Supplementary Material

Synthesis and photoreactivity of pyridinium-subsituted norbornadienes

Julian F. M. Hebborn, Robin Schulte, Thomas Paululat, Heiko Ihmels

Department of Chemistry and Biology, and Research Center of Micro- and Nanochemistry and (Bio-) Technology (Cμ), University of Siegen, Adolf-Reichwein-Str. 2, Siegen 57068, Germany
Email: ihmels@chemie.uni-siegen.de

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1. Equipment

NMR spectra: JEOL ECZ 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, 25 °C), Varian VNMR-S 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, 25 °C). Reference: residual signals of DMSO-d_6 [δ(^{1}H) 2.50 ppm, δ(^{13}C) = 39.5 ppm; usually contains significant amount of water: δ(^{1}H) 3.30 ppm], $CDCl_3$ [δ(^{13}C) = 77.16 ppm] and MeCN-d_3 [δ(^{1}H) = 1.94 ppm, δ(^{13}C) = 1.32 ppm], or tetramethylsilane (TMS) [δ(^{1}H) = 0.00 ppm]. Software: MestReNova. Melting points: BÜCHI 545 (Büchi, Flawil, CH), uncorrected. Elemental analysis: in-house (Organic Chemistry, University of Siegen), HEKAtech EUROEA combustion analyzer. Absorption spectra: Varian Cary 100 Bio, Analytik Jena SPECORD S, in quartz glass cuvettes (d = 10 mm); Software: Origin (OriginPro 8.5.1) with the implemented smoothing function "adjacent averaging", factor 10. Photoreactions: Thorlabs LED M340L5 (340 nm), LUMOS 43 Atlas Photonics; 275 nm, 315 nm, 360 nm, 420 nm). In situ NMR irradiations: 365 nm LEDs.[1]

2. Methods

Reaction mixtures were stirred with a magnetic stirring bar (400–750 rpm). Solvents were removed with a rotary evaporator at 20–40 °C under reduced pressure (360–15 mbar). Air-sensitive reactions were performed under an inert atmosphere (Ar) with Schlenk equipment. Solvents/solutions were deaerated by bubbling argon through the solution (approx. 5 min) prior to use. Room temperature (r.t.) was 22 °C.

3. Materials

Commercially available chemicals. Acros Organics: $NaBF_4$, benzyltributylammonium chloride; Alfa Aesar GmbH & Co KG: iodomethane, 2-bromopyridine, 3-bromopyridine, 4-bromopyridine hydrochloride, 2-naphthoic acid, trimethyloxonium tetrafluoroborate; Bernd Kraft GmbH: K_2CO_3; Carbolution Chemicals GmbH: tetrabutylammonium bromide, $Pd(PPh_3)_2Cl_2$, 2-bromopyridine, bis(pinacolato)diborone; Fisher scientific: MeI, *t*-BuOK, *n*-BuLi (2.5 M in hexanes); Fluorochem Ltd: NH_4PF_6, 3-bromopyridine, trimethylsilylacetylene; Silicycle: SiO_2 (particle size 40–63 μm).
4,4,5,5-Tetramethyl-2-(bicyclo[2.2.1]heptadien-2-yl)-1,3,2-dioxaborolane,[2] 2-(bicyclo[2.2.1]-hepta-2,5-dien-2-yl)pyridine,[2] 2-ethynylpyridine,[3] 3-ethynylpyridine,[3] 4-ethynylpyridine,[3] 4-bromopyridine[4] and cucurbit[7]uril[5] were prepared according to literature. 2-((Trimethylsilyl)-ethynyl)pyridine, 3-((trimethylsilyl)ethynyl)pyridine, 4-((trimethylsilyl) ethynyl)pyridine were synthesized in a varied procedure with Et_3N as the solvent.[3] Potassium 2-naphthoate was obtained by neutralization of a methanolic solution of the corresponding acid with equimolar amount of KOH. The solvent was removed under reduced pressure, and the crude was washed with $CHCl_3$ (10 mL) and dried under reduced pressure. *n*-Hexane was purified by distillation prior to use.

4. Absorption properties

Solutions (c = 20 μM, V = 2.00 mL) of the norbornadiene **3f**–**3i**, **3g^{Cl}**, **3g^{Br}** and **3g^{I}** in MeCN, MeOH and water were prepared by the evaporation of a stock solution of the norbornadiene in MeCN (c = 1 mM, V = 40 μL) under a nitrogen stream followed by the addition of the corresponding solvent. The absorption spectra were subsequently measured (T = 20 °C).

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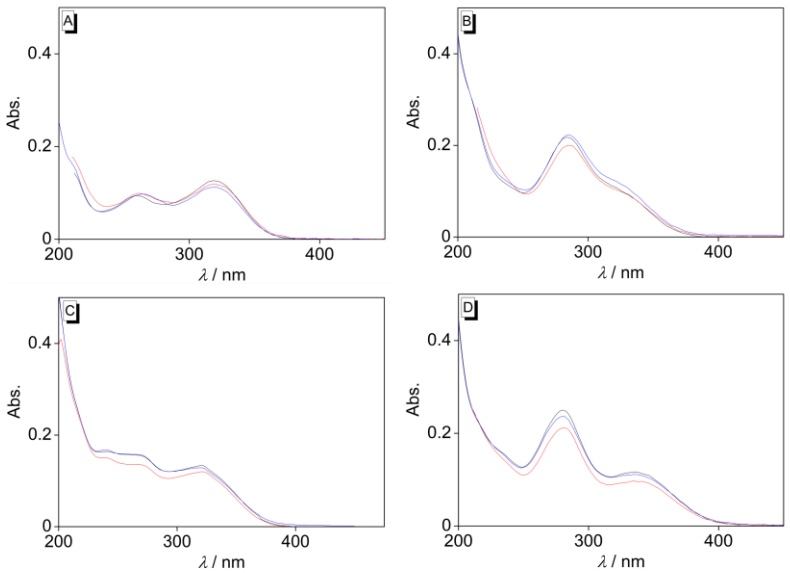


Figure S1. Absorption spectra of **3f**–**3i** (A–D) (*c* = 20 µM) in MeCN (black), MeOH (red), and H_2O (blue).

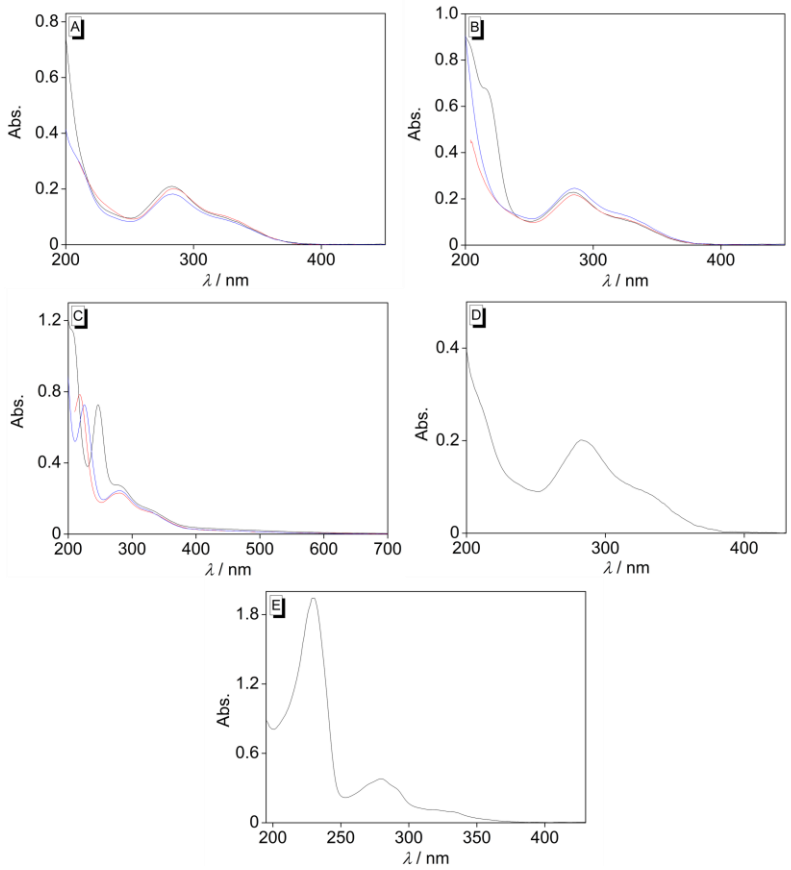


Figure S2. Absorption spectra of **3g^{Cl}**, **3g^{Br}**, **3g^{I}**, **3g^{PF6}** and **3g^{Nap}** (A–E) (*c* = 20 µM) in MeCN (black), MeOH (red), and H_2O (blue).

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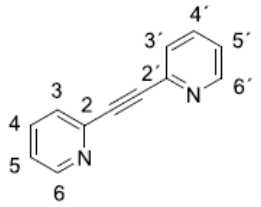
5. Synthesis

Synthesis of bispyridyl ethynes

General Procedure A (GP A) for Pd-catalyzed Sonogashira coupling reaction of ethynylarene derivatives with aryl halides[6]

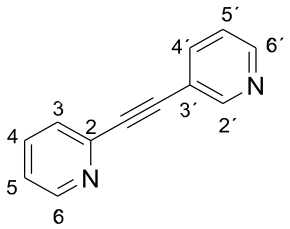
Under an argon atmosphere, bromoarene (1.4–2.3 g, 0.86–1.4 mL, 9.1–14 mmol) was added to a suspension of $Pd(PPh_3)_2Cl_2$ (2.5 mol%) and CuI (2.5 mol%) in deaerated Et_3N (9–15 mL). After stirring for 5 min, a solution of ethynyl arene (1.1 equiv.) in deaerated Et_3N (9.0–10 mL) was added. The mixture was stirred at 80 °C for 18 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography.

2,2′-(1,2-Ethynediyl)bispyridine (**4g**)



2-Bromopyridine (2.27 g, 1.38 mL, 14.4 mmol) and 2-ethynylpyridine (1.63 g, 15.8 mmol) were treated and purified according to GP A. The crude product was purified by column chromatography (SiO_2, EtOAc, *R*f = 0.30). The product was obtained as a dark brown oil which crystallized slowly upon cooling to r.t. (1.54 g, 8.55 mmol, 59%, lit.: 48%[6]); mp 71–73 °C (lit.: 71–73 °C[7]). – ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.27 (ddd, ^3J = 7.6 Hz, ^3J = 4.9 Hz, ^4J = 1.3 Hz, 2H, 5-H, 5′-H), 7.61 (dt, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 2H, 3-H, 3′-H), 7.69 (td, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 2H, 4-H, 4′-H), 8.63 (ddd, ^3J = 4.9 Hz, ^4J = 1.9 Hz, ^5J = 1.0 Hz, 2H, 6-H, 6′-H).

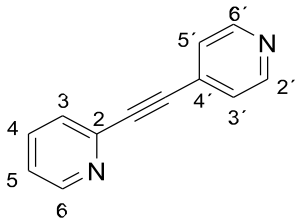
2-[2-(3-Pyridinyl)ethynyl]pyridine (**4h**)



2-Bromopyridine (1.2 mL, 1.9 g, 12 mmol) and 3-ethinylpyridine (1.34 g, 13.0 mmol) were treated and purified according to GP A. The crude product was purified by column chromatography (SiO_2, EtOAc, *R*f = 0.37) to yield the product as a yellow wax (1.95 g, 10.8 mmol, 90%); mp 38–41 °C (lit.: 41–42 °C[8]). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (ddd, ^3J = 6.1 Hz, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 1H, 5-H), 7.30 (ddd, ^3J = 7.9 Hz, ^3J = 4.9 Hz, ^5J = 0.9 Hz, 1H, 5′-H), 7.55 (dt, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, 3-H), 7.70 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, 4-H), 7.87 (ddd, ^3J = 7.9 Hz, ^4J = 2.2 Hz, ^4J = 1.7 Hz, 1H, 4′-H), 8.58 (dd, ^3J = 4.9 Hz, ^4J = 1.7 Hz, 1H, 6′-H), 8.63 (ddd, ^3J = 4.9 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1H, 6-H), 8.82 (dd, ^4J = 2.2 Hz, ^5J = 0.9 Hz, 1H, 2′-H).

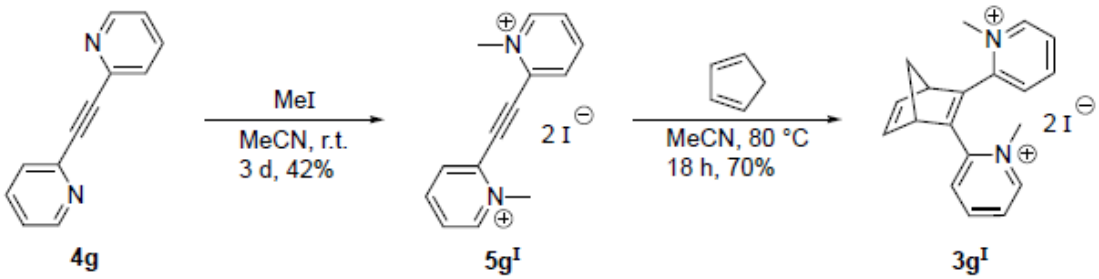
2-[2-(4-Pyridinyl)ethynyl]pyridine (**4i**)

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2-Bromopyridine (0.86 mL, 1.43 g, 9.05 mmol) and 4-ethinylpyridine (1.00 g, 9.70 mmol) were treated and purified according to GP A. The crude product was purified by column chromatography (SiO_2, EtOAc, *R*f = 0.40) to yield the product as an orange oil, which crystallized slowly upon cooling (1.63 g, 9.05 mmol, >95%); mp 60–62 °C (lit.: 64–65 °C[8]). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (ddd, ^3J = 7.7 Hz, ^3J = 4.9 Hz, ^5J = 1.2 Hz, 1H, 5-H), 7.43 (dd, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 2H, 3´-H, 5´-H), 7.55 (dt, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, 3-H), 7.71 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, 4-H), 8.62 (dd, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 2H, 2´-H, 6´-H), 8.64 (ddd, ^3J = 4.9 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1H, 6-H).

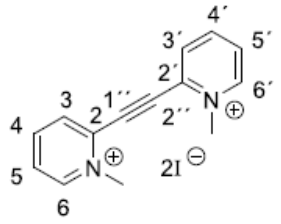
N-Methylation of bispyridiyl ethynes



4g **5g^I** **3g^I**

Scheme S1. Synthesis of the cationic norbornadiene **3g^I**.

2,2′-(1,2-Ethynediyl)bis-1-methylpyridinium bis(iodide) (**5g^I**)



A solution of **4g** (500 mg, 2.77 mmol) and methyl iodide (2.36 g, 1.0 mL, 16.7 mmol, 3 equiv.) in anhydrous MeCN (18 mL) was stirred under argon at r.t. for 3 d. The precipitate was filtered off and washed with MeCN (2 × 2 mL) and Et_2O (10 mL). The product was obtained as an amorphous dark red-brown powder (536 mg, 1.15 mmol, 42%); mp 235–238 °C. – ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 4.50 (s, 6H, 2 × CH_3), 8.28 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.6 Hz, 2H, 5-H, 5´-H), 8.64 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 2H, 3-H, 3´-H), 8.72 (td, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.24 (ddt, ^3J = 6.3 Hz, ^4J = 1.4 Hz, ^5J = 0.7 Hz, 2H, 6-H, 6´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.9 (N1CH_3, N1´CH_3), 91.6 (C1´´, C2´´), 129.1 (C5, C5´), 133.0 (C3, C3´), 134.3 (C2,

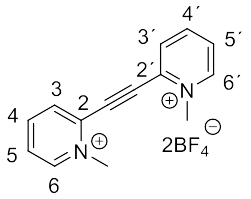
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C2´), 145.3 (C4, C4´), 148.5 (C6, C6´).

General Procedure B (GP B) for the synthesis methylation of pyridines with Me_3OBF_4

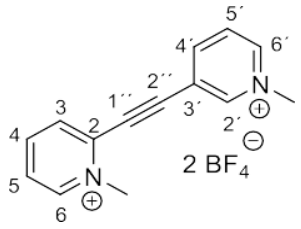
The methylated bispyridyl ethynes were prepared with modified literature procedure.[9] A mixture of bis(pyridiyl)ethyne (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) in anhydrous MeCN (18 mL) was stirred at r.t. for 2 d. The solution was poured into Et_2O, and the resulting precipitate was filtered and recrystallized from MeCN/EtOAc.

2,2′-(1,2-Ethynediyl)bis-1-methylpyridinium bis(tetrafluoroborate) (**5g**)



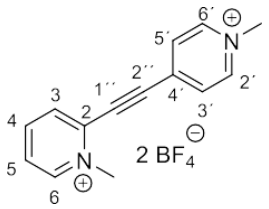
A solution of **4g** (500 mg, 2.77 mmol) and trimethyloxonium tetrafluoroborate (2.10 g, 14.2 mmol, 2.5 equiv.) were treated and purified according to GP B. The product was obtained as light-yellow microcrystalline solid (875 mg, 2.28 mmol, 82%, lit.: 100%[9]); mp 268–277 (lit.: 260–268 °C[9]). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.49 (s, 6H, 2 × CH_3), 8.27 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.6 Hz, 2H, 5-H, 5´-H), 8.61 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H, 3-H, 3´- H), 8.71 (td, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.23 (d, 2H, ^3J = 6.1 Hz, 6-H, 6´-H).

1-Methyl-2-((1-methylpyridinium-3-yl)ethynyl)pyridinium bis(tetrafluoroborate) (**5h**)



A solution of **4h** (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) were treated and purified according to GP B. The product was obtained as fine yellow crystals (571 mg, 1.49 mmol, 54%); mp 260–265 °C. – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.40 (s, 3H, 1´-CH3), 4.50 (s, 3H, 1-CH3), 8.22 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.5 Hz, 1H, 5-H), 8.30 (dd, ^3J = 8.2 Hz, ^3J = 6.1 Hz, 1H, 5´-H), 8.44 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1H, 3-H), 8.68 (td, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, 4-H), 8.94 (dt, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H, 4´-H), 9.14 (d, ^3J = 6.2 Hz, 1H, 6´-H), 9.19 (dt, ^3J = 6.2 Hz, ^5J = 0.6 Hz, 1H, 6-H), 9.56 (s, 1H, 2´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 48.1 (N1CH_3), 49.0 (N1´CH_3), 85.3 (C1´´), 96.8 (C2´´), 120.3 (C3´), 128.5 (C5´), 128.7 (C5), 132.6 (C3), 136.0 (C2), 145.8 (C4), 147.7 (C6´), 148.0 (C4´), 148.6 (C6), 149.4 (C2´). – El. Anal. for $C_{14}H_{14}B_2F_8N_2$, calc. (%): C 43.80, H 3.68, N 7.30, found (%): C 43.74, H 3.51, N 7.41.

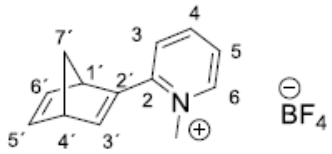
1-Methyl-2-((1-methylpyridinium-4-yl)ethynyl)pyridinium bis(tetrafluoroborate) (**5i**)



A solution of **4i** (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) were treated and purified according to GP B. The product was obtained as fine yellow crystals (510 mg, 1.33 mmol, 48%); mp 268–278 °C. – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.39 (s, 3H, 1´-CH_3), 4.51 (s, 3H, 1-CH_3), 8.26 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.6 Hz, 1H, 5-H), 8.50 (dd, ^3J = Hz, ^4J = 1.9 Hz, 2H, 3´-H, 5´-H), 8.52 (dd, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H, 3-H), 8.71 (td, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 1H, 4-H), 9.16 (dd, ^3J = 5.3 Hz, ^4J = 1.7 Hz, 2H, 2´-H, 6´-H), 9.22 (dt, ^3J = 6.2 Hz, ^5J = 0.6 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 48.2 (N1CH_3), 48.9 (N1´CH_3), 89.0 (C1´´), 97.8 (C2´´), 129.2 (C5), 130.4 (C3´, C5´), 133.3 (C3), 135.5 (C4´), 135.6 (C2), 145.8 (C4), 146.8 (C2´, C6´), 148.8 (C6). – El. Anal. for $C_{14}H_{14}B_2F_8N_2$, calc. (%): C 43.80, H 3.68, N 7.30, found (%): C 43.57, H 3.56, N 7.48.

Synthesis of cationic norbornadienes

2-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (**3f**)



A solution of MeI (0.24 g, 0.11 mL, 0.17 mmol) and 2-(2-pyridyl)norbornadiene (96.0 mg, 567 µmol) in anhydrous MeCN (5 mL) was stirred for 24 h at room temperature. Another portion of MeI (0.24 g, 0.11 mL, 0.17 mmol) was added, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was suspended in water (15 mL), and $NaBF_4$ (1.00 g, 9.11 mmol) was added. The aqueous suspension was washed with hexanes (3 × 15 mL) and extracted with $MeNO_2$ (5 × 15 mL). The organic layer was separated and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/MeOH, 9/1, *R*f = 0.31) to obtain the product as yellow needles (52.1 mg, 192 mmol, 34%); mp >105 °C (dec.). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.10 (d, 1H ^2J = 6.6 Hz, 7´-H), 2.24 (dt, 1H, ^3J = 1.7 Hz, ^2J = 6.6 Hz, 7´-H), 3.95–3.98 (m, 1H, 4´-H), 4.03–4.06 (m, 1H, 1´-H), 4.19 (s, 3H, CH3), 6.93 (dd, 1H, ^3J = 3.1 Hz, ^3J = 5.1 Hz, 5´-H), 7.15 (dd, 1H, ^3J = 3.0 Hz, ^3J = 5.1 Hz, 6´-H), 7.68 (d, 1H, ^3J = 3.3 Hz, 3´-H), 7.93 (m, 2H, 4-H, 5-H), 8.48 (td, 1H, ^4J = 1.5 Hz, ^3J = 7.9 Hz, 3-H), 8.95 (dd, 1H, ^4J = 1.5 Hz, ^4J = 6.7 Hz, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.5 (CH3), 52.7 (4´-C), 54.8 (C1´), 73.2 (C7´), 125.8 (C4), 127.1 (C5), 143.1 (C6´), 143.5 (C5´), 145.4 (C3), 147.2 (C6), 148.9 (C2´), 152.3 (C2), 154.9 (C3´). – El. Anal. for $C_{13}H_{14}BF_4N$, calc. (%): C 57.60, H 5.21, N 5.52, found (%) C 57.63, H 5.07, N 5.20.

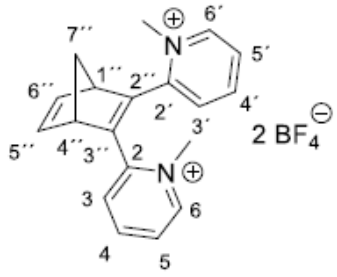
General Procedure C (GP C) for the synthesis of cationic norbornadienes by Diels-Alder reactions[9]

A solution of bis(methylpyridium)ethyne bis(tetrafluoroborate) (200–495 mg, 0.52–1.29 mmol) and freshly cracked cyclopentadiene (40 equiv.) in MeCN (18–45 mL) was stirred under reflux for 18 h. After cooling to r.t., the solution was filtered and slowly added to Et_2O (200–500 mL). The precipitate was filtered off and

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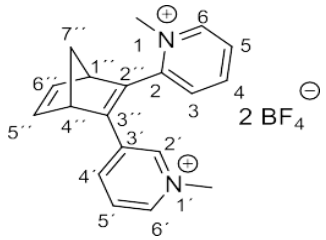
dried in vacuum.

2,3-Bis(1-methyl-2-pyridino)bicyclo[2.2.1]hepta-2,5-diene-bis*(tetrafluoroborate)* (**3g**)



A solution of **5g** (495 mg, 1.29 mmol) and cyclopentadiene (4.5 mL, 3.6 g, 55 mmol) were treated according to GP C. The crude product was recrystallized from acetone to give the product as colorless crystals (494 mg, 1.10 mmol, 85%, lit.: 74%[9]); mp 243–254°C (lit.: 235–255 °C[9]). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.27 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 1H, 7´´-H), 2.80 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 1H, 7´´-H), 4.19 (s, 6H, 2 × CH3), 4.36–4.38 (m, 2H, 1´´-H, 4´´-H), 7.24 (t, ^3J = 1.9 Hz, 2H, 5´´-H, 6´´-H), 7.73 (d, ^3J = 7.8 Hz, 2H, 3-H, 3´-H), 8.05 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.36 (td, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 2H, 4-H, 4´-H), 9.12 (ddd, ^3J = 6.1 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 2H, 6-H, 6´-H).

