Supplementary Information for

Generation of mono(amino)carbenes from N-triftosyl amino hydrazonates with blue light

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1) General Methods

For manipulations that were carried out in an argon-filled glovebox or using standard Schlenk techniques, glassware was dried overnight at 150 °C in an oven or by flame under vacuum. Microwave reaction vials and caps (10 mL, Biotage) were stored in an oven for at least 24 h at 150 °C before cycling into a glovebox immediately before use. Unless otherwise specified, starting materials were purchased from commercial sources and used without further purification. Dry solvents were distilled from sodium wire and benzophenone, calcium hydride, or phosphorous pentoxide as appropriate, degassed by three freeze-pump-thaw cycles, and stored over activated 3Å molecular sieves prior to use. Thin-layer chromatography was carried out on aluminum-backed silica gel 60 (F254) plates from MERCK (grain-size distribution 60/20 μm) and visualized using UV light. Column chromatography was performed with silica gel (spherical, particle size 60 μm, neutral) or neutral alumina (activated, Brockmann I) purchased from Silicycle or Sigma Aldrich.

Photochemistry was conducted using the following light sources: EvoluChem LED 450PF non-dimmable 110V-220V (Wavelength: 450 nm, Irradiance: 328 mW/cm^2, HepatoChem, SKU: HCK1012-01-002); EvoluChem LED 365PF non-dimmable 110V-220V (Wavelength: 365 nm, Irradiance: 190 mW/cm^2, HepatoChem, SKU: HCK1012-01-029).

NMR spectra were recorded on Bruker (300 MHz, 400 MHz, 600 MHz), Varian (500 MHz), or Joel (400 MHz, 500 MHz) spectrometers at 25 °C. ^{1}H NMR chemical shifts are reported relative to TMS (δ in ppm) and were referenced via residual proton resonances of the corresponding deuterated solvent ($CHCl_3$: 7.26 ppm; C_6D_5H : 7.16 ppm; THF-d_7: 3.58 ppm; ACN-d_2: 1.94 ppm; Acetone-d_5: 2.05 ppm; DMSO-d_5: 2.50 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.16 ppm; C_6D_6: 128.06 ppm; DCM-d_2: 53.84 ppm; ACN-d_3: 1.32 ppm; Acetone-d_5: 29.84 ppm, 206.26 ppm; DMSO-d_6: 39.52 ppm).

High Resolution Mass Spectrometry (HRMS) were recorded at the UC San Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOF-MS spectrometer.

UV-Visible absorption spectra were recorded on an Agilent Cary 60 spectrophotometer.

Single crystal X-ray diffraction data were collected on a Bruker D8-Venture diffractometer using Mo-Kα radiation (λ = 0.71073 Å).

2) Synthetic Procedures

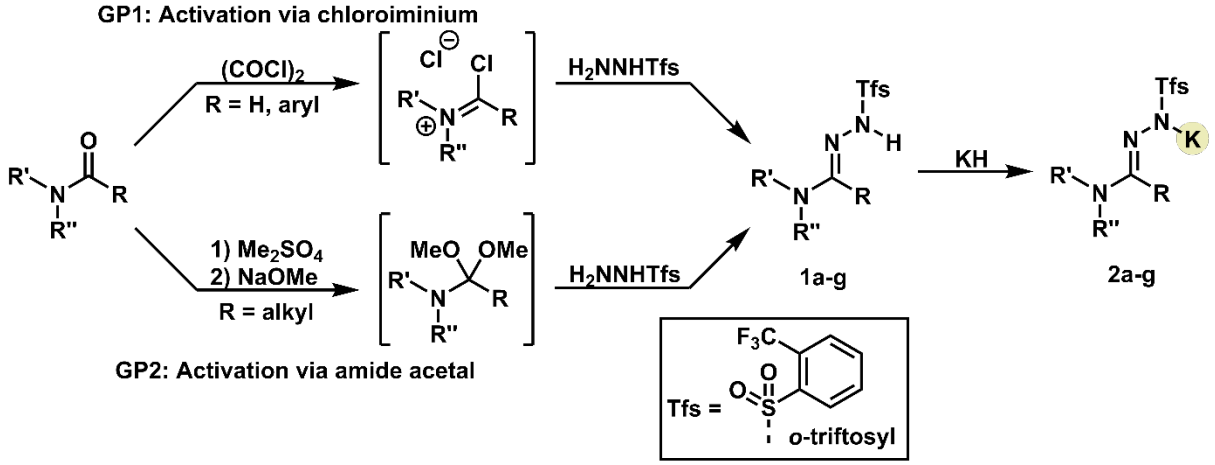
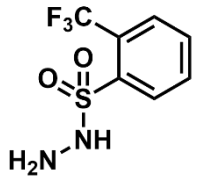


Figure S1. Synthetic approach to access potassium amino *N*-triftosyl hydrazonates.

Amino *N*-triftosyl hydrazonates **1a-g** were prepared from secondary amides and *o*-triftosyl hydrazide, $H_2NNHTfs$. Two different amide activation strategies were used, the choice of which depended on the amide substituents. Oxalyl chloride proved very convenient for the activation of formamides and benzamides. In our hands, activation of alkyl amides with oxalyl chloride or other common chlorinating agents produced intensely colored solutions which, upon addition of $H_2NNHTfs$, gave little to none of the desired hydrazone. Activation via the amide acetal gave superior results but is decidedly less convenient than the chloroiminium route. The corresponding potassium hydrazonates **2a-g** were prepared by deprotonation with KH.

2-(trifluoromethyl)benzenesulfonyl hydrazide (triftosyl hydrazide, $H_2NNHTfs$)

The title compound was prepared through an adapted literature procedure.[1]



In a flame-dried, 500 mL Schlenk flask equipped with a stir bar and rubber septum, 25 g (102 mmol, 1 eq.) of 2-(trifluoromethyl)benzenesulfonyl chloride was dissolved in 120 mL of dry THF then cooled to 0° C. To the resulting solution, 12 mL (11.65 g, 233 mmol, 2.3 eq.) of hydrazine monohydrate was added dropwise over *ca.* 5 minutes. The reaction mixture was then stirred for at least 90 minutes at 0° C. Then, the reaction was diluted with 120 mL of EtOAc and the resulting organic layer was washed twice with 2 x 120 mL of saturated NaCl brine in a separatory funnel. The organic layer was dried over $MgSO_4$, then filtered directly into 250 mL of vigorously stirred pentanes, resulting in immediate formation of a white, crystalline precipitate. Once the filtration was complete, the suspension was stirred for another 30 minutes. Vacuum filtration yielded a fluffy white, crystalline solid. Drying the solid at 50° C overnight under vacuum yielded 19.87 grams of $H_2NNHTfs$. The filtrate was stored at -4° C overnight, then similarly vacuum filtered and dried to obtain a second crop, 2.17 g, leading to an overall yield of 22.04 g (91.8 mmol, 90%).

^{1}H NMR (500 MHz, 25°C, ACN-d_3) δ = 8.16 (m, 1H), 7.97 (m, 1H), 7.82 (m, 2H), 6.77 (s, 1H), 3.85 (s, 2H).

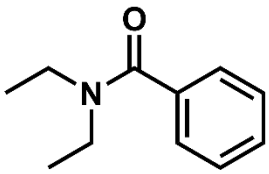
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) δ = 136.7, 134.2, 133.8, 133.5 (m), 129.4 (q, *J* = 6.5 Hz), 128.3 (q, *J* = 32.9 Hz), 124.0 (q, *J* = 273.0 Hz).

^{19}F NMR (376 MHz, 25°C, ACN-d_3) δ = -58.19.

Spectral data matched those reported previously.[1]

Synthesis of precursor amides

N,*N*-diethylbenzamide

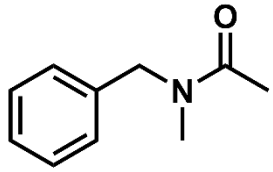


A 250 mL conical flask was charged with a stir bar, 5.7 mL of diethylamine (4.0 g, 55 mmol, 1.1 eq.), 8.7 mL (6.3 g, 62 mmol, 1.25 eq.) of triethylamine, and 100 mL of DCM. The mixture was chilled to 0 °C, then 5.8 mL of benzoyl chloride (7.0 g, 50 mmol, 1 eq.) was slowly added. The ice bath was removed and the reaction left to stir for 2 h at room temperature. The reaction was diluted with 300 mL of Et_2O, then washed with 150 mL of water, 150 mL of 0.5 M aq. HCl, 150 mL 20 % $NaHCO_3$, and another 150 mL of water. The organic fraction was collected, dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain the title compound. Colorless oil, 8.83 g (49.8 mmol, 100% yield).

^{1}H NMR (400 MHz, 25°C, $CDCl_3$) δ = 7.37 (m, 5H), 3.54 (broad, 2H), 3.24 (broad, 2H), 1.24 (broad, 3H), 1.10 (s, 3H).

Spectral data matched those reported previously.[2]

N-benzyl-*N*-methylacetamide

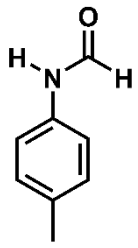


A 250 mL conical flask was charged with a stir bar, 11.7 mL of *N*-methyl benzylamine (11.0 g, 90.8 mmol, 1 eq.), 12.6 mL of triethylamine (9.14 g, 90.3 mmol, 1 eq.), and 90 mL of DCM. The mixture was chilled to 0 °C, then 10.2 mL of Ac_2O (11.0 g, 108 mmol, 1.2 eq.) was slowly added. The ice bath was removed and the reaction left to stir for 16 h at room temperature. The reaction was diluted with 300 mL of Et_2O, then washed with 150 mL of water, 150 mL of 0.5 M aq. HCl, 150 mL 20 % $NaHCO_3$, and another 150 mL of water. The organic fraction was collected, dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain the title compound. Colorless oil, which crystallizes upon standing, 12.63 g (77.4 mmol, 86% yield). Presents as a 55:45 mixture of rotamers.

^{1}H NMR (400 MHz, 25°C, $CDCl_3$) δ = 7.37 – 7.16 (m, 5H), 4.58 (s, 2H, MAJOR), 4.52 (s, 2H, minor), 2.94 (s, 3H, minor), 2.91 (s, 3H, MAJOR), 2.15 (s, 3H, MAJOR), 2.15 (s, 3H, minor).

Spectral data matched those reported previously.[3]

N-(p-tolyl)formamide



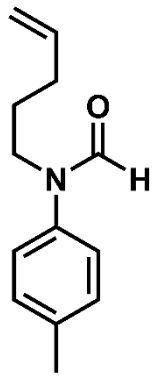
A 35 mL conical-bottom flask was charged with 10.64 g of *p*-toluidine (105.2 mmol, 1.05 eq.), 15 mL of toluene, 3.8 mL of 96% formic acid (4.6 g, 100 mmol, 1 eq.), and a stir bar. The flask was then equipped with a Dean Stark apparatus, the apparatus flushed with argon, and the reaction was set to vigorously reflux for 20 h, during which time *ca.* 1.8 mL of water (~ 100% theoretical yield) was collected. The reaction mixture was then left to cool. Concentration under vacuum yielded an oil which eventually solidifed upon trituration with hexanes. The solid was crushed till uniform, then collected by filtration and washed with pentanes. Drying under vacuum yielded the title compound as a tan powder, 13.24 g (98 mmol, 98% yield). Presents as a 55:45 mixture of rotamers.

^{1}H NMR (400 MHz, 25°C, $CDCl_3$) δ = 8.63 (d, *J* = 11.5 Hz, 1H, MAJOR), 8.35 (broad, 1H, minor), 8.34 (d, *J* = 1.9 Hz, 1H, minor), 7.47 (broad, 1H, minor), 7.42 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 2.33 (s, 3H, MAJOR), 2.32 (s, 3H, minor).

Spectral data matched those reported previously.[4]

N-(pent-4-en-1-yl)-*N*-(p-tolyl)formamide

The title compound was prepared through an adapted literature procedure.[5]



A 50 mL round-bottom flask was charged with freshly powdered KOH (2.24 g, 40 mmol, 4 eq.) and 20 mL of DMSO. After stirring for 5 minutes at room temperature, *N*-(p-tolyl)formamide (1.35 g, 10 mmol, 1 eq.) was added in one portion. The reaction was then chilled in an ice bath, partially freezing the mixture. 5-bromo-1-pentene (2.4 mL, 3.0 g, 20 mmol, 2 eq.) was added dropwise. The reaction was stirred for 5 minutes, then allowed to warm to rt. Reaction progress was monitored by TLC. Once the starting material was fully consumed (*ca.* 45 minutes), the reaction was diluted with 100 mL of DI H_2O, then extracted three times with 20 mL of DCM. The combined organic phases were diluted with 120 mL of Et_2O, then washed five times with 30 mL of 10% aqueous LiCl to remove the DMSO. The organic phase was then dried over $MgSO_4$, filtered, and concentrated under vacuum to yield the pure product as a brown oil, 1.81 g (8.9 mmol, 89% yield).

^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.32 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.80 – 5.71 (m, 1H), 4.99 – 4.93 (m, 2H), 3.80 – 3.77 (m, 2H), 2.37 (s, 3H), 2.07 – 2.03 (m, 2H), 1.65 – 1.59 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 162.4, 138.4, 137.5, 136.9, 130.2, 124.4, 115.2, 44.6, 30.9, 26.8, 20.9.

HR-ESI-TOFMS: calc. for $[C_{13}H_{17}NO]+H^+$ m/z: 204.1383; found 204.1383 (Δ = 0.0 ppm).

Synthesis of *N*-triftosyl amino hydrazones

General Procedure 1: Chloroiminium route

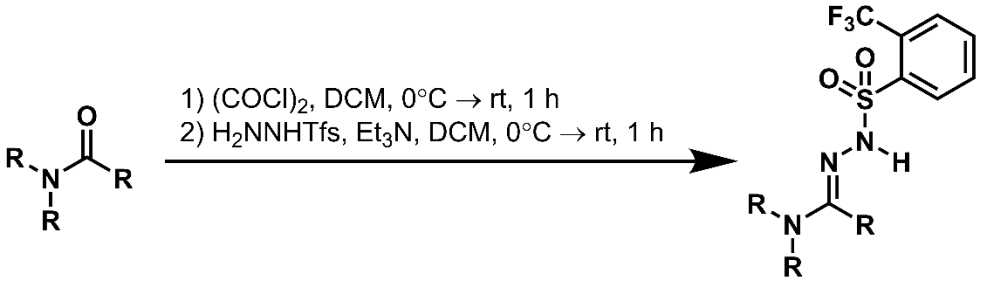


Figure S2. Synthetic scheme for synthesis of amino hydrazones via chlorominiums.

In a flame-dried Schlenk flask equipped with a stir bar under argon, the appropriate amide was dissolved in dry DCM (2 mL per mmol of amide). The solution was chilled to 0 °C, then 1.5 eq. of neat $(COCl)_2$ was added by syringe. The cold bath was removed and the reaction stirred for 1 h at room temperature. Volatiles were removed under vacuum to remove unreacted $(COCl)_2$. The resulting residue was redissolved in dry DCM (5 mL per mmol of amide). The reaction was chilled to 0° C and 1 eq. of $H_2NNHTfs$ was added in a single portion, followed by 1 eq. of dry Et_3N. The cold bath was removed and the reaction stirred at room temperature until the hydrazide is consumed by TLC (*ca.* 1 h). The reaction was quenched by the addition of sat. aq. $HNaCO_3$. The resulting biphasic mixture was extracted with DCM. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain the crude product. Purification by flash column chromatography over SiO_2 gave the pure amino hydrazone.

General Procedure 2: Amide acetal route

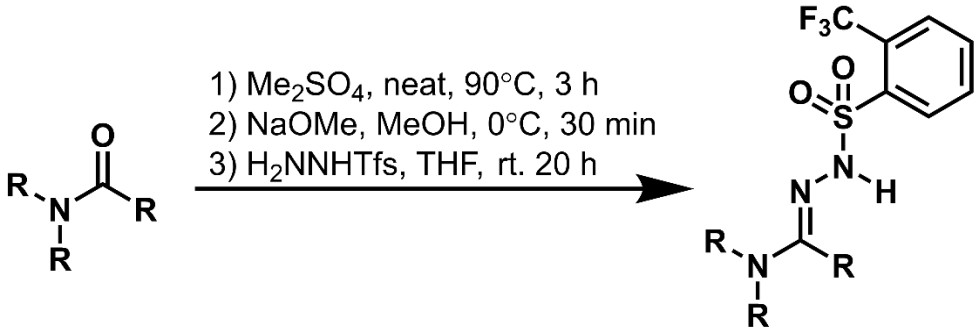
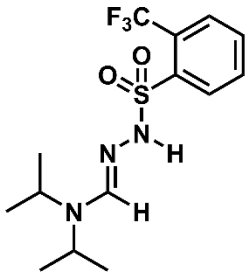


Figure S3. Synthetic scheme for synthesis of amino hydrazones via amide acetals.

In a flame-dried Schlenk flask equipped with a stir bar under argon, 1.08 eq. of Me_2SO_4 was added to the appropriate amide. The neat mixture was then heated to 90 °C and stirred for 3 h. The reaction was then chilled to 0 °C and 1.1 eq. of freshly prepared NaOMe in MeOH (from sodium metal and MeOH dried over 3Å molecular sieves, *ca.* 0.25 M) was added via cannulation. The resulting suspension was stirred at room temperature for 30 minutes, then filtered. The filtrate was diluted with dry pentanes, filtered again, concentrated under argon, then filtered once more to yield a mixture of the desired acetal and the starting amide. The purity of the acetal was estimated by ^1H NMR.

The crude acetal was transferred to a flame-dried Schlenk flask equipped with a stir bar and cycled to argon. Then, 0.95 eq. of $H_2NNHTfs$ (relative to acetal) was added in one portion, followed by dry THF (1 mL per mmol of acetal). The mixture was stirred for 20 h, then all volatiles were removed under vacuum. Purification by flash column chromatography over SiO_2 gave the pure amino hydrazone.

***N*,*N*-diisopropyl-*N'*-triftosyl formamide hydrazone (1a)**



Prepared according to GP1 from 1.33 g of *N*,*N*-diisopropylformamide (10.3 mmol). Eluted with 2:1 Hex:EtOAc. White solid, 2.68 g (7.6 mmol, 74% yield).

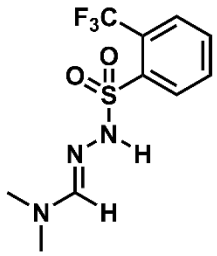
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.01 (d, *J* = 7.3 Hz, 1H), 7.91 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 6.70 (broad, 1H), 4.04 (broad, 1H), 3.53 (broad, 1H), 1.16 (broad, 12H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 161.8, 136.9, 134.0, 132.9, 131.6, 128.4 (q, *J* = 6.2 Hz), 128.2 (q, *J* = 32.6 Hz), 123.1 (q, *J* = 273.5 Hz), 46.5 (broad), 23.8 (broad), 19.6 (broad).

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -57.85

HR-ESI-TOFMS: calc. for $[C_{14}H_{20}F_3N_3O_2S]+H^+$ m/z: 352.1301; found 352.1301 (Δ = 0.0 ppm).

***N*,*N*-dimethyl-*N'*-triftosyl formamide hydrazone (1b)**



Prepared according to GP1 from 219 mg of *N*,*N*-dimethylformamide (3 mmol). Eluted with 1:3 Hex:EtOAc. White solid, 759 mg (2.57 mmol, 86% yield).

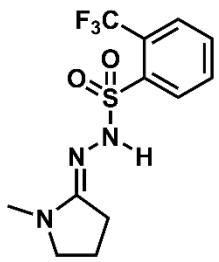
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.05 – 8.03 (m, 1H), 7.90 – 7.88 (m, 1H), 7.81 (s, 1H), 7.72 – 7.66 (m, 2H), 6.69 (broad, 1H), 2.83 (broad, 6H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 164.9, 164.8, 136.6, 133.8, 133.0 – 132.9 (m), 131.8 – 131.7 (m), 128.5 – 128.3 (m), 128.2 (q, *J* = 32.8 Hz), 123.1 (q, *J* = 273.5 Hz), 41.1, 35.0.

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -57.77.

HR-ESI-TOFMS: calc. for $[C_{10}H_{12}F_3N_3O_2S]+H^+$ m/z: 296.0675; found 296.0677 (Δ = 0.7 ppm).

***N*-methylpyrrolidone hydrazone (1c)**



Prepared according to GP2 from 1.98 g of *N*-methylpyrrolidone (20 mmol). Acetal intermediate was comprised of a 7:1 acetal:amide mixture, to which 1.64 g of H2NNHTfs (6.8 mmol) was added. Eluted with 100% EtOAc. White solid, 1.36 g (4.2 mmol, 62% yield based on H_2NNHTfs).

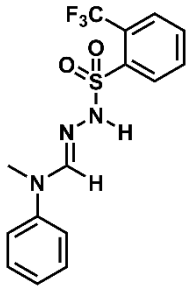
^{1}H NMR (500 MHz, 25°C, ACN-d_3) δ = 8.12 – 8.11 (m, 1H), 7.89 – 7.87 (m, 1H), 7.71 – 7.66 (m, 2H), 6.41 (broad, 1H), 3.36 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.70 (s, 3H), 2.01 – 1.95 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, ACN-d_3) δ = 175.0, 136.6, 134.1, 132.8, 131.6, 128.3 (q, *J* = 6.3 Hz), 128.1 (d, *J* = 32.8 Hz), 123.2 (q, *J* = 273.8 Hz), 52.9, 31.5, 29.1, 19.6.

^{19}F NMR (376 MHz, 25°C, ACN-d_3) δ = -57.79.

HR-ESI-TOFMS: calc. for $[C_{12}H_{14}F_3N_3O_2S]+H^+$ m/z: 322.0832; found 322.0833 (Δ = 0.3 ppm).

N-methyl-*N*-phenyl-*N'*-triftosyl formamide hydrazone (1d)



Prepared according to GP1 from 1.37 g of *N*-methylformanilide (10.1 mmol). Eluted with 1:1 Hex:EtOAc. White solid, 1.81 g (5.1 mmol, 50% yield).

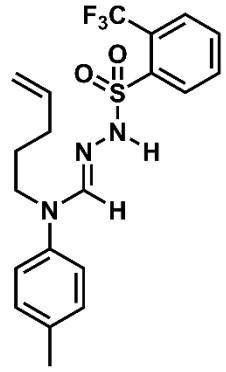
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.40 (s, 1H), 8.11 – 8.09 (m, 1H), 7.93 – 7.92 (m, 1H), 7.76 – 7.69 (m, 2H), 7.39 – 7.36 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 9.8 Hz, 2H), 6.89 (broad, 1H), 3.17 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, $CDCl_3$) δ = 162.2, 144.4, 136.6, 133.9, 133.2, 131.9, 128.5 (q, *J* = 6.4 Hz), 128.2 (q, *J* = 32.8 Hz), 124.2, 123.1 (q, *J* = 273.5 Hz). 119.9, 34.7.

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -57.78.

HR-ESI-TOFMS: calc. for $[C_{15}H_{14}F_3N_3O_2S]+H^+$ m/z: 358.0832; found 358.0834 (Δ = 0.6 ppm).

N-pentenyl-*N*-(p-tolyl)-*N'*-triftosyl formamide hydrazone (1e)



Prepared according to GP1 from 1.03 g of *N*-(pent-4-en-1-yl)-*N*-(p-tolyl)formamide (5.1 mmol). Eluted with 100% hexanes → 2:1 Hex:EtOAc. Off-white solid, 1.35 g (62% yield).

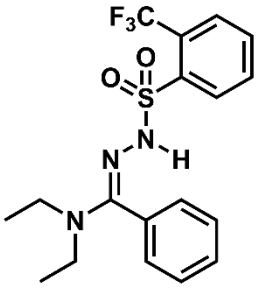
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.22 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 1H), 5.68 – 5.80 (m, 1H), 4.96 – 4.85 (m, 2H), 3.61 – 3.58 (m, 2H), 2.34 (s, 3H), 1.92 – 1.87 (m, 2H), 1.60 – 1.54 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, $CDCl_3$) δ = 162.0, 141.0, 137.6, 137.0, 135.3, 133.8, 133.0, 131.9, 130.2, 128.3 (q, *J* = 6.1 Hz), 128.2 (q, *J* = 33.0 Hz), 123.1 (q, *J* = 273.7 Hz), 121.9, 115.1, 47.6, 30.9, 25.9, 20.8.

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -57.80.

HR-ESI-TOFMS: calc. for $[C_{20}H_{22}F_3N_3O_2S]+H^+$ m/z: 426.1458; found 426.1460 (Δ = 0.5 ppm).

***N*,*N*-diethyl-*N'*-triftosyl benzamide hydrazone (1f)**



In a flame-dried Schlenk flask equipped with a stir bar under argon, 1.8 g (10.2 mmol) of *N*,*N*-diethyl benzamide was dissolved in 10 mL of dry toluene. 4 mL of neat $(COCl)_2$ (5.9 g, 47 mmol, 4.6 eq.) was added by syringe, and the resulting mixture was stirred at 60 °C for 16 h. Unreacted $(COCl)_2$ was subsequently removed under vacuum, and the residue was redissolved in 40 mL of dry DCM. The mixture was chilled to 0 °C, and then $H_2NNHTfs$ (2.4 g, 10 mmol, 0.98 eq.) was added in a single portion followed by dry Et_3N (1.6 mL, 1.2 g, 11.5 mmol, 1.1 eq.). The cold bath was removed and the reaction stirred at room temperature for 2 h. The reaction was quenched by the addition of sat. aq. $HNaCO_3$. The resulting biphasic mixture was extracted three times with 20 mL of DCM. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain the crude product. Purification by flash column chromatography over SiO_2 (3:1 Hex:EtOAc) gave the title compound. Colorless oil, which crystallizes upon standing, 3.00 g (7.5 mmol, 74% yield).

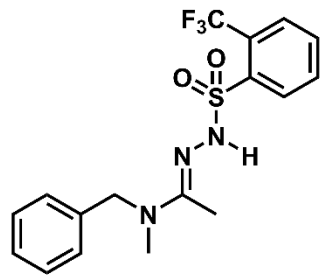
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 8.35 – 8.33 (m, 1H), 7.86 – 7.84 (m, 1H), 7.74 – 7.69 (m, 2H), 7.46 – 7.43 (m, 3H), 7.06 – 7.03 (m, 2H), 6.41 (broad, 1H), 3.02 (broad, 4H), 0.88 (t, *J* = 7.0 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 159.8, 137.2, 134.5, 132.7, 131.8, 130.5, 130.0, 129.5, 128.0 (q, *J* = 7.3 Hz), 127.8, 123.0 (d, *J* = 274.0 Hz), 42.4 (broad), 13.1 (broad).

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -58.20.

HR-ESI-TOFMS: calc. for $[C_{18}H_{20}F_3N_3O_2S]+H^+$ m/z: 400.1301; found 400.1302 (Δ = 0.3 ppm).

***N*-methyl-*N*-benzyl-*N'*-triftosyl acetamide hydrazone (1g)**



Prepared according to GP2 from 4.9 g of *N*-methyl-*N*-benzyl acetamide (30 mmol). Acetal intermediate was comprised of a 3:1 acetal:amide mixture, to which 2.35 g of $H_2NNHTfs$ (9.8 mmol) was added. Eluted with 1:1 Hex:EtOAc. Colorless oil, which crystallizes upon standing, 2.44 g (6.3 mmol, 65% yield based on $H_2NNHTfs$).

^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.47 (s, broad), 4.45 (s, 2H), 2.82 (s, 3H), 2.28 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 170.1, 137.5, 136.7, 134.2, 132.7, 131.6, 128.8, 128.2 (q, *J* = 6.5 Hz), 127.9 (q, *J* = 32.6 Hz), 127.3, 126.9, 123.2 (q, *J* = 273.8 Hz), 53.4, 36.5, 14.0.

^{19}F NMR (376 MHz, 25°C, $CDCl_3$) δ = -57.81.

HR-ESI-TOFMS: calc. for $[C_{17}H_{18}F_3N_3O_2S]+H^+$ m/z: 386.1145; found 386.1146 (Δ = 0.3 ppm).

Synthesis of potassium *N*-triftosyl amino hydrazonates

General Procedure 3: Deprotonation with potassium hydride

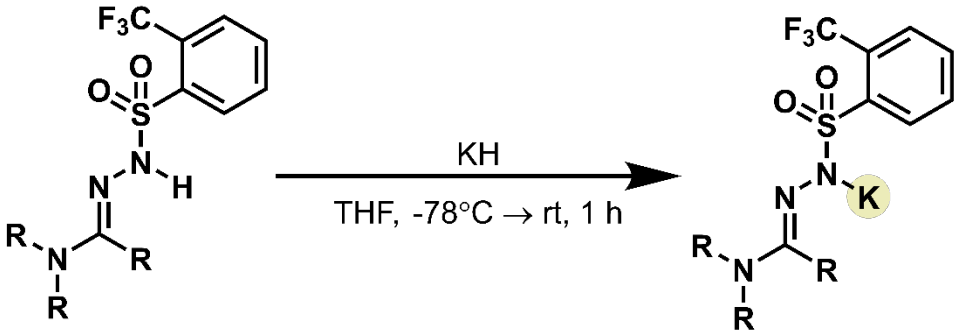
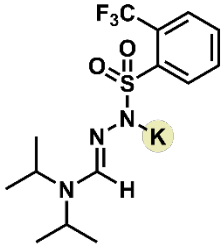


Figure S4. Synthesis of potassium hydrazonate salts.

In a glovebox, a Schlenk flask with stir bar was charged with equimolar quantities of hydrazone and KH. The flask was sealed, transferred to a Schlenk line, cycled to argon, and chilled to -78° C. Then, freshly distilled THF was slowly added via syringe (4 mL per 1 mmol of hydrazone). The resulting suspension was gently stirred for 5 minutes at low temperature, then allowed to slowly come to room temperature, at which point stirring was maintained for 1 hour longer. If necessary, additional THF was added to ensure effective stirring. Volatiles were removed under vacuum, yielding an orange-yellow residue which may present as a solid, foam, or thick oil. To obtain a free-flowing solid and remove traces of THF, the residue was treated with dry pentanes or hexanes, vigorously stirred, then dried under vacuum. Drying overnight at 60° C under vacuum yielded the potassium hydrazonate salt as a yellow solid.

Potassium *N*,*N*-diisopropyl *N'*-triftosyl formamidrazonate (2a)



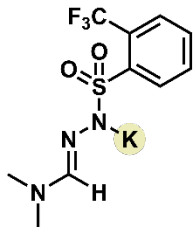
Prepared according to GP3 from 1.62 g (4.6 mmol) of the corresponding hydrazone. Yellow solid, 1.73 g (4.44 mmol, 97% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d_3) δ = 8.12 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.56 (s, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 3.72 (sept, *J* = 6.8 Hz, 2H), 1.04 (d, *J* = 6.8 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) δ = 148.2, 146.5, 132.8, 132.2, 130.2, 127.9 (q, *J* = 6.6 Hz), 127.2 (q, *J* = 31.9 Hz), 124.9 (d, *J* = 273.1 Hz), 45.8, 22.1.

^{19}F NMR (376 MHz, 25°C, ACN-d_3) δ = -57.62.

Potassium *N*,*N*-dimethyl *N'*-triftosyl formamidrazonate (2b)



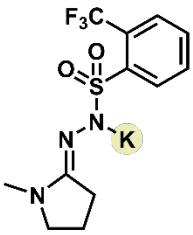
Prepared according to GP3 from 526 mg (1.8 mmol) of the corresponding hydrazone. Yellow solid, 586 mg (1.76 mmol, 98% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d$_3$) δ = 8.11 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.43 (s, 1H), 2.57 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d$_3$) δ = 151.3, 146.9, 132.5, 132.3, 130.2, 127.9 (q, *J* = 6.6 Hz), 127.3 (q, *J* = 31.8 Hz), 124.9 (d, *J* = 273.3 Hz), 38.2.

^{19}F NMR (376 MHz, 25°C, ACN-d$_3$) δ = -57.69.

***N*-methyl-*N'*-triftosyl γ-lactamidrazone (2c)**



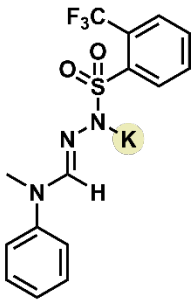
Prepared according to GP3 from 1.16 g (3.61 mmol) of the corresponding hydrazone. Bright yellow solid, 1.24 g (3.45 mmol, 96% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d$_3$) δ = 8.07 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 3.00 (t, *J* = 6.7 Hz, 2H), 2.52 (s, 3H), 2.47 (t, *J* = 7.8 Hz, 2H), 1.78 (p, *J* = 6.9 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d$_3$) δ = 159.9, 146.9, 132.5, 132.2, 130.1, 127.9 (q, *J* = 6.6 Hz), 127.3 (q, *J* = 31.9 Hz), 125.0 (q, *J* = 273.1 Hz), 53.0, 33.0, 27.2, 20.9.

^{19}F NMR (376 MHz, 25°C, ACN-d$_3$) δ = -57.67.

***N*-methyl-*N*-phenyl *N'*-triftosyl formamidrazone (2d)**



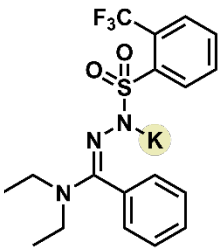
Prepared according to GP3 from 1.07 g (2.99 mmol) of the corresponding hydrazone. Faint yellow solid, 988 mg (2.50 mmol, 84% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d$_3$) δ = 8.20 (s, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.00 – 6.97 (m, 2H), 6.87 (tt, *J* = 7.3, 1.1 Hz, 1H), 3.11 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d$_3$) δ = 146.7, 146.6, 144.6, 132.6, 132.4, 130.4, 130.1, 128.0 (q, *J* = 6.6 Hz), 127.3 (q, *J* = 31.9 Hz), 124.9 (q, *J* = 273.3 Hz), 121.3, 117.04, 33.5.

^{19}F NMR (376 MHz, 25°C, ACN-d$_3$) δ = -57.68.

_N_,_N_-diethyl _N'_-triftosyl benzamidrazone (2f)



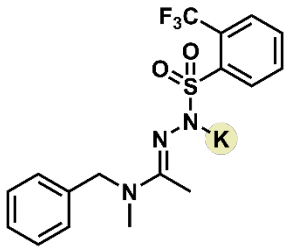
Prepared according to GP3 from 1.20 g (3.00 mmol) of the corresponding hydrazone. Bright yellow solid, 1.16 g (2.65 mmol, 88% yield).

^{1}H NMR (600 MHz, 25°C, acetone-d$_6$) δ = 8.21 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 2.95 (q, J = 6.9 Hz, 4H), 0.88 (t, J = 7.0 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, acetone-d$_6$) δ = 152.9, 147.1, 137.7, 133.1, 132.8, 131.7, 129.8, 129.7, 128.7, 128.2, 127.4 (q, *J* = 6.3 Hz), 124.9 (q, *J* = 273.8 Hz). 42.8, 13.2.

^{19}F NMR (376 MHz, 25°C, acetone-d$_6$) δ = -57.69.

_N_-methyl-_N_-benzyl _N'_-triftosyl acetamidrazone (2g)



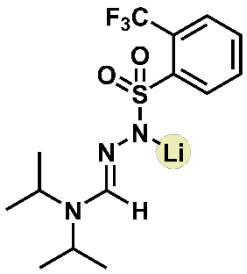
Prepared according to GP3 from 974 mg (2.53 mmol) of the corresponding hydrazone. Bright yellow solid, 1.03 g (2.43 mmol, 96% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d$_3$) δ = 8.05 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.12 (m, 5H), 4.22 (s, 2H), 2.54 (s, 3H), 1.96 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d$_3$) δ = 154.1, 146.3, 140.8, 132.7, 132.2, 130.2, 129.2, 128.5, 127.9 (q, *J* = 6.3 Hz), 127.1 (q, *J* = 31.6 Hz), 125.0 (q, *J* = 273.5 Hz), 54.4, 36.5, 13.3.

^{19}F NMR (376 MHz, 25°C, ACN-d$_3$) δ = -57.67.

Lithium _N_,_N_-diisopropyl _N'_-triftosyl formamidrazonate (2a-Li)



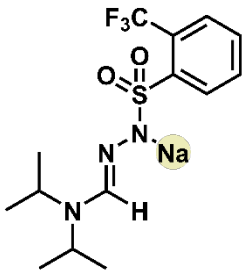
Prepared according to GP3, but substituting $LiNH_2$ for KH, from 351 mg (1.00 mmol) of the corresponding hydrazone. Off-white solid, 328 mg (0.92 mmol, 92% yield).

^{1}H NMR (500 MHz, 25°C, ACN-d$_3$) δ = 8.07 – 8.06 (m, 1H), 7.91 – 7.89 (m, 1H), 7.80 (s, 1H), 7.73 – 7.71 (m, 2H), 7.71, 3.76 (sept, *J* = 6.7 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d$_3$) δ = 157.6 (broad), 139.2 (broad), 132.6, 132.3, 132.1, 128.0 (q, *J* = 6.4 Hz), 127.2 (q, *J* = 32.6 Hz), 123.3 (q, *J* = 273.3 Hz), 46.0, 20.8.

^{19}F NMR (376 MHz, 25°C, ACN-d$_3$) δ = -57.86.

Sodium *N,N*-diisopropyl *N'*-triftosyl formamidrazonate (2a-Na)



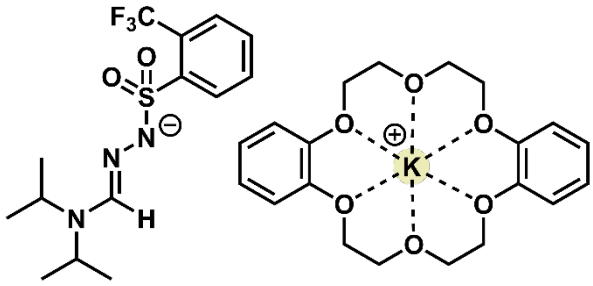
Prepared according to GP3, but substituting NaH for KH, from 351 mg (1.00 mmol) of the corresponding hydrazone. A thick suspension formed, requiring the addition of further THF as necessary to ensure efficient stirring. Light yellow solid, 306 mg (0.82 mmol, 82% yield).

^{1}H NMR (500 MHz, 25°C, acetone-d_6) δ = 8.24 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 3.77 (sept, *J* = 6.8 Hz, 2H), 1.04 (d, *J* = 6.7 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, DMSO-d_6) δ = 147.3 (broad), 143.9 (broad), 131.2, 130.9, 128.6, 126.4 (q, *J* = 6.4 Hz), 125.8 (q, *J* = 31.8 Hz), 123.8 (d, *J* = 274.3 Hz), 44.5, 21.7.

^{19}F NMR (376 MHz, 25°C, acetone-d_6) δ = -57.49.

Potassium(dibenzo-18-crown-6) *N,N*-diisopropyl *N'*-triftosyl formamidrazonate (2a')



Dissolve **1a-K** (80 mg, 0.21 mmol, 1 eq.) in 2 mL THF, then add a solution of dibenzo-18-crown-6 (76 mg, 0.21 mmol, 1 eq.). Within 5 minutes, a thick yellow suspension formed, which was fully dissolved in THF (*ca.* 20 mL total). X-ray diffraction quality crystals were obtained by slow evaporation of this THF solution under an argon atmosphere, yielding the product as yellow crystalline blocks, 151 mg (0.206 mmol, 98% yield).

^{1}H NMR (600 MHz, 25°C, ACN-d_3) δ = 8.16 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.98 – 6.94 (m, 8H), 4.17 – 4.16 (m, 8H), 3.97 – 3.96 (m, 8H), 3.72 (sept, *J* = 6.8 Hz, 2H). 3.64, 1.04 (d, *J* = 6.7 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, ACN-d_3) δ = 149.0 (broad), 148.1 (broad), 144.9, 132.7, 131.8, 129.2, 127.5 (q, *J* = 6.8 Hz), 127.4 (d, *J* = 31.6 Hz), 125.1 (d, *J* = 273.5 Hz), 112.4, 69.9, 68.1, 45.8, 22.2.

^{19}F NMR (376 MHz, 25°C, ACN-d_3) δ = -57.34.

m.p.: 119.1 – 123.5 °C

3) Photochemistry and Carbene Trapping Experiments

Photochemical experiments were performed using the apparatus shown in **Figure S5.** Photochemical reaction apparatus.Cardboard and a clamp were used to suspend four microwave reaction vials above a magnetic stirring plate and between an array of four light sources. Each light source was centered on a different reaction vial and placed at a 6 cm distance. A commercial box fan was used to provide air cooling.

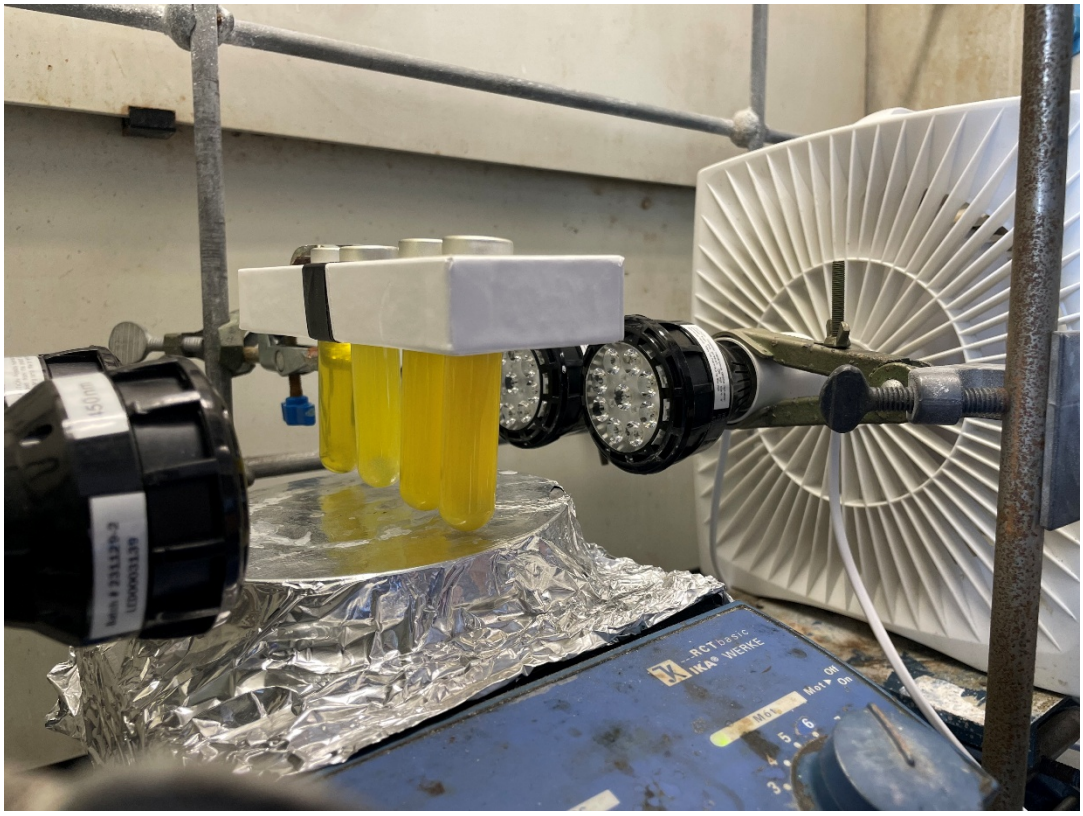
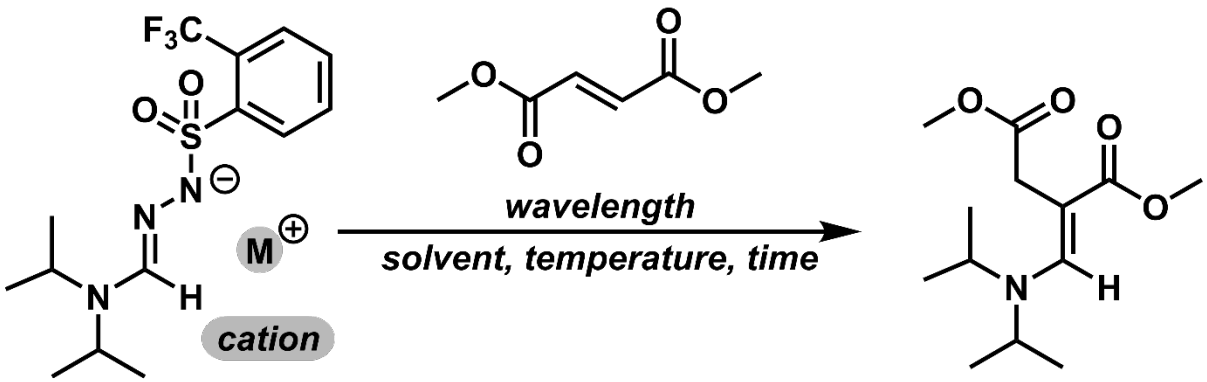


Figure S5. Photochemical reaction apparatus.

Optimization of photolysis conditions

In a glove box, a 10-mL microwave reaction vial was charged with 0.1 mmol of **2a**, 0.1 mmol of dimethyl fumarate, a stir bar, and 2 mL of dry solvent. The vial was sealed with a crimped cap and subjected to the specified conditions (**Figure S6**).

To analyze the reaction, the vial was opened and ~100 µL of an internal standard solution (~0.1 M hexamethylbenzene in benzene) was added while stirring. The reaction mixture was then diluted with 10 mL of hexanes. The resultant suspension was vacuum filtered through a 1-cm pad of Celite, which was subsequently rinsed with 5 mL of hexanes. The filtrate was concentrated under vacuum without heating to yield a residue which was fully dissolved in C_6D_6 for analysis by ^1H NMR.



