Supporting Information

for

Unusual Regio- and Stereo-selectivity in Diels-Alder Reactions between Bulky N-phenylmaleimides and Anthracene Derivatives

*Hao Chen, Erdong Yao, Chi Xu, Xiao Meng and Yuguo Ma**

Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Email: ygma@pku.edu.cn

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1. Experimental Section

General Information. Chemicals were purchased commercially and used without further purification. *N*-phenylmaleimide were prepared by literature methods.[1] ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV 400 (400 MHz), a Varian Mercury-300 (300 MHz) and a Bruker AV 500 (500 MHz) spectrometer using $CDCl_3$, TCE-d_2 and DMSO-d_6 as solvents. VT NMR and 2D NOSEY NMR experiments were recorded on a Bruker AV 500 (500 MHz) spectrometer. ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or TCE-d_2 (6.0 ppm), ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.16 ppm) and ^{19}F NMR chemical shifts were referenced to a CF_3CO_2H external standard (0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using the absorption mode in a 1 cm quartz cell. Fluorescence emission spectra were recorded in 1 cm quartz cuvette on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer, with graphite monochromator and Mo Kα radiation [λ (MoK_α) = 0.71073 Å]. Structures were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXS-97.

***In-situ* NMR experiments**

In a typical experiment, maleimide **2d** (0.06 mM) and diene **1h** (0.06 mM) were dissolved in 0.6 mL TEC-d_2 in an NMR tube. The sample was heated in an oil bath at 110 ℃ for certain time. The ratios of starting materials, 9,10-adduct **4d** and anti-1,4-adduct **3d** were monitored by integration of their typical peaks at δ8.57 (1H), 3.54 (1H) and 3.35 (2H) ppm, respectively.

Computational Methods

All geometry optimizations were performed with Gaussian 09 program using the B3LYP density functional theory (DFT) with the 6-31G(d) basis set.[2] B3LYP/6-31G* is the relatively computationally inexpensive DFT method and achieve high accuracy for many hydrocarbon pericyclic reactions.[3] However, B3LYP consistently underestimate the reaction exothermicities, and we have performed single point energy calculations with M06-2X[4] that are expected to deliver a more accurate treatment of medium-range correlation effects, such as van der Waals interactions. Such calculations give improved thermodynamics for C-C bond forming reactions.[5] Single point calculations with a larger 6-311+G(d,p) basis set have been also performed to confirm that the basis-set size does not affect the conclusions drawn. Harmonic vibrational frequencies were computed for all optimized structures to verify that they were either minima (only real frequencies) or transition states (a single imaginary frequency). Zero-point energies (unscaled) are included in all thermodynamic quantities. The effects of solvation on the reaction energetics were

evaluated using a polarizable continuum solvation model (PCM).[6]

2. Synthesis of Maleimides

N-(3,4,5-Trifluorophenyl)maleimide **2b.** Exemplary procedure for all maleimides **2a-2k**.

To a stirred solution of maleic anhydride (1.27 g, 13 mmol) in diethyl ether (25 mL), a solution of *N*-(3,4,5-Trifluorophenyl)maleimide (1.0 g, 6.6 mmol) in diethyl ether (5 mL) was added. Stirring of the mixture was continued for 1 h. The formed solid was collected and dried in vacuum to yield the intermediate acid. Without further purification, the intermediate acid and sodium acetate (0.53 g, 6.6 mmol) were added to acetic anhydride (5 mL). The mixture was heated in an oil bath for 1 hour at 90 ℃, and then cooled down by an ice bath. The solid was collected, washed three times with water and dried. Recrystallization from cyclohexane yielded 1.14 g (75%) of **2b** as white crystals. ^{1}H NMR (300 MHz, C*D*Cl$_3$):*δ*7.19-7.14 (2H, m), 6.89 (2H, s). ^{13}C NMR (100 MHz, C*D*Cl$_3$):*δ*168.5, 152.2, 149.8, 140.3, 137.8, 134.4, 126.8, 110.4. ^{19}F NMR (282 MHz, C*D*Cl$_3$):*δ*-56.80, -84.57. Elem. Anal.: Calcd. for $C_{10}H_4F_3NO_2$: C, 52.88; H, 1.78; N, 6.17. Found: C, 52.88; H, 1.82; N, 6.15. MS: Calcd. for $C_{10}H_4F_3NO_2$, 227 ([M$^+$]/z), Found: $C_{10}H_4F_3NO_2$, 227 ([M$^+$]/z).

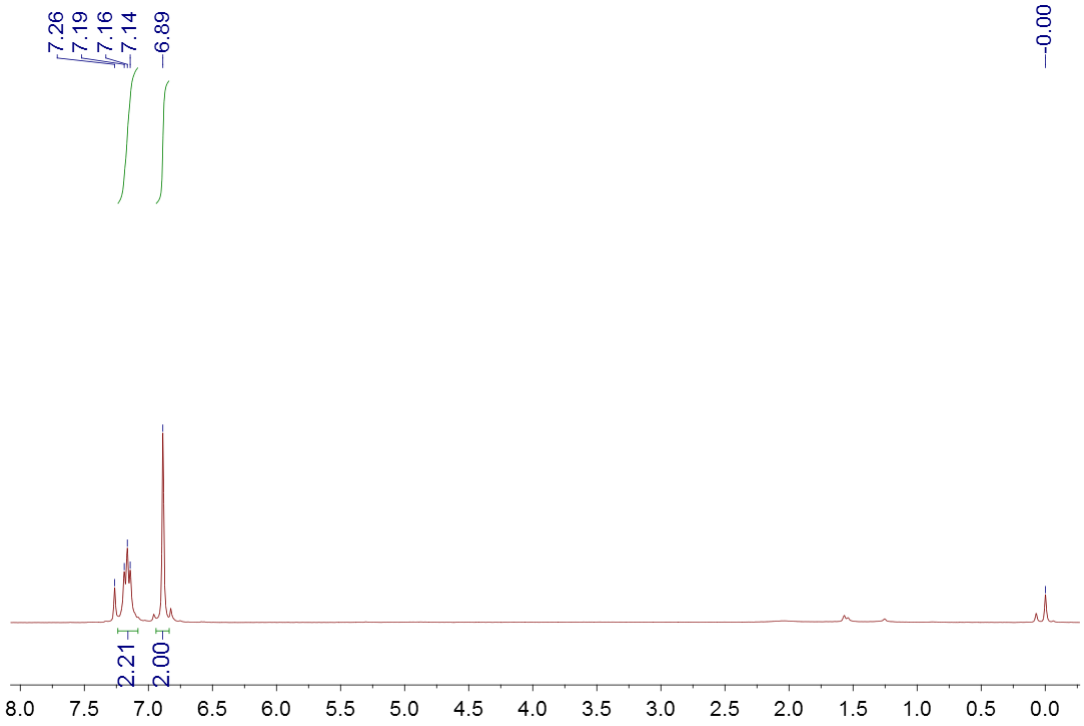


Figure S1. ^{1}H NMR spectrum (300 M) of **2b** in C*D*Cl$_3$.

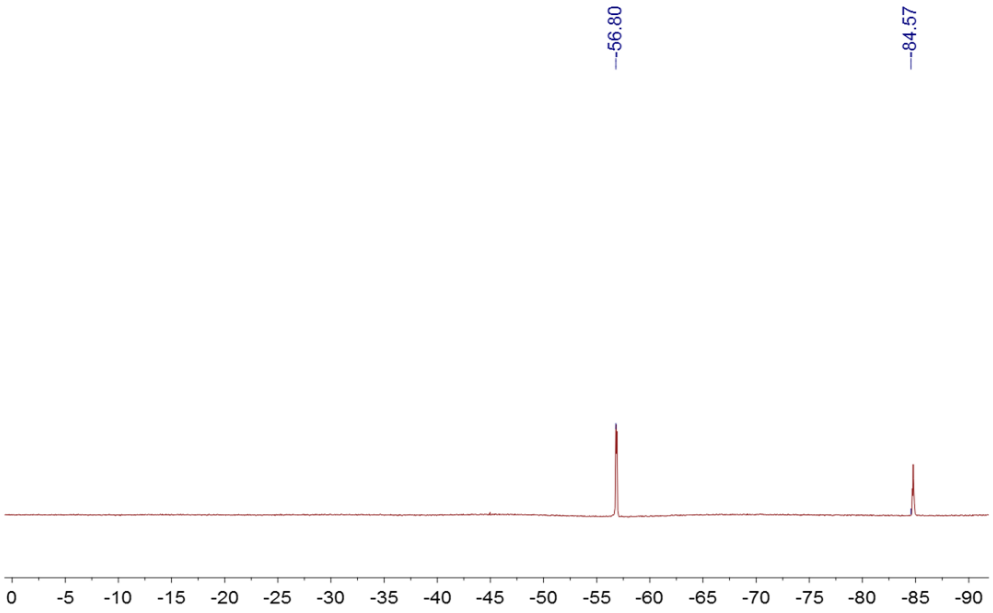


Figure S2. ^{19}F NMR spectrum (282 M) of **2b** in C*D*Cl$_3$.

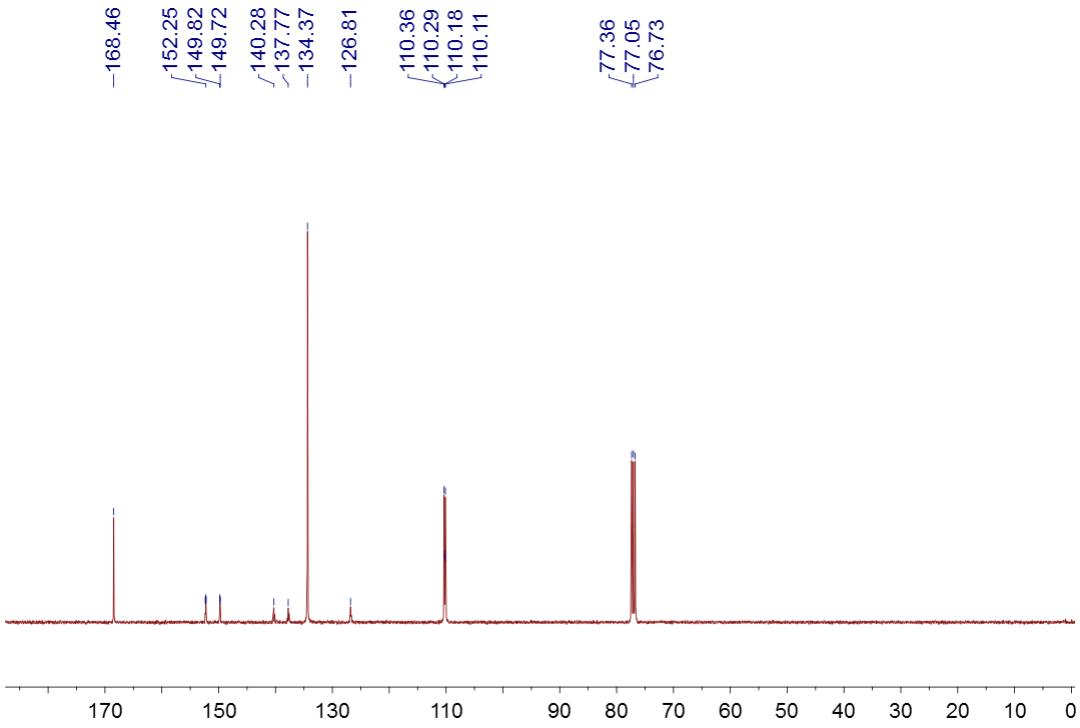


Figure S3. ^{13}C NMR spectrum (100 M) of **2b** in C*D*Cl$_3$.

3. ^{1}H NMR, ^{19}F NMR Spectra of Reaction Mixtures

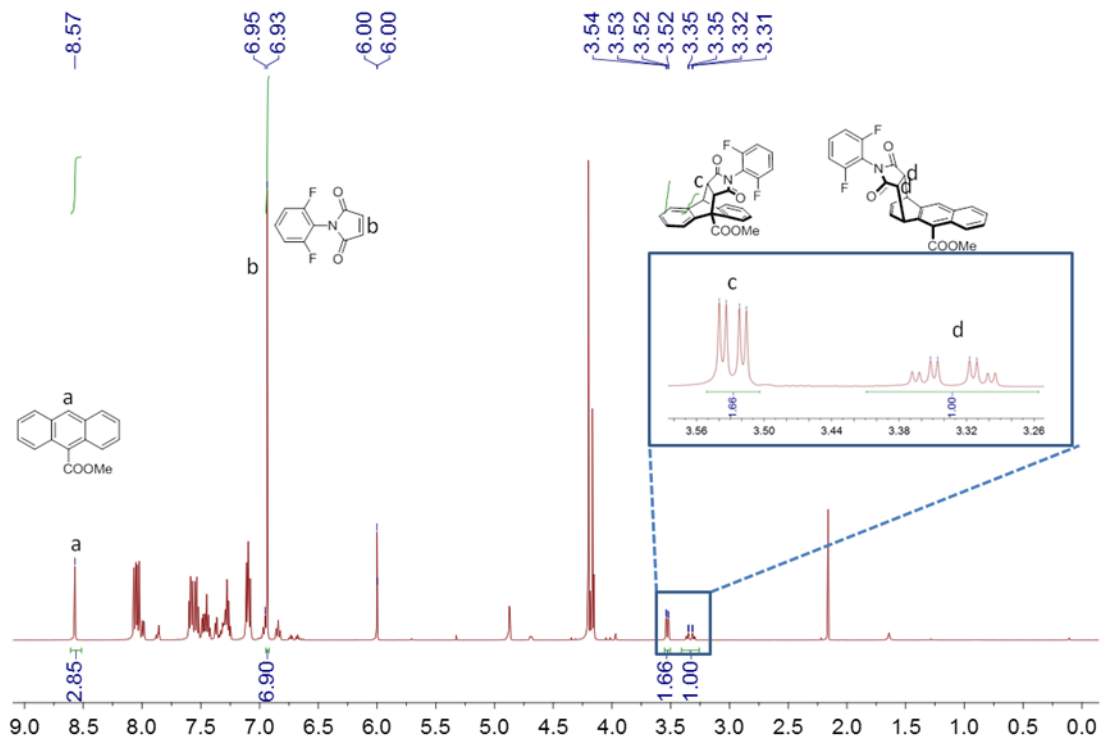


Figure S4. ^{1}H NMR spectrum (500 M) of crude reaction mixture (starting material: **1h** and **2d**) in TCE-d_2.

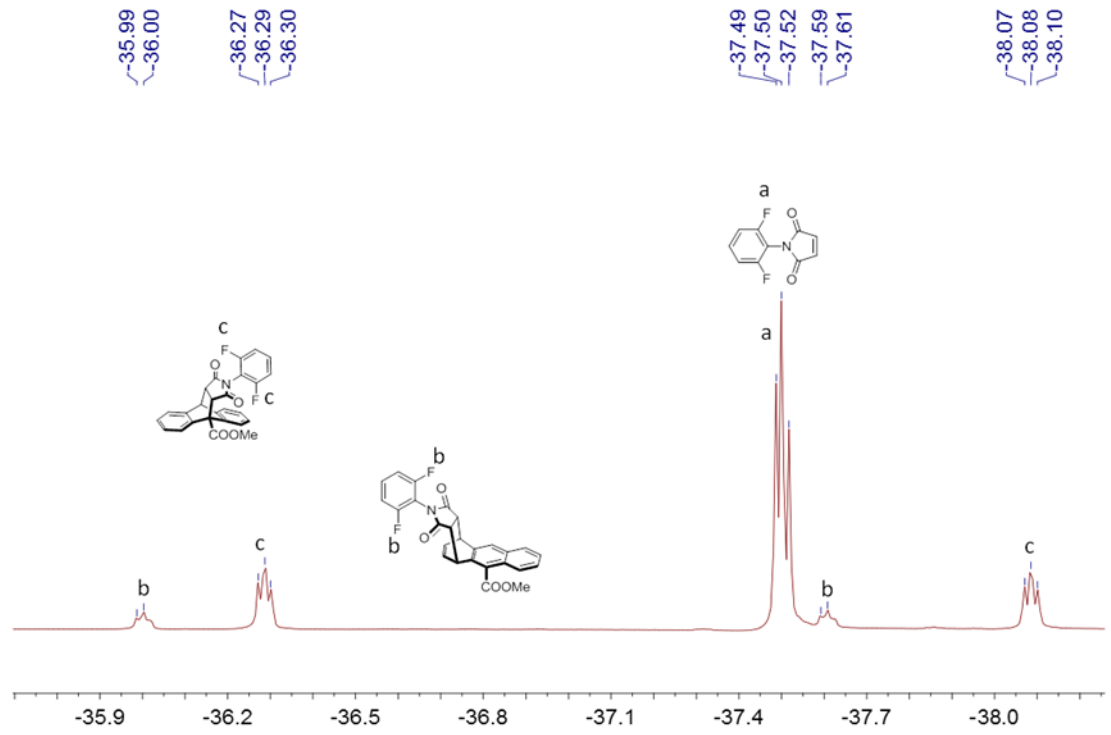


Figure S5. ^{19}F NMR spectrum (470 M) of crude reaction mixture (starting material: **1d** and **2d**) in TCE-d_2.

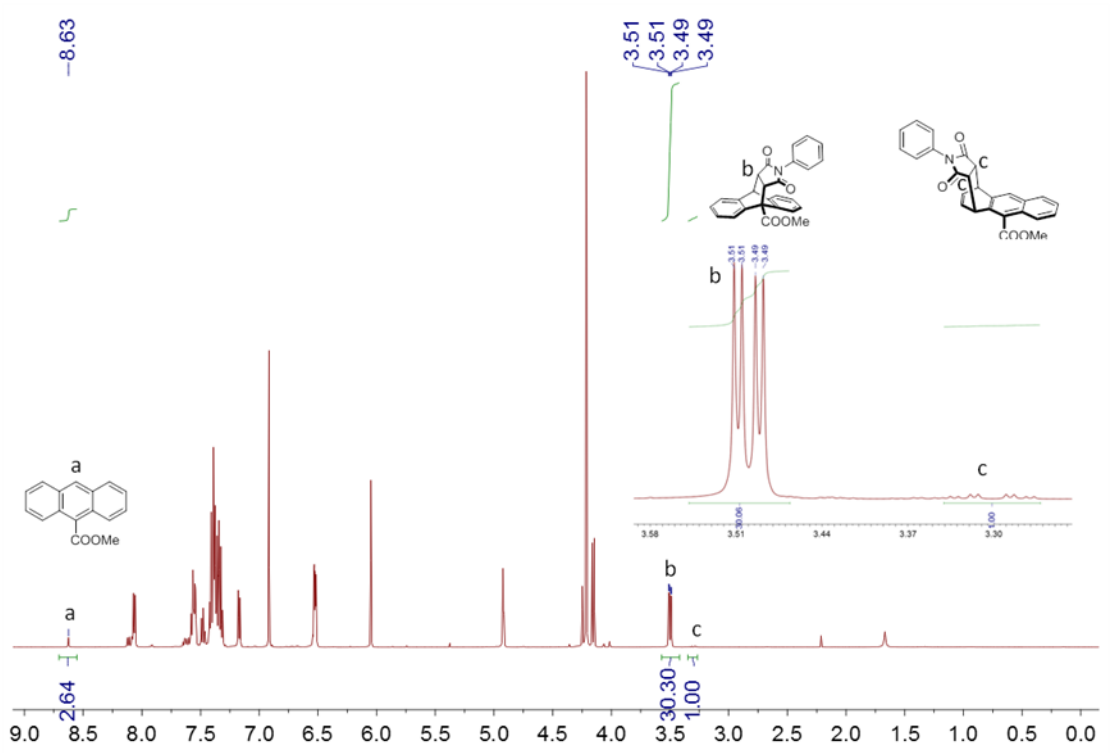


Figure S6. ^{1}H NMR spectrum (500 M) of crude reaction mixture (starting material: **1h** and **2a**) in TCE-d_2.

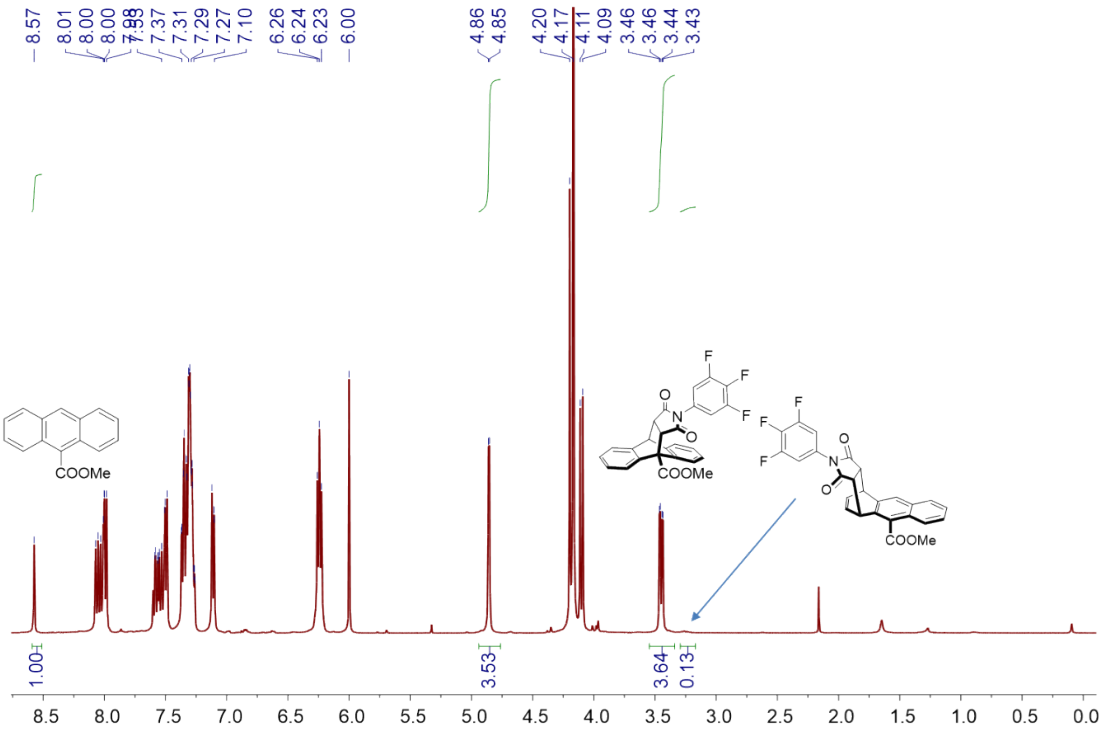


Figure S7. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2b**) in TCE-d_2.

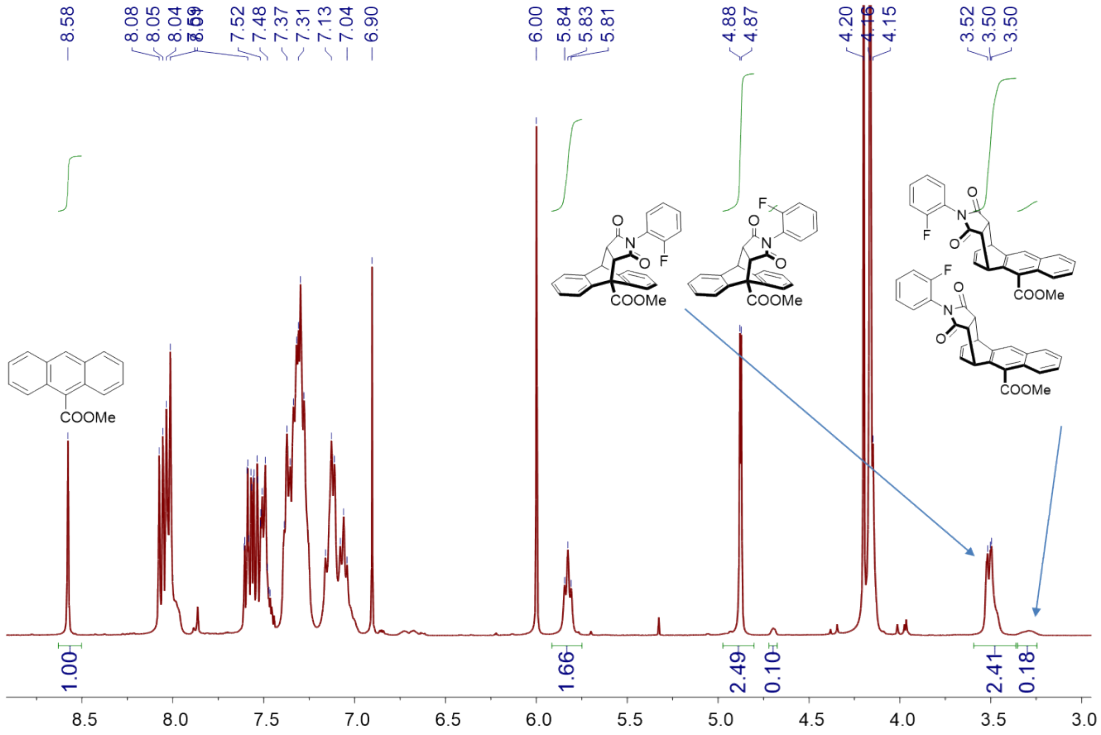


Figure S8. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2c**) in TCE-d_2.

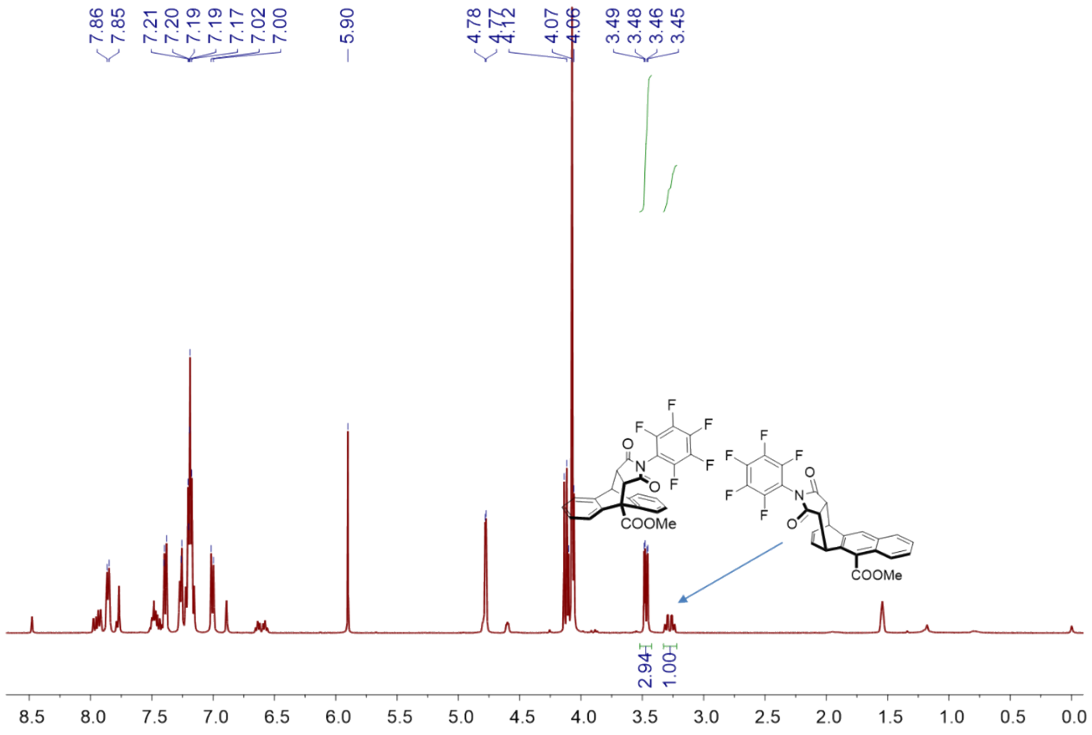


Figure S9. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2e**) in TCE-d_2.

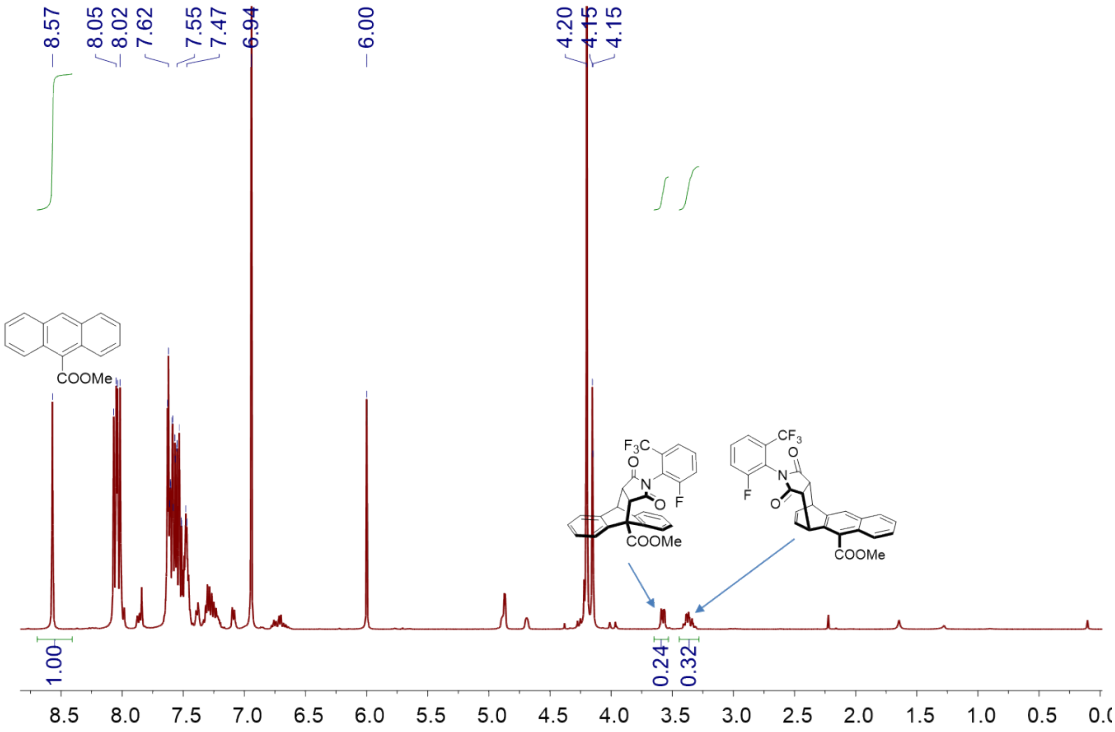


Figure S10. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2f**) in TCE-d_2.

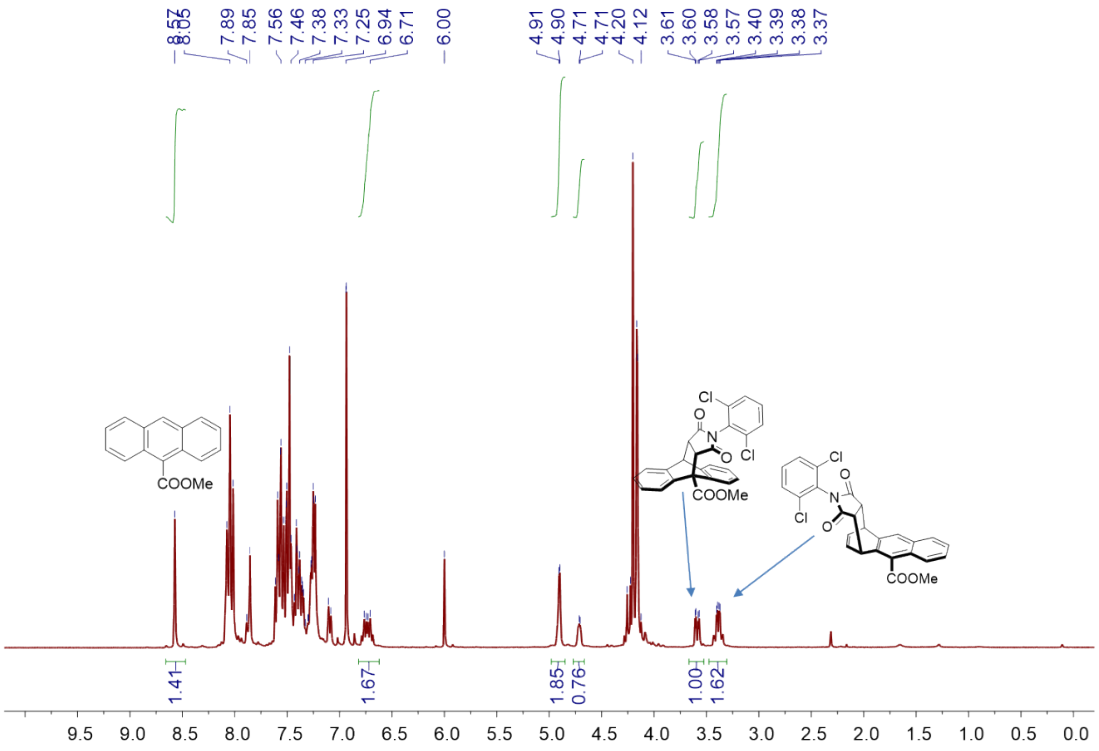


Figure S11. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2g**) in TCE-d_2.

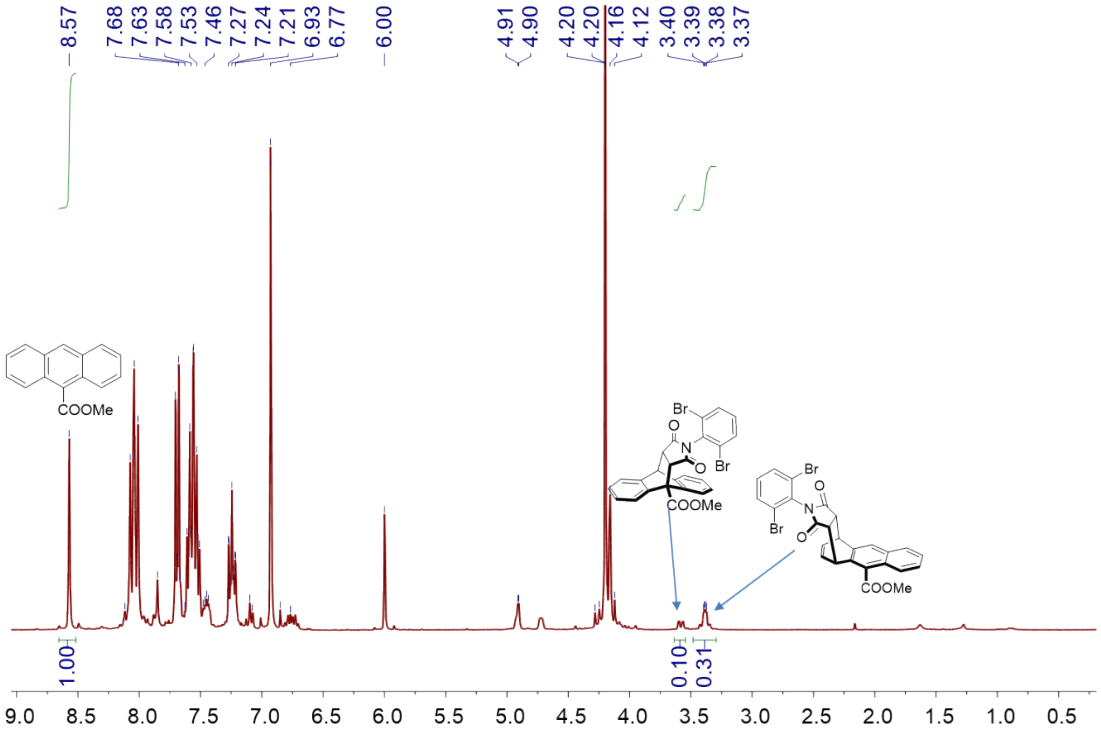


Figure S12. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2h**) in TCE-d_2.

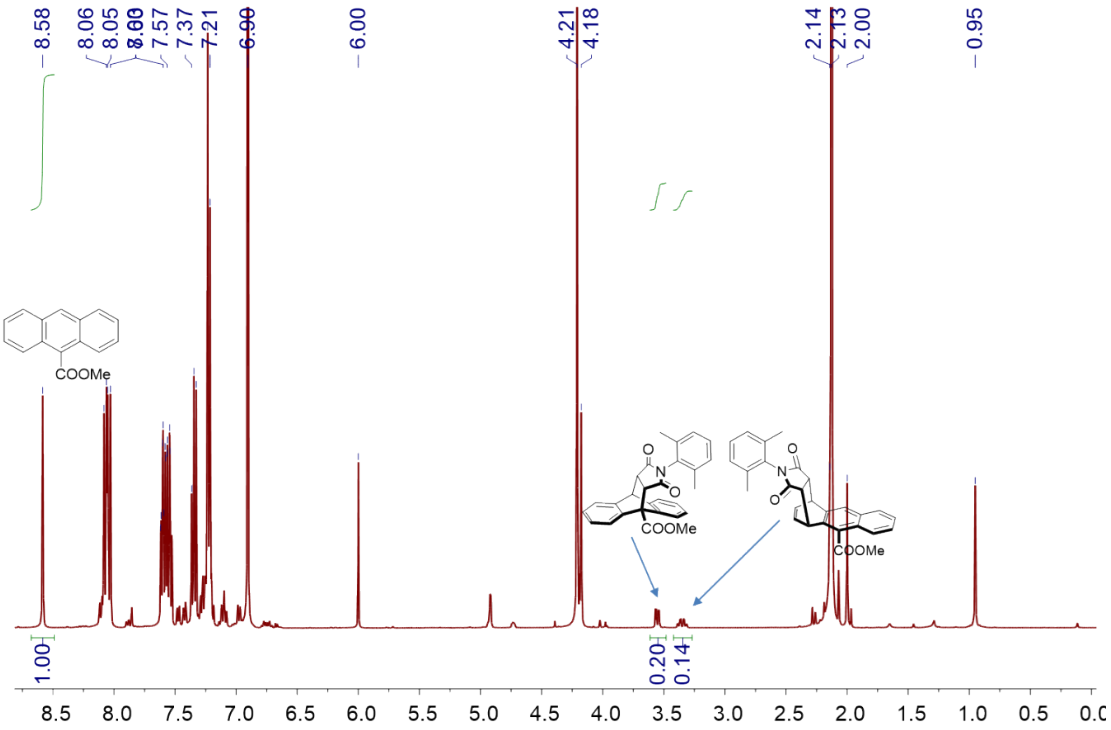


Figure S13. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2i**) in TCE-d_2.

