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Lewis Acid-Catalyzed Annulative Partial Dimerization of 3-Aryloxyacrylates to 4-Arylchroman-2-ones: Synthesis of Analogues of Tolterodine, RORγ Inhibitor and aGPR 40 Agonist

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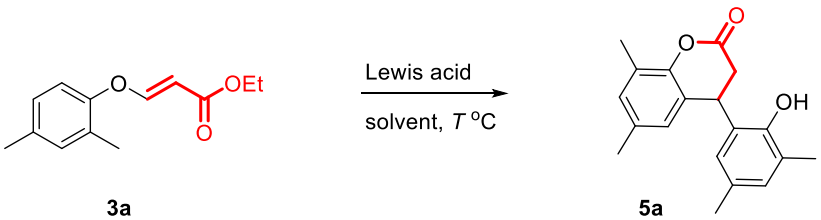
Experimental Procedures

General Information.
Solvents were dried by standard methods. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or under a UV lamp. ^1H and ^{13}C NMR were recorded with a spectrometer operating at 500 or 400 and 125 or 100 MHz for proton and carbon nuclei respectively. The chemical shifts are based on the TMS peak at δ = 0.00 pm for proton NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) in carbon NMR. IR spectra were obtained on an FT−IR spectrometer, and samples were prepared by evaporation from $CHCl_3$ on CsBr plates. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization by the TOF method.

Reaction Optimization.
We chose compound **3a** to investigate various Lewis acids and to optimize the reaction conditions (Table 1). In 1,2-dichloroethane (DCE) solvent, of the various acids investigated (Table 1, entries 1-11), $BF_3{\cdot}OEt$ and $Sc(OTf)_3$ provided reasonable yields of **5a**. $Zn(OTf)_2$, $Cu(OTf)_2$ and AgOTf were not successful for this reaction (entries 4-6) and the substrate **3a** was recovered in all cases even after heating to 80 °C. With *p*TsOH, the cleavage of **3a** into its corresponding phenol was observed at elevated temperature and no rearranged product **5a** was formed (entry 8). Among the other protic acids like AcOH, TfOH and H_3PO_4, only TfOH catalyzed the reaction giving **5a** in 56% yield (entries 9-11). With increase in temperature to 60 °C, the reaction was terminated by $BF_3{\cdot}OEt_2$ in a shorter period and higher yield to deliver **5a** in 91% yield (entry 12). The reaction was further improved and completed in 4 h at 80 °C cleanly providing **5a** in 94% yield (entry 13). Change of solvent to CH_2Cl_2, toluene, CH_3CN, or benzene did not prove better (entries 14-17). With $Sc(OTf)_3$, the reaction at 80 °C gave **5a** in 78% yield (entry 18). Thus among the Lewis acids: TMSOTf, $Sc(OTf)_3$ and $BF_3{\cdot}OEt$, the last worked well and was also cheaper than the rest. A change in concentration of $BF_3{\cdot}OEt$ from 0.5 to 0.25 or 1.0 equivalent was not superior (entries 19 and 20 respectively). The latter having higher concentration of $BF_3{\cdot}OEt$ resulted in partial cleavage of **3a** to the corresponding phenol. The reaction concentration was also found to be influential. Lowering the reaction concentration to 0.01 M gave lower yields of **3a** (entry 21), while higher concentration proved highly detrimental (entry 22). In the absence of $BF_3{\cdot}OEt$, no reaction was observed (entry 23) even after 48 h. When the corresponding (*Z*)-**3a** was used, it delivered the same product **5a** in 93% yield (entry 24). Similarly, the mixture of *E*/*Z*-**3a** as obtained during preparation (*E*:*Z* = ~4:1) also provided **5a** in 94% yield (entry 25.) Thus, the separation of the *E*/*Z*-isomers of 3-aryloxyacrylates **3** is not necessitated.

Table 1. Optimization of partial annulativedimeriztion/rearrangement of ethyl 3-aryloxyacrylate **3a** to **5a.**[a]



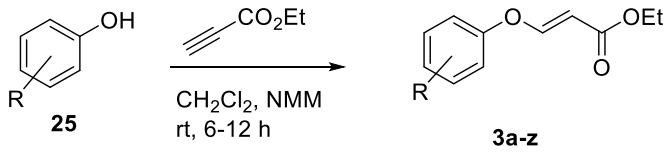
3a **5a**

entry	acid (equiv)	solvent (conc)	*T* (°C)	time (h)	yield **5a** (%)[b]
1	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	rt	12	68
2	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	0	24	28
3	TMSOTf(0.5)	DCE (0.02 M)	rt	12	48
4	$Zn(OTf)_2$ (0.5)	DCE (0.02 M)	rt–80	12	0
5	$Cu(OTf)_2$ (0.5)	DCE (0.02 M)	rt–80	12	0
6	AgOTf (0.5)	DCE (0.02 M)	rt–80	12	0
7	$Sc(OTf)_3$ (0.5)	DCE (0.02 M)	rt	12	63
8	*p*-TsOH (0.5)	DCE (0.02 M)	rt–80	12	0[c]
9	AcOH (0.5)	DCE (0.02 M)	rt–80	12	0
10	TfOH (0.5)	DCE (0.02 M)	rt–80	12	56
11	H_3PO_4 (0.5)	DCE (0.02 M)	rt–80	12	0
12	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	60	6	91
13	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	80	4	94

14	$BF_3{\cdot}OEt_2$ (0.5)	CH_2Cl_2 (0.02 M)	reflux	8	82
15	$BF_3{\cdot}OEt_2$ (0.5)	Toluene (0.02 M)	80	4	53
16	$BF_3{\cdot}OEt_2$ (0.5)	Benzene (0.02 M)	80	4	56
17	$BF_3{\cdot}OEt_2$ (0.5)	CH_3CN (0.02 M)	60	6	25
18	$Sc(OTf)_3$ (0.5)	DCE (0.02 M)	80	6	78
19	$BF_3{\cdot}OEt_2$ (0.25)	DCE (0.02 M)	80	7	82
20	$BF_3{\cdot}OEt_2$ (1.0)	DCE (0.02 M)	80	3	42[c]
21	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.01 M)	80	10	76
22	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.05 M)	80	3	42
23	None	DCE (0.05 M)	80	48	0
24	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	80	4	93[d]
25	$BF_3{\cdot}OEt_2$ (0.5)	DCE (0.02 M)	80	4	94[e]

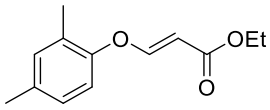
[a]Reaction conditions: **3a** (0.5 mmol), acid(0.125–0.5 mmol), solvent (10–50 mL), 0–80 °C. [b]Isolated yield.
[c]2,4-Dimethylphenol obtained. [d]Pure (*Z*)-**3a** was used. [e]Mixture of (*E*/*Z* = ~4:1)-**3a** was used.

General procedure for synthesis of ethyl 3-aryloxyacrylates, 3a-z



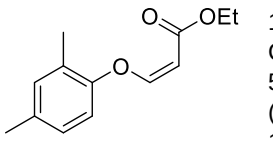
To a stirred solution of phenol **25** (2.0mmol) in dry CH_2Cl_2 (25 mL) was added *N*-methyl morpholine (NMM, 2.2 mmol, 1.1 equiv) at 0 °C. The mixture was stirred for 10 min and thenethylpropiolate (2.2 mmol, 1.1equiv) was added dropwise at 0 °C. The reaction mixture was stirred for additional 6-12 h at room temperature. The reaction progress was monitored by TLC. On complete consumption of the starting material, the reaction mixture was diluted with CH_2Cl_2(20 mL). The organic layer was washed with water (2 × 10 mL), brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (99:1 to 20:1) as an eluent to afford different ethyl3-aryloxyacrylates **3a-z** (~4:1, *E*/*Z*). Except **3a**, in all cases, only the major *E*-isomer was separated (for easy characterization) and used.

Ethyl (*E*)-3-(2,4-dimethylphenoxy)acrylate, *E*-3a



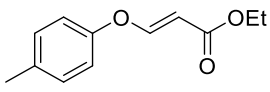
Yield = 343.6 mg, 78%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2982, 2925, 1715, 1649, 1632, 1610, 1593 1498, 1445, 1368, 1314, 1279, 1250, 1220, 1207, 1166, 1131, 1104, 1047, 958, 873, 833, 738, 527 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 12.3 Hz, 1H), 7.05–6.96 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.32 (d, *J* = 12.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 2.19 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.5, 160.5, 151.5, 135.0, 132.1, 128.6, 127.7, 118.5, 100.5, 59.9, 20.7, 15.7, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{16}O_3 + H]^+$ 221.1172, found 221.1170.

Ethyl (*Z*)-3-(2,4-dimethylphenoxy)acrylate, *Z*-3a



Yield = 83.7 mg, 19%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2983, 2959, 1720, 1705, 1647, 1592, 1500, 1413, 1385, 1276, 1249, 1172, 1130, 1081, 1066, 1032, 950, 805, 555 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.01 (s, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.80 (d, *J* = 6.9 Hz, 1H), 5.09 (d, *J* = 6.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 165.0, 155.1, 153.6, 134.2, 131.9, 128.3, 127.4, 116.4, 99.0, 59.8, 20.6, 15.8, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{16}O_3 + H]^+$ 221.1172, found 221.1169.

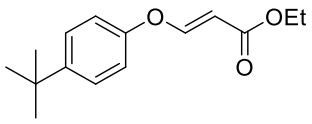
Ethyl (*E*)-3-(*p*-tolyloxy)acrylate, *E*-3b



Yield = 338.2 mg, 82%,colorless oil; **IR** ($CHCl_3$) ν_{max} = 3079, 2980, 1714, 1650, 1608, 1585, 1489, 1460, 1368, 1295, 1250, 1208, 1180, 1149, 1115, 1046, 952, 923, 840, 783, 690 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 12.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.50 (d, *J* = 12.2, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ =

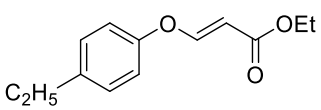
167.3, 159.5, 153.7, 134.5, 130.3, 117.9, 101.6, 59.9, 20.6, 14.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{14}O_3 + Na]^+$ 229.0835, found 229.0851.

Ethyl (*E*)-3-[4-(*tert*-butyl)phenoxy]acrylate, *E*-3c



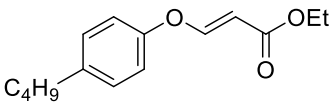
Yield = 412.2 mg, 83%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3042, 2964, 2906, 2871, 1716, 1650, 1632, 1601, 1508, 1464, 1394, 1366, 1280, 1268, 1231, 1175, 1158, 1123, 1103, 1047, 1014, 953, 835, 739, 666, 538 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79 (d, J = 12.2 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 5.51 (d, J = 12.2, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.32 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.4, 159.6, 153.5, 148.0, 126.8, 117.6, 101.6, 60.0, 34.4, 31.4, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{20}O_3 + Na]^+$ 271.1305, found 271.1304.

Ethyl (*E*)-3-(4-ethylphenoxy)acrylate, *E*-3d



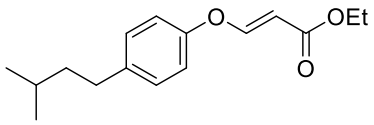
Yield = 365.6 mg, 83%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3040, 2967, 2933, 2873, 1715, 1650, 1634, 1603, 1506, 1463, 1368, 1322, 1284, 1229, 1189, 1171, 1118, 1048, 1016, 953, 835, 694, 540 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.78 (d, J = 12.2 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 5.50 (d, J = 12.2, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.6 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.4, 159.6, 153.8, 141.0, 129.2, 118.0, 101.6, 60.0, 28.1, 15.6, 14.3 ppm; **HRMS** (ESI−TOF) calcd for$[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0995.

Ethyl (*E*)-3-(4-butylphenoxy)acrylate, *E*-3e



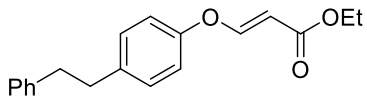
Yield = 377.5 mg, 76%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3040, 2955, 2931, 2859, 1716, 1650, 1632, 1603, 1506, 1466, 1368, 1322, 1284, 1227, 1191, 1171, 1118, 1046, 1015, 953, 836, 768 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 12.2 Hz, 1H), 7.16 (dd, J = 2.0, 8.4 Hz, 2H), 6.97 (dd, J = 2.0, 8.1 Hz, 2H), 5.51 (d, J = 12.2 Hz, 1H), 4.18 (q, J = 7.6 Hz, 2H), 2.59 (t, J = 7.7 Hz, 2H), 1.62–1.54 (m, 2H), 1.39–1.29 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.3, 159.6, 153.8, 139.7, 129.7, 117.9, 101.6, 60.0, 34.9, 33.6, 22.2, 14.3, 13.9 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{20}O_3 + Na]^+$ 271.1305, found 271.1304.

Ethyl (*E*)-3-(4-isopentylphenoxy)acrylate, *E*-3f



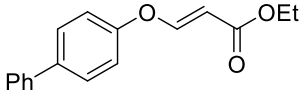
Yield = 398.8 mg, 76%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3037, 2956, 2932, 2869, 1715, 1651, 1632, 1603, 1506, 1467, 1385, 1368, 1321, 1283, 1227, 1190, 1170, 1153, 1116, 1047, 1016, 953, 838 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.78 (d, J = 12.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 5.51 (d, J = 12.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.59 (t, J = 8.0 Hz, 2H), 1.60 (sept, J = 6.6 Hz, 1H), 1.54 –148 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 0.93 (d, J = 6.6 Hz, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 159.6, 153.8, 139.9, 129.6, 117.9, 101.6, 60.0, 40.8, 33.0, 27.6, 22.5, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{16}H_{22}O_3 + Na]^+$ 285.1461, found 285.1463.

Ethyl (*E*)-3-(4-phenylethylphenoxy)acrylate, *E*-3g



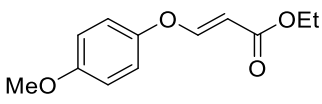
Yield = 426.8 mg, 72%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3064, 3028, 2982, 2930, 2859, 1713, 1650, 1630, 1603, 1505, 1454, 1368, 1318, 1288, 1228, 1191, 1172, 1118, 1046, 1019, 952, 837, 749, 699, 522 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (d, J = 12.2 Hz, 1H), 7.32–7.27 (m, 2H), 7.23–7.14 (m, 5H), 7.01 (d, J = 8.5 Hz, 2H), 5.53 (d, J = 12.2, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.95–2.89 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 159.4, 154.0, 141.3, 138.5, 129.8, 128.4, 128.3, 126.0, 117.9, 101.7, 60.0, 37.9, 37.1, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{20}O_3 + H]^+$ 297.1485, found 297.1489.

Ethyl (*E*)-3-([1,1'-biphenyl]-4-yloxy)acrylate, *E*-3h



Yield = 434.7 mg, 81%, white solid, **M.P.** 74–76 °C, lit.[1] 74–76 °C; **IR** ($CHCl_3$) ν_{max} = 3083, 2993, 2908, 1712, 1651, 1601, 1519, 1487, 1452, 1408, 1369, 1329, 1309, 1241, 1191, 1177, 1127, 1034, 1005, 952, 839, 838, 769, 717, 696, 485 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (d, J = 12.2 Hz, 1H), 7.62–7.53 (m, 4H), 7.45 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 8.7 Hz, 2H), 5.61 (d, J = 12.1, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.2, 158.9, 155.2, 140.0, 138.1, 128.8, 128.6, 127.4, 126.9, 118.3, 102.3, 60.1, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{16}O_3 + Na]^+$ 291.0992, found 291.0989

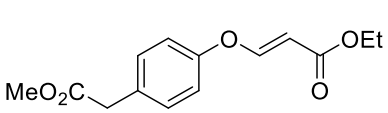
Ethyl (*E*)-3-(4-methoxyphenoxy)acrylate, *E*-3i



Yield = 324.5 mg, 73%, light yellow oil; **IR** ($CHCl_3$) ν_{max} = 2961, 2928, 2844, 1715, 1649, 1630, 1601, 1505, 1464, 1442, 1369, 1324, 1285, 1225, 1188, 1119, 1037, 954, 831, 700, 509 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 12.3 Hz, 1H), 6.99 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 5.43 (d, J = 12.2, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.27 (t, J = 7.1

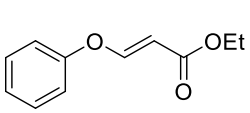
Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.4, 160.3, 156.8, 149.5, 119.4, 114.9, 101.2, 60.0, 55.6, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{14}O_4 + Na]^+$ 245.0784, found 245.0785.

Ethyl (*E*)-3-[4-(2-methoxy-2-oxoethyl)phenoxy]acrylate, *E*-3j



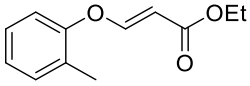
Yield = 359.4 mg, 68%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2983, 2955, 1742, 1711, 1651, 1634, 1605, 1507, 1436, 1369, 1320, 1230, 1192, 1173, 1118, 1046, 1017, 953, 838 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 12.3 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.01 (dd, J = 1.7, 8.3 Hz, 2H), 5.53 (d, J = 12.3, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.68 (s, 3H), 3.60 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 171.7, 167.1, 158.9, 154.9, 130.8, 130.6, 118.1, 102.2, 60.0, 52.0, 40.2, 14.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{14}H_{16}O_5 + Na]^+$ 287.0890, found 287.0888.

Ethyl (*E*)-3-phenoxyacrylate, *E*-3k



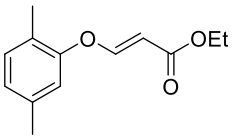
Yield = 303.7 mg, 79%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3078, 2980, 2903, 1713, 1651, 1631, 1588, 1489, 1367, 1320, 1284, 1226, 1187, 1168, 1118, 1153, 1045, 1002, 951, 898, 836, 691, 597, 494 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.79 (d, J = 12.2 Hz, 1H), 7.37 (t, J = 8.0, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.9 Hz, 2H), 5.55 (d, J = 12.2, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.2, 159.0, 155.8, 129.9, 124.9, 118.1, 102.1, 60.1, 14.3 ppm.

Ethyl (*E*)-3-(*o*-tolyloxy)acrylate, *E*-3l



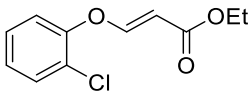
Yield = 338.2 mg, 82%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2980, 2916, 1713, 1650, 1614, 1590, 1467, 1451, 1367, 1288, 1207, 1183, 1145, 1115, 1046, 947, 840, 688 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.76 (d, J = 12.3 Hz, 1H), 7.18–7.22 (m, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 5.36 (d, J = 12.3, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.35 (s, 3 H), 1.27 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ =167.3, 160.0, 153.7, 131.5, 128.9, 127.3, 125.3, 118.5, 101.0, 60.0, 15.8, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{14}O_3 + H]^+$ 207.1016, found 207.1018.

Ethyl (*E*)-3-(2,5-dimethylphenoxy)acrylate, *E*-3m



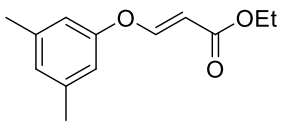
Yield = 339.2 mg, 77%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2979, 2926, 1713, 1649, 1632, 1619, 1578, 1510, 1461, 1408, 1367, 1315, 1278, 1248, 1208, 1174, 1149, 1128, 1103, 1046, 956, 838, 812, 738, 709, 446 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 12.3 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.80 (s, 1H), 5.36 (d, J = 12.3, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.4, 160.1, 153.5, 137.4, 131.2, 126.0, 125.5, 119.1, 100.7, 59.9, 20.9, 15.3, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0990.

Ethyl (l)-3-(2-chlorophenoxy)acrylate, *E*-3n



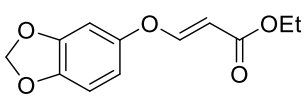
Yield = 344.5 mg, 76%,colorless oil; **IR** ($CHCl_3$) ν_{max} = 3091, 2981, 2934, 1713, 1650, 1631, 1589, 1551, 1486, 1445, 1368, 1323, 1294, 1274, 1232, 1187, 1166, 1118, 1091, 1046, 1011, 949, 828, 652, 497 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43 (d, J = 12.3 Hz, 1H), 7.38−7.29 (m, 2H), 7.07−6.95 (m, 2H), 5.55 (d, J = 12.2, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 166.9, 158.4, 154.3, 130.2, 130.0, 119.4, 102.8, 60.2, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{11}H_{11}O_3Cl + Na]^+$ 249.0289, found 249.0284.

Ethyl (*E*)-3-(3,5-dimethylphenoxy)acrylate, *E*-3o



Yield = 343.6 mg, 78%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2980, 2921, 1713, 1650, 1630, 1614, 1589, 1468, 1368, 1313, 1288, 1239, 1208, 1184, 1144, 1115, 1046, 998, 947, 840, 689, 638 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.77 (d, J = 12.2 Hz, 1H), 6.81 (s, 1H), 6.68 (s, 2H), 5.52 (d, J = 12.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.30 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.4, 159.3, 155.9, 139.9, 126.6, 115.6, 101.7, 60.0, 21.2, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0990.

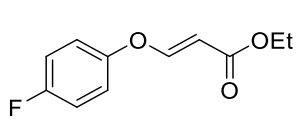
Ethyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yloxy)acrylate, *E*-3p



Yield = 401.6 mg, 85%, light yellow oil; **IR** ($CHCl_3$) ν_{max} = 3083, 2983, 2903, 2780, 1713, 1651, 1628, 1503, 1484, 1447, 1395, 1369, 1321, 1251, 1179, 1136, 1086, 1038, 941, 927, 845, 815, 738, 649, 607, 549, 468 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, J = 12.3 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.50 (dd, J = 2.4, 8.4 Hz, 1H), 5.97 (s, 2H), 5.45 (d, J = 12.4 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.2, 159.9, 150.5,

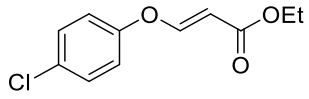
148.4, 144.8, 110.7, 108.2, 101.8, 101.5, 101.0, 60.0, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{12}O_5 + Na]^+$ 259.0577, found 259.0577.

Ethyl (*E*)-3-(4-fluorophenoxy)acrylate, *E*-3q



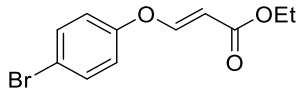
Yield = 353.1 mg, 84%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3080, 2983, 2925, 2898, 1714, 1651, 1632, 1610, 1598, 1503, 1446, 1390, 1369, 1324, 1282, 1244, 1212, 1200, 1184, 1159, 1118, 1047, 953, 835, 776, 700, 506 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 12.2 Hz, 1H), 7.07–6.99 (m, 4H), 5.48 (d, J = 12.2, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.0, 160.9, 159.3, 158.4, 151.7 and 151.65 ($J_{C\text{-}F}$ = 2.7 Hz), 119.7 and 119.64 ($J_{C\text{-}F}$ = 8.6 Hz), 116.6 and 116.4 ($J_{C\text{-}F}$ = 23.7 Hz), 102.1, 60.1, 14.2 ppm; **^{19}F NMR** (470 MHz, $CDCl_3$/TMS) δ = –117.7 ppm; **HRMS** (ESI−TOF)calcd for $[C_{11}H_{11}FO_3 + H]^+$ 211.0765, found 211.0766.

Ethyl (*E*)-3-(4-chlorophenoxy)acrylate, *E*-3r



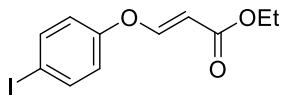
Yield = 367.2 mg, 81%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3091, 2981, 2932, 1884, 1713, 1650, 1589, 1486, 1368, 1322, 1298, 1275, 1232, 1188, 1117, 1092, 1047, 1011, 949, 832, 722, 652, 497 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 12.2 Hz, 1H), 7.67 (dd, J = 1.0, 8.2 Hz, 2H), 6.84 (dd, J = 0.9, 8.1 Hz, 2H), 5.53 (d, J = 12.2, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (q, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 166.9, 158.4, 154.3, 130.2, 129.9, 119.4, 102.7, 60.2, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{11}H_{11}O_3Cl + Na]^+$ 249.0289, found 249.0289.

Ethyl (*E*)-3-(4-bromophenoxy)acrylate, *E*-3s



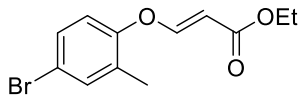
Yield = 422.9 mg, 78%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3083, 2980, 1713, 1653, 1631, 1579, 1473, 1443, 1367, 1314, 1232, 1189, 1130, 1109, 1046, 949, 836, 656 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 12.2 Hz, 1H), 7.48 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 5.54 (d, J = 12.2, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.28 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 166.9, 158.3, 154.8, 132.9, 119.8, 117.7, 102.8, 60.2, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{11}H_{11}O_3Br + Na]^+$ 292.9784, found 292.9784.

Ethyl (*E*)-3-(4-iodophenoxy)acrylate, *E*-3t



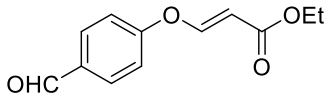
Yield = 483.5 mg, 76%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3088, 2980, 1713, 1652, 1634, 1579, 1482, 1397, 1369, 1322, 1296, 1231, 1189, 1172, 1156, 1117, 1057, 1007, 949, 838, 822, 736, 618, 542, 495 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, J = 12.2 Hz, 1H), 7.67 (dd, J = 1.2, 8.2 Hz, 2H), 6.84 (dd, J = 0.9, 8.0 Hz, 2H), 5.56 (d, J = 12.2, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.28 (q, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.9, 158.1, 155.7, 138.9, 120.1, 103.0, 88.3, 60.2, 14.3 ppm; **HRMS** (ESI−TOF) calcd for$[C_{11}H_{11}IO_3 + Na]^+$ 340.9645, found 340.9649.

Ethyl (*E*)-3-(4-bromo-2-methylphenoxy)acrylate, *E*-3u



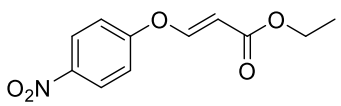
Yield = 393.5 mg, 69%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2979, 2930, 1713, 1649, 1628, 1482, 1366, 1319, 1278, 1234, 1176, 1129, 1045, 955, 815, 634 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.70 (d, J = 12.3 Hz, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.32 (dd, J = 2.4, 8.4 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 5.37 (d, J = 12.3 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.21 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.1, 159.3 152.7, 134.2, 131.3, 130.2, 120.1, 118.0, 101.6, 60.1, 15.7, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{13}BrO_3 + Na]^+$ 306.9940, found 306.9940.

Ethyl (*E*)-3-(4-formylphenoxy)acrylate, *E*-3v



Yield = 295.1 mg, 67%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2987, 1706, 1655, 1622, 1601, 1588, 1507, 1431, 1369, 1331, 1297, 1256, 1232, 1190, 1166, 1121, 1037, 954, 912, 856, 830, 810, 736, 619, 504 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.95 (s, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 12.1 Hz, 1H), 7.20 (d, J = 8.6 Hz, 2H), 5.70 (d, J = 12.1, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.28 (q, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 190.5, 166.6, 160.2, 156.4, 133.0, 132.0, 117.8, 104.6, 60.4, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{12}H_{12}O_4 + K]^+$ 259.0367, found 259.0369.

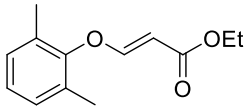
Ethyl (*E*)-3-(4-nitrophenoxy)acrylate, *E*-3w



Yield = 303.6 mg, 64%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3081, 2989, 1706, 1657, 1612, 1591, 1513, 1494, 1371, 1343, 1324, 1250, 1193, 1174, 1115, 952, 866, 848, 686, 649, 495 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.27 (d, J = 8.9 Hz, 2H), 7.75 (d, J = 12.1 Hz, 1H), 7.19 (d, J = 8.9 Hz, 2H), 5.75 (d, J = 12.1, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.30 (q, J = 7.1 Hz, 3H)

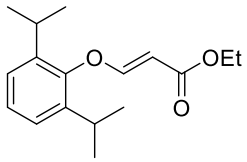
ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.3, 160.2, 155.7, 144.3, 126.0, 117.6, 105.4, 60.5, 14.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{11}H_{11}NO_5 + H]^+$ 238.0710, found 238.0710.

Ethyl (*E*)-3-(2,6-dimethylphenoxy)acrylate, *E*-3x



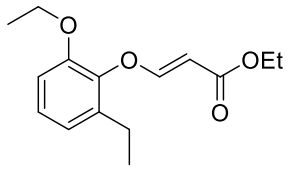
Yield = 312.8 mg, 71%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2983, 2959, 1715, 1631, 1588, 1475, 1444, 1368, 1313, 1279, 1264, 1223, 1188, 1176, 1152, 1121, 1084, 1047, 967, 836, 812, 775, 739 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$)δ = 7.74 (d, *J* = 12.4 Hz, 1H), 7.08−7.02 (m, 3H), 5.00 (d, *J* = 12.5, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.18 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.5, 160.5, 151.0, 129.9, 129.1, 125.9, 98.7, 59.9, 16.0, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0993.

Ethyl (*E*)-3-(2,6-diisopropyphenoxy)acrylate, 3y



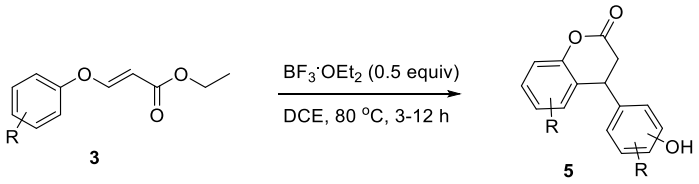
Yield = 370.4 mg, 67%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2967, 2928, 1716, 1642, 1629, 1465, 1445, 1367, 1333, 1315, 1279, 1249, 1219, 1186, 1155, 1121, 1046, 967, 837, 797, 781, 762, 666 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$)δ = 7.76 (d, *J* = 12.4 Hz, 1H), 7.24–7.12 (m, 3H), 5.09 (d, *J* = 12.4, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.05 (sept, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 12H), ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.5, 162.2, 149.1, 140.3, 126.5, 124.4, 99.2, 59.9, 26.9, 23.4, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{24}O_3 + Na]^+$ 299.1618, found 299.1617.

Ethyl (*E*)-3-(2-ethoxy-6-ethylphenoxy)acrylate, *E*-3z



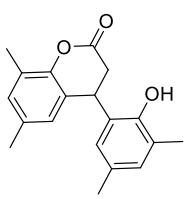
Yield = 375.3 mg, 71%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 2980, 2933, 1714, 1645, 1632, 1582, 1471, 1394, 1369, 1312, 1279, 1191, 1223, 1044, 952, 670 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 12.4 Hz, 1H), 7.09 (t, *J* = 8.1 Hz, 1H), 6.85–6.78 (m, 2H), 5.21 (d, *J* = 12.3, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 2.57 (q, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.7, 162.1, 150.2, 141.9, 137.3, 126.1, 121.2, 111.4, 98.9, 64.4, 59.8, 23.0, 14.7, 14.5, 14.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{20}O_4 + Na]^+$ 287.1254, found 287.1255.

General procedure for synthesis of 4-arylchroman-2-ones (5).



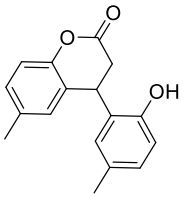
To a stirred solution of ethyl (*E*)-3-aryloxyacrylate **3** or *E*/*Z* mixture-**3** (1.0mmol) in dry $ClCH_2CH_2Cl$ (DCE, 50 mL, 0.02M) was added drop wise $BF_3{\cdot}OEt_2$ (46% solution, 0.5 mmol, 0.5 equiv) at room temperature. The mixture was stirred for 10 min and then stirred for additional 3-12 h at 80 °C. The reaction progress was monitored by TLC. On complete consumption of starting material, the mixture was quenched with sat. aqueous solution of $NaHCO_3$ (15 mL), stirred vigorously till two clear layers were formed. The aqueous layer was then extracted with CH_2Cl_2 (2 ×20 mL) and the combined organic layers were washed with water (10 mL), dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (17:3 to 7:3) as an eluent to afford 4-arylchroman-2-ones **5**. For **5j**, the reaction was carried out at room temperature for 3 d.

4-(2-Hydroxy-3,5-dimethylphenyl)-6,8-dimethylchroman-2-one, 5a



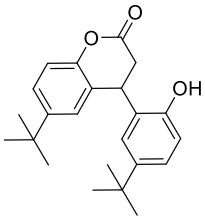
Yield = 139.3 mg, 94%, white solid, **M.P**. 210–212°C; **IR** ($CHCl_3$) ν_{max} = 3425, 2983, 2921, 1748, 1601, 1482, 1446, 1418, 1334, 1298, 1254, 1222, 1190, 1158, 1140, 1029, 906, 858, 789, 741, 652 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.96 (s, 1H), 6.85 (s, 1H), 6.68 (s, 1H), 6.48 (s, 1H), 4.77 (br s, 1H), 4.59 (t, *J* = 6.4 Hz, 1H), 3.14 (dd, *J* = 6.6, 15.6 Hz, 1H), 2.94 (dd, *J* = 6.4, 15.9 Hz, 1H), 2.33 (s, 3H),2.23 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.9, 149.1, 148.2, 133.6, 130.8, 130.6, 130.0, 126.9, 126.5, 126.0, 125.9, 124.5, 122.8, 35.6, 35.3, 20.7, 20.5, 15.8, 15.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{20}O_3 + Na]^+$ 319.1305, found 319.1306.

4-(2-Hydroxy-5-methylphenyl)-6-methylchroman-2-one, 5b



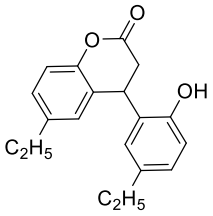
Yield = 124.8 mg, 93%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3386, 3020, 2922, 1743, 1611, 1509, 1494, 1414, 1341, 1255, 1201, 1161, 1095, 1042, 978, 929, 816 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.10 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.90 (d, J = 7.9 Hz,1H), 6.86 (s, 1H), 6.64 (d, J = 8.1Hz, 1H), 6.59 (s, 1H), 5.38 (br s, 1H), 4.60(t, J = 6.2 Hz, 1H), 3.18 (dd, J = 6.1, 16.0 Hz, 1H), 2.97 (dd, J = 6.5, 16.0 Hz, 1H), 2.18 (s, 3H), 2.27 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.1, 150.8, 149.9, 134.4, 130.4, 129.2, 129.1, 129.0, 128.7, 126.6, 124.6, 116.7, 115.6, 35.3, 35.26, 20.8, 20.6 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{16}O_3 + Na]^+$ 291.0992, found 291.0994.

4-(5-*tert*-Butyl-2-hydroxyphenyl)-6-*tert*-butylchroman-2-one, 5c



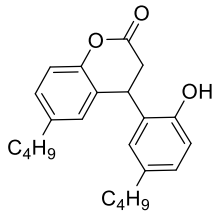
Yield = 155.1 mg, 88%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3398, 2962, 2906, 2871, 1748, 1611, 1509, 1497, 1462, 1416, 1365, 1340, 1272, 1223, 1178, 1150, 1124, 1091, 986, 927, 890, 823, 668 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 (dd, J = 2.2, 8.5 Hz, 1H), 7.11–7.07 (m, 3H), 6.79 (d, J = 2.2 Hz,1H), 6.66 (d, J = 8.3Hz, 1H), 5.50 (br s, 1H), 4.69 (t, J = 6.4 Hz, 1H), 3.19 (dd, J = 6.4, 16.1 Hz, 1H), 3.01 (dd, J = 6.4, 16.1 Hz, 1H), 1.25 (s, 9H), 1.17 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.3, 150.9, 149.9, 147.7, 143.8, 126.2, 125.6, 125.5, 125.3, 125.2, 124.2, 116.4, 115.1, 35.6, 35.5, 34.4, 34.1, 31.4, 31.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{23}H_{28}O_3 + Na]^+$ 375.1931, found 375.1928.

4-(5-Ethyl-2-hydroxyphenyl)-6-ethylchroman-2-one, 5d



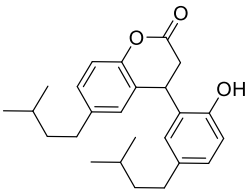
Yield = 128.9 mg, 87%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3400, 3013, 2963, 2932, 2868, 1744, 1614, 1510, 1495, 1424, 1377, 1341, 1251, 1202, 1160, 1099, 1056, 1017, 963, 924, 824, 668, 491 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 (dd, J = 1.8, 8.3 Hz, 1H), 7.06 (d, J = 8.3 Hz, 1H), 6.94–6.88 (m, 2H), 6.67 (d, J = 8.1 Hz,1H), 6.60 (d, J = 1.7 Hz, 1H), 6.09 (brs, 1H), 4.64 (t, J = 6.2 Hz, 1H), 3.19 (dd, J = 5.6, 16.1 Hz, 1H), 2.98 (dd, J = 6.6, 16.0 Hz, 1H), 2.57 (q, J = 7.6 Hz, 2H), 2.47 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H), 1.11 (t, J = 7.6 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.6, 151.2, 150.0, 140.8, 136.6, 127.9, 127.8, 127.7, 127.6, 126.5, 124.6, 116.7, 115.5, 35.3 (2C), 28.1, 27.9, 15.7, 15.6 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{20}O_3 + Na]^+$ 319.1305, found 319.1307.

4-(5-Butyl-2-hydroxyphenyl)-6-butylchroman-2-one, 5e



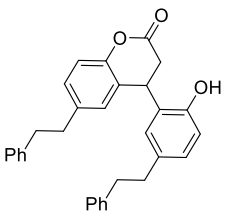
Yield = 137.5 mg, 78%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3385, 2955, 2929, 2857, 1745, 1613, 1510, 1494, 1464, 1435, 1378, 1340, 1258, 1199, 1160, 1098, 898, 823, 490 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.11 (dd, J = 2.0, 8.3 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 6.91 (dd, J = 2.1, 8.1 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 6.65 (d, J = 8.1 Hz,1H), 6.59 (d, J = 2.4 Hz,1H), 4.63 (t, J = 6.4 Hz, 1H), 3.18 (dd, J = 6.5, 16.0 Hz, 1H), 2.99 (dd, J = 6.5, 16.0 Hz, 1H), 2.52 (t, J = 7.7 Hz, 2H), 2.43 (t, J = 7.7 Hz, 2H), 1.56–1.42 (m, 4H), 1.35–1.21 (m, 4H), 0.92–0.84 (m, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.3, 151.1, 150.1, 139.4, 135.4, 128.5, 128.3, 128.1, 126.5, 124.6, 116.7, 115.5, 35.4, 35.3, 34.9, 34.7, 33.7, 33.6, 22.2, 22.16, 13.9 (2C) ppm; **HRMS** (ESI−TOF) calcd for $[C_{23}H_{28}O_3 + Na]^+$ 375.1931, found 375.1933.

4-(2-Hydroxy-5-isopentylphenyl)-6-isopentylchroman-2-one, 5f



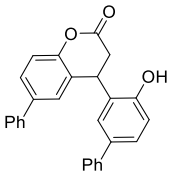
Yield = 137 mg, 72%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3385, 3023, 2959, 2929, 2871, 1745, 1610, 1508, 1494, 1437, 1351, 1258, 1199, 1160, 1100, 927, 823 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.11 (dd, J = 2.0, 8.3 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.93 (dd, J = 2.0, 8.2 Hz, 1H), 6.86 (d, J = 1.7 Hz, 1H), 6.67(d, J = 8.2 Hz, 1H), 6.61 (d, J = 2.1 Hz,1H), 5.15 (brs, 1H), 4.63 (t, J = 6.5 Hz, 1H), 3.17 (dd, J = 6.6, 16.0 Hz, 1H), 2.98 (dd, J = 6.3, 16.0 Hz, 1H), 2.52 (t, J = 8.2 Hz, 2H), 2.44 (t, J = 8.1 Hz, 2H), 1.60–1.33 (m, 6H), 0.91–0.85 (m, 12H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.0, 151.0, 150.1, 139.6, 135.8, 128.5, 128.4, 128.3, 128.0, 126.5, 124.6, 116.8, 115.6, 40.8, 35.34, 35.3, 33.1, 32.8, 27.6, 27.5, 22.5, 22.47, 22.4 ppm; **HRMS** (ESI−TOF) calcd for $[C_{25}H_{32}O_3 + Na]^+$ 403.2244, found 403.2242.

4-(2-Hydroxy-5-phenethylphenyl)-6-phenethylchroman-2-one, 5g



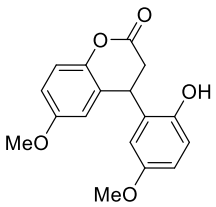
Yield = 163.7 mg, 73%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3377, 3027, 2929, 2857, 1744, 1603, 1512, 1495, 1454, 1435, 1339, 1259, 1199, 1160, 1095, 818, 699 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30–7.23 (m, 4H), 7.23–7.05 (m, 8H), 6.90 (dd, J = 2.1, 8.1 Hz,1H), 6.86 (d, J = 1.8 Hz, 1H), 6.65 (d, J = 8.1 Hz,1H), 6.58 (d, J = 2.1 Hz, 1H), 5.83 (brs, 1H), 4.63 (t, J = 6.3 Hz, 1H), 3.20 (dd, J = 6.2, 16.2 Hz, 1H), 2.97 (dd, J = 6.6, 16.1 Hz, 1H), 2.91–2.85 (m, 4H), 2.85–2.75 (m, 4H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.6, 151.4, 150.1, 141.5, 141.3, 138.2, 134.1, 128.6, 128.5, 128.4, 128.37, 128.3, 128.2, 128.18, 126.4, 125.9, 125.8, 124.6, 116.8, 115.6, 37.8, 37.7, 37.0, 36.8, 35.4, 35.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{31}H_{28}O_3 + Na]^+$ 471.1931, found 471.1932.

4-(5-Phenyl-2-hydroxyphenyl)-6-phenylchroman-2-one, 5h



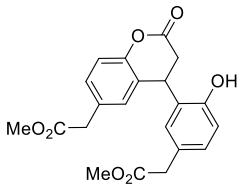
Yield = 164.8 mg, 84%, white solid, M.P. 232–233 °C; **IR** ($CHCl_3$) ν_{max} = 3331, 3057, 3024, 2923, 1727, 1606, 1515, 1479, 1451, 1406, 1334, 1276, 1239, 1211, 1165, 1146, 1100, 1020, 901, 825, 814, 732, 644, 564, 530, 495 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 2.2, 8.5 Hz, 1H),7.51–7.46 (m, 2H),7.44–7.21 (m, 11H), 7.09 (d, *J* = 2.2, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.86 (br s, 1H),4.80 (t, *J* = 6.2 Hz, 1H), 3.32 (dd, *J* = 5.8, 16.0 Hz, 1H), 2.99 (dd, *J* = 6.6, 16.1 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.9, 152.7, 151.5, 140.4, 140.0, 138.0, 134.4, 128.8, 128.7, 127.5, 127.4, 127.3, 127.03, 127.0, 126.8, 126.7, 125.0, 117.5, 116.1, 35.8, 35.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{27}H_{20}O_3 + Na]^+$ 415.1305, found 415.1307.

4-(2-Hydroxy-5-methoxyphenyl)-6-methoxychroman-2-one, 5i



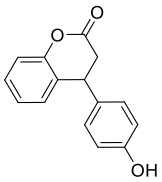
Yield = 111.1 mg, 74%, light yellow semi-solid; **IR** ($CHCl_3$) ν_{max} = 3395, 2935, 2835, 1754, 1592, 1546, 1508, 1494, 1466, 1430, 1342, 1278, 1198, 1038, 985, 907, 873, 813, 733, 607 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.06 (d, *J* = 8.9 Hz, 1H), 6.83 (dd, *J* = 3.0, 8.9 Hz, 1H), 6.68–6.60 (m, 3H), 6.35 (d, *J* = 2.9 Hz, 1H), 4.60(t, *J* = 6.3 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.18 (dd, *J* = 6.1, 16.1 Hz, 1H), 2.97 (dd, *J* = 6.4, 16.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.2, 156.4, 153.7, 147.2, 145.9, 127.6, 125.7, 117.8, 116.3, 114.7, 113.9, 113.3, 113.1, 55.64, 55.6, 35.7, 35.0 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{16}O_5 + Na]^+$ 323.0890, found 323.0895.

Methyl 2-(4-hydroxy-3-[6-(2-methoxy-2-oxoethyl)-2-oxochroman-4-yl]phenylacetate, 5j



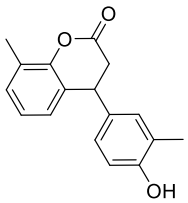
Yield = 84.6 mg, 44%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3389, 3021, 2959, 1736, 1612, 1513, 1495, 1438, 1347, 1254, 1200, 1161, 1041, 933, 825 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$)δ = 7.21 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 2.2, 8.3 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 4.61 (t, *J* = 6.6 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.55 (s, 2H), 3.47 (s, 2H), 3.15 (dd, *J* = 6.6, 16.1 Hz, 1H), 2.96 (dd, *J* = 6.6, 16.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 172.4, 172.0, 168.4, 152.5, 151.1, 130.3, 129.6, 129.5, 129.2, 126.8, 126.4, 124.9, 117.2, 116.0, 52.1, 52.0, 40.3, 40.2, 35.5, 35.0 ppm; **HRMS** (ESI−TOF) calcd for $[C_{21}H_{20}O_7 + Na]^+$ 407.1101, found 407.1106.

4-(4-Hydroxyphenyl)chroman-2-one, 5k



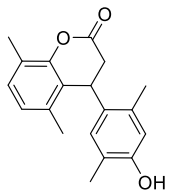
Yield = 64.9 mg, 54%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3386, 3020, 2916, 1763, 1611, 1594, 1514, 1484, 1455, 1344, 1280, 1221, 1176, 1140, 1104, 969, 919, 883, 835 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$)δ = 7.29 (td, *J* = 1.3, 7.1 Hz, 1H), 7.12–7.07 (m, 2H), 7.01–6.97 (m, 3H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.89 (br s, 1H), 4.28 (t, *J* = 6.7 Hz, 1H), 3.07–2.97 (m, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.5, 155.2, 151.5, 132.0, 128.7, 128.66, 128.3, 126.1, 124.8, 117.1, 115.9, 39.8, 37.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{12}O_3 + Na]^+$ 263.0679, found 263.0675.

4-(4-Hydroxy-3-methylphenyl)-8-methylchroman-2-one, 5l



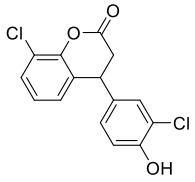
Yield = 80.5 mg, 60%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3403, 3025, 2979, 2923, 1741, 1623, 1584, 1502, 1460, 1414, 1377, 1343, 1276, 1241, 1147, 1024, 964, 864, 817, 597 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.83–6.80 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 5.37 (br s, 1H), 4.22 (t, *J* = 6.7 Hz, 1H), 3.04–2.95 (m, 2H), 2.35 (s, 3H), 2.21(s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.5, 155.4, 149.8, 132.2, 130.1, 130.0, 126.4, 126.04, 126.0, 125.8, 124.6, 124.1, 115.3, 40.0, 37.1, 15.9, 15.8 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{16}O_3 + Na]^+$ 291.0992, found 291.0991.

4-(4-Hydroxy-2,5-dimethylphenyl)-5,8-dimethylchroman-2-one, 5m



Yield = 71.1 mg, 48%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3365, 2920, 1726, 1590, 1407, 1285, 1245, 1128, 1156, 1073, 881, 802, 600 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 6.31 (s,1H), 4.45 (d, *J* = 6.0 Hz, 1H), 2.96 (dd, *J* = 7.2, 15.3 Hz, 1H), 2.84 (dd, *J* = 1.4, 15.3 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 167.9, 152.8, 150.8, 133.9, 133.7, 129.9, 129.8, 128.9, 125.8, 123.9, 123.7, 121.6, 117.4, 36.2, 34.2, 18.8, 18.3, 15.8, 15.4 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{20}O_3 + Na]^+$ 319.1305, found 319.1305.

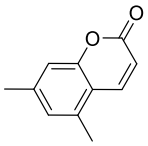
4-(3-Chloro-4-hydroxyphenyl)-8-chlororochroman-2-one, 5n



Yield = 85 mg, 55%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3447, 2920, 2854, 1774, 1497, 1480, 1423, 1338, 1277, 1228, 1177, 1111, 1085, 1024, 1003, 877, 822, 762, 641cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.29 (dd, *J* = 2.5, 6.2 Hz, 1H), 7.15–7.06 (m, 2H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.79 (d, *J* = 2.5 Hz,1H), 6.70 (d, *J* = 8.6 Hz, 1H), 5.41 (brs, 1H), 4.60 (t, *J* = 6.5 Hz, 1H), 3.18 (dd, *J* = 6.5, 16.1 Hz, 1H), 2.99 (dd, *J* = 6.5, 16.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$ + DMSO-d_6) δ = 167.3, 153.5, 150.3, 129.5, 128.5, 128.0, 127.9,

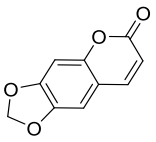
127.6, 126.3, 124.2, 118.2, 117.0, 35.4, 34.2 ppm; **HRMS** (ESI−TOF)calcd for $[C_{15}H_{10}Cl_2O_3 + Na]^+$ 330.9899, found 330.9898.

5,7-Dimethyl-2H-chromen-2-one, 5o



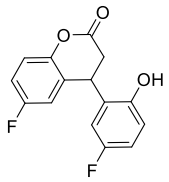
Yield = 99.3 mg, 57%, white solid, **M.P**. 132–134 °C, lit.[2] 132 °C; **IR** ($CHCl_3$) ν_{max} = 2972, 2923, 1722, 1618, 1451, 1380, 1298, 1242, 1198, 1143, 1121, 1067, 1028, 896, 880, 846, 824, 723, 587 cm^{-1};**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.86 (d, J = 9.8 Hz, 1H), 6.97 (s, 1H), 6.92 (s, 1H), 6.34 (d, J = 9.7 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 161.1, 154.7, 142.7, 140.4, 135.6, 127.0, 115.3, 115.0, 114.7, 21.6, 18.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{11}H_{10}O_2 + Na]^+$ 197.0573, found 197.0520.

6*H*-[1,3]Dioxolo[4,5-*g*]chromen-6-one, 5p



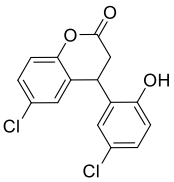
Yield = 136.9 mg, 72%, light green solid, **M.P**. 222–224 °C, lit.[3] 222–223 °C; **IR** ($CHCl_3$) ν_{max} = 3055, 2920, 2852, 1706, 1684, 1626, 1581, 1499, 1455, 1419, 1383, 1258, 1151, 1039, 941, 881, 837, 752, 732 cm^{-1};**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.58 (d, J = 9.5 Hz,1H), 6.83 (d, J = 1.8 Hz, 2H), 6.27 (d, J = 9.4 Hz, 1H), 6.07 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.2, 151.23, 151.2, 144.9, 143.5, 113.4, 112.7, 105.0, 102.3, 98.4 ppm; **HRMS** (ESI−TOF) calcd for $[C_{10}H_6O_4 + Na]^+$ 213.0158, found 213.0157.

4-(5-Fluoro-2-hydroxyphenyl)-6-fluorochroman-2-one, 5q



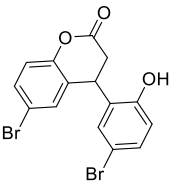
Yield = 98.1 mg, 71%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3393, 2923, 2854, 1750, 1508, 1490, 1438, 1340, 1264, 1184, 1141, 1080, 986, 906, 875, 817, 791, 598 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.15–7.09 (m, 1H), 7.02 (td, J = 2.7, 8.6 Hz, 1H), 6.87–6.75 (m, 2H), 6.70 (dd, J = 2.2, 8.8 Hz, 1H), 6.51 (dd, J = 2.9, 9.0 Hz, 1H),5.51 (brs, 1H), 4.63 (t, J = 6.4 Hz, 1H), 3.17 (dd, J = 6.6, 16.1 Hz, 1H), 2.99 (dd, J = 6.4, 16.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.3, 160.3, 158.3 and 158.0($J_{C\text{-}F}$ = 43.3 Hz), 156.1, 149.23 and 149.21 ($J_{C\text{-}F}$ = 2.4 Hz), 147.9, 127.4 and 127.3($J_{C\text{-}F}$ = 6.9 Hz), 126.0 and 125.9 ($J_{C\text{-}F}$ = 7.6 Hz), 118.55 and 118.48 ($J_{C\text{-}F}$ = 8.4 Hz), 116.51 and 116.45 ($J_{C\text{-}F}$ = 8.1 Hz), 115.85 and 115.66 ($J_{C\text{-}F}$ = 23.6 Hz), 115.3, 115.20 and 115.15 ($J_{C\text{-}F}$ = 6.4 Hz), 115.0 and 114.9 ($J_{C\text{-}F}$ = 9 Hz), 114.8, 35.4, 34.5 ppm; **^{19}F NMR** (470 MHz, $CDCl_3$/TMS) δ = –117.3, –122.5; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{10}F_2O_3 + H]^+$ 277.0671, found 277.0672.

4-(5-Chloro-2-hydroxyphenyl)-6-chlororochroman-2-one, 5r



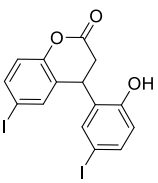
Yield = 98.9 mg, 64%, white solid, **M.P**. 282–284 °C; **IR** ($CHCl_3$) ν_{max} = 3477, 3079, 2916, 2847, 1774, 1499, 1480, 1424, 1342, 1277, 1227, 1177, 1114, 1085, 1050, 1025, 1003, 878, 822, 762, 641cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.22 (dd, J = 2.4, 8.7 Hz, 1H), 7.06–7.00 (m, 2H), 6.98 (d, J = 2.3 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 4.54 (t, J = 6.6 Hz, 1H), 3.14 (dd, J = 6.8, 16.2 Hz, 1H), 2.92 (dd, J = 6.6, 16.2 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.4, 153.4, 150.3, 129.5, 128.6, 128.04 128.0, 127.6, 126.2, 124.3, 118.3, 117.1, 35.5, 34.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{10}Cl_2O_3 + Na]^+$ 330.9899, found 330.9889.

4-(5-Bromo-2-hydroxyphenyl)-6-bromochroman-2-one, 5s



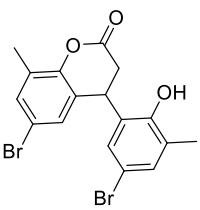
Yield = 125.4 mg, 63%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3353, 2979, 2915, 1732, 1603, 1495, 1477, 1415, 1404, 1332, 1310, 1269, 1221, 1174, 1144, 1101, 1020, 900, 870, 822, 812, 756 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 (dd, J = 2.2, 8.6 Hz, 1H), 7.20 (dd, J = 2.4, 8.6 Hz, 1H), 7.14 (d, J = 2.0 Hz,1H), 6.98 (d, J = 8.6 Hz, 1H), 6.90 (d, J = 2.3 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 4.54 (t, J = 6.4 Hz, 1H), 3.15 (dd, J = 6.7, 16.2 Hz, 1H), 2.94 (dd, J = 6.6, 16.2 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 153.9, 150.9, 131.6, 131.57, 131.0, 130.9, 128.2, 126.6, 118.7, 117.6, 117.1, 111.6, 35.5, 34.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{10}Br_2O_3 + Na]^+$ 418.8889, found 418.8887.

4-(2-Hydroxy-5-iodophenyl)-6-iodochroman-2-one, 5t



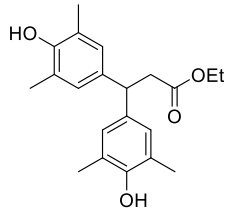
Yield = 127.9 mg, 52%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3312,2920, 1766, 1746, 1578, 1490, 1476, 1394, 1344, 1270, 1219, 1171, 818, 757, 650 cm^{-1}; **^{1}H NMR** (400 MHz, MeOD) δ = 7.65 (dd, J = 2.1, 8.5 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 7.38 (d, J = 1.5 Hz,1H), 7.00 (d, J = 8.9 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.66 (d, J = 8.5 Hz, 1H), 4.59 (t, J = 6.3 Hz, 1H), 3.13 (dd, J = 6.1, 16.2 Hz, 1H), 2.94 (dd, J = 6.7, 16.2 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, MeOD) δ = 167.8, 154.9, 151.9, 137.43, 137.4, 136.9, 136.6, 129.5, 127.4, 118.6, 117.5, 87.0, 80.3, 35.1, 33.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{15}H_{10}I_2O_3 + Na]^+$ 514.8612, found 514.8615.

4-(5-bromo-2-hydroxy-3-methylphenyl)-6-bromo-8-methylchroman-2-one, 5u



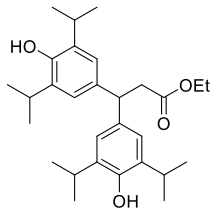
Yield = 140.6 mg, 66%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3424, 2919, 1751, 1605, 1470, 1447, 1380, 1339, 1321, 1248, 1185, 1150, 901, 867, 758, 670 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 (d, J = 2.0 Hz,1H), 7.21 (d, J = 1.9 Hz, 1H), 6.97 (d, J = 2.1 Hz,1H), 6.80 (d, J = 2.0 Hz, 1H), 4.94 (brs, 1H), 4.58 (t, J = 6.5 Hz, 1H), 3.13 (dd, J = 6.5, 16.1 Hz, 1H), 2.95 (dd, J = 6.6, 16.1 Hz, 1H), 2.34 (s, 3H), 2.24(s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 150.6, 149.3, 133.1, 132.9, 129.2, 128.8, 128.4, 128.2, 125.9, 125.2, 116.8, 113.0, 35.6, 34.5, 15.8, 15.6 ppm; **HRMS** (ESI−TOF) calcd for $[C_{17}H_{14}Br_2O_3, + Na]^+$ 446.9202, found 446.9194.

Ethyl 3,3-bis(4-hydroxy-3,5-dimethylphenyl)propanoate, 5x



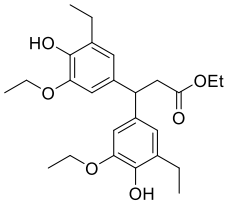
Yield = 140.4 mg, 82%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3474, 3466, 2979, 2918, 1714, 1603, 1489, 1463, 1440, 1373, 1332, 1284, 1254, 1204, 1147, 1027, 941, 880, 764, 734 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.83 (s, 4H), 4.30 (t, *J* = 8.1 Hz, 1H), 4.05 (qd, *J* = 0.8, 7.1 Hz, 2H), 2.95 (dd, *J* = 1.2, 8.0 Hz, 2H), 2.19 (s, 12H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ =172.3, 150.6, 135.6, 127.6, 122.9, 60.3, 45.5, 41.2, 16.0, 14.1 ppm; **HRMS** (ESI−TOF) calcd for $[C_{21}H_{26}O_4 + Na]^+$ 365.1723, found 365.1725.

Ethyl 3,3-bis(4-hydroxy-3,5-diisopropylphenyl)propanoate, 5y



Yield = 166 mg, 73%, light yellow oil; **IR** ($CHCl_3$) ν_{max} = 3492, 2960, 2935, 2870, 1715, 1596, 1470, 1447, 1385, 1371, 1340, 1301, 1271, 1256, 1200, 1151, 1123, 1034, 1028, 936, 876, 758, 691 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.93 (s, 4H), 4.39 (t, *J* = 8.3 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.11 (sept, *J* = 6.9 Hz, 4H), 2.98 (d, *J* = 8.1 Hz, 2H), 1.19–1.25 (m, 24H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 172.3, 148.2, 135.7, 133.3, 122.7, 60.2, 46.9, 42.3, 27.2, 22.8, 22.7, 14.1 ppm; **HRMS** (ESI−TOF) calcd for $[C_{29}H_{42}O_4 + Na]^+$ 477.2975, found 477.2975.

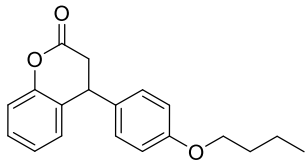
Ethyl 3,3-bis(4-hydroxy-5-ethoxy-3-ethylphenyl)propanoate, 5z



Yield = 183 mg, 85%, light yellow oil; **IR** ($CHCl_3$) ν_{max} = 3539, 2976, 2933, 2875, 1731, 1603, 1496, 1480, 1444, 1374, 1295, 1155, 1096, 1052, 950, 865, 695, 669 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.64 (d, *J* = 1.8 Hz, 2H), 6.55 (d, *J* = 1.8 Hz, 2H), 5.53 (brs, 2H), 4.35 (t, *J* = 8.1 Hz, 1H), 4.10–3.96 (m, 6H), 2.95 (d, *J* = 8.1 Hz, 2H), 2.62 (q, *J* = 7.5 Hz, 4H), 1.40 (t, *J* = 7.0 Hz, 6H), 1.19 (t, *J* = 7.5 Hz, 6H), 1.13 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 172.1, 145.3, 141.8, 134.9, 129.5, 120.2, 108.8, 64.4, 60.3, 46.6, 41.7, 23.0, 14.9, 14.2, 14.1 ppm; **HRMS** (ESI−TOF) calcd for $[C_{25}H_{34}O_6 + Na]^+$ 453.2248, found 453.2243.

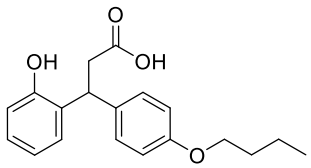
Synthesis of GPR-40 agonist, 8a

4-(4-Butoxyphenyl)chroman-2-one, 10



To a solution of 4-(4-hydroxyphenyl)chroman-2-one **5k** (40 mg, 0.167 mmol) in DMF (1.5 mL) was added CsF (76 mg, 0.5 mmol, 3.0 equiv) and *n*-butyl iodide (46 mg, 0.25 mmol, 1.5 equiv). The mixture was stirred at room temperature for 12 h and then diluted with EtOAc (20 mL).The organic layer was washed with water (3 × 5 mL), brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (10:1) as eluent to give **10** (40.1 mg, 81%) as a colorless oil; **IR** ($CHCl_3$) ν_{max} = 2959, 2932, 2873, 1772, 1611, 1586, 1512, 1456, 1279, 1251, 1221, 1178, 1135, 1070, 970, 919, 832 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.29 (dt, *J* = 2.1, 7.5 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.10–7.03 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.29 (t, *J* = 7.1 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.07–2.95 (m, 2H), 1.79–1.72 (m, 2H), 1.52–1.45 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.8, 158.6, 151.7, 132.0, 128.7, 128.6, 128.3, 126.3, 124.6, 117.1, 115.1, 67.8, 39.9, 37.2, 31.3, 19.2, 13.8 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{20}O_3 + Na]^+$ 319.1305, found 319.1306.

3-(4-Butoxyphenyl)-3-(2-hydroxyphenyl)propanoic acid, 8a



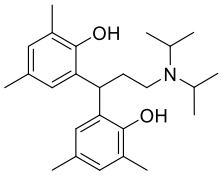
To a solution of 4-(4-butoxyphenyl)chroman-2-one **10** (36 mg, 0.12 mmol) in THF/MeOH/H_2O (4:1:1, v/v/v, 6.0 mL) was added LiOH (1M in H_2O, 1.0 mL, 1.0 mmol). The mixture was stirred at room temperature for 12 h and then aqueous 1N HCl solution (2 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2/MeOH (20:1) as eluent to give **8a** (23.3 mg, 61%) as a white semi-solid; **IR** ($CHCl_3$) ν_{max} = 2922, 2852, 1737, 1610, 1512, 1456, 1246, 1178, 1042, 976, 919 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 8.7 Hz, 2H), 7.11–7.05 (m, 2H), 6.91–6.74 (m, 4H), 4.76 (t, *J* = 7.6 Hz, 1H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.15–3.01 (m, 2H), 1.75 (quint., *J* = 6.5, 6.5 Hz, 2H), 1.52–1.40 (m, 2H), 0.96 (t, *J* = 7.6, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.5, 157.9, 153.1, 134.2, 130.3, 128.7, 128.1, 127.8, 121.1, 116.7, 114.6, 67.7, 39.5, 39.1, 31.3, 19.2, 13.8 ppm; **HRMS** (ESI−TOF) calcd for $[C_{19}H_{22}O_4 + Na]^+$337.1410, found 337.1416.

General procedure for synthesis of tolterodine analogues 7′a and 7′q

To a solution of 4-arylchroman-2-one **5a** or **5q** (0.25 mmol) in anhydrous CH_2Cl_2 (3 mL) was added DIBAL-H (1.75 M in toluene, 0.3mmol) dropwise under N_2 at −20 °C. After stirring for 6 h, the reaction was quenched with EtOAc and an aqueous solution of Rochelle salt was added. The mixture was stirred at room temperature for 1 h. The aqueous phase was extracted with EtOAc (2 × 15 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated. To a solution of the residue in EtOH (2

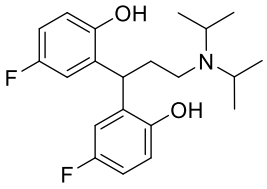
mL), placed in a glass cylinder in a stainless steel autoclave, were added Pd/C (10 mg) and R_2NH (0.3mmol), and the autoclave was pressurized with H_2 (20 atm). The reaction mixture was stirred for 12 h at 60 °C. The autoclave was cooled to room temperature and depressurized. The mixture was filtered through celite pad and the pad washed with EtOAc. The filtrate was concentrated and the residue was purified by silica gel column chromatography to give analogues of tolterodine **7′a** and **7′q** in good yields.

***N*,*N*-Diisopropyl-3,3-bis(2-hydroxy-3,5-dimethylphenyl)propan-1-amine, 7′a**



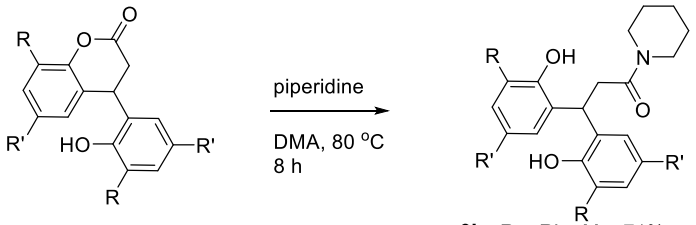
Yield =79.6 mg, 83%, light yellow semi-solid; **IR** ($CHCl_3$) ν_{max} = 3416, 2978, 2681, 1600, 1507, 1481, 1291, 1229, 857 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.83 (s, 2H), 6.76 (s, 2H), 6.21 (br s, 2H), 4.43 (t, *J* = 8.2 Hz, 1H), 3.21 (quint., *J* = 6.7 Hz, 2H), 2.53 (t, *J* = 6.0 Hz, 2H), 2.17−2.28 (m, 14H), 1.09 (d, *J* = 6.9 Hz, 12H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.6, 129.9, 129.7, 129.2, 125.9, 125.2, 47.7, 41.6, 33.3, 32.2, 20.8, 19.6, 16.4 ppm; **HRMS** (ESI−TOF) calcd for $[C_{25}H_{37}O_2N + H]^+$ 384.2897, found 384.2896.

***N*,*N*-Diisopropyl-3,3-bis(2-hydroxy-5-fluorophenyl)propan-1-amine, 7′q**



Yield = 67.2 mg, 74%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3277, 2959, 2923, 2855, 1607, 1586, 1496, 1463, 1397, 1385, 1358, 1258, 1124, 1098, 1038, 973, 937, 884, 819, 666, 542 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.86–6.73 (m, 6H), 4.57 (t, *J* = 8.1 Hz, 1H), 4.07 (br s, 2H), 3.22 (quint., *J* = 6.5 Hz, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.34(q, *J* = 7.3 Hz, 2H) 1.15 (d, *J* = 6.7 Hz, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.0, 155.7, 151.0, 132.0 and 131.9 ($J_{C\text{-}F}$ = 6.4 Hz), 118.0 and 117.9 ($J_{C\text{-}F}$ = 8.1 Hz), 113.9, 113.63 and 113.60 ($J_{C\text{-}F}$ = 2.4 Hz), 48.9, 42.6, 34.5, 32.3, 19.6 ppm; **^{19}F NMR** (470 MHz, $CDCl_3$/TMS) δ = –124.27 ppm; **HRMS** (ESI−TOF) calcd for $[C_{21}H_{27}O_2F_2N + H]^+$ 364.2083, found 364.2082.

Synthesis of 9′a and 9′q

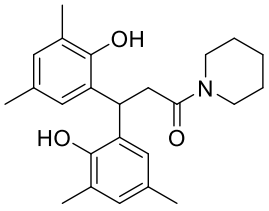


7a, 7q

9'a R = R' = Me, 71%
9'q R = H, R' = F, 76%

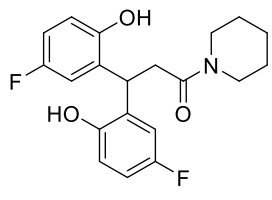
To a solution of **5a**, and **5q** (0.1 mmol, 1.0 equiv) in DMA (2.0 mL) was added piperidine (1.0 mmol, 10.0 equiv). The mixture was heated at 80 °C for 8 h, concentrated under reduced pressure and dissolved in CH_2Cl_2 (20 mL). The solution was washed with sat. aqueous $NaHCO_3$ (2 × 10 mL). The organic layer was dried ($NaSO_4$) and concentrated under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate/CH_2Cl_2 (3:1) to afford **9′a** and **9′q**, respectively.

3,3-*bis*(2-Hydroxy-3,5-dimethylphenyl)-1-(piperidin-1-yl)propan-1-one, 9′a



Yield = 27.1 mg, 71%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3576, 2935, 1611, 1480, 1222, 1144, 1081, 788 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 8.48 (s, 2H), 6.83 (s, 2H), 6.67 (s, 2H), 5.05 (t, *J* = 7.3Hz, 1H), 3.50 (t, *J* = 5.5 Hz, 2H), 3.38 (t, *J* = 5.7 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 6H), 2.08 (s, 6H), 1.61–1.50 (m, 2H), 1.49–1.41 (m, 2H), 1.39–1.30 (m, 2H) ppm; **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 170.6, 150.3, 132.2, 129.2, 127.9, 126.5, 124.7, 46.4, 42.8, 38.6, 32.9, 26.5, 25.8, 24.5, 21.0, 17.1ppm; **HRMS** (ESI−TOF) calcd for $[C_{24}H_{31}O_3N + Na]^+$ 404.2196, found 404.2196.

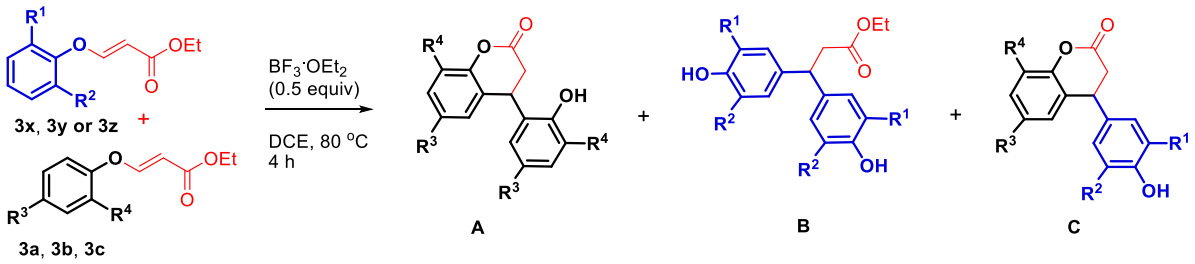
3,3-*bis*(5-Fluoro-2-hydroxyphenyl)-1-(piperidin-1-yl)propan-1-one, 9′q



Yield = 27.5 mg, 76%, white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3349, 2928, 2857, 1605, 1505, 1490, 1435, 1351, 1263, 1183, 909, 871, 812, 770, 707, 663 cm^{-1}; **^{1}H NMR** (500 MHz, DMSO–d_6) δ = 9.37 (br s, 2H), 6.87–6.77 (m, 4H), 6.74–6.67 (m, 2H), 4.96 (t, *J* = 7.6 Hz, 1H), 3.49 (t, *J* = 5.4 Hz, 2H), 2.96 (d, *J* = 7.7 Hz, 2H), 1.58–1.51 (m, 2H), 1.49–1.42 (m, 2H),1.36–1.29 (m, 2H) ppm; **^{13}C NMR** (125 MHz, DMSO–d_6) δ = 169.2, 156.7, 154.8, 151.6, 132.2 and 132.1 ($J_{C\text{-}F}$ = 6.6 Hz), 116.2 and 116.1 ($J_{C\text{-}F}$ = 7.6 Hz), 115.3 and 115.1 ($J_{C\text{-}F}$ = 23.4 Hz),113.3 and 113.1 ($J_{C\text{-}F}$ = 22.2 Hz), 46.4, 42.5, 36.2, 34.9, 26.6, 25.9, 24.5 ppm; **^{19}F NMR** (470 MHz, DMSO–d_6) δ = –125.9 ppm; **HRMS** (ESI−TOF) calcd for $[C_{20}H_{21}O_2F_2NO_3 + Na]^+$ 384.1382, found 384.1378.

