Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Eco-friendly, in water, catalyst-free assembly of acylethenylpyrroloimidazoindoles from 3*H*-indoles acylpyrrolylacetylenes

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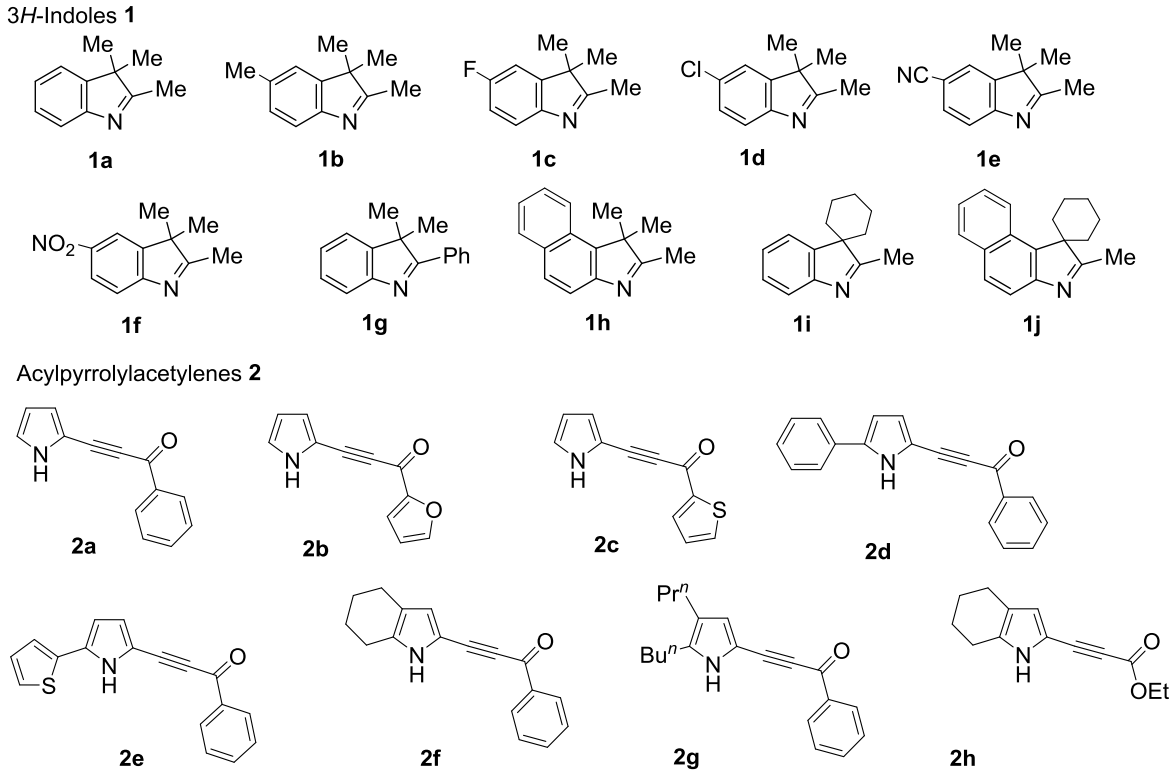
1. General Information

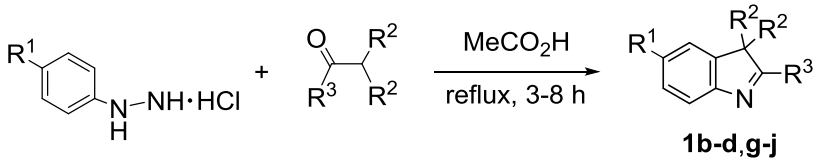
NMR spectra were recorded from solutions in $CDCl_3$ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^1H, 100.6 MHz for ^{13}C, 376.5 MHz for ^{19}F, and 40.5 MHz for ^{15}N). Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.27 and δ_C 77.10, was used as a reference. $CFCl_3$ was employed as external standard for ^{19}N NMR. Coupling constants (J) are reported in Hertz (Hz). The multiplicity abbreviations used are: s singlet, d doublet, dd doublet of doublet, t triplet, m multiplet, nr marrow, br broad signal. The values of the δ ^{15}N were measured through the 2D ^1H-^{15}N HMBC experiment. The ^{15}N chemical shifts were referenced to CH_3NO_2.

IR spectra were obtained on a Varian 3100 IF-IR spectrometer (400-4000 cm^{-1}) as thin films dispersed from $CDCl_3$. Mass spectra of synthesized compounds were recorded on a GCMS-QP5050A spectrometer made by Shimadzu Company. High-resolution mass spectra were recorded from acetonitrile solution with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with an electrospray ionization (ESI) source. Melting points (uncorrected) were measured on a melting point apparatus SGW-X-4. Thin layer chromatography was carried out on Merck silica gel 60 F254 pre-coated aluminium foil sheets and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Alfa Aesar silica gel (SiO_2), 70-230 mesh, pore size 60 Å.

2. The structure of 3*H*-indoles 1 and acylpyrrolylacetylenes 2

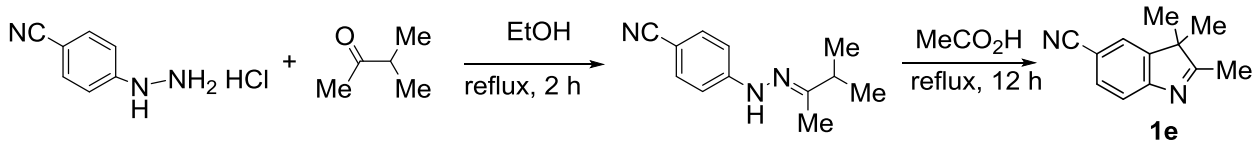


3*H*-Indoles **1a** and **1h** were purchased from commercial sources (Alfa Aesar), and were used without further purification. 3*H*-Indoles **1b-d**,**g-j** were prepared from corresponding aryl hydrazine hydrochlorides and ketones according to the literature procedures[1-3] and their characterization data were in accordance with the published ones.

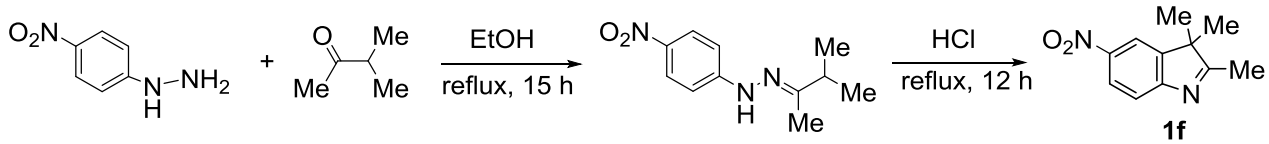


1b-d,**g-j**

3*H*-Indoles **1e** and **1f** were prepared from 5-cyano hydrazine hydrochloride and 5-nitro hydrazine and 3-methyl-2-butanone in two steps. Their characterization data were in accordance with the published ones.[4,5]

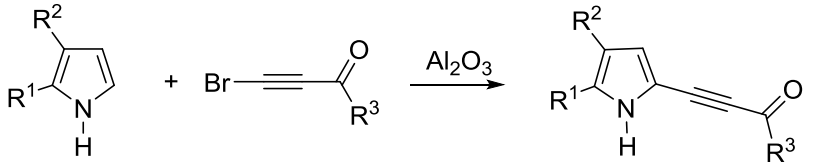


1e



1f

Starting acylpyrrolylacetylenes **2a-h** were obtained from corresponding pyrroles and acylbromoacetylenes in the presence of Al_2O_3. Pyrrole (5.0 mmol) and 1-acyl-2-bromoacetylene (5.0 mmol) were ground together at rt with 10-fold amount of Al_2O_3 (chromatography grade, Merck, pH 6.8–7.8) in a porcelain mortar for 1–2 min. After 3 h, the reaction mixture were chromatographed on a column (Al_2O_3, eluent *n*-hexane–Et_2O, gradient 9:1→0:1) to yield acylpyrrolylacetylene **2**.[6]



2a-h

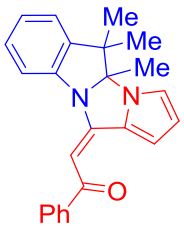
3. General procedure of pyrrolo[1',2':3,4]imidazo[1,2-*a*]indole 3 synthesis

Procedure A: To a 4.0 mL vial equipped with a magnetic stirrer, 3*H*-indole **1a-h** (0.5 mmol) and solution of acylpyrrolylacetylene **2a-f** (0.5 mmol) in MeCN (2 ml) added at room temperature. The vial was sealed with a screw-top septum cap and placed in a pre-heated oil bath at 80 ºC for 96 h. After cooling down to ambient temperature, the solvent was removed under reduced pressure and residue was purified by column chromatography on silica gel (eluent: hexane/Et_2O, 1:0→0:1, v/v) to give target adduct **3a-o**.

Procedure B: A 5 ml round bottomed flask equipped with a magnetic stirrer, was charged 3*H*-indole **1a-j** (0.5 mmol), acetylene **2a-h** (0.5 mmol) and H_2O (1 mL). After stirring for ~10 min (~200 min^{-1}) at rt, the sealed reaction flask was placed in a pre-heated oil bath at 100 ºC for 8 h. After cooling down to ambient temperature, water was decanted and solid residue was dissolved in CH_2Cl_2 and dried over Na_2SO_4. The solvent was removed under reduced pressure and residue was purified by column chromatography (SiO_2, hexane/Et_2O, 1:0→0:1, v/v) to give target adduct **3a-w**.

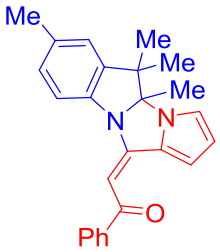
4. Characterization data of products

(*E*)-1-Phenyl-2-(4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3a).



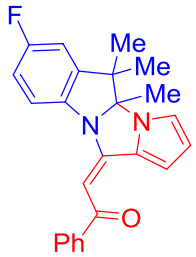
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Yellow solid: 120 mg (yield 68% − procedure A), 148 mg (yield 83% − procedure B); mp 160−162 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.00−7.98 (m, 2 H, H_o), 7.84 (dd, *J* = 3.9, 1.1 Hz, 1 H, H-1), 7.49−7.43 (m, 3 H, $H_{m,p}$), 7.41−7.40 (m, 2 H, H-8, H-9), 7.23−7.19 (m, 2 H, H-6, H-7), 7.01 (dd, *J* = 2.6, 1.1 Hz, 1 H, H-3), 6.74 (s, 1 H, =CH), 6.55 (dd, *J* = 3.9, 2.6 Hz, 1 H, H-2), 1.64 (s, 3 H, Me-4a), 1.58 (s, 3 H, Me-5), 0.78 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.0 (C=O), 148.9 (C-11), 144.8 (C-5a), 141.2 (C_i), 140.3 (C-9a), 133.0 (C-11a), 131.0 (C_p), 128.3 (C_m; C-8), 127.6 (C_o), 125.0 (C-7), 123.0 (C-6), 117.4 (C-9), 116.5 (C-3), 115.1 (C-2), 112.8 (C-1), 91.5 (C-4a), 89.6 (=CH), 47.7 (C-5), 26.1 (Me-5), 23.9 (Me-4a), 19.9 (Me-5) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –197.3 (N-4), –241.2 (N-10) ppm; IR (film): *v* = 1640 (C=O), 1534 (C=C) cm^{-1}; MS (EI) *m/z*: 354 (27) $[M]^+$, 249 (100) $[M - PhCO]^+$, 234 (83) $[249 - Me]^+$, 233 (17), 105 (27) $[PhCO]^+$, 77 (28) $[Ph]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O^+$: 355.1810, found: 355.1813.

(*E*)-1-Phenyl-2-(4a,5,5,7-tetramethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3b).



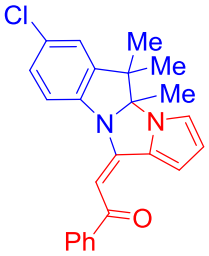
Obtained from 3*H*-indole **1b** (87 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Light yellow solid; 107 mg (yield 58 % − procedure A), 140 mg (yield 76 % − procedure B); mp 193−194 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2 H, H_o), 7.83 (dd, *J* = 3.6, 1.0 Hz, 1 H, H-1), 7.49−7.43 (m, 3 H, $H_{m,p}$), 7.30 (d, 1 H, *J* 8.0 Hz, H-9), 7.20 (d, 1 H, *J* 8.0 Hz, H-8), 7.02 (s, 1 H, H-6), 7.00 (dd, *J* = 2.7, 1.0 Hz, 1 H, H-3), 6.69 (s, 1 H, =CH), 6.55 (dd, *J* = 3.6, 2.7 Hz, 1 H, H-2), 2.40 (s, 3 H, Me-7), 1.64 (s, 3 H, Me-4a), 1.56 (s, 3 H, Me-5), 0.77 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.9 (C=O), 149.2 (C-11), 144.9 (C-5a), 141.4 (C_i), 138.0 (C-9a), 134.9 (C-11a), 133.1 (C-7), 130.9 (C_p), 128.7 (C-8), 128.3 (C_m), 127.6 (C_o), 123.8 (C-6), 117.2 (C-9), 116.3 (C-3), 115.0 (C-2), 112.7 (C-1), 91.6 (C-4a), 89.5 (=CH), 47.8 (C-5), 26.1 (Me-5), 23.9 (Me-4a), 21.2 (Me-7), 19.9 (Me-5) ppm; IR (film): *v* = 1640 (C=O), 1535 (C=C) cm^{-1}; MS (EI) *m/z*: 368 (18) $[M]^+$, 263 (100) $[M - PhCO]^+$, 248 (94) $[263 - Me]^+$, 115 (21), 105 (51) $[PhCO]^+$, 91 (18), 77 (66) $[Ph]^+$, 51 (19), 41 (13); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2O^+$: 369.1967, found: 369.1969.

(*E*)-2-(7-Fluoro-4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)-1-phenylethan-1-one (3c).



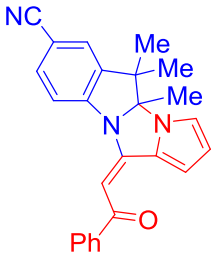
Obtained from 3*H*-indole **1c** (89 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Yellow solid; 67 mg (yield 36% − procedure A), 104 mg (yield 56% − procedure B); mp 208−209 ºC ($CHCl_3$/hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2 H, H_o), 7.83 (dd, *J* = 3.6, 1.0 Hz, 1 H, H-1), 7.49−7.44 (m, 3 H, $H_{m,p}$), 7.34 (dd, *J* = 8.6, 4.3 Hz, 1 H, H-9), 7.08 (ddd, *J* = 8.6, 8.0, 2.5 Hz, 1 H, H-8), 7.00 (dd, *J* = 2.7, 1.0 Hz, 1 H, H-3), 6.93 (dd, *J* = 8.0, 2.5 Hz, 1 H, H-6), 6.65 (s, 1 H, =CH), 6.55 (dd, *J* = 3.6, 2.7 Hz, 1 H, H-2), 1.65 (s, 3 H, Me-4a), 1.56 (s, 3 H, Me-5), 0.78 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 188.1 (C=O), 160.5 (d, *J* = 244.8 Hz, C-7), 149.1 (C-11), 147.1 (d, *J* = 7.5 Hz, C-5a), 141.2 (C_i), 136.6 (C-9a), 132.9 (C-11a), 131.2 (C_p), 128.4 (C_m), 127.6 (C_o), 118.4 (d, *J* 8.5 Hz, C-9), 116.4 (C-3), 115.3 (C-2), 114.7 (d, *J* 23.6 Hz, C-8), 113.0 (C-1), 111.0 (d, *J* 24.0 Hz, C-6), 91.8 (C-4a), 89.6 (=CH), 48.3 (C-5), 26.0 (Me-5), 23.8 (Me-4a), 19.9 (Me-5) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$): δ –243.7 (N-10), –198.5 (N-4) ppm; ^{19}F NMR (376.5 MHz, $CDCl^3$): δ –116.79 ppm; IR (film): *ν* = 1641 (C=O), 1538 (C=C) cm^{-1}; MS (EI) *m/z*: 372 (10) $[M]^+$, 267 (83) $[M - PhCO]^+$, 252 (88) $[267 - Me]^+$, 162 (14), 133 (16), 105 (82) $[PhCO]^+$, 77 (100) $[Ph]^+$, 51 (31), 39 (20); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}FN_2O^+$: 373.1716, found: 373.1717.

(*E*)-2-(7-Chloro-4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)-1-phenylethan-1-one (3d).



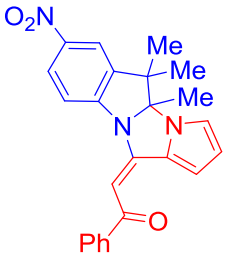
Obtained from 3*H*-indole **1d** (97 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Light yellow solid; 68 mg (yield 35% – procedure A), 111 mg (yield 57% – procedure B); mp 160–161 ºC ($CHCl_3$/hexane);^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.98–7.96 (m, 2 H, H_o), 7.83 (dd, *J* = 3.8, 1.0 Hz, 1 H, H-1), 7.50–7.44 (m, 3 H, $H_{m,p}$), 7.37 (dd, *J* = 8.3, 2.0 Hz, 1 H, H-8), 7.32 (d, *J* = 8.3 Hz, 1 H, H-9), 7.17 (d, *J* = 2.0 Hz, 1 H, H-6), 6.99 (dd, *J* = 2.5, 1.0 Hz, 1 H, H-3), 6.65 (s, 1 H, =CH), 6.55 (dd, *J* = 3.8, 2.5 Hz, 1 H, H-2), 1.64 (s, 3 H, Me-4a), 1.56 (s, 3 H, Me-5), 0.79 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.1 (C=O), 148.6 (C-11), 146.8 (C-5a), 141.1 (C_i), 139.1 (C-9a), 132.9 (C-11a), 131.2 (C_p), 130.4 (C-7), 128.4 (C_m), 128.3 (C-8), 127.6 (C_o), 123.6 (C-6), 118.3 (C-9), 116.4 (C-3), 115.4 (C-2), 113.1 (C-1), 91.6 (C-4a), 90.0 (=CH), 48.2 (C-5), 26.1 (Me-5), 23.9 (Me-4a), 19.8 (Me-5) ppm; IR (film): *ν* = 1642 (C=O), 1536 (C=C) cm^{-1}; MS (EI) *m/z*: 388 (12) $[M]^+$, 285 (28), 284 (15), 283 (73) $[M - PhCO]^+$, 270 (23), 269 (18), 268 (65) $[283 - Me]^+$, 115 (26), 105 (92) $[PhCO]^+$, 77 (100) $[Ph]^+$, 51 (29), 41 (10), 39 (17); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}ClN_2O^+$: 389.1421, found: 389.1424.

(*E*)-4a,5,5-Trimethyl-11-(2-oxo-2-phenylethylidene)-4a,5-dihydro-11H-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indole-carbonitrile (3e).



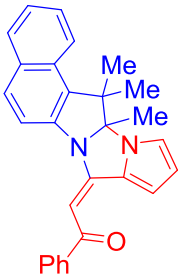
Obtained from 3*H*-indole **1e** (92 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Light yellow solid; yield: 28 mg (15% – procedure A), 65 mg (yield 34% – procedure B); mp 170–171 ºC (EtOH); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.98–7.97 (nr m, 2 H, H_o), 7.85 (dd, *J* = 3.8, 1.0 Hz, 1 H, H-1), 7.72 (d, *J* = 8.2 Hz, 1 H, H-9), 7.52–7.44 (m, 5 H, $H_{m,p}$; H-8; H-6), 7.00 (dd, *J* = 2.7, 1.0 Hz, 1 H, H-3), 6.71 (s, 1 H, =CH), 6.57 (dd, *J* = 3.8, 2.7 Hz, 1 H, H-2), 1.64 (s, 3 H, Me-4a), 1.61 (s, 3 H, Me-5), 0.83 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.1 (C=O), 147.3 (C-11), 146.0 (C-5a), 144.2 (C-9a), 140.8 (C_i), 133.5 (C-8), 132.6 (C-11a), 131.5 (C_p), 128.5 (C_m), 127.6 (C_o), 126.5 (C-6), 118.8 (CN), 117.0 (C-9), 116.8 (C-3), 115.8 (C-2), 113.5 (C-1), 107.9 (C-7), 91.5 (C-4a), 91.1 (=CH), 47.8 (C-5), 26.4 (Me-5), 24.29 (Me-4a), 19.7 (Me-5) ppm; IR (film): *ν* = 2225 (CN), 1644 (C=O), 1540 (C=C) cm^{-1}; MS (EI) *m/z*: 379 (15) $[M]^+$, 275 (21), 274 (72) $[M - PhCO]^+$, 259 (82) $[274 - Me]^+$, 278 (22), 115 (12), 105 (100) $[PhCO]^+$, 77 (98) $[Ph]^+$, 51 (27), 39 (19); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}N_3O^+$: 380.1763, found: 380.1764.

(*E*)-1-Phenyl-2-(4a,5,5-trimethyl-7-nitro-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3f).



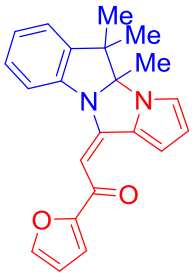
Obtained from 3*H*-indole **1f** (102 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Citric needles; 18 mg (yield 9% – procedure A), 39 mg (yield 20% – procedure B); mp 188–189 ºC (hexane/EtOAc); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.6 Hz, 1 H, H-8), 8.07 (s, 1 H, H-6), 7.99–7.97 (m, 2 H, H_o), 7.86 (dd, *J* = 3.8, 1.0 Hz, 1 H, H-1), 7.51−7.47 (m, 4 H, $H_{m,p}$; H-9), 7.02 (br s, 1 H, H-3), 6.75 (s, 1 H, =CH), 6.58 (dd, *J* = 3.8, 2.5 Hz, 1 H, H-2), 1.67 (s, 6 H, Me-4a; Me-5), 0.88 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.1 (C=O), 146.9 (C-11), 146.1 (C-5a), 145.9 (C-9a), 144.6 (C-7), 140.7 (C_i), 132.6 (C-11a), 131.5 (C_p), 128.5 (C_m), 127.6 (C_o), 125.5 (C-8), 118.9 (C-6), 116.9 (C-3), 116.0 (C-9), 115.9 (C-2), 113.7 (C-1), 91.9 (C-4a), 91.4 (=CH), 47.8 (C-5), 26.4 (Me-5), 24.3 (Me-4a), 19.7 (Me-5) ppm; IR (film): *ν* = 1645 (C=O), 1542 (C=C), 1519 (NO_2) cm^{-1}; MS (EI) *m/z*: 399 (14) $[M]^+$, 295 (20), 294 (92) $[M - PhCO]^+$, 233 (22), 115 (24), 105 (100) $[PhCO]^+$, 77 (94) $[Ph]^+$, 51 (22), 39 (12); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}N_3O^+$: 400.1661, found: 400.1662.