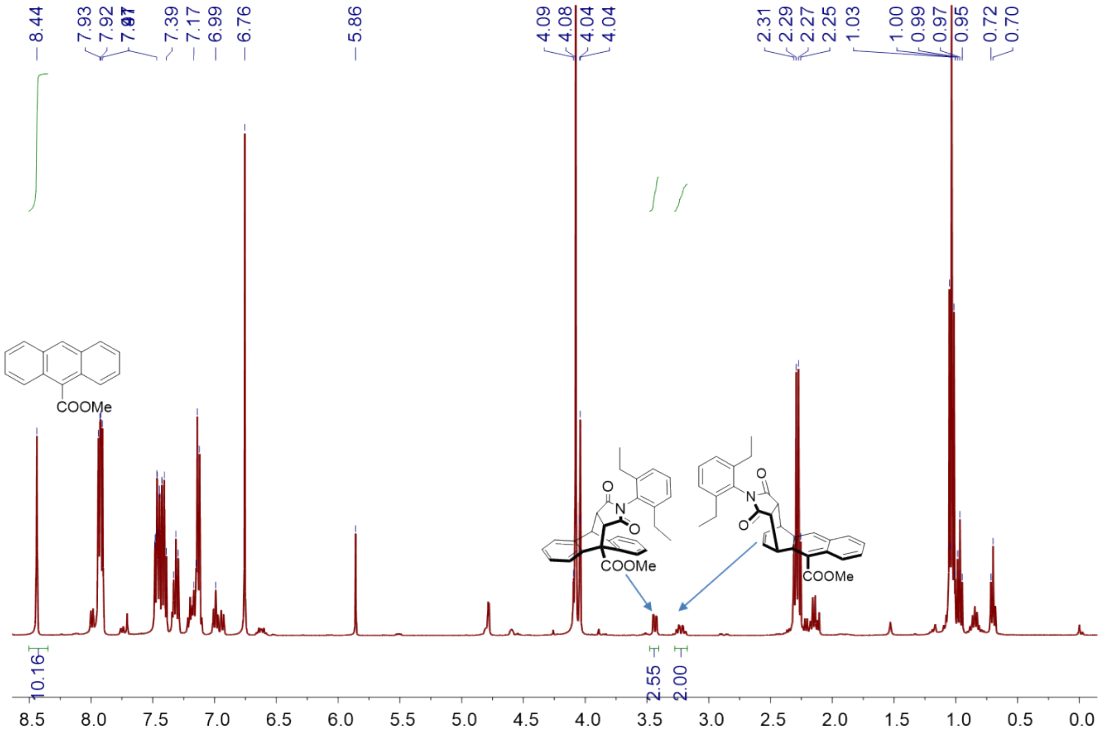


Figure S14. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2j**) in TCE-d_2.

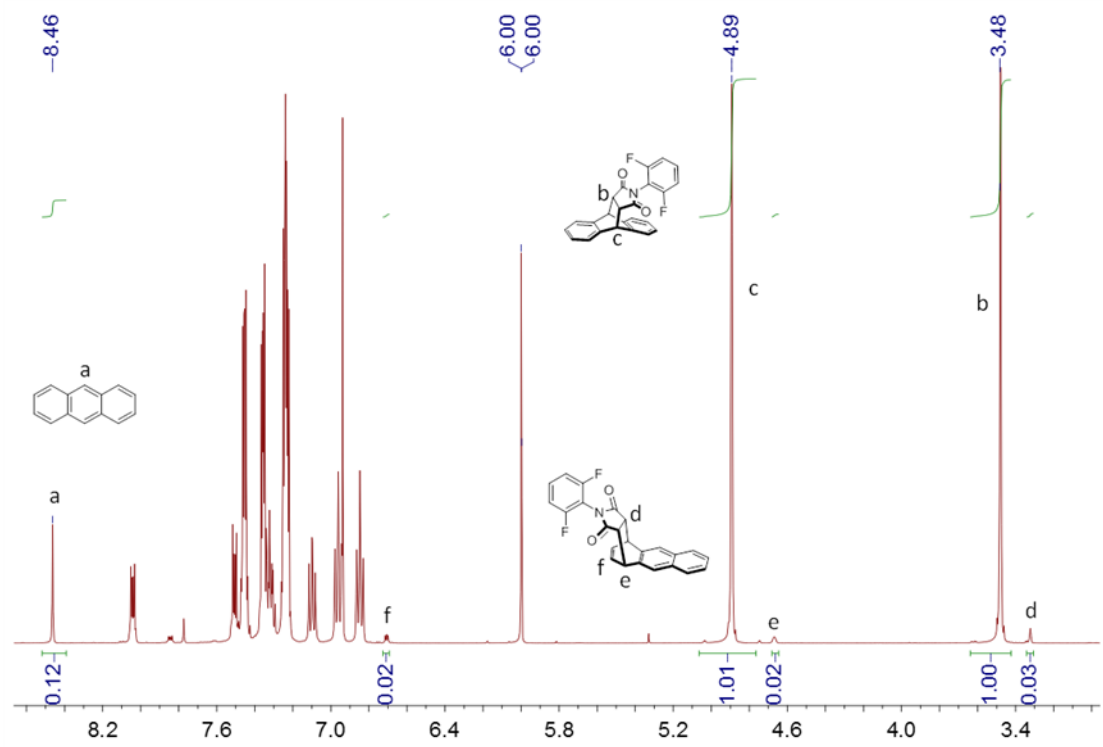


Figure S15. [1]H NMR spectrum (500 M) of crude reaction mixture (starting material: **2d** and **1a**) in TCE-d_2.

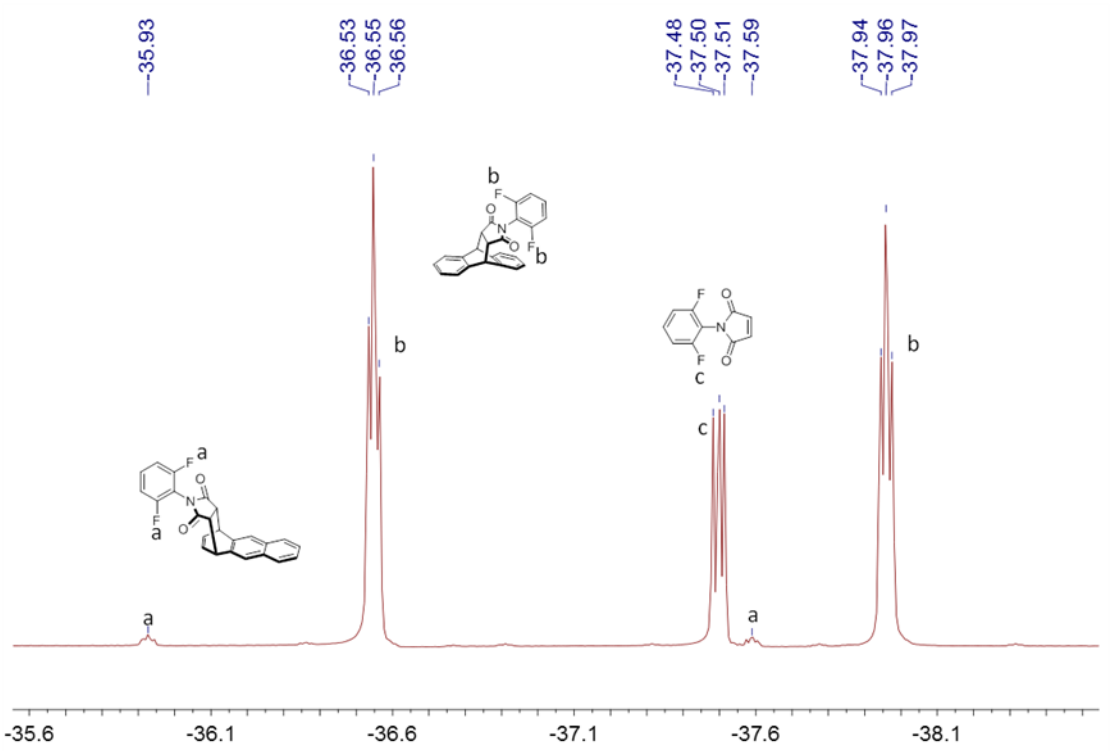


Figure S16. ^{19}F NMR spectrum (470 M) of crude reaction mixture (starting material: **2d** and **1a**) in TCE-d_2.

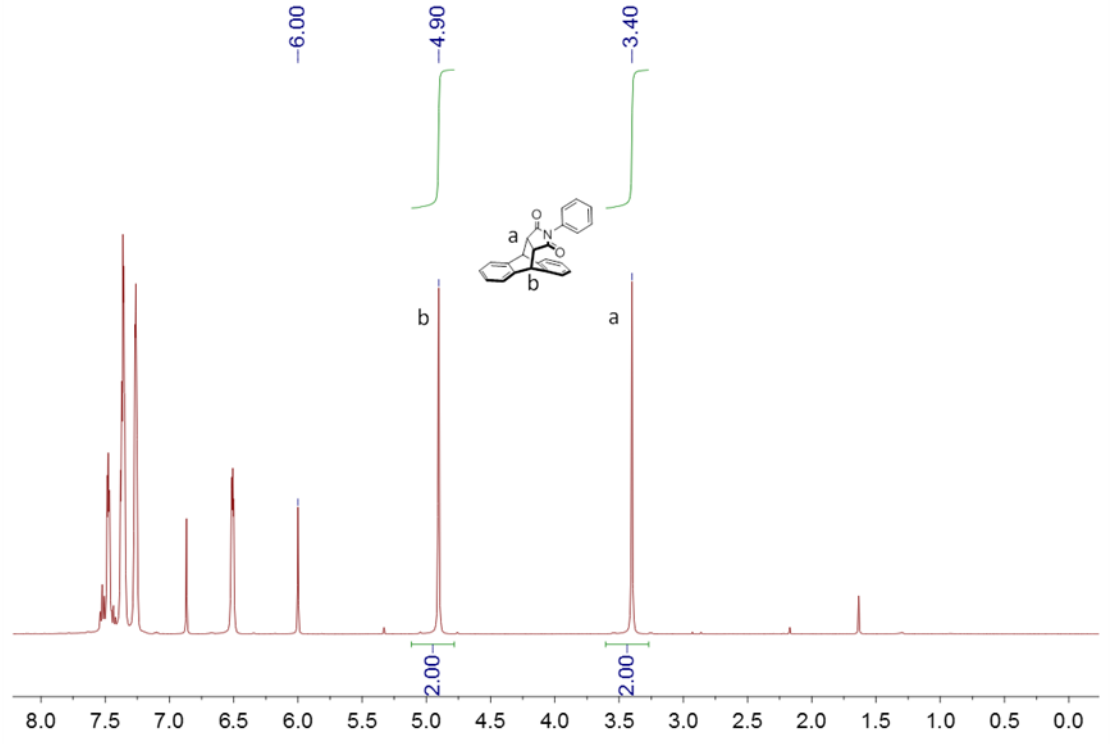


Figure S17. ^{1}H NMR spectrum (500 M) of crude reaction mixture (starting material: **1a** and **2b**) in TCE-d_2.

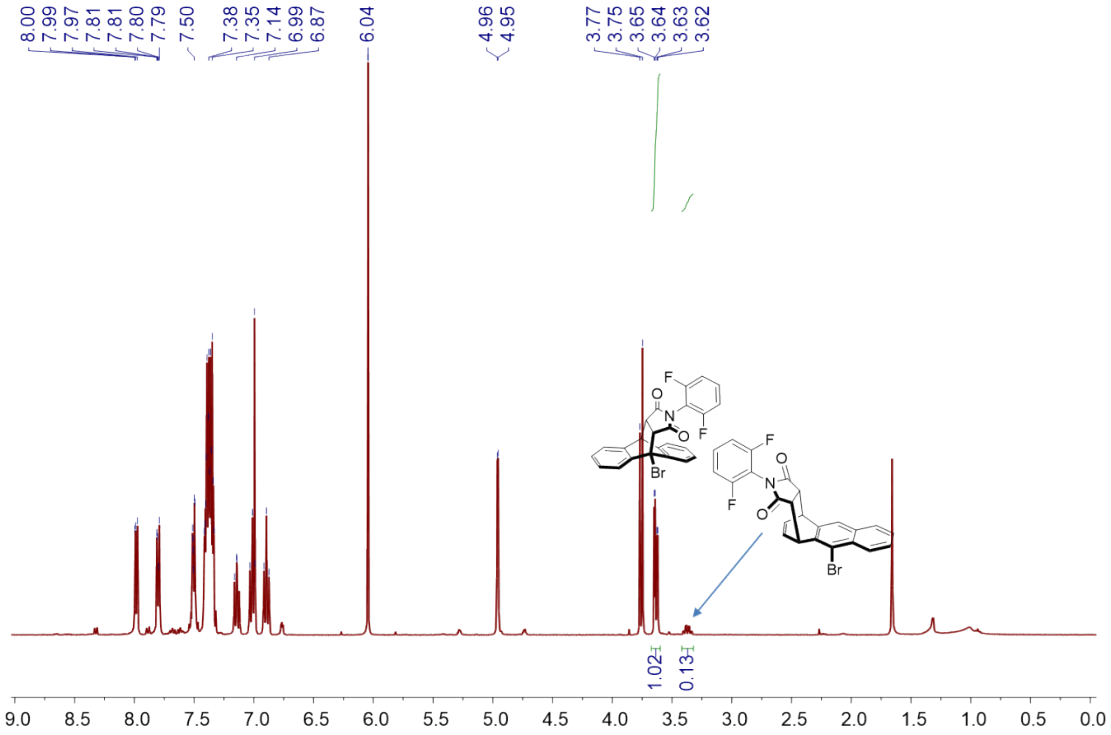


Figure S18. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1b**) in TCE-d_2.

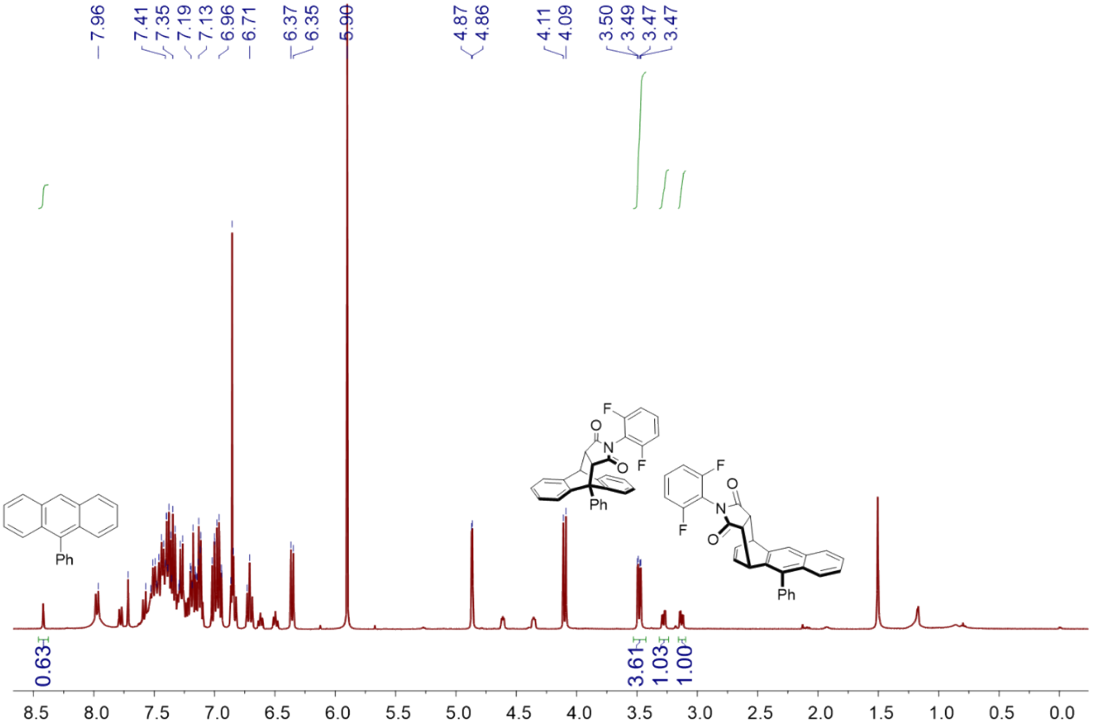


Figure S19. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1c**) in TCE-d_2.

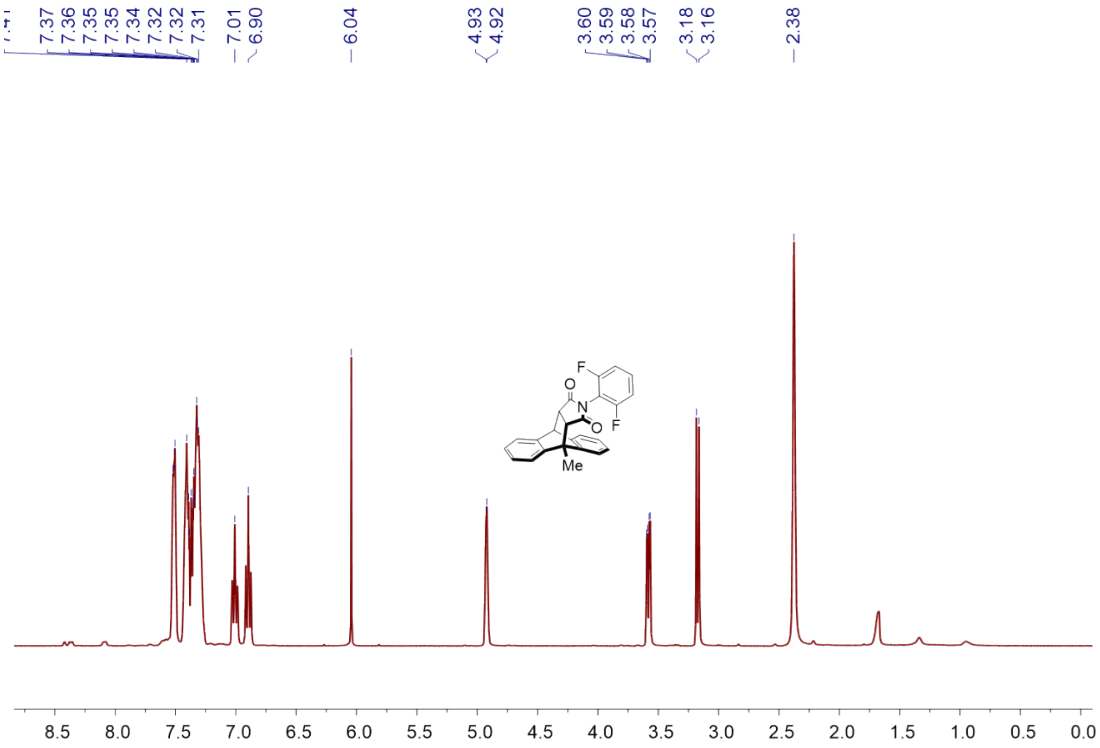


Figure S20. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1d**) in TCE-d_2.

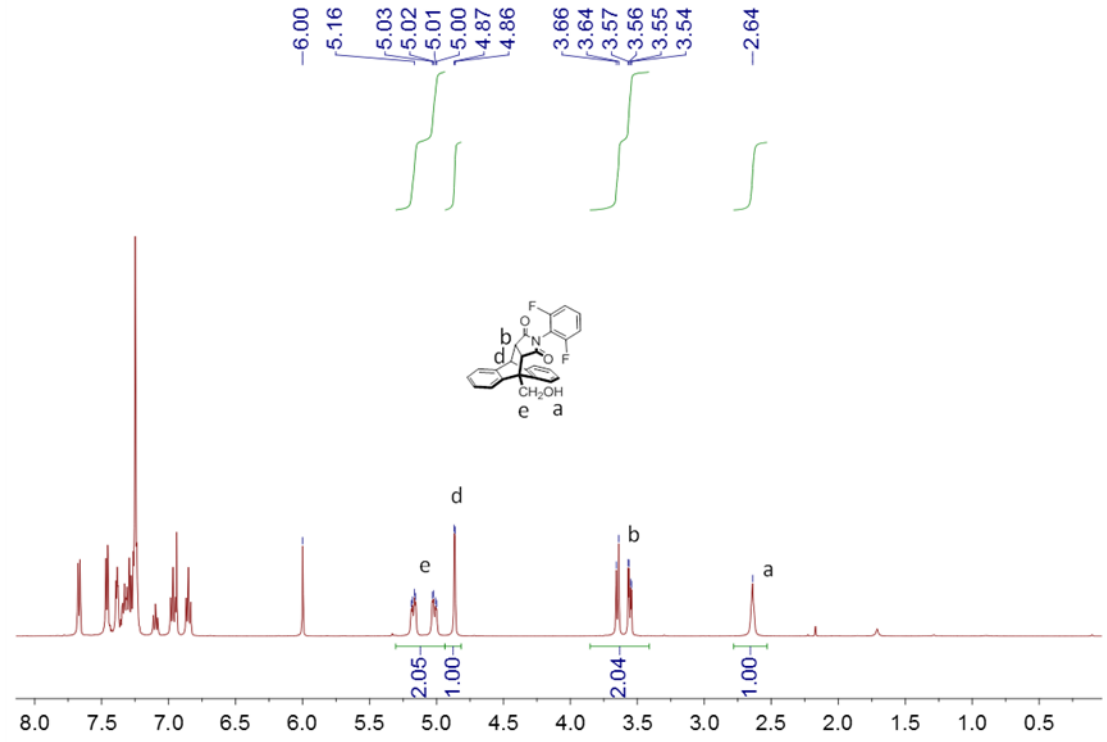


Figure S21. ^{1}H NMR spectrum (500 M) of crude reaction mixture (starting material: **2d** and **1e**) in TCE-d_2

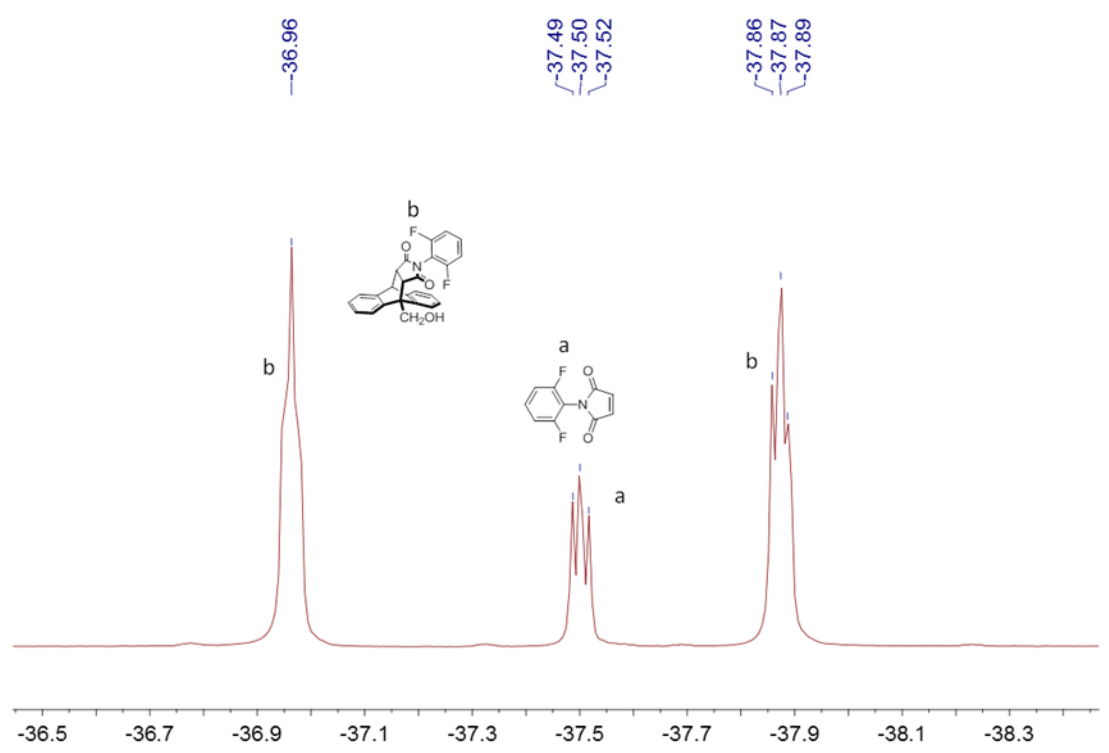


Figure S22. ^{19}F NMR spectrum (470 M) of crude reaction mixture (starting material: **2d** and **1e**) in TCE-d_2.

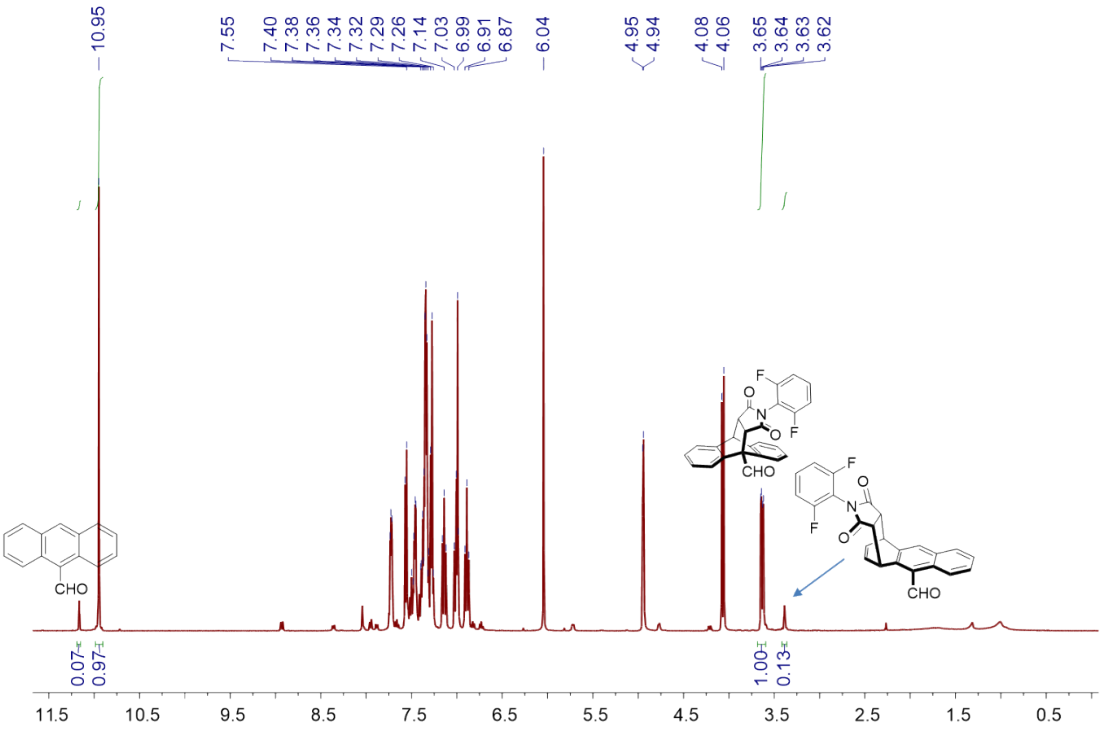


Figure S23. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1f**) in TCE-d_2.

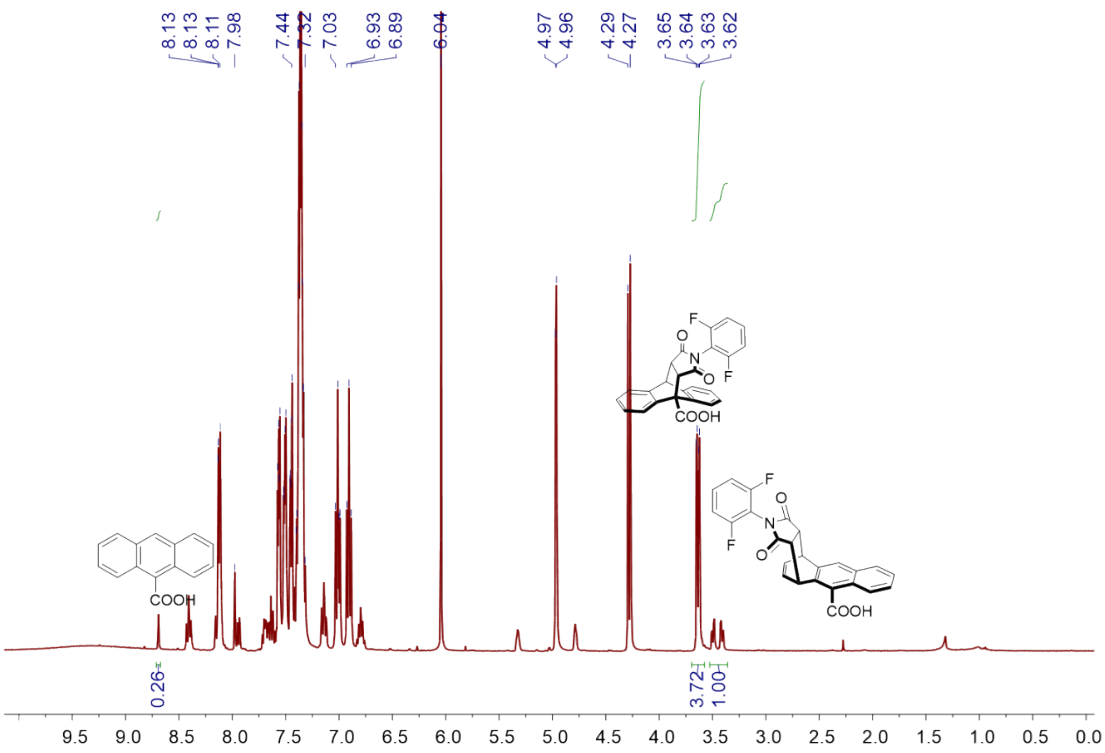


Figure S24. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1g**) in TCE-d_2.

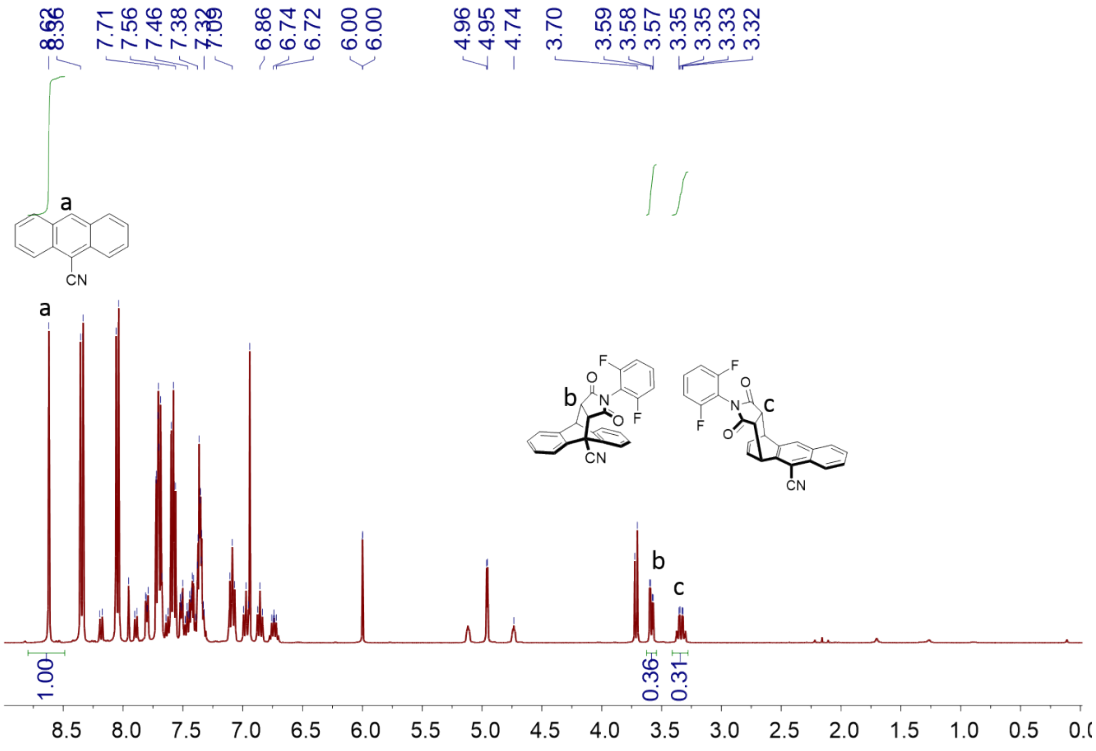


Figure S25. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1i**) in TCE-d_2.

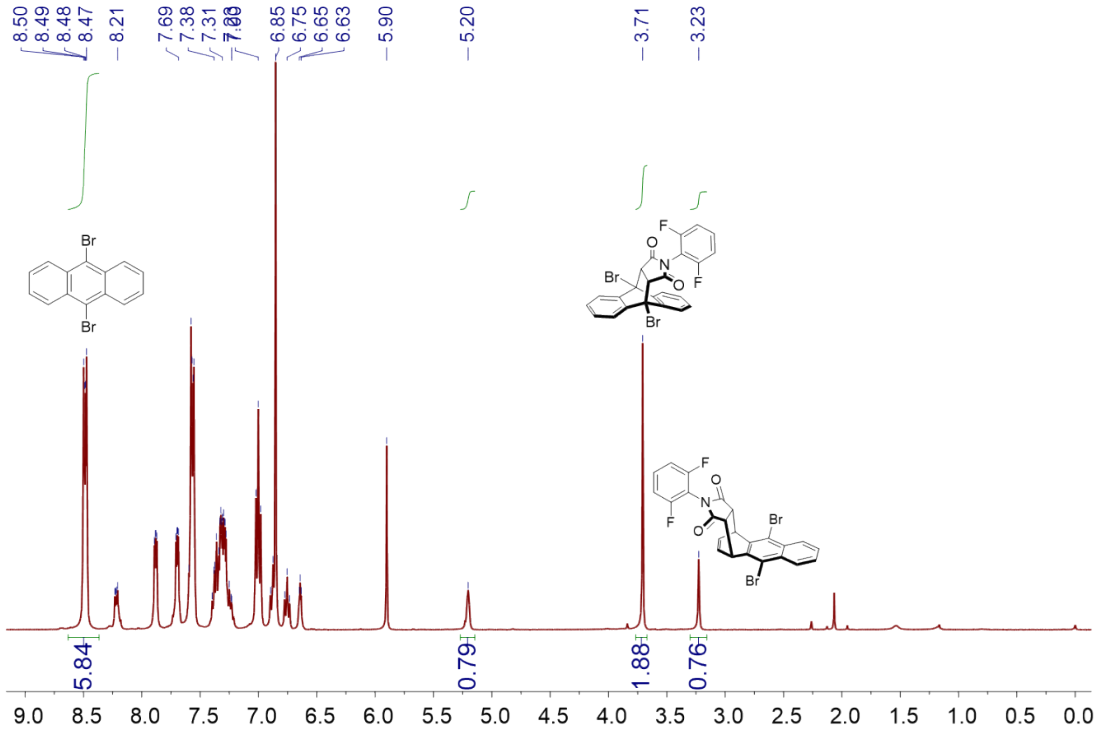


Figure S26. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1j**) in TCE-d_2.

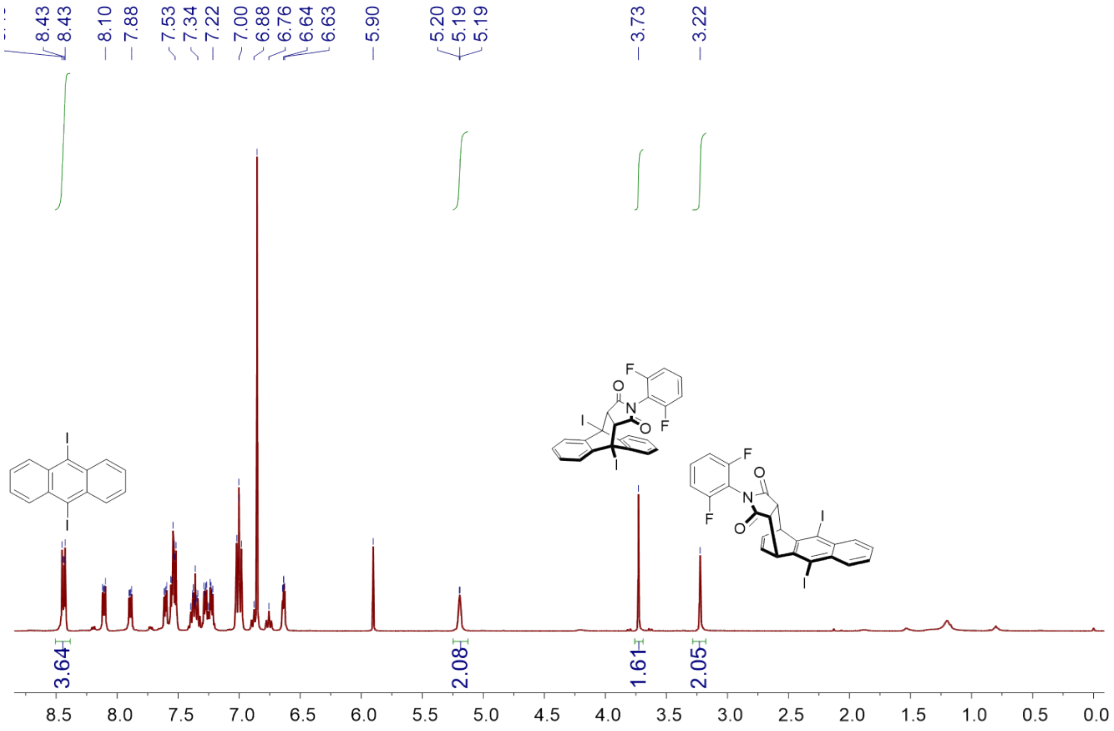


Figure S27. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1k**) in TCE-d_2.

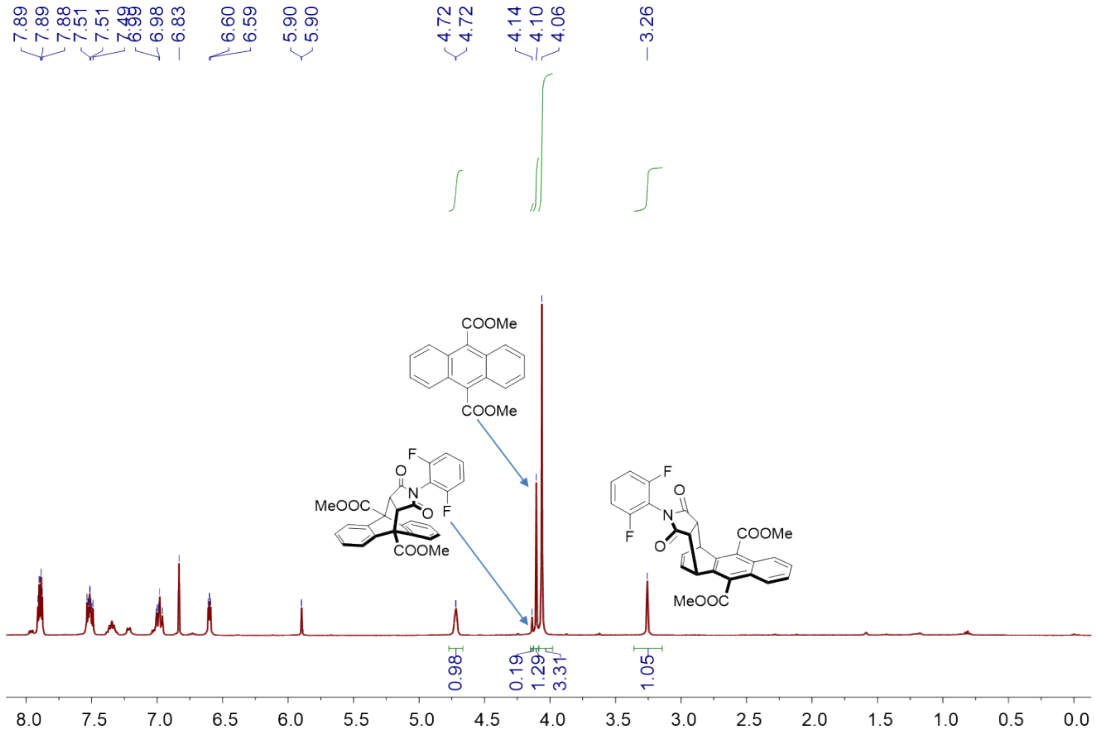


Figure S28. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1l**) in TCE-d_2.