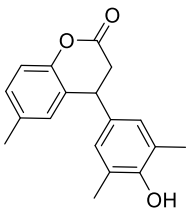
General procedure for cross over experiments of mixed 3-aryloxyacrylates

To a stirred solution of ethyl (*E*)-3-phenoxyacrylate **3x**, **3y** or **3z** (0.5 mmol) and ethyl (*E*)-3-phenoxyacrylate **3a**, **3b** or **3c** (0.5 mmol) in dry $ClCH_2CH_2Cl$ (DCE, 50 mL, 0.02M) was added drop wise $BF_3{\cdot}OEt_2$ (46% solution, 0.5 mmol, 1.0 equiv) at room temperature. The mixture was stirred for 10 min and then stirred for additional 4 h at 80 °C. The reaction progress was monitored by TLC. On complete consumption of starting material, the reaction mixture was quenched with sat. aqueous solution of $NaHCO_3$ (15 mL) and stirred vigorously till two clear layers were formed. The aqueous layer was then extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were washed with water (10 mL), dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (17:3 to 7:3) as an eluent to give the separated compounds in the order of elution as **C**, **B** and **A**. The characterization data of compounds corresponding to **A** and **B** is as given before. For new compounds corresponding to **C** is given below.



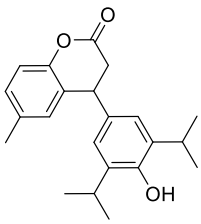
entry	R^1, R^2, R^3, R^4 (**3**)	yield **A**	yield **B**	yield **C**
1	$R^1 = R^2 = R^3$ = Me, R^4 = H (3**x** and **3b**)	**5b**, 27%	**5x**, 25%	**5bx**, 37%
2	$R^1 = R^2$ = *i*-Pr, R^3 = Me, R^4 = H (**3y** and **3b**)	**5b**,30%	**5y**, 25%	**5by**, 35%
3	$R^1 = R^2$ = *i*-Pr, $R^3 = R^4$ = Me (**3y** and **3a**)	**5a**, 32%	**5y**, 21%	**5ay**, 32
4	$R^1 = R^2$ = *i*-Pr, R^3 = *t*-Bu, R^4 = H (**3y** and **3c**)	**5c**, 28%	**5y**, 23%	**5cy**, 34%
5	R^1 = Et, R^2 = OEt, $R^3 = R^4$ = Me (**3z** and **3a**)	**5a**, 27%	**5z**, 24%	**5az**, 32%

4-(4-Hydroxy-3,5-dimethylphenyl)-6-methylchroman-2-one, 5bx



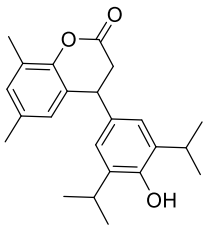
Yield = 52.2 mg, 37%, white solid, **M.P**. 196–198 °C; **IR** ($CHCl_3$) ν_{max} = 3500, 2922, 2854, 1747, 1600, 1495, 1412, 1378, 1342, 1313, 1283, 1247, 1197, 1165, 1139, 1122, 1025, 931, 868, 833, 482 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.08 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H), 6.74 (s, 2H), 4.16 (t, *J* = 6.7 Hz, 1H), 3.04–2.90 (m, 2H), 2.26 (s, 3H), 2.21 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.2, 151.6, 149.5, 134.3, 132.0, 129.1, 128.7, 127.6, 125.9, 123.7, 116.7, 40.0, 37.4, 20.8, 16.0 ppm; **HRMS** (ESI−TOF) calcd for $[C_{18}H_{18}O_3 + Na]^+$ 305.1148, found 305.1145.

4-(4-Hydroxy-3,5-diisopropylphenyl)-6-methylchroman-2-one, 5by



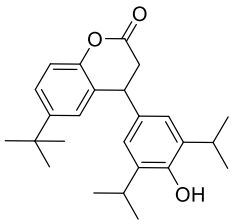
Yield = 59.2 mg, 35%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3515, 2958, 1759, 1493, 1472, 1249, 1200, 1151, 1042, 913, 819, 736 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.07 (dd, *J* = 2.0, 8.2 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 2H), 6.78 (d, *J* = 1.6 Hz, 1H), 4.80 (br s, 1H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.13 (sept, *J* = 6.9 Hz, 2H), 3.06–2.90 (m, 2H), 2.25 (s, 3H), 1.28–1.18 (m, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.4, 149.6, 149.3, 134.3, 134.1, 132.2, 129.0, 128.6, 126.1, 122.6, 116.6, 40.6, 37.4, 27.3, 22.6, 20.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{22}H_{26}O_3 + Na]^+$ 361.1774, found 361.1772.

4-(4-Hydroxy-3,5-diisopropylphenyl)-6,8-dimethylchroman-2-one, 5ay



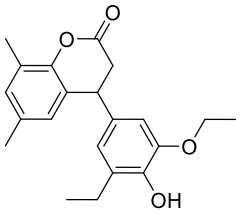
Yield = 56.4 mg, 32%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3503, 2962, 2925, 1759, 1472, 1446, 1265, 1198, 1150, 1036, 911, 736 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.94 (s, 1H), 6.82 (s, 2H), 6.59 (s, 1H), 4.81 (br s, 1H), 4.19 (t, *J* = 7.5 Hz, 1H), 3.12 (sept, *J* = 7.1 Hz, 2H), 3.05–2.90 (m, 2H), 2.32 (s, 3H), 2.21 (s, 3H), 1.30–1.18 (m, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.6, 149.3, 147.9, 134.2, 133.5, 132.3, 130.6, 126.1, 125.9, 122.7, 40.7, 37.4, 27.3, 22.64, 22.6, 20.7, 15.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{23}H_{28}O_3 + Na]^+$ 375.1931, found 375.1931.

4-(4-Hydroxy-3,5-diisopropylphenyl)-6-*tert*-butychroman-2-one, 5cy



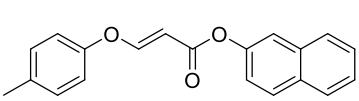
Yield = 64.7 mg, 34% colorless oil; **IR** ($CHCl_3$) ν_{max} = 3502, 2963, 2877, 1758, 1494, 1471, 1442, 1364, 1266, 1222, 1198, 1175, 1151, 1127, 927, 910, 825, 735, 667 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.29 (dd, *J* = 1.9, 8.5 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98 (s, 1H), 6.84 (s, 2H), 4.82 (br s, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.14 (sept, *J* = 6.7 Hz, 2H), 3.08–2.92 (m, 2H), 1.26–1.19 (m, 21H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.5, 149.5, 149.2, 147.4, 134.3, 132.0, 125.7, 125.3, 125.2, 122.6, 116.3, 40.6, 37.5, 34.4, 31.3, 27.2, 22.7, 22.6 ppm; **HRMS** (ESI−TOF) calcd for $[C_{25}H_{32}O_3 + Na]^+$ 403.2244, found 403.2242.

4-(3-Ethoxy-5-ethyl-4-hydroxyphenyl)-6,8-dimethylchroman-2-one, 5az



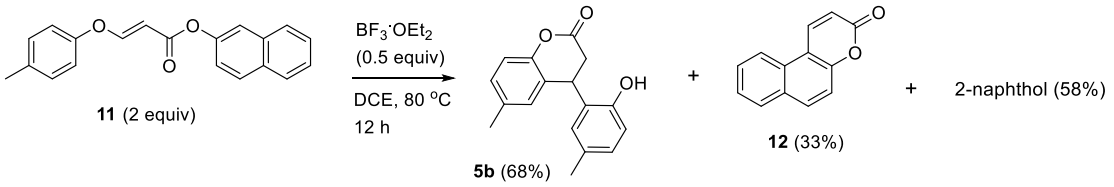
Yield = 54.5 mg, 32%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3401, 2971, 2928, 1765, 1617, 1499, 1474, 1450, 1334, 1304, 1222, 1201, 1142, 1091, 1055, 917, 858, 825, 770, 694, 588 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.94 (s, 1H), 6.61 (s, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 5.69 (br s, 1H), 4.16 (t, *J* = 6.3 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.02–2.91 (m, 2H), 2.63 (q, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 2.22 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H),1.19 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.4, 147.8, 145.7, 142.7, 133.6, 131.4, 130.7, 130.2, 126.1, 125.9, 125.86, 120.6, 108.1, 64.6, 40.7, 37.3, 23.0, 20.7, 15.7, 14.8, 14.0 ppm; **HRMS** (ESI−TOF) calcd for $[C_{21}H_{24}O_4 + Na]^+$ 363.1567, found 363.1566.

Naphthalen-2-yl (*E*)-3-(*p*-tolyloxy)acrylate, 11



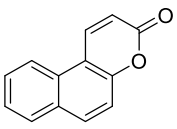
The title compound was prepared from *p*-cresol (108.1 mg, 1.0mmol) and naphthalen-2-ylpropiolate (215.8 mg, 1.1 mmol, 1.1 equiv) following similar reaction procedure as that described for compounds **3**, to give **11** (203.9 mg, 67%) as a white solid, **M.P.** 84–86 °C; **IR** ($CHCl_3$) ν_{max} = 3054, 1723, 1661, 1628, 1599, 1505, 1465, 1328, 1248, 1212, 1181, 1164, 1126, 1102, 1016, 1000, 957, 894, 867, 822, 736, 476 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 12.3 Hz, 1H), 7.88–7.83 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.52–7.43 (m, 2H), 7.28 (dd, *J* = 2.3, 8.4 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 5.75 (d, *J* = 12.3 Hz, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.0, 161.4, 153.6, 148.3, 135.0, 133.8, 131.4, 130.5, 129.3, 127.7, 127.6, 126.5, 125.6, 121.4, 118.6, 118.1, 100.8, 20.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{20}H_{16}O_3 + Na]^+$ 327.0992, found 367.0992.

Experiments to ascertain C3-O bond cleavage in 3-aryloxyacrylates



The above reaction was carried on **11** (152.2 mg, 0.5 mmol) using $BF_3{\cdot}OEt_2$ (46% solution, 0.25 mmol, 0.5 equiv) and following similar procedure as that described for compounds **7** to give **7b** (45.6 mg, 68%),**12** (32.4 mg, 33%) and 2-naphthol (41 mg, 58%).

3*H*-Benzo[*f*]chromen-3-one, **12**

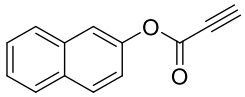


Yield = 32.4 mg, 33%, pale yellow solid, **M.P.** 116–118 °C, lit.[2] 117–118 °C; **IR** ($CHCl_3$) ν_{max} = 3057, 2928, 2861, 1722, 1684, 1634, 1586, 1566, 1516, 1463, 1439, 1336, 1280, 1247, 1208, 1176, 1159, 1112, 1032, 901, 812, 781 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 9.8 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 6.58 (d, *J* = 9.8 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 160.9, 153.9, 139.1, 133.1, 130.3, 129.0, 128.3, 126.0, 121.3, 117.1, 115.7, 113.0 ppm; ; **HRMS** (ESI−TOF) calcd for $[C_{13}H_8O_2 + H]^+$calcd: 197.0597, found 197.0592.

General procedure for DCC esterification to synthesize 13 and 16

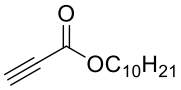
To a stirred solution of propiolic acid (70 mg, 1.0 mmol) in dry CH_2Cl_2 (10 mL) were added *N,N'*-dicyclohexylcarbodiimide (DCC, 206.3 mg, 1.0 mmol, 1.0 equiv) and DMAP (36.8 mg, 0.3 mmol, 0.3 equiv) at 0 °C. The mixture was stirred for 10 min and then a solution of 2-naphthol or *n*-decanol (1.2 mmol, 1.2 equiv) in dry CH_2Cl_2 (3 mL) was added dropwise at 0 °C. The reaction mixture was stirred for additional 5 h at room temperature. It was then filtered through cotton plug and the residue was washed with cold CH_2Cl_2 (5 mL). The filtrate were washed with water, brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (20:1) as eluent to give the corresponding esters **13** or **16**.

Naphthalen-2-ylpropiolate, 13[4]



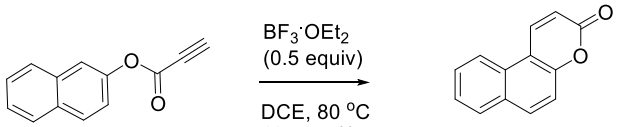
Yield = 111.8 mg, 57%, white solid, **M.P.** 72–74 °C, lit.[4] 71–73 °C; **IR** ($CHCl_3$) ν_{max} = 3420, 3245, 3057, 2117, 1711, 1679, 1601, 1574, 1511, 1461, 1435, 1379, 1249, 1219, 1197, 1154, 961, 932, 895, 875, 858, 814, 737, 480 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.93–7.80 (m, 3H), 7.65 (s, 1H), 7.56–7.48 (m, 2H), 7.30 (dd, J = 2.4, 8.4, Hz, 1H), 3.12 (s, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.1, 147.4, 133.6, 131.7, 129.7, 127.8, 127.76, 126.8, 126.1, 120.4, 118.5, 77.0, 74.3 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_8O_2$+ H]$^+$ 197.0597, found 197.0596.

***n*-Decylpropiolate, 16**



Yield = 134.6 mg, 64%, colorless oil; **IR** ($CHCl_3$) ν_{max} = 3305, 3283, 2955, 2925, 2856, 2121, 1718, 1467, 1379, 1235, 1042, 975, 783 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.18 (t, J = 6.8 Hz, 2H), 2.87 (s, 1H), 1.74–1.61 (m, 2H), 1.43–1.19 (m, 14H), 0.87 (t, J = 6.8 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ =152.8, 74.8, 74.4 66.5, 31.9, 29.5, 29.4, 29.3, 29.1, 28.3, 25.7, 22.6, 14.1 ppm; **HRMS** (ESI−TOF) calcd for $[C_{13}H_{22}O_2$+ K]$^+$ 249.1251, found 249.1255.

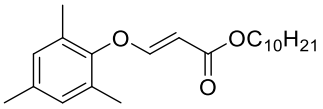
Reaction of compound 13 to give 12



13 **12**

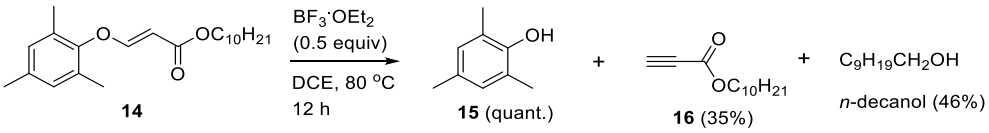
The above reaction was carried on **13** (70 mg, 0.357 mmol) using $BF_3{\cdot}OEt_2$ (46% solution, 0.178mmol, 0.5 equiv) and following similar procedure as that described for compounds **5** to give **12** (31.5 mg, 45%) as pale yellow solid. Characterization data is same as before.

***n*-Decyl (*E*)-3-(mesityloxy)acrylate, 14**



The title compound was prepared from mesitol (136.2 mg, 1.0mmol) and *n*-decylpropiolate **16** (231.3 mg, 1.1 mmol, 1.1 equiv) following similar reaction procedure as that described for compounds **5**, to give **14** (201 mg, 58%) as a colorless oil; **IR** ($CHCl_3$) ν_{max} = 2923, 2853, 1733, 1466, 1378, 1342, 1124, 1056, 721 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, J = 12.4 Hz, 1H), 6.86 (s, 2H), 5.00 (d, J = 12.4 Hz, 1H), 4.07 (t, J = 6.5 Hz, 2H), 2.27 (s, 3H), 2.13 (s, 6H), 1.44–1.14 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.7, 160.8, 148.9, 135.3, 129.6, 129.4, 98.6, 64.2, 31.9, 29.5, 29.3, 28.7, 25.9, 22.7, 20.7, 15.9, 14.1 ppm; **HRMS** (ESI−TOF) calcd for $[C_{22}H_{34}O_3$ + Na]$^+$ 369.2400, found 369.2401.

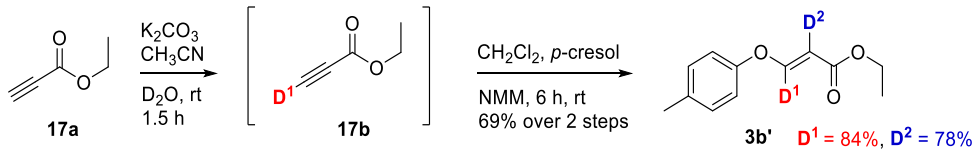
Reaction of compound 14 under standard conditions.



14 **15** (quant.) **16** (35%)

The above reaction was carried on **14** (173.2 mg, 0.5 mmol) using $BF_3{\cdot}OEt_2$ (46% solution, 0.25 mmol, 0.5 equiv) and following similar procedure as that described for compounds **5** to give **15** (67.9 mg, quant.), **16** (36.8 mg, 35%) and *n*-decanol (36.4 mg, 46%).

Preparation of di-deuterated ester 3b′

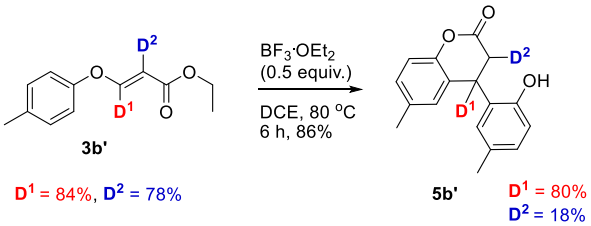


17a **17b** **3b'** D^1 = 84%, D^2 = 78%

To a stirred solution of ethyl propiolate **17a** (196.2 mg, 2.0 mmol, 1.0 equiv) in CH_3CN (8 mL) was added anhydrous K_2CO_3 (414.6 mg, 3 mmol, 1.5 equiv) and the mixture stirred for 30 min. To this solution was added D_2O (2.0 g, 100mmol, 50.0 equiv) and stirred for 1.5 h. The reaction mixture was then diluted with anhydrous CH_2Cl_2 (20 mL)and the organic layer was separated from D_2O.The organic layer was then dried (Na_2SO_4) and filtered. To this filtrate containing **17b** was added *p*-cresol (216.3 mg, 2.0 mmol, 1.0 equiv), few drops of D_2O and *N*-methyl morpholine (223 mg, 2.2 mmol, 1.1 equiv) and the reaction mixture was

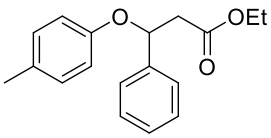
stirred for 6 h at room temperature. It was then concentrated and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (49:1 to 19:1) as eluent to give **3b′** (287.4 mg, 69%) as colorless oil; **IR** ($CHCl_3$) ν_{max} = 2979, 2927, 2854, 1710, 1623, 1599, 1506, 1446, 1367, 1282, 1226, 1205, 1172, 1144, 1121, 1062, 1017, 974, 818, 761, 701, 646, 497 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79–7.75 (m, 0.17 H), 7.16 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 5.47–5.12 (m, 0.27 H), 4.18 (q, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 159.5, 153.6, 134.6, 130.3, 117.9, 101.4, 60.0, 20.7, 14.3 ppm.

Reaction of 3b′ to give 5b′



The above reaction was carried on **3b′** (104.2 mg, 0.5 mmol) using $BF_3{\cdot}OEt_2$ (46% solution, 0.25 mmol, 0.5 equiv) and following similar procedure as that described for compounds **5** to give **5b′** (58.1 mg, 86%, the yield is based on assuming fully deuterated compound) as a white semi-solid; **IR** ($CHCl_3$) ν_{max} = 3386, 3015, 2924, 2856, 1745, 1614, 1511, 1493, 1463, 1416, 1370, 1280, 1253, 1200, 1124, 1075, 1034, 942, 816, 666, 590, 543, 489 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.10 (d, J = 8.3 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 6.91–6.85 (m, 2H), 6.63 (dt, J = 1.6, 8.0 Hz, 1H), 6.58 (td, J = 1.6, 7.6 Hz, 1H), 5.59 (br s, 1H), 4.60 (t, J = 6.5 Hz, 0.22 H), 3.22–3.13 (m, 0.81H), 3.00–2.91 (m, 0.83H), 2.28 (s, 3H), 2.17 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 169.3, 150.9, 149.9, 134.4, 130.2, 129.2, 129.0, 128.9, 128.73, 128.7, 126.5, 124.5, 116.7, 115.5, 35.2, 35.16, 20.8, 20.6 ppm.

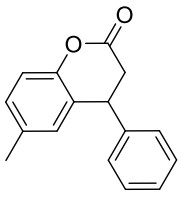
Ethyl 3-phenyl-3-(*p*-tolyloxy)propanoate, 24



To a stirred solution of *p*-cresol (130 mg, 1.2 mmol, 1.2 equiv) in DMF (5 mL) was added K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv) followed by ethyl 3-phenylpropiolate (174 mg, 1.0 mmol, 1.0 equiv) and the reaction mixture was stirred for 3 h at 60 °C. The reaction was monitored by TLC and after consumption of starting alkyne, it was then cooled to room temperature and diluted with Et_2O (30 mL) and H_2O (10 mL). The aqueous layer was then separated and extracted with Et_2O (2 ×15 mL) and the combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (49:1) as eluent to give ethyl 3-phenyl-3-(*p*-tolyloxy)acrylate (274 mg) as *E/Z* (2:1) mixture which was directly taken for next step.

To a stirred solution of the above mixture (274 mg) in EtOAc (5 mL) was added Pd/C (10% on carbon, 27 mg) and the reaction was stirred at 60 °C under H_2 pressure (20 atm) for 5 h. The mixture was then filtered through a pad of celiteand the pad washed with EtOAc (20 mL). The filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (49:1) as eluent to give **24** (238.9 mg, 84%, over two steps) as colorless oil; **IR** ($CHCl_3$): ν_{max} = 3030, 2981, 2927, 1737, 1613, 1586, 1509, 1454, 1374, 1354, 1288, 1270, 1232, 1174, 1079, 1026, 918, 876, 818, 763, 742, 701, 668, 606, 516 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.41 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.25–7.29 (m, 1H), 6.98 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 5.59 (dd, J = 4.6, 9.2 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.03 (dd, J = 9.1, 15.5 Hz, 1H), 2.76 (dd, J = 4.7, 15.5 Hz, 1H), 2.23 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H), ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.5, 155.6, 140.6, 130.4, 129.7, 128.7, 127.9, 126.0, 116.2, 77.1, 60.7, 43.9, 20.4, 14.2 ppm; **HRMS** (ESI−TOF) calcd for $[C_{18}H_{20}O_3 + Na]^+$ 307.1305, found 307.1307.

6-Methyl-4-phenylchroman-2-one, 5aa



The reaction of ethyl 3-phenyl-3-(*p*-tolyloxy)propanoate **24** (142.2 mg, 0.5 mmol) using $BF_3{\cdot}OEt_2$ (46% solution, 0.25 mmol, 0.5 equiv) by similar procedure as that described for **5** produced **5aa** (109.6 mg, 92%) as colorless oil; **IR** ($CHCl_3$)ν_{max} = 2924, 2851, 1770, 1610, 1587, 1514, 1487, 1455, 1344, 1280, 1222, 1177, 1138, 968, 920, 880, 823, 730 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38–7.28 (m, 3H), 7.18–7.14 (m, 2H), 7.09 (dd, J = 1.8, 8.2 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.79 (s, 1H), 4.30 (t, J = 6.9 Hz, 1H), 3.10–2.96 (m, 2H), 2.26 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$)δ = 167.8, 149.7, 140.5, 134.3, 129.3, 129.1, 128.6, 127.6, 127.5, 125.3, 116.9, 40.7, 37.1, 20.7 ppm; **HRMS** (ESI−TOF) calcd for $[C_{16}H_{14}O_2 + Na]^+$ 261.0886, found 261.0886.

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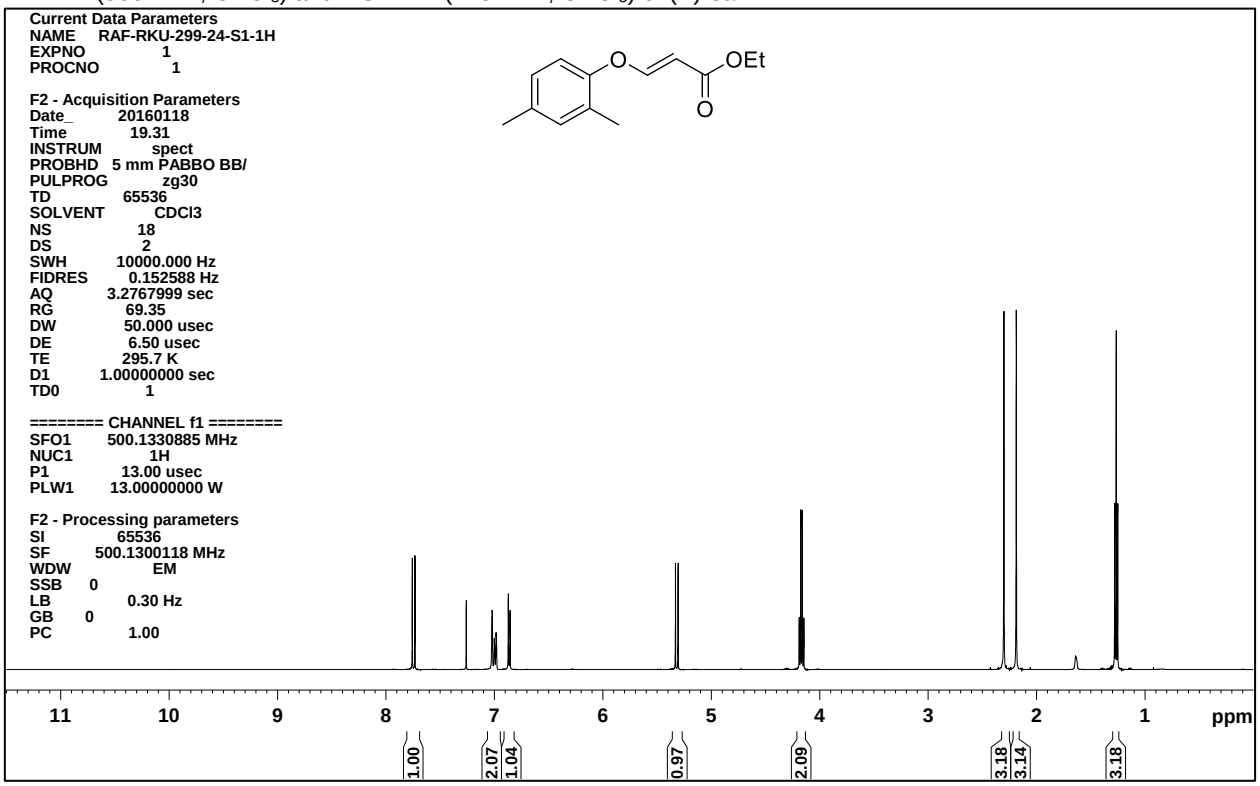
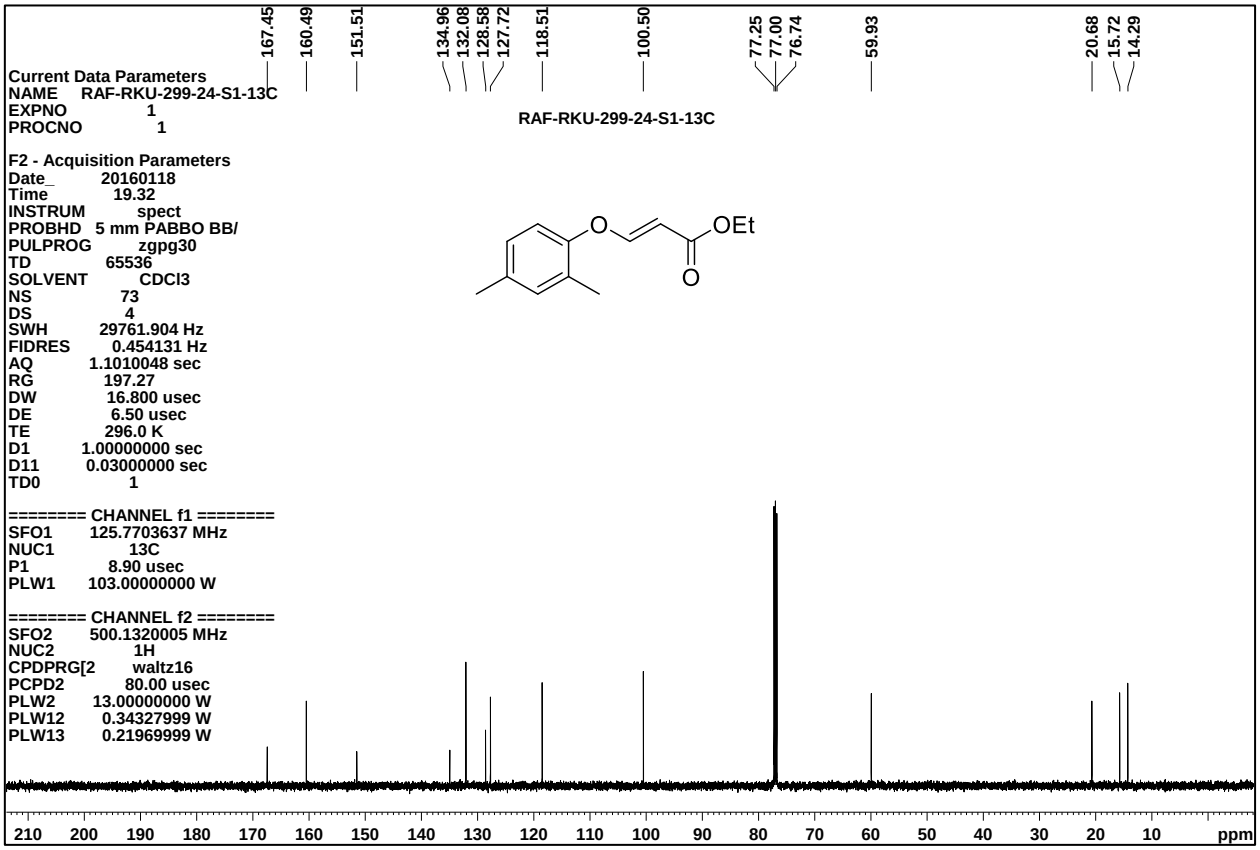
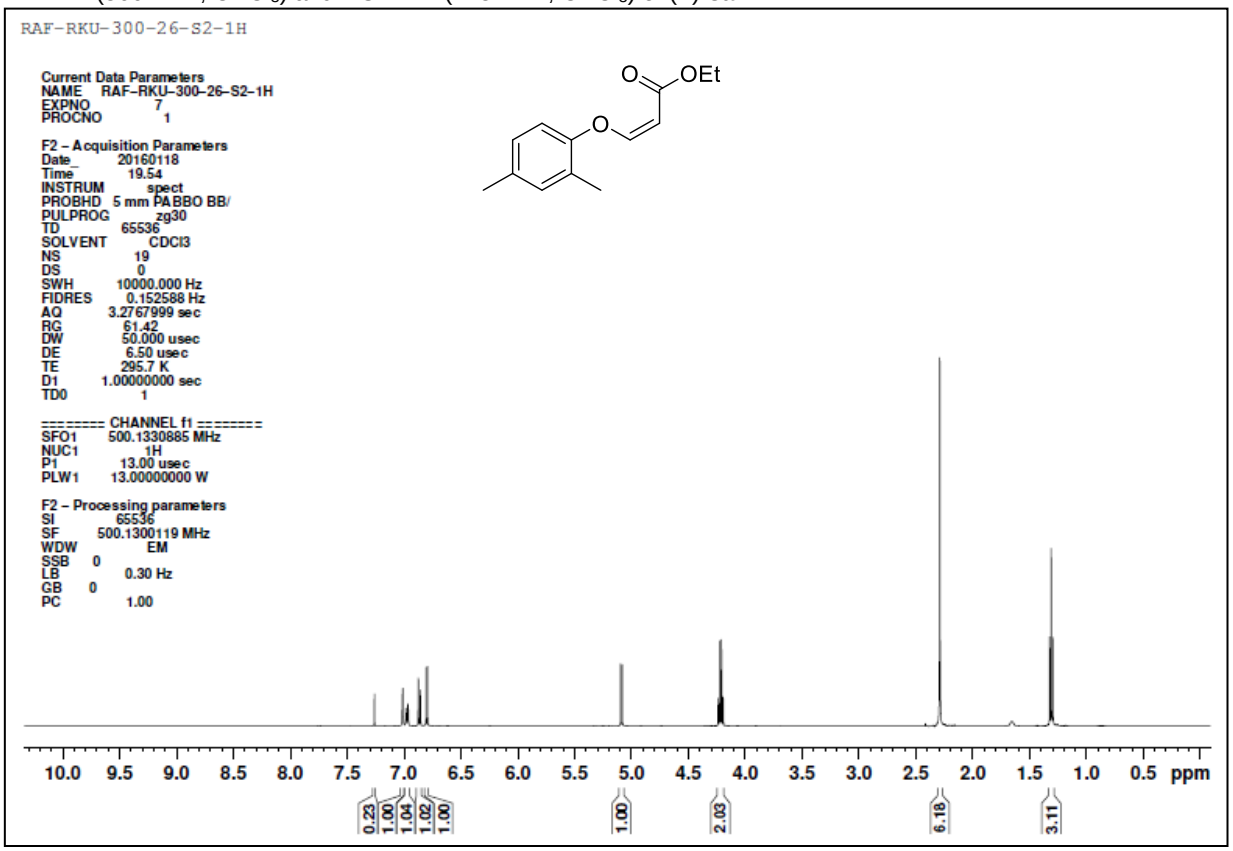
2. M. S. Kutubi, T. Hashimoto, T. Kitamura, *Synthesis,* 2011, 1283.
3. E. Fillion, A. M. Dumas, B. A. Kuropatwa, N. R. Malhotra, T. C. Sitler, *J. Org. Chem.,* 2006, **71**, 409.
4. K. Okamoto, T. Hayashi, V. H. Rawal, *Chem. Commun*., 2009, 4815.

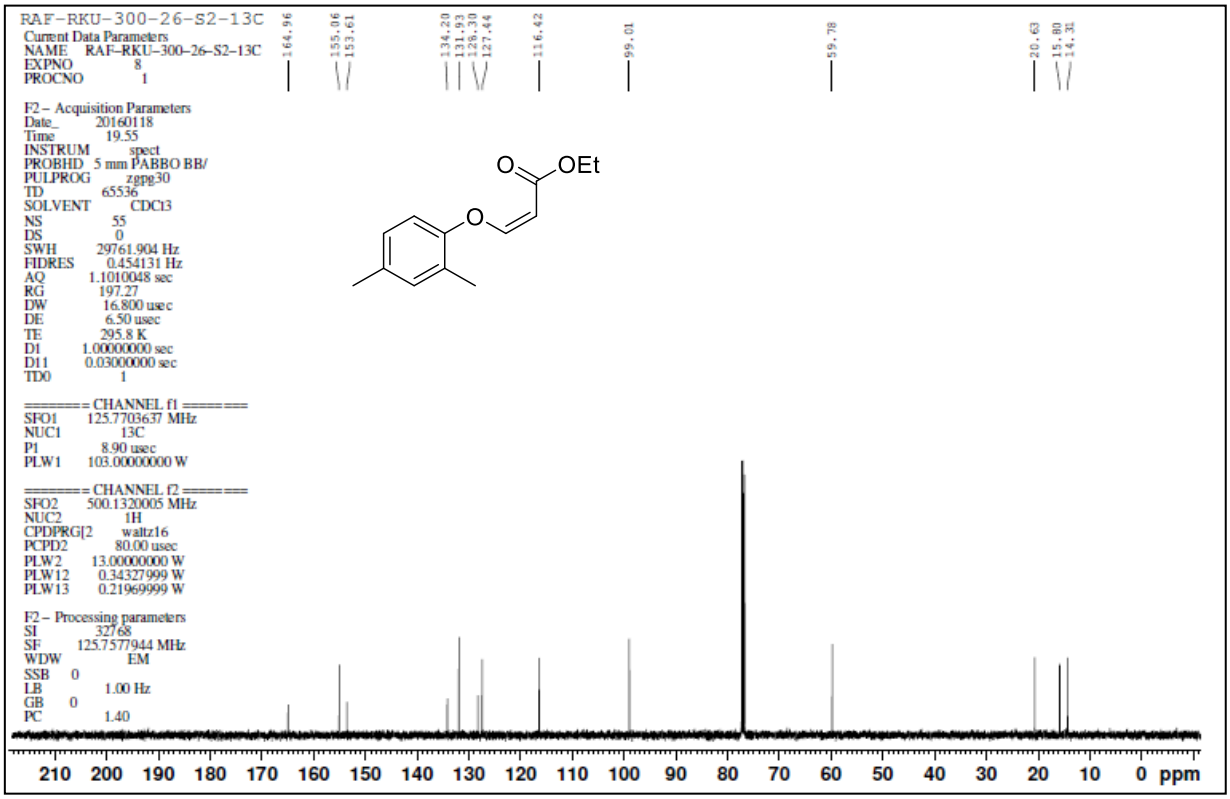
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3a**



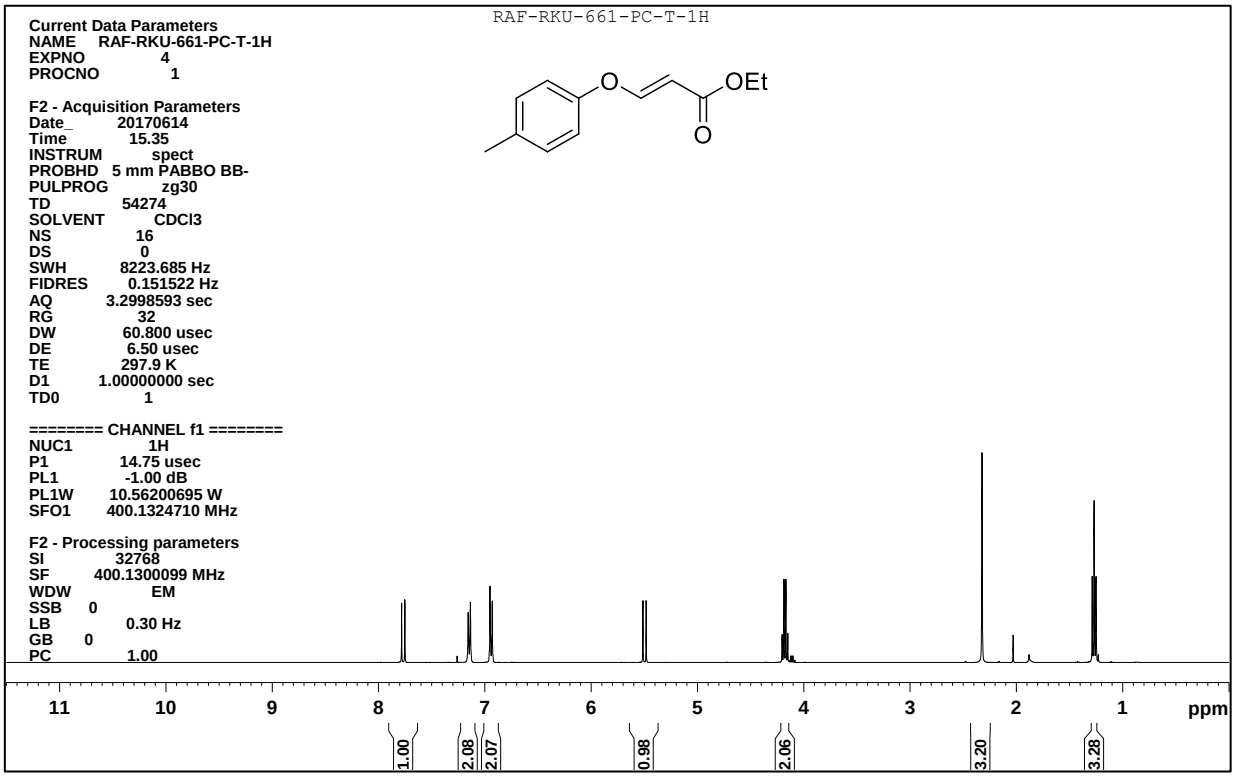


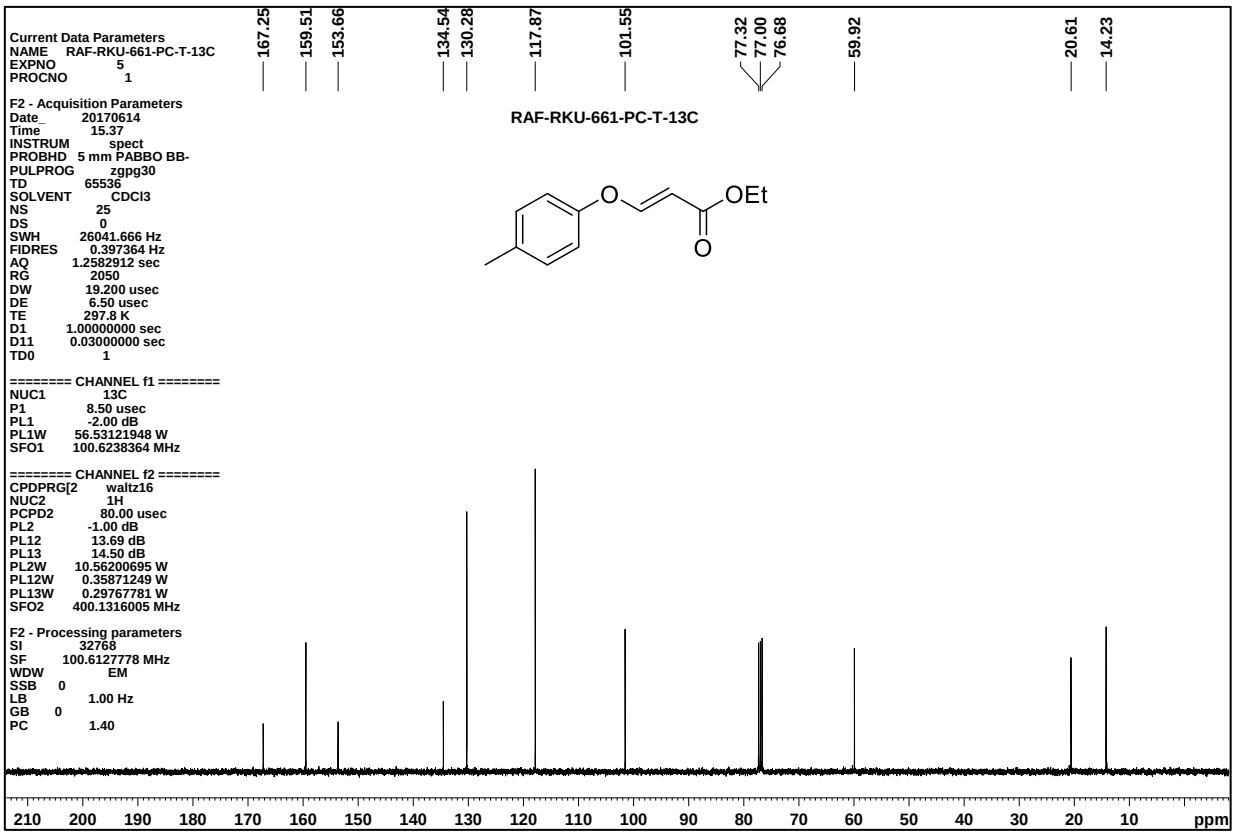
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*Z*)-**3a**



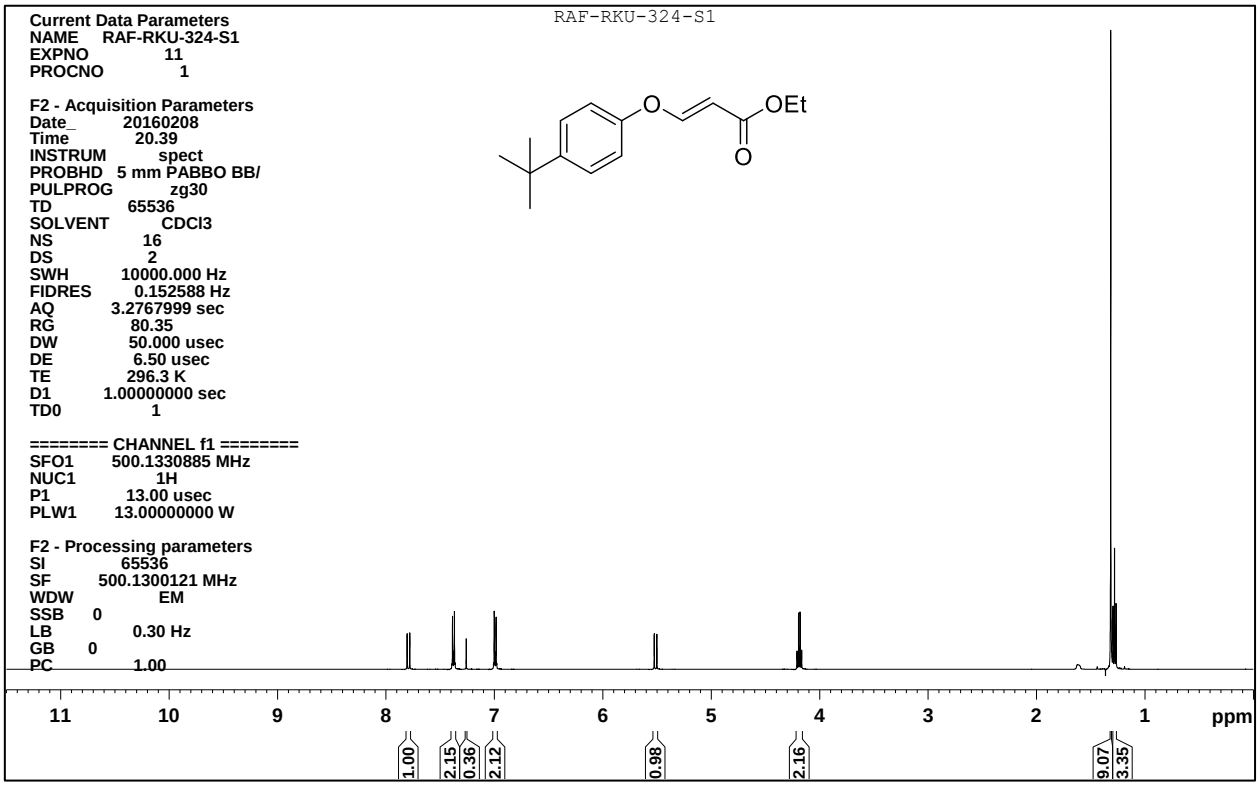


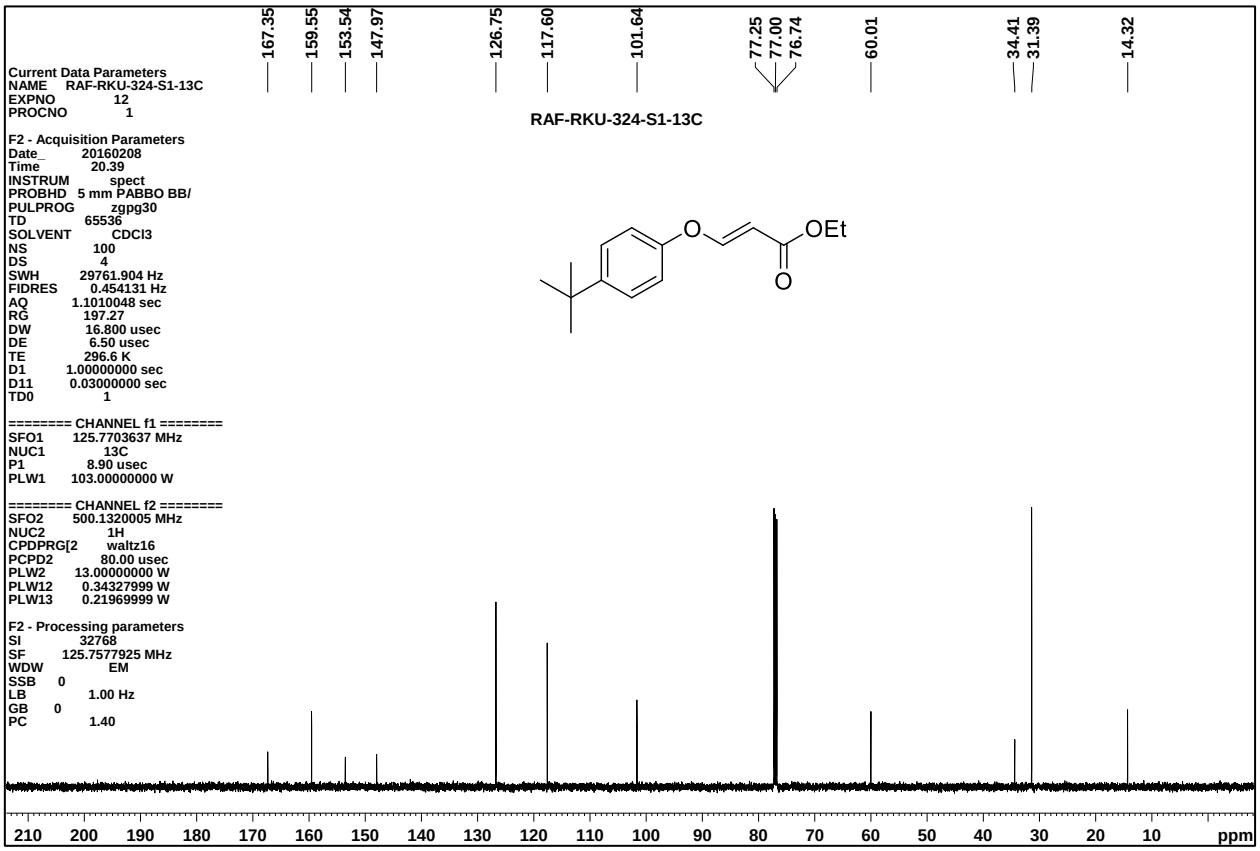
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3b**



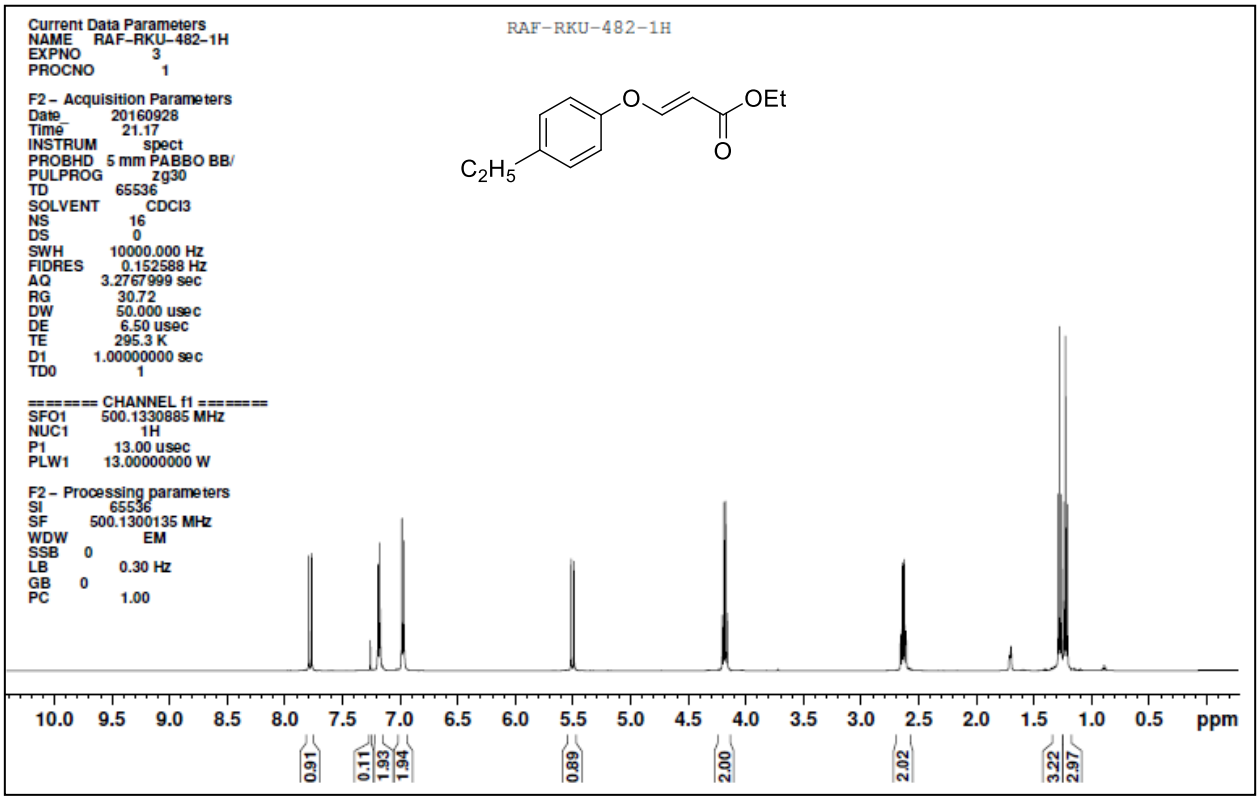


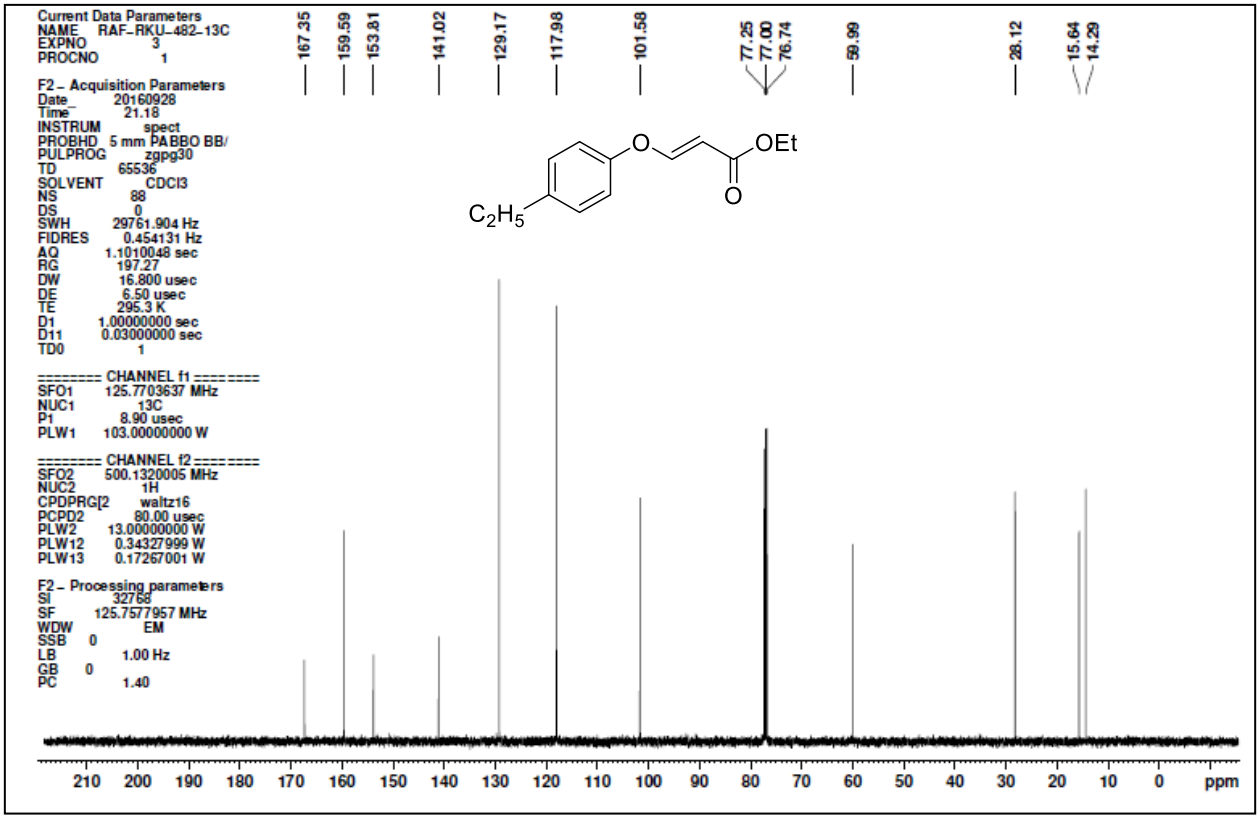
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3c**



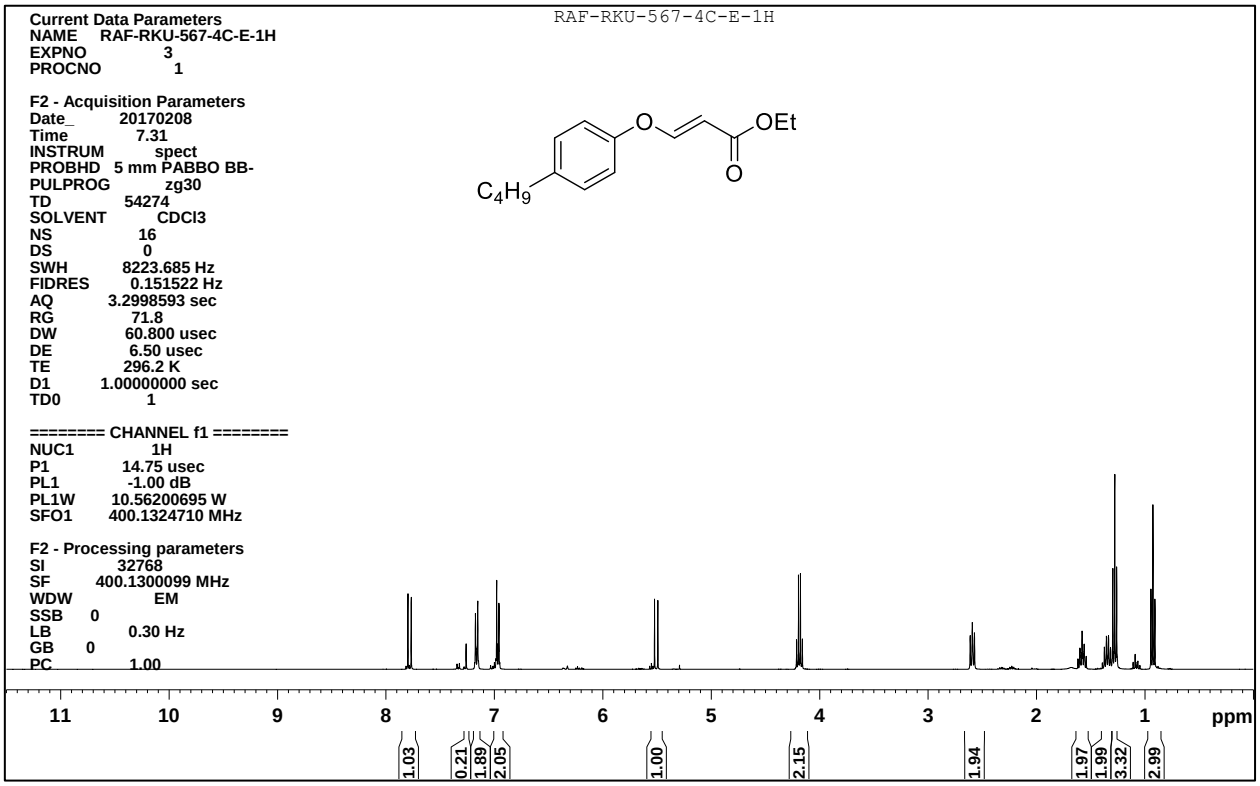


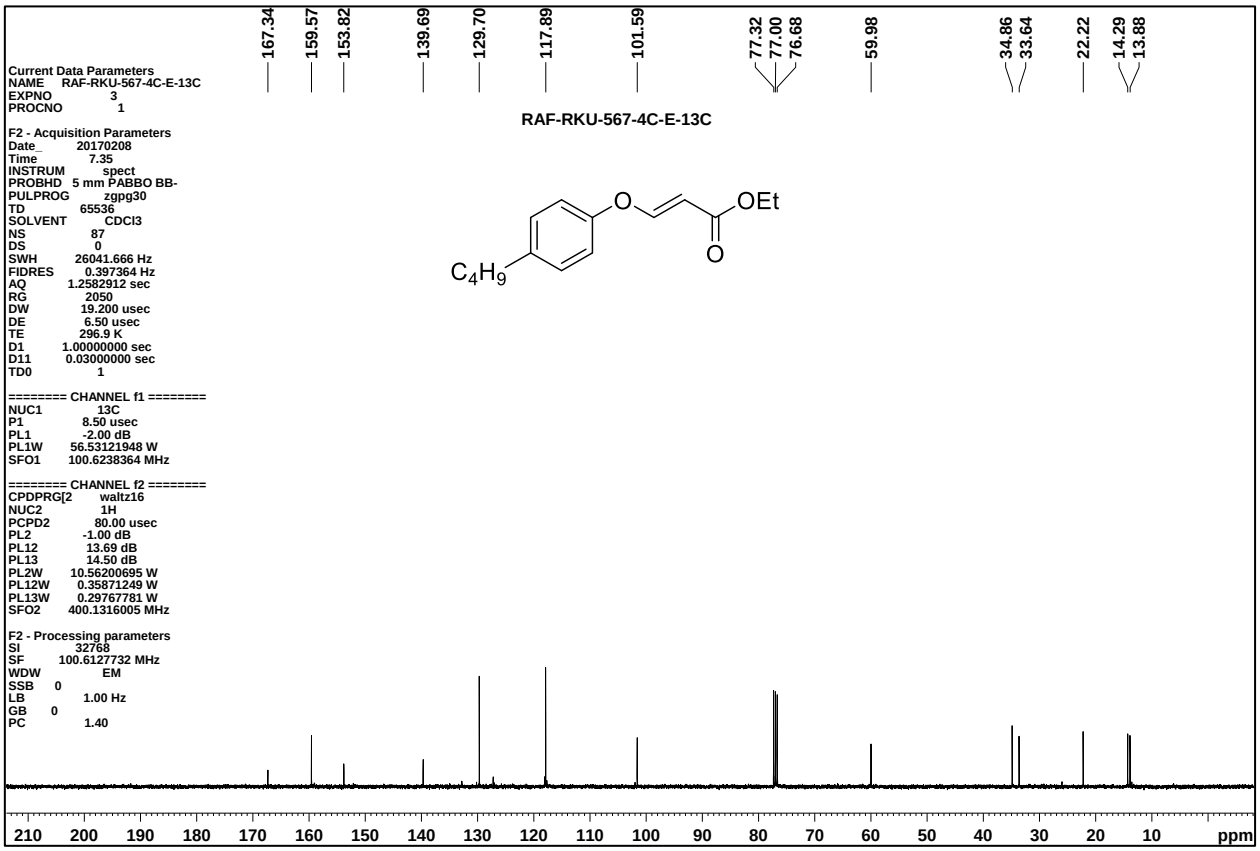
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3d**



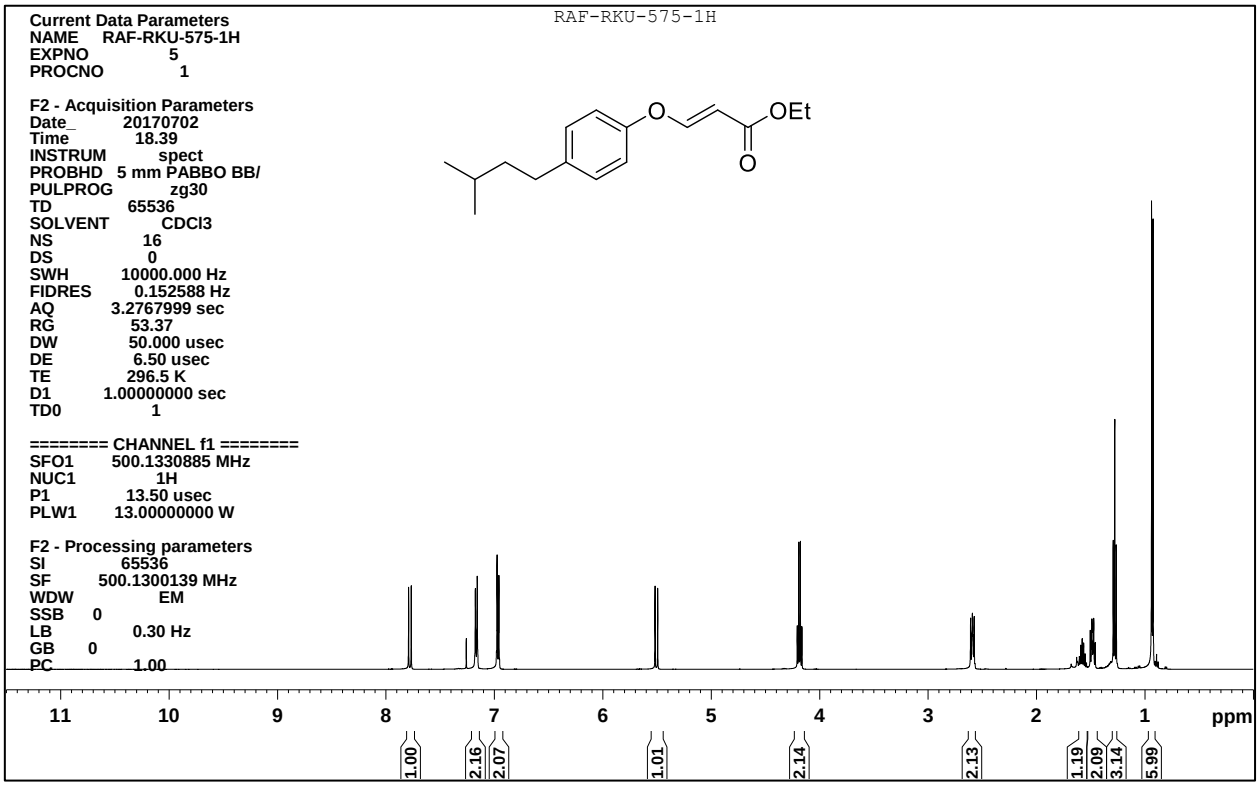


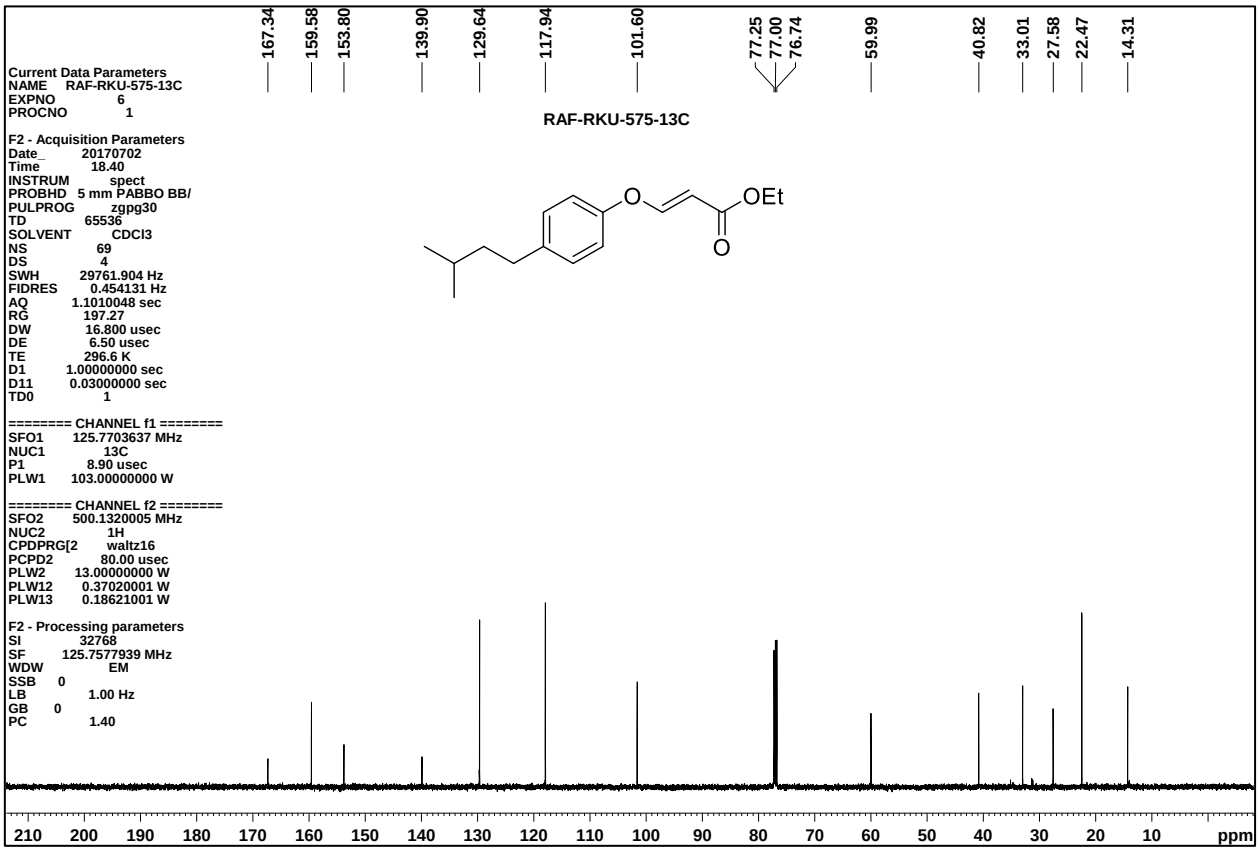
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3e**



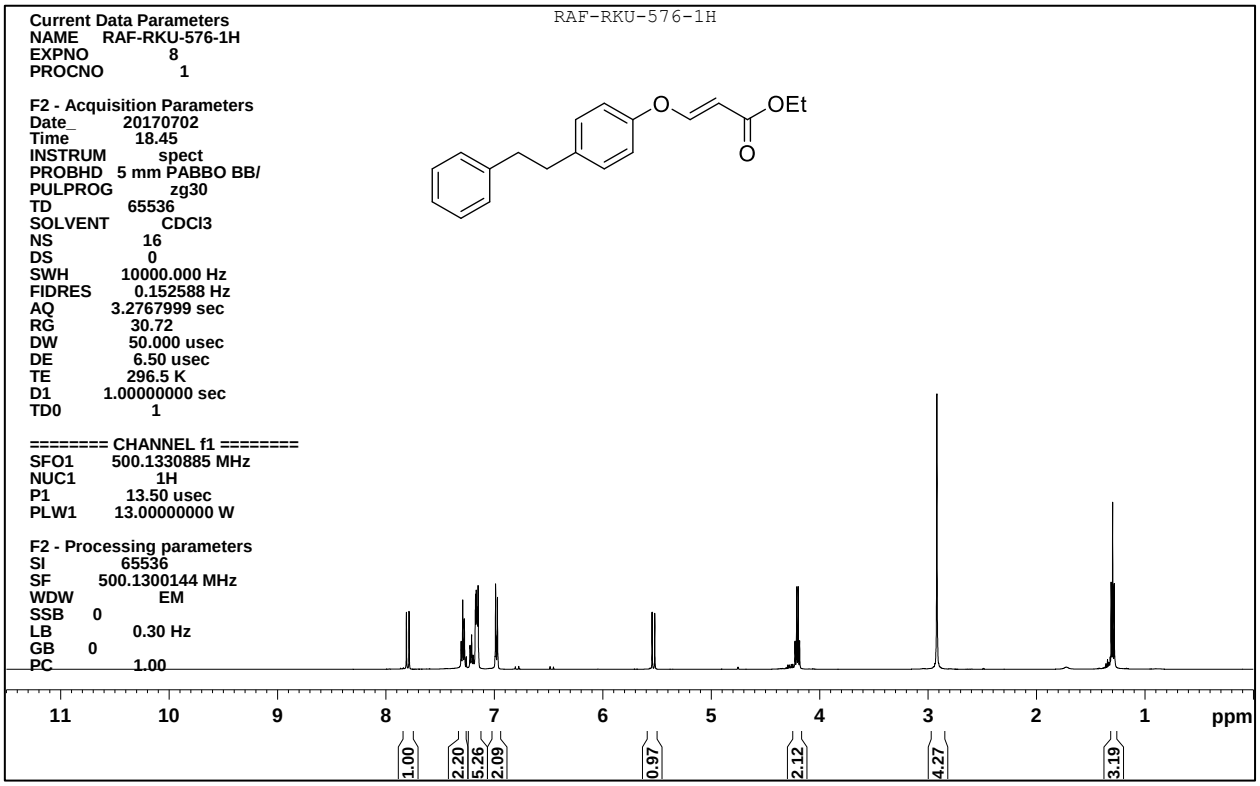


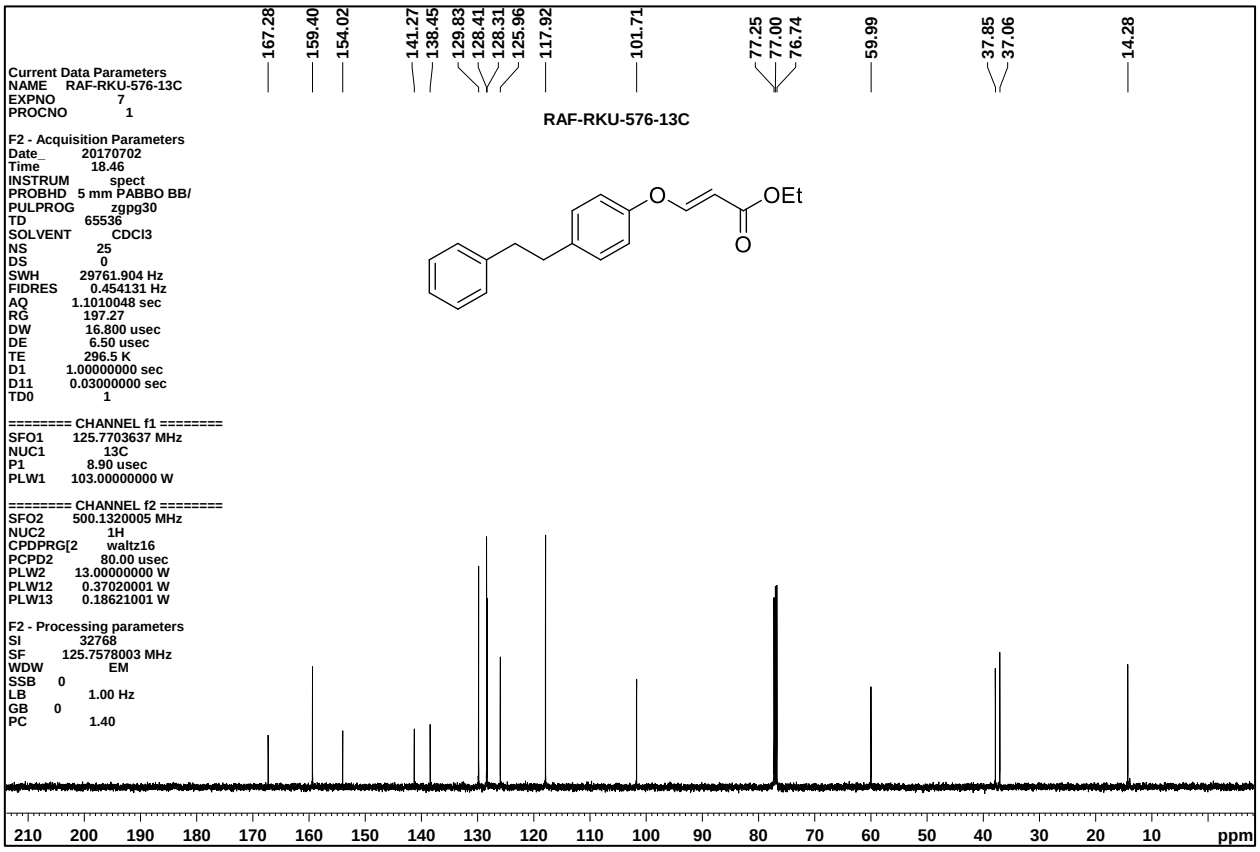
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3f**



