Supplementary Information

Diverse C(sp^3)–H Functionalization Through Electrochemical Benzylic Oxygenation

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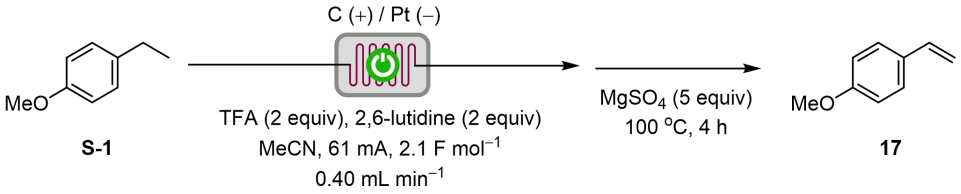
1. General Information

The commercially available reagents were used without purification. Flash column chromatography was performed with silica gel (200–300 mesh). NMR spectra were recorded on Bruker AV-400 instruments and Zhongke-Niujin Quantum-I^{plus} spectrometer. Data were reported as chemical shifts in ppm relative to $CDCl_3$ (7.29 ppm) for ^1H and $CDCl_3$ (77.2 ppm) for ^{13}C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br s = broad singlet. Infrared spectra were recorded on a Nicolet AVATER FTIR 330 spectrometer. GC analyses were carried out on Agilent 8860 GC system (column type: HP-5MS 5% Phenyl Methyl Silox, 30 m × 250 μm × 0.25 μm; rate flow: 1.2 mL/min). High-resolution mass spectra (ESI or APCI) were recorded by the instrumentation center of Department of Chemistry, Xiamen University, on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer.

2. Additional Optimization of Reaction Conditions

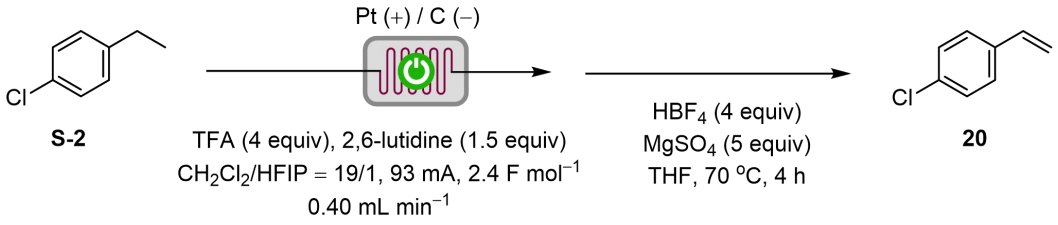
Table S1. Optimization of elimination conditions for the electron-rich substrate S-1.[a]



Entry	Deviations	Yield of **17** (%)[b]
1	None	80
2	In the absence of $MgSO_4$	26
3	$MgSO_4$ (2 equiv)	74
4	70 °C instead of 100 °C	62
5	1 h instead of 4 h	48
6	In the presence of HBF_4 (1 equiv)	11

[a]Reaction conditions: **S-1** (0.045 M), 8.0 mL of the outlet solution was collected and analyzed. [b]Yield determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

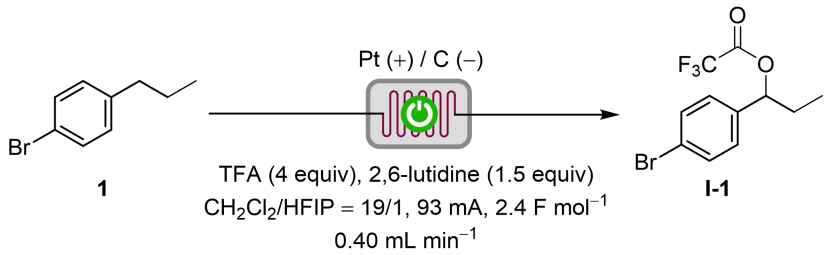
Table S2. Optimization of elimination conditions for the reaction of S-2.[a]



Entry	Deviations	Yield of **20** (%)[b]
1	None	67
2	No $MgSO_4$	41
3	4Å MS (150 mg) instead of $MgSO_4$	53

[a]Reaction conditions: **S-2** (0.06 M), 6.0 mL of the outlet solution was collected and analyzed. [b]Yield determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. Conditions for the formation of intermediate trifluoroacetic ester I-1 from substrate 1.[a]



Entry	Deviations	Conversion of **1** (%)	Yield of **I-1** (%)[b]
1	None	100	93
2	Reaction in batch (9.3 mA, 1.4 F mol^{-1}, 1.5 h)	71	54
3	Reaction in batch (9.3 mA, 2.4 F mol^{-1}, 2.5 h)	91	64
4	Reaction in batch (9.3 mA, 3.4 F mol^{-1}, 3.5 h)	98	32
5	Reaction in batch (30 mA, 2.4 F mol^{-1}, 0.8 h)	94	57

[a]Reaction conditions: **1** (0.06 M), 6.0 mL of the outlet solution was collected and analyzed, residence time= 22 seconds. [b]Yield determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

3. Detailed Steps for the Desaturation of Alkylarene

General procedure A. The electrolysis was conducted using a flow electrolytic cell equipped with a Pt anode and a graphite cathode with the exposed surface area of 10 cm^2 and interelectrode distance of 150 μ m (Figure S1). The solution containing substrate (0.06 M), TFA (4.0 equiv), 2,6-lutidine (1.5 equiv) in dry CH_2Cl_2/HFIP (19/1) was pushed using a syringe pump to pass through the flow cell operated with a flow rate of 0.40 mL min^{-1} and a constant current in the range of 93−144 mA. 6 mL of the outlet solution was collected (15 min) and concentrated under reduced pressure. The residue was treated with THF (2.4 mL), HBF_4•Et_2O (4 equiv, 50% w/w) and $MgSO_4$ (0 or 5 equiv). Then, the mixture was warmed to 100 ℃ and stirred for 4 h. After being cooled to room temperature, the mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the alkene product.

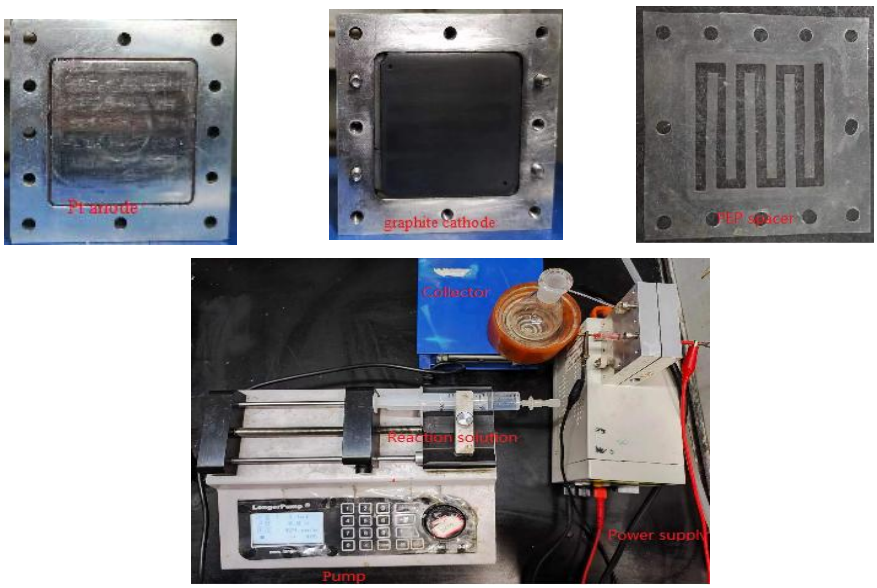


Figure S1. Assembling of the flow reactor and setup.

General Procedure B. The electrolysis was conducted using the same flow cell described above, but using graphite as anode and Pt as cathode. The solution containing substrate (0.045 M), TFA (2 equiv), 2,6-lutidine (2 equiv) in dry MeCN was pushed using a syringe pump to pass through the flow cell operated with a flow rate of 0.40 mL min^{-1} and a constant current in the range of 61 − 100 mA. The outlet solution was collected for 20 min (8 mL), treated with $MgSO_4$ (5 equiv), warmed to 100 ℃ and

stirred for 4 h. After being cooled to room temperature, the mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the alkene product.

Procedure for large scale synthesis of 38. Methyl dehydroabietate (25.7 g, 82 mmol, 1.0 equiv), TFA (25.1 mL, 328 mmol, 4 equiv), 2,6-lutidine (14.3 mL, 123 mmol, 1.5 equiv) were dissolved in dry CH_2Cl_2/HFIP (19/1, 1.4 L). The resulting solution was pumped through 8 flow cells with a flow rate of 0.4 mL min^{-1} for each reactor (Figure S2). The constant current for each reactor was 114 mA, and the electricity consumption was 2.9 F mol^{-1}. Upon complete passing of the reaction solution in 8.5 h, the collected outlet solution was concentrated under reduced pressure. The residue was treated with THF (360 mL), HBF_4•Et_2O (66.9 mL, 3 equiv, 50% w/w) and $MgSO_4$ (1.5 g, 1.5 equiv). Then, the mixture was warmed to 100 °C and stirred for 6 h. After being cooled to room temperature, the mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was then washed with 0.6 M H_2SO_4 to remove 2,6-lutidine and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give **38** (10.9 g, yield = 43%).

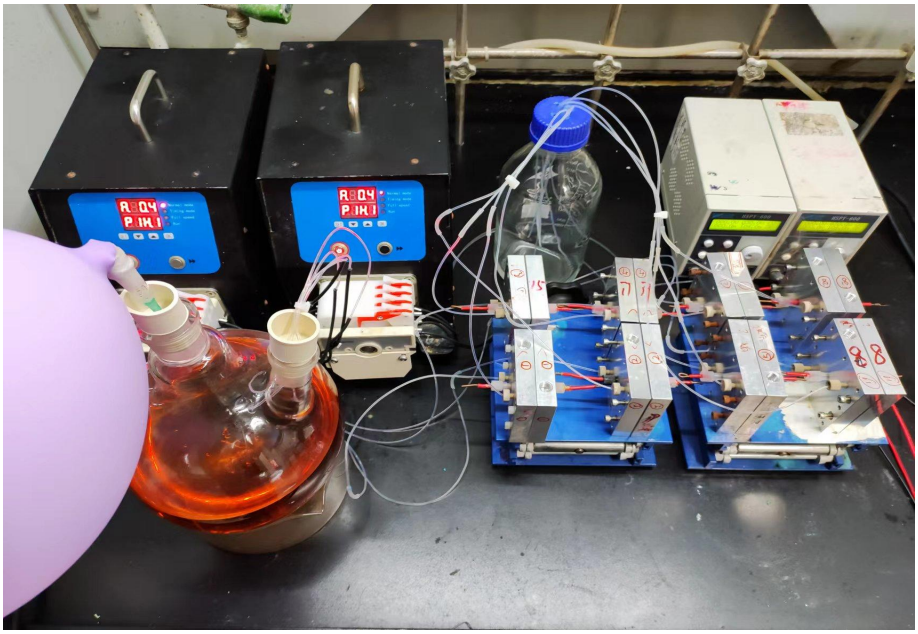
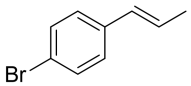
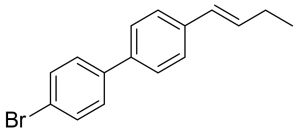


Figure S2. Reaction setup for scale-up with 8 parallel flow cells.

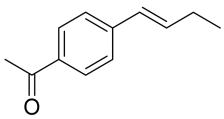
4. Characterization Data for the Alkene Products



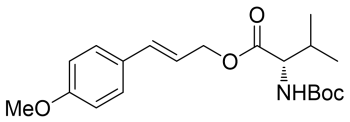
(*E*)-1-Bromo-4-(prop-1-en-1-yl)benzene (2). The title compound was obtained by following the **General Procedure A** but without the addition of $MgSO_4$. This compound known in the literature.[1] White solid, yield = 81% (57 mg, *E*/*Z* = 29/1, determined by GC analysis), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.30–6.23 (m, 1H), 1.91 (dd, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 131.5, 129.9, 127.4, 126.6, 120.3, 18.5.



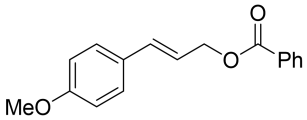
(*E*)-4-Bromo-4'-(but-1-en-1-yl)-1,1'-biphenyl (3). The title compound was obtained by following the **General Procedure A** but without the addition of $MgSO_4$. White solid, yield = 84% (86 mg, *E*/*Z* = 39/1, determined by GC analysis), current = 108 mA, electricity = 2.8 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.53–7.43 (m, 6H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.39–6.34 (m, 1H), 2.31–2.27 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.2, 137.4, 133.2, 131.8, 128.4, 128.2, 127.0, 126.4, 121.3, 26.1, 13.6. IR (neat, cm^{-1}): 3055, 2964, 1646, 1539, 1481, 1390, 1264, 969, 806, 738, 705. ESI HRMS *m/z* $(M+H)^+$ calcd 287.0430, obsd 287.0426.



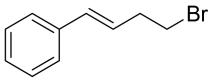
(*E*)-1-(4-(But-1-en-1-yl)phenyl)ethanone (4). The title compound was obtained through layer chromatography by following the **General Procedure A** but without the addition of $MgSO_4$. Colorless oil, yield = 44% (28 mg, *E* only, determined by GC analysis), current = 116 mA, electricity = 3.0 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.44 (m, 2H), 2.61 (s, 3H), 2.30–2.28 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 142.7, 135.9, 135.4, 128.7, 128.0, 125.9, 26.5, 26.1, 13.3. IR (neat, cm^{-1}): 2963, 2921, 2850, 1682, 1608, 1405, 1359, 1266, 959, 827. ESI HRMS *m/z* $(M+H)^+$ calcd 175.1117, obsd 175.1109.



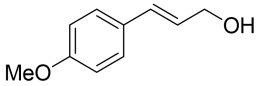
(*S*,*E*)-3-(4-Methoxyphenyl)allyl 2-((*tert*-butoxycarbonyl)amino)-3-methylbutanoate (5). The title compound was obtained by following the **General Procedure B**. White solid, yield = 72% (94 mg, *E*/*Z* = 47/1, determined by GC analysis), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.17–6.13 (m, 1H), 5.08 (d, *J* = 7.6 Hz, 1H), 4.79 (d, *J* = 5.2 Hz, 2H), 4.28 (br s, 1H), 3.82 (s, 3H), 2.17 (m, 1H), 1.46 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 159.7, 155.7, 134.5, 128.8, 127.9, 120.4, 114.1, 79.7, 65.9, 58.6, 55.2, 31.3, 28.3, 19.0, 17.5. IR (neat, cm^{-1}): 3374, 2972, 2837, 1717, 1607, 1577, 1497, 1368, 1250, 1092, 1031, 971, 848, 804, 778. ESI HRMS *m/z* $(M+Na)^+$ calcd 386.1938, obsd 386.1947.



(*E*)-3-(4-Methoxyphenyl)allyl benzoate (6). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[2] Colorless oil, yield = 74% (71 mg, *E*/*Z* > 49/1, determined by GC analysis), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.69-7.56 (m, 1H), 7.53-7.44 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.36–6.29 (m, 1H), 5.01 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.6, 134.1, 133.0, 130.3, 129.7, 129.0, 128.4, 127.9, 121.0, 114.1, 65.8, 55.3.

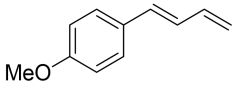


(*E*)-(4-Bromobut-1-en-1-yl)benzene (7). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[3] Colorless oil, yield = 74% (56 mg, *E* only, determined by GC analysis), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 4H), 7.29–7.24 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.25–6.18 (m, 1H), 3.51 (t, *J* = 7.2 Hz, 2H), 2.84–2.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 132.7, 128.5, 127.4, 126.6, 126.2, 36.3, 32.2.

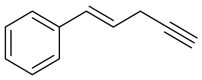


(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (8). The title compound was obtained by

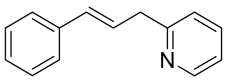
following the **General Procedure B**. This compound known in the literature.[4] Colorless oil, yield = 61% (36 mg, *E* only, determined by GC analysis), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.29–6.22 (m, 1H), 4.32 (dd, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 131.0, 129.4, 127.7, 126.2, 114.0, 63.9, 55.3.



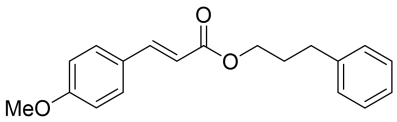
(*E*)-1-(Buta-1,3-dien-1-yl)-4-methoxybenzene (9). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[5] Colorless oil, yield = 70% (41 mg, *E* only, determined by GC analysis), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.74–6.68 (m, 1H), 6.57–6.48 (m, 2H), 5.32 (d, *J* = 16.0, 1H), 5.17–5.14 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 137.4, 132.4, 129.9, 127.6, 116.4, 114.1, 55.3.



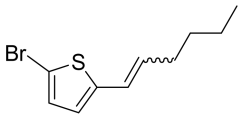
(*E*)-Pent-1-en-4-yn-1-ylbenzene (10). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[6] Colorless oil, yield = 50% (26 mg, *E* only, determined by GC analysis), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.38-7.30 (m, 2H), 7.29-7.23 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.24–6.17 (m, 1H), 3.18 (d, *J* = 2.0, 2H), 2.21 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 131.6, 128.5, 127.4, 126.2, 123.6, 81.2, 70.6, 21.9.



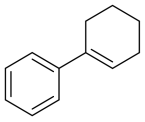
2-Cinnamylpyridine (11). The title compound was obtained by following the **General Procedure A**, the corresponding reaction mixture was diluted with saturated aqueous $NaHCO_3$ instead of H_2O. This compound known in the literature.[7] White solid, yield = 49% (34 mg, *E* only, determined by GC analysis), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.67–7.63 (m, 1H), 7.41–7.15 (m, 7H), 6.59–6.44 (m, 2H), 3.77 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 149.3, 137.3, 136.7, 132.0, 128.5, 127.4, 127.2, 126.2, 122.9, 121.4, 42.0.



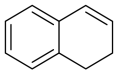
(*E*)-3-Phenylpropyl 3-(4-methoxyphenyl)acrylate (12). The title compound was obtained through layer chromatography by following the **General Procedure B**. Colorless oil, yield = 52% (55 mg, *E* only, determined by GC analysis), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 2H), 7.26–7.23 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.09–2.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 161.4, 144.4, 141.3, 129.7, 128.5, 127.2, 126.0, 115.6, 114.3, 63.7, 55.4, 32.3, 30.4. IR (neat, cm^{-1}): 3027, 2953, 2838, 1709, 1634, 1604, 1575, 1513, 1497, 1454, 1422, 1380, 1302, 1254, 1159, 1111, 1030, 982, 828, 751, 698. ESI HRMS *m/z* $(M+Na)^+$ calcd 319.1305, obsd 319.1311.



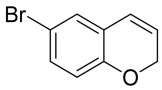
2-Bromo-5-(hex-1-en-1-yl)thiophene (13). The title compound was obtained by following the **General Procedure B**. Colorless oil, yield = 56% (49 mg, *E*/*Z* = 5/1, determined by ^1H NMR), current = 81 mA, electricity = 2.8 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 4.0 Hz, 0.15H), 6.90 (d, *J* = 4.0 Hz, 0.85H), 6.72 (d, *J* = 3.6 Hz, 0.15H), 6.61 (d, *J* = 3.6 Hz, 0.85H), 6.44–6.39 (m, 1H), 6.03–5.95 (m, 0.85H), 5.63–5.58 (m, 0.15H), 2.38–2.33 (m, 0.30H), 2.20–2.15 (m, 1.70H), 1.51–1.33 (m, 4H), 0.98–0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 131.9, 130.0, 129.4, 127.0, 124.2, 122.6, 121.4, 109.5, 32.5, 31.5, 31.2, 29.1, 22.4, 22.2, 13.9. IR (neat, cm^{-1}): 3098, 2957, 2929, 2871, 1713, 1674, 1531, 1507, 1416, 1327, 1247, 1085, 1048, 976, 805, 749. ESI HRMS *m/z* $(M+H)^+$ calcd 244.9994, obsd 244.9996.



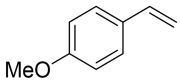
2,3,4,5-Tetrahydro-1,1'-biphenyl (14). The title compound was obtained through layer chromatography by following the **General Procedure A**. This compound known in the literature.[8] Colorless oil, yield = 54% (31 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.38-7.31 (m, 2H), 7.28-7.22 (m, 1H), 6.21-6.13 (m, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.29–2.27 (m, 2H), 1.87–1.76 (m, 2H), 1.76–1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 136.6, 128.2, 126.5, 124.9, 124.8, 27.4, 25.9, 23.1, 22.2.



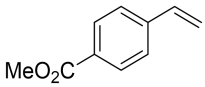
1,2-Dihydronaphthalene (15). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[9] Colorless oil, yield = 66% (31 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.06 (m, 4H), 6.54-6.46 (m, 1H), 6.11–6.06 (m, 1H), 2.85 (t, *J* = 8.0 Hz, 2H), 2.40–2.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 134.1, 128.6, 127.8, 127.5, 126.8, 126.4, 125.9, 27.5, 23.1.



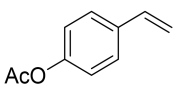
6-Bromo-2*H*-chromene (16). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[10] White solid, yield = 41% (31 mg), current = 78 mA, electricity = 2.7 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.38–6.35 (m, 1H), 5.84–5.80 (m, 1H), 4.85–4.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 131.6, 129.0, 124.1, 123.5, 123.1, 117.4, 113.2, 65.6.



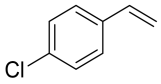
1-Methoxy-4-vinylbenzene (17). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[11] Colorless oil, yield = 79% (38 mg), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 2H), 6.93-6.86 (m, 2H), 6.70 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 136.2, 130.5, 127.4, 113.9, 111.5, 55.2.



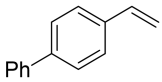
Methyl 4-vinylbenzoate (18). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[12] Colorless oil, yield = 64% (37 mg), current = 116 mA, electricity = 3.0 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06-7.98 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.77 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 11.2 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 141.9, 136.0, 129.9, 129.7, 126.1, 116.5, 52.0.



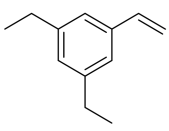
4-Vinylphenyl acetate (19). The title compound was obtained through layer chromatography by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[13] Colorless oil, yield = 59% (34 mg), current = 116 mA, electricity = 3.0 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.72 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 150.2, 135.9, 128.7, 127.2, 121.6, 114.0, 21.1.



1-Chloro-4-vinylbenzene (20). The title compound was obtained through layer chromatography by following the **General Procedure A**, with the modification of using THF (6 mL) at 70 ºC instead of THF (2.4 mL) at 100 ºC. This compound known in the literature.[14] Colorless oil, yield = 64% (32 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 4H), 6.69 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.29 (d, J = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 135.7, 133.4, 128.7, 127.4, 114.4.

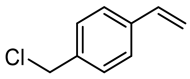


4-Vinyl-1,1'-biphenyl (21). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[11] Colorless oil, yield = 67% (43 mg), current = 108 mA, electricity = 2.8 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.60 (m, 4H), 7.53–7.46 (m, 4H), 7.40–7.38 (m, 1H), 6.80 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.84 (dd, J_1 = 17.6 Hz, J_2 = 0.4 Hz, 1H), 5.32 (dd, J_1 = 10.8 Hz, J_2 = 0.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 127.0, 126.7, 113.9.

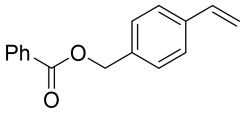


1,3-Diethyl-5-vinylbenzene (22). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[15] Colorless oil, yield = 54% (31 mg), current = 100 mA, electricity = 2.6 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.99 (s, 1H), 6.74 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1H), 5.78 (dd, J_1 = 17.6 Hz, J_2 = 0.4 Hz, 1H), 5.26 (dd, J_1 = 10.8 Hz, J_2 = 0.8 Hz, 1H), 2.67 (q, J = 7.6 Hz, 4H), 1.29 (t, J =

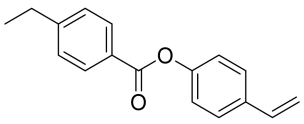
6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.2, 127.2, 124.8, 123.2, 113.3, 28.8, 15.6.



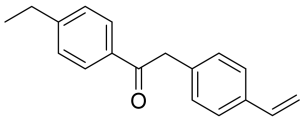
1-(Chloromethyl)-4-vinylbenzene (23). The title compound was obtained through layer chromatography by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[16] Colorless oil, yield = 46% (25 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.74 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 4.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.9, 136.2, 128.8, 126.5, 114.5, 46.0.



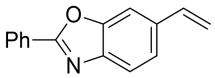
4-Vinylbenzyl benzoate (24). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). Colorless oil, yield = 54% (46 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 2H), 7.63-7.55 (m, 1H), 7.48–7.43 (m, 6H), 6.76 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 5.38 (s, 2H), 5.29 (d, J = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 137.6, 136.4, 135.5, 133.0, 130.1, 129.7, 128.5, 128.4, 126.4, 114.3, 66.4. IR (neat, cm^{-1}): 3062, 3006, 2924, 2852, 1721, 1601, 1514, 1450, 1374, 1314, 1268, 1175, 1107, 1026, 989, 908, 830, 709. ESI HRMS *m/z* $(M+Na)^+$ calcd 261.0886, obsd 261.0894.



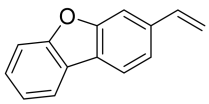
4-Vinylphenyl 4-ethylbenzoate (25). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[11] Colorless oil, yield = 42% (38 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 6.77 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 2.78 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.6, 136.0, 135.3, 130.3, 128.8, 128.1, 127.2, 121.8, 121.4, 113.9, 29.0, 15.2.



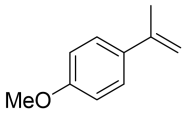
1-(4-Ethylphenyl)-2-(4-vinylphenyl)ethan-1-one (26). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). White solid, yield = 42% (38 mg), current = 128 mA, electricity = 3.3 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.32-7.26 (m, 4H), 6.73 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 4.29 (s, 2H), 2.73 (q, J = 8.0 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 150.1, 136.5, 136.2, 134.4, 134.3, 129.6, 128.8, 128.1, 126.5, 113.6, 45.2, 28.9, 15.1. IR (neat, cm^{-1}): 2964, 2926, 1682, 1605, 1407, 994, 894, 827. ESI HRMS *m/z* $(M+H)^+$ calcd 251.1430, obsd 251.1429.



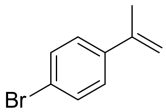
2-Phenyl-6-vinylbenzo[*d*]oxazole (27). The title compound was obtained through layer chromatography by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). White solid, yield = 68% (54 mg), current = 110 mA, electricity = 2.8 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32-8.25 (m, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.58–7.55 (m, 3H), 7.46 (d, J = 8.0 Hz, 1H), 6.87 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.35 (d, J = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 151.3, 141.9, 136.6, 135.4, 131.5, 128.9, 127.6, 127.1, 123.4, 119.7, 114.2, 107.9. IR (neat, cm^{-1}): 3048, 2928, 2850, 1626, 1494, 1457, 1425, 1406, 1322, 1264, 1204, 1129, 1104, 988, 928, 903, 823, 745. ESI HRMS *m/z* $(M+H)^+$ calcd 222.0913, obsd 222.0921.



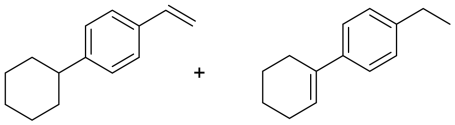
3-Vinyldibenzo[*b*,*d*]furan (28). The title compound was obtained through layer chromatography by following the **General Procedure B**. This compound known in the literature.[17] White solid, yield = 60% (42 mg), current = 100 mA, electricity = 3.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.62-7.55 (m, 1H), 7.49–7.43 (m, 2H), 7.39-7.32 (m, 1H), 6.89 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.89 (d, J = 17.6 Hz, 1H), 5.36 (d, J = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 137.2, 136.8, 127.1, 126.5, 124.1, 123.9, 122.8, 121.4, 120.6, 120.5, 114.3, 111.6, 109.0.



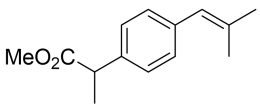
1-Methoxy-4-(prop-1-en-2-yl)benzene (29). The title compound was obtained by following the **General Procedure B**. The corresponding outlet solution was only need stirred at rt for 6 h without the addition of any additive to give product **29**. This compound known in the literature.[18] Colorless oil, yield = 56% (30 mg), current = 61 mA, electricity = 2.1 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.32 (s, 1H), 5.02 (s, 1H), 3.84 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 142.6, 133.8, 126.6, 113.5, 110.6, 55.2, 21.9.



1-Bromo-4-(prop-1-en-2-yl)benzene (30). The title compound was obtained by following the **General Procedure A**. The corresponding outlet solution was only need stirred at rt for 6 h without the addition of any additive to give product **30**. This compound known in the literature.[18] Colorless oil, yield = 51% (36 mg), current = 96 mA, electricity = 2.5 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 5.14 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 140.1, 131.3, 127.1, 121.3, 113.0, 21.6.

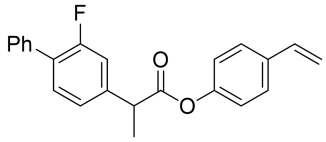


1-Cyclohexyl-4-vinylbenzene/4'-ethyl-2,3,4,5-tetrahydro-1,1'-biphenyl (31/31'). The title compound was obtained as a 7:1 mixture of isomers through layer chromatography by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[19] Colorless oil, yield = 48% (32 mg), current = 124 mA, electricity = 3.2 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.22–7.17 (m, 2H), 6.74 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 0.88H), 6.17-6.10 (m, 0.12H), 5.75 (d, *J* = 17.6 Hz, 0.88H), 5.23 (d, *J* = 10.8 Hz, 0.88H), 2.70–2.24 (m, 2H), 1.90–1.68 (m, 4H), 1.51–1.26 (m, 5.24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 136.8, 135.3, 127.0, 126.2, 112.8, 44.3, 34.4, 26.9, 26.1.

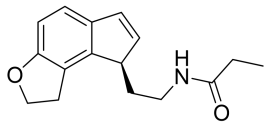


Methyl 2-(4-(2-methylprop-1-en-1-yl)phenyl)propanoate (32). The title compound

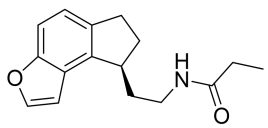
was obtained by following the **General Procedure A**. This compound known in the literature.[20] Colorless oil, yield = 73% (57 mg), current = 93 mA, electricity = 2.4 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 3.74 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 137.9, 137.6, 135.5, 129.0, 127.1, 124.7, 52.0, 45.1, 26.9, 19.4, 18.5.



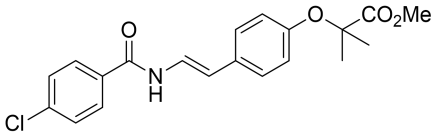
4-Vinylphenyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (33). The title compound was obtained by following the **General Procedure A**, with the modification of using THF (6 mL) instead of THF (2.4 mL). This compound known in the literature.[11] Colorless oil, yield = 61% (76 mg), current = 116 mA, electricity = 3.0 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.51–7.42 (m, 6H), 7.31–7.24 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 160.0 (d, $J_{C\text{-}F}$ = 248.0 Hz), 150.3, 141.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 135.8, 135.4 (d, $J_{C\text{-}F}$ = 5.1 Hz), 131.08, 131.04, 129.0 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.6 (d, $J_{C\text{-}F}$ = 23.7 Hz), 127.7, 127.1, 123.65, 123.62, 121.4, 115.3 (d, $J_{C\text{-}F}$ = 23.7 Hz), 114.1, 45.1, 18.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2.



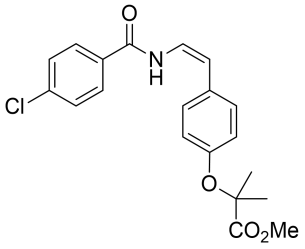
(*R*)-*N*-(2-(2,8-Dihydro-1*H*-indeno[5,4-*b*]furan-8-yl)ethyl)propionamide (34). The title compound was obtained by following the **General Procedure B**. White solid, yield = 44% (41 mg), current = 80 mA, electricity = 2.7 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.0 Hz, 1H), 6.80 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.36 (dd, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 1H), 5.34 (br s, 1H), 4.65–4.58 (m, 2H), 3.61 (br s, 1H), 3.39–3.07 (m, 4H), 2.26–2.20 (m, 1H), 2.07–1.97 (m, 3H), 1.06 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 158.9, 143.4, 137.4, 135.0, 131.7, 122.5, 120.4, 107.3, 71.3, 47.8, 37.1, 29.6, 28.5, 28.2, 9.7. IR (neat, cm^{-1}): 3303, 2926, 1646, 1552, 1460, 1439, 1374, 1227, 1124, 988, 940, 810. ESI HRMS *m/z* $(M+H)^+$ calcd 258.1489, obsd 258.1495.



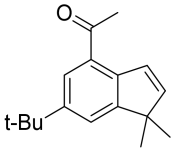
***(S)-N*-(2-(7,8-Dihydro-6*H*-indeno[5,4-*b*]furan-8-yl)ethyl)propionamide (34').** The title compound was obtained by following the **General Procedure B**. White solid, yield = 7% (6 mg), current = 80 mA, electricity = 2.7 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.79 (q, *J* = 1.2 Hz, 1H), 5.41 (br s, 1H), 3.51–3.37 (m, 3H), 3.09–2.91 (m, 2H), 2.44–2.38 (m, 1H), 2.22-2.13 (m, 3H), 1.98–1.92 (m, 1H), 1.81–1.76 (m, 1H), 1.13 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 154.7, 145.1, 138.6, 137.6, 123.6, 120.4, 109.6, 104.6, 42.4, 38.0, 34.5, 31.8, 31.3, 29.7, 9.8. IR (neat, cm^{-1}): 3294, 3100, 2937, 2852, 1646, 1548, 1463, 1431, 1354, 1249, 1138, 1109, 1045, 805, 759. ESI HRMS *m/z* $(M+H)^+$ calcd 258.1489, obsd 258.1496.



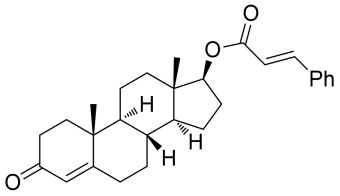
(*E*)-Methyl 2-(4-(2-(4-chlorobenzamido)vinyl)phenoxy)-2-methylpropanoate (35). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[21] White solid, yield = 35% (47 mg), current = 68 mA, electricity = 2.3 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 10.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.64–7.58 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.25 (d, *J* = 14.8 Hz, 1H), 3.81 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 163.3, 154.5, 138.4, 131.9, 130.0, 129.0, 128.5, 126.5, 121.8, 119.5, 113.5, 79.2, 52.5, 25.3.



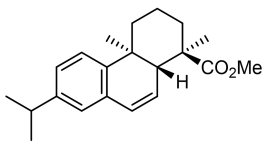
(*Z*)-Methyl 2-(4-(2-(4-chlorobenzamido)vinyl)phenoxy)-2-methylpropanoate (35'). The title compound was obtained by following the **General Procedure B**. This compound known in the literature.[21] White solid, yield = 6% (8 mg), current = 68 mA, electricity = 2.3 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 10.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.17–7.12 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.88 (d, *J* = 9.6 Hz, 1H), 3.82 (s, 3H), 1.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 163.3, 154.4, 138.5, 131.7, 129.3, 129.1, 128.8, 128.5, 121.5, 119.5, 110.9, 52.6, 25.4.



1-(6-(*tert*-Butyl)-1,1-dimethyl-1*H*-inden-4-yl)ethanone (36). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[11] White solid, yield = 84% (73 mg), current = 116 mA, electricity = 3.0 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 0.4 Hz, 1H), 7.39 (d, *J* = 5.6 Hz, 1H), 6.54 (d, *J* = 5.2 Hz, 1H), 2.66 (s, 3H), 1.41 (s, 9H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 155.0, 150.2, 148.2, 140.0, 130.3, 127.7, 124.3, 122.2, 48.9, 34.8, 31.5, 28.3, 24.2.



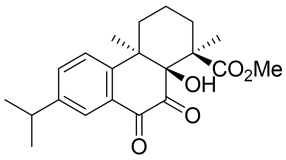
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl cinnamate (37). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[22] White solid, yield = 44% (66 mg, *E* only, determined by ^1H NMR), current = 144 mA, electricity = 3.7 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.61-7.53 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.77 (s, 1H), 4.79 (t, *J* = 8.0 Hz, 1H), 2.46–1.23 (m, 16H), 1.16 (s, 3H), 1.14–1.00 (m, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 171.0, 167.0, 144.5, 134.5, 130.2, 128.9, 128.0, 124.0, 118.5, 82.5, 53.7, 50.3, 42.7, 38.6, 35.7, 35.4, 33.9, 32.7, 31.5, 27.6, 23.5, 20.5, 17.4, 12.1.



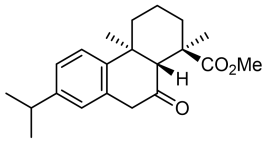
(1*R*,4a*S*,10a*R*)-Methyl 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,10a-hexahydrophenanthrene-1-carboxylate (38). The title compound was obtained by following the **General Procedure A**. This compound known in the literature.[23] White solid, yield = 51% (57 mg), current = 114 mA, electricity = 2.9 F mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.08 (m, 2H), 6.94 (s, 1H), 6.54 (dd, J_1 = 9.6 Hz, J_2 = 3.2 Hz, 1H), 5.75 (dd, J_1 = 9.6 Hz, J_2 = 2.4 Hz, 1H), 3.67 (s, 3H), 2.95 (s, 1H), 2.92–2.87 (m, 1H), 2.23 (d, *J* = 11.2 Hz, 1H), 1.83–1.72 (m, 5H), 1.43 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.11

(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 146.3, 145.1, 132.6, 129.8, 128.3, 125.7, 124.7, 121.6, 52.0, 46.6, 46.4, 37.1, 35.6, 35.3, 33.5, 23.9, 20.8, 18.4, 17.9.

5. Alkene Transformations

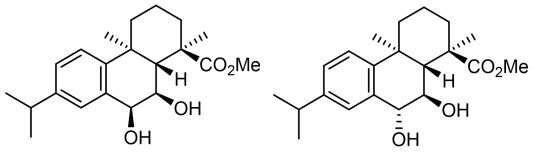


(1*R*,4a*R*,10a*S*)-Methyl 10a-hydroxy-7-isopropyl-1,4a-dimethyl-9,10-dioxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (40). To a round bottom flask was added **38** (62 mg, 0.2 mmol), *tert*-butanol (1 mL), and water (1 mL), followed by the addition of AD-mix (β) (750 mg) and K_2OsO_4•$2H_2O$ (3 mg, 7 μmol). The reaction mixture was stirred at room temperature for 3 days. Solid Na_2SO_3 (0.2 g) was added to the mixture, which then stirred at room temperature for 1 h. Next, the reaction mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography to give **40** as yellow solid (86%, 62 mg). This compound known in the literature.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.0 Hz, 1H), 7.53 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 6.79 (s, 1H), 3.79 (s, 3H), 2.99–2.40 (m, 1H), 2.40–2.36 (m, 1H), 2.19–2.12 (m, 2H), 1.97–1.89 (m, 2H), 1.73 (s, 3H), 1.69–1.65 (m, 1H), 1.36 (s, 3H), 1.29 (d, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 183.9, 180.9, 151.4, 147.4, 134.3, 130.8, 126.2, 123.8, 81.8, 53.1, 46.5, 44.9, 33.5, 32.5, 30.6, 29.5, 23.7, 18.5, 17.5.



(1*R*,4a*S*,10a*R*)-Methyl 7-isopropyl-1,4a-dimethyl-10-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (41). To an oven-dried round bottom flask was added **38** (62 mg, 0.2 mmol) and CH_2Cl_2 (1.5 mL). Then, *m*-CPBA (61 mg, 0.3 mmol, 85%) was added to the mixture slowly at 0 °C. The resultant mixture was warmed to room temperature and stirred in dark for 5 h. Then, Et_2O was added to the mixture, which was subsequently washed with saturated aqueous KI solution, $Na_2S_2O_3$ (2N) solution, and saturated aqueous $NaHCO_3$ solution. The aqueous phase was extracted twice with Et_2O. The combined organic phase was then washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue and TsOH•H_2O (46 mg,

0.24 mmol) were dissolved in 1 mL of benzene, stirred and heated at 80 °C under Ar for 2 h. After being cooled to room temperature, Et_2O was added to the reaction mixture. The organic layer was washed with brine, aqueous $NaHCO_3$ solution and H_2O and subsequently concentrated under reduced pressure. The residue was purified by a flash chromatography to give compound **41** as a colorless oil, yield = 44% (29 mg). This compound known in the literature.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 3.80-3.57 (m, 2H), 3.66 (s, 3H), 3.29 (s, 1H), 2.93–2.90 (m, 1H), 2.37–2.35 (m, 1H), 1.83–1.74 (m, 5H), 1.29 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 178.4, 147.1, 145.7, 131.5, 126.5, 125.1, 122.8, 59.0, 52.2, 43.8, 43.6, 38.1, 37.47, 37.40, 33.6, 24.1, 24.0, 23.9, 18.0, 17.0.

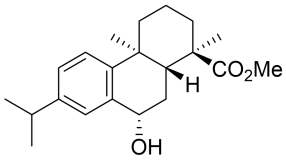


Methyl (1*R*,4a*S*,9*S*,10*R*,10a*R*)-9,10-dihydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (42) and (1*R*,4a*S*,9*R*,10*R*,10a*R*)-methyl 9,10-dihydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (42'). To a round bottom flask was added **38** (62 mg, 0.2 mmol) and CH_3CN/H_2O (2.6 mL, 1/1). Then, *m*-CPBA (61 mg, 0.3 mmol, 85%) was added to the mixture at 0 °C. The resultant mixture was warmed to room temperature and stirred for 0.5 h. Next, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted twice with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by a flash chromatography to give compound **42** (39 mg, 57%) and **42'** (14 mg, 20%) as colorless oil.

Compound 42: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.74 (d, *J* = 4.4 Hz, 1H), 4.14–4.11 (m, 1H), 3.68 (s, 3H), 2.93–2.90 (m, 1H), 2.70 (d, *J* = 12.0 Hz, 1H), 2.32–2.29 (m, 1H), 1.82–1.52 (m, 6H), 1.49 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 6H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 147.0, 146.2, 134.5, 128.7, 127.3, 124.0, 70.9, 67.8, 52.1, 44.6, 44.1, 38.6, 38.0, 37.6, 33.5, 25.2, 24.0, 23.8, 18.3, 16.3. IR (neat, cm^{-1}): 3447, 2957, 2868, 1703, 1497, 1459, 1250, 1039, 1006, 952, 892, 826, 734. ESI HRMS *m/z* $(M+Na)^+$ calcd 369.2036, obsd 369.2033.

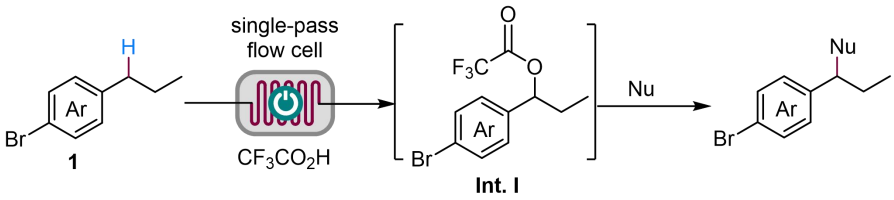
Compound 42': ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.03–3.98 (m, 1H), 3.69 (s, 3H), 2.93–2.90 (m, 1H), 2.65 (d, *J* = 12.0 Hz, 1H), 2.30 (d, *J* = 12.8 Hz, 1H), 1.82–1.51 (m, 6H), 1.47 (s, 3H), 1.30, (s, 3H), 1.27 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.1, 146.9, 145.6, 135.2,

126.1, 125.3, 123.8, 77.9, 72.8, 52.1, 47.7, 44.2, 38.9, 38.0, 37.5, 33.7, 26.2, 24.0, 23.8, 18.2, 16.7. IR (neat, cm^{-1}): 3420, 2955, 2869, 1708, 1496, 1459, 1257,1020, 986, 737. ESI HRMS *m/z* $(M+Na)^+$ calcd 369.2036, obsd 369.2033.



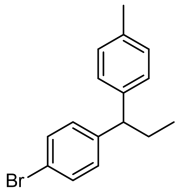
(1*R*,4a*S*,10*S*,10a*R*)-Methyl 10-hydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (43). To an oven-dried round bottom flask was added BH_3•SMe_2 (350 µL, 2.0 M in THF, 0.7 mmol). Then, a solution of **38** (62 mg, 0.2 mmol) in THF (0.6 mL) was added to the flask under Ar at 0 °C. The resultant mixture was warmed to room temperature and stirred overnight. Next, the reaction was cooled to 0 °C and added NaOH (0.8 mL, 3 M in H_2O, 0.8 mmol) and 30% H_2O_2 (0.3 mL). Then, the resultant mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous $NaHSO_3$ solution and extracted twice with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by a flash chromatography to give compound **43** as a colorless oil, yield = 67% (44 mg). This compound known in the literature.[23] ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.16 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 4.78 (d, J = 3.2 Hz, 1H), 3.72 (s, 3H), 2.94–2.87 (m, 1H), 2.55–2.52 (m, 1H), 2.34 (d, J = 12.4 Hz, 1H), 2.18–2.11 (m, 1H), 1.86–1.52 (m, 7H), 1.32 (s, 3H), 1.27 (d, J = 6.8 Hz, 6H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 146.6, 146.5, 136.1, 128.1, 126.5, 124.2, 68.1, 52.1, 47.2, 39.8, 37.7, 37.4, 36.5, 33.5, 31.2, 24.1, 24.0, 23.8, 18.6, 16.5. IR (neat, cm^{-1}): 3411, 2953, 1724, 1455, 1383, 1250, 1179, 1123, 1071, 1048, 982, 953, 869.

6. Details for the Diverse Transformations

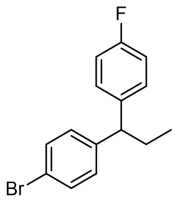


General Procedure for the benzylic functionalized products. The electrolysis was conducted using the same flow cell and electrodes described above in the procedure A. The solution containing 1-bromo-4-propylbenzene (0.06 M), TFA (4.0 equiv), 2,6-lutidine (1.5 equiv) in dry CH_2Cl_2/HFIP (19:1) was pushed using a syringe pump to pass

through the flow cell operated with a flow rate of 0.40 mL min^{-1} and a constant current of 93 mA. 4 mL of the outlet solution was collected (10 min) and concentrated under reduced pressure. Then, the crude **Int. I** was treated with different nucleophiles and acids in a certain solvent (2 mL). When the reaction was completed. The mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding products (**44-54**).