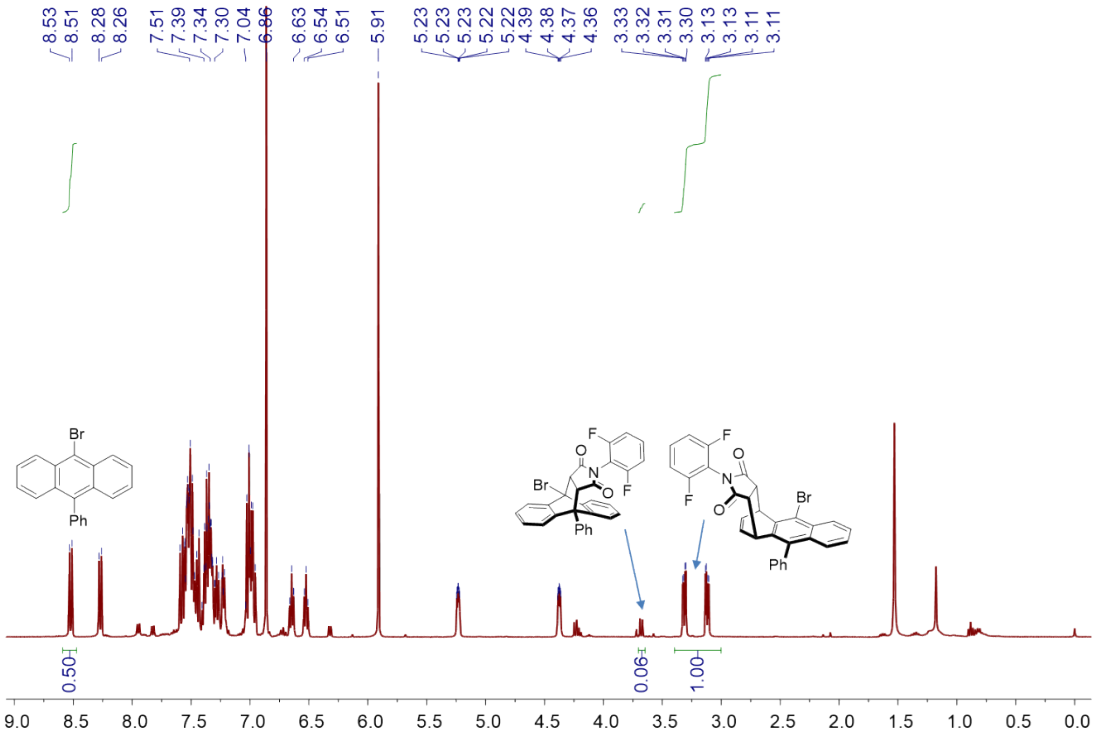


Figure S29. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1m**) in TCE-d_2.

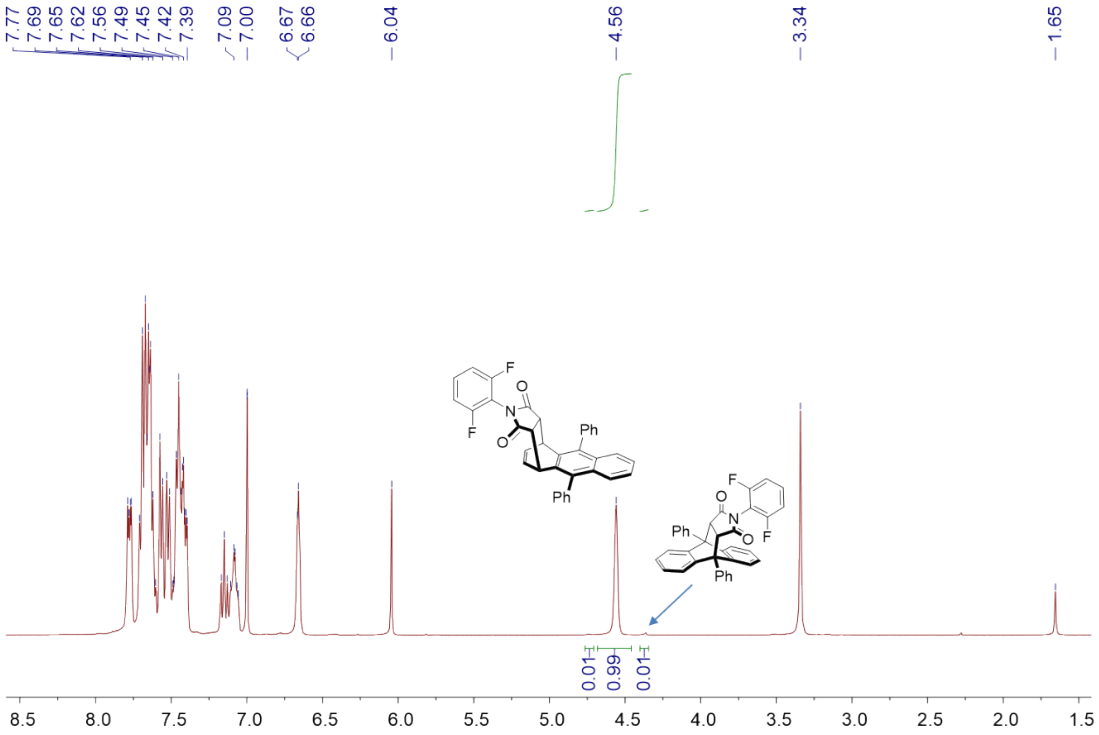


Figure S30. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **2d** and **1n**) in TCE-d_2.

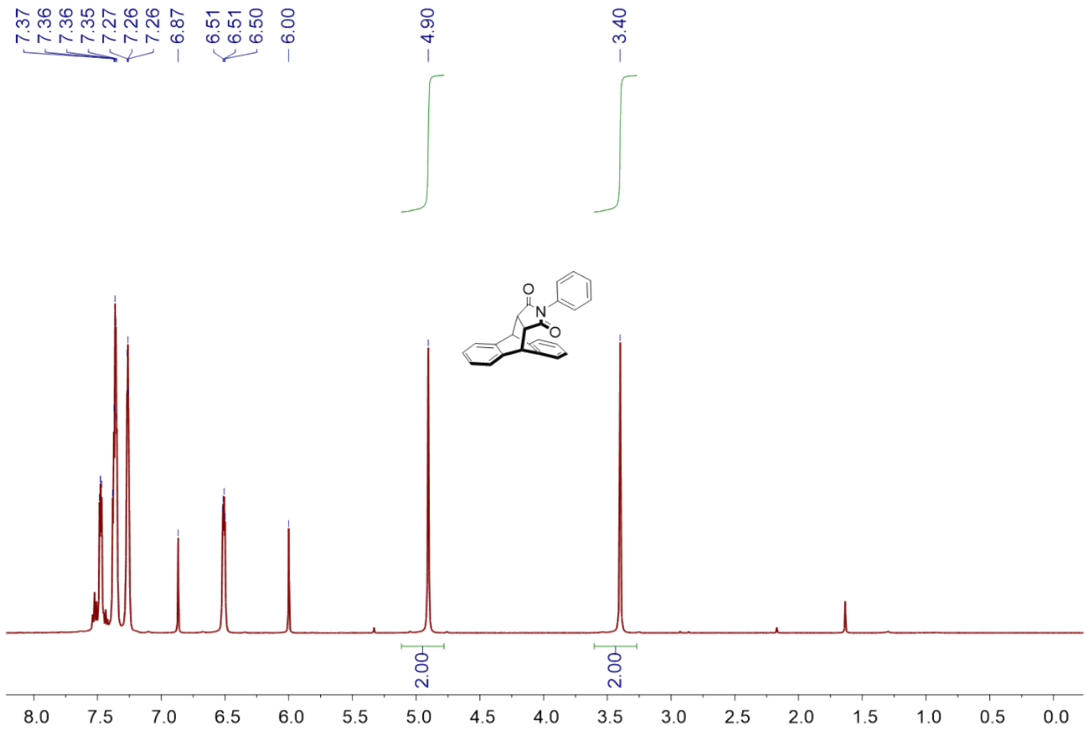


Figure S31. [1]H NMR spectrum (500 M) of crude reaction mixture (starting material: **1a** and **2a**) in TCE-d_2.

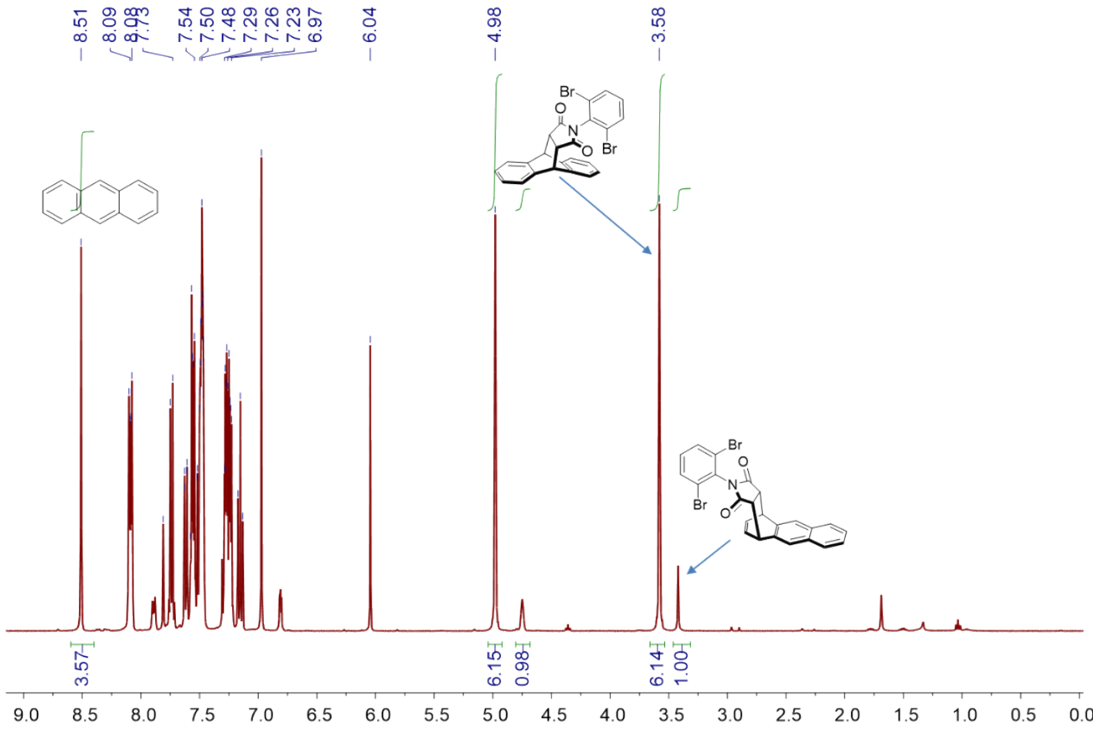


Figure S32. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1a** and **2h**) in TCE-d_2.

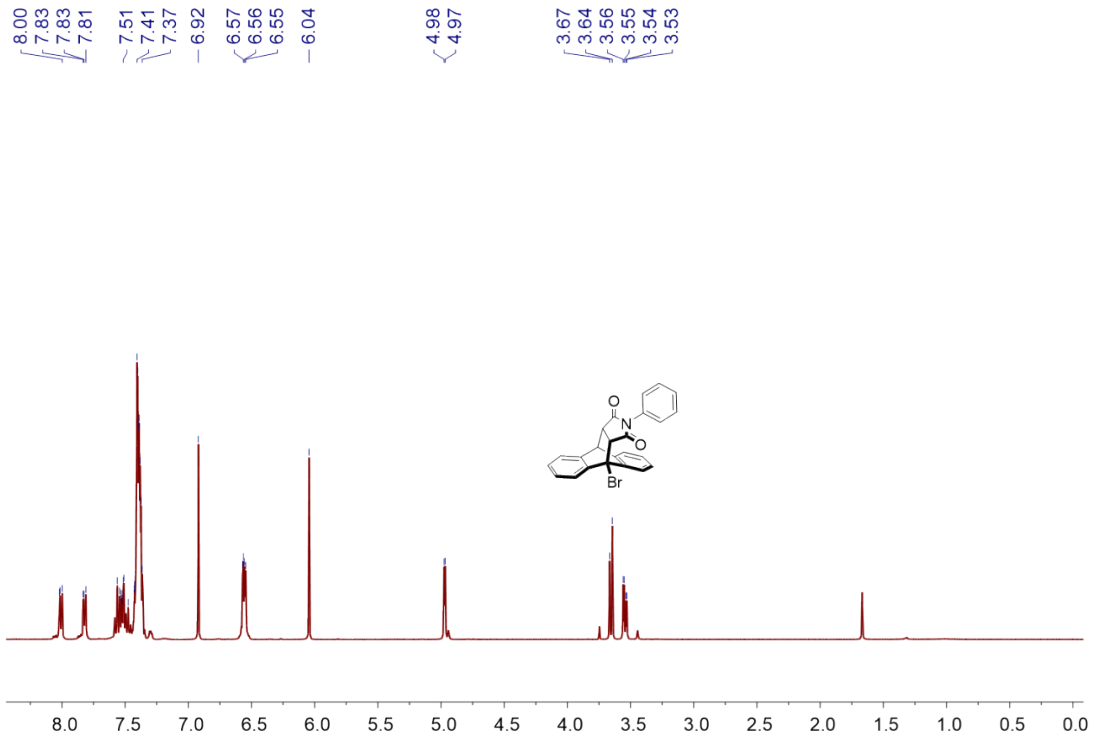


Figure S33. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1b** and **2a**) in TCE-d_2.

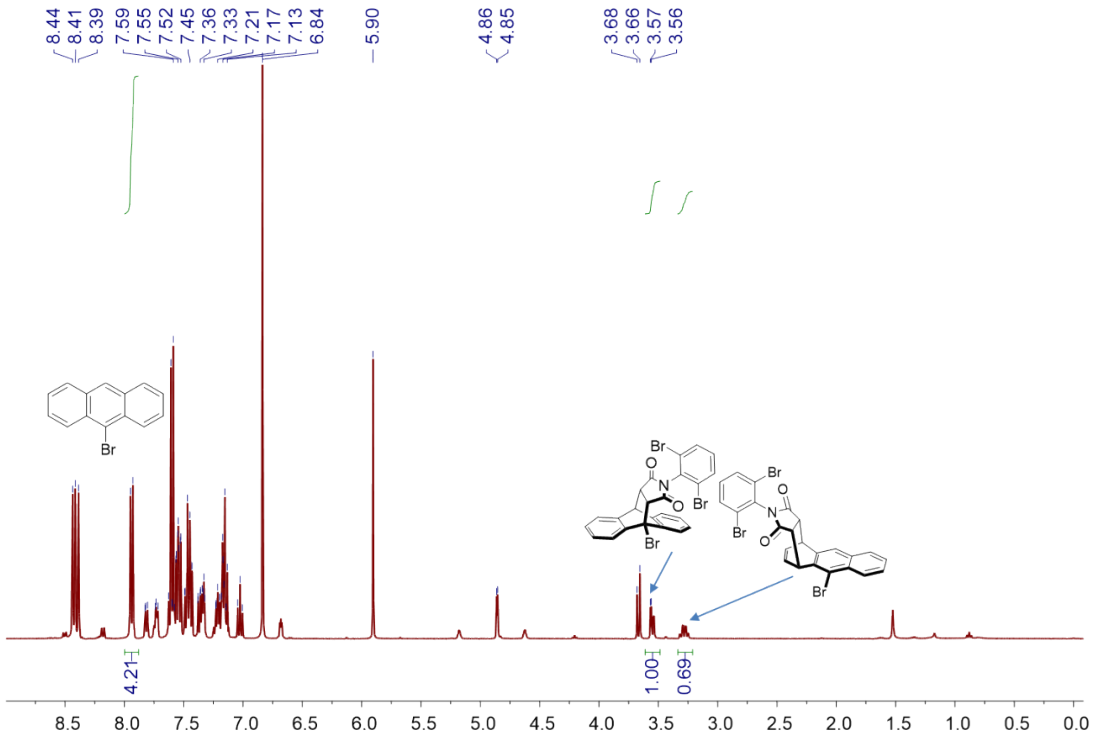


Figure S34. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1b** and **2h**) in TCE-d_2.

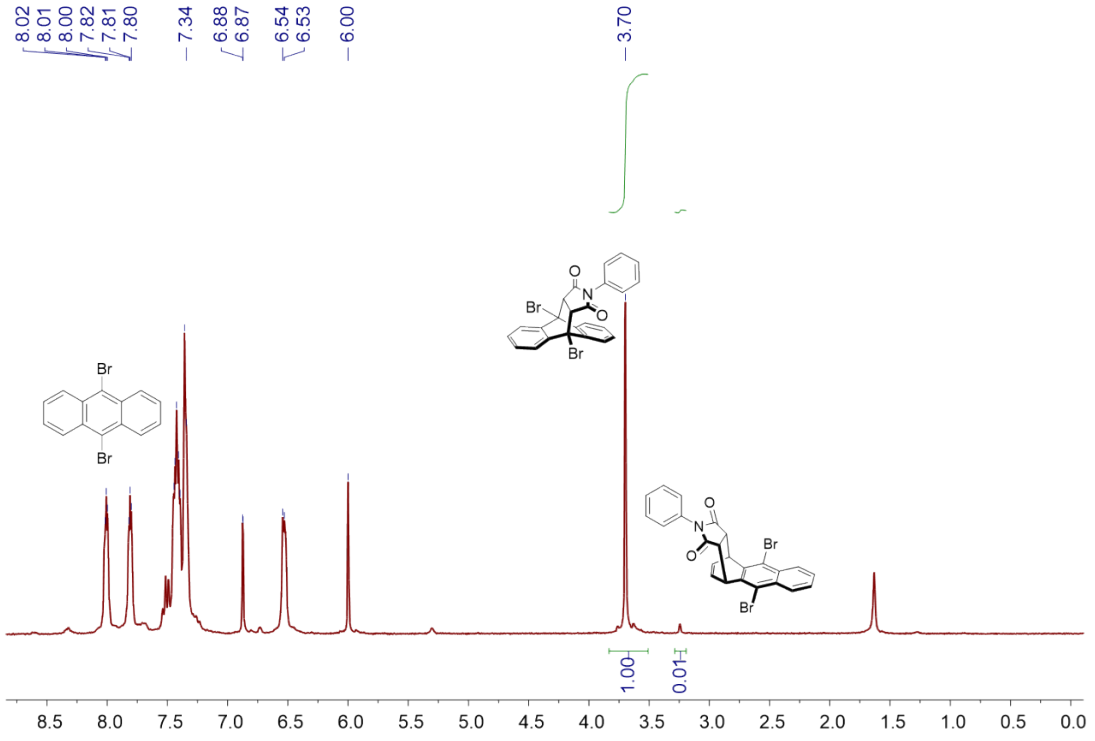


Figure S35. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1j** and **2a**) in TCE-d_2.

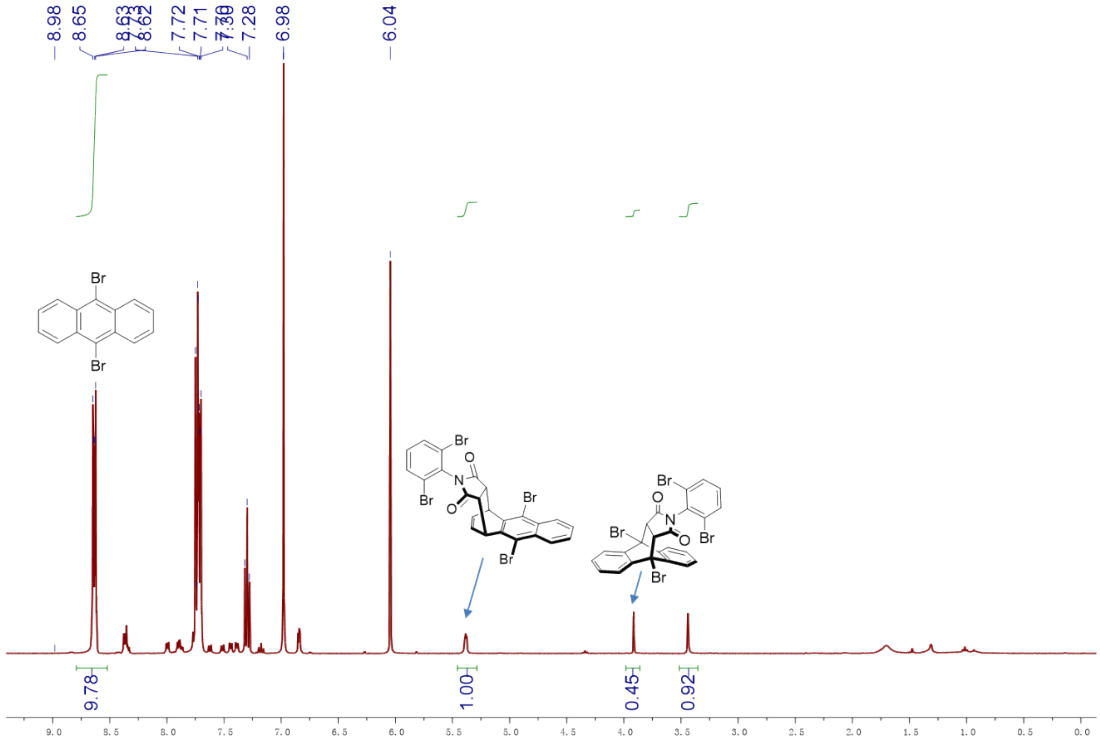


Figure S36. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1j** and **2h**) in TCE-d_2.

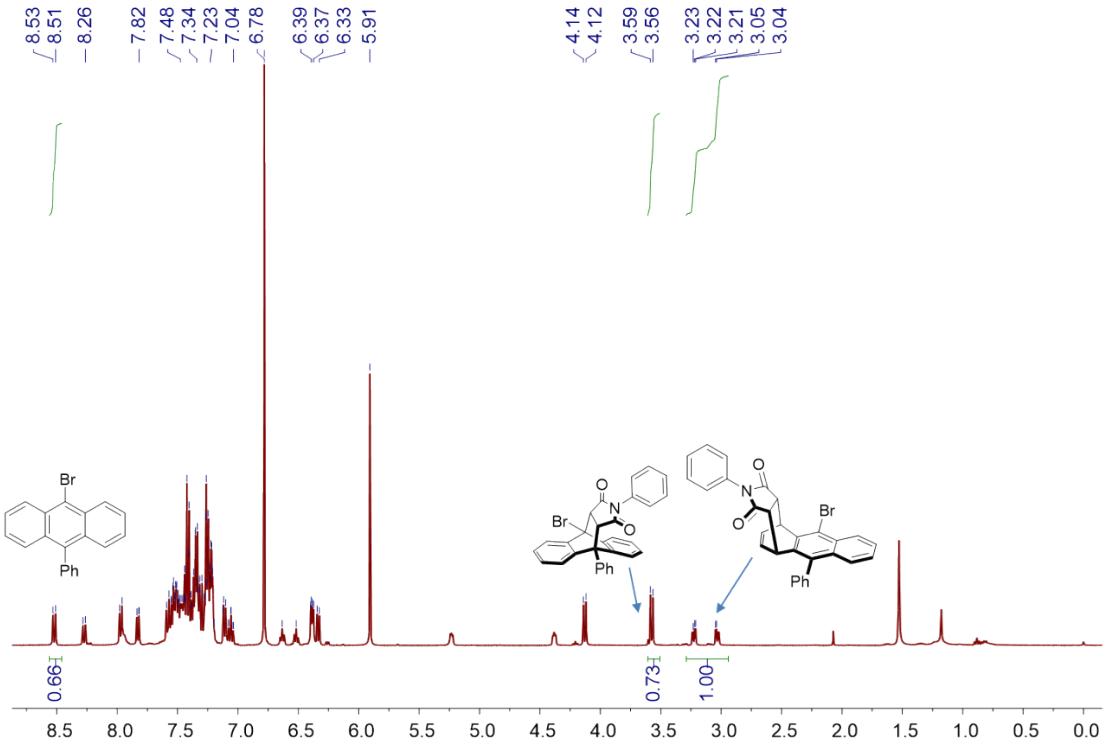


Figure S37. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1m** and **2a**) in TCE-d_2.

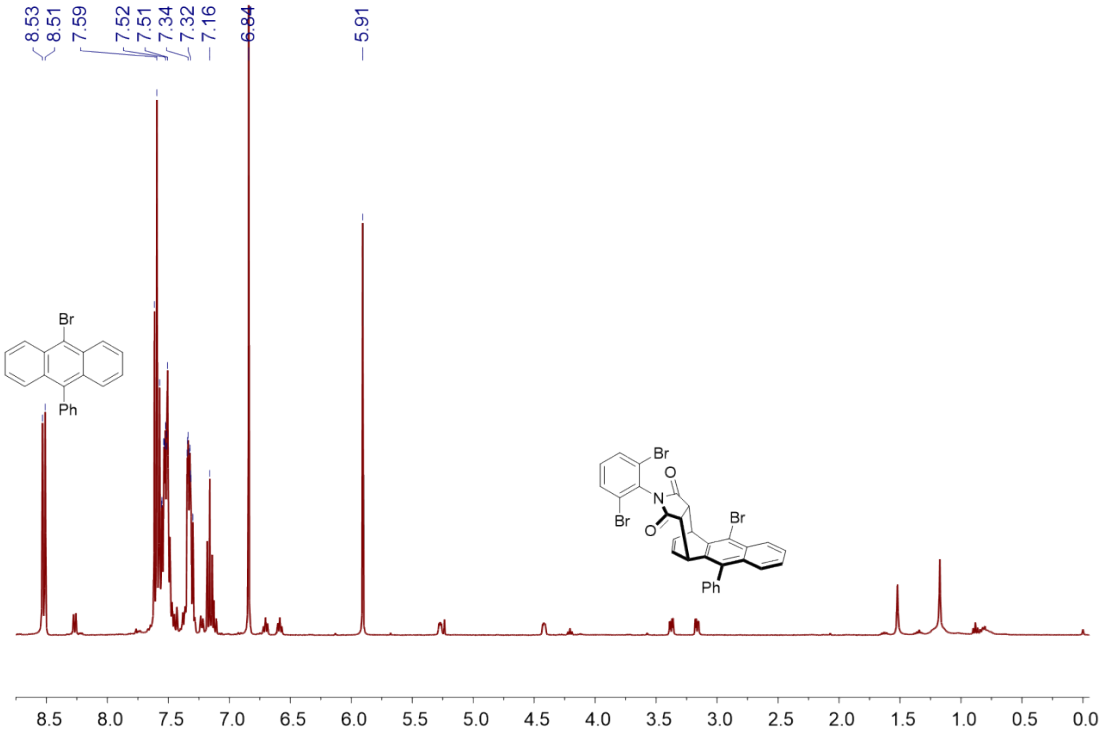


Figure S38. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1m** and **2h**) in TCE-d_2.

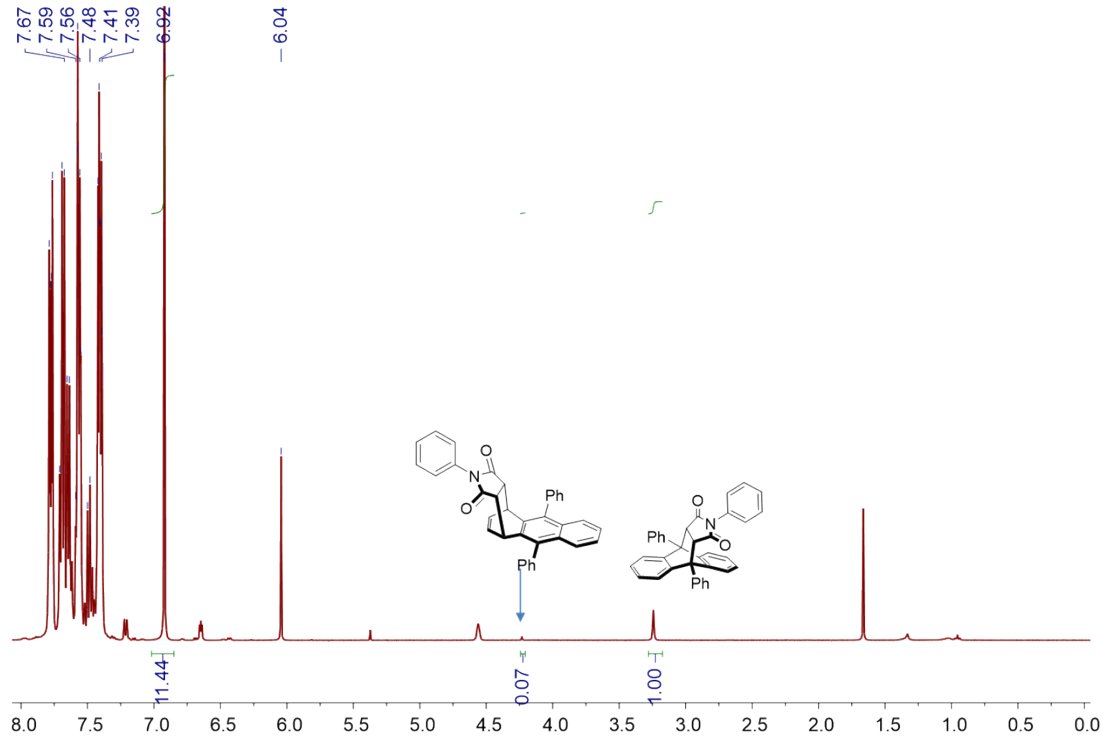


Figure S39. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1n** and **2a**) in TCE-d_2.

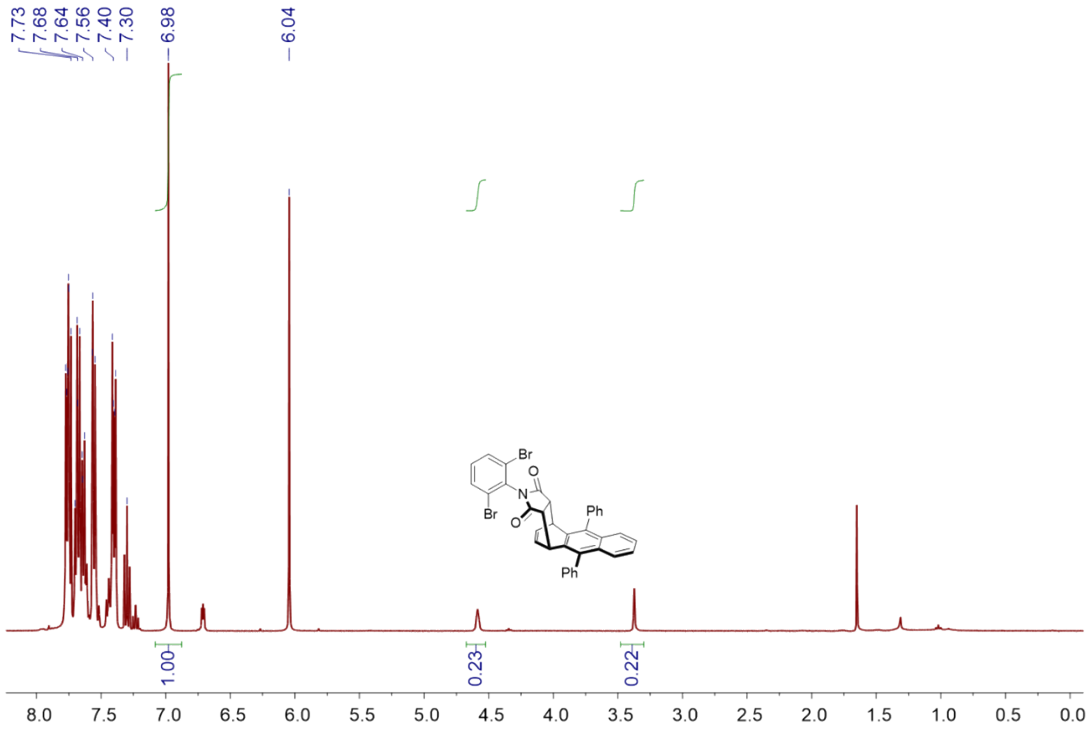


Figure S40. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1n** and **2h**) in TCE-d_2.

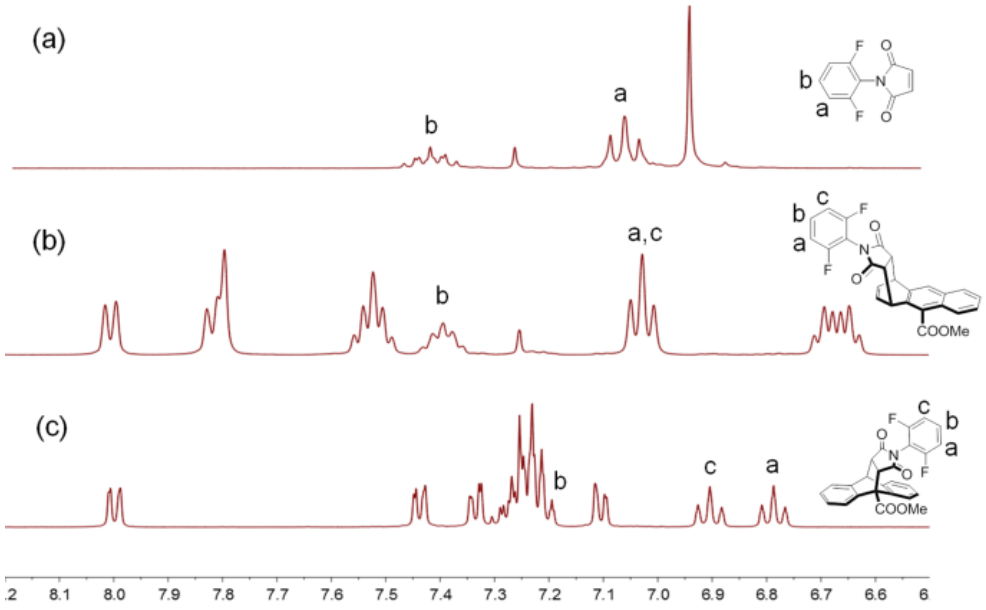


Figure S41. Aromatic region of ^{1}H NMR spectra of **2d**, **3d** and **4d** in C*D*Cl$_3$ from (a) to (c), respectively.

In ^{1}H NMR (***Figure S41***), we carefully assigned each resonance peak of **3d** and **4d**, especially the three phenyl protons marked with "a", "b" and "c". The proton "a", "b" and "c" of **4d** significantly shifted upfield, presumably resulting from shielding effect

of near phenyl ring. But in **3d**, the resonance of protons "a", "b" and "c" were only slightly shifted, indicating insignificant shield effect. Moreover, the resonance of protons "a" and "c" of **3d** was not distinguished. If **3d** was syn-1,4-adduct, the resonance of protons "a", "b" and "c" should have been shielded by naphthalene moieties and shifted upfield like those of **4d**. Therefore, we considered **3d** as an anti-1,4-adduct.

Table S1. DA reactions results between **1h** and **2d** in different solvents at 110 °C.

Entry	Solvent	$E_T(30)$ /kcal mol^{-1}	Ratio of anti-1,4-adduct /9,10-adduct
1	Octane	31.1	16:84
2	Toluene	33.9	19:81
3	TCE	39.4	22:78
4	DMSO	45.0	40:60

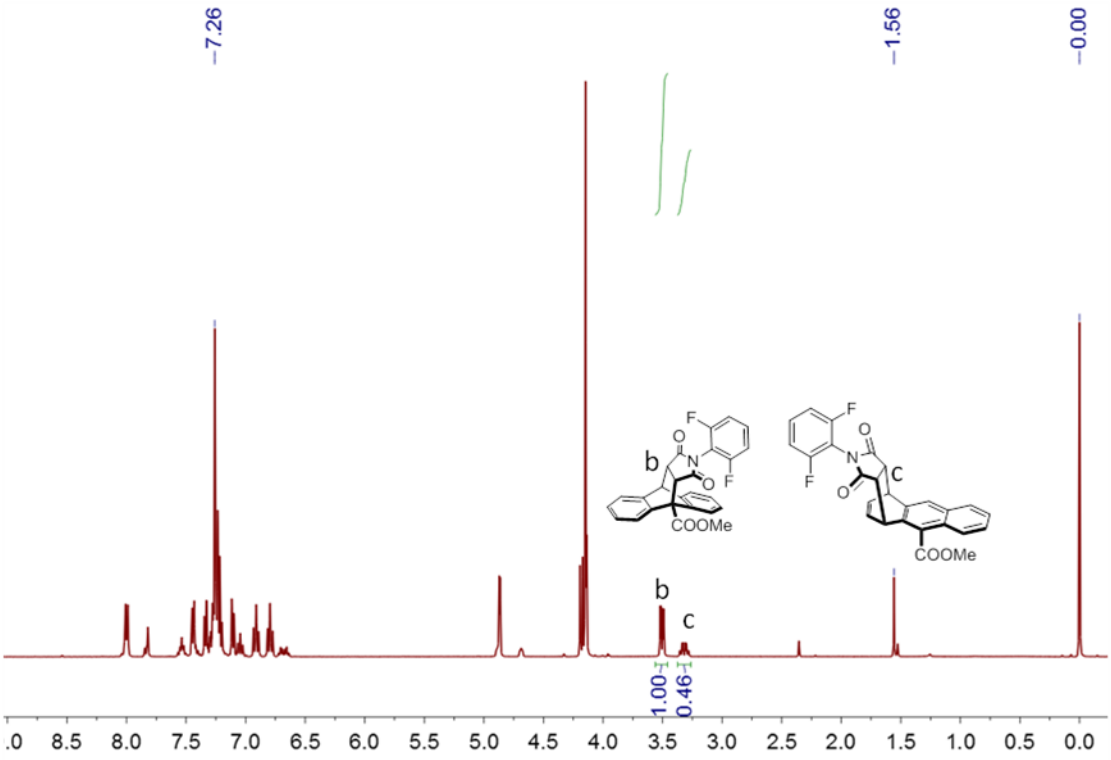


Figure S42. ^{1}H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2d**) in C*D*Cl_3. (The reaction was carried out in toluene.)

