Electronic Supplementary Information (ESI) for

Dialkylamino and trialkylammonium groups in close proximity: intra- and intermolecular ways of formation, structural consequences, and properties. A case of metal-free directed ortho alkylation

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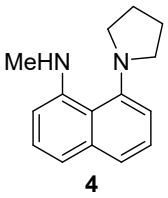
Experimental Data

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 (250 MHz) spectrometer with the solvent residual peaks as the internal standard (Scientific and Educational Laboratory of Resonance Spectroscopy, Department of Natural and High Molecular Compounds Chemistry of Southern Federal University). In some cases, a Bruker Avance 600 (600 MHz) and Varian Unity-300 (300 MHz) spectrometers were used. The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source; methanol was used as the solvent (Chemical Analysis and Materials Research Centre, St. Petersburg State University). The instrument was operated in positive mode using an *m*/*z* range of 50–1200. The capillary voltage of the ion source was set at 4000 V. The nebulizer gas pressure was 1.0 bar, and the drying gas flow was set to 4.0 L/min. The progress of reactions and the purity of products were monitored by TLC (Merck silica gel 60 F254); development with iodine vapor or UV-light. Products were purified by chromatography on silica gel (230−400 mesh, grade 60) or Al_2O_3 (Brockmann activity III). The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods.

1-Methylamino-8-(pyrrolidin-1-yl)naphthalene (4)



4

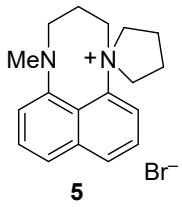
A mixture of 1-dimethylamino-8-(pyrrolidin-1-yl)naphthalene (**3**)[S1] (112 mg, 0.47 mmol), KI (390 mg, 2.35 mmol) and 37% aqueous HBr (0.08 mL, 0.49 mmol) in DMF (6 mL) was refluxed for 1 h. The resulting mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The solvent was evaporated, and the crude product was purified by column chromatography (silica gel, CH_2Cl_2) to afford **4** (73 mg, 69%) as a colourless solid (its solutions possess blue fluorescence under UV light) with mp 79–81 °C.[S2] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (br s, 1H), 7.48 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.33–7.25 (m, 2H), 7.15 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.41 (br d, *J* = 7.8 Hz, 1H), 3.40–3.35 (m, 2H), 2.94 (br s, 3H), 2.84–2.74 (m, 2H), 2.01–1.96 (m, 4H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 148.14, 147.90, 136.71, 126.83, 125.26, 125.14, 118.99, 114.82 (2C), 102.36, 54.05, 30.28, 24.02. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{19}N_2^+$: 227.1543; found: 227.1549.

Interaction of pyrrolidinonaphthalene 4 with 1,3-dibromopropane

A mixture of compound **4** (46 mg, 0.20 mmol), K_2CO_3 (21 mg, 0.15 mmol) and 1,3-dibromopropane (0.03 mL, 0.30 mmol) in acetonitrile (4 mL) was refluxed for 7 d. The resulting reaction suspension was basified with aqueous KOH and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (4 mL) and filtered. Diethyl ether (9 mL) was added to the concentrated filtrate (1 mL). The precipitate formed was filtered off and washed with Et_2O (2 × 5 mL) to afford **5** (26 mg, 38%). Next, diethyl ether was removed,

and the remaining neutral compounds were separated by column chromatography (silica gel, CH_2Cl_2), after isolation of unreacted **4** (11 mg, 24%), the solvent was changed to ethyl acetate to give **6** (8 mg, 15%).

5-Methyl-2,3,4,5-tetrahydrospiro[naphtho[1,8-*bc*][1,5]diazocine-1,1'-pyrrolidin]-1-ium bromide (5)

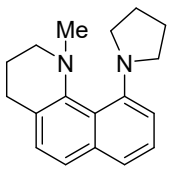


5

Beige solid; mp 168–170 °C (rearranges to **6** on heating; see below). Crystals suitable for XRD analysis were obtained from a 1:1 mixture of CH_2Cl_2/Et_2O. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.10 (br d, *J* = 7.8 Hz, 1H), 7.90 (br d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.58–7.49 (m, 2H), 7.42 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.12–5.00 (m, 2H), 4.74–4.65 (m, 2H), 4.46–4.28 (m, 2H), 3.27–3.15 (m, 1H), 3.05 (s, 3H), 2.79–2.71 (m, 1H), 2.47–2.35 (m, 2H), 2.12–1.99 (m, 2H), 1.90–1.80 (m, 1H), 1.68–1.61 (m, 1H). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 146.1, 137.24, 137.15, 132.6, 127.7, 126.1, 125.1, 125.0, 122.3, 121.0, 72.3, 71.0, 68.7, 57.0, 43.6, 26.4, 22.5, 21.1. HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{18}H_{23}N_2^+$: 267.1861; found: 267.1856.

The conversion of salt **5** (10 mg, 0.03 mmol) to **6** was conducted in a pre-heated silicone oil bath at 170 °C for 10 min. The reaction mixture was then allowed to cool to room temperature, dissolved in ethyl acetate (2 mL), poured into water, and basified with aqueous KOH to pH 10–11. The aqueous layer was additionally extracted with ethyl acetate (2 × 2 mL) to give crude tetrahydrobenzo[*h*]quinoline **6** (7 mg, 88%).

1-Methyl-10-(pyrrolidin-1-yl)-1,2,3,4-tetrahydrobenzo[*h*]quinoline (6)



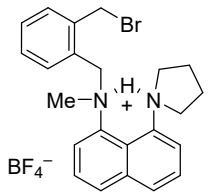
6

Dark beige oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22–7.15 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.80 (dd, *J* = 6.0, 2.7 Hz, 1H), 3.73–3.02 (br m, 5H), 2.91–2.86 (m, 3H), 2.75 (s, 3H), 2.06–1.81 (m, 6H). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 147.0, 144.9, 136.4, 127.4, 124.7, 123.2, 120.1, 119.5, 119.0, 109.9, 52.3, 51.3, 45.3, 29.1, 24.8, 20.0. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{23}N_2^+$: 267.1856; found: 267.1860.

Interaction of pyrrolidinonaphthalene 4 with *o*-xylylene dibromide

A mixture of compound **4** (30 mg, 0.14 mmol), K_2CO_3 (19 mg, 0.14 mmol) and *o*-xylylene dibromide (45 mg, 0.17 mmol) in 1,4-dioxane (4 mL) was stirred and refluxed for 15 hrs. The resulting mixture was poured into water (15 mL), basified with aqueous KOH to pH 10–11 and extracted with ethyl acetate (3 × 6 mL). The solvent was evaporated, and the crude product was purified by column chromatography (silica gel, CH_2Cl_2, after isolation of mobile precursors, the solvent was changed to ethyl acetate). TLC plate showed only one spot, but NMR and ESI-MS spectra indicated the presence of two compounds, salt **9** and bromide **10** (See Figs. S9–S10).

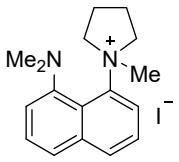
_N_-(2-(Bromomethyl)benzyl)-_N_-methyl-8-(pyrrolidin-1-yl)naphthalen-1-amine hydrogen tetrafluoroborate (11)



11

The isolated mixture of **9** and **10** (20 mg) was treated with 40% aqueous HBF_4 (0.01 mL, 0.06 mmol, 1.2 equiv) in a minimum volume of acetonitrile (0.4 mL). The solvent was removed, and the oily residue was washed with Et_2O (2 × 5 mL) to afford salt **11** (20 mg, 83%) as colourless oil. ^{1}H NMR (250 MHz, CD_3CN): δ = 19.96 (br s, 1H), 7.80–7.76 (m, 4H), 7.61–7.54 (m, 2H), 7.01–6.89 (m, 4H), 5.10–5.00 (m, 2H), 4.30–4.17 (m, 2H), 3.77–3.68 (m, 2H), 3.46–3.40 (m, 2H), 3.33 (d, *J* = 2.7 Hz, 3H), 1.91–1.83 (m, 2H), 1.79–1.51 (m, 2H). ^{13}C{^{1}H} NMR (62.9 MHz, CD_3CN): δ = 141.7, 139.3, 134.2, 133.4, 133.2, 131.9 (2C), 129.23, 129.20, 128.7, 128.6, 126.9, 126.8, 124.3, 121.7, 121.5, 63.5, 62.5, 53.9, 41.4, 33.2, 29.8, 25.5.

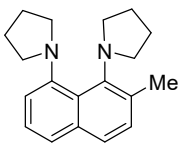
1-(8-(Dimethylamino)naphthalen-1-yl)-1-methylpyrrolidin-1-ium iodide (14)



14

Iodomethane was added (0.24 mL, 3.80 mmol) to a solution of 1-dimethylamino-8-(pyrrolidin-1-yl)naphthalene (**3**)[S1] (91 mg, 0.38 mmol) in acetonitrile (4 mL). The reaction mixture was kept tightly closed for 21 d at room temperature. The resulting solution was treated with aqueous 10% KOH (0.2 mL) and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (4 mL) and filtered. The solvent was removed, and the crude product was washed with diethyl ether (2 × 5 mL). Further purification was carried out by dissolving iodide **14** in CH_2Cl_2 (1 mL) and addition of diethyl ether (8 mL). The precipitate formed was washed with Et_2O (2 × 8 mL) to afford **14** (19 mg, 13%) as a beige solid with mp 134–136 °C (quantitatively decomp. to **3** on melting). Crystals suitable for XRD analysis were obtained from a 1:1 mixture of CH_2Cl_2/Et_2O. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.55 (br d, *J* = 7.8 Hz, 1H), 7.87 (br d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.62–7.50 (m, 3H), 5.36–5.26 (m, 2H), 4.27 (s, 3H), 3.85–3.73 (m, 2H), 2.66 (s, 6H), 2.51–2.39 (m, 2H), 2.16–2.05 (m, 2H). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 149.9, 144.1, 137.5, 131.6, 127.3, 127.1, 125.6, 124.8, 122.8, 121.5, 70.1, 54.0, 46.8, 21.8. HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{17}H_{23}N_2^+$: 255.1856; found: 255.1856.

1,1'-(2-Methylnaphthalene-1,8-diyl)dipyrrolidine (17)

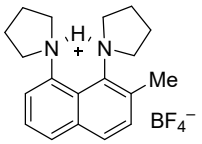


17

Iodomethane (0.19 mL, 3.00 mmol) was added to dipyrrolidinonaphthalene **15**[S3] (40 mg, 0.15 mmol) and K_2CO_3 (21 mg, 0.15 mmol) in acetonitrile (5 mL). The reaction mixture was stirred in inert atmosphere for 10 d at 50 °C. The resulting mixture was poured into water (20 mL), basified with aqueous KOH to pH 10–11 and extracted with CH_2Cl_2 (3 × 7 mL). The solvent was evaporated, and the crude product was purified by column chromatography (Al_2O_3, CH_2Cl_2), after isolation of dipyrrolidinonaphthalene **15** (6 mg, 15%), the solvent was changed to ethyl acetate to give **17** (35 mg, 83%) as a beige solid with mp 40–42 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ

= 7.43–7.36 (m, 2H), 7.26–7.21 (m, 2H), 7.04 (br d, *J* = 7.3 Hz, 1H), 3.44–3.39 (m, 4H), 3.13–2.90 (br m, 4H), 2.41 (s, 3H), 1.98–1.90 (m, 8H). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ = 148.2, 142.6, 135.9, 131.7, 130.3, 125.7, 124.6, 123.4, 122.4, 112.9, 53.1, 51.2, 26.5, 24.3, 20.7. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{25}N_2^+$: 281.2012; found: 281.2012.

1,1'-(2-Methylnaphthalene-1,8-diyl)dipyrrolidine hydrogen tetrafluoroborate (18b)



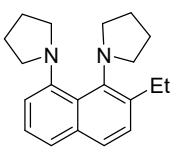
18b

Compound **17** (30 mg, 0.11 mmol) was treated with 40% aqueous HBF_4 (0.02 mL, 0.12 mmol, 1.1 equiv) in a minimum volume of acetonitrile (0.4 mL) followed by 3-fold dilution with Et_2O. The residue formed was washed with Et_2O and vacuum-dried to give **18b** (33 mg, 80%) as a beige solid with mp 214–216 °C (from EtOH). Crystals suitable for XRD analysis were obtained from CH_2Cl_2. ^1H NMR (250 MHz, CD_3CN): δ = 19.80 (br s, 1H), 8.01–7.94 (m, 2H), 7.84 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H) 3.87–3.77 (m, 2H), 3.69–3.55 (m, 4H), 3.50–3.37 (m, 2H), 2.59 (s, 3H), 2.45–2.33 (m, 4H), 2.24–2.12 (m, 4H). $^{13}C\{^1H\}$ NMR (62.9 MHz, CD_3CN): δ = 141.0, 136.6, 134.4, 133.9, 132.0, 129.3, 129.2, 126.4, 122.8, 122.6, 58.9, 54.0, 25.7, 24.2, 18.8.

Interaction of dipyrrolidinonaphthalene 15 with iodoethane

Iodoethane (1 mL, 12.40 mmol) was added to dipyrrolidinonaphthalene **15** [S3] (115 mg, 0.43 mmol) and K_2CO_3 (59 mg, 0.43 mmol) in acetonitrile (7 mL). The reaction mixture was refluxed for 4 d. The resulting mixture was poured into water (30 mL), basified with aqueous KOH to pH 10–11 and extracted with CH_2Cl_2 (3 × 10 mL). The solvent was evaporated, and the crude products were purified by column chromatography (Al_2O_3, CH_2Cl_2), after isolation of starting compound **15** (38 mg, 33%) and *para*-ethylated product **20** (18 mg, 14%), the solvent was changed to ethyl acetate to give *ortho*-isomer **19** (48 mg, 38%).

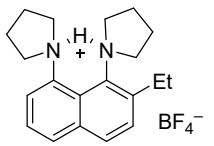
1,1'-(2-Ethylnaphthalene-1,8-diyl)dipyrrolidine (19)



19

Beige solid; mp 33–35 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.28–7.22 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 3.43–3.36 (m, 4H), 3.21–2.95 (m, 4H), 2.78 (q, *J* = 7.5 Hz, 2H), 2.00–1.89 (m, 8H), 1.24 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ = 148.5, 142.1, 138.0, 135.9, 128.8, 125.5, 124.7, 123.7, 122.4, 113.0, 53.1, 51.8, 26.4 (3C), 24.4, 16.0. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{27}N_2^+$: 295.2169; found: 295.2173.

