Supporting Information

Kinetics of Self-Immolation: Faster Signal Relay over a Longer Linear Distance?

Ho Yong Lee, Xuan Jiang, and Dongwhan Lee*

Department of Chemistry, Indiana University,
800 East Kirkwood Avenue, Bloomington, Indiana 47405

Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used as received unless otherwise noted. The solvents dichloromethane, MeCN, and THF were saturated with nitrogen and purified by passage through activated Al_2O_3 columns under nitrogen (Innovative Technology SPS 400). Triethylamine was saturated with nitrogen and used without further purification. The compound 5-ethynyl-2-hydroxybenzaldehyde[1] was prepared according to literature procedures. All air-sensitive manipulations were carried out under nitrogen atmosphere in an M.Braun drybox or by standard Schlenk-line techniques.

Physical Measurements. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400 MHz Varian Inova NMR Spectrometer. Chemical shifts were reported versus tetramethylsilane and referenced to the residual solvent peaks. High-resolution chemical ionization (CI) (using CH_4 as CI reagent) and electrospray ionization (ESI) mass spectra were obtained on a Thermo Electron Corporation MAT 95XP-Trap. High resolution GC-MS (CI, using CH_4 as CI reagent) was obtained on a Thermo Electron Corporation MAT 95XP-Trap equipped with a Thermo Electron Trace Gas Chromatograph. FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer with EZ OMNIC E.S.P. software. UV-vis spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Fluorescence spectra were recorded on a Photon Technology International QM-4-CW Spectrofluorometer with FeliX32 software.

Kinetic Measurements. Stock solutions of tetrabutylammonium fluoride (TBAF, 35 mM) were prepared using TBAF·$3H_2O$ and anhydrous THF in the glovebox. Solution samples (1.0 μM) were prepared with anhydrous CH_2Cl_2 or THF collected freshly from the solvent purification system. In order to minimize dilution effects, 2–10 μL aliquots of TBAF stock solution, corresponding to 20–100 equiv with respect to the substrate, were delivered using microsyringes into a 3.5 mL sample solution placed in a thermostated Peltier cuvette holder.

Time-dependent changes in the fluorescence intensity were monitored at 460 nm (λ_{ex} = 380 nm) at 293 K with constant stirring. For the compounds **1**, **4**, **5**, and **7**, the ΔI vs t kinetic traces were fitted by non-linear regression method (OriginPro 8) using eq (1), in which the parameters k_1' (= $k_1[F^-]_0$) and I (= intensity at $t \rightarrow \infty$) were allowed to vary.

$$\Delta I = I(1 - e^{-k_1' t}) \tag{1}$$

[1] Chang, K.-H.; Huang, C.-C.; Liu, Y.-H.; Hu, Y.-H.; Chou, P.-T.; Lin, Y.-C. *Dalton Trans.* **2004**, 1731–1738.

For the kinetic analysis of the compounds **2**, **3**, **6**, and **8**, eq (2) was used. For each fit, the parameter k_1' ($= k_1[F^-]_0$) was fixed to the value obtained from the corresponding structural analogue having a carbonate linker, and k_2 and I were allowed to vary.[2,3]

$$\Delta I = \frac{I}{k_2 - k_1'}\{k_2(1 - e^{-k_1' t}) - k_1'(1 - e^{-k_2 t})\} \quad (2)$$

For compounds **3**, **6**, and **8** undergoing multiple quinone methide rearrangements prior to the release the fluorophore, kinetic data at initial stages of the reaction suffer excessively from interference of multiple intermediates that build up and decay simultaneously.[2,3] As such, intensity changes at $t > 40$ sec were used to derive effective k_2 values that approximate the time delay between the initial SiO bond cleavage event and the eventual release of the final fragmentation product.

Carbonic acid 5-ethynyl-2-triisopropylsilanyloxy-benzyl ester 2-oxo-2H-chromen-7-yl ester (1). An oven-dried round-bottom flask was loaded with 7-hydroxycoumarin (0.15 g, 0.92 mmol) and triphosgene (0.09 g, 0.3 mmol), and kept at 0 °C using ice bath. Pre-cooled CH_2Cl_2 (100 mL) was delivered under nitrogen to the reaction vessel using syringe. A solution of pyridine (0.07 g, 0.9 mmol) in anhyd CH_2Cl_2 (10 mL) was added over a period of 1 h using a cannula. During the addition, the temperature of the reaction was maintained at 0–5 °C. After the addition was complete, the mixture was allowed to warm slowly to r.t. and stirring was continued for 2 h under nitrogen. The reaction mixture was cooled to 0 °C and treated with anhyd CH_2Cl_2 solution (10 mL) of **15** (0.14 g, 0.46 mmol) and pyridine (0.04 g, 0.5 mmol). After stirring for 1 h at r.t., sat'd aq solution (50 mL) of $NaHCO_3$ was added. The organic layer was separated, washed with brine, and dried over anhyd $MgSO_4$. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v) to furnish **1** as a colorless oil (0.074 g, 33%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.70 (d, J = 9.6 Hz, 1H), 7.54 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 4.8 Hz, 1H), 7.20 (s, 1H), 7.14 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 9.6 Hz, 1H), 5.29 (s, 2H), 3.01 (s, 1H), 1.33 (m, 3H), 1.12 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.4, 155.3, 154.8, 153.6, 152.9, 142.9, 134.5, 134.3, 128.8, 125.1, 118.4, 117.9, 117.0, 116.4, 114.7, 110.1, 83.3, 76.5, 66.5, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3299, 2945, 2924, 2867, 1766, 1743, 1618, 1567, 1495, 1463, 1424, 1376, 1284, 1227, 1153, 1125, 1098, 1045, 976, 947, 882, 836, 685, 668. HRMS (CI) calcd for $C_{28}H_{33}O_6Si$ $[M + H]^+$ 493.2041, found 493.2058.

7-(5-Ethynyl-2-triisopropylsilanyloxy-benzyloxy)-chromen-2-one (2). To an anhyd DMF (5 mL) solution of **11** (0.31 g, 0.74 mmol) was added potassium salt of 7-hydroxycoumarin (0.15 g, 0.81 mmol). After stirring for 1 h at r.t., water (100 mL) and EtOAc (70 mL) were added to the reaction mixture. The organic layer was separated, washed with brine (100 mL × 3), dried over anhyd $MgSO_4$, and filtered. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v) to furnish **2** as a white solid (0.10 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.65 (d, J = 9.6 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.39–7.34 (m, 2H), 6.91 (dd, J = 8.4, 2.4 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.27 (d, J = 9.6 Hz, 1H), 5.11 (s, 2H), 3.00 (s, 1H), 1.31 (m, 3H), 1.11 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 162.1, 161.4, 156.0, 154.5, 143.6, 133.5, 133.1, 129.0, 126.5, 118.3, 114.7, 113.3, 112.9, 101.8, 83.6, 76.3, 65.9, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3345, 2943, 2866, 1734, 1614, 1558, 1540, 1506,

[2]Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; Wiley-VCH: Weinheim, 1990.
[3]Wright, M. R. *An Introduction to Chemical Kinetics*; John Wiley & Sons: Chichester, UK, 2004.

1492, 1458, 1399, 1280, 1229, 1122, 883, 668, 650, 617, 578. HRMS (CI) calcd for $C_{27}H_{33}O_4Si$ [M + H]$^+$ 449.2143, found 449.2155.

4-(5-Ethynyl-2-(triisopropylsilyloxy)benzyloxy)benzyl 2-oxo-2H-chromen-7-yl carbonate (3). This compound was prepared using **12** (0.15 g, 0.36 mmol), N,N'-disuccinimidyl carbonate (0.11 g, 0.42 mmol), Et_3N (0.073g, 0.69 mmol), and 7-hydroxycoumarin (0.062 g, 0.37 mmol) in a manner similar to that described for **4**. The product was isolated as a colorless oil (18 mg, 8.2%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.69 (d, J = 12.8 Hz, 1H), 7.59 (d, J = 2.8 Hz, 1H), 7.49 (d, J = 11.6 Hz, 1H), 7.39 (d, J = 11.2 Hz, 2H), 7.34 (dd, J = 11.2, 2.8 Hz, 1H), 7.22 (d, J = 2.8 Hz, 1H), 7.15 (dd, J = 11.2, 2.8 Hz, 1H), 6.99 (d, J = 11.6, 2H), 6.80 (d, J = 11.2 Hz, 1H), 6.41 (d, J = 12.8 Hz, 1H), 5.23 (s, 2H), 5.09 (s, 2H), 2.99 (s, 1H), 1.32 (m, 3H), 1.12 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.4, 159.5, 154.8, 154.2, 153.6, 152.9, 142.9, 133.0, 132.9, 130.9, 128.8, 127.5, 126.7, 118.2, 117.9, 116.9, 116.4, 115.0, 114.7, 110.1, 83.8, 76.1, 71.0, 65.3, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 2945, 2866, 1764, 1743, 1614, 1513, 1493, 1381, 1280, 1224, 1175, 1154, 1099, 1042, 883, 686. HRMS (ESI) calcd for $C_{35}H_{38}O_7NaSi$ [M + Na]$^+$ 621.2285, found 621.2310.