Trial	Cation	Solvent	Wavelength	Temperature	Time	Yield
1	K	Hexane	450 nm	ambient	48 h	14%
2	K	Benzene	450 nm	ambient	48 h	38%
3	K	Toluene	450 nm	ambient	48 h	19%
4	K	Et_2O	450 nm	ambient	48 h	46%
5	K	THF	450 nm	ambient	48 h	13%
6	K	Et_2O	450 nm	ambient	24 h	20%
7	K	Et_2O	450 nm	ambient	72 h	78%
8	Li	Et_2O	450 nm	ambient	72 h	0%
9	Na	Et_2O	450 nm	ambient	72 h	12%
10	[K(crown)]*	Et_2O	450 nm	ambient	72 h	0%
11	K	Et_2O	dark	ambient	72 h	0%
12	K	Et_2O	dark	reflux	72 h	0%
13	K	Et_2O	365 nm	ambient	72 h	0%

Figure S6. Optimization of photolysis conditions and control experiments.

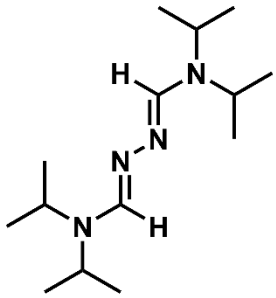
Carbene trapping experiments

General Procedure 4: Photolysis of potassium hydrazonate salts

In a glovebox, a 10-mL microwave reaction vial was charged with 0.5 mmol of hydrazonate salt, a stir bar, and 10 mL of dry Et_2O. If generating the salt *in situ*, the appropriate hydrazone was added, followed by 1 eq. of oil-free KH. Stirring for 10 minutes yields a solution of the hydrazonate salt. Then, the trapping agent (if used) was added. The vial was sealed with a crimped cap and irradiated at 450 nm while stirring for 72 h.

Once finished, the vial was carefully unsealed and gently stirred to liberate dissolved gases. The reaction mixture was then added to 20 mL of stirred hexanes. The resultant suspension was vacuum filtered through a 1-cm pad of celite, which was subsequently rinsed with 10 mL of hexanes. The filtrate was concentrated on a rotavap without heating to yield the crude product, which was further purified as necessary.

bis(*N*,*N*-diisopropylformamide) azine (3a)



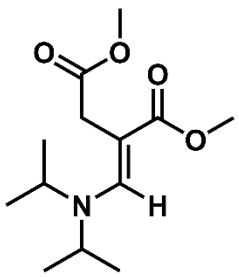
Prepared according to GP4 from 194 mg of **2a** (0.5 mmol). Trapping agent: none. Purification: The crude product was dissolved in 2 mL of pentanes and filtered through glass microfiber. Concentration under vacuum, followed by sublimation of the residue, yielded the azine. Off-white solid, 60 mg (0.24 mmol, 95% yield).

^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 8.32 (s, 2H), 3.87 (broad, 4H), 3.24 (broad, 2H), 1.01 (d, J = 6.9 Hz, 24H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 150.5, 45.5, 22.0.

HR-ESI-TOFMS: calc. for $[C_{14}H_{30}N_4]+H^+$ m/z: 255.2543; found 255.2545 (Δ = 0.8 ppm).

dimethyl 2-((diisopropylamino)methylene)succinate (4a)



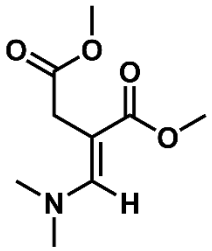
Prepared according to GP4 from 194 mg of **2a** (0.5 mmol). Trapping agent: 1 eq. of dimethyl fumarate (72 mg, 0.5 mmol). Purification: The crude product was purified by column chromatography over silica gel, eluting with 1:1 Et_2O:Hexane. Concentration under vacuum yielded the product. Pale yellow oil, 94 mg (0.37 mmol, 73% yield).

^{1}H NMR (500 MHz, 25°C, $CDCl_3$) δ = 7.62 (s, 1H), 3.78 (sept, J = 6.7 Hz, 2H), 3.66 (s, 3H), 3.66 (s, 3H), 3.43 (s, 2H), 1.19 (d, *J* = 6.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) δ = 173.7, 171.0, 144.5, 88.3, 52.0, 51.3, 47.9, 32.6, 22.6.

HR-ESI-TOFMS: calc. for $[C_{13}H_{23}NO_4]+H^+$ m/z: 258.1700; found 258.1702 (Δ = 0.8 ppm).

dimethyl 2-((dimethylamino)methylene)succinate (4b)



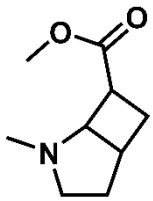
Prepared according to GP4 from 170 mg **2b** (0.5 mmol). Trapping agent: 1 eq. of dimethyl fumarate (72 mg, 0.5 mmol). Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C overnight, then filtered through glass microfiber. Concentration under vacuum yielded the product. Pale yellow oil, 80 mg (0.40 mmol, 80% yield).

^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 7.47 (s, 1H), 3.61 (s, 2H), 3.59 (s, 3H), 3.39 (s, 3H), 2.19 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 173.6, 170.1, 150.2, 90.8, 51.4, 51.0, 42.1, 31.6.

HR-ESI-TOFMS: calc. for $[C_9H_{15}NO_4]+Na^+$ m/z: 224.0893; found 224.0894 (Δ = 0.4 ppm).

methyl 2-methyl-2-azabicyclo[3.2.0]heptane-7-carboxylate (5c)



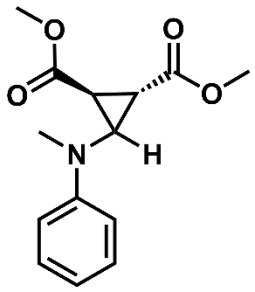
Prepared according to GP4 from 180 mg **2c** (0.5 mmol). Trapping agent: 5 eq. of methyl acrylate (215 mg, 2.5 mmol). Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C for 2 h, then filtered to remove unreacted hydrazonate salt. Attempts at further purification (e.g., distillation, column chromatography) led to decomposition or failed to improve purity. Pale yellow oil, 73 mg (0.43 mmol, 86% yield).

^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 3.81 (dd, *J* = 6.7, 3.8 Hz, 1H), 3.38 (s, 3H), 2.98 – 2.94 (m, 1H), 2.73 (dd, *J* = 9.4, 7.1 Hz, 1H), 2.71 – 2.68 (m, 1H), 2.57 – 2.53 (m, 1H), 2.26 (s, 3H), 1.27 (ddd, *J* = 13.1, 9.7, 4.0 Hz, 1H), 1.18 (dd, *J* = 12.4, 5.8 Hz, 1H). *One peak overlaps with the singlet at 2.26 ppm, as identified by 2D NMR, accounting for the final proton.*

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 175.1 (**C**O_2Me), 67.8 (**C**H), 52.5 (**C**H_2), 51.2 (O**C**H_3), 36.3 (**C**H), 35.9 (N**C**H_3), 34.5 (**C**H), 31.7 (**C**H_2), 25.2 (**C**H_2).

HR-ESI-TOFMS: calc. for $[C_9H_{15}NO_2]+H^+$ m/z: 170.1176; found 170.1175 (Δ = -0.6 ppm).

dimethyl 3-(methyl(phenyl)amino)cyclopropane-1,2-dicarboxylate (6d)



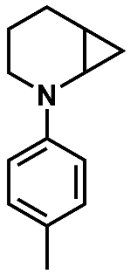
Prepared according to GP4 from 198 mg **2d** (0.5 mmol). Trapping agent: 1 eq. of dimethyl fumarate (72 mg, 0.5 mmol). Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C overnight, then filtered through glass microfiber. Concentration under vacuum yielded the product. Pale yellow oil, 126 mg (0.48 mmol, 96% yield).

^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 7.17 (t, J = 7.4 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 7.7 Hz, 2H), 3.28 (s, 3H), 3.24 (dd, J = 7.5 Hz, 4.6 Hz, 1H) 3.07 (s, 3H), 2.88 (dd, J = 5.4 Hz, 4.5 Hz, 1H) 2.61 (s, 3H), 2.60 (dd, J = 7.5 Hz, 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 170.5, 167.7, 149.2, 129.2, 118.5, 113.9, 51.8, 51.66, 47.3, 38.4, 32.1, 29.3.

HR-ESI-TOFMS: calc. for $[C_{14}H_{17}NO_4]+Na^+$ m/z: 264.1230; found 264.1231 (Δ = 0.4 ppm).

2-(p-tolyl)-2-azabicyclo[4.1.0]heptane (7e)



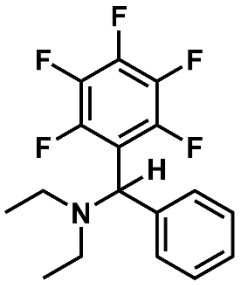
Prepared according to GP4 from **2e**, which was generated *in situ* by stirring 160 mg of **1e** (0.38 mmol), and 1.05 eq. of KH in Et_2O for 10 minutes at room temperature. Trapping agent: none. Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C overnight, then filtered through glass microfiber. Concentration under vacuum yielded the product. Pale yellow oil, 58 mg (0.31 mmol, 81% yield).

^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 7.17 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.03 – 3.00 (m, 1H), 2.67 (ddd, *J* = 11.5, 8.3, 3.5 Hz, 1H), 2.31 – 2.26 (m, 1H), 2.29 (s, 3H), 1.69 – 1.64, 1.31 – 1.24, 1.20 – 1.14, 0.96 – 0.90, 0.59 (dt, *J* = 9.5, 5.3 Hz, 1H), 0.03 – 0.00 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 148.2, 129.9, 125.1, 112.3, 43.2, 30.2, 22.9, 22.0, 20.6, 13.4, 13.3.

HR-ESI-TOFMS: calc. for $[C_{13}H_{12}N]+H^+$ m/z: 188.1434; found 188.1433 (Δ = -0.5 ppm).

***N*-ethyl-*N*-((perfluorophenyl)(phenyl)methyl)ethanamine (8f)**



Prepared according to GP4 from 218 mg of **2f** (0.5 mmol). Trapping agent: 10 eq. of pentafluorobenzene (840 mg, 5.0 mmol). Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C overnight, filtered through glass microfiber, then eluted through a column of neutral alumina using hexanes. Concentration under vacuum yielded the product. Pale yellow oil, 135 mg (0.41 mmol, 82% yield).

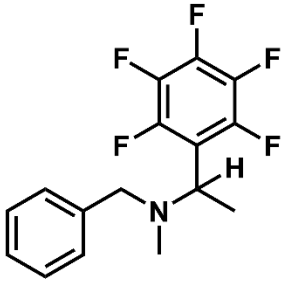
^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 7.49 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 5.27 (s, 1H), 2.56 (m, 2H), 2.28 (m, 2H), 0.88 (t, J = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 145.5 (d, *J* = 248.6 Hz), 141.2, 140.4 (d, *J* = 252.2 Hz), 138.0 (d, *J* = 251.3 Hz), 129.1, 128.1, 127.9, 115.6 (t, *J* = 14.8 Hz), 61.4, 43.5, 11.6.

^{19}F NMR (565 MHz, 25°C, C_6D_6) δ = -139.25 (d, J = 16.1 Hz, 2F), -155.41 (t, J = 21.8 Hz, 1F), -161.95 – -162.04 (m, 2F).

HR-ESI-TOFMS: calc. for $[C_{13}H_{17}NF_5]+Na^+$ m/z: 330.1276; found 330.1278 (Δ = 0.6 ppm).

***N*-benzyl-*N*-methyl-1-(perfluorophenyl)ethan-1-amine (8g)**



Prepared according to GP4 from 212 mg of **2g** (0.5 mmol). Trapping agent: 10 eq. of pentafluorobenzene (840 mg, 5.0 mmol). Purification: The crude product was dissolved in 2 mL of pentanes, stored at -4 °C overnight, filtered through glass microfiber, then eluted through a column of neutral alumina using hexanes. Concentration under vacuum yielded the product. Pale yellow oil, 110 mg (0.35 mmol, 70% yield).

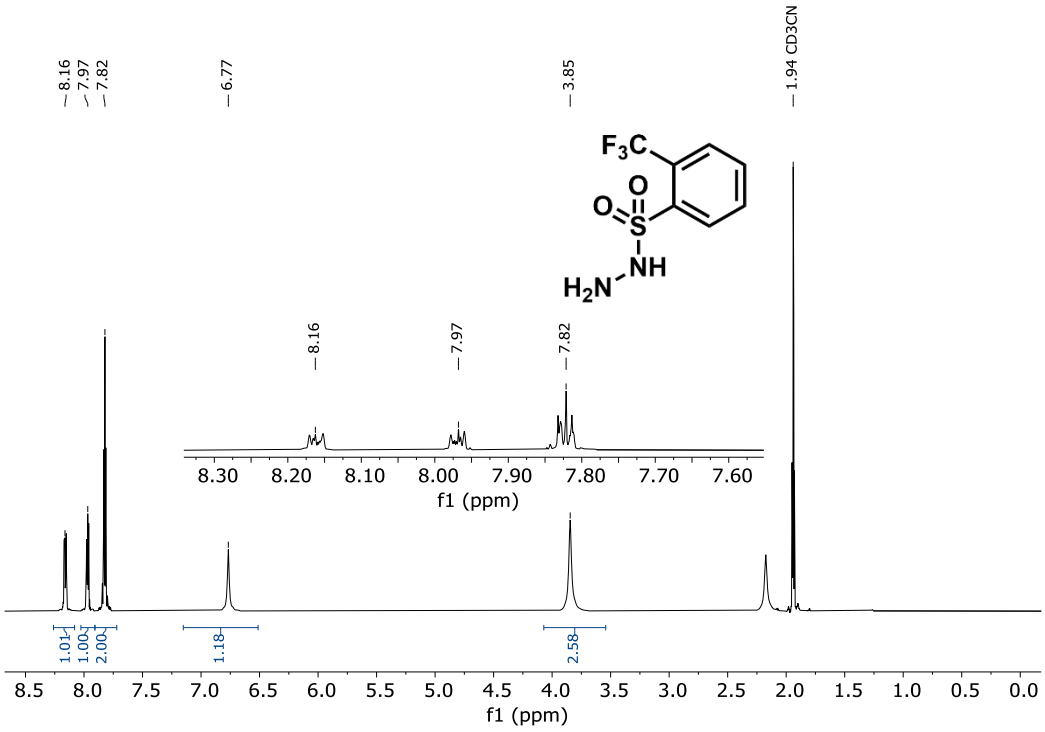
^{1}H NMR (600 MHz, 25°C, C_6D_6) δ = 7.29 (d, J = 7.8 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 3.99 (q, J = 7.2 Hz, 1H), 3.37 (d, J = 13.4 Hz, 1H), 3.20 (d, J = 13.3 Hz, 1H), 1.93 (s, 3H), 1.31 (d, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) δ = 145.6 (d, *J* = 245.9 Hz), 140.2 (d, *J* = 252.2 Hz), 139.8, 137.7 (d, *J* = 250.4 Hz), 128.8, 128.6, 127.4, 114.8 (t, *J* = 17.1 Hz), 59.1, 54.8, 37.8, 17.2.

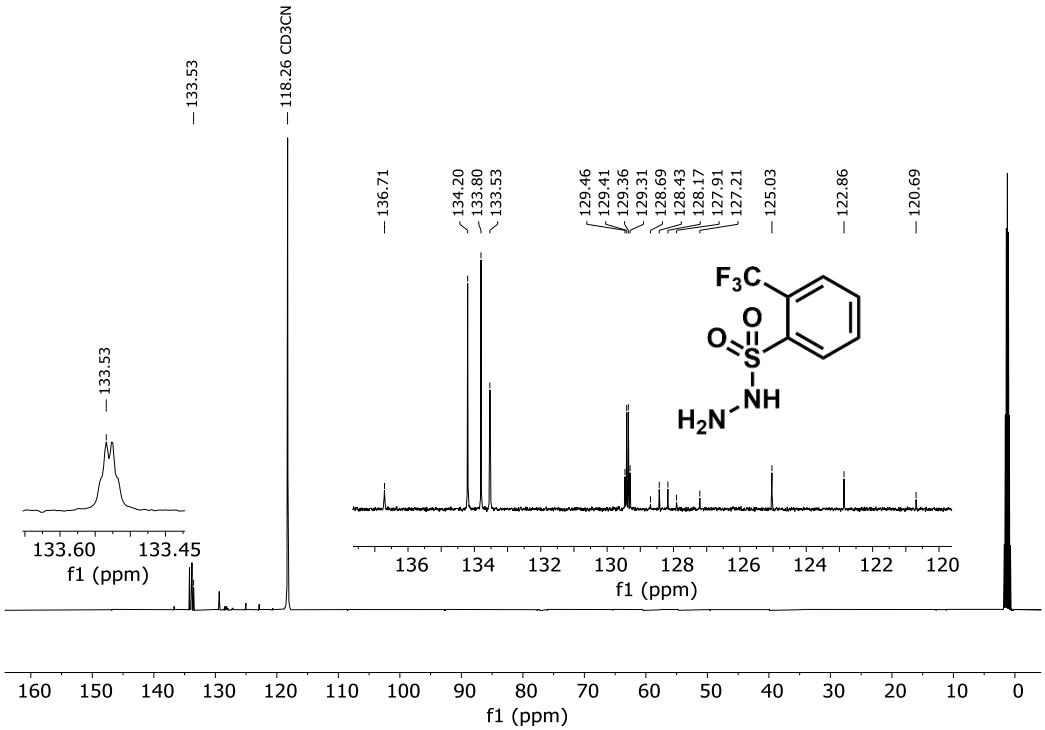
^{19}F NMR (565 MHz, 25°C, C_6D_6) δ = -139.88 (d, *J* = 15.1 Hz, 2F), -155.91 (t, *J* = 22.1 Hz, 1F), -162.40 – -162.49 (m, 2F).

HR-ESI-TOFMS: calc. for $[C_{16}H_{14}F_5N]+H^+$ m/z: 316.11195; found 316.1117 (Δ = -0.6 ppm).

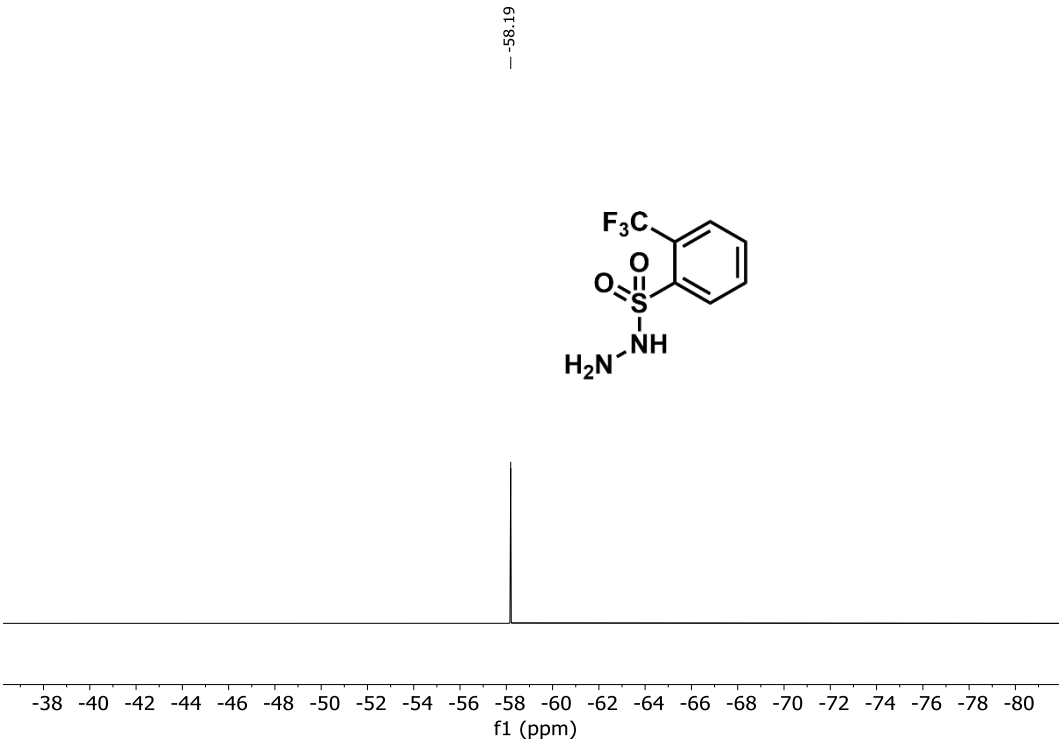
4) NMR Characterization



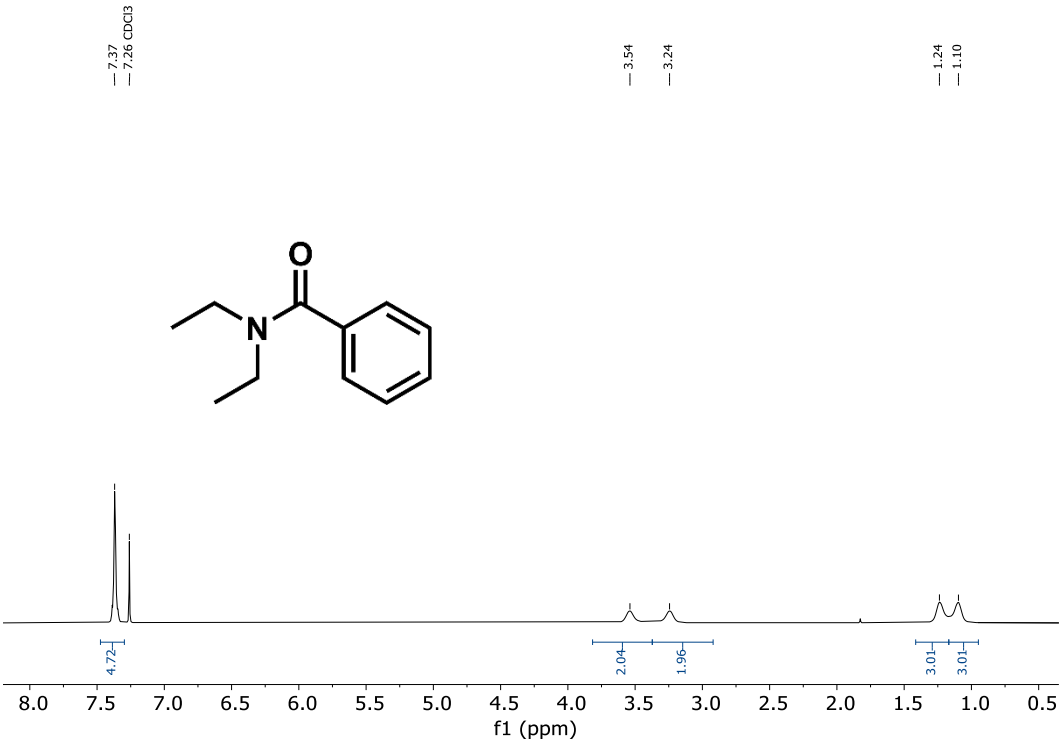
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **H_2NNHTfs**



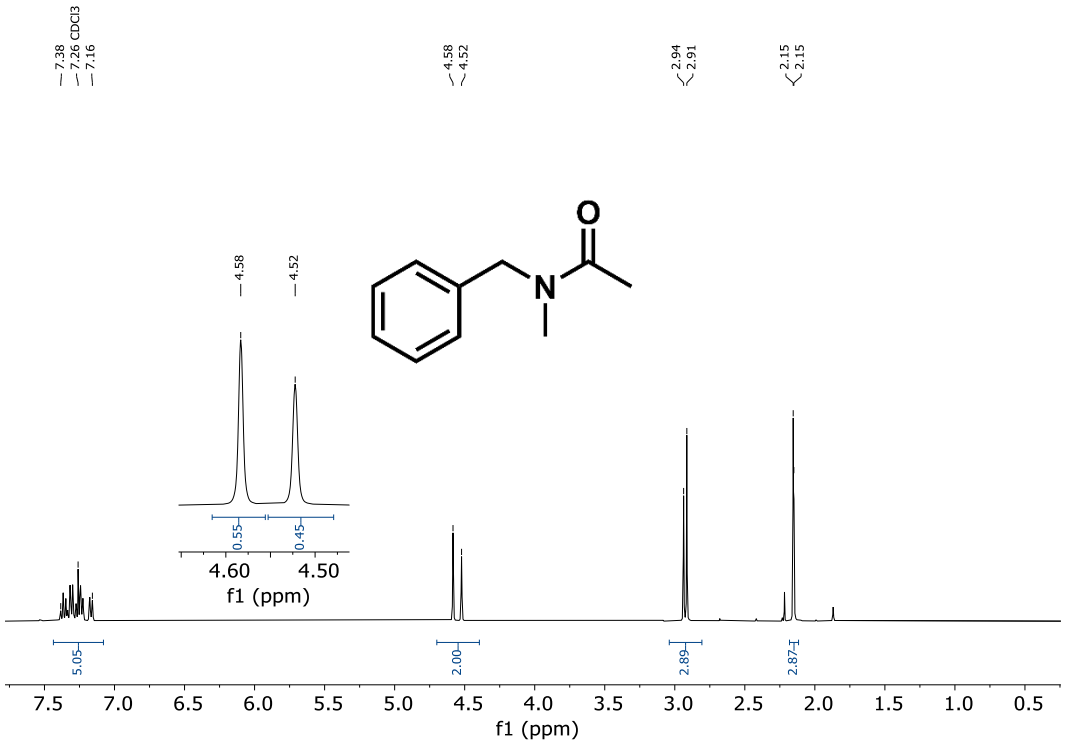
^{13}C{1H} NMR (126 MHz, 25°C, ACN-d_3) of **H_2NNHTfs**



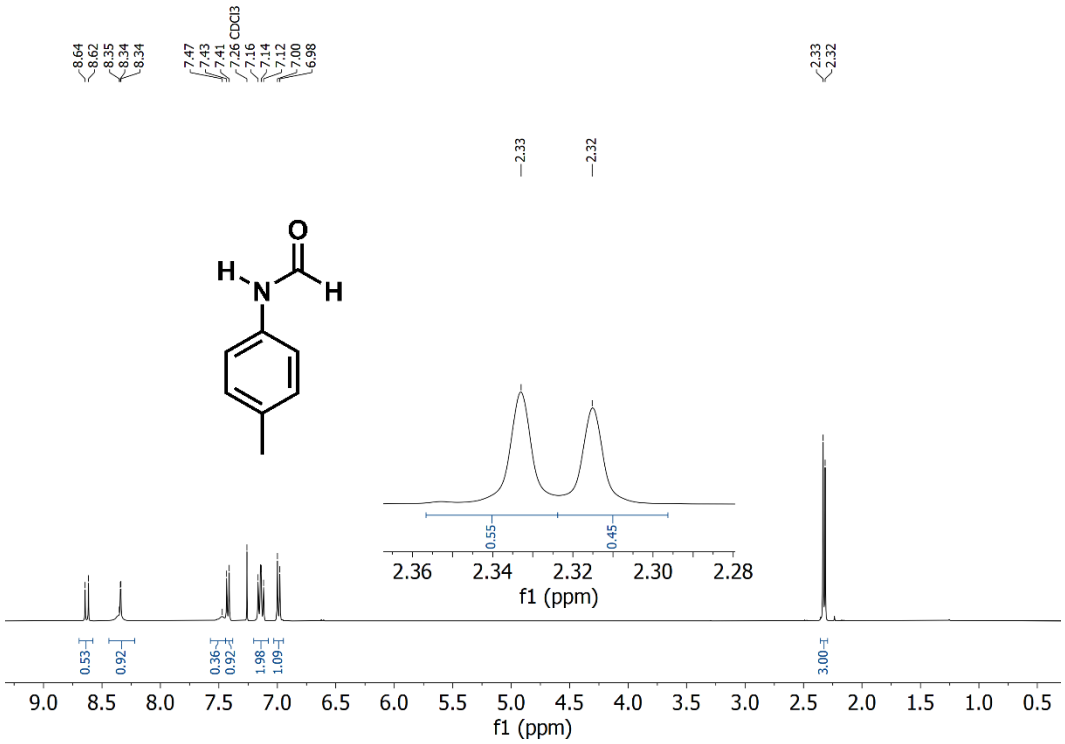
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **H_2NNHTfs**



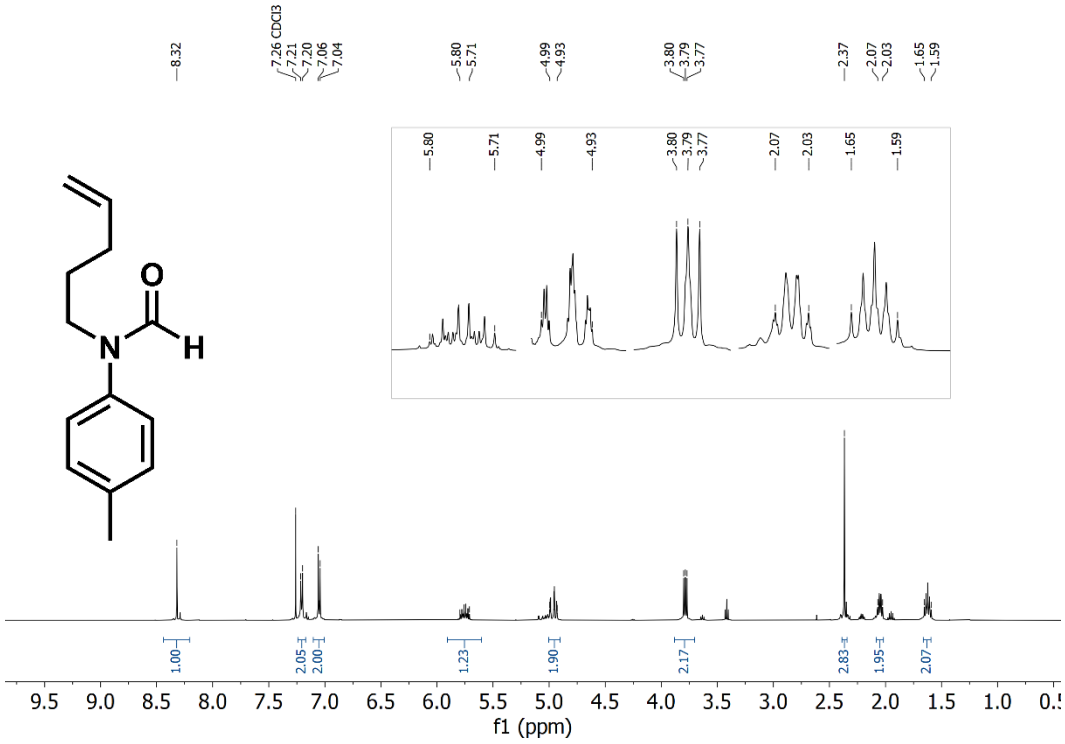
^{1}H NMR (400 MHz, 25°C, $CDCl_3$) of ***N*,*N*-diethylbenzamide**



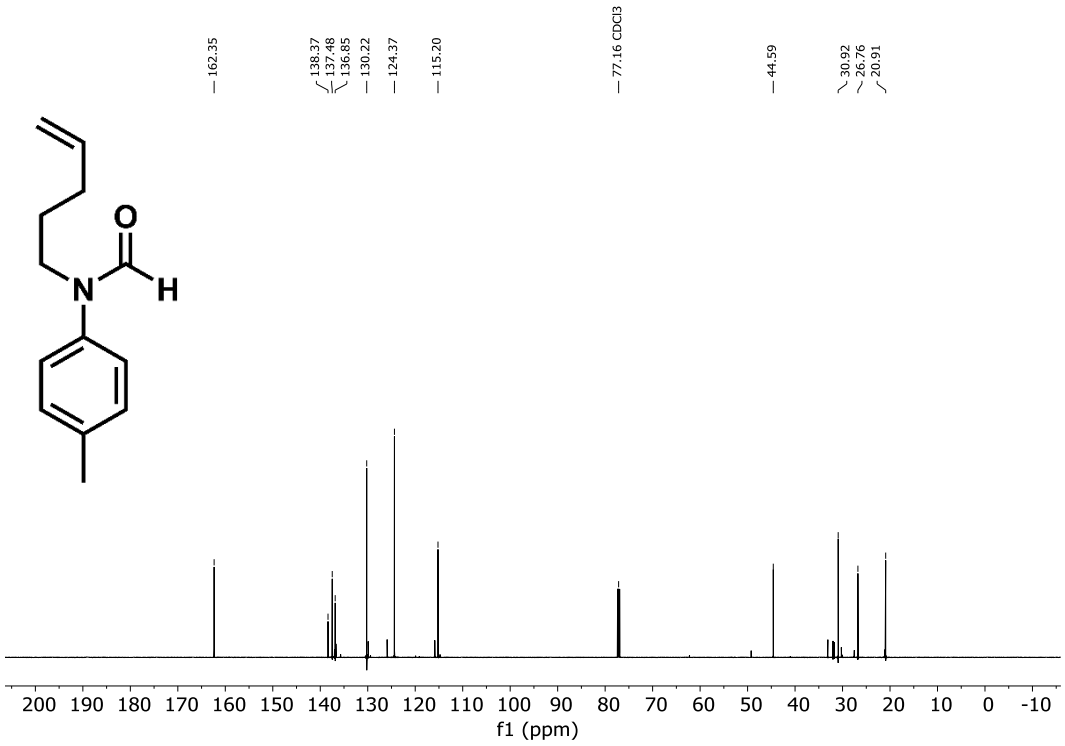
^{1}H NMR (400 MHz, 25°C, $CDCl_3$) of ***N*-benzyl-*N*-methyl acetamide**



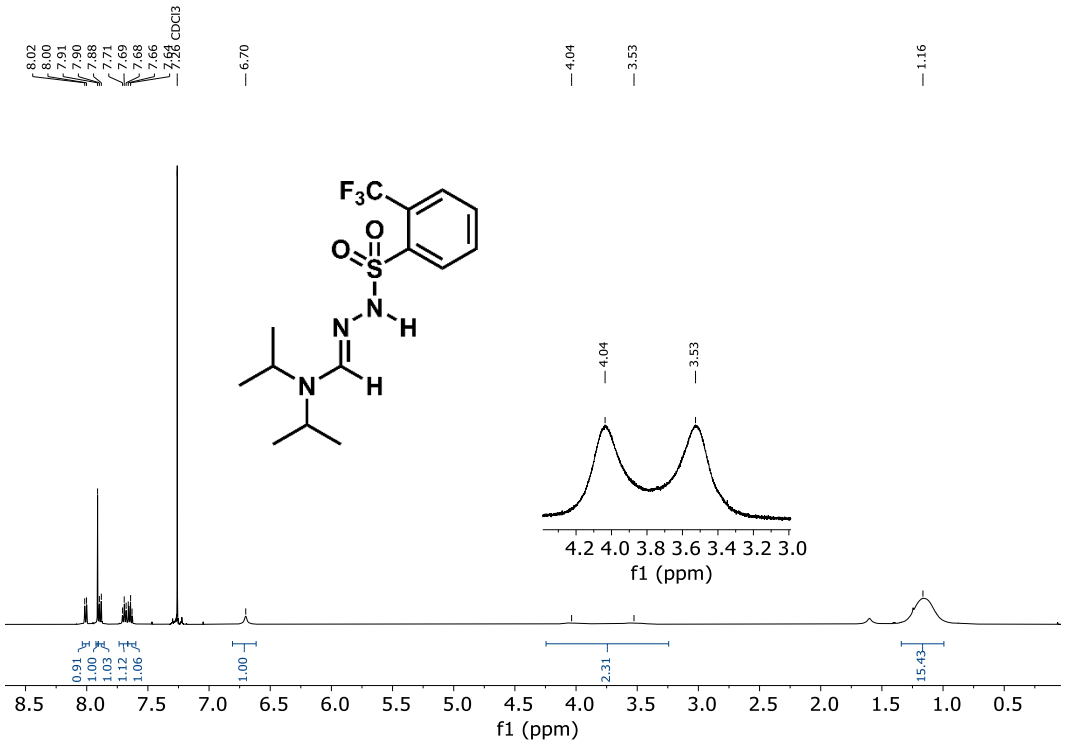
^{1}H NMR (400 MHz, 25°C, $CDCl_3$) of **p-tolyl formamide**



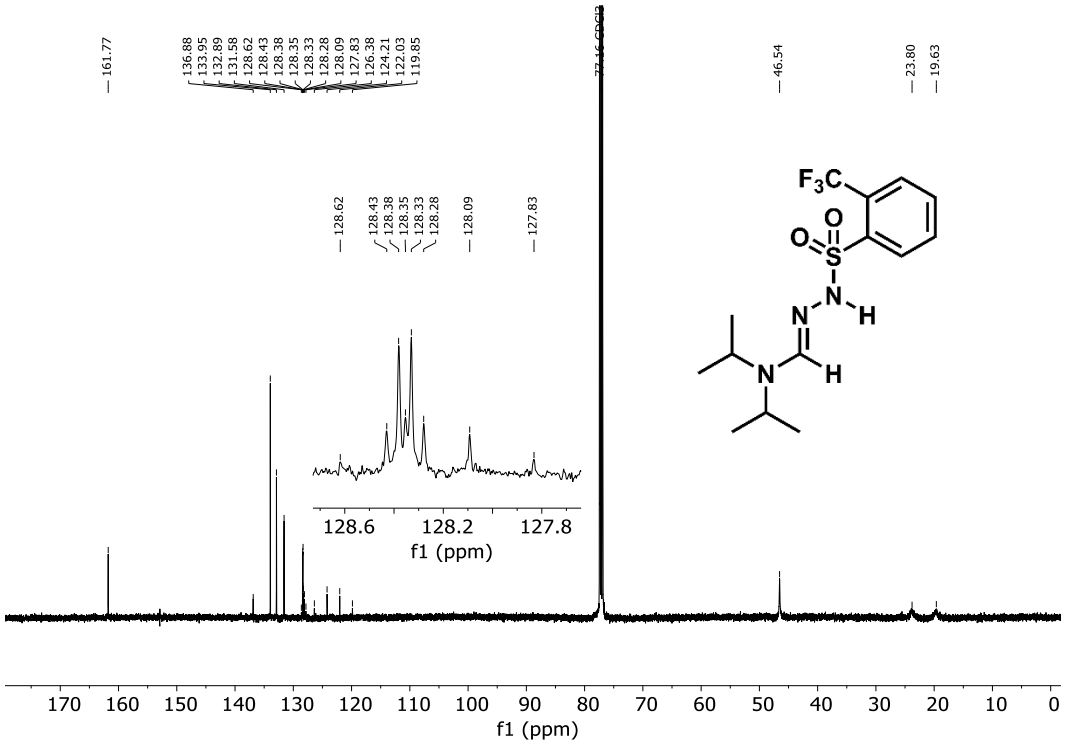
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of ***N*-(pent-4-en-1-yl)-*N*-(p-tolyl)formamide**



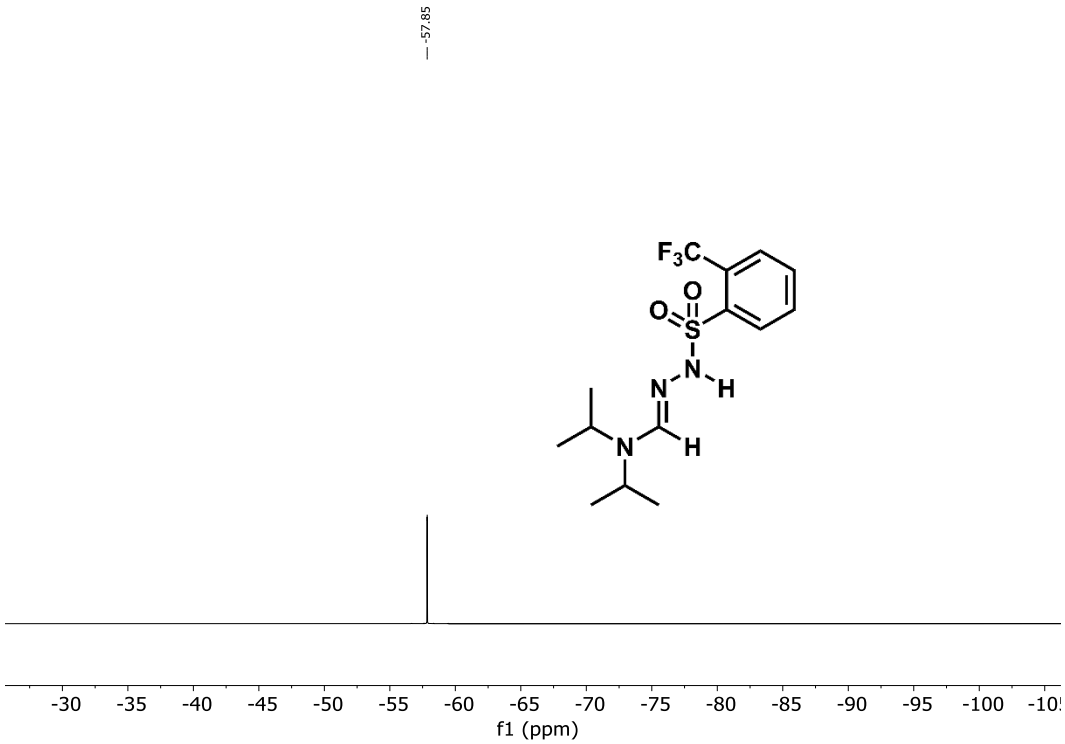
^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) of ***N*-(pent-4-en-1-yl)-*N*-(p-tolyl)formamide**



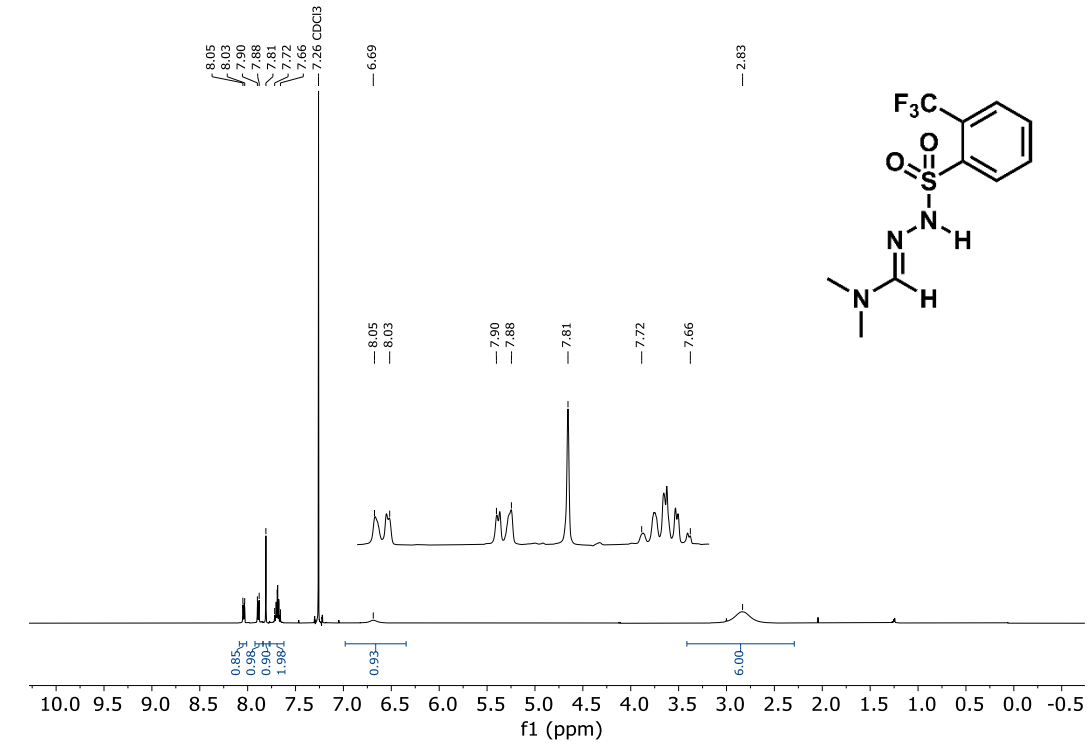
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1a**



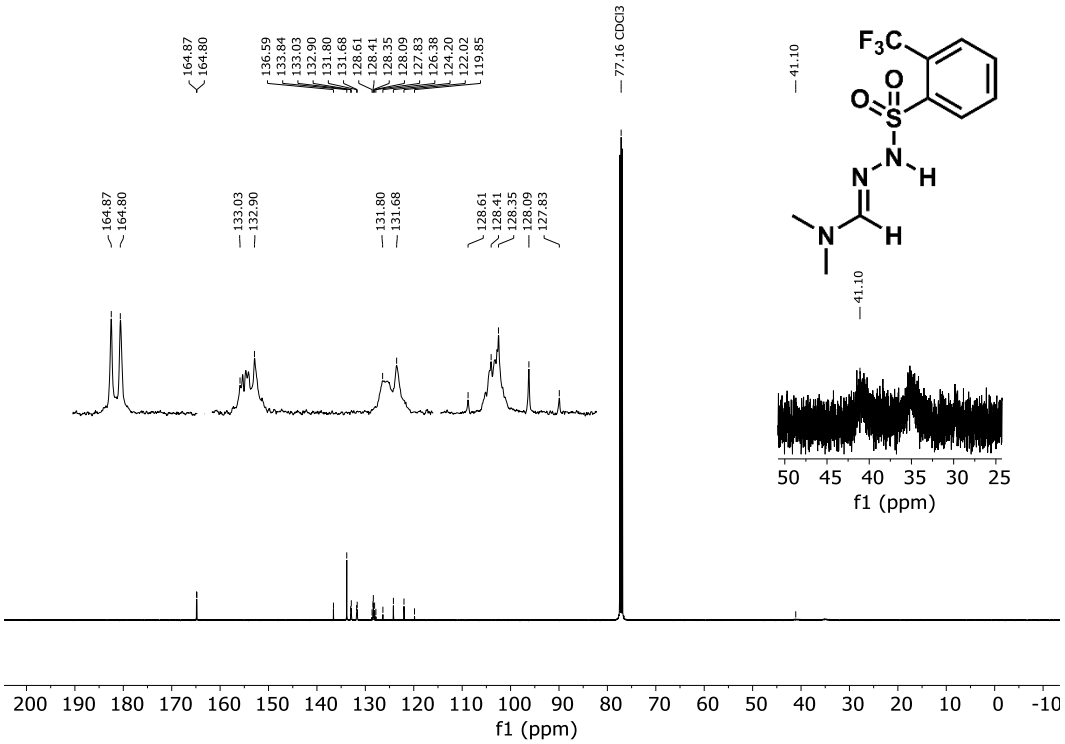
^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) of **1a**



