A Fluorescent and Switchable Rotaxane Dual Organocatalyst

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Supporting Information

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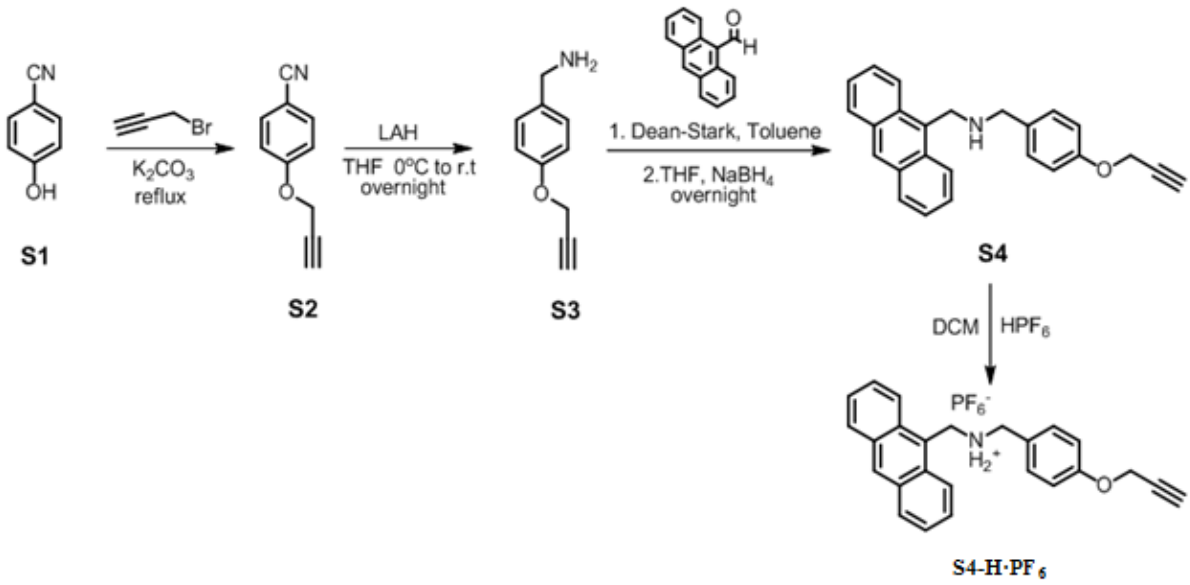
Experimental Section

General Methods

Unless otherwise noted, all the chemicals were purchased from Sigma-Aldrich and solvents were purchased commercially and used without further purification. All the reactions were conducted under anhydrous, high purity N_2 atmosphere protection. Thin-layer chromatography (TLC) was performed on aluminum plate, and the plates were visualized by UV light, staining with phosphomolybdic acid or ninhydrin with heating. Column chromatography purification was performed on silica gel (SiO_2) 60F (Merck 9385, 0.040–0.063 mm). ^{1}H NMR and ^{13}C NMR spectra characterization were recorded at 298K with a spectrometer Bruker Avance-III (^{1}H: 400 MHz and ^{13}C: 101 MHz). Chemical shifts of solvent ($CDCl_3$, CD_3CN) were calibrated reference to the solvent residue peak ($CDCl_3$ = 7.26 ppm, CD_3CN = 1.94 ppm). Coupling constants (*J*) were reported in hertz (Hz), with standard abbreviations indicating the multiplicity of the peaks (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad). Melting points of the compounds were collected by Electrothermal 9100 digital melting point apparatus. High-resolution mass spectrometry was performed with Bruker Autoflex spectrometer (MALDI-TOF-MS), and Thermofinnigan MAT 95 XL spectrometer (ESI-MS). Fluorescence was measured by Perkin Elmer LS55B Luminescence Spectrometer.

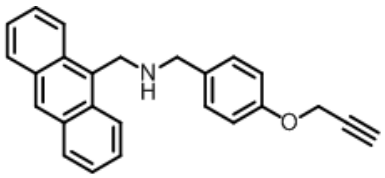
Synthesis Overview

Preparation of S4-H·PF_6



Scheme S1: Synthesis of S4-H·PF_6.

S1 to **S3** were prepared according to the literature reported procedures.[S1]

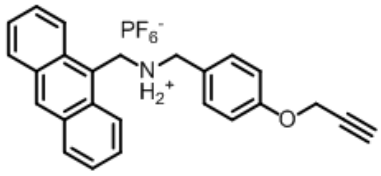


S4

Synthesis of S4

S3 (3.00 g, 18.0 mmol), and 9-anthracenecarboxaldehyde (3.80 g, 18.0 mmol), were dissolved in MeOH and refluxed overnight. Upon cooling to room temperature, yellow solid was filtered and redissolved in MeOH. $NaBH_4$ (2.80 g, 72.0 mmol) was added portionwise at 0 °C, and warm to room temperature. The reaction mixture was stirred overnight. H_2O (30 mL) was added to quench the excess $NaBH_4$ and the solvent was removed under reduced pressure. The suspension was extracted with DCM (3 x 100 mL) and water. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The yellow solid was purified by column chromatography (SiO_2; DCM) yielding a pale yellow solid (4.23 g, 65%). M.p. = 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.27 – 8.18 (m, 2H), 8.01 (dd, J = 8.3, 1.6 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.38 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 4.73 (d, J = 2.4 Hz, 2H), 4.68 (s, 2H), 3.99 (s, 2H), 2.55 (t, J = 2.4 Hz,

1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 133.5, 131.6, 131.6, 130.3, 129.6, 129.1, 127.2, 126.1, 124.9, 124.2, 114.9, 78.7, 75.6, 55.9, 53.7, 44.8. HRMS (MALDI-TOF): $C_{25}H_{21}NO$: *m/z* = 351.1590 $[M]^+$ (calcd. 351.1618).

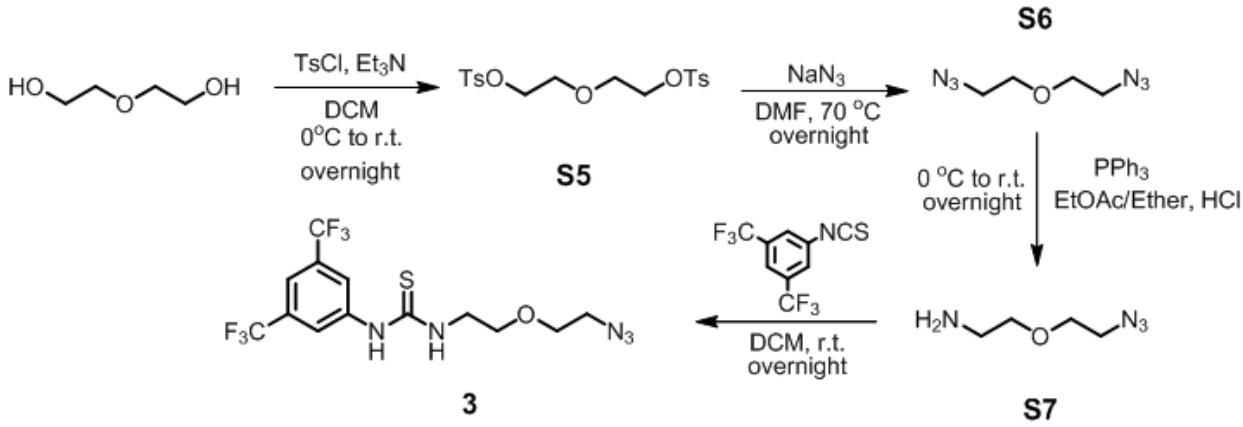


1-H.PF$_6$

Synthesis of S4-H·PF$_6$

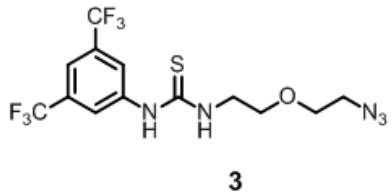
S4 (1.00 g, 2.80 mmol) was dissolved in DCM (10 mL), hexafluorophosphoric acid (1.50 mL) was added and the reaction mixture was stirred for 30 min. Then, H_2O (20 mL) was added, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, yielding a yellow glassy solid (0.80 g, 57%), and was pure enough to use without further purification. ^1H NMR (400 MHz, CD_3CN) δ 8.61 (s, 1H), 8.14 – 8.08 (m, 4H), 7.62 – 7.51 (m, 4H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 4.97 (s, 2H), 4.78 (d, *J* = 2.4 Hz, 2H), 4.24 (s, 2H), 2.84 (t, *J* = 2.4 Hz, 1H).

Preparation of 3



Scheme S2: Synthesis of 3

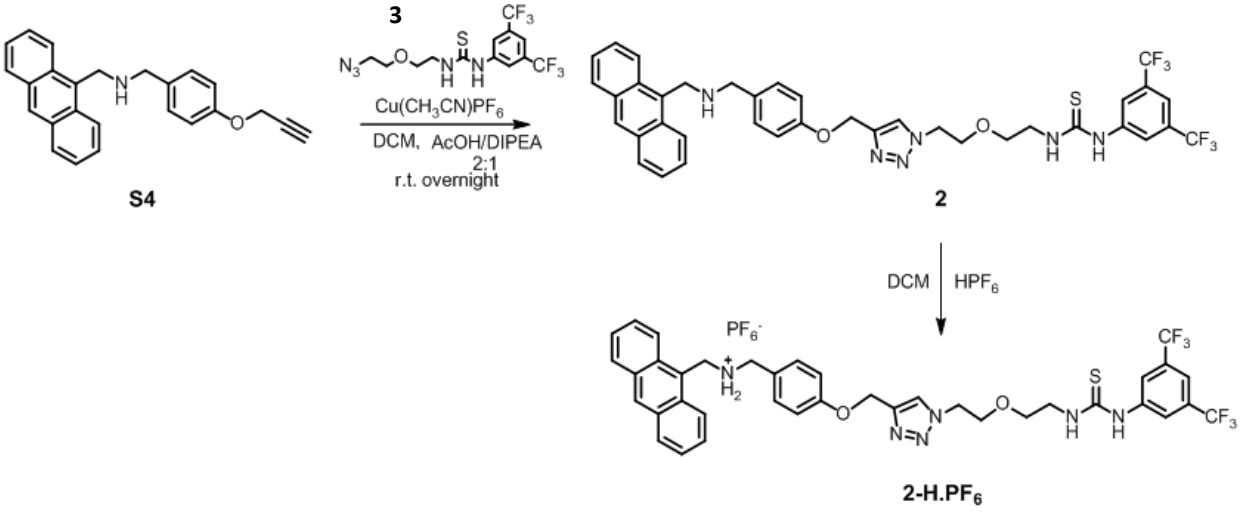
S5 to **S7** were prepared according to the literature reported procedures.[S2]



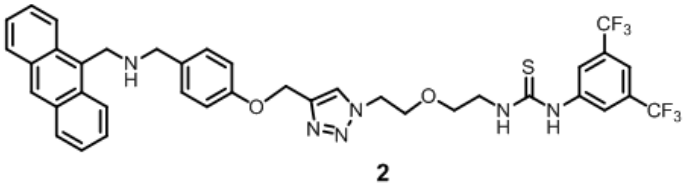
Synthesis of 3

S7 (5.00 g, 38.4 mmol) was dissolved in DCM, and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (7.00 mL, 38.4 mmol) was added dropwise and stirred at ambient temperature overnight. The solvent was removed by reduced pressure, yielding a pale yellow solid (14.2 g, 92 %), and was pure enough without further purification. M.p. = 81 °C. ^{1}H NMR (400 MHz, CD_3CN) δ 8.54 (br, 1H), 8.11 (s, 2H), 7.73 (s, 1H), 7.05 (br, 1H), 3.75 (br, 2H), 3.76 – 3.51 (m, 4H), 3.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 140.8, 130.8 (q, J_{CF} = 32.3 Hz), 124.4, 123.2, 121.7, 69.1, 50.2, 43.9. HRMS (MALDI-TOF): $C_{13}H_{13}F_6N_5OS$: *m/z* = 402.0823 $[M]^+$ (calcd. 402.0818).

Preparation of Thread 2-H·PF_6

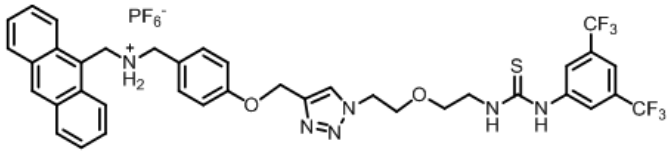


Scheme S3: Synthesis of Thread 2-H·PF_6



Synthesis of Thread 2

S4 (300 mg, 0.85 mmol) and **3** (350 mg, 0.85 mmol) was dissolved in degassed DCM (5 mL), $Cu(CH_3CN)_4PF_6$ (320 mg, 0.85 mmol) and DIPEA (140 μL, 0.85 mmol), were added to the reaction mixture, and stirred overnight at ambient temperature. After that, DCM was added to dilute the reaction mixture, and was washed with NaCN solution. The aqueous layer was extracted with DCM twice. The combined organic layers were dried over anhydrous $MgSO_4$ were concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; EtOAc) yielding a yellow solid (300 mg, 47%). M.p. = 93 °C. ^{1}H NMR (400 MHz, CD_3CN) δ 8.45 (s, 1H), 8.31 – 8.23 (m, 2H), 8.14 (s, 2H), 8.02 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.93 (s, 1H), 7.69 (s, 1H), 7.53 – 7.43 (m, 4H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.13 (s, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.14 (s, 2H), 4.59 (s, 2H), 4.56 – 4.50 (m, 2H), 3.92 (s, 2H), 3.89 – 3.81 (m, 2H), 3.64 (br, 2H), 3.59 (t, J = 4.5 Hz, 2H) (missing of one thiourea proton peak). ^{13}C NMR (101 MHz, CD_3CN) δ 181.1, 157.0, 143.3, 141.0, 133.3, 131.9, 131.2, 130.9, 130.5, 129.9, 129.2, 128.5, 126.5, 125.5, 124.7, 124.4, 124.3, 122.8, 121.7, 114.3, 68.5, 61.1, 52.8, 49.6, 44.3, 43.6 (1 peak is missing/overlapping). HRMS (ESI): $C_{38}H_{34}F_6N_6O_2S$: *m/z* = 753.2440 $[M+H]^+$ (calcd. 753.2368).

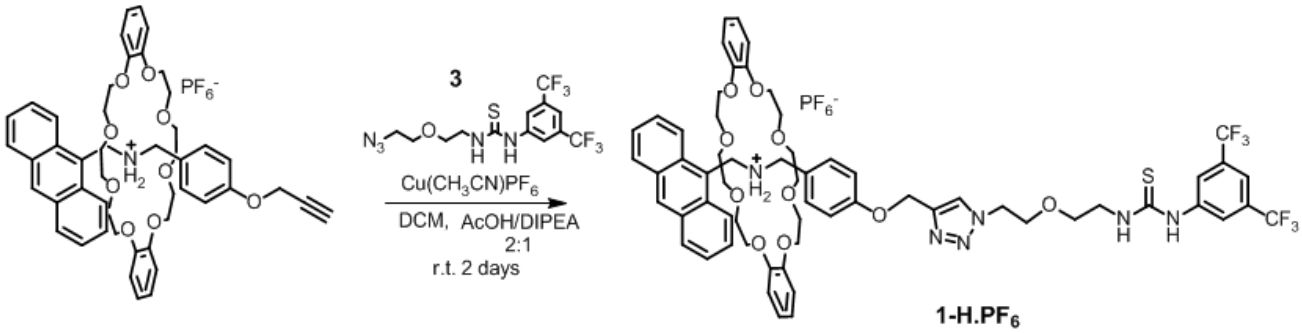


2-H.PF_6

Synthesis of Thread 2-H·PF_6

Thread **2** (100 mg, 0.13 mmol) was dissolved in DCM (8 mL), hexafluorophosphoric acid (1 mL) was added and the reaction mixture was stirred for 30 mins. Then, H_2O (20 mL) was added, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, yielding a yellow glassy solid, and was pure enough without further purification (70 mg, 60 %). ^{1}H NMR (400 MHz, CD_3CN) δ 8.72 (s, 1H), 8.62 (s, 1H), 8.14 (d, J = 7.2 Hz, 4H), 8.08 (d, J = 8.7 Hz, 2H), 7.97 (s, 1H), 7.70 (s, 1H), 7.66 – 7.55 (m, 4H), 7.47 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 5.20 (s, 2H), 5.18 (s, 2H), 4.57 – 4.52 (m, 2H), 4.43 (s, 2H), 3.90 – 3.82 (m, 2H), 3.65 (s, 2H), 3.61 (d, J = 4.3 Hz, 2H). (missing one thiourea proton peak).

Preparation of Rotaxane 1-H·PF_6

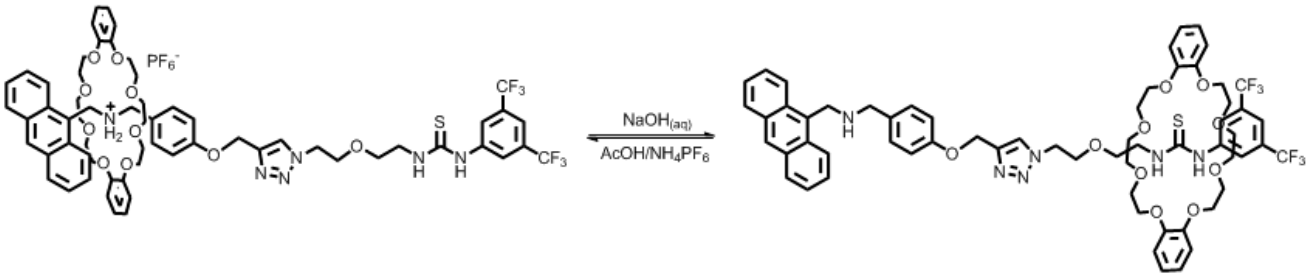


Scheme S4: Synthesis of Rotaxane 1-H·PF_6

Synthesis of Rotaxane 1-H·PF_6

S4-H·PF_6 (500 mg, 1.0 mmol) and DB24C8 (450 mg, 1.0 mmol) were dissolved in degassed DCM (8 mL), and stirred for 1 hour at ambient temperature. **3** (400 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (370 mg, 1.0 mmol), premixed AcOH (70 μL, 1.22 mmol) and DIPEA (106 μL, 0.61 mmol) in DCM (0.5 mL) were added to the reaction mixture, and stirred for 2 days at ambient temperature. After that, DCM (30 mL) was added to dilute the reaction mixture, and was washed with NaCN solution. Then, the reaction mixture was reprotonated by AcOH (2 mL), and final washed with NH_4PF_6 solution (20 mL, 2 M). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; EtOAc, then Acetone, then to Acetone with NH_4PF_6 (0.30 gL^{-1})) yielding a pale yellow glassy solid (800 mg, 59%). M.p. = 122 °C. ^{1}H NMR (400 MHz, CD_3CN) δ 8.62 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 2H), 8.15 (d, *J* = 11.4 Hz, 3H), 7.95 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.59 (ddd, *J* = 8.8, 5.0, 1.1 Hz, 2H), 7.49 – 7.42 (m, 4H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.64 – 6.60 (m, 4H), 6.37 – 6.32 (m, 4H), 5.55 (t, *J* = 6.8 Hz, 2H), 5.21 (t, *J* = 7.2 Hz, 2H), 5.09 (s, 2H), 4.55 (br, 2H), 3.87 (s, 2H), 3.84 – 3.77 (m, 6H), 3.77 – 3.70 (m, 6H), 3.68 – 3.63 (m, 11H), 3.46 – 3.38 (m, 4H) (missing of one thiourea proton peak). ^{13}C NMR (101 MHz, CD_3CN) δ 181.1, 173.1, 157.9, 153.9, 146.3, 142.7, 141.2, 130.4, 130.2, 129.0, 128.5, 126.8, 125.4, 124.7, 124.4, 124.2, 123.6, 122.7, 122.4, 121.2, 120.7, 114.4, 111.5, 70.5, 69.9, 68.4, 67.5, 61.1, 51.9, 49.6, 44.8, 43.7 (a peak is missing/overlapping). HRMS (ESI): $C_{62}H_{67}F_6N_6O_{10}S^+$: m/z = 1201.4571 $[M–PF_6]^+$ (calcd. 1201.4538).

Switching of [2]Rotaxane



Scheme S5: Acid-base switching of Rotaxane 1-H·PF_6 and Rotaxane 1

Deprotonation: **1-H·PF_6** (50 mg, 0.37 mmol) was dissolved in DCM (5 mL), NaOH solution (2 M, 5 mL) was then added to the reaction mixture and was stirred for one hour at ambient temperature. Two layers were separated, and the aqueous layer was extracted with DCM twice. The combined organic layer were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, yielding a pale yellow glassy solid. (40 mg, quantitative).

Reprotonation: **1** (40 mg, 0.33 mmol) was dissolved in DCM (5.00 mL), glacial AcOH (2.00 mL) was added to the reaction mixture and was stirred for one hour at ambient temperature. After that, water and NH_4PF_6 (0.10 g) was added, the reaction mixture was stirred for 30 minutes. Two layers were separated, and the aqueous layer was extracted with DCM twice. The combined organic layer were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, yielding a pale yellow glassy solid. (40 mg, quantitative).

Fluorescence Spectra

The measurement of fluorescence was performed in quartz cells using acetonitrile (MeCN) as solvent. Concentration of the analyte was 1 x 10^{-6} M, and the excitation wavelength was 368 nm.

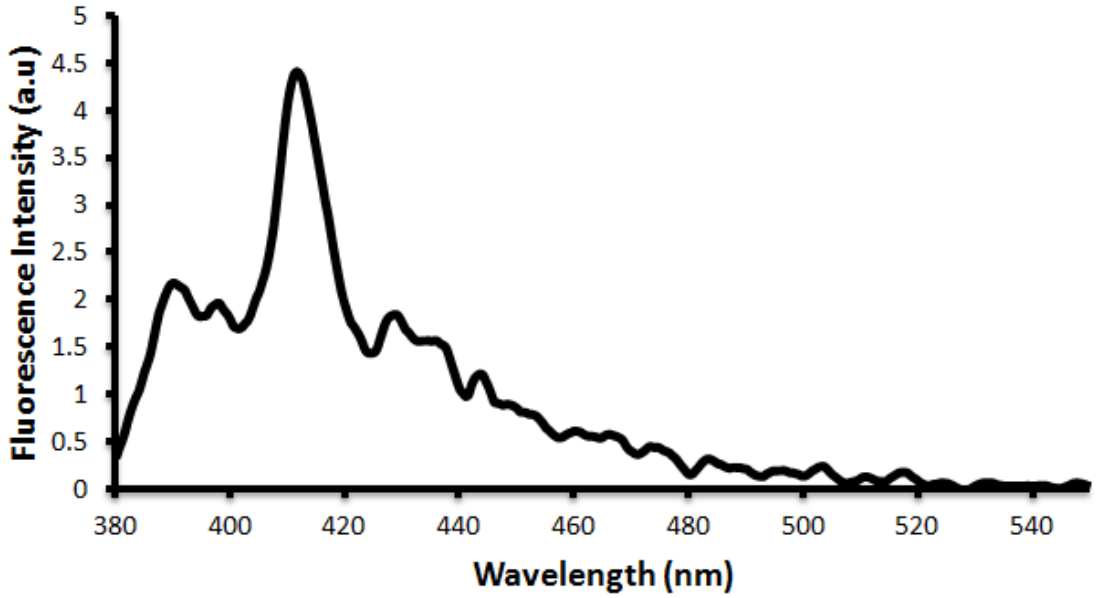


Figure S1 Fluorescence spectrum of rotaxane **1**-H·PF_6 dissolving only in absolute TEA.