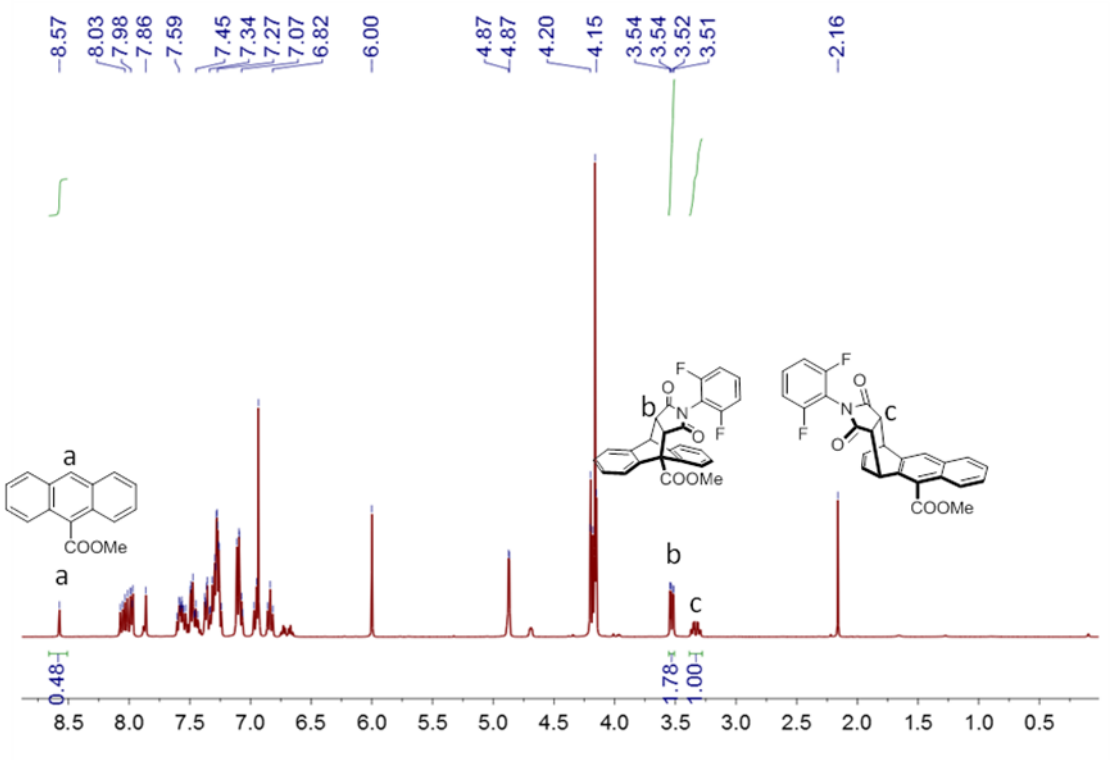


Figure S43. [1]H NMR spectrum (400 M) of crude reaction mixture (starting material: **1h** and **2d**) in TCE-d_2.

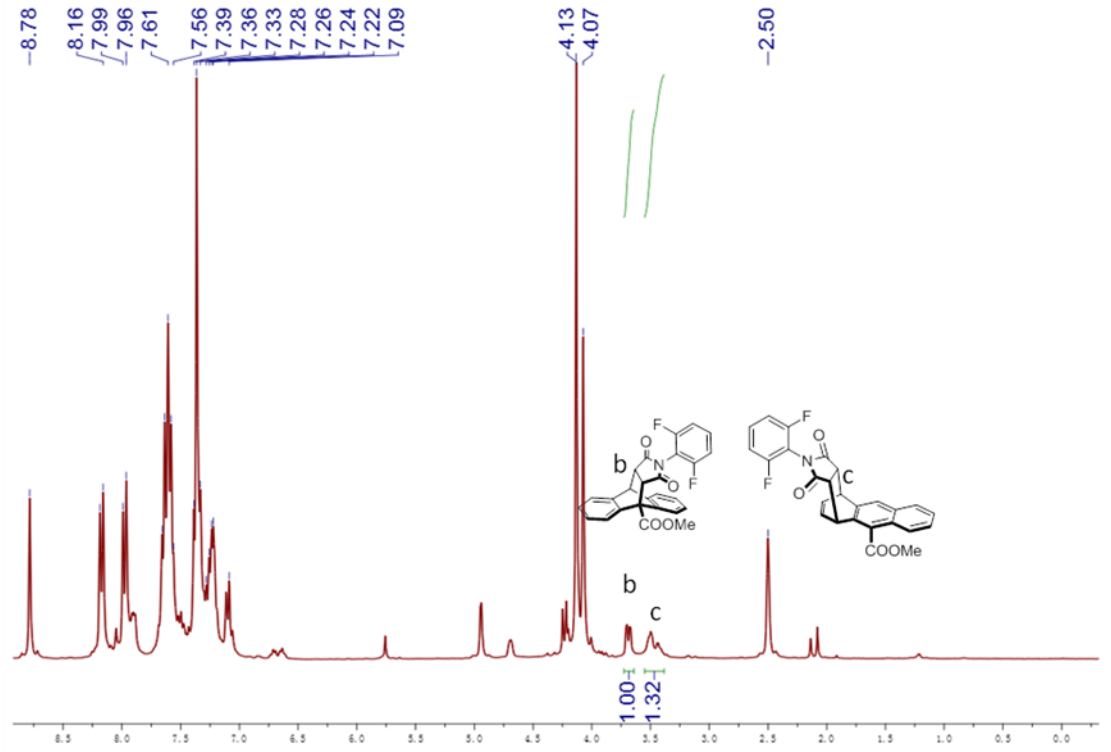


Figure S44. [1]H NMR spectrum (300 M) of crude reaction mixture (starting material: **1h** and **2d**) in DMSO-d_6.

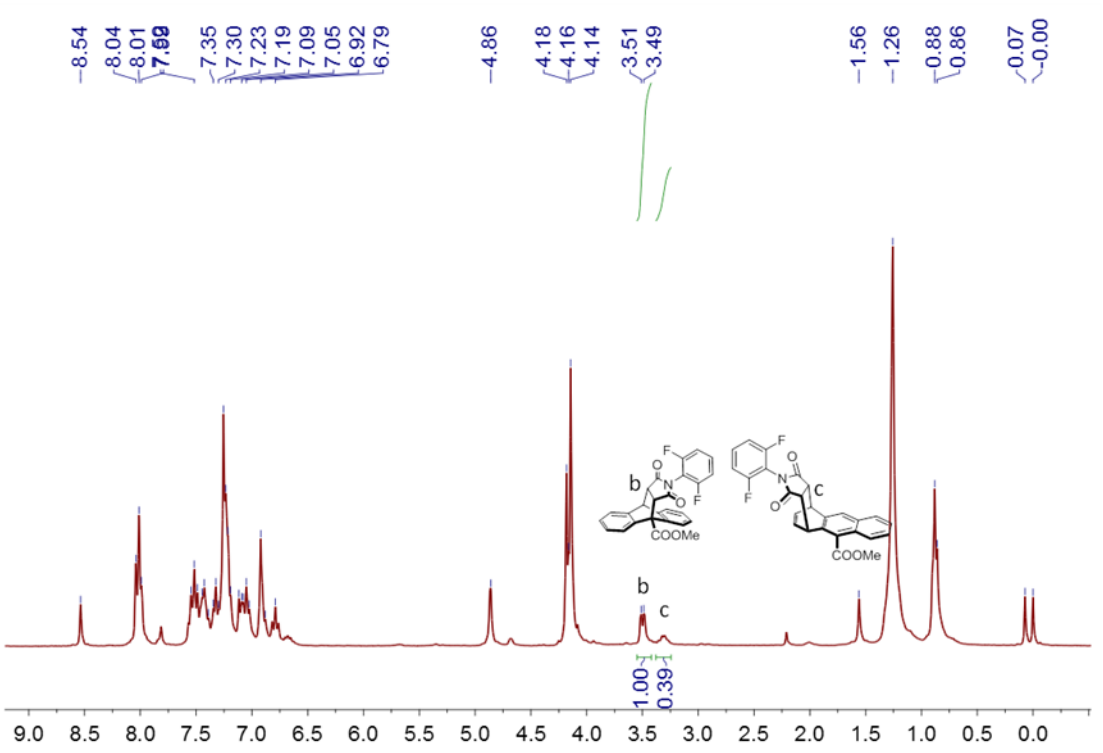
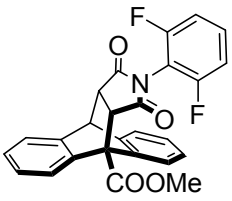
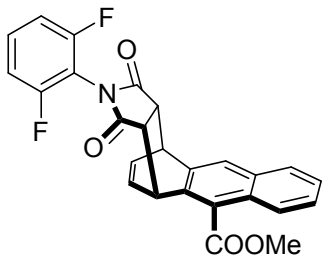


Figure S45. ^{1}H NMR spectrum (300 M) of crude reaction mixture (starting material: **1h** and **2d**) in C*D*Cl$_3$. (The reaction was carried out in octane.)

4. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra of Adducts



Methyl anthracene-9-carboxylate **1h** (310 mg, 1.31 mmol) and *N*-(2,6-Difluorophenyl)maleimide **2d** (274 mg, 1.29 mmol) were added to toluene (5 mL) in a flask. The reaction mixture was heated and stirred at 110 °C for 40 h. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (4:1, v/v) as eluent, to give **1h** and **2d** as pale solid (76 mg, 13%), with PE/CH_2Cl_2 (1:1, v/v) to CH_2Cl_2 as eluent, to give product **4d** as a white solid (328 mg, 56%), with PE/CH_2Cl_2 (1:2, v/v) to CH_2Cl_2 as eluent, to give product **3d** as a white solid (76 mg, 13%). **4d:** ^{1}H NMR (400 MHz, $CDCl_3$): δ8.01-7.99 (1H, dd), 7.45-7.43 (1H, dd), 7.35-7.32 (1H, dd), 7.29-7.19 (5H, m), 7.12-7.09 (1H, dd), 6.93-6.88 (1H, t), 6.81-6.77 (1H, t), 4.87-4.86 (1H, d), 4.19-4.16 (1H, d), 4.14 (3H, s), 3.51-3.48 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$): δ173.8, 173.2, 170.0, 158.0, 157.9, 141.0, 140.4, 137.5, 136.3, 131.1, 127.6, 127.6, 127.5, 127.0, 125.4, 125.3, 124.2, 123.1, 111.9, 108.6, 56.6, 52.6, 49.0, 47.8, 46.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ-38.2, -39.5. Elem. Anal.: Calcd. for $C_{26}H_{17}F_2NO_4$: C, 70.11; H, 3.85; N, 3.14. Found: C, 69.79; H, 3.85; N, 3.01.



3d: ^{1}H NMR (400 MHz, $CDCl_3$):δ8.01-7.99 (1H, d), 7.83-7.80 (2H, m), 7.56-7.49 (2H, m), 7.43-7.36 (1H, m), 7.05-7.01 (2H, t), 6.71-6.63 (2H, m), 4.88 (1H, s), 4.66 (1H, s), 4.13 (3H, s), 3.32-3.24 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$):δ174.8, 174.6, 168.5, 158.4, 138.7, 138.0, 134.2, 133.8, 132.0, 131.3, 128.8, 128.2, 127.3, 126.7, 126.1, 125.3, 124.6, 112.2, 109.3, 52.8, 46.6, 46.2, 41.9, 39.6. ^{19}F NMR (282 MHz, $CDCl_3$):δ-37.5, -39.0. HRMS: Calcd. for $C_{26}H_{18}F_2NO_4$, 446.11984 ([M+H$^+$]/z), Found: $C_{26}H_{18}F_2NO_4$, 446.12085 ([M+H$^+$]/z).

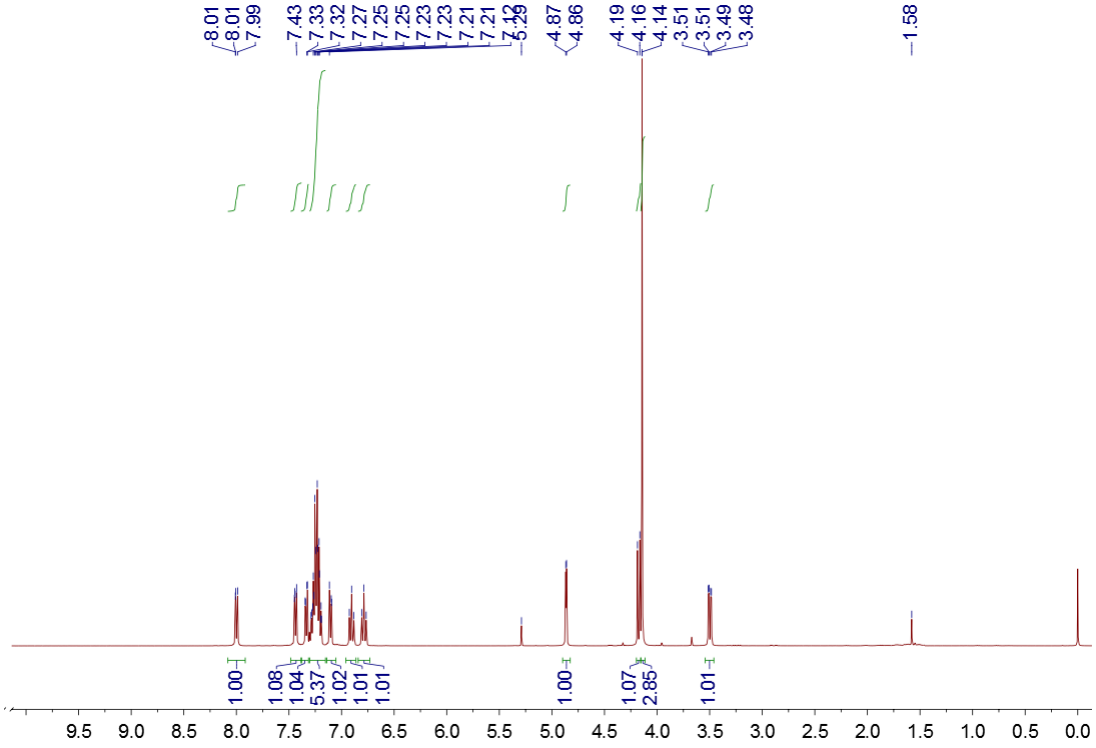


Figure S46. ^{1}H NMR spectrum (400 M) of **4d** in C*D*Cl_3.

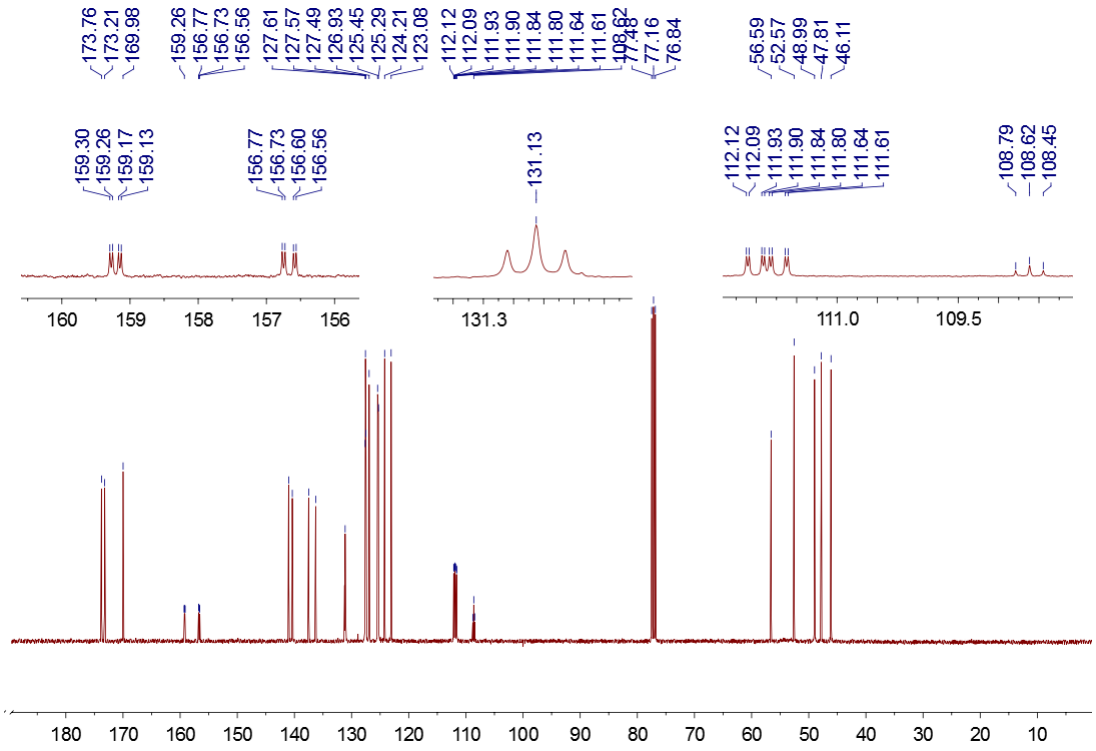


Figure S47. ^{13}C NMR spectrum (100 M) of **4d** in C*D*Cl$_3$.

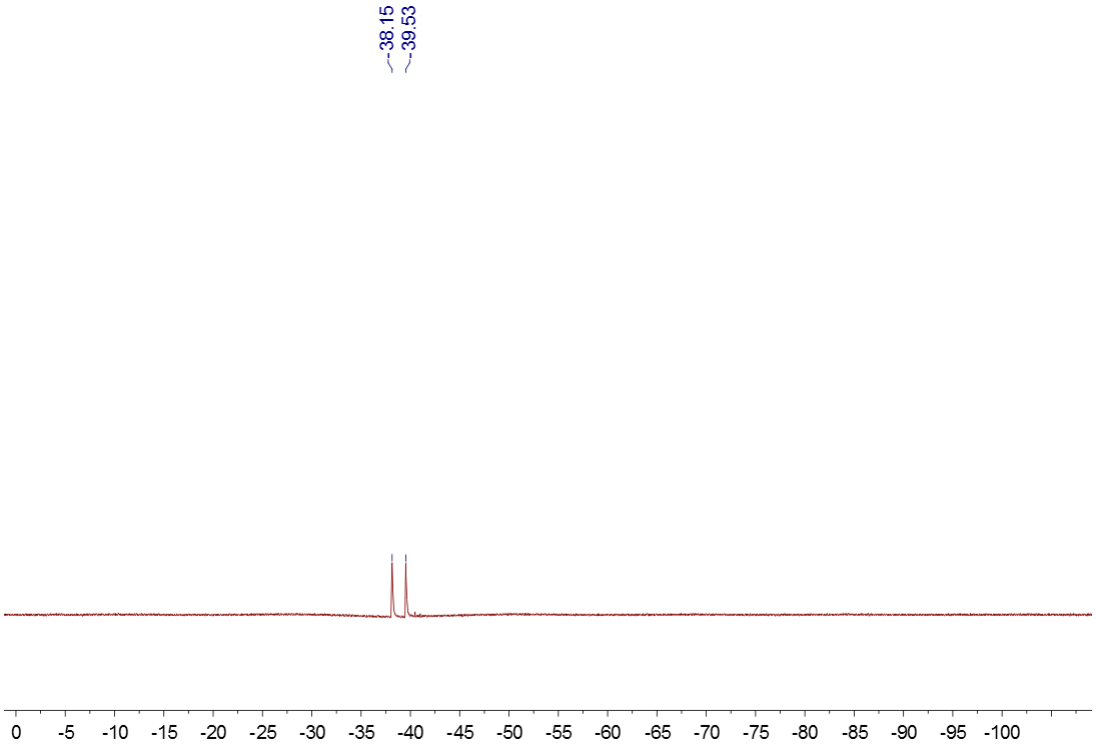


Figure S48. ^{19}F NMR spectrum (282 M) of **4d** in C*D*Cl$_3$.

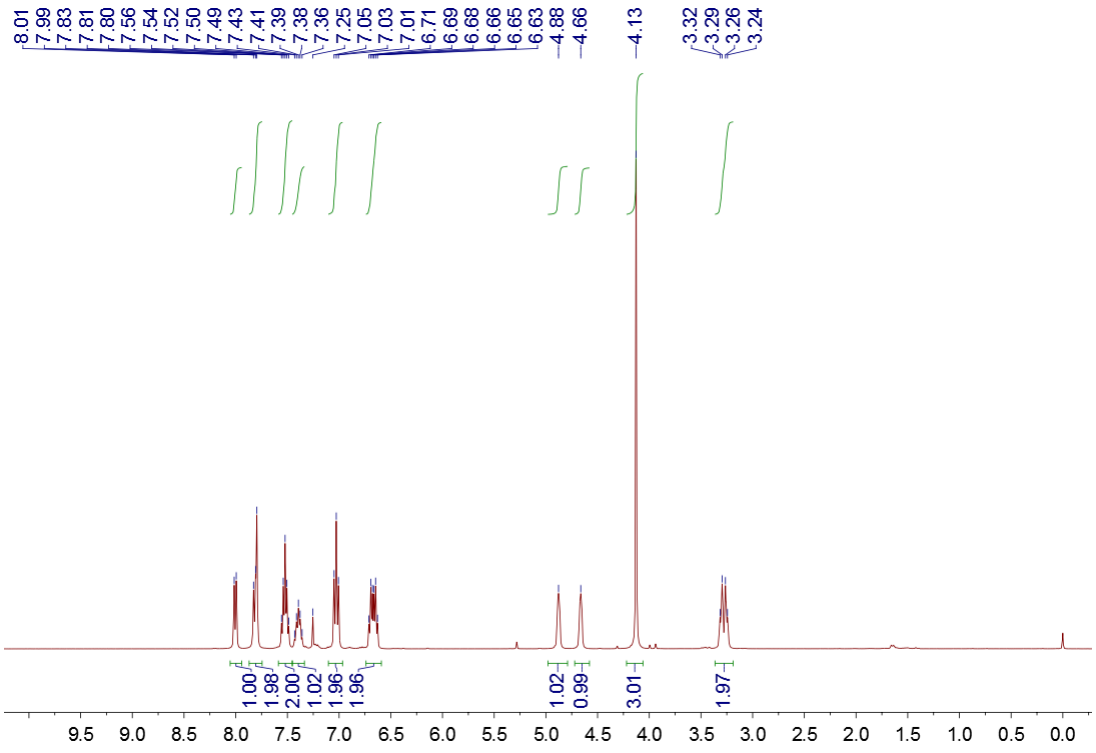


Figure S49. ^{1}H NMR spectrum (400 M) of **3d** in C*D*Cl$_3$.

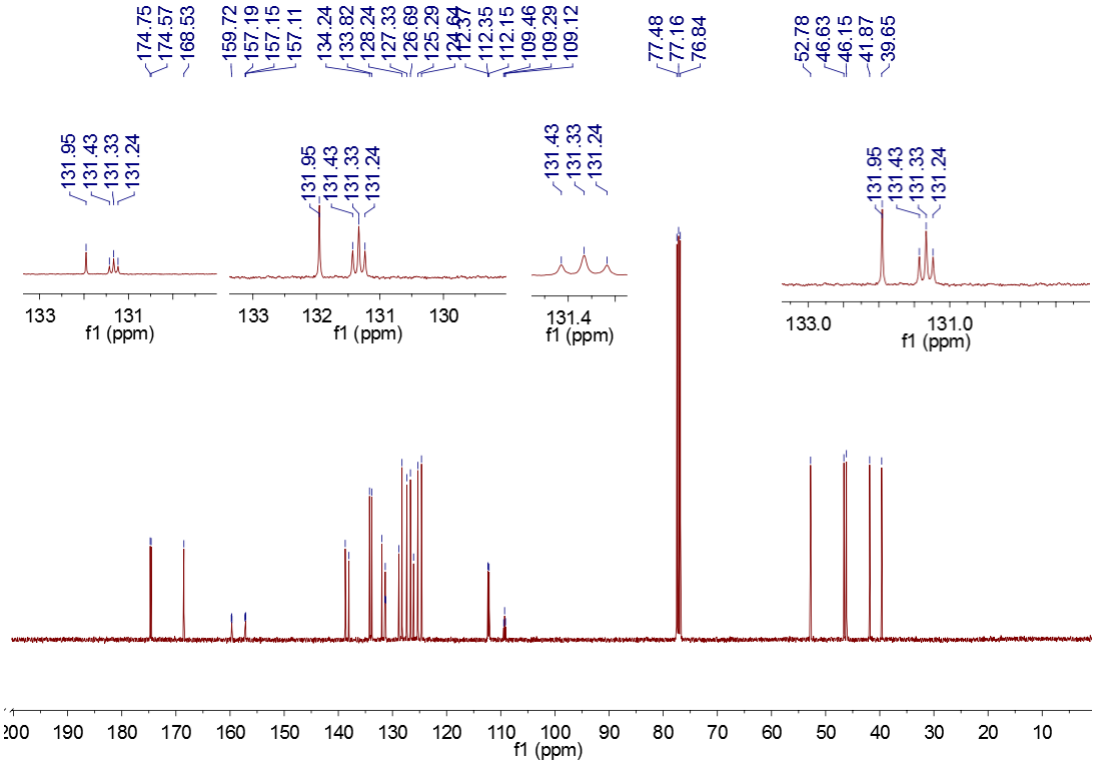


Figure S50. ^{13}C NMR spectrum (100 M) of **3d** in C*D*Cl$_3$.

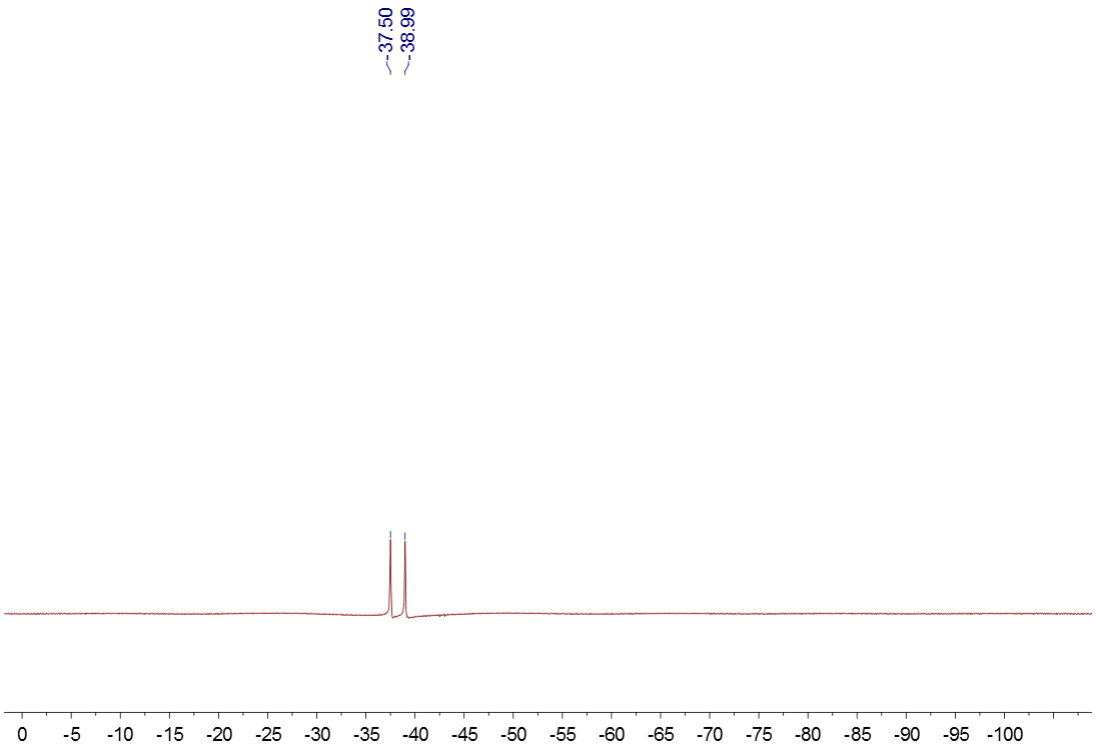
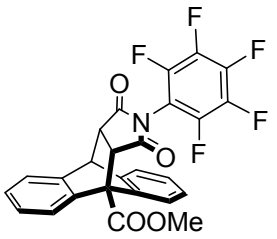
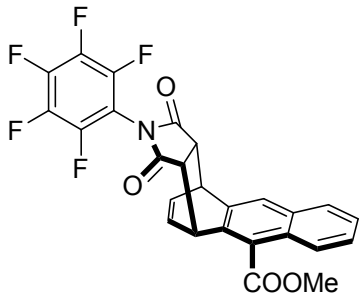


Figure S51. ^{19}F NMR spectrum (282 M) of **3d** in C*D*Cl_3.



Methyl anthracene-9-carboxylate **1h** (502 mg, 2.13 mmol), and *N*-(Pentafluorophenyl)maleimide **2e** (558 mg, 2.12 mmol) were added to toluene (5 mL) in a flask. The reaction mixture was heated and stirred at 110 °C for 40 h. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (4:1, v/v) as eluent, to give **1h** and **2e** as pale solid (138 mg, 12%), with PE/CH_2Cl_2 (1:1, v/v) as eluent, to give product **4e** as a white solid (625 mg, 59%), with PE/CH_2Cl_2 (1:2, v/v) as eluent, to give product **3e** as a white solid (106 mg, 10%). **4e**: ^1H NMR (400 MHz, $CDCl_3$):*δ*7.97-7.96 (1H, d), 7.46-7.44 (1H, d), 7.34-7.32 (1H, d), 7.28-7.21 (4H, m), 7.11-7.10 (1H, d), 4.86 (1H, s), 4.22-4.19 (1H, d), 4.16 (3H, s), 3.54-3.52 (1H, dd). ^{13}C NMR (100 MHz, $CDCl_3$):*δ*173.1, 172.5, 169.8, 143.2, 142.2, 140.7, 140.1, 137.8, 137.3, 136.2, 127.8, 127.7, 127.7, 127.1, 125.5, 125.3, 124.3, 123.2, 106.5, 56.7, 52.7, 49.2, 48.0, 46.1. ^{19}F NMR (282 MHz, $CDCl_3$):*δ*-64.0, -65.4, -73.0, -82.9, -83.4. Elem. Anal.: Calcd. for $C_{26}H_{14}F_5NO_4$: C, 62.53; H, 2.83; N, 2.80. Found: C, 62.54; H, 2.91; N, 2.71.



3e: ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.02-8.00 (2H, d), 7.85 (1H, d), 7.83 (1H, s), 7.58-7.52 (2H, m), 6.73-6.64 (2H, m), 4.89 (1H, s), 4.69 (1H, s), 4.14 (3H, s), 3.39-3.31 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$):δ174.0, 173.9, 168.4, 143.7, 142.4, 138.3, 138.1, 137.6, 134.3, 133.9, 132.0, 128.8, 128.3, 127.5, 126.8, 126.2, 125.3, 124.8, 107.1, 52.8, 46.8, 46.3, 41.8, 39.6. ^{19}F NMR (282 MHz, $CDCl_3$):δ-63.7, -65.1, -72.8, -82.8. HRMS: Calcd. for $C_{26}H_{18}F_5N_2O_4$, 517.11812 ([M+NH_4^+]/z), Found: $C_{26}H_{18}F_5N_2O_4$, 517.11814 ([M+NH_4^+]/z).

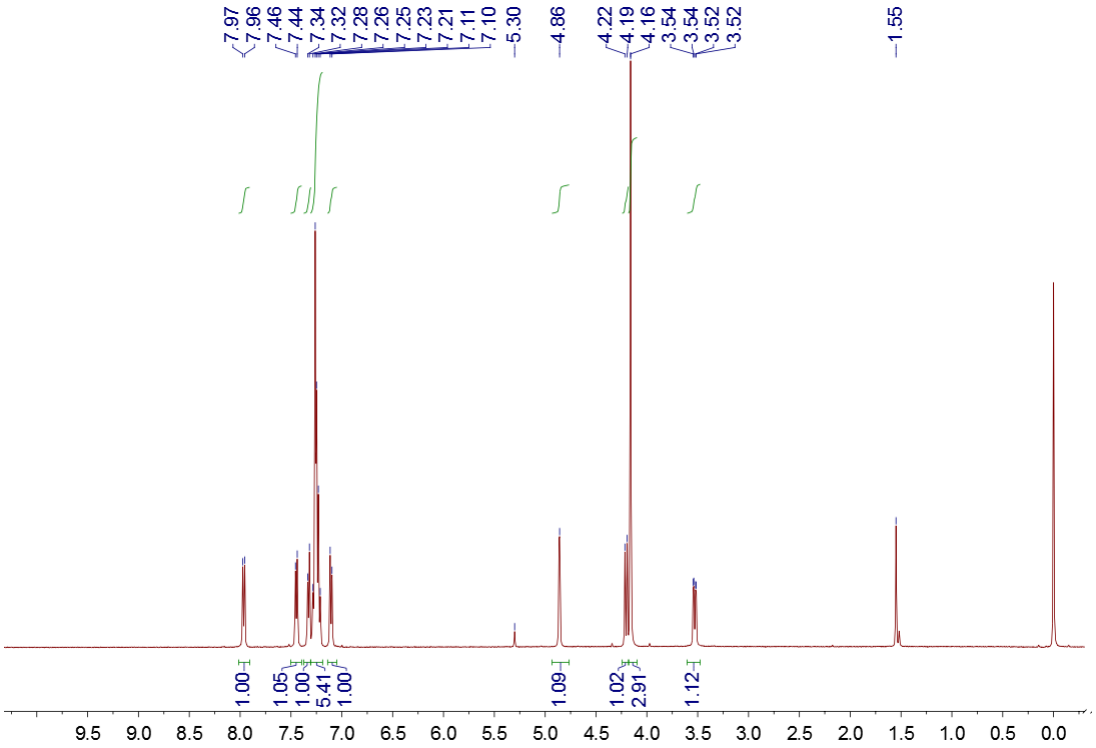


Figure S52. ^{1}H NMR spectrum (400 M) of **4e** in C*D*Cl_3.

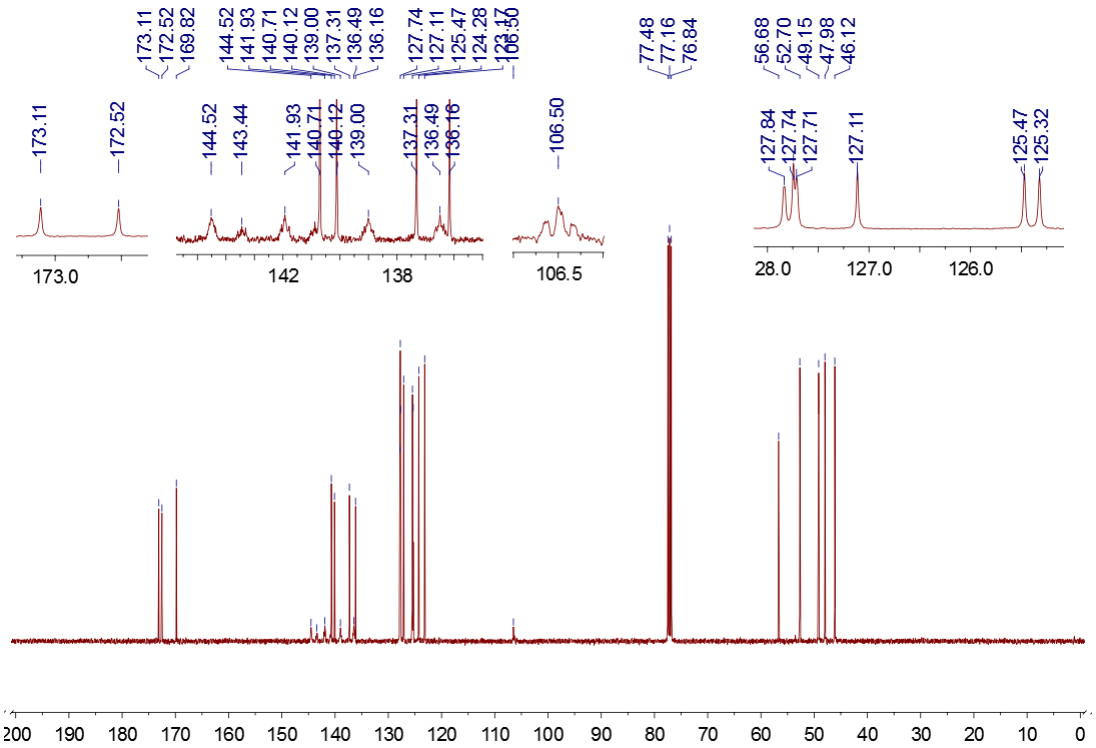


Figure S53. ^{13}C NMR spectrum (100 M) of **4e** in C*D*Cl$_3$.

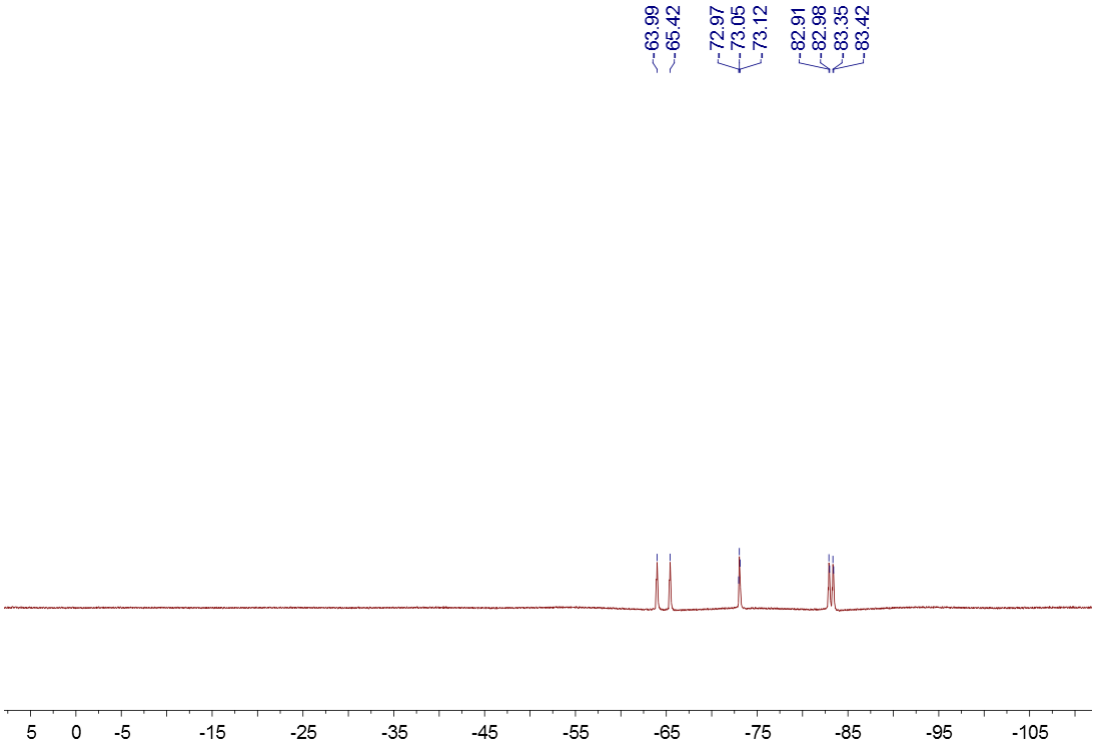


Figure S54. ^{19}F NMR spectrum (282 M) of **4e** in C*D*Cl$_3$.