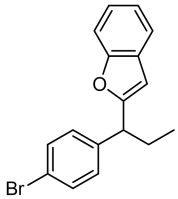


1-Bromo-4-(1-(*p*-tolyl)propyl)benzene (44). The crude **Int. I** was dissolved in toluene (2 mL), treated with concentrated H_2SO_4 (4 equiv) and then stirred at 100 °C for 4 h. After being cooled to room temperature, the mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **44** as a colorless oil, yield = 76% (53 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.14–7.16 (m, 6H), 3.76 (t, *J* = 8.0 Hz, 1H), 2.35 (s, 3H), 2.09–2.05 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 141.5, 135.7, 131.4, 129.6, 129.2, 127.6, 119.7, 52.2, 28.4, 20.9, 12.7. IR (neat, cm^{-1}): 3019, 2961, 2928, 2872, 1513, 1487, 1458, 1403, 1378, 1074, 1009, 803. ESI HRMS *m/z* $(M+Na)^+$ calcd 311.0408, obsd 311.0405

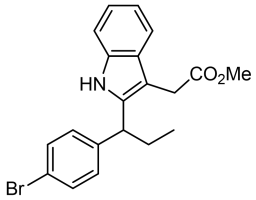


1-Bromo-4-(1-(4-fluorophenyl)propyl)benzene (45). The crude **Int. I** was treated with fluorobenzene (4 mL), HBF_4•Et_2O (4 equiv) and stirred at room temperature for 4 h. Then, the mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was obtained through layer chromatography with petroleum ether to give the corresponding compound **45** as a colorless oil, yield = 53% (37 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.18-7.15 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00-6.96 (m, 2H), 3.76 (t, *J* = 8.0 Hz, 1H), 2.07-1.99 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 243.6 Hz), 144.0, 140.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 131.5, 129.6, 129.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 119.9, 115.2 (d, $J_{C\text{-}F}$ = 21.0 Hz), 51.8, 28.5, 12.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0. IR (neat, cm^{-1}): 2963, 2927, 2873, 1603, 1507, 1487, 1222, 1157, 1009, 815. ESI HRMS *m/z* $(M+H)^+$ calcd 293.0336, obsd 293.0340.

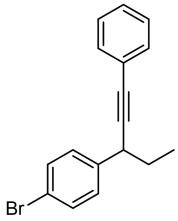


2-(1-(4-Bromophenyl)propyl)benzofuran (46). The crude **Int. I** was treated with benzofuran (5 equiv), CH_2Cl_2 (2 mL), HBF_4•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **46** as a colorless oil, yield = 55% (41 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.41 (m, 4H), 7.28–7.19 (m, 4H), 6.48 (s, 1H), 3.94 (t, *J* = 8.0 Hz, 1H), 2.31–2.24 (m, 1H), 2.03–1.96 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 154.8, 140.9, 131.6, 129.8, 128.5, 123.5, 122.5, 120.6, 120.5, 111.0, 102.5, 46.9, 27.4, 12.3. IR (neat, cm^{-1}): 2964, 2930, 2873, 1582, 1487, 1454, 1406, 1254, 1167, 1074, 1010, 955, 815, 798, 748. ESI HRMS *m/z* $(M)^+$ calcd 314.0300, obsd 314.0297.

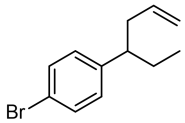


Methyl 2-(2-(1-(4-bromophenyl)propyl)-1*H*-indol-3-yl)acetate (47). The crude **Int. I** was treated with methyl 2-(1*H*-indol-3-yl)acetate (5 equiv), CH_2Cl_2 (2 mL), HBF_4•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **47** as a white solid, yield = 43% (40 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.61 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.29–7.28 (m, 1H), 7.18–7.13 (m, 4H), 4.23 (t, *J* = 8.4 Hz, 1H), 3.77 (s, 2H), 3.64 (s, 3H), 2.19–2.06 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 141.6, 137.8, 135.3, 131.7, 129.4, 128.3, 121.8, 120.4, 119.8, 110.6, 105.4, 51.9, 43.3, 30.3, 27.4, 12.4. IR (neat, cm^{-1}):

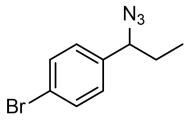
3393, 2961, 2931, 2873, 1727, 1488, 1461, 1435, 1309, 1271, 1239, 1164, 1074, 1009, 820, 743. ESI HRMS *m/z* $(M+H)^+$ calcd 386.0750, obsd 386.0750.



1-Bromo-4-(1-phenylpent-1-yn-3-yl)benzene (48). The crude **Int. I** was treated with trimethyl(phenylethynyl)silane (5 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **48** as a colorless oil, yield = 42% (30 mg). This compound known in the literature.[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 4H), 7.34–7.29 (m, 5H), 3.79 (t, *J* = 7.2 Hz, 1H), 1.90–1.85 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 131.6, 131.5, 129.3, 128.2, 127.9, 123.5, 120.4, 90.7, 83.7, 39.4, 31.5, 11.7.

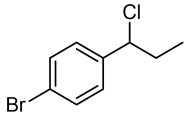


1-Bromo-4-(hex-5-en-3-yl)benzene (49). The crude **Int. I** was treated with allyltrimethylsilane (5 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **49** as a colorless oil, yield = 64% (37 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.65 (dd, J_1 = 17.2 Hz, J_2 = 7.6 Hz, 1H), 4.99–4.93 (m, 2H), 2.50–2.32 (m, 3H), 1.74–1.54 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 136.7, 131.3, 129.5, 119.5, 116.0, 47.1, 40.7, 28.7, 11.9. IR (neat, cm^{-1}): 3077, 2962, 2926, 2873, 1640, 1488, 1462, 1406, 1379, 1074, 1009, 994, 913, 824. ESI HRMS *m/z* $(M+Na)^+$ calcd 261.0249, obsd 261.0258.

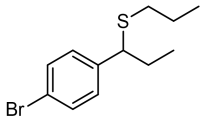


1-(1-Azidopropyl)-4-bromobenzene (50). The crude **Int. I** was treated with

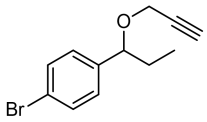
azidotrimethylsilane (5 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure.[26] The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **50** as a colorless oil, yield = 67% (38 mg). This compound known in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.20–7.18 (m, 2H), 4.34 (t, *J* = 7.2 Hz, 1H), 1.90–1.74 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 131.8, 128.6, 122.0, 67.1, 29.3, 10.5.



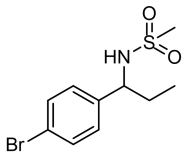
1-Bromo-4-(1-chloropropyl)benzene (51). The crude **Int. I** was treated with HCl (20 equiv), HFIP (2 mL) and then stirred at room temperature for 3 h. The mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **51** as a colorless oil, yield = 61% (34 mg). This compound known in the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.75 (t, *J* = 7.2 Hz, 1H), 2.13–2.05 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 131.7, 128.7, 122.0, 64.4, 33.1, 11.5.



(1-(4-Bromophenyl)propyl)(propyl)sulfane (52). The crude **Int. I** was treated with propane-1-thiol (20 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 1 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **52** as a colorless oil, yield = 83% (54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.67–3.64 (m, 1H), 2.32–2.20 (m, 2H), 1.95–1.77 (m, 2H), 1.56–1.49 (m, 2H), 0.95–0.90 (m, 6H) . ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 131.4, 129.6, 120.5, 50.9, 33.0, 29.7, 22.6, 13.5, 12.3. IR (neat, cm^{-1}): 2962, 2930, 2872, 1588, 1487, 1460, 1403, 1377, 1290, 1240, 1201, 1073, 1010, 816. ESI HRMS *m/z* $(M+H)^+$ calcd 273.0307, obsd 273.0311.



1-Bromo-4-(1-(prop-2-yn-1-yloxy)propyl)benzene (53). The crude **Int. I** was treated with prop-2-yn-1-ol (20 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was obtained through layer chromatography silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **53** as a colorless oil, yield = 50% (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 4.38 (t, J = 6.8 Hz, 1H), 4.13 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 3.88 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 2.43 (d, J = 2.0 Hz, 1H), 1.89–1.84 (m, 1H), 1.73–1.67 (m, 1H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 131.6, 128.7, 121.6, 81.7, 79.8, 74.1, 55.7, 30.6, 10.0. IR (neat, cm^{-1}): 3310, 2922, 2850, 2215, 1634, 1470, 1385, 1072, 1011, 817, 637. ESI HRMS *m/z* $(M+Na)^+$ calcd 275.0042, obsd 275.0039.

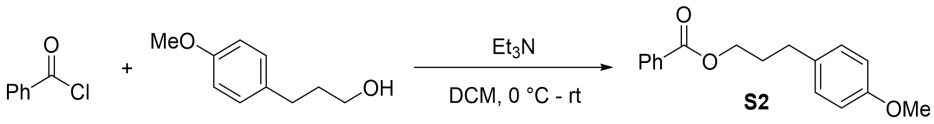


***N*-(1-(4-Bromophenyl)propyl)methanesulfonamide (54).** The crude **Int. I** was treated with methanesulfonamide (10 equiv), CH_2Cl_2 (2 mL), BF_3•Et_2O (4 equiv) and then stirred at room temperature for 6 h. The mixture was diluted with H_2O and extracted twice with CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the corresponding compound **54** as a colorless oil, yield = 72% (50 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.2 Hz, 2H), 5.48 (d, J = 16.4 Hz, 1H), 4.36–4.30 (m, 1H), 2.63 (s, 3H), 1.89–1.72 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 132.0, 128.5, 121.7, 59.2, 41.9, 30.6, 10.6. IR (neat, cm^{-1}): 3280, 2968, 2933, 2876, 1488, 1410, 1313, 1154, 1050, 1009, 976, 838, 821, 756. ESI HRMS *m/z* $(M+Na)^+$ calcd 313.9821, obsd 313.9827.

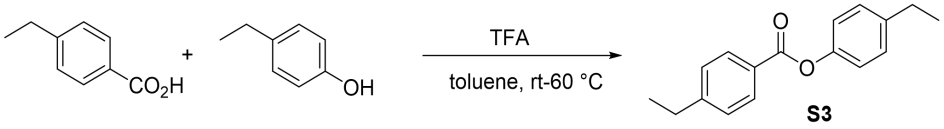
7. Synthesis and Characterization of New Substrates

S1

2-(4-Methoxyphenyl)propyl (*tert*-butoxycarbonyl)-*L*-valinate (S1). To an oven-dried round bottom flask was added (*tert*-butoxycarbonyl)-*L*-valine (0.61 g, 2.8 mmol), 3-(4-methoxyphenyl)propan-1-ol (0.42 g, 2.5 mmol), DMAP (0.03 g, 0.25 mmol) and CH_2Cl_2 (15 mL). Then, EDCI (0.58 g, 3 mmol) was added to the flask slowly at 0 °C. The resultant mixture was warmed to room temperature and stirred until complete consumption of 3-(4-methoxyphenyl)propan-1-ol. Next, the mixture was diluted with saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **S1** (0.78 g, 86% yield) as a colorless oil.[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.07 (d, *J* = 8.0 Hz, 1H), 4.25–4.13 (m, 3H), 3.80 (d, *J* = 0.8 Hz, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.18–1.92 (m, 3H), 1.00 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 157.9, 155.7, 133.0, 129.3, 113.9, 79.7, 64.4, 58.6, 55.2, 31.3, 31.1, 30.4, 26.3, 19.0, 17.6.

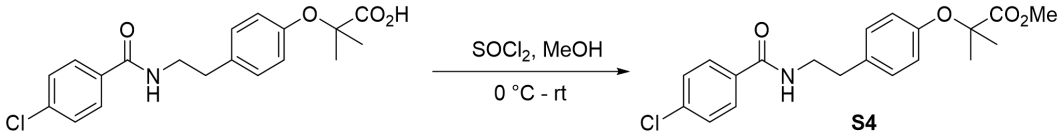


3-(4-Methoxyphenyl)propyl benzoate (S2). To an oven-dried round bottom flask was added 3-(4-methoxyphenyl)propan-1-ol (0.66 g, 4 mmol), Et_3N (1.0 mL, 7.2 mmol) and CH_2Cl_2 (12 mL). Then, benzoyl chloride (0.67 g, 4.8 mmol) was added to the flask slowly at 0 °C. The resultant mixture was warmed to room temperature and stirred until complete consumption of 3-(4-methoxyphenyl)propan-1-ol. Next, the mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic phase was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **S2** (0.98 g, 91% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.63-7.58 (m, 1H), 7.52-7.47 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.39 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.16–2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 158.0, 133.2, 132.9, 130.4, 129.6, 129.4, 128.4, 113.9, 64.3, 55.2, 31.4, 30.5. ESI HRMS *m/z* $(M+H)^+$ calcd 271.1329, obsd 271.1325.

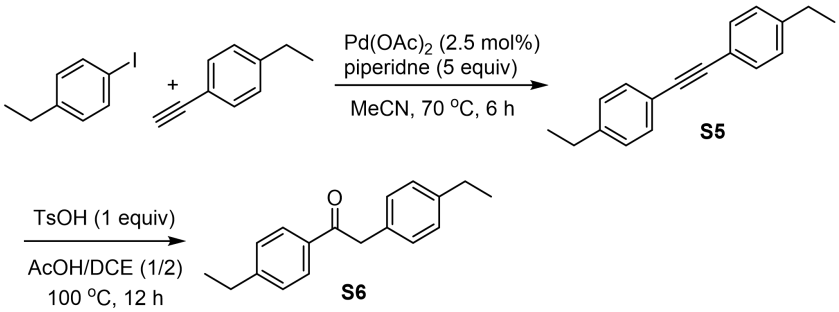


4-Ethylbenzyl benzoate (S3). To a round bottom flask was added 4-ethylbenzoic acid (0.83 mL, 5.5 mmol), 4-ethylphenol (0.61 mg, 5 mmol), TFA (1.53 mL, 11 mmol) and toluene (10 mL) at room temperature. The resultant mixture was warmed to 60 °C and

stirred until complete consumption of 4-ethylphenol. After being cooled to room temperature, the mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic phase was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **S3** (1.1 g, 87% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.18 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.20–7.17 (m, 2H), 2.83–2.71 (m, 4H), 1.37–1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 150.5, 148.9, 141.7, 130.3, 128.8, 128.1, 127.1, 121.5, 29.1, 28.3, 15.6, 15.3. ESI HRMS *m/z* $(M+H)^+$ calcd 255.1380, obsd 255.1386.



Methyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (S4). To an oven-dried round bottom flask was added 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoic acid (1.8 g, 5 mmol) and MeOH (30 mL). Then, $SOCl_2$ (0.5 mL, 7.5 mmol) was added to the flask slowly at 0 °C. The resultant mixture was warmed to room temperature and stirred until complete consumption of 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoic acid. Next, the mixture was diluted with aqueous saturated $NaHCO_3$ solution and extracted with EtOAc. The organic phase was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **S4** (1.7 g, 90% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.21 (br s, 1H), 3.79 (s, 3H), 3.68 (q, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 1.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 166.4, 154.0, 137.6, 133.0, 132.5, 129.5, 128.8, 128.3, 119.6, 79.2, 52.5, 41.2, 34.7, 25.3.ESI HRMS *m/z* $(M+Na)^+$ calcd 398.1130, obsd 398.1134.



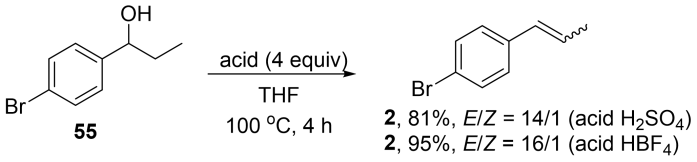
1,2-Bis(4-ethylphenyl)ethyne (S5). To a sealed tube was added 1-ethyl-4-iodobenzene (928 mg, 4 mmol). Then, 1-ethyl-4-ethynylbenzene (560 μL, 4 mmol), $Pd(OAc)_2$ (23 mg, 0.1 mmol), piperidine (2 mL), and MeCN (4 mL) were added to the tube at room

temperature. The resultant mixture was warmed to 70 °C and stirred for 6 h. After being cooled to room temperature, the reaction was quenched with 1.8 M HCl solution and extracted twice with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by a flash chromatography to give 1,2-bis(4-ethylphenyl)ethyne as a white solid, yield = 51% (477 mg).[29] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 2.71 (q, *J* = 7.6 Hz, 4H), 1.29 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 131.5, 127.9, 120.7, 88.9, 28.8, 15.4.

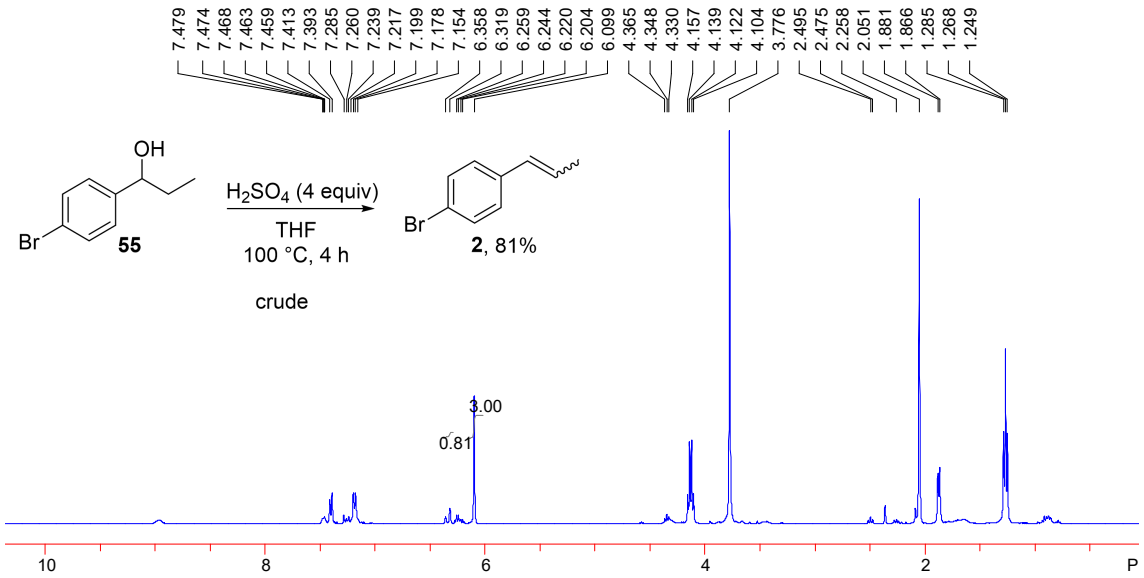
1,2-Bis(4-ethylphenyl)ethan-1-one (S6). To a sealed tube was added 1,2-bis(4-ethylphenyl)ethyne (302 mg, 1.3 mmol). Then, TsOH•H_2O (247 mg, 1.3 mmol), AcOH (650 μL), and DCE (1.3 mL) were added to the tube at room temperature. The resultant mixture was warmed to 100 °C and stirred for 12 h. After being cooled to room temperature, the reaction was quenched with saturated $NaHCO_3$ solution and extracted twice with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by a flash chromatography to give 1,2-bis(4-ethylphenyl)ethan-1-one as a yellow solid, yield = 75% (246 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.74 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H), 2.75-2.62 (m, 4H), 1.29-1.22 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 150.0, 142.7, 134.4, 131.9, 129.3, 128.9, 128.18, 128.13, 45.0, 28.9, 28.4, 15.4, 15.1. ESI HRMS *m/z* $(M+Na)^+$ calcd 275.1406, obsd 275.1401.

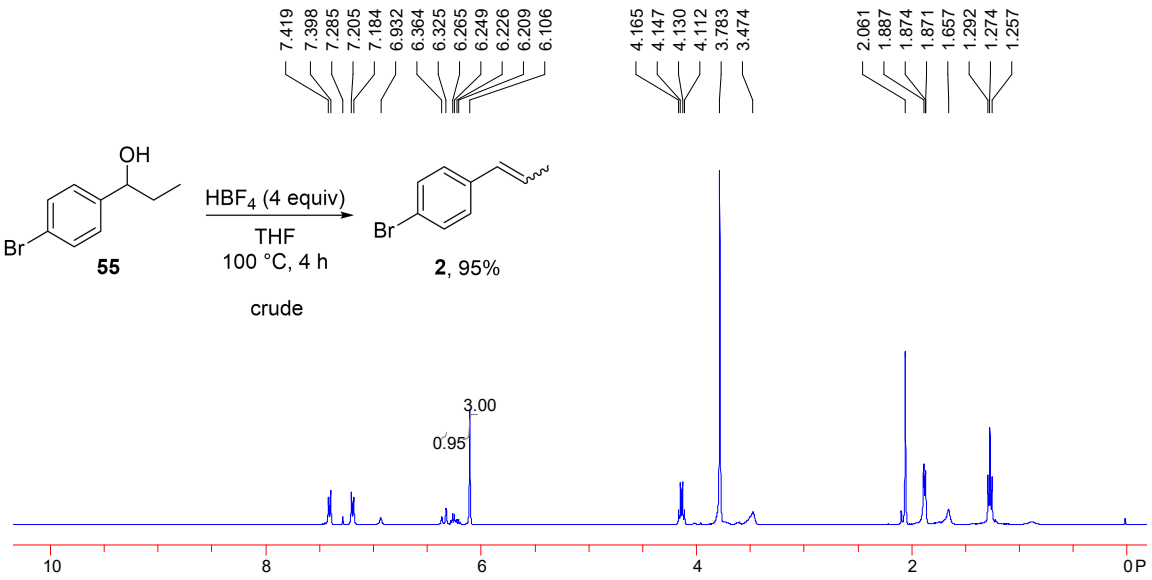
8. Mechanistic Studies

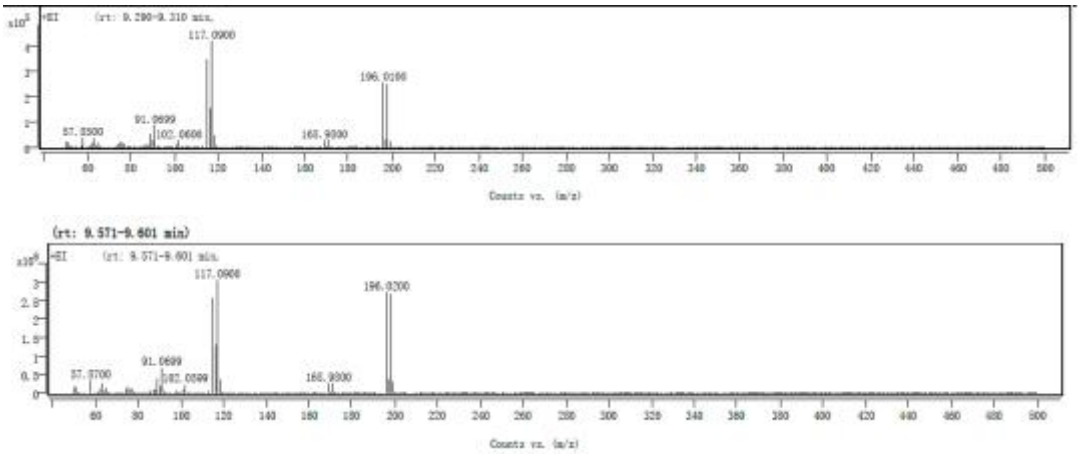
8.1 Dehydration of benzyl alcohol

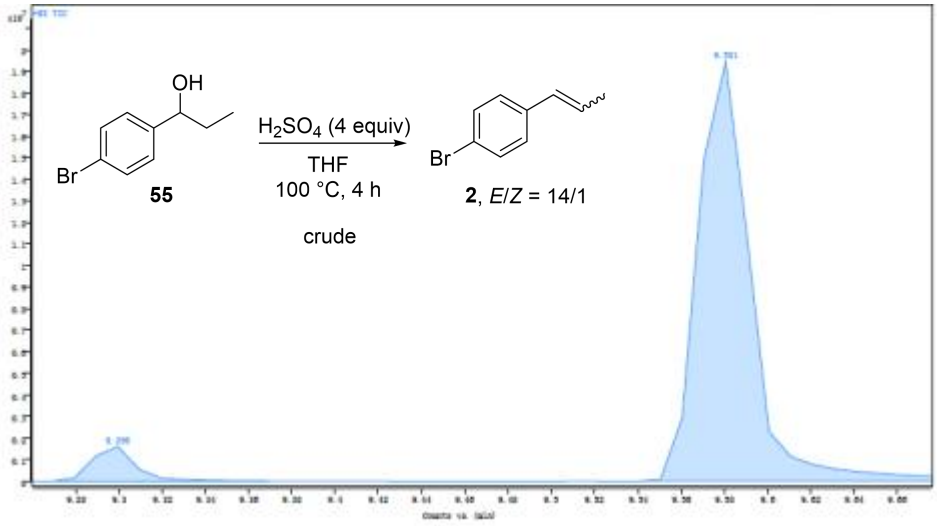


To an oven-dried round bottom flask was added 1-(4-bromophenyl)propan-1-ol **55** (22 mg, 0.1 mmol), acid (0.4 mmol) and THF (0.5 mL). The reaction mixture was warmed to 100 °C and stirred for 4 h. After being cooled to room temperature, the resulting mixture was concentrated under reduced pressure and analyzed by ^{1}H NMR in $CDCl_3$. Yield of **2** was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene (0.1 mmol) as the internal standard. The ratio of *E*/*Z* of **2** was determined by GC analysis (Figure S3).


7.479
7.474
7.468
7.463
7.459
7.413
7.393
7.285
7.260
7.239
7.217
7.199
7.178
7.154
6.358
6.319
6.259
6.244
6.220
6.204
6.099
4.365
4.348
4.330
4.157
4.139
4.122
4.104
3.776
2.495
2.475
2.258
2.051
1.881
1.866
1.285
1.268
1.249
OH
Br
55
H2SO4 (4 equiv)
THF
100 °C, 4 h
crude
Br
2, 81%
3.00
0.81
10
8
6
4
2
P


7.419
7.398
7.285
7.205
7.184
6.932
6.364
6.325
6.265
6.249
6.226
6.209
6.106
4.165
4.147
4.130
4.112
3.783
3.474
2.061
1.887
1.874
1.871
1.657
1.292
1.274
1.257
OH
Br
55
HBF4 (4 equiv)
THF
100 °C, 4 h
crude
Br
2, 95%
3.00
0.95
10
8
6
4
2
0P


117.0900
196.0100
91.0699
57.0300
168.9300
(rt: 9.571-9.601 min)
117.0900
196.0200
91.0699
57.0700
168.9300



RT	Areas	Areas%
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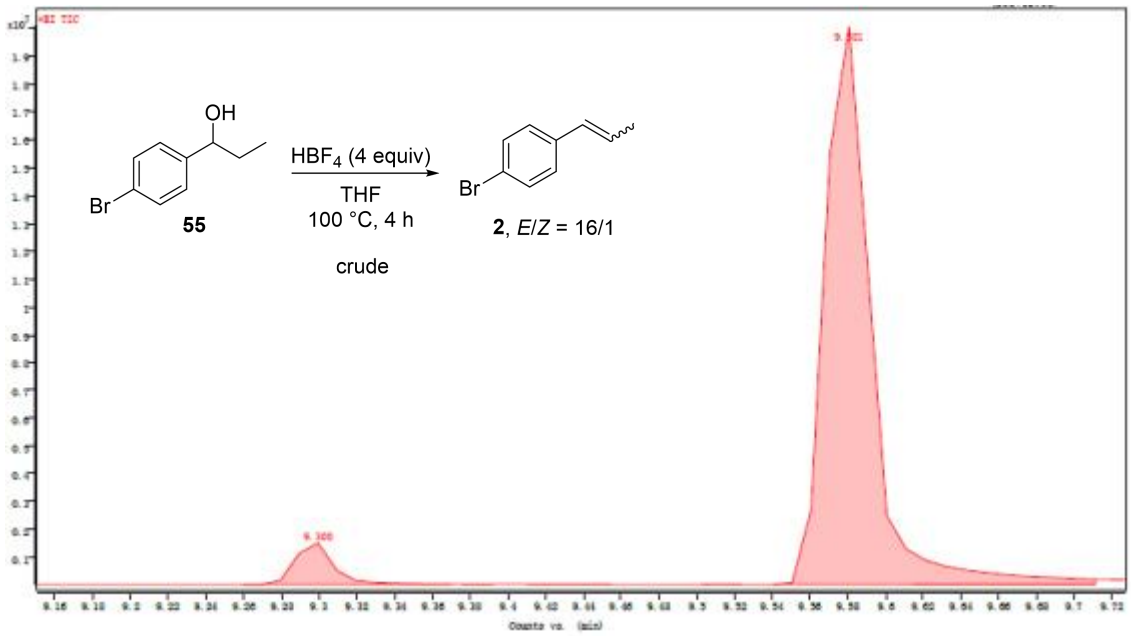
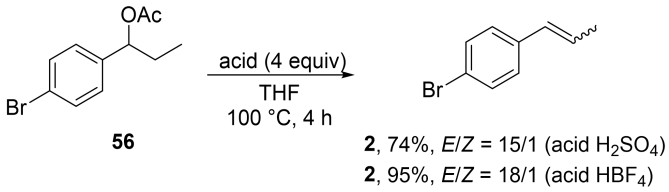
9.299	2322319	1



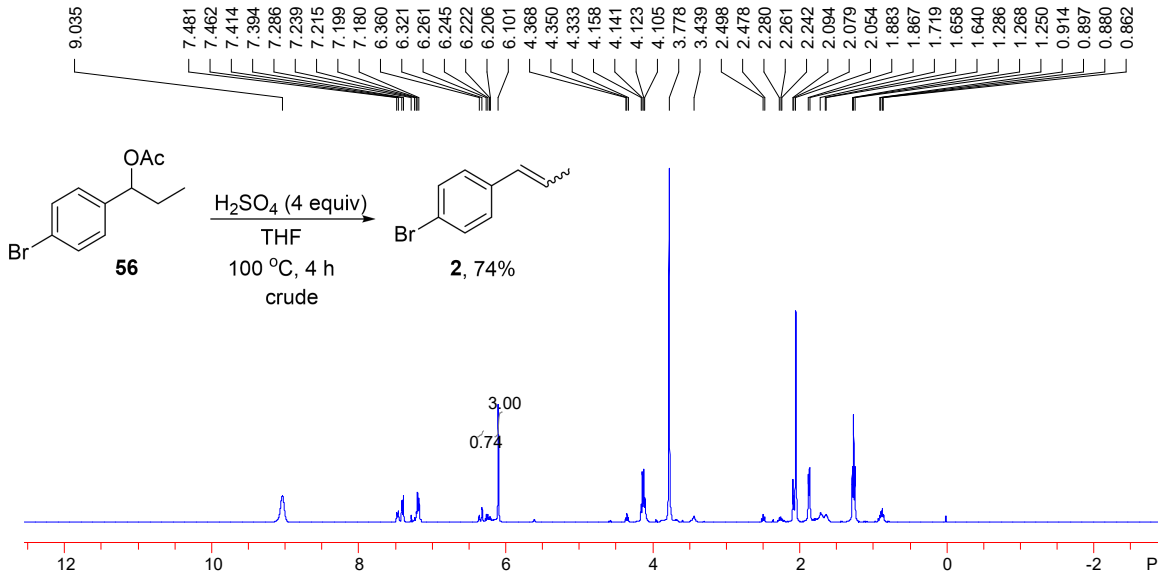
RT	Areas	Areas%
9.581	34514349	16
9.300	2164717	1

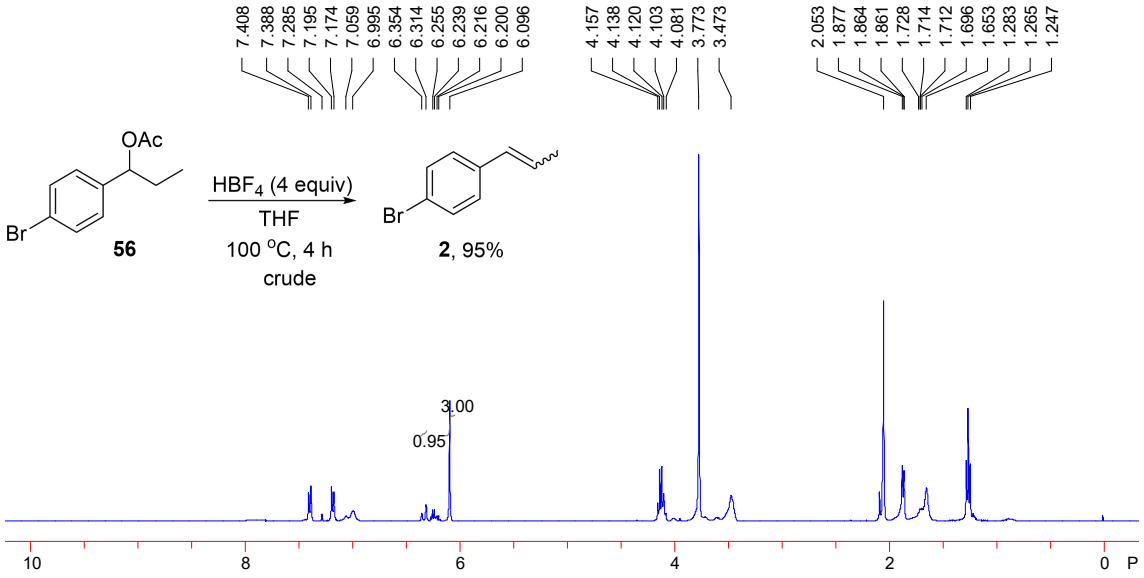
Figure S3. The crude ^{1}H NMR and GC spectra of the above reactions of **55**.

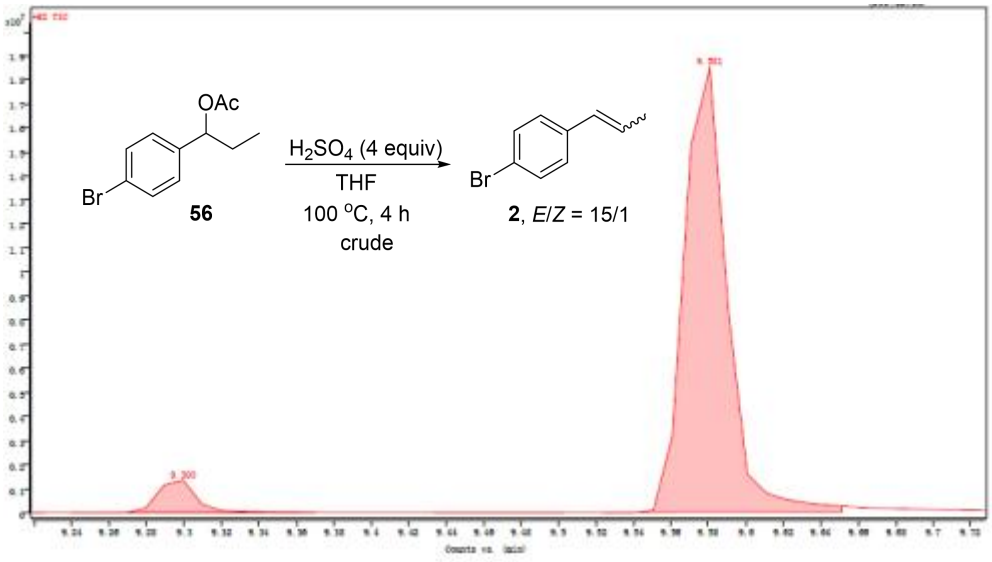
8.2 Elimination of acetate



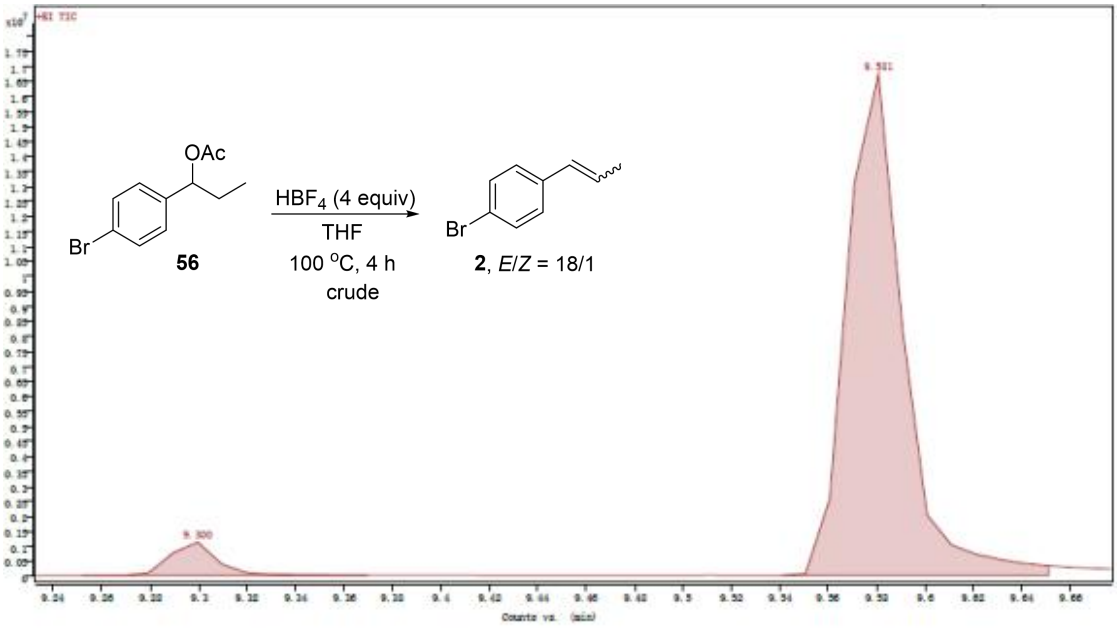
To an oven-dried round bottom flask was added 1-(4-bromophenyl)propyl acetate **56** (26 mg, 0.1 mmol), acid (0.4 mmol) and THF (0.5 mL) at room temperature. The resultant mixture was warmed to 100 °C and stirred for 4 h. After being cooled to room temperature, the resulting mixture was concentrated under reduced pressure and analyzed by ^{1}H NMR in $CDCl_3$. Yield of **2** was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene (0.1 mmol) as the internal standard. The ratio of *E*/*Z* of **2** was determined by GC analysis (Figure S4).







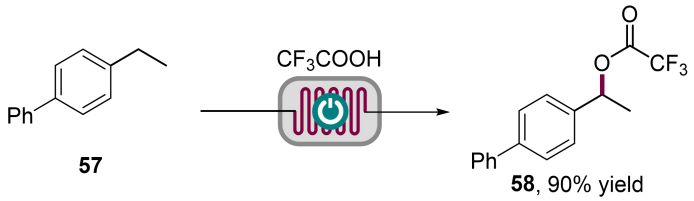
RT	Areas	Areas%
9.581	29470497	15
9.300	1963967	1



RT	Areas	Areas%
9.581	27346906	18
9.300	1559689	1

Figure S4. The crude ^{1}H NMR and GC spectra of the above reactions of **56**.

8.3 Probing trifluoroacetic ester as intermediate



The procedure is the same as the **General Procedure A** but without subsequent reaction with HBF_4. 6 mL of the outlet solution was collected and concentrated under reduced pressure. The residue was diluted with H_2O and extracted with CH_2Cl_2. The organic phase was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **58** (95 mg, 90% yield) as a white solid (Figure S5).

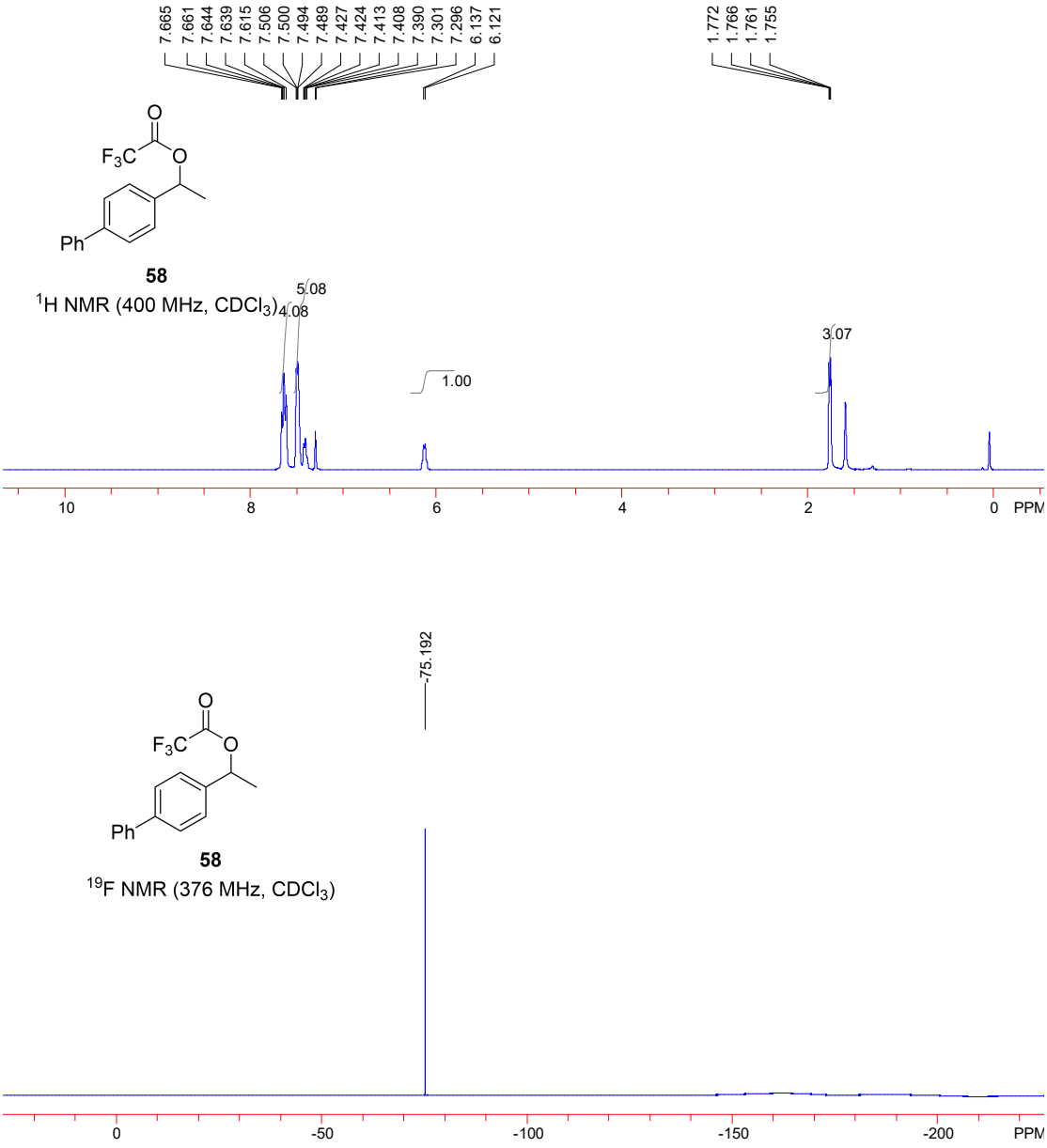
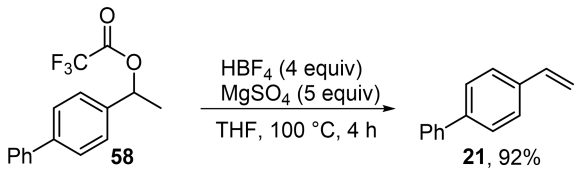


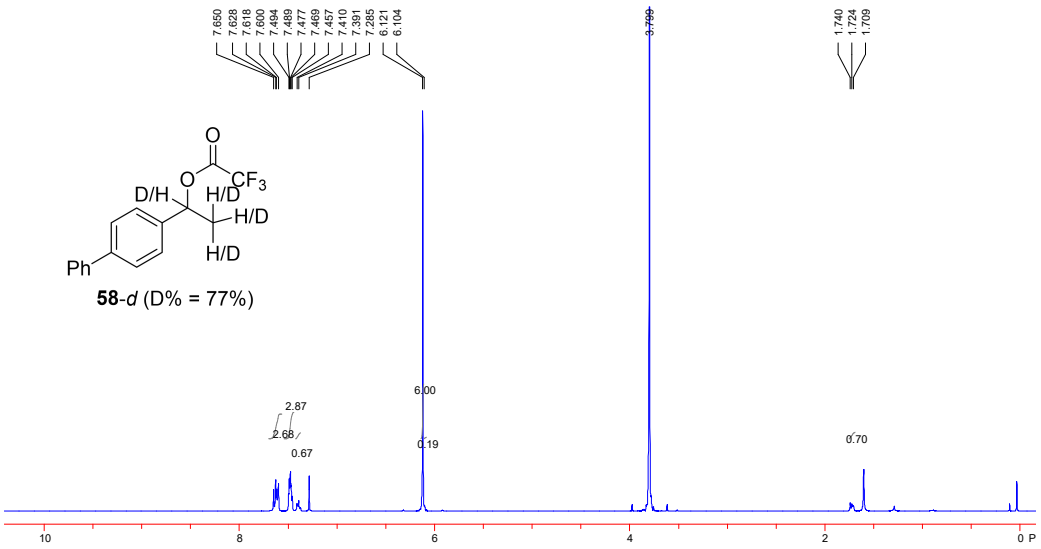
Figure S5. The ^{1}H NMR and ^{19}F NMR spectra of **58**.



To a sealed tube was added 1-([1,1'-biphenyl]-4-yl)ethyl 2,2,2-trifluoroacetate **58** (29 mg, 0.12 mmol), HBF_4 (130 μL, 0.48 mmol, 50% w/w), $MgSO_4$ (72 mg, 0.6 mmol) and THF (2 mL) at room temperature. The mixture was warmed to 100 °C and stirred for 4 h. After being cooled to room temperature, the reaction mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give **21** (20 mg, yield = 92%).

8.4 Kinetic isotope effect experiments

To a sealed tube was added 1-([1,1'-biphenyl]-4-yl)ethyl 2,2,2-trifluoroacetate **58** (24 mg, 0.082 mmol), **58**-*d* (48 mg, 0.158 mmol, D%, 77%), HBF_4•Et_2O (260 μL, 0.96 mmol, 50%), $MgSO_4$ (144 mg, 1.2 mmol) and THF (4 mL) at room temperature. The mixture was warmed to 100 °C and stirred for 15 min. After being cooled to room temperature, the reaction mixture was diluted with H_2O and extracted twice with EtOAc. The combined organic phase was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give **21**/**21**-*d* (8 mg, yield = 19%). Product **21**/**21**-*d* was analyzed by ^1H NMR in $CDCl_3$. A kinetic isotope effect (KIE = 1.5) was obtained (Figure S6).