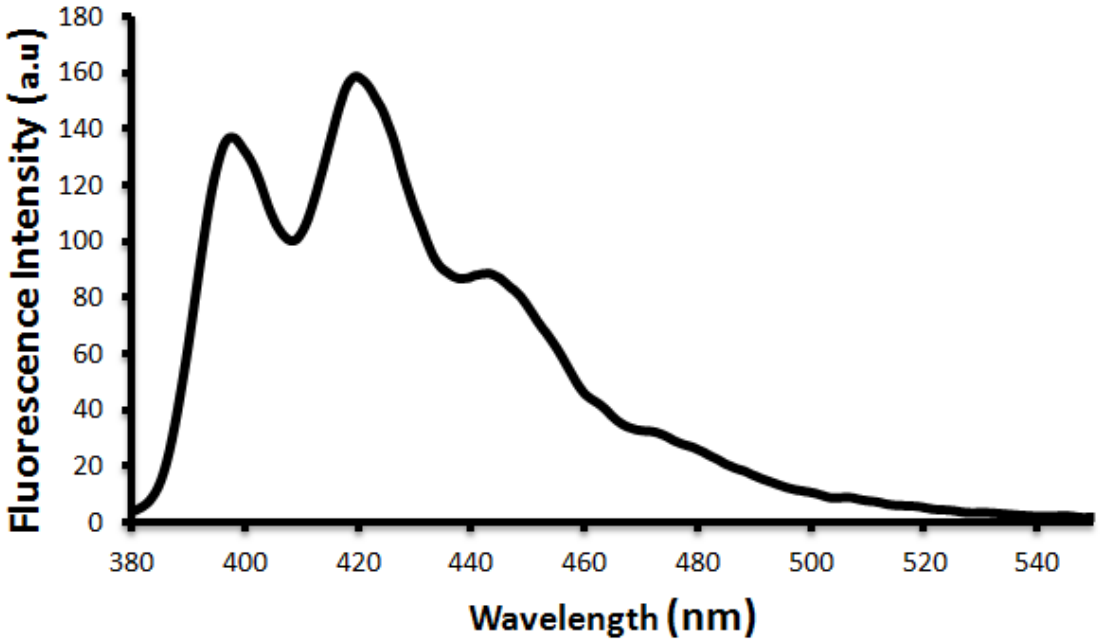


Figure S2 Fluorescence spectrum of rotaxane **1** dissolving only in absolute AcOH.

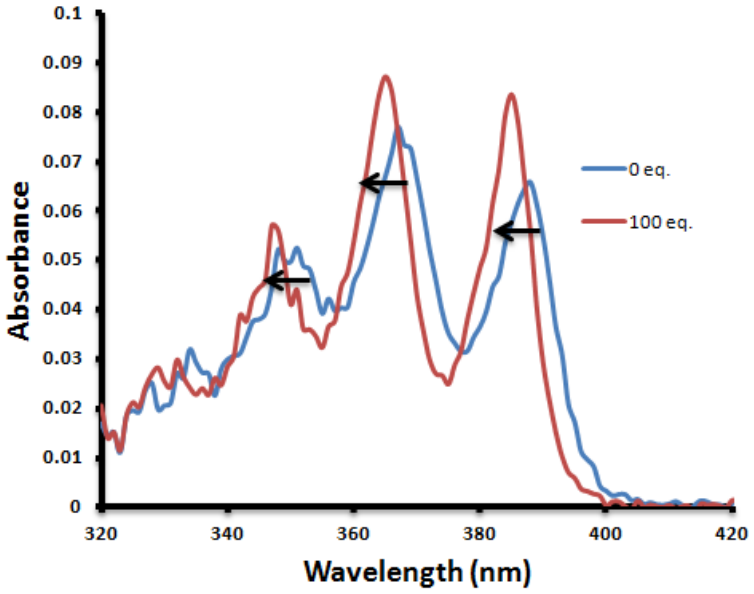


Figure S3 UV/Vis spectrum of rotaxane **1**-H·PF_6 in CH_3CN with addition of 100 eq. of TEA. A blue shift was observed.

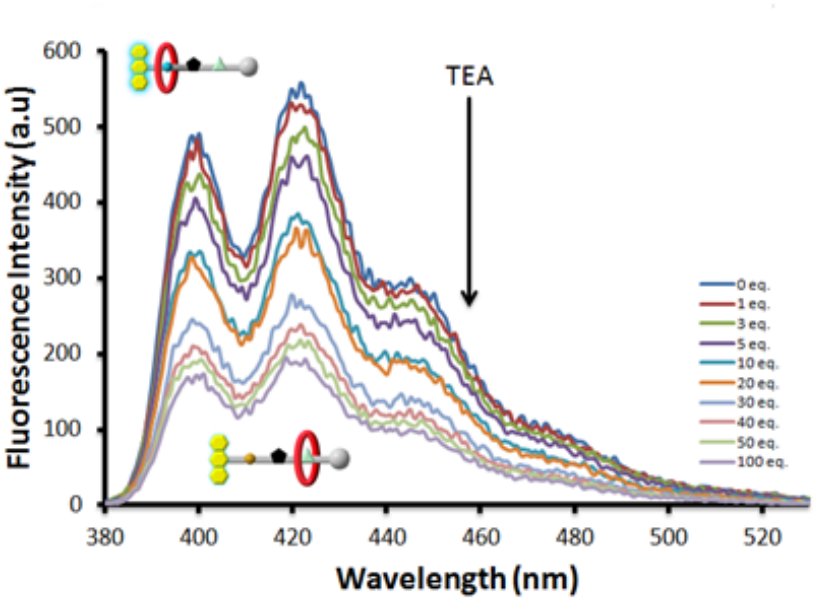


Figure S4 Fluorescence spectrum of rotaxane **1**-H·PF_6 (λ_{exc} = 368 nm, 1 x 10^{-6} M) in CH_3CN with addition of various equivalents TEA (0 to 100 equiv).

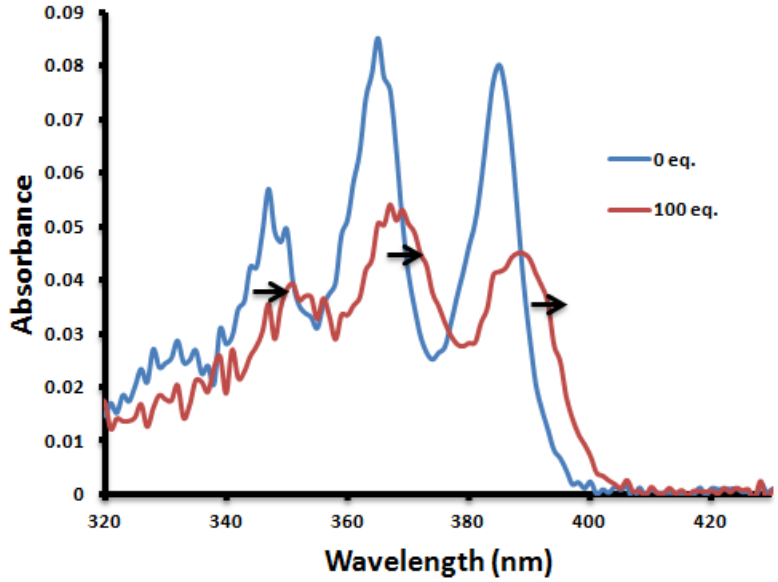


Figure S5 UV/Vis spectrum of rotaxane **1** in CH_3CN with addition of 100 eq. of AcOH. A red shift was observed.

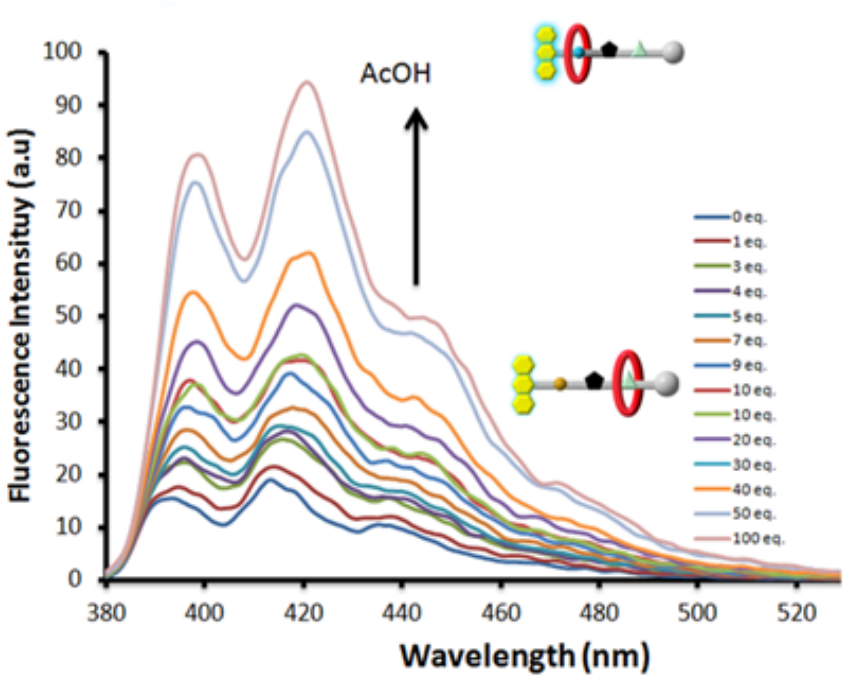


Figure S6 Fluorescence spectrum of rotaxane **1** (λ_{exc} = 368 nm, 1 x 10^{-6} M) in CH_3CN with addition of various equivalents AcOH (0 to 100 equiv).

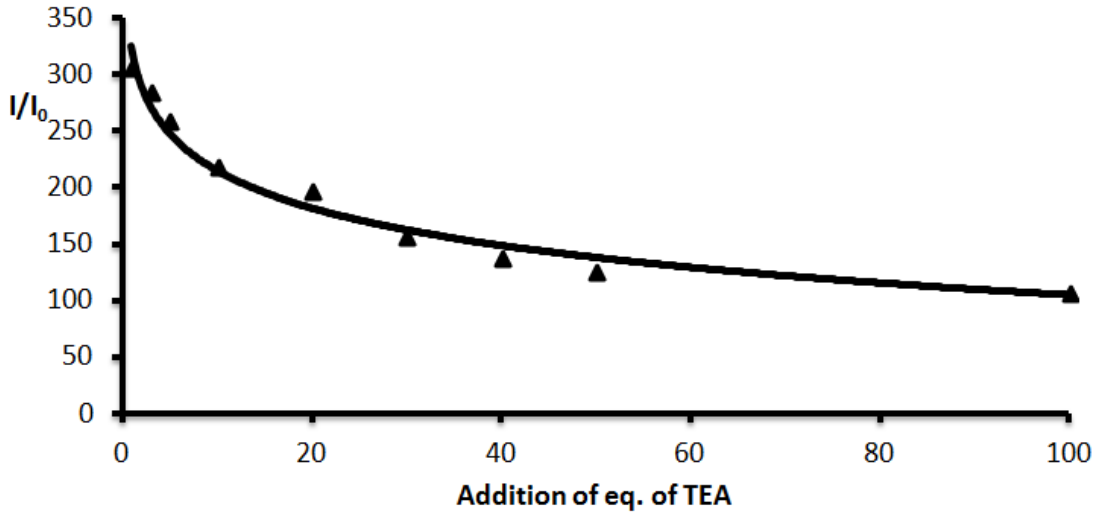


Figure S7 The plot of the relative fluorescence intensity I/I_o at 421 nm after the addition of TEA to **1**-H·PF_6.

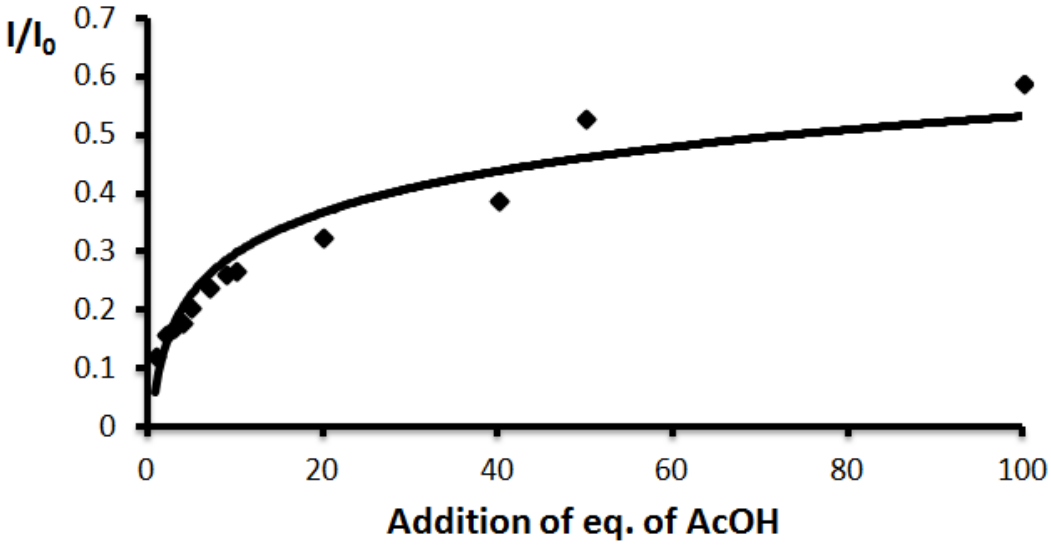


Figure S8 The plot of the relative fluorescence intensity I/I_o at 421 nm after the addition of AcOH to **1**.

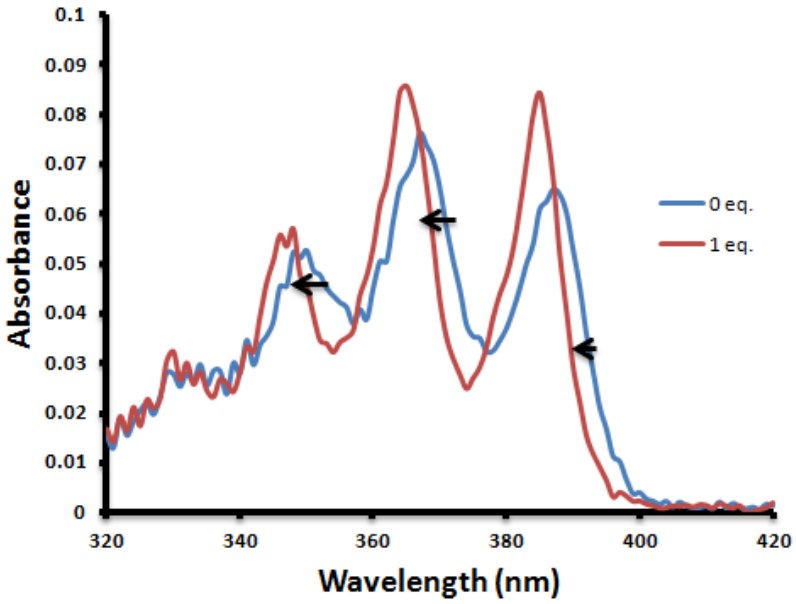


Figure S9 UV/Vis spectrum of thread **2**-H·PF_6 in CH_3CN with addition of 1 eq. of TEA. A blue shift was observed.

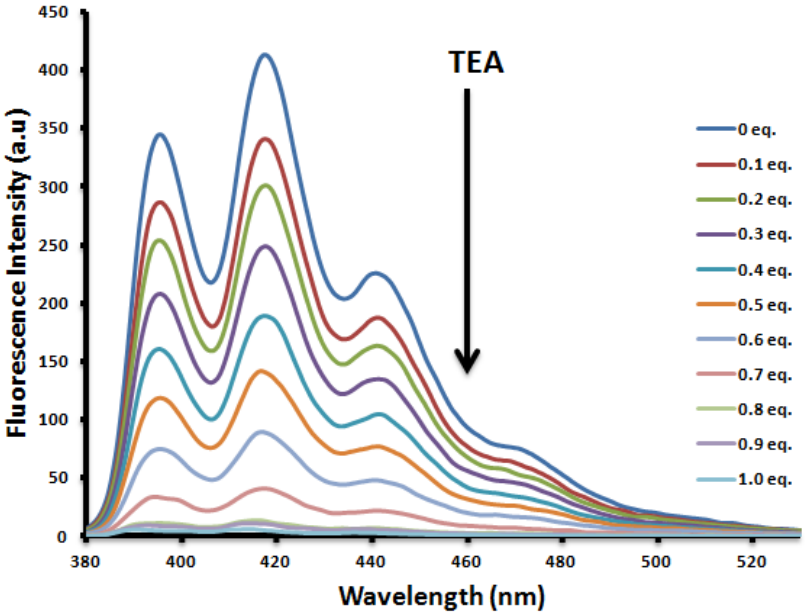


Figure S10 Fluorescence spectrum of thread **2**-H·PF_6 (λ_{exc} = 368 nm, 1 x 10^{-5} M) in CH_3CN with addition of various equivalents TEA (0 to 1 equiv).

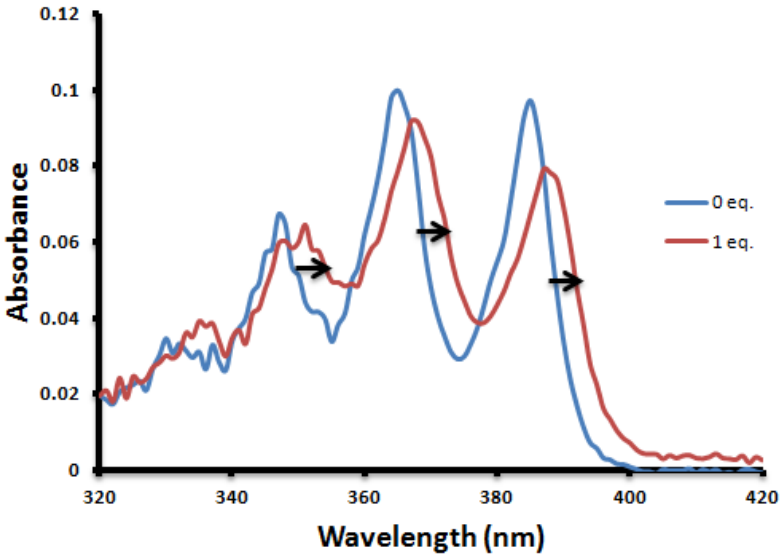


Figure S11 UV/Vis spectrum of thread **2** in CH_3CN with addition of 1 eq. of TFA. A red shift was observed.

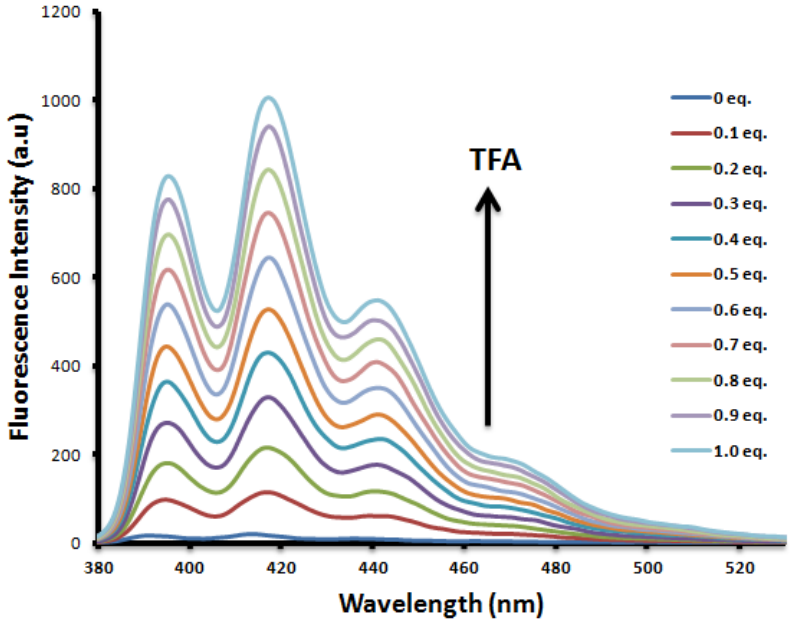


Figure S12 Fluorescence spectrum of thread **2** (λ_{exc} = 368 nm, 1 x 10^{-5} M) in CH_3CN with addition of various equivalents TFA (0 to 1 equiv).

The red-shift of anthracene bands of rotaxane **1** and thread **2** in UV-Vis upon addition of acid, and the blue-shift of rotaxane **1**-H·PF_6 and thread **2**-H·PF_6 upon addition of base were in agreement with the literature report.[S7]

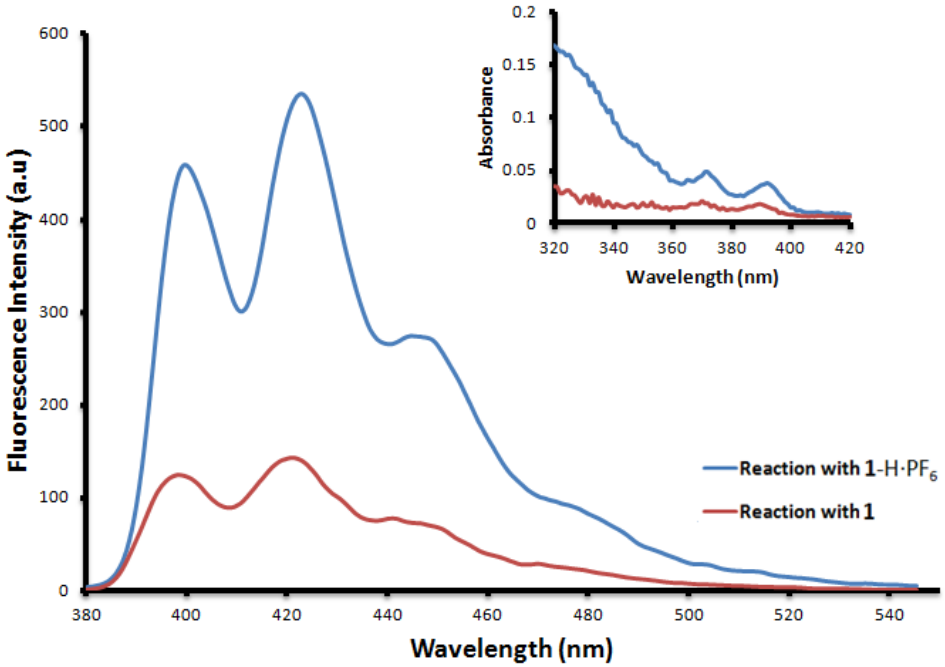
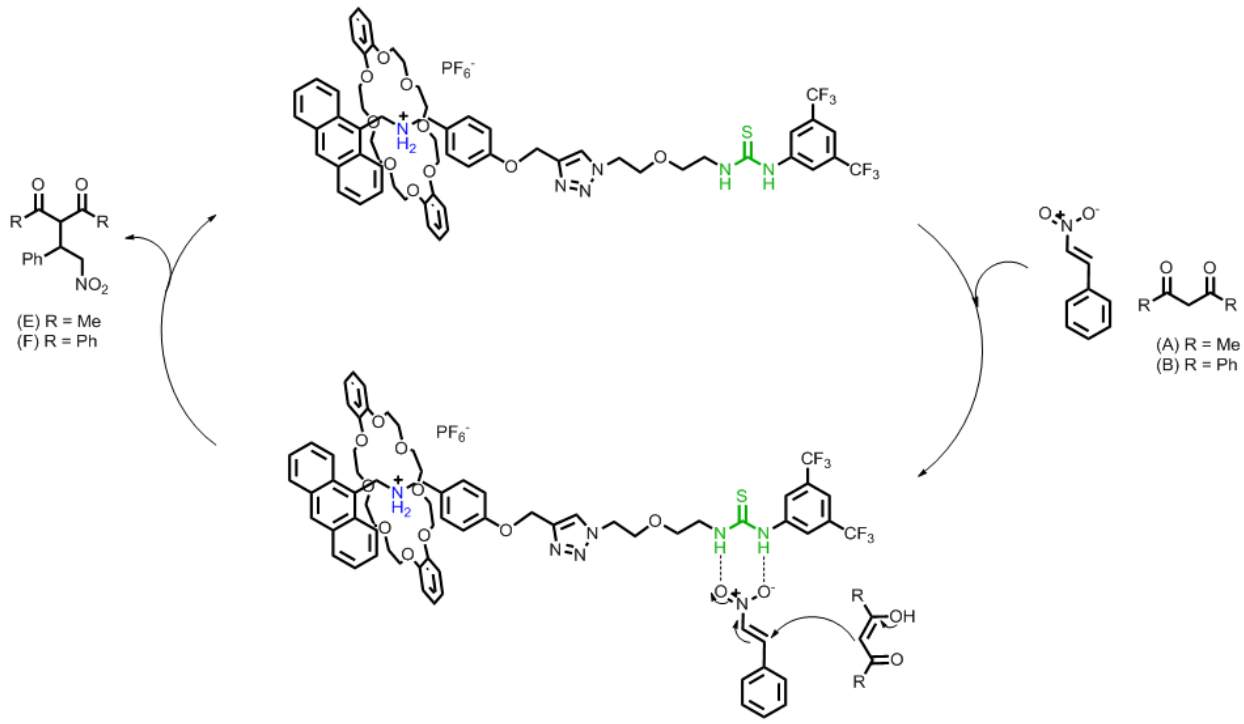


Figure S13 Fluorescence spectrum of **1**-H·PF_6 and **1** in the catalytic reaction entry 5 and 6 (λ_{exc} = 368 nm, 1 x 10^{-5} M) in CH_2Cl_2. Insert: UV/Vis spectrum of **1**-H·PF_6 and **1** in the reaction entry 5 and 6.