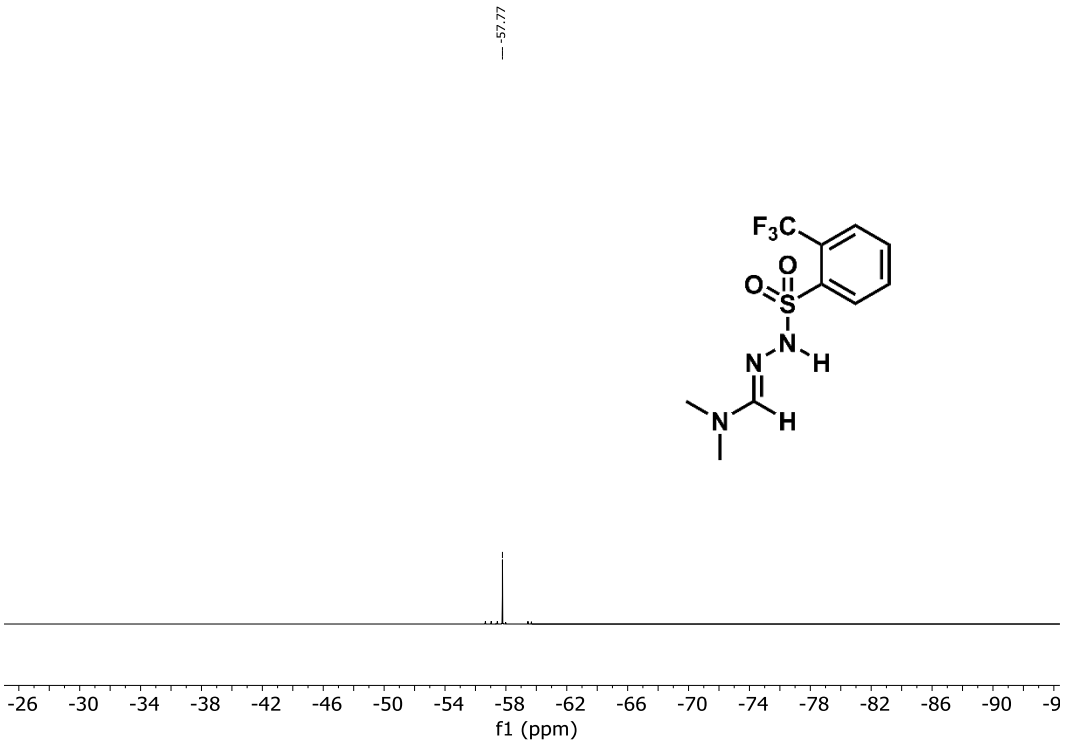
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1a**



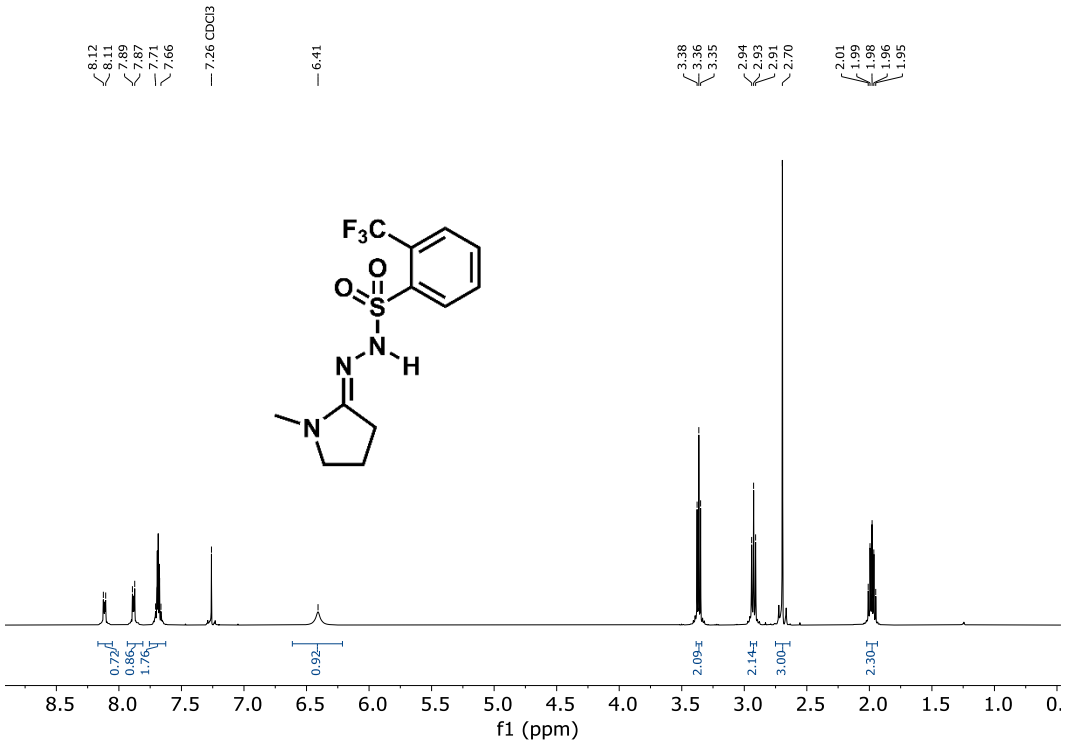
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1b**



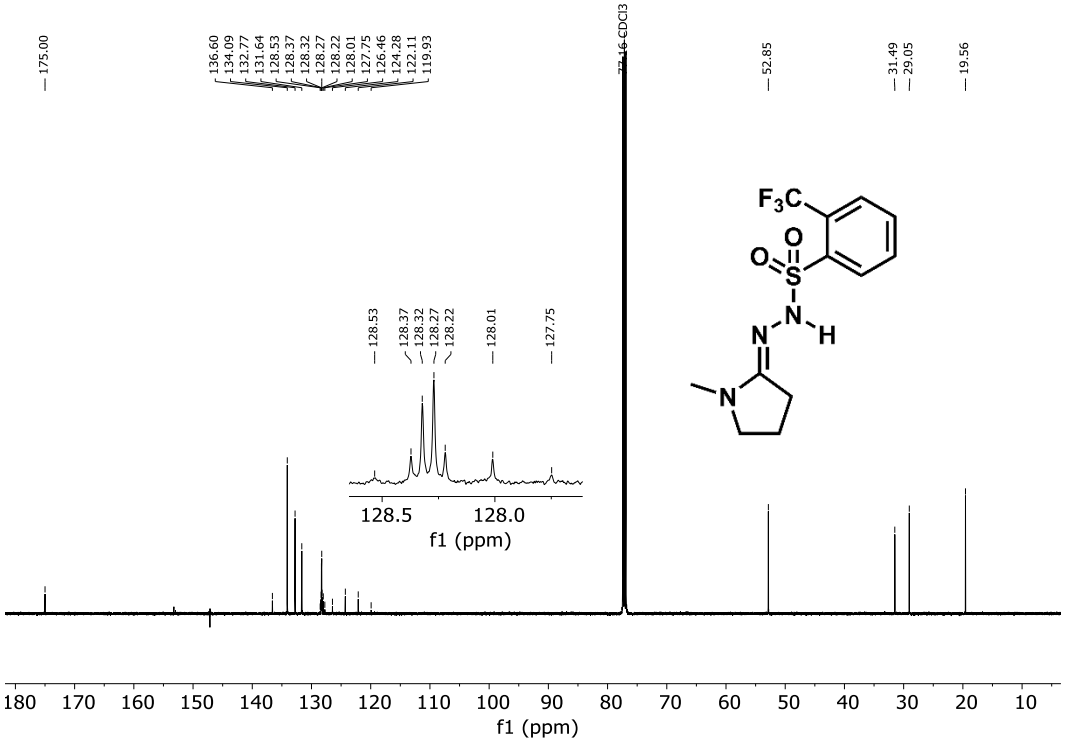
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, $CDCl_3$) of **1b**



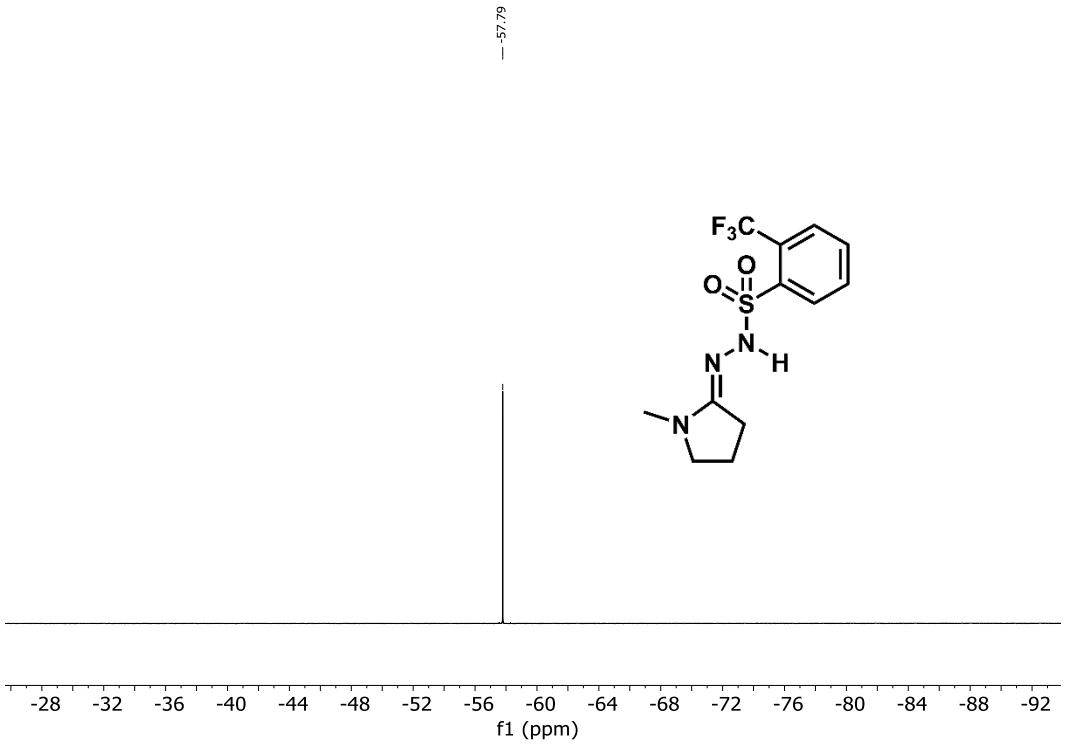
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1b**



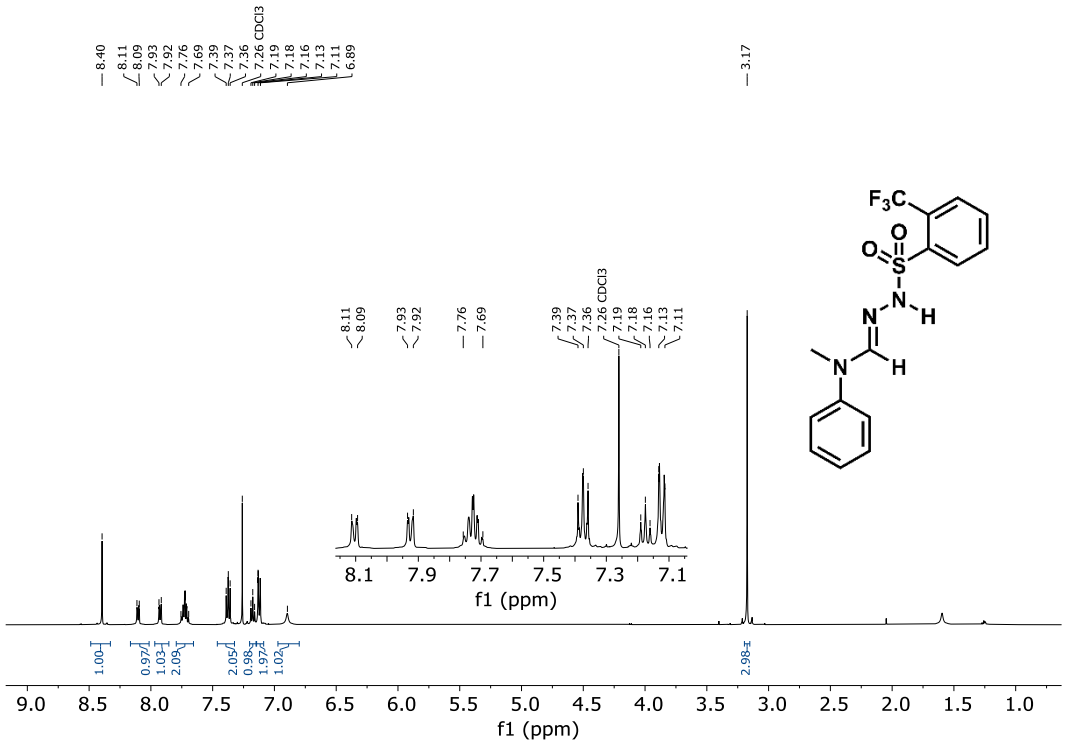
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1c**



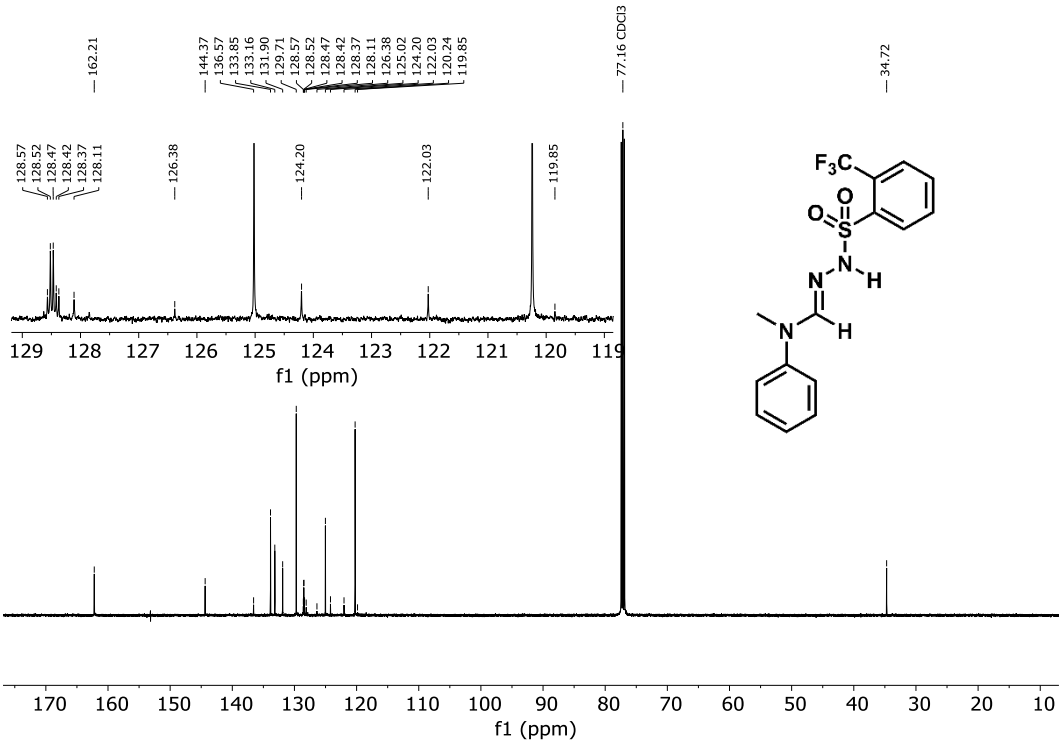
^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) of **1c**



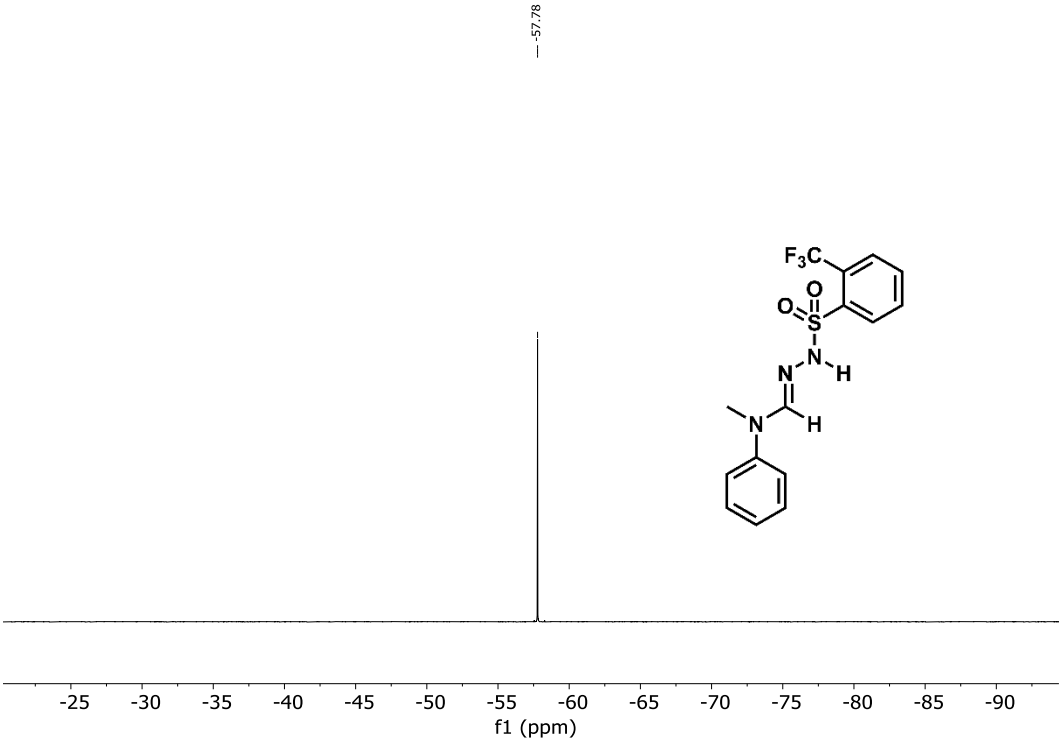
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1c**



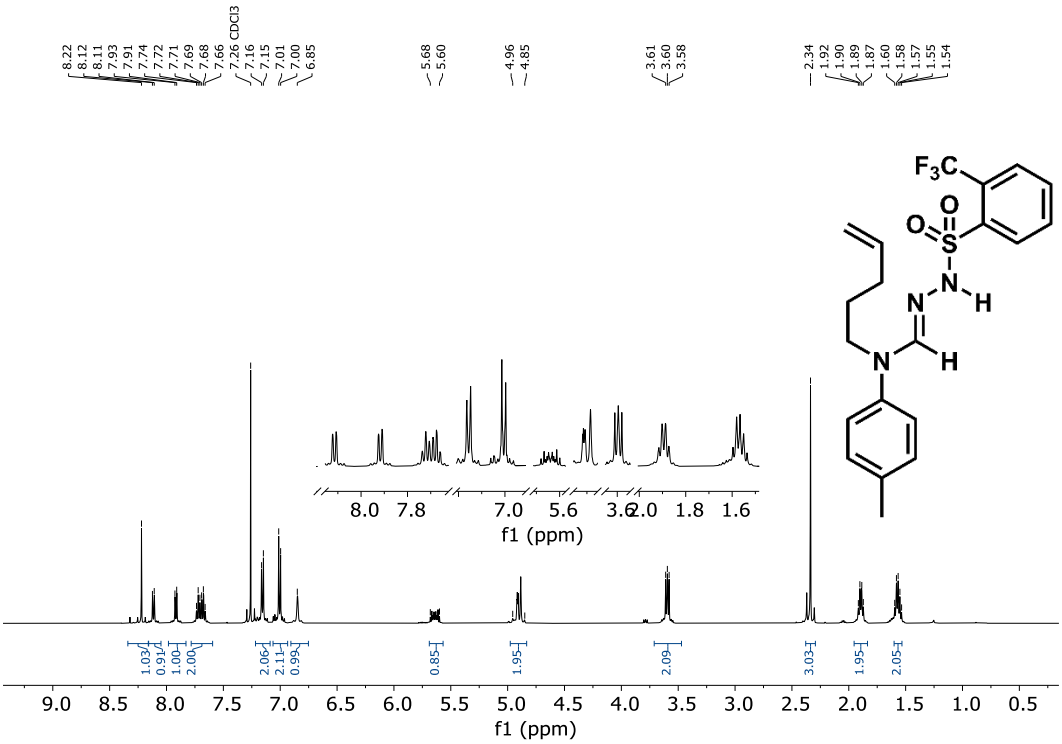
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1d**



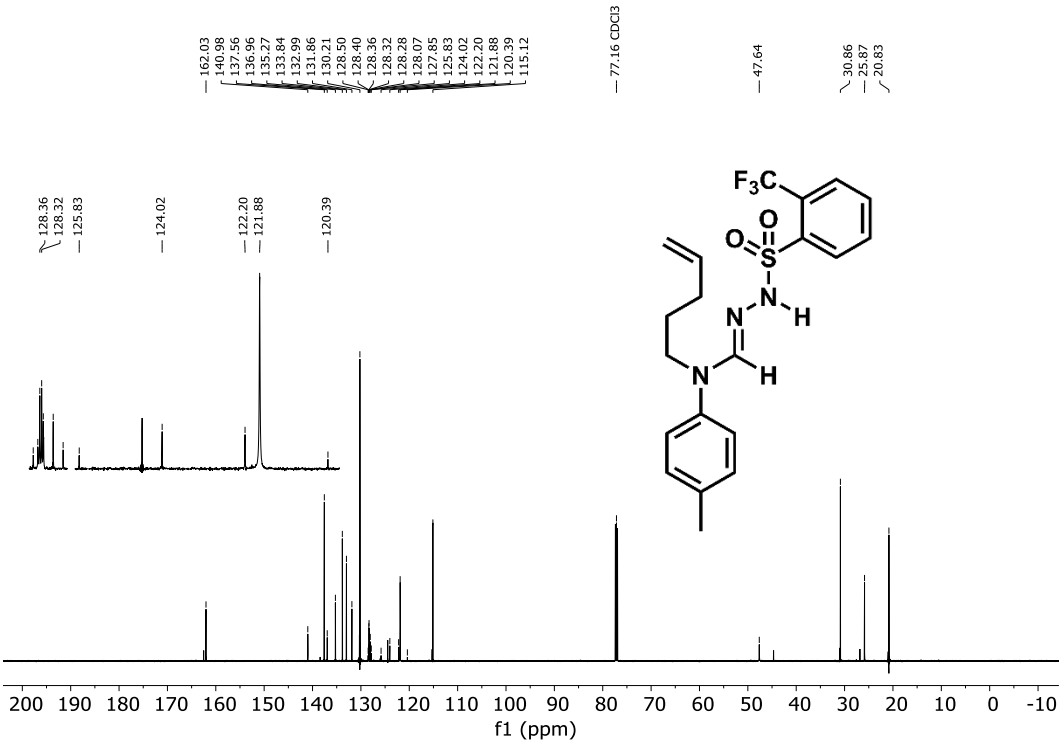
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, $CDCl_3$) of **1d**



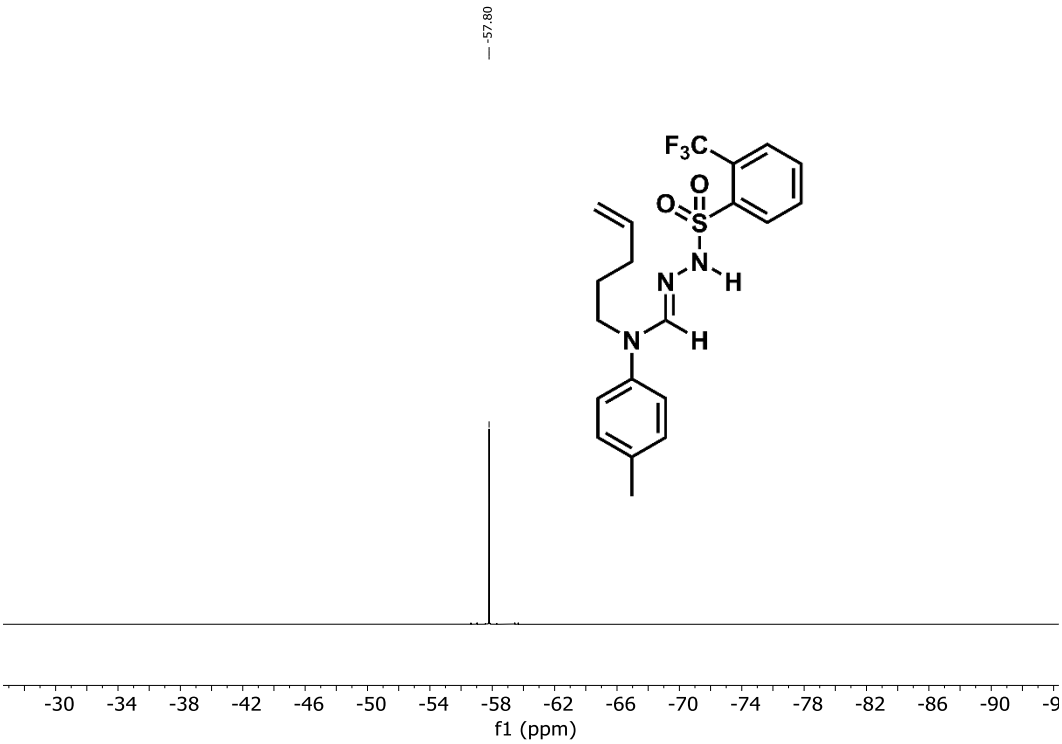
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1d**



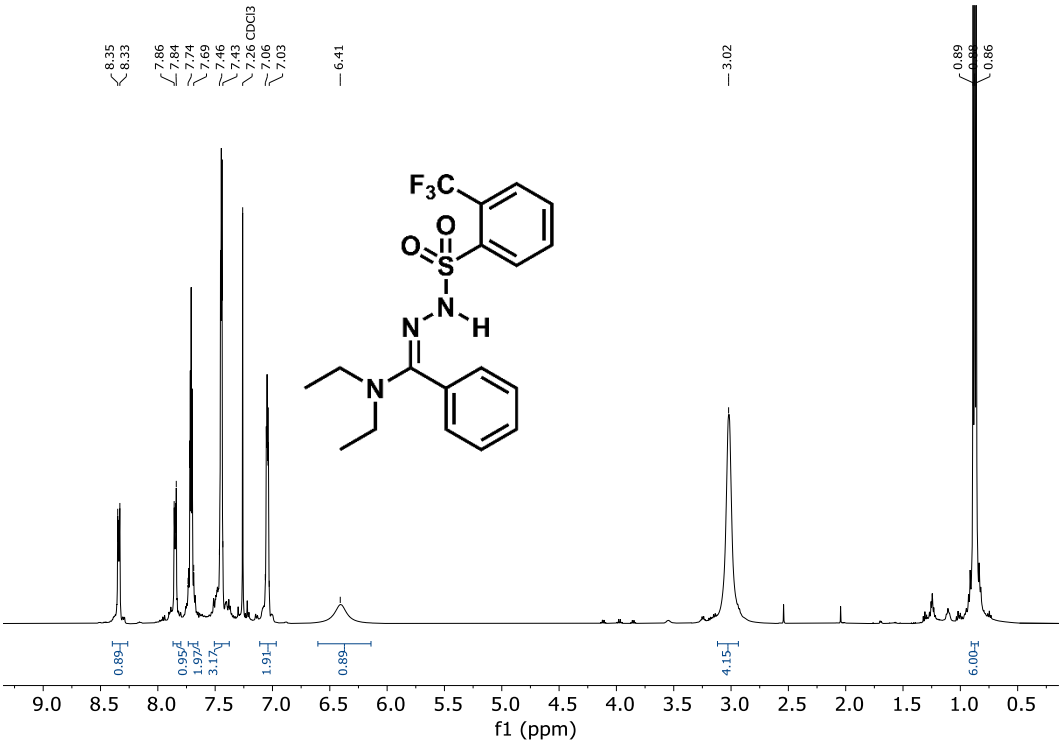
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1e**



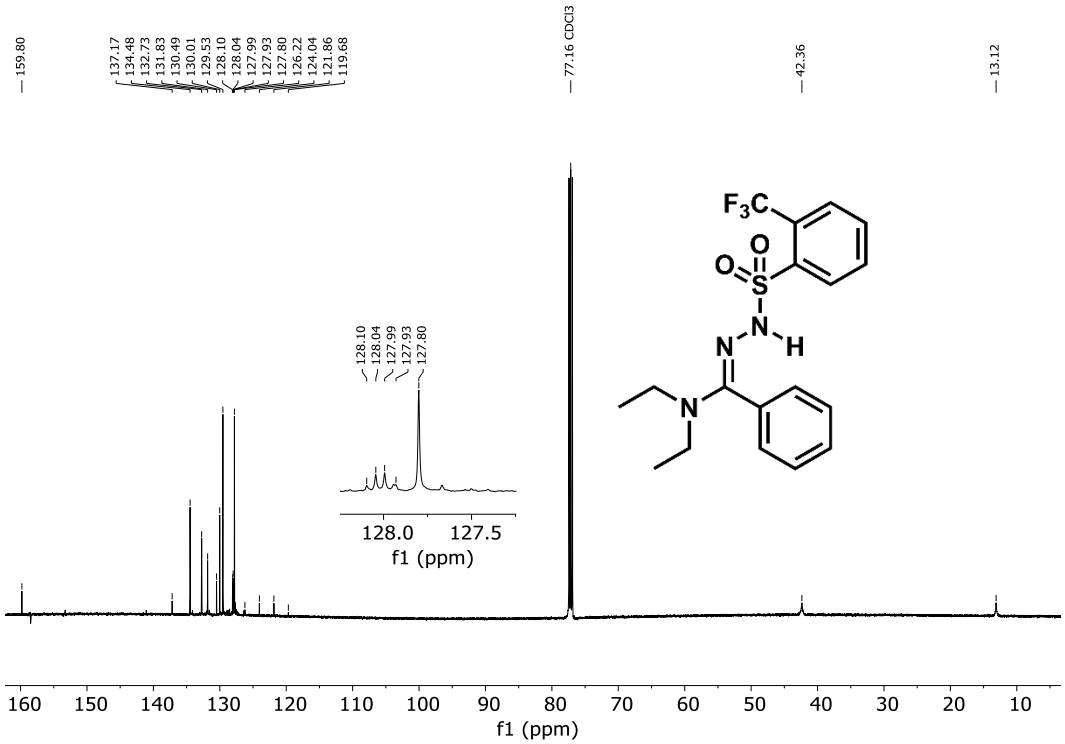
^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) of **1e**



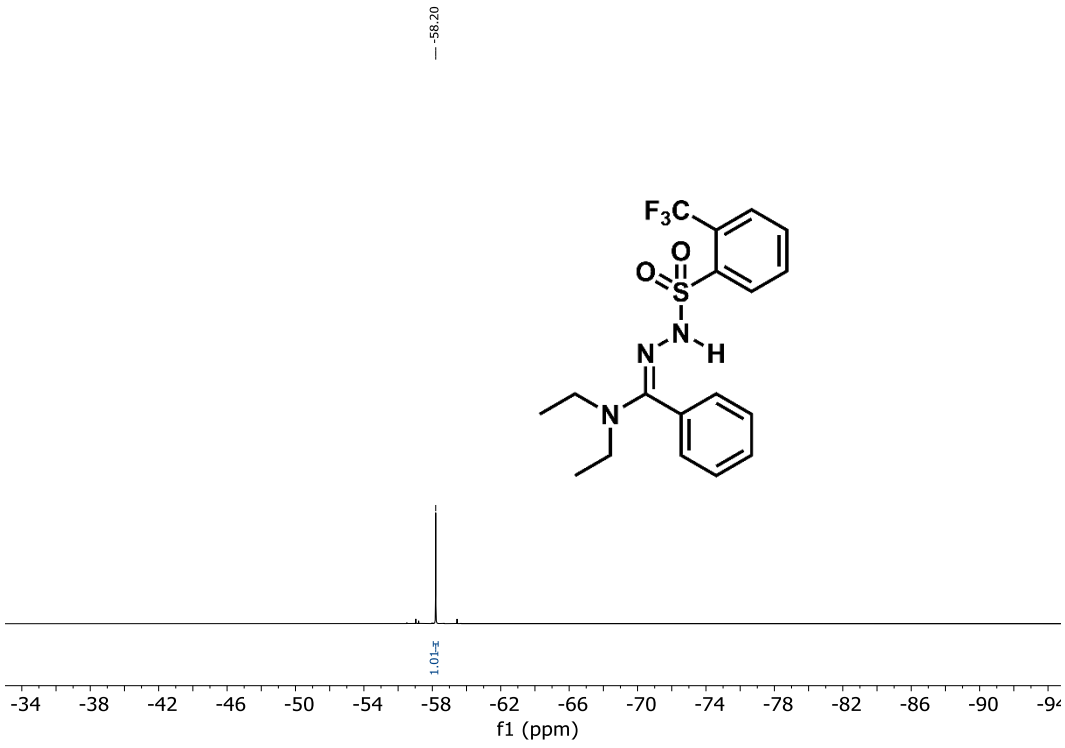
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1e**



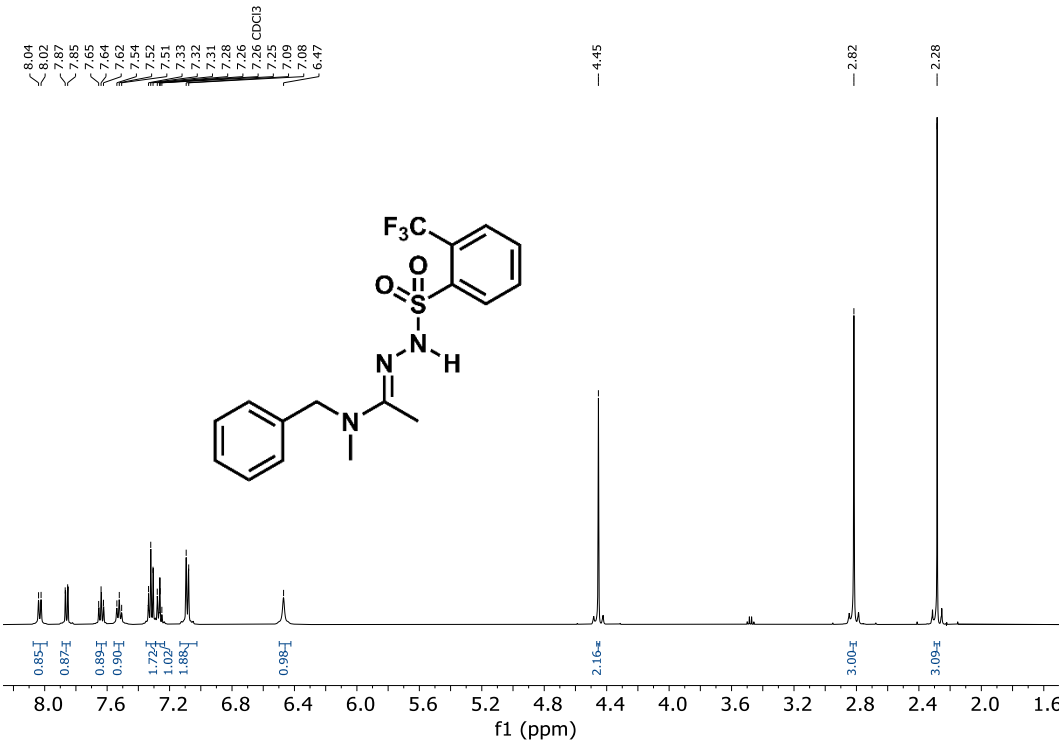
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1f**



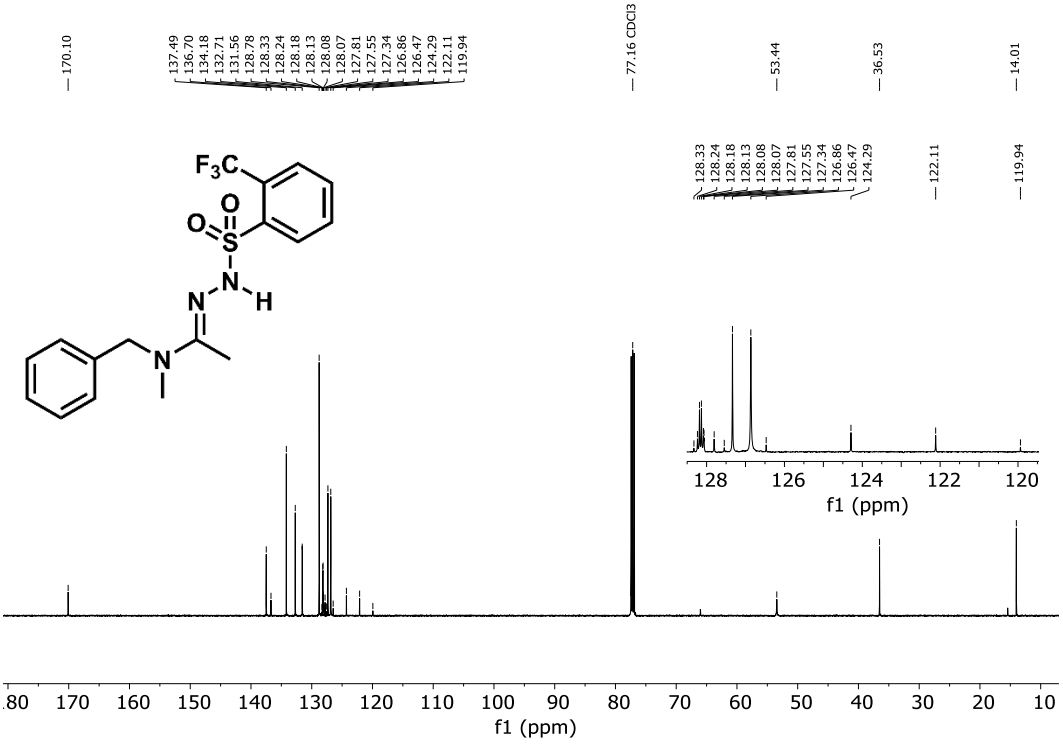
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, $CDCl_3$) of **1f**



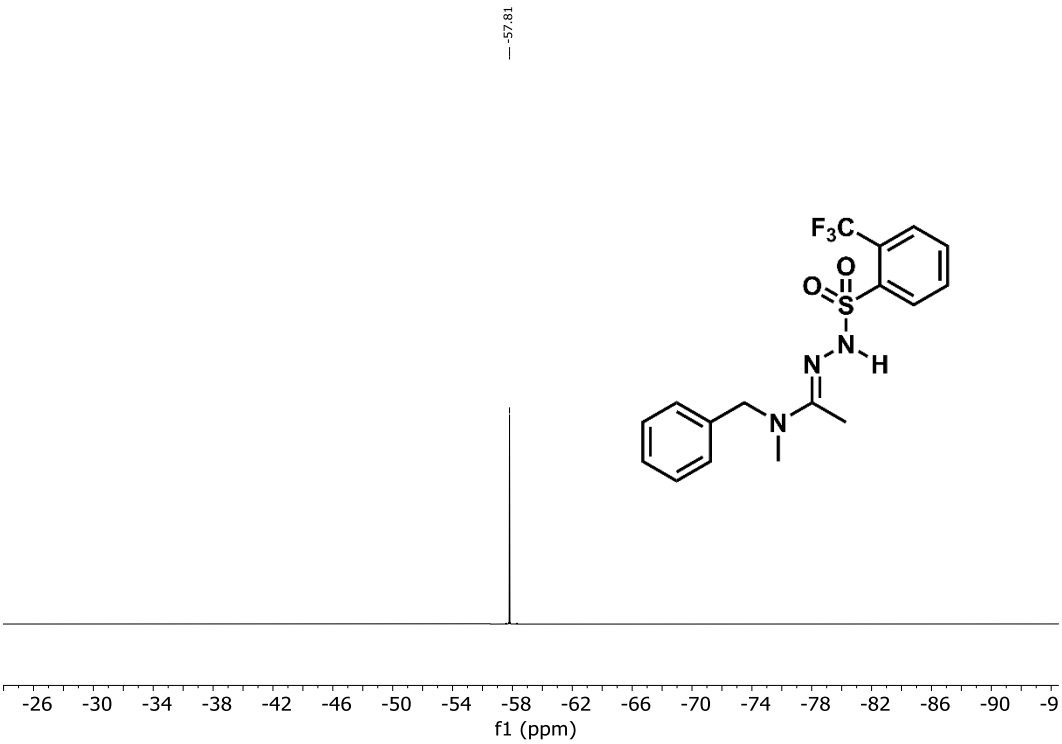
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1f**



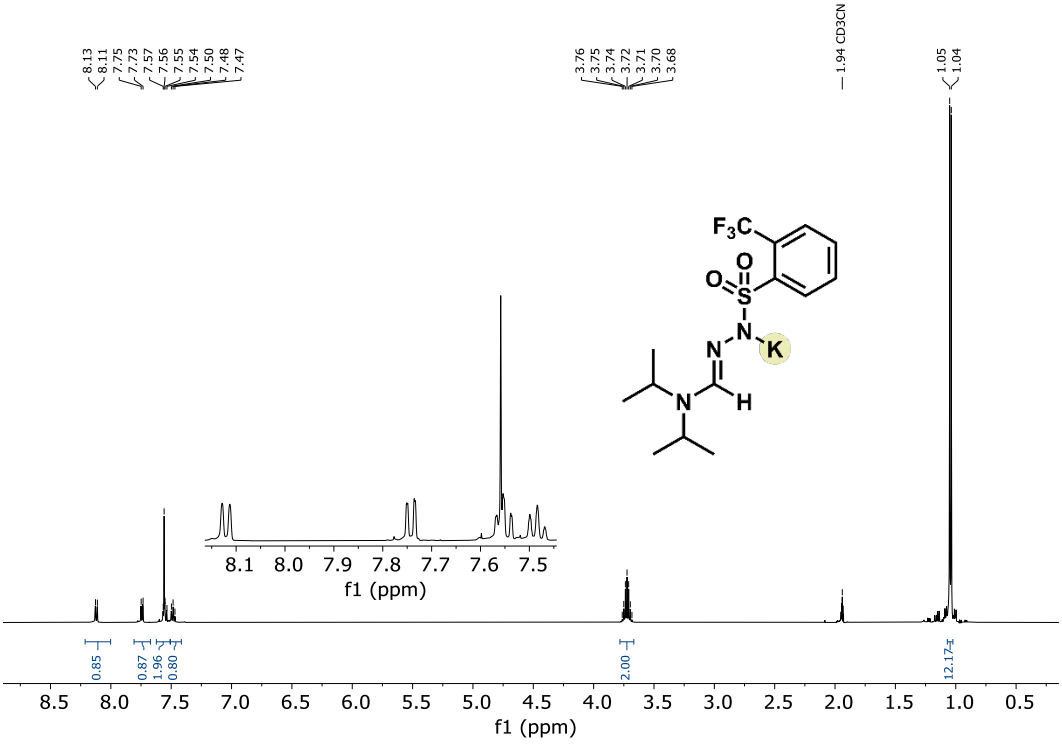
^{1}H NMR (500 MHz, 25°C, $CDCl_3$) of **1g**



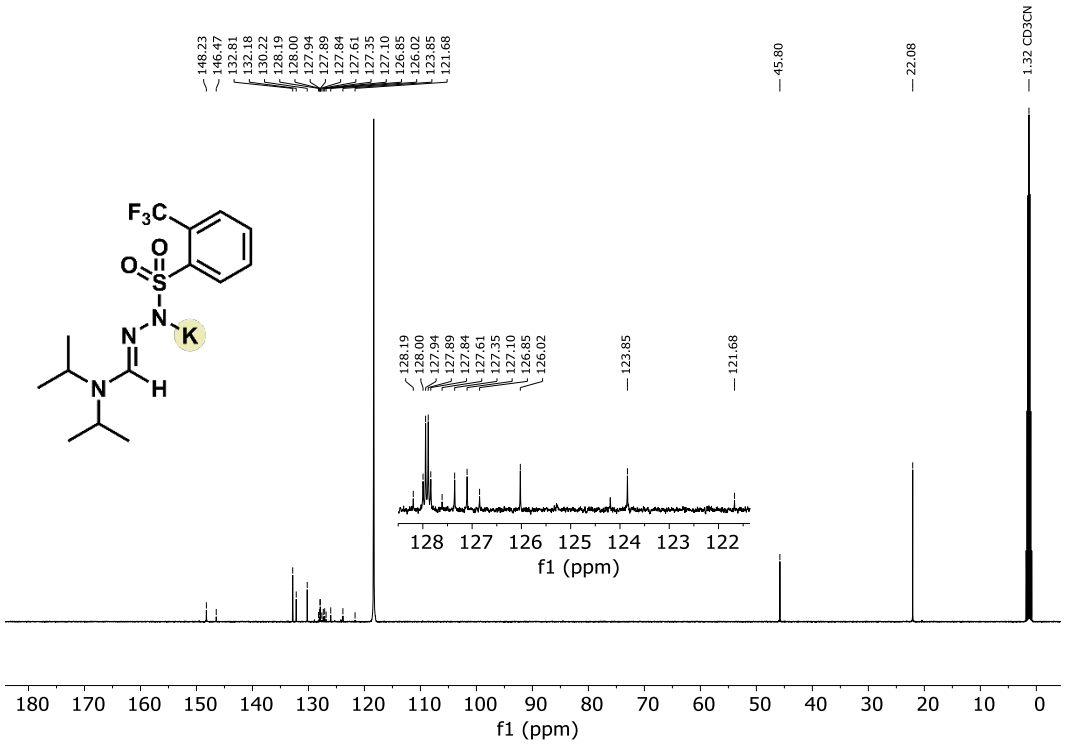
^{13}C{^{1}H} NMR (126 MHz, 25°C, $CDCl_3$) of **1g**



