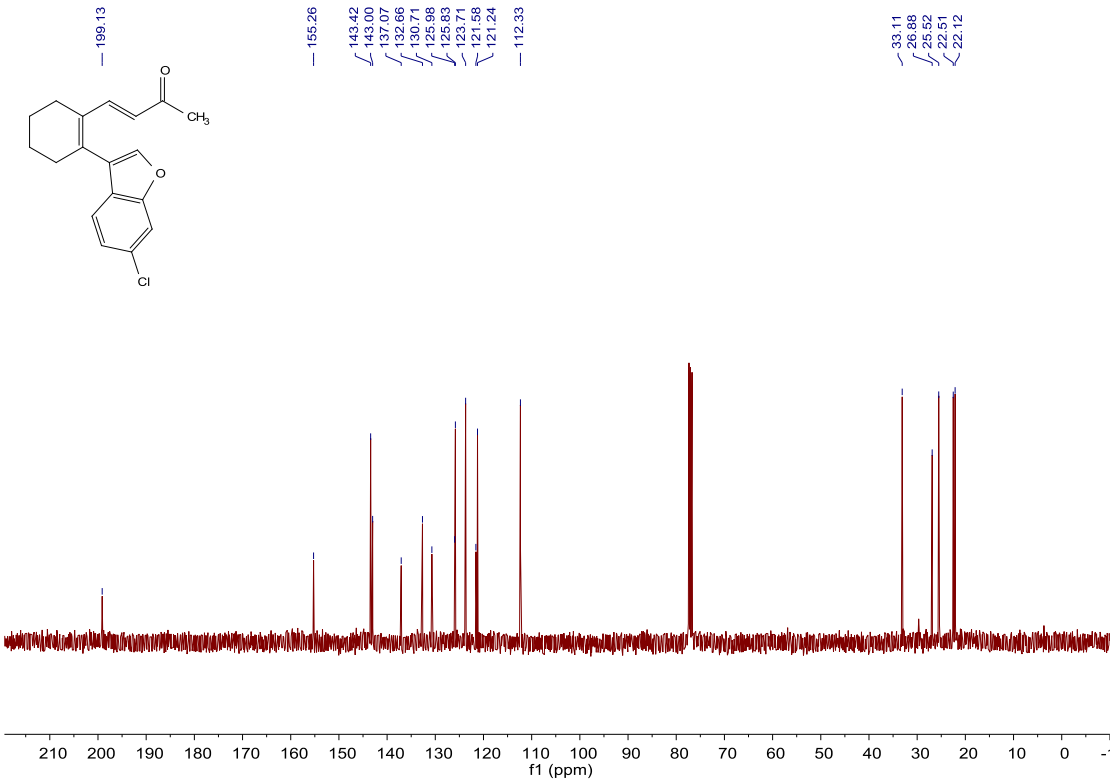

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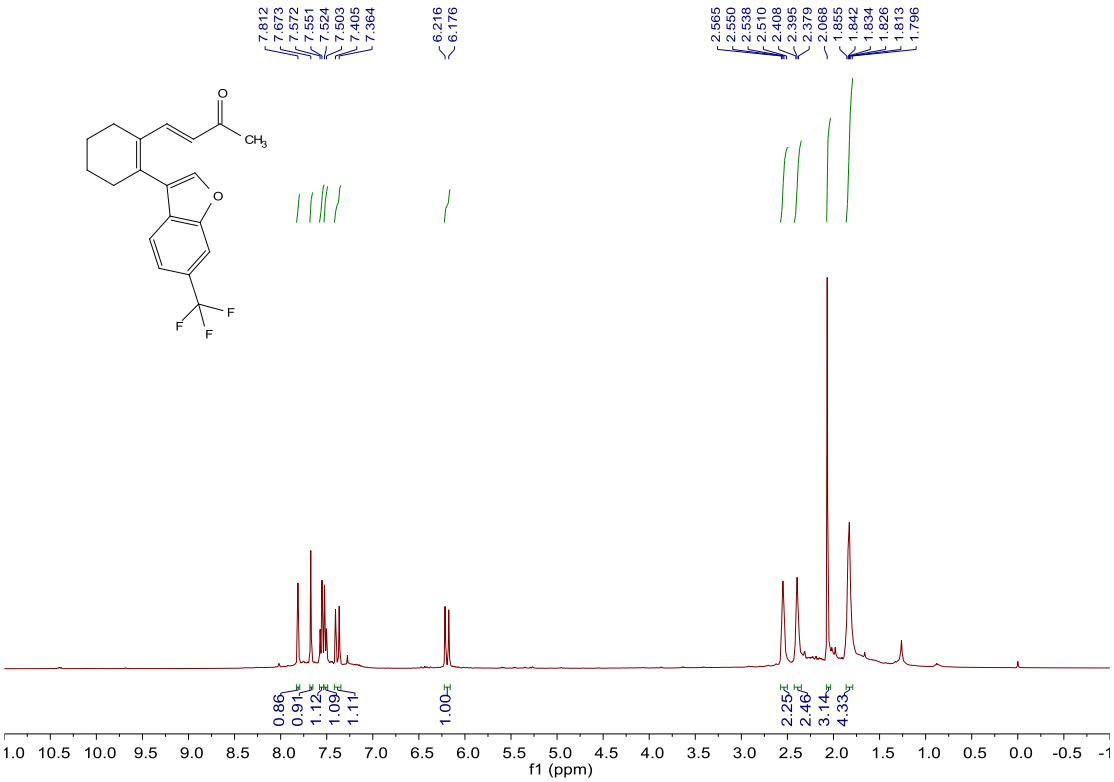

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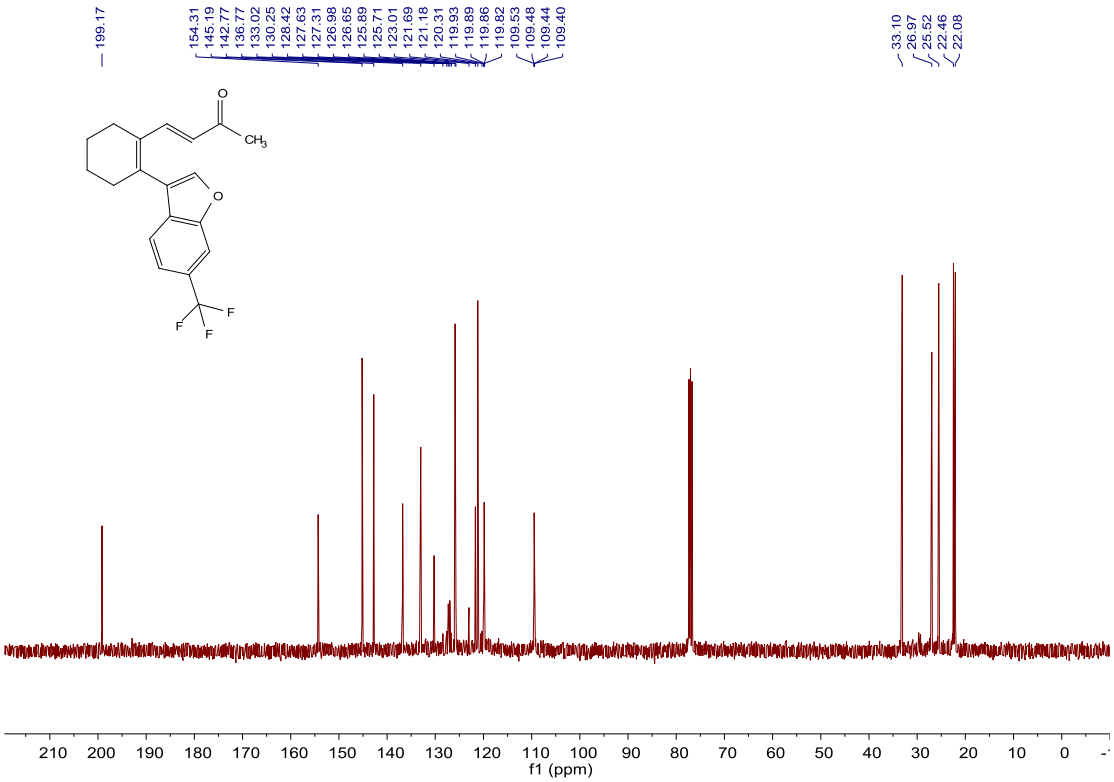

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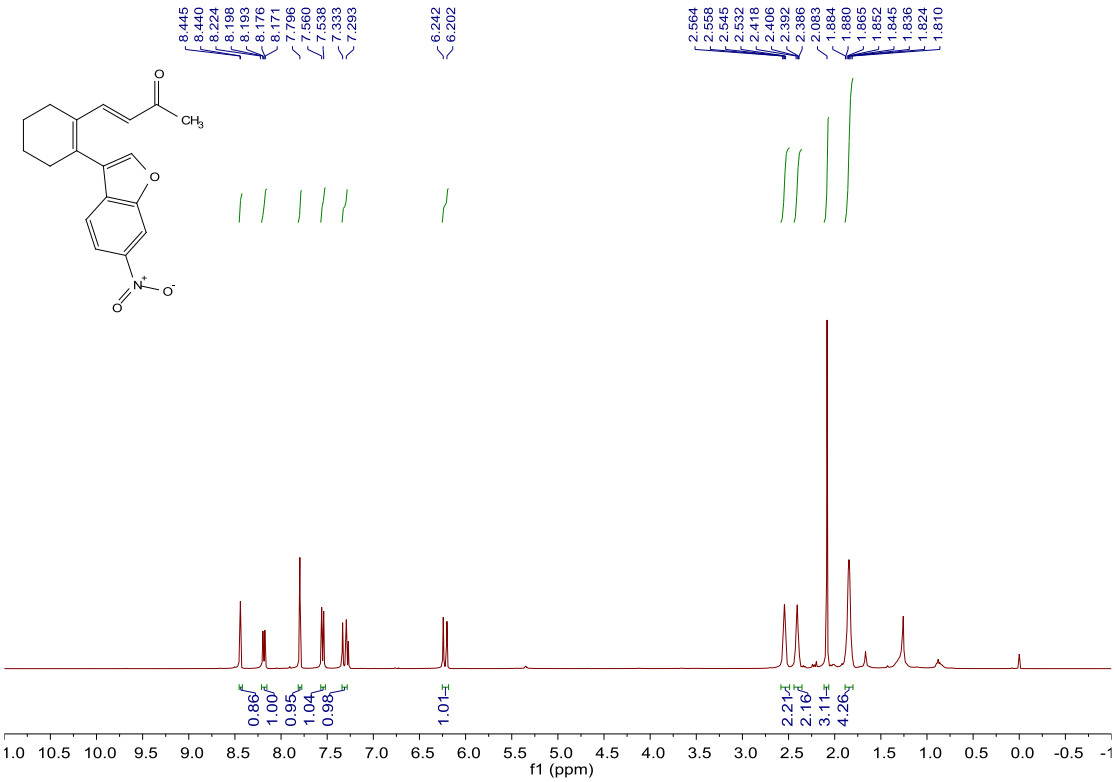

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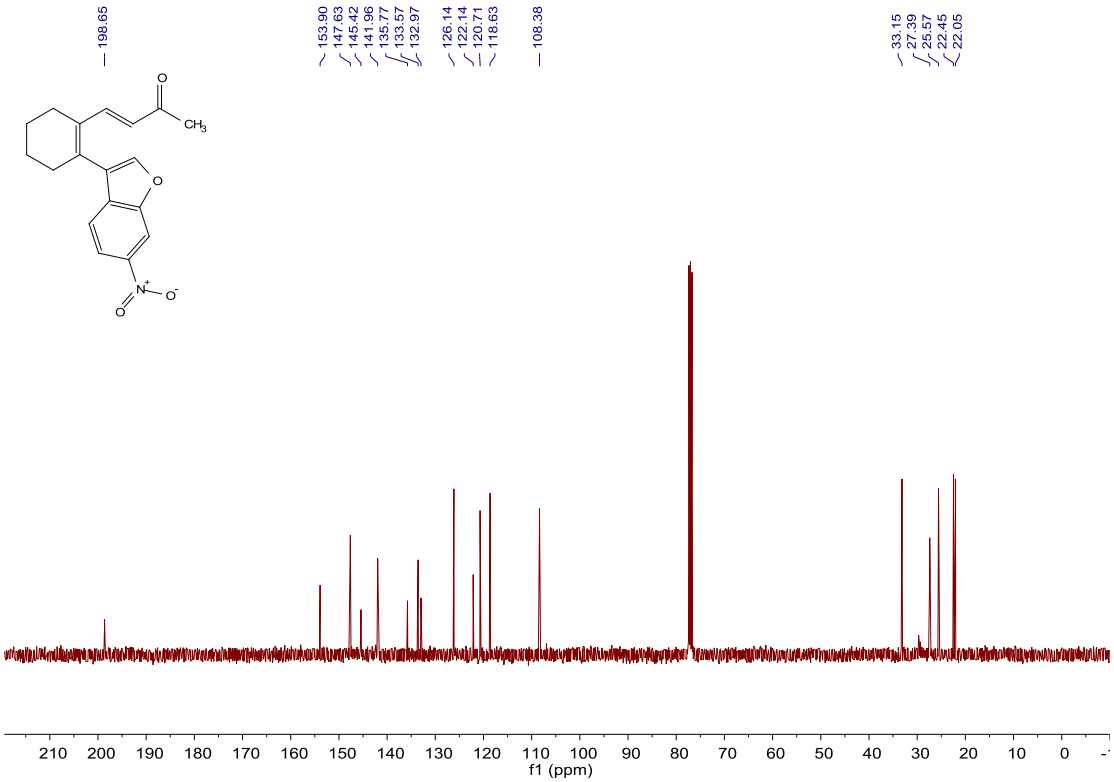

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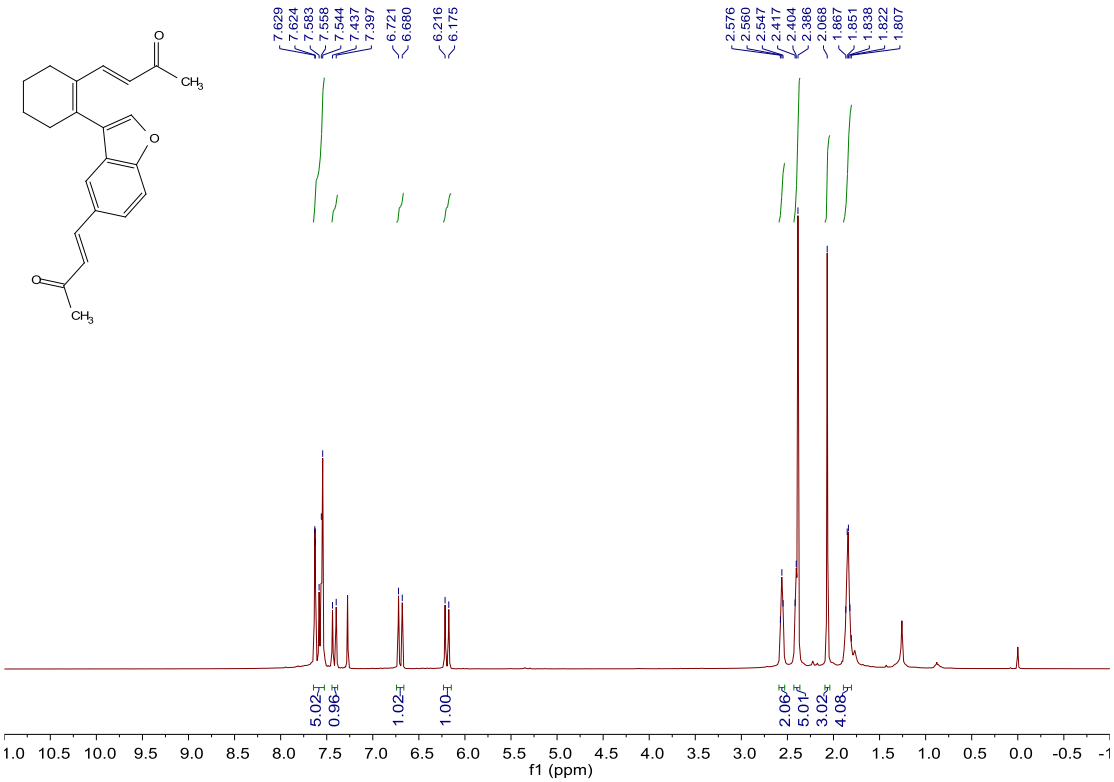

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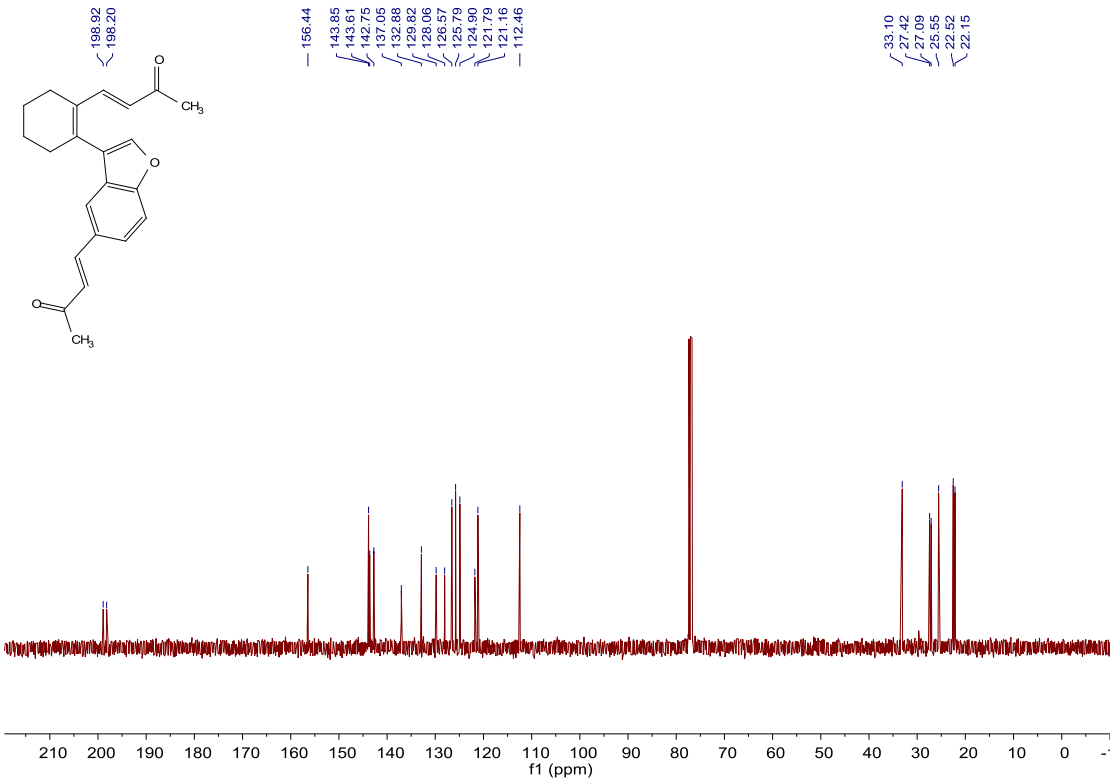

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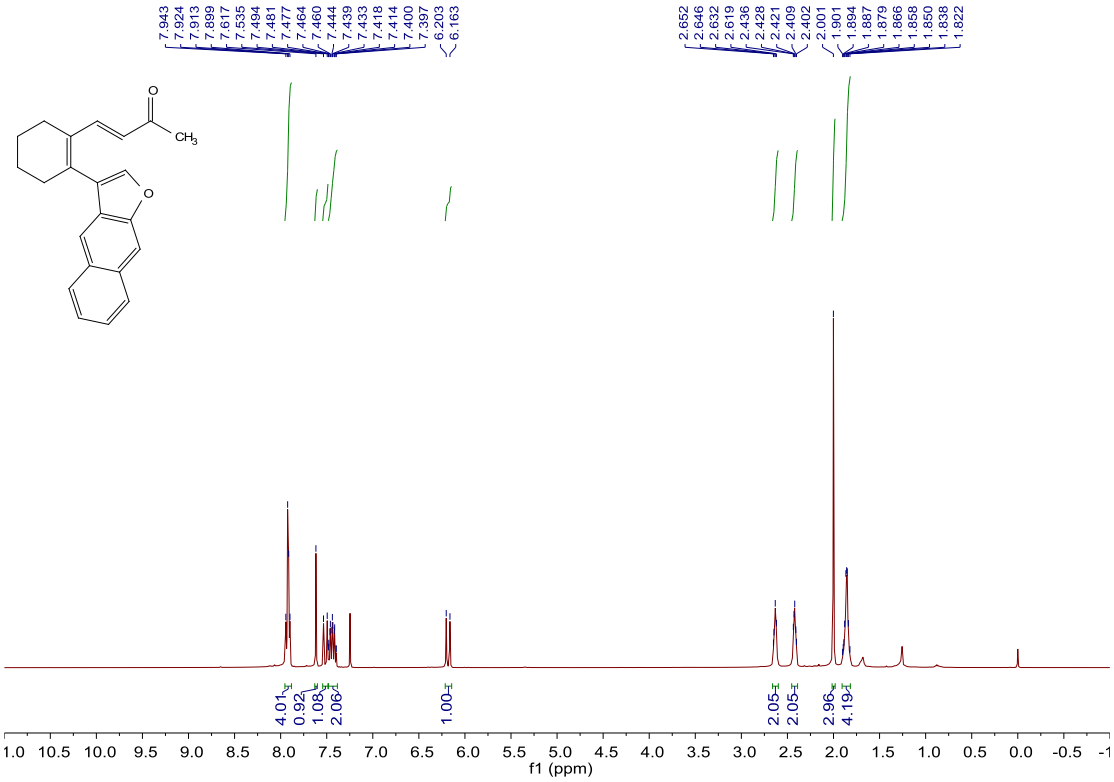

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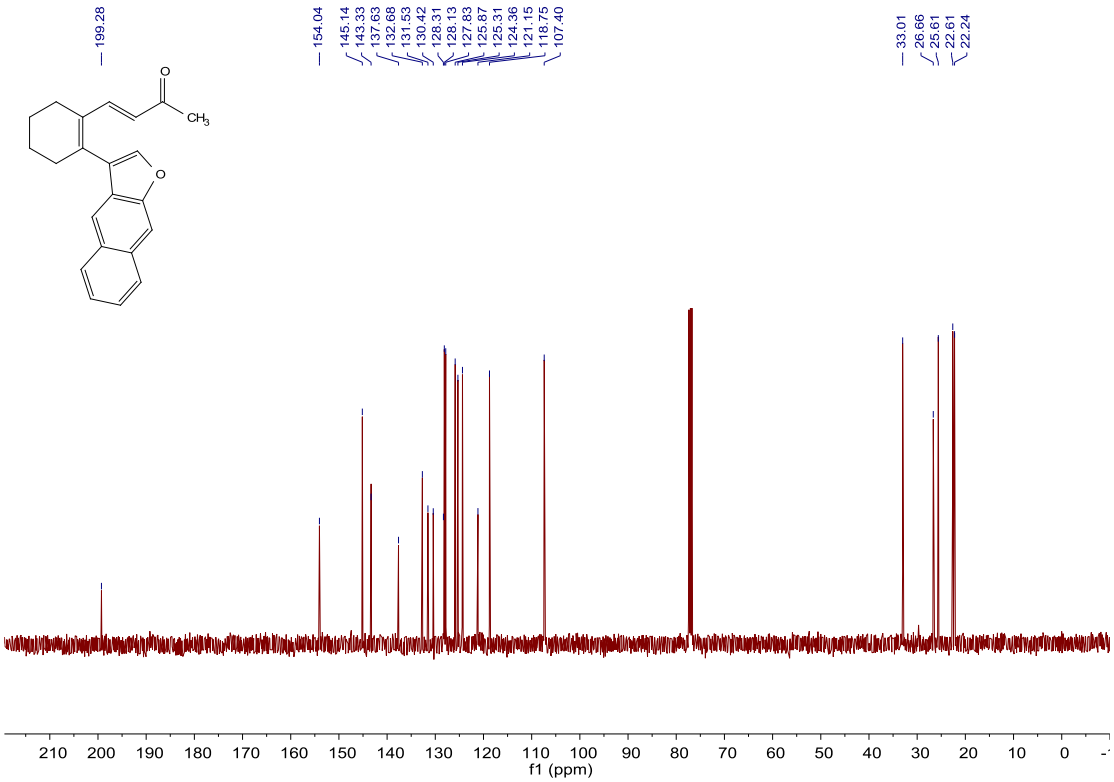

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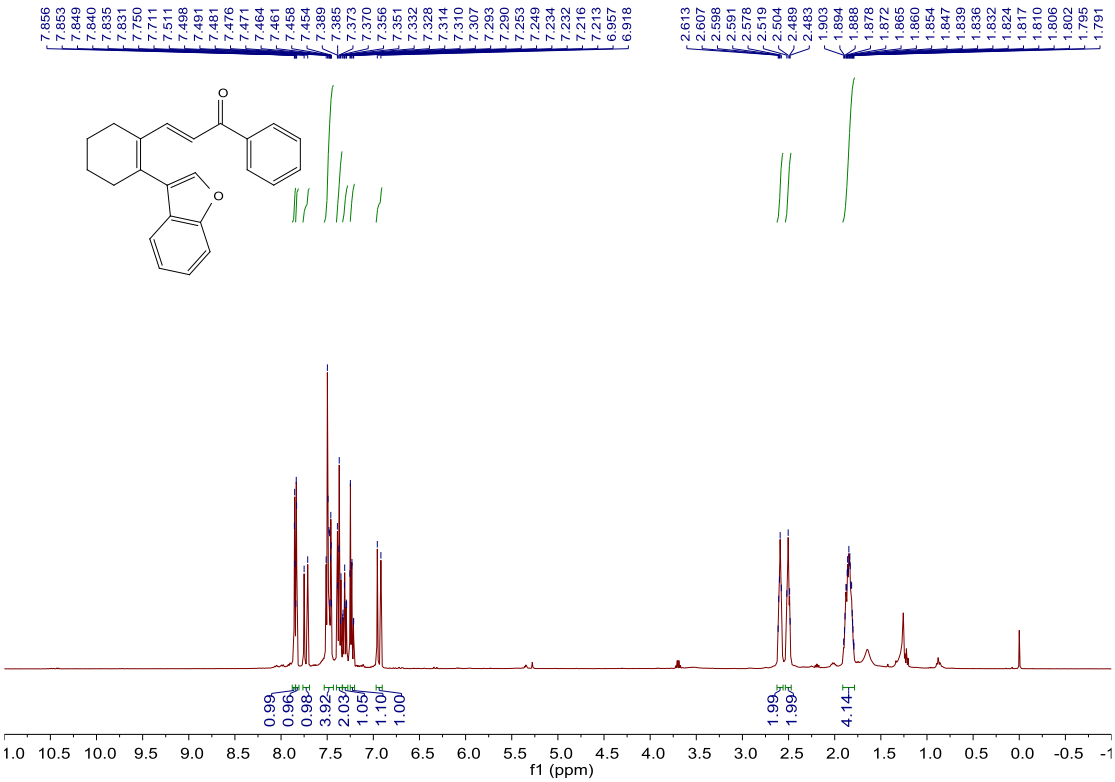

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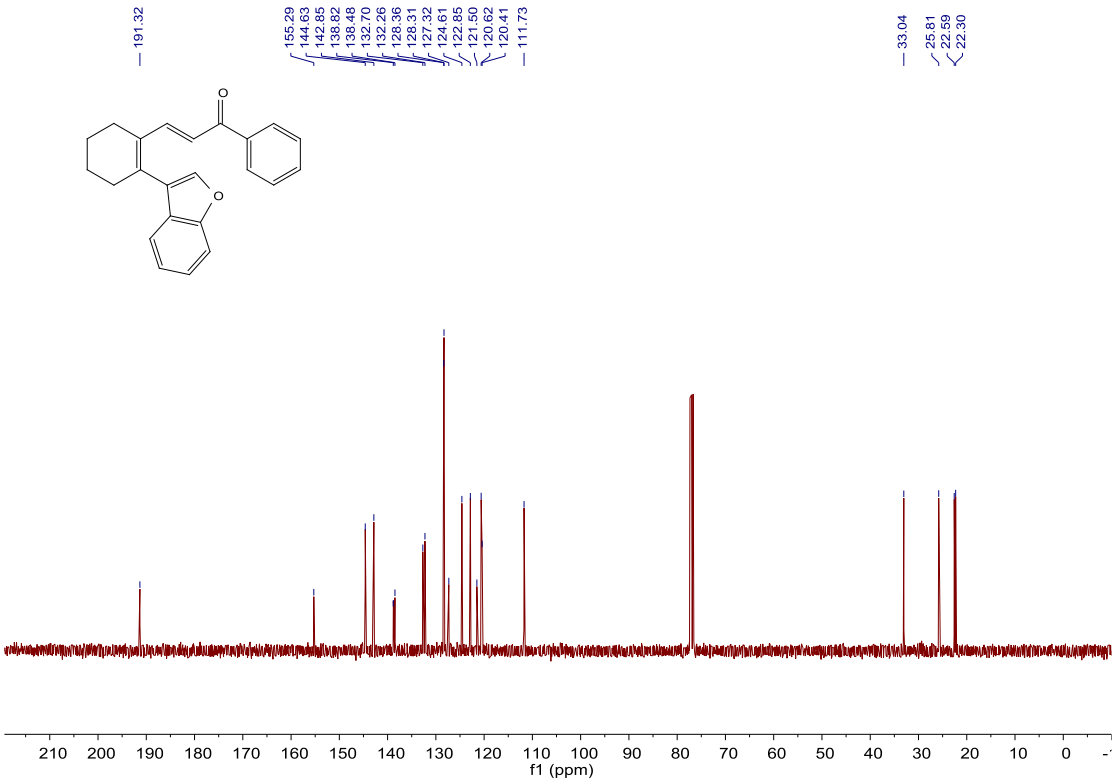

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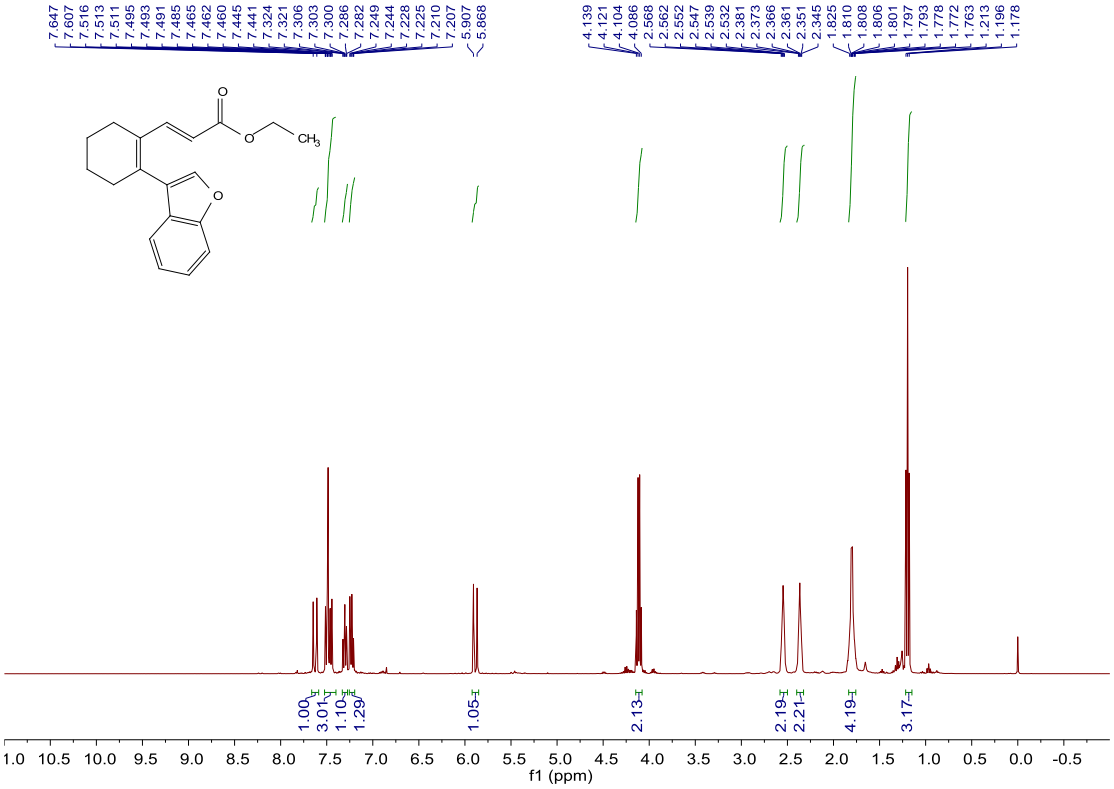

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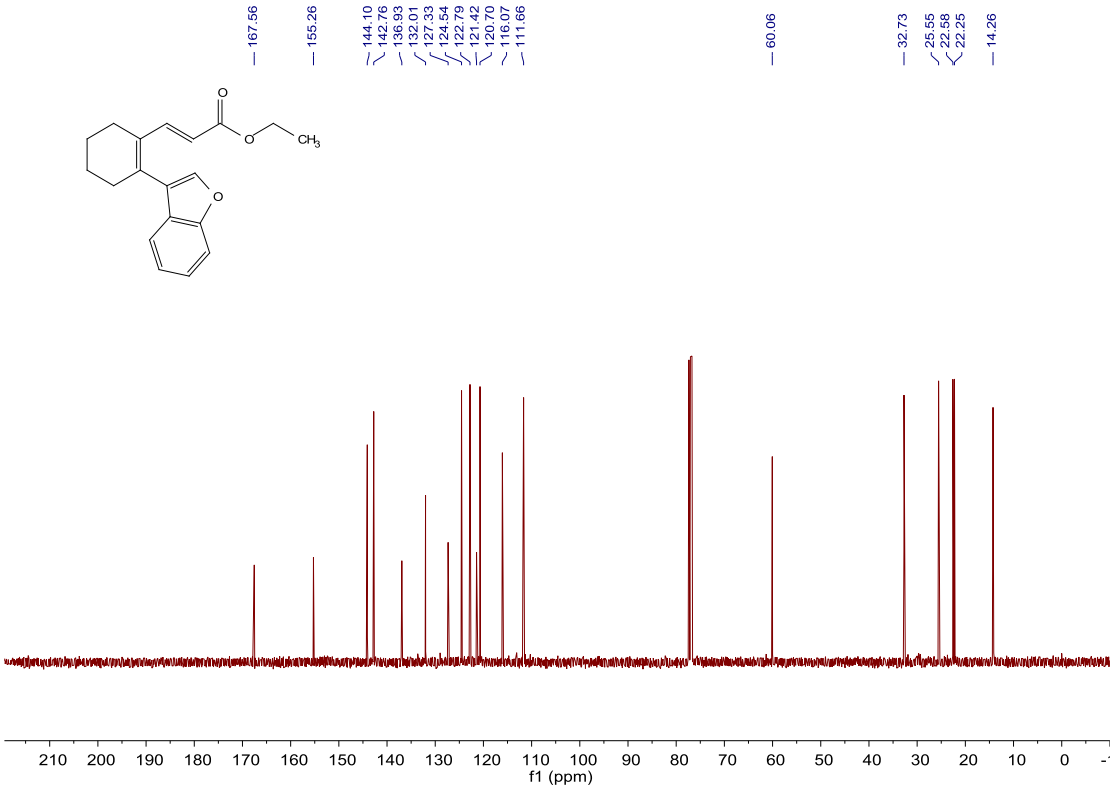

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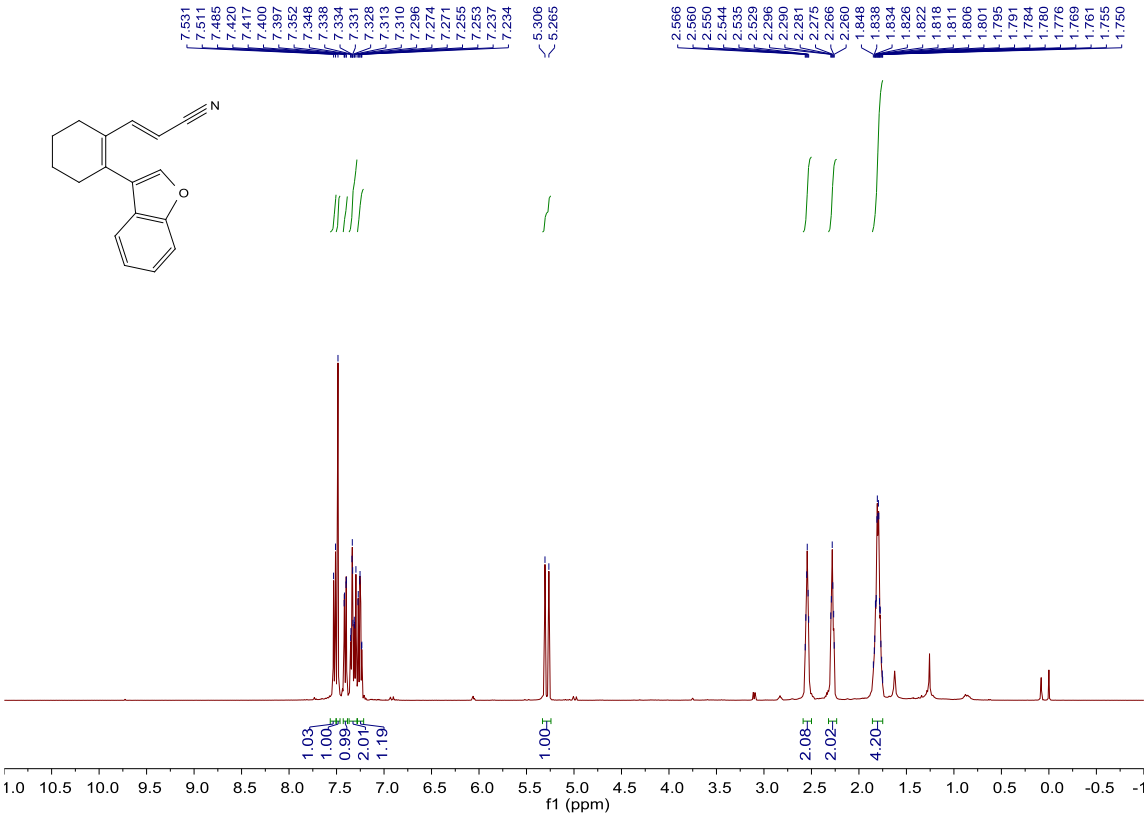

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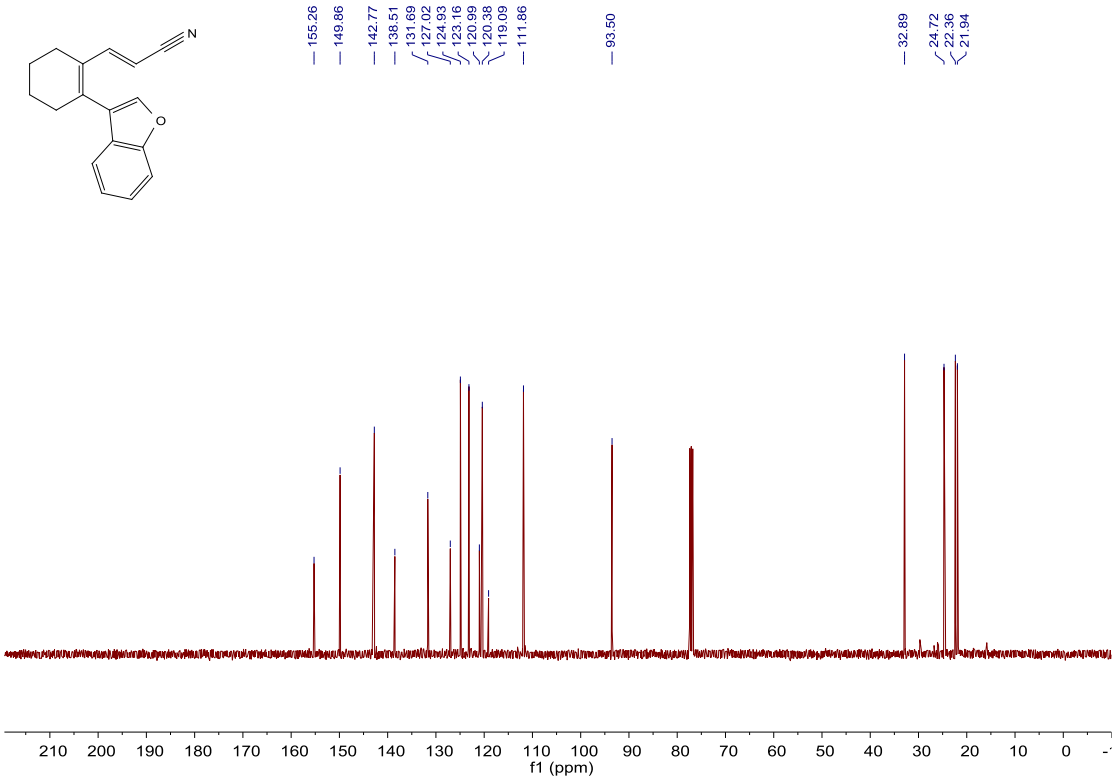

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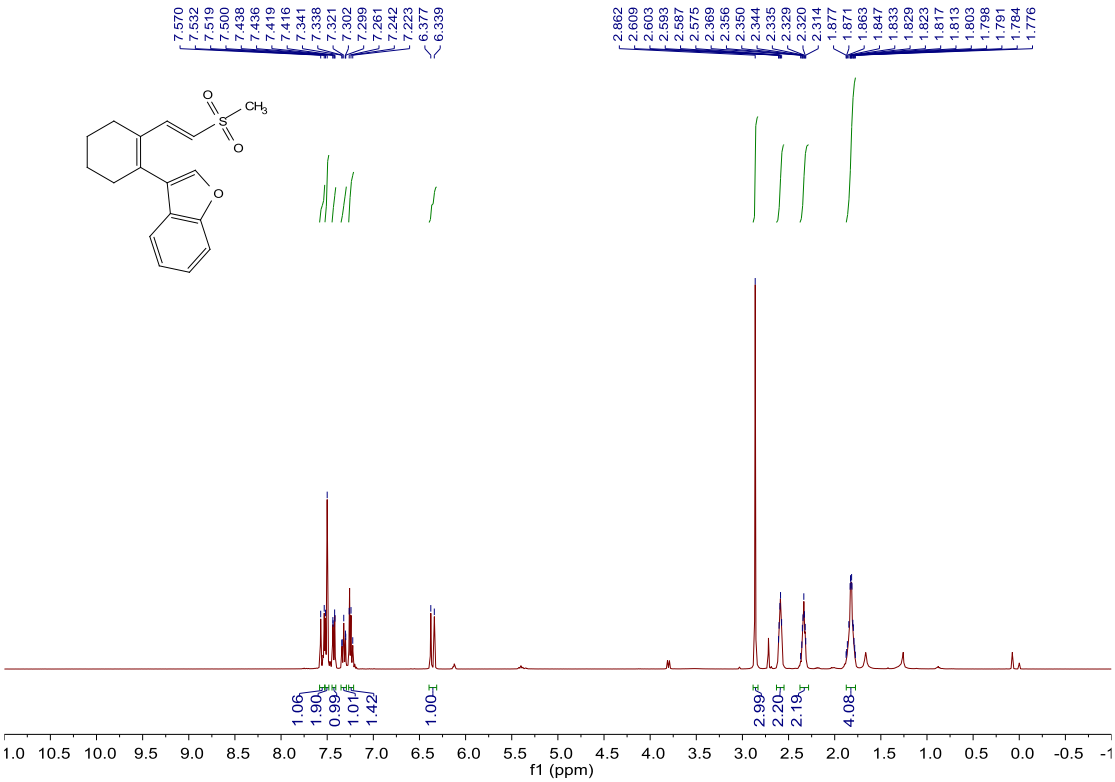

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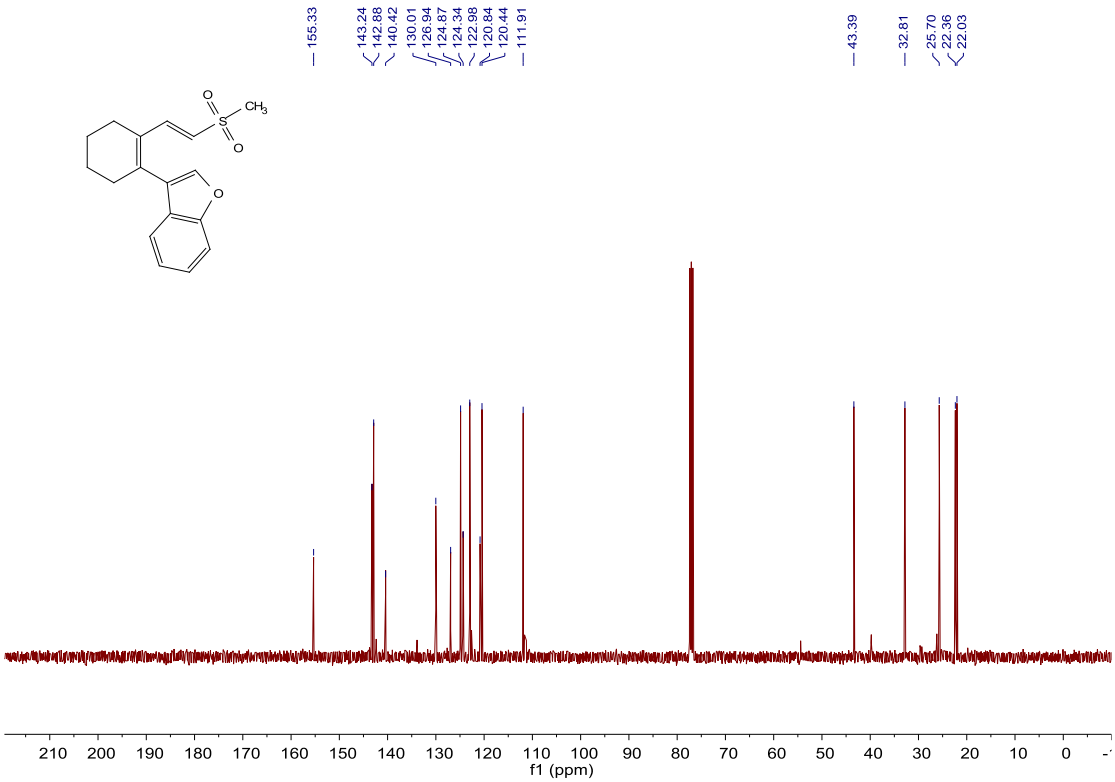

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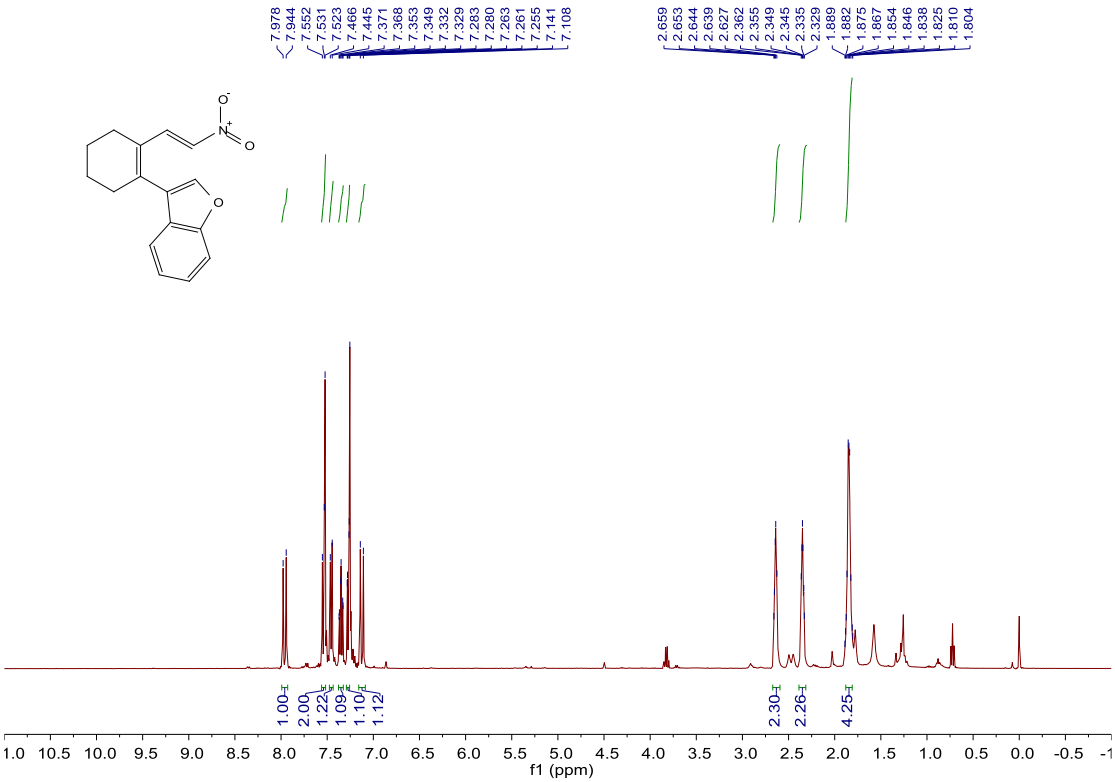

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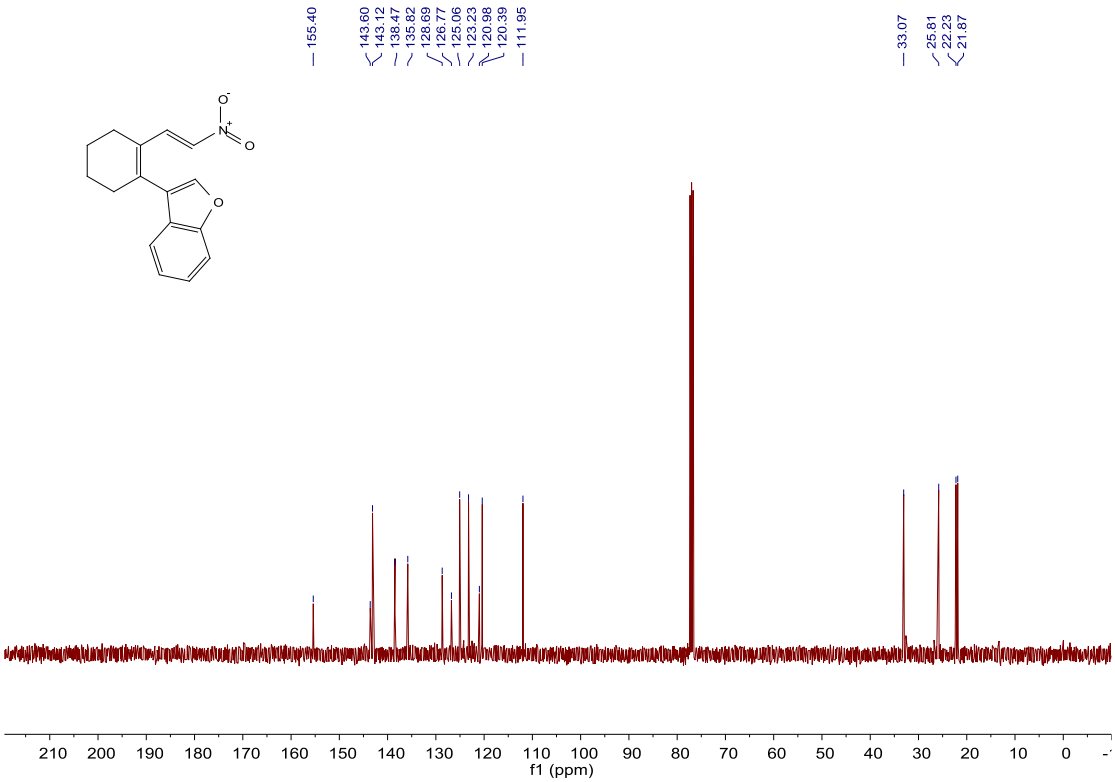

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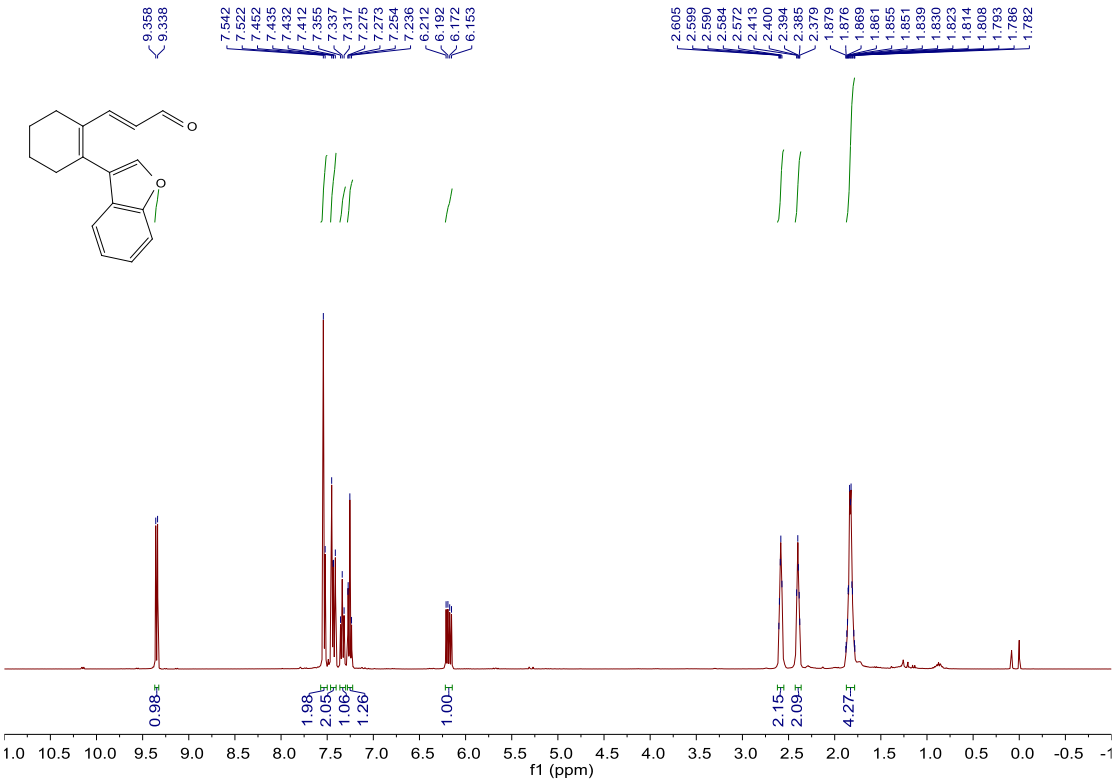

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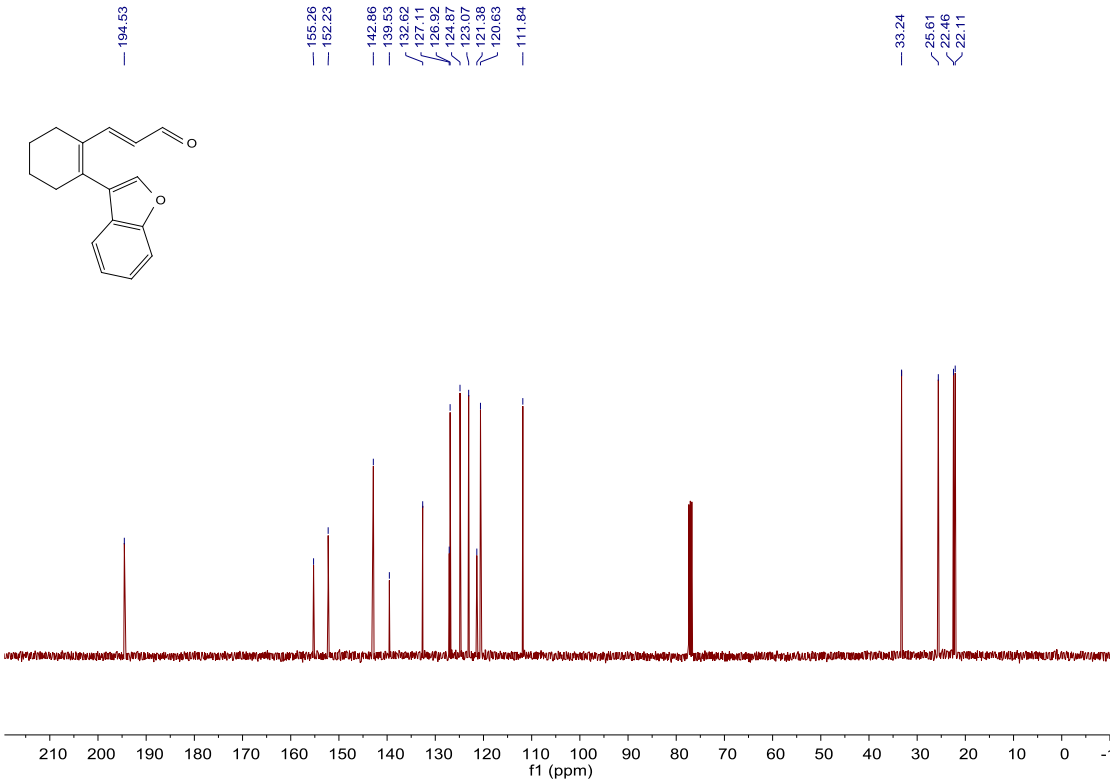
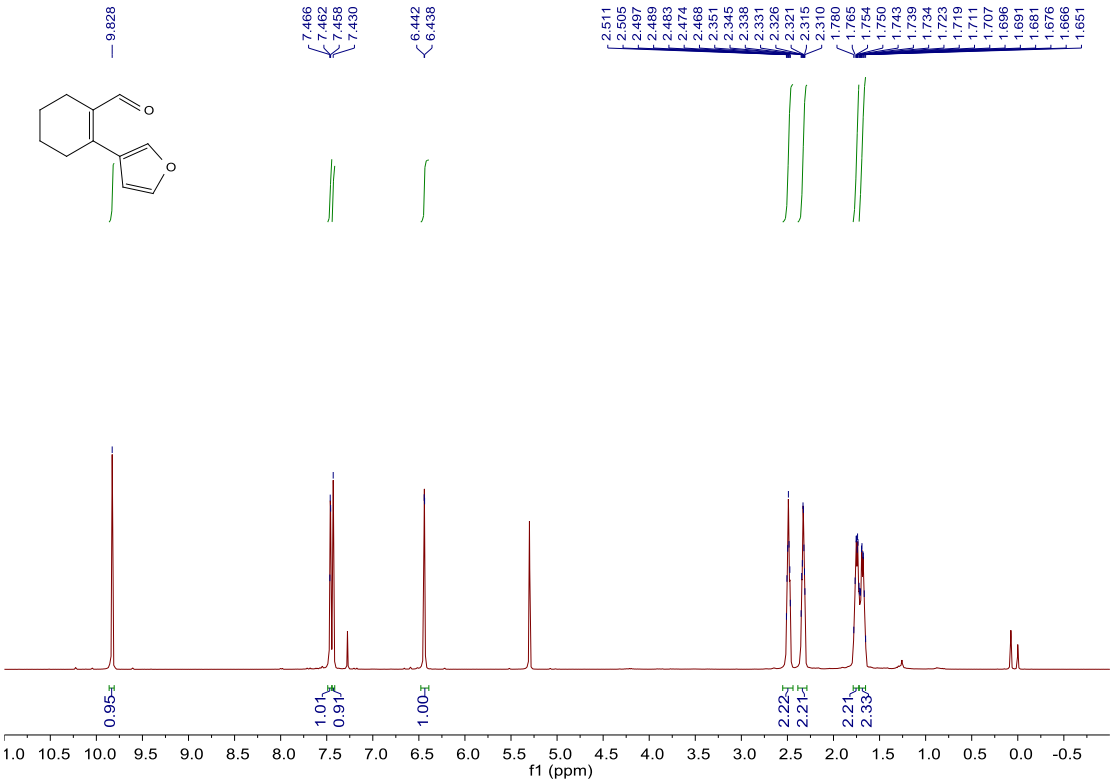


^{1}H NMR of In5-1p



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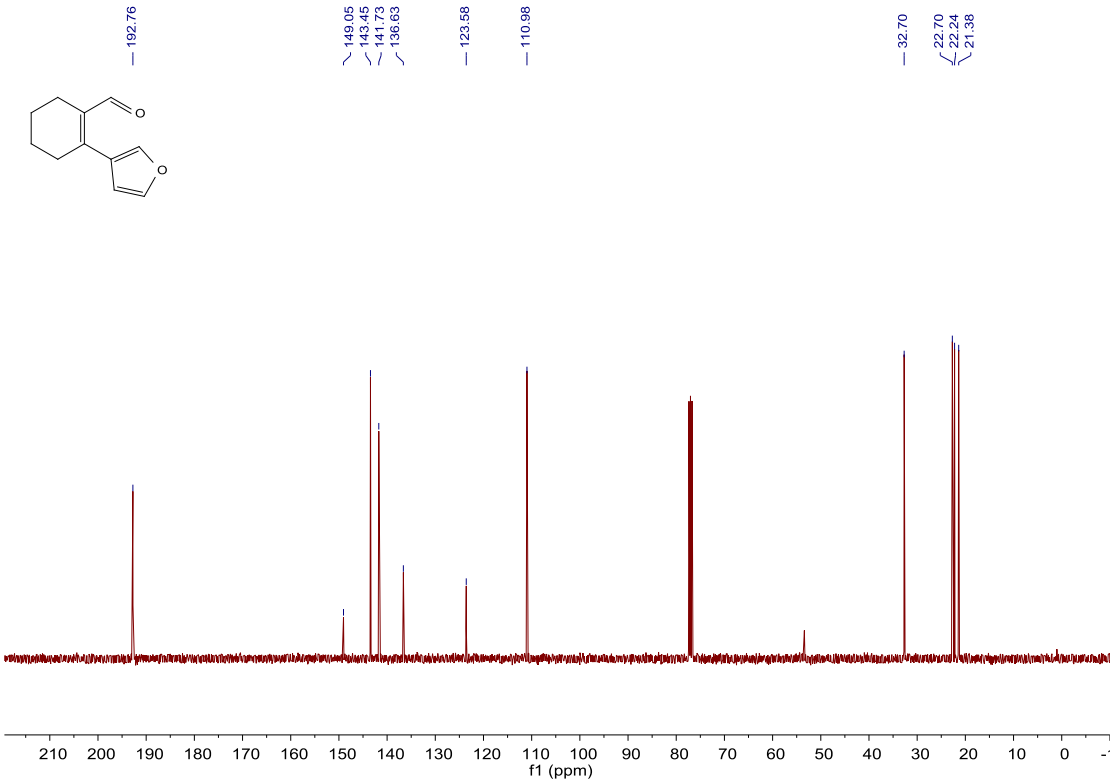