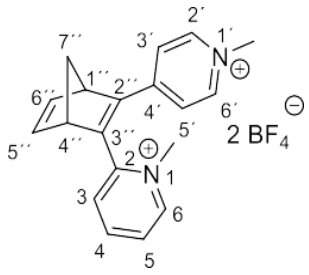
1-Methyl-2-(3-(1-methylpyridinium-3-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(tetrafluoroborate) (**3h**)



A solution of **5h** (200 mg, 521 µmol) and cyclopentadiene (2.1 mL, 1.7 g, 25 mmol) were treated to GP C. The product was suspended in MeCN (30 mL). After filtration, the solvent was removed under reduced pressure, and the product was obtained as a hygroscopic yellow amorphous powder (213 mg, 473 µmol, 91%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.22 (dt, ^2J = 6.9 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 2.58 (dt, ^2J = 6.9 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 4.18 (s, 3H, 1-CH_3), 4.24 (s, 1H, 1´´-H), 4.29 (s, 3H, 1´-CH_3), 4.34 (s, 1H, 4´´-H), 7.14 (s, 1H, 6´´-H), 7.19 (s, 1H, 5´´-H), 7.53 (s, 1H, 3-H), 7.93 (dd, ^3J = 8.2 Hz, ^3J = 6.0 Hz, 1H, 5´-H), 8.08 (ddd, ^3J = 7.7 Hz, ^3J = 6.1 Hz, ^4J = 1.5 Hz, 1H, 5-H), 8.19 (d, ^3J = 8.2 Hz, 1H, 4´-H), 8.38 (td, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 1H, 4-H), 8.85 (d, ^3J = 6.0 Hz, 1H, 6´-H), 9.00 (s, 1H, 2´-H), 9.18 (d, ^3J = 6.1 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.3 (1-CH_3), 48.6 (1´-CH3), 55.6 (C4´´), 57.1 (C1´´), 71.9 (C7´´), 127.4 (C5), 128.0 (C5´), 128.4 (C3), 133.8 (C3´), 143.0 (C4´), 143.1 (C6´´), 143.4 (C5´´), 144.0 (C2´), 145.2 (C6´), 146.2 (C4), 148.0 (C2´´), 148.5 (C6), 151.8 (C2), 154.8 (C3´´). – El. Anal. for $C_{19}H_{20}B_2F_8N_2$, calc. (%): C 50.71, H 4.48, N 6.23, found (%): C 50.45, H 4.13, N 6.62.

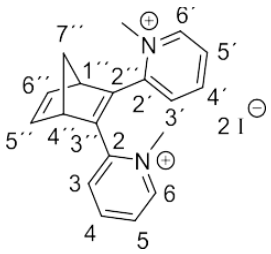
1-Methyl-2-(3-(1-methylpyridinium-4-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(tetrafluoroborate) (**3i**)

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A solution of **5i** (200 mg, 521 µmol) and cyclopentadiene (2.1 mL, 1.7 g, 25 mmol) were treated according to GP C. The product was suspended in MeCN (30 mL). After filtration, the solvent was removed under reduced pressure, and the product was obtained as a hygroscopic yellow amorphous powder (214 mg, 476 µmol, 92%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.23 (dt, ^2J = 7.1 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 2.61 (dt, ^3J = 7.1 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 4.20 (s, 3H, 1-CH_3), 4.25 (s, 3H, 1´-CH_3), 4.27 (s, 1H, 4´´-H), 4.38 (s, 1H, 1´´-H), 7.12 (s, 1H, 5´´-H), 7.24 (s, 1H, 6´´-H), 7.50 (s, 1H, 3-H), 7.87 (d, ^3J = 6.9 Hz, 2H, 3´-H, 5´-H), 8.12 (ddd, ^3J = 7.7 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 1H, 5-H), 8.41 (td, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1H, 4-H), 8.79 (d, ^3J = 6.9 Hz, 2H, 2´-H, 6´-H), 9.21 (d, ^3J = 6.2 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.3 (1-CH3), 47.8 (1´-CH3), 55.2 (C1´´), 57.8 (C4´´), 71.7 (C7´´), 125.3 (C3´, C5´), 127.7 (C5), 128.1 (C3), 142.9 (C5´´), 143.6 (C6´´), 145.9 (C2´, C6´), 146.3 (C4), 148.38 (C4´), 148.6 (C6), 151.5 (C2), 152.4 (C3´´), 156.0 (C2´´). – El. Anal. for $C_{19}H_{20}B_2F_8N_2$ × 0.5 H_2O, calc. (%): C 49.72, H 4.61, N 6.10, found (%): C 50.12, H 4.54, N 6.26.

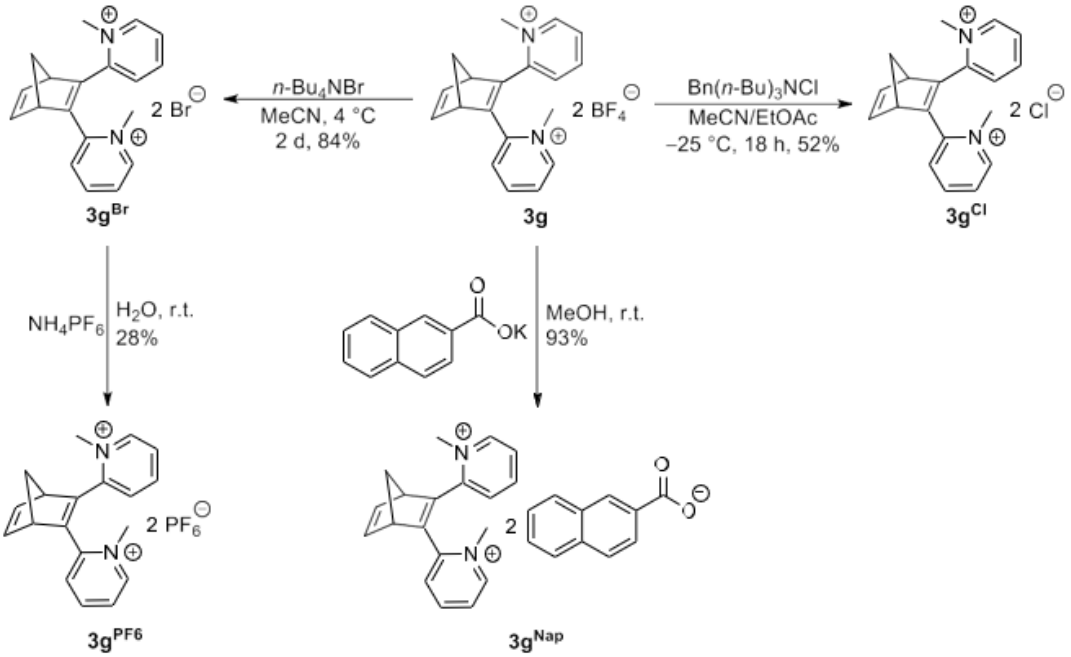
1-Methyl-2-(3-(1-methylpyridinium-4-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(iodide) (**3g^I**)



A solution of **5g^I** (195 mg, 420 µmol) and cyclopentadiene (1.20 g, 1.5 mL, 18.2 mmol) in MeCN (30 mL) was heated under reflux at 80 °C for 18 h. After cooling to room temperature, the mixture was poured in Et_2O (300 mL). The precipitate was filtered off, washed with MeCN and dissolved through the filter with MeOH. After removing the solvent under reduced pressure, the product was obtained as a black flaky powder (158 mg, 298 µmol, 71%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.26 (dt, ^3J = 7.1 Hz, ^4J = 1.6 Hz, 1H, 7´´-H), 2.81 (dt, ^3J = 7.0 Hz, ^4J = 1.6, 1H, 7´´-H), 4.20 (s, 6H, 2 × CH_3), 4.38 (p, ^3J = 1.6 Hz, 2H, 1´´-H, 4´´-H), 7.23 – 7.28 (m, 2H, 5´´-H, 6´´-H), 7.76 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 2H, 3-H, 3´-H), 8.06 (ddd, ^3J = 7.7 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.37 (td, ^3J = 7.9 Hz, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.13 (ddd, ^3J = 6.7 Hz, ^4J = 1.4 Hz, ^5J = 0.6 Hz, 2H, 6-H, 6´-H). –^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.2 (2 × CH3), 56.0 (C1´´, C4´´), 72.5 (C7´´), 128.8 (C5, C5´), 128.8 (C3, C3´), 142.9 (C5´´, C6´´), 145.3 (C4, C4´), 147.7 (C6, C6´), 149.3 (C2, C2´), 153.1 (C2´´, C3´´). – El. Anal. for $C_{19}H_{20}I_2N_2$, calc. (%): C 43.04, H 3.80, N 5.28, found (%) C 43.83, H 3.87, N 5.83.

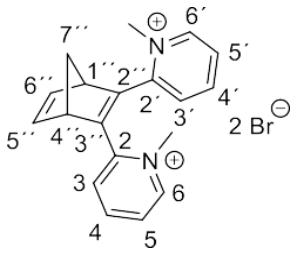
Counter ion exchange

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Scheme S2. Ion metathesis reactions of **3g**.

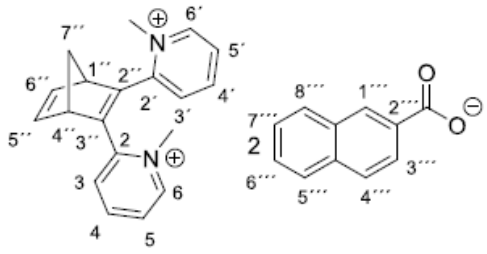
2,3-Bis(1-methyl-2-pyridino)bicyclo[2.2.1]hepta-2,5-diene bis(bromide) (**3gBr**)[10]



A solution of Bu_4NBr (420 mg, 1.30 mmol, 3 equiv.) in MeCN (0.4 mL) was added to a solution of **3g** (135 mg, 300 µmol) in MeCN (2.0 mL). The resulting suspension was placed in the fridge (4 °C) for 2 d. The crude product was filtered, washed with MeCN/EtOAc and Et_2O, and recrystallized from MeCN/EtOAc. The product was obtained as a colorless microcrystalline powder (110 mg, 0.25 mmol, 84%); mp 226–229 °C. – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.25 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 1H, 7´´-H), 2.82 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 1H, 7´´-H), 4.21 (s, 6H, 2 × CH_3), 4.39 (p, ^3J = 1.6 Hz, 2H, 1´´-H, 4´´-H), 7.25 (t, ^3J = 1.9 Hz, 2H, 5´´-H, 6´´-H), 7.77 (d, ^3J = 7.8 Hz, 2H, 3-H, 3´-H), 8.06 (ddd, ^3J = 7.7 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.37 (td, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.17 (d, ^3J = 6.0 Hz, 2H, 6-H, 6´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.7 (CH3), 56.6 (C1´´, C4´´), 73.1 (C7´´), 127.8 (C5, C5´), 129.4 (C3, C3´), 143.5 (C5´´, C6´´), 145.9 (C4, C4´), 148.3 (C6, C6´), 149.9 (C2, C2´), 153.7 (C2´´, C3´´). – El. Anal. for (%) for $C_{19}H_{20}N_2Br_2 \times H_2O$, calc. C 50.24, H 4.88, N 6.17, found (%) C 50.12, H 4.81, N 6.17.

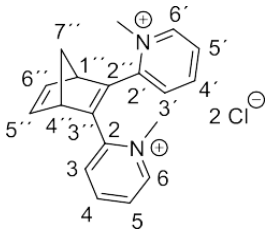
1-Methyl-2-(3-(1-methylpyridinium-3-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium di(2-naphthoate) (**3g^{Nap}**)

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A solution of the potassium 2-naphthoate (77.1 mg, 367 µmol) in MeOH (5 mL) was added under stirring at r.t. to a solution of the tetrafluoroborate **3g** (75.0 mg, 167 µmol) in MeCN (15 mL). The solvent was removed under reduced pressure. The residue was suspended in MeCN (15 mL), and the solid was filtered off. The solvent of the filtrate was removed under reduced pressure and the residue was washed with Et_2O (25 mL). The product was obtained as a yellow, highly hygroscopic powder (96.3 mg, 156 µmol, 93%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.26 (dt, ^2J = 7.0 Hz, ^3J = 1.5 Hz, 1H, 7´´-H), 2.80 (dt, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 4.20 (s, 6H, 2 × CH_3), 4.35–4.37 (m, 2H, 1´´-H, 4´´-H), 7.24 (t, ^3J = 1.9 Hz, 2H, 5´´- H, 6´´-H), 7.49–7.58 (m, 4H, 6´´´-H, 7´´´-H), 7.73 (d, ^3J = 7.9 Hz, 2H, 3-H, 3´-H), 7.87 (d, ^3J = 8.5 Hz, 2H, 8´´´-H), 7.89–7.96 (m, 2H, 5´´´-H), 7.99 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 2H, 3´´´-H), 8.01 (d, ^3J = 7.8 Hz, 2H, 4´´´-H), 8.04 (ddd, ^3J = 7.7 Hz, ^3J = 6.1 Hz, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.36 (td, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 2H, 4-H, 4´-H), 8.46 (s, 2H, 1´´´-H), 9.15 (d, ^3J = 6.1 Hz, 2H, 6-H, 6´-H).

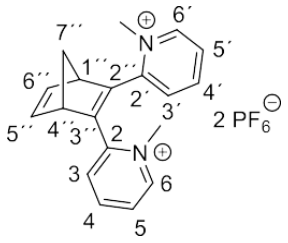
1-Methyl-2-(3-(1-methylpyridinium-3-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(chloride) (**3g^{Cl}**)[10]



A solution of **3g** (150 mg, 333 µmol) in MeCN (1.5 mL) was added to a solution of benzyltributylammonium chloride (BTBAC) (700 mg, 2.24 mmol, 7.5 equiv.) in MeCN (1.5 mL). The mixture was cooled to –25 °C for 18 h. The crude product was quickly filtered off (very hygroscopic even when filtered under a stream of argon) and was suspended in MeCN (15 mL). BTBAC (200 mg, 640 µmol) was added and the suspension was heated under reflux for 10 min. After the mixture was cooled to r.t., the precipitate was filtered off, leaving enough solvent to keep the precipitate covered. The precipitate was washed with MeCN/EtOAc (1/2, 5 × 5 mL), while always keeping the product covered. To recover the product, the remaining suspension was transferred into a storage vial, and the remaining solvent was removed under reduced pressure. The product was obtained as light green needles (59.8 mg, 172 µmol, 52%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.25 (dt, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 2.82 (dt, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 4.22 (s, 6H, 2 × CH3), 4.36–4.39 (m, 2H, 1´´-H, 4´´-H), 7.24 (t, ^3J = 2.0 Hz, 2H), 7.79 (dd, ^3J = 7.8 Hz, 2H, 3-H, 3´-H), 8.05 (ddd, ^3J = 7.8 Hz, ^3J = 6.1, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.37 (td, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.23 (d, ^3J = 6.1 Hz, 2H, 6-H, 6´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.7 (2 x CH3), 56.5 (C1´´, C4´´), 73.1 (C7´´), 127.7 (C5, C5´), 129.3 (3C, 3´C), 143.5 (5´´C, 6´´C), 145.9 (4C, 4´C), 148.4 (C6, C6´), 149.9 (C2, C2´), 153.7 (C2´´, C3´´).

1-Methyl-2-(3-(1-methylpyridinium-3-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(hexafluorophosphate) (**3g^{PF6}**)

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A solution of the bromide **3g^{Br}** (100 mg, 229 µmol) in water (200 mL) was treated with an aqueous solution of NH_4PF_6 (10 mL, 1.50 g, 9.20 mmol, 40 equiv.). The resulting suspension was extracted with $MeNO_2$ (3 × 50 mL). The combined organic layers were dried with Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was recrystalized from $MeNO_2$/$Cl(CH_2)_2Cl$ to yield the product as light-yellow crystals (36.9 mg, 65.2 µmol, 28%); mp >190 °C (dec.). – ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.22 (dt, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 2.77 (dt, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, 7´´-H), 4.15 (s, 6H 2 × CH_3), 4.31–4.35 (m, 2H, 1´´-H, 4´´-H), 7.21 (t, ^3J = 1.9 Hz, 2H, 5´´-H, 6´´-H), 7.68 (d, ^3J = 7.7 Hz, 2H, 3-H, 3´-H), 8.01 (ddd, ^3J = 7.7 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 2H, 5-H, 5´-H), 8.33 (td, ^3J = 7.7, ^4J = 1.4 Hz, 2H, 4-H, 4´-H), 9.08 (d, ^3J = 6.2 Hz, 2H, 6-H, 6´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ = 47.7 (2 × CH3), 56.6 (C1´´, C4´´), 73.1 (C7´´), 127.8 (C5, C5´), 129.3 (C3, C3´), 143.5 (C5´´, C6´´), 145.9 (C4, C4´), 148.3 (C6, C6´), 149.9 (C2, C2´), 153.7 (C2´´, C3´´). – El. Anal. for $C_{19}H_{20}F_{12}N_2P_2$, calc. (%): C 40.30, H 3.56, N 4.95, found (%): C 40.11, H 3.33, N 4.82.

6. Photoisomerisation of norbornadienes

Photometric investigation of the cycloaddition reaction

The cycloaddition reaction was investigated photometrically by the direct irradiation of **3f**–**3i**, **3g^{Cl}**, **3g^{Br}**, **3g^{I}**, **3g^{PF6}** and **3g^{Nap}** with LUMOS (λ_{ex} = 315 nm or, λ_{ex} = 360 nm, λex = 365 nm or λ_{ex} = 520 nm) or external LED (λ_{ex} = 365 nm) in MeCN, MeOH and H_2O (c = 20 µM, V = 2.00 mL) The irradiation was stopped, when only negligible change in absorption occurred.

The cycloaddition reaction of **3i** was investigated in H2O (c = 20 µM, V = 2.00 mL, λ_{ex} = 420 nm) in the absence and in the presence of cucurbit[7]uril (CB[7]). Because of precipitation upon complex formation, the irradiation of **3i** in the presence of CB[7] (10 equiv.) was performed with DMSO (5 *vol*%) as a cosolvent.

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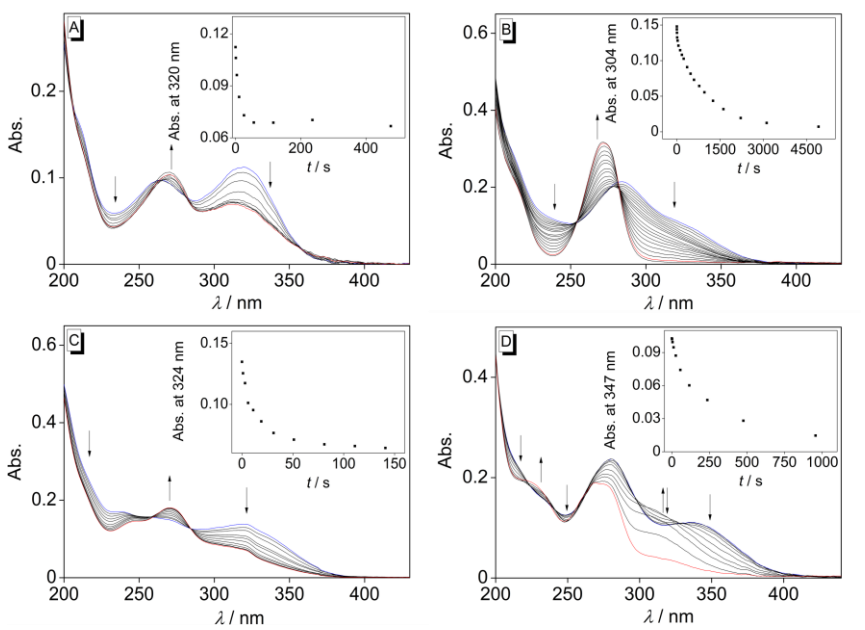


Figure S3. Photometric monitoring of the photoisomerization of **3f**–**3i** (A–D) in H2O (c = 20 µM, T = 20 °C) A–B: λ_{ex} = 315 nm; C: λ_{ex} = 365 nm; D: λ_{ex} = 360 nm. The arrows indicate the development of the absorption bands with reaction time. Inset: Plot of absorption at fixed wavelength versus t.

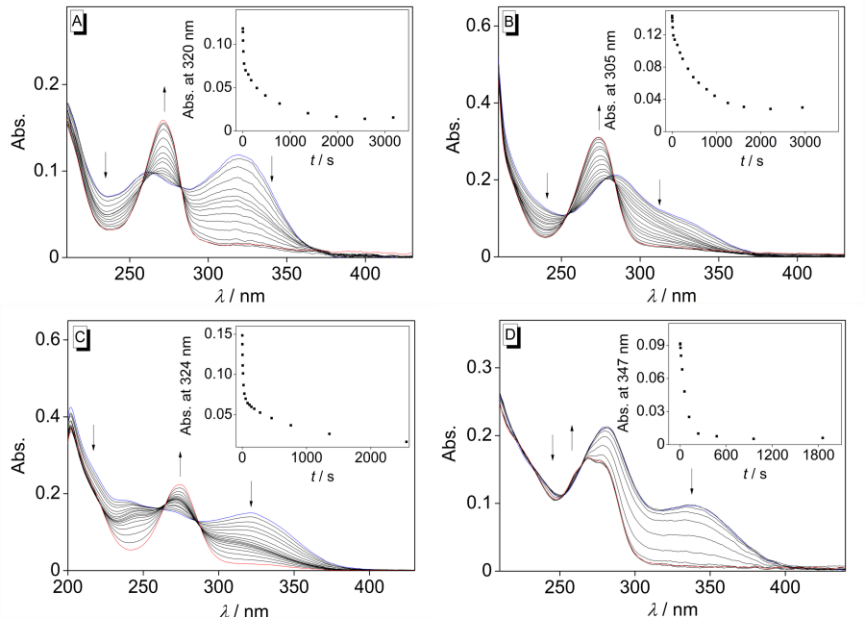


Figure S4. Photometric monitoring of the photoisomerization of **3f**–**3i** (A–D) in MeOH (c = 20 µM, T = 20 °C) A–B: λ_{ex} = 315 nm; C: λ_{ex} = 365 nm; D: λ_{ex} = 360 nm. The arrows indicate the development of the absorption bands with reaction time. Inset: Plot of absorption at fixed wavelength versus t.