2-(5-Ethynyl-2-(triisopropylsilyloxy)benzyloxy)benzyl 2-oxo-2H-chromen-7-yl carbonate (4). To a stirred solution of **13** (0.12 g, 0.29 mmol) in CH_2Cl_2 (10 mL) were added Et_3N (0.062 g, 0.59 mmol) and N,N'-disuccinimidyl carbonate (0.089 g, 0.35 mmol). After stirring overnight at r.t., 7-hydroxycoumarin (0.052 g, 0.30 mmol) was added and stirring was continued at r.t. for 4 h. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v) to furnish **4** as a colorless oil (12 mg, 6.6%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.68 (d, J = 9.6 Hz, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.44 (dd, J = 7.2, 1.6 Hz, 1H), 7.33 (m, 2H), 7.23 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.4, 2.4 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 9.2 Hz, 1H), 5.43 (s, 2H), 5.16 (s, 2H), 2.96 (s, 1H), 1.33 (m, 3H), 1.12 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.5, 157.0, 154.8, 154.0, 153.7, 153.0, 142.9, 133.0, 132.4, 130.7, 130.6, 128.7, 127.6, 123.1, 120.9, 118.1, 118.0, 116.8, 116.3, 114.7, 111.8, 110.1, 83.8, 76.2, 66.8, 65.4, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 2945, 2866, 1765, 1743, 1606, 1493, 1456, 1381, 1224, 1155, 1042, 982, 883, 842, 754, 665. HRMS (ESI) calcd for $C_{35}H_{38}O_7NaSi$ [M + Na]$^+$ 621.2285, found 621.2255.

2-Oxo-2H-chromen-7-yl 2-(triisopropylsilyloxy)benzyl carbonate (5). To a stirred solution of **14** (0.37 g, 1.3 mmol) in anhyd MeCN (10 mL) were added Et_3N (0.28 g, 2.7 mmol) and N,N-disuccinimidyl carbonate (0.41 g, 1.6 mmol). After stirring overnight at r.t. under nitrogen, 7-hydroxycoumarin (0.20 g, 1.2 mmol) was added, and stirring was continued for 4 h. Volatile fractions were removed under reduced pressure, and the residual material was extracted into EtOAc (50 mL). The organic layer was washed with sat'd aq solution of $NaHCO_3$ (100 mL) and brine (100 mL), dried over anhyd $MgSO_4$, and filtered. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **5** as a colorless oil (54 mg, 8.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.69 (d, J = 9.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 2.0, 8.0 Hz, 1H), 7.26 (m, 2H), 7.13 (dd, J = 2.4, 8.4 Hz, 1H), 6.97 (t, J = 7.6, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 9.2 Hz, 1H), 5.34 (s, 2H), 1.36 (m, 3H), 1.13 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.4, 154,8, 153.7, 153,0, 142.9, 130.9, 130.4, 128.8, 124.6, 121.0, 118.4, 117.9, 116.9, 116.3, 110.1, 67.3, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 2945, 2867, 1765, 1745, 1618, 1604, 1493, 1456, 1381, 1281, 1225, 1154, 1124, 983, 919, 883, 840, 758, 684. HRMS (CI) calcd for $C_{26}H_{32}O_6Si$ [M + H]$^+$ 469.2041, found 469.2026.

7-(2-(Triisopropylsilyloxy)benzyloxy)-2H-chromen-2-one (6). To an anhyd DMF (5 mL) solution of **15** (0.61 g, 1.5 mmol) was added potassium salt of 7-hydroxycoumarin (0.29 g, 1.5 mmol). After stirring for 1 h at r.t., the reaction was quenched by adding water (100 mL) and EtOAc (70 mL). The organic layer was separated, washed with brine (100 mL × 3), dried over anhyd $MgSO_4$, and filtered. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **6** as a white solid (0.30 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.63 (d, J = 9.6 Hz, 1H), 7.40 (m, 2H), 7.23 (t, J = 8.0 Hz, 1H), 6.90 (m, 4H), 6.24 (d, J = 9.6 Hz, 1H), 5.16 (s, 2H), 1.31 (m, 3H), 1.11(d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 162.4, 161.4, 156.0, 154.0, 143.6, 129.5, 128.9, 126.0, 121.1, 118.3, 113.2, 112.7, 101.8, 66.5, 18.2, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3072, 2941, 2891, 2866, 1738, 1613, 1507, 1491, 1455, 1429, 1401, 1383, 1348, 1279, 1230, 1120, 999, 919, 833, 757, 683. HRMS (CI) calcd for $C_{25}H_{32}O_4Si$ $[M + H]^+$ 425.2143, found 425.2150.

2-Oxo-2H-chromen-7-yl 4-(triisopropylsilyloxy)benzyl carbonate (7). This compound was prepared using **16** (0.36 g, 1.35 mmol), Et_3N (0.28 g, 2.7 mmol), *N*,*N*-disuccinimidyl carbonate (0.41 g, 1.6 mmol) and 7-hydroxycoumarin (0.19 g, 1.1 mmol) in a manner similar to that described for **5**. The product was isolated as a light yellow oil (0.31 g, 48%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.62 (d, J = 9.6 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.62 (m, 4H), 6.24 (d, J = 9.6 Hz, 1H), 5.02 (s, 2H), 1.27 (m, 3H), 1.10 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 162.2, 161.4, 156.5, 156.0, 143.6, 129.4, 128.9, 128.2, 120.2, 113.4, 113.3, 112.8, 102.0, 70.6, 18.1, 12.8. FT-IR (thin film on NaCl, cm^{-1}): 2945, 2892, 2867, 1765, 1744, 1613, 1512, 1463, 1424, 1379, 1229, 1169, 1154, 1125, 1099, 1014, 972, 912, 883, 842, 777, 679. HRMS (CI) calcd for $C_{26}H_{32}O_6Si$ $[M + H]^+$ 469.2041, found 469.2052.

7-(4-(Triisopropylsilyloxy)benzyloxy)naphthalen-2(1H)-one (8). This compound was prepared using **17** (0.59 g, 1.5 mmol) and potassium salt of 7-hydroxycoumarin (0.28 g, 1.5 mmol) in a manner similar to that described for **6**. The product was isolated as a light yellow oil (0.31 g, 48%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.62 (d, J = 9.6 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.62 (m, 4H), 6.24 (d, J = 9.6 Hz, 1H), 5.02 (s, 2H), 1.27 (m, 3H), 1.10 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 162.2, 161.4, 156.5, 156.0, 143.6, 129.4, 128.9, 128.2, 120.2, 113.4, 113.3, 112.8, 102.0, 70.6, 18.1, 12.8. FT-IR (thin film on NaCl, cm^{-1}): 3068, 2944, 2890, 2866, 1735, 1614, 1511, 1462, 1401, 1348, 1268, 1229, 1194, 1156, 1121, 998, 911, 883, 832, 684. HRMS (CI) calcd for $C_{25}H_{32}O_4Si$ $[M + H]^+$ 425.2143, found 425.2148.

5-Ethynyl-2-(triisopropylsilyloxy)benzaldehyde (9). An anhyd CH_2Cl_2 solution (100 mL) of 5-ethynyl-2-hydroxy-benzaldehyde (1.4 g, 9.9 mmol) and imidazole (0.81 g, 12 mmol) at 0 °C under nitrogen was treated with ^{i}Pr$_3$SiCl (2.3 g, 12 mmol). The reaction mixture was stirred overnight at r.t. under nitrogen. The crude reaction mixture was filtered through a pack of Celite and the filtrate concentrated under reduced pressure. The residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to afford **9** as a light-yellow solid (2.7 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 10.48 (s. 1H), 7.94 (d, J = 2.0 Hz , 1H), 7.55 (dd, J = 6.4, 2.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.02 (s, 1H), 1.35 (m, 3H), 1.13 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 189.4, 159.7, 139.1, 132.6, 126.8, 120.1, 115.3, 82.4, 77.1, 18.0, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3317, 2946, 2867, 2110, 1685, 1634, 1483, 1414, 1389, 1293, 1253, 1144, 1103, 950, 882, 827, 746, 665, 576. HRMS (CI) calcd for $C_{18}H_{27}O_2Si$ $[M + H]^+$ 303.1775, found 303.1773.

(5-Ethynyl-2-(triisopropylsilyloxy)phenyl)methanol (10). To a stirred solution of **9** (2.7 g, 8.9 mmol) in EtOH (100 mL) at 0 °C was added $NaBH_4$ (0.52 g, 13 mmol). After stirring for 10 min at 0 °C, the reaction mixture was quenched with sat'd aq solution of NH_4Cl (5 mL). Volatile fractions were removed under reduced pressure and the residual material was extracted into EtOAc (100 mL), and washed with water (100 mL) and brine (100 mL). The organic layer was dried over anhyd $MgSO_4$ and volatile fractions were removed under reduced pressure. The crude product was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **10** as a light yellow oil (2.6 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.48 (d, J = 2.0 Hz, 1H), 7.31 (dd, J = 6.4, 2.0 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 4.68 (s, 2H), 2.99 (s, 1H), 1.32 (m, 3H), 1.12 (d, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 154.5, 132.7, 131.5, 131.5, 118.1, 114.7, 83.8, 76.1, 61.7, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3310, 2945, 2892, 2867, 2105, 1604, 1492, 1463, 1385, 1281, 1265, 1385, 1281, 1265, 1117, 1041, 1015, 940, 882, 819, 734, 685, 667, 581. HRMS (CI) calcd for $C_{18}H_{29}O_2Si$ $[M + H]^+$ 305.1937, found 305.1950.