(*E*)-1-Phenyl-2-(12a,13,13-trimethyl-12a,13-dihydro-8*H*-benzo[*e*]pyrrolo[1',2':3,4]-imidazo[1,2-*a*]indol-8-ylidene)ethan-1-one (3h).



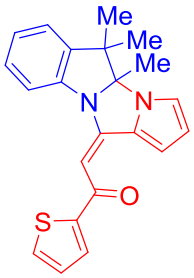
Obtained from 3*H*-indole **1h** (105 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Pale yellow solid; 146 mg (yield 72% − procedure A), 178 mg (yield 88% − procedure B); mp 215−216 ºC ($CHCl_3$/hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1 H, H-1), 7.98−7.93 (m, 4 H, H_o; H-5; H-6), 7.87 (dd, *J* = 3.9, 1.1 Hz, 1 H, H-9), 7.69 (d, *J* = 8.6 Hz, 1 H, H-4), 7.55−7.52 (m, 1 H, H-2), 7.48−7.43 (m, 4 H, H-3; $H_{m,p}$), 7.09 (dd, *J* = 2.6, 1.1 Hz, 1 H, H-11), 6.83 (s, 1 H, =CH), 6.58 (dd, *J* = 3.9, 2.6 Hz, 1 H, H-10), 1.99 (s, 3 H, Me-12a), 1.76 (s, 3 H, Me-13), 1.02 (s, 3 H, Me-13) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.0 (C=O), 149.5 (C-8), 141.3 (C_i), 138.6 (C-13a), 136.8 (C-6a), 133.3 (C-8a), 132.1 (C-4a), 131.0 (C_p), 130.4 (C-1a), 129.8 (C-4), 128.3 (C_m), 127.6 (C_o), 127.7 (C-3), 127.1 (C-2), 124.8 (C-3), 122.4 (C-1), 117.5 (C-11), 116.3 (C-6), 115.2 (C-10), 112.9 (C-9), 91.6 (C-12a), 89.3 (=CH), 49.9 (C-13), 24.4 (Me-13), 23.8 (Me-12a), 22.4 (Me-13) ppm; IR (film): *ν* = 1639 (C=O), 1513 (C=C) cm^{-1}; MS (EI) *m/z*: 404 (427) [M]$^+$, 299 (100) [M − PhCO]$^+$, 284 (75) [299 – Me]$^+$, 194 (21), 152 (12), 105 (47) [PhCO]$^+$, 77 (21) [Ph]$^+$; HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{28}H_{25}N_2O^+$: 405.1967, found: 405.1968.

(*E*)-1-(Furan-2-yl)-2-(4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3i).



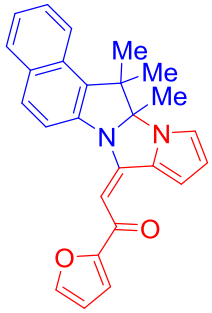
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2b** (93 mg, 0.5 mmol). Yellow solid; 125 mg (yield 73% − procedure A), 131 mg (yield 76% − procedure B); mp 133−135 ºC (hexane/$CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.9, 1.1 Hz, 1 H, H-1), 7.53 (dd, *J* = 1.7, 0.7 Hz, 1 H, H-5′), 7.47−7.45 (m, 1 H, H-9), 7.43−7.39 (m, 1 H, H-8), 7.21−7.16 (m, 2 H, H-6, H-7), 7.15 (dd, *J* = 3.4, 0.7 Hz, 1 H, H-3′), 6.98 (dd, *J* = 2.6, 1.1 Hz, 1 H, H-3), 6.70 (s, 1 H, =CH), 6.53 (dd, *J* = 3.9, 2.6 Hz, 1 H, H-2), 6.50 (dd, *J* = 3.4, 1.7 Hz, 1 H, H-4′), 1.63 (s, 3 H, Me-4a), 1.57 (s, 3 H, Me-5), 0.76 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.7 (C=O), 155.4 (C-2′), 148.8 (C-11), 144.8 (C-5a), 144.7 (C-5a), 144.4 (C-5′), 140.2 (C-9a), 133.1 (C-11a), 128.4 (C-8), 125.1 (C-7), 123.0 (C-6), 117.5 (C-9), 116.4 (C-3), 115.2 (C-2), 113.5 (C-3′), 112.1 (C-4′), 91.6 (C-4a), 88.8 (=CH), 47.7 (C-5), 26.1 (Me-5), 23.9 (Me-4a), 19.9 (Me-5) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –197.3 (N-4), –241.2 (N-10) ppm; IR (film): *ν* = 1637 (C=O), 1537 (C=C) cm^{-1}; MS (EI) *m/z*: 344 (34) [M]$^+$, 249 (84) [M − FurylCO]$^+$, 234 (100) [249 − Me]$^+$, 95 (87) [FurylCO]$^+$; HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{22}H_{21}N_2O_2^+$: 345.1603, found: 345.1605.

(*E*)-1-(Thien-2-yl)-2-(4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3j).



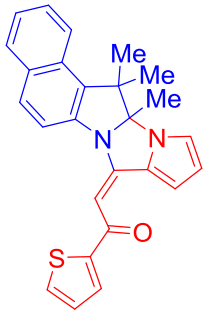
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2c** (101 mg, 0.5 mmol). Brownish solid; 126 mg (yield 70% − procedures A and B); mp 101−103 ºC (hexane/$CHCl_3$);^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.8, 1.0 Hz, 1 H, H-1), 7.70 (dd, *J* = 3.8, 0.9 Hz, 1 H, H-3′), 7.50 (dd, *J* = .8, 0.9 Hz, 1 H, H-5′), 7.42−7.41 (nr m, 2 H, H-8; H-9), 7.20−7.18 (m, 2 H, H-6; H-7), 7.11 (dd, *J* = 4.8, 3.8 Hz, 1 H, H-4′), 6.99 (dd, *J* = 2.6, 1.0 Hz, 1 H, H-3), 6.65 (s, 1 H, =CH), 6.53 (dd, *J* 3.7, 2.6 Hz, 1 H, H-2), 1.63 (s, 3 H, Me-4a), 1.57 (s, 3 H, Me-5), 0.77 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 180.2 (C=O), 148.7 (C-11), 148.3 (C-2′), 144.8 (C-5a), 140.3 (C-9a), 133.0 (C-11a), 130.7 (C-5′), 128.6 (C-8), 128.3 (C-3′), 127.8 (C-4′), 125.1 (C-7), 123.0 (C-6), 117.4 (C-9), 116.4 (C-3), 115.2 (C-2), 113.0 (C-1), 91.6 (C-4a), 88.8 (=CH), 47.8 (C-5), 26.1 (Me-5), 23.9 (Me-4a), 19.9 (Me-5) ppm; IR (film): *v* = 1627 (C=O), 1538 (C=C) cm^{-1}; MS (EI) *m/z*: 360 (21) $[M]^+$, 249 (92) $[M - ThCO]^+$, 234 (100) $[249 - Me]^+$, 111 (74) $[ThCO]^+$, 91 (18), 77 (18), 39 (52); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{21}N_2OS^+$: 361.1375, found: 361.1377.

(*E*)-1-(Furan-2-yl)-2-(12a,13,13-trimethyl-12a,13-dihydro-8*H*-benzo[*e*]pyrrolo[1',2':3,4]imidazo[1,2-a]indol-8-ylidene)ethan-1-one (3k).



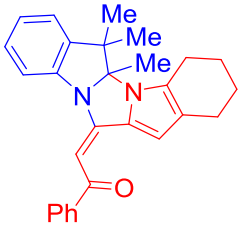
Obtained from 3*H*-indole **1h** (105 mg, 0.5 mmol) and pyrrolylacetylene **2b** (93 mg, 0.5 mmol). Yellow solid; 144 mg (yield 73% − procedure A), 154 mg (yield 78% − procedure B); mp 198−200 ºC; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1 H, H-1), 7.96 (d, *J* = 8.6 Hz, 1 H, H-5), 7.93 (d, *J* = 8.2 Hz, 1 H, H-6), 7.85 (dd, *J* = 3.9, 1.1 Hz, 1 H, H-9), 7.72 (d, *J* = 8.6 Hz, 1 H, H-4), 7.53−7.50 (m, 2 H, H-5′, H-2), 7.45 (t, *J* = 7.4 Hz, 1 H, H-3), 7.13 (dd, *J* = 3.4, 0.7 Hz, 1 H, H-3′), 7.08 (br s, 1 H, H-11), 6.79 (s, 1 H, =CH), 6.56 (dd, *J* = 3.9, 2.6 Hz, 1 H, H-10), 6.50 (dd, *J* = 3.4, 1.7 Hz, 1 H, H-4′), 1.97 (s, 3 H, Me-12a), 1.74 (s, 3 H, Me-13), 0.99 (s, 3 H, Me-12) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.6 (C=O), 155.4 (C-2′), 149.3 (C-8), 144.3 (C-5′), 138.3 (C-13a), 136.7 (C-6a), 133.3 (C-8a), 132.0 (C-4a), 130.3 (C-13b), 129.7 (C-4), 129.6 (C-5), 127.0 (C-2), 124.8 (C-3), 122.3 (C-1), 117.4 (C-11), 116.3 (C-6), 115.2 (C-10), 113.5 (C-3′), 113.0 (C-9), 112.0 (C-4′), 91.6 (C-12a), 88.4 (=CH), 49.8 (C-13), 24.3 (Me-13), 23.8 (Me-12a), 22.4 (Me-13) ppm; IR (film): *v* = 1636 (C=O), 1514 (C=C) cm^{-1}; MS (EI) *m/z*: 394 (52) $[M]^+$, 299 (100) $[M - FurylCO]^+$, 284 (75) $[299 – Me]^+$, 95 (29) $[FurylCO]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}N_2O_2^+$: 395.1760, found: 395.1761.

(*E*)-1-(Thien-2-yl)-2-(12a,13,13-trimethyl-12a,13-dihydro-8*H*-benzo[*e*]pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-8-ylidene)ethan-1-one (3l).



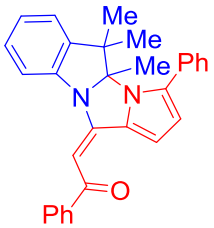
Obtained from 3*H*-indole **1h** (105 mg, 0.5 mmol) and pyrrolylacetylene **2c** (101 mg, 0.5 mmol). Yellow solid; 164 mg (yield 80% − procedure A); 166 mg (yield 81% − procedure B); mp 206−208 ºC (hexane/EtOAc); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1 H, H-1), 7.98−7.93 (m, 2 H, H-4, H-5), 7.83 (br s, 1 H, H-9), 7.70−7.68 (m, 2 H, H-6, H-3′), 7.55−7.45 (m, 3 H, H-2, H-3, H-5′), 7.11−7.10 (m, 2 H, H-11, H-4′), 6.73 (s, 1 H, =CH), 6.56 (br s, 1 H, H-10), 1.97 (s, 3 H, Me-12a), 1.75 (s, 3 H, Me-13), 1.00 (s, 3 H, Me-13) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 180.1 (C=O), 149.3 (C-8), 148.3 (C-2′), 138.4 (C-6a), 136.8 (C-13a), 133.2 (C-8a), 132.1 (C-4a), 130.7 (C-5′), 130.4 (C-13b), 129.8 (C-5), 129.7 (C-4), 128.6 (C-3′), 127.8 (C-4′), 127.1 (C-2), 124.8 (C-3), 122.4 (C-1), 117.3 (C-6), 116.4 (C-11), 115.2 (C-10), 113.0 (C-9), 91.7 (C-12a), 88.9 (=CH), 49.9 (C-13), 24.3 (Me-13), 23.8 (Me-12a), 22.4 (Me-13) ppm; IR (film): *v* = 1626 (C=O), 1513 (C=C) cm^{-1}; MS (EI) *m/z*: 410 (8) $[M]^+$, 299 (100) $[M - ThCO]^+$, 284 (52) $[299 – Me]^+$, 194 (20), 165 (19), 111 (100) $[ThCO]^+$, 83 (12) $[Th]^+$, 39 (37); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}N_2OS^+$: 411.1531, found: 411.1530.

(*E*)-1-Phenyl-2-(5a,6,6-trimethyl-1,2,3,4a,5-hexahydro-12*H*-imidazo[1,2-*a*:3,4-*a*']diindol-12-ylidene)ethan-1-one (3m).



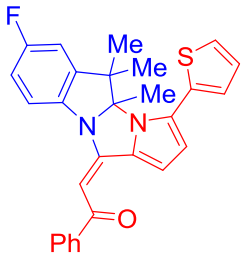
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2f** (125 mg, 0.5 mmol). Orange solid; 71 mg (yield 40% − procedure A), 96 mg (yield 54% − procedure B); mp 135−137 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.00−7.98 (m, 2 H, H_o), 7.71 (s, 1 H, H-13), 7.46−7.44 (m, 3 H, $H_{m,p}$), 7.39 (nr m, 2 H, H-9, H-10), 7.21−7.14 (m, 2 H, H-7, H-8), 6.66 (s, 1 H, =CH), 2.84−2.74 (m, 2 H, H-4), 2.69−2.66 (m, 2 H, H-1), 1.94−1.92 (m, 2 H, H-3), 1.87−1.73 (m, 2 H, H-2), 1.63 (s, 6 H, Me-5a, Me-6), 0.88 (s, 3 H, Me-6) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.5 (C=O), 148.5 (C-12), 144.7 (C-6a), 141.7 (C_i), 139.9 (C-10a), 131.5 (C-12a), 131.0 (C_p), 128.3 (C-4a), 128.2 (C_m; C-9), 127.5 (C_o), 125.2 (C-13a), 124.7 (C-8), 123.0 (C-7), 117.1 (C-10), 112.3 (C-13), 92.4 (C-5a), 88.4 (=CH), 47.7 (C-5), 29.8 (C-4), 27.0 (Me-6), 23.9 (C-1), 23.6, 23.3 (C-2, C-3), 22.2 (Me-5a), 20.7 (Me-6) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –203.2 (N-5), –241.2 (N-11) ppm; IR (film): *v* = 1640 (C=O), 1534 (C=C) cm^{-1}; MS (EI) *m/z*: 354 (27) $[M]^+$, 249 (100) $[M - PhCO]^+$, 234 (83) $[249 - Me]^+$, 233 (17), 105 (27) $[PhCO]^+$, 77 (28) $[Ph]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{28}H_{29}N_2O^+$: 355.1810, found: 355.1813.

(*E*)-1-Phenyl-2-(4a,5,5-trimethyl-3-phenyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)ethan-1-one (3n).



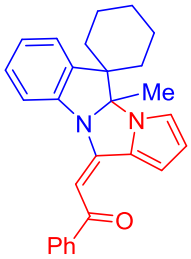
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2d** (136 mg, 0.5 mmol). Yellow solid; 93 mg (yield 43% − procedure A), 110 mg (yield 52% − procedure B); mp 169−171 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.01−8.00 (nr m, 3 H, H-1, H_o, Ph), 7.48 (nr m, 8 H, $H_{m,p}$, Ph; Ph′), 7.41−7.37 (m, 2 H, H-8, H-9), 7.14−7.08 (m, 2 H, H-6, H-7), 6.74 (s, 1 H, =CH), 6.44 (br s, 1 H, H-2), 1.67 (s, 3 H, Me-5), 0.88 (s, 3 H, Me-5), 0.82 (s, 3 H, Me-4a) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.8 (C=O), 148.4 (C-11), 145.2 (C-5a), 141.5 (C_i, Ph), 139.8 (C-9a), 133.7 (C_i, Ph′), 133.5 (C-3), 133.0 (C-11a), 131.1 (C_m, Ph′), 130.9 (C_p, Ph), 128.9 (C_p, Ph′), 128.3 (C_o, Ph′), 128.1 (C_m, Ph; C-8), 127.6 (C_o, Ph), 125.0 (C-7), 123.0 (C-6), 117.3 (C-9), 116.1 (C-2), 112.9 (C-1), 93.3 (C-4a), 89.1 (=CH), 48.0 (C-5), 26.2 (Me-5), 24.8 (Me-4a), 19.1 (Me-5) ppm; IR (film): *v* = 1640 (C=O), 1534 (C=C) cm^{-1}; MS (EI) *m/z*: 430 (87) $[M]^+$, 325 (37) $[M - PhCO]^+$, 310 (21) $[325 - Me]^+$, 105 (100) $[PhCO]^+$, 77 (77) $[Ph]^+$, 51 (12); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{30}H_{27}N_2O^+$: 431.2123, found: 431.2126.

(*E*)-2-(7-fluoro-4a,5,5-trimethyl-3-(thiophen-2-yl)-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)-1-phenylethan-1-one (3o).



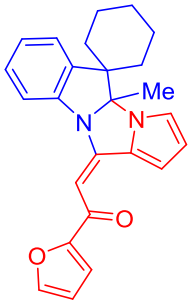
Obtained from 3*H*-indole **1c** (89 mg, 0.5 mmol) and pyrrolylacetylene **2e** (139 mg, 0.5 mmol). Orange solid; 98 mg (yield 43% − procedure A), 123 mg (yield 54% − procedure B); mp 123−125 ºC (hexane/EtOAc); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2 H, H_o), 7.94 (d, *J* = 3.9 Hz, 1 H, H-1), 7.50−7.44 (m, 4 H, $H_{m,p}$; H-5′), 7.33 (dd, *J* = 8.6, 4.3 Hz, 1 H, H-9), 7.21 (dd, *J* = 3.8, 0.9 Hz, 1 H, H-3′), 7.14 (dd, *J* = 4.8, 3.8 Hz, 1 H, H-4′), 7.06 (ddd, *J* = 8.7, 8.0, 2.6 Hz, 1 H, H-8), 6.85 (dd, *J* = 8.0, 2.6 Hz, 1 H, H-6), 6.66 (s, 1 H, =CH), 6.56 (d, *J* = 3.9 Hz, 1 H, H-2), 1.78 (s, 3 H, Me-5), 1.03 (s, 3 H, Me-4a), 0.85 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.9 (C=O), 160.4 (d, *J* = 244.8 Hz, C-7), 148.0 (C-11), 147.5 (d, *J* = 7.7 Hz, C-5a), 141.3 (C_i), 135.8 (d, *J* = 2.0 Hz, C-9a), 134.4 (C-2′), 132.8 (C-11a), 131.1 (C-5′), 130.1 (C_p), 128.4 (C_m), 127.6 (C_o; C-3′), 127.1 (C-4′), 124.7 (C-3), 118.9 (C-2), 118.1 (d, *J* 8.5 Hz, C-9), 114.6 (d, *J* = 23.7 Hz, C-8), 112.9 (C-1), 111.0 (d, *J* = 21.1 Hz, C-6), 93.7 (C-4a), 89.4 (=CH), 48.4 (C-5), 26.2 (Me-5), 24.7 (Me-4a), 19.3 (Me-5) ppm; ^{19}F NMR (376.5 MHz, $CDCl^3$): δ −116.79 ppm; IR (film): *v* = 1643 (C=O), 1538 (C=C) cm^{-1}; MS (EI) *m/z*: 454 (7) $[M]^+$, 349 (19) $[M - PhCO]^+$, 334 (10) $[349 - Me]^+$, 105 (100) $[PhCO]^+$, 77 (59) $[Ph]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{28}H_{24}FN_2OS^+$: 456.1672, found: 4563.1675.

(*E*)-2-(4a′-methyl-4a′*H*,11′*H*-spiro[cyclohexane-1,5′-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol]-11-ylidene)-1-phenylethan-1-one (3p).



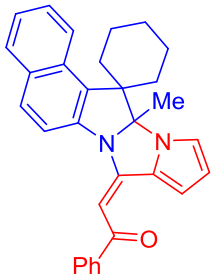
Obtained from 3*H*-indole **1i** (100 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Yellow solid; 138 mg (yield 70% − procedure B); mp 141−143 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2 H, H_o), 7.86 (d, *J* = 3.5 Hz, 1 H, H-1′), 7.53 (d, *J* = 7.5 Hz, 1 H, H-6′), 7.48−7.44 (m, 3 H, $H_{m,p}$), 7.41−7.40 (m, 2 H, H-8′, H-9′), 7.19−7.15 (m, 1 H, H-7′), 7.06 (d, *J* = 2.6 Hz, 1 H, H-3′), 6.72 (s, 1 H, =CH), 6.56 (dd, *J* = 3.5, 2.6 Hz, 1 H, H-2′), 2.22-2.18 (m, 1 H, Cy), 2.03-1.96 (m, 1 H, Cy), 1.91−1.88 (m, 2 H, Cy), 1.71−1.66 (m, 1 H, Cy), 1.61 (s, 3 H, Me-4a), 1.29−1.25 (m, 3 H, Cy), 1.03-1.01 (m, 2 H, Cy) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.1 (C=O), 148.9 (C-11′), 144.3 (C-5a'), 141.3 (C_i), 140.6 (C-9a'), 133.4 (C-11a'), 131.0 (C_p), 128.3 (C_m), 128.1 (C-8′), 127.6 (C_o), 125.8 (C-7′), 124.5 (C-6′), 118.0 (C-3′), 116.9 (C-9′), 115.1 (C-2′), 112.9 (C-1′), 92.0 (C-4a'), 88.8 (=CH), 51.2 (C-5′), 33.1, 29.1, 25.3 23.4 (4×C, Cy), 23.3 (Me-4a), 20.8 (Cy) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –241.3 (N-10), –198.3 (N-4) ppm; IR (film): *v* = 1640 (C=O), 1534 (C=C) cm^{-1}; MS (EI) *m/z*: 394 (11) $[M]^+$, 289 (100) $[M - PhCO]^+$, 246 (22), 105 (33) $[PhCO]^+$, 77 (43) $[Ph]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{27}N_2O^+$: 395.2123, found 395.2122.

(*E*)-1-(Furan-2-yl)-2-(4a′-methyl-4a′*H*,11′*H*-spiro[cyclohexane-1,5′-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol]-11′-ylidene)ethan-1-one (3q).