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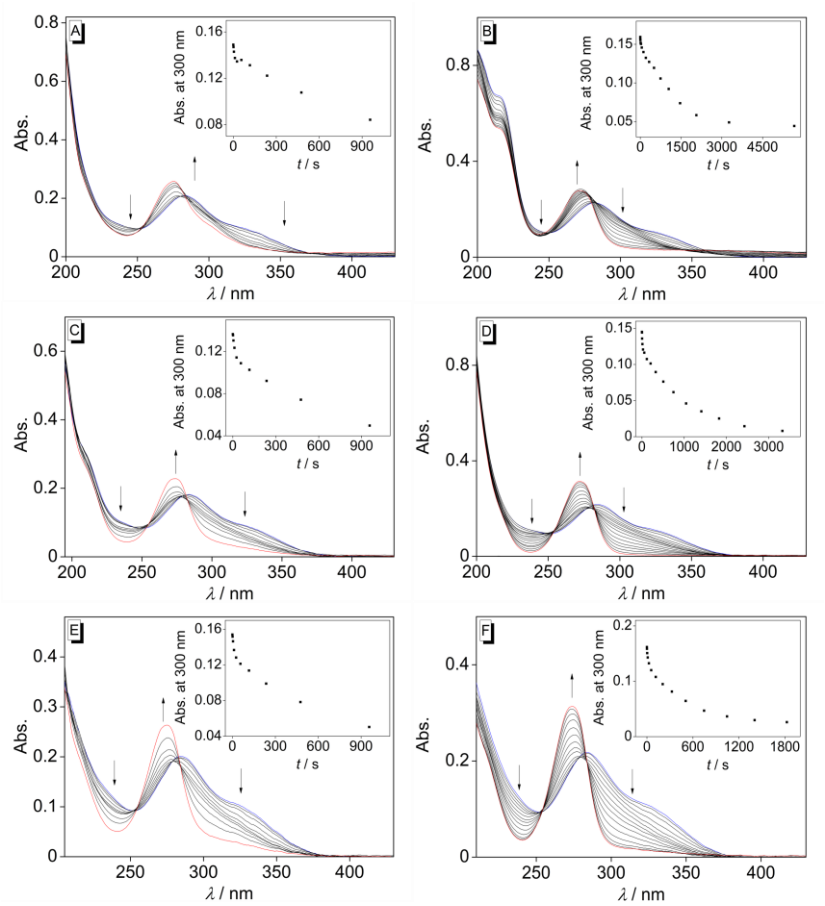


Figure S5. Photometric monitoring of the photoisomerization of **3g^{Cl}** (A, C, E) and **3g^{Br}** (B, D, F) in MeCN (A, B), H_2O (C, D) and MeOH (E, F) (*c* = 20 µM, *T* = 20 °C) A–F: λ_{ex} = 315 nm. The arrows indicate the development of the absorption bands with reaction time. Inset: Plot of absorption at fixed wavelength versus *t*.

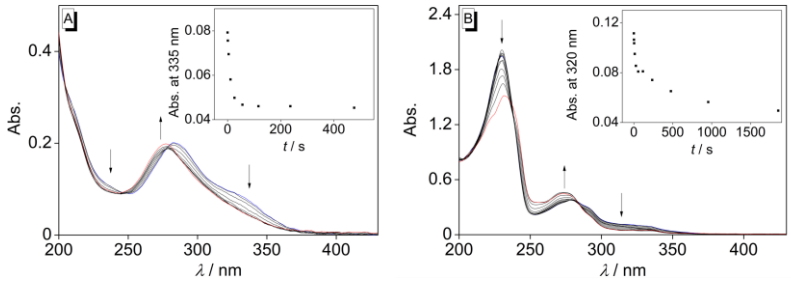


Figure S6. Photometric monitoring of the photoisomerization of **3g^{PF6}** and **3g^{Nap}** (A–D) in MeOH (*c* = 20 µM, *T* = 20 °C) A–B: λ_{ex} = 315 nm. The arrows indicate the development of the absorption bands with reaction time. Inset: Plot of absorption at fixed wavelength versus *t*.

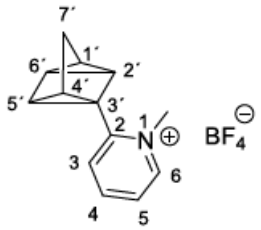
^{1}H NMR-spectroscopic investigation of the cycloaddition reaction

General Procedure D (GP D) for isomerisation of norbornadienes

Solutions of **3g**–**3i** (3.0 mg, 6.0–11 µmol) in MeCN-d_3 (600 µL) were irradiated externally with λ_{ex} = 340 nm or directly in the NMR probe head with λ_{ex} = 365 nm.[1] The ratios of the norbornadiene (**NBD**) and quadricyclane (**QC**) in the photostationary state were determined by ^{1}H NMR spectroscopy.

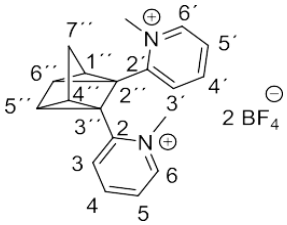
1-Methyl-2-(tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)pyridinium tetrafluoroborate (**6f**)

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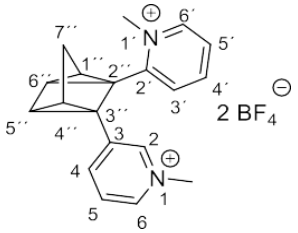
A solution of **3f** (3.0 mg, 11 µmol) in MeCN-d_3 (600 µL) was irradiated with λ_{ex} = 340 nm. During the photoreaction samples were examined photometrically until no further change in absorption occurred. (**NBD**:**QC**, 22:78). – ^{1}H-NMR (500 MHz, MeCN-d_3): δ = 1.83 (tq, ^3J = 4.6 Hz, ^4J = 1.4 Hz, 1H), 1.91–1.94 (m, 1H), 2.15 (dq, ^3J = 5.2 Hz, ^4J = 1.4 Hz, 1H), 2.21 (ddd, ^3J = 6.2 Hz, ^3J = 4.6 Hz, ^4J = 1.7 Hz, 1H), 2.27 (dt, ^2J = 12.0 Hz, ^4J = 1.4 Hz, 1H), 2.43 (dt, ^2J = 12.0 Hz, ^3J = 1.4 Hz, 1H), 2.71 (ddd, ^3J = 5.2 Hz, ^4J = 2.5 Hz, ^4J = 1.7 Hz, 1H), 4.10 (s, 3H, CH3), 7.64 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H), 7.73 (ddd, ^3J = 7.9 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 1H), 8.28 (td, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H), 8.50 (d, ^3J = 6.2 Hz, 1H).

2,2'-(Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-diyl)bis(1-methylpyridinium) bis(tetrafluoroborate) (**6g**)



A solution of **3g** (2.7 mg, 6.0 µmol) in MeCN-d3 (600 µL) was treated according to GP D. [**NBD**:**QC**, 33:67 (lit.: 29:71[9])]. – ^{1}H NMR (600 MHz, MeCN-d_3): δ = 2.48 (dt, ^3J = 5.1 Hz, ^4J = 1.4 Hz, 2H), 2.52 (dt, ^2J = 12.8 Hz, ^3J = 1.5 Hz, 1H), 2.91 (dt, ^2J = 12.8 Hz, ^3J =1.4 Hz, 1H), 2.97–3.05 (m, 2H), 4.08 (s, 6H, 2 × CH_3), 7.84 (ddd, ^3J = 7.9 Hz, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 2H), 8.06 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H), 8.38 (td, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2H), 8.48 (d, ^3J = 6.2 Hz, 1H).

1-Methyl-2-(5-(1-methylpyridinium-3-yl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)pyridinium (**6h**)

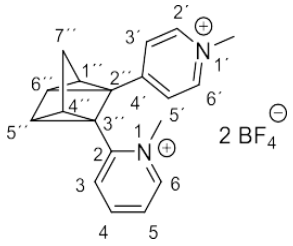


A solution of **3h** (2.7 mg, 6.0 µmol) in MeCN-d_3 (600 µL) was treated according to GP D (**NBD**:**QC**, 16:84). – ^{1}H NMR (600 MHz, MeCN-d_3): δ = 2.37–2.40 (m, 1H), 2.41–2.44 (m, 1H), 2.49–2.51 (m, 1H), 2.67–2.69 (m, 1H), 2.72–2.76 (m, 1H), 2.92–2.94 (m, 1H), 3.96–3.97 (m, 3H), 4.15–4.16 (m, 3H), 7.73 (t, ^3J = 7.3 Hz, 1H), 7.84–7.89 (m, 1H), 7.95 (d, ^3J = 8.0 Hz, 1H), 8.09 (d, ^3J = 7.9 Hz, 1H), 8.27 (s, 1H, 2-H), 8.38 (d, ^3J = 6.1 Hz, 1H), 8.45 (t, ^3J = 7.9 Hz, 1H), 8.53 (d, ^3J = 6.2 Hz, 1H).

1-Methyl-2-(5-(1-methylpyridinium-4-

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yl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)pyridinium (**6i**)



A solution of **3i** (2.7 mg, 6.0 µmol) in MeCN-*d*3 (600 µL) was treated according to GP D (**NBD**:**QC**, 10:90). – ^{1}H-NMR (600 MHz, MeCN-*d*3): δ = 2.42–2.47 (m, 1H), 2.50 (dt, ^2J = 12.5 Hz, ^3J = 1.4 Hz, 1H), 2.77 (dt, ^2J = 12.5 Hz, ^3J = 1.4 Hz, 1H), 2.83–2.88 (m, 1H), 2.98 (dd, ^3J = 5.2 Hz, ^4J = 2.6 Hz, 1H), 3.08 (dd, ^3J = 5.0 Hz, ^3J = 2.6 Hz, 1H), 4.08 (s, 3H, CH3), 4.11 (s, 3H, CH3), 7.02 (d, ^3J = 7.0 Hz, 2H), 7.98 (ddd, ^3J = 7.8 Hz, ^3J = 6.1 Hz, ^4J = 1.7 Hz, 1H), 8.10 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, 3-H), 8.18 (d, ^3J = 7.0 Hz, 2H), 8.51 (td, ^3J = 7.8 Hz, ^3J = 1.2 Hz, 1H), 8.67 (d, ^3J = 6.1 Hz, 1H).

7. NMR spectra

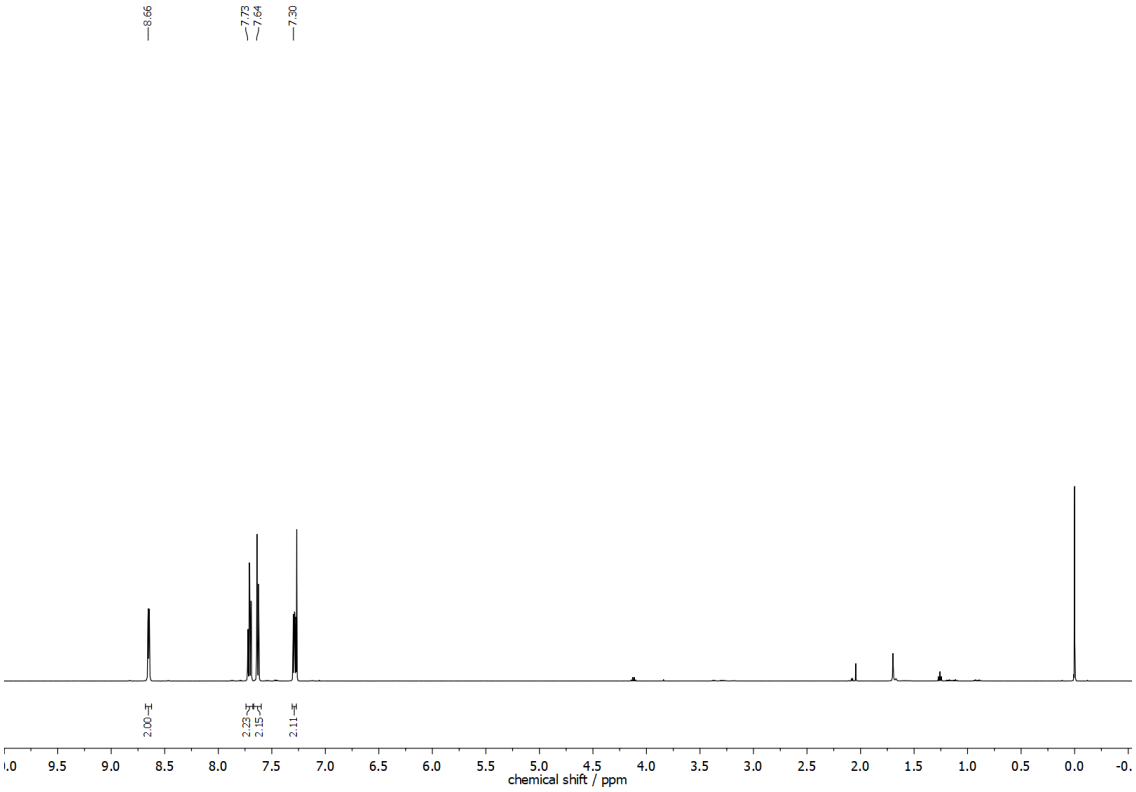


Figure S7. ^{1}H NMR spectrum (500 MHz) of **4g** in $CDCl_3$.

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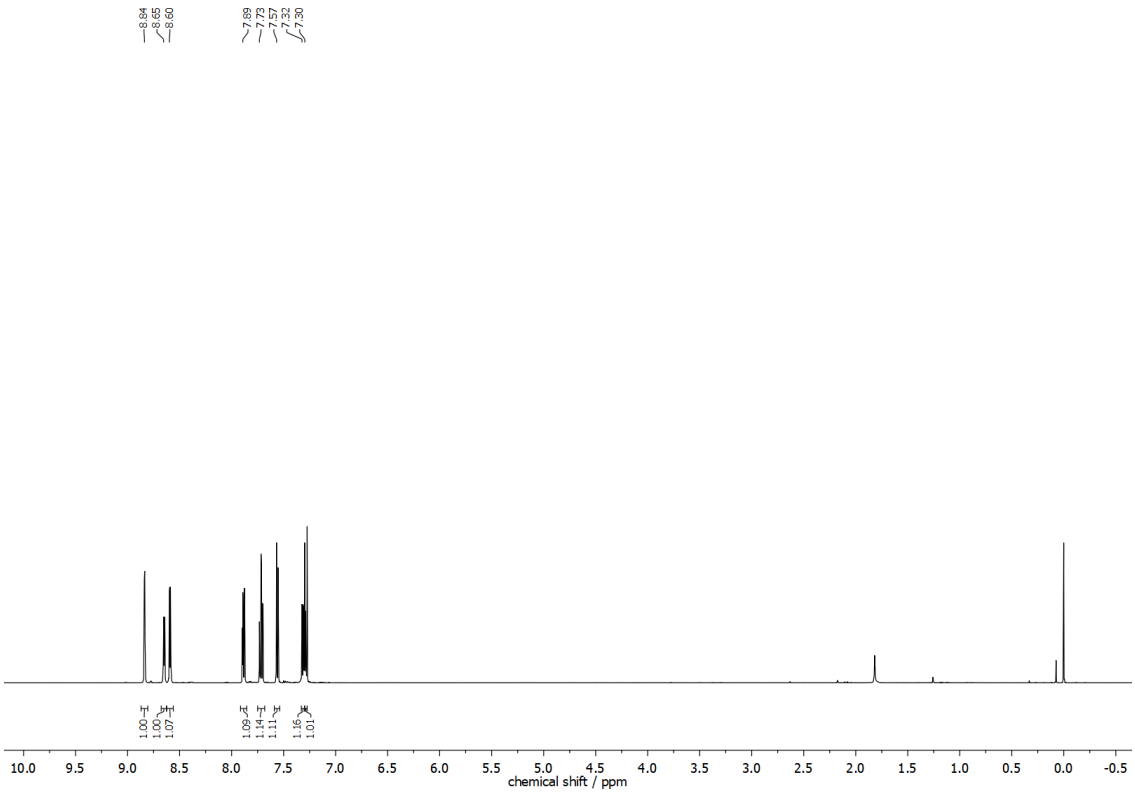


Figure S8. ^{1}H NMR spectrum (500 MHz) of **4h** in $CDCl_3$.

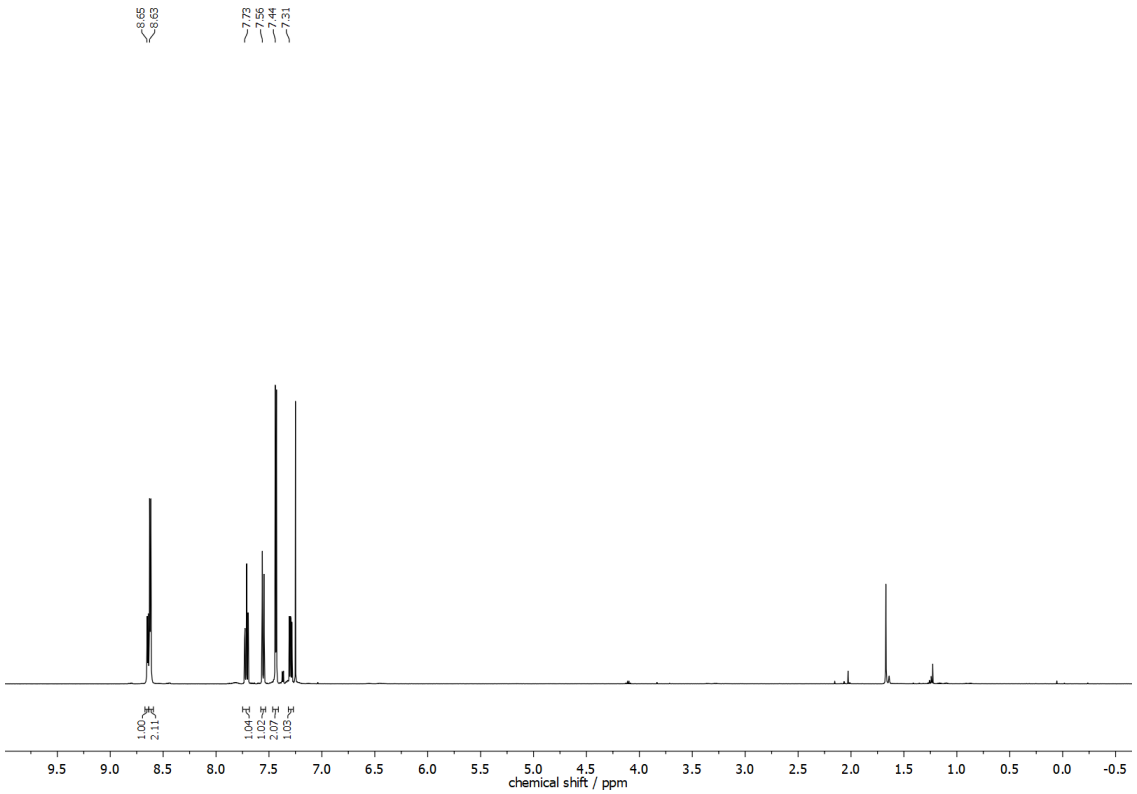


Figure S9. ^{1}H NMR spectrum (500 MHz) of **4i** in $CDCl_3$.

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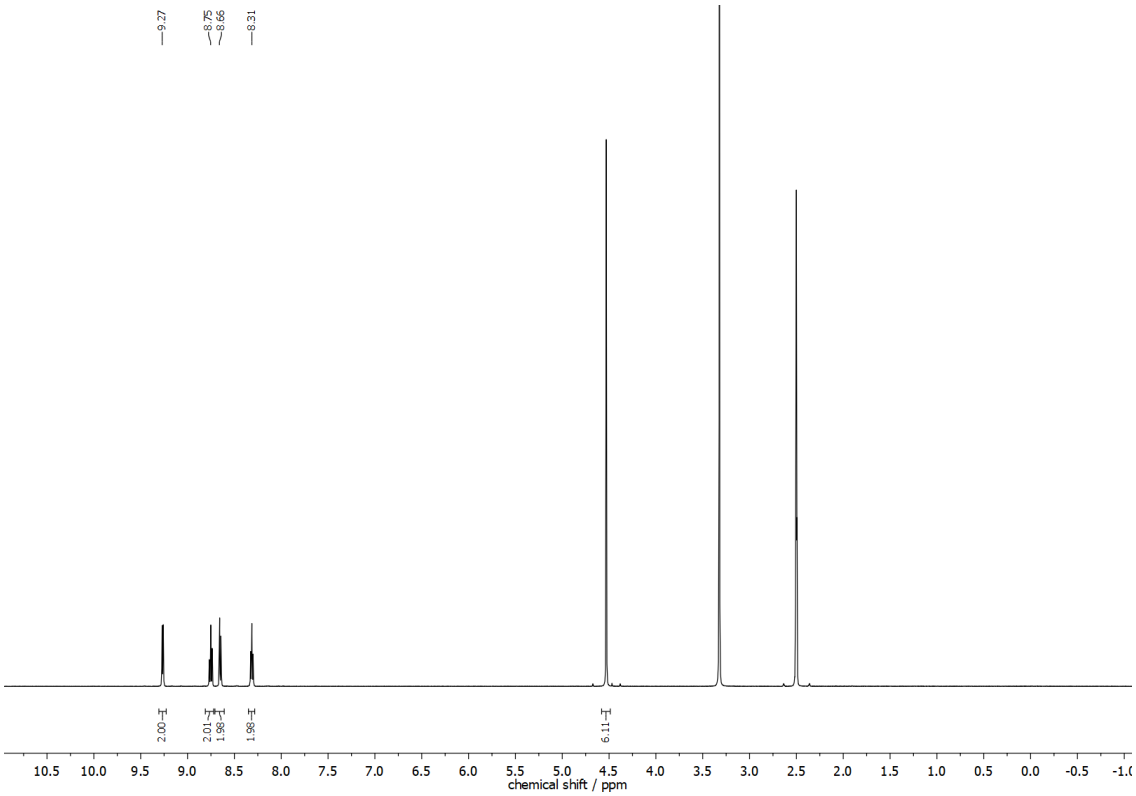


Figure S10. ^{1}H NMR spectrum (500 MHz) of **5g** in DMSO-d_6.

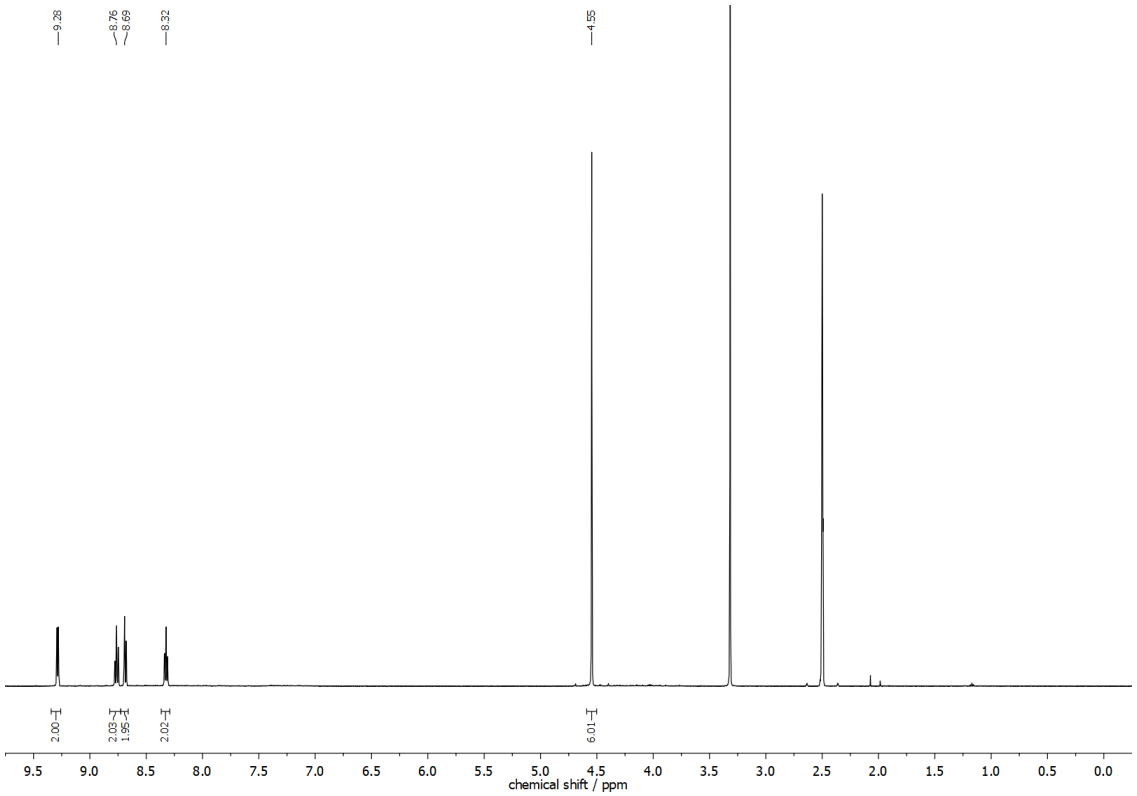


Figure S11. ^{1}H NMR spectrum (500 MHz) of **5g^{I}** in DMSO-d_6.