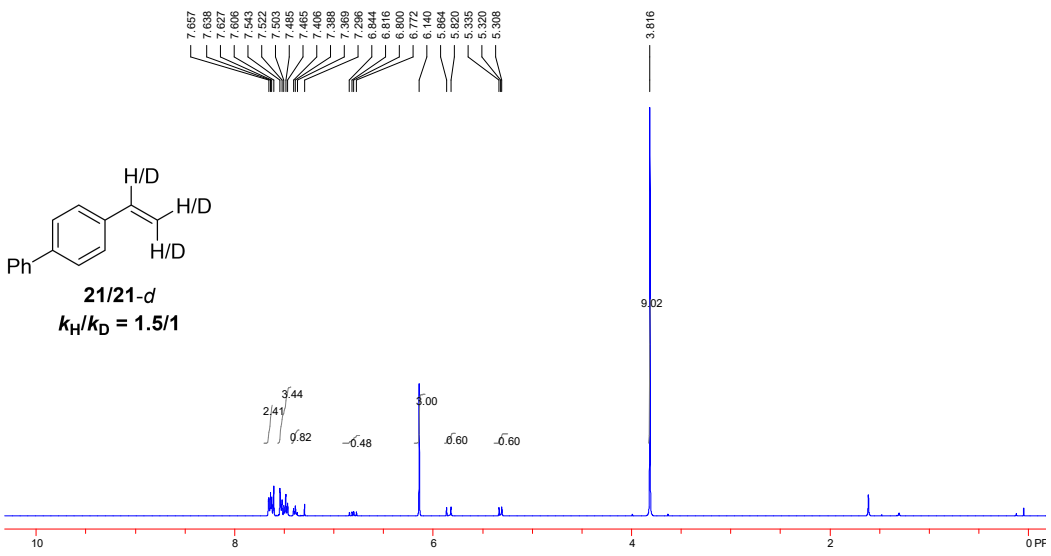
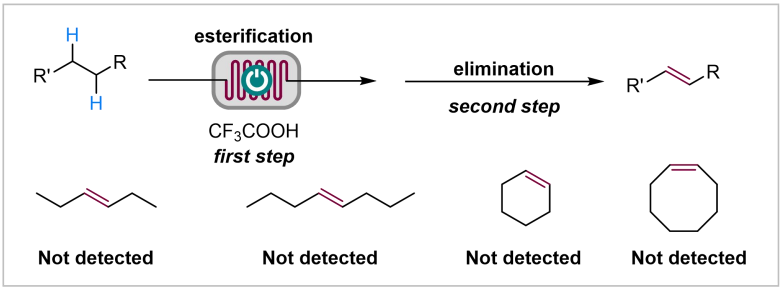
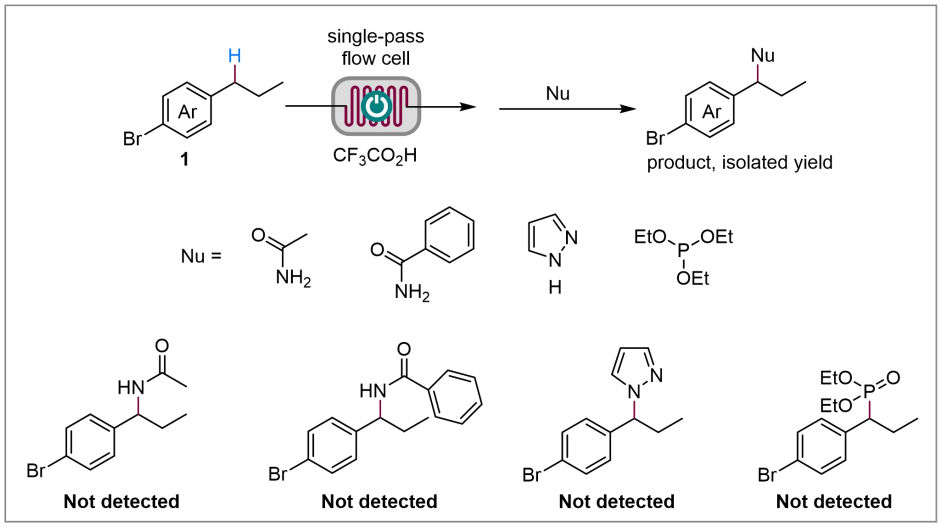


Figure S6. The ^{1}H NMR spectra of **58**-*d* and **21/21**-*d*.

9. Limitations





10. References

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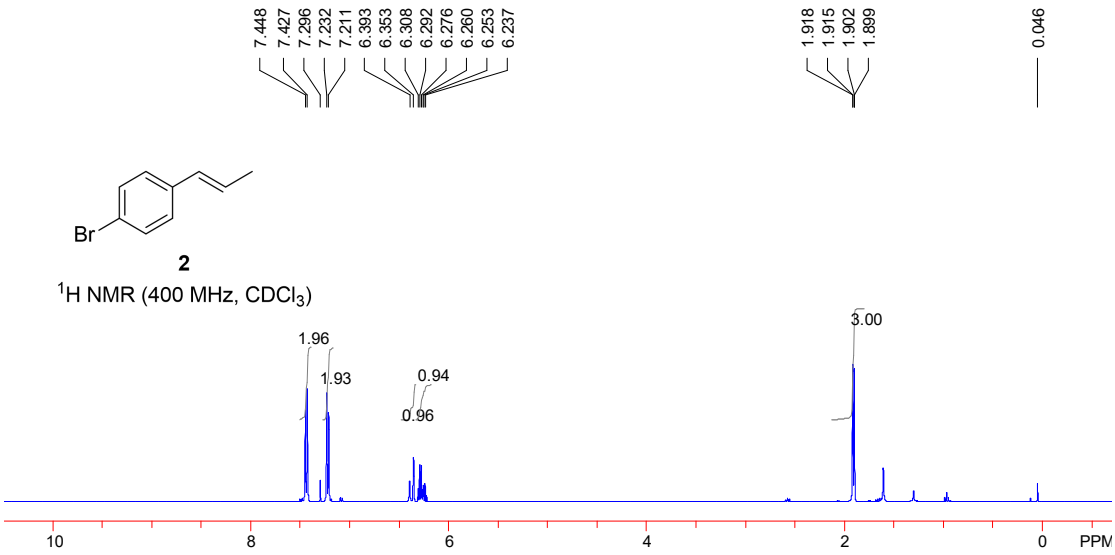
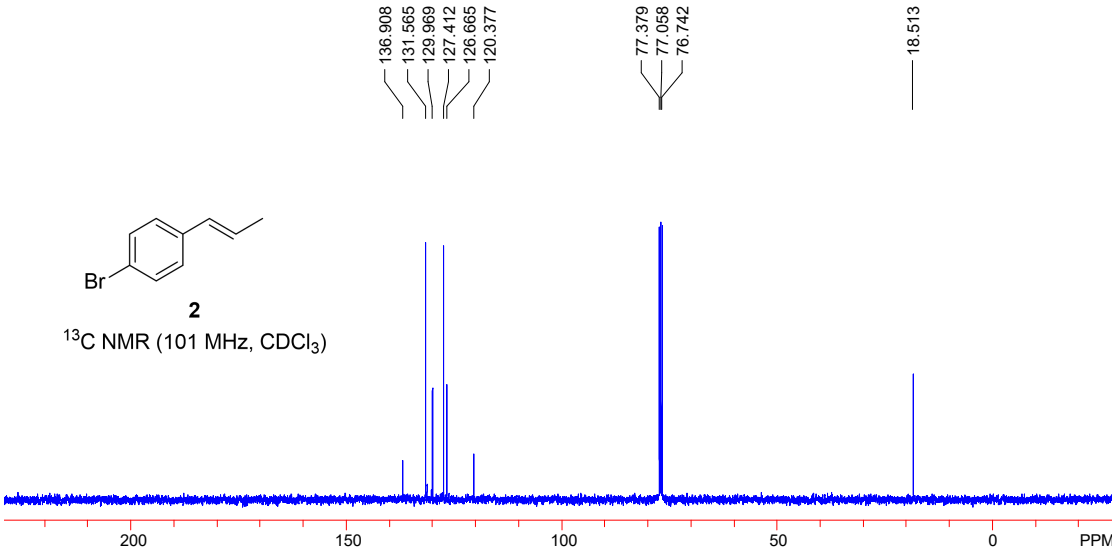
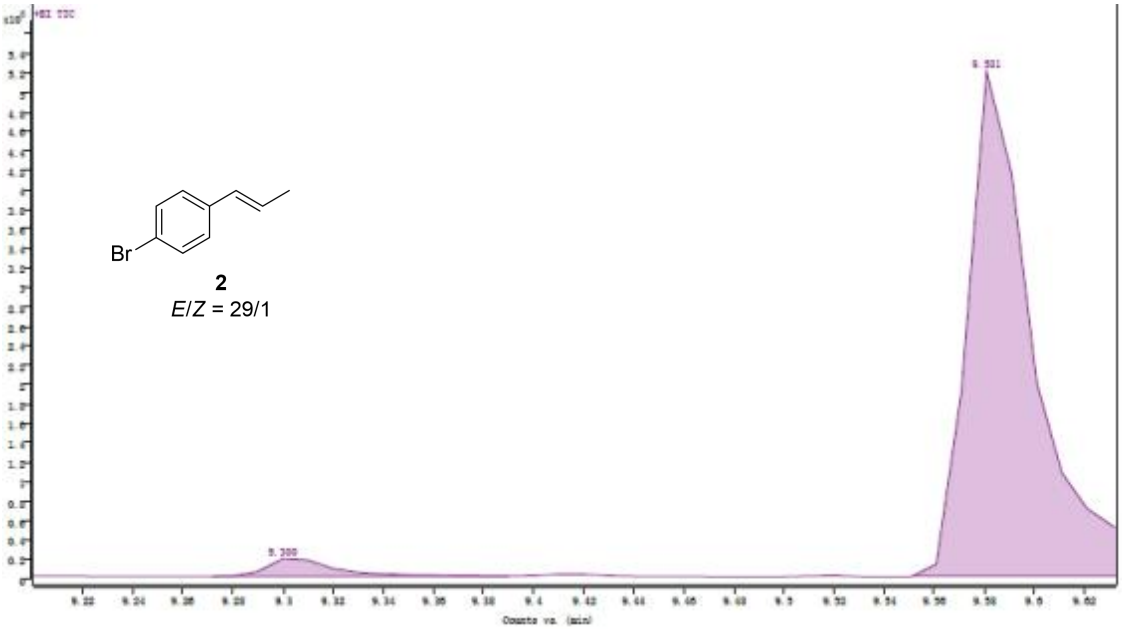
11. NMR and GC Spectra







RT	Areas	Areas%
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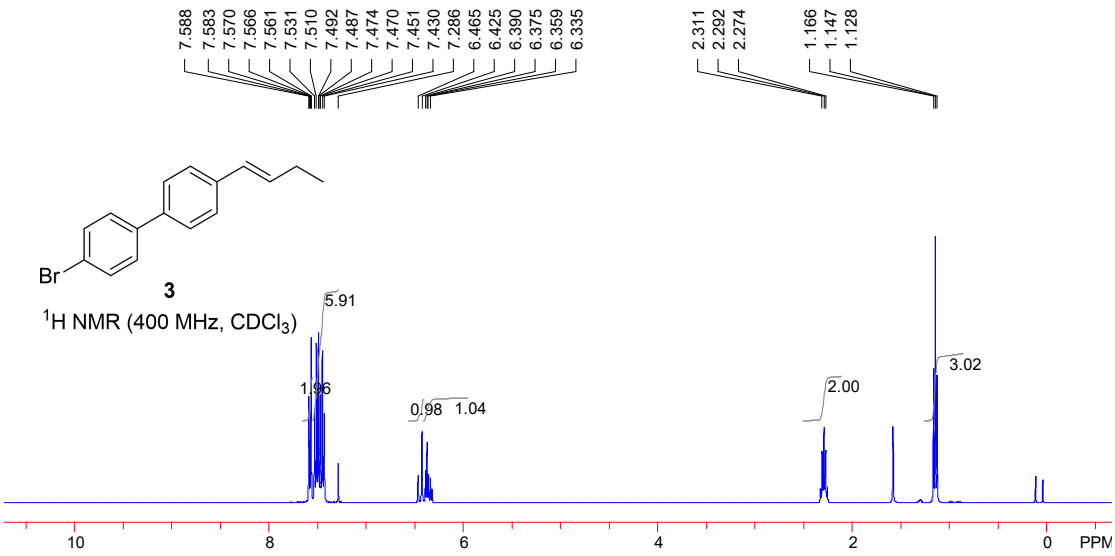
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7.561
7.531
7.510
7.492
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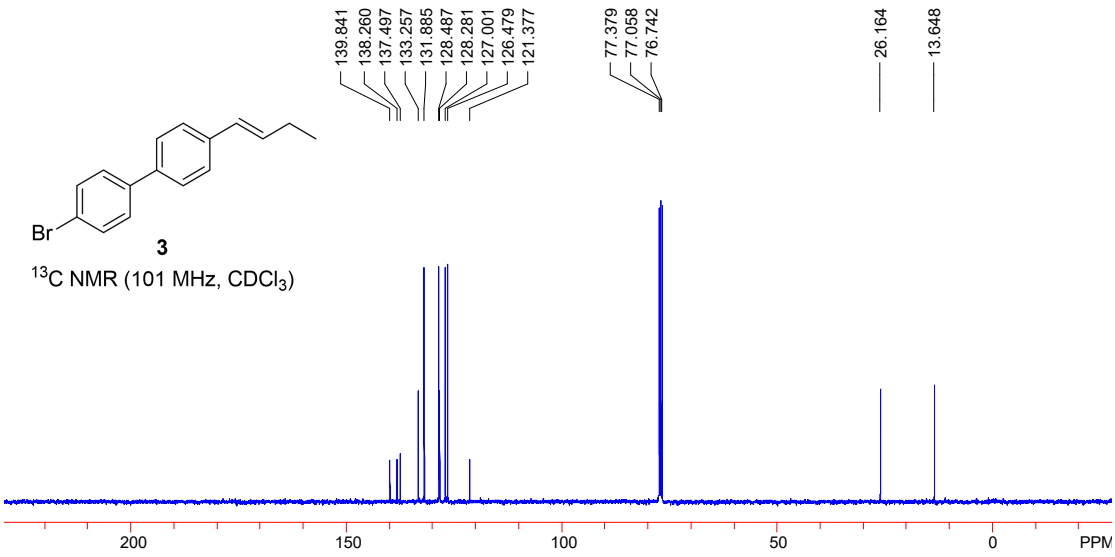
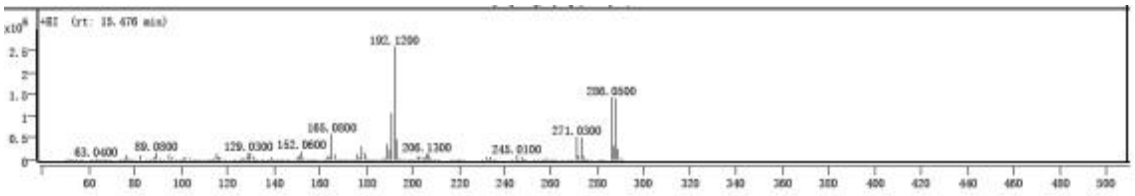
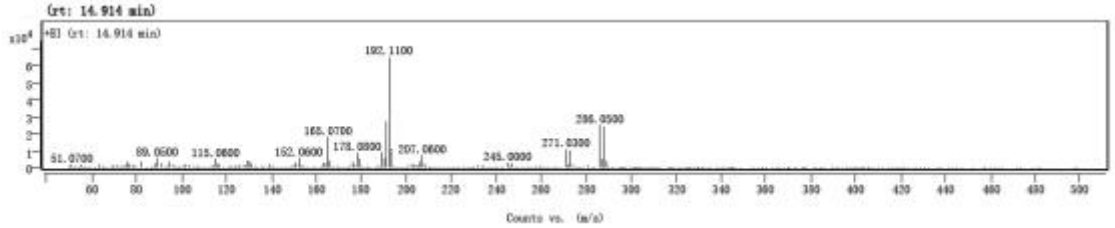
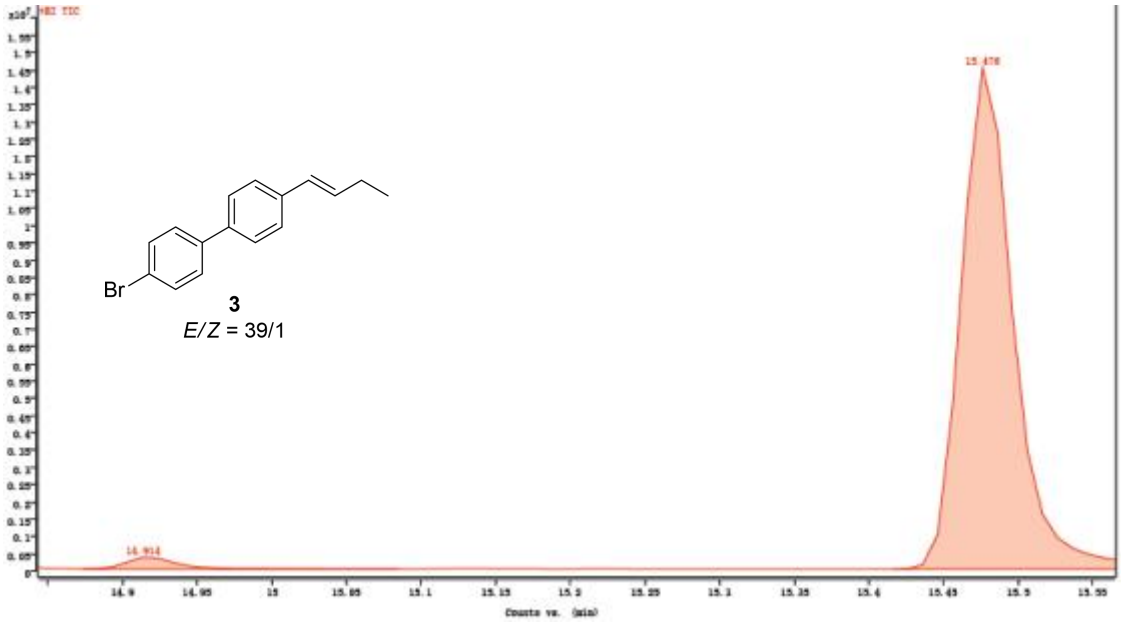
7.430
7.286
6.465
6.425
6.390
6.375
6.359
6.335
2.311
2.292
2.274
1.166
1.147
1.128
Br
3
1H NMR (400 MHz, CDCl3)
5.91
1.96
0.98
1.04
2.00
3.02
10
8
6
4
2
0
PPM

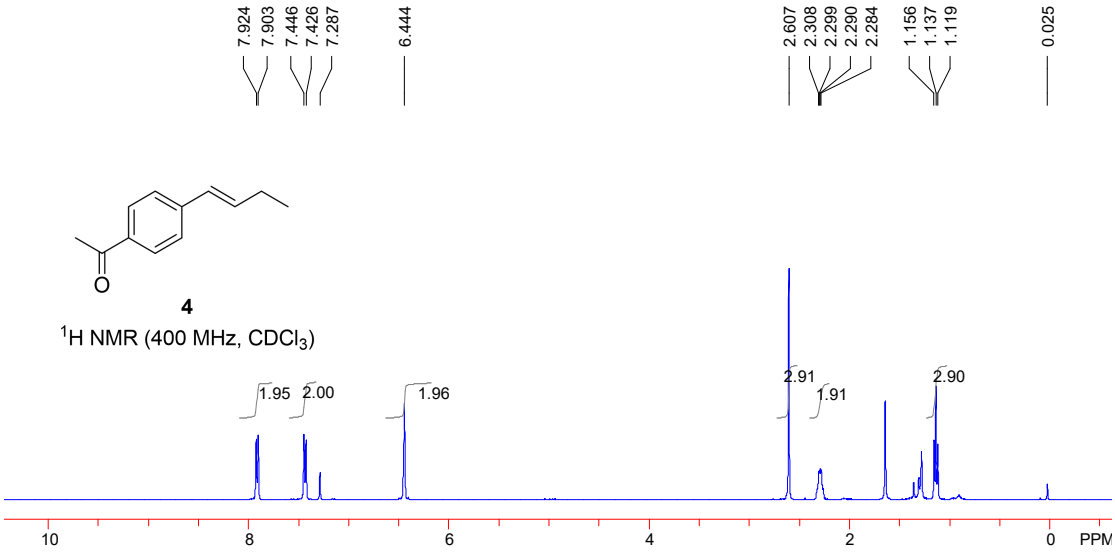

139.841
138.260
137.497
133.257
131.885
128.487
128.281
127.001
126.479
121.377
77.379
77.058
76.742
26.164
13.648
Br
3
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

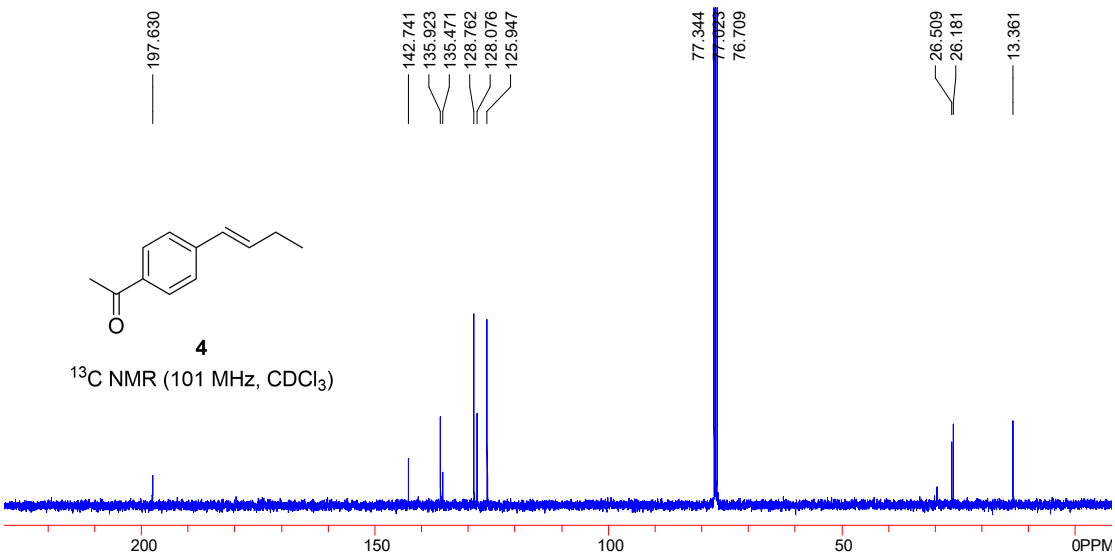


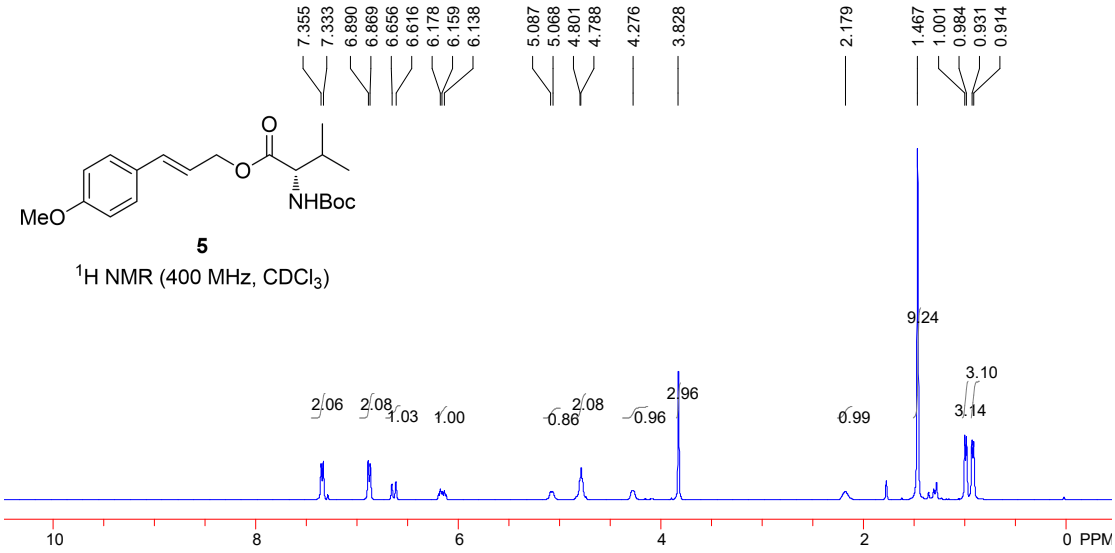


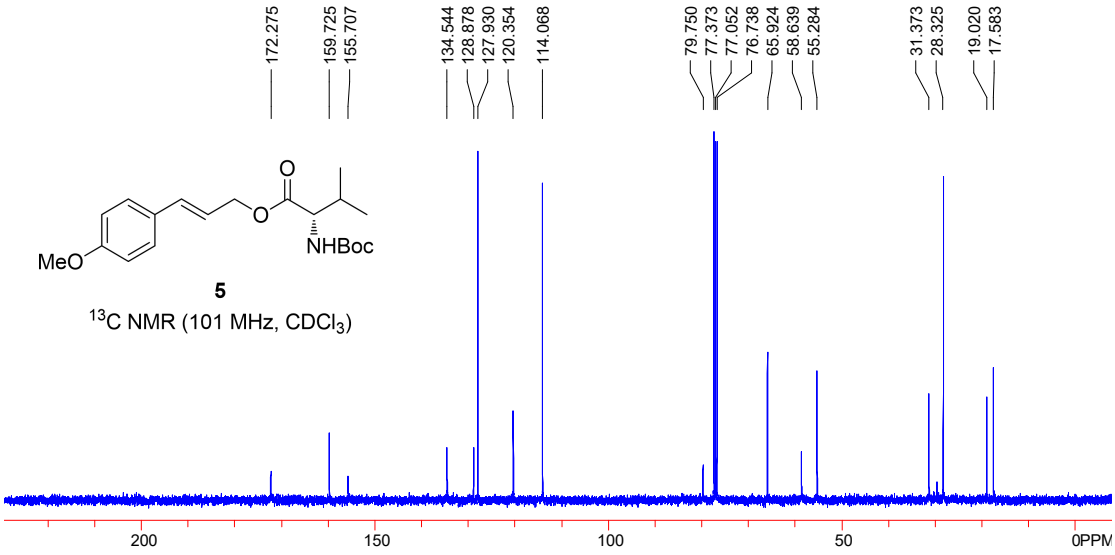


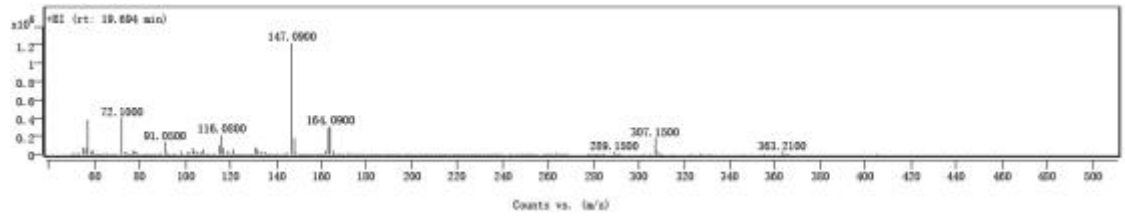
RT	Areas	Areas%
15.476	35977155	39
14.914	929562	1

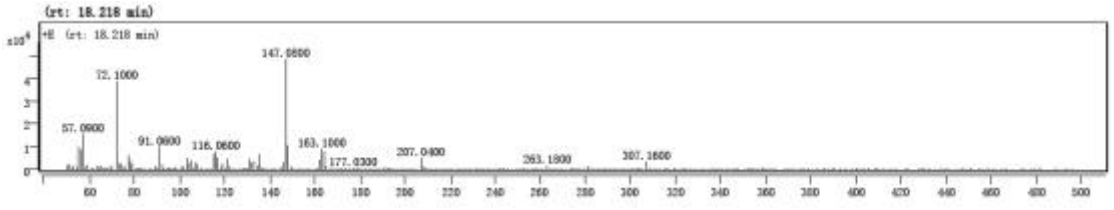

7.924
7.903
7.446
7.426
7.287
6.444
2.607
2.308
2.299
2.290
2.284
1.156
1.137
1.119
0.025
O
4
1H NMR (400 MHz, CDCl3)
1.95
2.00
1.96
2.91
1.91
2.90
10
8
6
4
2
0
PPM

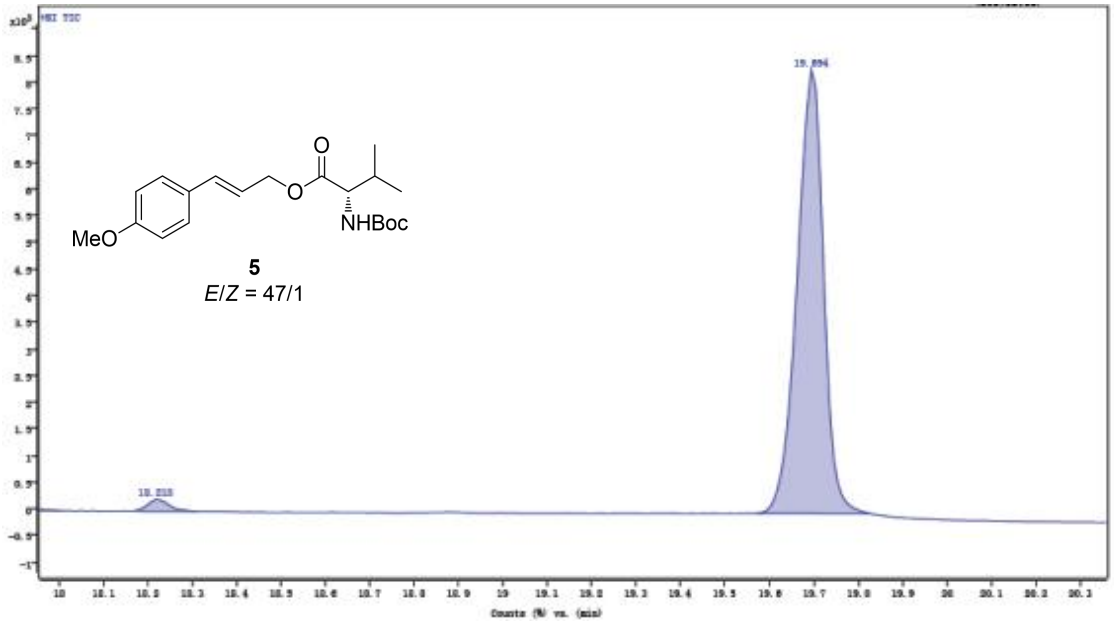

197.630
142.741
135.923
135.471
128.762
128.076
125.947
77.344
77.023
76.709
26.509
26.181
13.361
O
4
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


7.355
7.333
6.890
6.869
6.656
6.616
6.178
6.159
6.138
5.087
5.068
4.801
4.788
4.276
3.828
2.179
1.467
1.001
0.984
0.931
0.914
MeO
O
O
NHBoc
5
1H NMR (400 MHz, CDCl3)
9.24
3.10
3.14
2.96
2.06
2.08
1.03
1.00
2.08
0.86
0.96
0.99
10
8
6
4
2
0 PPM


172.275
159.725
155.707
134.544
128.878
127.930
120.354
114.068
79.750
77.373
77.052
76.738
65.924
58.639
55.284
31.373
28.325
19.020
17.583
MeO
O
O
NHBoc
5
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM



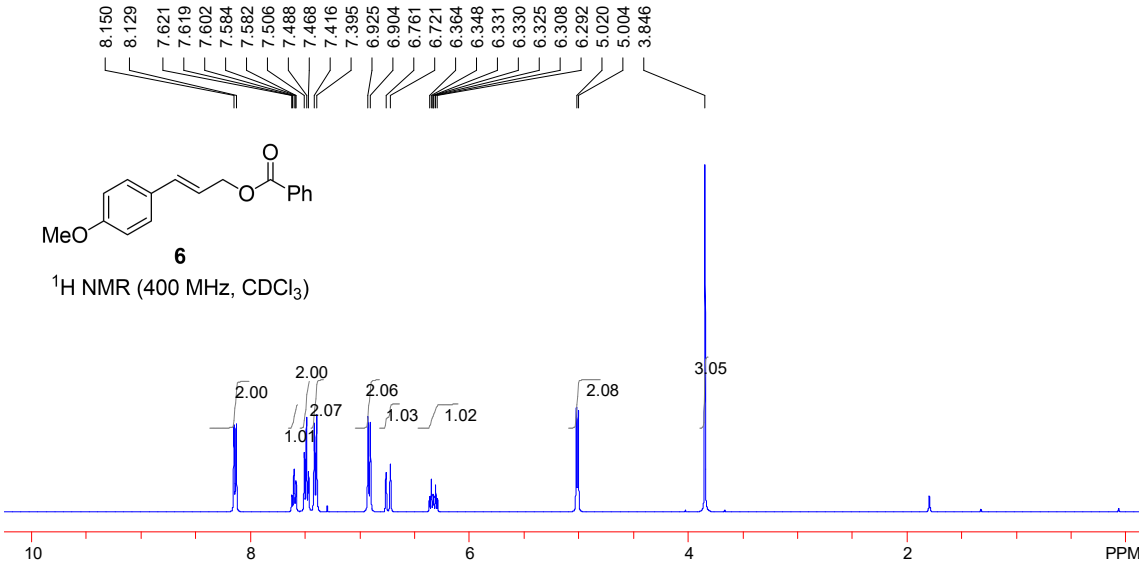


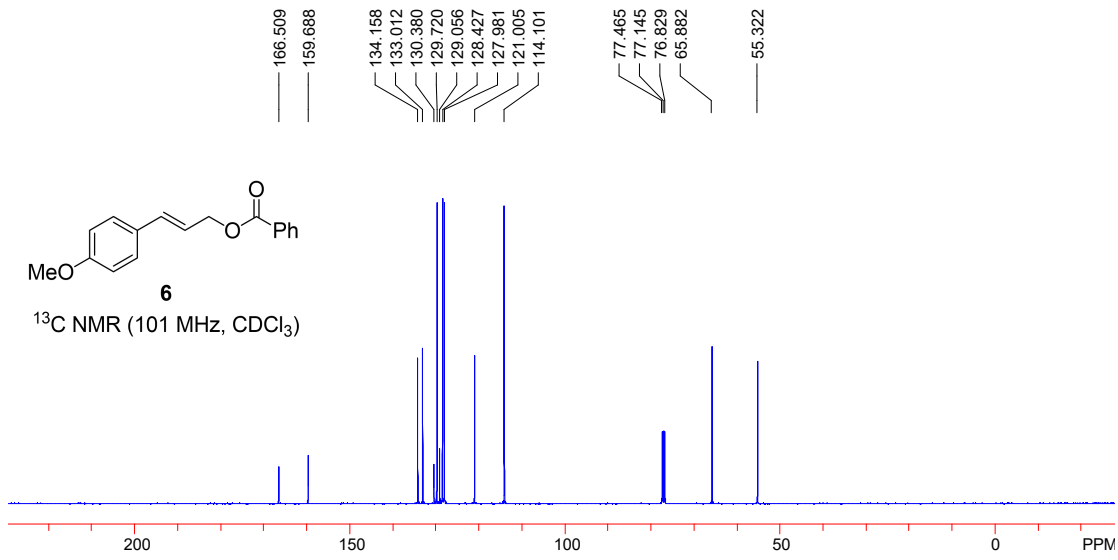


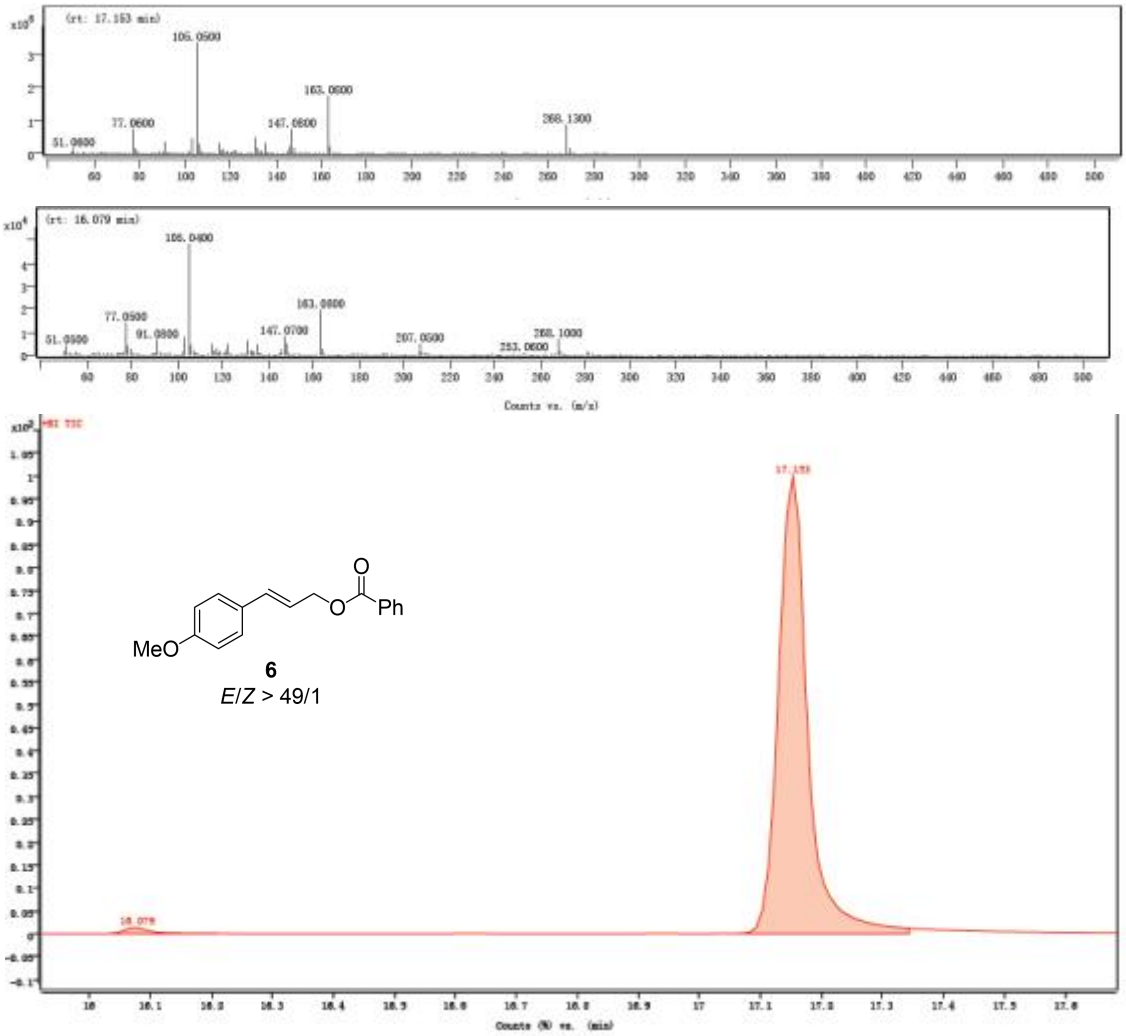
5

E/*Z* = 47/1

RT	Areas	Areas%
19.694	19304184	47
18.218	411330	1


8.150
8.129
7.621
7.619
7.602
7.584
7.582
7.506
7.488
7.468
7.416
7.395
6.925
6.904
6.761
6.721
6.364
6.348
6.331
6.330
6.325
6.308
6.292
5.020
5.004
3.846
O
O
Ph
MeO
6
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.07
1.01
2.06
1.03
1.02
2.08
3.05
10
8
6
4
2
PPM

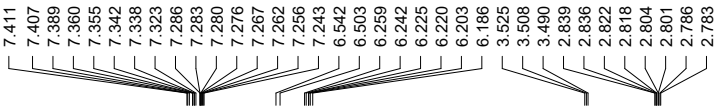

166.509
159.688
134.158
133.012
130.380
129.720
129.056
128.427
127.981
121.005
114.101
77.465
77.145
76.829
65.882
55.322
O
O
Ph
MeO
6
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

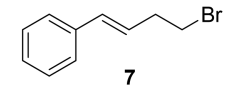


6

E/*Z* > 49/1

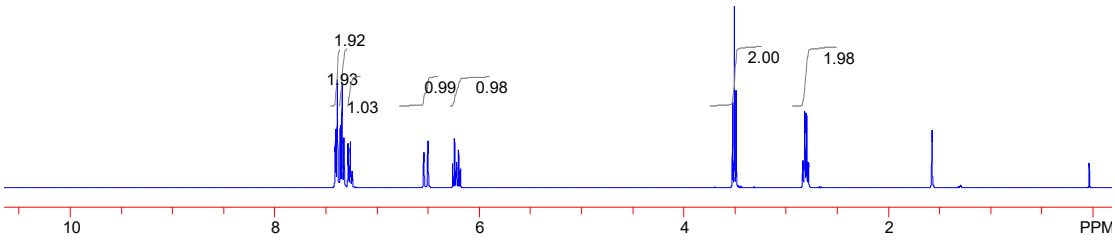
RT	Areas
17.153	42030584
16.079	511498

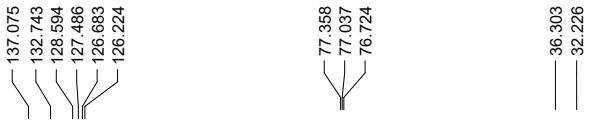


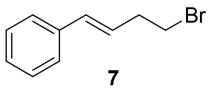


7

^{1}H NMR (400 MHz, $CDCl_3$)