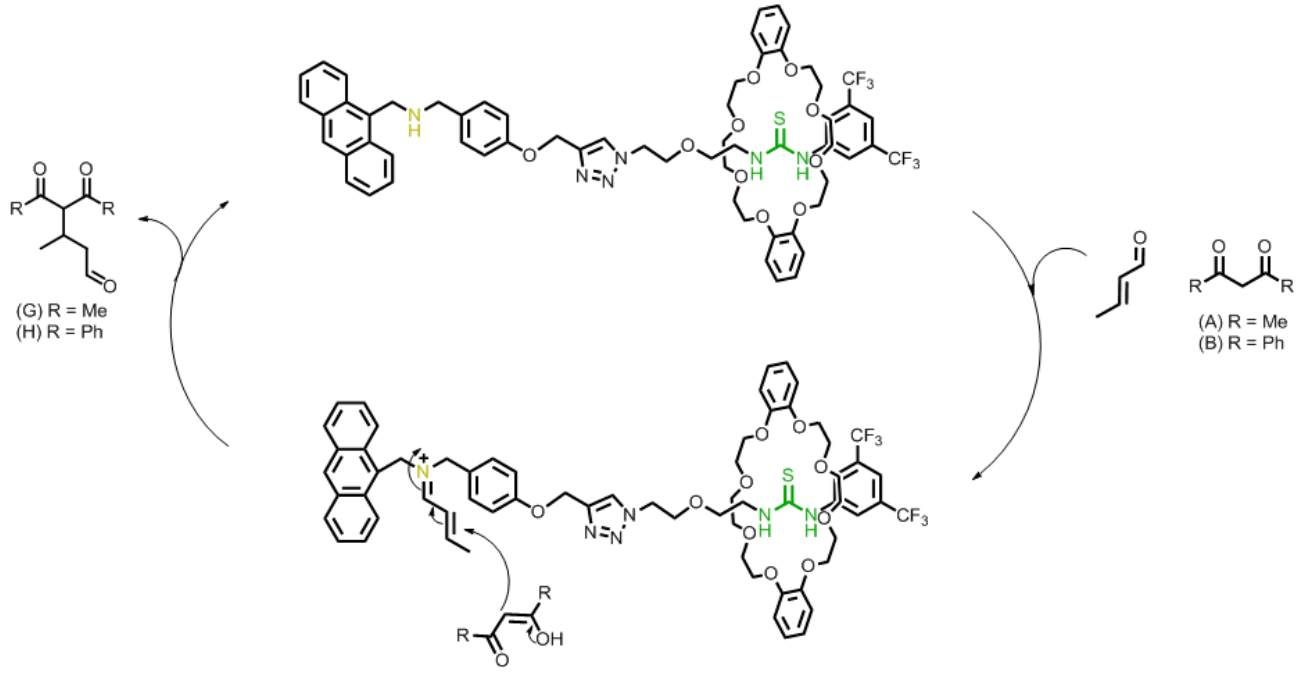
Catalysis Entries

General procedure for catalytic entry

Catalyst (**1**, **1**-H·PF_6 or **2**-H·PF_6 (15 μmol, 0.15 equiv.)), acetylacetone (**A**)/ dibenzoylmethane (**B**) (0.1 mmol, 2 equiv.), *trans*-β-nitrostyrene (**C**) (0.05 mmol, 1 equiv.), *(E)*-crotonaldehyde (**D**) (0.1 mmol, 2 equiv.) and NaOAc (20 μmol, 0.2 equiv.) were dissolved in 125μL of CH_2Cl_2, stirring for 5 days at ambient temperature in an ordinary vial. Sodium acetate is a weak base to activate the 1,3-diketone derivative **A** or **B**. The reaction progress of was monitored and analyzed by ^{1}H NMR spectroscopy, by taking out 1 μL of the reaction mixture, diluting with 600 μL of $CDCl_3$.

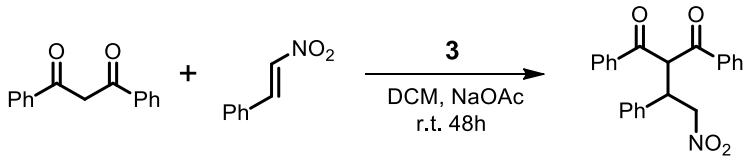


Scheme S1 Reaction mechanism of Michael addition between acetylacetone (**A**)/ dibenzoylmethane (**B**) and *trans*-β-nitrostyrene (**C**).



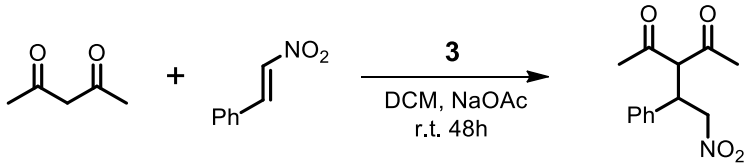
Scheme S2 Reaction mechanism of Michael addition between acetylacetone (**A**)/ dibenzoylmethane (**B**) and crotonaldehyde (**D**).

Synthesis of F



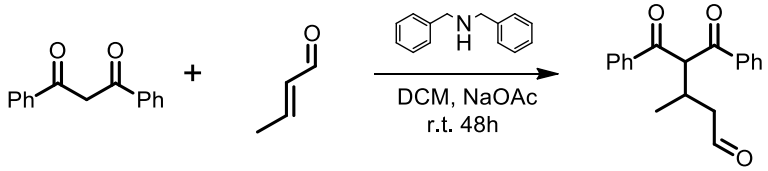
Dibenzoylmethane (**B**) (450 mg, 2.0 mmol) and *trans*-β-nitrostyrene (**C**) (290 mg, 2.0 mmol) were dissolved in 3 mL DCM, **3** (120 mg, 0.30 mmol) and sodium acetate (30 mg, 0.4 mmol) were added. The reaction mixture was stirred at room temperature for 48 hours. After that, the solvent was concentrated under reduced pressure, giving a yellow residue. Diethyl ether was added to the residue, yielding a white precipitate. The precipitate was filtered and washed with diethyl ether twice, yielding **F** (520 mg, 70%) as a white solid. The ^{1}H NMR was in agreement with previously literature reported data.[S5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.3, 1.3 Hz, 2H), 7.78 (dd, J = 8.3, 1.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.25 – 7.15 (m, 5H), 5.84 (d, J = 8.0 Hz, 1H), 5.00 (d, J = 6.8 Hz, 2H), 4.62 (q, J = 7.1 Hz, 1H).

Synthesis of E



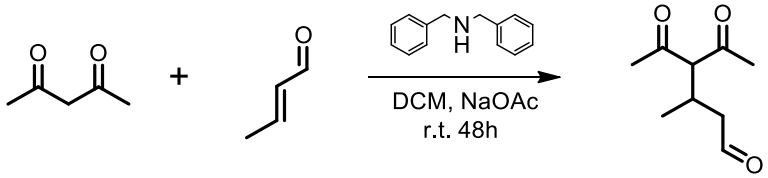
Acetylacetone (**A**) (200 µL, 2.0 mmol) and *trans*-β-nitrostyrene (**C**) (290 mg, 2.0 mmol) were dissolved in 3 mL DCM, **3** (120 mg, 0.30 mmol) and sodium acetate (30 mg, 0.4 mmol) were added. The reaction mixture was stirred at room temperature for 48 hours. After that, the solvent was concentrated under reduced pressure, giving a yellow residue. Diethyl ether was added to the residue, yielding a pale-yellow precipitate. The precipitate was filtered and washed with diethyl ether twice, yielding **F** (370 mg, 75%) as a pale-yellow solid. The ^{1}H NMR was in agreement with previously literature reported data.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 3H), 7.22 – 7.14 (m, 2H), 4.70 – 4.56 (m, 2H), 4.37 (d, J = 10.8 Hz, 1H), 4.24 (ddd, J = 10.7, 7.7, 4.9 Hz, 1H), 2.30 (s, 3H), 1.94 (s, 3H).

Synthesis of H



Dibenzoylmethane (**B**) (450 mg, 2.0 mmol) and crotonaldehyde (**D**) (330 µL, 4.0 mmol) were dissolved in 3 mL DCM, dibenzylamine (77 µL, 0.40 mmol) and sodium acetate (30 mg, 0.40 mmol) were added. The reaction mixture was stirred at room temperature for 48 hours. After that, the reaction mixture was extracted with water, the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; Hex/EtOAc 5:1) affording **H** (460 mg, 78%) as a pale yellow oil. The ^1H NMR was in agreement with previously literature reported data.[S6] ^1H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.98 (m, 4H), 7.54 (m, 2H), 7.43 (m, 4H), 5.52 (d, J = 7.5 Hz, 1H), 3.19 (m, 1H), 2.77 (dd, J = 17.9, 4.7 Hz, 1H), 2.55 (ddd, J = 18.0, 7.7, 1.8 Hz, 1H) 1.09 (d, J = 6.9 Hz, 3H).

Synthesis of G



Acetylacetone (**A**) (200 µL, 2.0 mmol) and crotonaldehyde (**D**) (330 µL, 4.0 mmol) were dissolved in 3 mL DCM, dibenzylamine (77 µL, 0.40 mmol) and sodium acetate (30 mg, 0.40 mmol) were added. The reaction mixture was stirred at room temperature for 48 hours. After that, the reaction mixture was extracted with water, the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; Hex/EtOAc 7:1) affording **G** (230 mg, 68%) as a pale yellow oil. The ^1H NMR was in agreement with previously literature reported data.[S4] ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 3.66 (d, J = 9.2 Hz, 1H), 2.86 (m, 1H), 2.39 (m, 1H), 2.26 (m, 1H), 2.17 (s, 6H), 0.94 (d, J = 5.1 Hz, 3H).

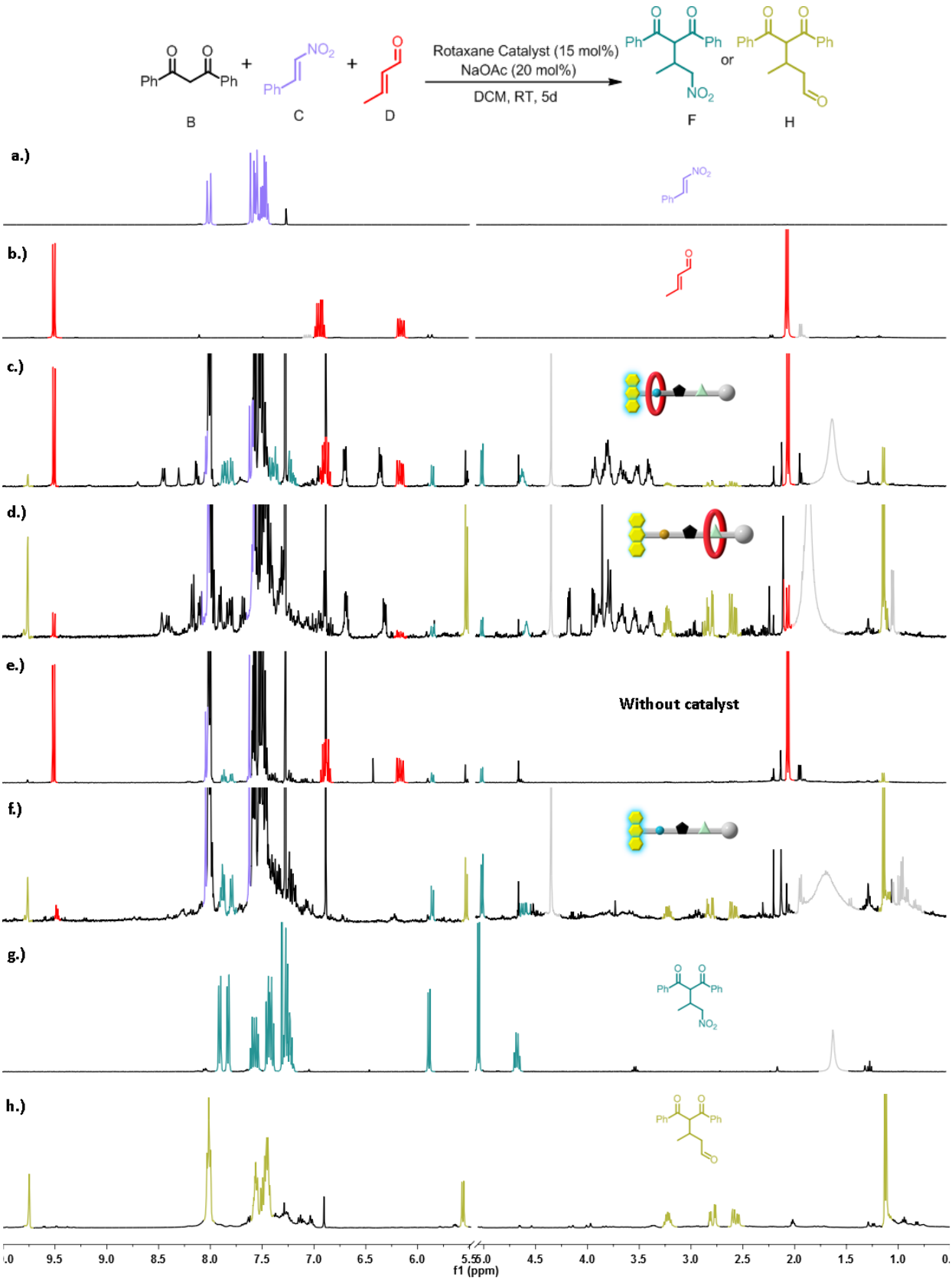


Figure S14 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) *trans*-β-nitrostyrene (**C**); b) crotonaldehyde (**D**); c) reaction mixture of dibenzoylmethane (**B**) (2 equiv), **C** (1 equiv), **D** (2 equiv), **1**-H·PF_6 (15 mol%), and

NaOAc (20 mol%), after stirring for 5 days; d) reaction mixture of dibenzoylmethane (**B**) (2 equiv), **C** (1 equiv), **D** (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 5 days.; e) reaction mixture of dibenzoylmethane (**B**) (2 equiv), **C** (1 equiv), **D** (2 equiv) and NaOAc (20 mol%) without catalyst, after stirring for 5 days.; f) reaction mixture of dibenzoylmethane (**B**) (1 equiv), **C** (1 equiv), **D** (1 equiv), **2**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days; g) Product **F**; h) Product **H**. The color-coding of the peaks represents the starting materials as well as the products.

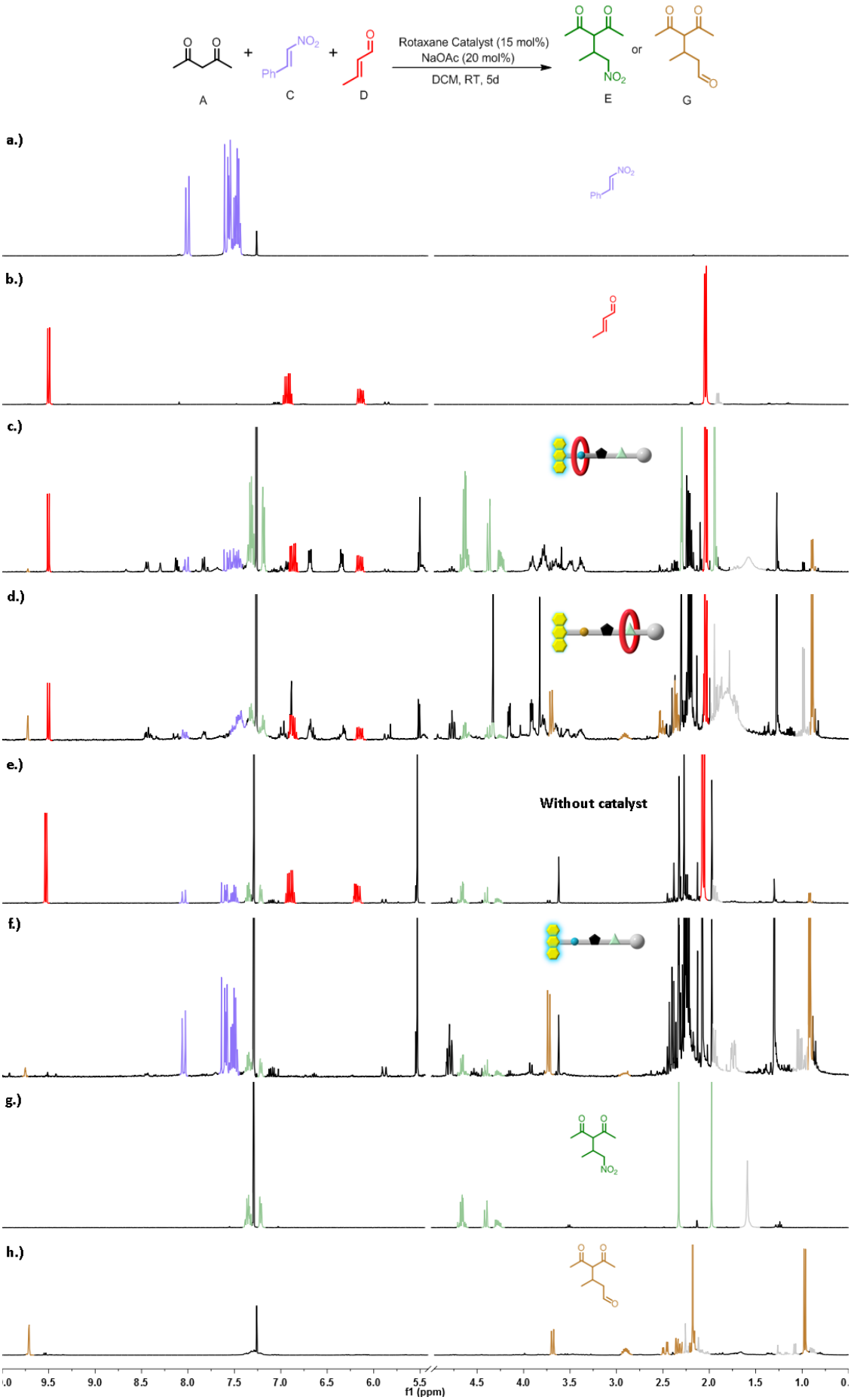

Rotaxane Catalyst (15 mol%)
NaOAc (20 mol%)
DCM, RT, 5d
or
A
C
D
E
G
a.)
b.)
c.)
d.)
e.)
Without catalyst
f.)
g.)
h.)
f1 (ppm)

Figure S15 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) *trans*-β-nitrostyrene (**C**); b) crotonaldehyde (**D**); c) reaction mixture of acetylacetone (**A**) (2 equiv), **C** (1 equiv), **D** (1 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days; d) reaction mixture of acetylacetone (**A**) (2 equiv), **C** (1 equiv), **D** (1 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 5 days.; e) reaction mixture of acetylacetone (**A**) (2 equiv), **C** (1 equiv), **D** (1 equiv) and NaOAc (20 mol%) without catalyst, after stirring for 5 days.; f) reaction mixture of acetylacetone (**A**) (1 equiv), **C** (1 equiv), **D** (1 equiv), **2**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days; g) Product **E**; h) Product **G**. The color-coding of the peaks represents the starting materials as well as the products.