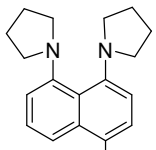
1,1'-(2-Ethylnaphthalene-1,8-diyl)dipyrrolidine hydrogen tetrafluoroborate (19·HBF$_4$)



19·HBF$_4$

Compound **19** (50 mg, 0.17 mmol) was treated with 40% aqueous HBF_4 (0.032 mL, 0.19 mmol, 1.1 equiv) in a minimum volume of acetonitrile (0.8 mL) followed by 3-fold dilution with Et_2O. The residue formed was washed with Et_2O and vacuum-dried to give **19·HBF$_4$** (47 mg, 72%) as a beige solid with mp 222–224 °C (from EtOH). ^{1}H NMR (250 MHz, CD_3CN): δ = 19.81 (br s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.70–7.64 (m, 2H), 3.88–3.67 (m, 4H), 3.55–3.38 (m, 4H), 2.86 (q, *J* = 7.5 Hz, 2H), 2.47–2.37 (m, 4H), 2.27–2.16 (m, 4H), 1.39 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (62.9 MHz, CD_3CN): δ = 141.7, 141.1, 136.7, 134.3, 130.7, 130.1, 129.9, 127.0, 123.3, 123.2, 59.5, 55.9, 26.1, 24.8, 24.7, 15.0.

1,1'-(4-Ethylnaphthalene-1,8-diyl)dipyrrolidine (20)



20

Dark beige oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.32–7.25 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.76 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 3.69–2.70 (m, 10H), 1.93–1.82 (m, 8H), 1.34 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 148.3, 146.4, 135.4, 130.2, 125.3, 124.5, 119.2, 114.5, 108.4, 108.2, 51.2, 51.1, 25.8, 25.0, 24.9, 14.8. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{27}N_2^+$: 295.2169; found: 295.2170.

Spectral Data

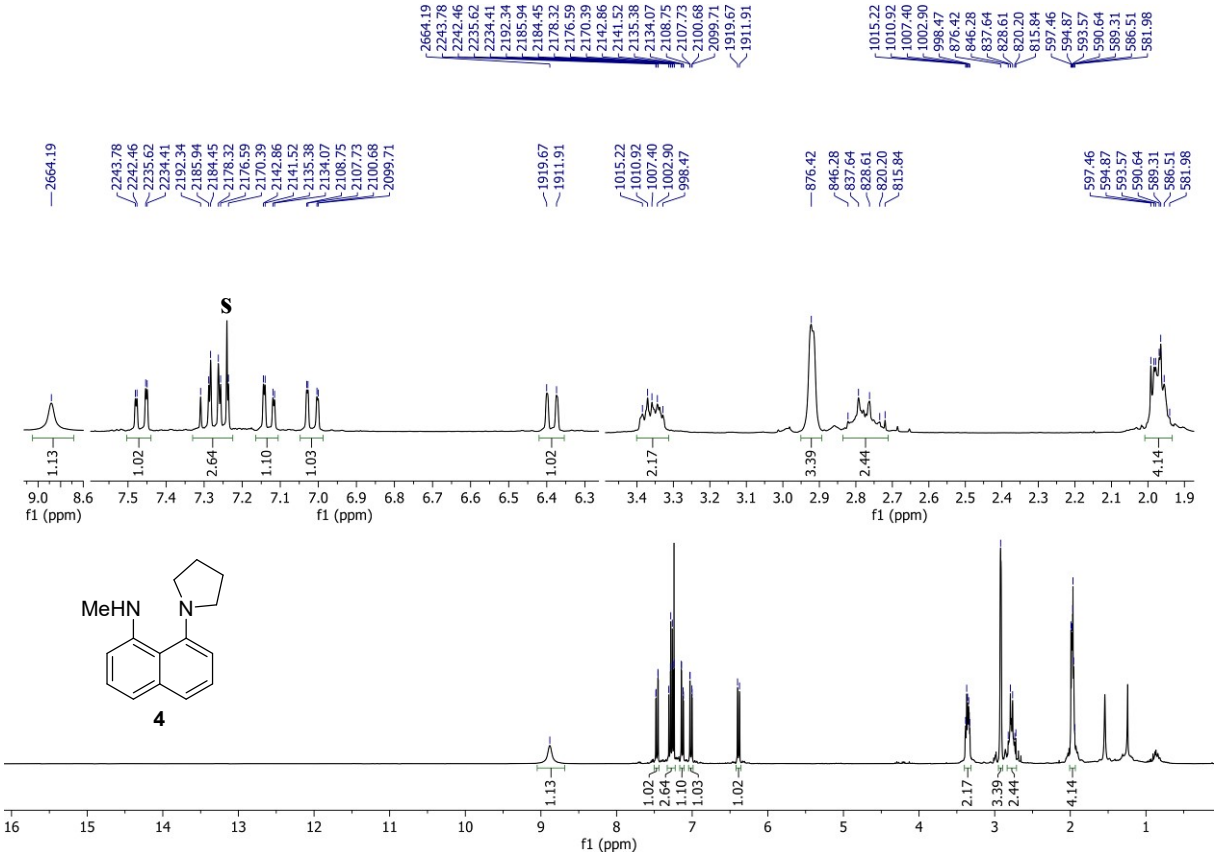


Fig. S1 ^{1}H NMR spectrum of **4** (300 MHz, $CDCl_3$).

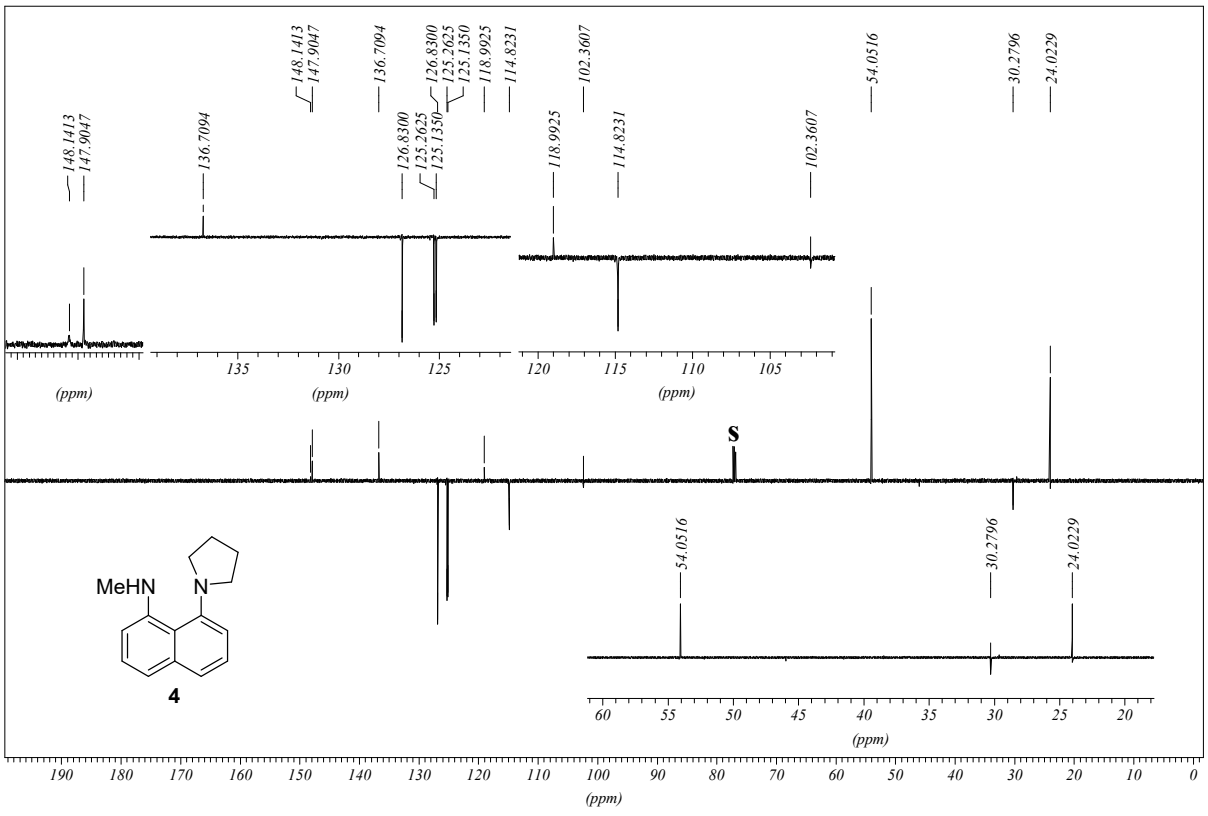


Fig. S2 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4** (150 MHz, $CDCl_3$).

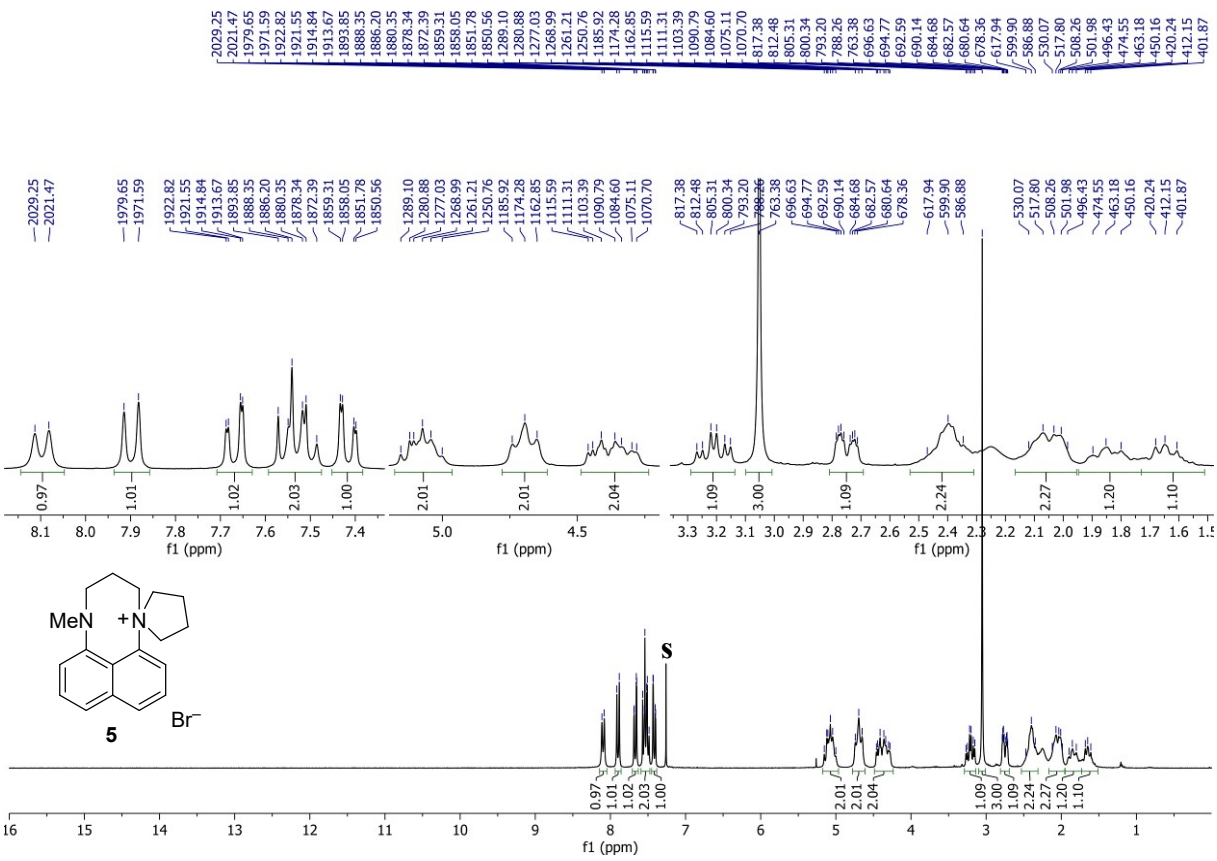


Fig. S3 ^{1}H NMR spectrum of **5** (250 MHz, $CDCl_3$).

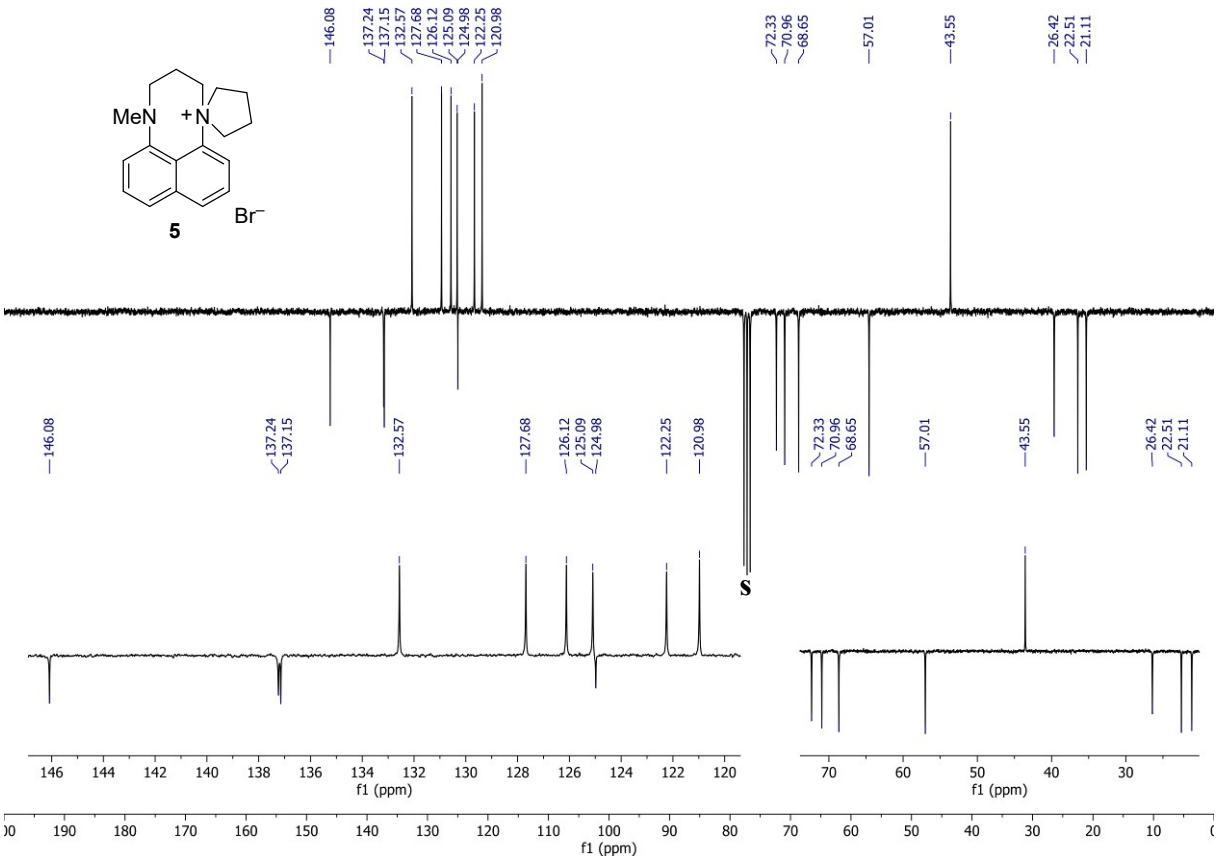


Fig. S4 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **5** (62.9 MHz, $CDCl_3$).

