Supporting Information for

Synthesis and properties of symmetric glycerol-derived (*E/Z*)-1,3-diether-2-alkenes

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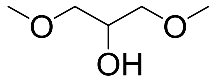
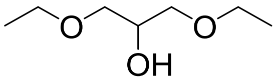
S1. Detailed Synthetic Procedures

S1.1 Synthesis of symmetric glycerol diether alcohols [R_1, 0, R_1]

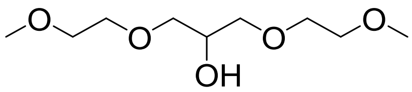
A primary (1°) alcohol (6 eq.) was added to a suitable round bottom flask loaded with NaOH powder (1.4 eq.), which was then heated to 65 °C and stirred for 1 h, followed by dropwise addition of epichlorohydrin (1.0 eq.). The reaction was allowed to run overnight before cooling to RT. The excess of 1° alcohol was removed by rotary evaporation under reduced pressure. 600 mL Et_2O was then added to the crude product, and the mixture was neutralized by 1 M HCl and dried over $MgSO_4$. The solids were filtered, and Et_2O was removed by rotary evaporation under reduced pressure, followed by vacuum distillation to afford [R_1, 0, R_1].



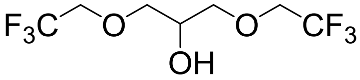
[M, 0, M] was prepared from methanol in 52.0% isolated yield (62.46 g, 0.52 mol) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 3.88 (tt, *J* = 6.3, 4.4 Hz, 1H), 3.39 (dd, *J* = 9.8, 4.4 Hz, 2H), 3.37 – 3.33 (m, 2H), 3.32 (s, 6H), 2.85 (d, *J* = 2.1 Hz, 1H).



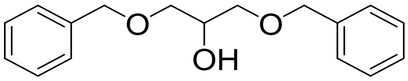
[E, 0, E] was prepared from ethanol in 55.8% isolated yield (81.64 g, 0.55 mol) as a clear, colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (dtd, *J* = 6.6, 4.3, 2.2 Hz, 1H), 3.53 – 3.47 (m, 4H), 3.47 – 3.43 (m, 2H), 3.42 – 3.38 (m, 2H), 2.71 (d, *J* = 3.6 Hz, 1H), 1.21 – 1.13 (m, 6H).



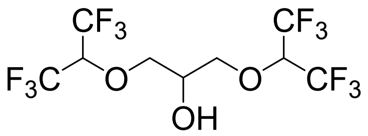
[ME, 0, ME] was prepared from 2-methoxyethanol in 74.8% isolated yield (155.74 g, 0.75 mol) as a clear, colorless liquid. ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.96 (dtd, *J* = 6.3, 4.1, 2.2 Hz, 1H), 3.66 – 3.60 (m, 4H), 3.57 – 3.51 (m, 4H), 3.51 – 3.44 (m, 4H), 3.35 (s, 6H), 3.03 (d, *J* = 4.1 Hz, 1H).



[F, 0, F] was prepared from 2,2,2-trifluoroethanol in 75.8% isolated yield (194.18 g, 0.76 mol) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (h, *J* = 4.9 Hz, 1H), 3.90 (d, *J* = 8.7 Hz, 2H), 3.87 (d, *J* = 8.7 Hz, 2H), 3.72 (dd, *J* = 9.6, 4.5 Hz, 2H), 3.68 (dd, *J* = 9.8, 5.8 Hz, 2H), 2.46 (d, *J* = 6.7 Hz, 1H).



[Bn, 0, Bn] was prepared from benzyl alcohol in 77.8% isolated yield (212.16 g, 0.78 mol) as a clear, light-yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 5H), 7.33 – 7.28 (m, 5H), 4.56 (s, 4H), 4.07 – 3.99 (m, 1H), 3.56 (qd, *J* = 9.6, 5.2 Hz, 4H), 2.42 (s, 1H).



[2F, 0, 2F] was prepared from 1,1,1,3,3,3-hexafluoro-2-propanol in 79.8% isolated yield (312.81 g, 0.80 mol) as a clear, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (p, *J* = 5.9 Hz, 2H), 4.13 – 4.04 (m, 1H), 3.95 (qd, *J* = 9.9, 5.0 Hz, 4H), 2.41 (s, 1H).

Table S1.1 Densities (ρ) of [2F, 0, 2F] measurements at different temperatures (T) and P = 101 kPa [a]

[2F, 0, 2F]						
T (K)	293.15	303.15	313.15	323.15	333.15	343.15
Density (g (cm^{-3}))	1.58739	1.56952	1.55119	1.53265	1.51393	1.49501

[a] Uncertainties are u(T) = 0.01 °C and u(ρ) = 0.00001 g (cm^{-3}).

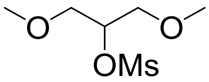
Table S1.2 Dynamic viscosities (η) of [2F, 0, 2F] at temperatures (T) from 293.15 to 333.15K and p = 101 kPa. [a]

[2F, 0, 2F]					
T (K)	293.15	303.15	313.15	323.15	333.15
Viscosity (mPa s)	15.24	9.69	6.63	4.78	3.60

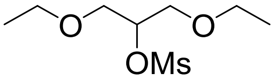
[a] Temperature variance is ±0.01 K

S1.2 Synthesis of symmetric glycerol diether mesylates [R_1, Ms, R_1]

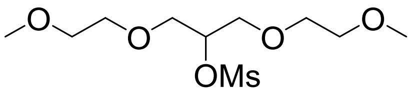
To a suitable round bottom flask loaded with [R_1, 0, R_1] (1 eq) and DCM (500 mL), triethylamine was added (1.2 eq). The mixture was cooled to 0 °C in an ice bath. Methane sulfonyl chloride (MsCl) (1.2 eq) dissolved in 100 mL DCM was added dropwise over 1 h, after which the ice bath was removed, and the reaction was allowed to run at RT for 4 h. DCM was removed by rotary evaporation under reduced pressure, and 400 mL Et_2O was added to extract the product. The residue was filtered, and the filtrate was washed with 50 mL DI water and 3 × 50 mL saturated $NaHCO_3$ solution and dried over $MgSO_4$. The solids were filtered, and Et_2O was removed by rotary evaporation under reduced pressure, followed by vacuum distillation to afford [R_1, Ms, R_1].



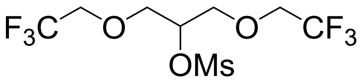
[M, Ms, M] was prepared in 86.3% isolated yield (170.87 g, 0.86 mol) using [M, 0, M] (120.17 g, 1.0 mol) following the procedure described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (dqd, *J* = 5.8, 4.4, 2.1 Hz, 1H), 3.62 – 3.58 (m, 2H), 3.58 – 3.54 (m, 2H), 3.36 (s, 6H), 3.06 (s, 3H).



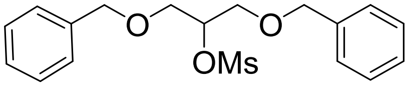
[E, Ms, E] was prepared in 88.1% isolated yield (198.88 g, 0.88 mol) using [E, 0, E] (148 g, 1.0 mol) following the procedure described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 – 4.79 (m, 1H), 3.64 (d, *J* = 1.9 Hz, 2H), 3.63 (d, *J* = 0.9 Hz, 2H), 3.59 – 3.53 (m, 2H), 3.53 – 3.49 (m, 2H), 3.09 (s, 3H), 1.20 (t, *J* = 6.2 Hz, 3H), 1.17 (t, *J* = 0.7 Hz, 3H).



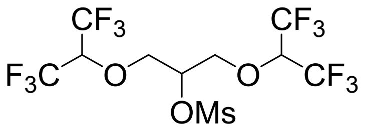
[ME, Ms, ME] was prepared in 92.1% isolated yield (263.6 g, 0.92 mol) using [ME, 0, ME] (208.4 g, 1.0 mol) following the procedure described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (p, *J* = 5.3 Hz, 1H), 3.71 (d, *J* = 5.3 Hz, 4H), 3.69 – 3.59 (m, 4H), 3.52 (ddd, *J* = 5.2, 3.8, 0.9 Hz, 4H), 3.35 (s, 6H), 3.11 (s, 3H).



[F, Ms, F] was prepared in 89.0% isolated yield (297.36.88 g, 0.89 mol) using [F, 0, F] (256.2 g, 1.0 mol) following the procedure described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (tt, *J* = 5.7, 4.3 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.92 – 3.90 (m, 2H), 3.89 (s, 2H), 3.89 – 3.85 (m, 2H), 3.10 (s, 3H).



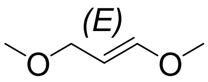
[Bn, Ms, Bn] was prepared in 91.4% isolated yield (319.9 g, 0.91 mol) using [Bn, 0, Bn] (272.14 g, 1.0 mol) following the procedure described above. ^{1}H NMR (500 MHz, DMSO) δ 7.39 – 7.34 (m, 5H), 7.34 – 7.28 (m, 5H), 4.95 – 4.88 (m, 1H), 4.58 – 4.49 (m, 4H), 3.69 (d, *J* = 4.6 Hz, 4H), 3.16 (s, 3H).

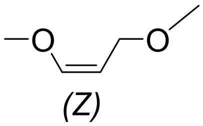


[2F, Ms, 2F] was prepared in 90.1% isolated yield (423.9 1, 0.90 mol) using [2F, 0, 2F] (272.14 g, 1.0 mol) following the procedure described above. ^{1}H NMR (360 MHz, CDCl3) δ 4.89 (p, *J* = 4.9 Hz, 1H), 4.21 – 4.14 (m, 2H), 4.13 (s, 2H), 4.12 (s, 2H), 3.06 (s, 3H).

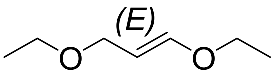
S1.3 Synthesis of symmetric (*E*/*Z*)-1,3-diether-2-alkenes [R_1, A, R_1]

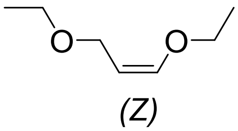
[R_1, Ms, R_1] (1 eq) was added to a suitable round bottom flask loaded with NaOH (3 eq) powder and 150 mL DMSO. The reaction temperature was increased slowly to 95 °C and then kept at this temperature overnight (~12 h) before the reaction was stopped and cooled to RT. The solids were filtered and washed with 50 mL Et_2O. 500 mL Et_2O was then added to extract the product from DMSO. The Et_2O phase was collected and washed sequentially with 3 × 80 mL H_2O and 2 × 60 mL saturated NaCl solution and dried over $MgSO_4$. The solid was filtered, and Et_2O was removed by rotary evaporation under reduced pressure, followed by vacuum distillation to afford [R_1, A, R_1].



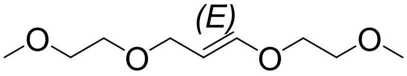


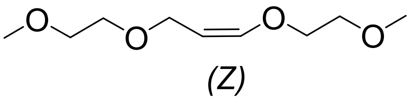
[M, A, M] was prepared in 67.6% isolated yield (34.68 g, 0.34 mol) using [M, Ms, M] (99.1 g, 0.5 mol) following the procedure described above. ^{1}H NMR (500 MHz, DMSO) δ 6.59 (d, *J* = 12.6 Hz, 1H), 6.15 (dt, *J* = 6.3, 1.1 Hz, 1H), 4.85 (dt, *J* = 12.6, 7.4 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 1H), 3.88 (dd, *J* = 7.0, 1.2 Hz, 2H), 3.77 (dd, *J* = 7.4, 0.8 Hz, 2H), 3.58 (s, 3H), 3.50 (s, 3H), 3.17 (s, 3H), 3.16 (s, 3H).



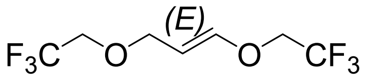


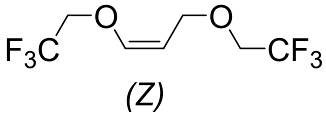
[E, A, E] was prepared in 73.1% isolated yield (47.52 g, 0.37 mol) using [E, Ms, E] (113.15 g, 0.5 mol) following the procedure described above. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.46 (d, *J* = 12.7 Hz, 1H), 6.14 – 6.02 (m, 1H), 4.90 (dt, *J* = 12.7, 7.4 Hz, 1H), 4.53 (q, *J* = 6.9 Hz, 1H), 4.04 (dd, *J* = 7.1, 1.1 Hz, 2H), 3.89 – 3.82 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 3.74 (q, *J* = 7.0 Hz, 2H), 3.49 – 3.40 (m, 4H), 1.24 (dt, *J* = 14.3, 7.0 Hz, 6H), 1.20 – 1.15 (m, 6H).