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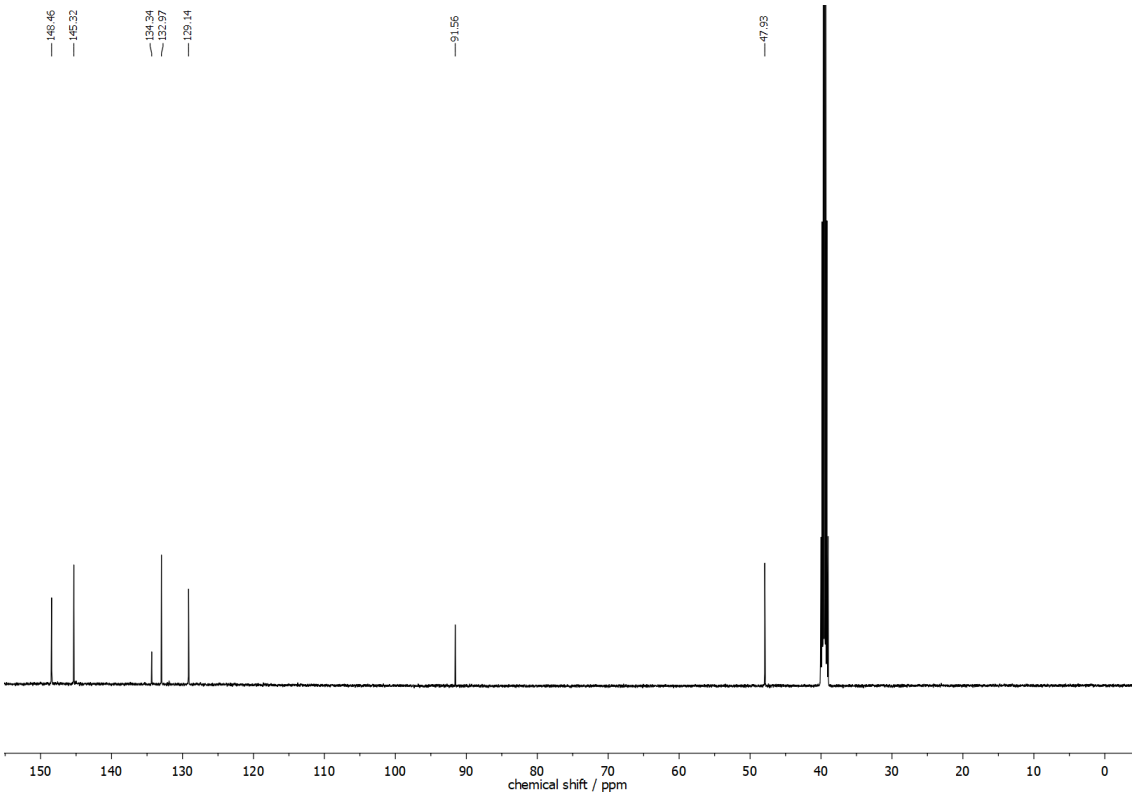


Figure S12. ^{13}C NMR spectrum (125 MHz) of **5g^{I}** in DMSO-d_6.

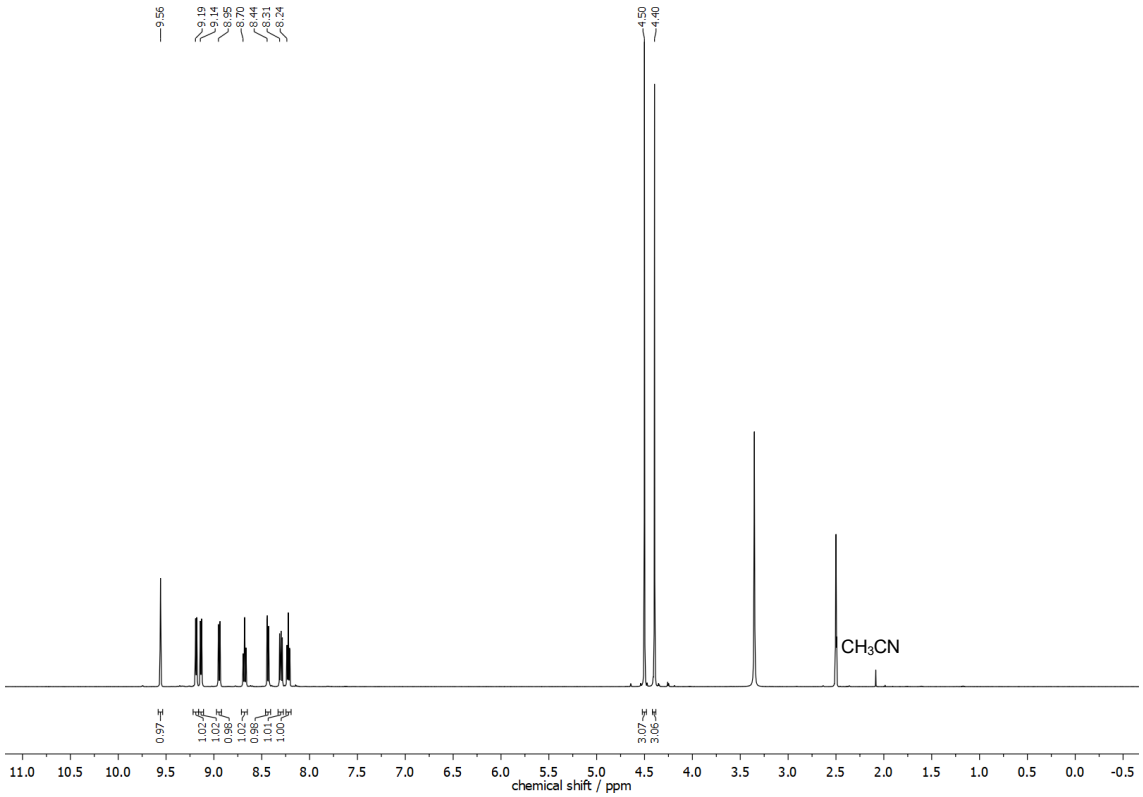


Figure S13. ^{1}H NMR spectrum (500 MHz) of **5h** in DMSO-d_6.

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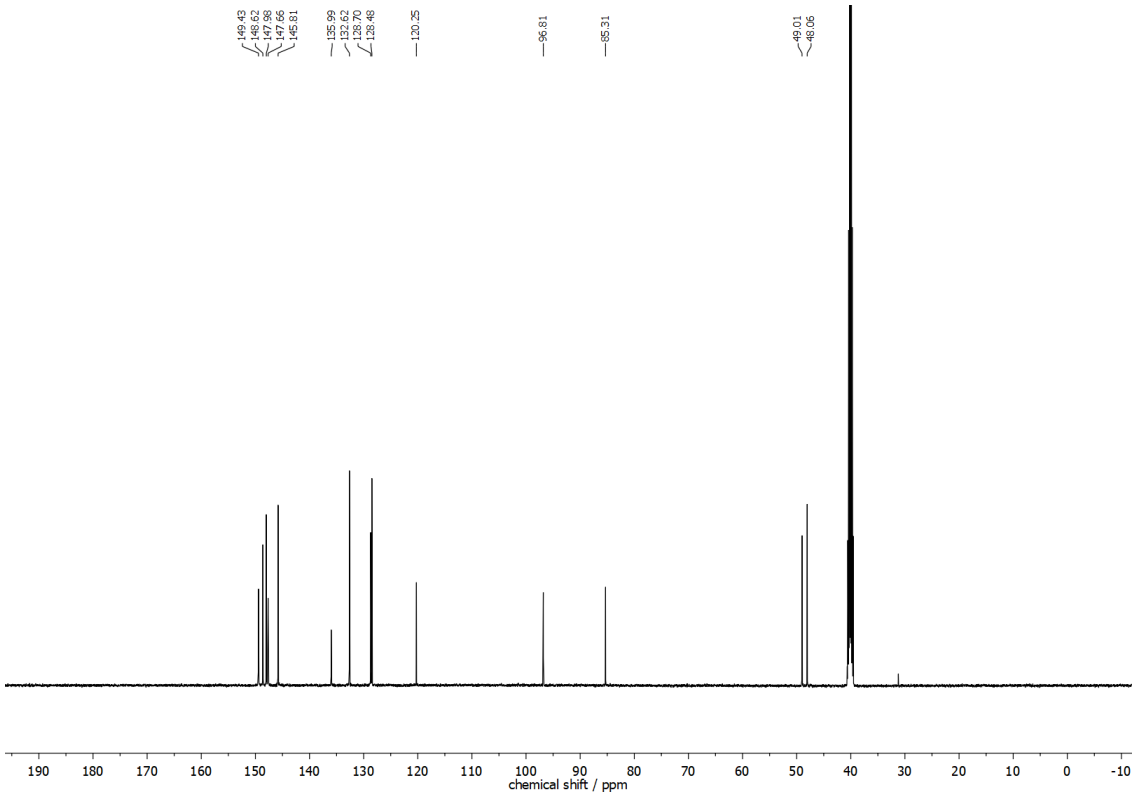


Figure S14. ^{13}C NMR spectrum (125 MHz) of **5h** in DMSO-d_6.

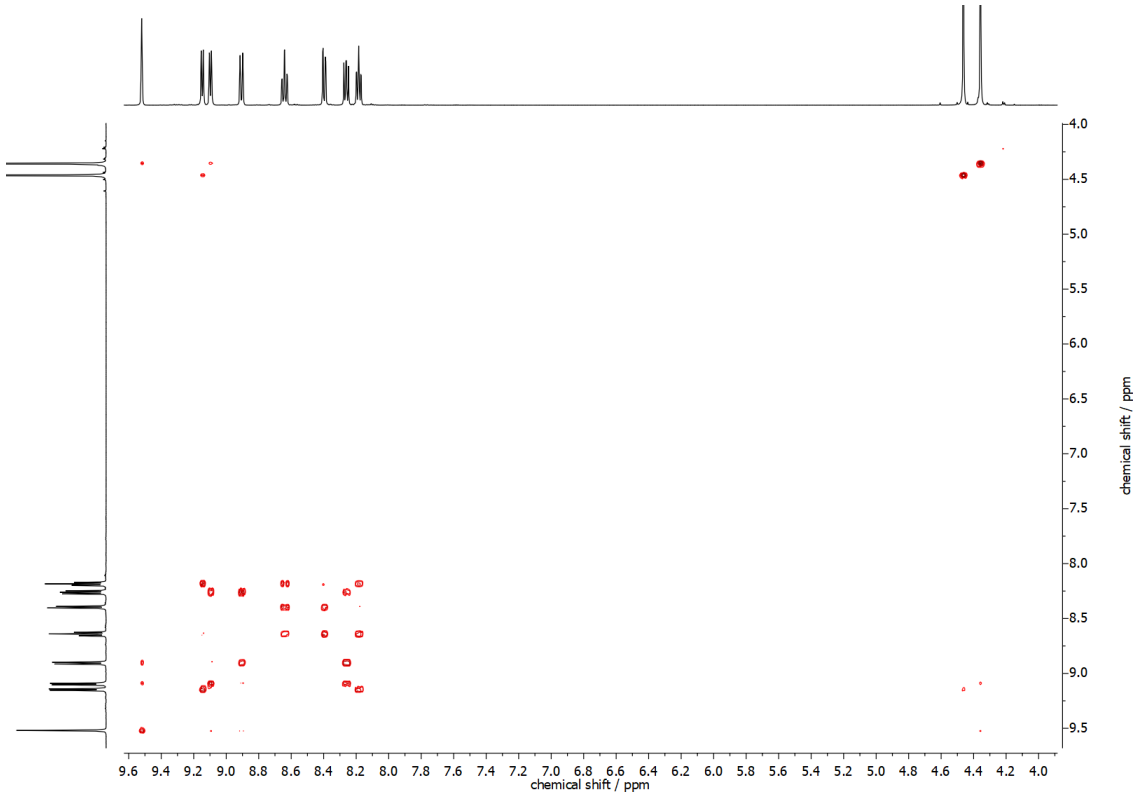


Figure S15. H,H-COSY spectrum (500 MHz) of **5h** in DMSO-d_6.

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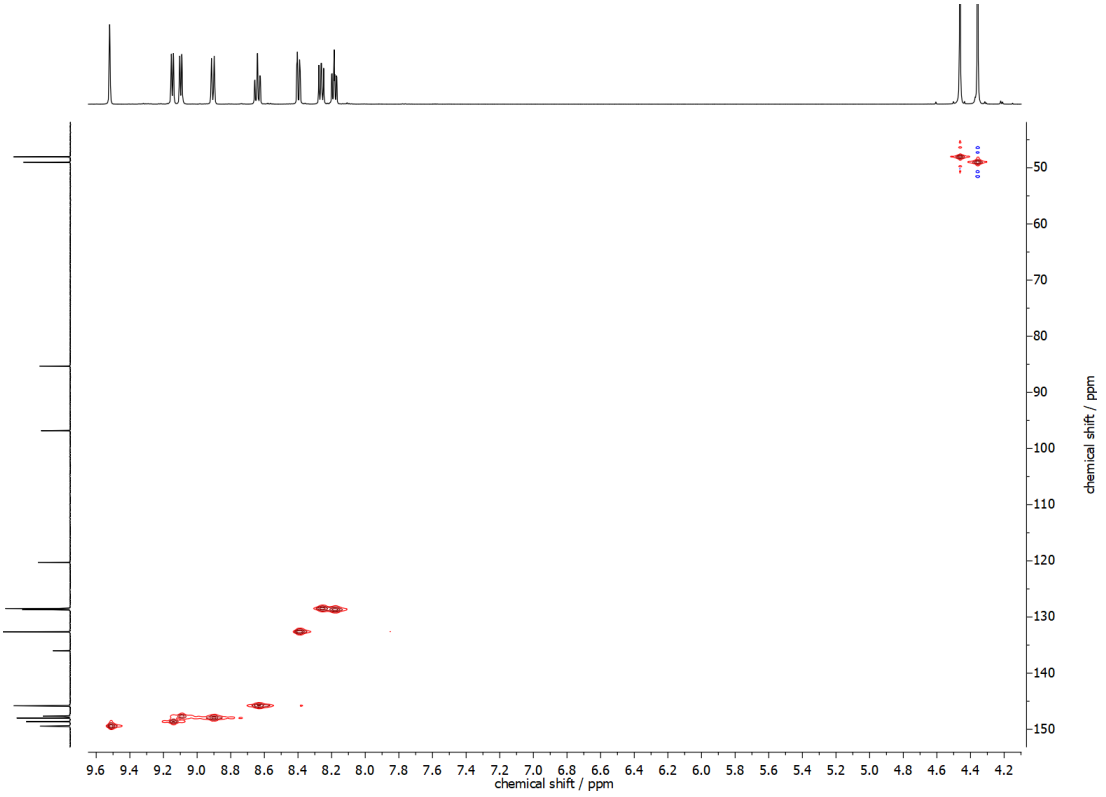


Figure S16. HSQC NMR spectrum (500 MHz) of **5h** in DMSO-d_6.

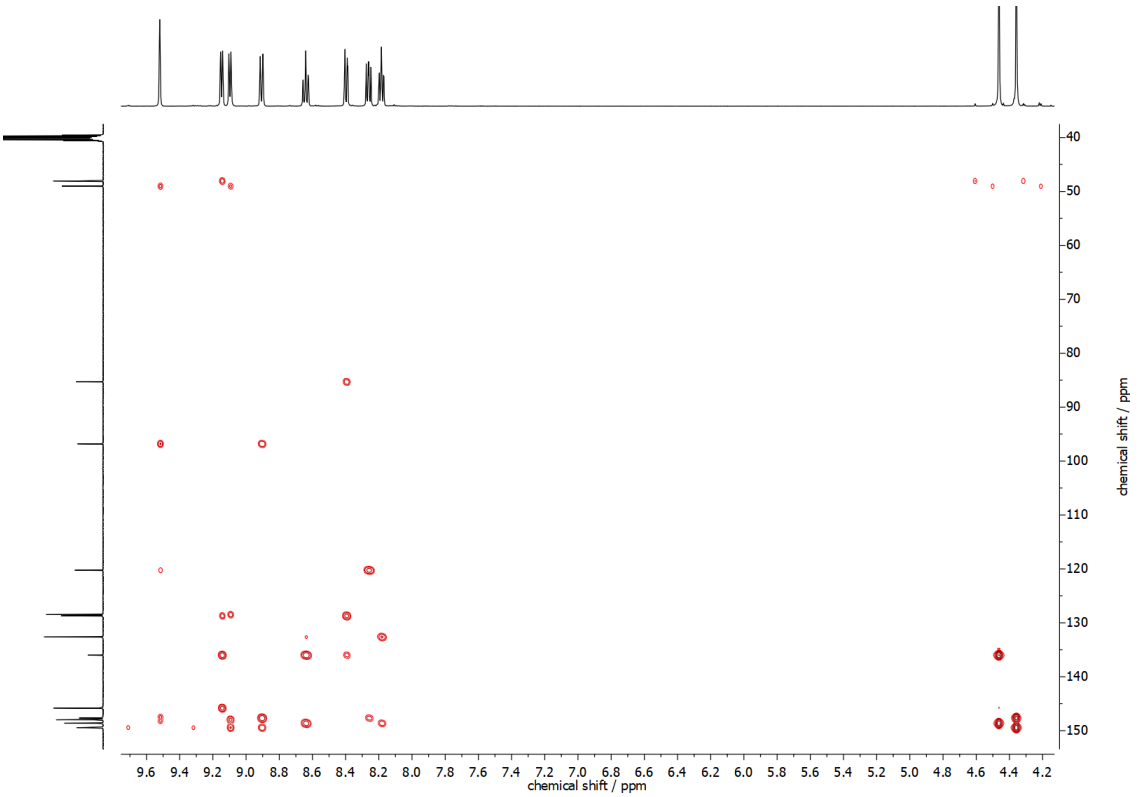


Figure S17. HMBC NMR spectrum (500 MHz) of **5h** in DMSO-d_6.

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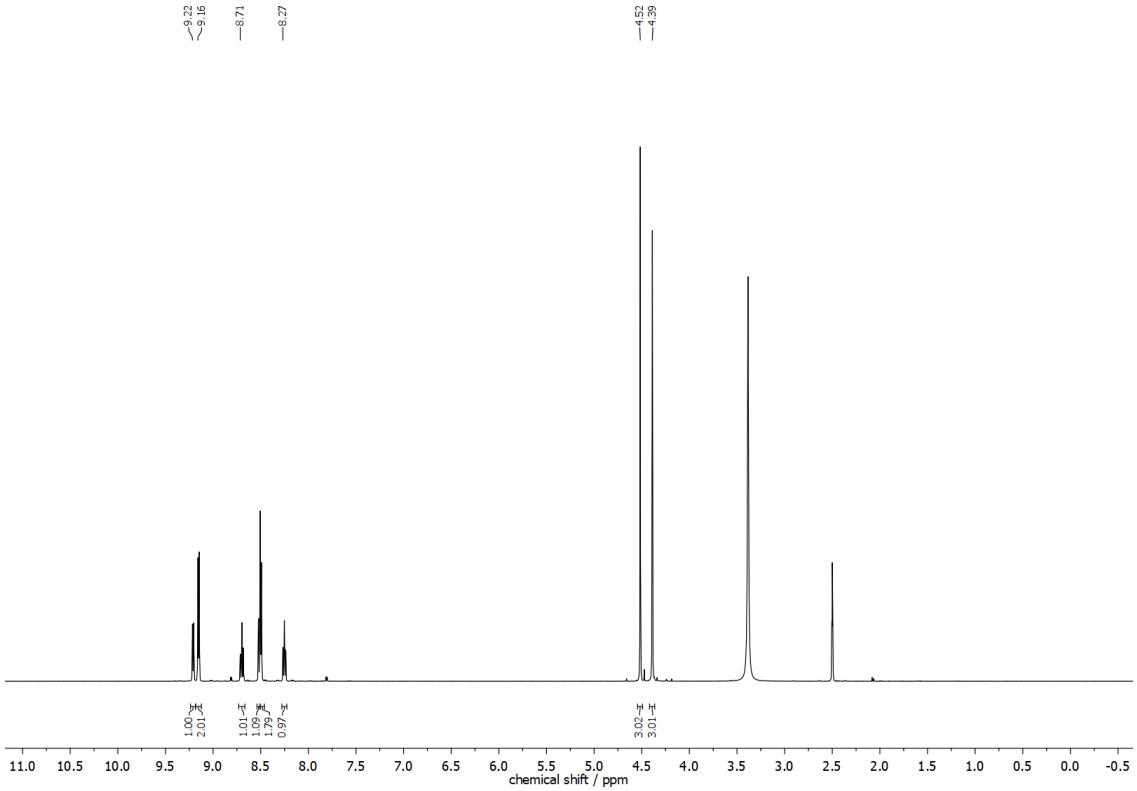


Figure S18. ^{1}H-NMR spectrum (500 MHz) of **5i** in DMSO-d_6.

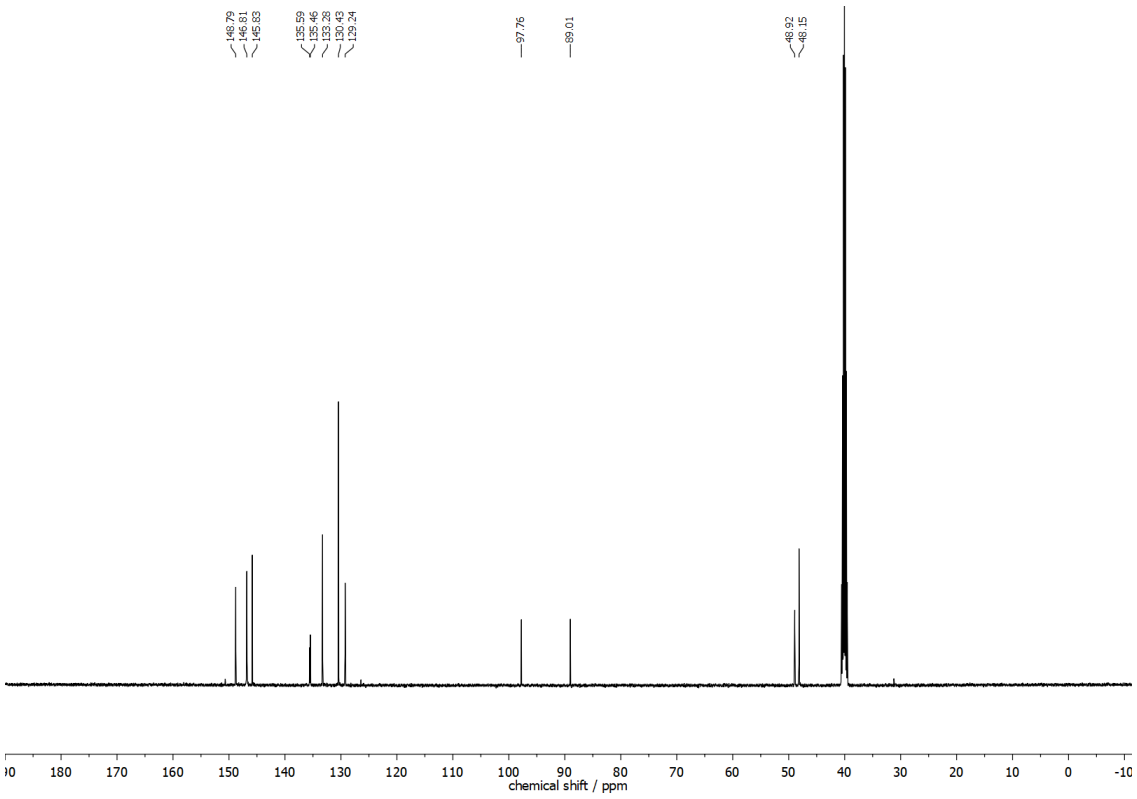


Figure S19. ^{13}C NMR spectrum (125 MHz) of **5i** in DMSO-d_6.