(4-Ethynyl-2-iodomethyl-phenoxy)-triisopropyl-silane (11). To a stirred solution of **10** (0.93 g, 3.0 mmol) in anhyd CH_2Cl_2 (50 mL) at 0 °C under nitrogen were added imidazole (0.31 g, 4.5 mmol) and PPh_3 (0.98 g, 3.7 mmol). After 10 min of stirring at 0 °C, I_2 (1.1 g, 4.5 mmol) was added and stirring was continued for 30 min at 0 °C under nitrogen. The mixture was filtered through a pack of Celite and the filtrate concentrated under reduced pressure. The residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to provide **11** as a light yellow oil (1.2 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.46 (d, J = 2.0 Hz, 1H), 7.27 (dd, J = 6.4, 2.0 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 4.42 (s, 2H), 2.98 (s, 1H), 1.37 (m, 3H), 1.15 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 154.6, 134.6, 133.4, 129.7, 118.4, 114.6, 83.3, 76.2, 18.3, 13.2. FT-IR (thin film on NaCl, cm^{-1}): 3307, 2944, 2866, 1601, 1493, 1460, 1283, 1158, 1135, 949, 883, 820, 722, 685, 662, 588. HRMS (CI) calcd for $C_{18}H_{28}OISi$ $[M + H]^+$ 415.0949, found 415.0930.

(4-(5-Ethynyl-2-(triisopropylsilyloxy)benzyloxy)phenyl)methanol (12). This compound was prepared using **11** (0.27 g, 0.65 mmol), potassium salt of 2-hydroxybenzaldehyde (0.10 g, 0.62 mmol), and $NaBH_4$ (0.022 g, 0.52 mmol) in a manner similar to that described for **13**. The product was isolated as a colorless oil (0.14 g, 52%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.61 (d, J = 1.6 Hz, 1H), 7.34 (dd, J = 8.4, 2.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.4 Hz, 1H), 5.08 (s, 2H), 4.60 (s, 2H), 2.99 (s, 1H), 1.32 (m, 3H), 1.12 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.5, 154.2, 133.5, 132.9, 128.8, 127.8, 118.1, 114.9, 114.6, 83.9, 76.1, 65.3, 65.2, 18.2, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3289, 2944, 2926, 2867, 1683, 1606, 1558, 1540, 1463, 1383, 1284, 1244, 1173, 1113, 1044, 1018, 950, 882, 759, 685, 664. HRMS (ESI) calcd for $C_{25}H_{34}O_3NaSi$ $[M + Na]^+$ 433.2175, found 433.2192.

(2-(5-Ethynyl-2-(triisopropylsilyloxy)benzyloxy)phenyl)methanol (13). To an anhyd DMF (5 mL) solution of **11** (0.34 g, 0.82 mmol) was added potassium salt of 4-hydroxybenzaldehyde (0.15 g, 0.93 mmol). The reaction mixture was stirred for 2 h at r.t. and treated with water (100 mL) and EtOAc (70 mL). Organic layer was separated, washed with water (100 mL) and brine (100 mL), dried over anhyd $MgSO_4$, and filtered. Volatile fractions were removed under reduced pressure and the crude product (0.20 g) was extracted into EtOH (10 mL). A portion of $NaBH_4$ (0.031 g, 0.79 mmol) was added at 0 °C and the mixture was stirred for 10 min. A sat'd aq solution (5 mL) of NH_4Cl was added and volatile fractions were removed under reduced pressure. The crude product was extracted into EtOAc (100 mL), and washed with water (100 mL) and brine (100 mL). The organic layer was dried over anhyd $MgSO_4$ and filtered. Volatile fractions were removed under

reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v) to provide **13** as a colorless oil (0.12 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.55 (d, J = 1.6 Hz, 1H), 7.32 (m, 2H), 7.24 (t, J = 8.0 Hz, 1H), 6.95 (t, J = 7,2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 5.12 (s, 2H), 4.74 (d, J = 4.4 Hz, 2H), 2.98 (s, 1H), 2.42 (s, 1H), 1.31 (m, 3H), 1.11 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 156.6, 154.3, 133.2, 132.8, 129.6, 129.0, 128.8, 127.6, 121.1, 118.3, 114.8, 111.4, 83.7, 76.4, 65.4, 62.1, 18.1, 13.1. FT-IR (thin film on NaCl, cm^{-1}): 3309, 2945, 2917, 286, 1605, 1493, 1455, 1382, 1283, 1236, 1124, 1049, 1014, 949, 882, 820, 757, 685, 667. HRMS (ESI) calcd for $C_{25}H_{34}O_3NaSi$ $[M + Na]^+$ 433.2175, found 433.2166.

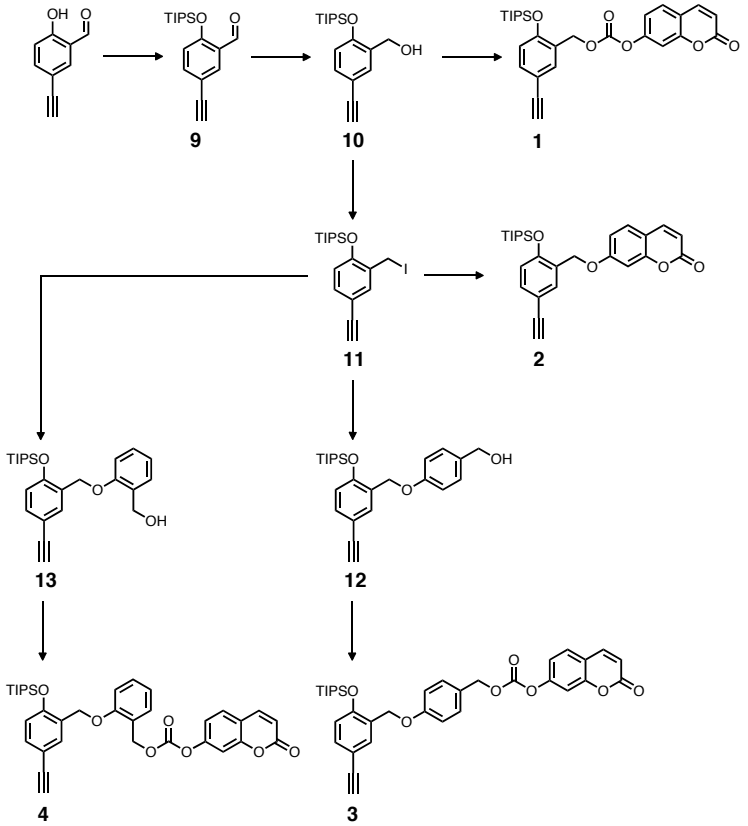
(2-(Triisopropylsilyloxy)phenyl)methanol (14). To an anhyd CH_2Cl_2 (70 mL) solution of 2-hydroxybezaldehyde (1.7 g, 14 mmol) and imidazole (1.9 g, 28 mmol) at 0 °C was added via syringe ^{i}Pr$_3$SiCl (3.3 g, 17 mmol) dissolved in anhyd CH_2Cl_2 (10 mL). The reaction mixture was stirred at r.t. for 12 h under nitrogen and filtered through a pack of Celite. The filtrate was concentrated under reduced pressure to furnish the crude product (4.1 g), which was extracted into EtOH (10 mL). A portion of $NaBH_4$ (0.58 g, 15 mmol) was added at 0 °C. After stirring at 0 °C for 20 min, the reaction was quenched by adding sat'd aq solution of NH_4Cl (2 mL). Volatile fractions were removed under reduced pressure, and the residual material was extracted into EtOAc (100 mL), and washed with water (100 mL) and brine (100 mL). The organic layer was separated, dried over anhyd $MgSO_4$, and filtered. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **14** as a colorless oil (1.9 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.31 (dd, J = 1.6, 7.2 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8 Hz, 1H), 4.72 (d, J = 5.6 Hz, 2H), 2.15 (t, J = 6.4 Hz, 1H), 1.35 (m, 3H), 1.13 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 154.0, 131.2, 128.9, 128.8, 121.2, 118.1, 62.4, 18.2, 13.2. FT-IR (thin film on NaCl, cm^{-1}): 3345, 3069, 3037, 2944, 2891, 2867, 1061, 1583, 1488, 1454, 1384, 1367, 1277, 1256, 1109, 1041, 1014, 997, 920, 882, 755, 682, 661. HRMS (CI) calcd for $C_{16}H_{28}O_2Si$ $[M + H]^+$ 280.1853, found 280.1856.

(2-(Iodomethyl)phenoxy)triisopropylsilane (15). To a stirred anhyd CH_2Cl_2 (50 mL) solution of **14** (0.58 g, 2.0 mmol) at 0 °C under nitrogen were added imidazole (0.23 g, 3.3 mmol) and PPh_3 (0.69 g, 2.6 mmol). After stirring for 10 min at 0 °C, I_2 (0.79 g, 3.1 mmol) was added, and stirring was continued for 0.5 h at 0 °C under nitrogen. The reaction mixture was filtered through a pack of Celite and the filtrate concentrated under reduced pressure. The residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to afford **15** as a light yellow oil (0.61 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.34 (dd, J = 1.6, 7.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 4.53 (s, 2H), 1.43 (m, 3H), 1.20 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 154.1, 130.8, 129.5, 129.4, 121.2, 118.5, 18.4, 13.4, 2.35. FT-IR (thin film on NaCl, cm^{-1}): 2944, 2891, 2866, 1609, 1463, 1460, 1263, 1158, 1135, 996, 882, 831, 731, 680. HRMS (CI) calcd for $C_{16}H_{27}IOSi$ $[M + H]^+$ 391.0949, found 391.0951.