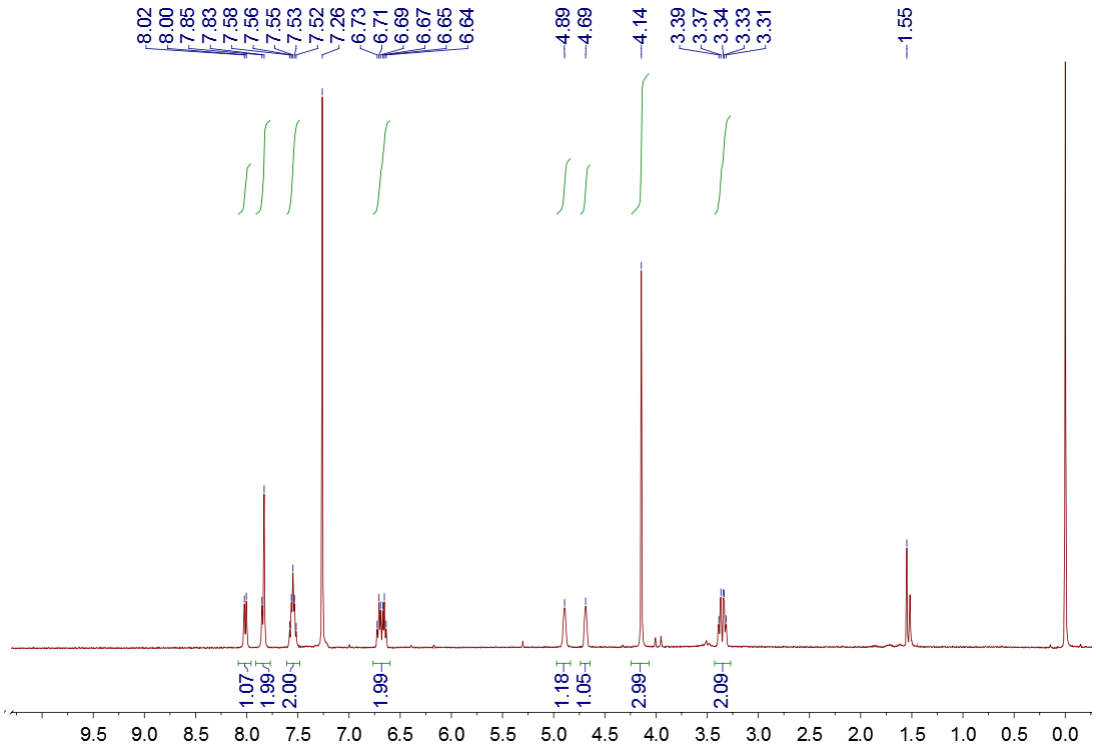


Figure S55. ^{1}H NMR spectrum (400 M) of **3e** in C*D*Cl$_3$.

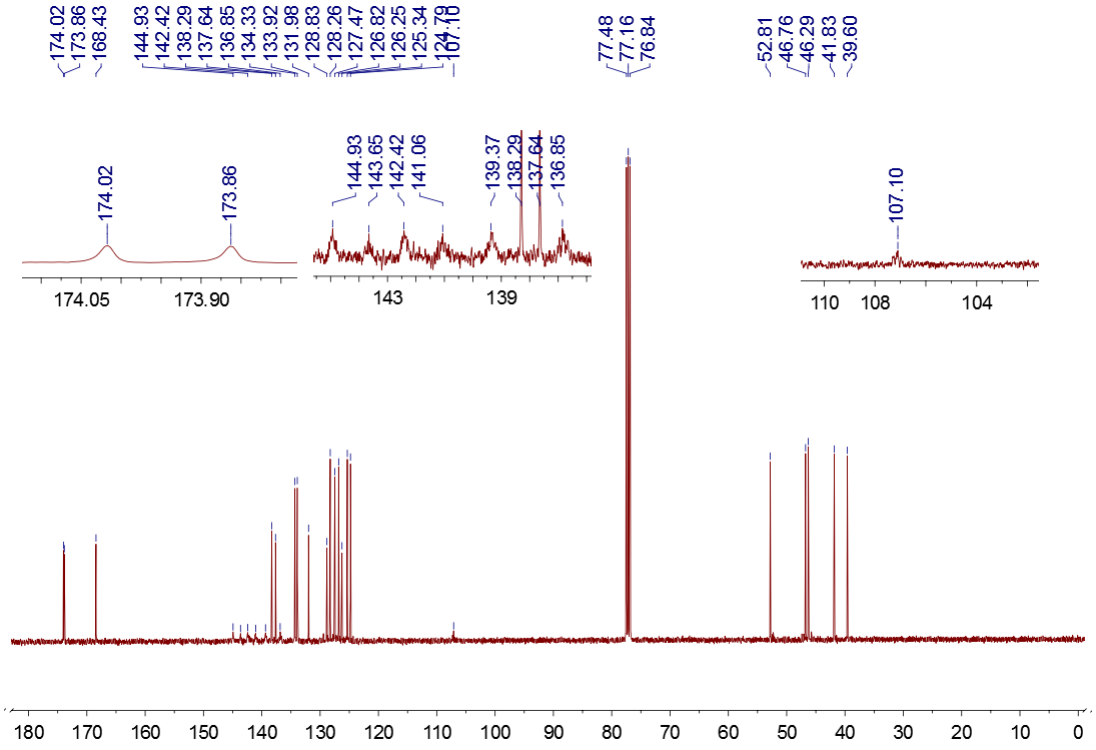


Figure S56. ^{13}C NMR spectrum (100 M) of **3e** in C*D*Cl$_3$.

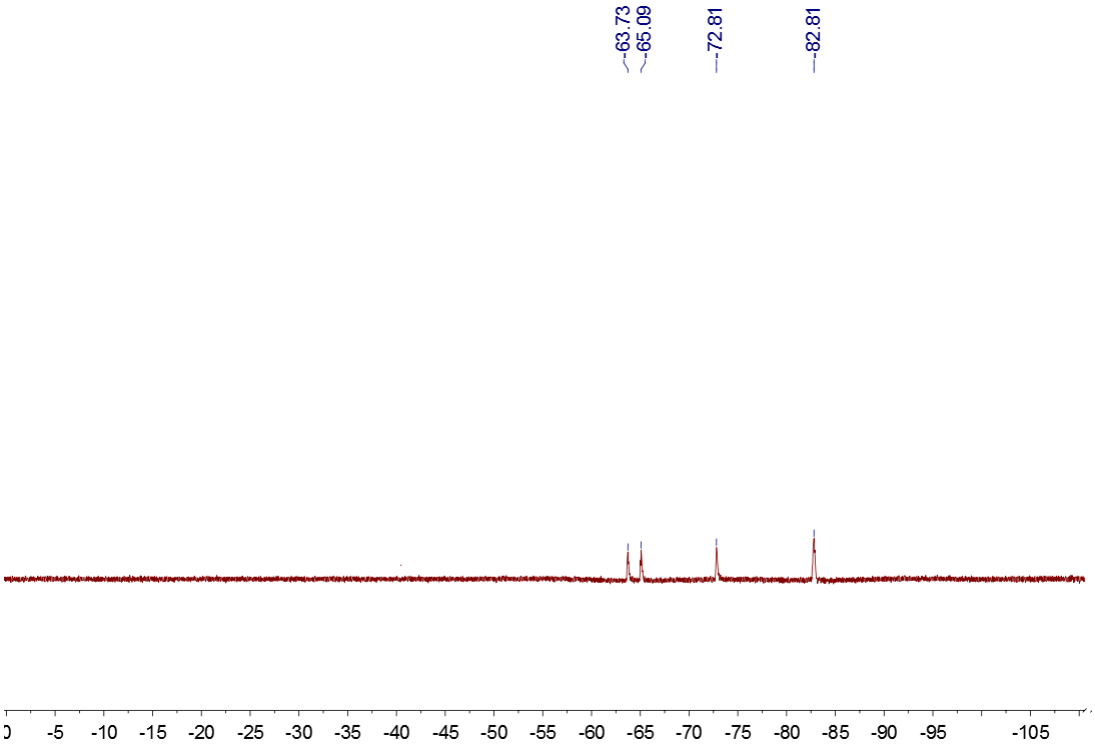
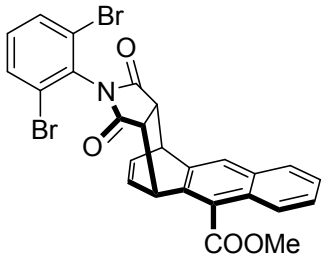


Figure 57. ^{19}F NMR spectrum (282 M) of **3e** in C*D*Cl$_3$.



3h: Methyl anthracene-9-carboxylate **1h** (120 mg, 0.51 mmol) and N-(2,6-Dibromobenzyl)maleimide **2h** (165 mg, 0.50 mmol) were added to TCE-d_2 (0.3 mL) in a NMR tube. The reaction mixture was heated and stirred at 110 °C for 5 d. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (4:1, v/v) as eluent, to give **1h** and **2h** as pale solid (28 mg, 10%), with PE/CH_2Cl_2 (1:2, v/v) to CH_2Cl_2 as eluent, to give product **3h** as a white solid (146 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$):δ8.01-7.99 (1H, d), 7.81-7.78 (2H, m), 7.62-7.58 (2H, m), 7.54-7.48 (2H, m), 7.12-7.15 (1H, t), 6.76-6.68 (2H, m), 4.92 (1H, s), 4.69 (1H, s), 4.12 (3H, s), 3.38-3.30 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$):δ174.14, 173.99, 168.43, 138.92, 138.21, 135.00, 134.48, 132.82, 132.40, 131.98, 131.86, 131.48, 128.71, 128.15, 127.20, 126.56, 126.01, 125.22, 124.46, 123.98, 123.84, 77.37, 77.11, 76.86, 52.64, 46.91, 46.46, 41.63, 39.40. HRMS: Calcd. for $C_{26}H_{18}Br_2NO_4$, 565.95971 ([M+H$^+$]/z), Found: $C_{26}H_{18}Br_2NO_4$, 565.96102 ([M+H$^+$]/z).

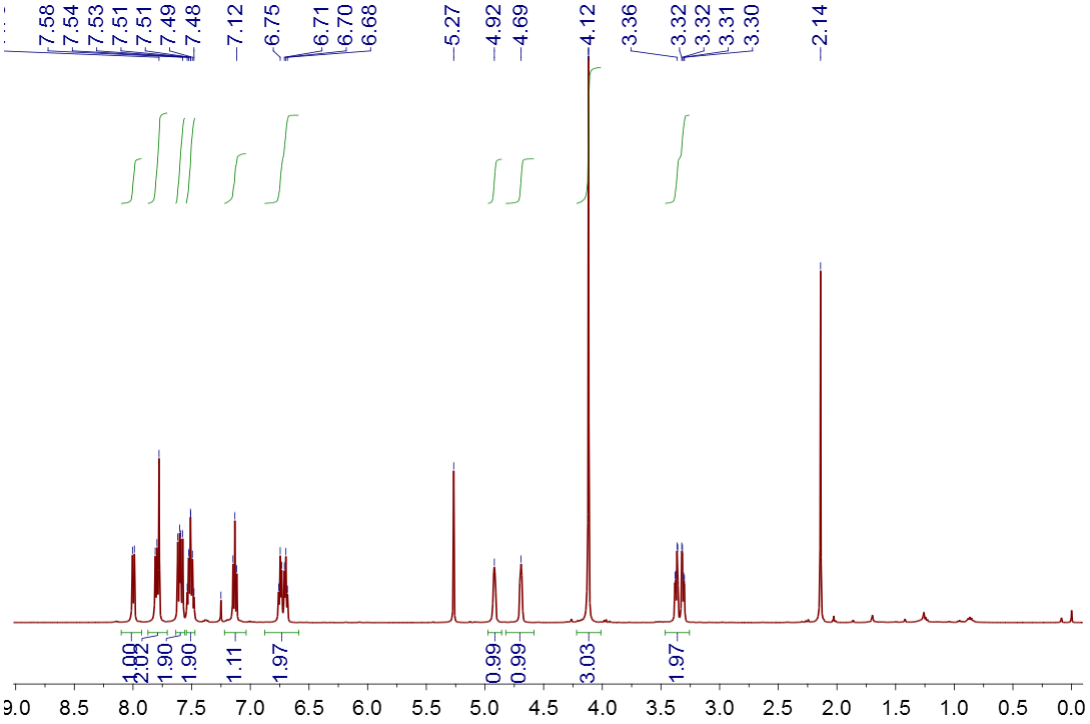


Figure S59. ^{1}H NMR spectrum (500 M) of **3h** in C*D*Cl$_3$.

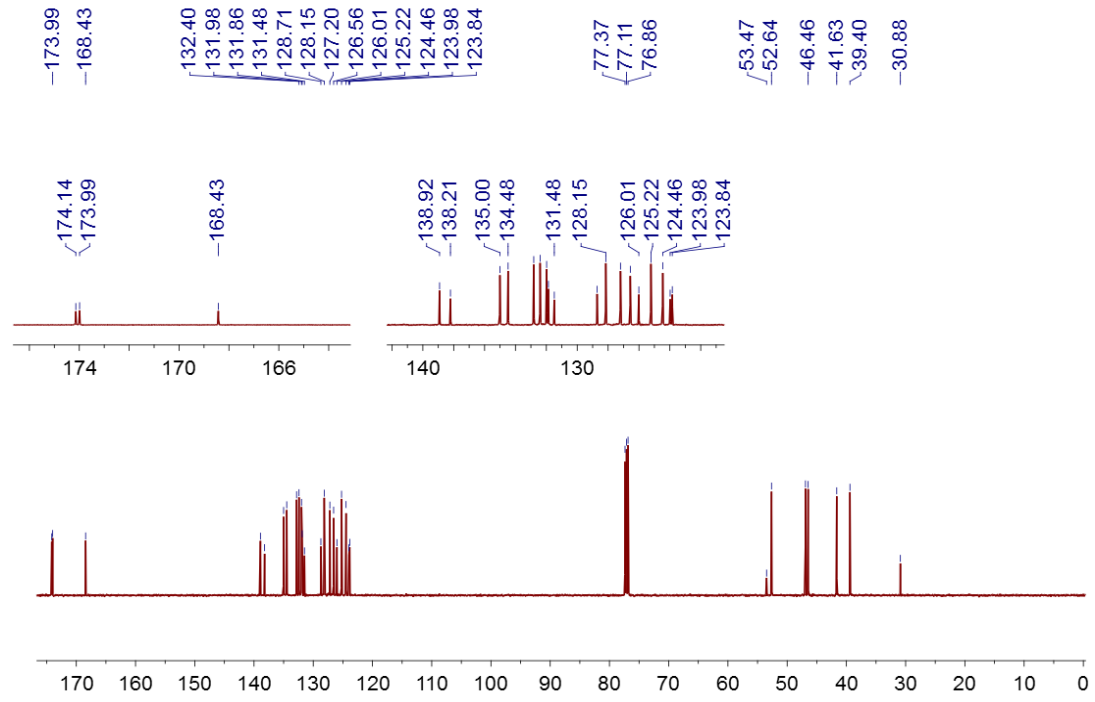
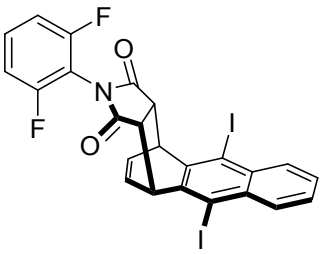


Figure S60. ^{13}C NMR spectrum (125 M) of **3h** in C*D*Cl$_3$.



5k: **1k** (706 mg, 1.6 mmol) and N-(2,6-difluorobenzyl)maleimide **2d** (344 mg, 1.6 mmol) were added to TCE (10 mL) in a flask. The reaction mixture was heated and stirred at 110 °C for 5 d. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (1:1, v/v) as eluent, to give product **5k** as a white solid (158 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$): δ8.21-8.19 (2H, dd), 7.63 – 7.60 (2H, dd), 7.45 – 7.39 (1H, m), 7.07-7.03 (2H, t), 6.72-6.70 (2H, t), 5.31 (2H, s), 3.30 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$):*δ*174.05, 159.8, 157.12, 139.48, 134.08, 131.19, 128.15, 128.11, 118.14, 112.31, 109.18, 77.37, 77.11, 76.86, 45.29, 42.54. HRMS: Calcd. for $C_{24}H_{14}F_2I_2NO_2$, 639.90765 ([M+H$^+$]/z), Found: $C_{26}H_{18}Br_2NO_4$, 639.91008 ([M+H$^+$]/z).

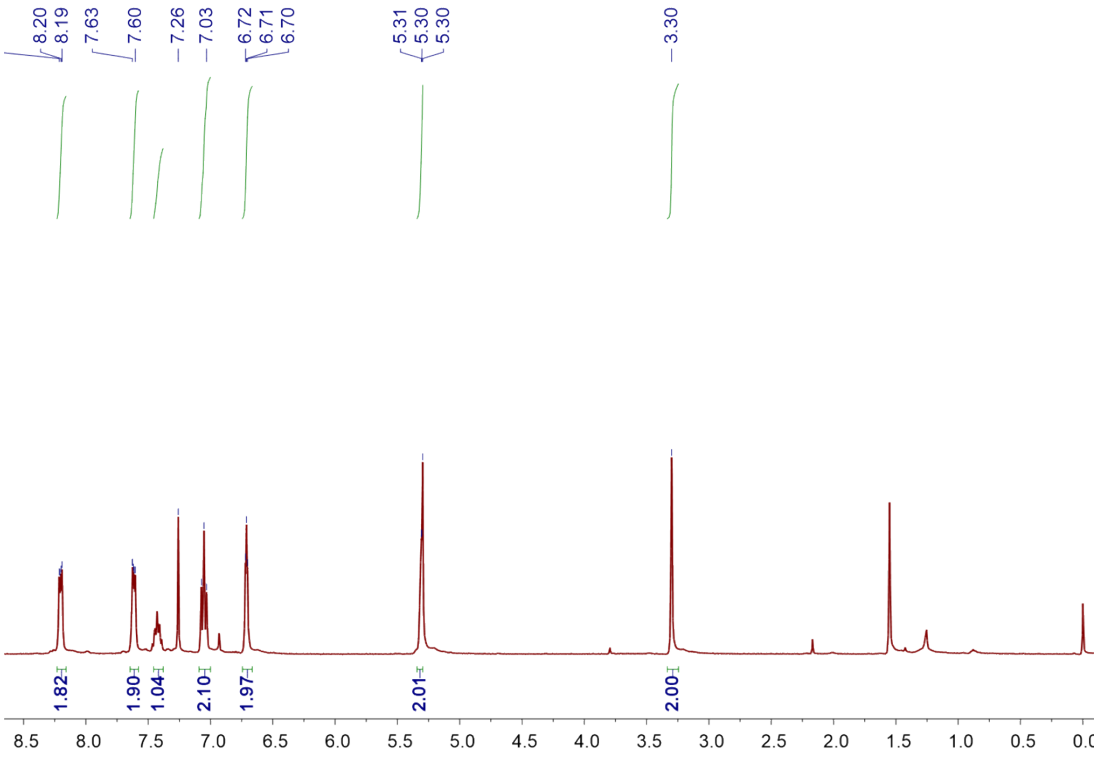


Figure S61. ^{1}H NMR spectrum (400 M) of **5k** in C*D*Cl_3.

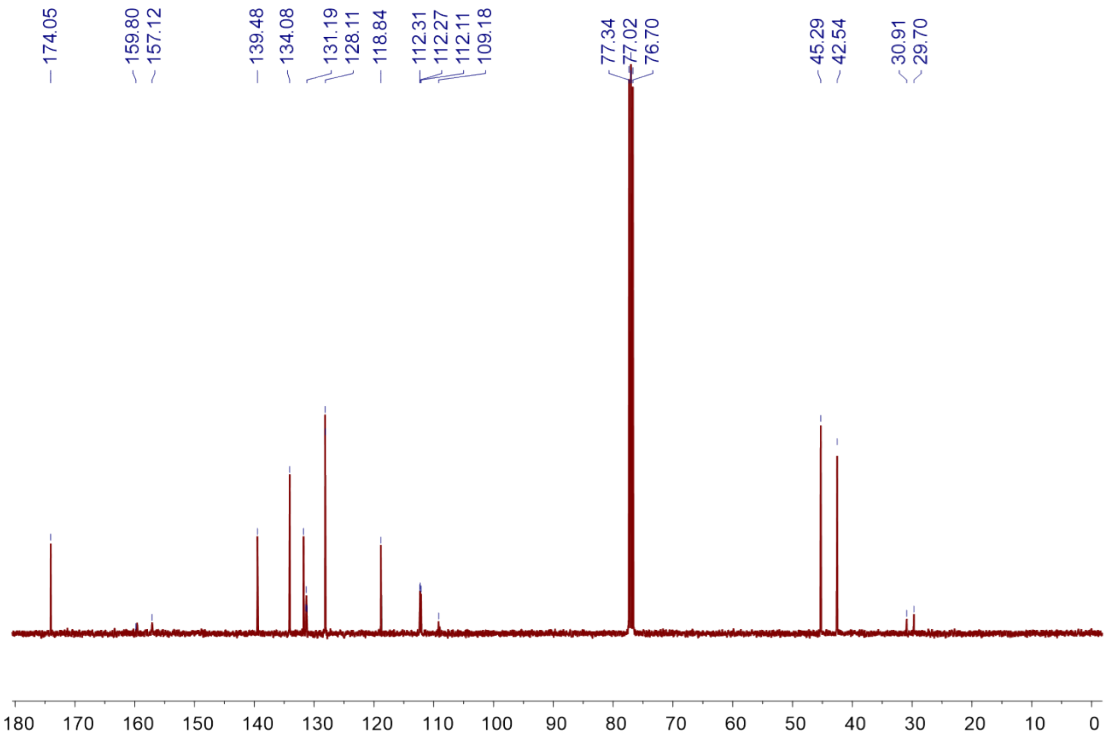
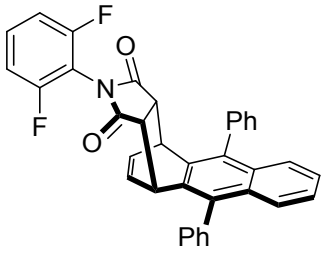


Figure S62. ^{13}C NMR spectrum (100 M) of **5k** in C*D*Cl$_3$.



5n: **1n** (26 mg, 0.08 mmol) and N-(2,6-difluorobenzyl)maleimide **2d** (18 mg, 0.09 mmol) were added to TCE-d_2 (0.2 mL) in a NMR tube. The reaction mixture was heated and stirred at 140 ^{o}C for 5 d. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (1:1, v/v) as eluent, to give product **5n** as a white solid (39 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.61-7.52 (8H, m), 7.43-7.42(2H, d), 7.36-7.33 (5H, m), 7.00-6.98 (2H, m), 4.54(2H, s), 3.27 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$):*δ*174.70, 159.70-159.60, 157.17-157.05, 137.75, 136.32, 134.50, 134.47, 131.23, 131.07, 130.49, 130.12, 128.85, 128.77, 127.87, 126.74, 125.85, 112.20, 109.52, 77.37, 77.11, 76.86, 46.51, 39.54.

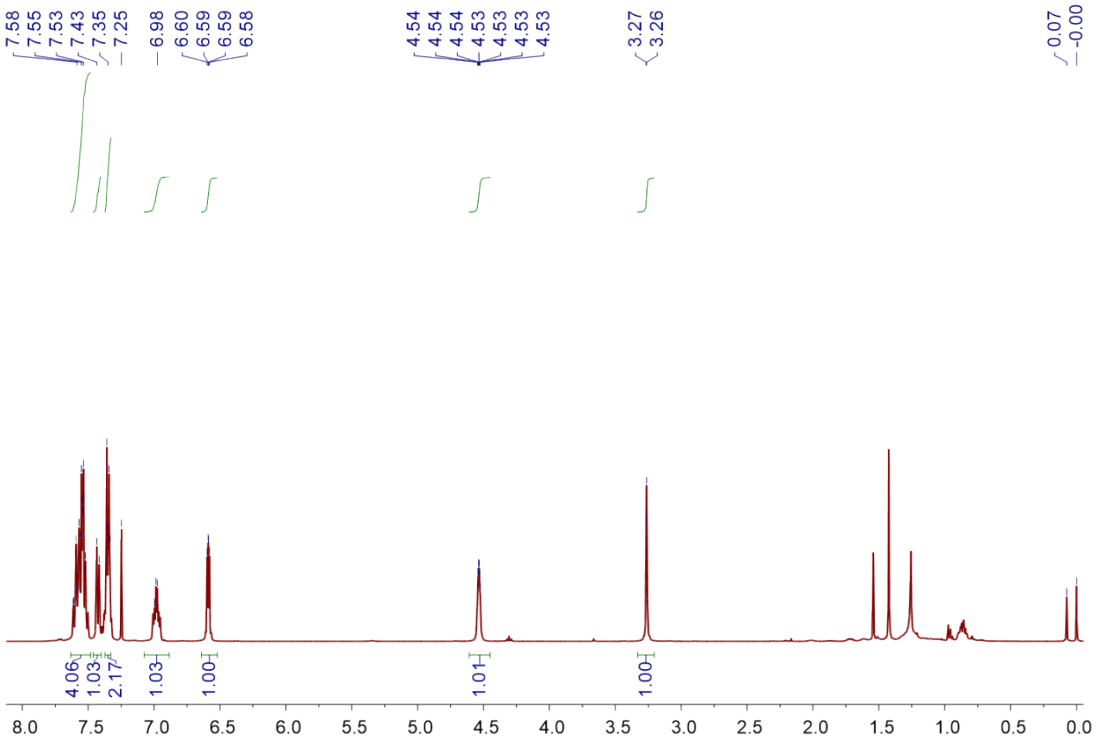


Figure S63. ^{1}H NMR spectrum (400 M) of **5n** in C*D*Cl$_3$.

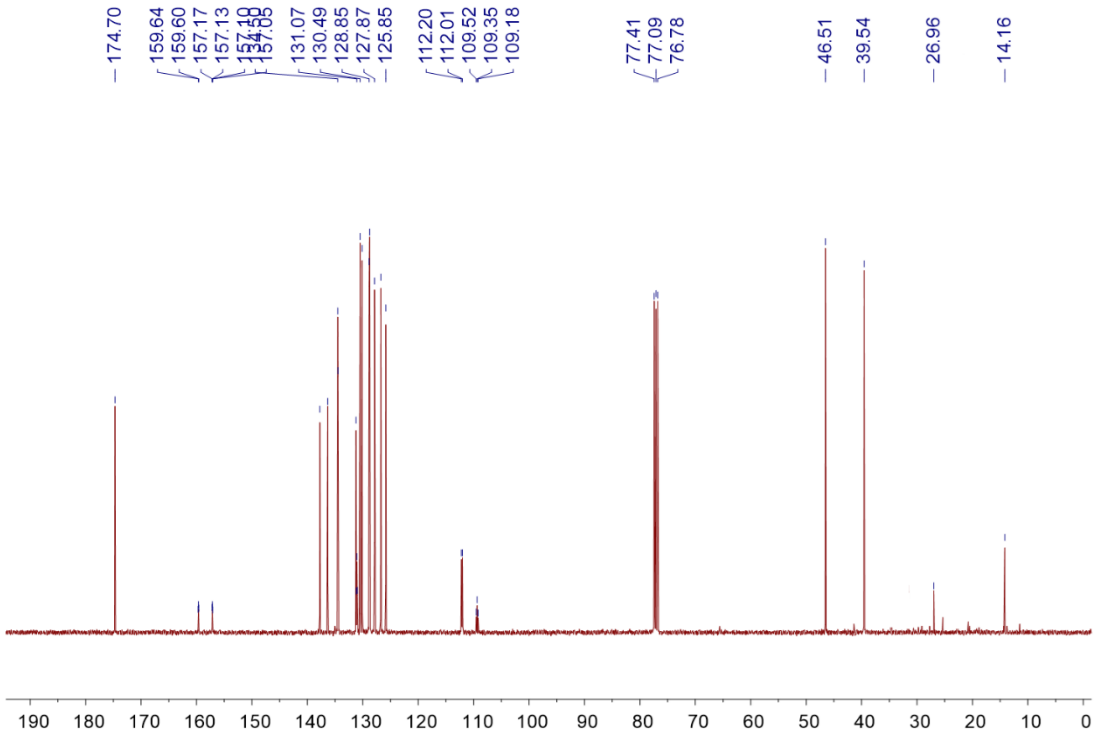
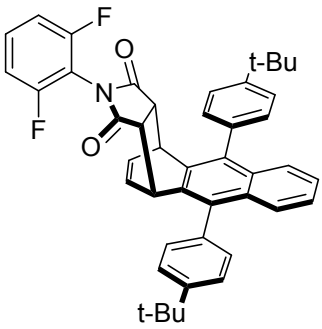


Figure S64. ^{13}C NMR spectrum (100 M) of **5n** in C*D*Cl$_3$.



7a: A schlenk tube containing **5k** (27 mg, 0.04 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), K_2CO_3 (58 mg, 0.42 mmol) and (4-(tert-butyl)phenyl)boronic acid (22 mg, 0.12 mmol) was evacuated and back-filled with nitrogen for three times. Then water (1 mL) and THF (2 mL) were added to the tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred at 80 °C for 12 hours. Then the reaction mixture was cooled to room temperature. The organic layer was washed with saturated aqueous NH_4Cl solution and dried over anhydrous Na_2SO_4. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (1:1, v/v) as eluent, to give product **7a** as a white solid (24 mg, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ7.60-7.56 (6H, m), 7.36-7.33 (5H, m), 7.28-7.26 (2H, dd), 7.00-6.99 (2H, dd), 6.61-6.59 (2H, t), 4.59 (2H, s), 3.27 (2H, s), 1.46 (18H, s). ^{13}C NMR (100 MHz, $CDCl_3$):*δ*173.88, 149.49, 133.35, 129.98, 128.77, 124.56, 111.16, 110.25, 77.37, 77.11, 76.86,45.51, 38.50, 33.73, 30.46, 28.68. HRMS: Calcd. for $C_{44}H_{40}F_2NO_2$, 652.30216 ([M+H$^+$]/z), Found: $C_{26}H_{18}Br_2NO_4$, 652.30045 ([M+H$^+$]/z).

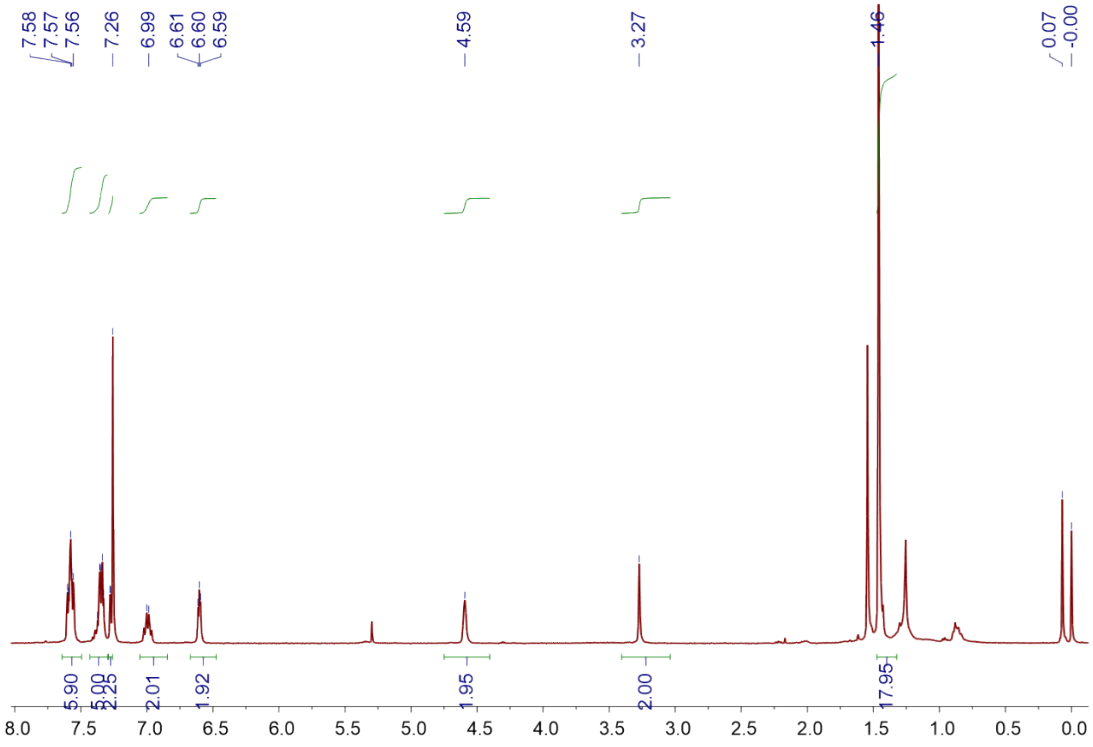


Figure S65. ^1H NMR spectrum (400 M) of **7a** in C*D*Cl_3.

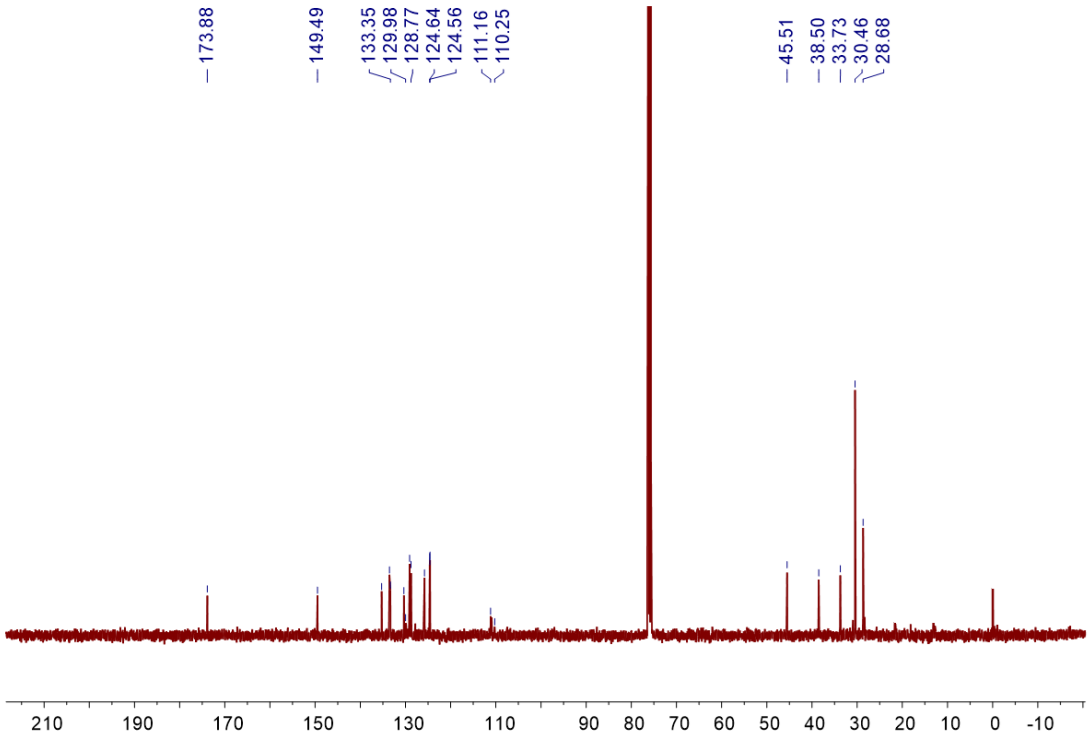
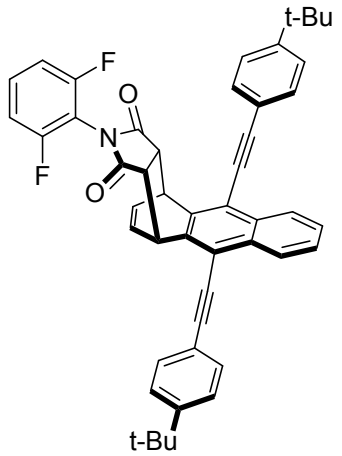


Figure S66. ^{13}C NMR spectrum (100 M) of **7a** in C*D*Cl$_3$.



7b: A schlenk tube containing **5k** (28 mg, 0.04 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), CuI (1 mg, 0.005 mmol) and 1-(tert-butyl)-4-ethynylbenzene (21 mg, 0.12 mmol) was evacuated and back-filled with nitrogen for three times. Then Et_3N (2 mL) and THF (2 mL) were added to the tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred at 40 ^oC for 12 hours. Then the reaction mixture was cooled to room temperature. Upon removal of the solvent *in vacuo*, the residue was applied to silica gel column chromatography, with PE/CH_2Cl_2 (1:1, v/v) as eluent, to give product **7b** as a pale solid (27 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.47-8.44 (2H, dd), 7.69-7.62 (5H, m), 7.48-7.42 (6H, m), 7.08-7.02 (2H, t), 6.76 (2H, t), 5.31(2H, s), 3.36 (2H, s), 1.37 (18H, s). ^{13}C NMR (100 MHz, $CDCl_3$):*δ*174.23, 152.03, 141.06, 134.03, 131.62, 127.16, 126.84, 125.58, 120.00, 119.83, 119.39, 116.15,

112.09, 111.90, 99.59, 83.57, 77.37, 77.11, 76.86, 46.06, 40.55, 34.92, 31.20, 29.43. HRMS: Calcd. for $C_{48}H_{40}F_2NO_2$, 700.30216 ([M+H$^+$]/z), Found: $C_{26}H_{18}Br_2NO_4$, 700.30349 ([M+H$^+$]/z).

