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Supplementary Material

$BiCl_3$-Facilitated Removal of Methoxymethyl-Ether/Ester Derivatives and DFT Study of -O-C-O- Bond Cleavage

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S1. General Information

Commercial grade reagents and solvents were used as received without further purification. ^{1}HNMR and ^{13}CNMR spectra were recorded in deuterated chloroform ($CDCl_3$) on an Agilent/Varian VNMRS 400 MHz instrument. Chemical shifts (δ) are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity, coupling constants (*J)* reported in Hertz (Hz) and integration and the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br = broad, m = multiplet, td = triplet of doublets. IR spectra were recorded on a Thermo/Nicolet 6700 FT-IR Spectrometer and only the more significant peaks are reported. Reactions were monitored by thin layer chromatography (TLC) on glass-backed plates coated with a 0.2 mm thickness of silica gel 60 F254; chromatograms were visualized by UV radiation (254 nm) or by staining with $KMnO_4$ or phosphomolybdic acid. Flash column chromatography was performed on 300–400 mesh silica gel using mixtures of ethyl acetate and hexane as the eluent system.

S2. General experimental procedure & characterization data for MOM protection

General experimental procedure for MOM ethers and esters

MOMCl (1.5 mmol) was added to a stirred solution of the alcohol or carboxylic acid substrate (1 mmol) in CH_2Cl_2 (15 mL) at 0 ^{o}C. DIPEA (2 mmol) was slowly added to the reaction mixture. The ice-bath was removed and the mixture was stirred at room temperature for 12 h. Distilled water (15 mL) was added in the reaction mixture and the organic phase was separated, washed with 0.5 M of HCl, distilled water, 1M of NaOH, and brine. The organic phase was dried using anhydrous sodium sulphate, filtered and concentrated. Flash column chromatography of the residue over silica gel (hexane: EtOAc mixture) gave the desired MOM protected alcohol or ester. (Note: In some cases, the crude MOM protected alcohols and esters were pure (as indicated by ^{1}HNMR and TLC) and were used directly for the next step without further purification).

2.1) Preparation of 1-(methoxymethoxy)hexane (1a)

Following the general procedure for MOM protection, 1-(methoxymethoxy)hexane (**1a**) was obtained as an oil in 84 % yield. FTIR ($CDCl_3$) 2929, 2860, 1467, 1110, 1048 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 0.78 (t, *J* = 5.2 Hz, 3H), 1.18-1.24 (m, 6H), 1.42-1.48 (m, 2H), 3.30 (s, 3H), 3.39 (t, *J* = 6.4 Hz, 2H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.5, 25.8, 29.6, 31.5, 54.7, 67.6, 96.1 ppm; spectra data was consistent with previous literature report.[1]

2.2) Preparation of 1-(methoxymethoxy)octane (2a)

Following the general procedure for MOM protection, 1-(methoxymethoxy)octane (**2a**) was obtained as a colorless liquid in 70 % yield. FTIR (neat) 2931, 1592, 1380, 1256 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 6.8 Hz, 3H), 1.14-1.38 (m, 10H), 1.48-1.60 (m, 2H), 3.30 (s, 3H), 3.46 (t, *J* = 6.8 Hz, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.6, 26.2, 29.2, 29.3, 29.7, 31.8, 54.5, 67.8, 96.3, ppm; spectra data was consistent with previous literature report.[2]

2.3) Preparation of (3-(methoxymethoxy)propyl)benzene (3a)

Following the general procedure for MOM protection, (3-(methoxymethoxy)propyl)benzene (**3a**) was obtained as an oil in 80 % yield. FTIR (neat) 3005, 1510, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83-1.98 (m, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 3.36 (s, 3H), 3.54 (t, *J* = 6.4 Hz, 2H), 4.62 (s, 2H), 7.17-7.24 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 32.4, 55.2, 67.1, 96.5, 125.8, 128.3, 128.4, 141.8 ppm; spectra data was consistent with previous literature report.[3]

2.4) Preparation of (2-(methoxymethoxy)propyl)benzene (4a)

Following the general procedure for MOM protection, (2-(methoxymethoxy)propyl)benzene (**4a**) was obtained as an oil in 72 % yield. FTIR (neat) 2986, 1495, 1215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.8 Hz, 3H), 2.71 (dd, *J* = 6.0, 13.6 Hz, 1H), 2.88 (dd, *J* = 7.2, 13.6 Hz, 1H), 3.18 (s, 3H), 3.92-3.97 (m, 1H), 4.53 (d, *J* = 7.0, 1H), 4.65 (d, *J* = 6.8, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 43.6, 55.0, 73.9, 94.7, 126.1, 128.2, 129.5, 138.9 ppm; spectra data was consistent with previous literature report.[4]

2.5) Preparation of trans-2-(methoxymethoxy)cyclohexyl)benzene (5a)

Following the general procedure for MOM protection, trans-2-(methoxymethoxy)cyclohexyl)benzene (**5a**) was obtained as an oil in 74 % yield. FTIR (neat) 2930, 2859, 1455 cm^{-1}; δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.62 (m, 4H), 1.82-1.86 (m, 2H), 2.07-2.18 (m, 1H), 2.39-2.52 (m, 1H), 3.42 (s, 3H), 3.59-3.68 (m, 1H), 4.13 (d, *J* = 7.2, 1H), 4.46 (d, *J* = 7.2, 1H), 7.14-7.24 (m, 3H), 7.30-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 25.9, 33.3, 34.4, 53.2, 74.4, 79.4, 94.6, 126.8, 128.1, 128.8, 144.6 ppm.

2.6) Preparation of 3-(methoxymethoxy)-1,5,5-trimethylcyclohex-1-ene (6a)

Following the general procedure for MOM protection, 3-(methoxymethoxy)-1,5,5-trimethylcyclohex-1-ene **(6a)** was obtained as an oil in 87 % yield. FTIR (neat) 2996, 1672, 1490, 1211 cm^{-}1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 3H), 0.96 (s, 3H), 1.31 (dd, *J* = 8.8, 12.4 Hz, 1H), 1.58 (d, *J* = 17.2 Hz, 1H), 1.66 (s, 3H), 1.73 (dd, *J* = 6.0, 12.4 Hz, 1H), 1.84 (d, *J* = 17.2 Hz, 1H), 3.36 (s, 3H), 4.12-4.18 (m, 1H), 4.67 (q, *J* = 6.8, 2H), 5.41 (d, *J* = 3.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 26.3, 30.8, 31.1, 42.0, 44.1, 55.2, 72.5, 95.2, 121.4, 136.5 ppm.

2.7) Preparation of 6-(methoxymethoxy)-2,6-dimethylhept-1-ene (7a)

Following the general procedure for MOM protection, 6-(methoxymethoxy)-2,6-dimethylhept-1-ene **(7a)** was obtained as an oil in 82 % yield. FTIR (neat) 2972, 2943, 1649, 1449, 1382, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 6H), 1.42-1.56 (m, 4H), 1.70 (s, 3H), 1.98-2.40 (m, 2H), 3.34 (s 3H), 4.66 (s, 2H), 4.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 21.9, 22.3, 26.3, 38.1, 41.4, 55.0, 76.2, 90.9, 109.8, 145.9 ppm.

2.8) Preparation of 1-(methoxymethoxy)but-2-yne (8a)

Following the general procedure for MOM protection, 1-(methoxymethoxy)but-2-yne **(8a)** was obtained as an oil in 70 % yield. FTIR (neat) 2923, 2889, 2222, 1448, 1148, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (t, *J* = 2.4 Hz, 3H), 3.36 (s, 3H), 4.16 (q, *J* = 2.4 Hz, 2H), 4.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.6, 54.7, 55.5, 74.5, 82.4, 94.6 ppm; spectra data was consistent with previous literature report.[5]

2.9) Preparation of 1-(methoxymethoxy)hept-3-yne (9a)

Following the general procedure for MOM protection, 1-(methoxymethoxy)hept-3-yne **(9a)** was obtained as an oil in 75 % yield. FTIR (neat) 2961, 2932, 2875, 1465, 1208, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.39 (sextet, *J* = 7.2 Hz, 2H), 2.00-2.04 (m, 2H), 2.33-2.37 (m, 2H), 3.27 (s, 3H), 3.51 (t, *J* = 7.2 Hz, 2H), 4.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 20.2, 20.7, 22.3, 55.2, 66.5, 76.7, 81.3, 96.3 ppm.

2.10) Preparation of (3-(methoxymethoxy)prop-1-yn-1-yl)benzene (10a)

Following the general procedure for MOM protection, (3-(methoxymethoxy)prop-1-yn-1-yl)benzene **(10a)** was obtained as an oil in 68 % yield. FTIR (neat) 2948, 2888, 2237, 1490, 1149, 1041 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 3H), 4.43 (s, 2H), 4.77 (s, 2H), 7.24-7.30 (m, 3H), 7.42-7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.9, 55.6, 84.6, 86.1, 94.9, 122.5, 128.2, 128.4, 131.7 ppm; spectra data was consistent with previous literature report.[6]

2.11) Preparation of 1-bromo-4-((methoxymethoxy)methyl)benzene (11a)

Following the general procedure for MOM protection, 1-bromo-4-((methoxymethoxy)methyl)benzene **(11a)** was obtained as a clear oil in 82 % yield. FTIR (neat) 2934, 2884, 1594, 1487, 1208, 1148, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (s, 3H), 4.53 (s, 2H), 4.68 (s, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 68.4, 95.7, 121.5, 129.4, 131.5, 136.9 ppm; spectra data was consistent with previous literature report.[7]

2.12) Preparation of 9-((methoxymethoxy)methyl)anthracene (12a)

Following the general procedure for MOM protection, 9-((methoxymethoxy)methyl)anthracene **(12a)** was obtained as a pale yellow solid in 85 % yield; m.p. = 81-82 °C. FTIR (neat) 3003, 2962, 2885, 1526, 1446, 1146, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 3H), 4.79 (s, 2H), 5.60 (s, 2H), 7.45-7.49 (m, 2H), 7.53-7.57 (m, 2H), 8.01 (d, J = 8.8 Hz, 2H), 8.42 (d, J = 9.2 Hz, 2H), 8.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 61.0, 95.6, 124.2, 125.0, 126.3, 128.2, 128.5, 129.0, 131.1, 131.4 ppm; spectra data was consistent with previous literature report.[8]

2.13) Preparation of methoxymethyl hexanoate (13a)

Following the general procedure for MOM protection, methoxymethyl hexanoate **(13a)** was obtained as an oil in 76 % yield. FTIR (neat) 2958, 2933, 2873, 1737, 1150, 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 6.8 Hz, 3H), 1.23-1.26 (m, 4H), 1.55-1.58 (m, 2H), 2.26 (t, J = 7.2 Hz, 2H), 3.34 (s, 3H), 5.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 22.0, 24.2, 31.0, 33.9, 56.9, 89.8, 172.9 ppm; spectra data was consistent with previous literature report.[9]

2.14) Preparation of methoxymethyl benzoate (14a)

Following the general procedure for MOM protection, methoxymethyl benzoate **(14a)** was obtained as a clear oil in 88 % yield. FTIR (neat) 2930, 2860, 1719, 1636, 1455, 1260, 1163, 1055 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 3H), 5.48 (s, 2H), 7.42-7.46 (m, 2H), 7.55-7.58 (m, 1H), 8.06-8.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.7, 90.9, 128.4, 129.7, 129.8, 133.2, 166.0 ppm; spectra data was consistent with previous literature report.[10]

2.15) Preparation of methoxymethyl 2-phenylacetate (15a)

Following the general procedure for MOM protection, methoxymethyl 2-phenylacetate **(15a)** was obtained as an oil in 76 % yield. FTIR (neat) 2962, 1735, 1475, 1126, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.61 (s, 2H), 5.20 (s, 2H), 7.21-7.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.6, 56.7, 90.2, 127.3, 128.2, 129.1, 130.2, 172.3 ppm; spectra data was consistent with previous literature report.[11]

2.16) Preparation of methoxymethyl 2-(4-bromophenyl)acetate (16a)

Following the general procedure for MOM protection, methoxymethyl 2-(4-bromophenyl)acetate **(16a)** was obtained as an oil in 72 % yield. FTIR (neat) 2959, 1738, 1488, 1130, 1088 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.60 (s, 2H), 5.22 (s, 2H), 7.16 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.7, 57.7, 90.8, 121.3, 130.9, 131.7, 132.6, 170.6 ppm.

2.17) Preparation of trans-methoxymethyl cinnamate (17a)

Following the general procedure for MOM protection, methoxymethyl cinnamate **(17a)** was obtained as a clear oil in 90 % yield. FTIR (neat) 2959, 1715, 1638, 1455, 1138, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 3H), 5.36 (s, 2H), 6.45 (d, J = 16 Hz, 1H), 7.38-7.39 (m, 3H), 7.51-7.54 (m, 2H), 7.74 (d, J = 16 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.7, 90.5, 117.6, 128.2, 128.9, 130.5, 134.2, 145.7, 166.3 ppm; spectra data was consistent with previous literature report.[10]

2.18) Preparation of methoxymethyl 2-acetoxybenzoate (18a)

Following the general procedure for MOM protection, methoxymethyl 2-acetoxybenzoate **(18a)** was obtained as an oil in 79 % yield. FTIR (neat) 2990, 2860, 1740, 1718, 1610, 1459, 1310, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.51 (s, 3H), 5.43 (s, 2H), 7.11

(dd, *J* = 1.2, 8.4 Hz, 1H), 7.30-7.34 (m, 1H), 7.55-7.57 (m, 1H), 8.06 (dd, *J* = 1.6, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 57.8, 91.2, 122.9, 123.9, 126.0, 131.9, 134.2, 150.9, 166.9, 169.7 ppm.

S3. General experimental procedure & characterization data for $BiCl_3$ mediated MOM cleavage

$BiCl_3$ (100 mol%) was added to a stirred solution of MOM protected alcohol MOM ethers or carboxylic MOM esters (1 mmol) in $MeCN/H_2O$ (5 mL/0.1 mL; 5:0.1 v/v) and the mixture was stirred at 50 °C until reaction was complete (TLC control). The mixture was filtered over a pad of celite using CH_2Cl_2 (10 mL), the resulting filtrate was dried over anhydrous sodium sulphate and concentrated under reduced pressure. Flash column chromatography of the residue over silica gel (hexane:EtOAc mixture) afforded the desired pure alcohol or carboxylic acid. All products were characterized from their spectra (FTIR, ^{1}HNMR, ^{13}CNMR) and by comparison with authentic samples.

3.1) 1-hexanol (1b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 1-(methoxymethoxy)hexane (**1b**) was obtained as an oil in 79 % yield. FTIR (neat) 3324, 2928, 2859, 1467, 1379, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.21-1.34 (m, 6H), 1.48-1.55 (quintet, *J* = 6.8 Hz, 2H), 2.07 (br s, 1H), 3.57 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.6, 25.4, 31.6, 32.7, 62.8 ppm; spectra data was consistent by comparison with authentic sample.

3.2) 1-octanol (2b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 1-octanol (**2b**) was obtained as a colorless liquid in 84 % yield. FTIR (neat) 3317, 2895, 1599, 1362 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.20-1.38 (m, 10H), 1.50-1.60 (m, 2H), 3.62 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.7, 29.2, 29.4, 31.8, 32.7, 63.1 ppm; spectra data was consistent by comparison with authentic sample.

3.3) 3-phenyl-propan-1-ol (3b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 3-phenyl-propan-1-ol (**3b**) was obtained as an oil in 88 % yield. FTIR (neat) 3383, 2968, 2940, 1456, 1375, 1186 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.84-1.94 (m, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 3.68 (t, *J* = 6.8 Hz, 2H), 7.18-7.24 (m, 3H), 7.26-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 34.2, 62.3, 125.8, 128.4, 128.5, 141.8 ppm; spectra data was consistent by comparison with authentic sample.

3.4) 1-phenyl-propan-2-ol (4b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 1-phenyl-propan-2-ol (**4b**) was obtained as an oil in 78 % yield. FTIR (neat) 3475, 2973, 2929, 1605, 1496, 1452, 1065 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.0 Hz, 3H), 1.92 (br s, 1H), 2.78-2.67 (m, 2H), 4.00 (sextet, *J* = 6, 1H), 7.20-7.25 (m, 3H), 7.29-7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 45.8, 68.8, 126.4, 128.5, 129.4, 138.6 ppm; spectra data was consistent by comparison with authentic sample.

3.5) trans-2-phenylcyclohexan-1-ol (5b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, trans-2-phenylcyclohexan-1-ol (**5b**) was obtained as an oil in 81 % yield. FTIR (neat) 3296, 2928, 2854, 1580, 1446, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73-1.77 (m, 4H), 1.84-1.87 (m, 2H), 2.09-2.12 (m, 1H), 2.39-2.45 (m, 1H), 3.65 (td, *J* = 4.4, 10 Hz, 1H), 7.21-7.25 (m, 3H), 7.30-7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 26.0, 33.3, 34.4, 53.2, 74.4, 126.8, 127.9, 128.7, 143.3 ppm; spectra data was consistent by comparison with authentic sample.