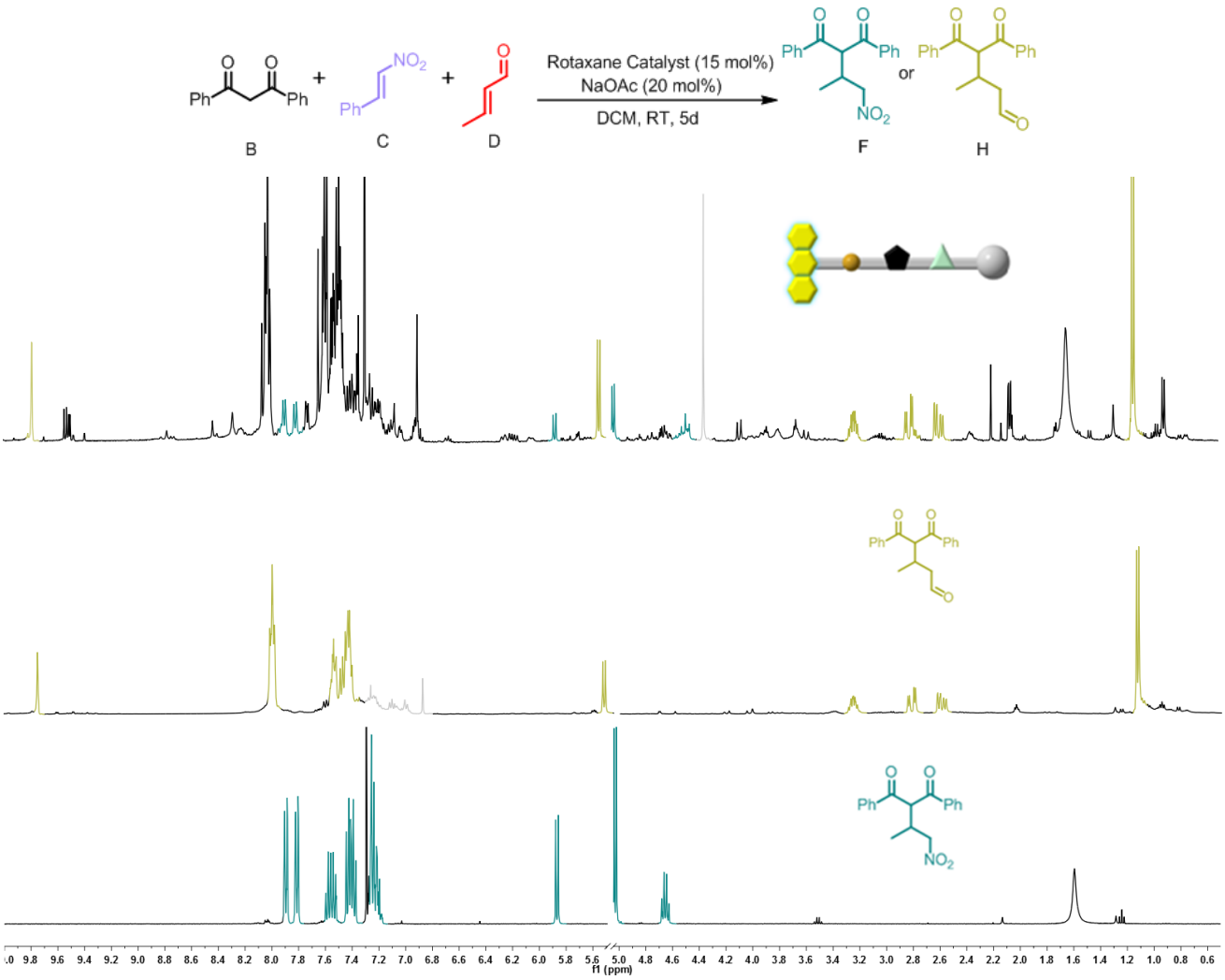


Figure S16 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of reaction mixture of dibenzoylmethane (**B**) (1 equiv), **C** (1 equiv), **D** (1 equiv), **2** (15 mol%), and NaOAc (20 mol%), after stirring for 5 days.

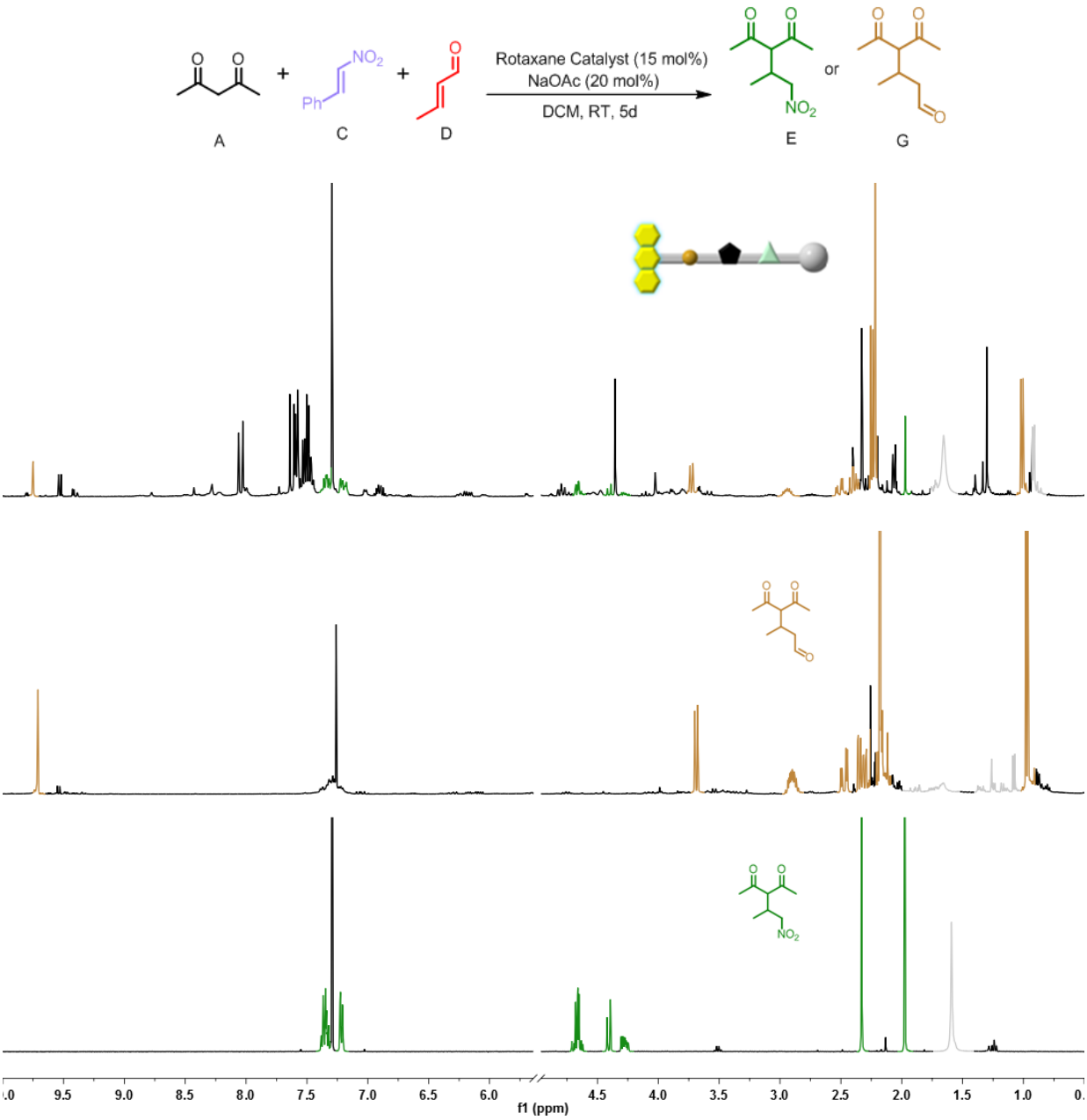


Figure S17 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of reaction mixture of acetylacetone (**A**) (1 equiv), **C** (1 equiv), **D** (1 equiv), **2** (15 mol%), and NaOAc (20 mol%), after stirring for 5 days.

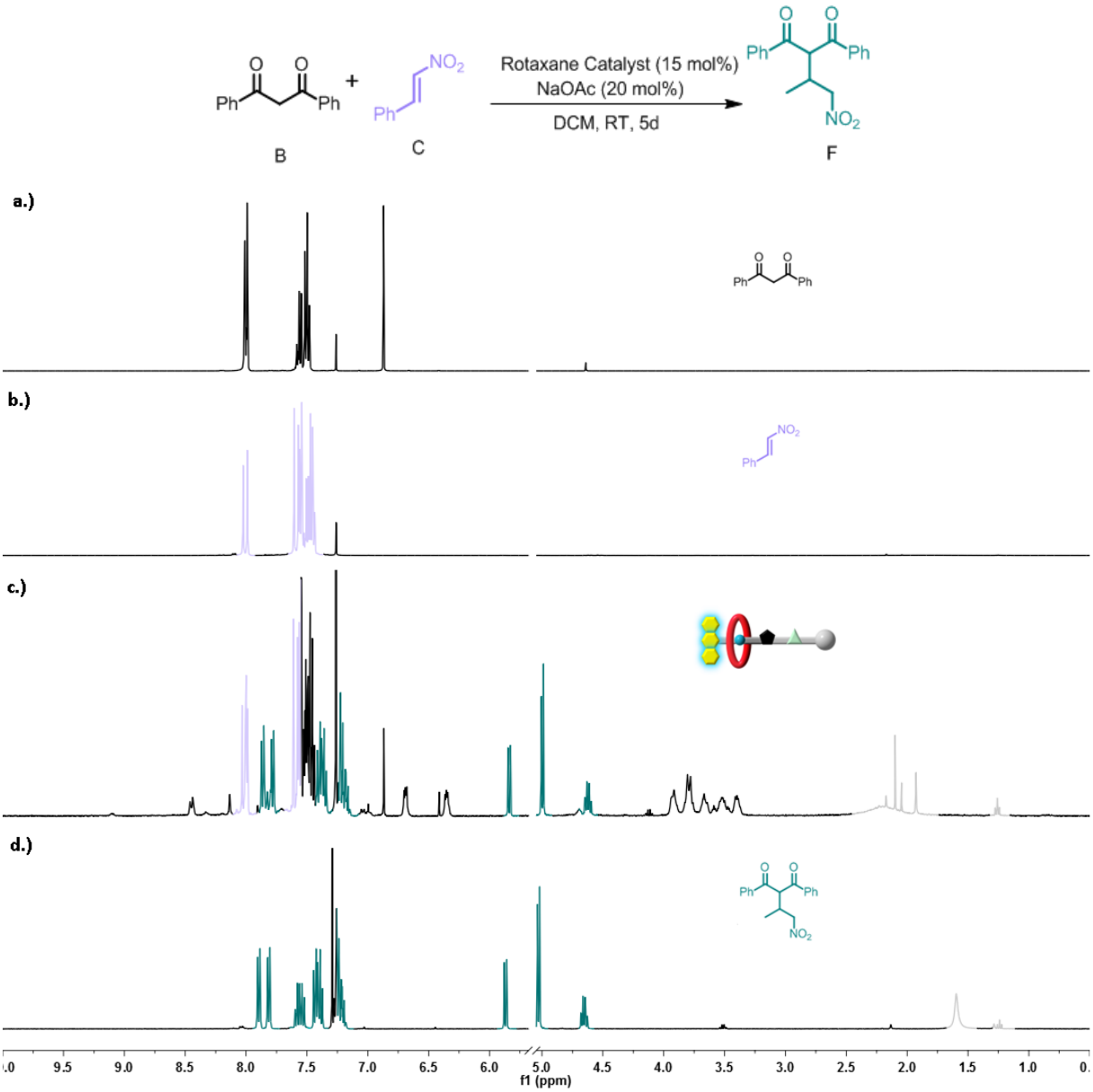


Figure S18 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) dibenzoylmethane (**B**); b) *trans*-β-nitrostyrene (**C**); c) reaction mixture of **B** (1 equiv), **C** (2 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days; d) Product **F**. The color-coding of the peaks represents the starting materials as well as the products.

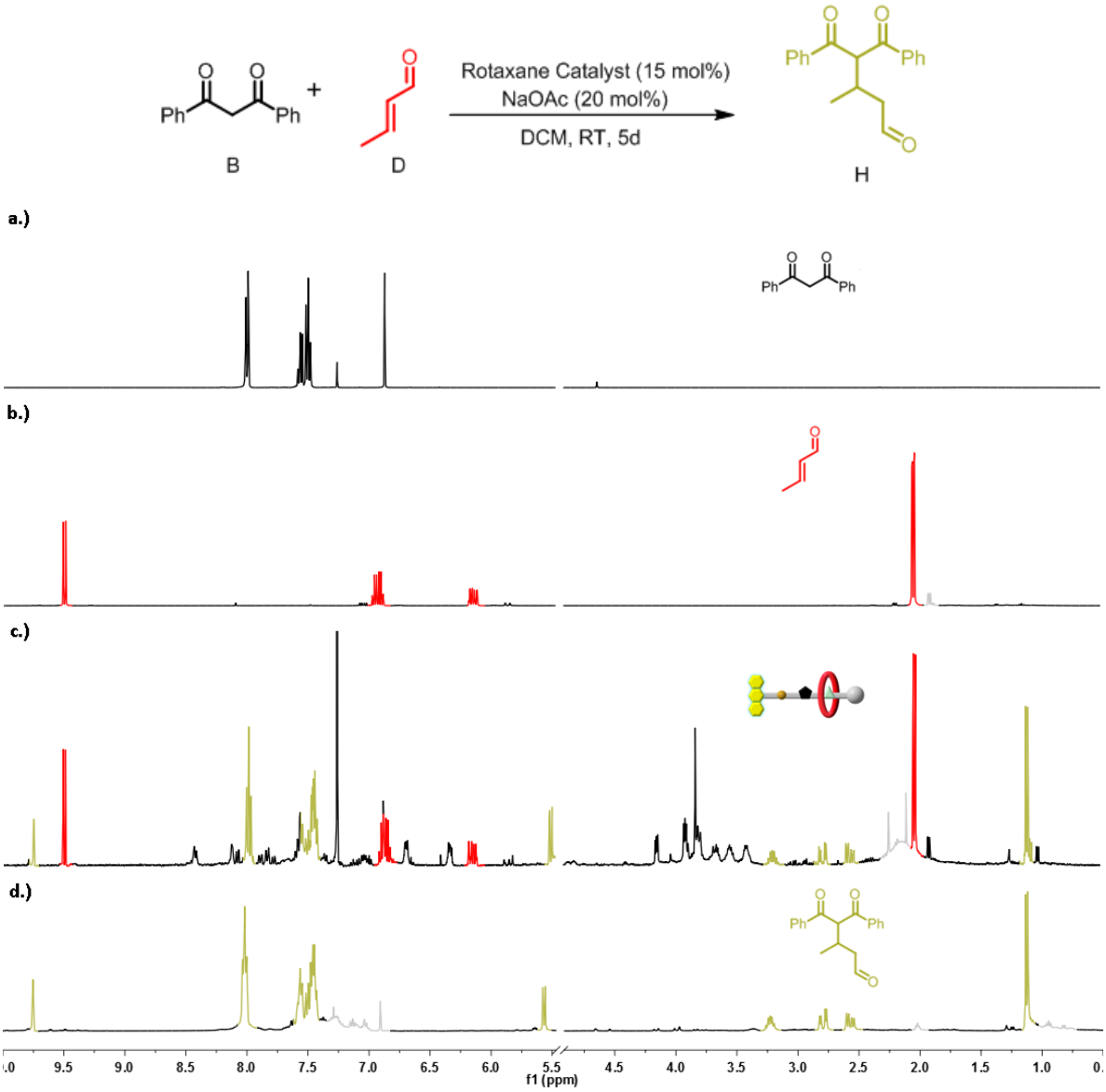


Figure S19 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) dibenzoylmethane (**B**); b) crotonaldehyde (**D**); c) reaction mixture of **B** (1 equiv), **D** (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 3 days; d) Product **H**. The color-coding of the peaks represents the starting materials as well as the products.

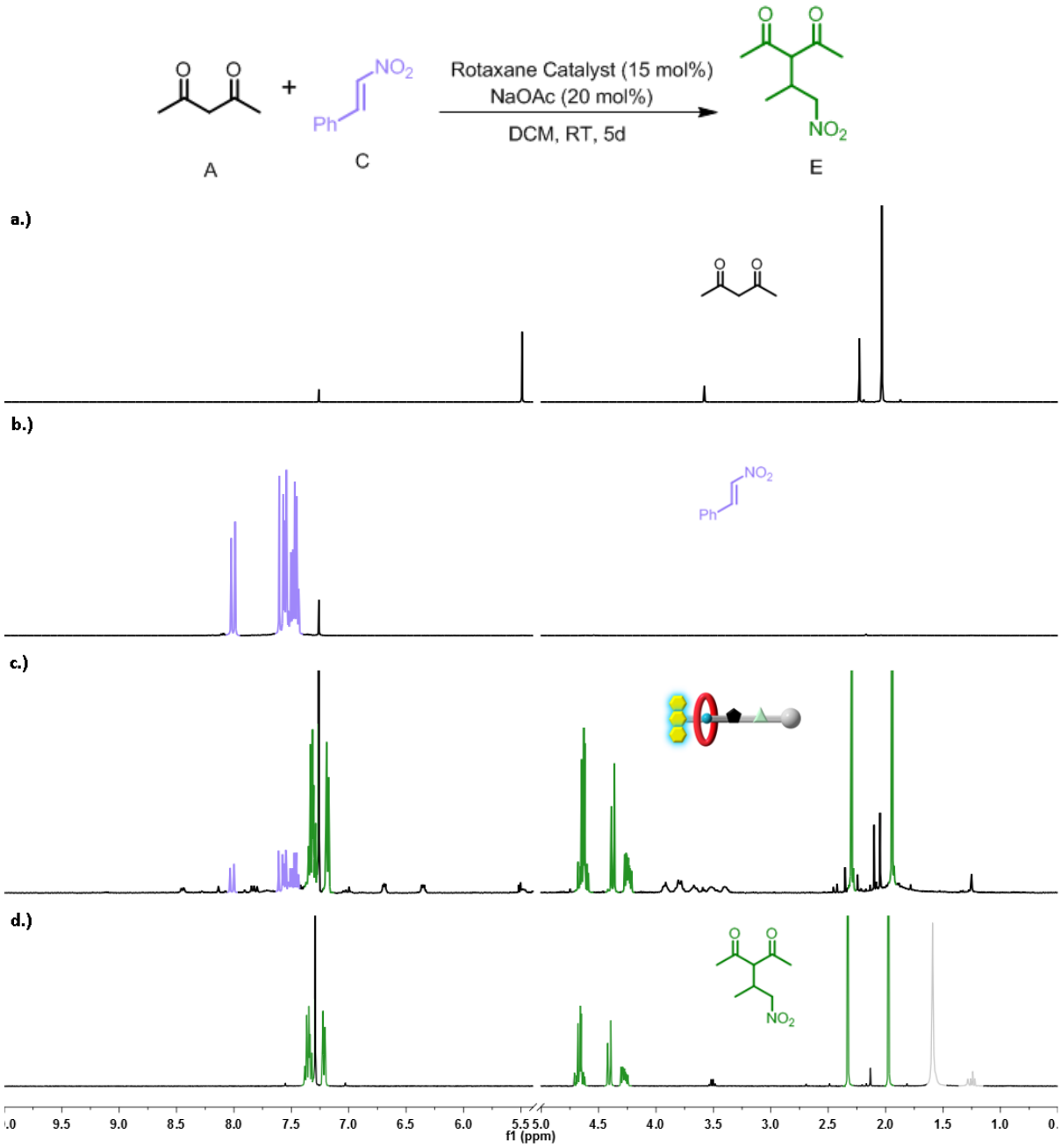


Figure S20 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) acetylacetone (**A**); b) *trans*-β-nitrostyrene (**C**); c) reaction mixture of **A** (1 equiv), **C** (2 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 3 days; d) Product **E**. The color-coding of the peaks represents the starting materials as well as the products.

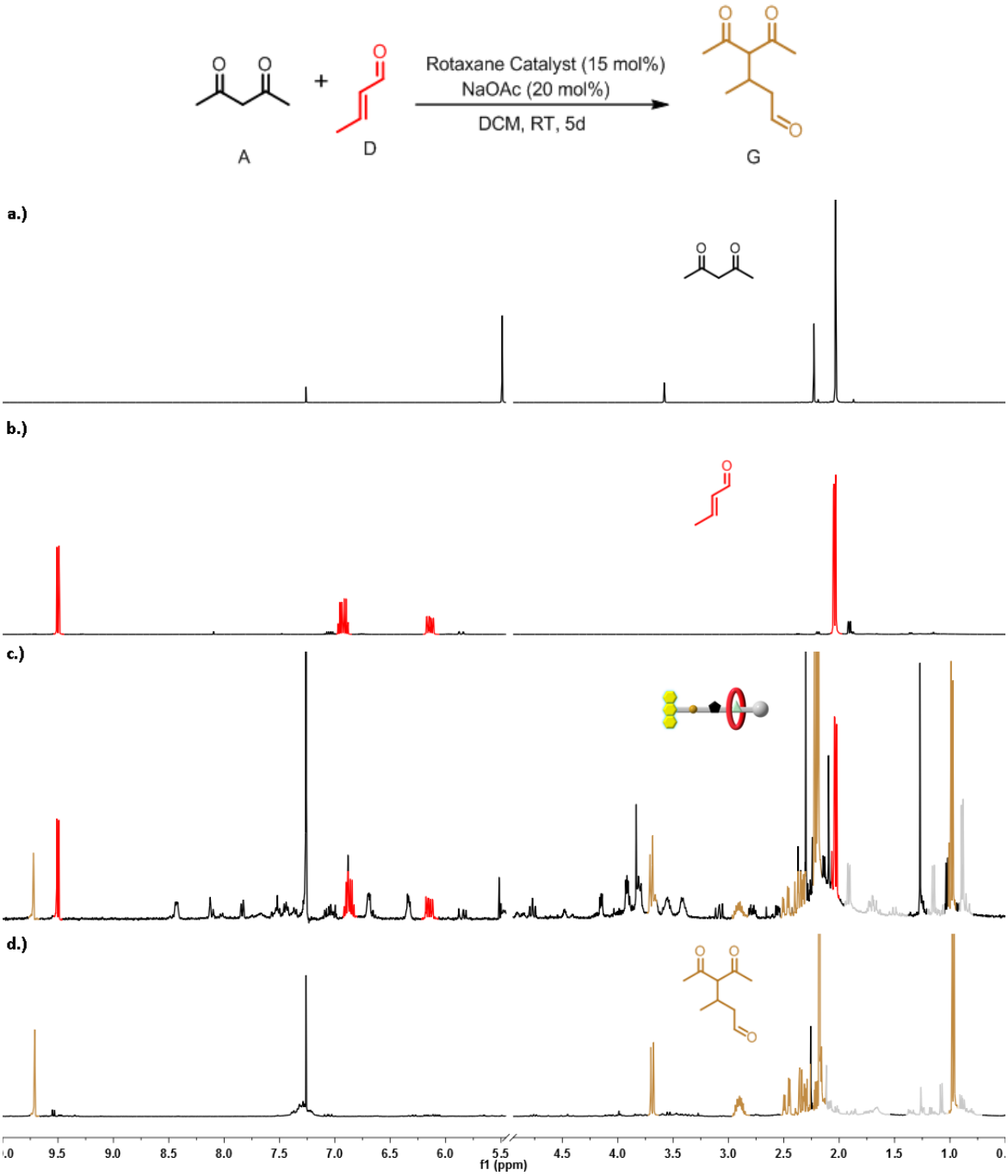


Figure S21 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) acetylacetone (**B**); b) crotonaldehyde (**D**); c) reaction mixture of **B** (1 equiv), **D** (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 3 days; d) Product **G**. The color-coding of the peaks represents the starting materials as well as the products.