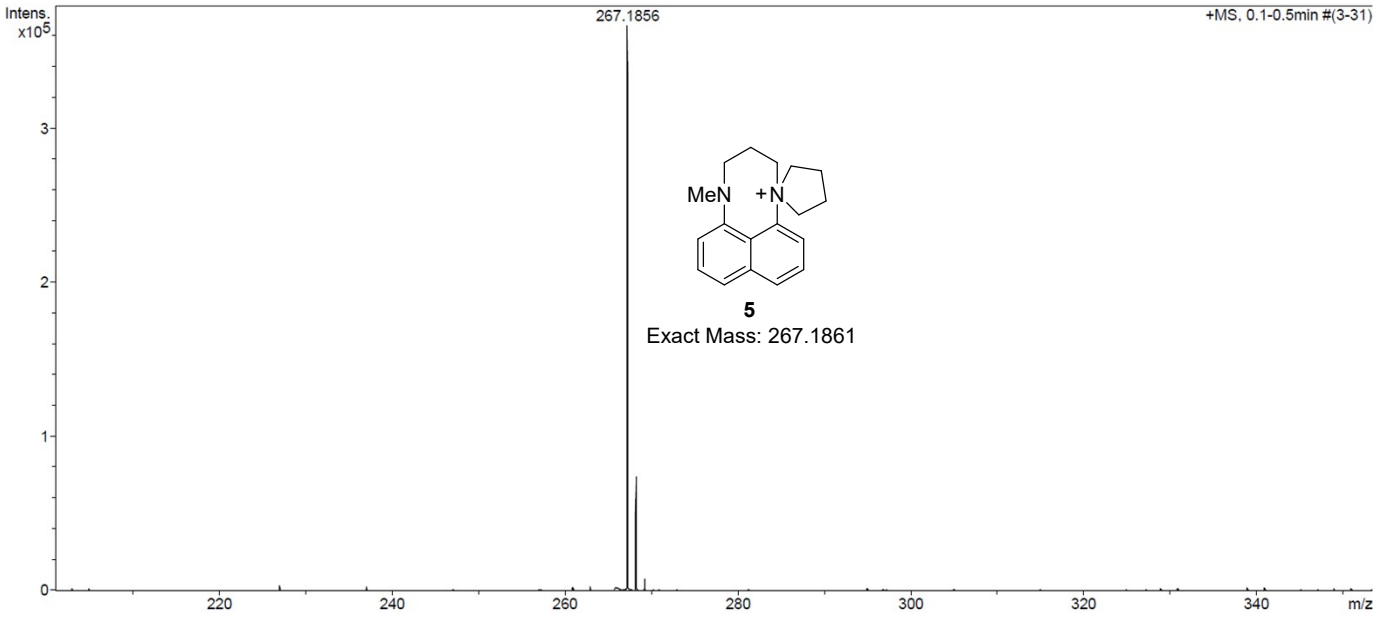


Fig. S5 HRMS (ESI) of **5**.

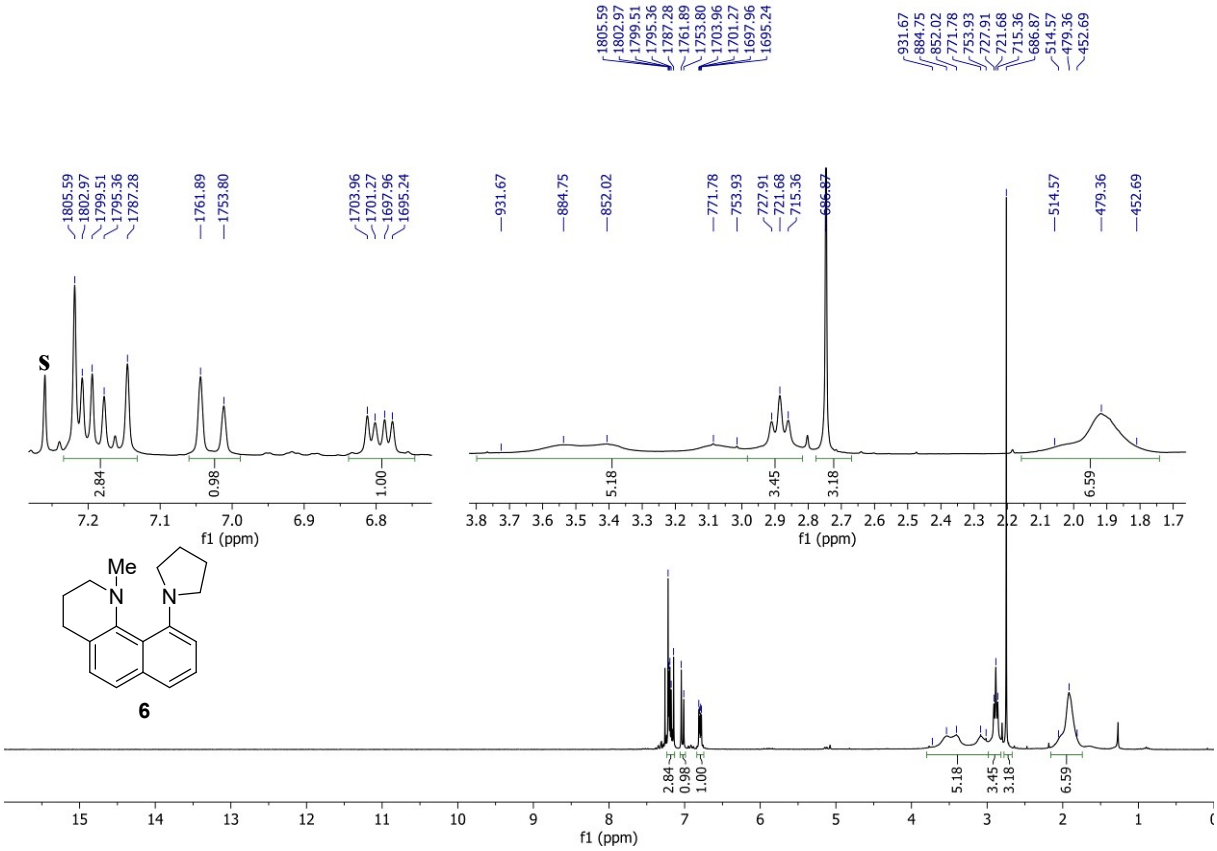


Fig. S6 ^{1}H NMR spectrum of **6** (250 MHz, $CDCl_3$).

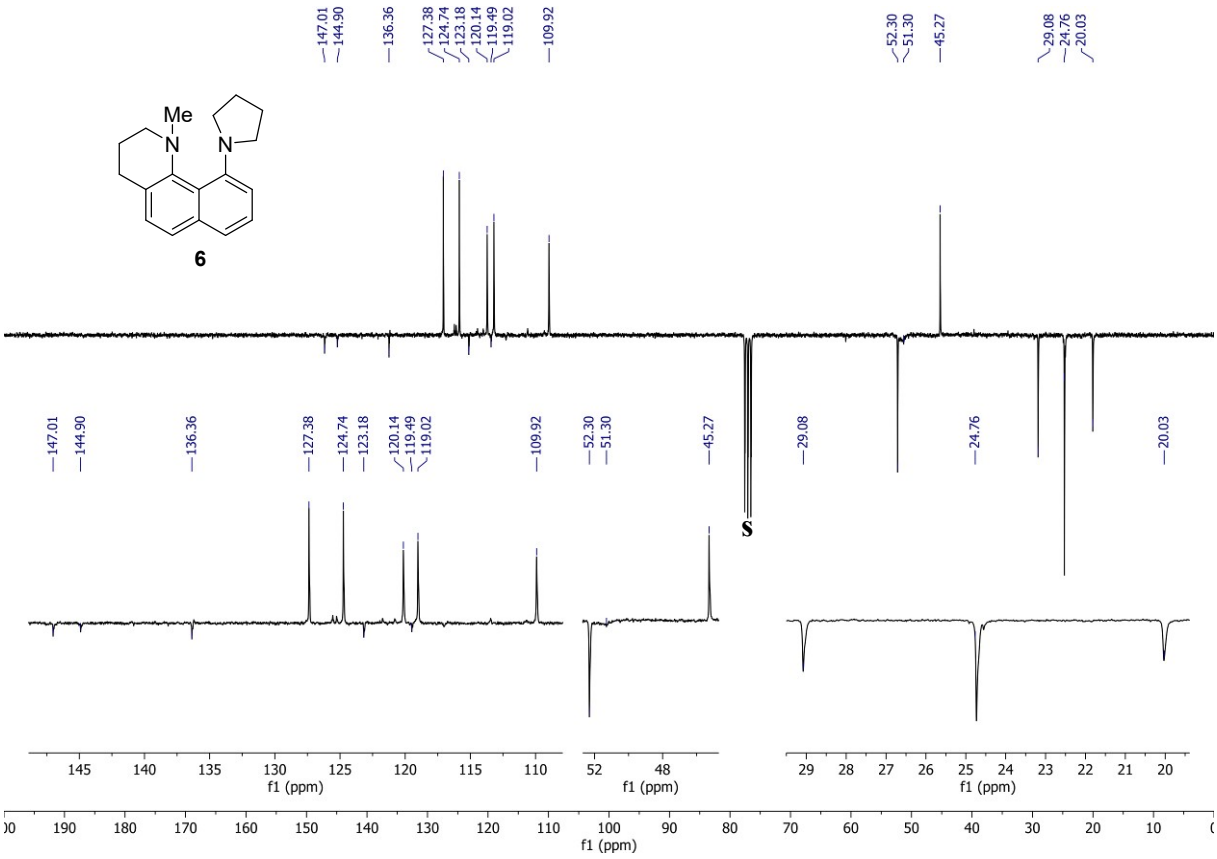


Fig. S7 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **6** (62.9 MHz, $CDCl_3$).

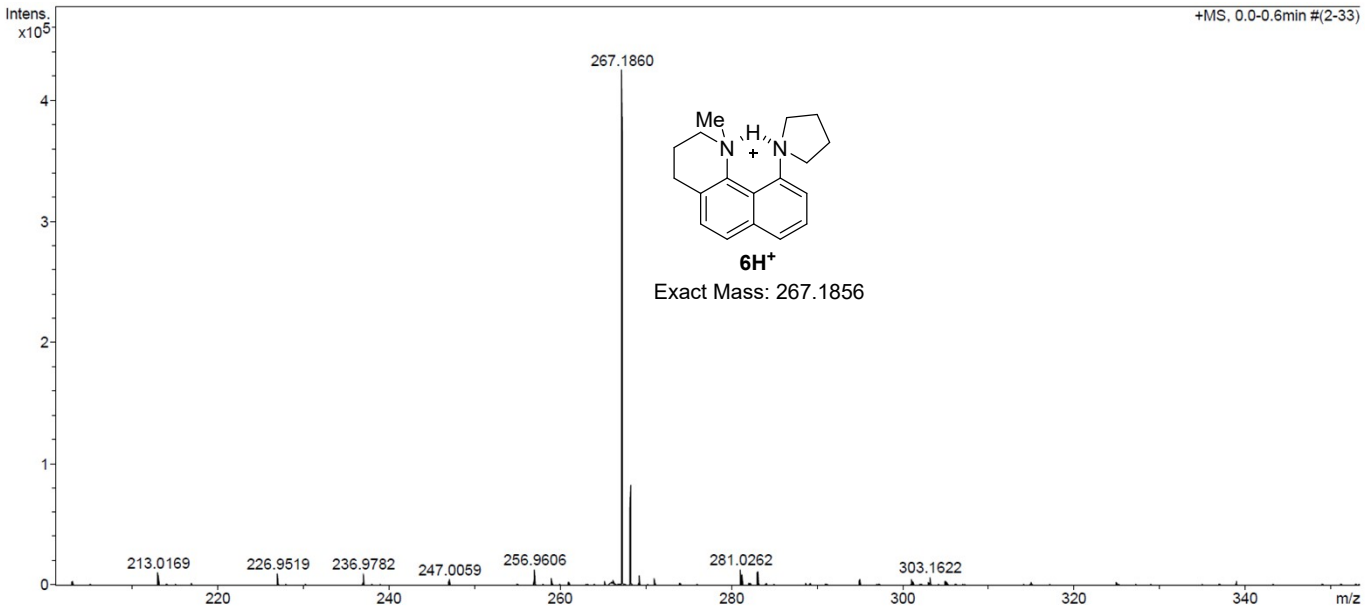


Fig. S8 HRMS (ESI) of **6**.