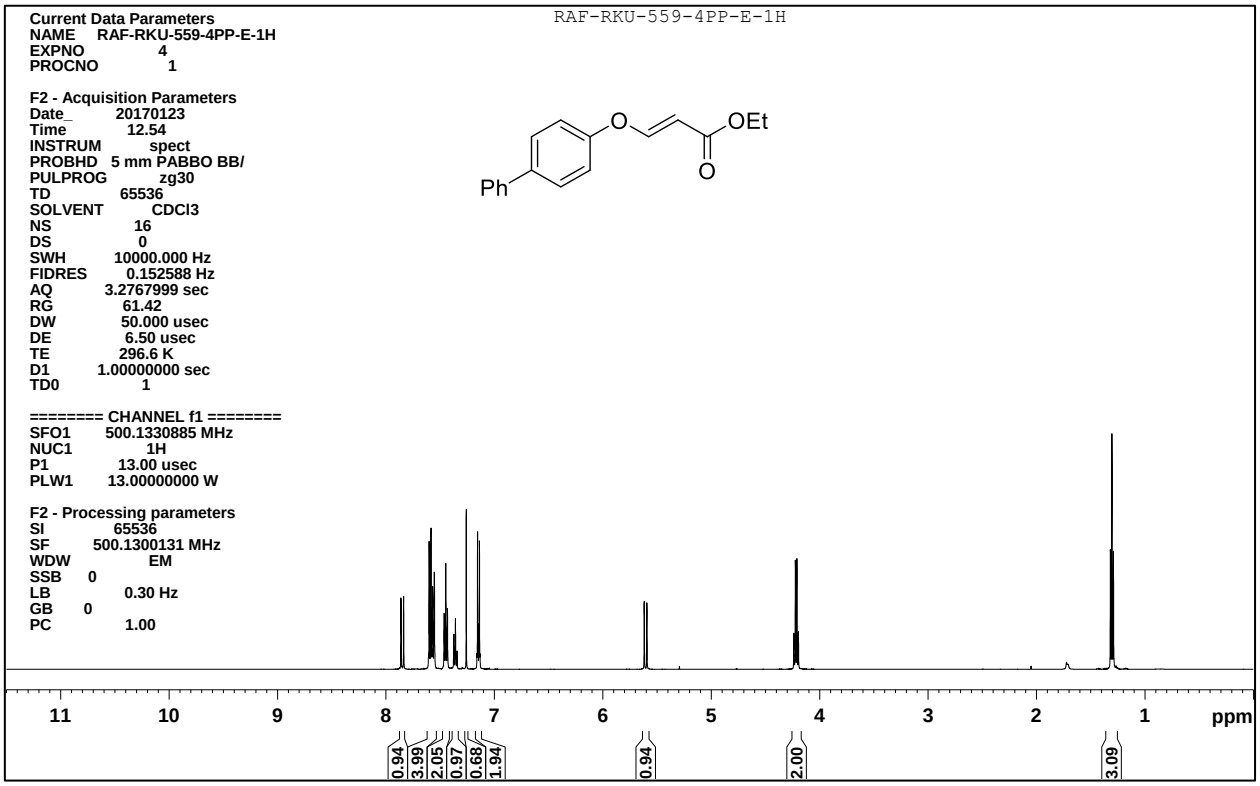


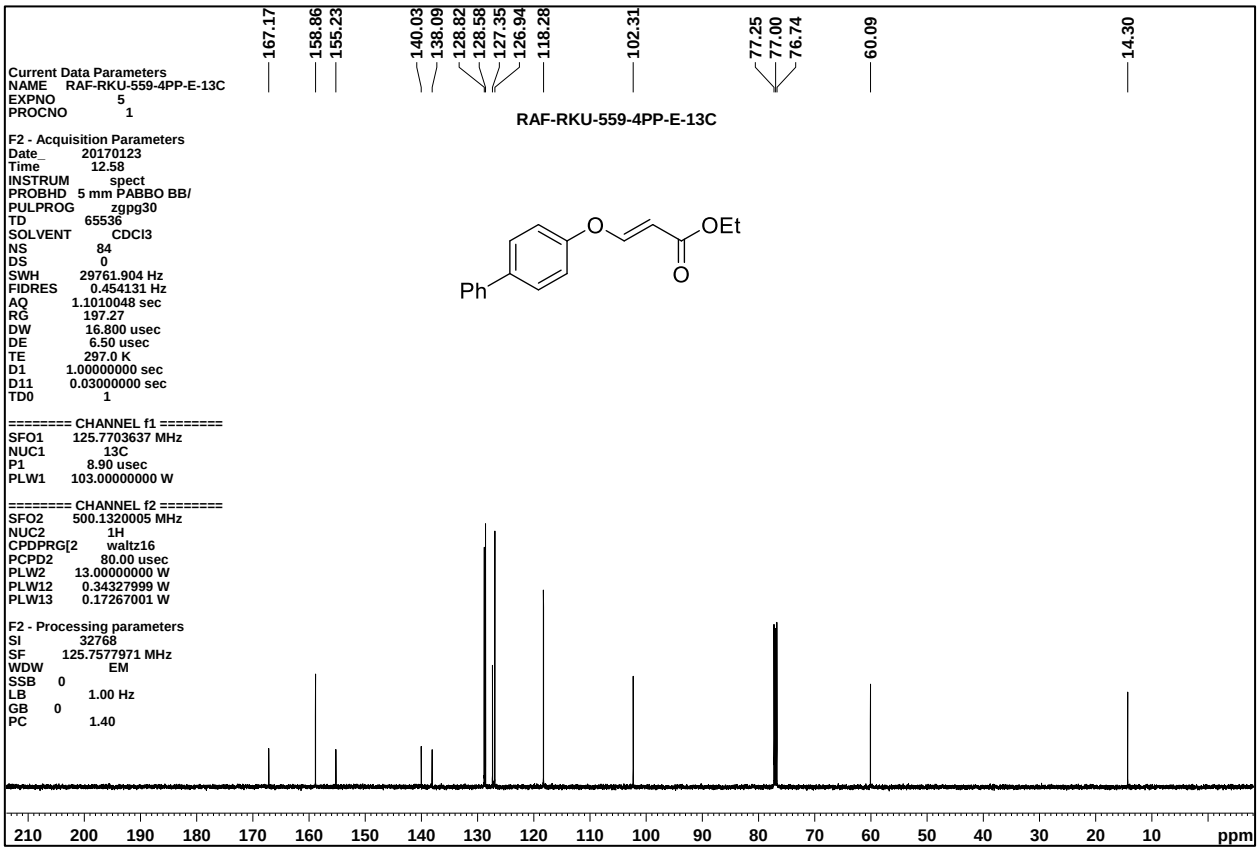
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3g**



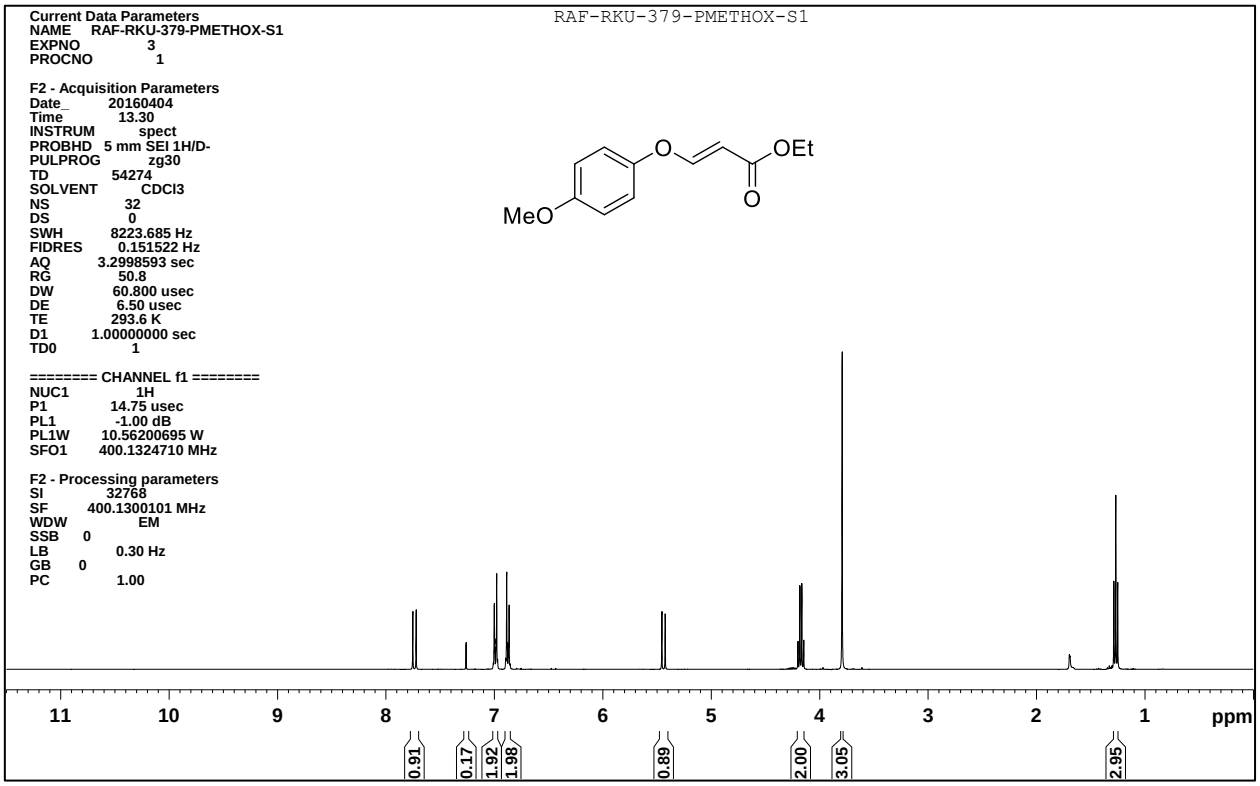


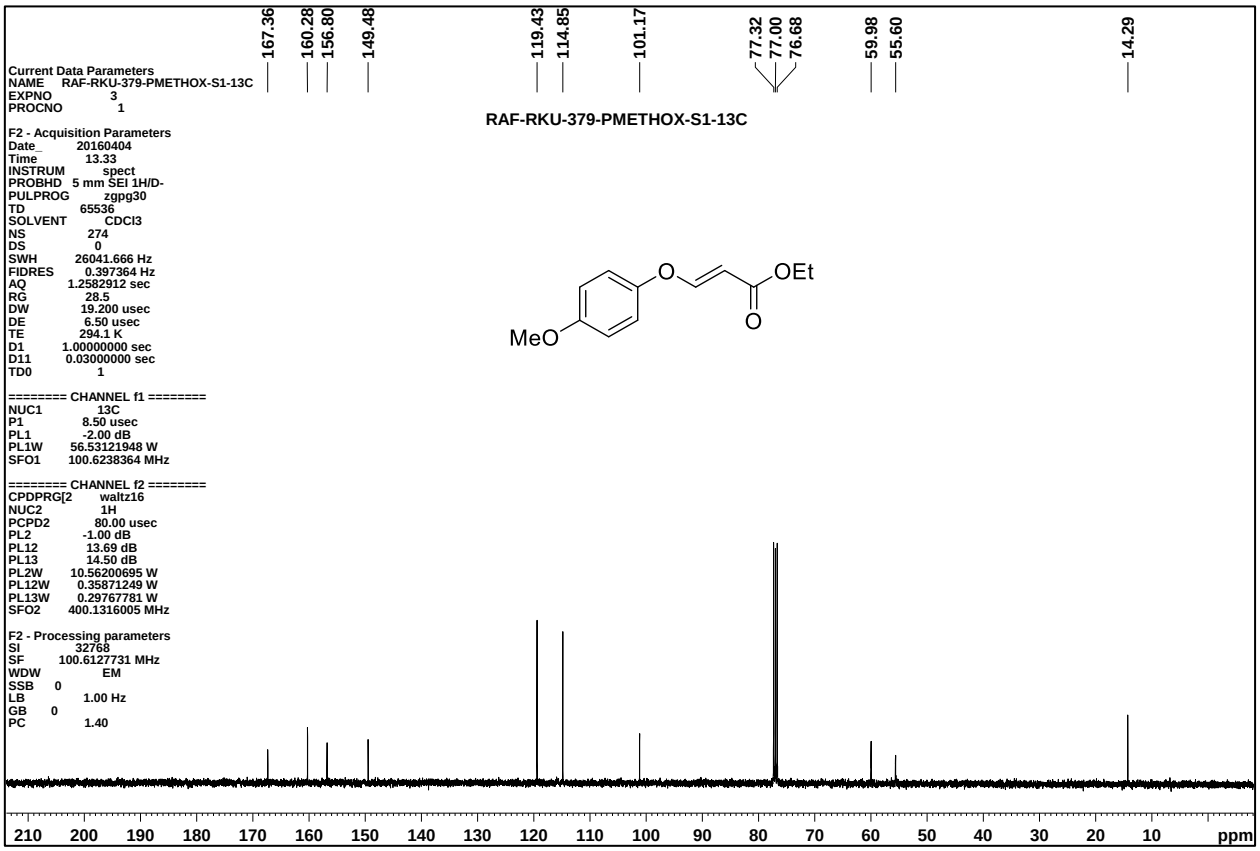
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3h**



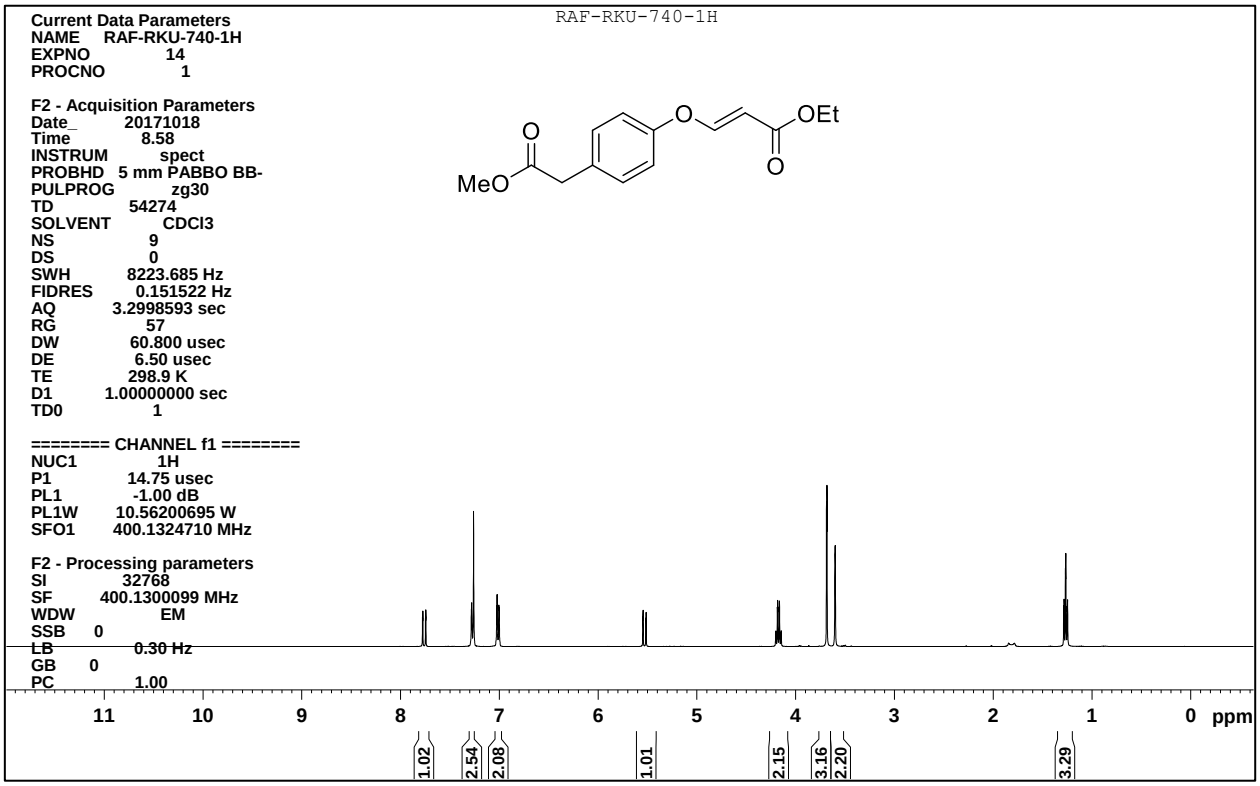


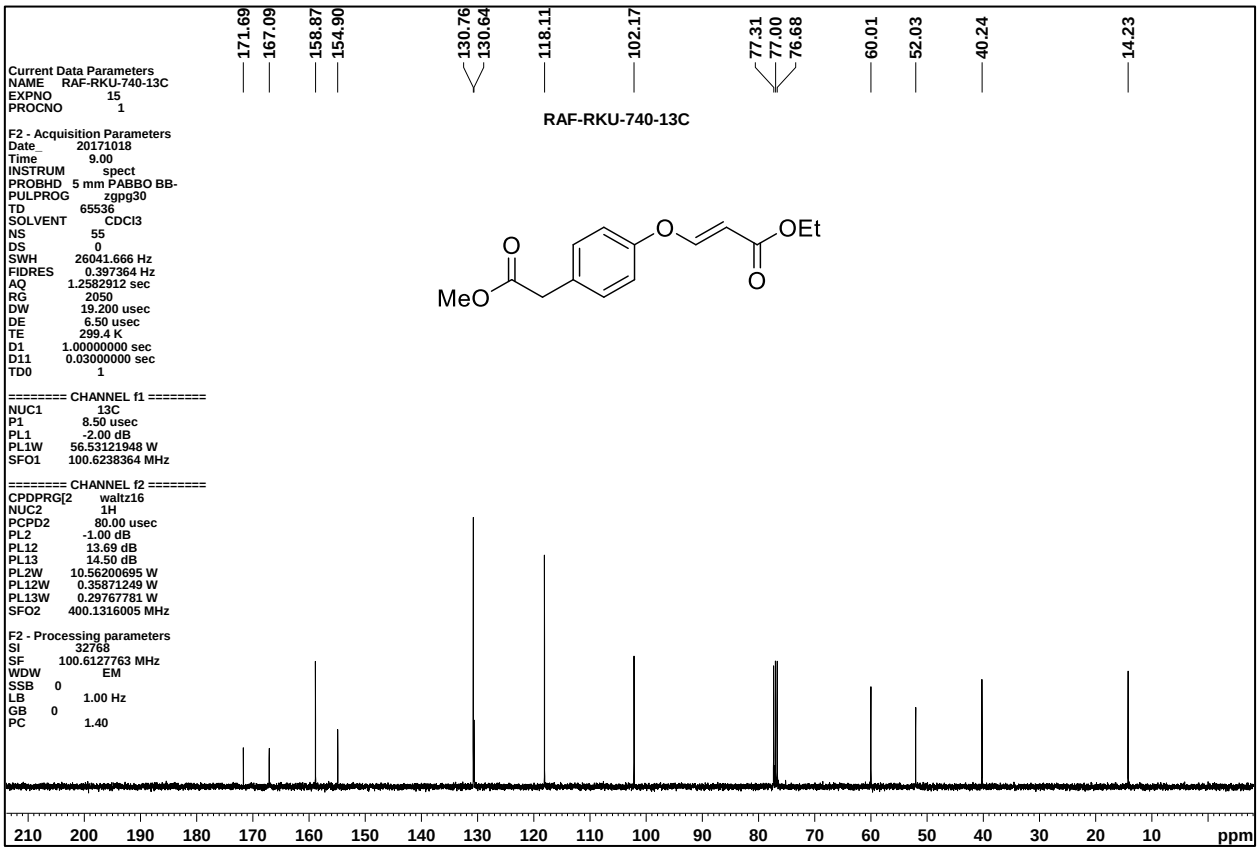
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3i**



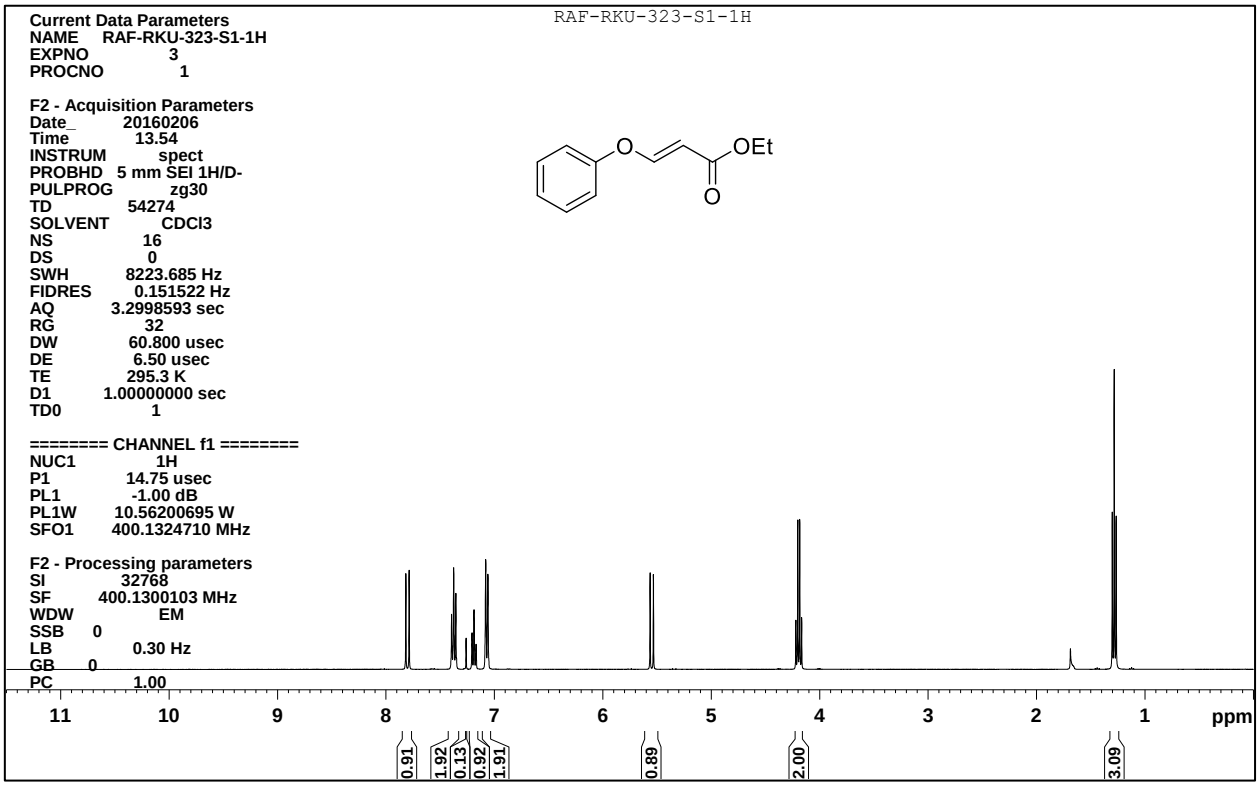


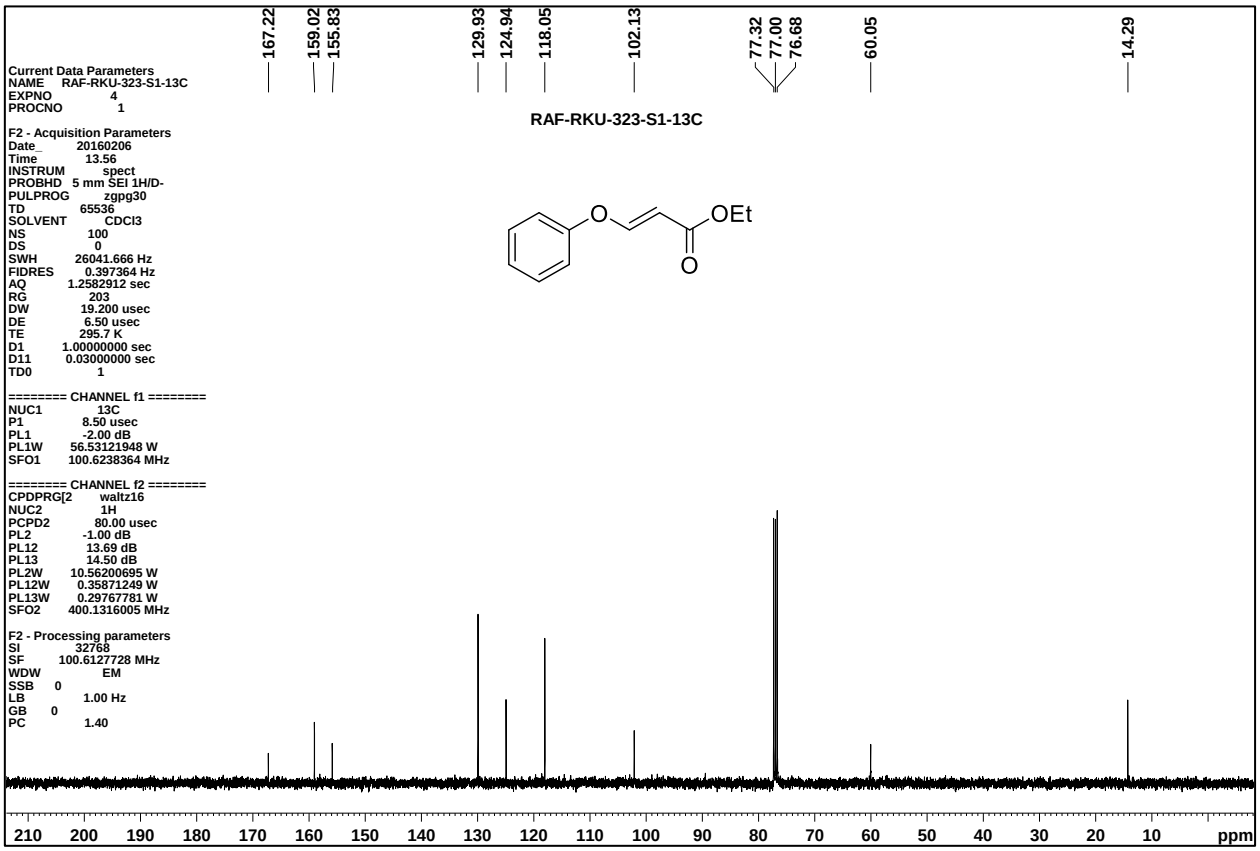
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3j**



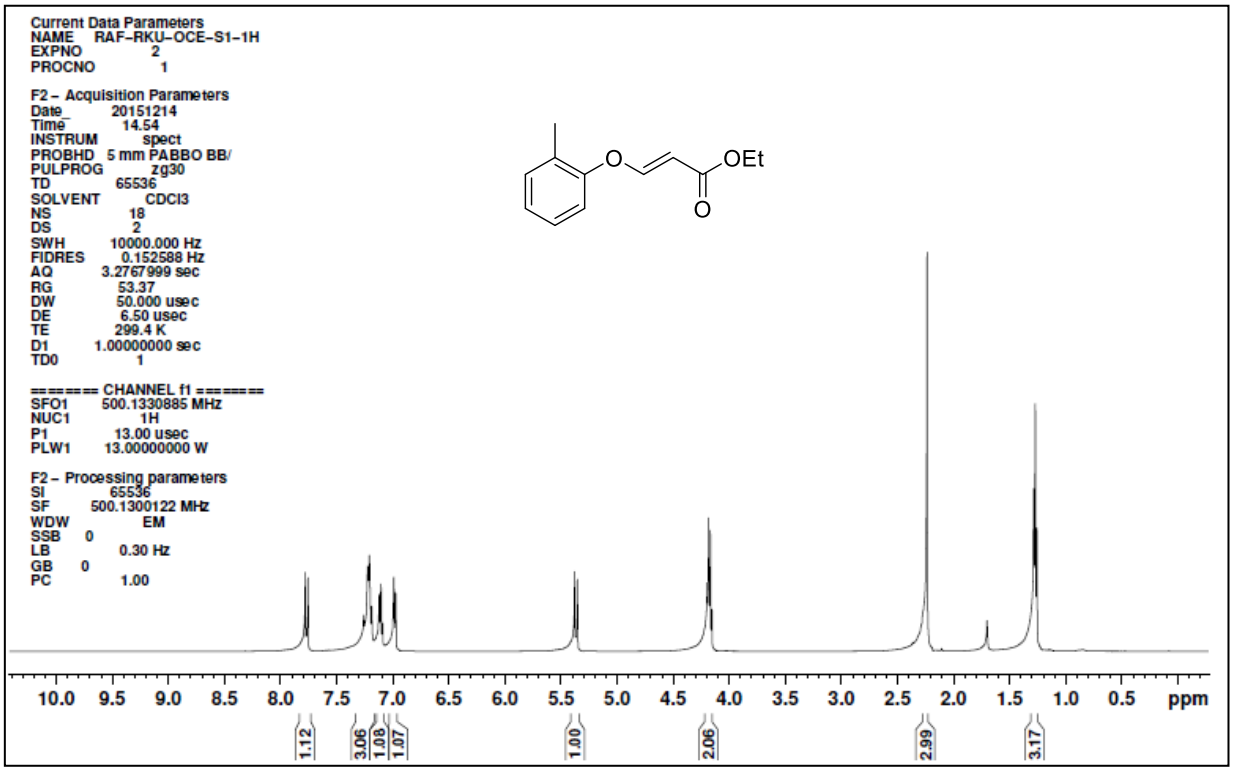


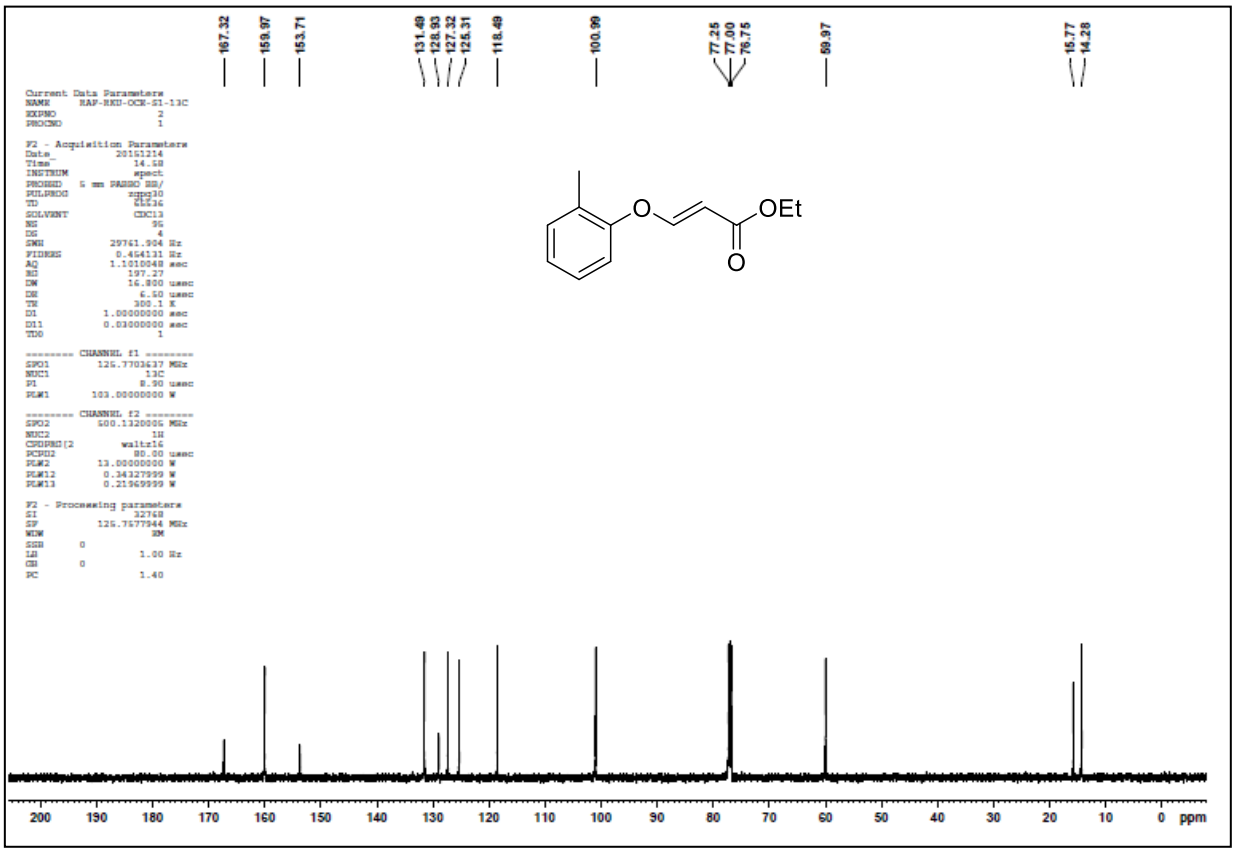
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3k**



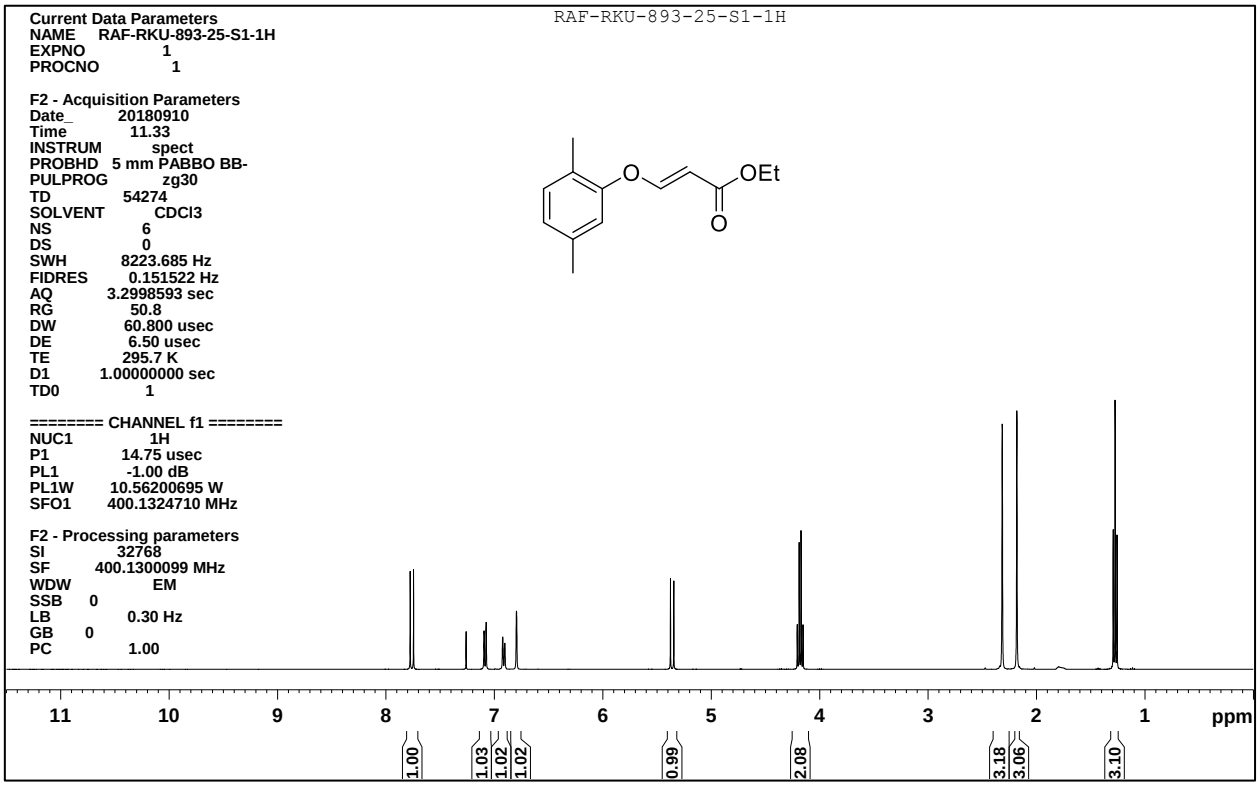


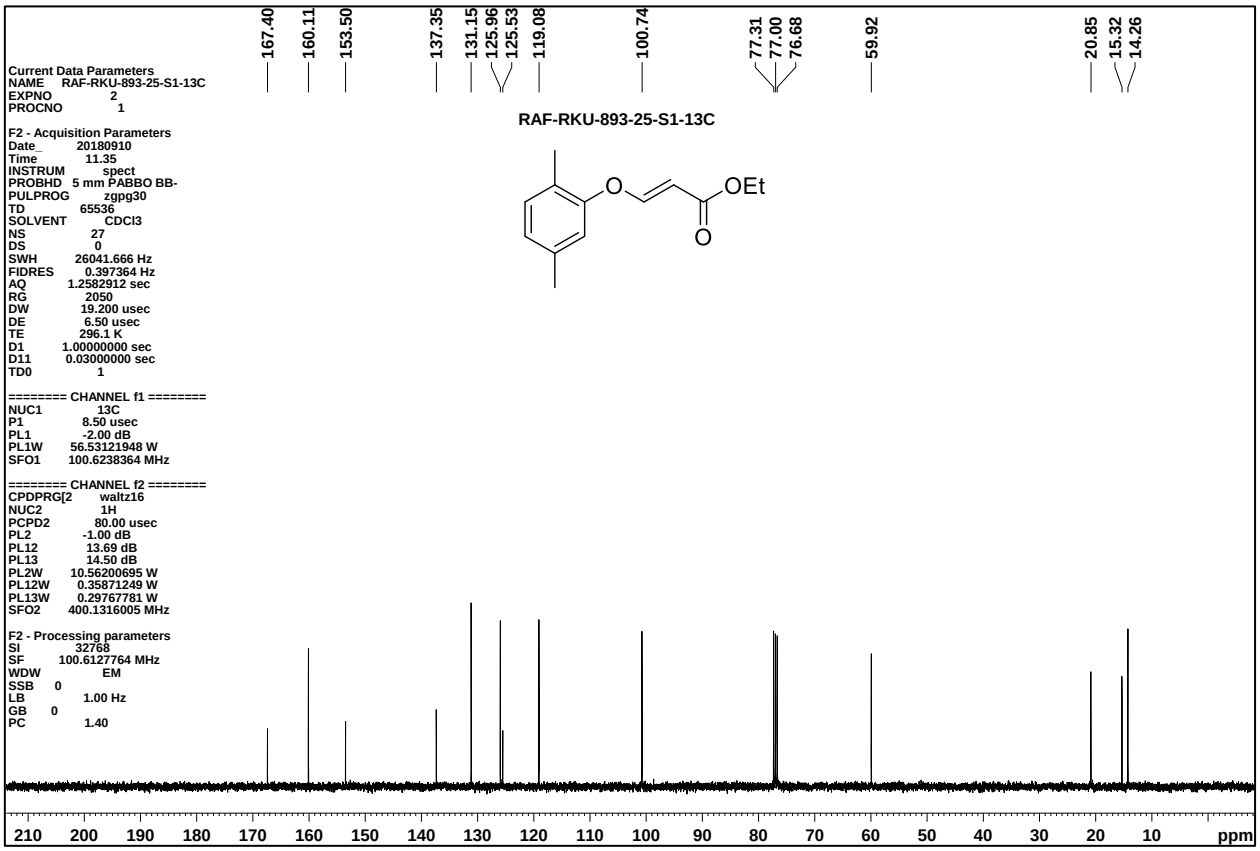
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3l**



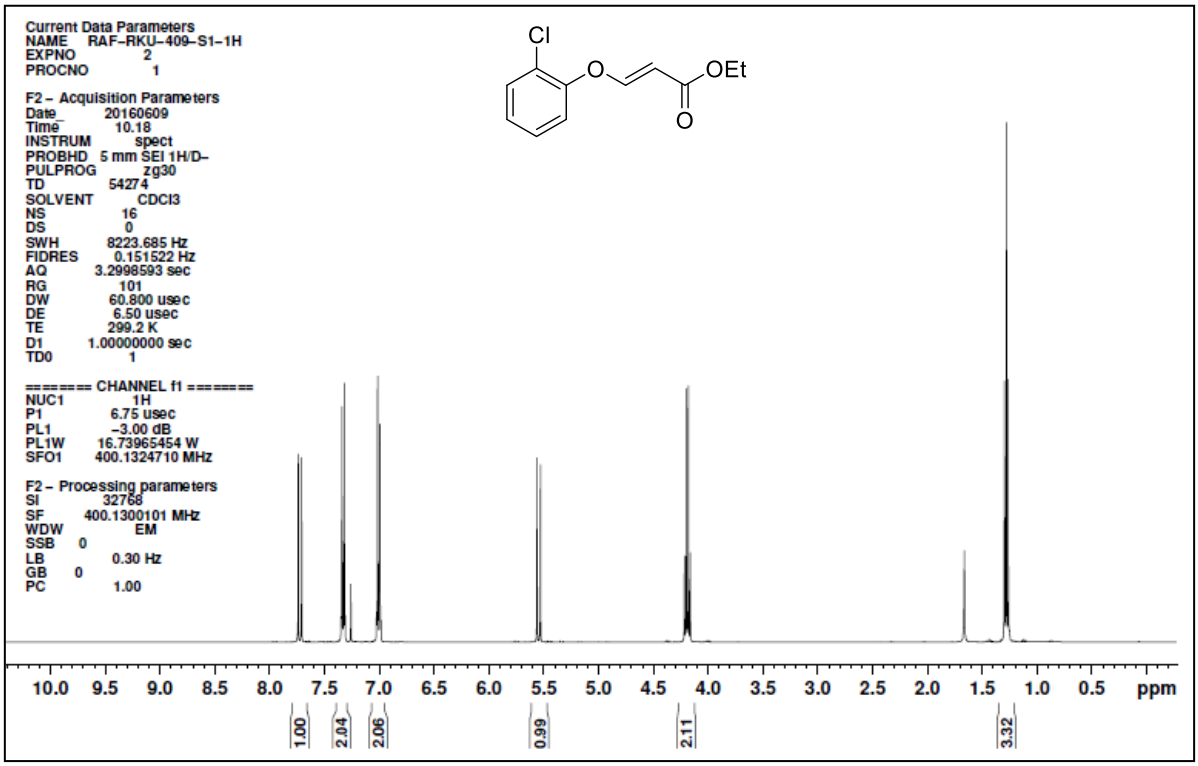


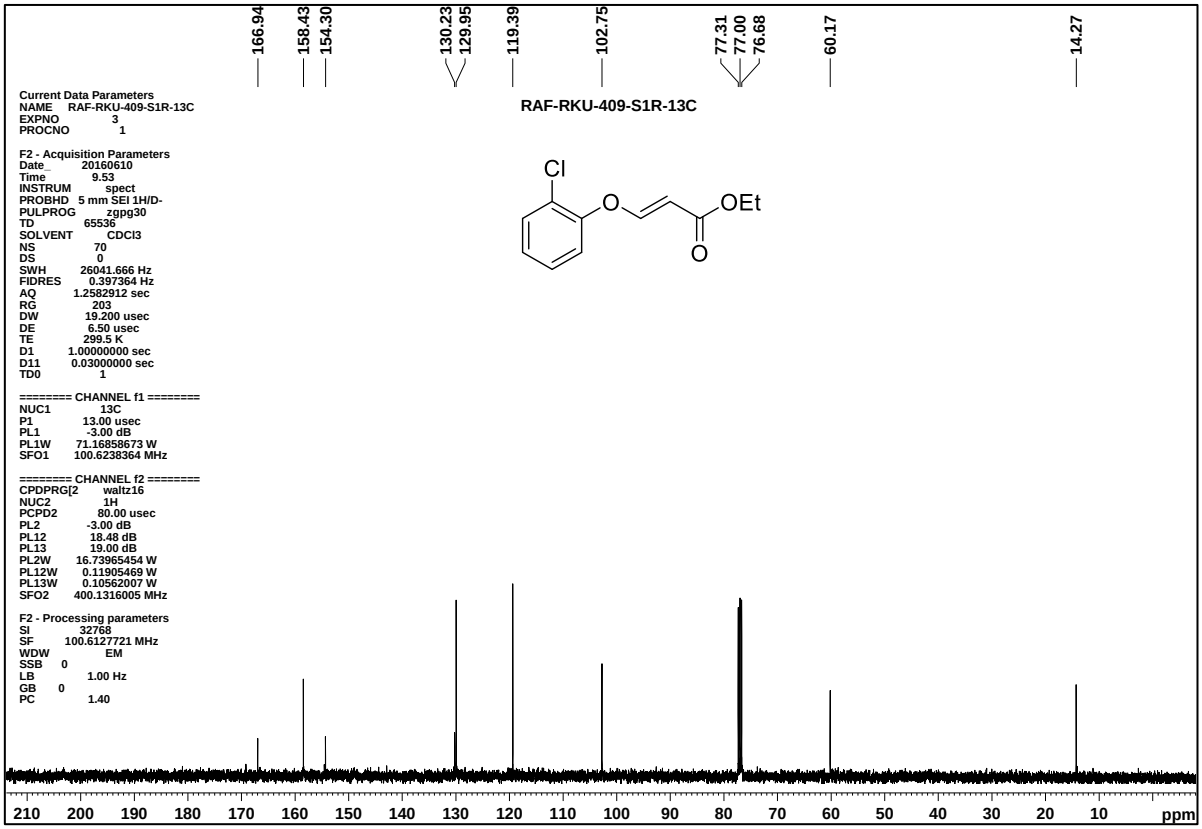
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3m**



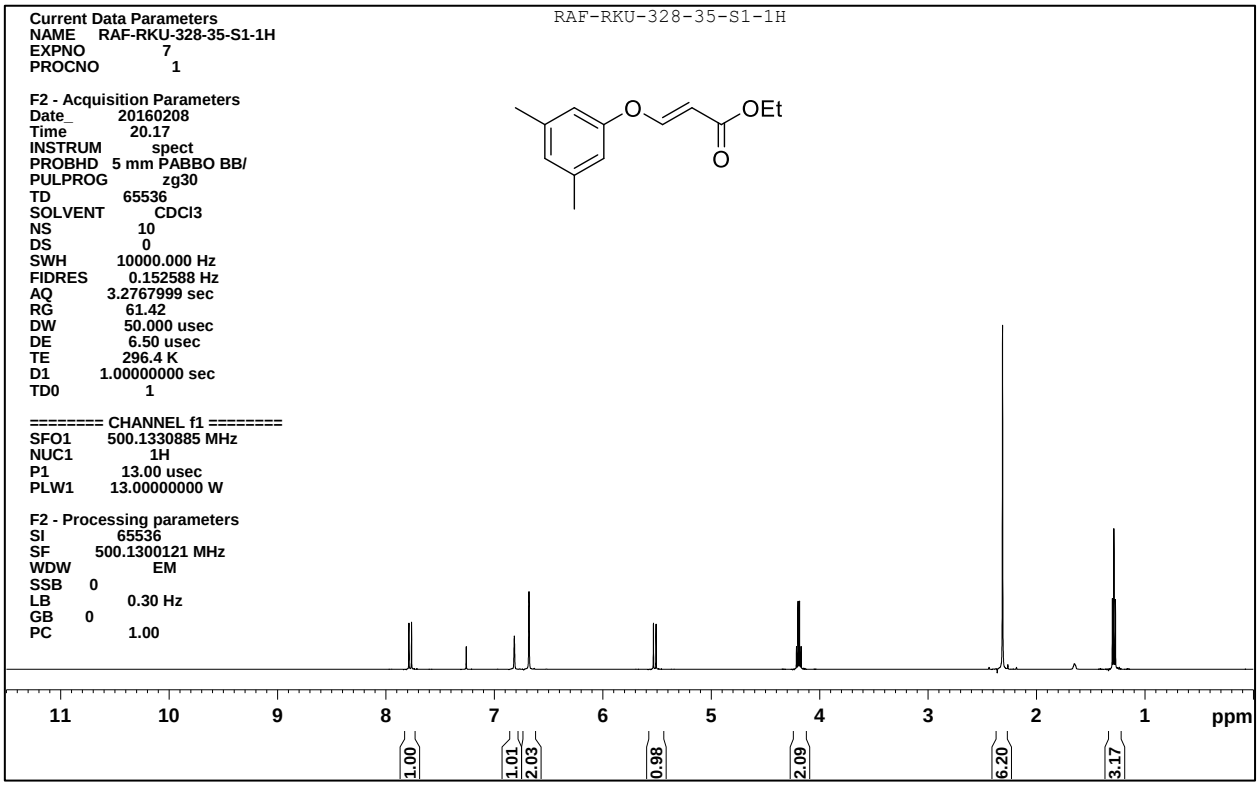


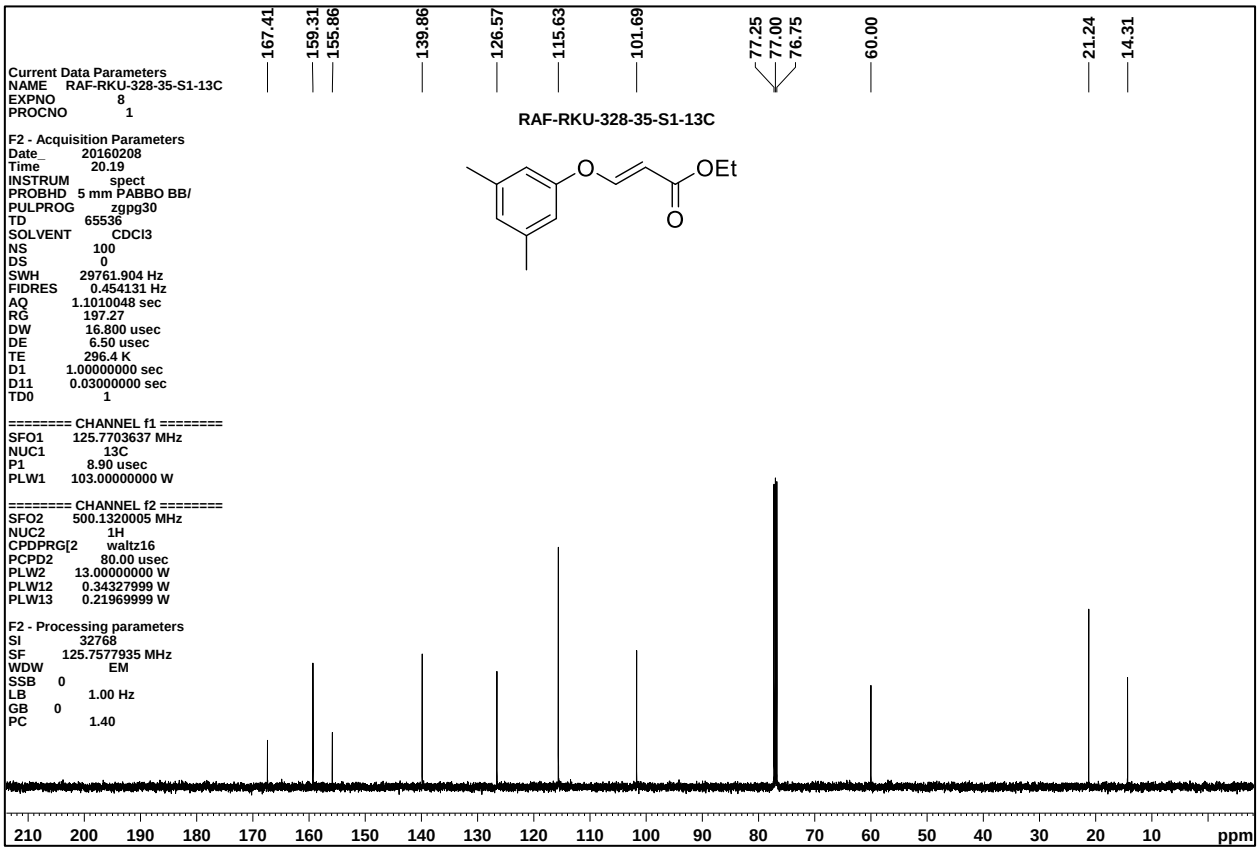
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3n**



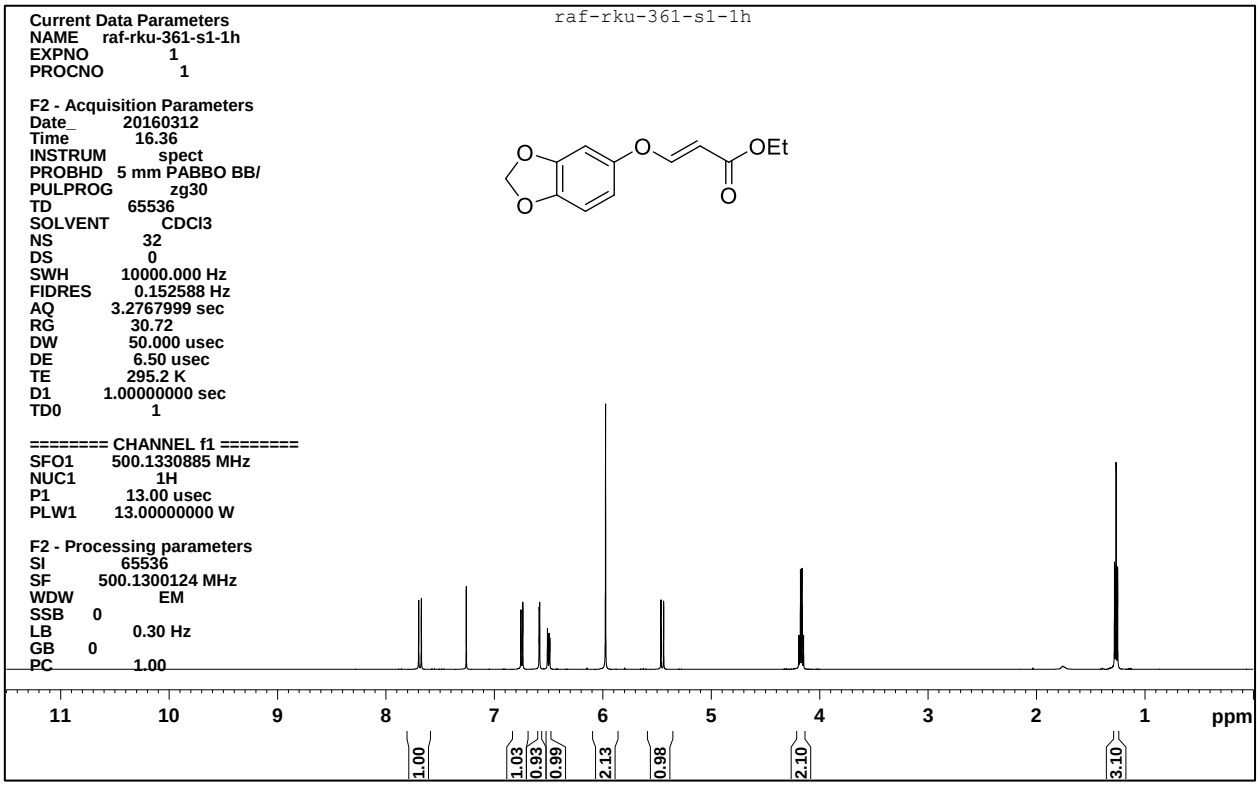


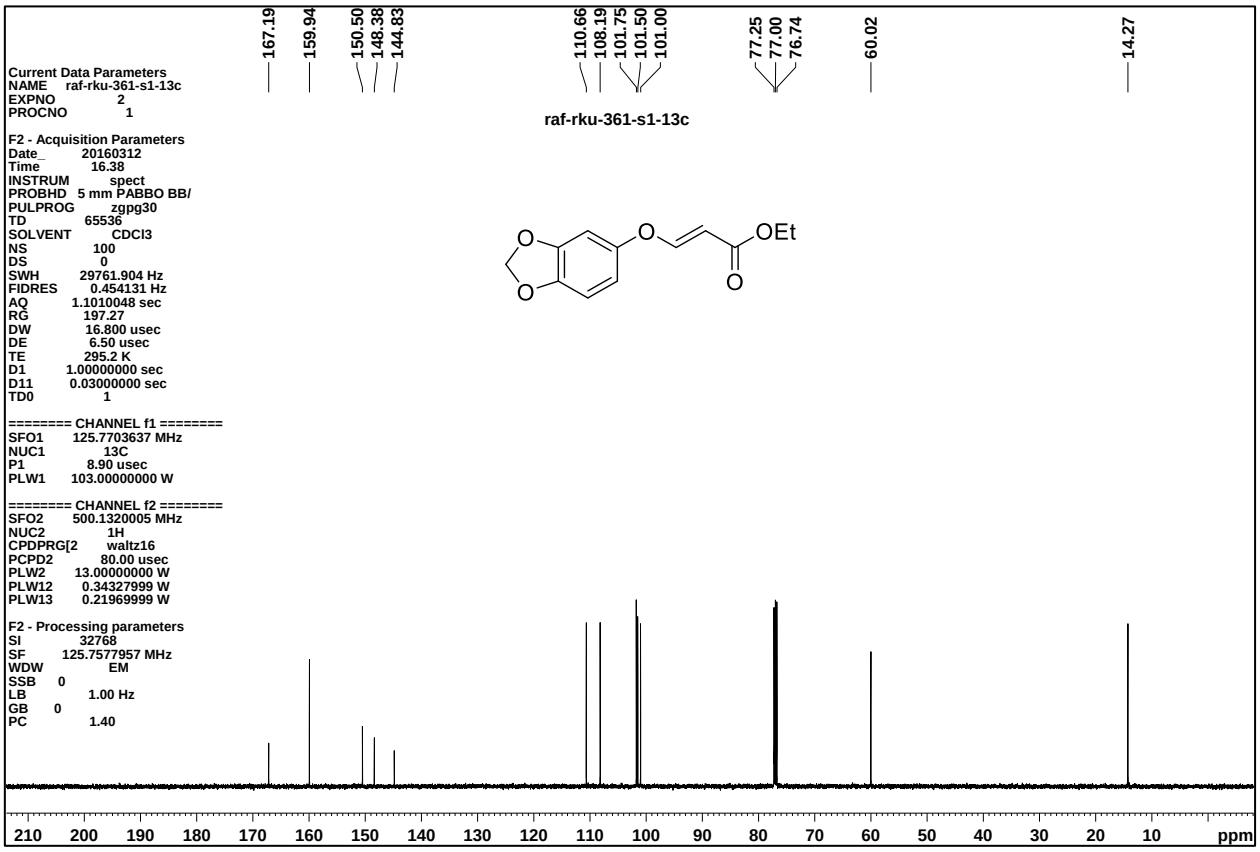
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3o**



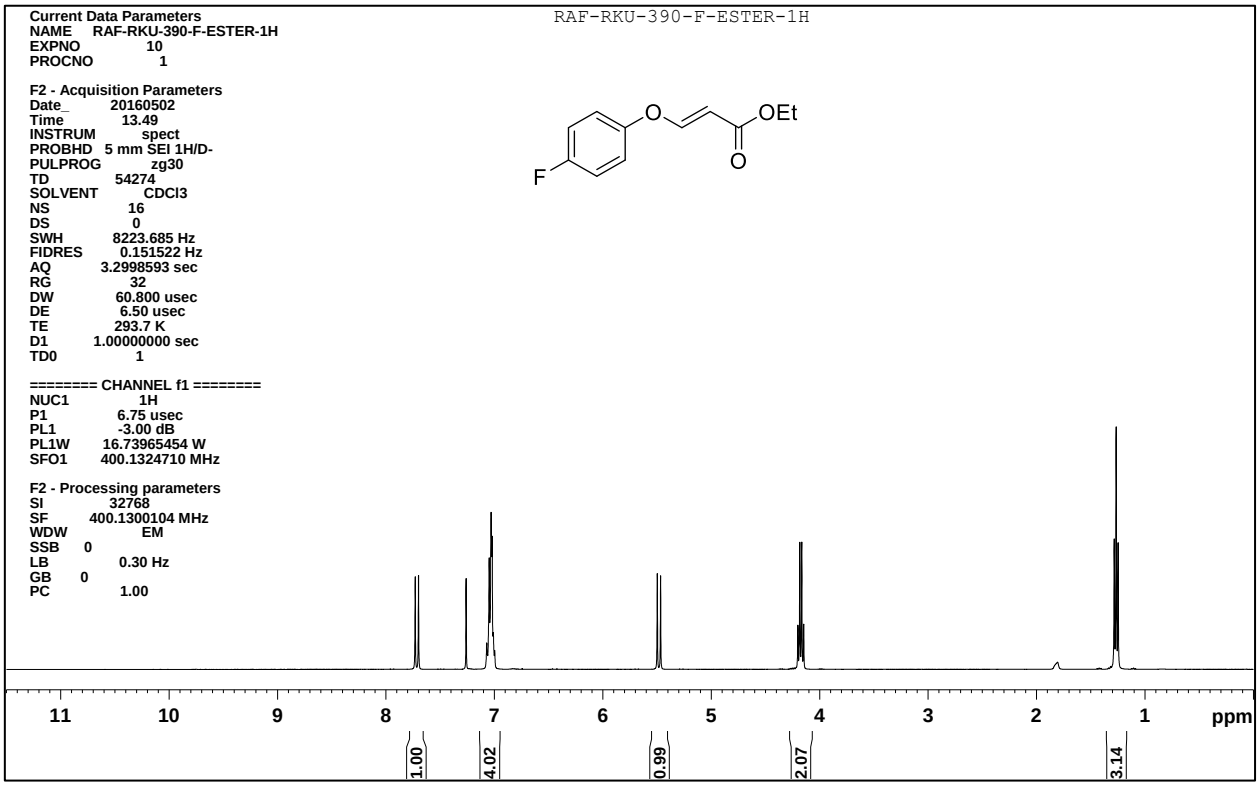


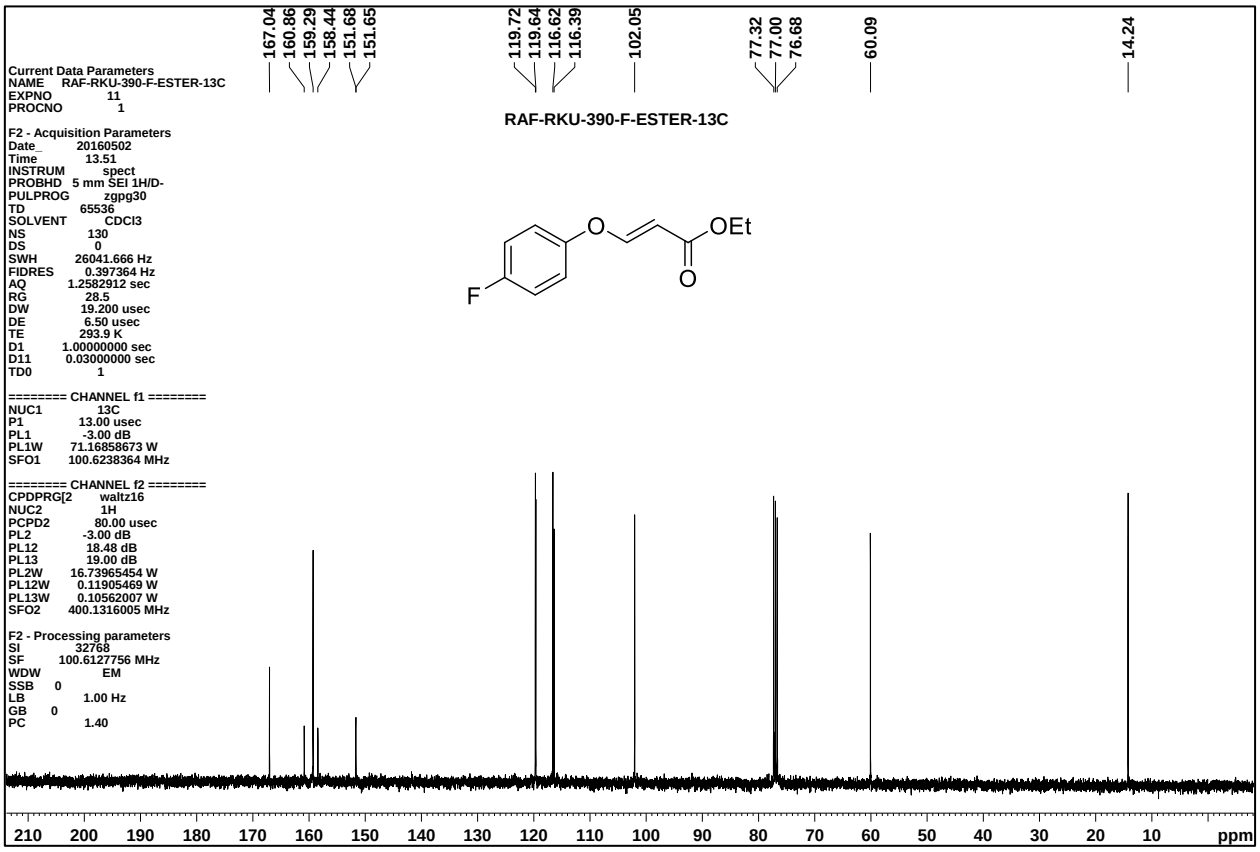
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3p**