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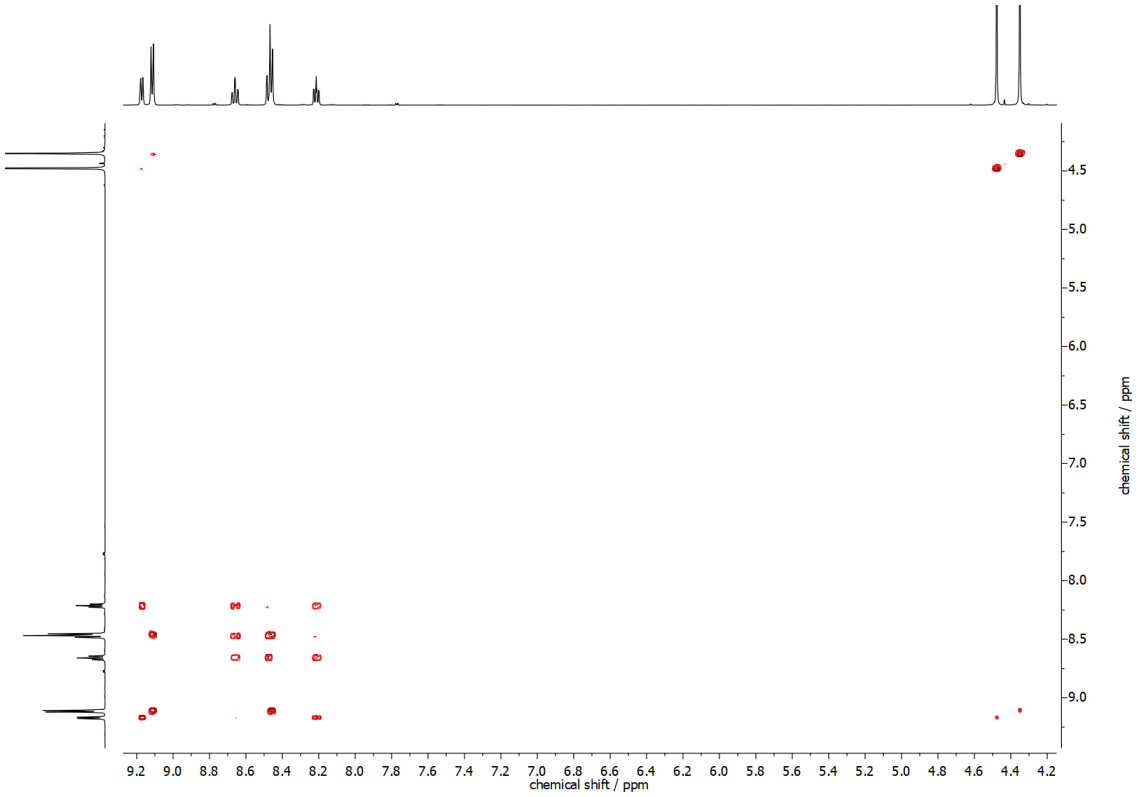


Figure S20. H,H-COSY spectrum (500 MHz) of **5i** in DMSO-d_6.

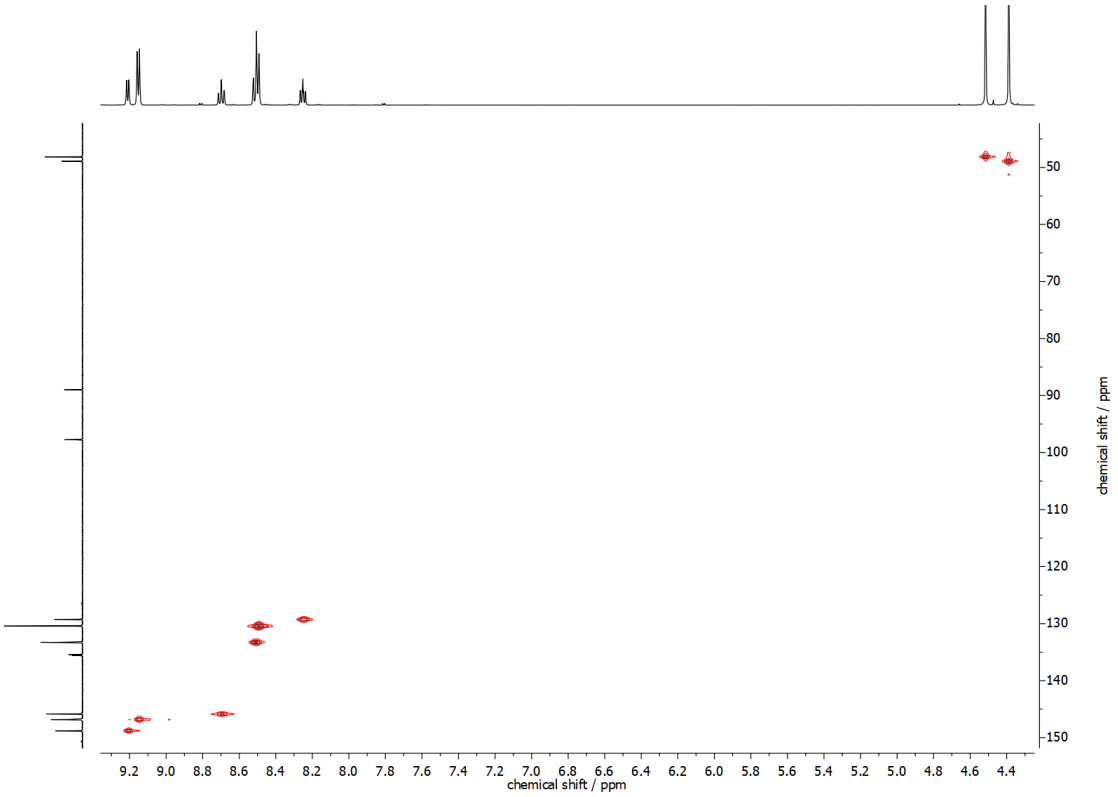


Figure S21. HSQC NMR spectrum (500 MHz) of **5i** in DMSO-d_6.

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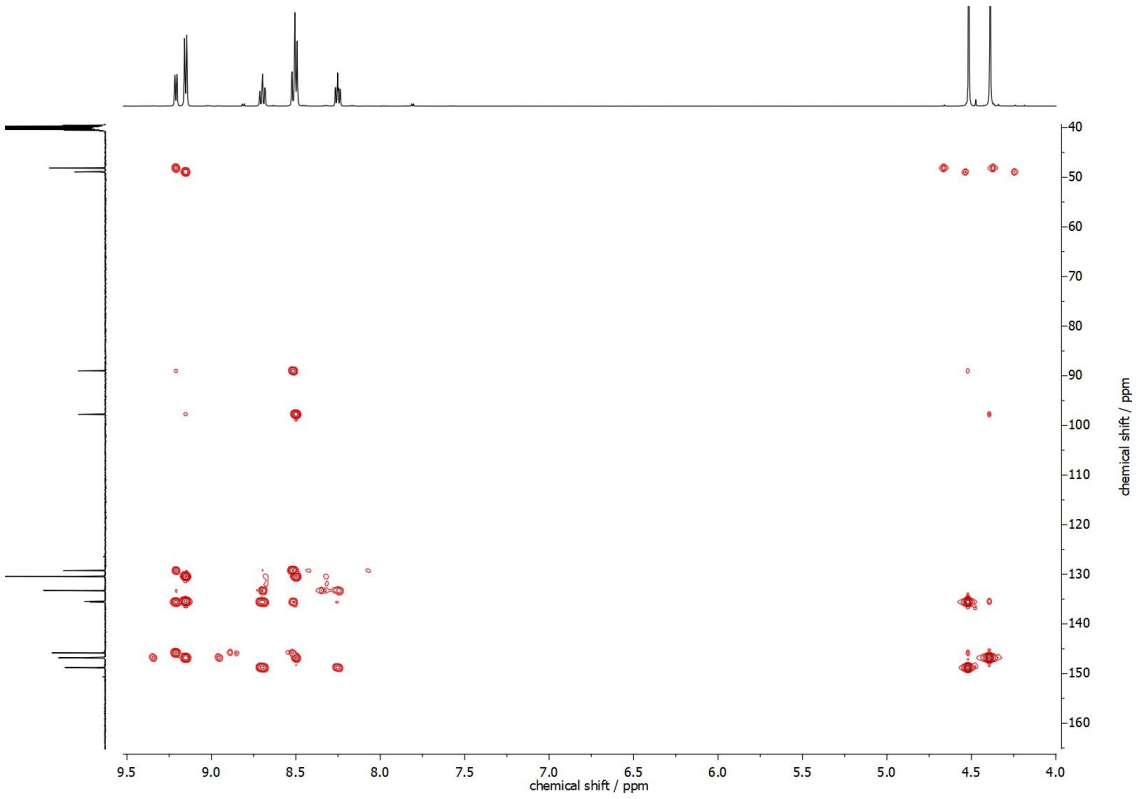


Figure S22. HMBC NMR spectrum (500 MHz) of **5i** in DMSO-d_6.

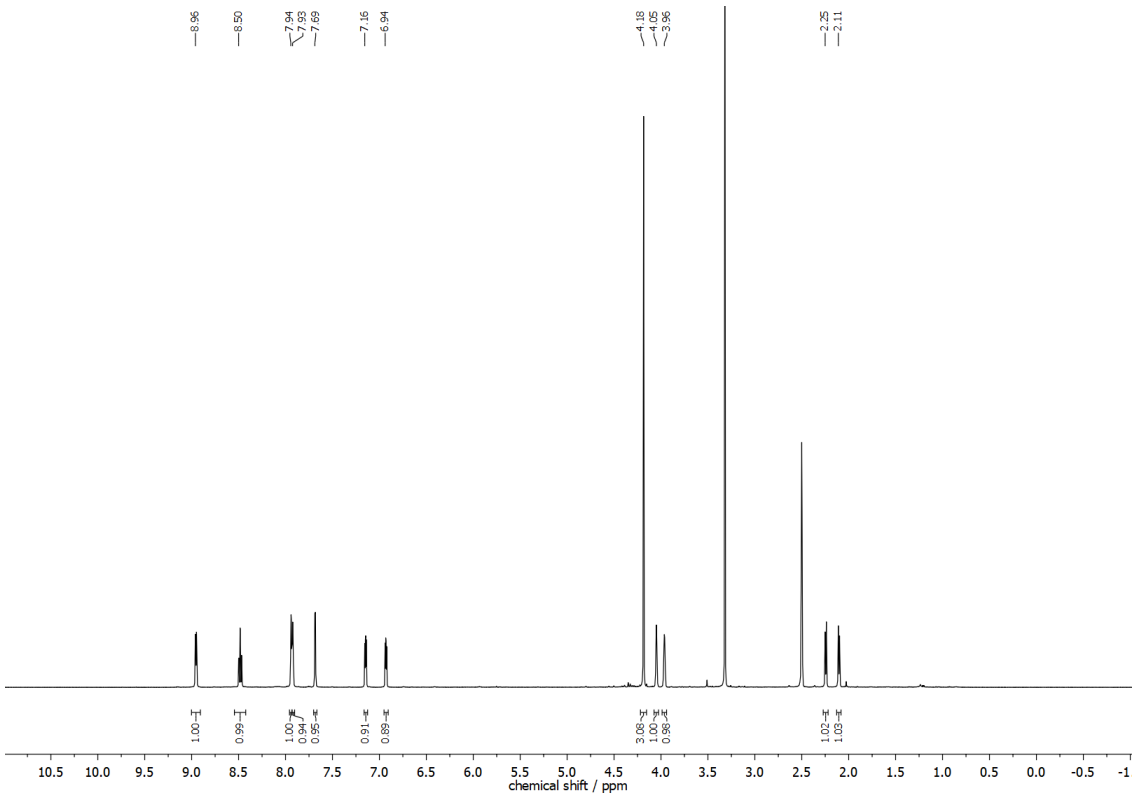


Figure S23. ^{1}H NMR spectrum (500 MHz) of **3f** in DMSO-d_6.

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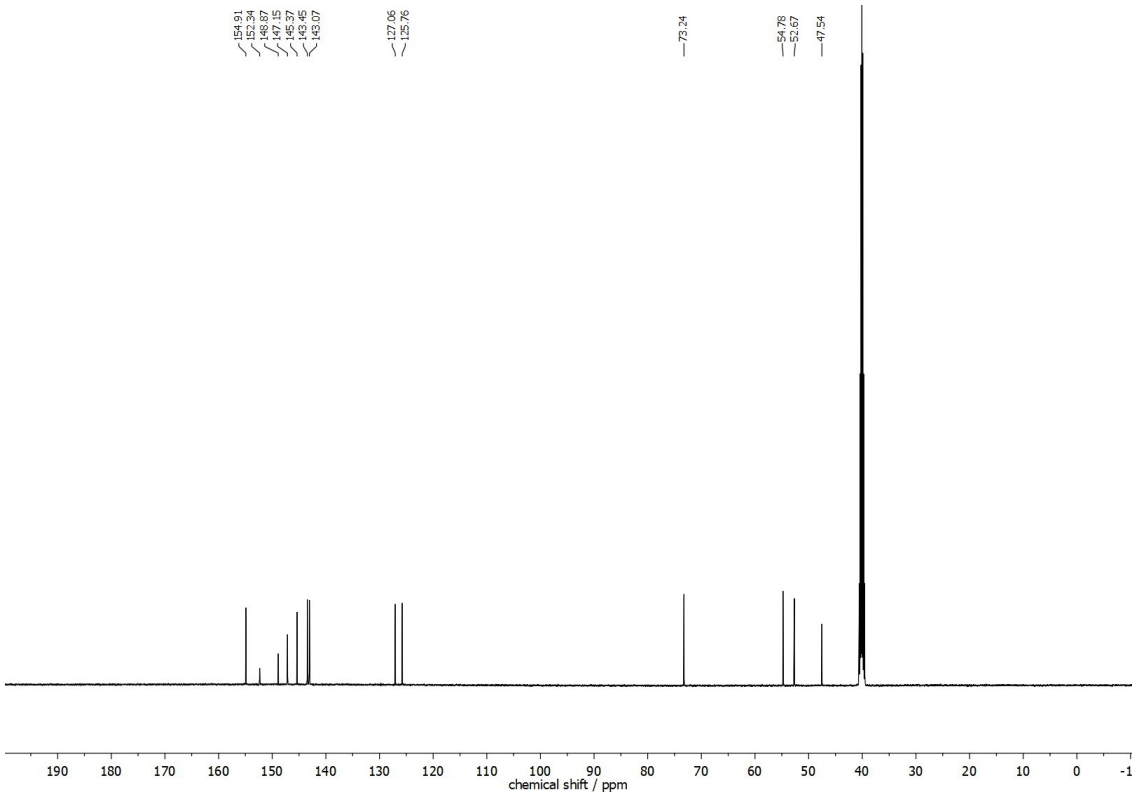


Figure S24. ^{13}C NMR spectrum (125 MHz) of **3f** in DMSO-d_6.

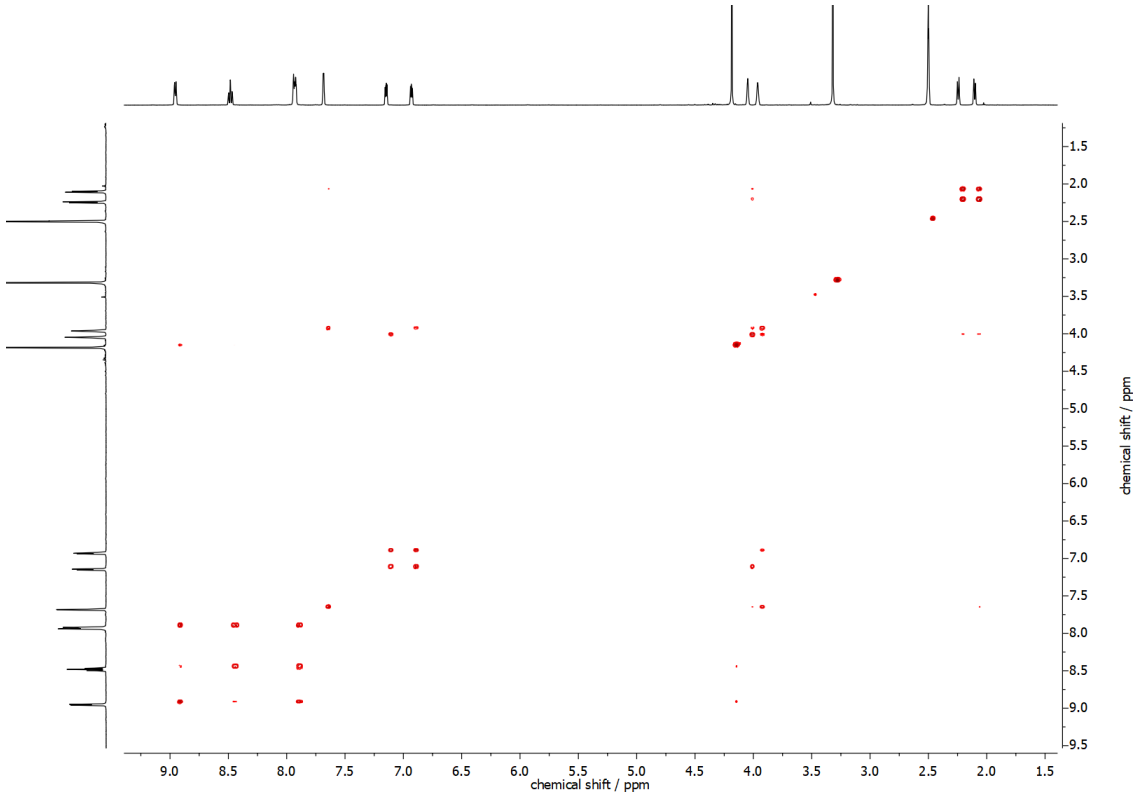


Figure S25. H,H-COSY spectrum (500 MHz) of **3f** in DMSO-d_6.

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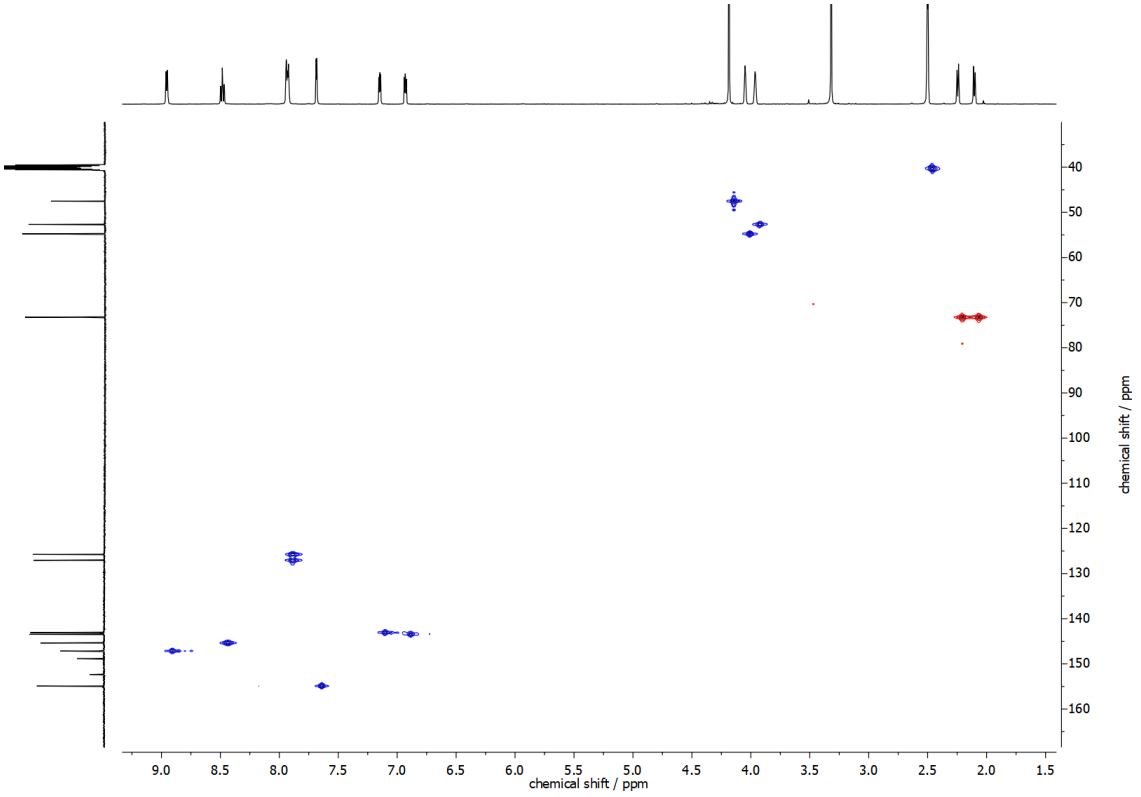


Figure S26. HSQC NMR spectrum (500 MHz) of **3f** in DMSO-d_6.

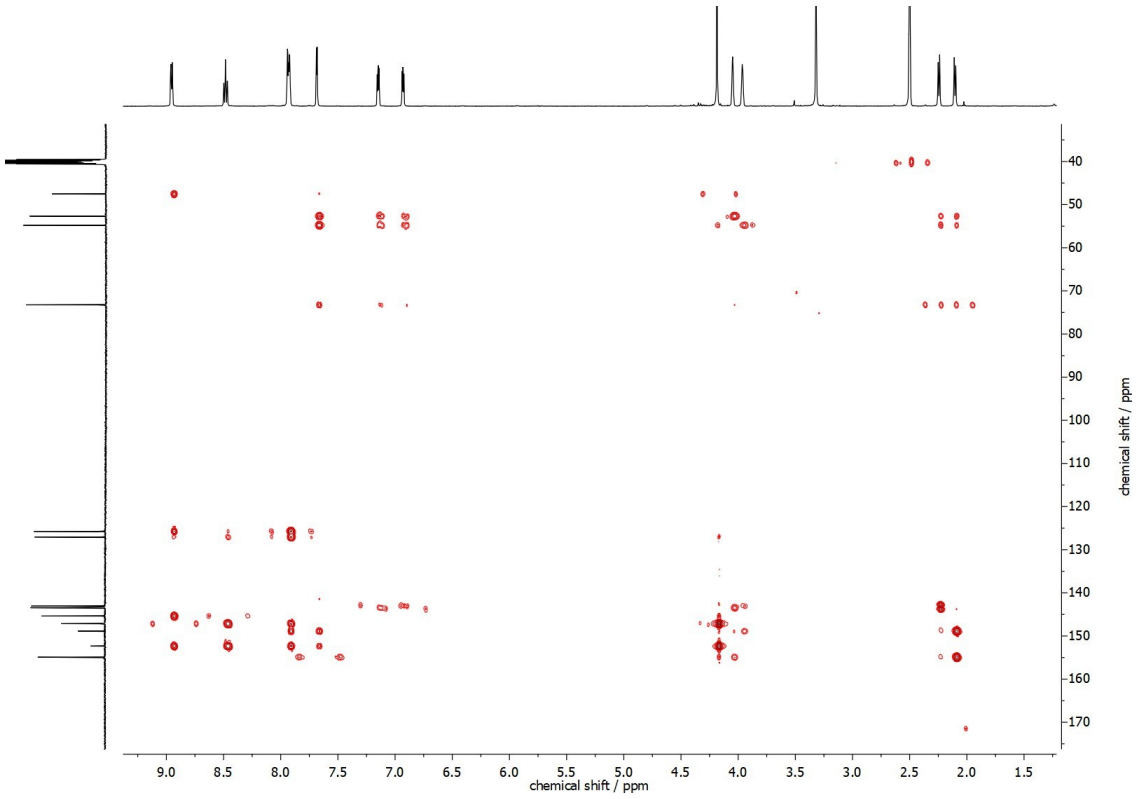


Figure S27. HMBC NMR spectrum (500 MHz) of **3f** in DMSO-d_6.