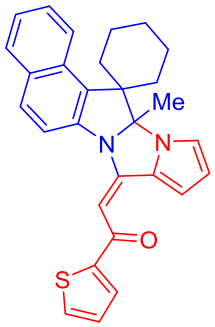
Obtained from 3*H*-indole **1i** (100 mg, 0.5 mmol) and pyrrolylacetylene **2b** (93 mg, 0.5 mmol). Light yellow solid; 107 mg (yield 56% − procedure B); mp 162−164 ºC; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.83 (d, *J* = 3.6 Hz, 1 H, H-1′), 7.52 (s, 1 H, H-5″), 7.51 (d, *J* = 6.7 Hz, 1 H, H-6′), 7.47−7.40 (m, 2 H, H-8′, H-9′), 7.17 (t, *J* = 7.5 Hz, 1 H, H-7′), 7.13 (d, *J* = 3.0 Hz, 1 H, H-3″), 7.04 (br s, 1 H, H-3′), 6.68 (s, 1 H, =CH), 6.54 (dd, *J* = 3.6, 2.6 Hz, 1 H, H-2′), 6.50 (dd, *J* = 3.4, 1.7 Hz, 1 H, H-4″), 2.20−2.17 (m, 1 H, Cy), 2.02−1.95 (m, 1 H, Cy), 1.90−1.82 (m, 2 H, Cy), 1.72−1.66 (m, 1 H, Cy), 1.60 (s, 3 H, Me-4a), 1.31−1.23 (m, 3 H, Cy), 1.03−0.95 (m, 2 H, Cy) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.7 (C=O), 155.5 (C-2″), 148.7 (C-11′), 144.3 (C-5a'), 144.2 (C-5″), 140.5 (C-9a'), 133.5 (C-11a'), 128.1 (C-8′), 125.8 (C-7′), 124.5 (C-6′), 118.0 (C-9′), 116.9 (C-3′), 115.1 (C-2′), 113.4 (C-3″), 113.0 (C-1′), 112.0 (C-4″), 92.1 (C-4a'), 87.9 (=CH), 51.1 (C-5′), 33.0, 29.1 (2×C, Cy), 25.2 (Me-4a), 23.4, 23.3, 20.8 (3×C, Cy) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –198.2 (N-4), –240.8 (N-10) ppm; IR (film): *v* = 1636 (C=O), 1535 (C=C) cm^{-1}; MS (EI) *m/z*: 384 (21) $[M]^+$, 289 (100) $[M - Furoyl]^+$, 115 (13), 95 (36) $[Furoyl]^+$, 41 (11), 39 (21); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_2^+$: 385.1916, found: 385.1918.

(*E*)-2-(12a-Methyl-8*H*,12a*H*-spiro[benzo[*e*]pyrrolopyrrolo[1',2':3,4]imidazo[1,2-*a*]indole-13,1′-cyclohexan]-8-ylidene)-1-phenylethan-1-one (3r).



Obtained from 3*H*-indole **1j** (125 mg, 0.5 mmol) and pyrrolylacetylene **2a** (98 mg, 0.5 mmol). Purified by washing with diethyl ether. Light yellow solid; 187 mg (yield 84% − procedure B); mp 299−300 ºC ($CHCl_3$/EtOAc); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.33 (d, *J* 8.7 Hz, 1 H, H-1), 7.95−7.93 (m, 4 H, H_o; H-4, H-5), 7.89 (d, *J* = 3.5, 1.0 Hz, 1 H, H-9), 7.65 (d, *J* = 8.7 Hz, 1 H, H-6), 7.55−7.51 (m, 1 H, H-2), 7.46−7.40 (m, 4 H, $H_{m,p}$; H-4), 7.25 (dd, *J* = 2.5, 1.0 Hz, 1 H, H-11), 6.77 (s, 1 H, =CH), 6.58 (dd, *J* = 3.5, 2.5 Hz, 1 H, H-10), 2.98 (td, *J* = 14.3, 3.9 Hz, 1 H, H-2′), 2.40 (d, *J* = 14.3 Hz, 1 H, H-2′), 2.08 (d, *J* = 14.0 Hz, 1 H, Cy), 1.92−1.75 (m, 3 H, Cy), 1.75 (s, 3 H, Me-12a), 1.68−1.09 (m, 4 H, Cy) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 188.0 (C=O), 149.4 (C-8), 141.4 (C_i), 137.7 (C-6a), 136.4 (C-13a), 134.1 (C-8a), 132.5 (C-4a), 131.0 (C_p, Ph), 130.2 (2×C, C-4, C-5), 129.9 (C-1a), 128.3 (C_m), 127.6 (C_o), 126.8 (C-2), 124.5 (C-3), 122.5 (C-1), 120.0 (C-11), 117.5 (C-6), 115.2 (C-10), 113.4 (C-9), 92.3 (C-12a), 88.2 (=CH), 54.3 (C-13), 32.6, 29.4, 25.5 (3×C, Cy), 25.4 (Me-12a), 23.5, 22.5 (2×C, Cy) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –198.1 (N-12), –241.2 (N-7) ppm; IR (film): *ν* = 1637 (C=O), 1537 (C=C) cm^{-1}; MS (EI) *m/z*: 444 (8) $[M]^+$, 339 (100) $[M - PhCO]^+$, 194 (14), 165 (18), 105 (88) $[PhCO]^+$, 77 (76) $[Ph]^+$, 51 (12), 44 (18), 41 (13); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{31}H_{29}N_2O^+$: 445.22799, found: 445.22799.

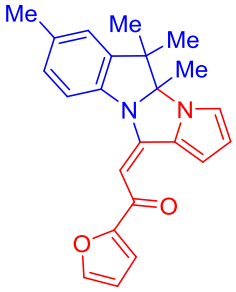
(*E*)-2-(12a-Methyl-8*H*,12a*H*-spiro[benzo[*e*]pyrrolo[1',2':3,4]imidazo[1,2-*a*]indole-13,1'-cyclohexan]-8-ylidene)-1-(thiophen-2-yl)ethan-1-one (3s).



Obtained from 3*H*-indole **1j** (125 mg, 0.5 mmol) and pyrrolylacetylene **2c** (101 mg, 0.5 mmol). Light yellow solid; 135 mg (yield 60% − procedure B); mp 283−285 ºC ($CHCl_3$/hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.6 Hz, 1 H, H-1), 7.92−7.89 (m, 2 H, H-4, H-5), 7.84 (d, *J* = 3.7 Hz, 1 H, H-9), 7.65 (dd, *J* = 8.7, 8.8 Hz, 1 H, H-6), 7.62 (d, *J* = 3.7 Hz, 1 H, H-3″), 7.54 (dd, *J* = 8.7, 8.6 Hz, 1 H, H-2), 7.49 (d, *J* = 4.9 Hz, 1 H, H-5″), 7.45 (dd, *J* = 8.7, 8.6 Hz, 1 H, H-3), 7.24 (dd, *J* = 2.5, 1.0 Hz, 1 H, H-11), 7.09−7.07 (m, 1 H, H-4″), 6.68 (s, 1 H, =CH), 6.57 (dd, *J* = 3.7, 2.5 Hz, 1 H, H-10), 2.98 (td, *J* = 14.2, 3.6 Hz, 1 H, H-2′), 2.40 (d, *J* = 14.1 Hz, 1 H, Cy), 2.07 (d, *J* = 13.9 Hz, 1 H, Cy), 1.90 (d, *J* = 13.9 Hz, 1 H, Cy), 1.82 (dd, *J* = 14.1, 5.2 Hz, 1 H, Cy), 1.75 (s, 3 H, Me-12a), 1.75−1.73 (m, 1 H, H-6′), 1.66 (d, *J* = 15.2 Hz, 1 H, Cy), 1.51 (dt, *J* = 12.9, 3.9 Hz, 1 H, Cy), 1.36 (d, *J* = 14.1 Hz, 1 H, Cy), 1.10 (tt, *J* = 13.0, 4.3 Hz, 1 H, H-5′) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 180.2 (C=O), 149.1 (C-8), 148.5 (C-2″), 137.6 (C-6a), 136.4 (C-13a), 134.0 (C-8a), 132.6 (C-4a), 130.6 (C-5″), 130.2 (2×C, C-5, C-13b), 129.9 (C-4), 128.5 (C-3″), 127.7 (C-4″), 126.8 (C-2), 124.6 (C-3), 122.5 (C-1), 120.0 (C-11), 117.3 (C-6), 115.2 (C-10), 113.6 (C-9), 91.4 (C-12a), 87.8 (=CH), 54.3 (C-13), 32.6, 29.4 (2×C, C-2′, C-6′), 25.4 (2×C, Me-12a, C-4′), 23.4, 22.5 (2×C, C-3′, C-5′) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –198.1 (N-12), –241.2 (N-7) ppm; IR (film): *ν* = 1625 (C=O), 1513 (C=C) cm^{-1}; MS (EI) *m/z*:

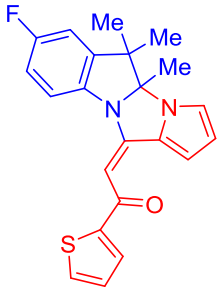
450 (18) $[M]^+$, 340 (27), 339 (100) $[M - ThCO]^+$, 165 (12), 111 (53) $[ThCO]^+$, 39 (15); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{27}N_2OS^+$: 451.1844, found: 451.1844.

(*E*)-1-(Furan-2-yl)-2-(4a,5,5,7-tetramethyl-4a,5-dihydro-11H-pyrrolo[1',2':3,4]imidazo[1,2-a]indol-11-ylidene)ethan-1-one (3t).



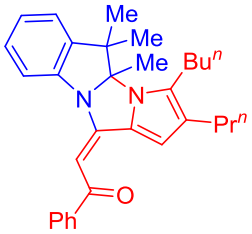
Obtained from 3*H*-indole **1b** (87 mg, 0.5 mmol) and pyrrolylacetylene **2b** (93 mg, 0.5 mmol). Light yellow solid; 142 mg (yield 79% − procedure B); mp 167−169 ºC ($CHCl_3$/hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.8, 1.1 Hz, 1 H, H-1), 7.53 (dd, *J* = 1.7, 0.6 Hz, 1 H, H-5′), 7.34 (d, *J* = 7.9 Hz, 1 H, H-9), 7.20 (d, *J* = 7.9 Hz, 1 H, H-8), 7.13 (dd, *J* = 3.4, 0.6 Hz, 1 H, H-3′), 7.00 (s, 1 H, H-6), 6.98 (dd, *J* = 2.6, 1.1 Hz, 1 H, H-3), 6.66 (s, 1 H, =CH), 6.52 (dd, *J* = 3.8, 2.6 Hz, 1 H, H-2), 6.50 (dd, *J* = 3.4, 1.7 Hz, 1 H, H-4′), 2.39 (s, 3 H, Me-7), 1.62 (s, 3 H, Me-4a), 1.55 (s, 3 H, Me-5), 0.75 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.6 (C=O), 155.5 (C-2′), 149.0 (C-11), 144.8 (C-5a), 144.2 (C-5′), 137.8 (C-9a), 134.9 (C-7), 133.1 (C-11a), 128.7 (C-8), 123.7 (C-6), 117.2 (C-9), 116.3 (C-3), 115.1 (C-2), 113.3 (C-3′), 112.8 (C-1), 112.0 (C-4′), 91.7 (C-4a), 88.6 (=CH), 47.7 (C-5), 26.0 (Me-5), 23.8 (Me-4a), 21.3 (Me-7), 19.9 (Me-5) ppm; IR (film): *v* = 1638 (C=O), 1542 (C=C) cm^{-1}; MS (EI) *m/z*: 358 (37) $[M]^+$, 263 (90) $[M - FurylCO]^+$, 248 (100) $[263 - Me]^+$, 95 (29) $[FurylCO]^+$, 39 (16); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2^+$: 359.1759, found: 359.1760.

(*E*)-2-(7-Fluoro-4a,5,5-trimethyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-*a*]indol-11-ylidene)-1-(thiophen-2-yl)ethan-1-one (3u).



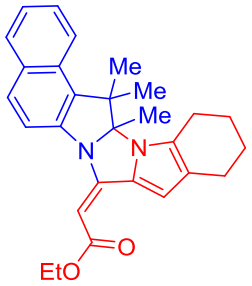
Obtained from 3*H*-indole **1c** (89 mg, 0.5 mmol) and pyrrolylacetylene **2c** (101 mg, 0.5 mmol). Yellow solid; 121 mg (yield 64% − procedure B); mp 191−192 ºC (hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 3.8, 1.0 Hz, 1 H, H-1), 7.68 (dd, *J* = 3.7, 1.0 Hz, 1 H, H-3′), 7.50 (dd, *J* = 4.9, 1.0 Hz, 1 H, H-5′), 7.34 (dd, *J* = 8.5, 4.3 Hz, 1 H, H-9), 7.12−7.06 (m, 2 H, H-8, H-4′), 6.98 (dd, *J* = 2.6, 1.0 Hz, 1 H, H-3), 6.92 (dd, *J* = 7.9, 2.6 Hz, 1 H, H-6), 6.56 (s, 1 H, =CH), 6.52 (dd, *J* = 3.8, 2.6 Hz, 1 H, H-2), 1.63 (s, 3 H, Me-4a), 1.54 (s, 3 H, Me-5), 0.75 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 180.2 (C=O), 160.5 (d, *J* = 245.0 Hz, C-7), 148.8 (C-11), 148.2 (C-2′), 147.1 (d, *J* = 7.6 Hz, C-5a), 136.5 (C-9a), 132.8 (C-11a), 130.8 (C-5′),), 128.7 (C-3′), 127.8 (C-4′), 118.3 (d, *J* = 8.6 Hz, C-9), 116.4 (C-3), 115.4 (C-2), 114.7 (d, *J* = 23.6 Hz, C-6), 111.1 (C-1), 111.9 (d, *J* = 24.2 Hz, C-8), 91.8 (C-4a), 89.2 (=CH), 48.3 (C-5), 25.9 (Me-5), 23.7 (Me-4a), 19.8 (Me-5) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –198.1 (N-4), –244.2 (N-10) ppm; ^{19}F NMR (376.5 MHz, $CDCl^3$): δ –116.70 ppm; IR (film): *v* = 1629 (C=O), 1539 (C=C) $cm^{-1;}$. MS (EI) *m/z*: 378 (22) $[M]^+$, 267 (88) $[M - ThCO]^+$, 252 (100) $[267 - Me]^+$, 251 (23), 162 (11), 133 (13), 111 (74) $[ThCO]^+$, 83 (12), 39 (31); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{20}FN_2OS^+$: 379.1280, found: 379.1277.

(*E*)-2-(3-Butyl-4a,5,5-trimethyl-2-propyl-4a,5-dihydro-11*H*-pyrrolo[1',2':3,4]imidazo[1,2-a]indol-11-ylidene) phenyl ethan-1-one (3v).



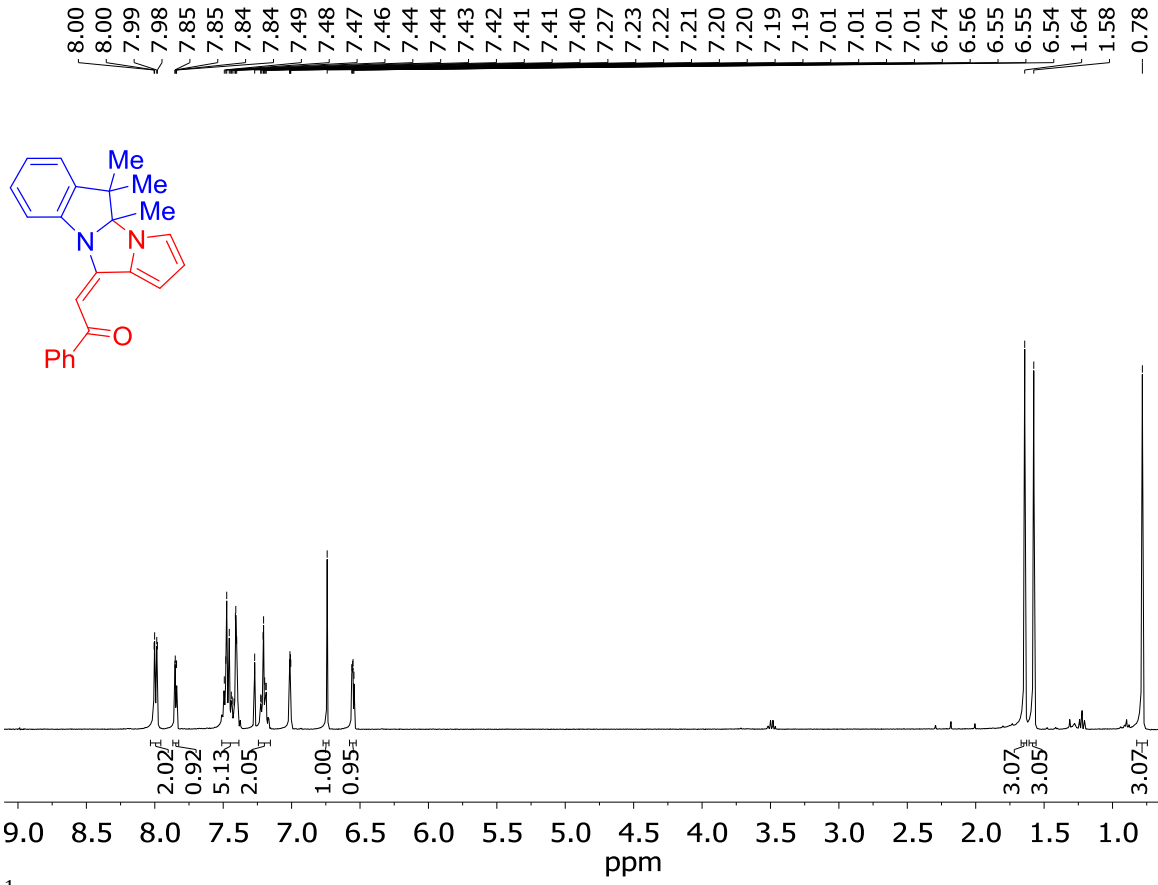
Obtained from 3*H*-indole **1a** (80 mg, 0.5 mmol) and pyrrolylacetylene **2g** (147 mg, 0.5 mmol). Brownish gum; 93 mg (yield 41% − procedure B); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.99−7.96 (m, 2 H, H_o), 7.80 (s, 1 H, H-1), 7.45−7.44 (m, 3 H, $H_{m,p}$), 7.39 (nr m, 2 H, H-8, H-9), 7.21−7.17 (m, 2 H, H-6, H-7), 6.62 (s, 1 H, =CH), 2.78-2.70 (m, 2 H, H-4, Bu), 2.47 (t, *J* = 7.6 Hz, 2 H, H-3, Pr), 1.75−1.69 (m, 2 H, H-2, Pr), 1.67 (br s, 6 H, Me-4a, Me-5), 1.62−1.59 (m, 2 H, H-3, Bu), 1.53−1.46 (m, 2 H, H-2, Bu), 1.02 (t, *J* = 7.6 Hz, 3 H, H-1, Pr), 1.00 (t, *J* = 7.6 Hz, 3 H, H-1, Bu), 0.86 (s, 3 H, Me-5) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 187.7 (C=O), 148.6 (C-11), 145.0 (C-5a), 141.8 (C_i), 139.9 (C-9a), 131.0 (C-3), 130.7 (C_p), 130.6 (C-2), 128.3 (3×C, C_m; C-8), 127.6 (C_o, Ph), 124.8 (C-7), 123.0 (C-6), 117.3 (C-9), 113.8 (C-1), 93.0 (C-4a), 88.3 (=CH), 47.9 (C-5), 32.7 (C-3, Bu), 28.8 (C-3, Pr), 26.5 (C-4, Bu), 26.4 (Me-5), 24.0 (Me-4a), 23.6 (C-2, Pr), 23.2 (C-2, Bu), 20.8 (Me-5), 14.3 (C-1, Pr), 13.9 (C-1, Bu) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –240.9 (N-10), –200.6 (N-4) ppm; IR (film): *v* = 1641 (C=O), 1534 (C=C) cm^{-1}; MS (EI) *m/z*: 452 (19) $[M]^+$, 437 (15) $[M - Me]^+$, 347 (77) $[M - PhCO]^+$, 105 (100) $[PhCO]^+$, 77 (42) $[Ph]^+$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{31}H_{37}N_2O^+$: 453.2906, found: 453.2903.

Ethyl (2*E*)-2-(14a,15,15-trimethyl-10,11,12,13,14a,15-hexahydro-8*H*-benzo[*e*]imidazo[1,2-*a*:3,4-*a*']diindol-8-ylidene)ethanoate (3w).