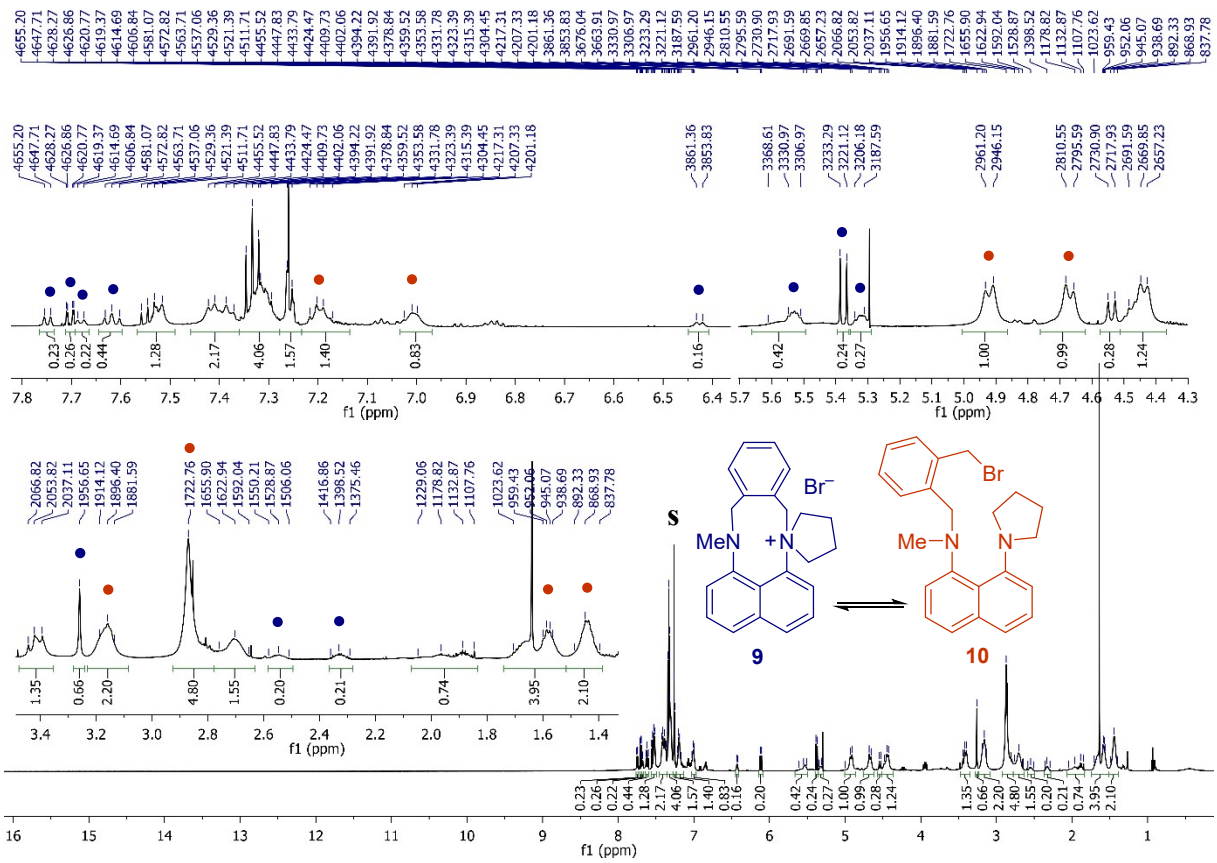


Fig. S9 ^{1}H NMR spectrum of an inseparable mixture of **9** and **10** (600 MHz, $CDCl_3$).

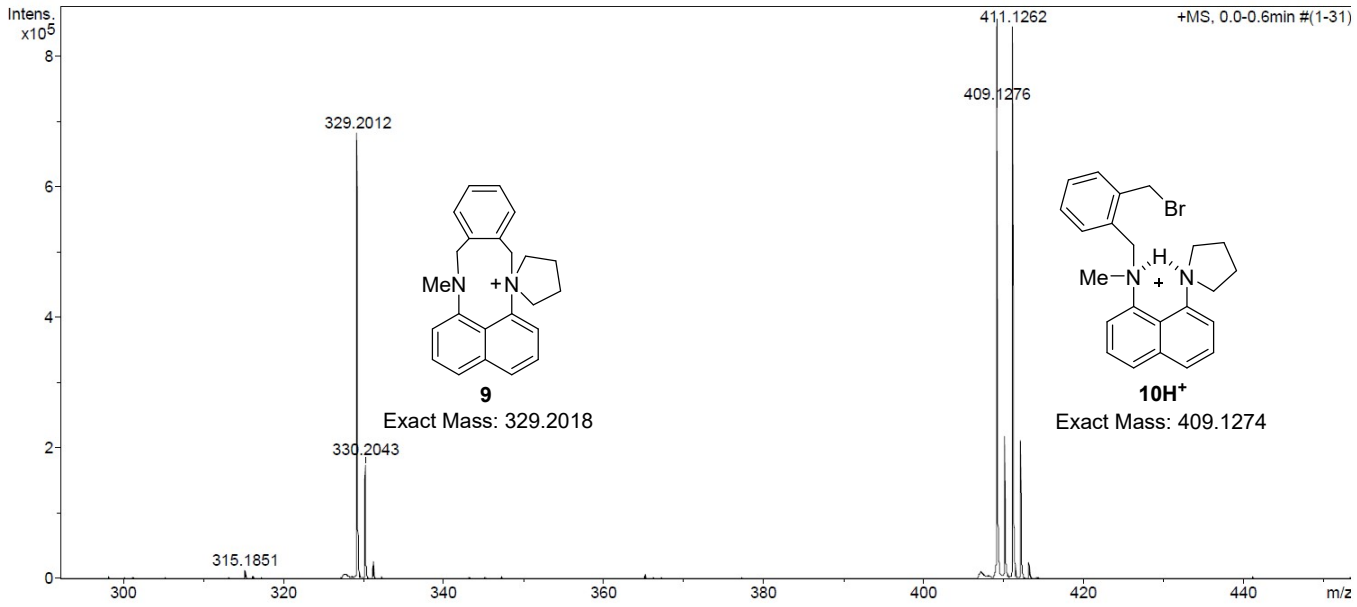


Fig. S10 HRMS (ESI) of a 3:7 mixture of **9** and **10**.

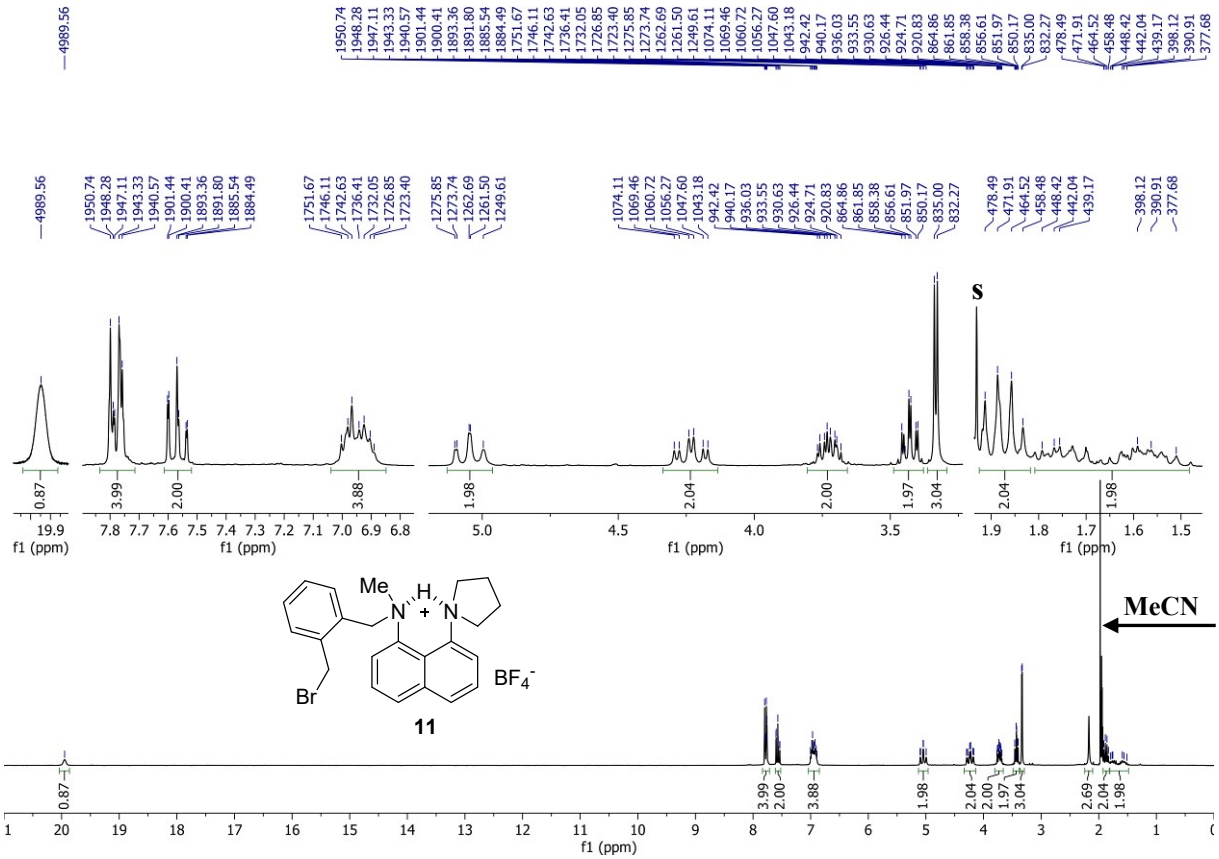


Fig. S11 ^{1}H NMR spectrum of **11** (250 MHz, CD_3CN).

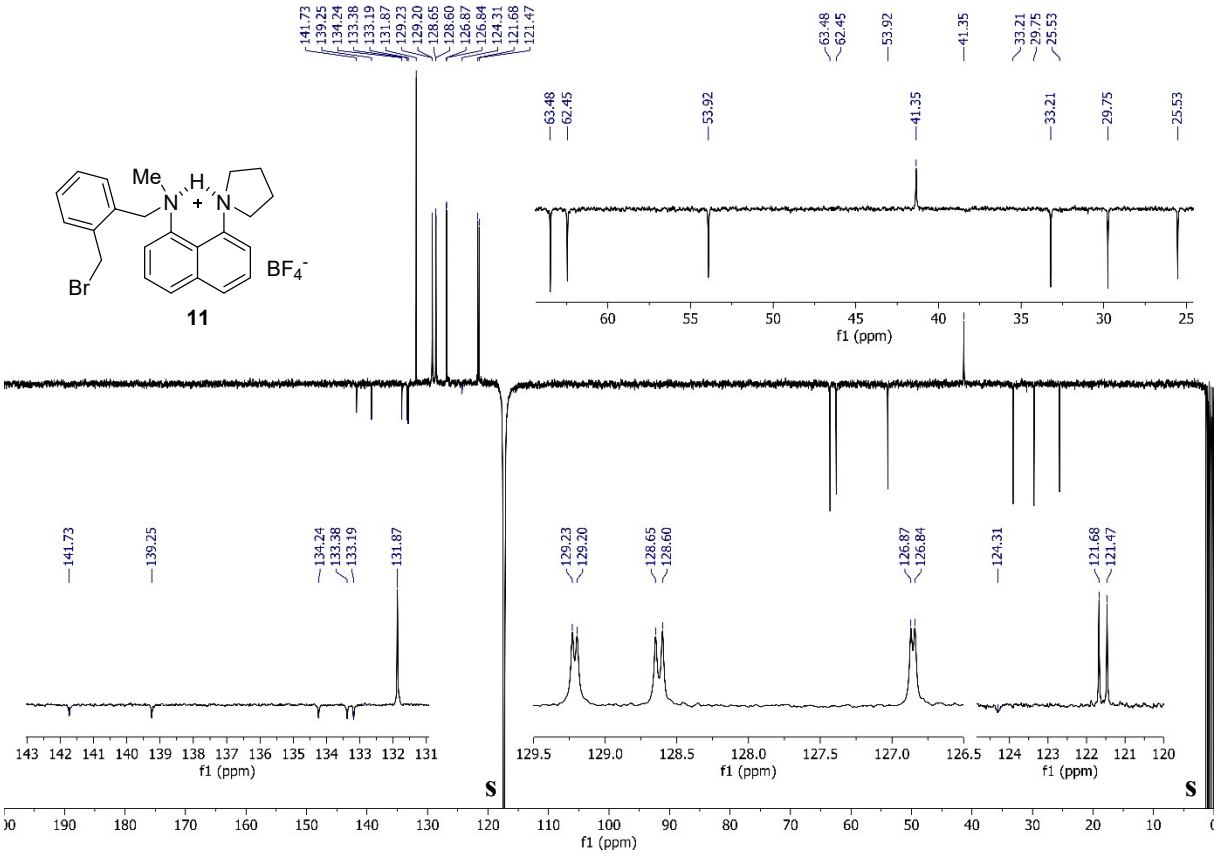


Fig. S12 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **11** (62.9 MHz, CD_3CN).

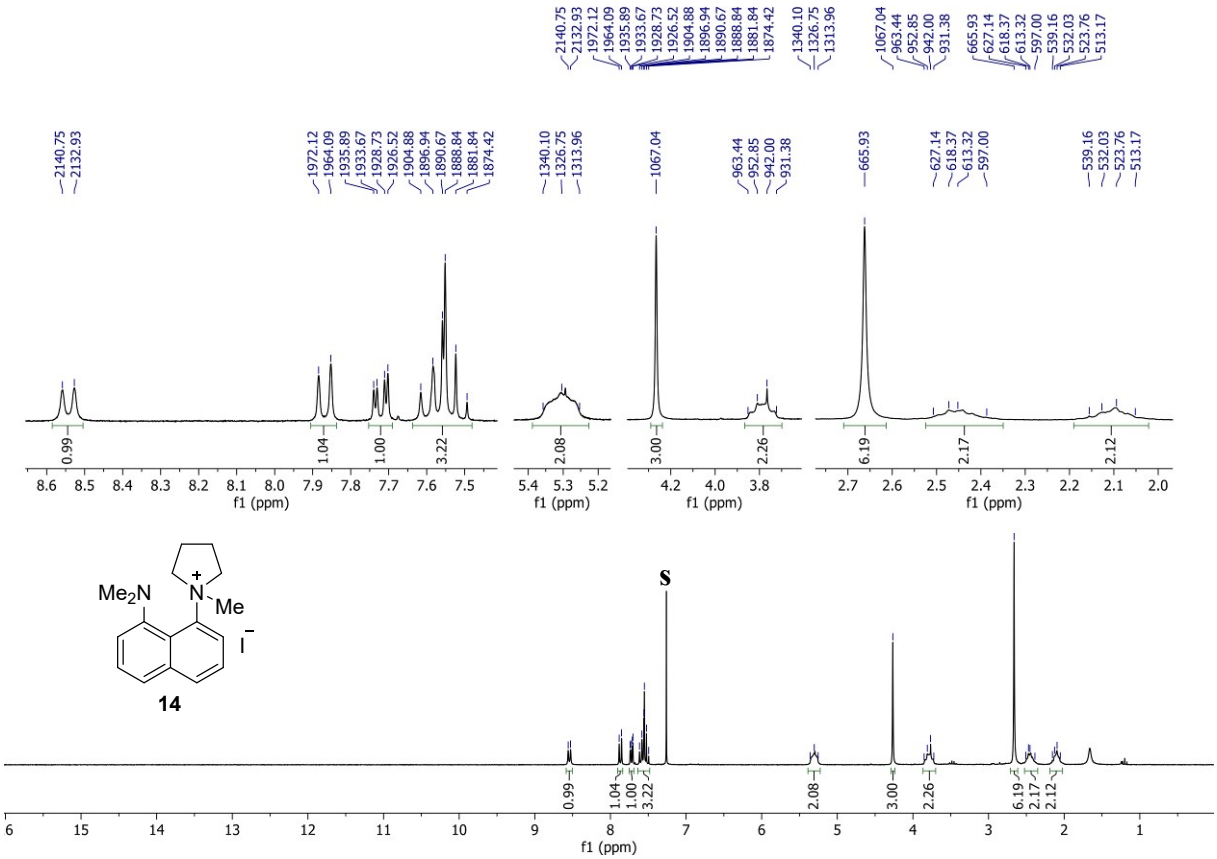


Fig. S13 ^{1}H NMR spectrum of **14** (250 MHz, $CDCl_3$).