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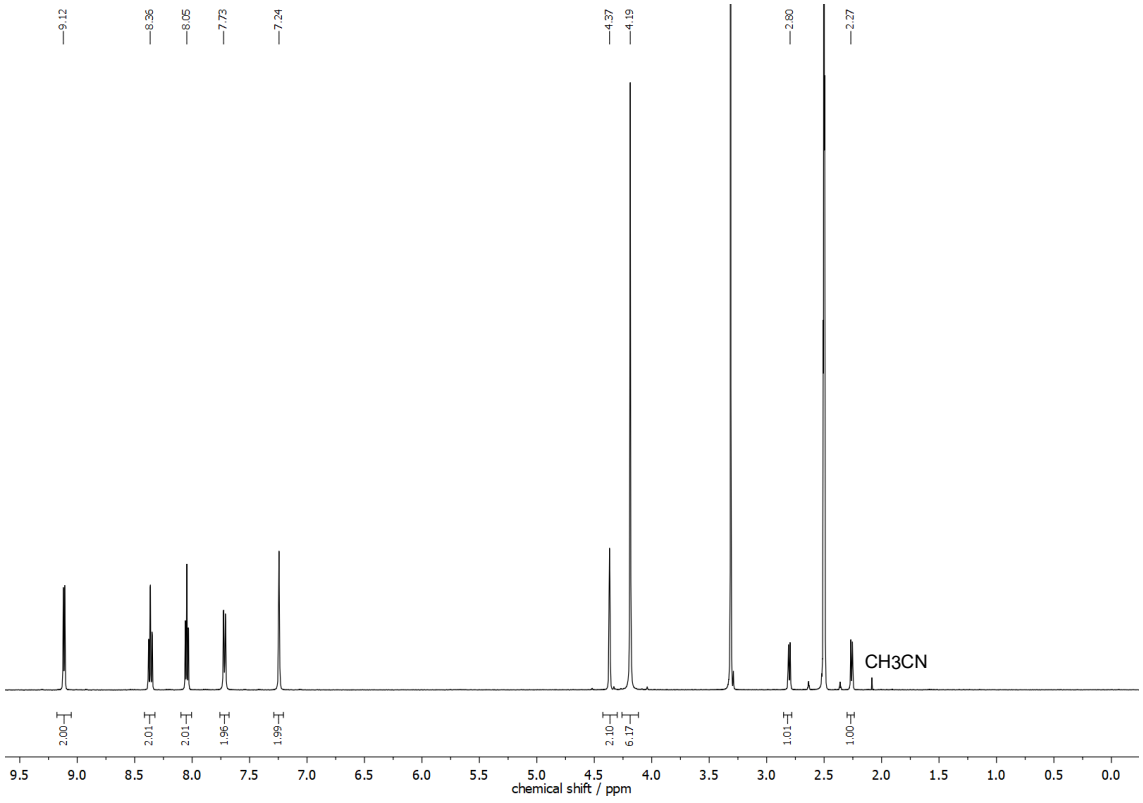


Figure S28. ^{1}H NMR spectrum (500 MHz) of **3g** in DMSO-d_6.

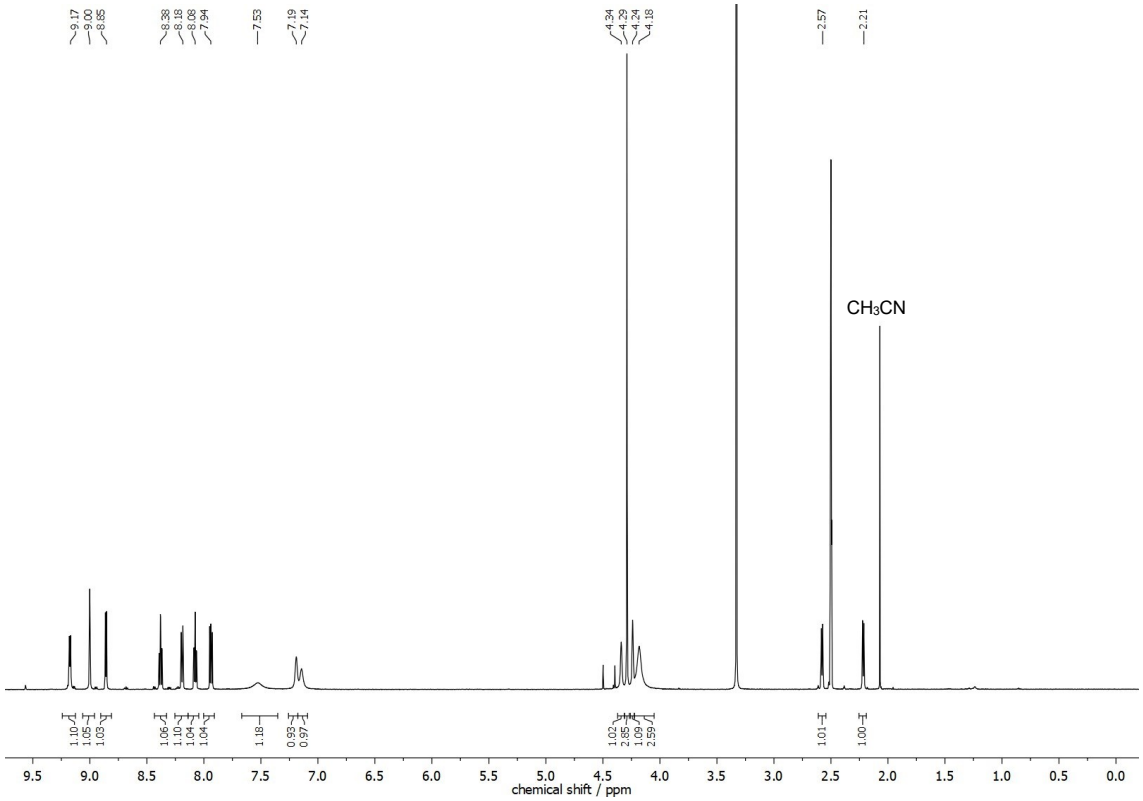


Figure S29. ^{1}H NMR spectrum (600 MHz) of **3h** in DMSO-d_6.

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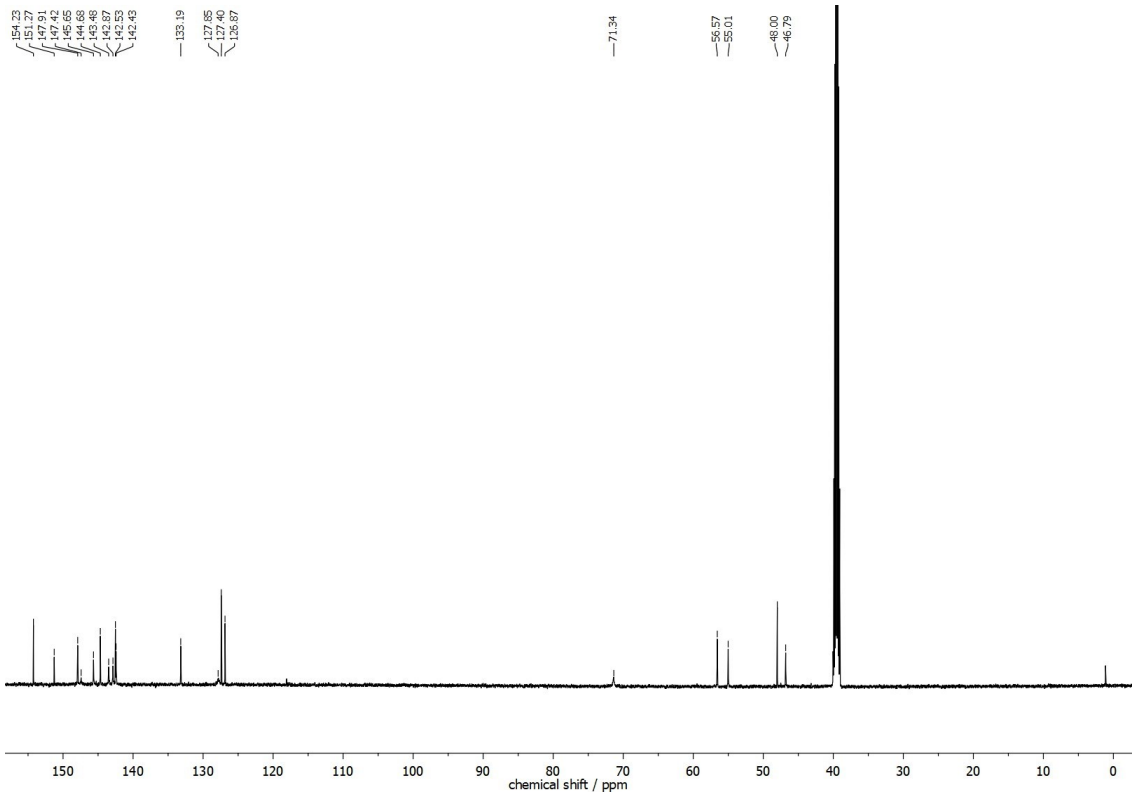


Figure S30. ^{13}C NMR spectrum (150 MHz) of **3h** in DMSO-d_6.

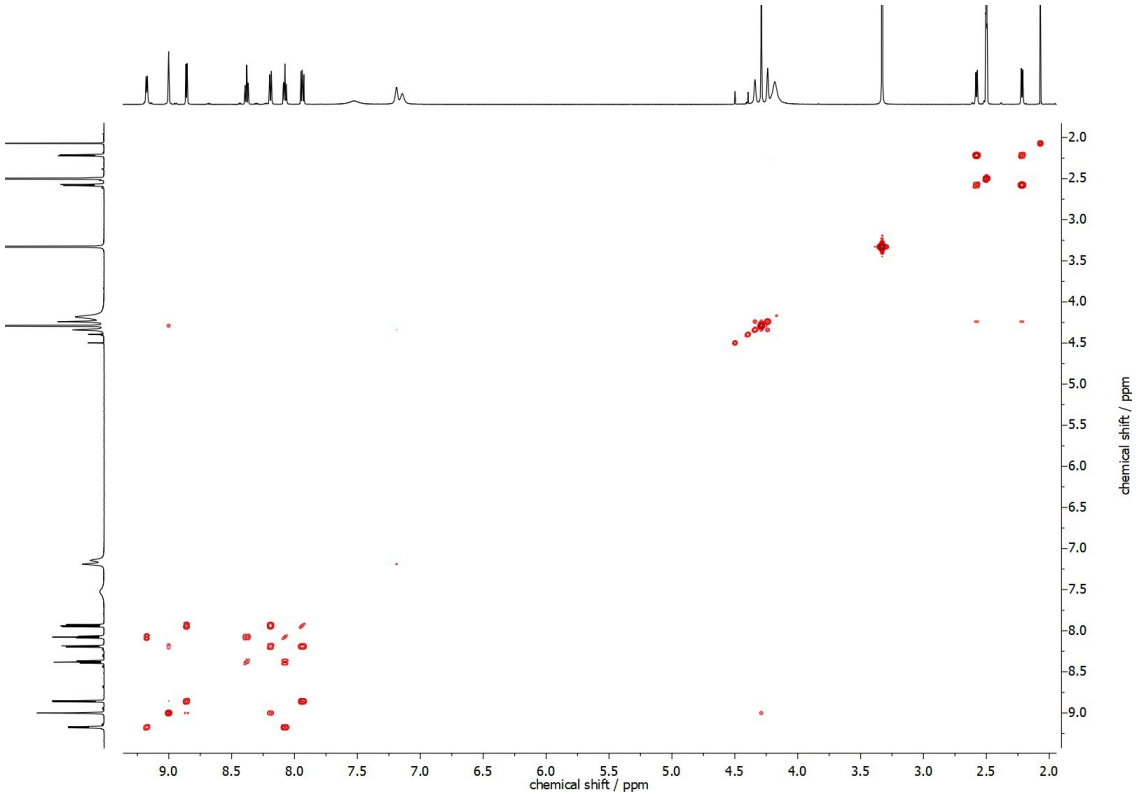


Figure S31. H,H-COSY spectrum (600 MHz) of **3h** in DMSO-d_6.

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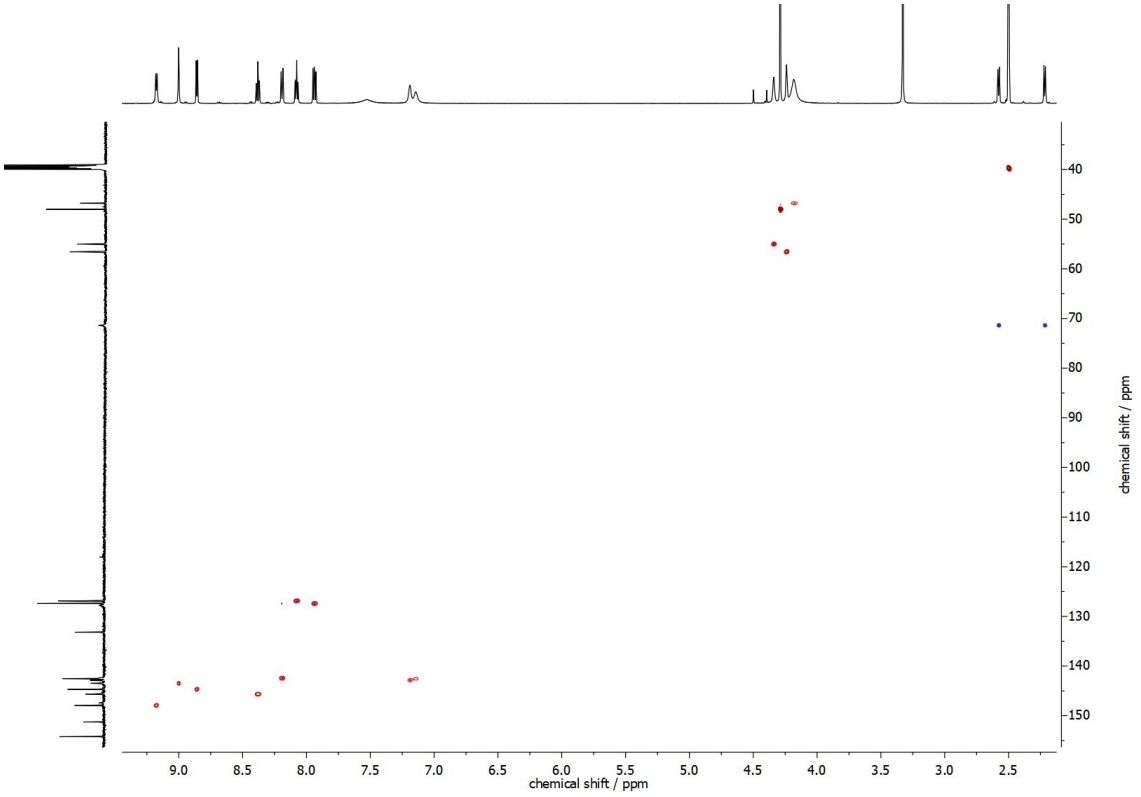


Figure S32. HSQC NMR spectrum (600 MHz) of **3h** in DMSO-d_6.

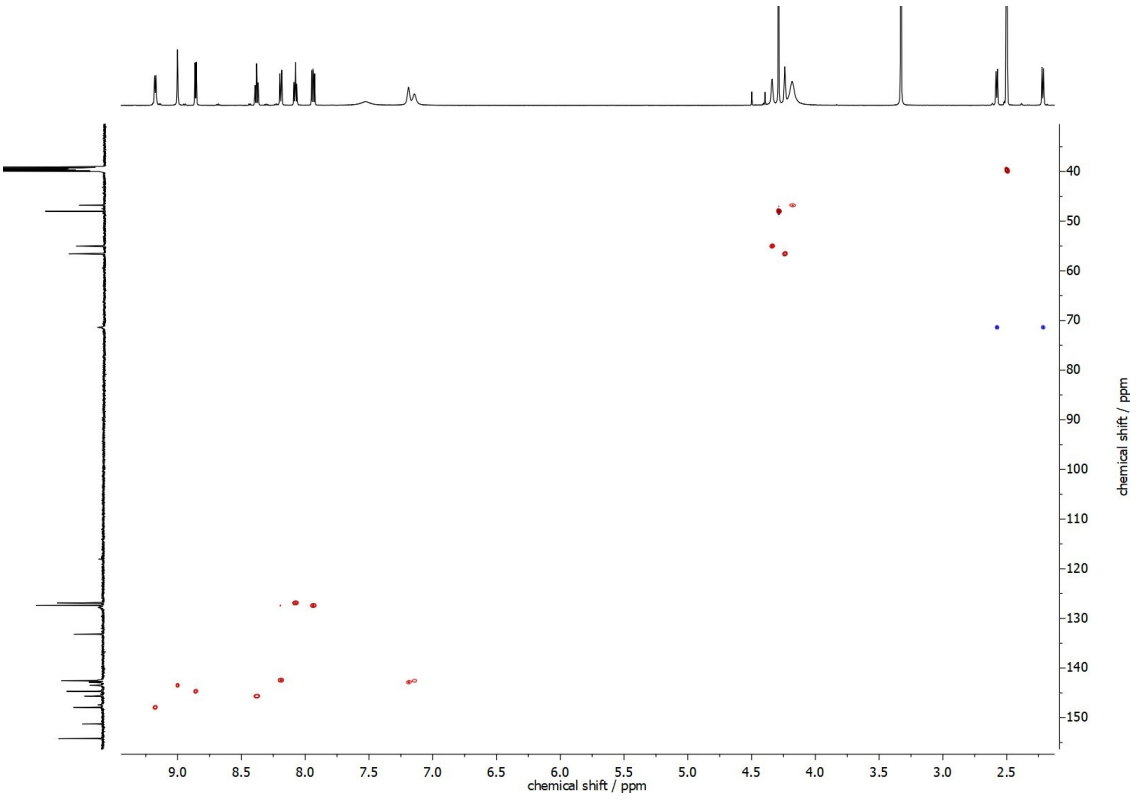


Figure S33. HMBC NMR spectrum (600 MHz) of **3h** in DMSO-d_6.

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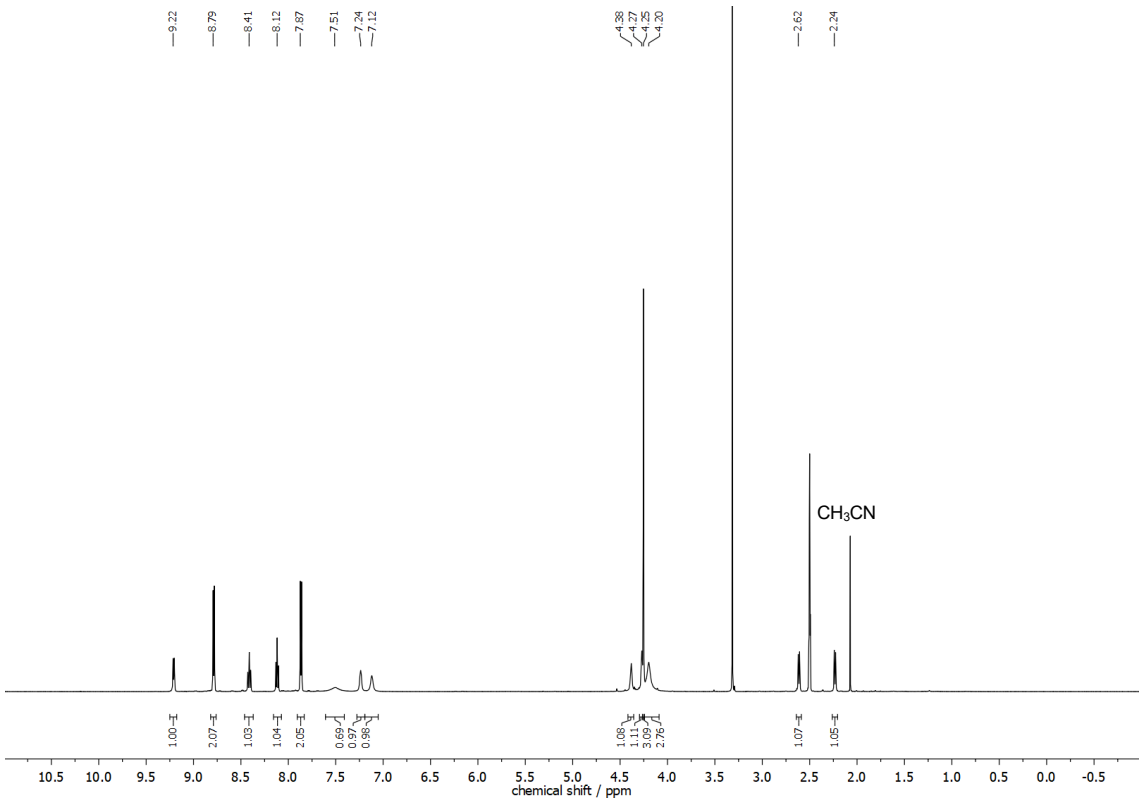


Figure S34. ^{1}H NMR spectrum (500 MHz) of **3i** in DMSO-d_6.

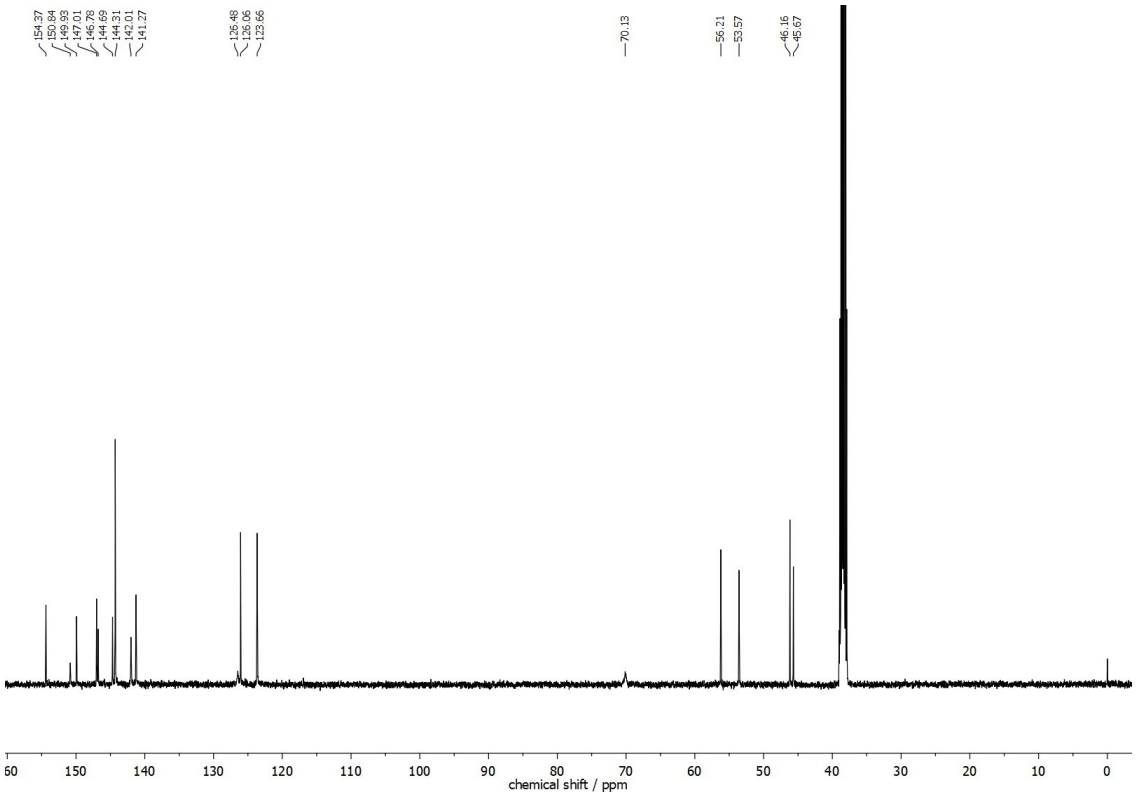


Figure S35. ^{13}C NMR spectrum (125 MHz) of **3i** in DMSO-d_6.