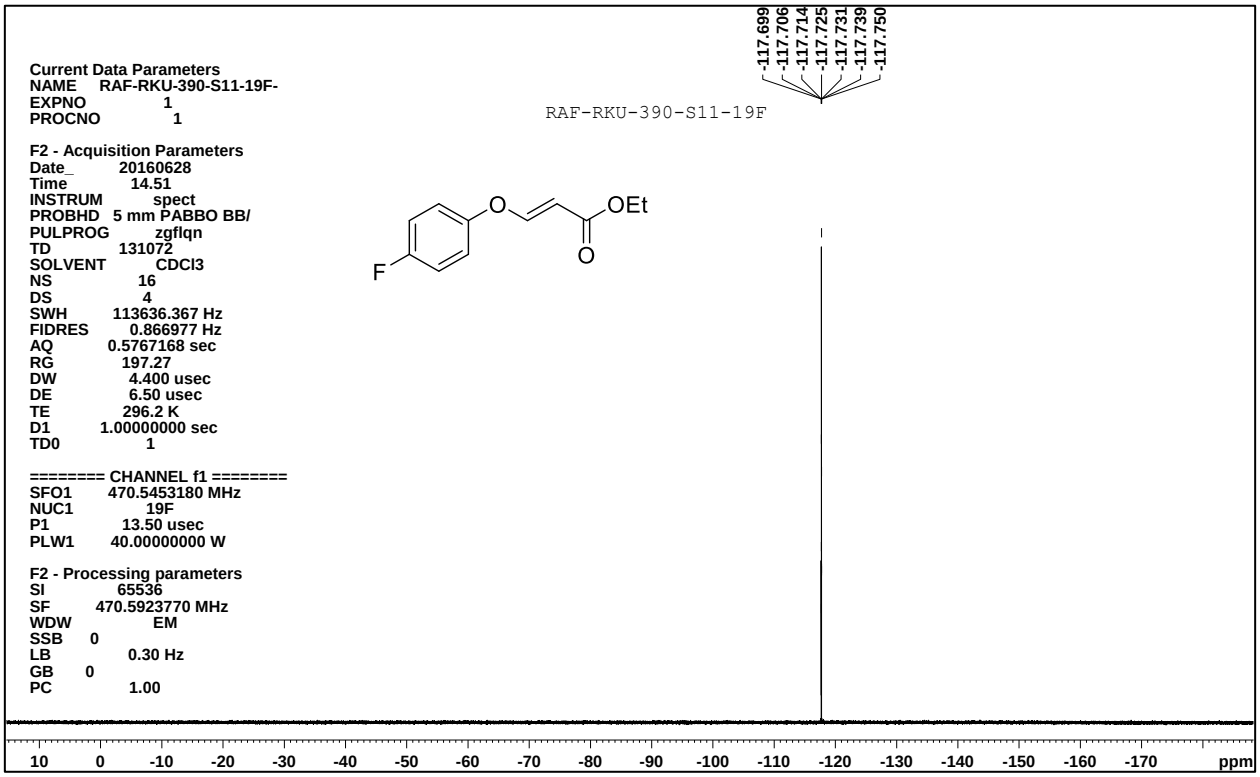


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3q**

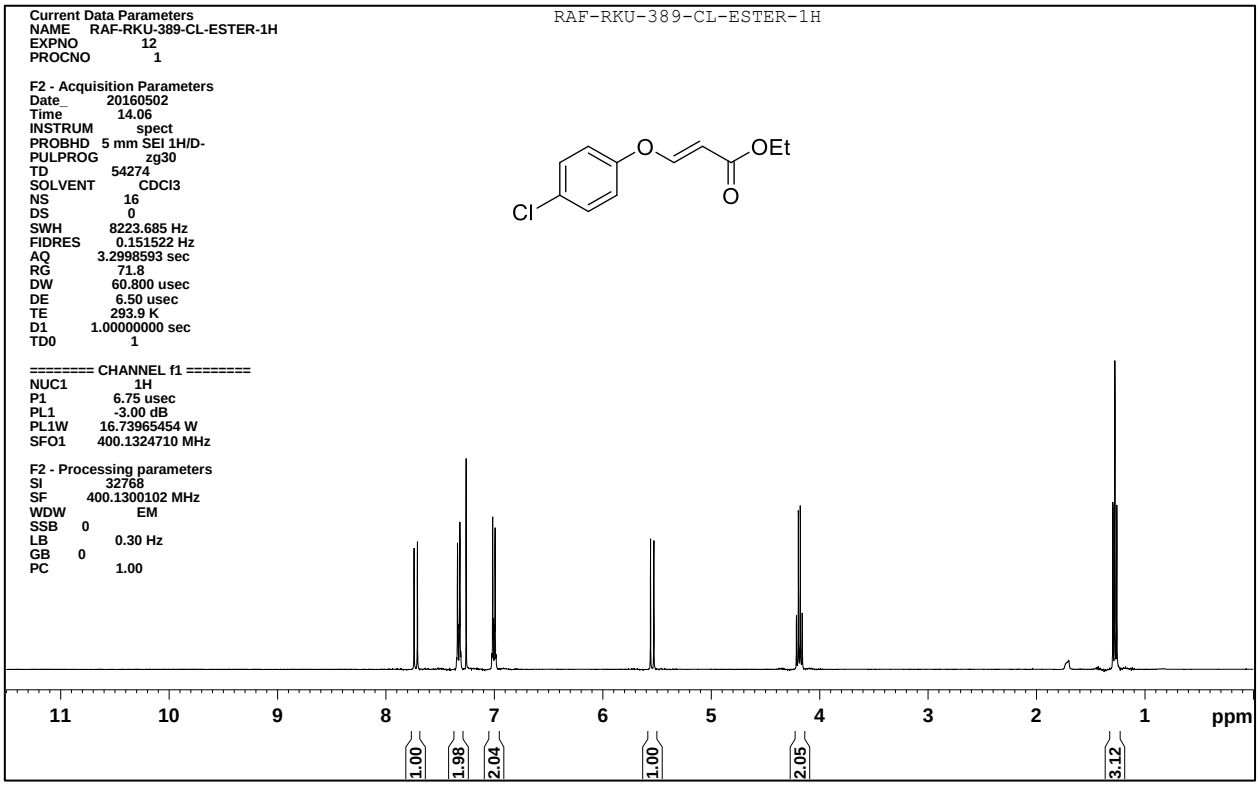


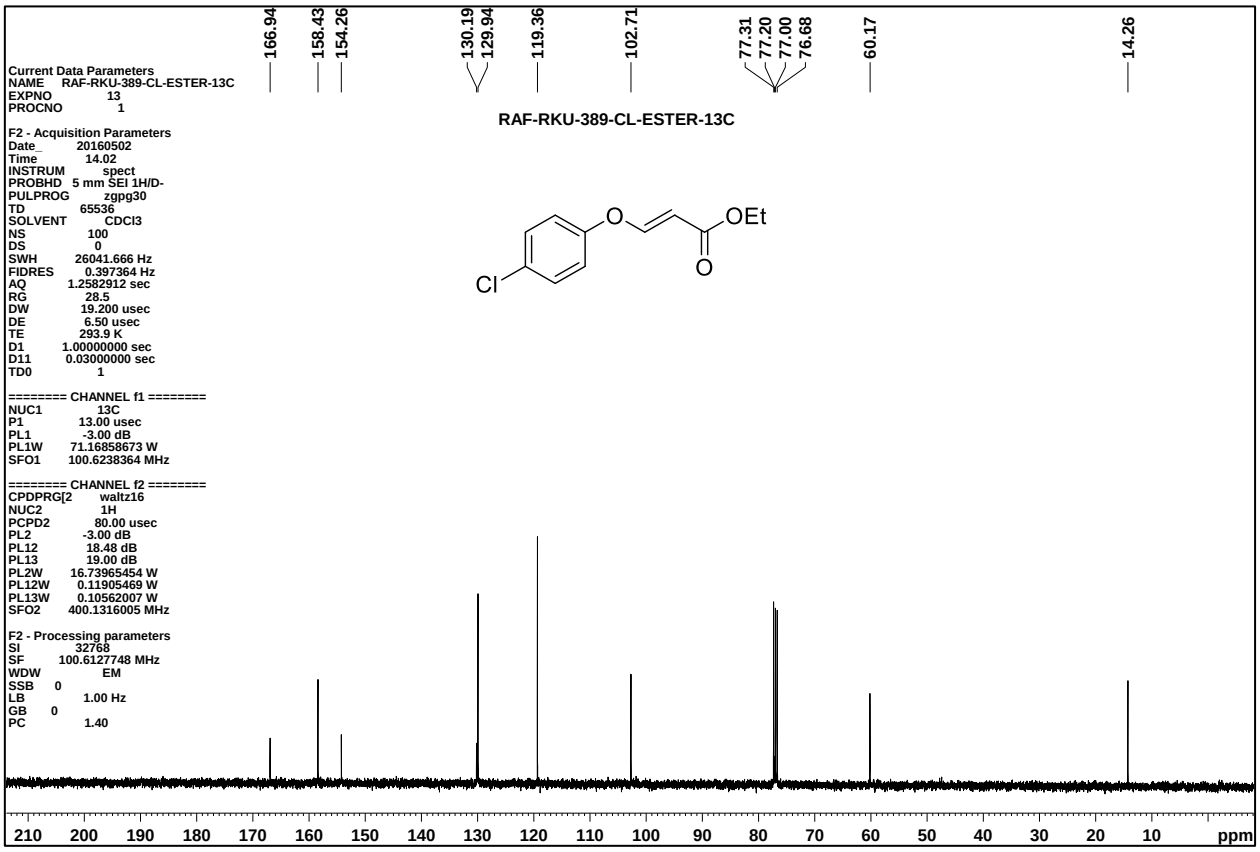


^{19}F NMR (470 MHz, $CDCl_3$) of (*E*)-**3q**

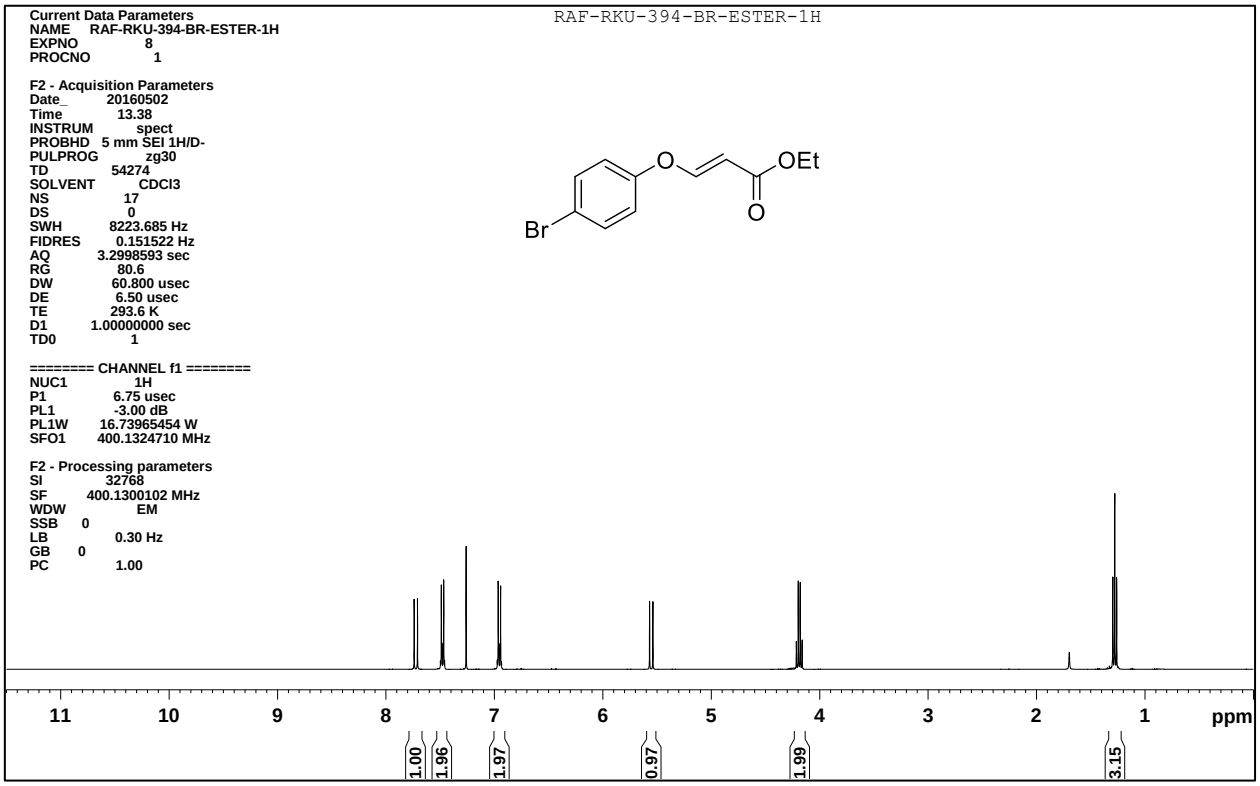


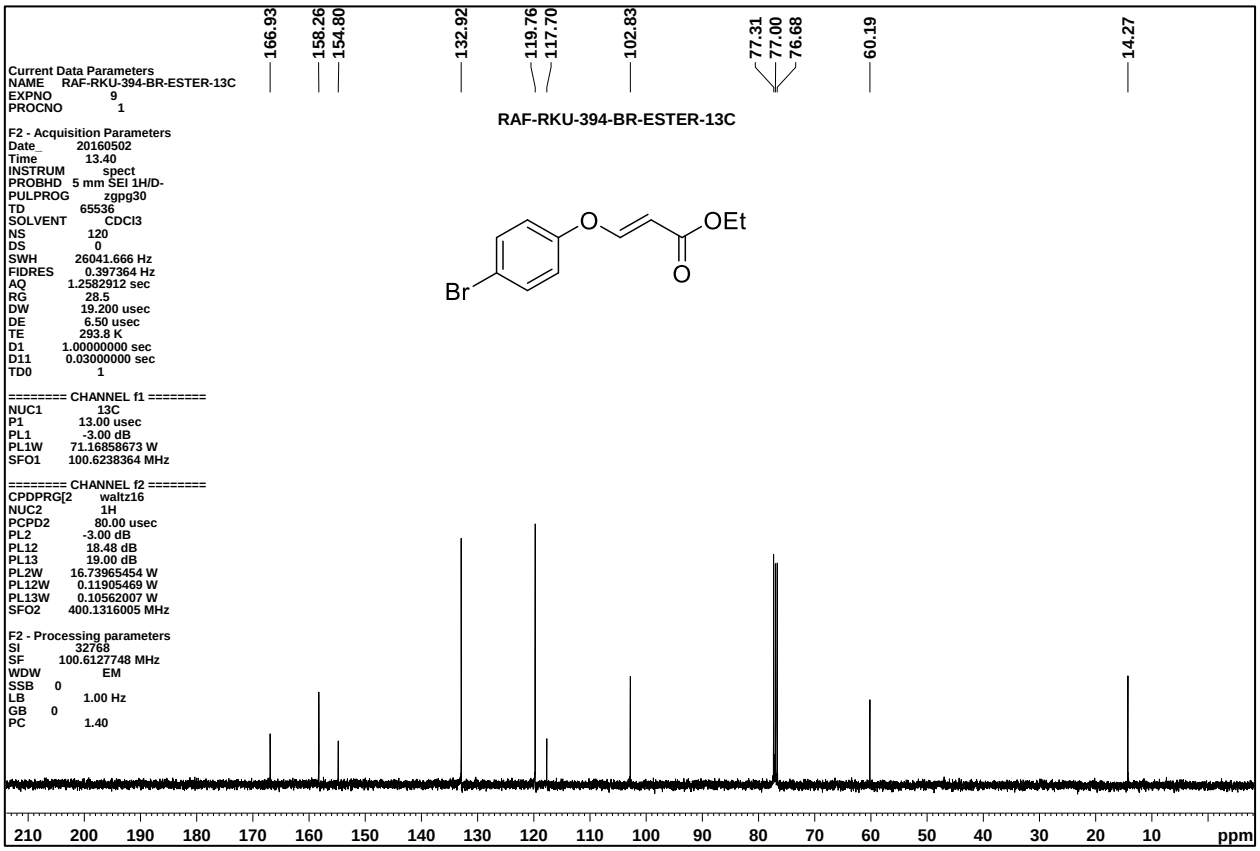
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3r**



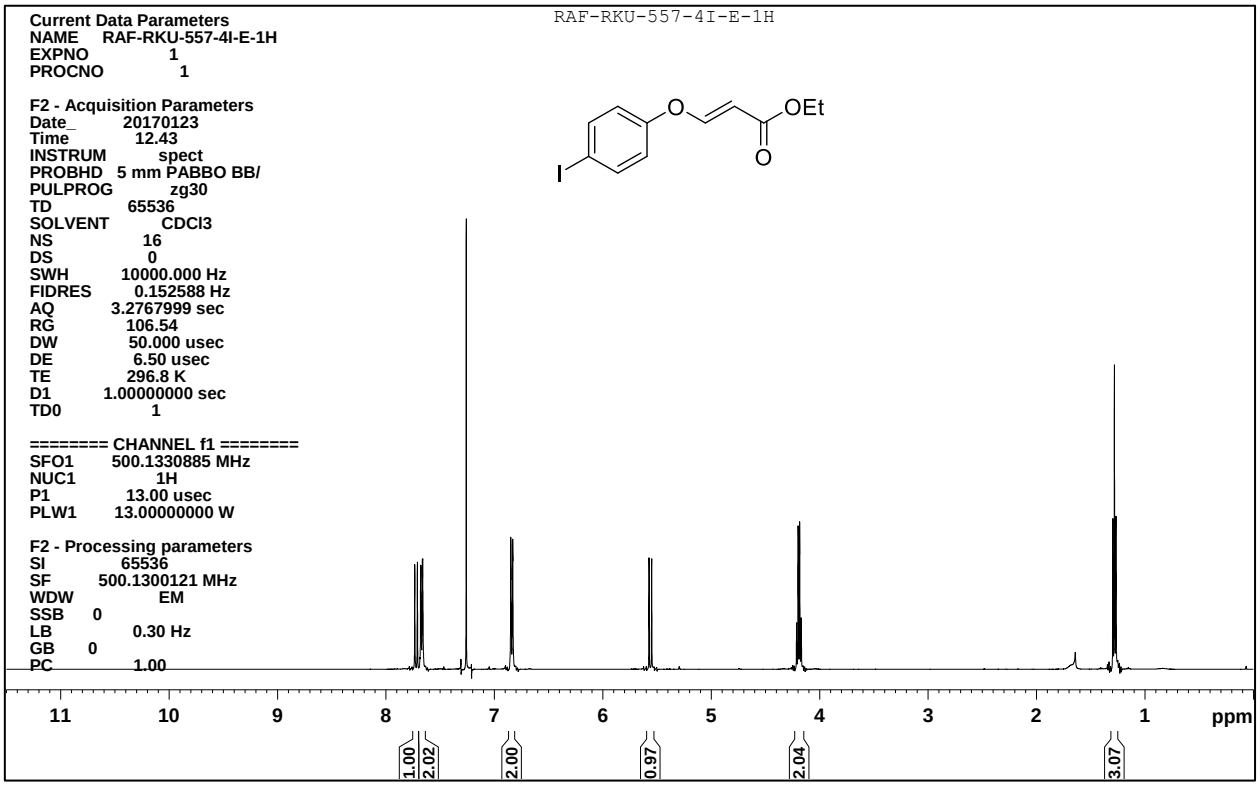


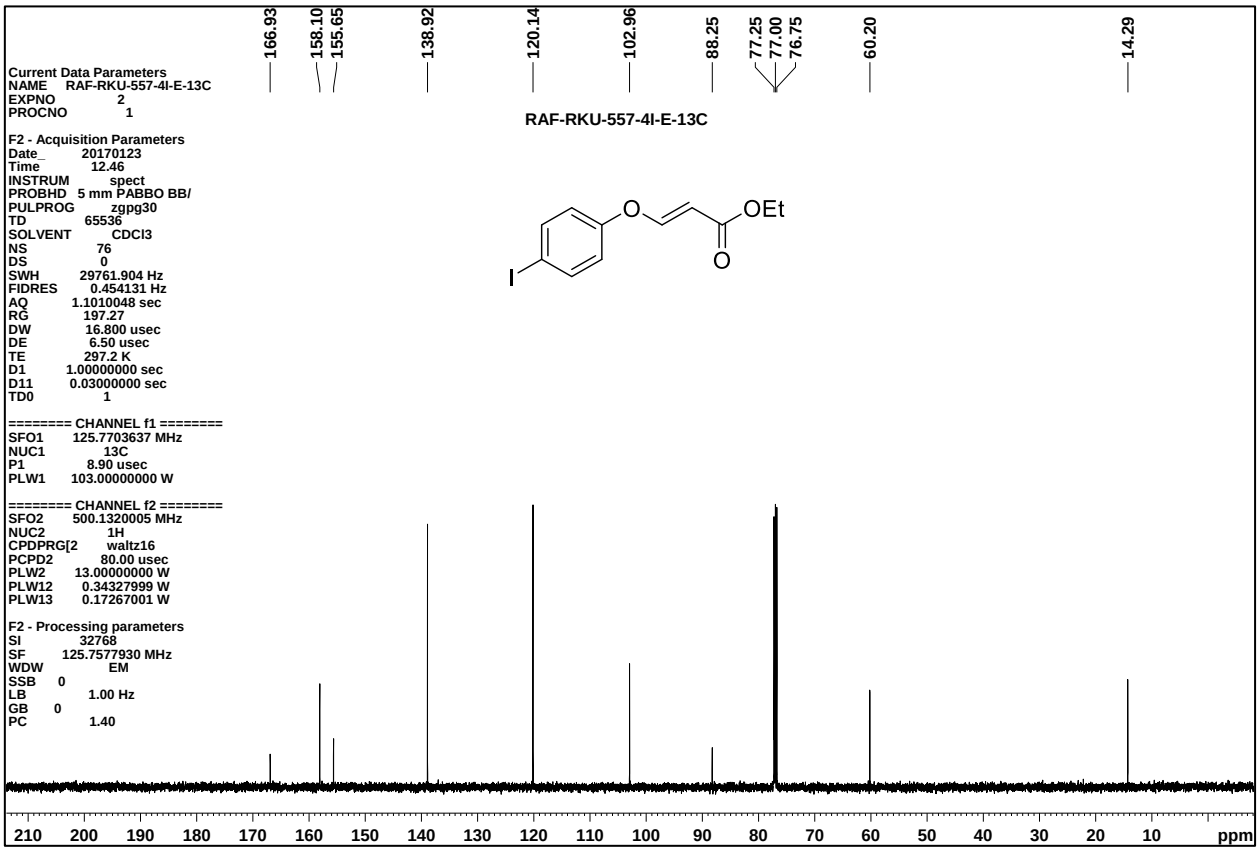
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3s**



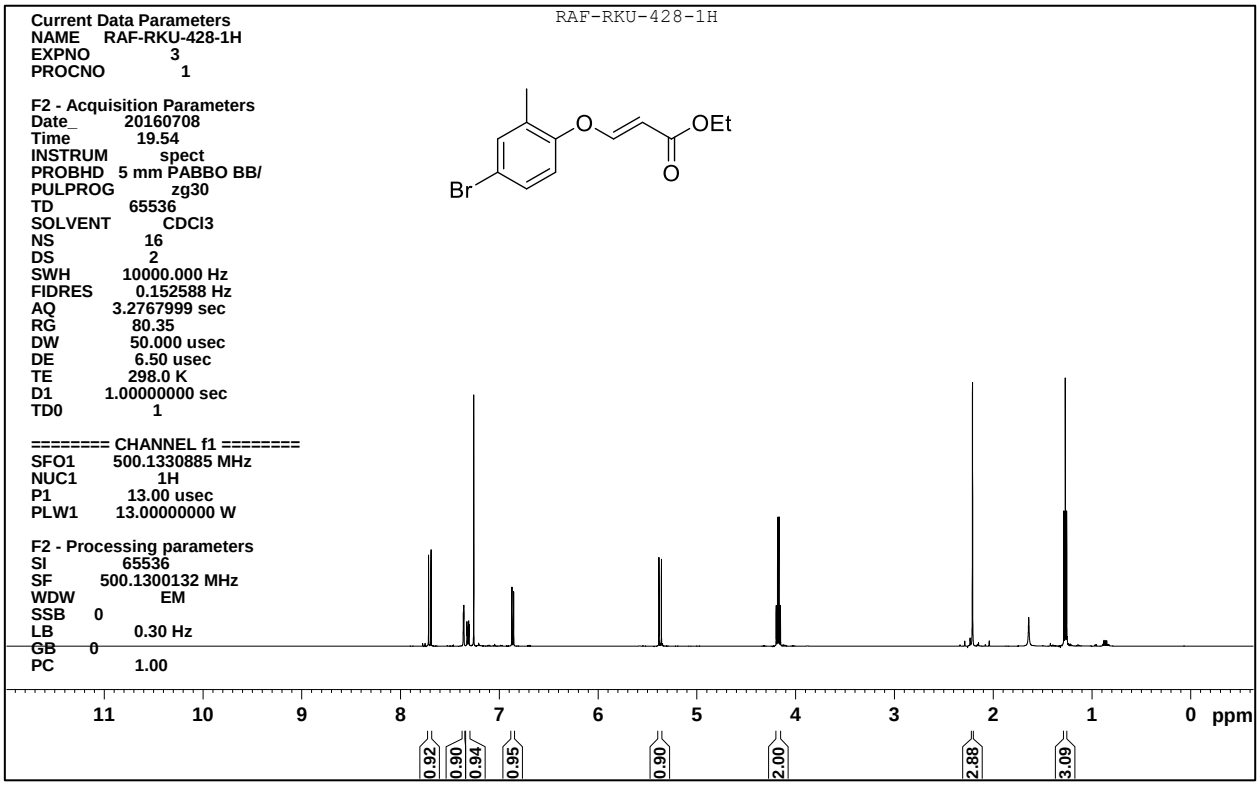


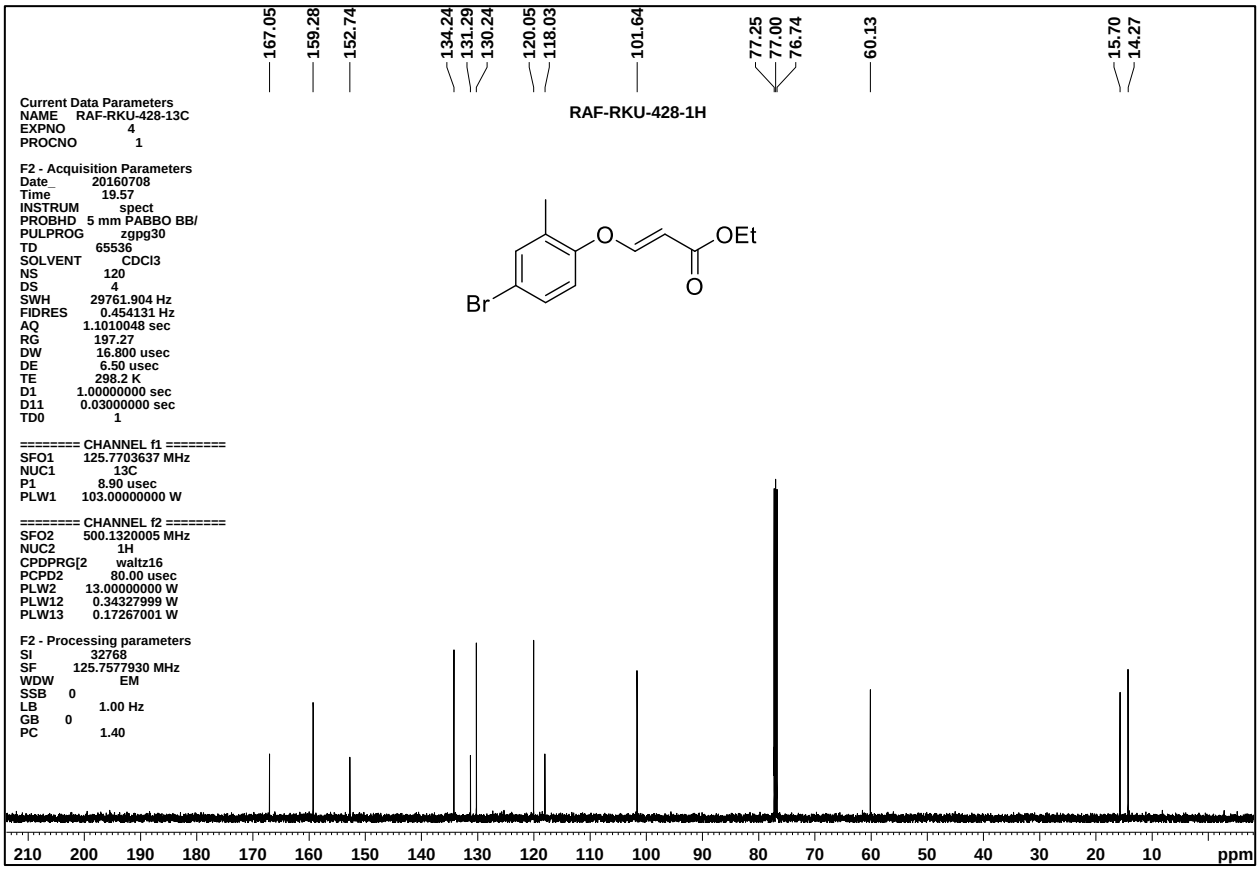
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3t**



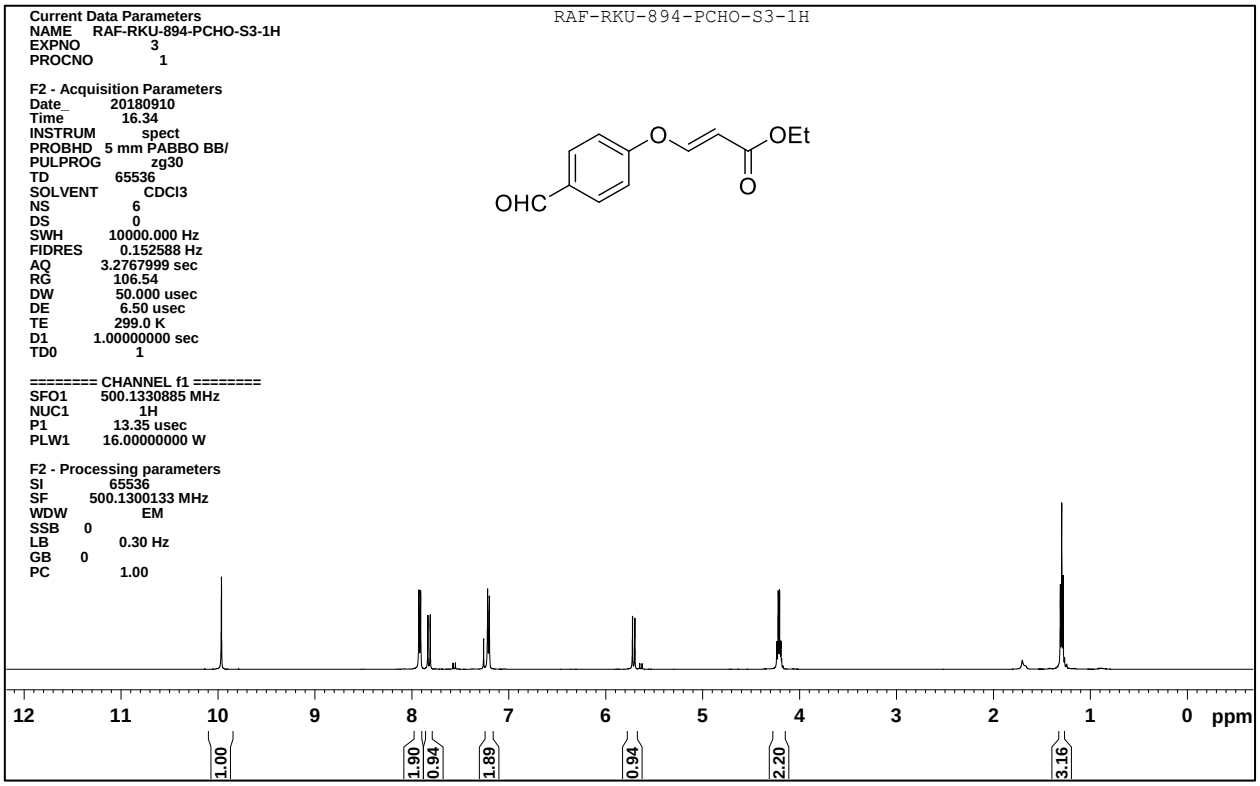


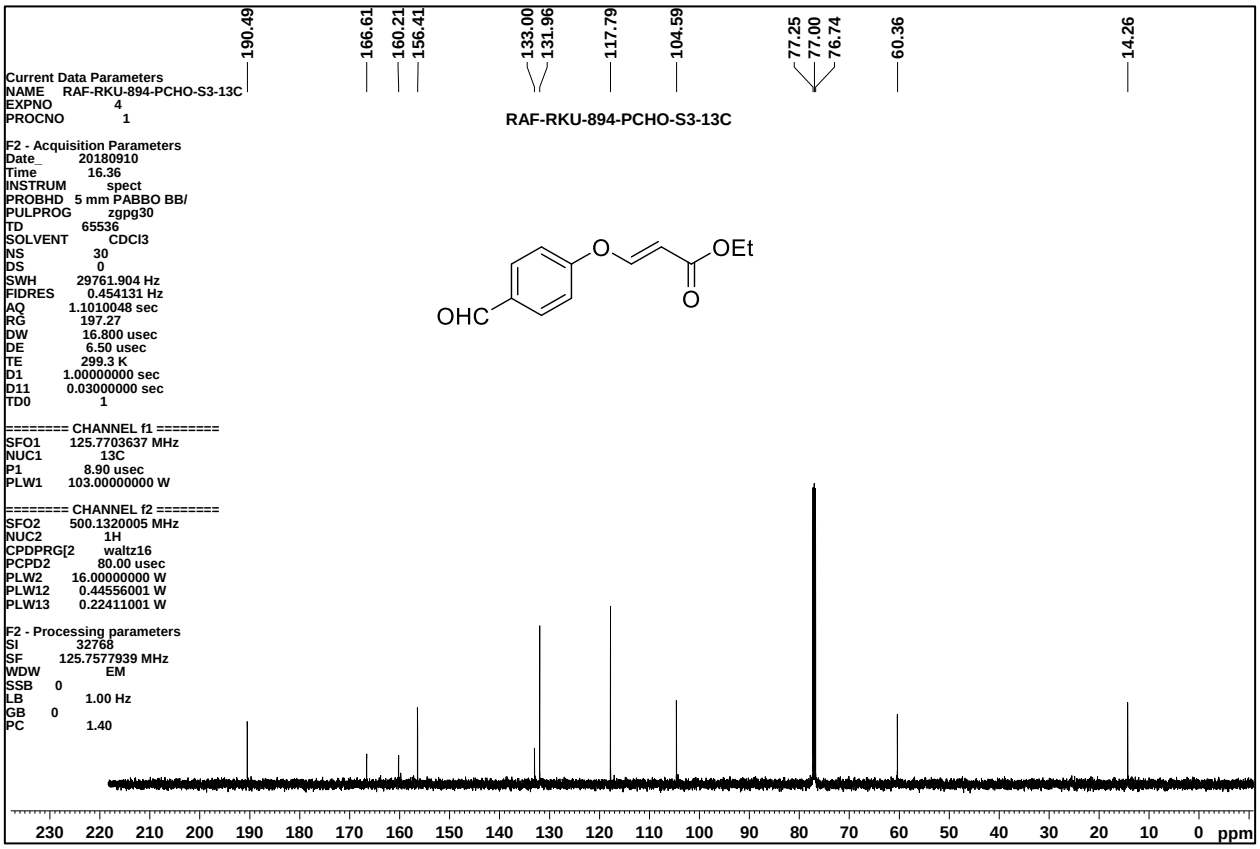
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3u**



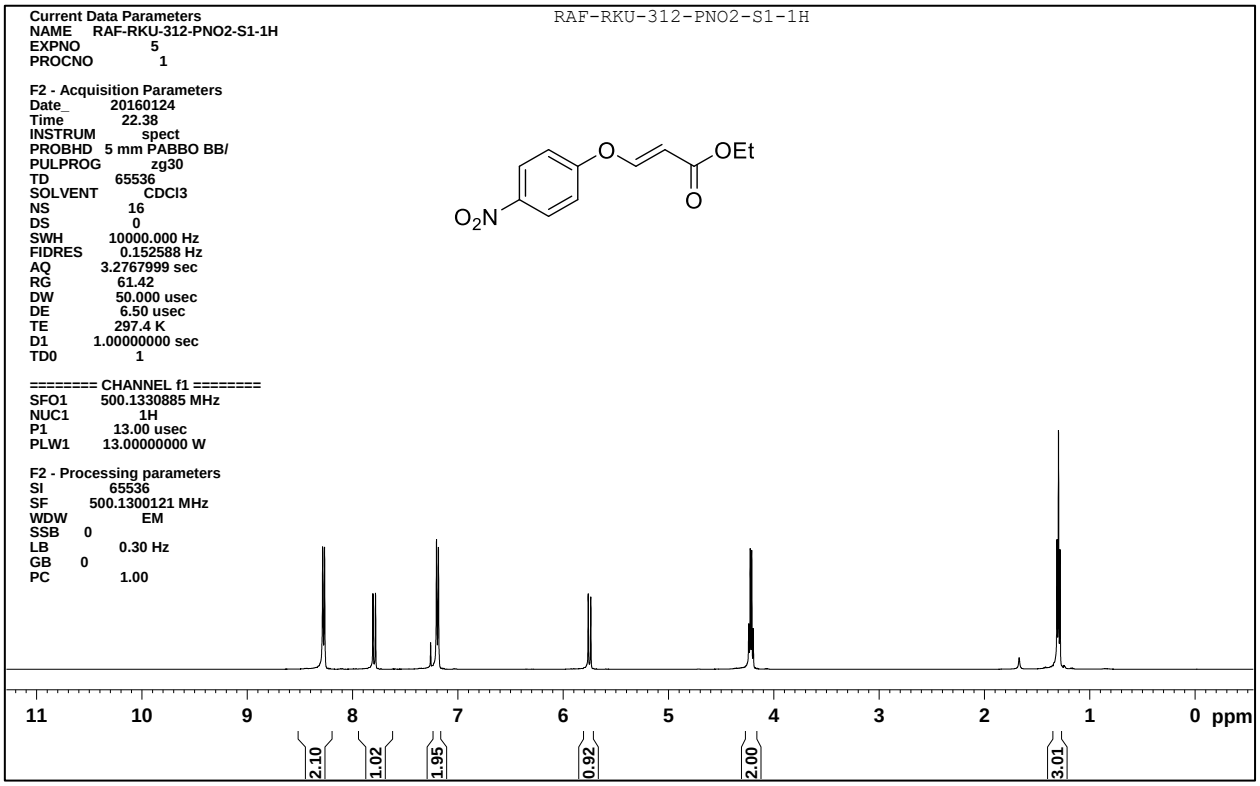


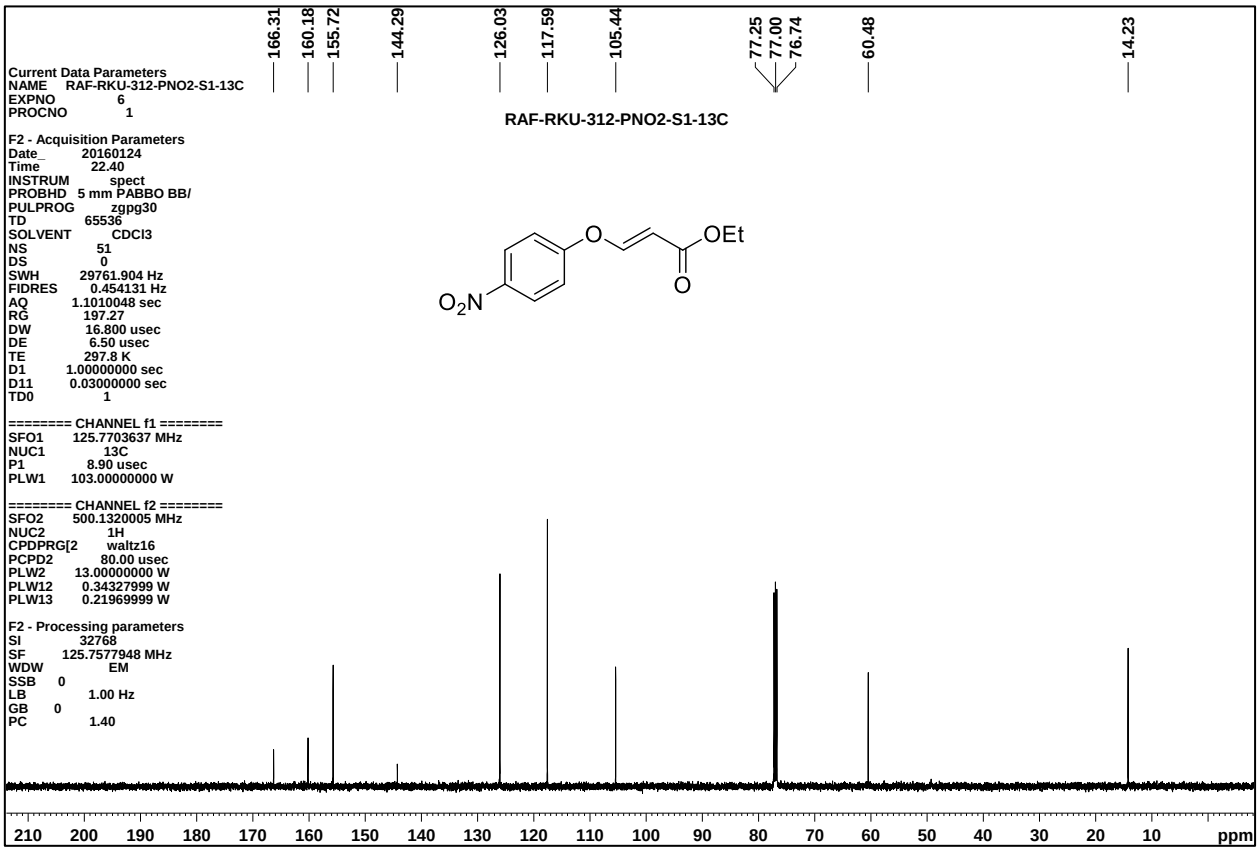
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3v**



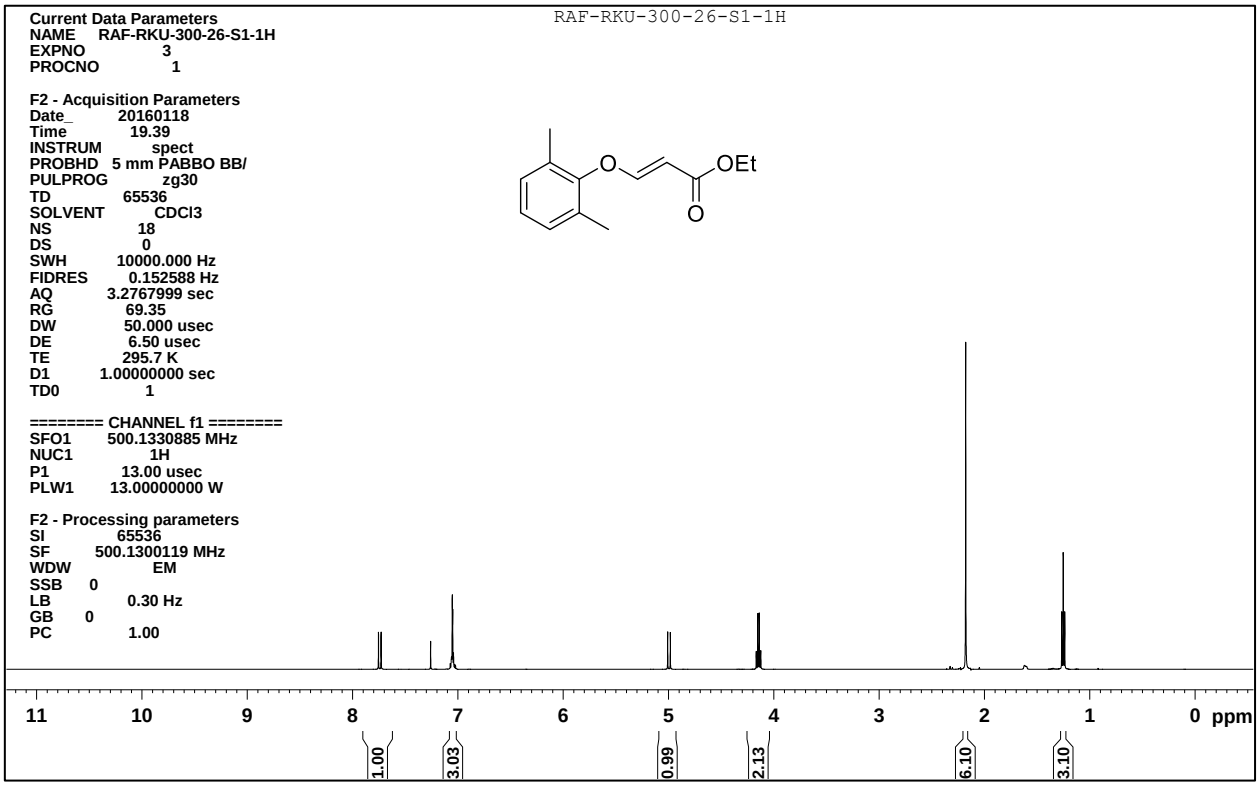


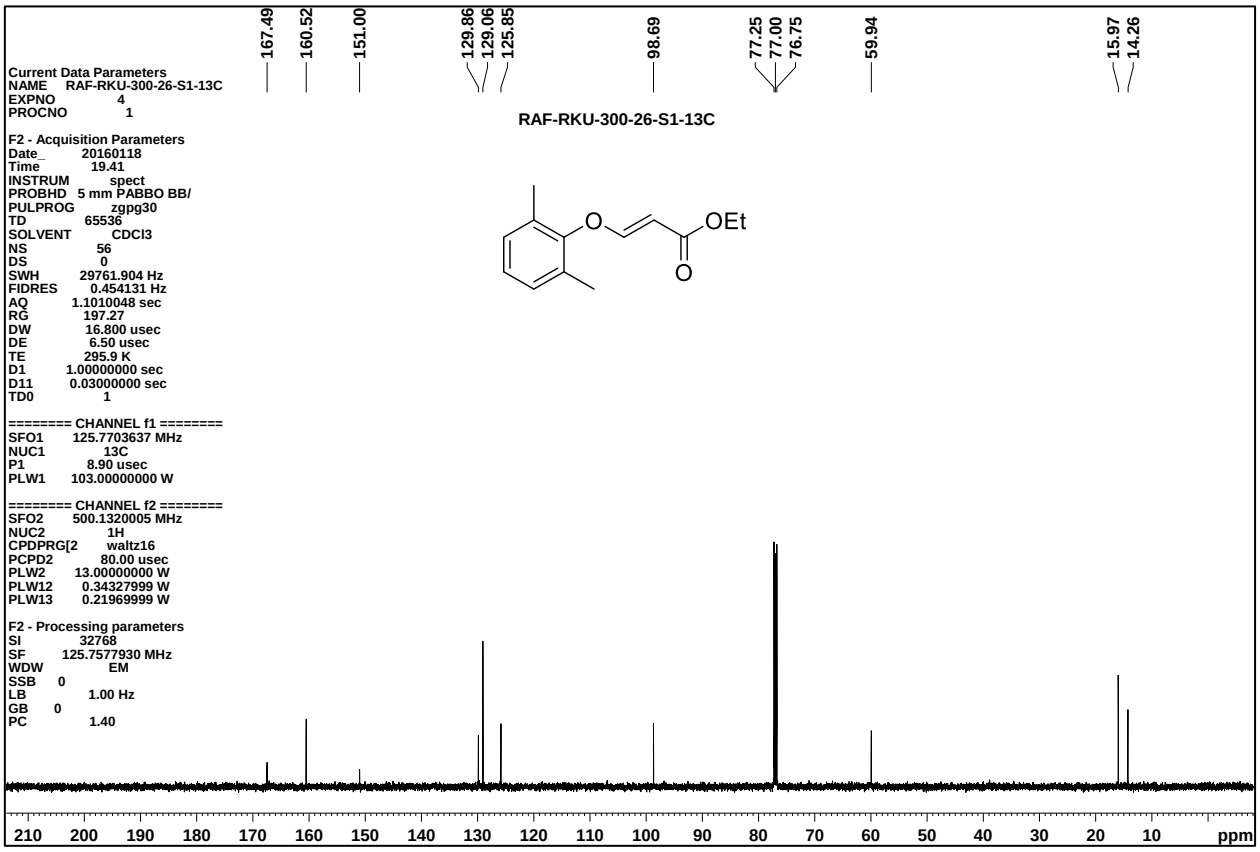
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3w**



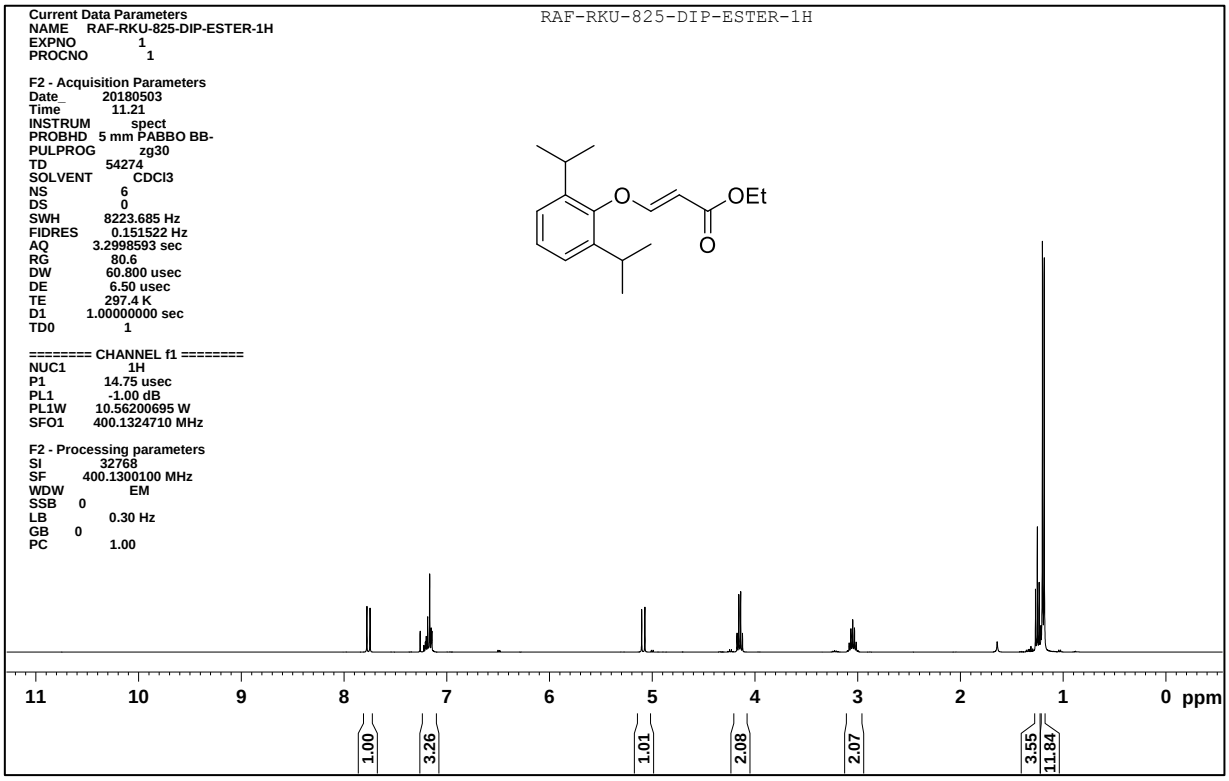


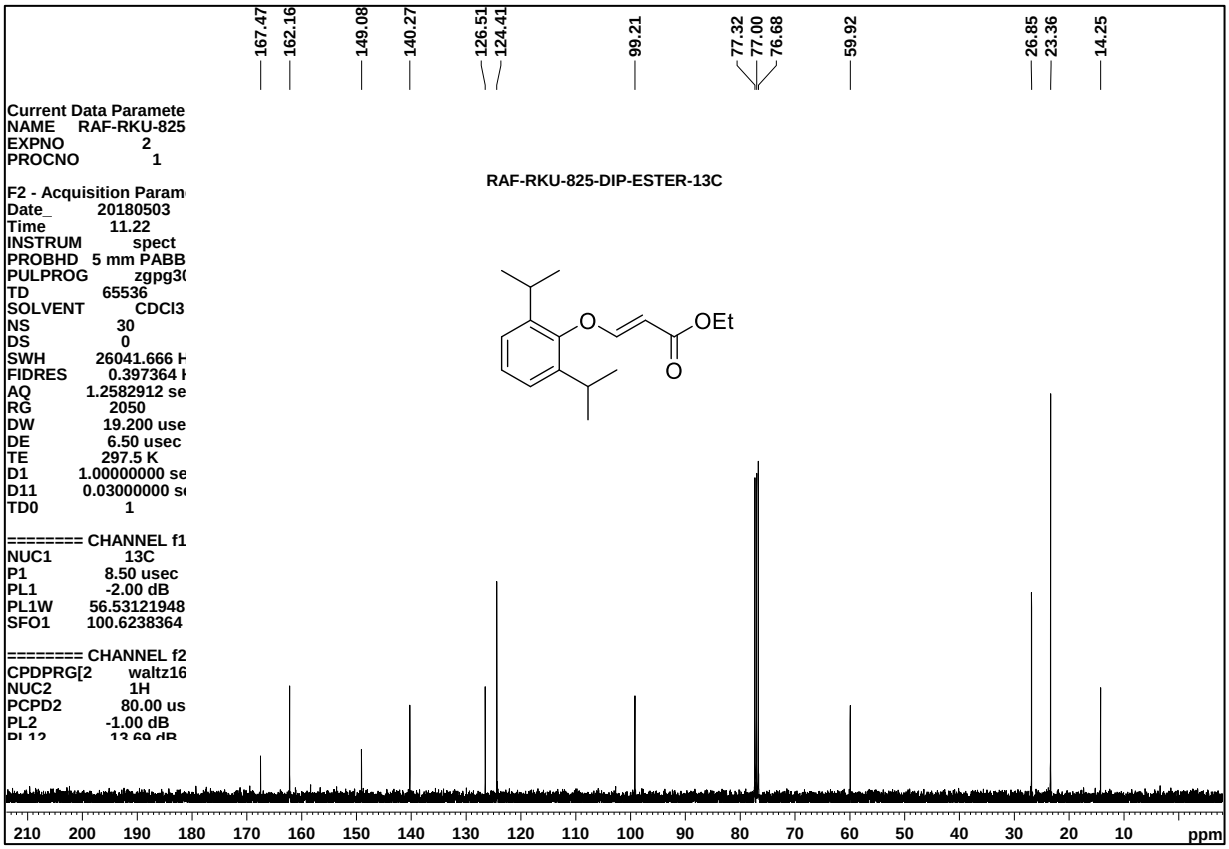
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3x**



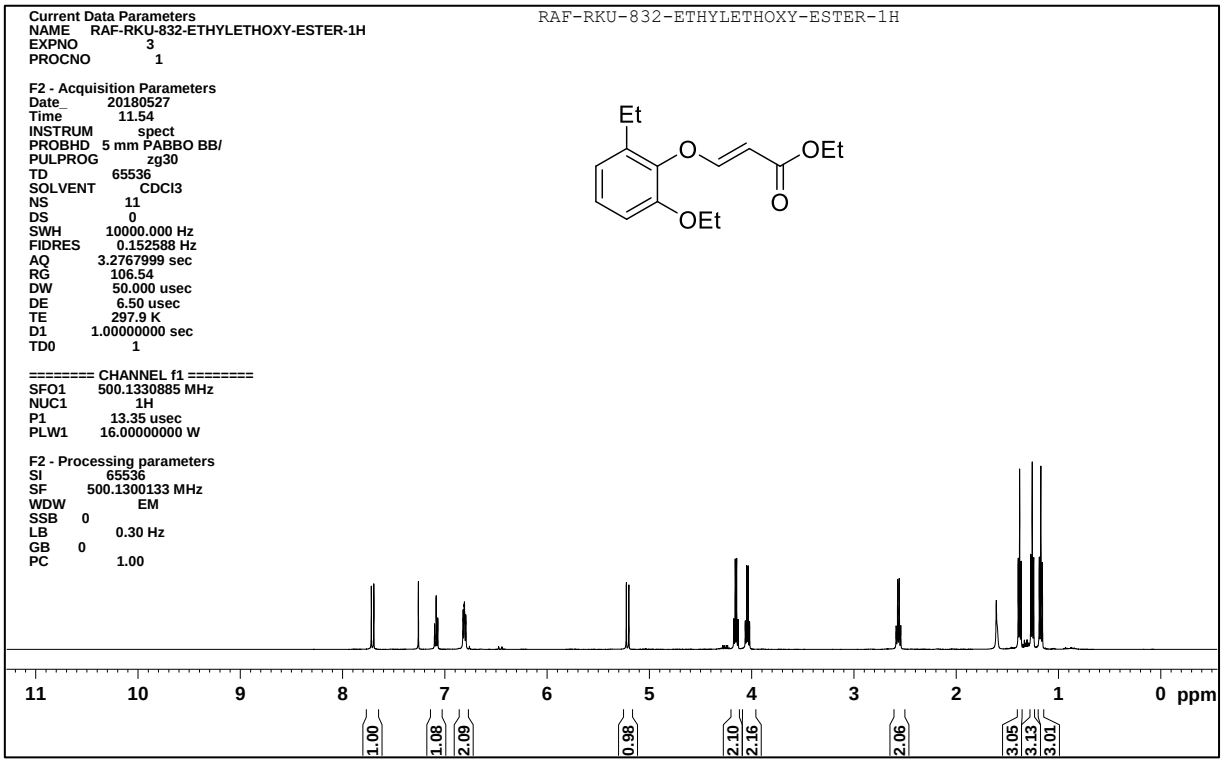


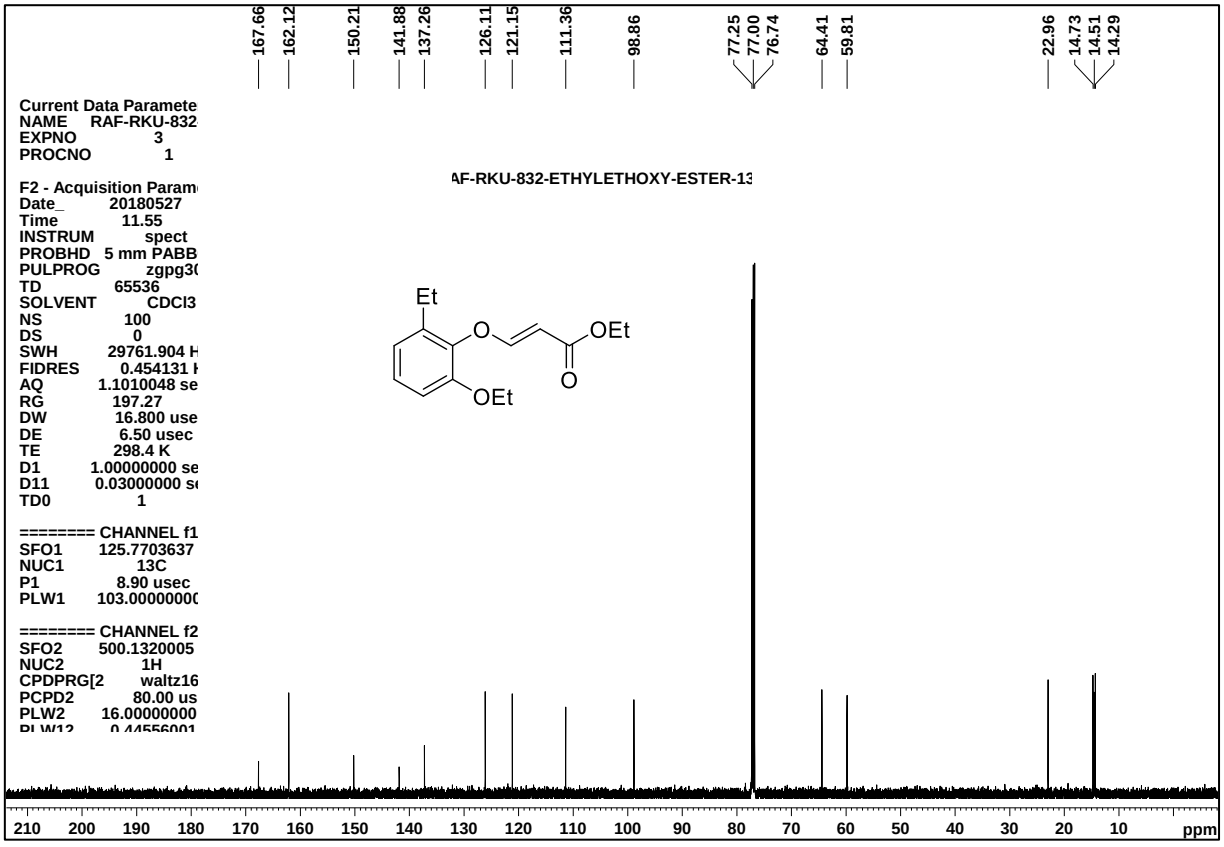
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of (*E*)-**3y**



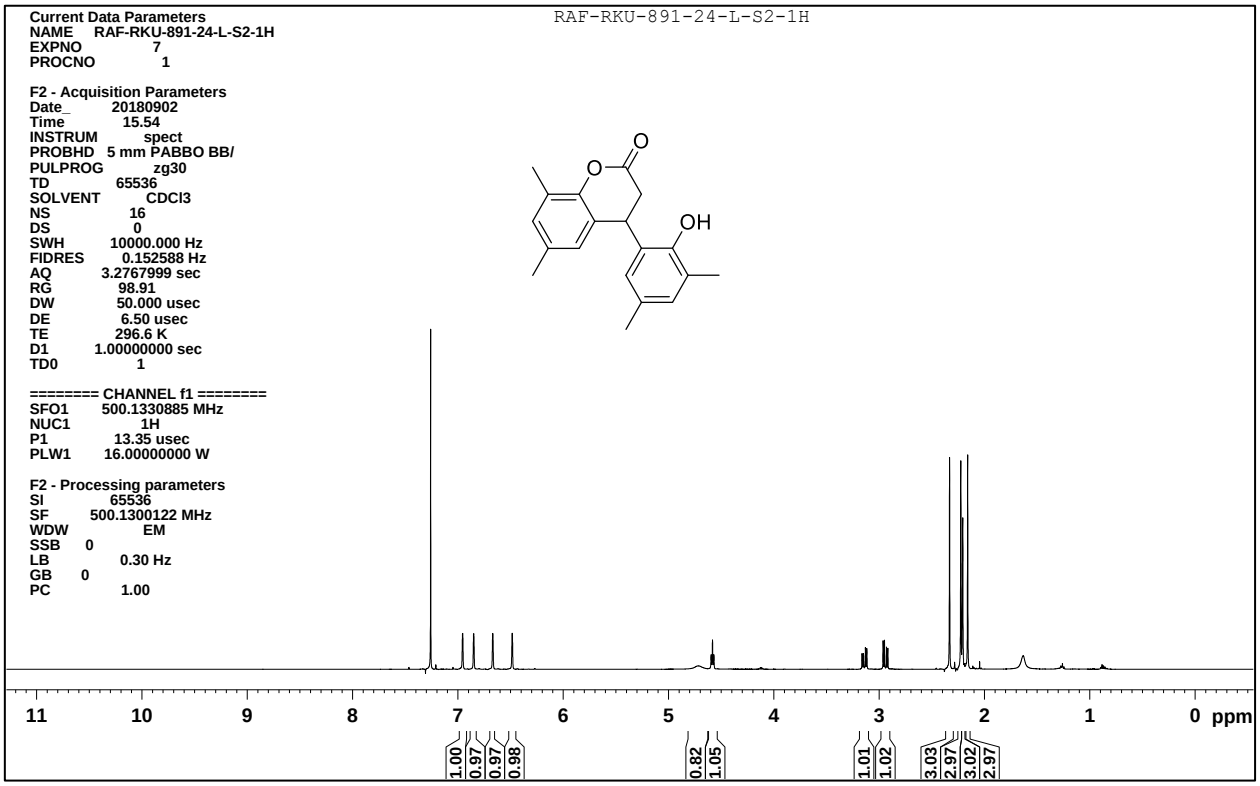


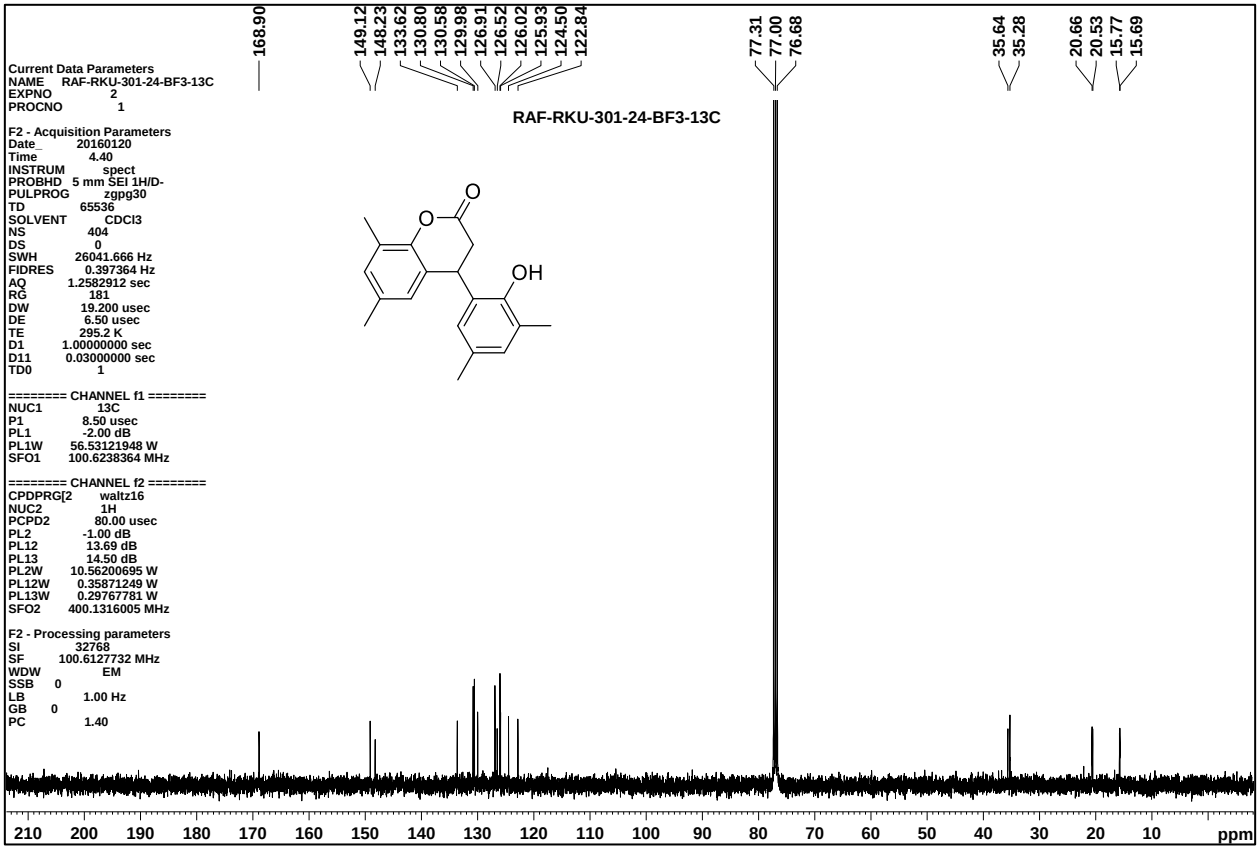
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**3z**



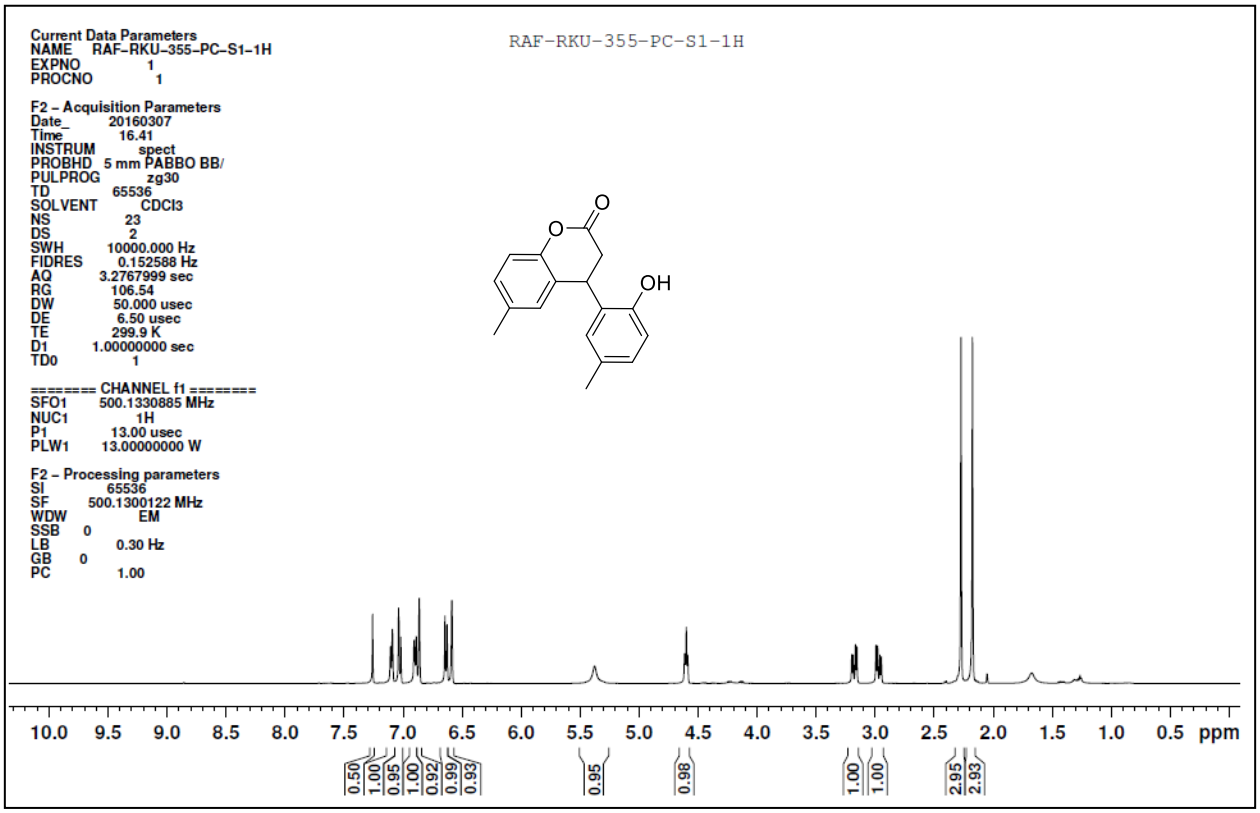


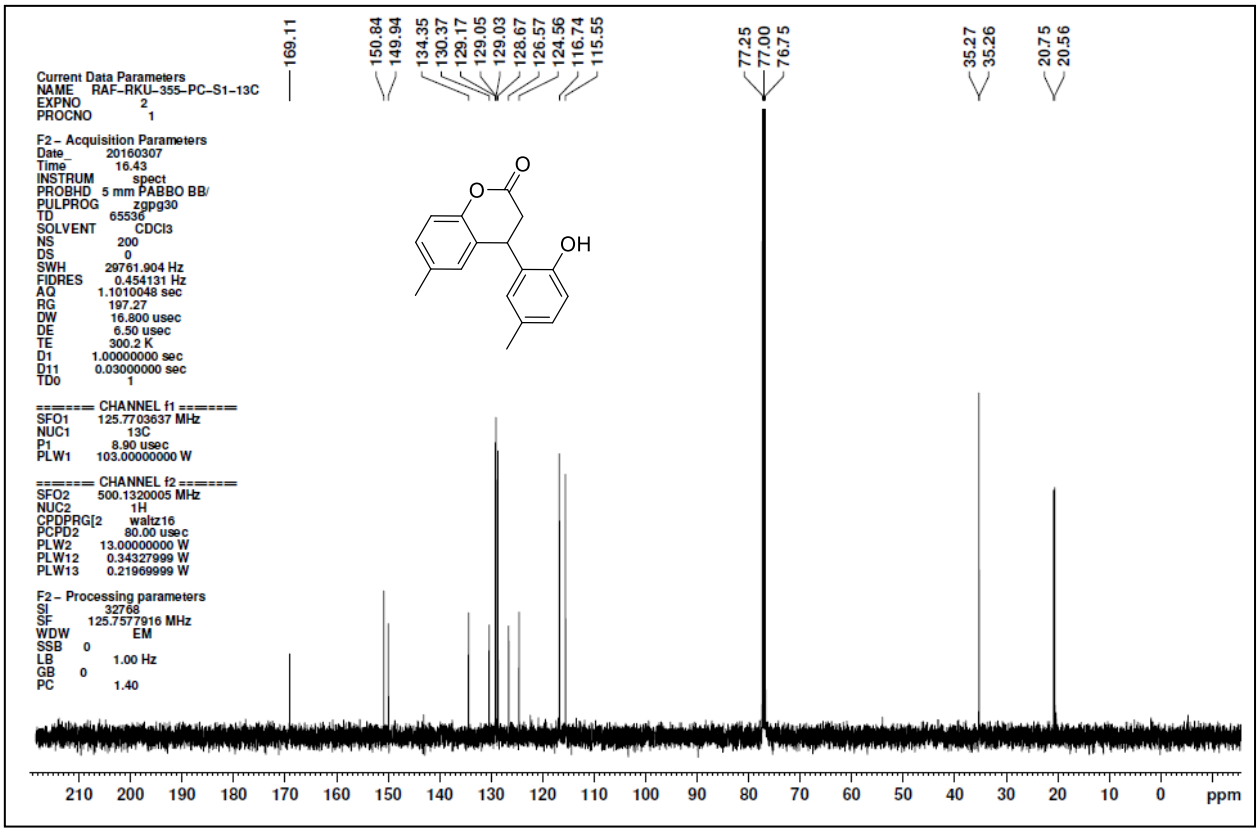
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (100MHz, $CDCl_3$) of **5a**



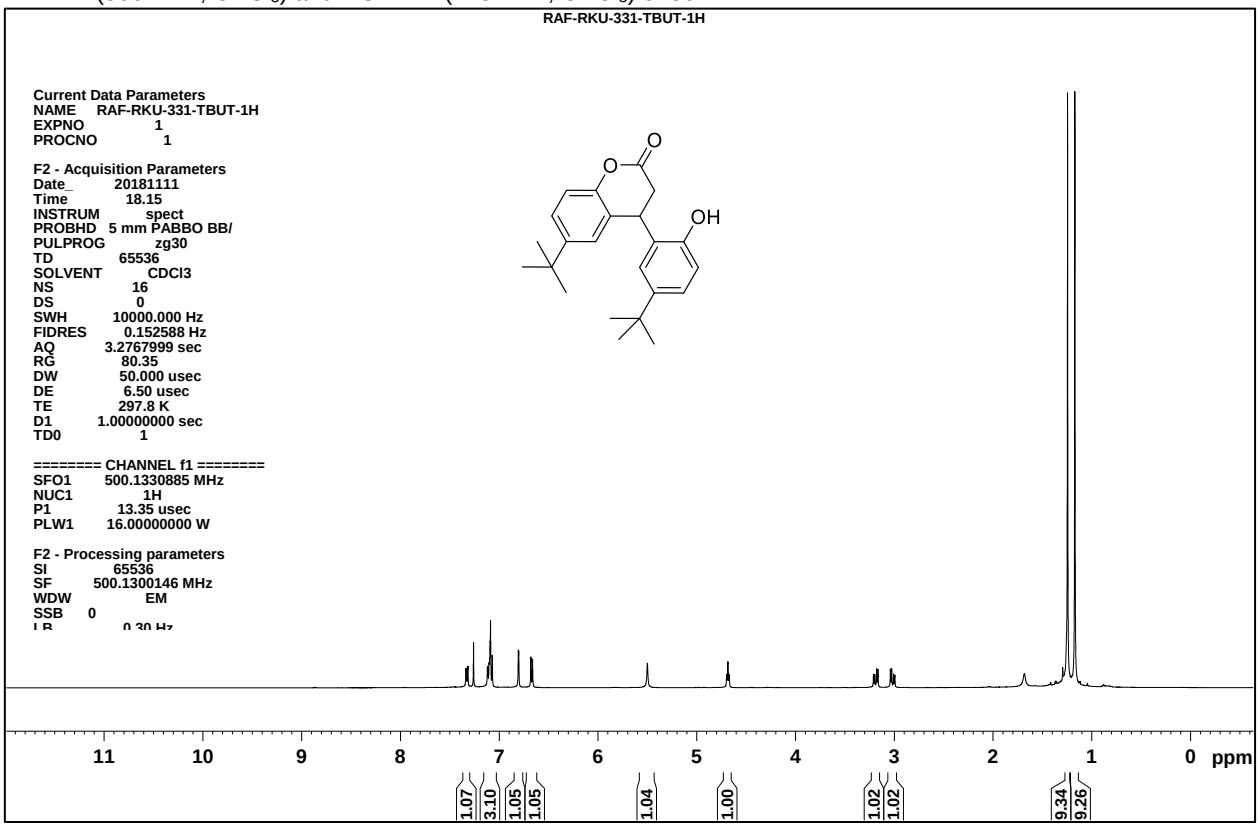


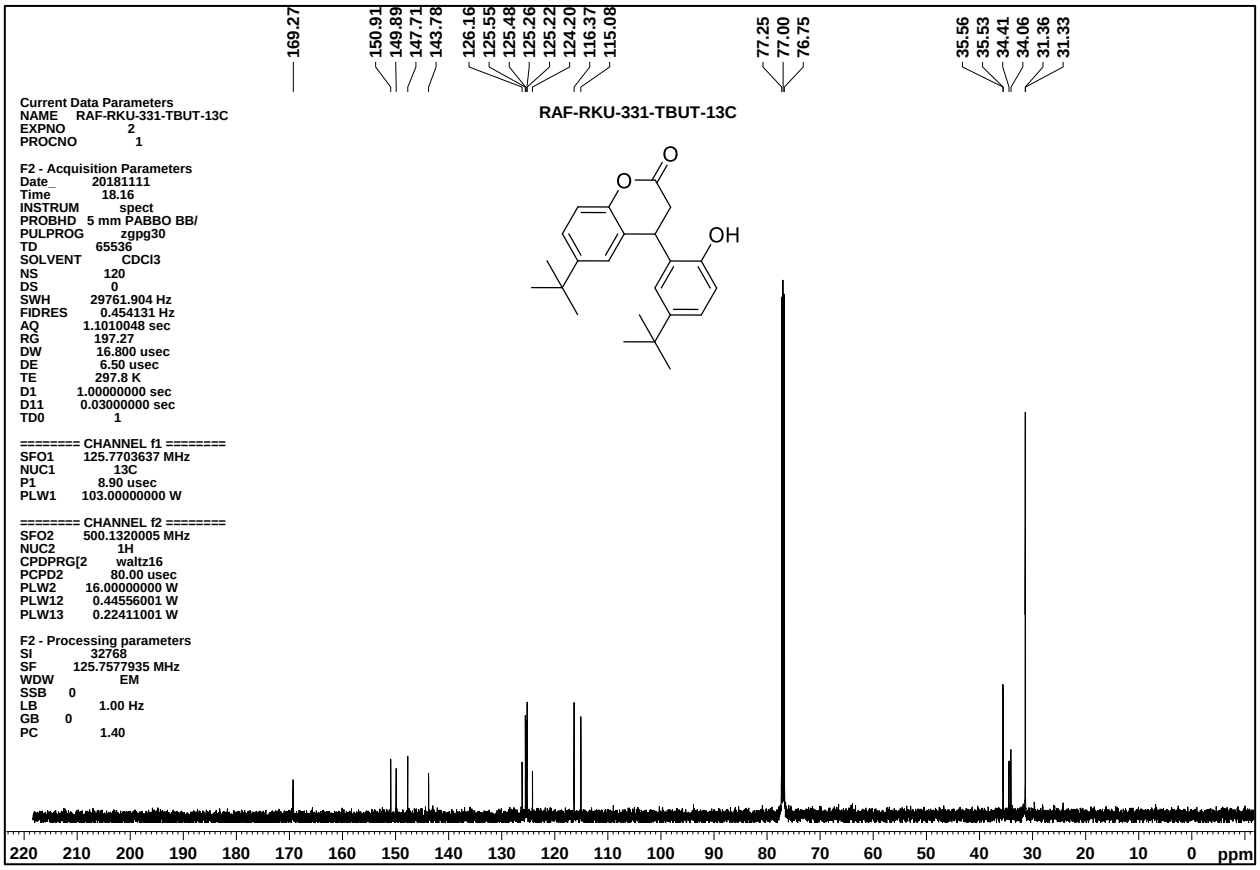
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5b**