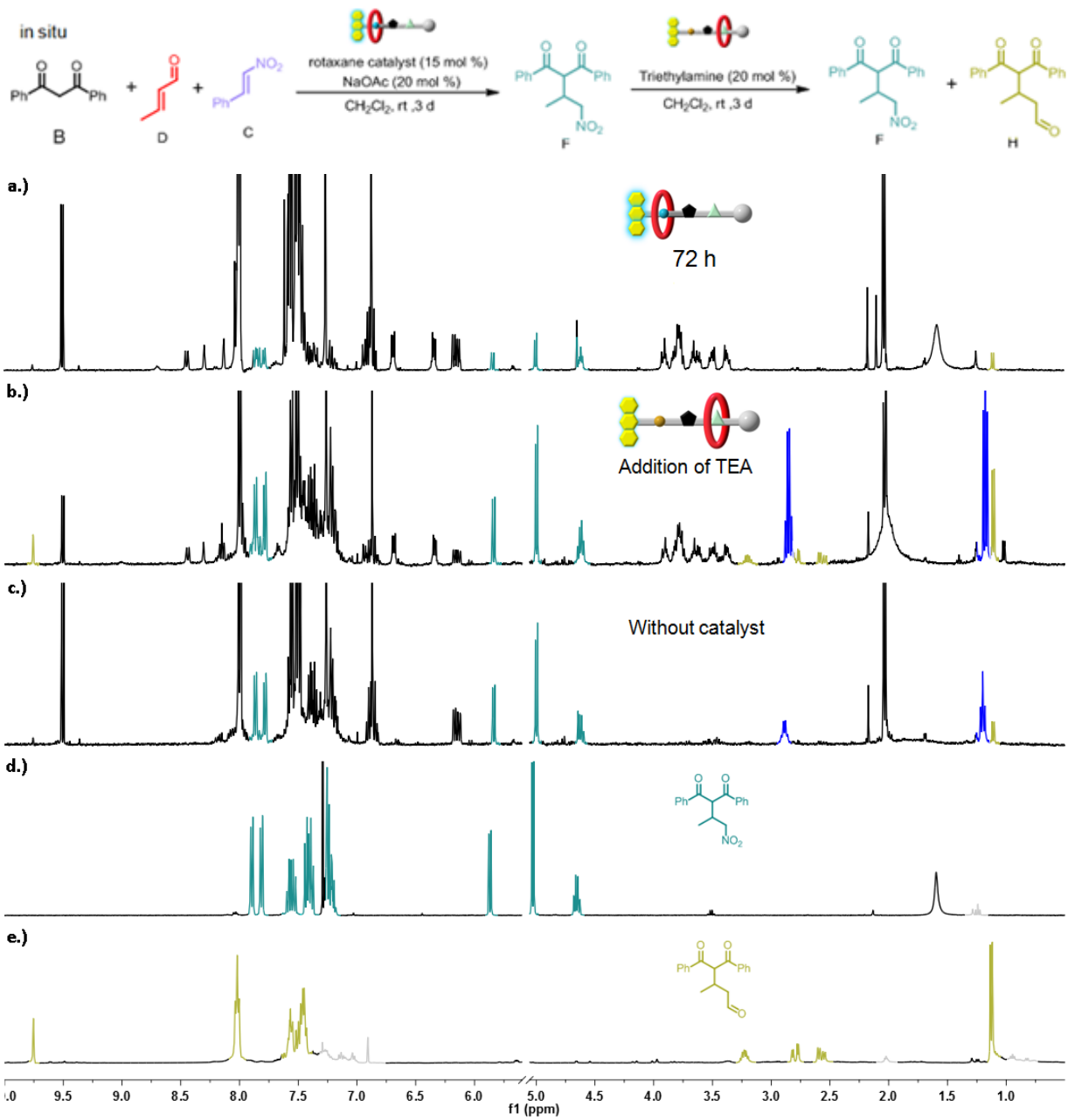


Figure S22 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of in situ experiment of entry 8: a) reaction mixture of **B** (2 equiv), **C** (1 equiv), **D** (1 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 3 days; b) addition of TEA (20 mol%) to the reaction mixture of a) stirring for 4 days more.; c) reaction mixture of **B** (2 equiv), **C** (1 equiv), **D** (1 equiv), and NaOAc (20 mol%) without catalyst after stirring for 3 days, showing no reaction, and addition of TEA (20 mol%) stirring for 4 days more.; d) Product **F**.; e) Product **H**. The color-coding of the peaks represents the starting materials as well as the products. Blue color represents the peaks of TEA. However, at the same time, TEA catalyzes the reaction between **B** and **C** readily, indicating in this system that, TEA not only acts as a base for switching, but also as a co-catalyst for the reaction between **B** and **C**.

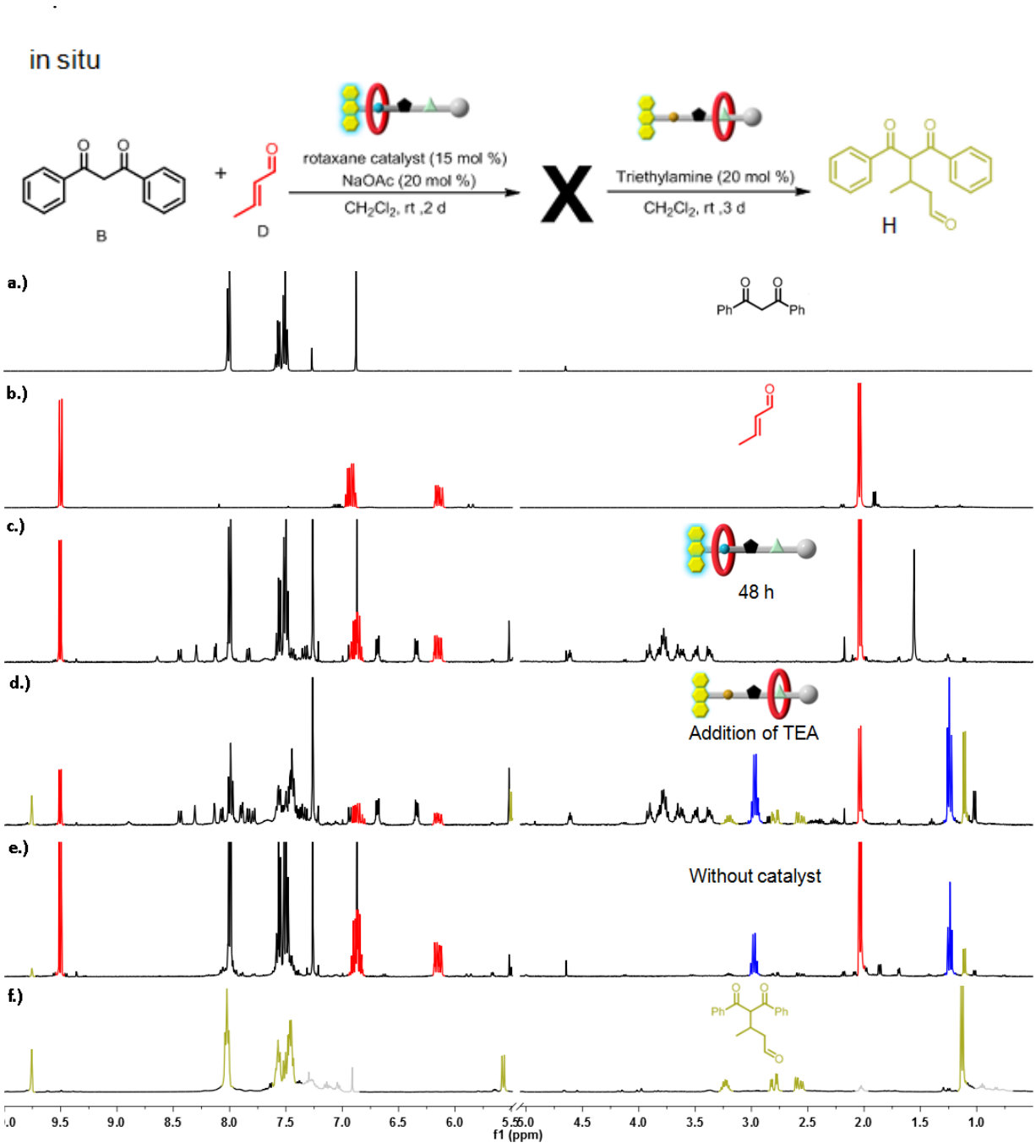


Figure S23 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of in situ switch on of entry 10: a) dibenzoylmethane (**B**); b) crotonaldehyde (**D**); c) reaction mixture of **B** (1 equiv), **D** (2 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 2 days; d) addition of TEA (20 mol%) to the reaction mixture of c) stirring for 3 days more.; e) reaction mixture of **B** (1 equiv), **D** (2 equiv), and NaOAc (20 mol%) without catalyst, after stirring for 2 days, addition of TEA (20 mol%) stirring for 3 days more; f) Product **H**. The color-coding of the peaks represents the starting materials as well as the products. Blue color represents the peaks of TEA.

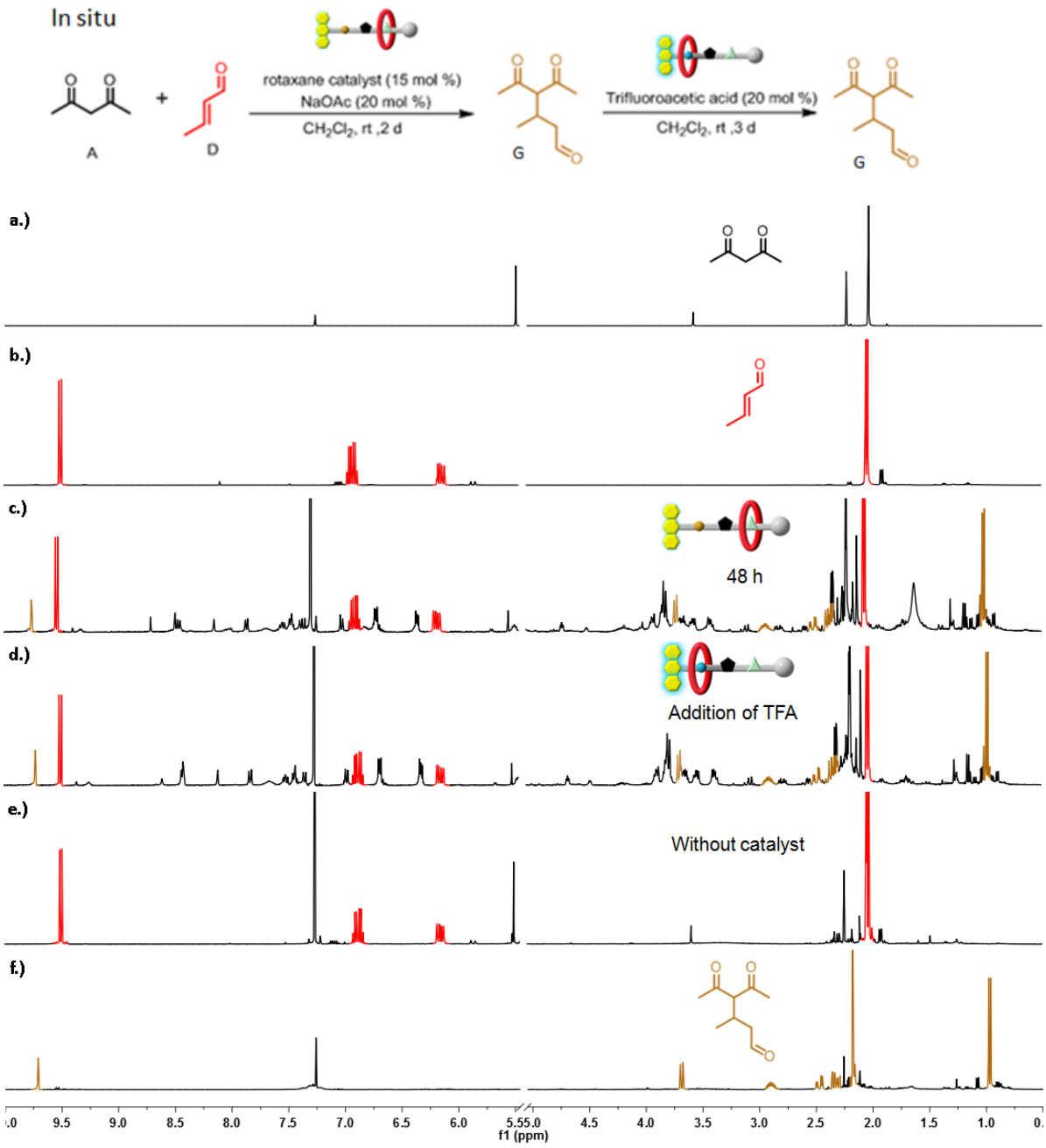


Figure S24 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of in situ switch off of entry 12: a) acetylacetone (**A**); b) crotonaldehyde (**D**); c) reaction mixture of **A** (1 equiv), **D** (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 2 days; d) addition of TFA (20 mol%) to the reaction mixture of c) stirring for 3 days more; e) reaction mixture of **A** (1 equiv), **D** (2 equiv), and NaOAc (20 mol%) without catalyst, after stirring for 2 days, addition of TFA (20 mol%) stirring for 3 days more; f) Product **G**. The color-coding of the peaks represents the starting materials as well as the products.

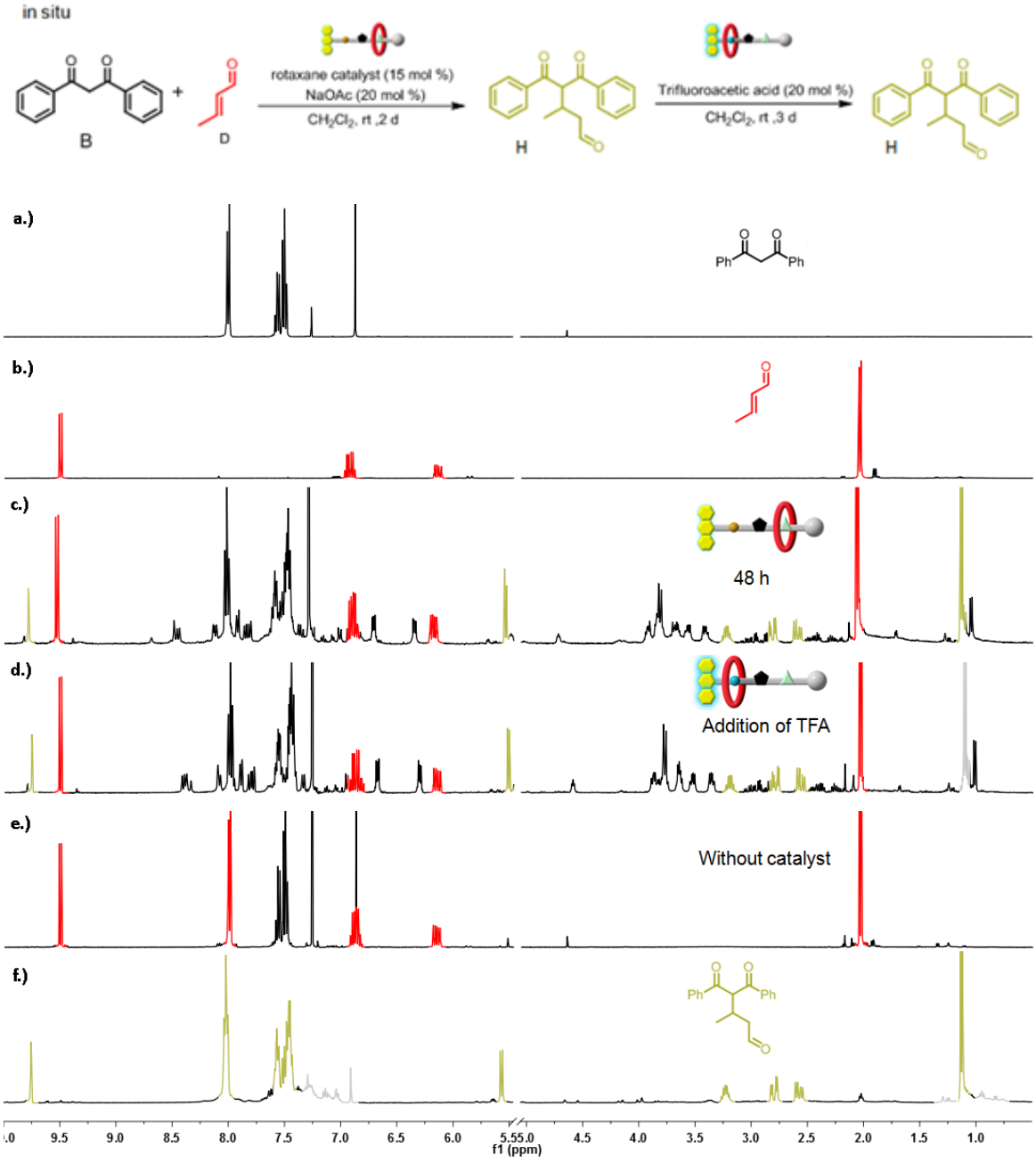


Figure S25 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of in situ switch off of entry 10: a) dibenzoylmethane (**B**); b) crotonaldehyde (**D**); c) reaction mixture of **A** (1 equiv), **D** (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 2 days; d) addition of TFA (20 mol%) to the reaction mixture of c) stirring for 3 days more; e) reaction mixture of **A** (1 equiv), **D** (2 equiv), and NaOAc (20 mol%) without catalyst, after stirring for 2 days, addition of TFA (20 mol%) stirring for 3 days more; f) Product **H**. The color-coding of the peaks represents the starting materials as well as the products.

Table S1 Summary of in situ experiment of entry 8, 12, 15, 18. TEA: triethylamine; TFA: trifluoroacetic acid.

Entry	Catalyst	Switching agent	Yield before switching (%)	Yield after switching (%)
8	**1**-H·PF_6	TEA	34 (**F**)	80 (**F**), 41 (**H**)
Control 8	–	TEA	–	78 (**F**)
9	**1**-H·PF_6	TEA	–	72 (**H**)
Control 9	–	TEA	–	–
12	**1**	TFA	39 (**G**)	39 (**G**)
Control 12	–	TFA	–	–
10	**1**	TFA	69 (**H**)	70 (**H**)
Control 10	–	TFA	–	–

In control 8, TEA catalyzes the reaction between **A** and **C** readily.[S8]

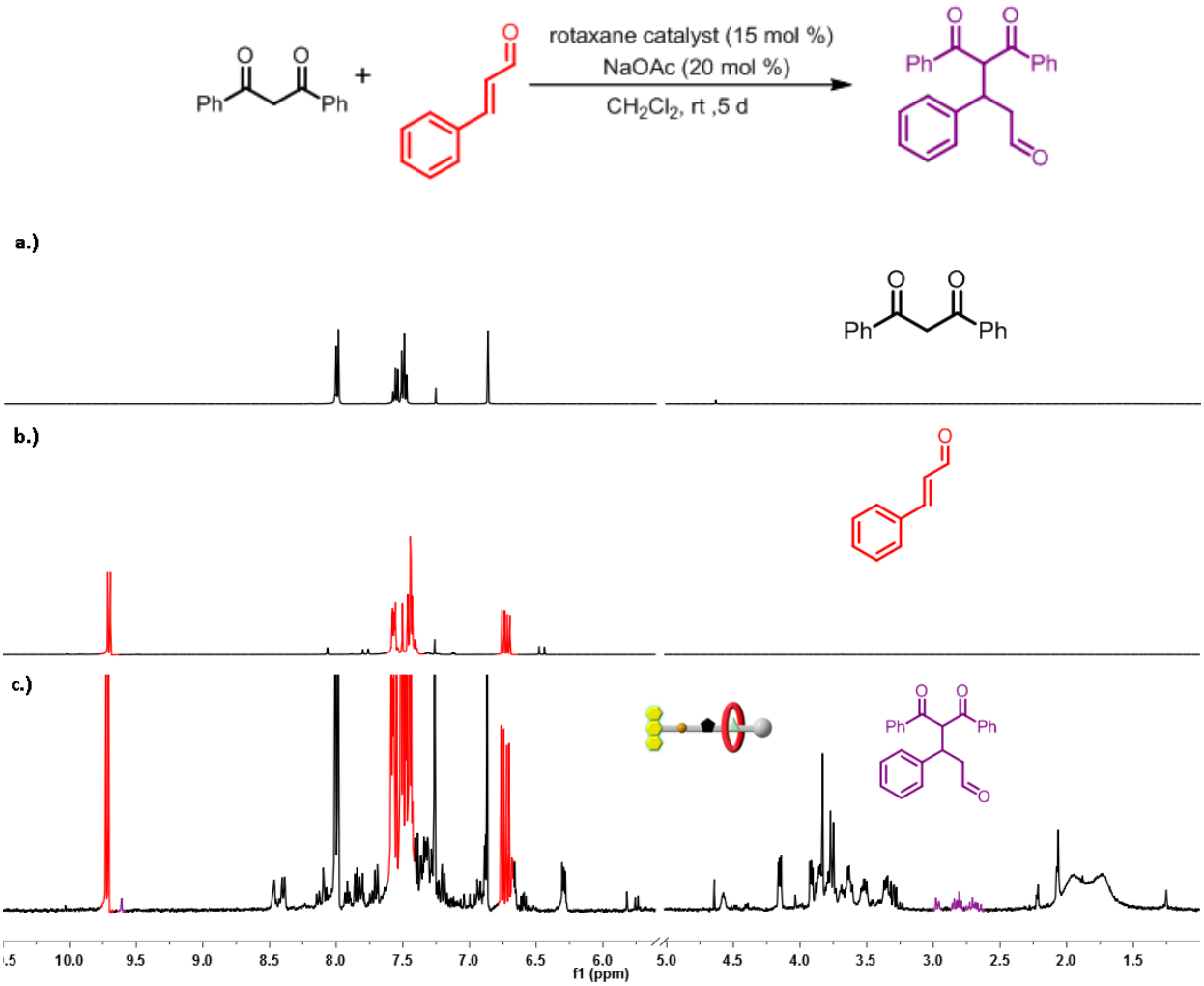


Figure S26 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) dibenzoylmethane; b) *trans*-cinnamaldehyde; c) reaction mixture of dibenzoylmethane (1 equiv), *trans*-cinnamaldehyde (2 equiv), **1** (15 mol%), and NaOAc (20 mol%), after stirring for 5 days. The color-coding of the peaks represents the starting materials as well as the products.

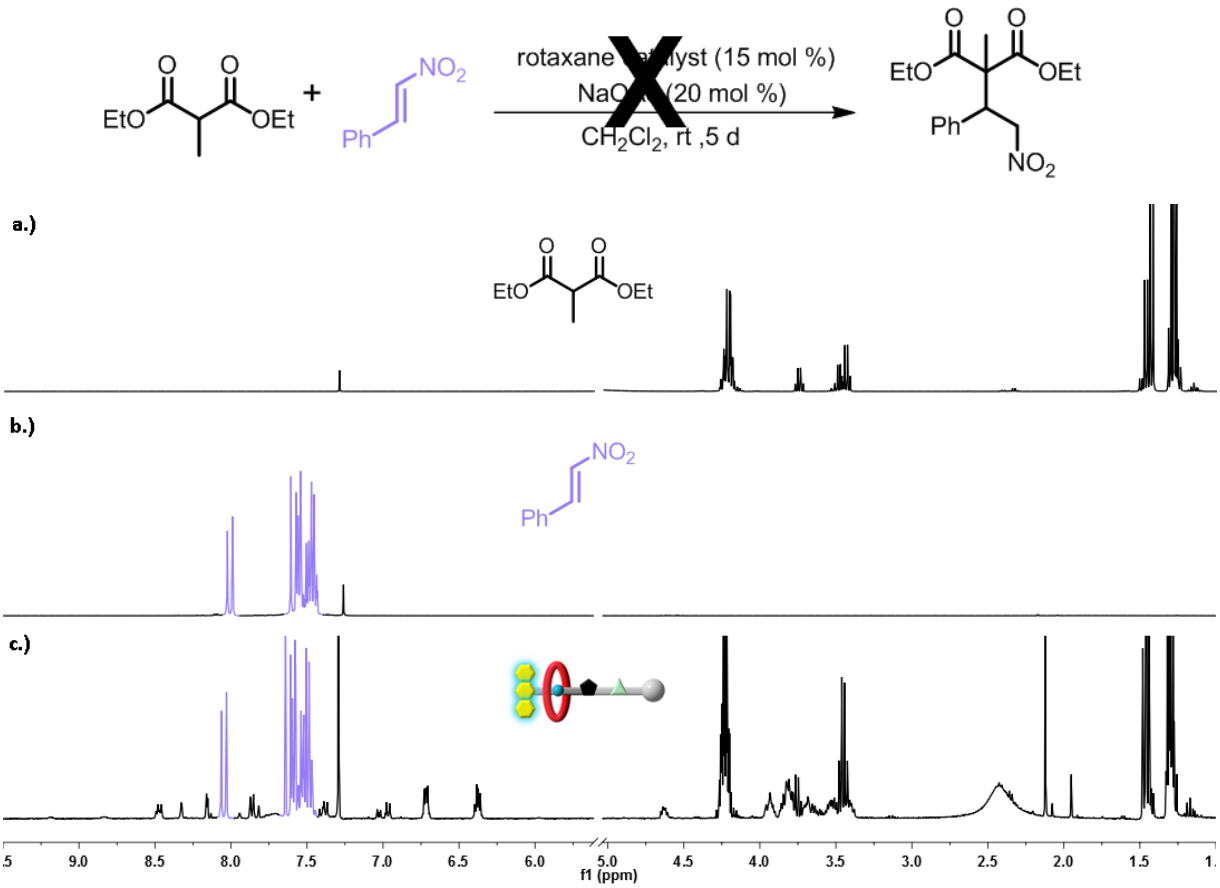


Figure S27 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) diethyl methylmalonate; b) *trans*-β-nitrostyrene; c) reaction mixture of diethyl methylmalonate (1 equiv), *trans*-β-nitrostyrene (2 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days. The color-coding of the peaks represents the starting materials.