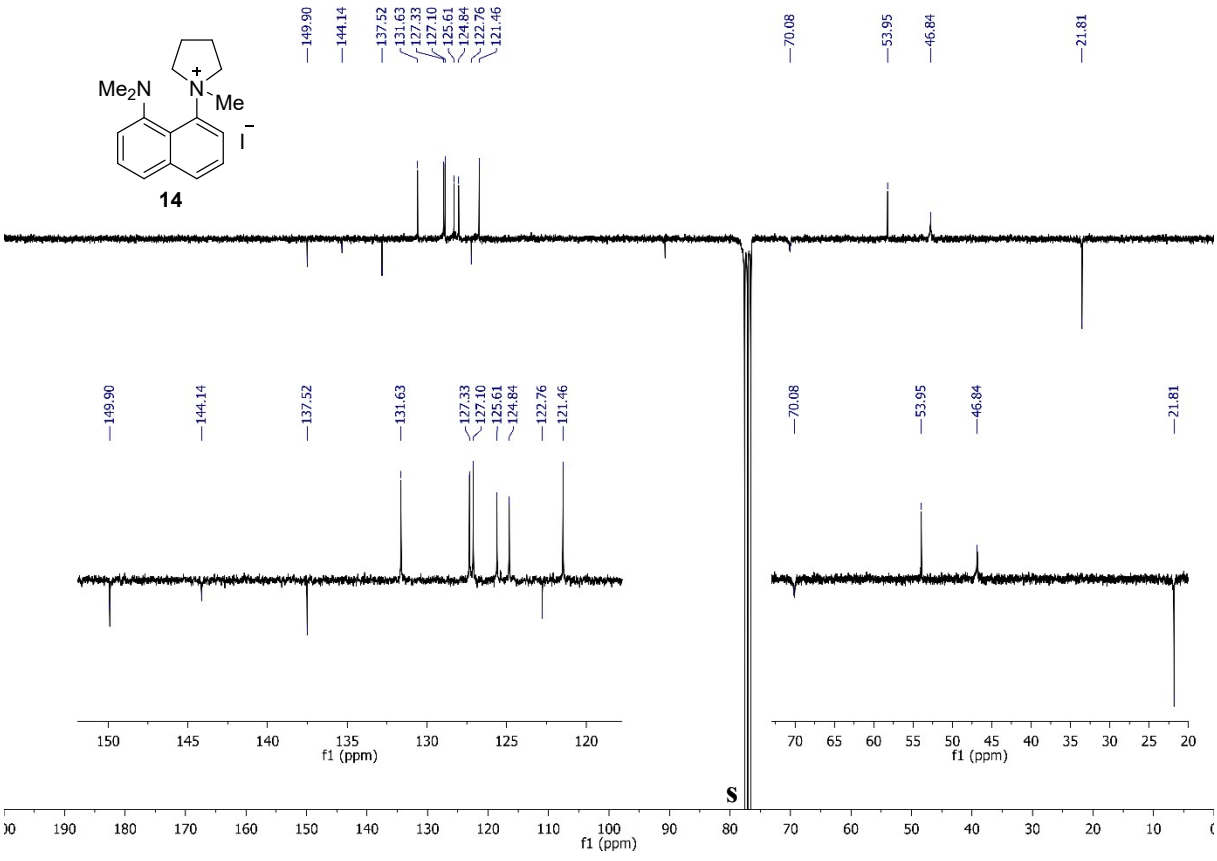


Fig. S14 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **14** (62.9 MHz, $CDCl_3$).

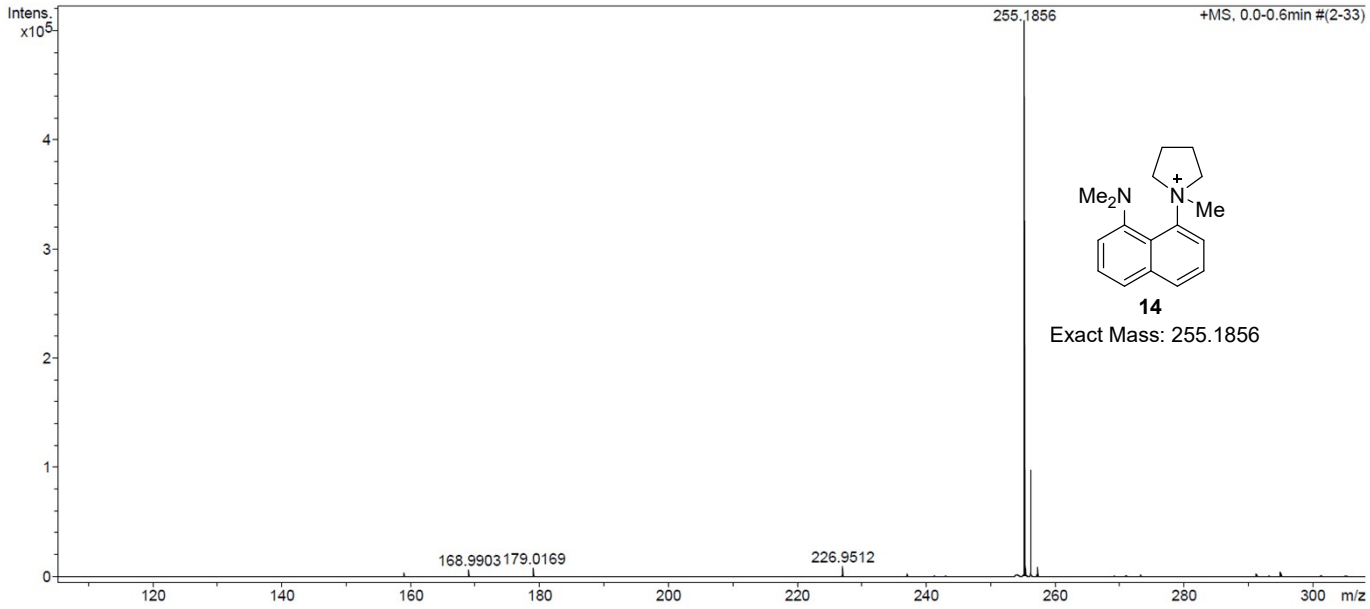


Fig. S15 HRMS (ESI) of **14**.

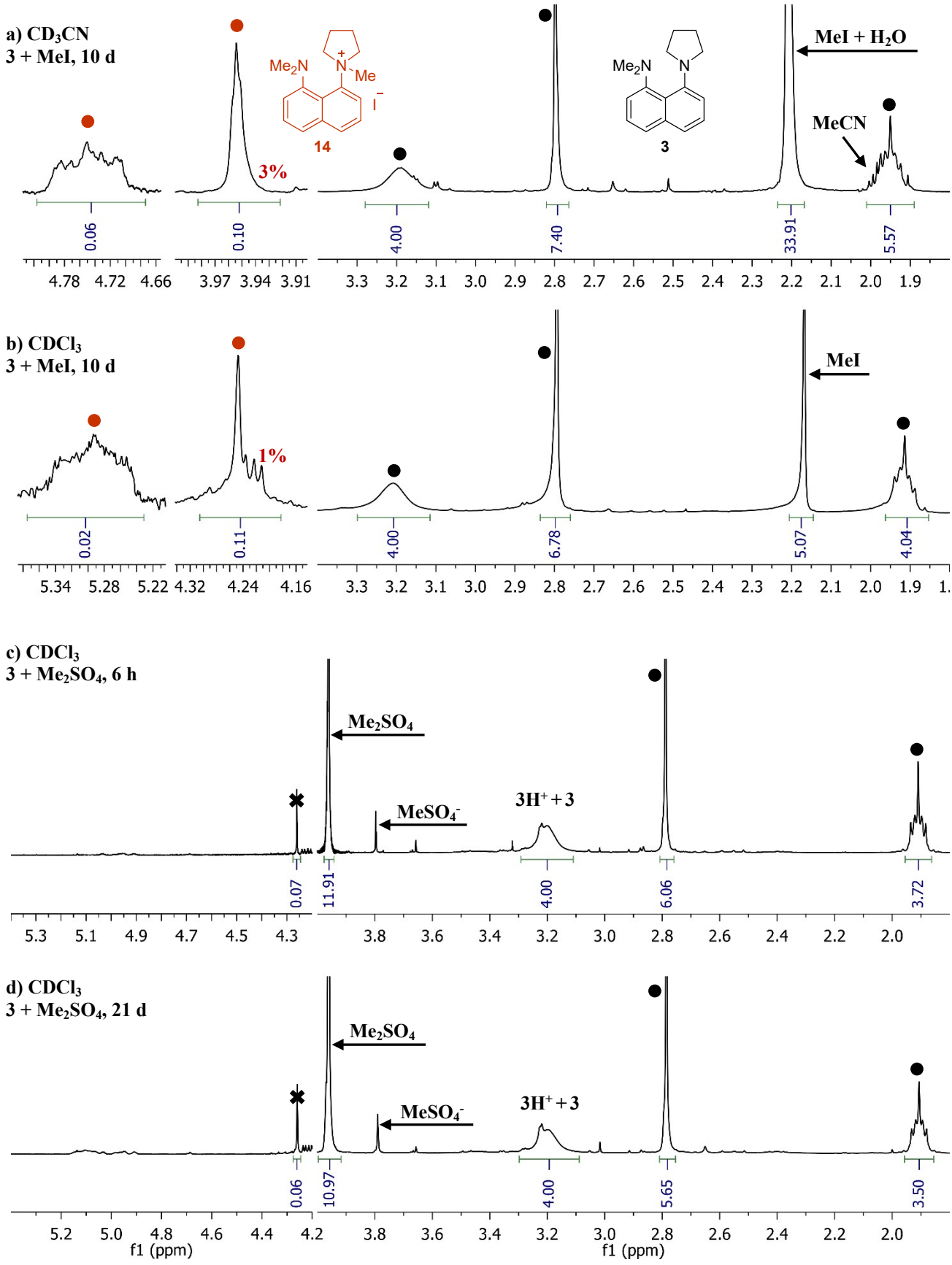


Fig. S16 ^{1}H NMR-monitoring of the **3** + MeI (1:10) and **3** + Me_2SO_4 (1:2) mixtures (250 MHz, 22 °C, only aliphatic regions are shown).

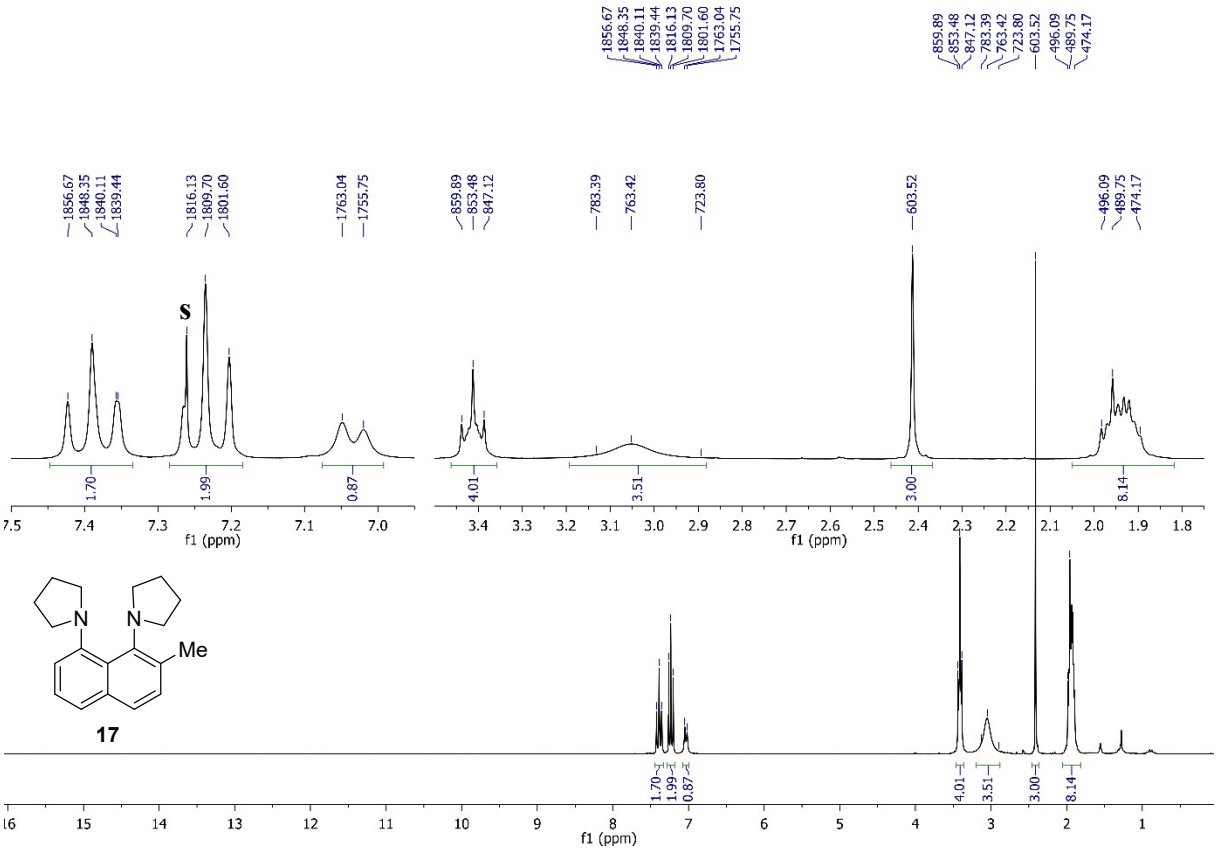


Fig. S17 ^{1}H NMR spectrum of **17** (250 MHz, $CDCl_3$).