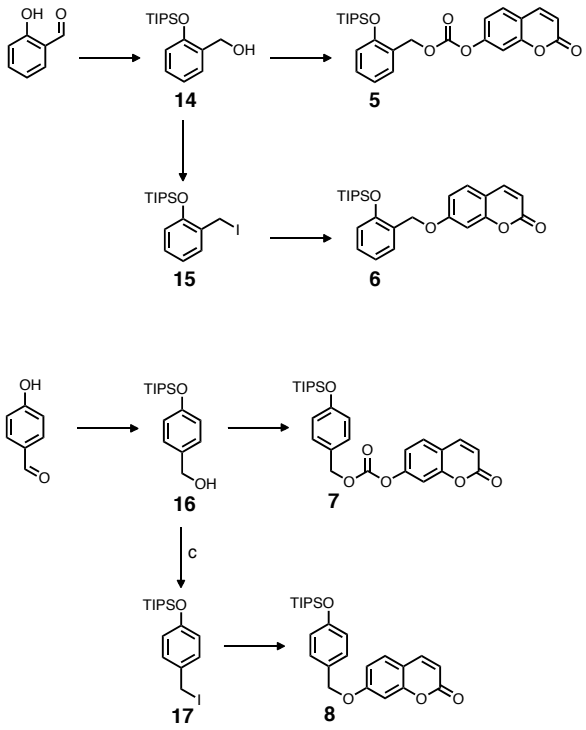
(4-(Triisopropylsilyloxy)phenyl)methanol (16). This compound was prepared using 4-hydroxybenzaldehyde (2.5 g, 20 mmol), imidazole (1.8, 26 mmol), ^{i}Pr$_3$SiCl (5.0 g, 25 mmol), and $NaBH_4$ (0.81 g, 21 mmol) in a manner similar to that described for **14**. The product was isolated as a colorless oil (4.1 g, 77%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.22 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 1H), 4.59 (s, 2H), 1.63 (s, 1H), 1.28 (m, 3H), 1.10 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 155.9, 133.6, 128.7, 120.1, 65.3, 18.1, 12.8. FT-IR (thin film on NaCl, cm^{-1}): 3408, 2944, 2891,

2866, 1651, 1609, 1509, 1463, 1417, 1384, 1263, 1166, 1010, 996, 912, 882, 831, 805, 680. HRMS (CI) calcd for $C_{16}H_{28}O_2Si$ $[M + H]^+$ 280.1853, found 280.1857.

(4-(Iodomethyl)phenoxy)triisopropylsilane (17). This compound was prepared using **16** (0.59 g, 2.1 mmol), imidazole (0.24 g, 3.5 mmol), PPh_3 (0.67 g, 2.5 mmol), and I_2 (0.80 g, 3.1 mmol) in a manner similar to that described for **15**. The product was isolated as a light yellow oil (0.59 g, 72%) after flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.31 (d, J = 6.4 Hz, 2H), 6.87 (d, J = 6.4 Hz, 1H), 4.51 (s, 2H), 1.34 (m, 3H), 1.17 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 156.0, 131.8, 130.2, 120.4, 18.1, 12.9, 6.9. FT-IR (thin film on NaCl, cm^{-1}): 2943, 2891, 2866, 1609, 1463, 1250, 1053, 1014, 882, 800, 682. HRMS (CI) calcd for $C_{16}H_{27}IOSi$ $[M + H]^+$ 391.0949, found 391.0958.



Scheme S1. Synthetic routes to compounds **1**–**4**.



Scheme S2. Synthetic routes to compounds **5**–**8**.

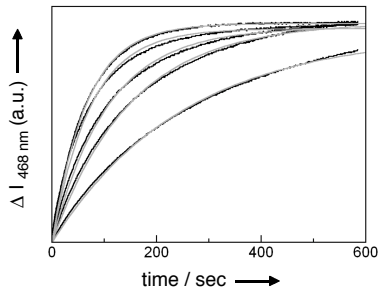


Figure S1. Time-dependent changes in the fluorescence intensity at λ = 460 nm (λ_{exc} = 380 nm) from the reaction between **1** (= 1.0 μM) and F^- (0.02–0.10 mM) in CH_2Cl_2 at T = 293 K. The gray curves overlaid on the experimental data are theoretical fits generated using eq 1.

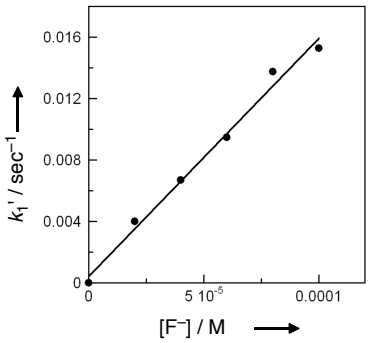


Figure S2. A plot of k_1' vs $[F^-]_0$ obtained from the data shown in Figure S1.

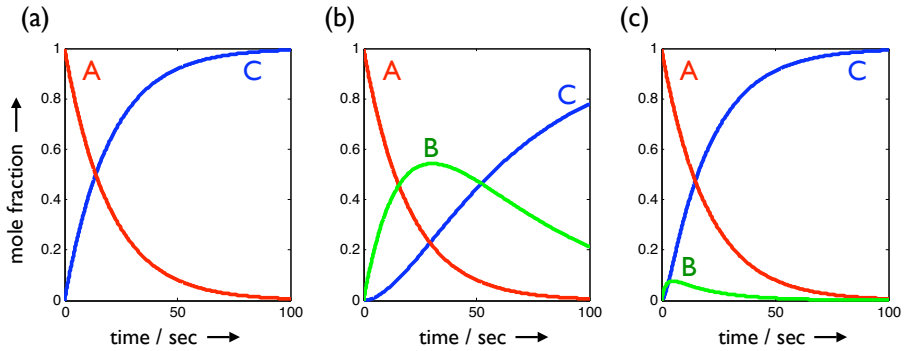


Figure S3. Plots describing idealized single-step (a) and two-step (b and c) reactions simulated using MATLAB. Time-dependent changes in the mole fractions of the reactant (A), intermediate (B), and product (C) are plotted for three different scenarios. Plot (a) represents first-order reaction $\mathsf{A} \xrightarrow{k_1} \mathsf{C}$ with $k_1 = 0.05$ sec^{-1}. Plots (b) and (c) represent two consecutive first-order reactions $\mathsf{A} \xrightarrow{k_1} \mathsf{B} \xrightarrow{k_2} \mathsf{C}$, where $k_1 = 0.05$ sec^{-1} and $k_2 = 0.02$ sec^{-1} for (b); $k_1 = 0.05$ sec^{-1} and $k_2 = 0.5$ sec^{-1} for (c). Note that the k_1 parameters of (a)–(c) are kept identical so that the mole fraction of the reactant A always decays with the same rate. With $k_1 \sim k_2$, as in (b), there is significant build-up of **B** at the early stage of the reaction and therefore a time delay (= induction period; lagtime) between the start of the reaction and the rise of the product **C**. With $k_1 \ll k_2$, as in (c), the system approaches the behavior of (a).

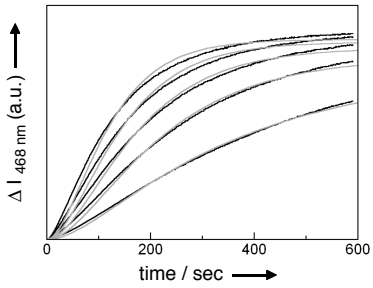


Figure S4. Time-dependent changes in the fluorescence intensity at $\lambda = 460$ nm ($\lambda_{exc} = 380$ nm) from the reaction between **2** (= 1.0 μM) and F^- (0.02–0.10 mM) in CH_2Cl_2 at T = 293 K. The gray curves overlaid on the experimental data are theoretical fits generated using eq 2 with k_1' fixed at the value obtained from data shown in Figures S1 and S2, and with k_2 allowed to vary in a global fitting scheme using a total of 2950 data points obtained for the entire $[F^-]$ concentration range.

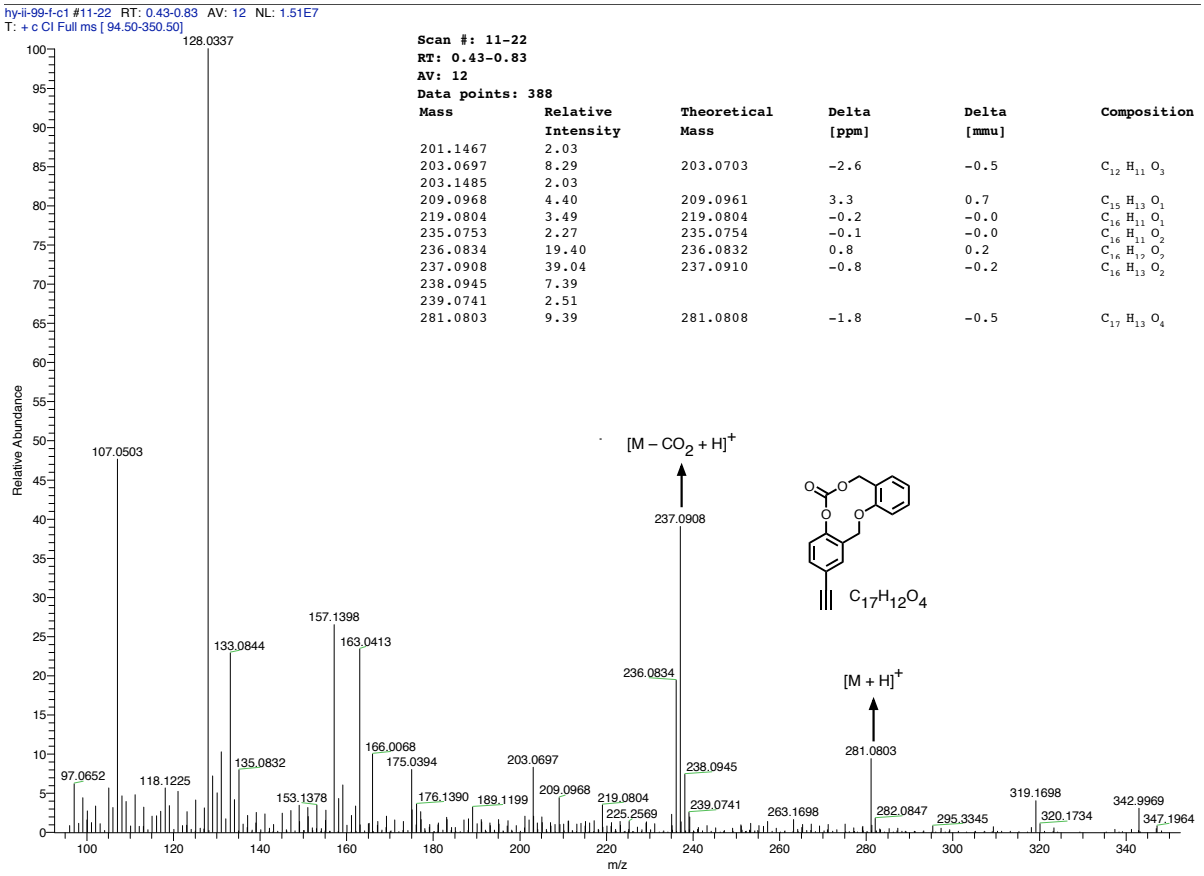


Figure S5. High-resolution mass spectrum recorded for the fluoride-induced cleavage reaction products of **4** showing the protonated parent at $m/z = 281.0803$ and decarboxylated fragment ion at $m/z = 237.0908$.