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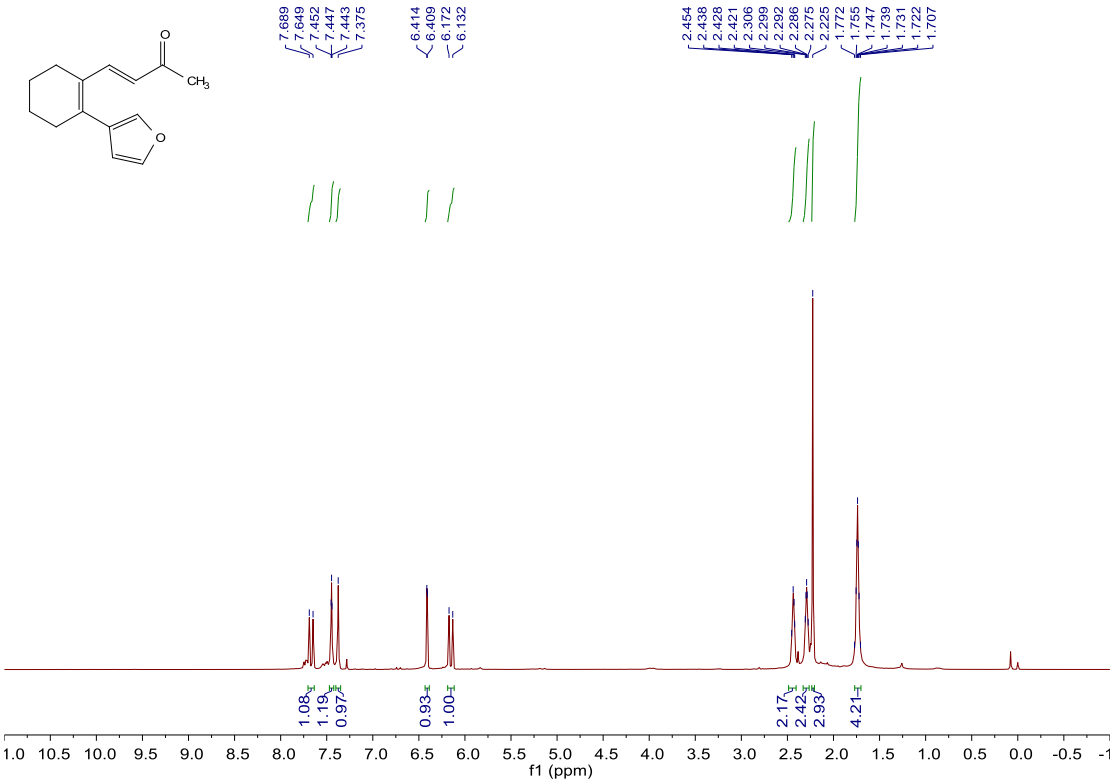

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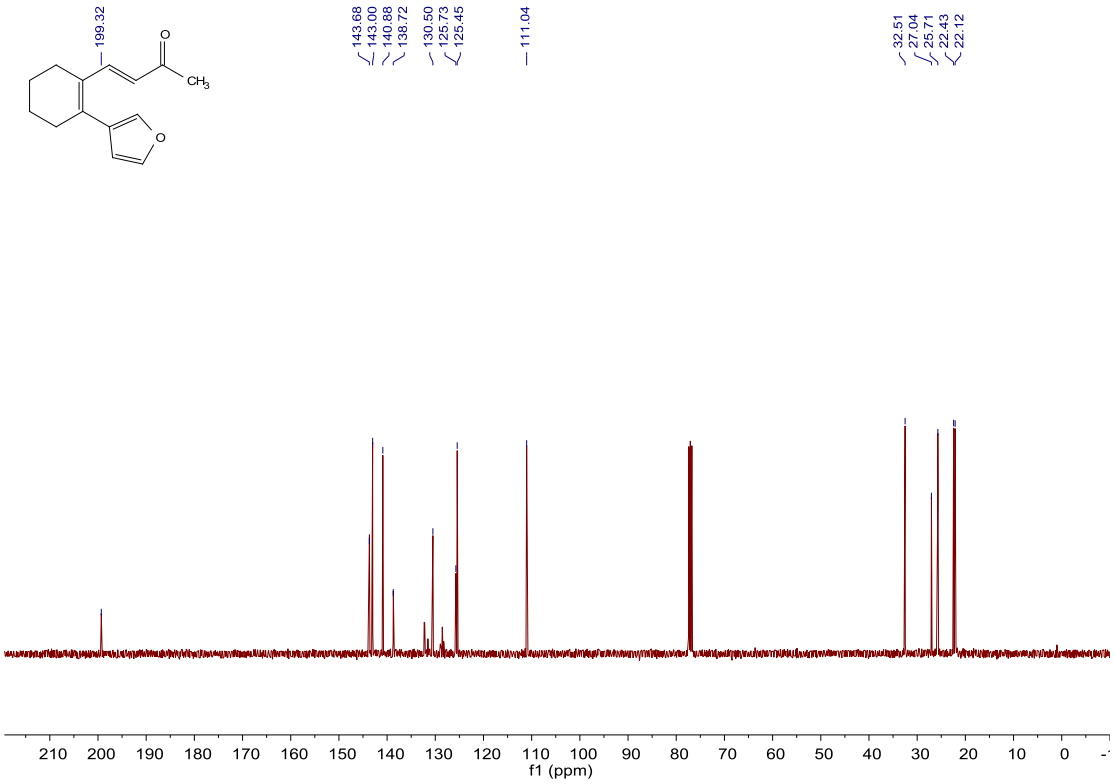
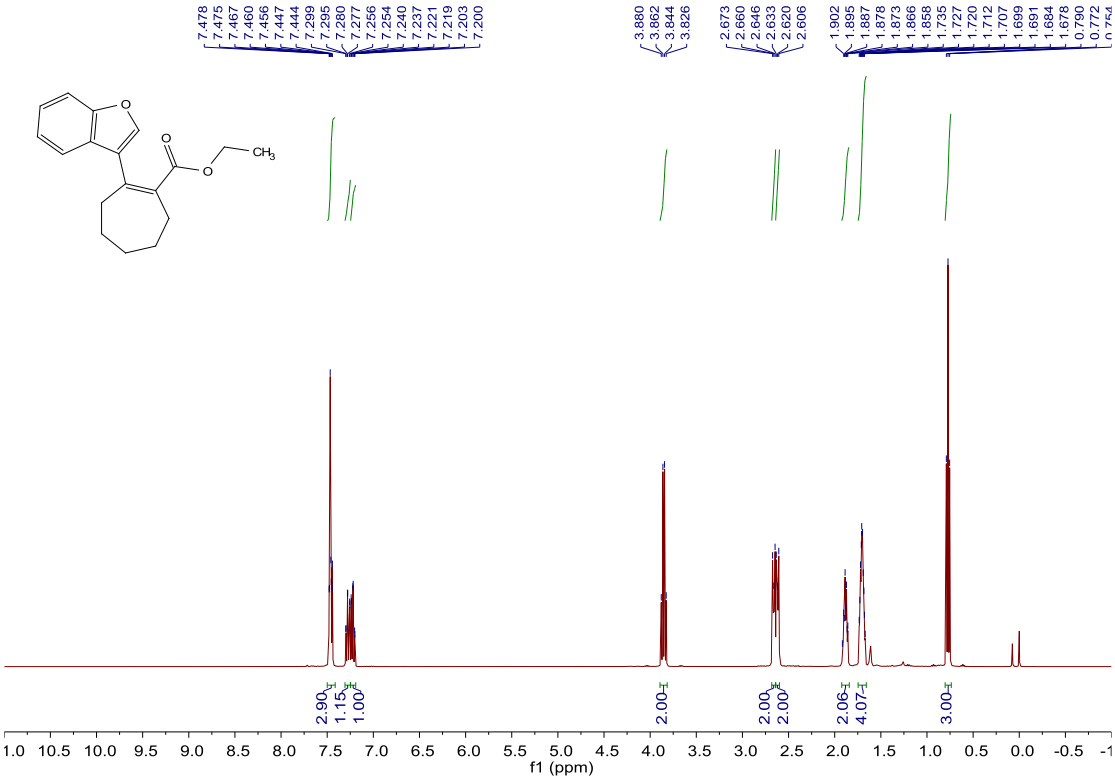


^{1}H NMR of In6-1q



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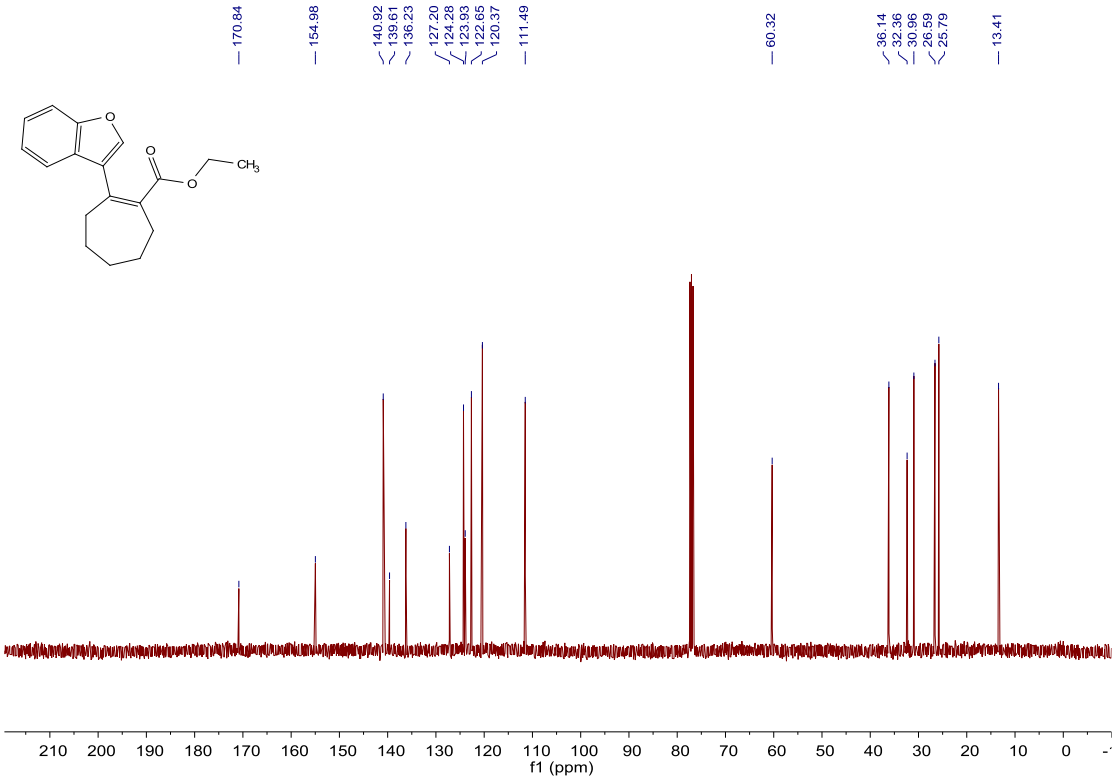
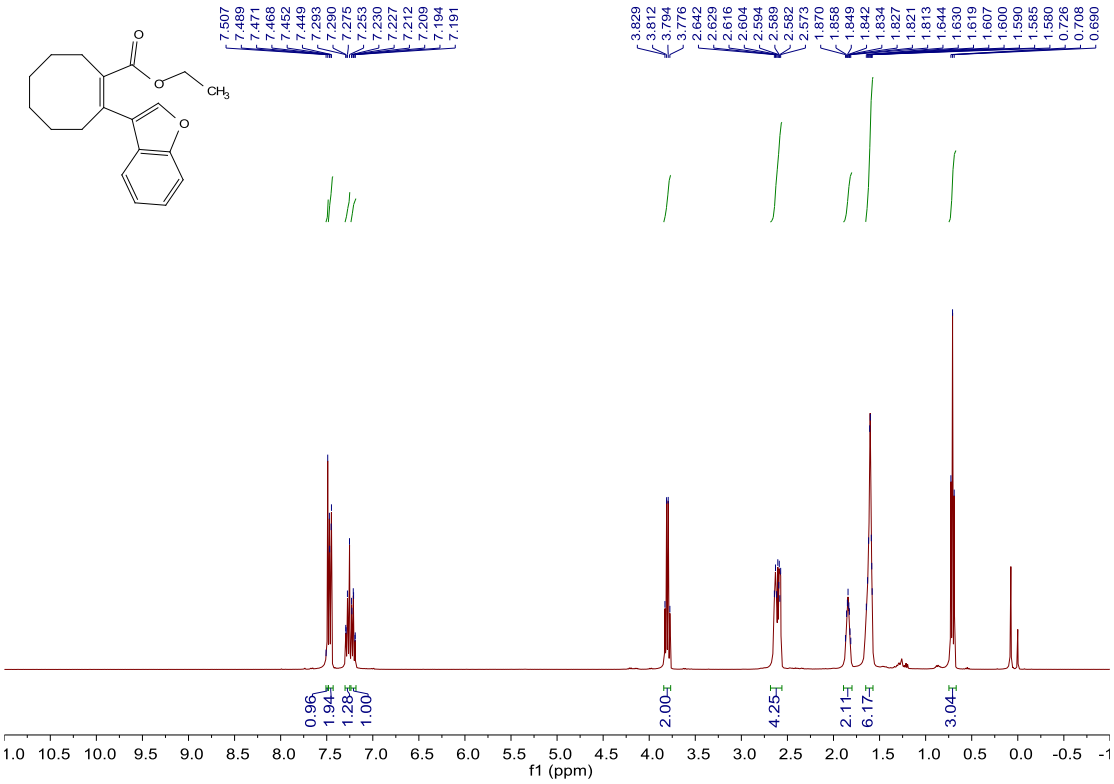


^{1}H NMR of In6-1r



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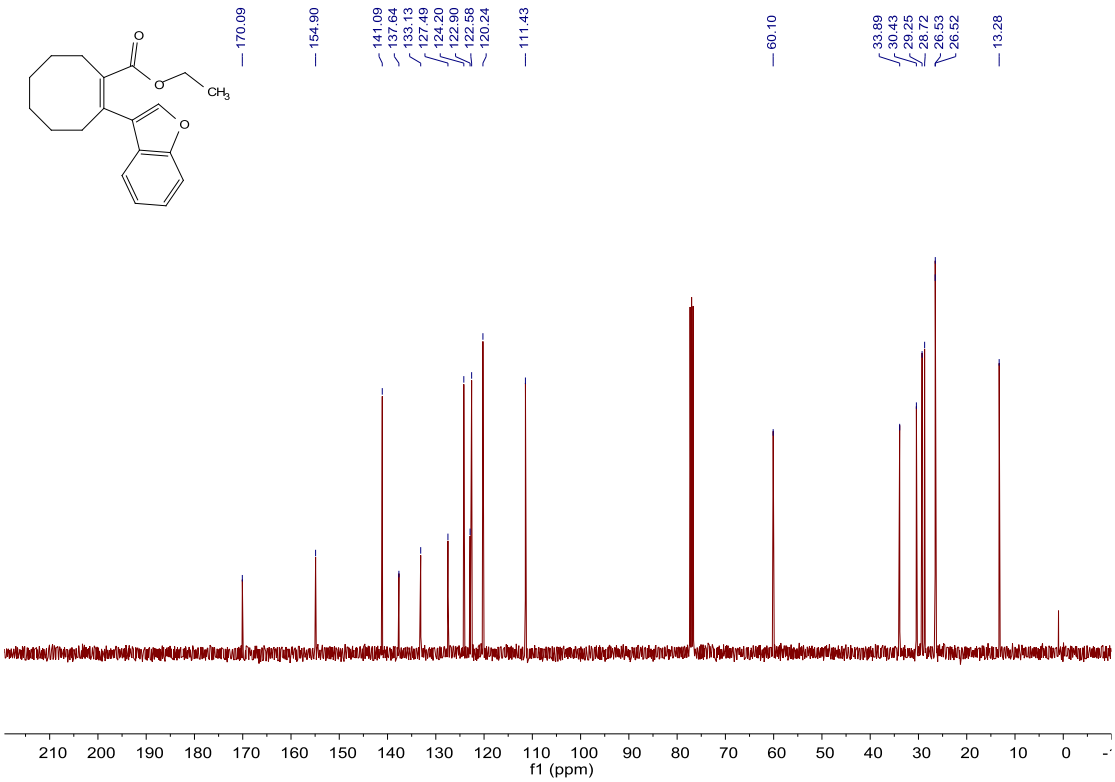

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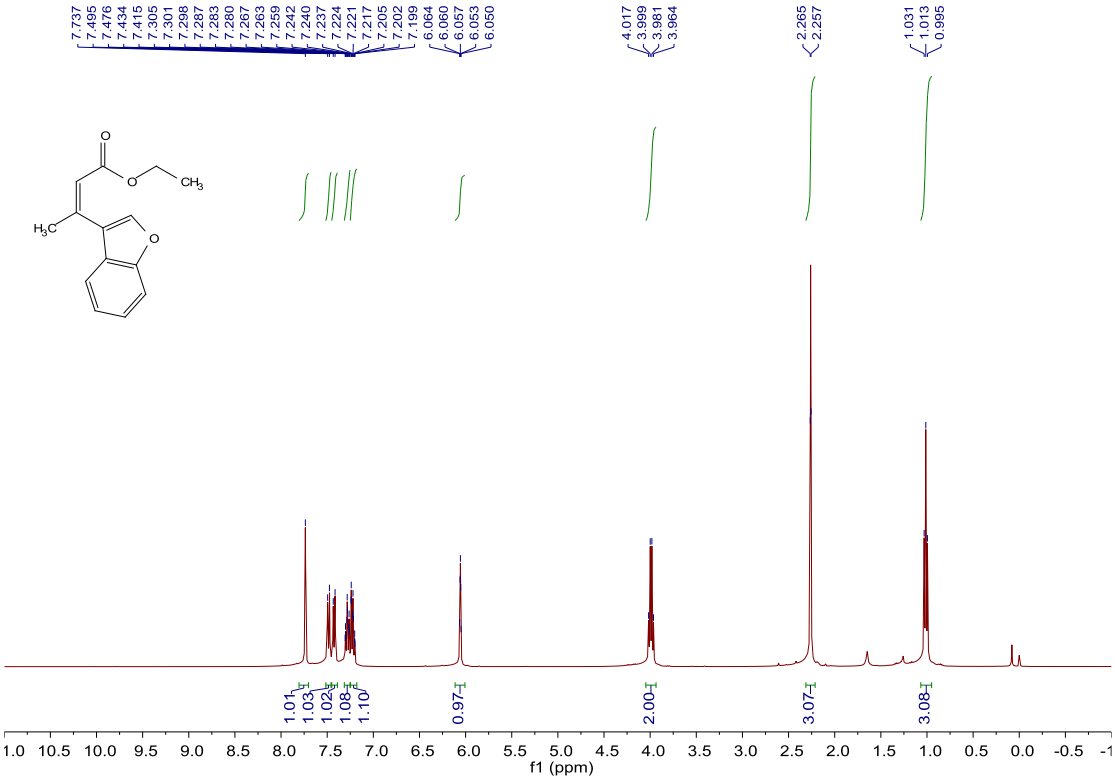
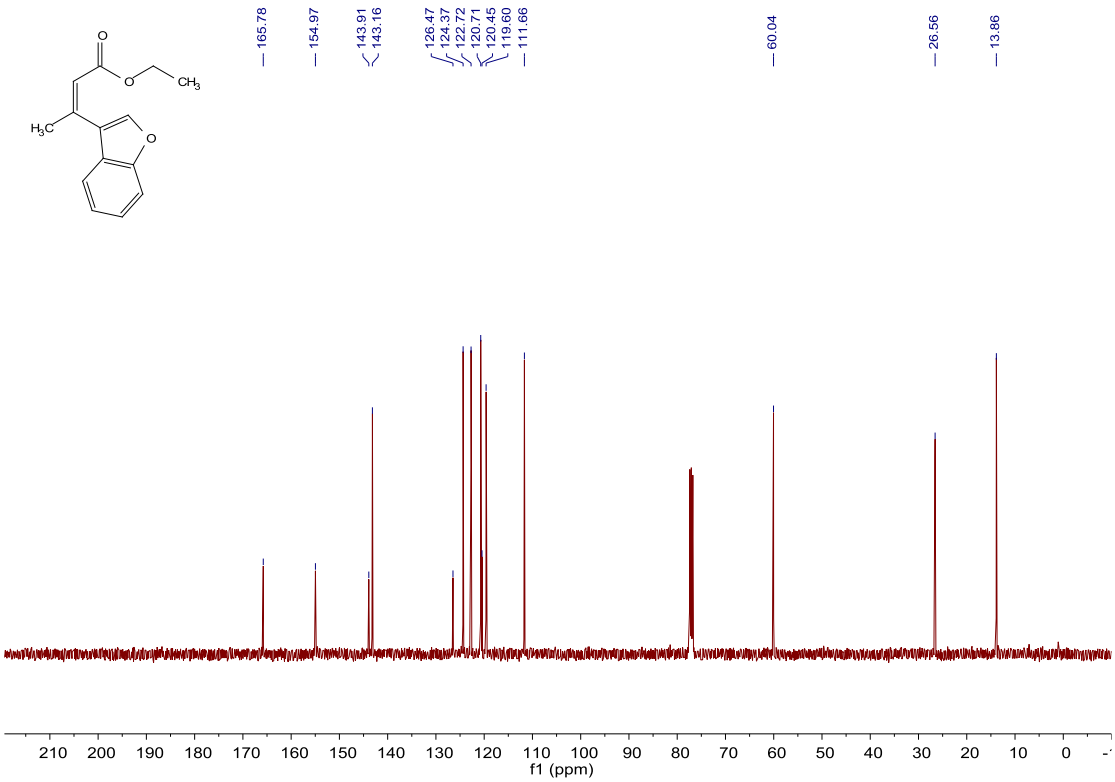
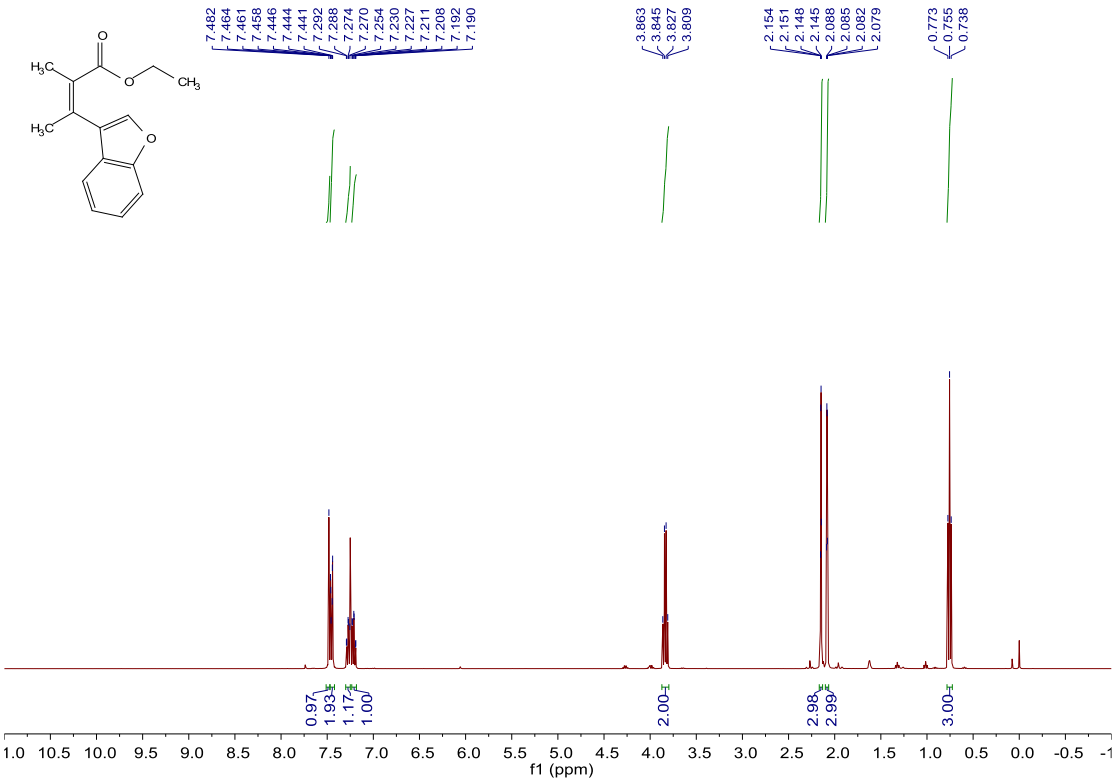


^{13}C NMR of In6-1s



^{1}H NMR of In6-1t



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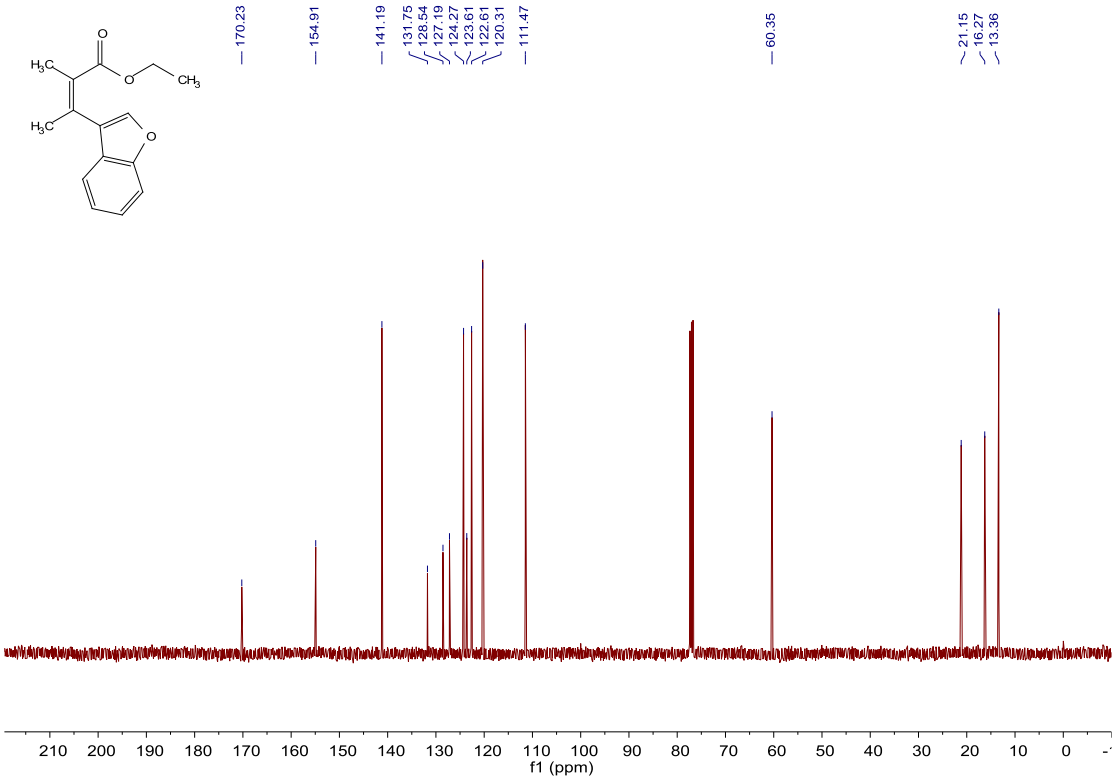

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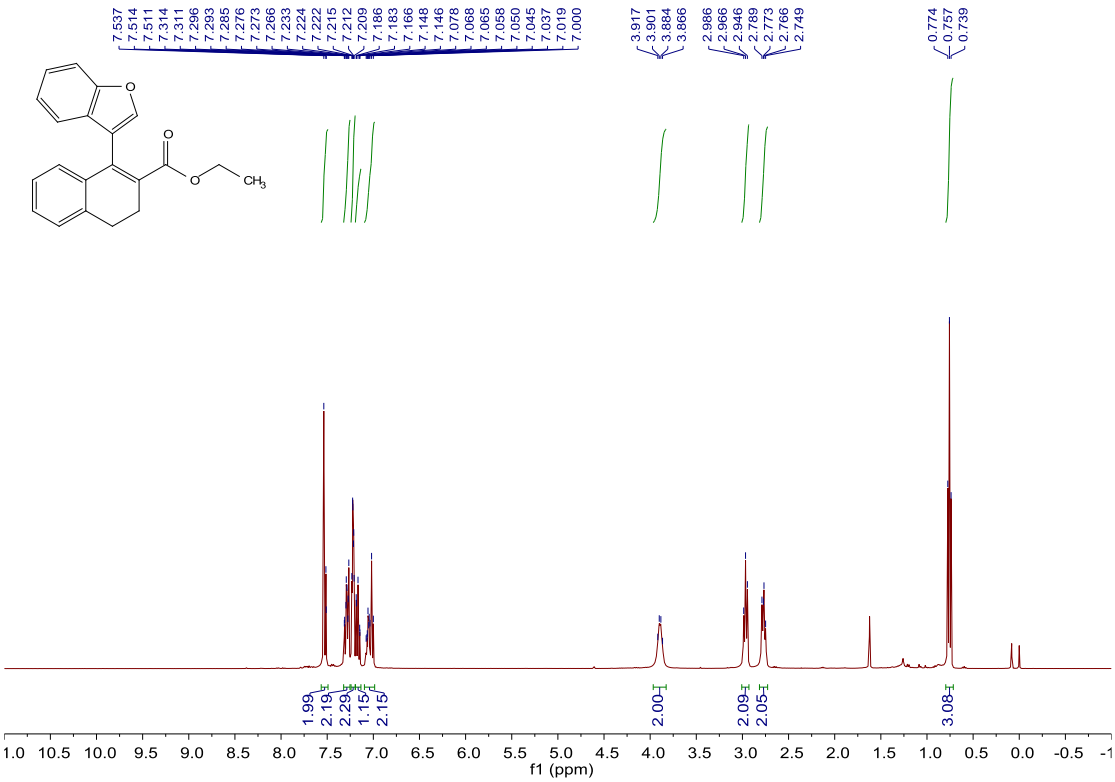

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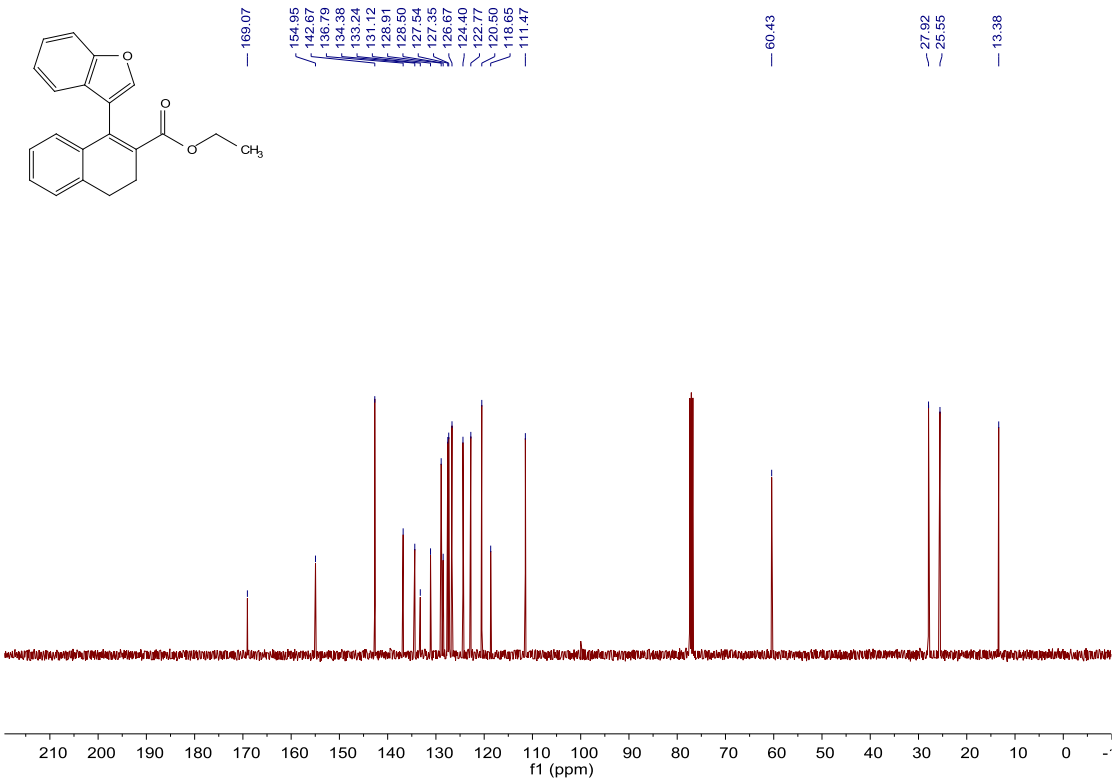

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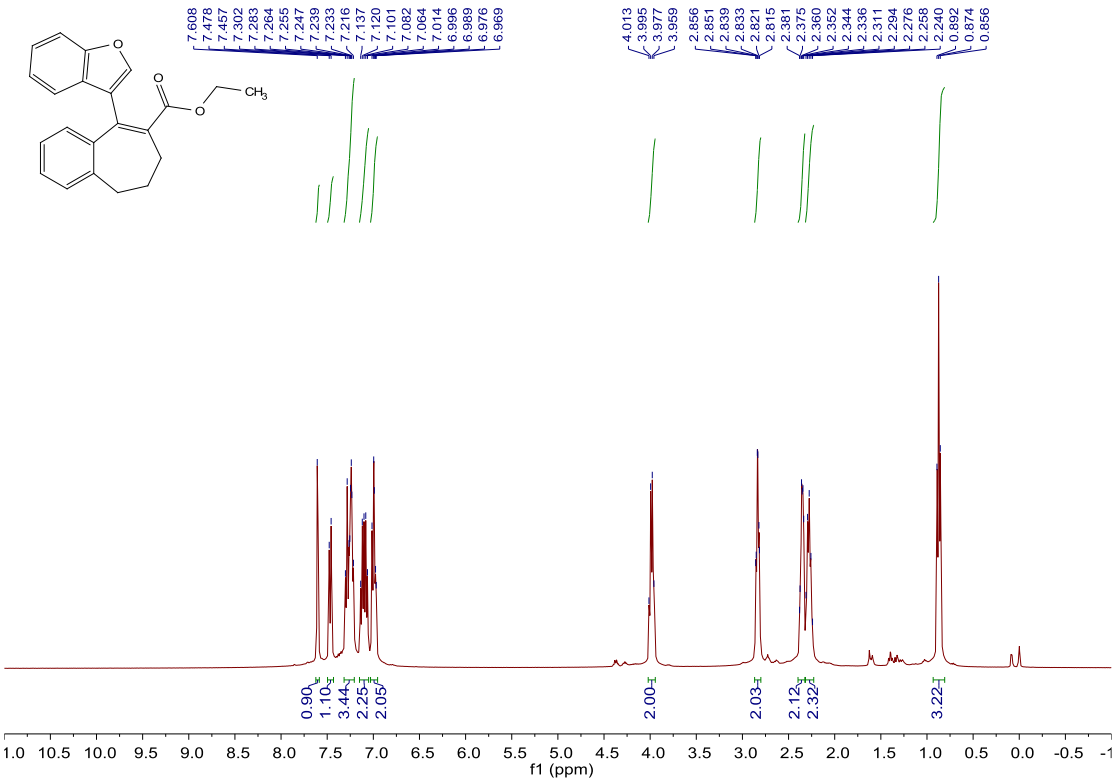
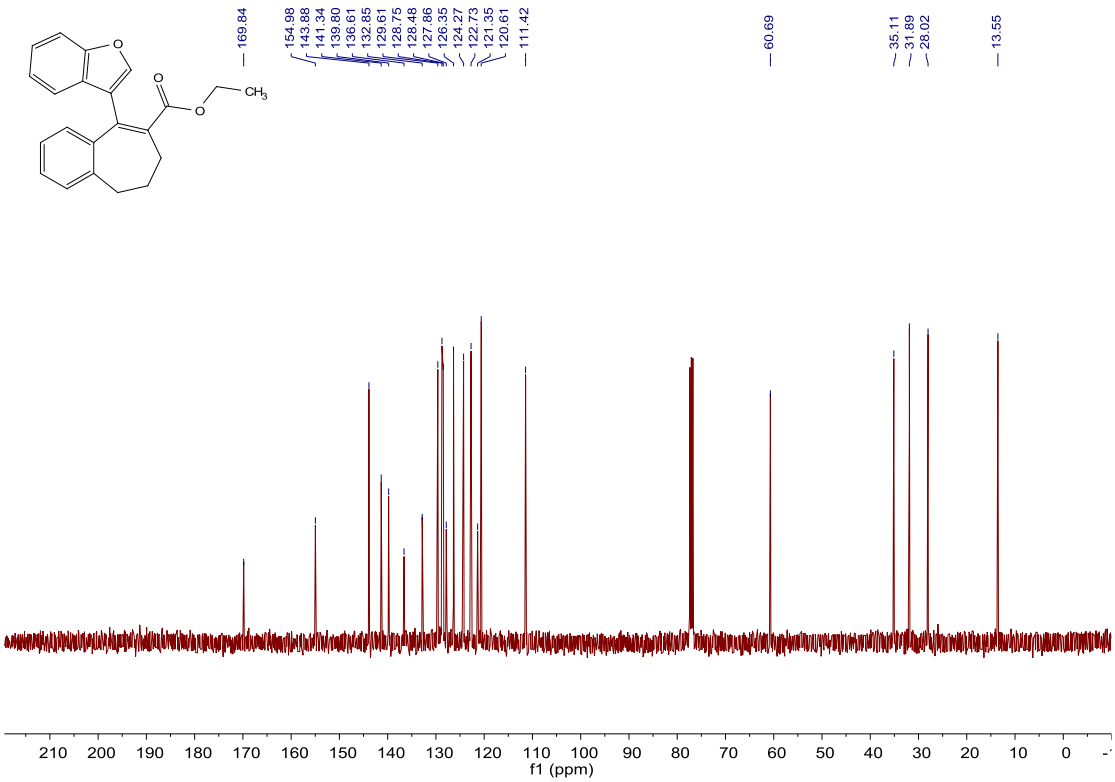
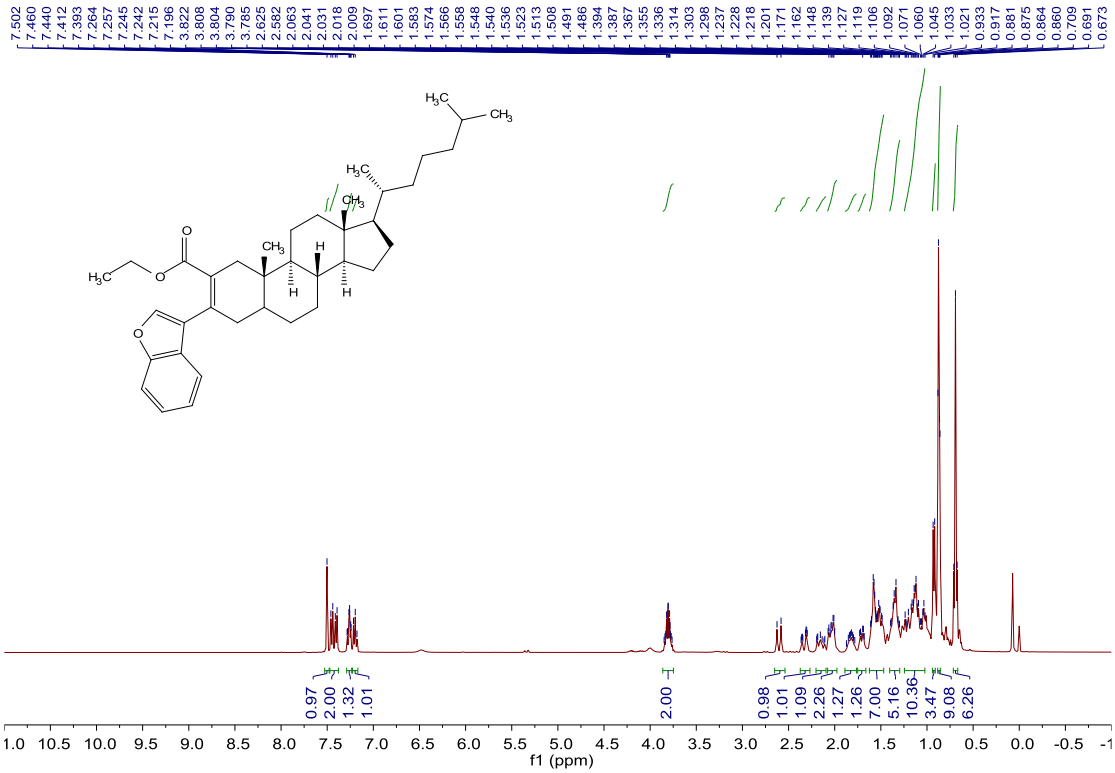


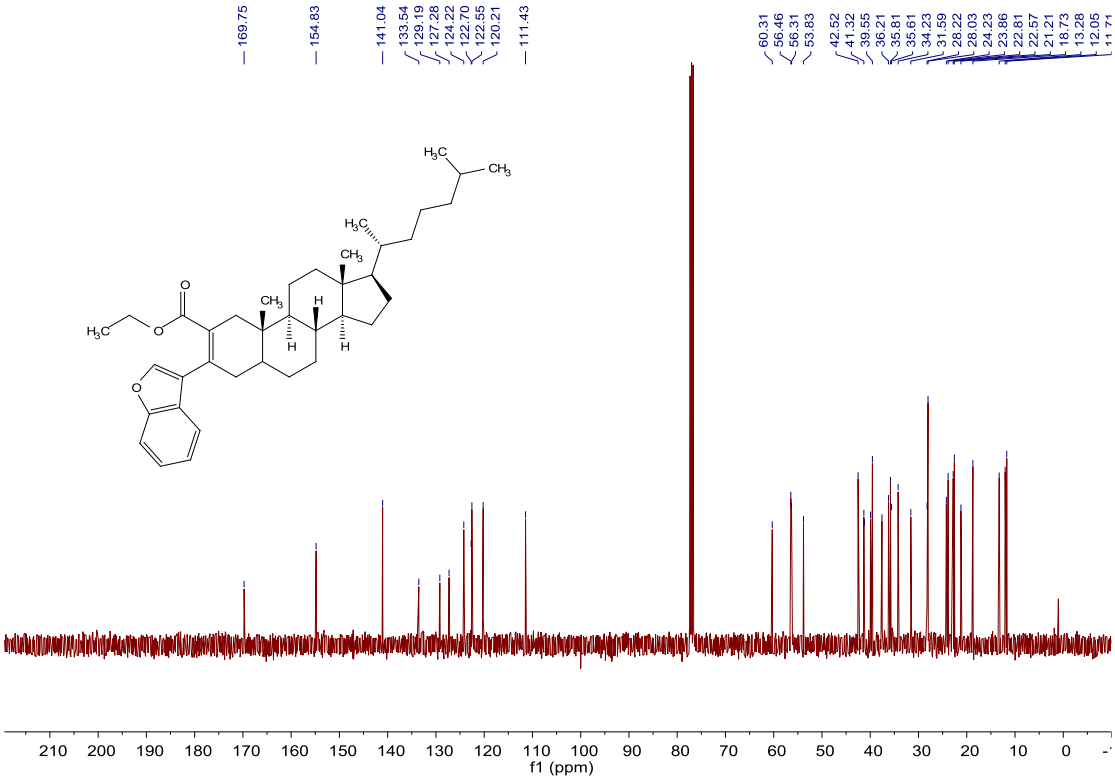
^{13}C NMR of In6-1v



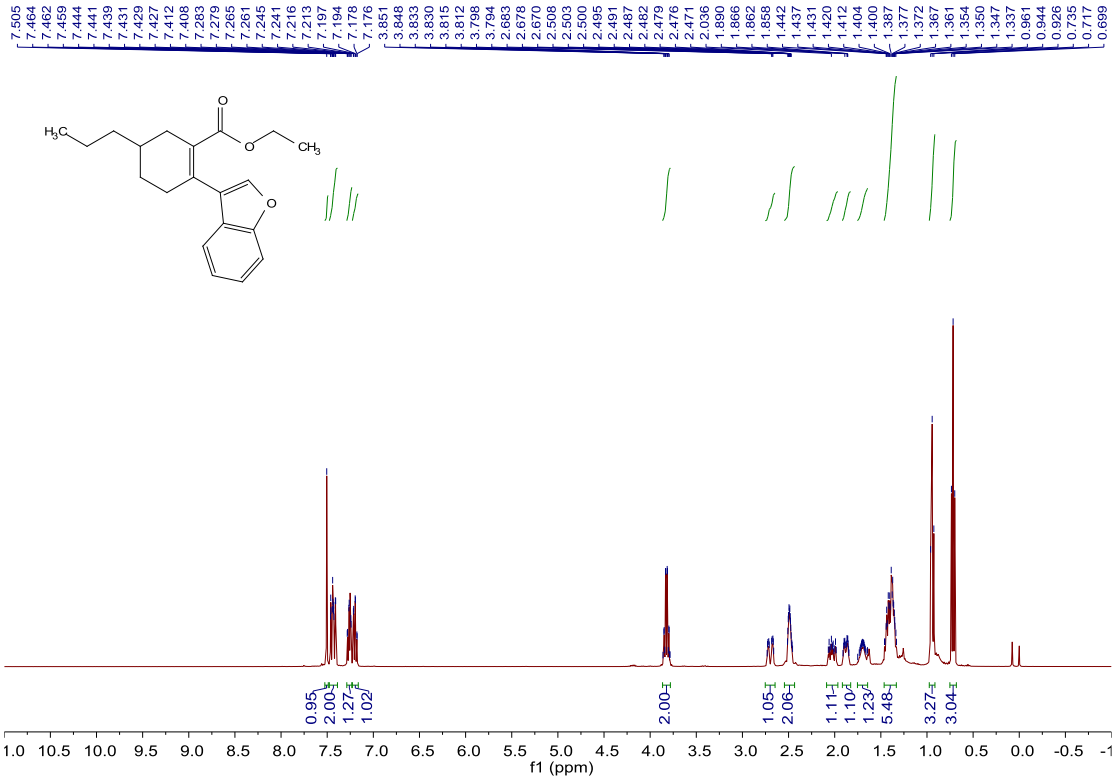
^{1}H NMR of In6-1w



^{13}C NMR of In6-1w



^{1}H NMR of In6-1x



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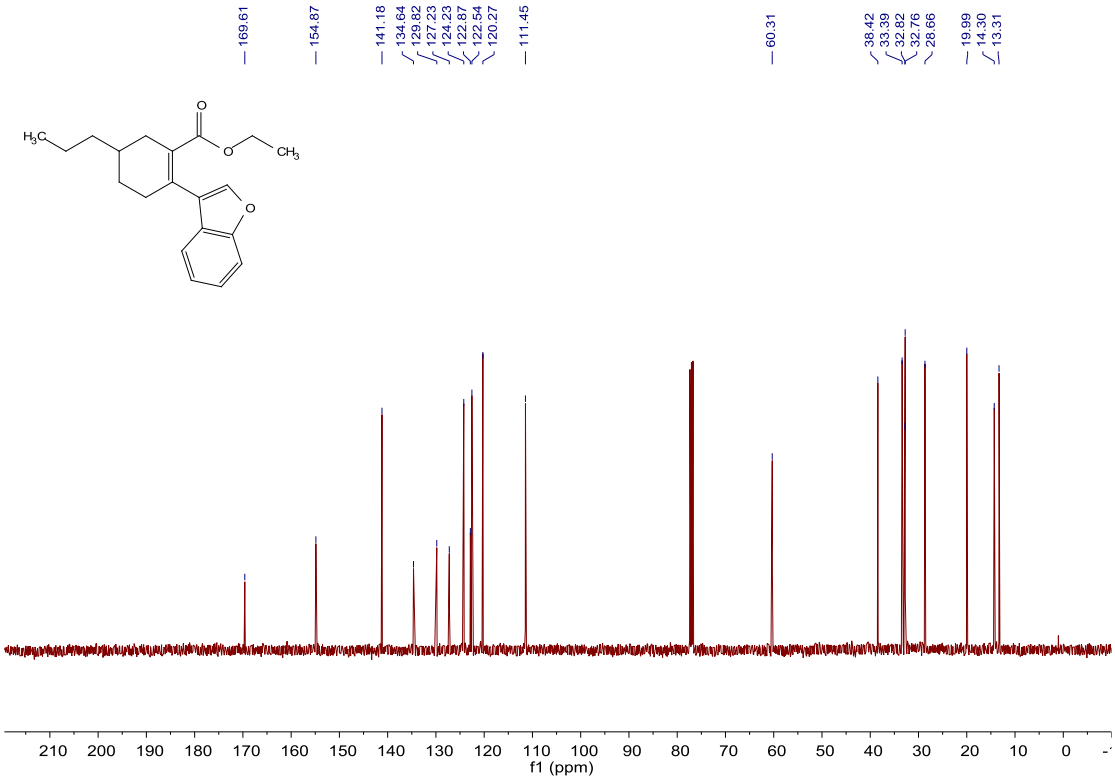

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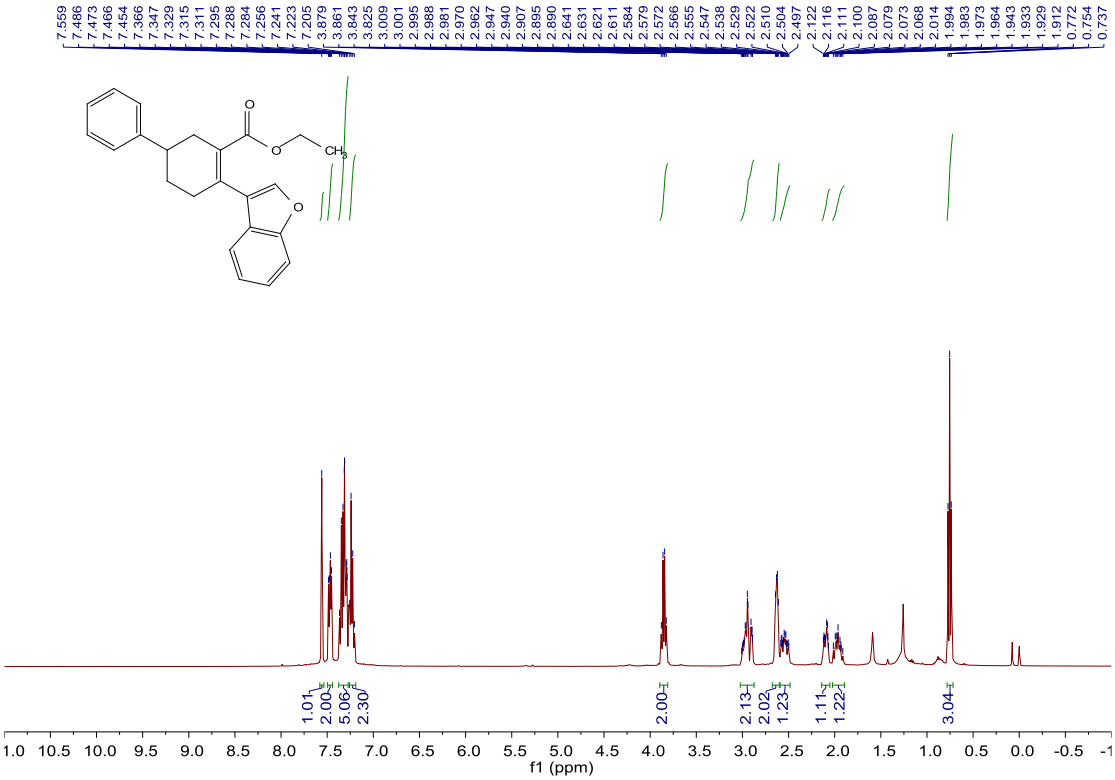

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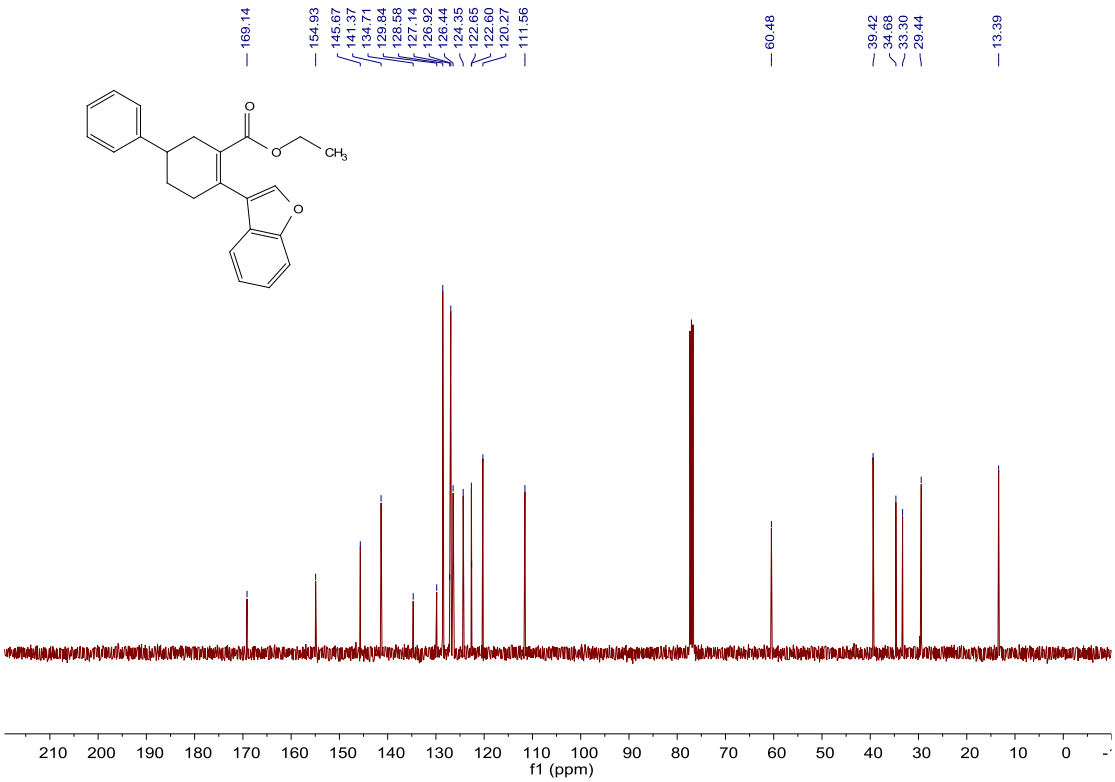
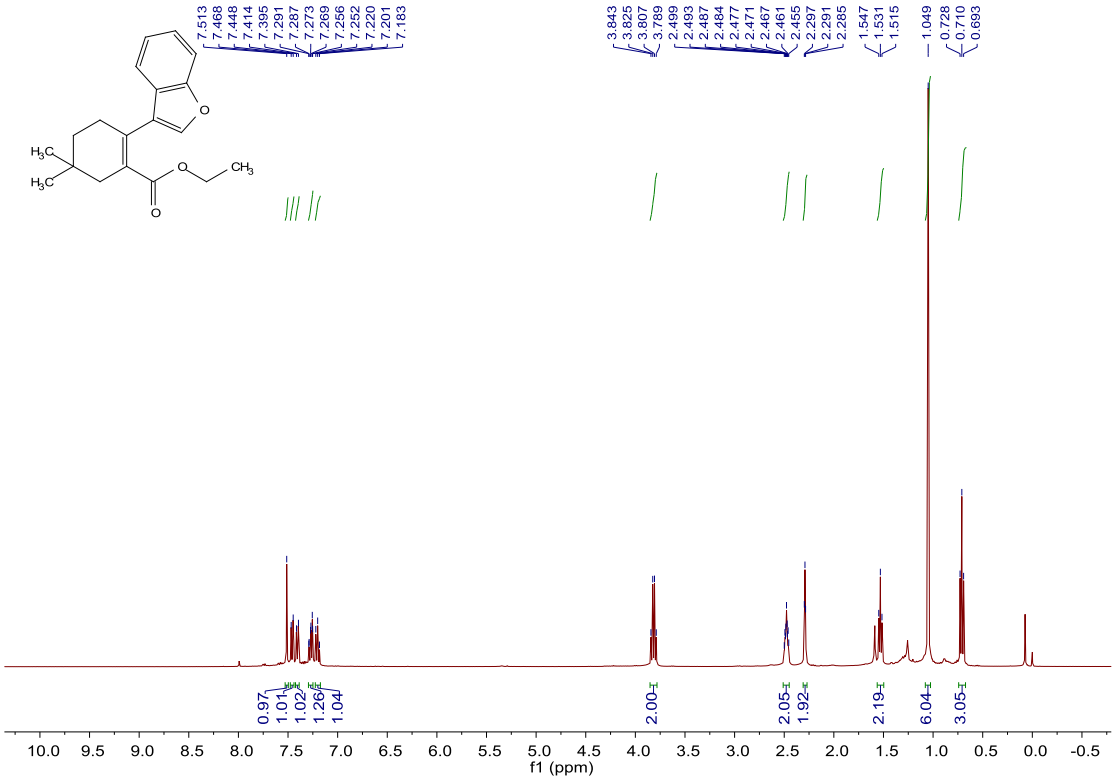


^{1}H NMR of In6-1aa



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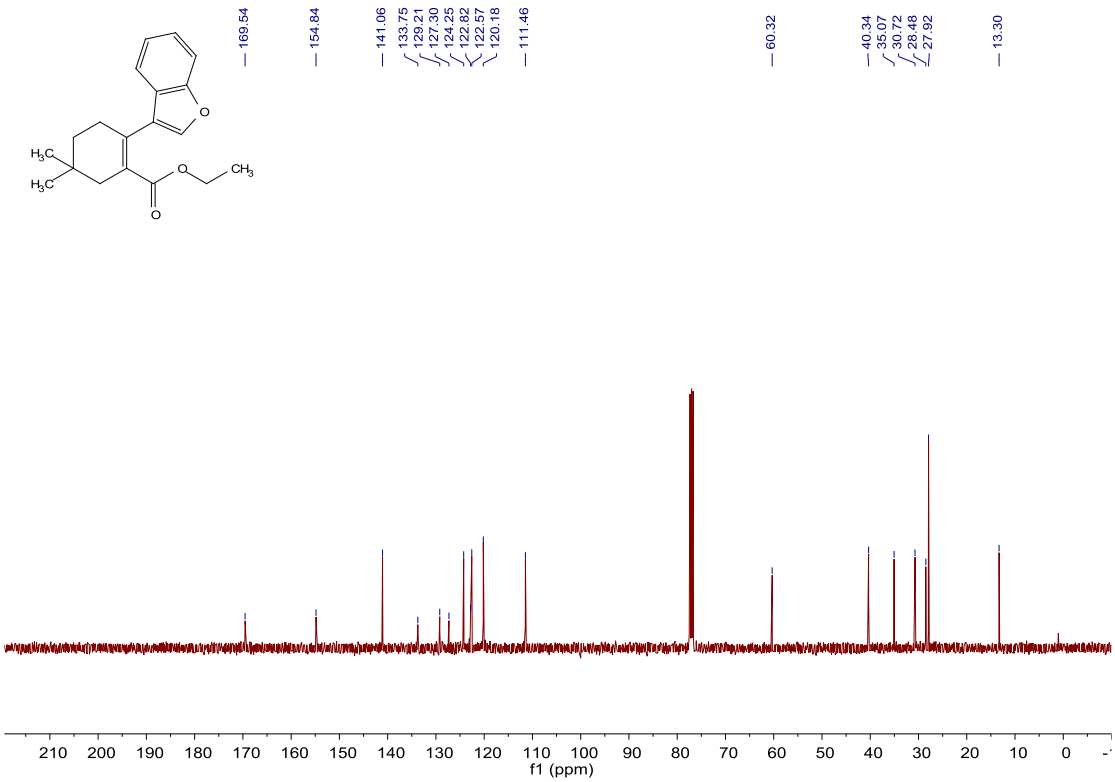
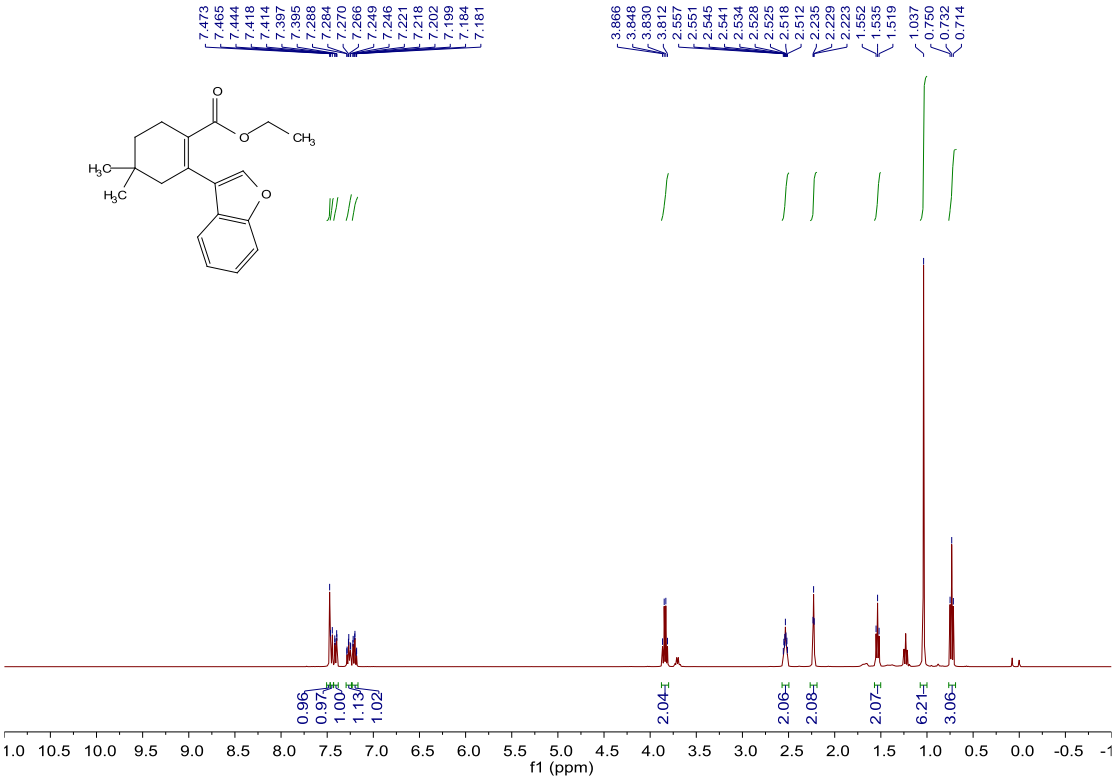