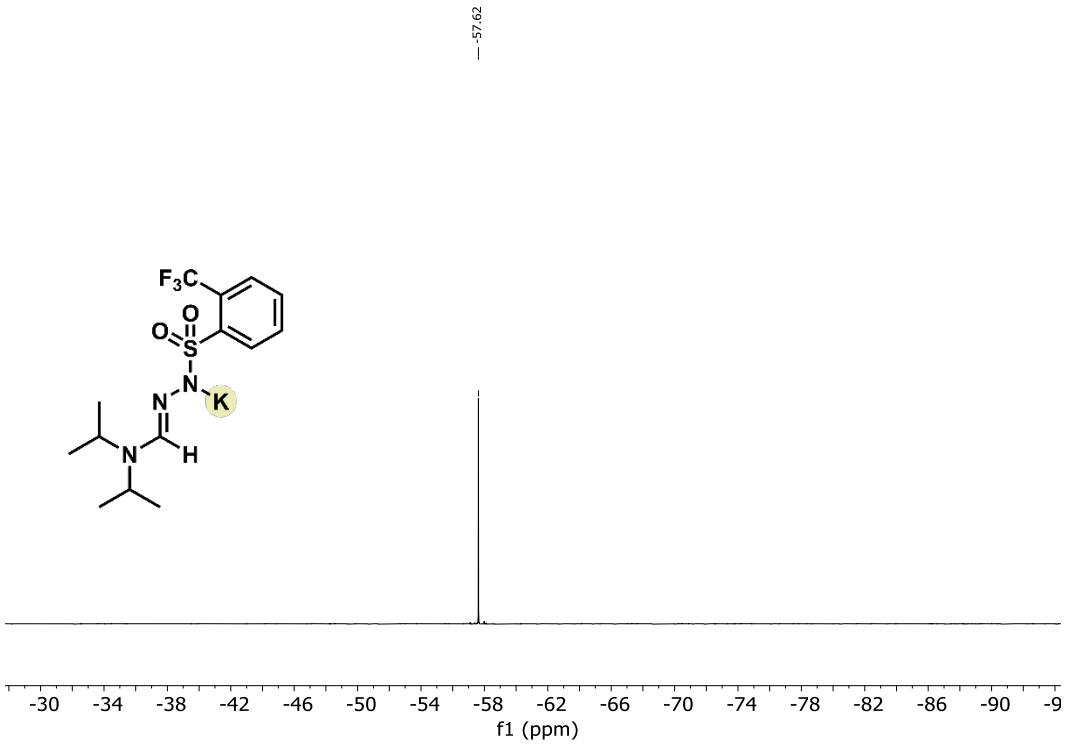
^{19}F NMR (376 MHz, 25°C, $CDCl_3$) of **1g**



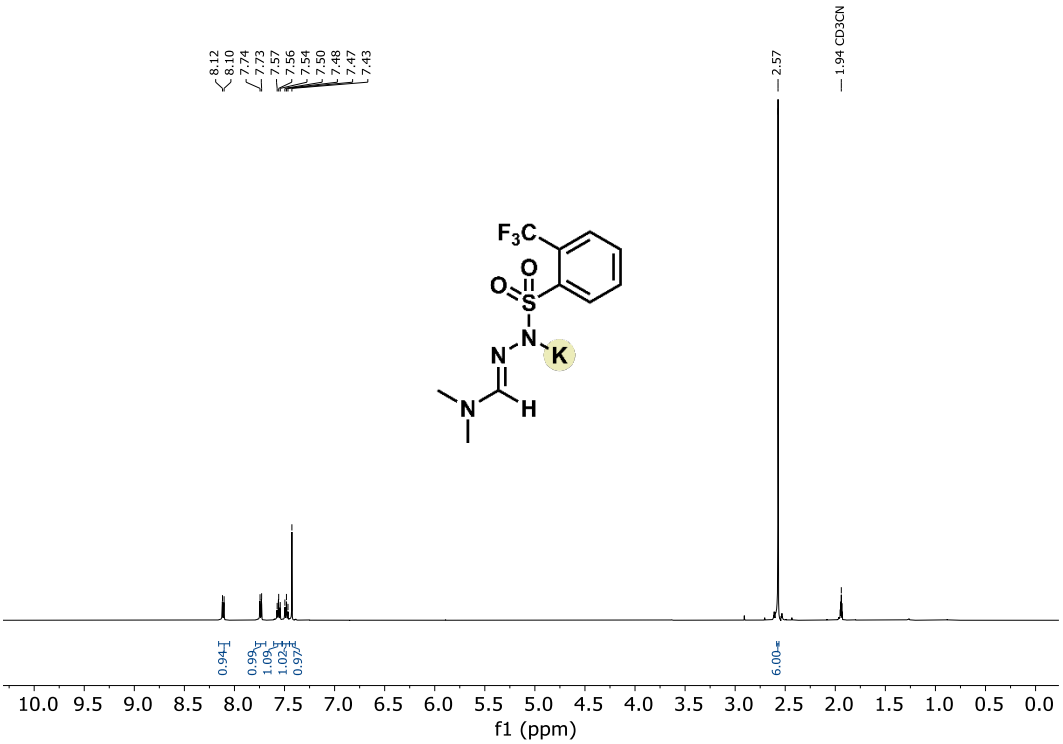
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2a**



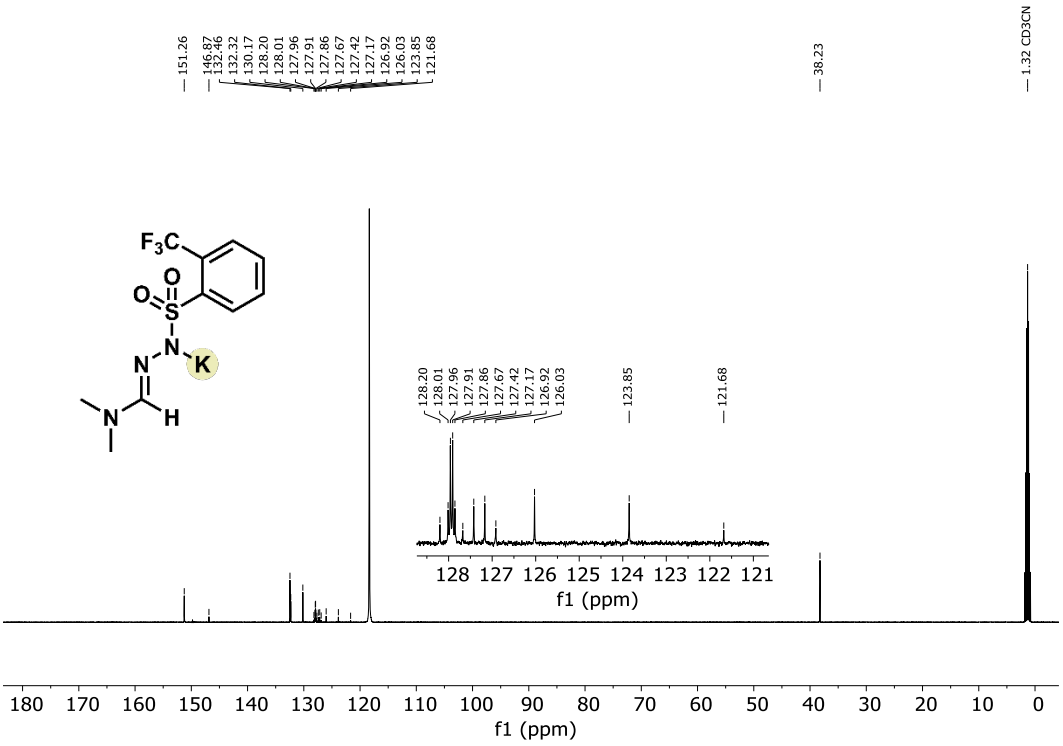
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, ACN-d_3) of **2a**



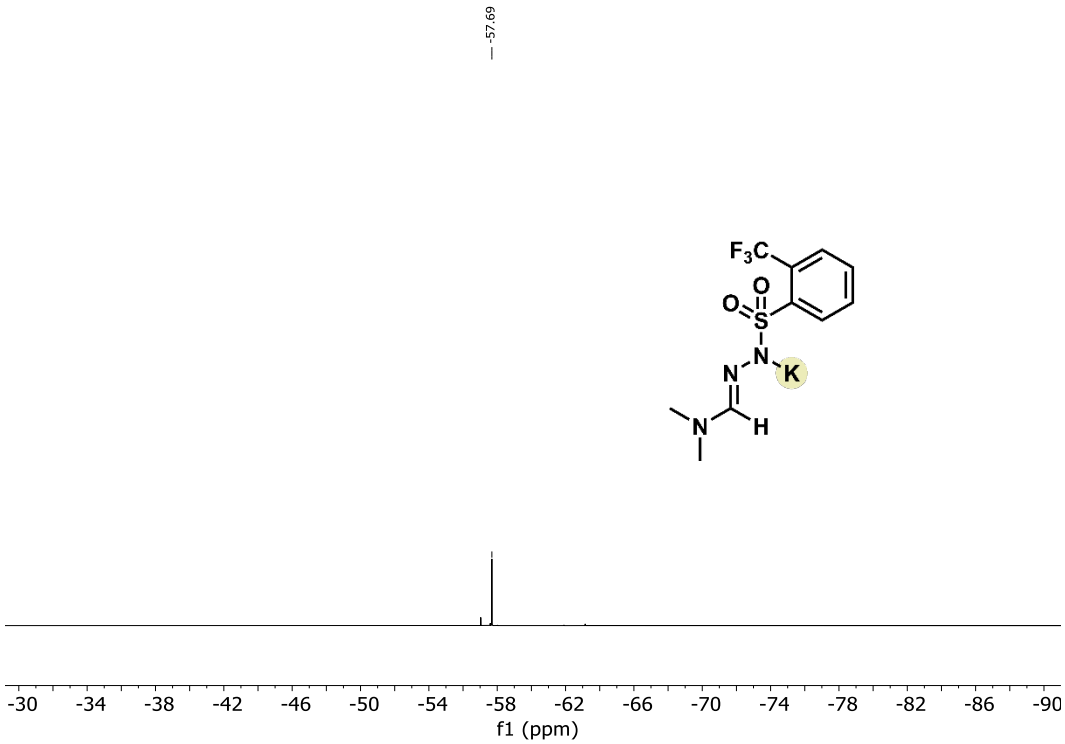
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2a**



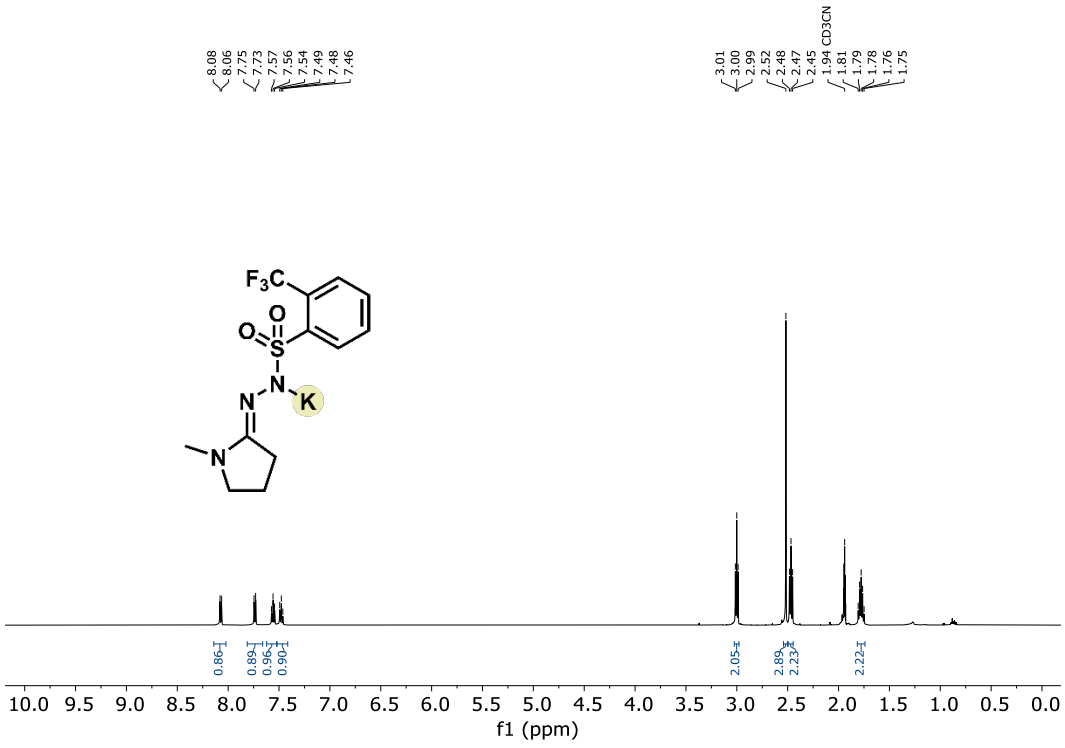
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2b**



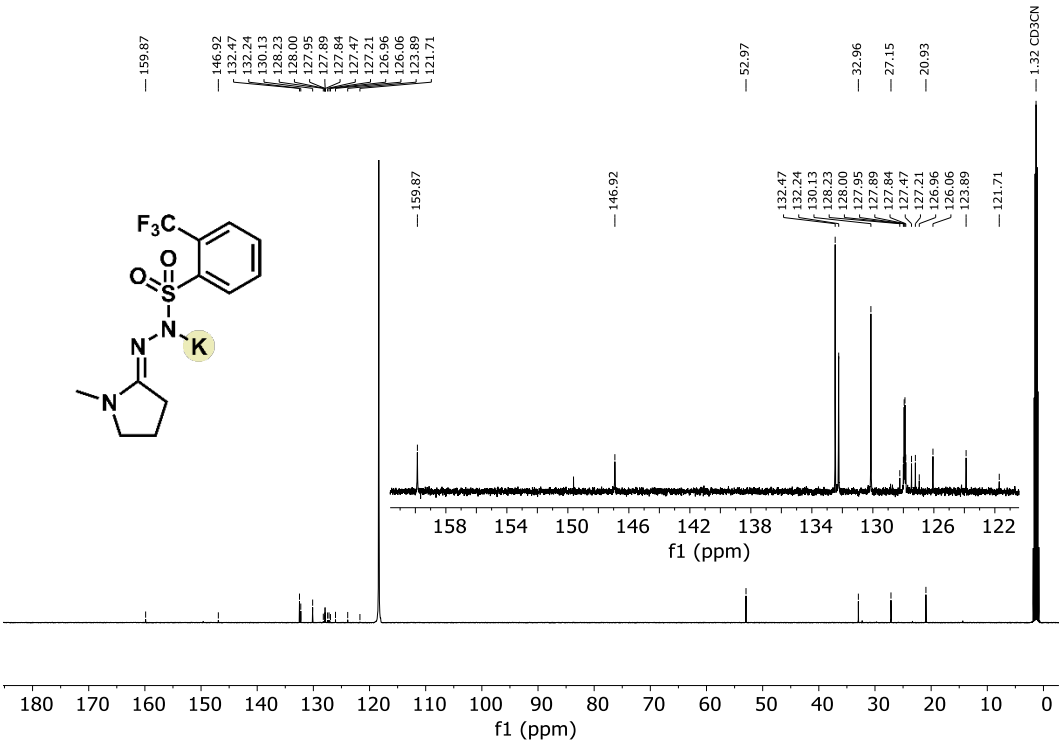
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) of **2b**



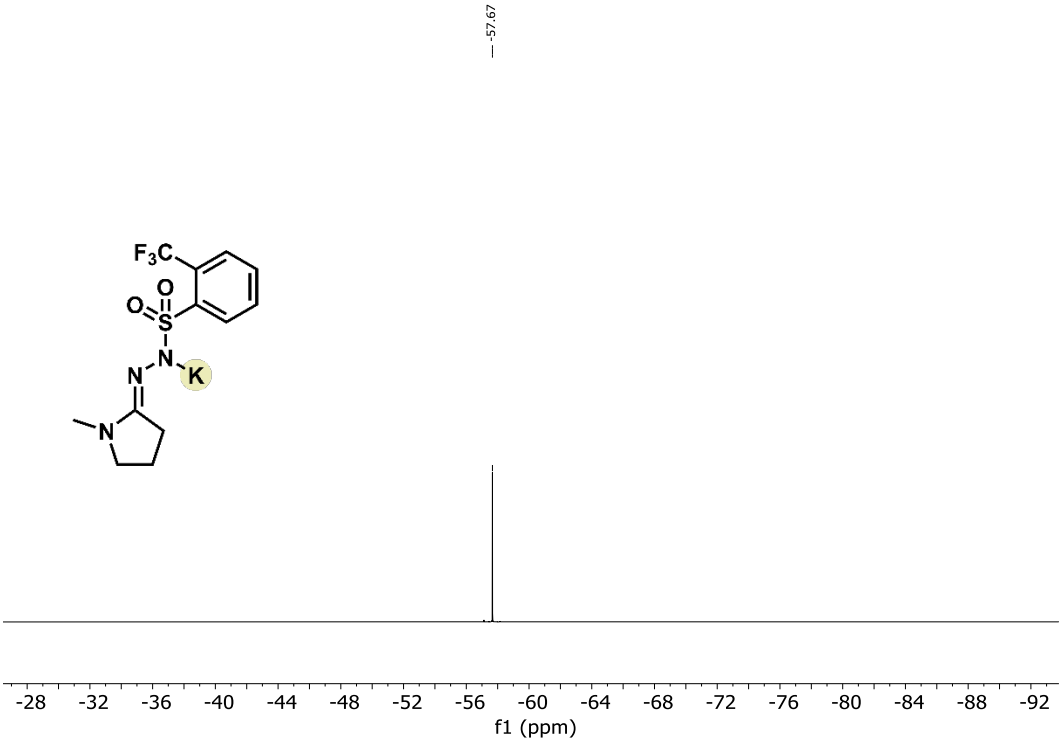
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2b**



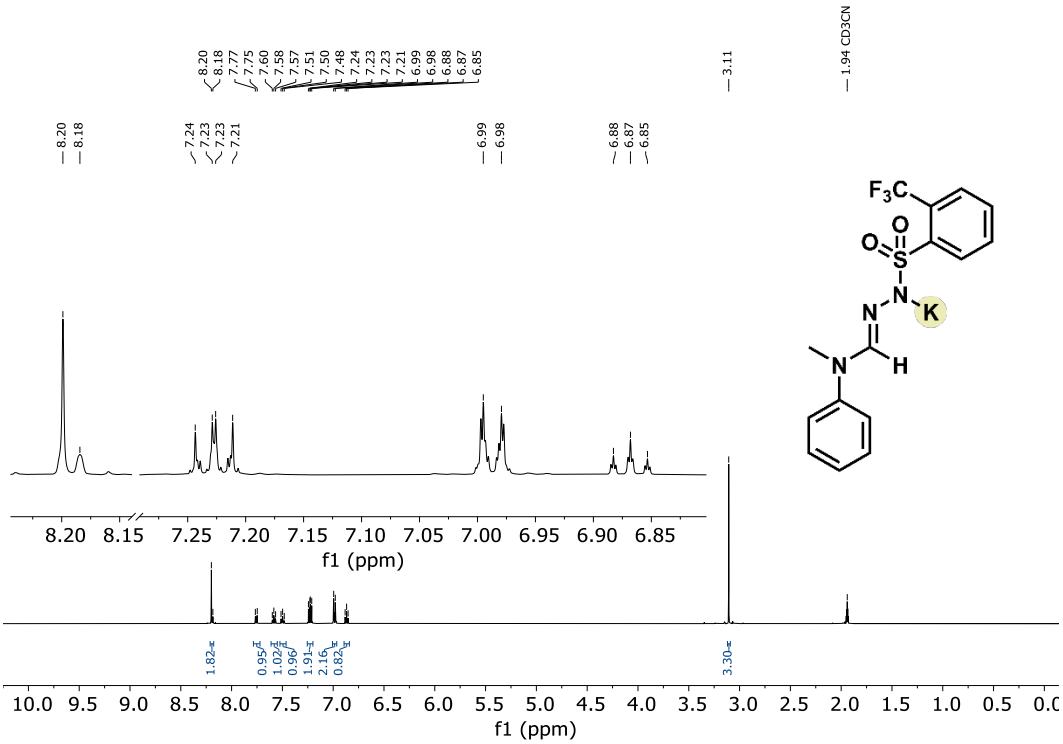
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2c**



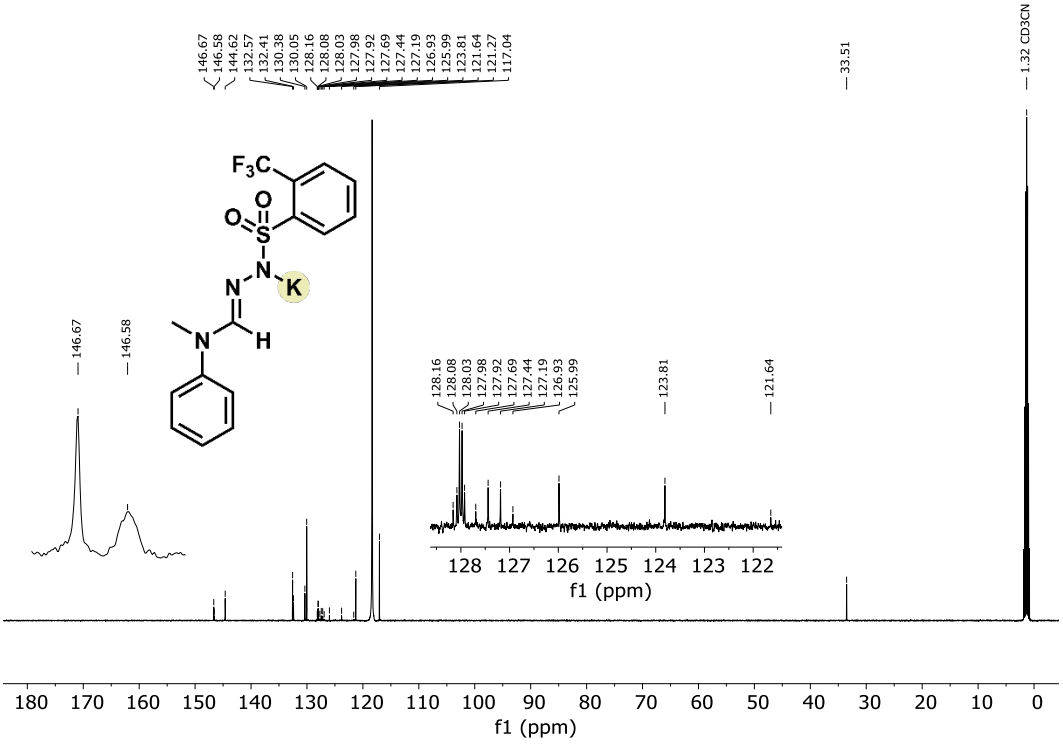
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, ACN-d_3) of **2c**



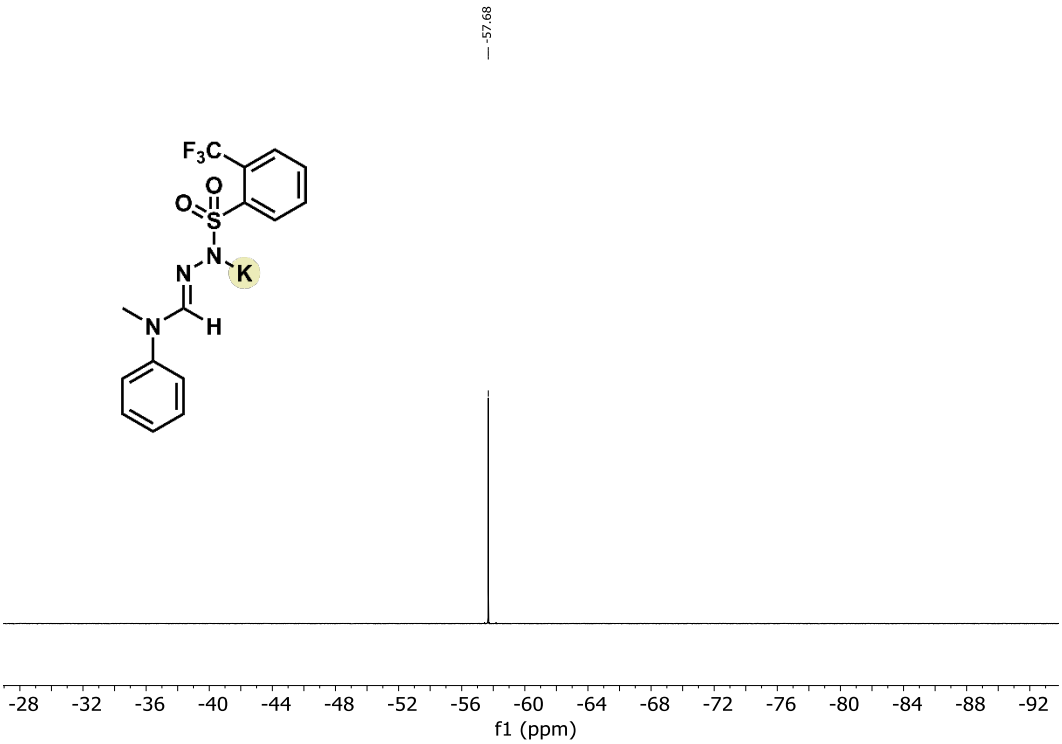
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2c**



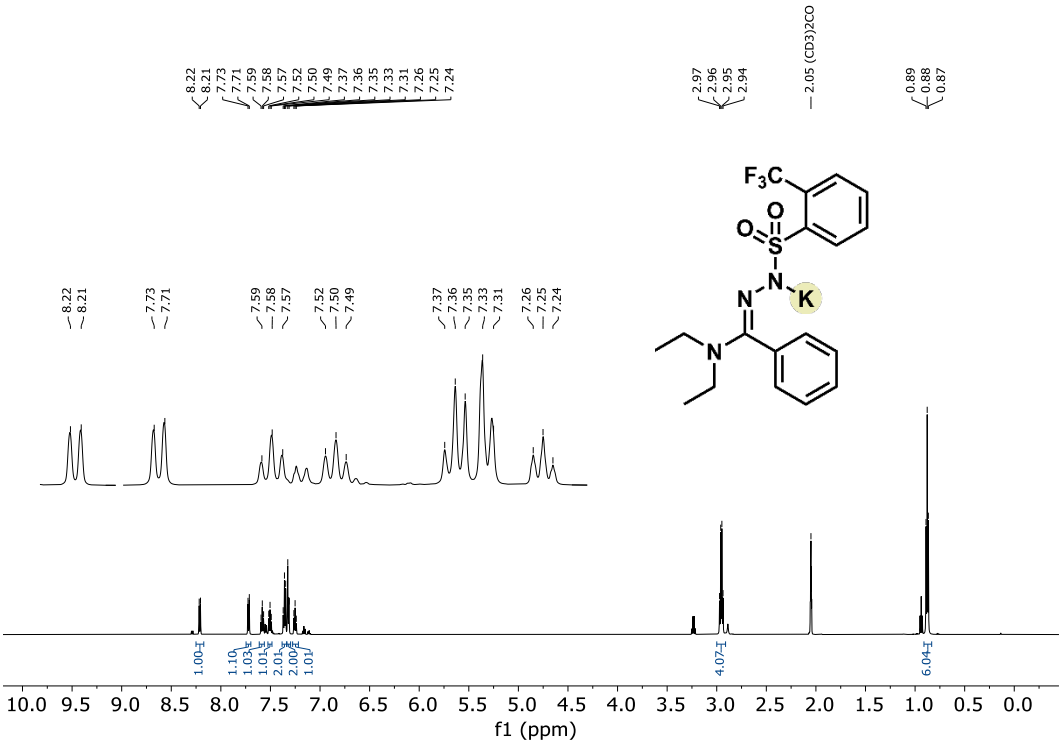
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2d**



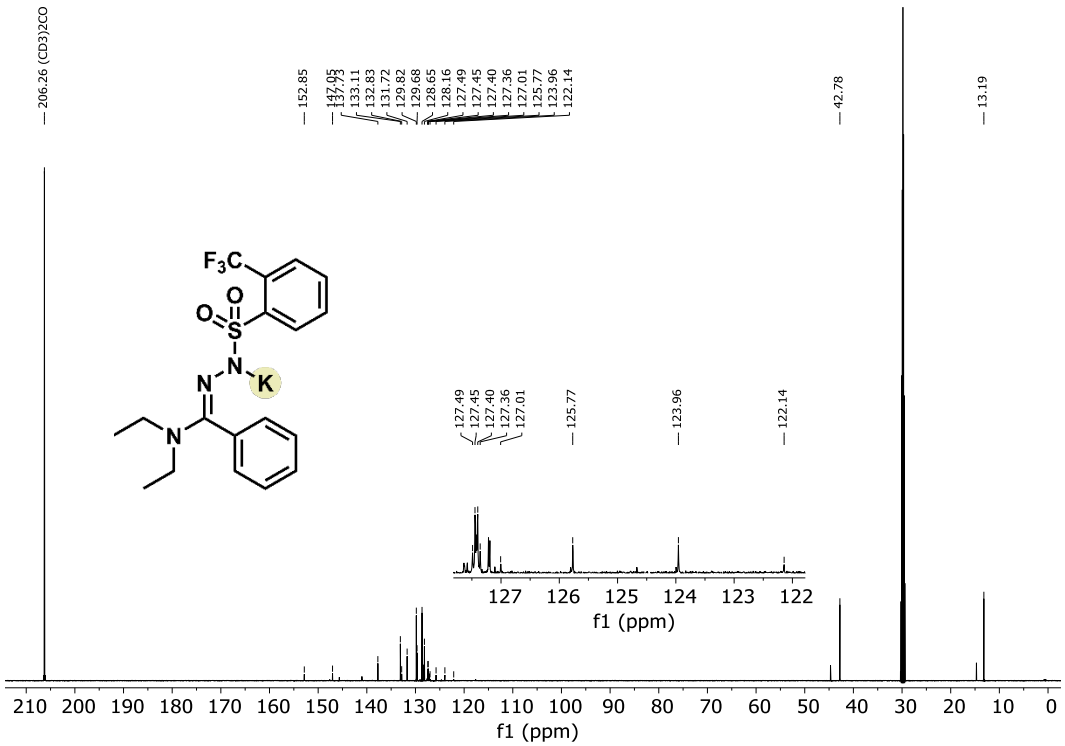
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) of **2d**



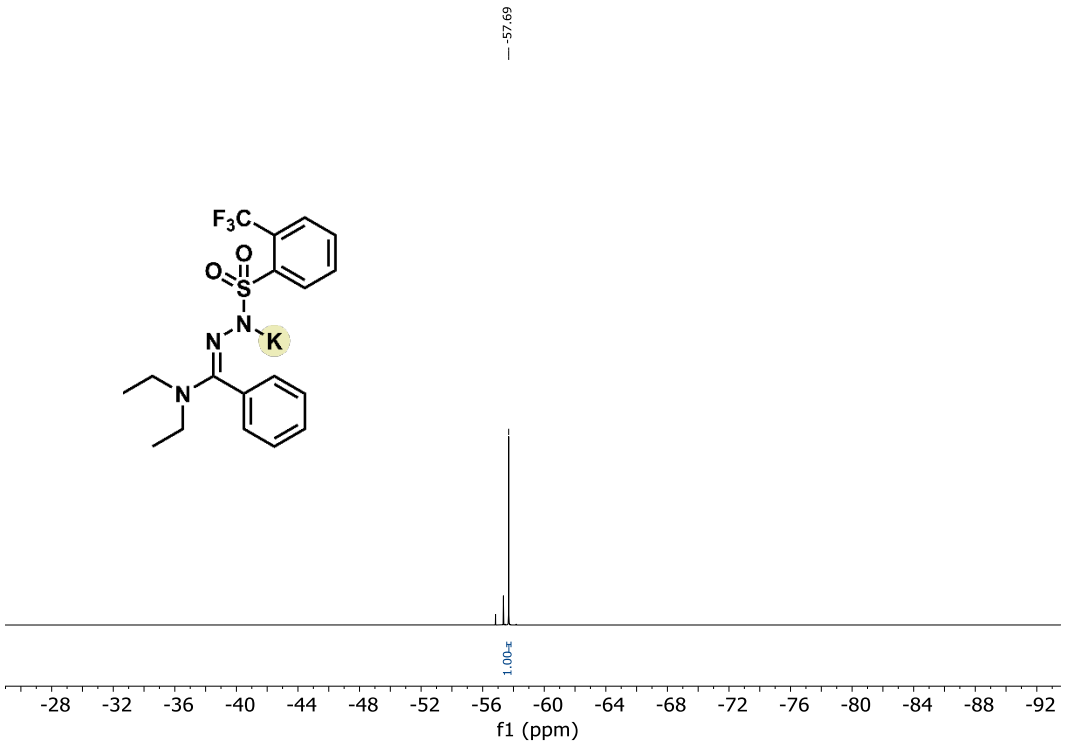
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2d**



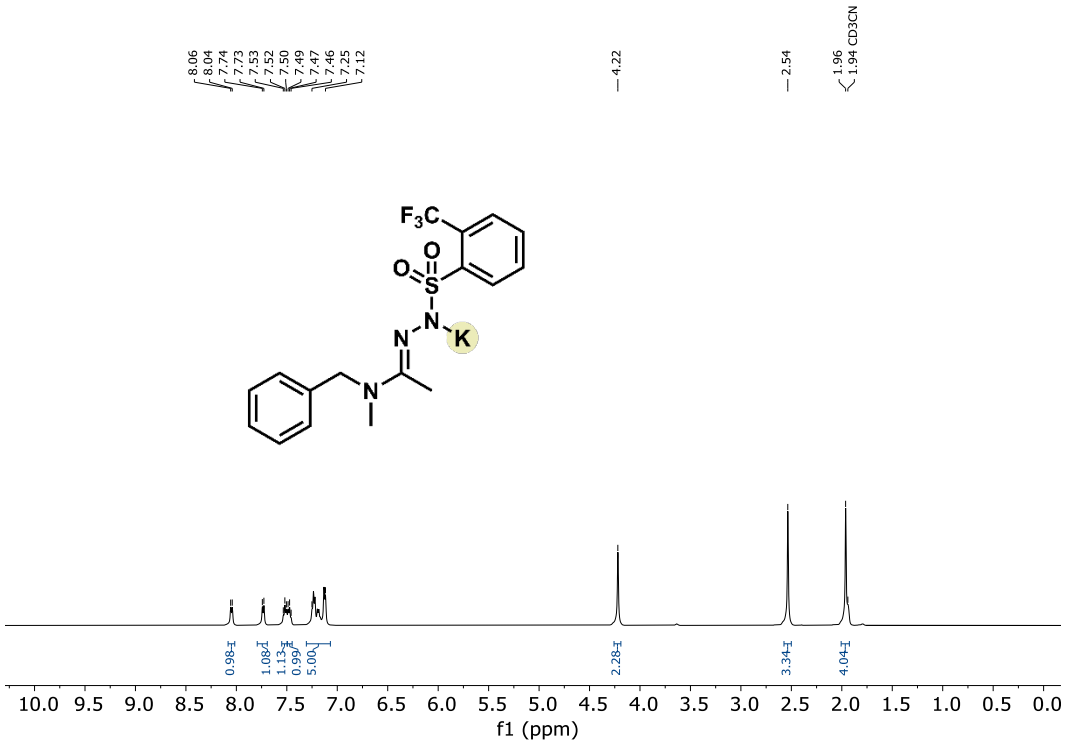
^{1}H NMR (600 MHz, 25°C, acetone-d_6) of **2f**



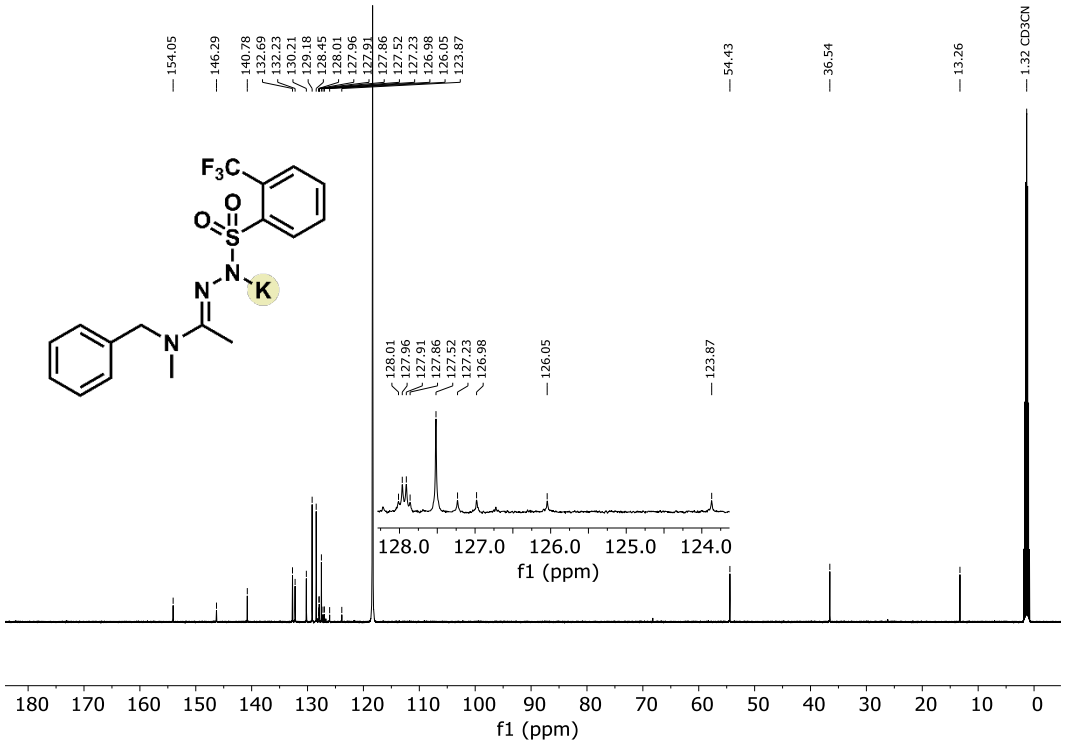
$^{13}C\{^{1}H\}$ NMR (151 MHz, 25°C, acetone-d_6) of **2f**



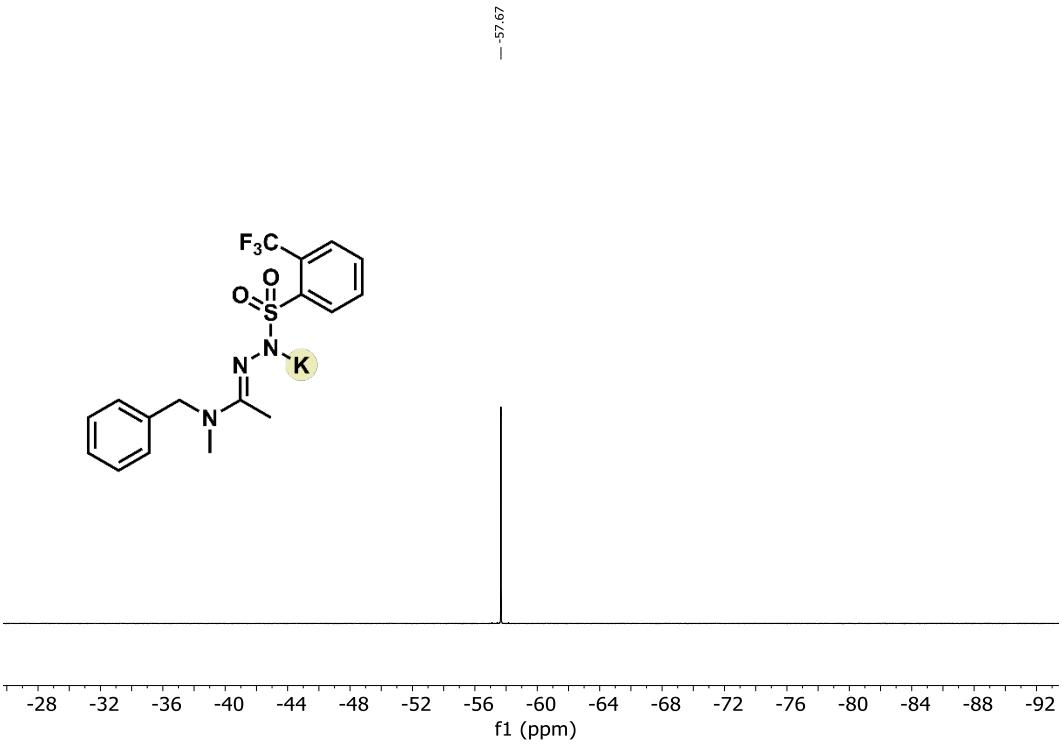
^{19}F NMR (376 MHz, 25°C, acetone-d_6) of **2f**



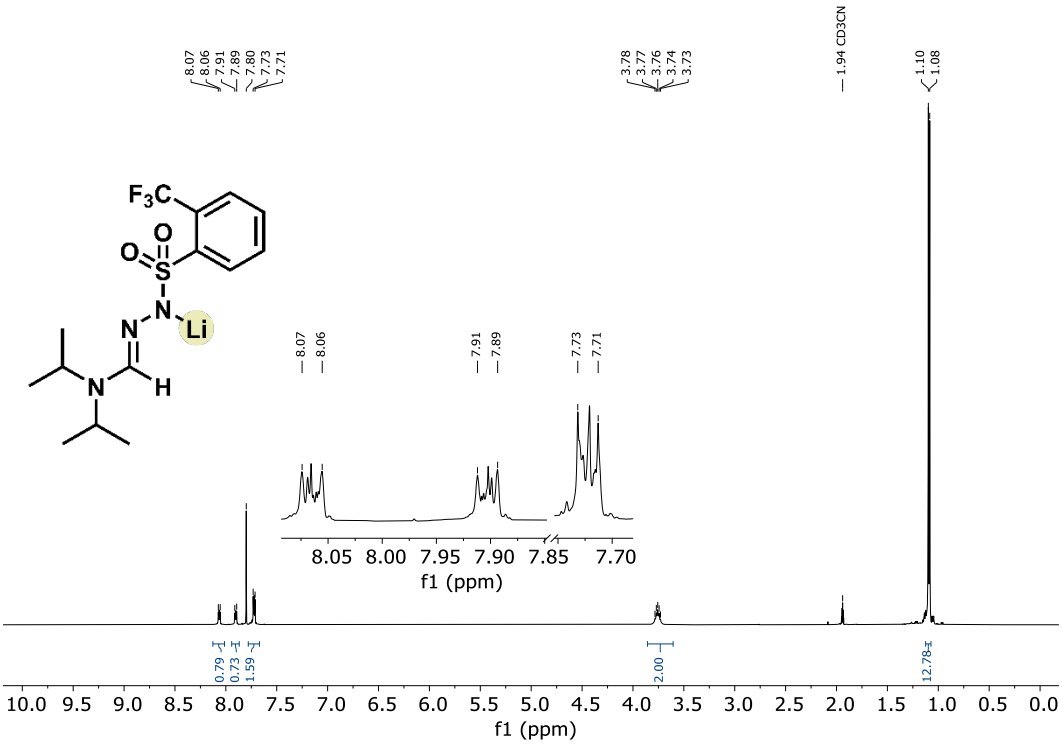
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2g**



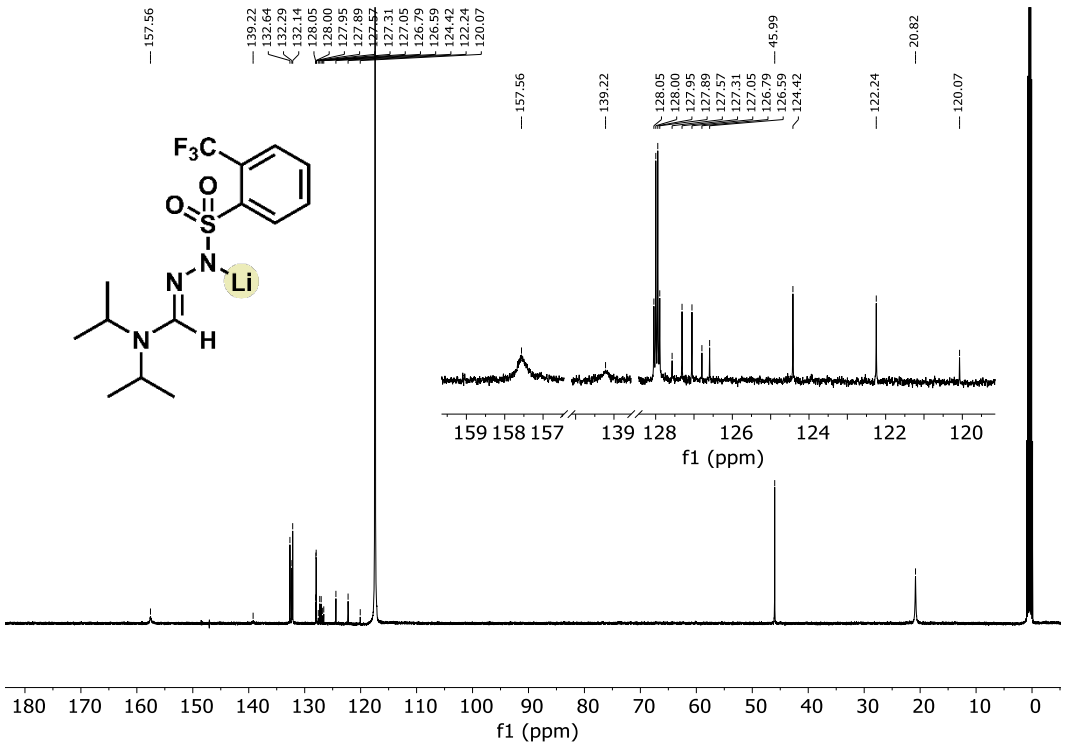
^{13}C{^{1}H} NMR (126 MHz, 25°C, ACN-d_3) of **2g**