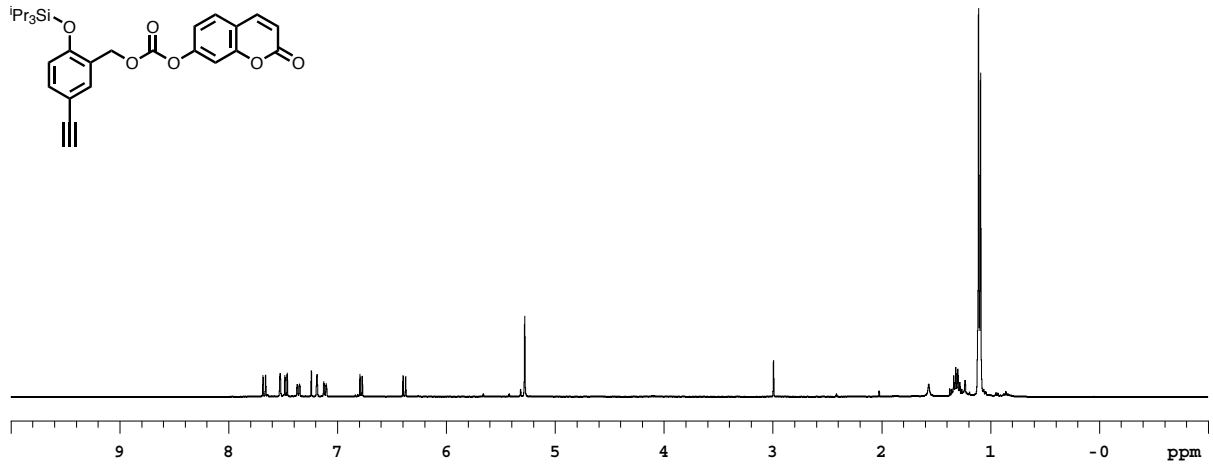


Figure S6. ^{1}H-NMR spectrum of **1** in $CDCl_3$ at $T = 298$ K.

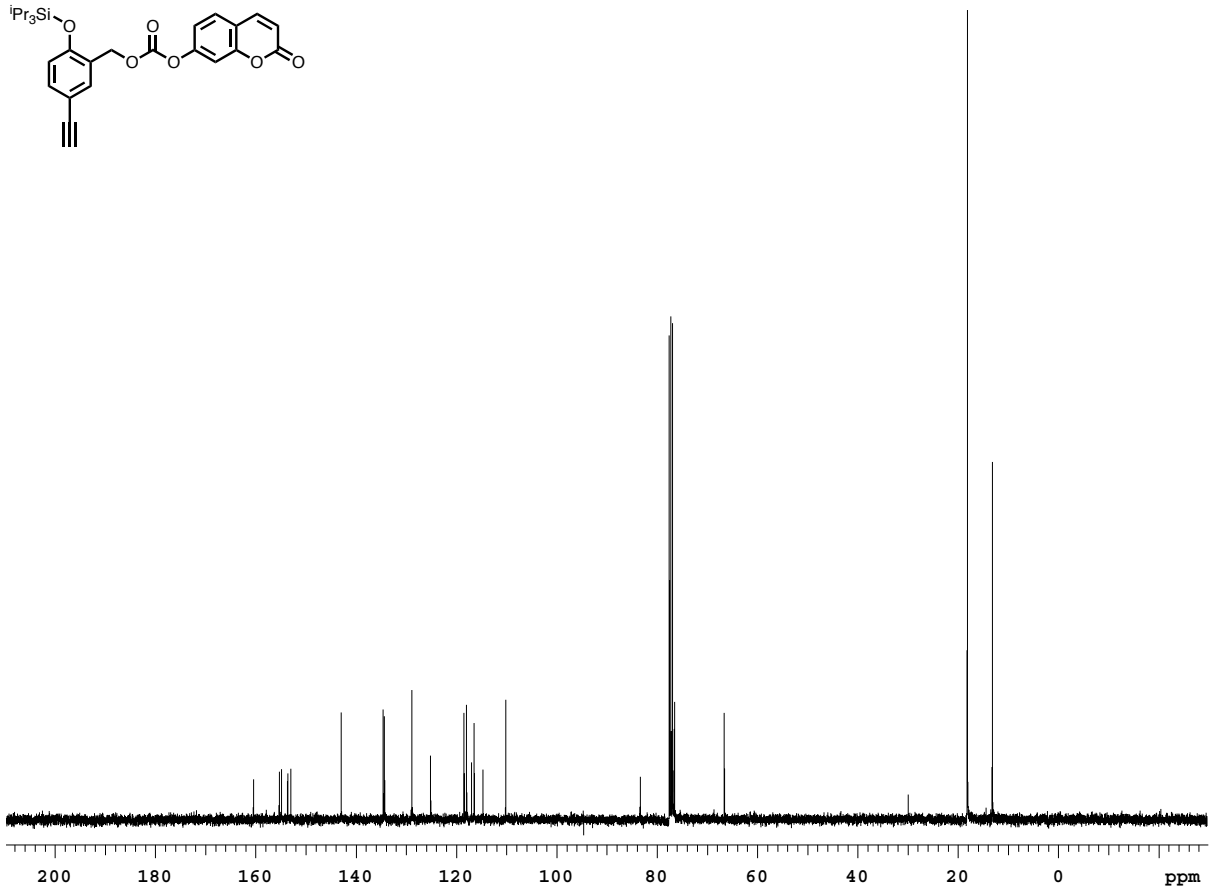


Figure S7. ^{13}C-NMR spectrum of **1** in $CDCl_3$ at $T = 298$ K.

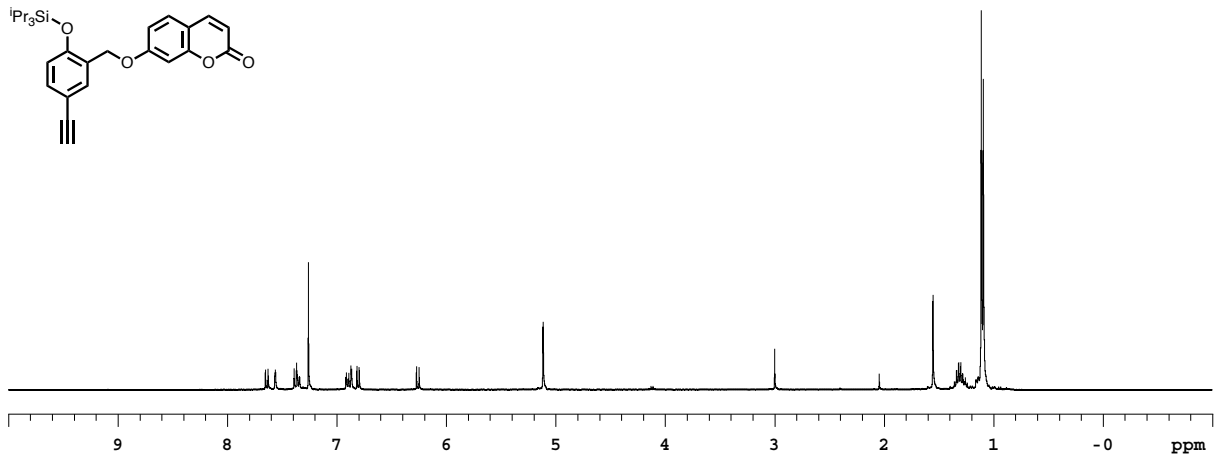


Figure S8. ^{1}H-NMR spectrum of **2** in $CDCl_3$ at $T = 298$ K.