3.6) 3,5,5-trimethylcyclohex-2-en-1-ol (6b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 3,5,5-trimethylcyclohex-2-en-1-ol (**6b**) was obtained as an oil in 78 % yield. FTIR (neat) 3318, 2924, 2866, 1672, 1455, 1364, 1019 cm^{-1}; ; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3H), 0.99 (s, 3H), 1.23 (dd, *J* = 9.2, 12.4 Hz, 1H), 1.59 (d, *J* = 17.6 Hz, 1H), 1.67 (s, 3H), 1.66-1.73 (m, 1H), 1.84 (d, *J* = 17.2 Hz, 1H), 4.19-4.25 (m, 1H), 5.41 (m 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 26.0, 31.0, 31.3, 44.1, 45.0, 66.5, 123.8, 136.5 ppm; spectra data was consistent by comparison with authentic sample.

3.7) 2,6-dimethylhept-6-en-2-ol (7b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 3,5,5-trimethylcyclohex-2-en-1-ol (**7b**) was obtained as an oil in 85 % yield. FTIR (neat) 3383, 2969, 29740, 1650, 1456, 1374, 1151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 6H), 1.40-1.50 (m, 4H), 1.69 (s, 3H), 1.99 (t, *J* = 7.0 Hz, 2H), 4.68 (d, *J* = 11.2 Hz, 2H)). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.3, 29.2, 38.1, 43.4, 70.9, 109.9, 145.7 ppm; spectra data was consistent by comparison with authentic sample.

3.8) but-2-yn-1-ol (8b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, but-2-yn-1-ol (**8b**) was obtained as an oil in 85 % yield. FTIR (neat) 3378, 2922, 2223, 1668, 1439, 1366, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (br s, 1H), 1.83 (t, *J* = 2.4 Hz, 3H), 4.21(q, *J* = 2.4 Hz, 2H), 4.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.5, 51.4, 77.4, 82.0 ppm; spectra data was consistent by comparison with authentic sample.

3.9) hept-3-yn-1-ol (9b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, hept-3-yn-1-ol (**9b**) was obtained as an oil in 75 % yield. FTIR (neat) 3337, 2962, 2934, 1457, 1340, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.50 (sextet, *J* = 7.2 Hz, 2H), 1.63 (br s, 1H), 2.10-2.15 (m, 2H), 2.34-2.44 (m, 2H), 3.66 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 20.2, 20.7, 22.3, 55.2, 66.5, 76.7, 81.3, 96.3 ppm; spectra data was consistent by comparison with authentic sample.

3.10) 3-phenylprop-2-yn-1-ol (10b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 3-phenylprop-2-yn-1-ol (**10b**) was obtained as an oil in 82 % yield. FTIR (neat) 3306, 2920, 2932, 2863, 2238, 1489, 1441, 1256, 1019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.70 (s, 1H), 4.49 (s, 2H), 7.24-7.31 (m, 3H), 7.42-7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 85.7, 87.1, 122.5, 128.3, 128.5, 131.7 ppm; spectra data was consistent by comparison with authentic sample.

3.11) (4-bromophenyl)methanol (11b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, (4-bromophenyl)methanol **(11b)** was obtained as an oil in 88 % yield. FTIR (neat) 3353, 2921, 1591, 1486, 1403, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 1H), 4.60 (s, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.5, 121.4, 128.6, 131.6, 136.7 ppm; spectra data was consistent by comparison with authentic sample.

3.12) 9-anthracenemethanol (12b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 9-anthracenemethanol (**12b**) was obtained as a solid in 92 % yield. FTIR (neat) 3417, 2927, 2861, 1475 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 2H), 5.98 (s, 1H), 7.45-7.49 (m, 2H), 7.45-7.50 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 8.42 (d, *J* = 8.8 Hz, 2H), 8.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 121.8, 123.6, 123.8, 125.1, 126.5, 128.4, 129.1, 131.5 ppm; spectra data was consistent by comparison with authentic sample.

3.13) hexanoic acid (13b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, hexanoic acid (**13b**) was obtained as an oil in 77 % yield. FTIR (neat) 2958, 2932, 1704, 1412, 1291 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.27-1.31 (m, 4H), 1.56-1.64 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 11.7 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.2, 24.3, 31.1, 34.0, 180.7 ppm; spectra data was consistent by comparison with authentic sample.

3.14) benzoic acid (14b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, benzoic acid (**14b**) was obtained as a solid in 89 % yield. FTIR (neat) 3071, 2927, 2849, 1678, 1481, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.49 (m, 2H), 7.59-7.64 (m, 1H), 8.10-8.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.5, 129.2, 130.2, 133.8, 172.0 ppm; spectra data was consistent by comparison with authentic sample.

3.15) 2-phenylacetic acid (15b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 2-phenylacetic acid **(15b)** was obtained as a white solid in 83 % yield. FTIR (neat) 3032, 2921, 2849, 1692, 1407, 1226 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 2H), 7.26-7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.9, 127.3, 128.6, 129.3, 133.2, 177.3 ppm; spectra data was consistent by comparison with authentic sample.

3.16) 2-(4-bromophenyl)acetic acid (16b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, 2-(4-bromophenyl)acetic acid (**16b**) was obtained as a solid in 85 % yield. FTIR (neat) 3375, 2916, 1693, 1487, 1244, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 2H), 5.22 (s, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 10.8 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 121.5, 131.1, 131.7, 132.1, 177.3 ppm; spectra data was consistent by comparison with authentic sample.

3.17) trans-cinnamic acid (17b)

Following the general procedure for $BiCl_3$ mediated MOM deprotection, trans-cinnamic acid (**17b**) was obtained as a solid in 87 % yield. FTIR (neat) 3370, 3027, 2814, 1668, 1628, 1578, 1449, 1220 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, J = 16 Hz, 1H), 7.39-7.41 (m, 3H), 7.54-7.56 (m, 2H), 7.79 (d, J = 16 Hz, 1H), 9.61 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.3, 128.4, 128.9, 130.7, 134.0, 147.1, 172.4 ppm; spectra data was consistent by comparison with authentic sample.

3.18) 2-acetoxybenzoic acid (18b)

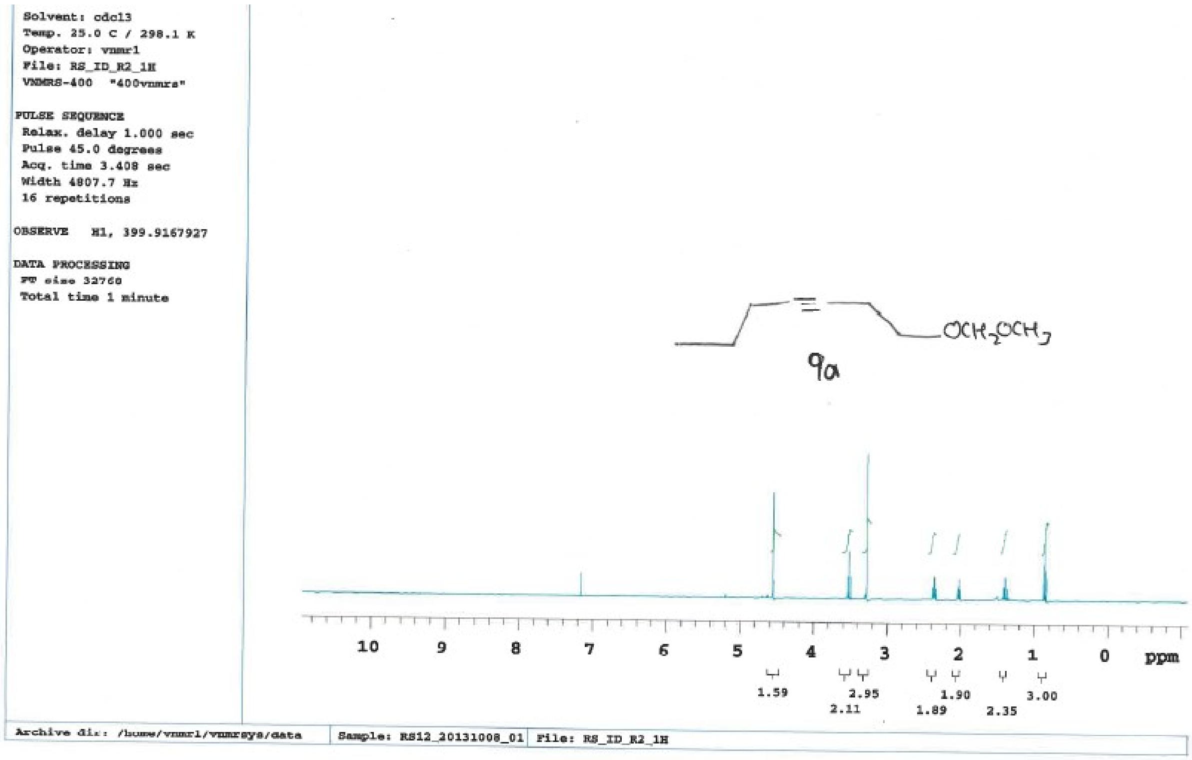
Following the general procedure for $BiCl_3$ mediated MOM deprotection, 2-acetoxybenzoic acid (**18b**) was obtained as a solid in 85 % yield. FTIR (neat) 3410, 2993, 2867, 1749, 1679, 1604, 1456, 1304, 1183 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 7.12 (dd, J = 0.8, 8.0 Hz, 1H), 7.32-7.36 (m, 1H), 7.59-7.63 (m, 1H), 8.11 (dd, J = 1.6, 8.0 Hz, 1H), 11.2 (br s, IH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 122.2, 124.0, 126.1, 132.5, 134.9, 151.2, 169.7, 170.2 ppm; spectra data was consistent by comparison with authentic sample.

Control experiment for reaction of HCl with phenolic MOM ether 19

3M HCl (0.1 mL, 0.3 mmol) was added to a stirred solution of the phenolic MOM ether **19** (0.138 g, 1 mmol) in $MeCN/H_2O$ (5 mL/0.1 mL; 5:0.1 v/v) and the mixture was stirred at 50 ^oC for 24h. The mixture was extracted with EtOAc (3 x 10 mL), washed with brine (10 mL) and the resulting filtrate was dried over anhydrous sodium sulphate and concentrated under reduced pressure. Flash column chromatography of the residue over silica gel (hexane:EtOAc mixture) afforded the desired pure phenol[12] (0.06 g, 64%). FTIR ($CDCl_3$) 3326, 3045, 1594, 1498, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 6.91-7.06 (m, 3H), 7.28-7.32 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 115.8, 121.5, 129.9, 156.3 ppm; spectra data was consistent by comparison with authentic sample.

S4. ^{1}HNMR and ^{13}CNMR spectra of MOM ethers and esters and deprotected products



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Operator: vnmr1
File: RS_ID_R2_1H
VNMRS-400  "400vnmrs"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.408 sec
 Width 4807.7 Hz
 16 repetitions

OBSERVE   H1, 399.9167927

DATA PROCESSING
 FT size 32768
 Total time 1 minute

Archive dir: /home/vnmr1/vnmrsys/data   Sample: RS12_20131008_01   File: RS_ID_R2_1H
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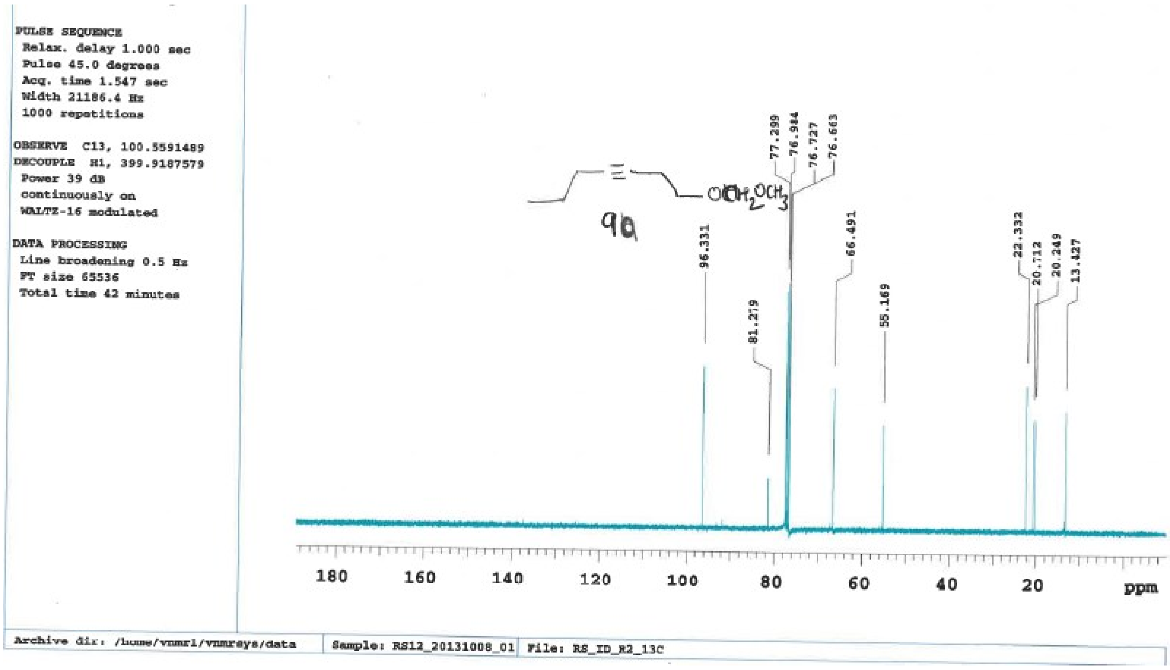

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PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.547 sec
 Width 21186.4 Hz
 1000 repetitions

OBSERVE  C13, 100.5591489
DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 42 minutes
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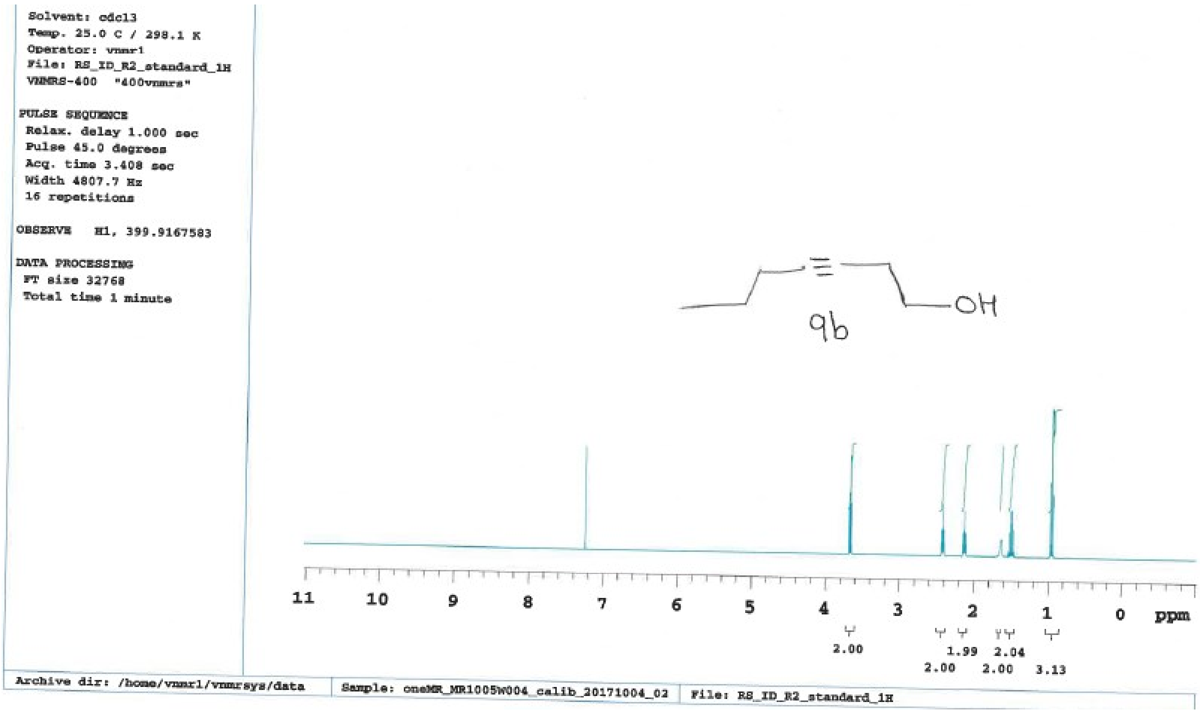

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Solvent: cdcl3
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Operator: vnmr1
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VNMRS-400  "400vnmrs"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.408 sec
 Width 4807.7 Hz
 16 repetitions

OBSERVE   H1, 399.9167583

DATA PROCESSING
 FT size 32768
 Total time 1 minute
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Archive dir: /home/vnmr1/vnmrsys/data    Sample: oneMR_MR1005W004_calib_20171004_02    File: RS_ID_R2_standard_1H
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Solvent: cdcl3
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Operator: vnmr1
File: RS_ID_R2_standard_13C
VNMRS-400  "400vnmrs"

ULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.547 sec
Width 21186.4 Hz
1000 repetitions

BSERVE  C13, 100.5591489
ECOUPLE  H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

ATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 minutes
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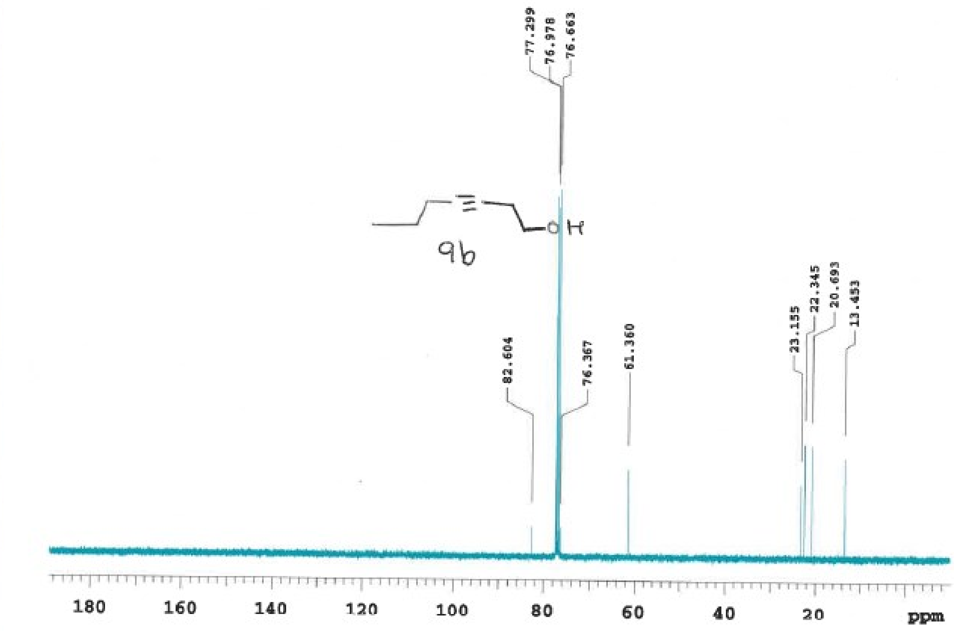

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OBSERVE  H1, 399.9167583

DATA PROCESSING
 FT size 32768
 Total time 1 minute
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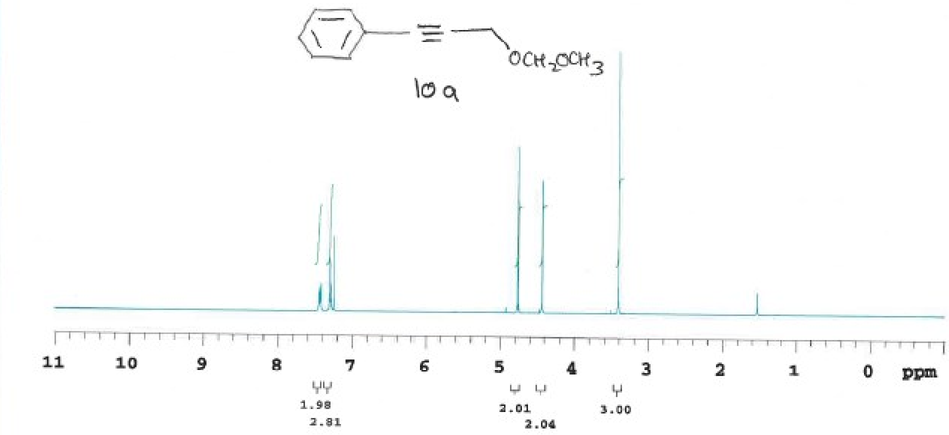

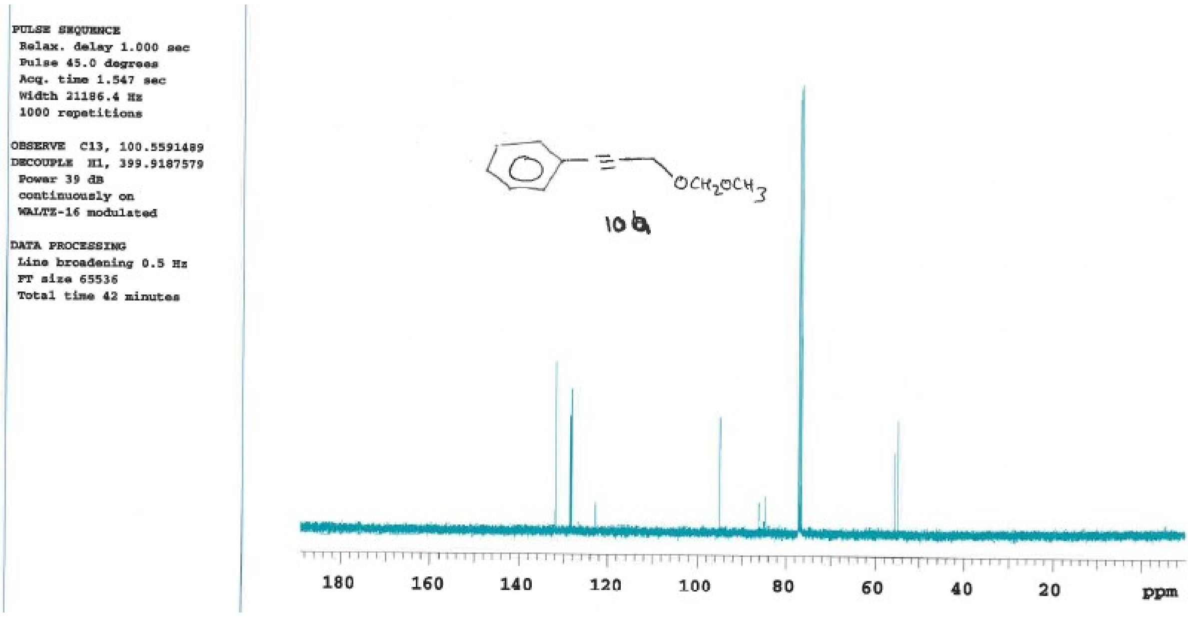

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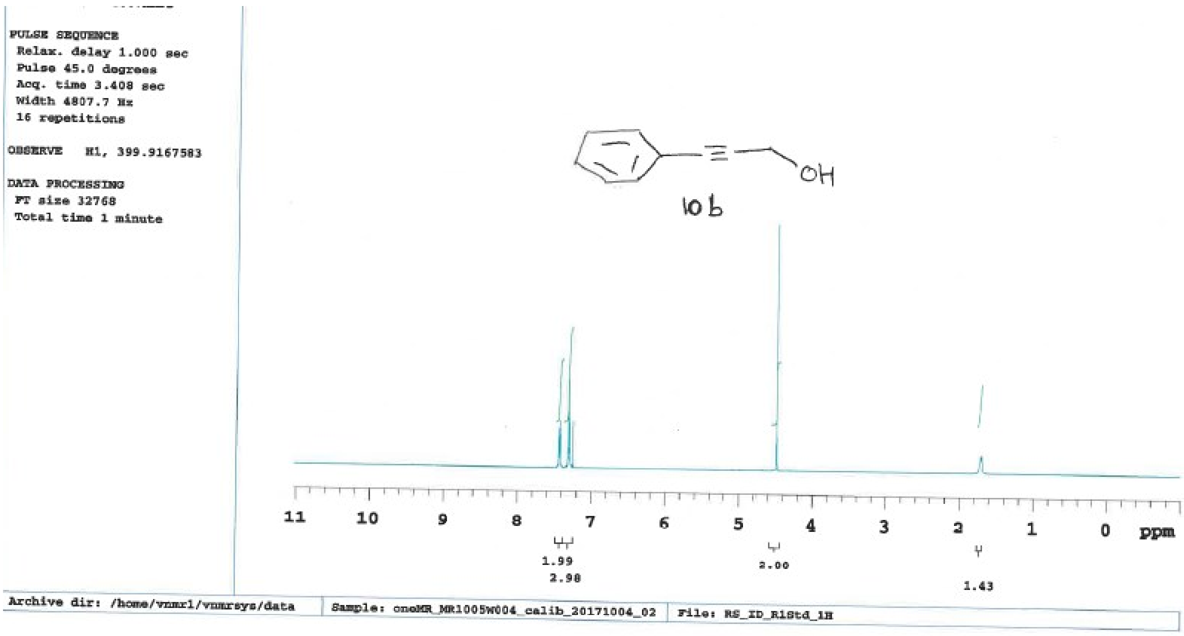
Pulse 45.0 degrees
Acq. time 1.547 sec
Width 21186.4 Hz
1000 repetitions

OBSERVE C13, 100.5591489
DECOUPLE H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 minutes



PULSE SEQUENCE
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Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
16 repetitions

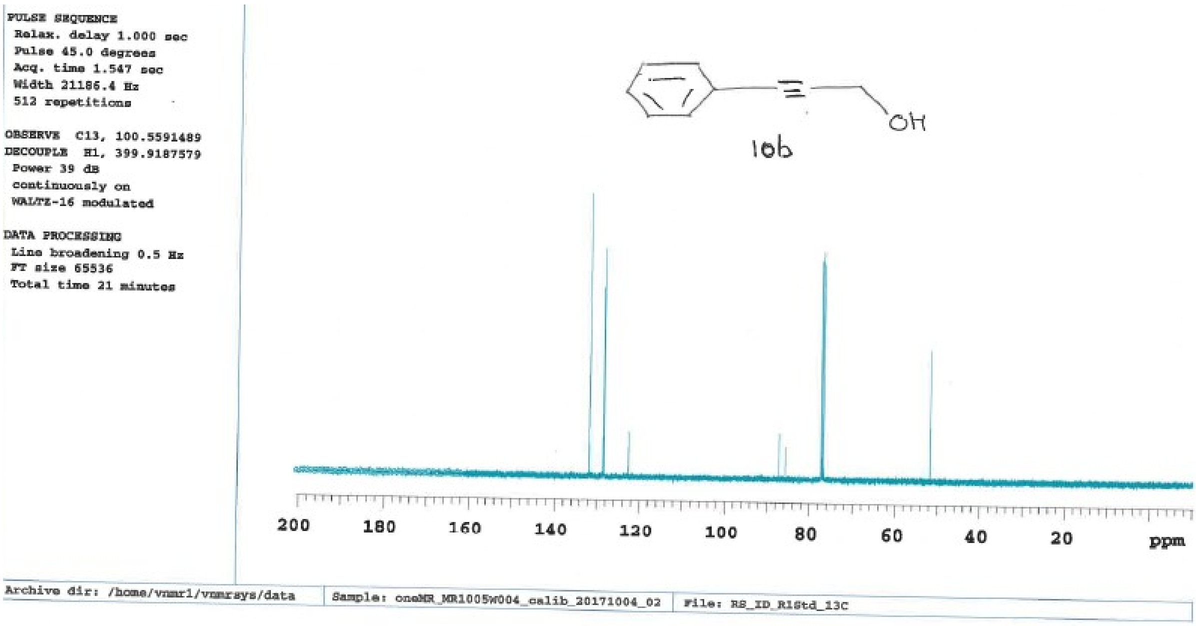
OBSERVE H1, 399.9167583

DATA PROCESSING
FT size 32768
Total time 1 minute

Archive dir: /home/vnmr1/vnmrsys/data

Sample: oneMR_MR1005W004_calib_20171004_02

File: RS_ID_R1Std_1H



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PULSE SEQUENCE
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 Acq. time 1.547 sec
 Width 21186.4 Hz
 512 repetitions

OBSERVE  C13, 100.5591489
DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 21 minutes
```

10b

```
Archive dir: /home/vnmr1/vnmrsys/data   Sample: oneMR_MR1005W004_calib_20171004_02   File: RS_ID_R1Std_13C
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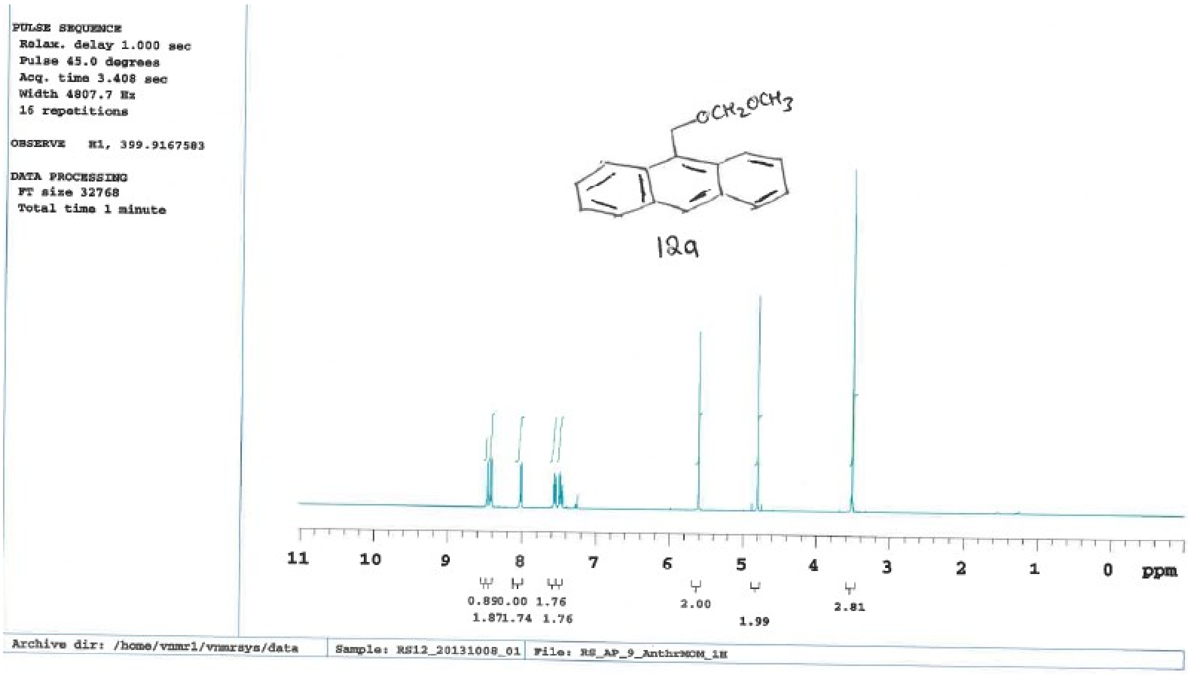

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PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.408 sec
 Width 4807.7 Hz
 16 repetitions