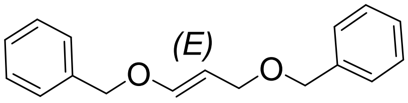


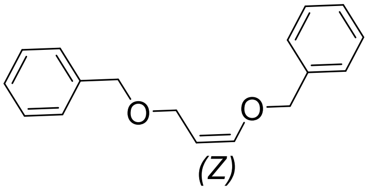
[ME, A, ME] was prepared in 82.5% isolated yield (78.38 g, 0.41 mol) using [ME, Ms, ME] (143.17 g, 0.5 mol) following the procedure described above. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.53 (d, *J* = 12.6 Hz, 1H), 6.12 (ddd, *J* = 6.3, 2.1, 0.9 Hz, 1.5H), 4.94 (dtd, *J* = 12.7, 7.5, 2.1 Hz, 1H), 4.58 (qd, *J* = 7.0, 2.3 Hz, 1.5H), 4.13 (ddd, *J* = 7.1, 2.2, 1.2 Hz, 3H), 3.95 – 3.91 (m, 2H), 3.89 (ddt, *J* = 4.9, 3.3, 2.0 Hz, 3H), 3.84 (td, *J* = 4.8, 2.1 Hz, 2H), 3.60 (dq, *J* = 5.0, 2.1 Hz, 2H), 3.58 (ddt, *J* = 7.4, 3.3, 1.6 Hz, 4H), 3.56 – 3.54 (m, 3H), 3.54 – 3.52 (m, 6H), 3.39 (d, *J* = 2.2 Hz, 3H), 3.37 (s, 3H), 3.37 (d, *J* = 1.3 Hz, 4.5H). 3.36 (d, *J* = 1.2 Hz, 4.5H).





[F, A, F] was prepared in 79.7% isolated yield (47.45 g, 0.20 mol) using [F, Ms, F] (83.56 g, 0.25 mol) following the procedure described above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (d, *J* = 12.5 Hz, 1H), 6.22 – 6.14 (m, 1H), 5.04 (dt, *J* = 12.3, 7.4 Hz, 1H), 4.79 – 4.71 (m, 1H), 4.26 (d, *J* = 7.3 Hz, 2H), 4.12 (s, 2H), 4.09 (d, *J* = 7.6 Hz, 2H), 4.08 – 4.05 (m, 2H), 3.79 (d, *J* = 1.5 Hz, 2H), 3.77 (d, *J* = 1.4 Hz, 2H).





[Bn, A, Bn] was prepared in 86.8% isolated yield (55.19 g, 0.22 mol) using [Bn, Ms, Bn] (99.1 g, 0.25 mol) following the procedure described above. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 6H), 7.37 – 7.34 (m, 6H), 7.33 – 7.30 (m, 5H), 7.29 – 7.26 (m, 5H), 6.63 (d, *J* = 12.6 Hz, 1H), 6.29 – 6.22 (m, 1H), 5.11 (dt, *J* = 12.7, 7.4 Hz, 1H), 4.85 (s, 2H), 4.80 (s, 2H), 4.70 (q, *J* = 6.7 Hz, 1H), 4.52 (s, 2H), 4.51 (s, 2H), 4.27 – 4.19 (m, 2H), 3.99 (d, *J* = 7.4 Hz, 2H).

Elimination reaction mechanism

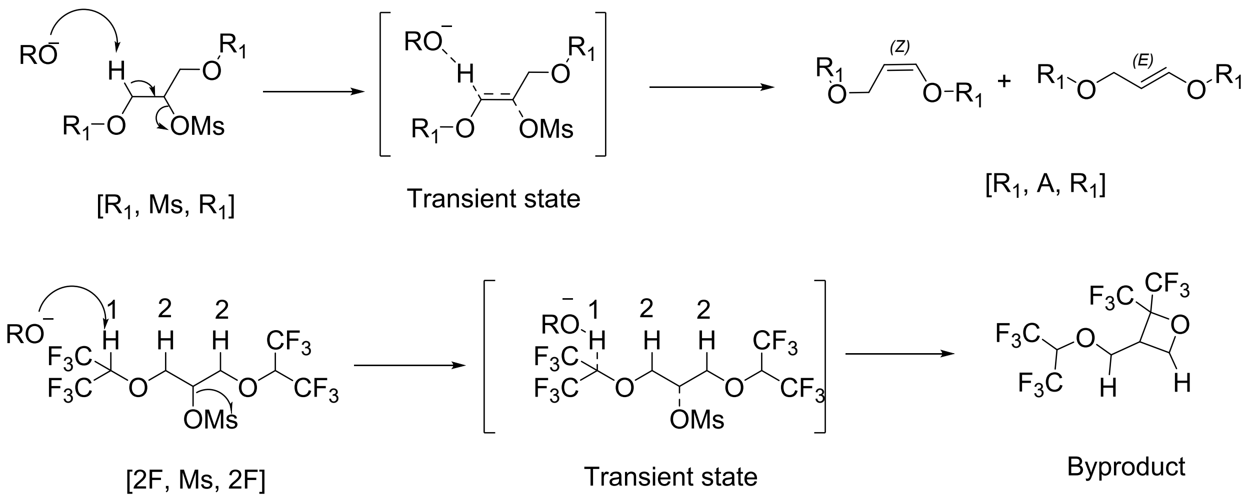
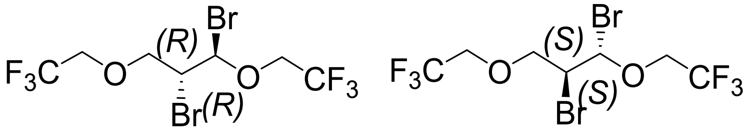


Figure S1. Proposed [2F, 0, 2F] elimination mechanism.

S1.4 Synthesis of [R_1, Br_2, R_1]

Alkene (10 mmol) and anhydrous DCM (20 mL) in an ordinary round-bottomed flask with a magnetic stirring bar under an N_2 atmosphere. Br_2 (1.2 eq.) was added dropwise to the above solution over 5 min at 0 °C. After addition, stir the mixture in an ice bath for 1-2 h under N_2 atmosphere. After completion of the reaction, as the TLC indicates, the reaction was quenched with saturated $Na_2S_2O_3$. The reaction mixture was stirred vigorously until the orange color disappeared. The reaction mixture was then filtered through a pad of Celite and washed with deionized water (2 x 5 mL). The reaction mixture was then dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure, and obtained product via column chromatography (silica gel, hexane).



[F, Br_2, F] was prepared in 70.3% isolated yield (6.995 g, 0.018 mol) using [F, A, F] (5.96 g, 0.025 mol) following the procedure described above. ^1H NMR (360 MHz, $CDCl_3$) δ 6.09 (d, *J* = 2.7 Hz, 1H), 6.05 (d, *J* = 5.3 Hz, 1H), 4.40 (td, *J* = 4.8, 2.7 Hz, 1H), 4.38 – 4.34 (m, 1H), 4.29 – 4.18 (m, 2H), 4.18 – 4.11 (m, 2H), 4.05 – 3.98 (m, 2H), 3.96 (dd, *J* = 7.9, 4.3 Hz, 2H), 3.93 – 3.91 (m, 2H), 3.90 – 3.85 (m, 2H).

S2. NMR Spectra

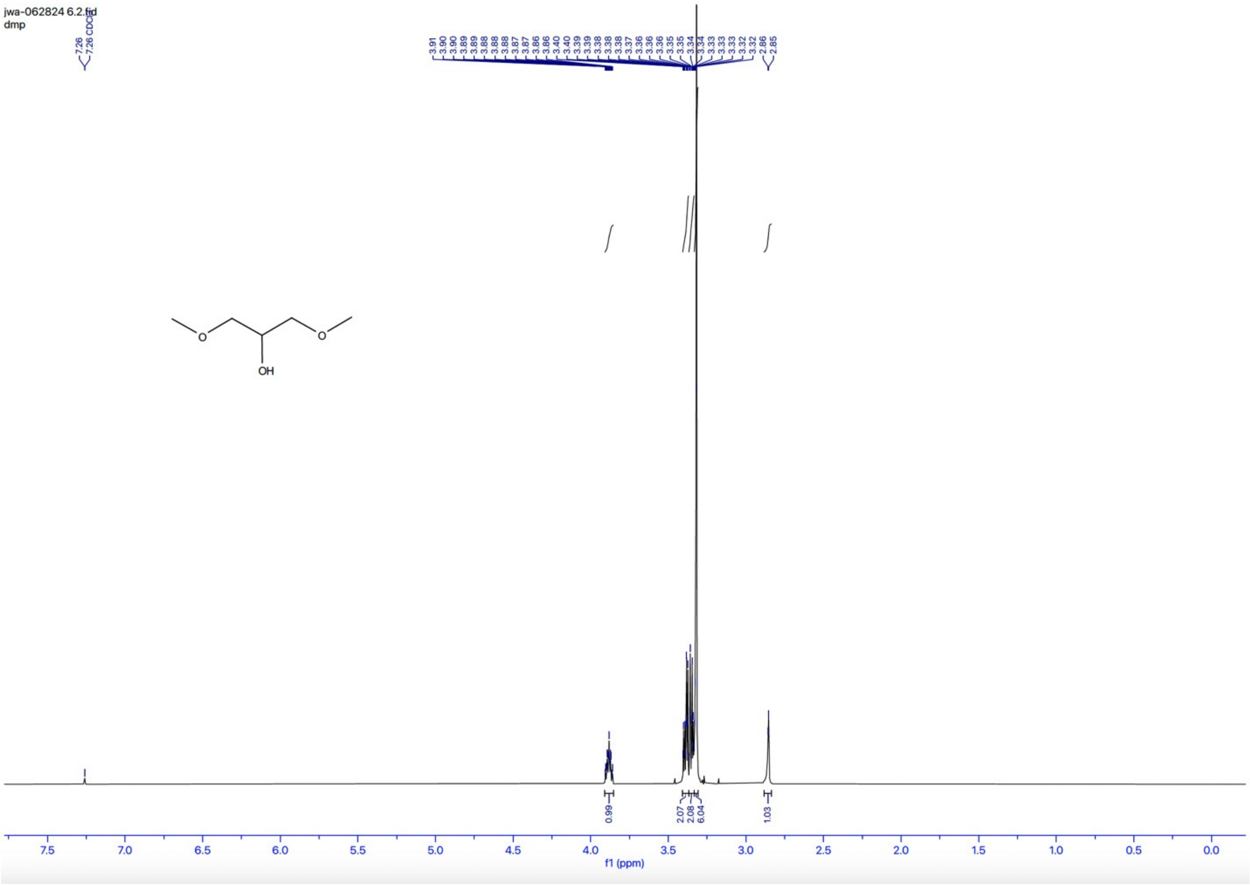


Figure S2.1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (tt, *J* = 6.3, 4.4 Hz, 1H), 3.39 (dd, *J* = 9.8, 4.4 Hz, 2H), 3.37 – 3.33 (m, 2H), 3.32 (s, 6H), 2.85 (d, *J* = 2.1 Hz, 1H).