^{1}H NMR of In6-1ab



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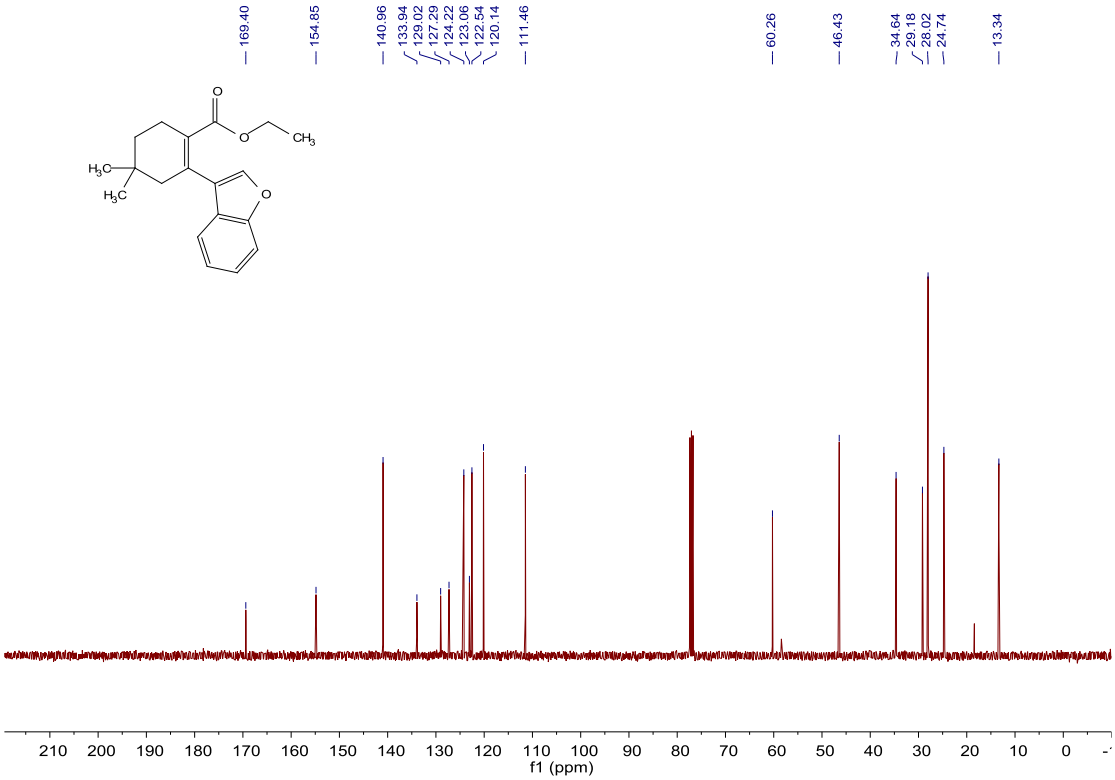
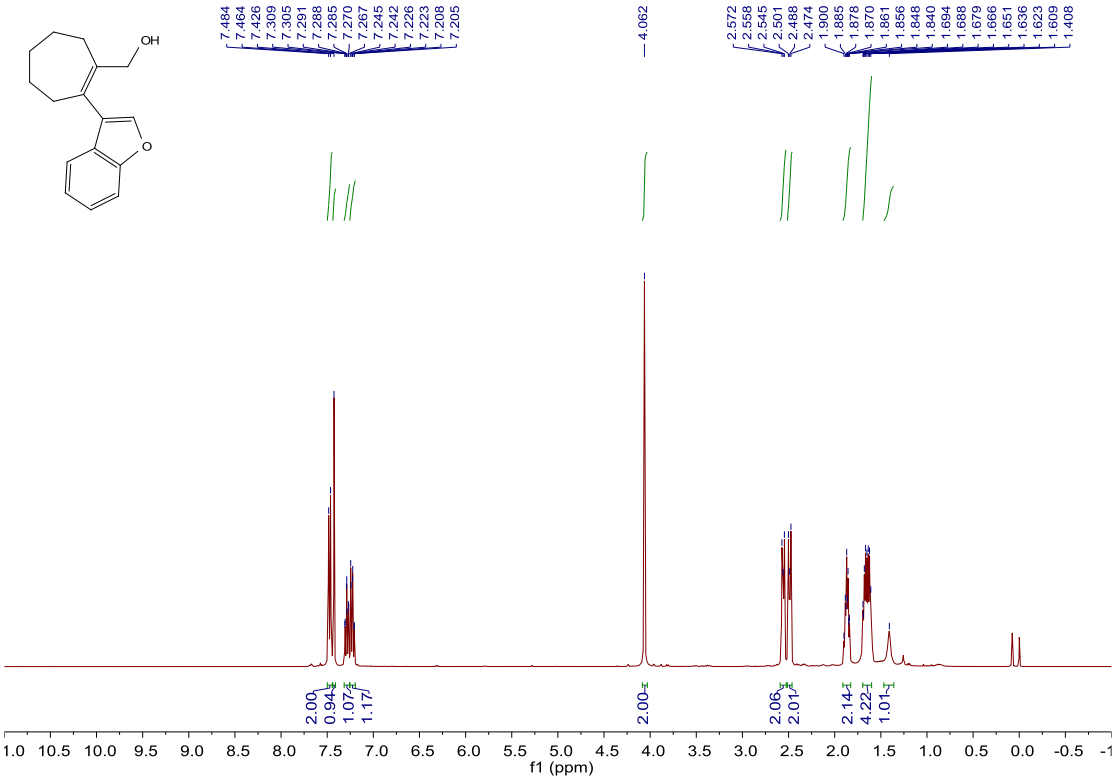
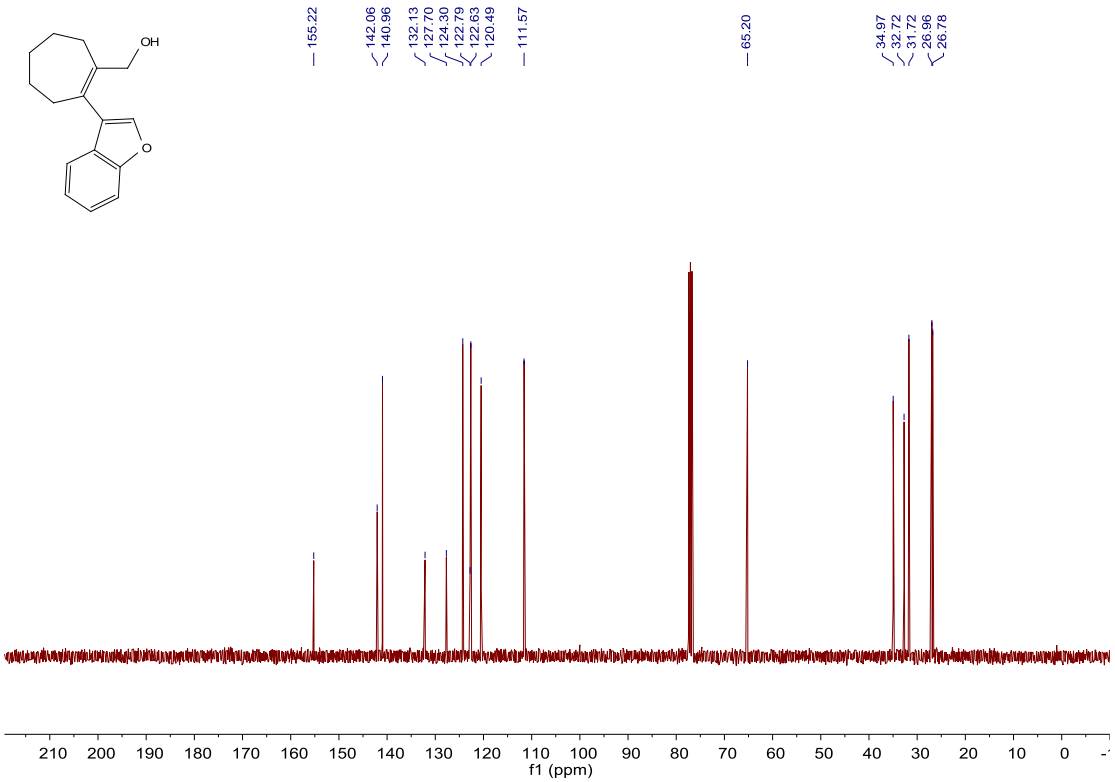


^{1}H NMR of In7-1q



^{13}C NMR of In7-1q



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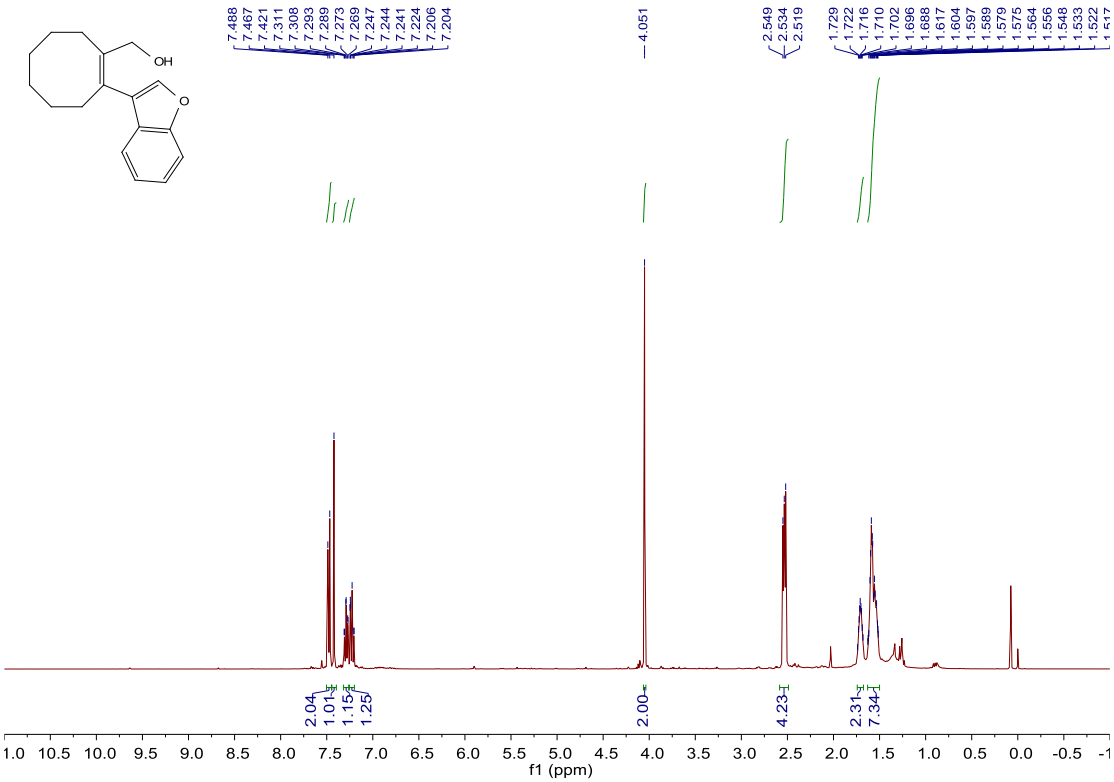

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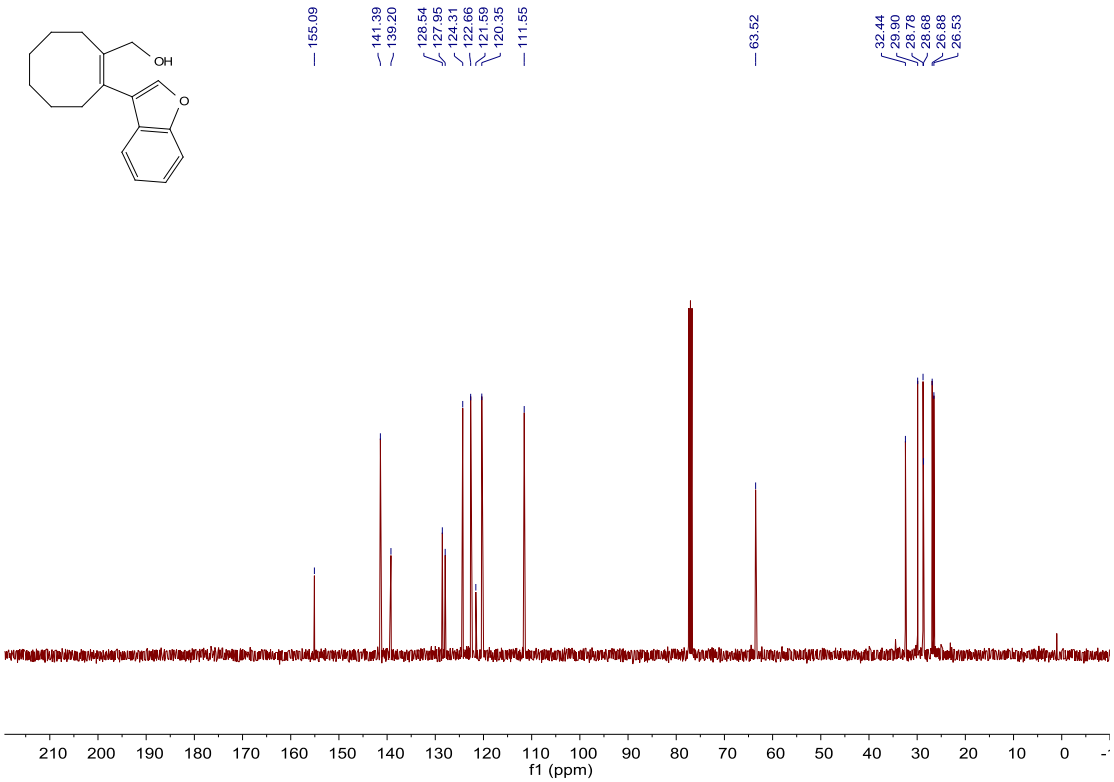

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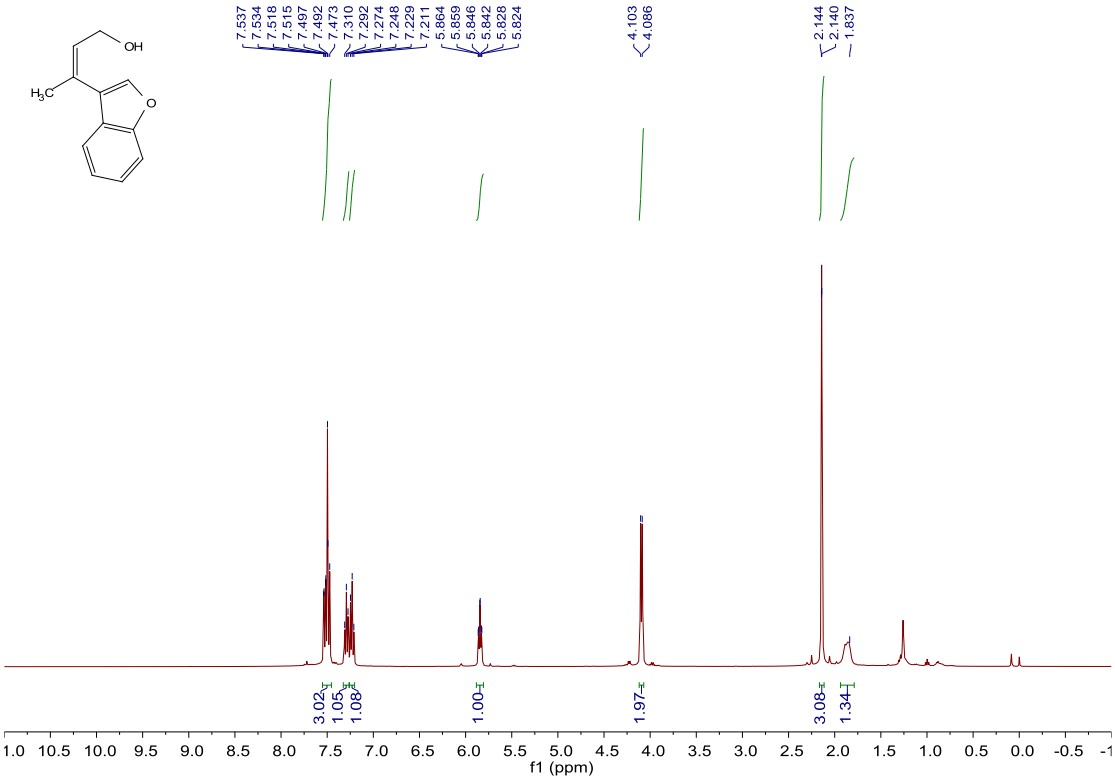

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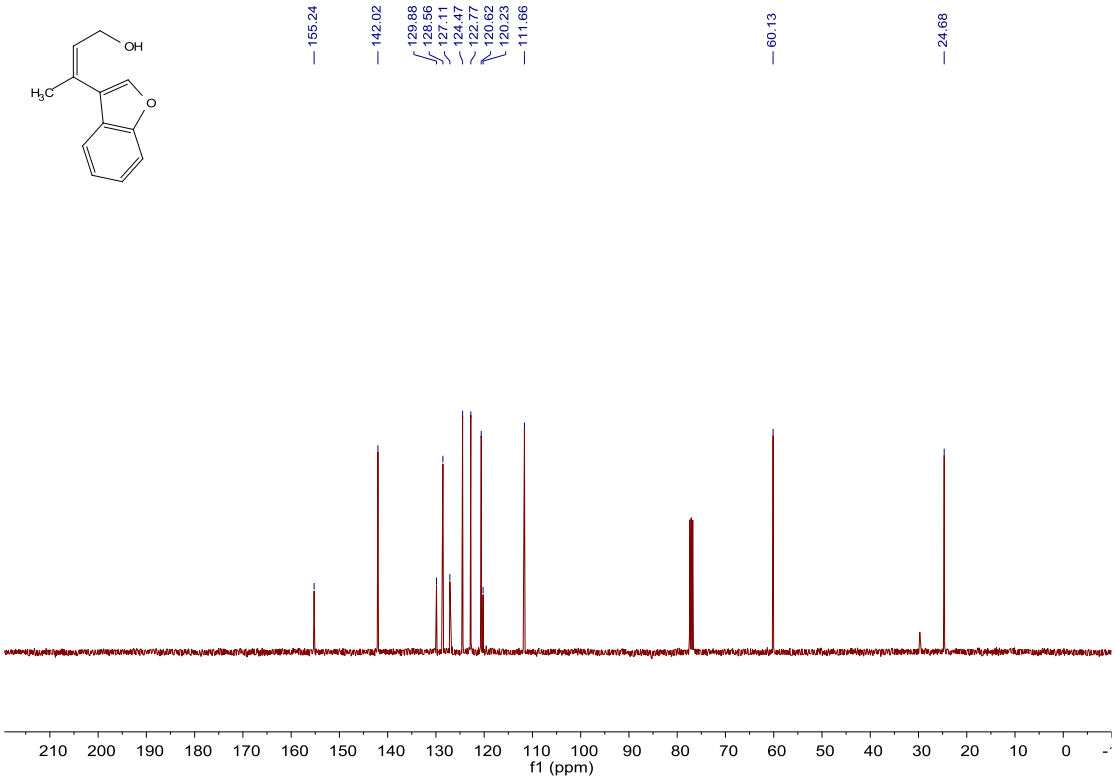

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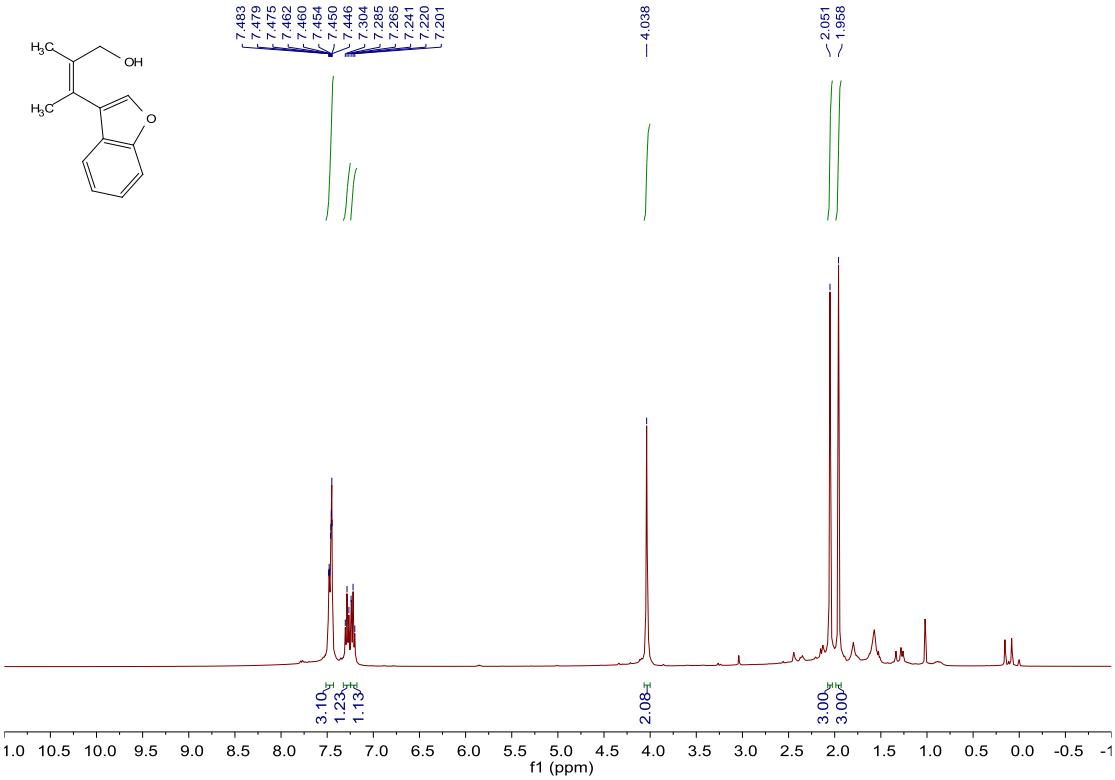

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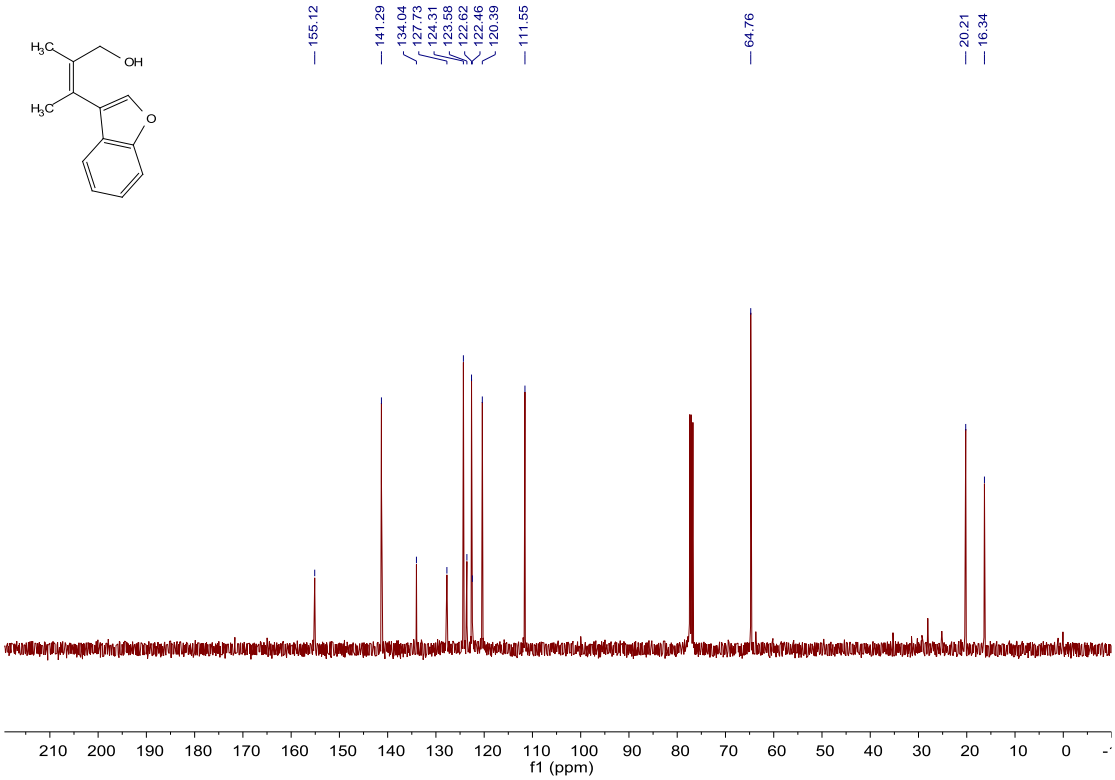

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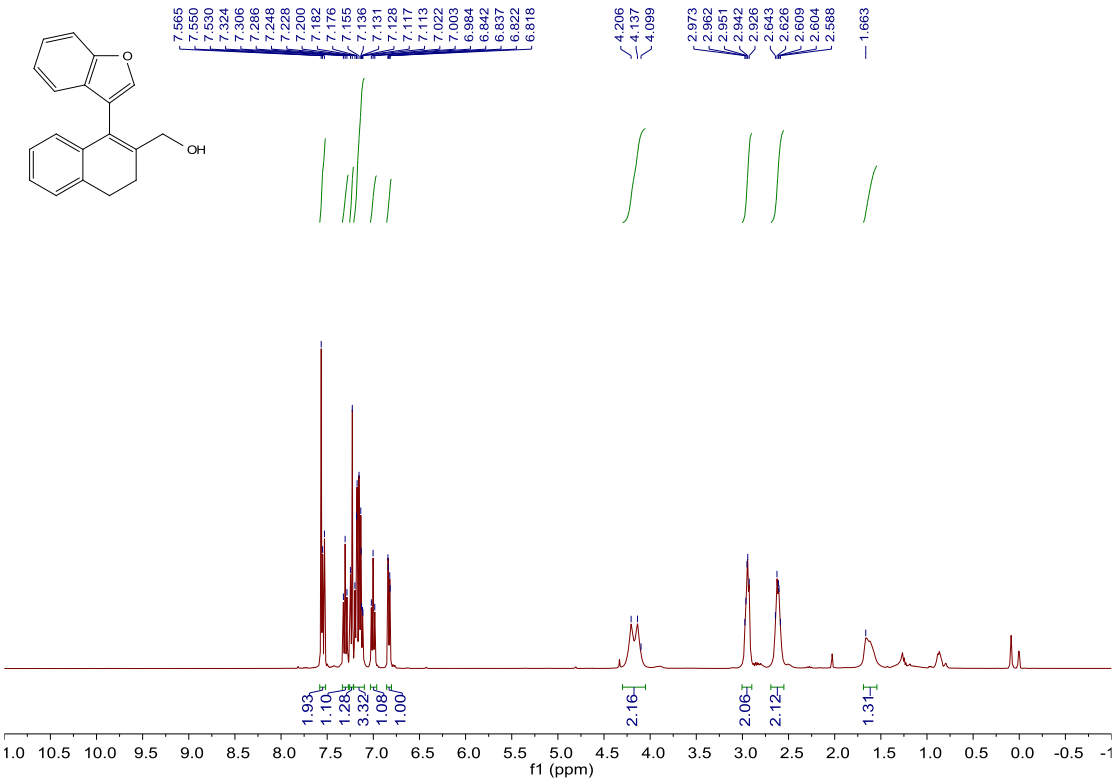

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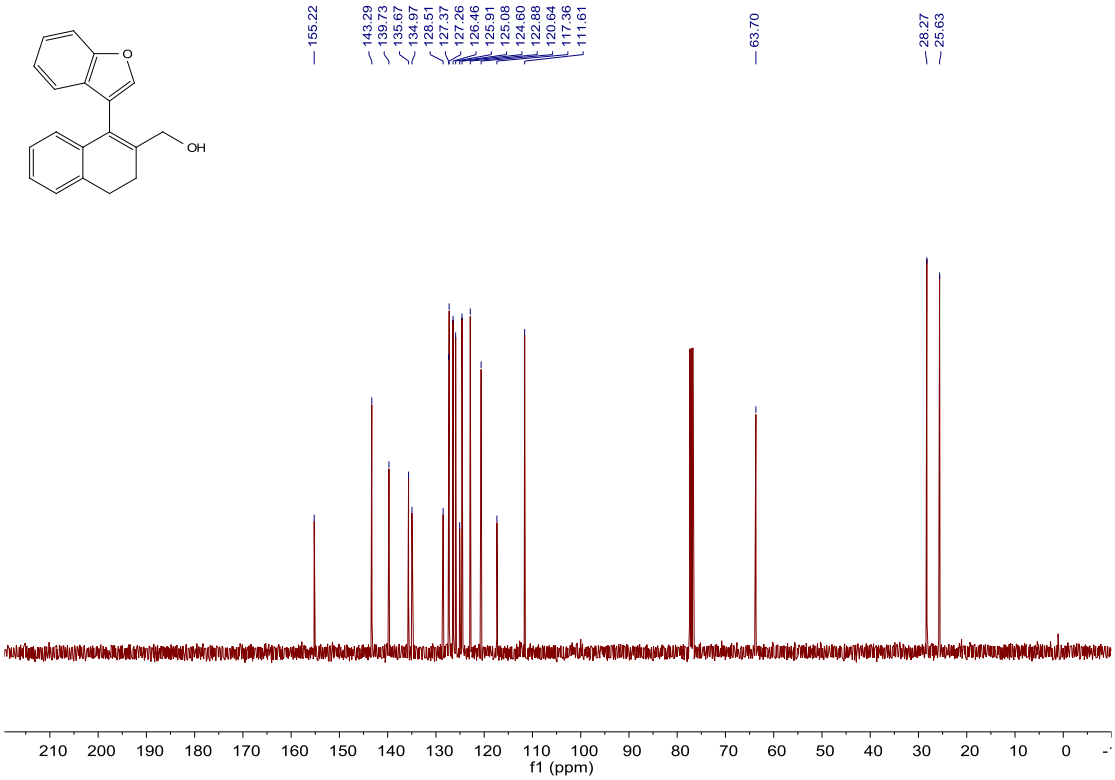

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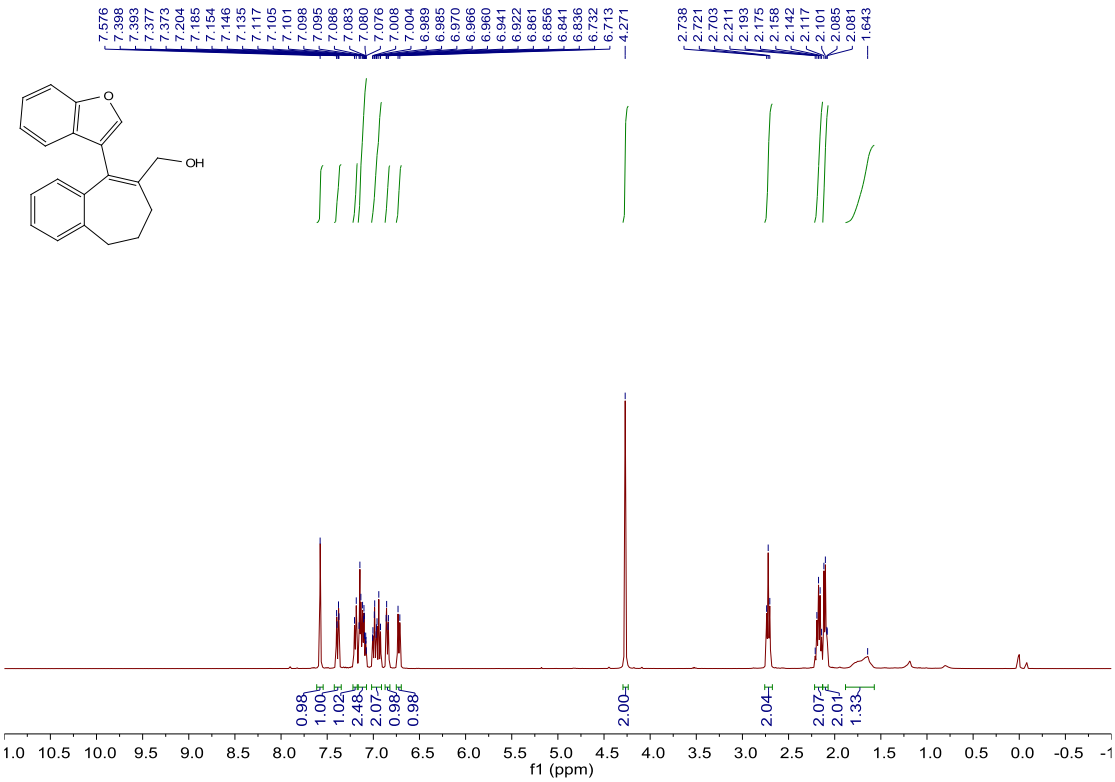

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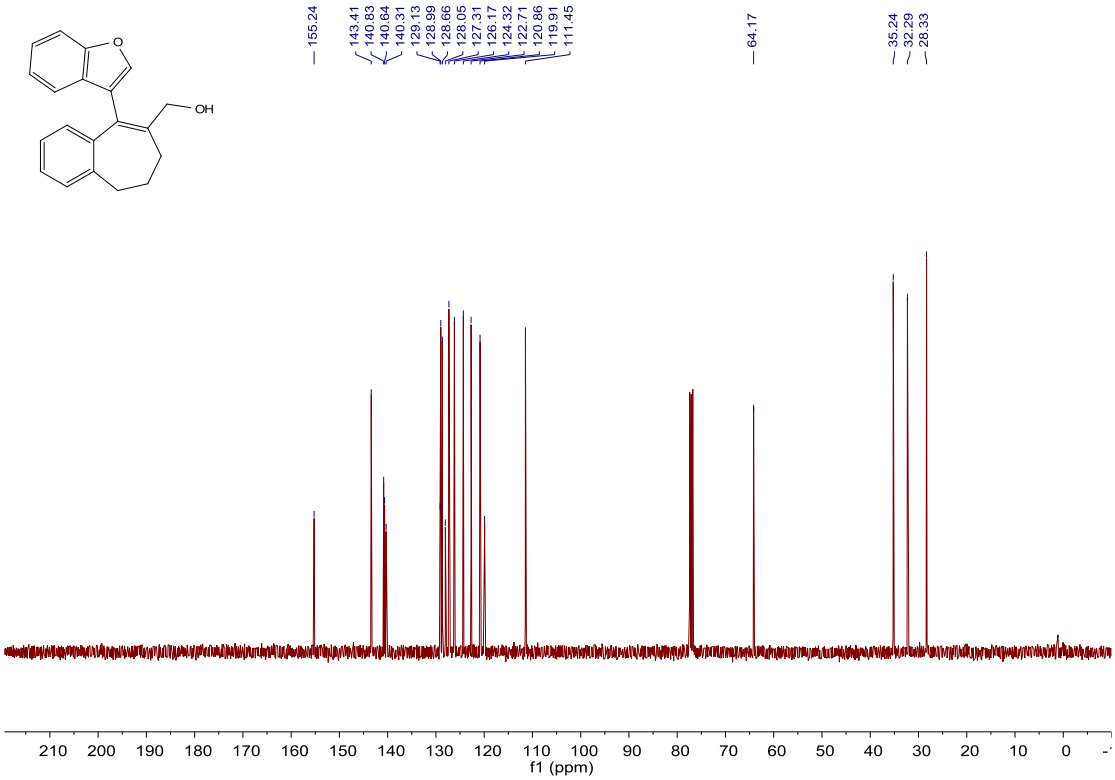
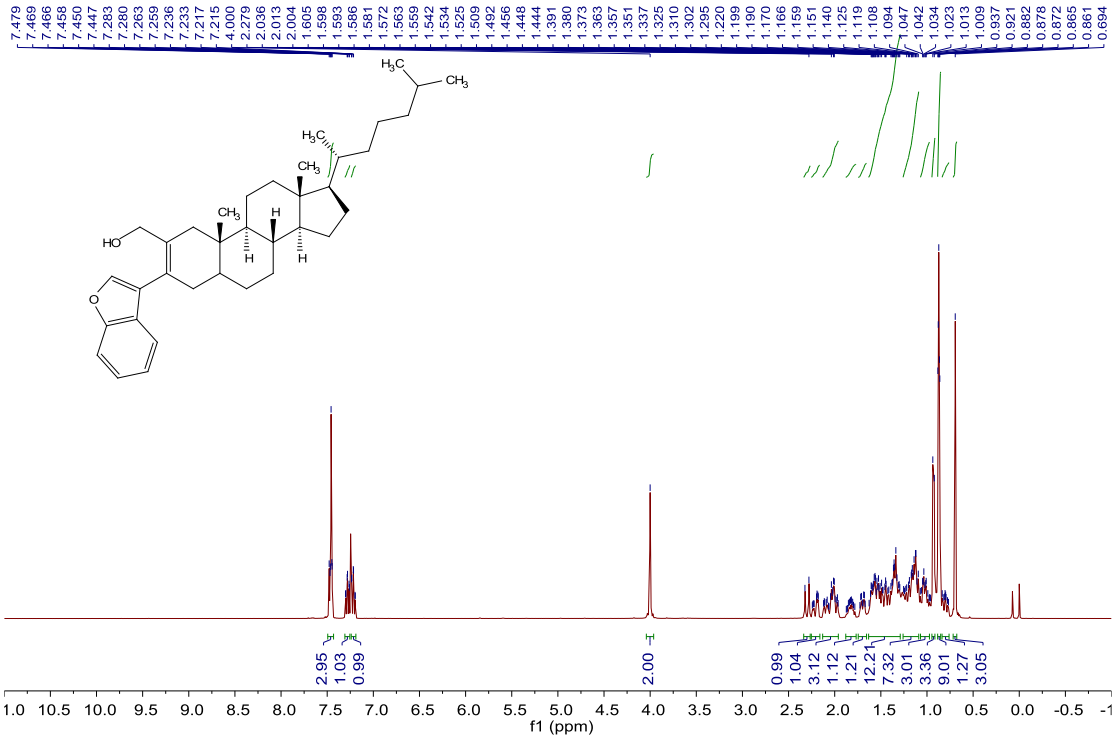


^{1}H NMR of In7-1w



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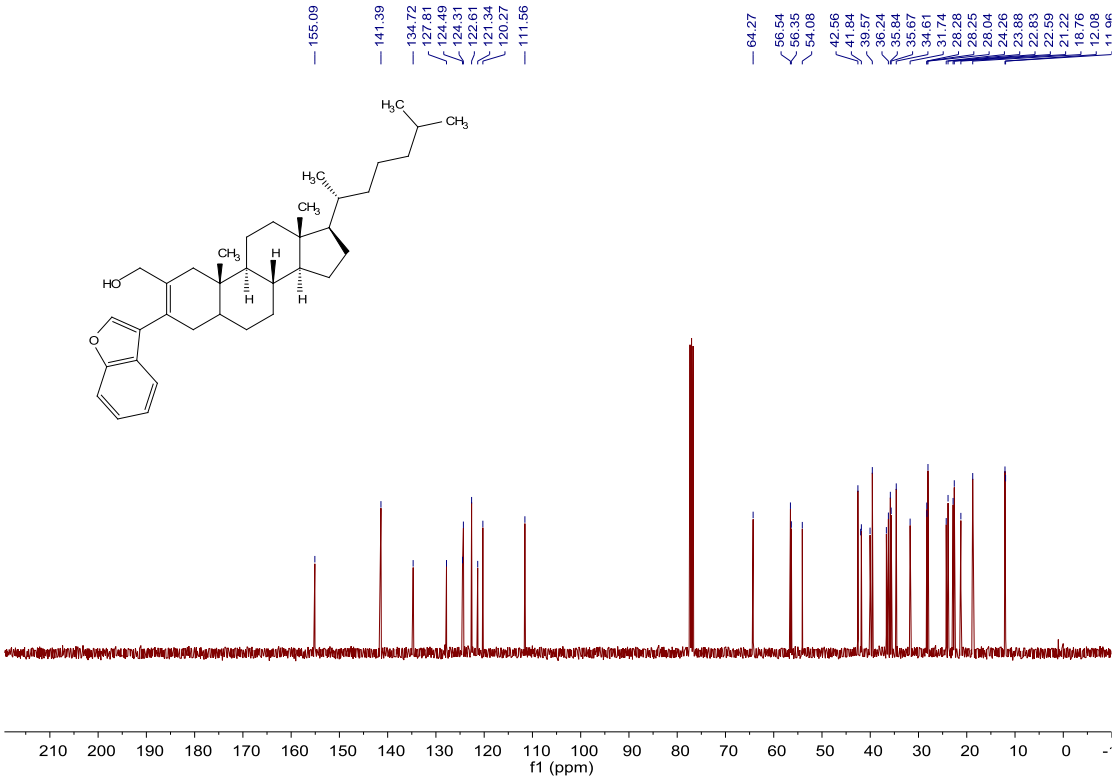
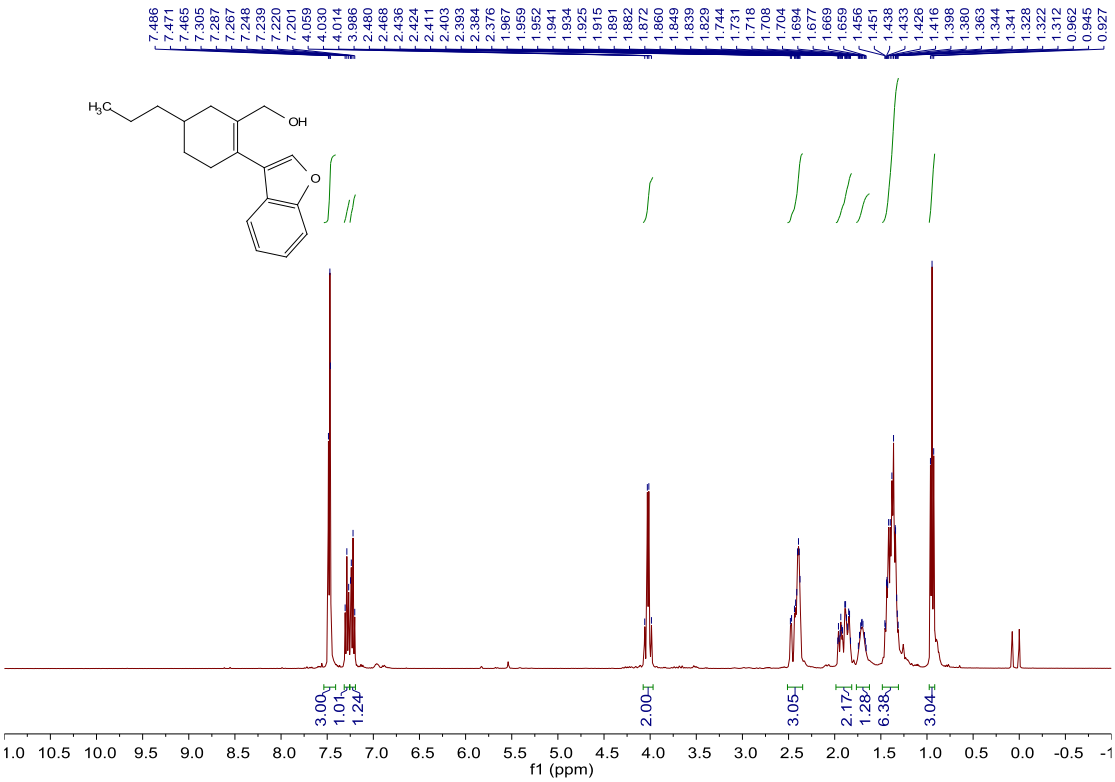
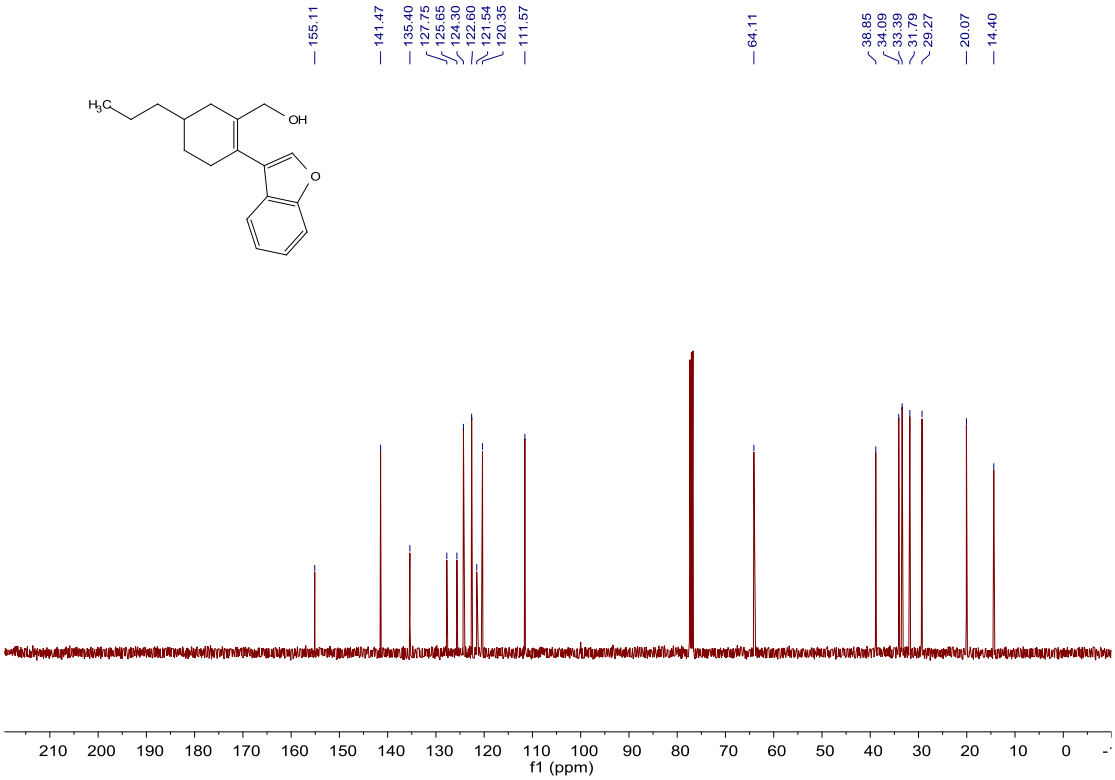


^{1}H NMR of In7-1x



^{13}C NMR of In7-1x



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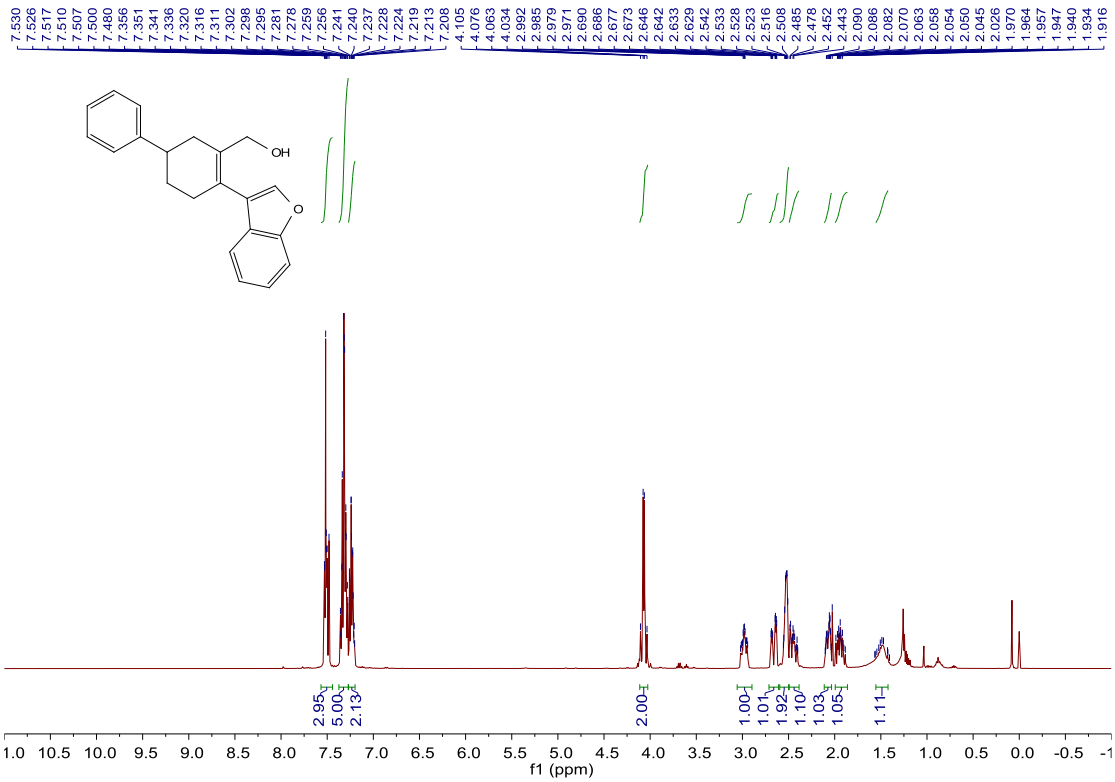

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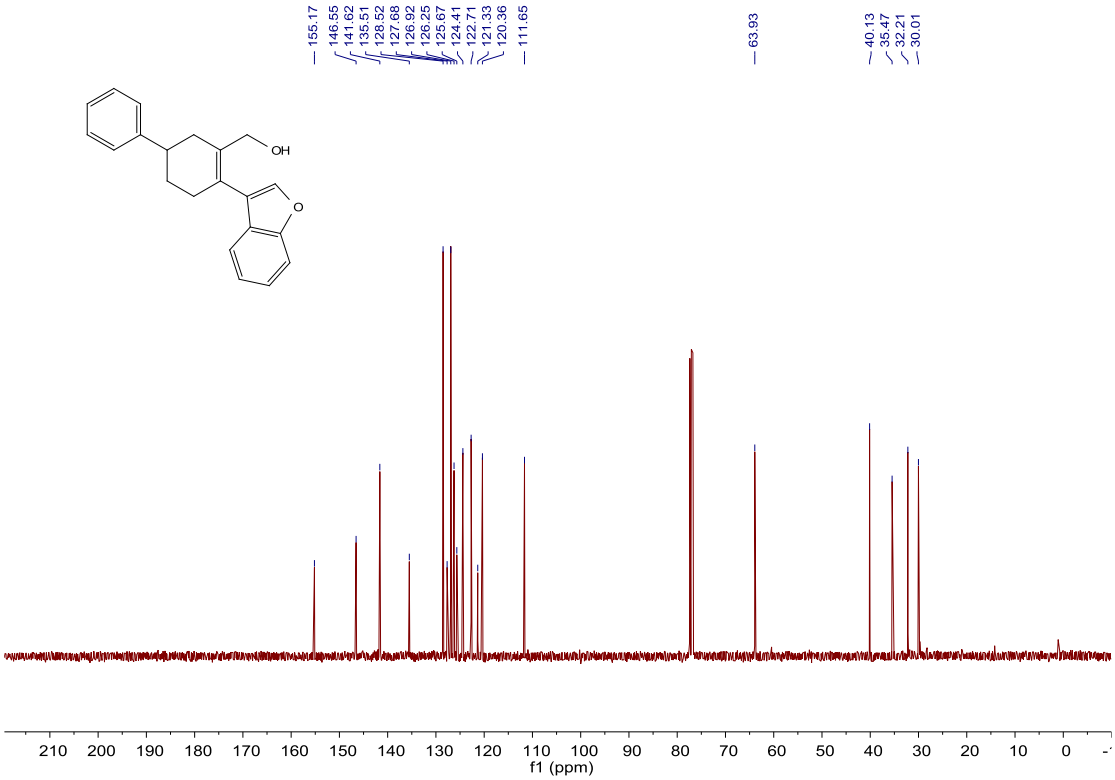
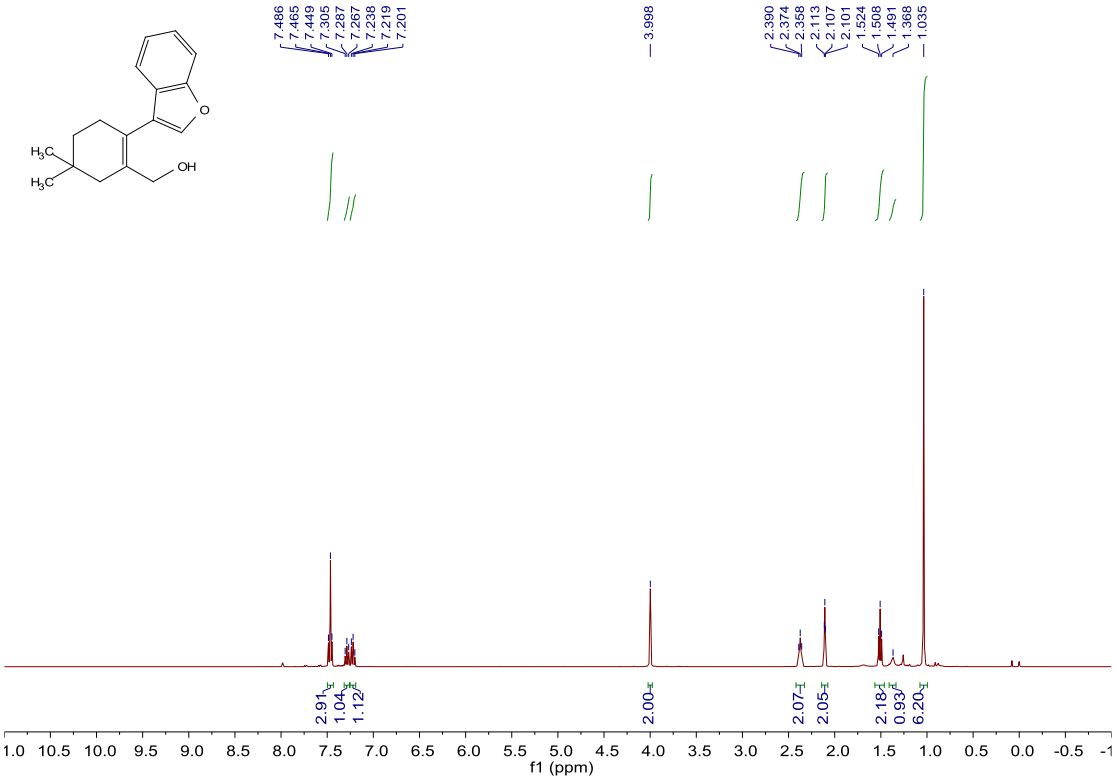
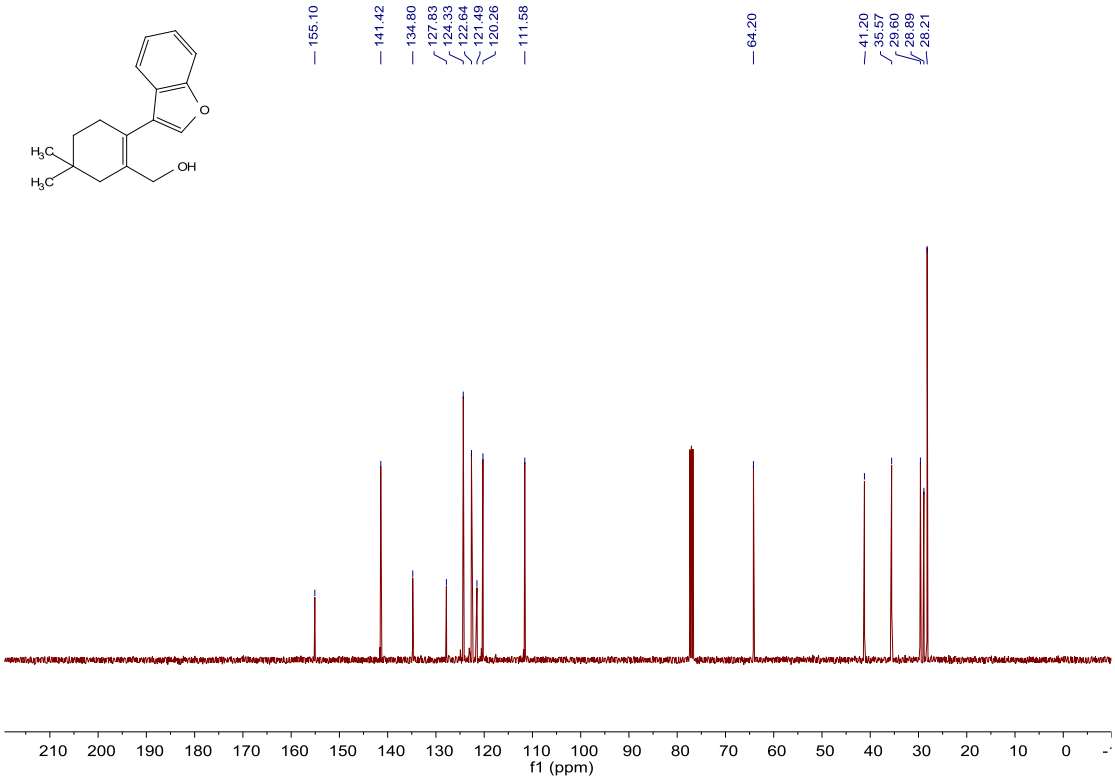