OBSERVE   H1, 399.9167583

DATA PROCESSING
 FT size 32768
 Total time 1 minute
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12a

```
Archive dir: /home/vnmr1/vnmrsys/data   Sample: RS12_20131008_01   File: RS_AP_9_AnthrMOM_1H
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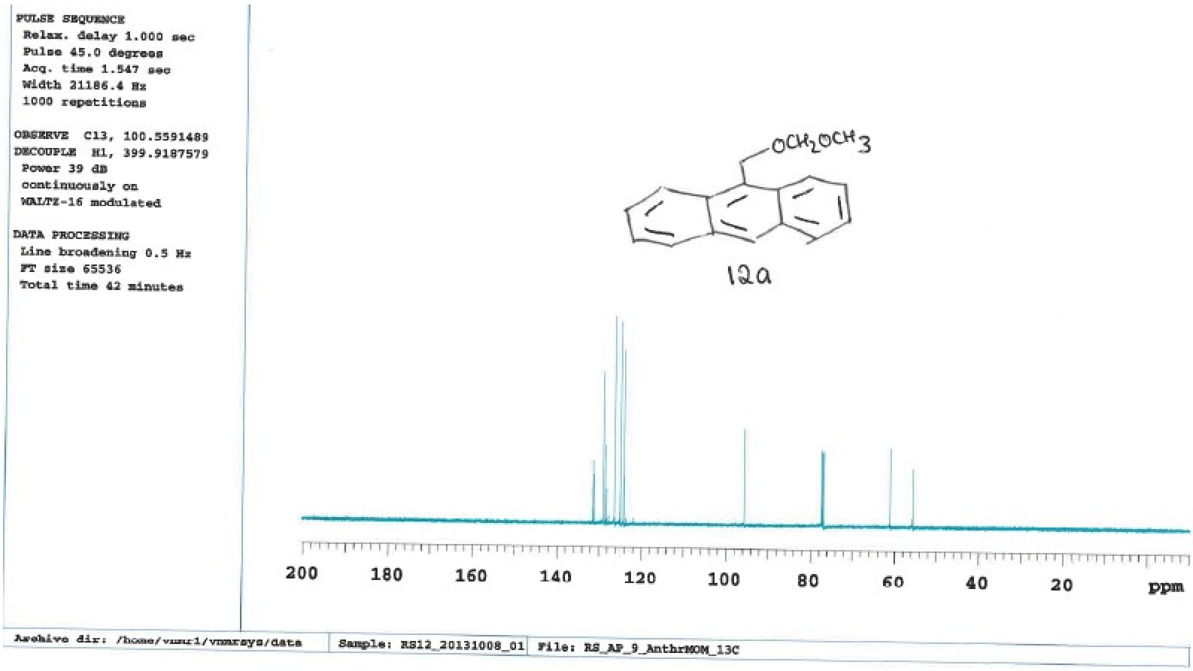

12a

PULSE SEQUENCE
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Pulse 45.0 degrees
Acq. time 1.547 sec
Width 21186.4 Hz
1000 repetitions

OBSERVE C13, 100.5591489
DECOUPLE H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 minutes

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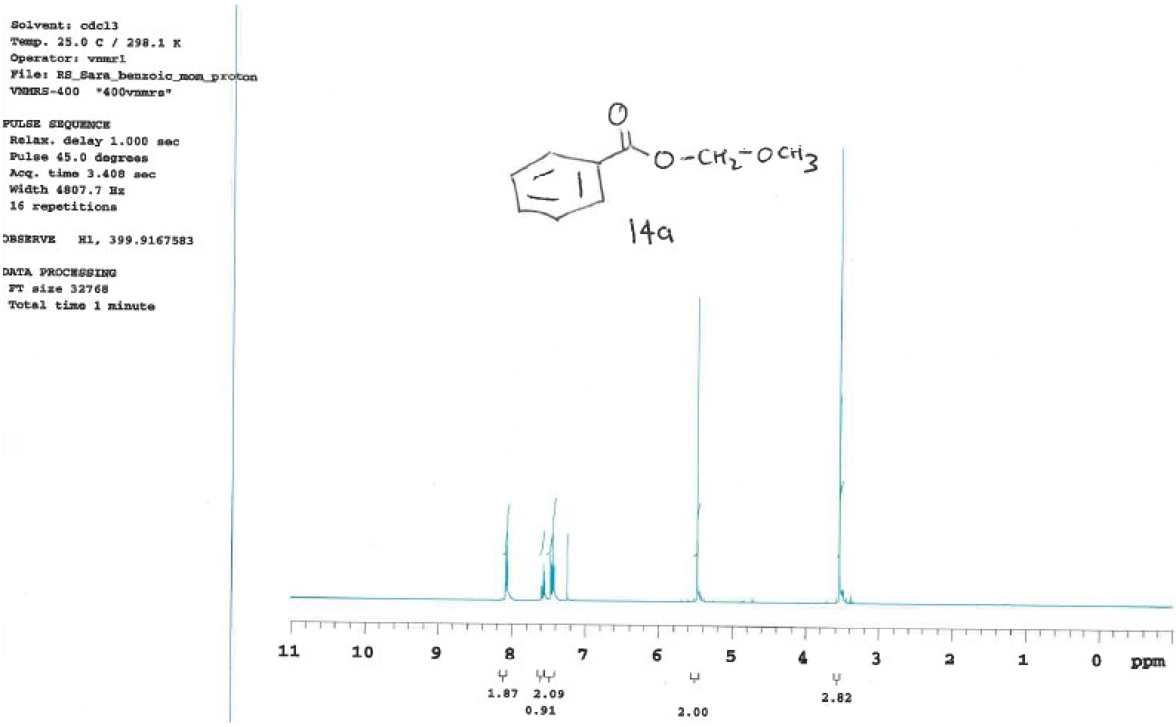
Sample: RS12_20131008_01
File: RS_AP_9_AnthrMOM_13C



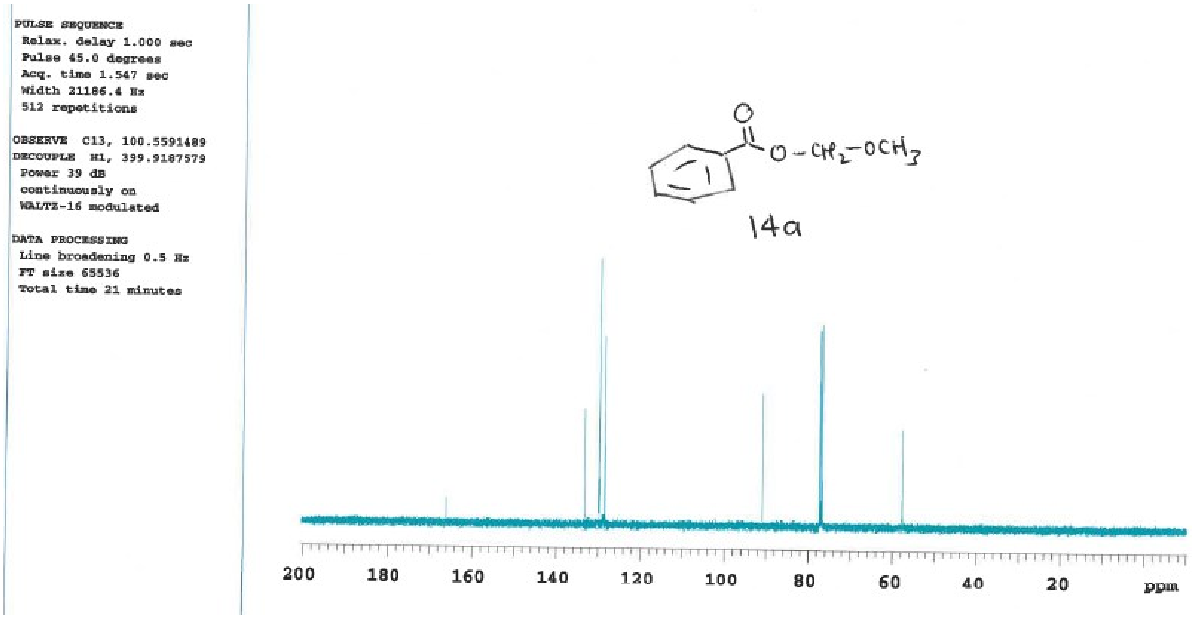
14a

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: RS_Sara_benzoic_mom_proton
VNMRS-400 "400vnmrs"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
16 repetitions

OBSERVE H1, 399.9167583

DATA PROCESSING
FT size 32768
Total time 1 minute



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PULSE SEQUENCE
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 Acq. time 1.547 sec
 Width 21186.4 Hz
 512 repetitions

OBSERVE  C13, 100.5591489
DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 21 minutes
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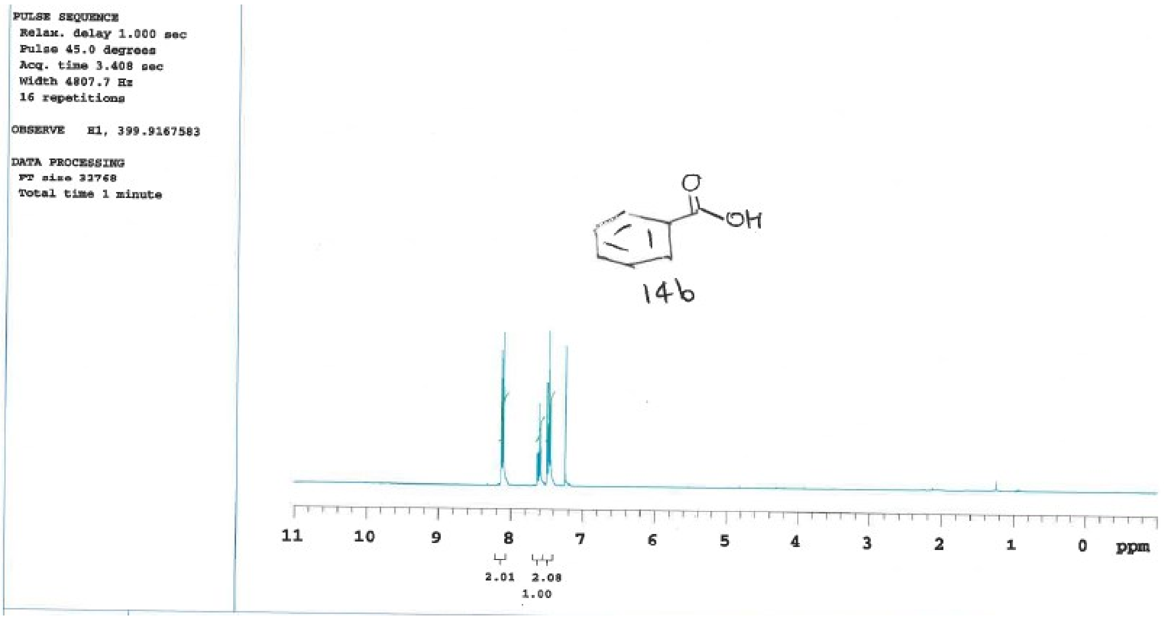
14a



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PULSE SEQUENCE
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 Acq. time 3.408 sec
 Width 4807.7 Hz
 16 repetitions

OBSERVE   H1, 399.9167583

DATA PROCESSING
 FT size 32768
 Total time 1 minute
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14b

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
16 repetitions

OBSERVE H1, 399.9167583

DATA PROCESSING
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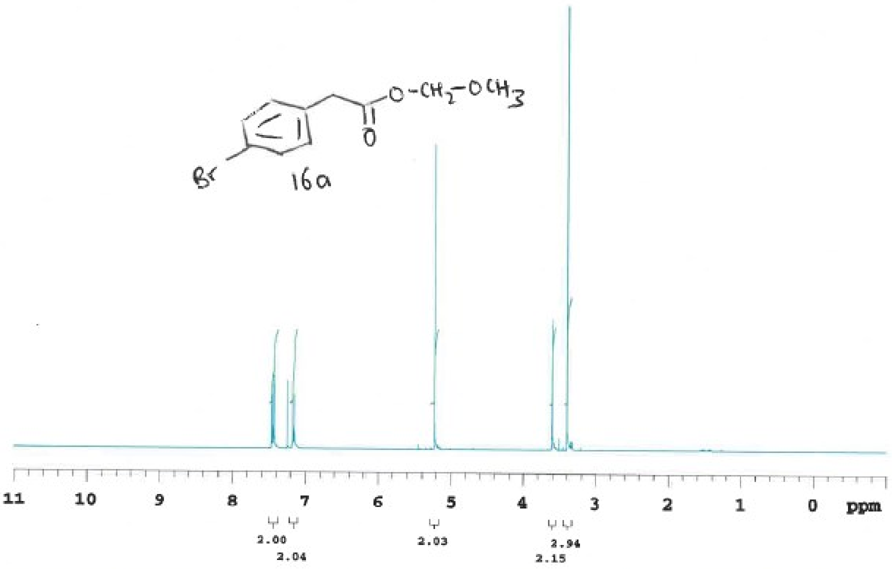
Total time 1 minute



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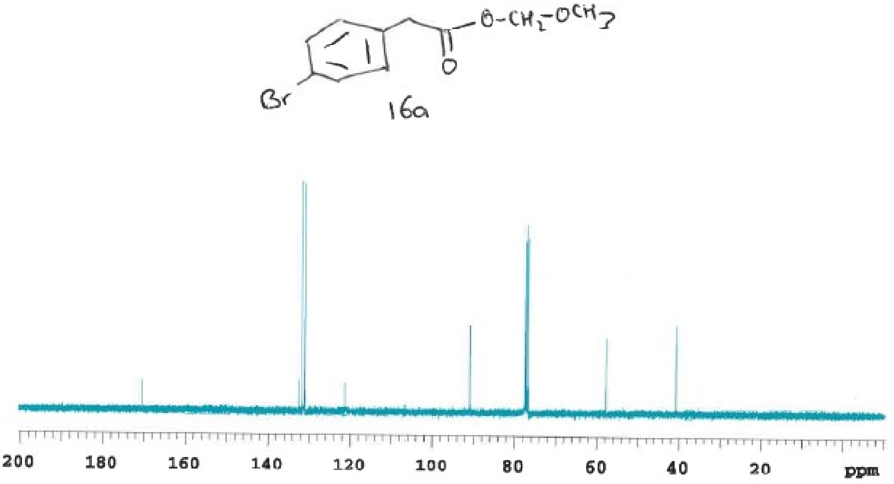
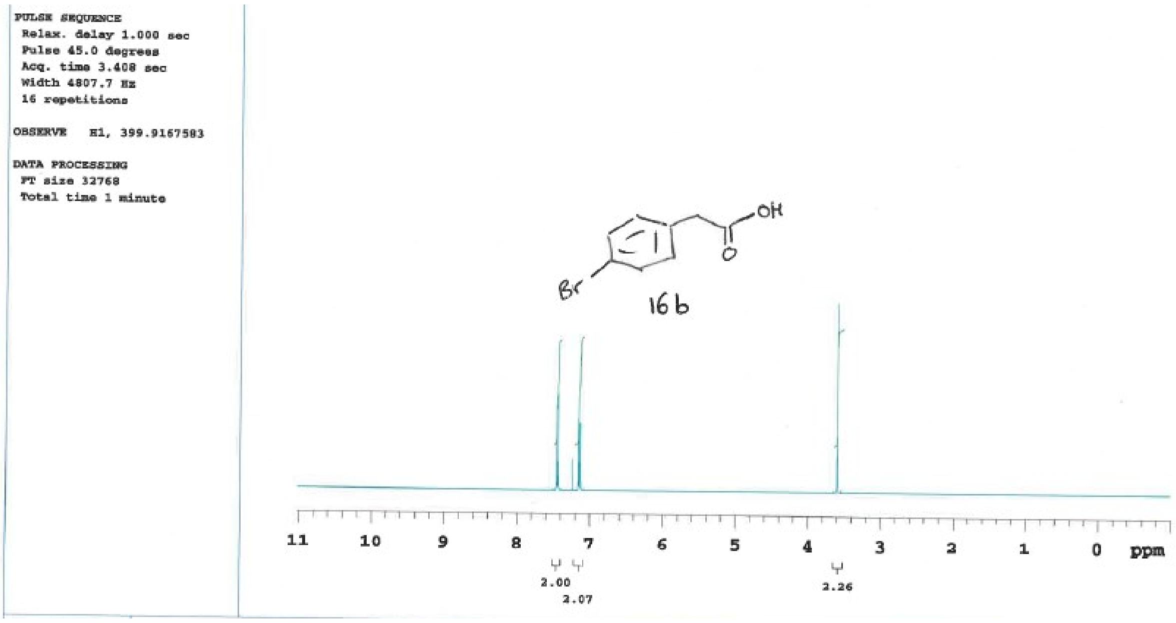
Width 21186.4 Hz
512 repetitions

OBSERVE C13, 100.5591489
DECOUPLE H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 21 minutes

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Acq. time 3.408 sec
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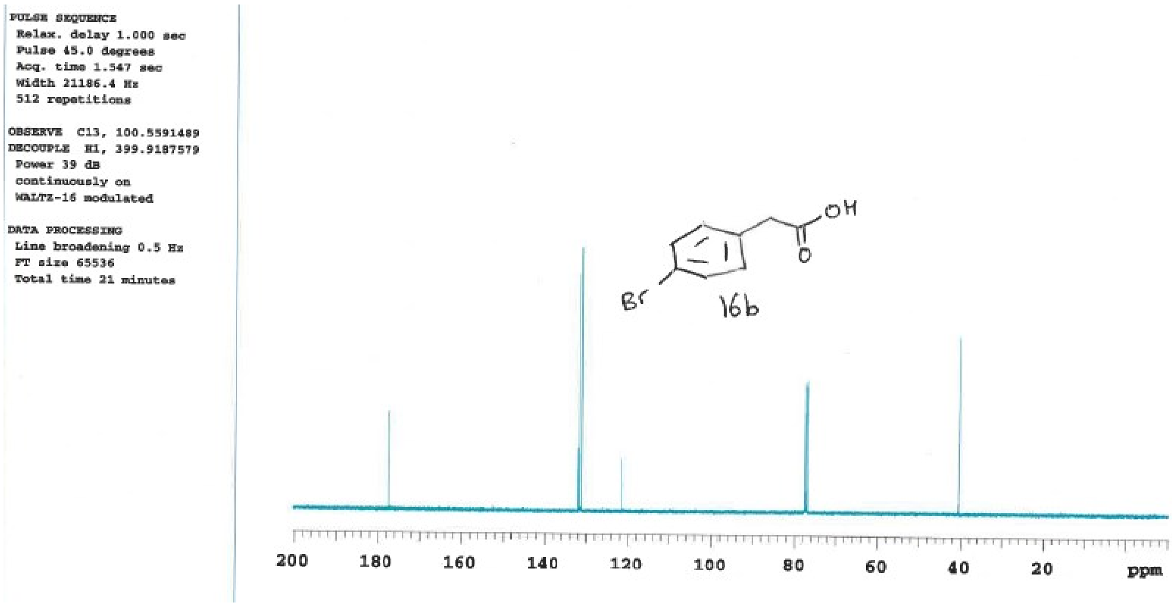
16 repetitions

OBSERVE H1, 399.9167583

DATA PROCESSING
FT size 32768
Total time 1 minute

16b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Acq. time 1.547 sec
Width 21186.4 Hz
512 repetitions

OBSERVE C13, 100.5591489
DECOUPLE H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

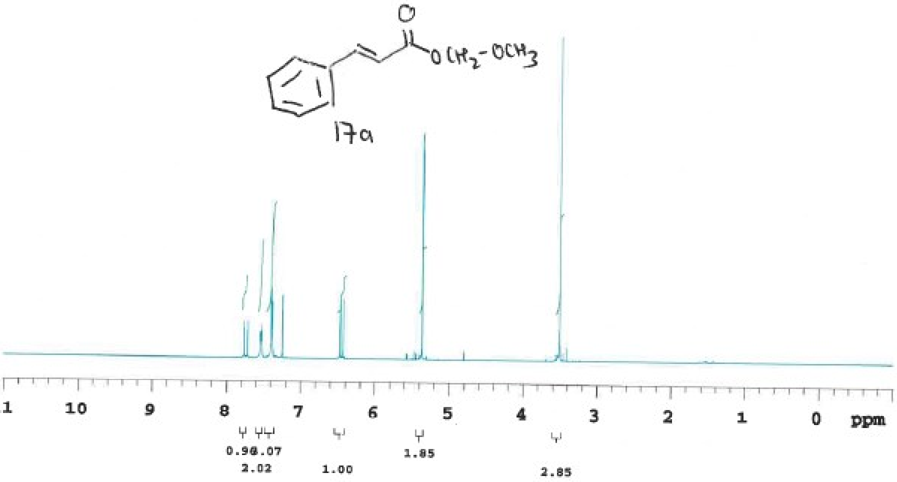
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 21 minutes

16b

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
16 repetitions

OBSERVE H1, 399.9167583

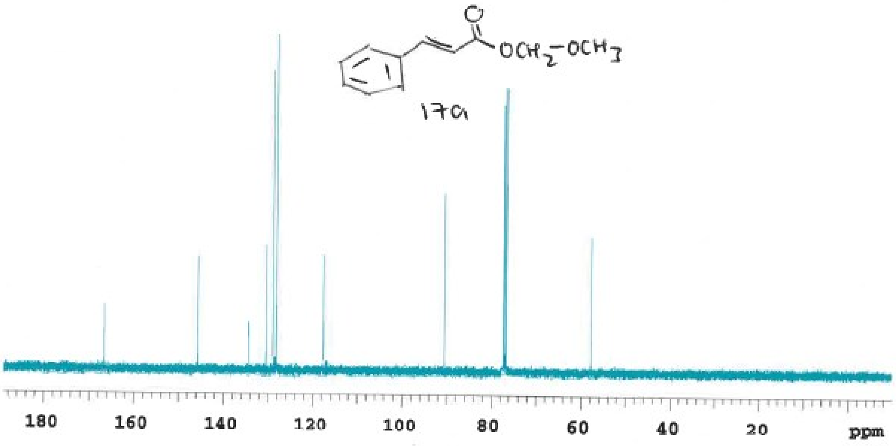
DATA PROCESSING
FT size 32768
Total time 1 minute

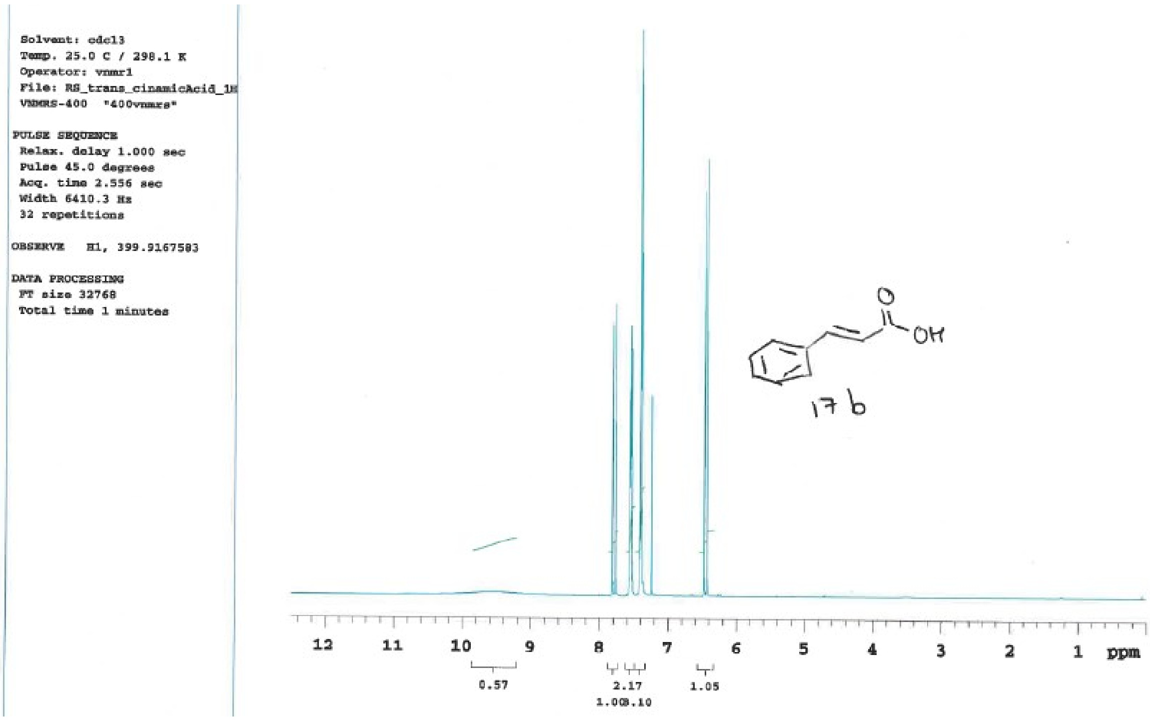


PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.547 sec
Width 21186.4 Hz
512 repetitions

OBSERVE C13, 100.5591489
DECOUPLE H1, 399.9187579
Power 39 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 21 minutes





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Operator: vnmr1
File: RS_trans_cinamicAcid_1H
VNMRS-400  "400vnmrs"

PULSE SEQUENCE
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 Pulse 45.0 degrees
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OBSERVE   H1, 399.9167583

DATA PROCESSING
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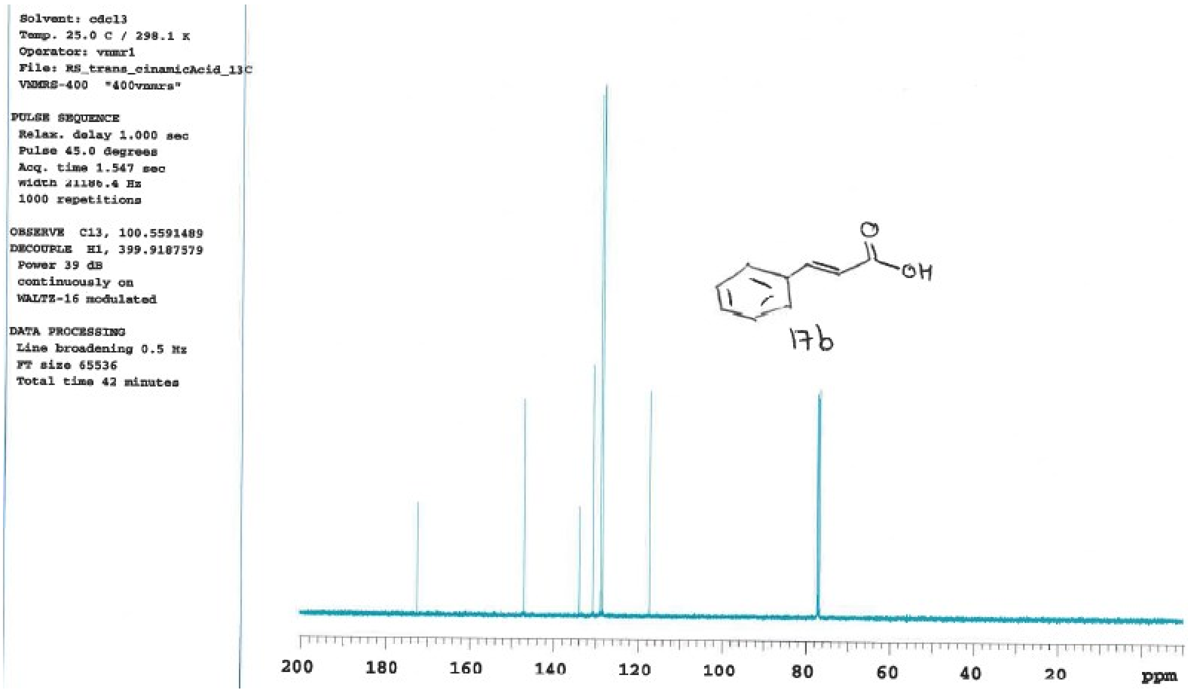

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Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: RS_trans_cinamicAcid_13C
VNMRS-400  "400vnmrs"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.547 sec
 Width 21186.4 Hz
 1000 repetitions

OBSERVE  C13, 100.5591489
DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 42 minutes
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```
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
File: RS_Tania_MOM_1H
VNMRS-400  "400vnmrs"

PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.408 sec
 Width 4807.7 Hz
 16 repetitions

OBSERVE   H1, 399.9167583

DATA PROCESSING
 FT size 32768