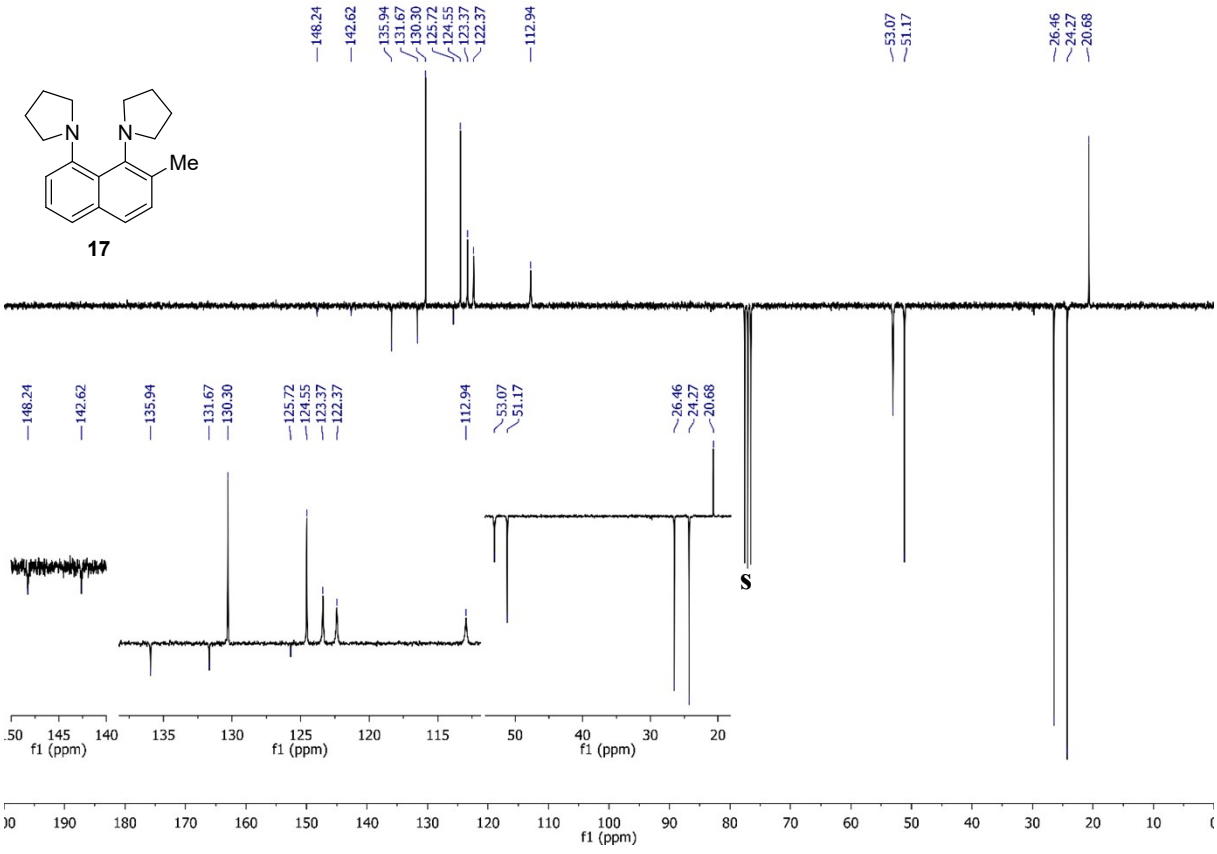


Fig. S18 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **17** (62.9 MHz, $CDCl_3$).

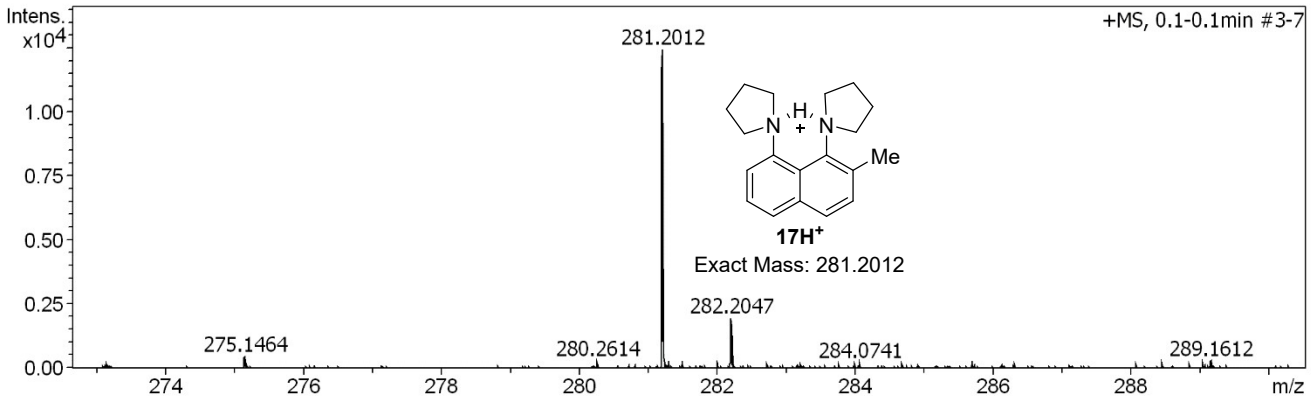


Fig. S19 HRMS (ESI) of **17**.

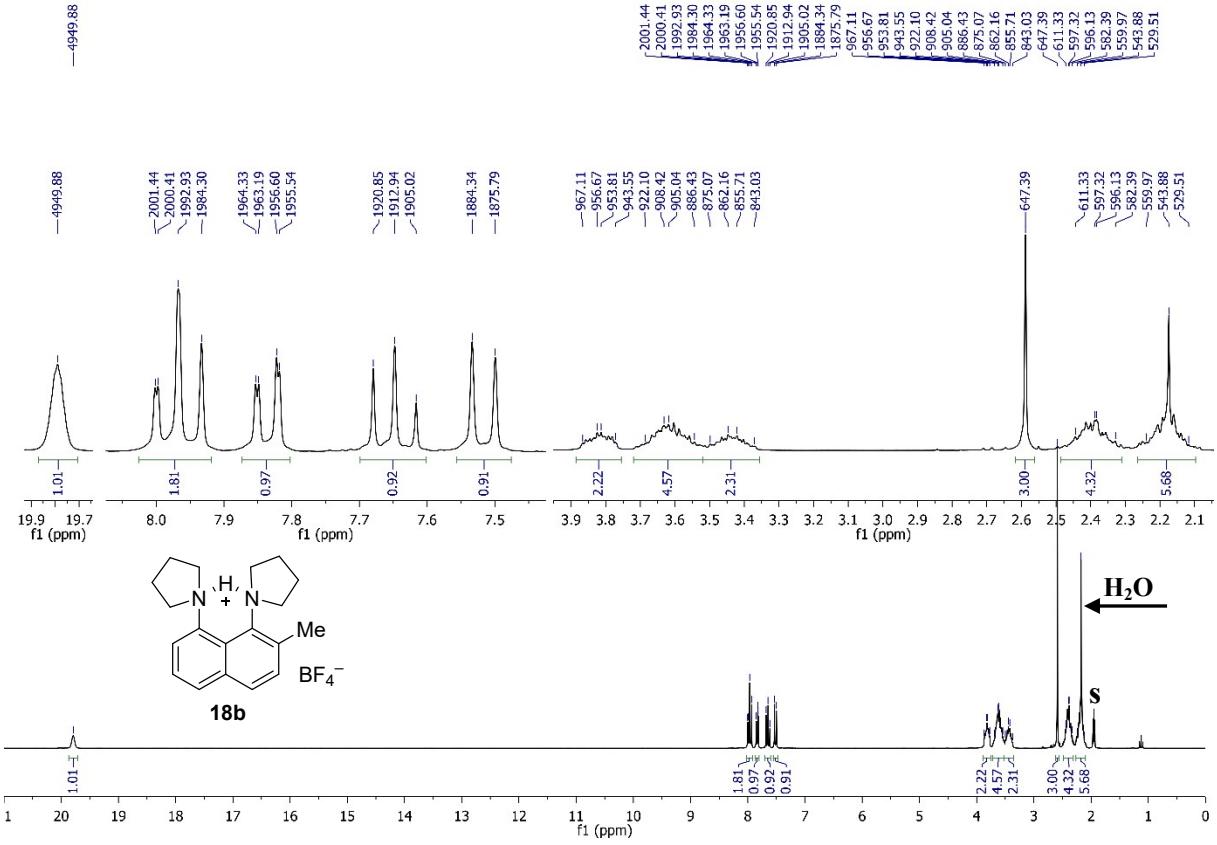


Fig. S20 ^{1}H NMR spectrum of **18b** (250 MHz, CD_3CN).

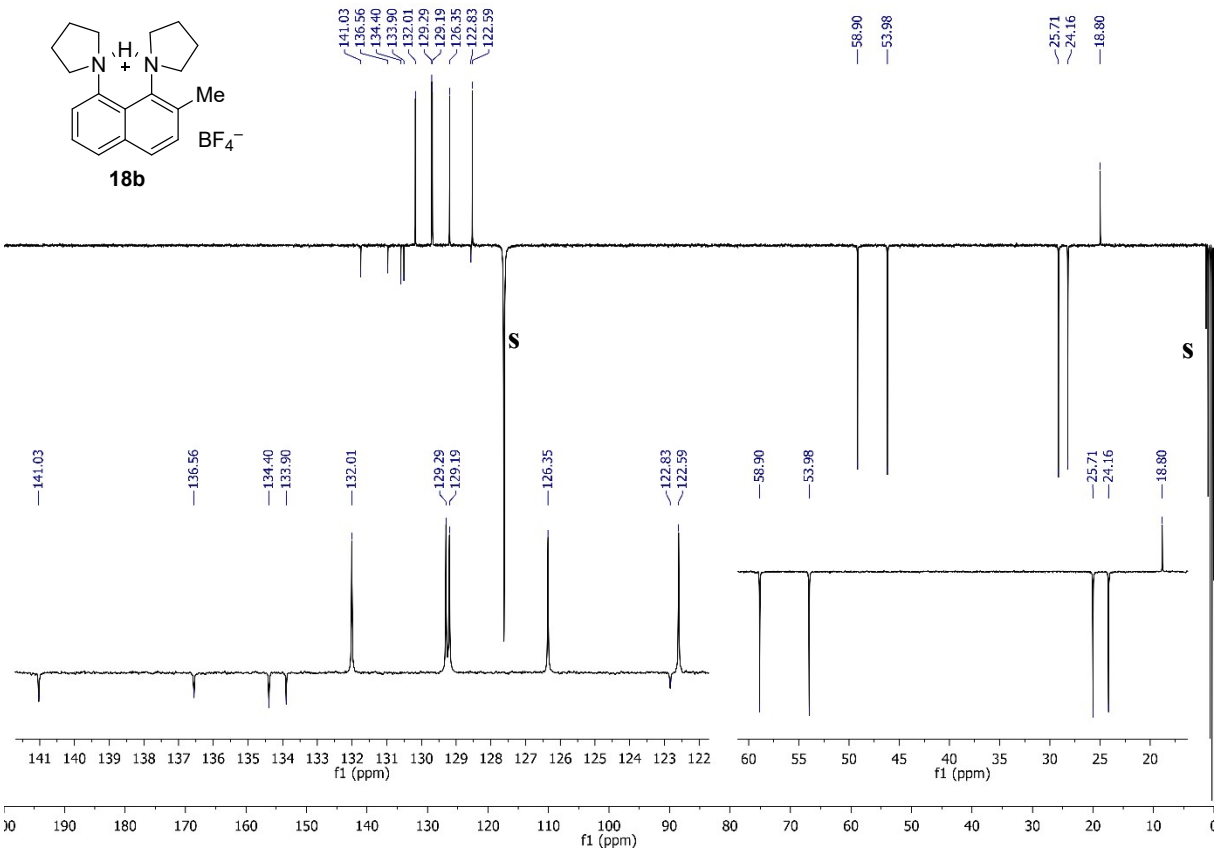


Fig. S21 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **18b** (62.9 MHz, CD_3CN).

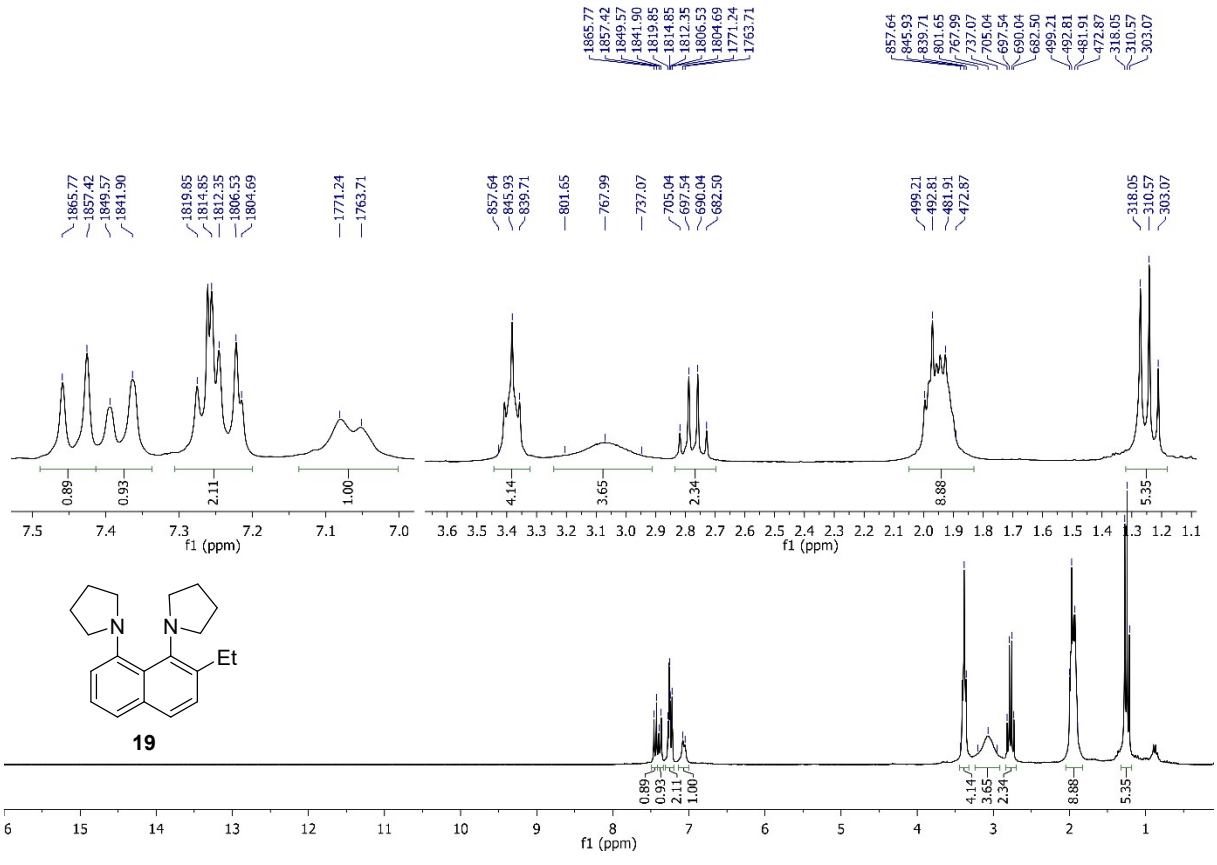


Fig. S22 ^{1}H NMR spectrum of **19** (250 MHz, $CDCl_3$).