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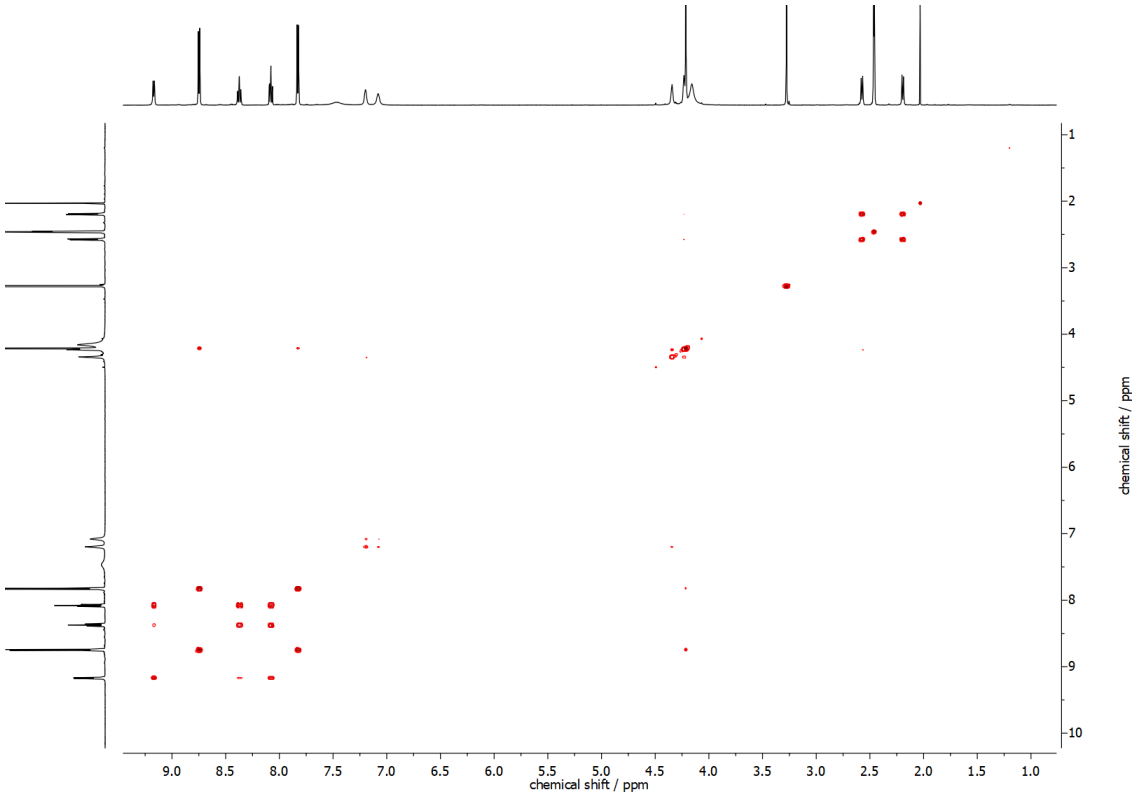


Figure S36. H,H-COSY spectrum (500 MHz) of **3i** in DMSO-d_6.

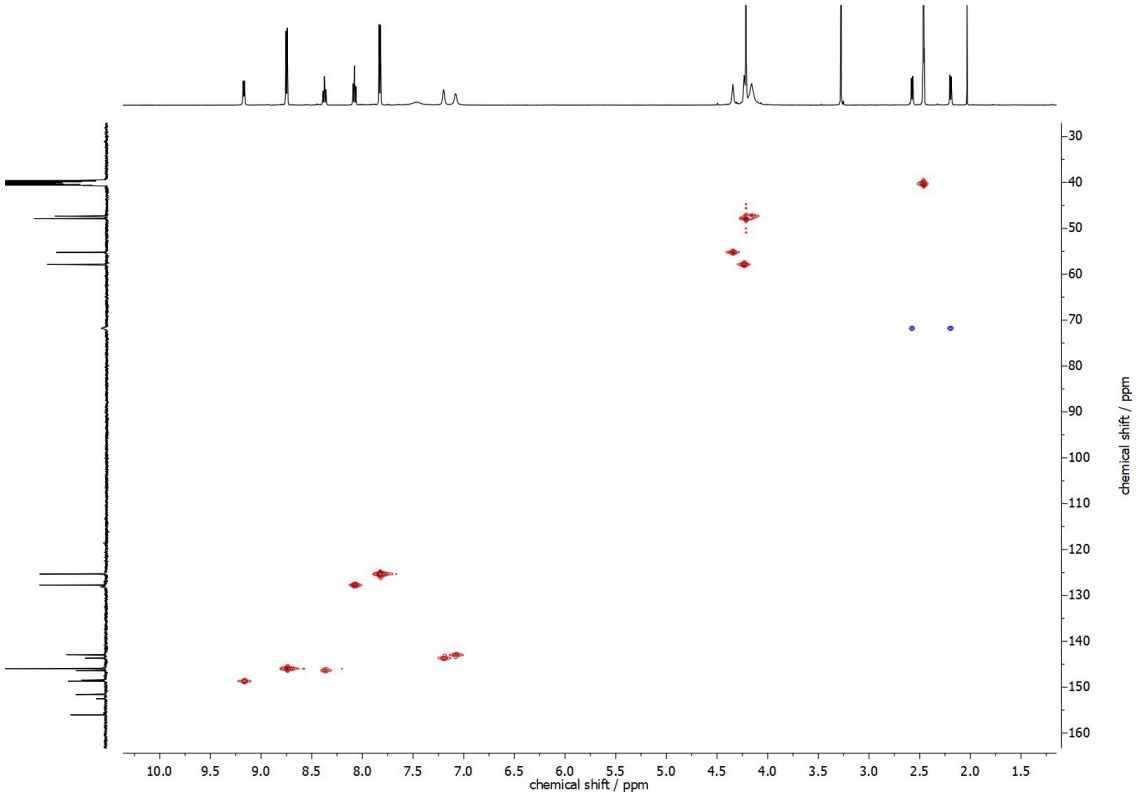


Figure S37. HSQC NMR spectrum (500 MHz) of **3i** in DMSO-d_6.

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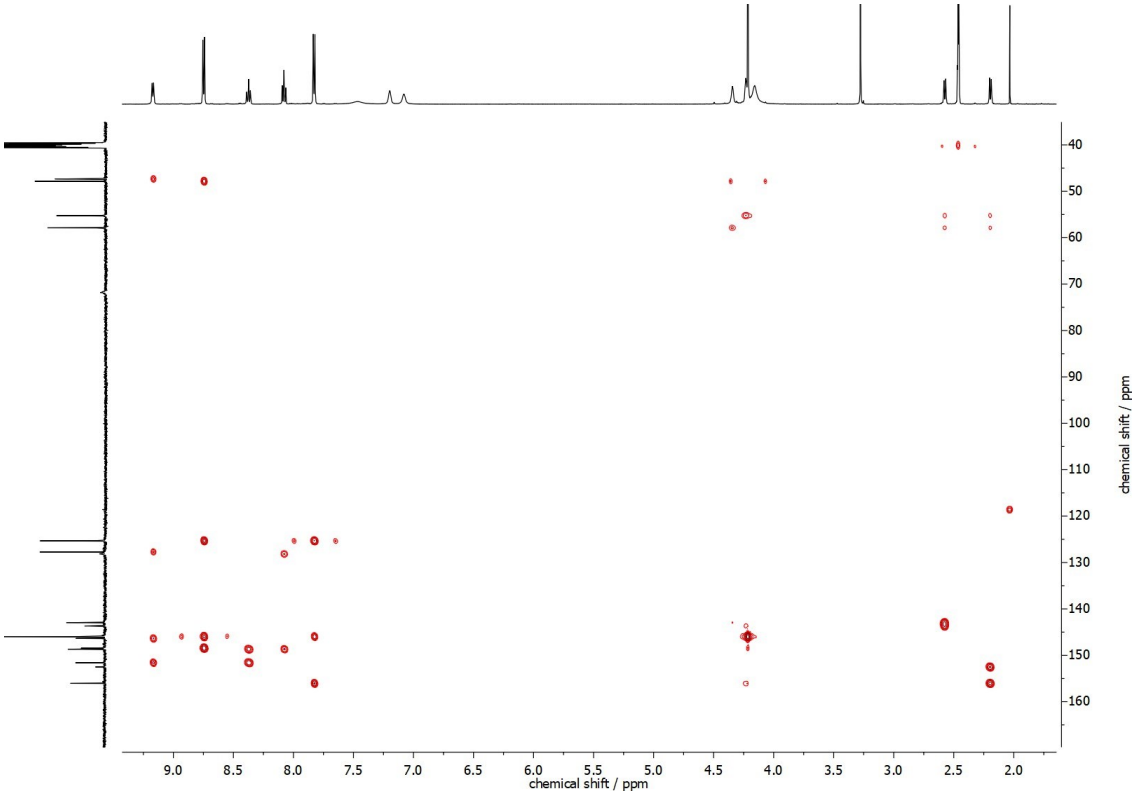


Figure S38. HMBC NMR spectrum (500 MHz) of **3i** in DMSO-d_6.

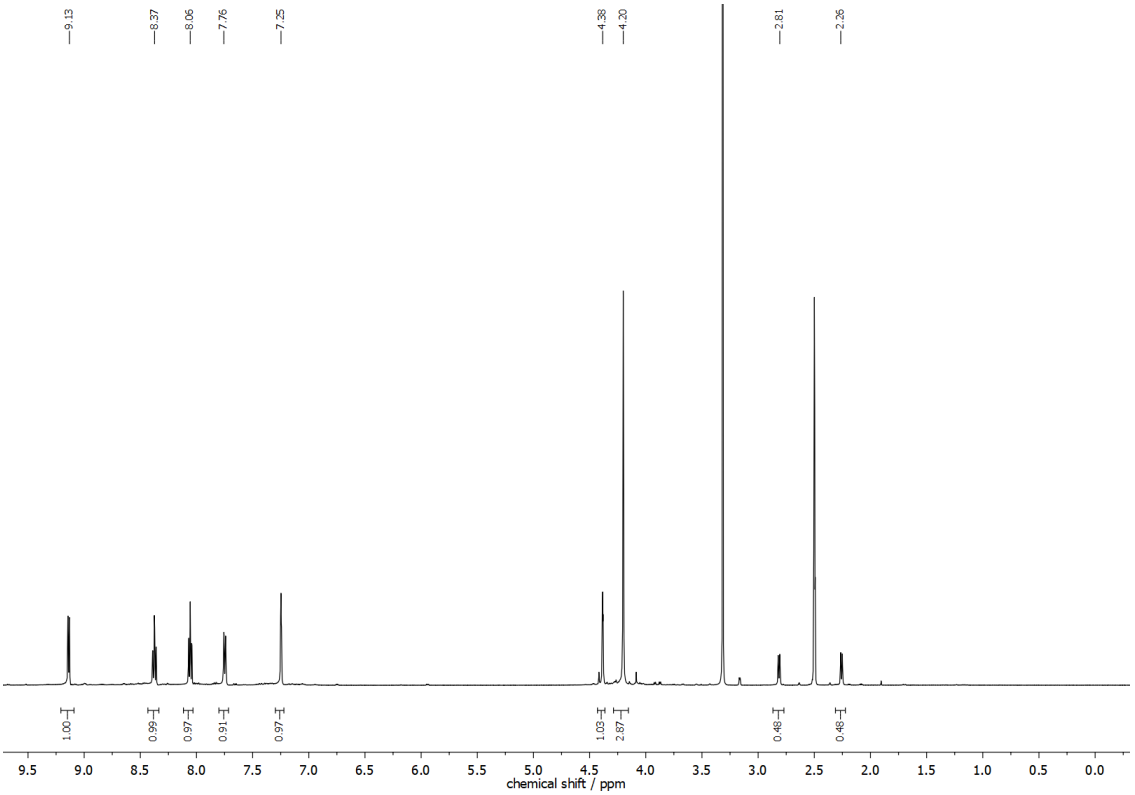


Figure S39. ^{1}H NMR spectrum (500 MHz) of **3g'** in DMSO-d_6.

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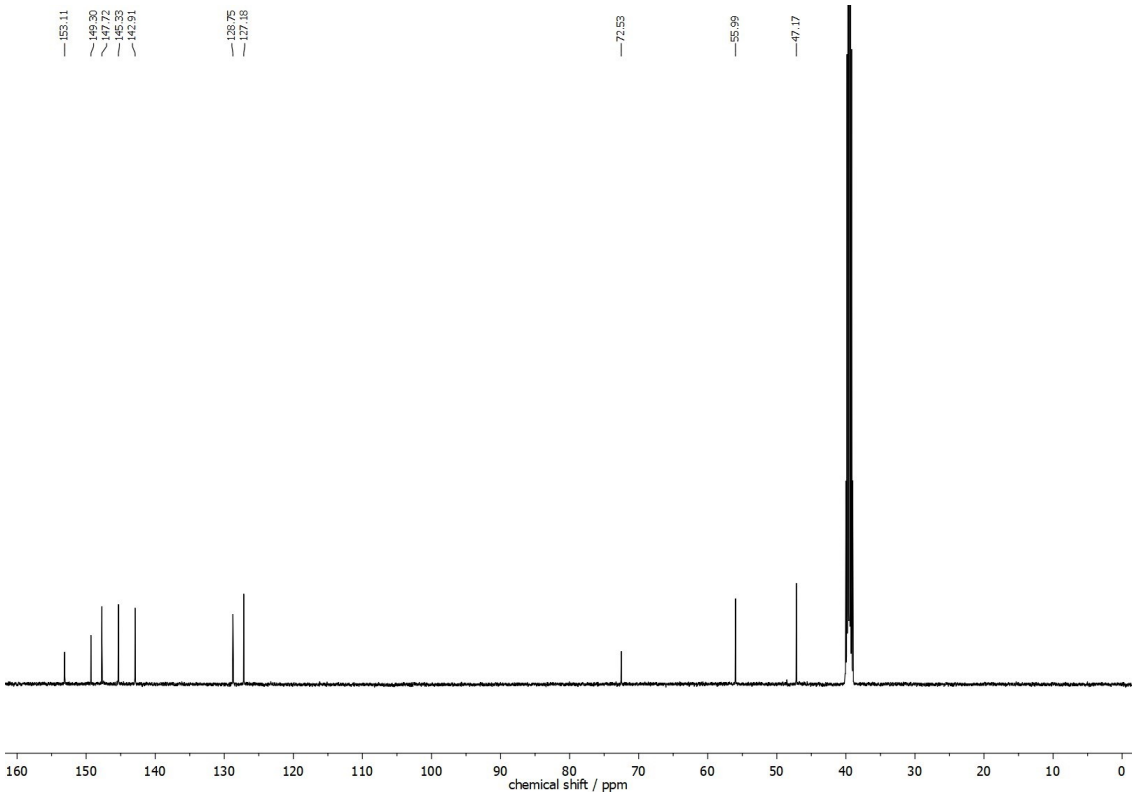


Figure S40. ^{13}C NMR spectrum (125 MHz) of **3g^{I}** in DMSO-d_6.

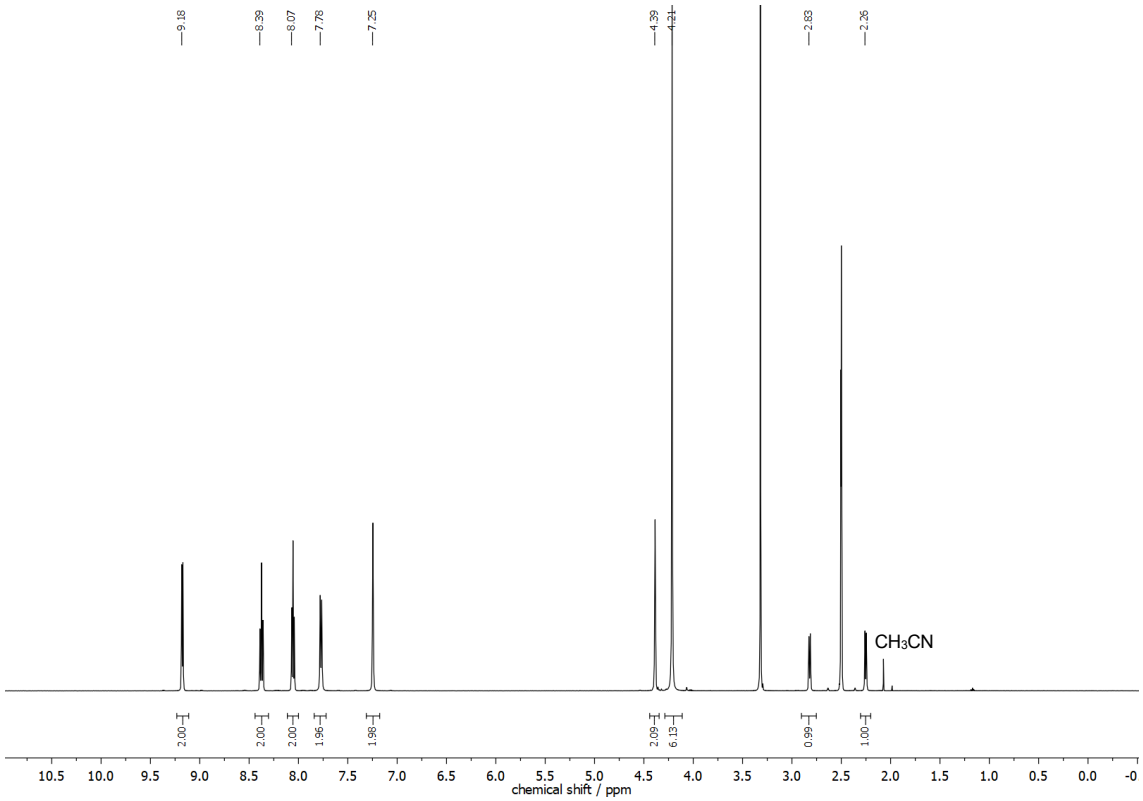


Figure S41. ^{1}H NMR spectrum (500 MHz) of **3g^{Br}** in DMSO-d_6.

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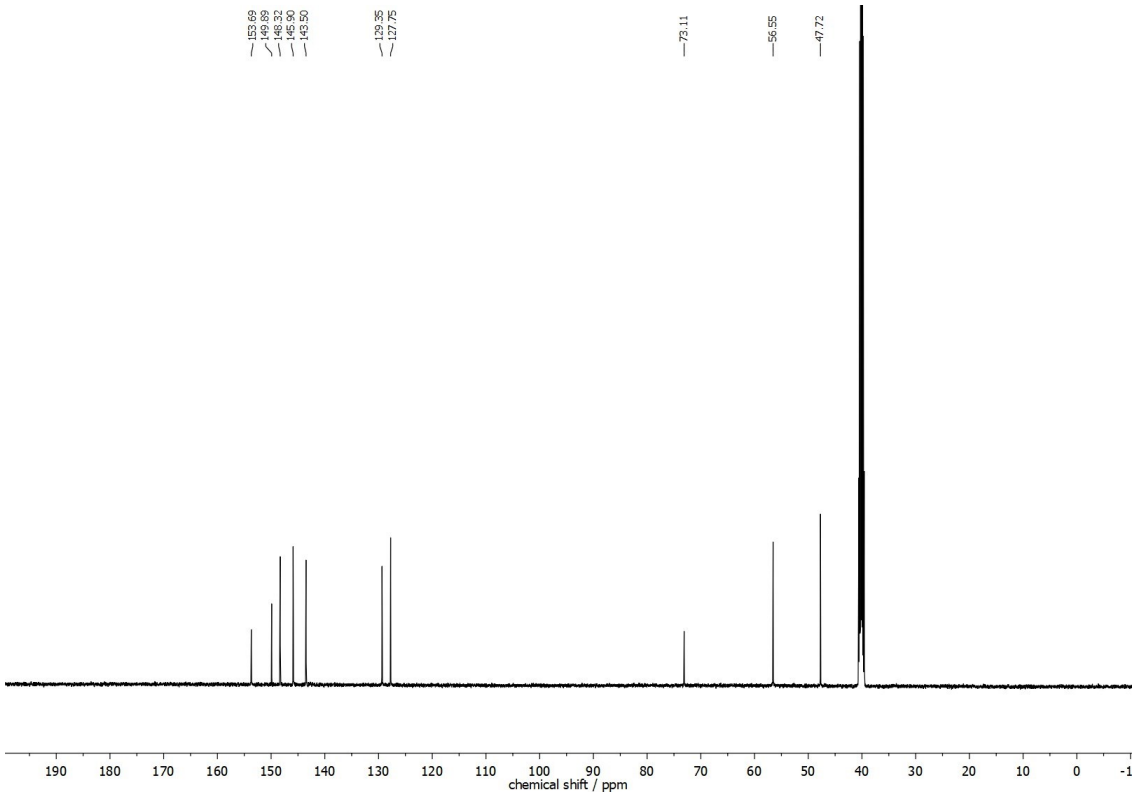


Figure S42. ^{13}C NMR spectrum (500 MHz) of **3g^{Br}** in DMSO-d_6.

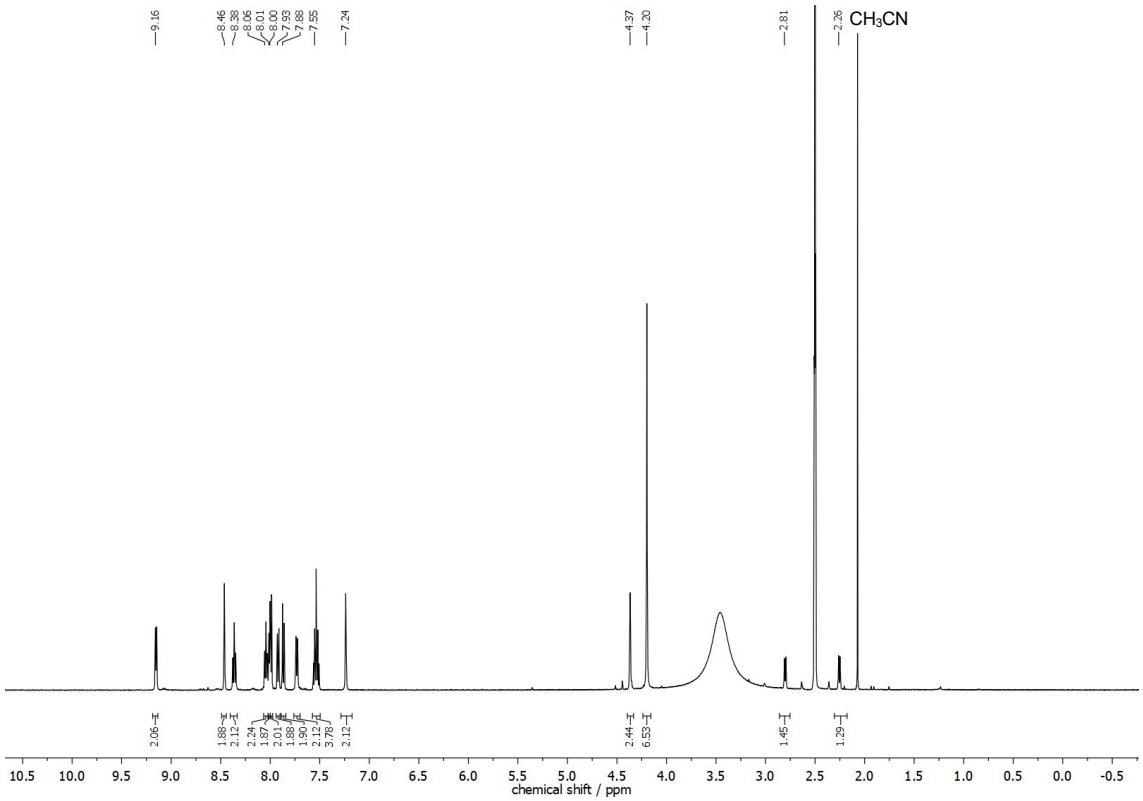


Figure S43. ^{1}H NMR spectrum (500 MHz) of **3g^{Nap}** in DMSO-d_6.