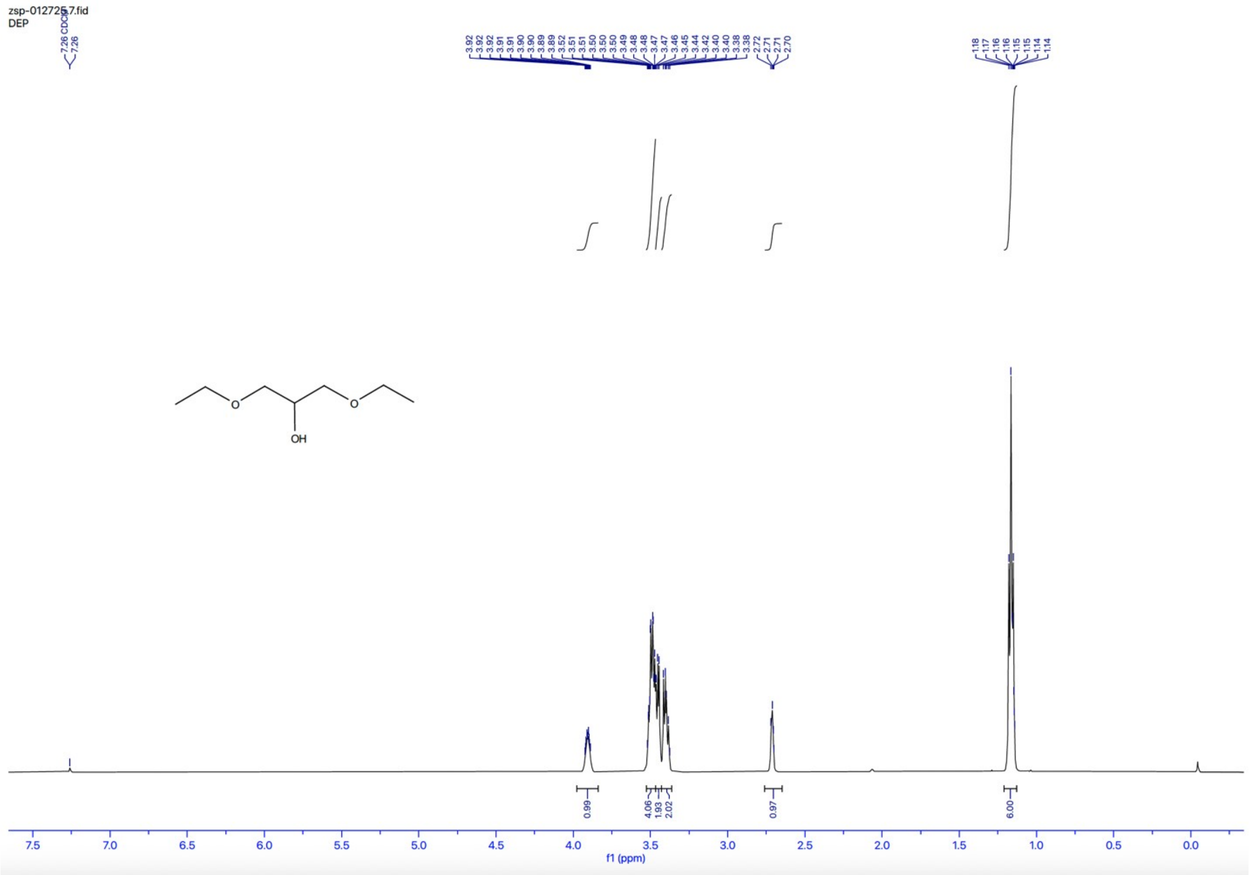


Figure S2.2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (dtd, *J* = 6.6, 4.3, 2.2 Hz, 1H), 3.53 – 3.47 (m, 4H), 3.47 – 3.43 (m, 2H), 3.42 – 3.38 (m, 2H), 2.71 (d, *J* = 3.6 Hz, 1H), 1.21 – 1.13 (m, 6H).

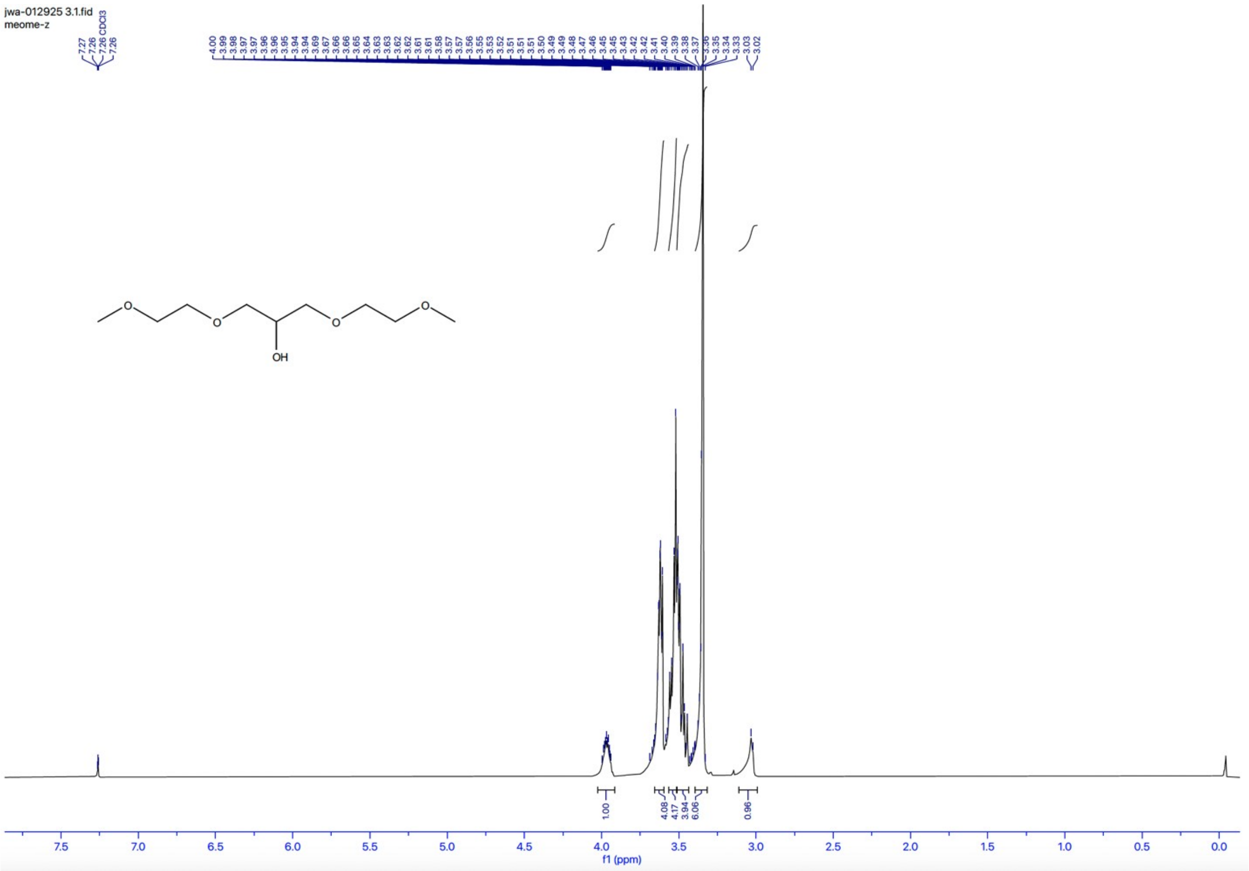


Figure S2.3: ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.96 (dtd, *J* = 6.3, 4.1, 2.2 Hz, 1H), 3.66 – 3.60 (m, 4H), 3.57 – 3.51 (m, 4H), 3.51 – 3.44 (m, 4H), 3.35 (s, 6H), 3.03 (d, *J* = 4.1 Hz, 1H).

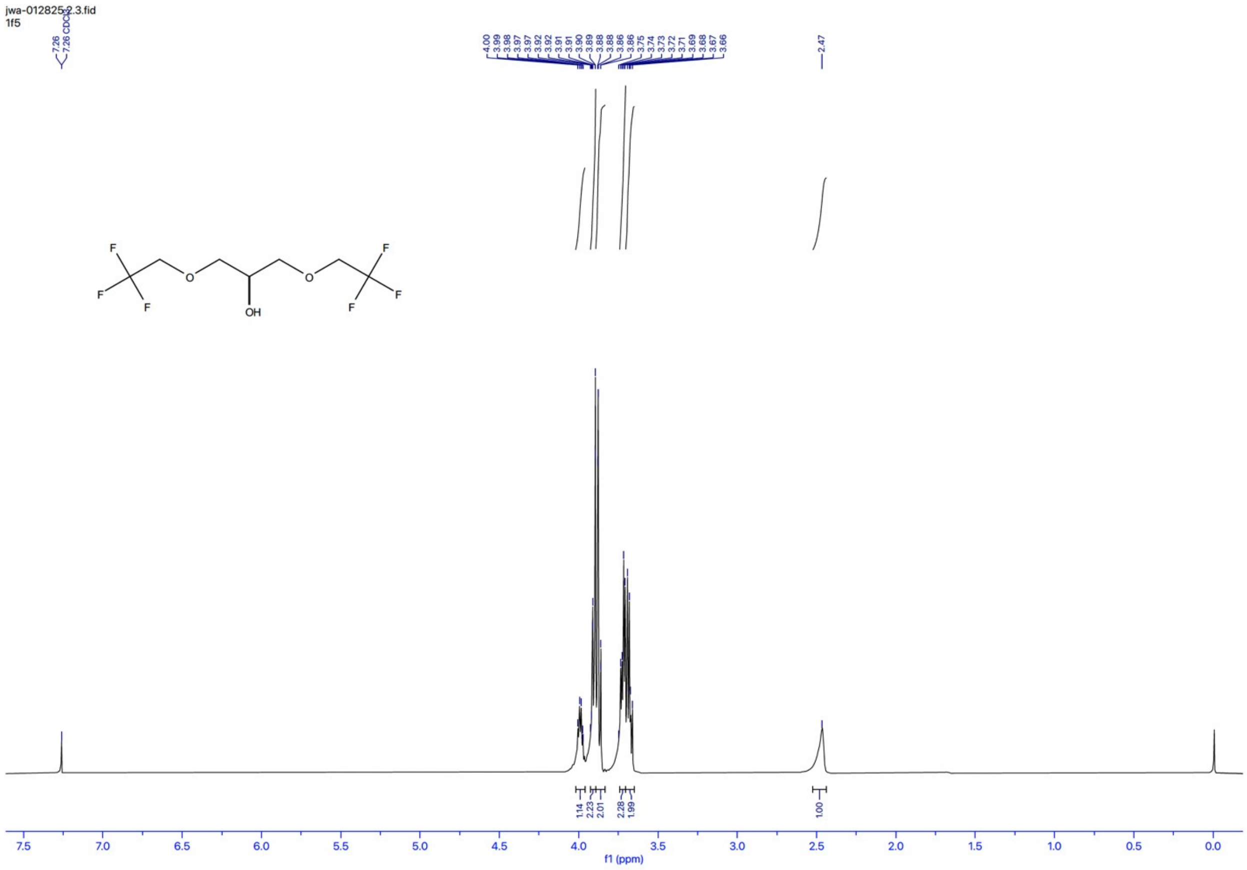


Figure S2.4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (h, *J* = 4.9 Hz, 1H), 3.90 (d, *J* = 8.7 Hz, 2H), 3.87 (d, *J* = 8.7 Hz, 2H), 3.72 (dd, *J* = 9.6, 4.5 Hz, 2H), 3.68 (dd, *J* = 9.8, 5.8 Hz, 2H), 2.46 (d, *J* = 6.7 Hz, 1H).

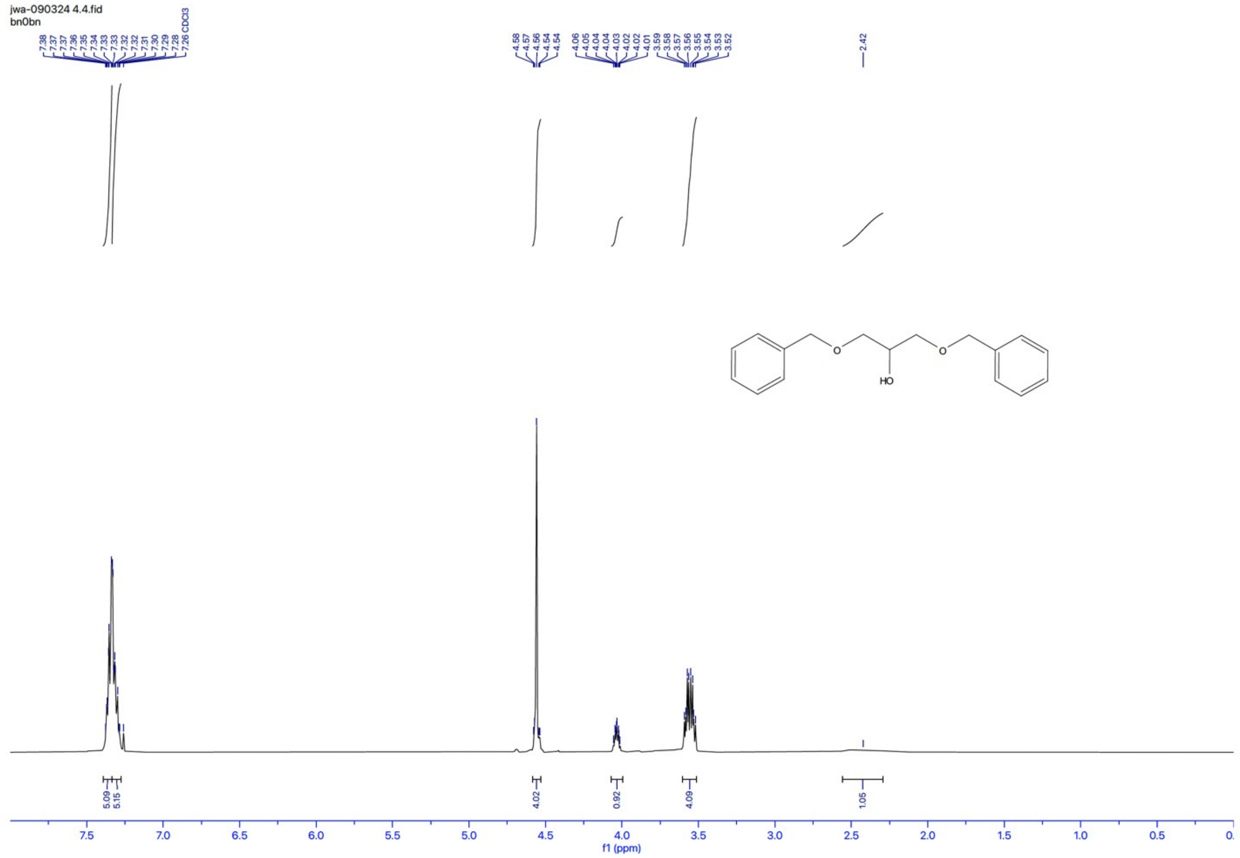


Figure S2.5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 5H), 7.33 – 7.28 (m, 5H), 4.56 (s, 4H), 4.07 – 3.99 (m, 1H), 3.56 (qd, *J* = 9.6, 5.2 Hz, 4H), 2.42 (s, 1H).