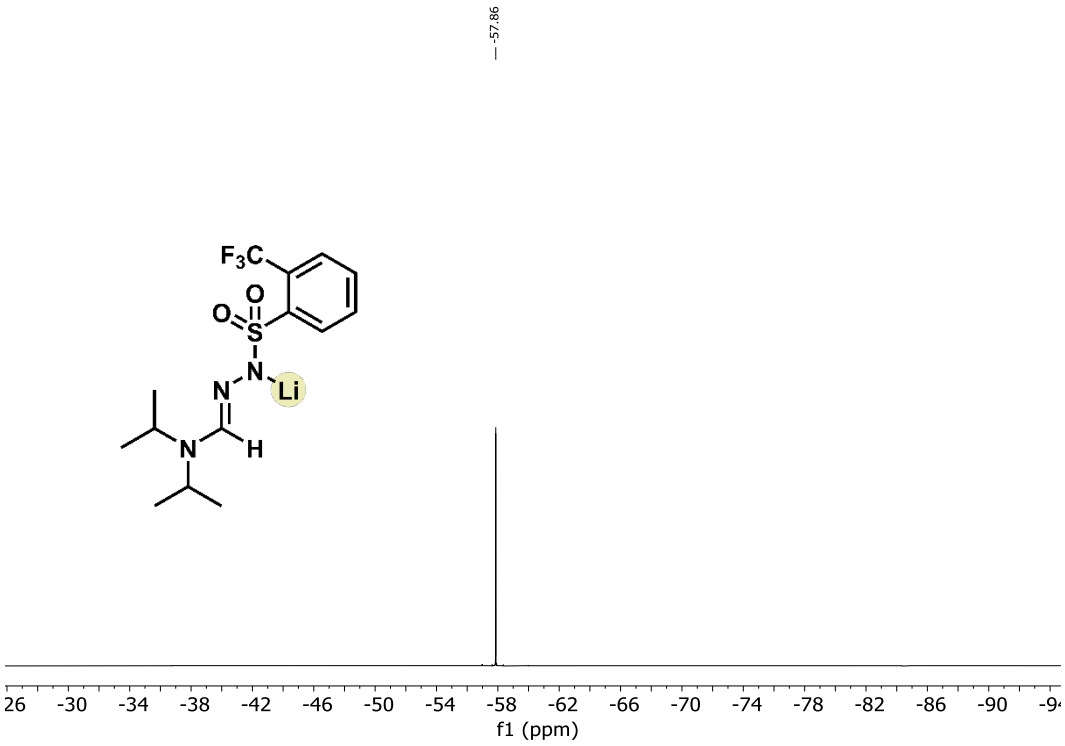
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2g**



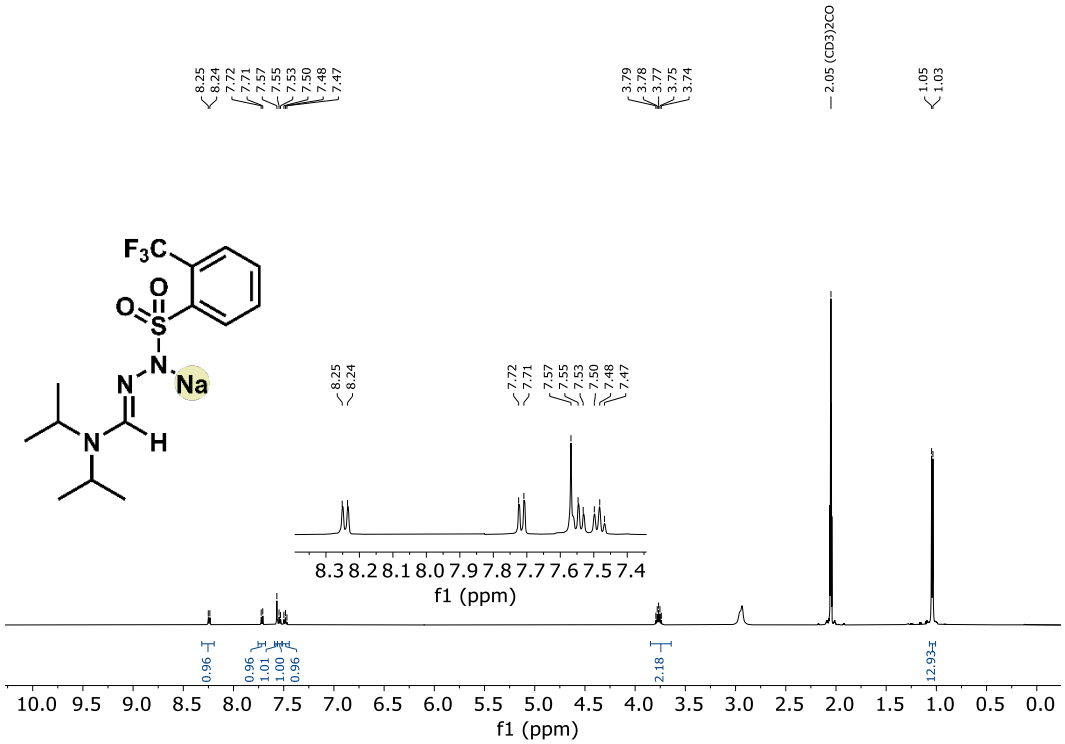
^{1}H NMR (500 MHz, 25°C, ACN-d_3) of **2a-Li**



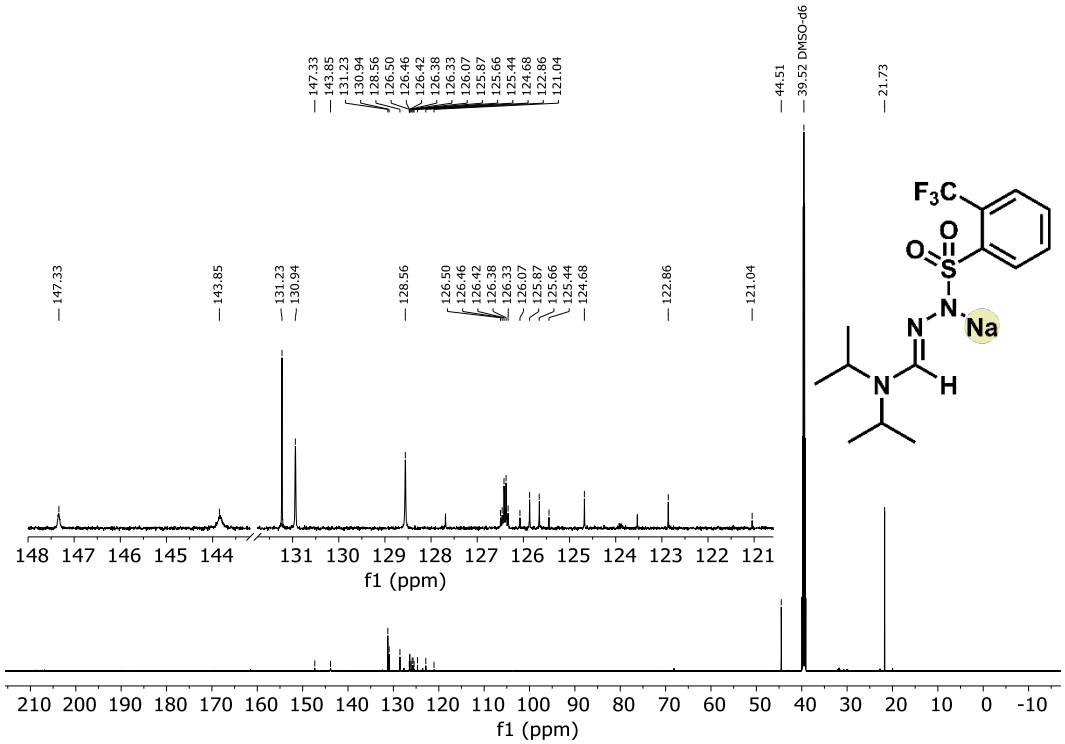
$^{13}C\{^{1}H\}$ NMR (126 MHz, 25°C, ACN-d_3) of **2a-Li**



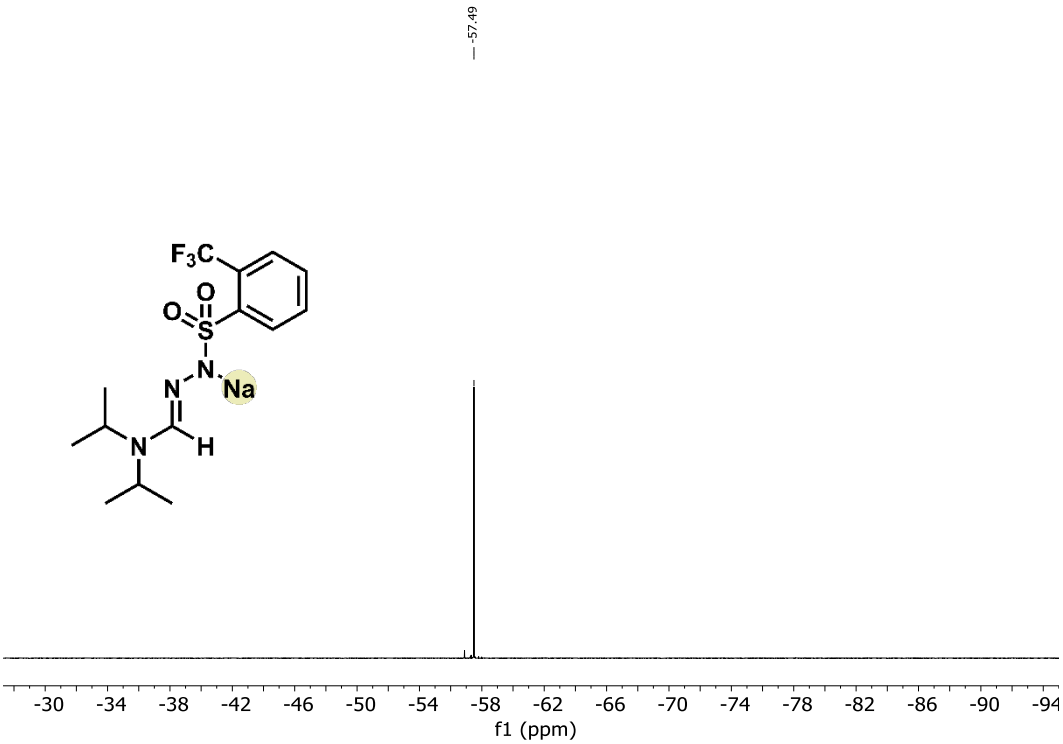
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2a-Li**



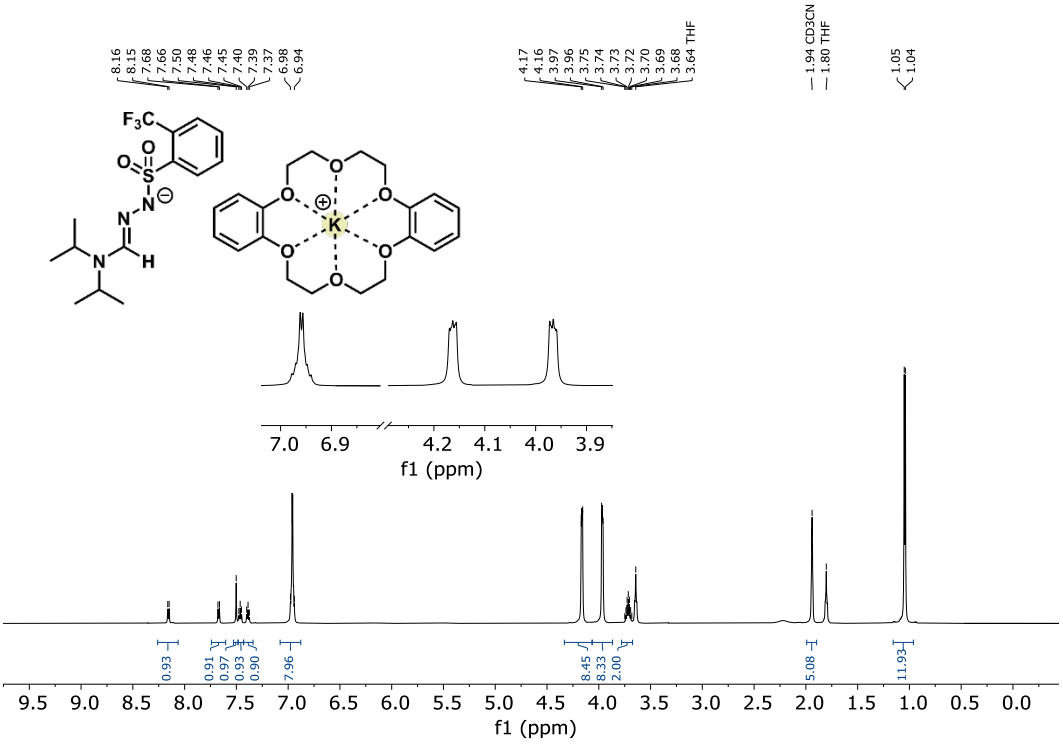
^{1}H NMR (500 MHz, 25°C, acetone-d_6) of **2a-Na**



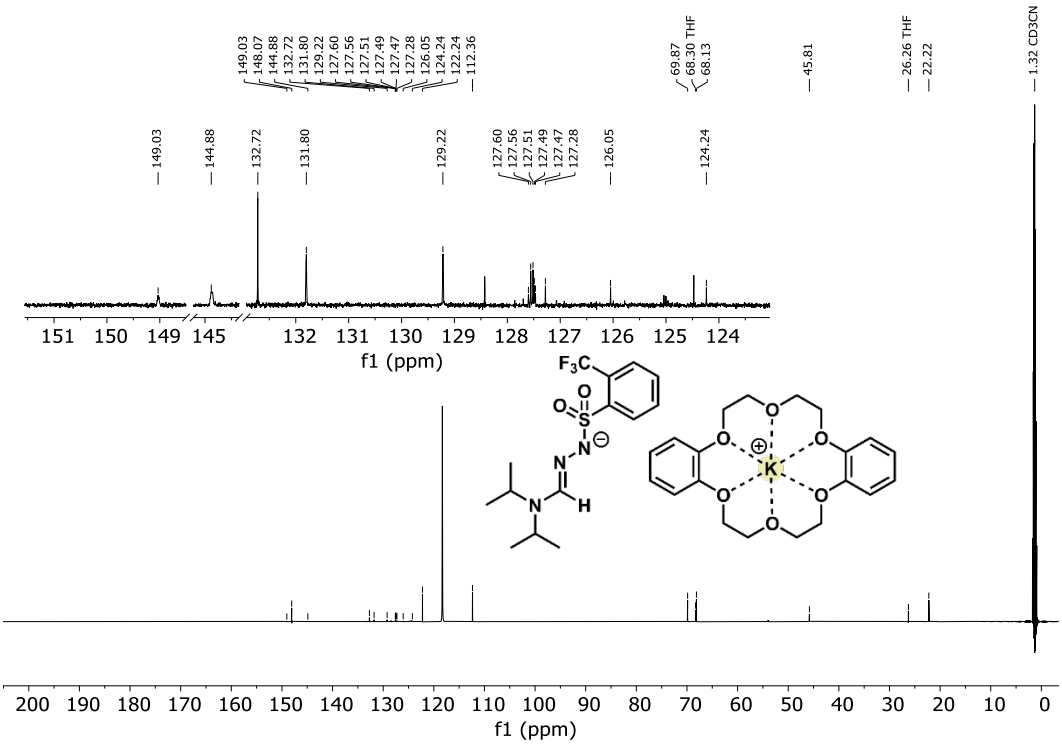
^{13}C{^{1}H} NMR (151 MHz, 25°C, DMSO-d_6) of **2a-Na**



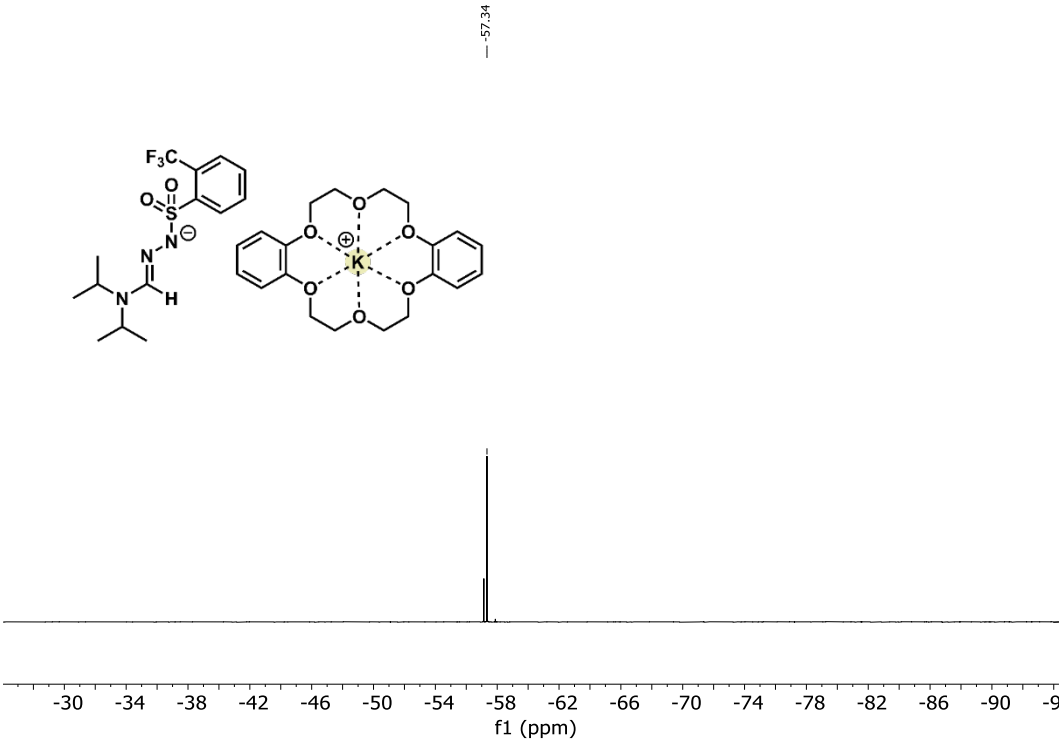
^{19}F NMR (376 MHz, 25°C, acetone-d_6) of **2a-Na**



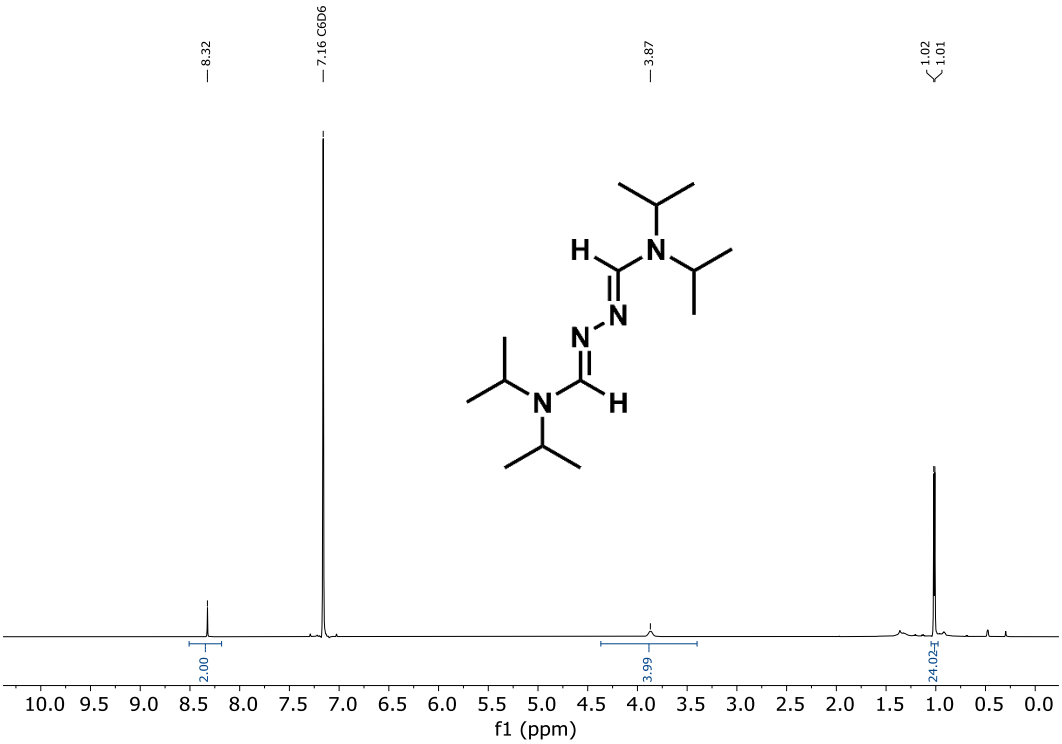
^{1}H NMR (600 MHz, 25°C, ACN-d_3) of **2a'**



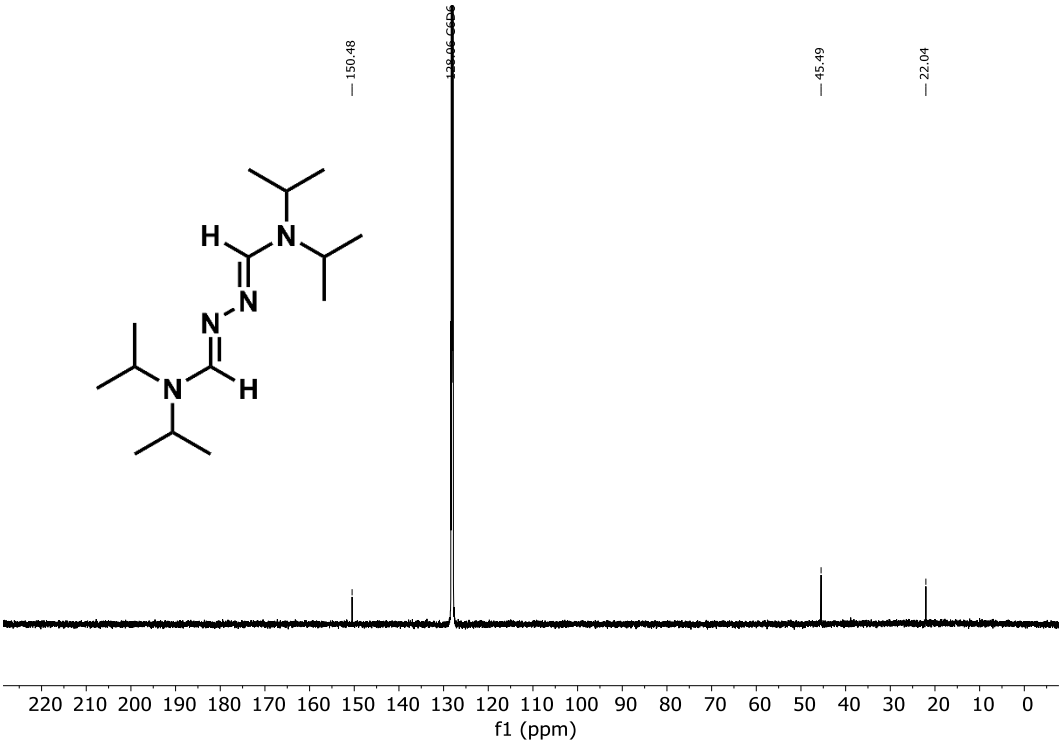
$^{13}C\{^{1}H\}$ NMR (151 MHz, 25°C, ACN-d_3) of **2a'**



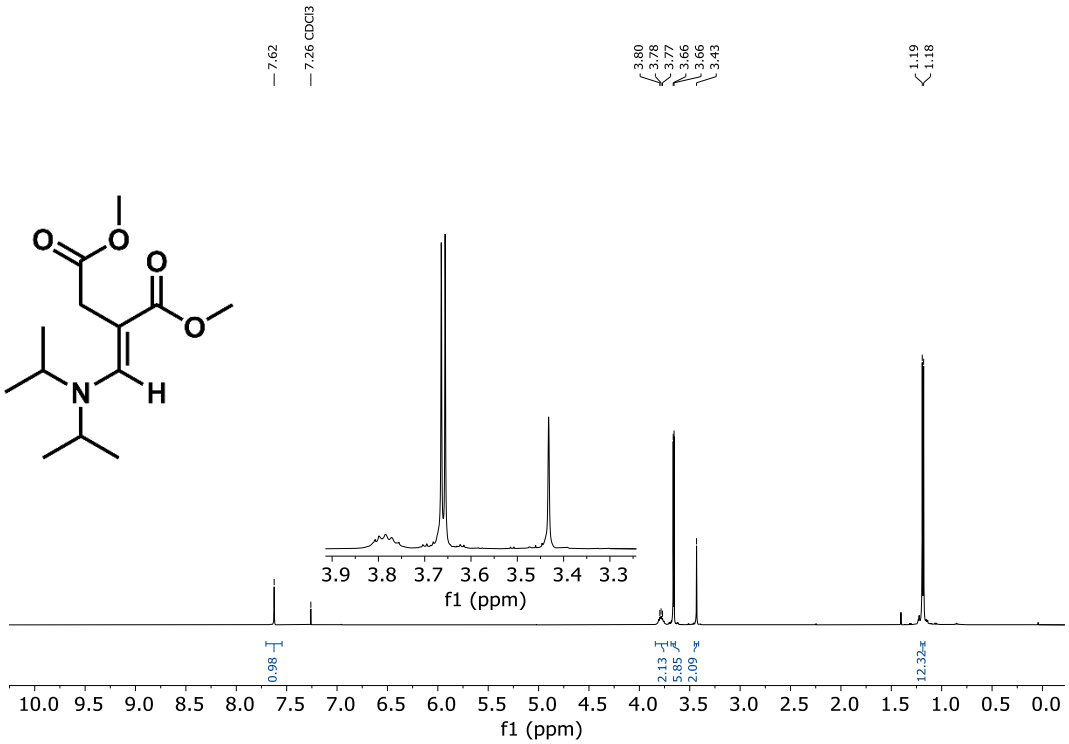
^{19}F NMR (376 MHz, 25°C, ACN-d_3) of **2a'**



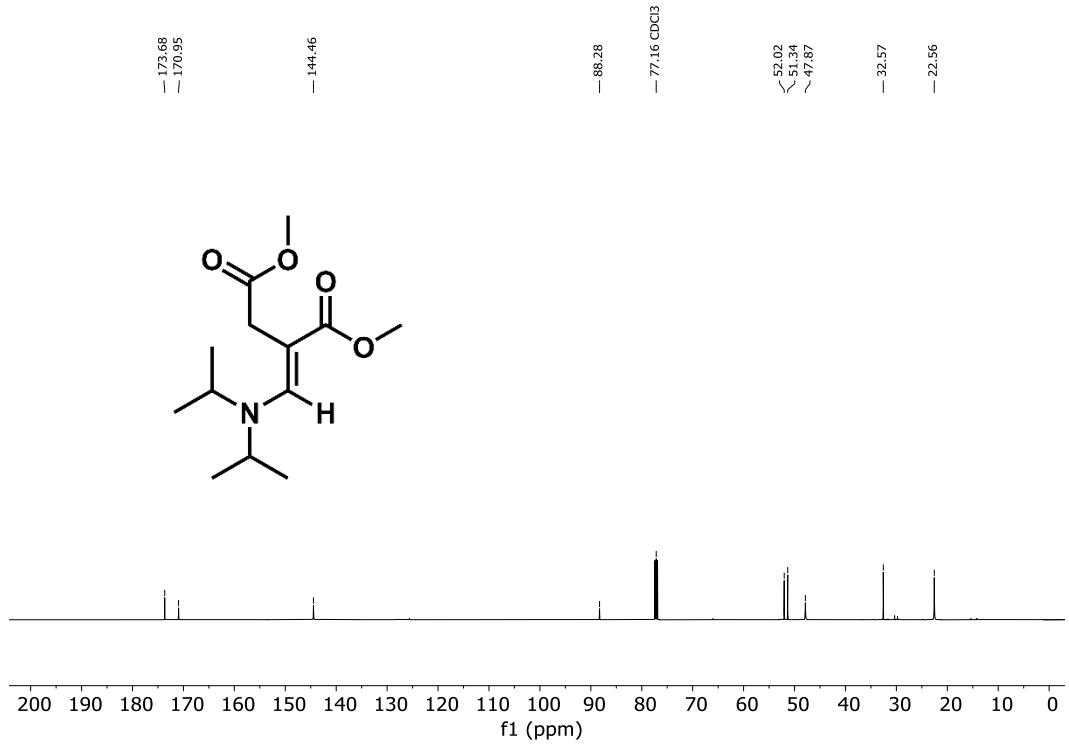
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **3a**



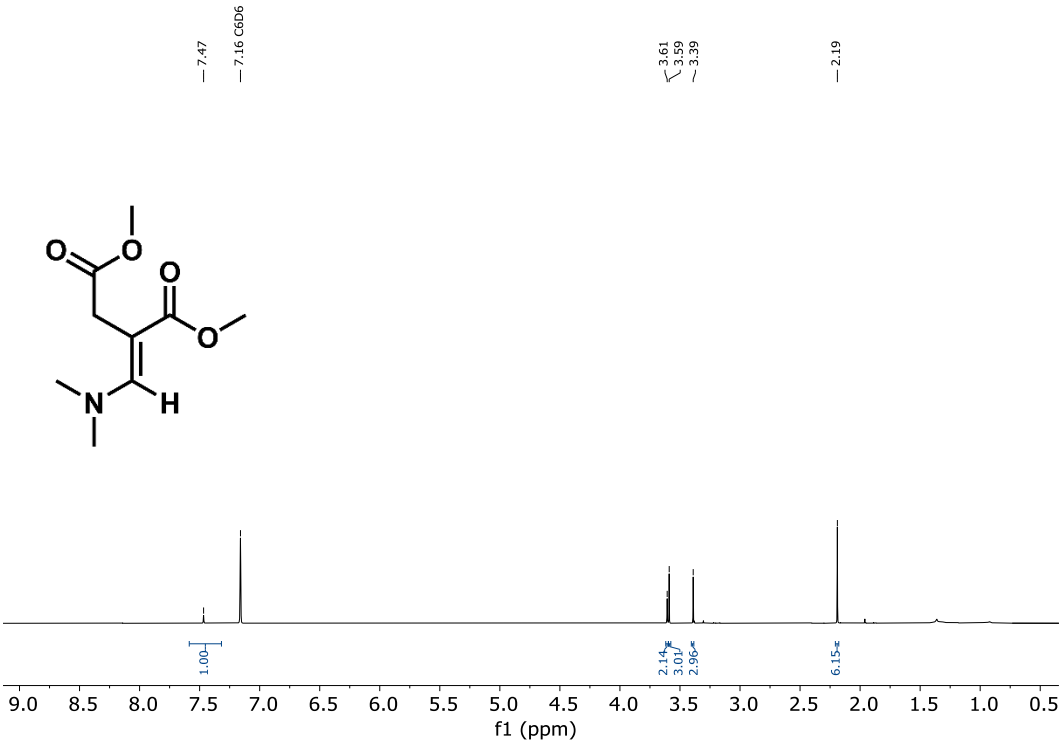
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **3a**



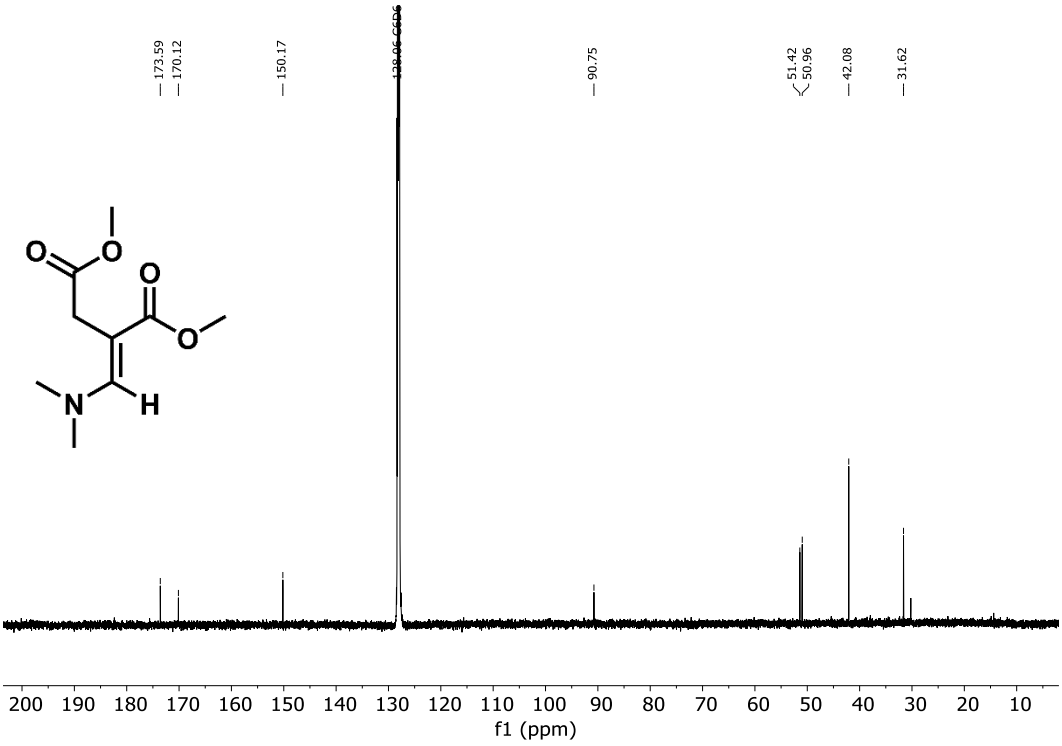
^{1}H NMR (500 MHz, 25°C, C_6D_6) of **4a**



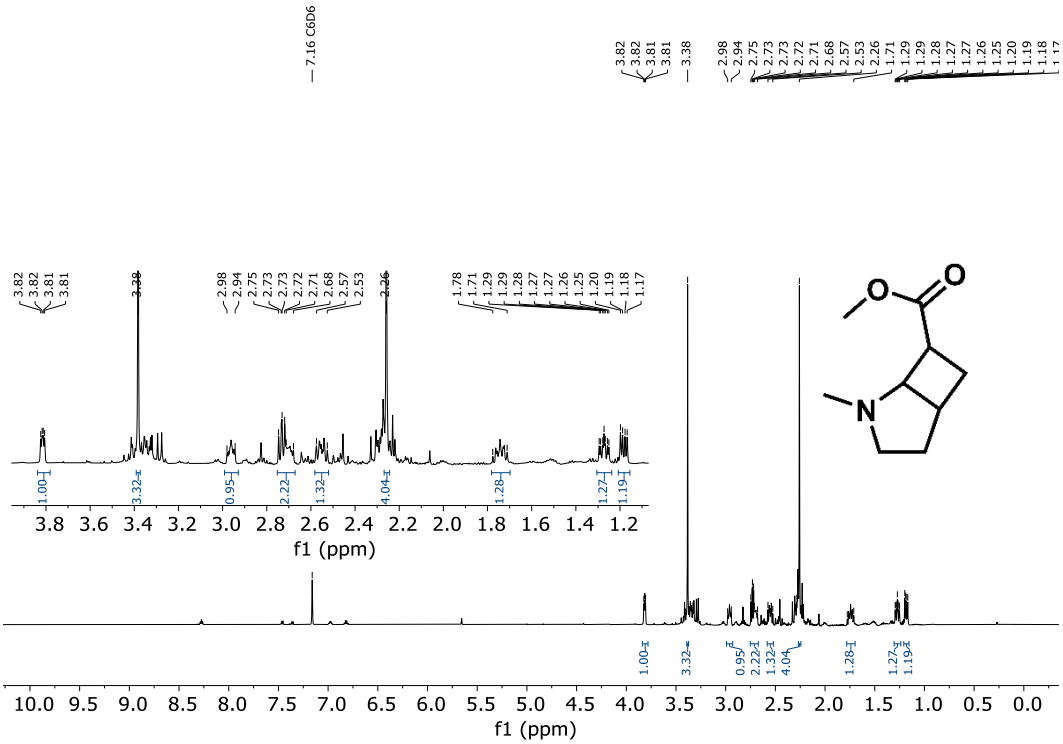
^{13}C{^{1}H} NMR (126 MHz, 25°C, C_6D_6) of **4a**



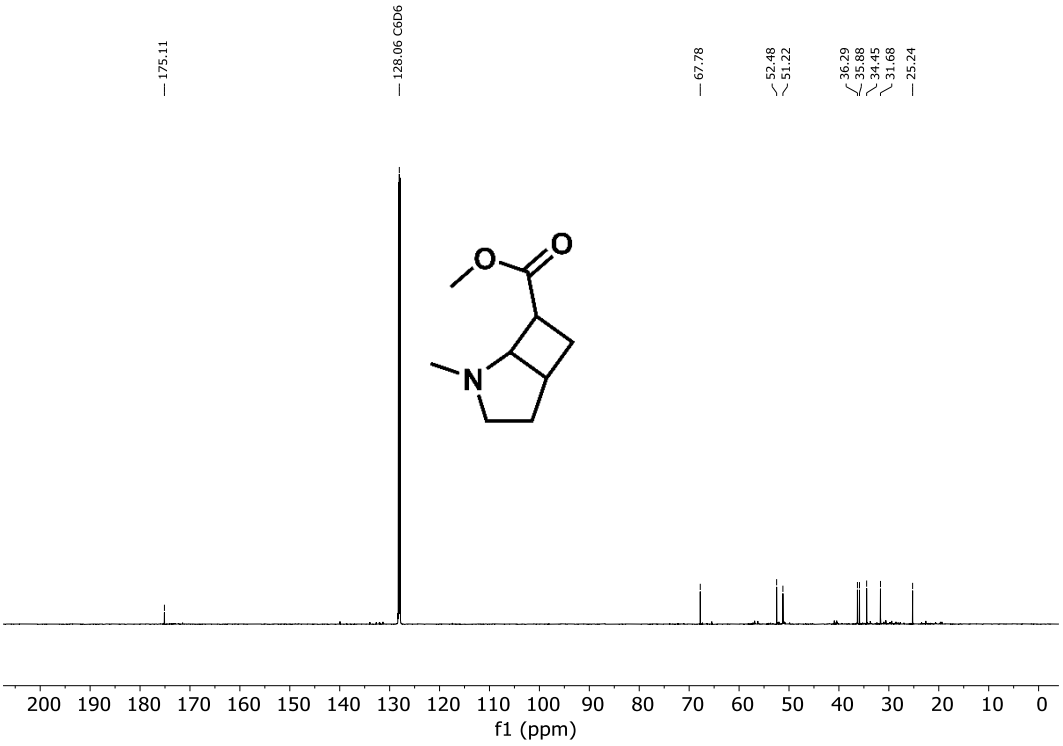
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **4b**



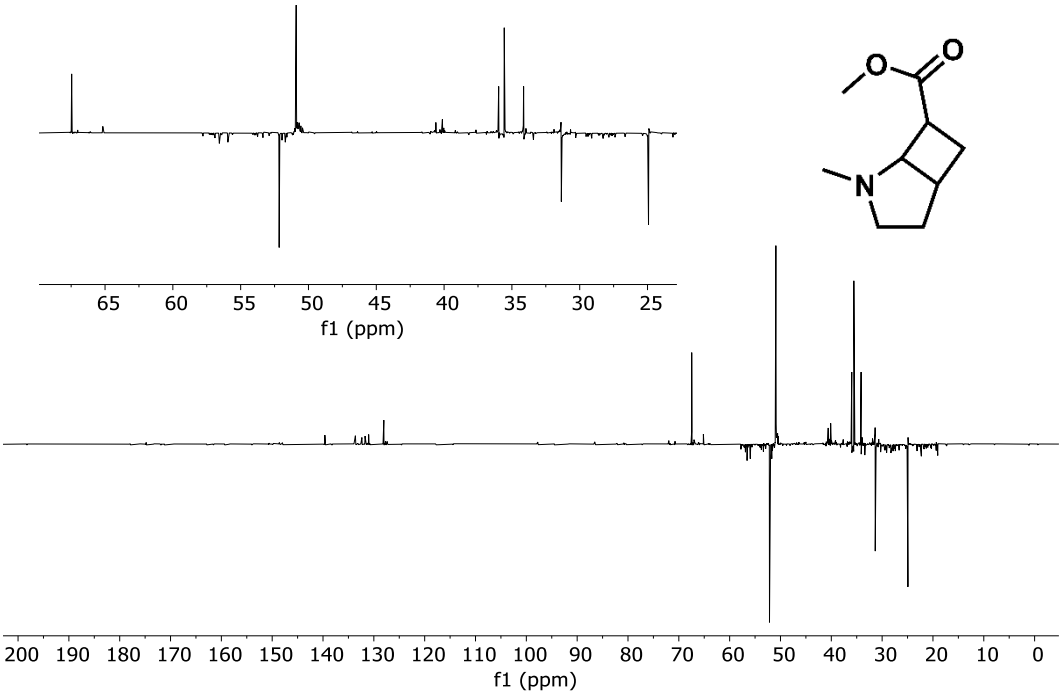
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **4b**



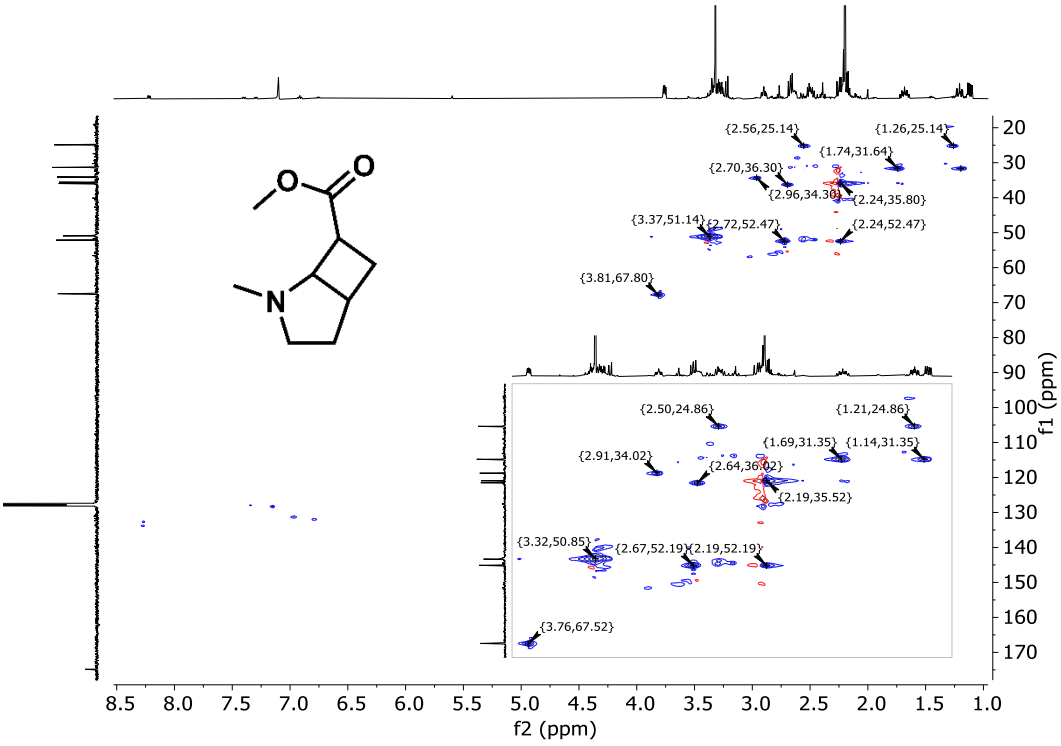
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **5c**



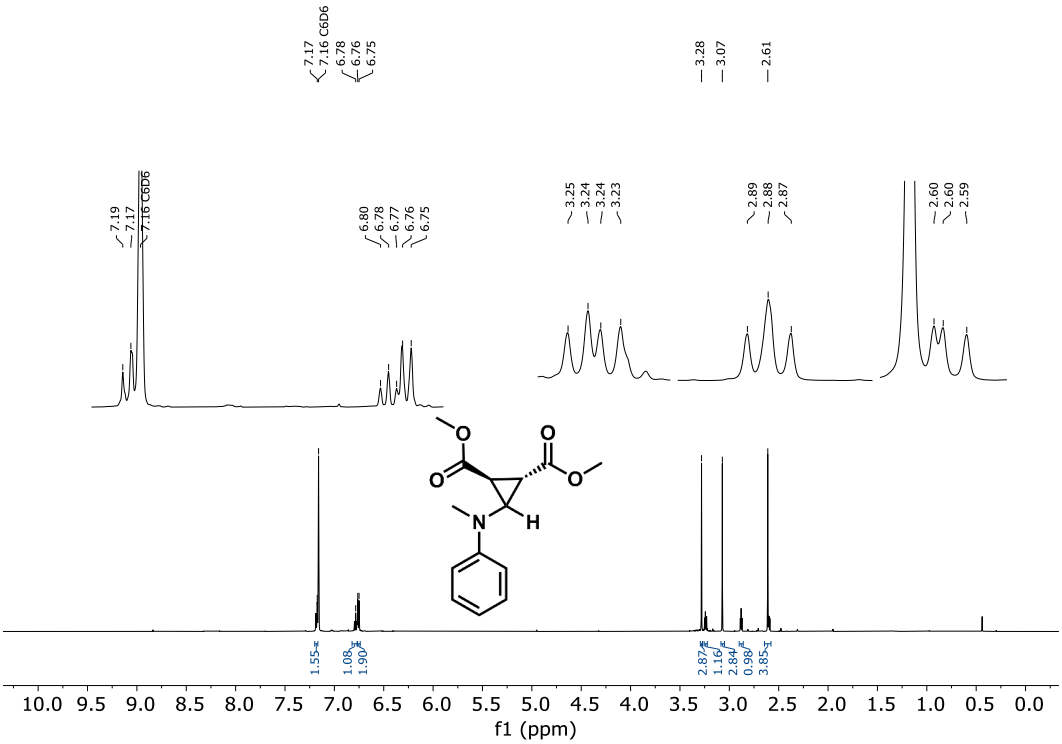
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **5c**