 Total time 1 minute
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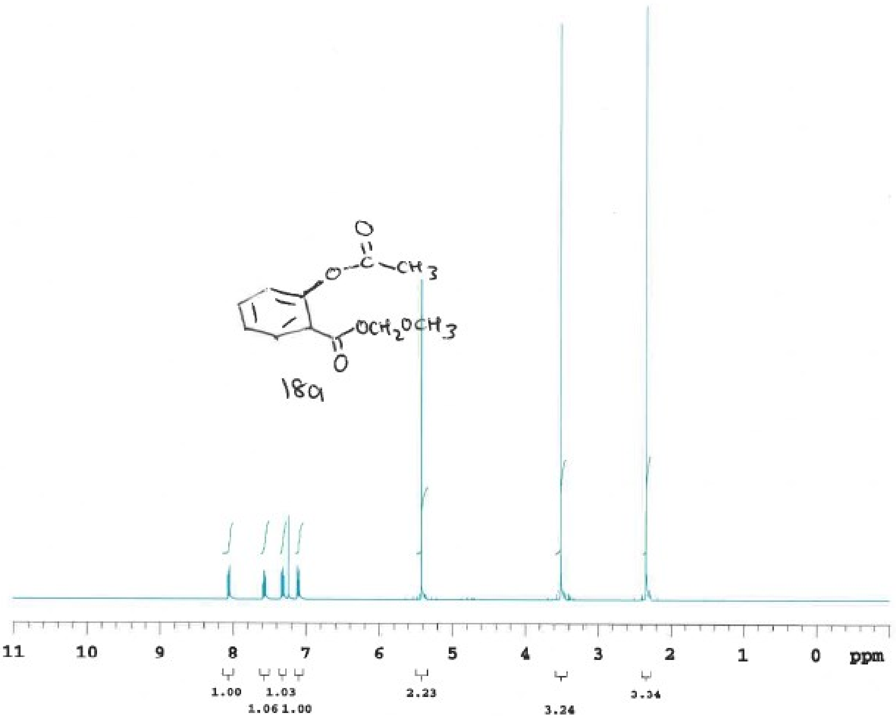

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PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.547 sec
 Width 21186.4 Hz
 512 repetitions

OBSERVE  C13, 100.5591489
DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 21 minutes
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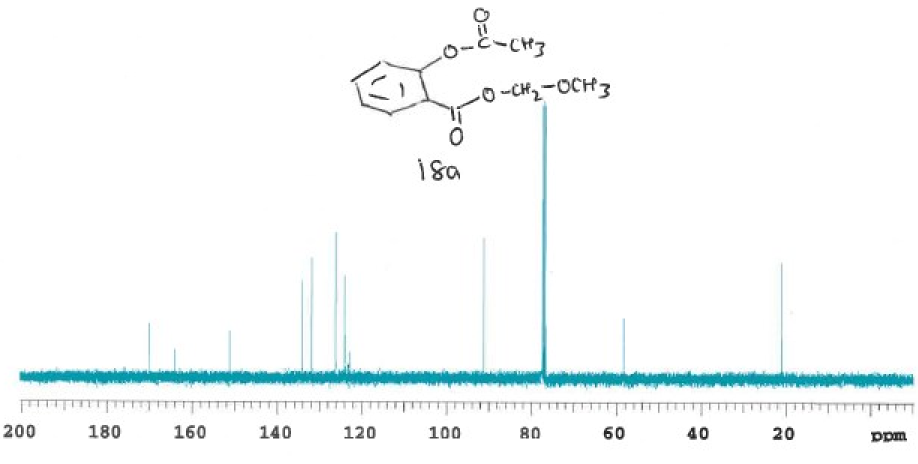

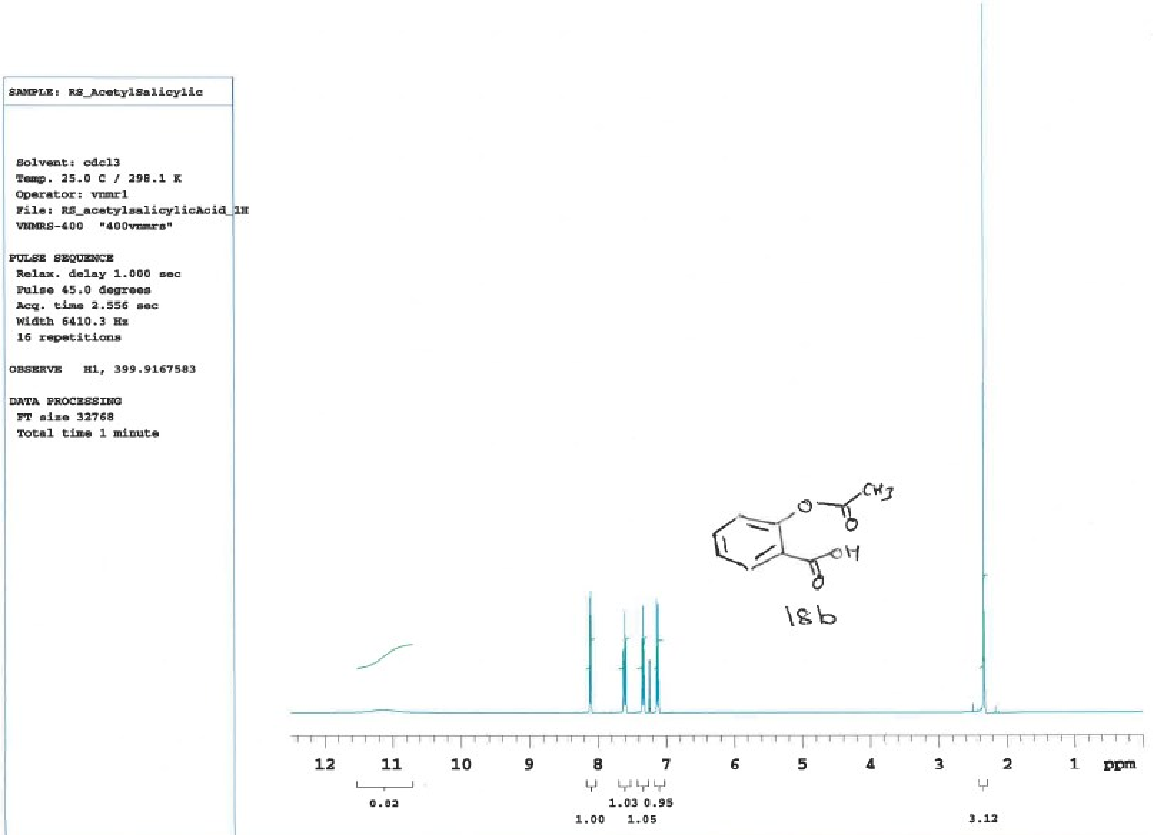

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 Pulse 45.0 degrees
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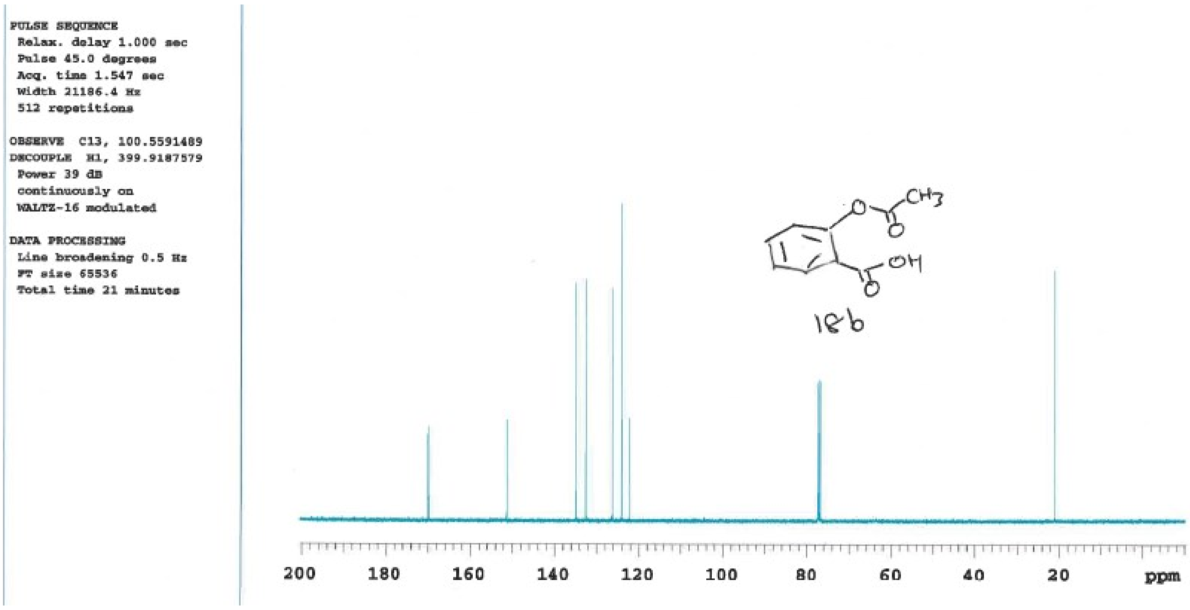
18b



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 Width 21186.4 Hz
 512 repetitions

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DECOUPLE  H1, 399.9187579
 Power 39 dB
 continuously on
 WALTZ-16 modulated

DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 21 minutes
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18b

S5. Computational data

Table S5.1: Selected interatomic distances (in Å) in the MCs, TSs and INs for the reaction **20** + $BiCl_3$ according to M06-2X/6-31G(d) calculations in the gas phase. Interatomic distances corresponding to Bi-Cl cleavage are shown in blue.

	Pathway 1					**Pathway 2**			
	***d*(Bi-O1)**	***d*(O1-C)**				***d*(Bi-O2)**	***d*(O2-C)**		
20MC1	2.404	1.481	***d*(Bi-Cl1)**	2.484	**20MC2**	2.379	1.445	***d*(Bi-Cl1)**	2.504
			***d*(Bi-Cl2)**	2.536				***d*(Bi-Cl2)**	2.488
			***d*(Bi-Cl3)**	2.504				***d*(Bi-Cl3)**	2.543
20TS1	2.083	2.513	***d*(Bi-Cl1)**	2.525	**20TS2**	2.048	2.444	***d*(Bi-Cl1)**	2.482
			***d*(Bi-Cl2)**	2.496				***d*(Bi-Cl2)**	2.744
			***d*(Bi-Cl3)**	2.682				***d*(Bi-Cl3)**	2.531
20IN1	2.032	3.073	***d*(Bi-Cl1)**	2.440	**20IN2**	1.996	2.916	***d*(Bi-Cl1)**	2.464
			***d*(Bi-Cl2)**	2.457				***d*(Bi---Cl2)**	3.574
			***d*(Bi---Cl3)**	3.164				***d*(Bi-Cl3)**	2.454

Table S5.2: Selected interatomic distances (in Å) in the MCs, TSs and INs for the reaction **21** + $BiCl_3$ according to M06-2X/6-31G(d) calculations in the gas phase. Interatomic distances corresponding to Bi-Cl cleavage are shown in blue.

Pathway 1					**Pathway 2**				
	***d*(Bi-O1)**	***d*(O1-C)**				***d*(Bi-O2)**	***d*(O2-C)**		
21MC1	2.255	1.476	***d*(Bi-Cl1)**	2.580	**21MC2**	2.327	1.460	***d*(Bi-Cl1)**	2.512
			***d*(Bi-Cl2)**	2.437				***d*(Bi-Cl2)**	2.494
			***d*(Bi-Cl3)**	2.553				***d*(Bi-Cl3)**	2.553
21TS1	2.074	2.426	***d*(Bi-Cl1)**	2.534	**21TS2**	2.043	2.493	***d*(Bi-Cl1)**	2.481
			***d*(Bi-Cl2)**	2.513				***d*(Bi-Cl2)**	2.731
			***d*(Bi-Cl3)**	2.663				***d*(Bi-Cl3)**	2.545
21IN1	2.022	3.107	***d*(Bi-Cl1)**	2.450	**21IN2**	1.996	2.904	***d*(Bi-Cl1)**	2.468
			***d*(Bi-Cl2)**	2.437				***d*(Bi---Cl2)**	3.548
			***d*(Bi---Cl3)**	3.258				***d*(Bi-Cl3)**	2.465

Table S5.3: Selected interatomic distances (in Å) in the MCs, TSs and INs for the reaction **22** + $BiCl_3$ according to M06-2X/6-31G(d) calculations in the gas phase. Interatomic distances corresponding to Bi-Cl cleavage are shown in blue.

Pathway 1					**Pathway 2**				
	***d*(Bi-O1)**	***d*(O1-C)**				***d*(Bi-O2)**	***d*(O2-C)**		
22MC1	2.334	1.480	***d*(Bi-Cl1)**	2.490	**22MC2**	2.337	1.437	***d*(Bi-Cl1)**	2.535
			***d*(Bi-Cl2)**	2.554				***d*(Bi-Cl2)**	2.445
			***d*(Bi-Cl3)**	2.514				***d*(Bi-Cl3)**	2.592
22TS1	2.075	2.431	***d*(Bi-Cl1)**	2.535	**22TS2**	2.043	2.586	***d*(Bi-Cl1)**	2.478
			***d*(Bi-Cl2)**	2.513				***d*(Bi-Cl2)**	2.535
			***d*(Bi-Cl3)**	2.661				***d*(Bi-Cl3)**	2.744
22IN1	2.020	2.884	***d*(Bi-Cl1)**	2.456	**22IN2**	1.996	2.914	***d*(Bi-Cl1)**	2.468
			***d*(Bi-Cl2)**	2.445				***d*(Bi-Cl2)**	2.464
			***d*(Bi---Cl3)**	3.427				***d*(Bi---Cl3)**	3.570

Table S5.4: Selected interatomic distances (in Å) in the MCs, TSs and INs for the reaction **2a** + $BiCl_3$ according to M06-2X/6-31G(d) calculations in the gas phase. Interatomic distances corresponding to Bi-Cl cleavage are shown in blue.

Pathway 1					**Pathway 2**				
	***d*(Bi-O1)**	***d*(O1-C)**				***d*(Bi-O2)**	***d*(O2-C)**		
2aMC1	2.295	1.458	***d*(Bi-Cl1)**	2.522	**2aMC2**	2.294	1.472	***d*(Bi-Cl1)**	2.484
			***d*(Bi-Cl2)**	2.541				***d*(Bi-Cl2)**	2.554
			***d*(Bi-Cl3)**	2.520				***d*(Bi-Cl3)**	2.533
2aTS1	2.037	2.523	***d*(Bi-Cl1)**	2.737	**2aTS2**	2.034	2.548	***d*(Bi-Cl1)**	2.477