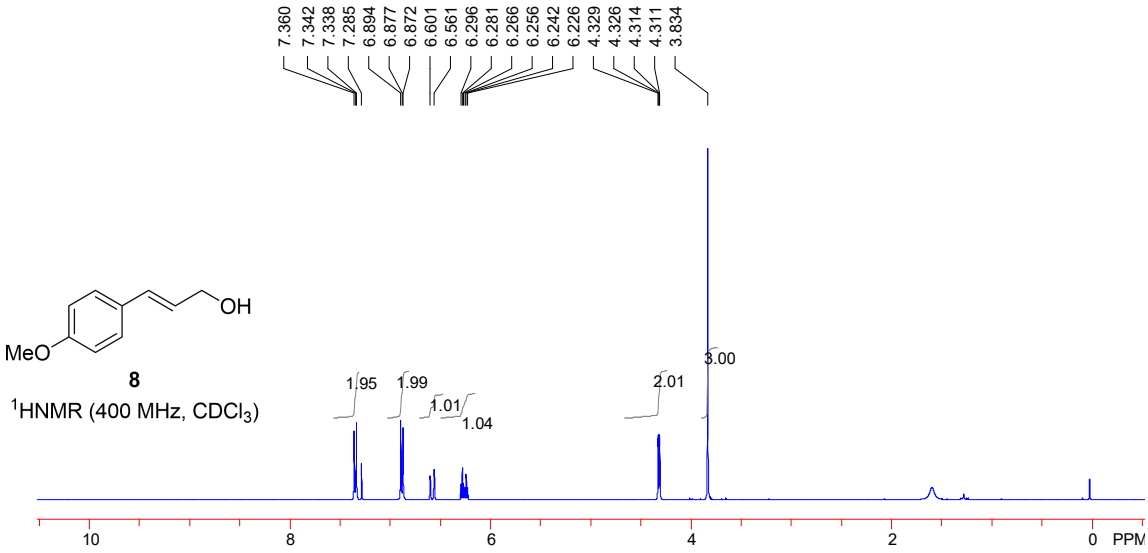


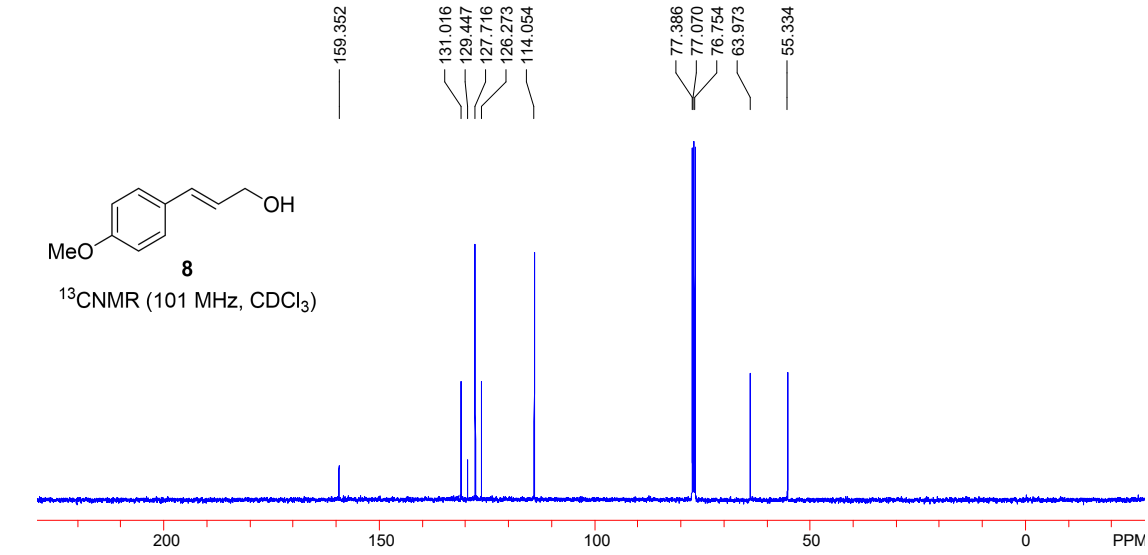


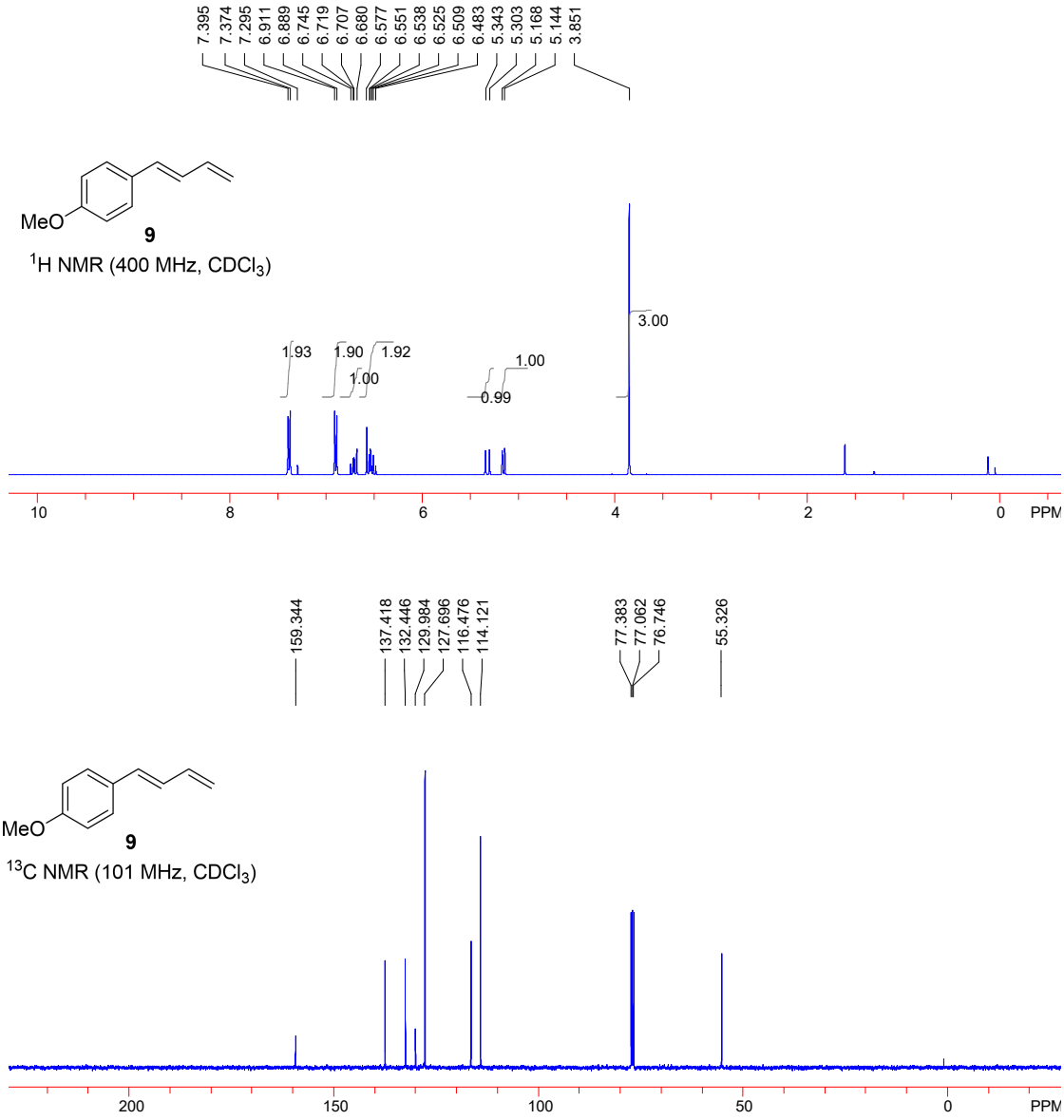


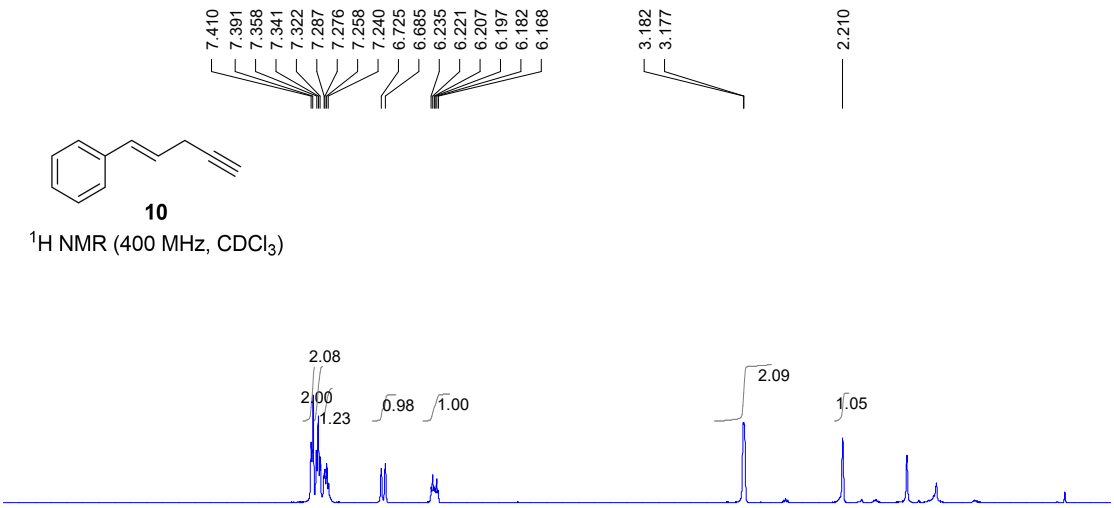
7

^{13}C NMR (101 MHz, $CDCl_3$)


7.360
7.342
7.338
7.285
6.894
6.877
6.872
6.601
6.561
6.296
6.281
6.266
6.256
6.242
6.226
4.329
4.326
4.314
4.311
3.834
OH
MeO
8
1HNMR (400 MHz, CDCl3)
1.95
1.99
1.01
1.04
2.01
3.00
10
8
6
4
2
0
PPM

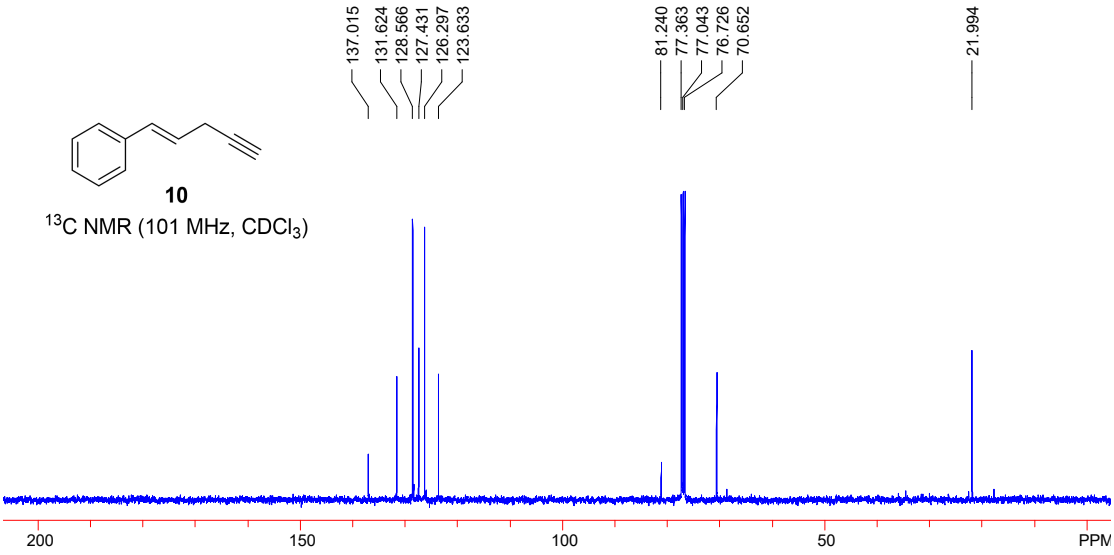

159.352
131.016
129.447
127.716
126.273
114.054
77.386
77.070
76.754
63.973
55.334
OH
MeO
8
13CNMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.395
7.374
7.295
6.911
6.889
6.745
6.719
6.707
6.680
6.577
6.551
6.538
6.525
6.509
6.483
5.343
5.303
5.168
5.144
3.851
MeO
9
1H NMR (400 MHz, CDCl3)
3.00
1.93
1.90
1.92
1.00
1.00
0.99
10
8
6
4
2
0
PPM
159.344
137.418
132.446
129.984
127.696
116.476
114.121
77.383
77.062
76.746
55.326
MeO
9
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM



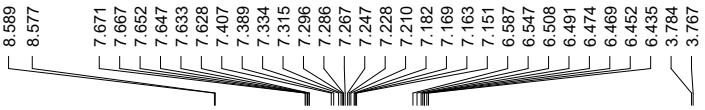
10

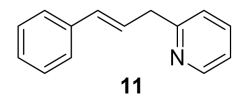
^{1}H NMR (400 MHz, $CDCl_3$)



10

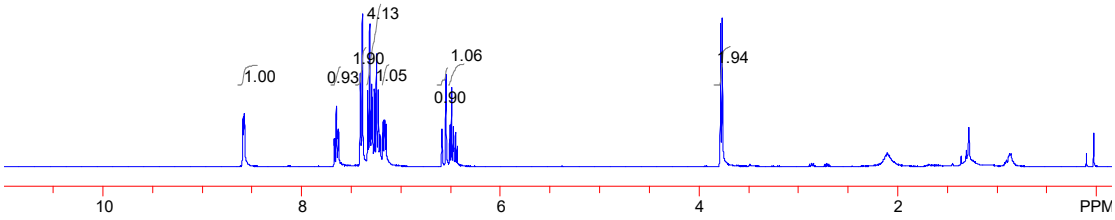
^{13}C NMR (101 MHz, $CDCl_3$)

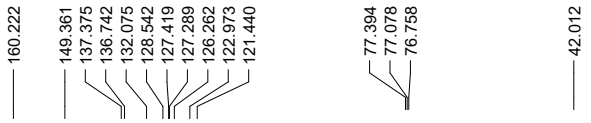


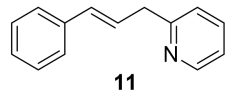


11

^{1}H NMR (400 MHz, $CDCl_3$)

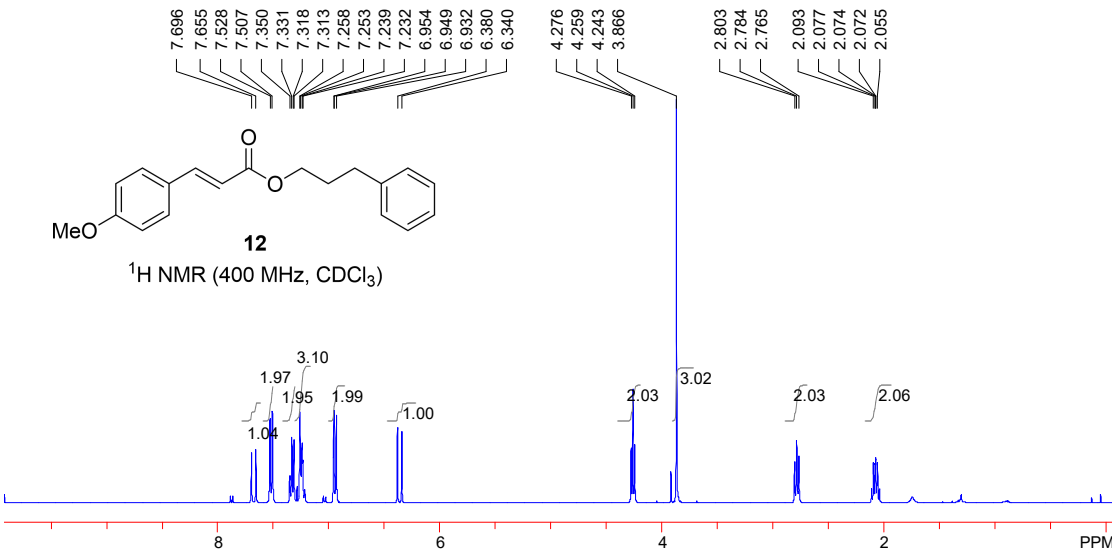


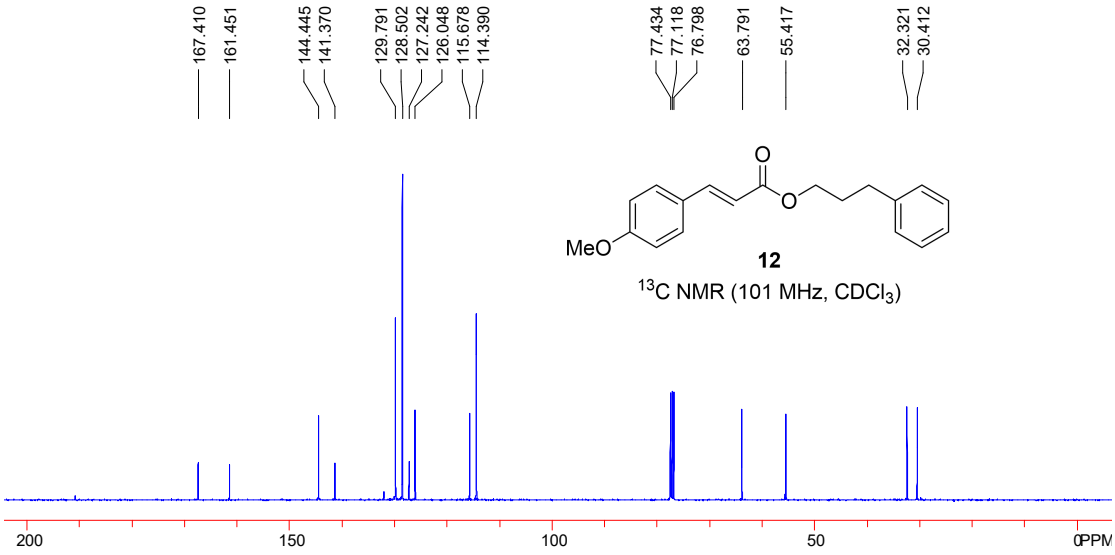


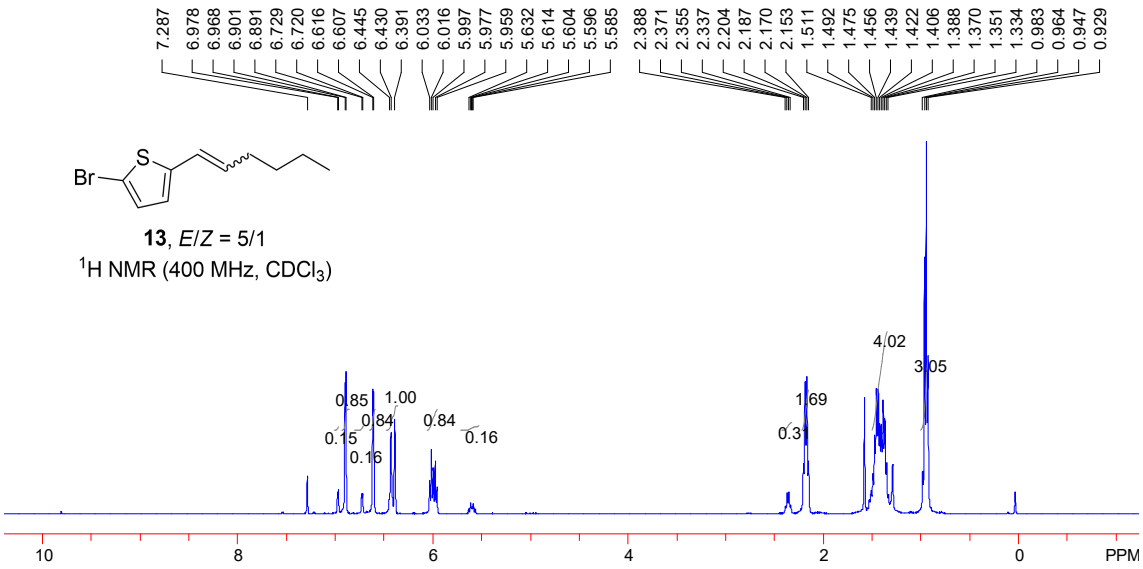


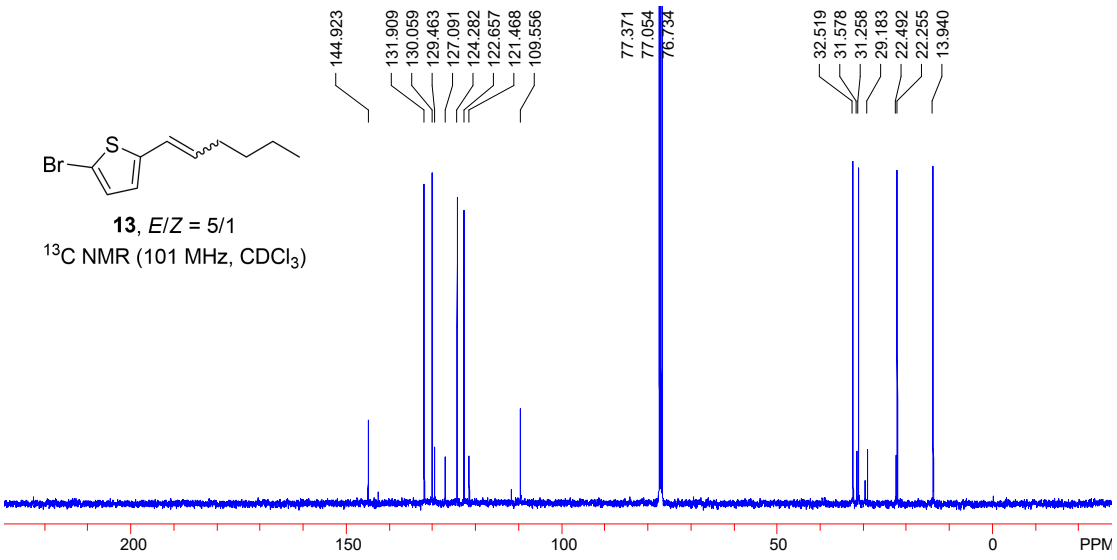
11

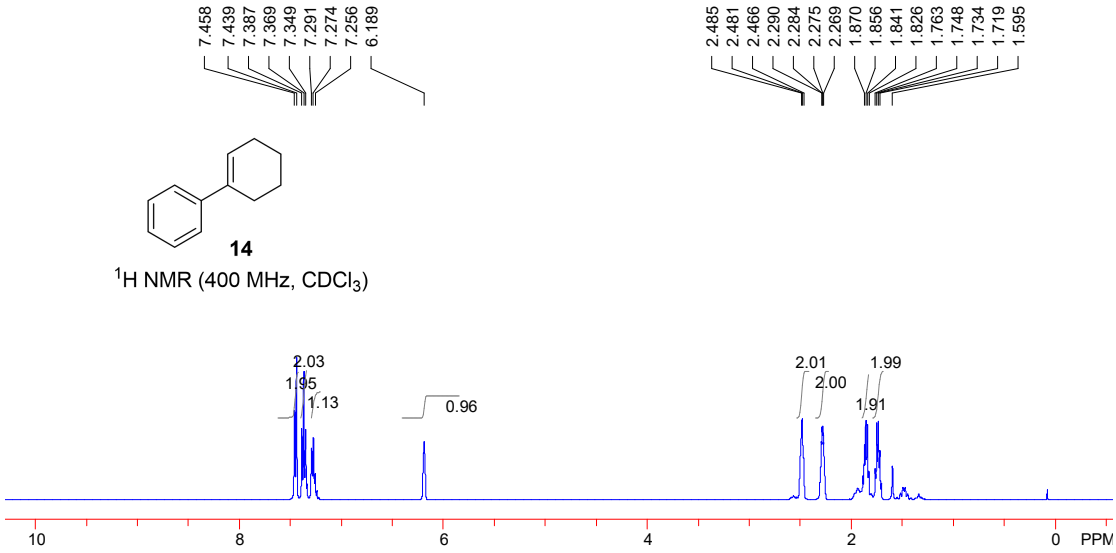
^{13}CNMR (101 MHz, $CDCl_3$)


7.696
7.655
7.528
7.507
7.350
7.331
7.318
7.313
7.258
7.253
7.239
7.232
6.954
6.949
6.932
6.380
6.340
4.276
4.259
4.243
3.866
2.803
2.784
2.765
2.093
2.077
2.074
2.072
2.055
O
O
MeO
12
1H NMR (400 MHz, CDCl3)
3.10
1.97
1.95
1.99
1.00
1.04
2.03
3.02
2.03
2.06
8
6
4
2
PPM


167.410
161.451
144.445
141.370
129.791
128.502
127.242
126.048
115.678
114.390
77.434
77.118
76.798
63.791
55.417
32.321
30.412
O
O
MeO
12
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

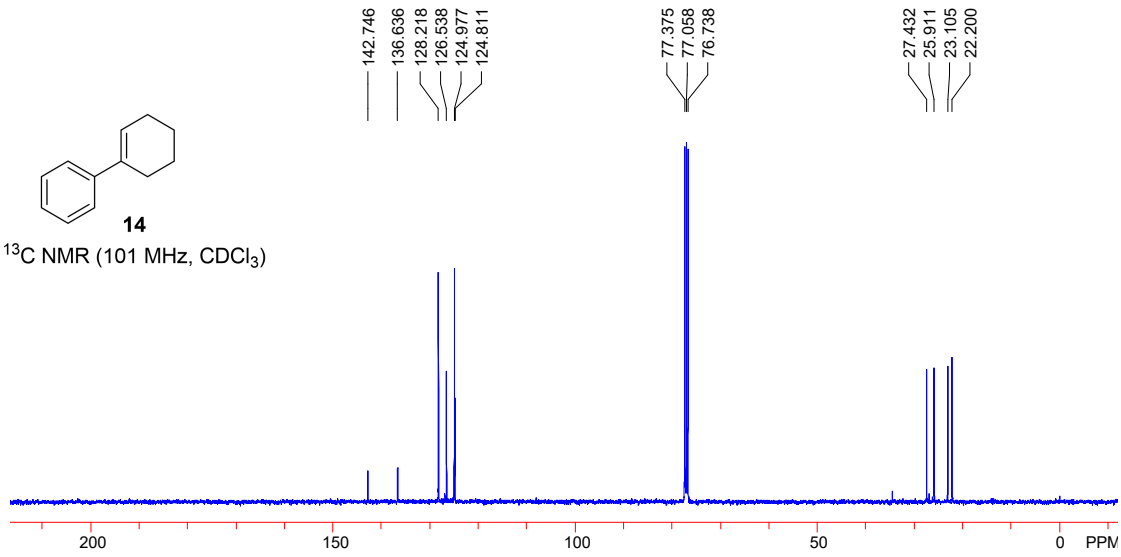

7.287
6.978
6.968
6.901
6.891
6.729
6.720
6.616
6.607
6.445
6.430
6.391
6.033
6.016
5.997
5.977
5.959
5.632
5.614
5.604
5.596
5.585
2.388
2.371
2.355
2.337
2.204
2.187
2.170
2.153
1.511
1.492
1.475
1.456
1.439
1.422
1.406
1.388
1.370
1.351
1.334
0.983
0.964
0.947
0.929
Br
S
13, E/Z = 5/1
1H NMR (400 MHz, CDCl3)
0.85
1.00
0.84
0.84
0.15
0.16
0.16
1.69
0.31
4.02
3.05
10
8
6
4
2
0
PPM


144.923
131.909
130.059
129.463
127.091
124.282
122.657
121.468
109.556
77.371
77.054
76.734
32.519
31.578
31.258
29.183
22.492
22.255
13.940
Br
S
13, E/Z = 5/1
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM



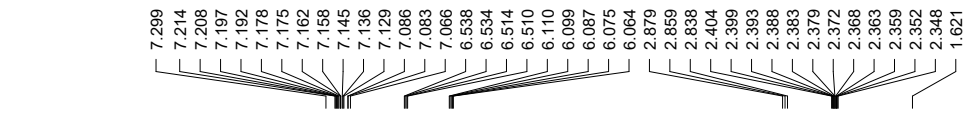
14

^{1}H NMR (400 MHz, $CDCl_3$)



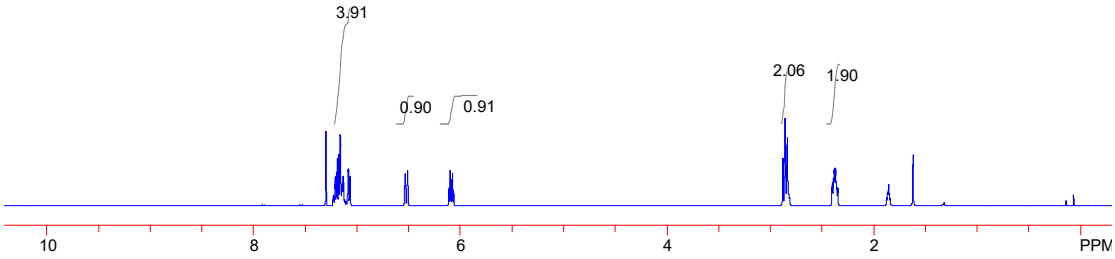
14

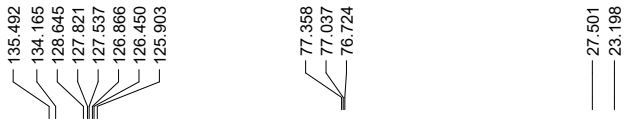
^{13}C NMR (101 MHz, $CDCl_3$)

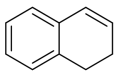


15

^{1}H NMR (400 MHz, $CDCl_3$)

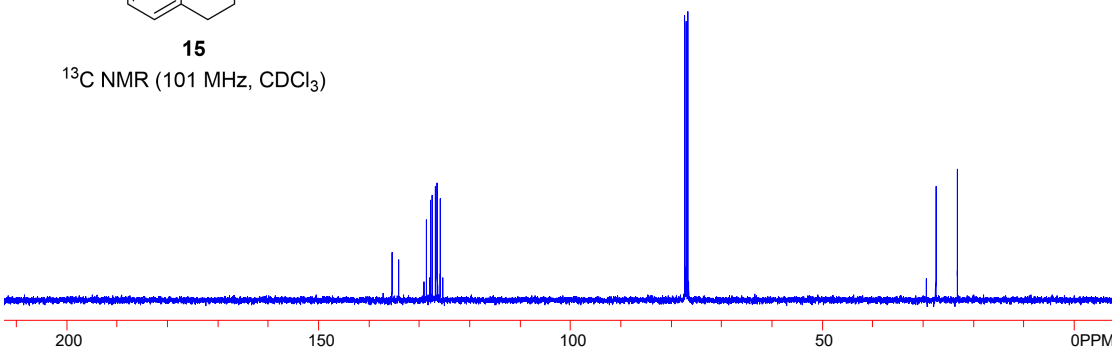


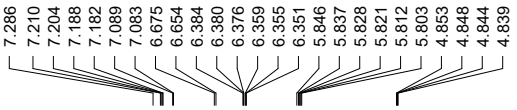


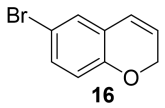


15

^{13}C NMR (101 MHz, $CDCl_3$)

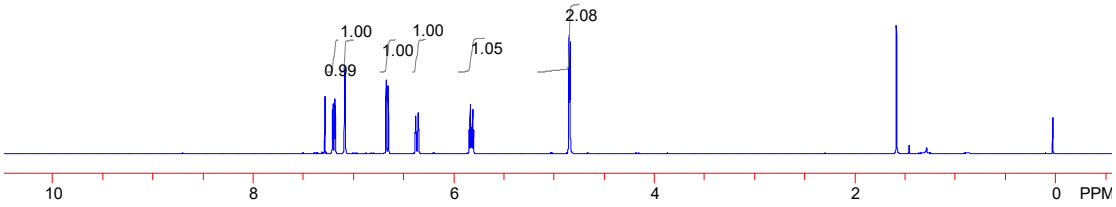


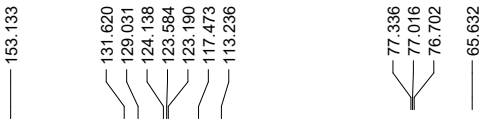


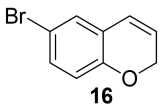


16

^{1}H NMR (400 MHz, $CDCl_3$)

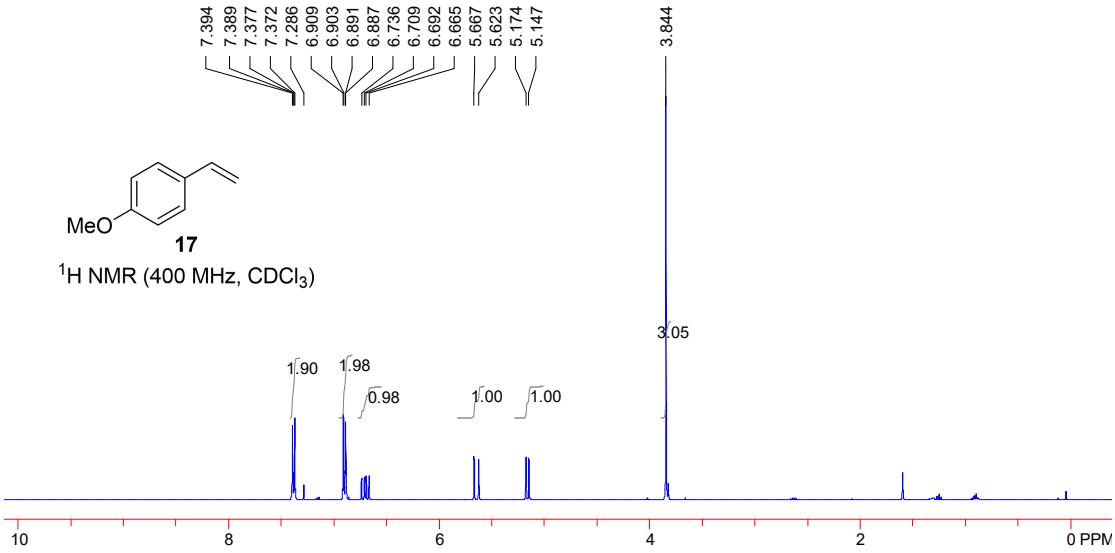


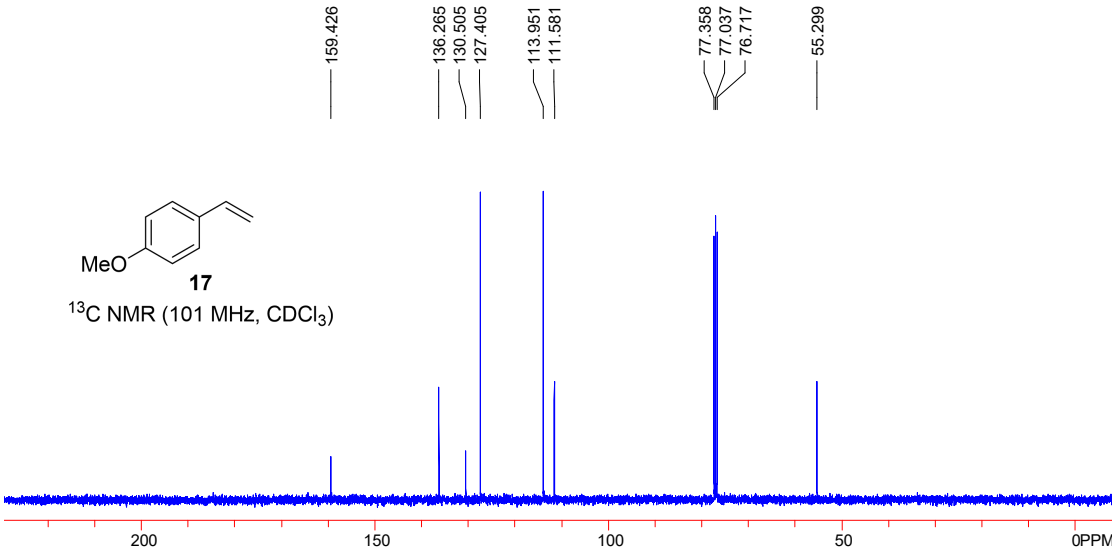


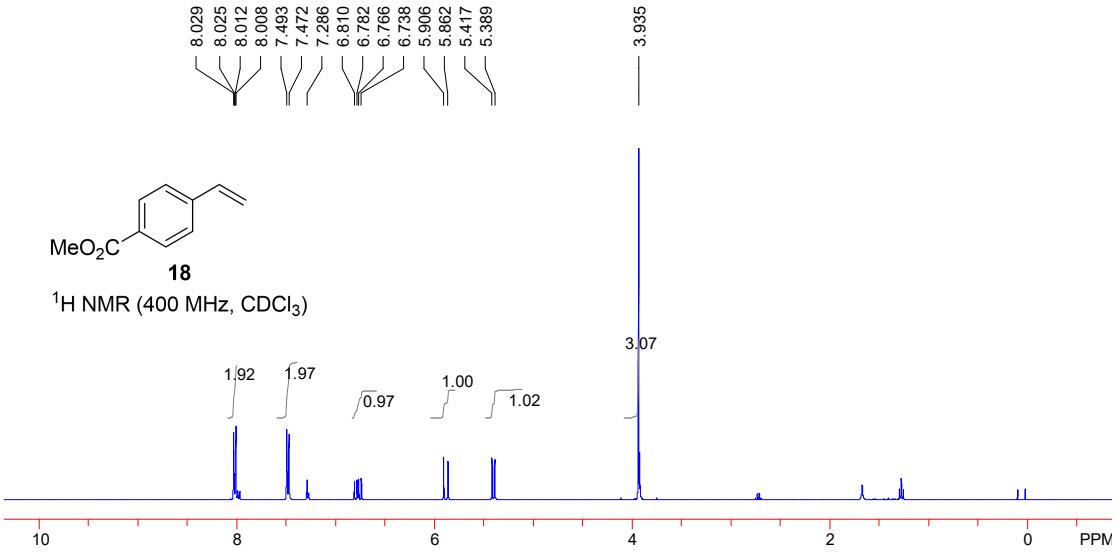


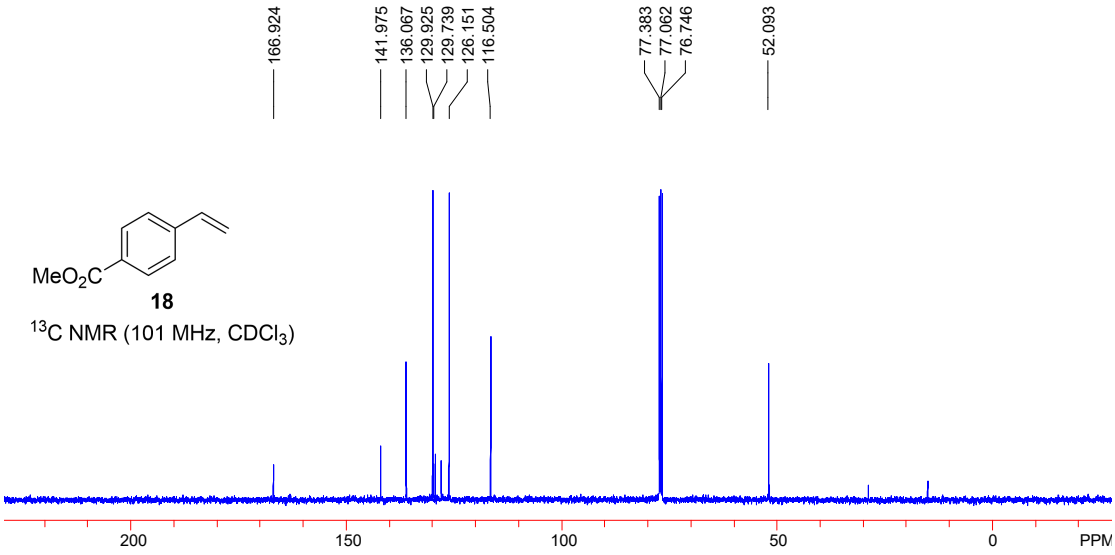
16

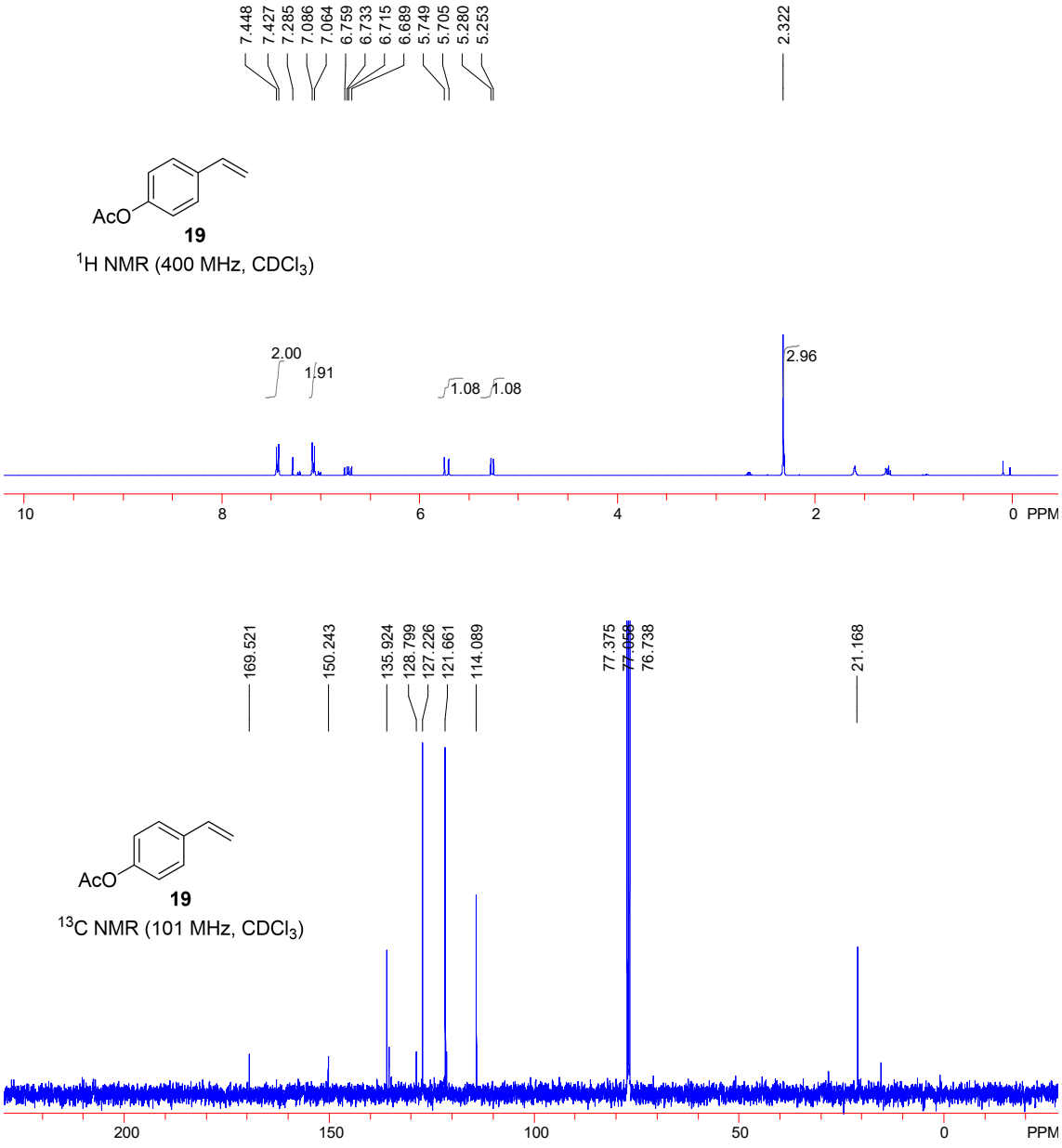
^{13}C NMR (101 MHz, $CDCl_3$)

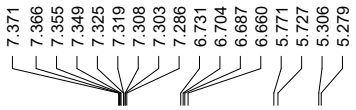

7.394
7.389
7.377
7.372
7.286
6.909
6.903
6.891
6.887
6.736
6.709
6.692
6.665
5.667
5.623
5.174
5.147
3.844
MeO
17
1H NMR (400 MHz, CDCl3)
3.05
1.90
1.98
0.98
1.00
1.00
10
8
6
4
2
0 PPM

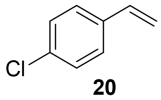

159.426
136.265
130.505
127.405
113.951
111.581
77.358
77.037
76.717
55.299
MeO
17
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


8.029
8.025
8.012
8.008
7.493
7.472
7.286
6.810
6.782
6.766
6.738
5.906
5.862
5.417
5.389
3.935
MeO2C
18
1H NMR (400 MHz, CDCl3)
3.07
1.92
1.97
0.97
1.00
1.02
10
8
6
4
2
0
PPM


166.924
141.975
136.067
129.925
129.739
126.151
116.504
77.383
77.062
76.746
52.093
MeO2C
18
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

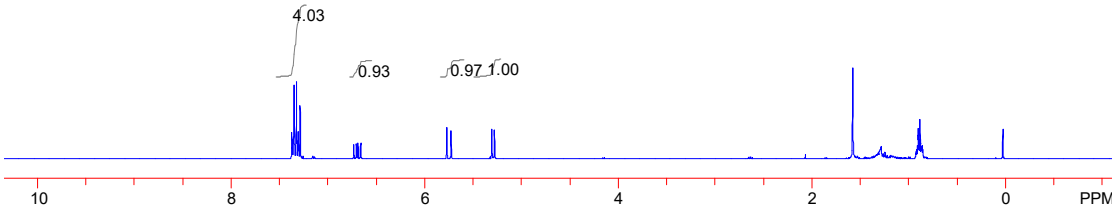

7.448
7.427
7.285
7.086
7.064
6.759
6.733
6.715
6.689
5.749
5.705
5.280
5.253
2.322
AcO
19
1H NMR (400 MHz, CDCl3)
2.00
1.91
1.08
1.08
2.96
10
8
6
4
2
0 PPM
169.521
150.243
135.924
128.799
127.226
121.661
114.089
77.375
77.063
76.738
21.168
AcO
19
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

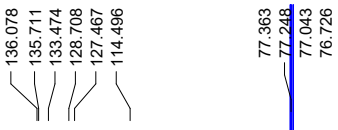


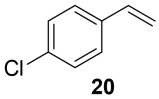


20

^{1}H NMR (400 MHz, $CDCl_3$)

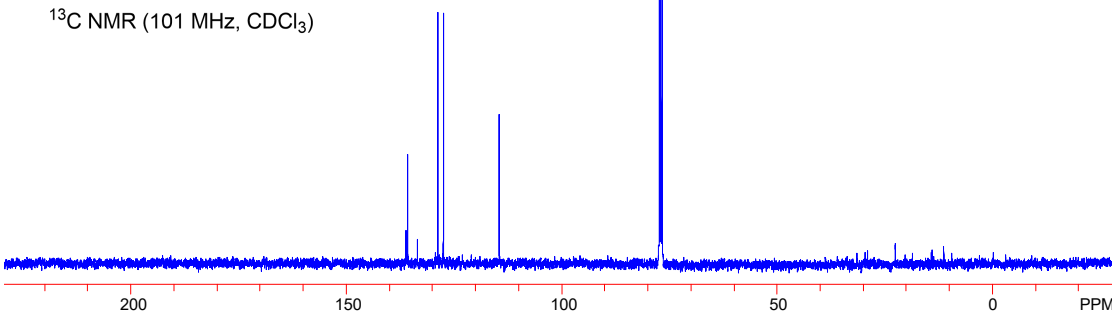


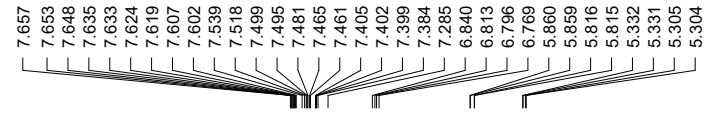




20

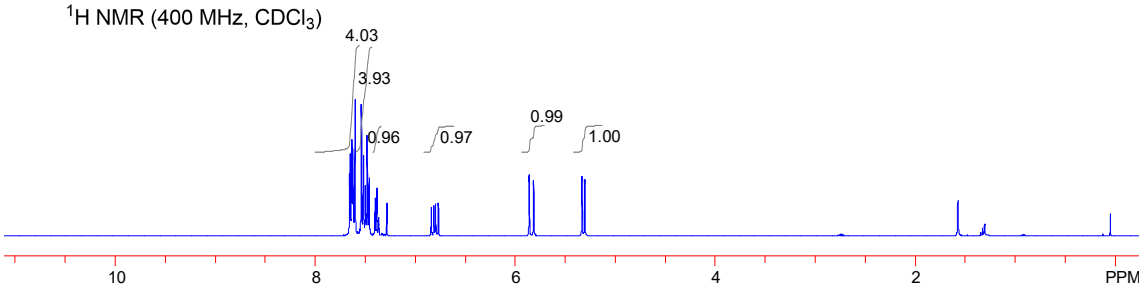
^{13}C NMR (101 MHz, $CDCl_3$)

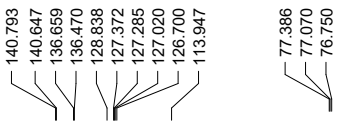


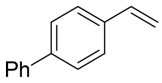


21

^{1}H NMR (400 MHz, $CDCl_3$)