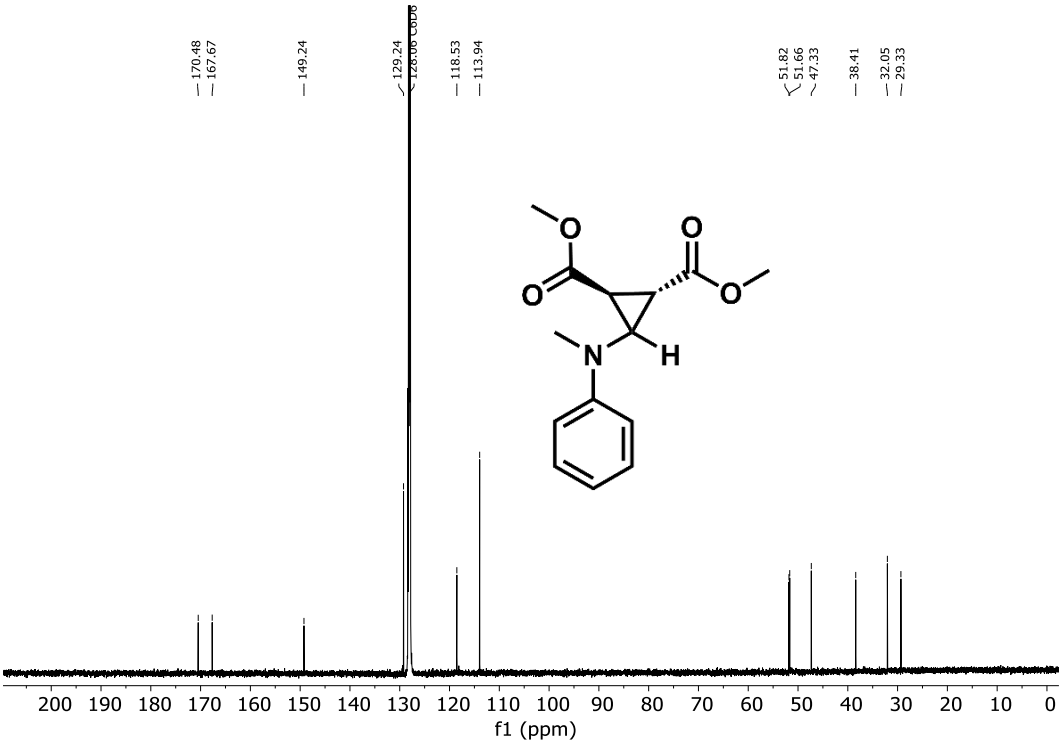
DEPT 135 (151 MHz, 25°C, C_6D_6) of **5c**



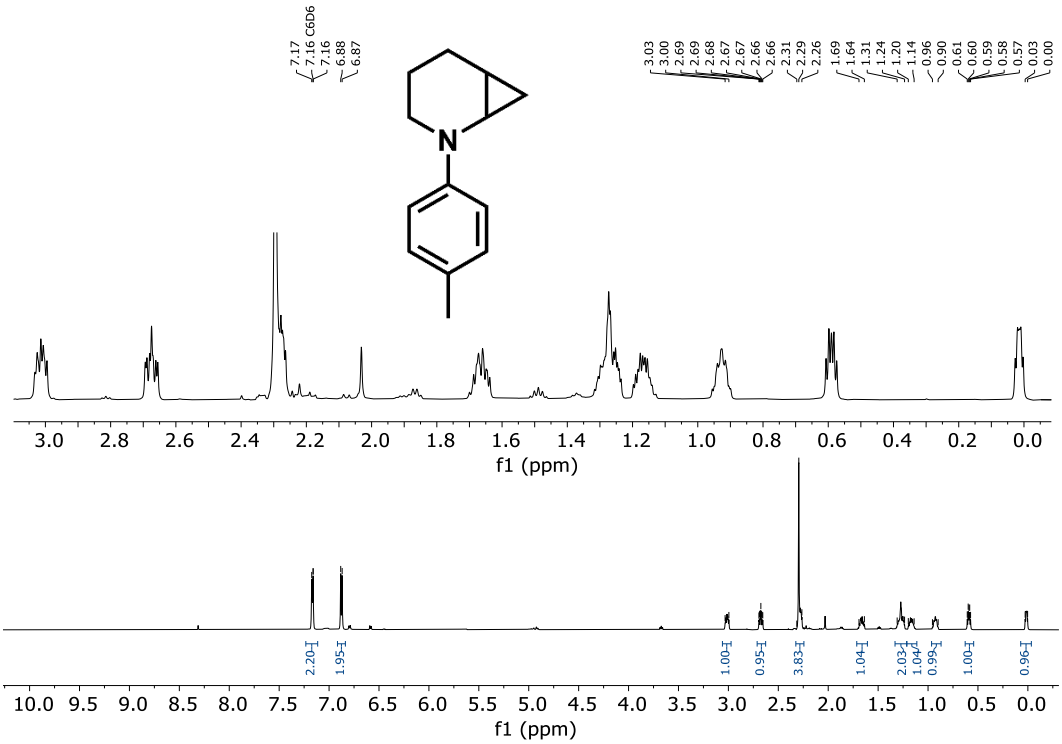
HSQC (151 MHz, 25°C, C_6D_6) of **5c**



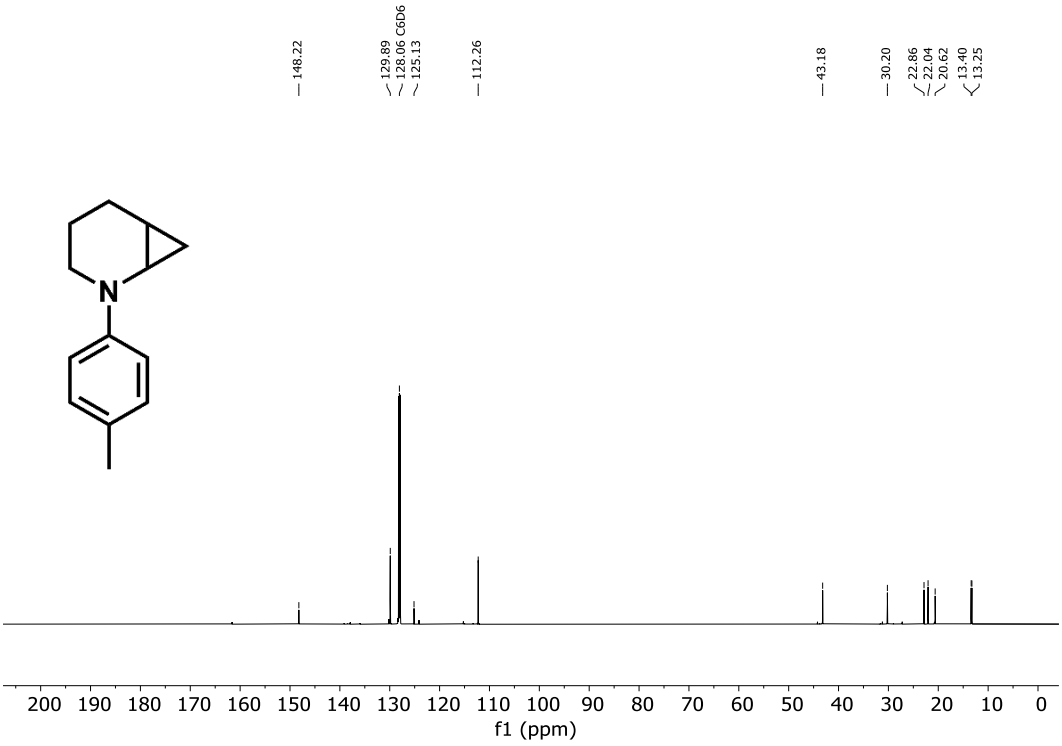
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **6d**



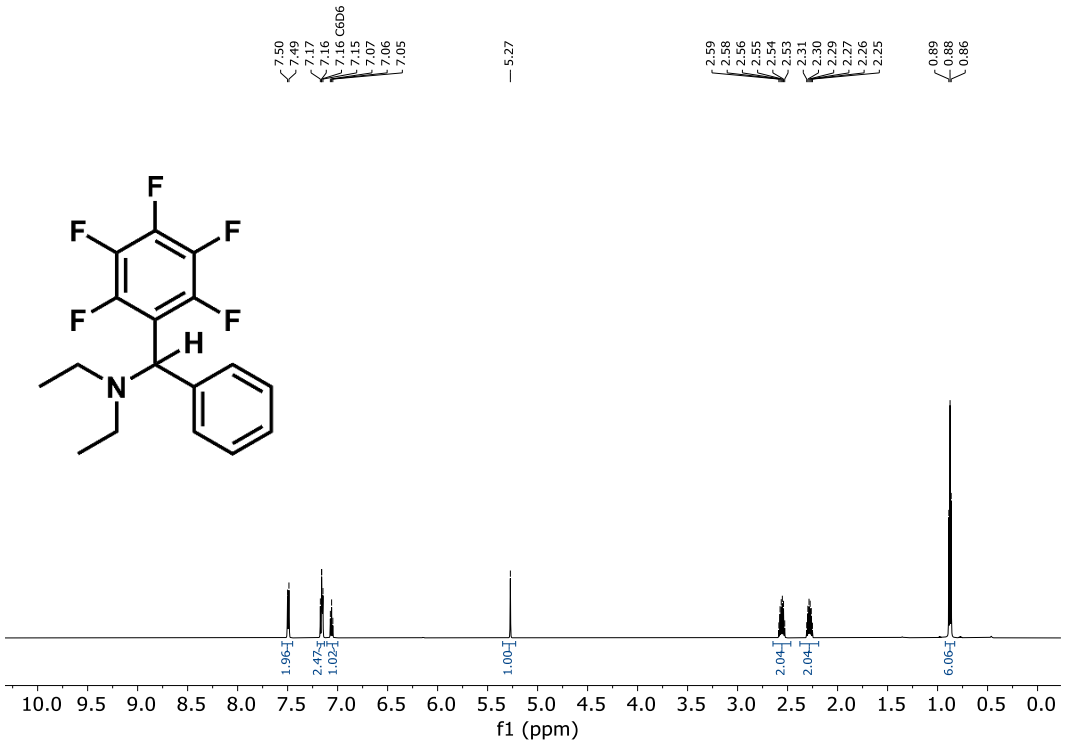
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **6d**



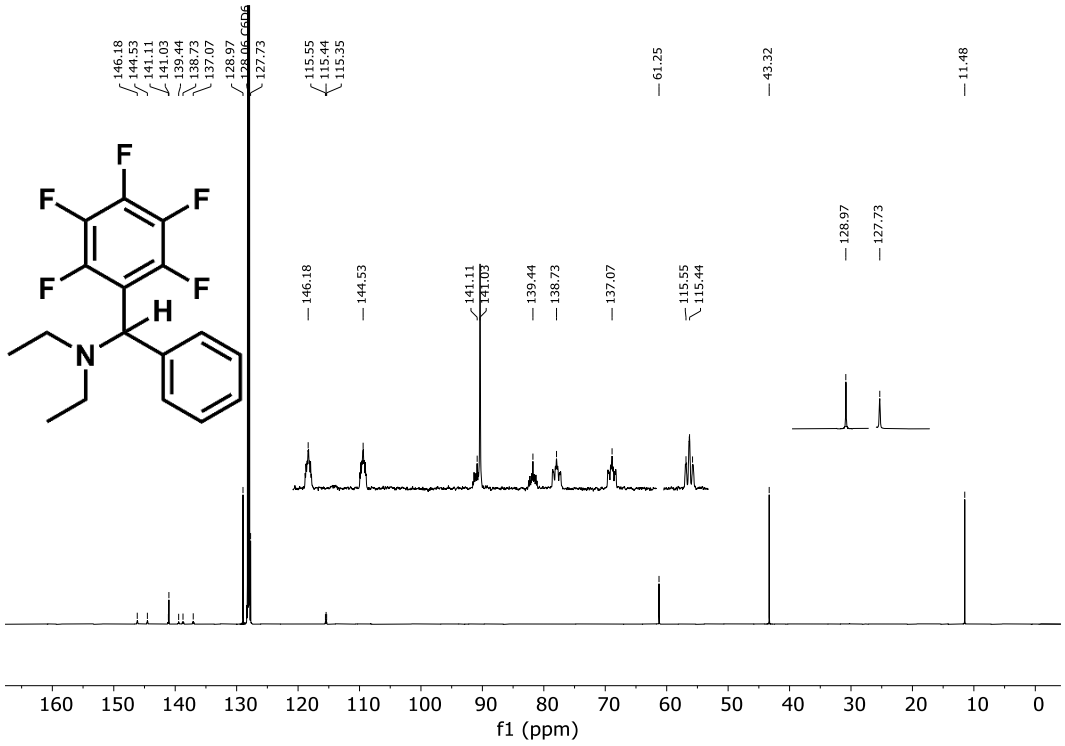
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **7e**



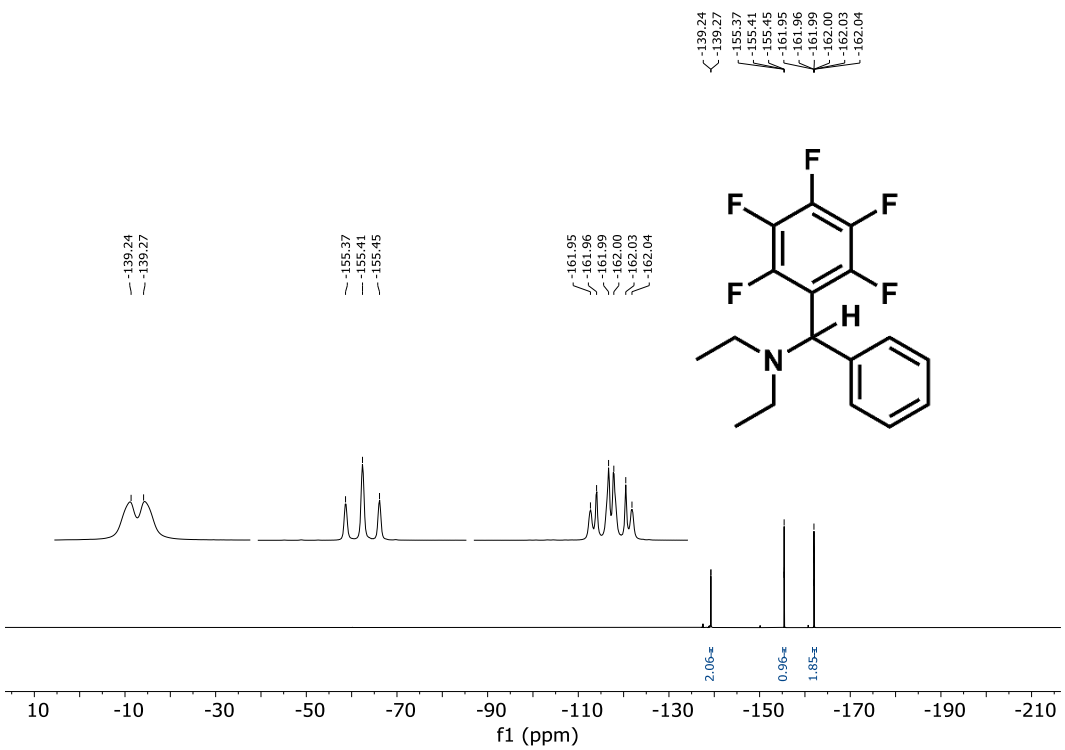
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **7e**



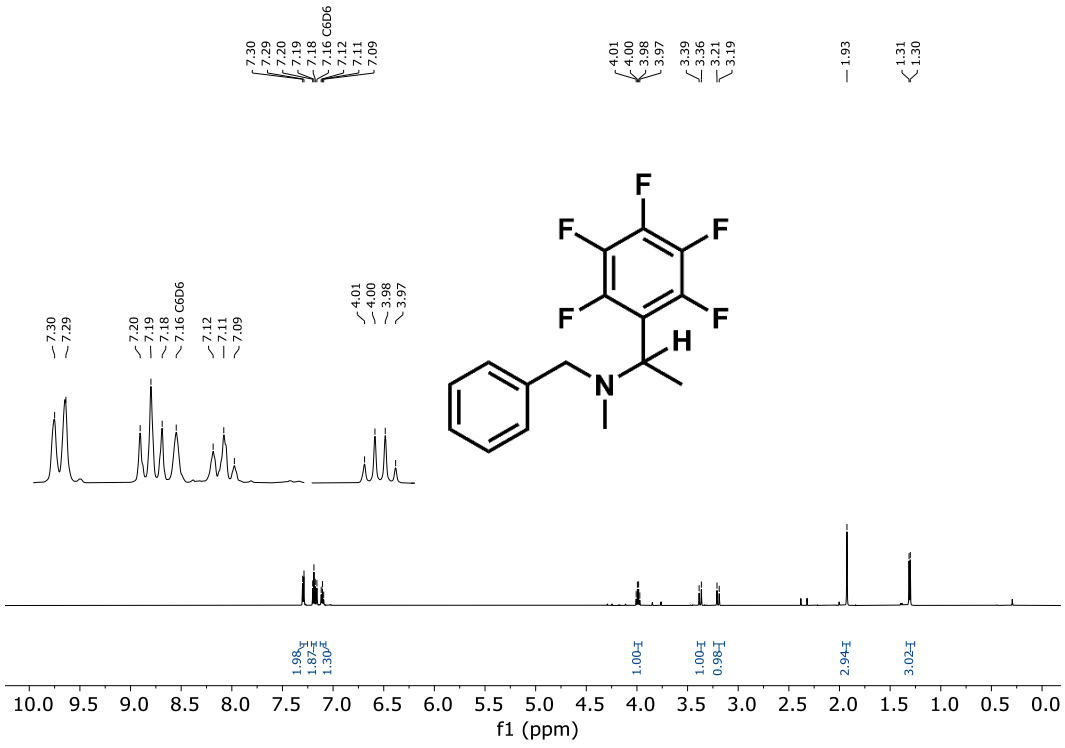
^{1}H NMR (600 MHz, 25°C, C_6D_6) of **8f**



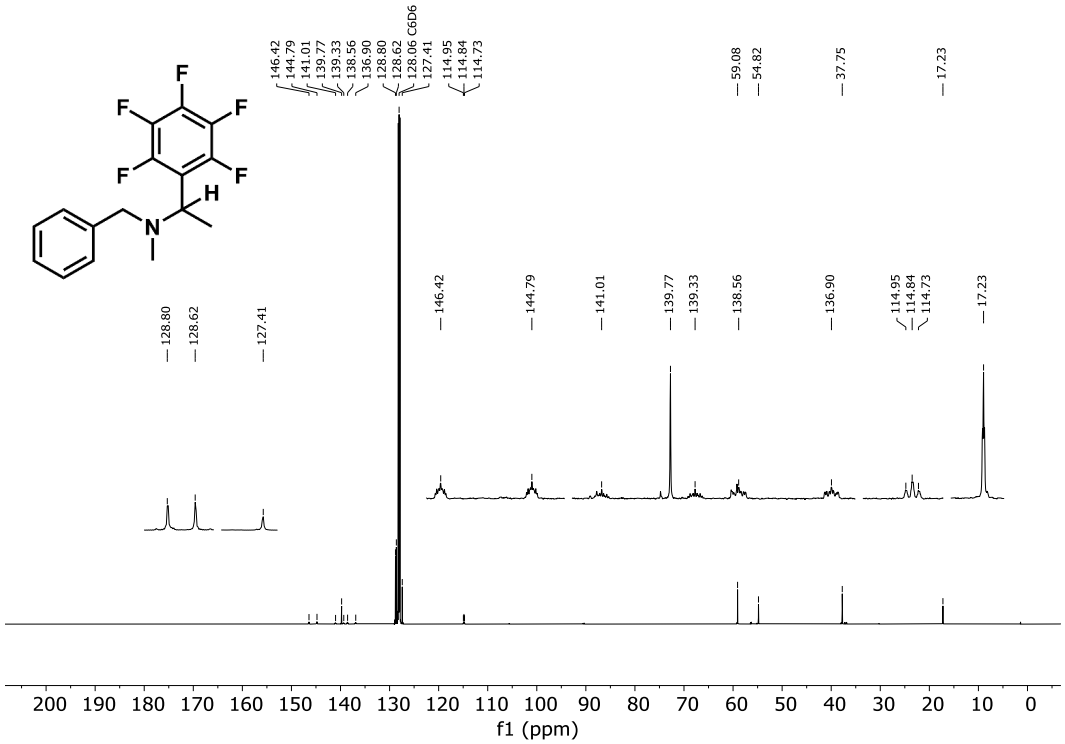
^{13}C{^{1}H} NMR (151 MHz, 25°C, C_6D_6) of **8f**



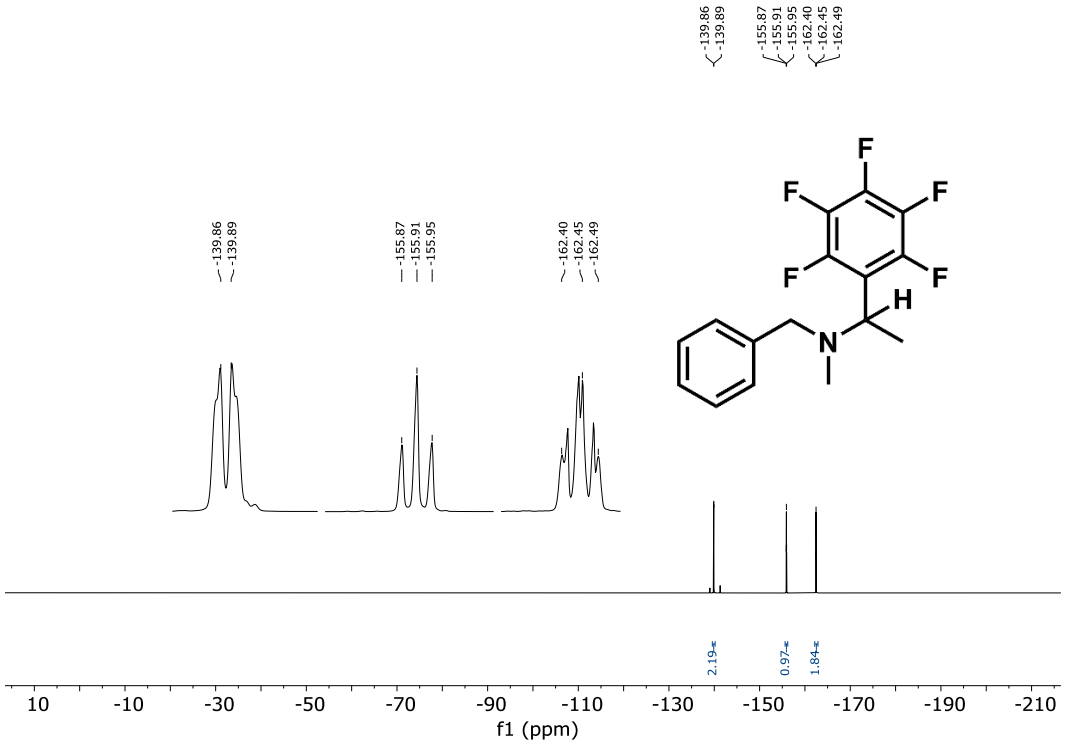
^{19}F NMR (565 MHz, 25°C, C_6D_6) of **8f**



^{1}H NMR (600 MHz, 25°C, C_6D_6) of **8g**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 25°C, C_6D_6) of **8g**



^{19}F NMR (565 MHz, 25°C, C_6D_6) of **8g**

5) UV-Visible Spectroscopy

UV-Visible spectra were acquired on an Agilent Cary 60 UV-Vis spectrophotometer. Acquisition parameters: 300 nm/min scan speed, 0.5 data interval, 0.1 averaging time, dual beam mode. All spectra are baseline corrected. Samples were prepared using distilled THF.

Table S1. Tabulated spectroscopic data for all compounds in THF.

Compound	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)
1a	300	968
2a-Li	340	855
2a-Na	340	1197
2a	340	1300
2a'	340	1516

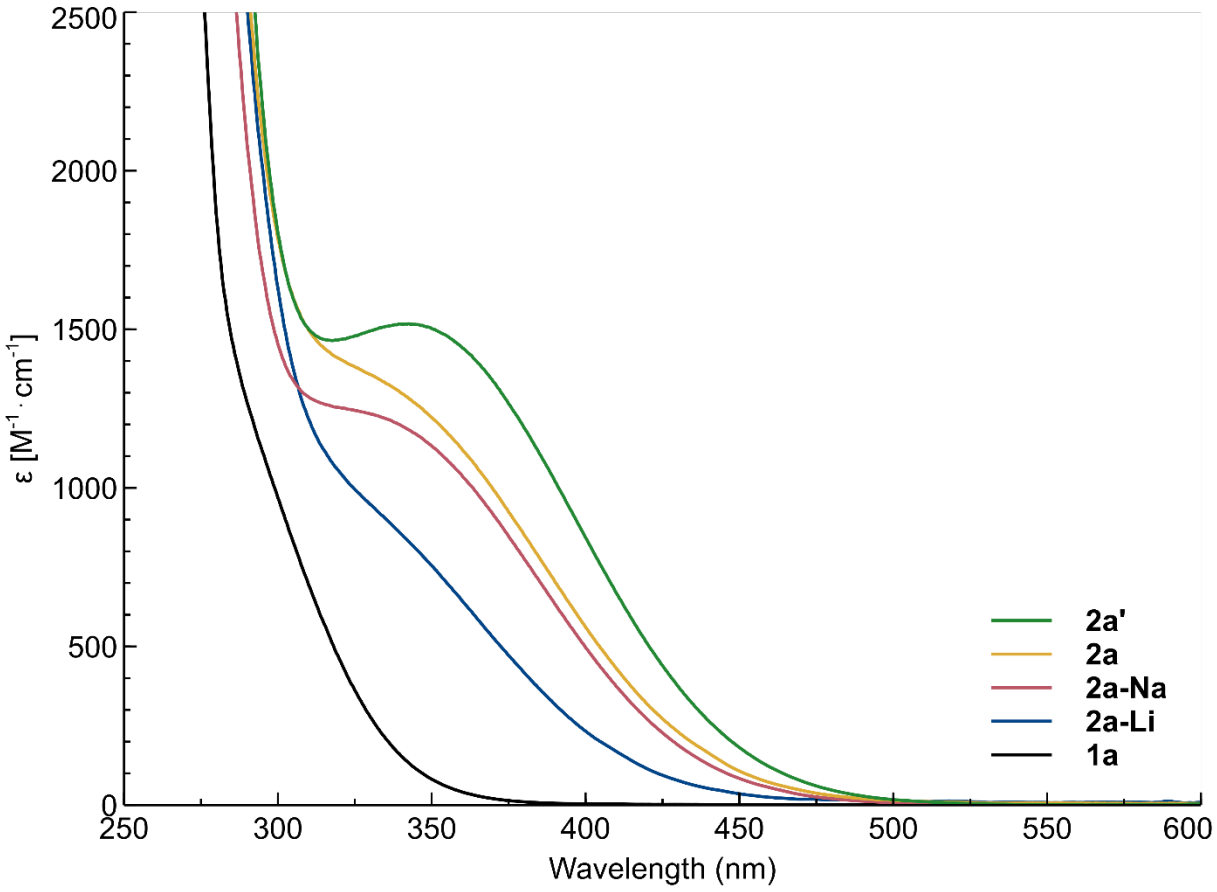


Figure S7. UV-vis spectra of **1a** and hydrazonate salts derived therefrom with various countercations in THF at *ca.* 1 mM.

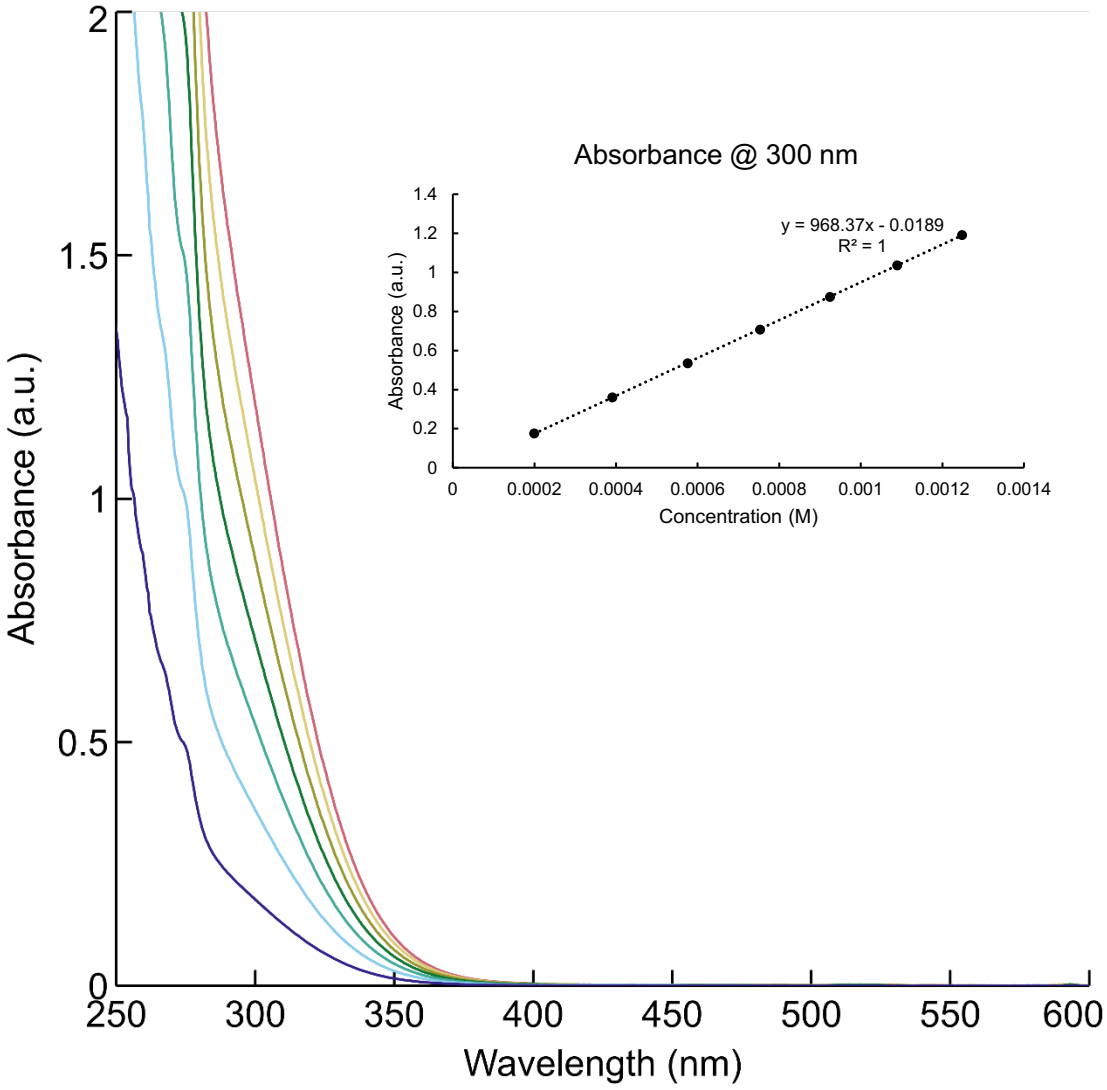


Figure S8. UV-Vis spectra for determining the molar absorptivity of **1a** in THF.

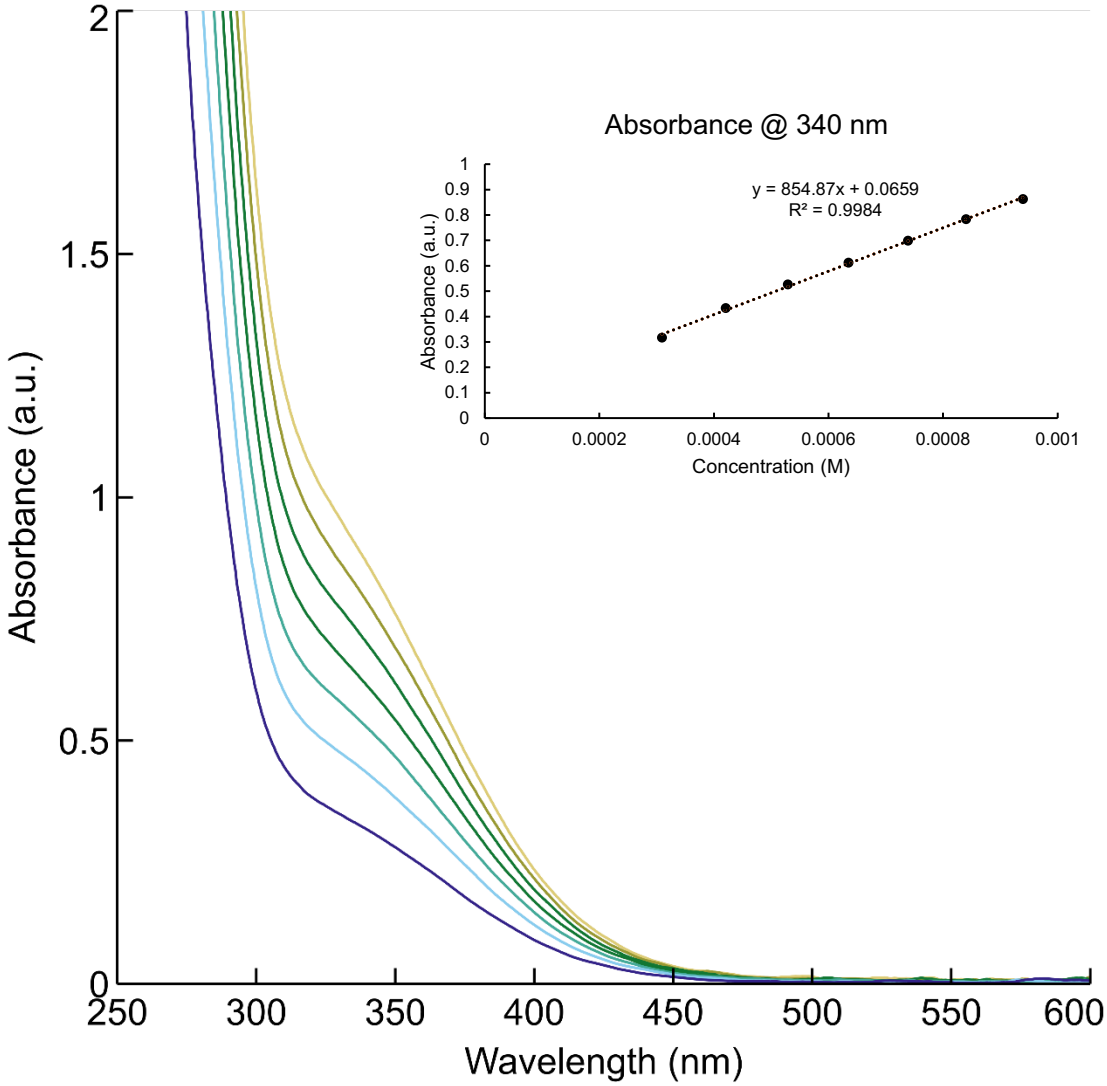


Figure S9. UV-Vis spectra for determining the molar absorptivity of **2a-Li** in THF.

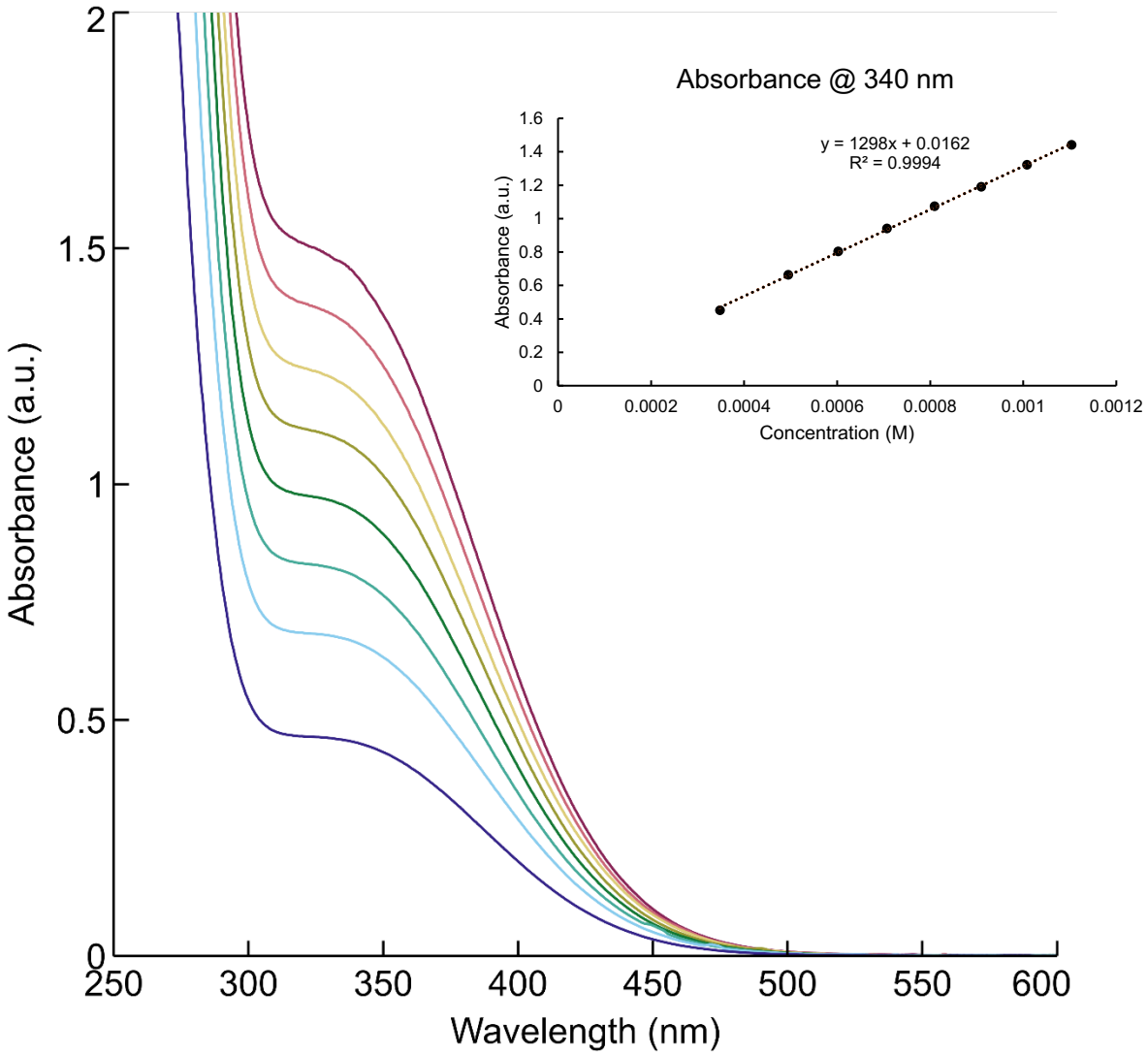


Figure S10. UV-Vis spectra for determining the molar absorptivity of **2a-Na** in THF.

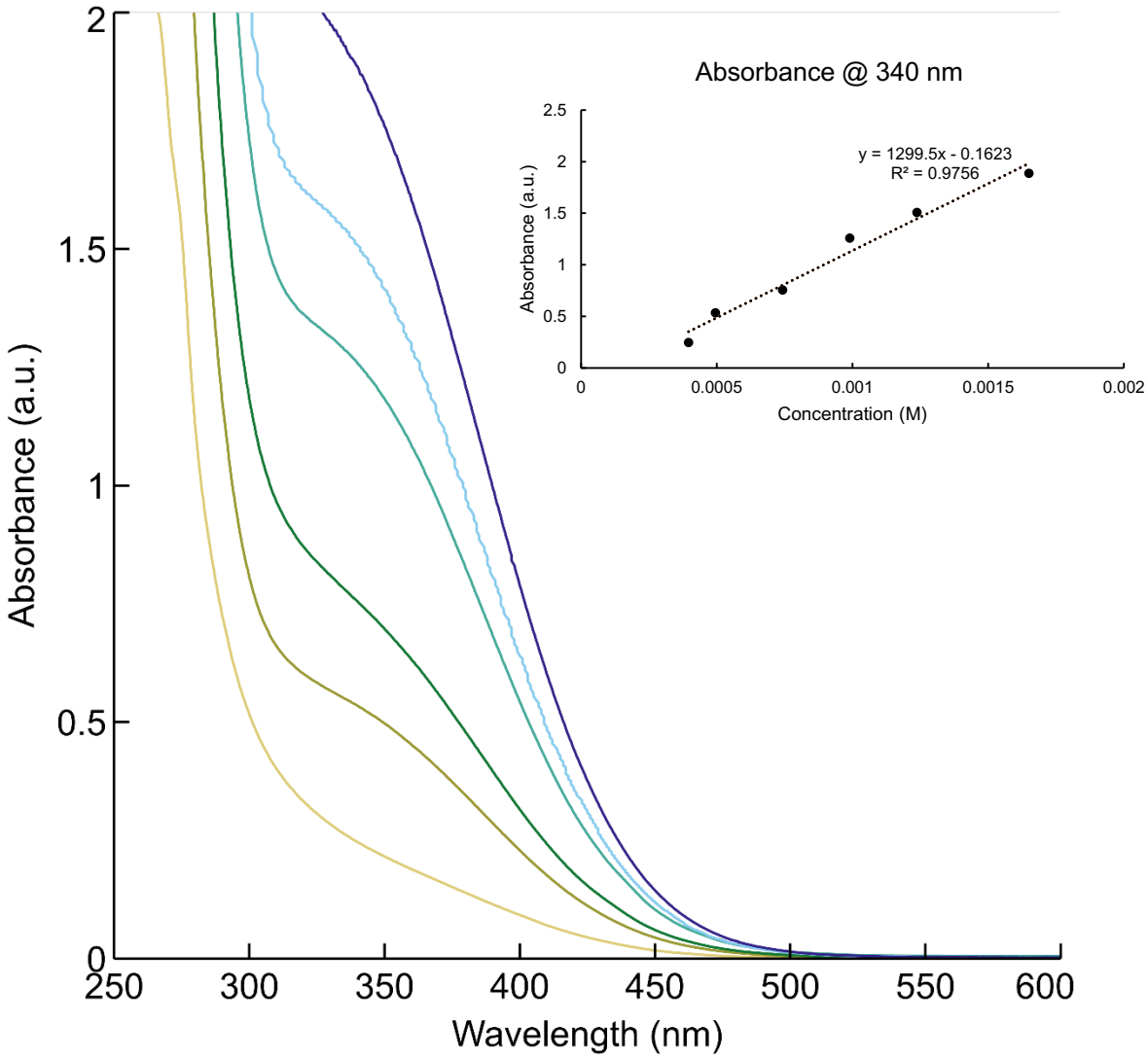


Figure S11. UV-Vis spectra for determining the molar absorptivity of **2a** in THF.

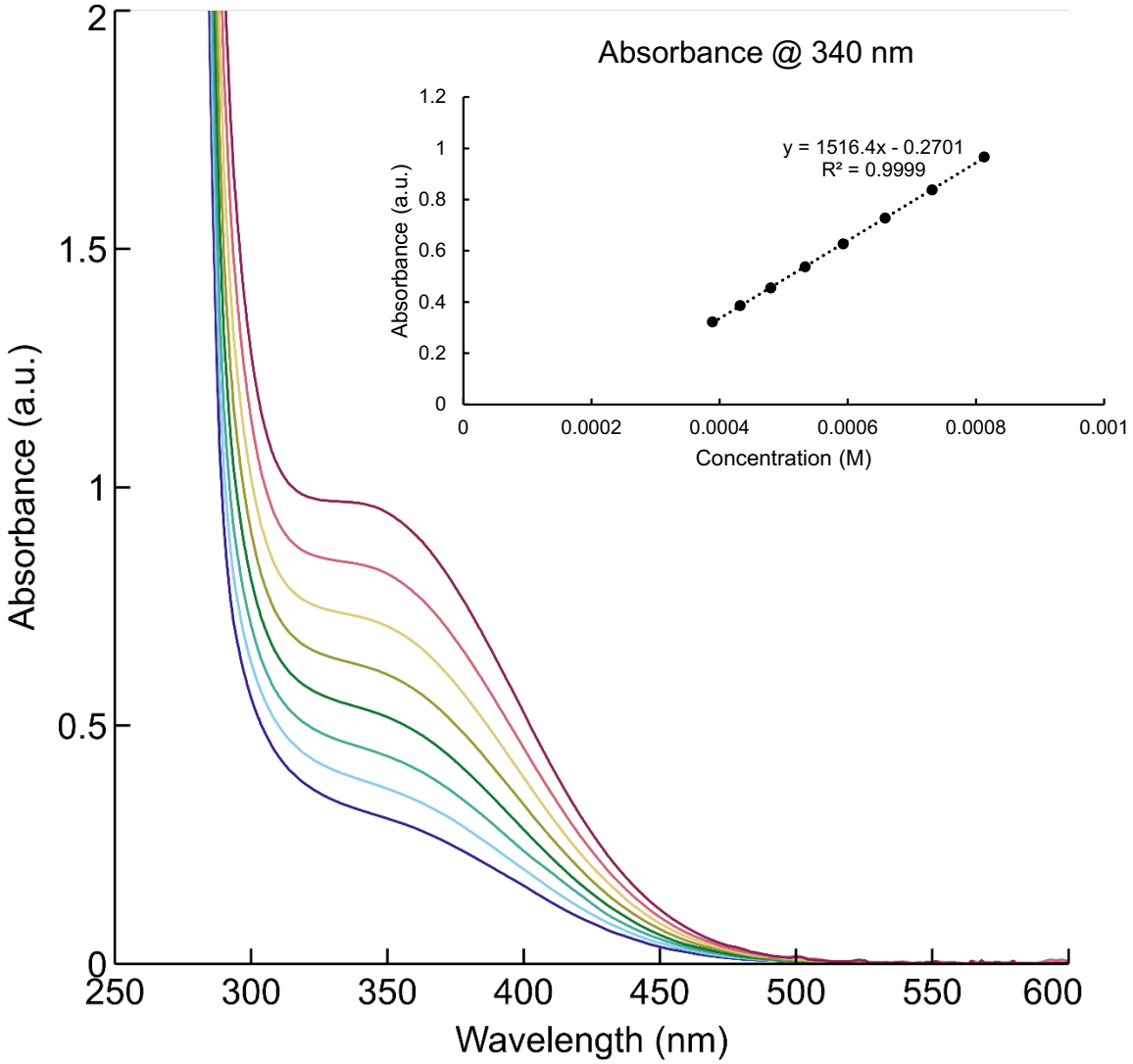


Figure S12. UV-Vis spectra for determining the molar absorptivity of **2a'** in THF.