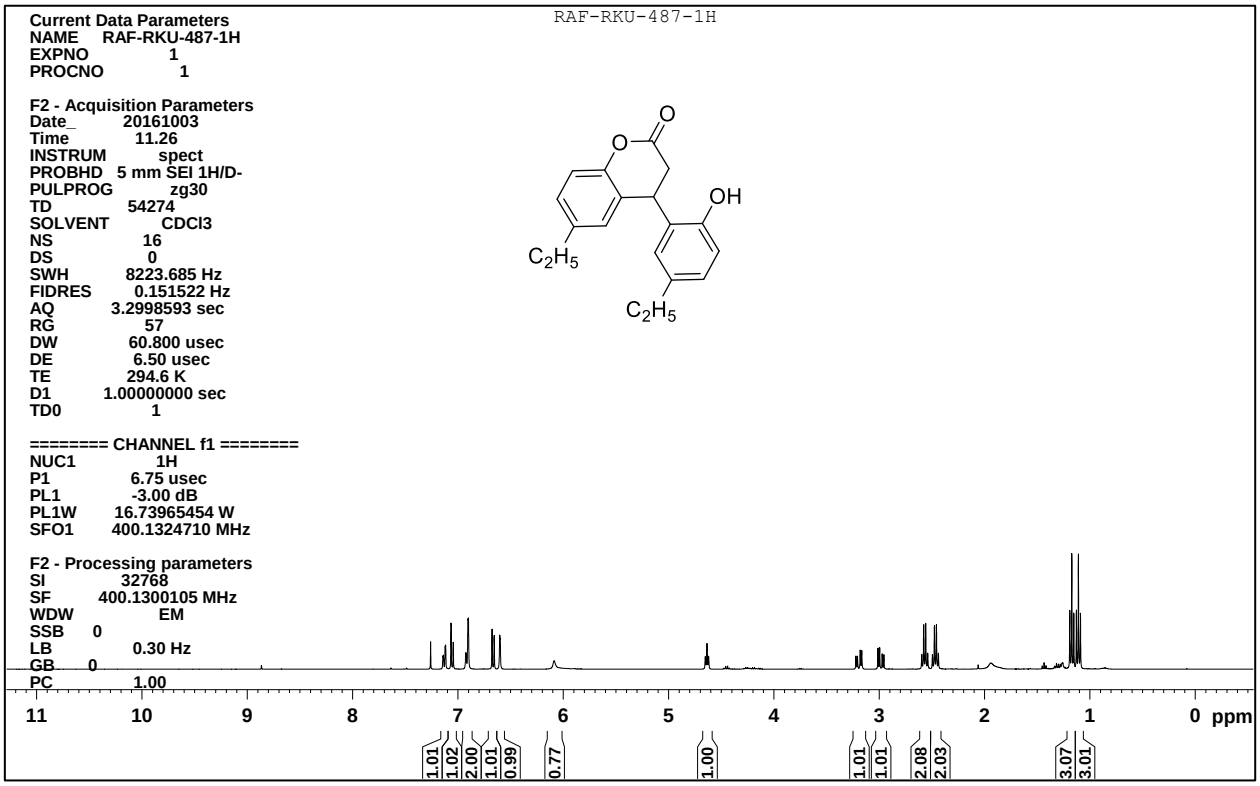


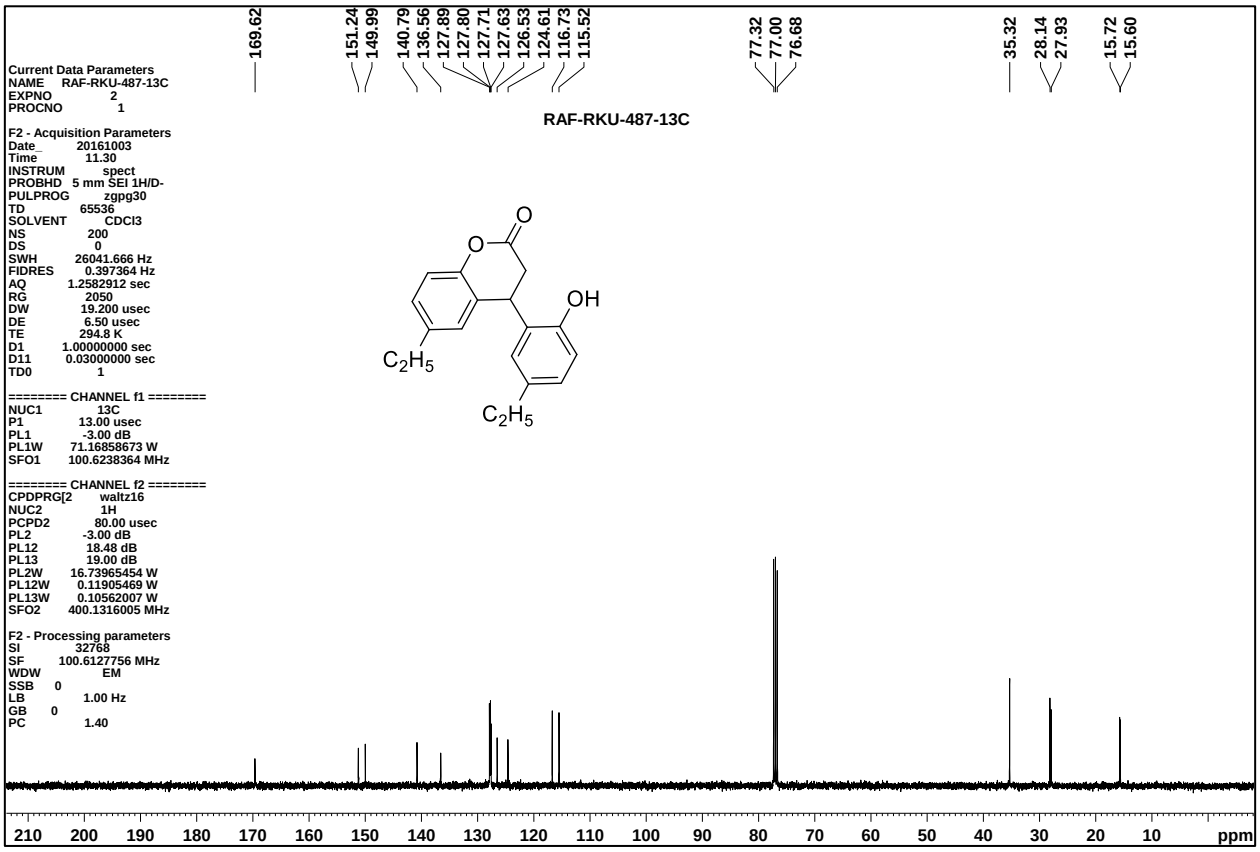
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5c**



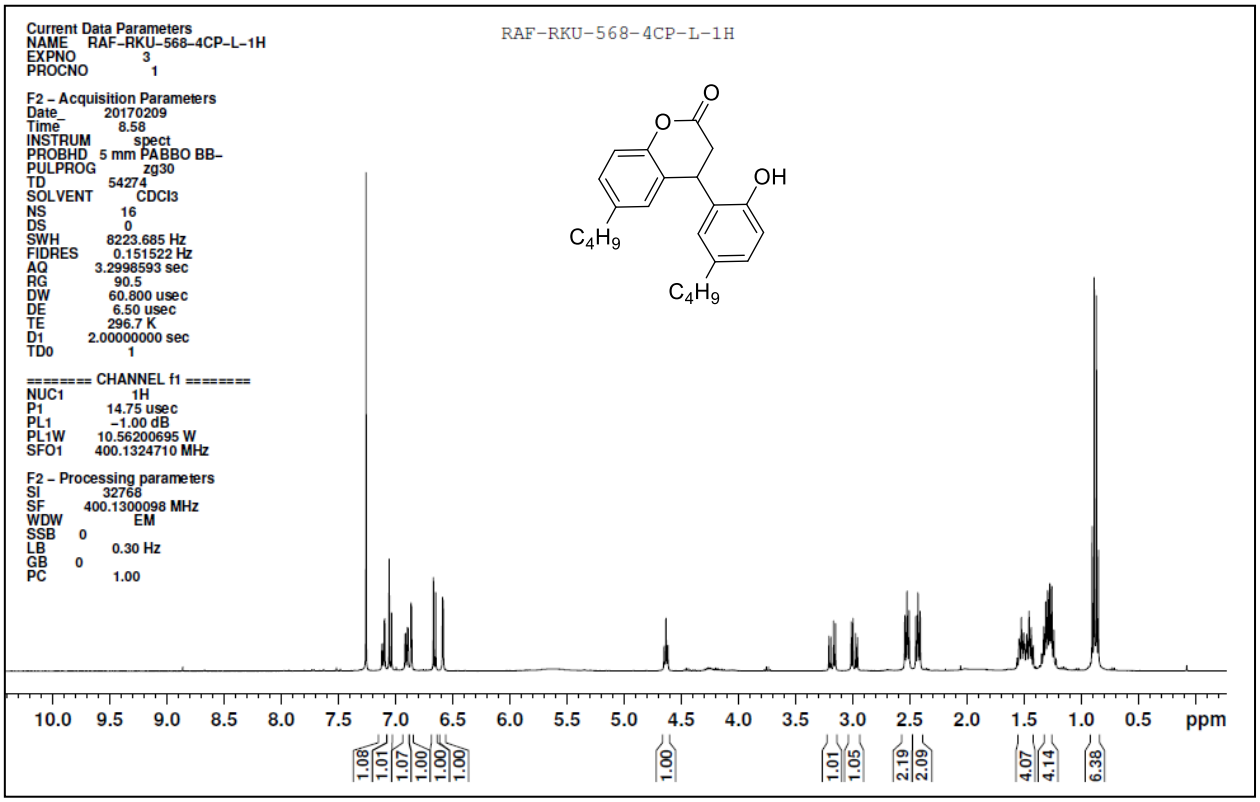


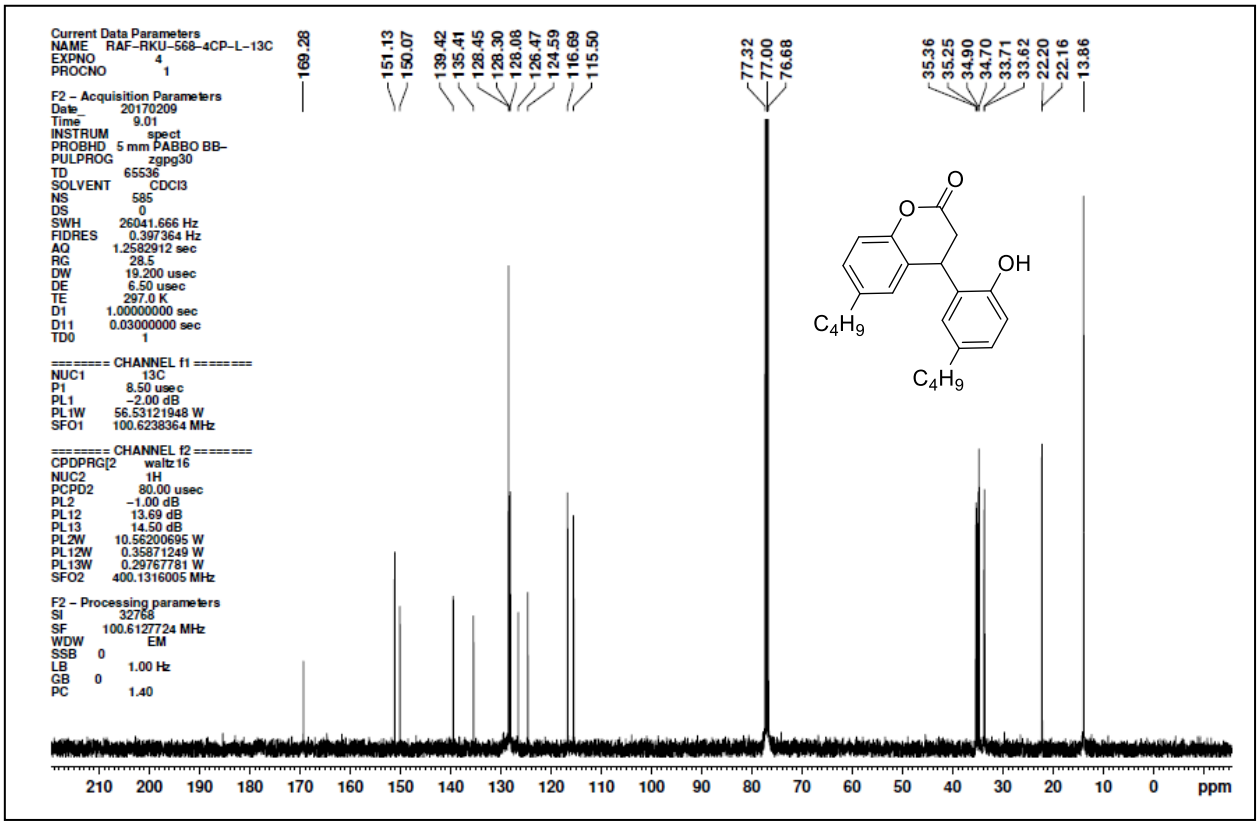
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100MHz, $CDCl_3$) of **5d**



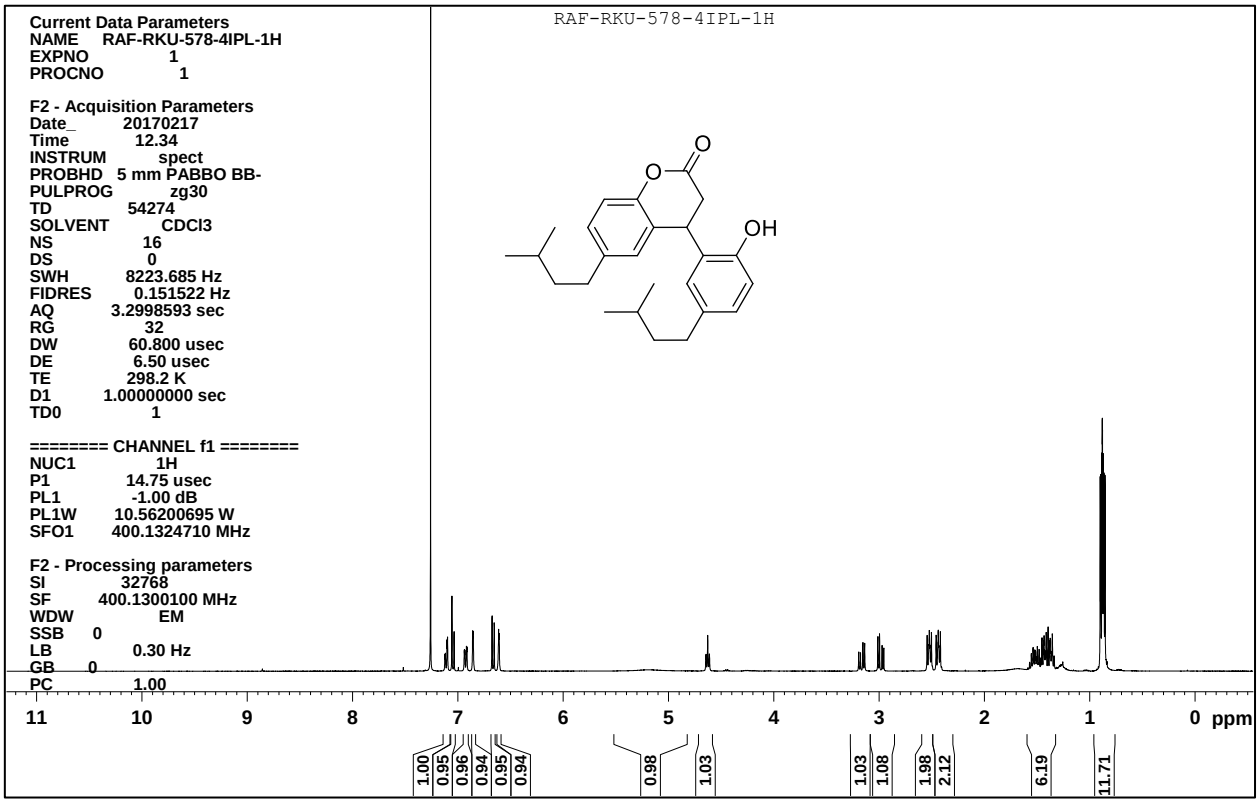


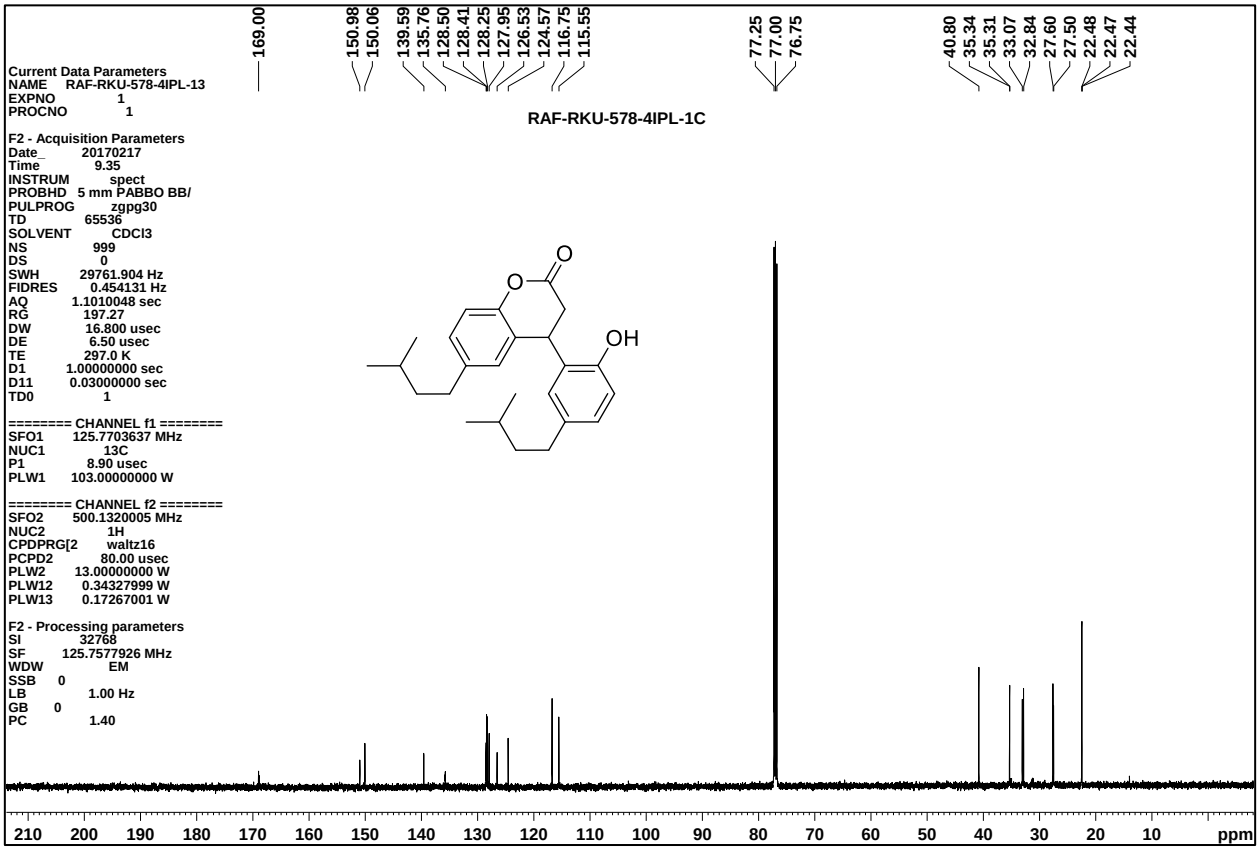
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100MHz, $CDCl_3$) of **5e**



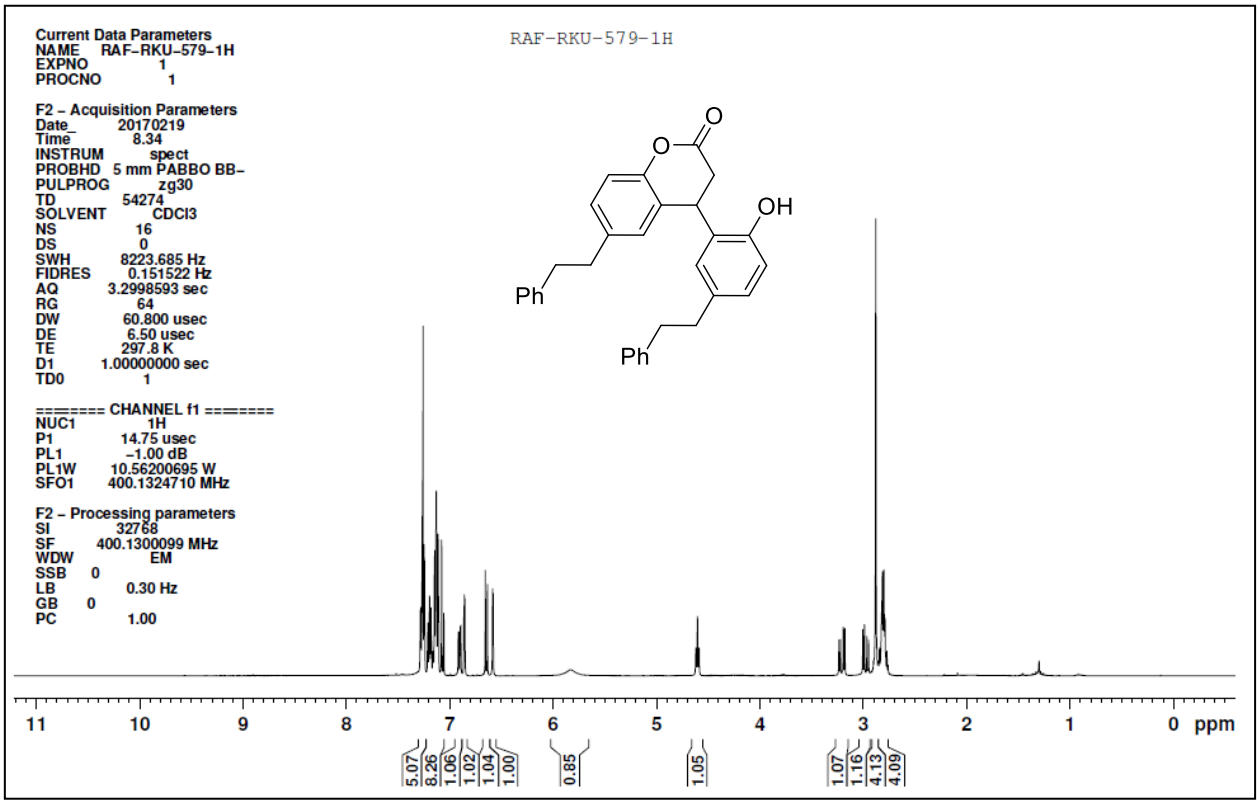


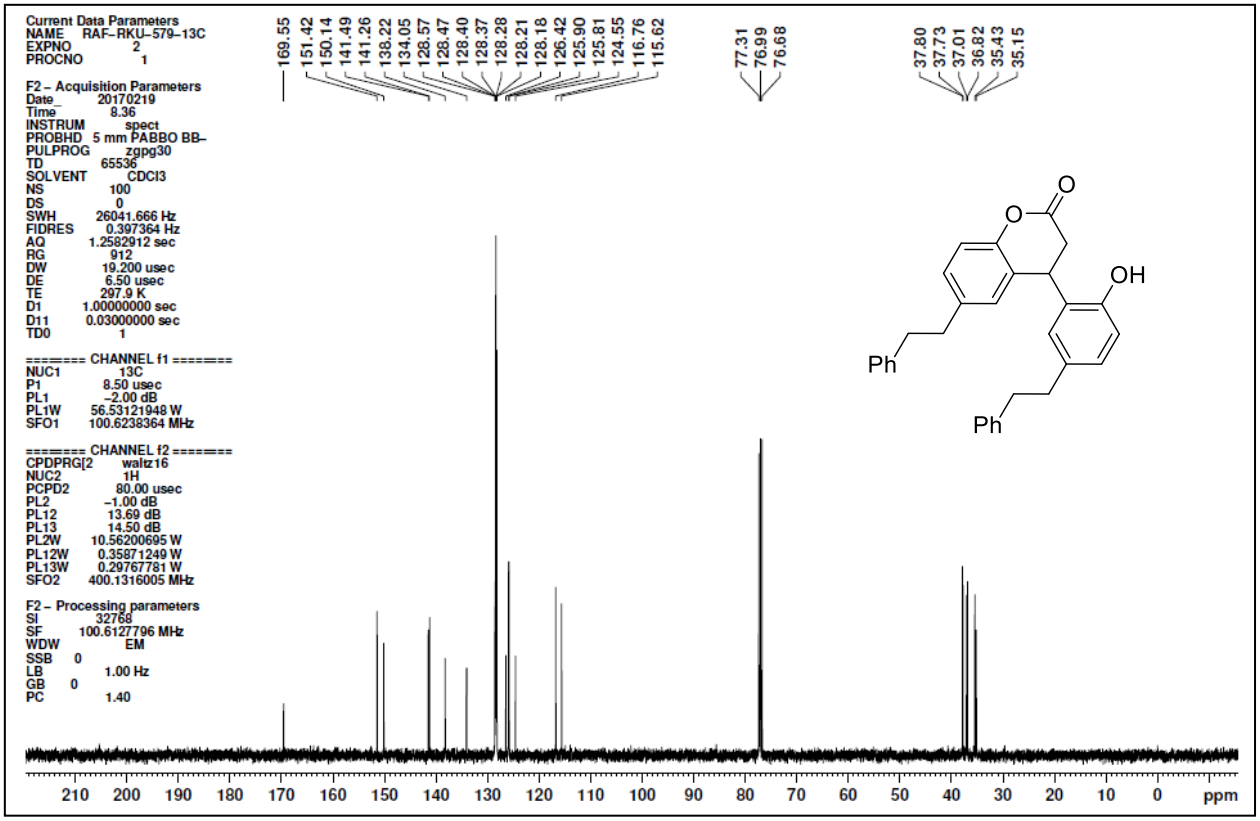
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5f**



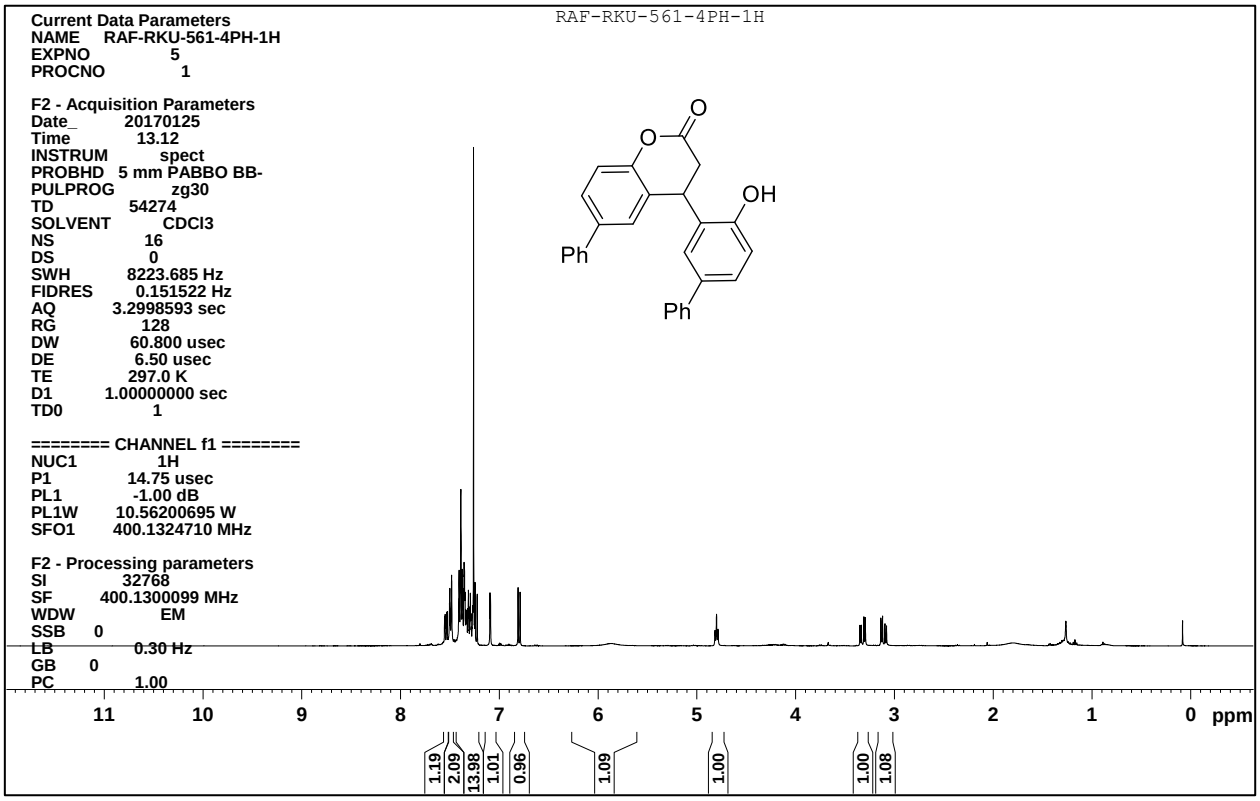


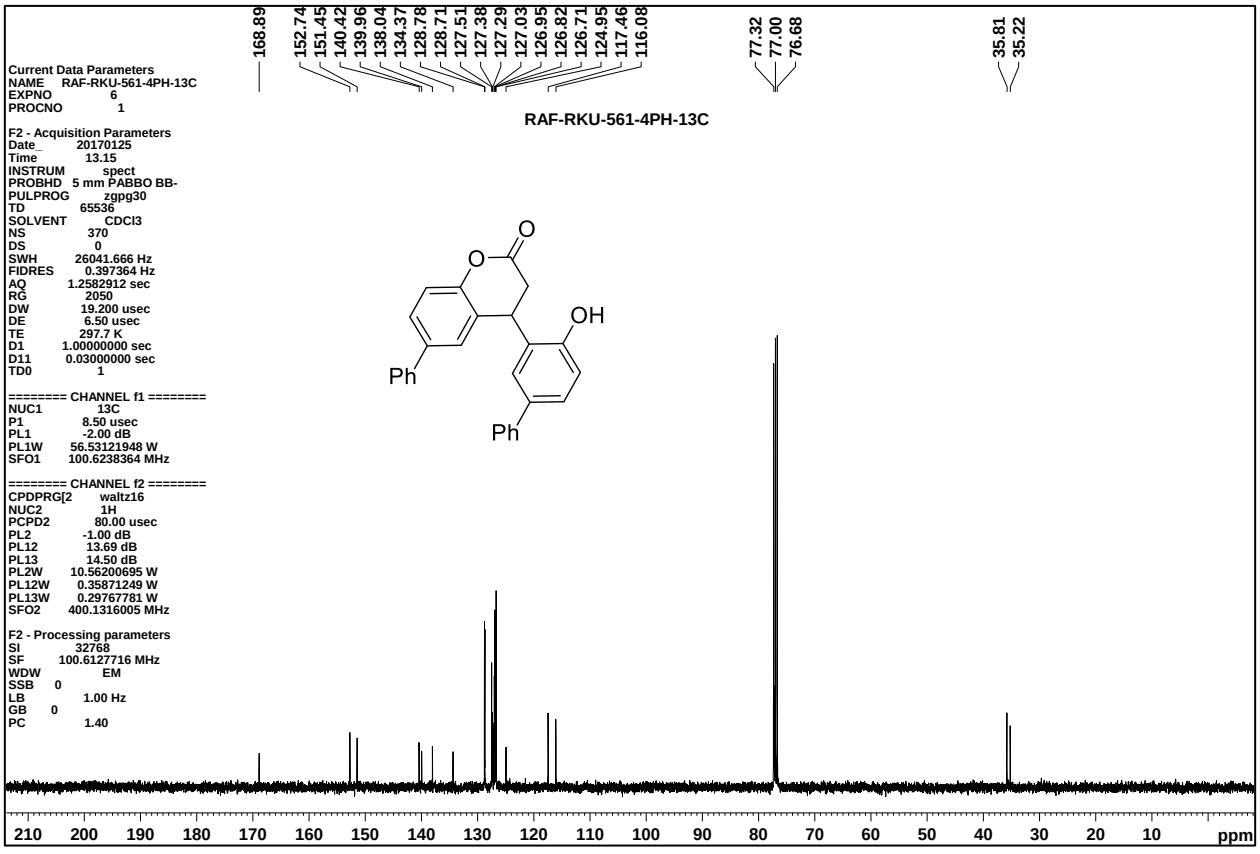
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100MHz, $CDCl_3$) of **5g**



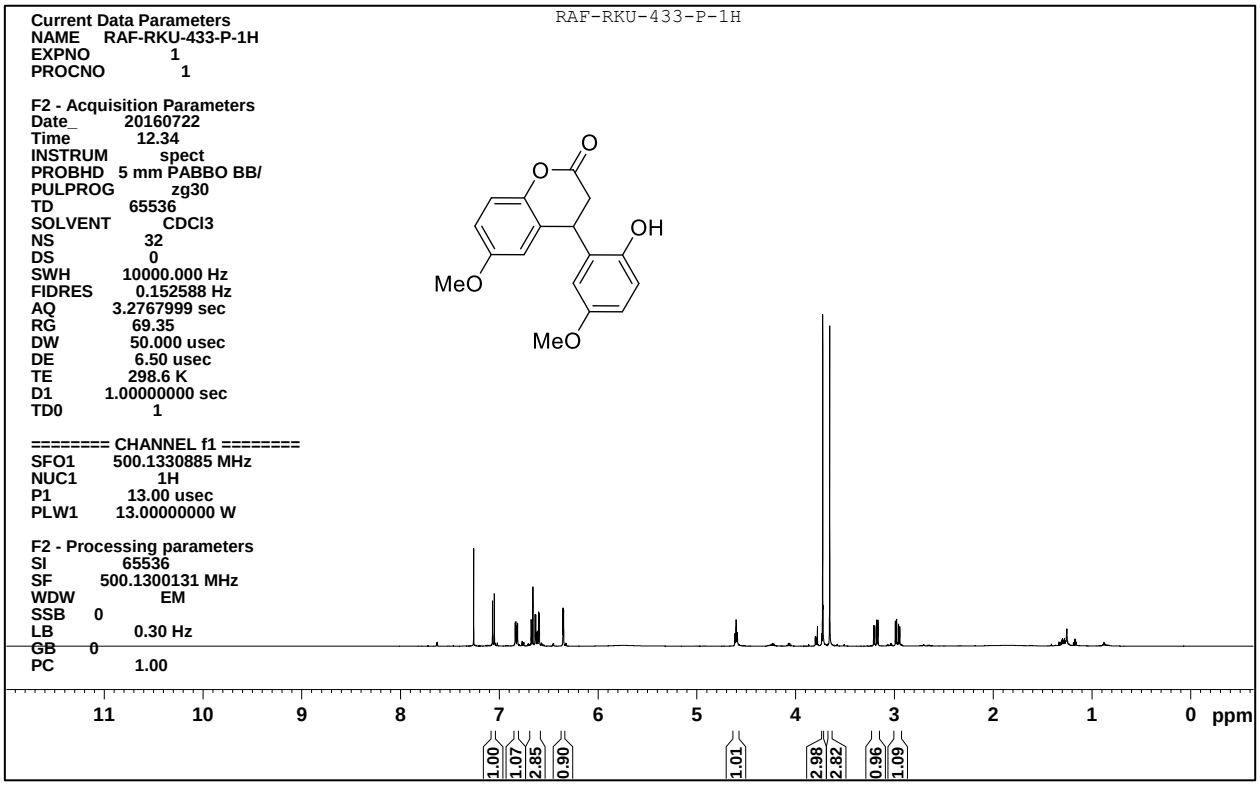


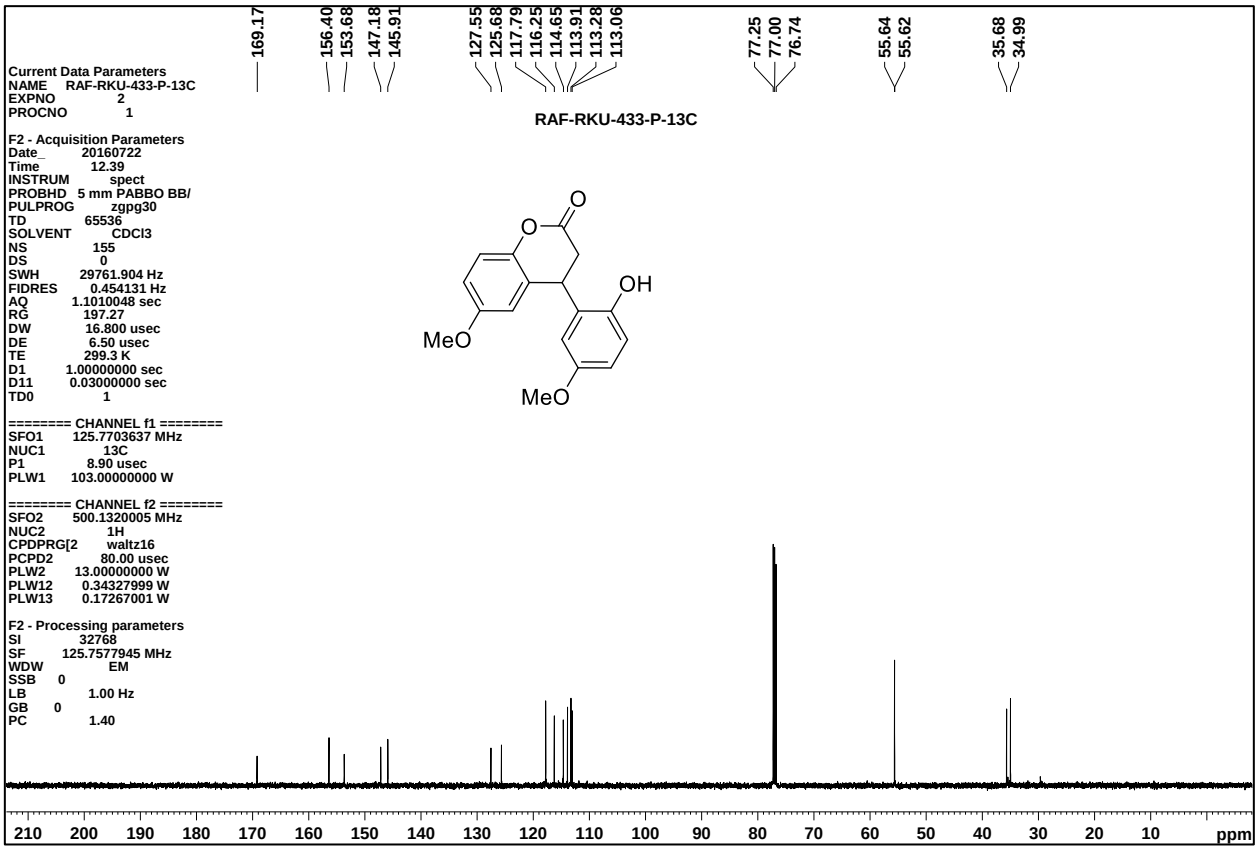
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100MHz, $CDCl_3$) of **5h**



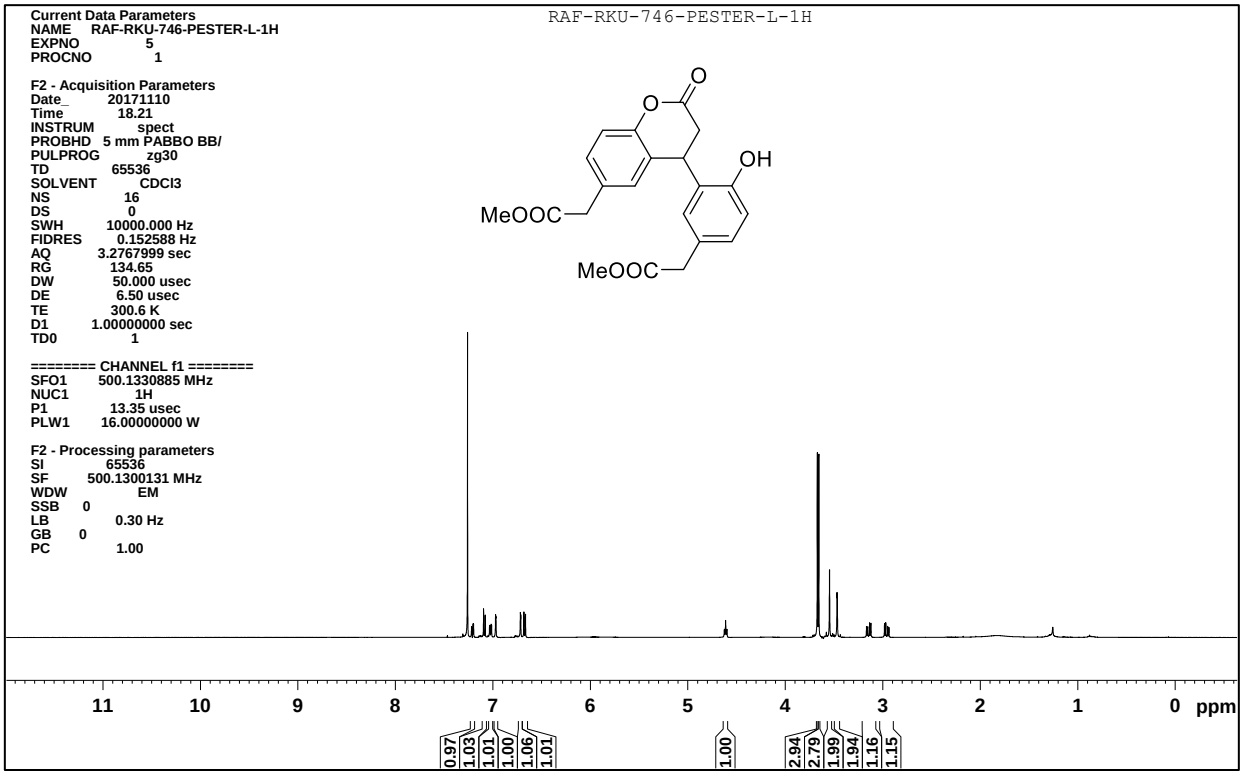


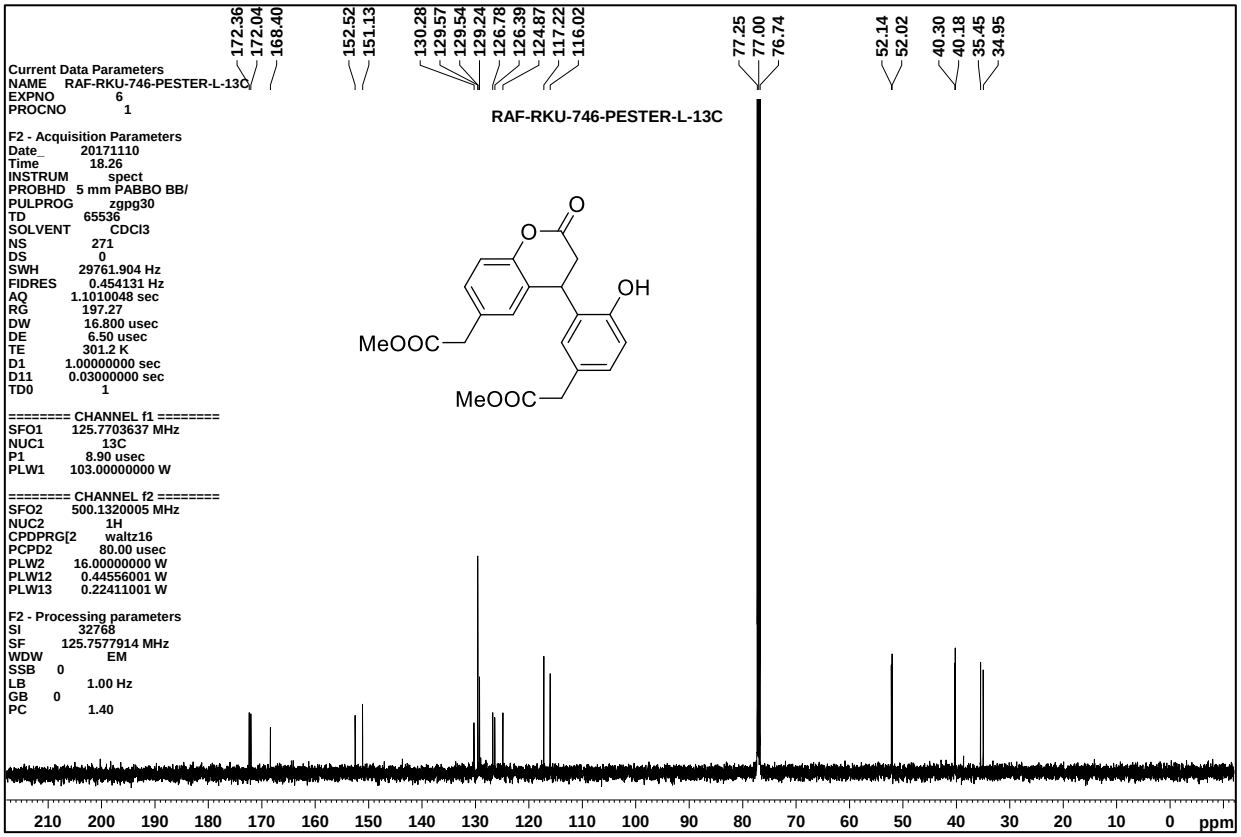
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5i**



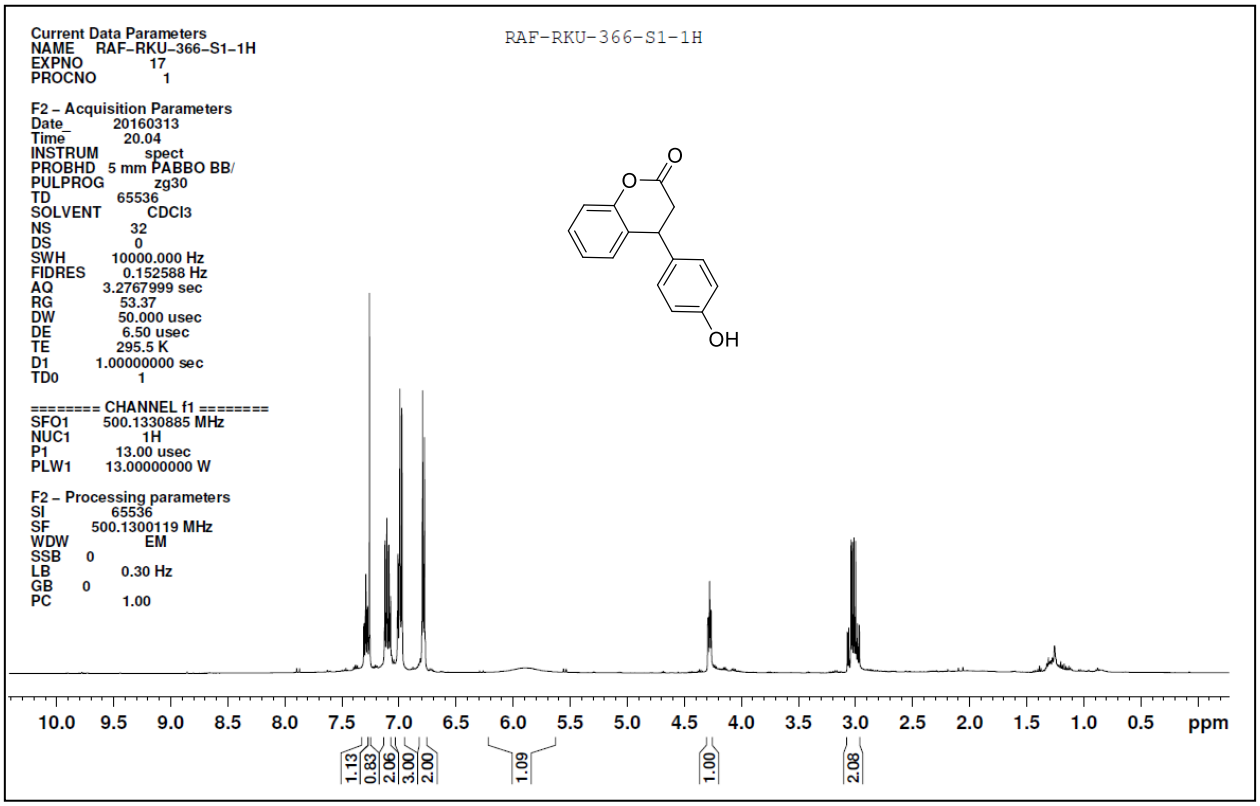


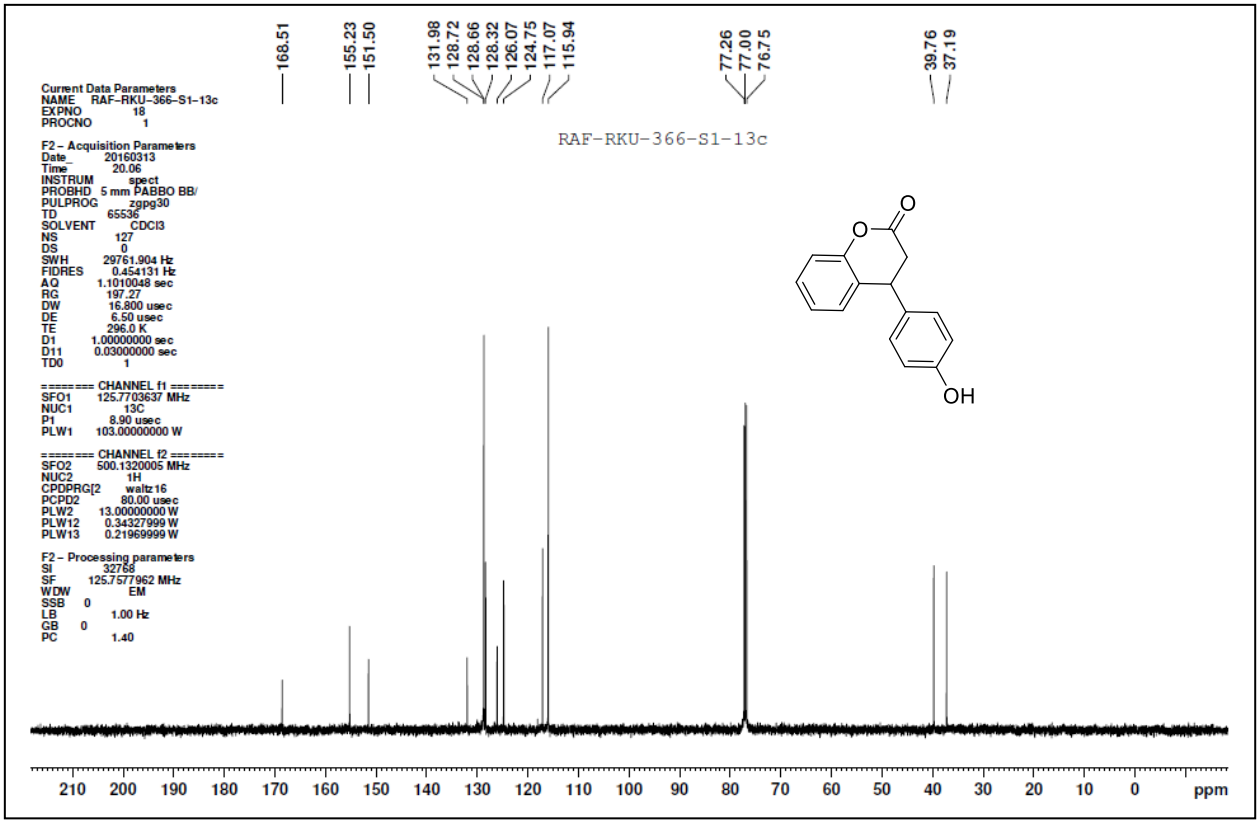
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5j**



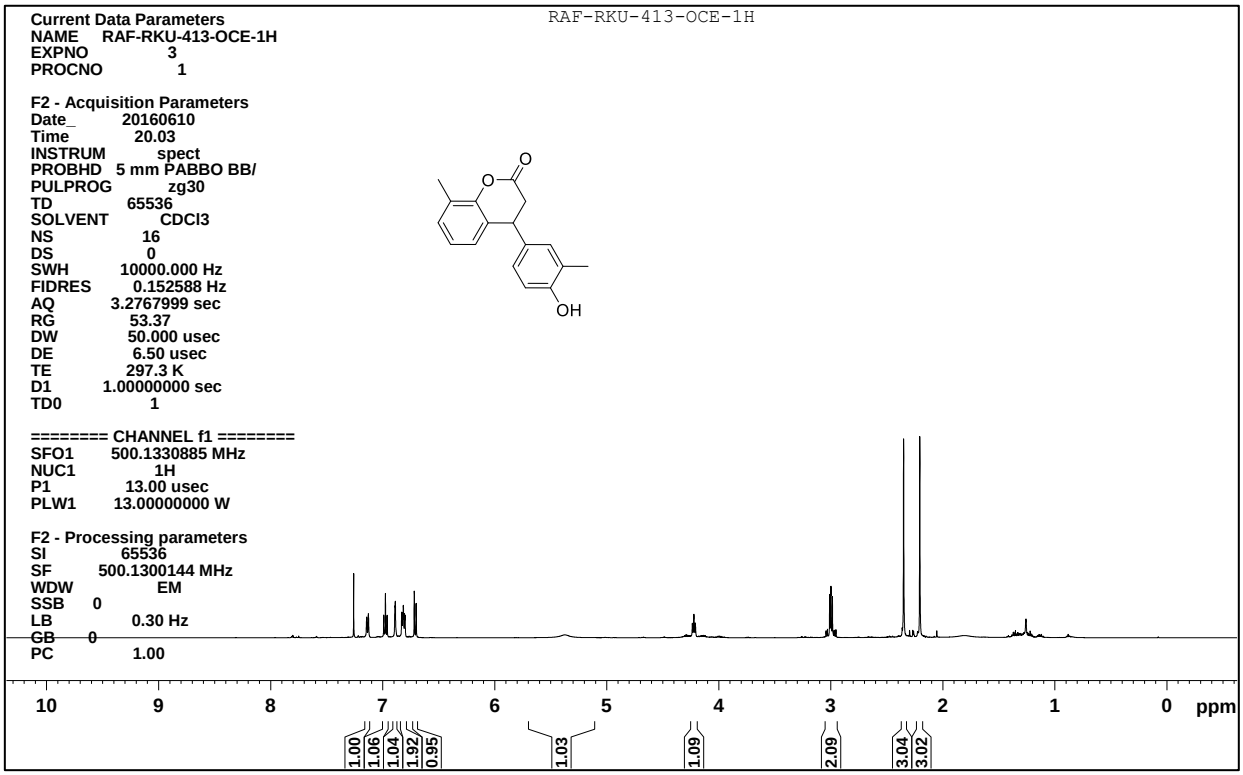


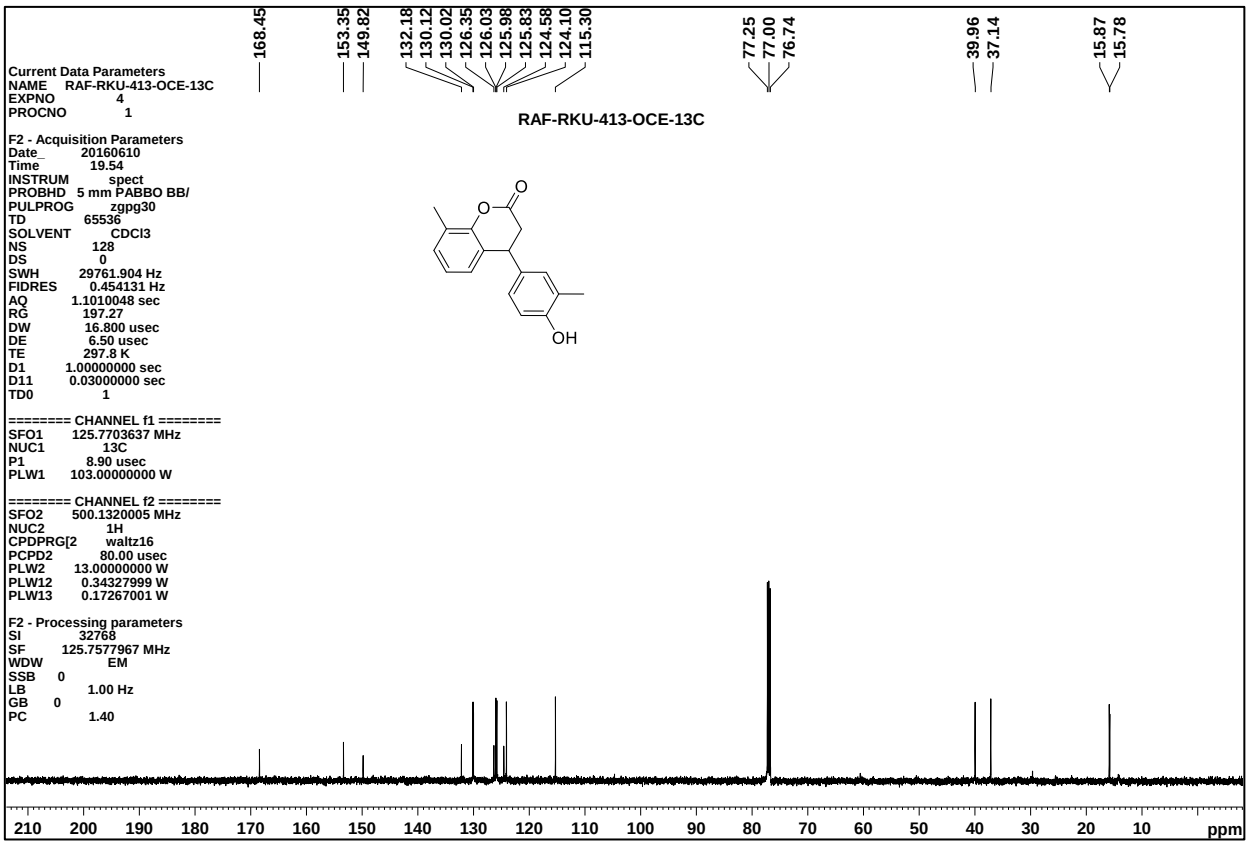
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5k**



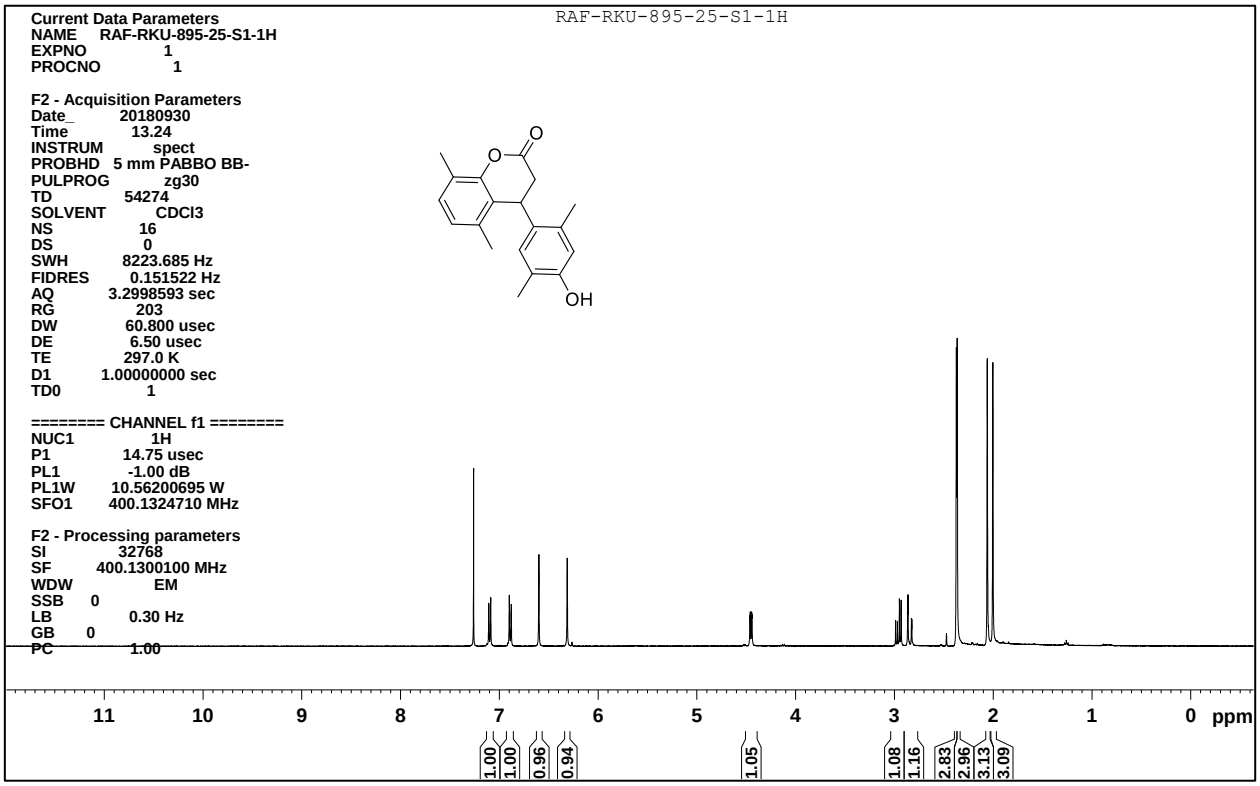


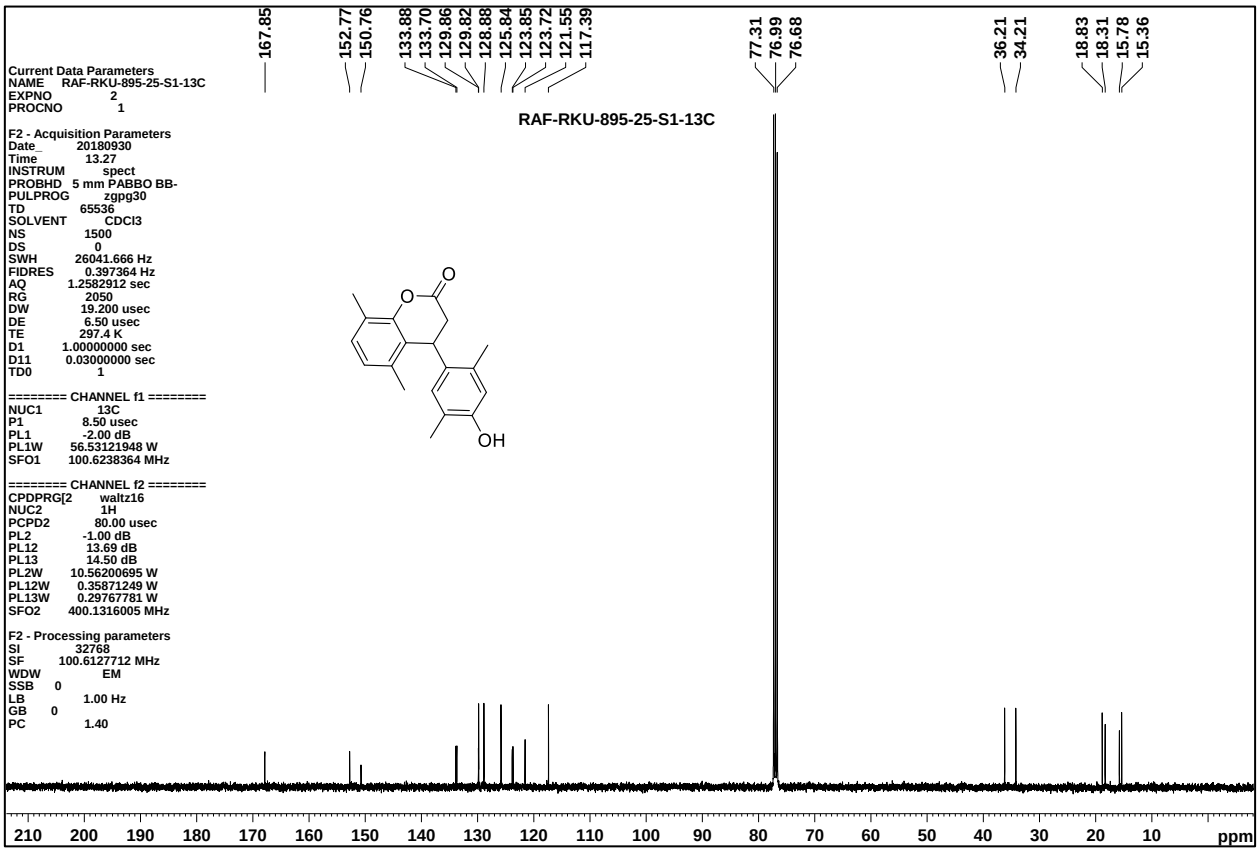
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5l**



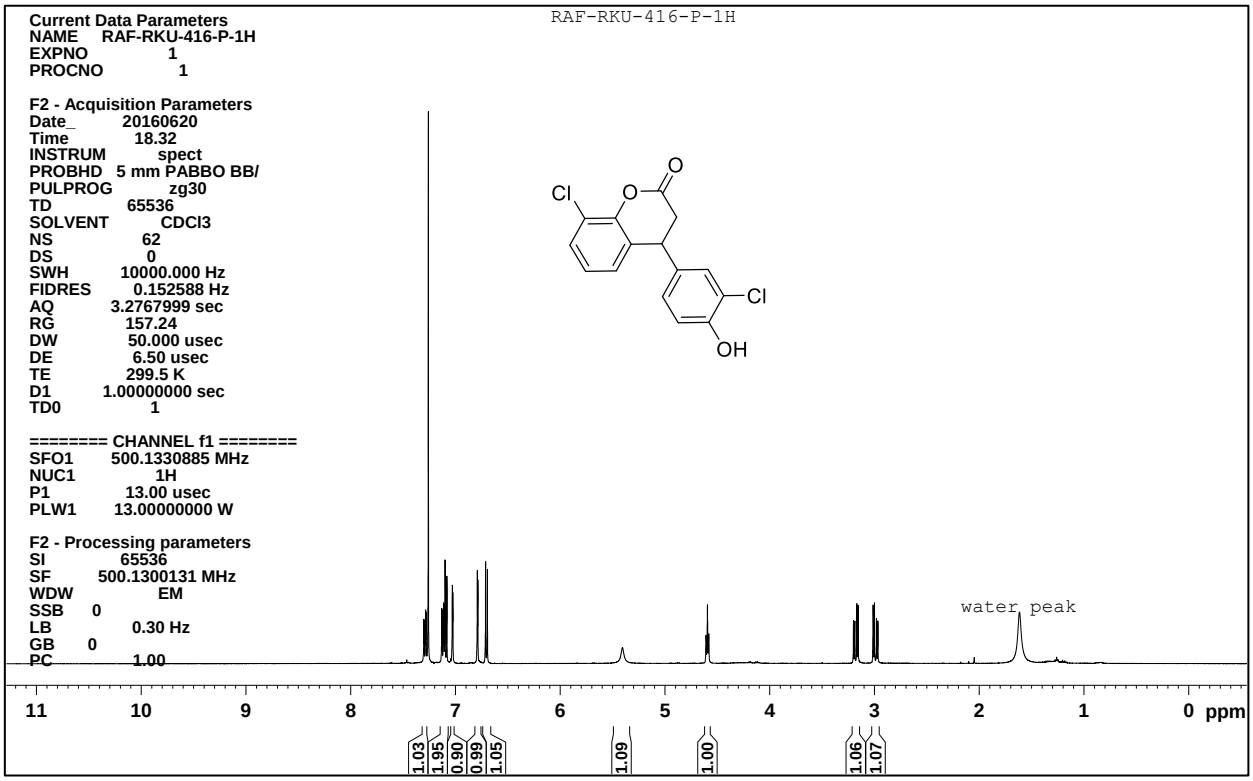


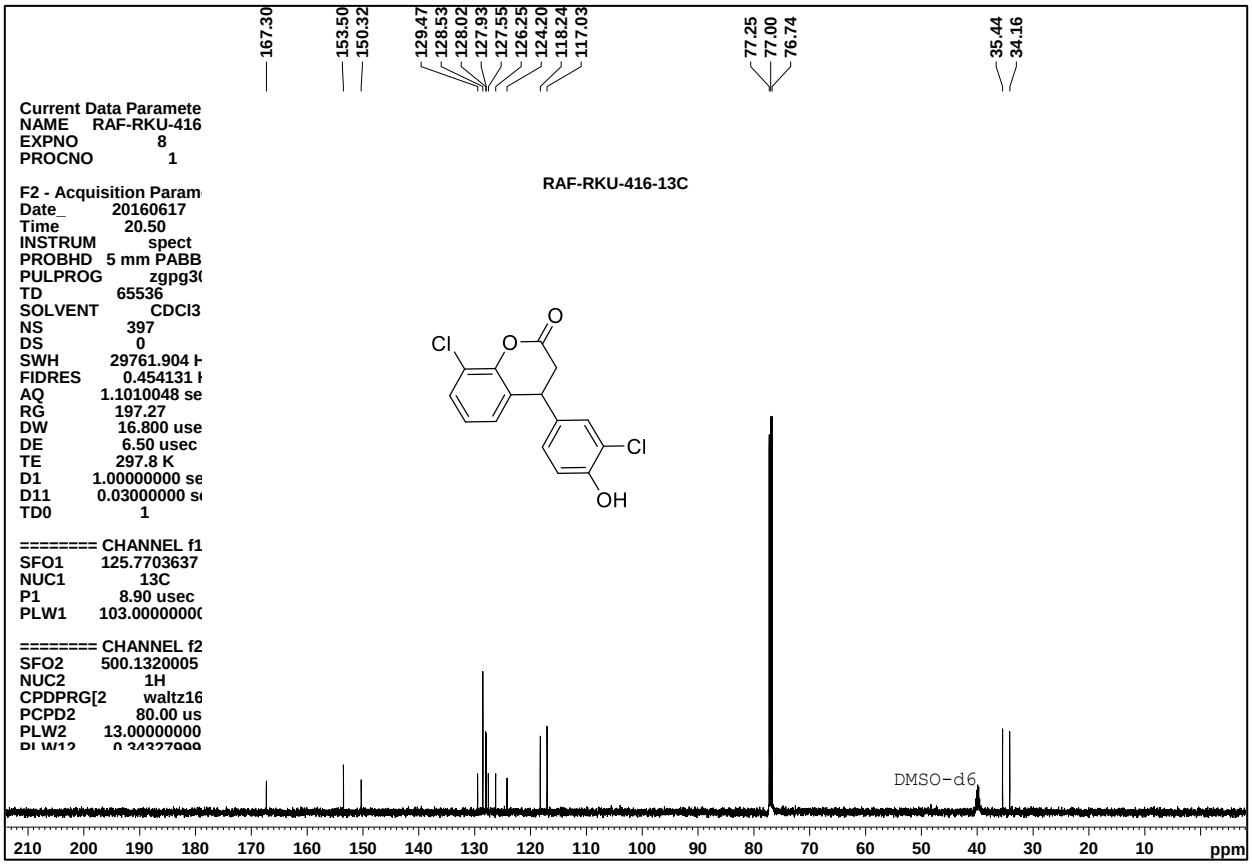
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5m**