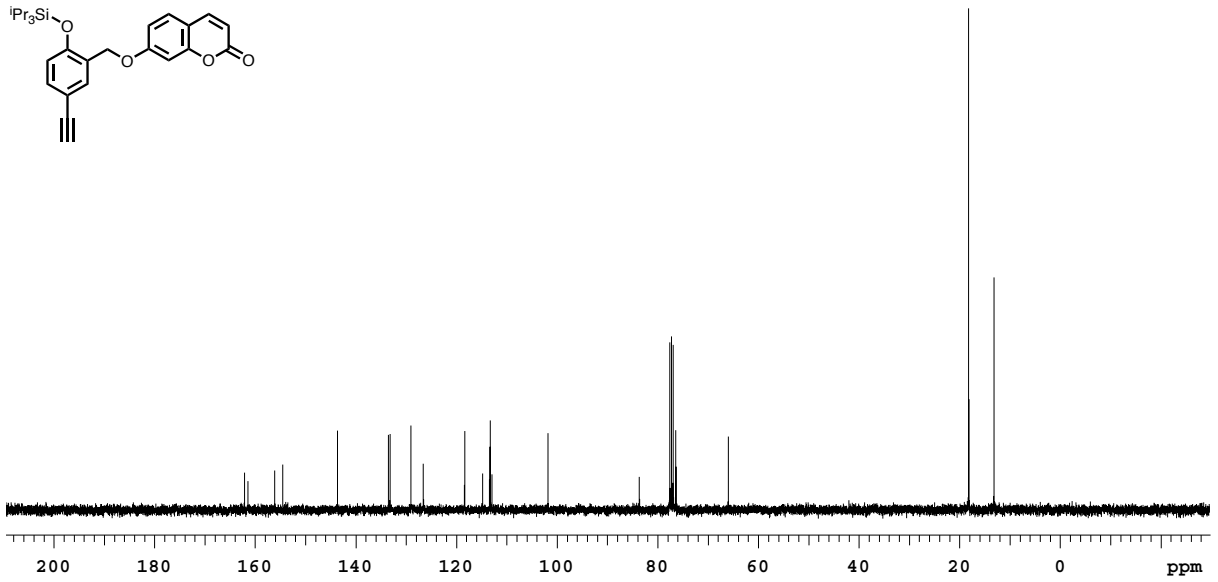


Figure S9. ^{13}C-NMR spectrum of **2** in $CDCl_3$ at $T = 298$ K.

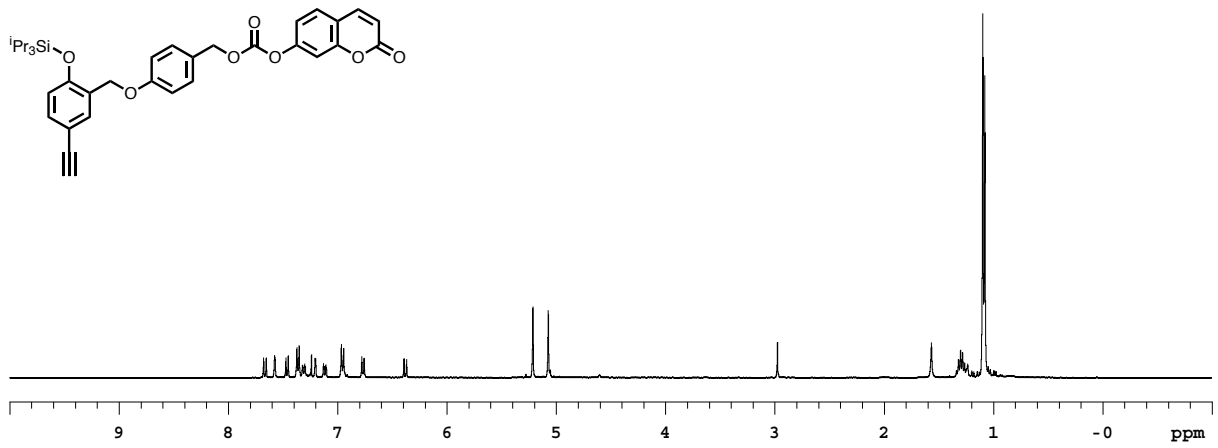


Figure S10. ^{1}H-NMR spectrum of **3** in $CDCl_3$ at $T = 298$ K.

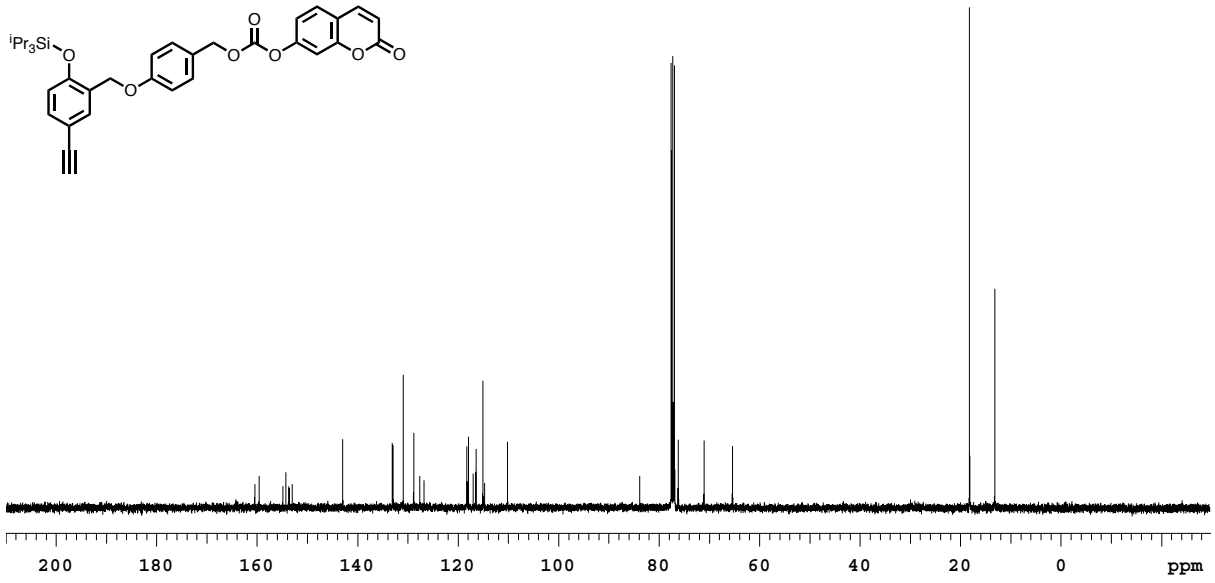


Figure S11. ^{13}C-NMR spectrum of **3** in $CDCl_3$ at $T = 298$ K.

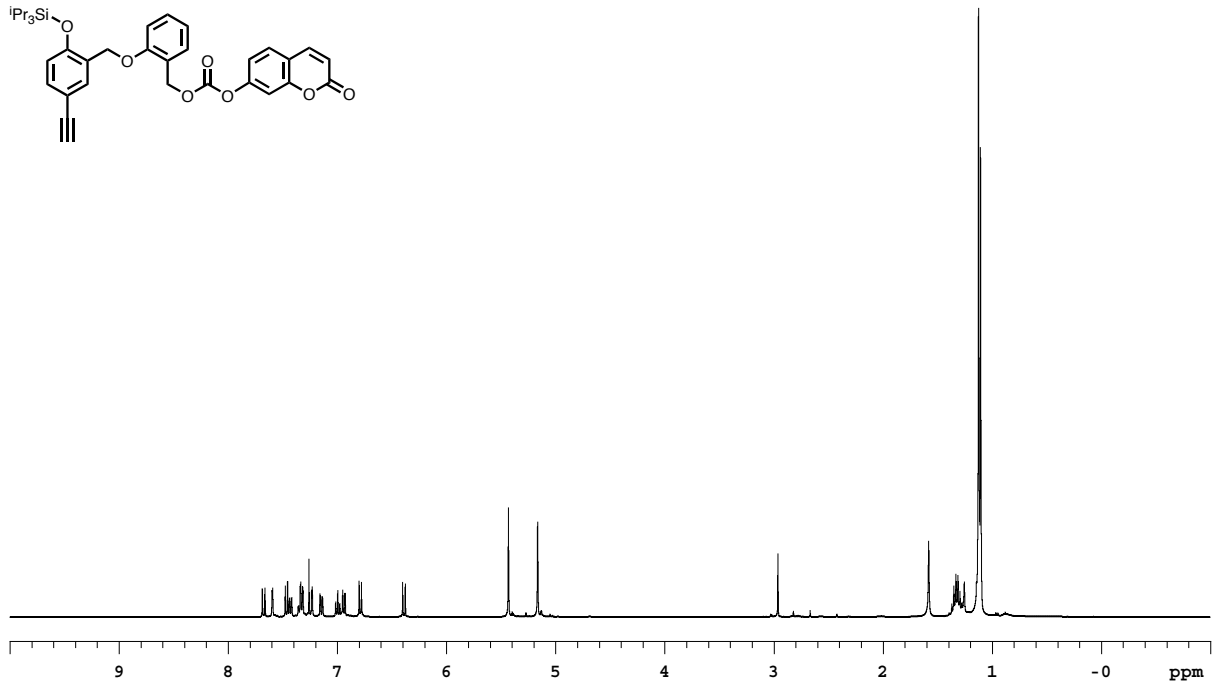


Figure S12. ^{1}H-NMR spectrum of **4** in $CDCl_3$ at $T = 298$ K.