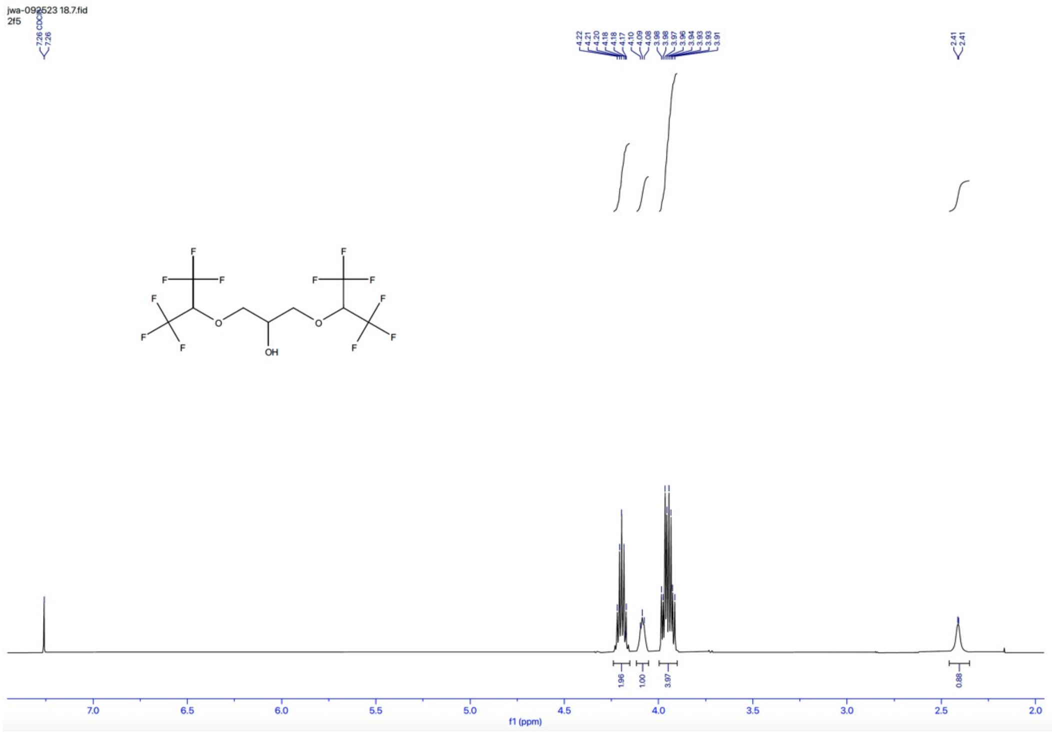


Figure S2.6: ^{1}H-NMR spectrum of [2F, 0, 2F]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (p, *J* = 5.9 Hz, 2H), 4.13 – 4.04 (m, 1H), 3.95 (qd, *J* = 9.9, 5.0 Hz, 4H), 2.41 (s, 1H).

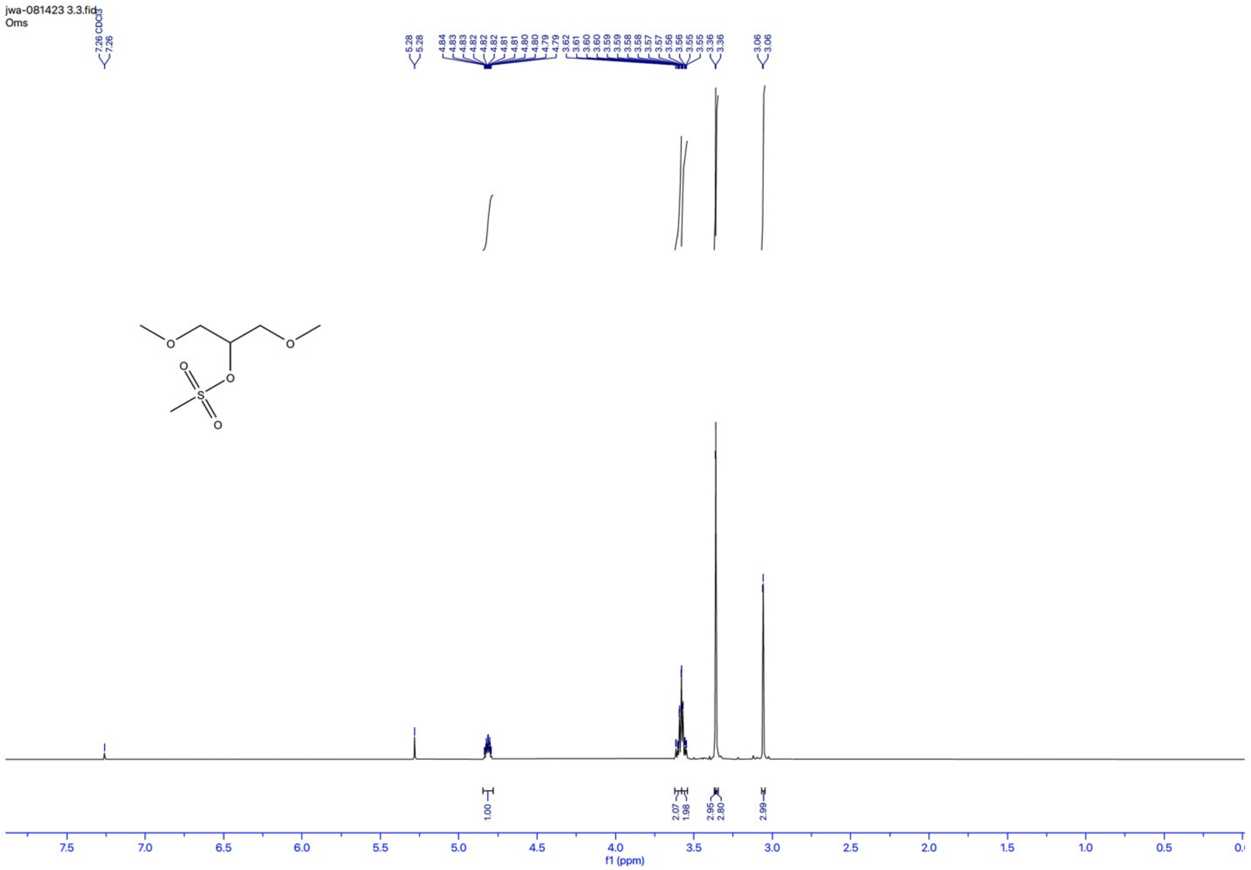


Figure S2.7: ^{1}H-NMR spectrum of [M, Ms, M]. ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.81 (dqd, *J* = 5.8, 4.4, 2.1 Hz, 1H), 3.62 – 3.58 (m, 2H), 3.58 – 3.54 (m, 2H), 3.36 (s, 6H), 3.06 (s, 3H).

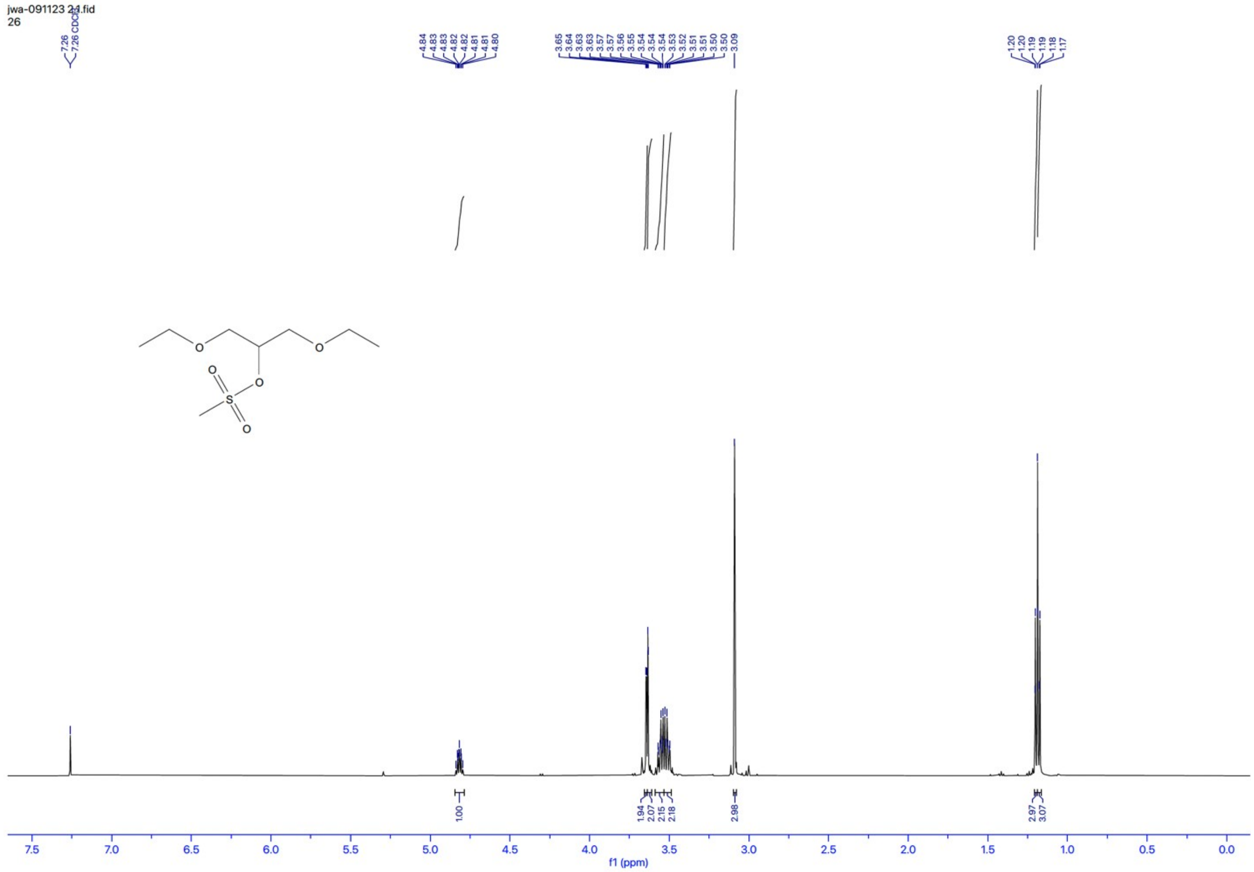


Figure S2.8: ^{1}H-NMR spectrum of [E, Ms, E]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 – 4.79 (m, 1H), 3.64 (d, *J* = 1.9 Hz, 2H), 3.63 (d, *J* = 0.9 Hz, 2H), 3.59 – 3.53 (m, 2H), 3.53 – 3.49 (m, 2H), 3.09 (s, 3H), 1.20 (t, *J* = 6.2 Hz, 3H), 1.17 (t, *J* = 0.7 Hz, 3H).