			***d*(Bi-Cl2)**	2.544				***d*(Bi-Cl2)**	2.531
			***d*(Bi-Cl3)**	2.488				***d*(Bi-Cl3)**	2.777
2aIN1	1.989	2.919	***d*(Bi---Cl1)**	3.236	**2aIN2**	1.991	2.935	***d*(Bi-Cl1)**	2.461
			***d*(Bi-Cl2)**	2.464				***d*(Bi-Cl2)**	2.462
			***d*(Bi-Cl3)**	2.457				***d*(Bi---Cl3)**	3.228

Table S5.5: Selected interatomic distances (in Å) in the MCs, TSs and INs for the reaction **3a** + $BiCl_3$ according to M06-2X/6-31G(d) calculations in the gas phase. Interatomic distances corresponding to Bi-Cl cleavage are shown in blue.

Pathway 1					**Pathway 2**				
	***d*(Bi-O1)**	***d*(O1-C)**				***d*(Bi-O2)**	***d*(O2-C)**	***d*(Bi-Cl)**	
3aMC1	2.298	1.459	***d*(Bi-Cl1)**	2.530	**3aMC2**	2.292	1.471	***d*(Bi-Cl1)**	2.482
			***d*(Bi-Cl2)**	2.547				***d*(Bi-Cl2)**	2.555
			***d*(Bi-Cl3)**	2.506				***d*(Bi-Cl3)**	2.538
3aTS1	2.039	2.513	***d*(Bi-Cl1)**	2.731	**3aTS2**	2.034	2.544	***d*(Bi-Cl1)**	2.471
			***d*(Bi-Cl2)**	2.551				***d*(Bi-Cl2)**	2.528
			***d*(Bi-Cl3)**	2.485				***d*(Bi-Cl3)**	2.787
3aIN1	1.989	2.932	***d*(Bi---Cl1)**	3.247	**3aIN2**	1.990	2.948	***d*(Bi-Cl1)**	2.464
			***d*(Bi-Cl2)**	2.465				***d*(Bi-Cl2)**	2.461
			***d*(Bi-Cl3)**	2.455				***d*(Bi---Cl3)**	3.233

Compound 19

Table S5.6: Relative electronic energies (ΔE, in kcal mol^{-1}), enthalpies (ΔH, in kcal mol^{-1}), Gibbs free energies (ΔG, in kcal mol^{-1}) and entropies (ΔS, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using the M06-2X functional in correlation with 6-31+G(d) and 6-311G(d) basis sets, respectively for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **19** + BiCl$_3$ (**19** = (methoxymethoxy)benzene) at 25°C.

O1 (Pathway 1)					O2 (Pathway 2)				
	ΔE	ΔH	ΔG	ΔS		ΔE	ΔH	ΔG	ΔS
M06-2X/6-31+G(d)									
19MC1	-11.7	-11.5	1.9	-45.2	**19MC2**	-15.2	-15.3	-0.1	-51.2
19TS1	11.1	11.3	25.2	-46.6	**19TS2**	21.2	21.6	34.6	-43.6
19IN1	-10.0	-9.5	2.9	-41.6	**19IN2**	-9.0	-8.6	3.8	-41.8
M06-2X/6-311G(d)									
19MC1	-14.4	-14.2	-0.6	-45.9	**19MC2**	-18.7	-18.8	-3.8	-50.2
19TS1	7.2	7.3	21.4	-47.0	**19TS2**	17.0	17.3	30.1	-42.7
19IN1	-12.3	-11.7	0.2	-40.0	**19IN2**	-12.4	-12.0	0.6	-42.5

Table S5.7: Relative electronic energies (ΔE, in kcal mol^{-1}), enthalpies (ΔH, in kcal mol^{-1}), free energies (ΔG, in kcal mol^{-1}) and entropies (ΔS, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using the B3LYP functional and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **19** + BiCl$_3$ (**19** = (methoxymethoxy)benzene).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^{a}	ΔH^{a}	ΔG^{a}	ΔG^{b}	ΔS^{a}		ΔE^{a}	ΔH^{a}	ΔG^{a}	ΔG^{b}	ΔS^{a}
B3LYP/6-31G(d)											
19MC1	1.9	2.4	15.9	17.0	-45.2	**19MC2**	1.5	1.9	14.4	15.4	-41.9
19TS1	22.6	23.1	36.4	37.5	-44.5	**19TS2**	29.3	29.8	42.7	43.7	-43.0
19IN1	2.4	3.3	13.9	14.9	-35.8	**19IN2**	3.7	4.4	16.2	17.3	-39.8
MP2/6-31G(d)											
19MC1	-1.0	-0.7	12.4	13.5	-43.9	**19MC2**	-2.2	-2.1	12.4	13.7	-48.8
19TS1	22.6	22.9	35.8	36.9	-43.4	**19TS2**	31.9	32.3	44.5	45.4	-40.6
19IN1	-3.6	-3.0	8.1	9.0	-37.1	**19IN2**	-4.1	-3.6	8.2	9.1	-39.4

[a] at 25 °C

[b] at 50 °C

Compound 20

Table S5.8: Relative electronic energies (Δ*E*, in kcal mol^{-1}), enthalpies (Δ*H*, in kcal mol^{-1}), Gibbs free energies (Δ*G*, in kcal mol^{-1}) and entropies (Δ*S*, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **20** + BiCl$_3$ (**20** = 1-(methoxymethoxy)-4-nitrobenzene).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a		ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a
B3LYP/6-31G(d)											
20MC1	9.7	10.4	21.7	22.7	-38.1	**20MC2**	5.7	6.0	18.1	19.1	-40.4
20TS1	27.9	28.6	39.7	40.6	-37.3	**20TS2**	39.5	40.1	51.0	51.9	-36.3
20IN1	7.1	8.2	15.5	16.1	-24.7	**20IN2**	10.6	11.4	21.3	22.1	-33.2
M06-2X/6-31G(d)											
20MC1	-3.6	-3.2	9.1	10.1	-41.2	**20MC2**	-6.2	-6.0	6.1	7.1	-40.5
20TS1	18.8	19.2	31.4	32.4	-40.9	**20TS2**	31.7	32.1	44.5	45.5	-41.6
20IN1	-2.5	-1.7	9.0	9.9	-35.9	**20IN2**	-0.5	0.0	11.8	12.8	-39.7
MP2/6-31G(d)											
20MC1	7.6	8.0	20.3	21.4	-41.3	**20MC2**	5.9	6.2	18.6	19.6	-41.6
20TS1	29.2	29.6	41.4	42.4	-39.7	**20TS2**	42.8	43.3	55.3	56.3	-40.1
20IN1	-0.9	-0.3	10.1	11.0	-35.0	**20IN2**	4.3	4.9	15.8	16.7	-36.4

[a] at 25°C

[b] at 50°C

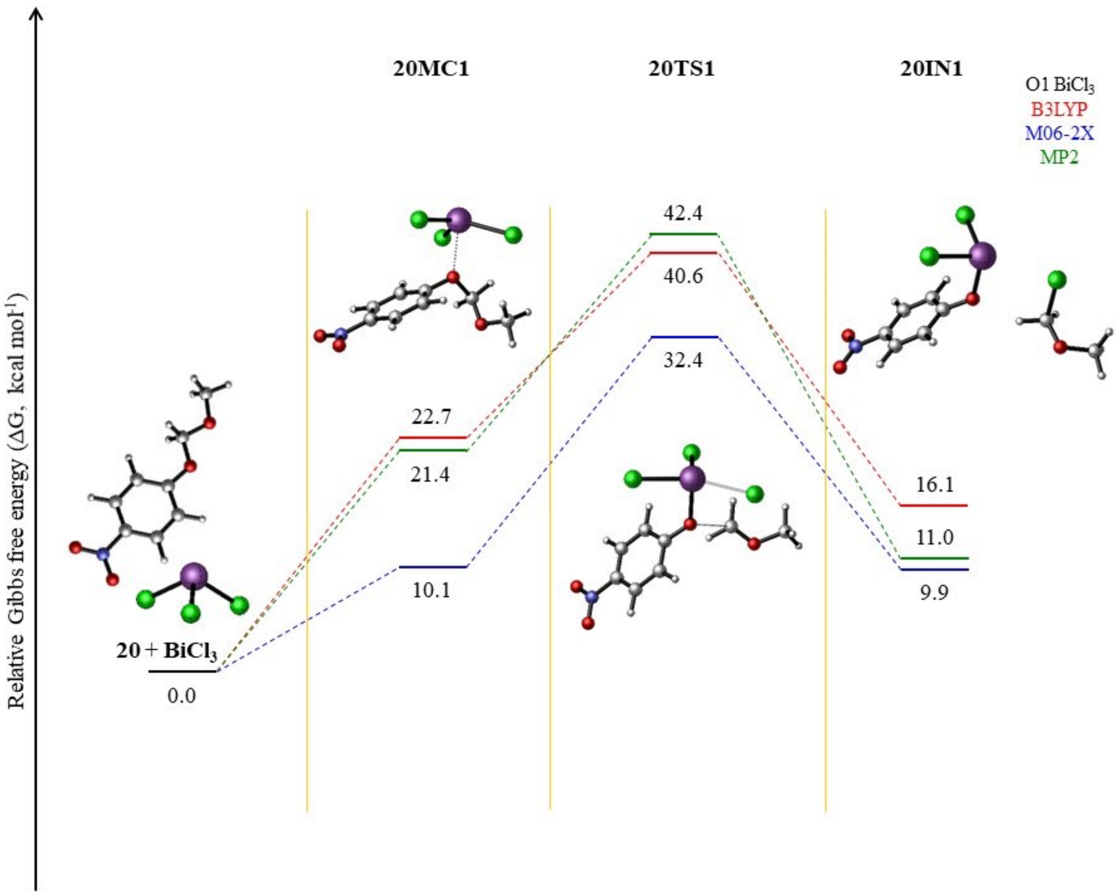