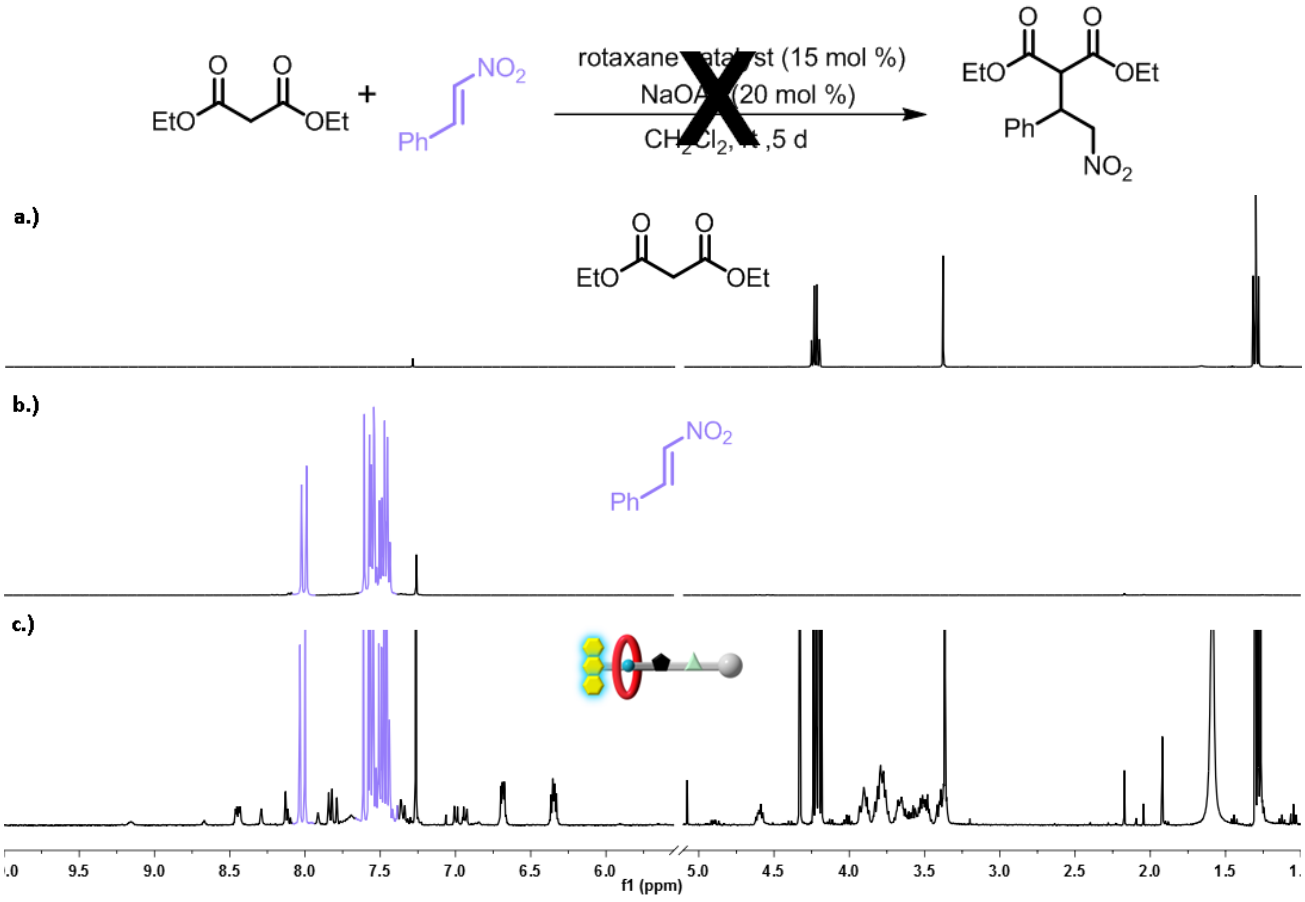


Figure S28 Stack ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of: a) diethylmalonate; b) *trans*-β-nitrostyrene; c) reaction mixture of diethylmalonate (1 equiv), *trans*-β-nitrostyrene (2 equiv), **1**-H·PF_6 (15 mol%), and NaOAc (20 mol%), after stirring for 5 days. The color-coding of the peaks represents the starting materials.

Kinetics study of selected organocatalysis

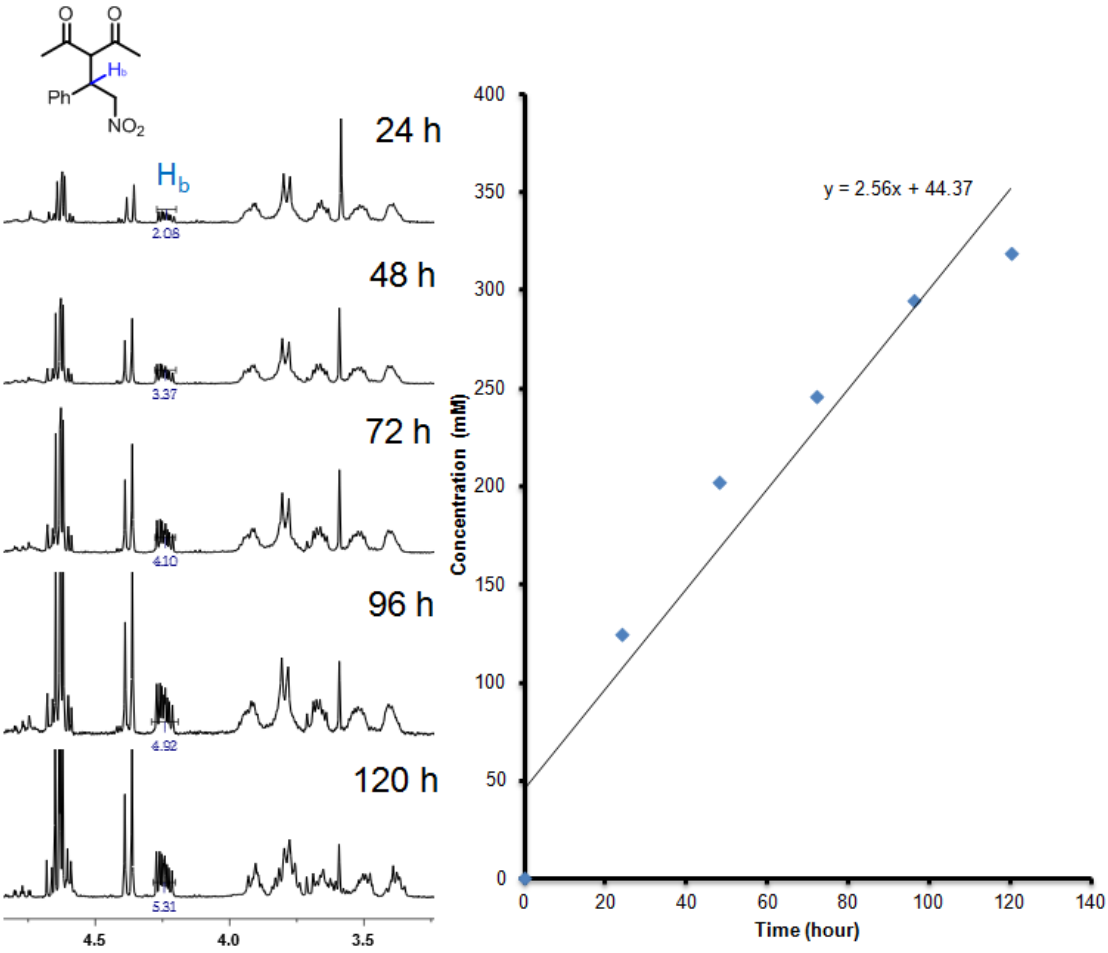


Figure S29 Partial ^{1}H NMR spectrum of entry 1 with respect to time, and the kinetics study of product **E**.

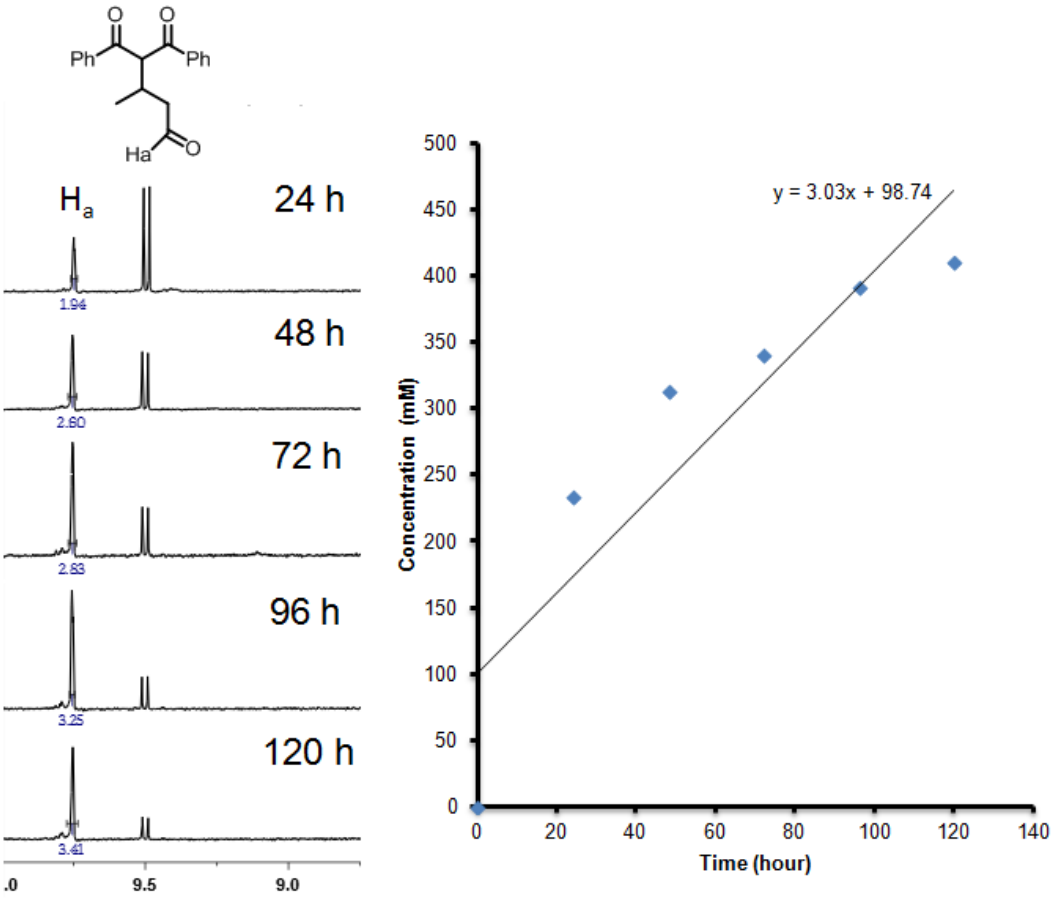


Figure S30 Partial ^{1}H NMR spectrum of entry 6 with respect to time, and the kinetics study of product **H**.

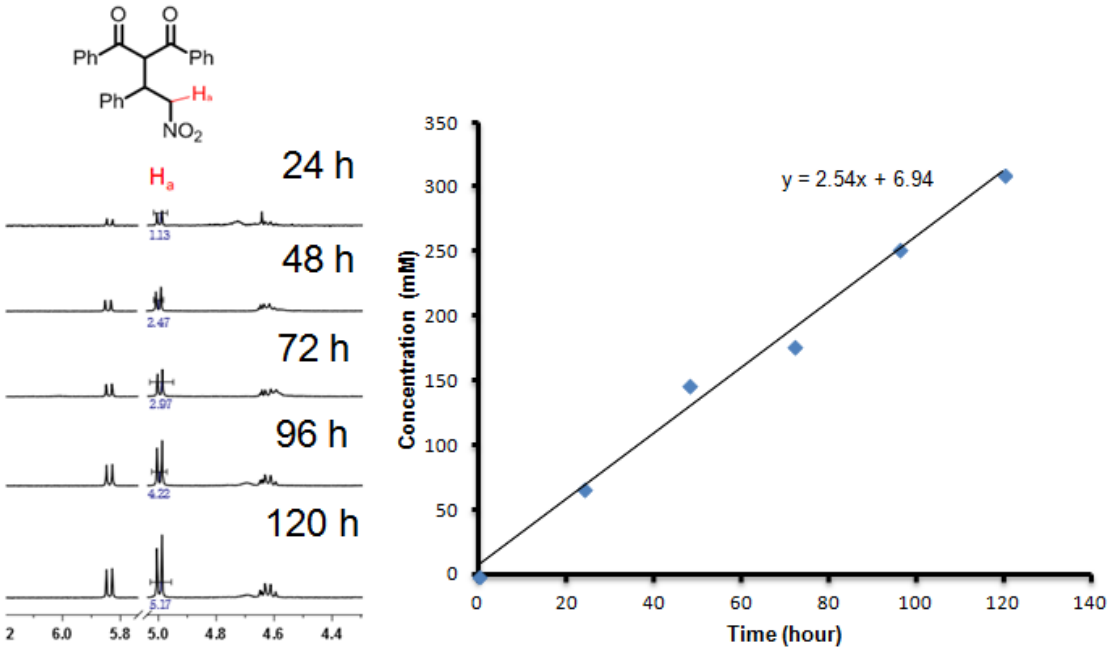


Figure S31 Partial ^{1}H NMR spectrum of entry 9 with respect to time, and the kinetics study of product **F**.

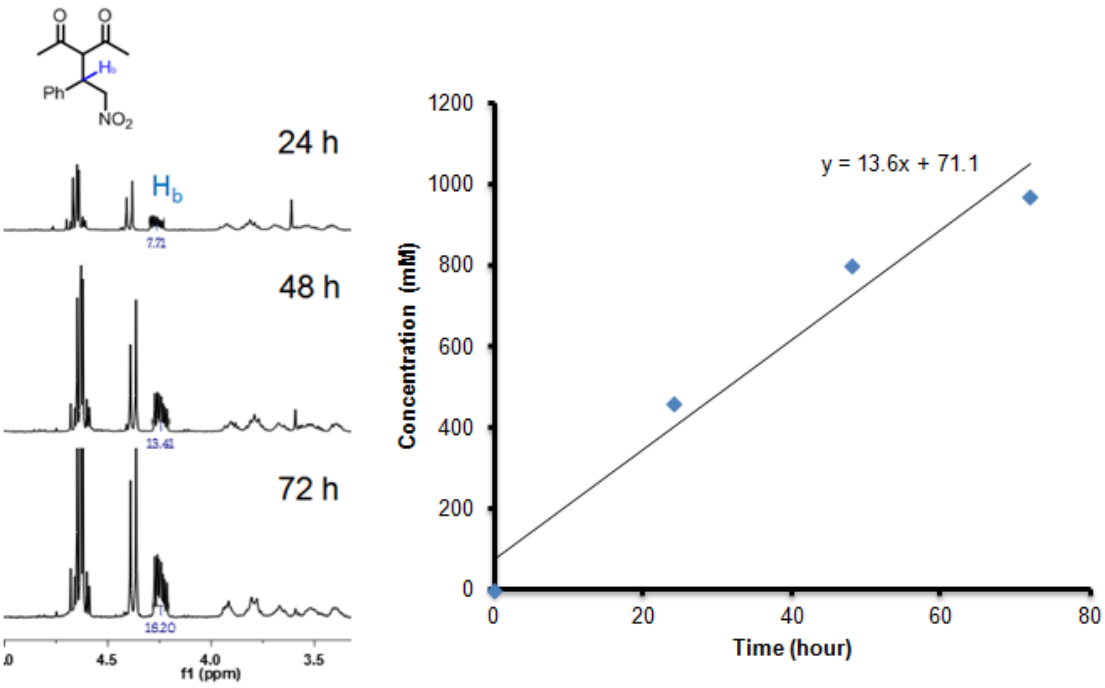


Figure S32 Partial ^{1}H NMR spectrum of entry 11 with respect to time, and the kinetics study of product **E**.

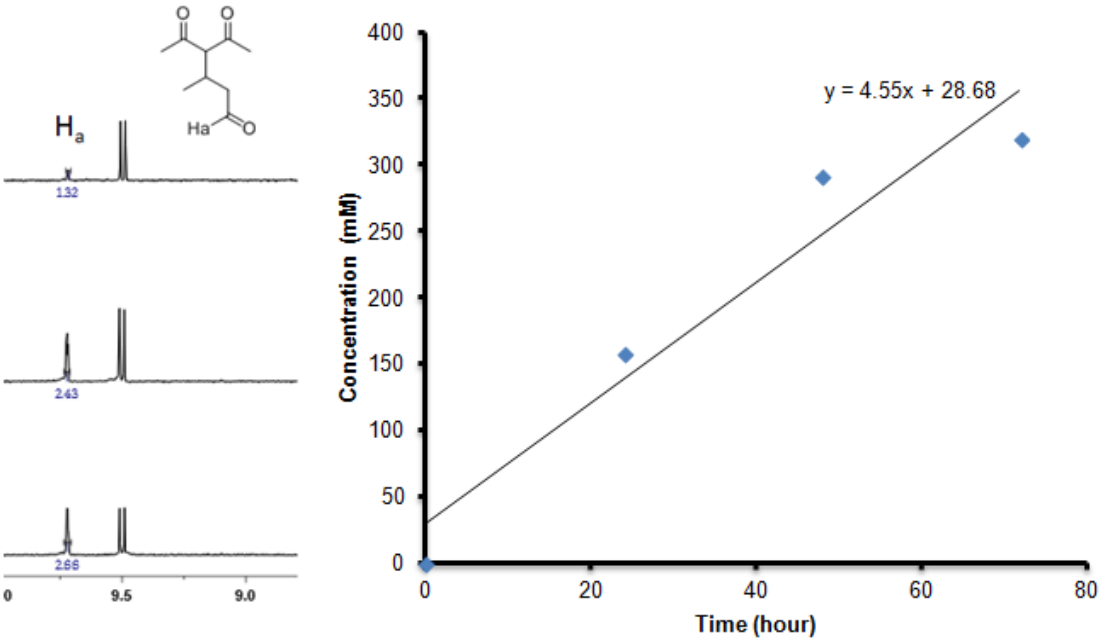


Figure S33 Partial ^{1}H NMR spectrum of entry 12 with respect to time, and the kinetics study of product **G**.

NMR Spectra of selected compounds

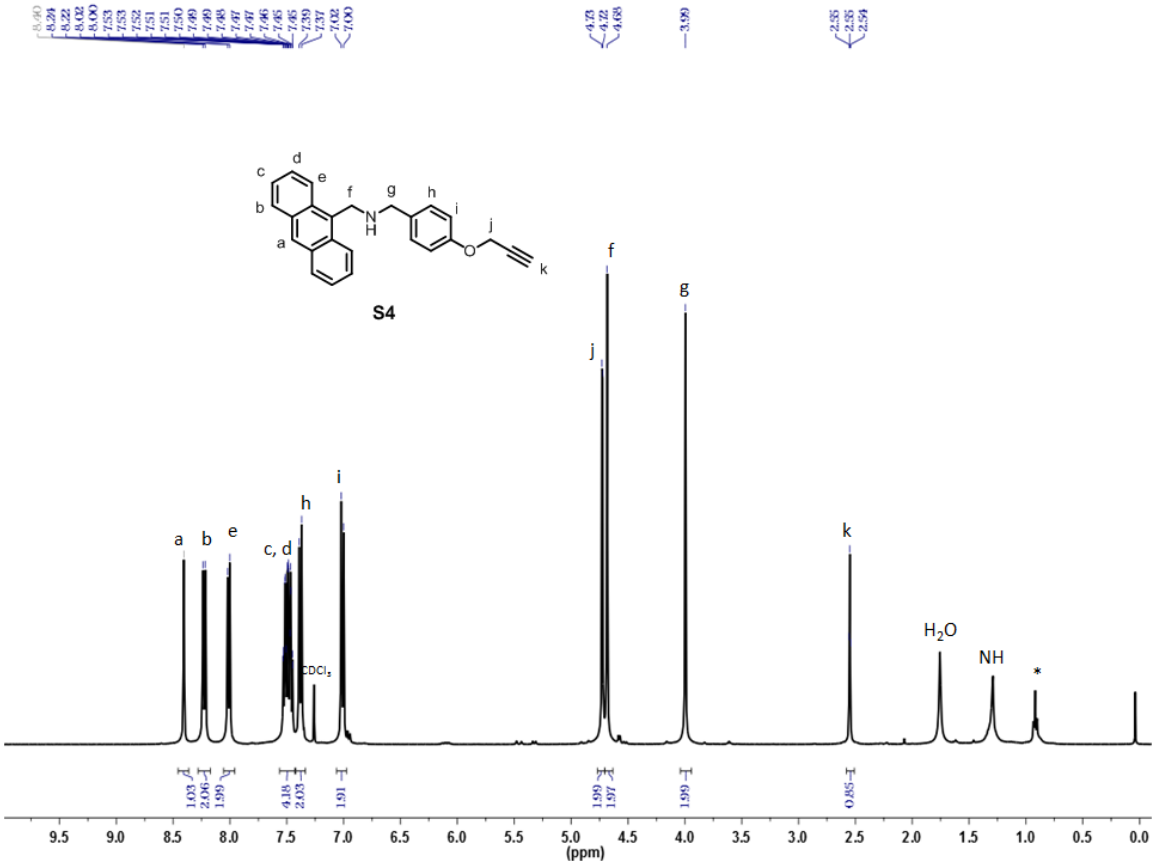


Figure S34 ^{1}H NMR spectrum of (400 MHz, $CDCl_3$) **S4** (Asterisk: solvent residual signal).