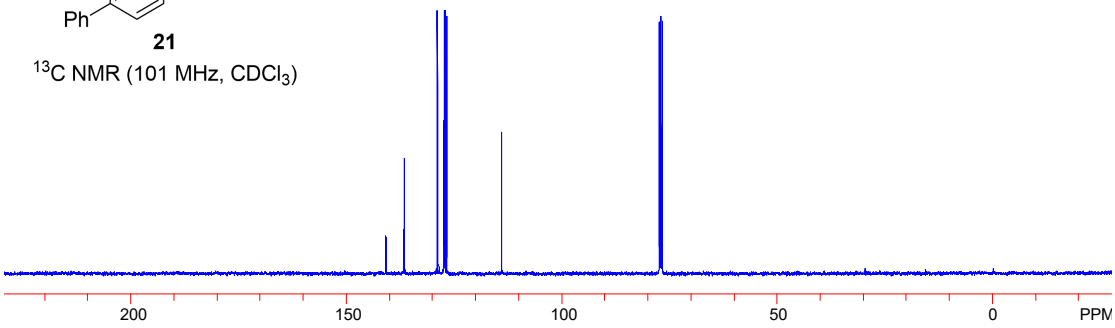


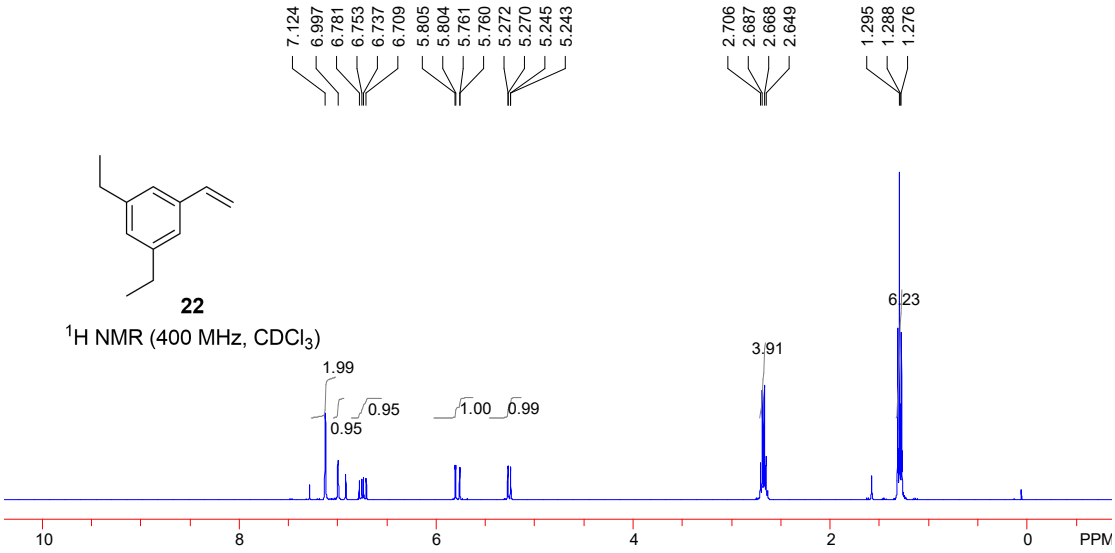


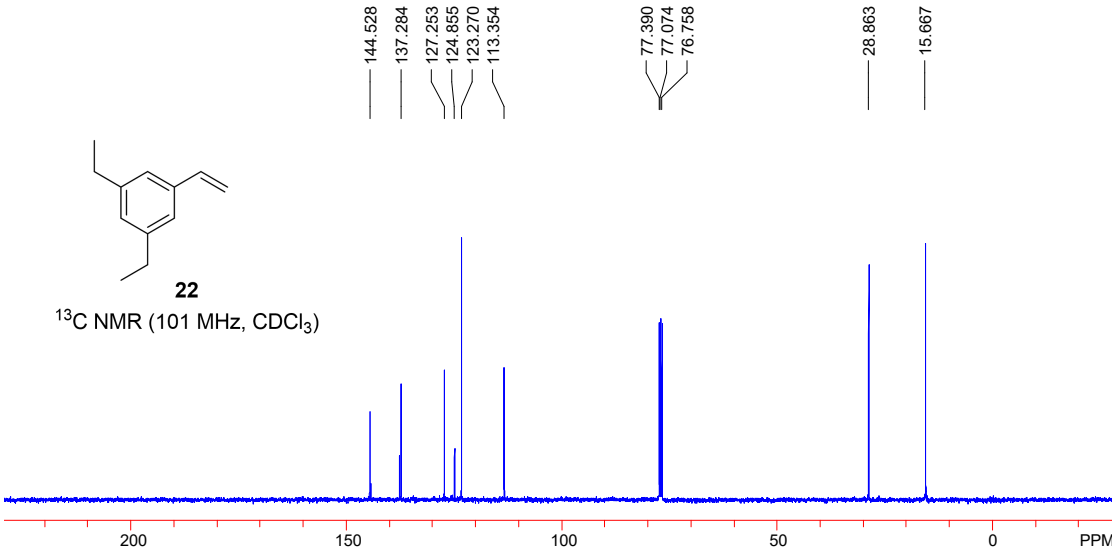


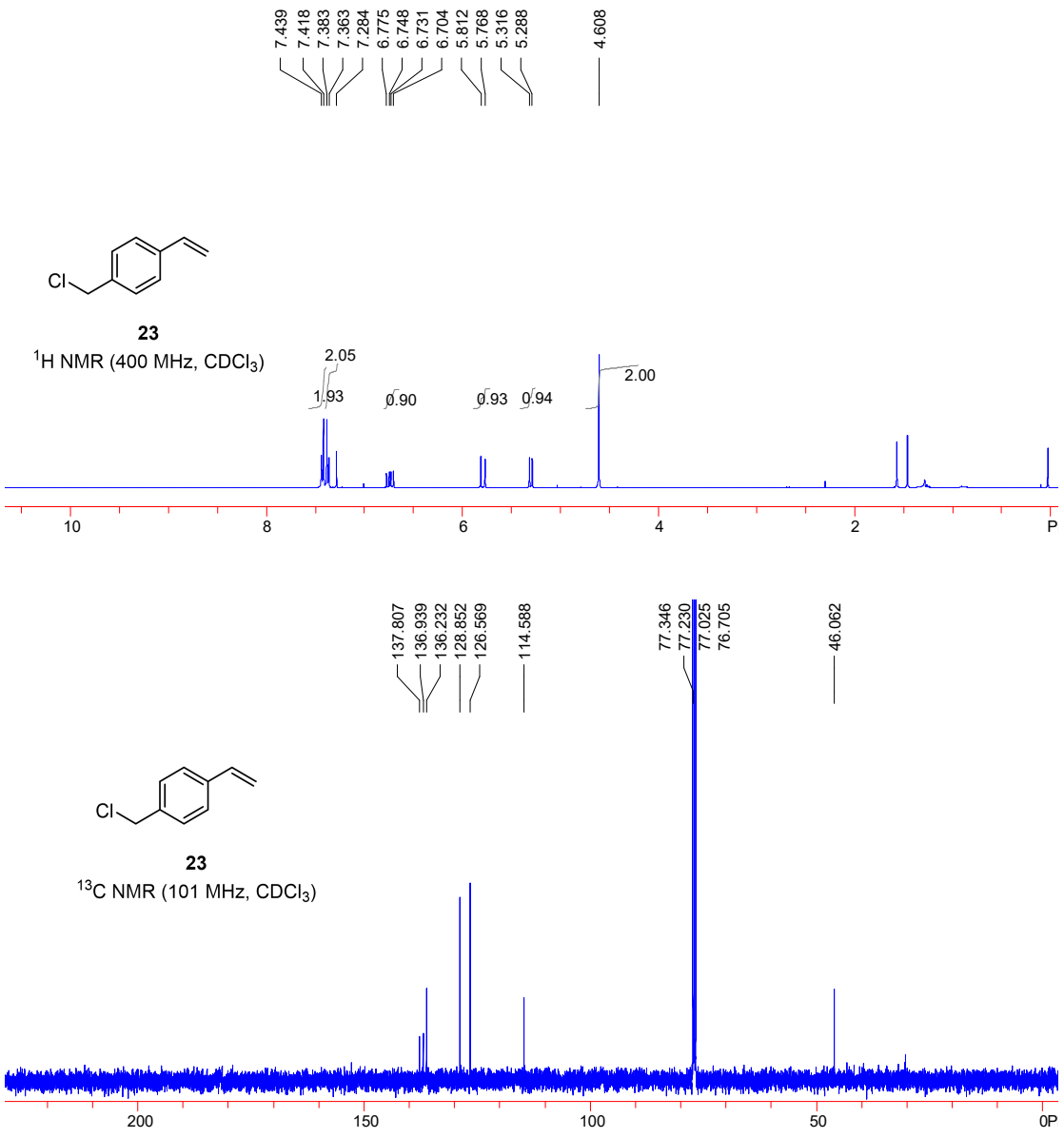
21

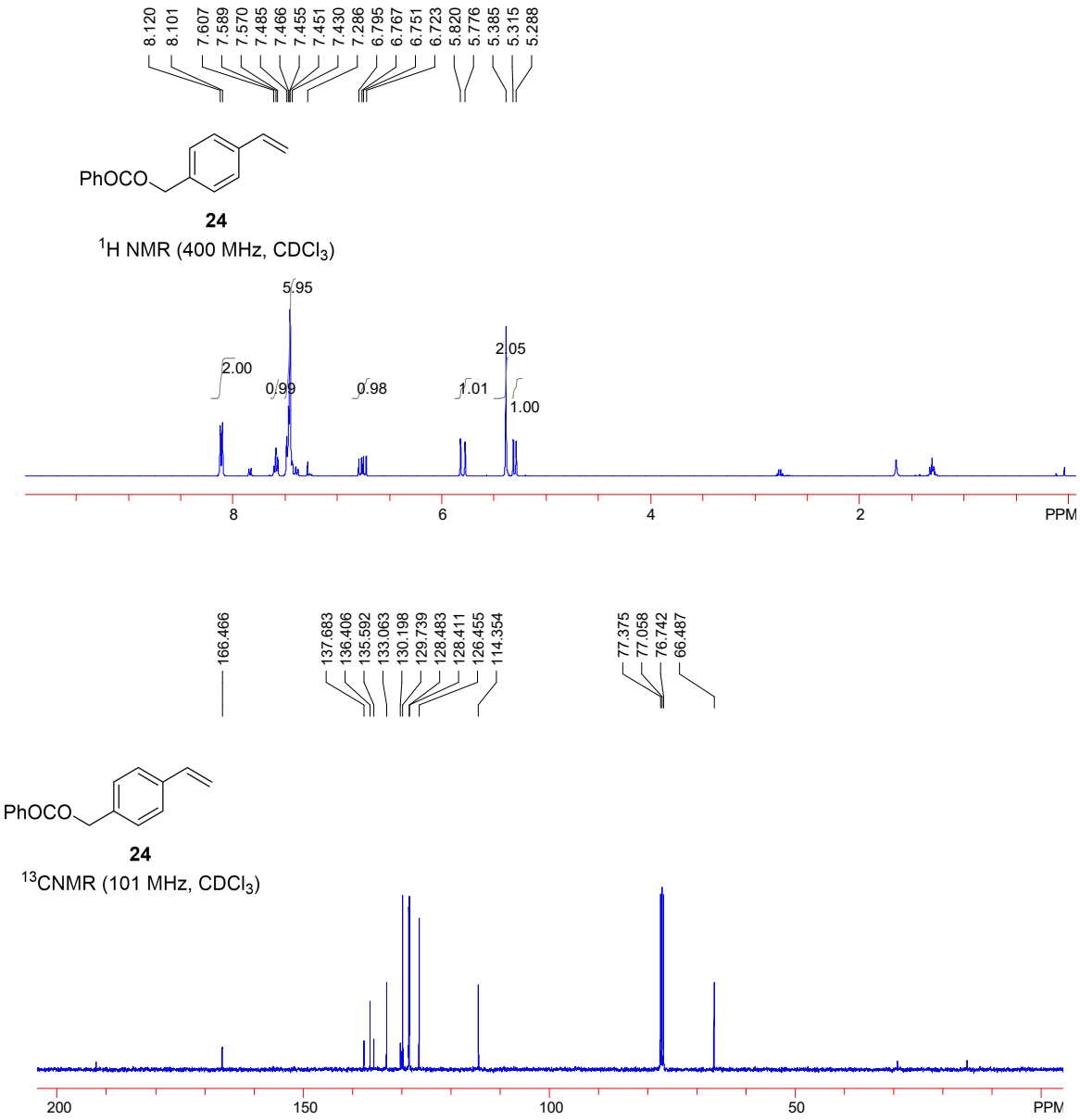
^{13}C NMR (101 MHz, $CDCl_3$)

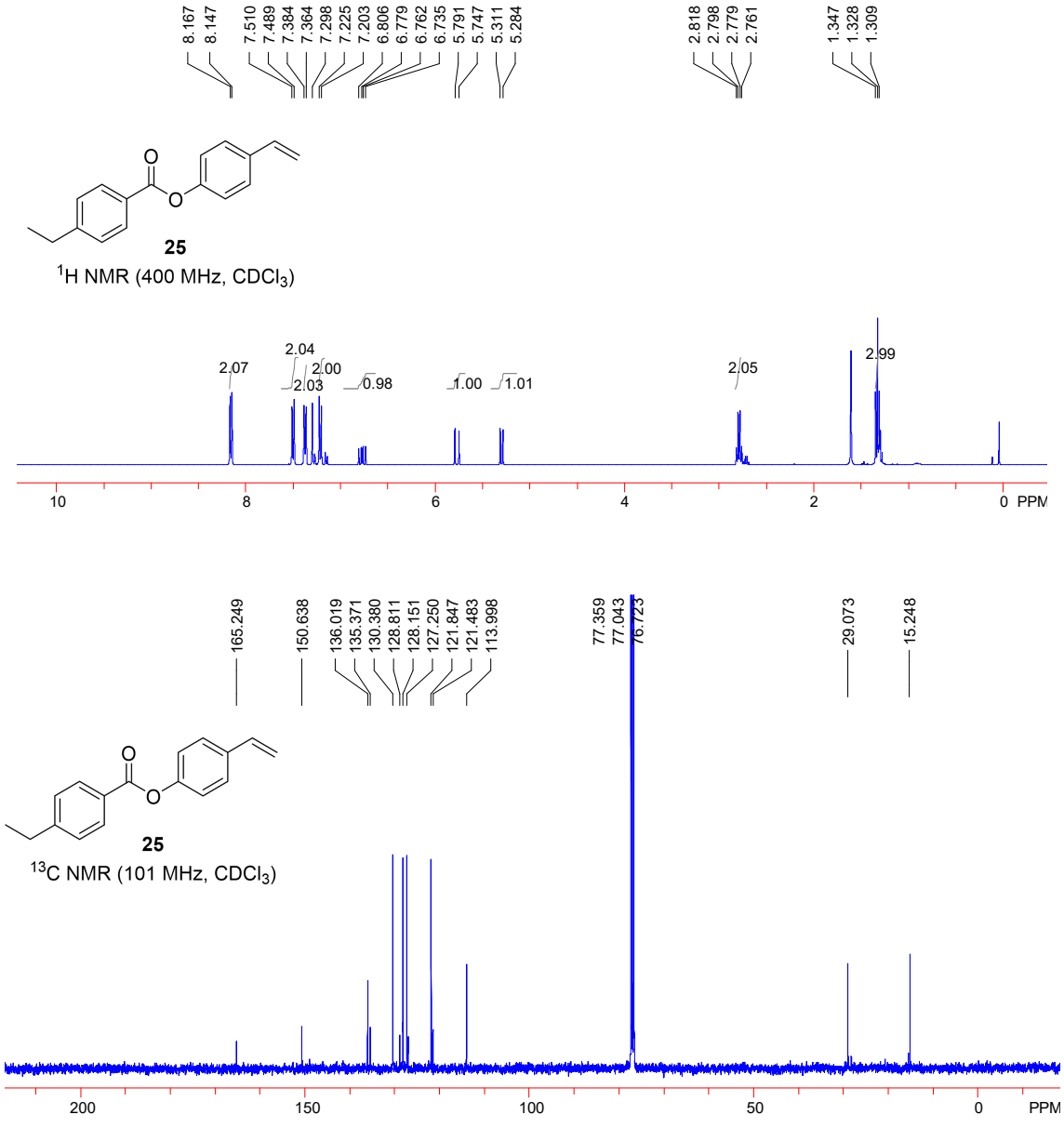


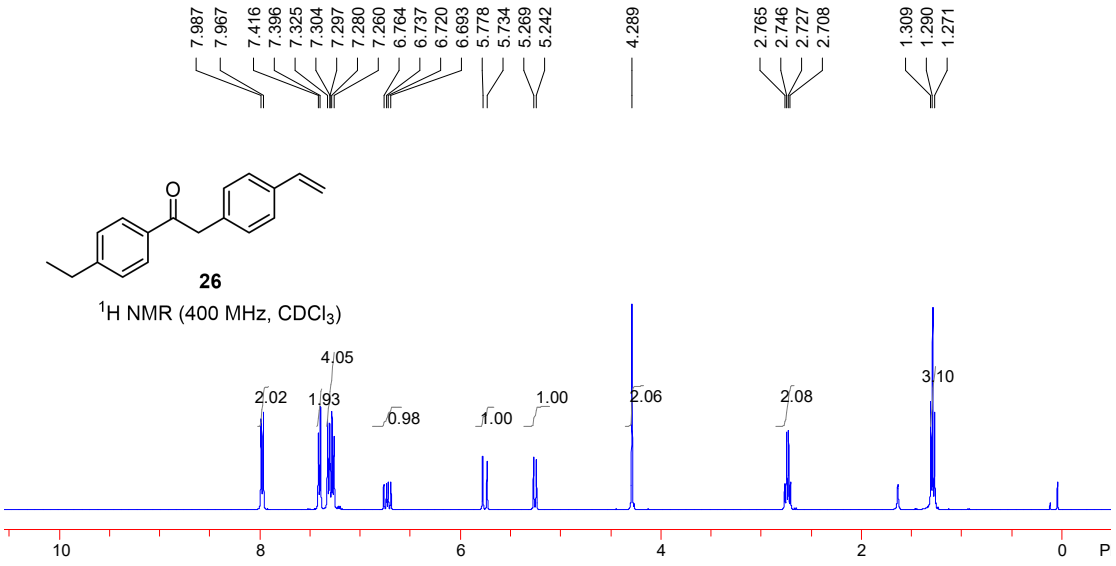

7.124
6.997
6.781
6.753
6.737
6.709
5.805
5.804
5.761
5.760
5.272
5.270
5.245
5.243
2.706
2.687
2.668
2.649
1.295
1.288
1.276
22
1H NMR (400 MHz, CDCl3)
1.99
0.95
0.95
1.00
0.99
3.91
6.23
10
8
6
4
2
0
PPM

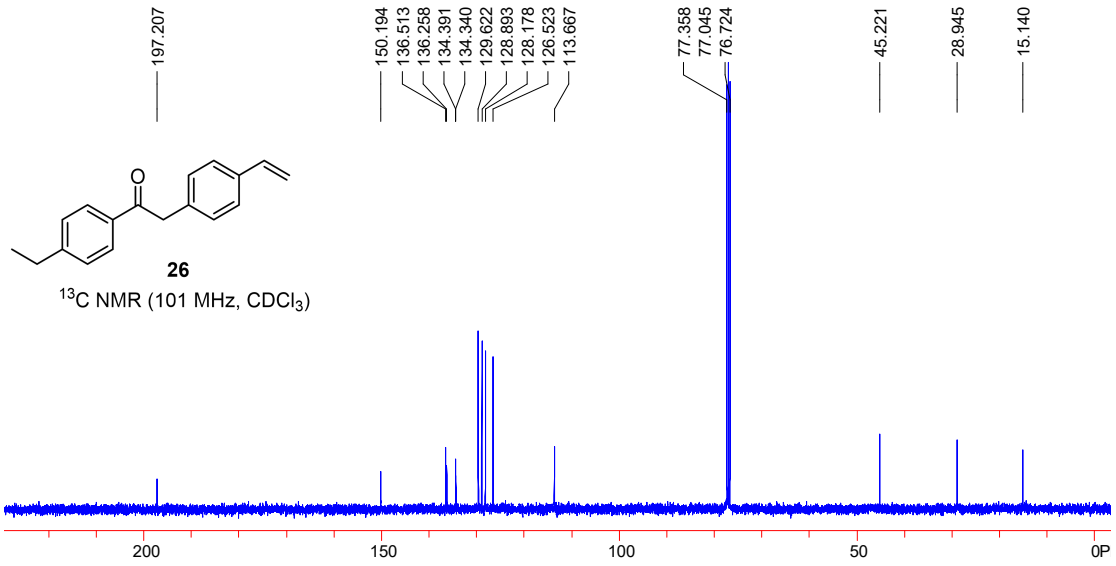

144.528
137.284
127.253
124.855
123.270
113.354
77.390
77.074
76.758
28.863
15.667
22
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

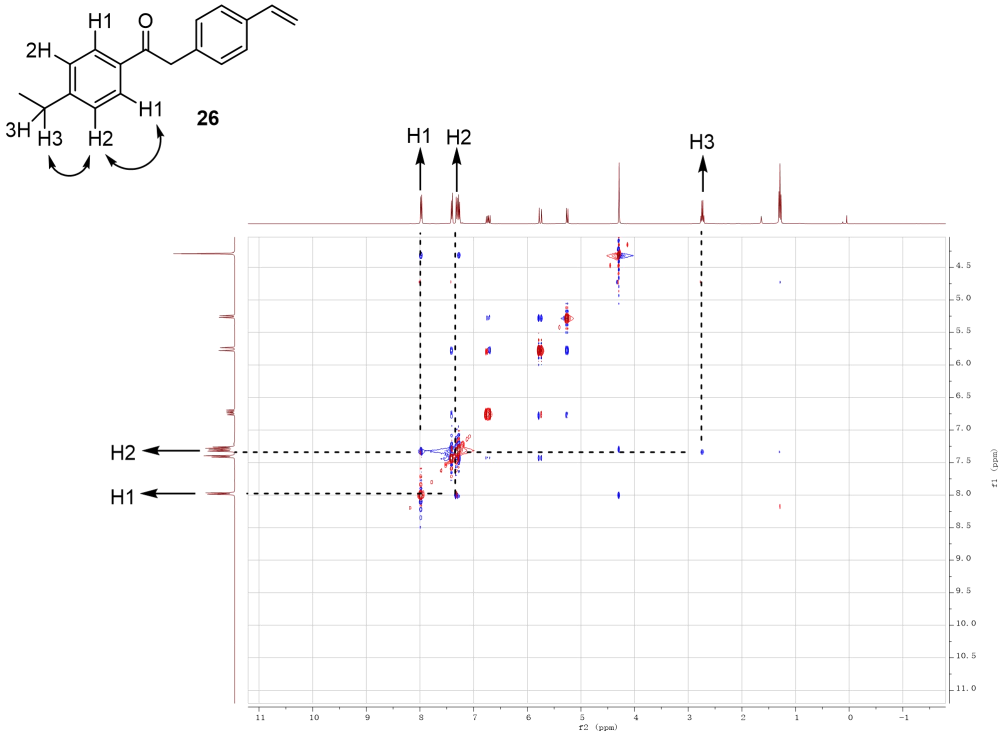

7.439
7.418
7.383
7.363
7.284
6.775
6.748
6.731
6.704
5.812
5.768
5.316
5.288
4.608
Cl
23
1H NMR (400 MHz, CDCl3)
2.05
1.93
0.90
0.93
0.94
2.00
10
8
6
4
2
P
137.807
136.939
136.232
128.852
126.569
114.588
77.346
77.230
77.025
76.705
46.062
Cl
23
13C NMR (101 MHz, CDCl3)
200
150
100
50
0P

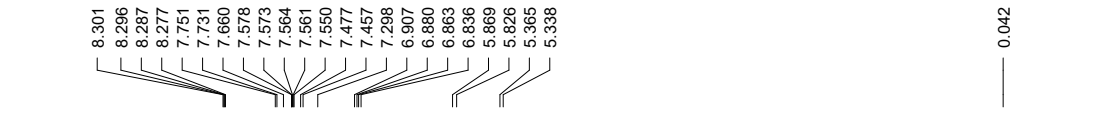

8.120
8.101
7.607
7.589
7.570
7.485
7.466
7.455
7.451
7.430
7.286
6.795
6.767
6.751
6.723
5.820
5.776
5.385
5.315
5.288
PhOCO
24
1H NMR (400 MHz, CDCl3)
5.95
2.00
0.99
0.98
1.01
2.05
1.00
8
6
4
2
PPM
166.466
137.683
136.406
135.592
133.063
130.198
129.739
128.483
128.411
126.455
114.354
77.375
77.058
76.742
66.487
PhOCO
24
13CNMR (101 MHz, CDCl3)
200
150
100
50
PPM

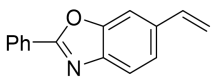

8.167
8.147
7.510
7.489
7.384
7.364
7.298
7.225
7.203
6.806
6.779
6.762
6.735
5.791
5.747
5.311
5.284
2.818
2.798
2.779
2.761
1.347
1.328
1.309
25
1H NMR (400 MHz, CDCl3)
2.07
2.04
2.03
2.00
0.98
1.00
1.01
2.05
2.99
10
8
6
4
2
0 PPM
165.249
150.638
136.019
135.371
130.380
128.811
128.151
127.250
121.847
121.483
113.998
77.359
77.043
76.723
29.073
15.248
25
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.987
7.967
7.416
7.396
7.325
7.304
7.297
7.280
7.260
6.764
6.737
6.720
6.693
5.778
5.734
5.269
5.242
4.289
2.765
2.746
2.727
2.708
1.309
1.290
1.271
O
26
1H NMR (400 MHz, CDCl3)
4.05
2.02
1.93
0.98
1.00
1.00
2.06
2.08
3.10
10
8
6
4
2
0
P


197.207
150.194
136.513
136.258
134.391
134.340
129.622
128.893
128.178
126.523
113.667
77.358
77.045
76.724
45.221
28.945
15.140
O
26
13C NMR (101 MHz, CDCl3)
200
150
100
50
0P

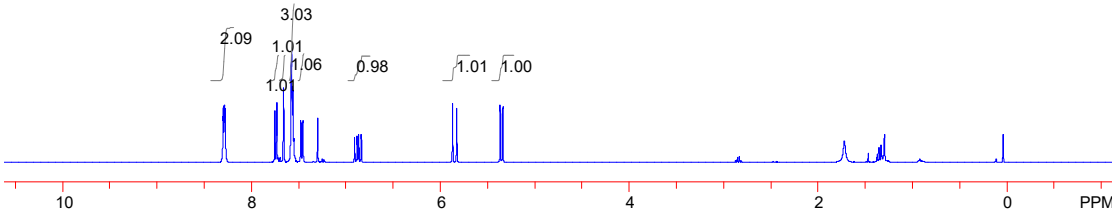

H1
O
2H
H1
3H
H3
H2
26
H1
H2
H3
H2
H1
f2 (ppm)
f1 (ppm)

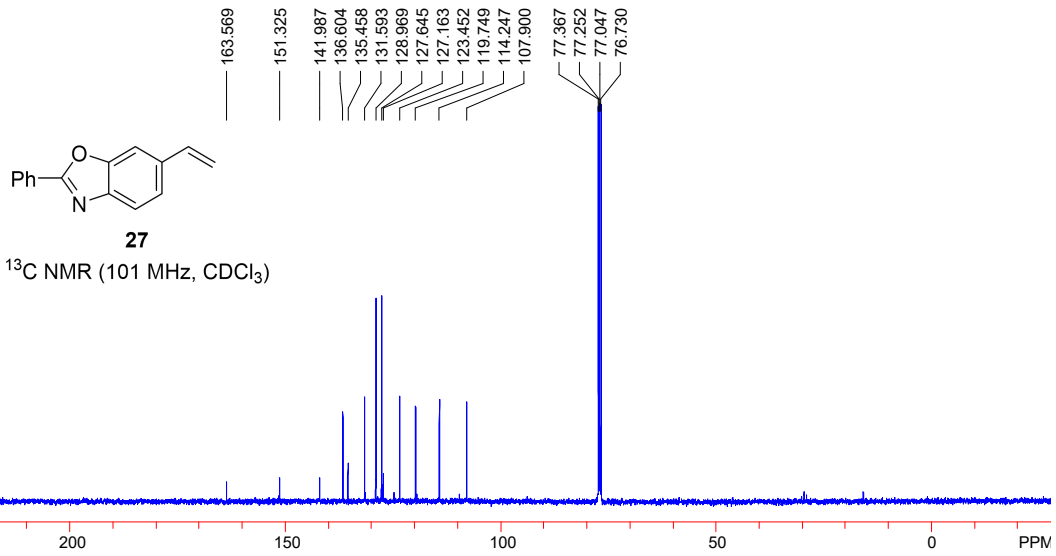




27

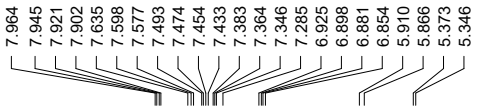
^{1}H NMR (400 MHz, $CDCl_3$)

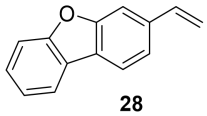




27

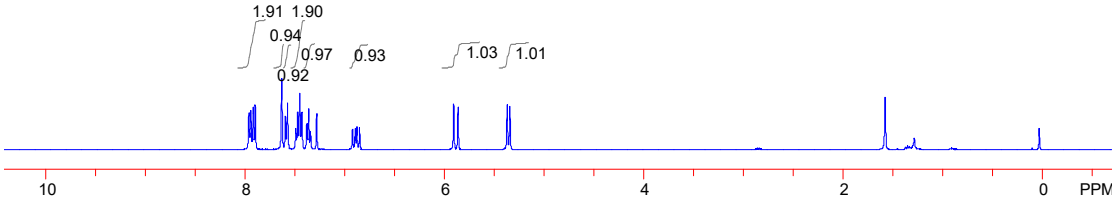
^{13}C NMR (101 MHz, $CDCl_3$)

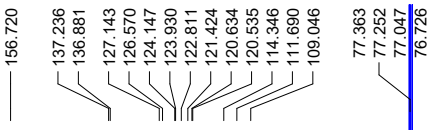


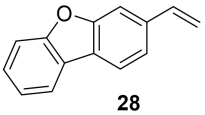


28

^{1}H NMR (400 MHz, $CDCl_3$)

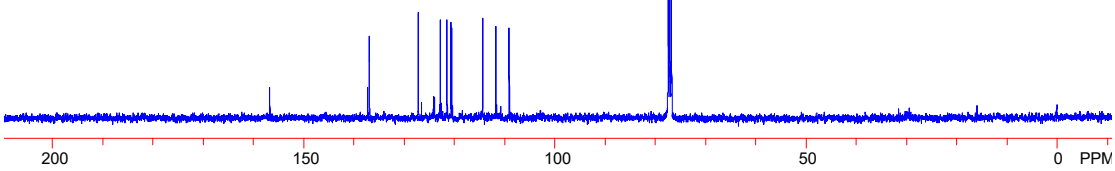


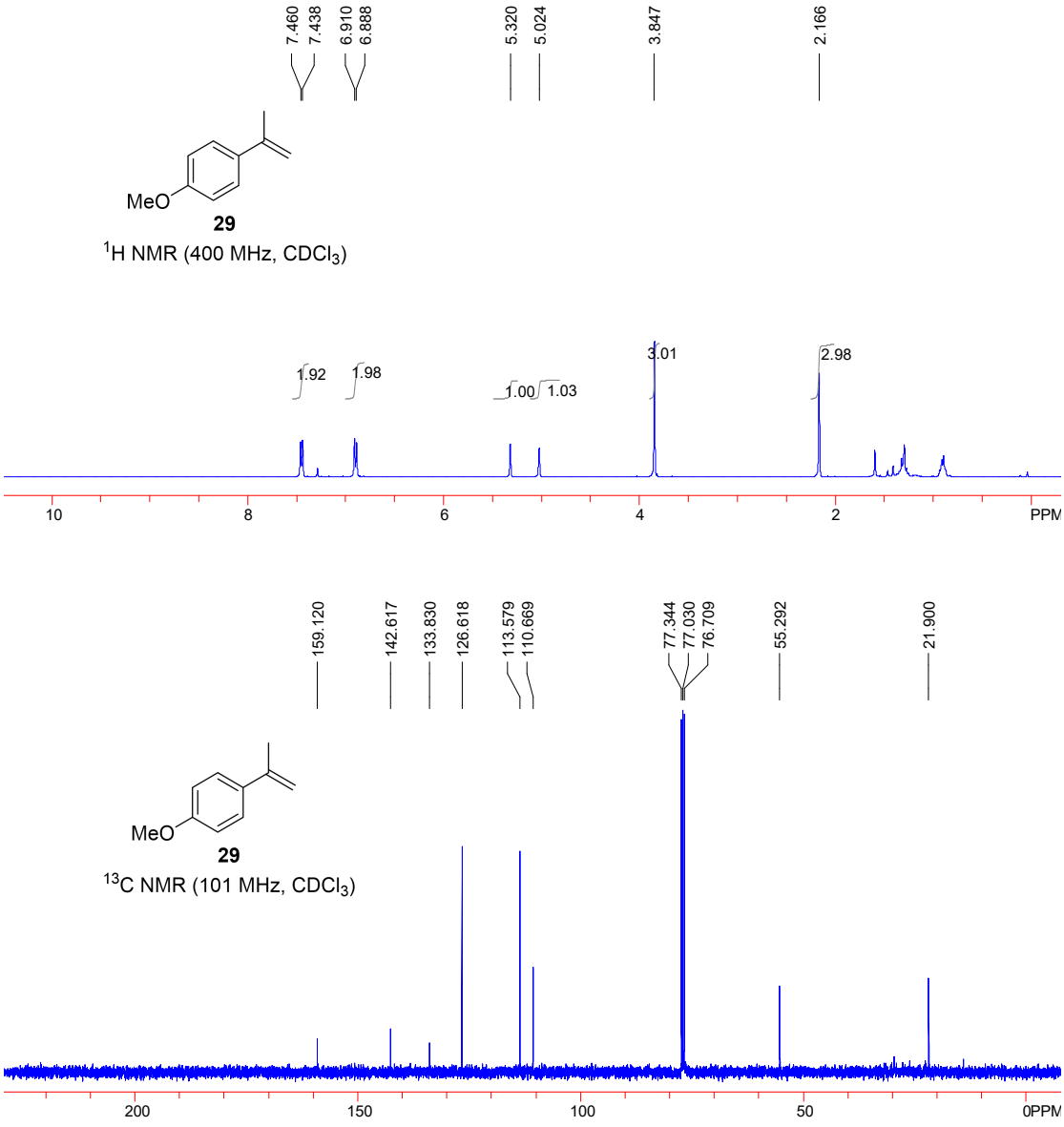


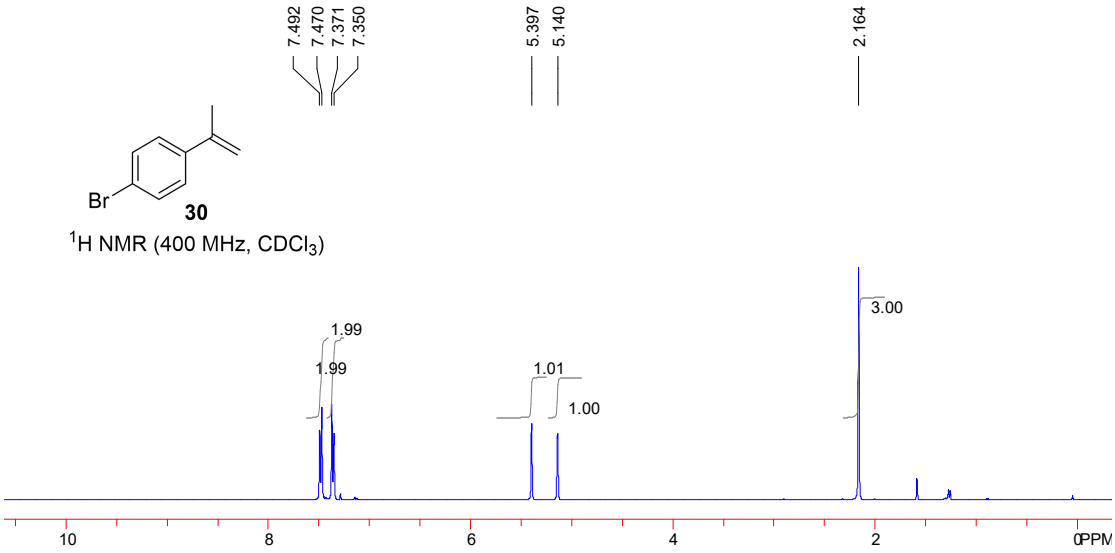


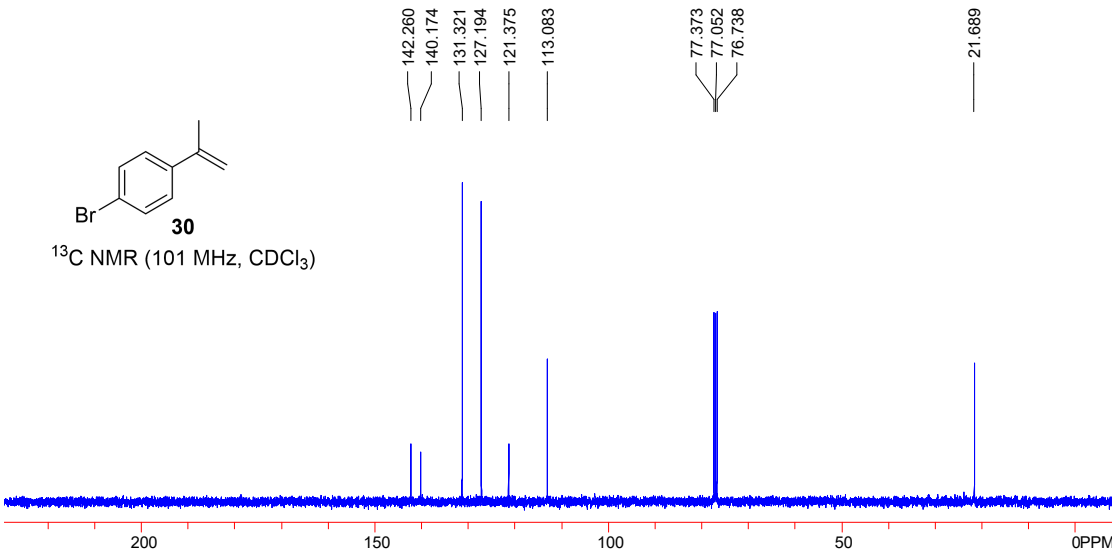
28

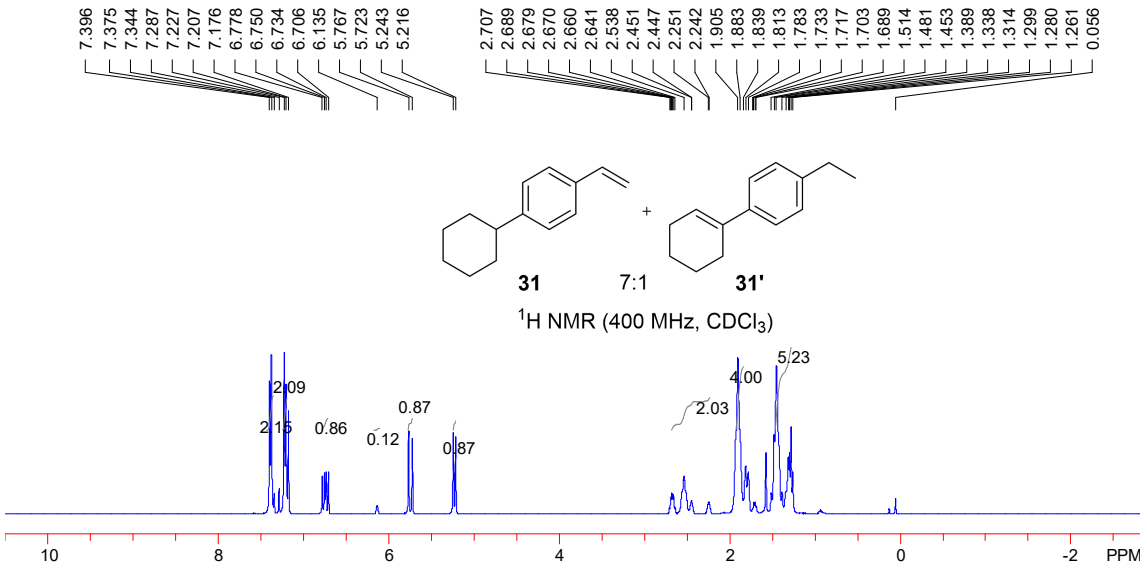
^{13}C NMR (101 MHz, $CDCl_3$)

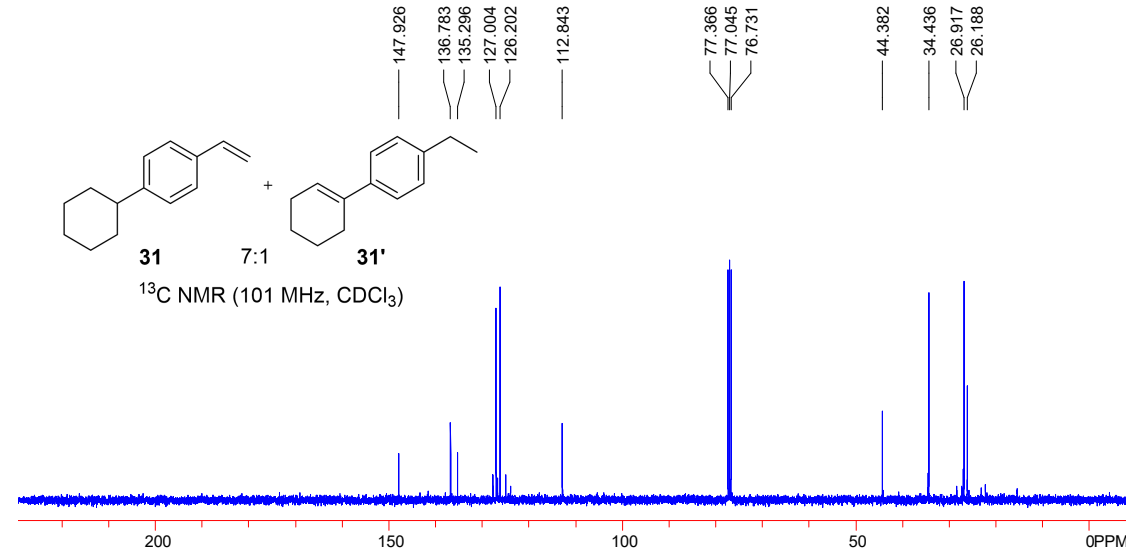


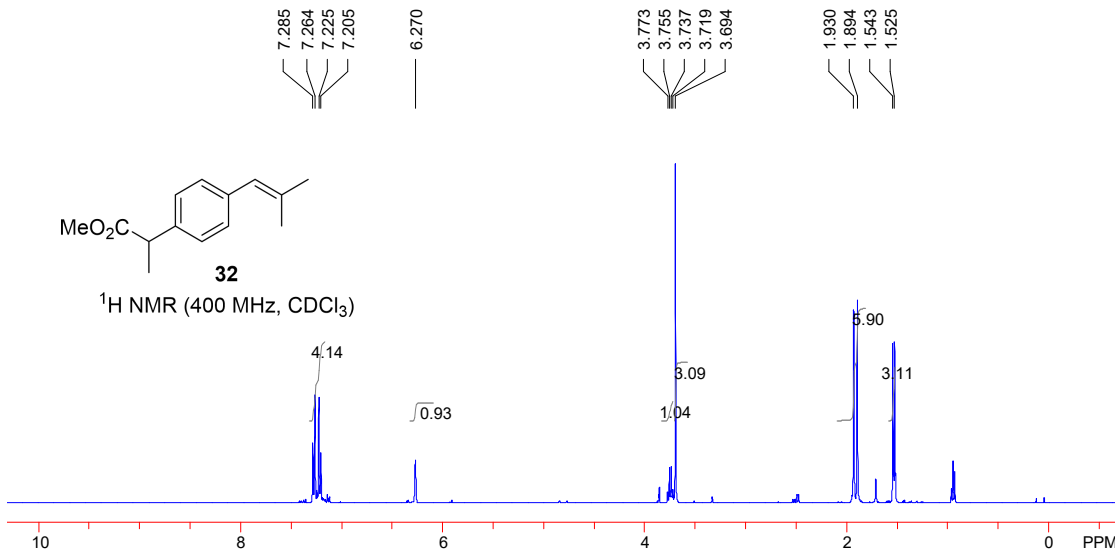

7.460
7.438
6.910
6.888
5.320
5.024
3.847
2.166
MeO
29
1H NMR (400 MHz, CDCl3)
1.92
1.98
1.00
1.03
3.01
2.98
10
8
6
4
2
PPM
159.120
142.617
133.830
126.618
113.579
110.669
77.344
77.030
76.709
55.292
21.900
MeO
29
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

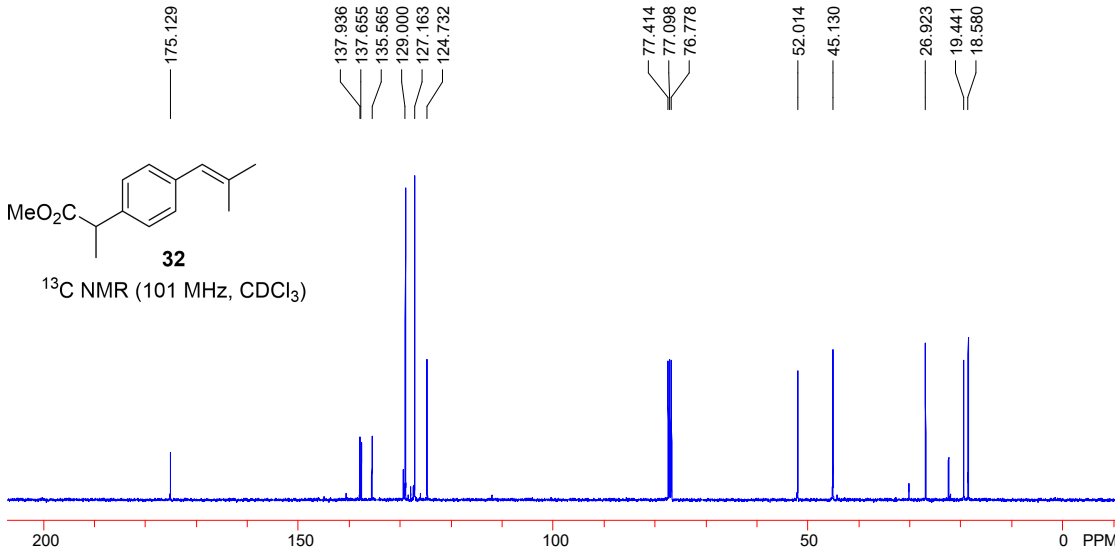

7.492
7.470
7.371
7.350
5.397
5.140
2.164
Br
30
1H NMR (400 MHz, CDCl3)
1.99
1.99
1.01
1.00
3.00
10
8
6
4
2
0PPM

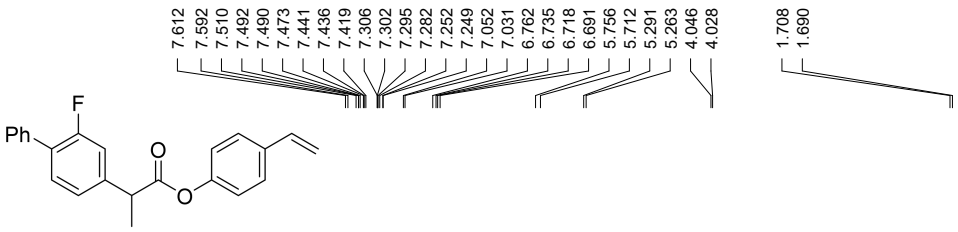

142.260
140.174
131.321
127.194
121.375
113.083
77.373
77.052
76.738
21.689
Br
30
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