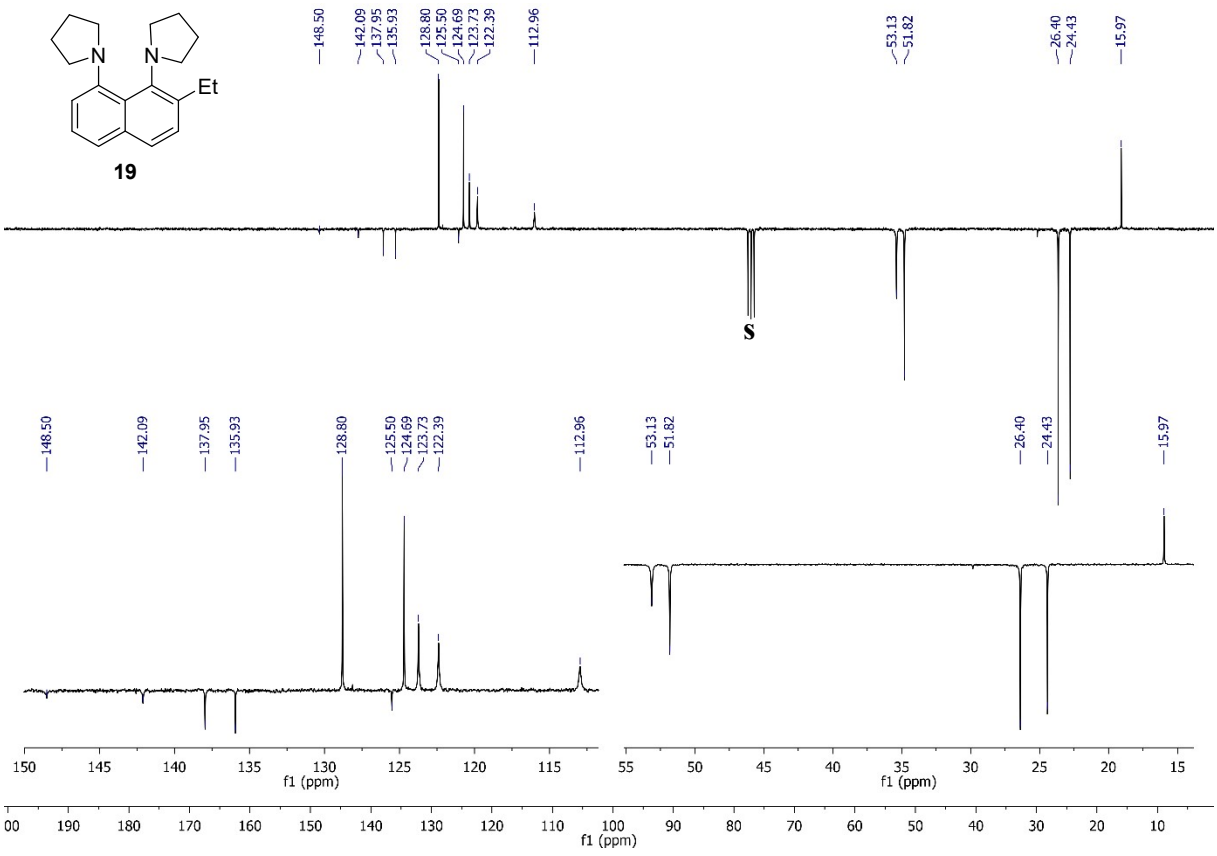


Fig. S23 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **19** (62.9 MHz, $CDCl_3$).

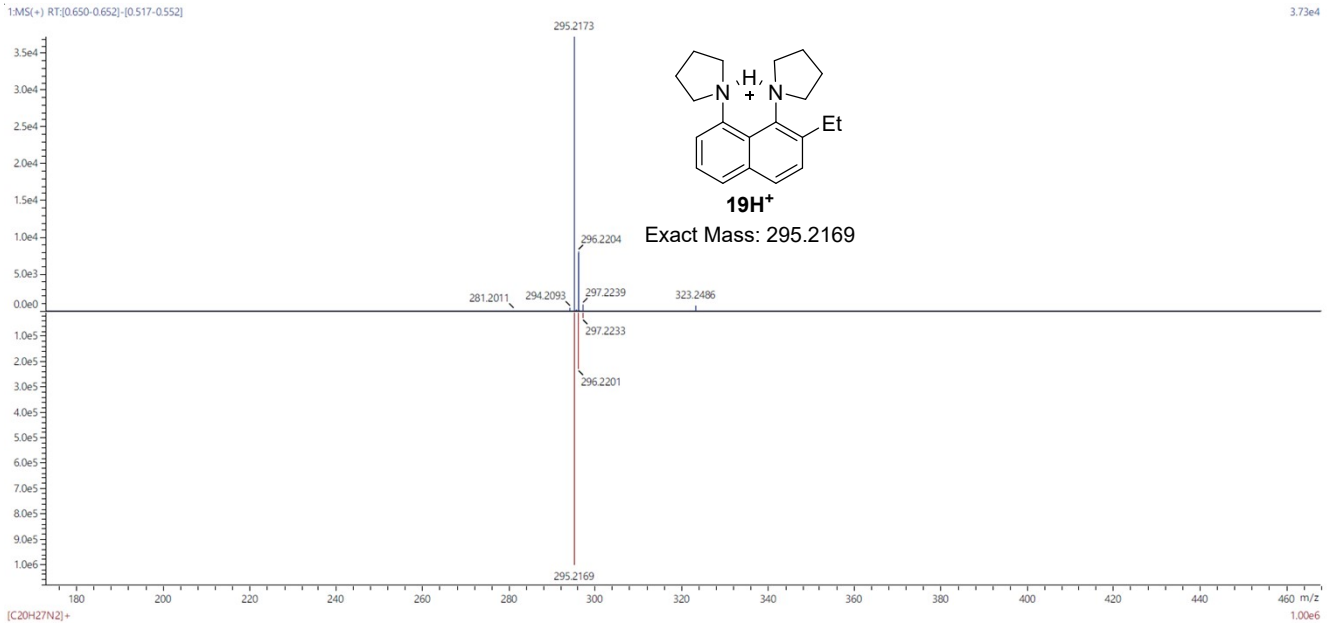


Fig. S24 HRMS (ESI) of **19**.

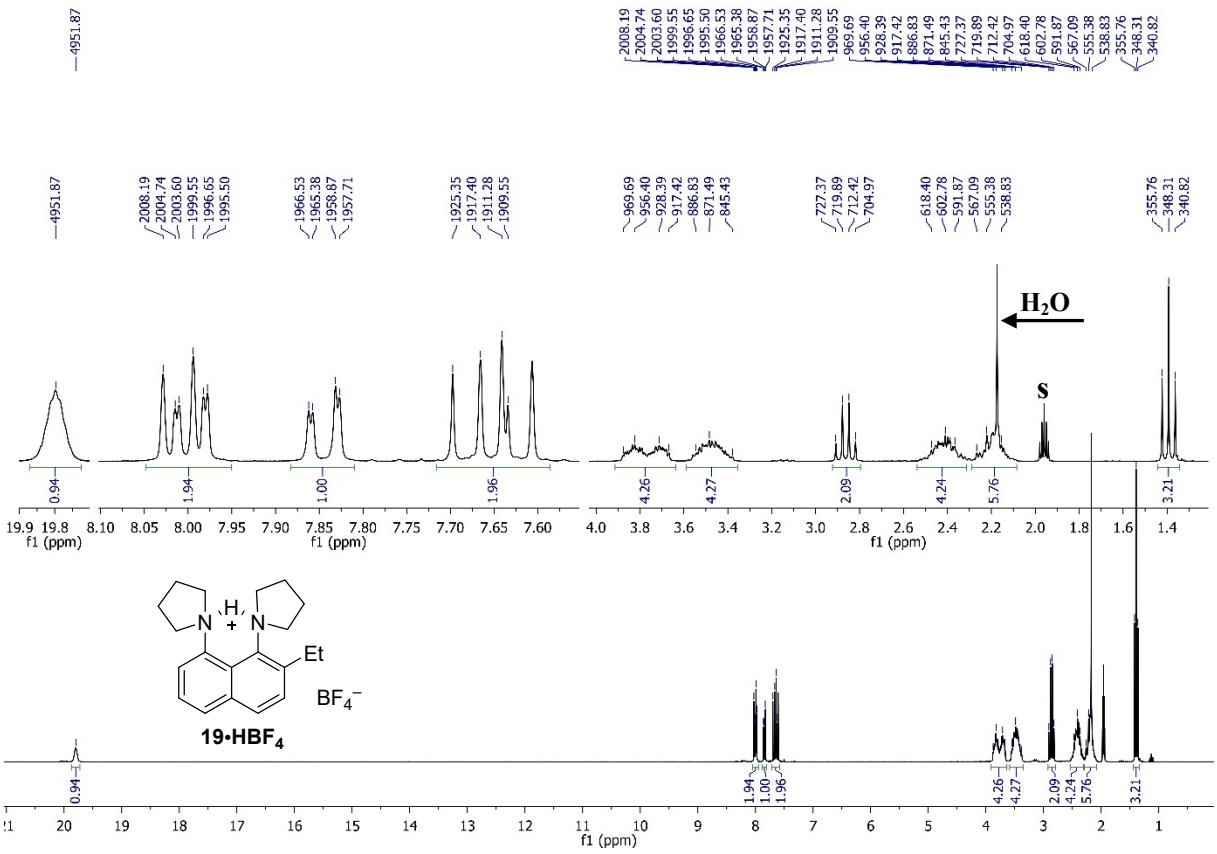


Fig. S25 ^{1}H NMR spectrum of **19·HBF$_4$** (250 MHz, CD_3CN).

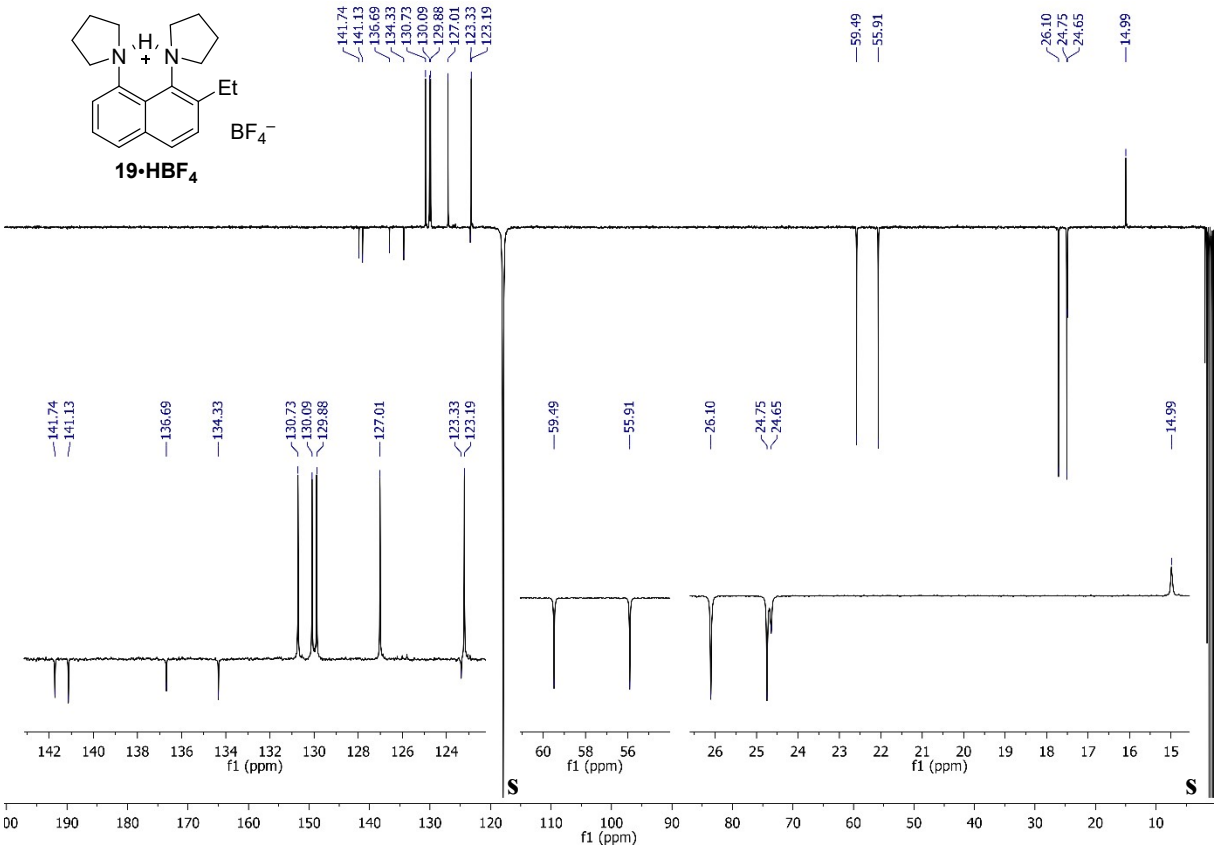


Fig. S26 ^{13}C{^{1}H} APT-NMR spectrum of **19·HBF$_4$** (62.9 MHz, CD_3CN).