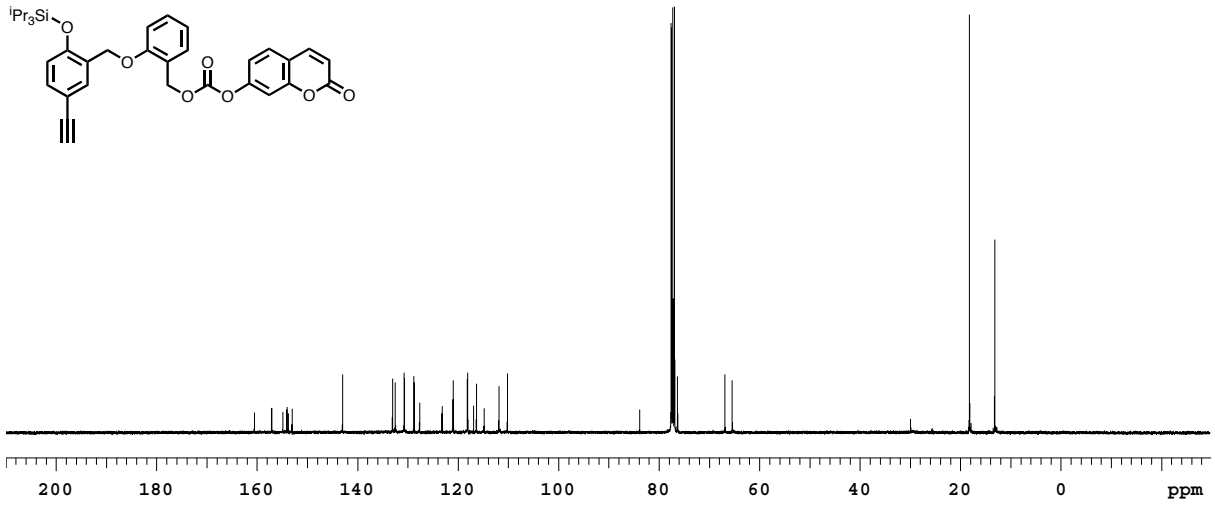


Figure S13. ^{13}C-NMR spectrum of **4** in $CDCl_3$ at $T = 298$ K.

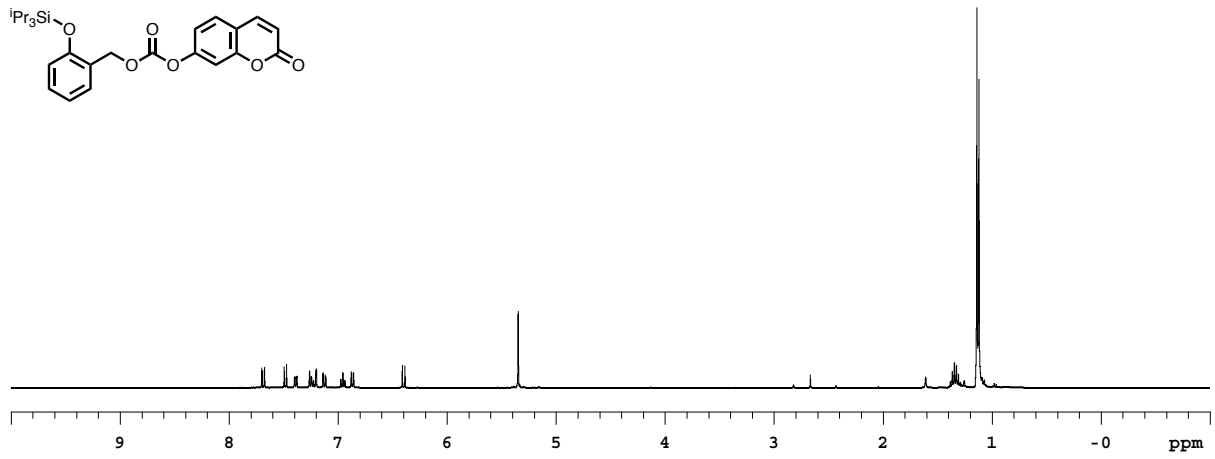


Figure S14. ^{1}H-NMR spectrum of **5** in $CDCl_3$ at $T = 298$ K.

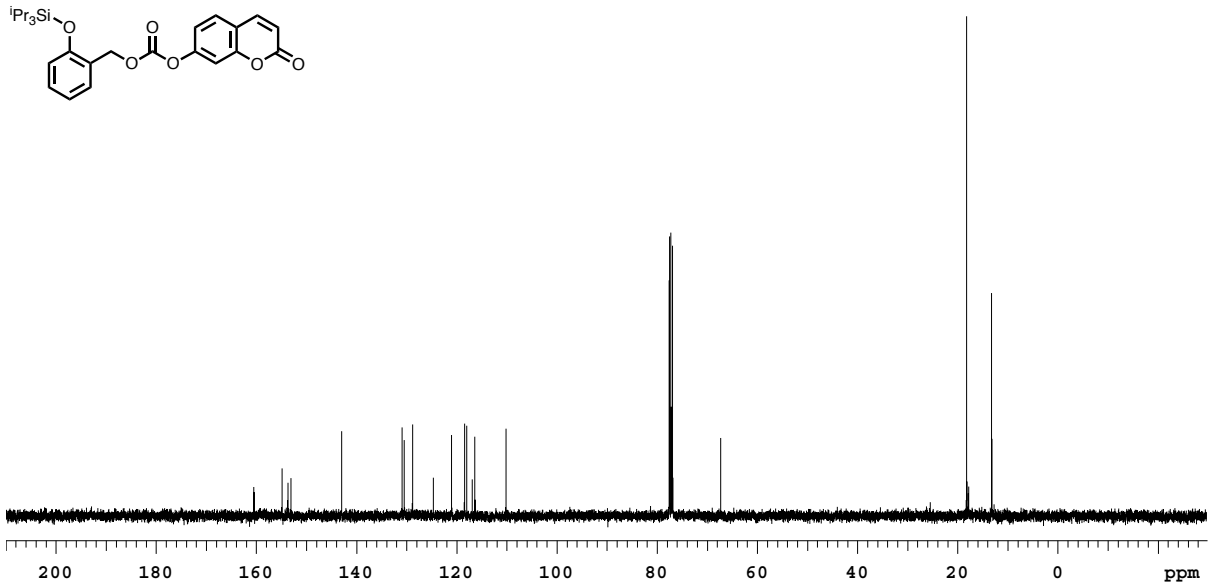


Figure S15. ^{13}C-NMR spectrum of **5** in $CDCl_3$ at $T = 298$ K.

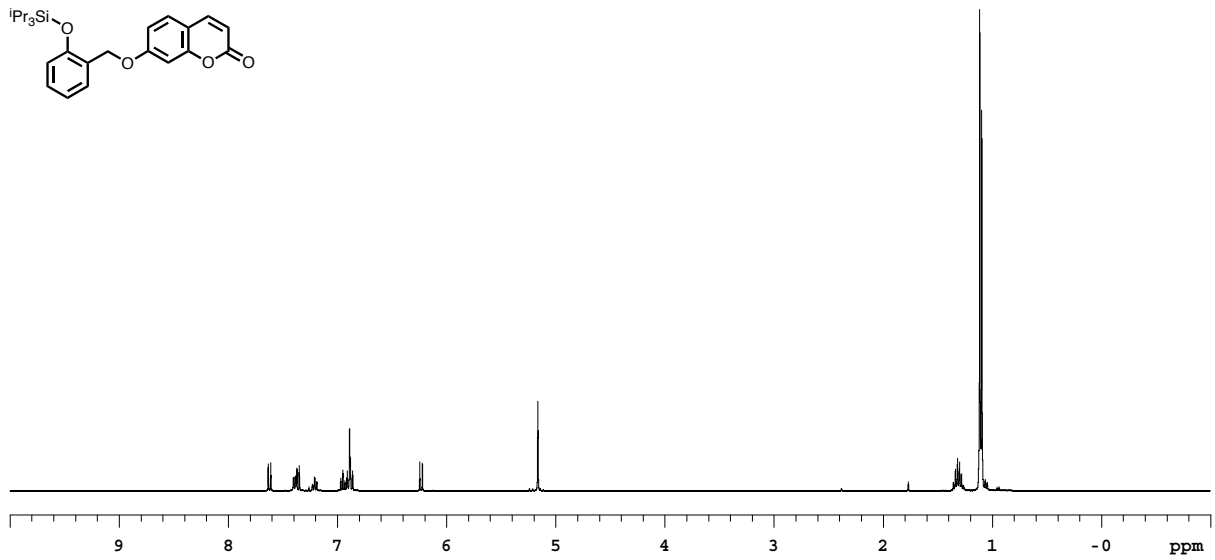


Figure S16. ^{1}H-NMR spectrum of **6** in $CDCl_3$ at $T = 298$ K.

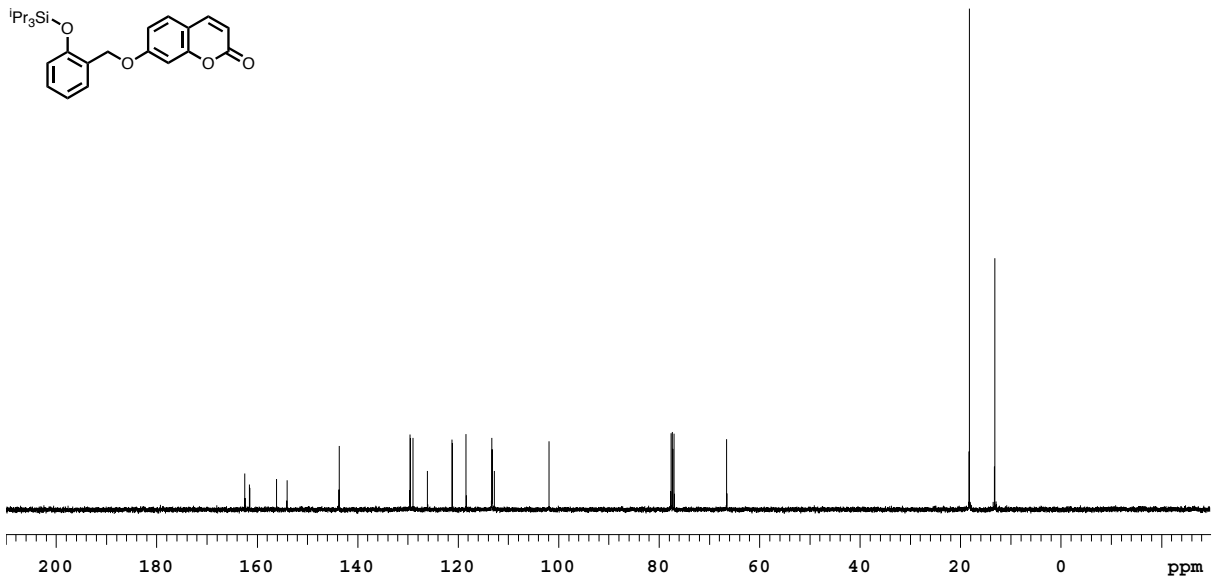


Figure S17. ^{13}C-NMR spectrum of **6** in $CDCl_3$ at $T = 298$ K.