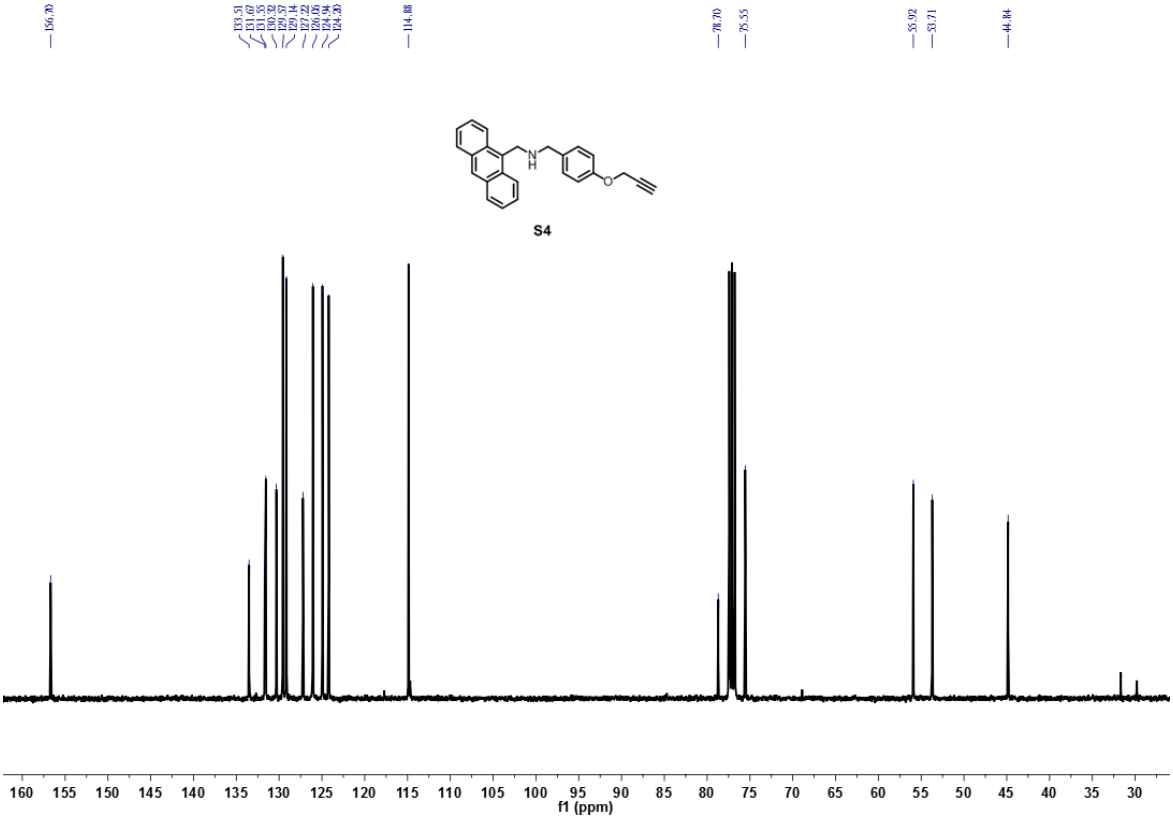


Figure S35 ^{13}C NMR spectrum of (101 MHz, $CDCl_3$) **S4**.

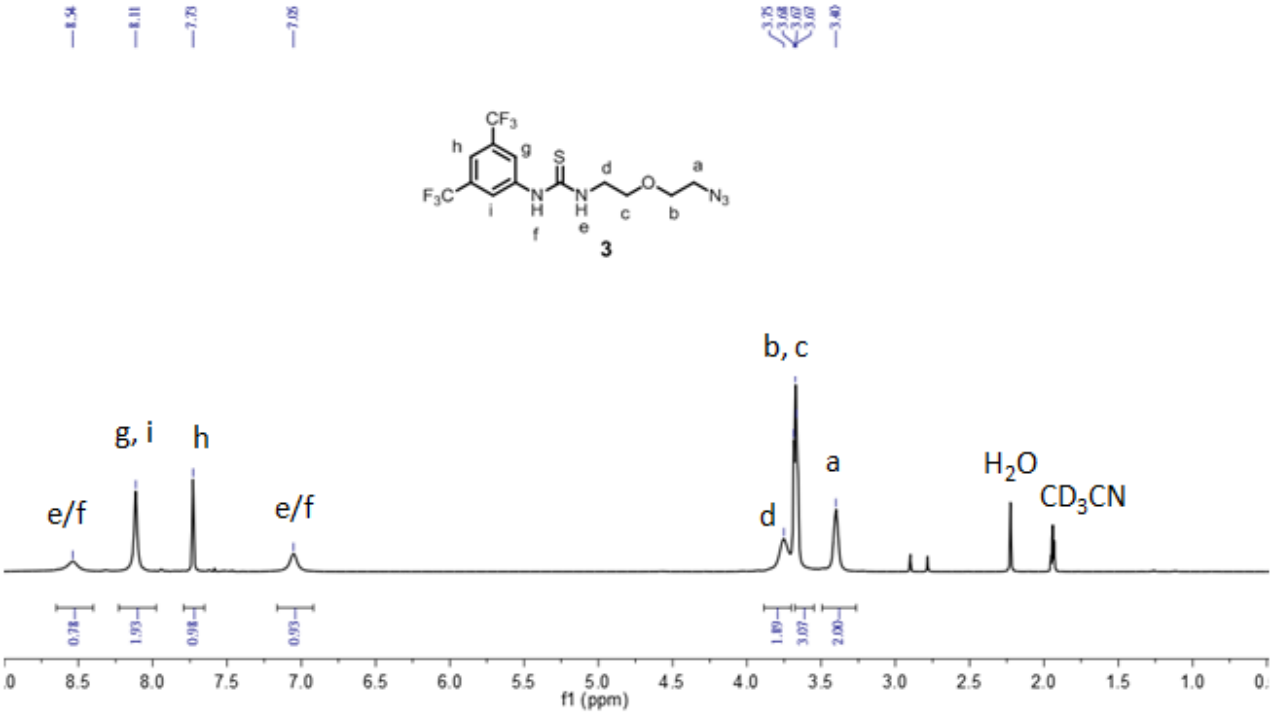


Figure S36 ^{1}H NMR spectrum of (400 MHz, CD_3CN) **3**.

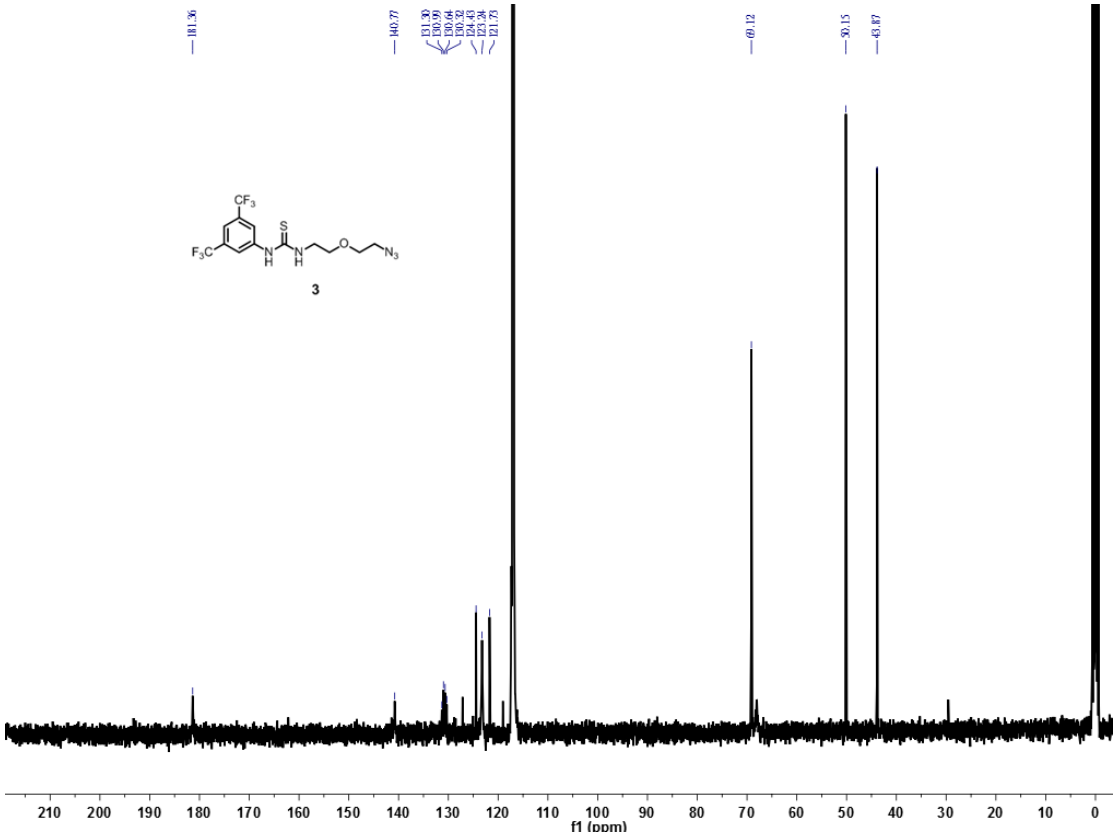


Figure S37 ^{13}C NMR spectrum of (101 MHz, CD_3CN) **3**.

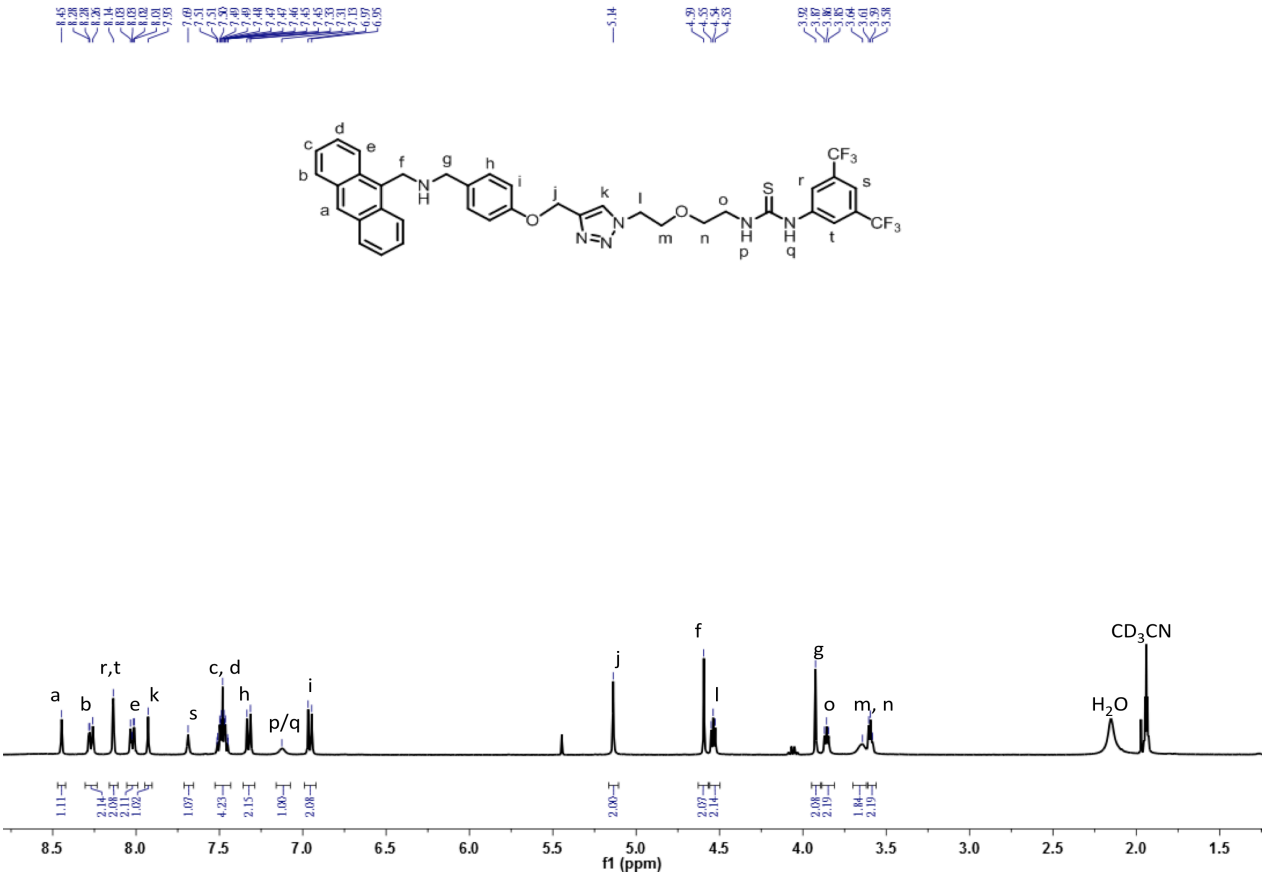


Figure S38 ^{1}H NMR spectrum of (400 MHz, CD_3CN) **2**.

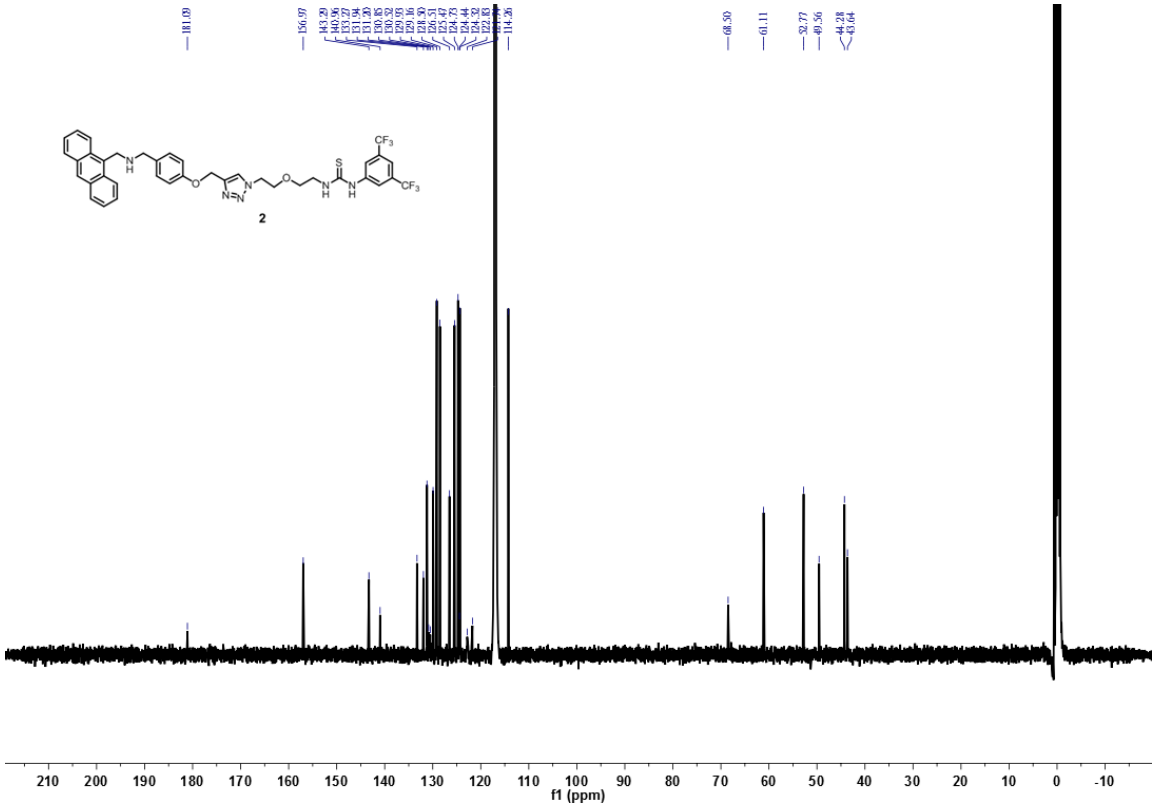


Figure S39 ^{13}C NMR spectrum of (101 MHz, CD_3CN) **2**.

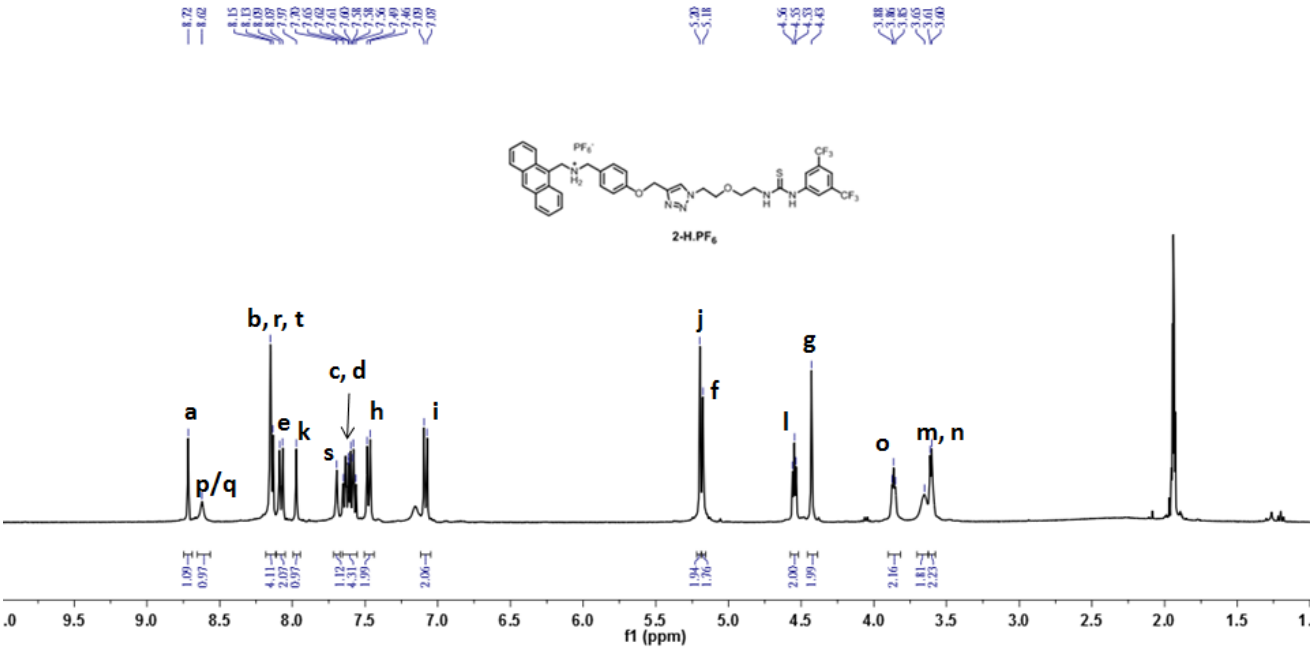


Figure S40 ^{1}H NMR spectrum of (400 MHz, CD_3CN) **2**-H·PF_6.

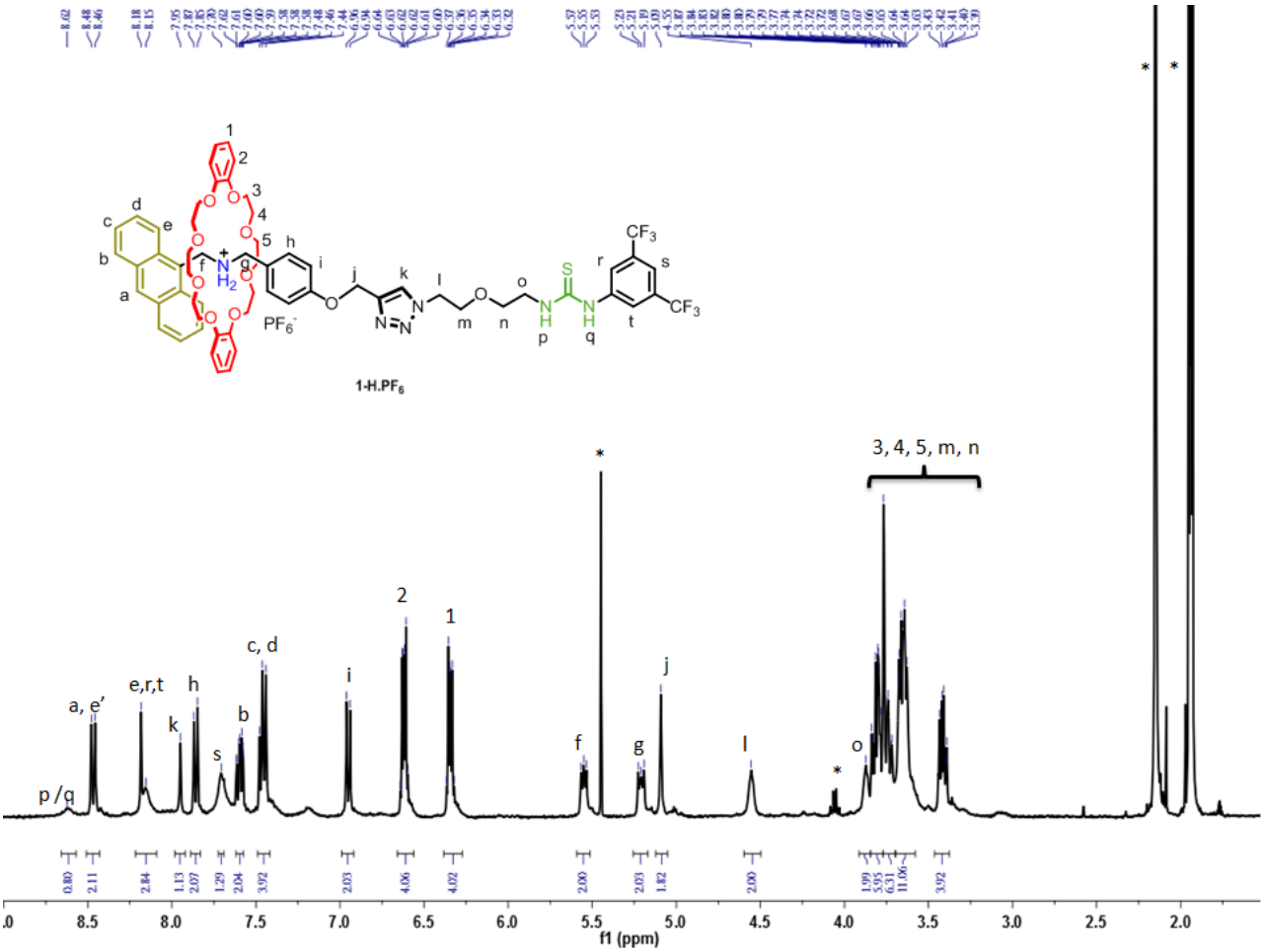


Figure 41 ^{1}H NMR spectrum of (400 MHz, CD_3CN) **1**-H·PF_6 (Asterisk: solvent residual signal)

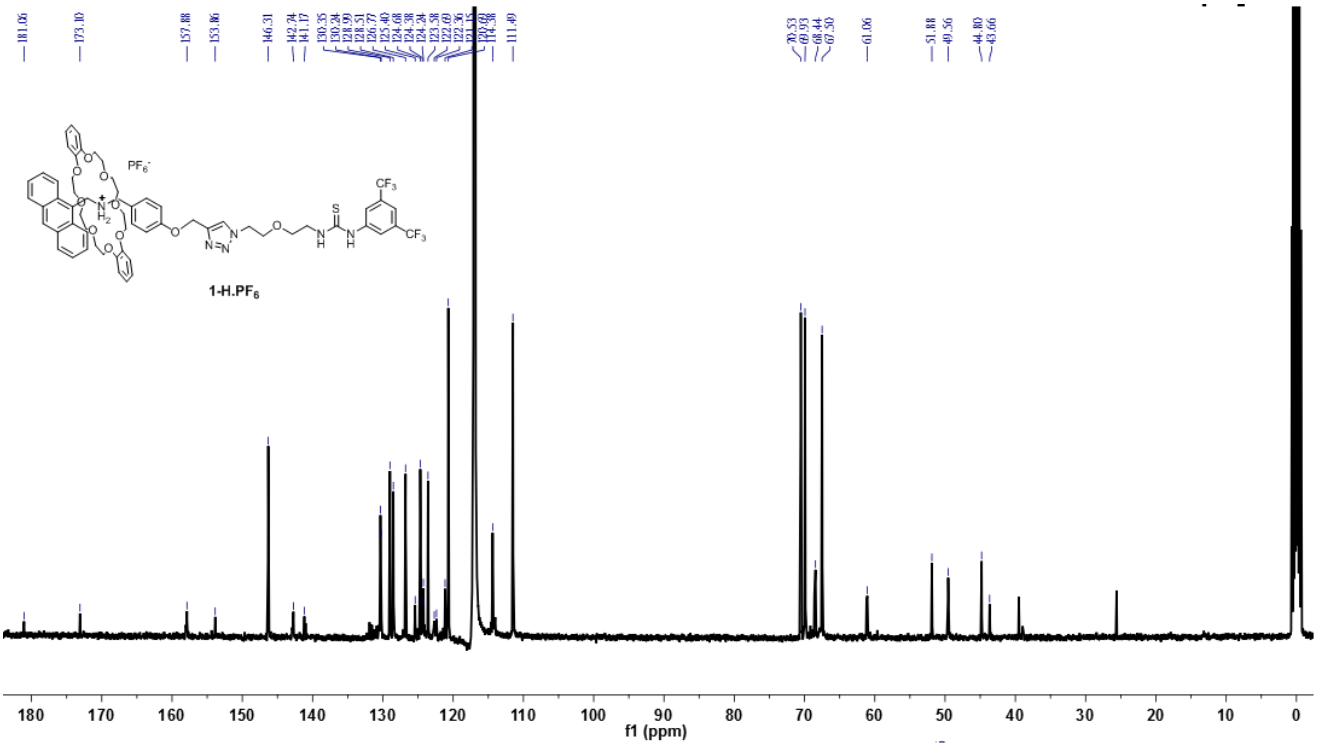


Figure S42 ^{13}C NMR spectrum of (101 MHz, CD_3CN) **1**-H·PF_6.