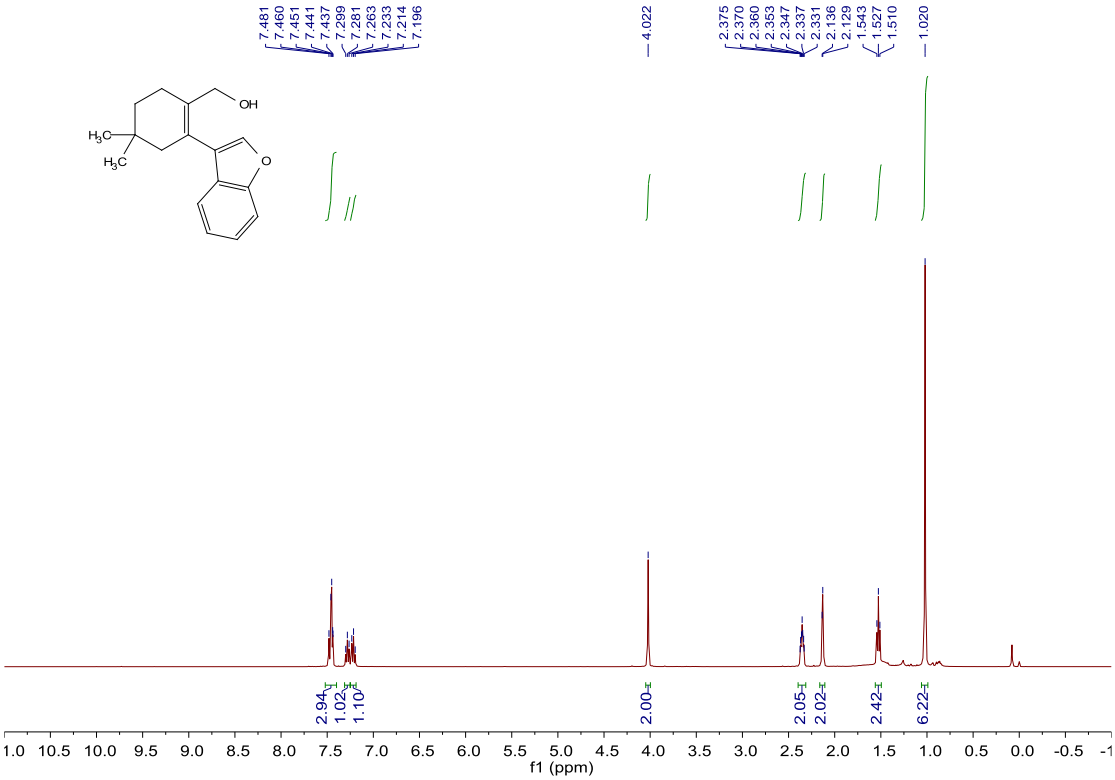
^{1}H NMR of In7-1aa



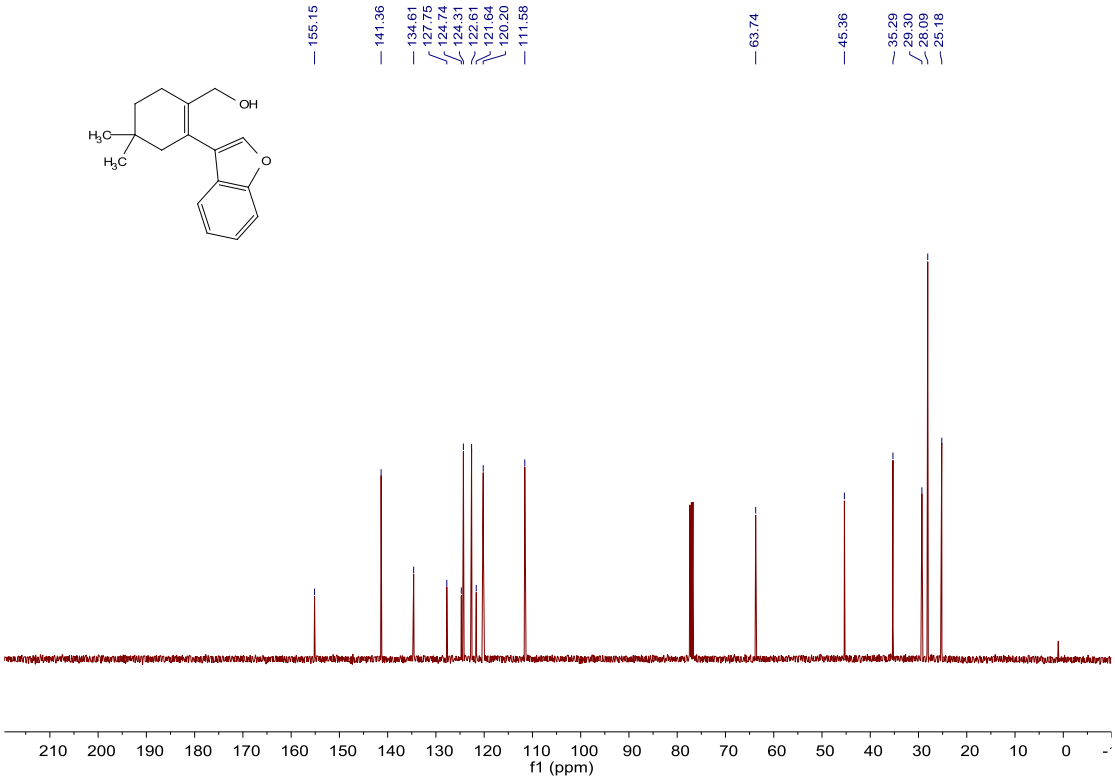
^{13}C NMR of In7-1aa



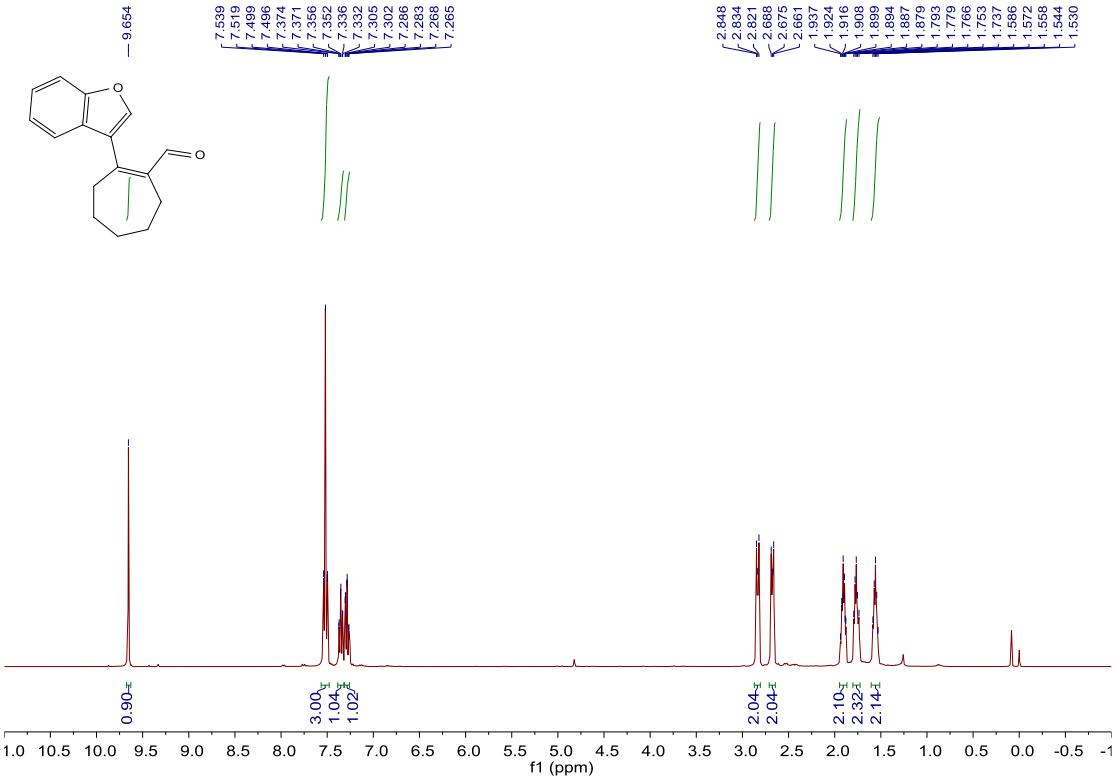
^{1}H NMR of In7-1ab



^{13}C NMR of In7-1ab



^{1}H NMR of In8-1q



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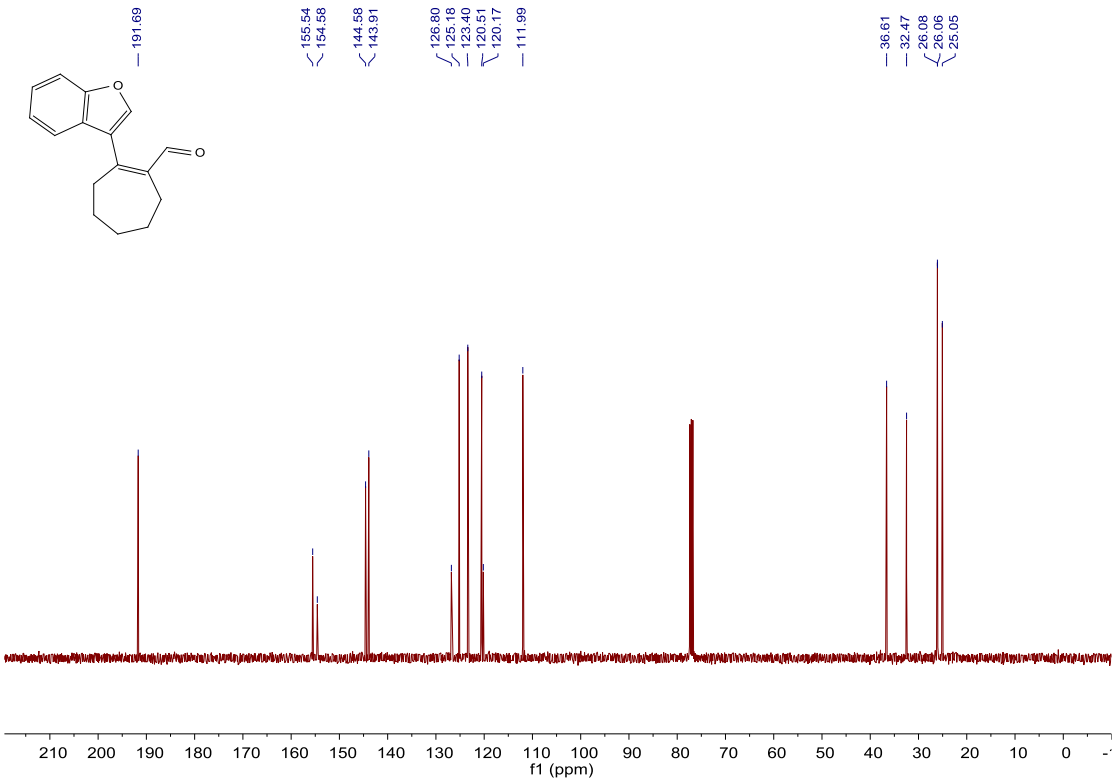
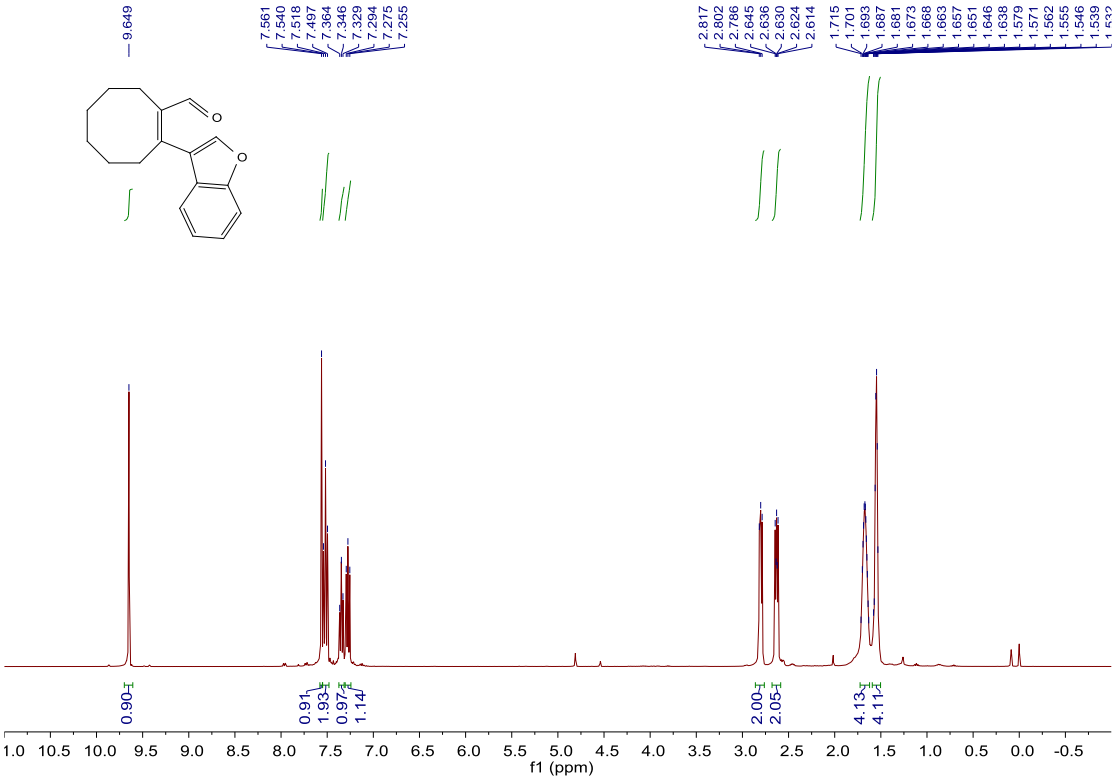
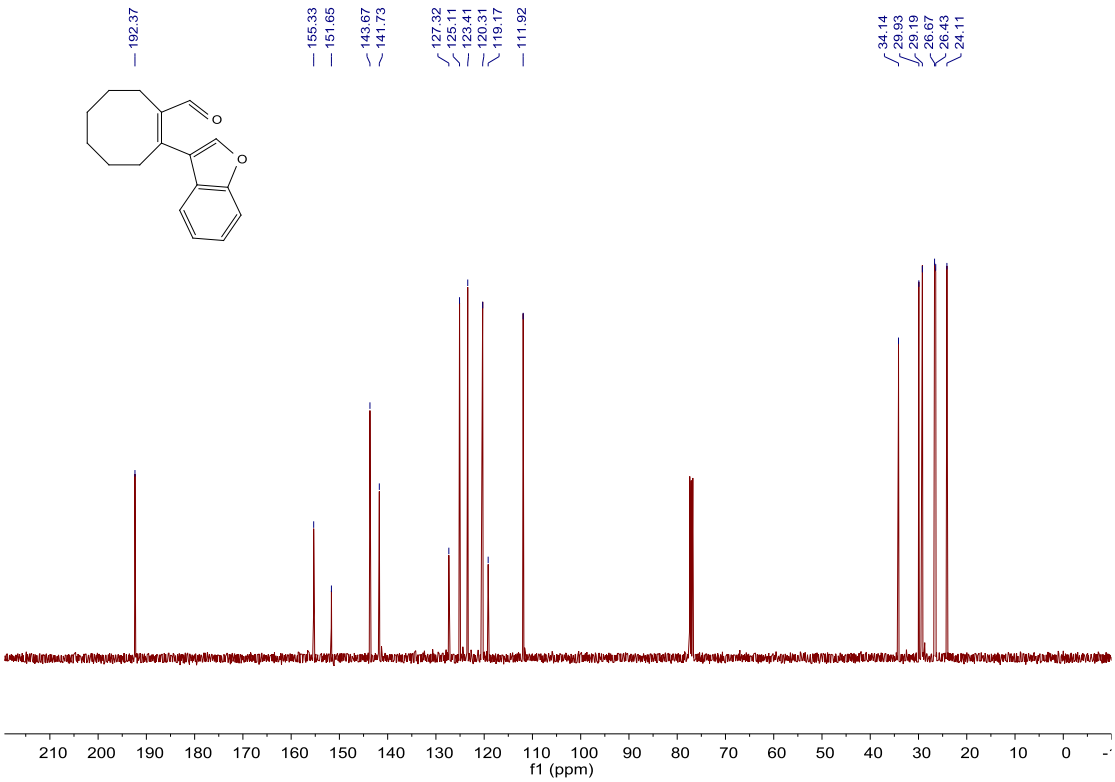


^{1}H NMR of In8-1r



^{13}C NMR of In8-1r



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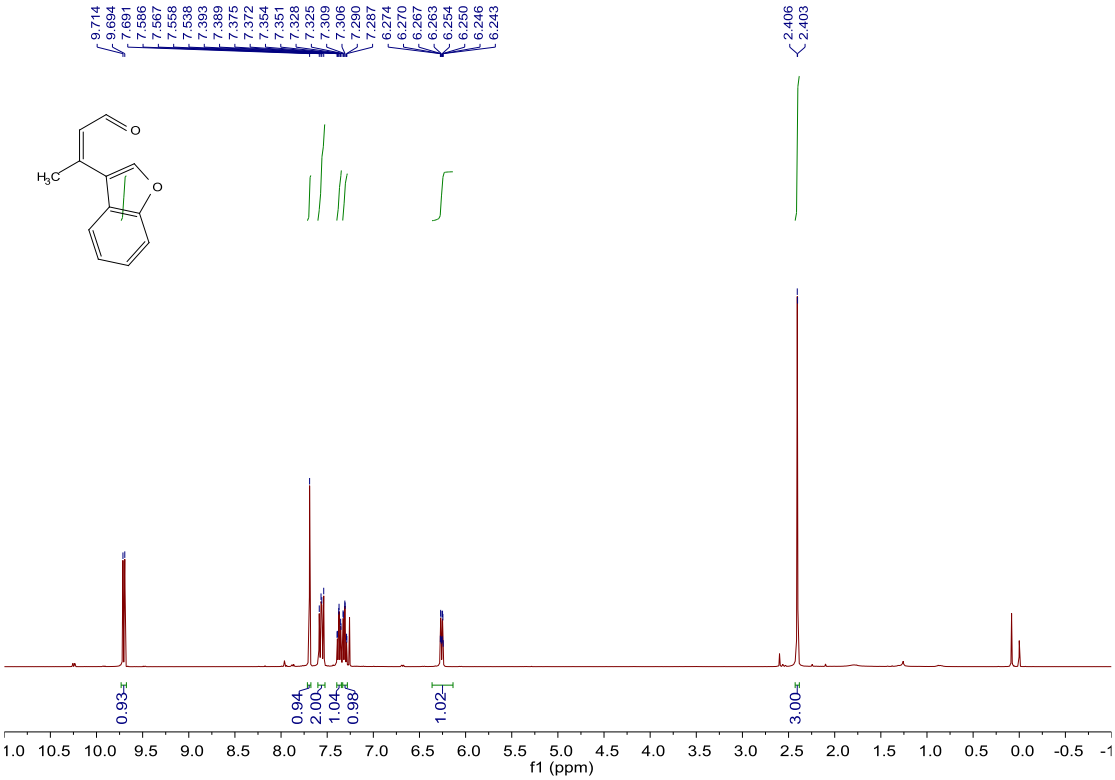
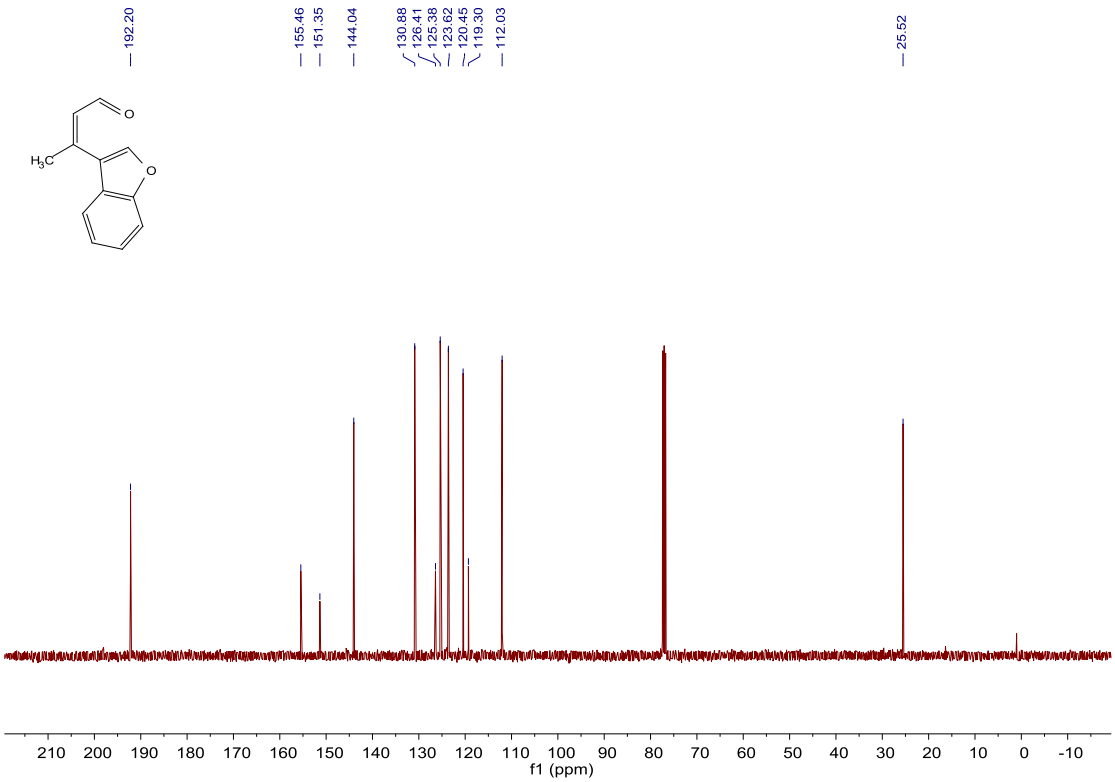


^{13}C NMR of In8-1s



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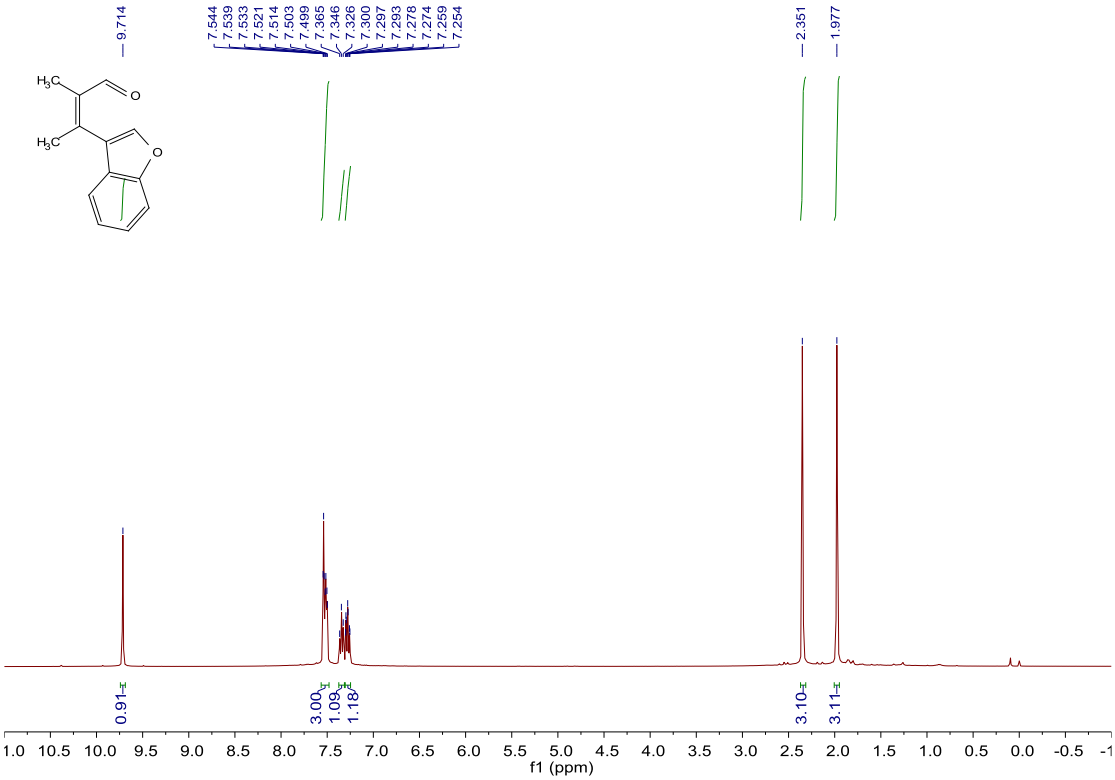

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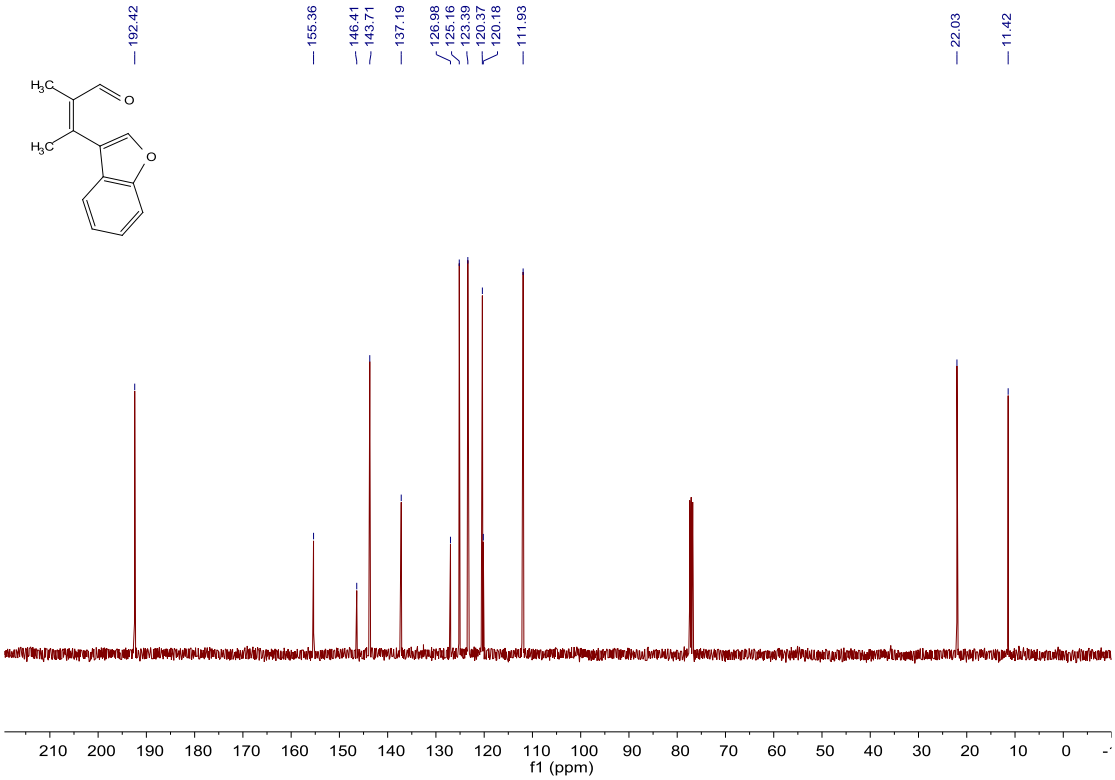

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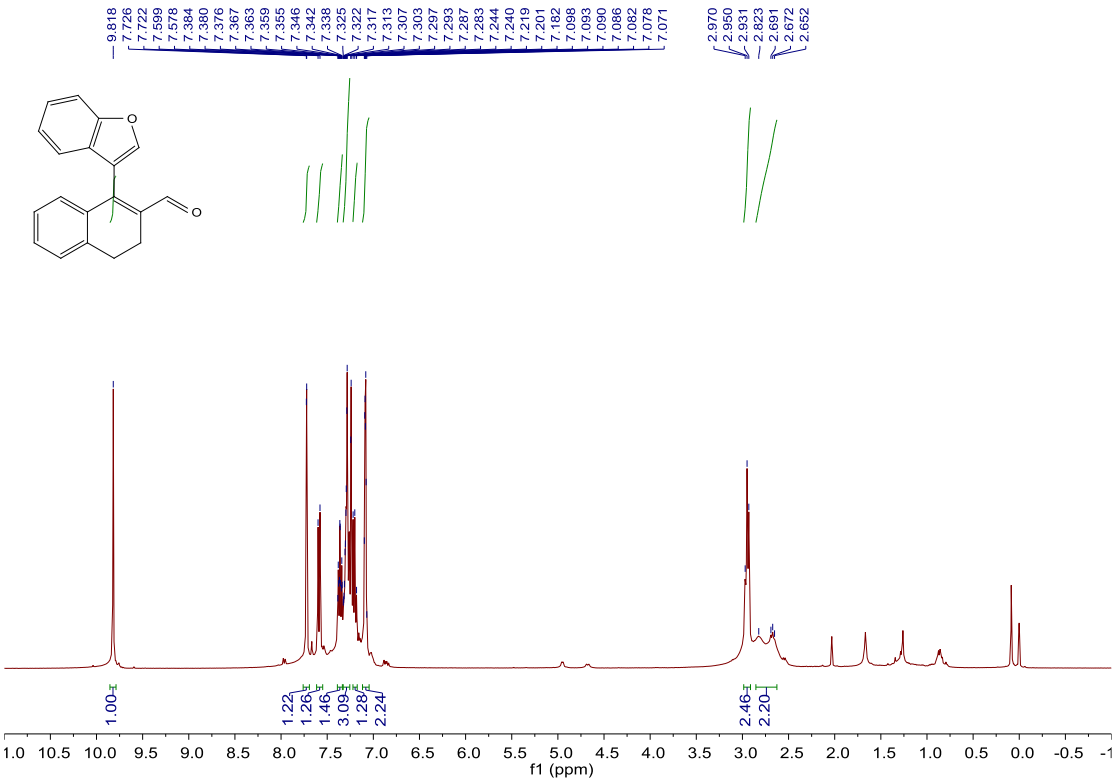

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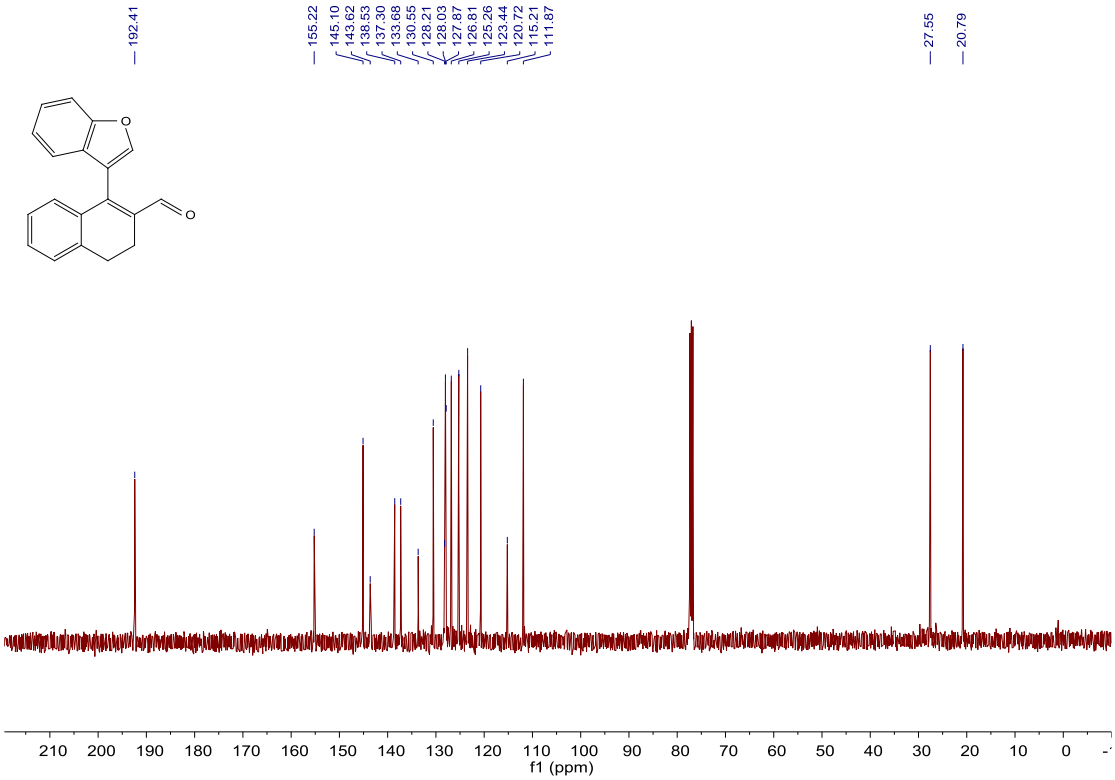

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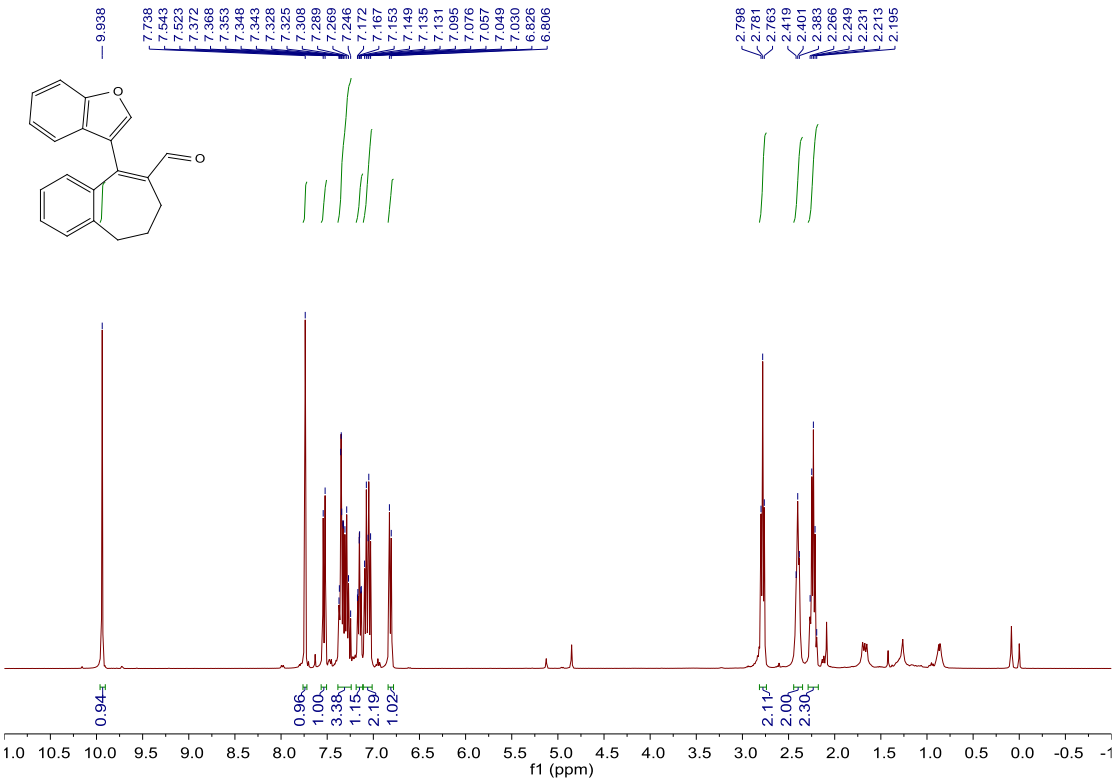
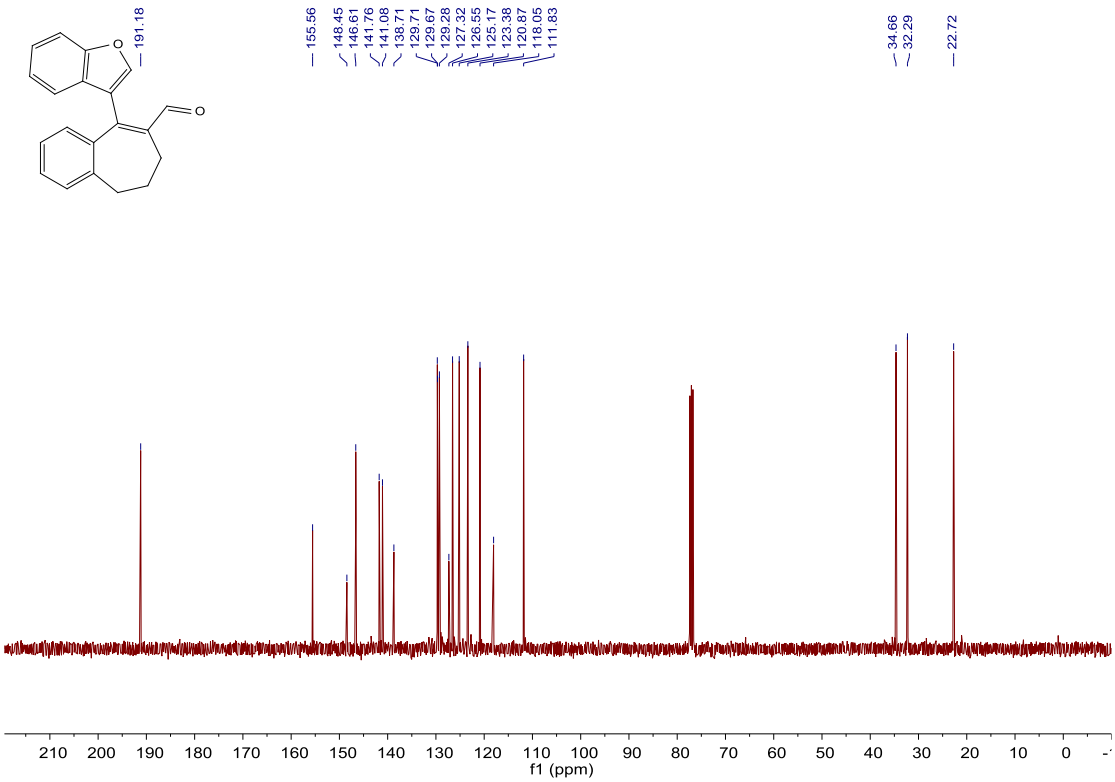
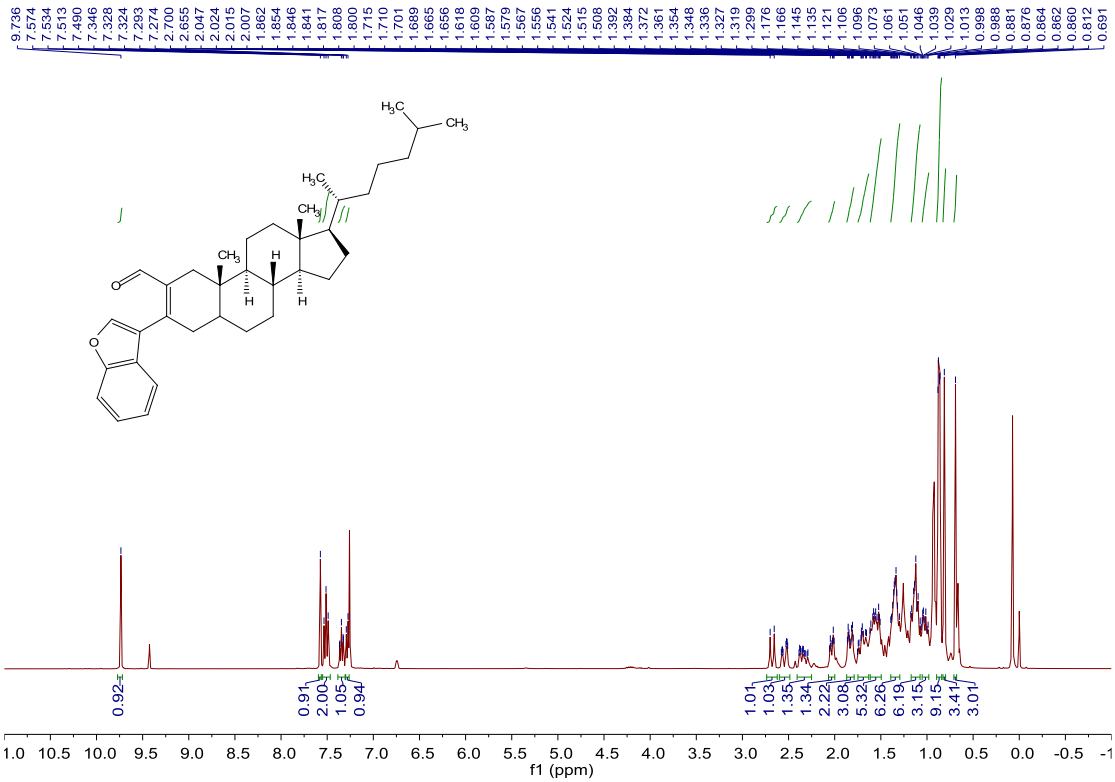


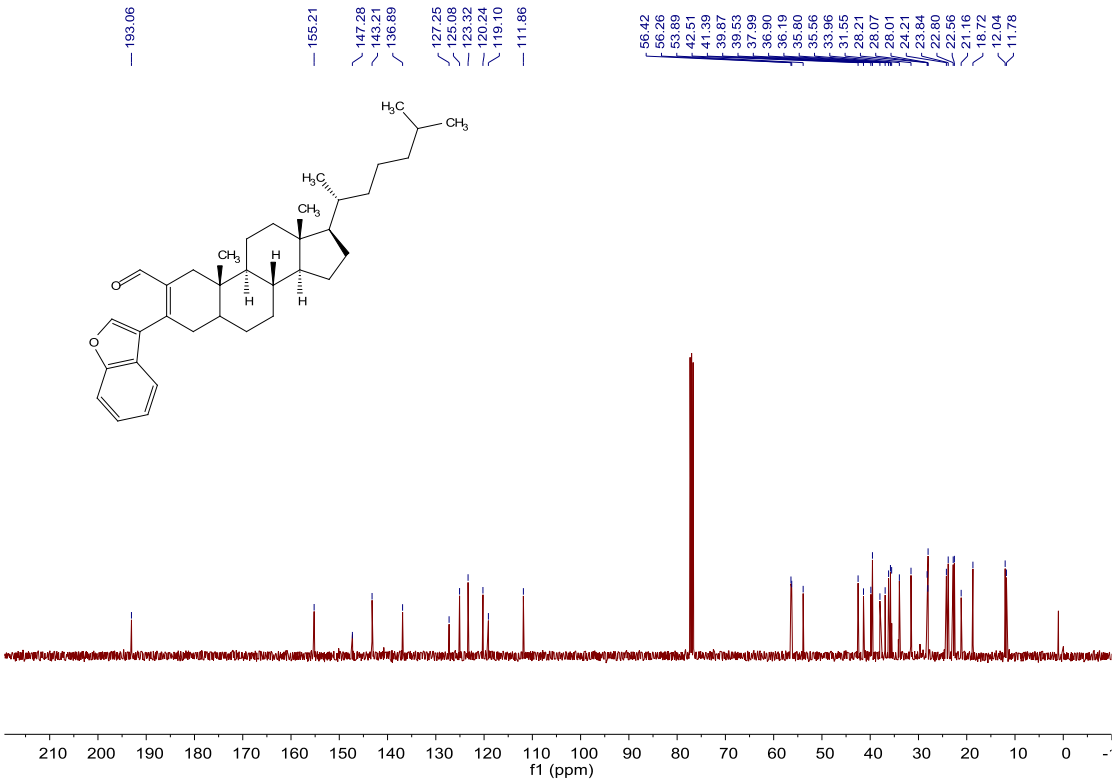
^{13}C NMR of In8-1v



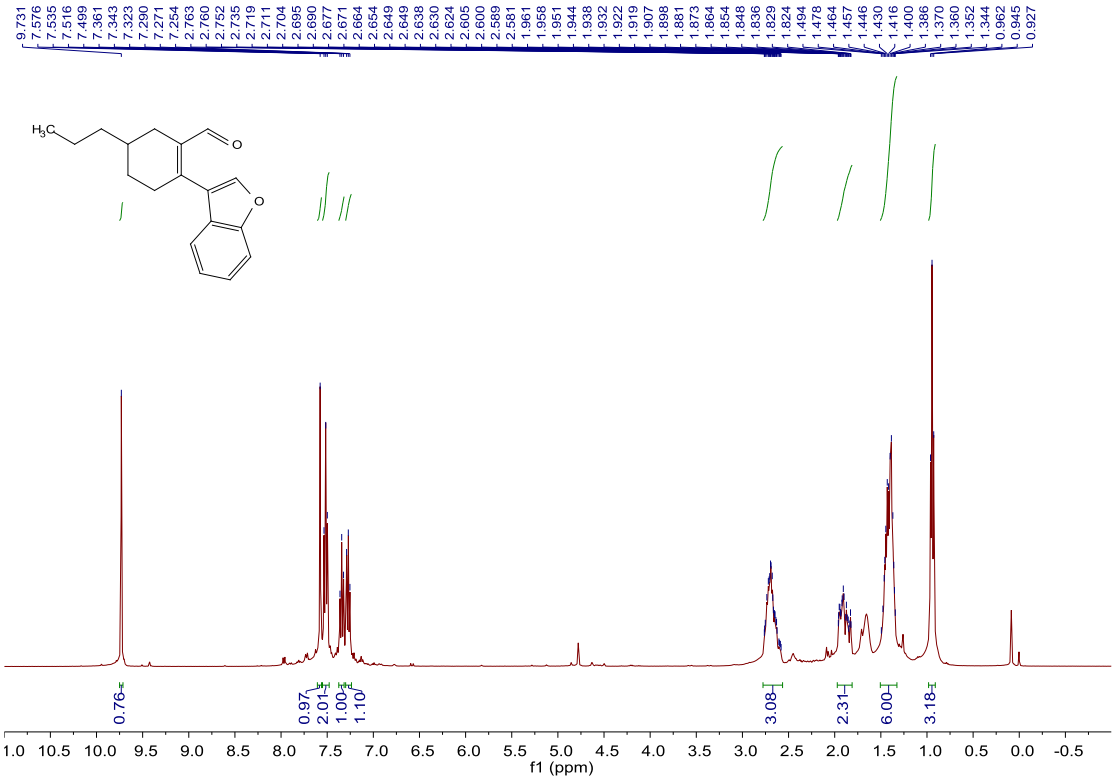
^{1}H NMR of In8-1w



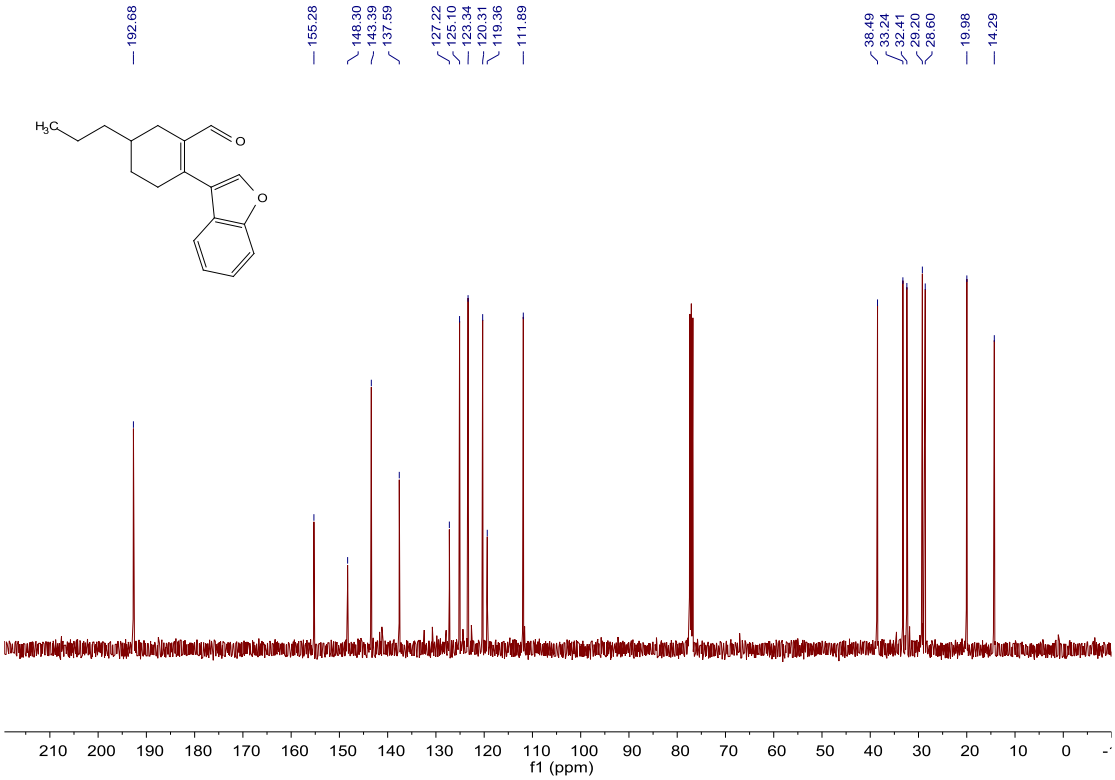
^{13}C NMR of In8-1w



^{1}H NMR of In8-1x



^{13}C NMR of In8-1x



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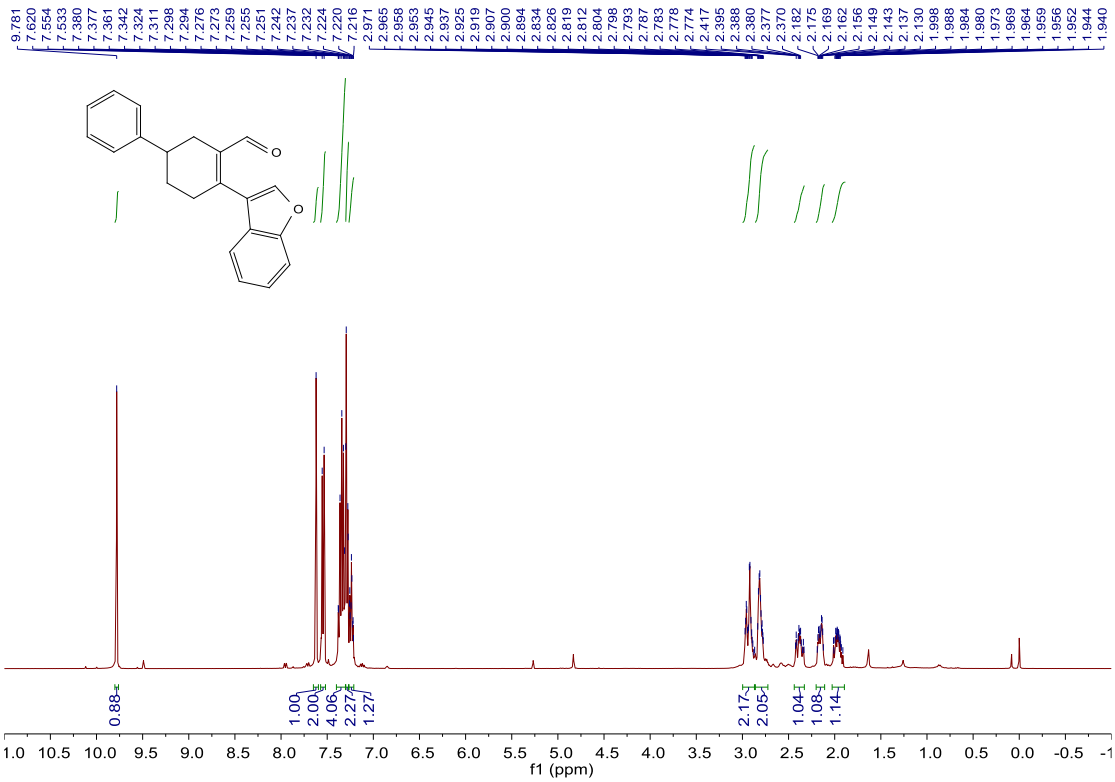

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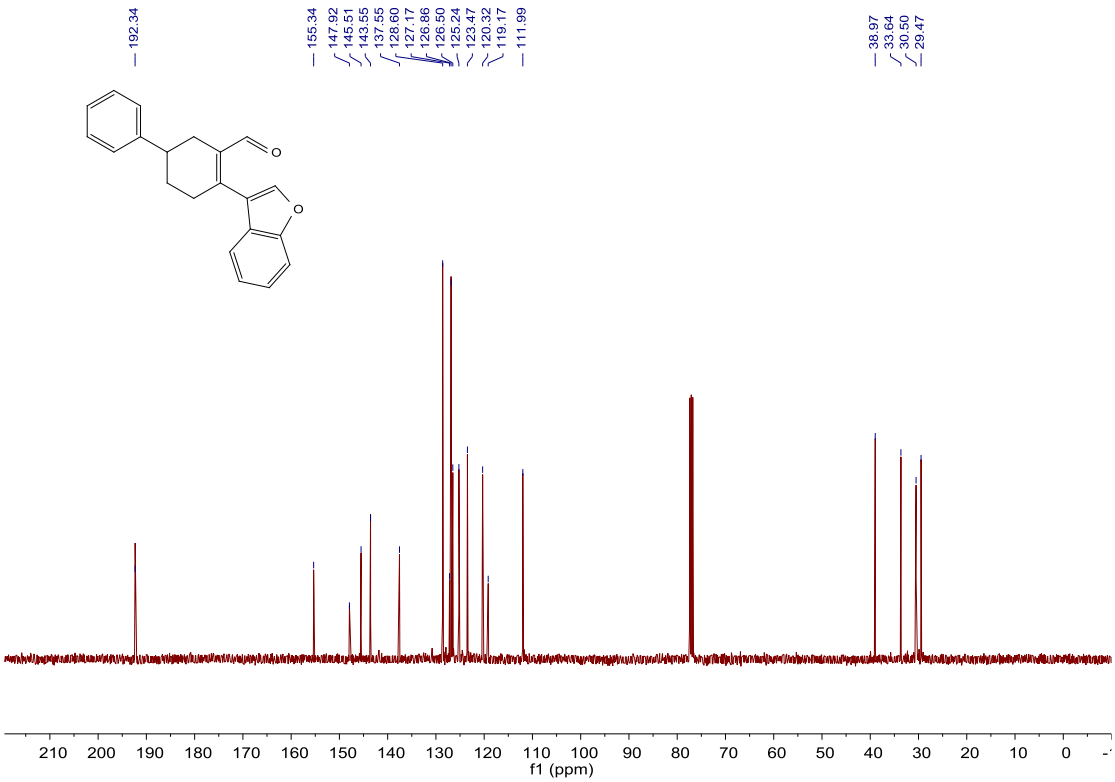

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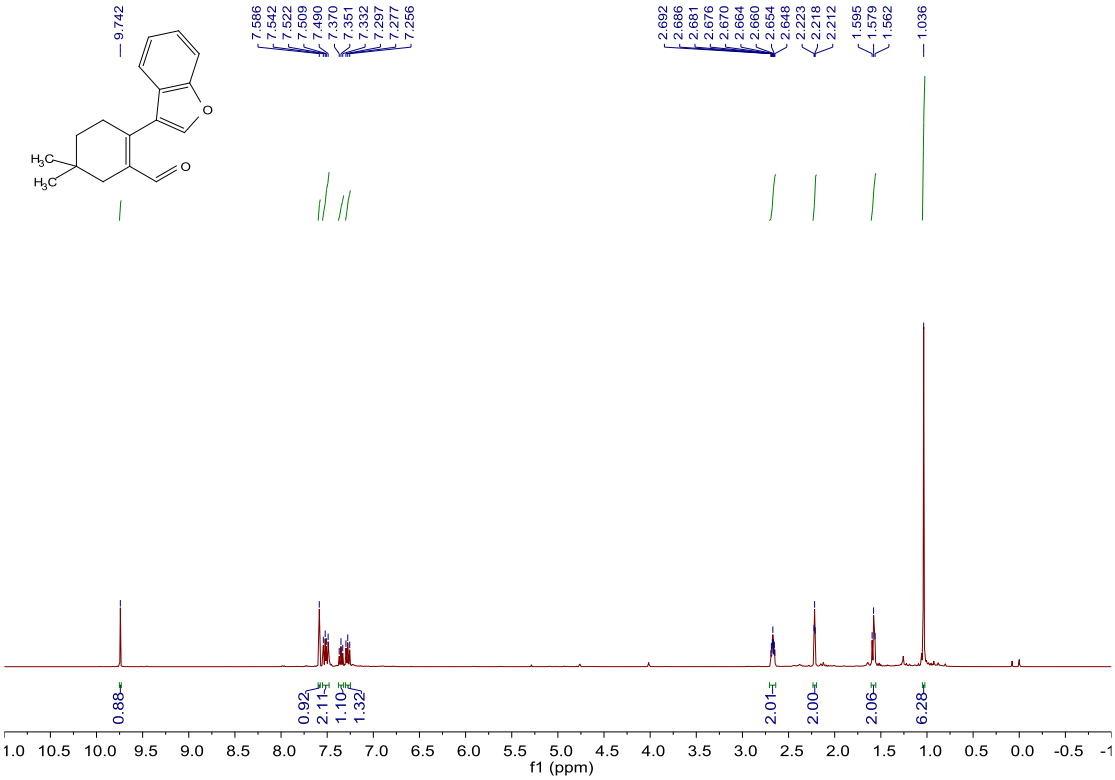

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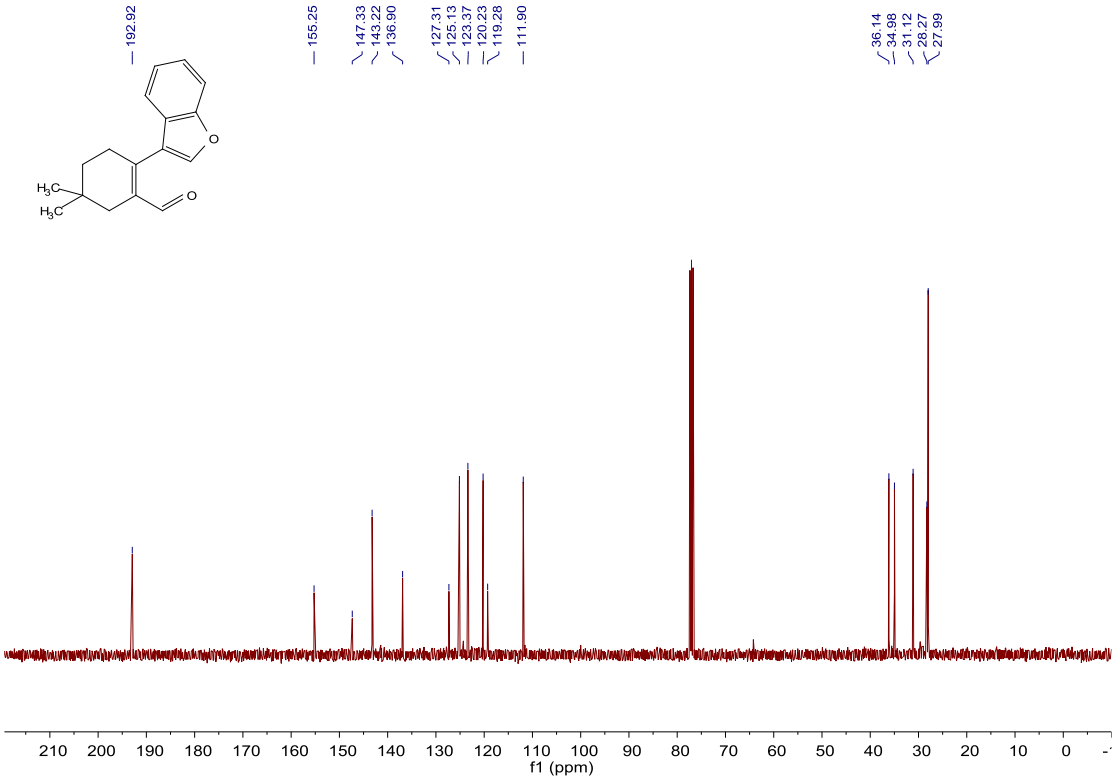
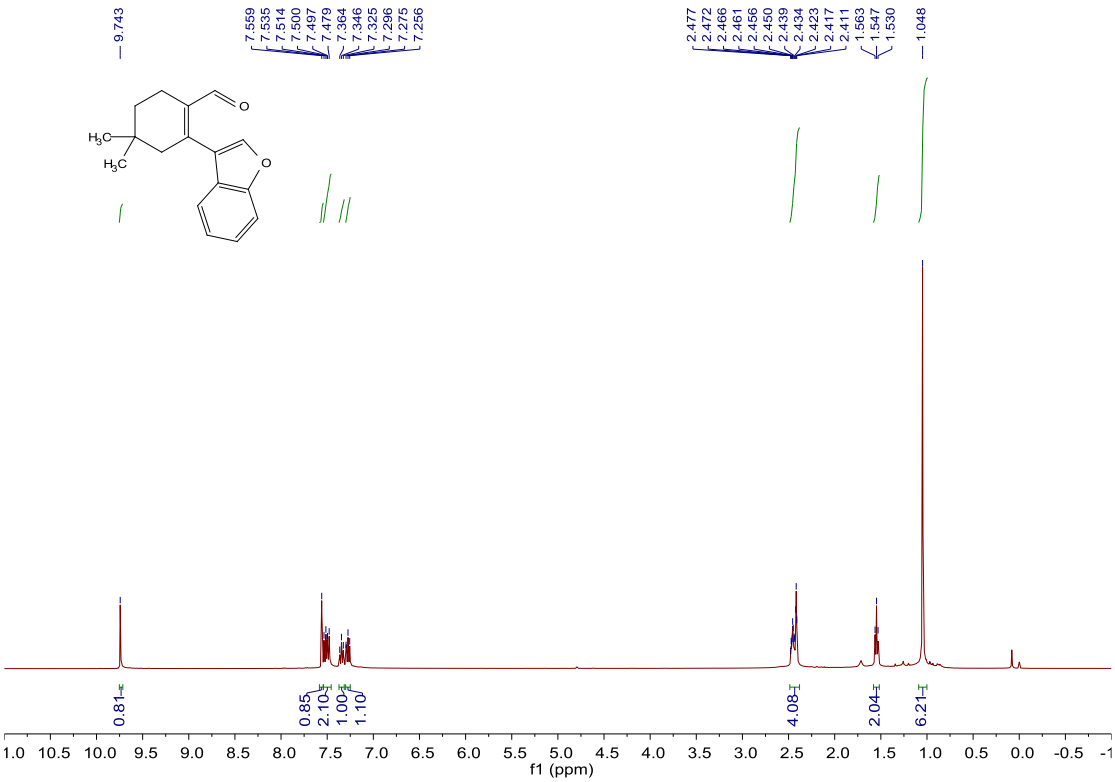
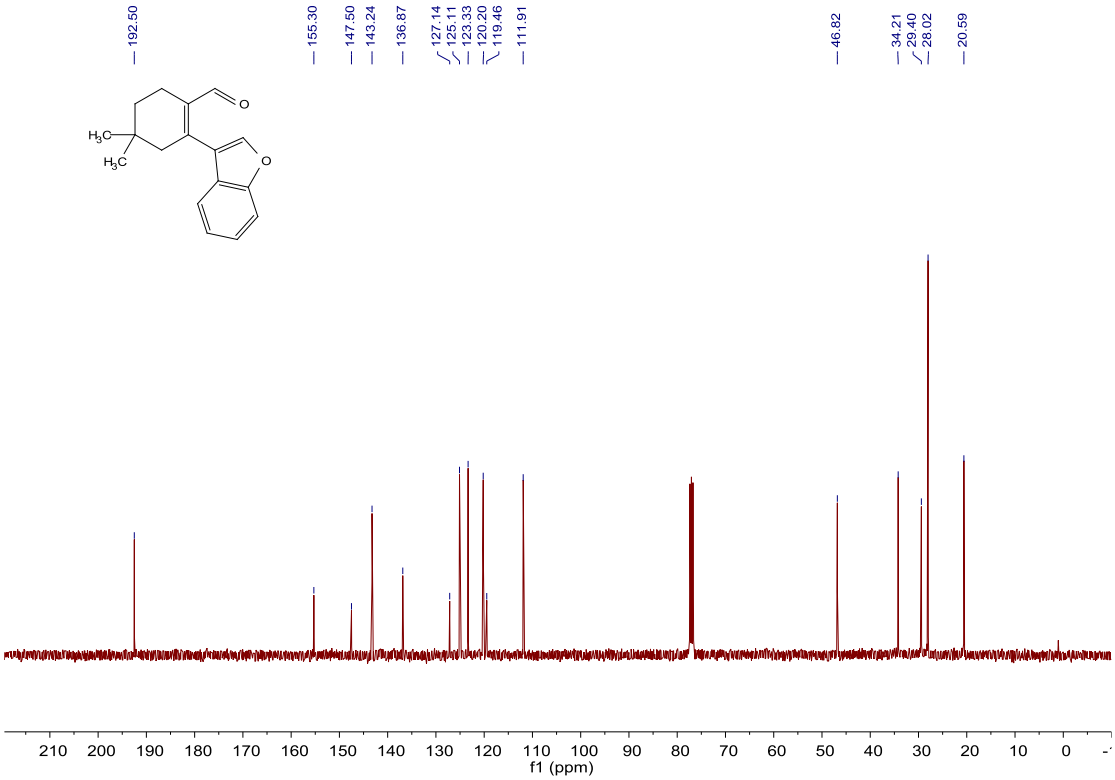