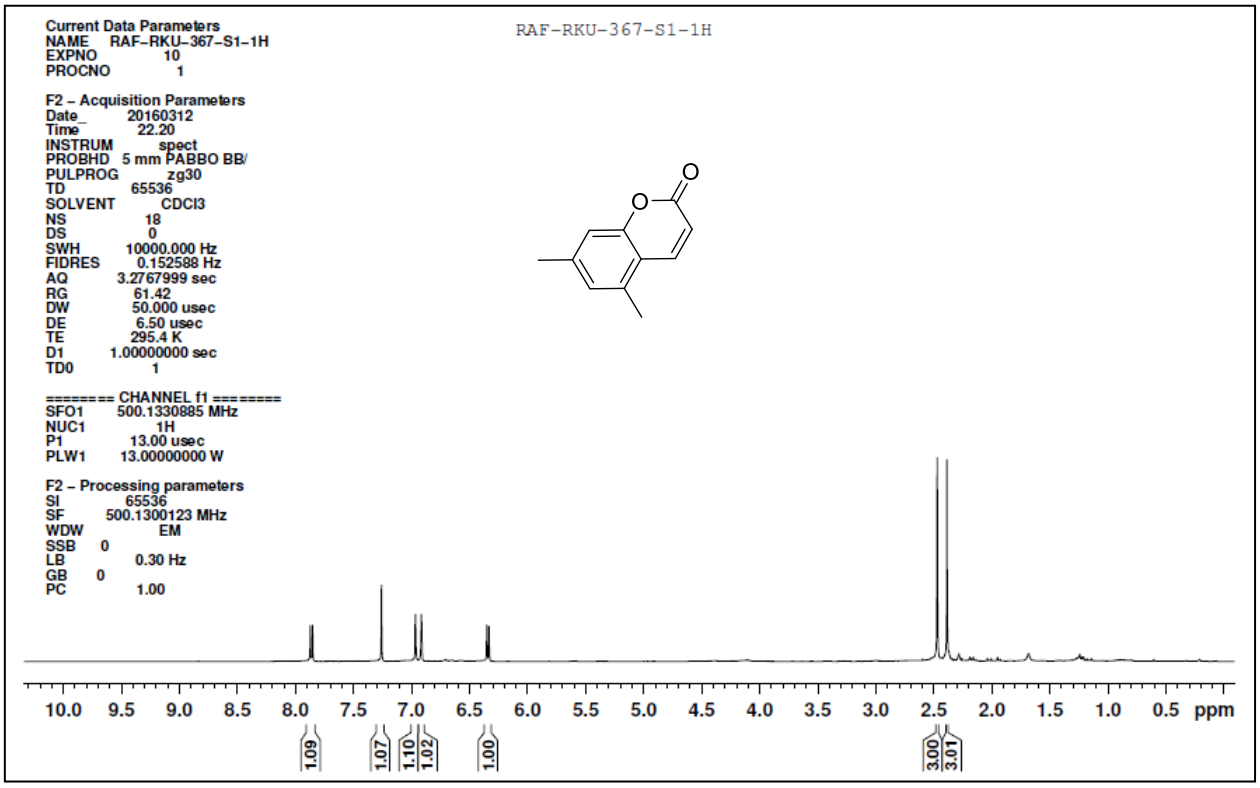


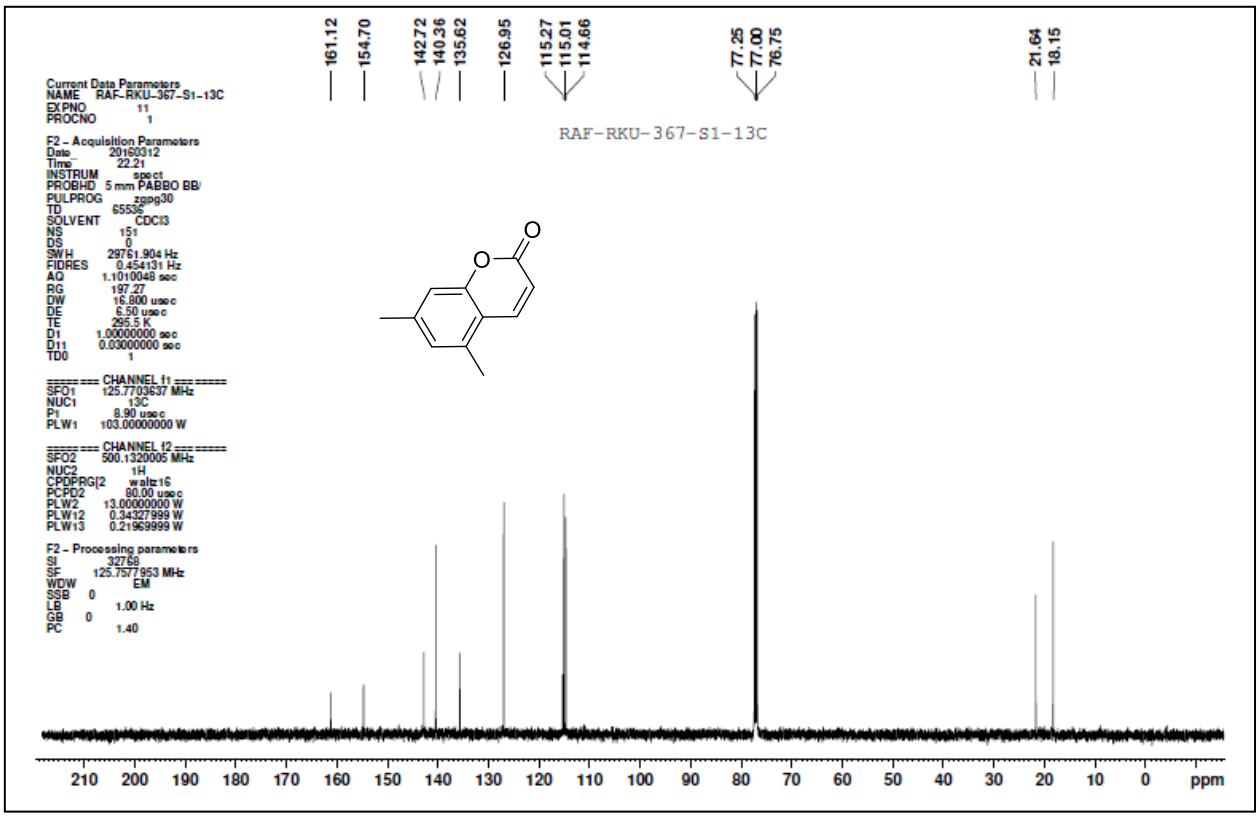
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$ + DMSO-d_6) of **5n**



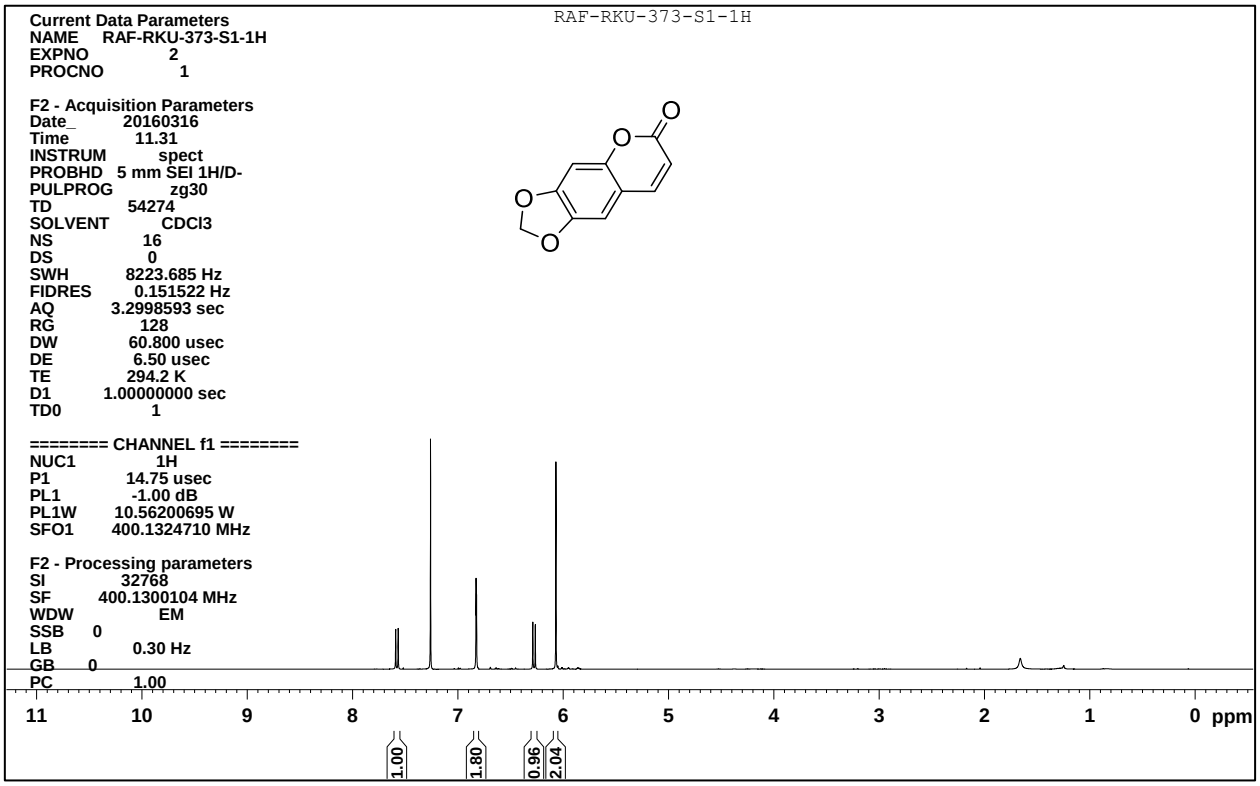


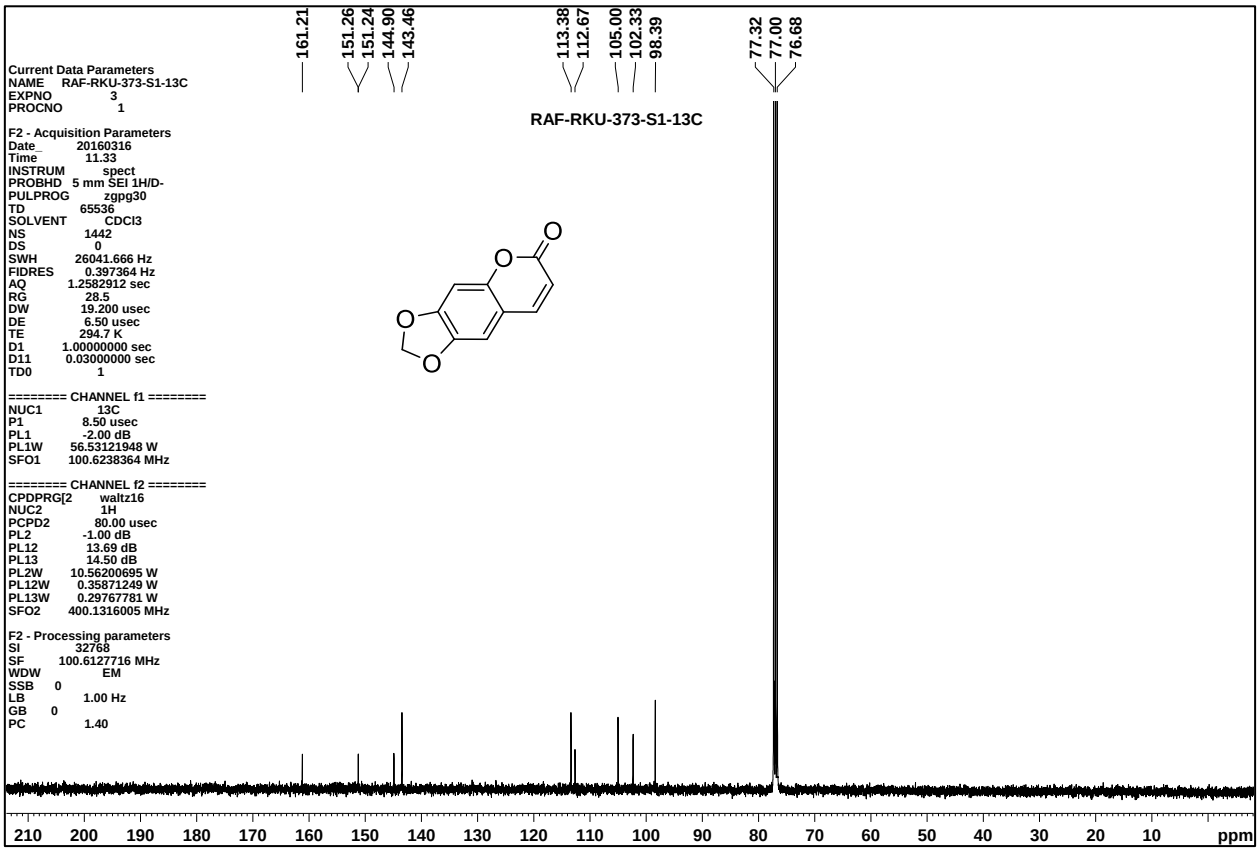
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5o**



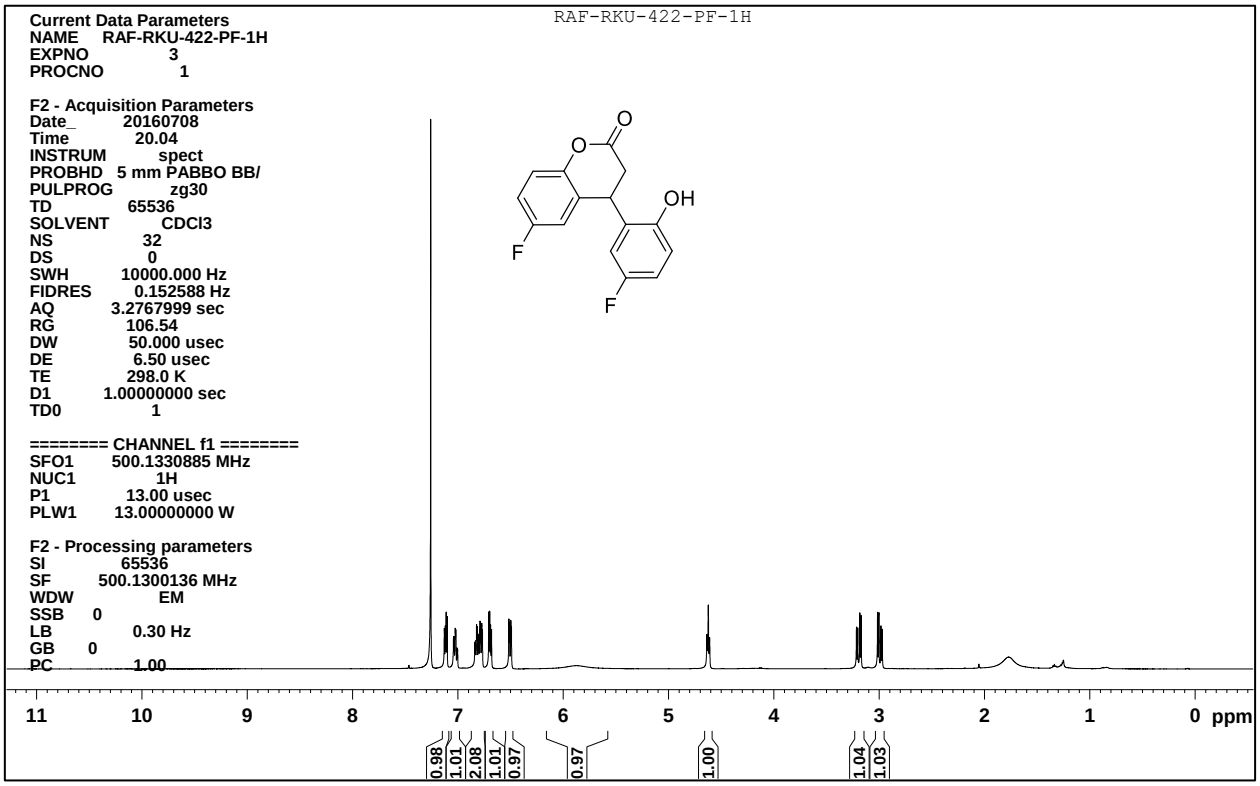


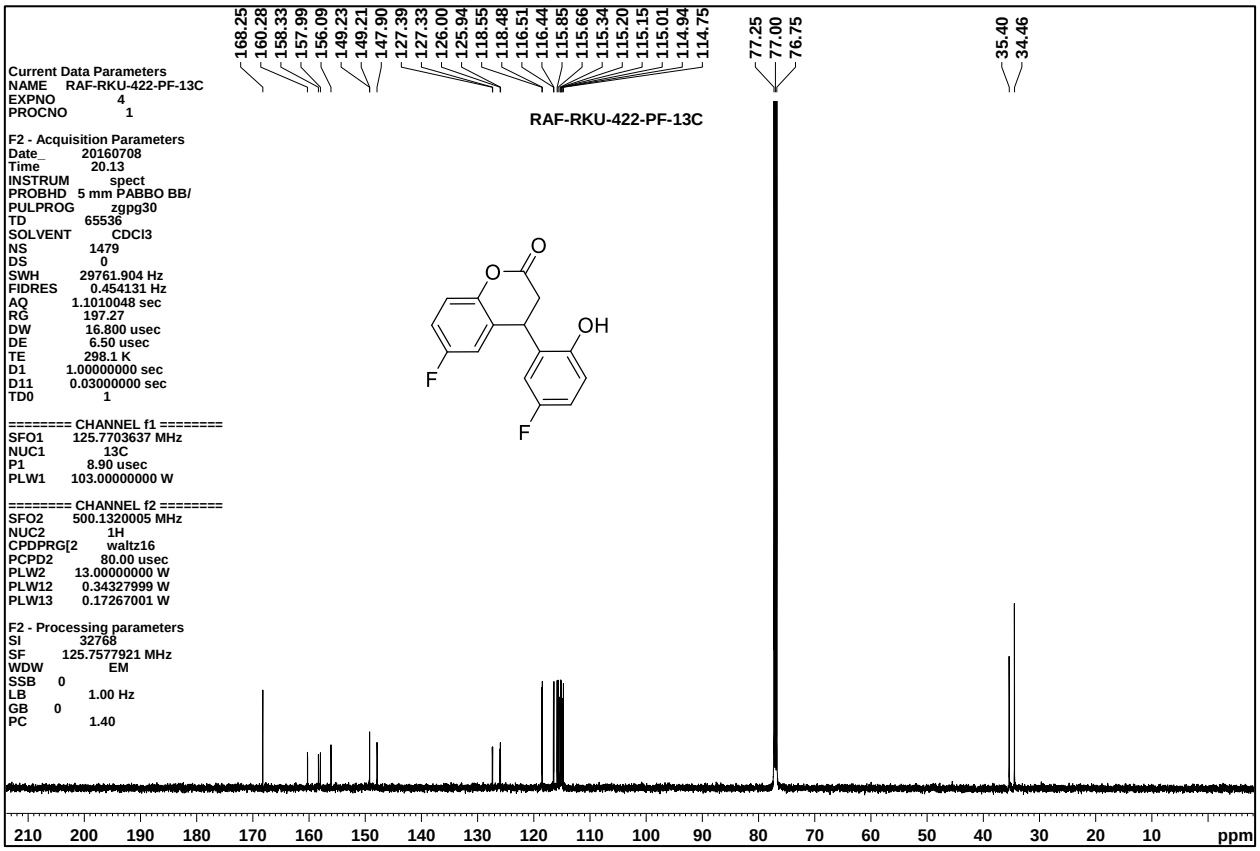
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5p**



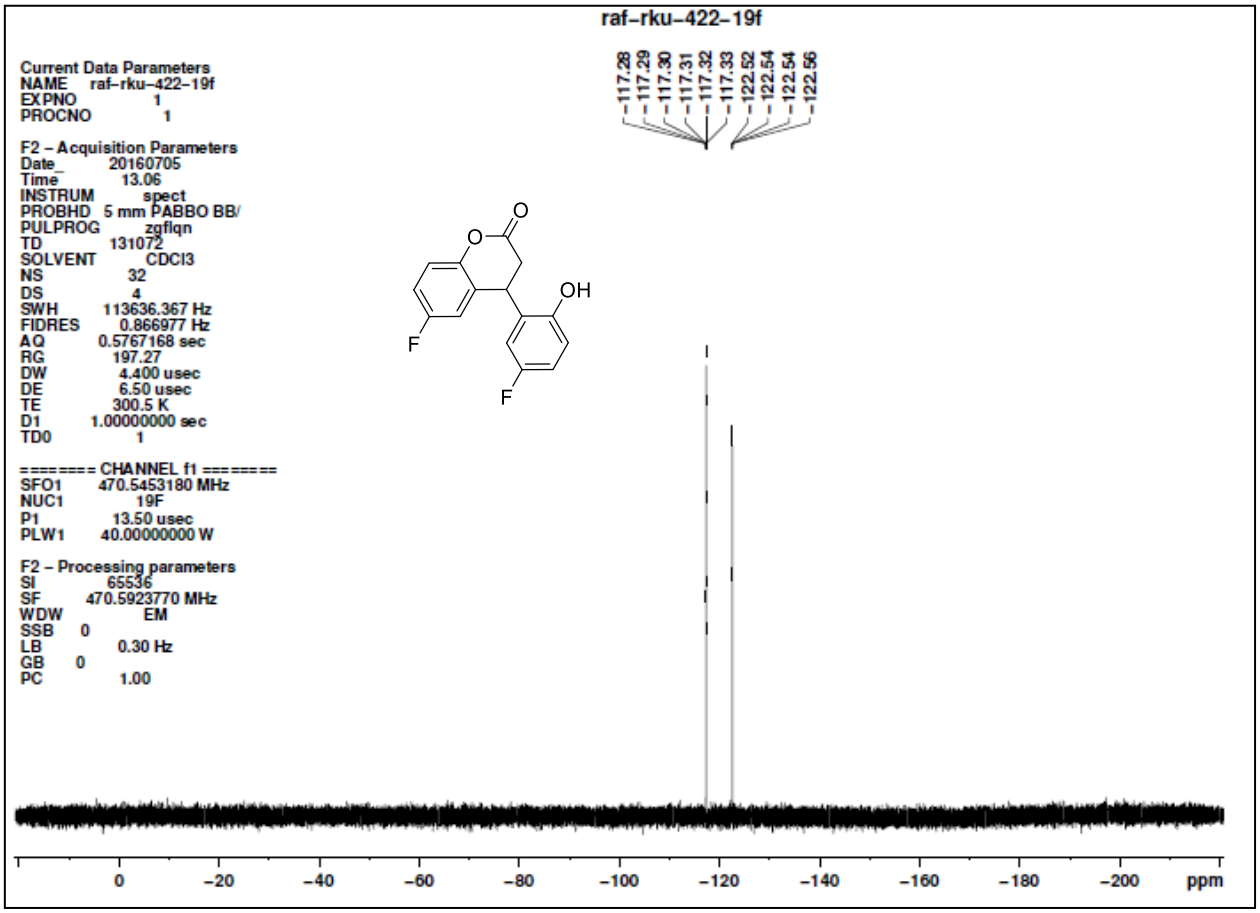


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5q**

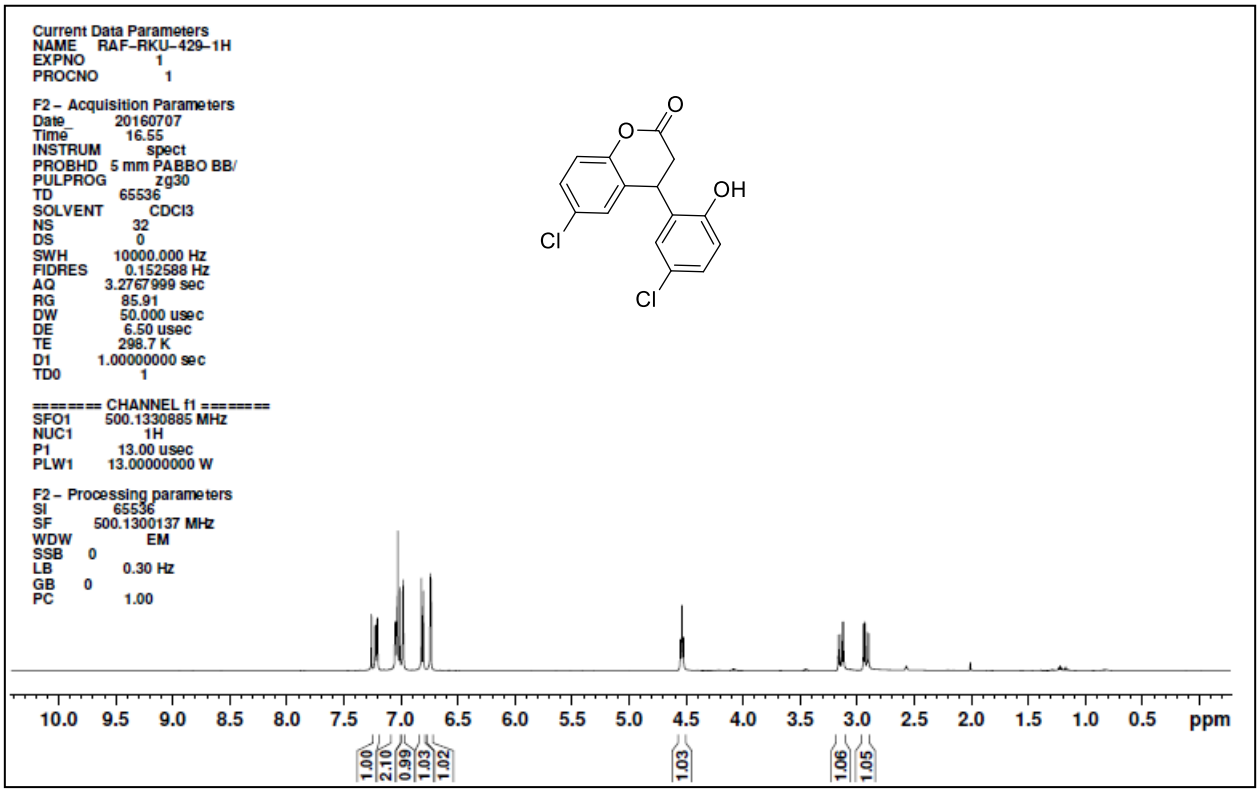


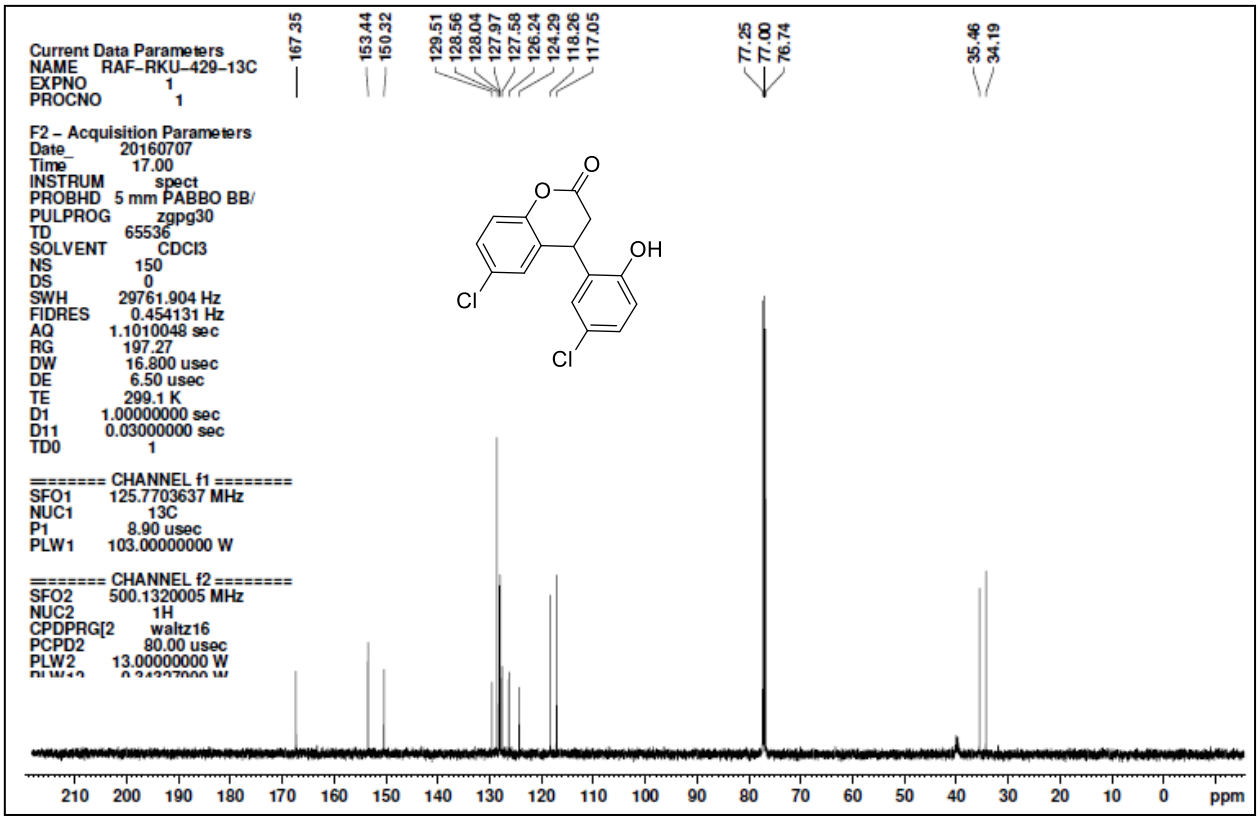


^{19}F NMR(470 MHz, $CDCl_3$) of **5q**

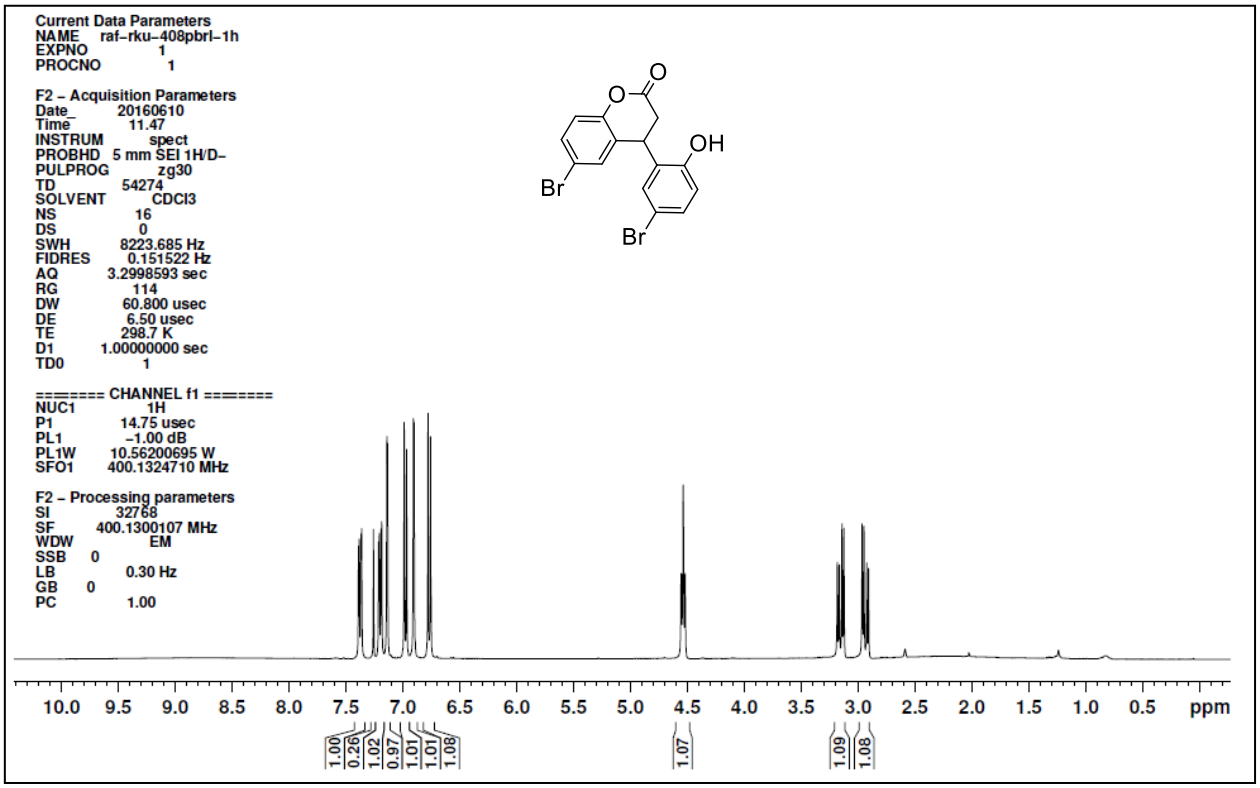


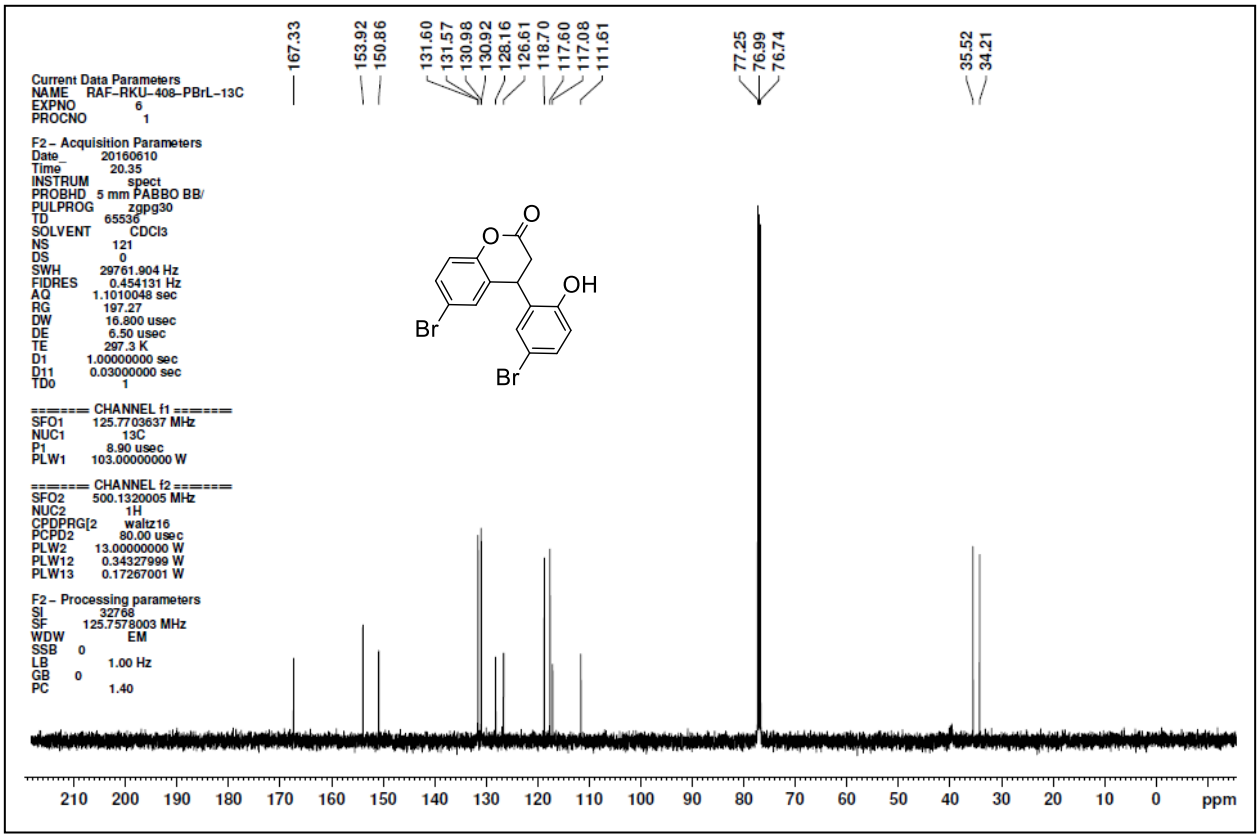
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5r**



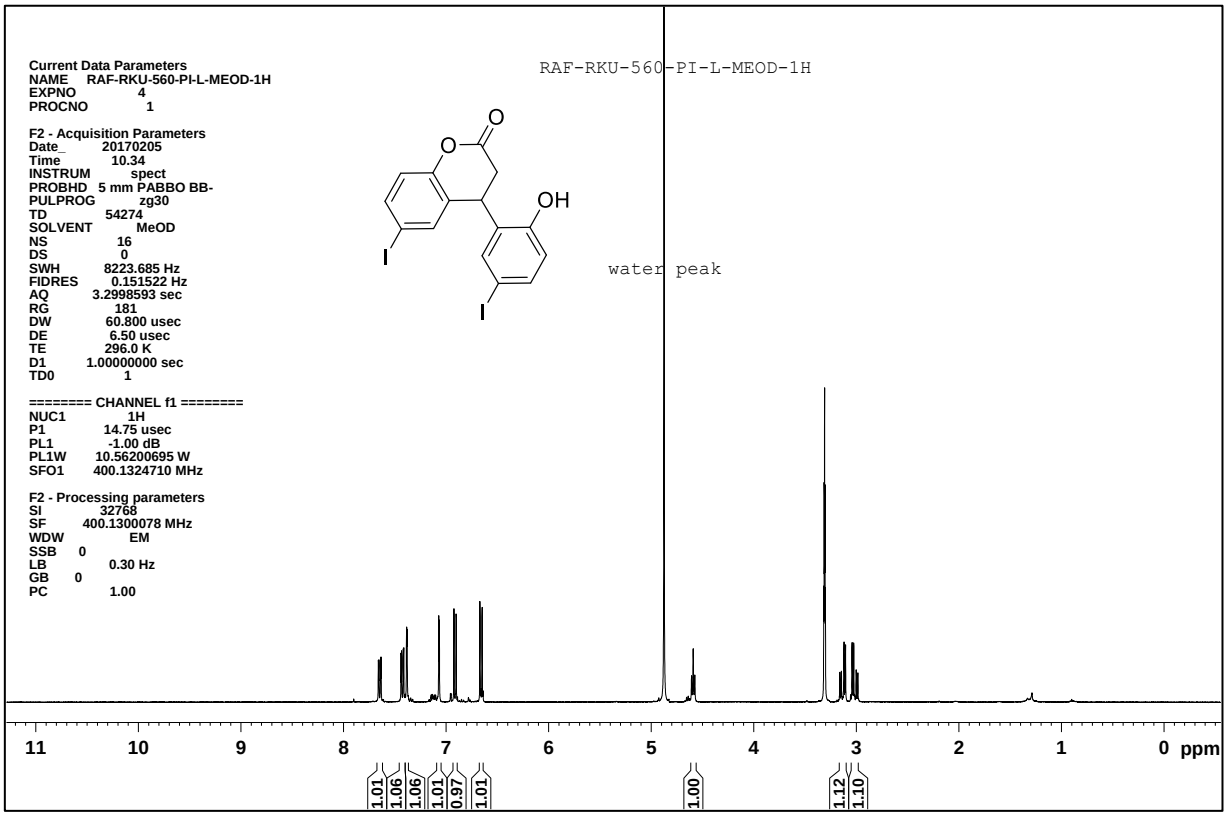


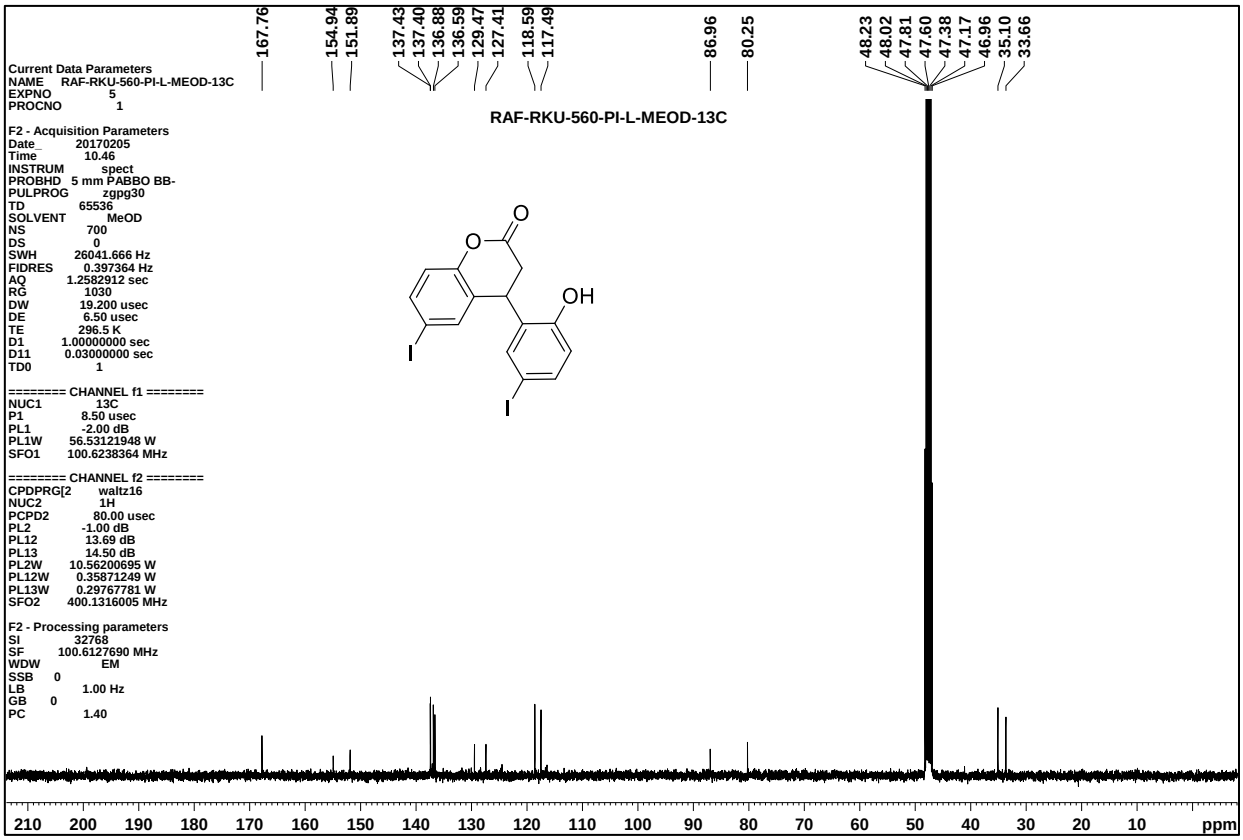
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5s**



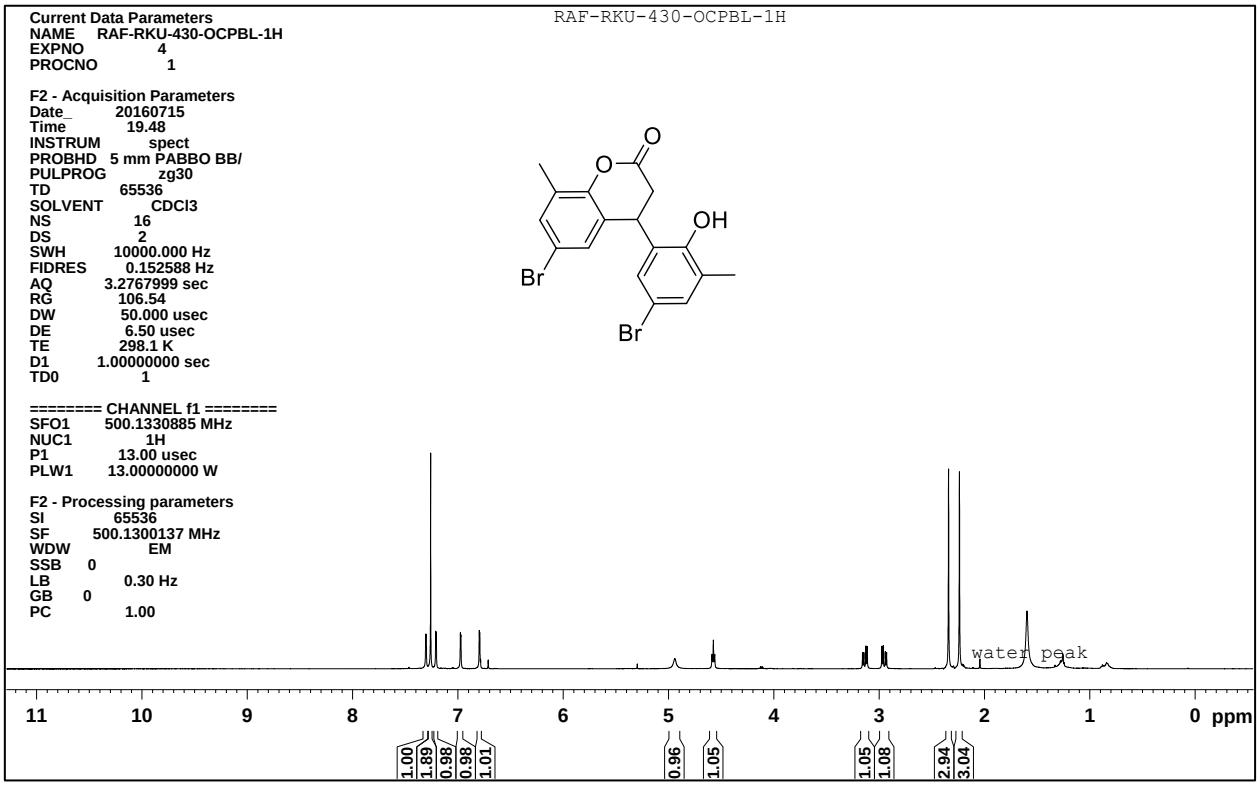


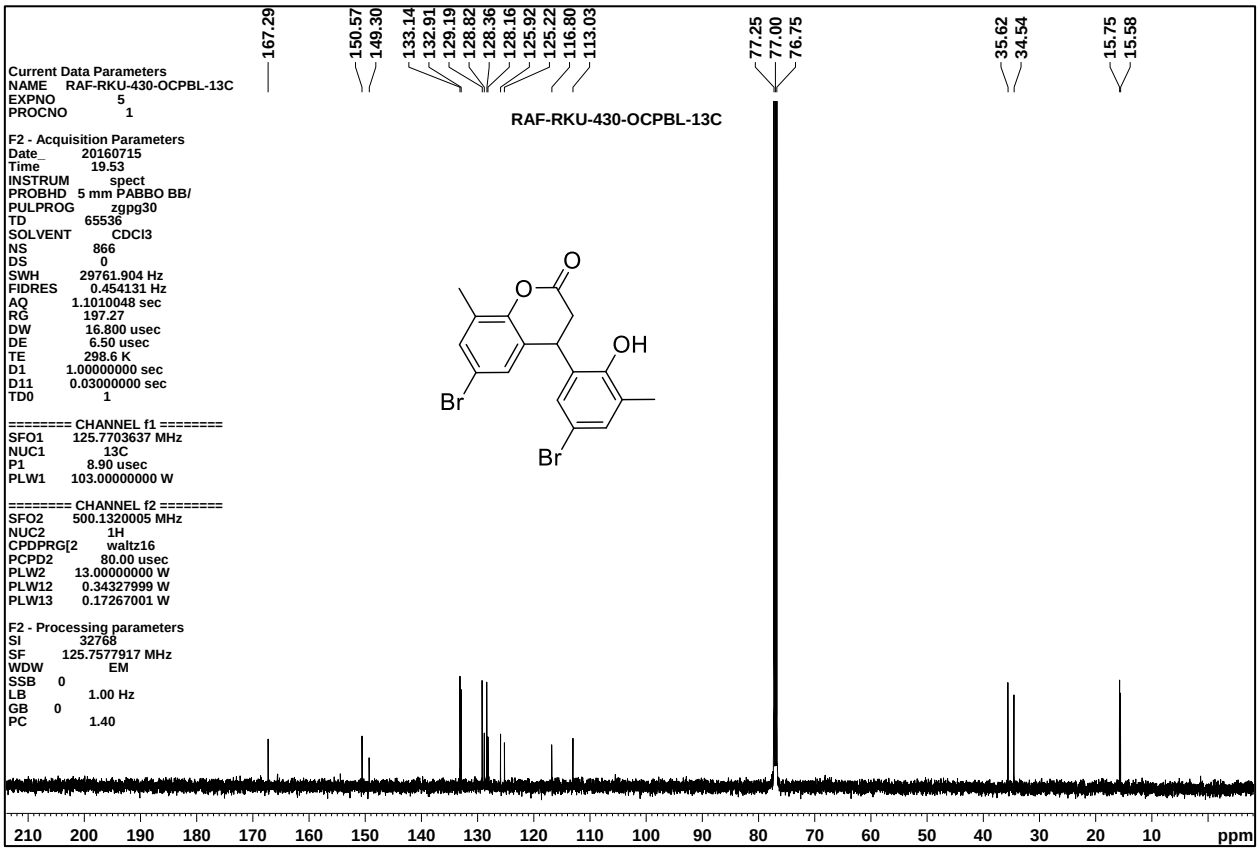
^{1}H NMR (400 MHz, MeOD) and **^{13}C NMR** (100 MHz, MeOD) of **5t**



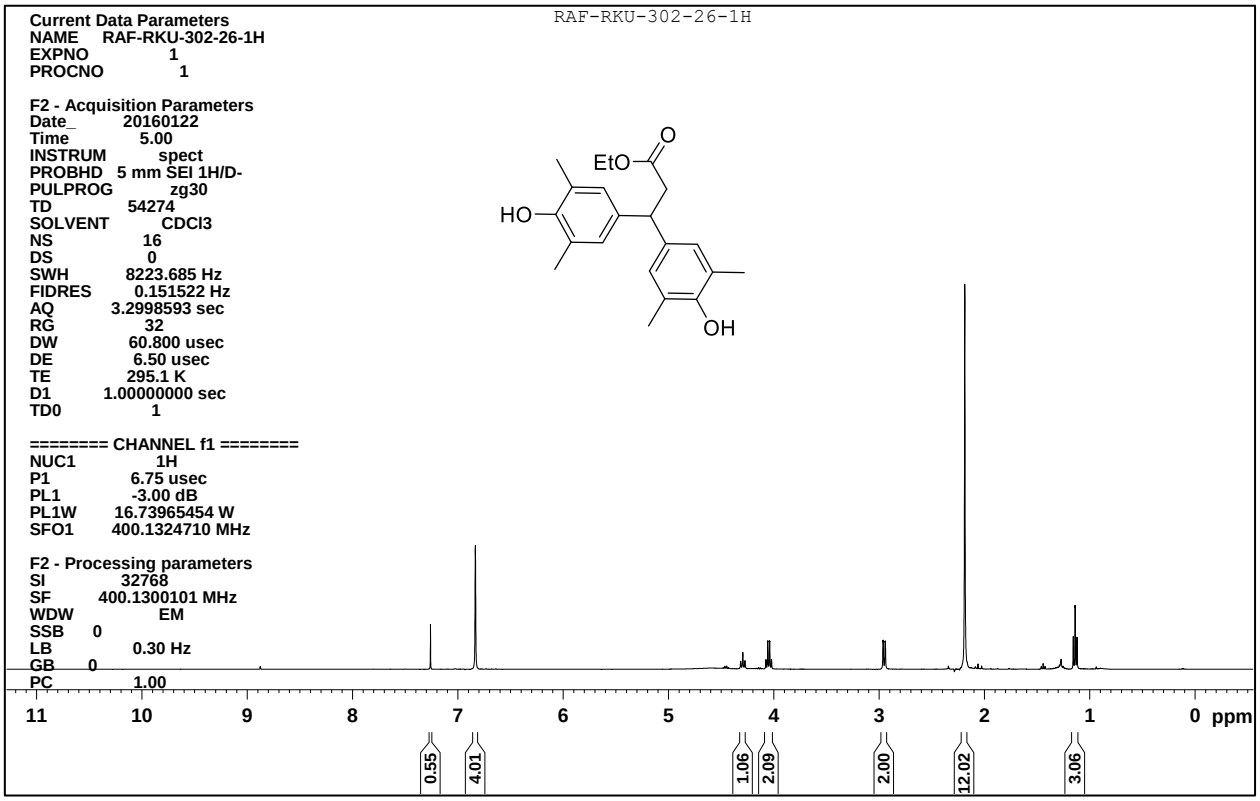


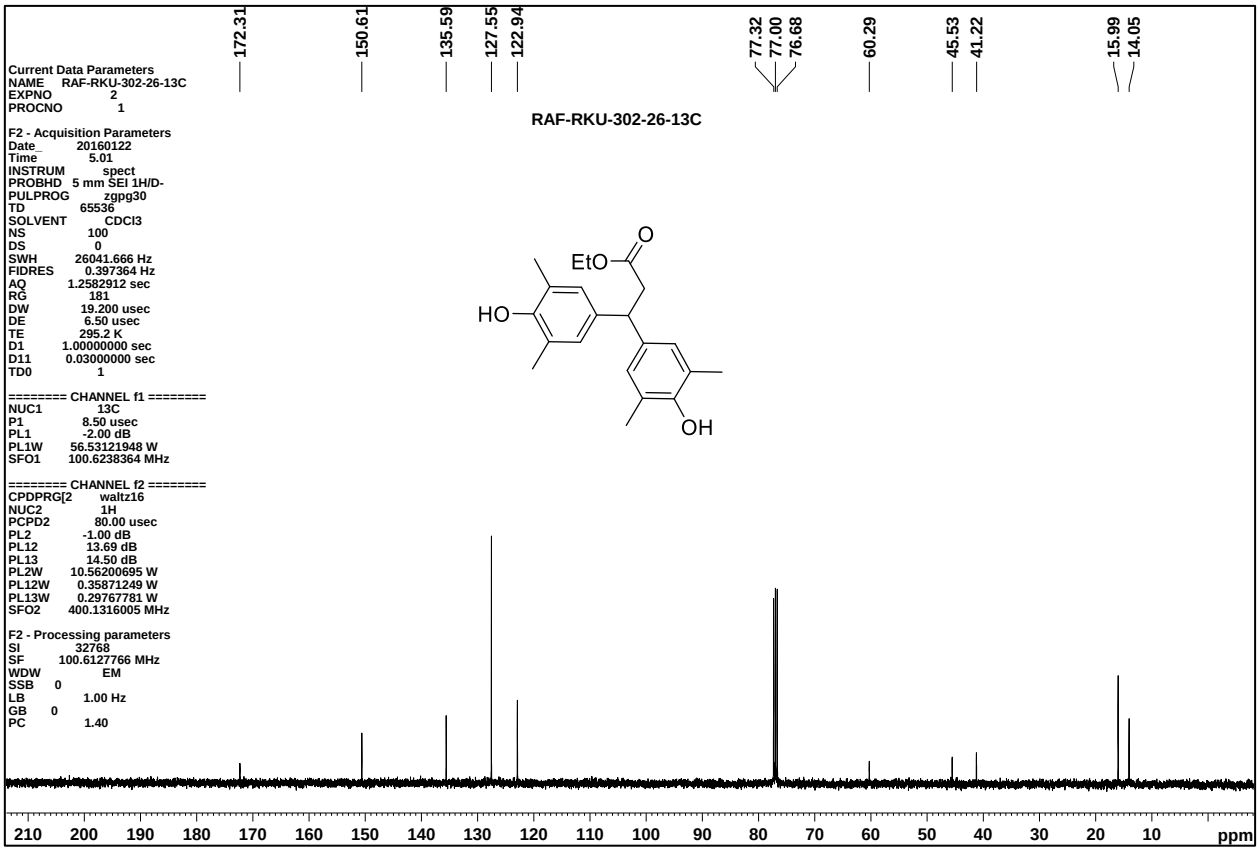
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5u**



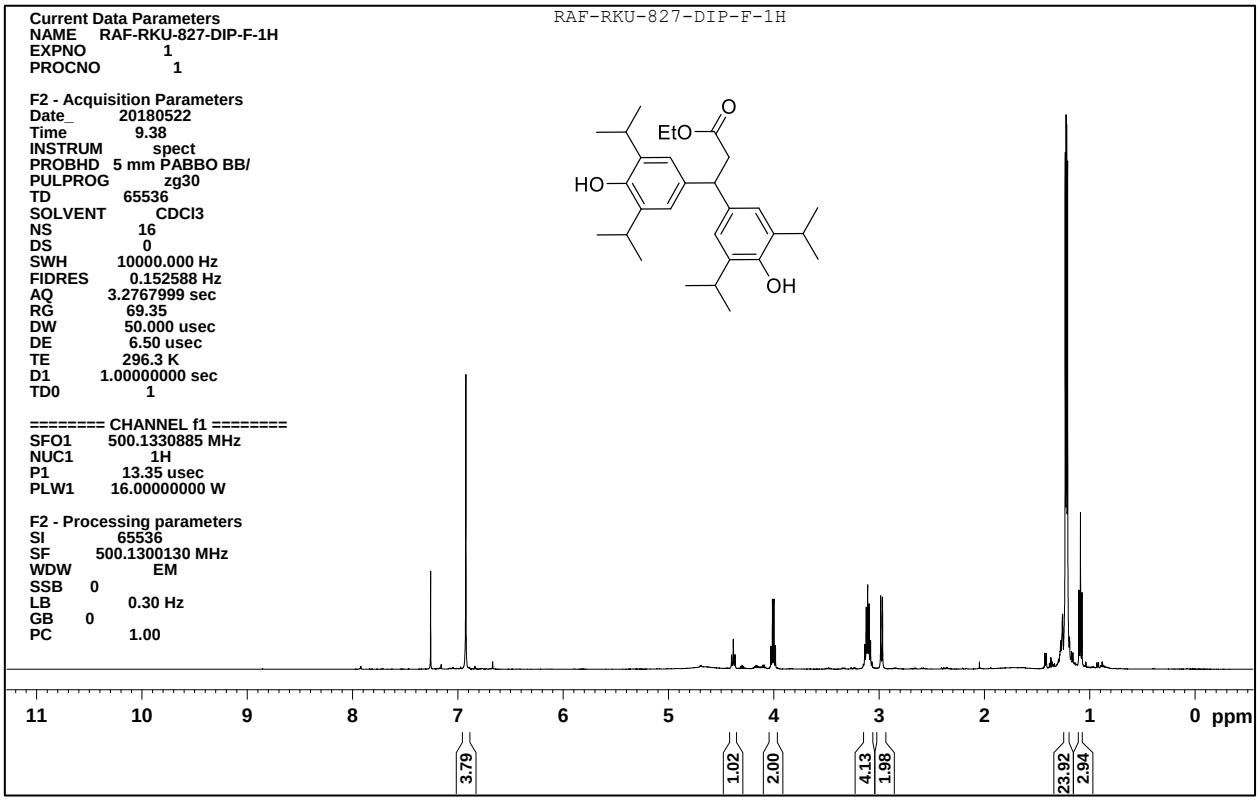


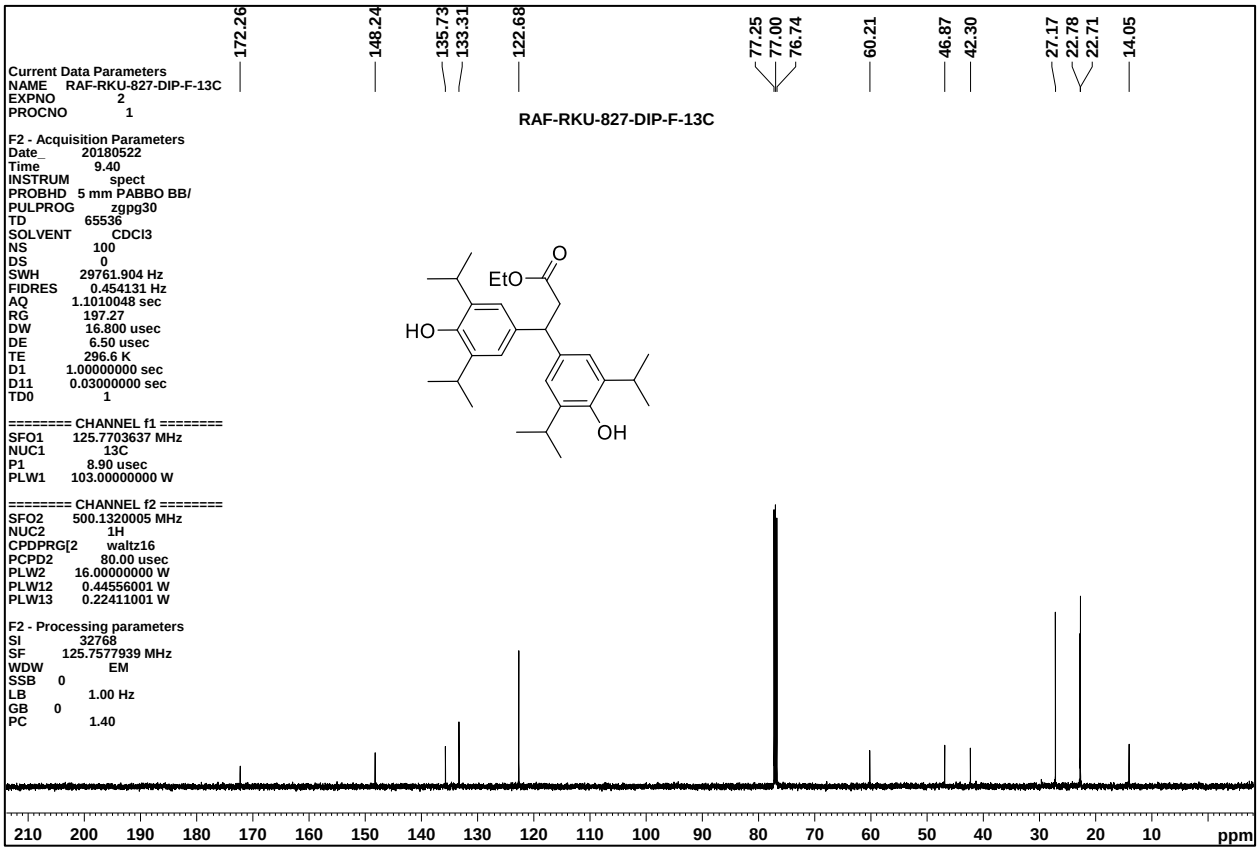
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5x**



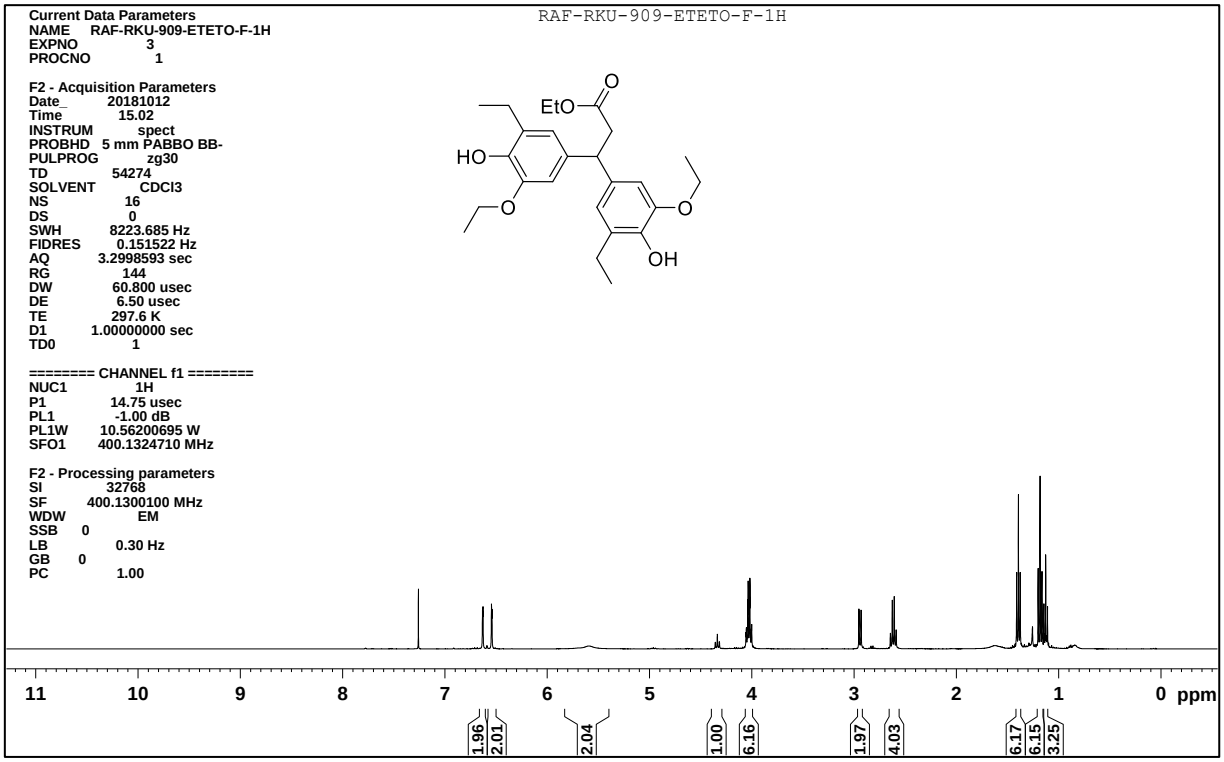


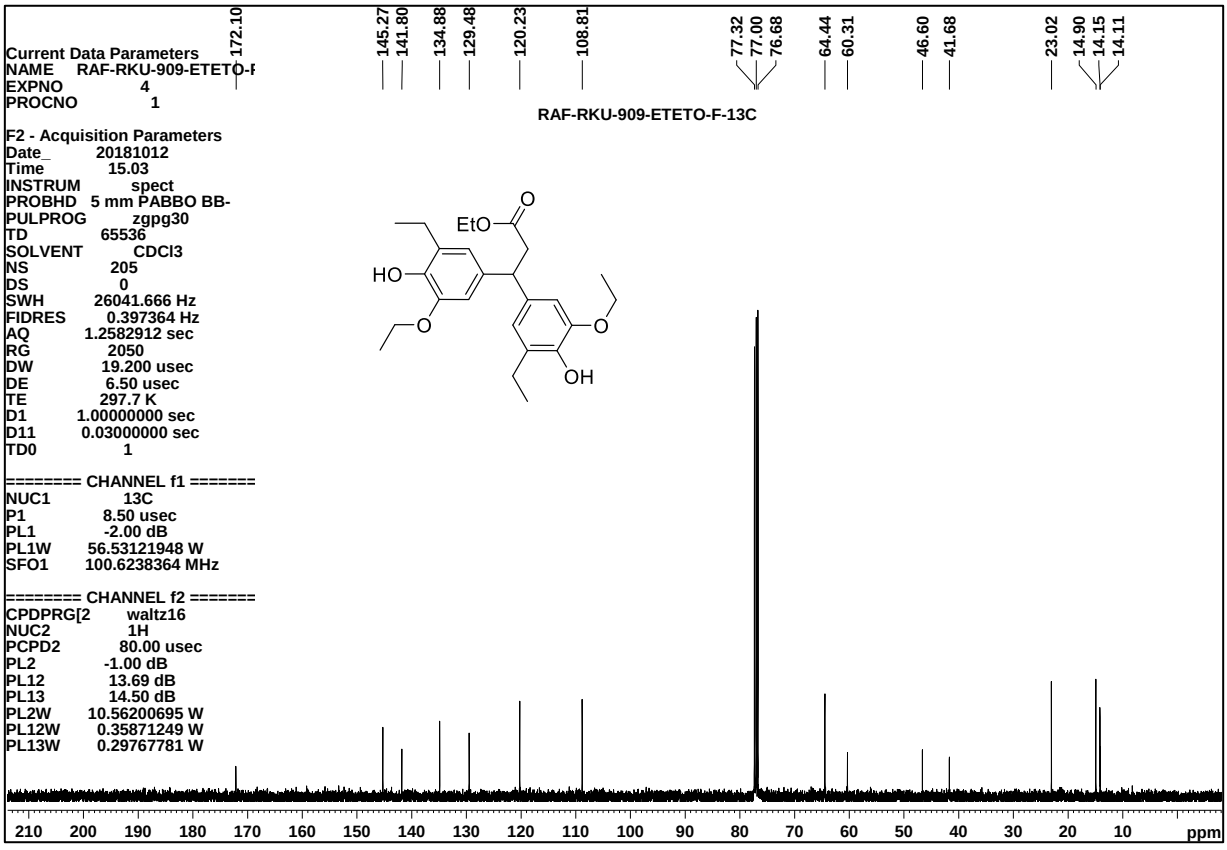
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5y**



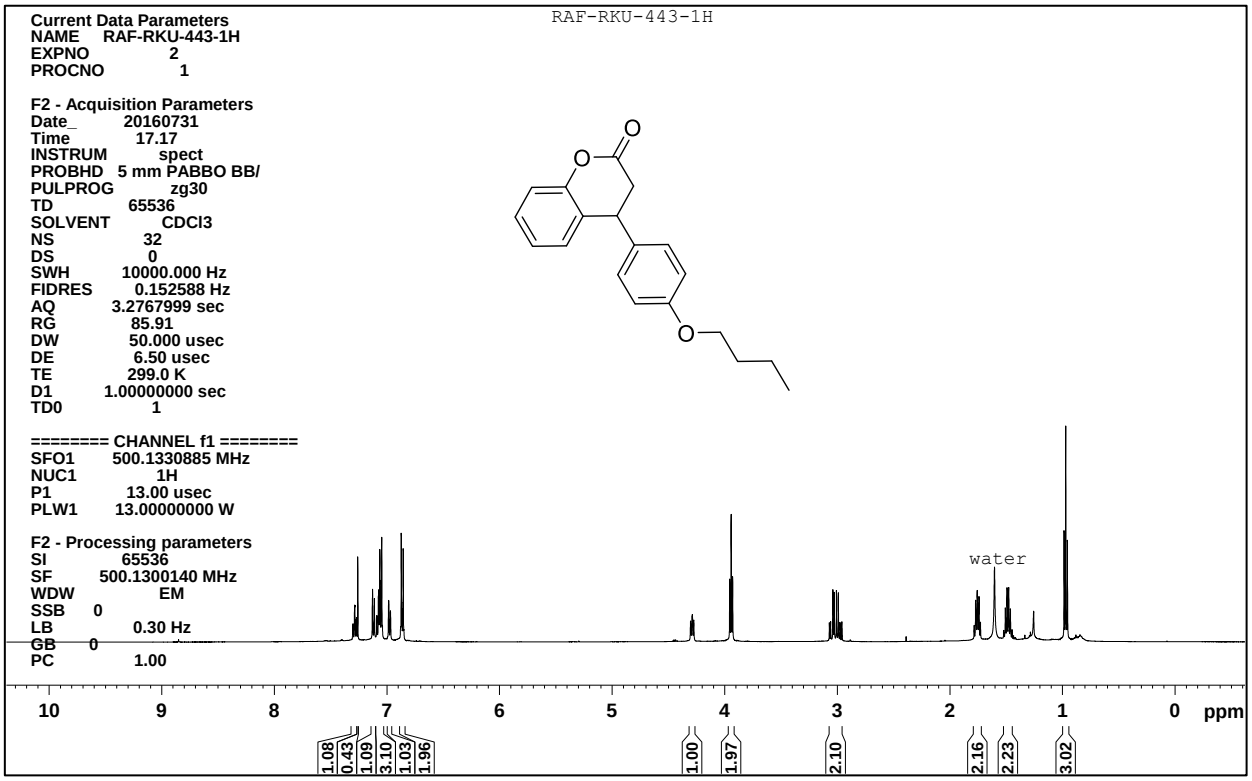


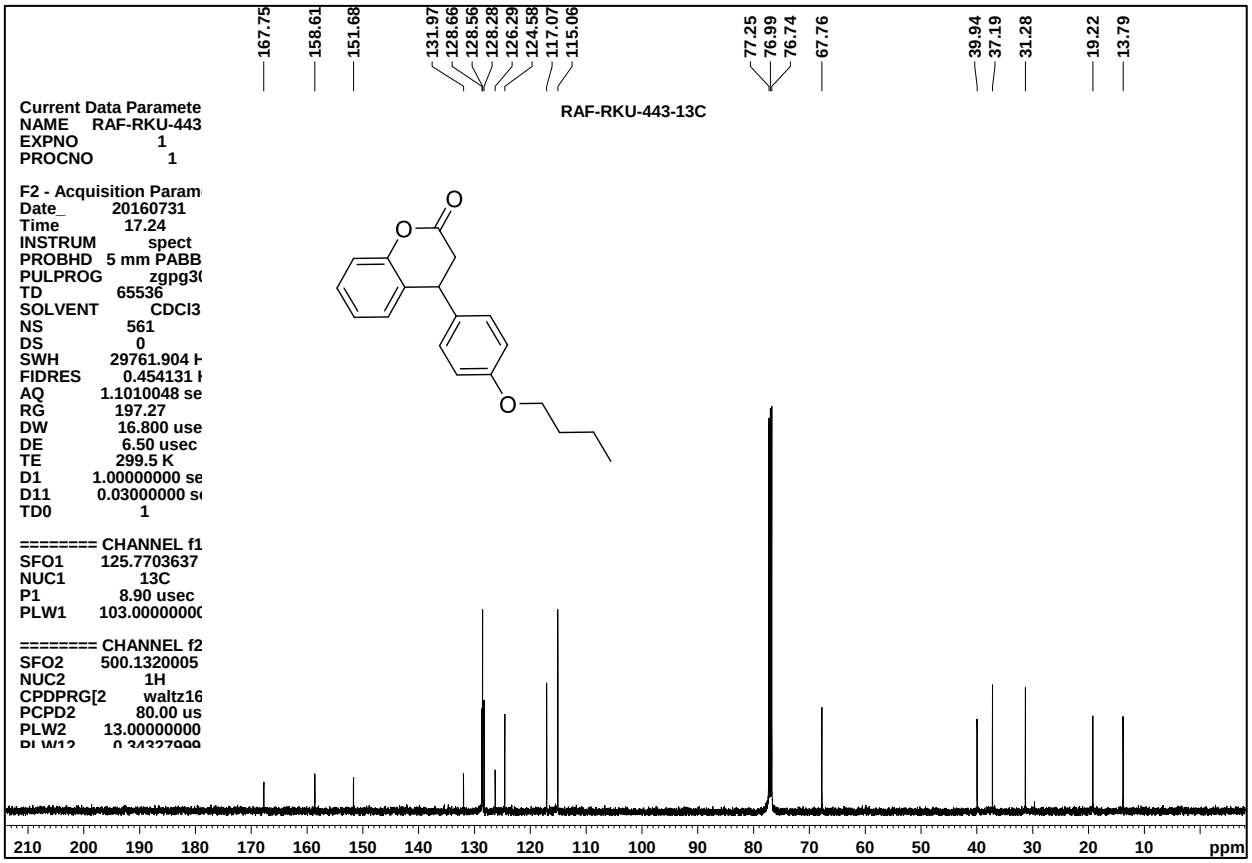
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5z**