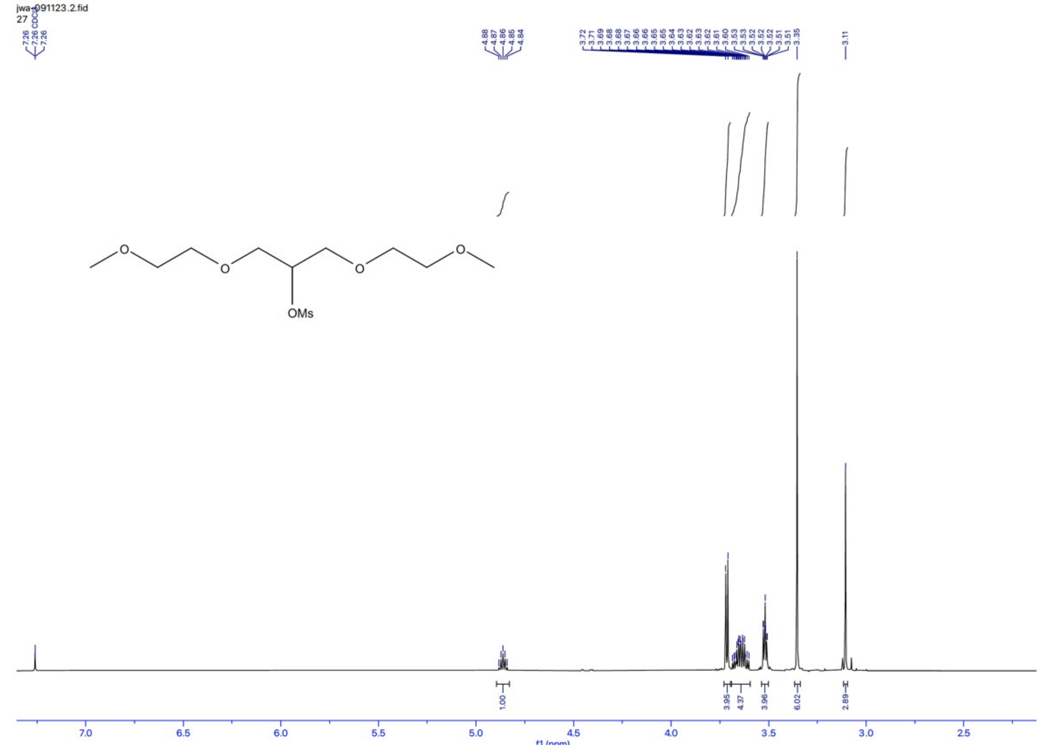


Figure S2.9: ^{1}H-NMR spectrum of [ME, Ms, ME]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (p, *J* = 5.3 Hz, 1H), 3.71 (d, *J* = 5.3 Hz, 4H), 3.69 – 3.59 (m, 4H), 3.52 (ddd, *J* = 5.2, 3.8, 0.9 Hz, 4H), 3.35 (s, 6H), 3.11 (s, 3H).

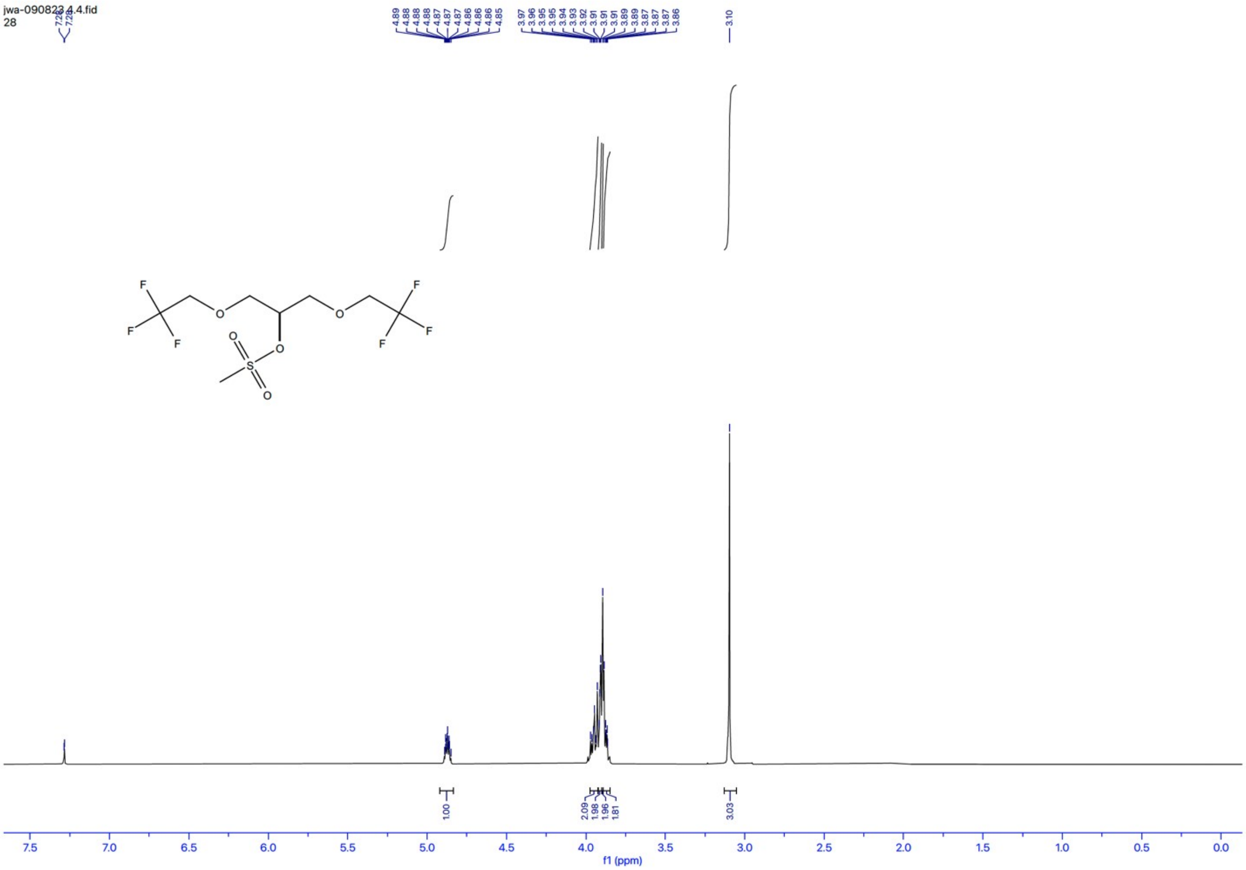


Figure S2.10: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (tt, *J* = 5.7, 4.3 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.92 – 3.90 (m, 2H), 3.89 (s, 2H), 3.89 – 3.85 (m, 2H), 3.10 (s, 3H).

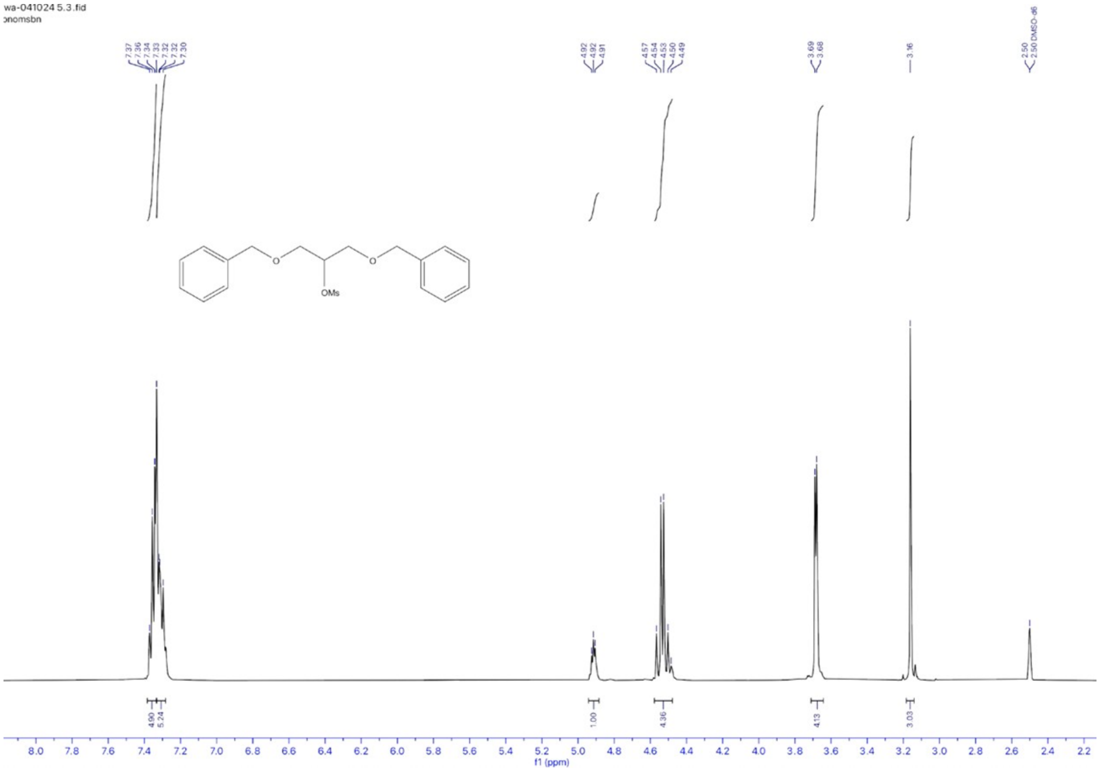


Figure S2.11: ^{1}H-NMR spectrum of [Bn, Ms, Bn]. ^{1}H NMR (500 MHz, DMSO) δ 7.39 – 7.34 (m, 5H), 7.34 – 7.28 (m, 5H), 4.95 – 4.88 (m, 1H), 4.58 – 4.49 (m, 4H), 3.69 (d, *J* = 4.6 Hz, 4H), 3.16 (s, 3H).

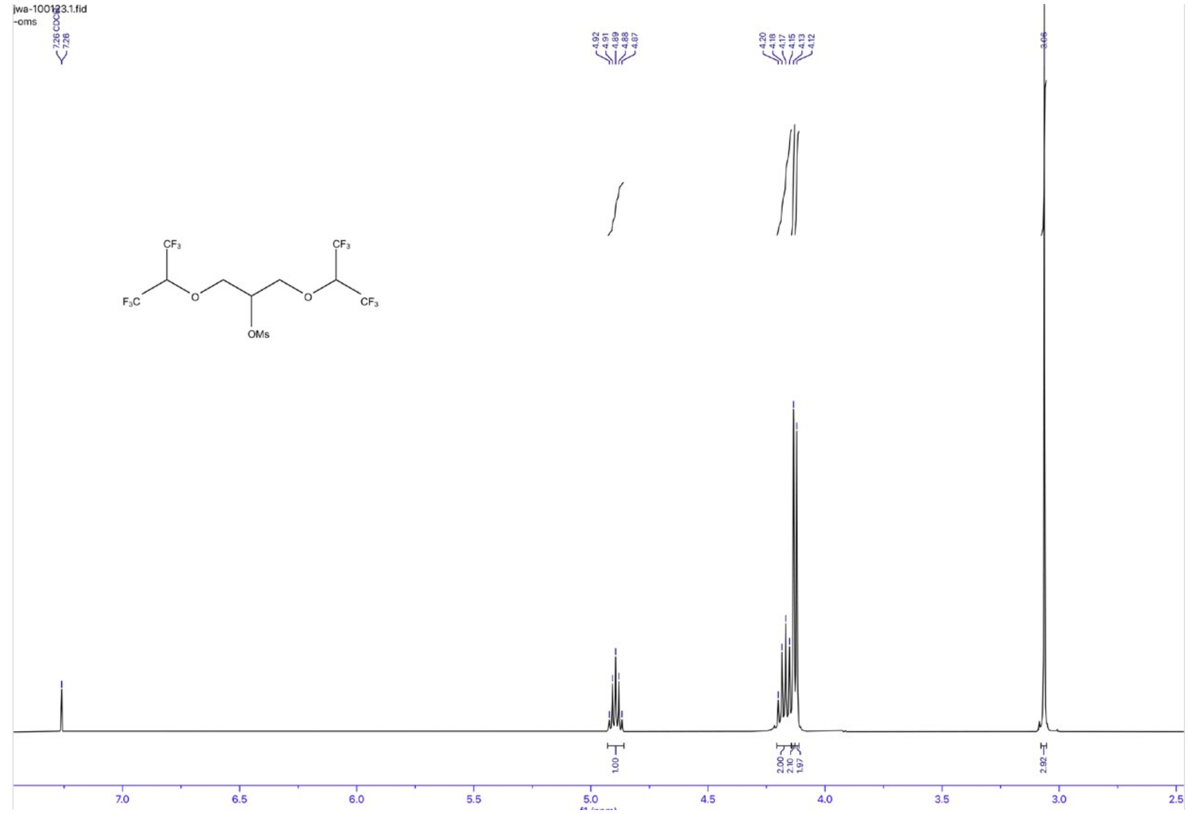


Figure S2.12: ^{1}H-NMR spectrum of [2F, Ms, 2F]. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.89 (p, *J* = 4.9 Hz, 1H), 4.21 – 4.14 (m, 2H), 4.13 (s, 2H), 4.12 (s, 2H), 3.06 (s, 3H).