^{1}H NMR of In8-1ab



^{13}C NMR of In8-1ab



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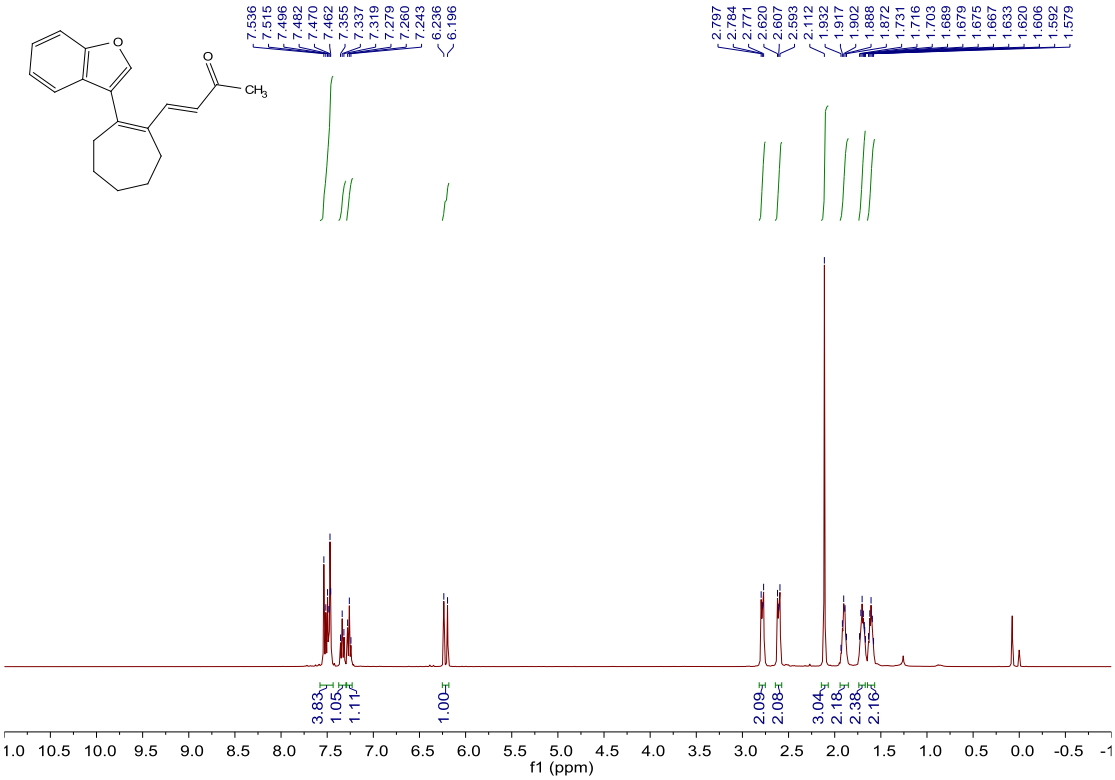
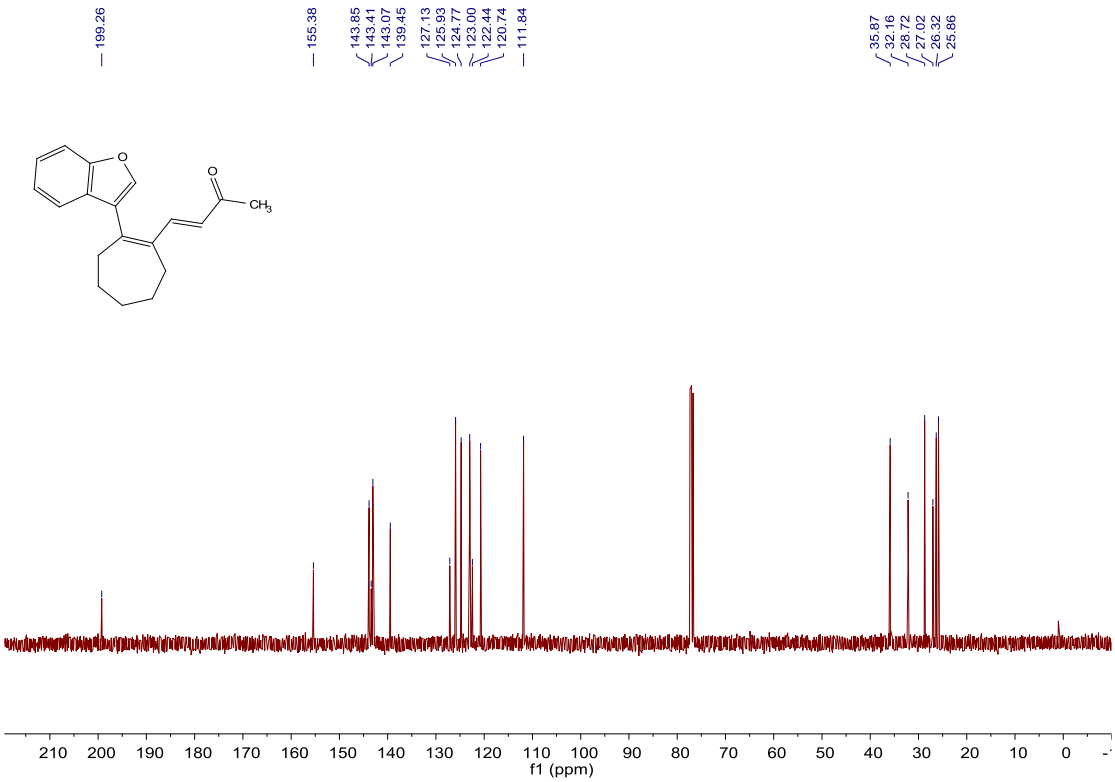


^{13}C NMR of 1q



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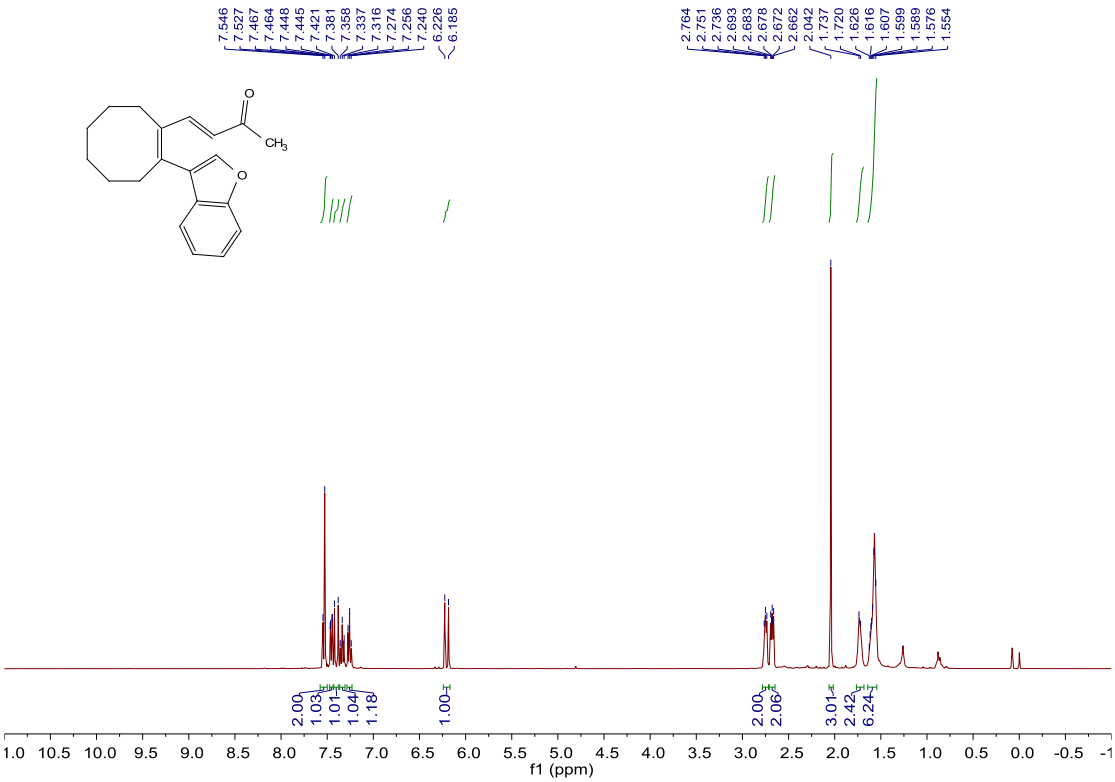
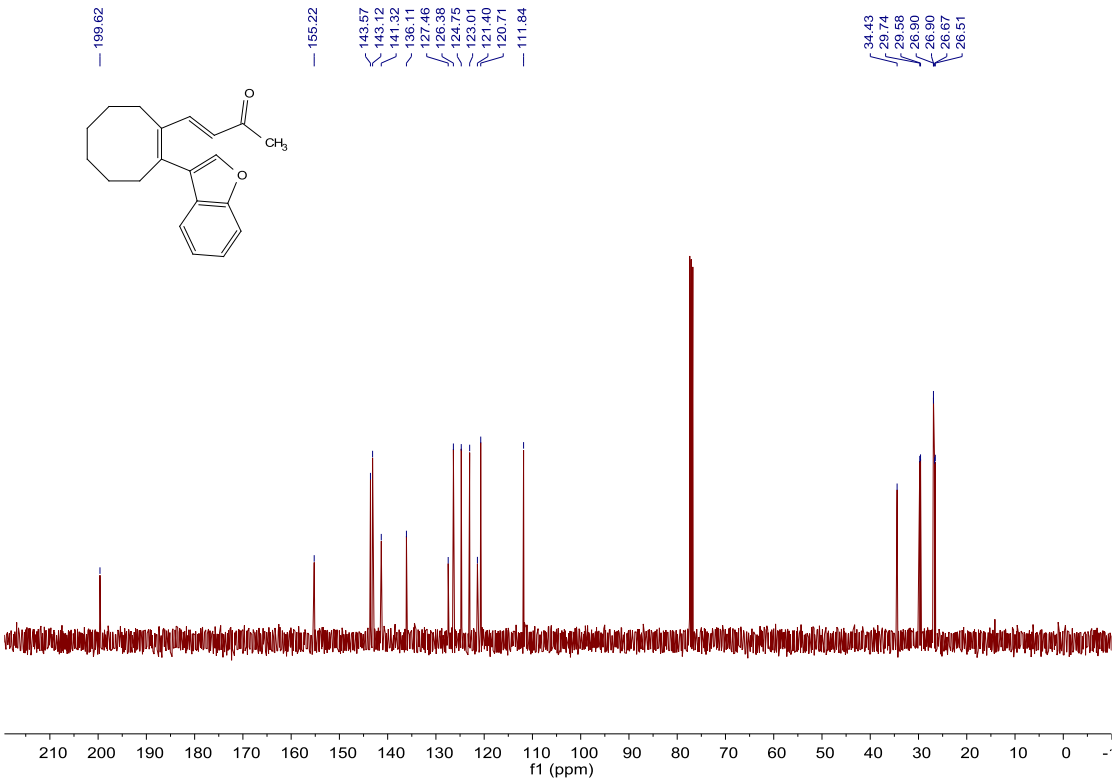
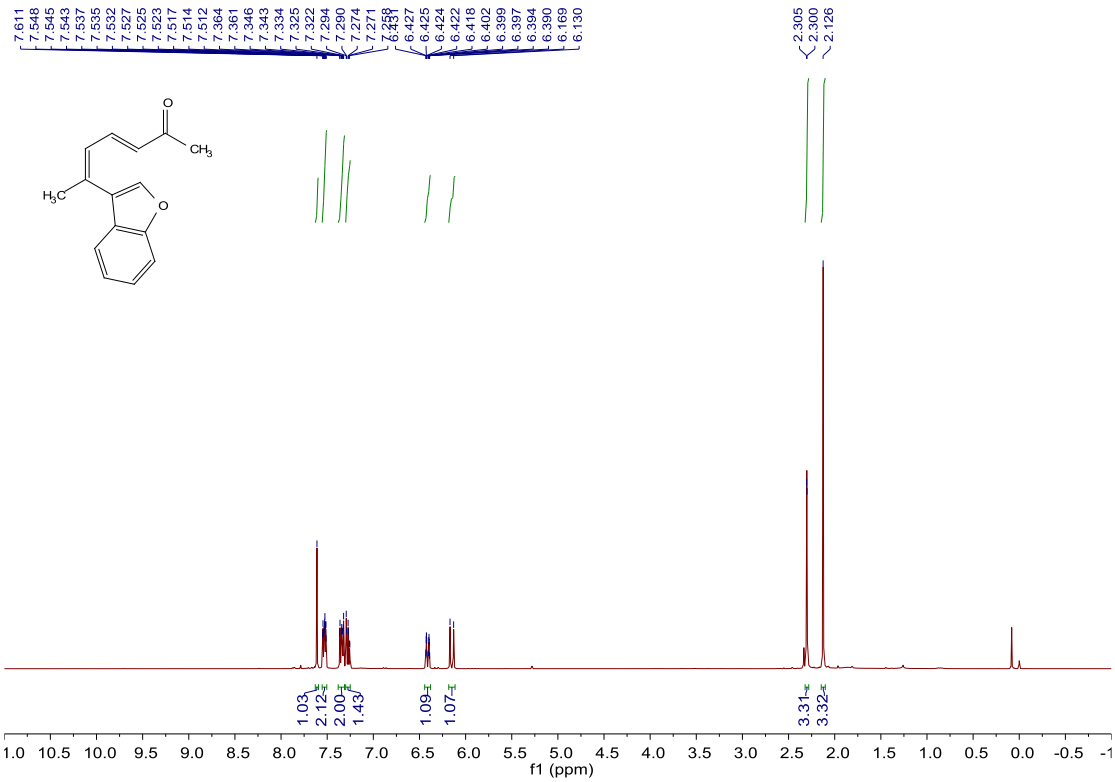


^{13}C NMR of 1r



^{1}H NMR of 1s



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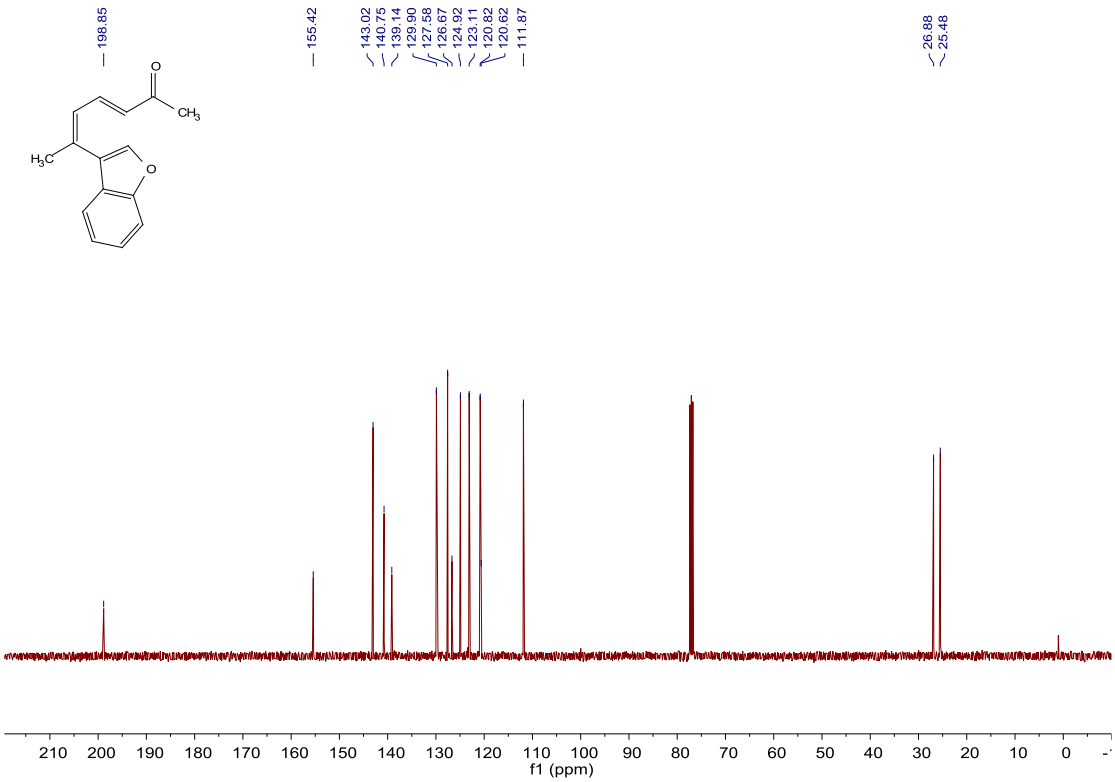
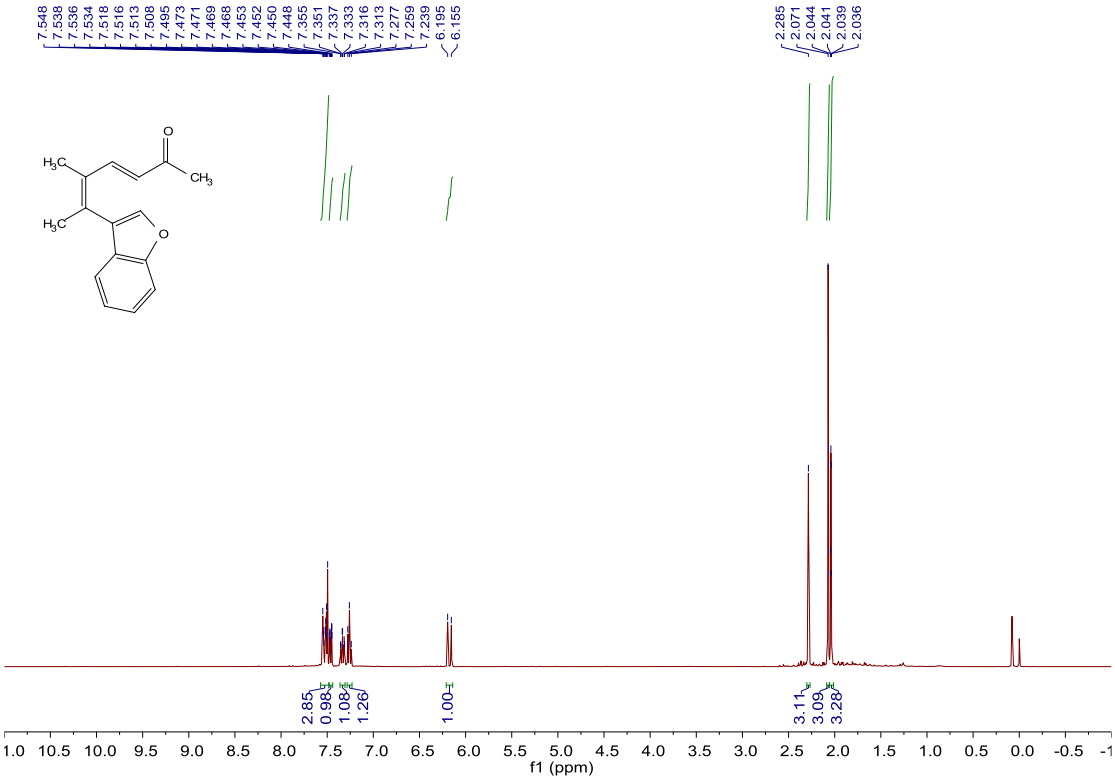


^{1}H NMR of 1t



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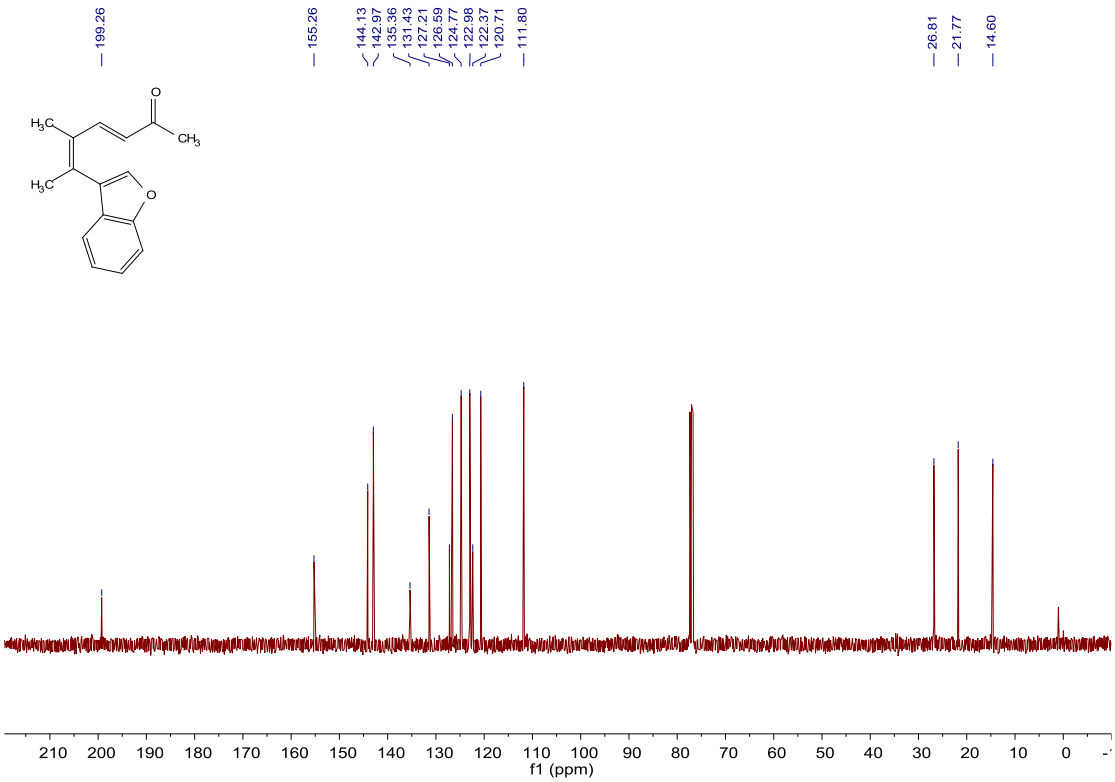

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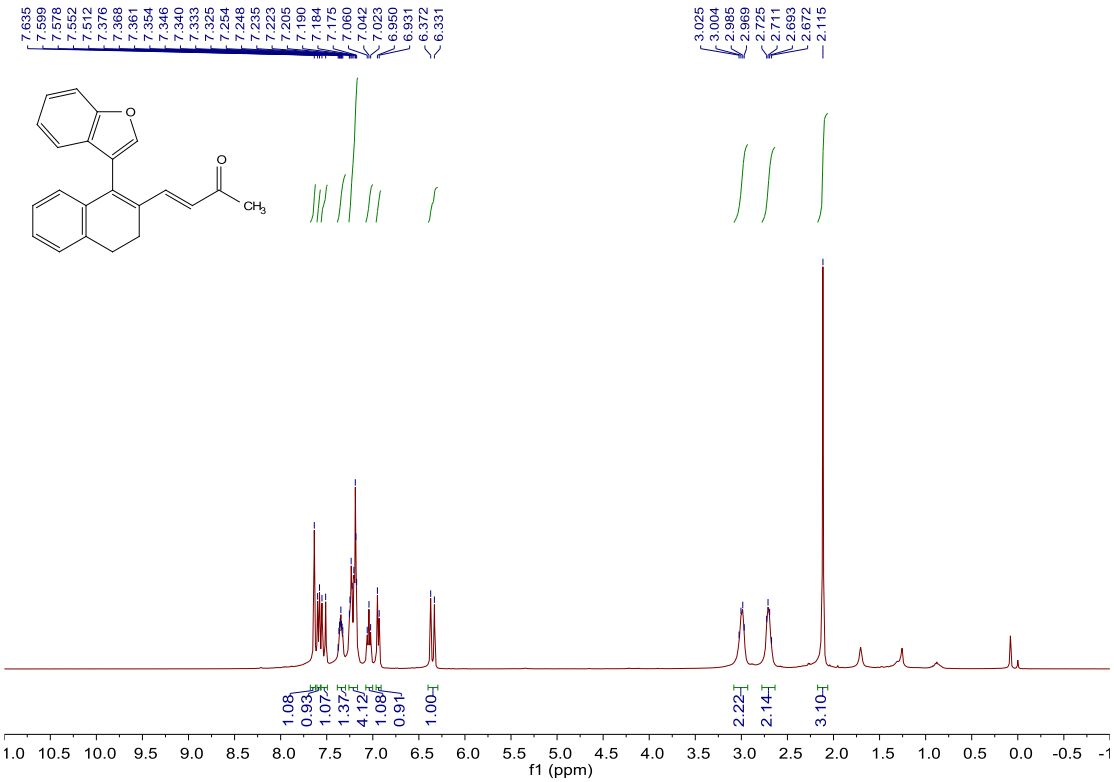

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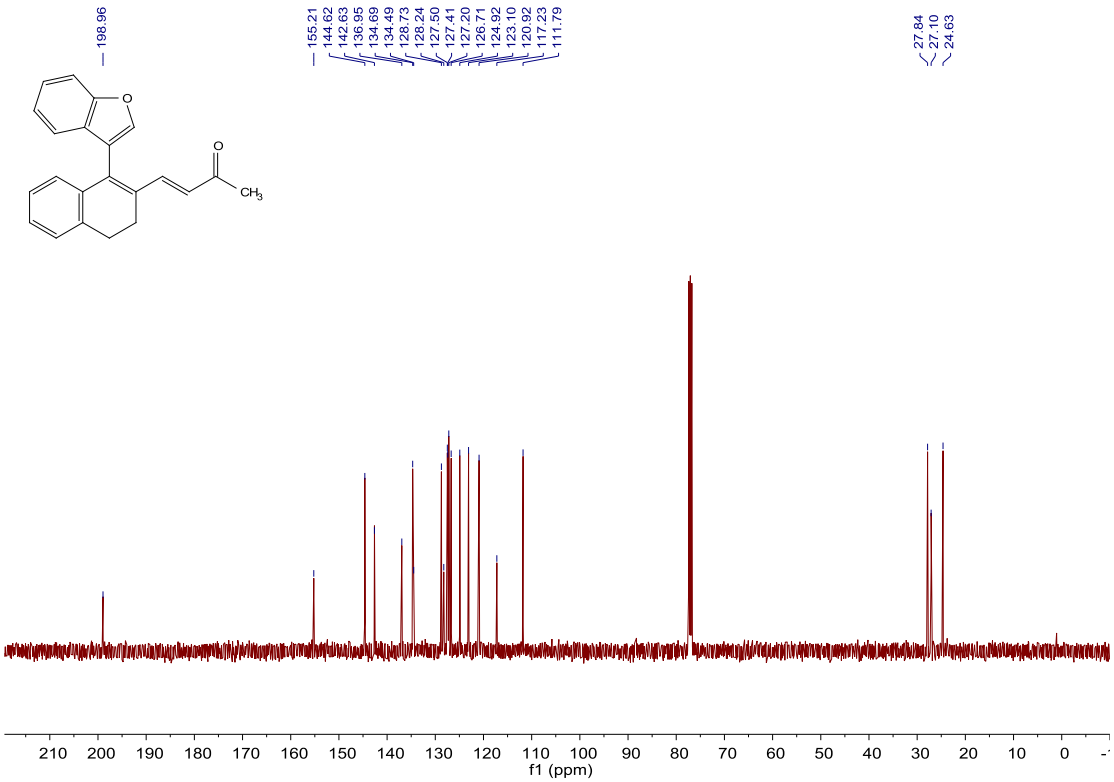

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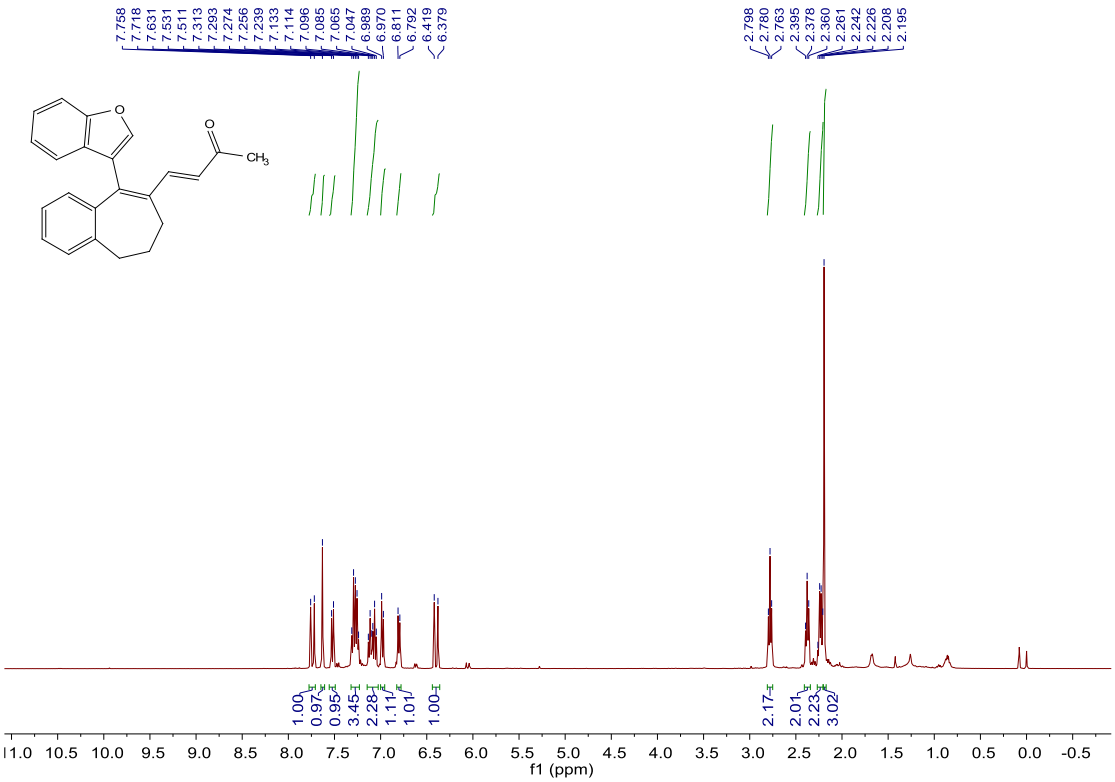

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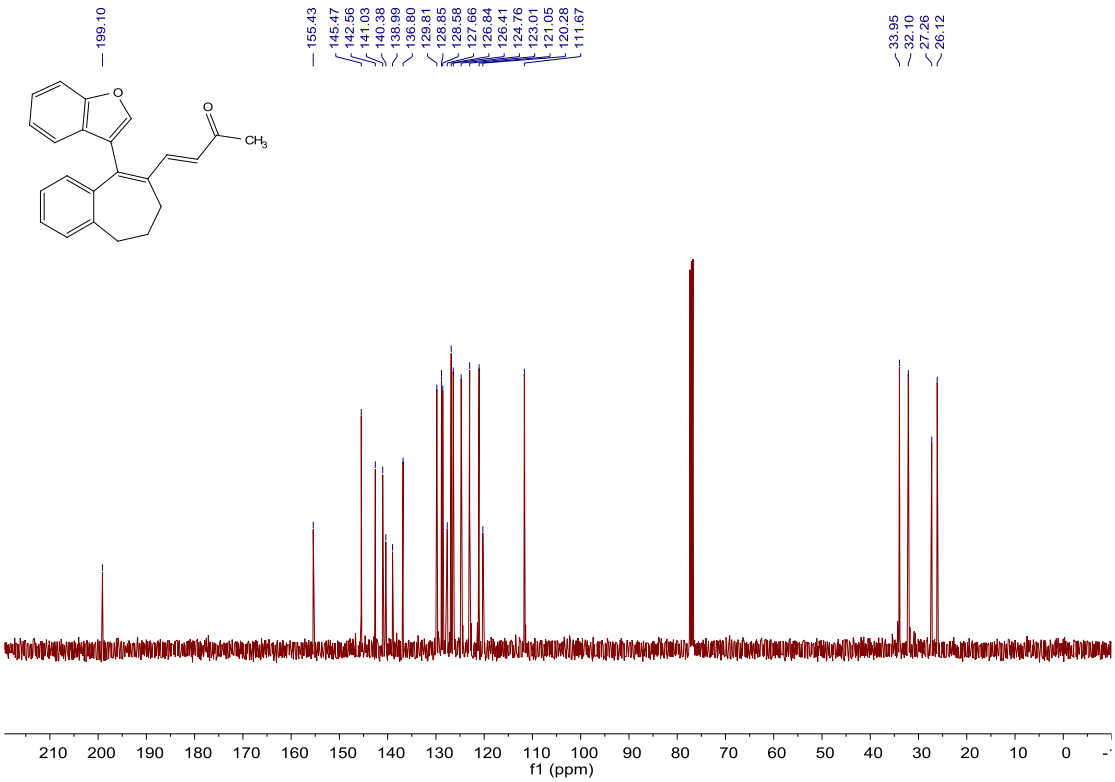

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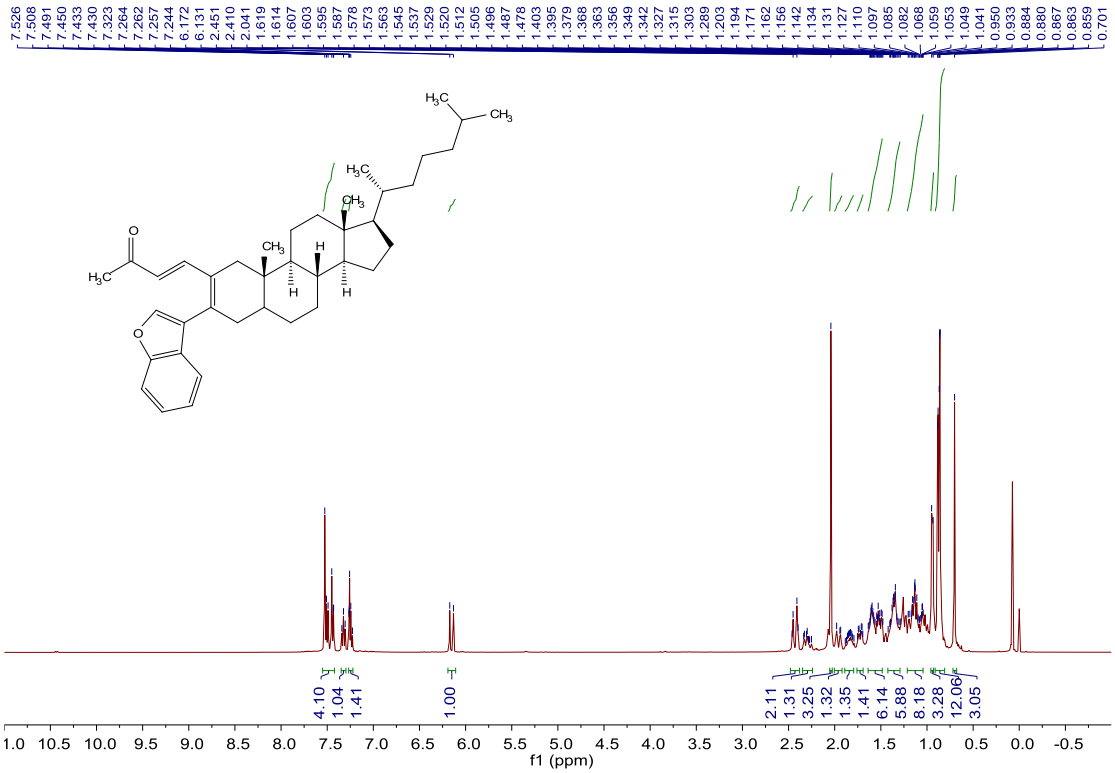

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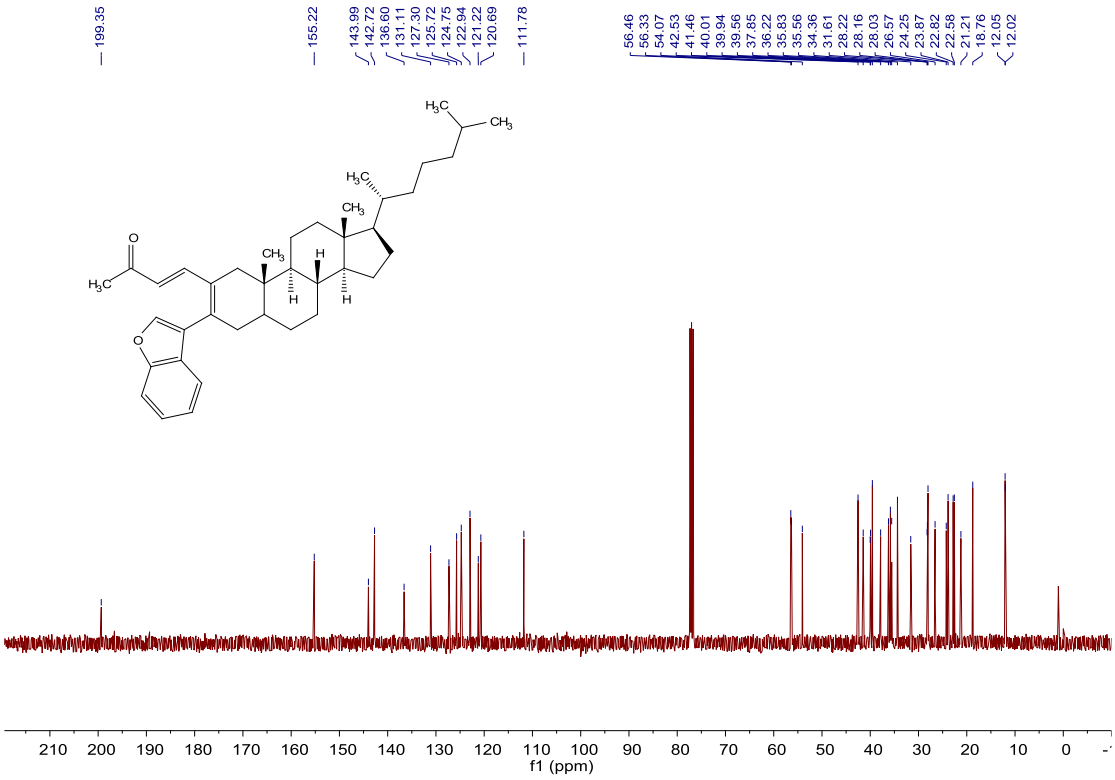

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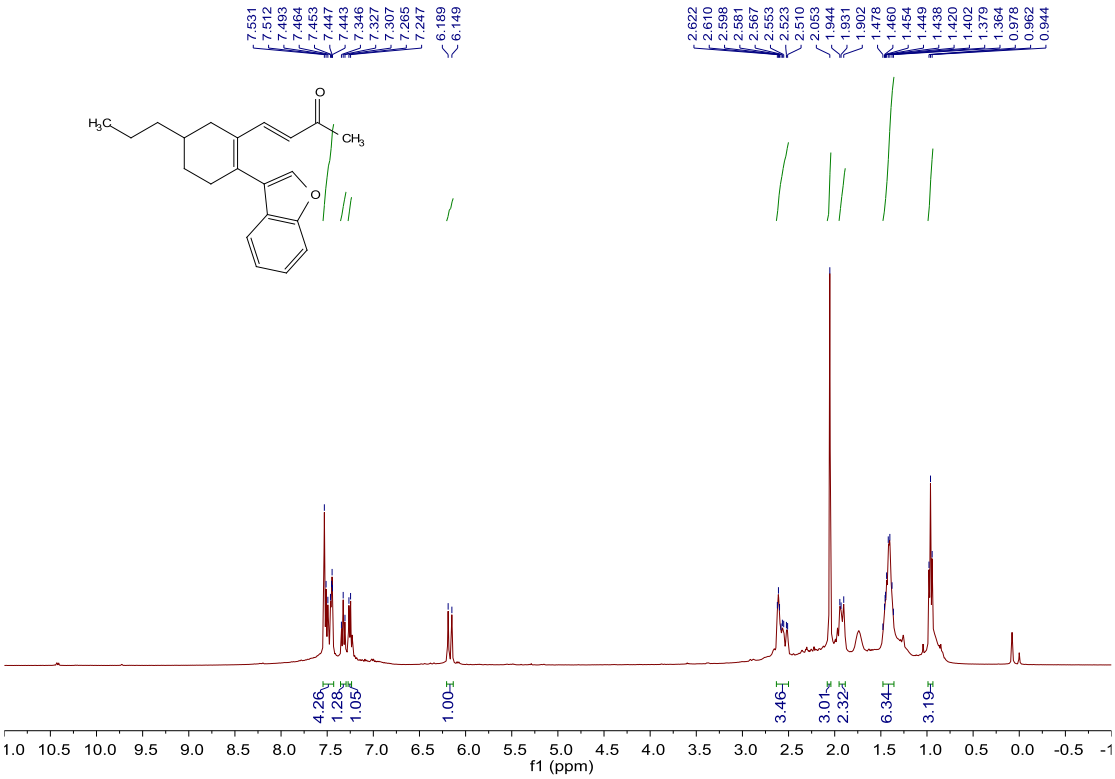

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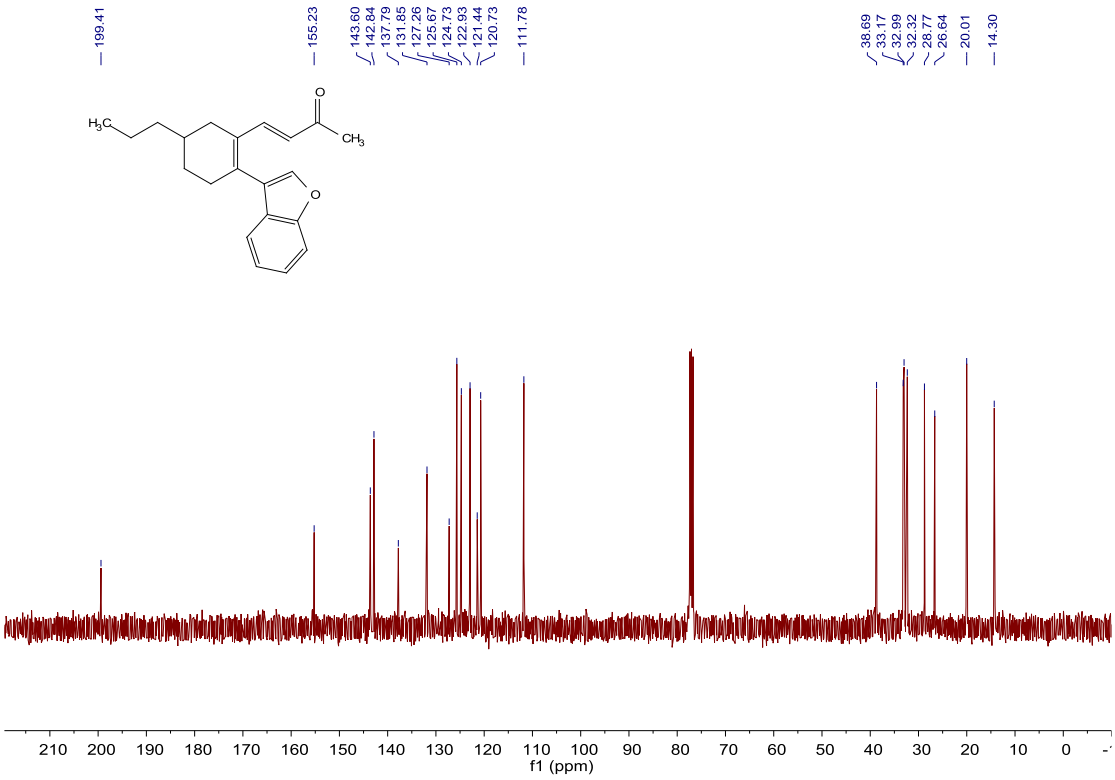

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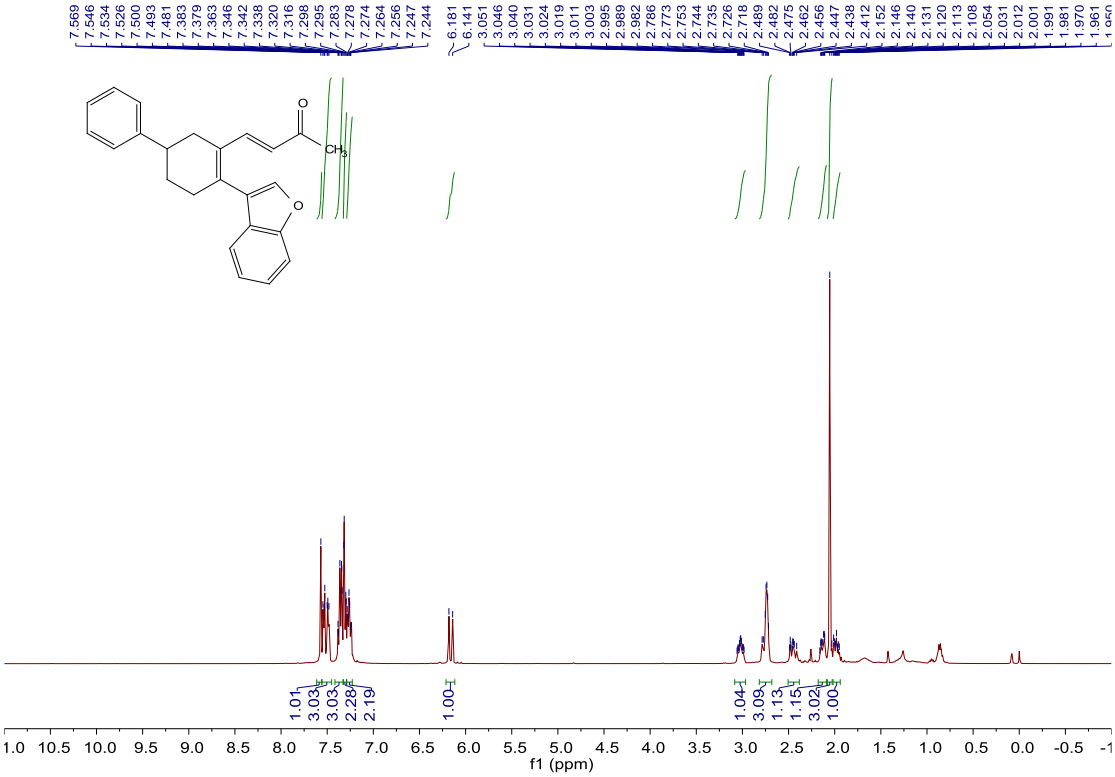

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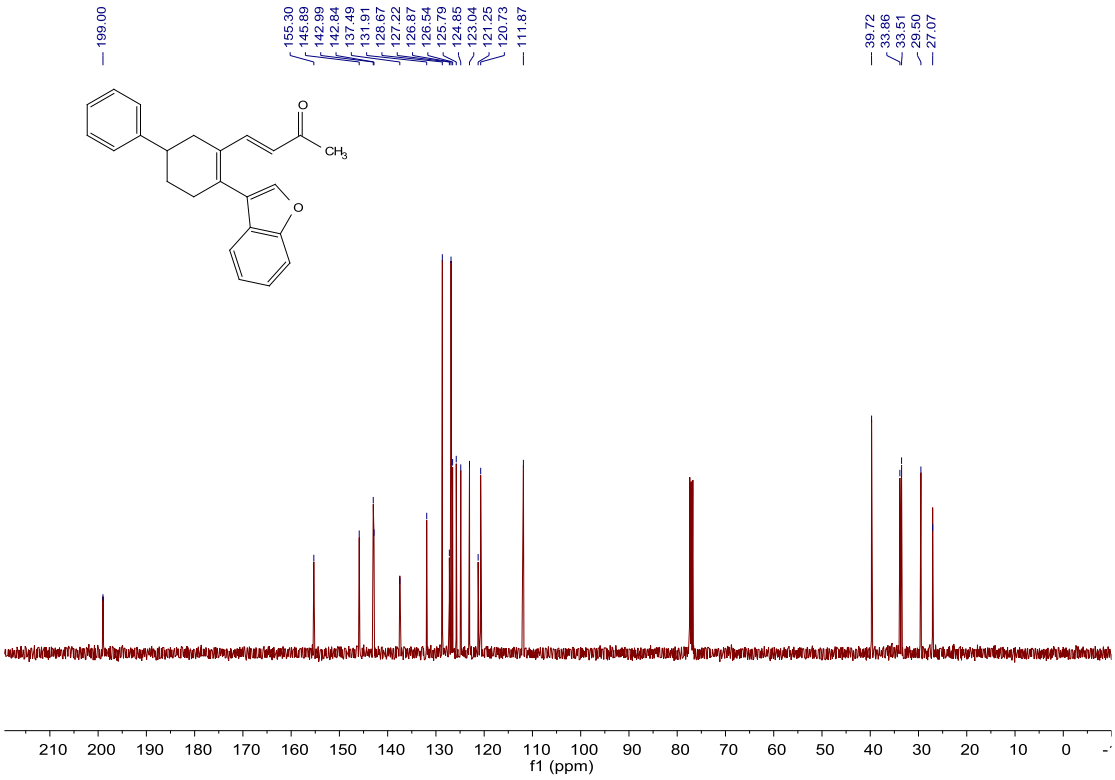

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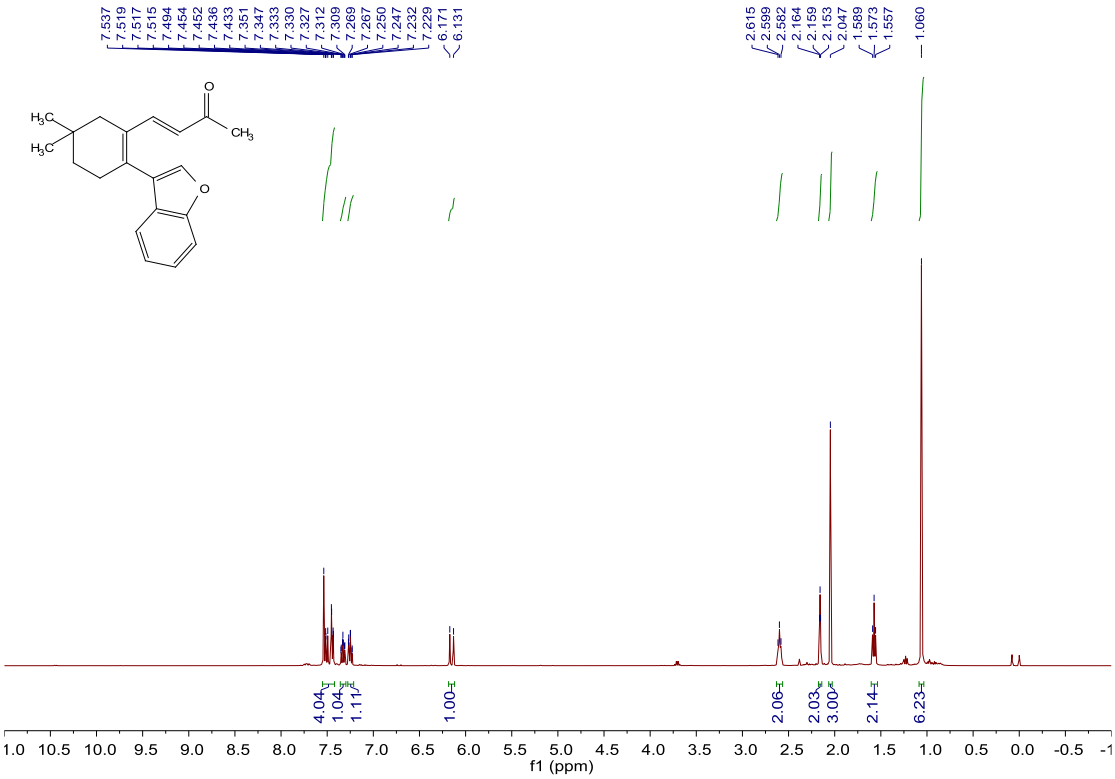

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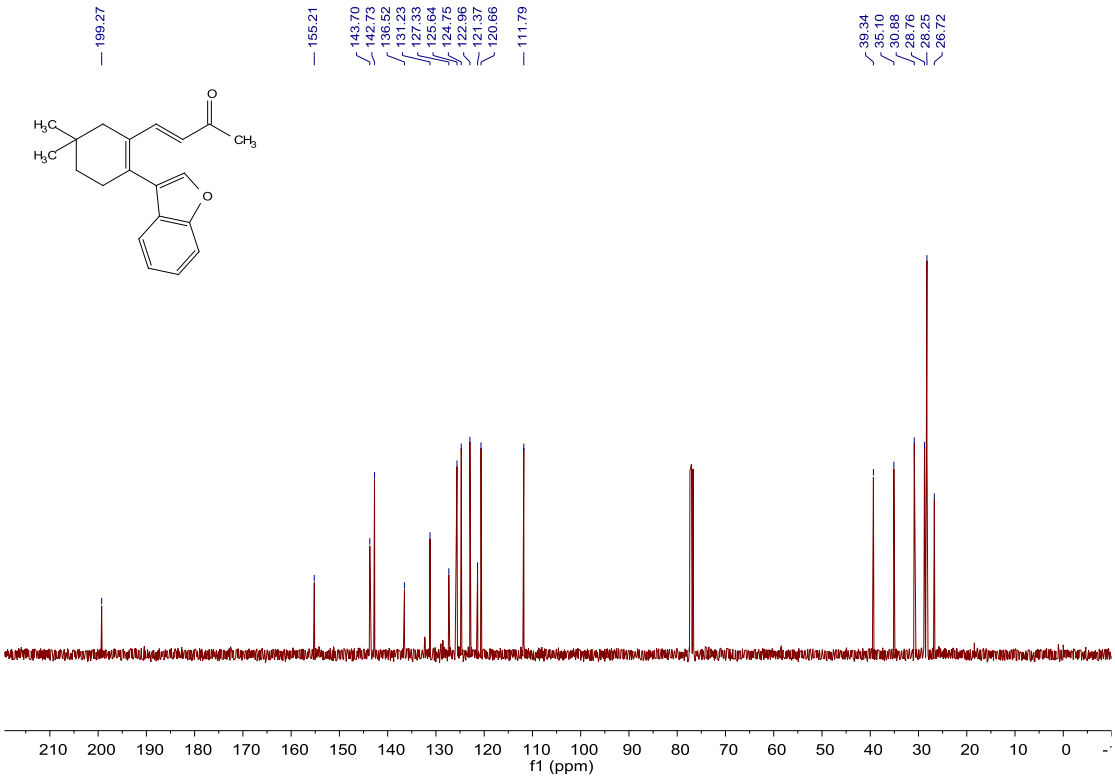

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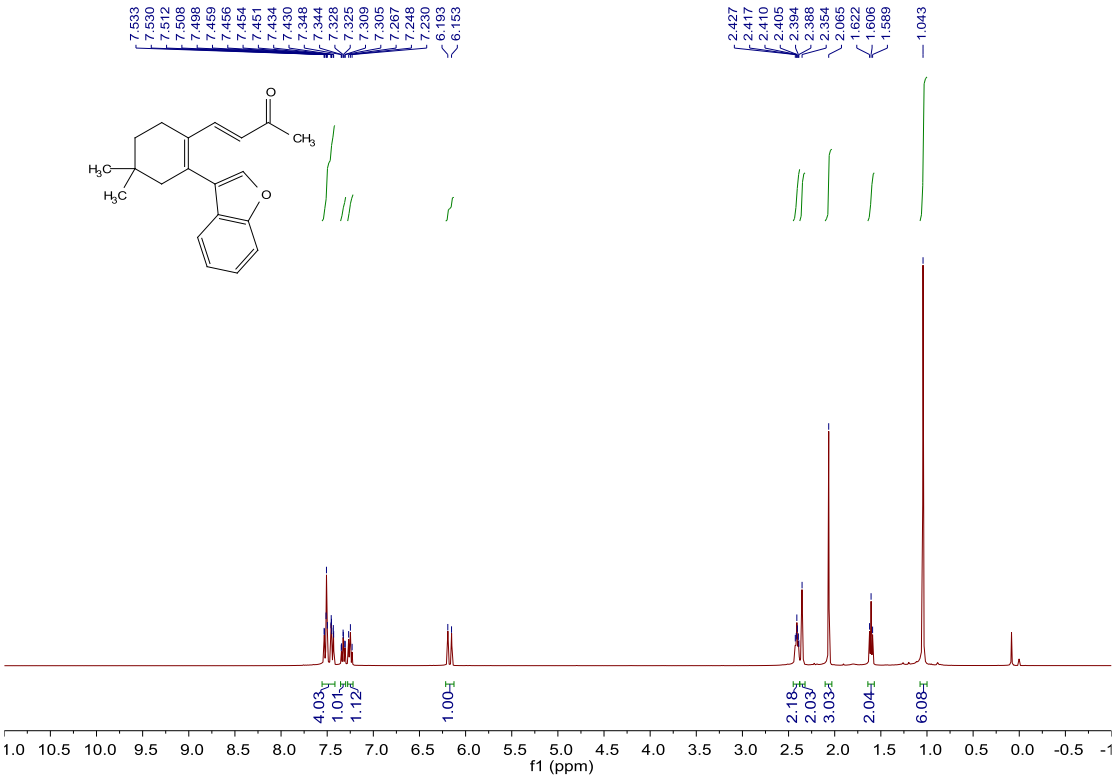