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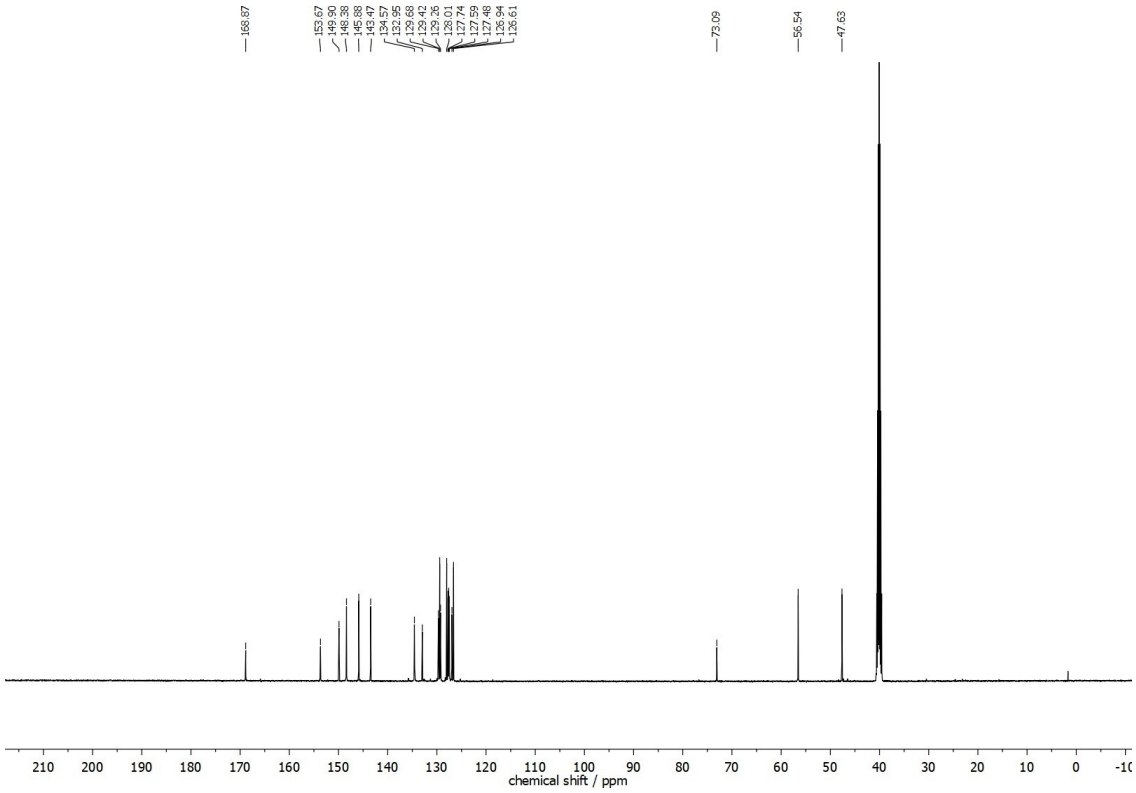


Figure S44. ^{13}C NMR spectrum (125 MHz) of **3g^{Nap}** in DMSO-d_6.

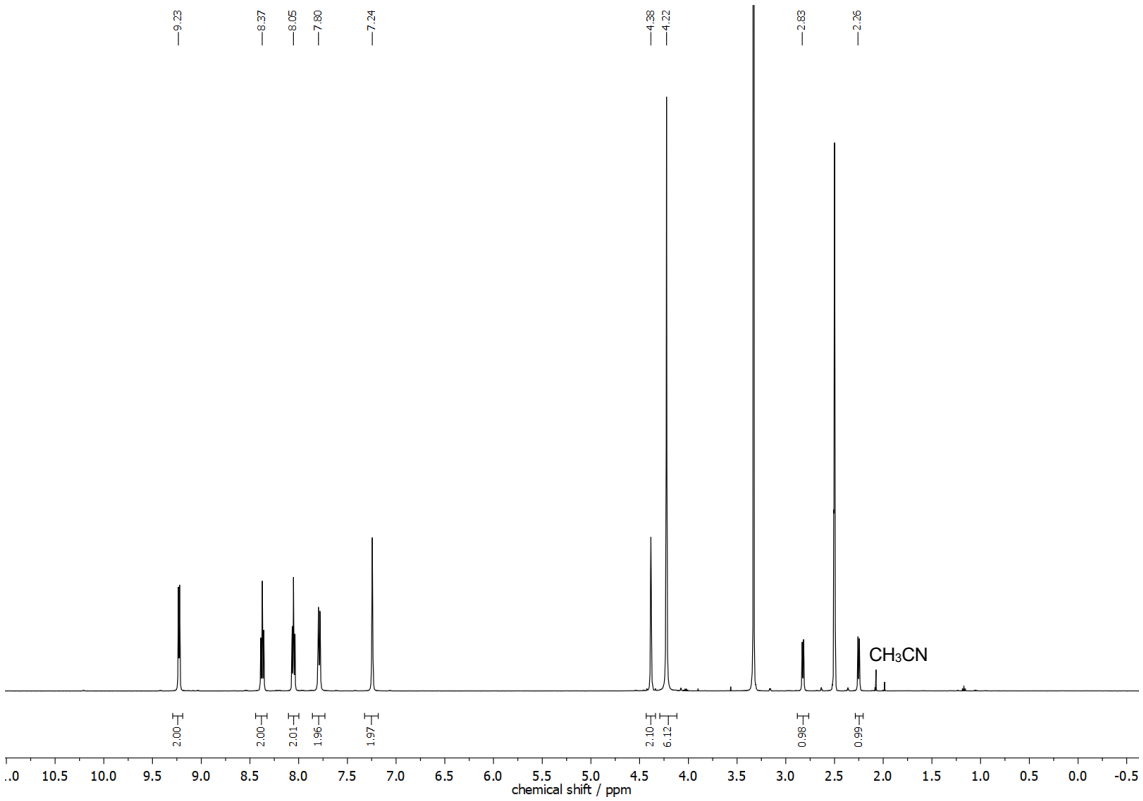


Figure S45. ^{1}H NMR spectrum (500 MHz) of **3g^{Cl}** in DMSO-d_6.

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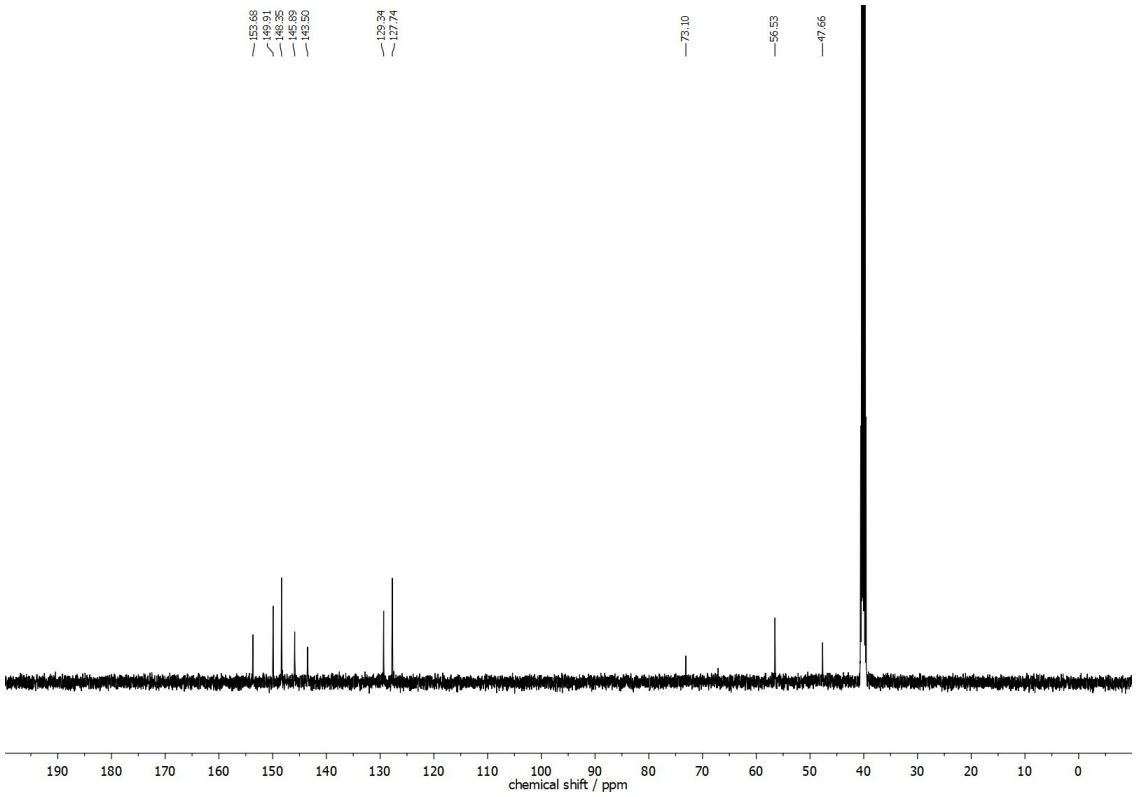


Figure S46. ^{13}C NMR spectrum (125 MHz) of **3g^{Cl}** in DMSO-d_6.

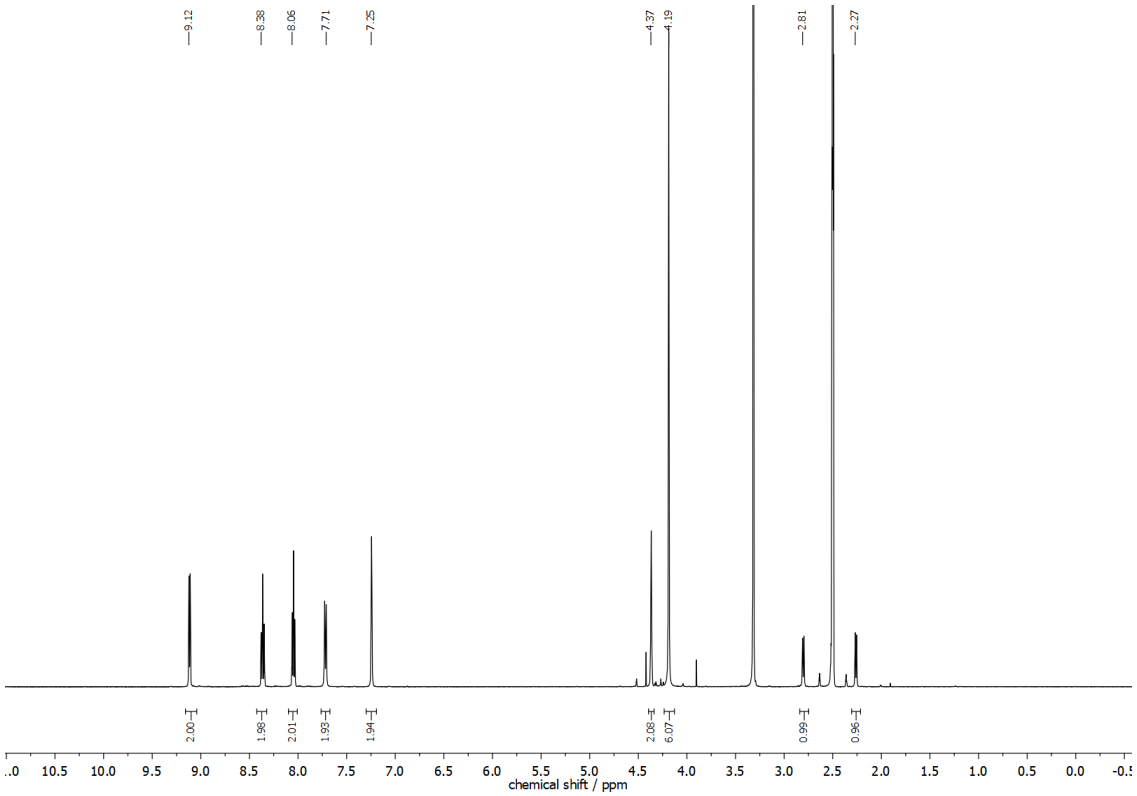


Figure S47. ^{1}H NMR spectrum (500 MHz) of **3g^{PF6}** in DMSO-d_6.

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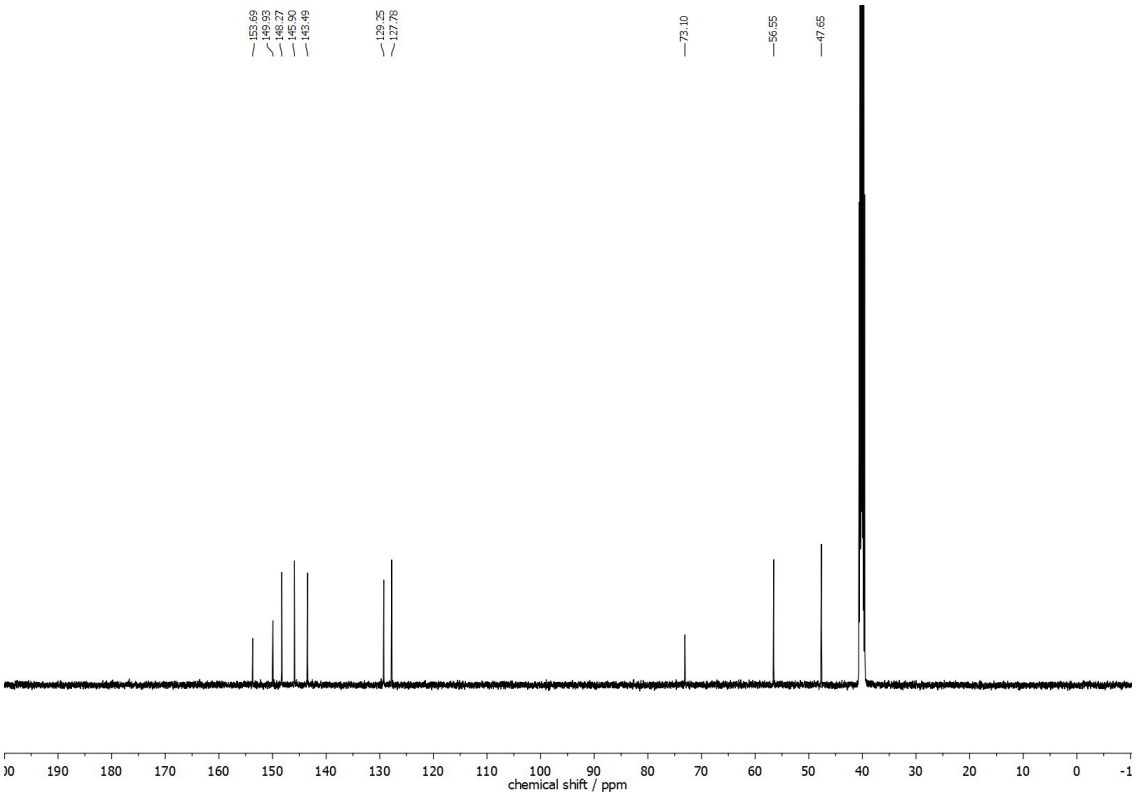


Figure S48. ^{13}C NMR spectrum (125 MHz) of **3g^{PF6}** in DMSO-d_6.

8. NMR-spectroscopic monitoring of the photoreactions

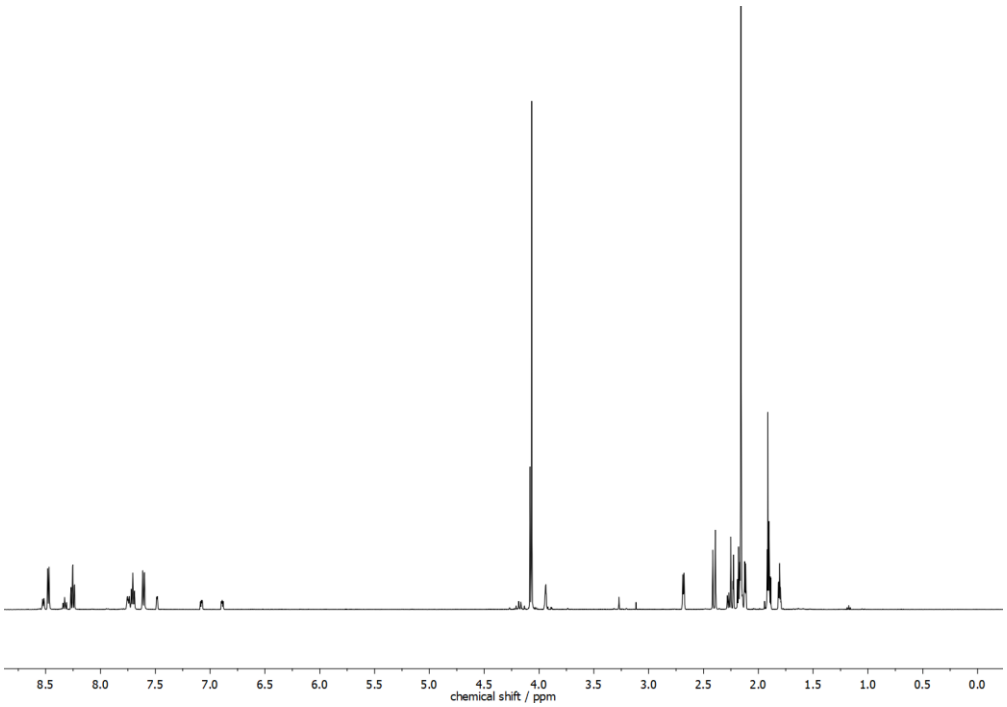


Figure S49. Determination of the photostationary state (PSS) by monitoring the cycloaddition reaction of **3f** (*c* = 11 mM) in MeCN-*d*3 upon irradiation with Thorlabs M340L5 (λex = 340 nm) with ^{1}H NMR spectroscopy (500 MHz).

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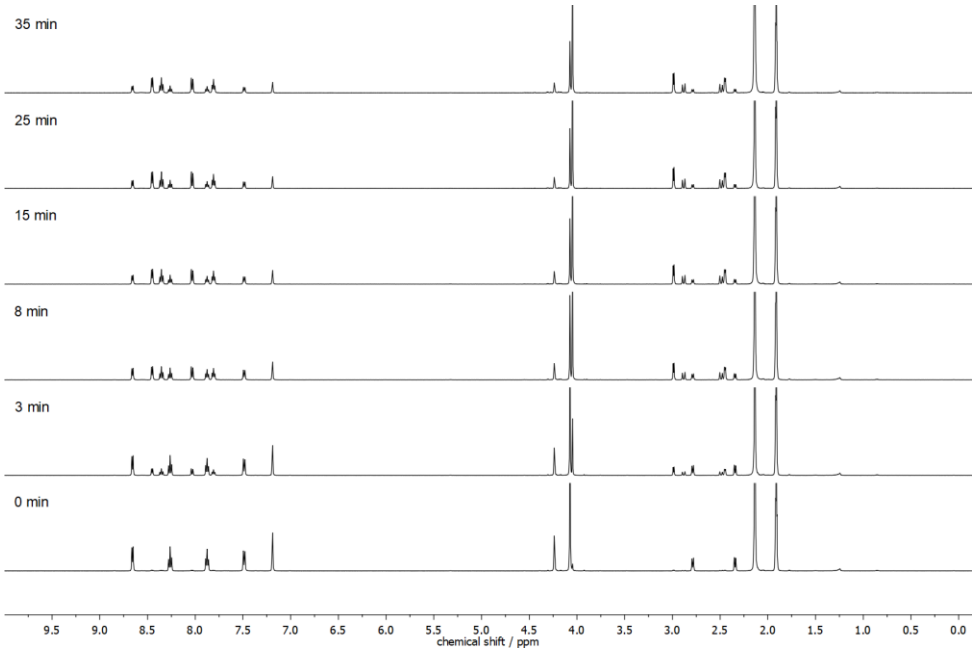


Figure S50. Determination of the photostationary state (PSS) by monitoring the cycloaddition reaction of **3g** (*c* = 10 mM) in MeCN-*d*3 upon irradiation with Thorlabs M340L5 (*λ*ex = 340 nm) with ^{1}H NMR spectroscopy (500 MHz).

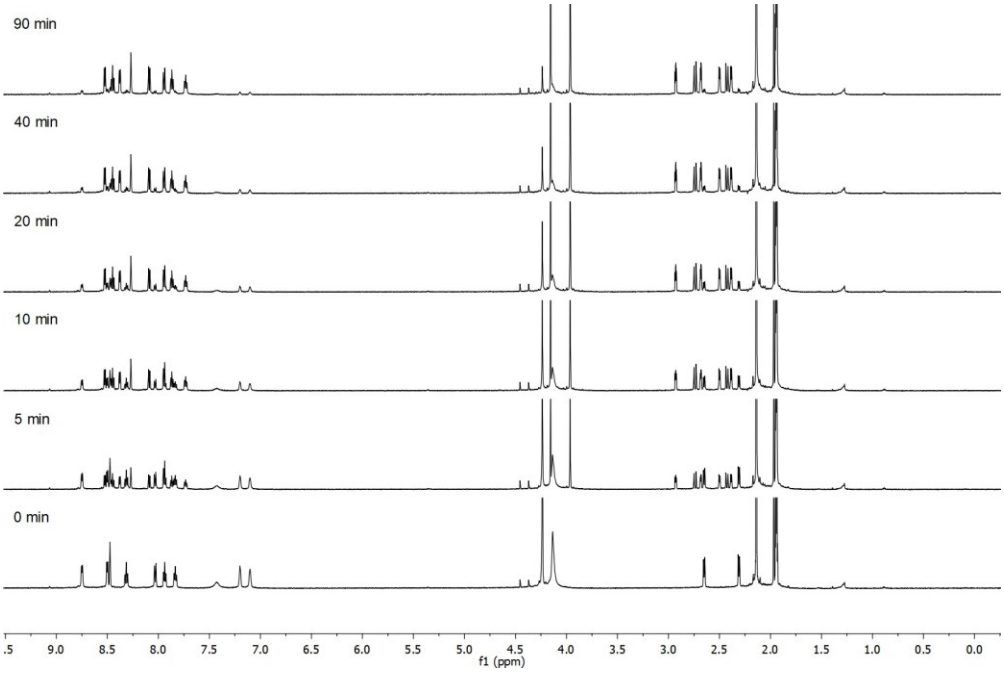


Figure S51. In situ ^{1}H NMR-spectroscopic analysis (600 MHz) of the photoreaction of **3h** (10 mM) in MeCN-*d*3 at different irradiation times (*λ*ex = 365 nm, 1 mW). Spectra were recorded in intervals of 1 min, only selected spectra are shown.

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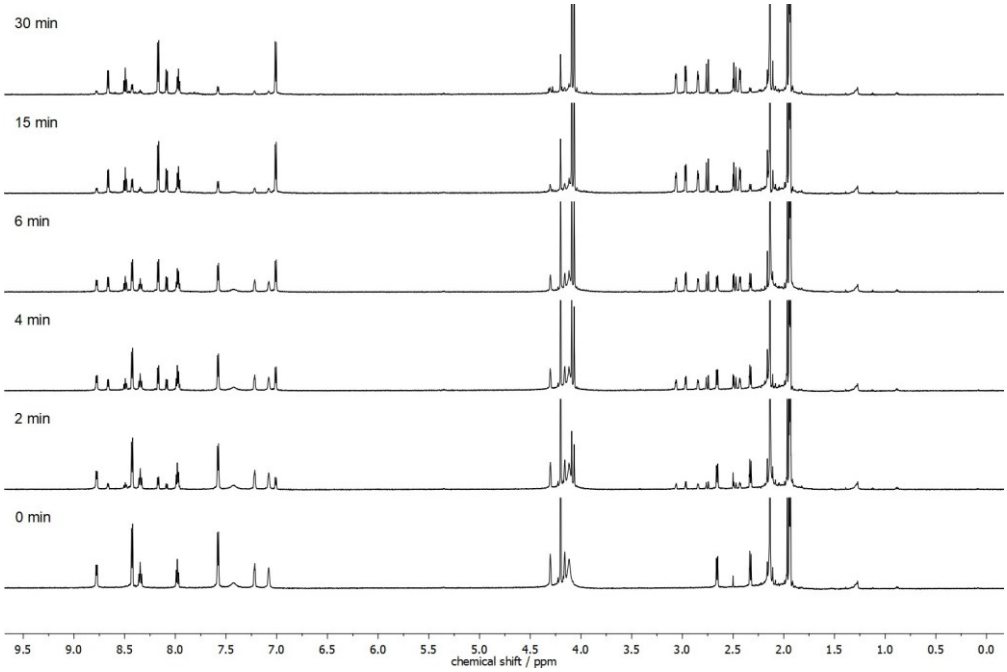


Figure S52. In situ ^{1}H NMR-spectroscopic analysis (600 MHz) of the photoreaction of **3i** (10 mM) in MeCN-*d*3 at different irradiation times (*λ*ex = 365 nm, 1 mW). Spectra were recorded in intervals of 1 min, only selected spectra are shown.

9. References

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