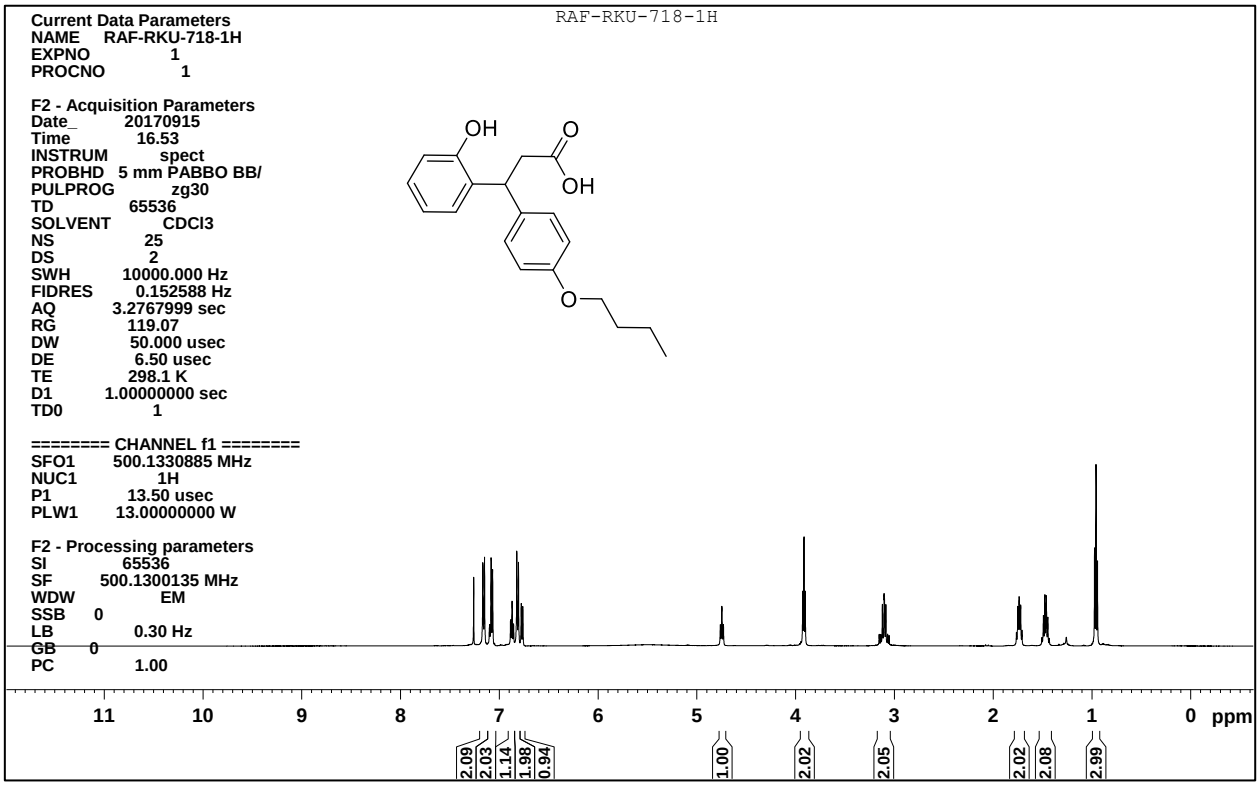


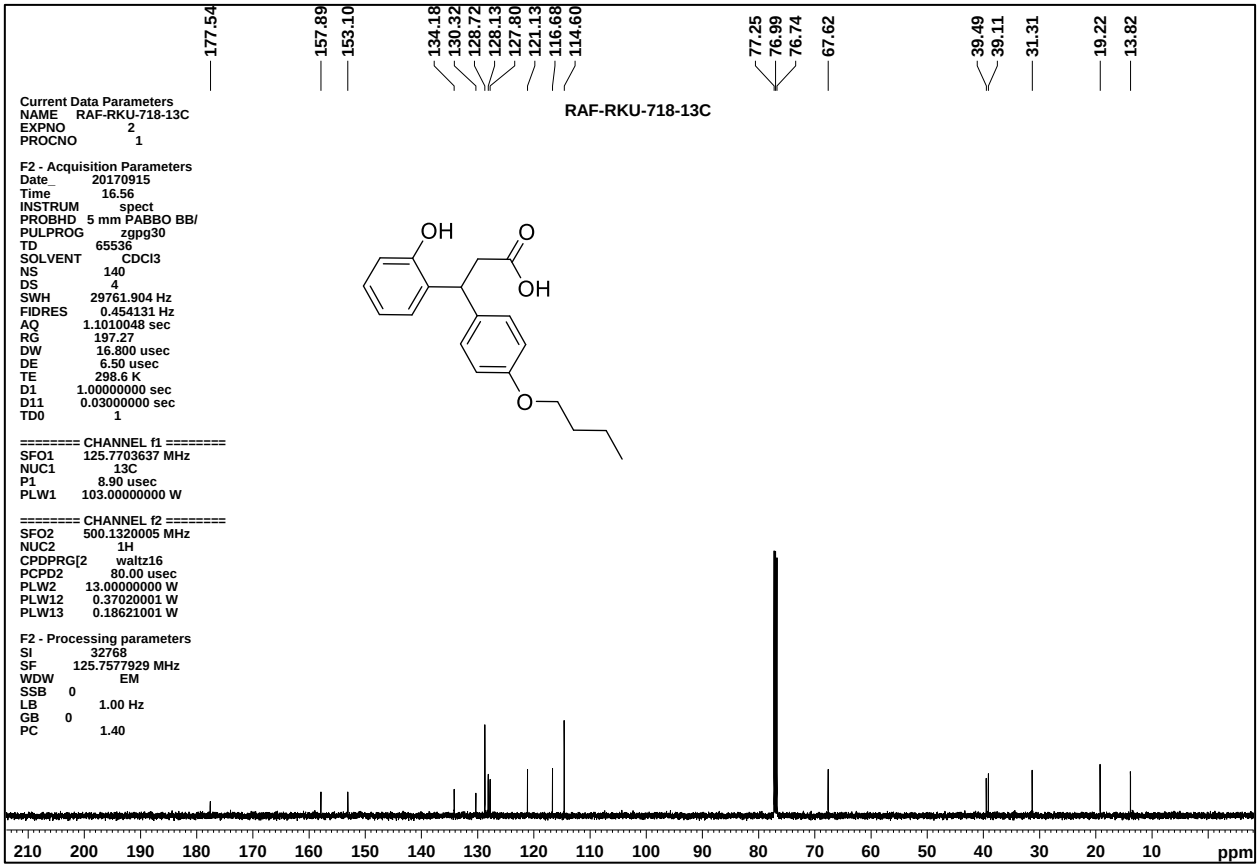
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **10**



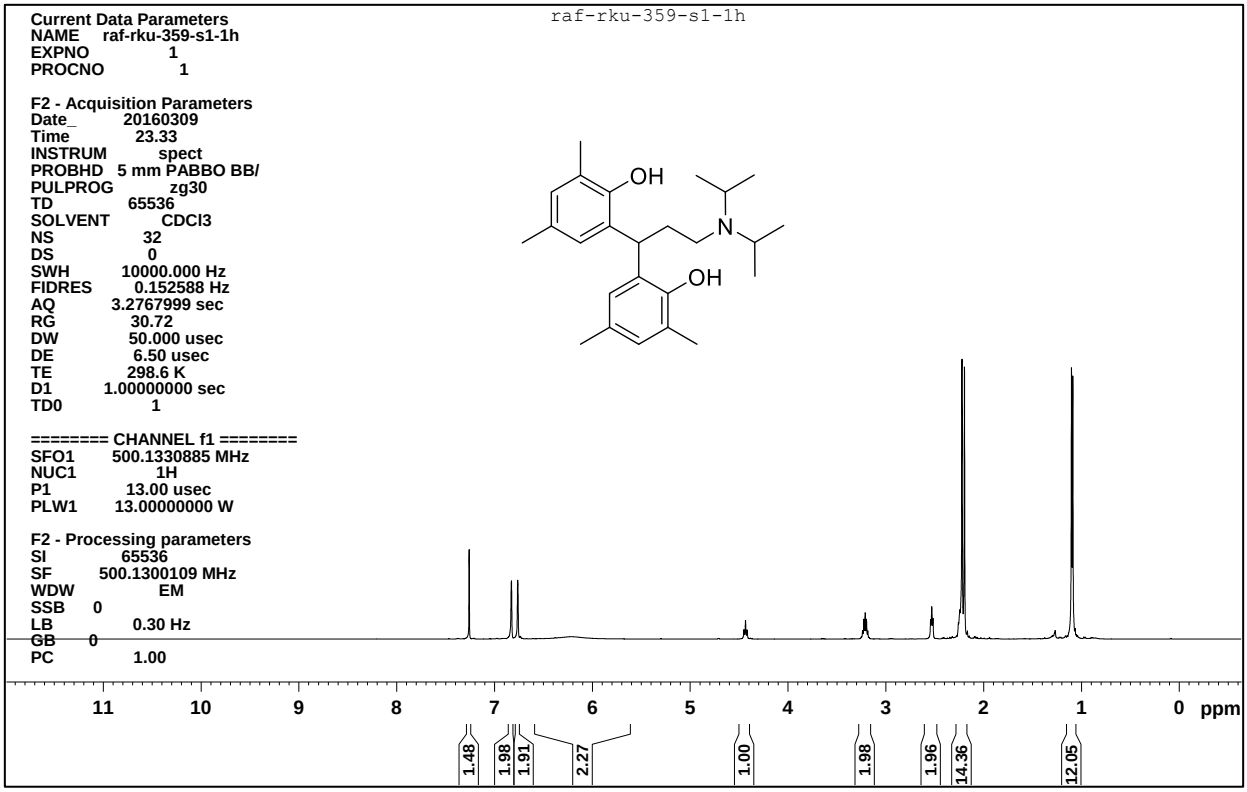


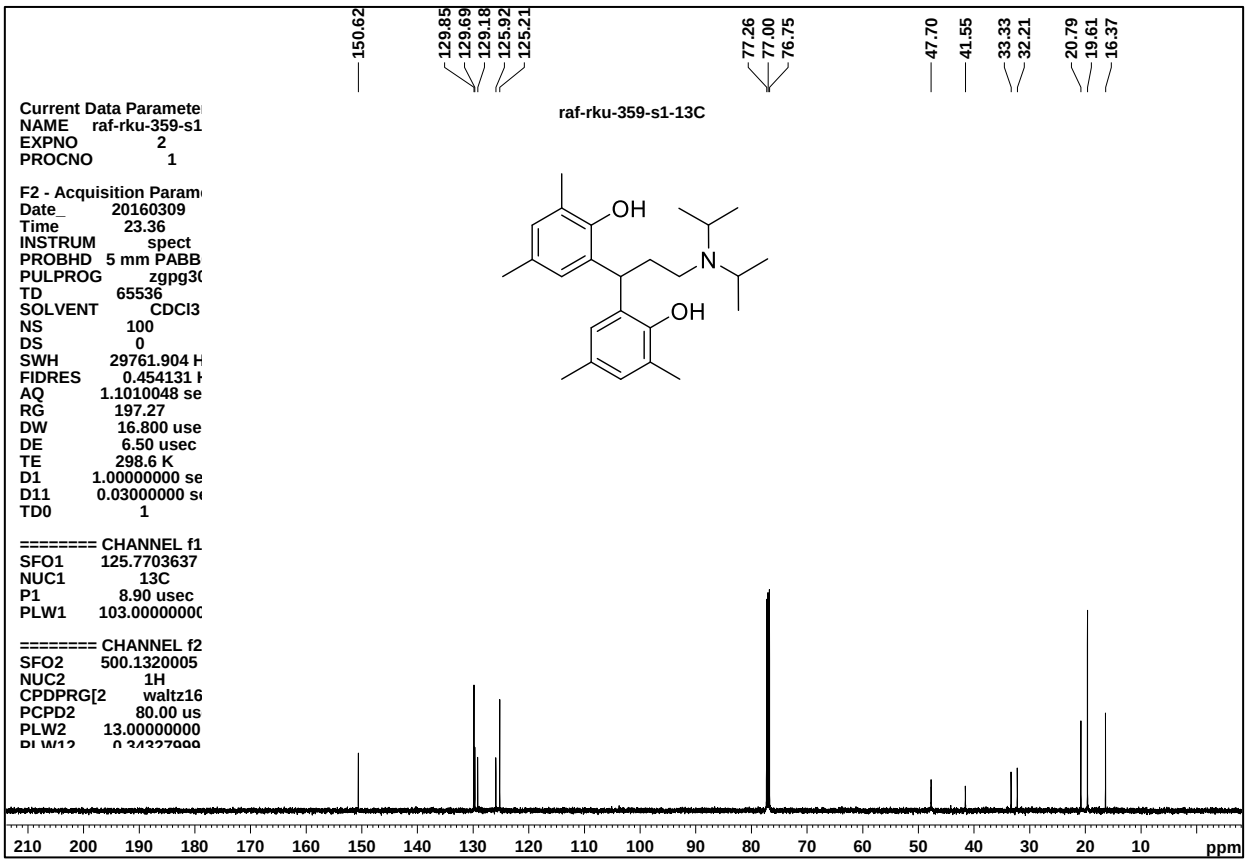
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **8a**



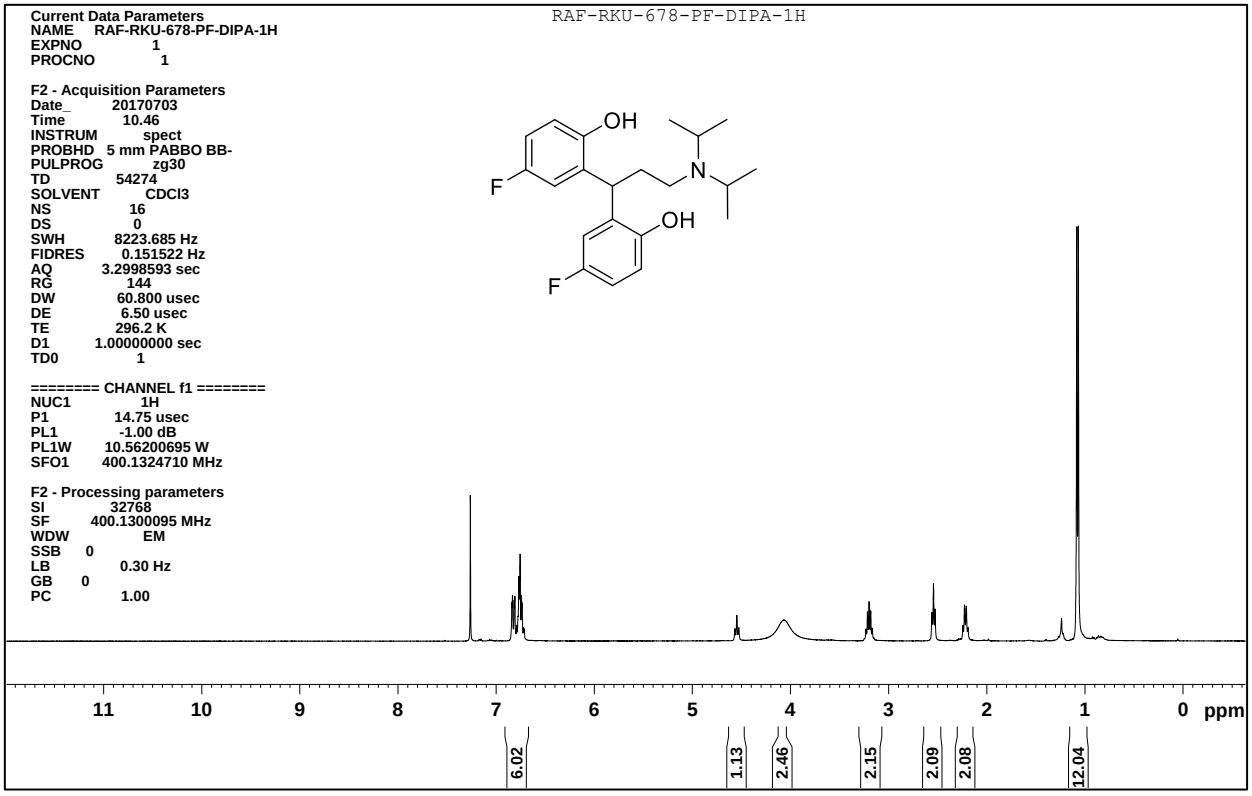


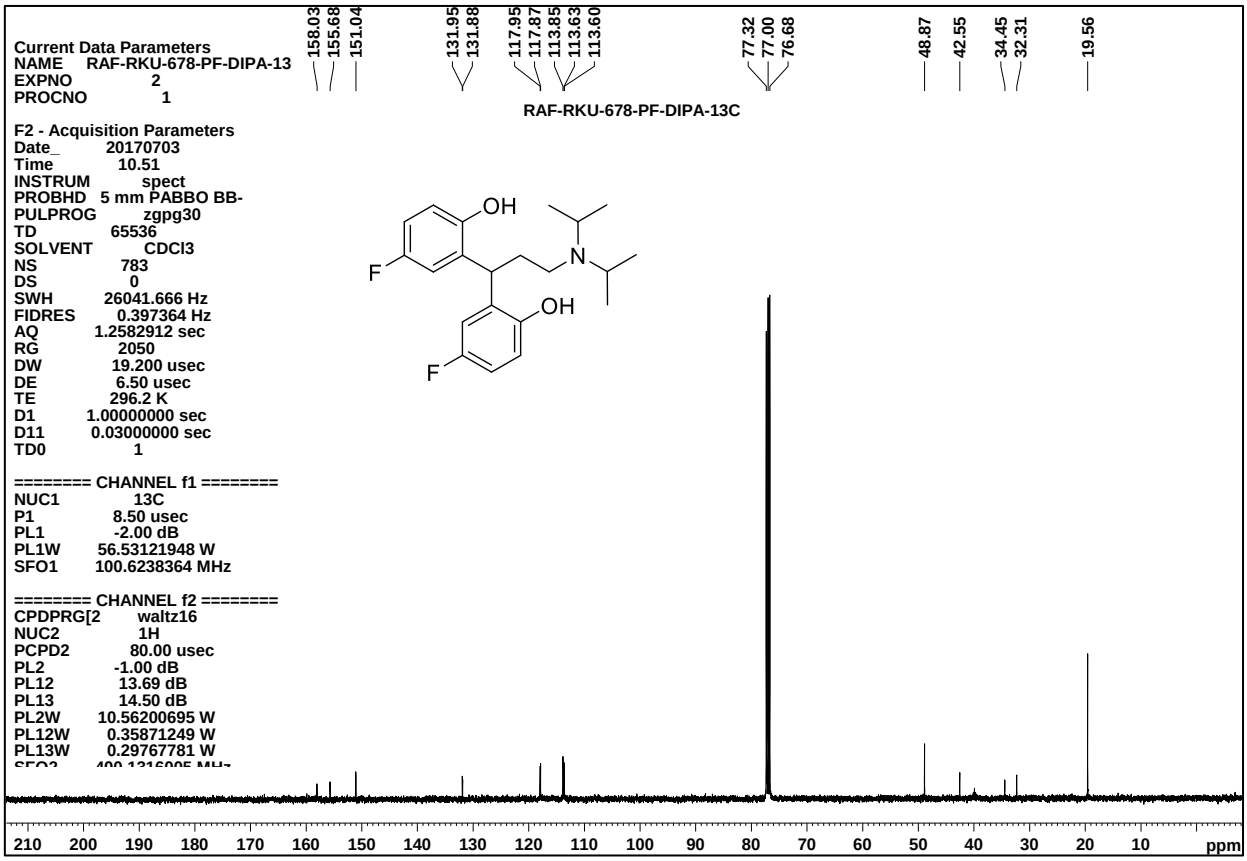
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **7′a**



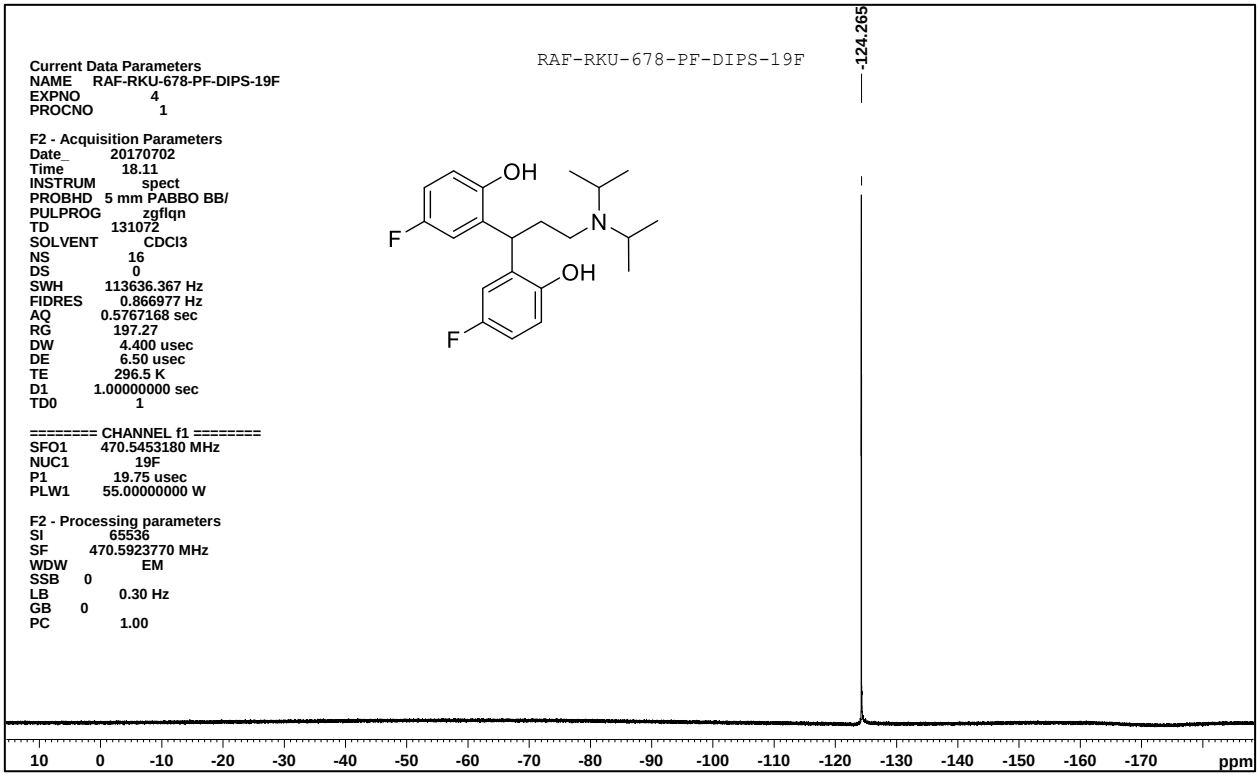


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **7′q**

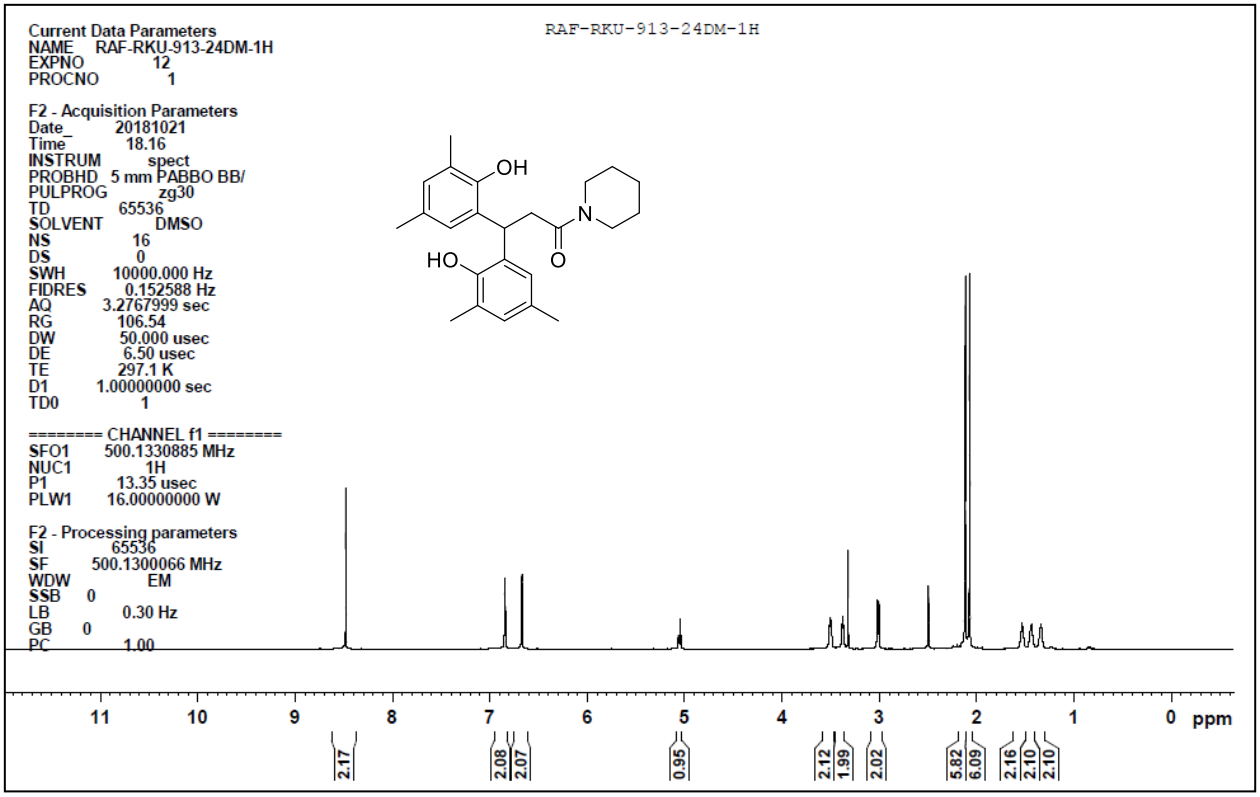


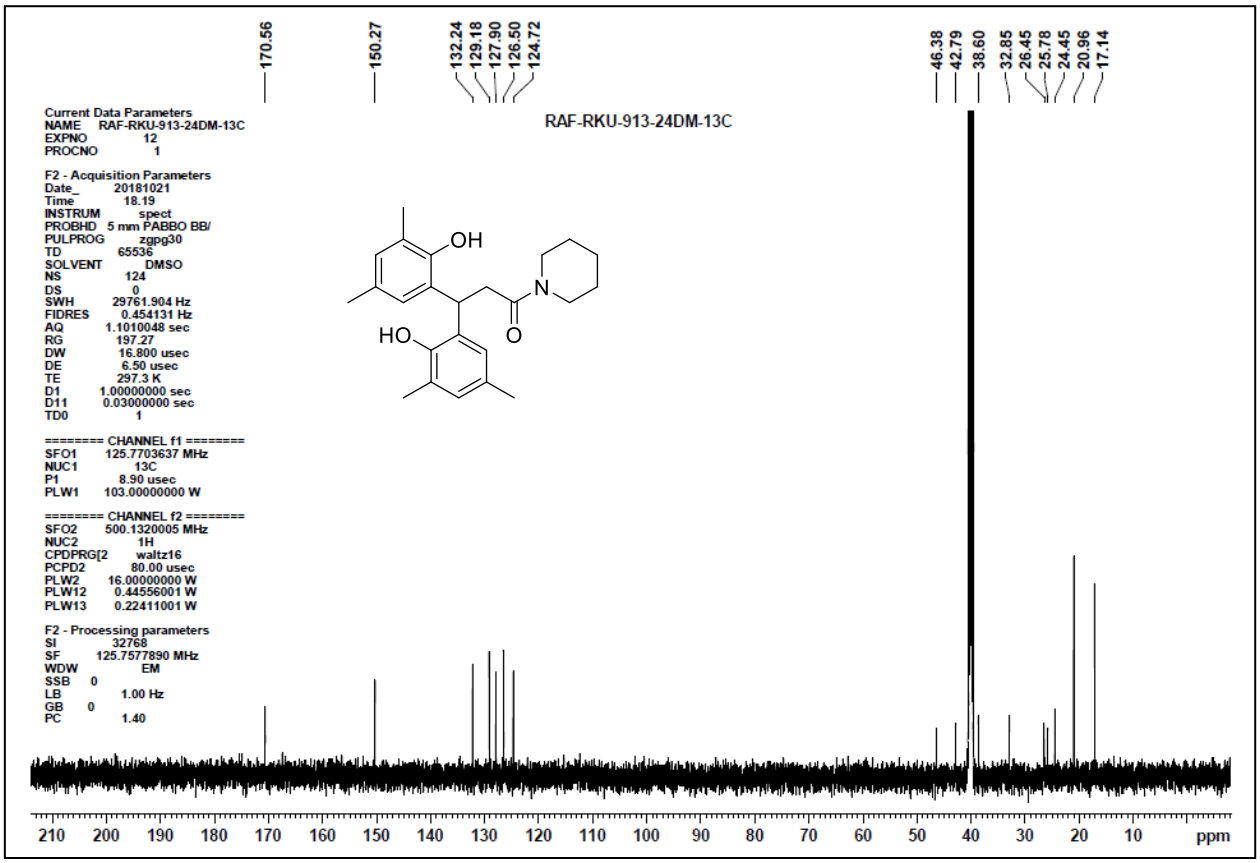


^{19}F NMR (470 MHz, $CDCl_3$) of **7′q**

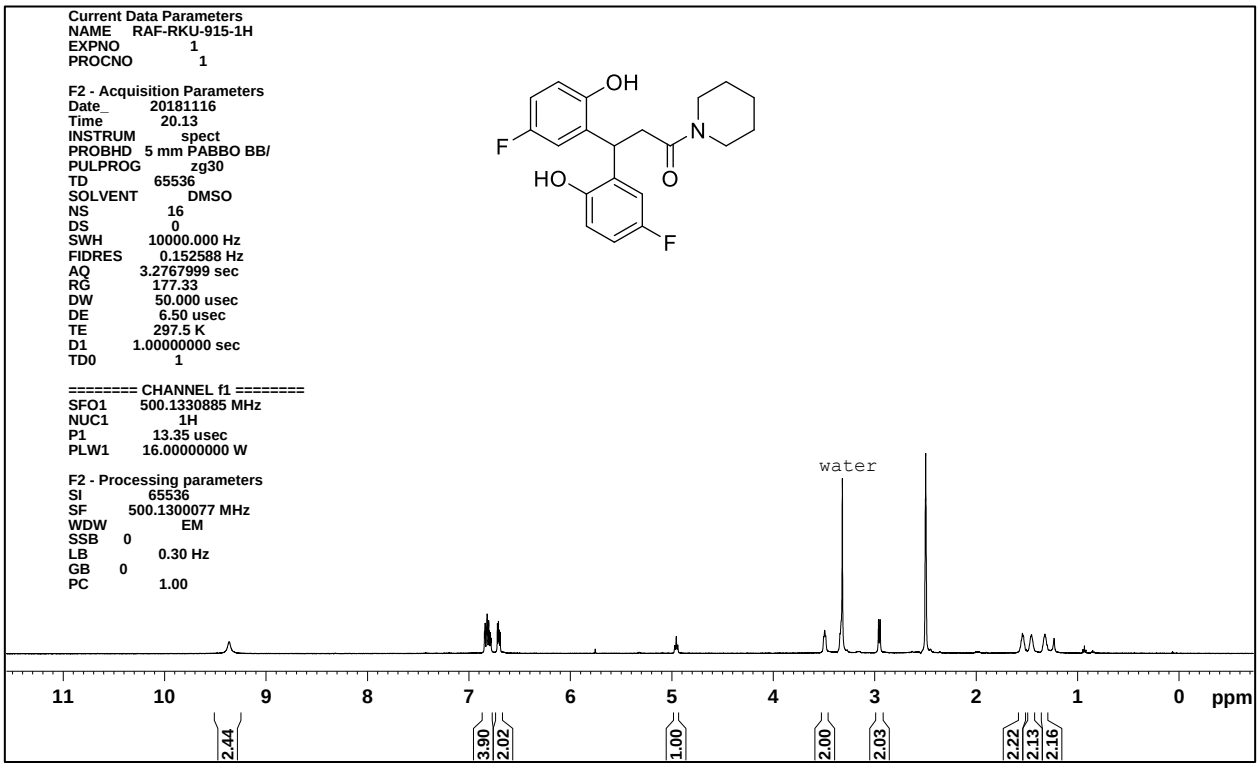


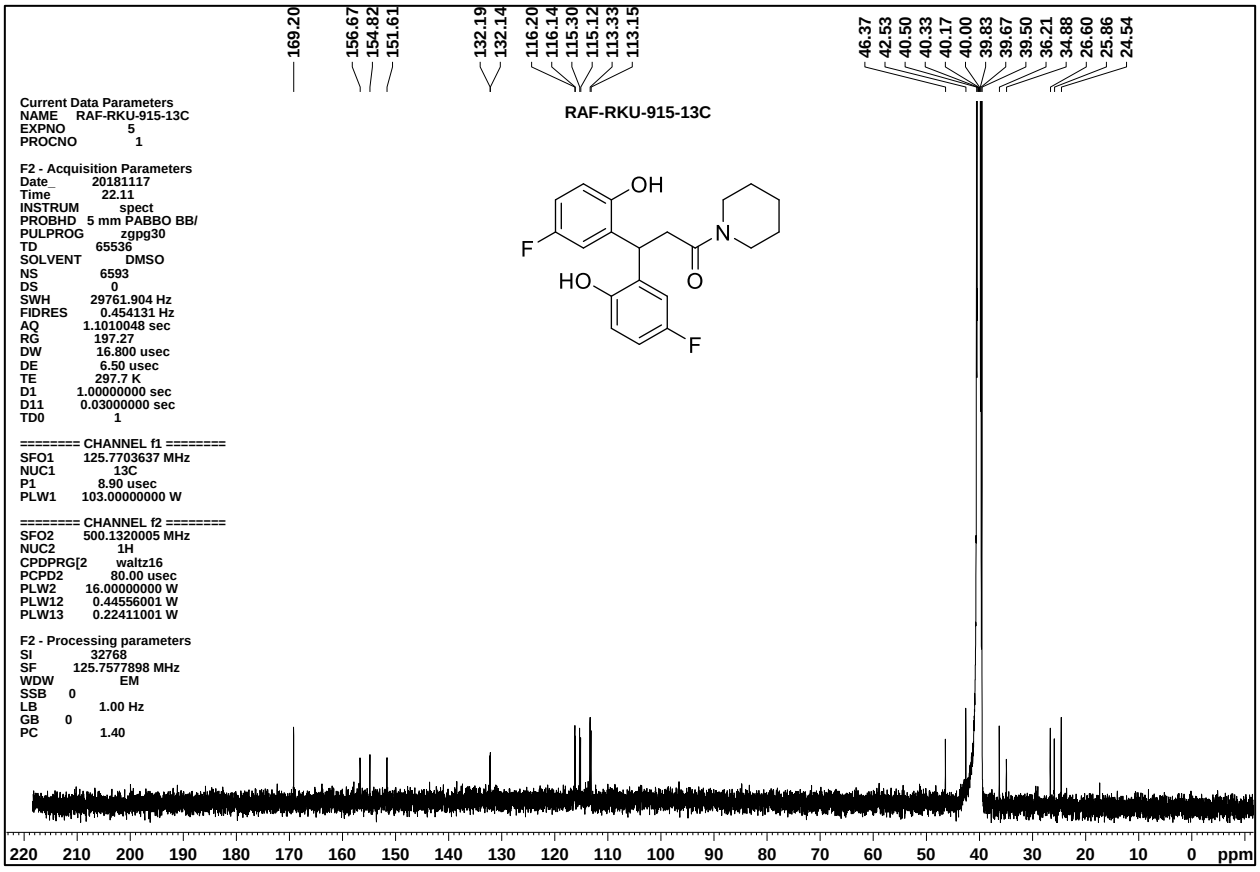
^{1}H NMR (500 MHz, DMSO-d_6) and **^{13}C NMR** (125 MHz, DMSO-d_6) of **9′a**



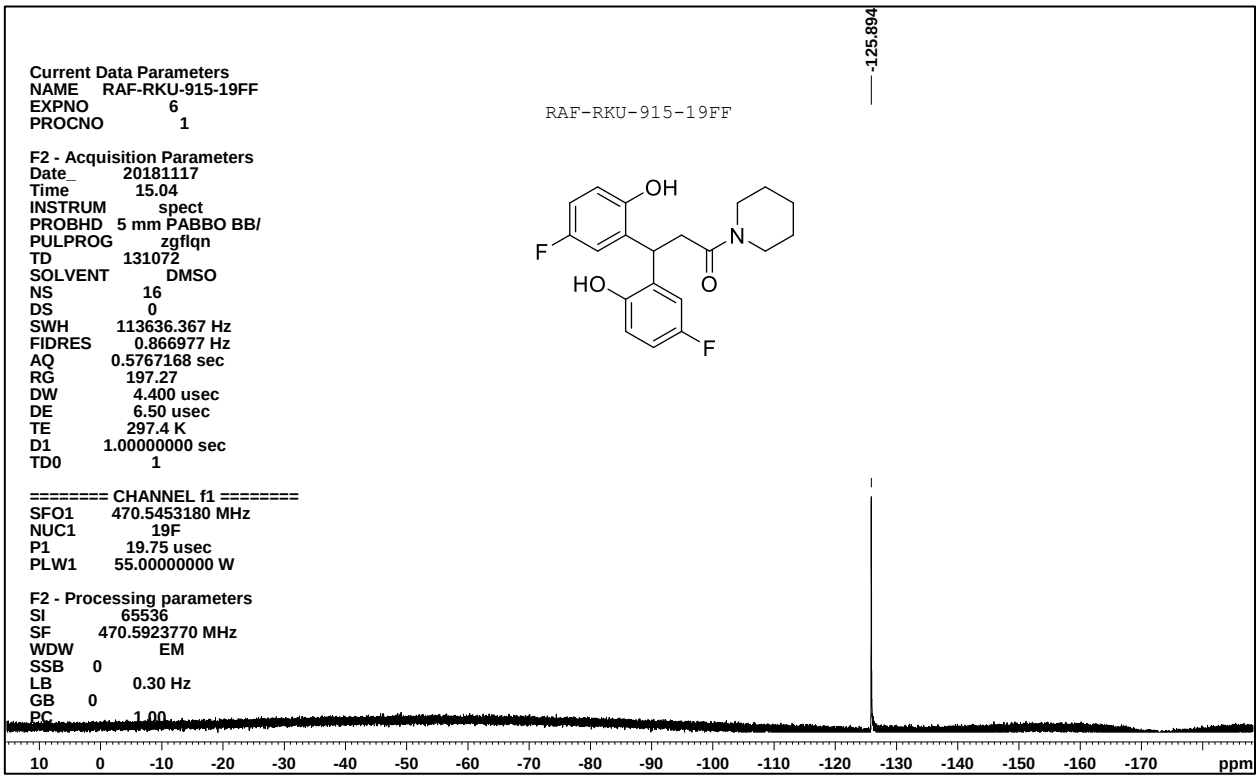


^{1}H NMR (500 MHz, DMSO–d_6) and **^{13}C NMR** (125 MHz, DMSO–d_6) of **9′q**

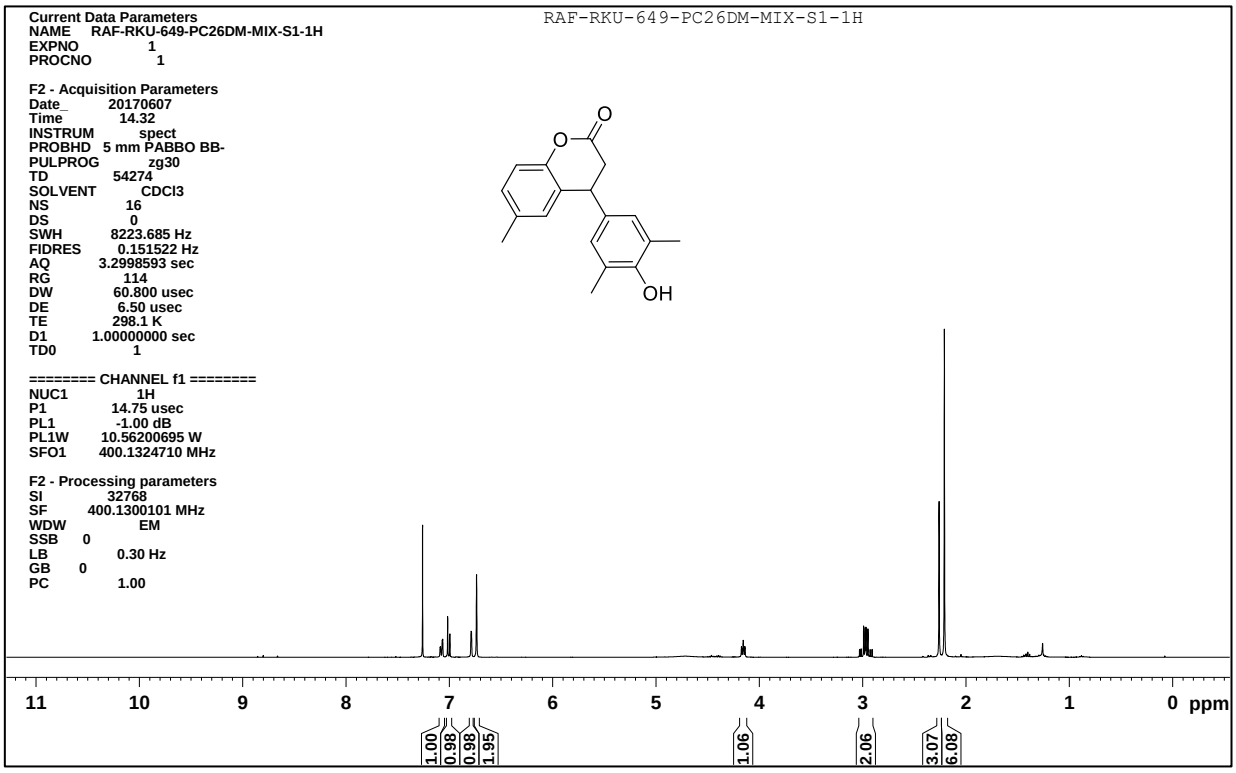


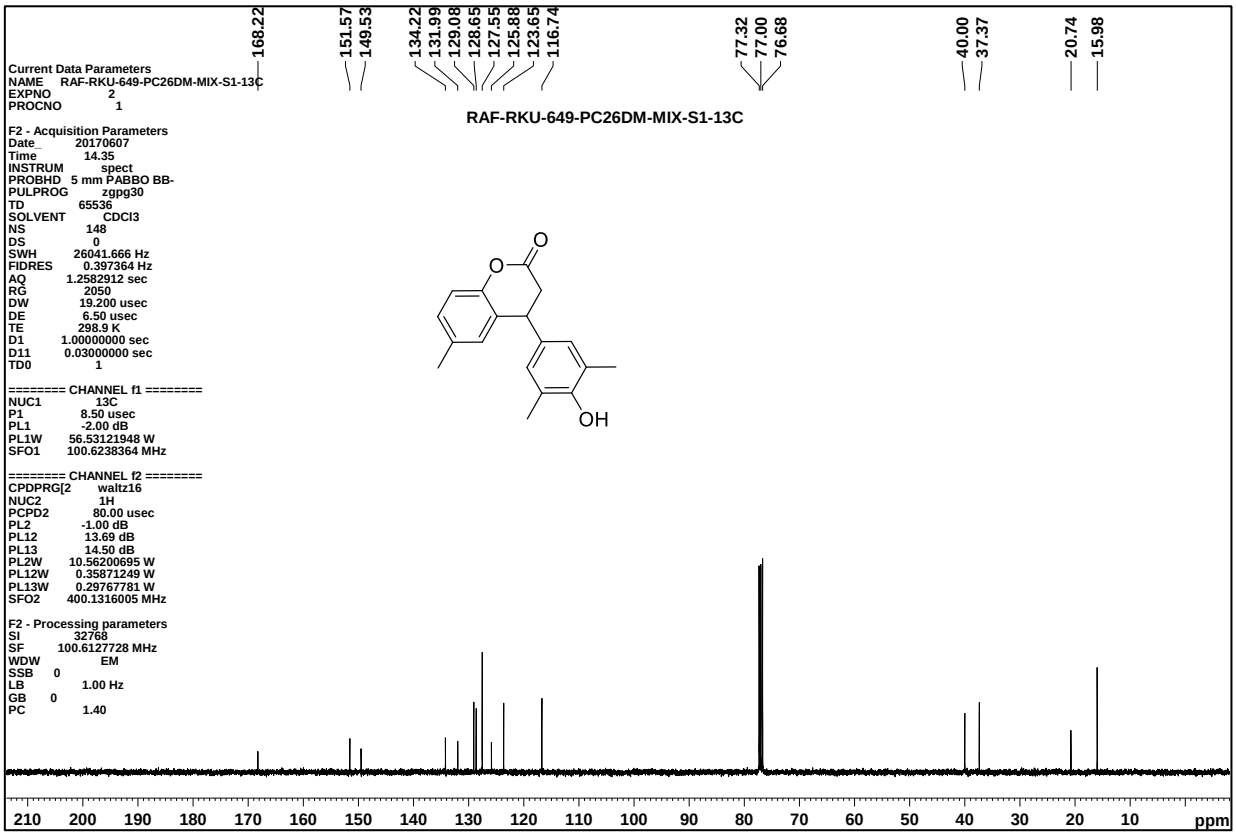


^{19}F NMR(470 MHz, DMSO–d_6) of **9′q**

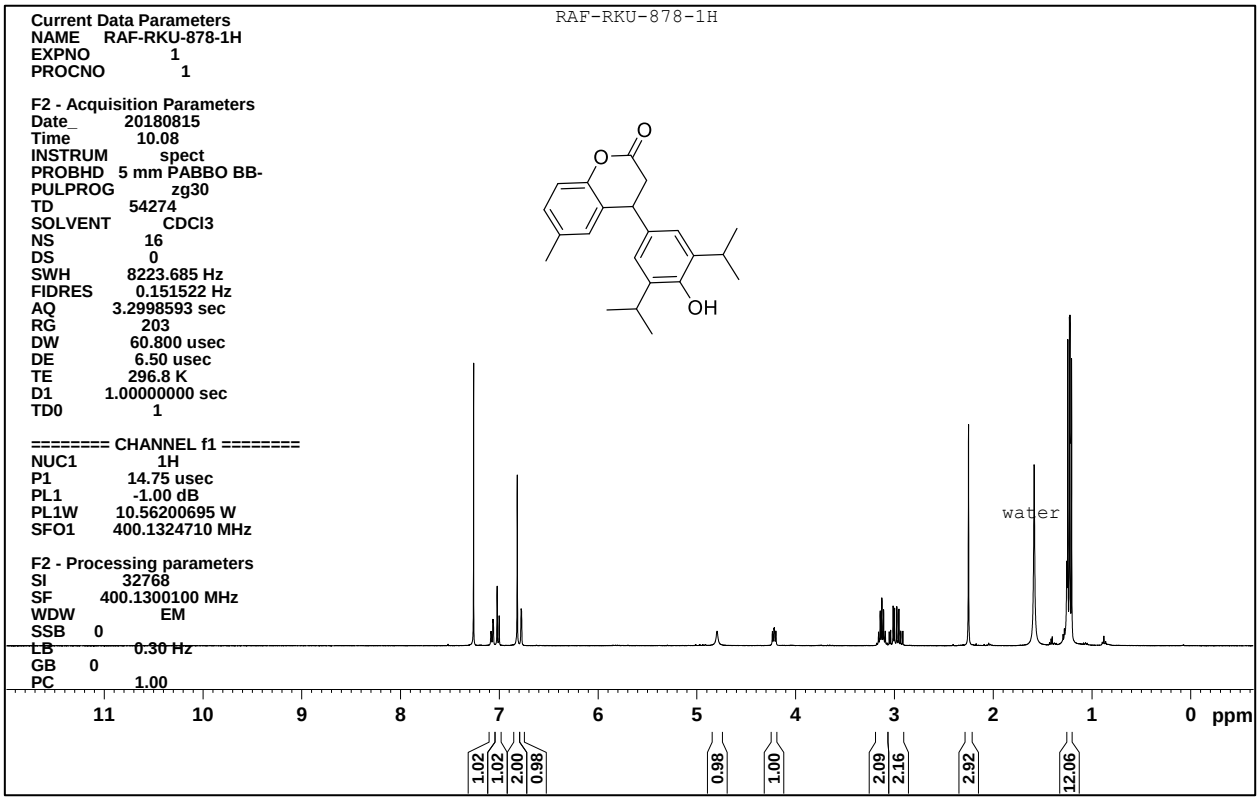


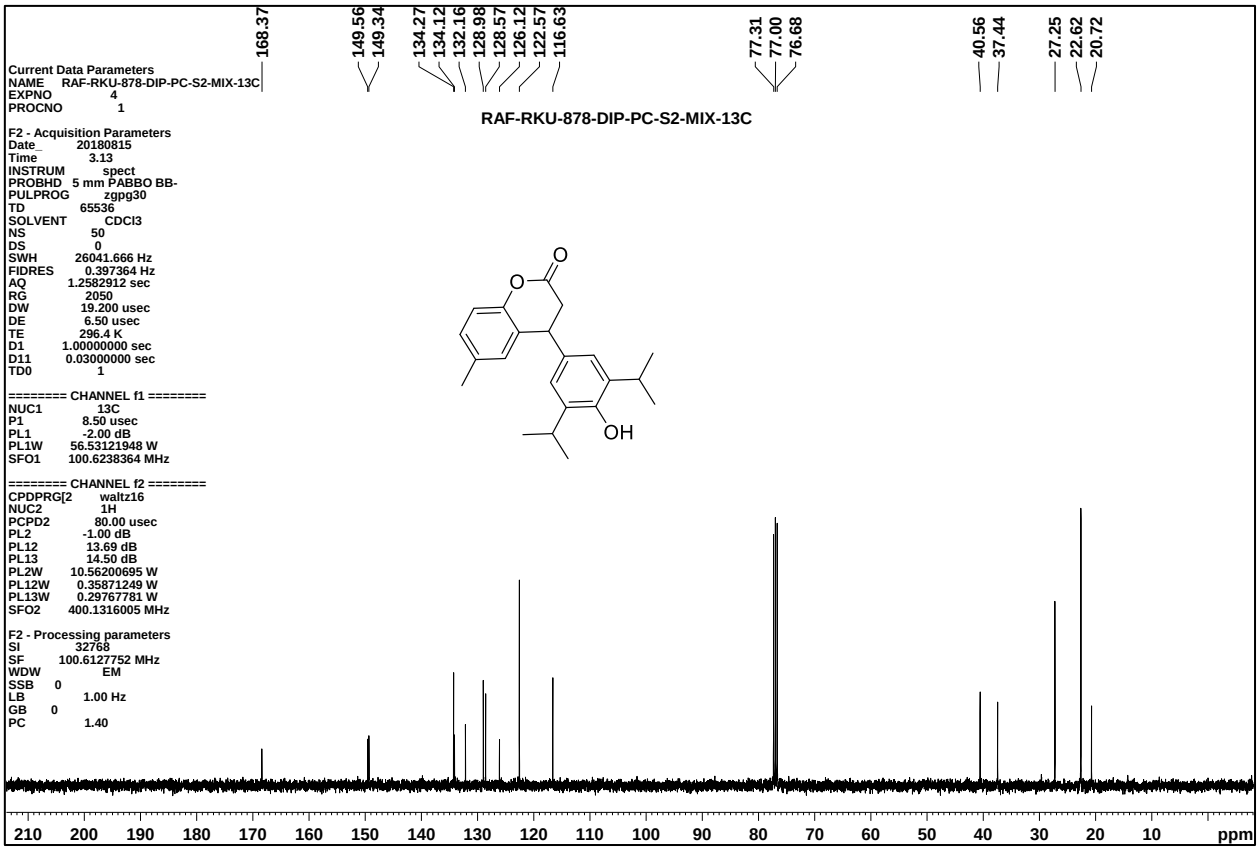
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5bx**



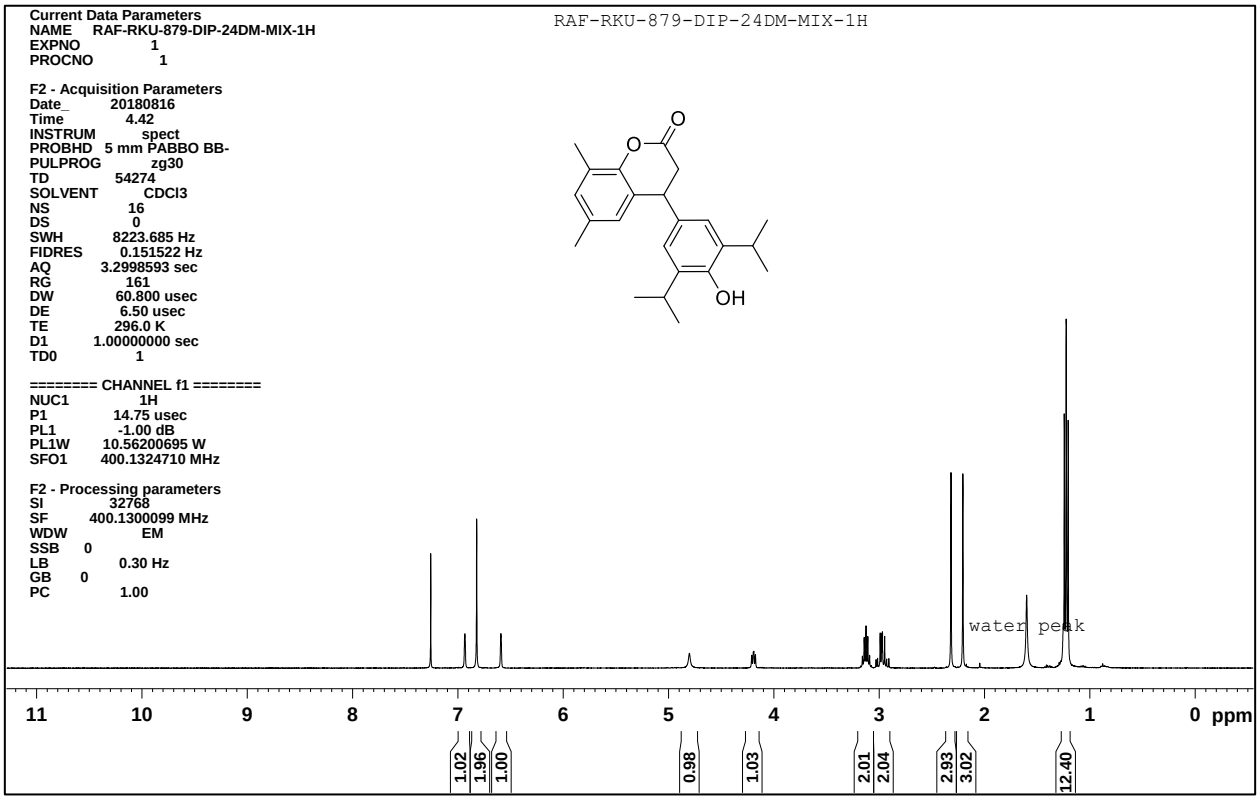


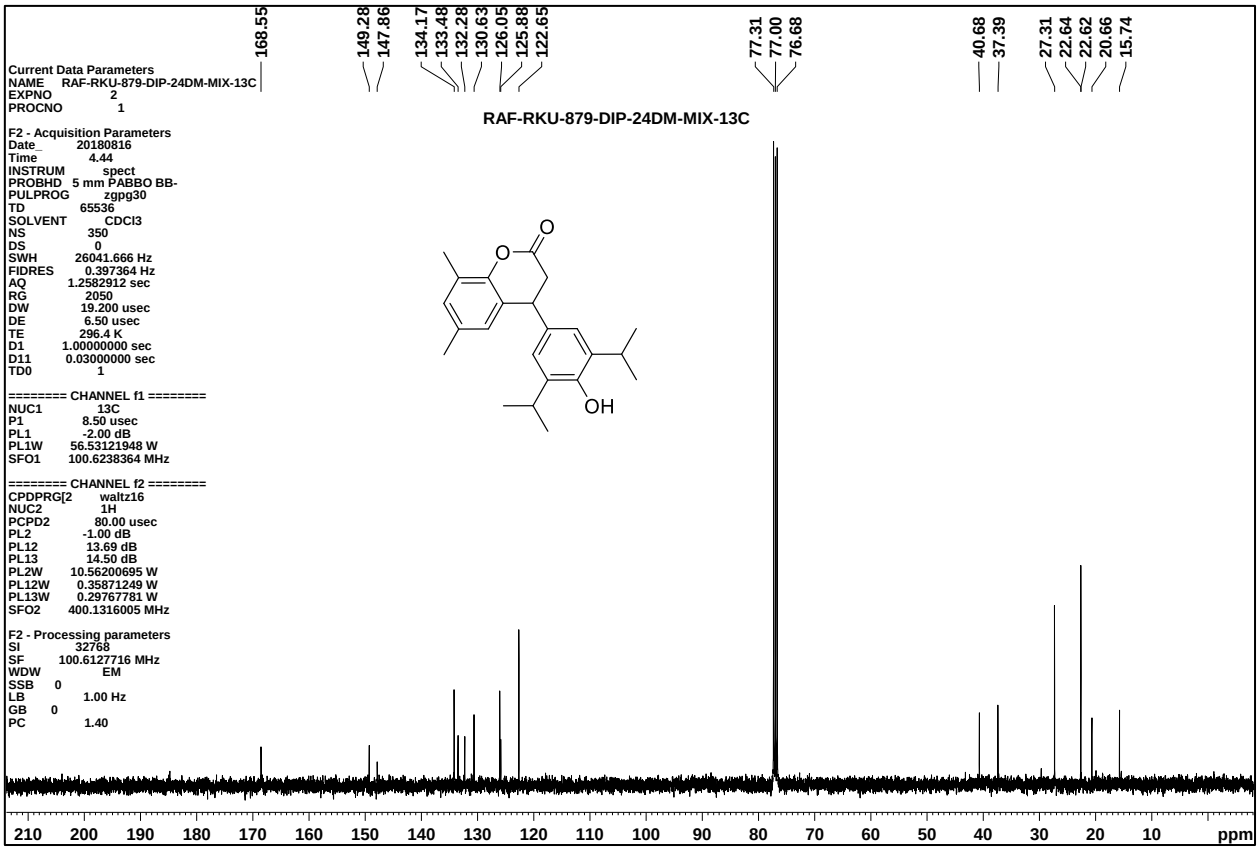
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5by**



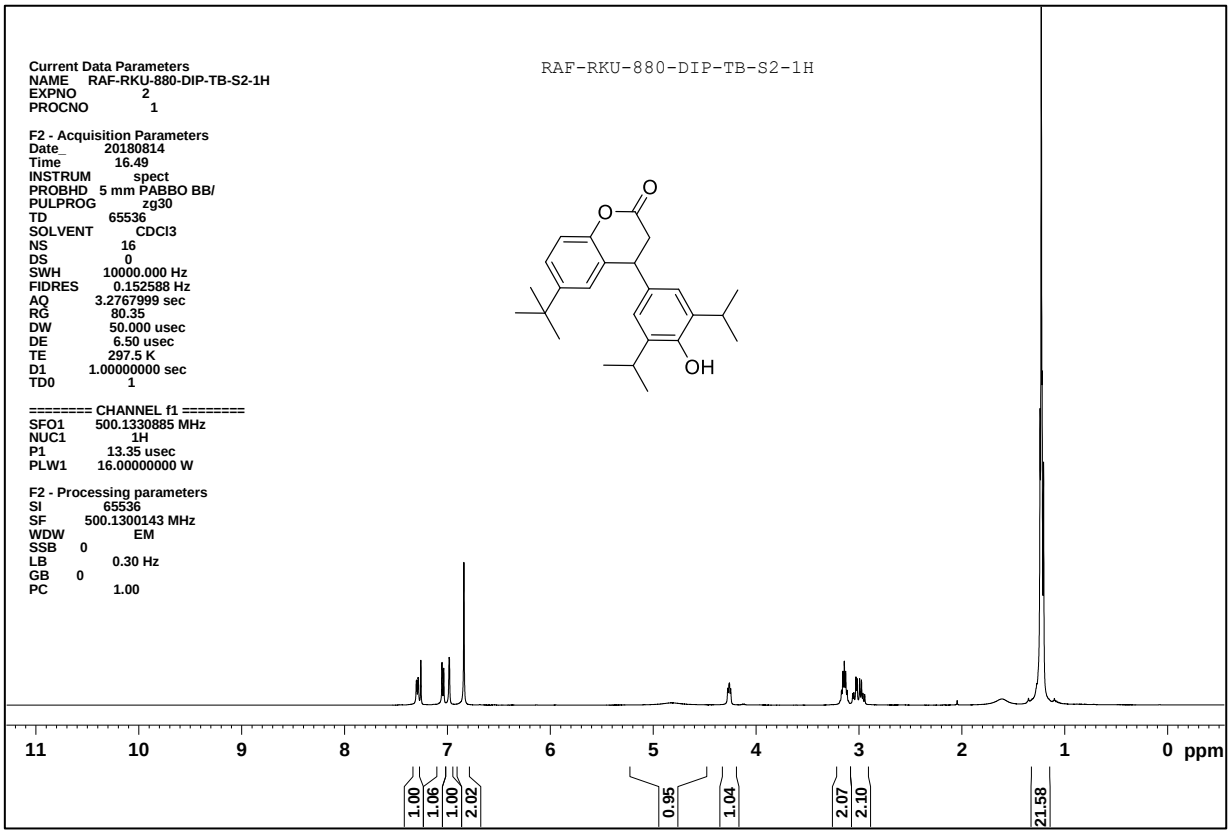


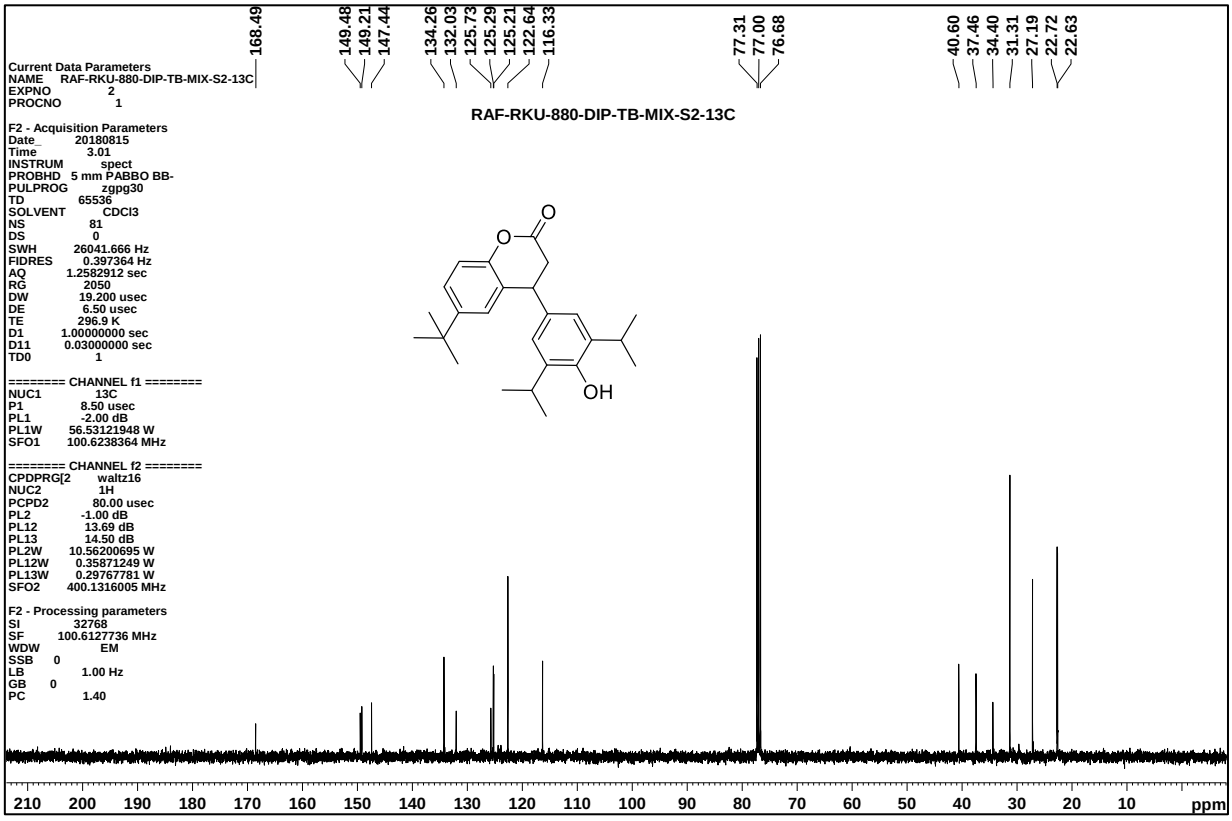
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5ay**



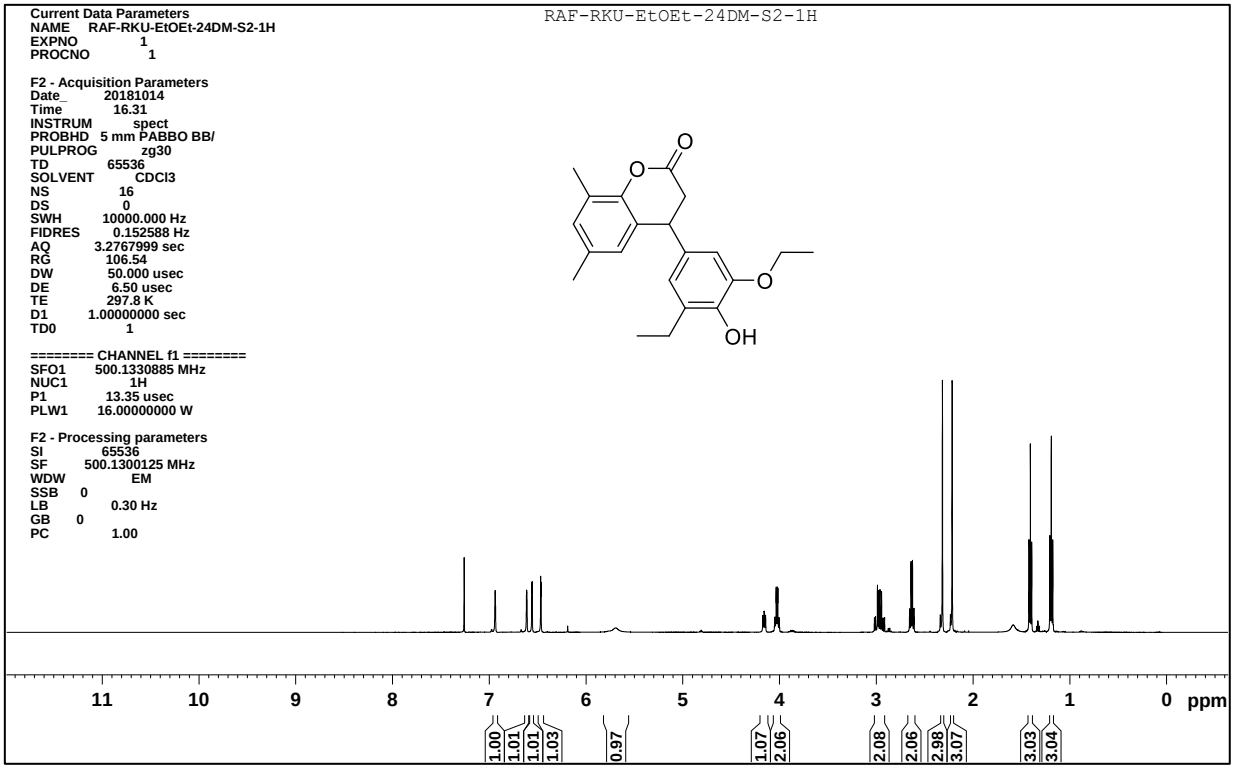


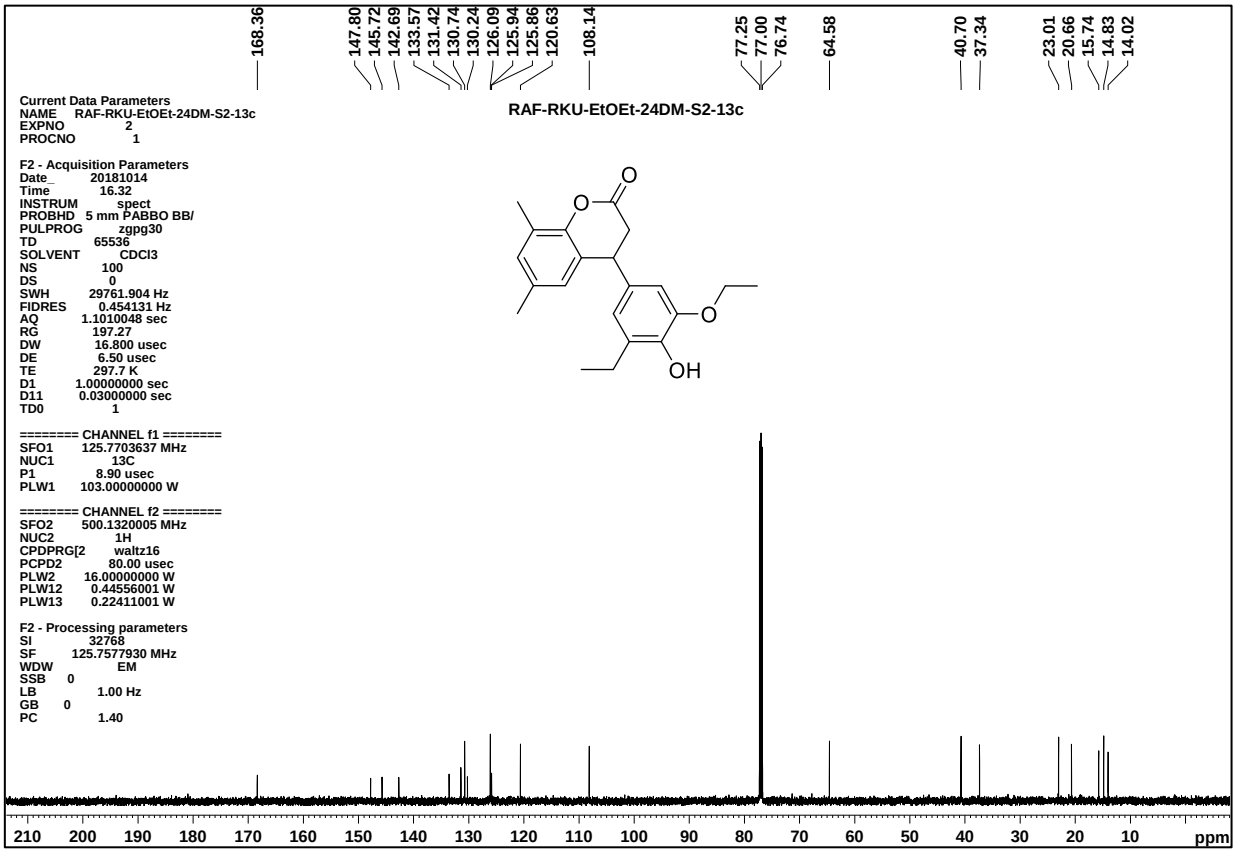
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5cy**