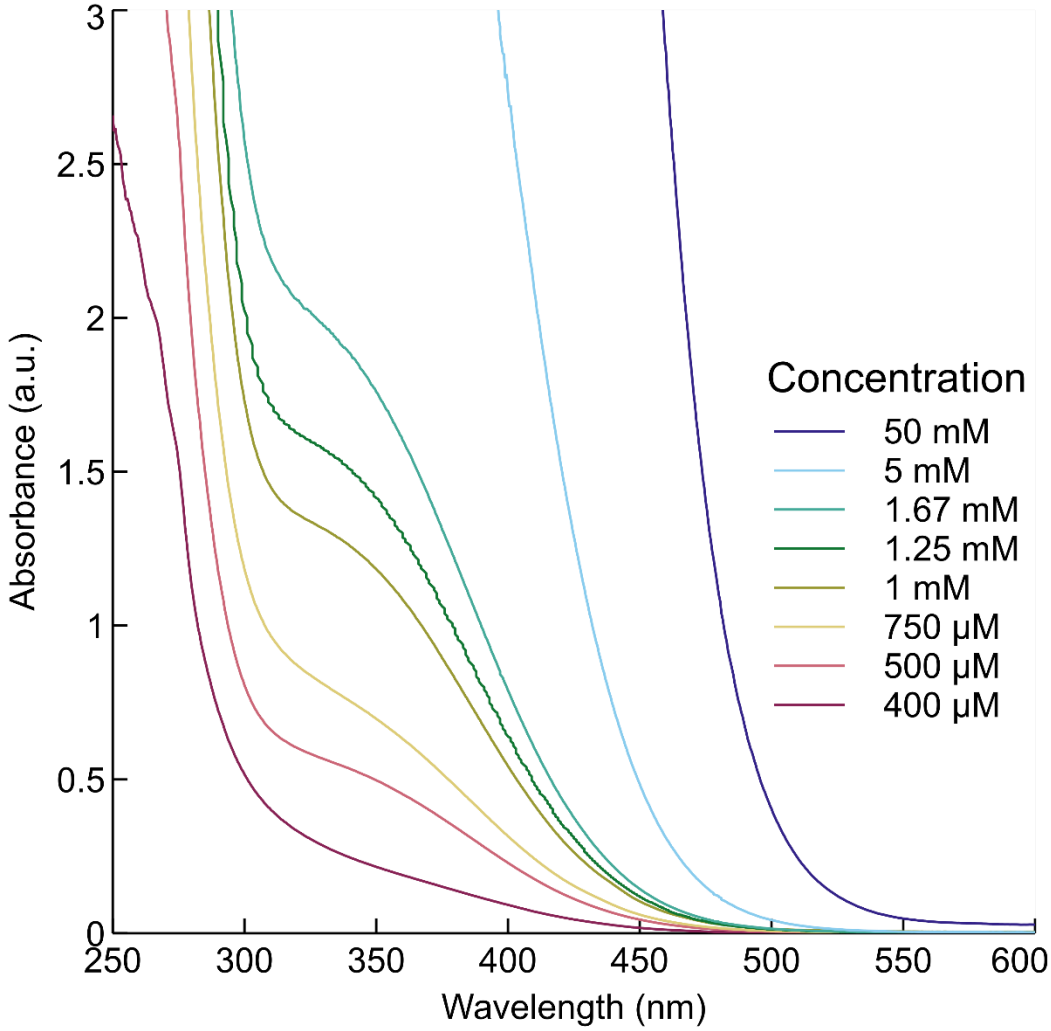


Figure S13. UV-Vis spectra of **2a** at varying concentrations in THF.

6) Crystallography

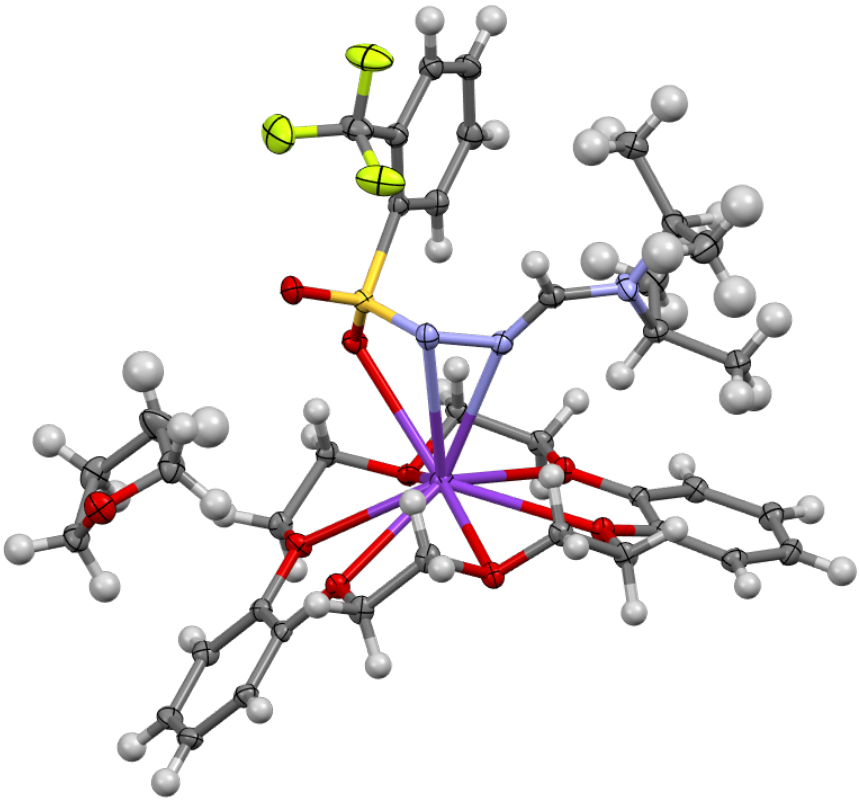


Figure S14. Crystal structure of **2a'** with thermal ellipsoids set to 50%.

Crystal data and structure refinement features for 1a-[K(crown)]

CCDC Deposition Number	2530033
Empirical formula	$C_{38}H_{51}F_3KN_3O_9S$
Formula weight	821.97
Temperature (K)	273.15
Crystal system	triclinic
Space group	P-1
a (Å)	9.1895(5)
b (Å)	9.7786(5)
c (Å)	22.9310(10)
α (°)	80.550(2)
β (°)	86.176(2)

γ (°)	78.805(2)
Volume ($Å^3$)	1992.66(17)
Z	2
ρ_{calc} (g/cm^3)	1.370
μ (mm^{-1})	0.257
F(000)	868.0
Crystal size (mm^3)	0.16 × 0.14 × 0.125
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	3.604 to 53.434
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	85746
Independent reflections	8461 [R_{int} = 0.0547, R_{sigma} = 0.0251]
Data / restraints / parameters	8461 / 0 / 501
Goodness-of-fit on F2	1.018
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0322, wR_2 = 0.0727
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0764
Largest diff. peak/hole ($e•Å^{-3}$)	0.38/-0.36

-

7) Computational Modeling

All calculations were performed using Orca 6.0.0 or Orca 6.0.1.[6] Unless stated otherwise, all default parameters were used. For all calculations, options DefGrid2 and TightSCF were employed. All calculations using the Global Optimizer Algorithm (GOAT), as implemented in ORCA, used Grimme's semi-empirical GFN2-XTB[7] method for downhill steps and the GFN-FF[8] method for uphill steps, with the ALPB solvation model.[9] Minima and transition states were verified by the presence of zero or one imaginary vibrational mode, respectively. Final reported Gibbs free energies were obtained by adding the Gibbs free energy minus the electronic energy from frequency calculations to the relevant single point electronic energies. Cartesian coordinates (Å) and isosurfaces were visualized using ChemCraft.

Simplified TD-DFT (sTD-DFT)[10,11] calculations were performed using the ωB97x-D3[12] and CAM-B3LYP[13] functionals, as well as the def2-TZVPP[14] basis set and CPCM solvation with parameters for THF. Further, the RIJCOSX approximation was employed,[15,16] using the def2/J auxiliary basis set.[17] Ultimately, the ωB97X-D3 functional was determined to be in best agreement with the experimental data. Spectral convolution was performed in ChemCraft.

For modeling UV-Visible spectra, a multistep computational workflow was applied, an adaptation of the *CREST/CENSO* workflow developed by Grimme and coworkers.[18]

Step 1: For each salt, an initial conformational ensemble was generated using GOAT.

Step 2: The electronic energies of these conformers were re-evaluated at the r^2SCAN-3c/CPCM(THF) level of theory.[19] For each salt, all conformers with an electronic energy 3 kcal/mol or greater than the minimum were excluded.

Step 3: Geometries were reoptimized at the r^2SCAN-3c/CPCM(THF) level of theory. On a case-by-case basis, conformers which were absent from the ensembles of some salts were added to others and found to be more thermodynamically stable than those generated by GOAT.

Step 4: Frequency calculations were performed using the most stable conformer from Step 3.

Step 5: sTD-DFT calculations were performed using the geometry of the most stable conformer from Step 3.

The workflow is represented graphically in **Figure S15**. Cartesian coordinates for the most stable conformers identified in Step 3 are provided in "Cartesian Coordinates."

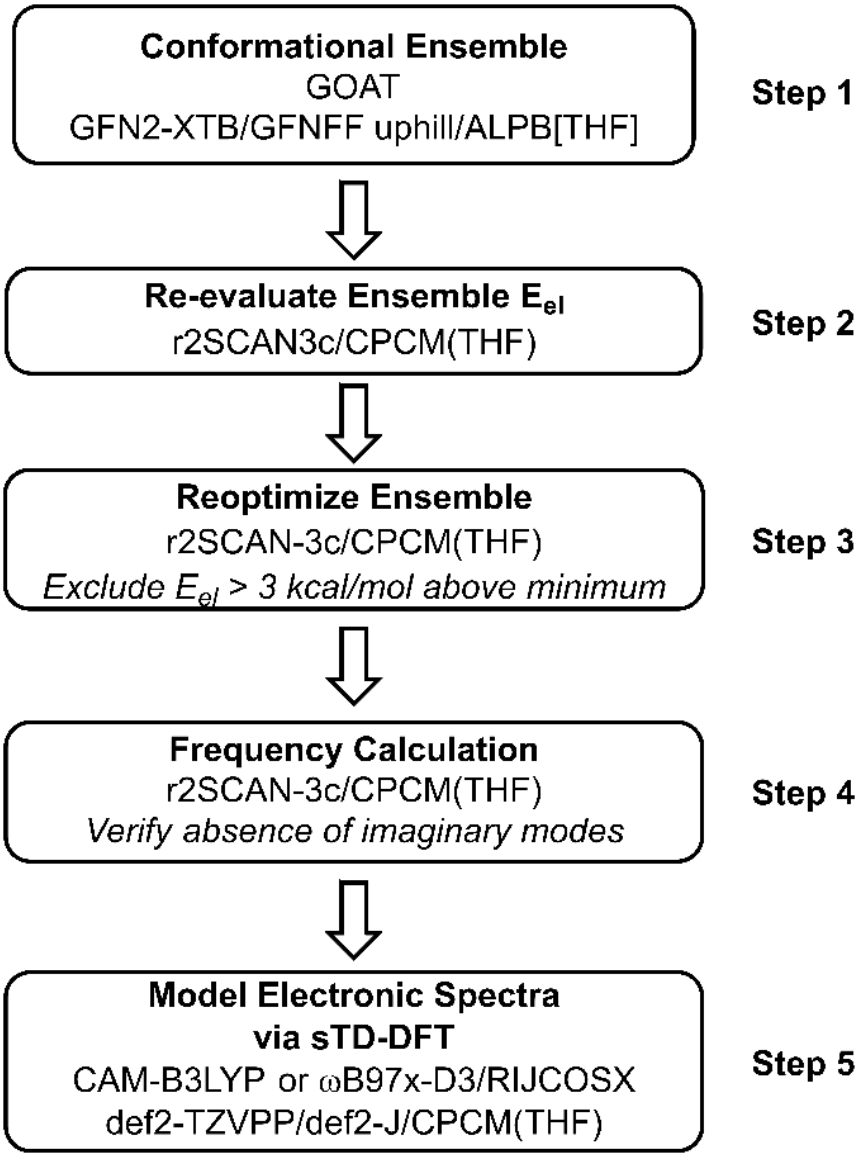


Figure S15. Graphical depiction of computational workflow for modeling the UV-Visible spectra of various hydrazonate salts.

To model the carbene generation mechanism, the following workflow was applied:

Step 1: To identify the global minimum of conformationally flexible structures, an initial conformational ensemble in the singlet or triplet state, as appropriate, was generated using GOAT. In some cases, the full ensemble was reoptimized at the r^2SCAN-3c/CPCM(Et_2O) level of theory. For others, the ensemble energies were first re-assessed via single point calculations, then a sub-ensemble was reoptimized. For

transition states, coordinate scans were used to identify the saddlepoint geometry, which was then optimized.

Step 2: Thermostatistical corrections to the electronic energy for the geometries obtained from Step 1 were calculated at the r^{2}SCAN-3c/CPCM(Et_2O) of theory.

Step 3: Final Gibbs free energies were obtained by recalculating the electronic energies at the ωB97X-V/def2-mTZVPP/SMD(Et_2O) level of theory using the Step 1 geometries.[20] Thermostatistical corrections obtained from Step 2 were applied to the resulting electronic energies.

The resulting data are tabulated in **Table S8**. Cartesian coordinates for reactants, products, byproducts, intermediates, and transition states provided in "Cartesian Coordinates."

Electronic structure of transient mono(amino)carbenes

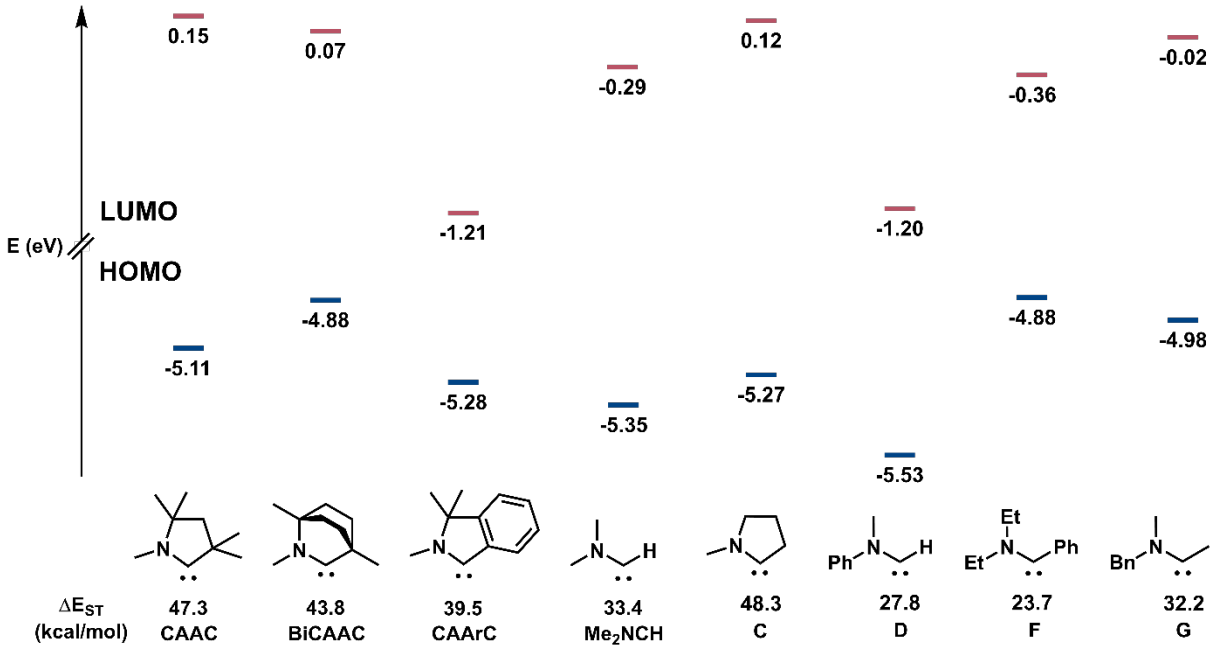


Figure S16. Calculated HOMO and LUMO eigenvalues and adiabatic singlet-triplet gaps (ΔE_{ST}) for carbenes from prior work and representative examples from this work. The B3LYP/def2-TZVPP level of theory was employed.

To predict the degree to which the electronic structure of the transient aminocarbenes we access resembles that of known stable aminocarbenes, such as **CAAC**,[21] **BiCAAC**,[22] and **CAArC**,[23] we modelled the electronic structure of representative examples using DFT at the B3LYP/def2-TZVPP level of theory (**Figure S16**). Based upon the calculated HOMO eigenvalues, which can be used to predict the relative nucleophilicity of carbenes, those generated in this work should exhibit similar nucleophilicity to stable mono(amino)carbenes. However, as indicated by their lower adiabatic singlet-triplet

gaps (ΔE_{ST}), our transient mono(amino)carbenes should be more ambiphilic than most stable examples.[24,25] This accords well with the fact that acyclic carbenes are generally more ambiphilic than cyclic carbenes. The slight differences between **G** and the closely related **CAAC** are likely due to the absence of electron-releasing quaternary carbons which destabilize the HOMO.

Table S2. Relevant electronic structure and thermochemical data for assessing substituent effects in carbenes at the B3LYP/def2-TZVPP level of theory.

Structure	HOMO (H)	LUMO (H)*	G (H)	v (cm^{-1})
CAAC – S0	-0.1878	0.0054	-407.5541833	64.52
CAAC – T1	---	---	-407.47877	56.32
BiCAAC – S0	-0.1795	0.0024	-445.6325355	109.26
BiCAAC – T1	---	---	-445.5627098	80.67
CAArC – S0	-0.1942	-0.0446	-481.3824689	90.79
CAArC – T1	---	---	-481.3195533	72.07
Me_2NCH – S0	-0.1968	-0.0106	-173.08216	161.28
Me_2NCH – T1	---	---	-173.0288684	174.99
C – S0	-0.1937	0.0043	-250.4590738	112.95
C – T1	---	---	-250.3820507	80.82
D – S0	-0.2034	-0.0442	-364.7194908	30.24
D – T1	---	---	-364.6751269	61.61
F – S0	-0.1793	-0.0132	-482.5532543	31.49
F – T1	---	---	-482.5154376	35.75
G – S0	-0.1831	-0.0009	-443.2749471	32.52
G – T1	---	---	-443.2236849	29.94

TD-DFT Calculations

Both the CAM-B3LYP and ωB97X-D3 range-adjusted hybrid functionals were used to simulate the absorption of **1b** and the corresponding hydrazonate salts, serving as simpler models in place of the **1a** series. Overall, ωB97X-D3 better replicates the structure of the absorption bands observed in the potassium hydrazonate salts. Note, CAM-B3LYP produces a distinct absorption band corresponding to the first excitation, rather than a "shoulder" which begins at *ca.* 300 nm.

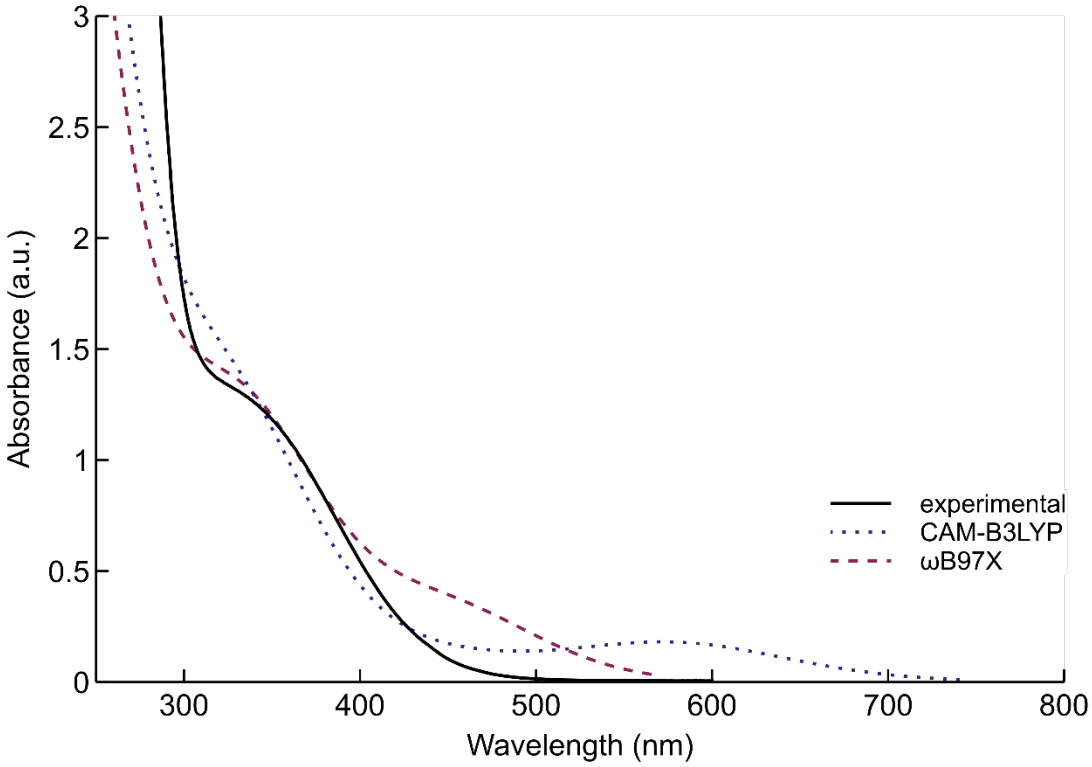


Figure S17. Comparison of experimental UV-Vis spectrum (black, solid) of **2a** with computed spectra (Gaussian broadening, FWHM = 50 nm) obtained using the CAM-B3LYP (blue, dotted) or ωB97X-D3 (red, dashed) functionals. Both computed spectra are offset by -12000 cm^{-1}, with intensity adjusted for clarity.

Noting the dramatic influence of the cation identity on the photolysis reactions (Figure S6) and the UV-Vis spectra of the hydrazonate salts (Figure S7), we modelled the low-lying excitations for the neutral hydrazone **1b** and the corresponding hydrazonates (Figures S18 – S22, Tables S3 – S7). As observed experimentally, the calculated lowest energy absorption band in the salts is bathochromically shifted as compared to that of the neutral hydrazone. Furthermore, this band is increasingly red-shifted for hydrazonates with larger cations, as has been observed for other organic anions.[26] This explains the poor productivity of **2a-Li** as compared to **2a**; the lithium salt is much less sensitive to 450 nm light than the potassium salt. As for the sodium salt (**2a-Na**) and potassium crown etherate complex (**2a'**), these are significantly less soluble in Et_2O as compared to the potassium salt, forming suspensions with barely colored supernatant. The hydrazonate salts may need to be in solution to undergo photolysis. Thus, despite being equally or more sensitive to 450 nm light as **2a**, **2a-Na** and **2a'** give little to no trapping products under photolytic conditions.

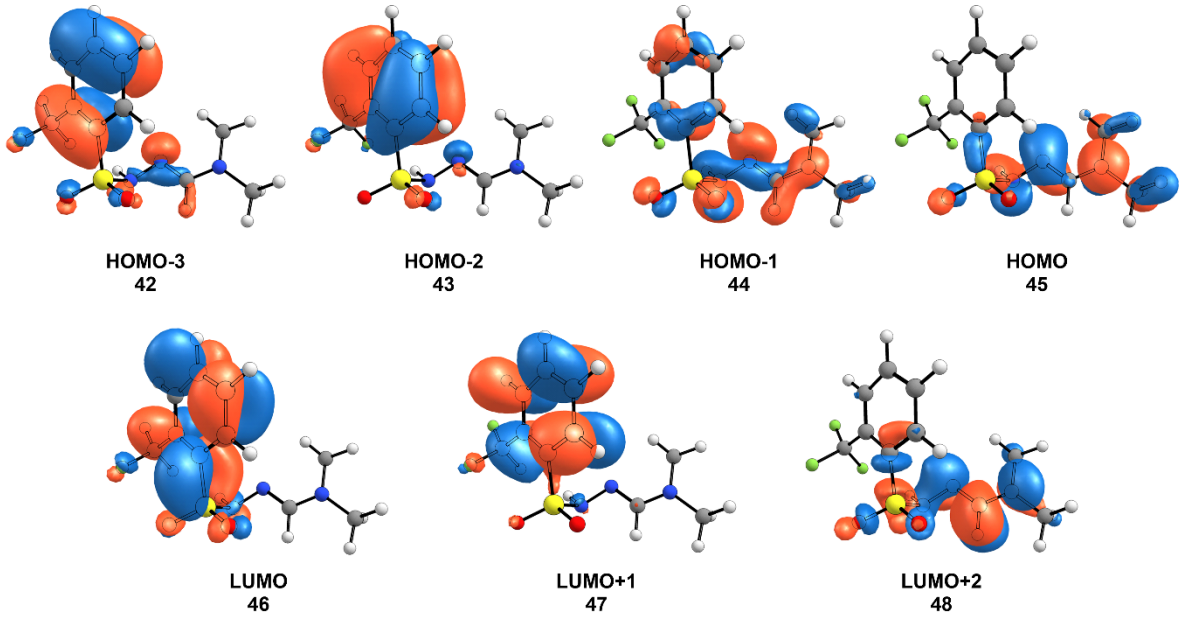


Figure S18. Canonical orbitals of **1b** obtained via sTD-DFT using the ωB97X-D3 functional.

Table S3. Nature of selected electronic transitions for **1b** obtained via sTD-DFT using the ωB97X-D3 functional.

Transition	eV	nm	Amplitudes		
S1	5.086	243.8	0.63 (45-> 46)	0.11 (44-> 46)	0.09 (42-> 46)
S2	5.172	239.7	0.59 (43-> 46)	0.26 (42-> 47)	0.06 (44-> 46)
S3	5.336	232.4	0.41 (42-> 46)	0.26 (43-> 47)	0.23 (45-> 46)
S4	5.671	218.6	0.60 (45-> 48)	0.24 (44-> 48)	0.05 (45-> 47)

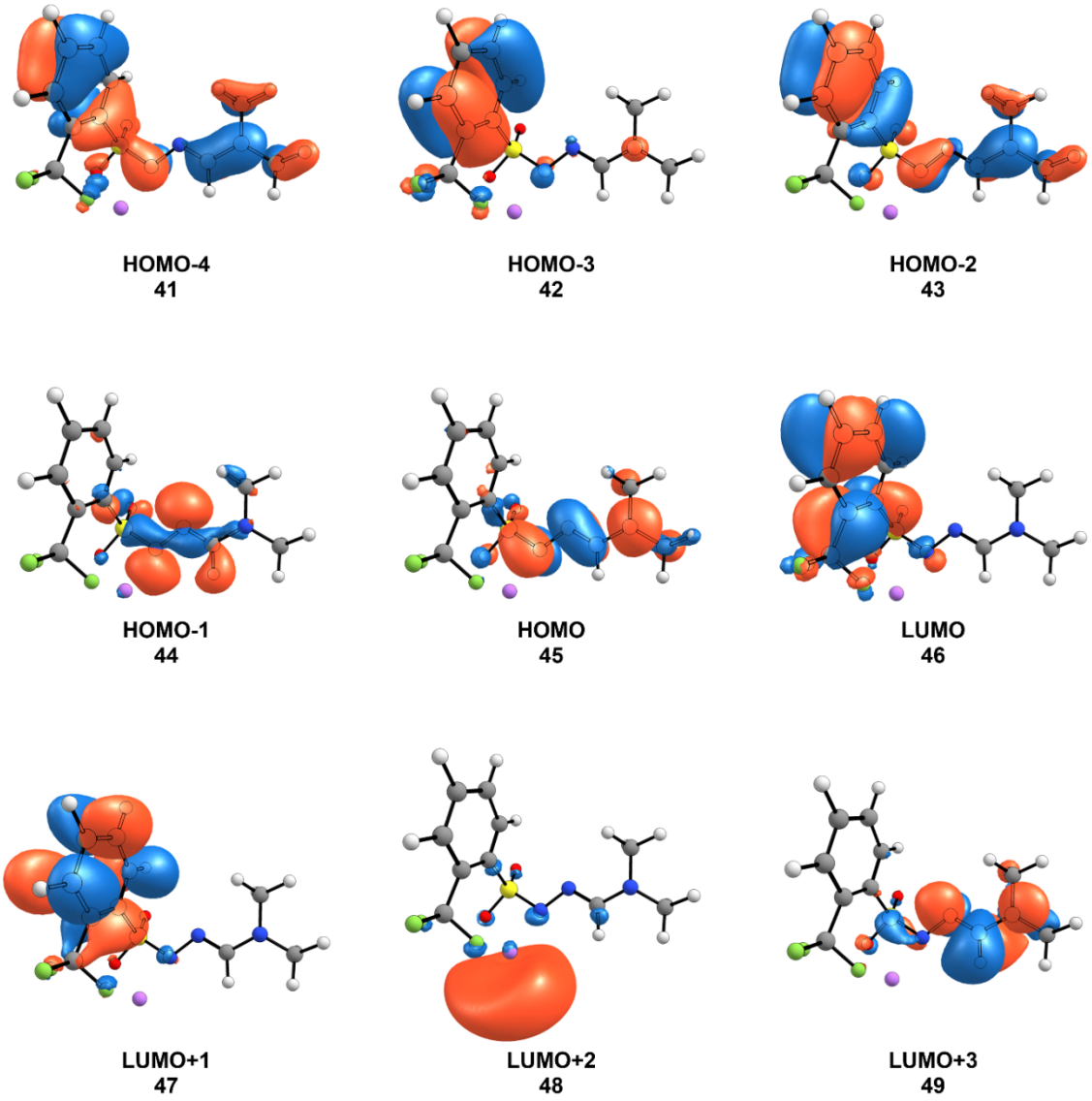


Figure S19. Canonical orbitals of **2b-Li** obtained via sTD-DFT using the ωB97X-D3 functional.

Table S4. Nature of selected electronic transitions for **2b-Li** obtained via sTD-DFT using the ωB97X-D3 functional.

Transition	eV	nm	Amplitudes		
S1	4.253	291.5	0.88 (45-> 46)	0.05 (43-> 46)	0.02 (45-> 47)
S2	4.939	251.0	0.77 (45-> 48)	0.14 (45-> 47)	0.02 (41-> 48)
S3	5.041	246.0	0.40 (45-> 47)	0.17 (42-> 46)	0.15 (45-> 48)
S4	5.230	237.0	0.52 (45-> 49)	0.17 (43-> 46)	0.08 (42-> 47)

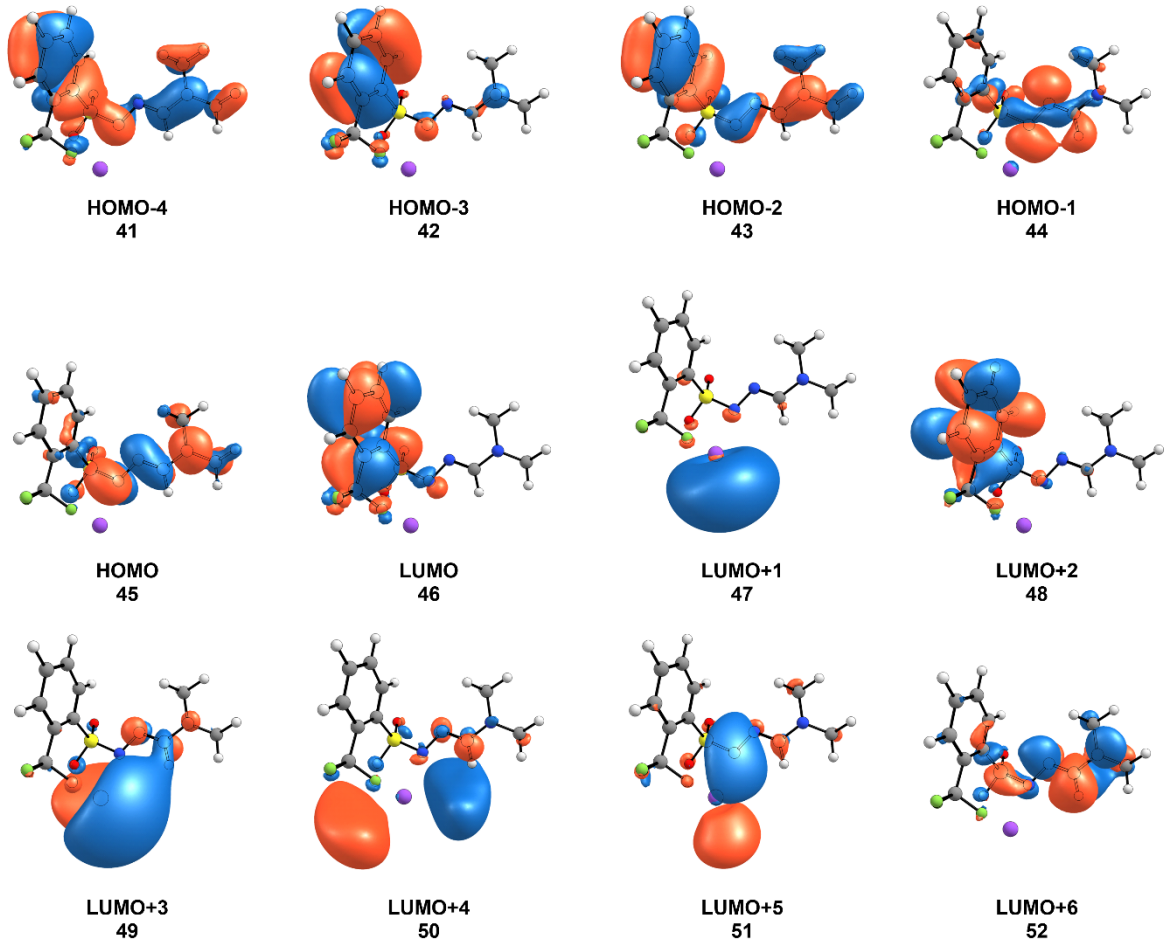


Figure S20. Canonical orbitals of **2b-Na** obtained via sTD-DFT using the ωB97X-D3 functional.

Table S5. Nature of selected electronic transitions for **2b-Na** obtained via sTD-DFT using the ωB97X-D3 functional.

Transition	eV	nm	Amplitudes		
S1	4.245	292.1	0.88 (45-> 46)	0.04 (43-> 46)	0.03 (45-> 48)
S2	4.327	286.6	0.94 (45-> 47)	0.02 (41-> 47)	0.02 (43-> 47)
S3	4.980	249.0	0.60 (45-> 48)	0.12 (42-> 46)	0.08 (43-> 48)
S4	5.180	239.3	0.27 (45-> 49)	0.27 (45-> 52)	0.10 (43-> 46)

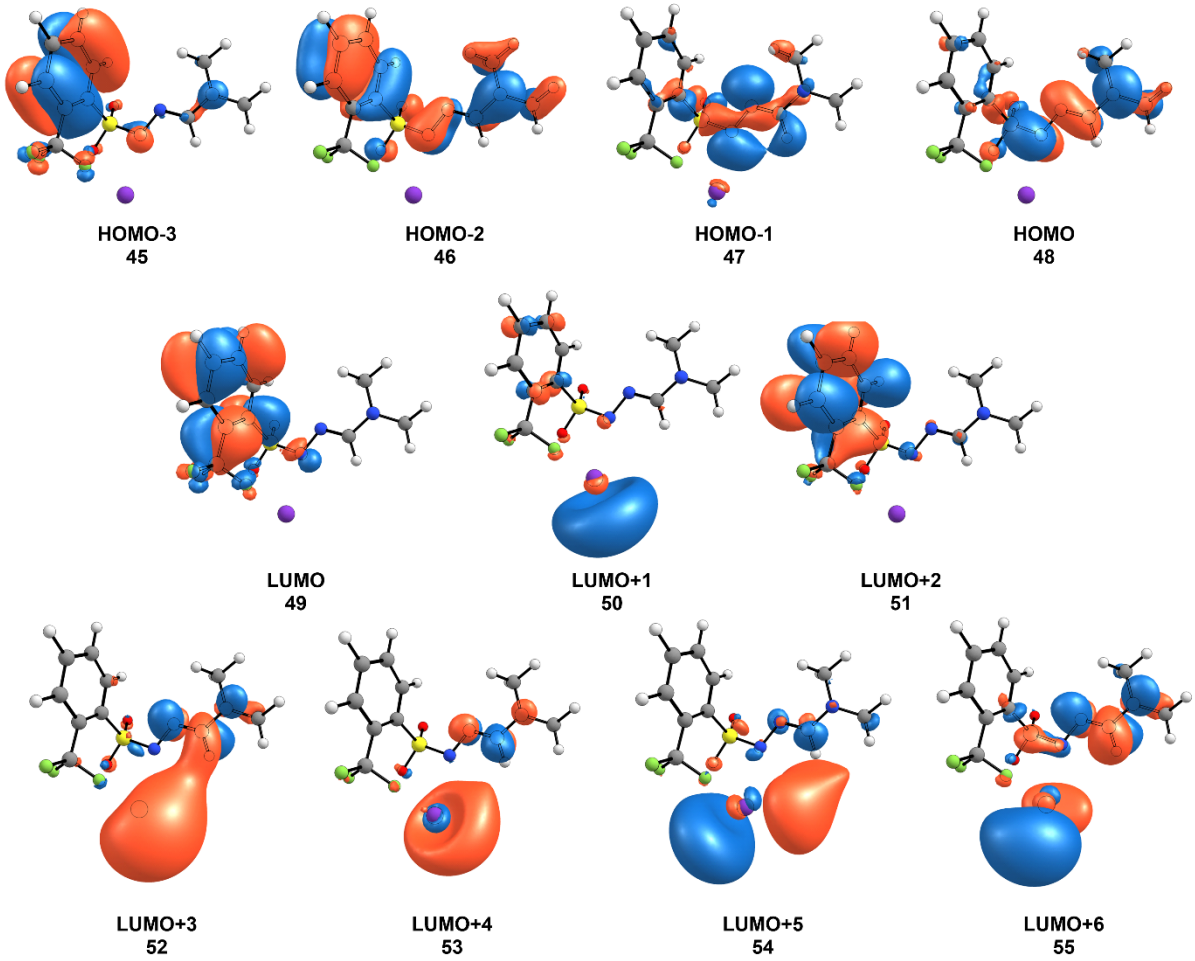


Figure S21. Canonical orbitals of **2b** obtained via sTD-DFT using the ωB97X-D3 functional.

Table S6. Nature of selected electronic transitions for **2b** obtained via sTD-DFT using the ωB97X-D3 functional.

Transition	eV	nm	Amplitudes		
S1	4.230	293.1	0.51 (48-> 49)	0.42 (48-> 50)	0.02 (46-> 49)
S2	4.256	291.3	0.53 (48-> 50)	0.38 (48-> 49)	0.02 (46-> 49)
S3	4.949	250.5	0.65 (48-> 51)	0.09 (45-> 49)	0.07 (46-> 51)
S4	5.193	238.8	0.35 (48-> 52)	0.20 (48-> 55)	0.09 (46-> 49)

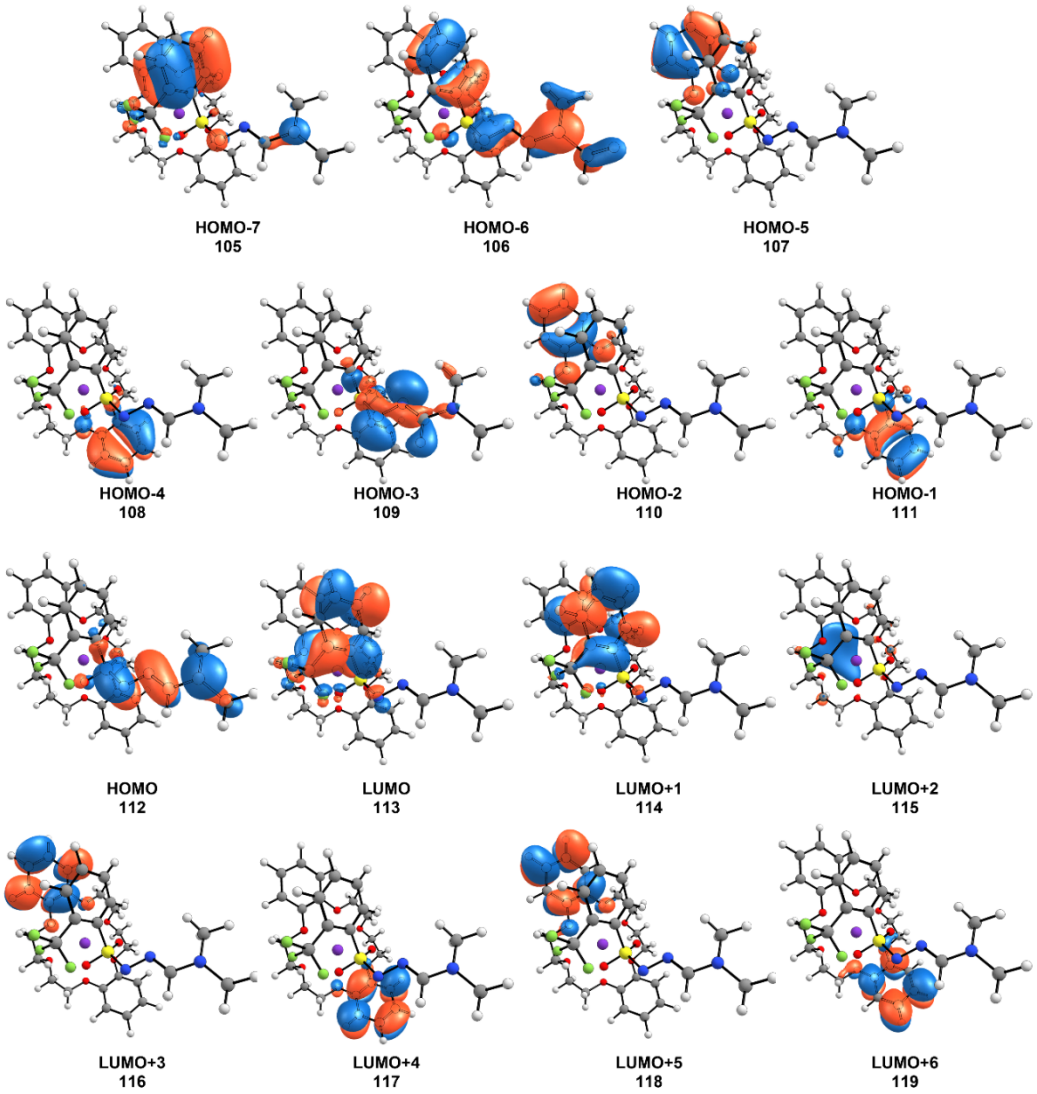


Figure S22. Canonical orbitals of **2b'** obtained via sTD-DFT using the ωB97X-D3 functional.

Table S7. Nature of selected electronic transitions for **2b'** obtained via sTD-DFT using the ωB97X-D3 functional.

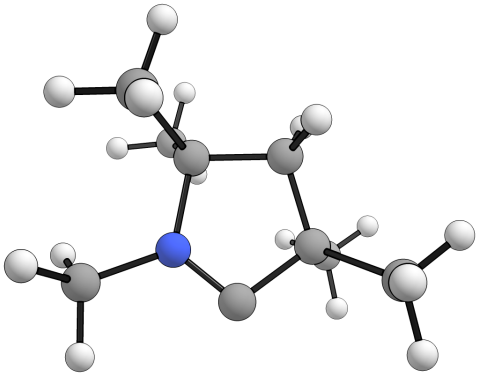
Transition	eV	nm	Amplitudes		
S1	4.252	291.6	0.87 (112-> 113)	0.04 (106-> 113)	0.03 (112-> 114)
S2	4.833	256.6	0.59 (110-> 116)	0.22 (107-> 118)	0.11 (111-> 117)
S3	4.839	256.2	0.59 (111-> 117)	0.23 (108-> 119)	0.10 (110-> 116)
S4	4.940	251.0	0.62 (112-> 114)	0.12 (112-> 120)	0.08 (105-> 113)

Table S8. Absolute contributions to the Gibbs free energies for mechanistic calculations.