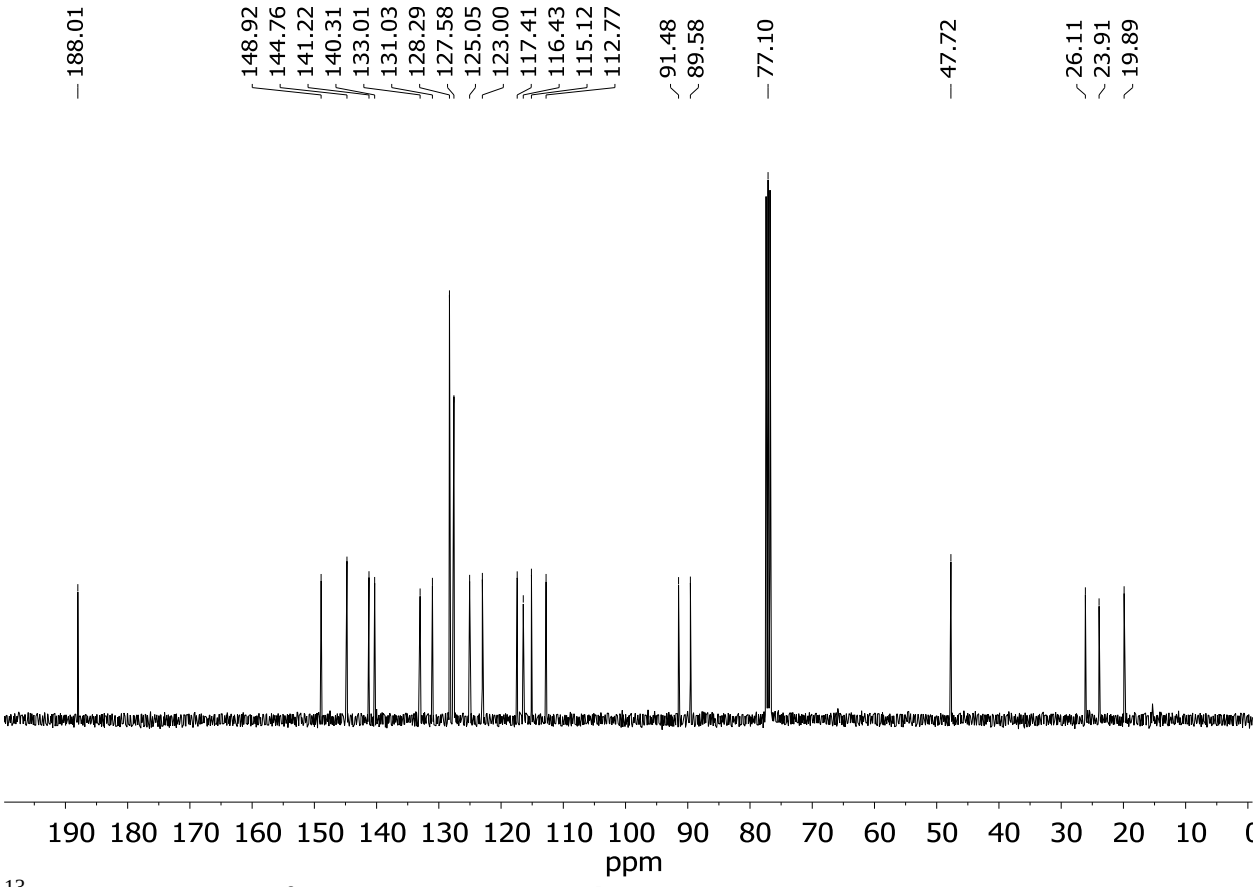


Obtained from 3*H*-indole **1h** (105 mg, 0.5 mmol) and pyrrolylacetylene **2h** (109 mg, 0.5 mmol). Pale yellow solid; 98 mg (yield 46% − procedure B); mp 181−182 ºC ($CHCl_3$/hexane); ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 1 H, H-1), 7.89 (d, *J* = 8.2 Hz, 1 H, H-4), 7.85 (d, *J* = 8.7 Hz, 1 H, H-5), 7.55 (d, *J* = 8.7 Hz, 1 H, H-6), 7.49 (t, *J* = 7.6 Hz, 1 H, H-2), 7.41 (t, *J* = 7.4 Hz, 1 H, H-3), 7.28 (s, 1 H, H-9), 5.56 (s, 1 H, =CH), 4.19 (dq, *J* = 7.1, 1.7 Hz, 2 H, OCH_2), 2.88−2.82 (m, 2 H, H-10), 2.66 (nr m, 2 H, H-13), 1.99 (s, 3 H, Me-15), 1.98−1.93 (m, 2 H, H-11), 1.86−1.76 (m, 2 H, H-12), 1.71 (s, 3 H, Me-14a), 1.30 (t, *J* = 7.1 Hz, 3 H, *Me*CH_2), 1.09 (s, 3 H, Me-15) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.1 (C=O), 148.8 (C-8), 138.4 (C-15a), 135.9 (C-6a), 131.9 (C-8a), 130.8 (C-4a), 130.2 (C-15b), 129.8 (C-4), 129.4 (C-5), 127.8 (C-2), 127.7 (C-13a), 125.2 (C-9a), 124.3 (C-3), 122.3 (C-1), 117.6 (C-6), 110.5 (C-9), 92.6 (C-14a), 81.1 (=CH), 58.9 (CH_2O), 49.6 (C-15), 25.3 (Me-15), 24.1 (C-13), 23.7 (C-10), 23.4, 23.3 (C-11, C-12), 22.9 (Me-14a), 22.3 (Me-15), 14.8 (*Me*CH_2) ppm; ^{15}N NMR (40.6 MHz, $CDCl_3$) δ –203.9 (N-14), –247.1 (N-7) ppm; IR (film): *v* = 1694 (C=O), 1518 (C=C) cm^{-1}; MS (EI) *m/z*: 427 (19), 426 (75) $[M]^+$, 411 (100) $[M - Me]^+$, 353 (41) $[M - CO_2Et]^+$, 338 (21), 194 (37), 169 (25), 161 (22), 148 (21); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{28}H_{31}N_2O_2^+$: 427.2386, found: 427.2387.

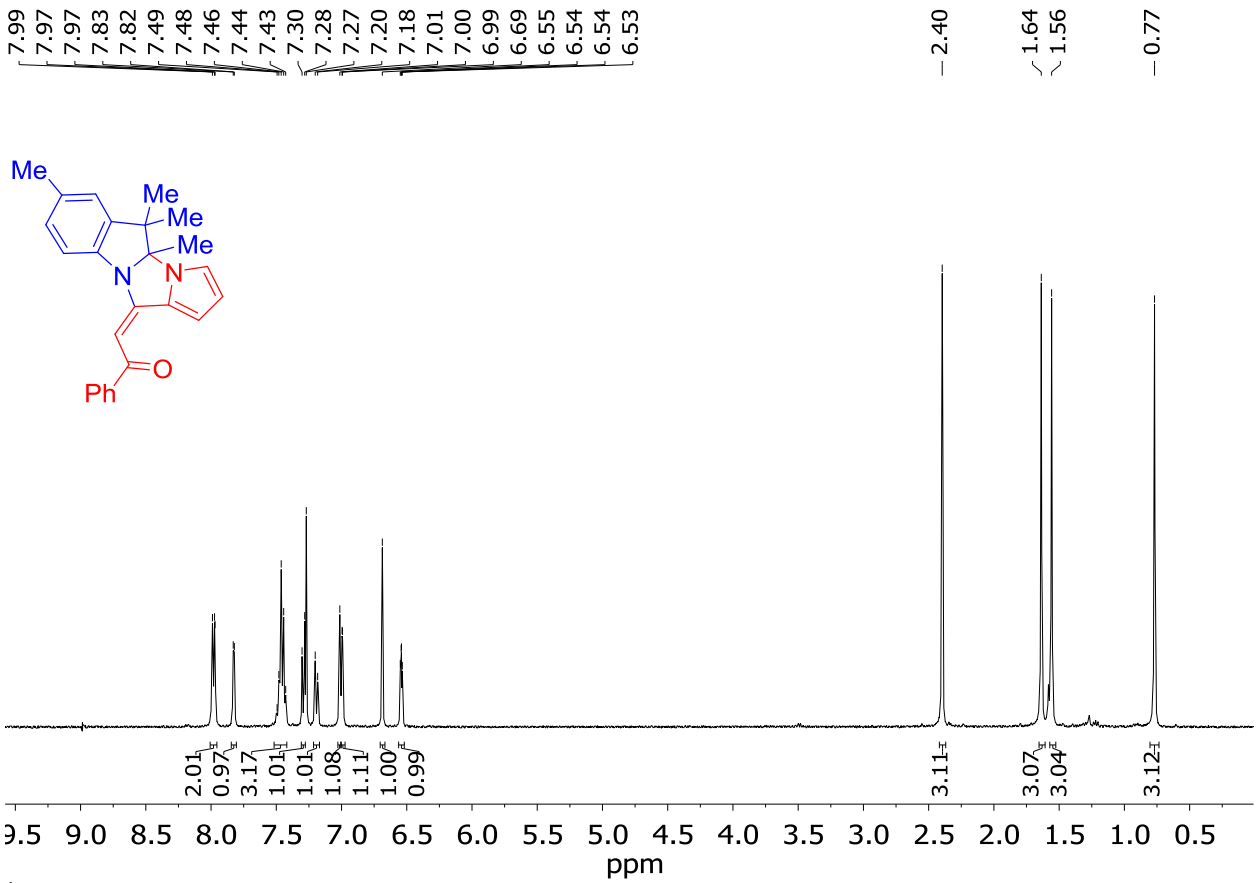
5. NMR spectra for products



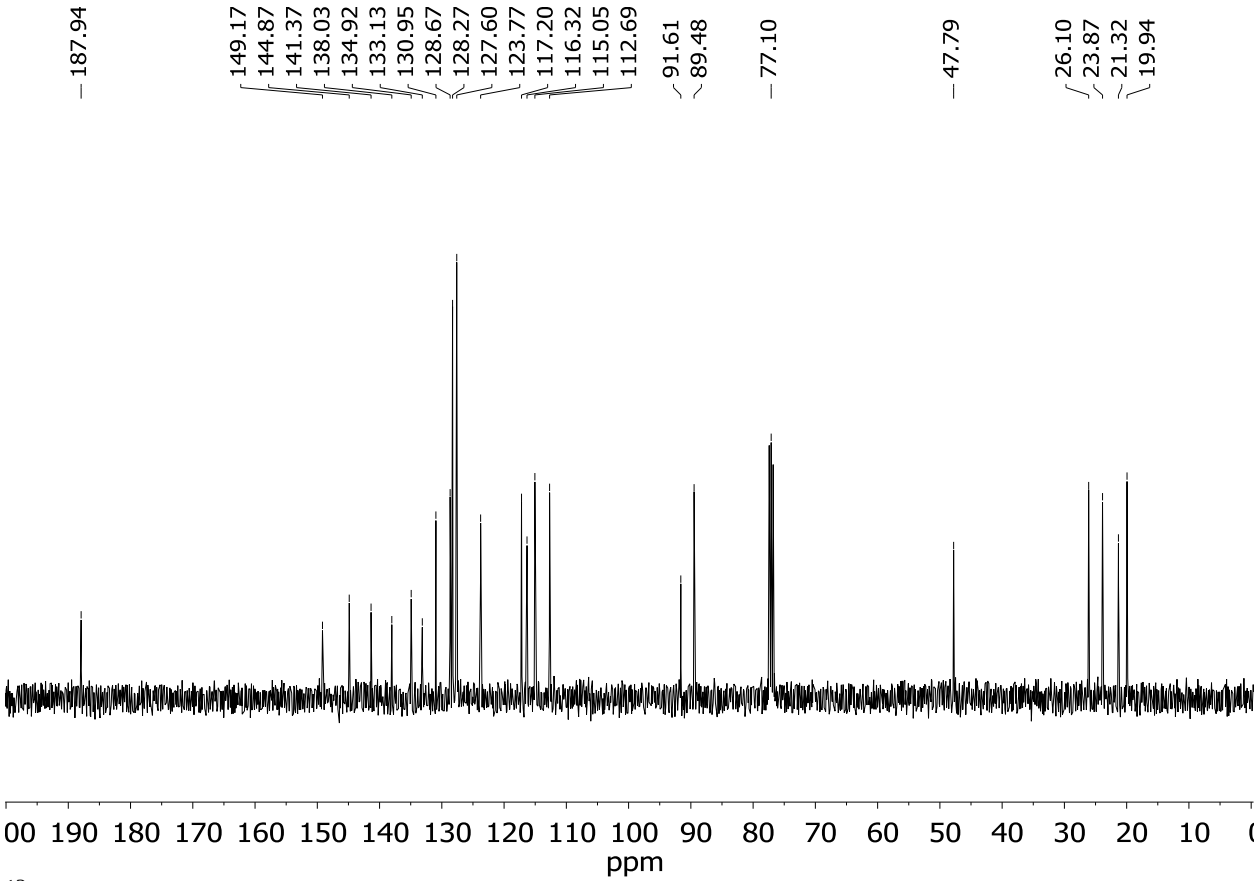
^{1}H NMR Spectrum of **3a** (400.13 MHz, $CDCl_3$)



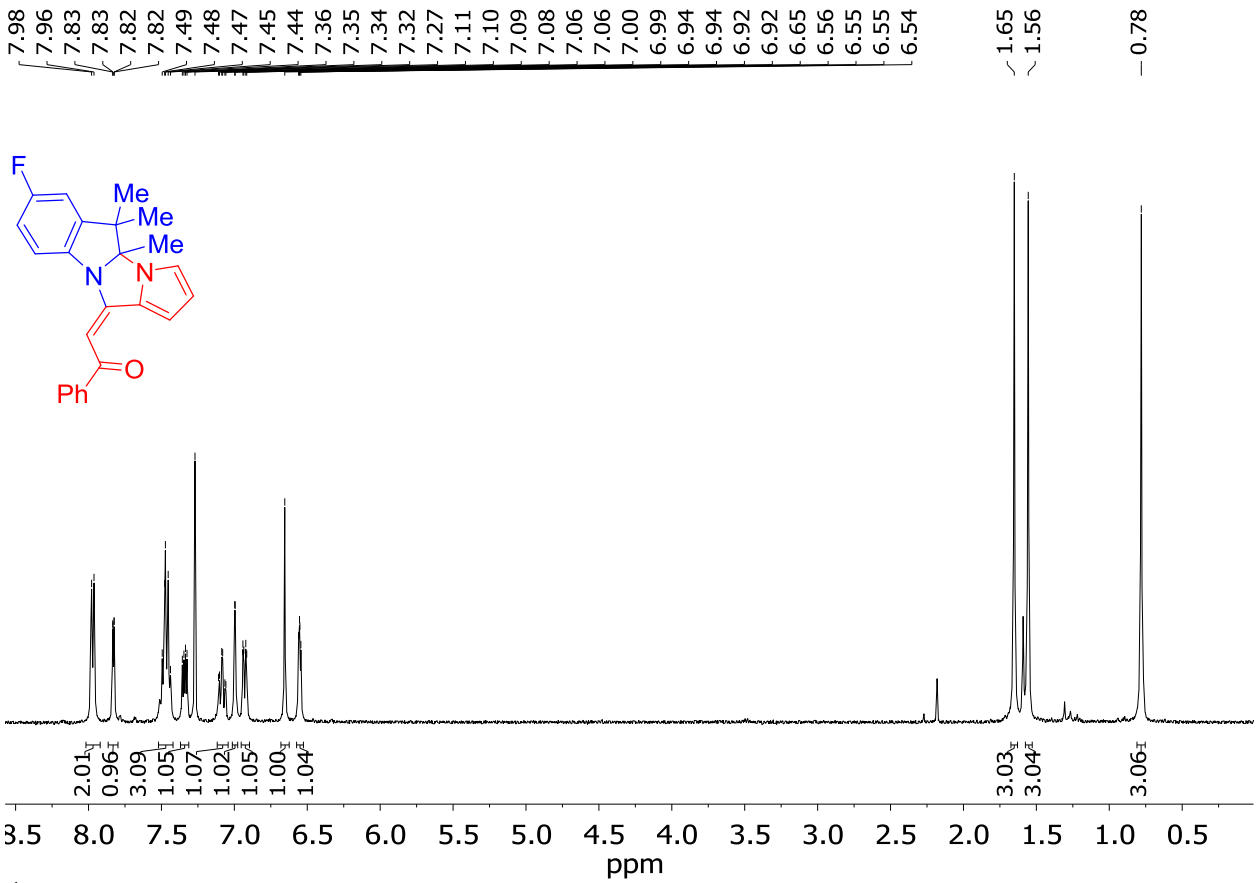
^{13}C NMR Spectrum of **3a** (100.62 MHz, $CDCl_3$)



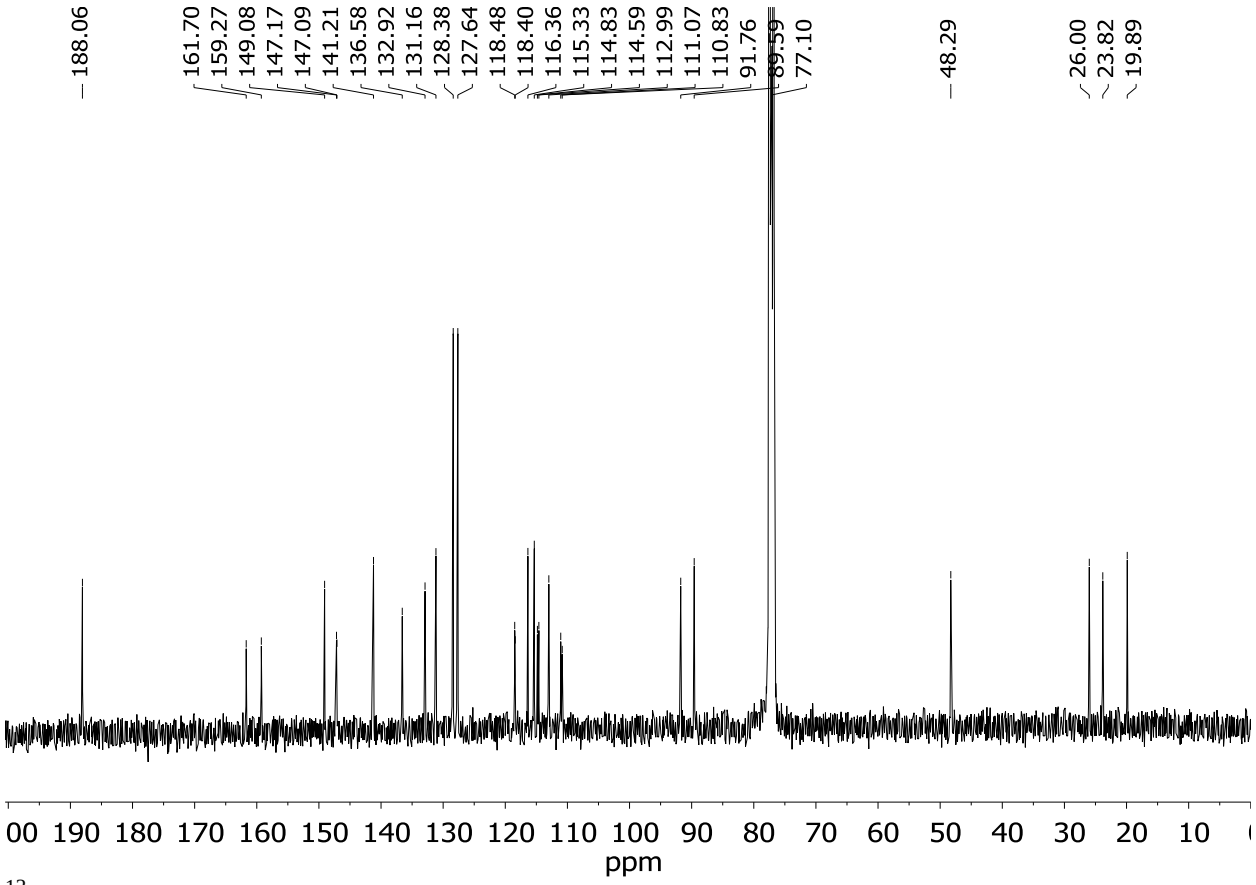
^{1}H NMR Spectrum of **3b** (400.13 MHz, $CDCl_3$)



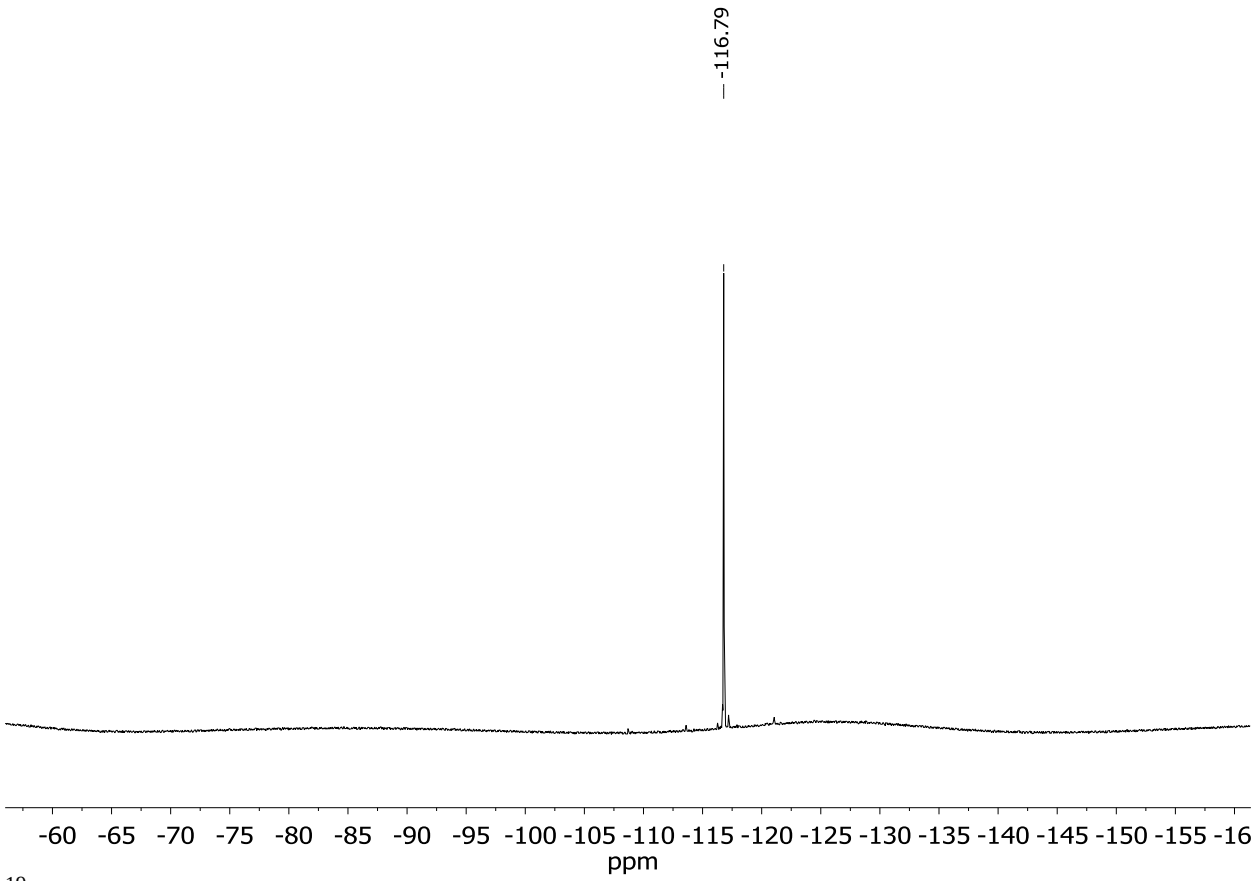
^{13}C NMR Spectrum of **3b** (100.62 MHz, $CDCl_3$)