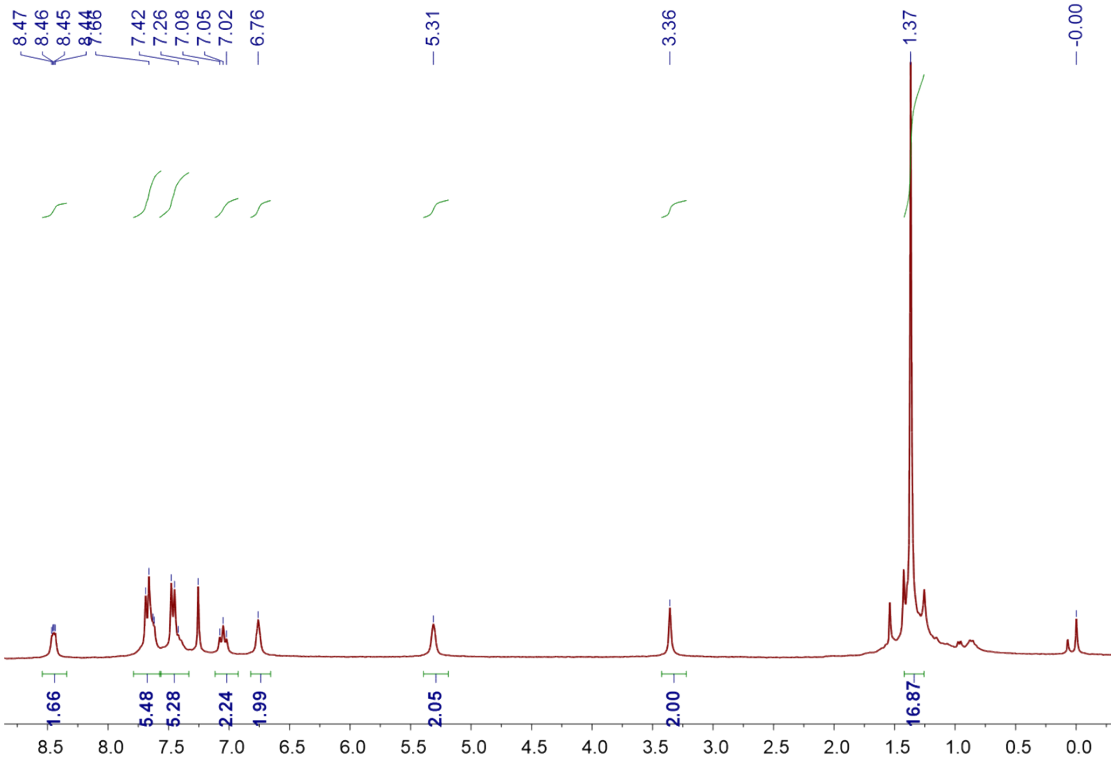


Figure S67. ^{1}H NMR spectrum (400 M) of **7b** in C*D*Cl$_3$.

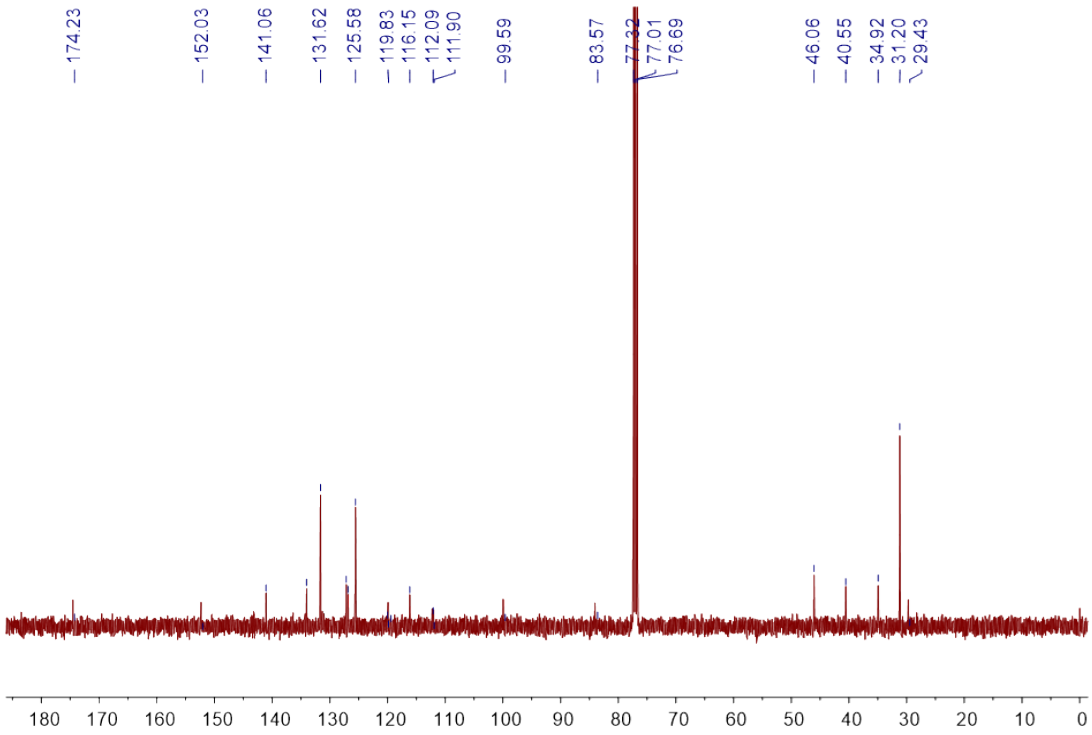


Figure S68. ^{13}C NMR spectrum (100 M) of **7b** in C*D*Cl$_3$.

5. Emission Spectra and UV-Vis Absorption Spectra

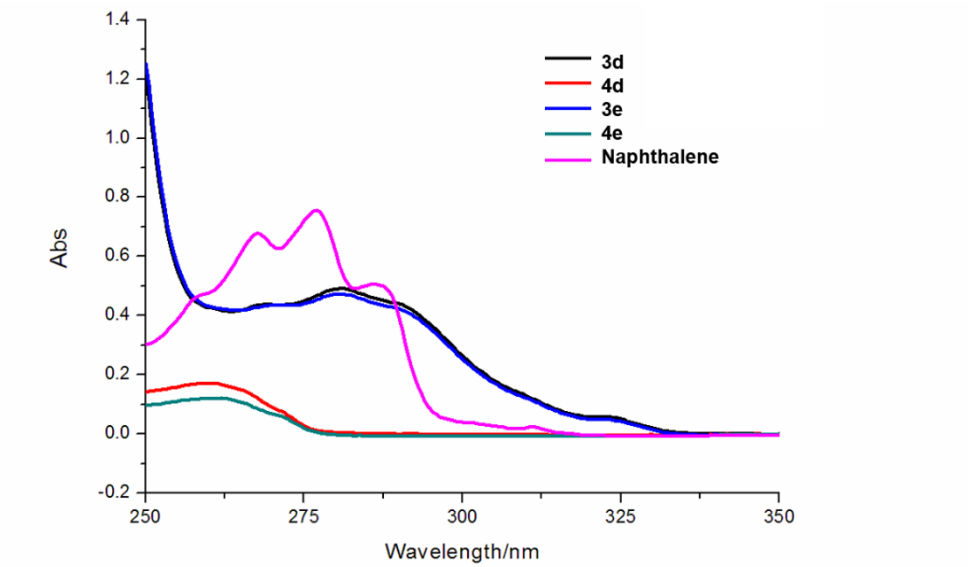


Figure S69. Absorption spectra for **3d**, **4d**, **3e**, **4e** and naphthalene in $CHCl_3$ (1×10^{-4} M) at 298 K, respectively.

The UV-vis absorption spectra of **3d/3e** supported the existent of naphthalene moiety, while that of **4d/4e** showed absorption feature of nonconjugated phenyl ring, implying that **3d/3e** were 1,4-adducts and **4d/4e** were 9,10-adducts.

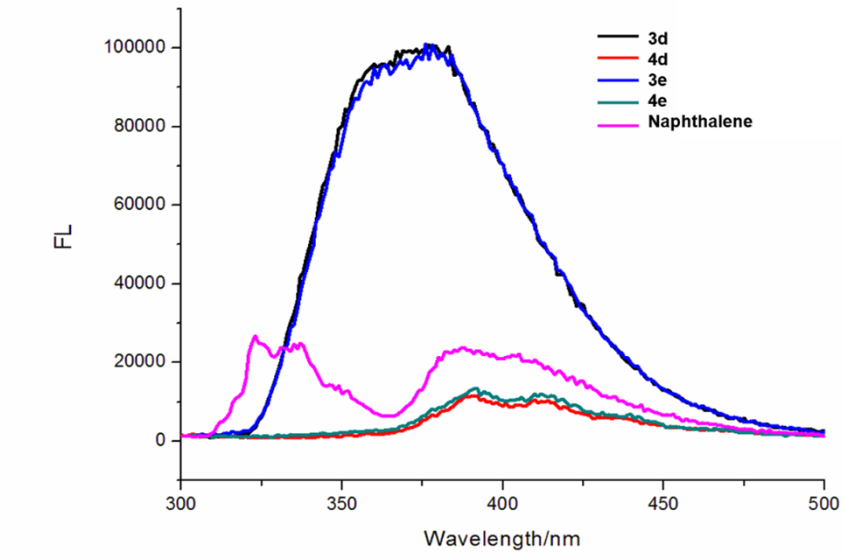


Figure S70. Emission spectra for **3d**, **4d**, **3e**, **4e** and naphthalene in $CHCl_3$ (1×10^{-4} M) at 298 K, respectively. (The spectra for **3d**, **3e** and naphthalene were excited at 280 nm. The spectra for **4d** and **4e** were excited at 260 nm.)

The fluorescence emission spectra of **3d/3e** also showed emission due to the naphthalene moiety.

6. 2D NOSEY NMR Spectra

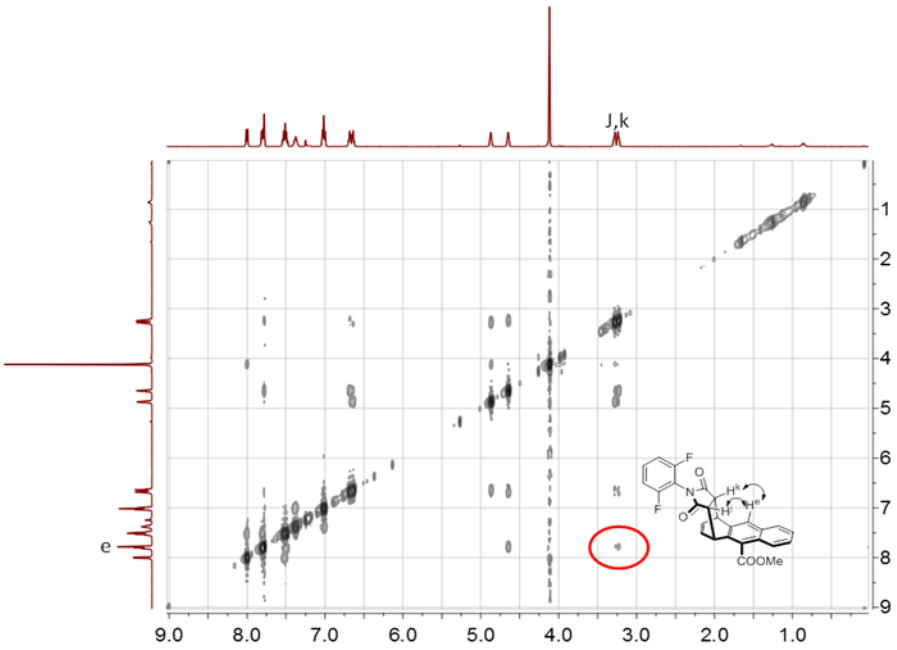


Figure S71. 2D NOSEY NMR (500 M) spectrum of **3d**.

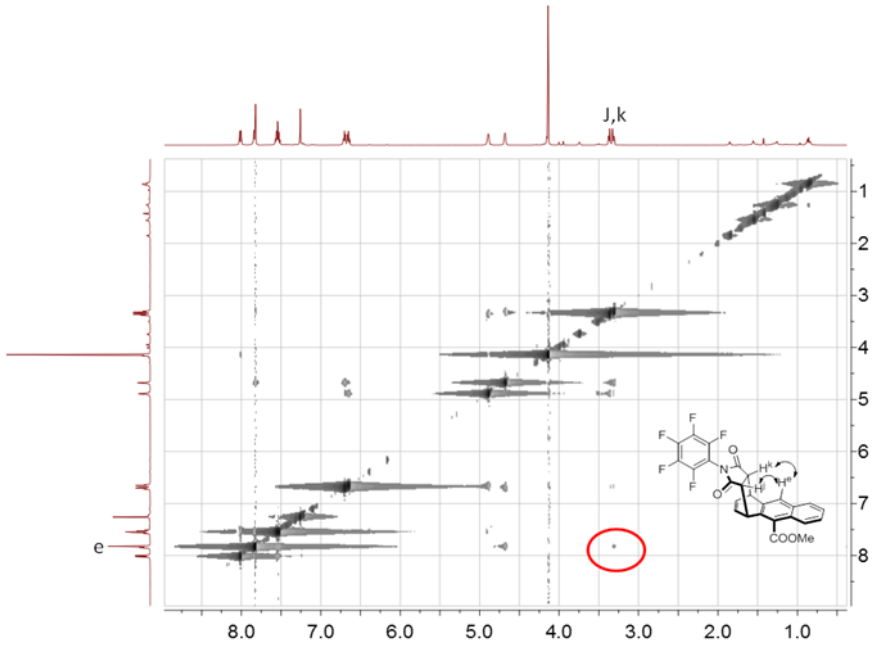


Figure S72. 2D NOSEY NMR (500 M) spectrum of **3e**.

7. Variable Temperature NMR

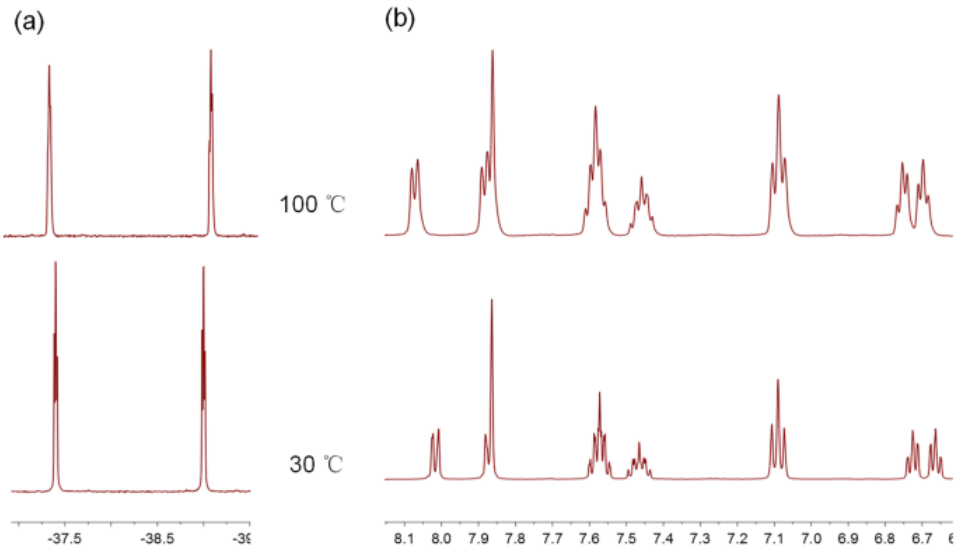


Figure S73. (a) ^{19}F NMR (470 MHz, TCE-d_2) spectra of **3d** at 100 ℃ (top) and 30℃ (bottom). (b) Partial ^{1}H NMR (500 MHz, TCE-d_2) spectra of **3d** at 100 ℃ (top) and 30℃ (bottom).

8. Computational Studies

Table S2. Predicted free energies at 110 ºC (Simulation experimental conditions) and relative rates for the reaction of **1h** with **2d**. Optimizations performed with B3LYP/6-31G(d), single point energies performed with M06-2X/6-31G(d) and the B3LYP/6-311+G(d,p) (applying transition-state theory at 298 K). The effects of solvation were evaluated using PCM in toluene.

	B3LYP/6-31G*	**B3LYP/6-311+G** //B3LYP/6-31G***	**M062X/6-31G* //B3LYP/6-31G***
3d'(syn-1,4-adduct)	15.2	18.9	-4.5
3d(anti-1,4-adduct)	12.1	15.9	-6.6
4d(9,10-adduct)	4.6	8.7	-17.8
3d'-TS	46.5	49.7	33.4
3d-TS	42.3	45.2	30.1
4d-TS	40.7	44.3	27.1
k_{4d}/k_{3d}	8.6	3.5	51.3

$k_{4d}/k_{3d'}$	1981	1312	3811

Table S3. Predicted free energies at 110 °C (Simulation experimental conditions) and relative rates for the reaction of **1h** with **2a**. Optimizations performed with B3LYP/6-31G(d), single point energies performed with M06-2X/6-31G(d) and the B3LYP/6-311+G(d,p) (applying transition-state theory at 298 K). The effects of solvation were evaluated using PCM in toluene.

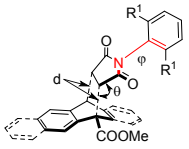
	B3LYP/6-31G*	B3LYP/6-311+G** //B3LYP/6-31G*	M062X/6-31G* //B3LYP/6-31G*
3a'(syn-1,4-adduct)	15.6	19.0	-3.7
3a(anti-1,4-adduct)	12.9	16.5	-5.6
4a(9,10-adduct)	5.5	9.2	-16.6
3a'-TS	48.5	51.1	34.8
3a-TS	43.8	46.2	31.8
4a-TS	40.3	43.3	26.2
k_{4a}/k_{3a}	102	45.9	1600
$k_{4a}/k_{3a'}$	47317	26926	81669

Table S4. Computed rotational barriers and dihedral angles. Optimizations performed with B3LYP/6-31G* (applying transition-state theory at 298 K). The effects of solvation were evaluated using PCM in toluene.

TS	**Barrier /kcal mol^{-1}**	**Φ Imide/phenyl dihedral angle/degree[b]**
2a	2.7	46(49)
2b	2.1	35(-)
2c	11.3	56(61)
2d	22.8	62(60)
2e	22.3	62(-)

[b] φ (imide/phenyl dihedral angle) were from DFT at B3LYP/6-31G* level and single crystal data in parentheses.

Table S5. Computed geometry parameters of adducts'TS with **2d** and **2a** for comparison. Optimizations performed with B3LYP/6-31G(d) applying transition-state theory at 298 K.



TS	Distance (d)/Å	Angle (θ)/°	Dihedral angle (φ)/°
4d (9,10-adduct)	2.252	103.0	56.78 (-5.81)[a]
3d (anti-1,4-adduct)	2.170	100.7	62.48 (-0.09)[a]
3d' (syn-1,4-adduct)	2.197	103.9	57.24 (-5.35)[a]
4a (9,10-adduct)	2.249	101.3	37.26 (-3.04)[b]
3a (anti-1,4-adduct)	2.172	100.8	37.72 (-2.58)[b]
3a' (syn-1,4-adduct)	2.190	102.6	39.31 (-0.99)[b]

From geometry parameters of TS (***Table S5***), we found that **3d**-TS displayed the shortest carbon-carbon bond forming distance (2.170 Å), while **4d**-TS and **3d'**-TS showed longer distances of 2.252 Å and 2.197 Å, respectively. The different distances between reactions sites might be induced by the steric effect due to rotationally restricted **2d**. At the same time, the degree of angles (θ) between the reaction sites also revealed that **4d**-TS (103.0°) and **3d'**-TS (103.9°) displayed larger repellant than **3d**-TS (100.7°). Finally, the decrease of dihedral angle (φ) of TS demonstrated the repellant between rotationally restricted **2d** and anthracene framework. Dihedral angle (φ) of **3d**-TS was almost equal to that of **2d**; while **4d**-TS and **3d'**-TS displayed a decreasing dihedral angle (φ) comparing to that of **2d** (-5.81 and -5.35 degree), respectively. In **4a**-TS, **3a**-TS and **3a'**-TS, the distances between the reaction sites, the dihedral angles (φ) and the angles (θ) between the reaction sites did not change too much because the free rotation of phenyl ring of maleimide **2a** induced much smaller repellent with anthracene framework comparing to rotationally restricted **2d**.

Cartesian Coordinates of B3LYP/6-31G(d) optimized stationary points. B3LYP/6-31G(d), M06-2X/6-31G(d) and B3LYP/6-311+G energies.**

2a

E(B3LYP/6-31G*) -590.4788369
H(B3LYP/6-31G*) -590.318632
G(B3LYP/6-31G*) -590.365685

E(M06-2X/6-31G*) -590.240575
E(B3LYP/6-311+G**) -590.639813

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-1.57576400	-1.12884300	-0.23956500
C	-2.99415300	-0.65249500	-0.13977500
C	-2.99415200	0.65249600	0.13977900
C	-1.57576300	1.12884400	0.23956000
N	-0.76221400	0.00000000	-0.00000200
H	-3.82686300	-1.32845900	-0.28605400
H	-3.82686200	1.32845900	0.28606400
C	0.66596100	0.00000000	-0.00000100
C	1.36275200	1.06836300	-0.57576500
C	1.36275200	-1.06836300	0.57576500
C	2.75684000	1.06580800	-0.56454900
C	2.75683900	-1.06580900	0.56455000
C	3.45892800	-0.00000100	0.00000100
O	-1.19539400	-2.25485300	-0.47601800
O	-1.19539100	2.25485300	0.47601800
H	3.29346400	-1.90071600	1.00651900
H	4.54532400	-0.00000100	0.00000200
H	3.29346500	1.90071600	-1.00651700
H	0.81890700	1.89608100	-1.01395800
H	0.81890600	-1.89608200	1.01395800

2b

E(B3LYP/6-31G*) -888.161893
H(B3LYP/6-31G*) -888.161893
G(B3LYP/6-31G*) -888.077380
E(M06-2X/6-31G*) -887.841410
E(B3LYP/6-311+G**) -888.427736

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-2.39842100	1.08701400	0.39242500
C	-3.81437500	0.62692400	0.22858700
C	-3.81437500	-0.62691400	-0.22861600
C	-2.39842300	-1.08702900	-0.39238900
N	-1.58116600	-0.00000600	0.00001200
H	-4.64710000	1.27604200	0.46671600
H	-4.64710100	-1.27601700	-0.46678400
C	-0.15834400	-0.00000400	0.00000600
C	0.53635200	-1.17485300	0.31415500
C	0.53634500	1.17484900	-0.31414800
C	1.92369600	-1.15700200	0.29983600

H	0.02380800	-2.09801400	0.54544200
C	1.92368900	1.15700400	-0.29983800
H	0.02379500	2.09800800	-0.54543100
C	2.63772500	0.00000300	-0.00000300
O	-2.01792200	2.17012300	0.77801200
O	-2.01792500	-2.17012600	-0.77801100
F	2.60970900	2.27261300	-0.59068800
F	3.97593800	0.00000500	-0.00000800
F	2.60972300	-2.27260700	0.59068200

2c

E(B3LYP/6-31G*) -689.708829
H(B3LYP/6-31G*) -689.556046
G(B3LYP/6-31G*) -689.605259
E(M06-2X/6-31G*) -689.443293
E(B3LYP/6-311+G**) -689.904681

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-1.59925100	-0.94379700	-0.56978800
C	-3.02854300	-0.57282900	-0.30590900
C	-3.06886000	0.63954500	0.25348000
C	-1.66873700	1.15593300	0.40470400
N	-0.82831500	0.14280200	-0.10192100
H	-3.84206100	-1.23715000	-0.56802100
H	-3.92346200	1.22416000	0.56936800
C	0.58940600	0.19890900	-0.12625100
C	1.26492100	1.25115400	-0.75018300
C	1.33777400	-0.80293300	0.49902500
C	2.65858700	1.28946700	-0.75043400
C	2.72589900	-0.78943100	0.48790300
C	3.38717500	0.26657900	-0.13989300
O	-1.17216100	-1.94710200	-1.09295900
O	-1.31117200	2.22108000	0.85657200
H	3.26259300	-1.59489800	0.97797300
H	4.47296300	0.28874600	-0.14780600
H	3.17317400	2.11374900	-1.23441100
F	0.69375700	-1.79761500	1.13519800
H	0.68762600	2.03690100	-1.22526300

2d

E(B3LYP/6-31G*) -788.93887155
H(B3LYP/6-31G*) -788.793382
G(B3LYP/6-31G*) -788.844754
E(M06-2X/6-31G*) -788.646087

E(B3LYP/6-311+G**) -789.169288

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.67657400	-0.90670900	0.72365600
C	3.09315000	-0.52438500	0.41389600
C	3.09310400	0.52421200	-0.41449700
C	1.67648700	0.90761700	-0.72274000
N	0.87247400	0.00027500	0.00028200
H	3.92985100	-1.06347500	0.83953500
H	3.92975900	1.06263300	-0.84107100
C	-0.53921400	0.00004500	0.00008300
C	-1.26606100	1.09081500	0.48623000
C	-1.26559200	-1.09095400	-0.48625500
C	-2.65447000	1.11295900	0.48508600
C	-2.65399300	-1.11354200	-0.48546900
C	-3.34182600	-0.00040000	-0.00028100
O	1.27646100	-1.79151500	1.44431700
O	1.27628800	1.79171800	-1.44421900
H	-3.16951700	-1.98715100	-0.86817000
H	-4.42741100	-0.00057200	-0.00042000
H	-3.17036800	1.98640400	0.86765600
F	-0.58456700	-2.14178600	-0.96923100
F	-0.58549700	2.14186000	0.96939200

2e

E(B3LYP/6-31G*) -1086.60279222
H(B3LYP/6-31G*) -1086.479284
G(B3LYP/6-31G*) -1086.53731
E(M06-2X/6-31G*) -1086.226846
E(B3LYP/6-311+G**) -1086.937762

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
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C	0.16239200	-0.00002000	-0.00001400
C	-0.55241900	1.16647900	0.28829800
C	-1.94404800	1.17560600	0.27692100
C	-2.63931200	0.00002300	0.00001000
N	1.57074200	-0.00003700	-0.00002500
C	2.37614200	-0.78227500	0.86015100
C	2.37614600	0.78218100	-0.86021500
C	3.79072000	-0.45169100	0.49268700
C	3.79072200	0.45170200	-0.49265100
H	4.62813900	-0.91487700	0.99856000

H	4.62814400	0.91494500	-0.99846700
O	1.97176500	-1.54010800	1.71011100
O	1.97177200	1.54012900	-1.71007400
F	-2.61398100	-2.29944000	-0.54815300
F	0.10153100	-2.29250800	-0.58358900
F	0.10161400	2.29247100	0.58355300
F	-2.61389800	2.29948600	0.54817200
F	-3.97332300	0.00004400	0.00002300

1h

E(B3LYP/6-31G*) -767.39775660
H(B3LYP/6-31G*) -767.145168
G(B3LYP/6-31G*) -767.201306
E(M06-2X/6-31G*) -767.0781664
E(B3LYP/6-311+G**) -767.5941133

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	3.48404100	-1.02901800	0.18060700
C	2.49559300	-0.07982500	0.19730100
C	1.11321800	-0.43968600	0.07891300
C	0.80449600	-1.84697400	-0.04114800
C	1.86702400	-2.80375800	-0.06213300
C	3.17286600	-2.41112200	0.04398300
C	0.04797600	0.49480900	0.11847200
C	-0.52893300	-2.25351100	-0.13074600
C	-1.58618200	-1.34152900	-0.08597200
C	-1.30382600	0.06844000	0.05834500
C	-2.42199100	0.96417400	0.10149700
H	-2.24231000	2.02362700	0.22908600
C	-3.70774000	0.49864200	0.00651800
C	-3.97891800	-0.89134900	-0.13591100
C	-2.94286800	-1.78325300	-0.17987100
H	4.52243900	-0.72277100	0.27482100
H	2.76239300	0.96419300	0.29625100
H	1.60821900	-3.85543900	-0.15871700
H	3.97287600	-3.14601600	0.03021000
H	-0.75103000	-3.31397500	-0.23254100
H	-4.53531300	1.20191900	0.04448300
H	-5.00664000	-1.23629800	-0.20814500
H	-3.12925200	-2.84898300	-0.28862400
C	0.31816700	1.96413200	0.24822300
O	-0.21427900	2.70780200	1.04828500
O	1.21505800	2.40682000	-0.66655600

3d

E(B3LYP/6-31G*) -1556.35149114

H(B3LYP/6-31G*) -1555.94884

G(B3LYP/6-31G*) -1556.032494

E(M06-2X/6-31G*) -1555.768915

E(B3LYP/6-311+G**) -1556.772312

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-0.05125100	-0.19702600	1.89397500
C	0.55502800	0.62135100	0.76433900
C	1.88179300	-0.02568400	0.37096500
C	1.72694200	-1.41941100	0.10974800
C	0.29166200	-1.90173500	0.24500000
C	-0.19947100	-1.49778300	1.62473100
C	3.12409500	0.57608300	0.26496500
C	2.80133200	-2.18917700	-0.24579500
C	4.10127800	-1.61891300	-0.33153900
C	4.28213500	-0.22107800	-0.06343700
C	5.59754000	0.31078500	-0.16122000
H	5.76061300	1.35811900	0.05713800
C	6.66456300	-0.49179800	-0.50461100
C	6.48150000	-1.86742800	-0.76839100
C	5.22237600	-2.41564400	-0.68178200
H	-0.35308800	0.27728400	2.82260500
H	0.64110400	1.67690800	1.00536200
H	0.18518400	-2.96937000	0.04355300
H	-0.63858800	-2.22342000	2.30189300
H	2.67690600	-3.24922000	-0.45810200
H	7.65950600	-0.05966300	-0.56900700
H	7.33234500	-2.48733900	-1.03733700
H	5.06412800	-3.47279500	-0.88175700
C	3.29261400	2.04840200	0.48595900
O	4.17855300	2.57379700	1.12947900
O	2.33631800	2.76460300	-0.15586600
C	-6.83781800	0.15589500	0.17861300
C	-6.23038200	0.89196500	-0.83952800
C	-4.85875100	0.77291100	-1.02060400
C	-4.07103400	-0.04668900	-0.20870800
C	-4.71512400	-0.75986200	0.80561700
C	-6.08670300	-0.67885800	1.00721200
N	-2.67190600	-0.14532900	-0.40315100
C	-2.02163600	-1.34972000	-0.73185800
C	-1.79087900	0.93803300	-0.21913200
C	-0.52683200	-1.06462000	-0.80609600

C	-0.37623300	0.43823200	-0.48842300
H	-0.17853700	-1.32167800	-1.81113200
H	0.04181700	1.01151600	-1.32141300
O	-2.12854300	2.05157500	0.11067800
O	-2.57899500	-2.40729500	-0.91609600
F	-3.97141900	-1.53658600	1.60900700
F	-4.25758100	1.45497200	-2.00796600
H	-6.53944200	-1.25672400	1.80505500
H	-7.91015400	0.23405700	0.32859500
H	-6.79613400	1.54515200	-1.49426200
C	2.42075800	4.19202700	0.01082500
H	3.36258100	4.56665700	-0.39814400
H	1.57182700	4.59808100	-0.53921100
H	2.36059300	4.46126900	1.06834400

3d'

E(B3LYP/6-31G*) -1556.35012149
H(B3LYP/6-31G*) -1555.947501
G(B3LYP/6-31G*) -1556.03053
E(M06-2X/6-31G*) -1555.769111
E(B3LYP/6-311+G**) -1556.770921

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-1.63095700	3.63736700	-0.05991600
C	-1.02578800	2.45205500	0.67798200
C	-1.51037800	1.18179700	-0.01596200
C	-1.23834800	1.20860400	-1.41436200
C	-0.55353200	2.48673200	-1.86993200
C	-1.38578300	3.65957200	-1.37377900
C	-2.07790300	0.06399400	0.57282100
C	-1.55399400	0.13978700	-2.20976200
C	-2.18713700	-1.00610700	-1.65613400
C	-2.45513300	-1.06008700	-0.24705400
C	-3.12107200	-2.21154700	0.25652300
H	-3.34009800	-2.27603200	1.31458500
C	-3.48211700	-3.24915600	-0.57549900
C	-3.19893400	-3.19849000	-1.95876000
C	-2.56502100	-2.09599300	-2.48340400
H	-2.20873100	4.38612400	0.47302500
H	-1.24105600	2.45578500	1.74252500
H	-0.37519700	2.49586500	-2.94698000
H	-1.73316900	4.43107400	-2.05433900
H	-1.32955300	0.15587500	-3.27392000
H	-3.99034300	-4.11584000	-0.16135300

H	-3.48534000	-4.02538200	-2.60279400
H	-2.34628200	-2.03776500	-3.54693700
C	-2.27973700	0.07545300	2.05916900
O	-2.72409800	1.01531200	2.68982200
O	-1.86570900	-1.06784000	2.64654800

4d

E(B3LYP/6-31G*) -1556.36563019
H(B3LYP/6-31G*) -1555.962962
G(B3LYP/6-31G*) -1556.045719
E(M06-2X/6-31G*) -1555.789066
E(B3LYP/6-311+G**) -1556.785932

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	0.76275800	-0.56028700	2.55950200
C	1.11365900	-0.60907200	1.21000000
C	0.89202500	-1.79057200	0.47593000
C	0.32776900	-2.90863700	1.08318800
C	-0.01261600	-2.85916000	2.43734300
C	1.68276200	0.52468600	0.33990800
C	1.28188400	-1.70284600	-0.98726100
C	2.71695800	-1.22044100	-1.05526300
C	2.94480200	-0.02626100	-0.34982200
C	4.21901900	0.53456500	-0.32312800
H	4.40995300	1.45254000	0.22449900
C	5.26610000	-0.09900300	-1.00167800
C	5.03816400	-1.28043100	-1.70669300
C	3.75805900	-1.84358600	-1.73636500
H	-0.05984600	-1.65132600	4.21945800
H	0.93105500	0.34171300	3.13258800
H	0.15044200	-3.80971900	0.50160700
H	-0.44898300	-3.73038600	2.91821900
H	1.12018600	-2.64227700	-1.52131000
H	6.26187000	0.33479100	-0.97498900
H	5.85551400	-1.76752000	-2.23137800
H	3.57567800	-2.76630700	-2.28213700
C	1.98487400	1.83429000	1.07082300
O	2.24284500	1.94616700	2.24873000
O	2.01078500	2.87404500	0.21205800
C	-5.01867400	-0.82675700	0.53397400
C	-3.66175100	-0.84075900	0.23716500
C	-3.05006500	0.19331000	-0.47674400
C	-3.85392600	1.26178900	-0.88132800
C	-5.21028000	1.31757500	-0.58990800

C	-5.78619900	0.26179900	0.11811800
N	-1.66685700	0.16347100	-0.78029100
C	-0.74748800	1.09874300	-0.27170000
C	-1.06992700	-0.84073900	-1.56604200
C	0.63222900	0.74333900	-0.82119900
C	0.42609600	-0.55729800	-1.62517500
H	0.97480900	1.56870400	-1.44788500
H	0.70898100	-0.44755700	-2.67651900
O	-1.02949700	2.00539800	0.47818200
O	-1.66567200	-1.75198800	-2.09214100
F	-3.28344700	2.25591700	-1.58073800
F	-2.90425600	-1.86742400	0.64839600
C	0.20558900	-1.69100700	3.16642400
H	-5.44693600	-1.65529600	1.08673400
H	-6.84665300	0.28806700	0.34903300
H	-5.78905500	2.17163800	-0.92307200
C	2.25284300	4.16081400	0.80716000
H	2.25005500	4.86861600	-0.02185400
H	1.45848600	4.39787000	1.51878500
H	3.21610200	4.17239800	1.32334000

3d-TS

E(B3LYP/6-31G*) -1556.29872878
H(B3LYP/6-31G*) -1555.899697
G(B3LYP/6-31G*) -1555.984288
E(M06-2X/6-31G*) -1555.705829
E(B3LYP/6-311+G**) -1556.72092

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	0.53626400	0.39900500	1.80424000
C	1.45249800	1.00646500	0.90036700
C	2.67140100	0.26913400	0.55860200
C	2.51343100	-1.15314400	0.52813000
C	1.17787400	-1.66641200	0.80787200
C	0.38231100	-0.96575800	1.74989700
C	3.91001400	0.83903000	0.23927300
C	3.57914000	-1.96573000	0.18602800
C	4.85021600	-1.42234500	-0.08757400
C	5.03583600	0.00509300	-0.05082500
C	6.33821000	0.51289700	-0.33966600
H	6.50842100	1.58079700	-0.29783300
C	7.37728200	-0.33363000	-0.64544400
C	7.18896500	-1.73843400	-0.68091400
C	5.95276100	-2.26612200	-0.40618700

H	-0.14468400	1.02261000	2.37552800
H	1.48331800	2.08739800	0.86009300
H	1.01451300	-2.73271600	0.67273300
H	-0.42792700	-1.46803500	2.26669000
H	3.44597900	-3.04478000	0.14496700
H	8.35901100	0.08037200	-0.85867200
H	8.02317600	-2.39069700	-0.92364500
H	5.79047400	-3.34103000	-0.42788700
C	4.08887900	2.32723500	0.20631700
O	4.99623100	2.94485700	0.72478400
O	3.11506500	2.93190400	-0.51797000
C	-5.35322900	1.03323000	-0.86786900
C	-3.99715500	0.89248400	-1.13398100
C	-3.13697600	0.19738300	-0.27734700
C	-3.70411700	-0.37632800	0.86411200
C	-5.05761100	-0.27389100	1.15509500
C	-5.87776800	0.44099400	0.28118500
N	-1.76016200	0.07166800	-0.56024900
C	-1.11921700	-1.16059600	-0.85013800
C	-0.87292900	1.16521200	-0.70178800
C	0.32058800	-0.83365600	-1.03764900
C	0.47344200	0.56760900	-0.95195000
H	0.92048700	-1.48152600	-1.66273800
H	1.19458200	1.14632200	-1.51437400
F	-3.48646700	1.42744900	-2.25277400
F	-2.89945700	-1.04467100	1.71174500
O	-1.68205900	-2.23204100	-0.91886000
O	-1.18688700	2.33217600	-0.60623500
C	3.20247900	4.36755900	-0.59942400
H	3.18855700	4.81025900	0.39955400
H	4.12433800	4.66241800	-1.10707100
H	2.32842100	4.67736800	-1.17188800
H	-5.97265900	1.58824100	-1.56345900
H	-6.93732800	0.53595900	0.49757500
H	-5.44334400	-0.74314700	2.05318400

3d'-TS

E(B3LYP/6-31G*) -1556.29340904
H(B3LYP/6-31G*) -1555.894601
G(B3LYP/6-31G*) -1555.978214
E(M06-2X/6-31G*) -1555.701889
E(B3LYP/6-311+G**) -1556.715065