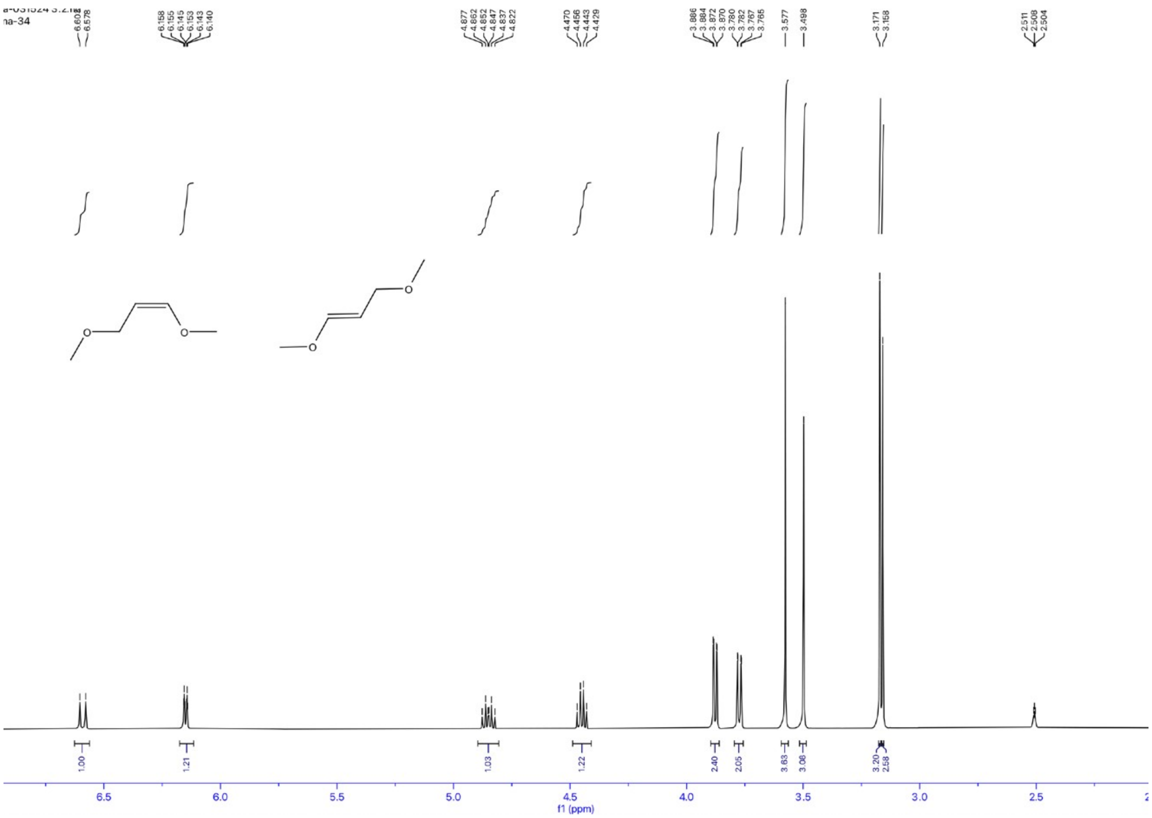


Figure S2.13: ^{1}H-NMR spectrum of [M, A, M]. ^{1}H NMR (500 MHz, DMSO) δ 6.59 (d, *J* = 12.6 Hz, 1H), 6.15 (dt, *J* = 6.3, 1.1 Hz, 1H), 4.85 (dt, *J* = 12.6, 7.4 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 1H), 3.88 (dd, *J* = 7.0, 1.2 Hz, 2H), 3.77 (dd, *J* = 7.4, 0.8 Hz, 2H), 3.58 (s, 3H), 3.50 (s, 3H), 3.17 (s, 3H), 3.16 (s, 3H).

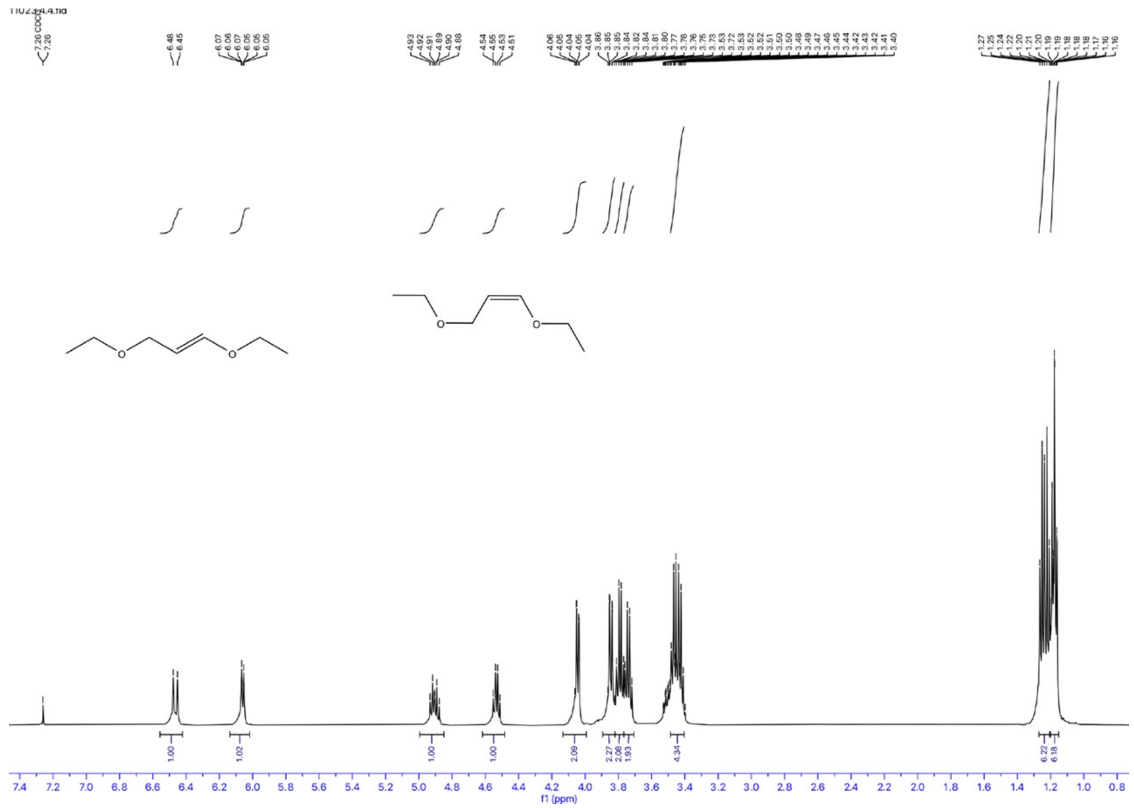


Figure S2.14: ^{1}H-NMR spectrum of [E, A, E]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.46 (d, *J* = 12.7 Hz, 1H), 6.14 – 6.02 (m, 1H), 4.90 (dt, *J* = 12.7, 7.4 Hz, 1H), 4.53 (q, *J* = 6.9 Hz, 1H), 4.04 (dd, *J* = 7.1, 1.1 Hz, 2H), 3.89 – 3.82 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 3.74 (q, *J* = 7.0 Hz, 2H), 3.49 – 3.40 (m, 4H), 1.24 (dt, *J* = 14.3, 7.0 Hz, 6H), 1.20 – 1.15 (m, 6H).

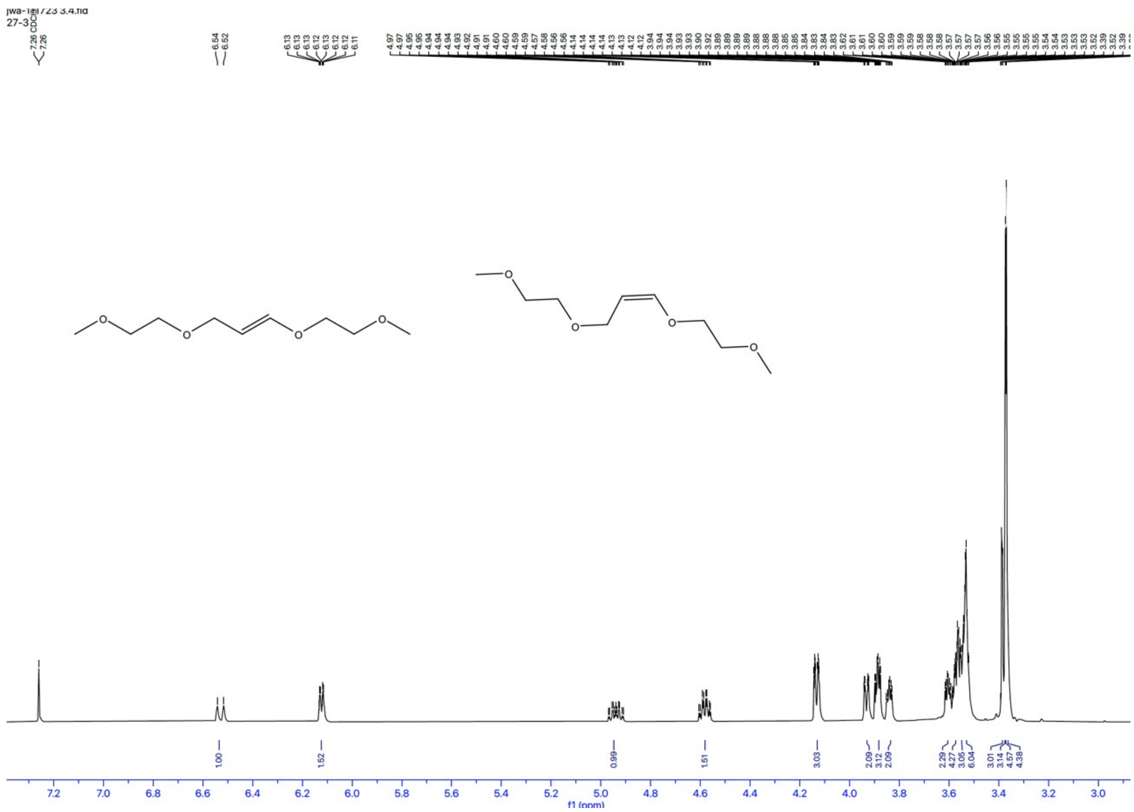


Figure S2.15: ^{1}H-NMR spectrum of [ME, A, ME]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (d, *J* = 12.6 Hz, 1H), 6.12 (ddd, *J* = 6.3, 2.1, 0.9 Hz, 1.5H), 4.94 (dtd, *J* = 12.7, 7.5, 2.1 Hz, 1H), 4.58 (qd, *J* = 7.0, 2.3 Hz, 1.5H), 4.13 (ddd, *J* = 7.1, 2.2, 1.2 Hz, 3H), 3.95 – 3.91 (m, 2H), 3.89 (ddt, *J* = 4.9, 3.3, 2.0 Hz, 3H), 3.84 (td, *J* = 4.8, 2.1 Hz, 2H), 3.60 (dq, *J* = 5.0, 2.1 Hz, 2H), 3.58 (ddt, *J* = 7.4, 3.3, 1.6 Hz, 4H), 3.56 – 3.54 (m, 3H), 3.54 – 3.52 (m, 6H), 3.39 (d, *J* = 2.2 Hz, 3H), 3.37 (s, 3H), 3.37 (d, *J* = 1.3 Hz, 4.5H). 3.36 (d, *J* = 1.2 Hz, 4.5H).