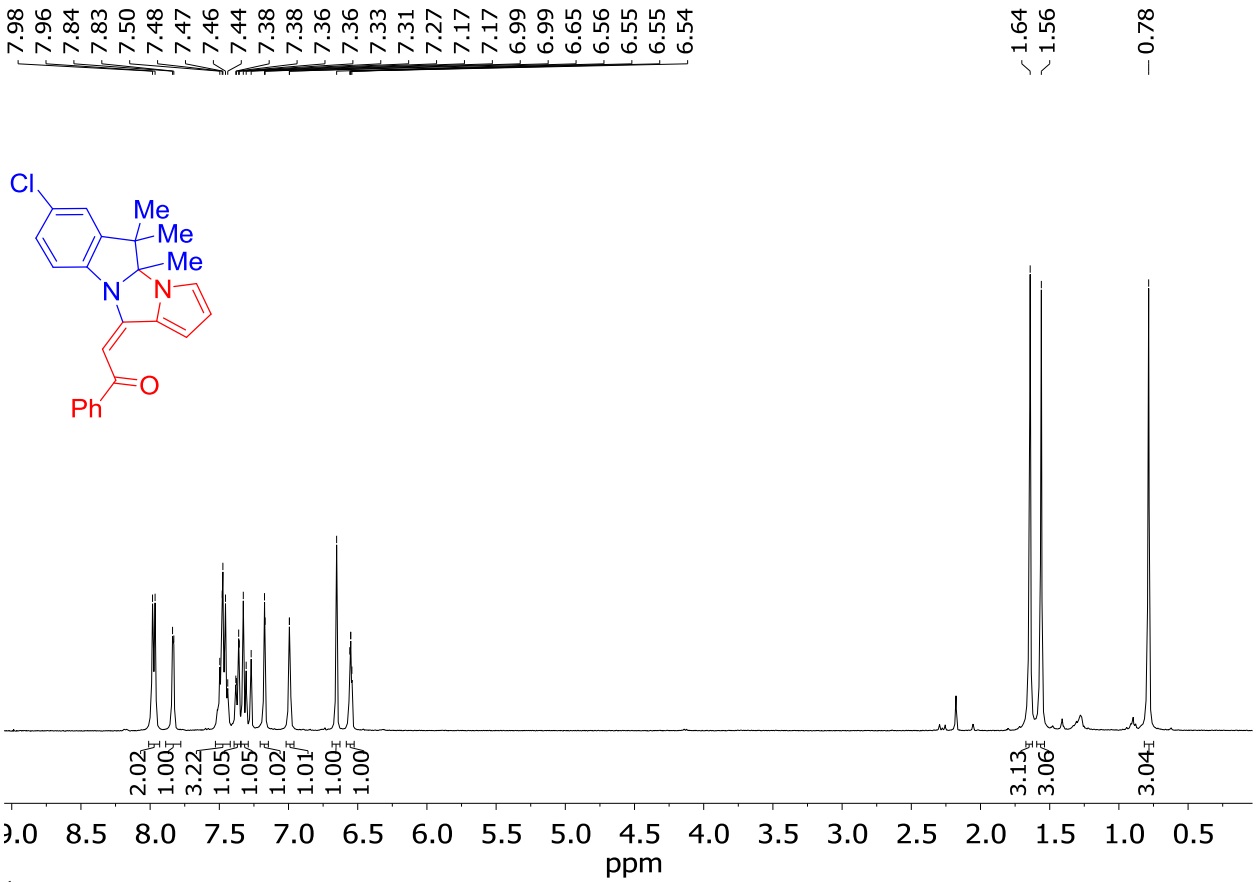
^{1}H NMR Spectrum of **3c** (100.62 MHz, $CDCl_3$)



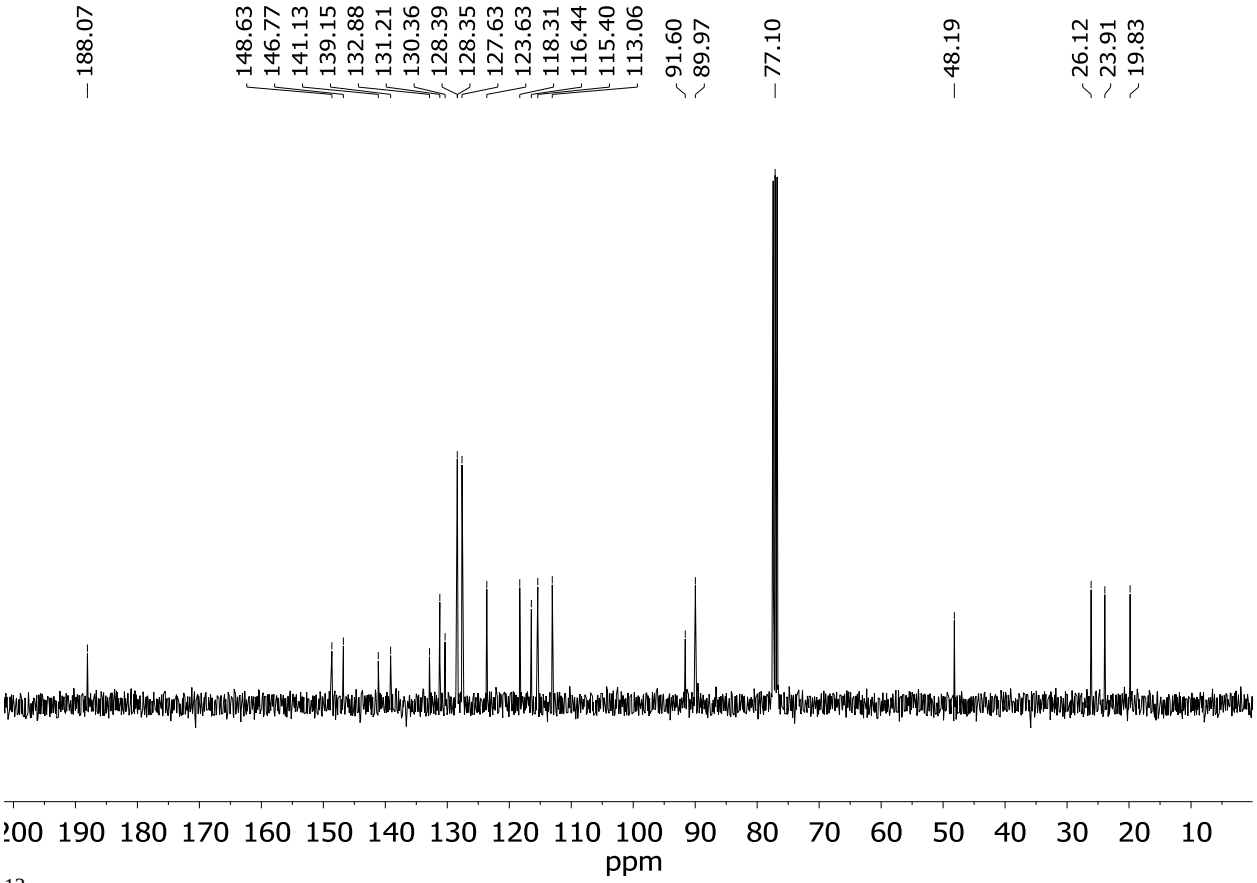
^{13}C NMR Spectrum of **3c** (100.62 MHz, $CDCl_3$)



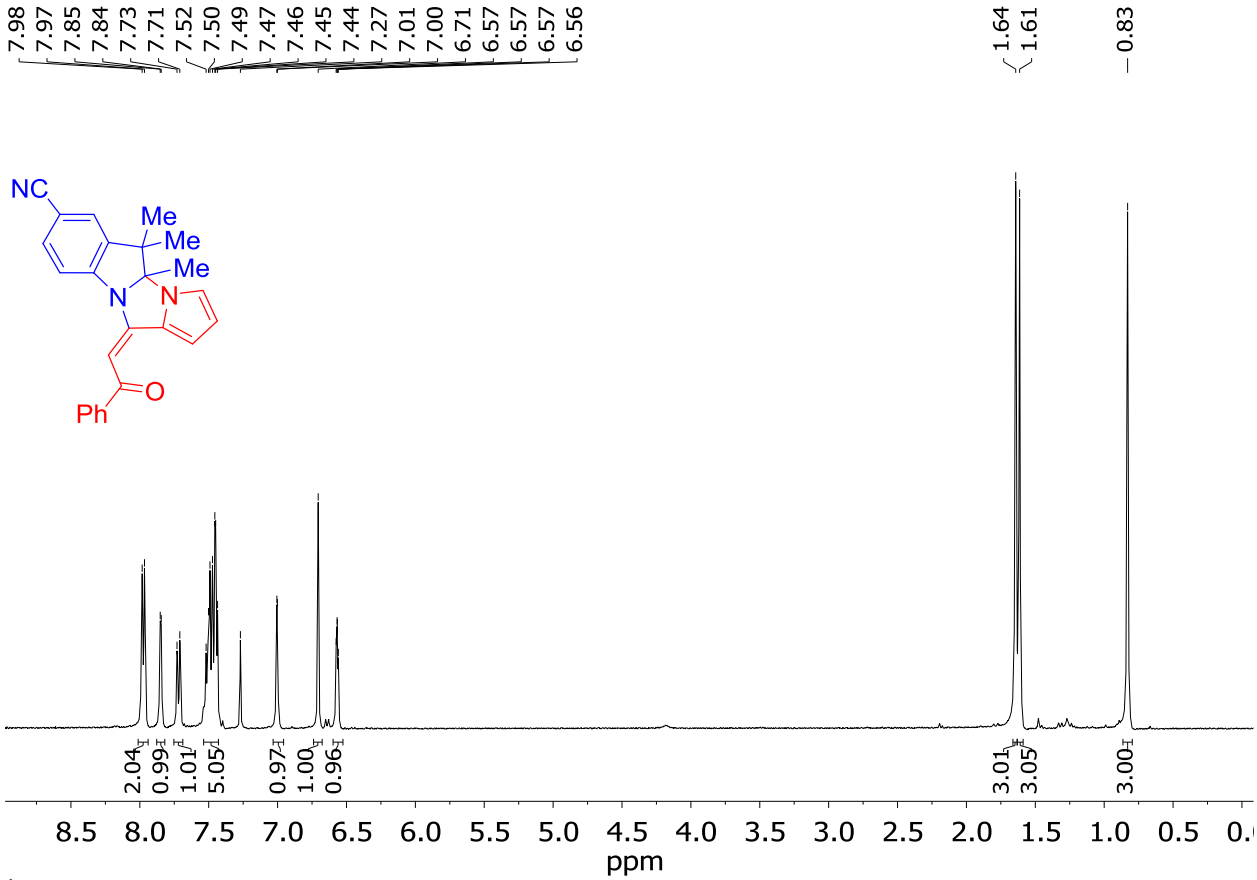
^{19}F NMR Spectrum of **3c** (376.50 MHz, $CDCl_3$)



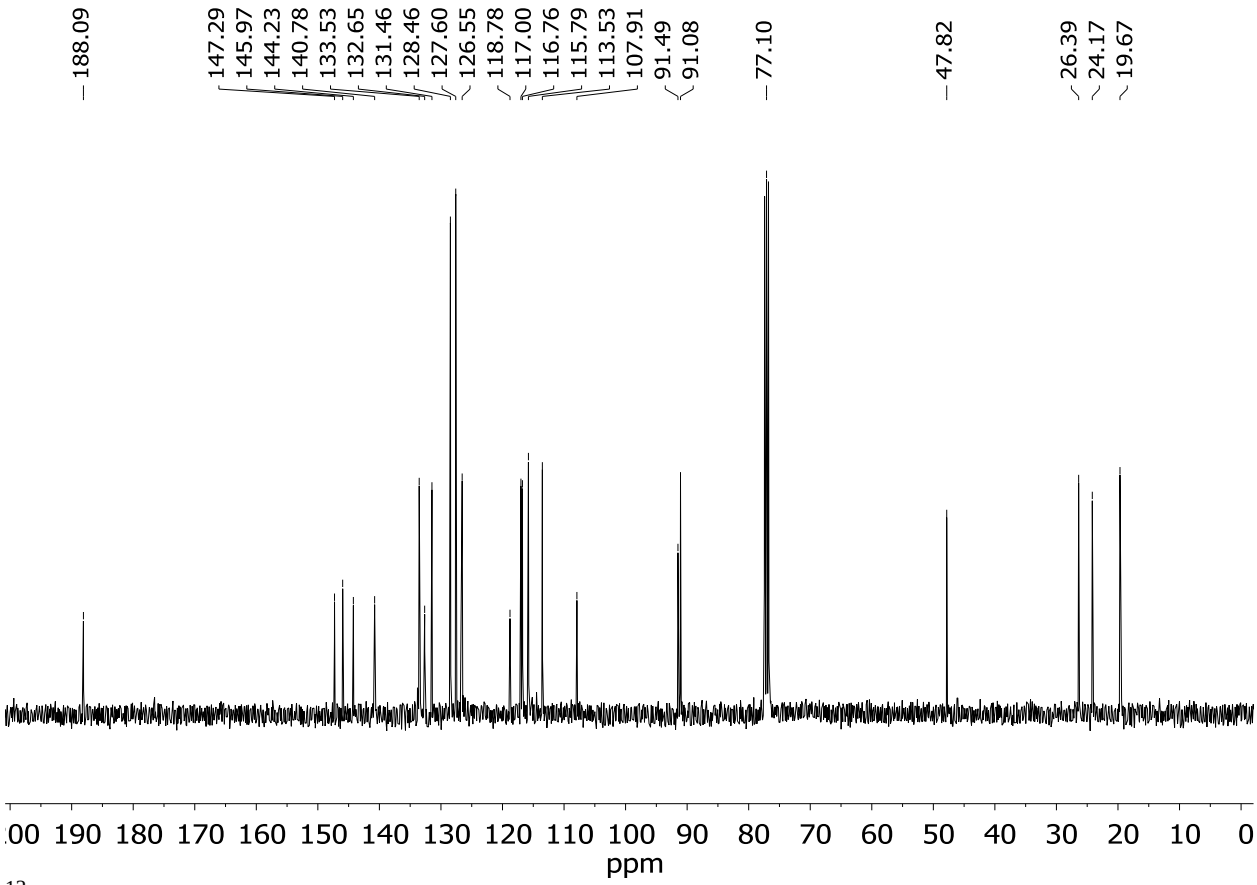
^{1}H NMR Spectrum of **3d** (400.13 MHz, $CDCl_3$)



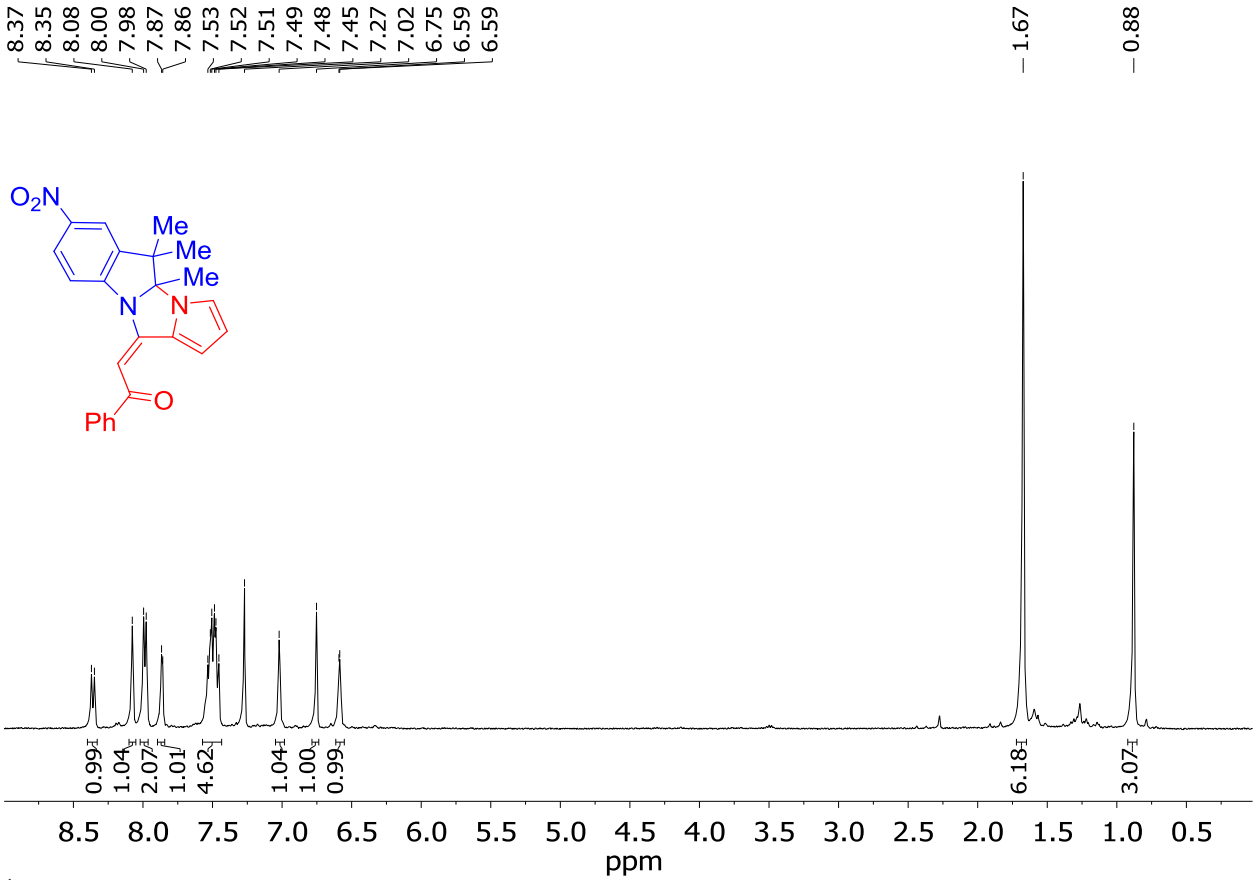
^{13}C NMR Spectrum of **3d** (100.62 MHz, $CDCl_3$)



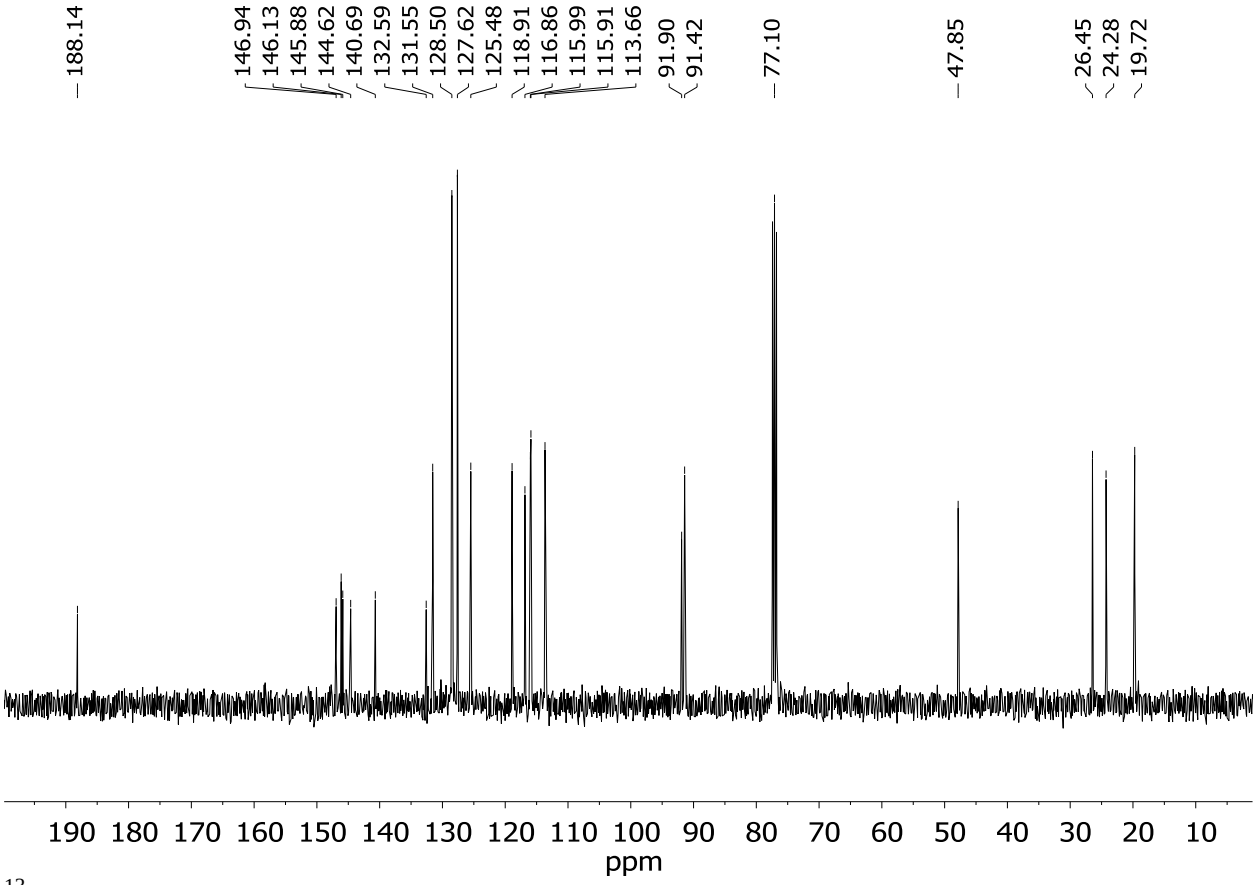
^{1}H NMR Spectrum of **3e** (400.13 MHz, $CDCl_3$)