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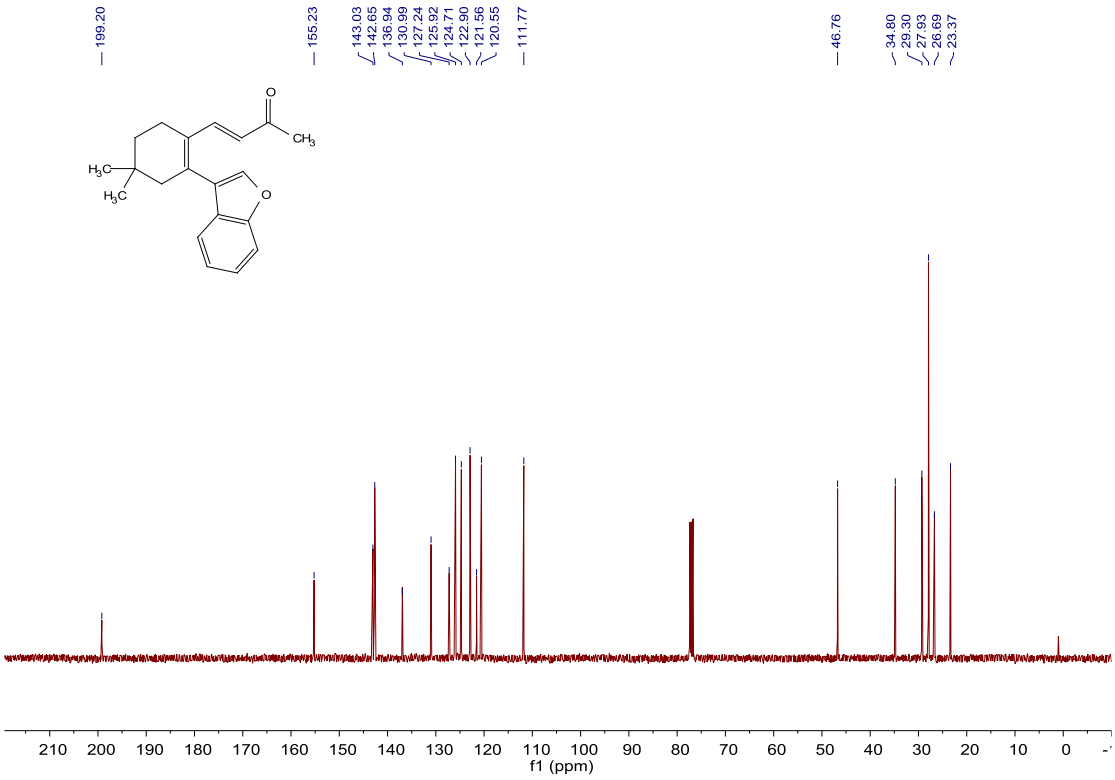
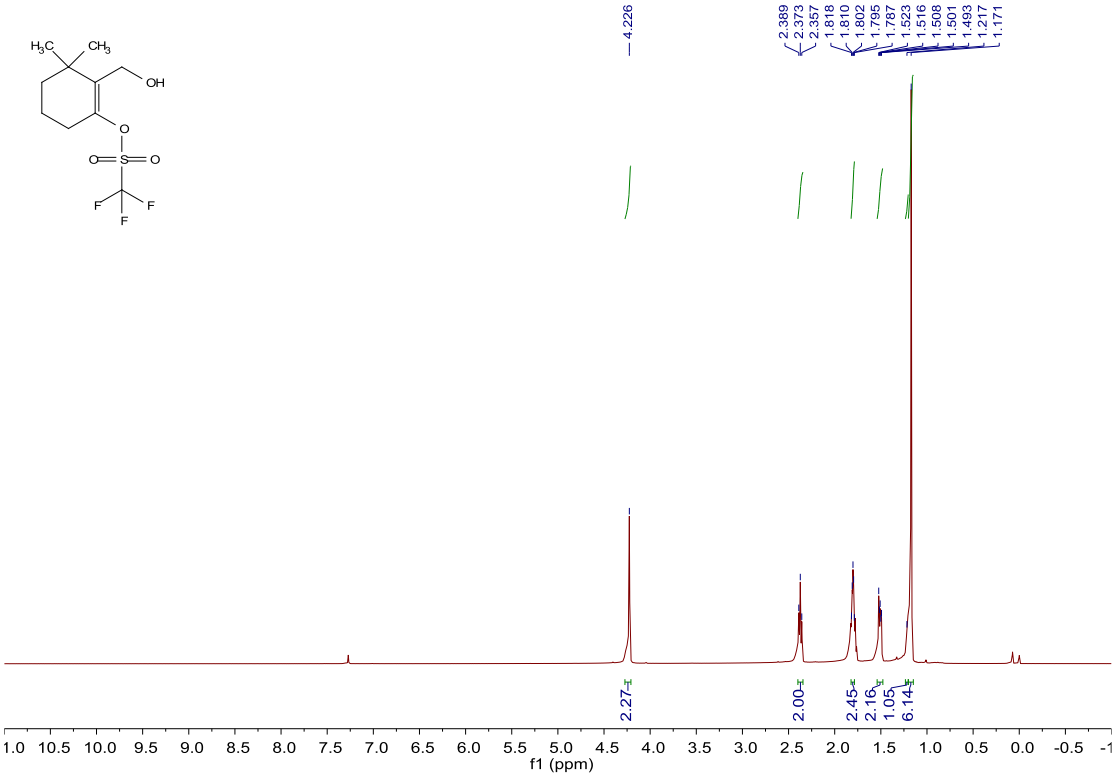
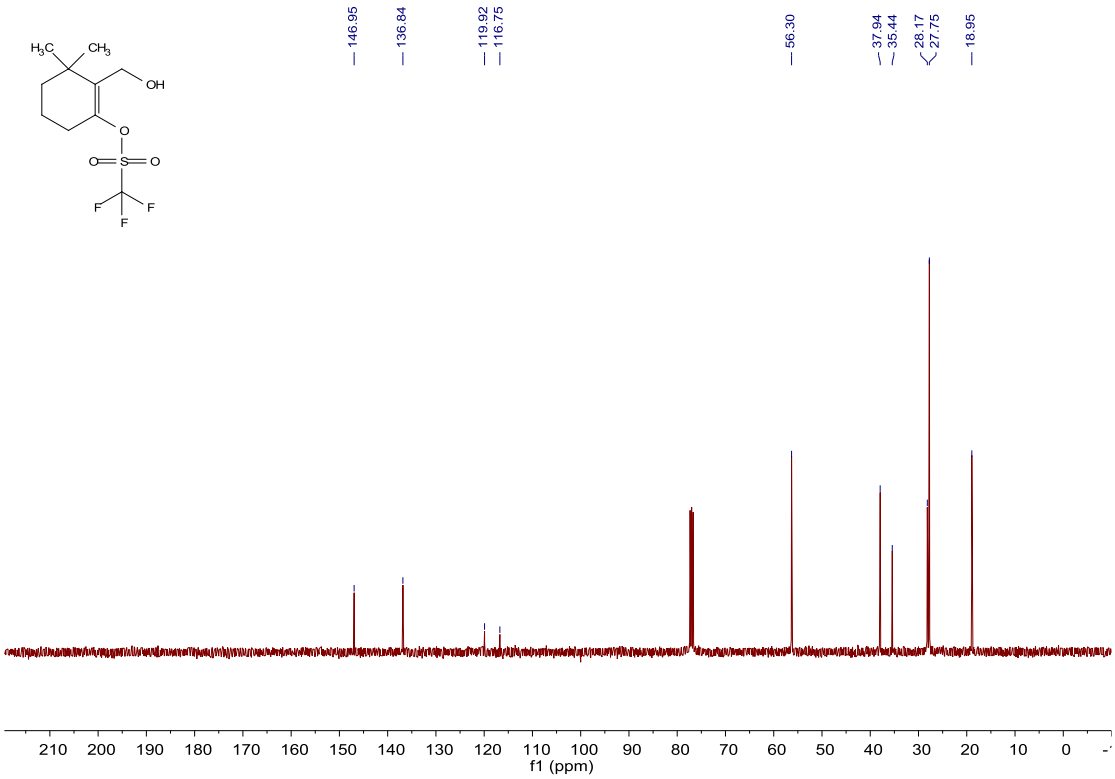


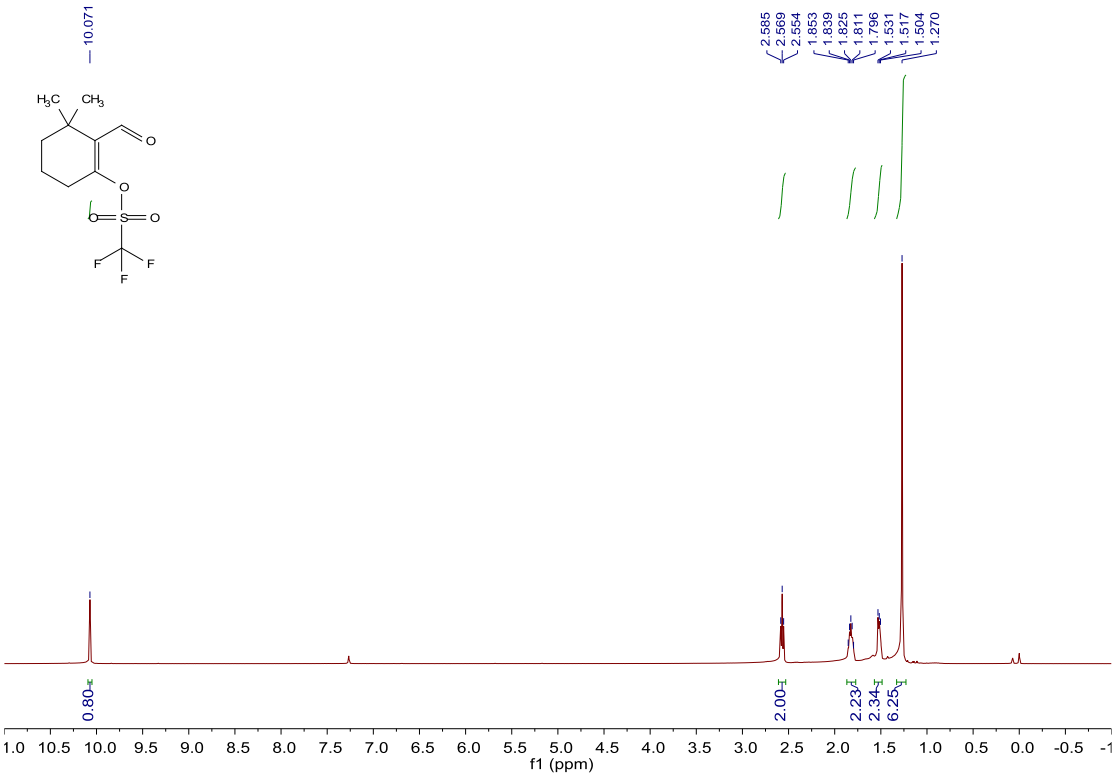
^{1}H NMR of M5-1z



^{13}C NMR of M5-1z



^{1}H NMR of M6-1z



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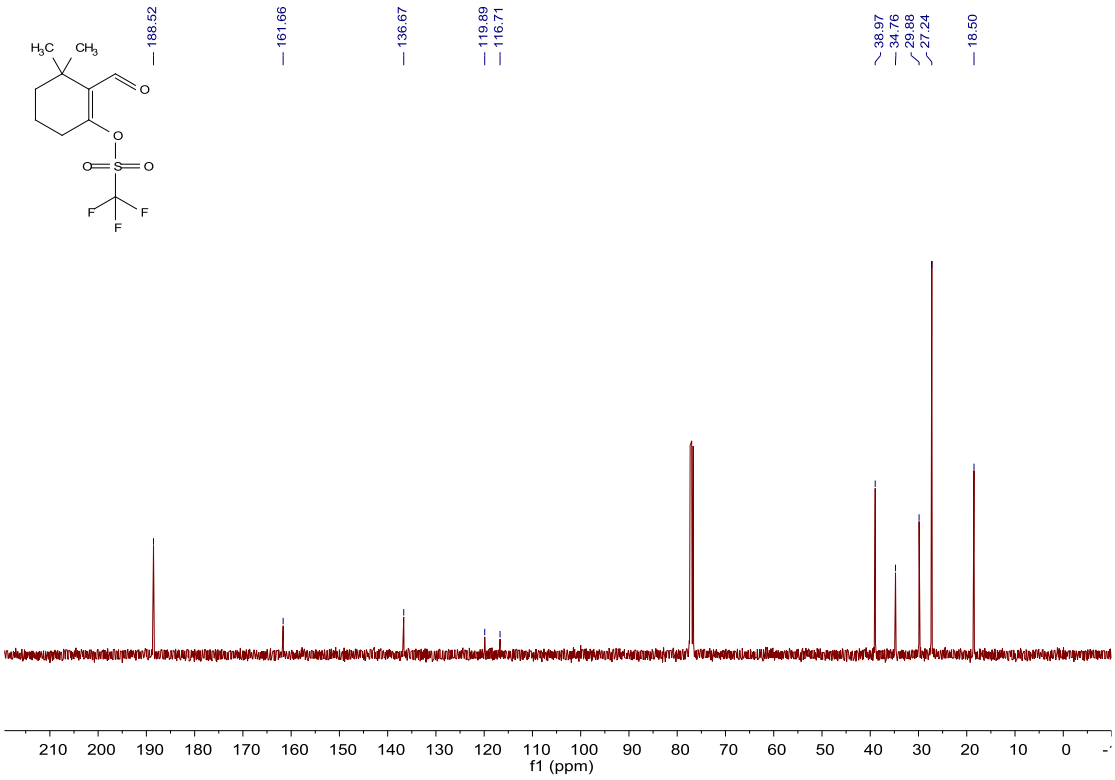
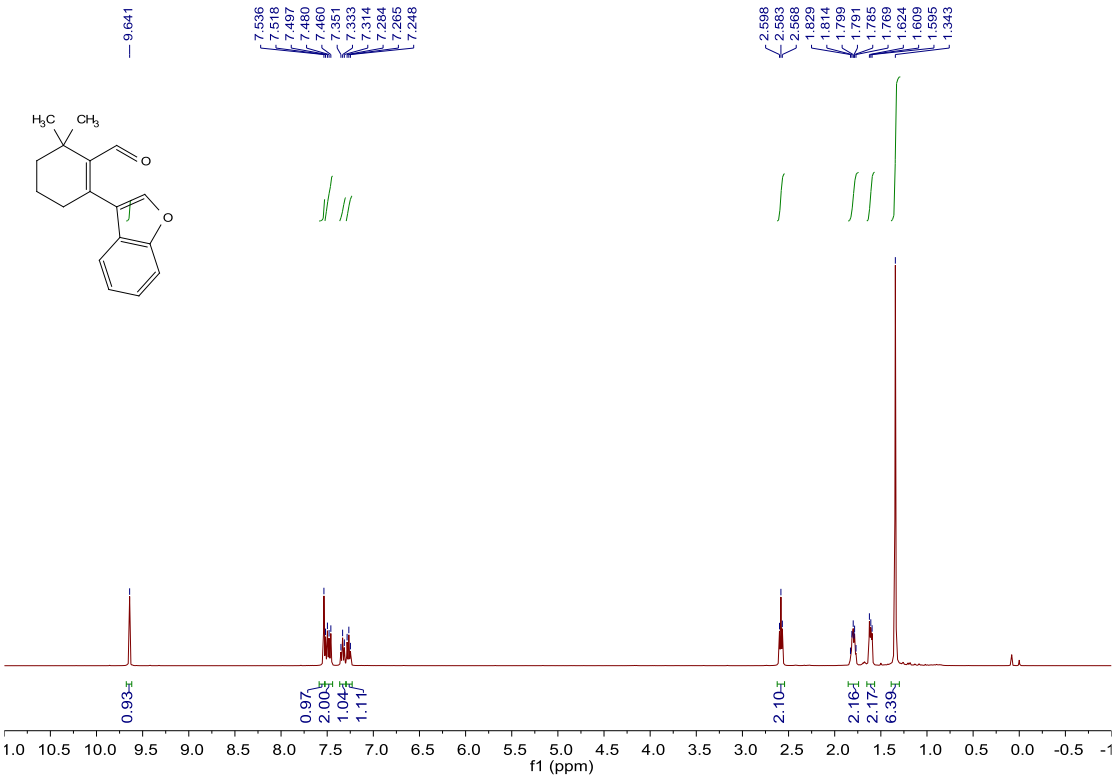


^{1}H NMR of In8-1z



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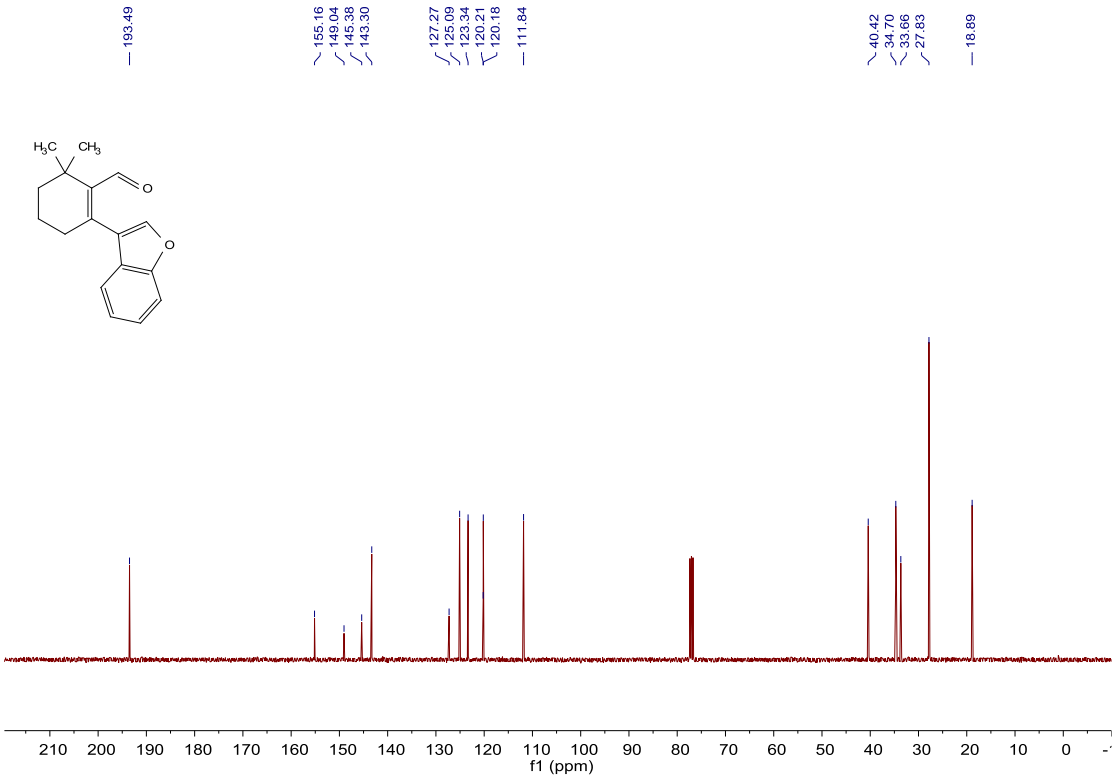
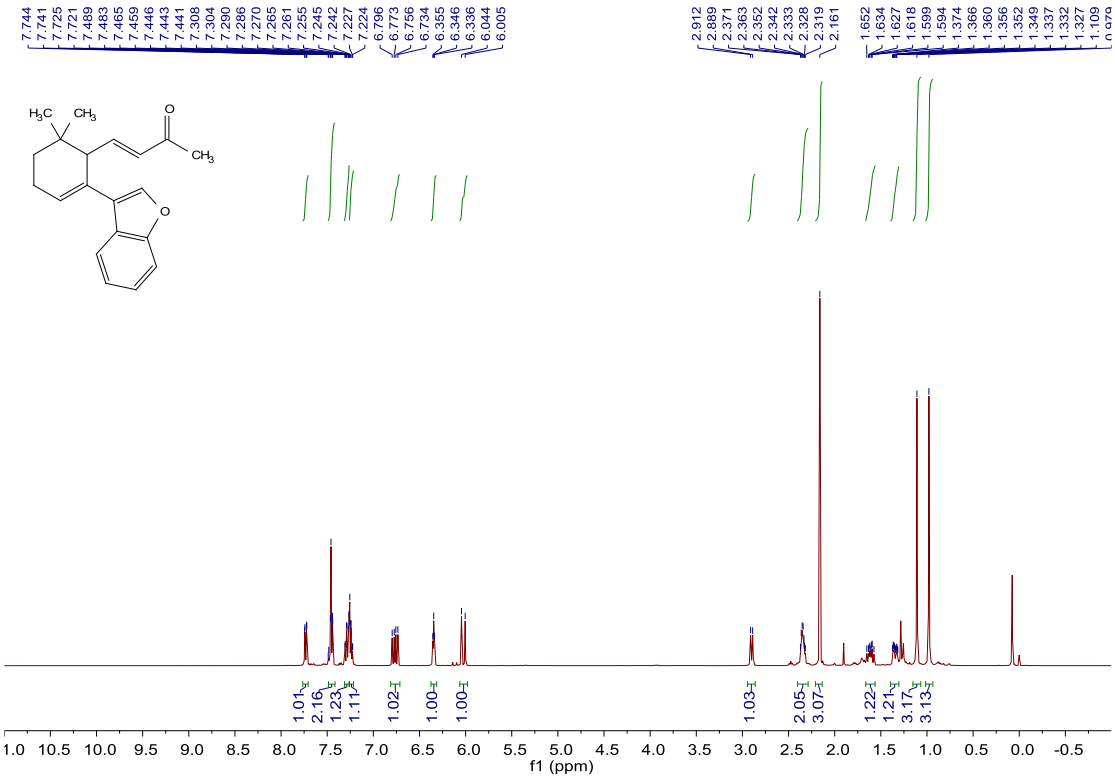


^{1}H NMR of 1ac'



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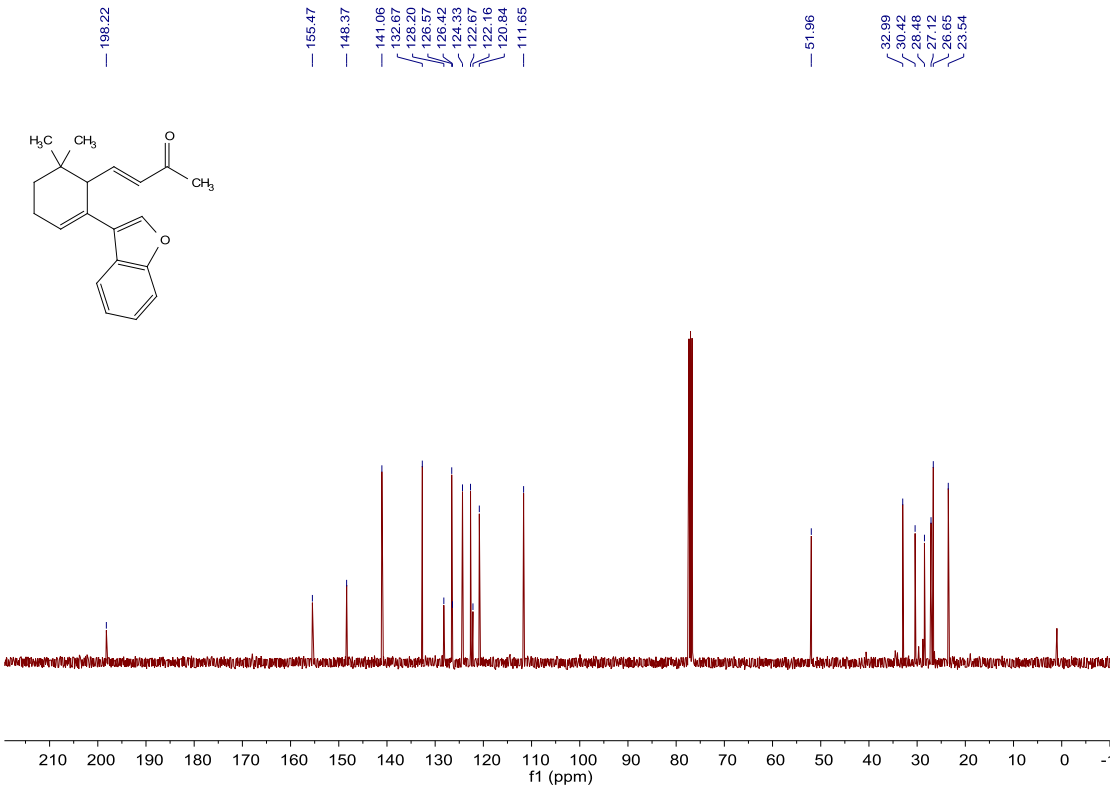

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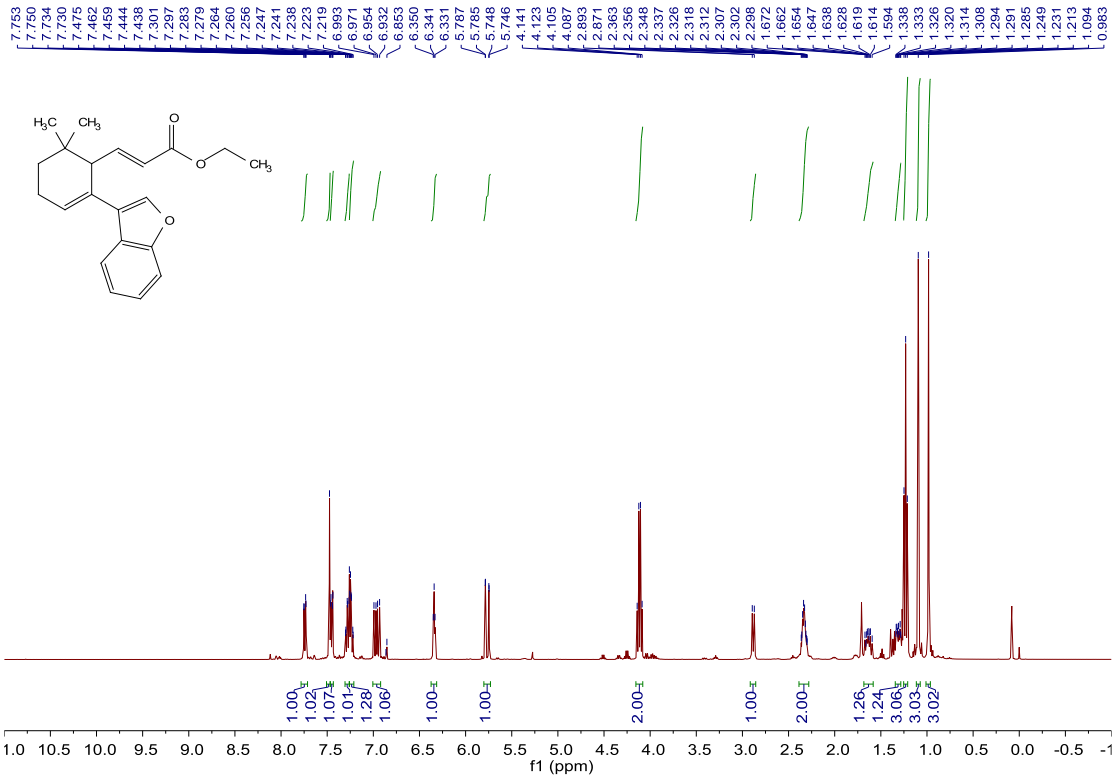

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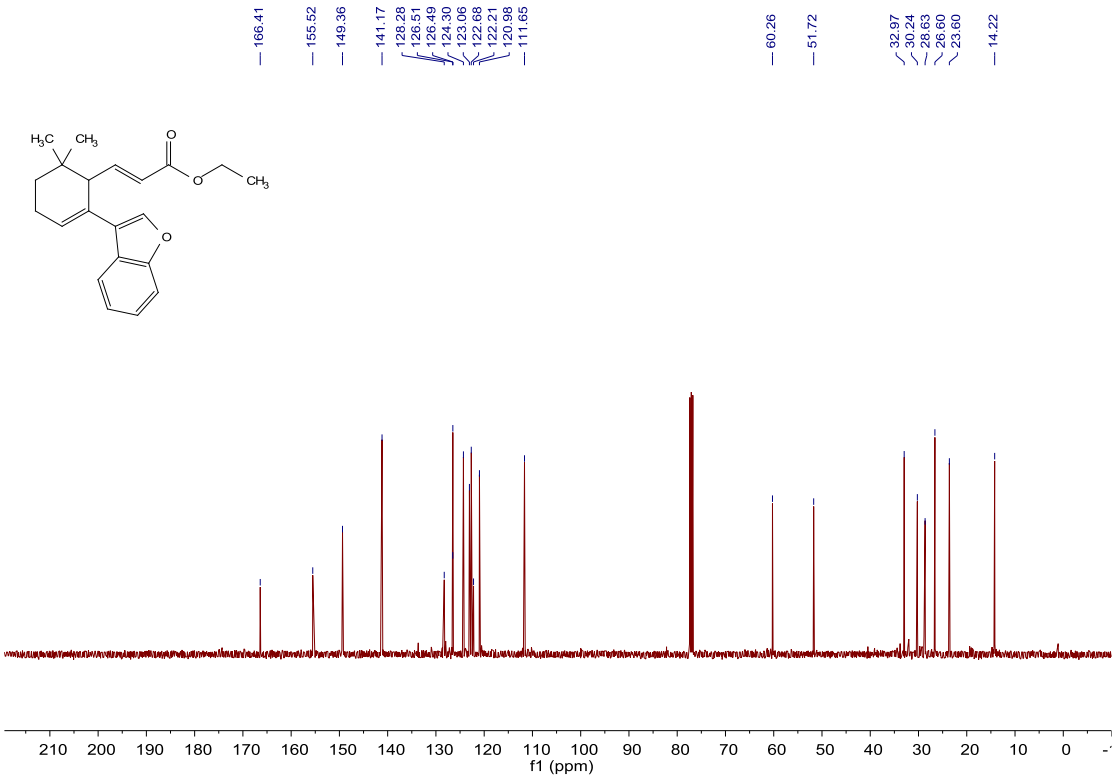
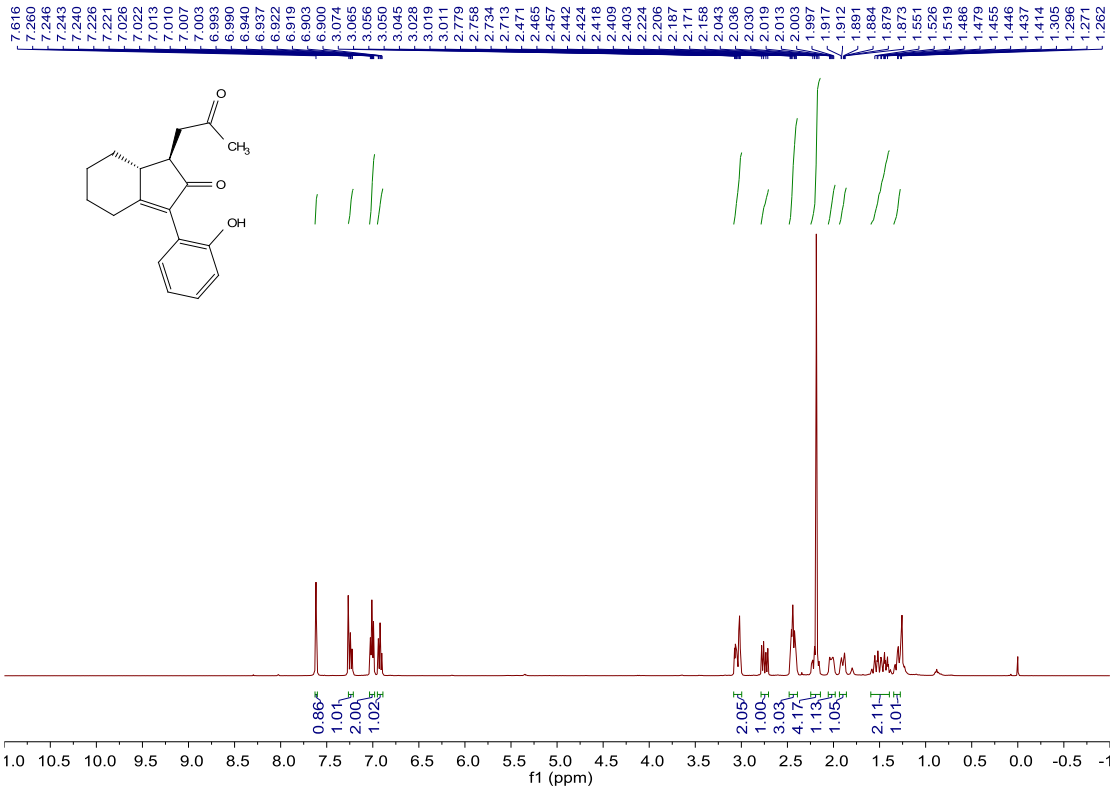
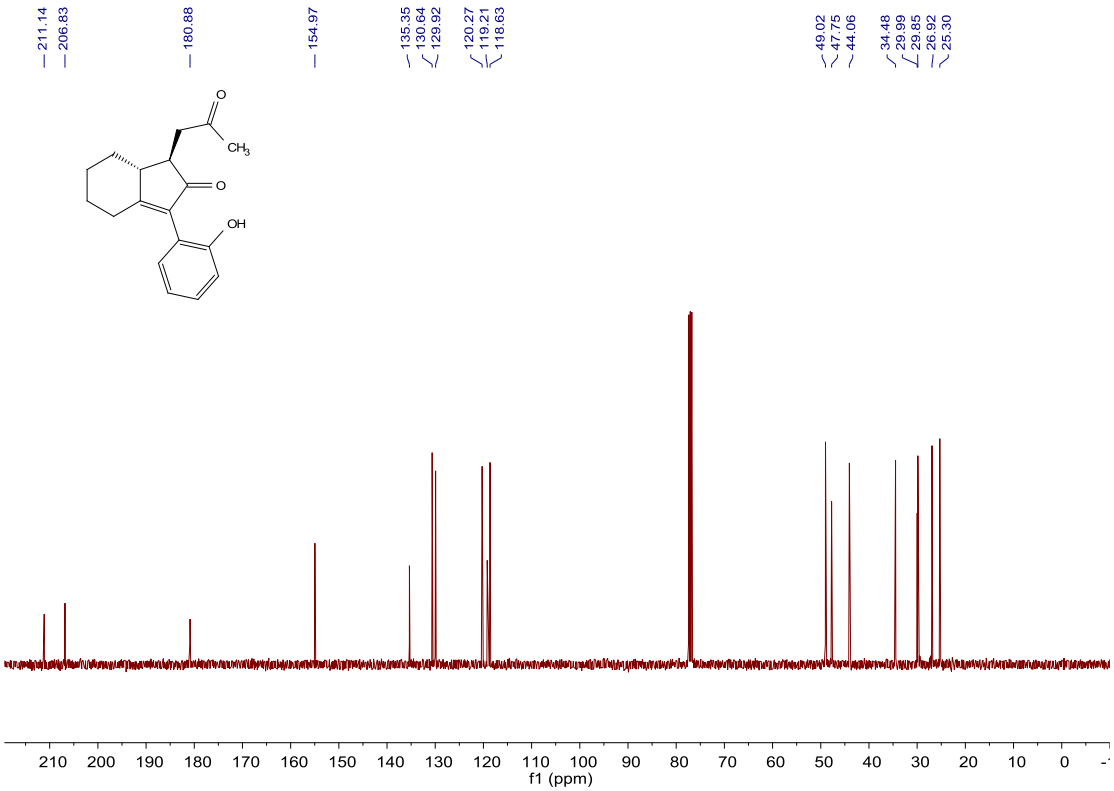


^{1}H NMR of 2a



^{13}C NMR of 2a



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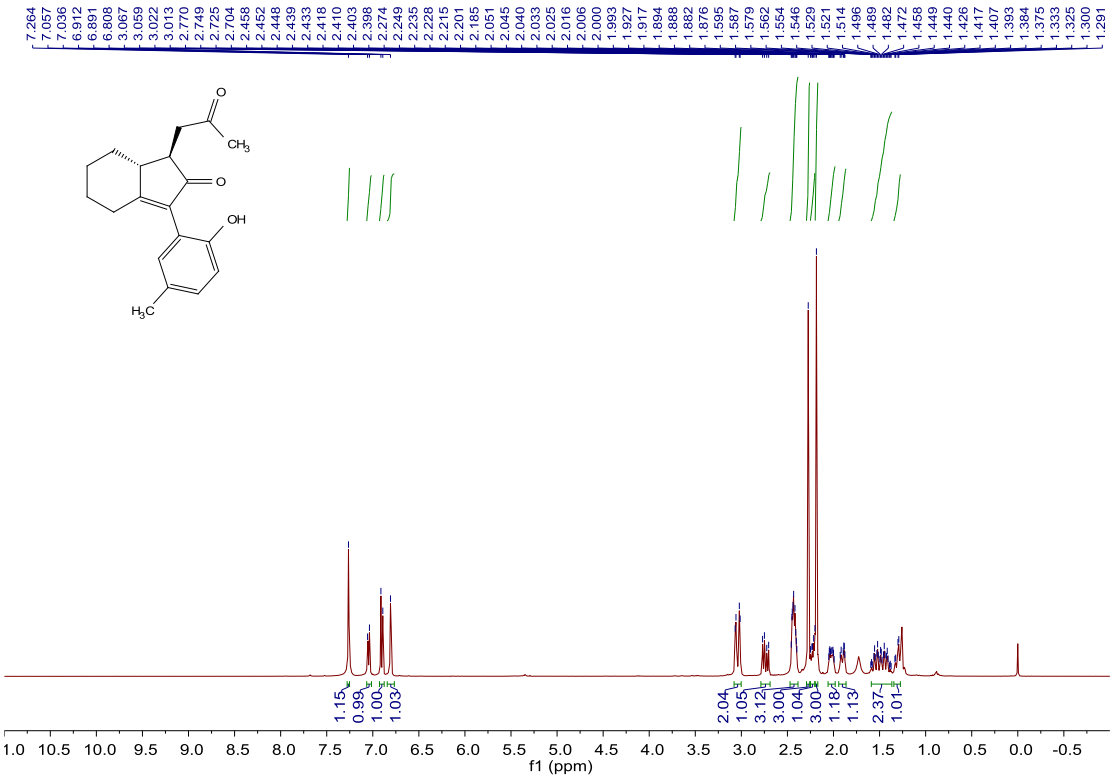
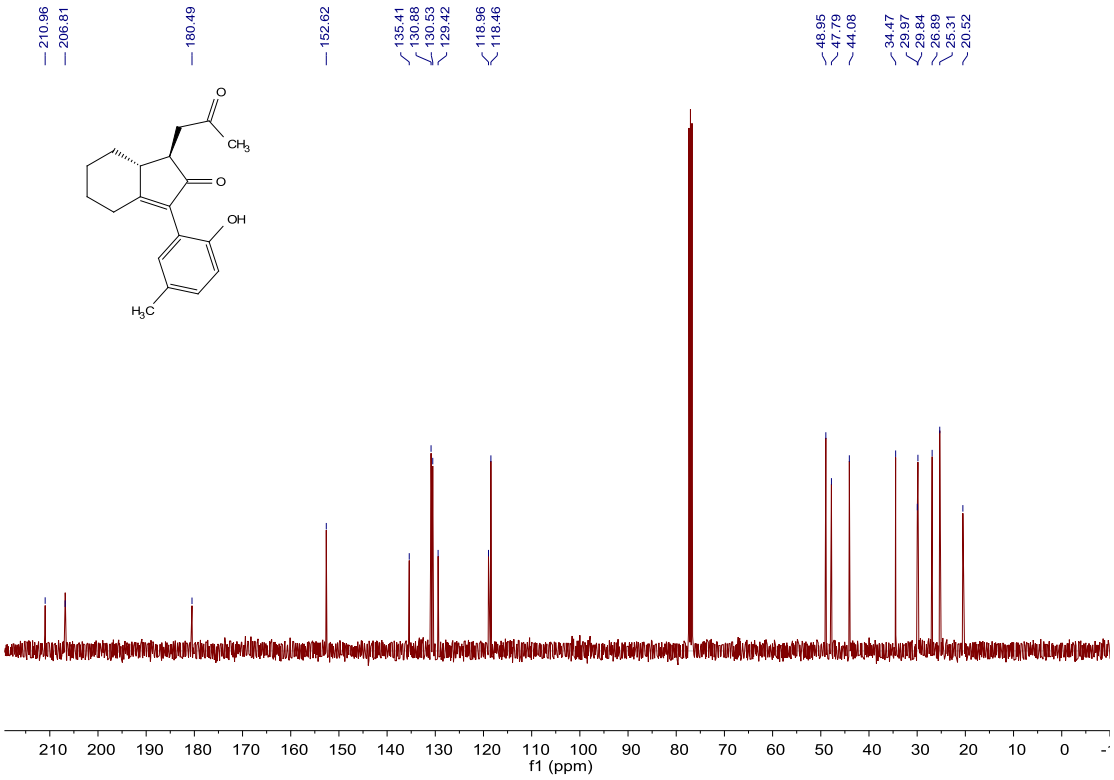
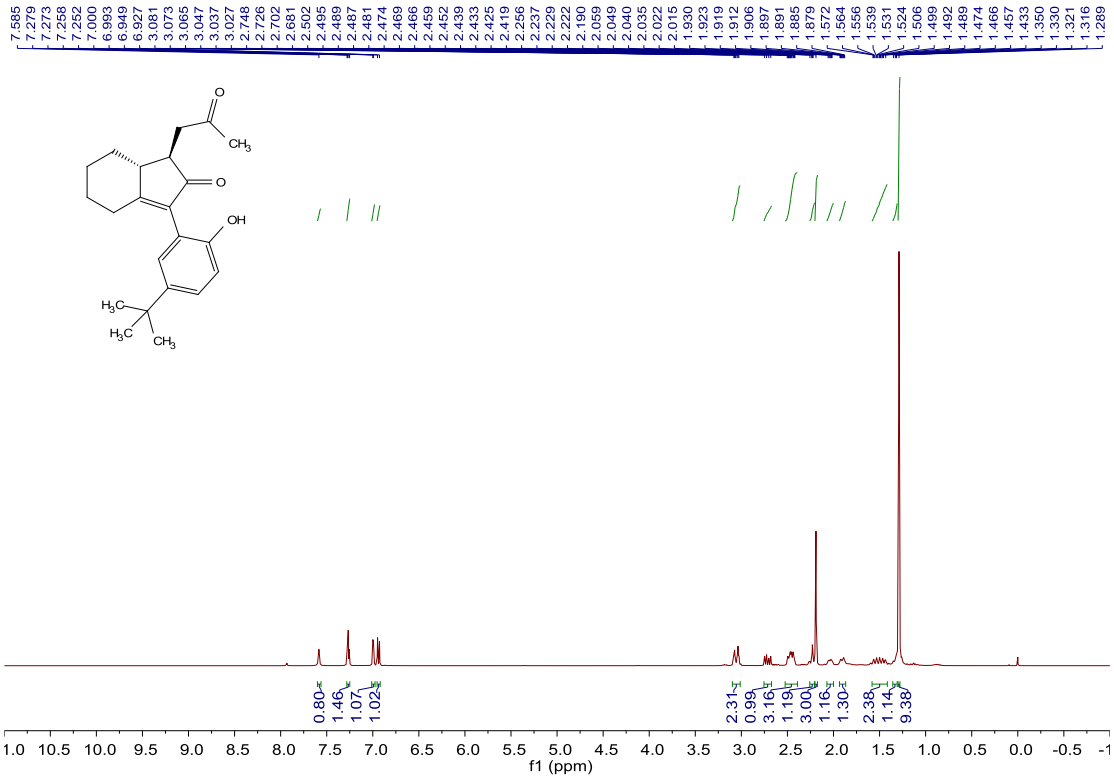


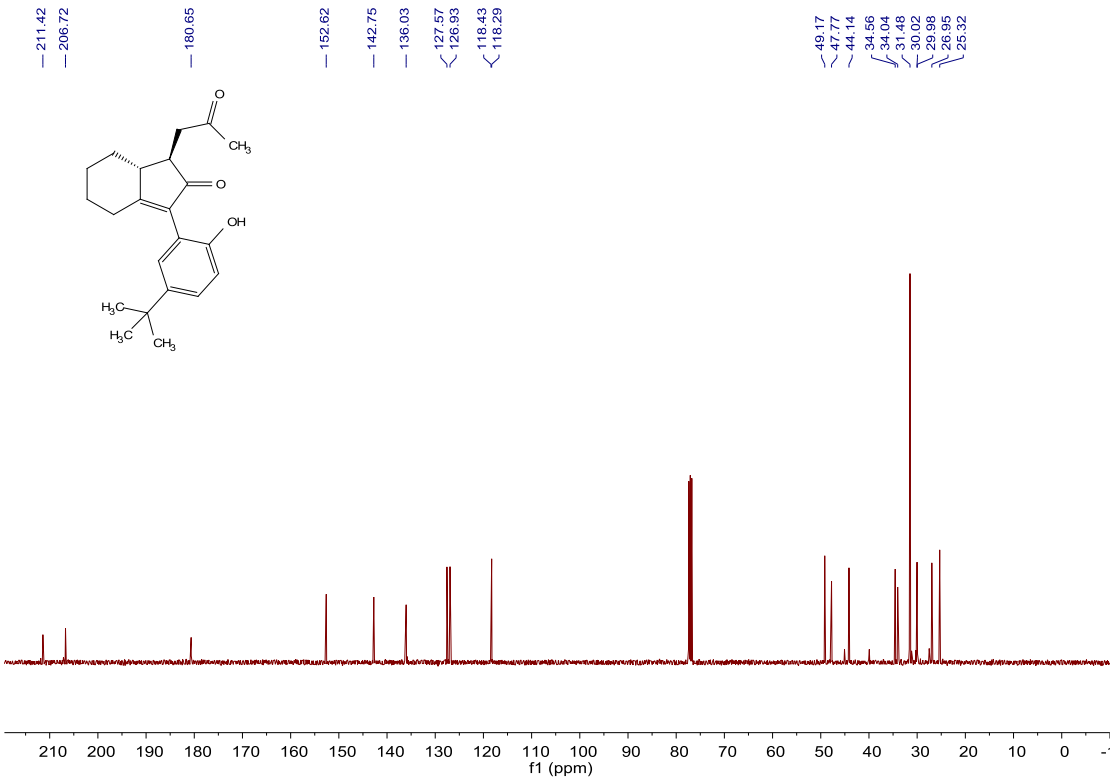
^{13}C NMR of 2b



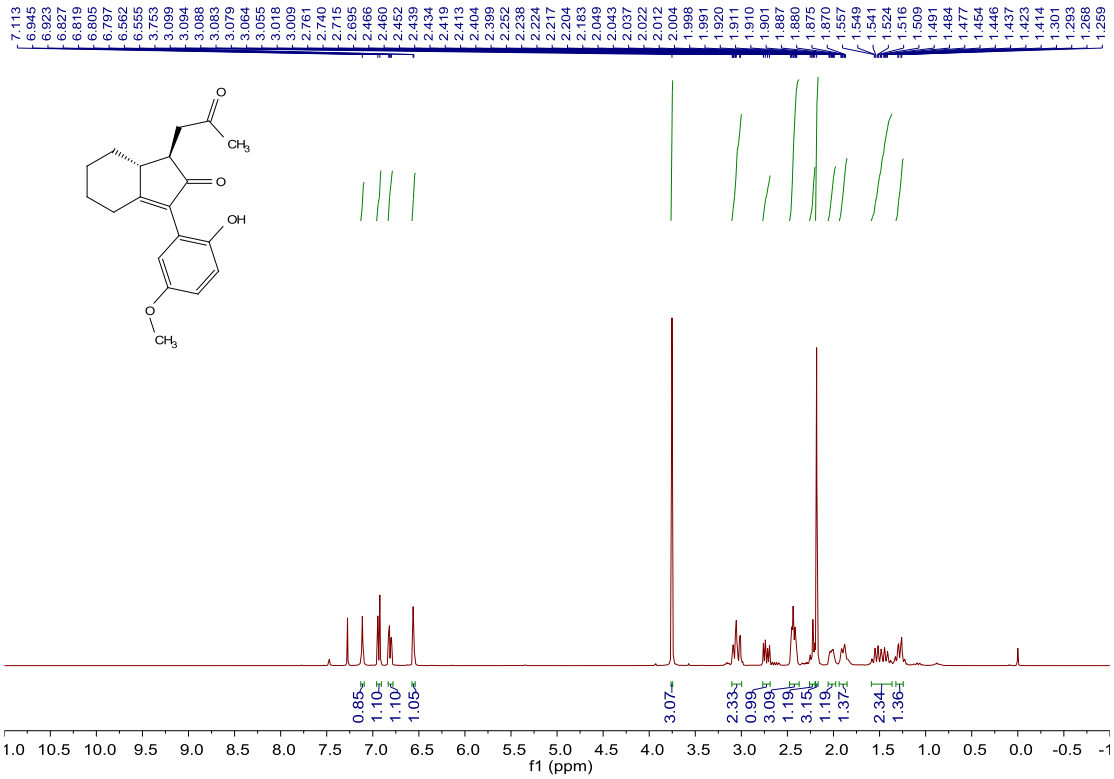
^{1}H NMR of 2c



^{13}C NMR of 2c



^{1}H NMR of 2d



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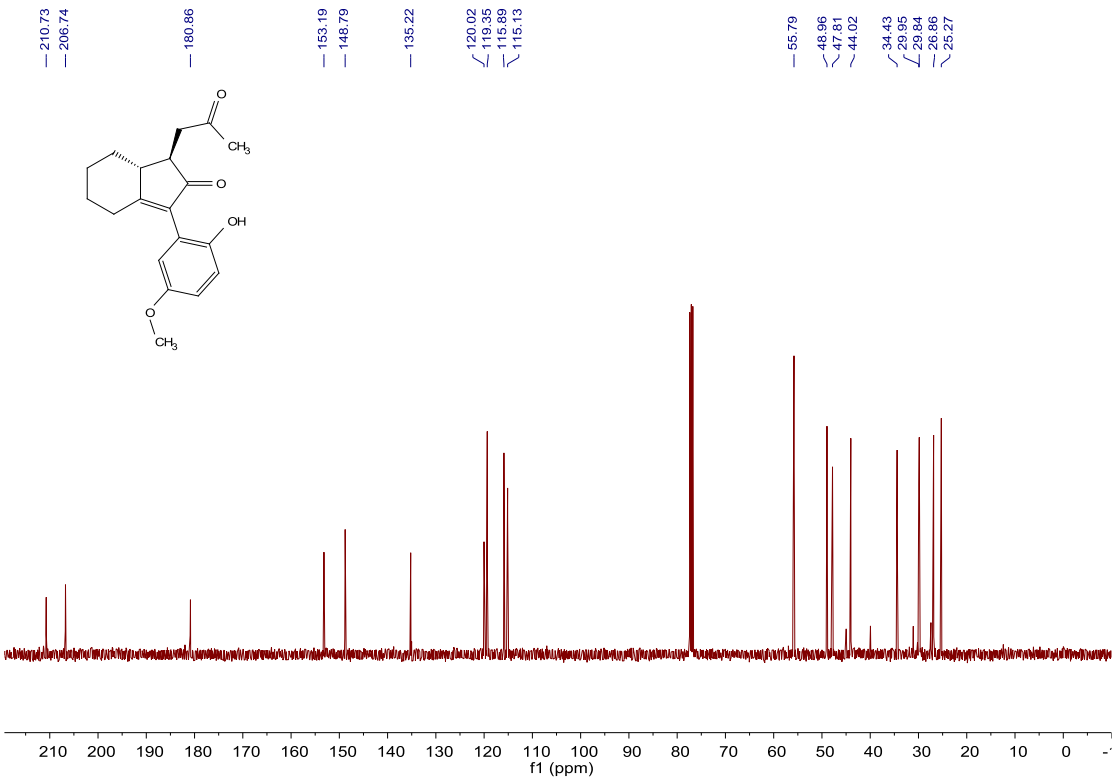
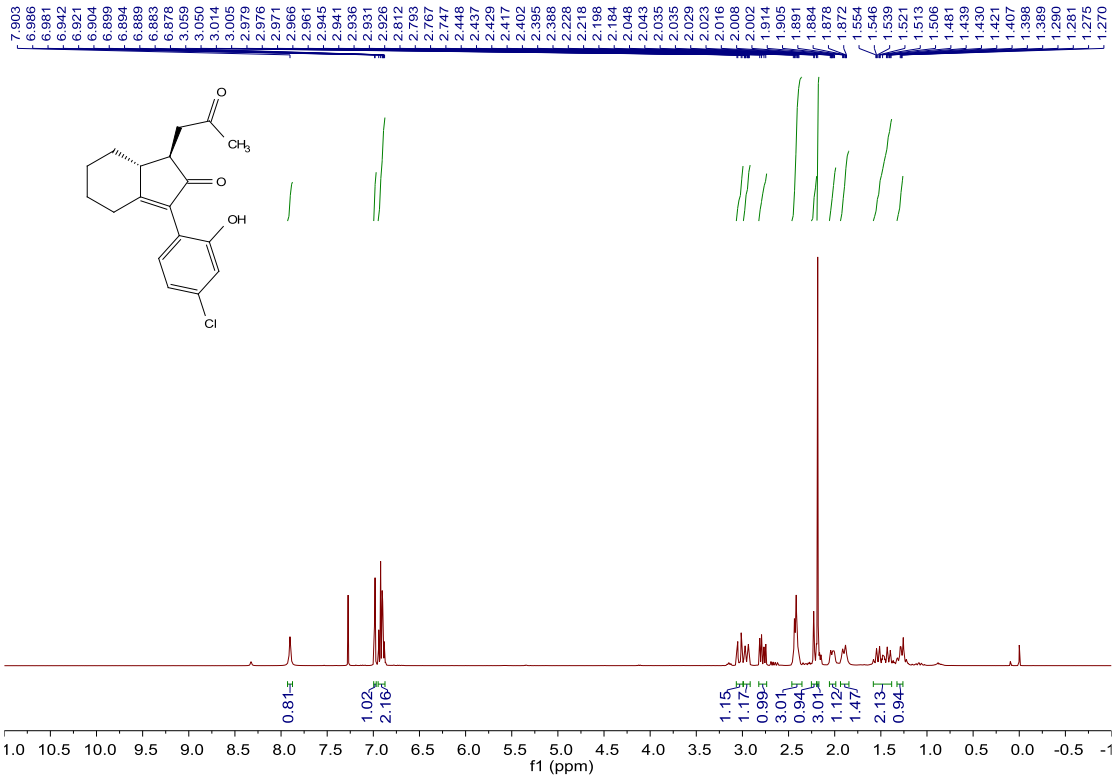


^{1}H NMR of 2e



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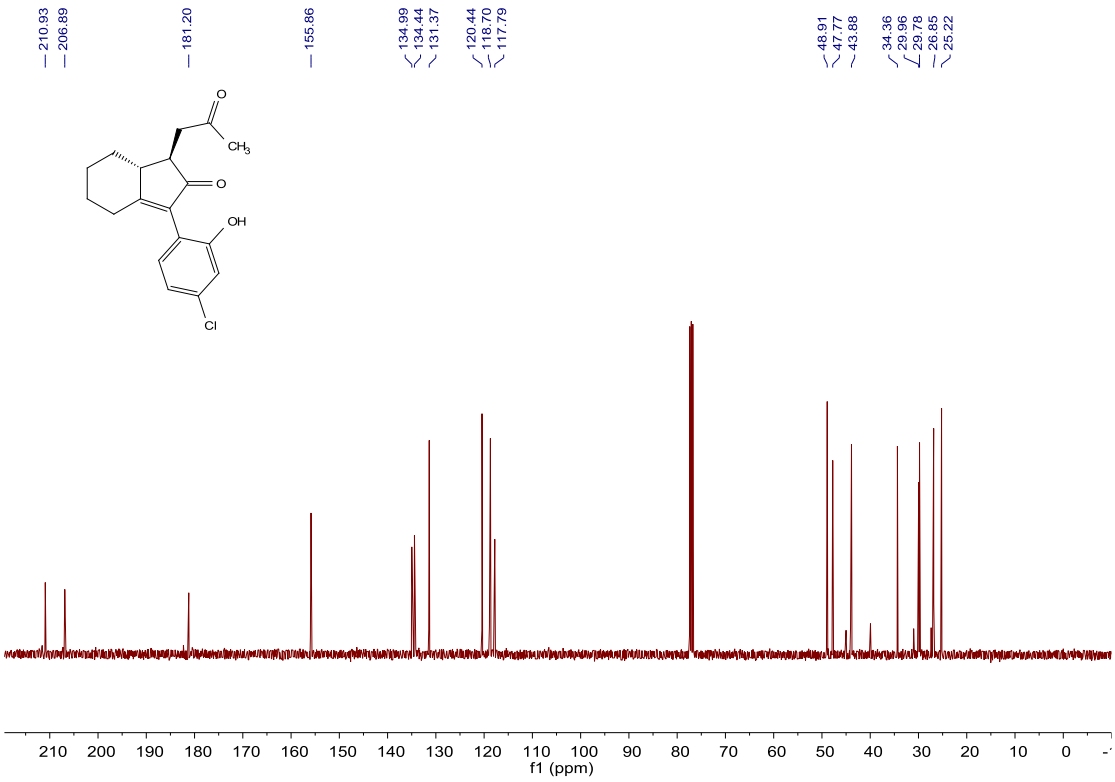

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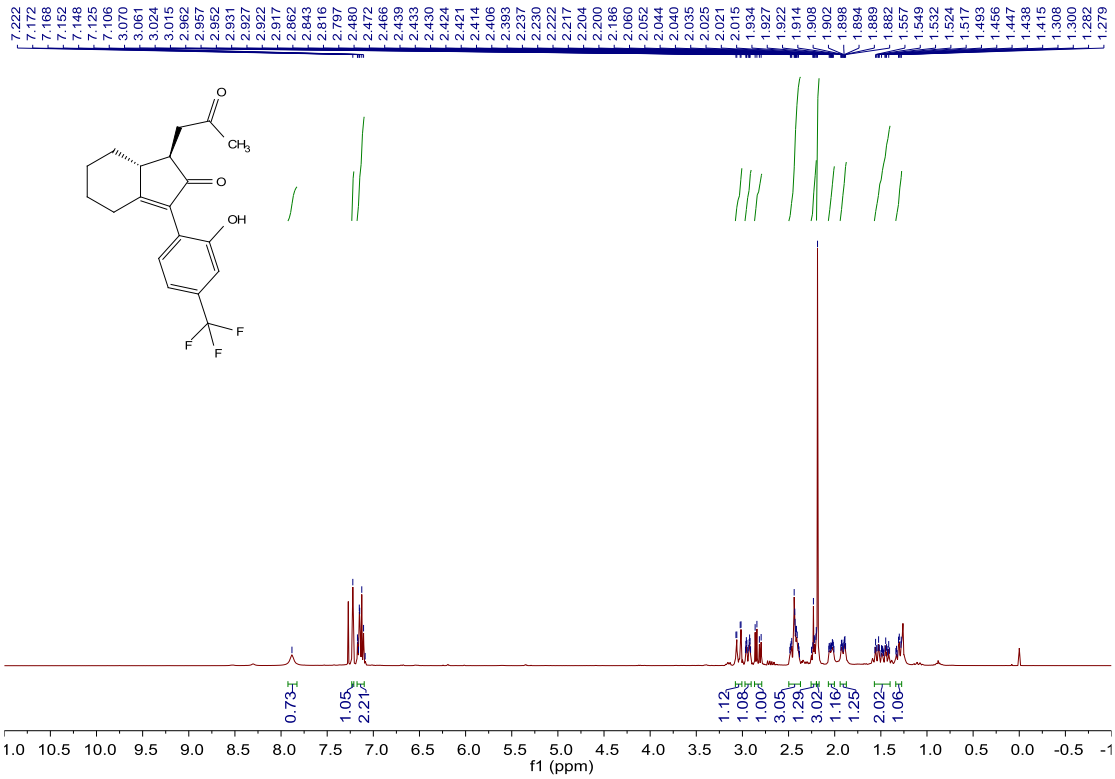
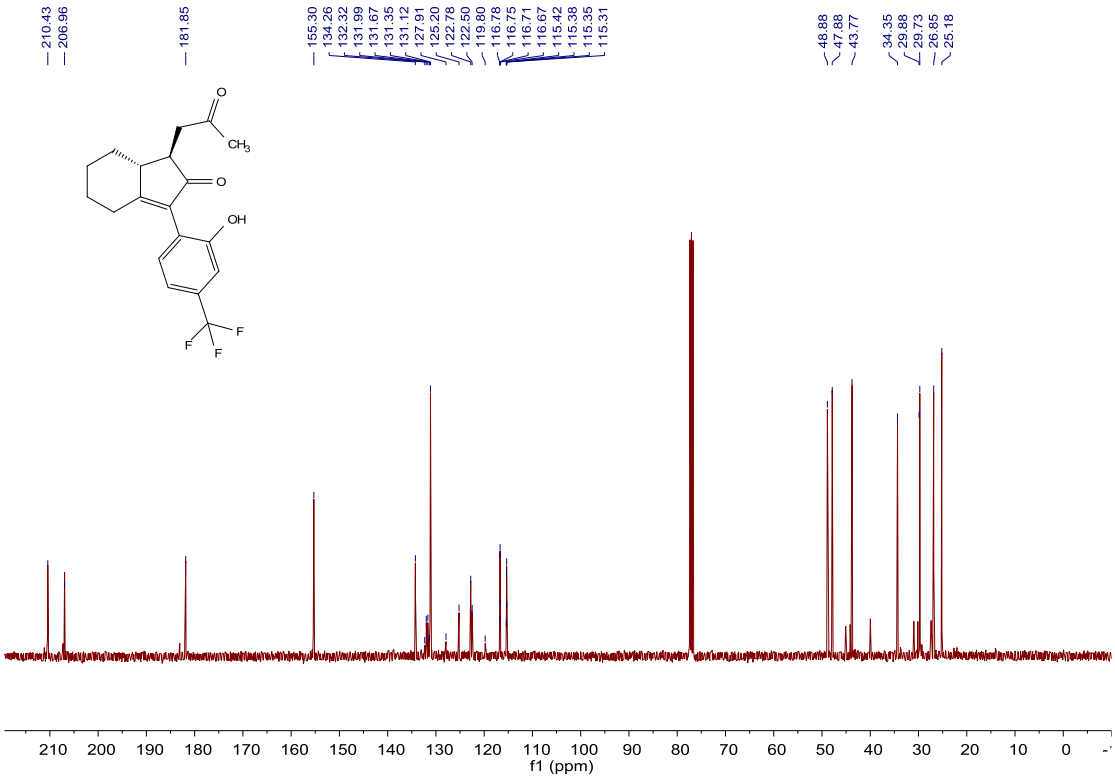
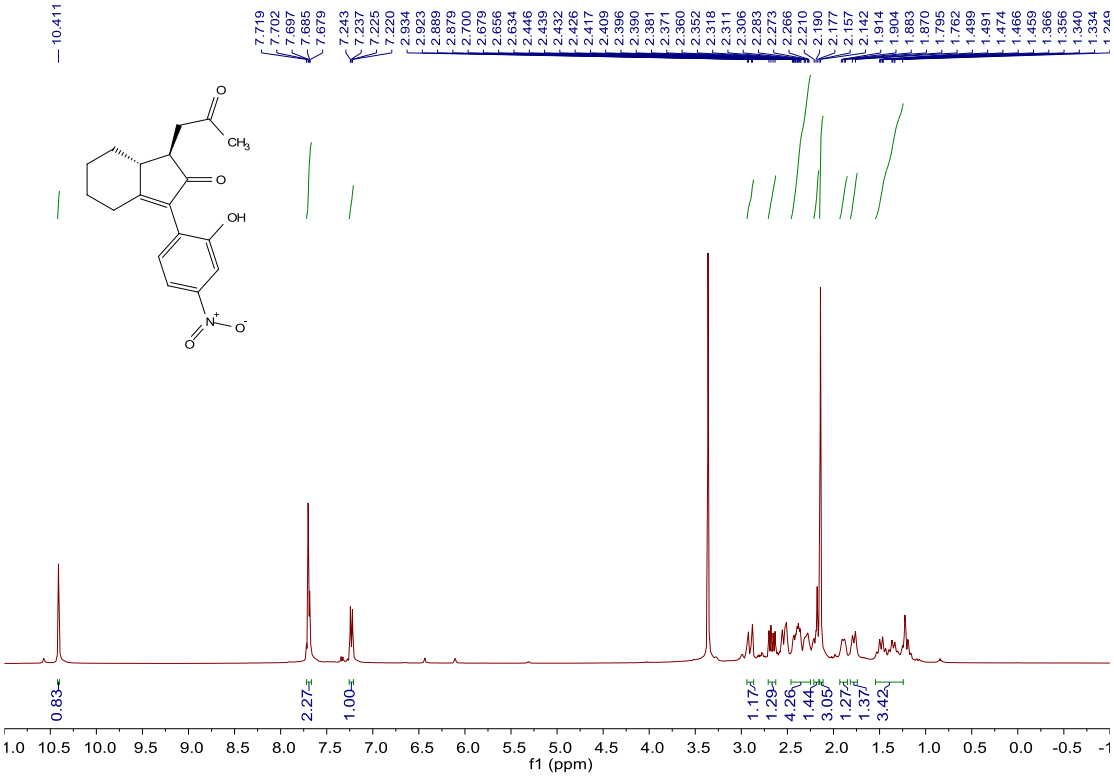