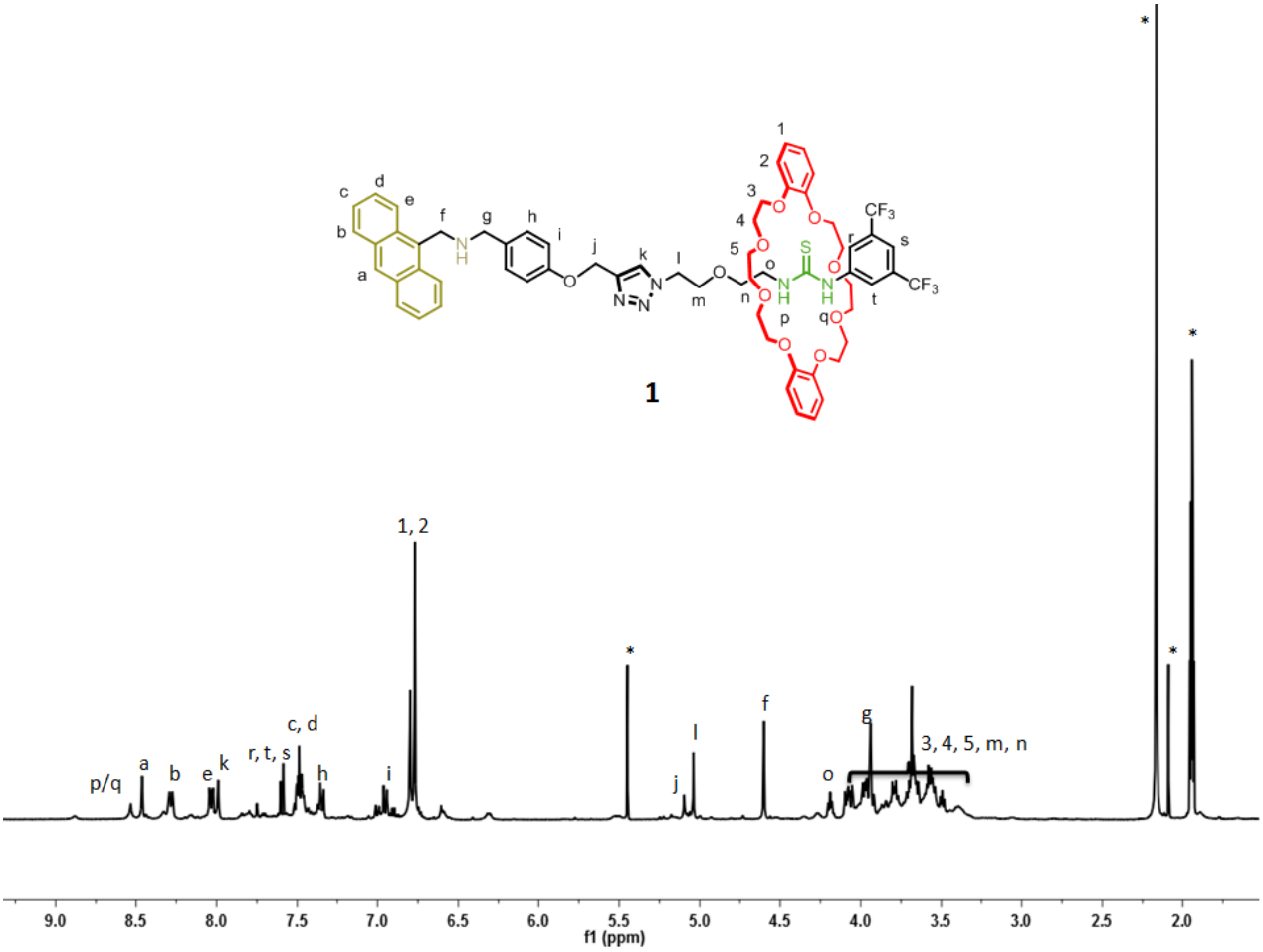


Figure S43 ^{1}H NMR spectrum of (400 MHz, CD_3CN) **1** (Asterisk: solvent residual signal).

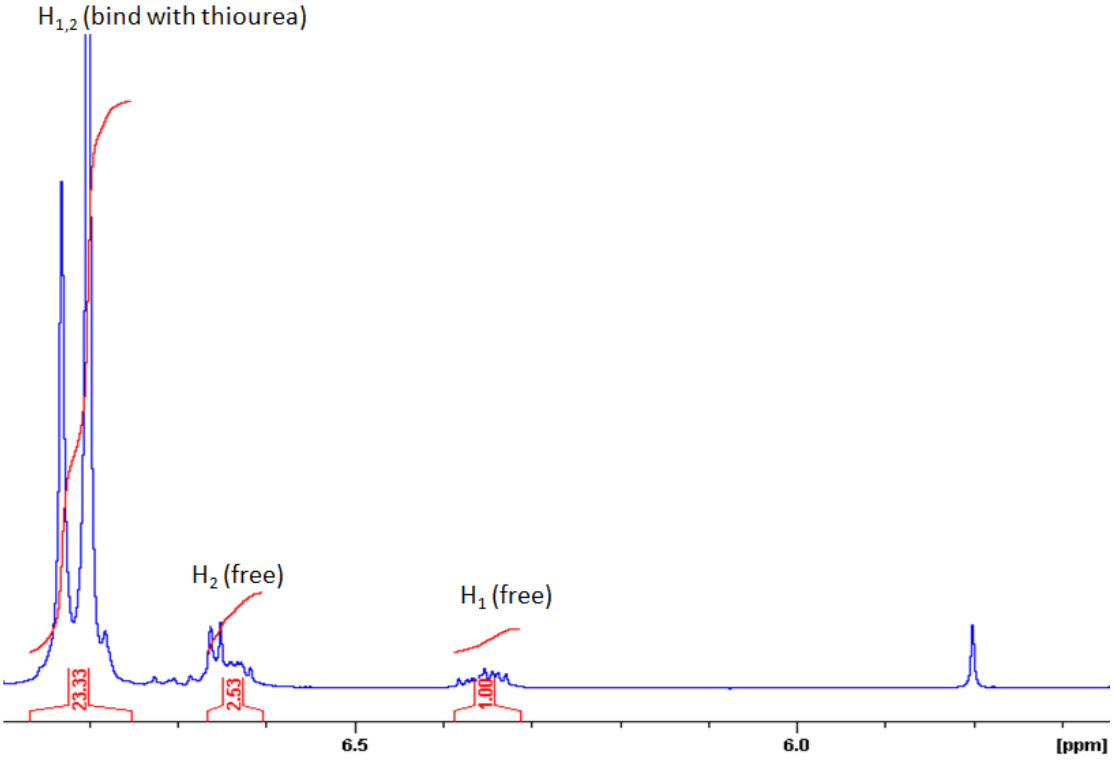


Figure S44 Partial enlarged ^{1}H NMR spectrum of **1** (CD_3CN, 20 mM) for binding constant determination. The binding constant K_a was calculated from the integration ratio of H_1 and H_2 (bound and free) of DB24C8's aryl proton binding with thiourea, whereas K_a = 5029 M^{-1}.

Mass Spectra of selected compounds

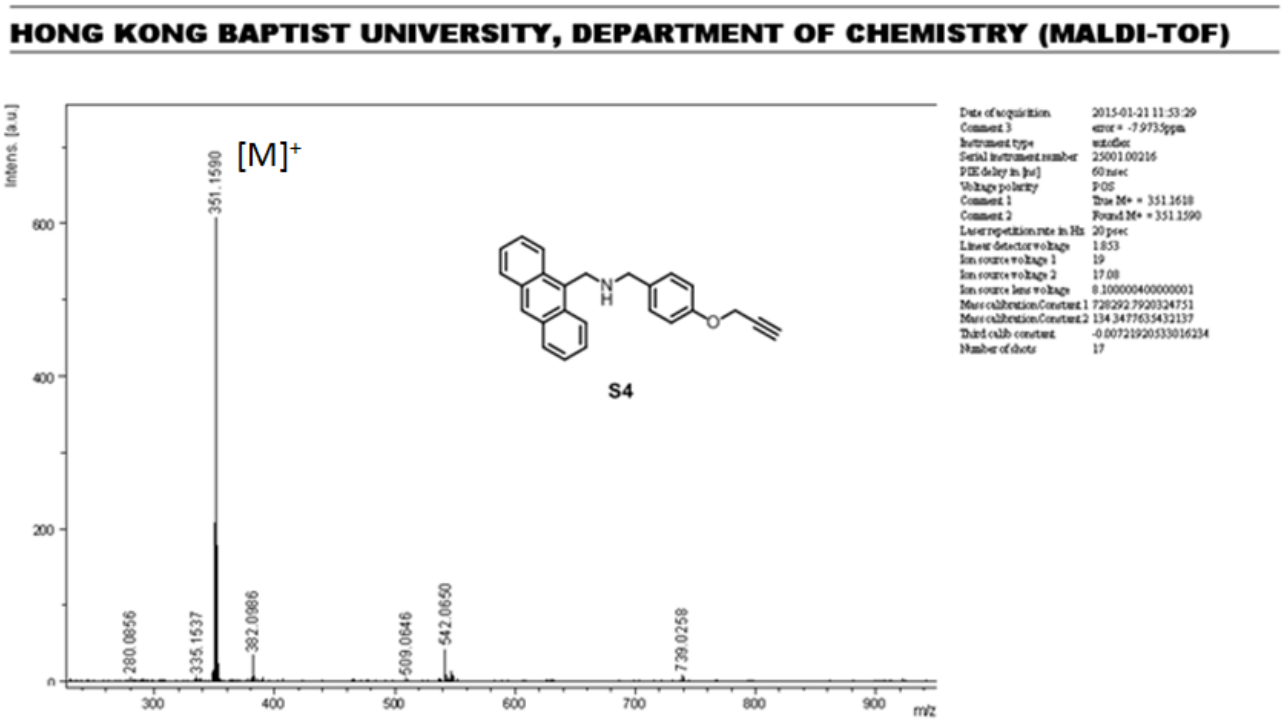


Figure S45 HRMS (MALDI-TOF) of **S4**.

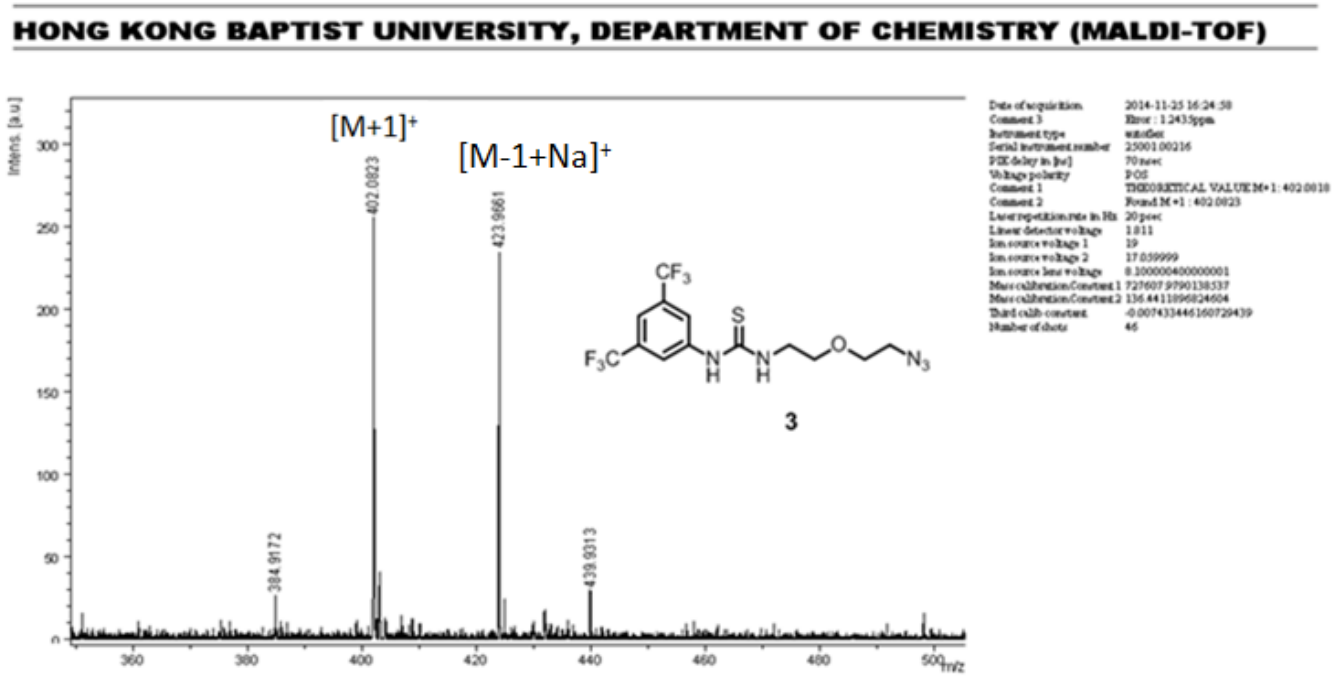


Figure S46 HRMS (MALDI-TOF) of **3**.

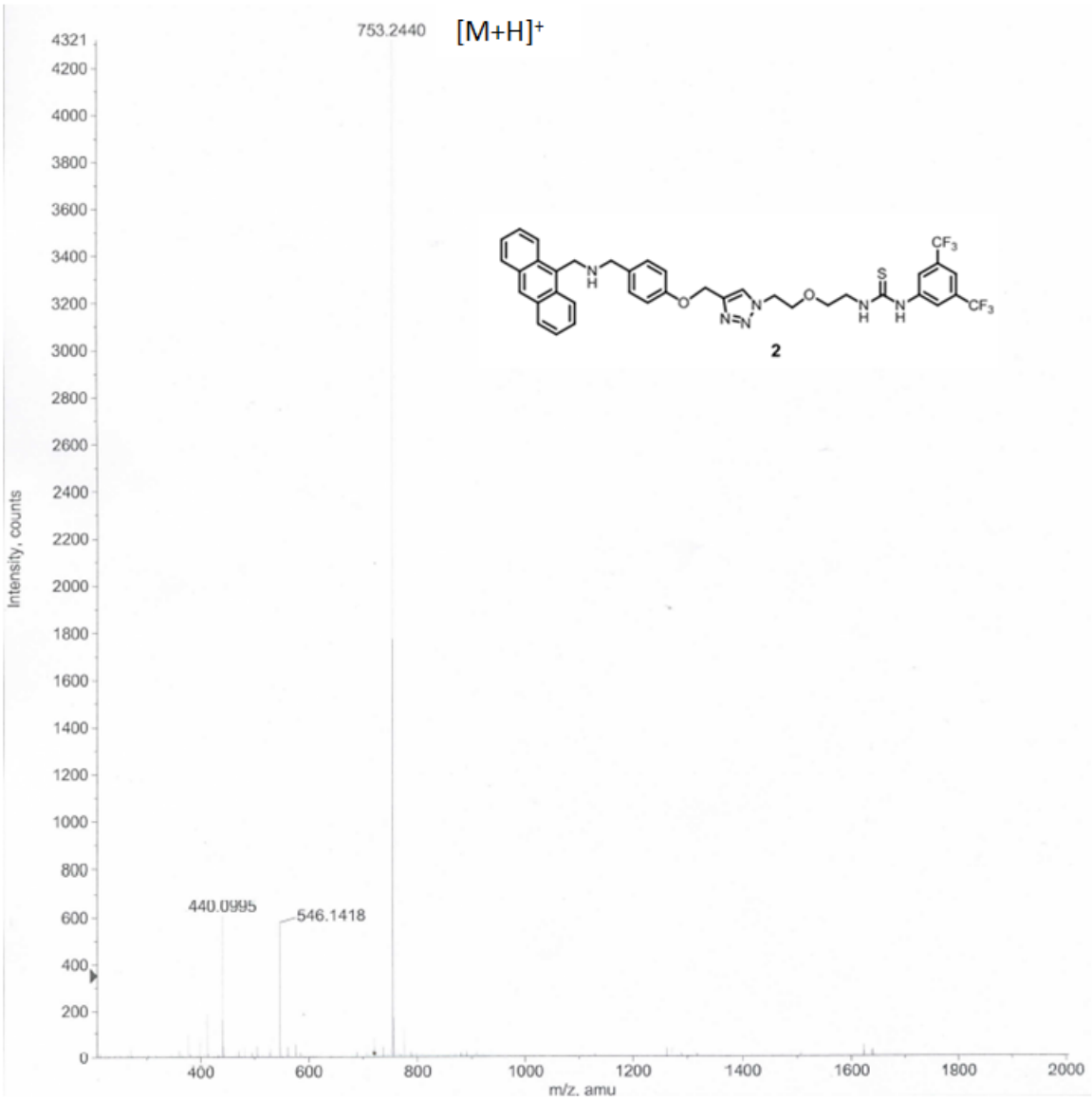


Figure S47 HRMS (ESI) of **2**.

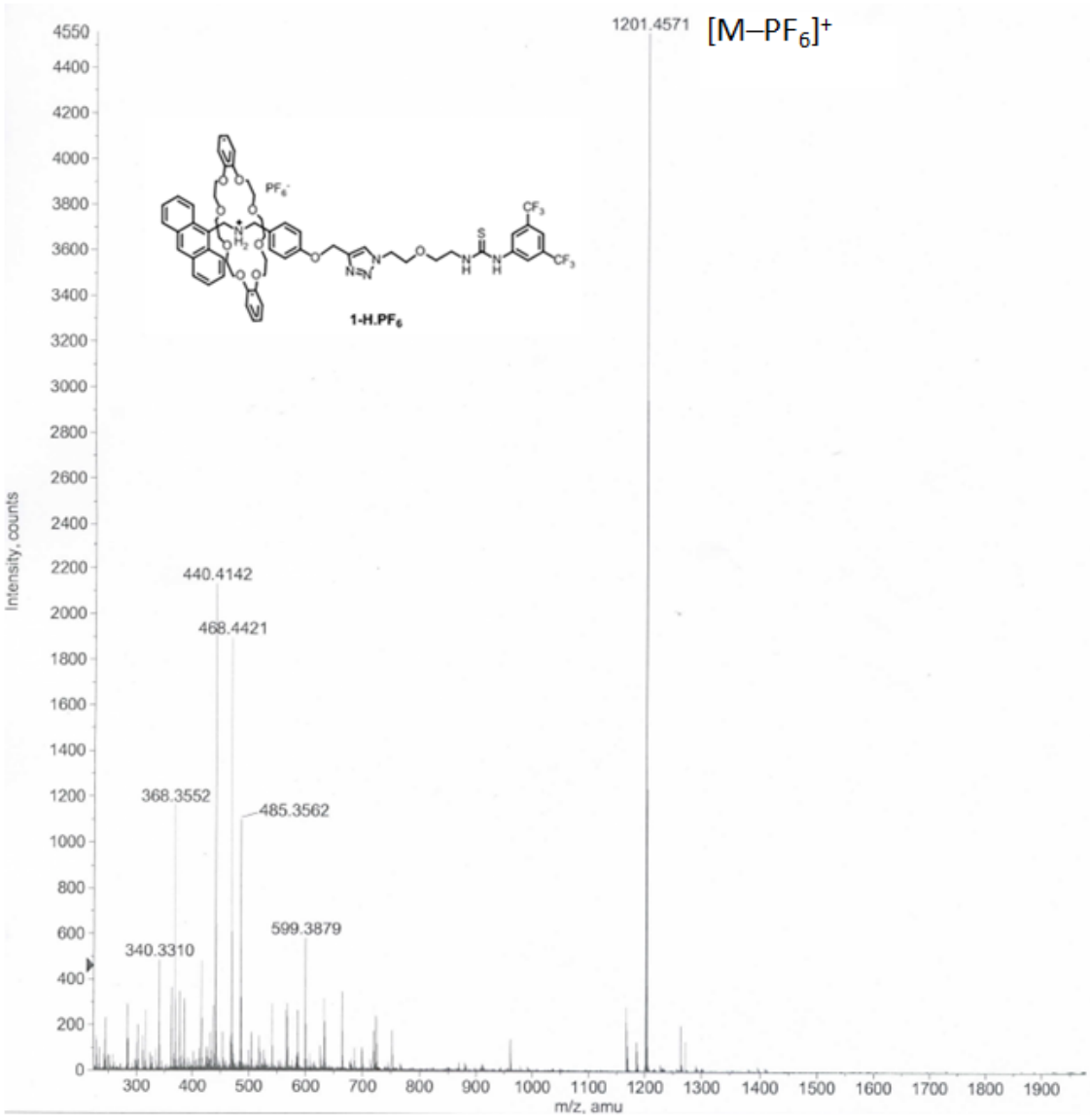


Figure S48 HRMS (ESI) of **1**-H·PF_6.

Notes and References

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