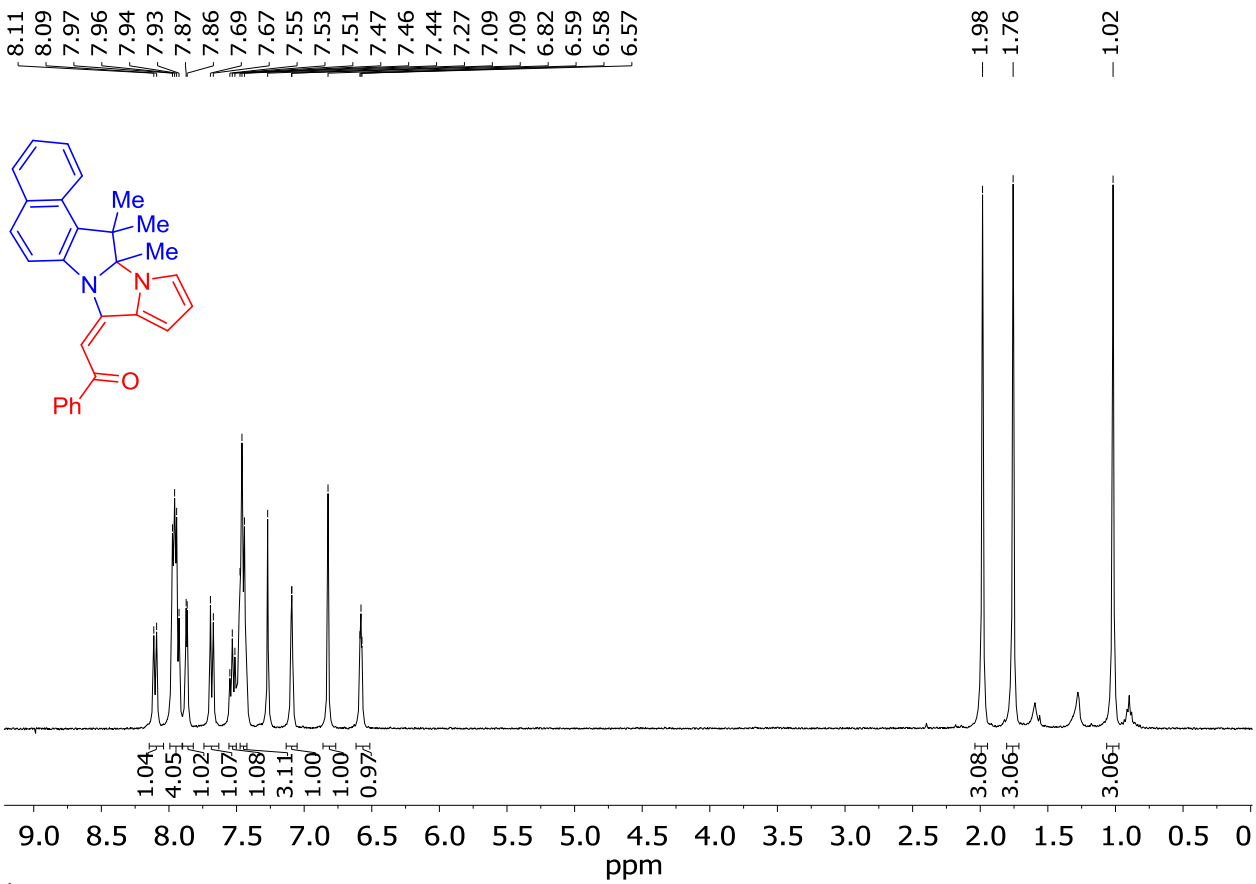
^{13}C NMR Spectrum of **3e** (100.62 MHz, $CDCl_3$)



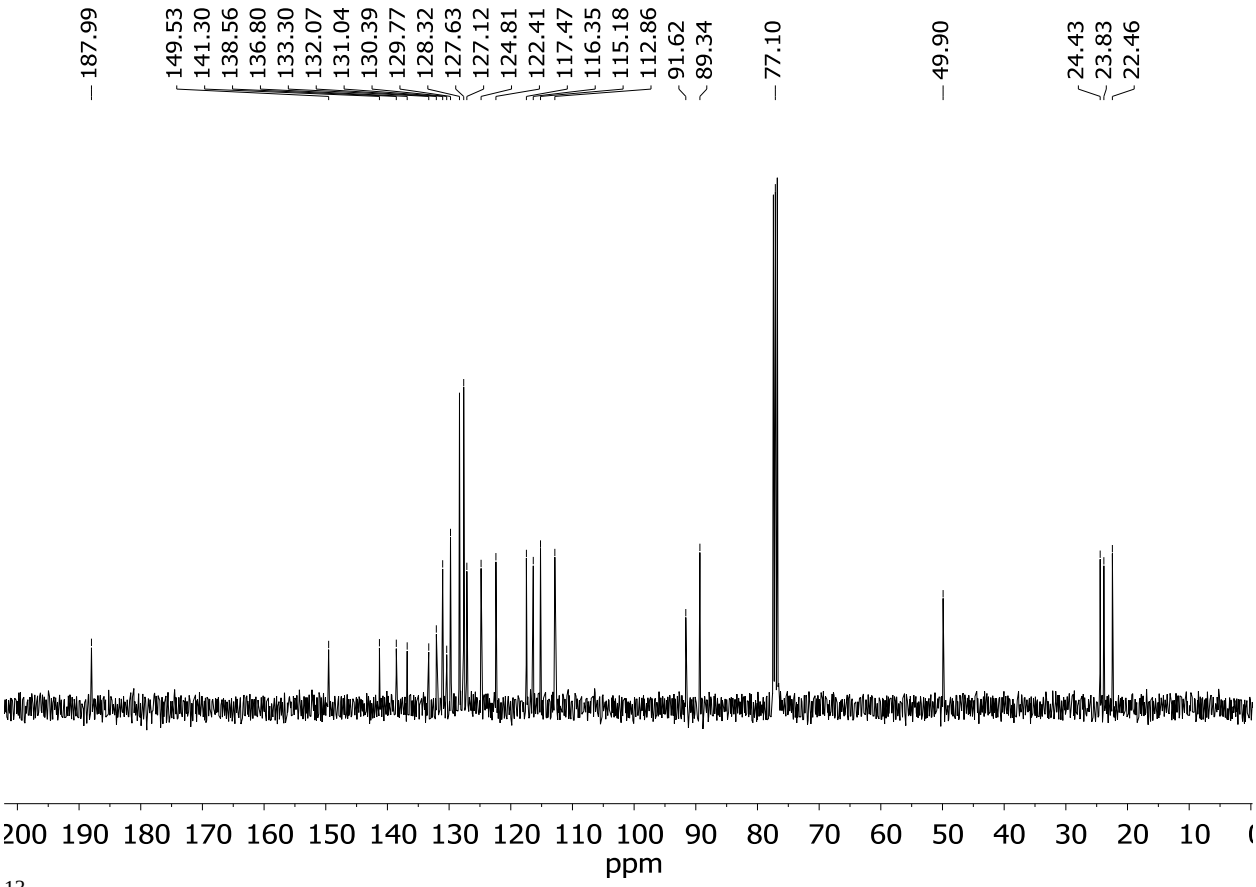
^{1}H NMR Spectrum of **3f** (400.13 MHz, $CDCl_3$)



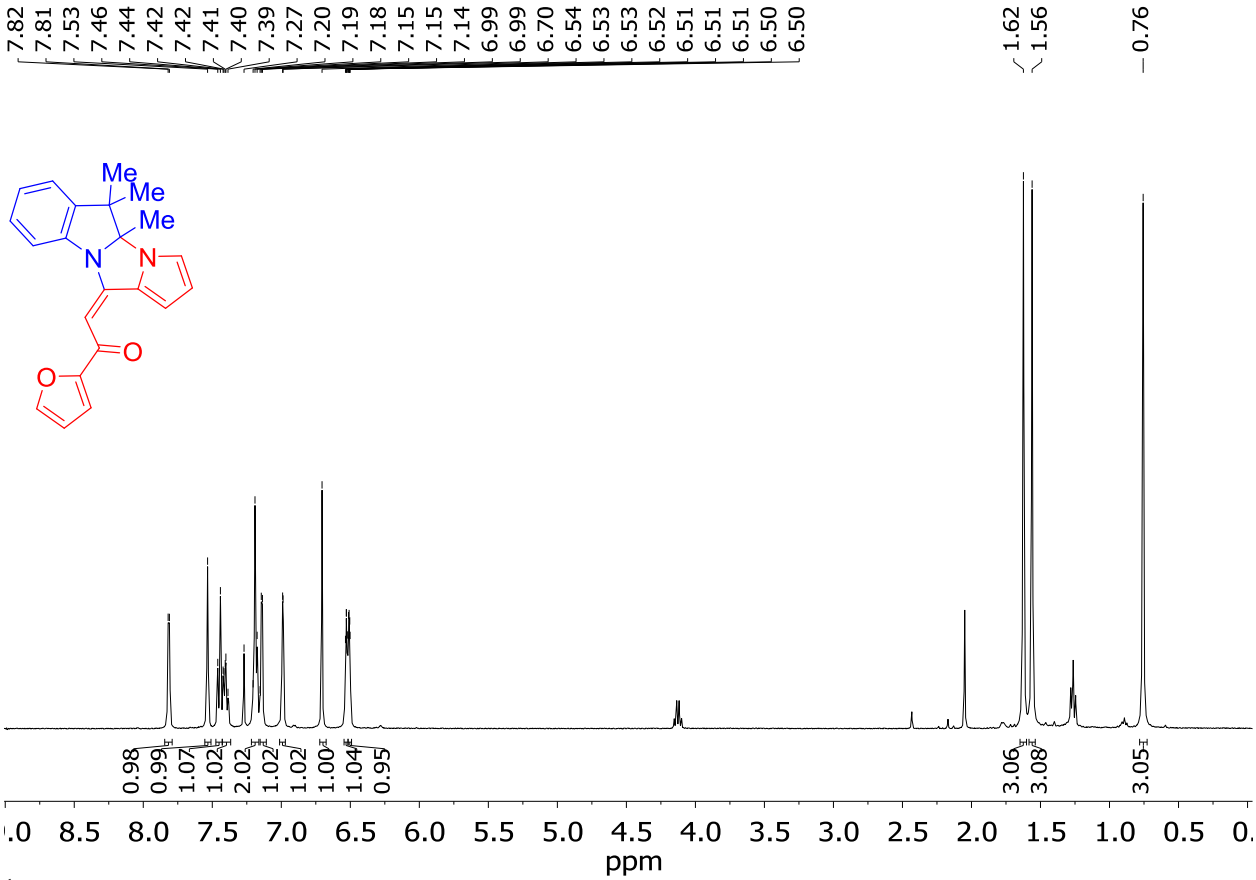
^{13}C NMR Spectrum of **3f** (100.62 MHz, $CDCl_3$)



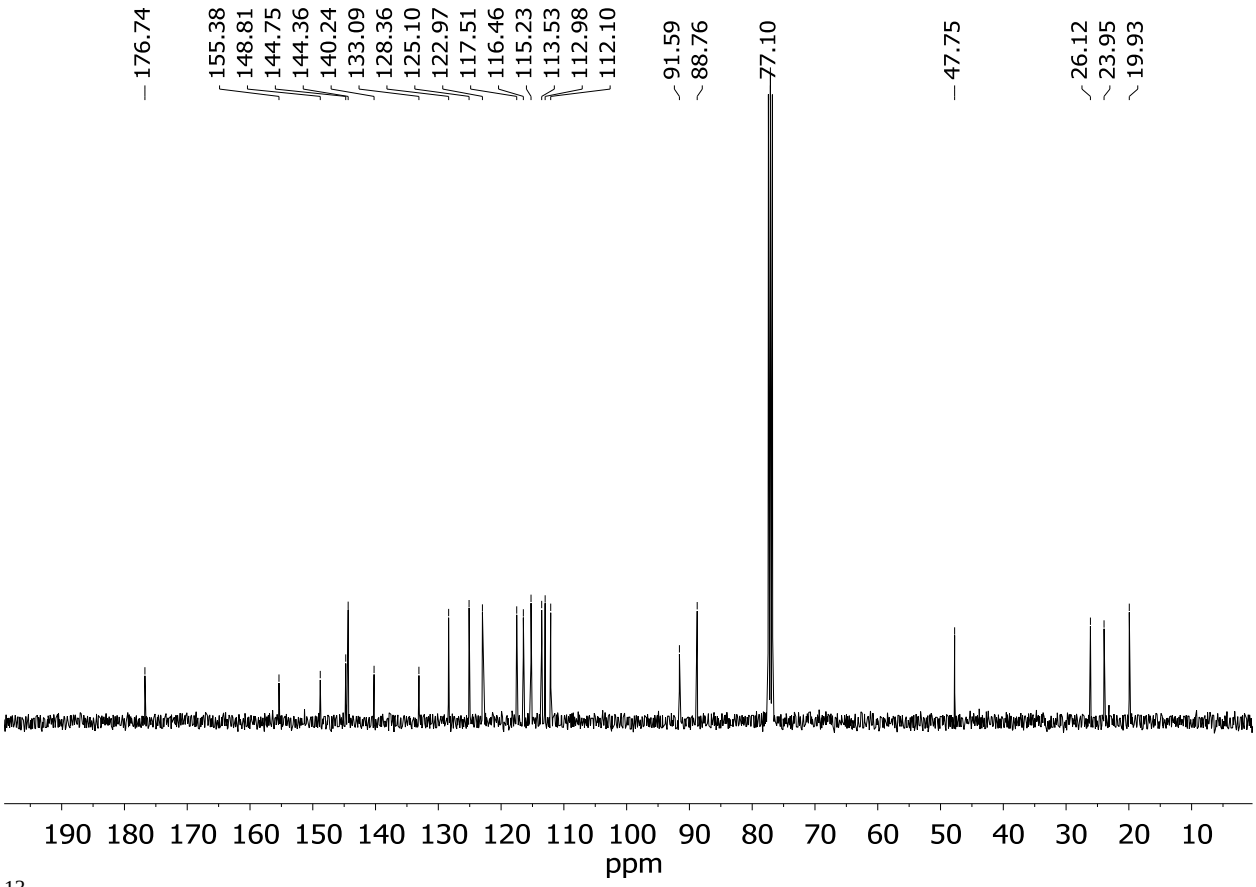
^{1}H NMR Spectrum of **3h** (400.13 MHz, $CDCl_3$)



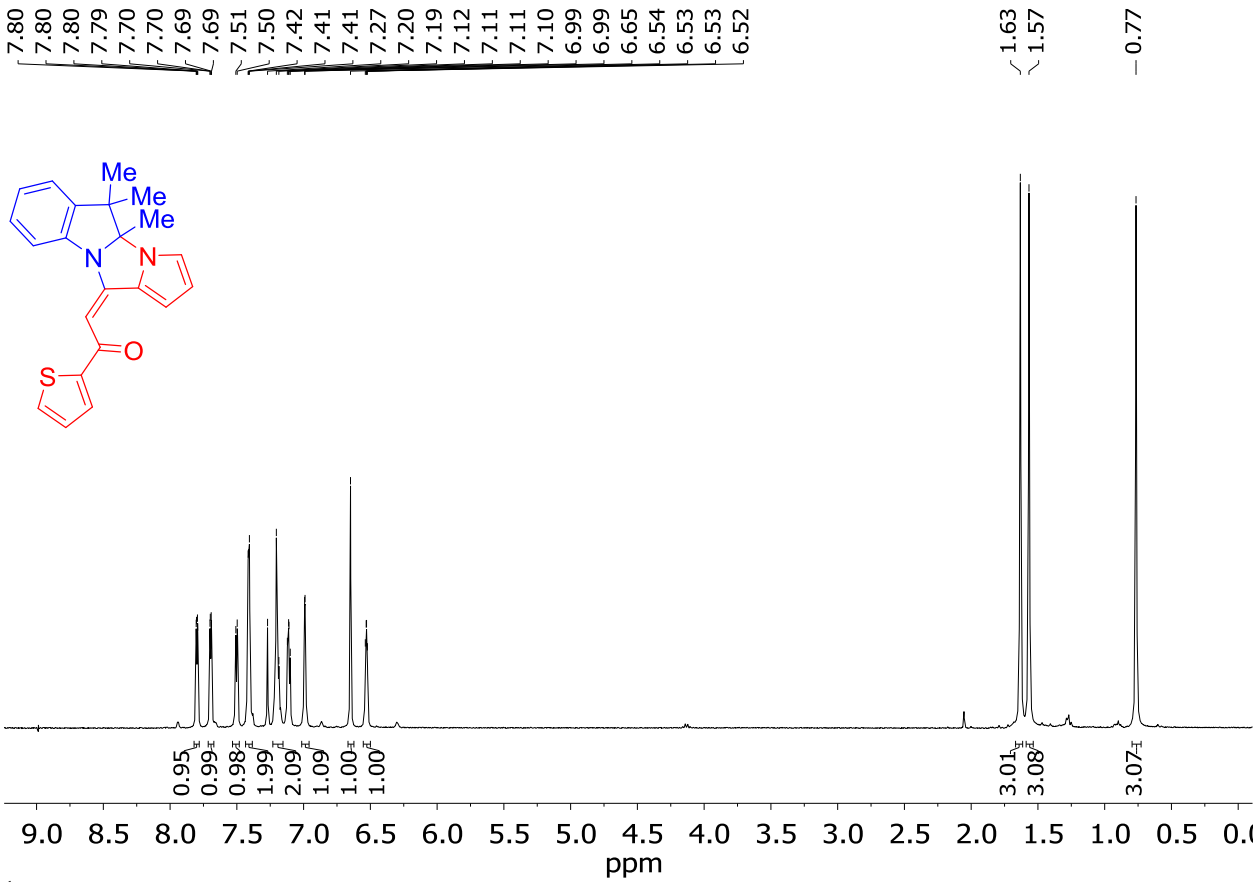
^{13}C NMR Spectrum of **3h** (100.62 MHz, $CDCl_3$)



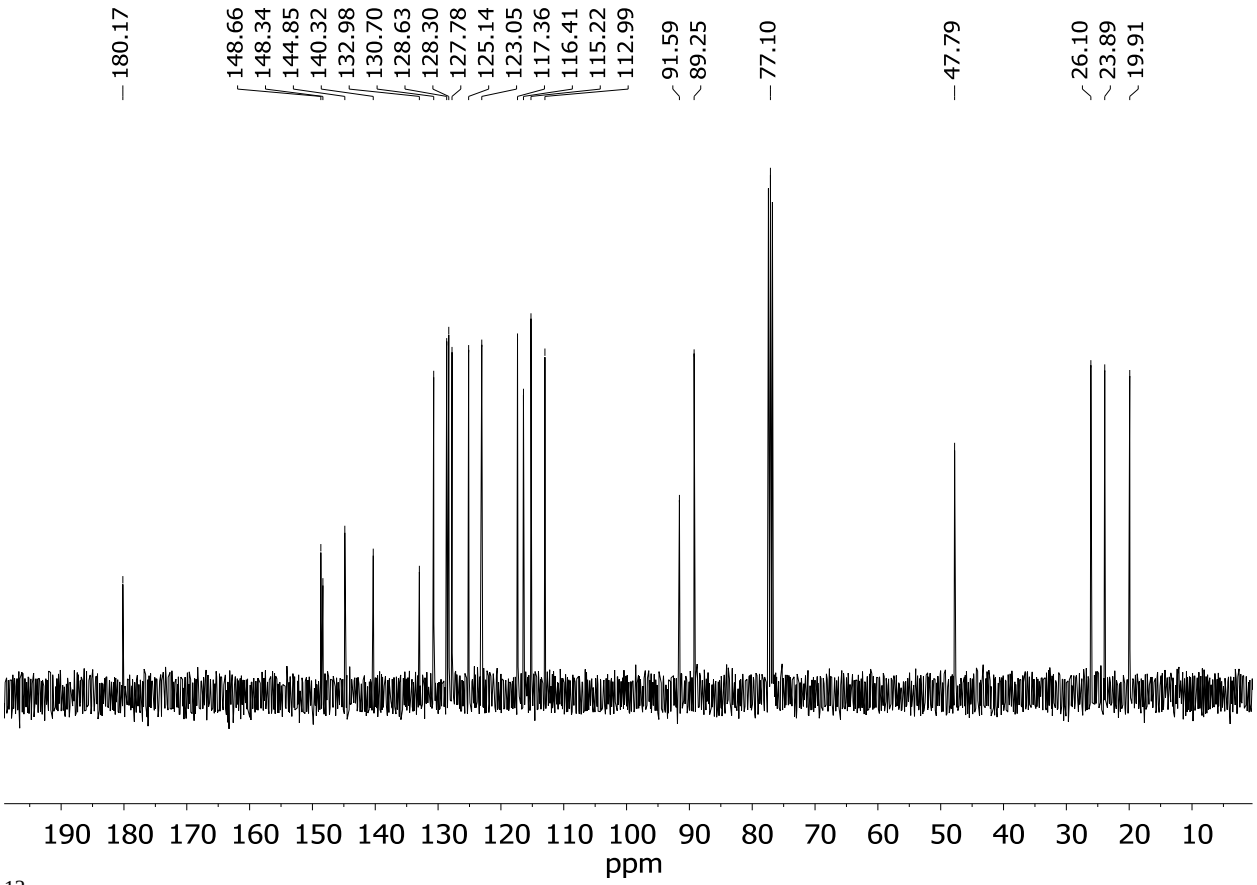
^{1}H NMR Spectrum of **3i** (400.13 MHz, $CDCl_3$)



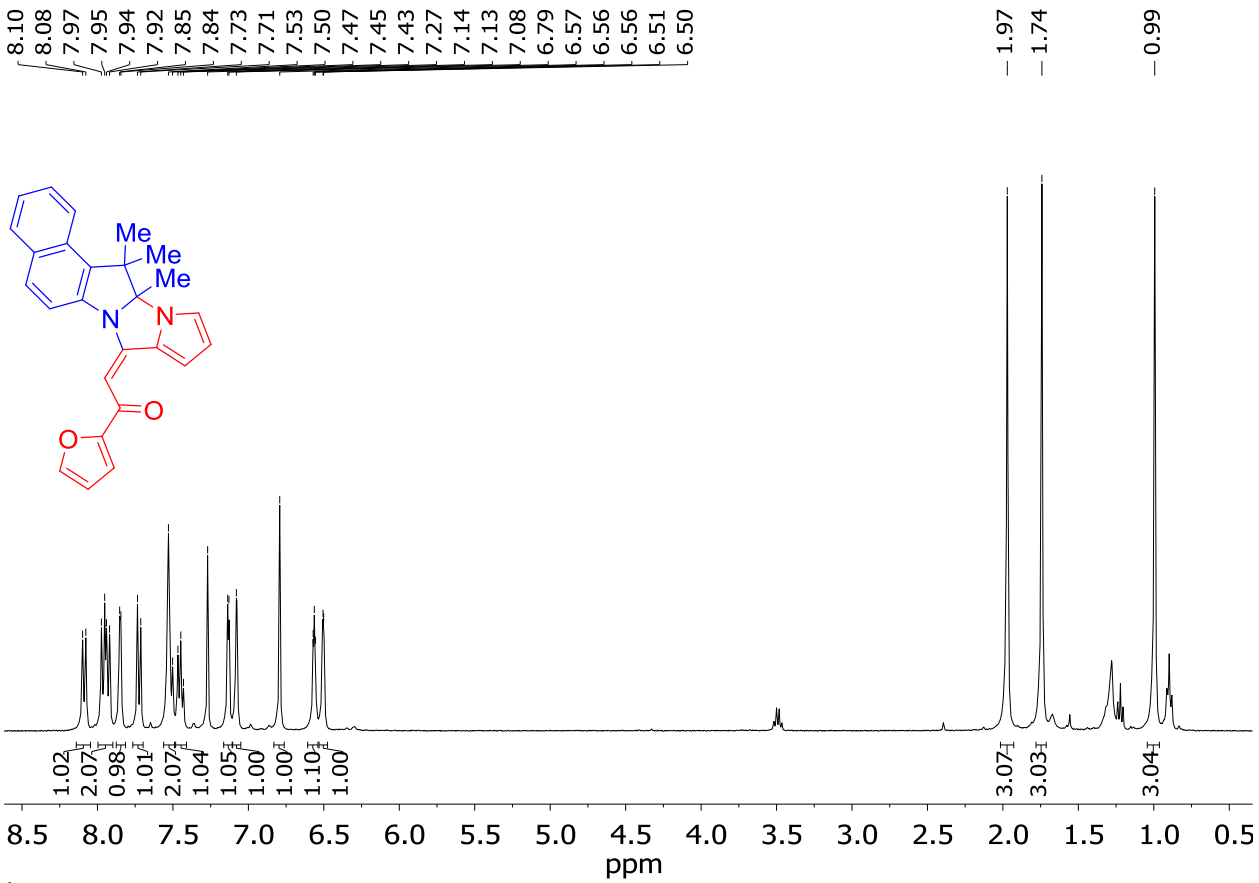
^{13}C NMR Spectrum of **3i** (100.62 MHz, $CDCl_3$)