^{13}C NMR of 2f



^{1}H NMR of 2g



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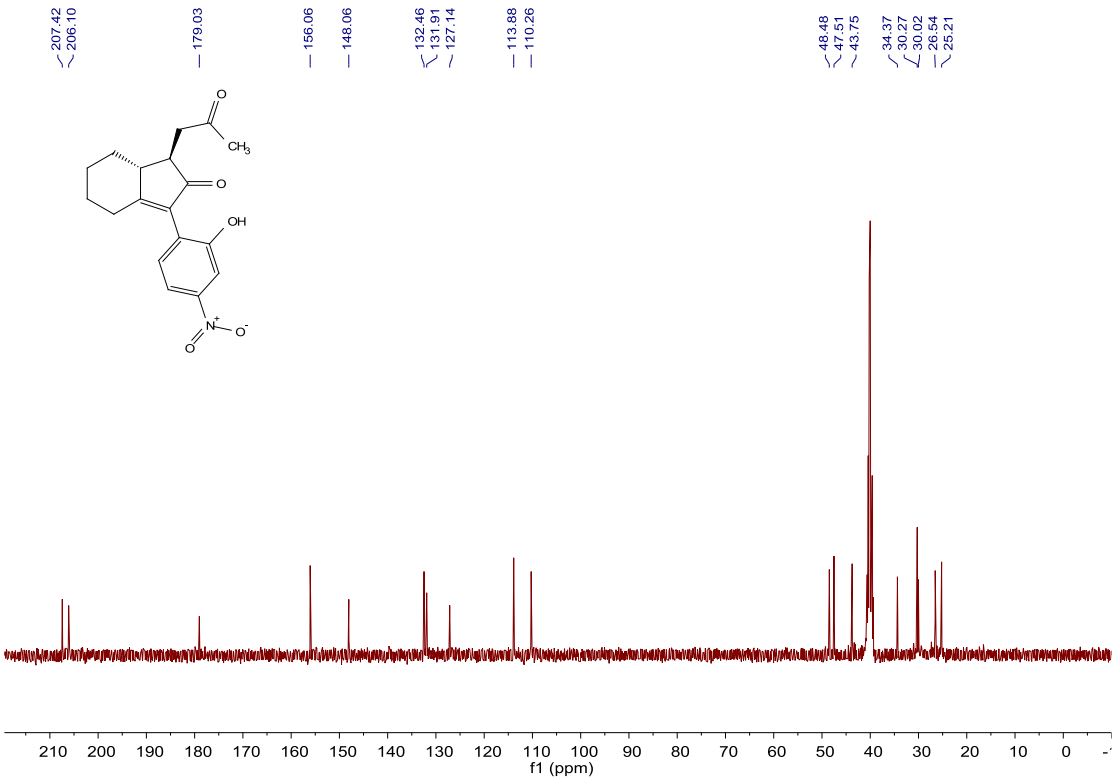

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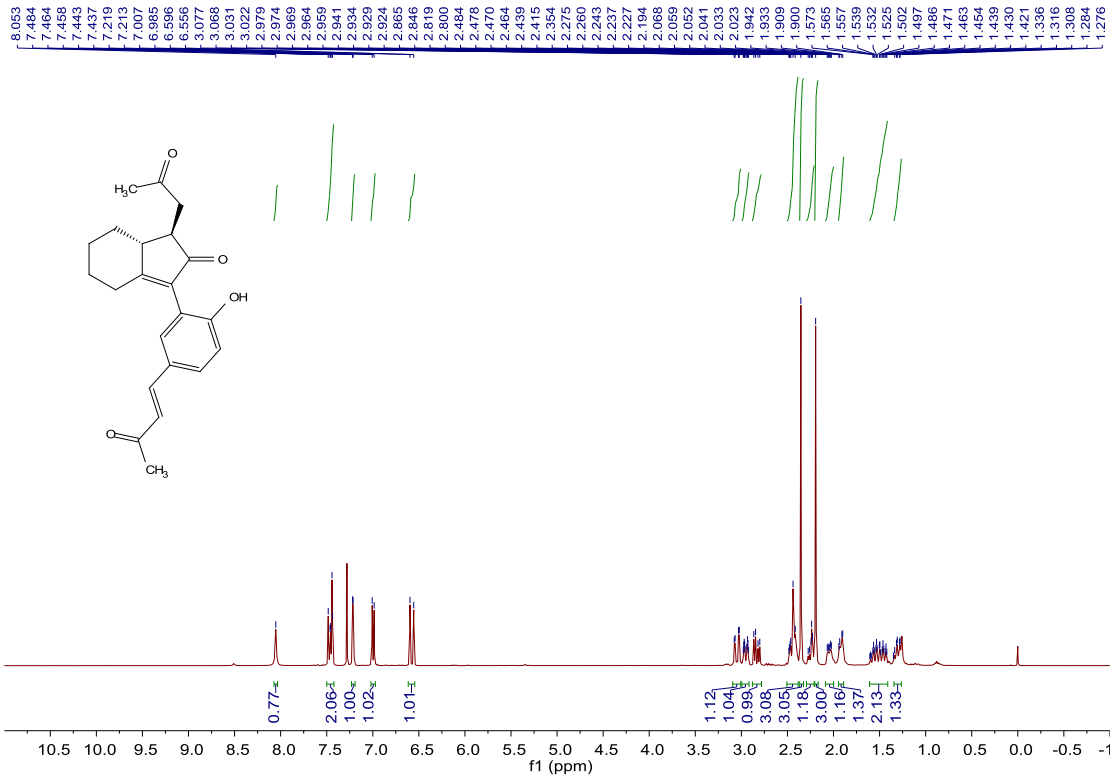

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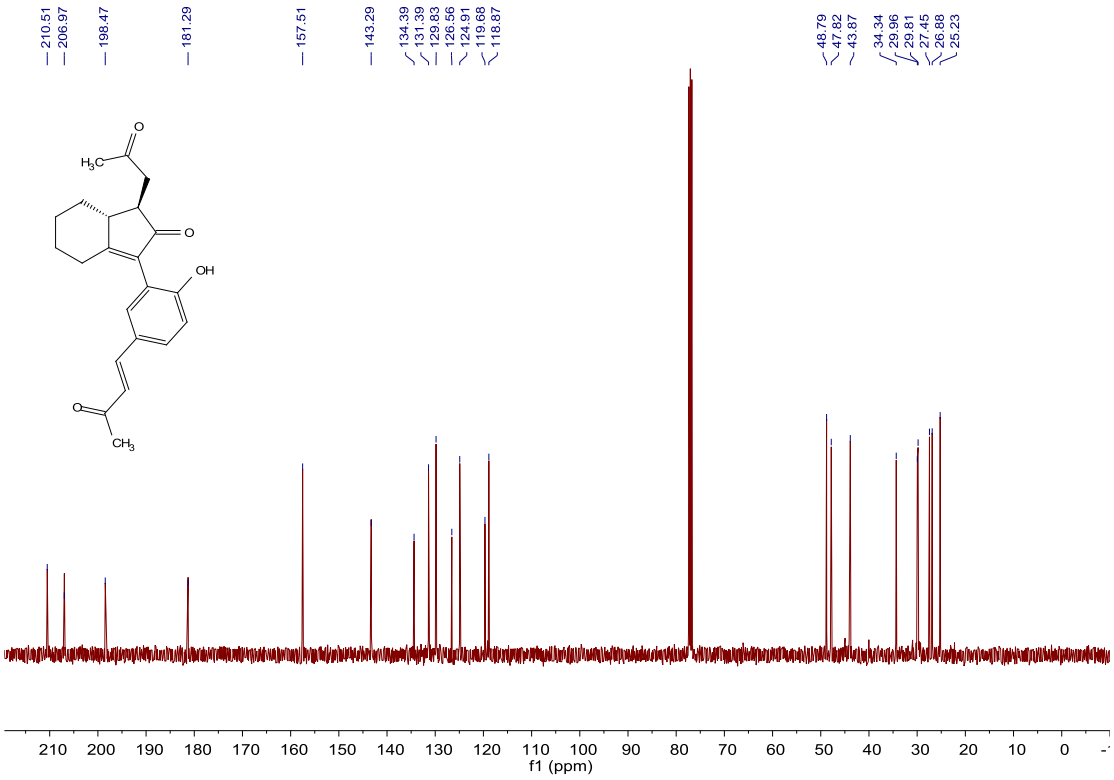

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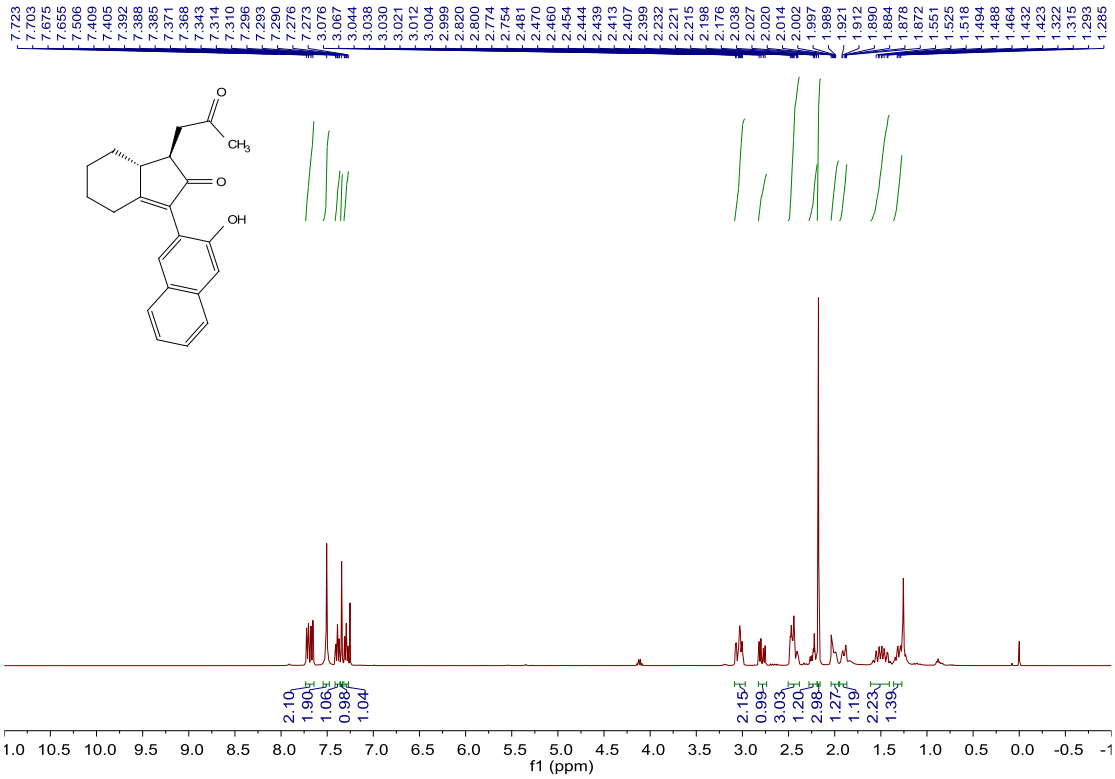
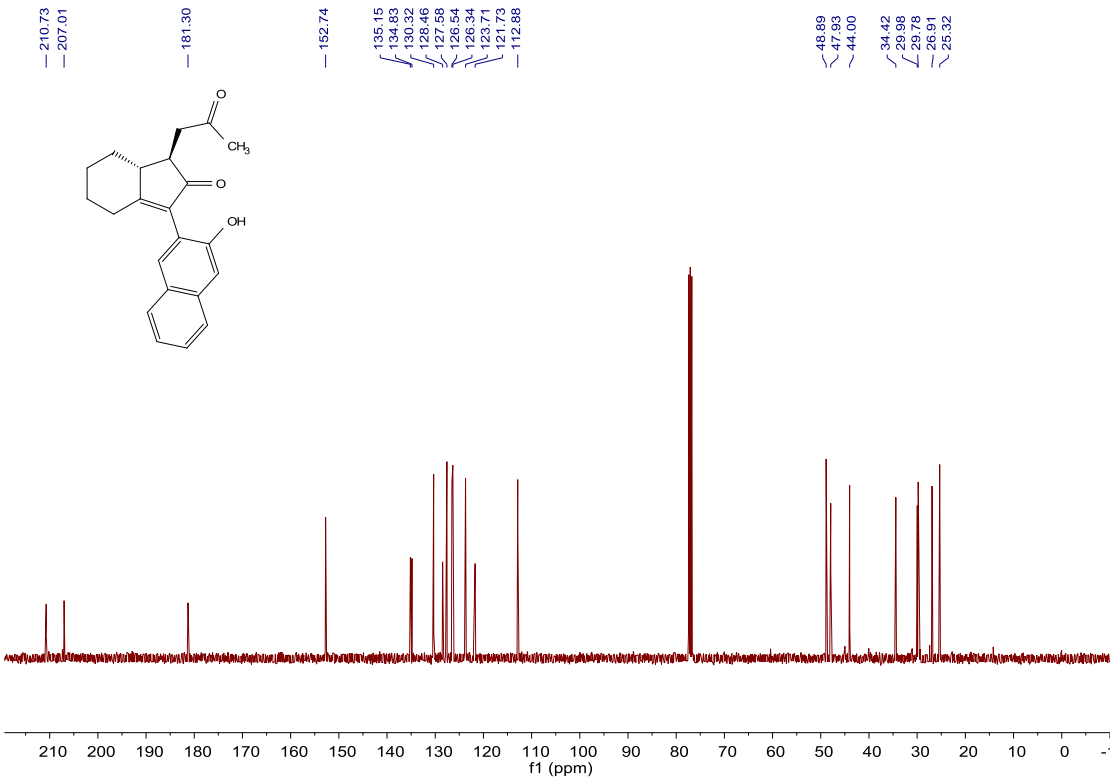


^{13}C NMR of 2i



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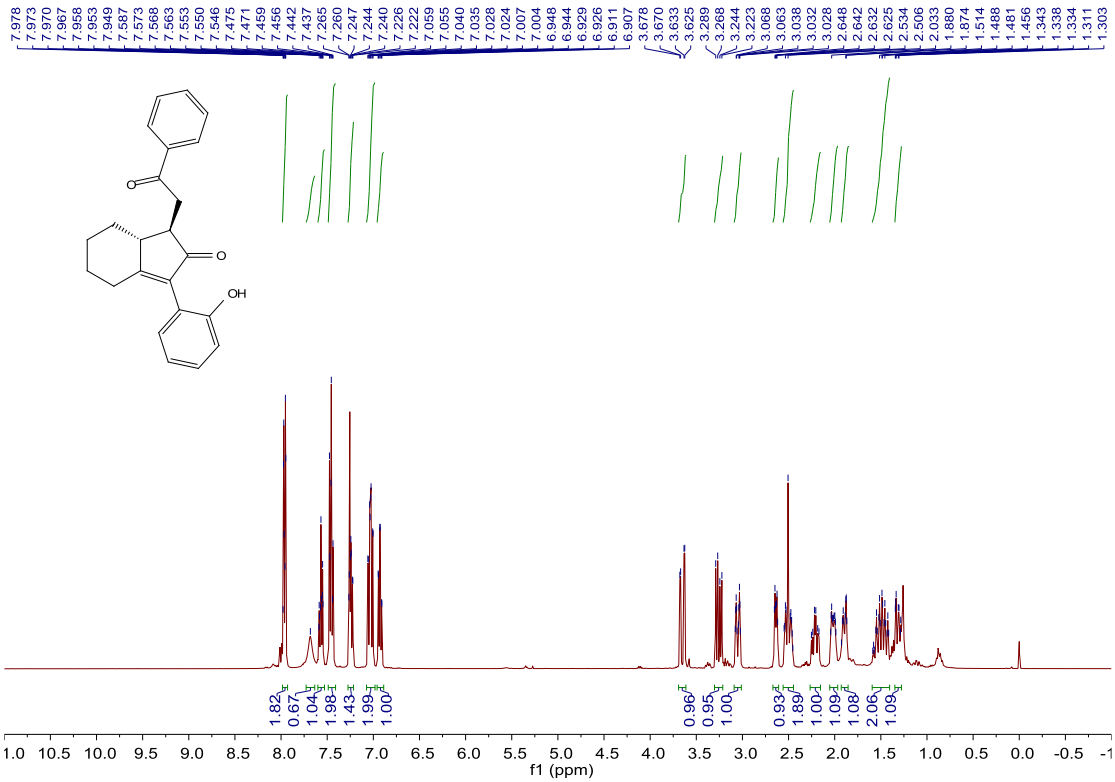

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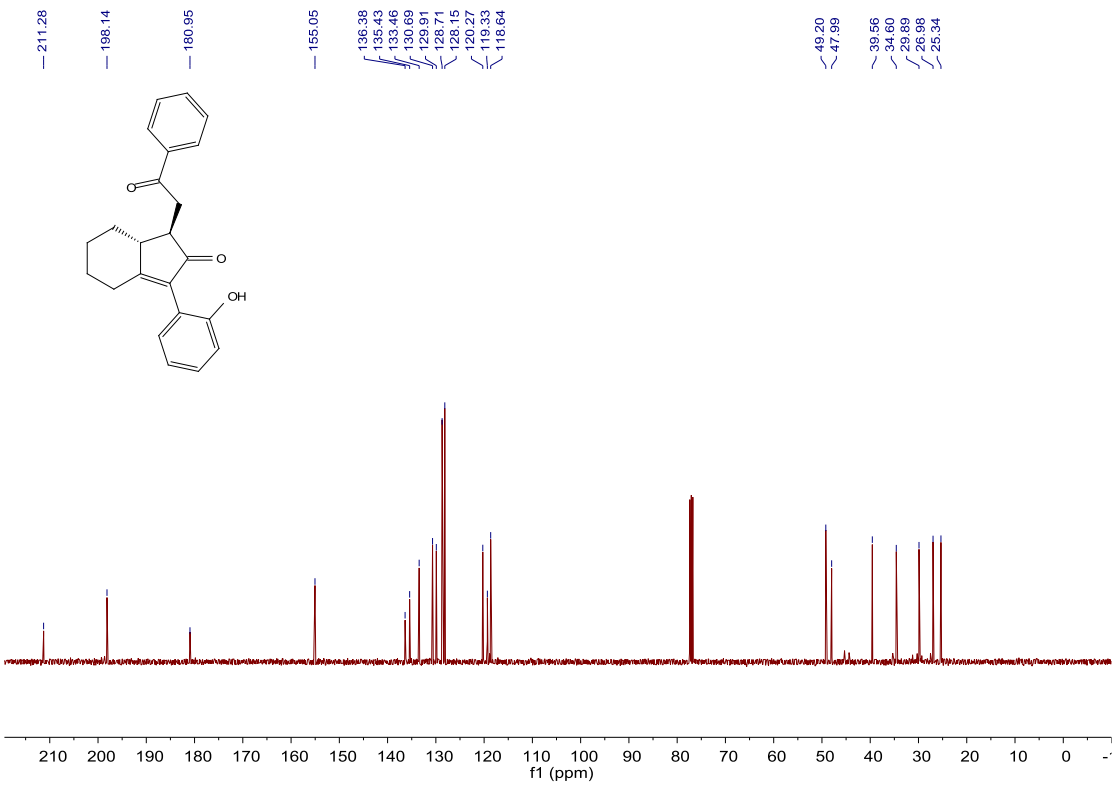

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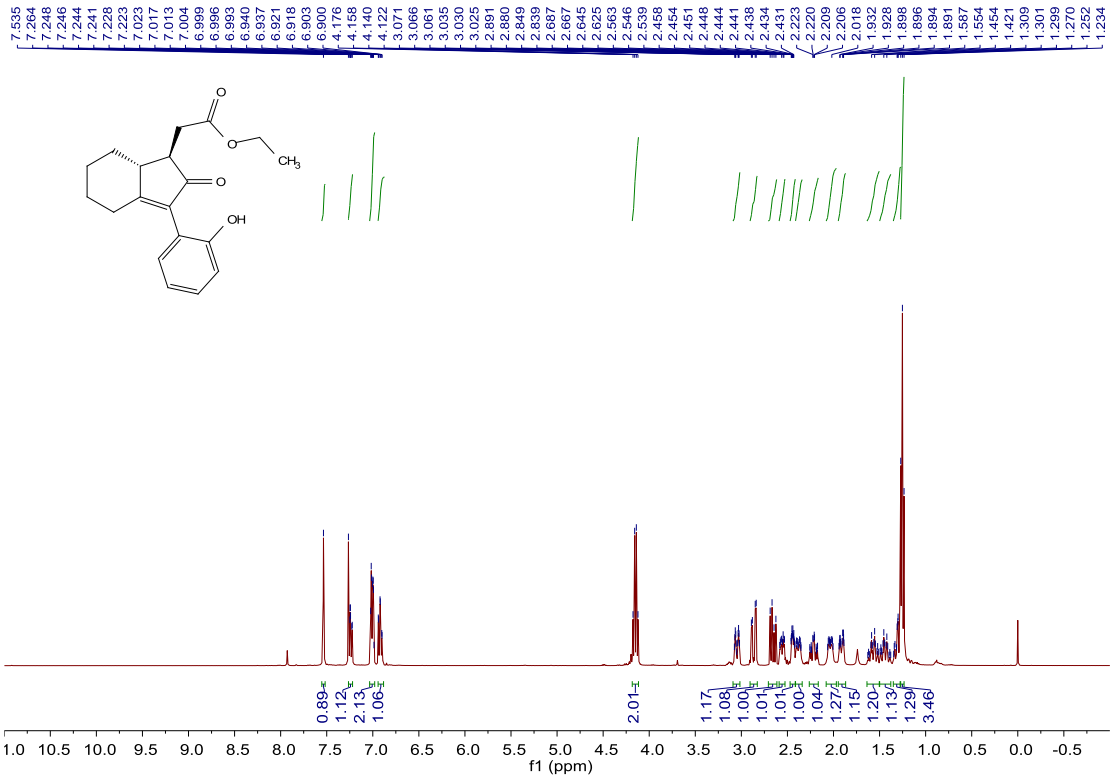

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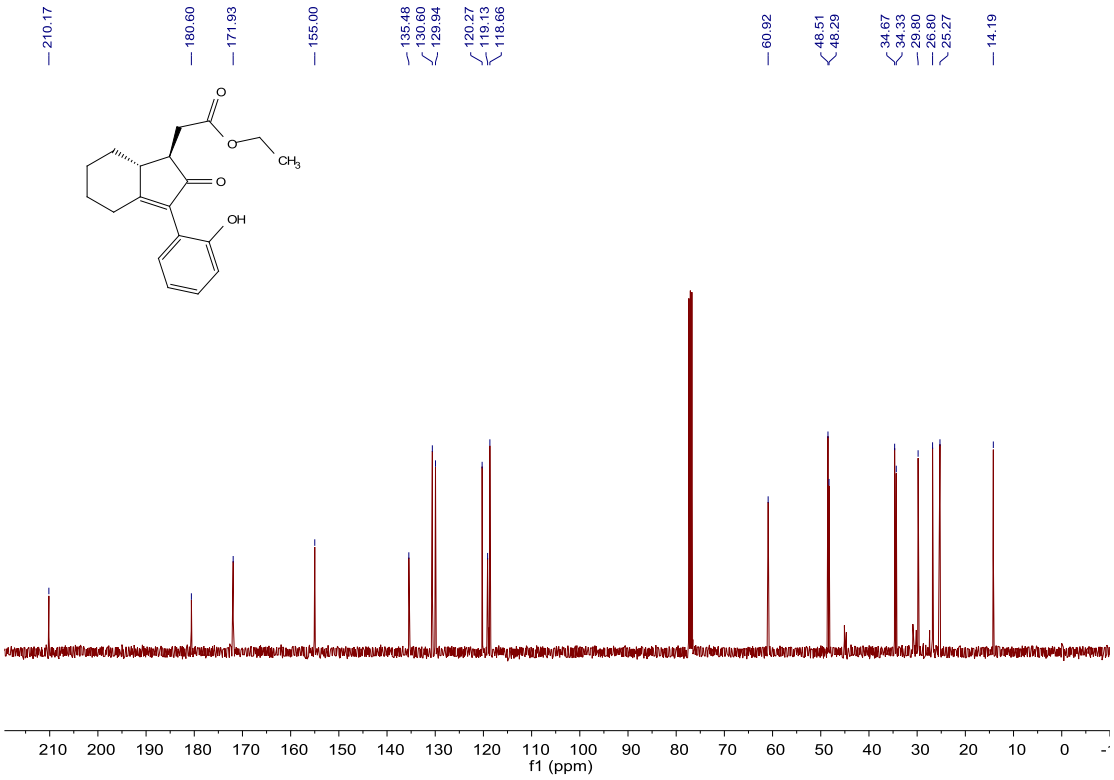

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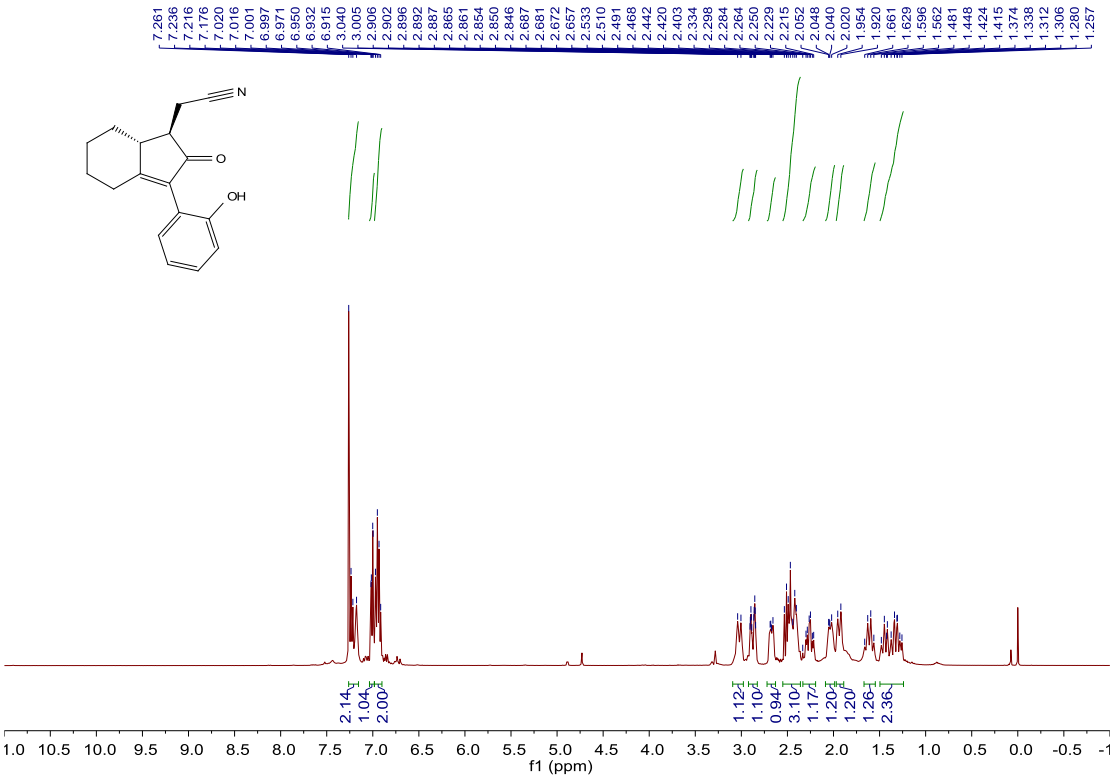

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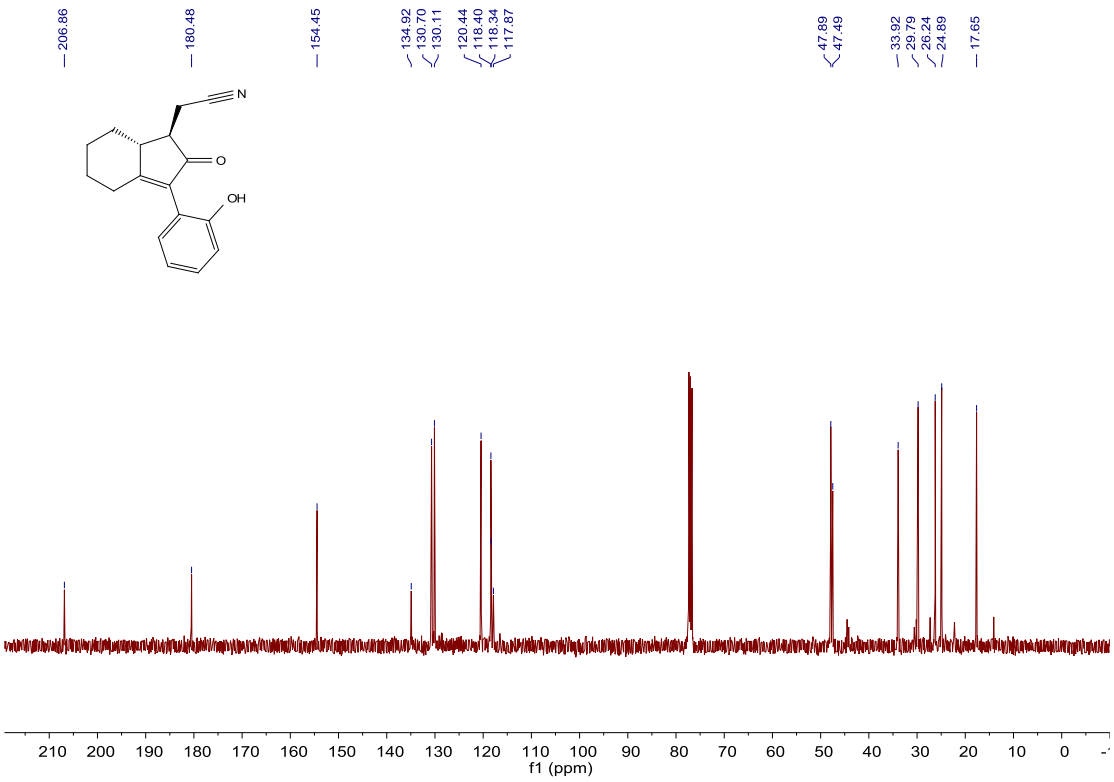

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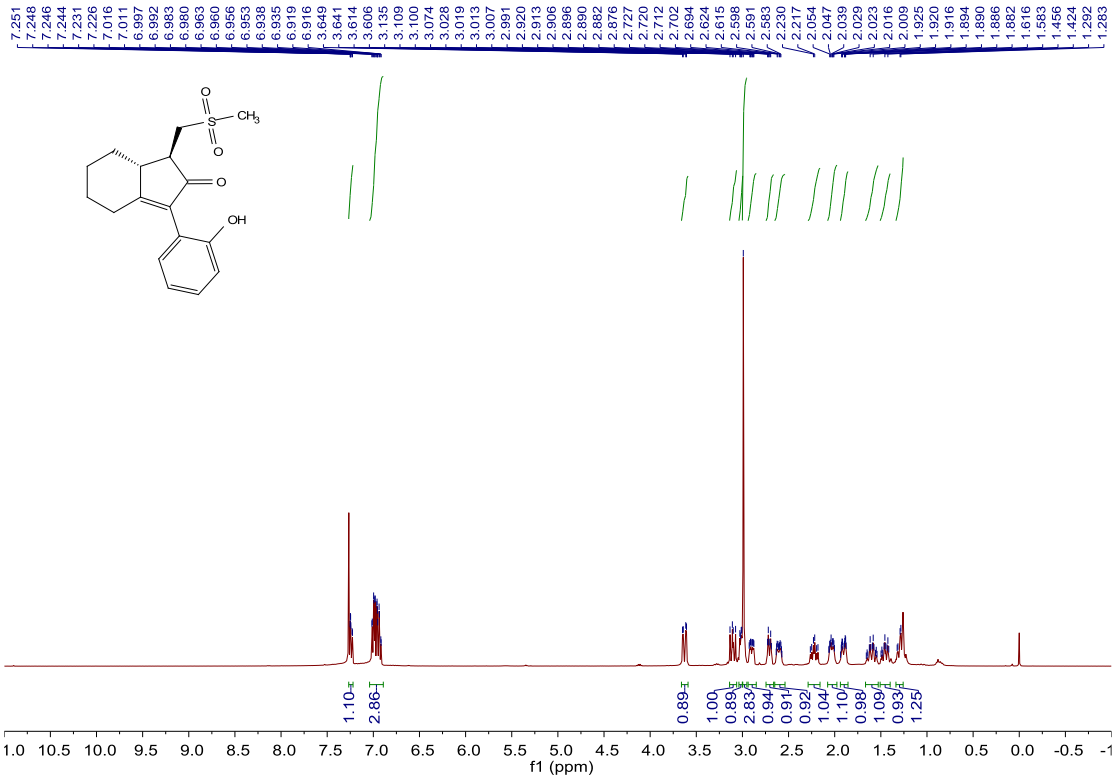

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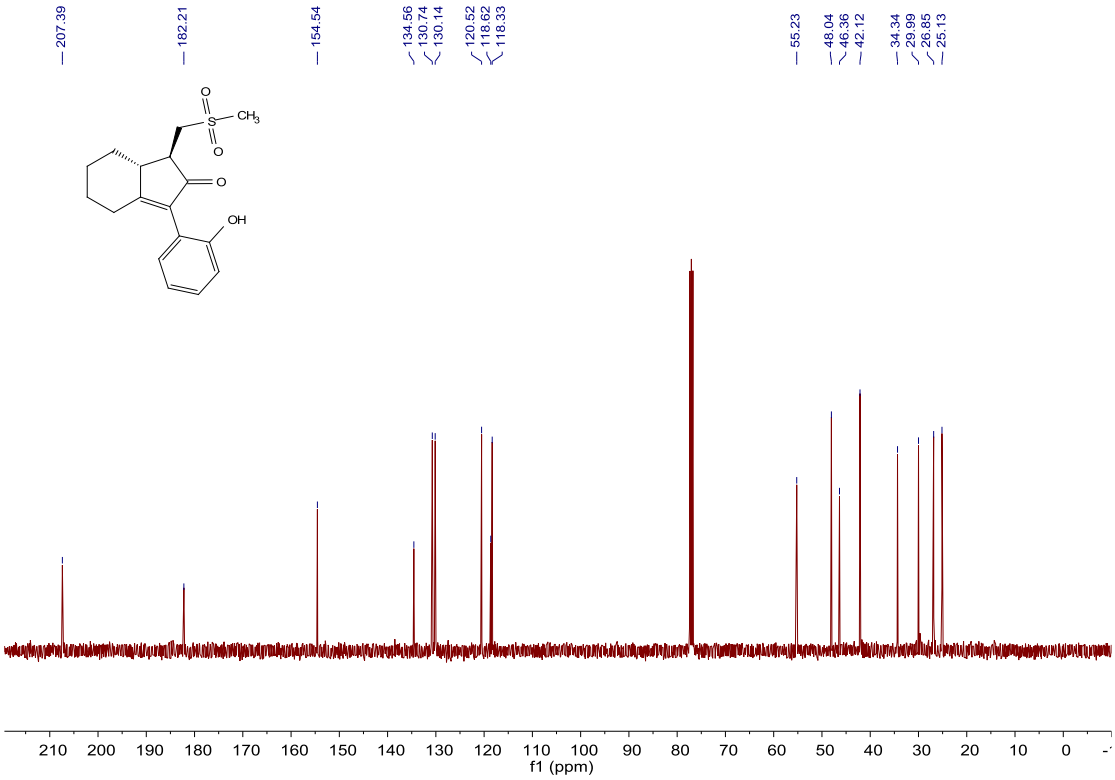

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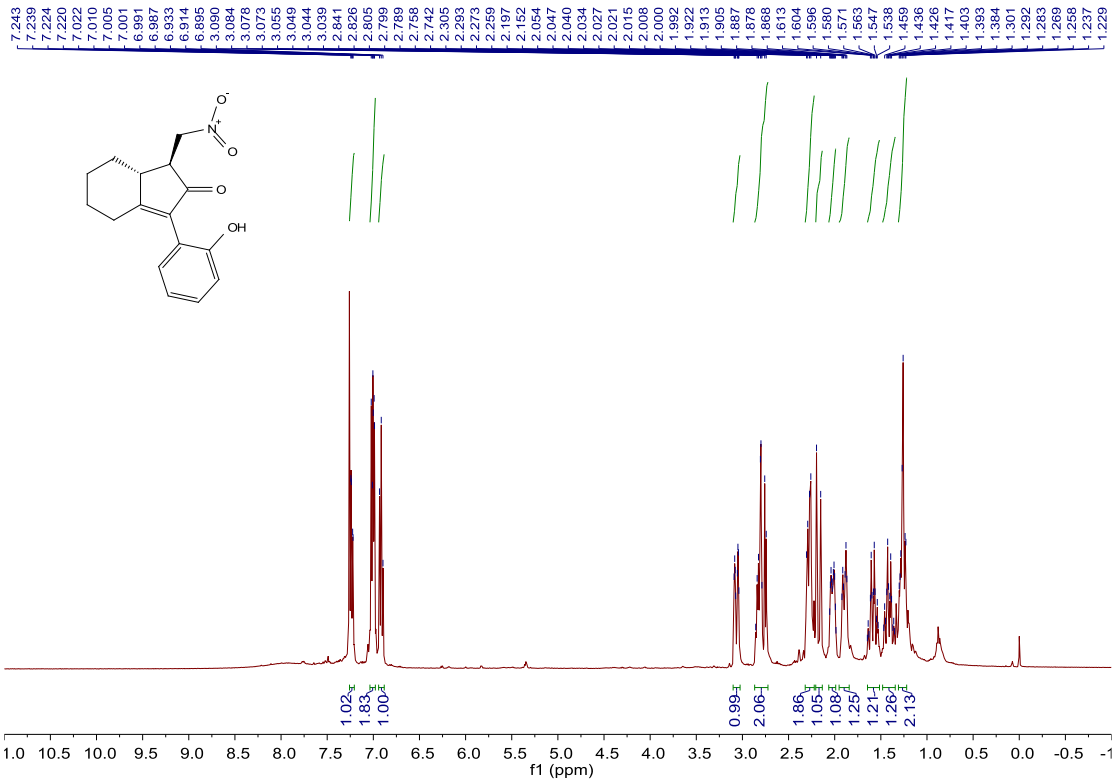

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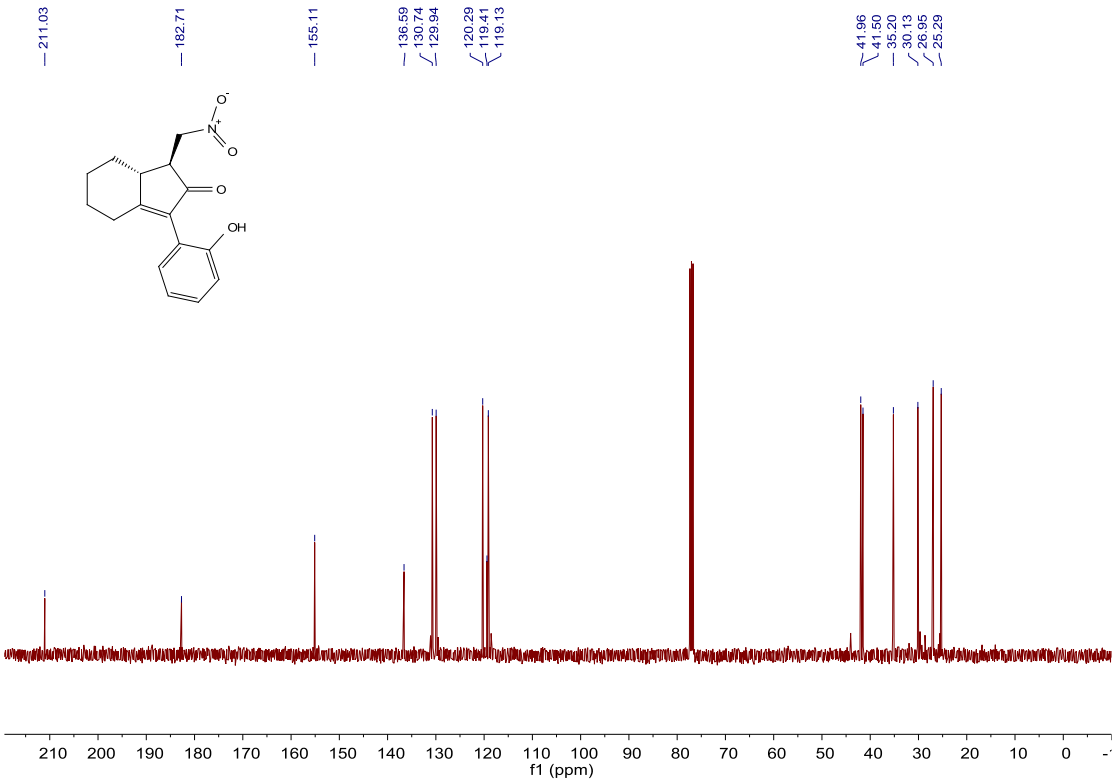

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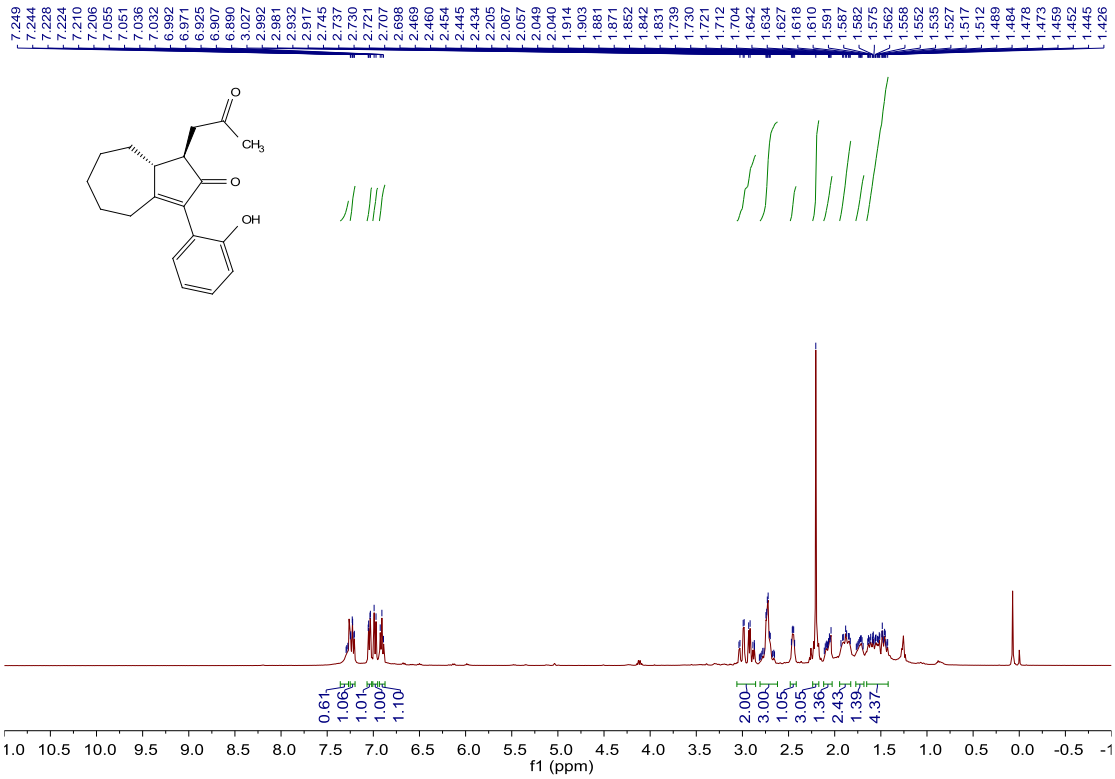
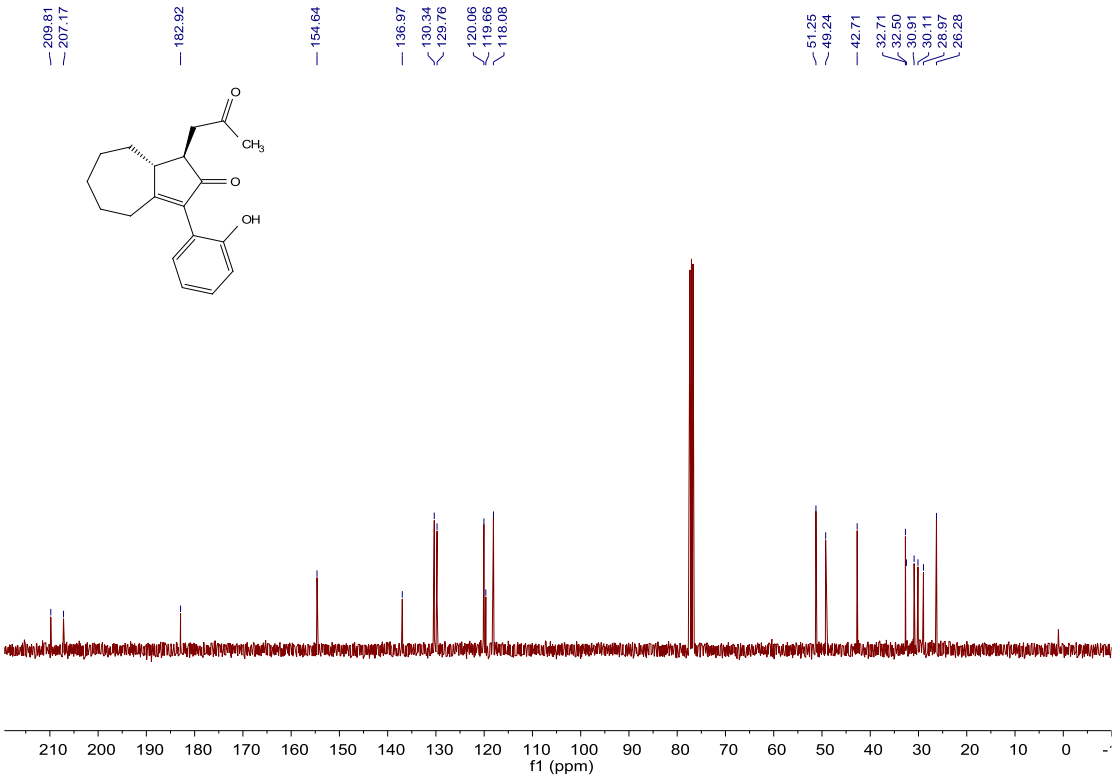
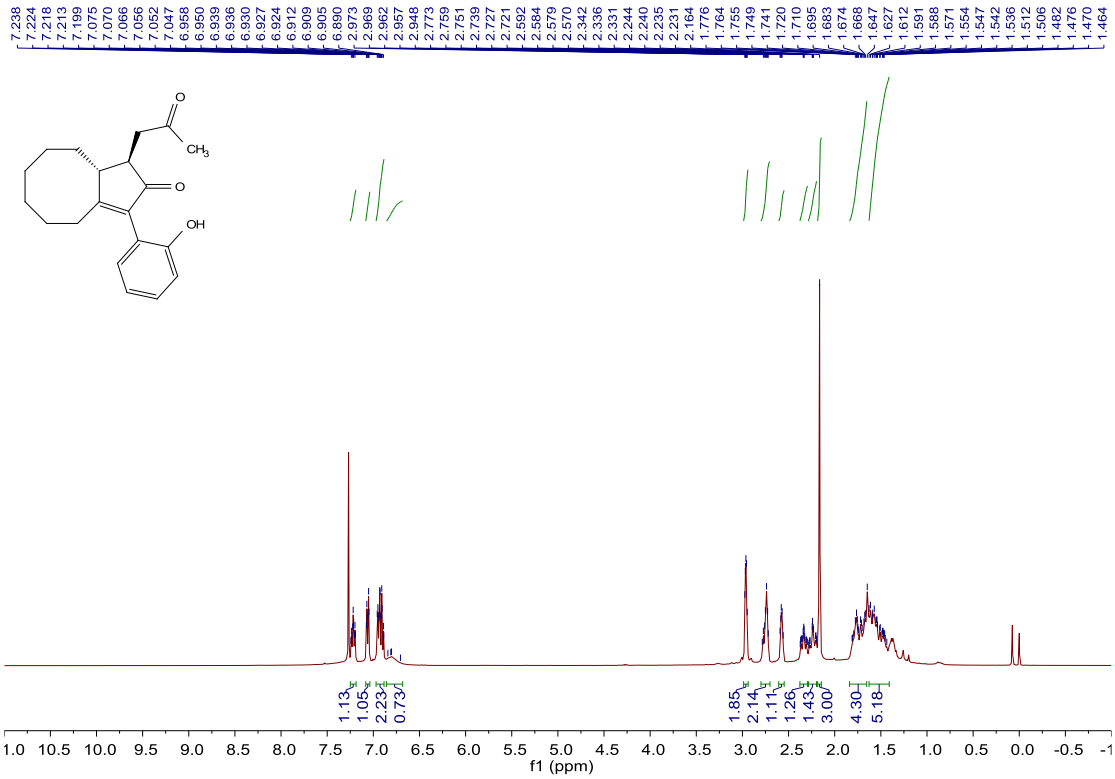


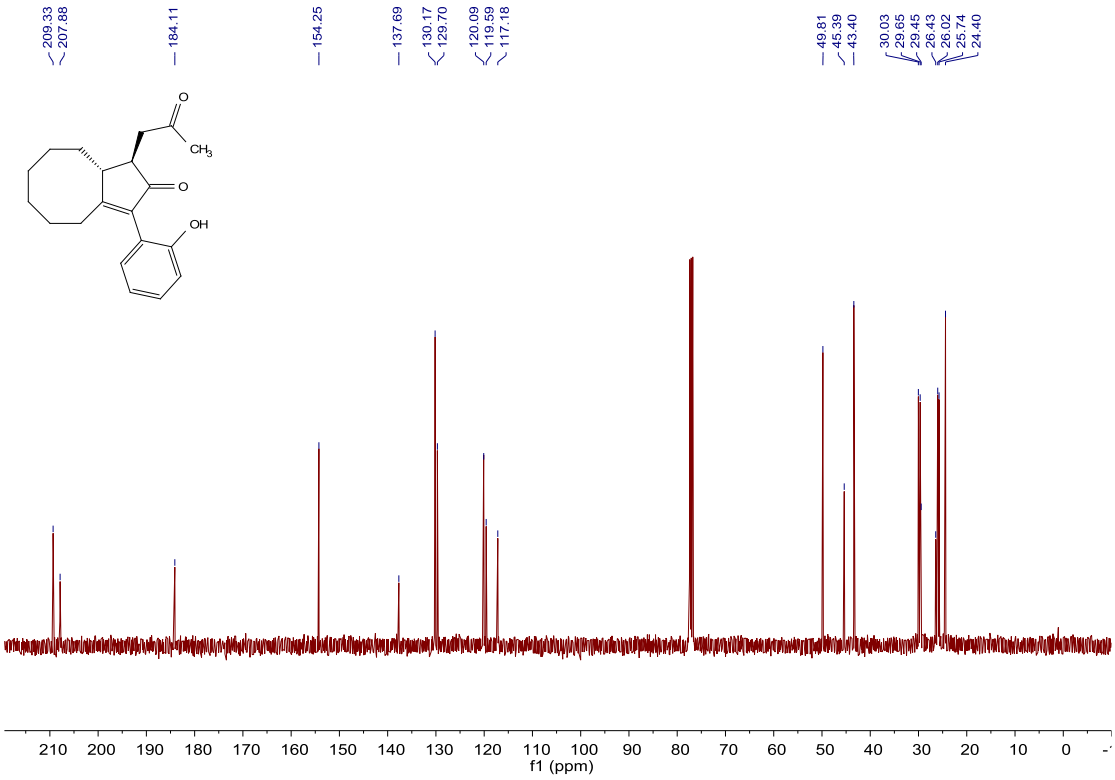
^{13}C NMR of 2q



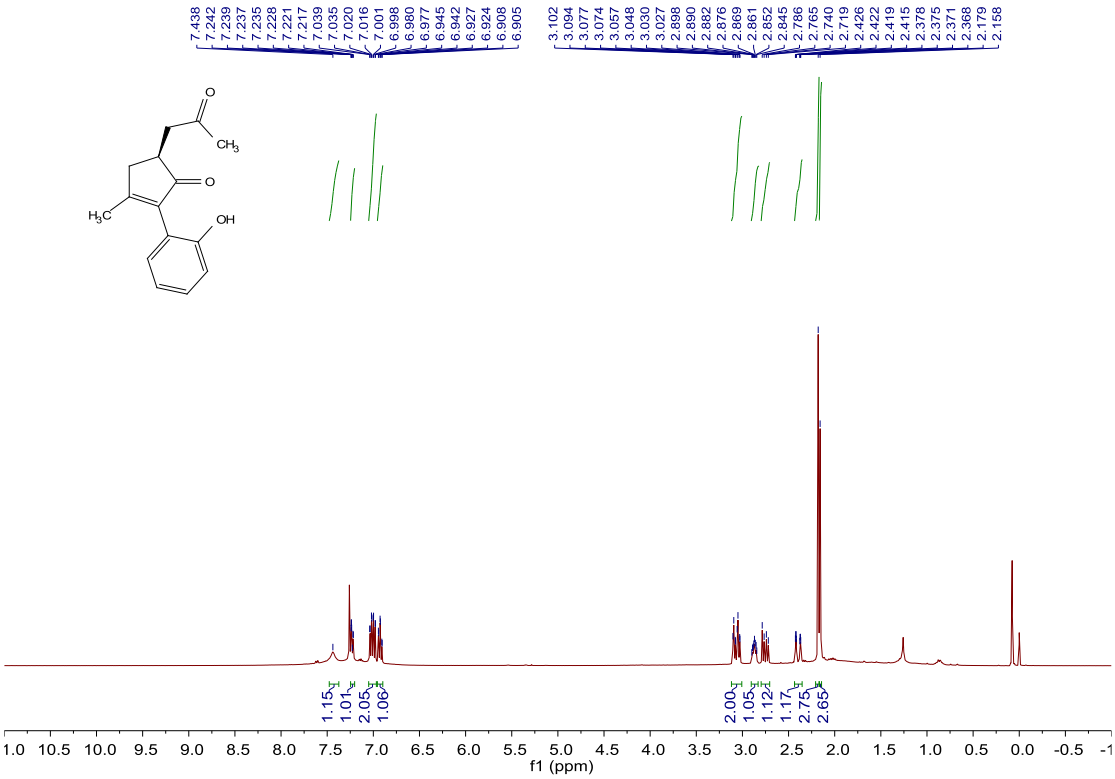
^{1}H NMR of 2r



^{13}C NMR of 2r



^{1}H NMR of 2s



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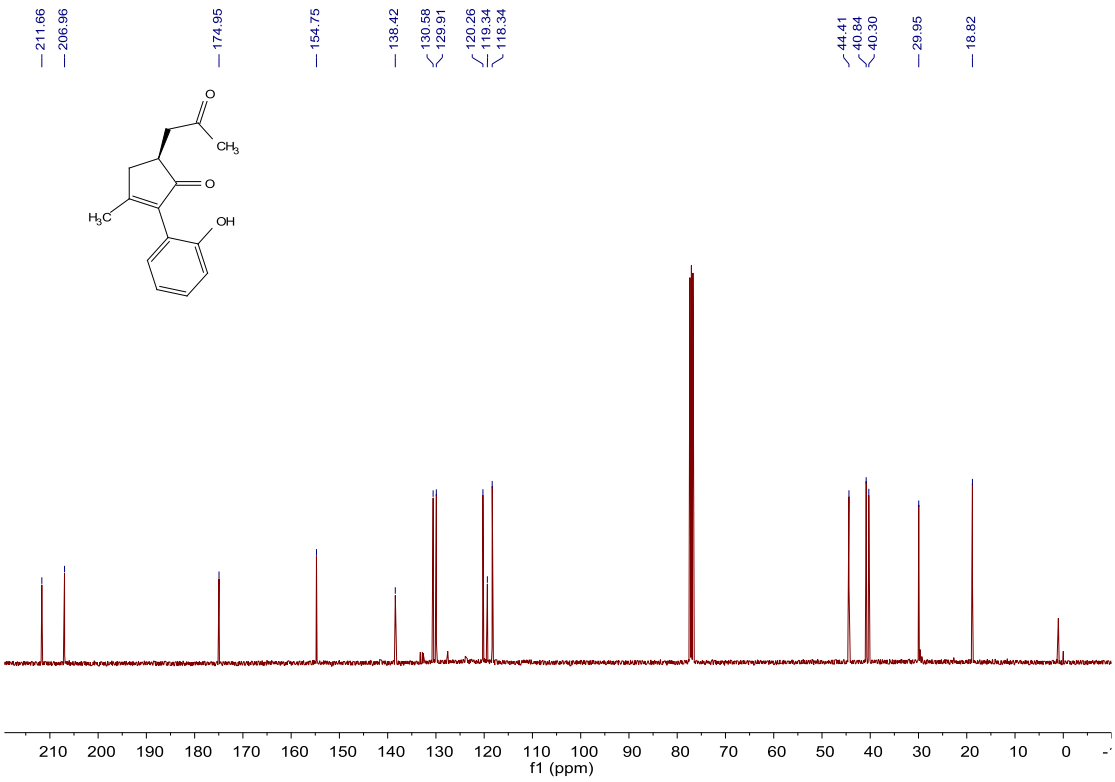
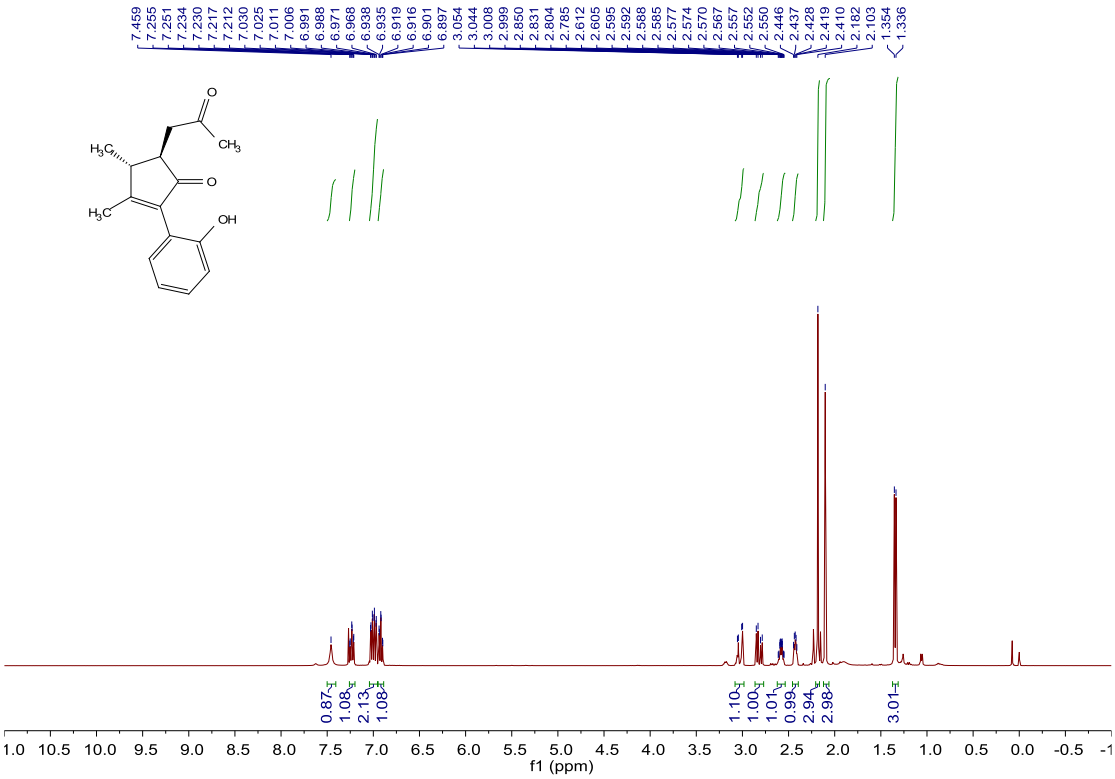