Figure S5.1(a): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **20** + $BiCl_3$ via pathway 1, where $BiCl_3$ is attached to O1 in the gas phase at 50°C.

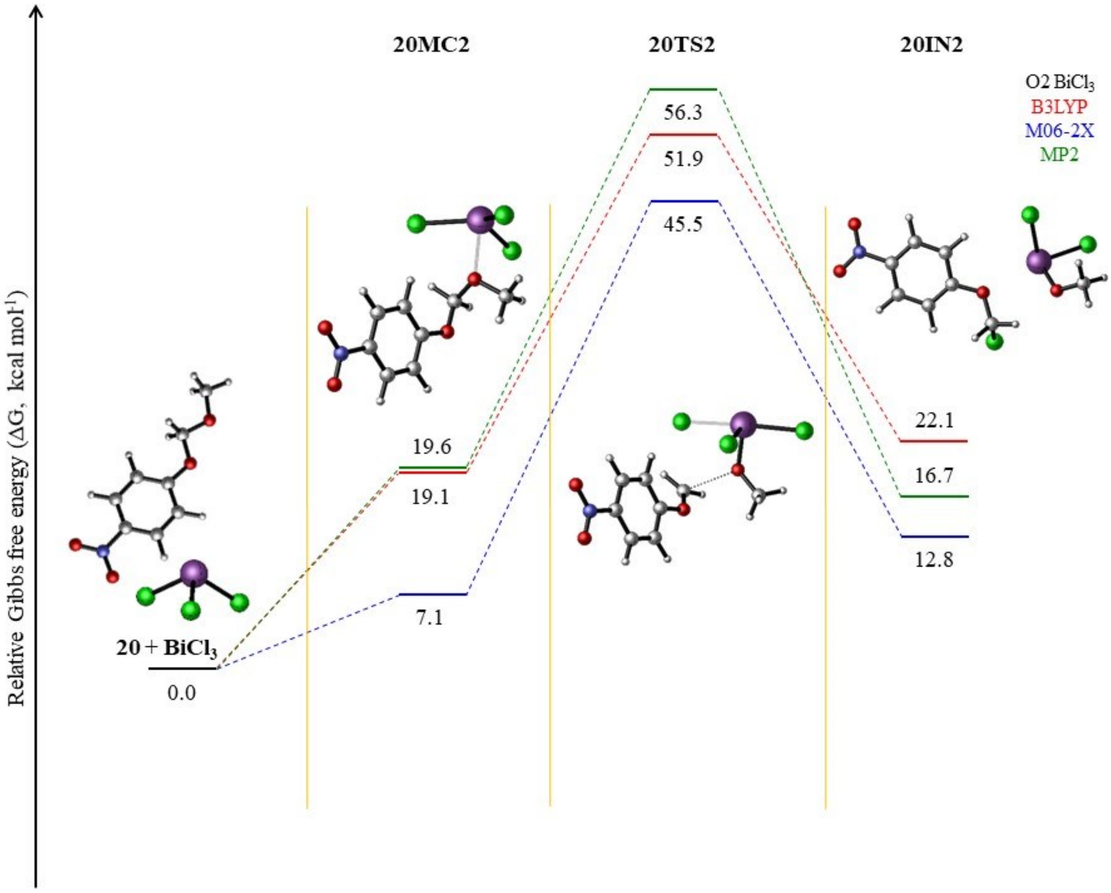

Figure S5.1(b): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **20** + $BiCl_3$ via pathway 2, where $BiCl_3$ is attached to O2 in the gas phase at 50°C.

Compound 21

Table S5.9: Relative electronic energies (Δ*E*, in kcal mol^{-1}), enthalpies (Δ*H*, in kcal mol^{-1}), Gibbs free energies (Δ*G*, in kcal mol^{-1}) and entropies (Δ*S*, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **21** + $BiCl_3$ (**21** = 1-methoxy-4-(methoxymethoxy)benzene).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a		ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a
B3LYP/6-31G(d)											
21MC1	3.2	3.7	15.8	16.9	-40.7	**21MC2**	0.7	0.9	13.6	14.7	-42.5
21TS1	23.4	23.9	36.3	37.3	-41.5	**21TS2**	28.3	28.9	40.6	41.6	-39.2
21IN1	3.2	4.1	13.5	14.3	-31.6	**21IN2**	4.6	5.3	16.5	17.4	-37.5
M06-2X/6-31G(d)											
21MC1	-13.4	-13.5	1.1	2.3	-48.9	**21MC2**	-12.4	-12.5	0.9	2.0	-45.0
21TS1	12.8	12.7	27.4	28.7	-49.4	**21TS2**	19.8	19.9	33.5	34.6	-45.6
21IN1	-6.2	-5.8	6.3	7.3	-40.8	**21IN2**	-8.3	-8.1	5.2	6.3	-44.7
MP2/6-31G(d)											
21MC1	1.2	1.6	14.2	15.3	-42.4	**21MC2**	1.2	1.4	14.2	15.3	-43.1
21TS1	25.2	25.6	38.4	39.4	-42.8	**21TS2**	33.2	33.7	46.0	47.0	-41.1
21IN1	-3.7	-3.1	8.2	9.1	-37.9	**21IN2**	-1.6	-1.0	10.5	11.5	-38.6

[a] at 25°C

[b] at 50°C

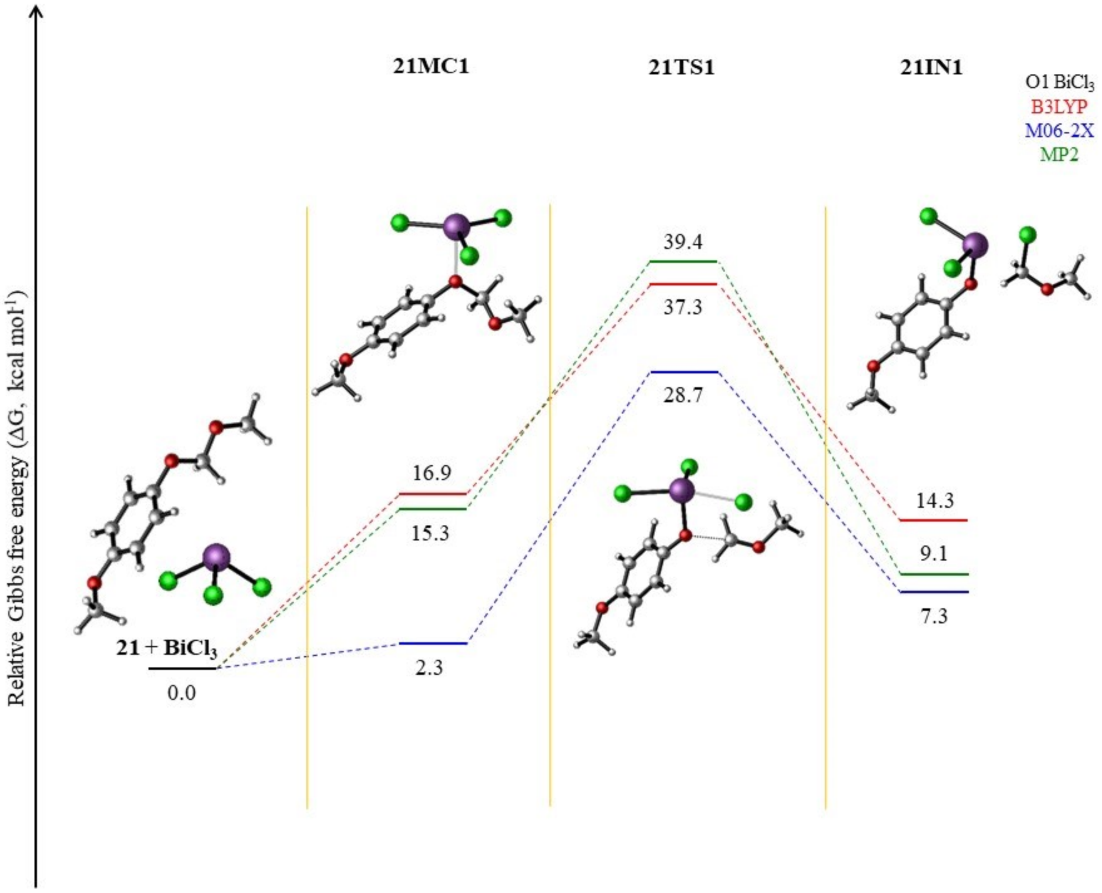

Figure S5.2(a): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **21** + $BiCl_3$ via pathway 1, where $BiCl_3$ is attached to O1 in the gas phase at 50°C.

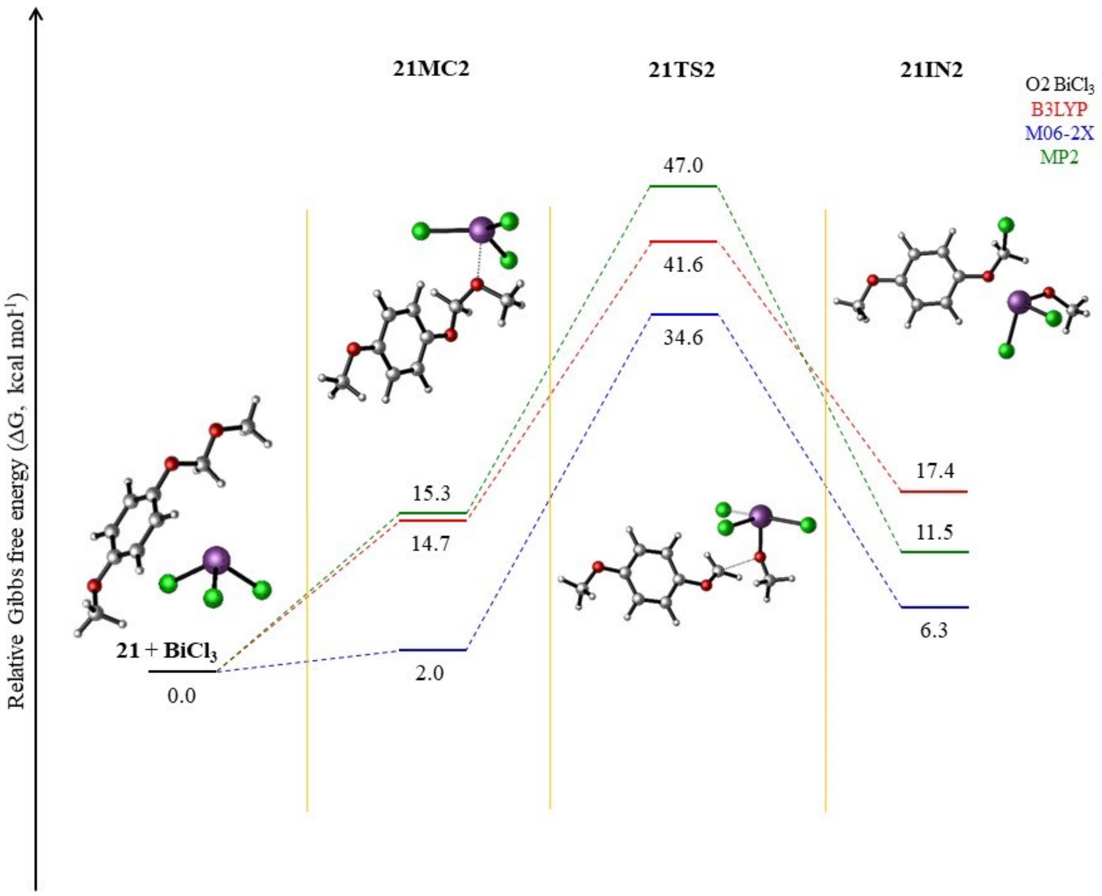

Figure S5.2(b): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **21** + $BiCl_3$ via pathway 2, where $BiCl_3$ is attached to O2 in the gas phase at 50°C.

Compound 22

Table S5.10: Relative electronic energies (ΔE, in kcal mol^{-1}), enthalpies (ΔH, in kcal mol^{-1}), Gibbs free energies (ΔG, in kcal mol^{-1}) and entropies (ΔS, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **22** + $BiCl_3$ (**22** = 1-ethyl-4-(methoxymethoxy)benzene).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a		ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a
B3LYP/6-31G(d)											
22MC1	4.2	4.8	16.4	17.3	-38.8	**22MC2**	3.6	4.0	16.4	17.5	-41.8
22TS1	25.1	25.7	36.9	37.8	-37.4	**22TS2**	33.7	34.5	45.2	46.1	-36.1
22IN1	4.8	5.7	14.4	15.1	-29.0	**22IN2**	6.2	7.0	17.1	18.0	-34.0
M06-2X/6-31G(d)											
22MC1	-9.6	-9.3	3.5	4.6	-43.1	**22MC2**	-12.0	-11.9	1.6	2.8	-45.5
22TS1	14.6	14.8	27.9	29.0	-43.8	**22TS2**	25.8	26.4	37.8	38.8	-38.3
22IN1	-7.1	-6.6	4.7	5.7	-37.9	**22IN2**	-6.5	-5.9	4.7	5.6	-35.6
MP2/6-31G(d)											
22MC1	0.2	0.6	13.6	14.7	-43.8	**22MC2**	-0.2	-0.1	13.9	15.1	-46.8
22TS1	24.0	24.4	37.3	38.4	-43.5	**22TS2**	36.1	36.7	48.5	49.5	-39.5
22IN1	-5.7	-5.2	6.3	7.2	-38.3	**22IN2**	-2.7	-2.1	9.6	10.6	-39.2

[a] at 25°

[b] at 50°C

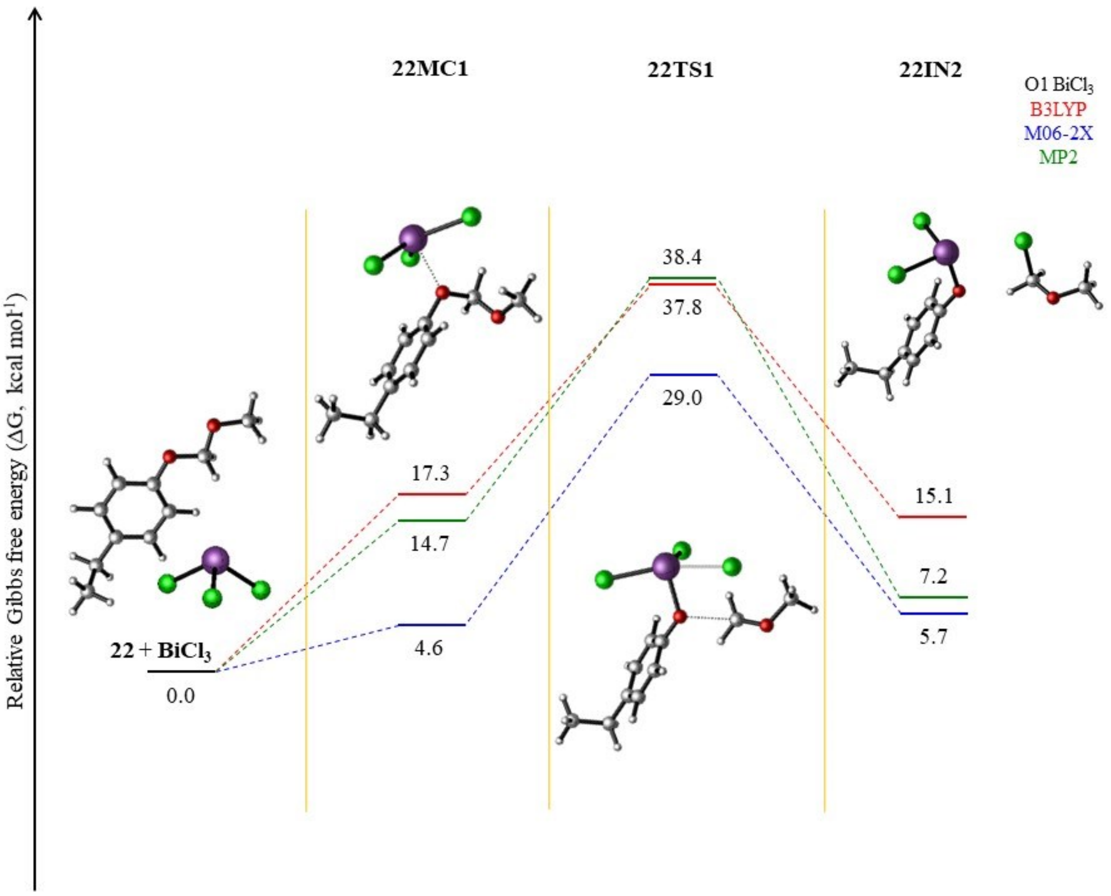

Figure S5.3(a): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **22** + $BiCl_3$ via pathway 1, where $BiCl_3$ is attached to O1 in the gas phase at 50°C.

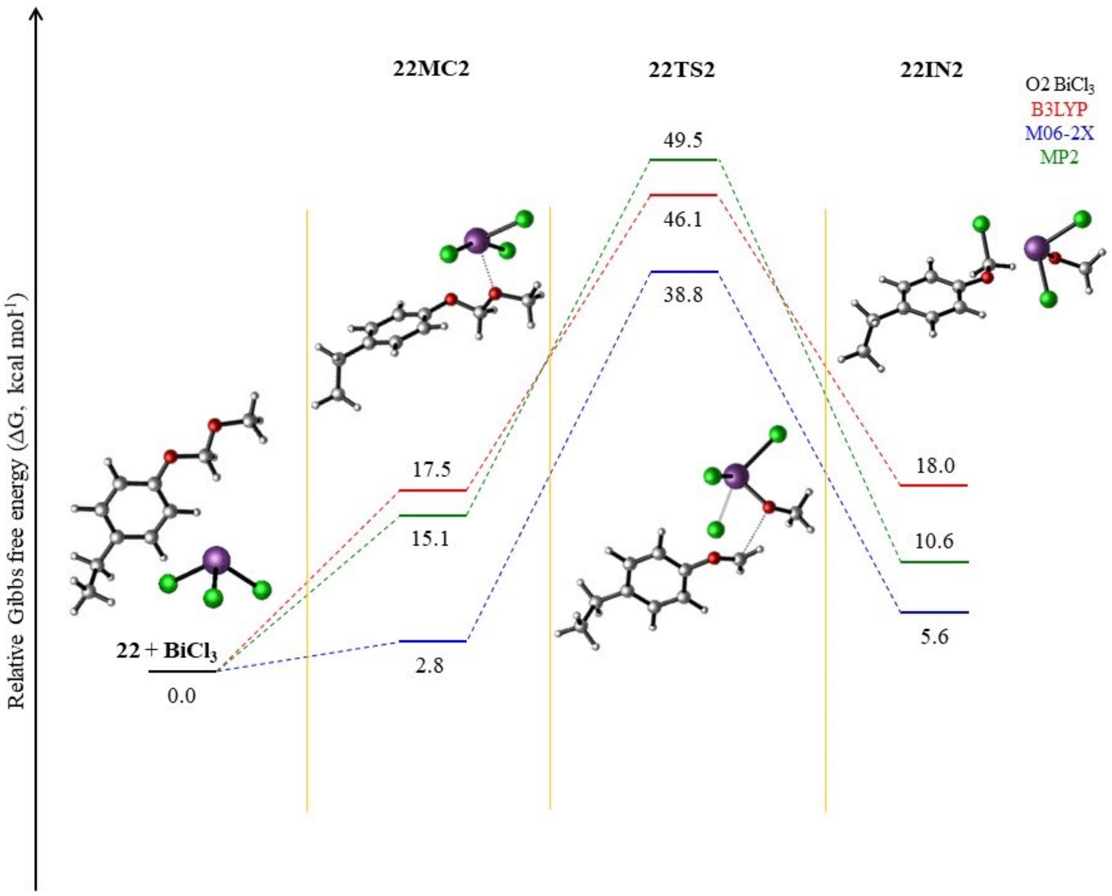

Figure S5.3(b): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **22** + $BiCl_3$ via pathway 2, where $BiCl_3$ is attached to O2 in the gas phase at 50°C.

Table S5.11(a): Mulliken charges (e) of the coordinating sites of $BiCl_3$ and phenolic MOM substrates.

	BiCl3	**19**	**20**	**21**	**22**
Bi	1.19				
Cl	-0.40				
O1		-0.54	-0.52	-0.54	-0.54
O2		-0.48	-0.48	-0.48	-0.48

Table S5.11(b): Interaction energies (kcal/mol) obtained from Natural Bond Orbital (NBO) analysis of the coordination of Bi with O1 or O2 for phenolic MOM molecular complexes.

	19MC	**20MC**	**21MC**	**22MC**
O1-Bi	54.92	47.22	47.44	56.01
O2-Bi	47.77	47.53	37.37	37.76

Compound 2a

Table S5.12: Relative electronic energies (ΔE, in kcal mol^{-1}), enthalpies (ΔH, in kcal mol^{-1}), Gibbs free energies (ΔG, in kcal mol^{-1}) and entropies (ΔS, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **2a** + $BiCl_3$ (**2a** = 1-(methoxymethoxy)octane).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a		ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a
B3LYP/6-31G(d)											
2aMC1	0.8	1.2	13.0	13.9	-39.4	**2aMC2**	-0.5	-0.2	11.4	12.4	-38.9