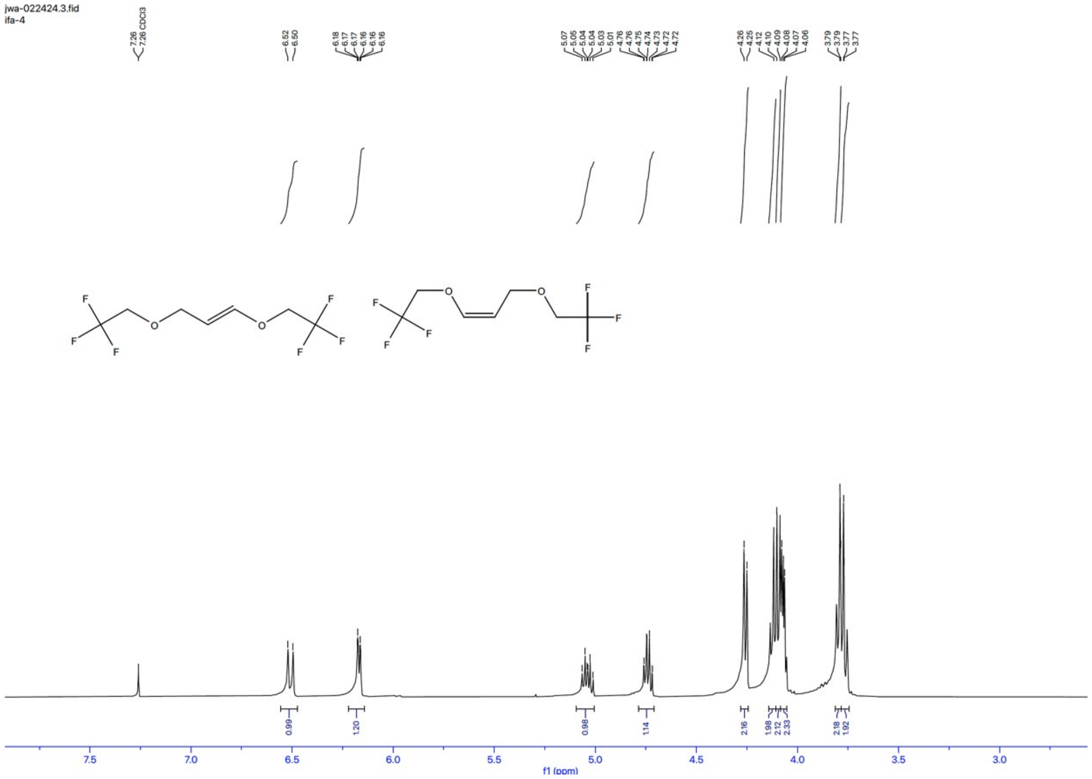


Figure S2.16: ^{1}H-NMR spectrum of [F, A, F]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (d, *J* = 12.5 Hz, 1H), 6.22 – 6.14 (m, 1H), 5.04 (dt, *J* = 12.3, 7.4 Hz, 1H), 4.79 – 4.71 (m, 1H), 4.26 (d, *J* = 7.3 Hz, 2H), 4.12 (s, 2H), 4.09 (d, *J* = 7.6 Hz, 2H), 4.08 – 4.05 (m, 2H), 3.79 (d, *J* = 1.5 Hz, 2H), 3.77 (d, *J* = 1.4 Hz, 2H).

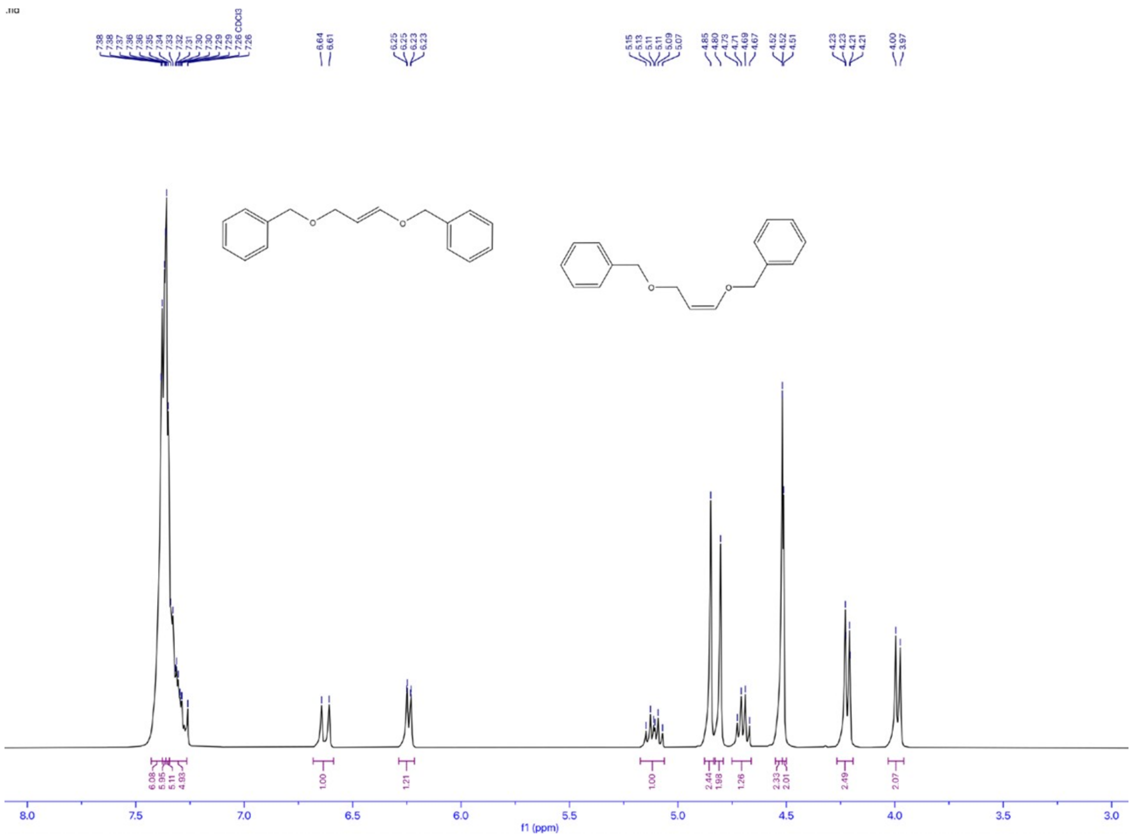


Figure S2.17: ^{1}H-NMR spectrum of [Bn, A, Bn]. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 6H), 7.37 – 7.34 (m, 6H), 7.33 – 7.30 (m, 5H), 7.29 – 7.26 (m, 5H), 6.63 (d, *J* = 12.6 Hz, 1H), 6.29 – 6.22 (m, 1H), 5.11 (dt, *J* = 12.7, 7.4 Hz, 1H), 4.85 (s, 2H), 4.80 (s, 2H), 4.70 (q, *J* = 6.7 Hz, 1H), 4.52 (s, 2H), 4.51 (s, 2H), 4.27 – 4.19 (m, 2H), 3.99 (d, *J* = 7.4 Hz, 2H).

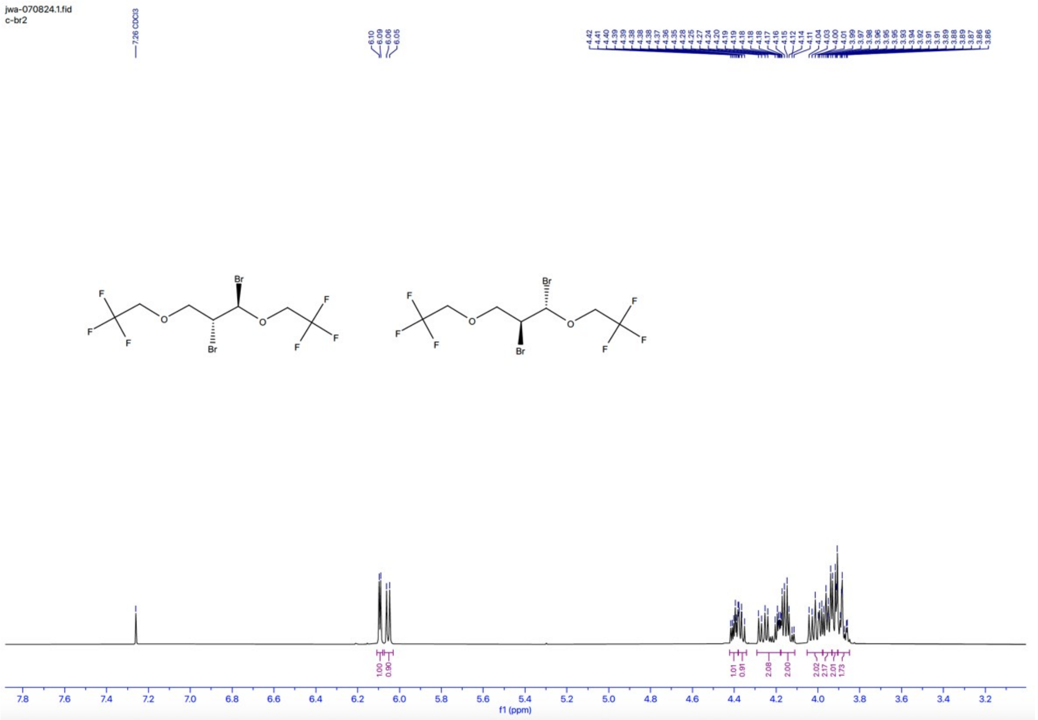


Figure S2.18: ^{1}H-NMR spectrum of [F, Br$_2$, F]. ^{1}H NMR (360 MHz, CDCl$_3$) δ 6.09 (d, *J* = 2.7 Hz, 1H), 6.05 (d, *J* = 5.3 Hz, 1H), 4.40 (td, *J* = 4.8, 2.7 Hz, 1H), 4.38 – 4.34 (m, 1H), 4.29 – 4.18 (m, 2H), 4.18 – 4.11 (m, 2H), 4.05 – 3.98 (m, 2H), 3.96 (dd, *J* = 7.9, 4.3 Hz, 2H), 3.93 – 3.91 (m, 2H), 3.90 – 3.85 (m, 2H).

S3. Computational Results

Table S3.1. Calculated temperature-dependent density of the studied solvent compounds in g/cm^3.

Property	**Density (g/cm^3)**									
	Structure									
T (K)	**[M, A, M]**		**[E, A, E]**		**[ME, A, ME]**		**[F, A, F]**		**[Bn, A, Bn]**	
S	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**
283.2	0.9267	0.9169	0.9212	0.9109	1.0335	1.0245	1.4318	1.3984	1.1048	1.0959
286.3	0.9235	0.9137	0.9180	0.9077	1.0302	1.0212	1.4272	1.3938	1.1016	1.0926
289.5	0.9203	0.9105	0.9148	0.9046	1.0269	1.0179	1.4227	1.3893	1.0983	1.0893
292.6	0.9171	0.9073	0.9117	0.9014	1.0236	1.0146	1.4182	1.3848	1.0950	1.0861
295.8	0.9139	0.9041	0.9086	0.8983	1.0204	1.0114	1.4137	1.3803	1.0918	1.0828
298.9	0.9108	0.9010	0.9055	0.8952	1.0171	1.0081	1.4092	1.3759	1.0885	1.0796
302.1	0.9076	0.8978	0.9024	0.8921	1.0139	1.0048	1.4048	1.3714	1.0853	1.0763
305.3	0.9045	0.8947	0.8993	0.8890	1.0106	1.0016	1.4003	1.3670	1.0821	1.0731
308.4	0.9014	0.8916	0.8962	0.8859	1.0074	0.9984	1.3958	1.3625	1.0788	1.0698
311.6	0.8983	0.8885	0.8932	0.8829	1.0042	0.9951	1.3914	1.3581	1.0756	1.0666
314.7	0.8953	0.8854	0.8901	0.8798	1.0010	0.9919	1.3870	1.3537	1.0723	1.0633
317.9	0.8922	0.8823	0.8871	0.8768	0.9978	0.9887	1.3825	1.3493	1.0691	1.0601
321.0	0.8892	0.8793	0.8841	0.8738	0.9946	0.9855	1.3781	1.3449	1.0659	1.0569
324.2	0.8861	0.8763	0.8811	0.8708	0.9914	0.9823	1.3737	1.3405	1.0627	1.0537
327.4	0.8831	0.8732	0.8781	0.8678	0.9882	0.9791	1.3693	1.3362	1.0594	1.0504
330.5	0.8801	0.8702	0.8751	0.8648	0.9851	0.9760	1.3650	1.3319	1.0562	1.0472
333.7	0.8771	0.8672	0.8722	0.8619	0.9819	0.9728	1.3606	1.3275	1.0530	1.0440
336.8	0.8741	0.8643	0.8692	0.8589	0.9787	0.9697	1.3563	1.3232	1.0498	1.0408
340.0	0.8712	0.8613	0.8663	0.8560	0.9756	0.9665	1.3519	1.3189	1.0466	1.0376
343.2	0.8682	0.8583	0.8634	0.8531	0.9725	0.9634	1.3476	1.3146	1.0434	1.0344

Table S3.2. Calculated temperature-dependent viscosity of the studied solvent compounds in mPa·s.