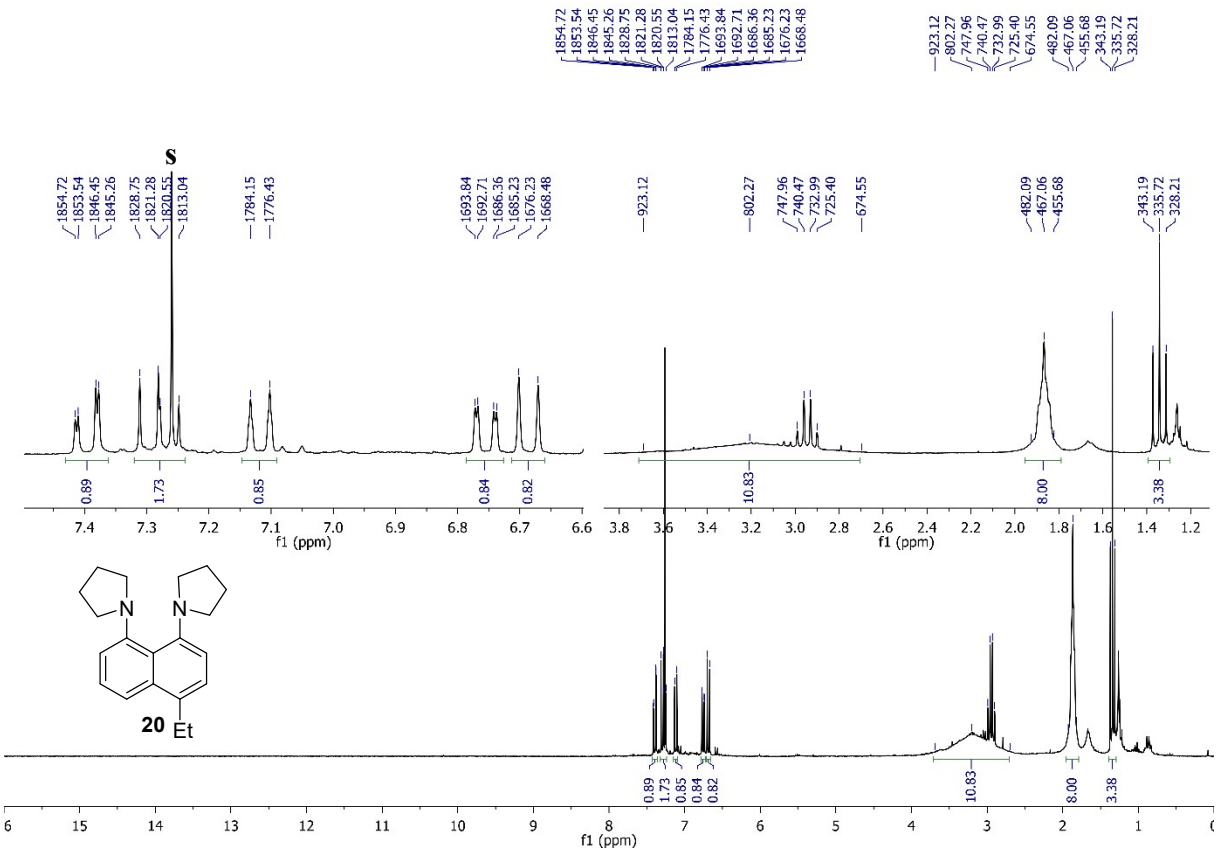


Fig. S27 ^{1}H NMR spectrum of **20** (250 MHz, $CDCl_3$).

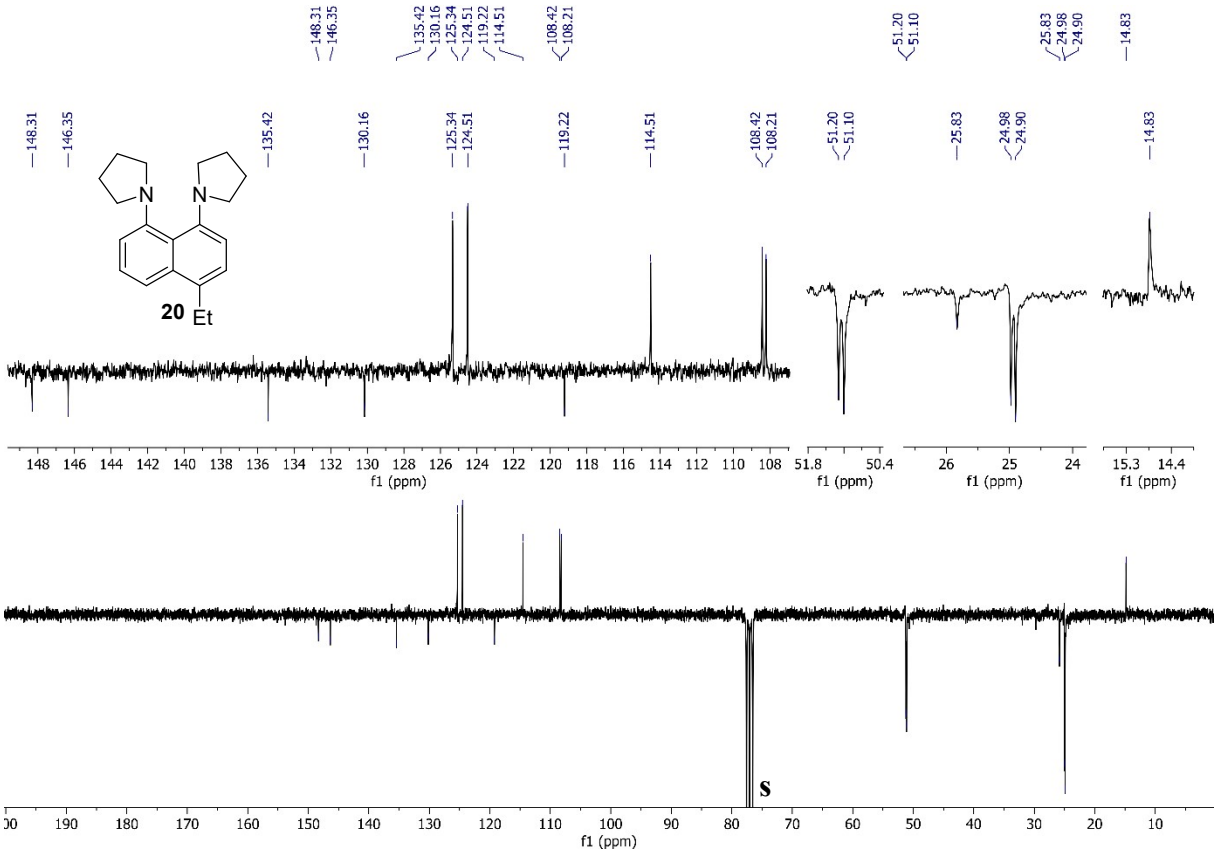


Fig. S28 $^{13}C\{^{1}H\}$ APT-NMR spectrum of **20** (62.9 MHz, $CDCl_3$).

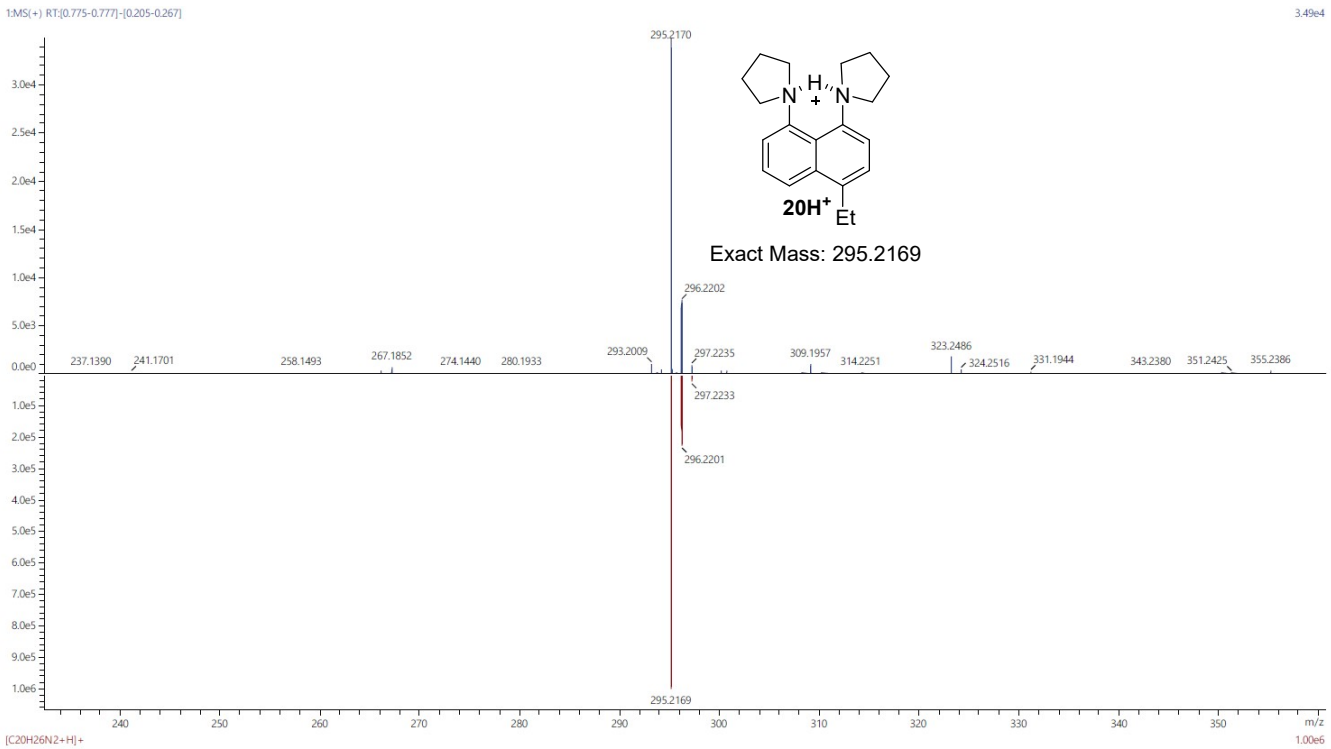
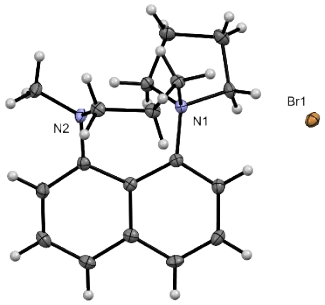
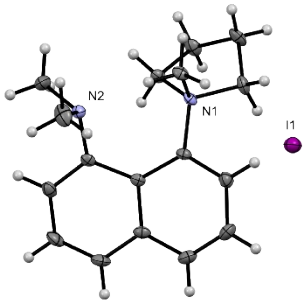
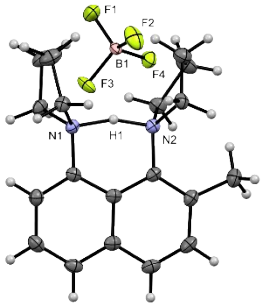


Fig. S29 HRMS (ESI) of **20**.

XRD Data

Table S1. Crystal data and structure refinement for the studied compounds.

			
Identification code	Structure-**5**	Structure-**14**	Structure-**18b**
Empirical formula	$C_{18}H_{23}BrN_2$	$C_{17}H_{23}IN_2$	$C_{19}H_{25}BF_4N_2$
Formula weight	347.29	382.27	368.22
Temperature/K	99.97(15)	100.00(10)	100.00(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*Cc*	$P2_1/c$	$P2_1/n$
a/Å	7.79650(10)	11.96030(10)	9.7812(1)
b/Å	18.2667(2)	9.88890(10)	10.3437(1)
c/Å	11.37140(10)	27.9480(2)	17.7597(2)
α/°	90	90	90
β/°	91.6140(10)	93.0630(10)	95.106(1)
γ/°	90	90	90
Volume/Å^3	1618.83(3)	3300.81(5)	1789.69(3)
Z	4	8	4
ρ_{calc} g/cm^3	1.425	1.538	1.367
μ/mm^{-1}	3.405	15.169	0.917
F(000)	720.0	1536.0	776.0
Crystal size/mm^3	0.14 × 0.1 × 0.08	0.12 × 0.1 × 0.08	0.24 × 0.18 × 0.15
Radiation	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)
2Θ range for data collection/°	9.684 to 139.948	6.334 to 139.986	9.906 to 152.564
Index *h k l* max	9, 22, 13	14, 12, 30	12, 13, 22
Reflections collected	22273	24250	18984
Independent reflections	2966 [R_{int} = 0.0280, R_{sigma} = 0.0146]	6246 [R_{int} = 0.0339, R_{sigma} = 0.0265]	3735 [R_{int} = 0.0263, R_{sigma} = 0.0166]
Data/restraints/parameters	2966/2/191	6246/0/367	3735/0/259
Goodness-of-fit on F^2	1.111	1.068	1.046
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0139, wR_2 = 0.0359	R_1 = 0.0343,wR_2 = 0.0978	R_1 = 0.0384,wR_2 = 0.1024
Final *R* indexes [all data]	R_1 = 0.0139, wR_2 = 0.0360	R_1 = 0.0362,wR_2 = 0.0993	R_1 = 0.0407,wR_2 = 0.1044
Largest diff. peak/hole / e Å^{-3}	0.13/–0.18	1.23/–1.79	0.35/–0.22

References

S1 E. V. Kolupaeva, V. A. Ozeryanskii and A. F. Pozharskii, *Synthesis*, 2020, **52**, 3427–3438.

S2 In the original paper, this compound was described as red oil. Other properties including spectral characteristics are consistent with data published in: L. S. Kovacevic, C. Idziak, A. Markevicius, C. Scullion, M. J. Corr, A. R. Kennedy, T. Tuttle and J. A. Murphy, *Angew. Chem. Int. Ed*, 2012, **51**, 8516–8519.

S3 R. W. Alder, M. R. Bryce, N. C. Goode, N. Miller and J. Owen, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2840–2847.