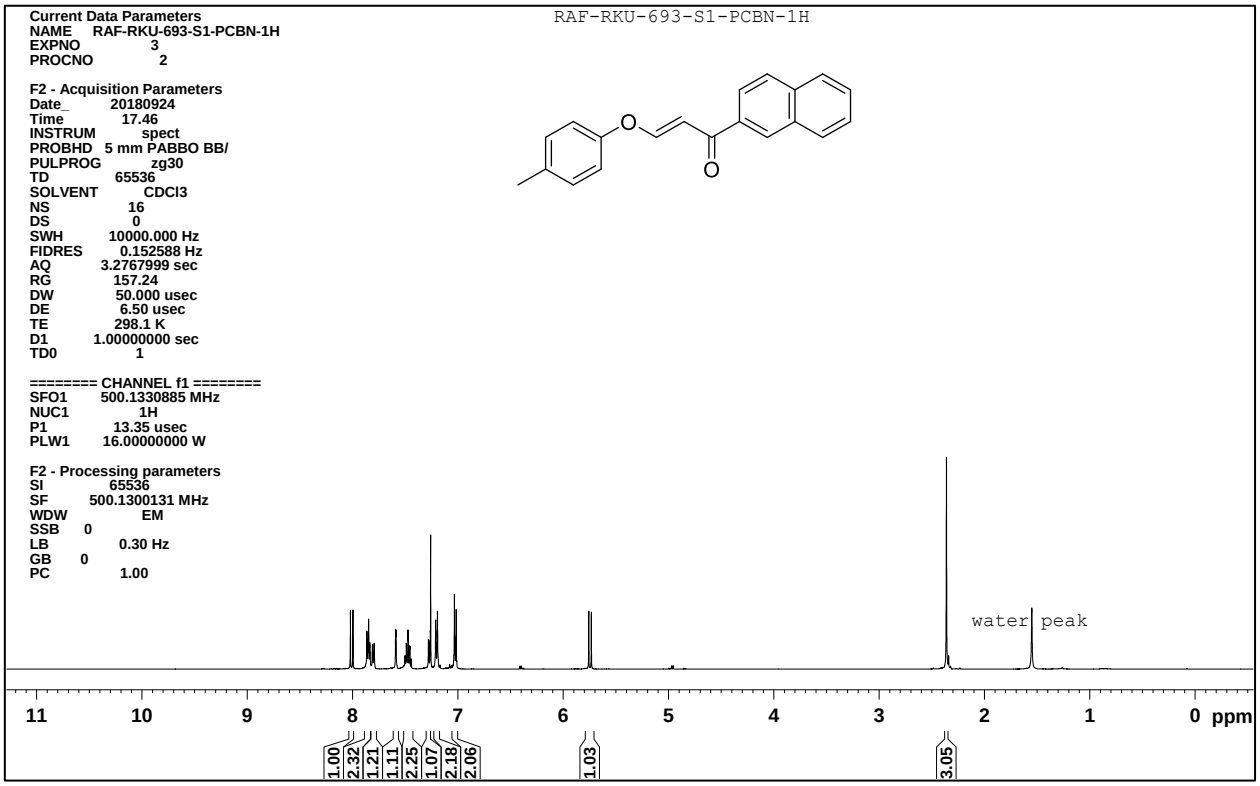


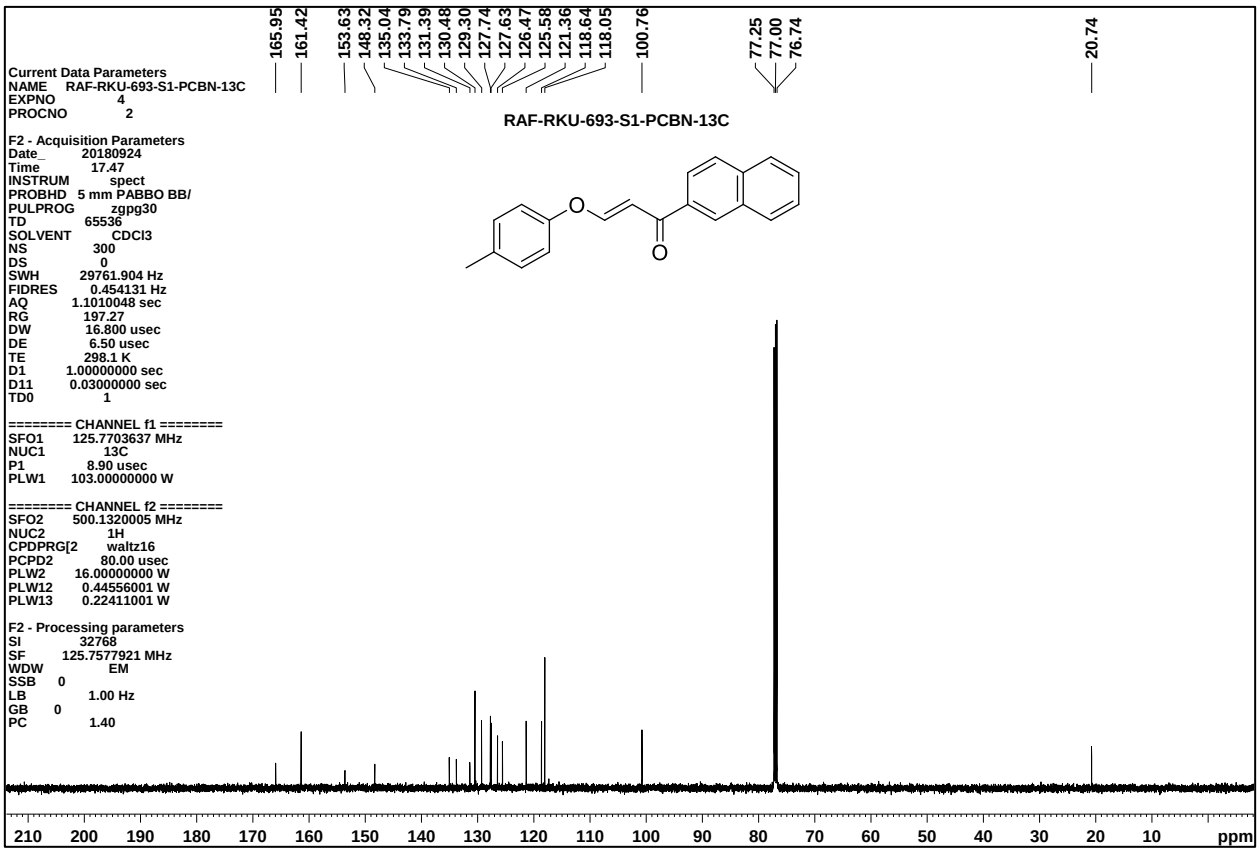
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5az**



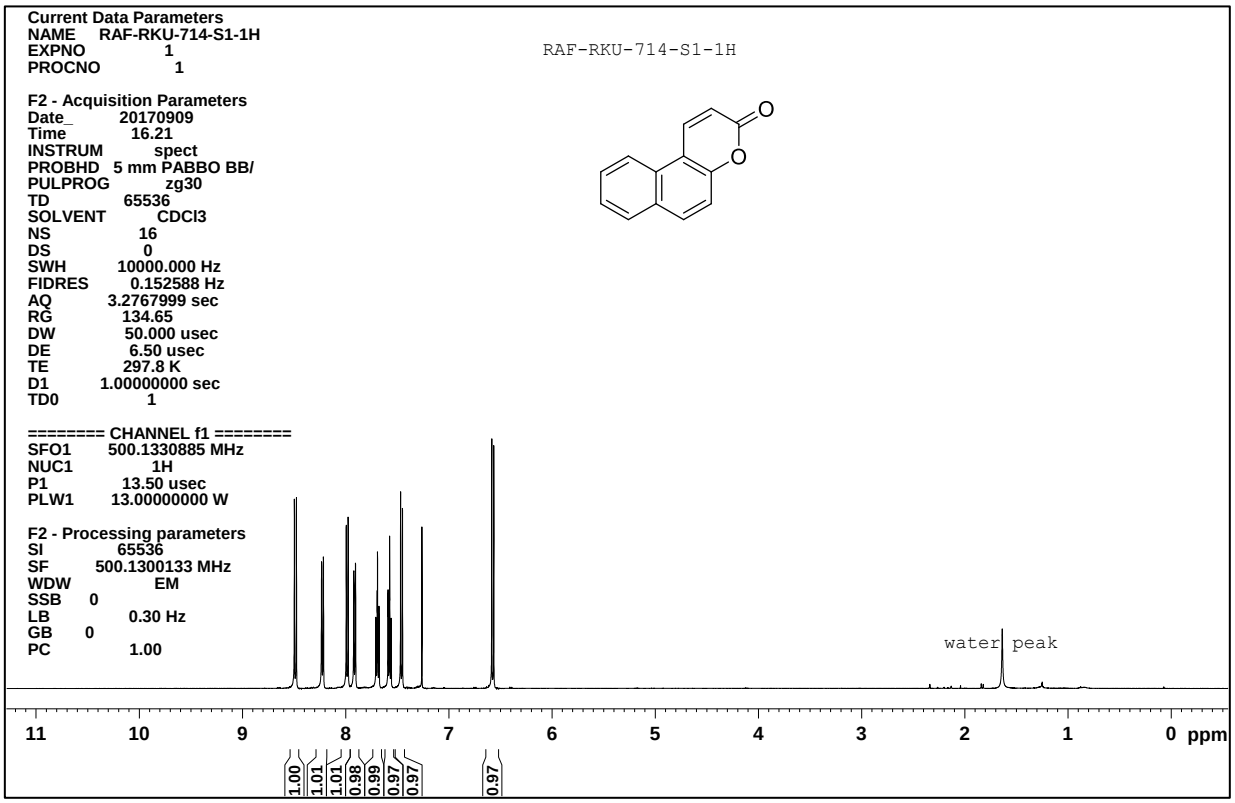


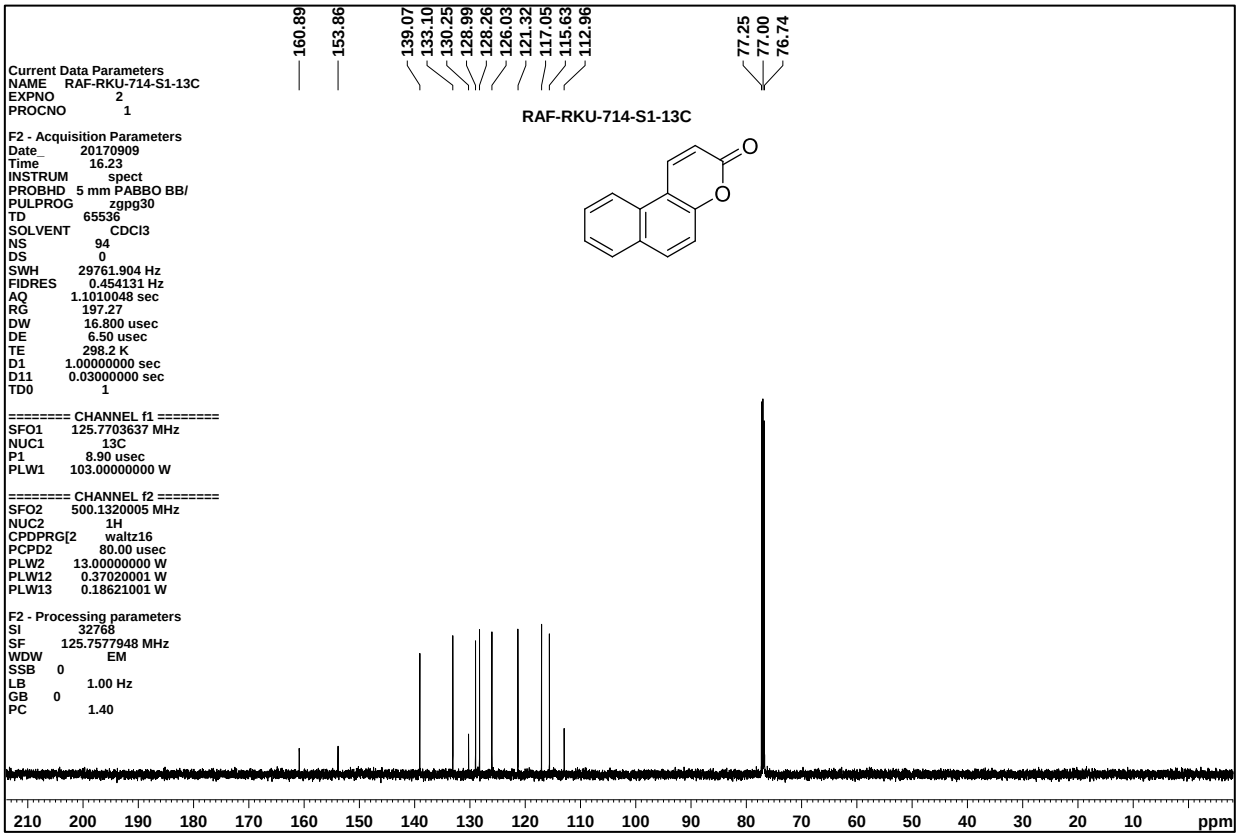
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**11**



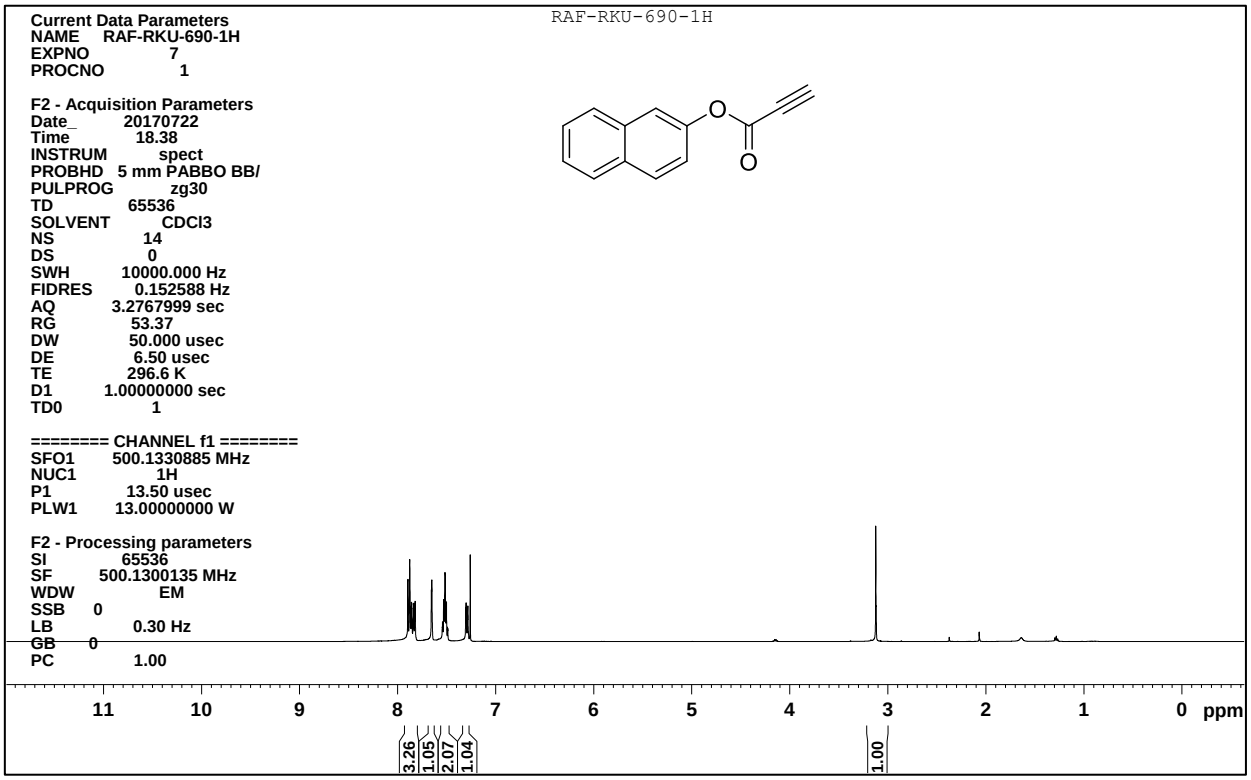


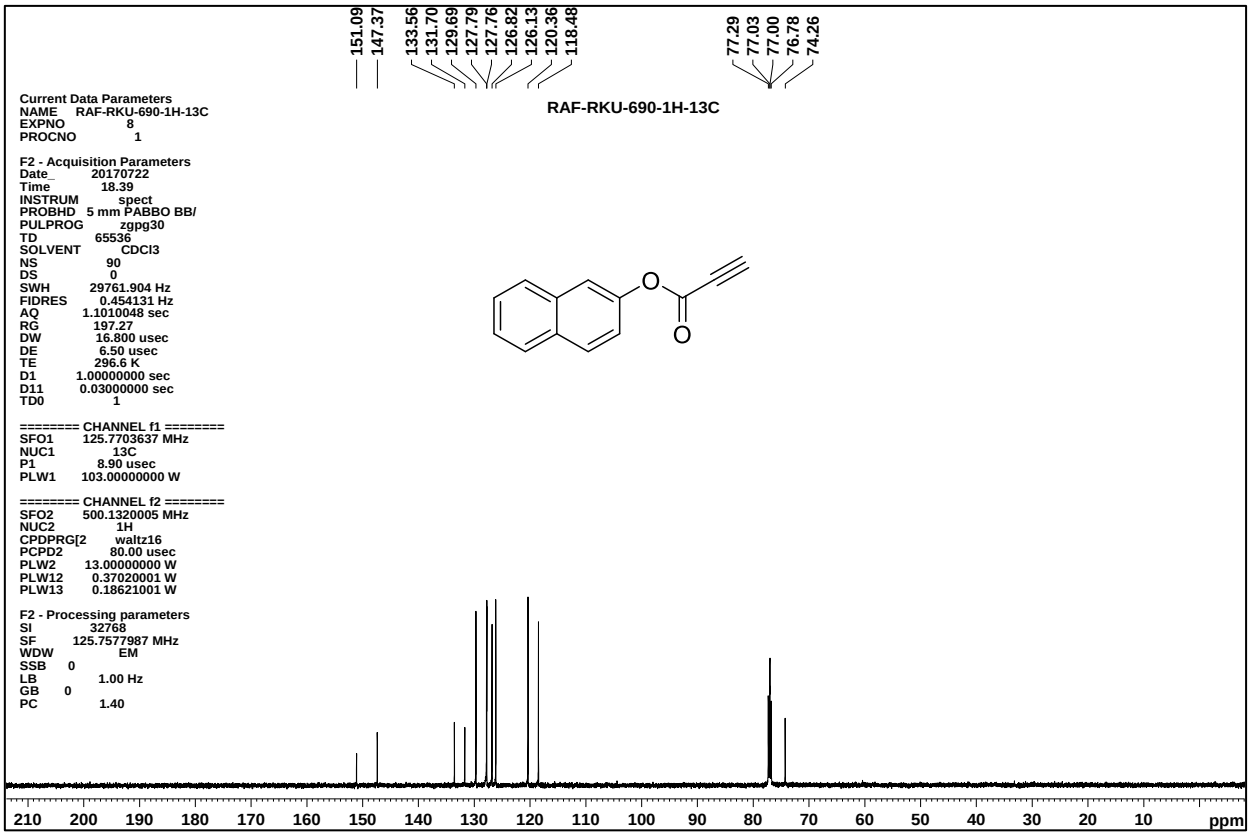
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **12**



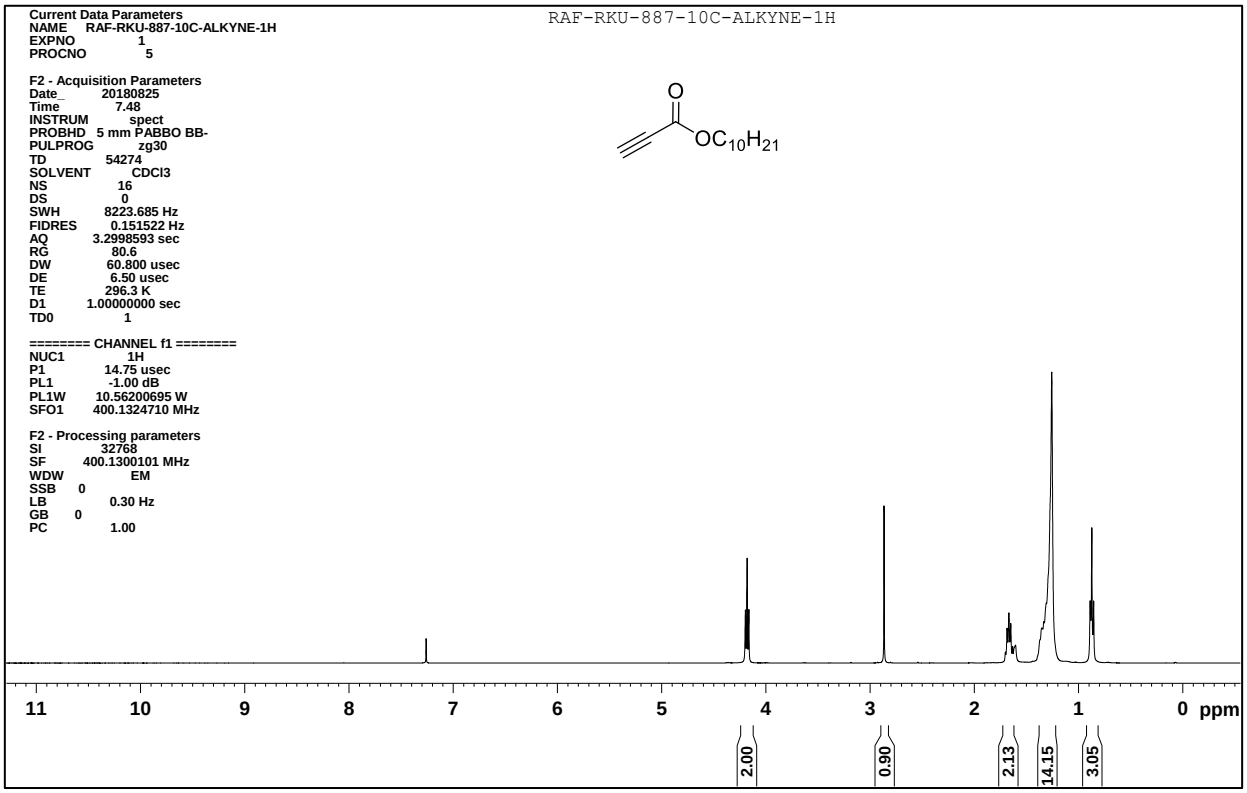


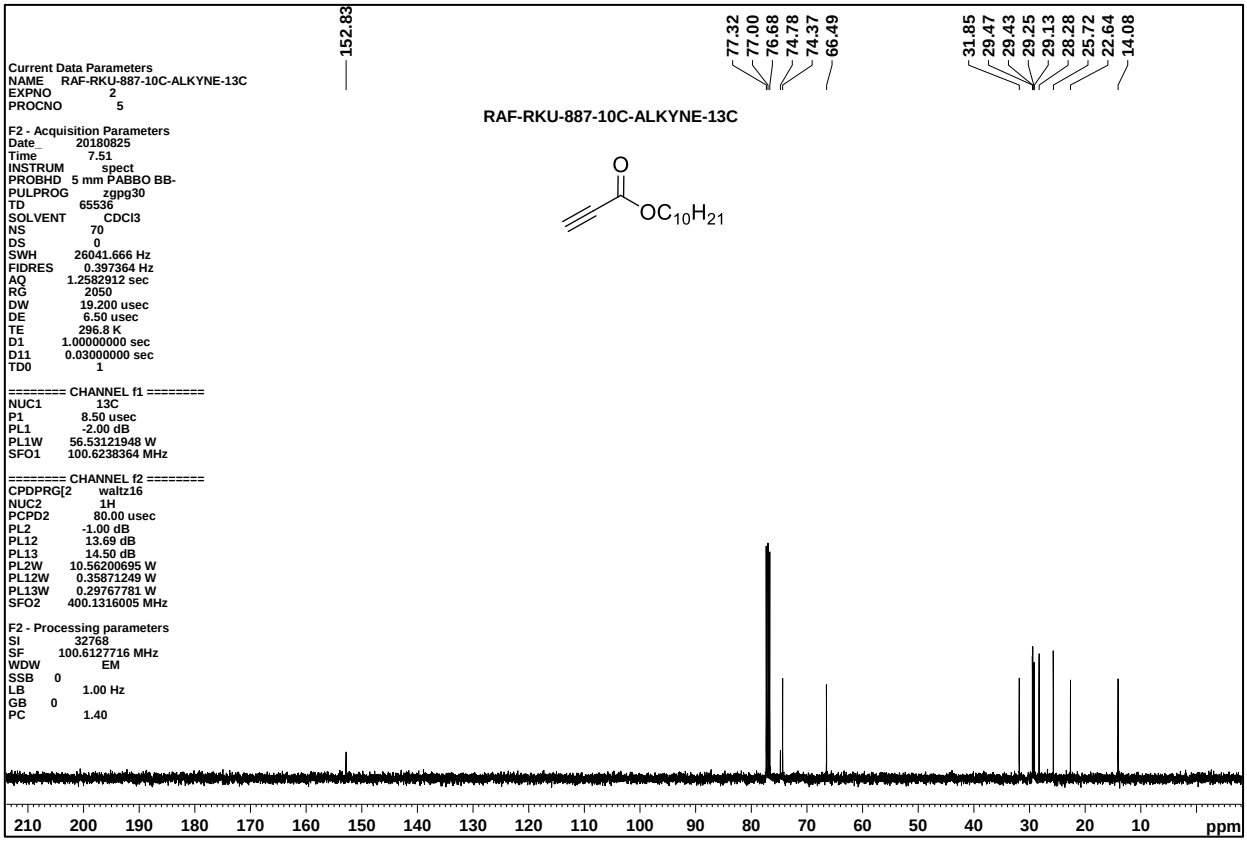
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **13**



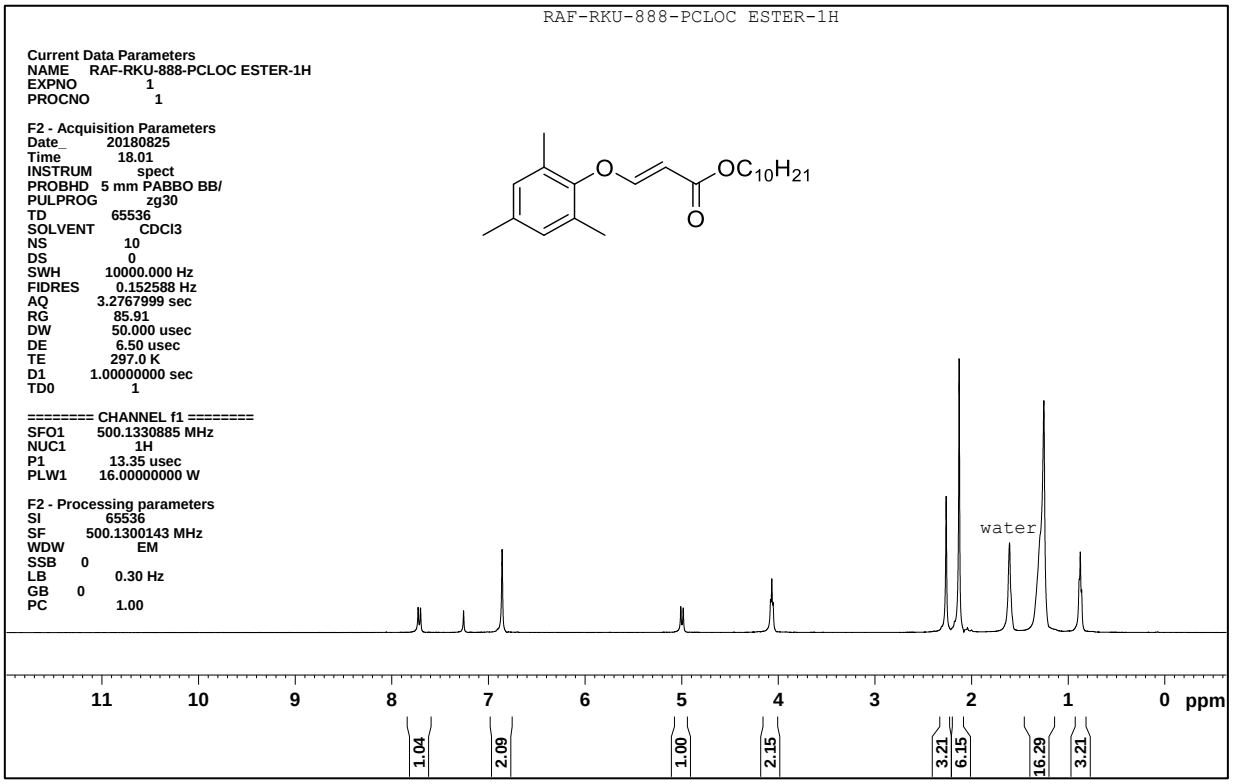


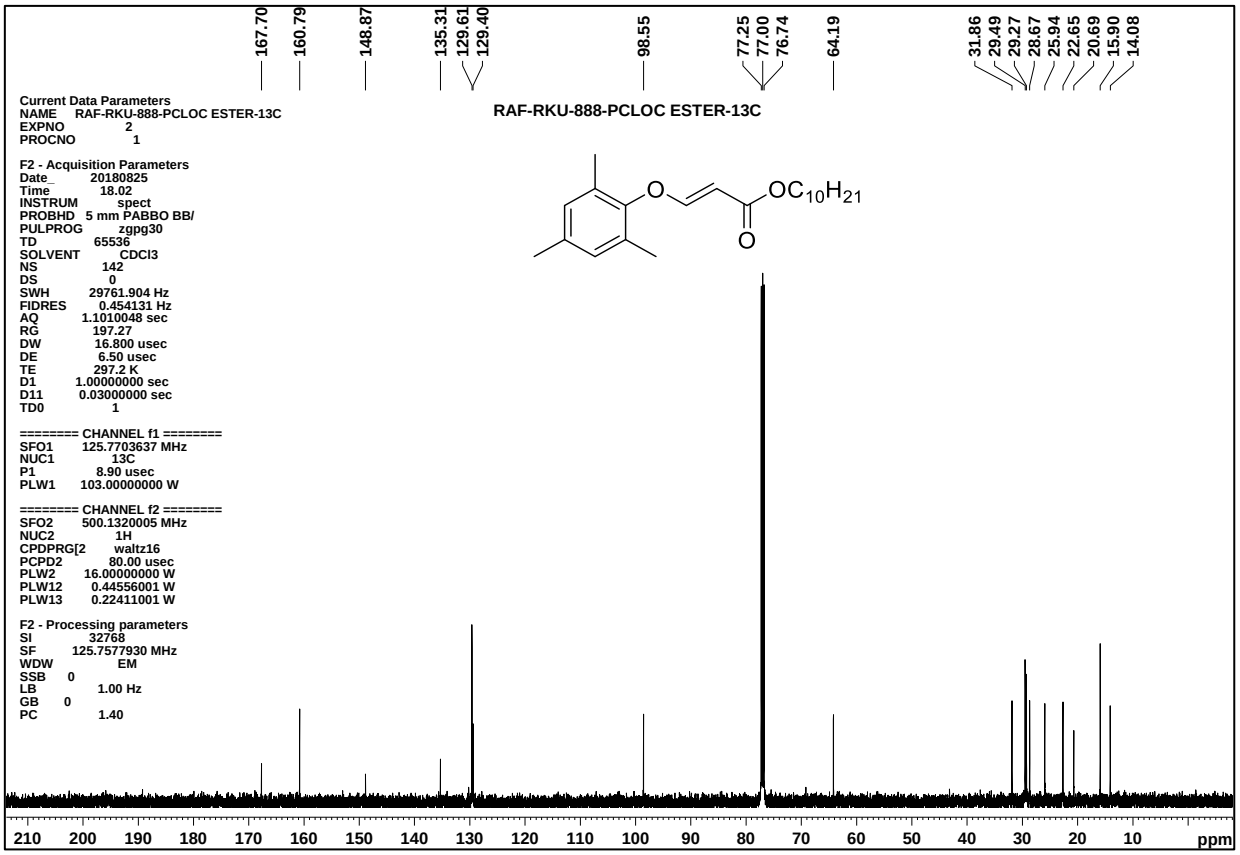
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **16**



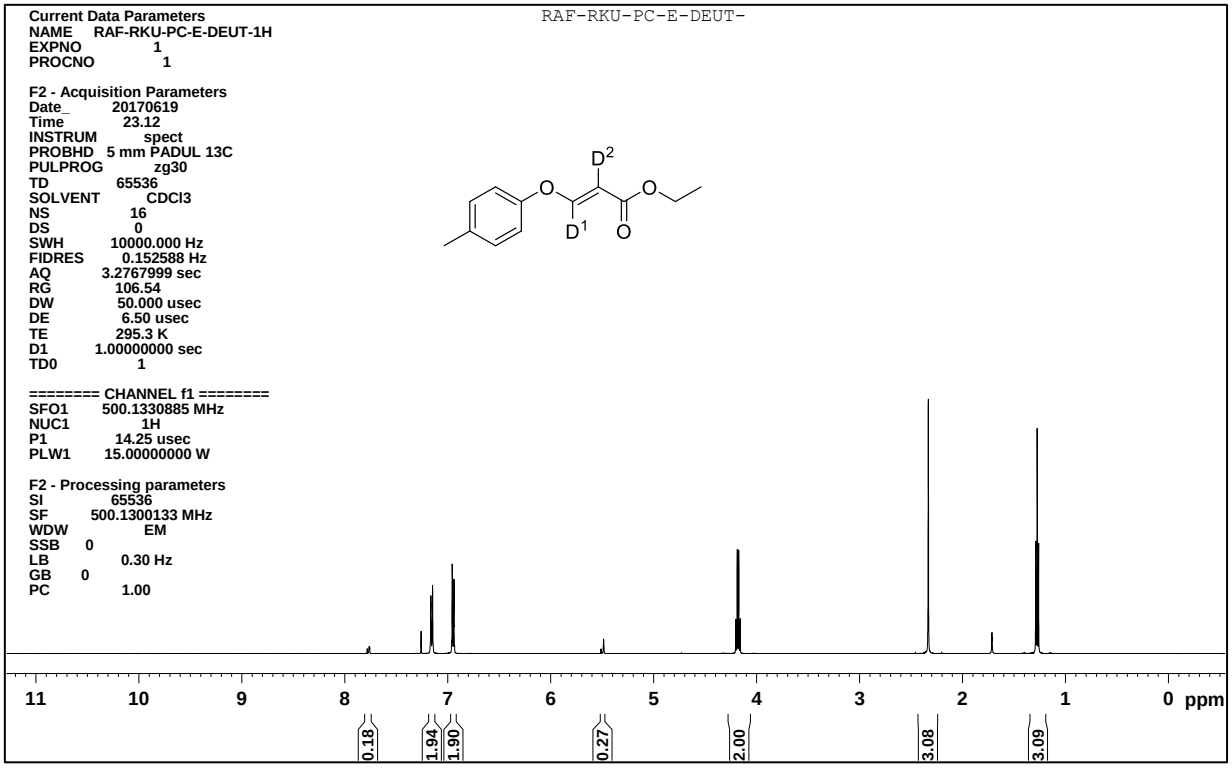


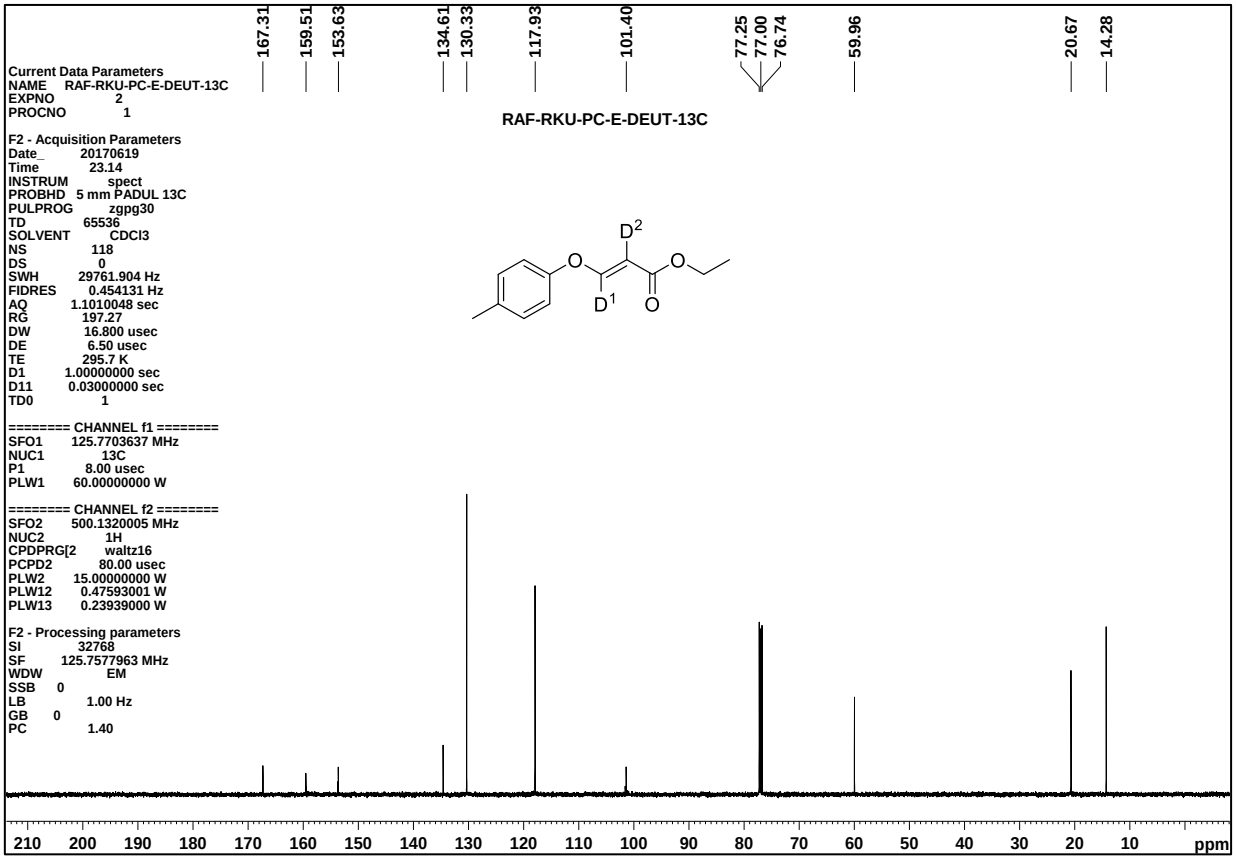
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of (*E*)-**14**



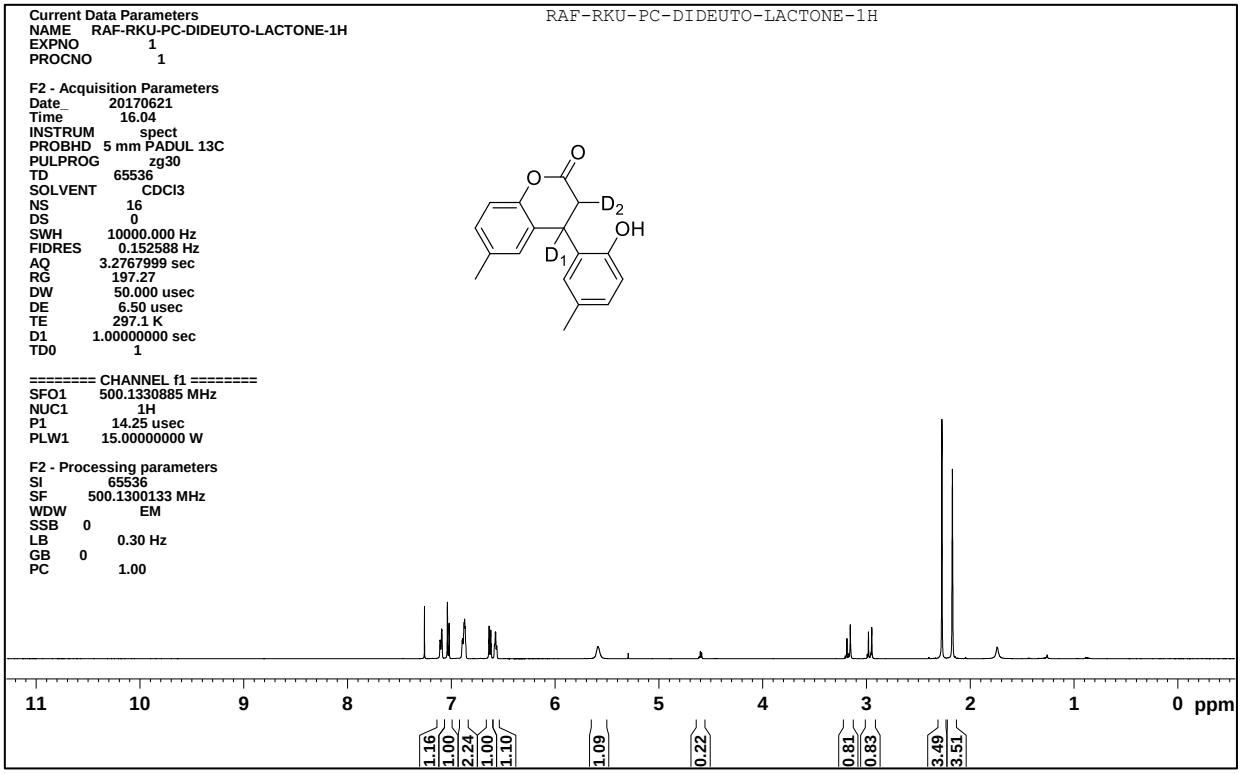


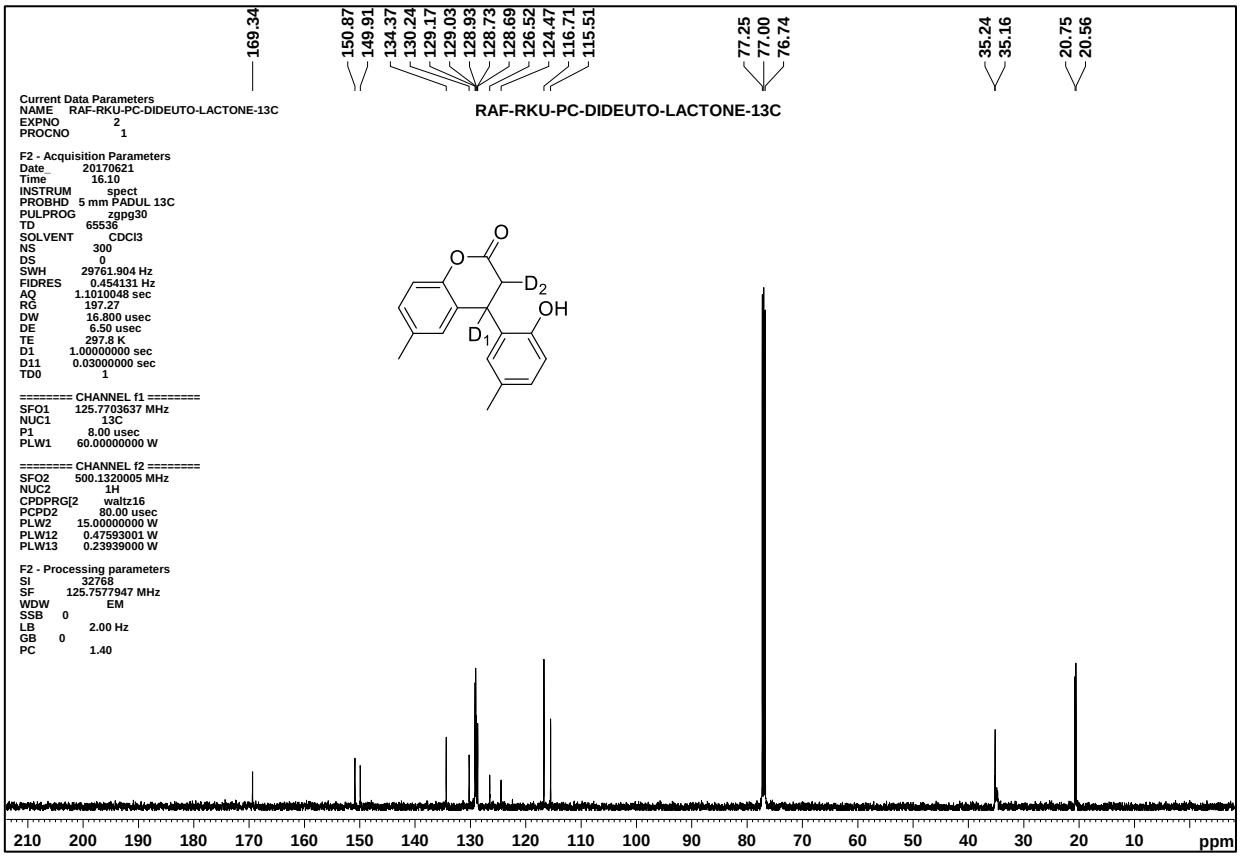
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **3b′**



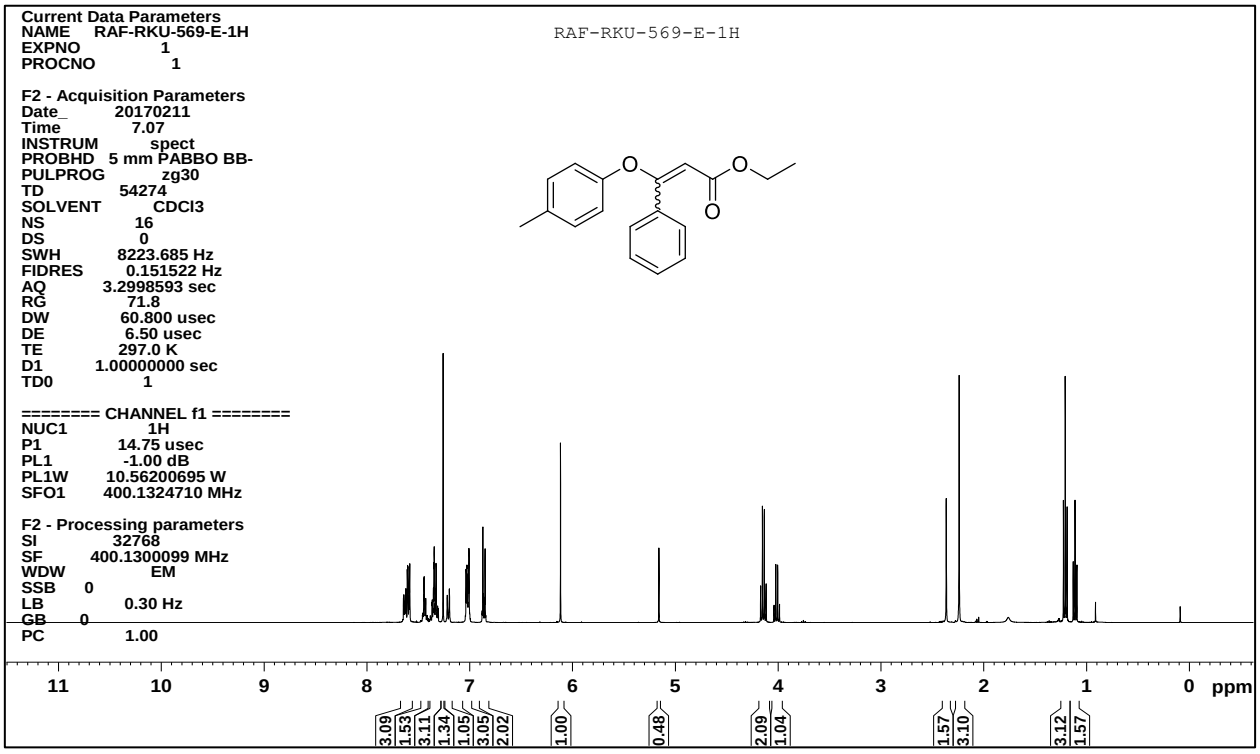


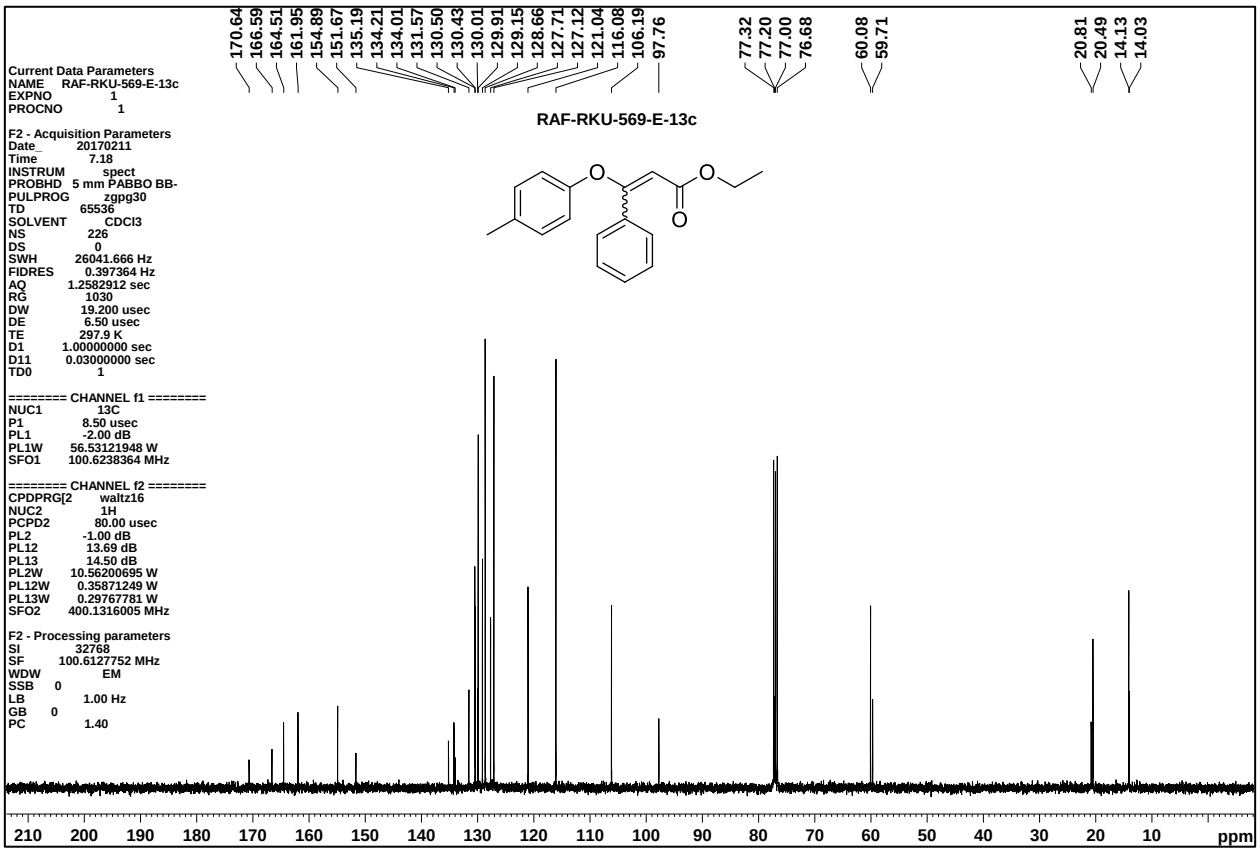
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **5b′**



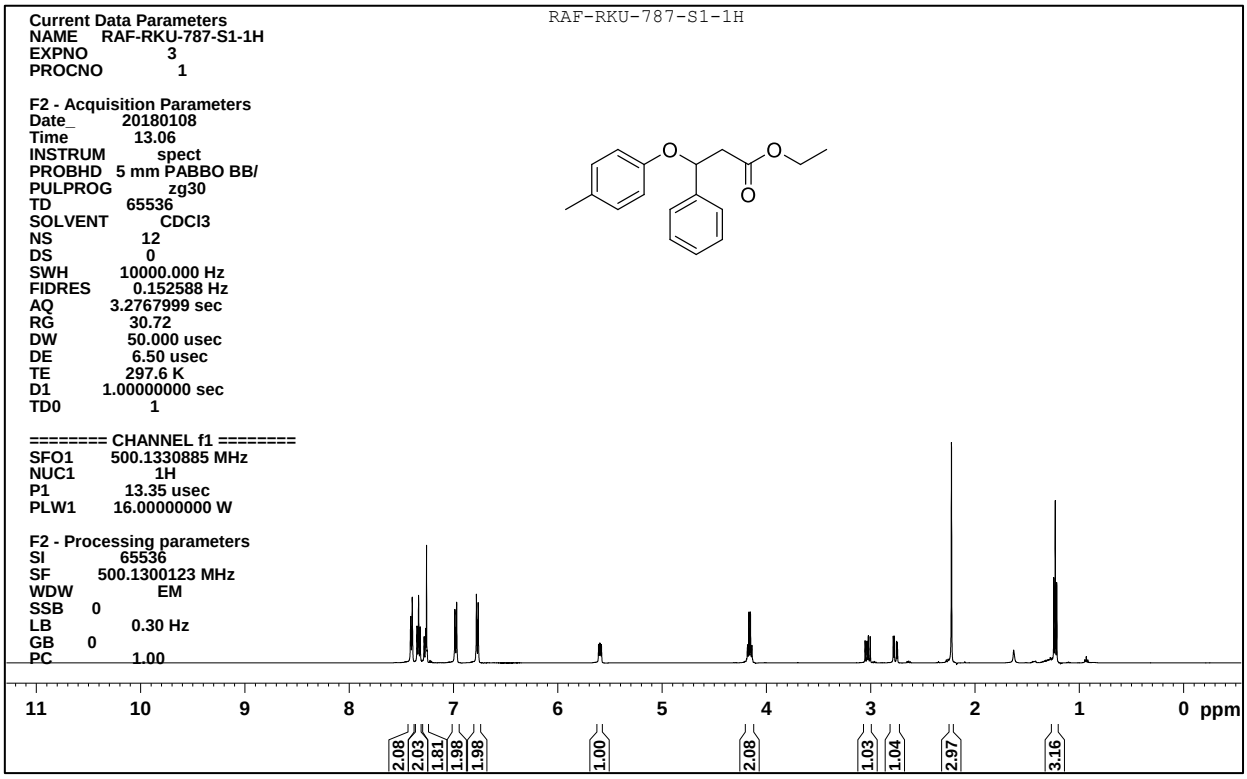


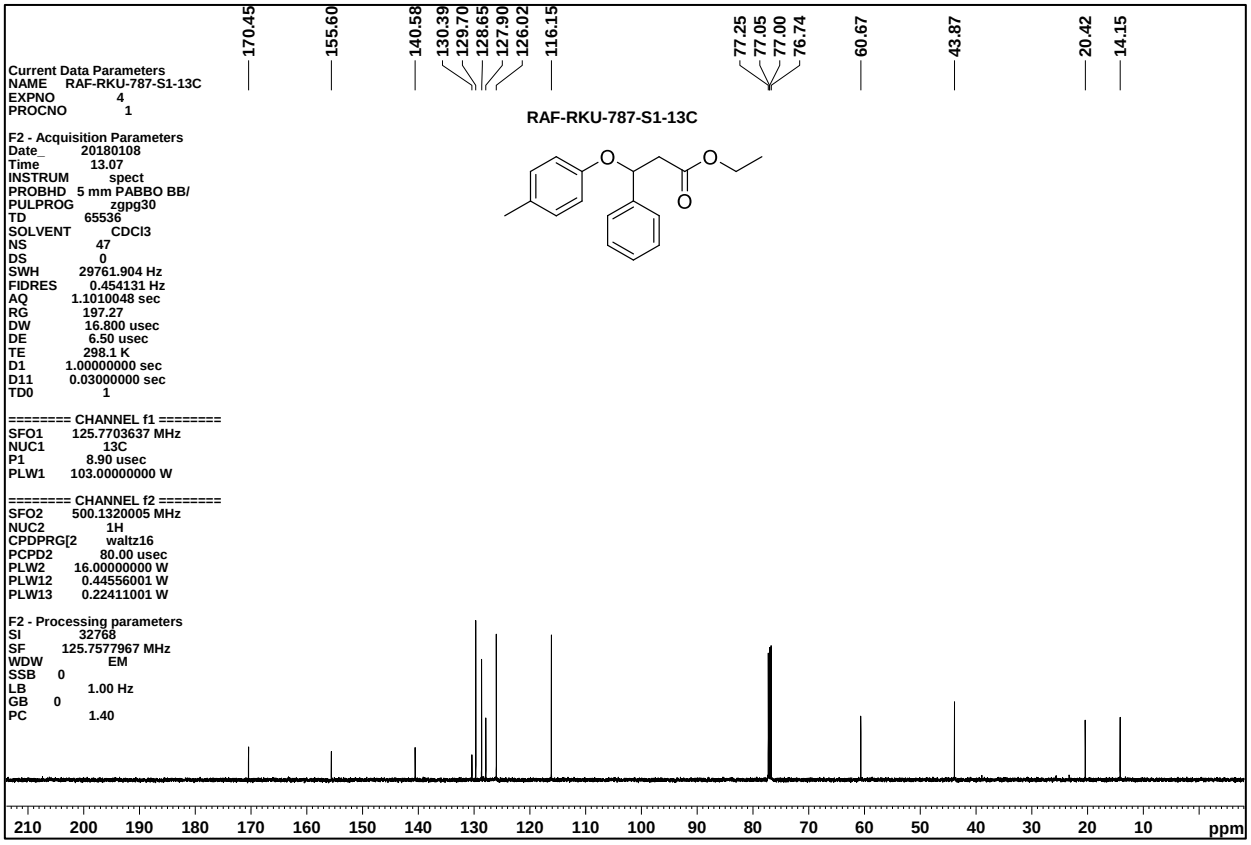
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of 3-phenyl-3-(*p*-tolyloxy)acrylate, *E/Z* (2:1)



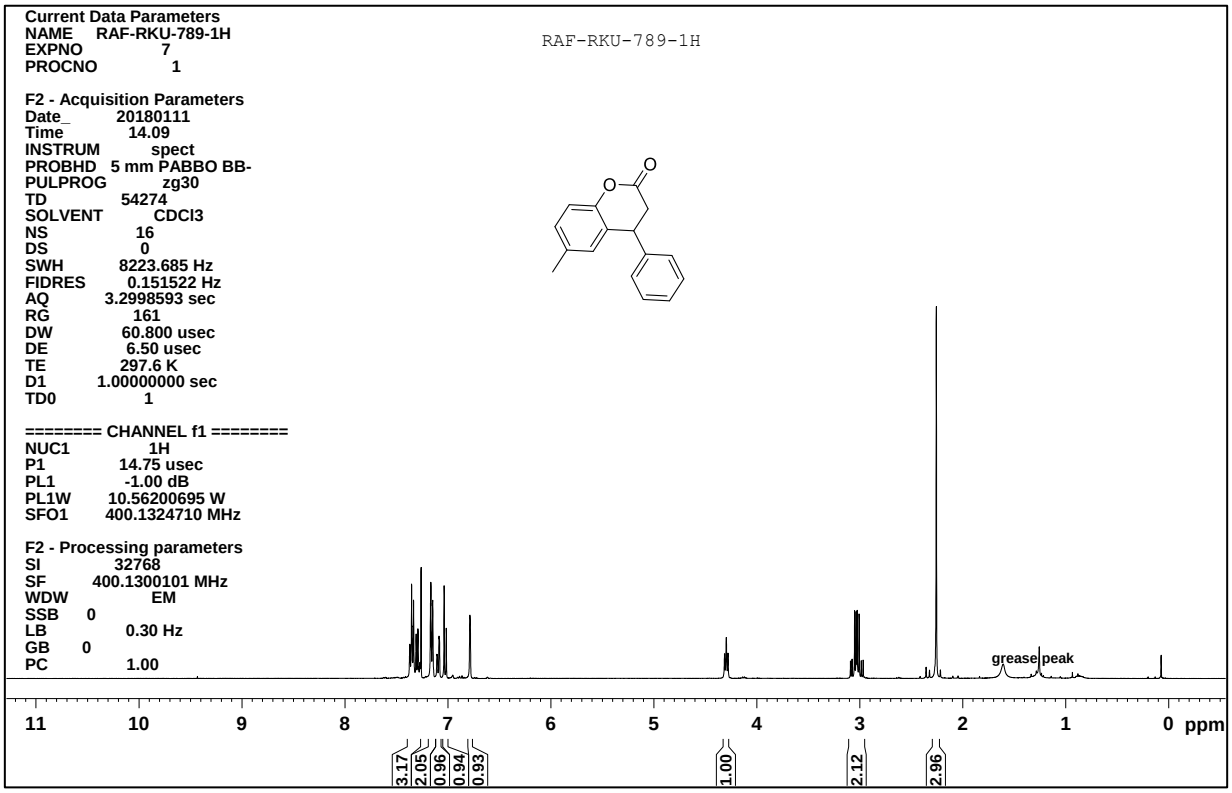


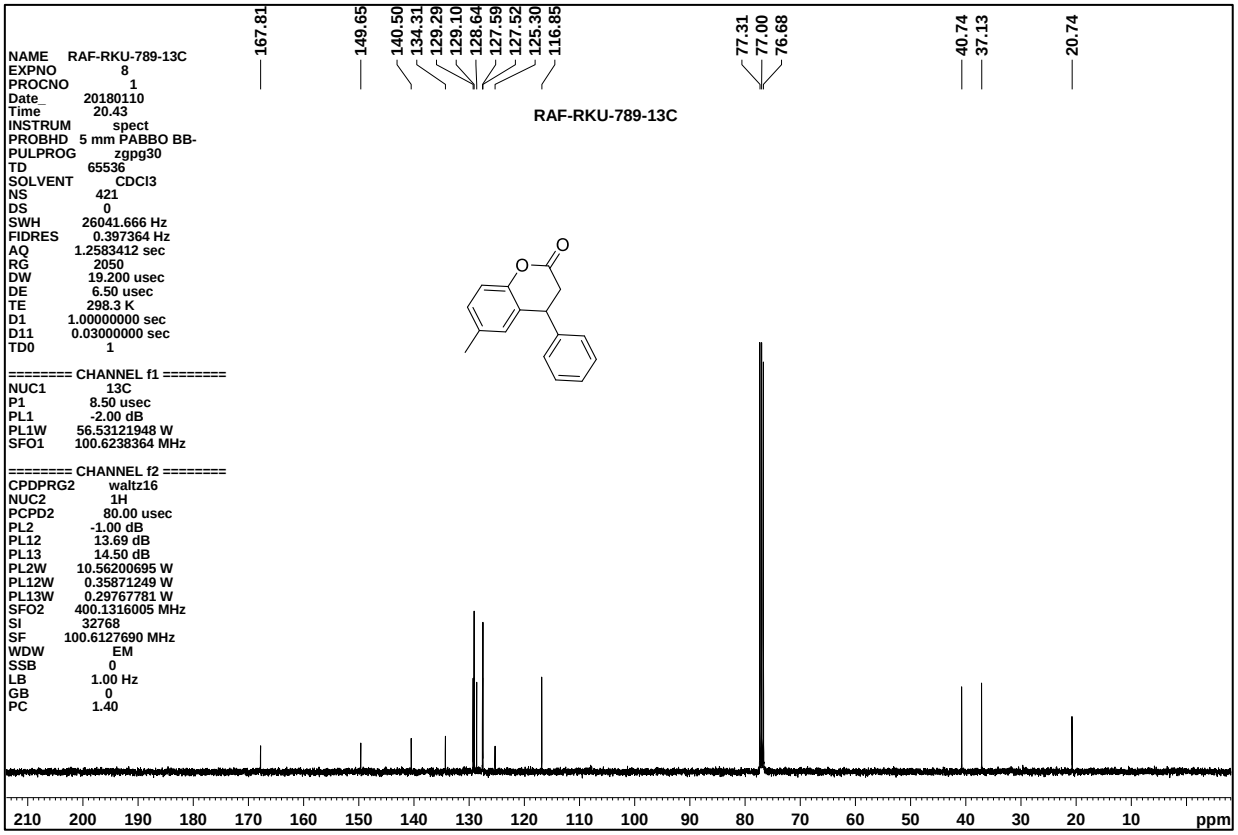
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (125 MHz, $CDCl_3$) of **24**



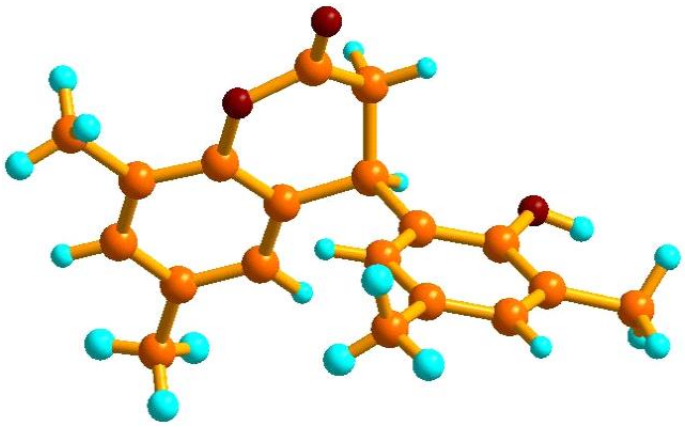


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (100 MHz, $CDCl_3$) of **5aa**





XRD parameters of **5a**



CCDC	1873459
Empirical formula	$C_{19}H_{20}O_3$
Formula weight	296.35
Temperature/K	150
Crystal system	orthorhombic
Space group	Pbca
a/Å	25.6777(10)
b/Å	15.169(6)
c/Å	8.027(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3126.6(17)
Z	8
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	0.084
F(000)	1264.0
Crystal size/mm^3	0.32 × 0.17 × 0.06
Radiation	MoKα (λ = 0.7107)
2Θ range for data collection/°	6.238 to 49.994
Reflections collected	13130
Independent reflections	2743 [R_{int} = 0.0645, R_{sigma} = 0.0437]
Data/restraints/parameters	2743/0/204
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.0670, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	0.26/-0.25

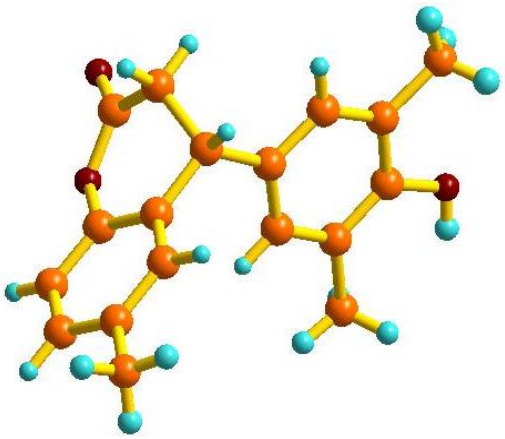
Table 2. Bond Lengths for **5a**

Atom	Atom	Length/Å	Atom	Atom
O2	C13	1.410(2)	C4	C3
O2	C14	1.366(2)	C4	C17
O1	C5	1.369(2)	C14	C15
O3	C14	1.208(2)	C8	C9
C5	C6	1.400(3)	C3	C2
C5	C4	1.395(3)	C1	C2
C7	C6	1.518(3)	C9	C10
C7	C15	1.537(3)	C2	C16
C7	C8	1.507(3)	C12	C11
C13	C8	1.382(3)	C12	C19
C13	C12	1.395(3)	C11	C10
C6	C1	1.388(3)	C10	C18

Table 3. Bond Angles for **5a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O2	C13	120.27(15)	O3	C14	C15	126.55(19)
O1	C5	C6	116.40(16)	C14	C15	C7	112.05(16)
O1	C5	C4	122.23(17)	C13	C8	C7	120.05(18)
C4	C5	C6	121.37(17)	C13	C8	C9	117.88(18)
C6	C7	C15	111.59(16)	C9	C8	C7	121.99(17)
C8	C7	C6	114.91(16)	C4	C3	C2	122.49(19)
C8	C7	C15	107.62(15)	C6	C1	C2	122.01(19)
C8	C13	O2	120.93(17)	C10	C9	C8	121.57(19)
C8	C13	C12	123.05(19)	C3	C2	C16	120.5(2)
C12	C13	O2	115.95(17)	C1	C2	C3	117.73(18)
C5	C6	C7	118.98(16)	C1	C2	C16	121.73(19)
C1	C6	C5	118.43(18)	C13	C12	C19	121.8(2)
C1	C6	C7	122.52(17)	C11	C12	C13	116.86(18)
C5	C4	C17	120.64(18)	C11	C12	C19	121.38(19)
C3	C4	C5	117.88(18)	C10	C11	C12	122.3(2)
C3	C4	C17	121.48(18)	C9	C10	C18	120.31(19)
O2	C14	C15	116.63(17)	C11	C10	C9	118.4(2)
O3	C14	O2	116.76(17)	C11	C10	C18	121.3(2)

XRD parameters of **5bx**



CCDC	1873458
Empirical formula	$C_{18}H_{18}O_3$
Formula weight	282.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.2851(6)
b/Å	11.5101(10)
c/Å	23.475(2)
α/°	90
β/°	93.360(9)
γ/°	90
Volume/Å^3	1425.6(2)
Z	6
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.089
F(000)	600.0
Crystal size/mm^3	0.241 × 0.057 × 0.037
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.476 to 49.99
Reflections collected	5338
Independent reflections	2453 [R_{int} = 0.0695, R_{sigma} = 0.0855]
Data/restraints/parameters	2453/0/194
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1223
Final R indexes [all data]	R_1 = 0.0865, wR_2 = 0.1507
Largest diff. peak/hole / e Å^{-3}	0.28/-0.31

Table 4. Bond lengths for **5bx**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C11	1.407(3)	C6	C7	1.396(3)
O3	C10	1.358(3)	C8	C9	1.541(3)
O2	C10	1.208(3)	C16	C11	1.375(3)
O1	C3	1.370(3)	C16	C15	1.387(3)
C5	C4	1.396(3)	C7	C2	1.384(4)
C5	C6	1.396(3)	C10	C9	1.485(3)
C12	C8	1.505(3)	C13	C14	1.386(3)
C12	C11	1.382(3)	C15	C14	1.391(3)
C12	C13	1.394(3)	C14	C17	1.507(4)
C4	C3	1.393(3)	C3	C2	1.404(4)
C4	C18	1.511(3)	C2	C1	1.503(3)
C6	C8	1.518(3)			

Table 5. Bond Angles for **5bx**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C10	O3	C11	119.82(18)	C16	C11	O3	116.0(2)
C6	C5	C4	122.3(2)	C16	C11	C12	123.0(2)
C11	C12	C8	118.7(2)	O3	C10	C9	117.9(2)
C11	C12	C13	116.7(2)	O2	C10	O3	116.6(2)
C13	C12	C8	124.6(2)	O2	C10	C9	125.5(2)
C5	C4	C18	121.1(2)	C10	C9	C8	112.0(2)
C3	C4	C5	118.4(2)	C14	C13	C12	122.6(2)
C3	C4	C18	120.5(2)	C16	C15	C14	121.0(2)
C5	C6	C8	124.2(2)	C13	C14	C15	118.1(2)
C5	C6	C7	117.1(2)	C13	C14	C17	121.3(2)
C7	C6	C8	118.7(2)	C15	C14	C17	120.6(2)
C12	C8	C6	115.7(2)	O1	C3	C4	123.4(2)
C12	C8	C9	106.86(19)	O1	C3	C2	115.3(2)
C6	C8	C9	110.5(2)	C4	C3	C2	121.3(2)
C11	C16	C15	118.6(2)	C7	C2	C3	118.1(2)
C2	C7	C6	122.9(2)	C7	C2	C1	121.3(2)
C12	C11	O3	120.9(2)	C3	C2	C1	120.6(2)