Structure	E_{el} (H)	H (H)	-T*S (H)	G (H)	G-E_{el} (H)	v (cm^{-1})	E_{el} SPC (H)	G_{final}	G_{rel} (kcal/mol)
2b-S0	-1999.832593	-1999.599169	-0.06846363	-1999.667633	0.16496034	27.9	-1999.955472	-1999.790512	--
2b-T1	-1999.771882	-1999.541118	-0.07213197	-1999.61325	0.15863201	17.55	-1999.882938	-1999.724306	--
TS1-S0	-1999.793418	-1999.563053	-0.06942584	-1999.632479	0.16093847	-193.68	-1999.895808	-1999.73487	--
TS1-T1	-1999.771614	-1999.541905	-0.07120951	-1999.613115	0.15849971	-137.6	-1999.87703	-1999.71853	--
TfsK	-1717.187309	-1717.070923	-0.05430944	-1717.125233	0.06207648	33.56	-1717.221143	-1717.159066	--
diazo_S0	-282.6273706	-282.5145128	-0.038634	-282.5531468	0.07422384	47.07	-282.7057569	-282.631533	--
diazo_T1	-282.619819	-282.5070135	-0.03999805	-282.5470116	0.07280739	114.34	-282.6991763	-282.6263689	--
TS_dediazotization_S0	-282.6169787	-282.5057162	-0.03868108	-282.5443973	0.07258143	-491.45	-282.6922456	-282.6196642	--
TS_dediazotization_T1	-282.5764589	-282.4670963	-0.04174214	-282.5088385	0.06762043	-391.66	-282.6494409	-282.5818204	--
carbene_S0	-173.1410296	-173.0390928	-0.03310387	-173.0721967	0.06883294	165.57	-173.2079845	-173.1391515	--
carbene_T1	-173.0870619	-172.9874685	-0.03497281	-173.0224413	0.06462052	195.12	-173.1401832	-173.0755627	--
N_2	-109.5075002	-109.4986168	-0.02238928	-109.5210061	-0.01350587	2448.75	-109.5312946	-109.5448005	--
2b-S0								-1999.790512	0.00
2b-T1								-1999.724306	41.54423332
TS1-S0								-1999.73487	34.91560532
TS1-T1								-1999.71853	45.16842073
INT1-S0	(diazo_S0 + TfsK)							-1999.790599	-0.054779008
INT1-T1	(diazo_T1 + TfsK)							-1999.785435	3.185693973
TS2-S0	(TS_dediazotization_S0 + TfsK)							-1999.77873	7.392927111
TS2-T1	(TS_dediazotization_T1 + TfsK)							-1999.740887	31.13986357
Me_2NCH-S0	(carbene_S0 + TfsK + N_2)							-1999.843018	-32.94770835
Me_2NCH -T1	(carbene_T1 + TfsK + N_2)							-1999.779429	6.954266453

Cartesian Coordinates

CAAC – S0



C	-0.151858335427	-0.092916948580	-1.768897243109
C	0.070566143525	1.138585875203	-0.869950164253
N	-0.410763071963	-1.156568295574	-0.719837989342
C	0.252186834067	0.589109870773	0.575904170940
C	-0.208744832077	-0.859686253461	0.533372416260
H	-0.802960108763	1.790979076662	-0.914245657132
H	0.925694565921	1.727038049483	-1.204059562884
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H	-1.651584863019	1.334450340324	1.338699072008
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H	-1.205895719986	0.929543235281	-3.350478817237
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H	0.946702566475	-1.381895807197	-3.153515852527
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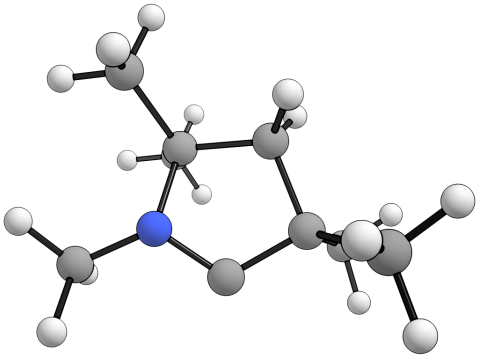
CAAC – T1



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C	0.293959753757	0.586901810613	0.609964135800
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H	-1.422520900263	-0.686592396967	-3.492436291699
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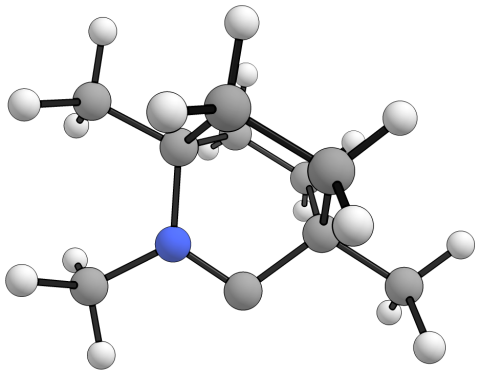

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H	-0.795403069100	-2.097279240871	-1.291238676589
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H	-2.372211452660	1.528733169382	0.607596439548
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C	-3.449971175665	-0.277392098706	-0.006638013232
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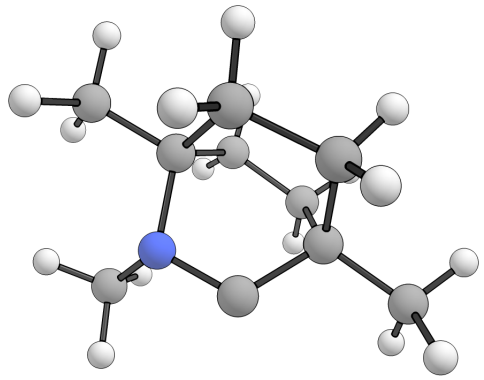
biCAAC – T1



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C	-3.307458321917	-0.621266881530	-2.175222959325
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H	-2.412724218631	1.619066024934	0.664652236244
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C	-3.318501646316	-0.322819782095	0.220625863440
H	-2.847276761224	-0.629812947542	1.160167230238
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H	-0.946398590830	2.924938383436	-0.774617650732
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H	-2.260534076898	3.185574677898	-1.927412447113
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H	-1.173291785373	0.082652641892	-3.947564060193
H	-2.821791709820	0.192518812885	-4.577462509910
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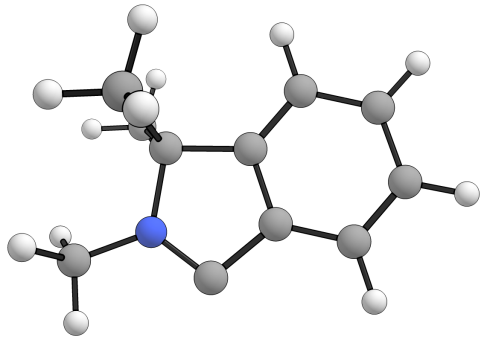
CAArC – S0



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C	0.600230093021	1.440241280259	-1.859460705448
N	-2.325899655308	-2.106427531283	-1.743622222700
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H	1.604571979011	-0.463182757304	-1.812800398196
H	-2.772566706567	1.922446844286	-1.852533175044
H	-0.628211898604	3.198957327390	-1.900640528131
H	1.523790729925	2.004637464095	-1.880765389610
C	-0.814622160952	-2.131952981738	-1.750797562336
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H	0.798771031081	-2.766043921143	-3.045439421038
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H	-2.852144260386	-3.971491110372	-2.577320321901
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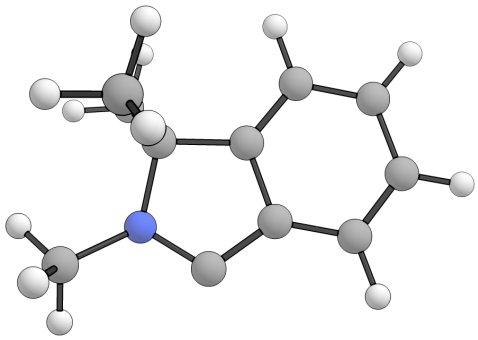
CAArC – T1



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C	-0.615281340200	2.129639040811	-1.954774703916
C	0.601485512242	1.445431997006	-1.871594417903
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H	-2.762724786752	1.999133778422	-1.983618382332
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C	-0.821124005817	-2.146029025739	-1.639308109707
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H	0.726445002014	-2.725973696037	-3.033241900738
H	-0.552969010035	-3.930243600033	-2.877317511298
H	-0.837148813273	-2.440635681424	-3.798720959670
C	-0.187358214369	-2.779063997755	-0.395235266029
H	-0.521921273351	-2.267997873339	0.506093058089
H	-0.450392343323	-3.835778050727	-0.316233373290
H	0.900345907440	-2.709808260264	-0.448872935693
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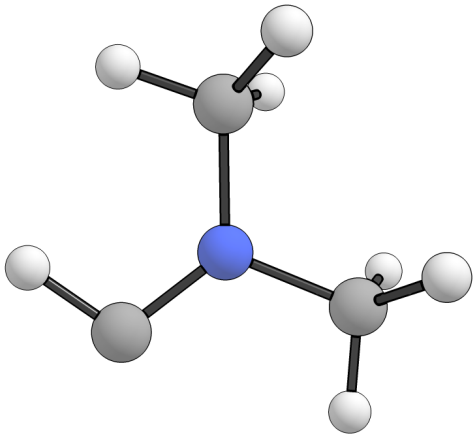
Me_2NCH – S0



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C	0.850608220602	-0.236096906072	1.240883017401
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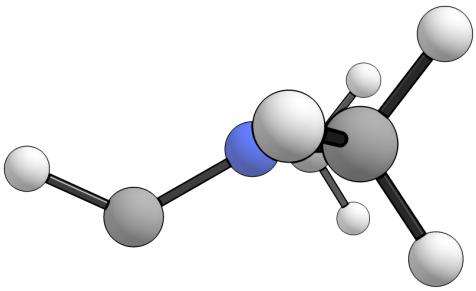
Me_2NCH – T1



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C	0.856569647898	-0.270199194728	1.371997128226
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H	1.756763882677	-0.655788826608	1.866627879811
H	0.883365355787	0.816642177987	1.403730042632
C	0.587675463943	-2.151785756049	-0.186473521868
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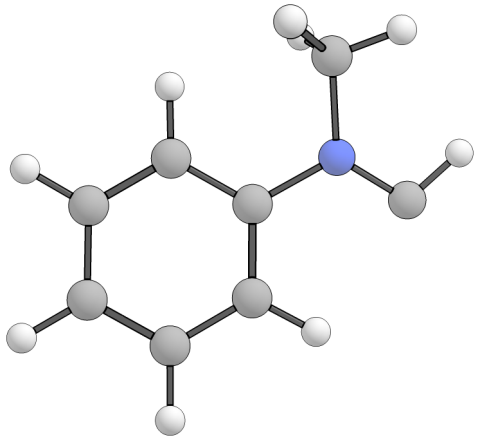
D – S0



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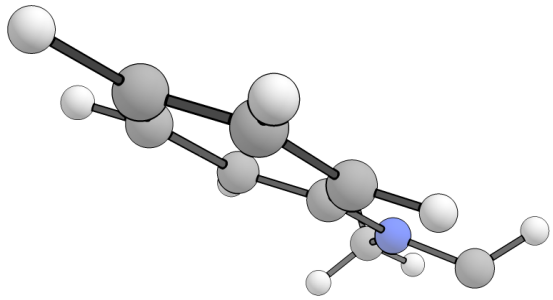
D – T1



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H	1.011647000000	-0.594355000000	2.062979000000
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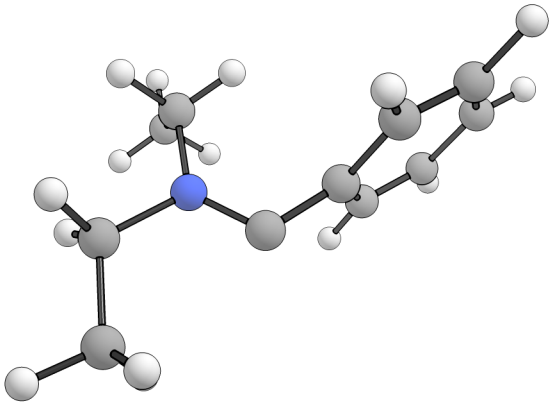
E – S0



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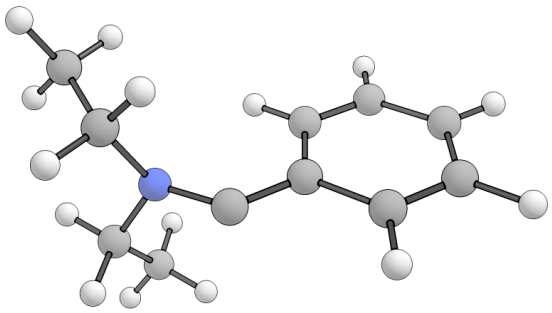
E – T1



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C	0.790244000000	-0.997476000000	1.969229000000
H	1.350288000000	-1.895667000000	2.259336000000
H	1.290971000000	-0.149813000000	2.434168000000
C	0.678538000000	-2.032374000000	-0.284801000000
H	1.581632000000	-2.655062000000	-0.234739000000
H	-0.124475000000	-2.595485000000	0.191413000000
C	1.672493000000	1.399738000000	-0.382950000000
C	0.402804000000	2.040335000000	-0.467770000000
C	2.812510000000	2.157502000000	-0.767745000000
C	0.295557000000	3.346900000000	-0.904906000000
C	2.686462000000	3.460881000000	-1.205080000000
C	1.430524000000	4.070142000000	-1.277607000000
H	-0.479511000000	1.482670000000	-0.184158000000
H	3.786172000000	1.688889000000	-0.709490000000
H	-0.680809000000	3.812759000000	-0.960297000000
H	3.570490000000	4.015892000000	-1.493095000000
H	1.338388000000	5.092303000000	-1.619643000000
C	-0.648261000000	-1.086020000000	2.468592000000
H	-1.196420000000	-0.172206000000	2.238323000000
H	-1.186852000000	-1.925499000000	2.027741000000
H	-0.654956000000	-1.224395000000	3.551505000000
C	0.318547000000	-1.748740000000	-1.735187000000
H	1.108714000000	-1.190078000000	-2.236092000000
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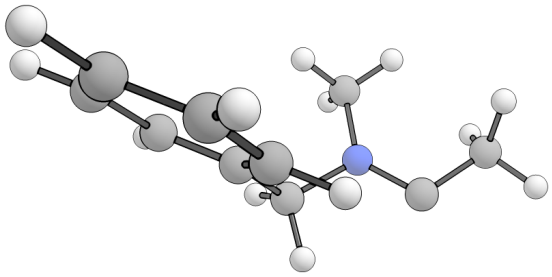
H	-0.602977000000	-1.169843000000	-1.804326000000

F – S0



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C	0.769489000000	-0.031560000000	1.330280000000
H	-0.274499000000	0.098143000000	1.623572000000
H	1.274296000000	-0.619584000000	2.095397000000
H	1.244164000000	0.941096000000	1.267473000000
C	0.608306000000	-2.191609000000	0.153288000000
H	-0.313098000000	-2.345696000000	0.721195000000
H	0.452274000000	-2.542166000000	-0.864000000000
C	1.305752000000	1.253635000000	-1.187595000000
H	0.518150000000	1.828202000000	-0.684203000000
H	2.256353000000	1.513655000000	-0.703771000000
H	1.365886000000	1.597265000000	-2.218250000000
C	1.746126000000	-2.941631000000	0.811769000000
C	1.546671000000	-3.668575000000	1.984116000000
C	3.017786000000	-2.935025000000	0.233039000000
C	2.591952000000	-4.376469000000	2.571247000000
C	4.063279000000	-3.636997000000	0.818378000000
C	3.853414000000	-4.360322000000	1.989832000000
H	0.564081000000	-3.685639000000	2.441126000000
H	3.179001000000	-2.375823000000	-0.680090000000
H	2.419305000000	-4.937008000000	3.480920000000
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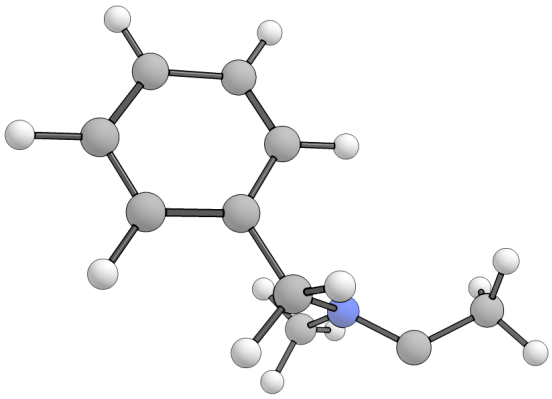
H	4.668662000000	-4.908939000000	2.443298000000

F – T1



C	0.422842000000	0.245224000000	-0.675601000000

N	0.867138000000	-0.559907000000	0.337661000000
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H	1.376864000000	-0.625092000000	2.373206000000
H	0.965740000000	0.981373000000	1.748660000000
C	0.709888000000	-2.013235000000	0.179173000000
H	-0.263650000000	-2.335329000000	0.571684000000
H	0.699271000000	-2.213313000000	-0.892851000000
C	1.260605000000	0.998376000000	-1.641795000000
H	1.938230000000	1.699374000000	-1.133259000000
H	1.889762000000	0.327861000000	-2.245599000000
H	0.639549000000	1.574409000000	-2.327442000000
C	1.810039000000	-2.814544000000	0.842644000000
C	1.505181000000	-3.834551000000	1.741824000000
C	3.151358000000	-2.567786000000	0.541066000000
C	2.513098000000	-4.597633000000	2.325375000000
C	4.159909000000	-3.324178000000	1.123209000000
C	3.843580000000	-4.344007000000	2.017368000000
H	0.469282000000	-4.034814000000	1.988853000000
H	3.401898000000	-1.771373000000	-0.148414000000
H	2.256973000000	-5.385590000000	3.021917000000
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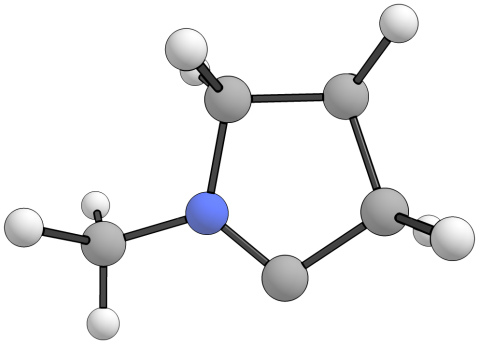
C – S0



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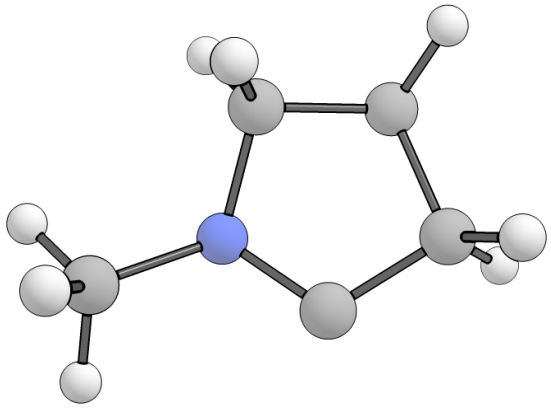
N	-0.046236000000	-0.174977000000	-0.075619000000
C	-0.534730000000	-2.473338000000	-0.246113000000
C	0.052466000000	-0.534174000000	1.174702000000
C	-0.069762000000	-2.039587000000	1.171424000000
H	0.694492000000	-1.341893000000	-1.681442000000
H	-1.605504000000	-2.678643000000	-0.248340000000
H	-0.734356000000	-2.379586000000	1.966385000000
H	0.919896000000	-2.437632000000	1.422338000000
H	-0.029340000000	-3.366693000000	-0.609724000000
H	-1.027197000000	-0.970172000000	-1.790210000000
C	0.074883000000	1.197788000000	-0.540883000000
H	0.925375000000	1.295919000000	-1.220150000000
H	-0.827872000000	1.498593000000	-1.077793000000
H	0.220630000000	1.838035000000	0.323318000000

C – T1



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N	-0.402520000000	-0.091067000000	-0.115534000000
C	-0.569580000000	-2.443470000000	-0.202008000000
C	0.051306000000	-0.604530000000	1.091348000000
C	0.062202000000	-2.087902000000	1.178233000000
H	0.687274000000	-1.244252000000	-1.526944000000
H	-1.642567000000	-2.591645000000	-0.080989000000
H	-0.526240000000	-2.495100000000	2.005496000000
H	1.073200000000	-2.502047000000	1.273650000000
H	-0.145349000000	-3.348136000000	-0.635275000000
H	-1.048632000000	-1.080781000000	-1.872327000000
C	0.055941000000	1.209525000000	-0.558081000000
H	1.126316000000	1.211930000000	-0.815519000000
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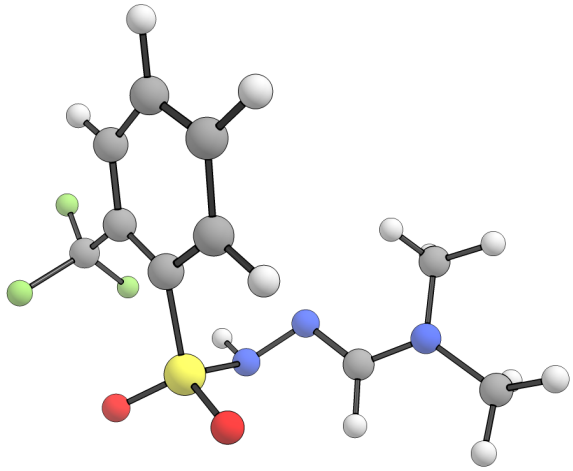
H	-0.106574000000	1.939882000000	0.233665000000

1b



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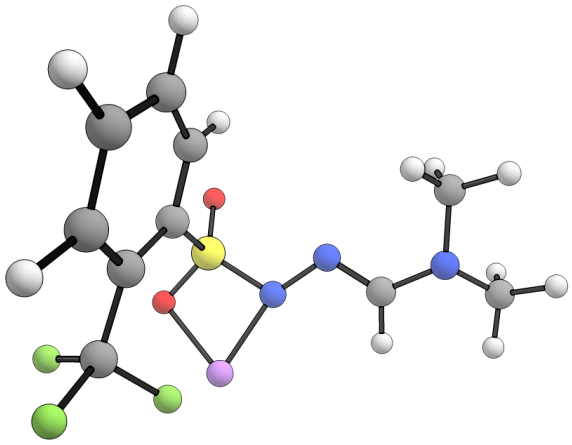
H	-1.82212297665853	0.72189478950351	-1.69290815081493
N	-0.47920149739861	-0.64968528258841	-0.93107760773046
C	-1.06253495714477	-0.58468484775144	0.40349505571506
H	-1.76984806748220	0.24626939575391	0.45741157876981
H	-1.59202497078866	-1.51562941834169	0.64813646103573
H	-0.27219582060160	-0.42709148029428	1.14521725919860
C	0.54433818448661	-1.66162120136099	-1.16490166259051
H	0.09871662414033	-2.62816844335438	-1.43807552319414
H	1.19946056591005	-1.33984951521930	-1.97903120601729
H	1.12988456362622	-1.78746635731345	-0.25016857973638
N	-0.72644271596542	-0.25718397140487	-3.19920463392022
N	-1.38639634929957	0.66686413208422	-4.06927161100651
S	-0.50323624371401	2.12911391431054	-4.32237964189792
C	1.17912097079322	1.66118889688934	-4.83258898855832
C	2.10633639004319	1.60892377694976	-3.79486777247309
C	1.56299137113626	1.30733295685057	-6.14019774600021
C	3.42099728242412	1.22630638088985	-4.04162863128670
C	2.88813989999549	0.94034150272961	-6.36968501910346
C	3.81242340073149	0.89805775974540	-5.33060673180658

H	1.79627818779241	1.88027729835032	-2.79261941590626
H	4.13152110931456	1.19198718385829	-3.22160597727407
H	3.20392186089441	0.68119112615814	-7.37317946048067
H	4.83671444332005	0.60493045518944	-5.53858853207957
C	0.63314244267536	1.32240375382503	-7.33440842633168
F	0.33513723364051	2.57506039562991	-7.74125650179672
F	1.18616548903179	0.69709449908767	-8.39885614699196
F	-0.53589513695758	0.67857516731108	-7.09014193273216
O	-1.19589169435776	2.84623596484885	-5.40070101663537
O	-0.36717598331631	2.74897728084714	-2.99603489944946
H	-1.49020965532007	0.22494655175985	-4.98388795017973

2b-Li



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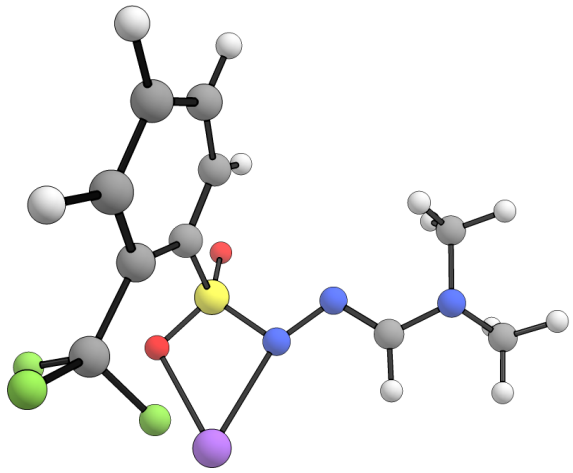
H	-1.95359017779248	-1.13373300523404	-3.28533920044502
N	-1.39586958991504	-0.64247941641353	-1.33564651653607
C	-2.51882044087641	-1.38801009253089	-0.77413167743450
H	-2.22649573145562	-2.40181277361336	-0.45611149819936
H	-2.91385310105888	-0.85186162400395	0.09461830361048
H	-3.31425424511638	-1.47475692742518	-1.52023253329848
C	-0.29436345702183	-0.38172337234380	-0.41870736368989
H	0.33512949071381	-1.27338329552063	-0.26676964272546
H	0.33897588491110	0.41628326537820	-0.81643811336641
H	-0.70534549548095	-0.07002052020280	0.54586333817626
N	0.08952516196046	-0.69402260520005	-3.13190053296821
N	0.15403254703627	-0.83129935130141	-4.52960038689783
S	1.63475729535667	-0.54324197400188	-5.10641190949082
C	2.03854206364049	1.20872437419287	-4.78222279850922
C	2.86534160038360	1.41837737511628	-3.68056760086445
C	1.49118822183162	2.31994199390493	-5.45824651824808
C	3.16857324445262	2.70480603795946	-3.24704745335473
C	1.81856636501842	3.60400169401076	-5.01920548175280
C	2.64748784975833	3.79976407139120	-3.91977019445082
H	3.27865544074166	0.55908040022540	-3.16508031787257
H	3.81632619028660	2.84147824143574	-2.38643554779683
H	1.42460733455073	4.46630085738096	-5.54355510441180
H	2.88080008022475	4.81016212939414	-3.59915742604877
C	0.61074410723494	2.23650749298220	-6.68340199781775
F	-0.47996616371030	1.40033251539089	-6.50711643440792
F	0.07047931314164	3.42849115260818	-6.99827331505147
F	1.25982574761186	1.80398110644555	-7.77825166434013
O	2.76259698436573	-1.30204566177662	-4.52719935677645
O	1.40415871419818	-0.70378736492043	-6.58717945004612
Li	-0.54031178468103	-0.67887089183281	-6.37383717563641

2b-Na



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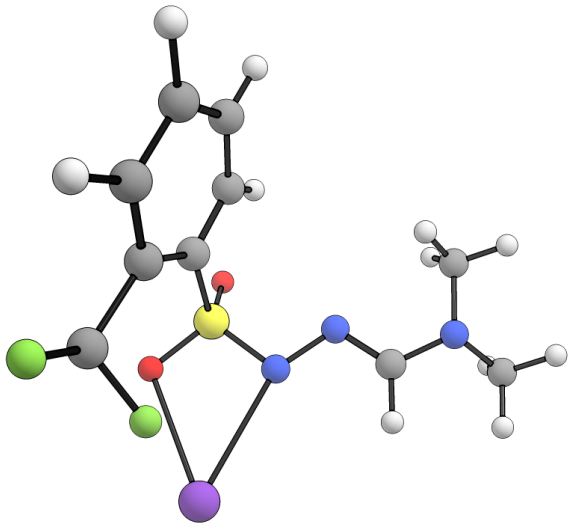
H	-1.88191848597757	-0.44859297320525	-1.96895449023249
N	-0.43094482783756	0.02447707279780	-0.54341230375273
C	-1.30930171104388	-0.37859893843108	0.55158786679198
H	-1.11609230302572	-1.41273332930313	0.88090624720242
H	-1.15964832708415	0.29105521500113	1.40459716078502
H	-2.35347562039885	-0.30618424647262	0.23271313174792
C	0.99025574954958	0.04404327456178	-0.22443251907417
H	1.41898959795562	-0.97068944075237	-0.18368268582179
H	1.53353671070666	0.61042152648304	-0.98615624065243
H	1.12649064805473	0.52456125529378	0.74890586276130
N	0.05897858101706	-0.56704748631744	-2.74868099603329
N	-0.52972650873673	-0.81600557770071	-4.00181928936931
S	0.59472863528597	-1.07044104813163	-5.13495776025177
C	1.51545367198896	0.49523522577615	-5.37716921184315
C	2.72056051901684	0.56893336906060	-4.67951866315698
C	1.06049571898794	1.62887749388263	-6.08323866068044
C	3.48211449996704	1.73246811284133	-4.68049339330378
C	1.84543584158090	2.78383824516263	-6.08829817100244
C	3.04664576224190	2.84164707469086	-5.39067694752975
H	3.06398155019221	-0.30463992598966	-4.13761490448232
H	4.41729404157163	1.76166589423042	-4.12925968884209
H	1.51647424548657	3.65224484749704	-6.64617659261530
H	3.63364227668521	3.75453963739906	-5.40948906850927
C	-0.21478471834223	1.68045178360750	-6.89147182117212
F	-0.49945062726284	2.93378044797292	-7.30377742704578
F	-0.18066845466933	0.91426543136768	-7.99824504579554
F	-1.31910579917091	1.29178760340819	-6.16626344314431
O	1.64934028971431	-2.06281648201287	-4.81764310560884
O	-0.20151402414620	-1.33691257943574	-6.37710975928782
Na	-2.25946131703407	-0.80340001416513	-5.55213018509479

2b



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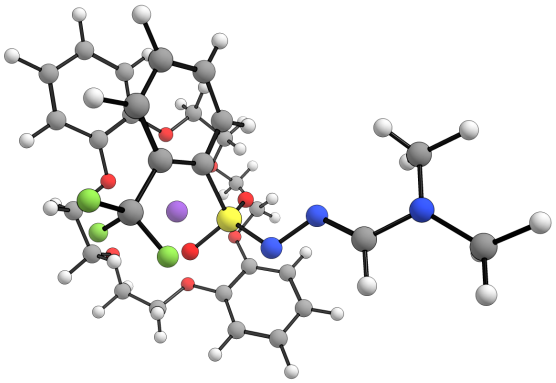
H	-1.95071703547745	0.19150284167676	-1.77637713200009
N	-0.32063212001643	-0.28220799611301	-0.55714287486093
C	-1.20072657351247	-0.66127755272625	0.54575875908313
H	-0.73865470514787	-0.37462815478932	1.49583031300599
H	-2.15633371983439	-0.13606429584579	0.45272647139368
H	-1.39993889036666	-1.74568593896756	0.56705433330643
C	1.01584530493863	-0.85993905913667	-0.50234060250246
H	1.01714411922164	-1.92775237250492	-0.77719515906967
H	1.67680869569209	-0.33239024457624	-1.19589850686266
H	1.40285649853957	-0.75641043003311	0.51576527764029
N	-0.27834540914948	-0.39714438413272	-2.89246994022712
N	-1.01214600723347	-0.07162292881509	-4.04895571669333
S	-0.17606497010289	-0.46864565734988	-5.37366978164396
C	1.29894075993028	0.62478905077874	-5.45190711540775
C	2.45776041308239	0.06952677087060	-4.90891767542726
C	1.32344352285988	1.96713797463788	-5.88452260090633
C	3.62868103311712	0.81127676075640	-4.79720491642667
C	2.51179376503047	2.69402109610353	-5.78269755917890
C	3.65849298782097	2.12624021715792	-5.23927794825431
H	2.43530689137150	-0.96230534724036	-4.57809534549540
H	4.51503489821146	0.35234423736779	-4.36917276804229
H	2.54443210570319	3.71863397592514	-6.13321841420661
H	4.56691286473500	2.71616714290988	-5.16715453626810
C	0.14497140830711	2.68368847523334	-6.49958982528948
F	-0.97932657644963	2.61234770496715	-5.72209196259176
F	0.38332077793294	4.00708965636385	-6.65130952237604
F	-0.18531851574640	2.21981825766418	-7.72265980275830
O	0.40464636810052	-1.83634985680702	-5.39756846383646
O	-1.06889411543434	-0.12598861505383	-6.52123057724134
K	-3.18869052208203	0.99790296136753	-5.34101720351298

2b’



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C	3.807442000000	4.726659000000	3.678448000000
H	3.567902000000	5.142970000000	4.661681000000
H	3.865191000000	3.628937000000	3.770320000000
H	4.789810000000	5.101236000000	3.373075000000
C	3.050146000000	4.711536000000	1.340560000000
H	4.100818000000	4.895663000000	1.096258000000
H	2.836029000000	3.638085000000	1.203602000000
H	2.415118000000	5.272346000000	0.649056000000
N	0.496906000000	4.932598000000	2.360059000000
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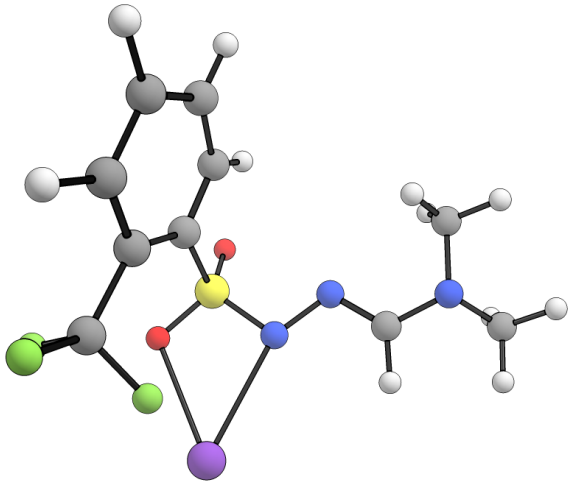

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S	0.19489857839154	-0.63139393085317	-5.41356764924695
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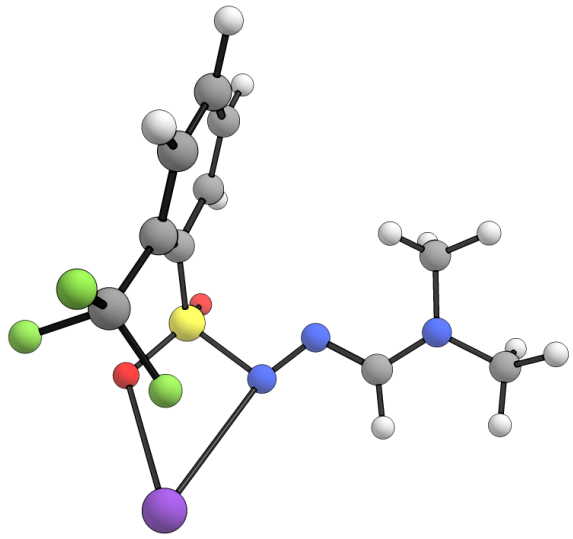

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H	1.32588952014449	0.37455169288672	-1.66670257891662
H	1.08107620728325	0.48933406320471	0.10266110353375
H	1.45256772590539	-1.08284775912765	-0.65303746940378
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C	1.28430851752112	1.90242998205325	-5.53549746841096
C	3.69169080453622	0.86179086477864	-4.47013910286623
C	2.25495754182899	2.74220427374191	-4.97274709958359
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H	2.94497778768734	-1.06949457983322	-4.97639279377135
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H	2.07655387729826	3.81240248993839	-4.97013586435347
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F	-1.11003493599219	2.13595267001684	-5.51553339522323
O	0.91093648374724	-2.09749675435789	-5.68790508469862
O	-0.59740096195018	-0.46103651606713	-6.89904497767558
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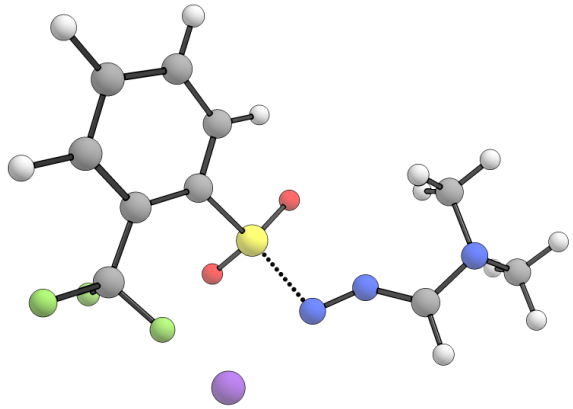

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C	1.75405661280411	0.94996701419861	-5.30388732800821
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O	1.09034411230218	-1.36508741520270	-4.19528660400529
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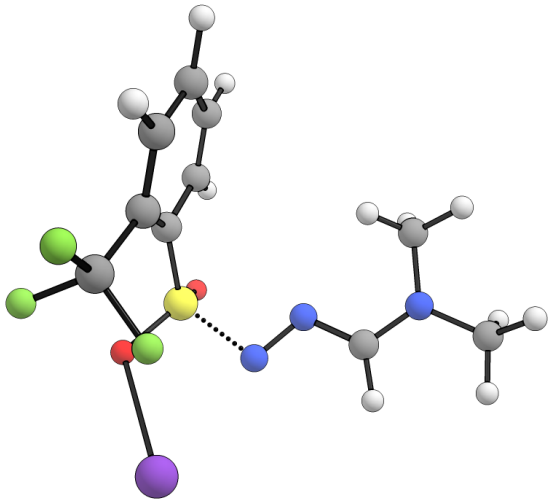

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S	0.34535545267255	-0.72034943556356	-5.74139441457908
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F	-1.01178363594660	2.14021230608398	-5.57748448375490
O	0.95414268836320	-2.08120372888226	-5.69244658868846
O	-0.53054959234072	-0.44042268605296	-6.92983099981013
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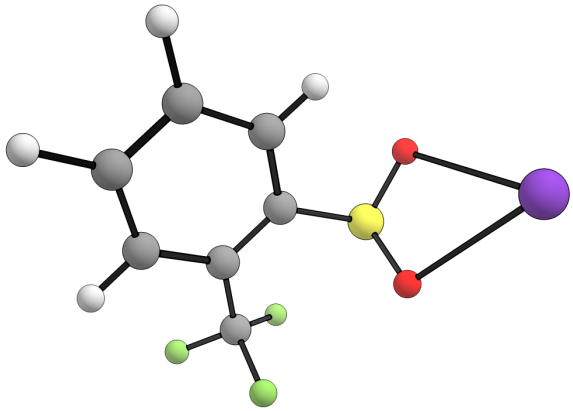

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H	3.55446633538707	3.98817131150937	-5.95436177331242
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C	0.89836589240079	4.01757622775122	-5.97155976225192
F	0.56885984705956	4.81284416499825	-4.92139067497225
F	1.53076154567266	4.81915053835813	-6.86707068197764
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O	-0.95827058541969	2.28220653674518	-3.77164405139870
O	-0.56833025214879	-0.14231592305112	-4.32414455768764
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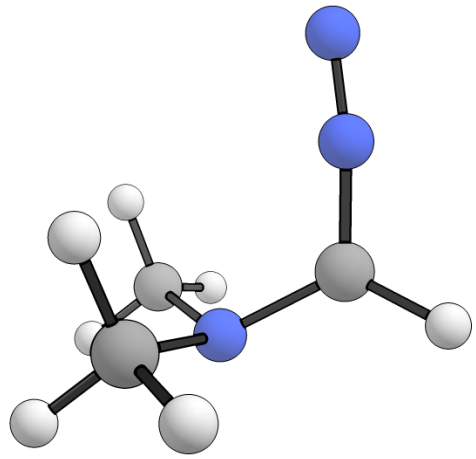

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C	0.58128382384678	2.63515687665880	-0.71343949090927
H	1.22031753135619	2.95666211494034	-1.54102501064396
H	-0.39513699338981	3.14327884197928	-0.80240536173847
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N	-2.35112606183717	0.71760683087167	-2.41855647150809
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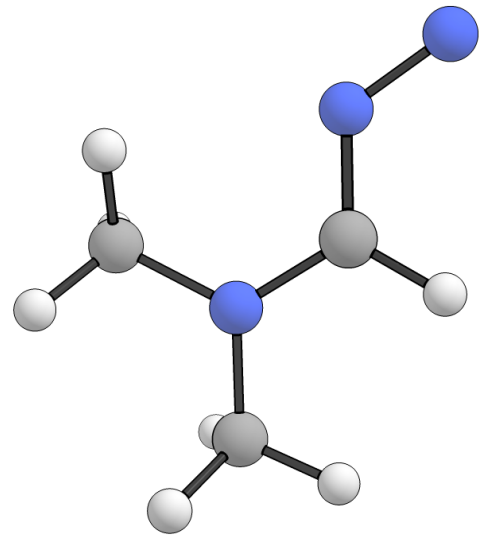

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H	-0.82702001903201	0.63669917080297	1.12404758680474
C	-0.01504984843571	2.74649205329690	-0.52234396028984
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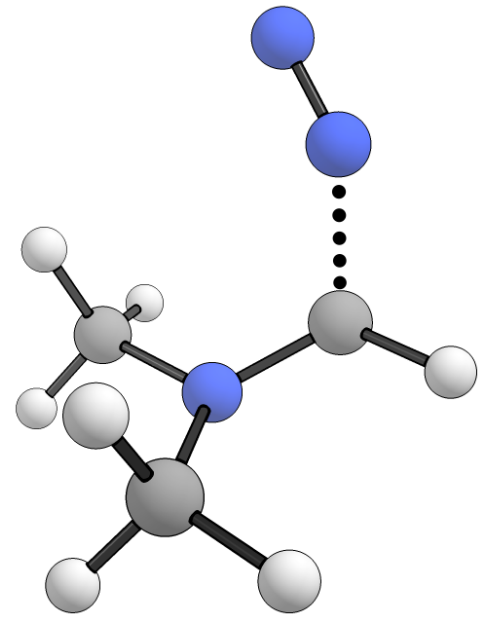

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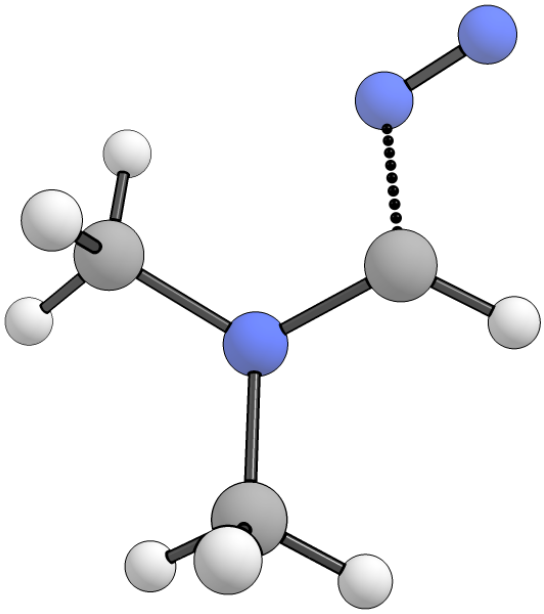
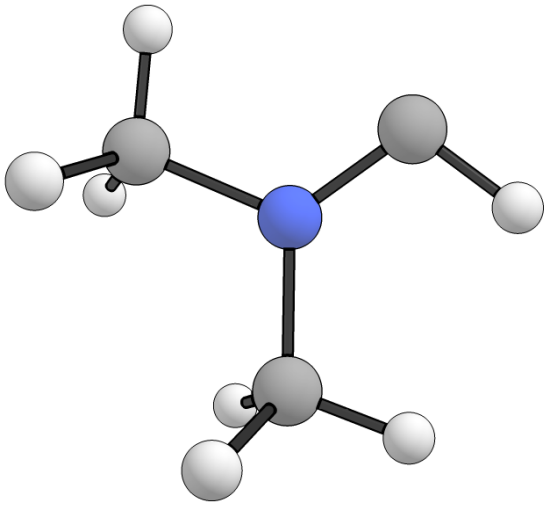
N	0.34086307544437	1.18602697302104	-0.76101681745298
C	-0.42971497421946	0.71147562388105	0.38235304471289
H	-1.45079742851397	1.13053426699886	0.37914125422353
H	-0.49590680638706	-0.37821462478823	0.34445391064371
H	0.06055836781625	1.01431906114064	1.31331881804526
C	0.66626500366724	2.61627894773027	-0.72821798705523
H	1.35148978171689	2.85075631544989	-1.54658879702814
H	-0.24491564026289	3.22555350822578	-0.84276892143263
H	1.14192731640742	2.87268928395745	0.22437143820605
N	-1.33120550232329	0.62464908381608	-2.44229350194862
N	-2.38352511291979	0.27384965189795	-2.23002076656426
H	0.76355563548107	0.94461814487027	-2.75599926747135

TS_dediazotization_T1



C	0.04618213660252	0.65345315355725	-1.78119789318411
N	-0.34416644580060	1.25469564206310	-0.62016072985024
C	-0.05213010346199	0.50110523094728	0.60770914256464
H	-0.29714347656342	-0.55379622241927	0.45853535701398
H	1.00793828295190	0.58639394035033	0.89258591270188
H	-0.67128878590711	0.89627529127562	1.42000434649458
C	-0.13051272107642	2.69677994705014	-0.48149019248656
H	-0.74460634980203	3.06763528402582	0.34475124404493
H	0.92599785164737	2.92480546262363	-0.26727818198535
H	-0.42478498635844	3.20779928557138	-1.39888037641169
N	-0.65806642876056	1.59902608671244	-3.34353751429025
N	-0.44880668359971	1.15827254259140	-4.35824323832837
H	-0.14452806852923	-0.39442777125466	-1.99226691635564

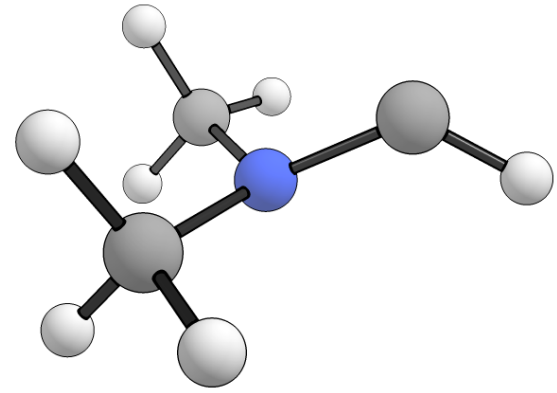
carbene_S0



C	-1.26149046092305	-0.37424986228398	-2.29713668756984
H	-1.34511009649488	-1.43030405851704	-2.62365375230054
N	-1.28181332201978	0.35116864481937	-3.37656869579213
C	-1.18812177924172	1.81924913531271	-3.30534088961512

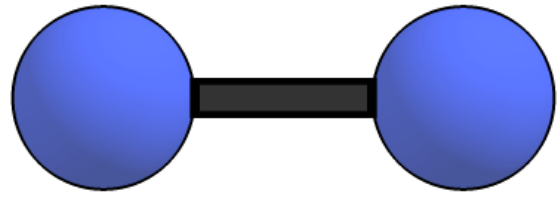
H	-2.07964935232260	2.26936727934381	-3.75717240944746
H	-1.10909682516785	2.10999093721915	-2.25832858328005
H	-0.30738171652538	2.16119044391906	-3.86119835409011
C	-1.39490099890970	-0.14070725024206	-4.76931002478629
H	-0.51755943514590	0.17486551471407	-5.34525661650366
H	-1.46172788214913	-1.22924506924028	-4.76162687310102
H	-2.28861949110001	0.28442063495518	-5.23993701351376

carbene_T1



C	-1.76994927421974	-0.48638747778260	-2.53993421511275
H	-1.20955515907683	-1.14864828974632	-1.87119269651523
N	-1.18711062627020	0.28588219686288	-3.50286379810592
C	-1.13083679436139	1.73463862354357	-3.28669376651347
H	-2.08391513708741	2.21977067576513	-3.54978119673502
H	-0.91092998766611	1.93690674234059	-2.23549673683596
H	-0.33711104982693	2.16422387151959	-3.90848161310322
C	-1.37036436632825	-0.10213164987971	-4.90431854009398
H	-0.57763611949414	0.34798789483855	-5.51279260826062
H	-1.31354391514002	-1.19013172989845	-4.99073688194228
H	-2.34451893052897	0.23363549243676	-5.29323784678150

N_2



N	-0.75143250600000	0.00000000000000	-2.15411917291891
N	-0.75143250600000	0.00000000000000	-3.2478591890810

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