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z

C	-3.82478800	-2.54422700	-0.13172900
C	-3.05521700	-1.52947900	-0.77023500
C	-2.56417200	-0.43189100	0.05776400
C	-2.23899900	-0.79527000	1.40355100
C	-2.42834100	-2.18906400	1.76876000
C	-3.50219000	-2.88912100	1.15850600
C	-2.33064700	0.87815000	-0.38895000
C	-1.74753400	0.15523500	2.28254300
C	-1.60187600	1.49783700	1.88906600
C	-1.88192800	1.87681600	0.52764300
C	-1.73719800	3.25577900	0.18462600
H	-1.94793600	3.57269400	-0.82833500
C	-1.33065700	4.18267200	1.11342600
C	-1.03810900	3.79885100	2.44750400
C	-1.17265800	2.48672600	2.82118200
H	-4.52552700	-3.13253900	-0.71764900
H	-3.24568400	-1.32008100	-1.81440200
H	-2.08298000	-2.49270500	2.75379600
H	-3.93301200	-3.76202400	1.64100000
H	-1.49057300	-0.12943700	3.29993600
H	-1.23315800	5.22508200	0.82224800
H	-0.71322300	4.54545700	3.16683600
H	-0.95779600	2.17467400	3.84016400
C	-2.57407500	1.18170800	-1.83799000
O	-3.53229300	0.79510400	-2.47982100
O	-1.57095400	1.89995000	-2.38378600
C	3.26202300	1.09732400	0.52274400
C	2.12076200	0.30786500	0.58228600
C	1.84992100	-0.68916900	-0.35993900
C	2.79830100	-0.87655400	-1.37306200
C	3.94014600	-0.09321600	-1.47698500
C	4.16702400	0.89519400	-0.51892300
N	0.69428100	-1.49752200	-0.28565400
C	-0.21799300	-1.68067800	-1.35087300
C	0.38490600	-2.35076400	0.80597400
C	-1.22487300	-2.67937600	-0.87419200
C	-0.87004400	-3.06419800	0.43526200
H	-1.64922700	-3.34484400	-1.61412900
H	-1.02278700	-4.05035700	0.85161500
F	1.24226300	0.50514600	1.57678800
F	2.59738400	-1.86095900	-2.26354200
O	-0.16603500	-1.11049900	-2.41962100
O	1.05622100	-2.46029800	1.80893700
H	4.63407600	-0.27947700	-2.28902500

H	3.41737800	1.85475500	1.28279800
H	5.05965700	1.50985300	-0.58229300
C	-1.66102500	2.09738100	-3.80565100
H	-2.59692300	2.59548600	-4.07091800
H	-0.80314800	2.71798200	-4.06514400
H	-1.60444200	1.13310700	-4.31637400

4d-TS

E(B3LYP/6-31G*) -1556.30272030
H(B3LYP/6-31G*) -1555.903859
G(B3LYP/6-31G*) -1555.987575
E(M06-2X/6-31G*) -1555.711994
E(B3LYP/6-311+G**) -1556.723811

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.06458200	0.18276100	2.63607500
C	1.76915600	-0.19412200	1.46486800
C	1.57892000	-1.51430200	0.95901700
C	0.72057500	-2.41579800	1.62410400
C	0.09173200	-2.04017400	2.79365700
C	2.62780300	0.67626000	0.67950300
C	2.23565500	-1.85181000	-0.27219800
C	3.52472100	-1.26251600	-0.52174900
C	3.73260300	0.05904800	-0.03887900
C	4.96718500	0.69052300	-0.32014600
H	5.15083000	1.69677800	0.03626100
C	5.94994900	0.02804400	-1.03401500
C	5.72928500	-1.27294900	-1.52612200
C	4.52265400	-1.90344600	-1.28488900
H	-0.23742100	-0.43912900	4.20979700
H	1.18910600	1.18121300	3.02960500
H	0.57551600	-3.40909600	1.20853600
H	-0.54740200	-2.74352400	3.31951300
H	2.03578100	-2.83548700	-0.69232800
H	6.90163300	0.51921200	-1.21697900
H	6.50753900	-1.77993500	-2.08951600
H	4.33956600	-2.90848600	-1.65710600
C	2.69170900	2.14485900	1.01054100
O	2.46041600	2.64223300	2.09313300
O	3.03231800	2.88668000	-0.06805100
C	-4.29212700	-0.62771600	0.54040300
C	-2.93063700	-0.70304400	0.27450900
C	-2.28212300	0.20251700	-0.57133600
C	-3.07623500	1.19158200	-1.16570100

C	-4.43514400	1.31101000	-0.90657000
C	-5.03941400	0.39133800	-0.04932300
N	-0.90014900	0.11644600	-0.85026500
C	0.00633700	1.20337900	-0.72520500
C	-0.27972800	-0.99519900	-1.46772000
C	1.30433400	0.71988300	-1.26100300
C	1.15508000	-0.61428500	-1.66623700
H	2.01307900	1.43370300	-1.65082500
H	1.67822700	-1.05951100	-2.50276000
O	-0.27348600	2.29010900	-0.26343700
O	-0.83969000	-2.02400400	-1.77746300
C	0.26536300	-0.73475500	3.29293100
F	-2.49899900	2.04183400	-2.02941500
F	-2.20867700	-1.67721700	0.84776400
H	-4.99517000	2.10436800	-1.38878100
H	-6.10273000	0.46633300	0.15634100
H	-4.73896100	-1.35976100	1.20383000
C	2.97159100	4.31185900	0.12674300
H	1.94295800	4.60862000	0.34464000
H	3.62287300	4.61843500	0.94852200
H	3.30599700	4.74550700	-0.81597200

3a

E(B3LYP/6-31G*) -1357.890985
H(B3LYP/6-31G*) -1357.473558
G(B3LYP/6-31G*) -1357.552773
E(M06-2X/6-31G*) -1357.362584
E(B3LYP/6-311+G**) -1358.24266

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-0.35429700	-0.06314300	1.90826100
C	0.24515200	0.66239100	0.71401000
C	1.57691900	-0.00626600	0.37552100
C	1.43059600	-1.41754700	0.22717200
C	-0.00122800	-1.89663700	0.40604700
C	-0.48862400	-1.38370300	1.75027000
C	2.81510300	0.59283700	0.21972900
C	2.50947300	-2.20638300	-0.06777600
C	3.80529200	-1.63628000	-0.20339700
C	3.97748600	-0.22045800	-0.04842100
C	5.28854200	0.31096800	-0.19416500
H	5.44468800	1.37360300	-0.06138900
C	6.36000800	-0.50913600	-0.47700000
C	6.18569200	-1.90271500	-0.62863800

C	4.93086900	-2.45088100	-0.49289900
H	-0.65517400	0.48412800	2.79626900
H	0.32345600	1.73505100	0.86571100
H	-0.10138700	-2.97776100	0.29343900
H	-0.90974300	-2.05564100	2.49167000
H	2.39199100	-3.28093900	-0.19338300
H	7.35155800	-0.07677100	-0.58031700
H	7.03995700	-2.53639500	-0.85051200
H	4.77964200	-3.52175500	-0.60674300
C	2.97562900	2.07865800	0.32812800
O	3.85776400	2.65545900	0.93154200
O	2.01638200	2.73943200	-0.36642200
C	-7.16850800	0.19410700	0.04092400
C	-6.46060900	1.09130500	-0.76034100
C	-5.08073000	0.96466300	-0.91252300
C	-4.40512600	-0.06404600	-0.24798800
C	-5.10627200	-0.96402700	0.56103500
C	-6.48758100	-0.83231700	0.69712500
N	-2.98682200	-0.19312500	-0.39909300
C	-2.32609800	-1.42254700	-0.58592000
C	-2.09325600	0.89411800	-0.32509200
C	-0.83127000	-1.15255100	-0.70375200
C	-0.67759400	0.36792700	-0.52368500
H	-0.49780200	-1.49927200	-1.68695800
H	-0.24716000	0.86371500	-1.39904500
O	-2.41020400	2.04818500	-0.13454300
O	-2.86408500	-2.50756700	-0.63674600
H	-7.03056500	-1.53570200	1.32221500
H	-8.24452000	0.29426500	0.15317200
H	-6.98197500	1.89419600	-1.27399400
C	2.09007400	4.17580500	-0.30284300
H	3.03056600	4.52715800	-0.73483800
H	1.24000900	4.53484300	-0.88298600
H	2.02409500	4.51964800	0.73246000
H	-4.52939300	1.66343400	-1.52977200
H	-4.57720200	-1.76287700	1.06530700

3a'

E(B3LYP/6-31G*) -1357.889634
H(B3LYP/6-31G*) -1357.472277
G(B3LYP/6-31G*) -1357.551569
E(M06-2X/6-31G*) -1357.362545
E(B3LYP/6-311+G**) -1358.241575

Atomic	Coordinates (Angstroms)

No.	X	Y	Z
C	-1.50407700	3.54859000	0.32350900
C	-0.89488600	2.29248100	0.92999100
C	-1.32859600	1.10995900	0.06792300
C	-1.01822500	1.31798600	-1.30745000
C	-0.34238600	2.65213400	-1.57578300
C	-1.21574900	3.73945400	-0.96782500
C	-1.89386500	-0.08108800	0.49227100
C	-1.30093100	0.35817600	-2.24259800
C	-1.93381100	-0.85578500	-1.85844600
C	-2.23268100	-1.09503700	-0.47493900
C	-2.89159900	-2.31038800	-0.14082300
H	-3.13130500	-2.51496000	0.89463900
C	-3.21940100	-3.23500500	-1.10875300
C	-2.90826100	-3.00099800	-2.46693500
C	-2.27881000	-1.83256500	-2.82921600
H	-2.11597600	4.21415600	0.92443400
H	-1.14420400	2.15965700	1.97870900
H	-0.12857600	2.79804600	-2.63632800
H	-1.55849600	4.58295200	-1.55950800
H	-1.05486900	0.51643200	-3.29042300
H	-3.72271100	-4.15458000	-0.82261900
H	-3.16961100	-3.73995300	-3.21935700
H	-2.03945800	-1.63332200	-3.87110700
C	-2.13492600	-0.26433100	1.96200700
O	-2.61485600	0.57872500	2.69489100
O	-1.71297000	-1.46656700	2.40767100
C	3.60261700	-2.54721300	-0.99549400
C	2.81020500	-1.40035400	-1.00718100
C	2.93279300	-0.46936100	0.02864400
C	3.83589600	-0.68593600	1.07378000
C	4.61566000	-1.84157000	1.07917000
C	4.50486300	-2.77279800	0.04534000
N	2.12722200	0.71437100	0.02072500
C	1.41689500	1.18164800	1.14390200
C	1.92414800	1.51521800	-1.12056200
C	0.66001800	2.44237200	0.74286500
C	0.99186400	2.66078900	-0.74341600
H	1.00523200	3.26368500	1.37830400
H	1.51664300	3.60269900	-0.92944400
O	1.41150300	0.65655600	2.23642400
O	2.40807700	1.31308600	-2.21302900
C	-1.81906400	-1.66587900	3.82856700
H	-1.19802800	-0.93784700	4.35614900

H	-2.85582200	-1.56059700	4.15843400
H	-1.45663700	-2.67868600	4.00546800
H	5.31344000	-2.01045300	1.89463300
H	5.11737200	-3.67018400	0.05152600
H	3.50866800	-3.26809200	-1.80284700
H	2.10748700	-1.22314200	-1.81217600
H	3.91612400	0.03620100	1.87751400

4a

E(B3LYP/6-31G*) -1357.905404
H(B3LYP/6-31G*) -1357.487905
G(B3LYP/6-31G*) -1357.56662
E(M06-2X/6-31G*) -1357.382829
E(B3LYP/6-311+G**) -1358.256863

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	0.46553700	-0.11883600	2.59260100
C	0.84689500	-0.39822900	1.27959900
C	0.63601200	-1.68802300	0.75385500
C	0.05492100	-2.68610900	1.53161000
C	-0.31522200	-2.40506900	2.84965500
C	1.44760300	0.56678000	0.24255500
C	1.05761200	-1.85266300	-0.69353800
C	2.49791500	-1.39601900	-0.80878200
C	2.72077000	-0.10088400	-0.31002200
C	3.99967300	0.44853900	-0.34809300
H	4.18754000	1.44594000	0.03777600
C	5.05572700	-0.29693700	-0.88417200
C	4.83260500	-1.57911400	-1.38496200
C	3.54798900	-2.13144300	-1.34975200
H	-0.39929700	-0.90855500	4.39569400
H	0.62550100	0.86768800	3.00642600
H	-0.10777400	-3.67510800	1.11031500
H	-0.76222300	-3.18169700	3.46444700
H	0.89788900	-2.86852700	-1.06251500
H	6.05469700	0.12967200	-0.90718000
H	5.65685300	-2.15261300	-1.80000500
H	3.36887700	-3.13216500	-1.73575900
C	1.74059000	1.98261900	0.74263200
O	1.94198200	2.30282500	1.89298200
O	1.82912200	2.85083200	-0.28620800
C	-5.33483700	-0.80696700	0.22738800
C	-3.96624000	-0.91292200	-0.01642100
C	-3.29015400	0.15567300	-0.61249700

C	-3.97373400	1.32585000	-0.95553800
C	-5.34014100	1.42355700	-0.69706600
C	-6.02491800	0.35865000	-0.10940300
N	-1.88601400	0.05298900	-0.87487800
C	-0.95714100	1.05343800	-0.53737600
C	-1.27666800	-1.08411000	-1.43902500
C	0.43103800	0.58767100	-0.96902900
C	0.22267400	-0.82850100	-1.53277800
H	0.80838800	1.28498500	-1.71905100
H	0.51698200	-0.90875900	-2.58384300
O	-1.22679600	2.10336100	0.00568300
O	-1.85463300	-2.09184600	-1.78270900
C	-0.11030300	-1.12842300	3.37153100
H	-5.86035700	-1.63935500	0.68698400
H	-7.09071400	0.43736700	0.08641200
H	-5.86918200	2.33538300	-0.95965800
C	2.06133300	4.22148300	0.08213900
H	2.12827200	4.76728800	-0.85912700
H	1.22758400	4.59156700	0.68355800
H	2.98880000	4.31647500	0.65224300
H	-3.43824200	2.15215900	-1.40789000
H	-3.42610700	-1.81410900	0.24663800

3a-TS

E(B3LYP/6-31G*) -1357.837436
H(B3LYP/6-31G*) -1357.423638
G(B3LYP/6-31G*) -1357.50414
E(M06-2X/6-31G*) -1357.298703
E(B3LYP/6-311+G**) -1358.190936

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-0.32421800	-0.05174700	1.83174100
C	0.60990000	0.64773900	1.01735600
C	1.82691100	-0.05606900	0.60700500
C	1.65893200	-1.46366900	0.40861300
C	0.31581600	-1.99399800	0.60866200
C	-0.48514800	-1.40002300	1.61768500
C	3.07423200	0.53592700	0.37252200
C	2.72335600	-2.24058300	-0.01156900
C	4.00248400	-1.68075100	-0.20141100
C	4.19812800	-0.26887900	0.00373200
C	5.50867600	0.25712900	-0.20438000
H	5.68584900	1.31120500	-0.03534200
C	6.54620900	-0.55776700	-0.59064100

C	6.34798200	-1.94718000	-0.79214600
C	5.10369300	-2.49190500	-0.59948400
H	-1.00441000	0.50749900	2.46709100
H	0.64899600	1.72571500	1.10313000
H	0.14678500	-3.03617100	0.34928900
H	-1.29397600	-1.95954700	2.07766500
H	2.58265100	-3.30613500	-0.18044500
H	7.53440300	-0.13106800	-0.73908900
H	7.18121300	-2.57444900	-1.09632300
H	4.93395100	-3.55549700	-0.74843600
C	3.26401300	2.01661700	0.51272000
O	4.16822700	2.56348800	1.11004400
O	2.30476000	2.70806700	-0.15082300
C	-6.07867300	1.21582600	-0.28676700
C	-4.72642100	1.13897300	-0.61852400
C	-3.98673500	0.00800100	-0.25011100
C	-4.60859400	-1.04145200	0.43896100
C	-5.96371300	-0.95605800	0.75265800
C	-6.70413000	0.17206800	0.39591000
N	-2.60034100	-0.08347000	-0.57493200
C	-1.95403900	-1.27354800	-1.00323200
C	-1.69389700	1.00390500	-0.59102700
C	-0.50929200	-0.94460000	-1.13847900
C	-0.34783400	0.43252000	-0.88960600
H	0.09033200	-1.52461400	-1.82721500
H	0.38349800	1.07099100	-1.36770000
O	-2.50208700	-2.33871900	-1.20329700
O	-1.97701500	2.16833300	-0.38845900
C	2.40399600	4.14296600	-0.06749200
H	2.38247300	4.46940200	0.97509400
H	3.33362600	4.48525500	-0.52910800
H	1.53872600	4.52344600	-0.60991800
H	-6.64482000	2.09854900	-0.57144500
H	-7.75944300	0.23591500	0.64633300
H	-6.43961900	-1.77719500	1.28182700
H	-4.24262300	1.95187300	-1.14346200
H	-4.03916600	-1.92201600	0.70840500

3a'-TS

E(B3LYP/6-31G*) -1357.834106
H(B3LYP/6-31G*) -1357.42046
G(B3LYP/6-31G*) -1357.500521
E(M06-2X/6-31G*) -1357.298045
E(B3LYP/6-311+G**) -1358.187314

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-3.86921200	-2.53257700	-0.12493100
C	-3.06638600	-1.55107600	-0.77375500
C	-2.53716900	-0.45954200	0.03815000
C	-2.23085300	-0.81296200	1.39086100
C	-2.46728100	-2.19523900	1.77410800
C	-3.56404100	-2.86802200	1.17147500
C	-2.23995000	0.82989900	-0.43111200
C	-1.68768400	0.12596600	2.25221400
C	-1.46778200	1.45125700	1.83295000
C	-1.73466600	1.81971700	0.46511400
C	-1.51781900	3.18234600	0.09608500
H	-1.71544300	3.49101700	-0.92193200
C	-1.05696000	4.10292500	1.00533000
C	-0.77902800	3.72913800	2.34533200
C	-0.98261600	2.43363000	2.74517300
H	-4.58703800	-3.10517100	-0.70565700
H	-3.24195700	-1.35491600	-1.82310500
H	-2.13804200	-2.49309000	2.76642000
H	-4.02610300	-3.71778400	1.66609400
H	-1.44956300	-0.15349600	3.27580200
H	-0.90373600	5.13256900	0.69387200
H	-0.41192400	4.47085700	3.04918200
H	-0.78487200	2.13126600	3.77070600
C	-2.47179800	1.11858400	-1.88572900
O	-3.45030900	0.76731500	-2.51706500
O	-1.43598100	1.77485300	-2.44600500
C	3.10663900	1.06001200	0.76120600
C	2.02679400	0.17995300	0.80899300
C	1.72410400	-0.60682900	-0.30840300
C	2.50227800	-0.50691000	-1.46848000
C	3.57139300	0.38691800	-1.50661800
C	3.88099000	1.17075500	-0.39434600
N	0.63099800	-1.52373200	-0.26124200
C	-0.24393500	-1.79599000	-1.33711700
C	0.30599500	-2.33503200	0.85585700
C	-1.25946800	-2.76838600	-0.83508800
C	-0.92289200	-3.09880100	0.49194200
H	-1.69245500	-3.45323300	-1.55169200
H	-1.05990100	-4.07295900	0.94145400
O	-0.17109500	-1.31358900	-2.45084500
O	0.92661700	-2.37924600	1.89840700
H	4.16793900	0.46317500	-2.41175000

H	3.33666800	1.66594300	1.63329800
H	4.71889100	1.86178400	-0.42772400
C	-1.51689500	1.94881700	-3.87147500
H	-2.42825500	2.48535200	-4.14692600
H	-0.63045400	2.52266300	-4.14197700
H	-1.50611200	0.97303100	-4.36307700
H	1.42658400	0.09712700	1.70544400
H	2.26199000	-1.11226900	-2.33289800

4a-TS

E(B3LYP/6-31G*) -1357.844356
H(B3LYP/6-31G*) -1357.430574
G(B3LYP/6-31G*) -1357.510155
E(M06-2X/6-31G*) -1357.308958
E(B3LYP/6-311+G**) -1358.19688

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	0.88445300	0.27767500	2.48716000
C	1.66895100	-0.13979900	1.38121600
C	1.50059800	-1.47221700	0.90158200
C	0.58374300	-2.34568700	1.52659500
C	-0.13200700	-1.92680400	2.63059400
C	2.58110700	0.70298400	0.62737700
C	2.22270900	-1.84414500	-0.28274000
C	3.52837900	-1.26922000	-0.47643000
C	3.71851900	0.06240800	-0.01528700
C	4.97133000	0.67955700	-0.24250400
H	5.14254800	1.69293600	0.09962900
C	5.98669500	-0.00576000	-0.88590200
C	5.78394300	-1.31679500	-1.35818400
C	4.56144900	-1.93447600	-1.16790900
H	-0.54824100	-0.27910400	3.96890200
H	0.99257500	1.28578200	2.86068900
H	0.46549600	-3.35223500	1.13472700
H	-0.81473600	-2.60825800	3.13041000
H	2.04048700	-2.83841700	-0.68552400
H	6.95039100	0.47532900	-1.02821100
H	6.58800700	-1.84172000	-1.86615100
H	4.39208600	-2.94736100	-1.52504800
C	2.63190500	2.18041400	0.91680900
O	2.33900500	2.71011900	1.96883100
O	3.03743000	2.88753000	-0.16200900
C	-4.15348300	-0.85890200	0.47143800
C	-2.81383300	-0.91894500	0.09119500

C	-2.21948500	0.18569800	-0.53157600
C	-2.96922200	1.34582600	-0.76525400
C	-4.30425100	1.39579800	-0.36681200
C	-4.90390400	0.29631500	0.24851700
N	-0.85346000	0.12318300	-0.94059900
C	0.05767400	1.21084300	-0.90831800
C	-0.23482000	-1.01699000	-1.50474000
C	1.35746800	0.69094700	-1.39412400
C	1.20094000	-0.65853100	-1.73502300
H	2.09062300	1.37712900	-1.78864500
H	1.72008300	-1.14822800	-2.54920200
O	-0.20589500	2.34407900	-0.55066600
O	-0.77781300	-2.07620200	-1.74339900
C	0.02137100	-0.60842600	3.10437500
H	-4.87769600	2.30118200	-0.54638100
H	-5.94659100	0.33918500	0.55117800
H	-4.60905100	-1.72215000	0.94920100
C	2.96677000	4.31806100	-0.01651400
H	1.92672100	4.62017700	0.12674800
H	3.56563600	4.65098600	0.83435000
H	3.36027300	4.72184100	-0.94964600
H	-2.50626400	2.20136000	-1.23895500
H	-2.23342500	-1.81461500	0.26747700

Rotational Barriers:

2a-TS

E(B3LYP/6-31G*) -590.476490
H(B3LYP/6-31G*)-590.316970
G(B3LYP/6-31G*) -590.361382
E(M06-2X/6-31G*) -590.237717
E(B3LYP/6-311+G**) -590.636614

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.70650300	-1.14100100	0.12998400
C	3.12230400	-0.66055600	0.07126100
C	3.12184600	0.66122200	-0.08792500
C	1.70570900	1.14100100	-0.14416400
N	0.87273400	-0.00020300	-0.00632600
H	3.94900800	-1.35411500	0.15400100
H	3.94807200	1.35516800	-0.17218300
C	-0.56662600	-0.00060500	-0.00472600
C	-1.27811200	1.20078500	-0.16056700
C	-1.27701400	-1.20242800	0.15277600

C	-2.67231600	1.18829700	-0.15727100
C	-2.67122600	-1.19080600	0.15272100
C	-3.38109900	-0.00147100	-0.00145100
O	1.36467000	-2.29642800	0.26872000
O	1.36310300	2.29625700	-0.28239400
H	-3.20062800	-2.13185000	0.27606400
H	-4.46746100	-0.00180300	-0.00018500
H	-3.20258400	2.12901500	-0.27937900
H	-0.74749100	-2.13492200	0.27298100
H	-0.74945200	2.13360700	-0.28201000

2b-TS

E(B3LYP/6-31G*) -888.160796
H(B3LYP/6-31G*) -888.023510
G(B3LYP/6-31G*) -888.074012
E(M06-2X/6-31G*) -887.839822
E(B3LYP/6-311+G**) -888.425933

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.70408000	-1.14374200	0.12785700
C	3.11802300	-0.66099300	0.07058500
C	3.11762000	0.66192600	-0.08507000
C	1.70337700	1.14390100	-0.14082000
N	0.87087500	-0.00017100	-0.00573700
H	3.94596100	-1.35318800	0.15148200
H	3.94513300	1.35450900	-0.16698000
C	-0.56002800	-0.00063400	-0.00505500
C	-1.26684800	1.20263700	-0.16332500
C	-1.26574400	-1.20439600	0.15432400
C	-2.65384200	1.17830400	-0.15917300
C	-2.65276400	-1.18111400	0.15199600
C	-3.37296500	-0.00167200	-0.00309200
O	1.35413800	-2.29619400	0.26294200
O	1.35259200	2.29605700	-0.27614800
H	-0.76132900	-2.15016700	0.27741000
H	-0.76335900	2.14880700	-0.28716300
F	-3.33307400	-2.32829700	0.30404300
F	-4.71174100	-0.00216200	-0.00220100
F	-3.33520900	2.32499200	-0.31025300

2c-TS

E(B3LYP/6-31G*) -689.692267
H(B3LYP/6-31G*) -689.540554
G(B3LYP/6-31G*) -689.587234

E(M06-2X/6-31G*) -689.425949
E(B3LYP/6-311+G**) -689.885589

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	-1.72904000	-1.07697700	-0.00279800
C	-3.12505800	-0.54521200	-0.00470800
C	-3.09039700	0.78099800	-0.07642400
C	-1.66841800	1.22499100	-0.12663700
N	-0.84531400	0.05898900	-0.07929800
H	-3.96663100	-1.22361100	0.04715000
H	-3.89420700	1.50536700	-0.10032600
C	0.60053500	0.09447800	-0.10733500
C	1.25764500	1.34181400	-0.18474700
C	1.44646400	-1.03487600	-0.06311000
C	2.64432000	1.45464900	-0.21656800
H	0.66450900	2.23989700	-0.22081100
C	2.83435700	-0.92055700	-0.09516300
C	3.45043400	0.32093900	-0.17220800
O	-1.45620300	-2.24917700	0.05354200
O	-1.32581500	2.38756600	-0.19522600
H	3.40221000	-1.84447800	-0.05687800
H	4.53332900	0.39643600	-0.19648000
H	3.08493200	2.44536900	-0.27674700
F	0.98991300	-2.29390500	0.01262400

2d-TS

E(B3LYP/6-31G*) -788.903701
H(B3LYP/6-31G*) -788.760001
G(B3LYP/6-31G*) -788.808453
E(M06-2X/6-31G*) -788.611051
E(B3LYP/6-311+G**) -789.130985

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.76071600	-1.15565000	0.00263100
C	3.15211700	-0.64609700	0.18164200
C	3.15141000	0.67380500	0.01657300
C	1.75966200	1.12180800	-0.28296300
N	0.89208600	0.00007600	-0.00195100
H	3.97776300	-1.33368100	0.31273600
H	3.97627100	1.37344600	-0.02546800
C	-0.54167500	0.00397500	0.03165200
C	-1.32503800	1.18457600	-0.03969200
C	-1.32408700	-1.15788200	0.25627100
C	-2.71171800	1.18313600	-0.14090400

C	-2.71072400	-1.18281300	0.15818800
C	-3.41744000	-0.01065600	-0.07458000
O	1.48197800	-2.30555700	-0.22681100
O	1.47992900	2.17884200	-0.79000100
H	-3.20178700	-2.13769500	0.30977400
H	-4.49954600	-0.02107300	-0.15312500
H	-3.20359700	2.14527800	-0.23174400
F	-0.76421100	-2.31228100	0.64465900
F	-0.76647700	2.39990800	0.04939100

2e-TS

E(B3LYP/6-31G*) -1086.568398
H(B3LYP/6-31G*) -1086.446627
G(B3LYP/6-31G*) -1086.501715
E(M06-2X/6-31G*) -1086.192641
E(B3LYP/6-311+G**) -1086.900161

Atomic	Coordinates (Angstroms)		
No.	X	Y	Z
C	1.76604300	-1.15800000	0.00764700
C	3.15436900	-0.64527000	0.18949300
C	3.15385100	0.67472900	0.02394700
C	1.76525600	1.12557600	-0.27887800
N	0.89494500	-0.00076100	-0.01048600
H	3.98006700	-1.33140400	0.32726900
H	3.97898400	1.37430900	-0.01210800
C	-0.53632100	0.00178300	0.01372900
C	-1.31067300	1.18825900	-0.05986800
C	-1.30951600	-1.16651500	0.23755900
C	-2.70333000	1.17596200	-0.13920800
C	-2.70213800	-1.17549500	0.15784300
C	-3.41792200	-0.00714100	-0.04618100
O	1.48485100	-2.30878700	-0.20839800
O	1.48341800	2.18711500	-0.77261800
F	-0.78390200	-2.34050800	0.59208100
F	-0.78641800	2.41408300	-0.00842800
F	-3.35122500	2.34037500	-0.25167900
F	-4.75055500	-0.01591100	-0.10860200
F	-3.34919600	-2.33169600	0.33885900

9. Crystal Data and Structure Refinement

Table S6-1. Crystal data and structure refinement for **2c**.

Identification code	**2c**
Empirical formula	$C_{10}H_6FNO_2$

Formula weight	191.16
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.892(2) Å alpha = 90 deg. b = 7.9279(18) Å beta = 90 deg. c = 19.835(4) Å gamma = 90 deg.
Volume	1712.9(7) $Å^3$
Z, Calculated density	8, 1.483 Mg/m^3
Absorption coefficient	0.119 mm^{-1}
F(000)	784
Crystal size	0.30 x 0.27 x 0.15 mm
Theta range for data collection	2.05 to 25.00 deg.
Limiting indices	$-12\leq h\leq 9$, $-7\leq k\leq 9$, $-19\leq l\leq 23$
Reflections collected / unique	4891 / 1498 [R(int) = 0.0398]
Completeness to theta = 25.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9824 and 0.9652
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1498 / 13 / 137
Goodness-of-fit on F^2	1.287
Final R indices [I>2sigma(I)]	R_1 = 0.0601, wR_2 = 0.1140
R indices (all data)	R_1 = 0.0680, wR_2 = 0.1175
Largest diff. peak and hole	0.155 and -0.168 e. $Å^{-3}$

Table *S6-2*. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2c**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	4475(1)	-244(2)	6606(1)	53(1)
F(1')	8138(6)	2589(10)	6563(4)	59(3)
O(1)	8023(2)	347(3)	5639(1)	73(1)
O(2)	4328(1)	2970(2)	5848(1)	57(1)
N(1)	6185(2)	1577(2)	5935(1)	42(1)
C(1)	6247(2)	1391(3)	6648(1)	39(1)
C(2)	5353(2)	501(3)	6986(1)	41(1)
C(3)	5364(2)	303(3)	7673(1)	48(1)
C(4)	6323(2)	990(3)	8033(1)	50(1)
C(5)	7241(2)	1870(3)	7707(1)	53(1)
C(6)	7197(2)	2081(3)	7018(1)	47(1)
C(7)	7079(2)	1037(3)	5480(1)	51(1)
C(8)	6619(2)	1499(3)	4801(1)	53(1)
C(9)	5554(2)	2265(3)	4864(1)	51(1)
C(10)	5224(2)	2362(3)	5589(1)	44(1)

Table *S6-3*. Bond lengths [Å] and angles [deg] for **2c.**

F(1)-C(2)	1.354(3)
F(1)-H(1)	0.4023
F(1')-C(6)	1.424(7)
F(1')-H(1')	0.5755
O(1)-C(7)	1.206(3)
O(2)-C(10)	1.204(3)
N(1)-C(7)	1.395(3)
N(1)-C(10)	1.398(3)
N(1)-C(1)	1.423(3)
C(1)-C(2)	1.376(3)
C(1)-C(6)	1.381(3)
C(2)-C(3)	1.372(3)
C(2)-H(1)	0.9596
C(3)-C(4)	1.377(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.380(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.379(3)
C(5)-H(5)	0.9500
C(6)-H(1')	0.9601
C(7)-C(8)	1.483(4)
C(8)-C(9)	1.315(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.484(3)
C(9)-H(9)	0.9500
C(2)-F(1)-H(1)	9.5
C(6)-F(1')-H(1')	28.7
C(7)-N(1)-C(10)	110.0(2)
C(7)-N(1)-C(1)	125.3(2)
C(10)-N(1)-C(1)	124.70(18)
C(2)-C(1)-C(6)	118.3(2)
C(2)-C(1)-N(1)	120.2(2)
C(6)-C(1)-N(1)	121.5(2)
F(1)-C(2)-C(3)	120.6(2)
F(1)-C(2)-C(1)	116.9(2)
C(3)-C(2)-C(1)	122.5(2)
F(1)-C(2)-H(1)	4.0
C(3)-C(2)-H(1)	118.4
C(1)-C(2)-H(1)	119.2
C(2)-C(3)-C(4)	118.4(2)
C(2)-C(3)-H(3)	120.8
C(4)-C(3)-H(3)	120.8

C(3)-C(4)-C(5)	120.4(2)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(6)-C(5)-C(4)	120.0(2)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	120.3(2)
C(5)-C(6)-F(1')	129.6(4)
C(1)-C(6)-F(1')	108.4(4)
C(5)-C(6)-H(1')	119.8
C(1)-C(6)-H(1')	119.9
F(1')-C(6)-H(1')	16.7
O(1)-C(7)-N(1)	124.5(3)
O(1)-C(7)-C(8)	129.6(2)
N(1)-C(7)-C(8)	106.0(2)
C(9)-C(8)-C(7)	109.0(2)
C(9)-C(8)-H(8)	125.5
C(7)-C(8)-H(8)	125.5
C(8)-C(9)-C(10)	109.2(2)
C(8)-C(9)-H(9)	125.4
C(10)-C(9)-H(9)	125.4
O(2)-C(10)-N(1)	125.1(2)
O(2)-C(10)-C(9)	129.2(2)
N(1)-C(10)-C(9)	105.7(2)

Table *S6-4*. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2c**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
F(1)	44(1)	57(1)	57(1)	-3(1)	3(1)	-19(1)
F(1')	44(4)	54(5)	77(5)	5(4)	-7(4)	-10(4)
O(1)	60(1)	82(2)	77(1)	20(1)	25(1)	31(1)
O(2)	42(1)	76(1)	53(1)	-3(1)	3(1)	15(1)
N(1)	34(1)	44(1)	48(1)	4(1)	8(1)	3(1)
C(1)	34(1)	33(1)	49(1)	4(1)	5(1)	6(1)
C(2)	34(1)	34(1)	55(2)	-4(1)	2(1)	-3(1)
C(3)	47(1)	47(2)	50(2)	6(1)	10(1)	-1(1)
C(4)	56(2)	42(1)	52(2)	0(1)	-5(1)	10(1)
C(5)	47(2)	41(1)	70(2)	5(1)	-17(1)	0(1)
C(6)	34(1)	41(2)	67(2)	13(1)	0(1)	-3(1)
C(7)	44(1)	47(2)	63(2)	6(1)	16(1)	3(1)
C(8)	51(2)	57(2)	50(2)	-2(1)	16(1)	-3(1)
C(9)	46(1)	62(2)	47(2)	-1(1)	3(1)	-6(1)
C(10)	37(1)	47(1)	50(1)	-3(1)	5(1)	-3(1)

Table *S6-5*. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2c.**

	x	y	z	U(eq)
H(1)	4689	13	6735	49
H(3)	4725	-294	7895	58
H(4)	6352	856	8509	60
H(5)	7903	2332	7958	63
H(1')	7831	2709	6793	57
H(8)	7027	1278	4387	63
H(9)	5073	2689	4503	62

Table *S6-6*. Torsion angles [deg] for **2c.**

C(7)-N(1)-C(1)-C(2)	-120.7(2)
C(10)-N(1)-C(1)-C(2)	60.6(3)
C(7)-N(1)-C(1)-C(6)	58.9(3)
C(10)-N(1)-C(1)-C(6)	-119.8(2)
C(6)-C(1)-C(2)-F(1)	-176.2(2)
N(1)-C(1)-C(2)-F(1)	3.4(3)
C(6)-C(1)-C(2)-C(3)	1.1(3)
N(1)-C(1)-C(2)-C(3)	-179.2(2)
F(1)-C(2)-C(3)-C(4)	175.7(2)
C(1)-C(2)-C(3)-C(4)	-1.6(4)
C(2)-C(3)-C(4)-C(5)	0.7(4)
C(3)-C(4)-C(5)-C(6)	0.6(4)
C(4)-C(5)-C(6)-C(1)	-1.0(4)
C(4)-C(5)-C(6)-F(1')	-164.4(5)
C(2)-C(1)-C(6)-C(5)	0.2(3)
N(1)-C(1)-C(6)-C(5)	-179.4(2)
C(2)-C(1)-C(6)-F(1')	166.8(4)
N(1)-C(1)-C(6)-F(1')	-12.9(4)
C(10)-N(1)-C(7)-O(1)	178.6(3)
C(1)-N(1)-C(7)-O(1)	-0.3(4)
C(10)-N(1)-C(7)-C(8)	-1.1(3)
C(1)-N(1)-C(7)-C(8)	-179.9(2)
O(1)-C(7)-C(8)-C(9)	-178.8(3)
N(1)-C(7)-C(8)-C(9)	0.8(3)
C(7)-C(8)-C(9)-C(10)	-0.3(3)
C(7)-N(1)-C(10)-O(2)	-179.2(2)
C(1)-N(1)-C(10)-O(2)	-0.4(4)
C(7)-N(1)-C(10)-C(9)	0.9(3)
C(1)-N(1)-C(10)-C(9)	179.8(2)
C(8)-C(9)-C(10)-O(2)	179.8(3)
C(8)-C(9)-C(10)-N(1)	-0.4(3)

Table S7-1. Crystal data and structure refinement for **4e.**

Identification code	**4e**
Empirical formula	$C_{26}H_{14}F_5NO_4$
Formula weight	499.38
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.761(3) Å alpha = 90 deg. b = 20.483(4) Å beta = 98.692(3) deg. c = 8.2482(15) Å gamma = 90 deg.
Volume	2131.2(7) $Å^3$
Z, Calculated density	4, 1.556 Mg/m^3
Absorption coefficient	0.134 mm^{-1}
F(000)	1016
Crystal size	0.52 x 0.29 x 0.24 mm
Theta range for data collection	1.99 to 27.49 deg.
Limiting indices	$-16 \leq h \leq 16$, $-26 \leq k \leq 24$, $-6 \leq l \leq 10$
Reflections collected / unique	14409 / 4881 [R(int) = 0.0387]
Completeness to theta = 27.49	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9685 and 0.9335
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4881 / 0 / 326
Goodness-of-fit on F^2	1.158
Final R indices [I>2sigma(I)]	$R_1 = 0.0548$, $wR_2 = 0.1284$
R indices (all data)	$R_1 = 0.0600$, $wR_2 = 0.1316$
Largest diff. peak and hole	0.363 and -0.227 e. $Å^{-3}$