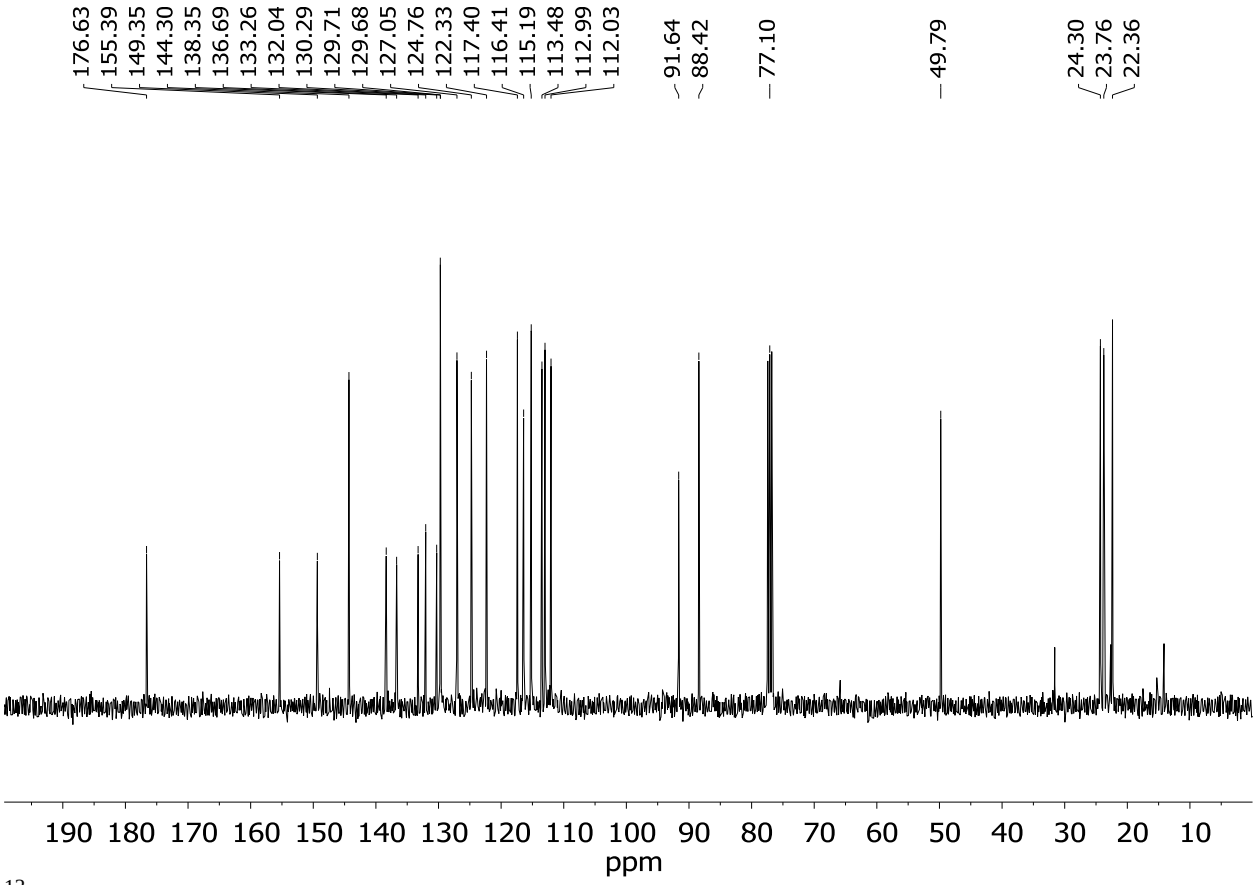
^{1}H NMR Spectrum of **3j** (400.13 MHz, $CDCl_3$)



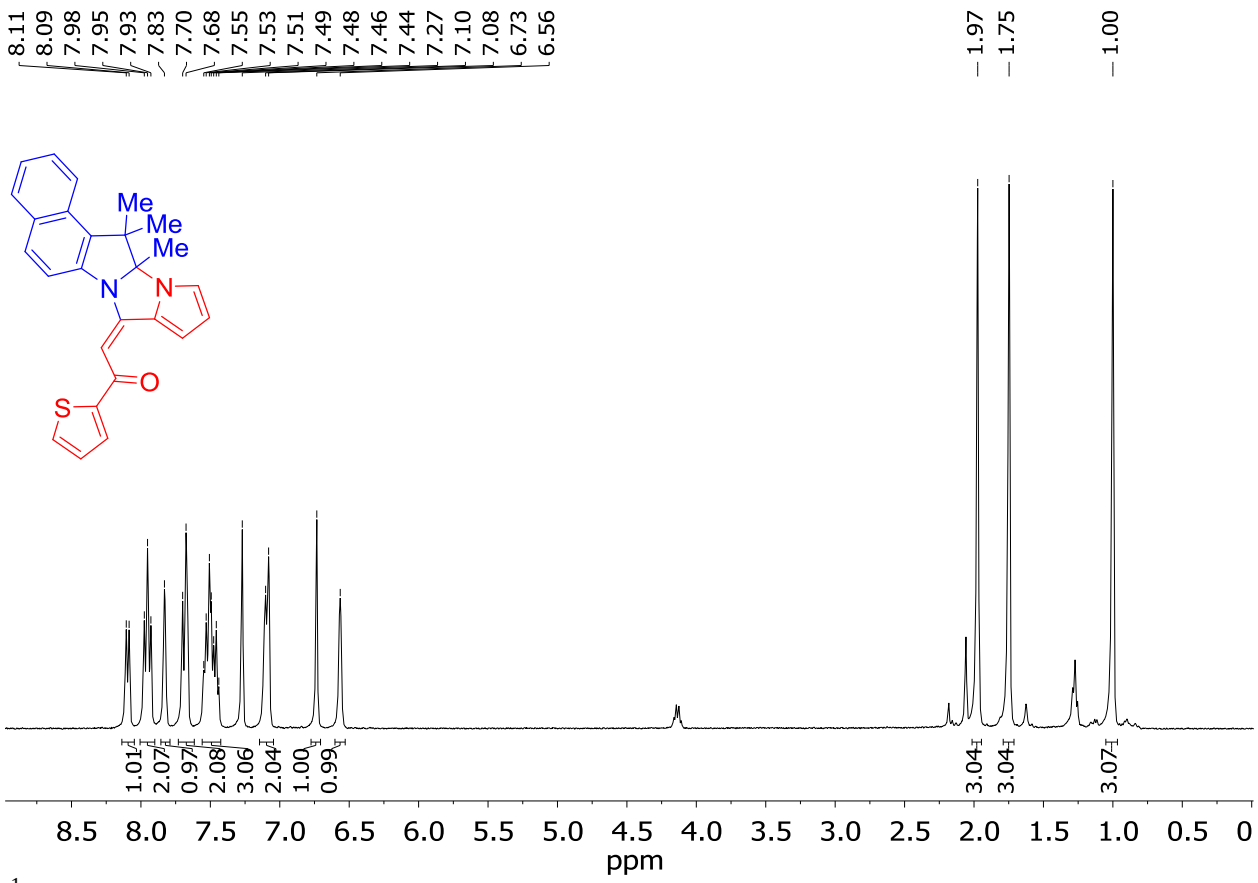
^{13}C NMR Spectrum of **3j** (100.62 MHz, $CDCl_3$)



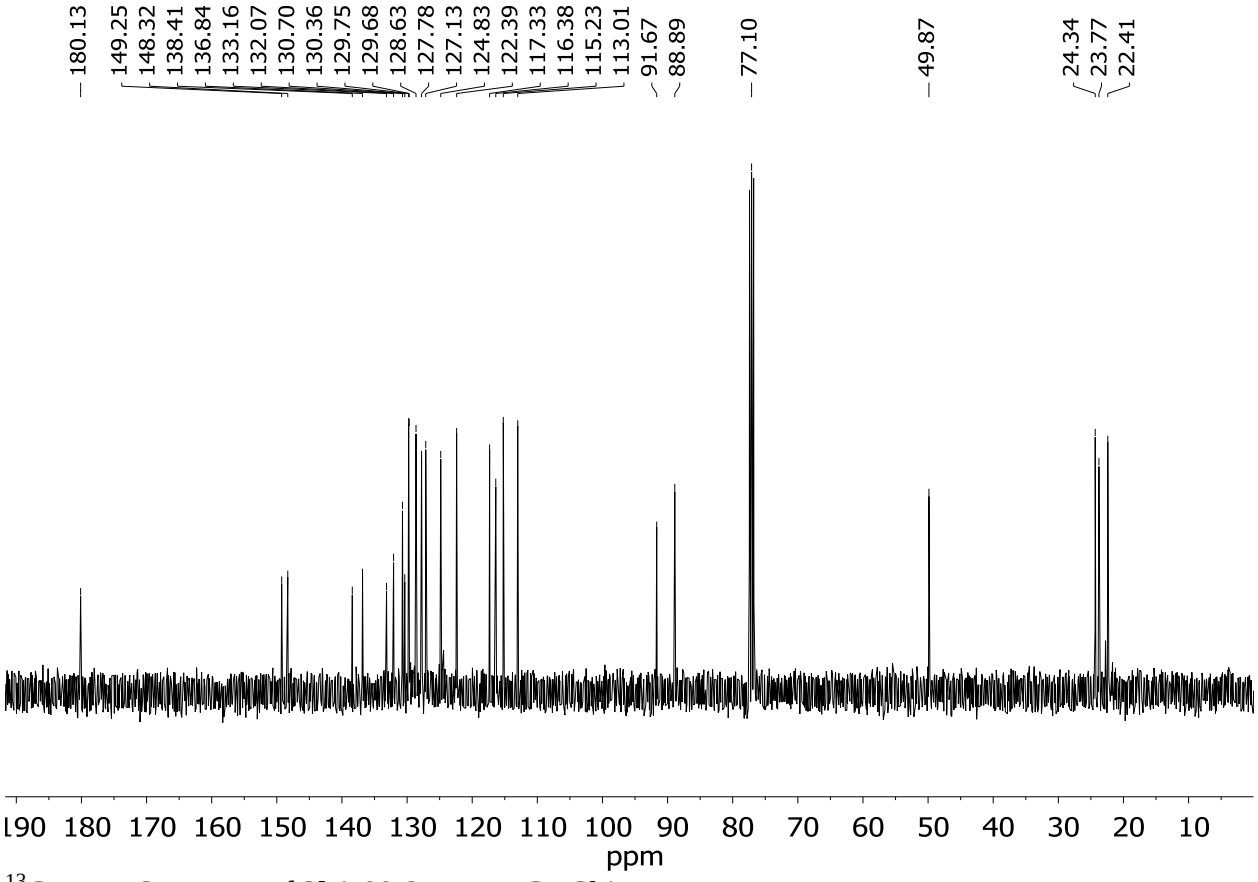
^{1}H NMR Spectrum of **3k** (400.13 MHz, $CDCl_3$)



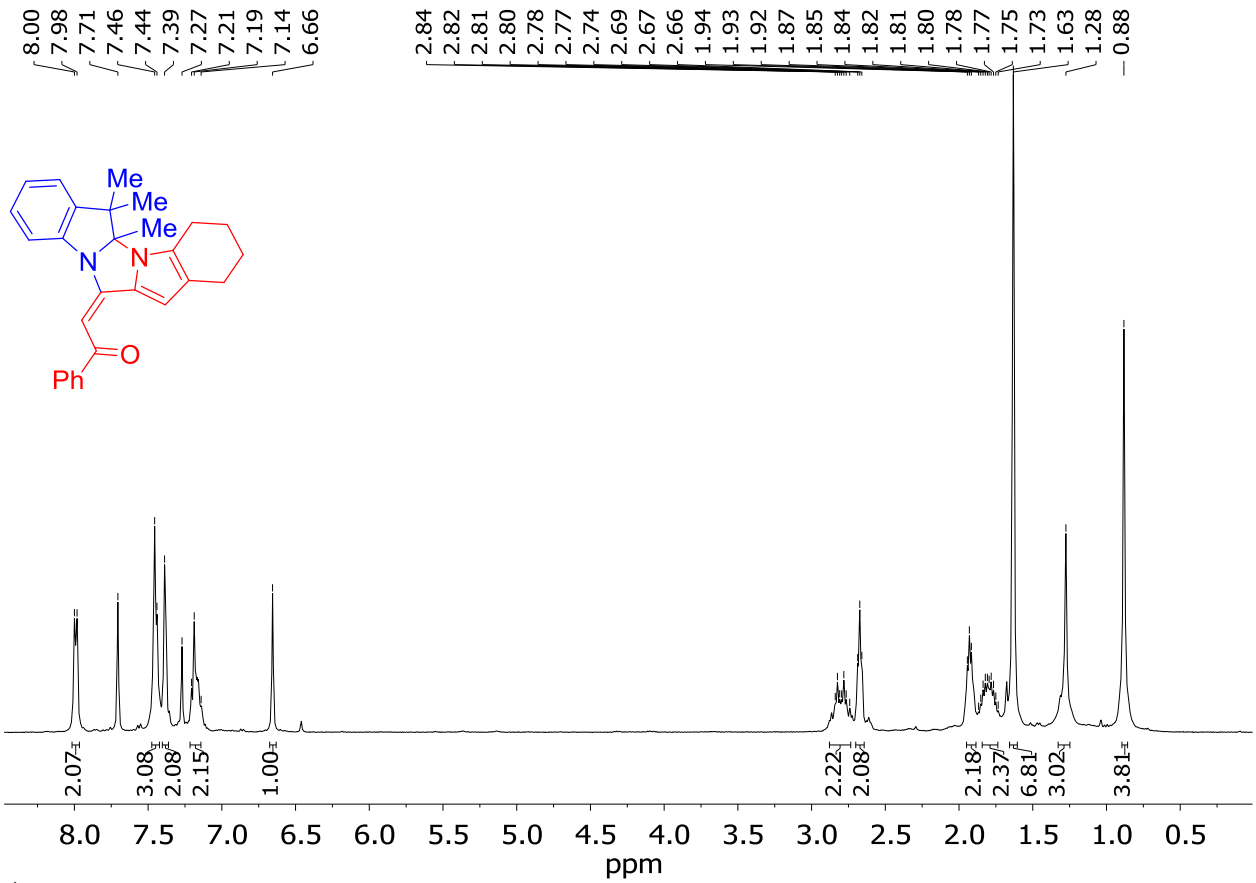
^{13}C NMR Spectrum of **3k** (100.62 MHz, $CDCl_3$)



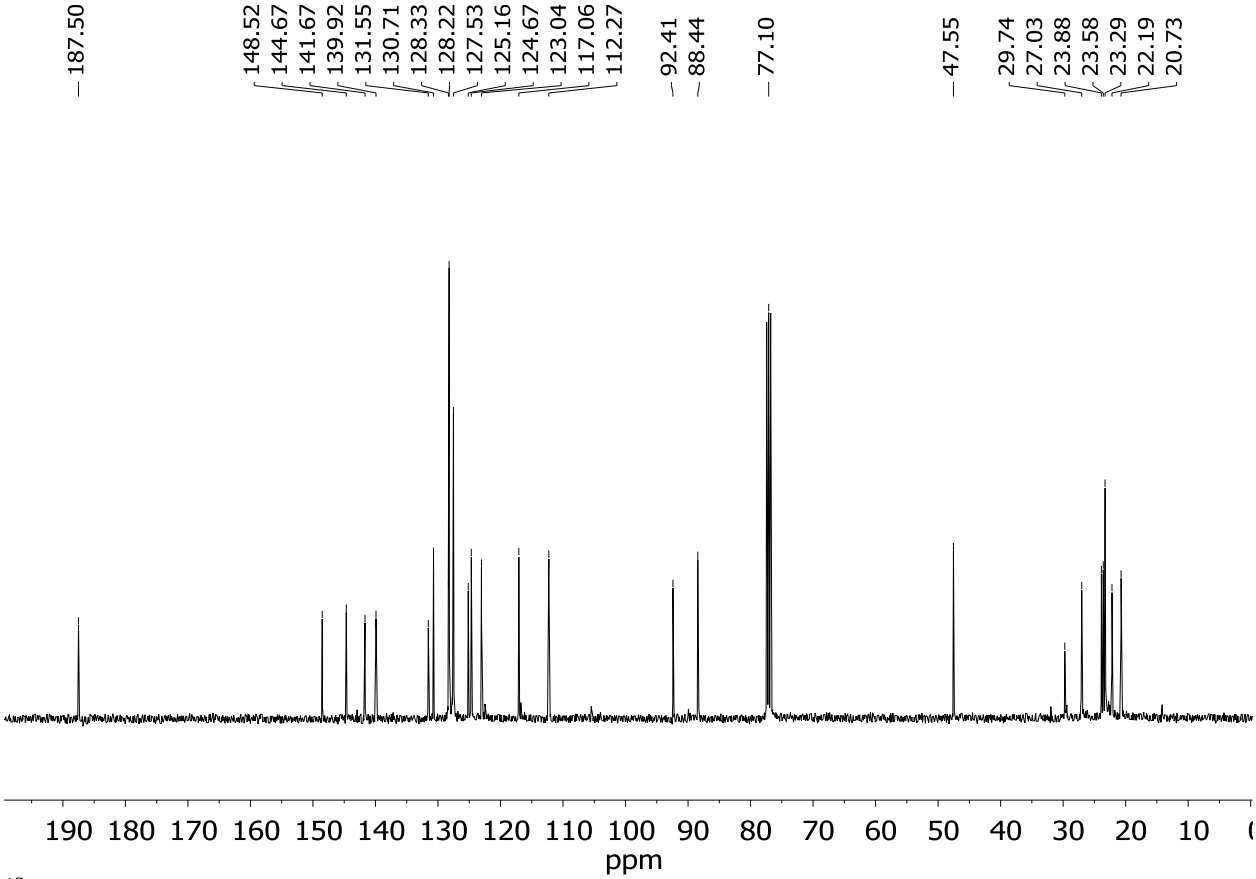
^{1}H NMR Spectrum of **3l** (400.13 MHz, $CDCl_3$)



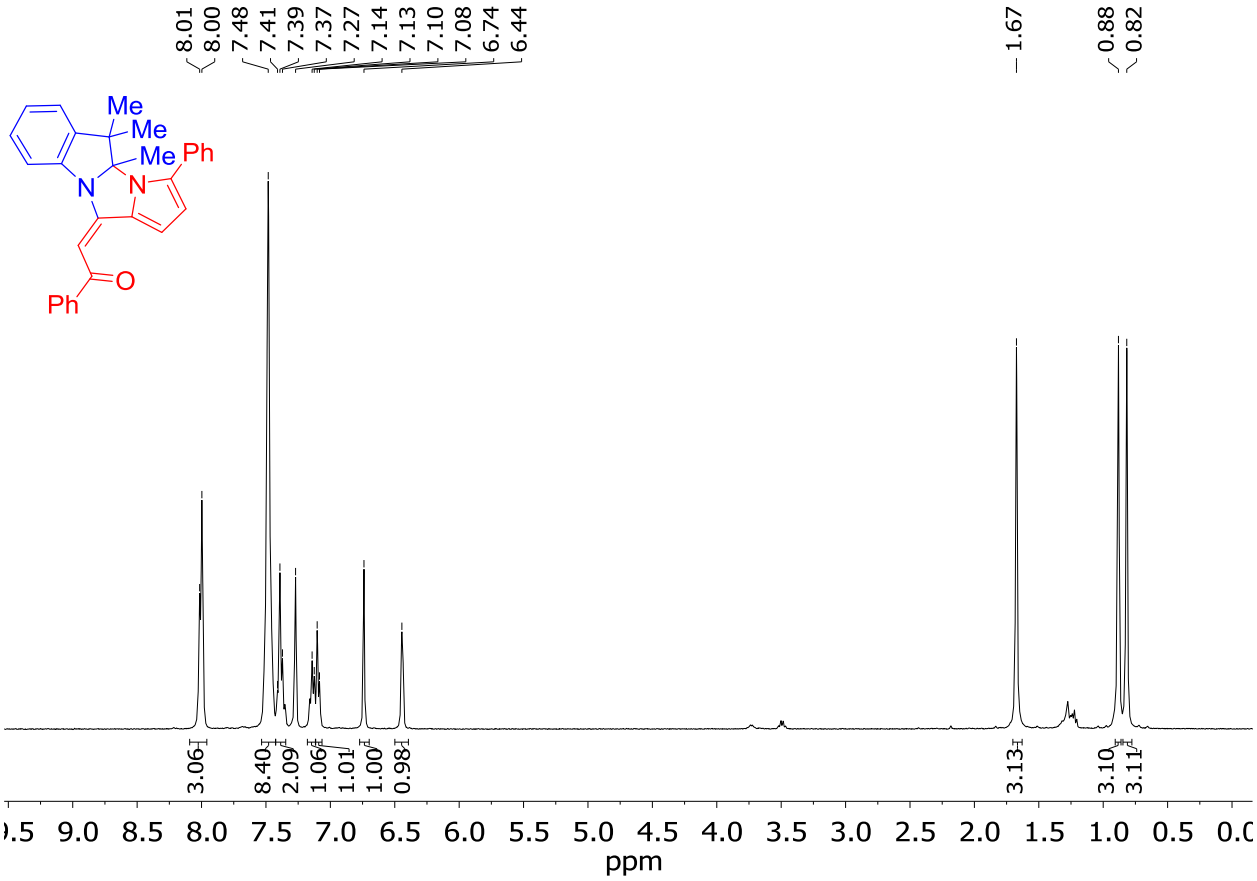
^{13}C NMR Spectrum of **3l** (100.62 MHz, $CDCl_3$)