7.396
7.375
7.344
7.287
7.227
7.207
7.176
6.778
6.750
6.734
6.706
6.135
5.767
5.723
5.243
5.216
2.707
2.689
2.679
2.670
2.660
2.641
2.538
2.451
2.447
2.251
2.242
1.905
1.883
1.839
1.813
1.783
1.733
1.717
1.703
1.689
1.514
1.481
1.453
1.389
1.338
1.314
1.299
1.280
1.261
0.056
31
7:1
31'
1H NMR (400 MHz, CDCl3)
2.09
2.15
0.86
0.12
0.87
0.87
2.03
4.00
5.23
10
8
6
4
2
0
-2
PPM


147.926
136.783
135.296
127.004
126.202
112.843
77.366
77.045
76.731
44.382
34.436
26.917
26.188
31
7:1
31'
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

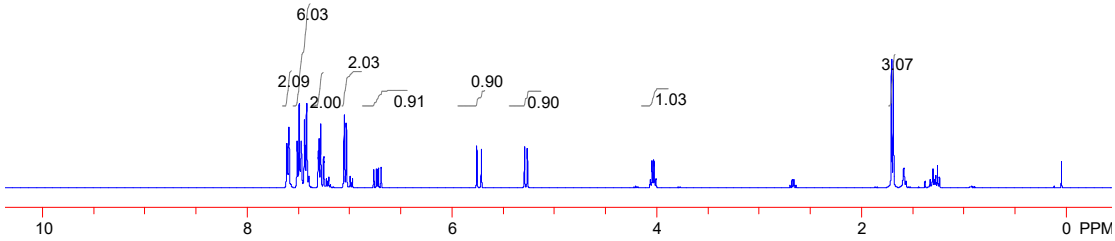

7.285
7.264
7.225
7.205
6.270
3.773
3.755
3.737
3.719
3.694
1.930
1.894
1.543
1.525
MeO2C
32
1H NMR (400 MHz, CDCl3)
4.14
0.93
3.09
1.04
5.90
3.11
10
8
6
4
2
0
PPM

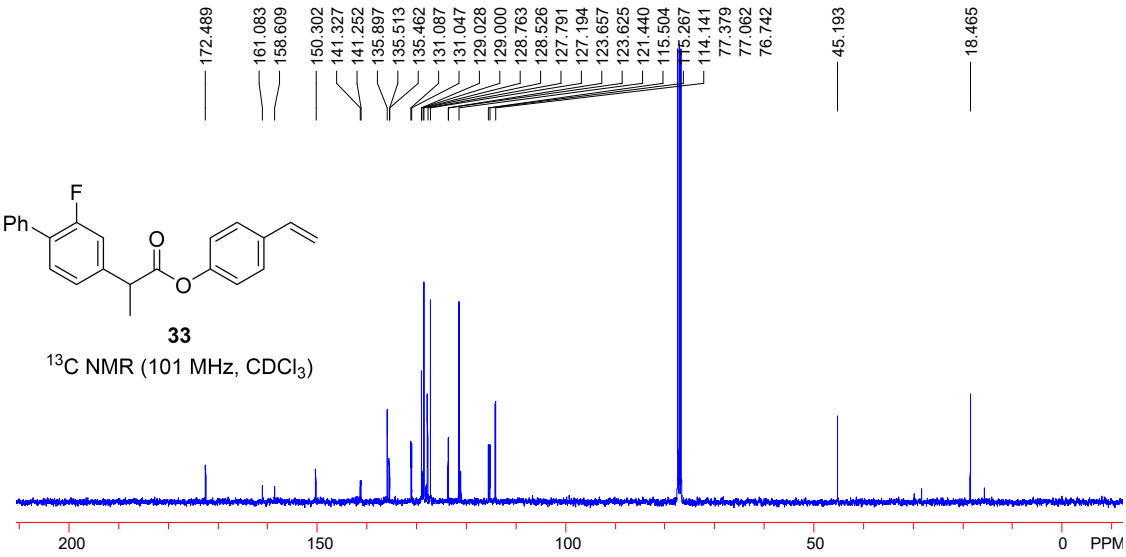

175.129
137.936
137.655
135.565
129.000
127.163
124.732
77.414
77.098
76.778
52.014
45.130
26.923
19.441
18.580
MeO2C
32
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM



33

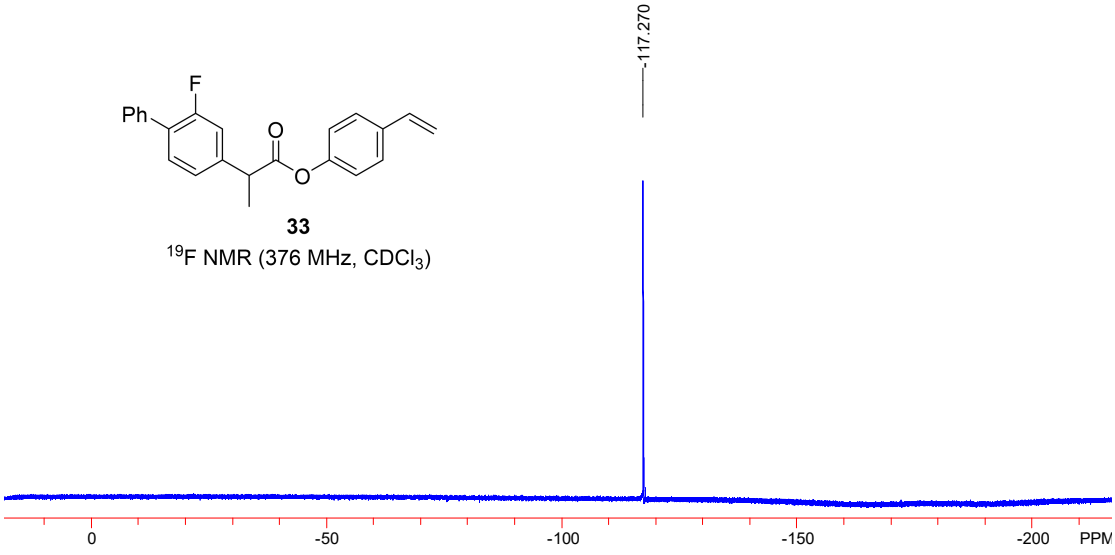
^{1}H NMR (400 MHz, $CDCl_3$)





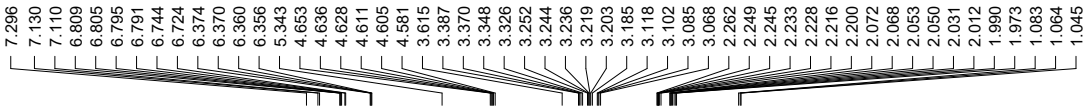
33

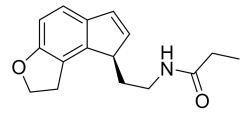
^{13}C NMR (101 MHz, $CDCl_3$)



33

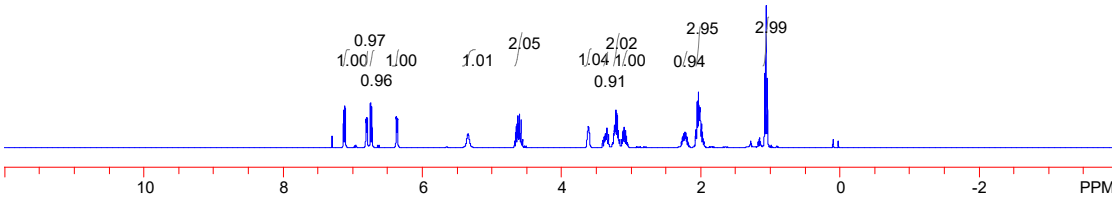
^{19}F NMR (376 MHz, $CDCl_3$)

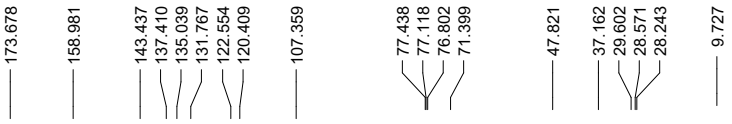


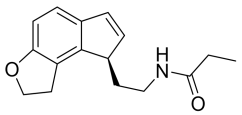


34

^{1}H NMR (400 MHz, $CDCl_3$)

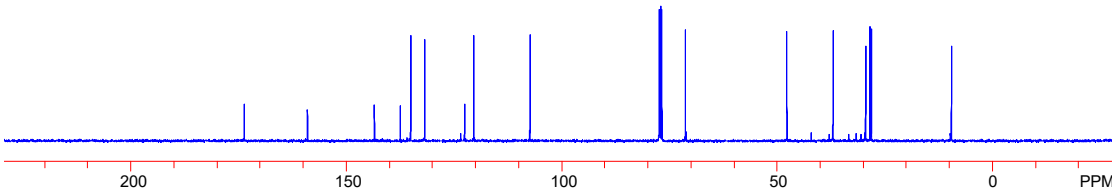


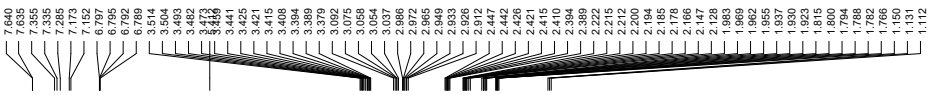


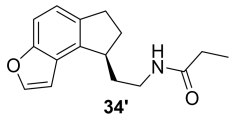


34

^{13}C NMR (101 MHz, $CDCl_3$)

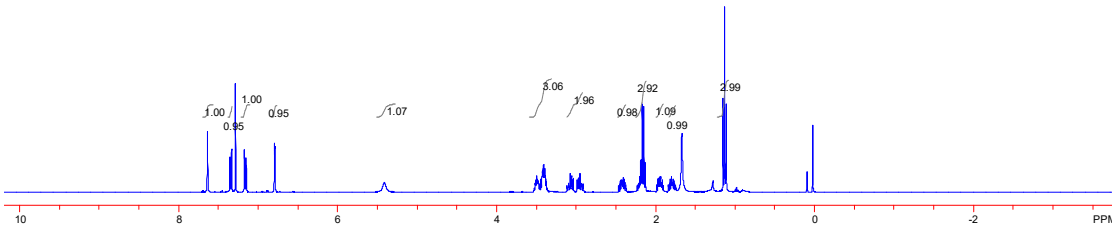


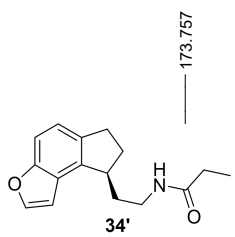




34'

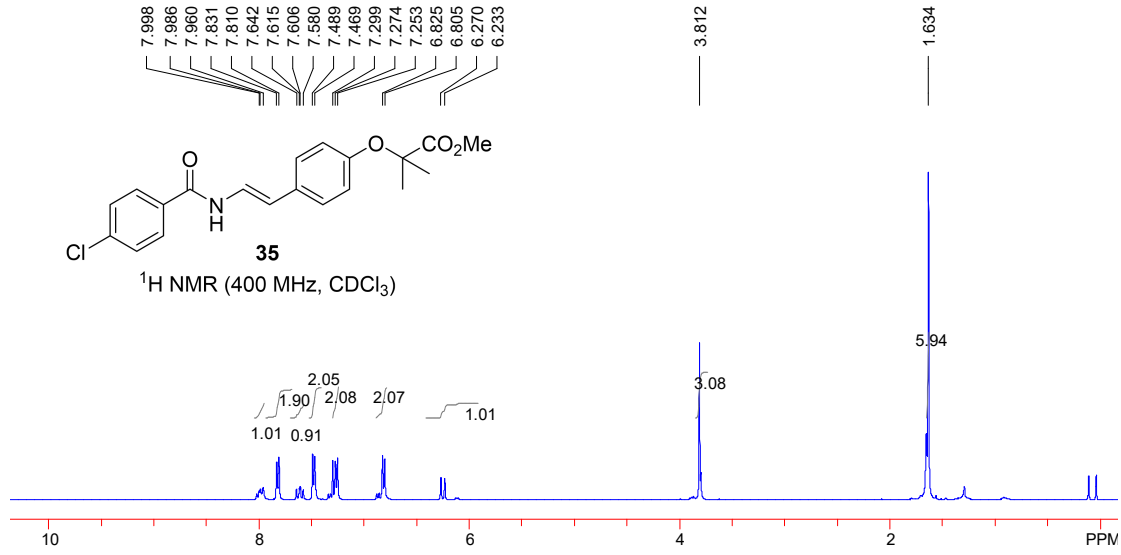
^{1}H NMR (400 MHz, $CDCl_3$)

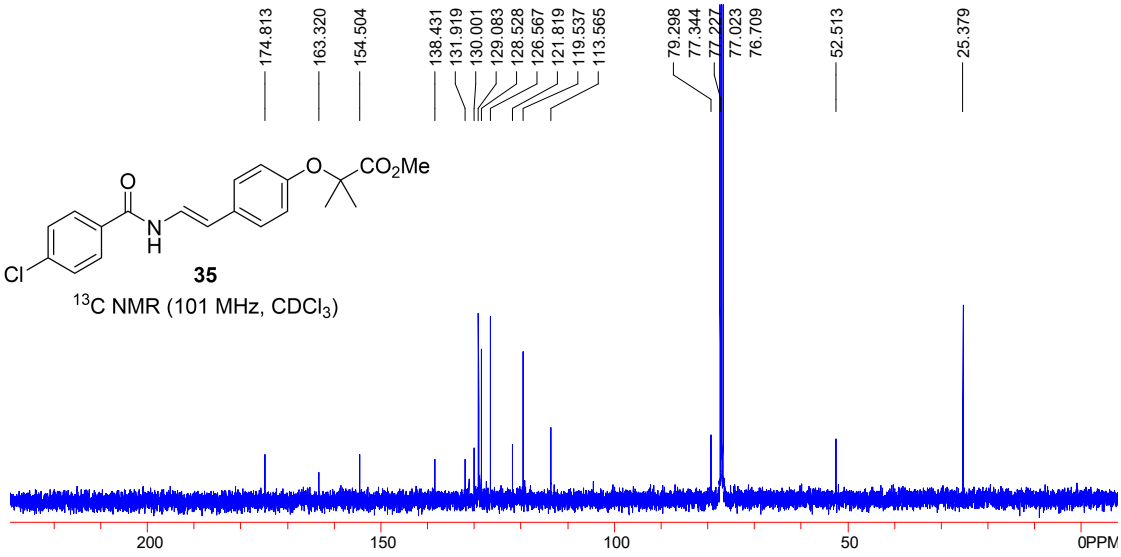


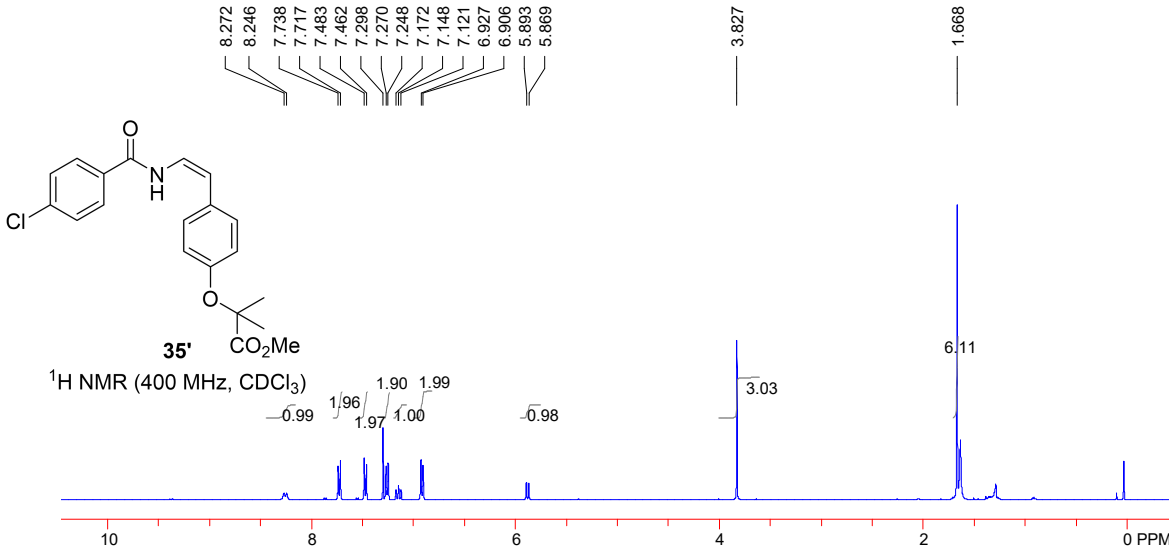


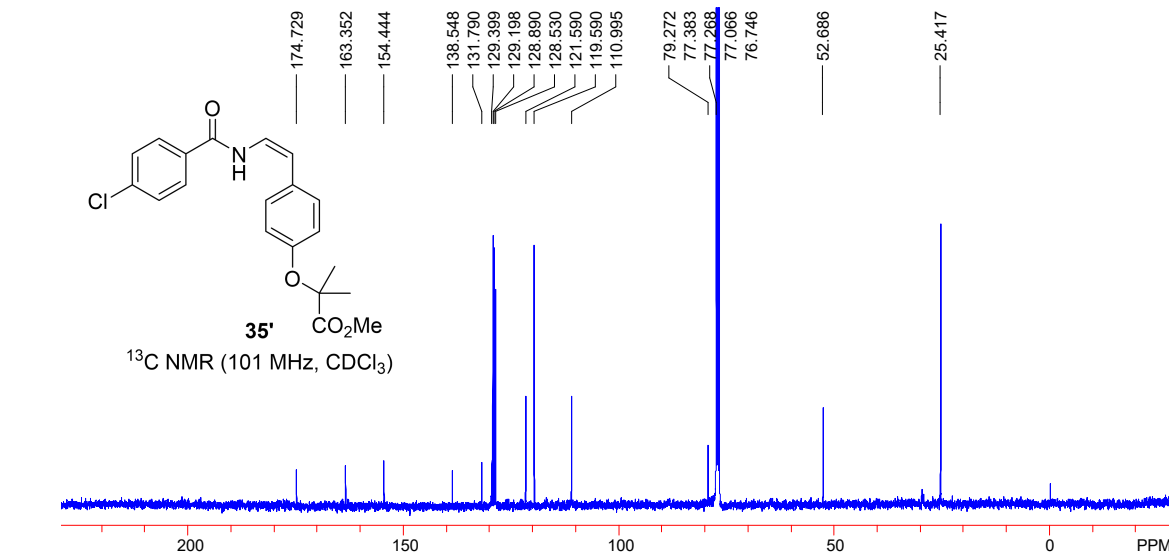
34'

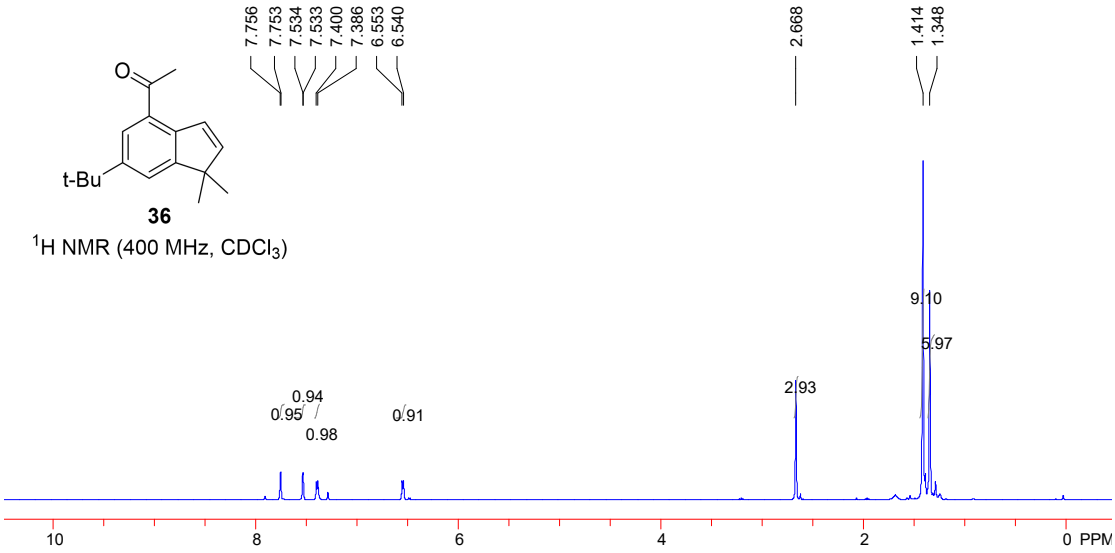
^{13}C NMR (101 MHz, $CDCl_3$)

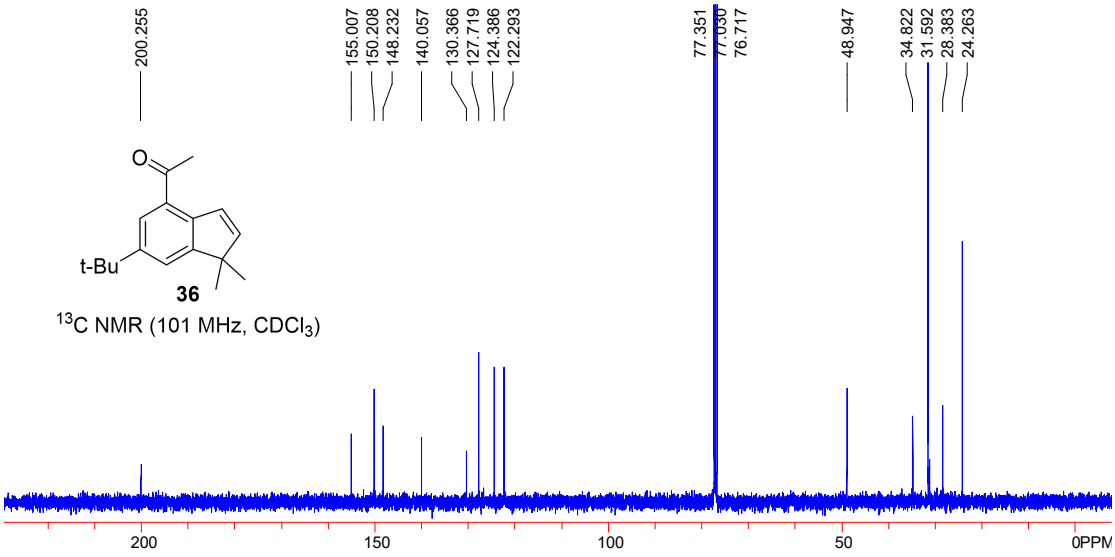

7.998
7.986
7.960
7.831
7.810
7.642
7.615
7.606
7.580
7.489
7.469
7.299
7.274
7.253
6.825
6.805
6.270
6.233
3.812
1.634
O
O
CO2Me
N
H
Cl
35
1H NMR (400 MHz, CDCl3)
2.05
1.90
2.08
2.07
1.01
1.01
0.91
3.08
5.94
10
8
6
4
2
PPM

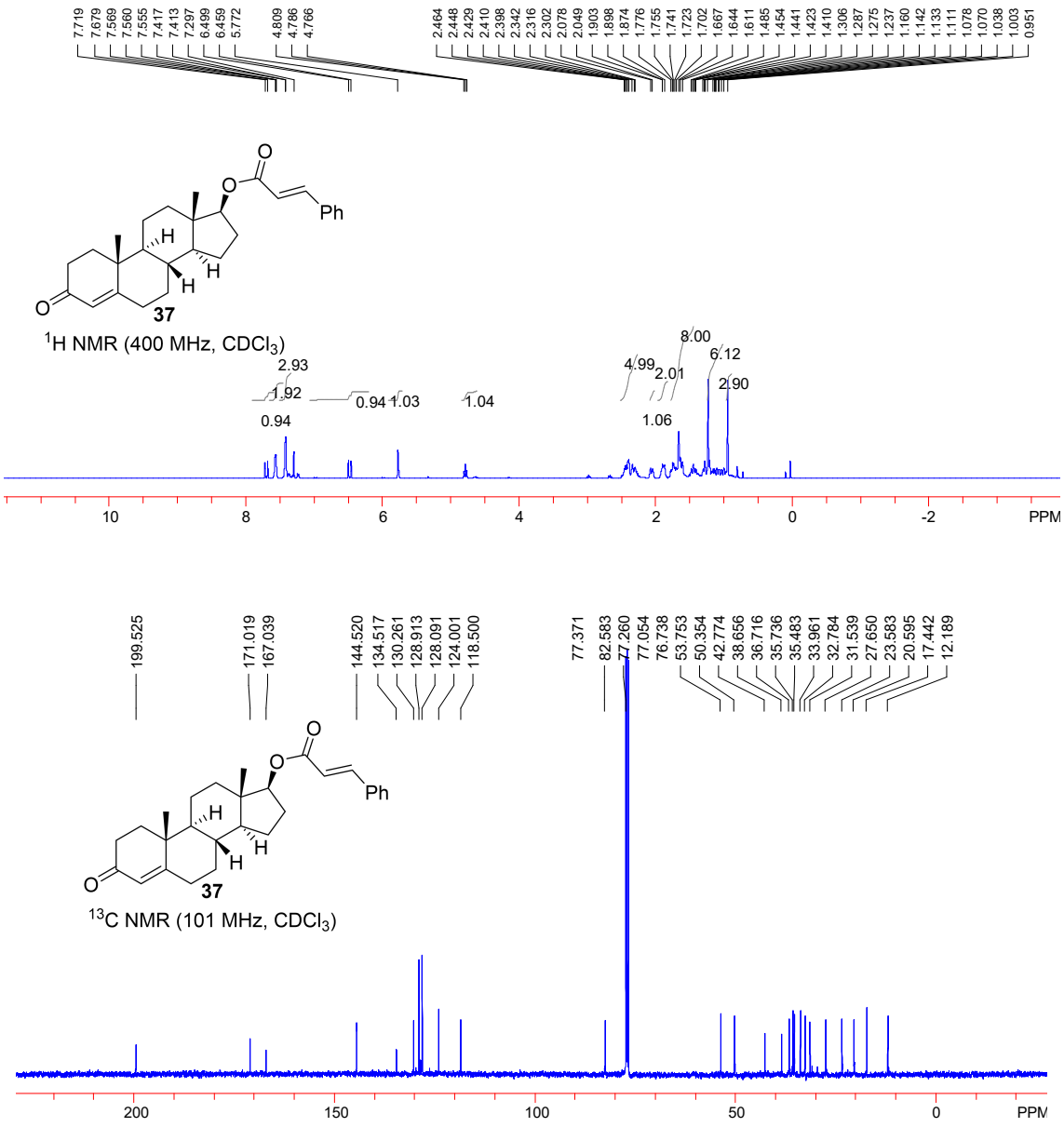

174.813
163.320
154.504
138.431
131.919
130.001
129.083
128.528
126.567
121.819
119.537
113.565
79.298
77.344
77.227
77.023
76.709
52.513
25.379
O
O
CO2Me
N
H
Cl
35
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


8.272
8.246
7.738
7.717
7.483
7.462
7.298
7.270
7.248
7.172
7.148
7.121
6.927
6.906
5.893
5.869
3.827
1.668
Cl
O
N
H
O
CO2Me
35'
1H NMR (400 MHz, CDCl3)
0.99
1.96
1.97
1.90
1.00
1.99
0.98
3.03
6.11
10
8
6
4
2
0 PPM

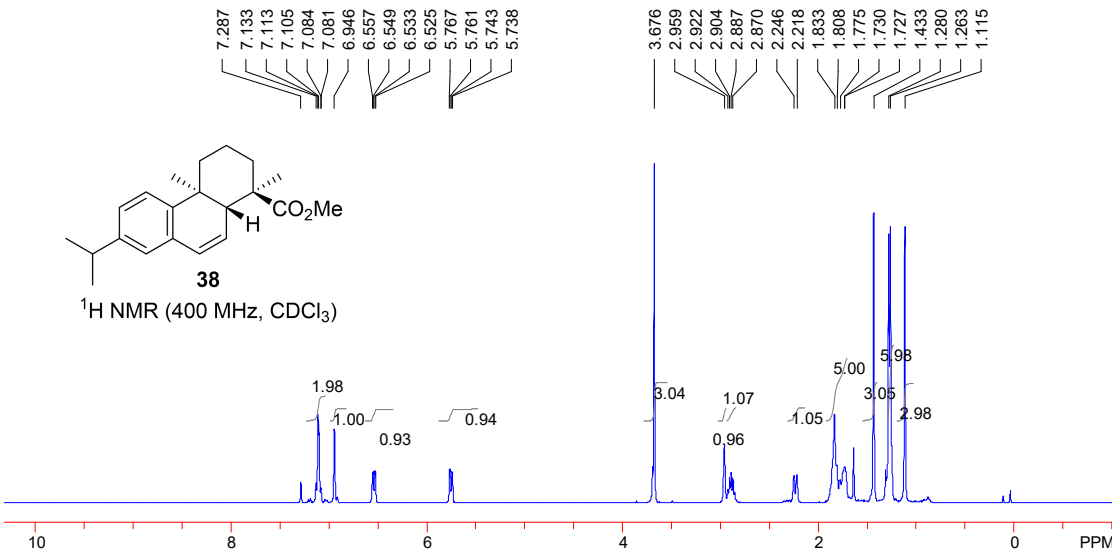

174.729
163.352
154.444
138.548
131.790
129.399
129.198
128.890
128.530
121.590
119.590
110.995
79.272
77.383
77.268
77.066
76.746
52.686
25.417
Cl
O
N
H
O
CO2Me
35'
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

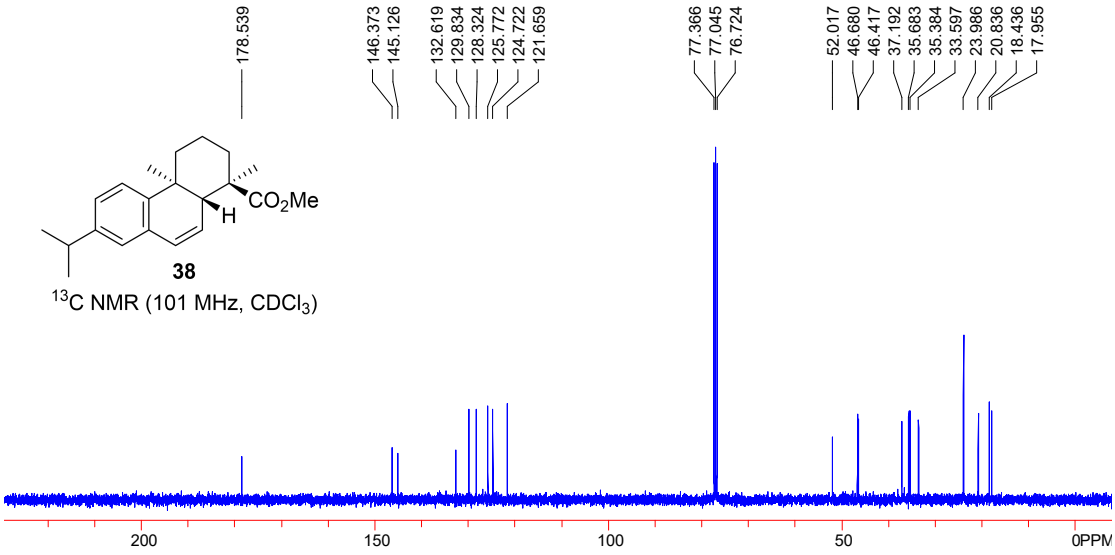

7.756
7.753
7.534
7.533
7.400
7.386
6.553
6.540
2.668
1.414
1.348
O
t-Bu
36
^{1}H NMR (400 MHz, $CDCl_3$)
9.10
5.97
2.93
0.94
0.95
0.98
0.91
10
8
6
4
2
0 PPM

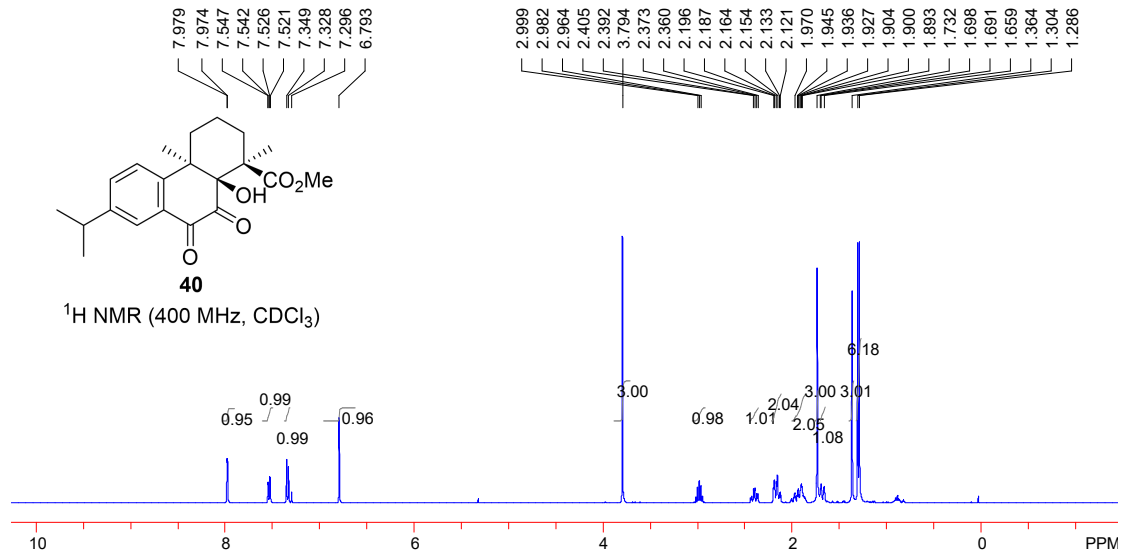

200.255
155.007
150.208
148.232
140.057
130.366
127.719
124.386
122.293
77.351
77.030
76.717
48.947
34.822
31.592
28.383
24.263
O
t-Bu
36
^{13}C NMR (101 MHz, $CDCl_3$)
200
150
100
50
0PPM

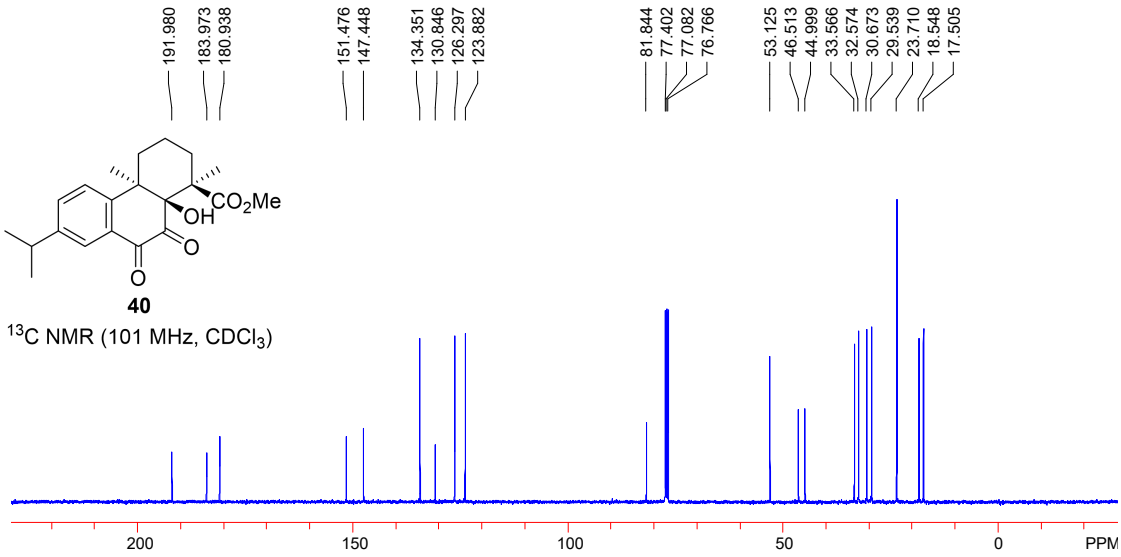

7.719
7.679
7.569
7.560
7.555
7.417
7.413
7.297
6.499
6.459
5.772
4.809
4.786
4.766
2.464
2.448
2.429
2.410
2.398
2.342
2.316
2.302
2.078
2.049
1.903
1.898
1.874
1.776
1.755
1.741
1.723
1.702
1.667
1.644
1.611
1.485
1.454
1.441
1.423
1.410
1.306
1.287
1.275
1.237
1.160
1.142
1.133
1.111
1.078
1.070
1.038
1.003
0.951
O
O
Ph
H
H
O
37
1H NMR (400 MHz, CDCl3)
2.93
1.92
0.94
0.94
1.03
1.04
8.00
6.12
4.99
2.01
2.90
1.06
10
8
6
4
2
0
-2
PPM

199.525
171.019
167.039
144.520
134.517
130.261
128.913
128.091
124.001
118.500
77.371
82.583
77.260
77.054
76.738
53.753
50.354
42.774
38.656
36.716
35.736
35.483
33.961
32.784
31.539
27.650
23.583
20.595
17.442
12.189
O
O
Ph
H
H
O
37
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.287
7.133
7.113
7.105
7.084
7.081
6.946
6.557
6.549
6.533
6.525
5.767
5.761
5.743
5.738
3.676
2.959
2.922
2.904
2.887
2.870
2.246
2.218
1.833
1.808
1.775
1.730
1.727
1.433
1.280
1.263
1.115
CO2Me
H
38
1H NMR (400 MHz, CDCl3)
1.98
1.00
0.93
0.94
3.04
1.07
0.96
1.05
5.00
5.98
3.05
2.98
10
8
6
4
2
0
PPM


178.539
146.373
145.126
132.619
129.834
128.324
125.772
124.722
121.659
77.366
77.045
76.724
52.017
46.680
46.417
37.192
35.683
35.384
33.597
23.986
20.836
18.436
17.955
CO2Me
H
38
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


7.979
7.974
7.547
7.542
7.526
7.521
7.349
7.328
7.296
6.793
2.999
2.982
2.964
2.405
2.392
3.794
2.373
2.360
2.196
2.187
2.164
2.154
2.133
2.121
1.970
1.945
1.936
1.927
1.904
1.900
1.893
1.732
1.698
1.691
1.659
1.364
1.304
1.286
CO2Me
OH
O
O
40
1H NMR (400 MHz, CDCl3)
0.95
0.99
0.99
0.96
3.00
0.98
1.01
2.04
2.05
3.00
3.01
1.08
6.18
10
8
6
4
2
0
PPM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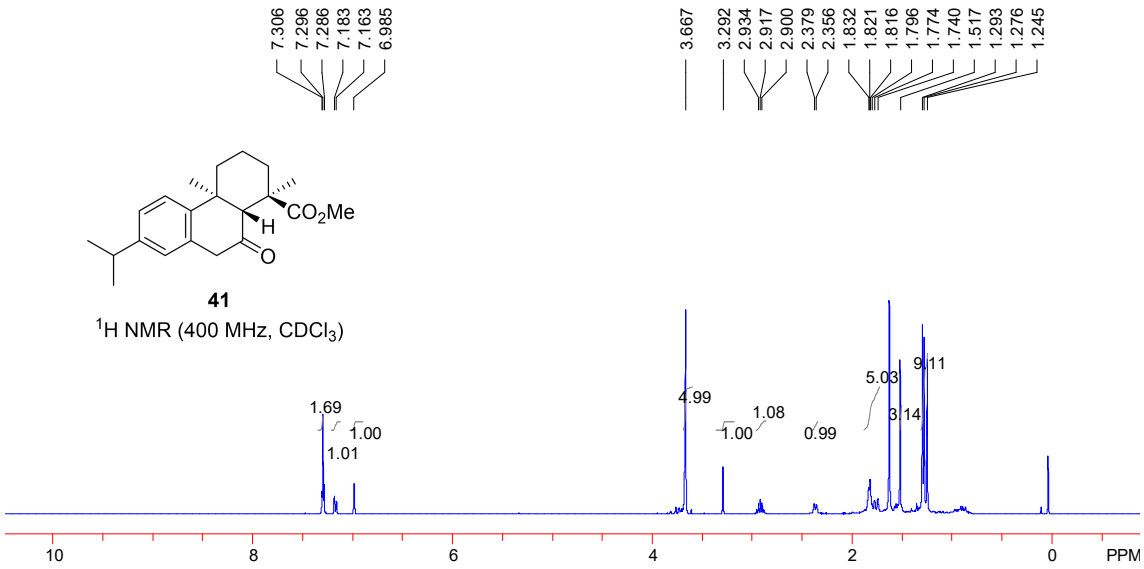
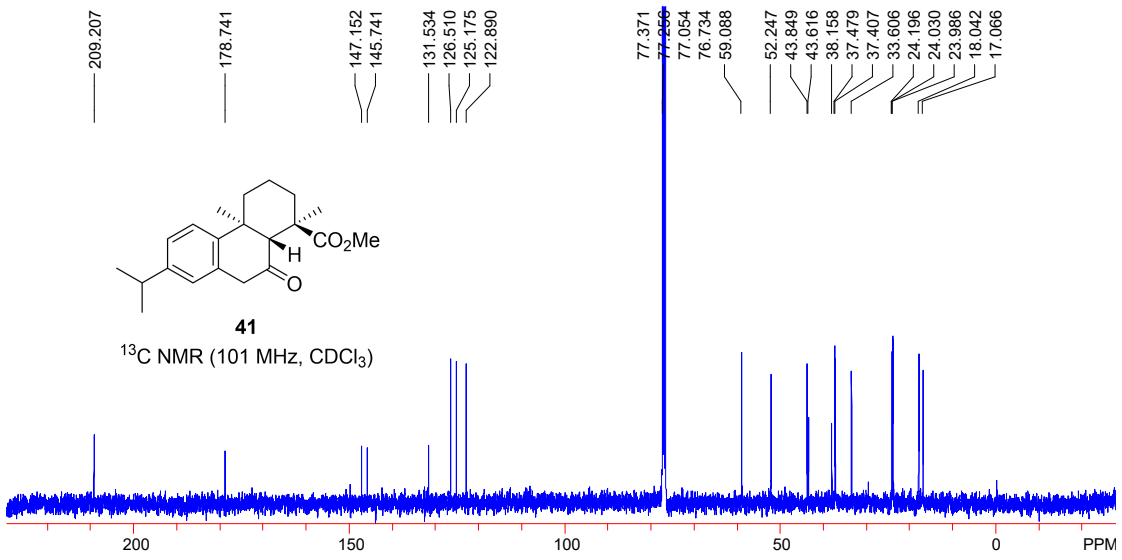
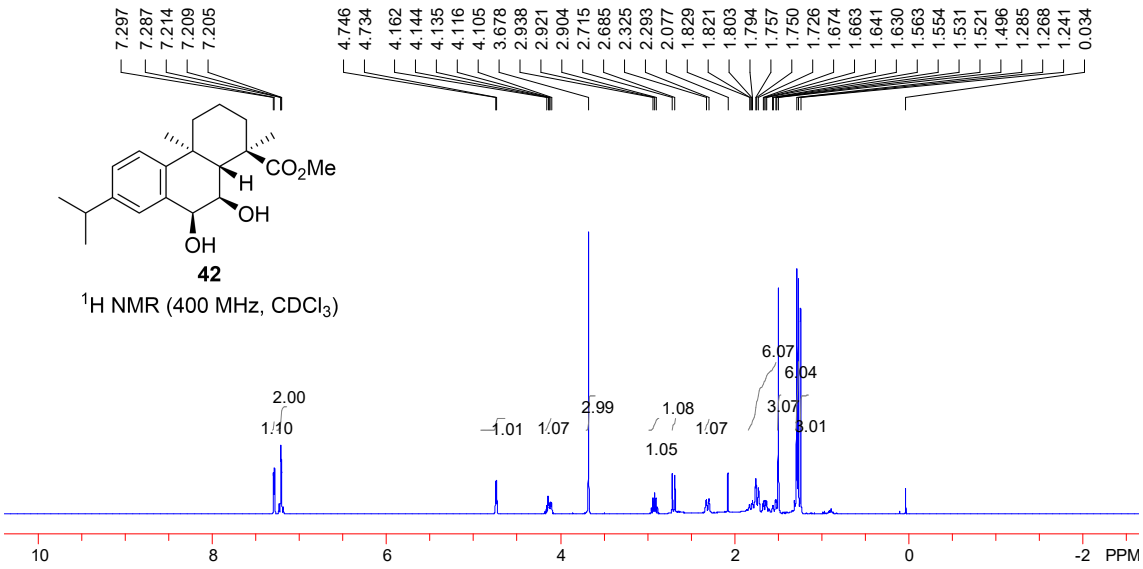
183.973
180.938
151.476
147.448
134.351
130.846
126.297
123.882
81.844
77.402
77.082
76.766
53.125
46.513
44.999
33.566
32.574
30.673
29.539
23.710
18.548
17.505
CO2Me
OH
O
O
40
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.306
7.296
7.286
7.183
7.163
6.985
3.667
3.292
2.934
2.917
2.900
2.379
2.356
1.832
1.821
1.816
1.796
1.774
1.740
1.517
1.293
1.276
1.245
CO2Me
H
O
41
1H NMR (400 MHz, CDCl3)
1.69
1.00
1.01
4.99
1.00
1.08
0.99
5.03
3.14
9.11
10
8
6
4
2
0
PPM