Table *S7-2*. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	-704(1)	3900(1)	3300(2)	40(1)
F(2)	-2585(1)	3420(1)	1829(2)	56(1)
F(3)	-3000(1)	2128(1)	1994(2)	58(1)
F(4)	-1598(1)	1327(1)	3808(2)	54(1)
F(5)	268(1)	1808(1)	5355(2)	39(1)
O(1)	217(1)	3813(1)	6902(2)	29(1)
O(2)	1855(1)	2502(1)	3587(2)	30(1)
O(3)	4395(1)	3305(1)	2515(2)	40(1)
O(4)	4326(1)	2650(1)	4671(2)	32(1)
N(1)	825(1)	3105(1)	5089(2)	23(1)
C(1)	2109(1)	3744(1)	6722(2)	22(1)
C(2)	2345(1)	4458(1)	6218(2)	23(1)
C(3)	3533(2)	4532(1)	6616(2)	24(1)
C(4)	4097(1)	4093(1)	5778(2)	24(1)
C(5)	3378(1)	3636(1)	4617(2)	22(1)
C(6)	2674(1)	3260(1)	5713(2)	21(1)
C(7)	1789(1)	2896(1)	4649(2)	23(1)
C(8)	945(1)	3583(1)	6323(2)	23(1)
C(9)	2051(1)	4500(1)	4372(2)	23(1)
C(10)	1294(2)	4918(1)	3565(2)	26(1)
C(11)	1079(2)	4903(1)	1861(2)	30(1)
C(12)	1611(2)	4466(1)	991(2)	31(1)
C(13)	2374(2)	4045(1)	1795(2)	26(1)
C(14)	2605(1)	4068(1)	3494(2)	22(1)
C(15)	-173(1)	2863(1)	4343(2)	25(1)
C(16)	-917(2)	3267(1)	3458(2)	30(1)
C(17)	-1876(2)	3024(1)	2692(3)	38(1)
C(18)	-2090(2)	2367(1)	2787(3)	39(1)
C(19)	-1369(2)	1959(1)	3684(3)	36(1)
C(20)	-417(2)	2205(1)	4462(2)	29(1)
C(21)	4069(2)	4985(1)	7685(2)	30(1)
C(22)	5170(2)	5001(1)	7910(2)	34(1)
C(23)	5730(2)	4565(1)	7077(2)	33(1)
C(24)	5195(2)	4109(1)	6005(2)	28(1)
C(25)	4068(1)	3183(1)	3770(2)	25(1)
C(26)	5067(2)	2205(1)	4094(3)	41(1)

Table *S7-3*. Bond lengths [Å] and angles [deg] for **4e.**

F(1)-C(16)	1.335(2)
F(2)-C(17)	1.336(2)
F(3)-C(18)	1.337(2)
F(4)-C(19)	1.334(2)
F(5)-C(20)	1.332(2)
O(1)-C(8)	1.203(2)
O(2)-C(7)	1.203(2)
O(3)-C(25)	1.199(2)
O(4)-C(25)	1.334(2)
O(4)-C(26)	1.445(2)
N(1)-C(7)	1.401(2)
N(1)-C(8)	1.403(2)
N(1)-C(15)	1.418(2)
C(1)-C(8)	1.509(2)
C(1)-C(6)	1.542(2)
C(1)-C(2)	1.561(2)
C(1)-H(1)	1.0000
C(2)-C(3)	1.509(3)
C(2)-C(9)	1.515(2)
C(2)-H(2)	1.0000
C(3)-C(21)	1.387(3)
C(3)-C(4)	1.399(3)
C(4)-C(24)	1.386(3)
C(4)-C(5)	1.539(2)
C(5)-C(25)	1.519(2)
C(5)-C(14)	1.529(2)
C(5)-C(6)	1.570(2)
C(6)-C(7)	1.517(2)
C(6)-H(6)	1.0000
C(9)-C(10)	1.383(2)
C(9)-C(14)	1.401(2)
C(10)-C(11)	1.391(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.388(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.391(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.389(2)
C(13)-H(13)	0.9500
C(15)-C(16)	1.382(3)
C(15)-C(20)	1.390(3)
C(16)-C(17)	1.383(3)

C(17)-C(18)	1.378(3)
C(18)-C(19)	1.374(3)
C(19)-C(20)	1.381(3)
C(21)-C(22)	1.389(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.389(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.392(3)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(25)-O(4)-C(26)	116.94(15)
C(7)-N(1)-C(8)	113.42(15)
C(7)-N(1)-C(15)	123.13(14)
C(8)-N(1)-C(15)	123.45(15)
C(8)-C(1)-C(6)	105.43(14)
C(8)-C(1)-C(2)	111.71(14)
C(6)-C(1)-C(2)	109.50(13)
C(8)-C(1)-H(1)	110.0
C(6)-C(1)-H(1)	110.0
C(2)-C(1)-H(1)	110.0
C(3)-C(2)-C(9)	107.53(14)
C(3)-C(2)-C(1)	105.30(14)
C(9)-C(2)-C(1)	107.06(13)
C(3)-C(2)-H(2)	112.2
C(9)-C(2)-H(2)	112.2
C(1)-C(2)-H(2)	112.2
C(21)-C(3)-C(4)	120.18(18)
C(21)-C(3)-C(2)	126.04(17)
C(4)-C(3)-C(2)	113.78(15)
C(24)-C(4)-C(3)	120.24(17)
C(24)-C(4)-C(5)	126.46(16)
C(3)-C(4)-C(5)	113.29(15)
C(25)-C(5)-C(14)	116.11(14)
C(25)-C(5)-C(4)	108.96(14)
C(14)-C(5)-C(4)	107.14(14)
C(25)-C(5)-C(6)	112.78(14)
C(14)-C(5)-C(6)	105.04(14)
C(4)-C(5)-C(6)	106.23(13)
C(7)-C(6)-C(1)	105.11(14)
C(7)-C(6)-C(5)	110.46(13)
C(1)-C(6)-C(5)	110.49(14)

C(7)-C(6)-H(6)	110.2
C(1)-C(6)-H(6)	110.2
C(5)-C(6)-H(6)	110.2
O(2)-C(7)-N(1)	123.71(17)
O(2)-C(7)-C(6)	128.47(16)
N(1)-C(7)-C(6)	107.81(14)
O(1)-C(8)-N(1)	123.73(17)
O(1)-C(8)-C(1)	128.38(16)
N(1)-C(8)-C(1)	107.88(14)
C(10)-C(9)-C(14)	120.84(16)
C(10)-C(9)-C(2)	124.63(16)
C(14)-C(9)-C(2)	114.52(15)
C(9)-C(10)-C(11)	119.30(17)
C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	119.96(17)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	120.98(17)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(14)-C(13)-C(12)	119.17(17)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(13)-C(14)-C(9)	119.71(16)
C(13)-C(14)-C(5)	127.68(16)
C(9)-C(14)-C(5)	112.50(14)
C(16)-C(15)-C(20)	118.34(17)
C(16)-C(15)-N(1)	121.33(16)
C(20)-C(15)-N(1)	120.32(17)
F(1)-C(16)-C(15)	119.98(17)
F(1)-C(16)-C(17)	118.91(18)
C(15)-C(16)-C(17)	121.08(18)
F(2)-C(17)-C(18)	119.91(19)
F(2)-C(17)-C(16)	120.5(2)
C(18)-C(17)-C(16)	119.6(2)
F(3)-C(18)-C(19)	120.1(2)
F(3)-C(18)-C(17)	119.7(2)
C(19)-C(18)-C(17)	120.25(19)
F(4)-C(19)-C(18)	119.74(19)
F(4)-C(19)-C(20)	120.4(2)
C(18)-C(19)-C(20)	119.88(19)
F(5)-C(20)-C(19)	119.50(17)
F(5)-C(20)-C(15)	119.69(17)

C(19)-C(20)-C(15)	120.80(19)
C(3)-C(21)-C(22)	119.52(19)
C(3)-C(21)-H(21)	120.2
C(22)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.27(18)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(22)-C(23)-C(24)	120.41(19)
C(22)-C(23)-H(23)	119.8
C(24)-C(23)-H(23)	119.8
C(4)-C(24)-C(23)	119.37(18)
C(4)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
O(3)-C(25)-O(4)	124.18(17)
O(3)-C(25)-C(5)	124.87(17)
O(4)-C(25)-C(5)	110.79(14)
O(4)-C(26)-H(26A)	109.5
O(4)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(4)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Table *S7-4*. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4e**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
F(1)	38(1)	30(1)	49(1)	8(1)	-1(1)	2(1)
F(2)	32(1)	69(1)	61(1)	5(1)	-11(1)	9(1)
F(3)	28(1)	76(1)	69(1)	-26(1)	2(1)	-16(1)
F(4)	46(1)	34(1)	86(1)	-17(1)	24(1)	-17(1)
F(5)	39(1)	26(1)	51(1)	4(1)	8(1)	3(1)
O(1)	28(1)	29(1)	32(1)	-2(1)	9(1)	5(1)
O(2)	31(1)	28(1)	33(1)	-10(1)	7(1)	-1(1)
O(3)	46(1)	43(1)	33(1)	4(1)	18(1)	11(1)
O(4)	33(1)	33(1)	32(1)	3(1)	9(1)	14(1)
N(1)	21(1)	22(1)	26(1)	-2(1)	3(1)	0(1)
C(1)	23(1)	22(1)	21(1)	-1(1)	3(1)	2(1)
C(2)	27(1)	20(1)	22(1)	-1(1)	4(1)	0(1)
C(3)	28(1)	24(1)	20(1)	3(1)	1(1)	-3(1)
C(4)	26(1)	23(1)	20(1)	3(1)	1(1)	-3(1)
C(5)	22(1)	23(1)	22(1)	1(1)	3(1)	0(1)
C(6)	21(1)	19(1)	22(1)	1(1)	4(1)	2(1)
C(7)	25(1)	20(1)	25(1)	1(1)	5(1)	1(1)
C(8)	26(1)	20(1)	23(1)	3(1)	5(1)	3(1)
C(9)	25(1)	20(1)	23(1)	1(1)	2(1)	-4(1)
C(10)	29(1)	20(1)	30(1)	1(1)	2(1)	0(1)
C(11)	31(1)	27(1)	30(1)	5(1)	-4(1)	-1(1)
C(12)	36(1)	32(1)	23(1)	2(1)	-3(1)	-3(1)
C(13)	29(1)	27(1)	24(1)	-2(1)	3(1)	-4(1)
C(14)	23(1)	19(1)	22(1)	0(1)	1(1)	-3(1)
C(15)	22(1)	27(1)	27(1)	-4(1)	5(1)	0(1)
C(16)	27(1)	29(1)	32(1)	-1(1)	5(1)	0(1)
C(17)	25(1)	50(1)	37(1)	-3(1)	0(1)	5(1)
C(18)	22(1)	52(1)	43(1)	-16(1)	7(1)	-9(1)
C(19)	33(1)	30(1)	49(1)	-13(1)	16(1)	-9(1)
C(20)	27(1)	26(1)	34(1)	-3(1)	8(1)	1(1)
C(21)	38(1)	29(1)	23(1)	-1(1)	3(1)	-7(1)
C(22)	39(1)	36(1)	27(1)	0(1)	-2(1)	-14(1)
C(23)	29(1)	39(1)	30(1)	6(1)	-2(1)	-9(1)
C(24)	26(1)	31(1)	27(1)	6(1)	3(1)	-3(1)
C(25)	24(1)	27(1)	25(1)	-3(1)	3(1)	0(1)
C(26)	40(1)	47(1)	37(1)	-2(1)	7(1)	22(1)

Table *S7-5*. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4e.**

	x	y	z	U(eq)
H(1)	2359	3679	7920	26
H(2)	1960	4788	6799	28
H(6)	3118	2949	6458	25
H(10)	924	5211	4169	32
H(11)	570	5193	1293	36
H(12)	1451	4453	-172	37
H(13)	2733	3747	1189	32
H(21)	3686	5281	8260	36
H(22)	5541	5312	8637	41
H(23)	6483	4578	7240	40
H(24)	5579	3812	5434	34
H(26A)	4819	2094	2944	62
H(26B)	5117	1806	4759	62
H(26C)	5766	2411	4189	62

Table *S7-6*. Torsion angles [deg] for **4e.**

C(8)-C(1)-C(2)-C(3)	-177.35(14)
C(6)-C(1)-C(2)-C(3)	-60.94(17)
C(8)-C(1)-C(2)-C(9)	-63.11(18)
C(6)-C(1)-C(2)-C(9)	53.30(18)
C(9)-C(2)-C(3)-C(21)	125.42(18)
C(1)-C(2)-C(3)-C(21)	-120.67(18)
C(9)-C(2)-C(3)-C(4)	-53.96(19)
C(1)-C(2)-C(3)-C(4)	59.95(18)
C(21)-C(3)-C(4)-C(24)	-0.2(3)
C(2)-C(3)-C(4)-C(24)	179.17(15)
C(21)-C(3)-C(4)-C(5)	-178.73(15)
C(2)-C(3)-C(4)-C(5)	0.7(2)
C(24)-C(4)-C(5)-C(25)	1.5(2)
C(3)-C(4)-C(5)-C(25)	179.84(14)
C(24)-C(4)-C(5)-C(14)	-124.89(18)
C(3)-C(4)-C(5)-C(14)	53.47(18)
C(24)-C(4)-C(5)-C(6)	123.23(18)
C(3)-C(4)-C(5)-C(6)	-58.40(18)
C(8)-C(1)-C(6)-C(7)	5.93(17)
C(2)-C(1)-C(6)-C(7)	-114.39(15)
C(8)-C(1)-C(6)-C(5)	125.10(14)
C(2)-C(1)-C(6)-C(5)	4.78(19)
C(25)-C(5)-C(6)-C(7)	-71.87(18)
C(14)-C(5)-C(6)-C(7)	55.51(17)
C(4)-C(5)-C(6)-C(7)	168.84(14)
C(25)-C(5)-C(6)-C(1)	172.26(14)
C(14)-C(5)-C(6)-C(1)	-60.37(17)
C(4)-C(5)-C(6)-C(1)	52.96(17)
C(8)-N(1)-C(7)-O(2)	-177.91(17)
C(15)-N(1)-C(7)-O(2)	1.4(3)
C(8)-N(1)-C(7)-C(6)	0.98(19)
C(15)-N(1)-C(7)-C(6)	-179.76(15)
C(1)-C(6)-C(7)-O(2)	174.44(18)
C(5)-C(6)-C(7)-O(2)	55.3(2)
C(1)-C(6)-C(7)-N(1)	-4.38(17)
C(5)-C(6)-C(7)-N(1)	-123.57(15)
C(7)-N(1)-C(8)-O(1)	-177.97(16)
C(15)-N(1)-C(8)-O(1)	2.8(3)
C(7)-N(1)-C(8)-C(1)	2.97(19)
C(15)-N(1)-C(8)-C(1)	-176.29(15)
C(6)-C(1)-C(8)-O(1)	175.47(17)
C(2)-C(1)-C(8)-O(1)	-65.7(2)

C(6)-C(1)-C(8)-N(1)	-5.53(18)
C(2)-C(1)-C(8)-N(1)	113.33(15)
C(3)-C(2)-C(9)-C(10)	-127.43(18)
C(1)-C(2)-C(9)-C(10)	119.84(18)
C(3)-C(2)-C(9)-C(14)	53.36(19)
C(1)-C(2)-C(9)-C(14)	-59.37(19)
C(14)-C(9)-C(10)-C(11)	0.3(3)
C(2)-C(9)-C(10)-C(11)	-178.84(17)
C(9)-C(10)-C(11)-C(12)	1.1(3)
C(10)-C(11)-C(12)-C(13)	-1.2(3)
C(11)-C(12)-C(13)-C(14)	-0.1(3)
C(12)-C(13)-C(14)-C(9)	1.5(3)
C(12)-C(13)-C(14)-C(5)	177.49(17)
C(10)-C(9)-C(14)-C(13)	-1.7(3)
C(2)-C(9)-C(14)-C(13)	177.59(16)
C(10)-C(9)-C(14)-C(5)	-178.19(15)
C(2)-C(9)-C(14)-C(5)	1.1(2)
C(25)-C(5)-C(14)-C(13)	7.8(3)
C(4)-C(5)-C(14)-C(13)	129.77(18)
C(6)-C(5)-C(14)-C(13)	-117.54(19)
C(25)-C(5)-C(14)-C(9)	-176.03(15)
C(4)-C(5)-C(14)-C(9)	-54.03(18)
C(6)-C(5)-C(14)-C(9)	58.65(18)
C(7)-N(1)-C(15)-C(16)	-116.80(19)
C(8)-N(1)-C(15)-C(16)	62.4(2)
C(7)-N(1)-C(15)-C(20)	62.0(2)
C(8)-N(1)-C(15)-C(20)	-118.82(19)
C(20)-C(15)-C(16)-F(1)	-179.17(17)
N(1)-C(15)-C(16)-F(1)	-0.4(3)
C(20)-C(15)-C(16)-C(17)	-0.8(3)
N(1)-C(15)-C(16)-C(17)	178.06(17)
F(1)-C(16)-C(17)-F(2)	-1.0(3)
C(15)-C(16)-C(17)-F(2)	-179.42(18)
F(1)-C(16)-C(17)-C(18)	177.35(18)
C(15)-C(16)-C(17)-C(18)	-1.1(3)
F(2)-C(17)-C(18)-F(3)	1.0(3)
C(16)-C(17)-C(18)-F(3)	-177.39(18)
F(2)-C(17)-C(18)-C(19)	-179.42(19)
C(16)-C(17)-C(18)-C(19)	2.2(3)
F(3)-C(18)-C(19)-F(4)	-2.4(3)
C(17)-C(18)-C(19)-F(4)	178.02(19)
F(3)-C(18)-C(19)-C(20)	178.10(18)
C(17)-C(18)-C(19)-C(20)	-1.5(3)
F(4)-C(19)-C(20)-F(5)	-0.8(3)

C(18)-C(19)-C(20)-F(5)	178.72(18)
F(4)-C(19)-C(20)-C(15)	-179.89(17)
C(18)-C(19)-C(20)-C(15)	-0.4(3)
C(16)-C(15)-C(20)-F(5)	-177.60(16)
N(1)-C(15)-C(20)-F(5)	3.6(3)
C(16)-C(15)-C(20)-C(19)	1.5(3)
N(1)-C(15)-C(20)-C(19)	-177.35(17)
C(4)-C(3)-C(21)-C(22)	0.3(3)
C(2)-C(3)-C(21)-C(22)	-179.01(17)
C(3)-C(21)-C(22)-C(23)	-0.3(3)
C(21)-C(22)-C(23)-C(24)	0.2(3)
C(3)-C(4)-C(24)-C(23)	0.1(3)
C(5)-C(4)-C(24)-C(23)	178.41(16)
C(22)-C(23)-C(24)-C(4)	-0.1(3)
C(26)-O(4)-C(25)-O(3)	1.4(3)
C(26)-O(4)-C(25)-C(5)	-174.13(16)
C(14)-C(5)-C(25)-O(3)	33.1(3)
C(4)-C(5)-C(25)-O(3)	-88.0(2)
C(6)-C(5)-C(25)-O(3)	154.33(19)
C(14)-C(5)-C(25)-O(4)	-151.46(15)
C(4)-C(5)-C(25)-O(4)	87.52(17)
C(6)-C(5)-C(25)-O(4)	-30.2(2)

Table S8-1. Crystal data and structure refinement for **3d**.

Identification code	**3d**
Empirical formula	$C_{26}H_{17}F_2NO_4$
Formula weight	445.41
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.309(2) Å alpha = 76.314(10) deg. b = 9.593(2) Å beta = 76.794(10) deg. c = 12.074(3) Å gamma = 79.813(10) deg.
Volume	1011.3(4) $Å^3$
Z, Calculated density	2, 1.463 Mg/ m^3
Absorption coefficient	0.111 mm^{-1}
F(000)	460
Crystal size	0.36 x 0.23 x 0.10 mm
Theta range for data collection	1.77 to 27.48 deg.
Limiting indices	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected / unique	13365 / 4630 [R(int) = 0.0424]
Completeness to theta = 27.48	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4630 / 0 / 299
Goodness-of-fit on F^2	1.133
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1158
R indices (all data)	R1 = 0.0597, wR2 = 0.1198
Largest diff. peak and hole	0.274 and -0.208 e. $Å^{-3}$

Table *S8-2*. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
F(1)	1325(1)	2697(1)	3548(1)	39(1)
F(2)	5055(1)	3152(1)	5418(1)	41(1)
O(1)	2309(2)	32(1)	5229(1)	35(1)
O(2)	1900(1)	4291(1)	6407(1)	34(1)
O(3)	-2521(2)	4254(1)	9880(1)	43(1)
O(4)	-1378(1)	2586(1)	11135(1)	35(1)
N(1)	2325(2)	2275(1)	5597(1)	25(1)
C(1)	872(2)	697(2)	7037(1)	23(1)
C(2)	-746(2)	533(2)	6968(1)	25(1)
C(3)	-1607(2)	436(2)	8211(1)	24(1)
C(4)	-1625(2)	1693(2)	8650(1)	23(1)
C(5)	-797(2)	2828(2)	7757(1)	24(1)
C(6)	837(2)	2090(2)	7472(1)	23(1)
C(7)	-1370(2)	1922(2)	6241(1)	26(1)
C(8)	-1406(2)	3095(2)	6651(1)	26(1)
C(9)	1731(2)	3054(2)	6476(1)	25(1)
C(10)	1895(2)	887(2)	5862(1)	25(1)
C(11)	3177(2)	2889(2)	4512(1)	25(1)
C(12)	4522(2)	3366(2)	4437(2)	30(1)
C(13)	5308(2)	4061(2)	3405(2)	38(1)
C(14)	4745(2)	4258(2)	2407(2)	38(1)
C(15)	3421(2)	3771(2)	2433(2)	34(1)
C(16)	2663(2)	3111(2)	3486(2)	28(1)
C(17)	-2277(2)	-707(2)	8892(2)	26(1)
C(18)	-3039(2)	-655(2)	10046(1)	26(1)
C(19)	-3827(2)	-1799(2)	10743(2)	30(1)
C(20)	-4589(2)	-1728(2)	11845(2)	31(1)
C(21)	-4620(2)	-496(2)	12298(2)	30(1)
C(22)	-3859(2)	624(2)	11650(1)	27(1)
C(23)	-3040(2)	578(2)	10509(1)	24(1)
C(24)	-2272(2)	1746(2)	9785(1)	23(1)
C(25)	-2109(2)	3007(2)	10256(1)	24(1)
C(26)	-1017(2)	3713(2)	11597(2)	40(1)

Table *S8-3*. Bond lengths [Å] and angles [deg] for **3d.**

F(1)-C(16)	1.353(2)
F(2)-C(12)	1.345(2)
O(1)-C(10)	1.206(2)
O(2)-C(9)	1.205(2)
O(3)-C(25)	1.202(2)
O(4)-C(25)	1.336(2)
O(4)-C(26)	1.446(2)
N(1)-C(9)	1.397(2)
N(1)-C(10)	1.402(2)
N(1)-C(11)	1.420(2)
C(1)-C(10)	1.509(2)
C(1)-C(6)	1.540(2)
C(1)-C(2)	1.564(2)
C(1)-H(1)	1.0000
C(2)-C(7)	1.513(2)
C(2)-C(3)	1.522(2)
C(2)-H(2)	1.0000
C(3)-C(17)	1.360(2)
C(3)-C(4)	1.423(2)
C(4)-C(24)	1.374(2)
C(4)-C(5)	1.518(2)
C(5)-C(8)	1.518(2)
C(5)-C(6)	1.558(2)
C(5)-H(5)	1.0000
C(6)-C(9)	1.511(2)
C(6)-H(6)	1.0000
C(7)-C(8)	1.325(2)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(11)-C(12)	1.384(2)
C(11)-C(16)	1.385(2)
C(12)-C(13)	1.377(3)
C(13)-C(14)	1.382(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.373(2)
C(15)-H(15)	0.9500
C(17)-C(18)	1.420(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.419(2)
C(18)-C(23)	1.423(2)

C(19)-C(20)	1.368(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.408(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.374(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.420(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.437(2)
C(24)-C(25)	1.497(2)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(25)-O(4)-C(26)	116.97(14)
C(9)-N(1)-C(10)	113.23(13)
C(9)-N(1)-C(11)	122.55(13)
C(10)-N(1)-C(11)	124.04(13)
C(10)-C(1)-C(6)	105.23(13)
C(10)-C(1)-C(2)	112.41(13)
C(6)-C(1)-C(2)	109.06(13)
C(10)-C(1)-H(1)	110.0
C(6)-C(1)-H(1)	110.0
C(2)-C(1)-H(1)	110.0
C(7)-C(2)-C(3)	107.74(13)
C(7)-C(2)-C(1)	107.69(13)
C(3)-C(2)-C(1)	104.29(12)
C(7)-C(2)-H(2)	112.2
C(3)-C(2)-H(2)	112.2
C(1)-C(2)-H(2)	112.2
C(17)-C(3)-C(4)	120.65(15)
C(17)-C(3)-C(2)	126.48(15)
C(4)-C(3)-C(2)	112.85(14)
C(24)-C(4)-C(3)	120.36(15)
C(24)-C(4)-C(5)	127.39(15)
C(3)-C(4)-C(5)	112.15(14)
C(8)-C(5)-C(4)	107.81(13)
C(8)-C(5)-C(6)	106.22(12)
C(4)-C(5)-C(6)	105.35(13)
C(8)-C(5)-H(5)	112.3
C(4)-C(5)-H(5)	112.3
C(6)-C(5)-H(5)	112.3
C(9)-C(6)-C(1)	105.26(13)
C(9)-C(6)-C(5)	110.20(13)
C(1)-C(6)-C(5)	110.07(12)

C(9)-C(6)-H(6)	110.4
C(1)-C(6)-H(6)	110.4
C(5)-C(6)-H(6)	110.4
C(8)-C(7)-C(2)	114.30(14)
C(8)-C(7)-H(7)	122.9
C(2)-C(7)-H(7)	122.9
C(7)-C(8)-C(5)	114.90(14)
C(7)-C(8)-H(8)	122.5
C(5)-C(8)-H(8)	122.5
O(2)-C(9)-N(1)	124.29(15)
O(2)-C(9)-C(6)	127.68(15)
N(1)-C(9)-C(6)	108.01(13)
O(1)-C(10)-N(1)	123.65(15)
O(1)-C(10)-C(1)	128.33(15)
N(1)-C(10)-C(1)	108.02(13)
C(12)-C(11)-C(16)	116.83(15)
C(12)-C(11)-N(1)	121.60(15)
C(16)-C(11)-N(1)	121.48(15)
F(2)-C(12)-C(13)	119.55(16)
F(2)-C(12)-C(11)	118.08(15)
C(13)-C(12)-C(11)	122.36(17)
C(12)-C(13)-C(14)	118.55(18)
C(12)-C(13)-H(13)	120.7
C(14)-C(13)-H(13)	120.7
C(13)-C(14)-C(15)	121.21(17)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	118.05(17)
C(16)-C(15)-H(15)	121.0
C(14)-C(15)-H(15)	121.0
F(1)-C(16)-C(15)	119.33(16)
F(1)-C(16)-C(11)	117.66(15)
C(15)-C(16)-C(11)	122.97(17)
C(3)-C(17)-C(18)	120.57(15)
C(3)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(19)-C(18)-C(17)	121.28(16)
C(19)-C(18)-C(23)	119.16(16)
C(17)-C(18)-C(23)	119.54(15)
C(20)-C(19)-C(18)	121.06(17)
C(20)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(19)-C(20)-C(21)	120.00(16)
C(19)-C(20)-H(20)	120.0

C(21)-C(20)-H(20)	120.0
C(22)-C(21)-C(20)	120.39(16)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	121.07(16)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(22)-C(23)-C(18)	118.29(15)
C(22)-C(23)-C(24)	123.00(15)
C(18)-C(23)-C(24)	118.65(15)
C(4)-C(24)-C(23)	120.03(15)
C(4)-C(24)-C(25)	118.76(14)
C(23)-C(24)-C(25)	121.18(14)
O(3)-C(25)-O(4)	123.02(15)
O(3)-C(25)-C(24)	125.58(15)
O(4)-C(25)-C(24)	111.35(14)
O(4)-C(26)-H(26A)	109.5
O(4)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(4)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Table *S8-4*. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3d**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
F(1)	39(1)	45(1)	39(1)	-7(1)	-16(1)	-10(1)
F(2)	37(1)	58(1)	33(1)	-11(1)	-8(1)	-17(1)
O(1)	41(1)	31(1)	35(1)	-15(1)	3(1)	-9(1)
O(2)	38(1)	29(1)	36(1)	-12(1)	2(1)	-15(1)
O(3)	75(1)	25(1)	32(1)	-7(1)	-20(1)	3(1)
O(4)	41(1)	31(1)	39(1)	-10(1)	-20(1)	-5(1)
N(1)	26(1)	26(1)	22(1)	-6(1)	-2(1)	-7(1)
C(1)	25(1)	22(1)	24(1)	-5(1)	-6(1)	-5(1)
C(2)	25(1)	26(1)	26(1)	-8(1)	-5(1)	-7(1)
C(3)	22(1)	26(1)	26(1)	-6(1)	-7(1)	-5(1)
C(4)	22(1)	25(1)	24(1)	-4(1)	-7(1)	-5(1)
C(5)	25(1)	23(1)	24(1)	-7(1)	-4(1)	-5(1)
C(6)	25(1)	25(1)	21(1)	-6(1)	-6(1)	-7(1)
C(7)	25(1)	33(1)	23(1)	-7(1)	-7(1)	-5(1)
C(8)	25(1)	27(1)	25(1)	-3(1)	-5(1)	-1(1)
C(9)	24(1)	27(1)	26(1)	-8(1)	-4(1)	-7(1)
C(10)	25(1)	24(1)	27(1)	-6(1)	-5(1)	-6(1)
C(11)	29(1)	22(1)	23(1)	-6(1)	-2(1)	-5(1)
C(12)	33(1)	33(1)	26(1)	-10(1)	-3(1)	-9(1)
C(13)	37(1)	39(1)	38(1)	-13(1)	8(1)	-16(1)
C(14)	50(1)	30(1)	27(1)	-7(1)	8(1)	-10(1)
C(15)	52(1)	26(1)	24(1)	-6(1)	-7(1)	0(1)
C(16)	31(1)	24(1)	31(1)	-8(1)	-7(1)	-3(1)
C(17)	25(1)	25(1)	31(1)	-8(1)	-7(1)	-6(1)
C(18)	23(1)	27(1)	29(1)	-3(1)	-9(1)	-4(1)
C(19)	28(1)	28(1)	34(1)	-2(1)	-9(1)	-9(1)
C(20)	26(1)	33(1)	32(1)	3(1)	-7(1)	-11(1)
C(21)	24(1)	36(1)	27(1)	-1(1)	-4(1)	-5(1)
C(22)	22(1)	30(1)	28(1)	-5(1)	-6(1)	-3(1)
C(23)	20(1)	26(1)	25(1)	-2(1)	-7(1)	-3(1)
C(24)	21(1)	25(1)	25(1)	-5(1)	-6(1)	-3(1)
C(25)	25(1)	27(1)	20(1)	-5(1)	0(1)	-5(1)
C(26)	45(1)	44(1)	42(1)	-18(1)	-14(1)	-13(1)

Table *S8-5*. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3d.**

	x	y	z	U(eq)
H(1)	1284	-160	7579	28
H(2)	-778	-335	6655	29
H(5)	-864	3737	8045	28
H(6)	1303	1868	8173	28
H(7)	-1707	1950	5549	32
H(8)	-1784	4033	6280	32
H(13)	6217	4399	3381	46
H(14)	5277	4736	1689	45
H(15)	3049	3890	1741	41
H(17)	-2235	-1548	8593	31
H(19)	-3825	-2627	10439	35
H(20)	-5096	-2510	12304	37
H(21)	-5172	-440	13055	36
H(22)	-3880	1443	11971	32
H(26A)	-99	4062	11119	61
H(26B)	-878	3326	12398	61
H(26C)	-1831	4516	11586	61

Table *S8-6*. Torsion angles [deg] for **3d.**

C(10)-C(1)-C(2)-C(7)	-62.87(17)
C(6)-C(1)-C(2)-C(7)	53.43(16)
C(10)-C(1)-C(2)-C(3)	-177.15(13)
C(6)-C(1)-C(2)-C(3)	-60.84(16)
C(7)-C(2)-C(3)-C(17)	128.42(17)
C(1)-C(2)-C(3)-C(17)	-117.33(17)
C(7)-C(2)-C(3)-C(4)	-53.39(17)
C(1)-C(2)-C(3)-C(4)	60.86(17)
C(17)-C(3)-C(4)-C(24)	2.5(2)
C(2)-C(3)-C(4)-C(24)	-175.78(14)
C(17)-C(3)-C(4)-C(5)	179.19(14)
C(2)-C(3)-C(4)-C(5)	0.89(19)
C(24)-C(4)-C(5)-C(8)	-131.60(17)
C(3)-C(4)-C(5)-C(8)	52.02(17)
C(24)-C(4)-C(5)-C(6)	115.29(17)
C(3)-C(4)-C(5)-C(6)	-61.09(16)
C(10)-C(1)-C(6)-C(9)	4.95(16)
C(2)-C(1)-C(6)-C(9)	-115.85(14)
C(10)-C(1)-C(6)-C(5)	123.68(13)
C(2)-C(1)-C(6)-C(5)	2.88(17)
C(8)-C(5)-C(6)-C(9)	58.65(16)
C(4)-C(5)-C(6)-C(9)	172.87(12)
C(8)-C(5)-C(6)-C(1)	-57.01(16)
C(4)-C(5)-C(6)-C(1)	57.21(16)
C(3)-C(2)-C(7)-C(8)	53.30(18)
C(1)-C(2)-C(7)-C(8)	-58.66(18)
C(2)-C(7)-C(8)-C(5)	0.8(2)
C(4)-C(5)-C(8)-C(7)	-54.56(18)
C(6)-C(5)-C(8)-C(7)	57.97(18)
C(10)-N(1)-C(9)-O(2)	-176.42(16)
C(11)-N(1)-C(9)-O(2)	-1.2(3)
C(10)-N(1)-C(9)-C(6)	2.07(18)
C(11)-N(1)-C(9)-C(6)	177.31(14)
C(1)-C(6)-C(9)-O(2)	174.04(16)
C(5)-C(6)-C(9)-O(2)	55.4(2)
C(1)-C(6)-C(9)-N(1)	-4.38(17)
C(5)-C(6)-C(9)-N(1)	-123.02(14)
C(9)-N(1)-C(10)-O(1)	-178.52(16)
C(11)-N(1)-C(10)-O(1)	6.3(3)
C(9)-N(1)-C(10)-C(1)	1.24(18)
C(11)-N(1)-C(10)-C(1)	-173.92(14)
C(6)-C(1)-C(10)-O(1)	175.84(17)

C(2)-C(1)-C(10)-O(1)	-65.6(2)
C(6)-C(1)-C(10)-N(1)	-3.90(17)
C(2)-C(1)-C(10)-N(1)	114.68(14)
C(9)-N(1)-C(11)-C(12)	62.9(2)
C(10)-N(1)-C(11)-C(12)	-122.43(18)
C(9)-N(1)-C(11)-C(16)	-113.57(18)
C(10)-N(1)-C(11)-C(16)	61.2(2)
C(16)-C(11)-C(12)-F(2)	-179.40(14)
N(1)-C(11)-C(12)-F(2)	4.0(2)
C(16)-C(11)-C(12)-C(13)	1.6(3)
N(1)-C(11)-C(12)-C(13)	-174.98(16)
F(2)-C(12)-C(13)-C(14)	179.47(16)
C(11)-C(12)-C(13)-C(14)	-1.5(3)
C(12)-C(13)-C(14)-C(15)	0.0(3)
C(13)-C(14)-C(15)-C(16)	1.3(3)
C(14)-C(15)-C(16)-F(1)	176.28(15)
C(14)-C(15)-C(16)-C(11)	-1.3(3)
C(12)-C(11)-C(16)-F(1)	-177.74(14)
N(1)-C(11)-C(16)-F(1)	-1.2(2)
C(12)-C(11)-C(16)-C(15)	-0.2(3)
N(1)-C(11)-C(16)-C(15)	176.43(15)
C(4)-C(3)-C(17)-C(18)	1.5(2)
C(2)-C(3)-C(17)-C(18)	179.56(15)
C(3)-C(17)-C(18)-C(19)	175.84(15)
C(3)-C(17)-C(18)-C(23)	-2.9(2)
C(17)-C(18)-C(19)-C(20)	-178.43(15)
C(23)-C(18)-C(19)-C(20)	0.3(2)
C(18)-C(19)-C(20)-C(21)	1.1(3)
C(19)-C(20)-C(21)-C(22)	-1.6(3)
C(20)-C(21)-C(22)-C(23)	0.8(2)
C(21)-C(22)-C(23)-C(18)	0.6(2)
C(21)-C(22)-C(23)-C(24)	177.69(15)
C(19)-C(18)-C(23)-C(22)	-1.1(2)
C(17)-C(18)-C(23)-C(22)	177.63(14)
C(19)-C(18)-C(23)-C(24)	-178.36(14)
C(17)-C(18)-C(23)-C(24)	0.4(2)
C(3)-C(4)-C(24)-C(23)	-5.0(2)
C(5)-C(4)-C(24)-C(23)	178.86(14)
C(3)-C(4)-C(24)-C(25)	172.70(14)
C(5)-C(4)-C(24)-C(25)	-3.4(2)
C(22)-C(23)-C(24)-C(4)	-173.55(15)
C(18)-C(23)-C(24)-C(4)	3.5(2)
C(22)-C(23)-C(24)-C(25)	8.8(2)
C(18)-C(23)-C(24)-C(25)	-174.13(14)

C(26)-O(4)-C(25)-O(3)	-3.2(2)
C(26)-O(4)-C(25)-C(24)	174.19(14)
C(4)-C(24)-C(25)-O(3)	59.4(2)
C(23)-C(24)-C(25)-O(3)	-122.89(19)
C(4)-C(24)-C(25)-O(4)	-117.88(16)
C(23)-C(24)-C(25)-O(4)	59.81(19)

10. Full reference 27 for Gaussian09

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