Property	**Viscosity (mPa·s)**									
	Structure									
T (K)	**[M, A, M]**		**[E, A, E]**		**[ME, A, ME]**		**[F, A, F]**		**[Bn, A, Bn]**	
S	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**
283.2	1.23	1.04	1.98	1.66	11.83	9.78	4.79	3.89	120.32	101.31
286.3	1.16	0.99	1.86	1.57	10.71	8.89	4.42	3.60	103.89	87.81
289.5	1.10	0.94	1.75	1.48	9.71	8.09	4.08	3.34	90.00	76.33
292.6	1.05	0.89	1.64	1.39	8.83	7.38	3.77	3.10	78.20	66.54
295.8	1.00	0.85	1.55	1.32	8.04	6.7	3.50	2.89	68.16	58.19
298.9	0.95	0.81	1.46	1.25	7.34	6.18	3.24	2.69	59.57	51.02
302.1	0.90	0.78	1.38	1.18	6.71	5.67	3.01	2.51	52.22	44.86
305.3	0.86	0.74	1.30	1.12	6.15	5.21	2.81	2.34	45.90	39.55
308.4	0.82	0.71	1.23	1.06	5.64	4.80	2.62	2.19	40.45	34.96
311.6	0.78	0.68	1.17	1.01	5.19	4.42	2.44	2.05	35.74	30.98
314.7	0.75	0.65	1.11	0.96	4.78	4.09	2.28	1.93	31.65	27.52
317.9	0.72	0.63	1.05	0.92	4.40	3.78	2.14	1.81	28.10	24.50
321.0	0.69	0.60	1.00	0.87	4.07	3.50	2.00	1.70	25.01	21.86
324.2	0.66	0.58	0.95	0.83	3.76	3.25	1.88	1.60	22.31	19.55
327.4	0.63	0.56	0.91	0.80	3.49	3.02	1.77	1.51	19.94	17.53
330.5	0.61	0.54	0.87	0.76	3.24	2.81	1.66	1.43	17.86	15.74
333.7	0.58	0.52	0.83	0.73	3.01	2.62	1.56	1.35	16.04	14.17
336.8	0.56	0.50	0.79	0.70	2.80	2.45	1.48	1.27	14.42	12.78
340.0	0.54	0.48	0.75	0.67	2.61	2.28	1.39	1.21	13.00	11.54
343.2	0.52	0.46	0.72	0.64	2.43	2.14	1.32	1.14	11.74	10.45

Table S3.3. Calculated temperature-dependent vapor pressure of the studied solvent compounds in kPa.

Property	**Vapor Pressure (kPa)**									
	Compound									
T (K)	**[M, A, M]**		**[E, A, E]**		**[ME, A, ME]**		**[F, A, F]**		**[Bn, A, Bn]**	
S	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**
283.2	0.3731	0.7527	0.0344	0.0666	0.0005	0.0008	0.0037	0.0096	2.39E-08	5.86E-08
286.3	0.4567	0.9126	0.0436	0.0838	0.0007	0.0010	0.0049	0.0125	3.73E-08	9.05E-08
289.5	0.5564	1.1014	0.0551	0.1048	0.0009	0.0014	0.0064	0.0162	5.78E-08	1.38E-07
292.6	0.6749	1.3235	0.0692	0.1305	0.0012	0.0019	0.0083	0.0208	8.84E-08	2.09E-07
295.8	0.8150	1.5837	0.0865	0.1617	0.0016	0.0025	0.0107	0.0265	1.34E-07	3.14E-07
298.9	0.9799	1.8875	0.1075	0.1993	0.0021	0.0033	0.0138	0.0337	2.01E-07	4.66E-07
302.1	1.1734	2.2406	0.1330	0.2445	0.0028	0.0043	0.0177	0.0425	3.00E-07	6.86E-07
305.3	1.3994	2.6496	0.1638	0.2987	0.0037	0.0057	0.0224	0.0534	4.43E-07	1.00E-06
308.4	1.6624	3.1216	0.2009	0.3633	0.0048	0.0073	0.0284	0.0667	6.48E-07	1.45E-06
311.6	1.9675	3.6646	0.2452	0.4400	0.0063	0.0095	0.0357	0.0829	9.40E-07	2.08E-06
314.7	2.3200	4.2871	0.2979	0.5307	0.0081	0.0121	0.0447	0.1025	1.35E-06	2.97E-06
317.9	2.7260	4.9984	0.3606	0.6375	0.0104	0.0155	0.0556	0.1262	1.93E-06	4.20E-06
321.0	3.1920	5.8085	0.4346	0.7628	0.0133	0.0197	0.0689	0.1547	2.74E-06	5.90E-06
324.2	3.7252	6.7284	0.5218	0.9094	0.0169	0.0248	0.0850	0.1887	3.86E-06	8.23E-06
327.4	4.3333	7.7699	0.6241	1.0801	0.0214	0.0312	0.1044	0.2293	5.39E-06	1.14E-05
330.5	5.0247	8.9456	0.7438	1.2783	0.0269	0.0391	0.1277	0.2775	7.48E-06	1.57E-05
333.7	5.8085	10.2692	0.8831	1.5077	0.0336	0.0486	0.1554	0.3343	1.03E-05	2.14E-05
336.8	6.6947	11.7550	1.0449	1.7723	0.0419	0.0603	0.1885	0.4013	1.41E-05	2.91E-05
340.0	7.6935	13.4186	1.2320	2.0764	0.0520	0.0744	0.2276	0.4799	1.92E-05	3.93E-05
343.2	8.8165	15.2764	1.4479	2.4251	0.0642	0.0914	0.2737	0.5717	2.60E-05	5.27E-05

Table S3.4. Calculated temperature-dependent heat of vaporization of the studied solvent compounds in kJ/mol.

Property	**Enthalpy of Vaporization (kJ/mol)**									
	Structure									
T (K)	**[M, A, M]**		**[E, A, E]**		**[ME, A, ME]**		**[F, A, F]**		**[Bn, A, Bn]**	
S	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**
283.2	43.20	41.12	51.01	49.00	66.90	65.28	59.08	56.06	95.32	92.69
286.3	43.14	41.06	50.94	48.9	66.80	65.18	58.96	55.94	95.20	92.57
289.5	43.07	41.00	50.87	48.88	66.70	65.09	58.84	55.82	95.07	92.45
292.6	43.00	40.94	50.81	48.81	66.60	64.99	58.72	55.70	94.94	92.33
295.8	42.94	40.87	50.74	48.75	66.50	64.89	58.59	55.58	94.81	92.21
298.9	42.87	40.81	50.67	48.67	66.39	64.80	58.47	55.46	94.68	92.08
302.1	42.80	40.74	50.60	48.62	66.29	64.70	58.34	55.34	94.55	91.96
305.3	42.73	40.63	50.53	48.55	66.18	64.59	58.22	55.22	94.41	91.83
308.4	42.66	40.60	50.45	48.48	66.07	64.49	58.09	55.09	94.28	91.70
311.6	42.58	40.53	50.38	48.41	65.96	64.38	57.97	54.97	94.14	91.57
314.7	42.51	40.46	50.30	48.34	65.85	64.28	57.84	54.85	94.00	91.43
317.9	42.44	40.39	50.22	48.26	65.74	64.17	57.71	54.72	93.86	91.30
321.0	42.36	40.32	50.14	48.19	65.62	64.06	57.58	54.60	93.71	91.16
324.2	42.29	40.25	50.06	48.11	65.50	63.95	57.45	54.47	93.57	91.02
327.4	42.21	40.17	49.98	48.04	65.39	63.83	57.32	54.34	93.42	90.88
330.5	42.13	40.10	49.90	47.96	65.27	63.72	57.19	54.22	93.27	90.74
333.7	42.05	40.02	49.81	47.88	65.14	63.60	57.06	54.09	93.12	90.59
336.8	41.97	39.94	49.73	47.80	65.02	63.48	56.93	53.96	92.96	90.44
340.0	41.89	39.87	49.64	47.71	64.89	63.36	56.79	53.83	92.80	90.29
343.2	41.80	39.79	49.55	47.63	64.76	63.23	56.66	53.70	92.64	90.14

Table S3.5. Calculated Dipole Moments (μ) of symmetric (*E/ Z*)-1,3-diethers-2-alkenes in Debye (D).

Property	**Dipole Moment (D)**									
	Structure									
	[M, A, M]		**[E, A, E]**		**[ME, A, ME]**		**[F, A, F]**		**[Bn, A, Bn]**	
S	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**	**E**	**Z**
	3.16	2.30	3.11	2.40	1.79	1.62	4.86	4.70	3.54	2.93

Table S3.6. Calculated density (g/cm^3), heat of vaporization (kJ/mol), vapor pressure (kPa), and viscosity (mPa·s) of [F, Br_2, F].

	Density (g/cm^3)		**Heat of vaporization (kJ/mol)**		**Vapor Pressure (kPa)**		**Viscosity (mPa·s)**	
T (K)	**R**	**S**	**R**	**S**	**R**	**S**	**R**	**S**
283.2	1.9757	1.9779	61.87	61.63	0.0015	0.0016	4.82	4.77
286.3	1.9697	1.9719	61.77	61.53	0.0020	0.0022	4.44	4.39
289.5	1.9637	1.9659	61.66	61.43	0.0027	0.0029	4.10	4.06
292.6	1.9577	1.9599	61.56	61.33	0.0036	0.0038	3.80	3.75
295.8	1.9518	1.9540	61.46	61.23	0.0047	0.0050	3.52	3.48
298.9	1.9458	1.9480	61.35	61.12	0.0061	0.0065	3.26	3.23
302.1	1.9399	1.9420	61.24	61.01	0.0079	0.0084	3.03	3.00
305.3	1.9340	1.9361	61.14	60.91	0.0101	0.0108	2.82	2.79
308.4	1.9280	1.9302	61.03	60.80	0.0129	0.0138	2.63	2.61
311.6	1.9221	1.9242	60.91	60.68	0.0165	0.0175	2.46	2.43
314.7	1.9162	1.9183	60.80	60.57	0.0208	0.0222	2.30	2.27
317.9	1.9103	1.9124	60.69	60.46	0.0262	0.0279	2.15	2.13
321.0	1.9044	1.9065	60.57	60.34	0.0329	0.0350	2.01	2.00
324.2	1.8986	1.9006	60.45	60.22	0.0410	0.0435	1.89	1.87
327.4	1.8927	1.8948	60.33	60.10	0.0509	0.0540	1.78	1.76
330.5	1.8868	1.8889	60.21	59.98	0.0629	0.0667	1.67	1.66
333.7	1.8810	1.8830	60.09	59.86	0.0773	0.0820	1.57	1.56
336.8	1.8752	1.8772	59.96	59.74	0.0947	0.1003	1.48	1.47
340.0	1.8693	1.8714	59.83	59.61	0.1155	0.1223	1.40	1.39
343.2	1.8635	1.8655	59.71	59.48	0.1403	0.1484	1.32	1.31

Table S3.7. Calculated Dipole Moments (μ) of [F, Br_2, F] in Debye (D).

Dipole moment (D)	
R	4.17
S	4.15

Table S4.1 Miscibility of compounds with common solvents at ambient temperature. [a]

Solvents	[M, A, M]	[E, A, E]	[ME, A, ME]	[F, A, F]	[Bn, A, Bn]
Hexane	+	+	+	+	+
Water	-	-	-	-	-
Toluene	+	+	+	+	+
CH_2Cl_2	+	+	+	+	+
MeOH	+	+	+	+	+
Et_2O	+	+	+	+	+
THF	+	+	+	+	+
Acetone	+	+	+	+	+
DMF	+	+	+	+	+
DMSO	+	+	+	+	+

[a] '+'= miscible and '-'=immiscible