209.207
178.741
147.152
145.741
131.534
126.510
125.175
122.890
77.371
77.054
76.734
59.088
52.247
43.849
43.616
38.158
37.479
37.407
33.606
24.196
24.030
23.986
18.042
17.066
CO2Me
H
O
41
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM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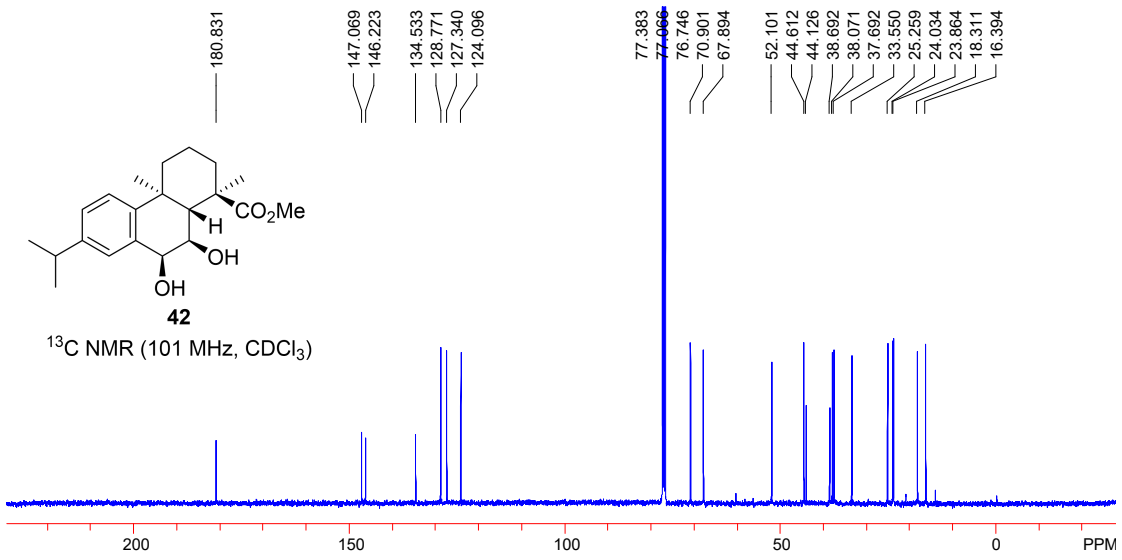
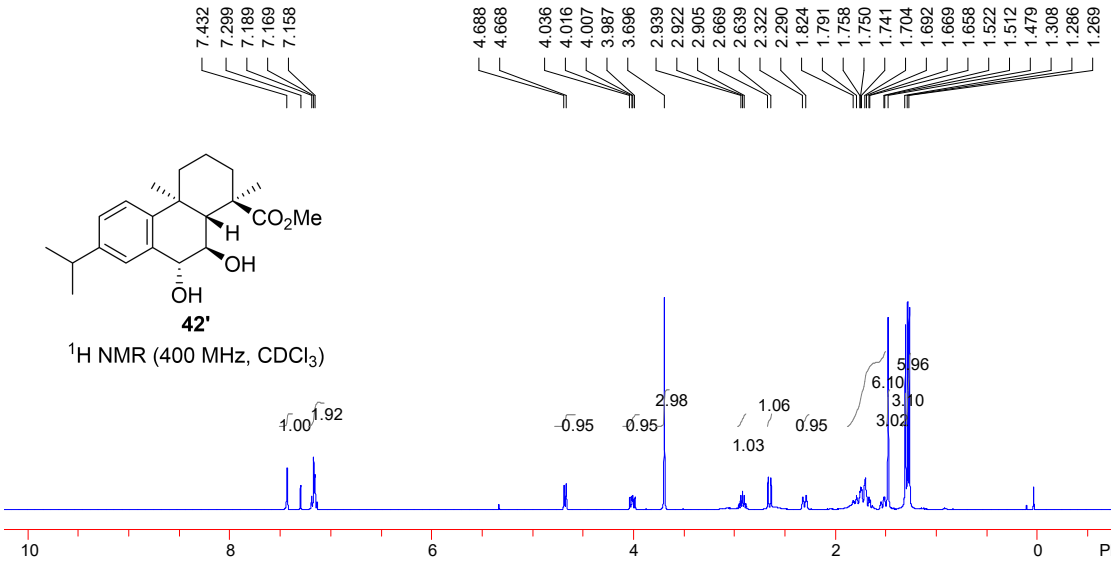
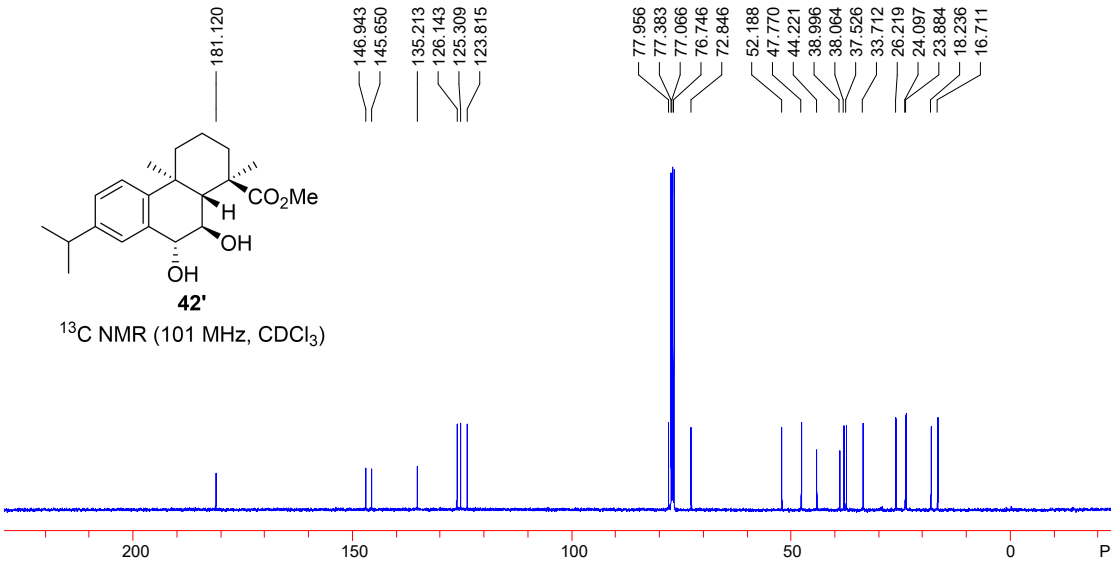
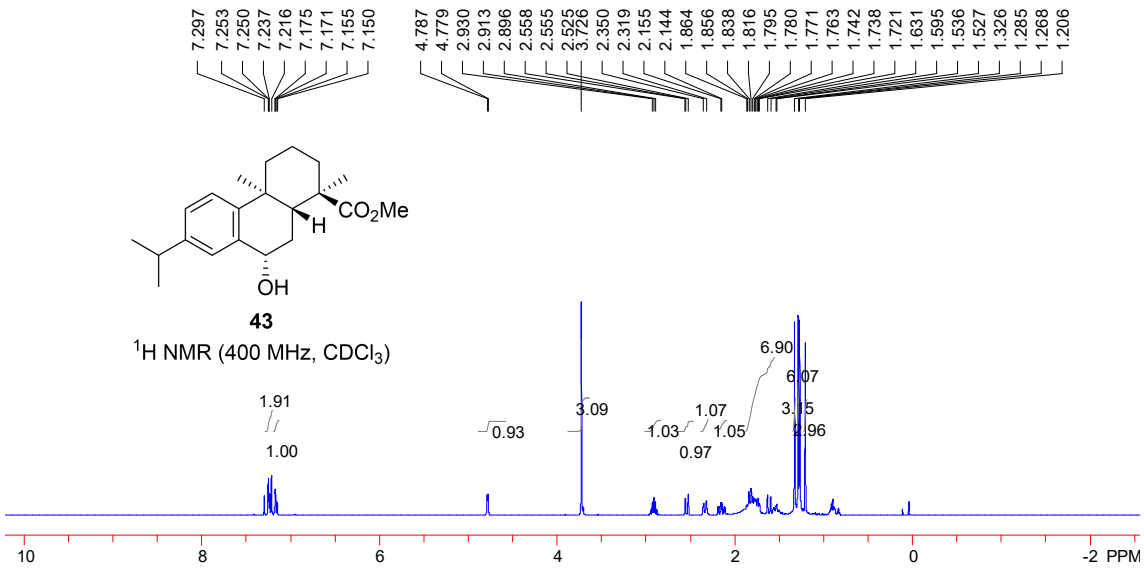
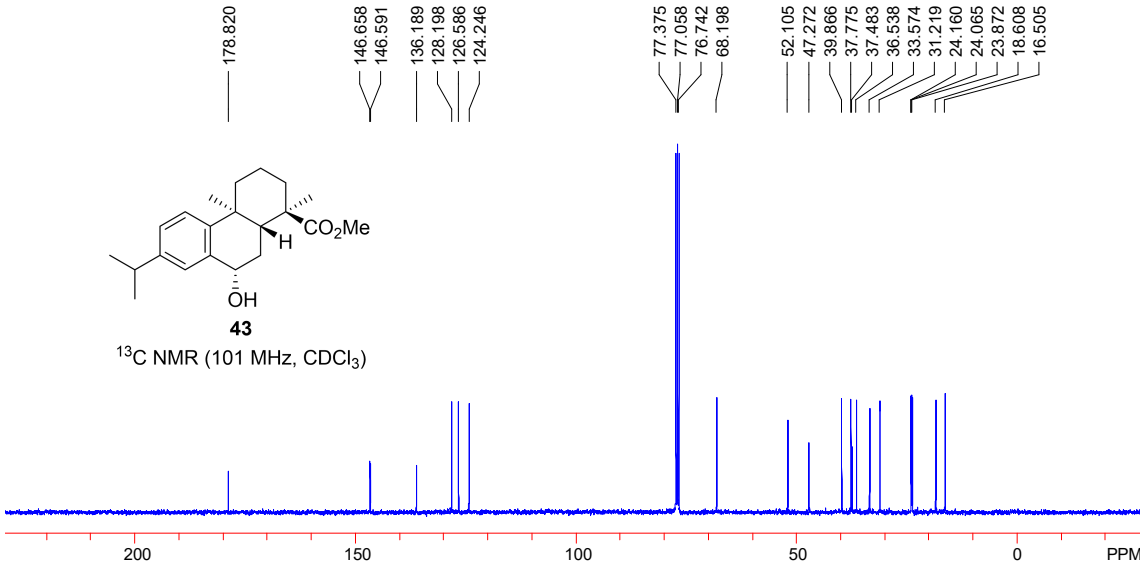
7.287
7.214
7.209
7.205
4.746
4.734
4.162
4.144
4.135
4.116
4.105
3.678
2.938
2.921
2.904
2.715
2.685
2.325
2.293
2.077
1.829
1.821
1.803
1.794
1.757
1.750
1.726
1.674
1.663
1.641
1.630
1.563
1.554
1.531
1.521
1.496
1.285
1.268
1.241
0.034
CO2Me
H
OH
OH
42
1H NMR (400 MHz, CDCl3)
2.00
1.10
1.01
1.07
2.99
1.08
1.05
1.07
6.07
6.04
3.07
3.01
10
8
6
4
2
0
-2
PPM

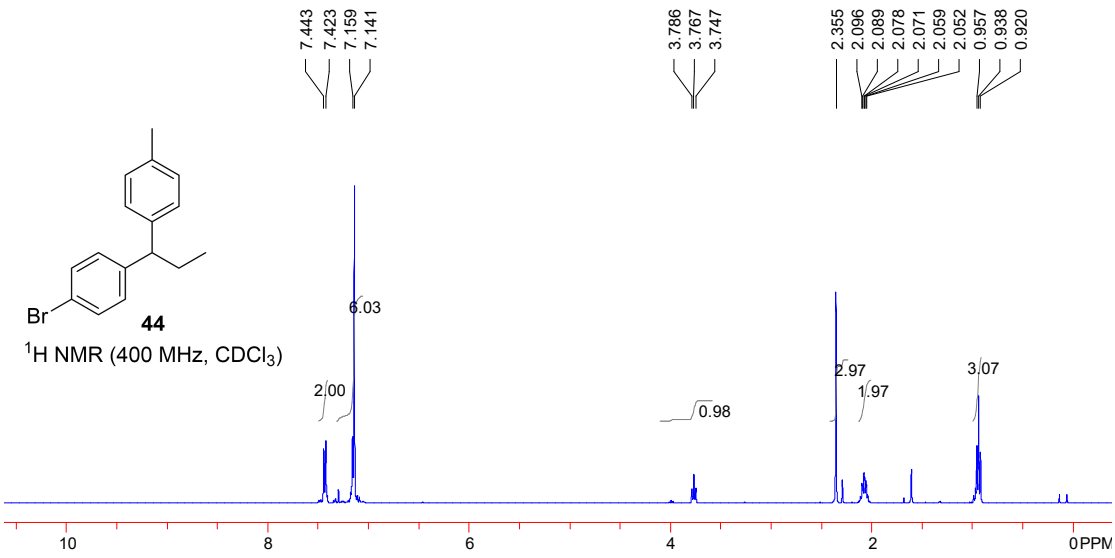

180.831
147.069
146.223
134.533
128.771
127.340
124.096
77.383
77.066
76.746
70.901
67.894
52.101
44.612
44.126
38.892
38.071
37.692
33.550
25.259
24.034
23.864
18.311
16.394
CO2Me
H
OH
OH
42
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

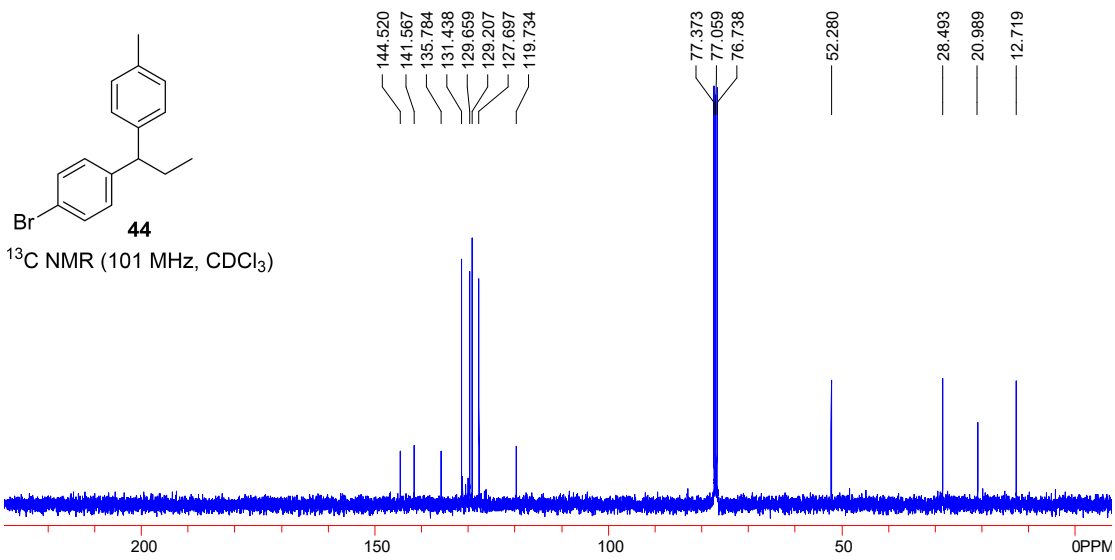

7.432
7.299
7.189
7.169
7.158
4.688
4.668
4.036
4.016
4.007
3.987
3.696
2.939
2.922
2.905
2.669
2.639
2.322
2.290
1.824
1.791
1.758
1.750
1.741
1.704
1.692
1.669
1.658
1.522
1.512
1.479
1.308
1.286
1.269
CO2Me
H
OH
OH
42'
1H NMR (400 MHz, CDCl3)
1.00
1.92
0.95
0.95
2.98
1.03
1.06
0.95
3.02
6.10
5.96
3.10
10
8
6
4
2
0
P

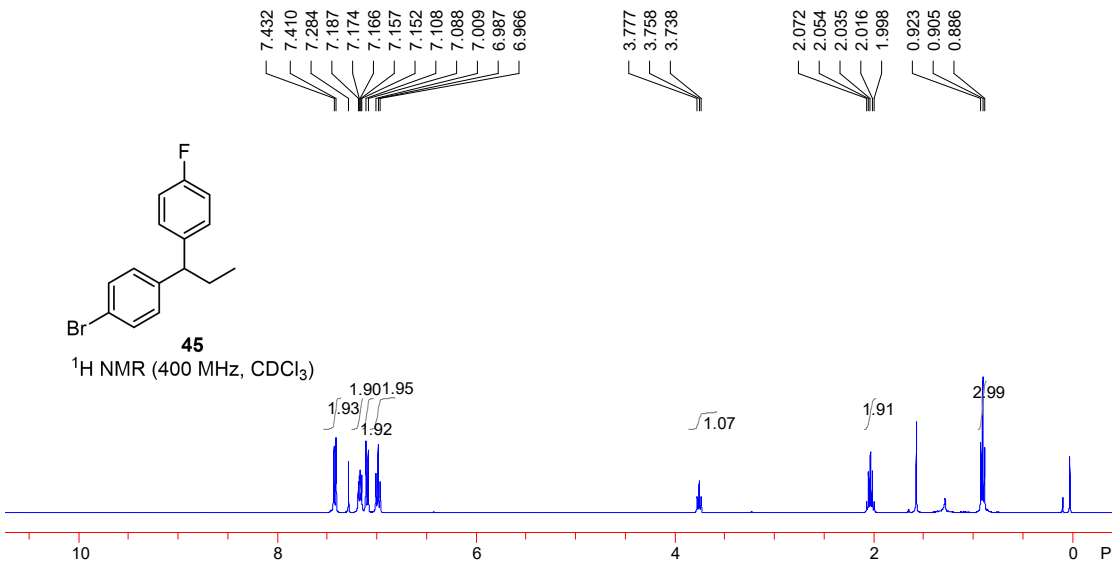

181.120
146.943
145.650
135.213
126.143
125.309
123.815
77.956
77.383
77.066
76.746
72.846
52.188
47.770
44.221
38.996
38.064
37.526
33.712
26.219
24.097
23.884
18.236
16.711
CO2Me
H
OH
OH
42'
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
P

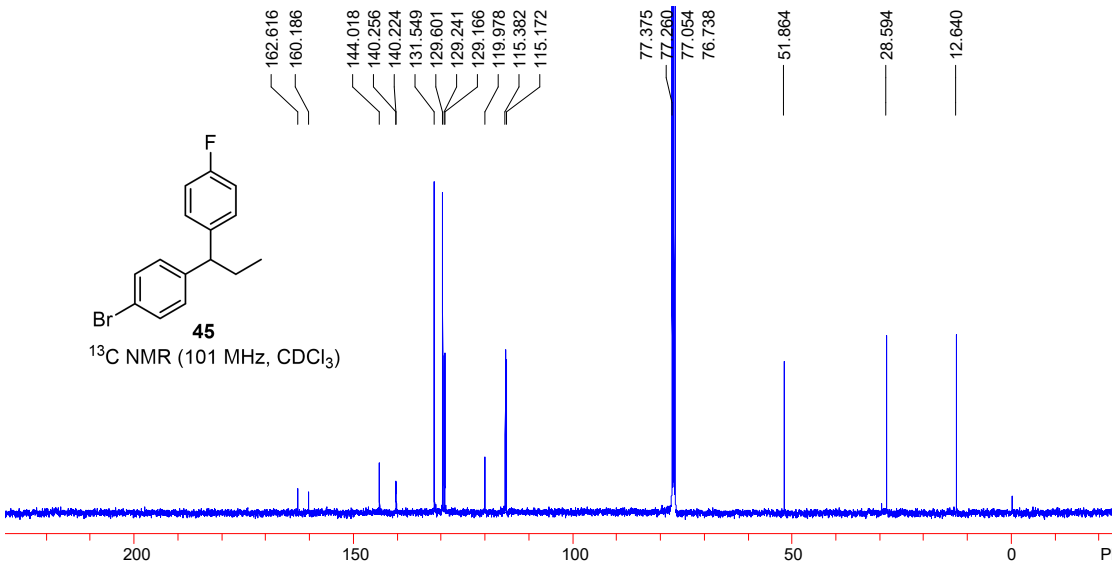

7.297
7.253
7.250
7.237
7.216
7.175
7.171
7.155
7.150
4.787
4.779
2.930
2.913
2.896
2.558
2.555
2.525
3.726
2.350
2.319
2.155
2.144
1.864
1.856
1.838
1.816
1.795
1.780
1.771
1.763
1.742
1.738
1.721
1.631
1.595
1.536
1.527
1.326
1.285
1.268
1.206
CO2Me
H
OH
43
1H NMR (400 MHz, CDCl3)
1.91
1.00
0.93
3.09
1.03
1.07
0.97
1.05
6.90
6.07
3.05
2.96
10
8
6
4
2
0
-2 PPM

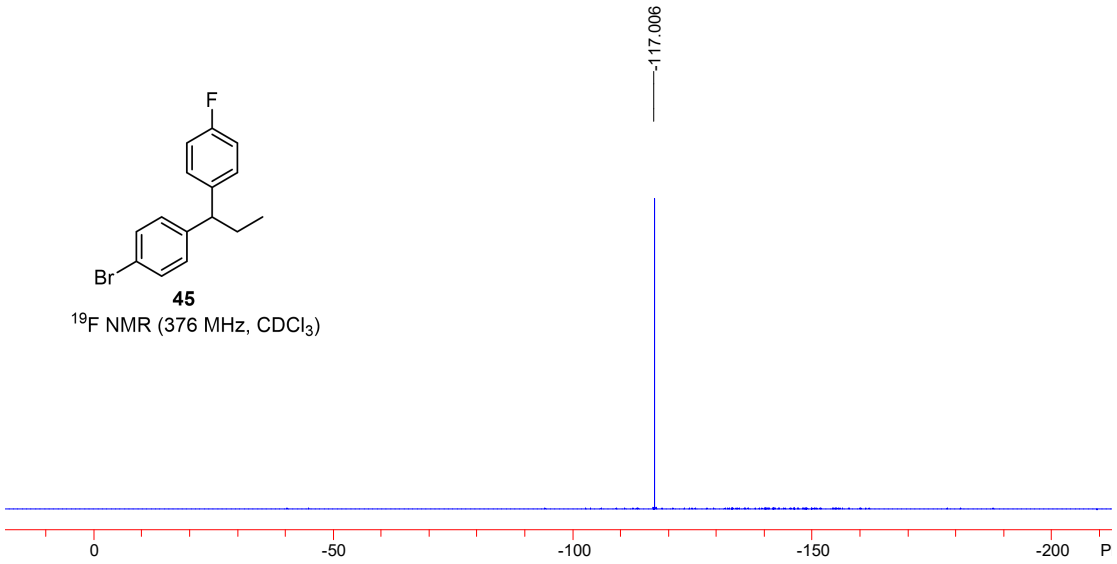

178.820
146.658
146.591
136.189
128.198
126.586
124.246
77.375
77.058
76.742
68.198
52.105
47.272
39.866
37.775
37.483
36.538
33.574
31.219
24.160
24.065
23.872
18.608
16.505
CO2Me
H
OH
43
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.443
7.423
7.159
7.141
3.786
3.767
3.747
2.355
2.096
2.089
2.078
2.071
2.059
2.052
0.957
0.938
0.920
Br
44
1H NMR (400 MHz, CDCl3)
6.03
2.00
0.98
2.97
1.97
3.07
10
8
6
4
2
0PPM


144.520
141.567
135.784
131.438
129.659
129.207
127.697
119.734
77.373
77.059
76.738
52.280
28.493
20.989
12.719
Br
44
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

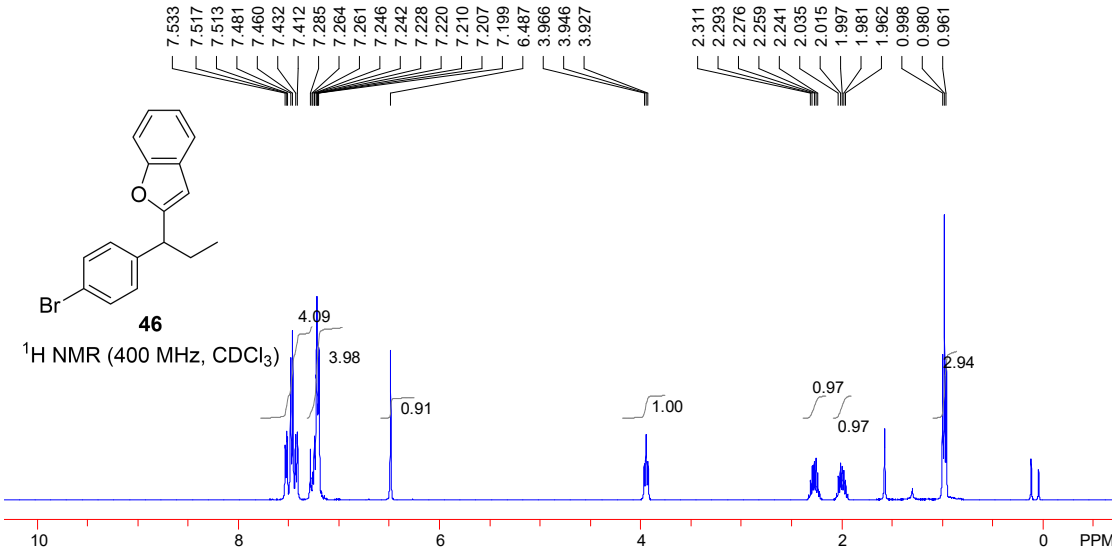

7.432
7.410
7.284
7.187
7.174
7.166
7.157
7.152
7.108
7.088
7.009
6.987
6.966
3.777
3.758
3.738
2.072
2.054
2.035
2.016
1.998
0.923
0.905
0.886
F
Br
45
1H NMR (400 MHz, CDCl3)
1.93
1.90
1.95
1.92
1.07
1.91
2.99
10
8
6
4
2
0
P

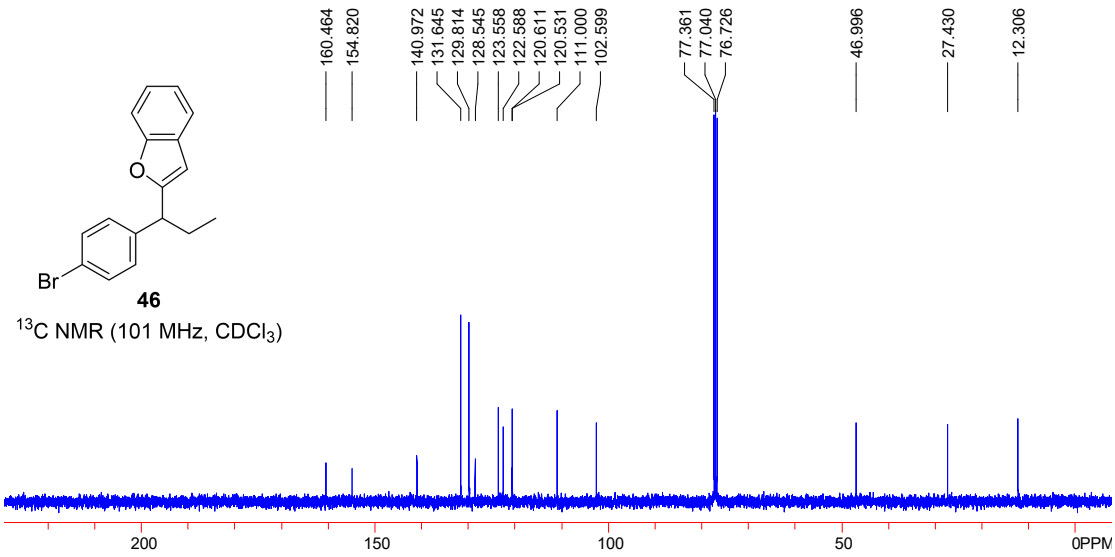

162.616
160.186
144.018
140.256
140.224
131.549
129.601
129.241
129.166
119.978
115.382
115.172
77.375
77.260
77.054
76.738
51.864
28.594
12.640
F
Br
45
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
P

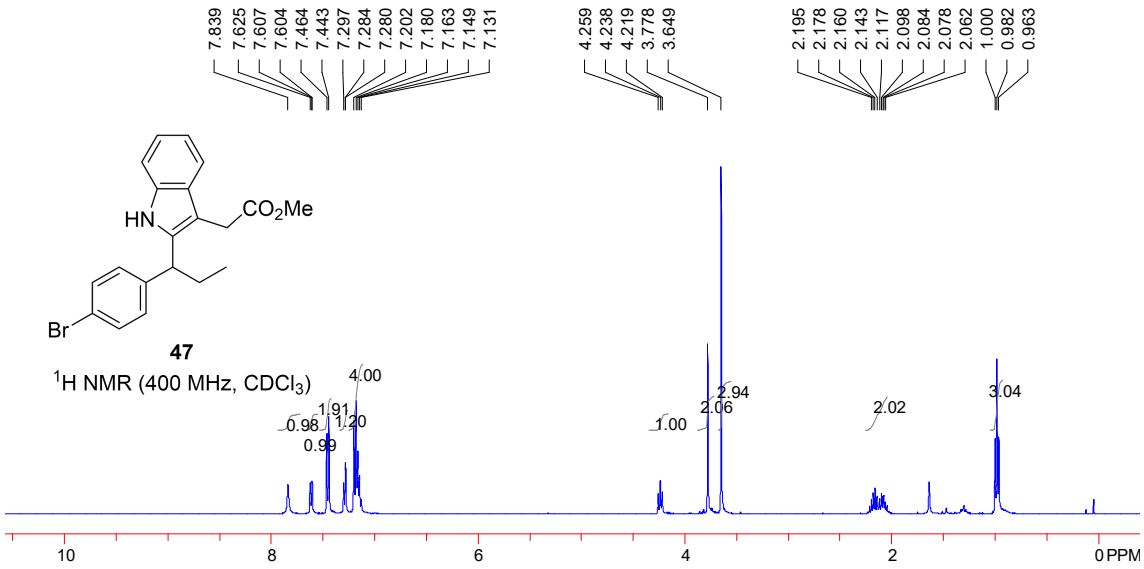


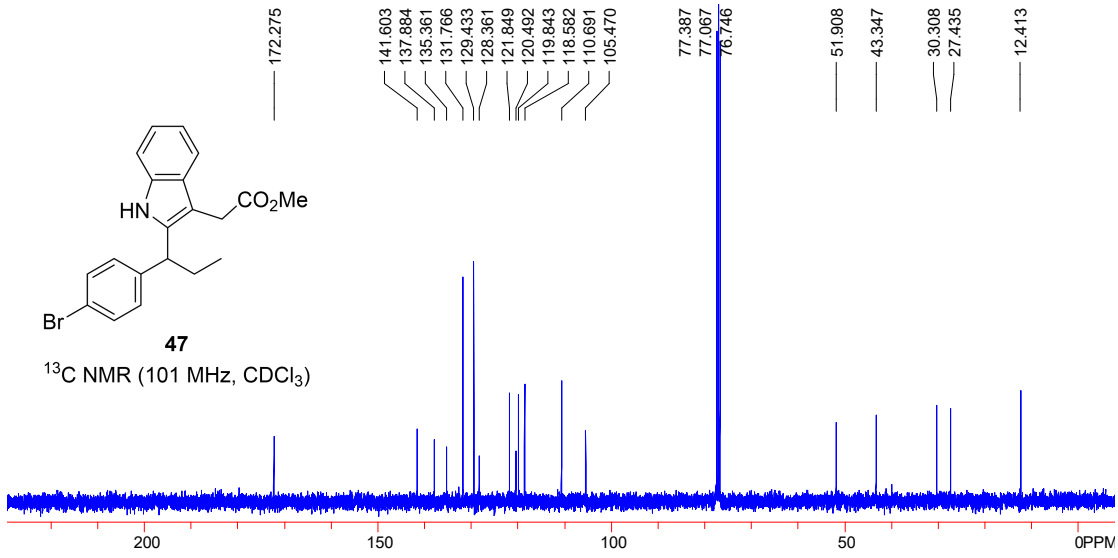
45

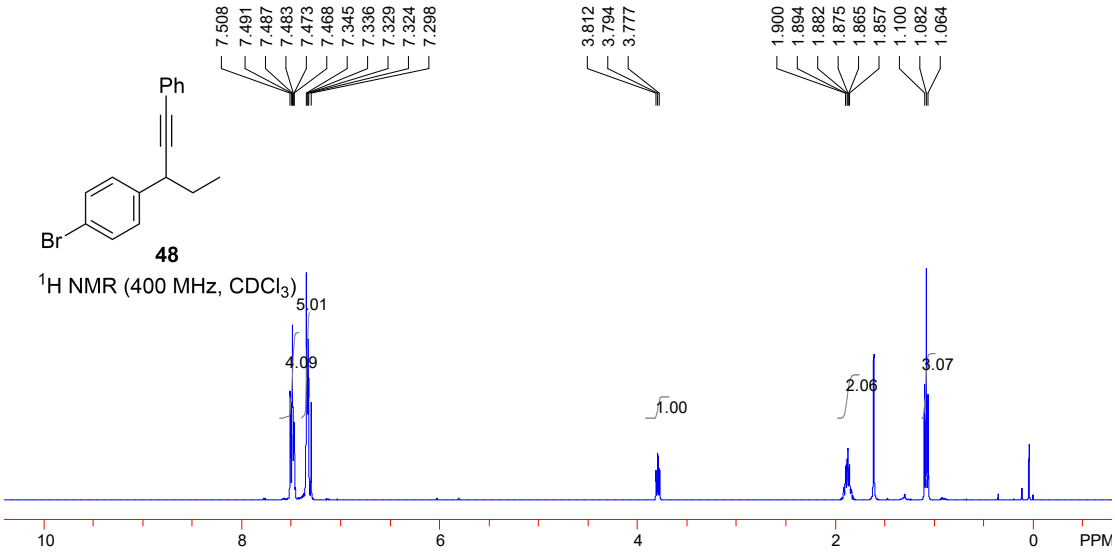
^{19}F NMR (376 MHz, $CDCl_3$)

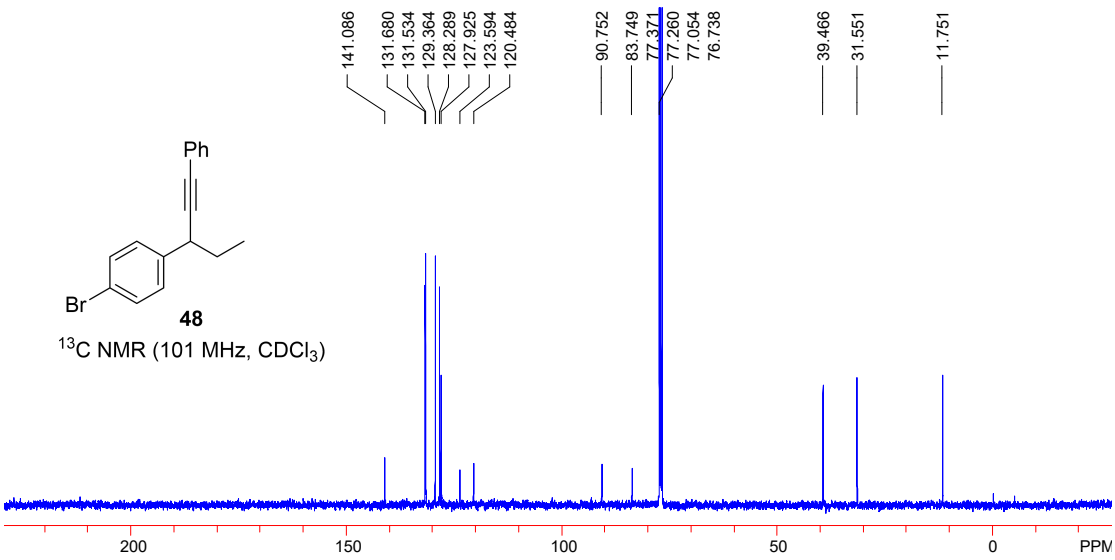

7.533
7.517
7.513
7.481
7.460
7.432
7.412
7.285
7.264
7.261
7.246
7.242
7.228
7.220
7.210
7.207
7.199
6.487
3.966
3.946
3.927
2.311
2.293
2.276
2.259
2.241
2.035
2.015
1.997
1.981
1.962
0.998
0.980
0.961
Br
O
46
1H NMR (400 MHz, CDCl3)
4.09
3.98
0.91
1.00
0.97
0.97
2.94
10
8
6
4
2
0
PPM

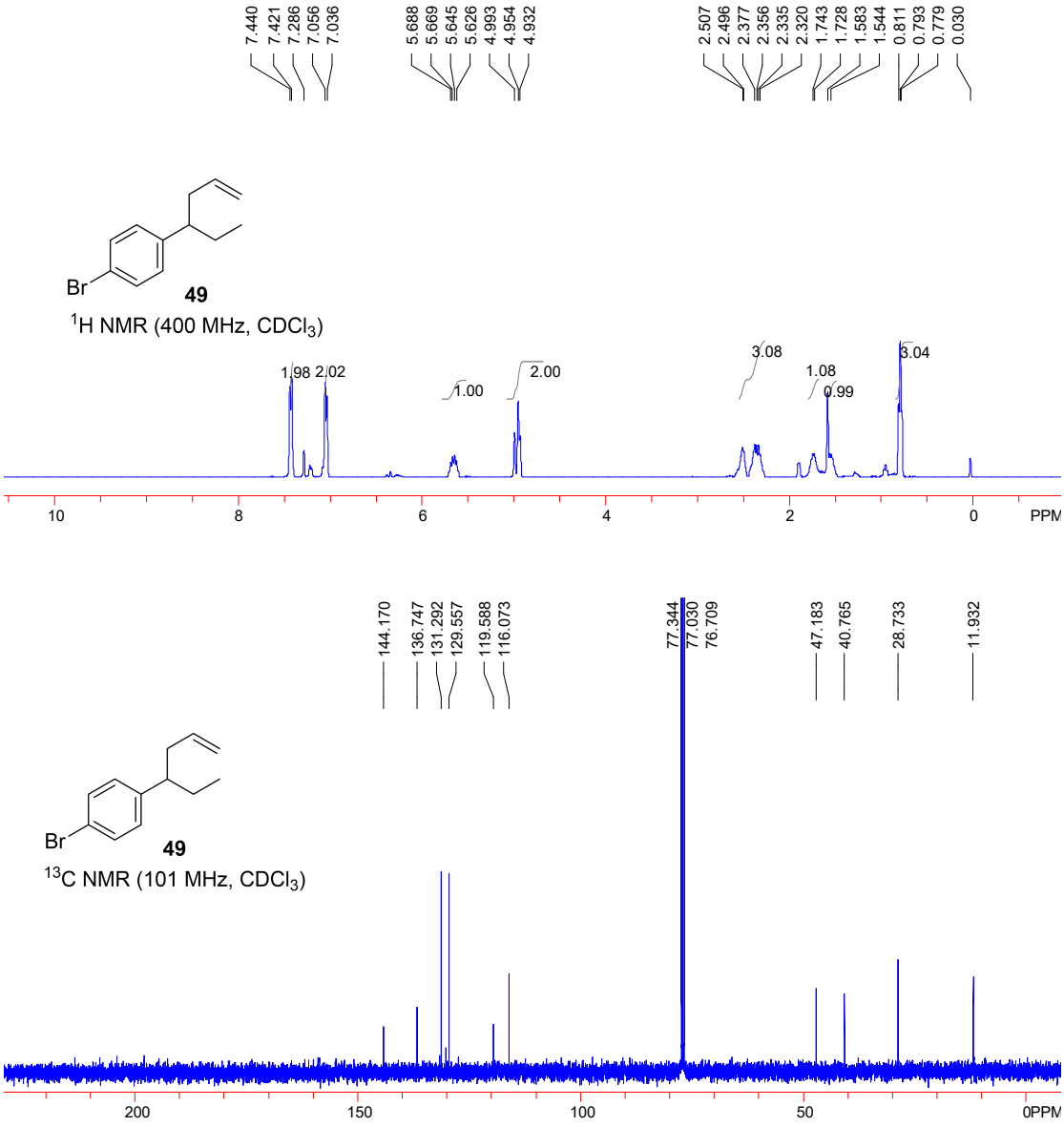

160.464
154.820
140.972
131.645
129.814
128.545
123.558
122.588
120.611
120.531
111.000
102.599
77.361
77.040
76.726
46.996
27.430
12.306
Br
O
46
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

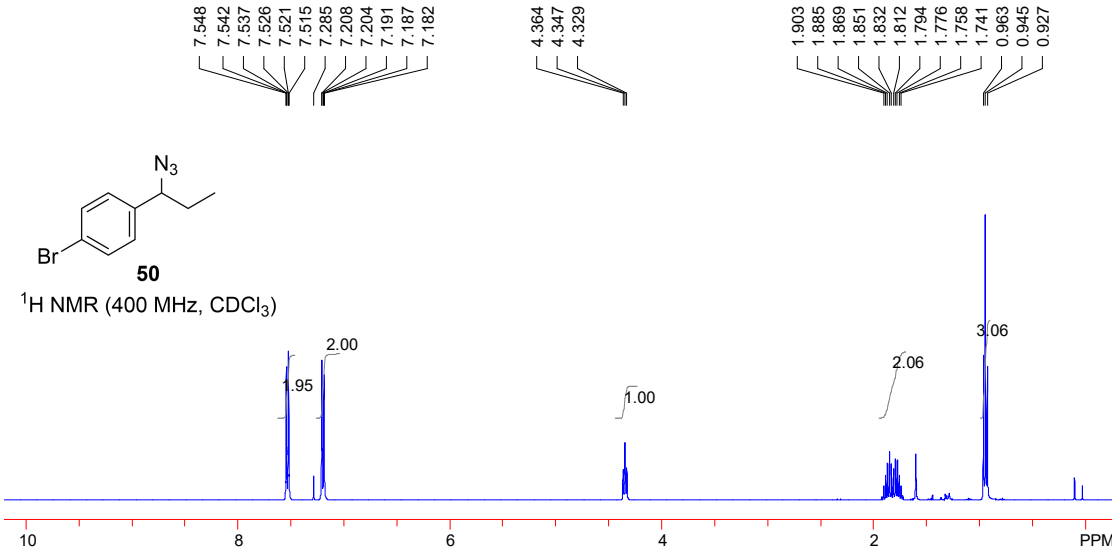

7.839
7.625
7.607
7.604
7.464
7.443
7.297
7.284
7.280
7.202
7.180
7.163
7.149
7.131
4.259
4.238
4.219
3.778
3.649
2.195
2.178
2.160
2.143
2.117
2.098
2.084
2.078
2.062
1.000
0.982
0.963
HN
CO2Me
Br
47
1H NMR (400 MHz, CDCl3)
4.00
1.91
1.20
0.98
0.99
1.00
2.94
2.06
2.02
3.04
10
8
6
4
2
0 PPM

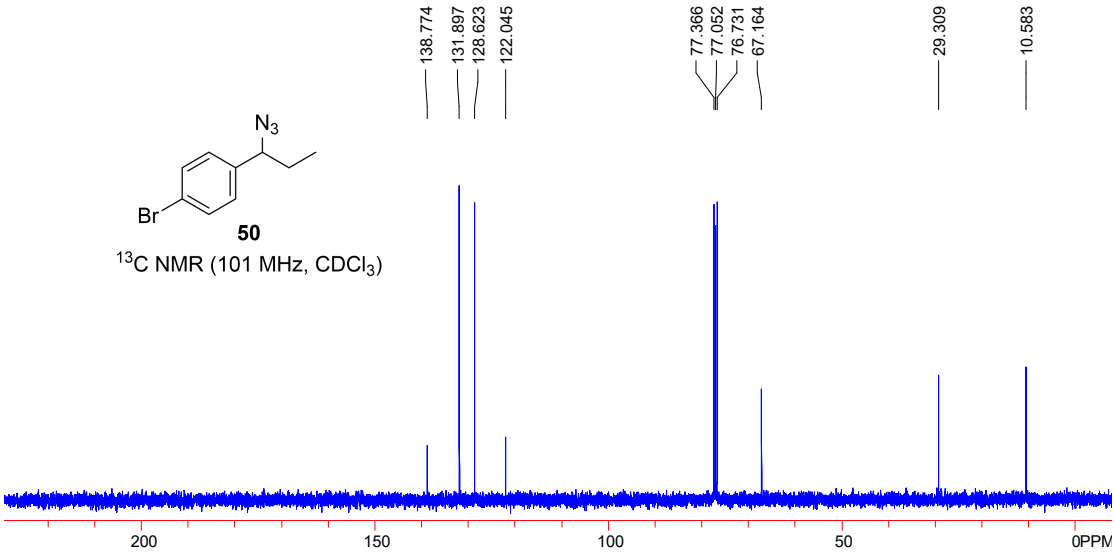

172.275
141.603
137.884
135.361
131.766
129.433
128.361
121.849
120.492
119.843
118.582
110.691
105.470
77.387
77.067
76.746
51.908
43.347
30.308
27.435
12.413
HN
CO2Me
Br
47
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

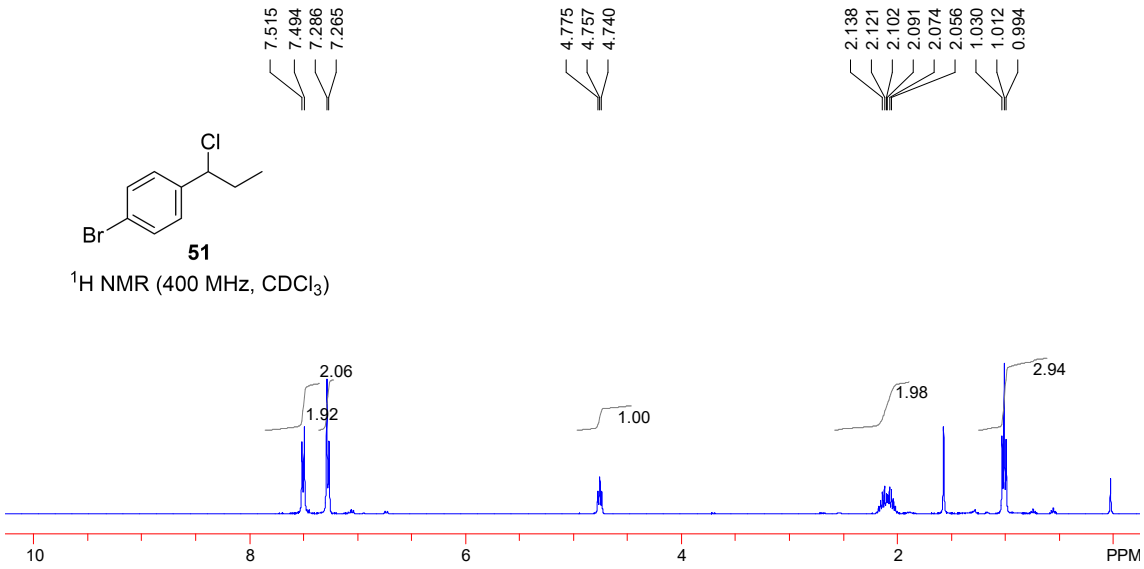

7.508
7.491
7.487
7.483
7.473
7.468
7.345
7.336
7.329
7.324
7.298
3.812
3.794
3.777
1.900
1.894
1.882
1.875
1.865
1.857
1.100
1.082
1.064
Ph
Br
48
1H NMR (400 MHz, CDCl3)
5.01
4.09
1.00
2.06
3.07
10
8
6
4
2
0
PPM