2aTS1	26.2	26.8	38.1	39.0	-37.9	**2aTS2**	24.2	24.8	35.6	36.5	-36.0
2aIN1	4.4	5.3	13.4	14.0	-27.0	**2aIN2**	4.3	5.3	13.4	14.1	-27.3
M06-2X/6-31G(d)											
2aMC1	-11.1	-10.8	0.7	1.6	-38.3	**2aMC2**	-12.8	-12.7	-0.1	0.9	-42.2
2aTS1	18.4	18.5	31.8	32.9	-44.5	**2aTS2**	17.2	17.5	30.6	31.7	-43.9
2aIN1	-4.3	-4.0	8.5	9.6	-42.0	**2aIN2**	-5.3	-4.9	6.9	7.9	-39.7
MP2/6-31G(d)											
2aMC1	-0.6	-0.3	11.9	12.9	-41.0	**2aMC2**	-1.7	-1.5	10.8	11.8	-41.2
2aTS1	27.4	27.8	39.8	40.8	-40.2	**2aTS2**	25.8	26.3	37.6	38.6	-37.8
I2aN1	-4.2	-3.6	6.5	7.4	-34.0	**2aIN2**	-0.4	0.2	10.8	11.7	-35.5

[a] at 25°C

[b] at 50°C

Compound 3a

Table S5.13: Relative electronic energies (ΔE, in kcal mol^{-1}), enthalpies (ΔH, in kcal mol^{-1}), Gibbs free energies (ΔG, in kcal mol^{-1}) and entropies (ΔS, in cal mol^{-1} K^{-1}) including zero-point energy corrections computed using the M06-2X functional in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set in the gas phase for the reactions **3a** + BiCl$_3$ (**3a** = (3-(methoxymethoxy)propyl)benzene).

O1 (Pathway 1)						O2 (Pathway 2)					
	ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a		ΔE^a	ΔH^a	ΔG^a	ΔG^b	ΔS^a
B3LYP/6-31G(d)											
3aMC1	14.2	14.8	26.9	27.9	-40.7	**3aMC2**	-0.9	-0.7	-38.1	14.2	-46.1
3aTS1	30.1	30.7	42.5	43.5	-39.8	**3aTS2**	39.5	40.3	0.0	52.1	-36.3
3aIN1	13.7	14.7	24.7	25.5	-33.6	**3aIN2**	10.0	10.8	-31.1	20.9	-31.1
M06-2X/6-31G(d)											
3aMC1	-10.5	-10.4	2.5	3.6	-43.2	**3aMC2**	-12.8	-12.8	0.5	1.7	-44.8
3aTS1	18.1	18.3	31.6	32.7	-44.6	**3aTS2**	17.5	17.8	30.5	31.6	-42.6
3aIN1	-4.5	-4.0	8.0	9.0	-40.3	**3aIN2**	-5.2	-4.8	7.3	8.3	-40.6
MP2/6-31G(d)											
3aMC1	0.6	0.9	13.2	14.3	-41.4	**3aMC2**	-0.7	-0.5	12.3	13.4	-43.1
3aTS1	28.4	28.8	41.1	42.1	-41.1	**3aTS2**	27.1	27.6	39.5	40.5	-39.9
3aN1	-2.9	-2.4	8.6	9.5	-36.7	**3aIN2**	0.8	1.4	12.3	13.2	-36.6

[a] at 25°C

[b] at 50°C

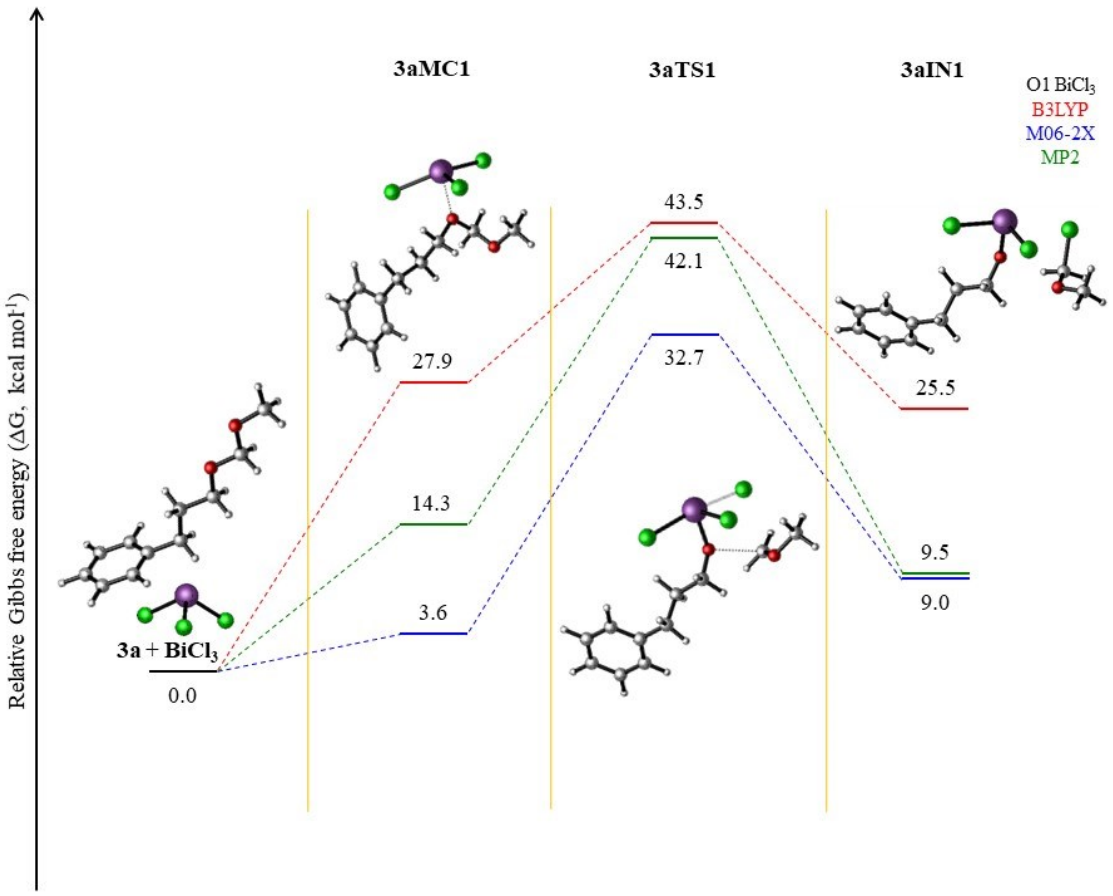

Figure S5.4(a): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **3a** + $BiCl_3$ via pathway 1, where $BiCl_3$ is attached to O1 in the gas phase at 50°C.

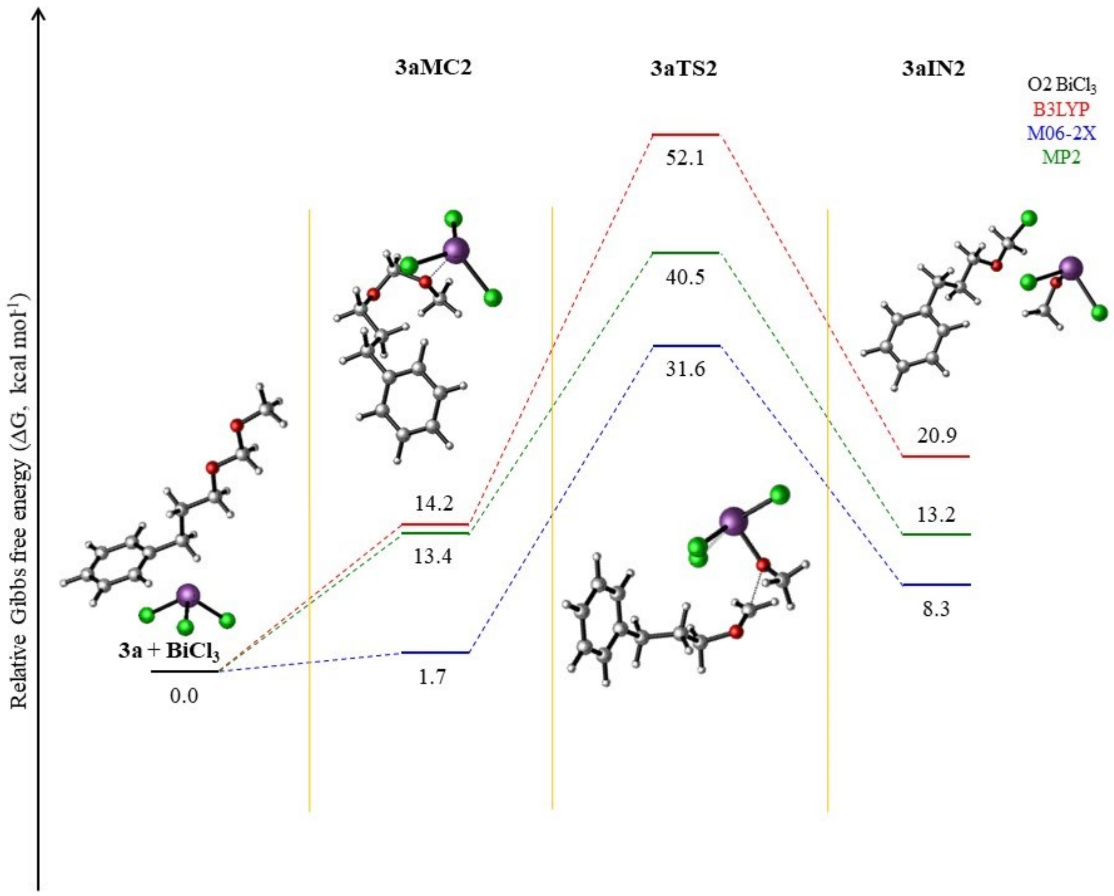

Figure S5.4(b): Relative Gibbs free energy profile computed using B3LYP and M06-2X functionals and MP2 method in correlation with 6-31G(d) basis set for all atoms, excluding bismuth where LANL2DZ was used as basis set for the reaction **3a** + $BiCl_3$ via pathway 2, where $BiCl_3$ is attached to O2 in the gas phase at 50°C.

Table S5.14: Relative electronic energies (Δ*E*, in kcal mol^{-1}), enthalpies (Δ*H*, in kcal mol^{-1}), Gibbs free energies (Δ*G*, in kcal mol^{-1}) and entropies (Δ*S*, in cal mol^{-1} K^{-1}) for the reaction of one water molecule with the intermediate to form alcohol via hemiacetal cleavage computed using M06-2X/6-31G(d) in the gas phase and solvent. The values in parentheses and square brackets are for acetonitrile and water, respectively

Substrates	**ΔE**	**ΔH**	**ΔG^a**	**ΔG^b**	**ΔS**
O1 M06-2X [(R-OH + BiCl$_2$(OH)]					
19	-1.7	-2.7	-4.1	-4.2	4.5
	(-0.7)	(-1.7)	(-3.2)	(-3.4)	(5.3)
	[-0.6]	[-1.6]	[-3.2]	[-3.3]	[5.3]
20	-3.6	-4.7	-6.0	-6.1	4.3
	(-2.4)	(-3.0)	(-6.2)	(-6.5)	(10.8)
	[-2.3]	[-3.5]	[-3.9]	[-4.0]	[1.5]
21	-1.3	-2.3	-4.0	-4.1	5.5
	(-0.5)	(-1.4)	(-3.5)	(-3.6)	(6.8)
	[-0.4]	[-1.3]	[-3.4]	[-3.5]	[6.8]
22	-1.9	-3.0	-4.5	-4.6	5.0
	(-0.9)	(-1.9)	(-3.4)	(-3.5)	(4.9)
	[-0.8]	[-1.9]	[-3.4]	[-3.5]	[5.2]
2a	0.6	-0.4	-1.7	-1.8	4.2
	(0.6)	(-0.3)	(-1.9)	(-2.0)	(5.3)
	[0.6]	[-0.3]	[-1.9]	[-2.0]	[5.3]
3a	0.0	-1.0	-2.2	-2.3	4.0
	(0.0)	(-0.9)	(-2.7)	(-2.8)	(5.9)
	[0.0]	[-0.9]	[-2.6]	[-2.8]	[5.7]
O2 M06-2X [R−OH + CH$_2$=O + HCl]					
19	12.9	13.7	2.0	1.0	39.3
	(11.9)	(12.7)	(1.1)	(0.1)	(39.0)
	[11.9]	[12.7]	[1.0]	[0.1]	[39.0]
20	11.8	12.5	0.8	-0.2	39.2
	(10.3)	(11.0)	(-0.6)	(-1.6)	(39.1)
	[10.3]	[11.0]	[-0.6]	[-1.6]	[39.1]
21	13.4	14.2	2.4	1.4	39.5
	(12.5)	(13.2)	(1.5)	(0.5)	(39.2)
	[12.4]	[13.2]	[1.5]	[0.5]	[39.2]
22	13.1	13.9	2.2	1.3	39.1
	(1.3)	(13.0)	(1.4)	(0.5)	(38.7)
	[12.2]	[12.9]	[1.4]	[0.4]	[38.7]
2a	17.5	18.3	6.8	5.9	38.3
	(17.1)	(17.7)	(6.7)	(5.8)	(36.9)

	[17.0]	[17.7]	[6.7]	[5.8]	[36.9]
3a	17.3	18.0	7.0	6.1	36.8
	(16.7)	(17.4)	(6.3)	(5.4)	(37.4)
	[16.7]	[17.4]	[6.3]	[5.4]	[37.2]

[a] at 25°C [b] at 50°C

S6. References

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