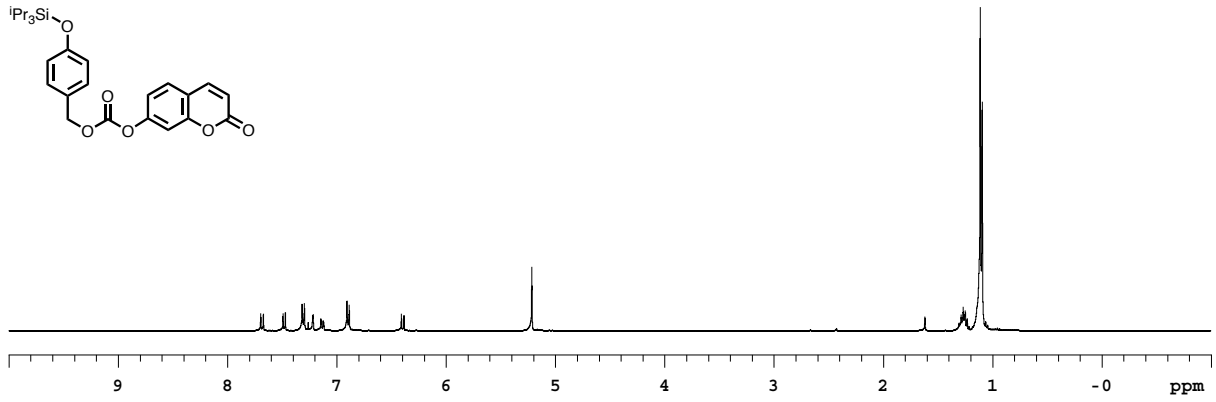


Figure S18. ^{1}H-NMR spectrum of **7** in $CDCl_3$ at $T = 298$ K.

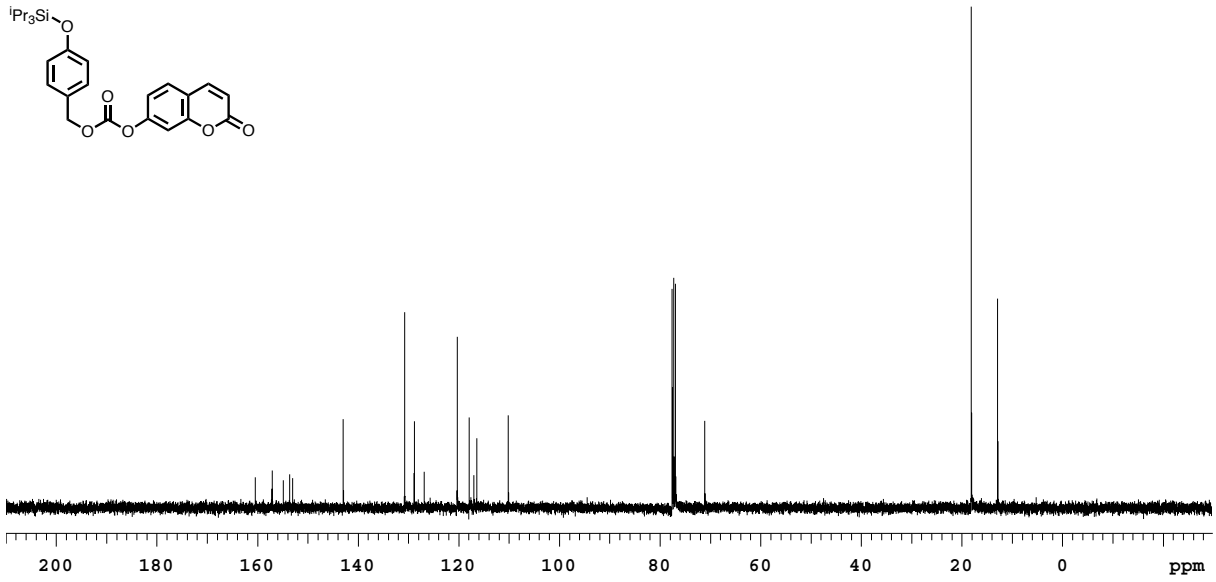


Figure S19. ^{13}C-NMR spectrum of **7** in $CDCl_3$ at $T = 298$ K.

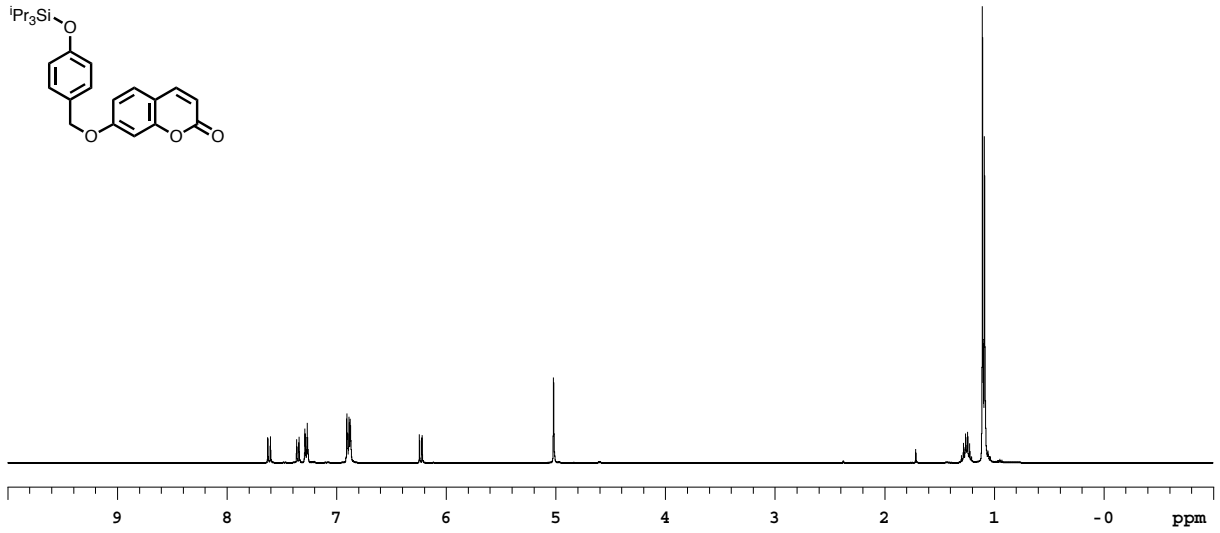


Figure S20. ^{1}H-NMR spectrum of **8** in $CDCl_3$ at $T = 298$ K.

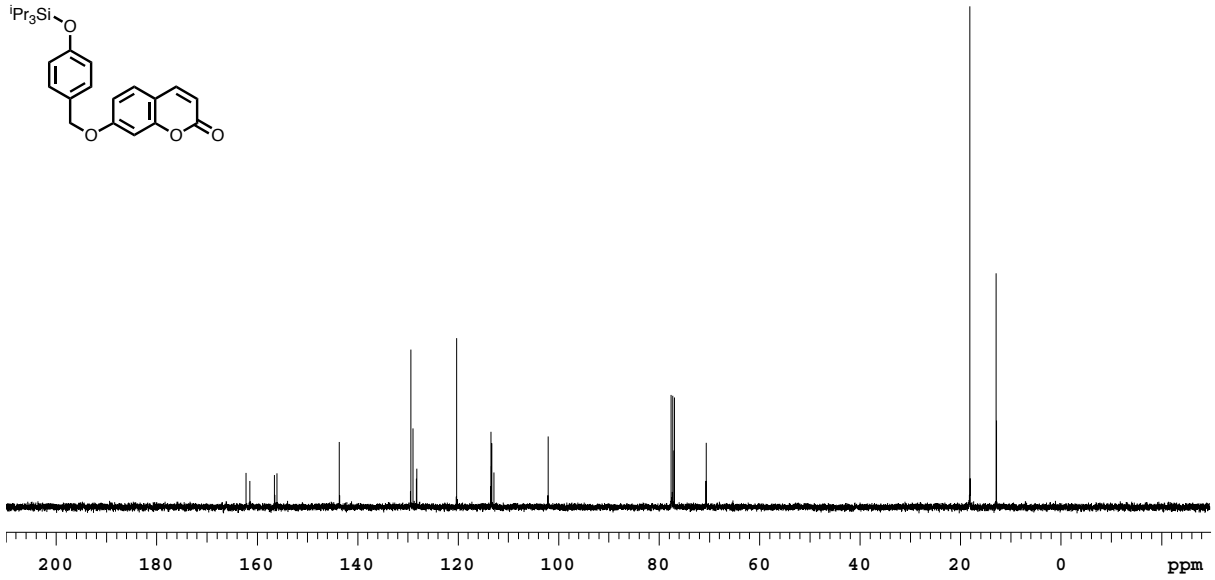


Figure S21. ^{13}C-NMR spectrum of **8** in $CDCl_3$ at $T = 298$ K.