^{1}H NMR of 2t



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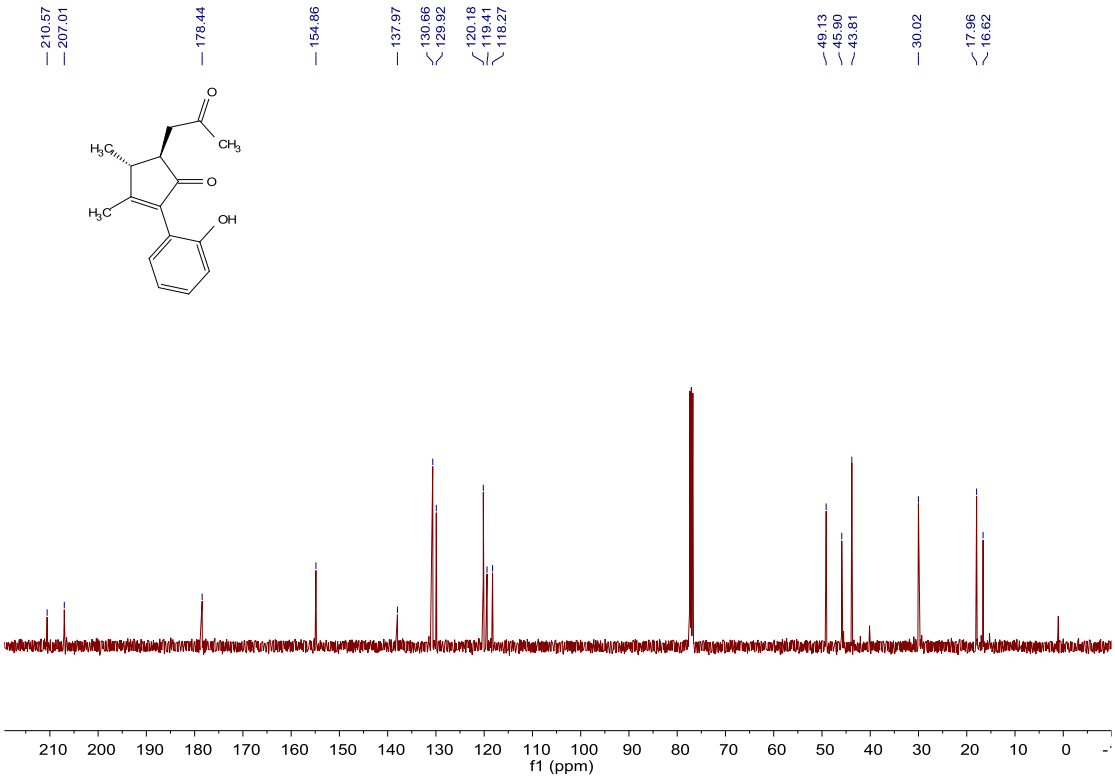

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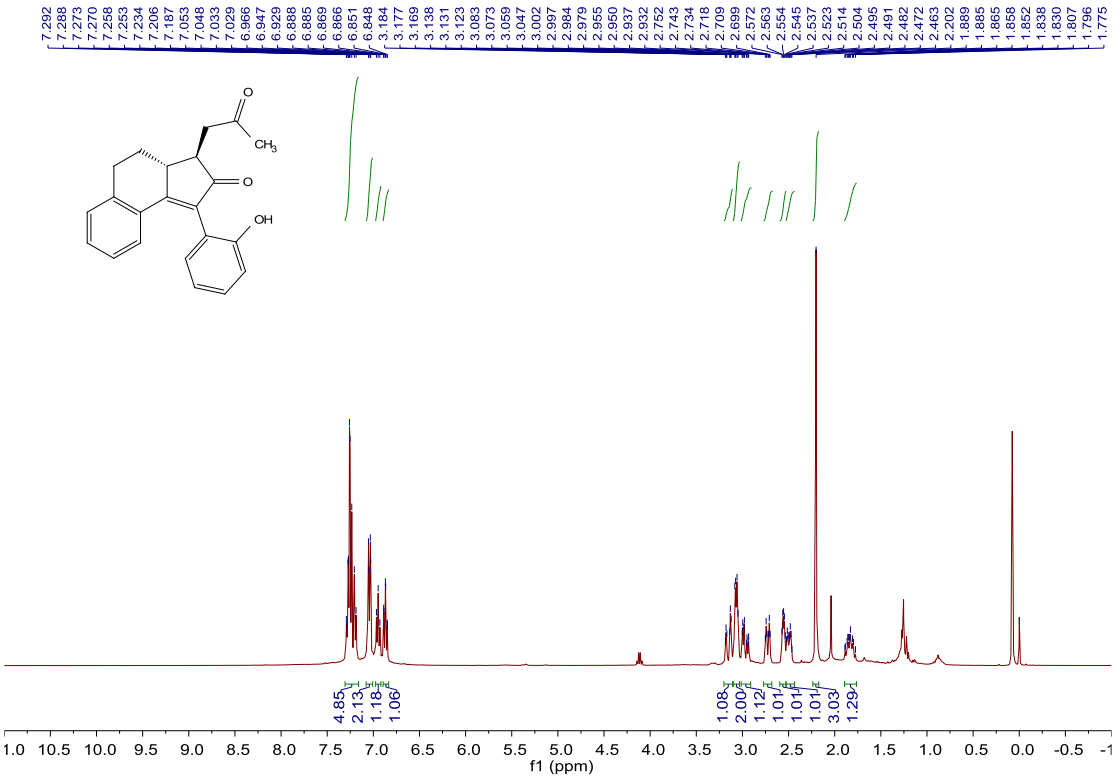

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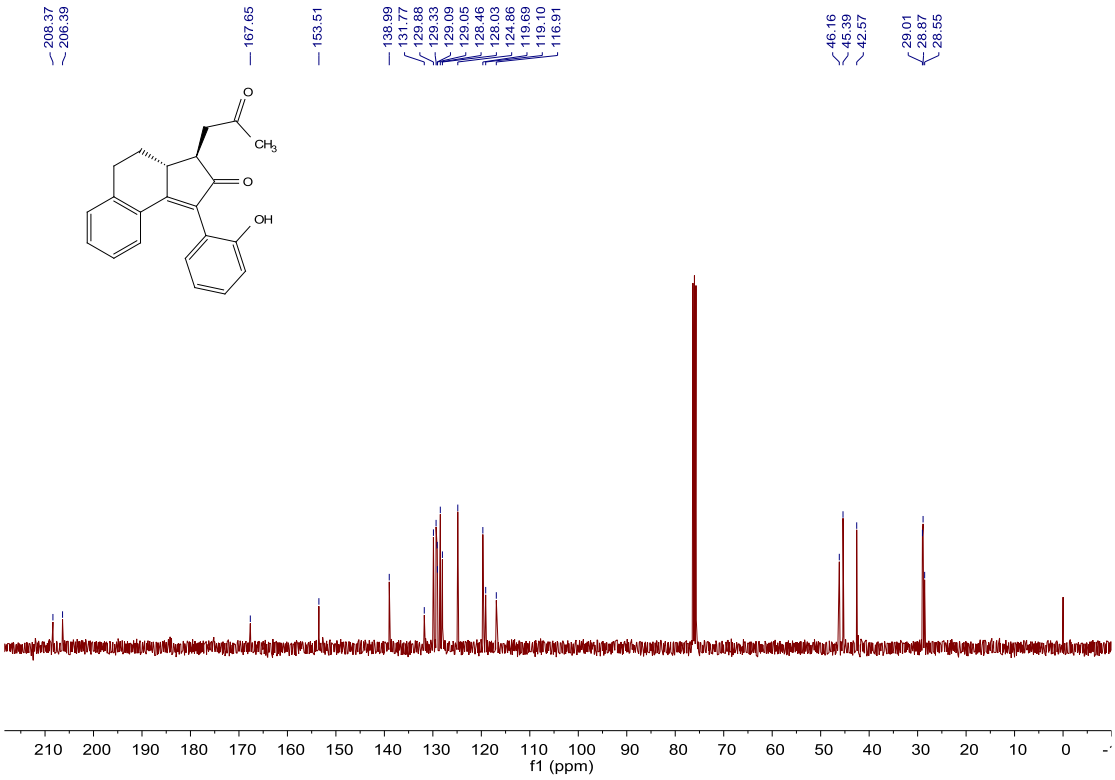

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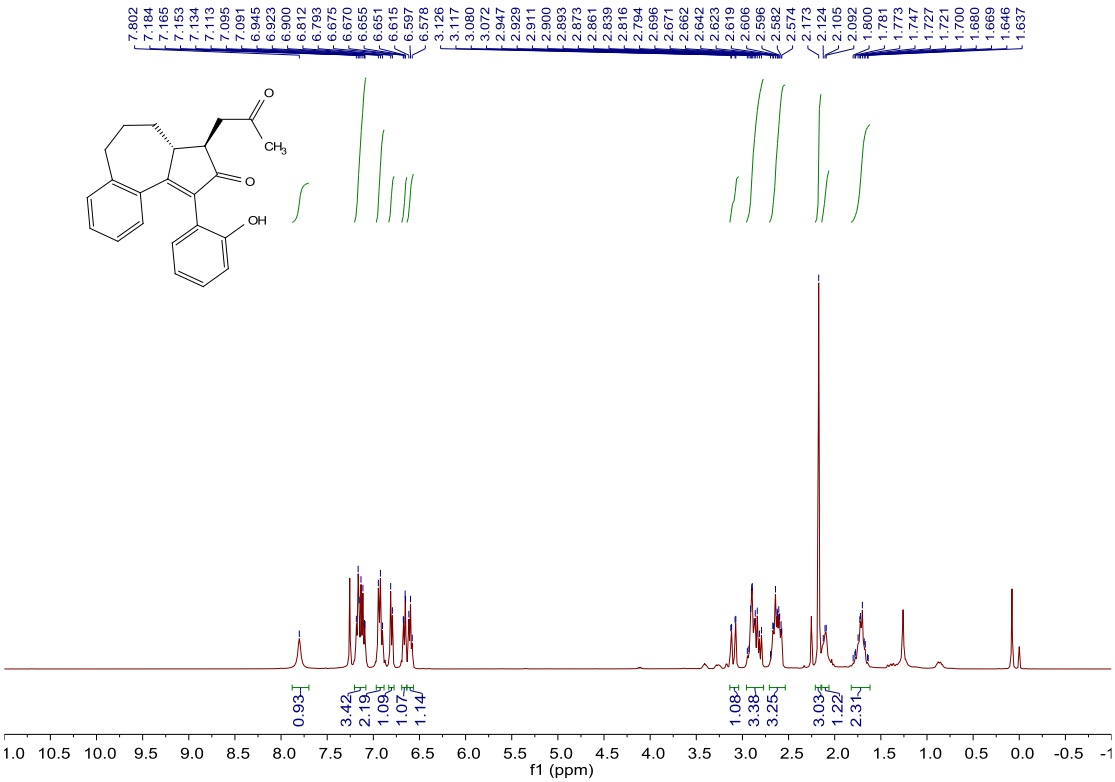

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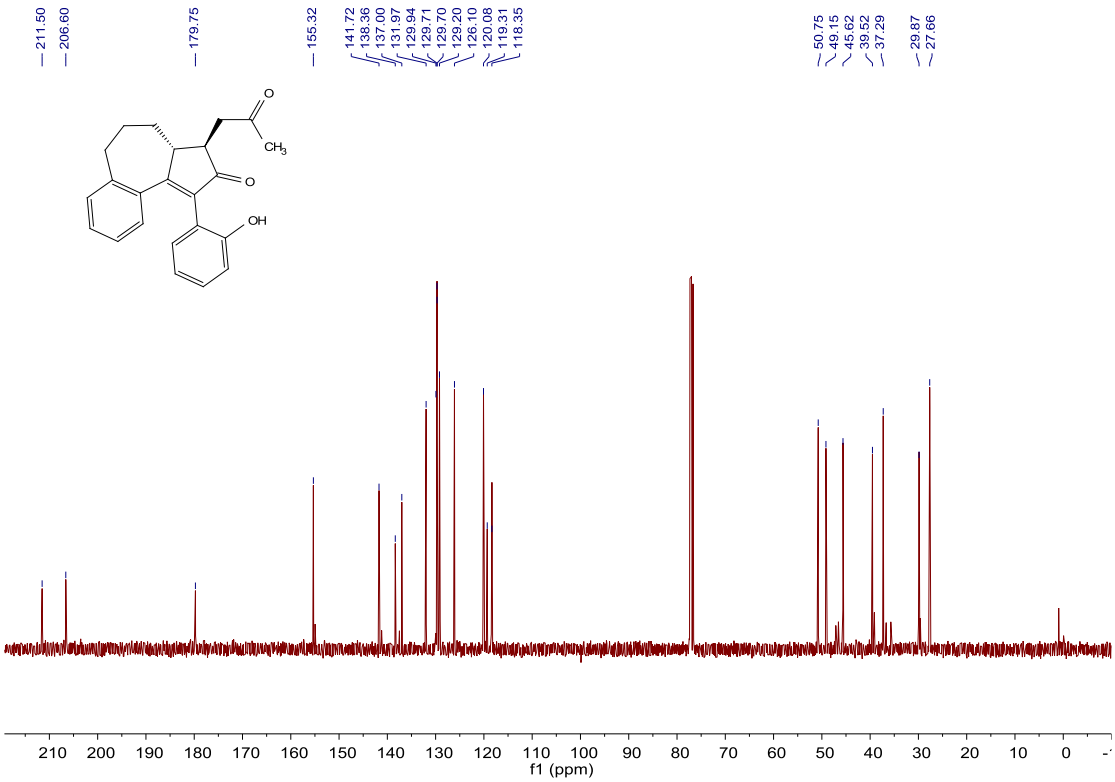

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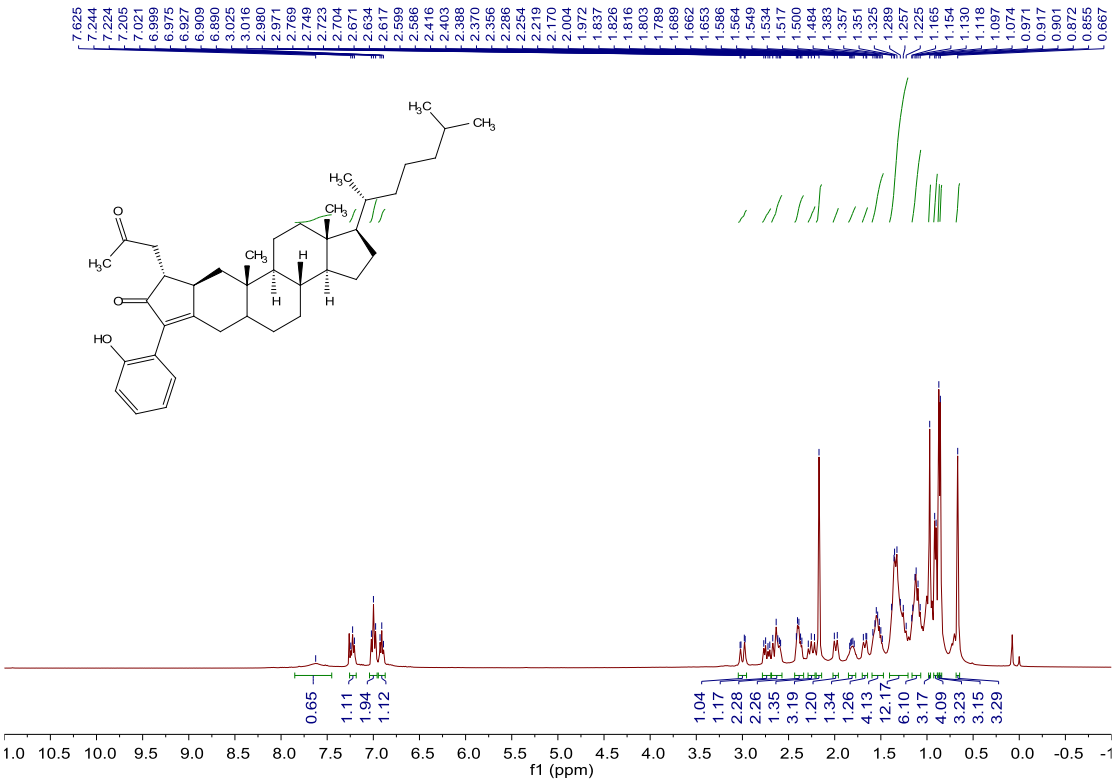

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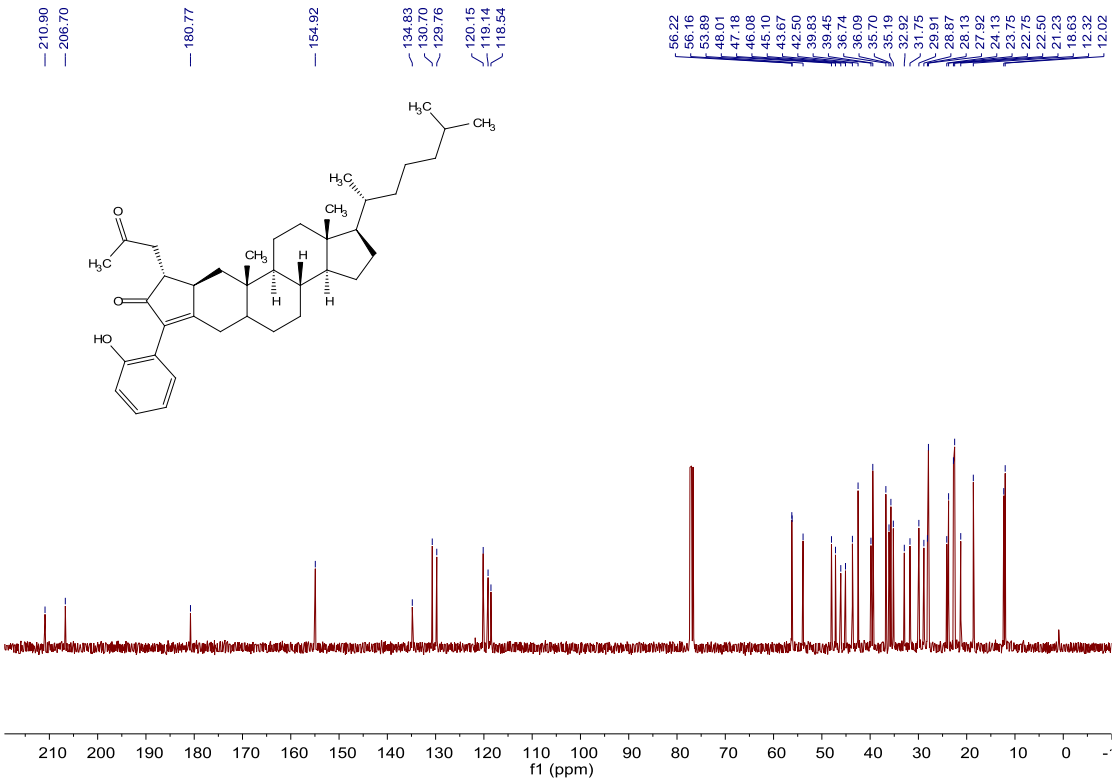

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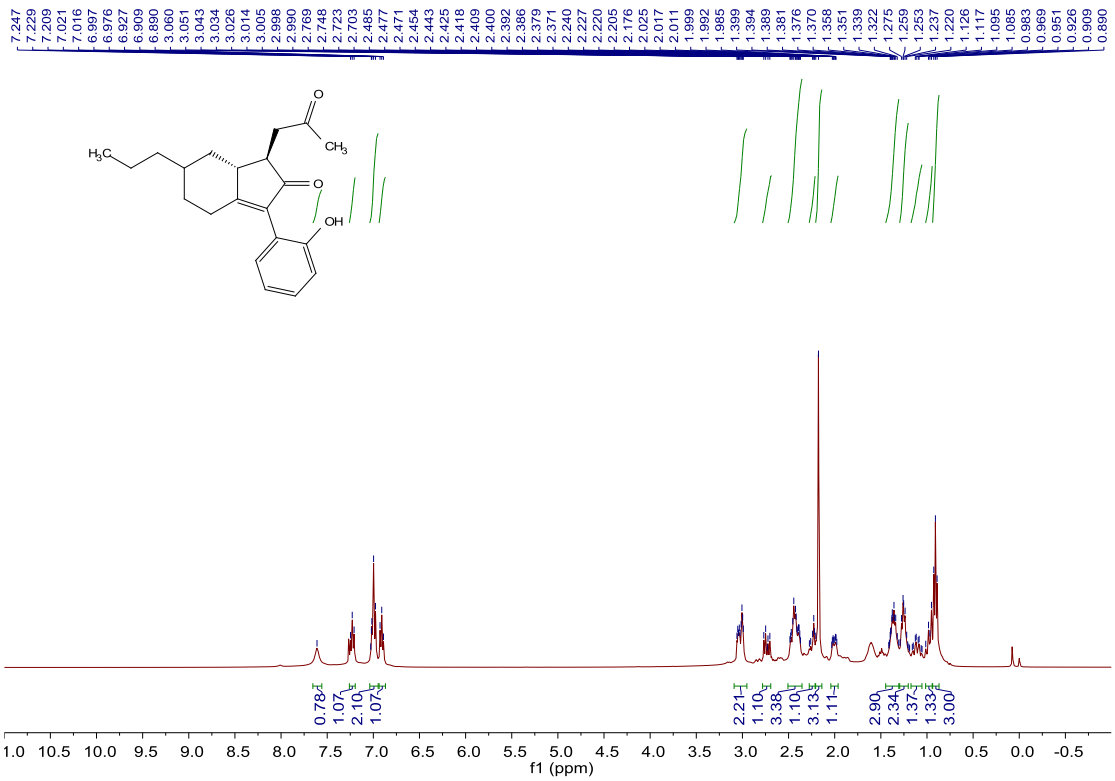

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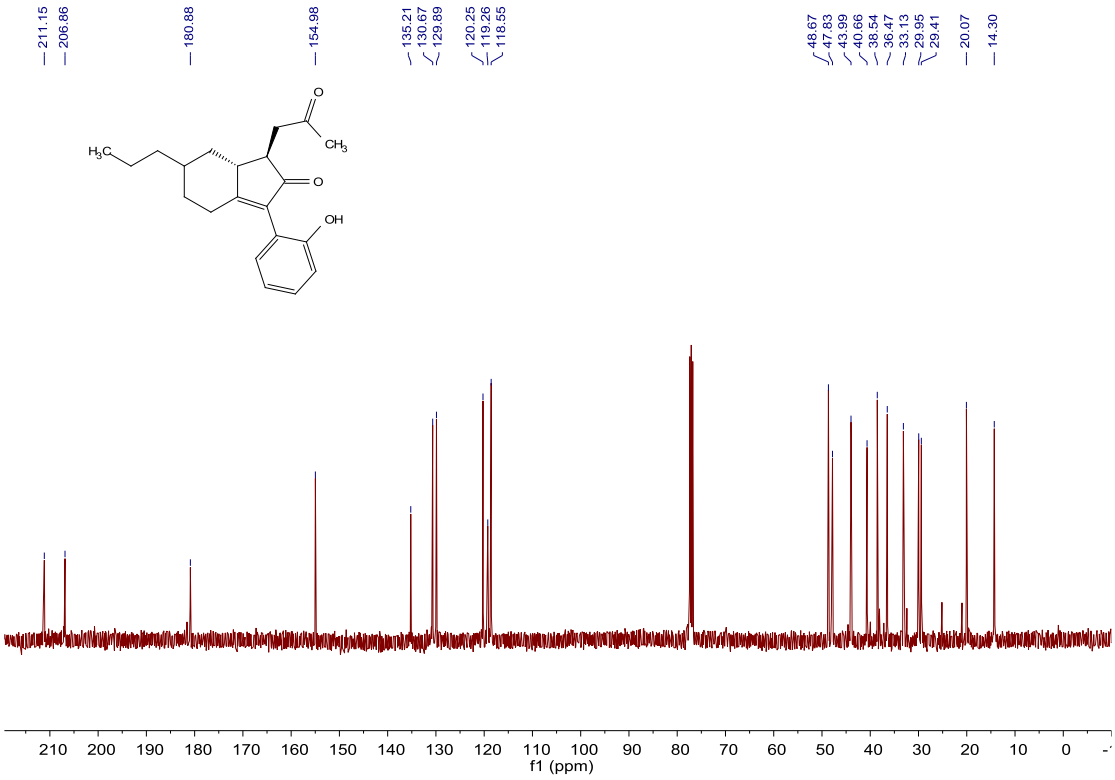

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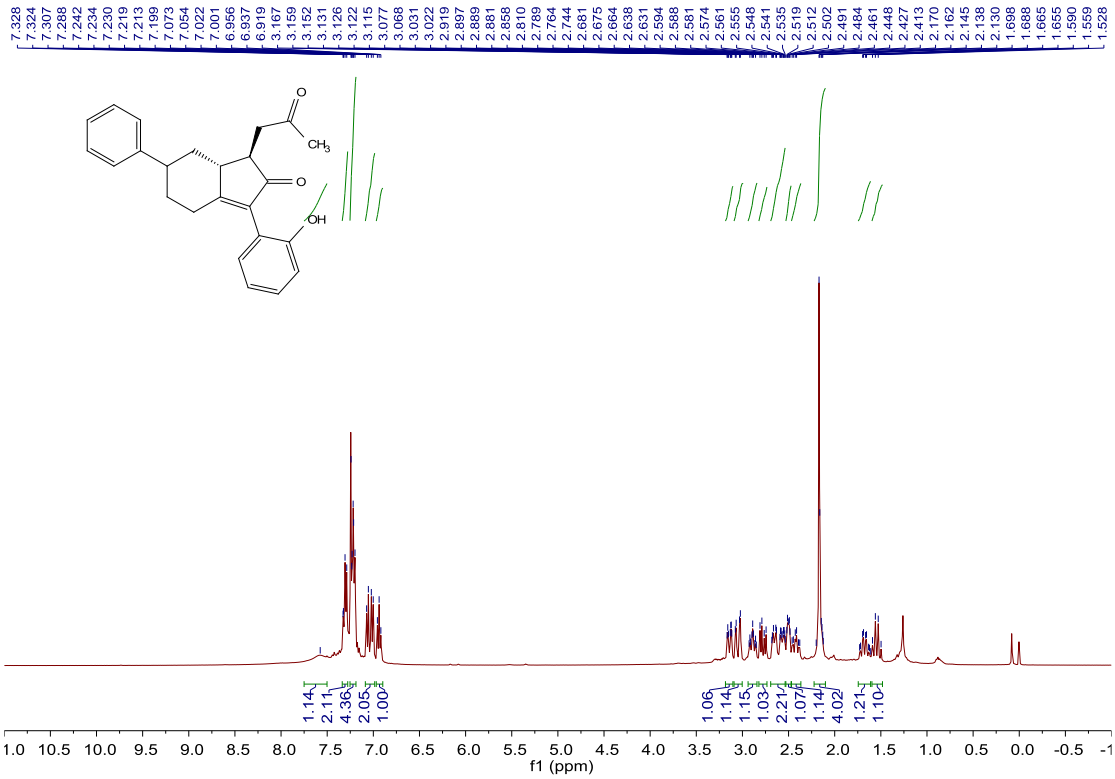

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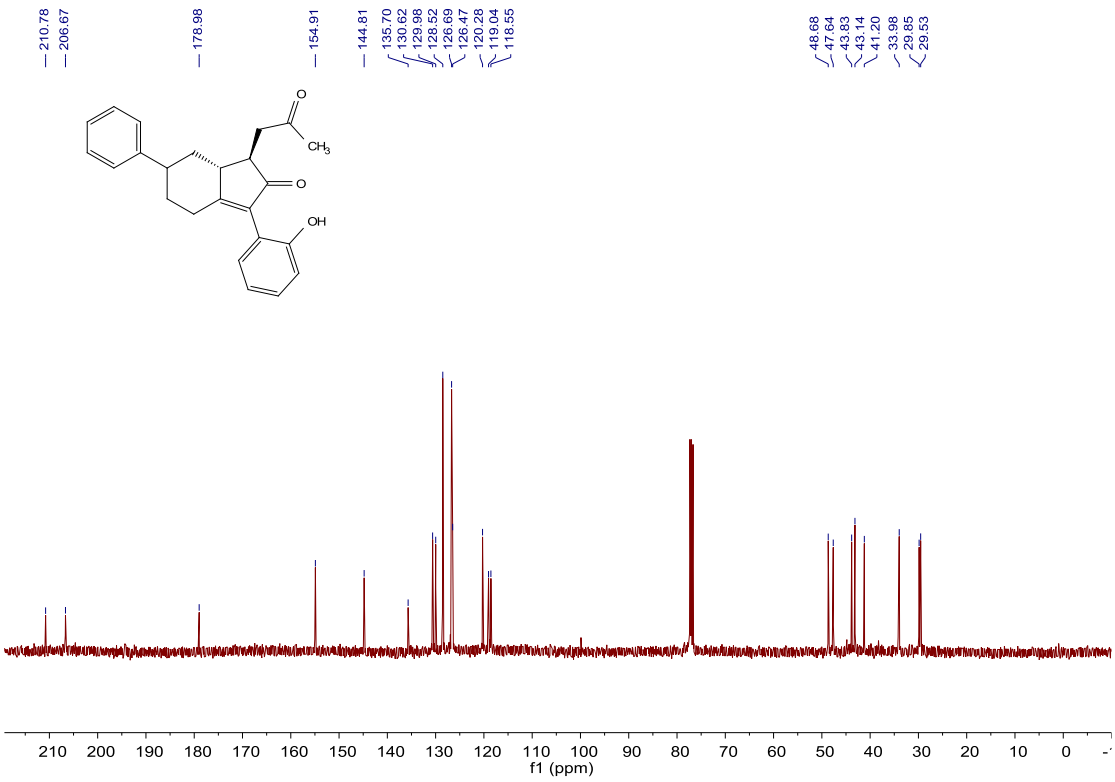
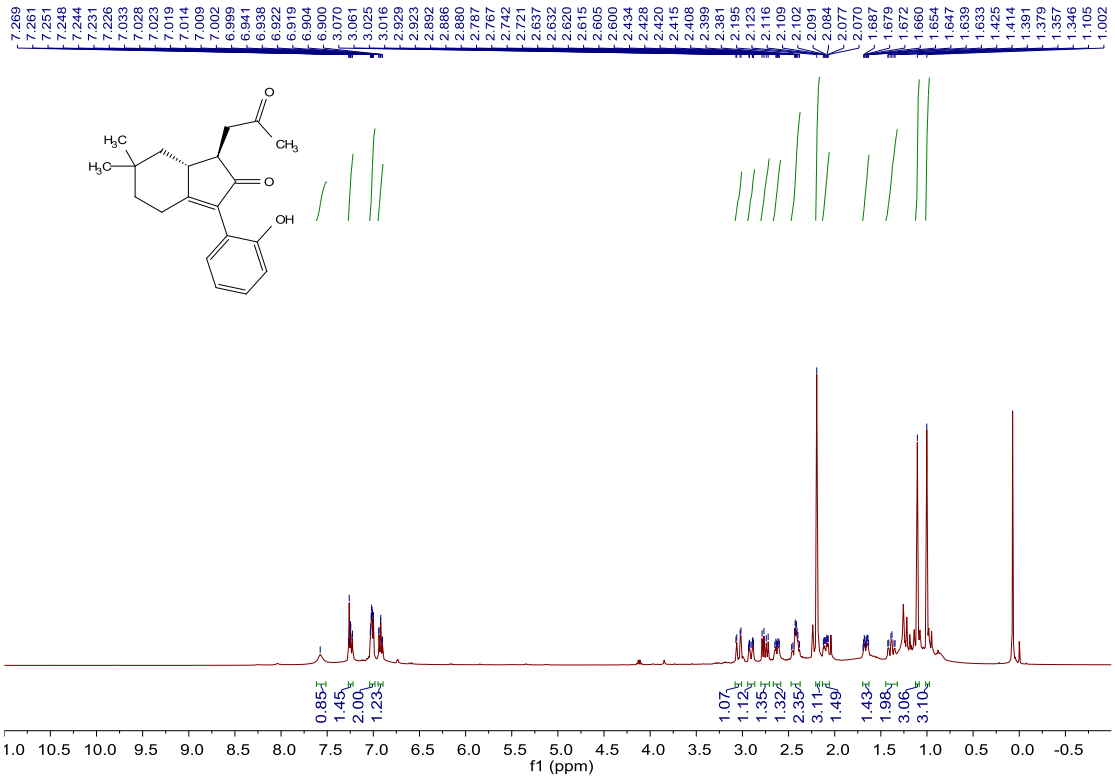
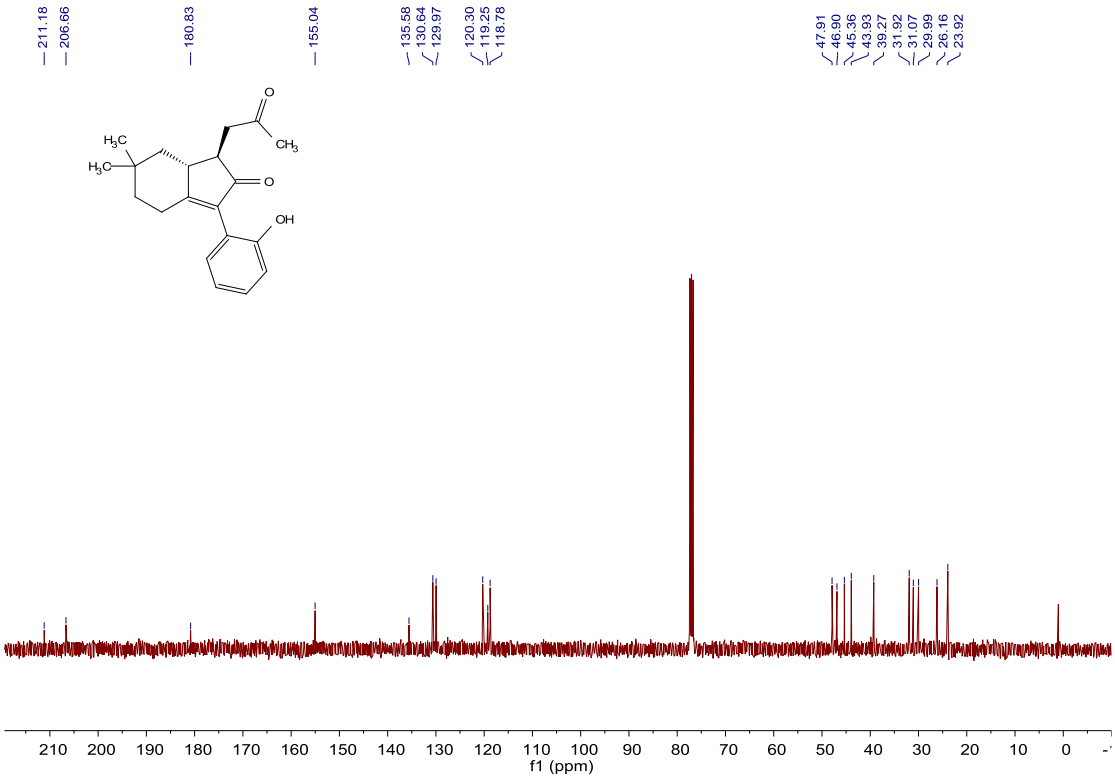


^{1}H NMR of 2aa



^{13}C NMR of 2aa



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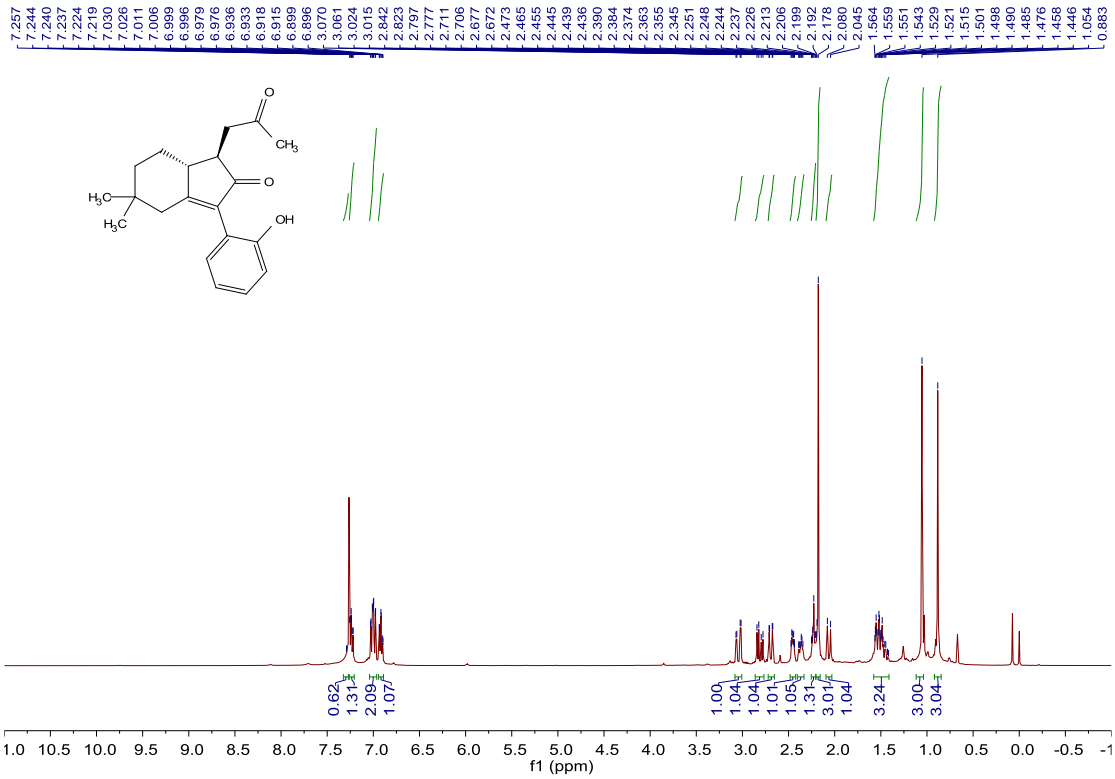

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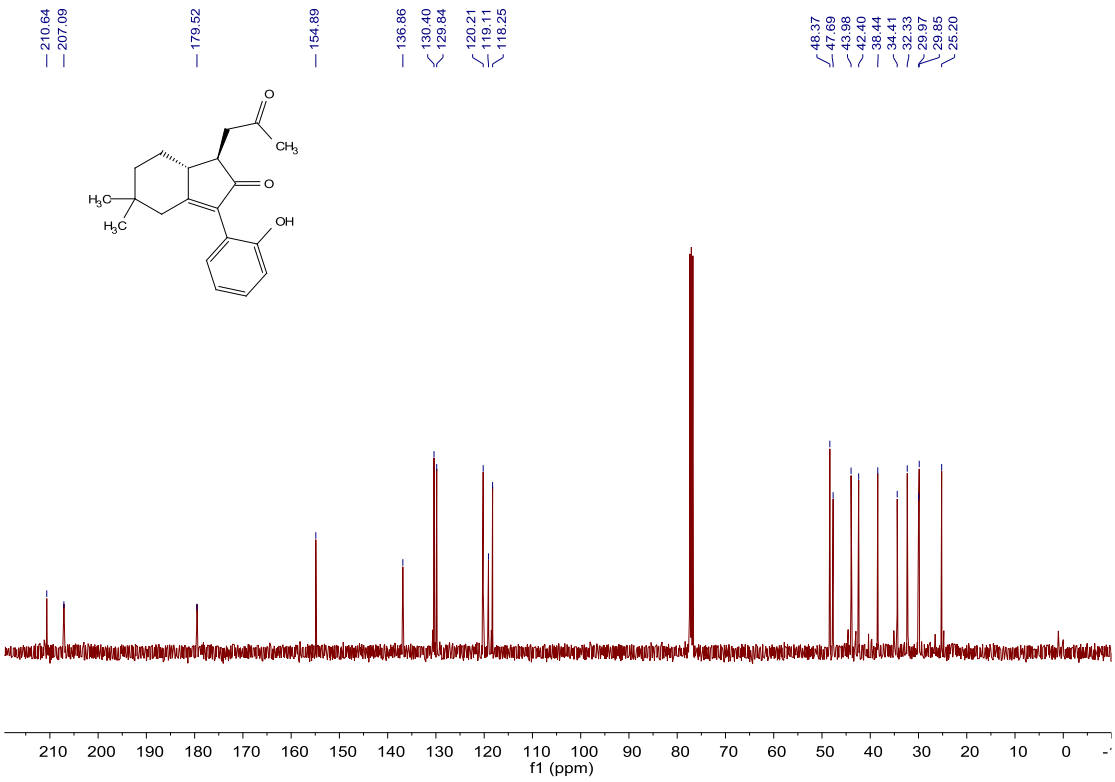

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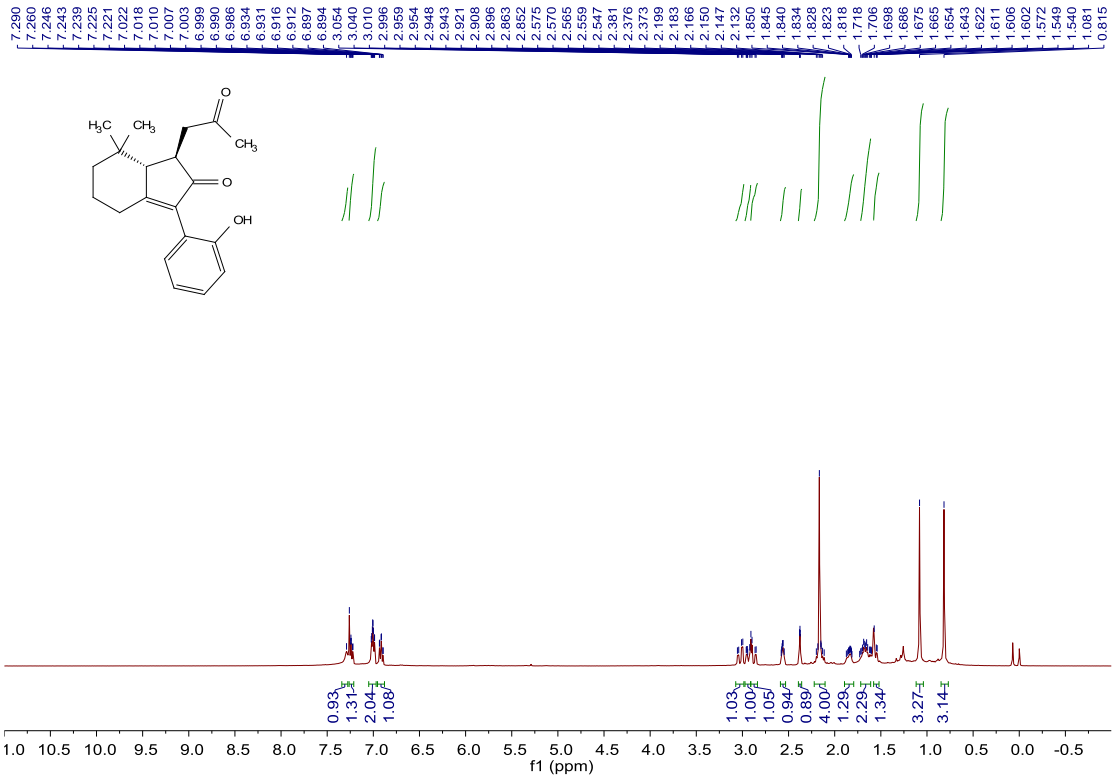

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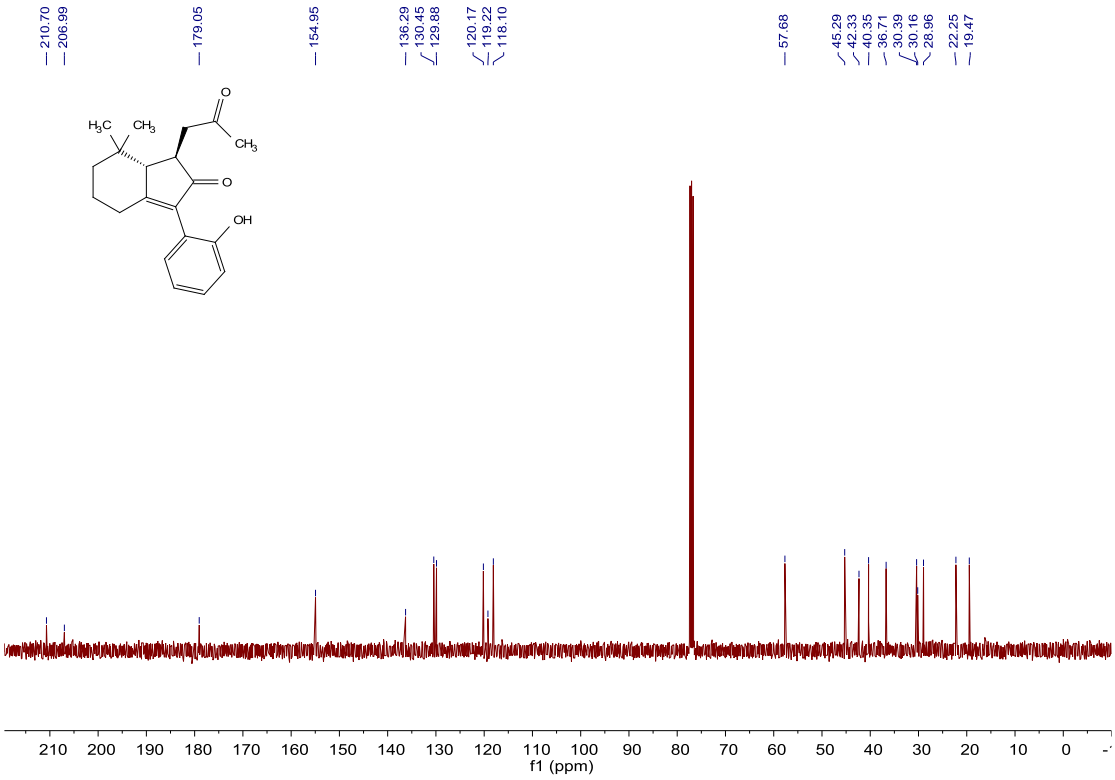
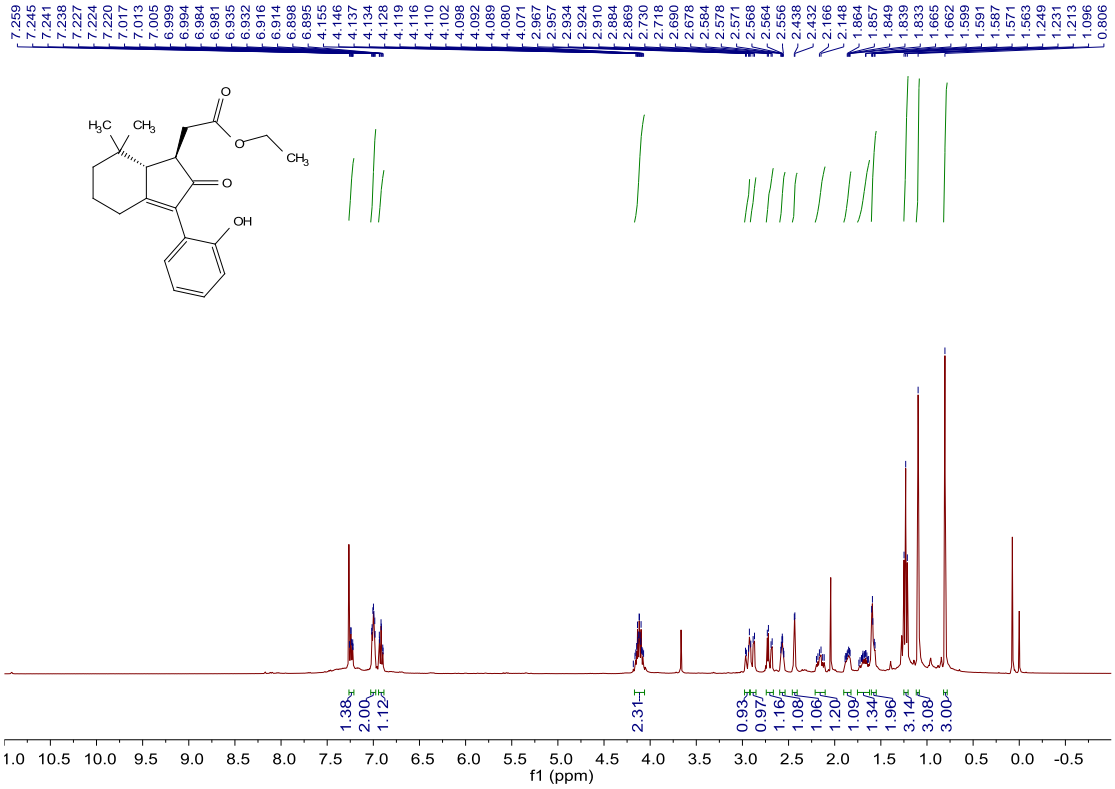


^{1}H NMR of 2ad



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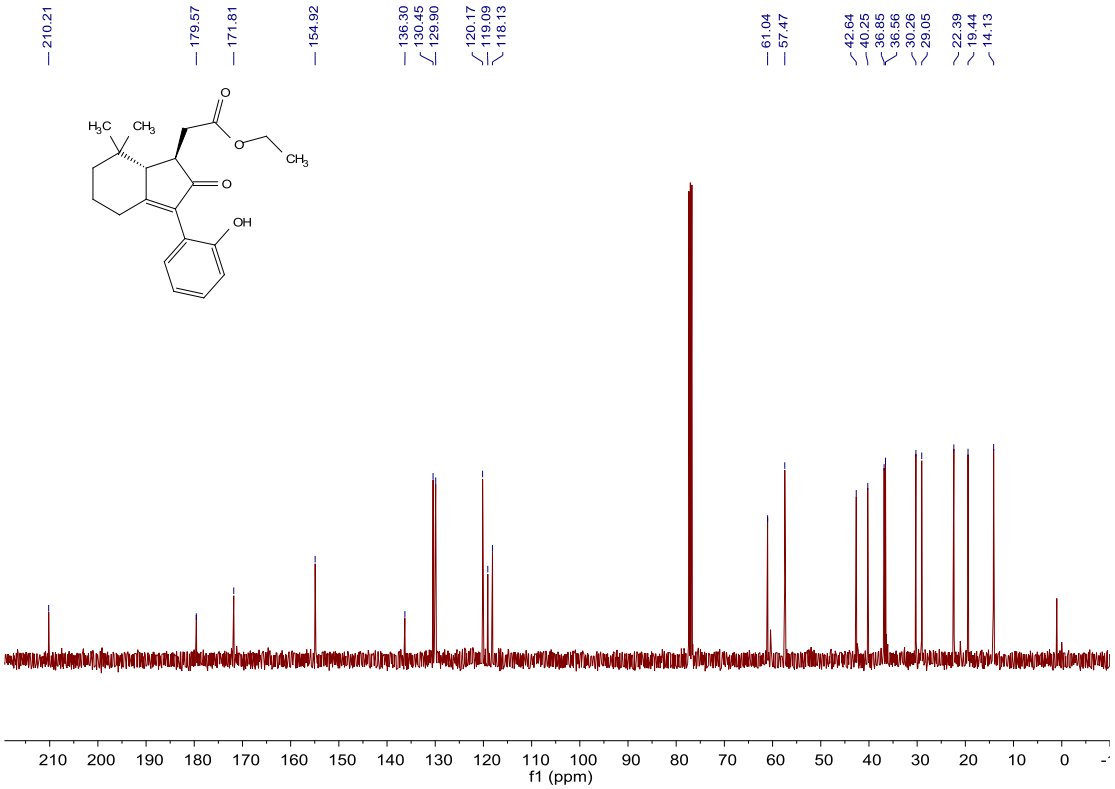
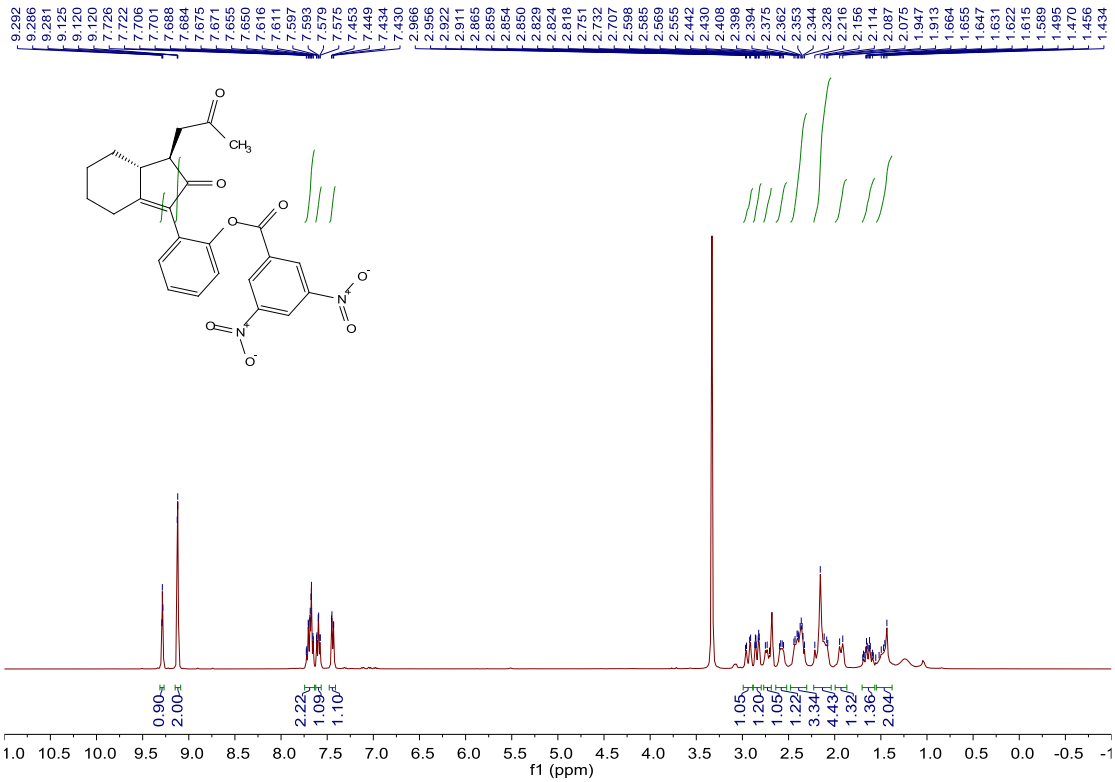


^{1}H NMR of 2a-1



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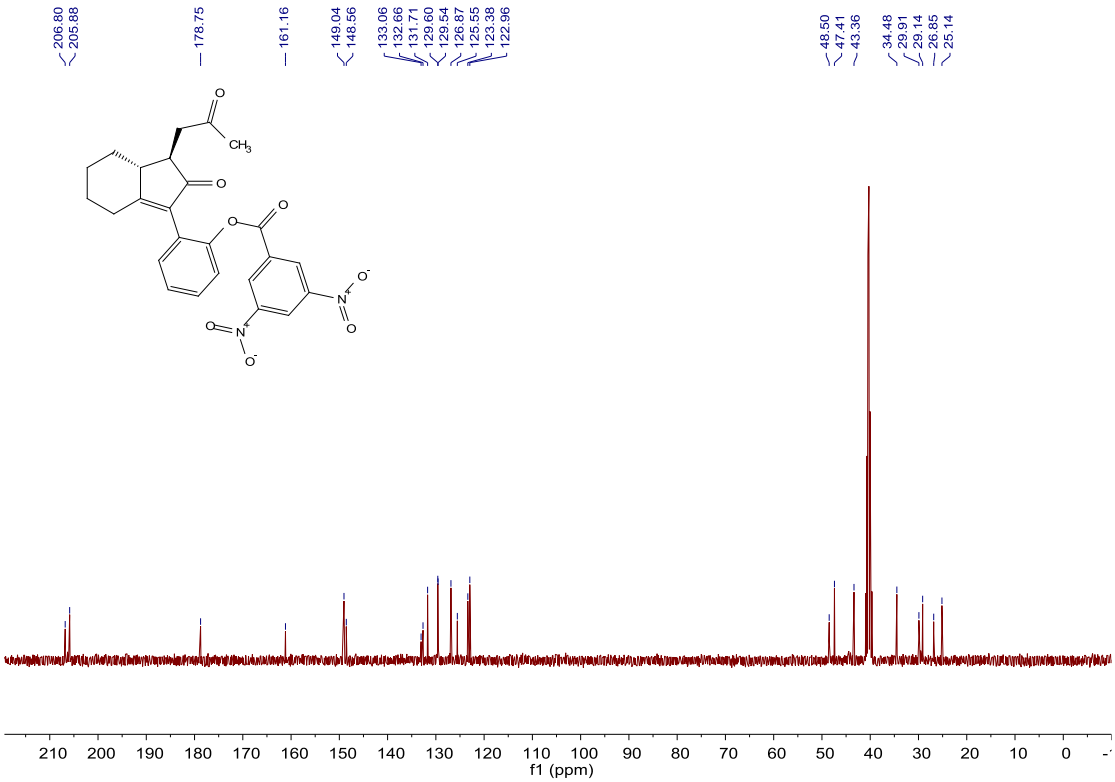
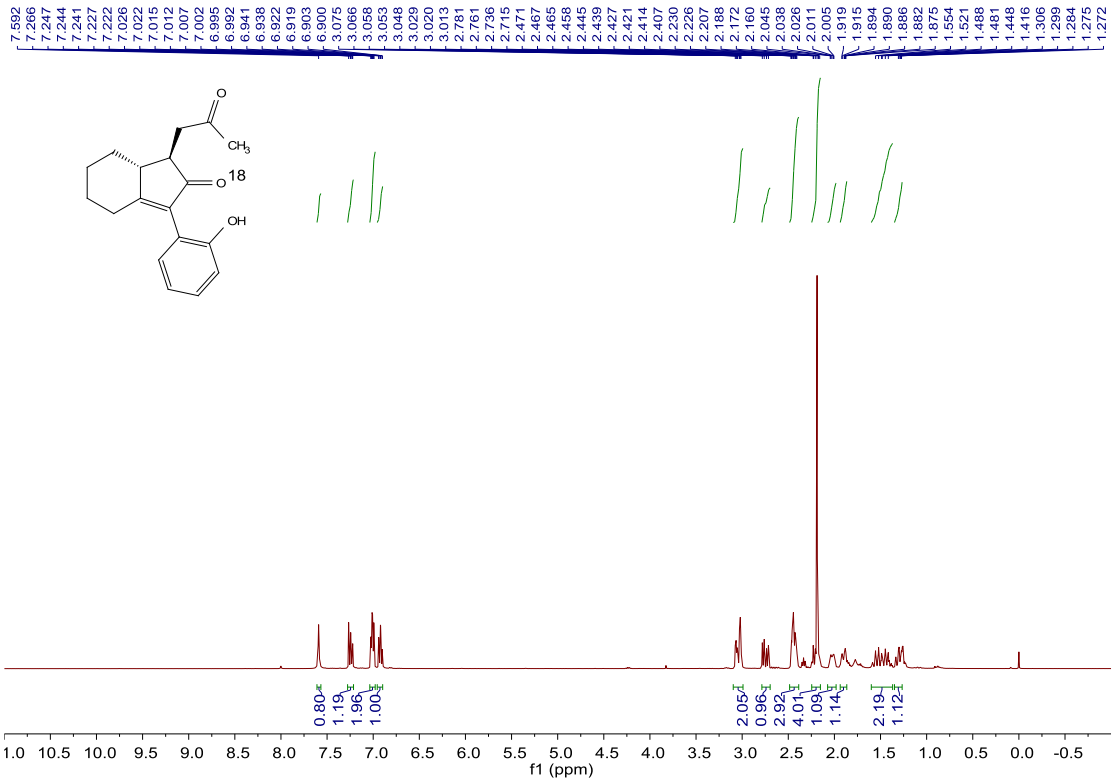
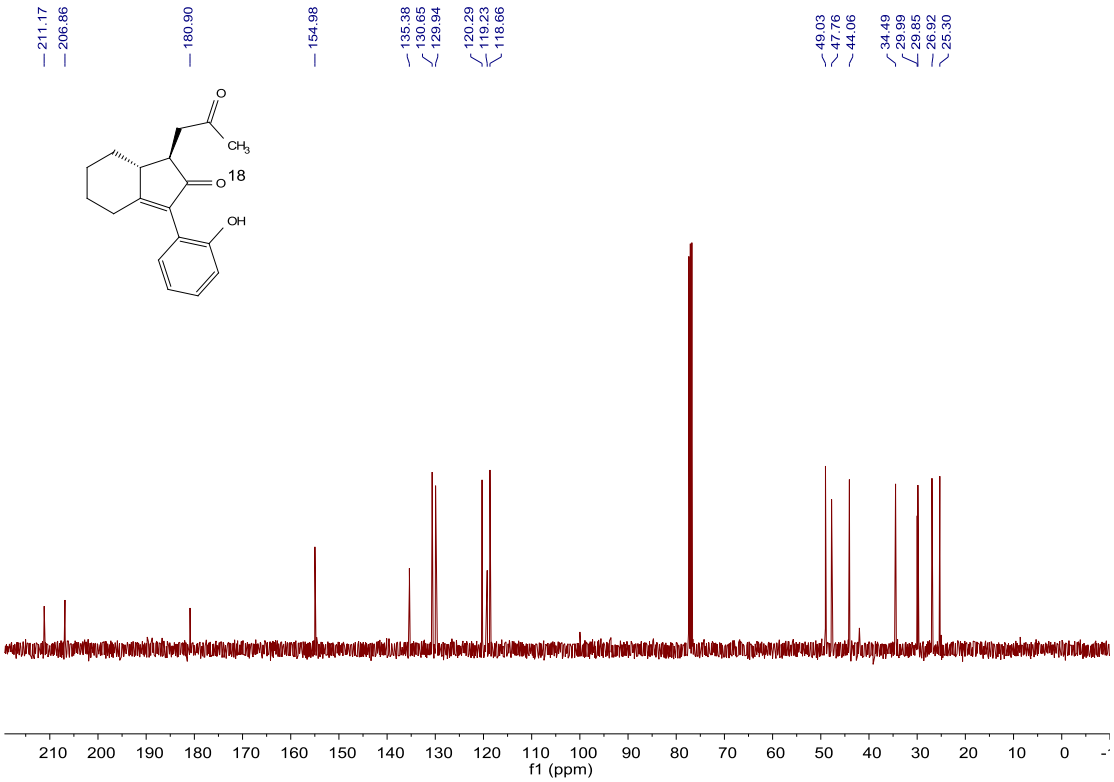


^{1}H NMR of 2a-^{18}O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