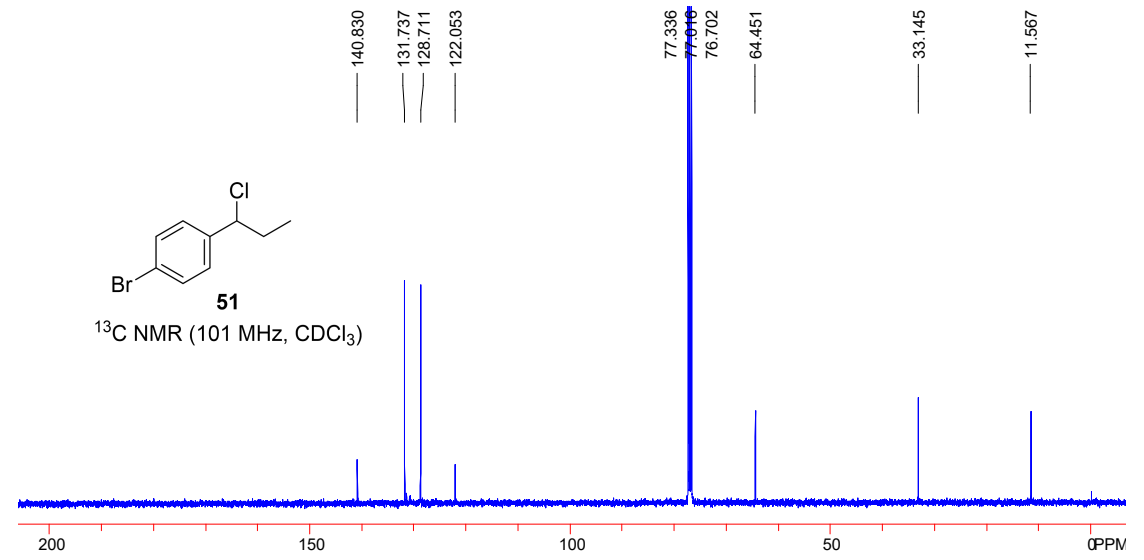

141.086
131.680
131.534
129.364
128.289
127.925
123.594
120.484
90.752
83.749
77.371
77.260
77.054
76.738
39.466
31.551
11.751
Ph
Br
48
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

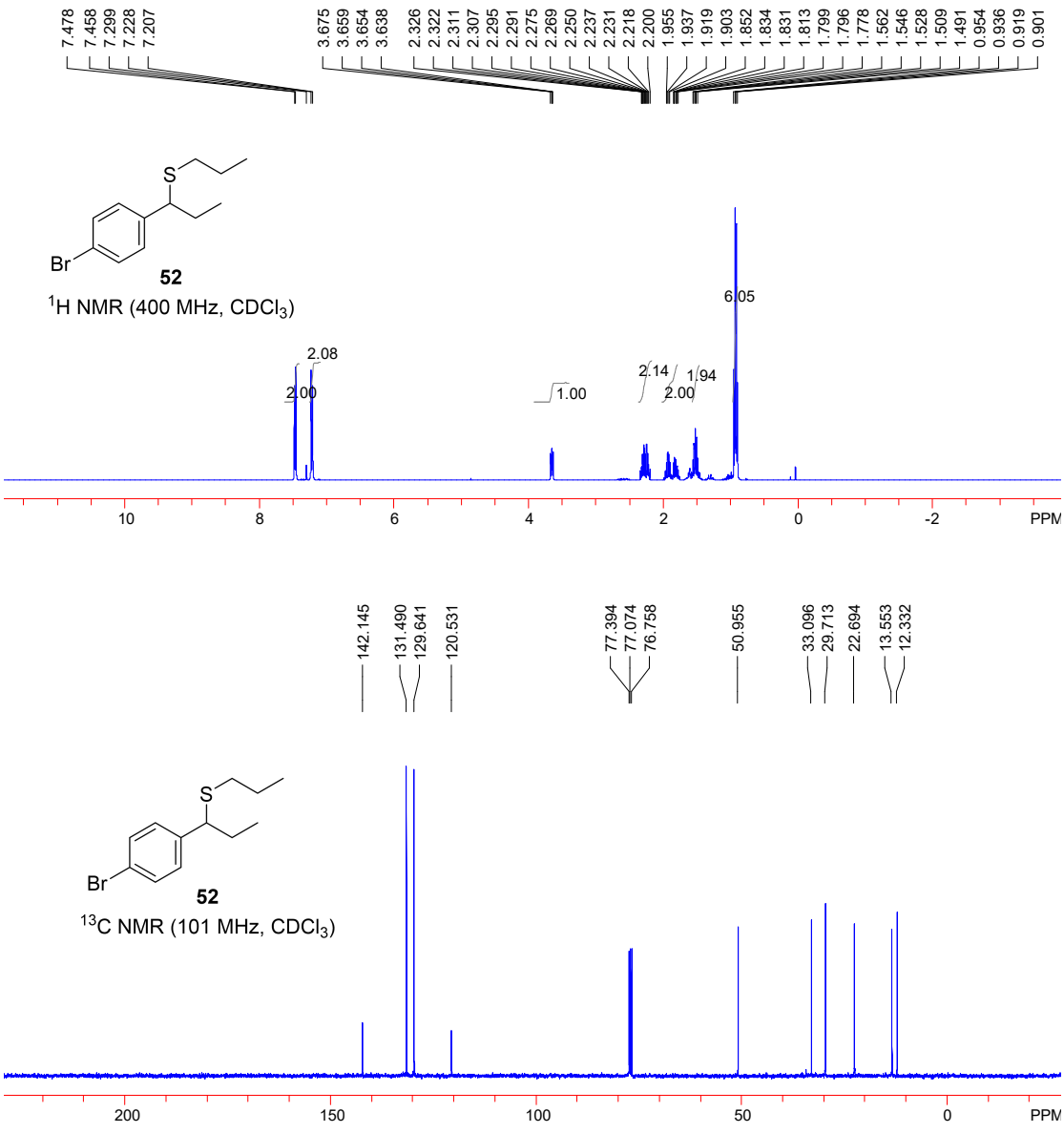

7.440
7.421
7.286
7.056
7.036
5.688
5.669
5.645
5.626
4.993
4.954
4.932
2.507
2.496
2.377
2.356
2.335
2.320
1.743
1.728
1.583
1.544
0.811
0.793
0.779
0.030
Br
49
1H NMR (400 MHz, CDCl3)
1.98
2.02
1.00
2.00
3.08
1.08
0.99
3.04
10
8
6
4
2
0
PPM
144.170
136.747
131.292
129.557
119.588
116.073
77.344
77.030
76.709
47.183
40.765
28.733
11.932
Br
49
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM

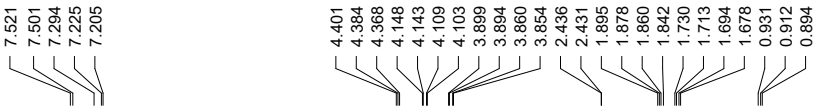

7.548
7.542
7.537
7.526
7.521
7.515
7.285
7.208
7.204
7.191
7.187
7.182
4.364
4.347
4.329
1.903
1.885
1.869
1.851
1.832
1.812
1.794
1.776
1.758
1.741
0.963
0.945
0.927
N3
Br
50
1H NMR (400 MHz, CDCl3)
2.00
1.95
1.00
2.06
3.06
10
8
6
4
2
PPM

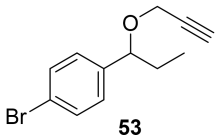

138.774
131.897
128.623
122.045
77.366
77.052
76.731
67.164
29.309
10.583
N3
Br
50
13C NMR (101 MHz, CDCl3)
200
150
100
50
0PPM


7.515
7.494
7.286
7.265
4.775
4.757
4.740
2.138
2.121
2.102
2.091
2.074
2.056
1.030
1.012
0.994
Cl
Br
51
1H NMR (400 MHz, CDCl3)
2.06
1.92
1.00
1.98
2.94
10
8
6
4
2
PPM


140.830
131.737
128.711
122.053
77.336
77.016
76.702
64.451
33.145
11.567
Cl
Br
51
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

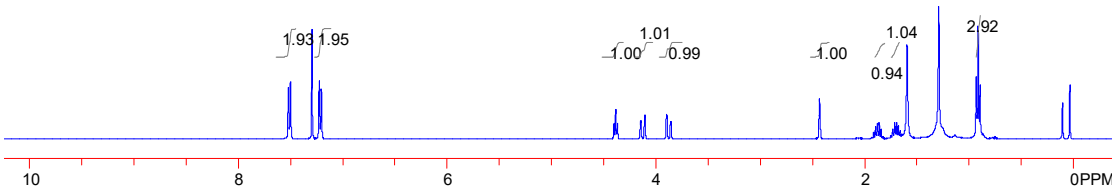

7.478
7.458
7.299
7.228
7.207
3.675
3.659
3.654
3.638
2.326
2.322
2.311
2.307
2.295
2.291
2.275
2.269
2.250
2.237
2.231
2.218
2.200
1.955
1.937
1.919
1.903
1.852
1.834
1.831
1.813
1.799
1.796
1.778
1.562
1.546
1.528
1.509
1.491
0.954
0.936
0.919
0.901
S
Br
52
1H NMR (400 MHz, CDCl3)
2.08
2.00
1.00
2.14
1.94
2.00
6.05
10
8
6
4
2
0
-2
PPM
142.145
131.490
129.641
120.531
77.394
77.074
76.758
50.955
33.096
29.713
22.694
13.553
12.332
S
Br
52
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

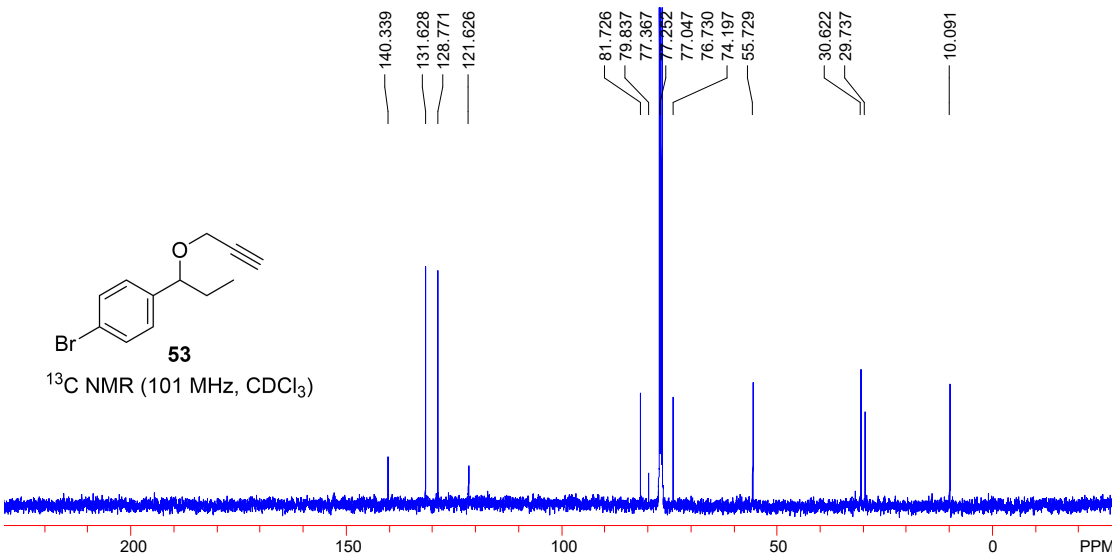




53

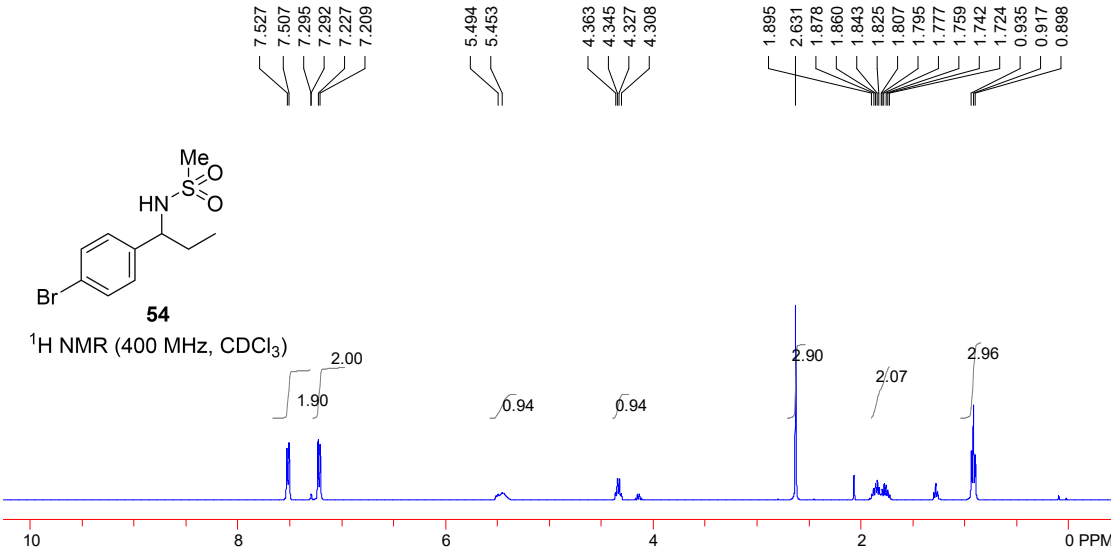
^{1}H NMR (400 MHz, $CDCl_3$)

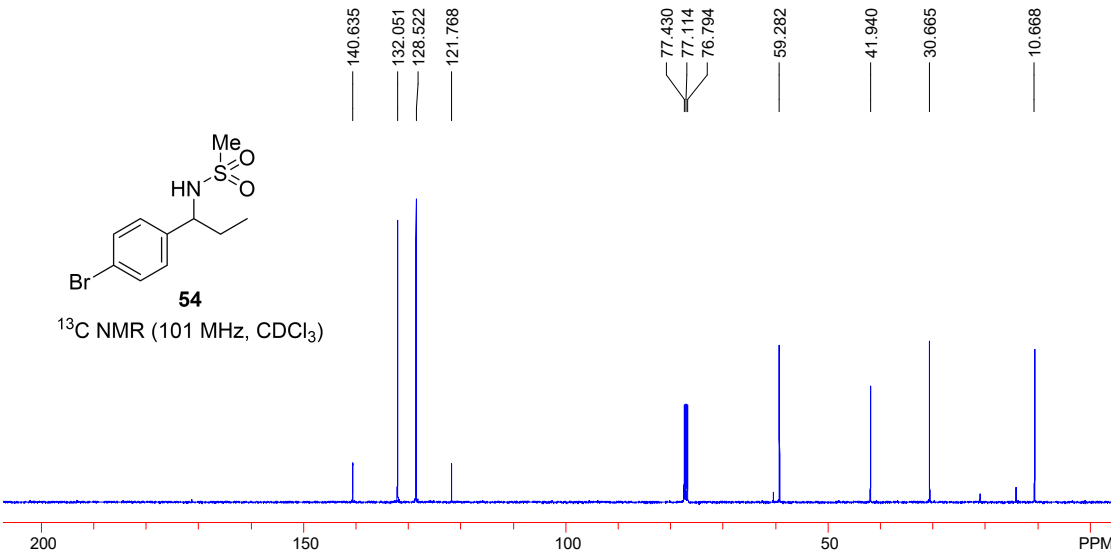


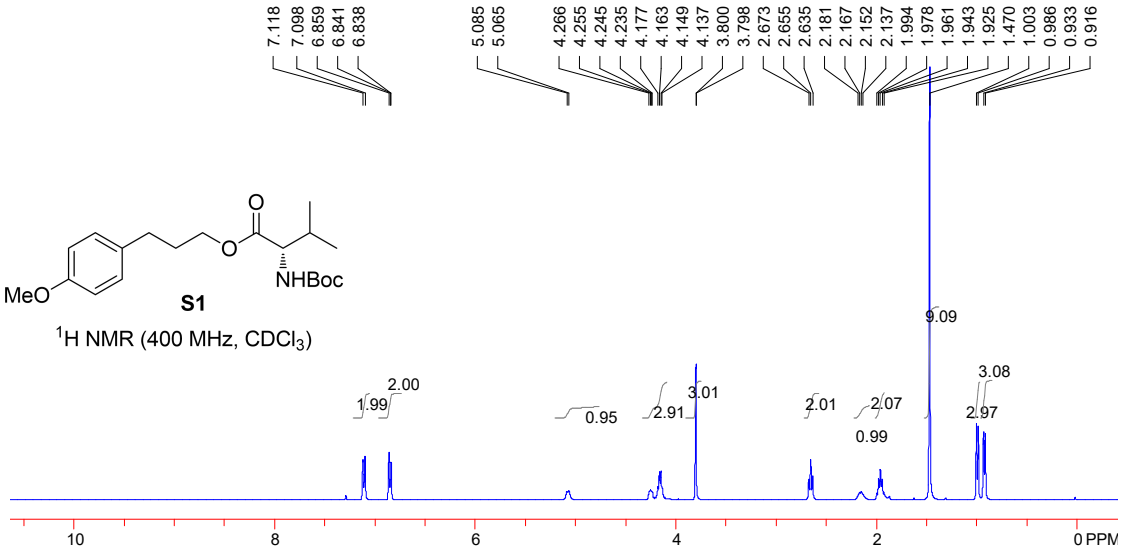


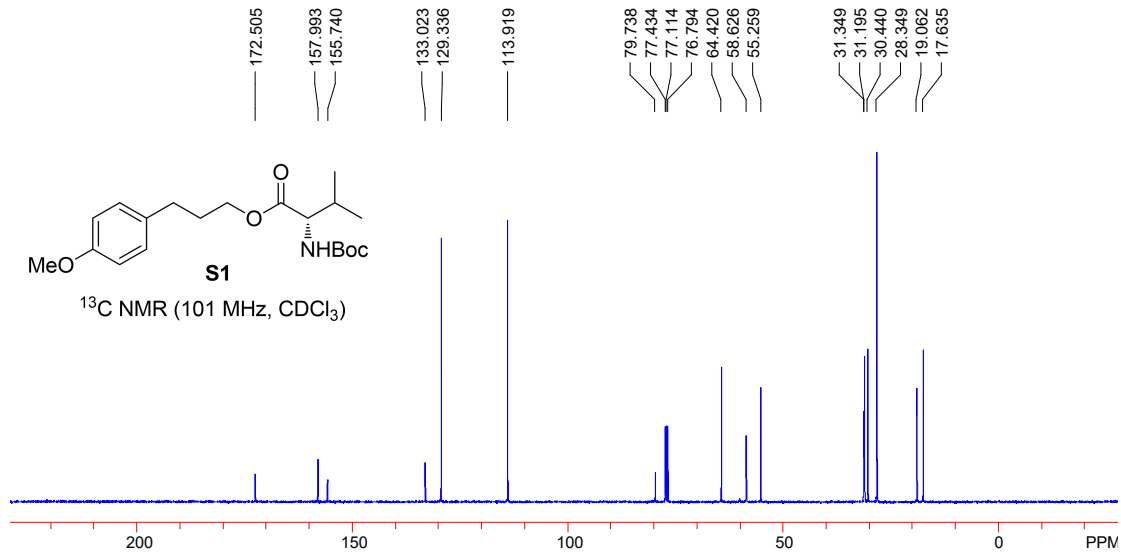
53

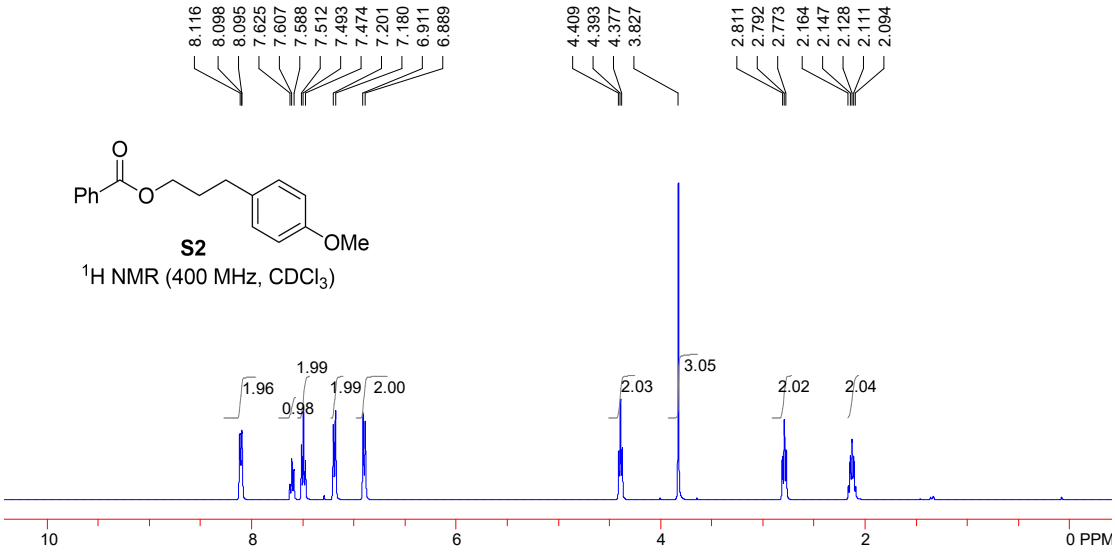
^{13}C NMR (101 MHz, $CDCl_3$)

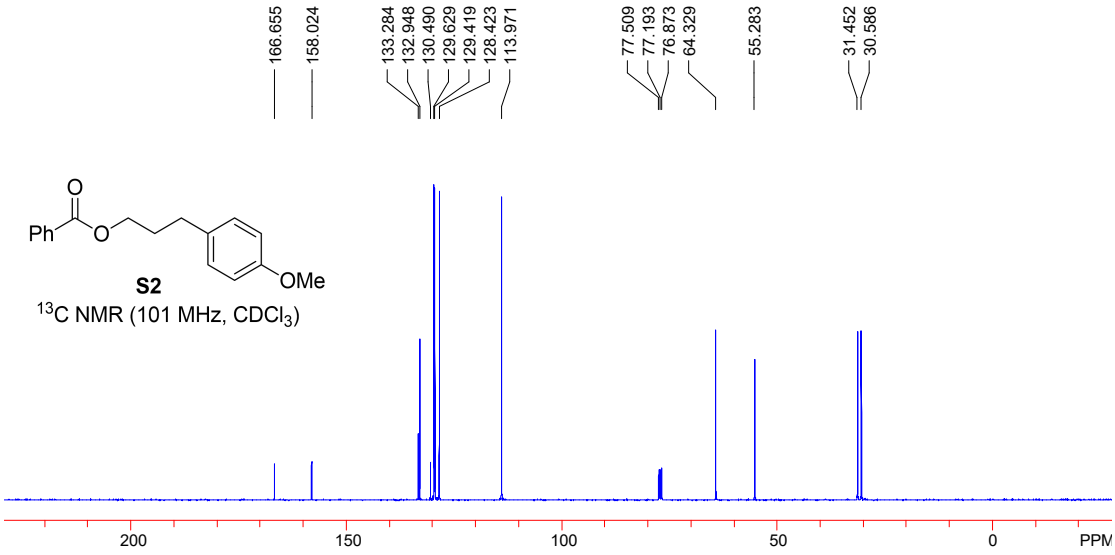

7.527
7.507
7.295
7.292
7.227
7.209
5.494
5.453
4.363
4.345
4.327
4.308
1.895
2.631
1.878
1.860
1.843
1.825
1.807
1.795
1.777
1.759
1.742
1.724
0.935
0.917
0.898
Me
HN
S
O
O
Br
54
1H NMR (400 MHz, CDCl3)
2.00
1.90
0.94
0.94
2.90
2.07
2.96
10
8
6
4
2
0 PPM

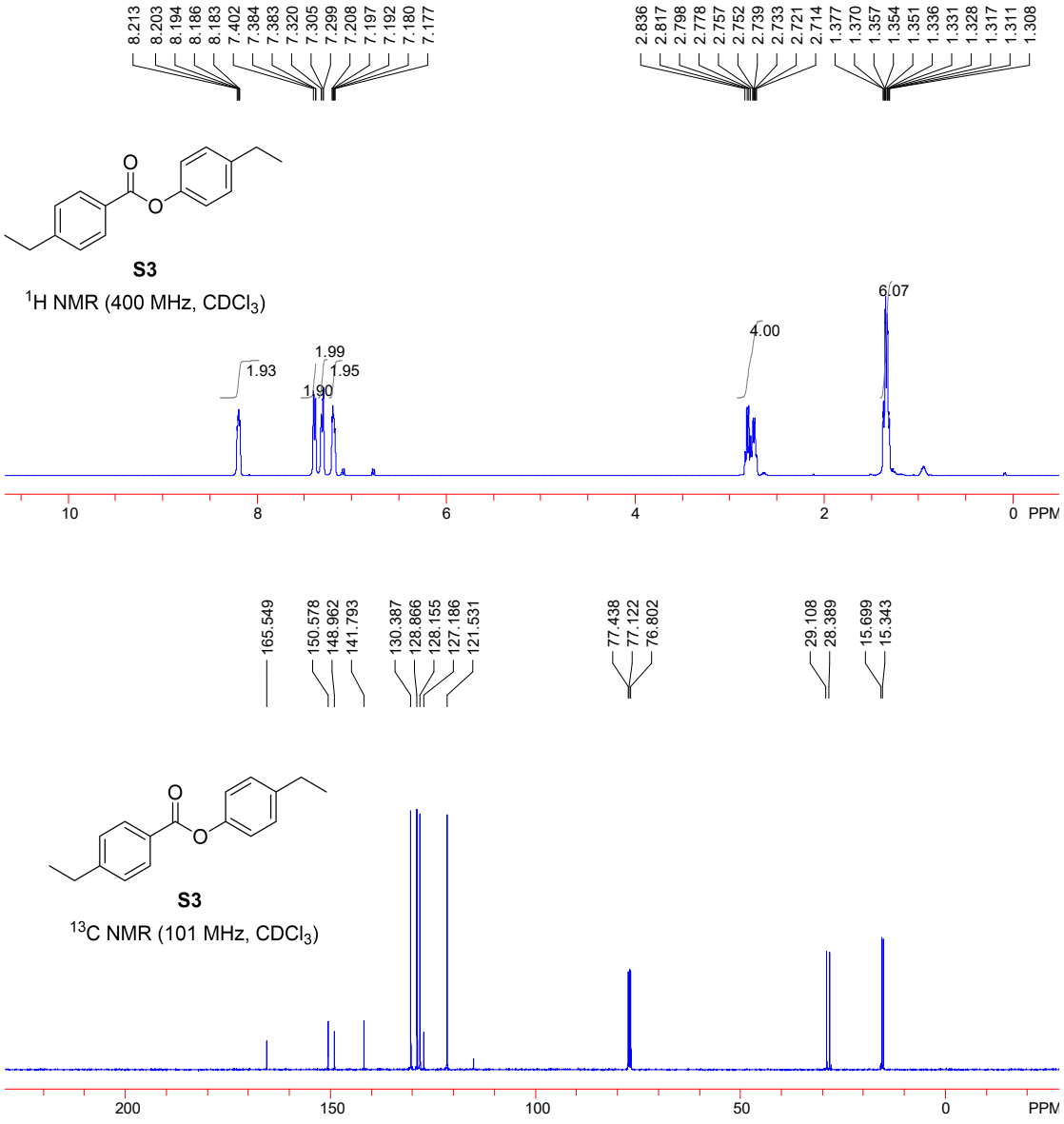

140.635
132.051
128.522
121.768
77.430
77.114
76.794
59.282
41.940
30.665
10.668
Me
HN
S
O
O
Br
54
13C NMR (101 MHz, CDCl3)
200
150
100
50
PPM

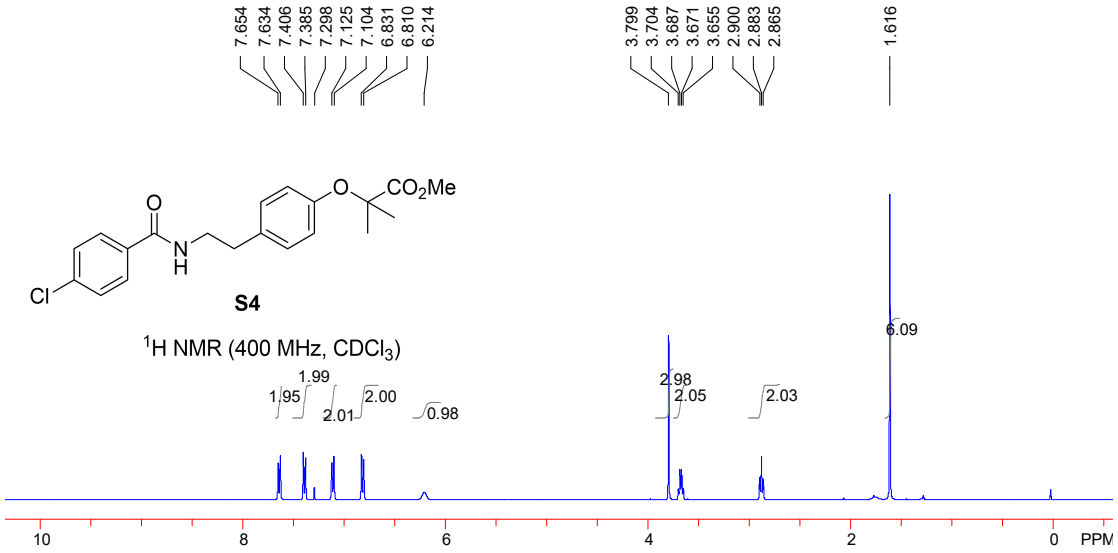

7.118
7.098
6.859
6.841
6.838
5.085
5.065
4.266
4.255
4.245
4.235
4.177
4.163
4.149
4.137
3.800
3.798
2.673
2.655
2.635
2.181
2.167
2.152
2.137
1.994
1.978
1.961
1.943
1.925
1.470
1.003
0.986
0.933
0.916
MeO
NHBoc
O
O
S1
1H NMR (400 MHz, CDCl3)
2.00
1.99
0.95
2.91
3.01
2.01
2.07
0.99
9.09
3.08
2.97
10
8
6
4
2
0 PPM

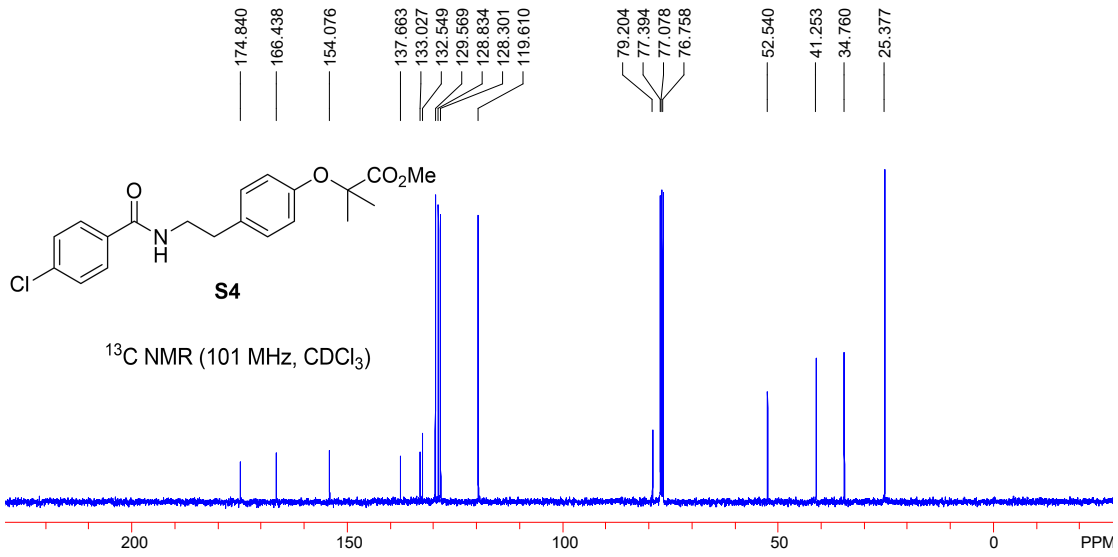

172.505
157.993
155.740
133.023
129.336
113.919
79.738
77.434
77.114
76.794
64.420
58.626
55.259
31.349
31.195
30.440
28.349
19.062
17.635
MeO
NHBoc
O
O
S1
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

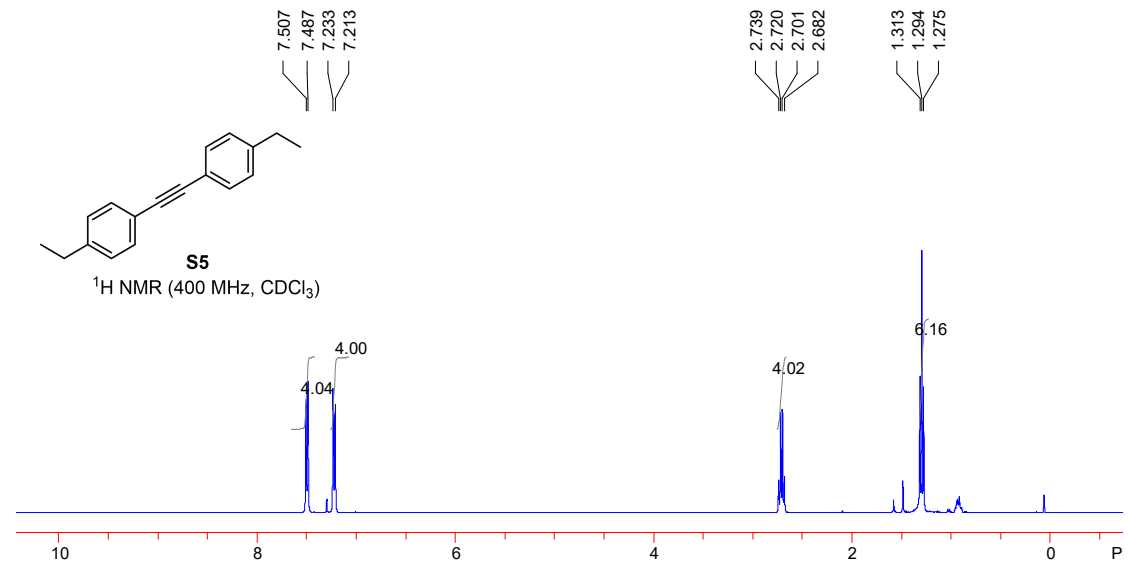

8.116
8.098
8.095
7.625
7.607
7.588
7.512
7.493
7.474
7.201
7.180
6.911
6.889
4.409
4.393
4.377
3.827
2.811
2.792
2.773
2.164
2.147
2.128
2.111
2.094
Ph
O
O
OMe
S2
1H NMR (400 MHz, CDCl3)
1.96
1.99
0.98
1.99
2.00
2.03
3.05
2.02
2.04
10
8
6
4
2
0 PPM

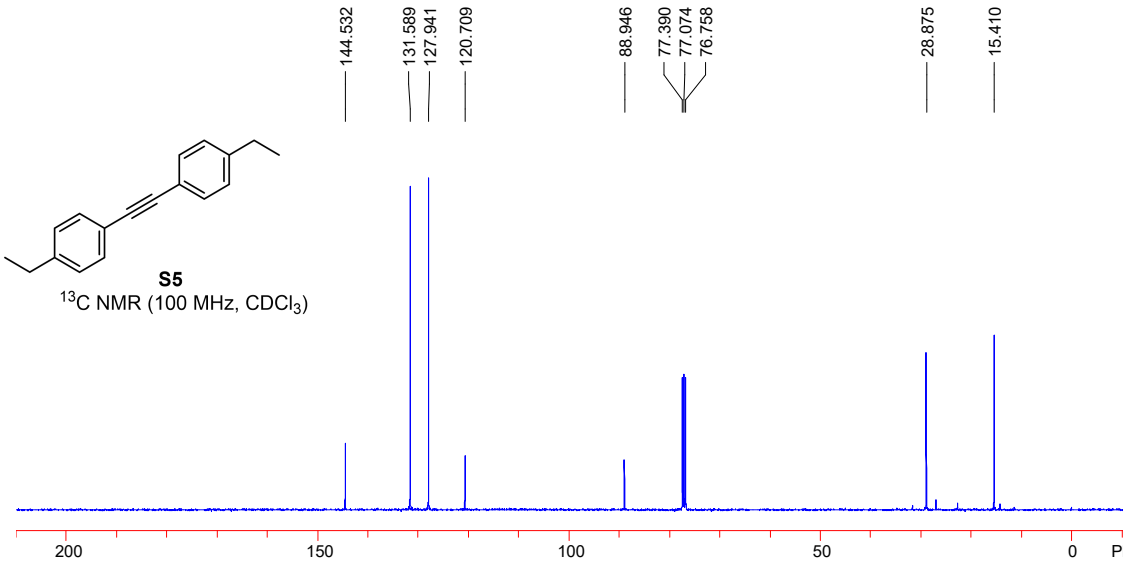

166.655
158.024
133.284
132.948
130.490
129.629
129.419
128.423
113.971
77.509
77.193
76.873
64.329
55.283
31.452
30.586
Ph
O
O
OMe
S2
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

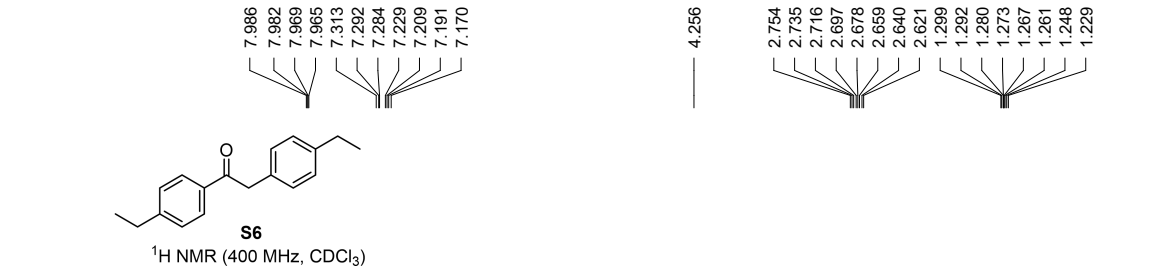

8.213
8.203
8.194
8.186
8.183
7.402
7.384
7.383
7.320
7.305
7.299
7.208
7.197
7.192
7.180
7.177
2.836
2.817
2.798
2.778
2.757
2.752
2.739
2.733
2.721
2.714
1.377
1.370
1.357
1.354
1.351
1.336
1.331
1.328
1.317
1.311
1.308
O
O
S3
1H NMR (400 MHz, CDCl3)
1.93
1.99
1.95
1.90
4.00
6.07
10
8
6
4
2
0 PPM
165.549
150.578
148.962
141.793
130.387
128.866
128.155
127.186
121.531
77.438
77.122
76.802
29.108
28.389
15.699
15.343
O
O
S3
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM


7.654
7.634
7.406
7.385
7.298
7.125
7.104
6.831
6.810
6.214
3.799
3.704
3.687
3.671
3.655
2.900
2.883
2.865
1.616
O
N
H
O
CO2Me
Cl
S4
1H NMR (400 MHz, CDCl3)
1.95
1.99
2.01
2.00
0.98
2.98
2.05
2.03
6.09
10
8
6
4
2
0
PPM


174.840
166.438
154.076
137.663
133.027
132.549
129.569
128.834
128.301
119.610
79.204
77.394
77.078
76.758
52.540
41.253
34.760
25.377
O
N
H
O
CO2Me
Cl
S4
13C NMR (101 MHz, CDCl3)
200
150
100
50
0
PPM

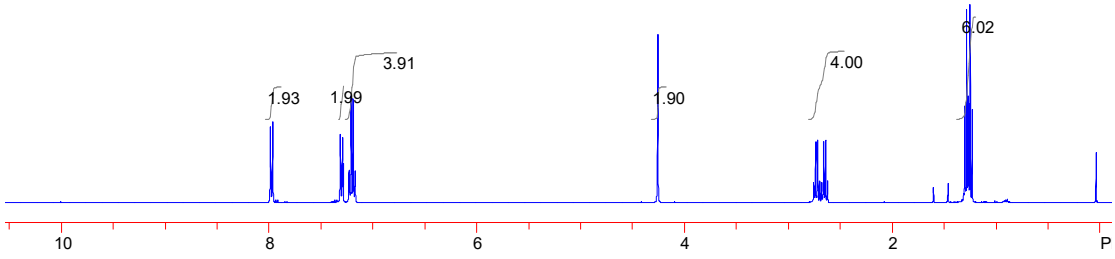

7.507
7.487
7.233
7.213
2.739
2.720
2.701
2.682
1.313
1.294
1.275
S5
1H NMR (400 MHz, CDCl3)
4.00
4.04
4.02
6.16
10
8
6
4
2
0
P

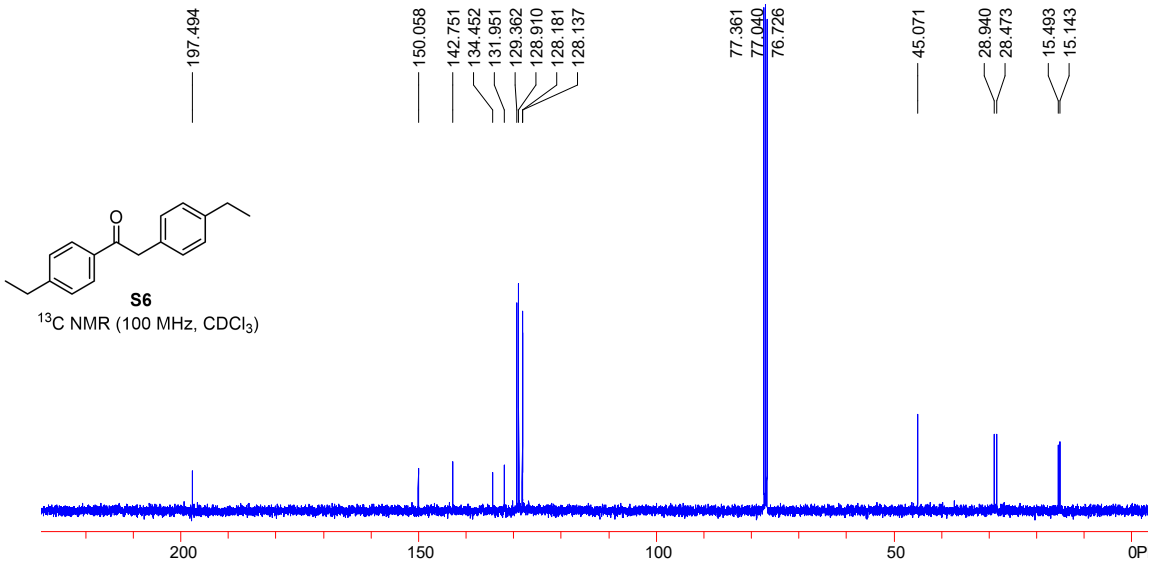

144.532
131.589
127.941
120.709
88.946
77.390
77.074
76.758
28.875
15.410
S5
13C NMR (100 MHz, CDCl3)
200
150
100
50
0
P



S6

^{1}H NMR (400 MHz, $CDCl_3$)

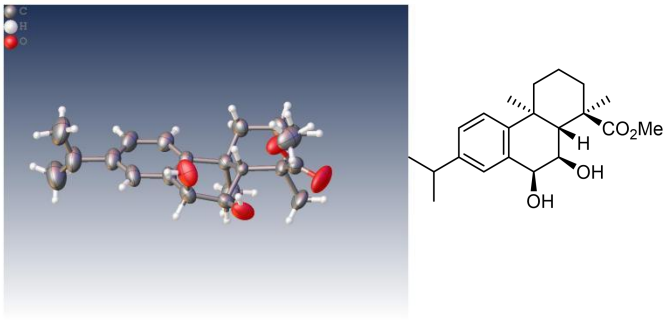




S6

^{13}C NMR (100 MHz, $CDCl_3$)

12. X-ray Crystal Structures and Data of 42 and 42'



X-ray structure of **42** with 50% ellipsoid probability

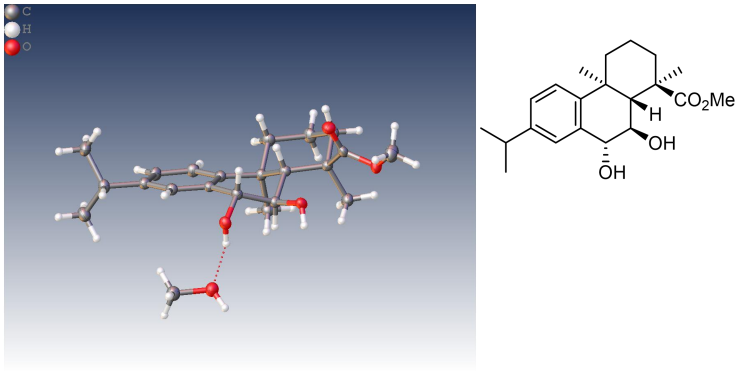
CCDC 2325618

X-ray structure determination. Single crystals suitable for X-ray diffraction was obtained by slow evaporation of the solvent from a CH_3OH solution of **42**. Crystal data collection and refinement parameters of **42** are summarized in Table S4. Intensity data were collected at 293 K on a SuperNova Dualdiffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S4 Crystallographic data and structure refinement results of **42**

Empirical formula	$C_{21}H_{29}O_4$
Formula weight	345.44
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.09540(10)
b/Å	12.03060(10)
c/Å	26.9927(3)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	1979.41(4)
Z	4
ρ_{calc}g/cm^3	1.159
μ/mm^{-1}	0.631
F(000)	748.0
Crystal size/mm^3	0.25 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.046 to 142.926
Index ranges	-5 ≤ h ≤ 7, -14 ≤ k ≤ 14, -33 ≤ l ≤ 33
Reflections collected	26116
Independent reflections	3832 [R_{int} = 0.0268, R_{sigma} = 0.0157]
Data/restraints/parameters	3832/972/233
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0807, wR_2 = 0.2370
Final R indexes [all data]	R_1 = 0.0833, wR_2 = 0.2405
Largest diff. peak/hole / e Å^{-3}	0.70/-0.48
Flack parameter	-0.02(7)



X-ray structure of **42'** with 50% ellipsoid probability

CCDC 2325639

X-ray structure determination. Single crystals suitable for X-ray diffraction was obtained by slow evaporation of the solvent from a CH_3OH solution of **42'**. Crystal data collection and refinement parameters of **42'** are summarized in Table S5. Intensity data were collected at 100 K on a SuperNova Dualdiffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54178 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S5 Crystallographic data and structure refinement results of **42'**

Empirical formula	$C_{22}H_{34}O_5$
Formula weight	378.49
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.6015(7)
b/Å	6.0925(2)
c/Å	13.7972(7)
α/°	90
β/°	116.481(7)
γ/°	90

Volume/Å^3	1023.38(10)
Z	2
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.688
F(000)	412.0
Crystal size/mm^3	0.13 × 0.13 × 0.06
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.158 to 154.14
Index ranges	-16 ≤ h ≤ 16, -7 ≤ k ≤ 6, -16 ≤ l ≤ 17
Reflections collected	9110
Independent reflections	3636 [R_{int} = 0.0371, R_{sigma} = 0.0404]
Data/restraints/parameters	3636/1/256
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.1024
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.1037
Largest diff. peak/hole / e Å^{-3}	0.26/-0.20
Flack parameter	-0.01(13)