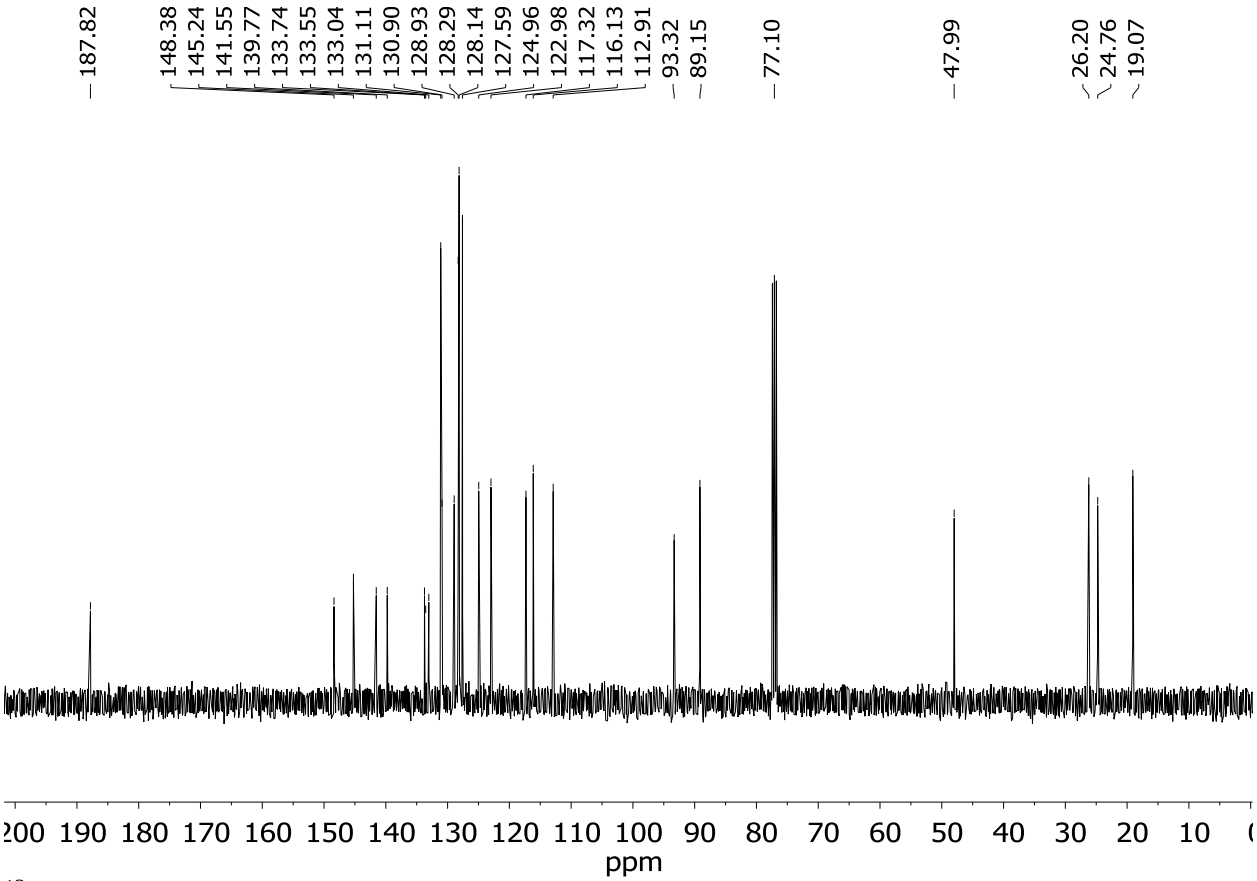
^{1}H NMR Spectrum of **3m** (400.13 MHz, $CDCl_3$)



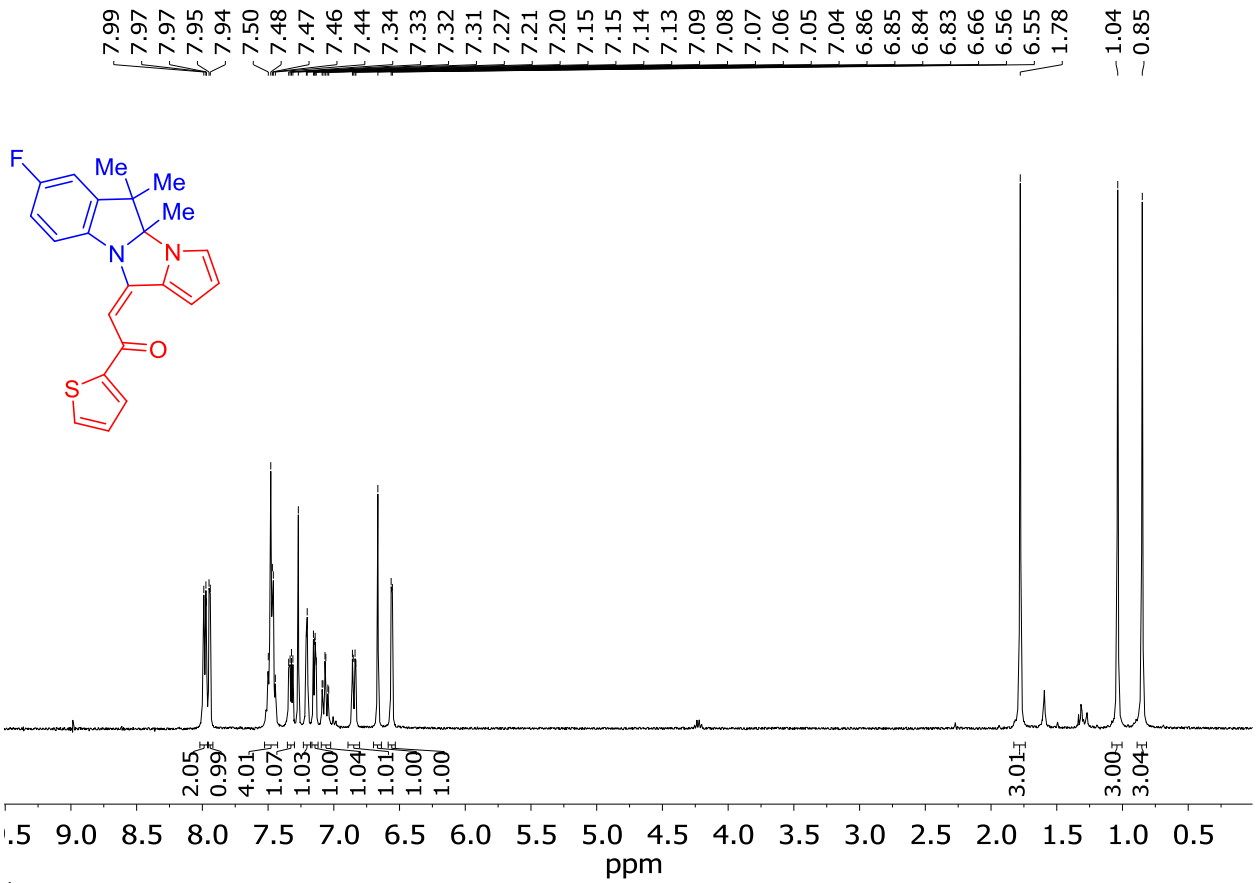
^{13}C NMR Spectrum of **3m** (100.62 MHz, $CDCl_3$)



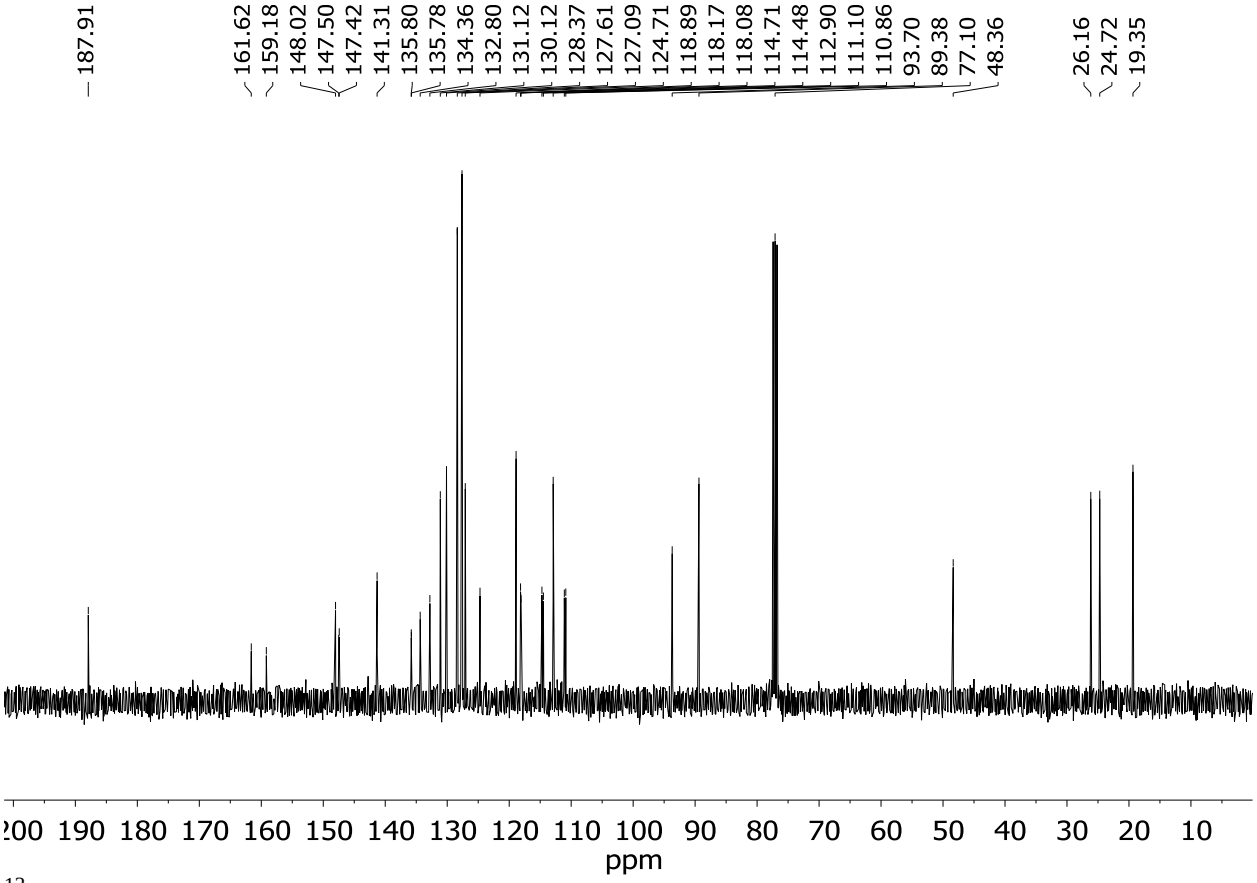
^{1}H NMR Spectrum of **3n** (400.13 MHz, $CDCl_3$)



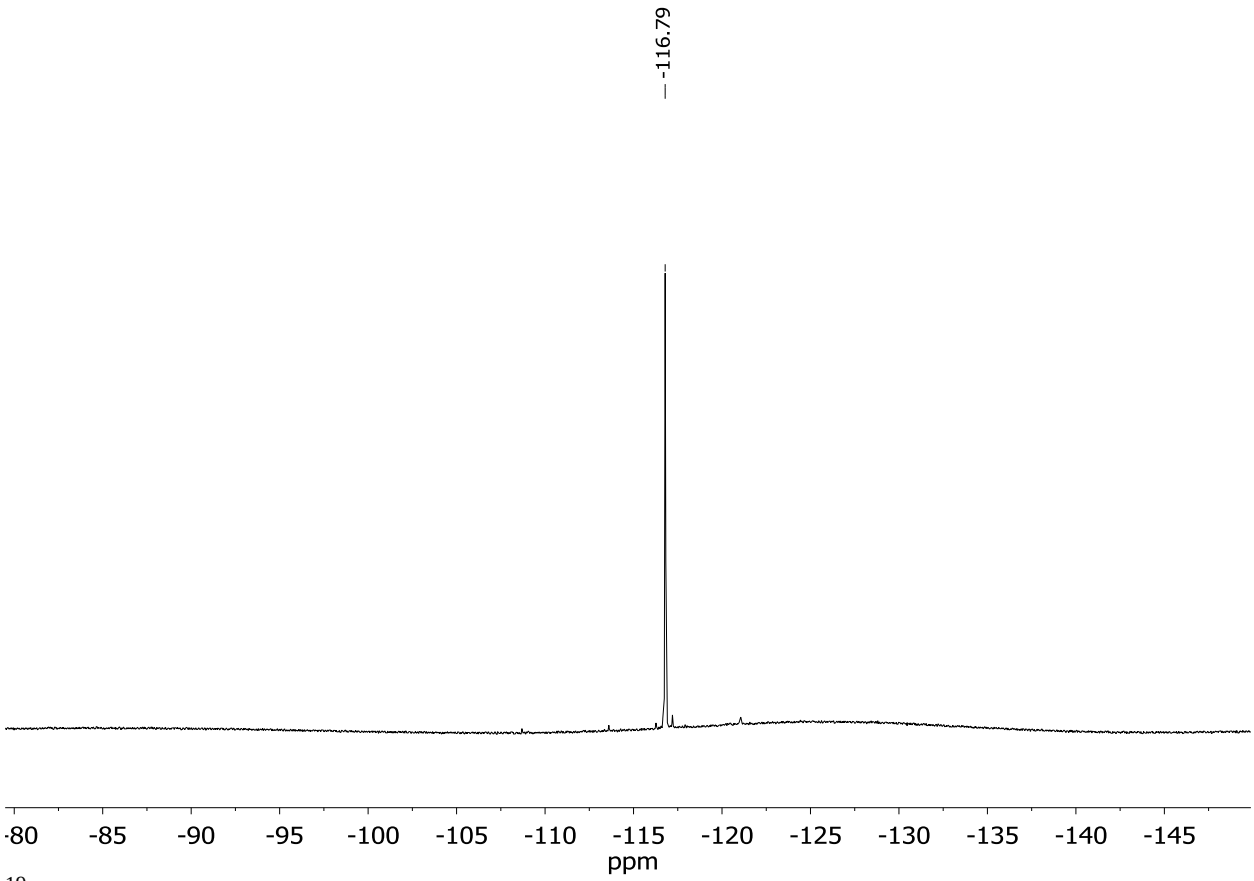
^{13}C NMR Spectrum of **3n** (100.62 MHz, $CDCl_3$)



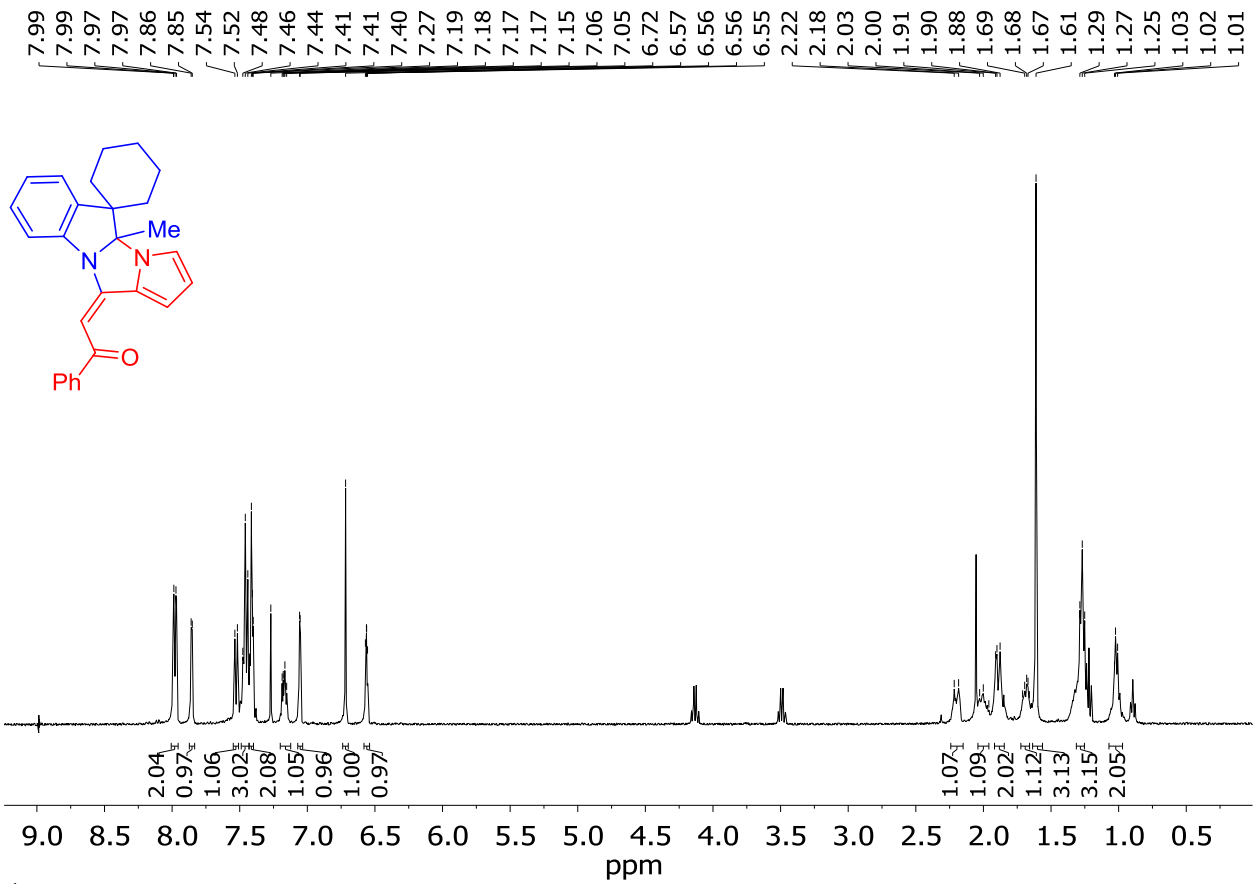
^{1}H NMR Spectrum of **3o** (400.13 MHz, $CDCl_3$)



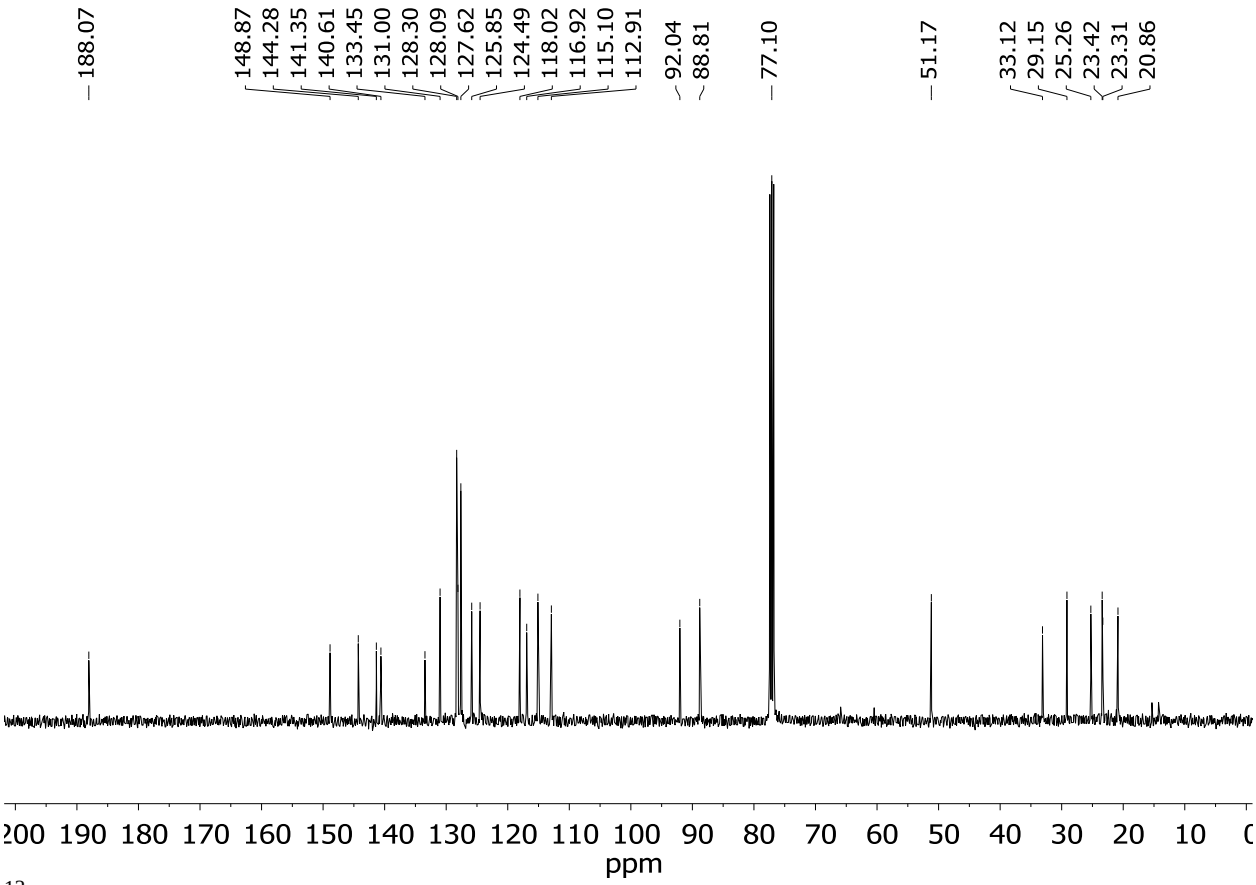
^{13}C NMR Spectrum of **3o** (100.62 MHz, $CDCl_3$)



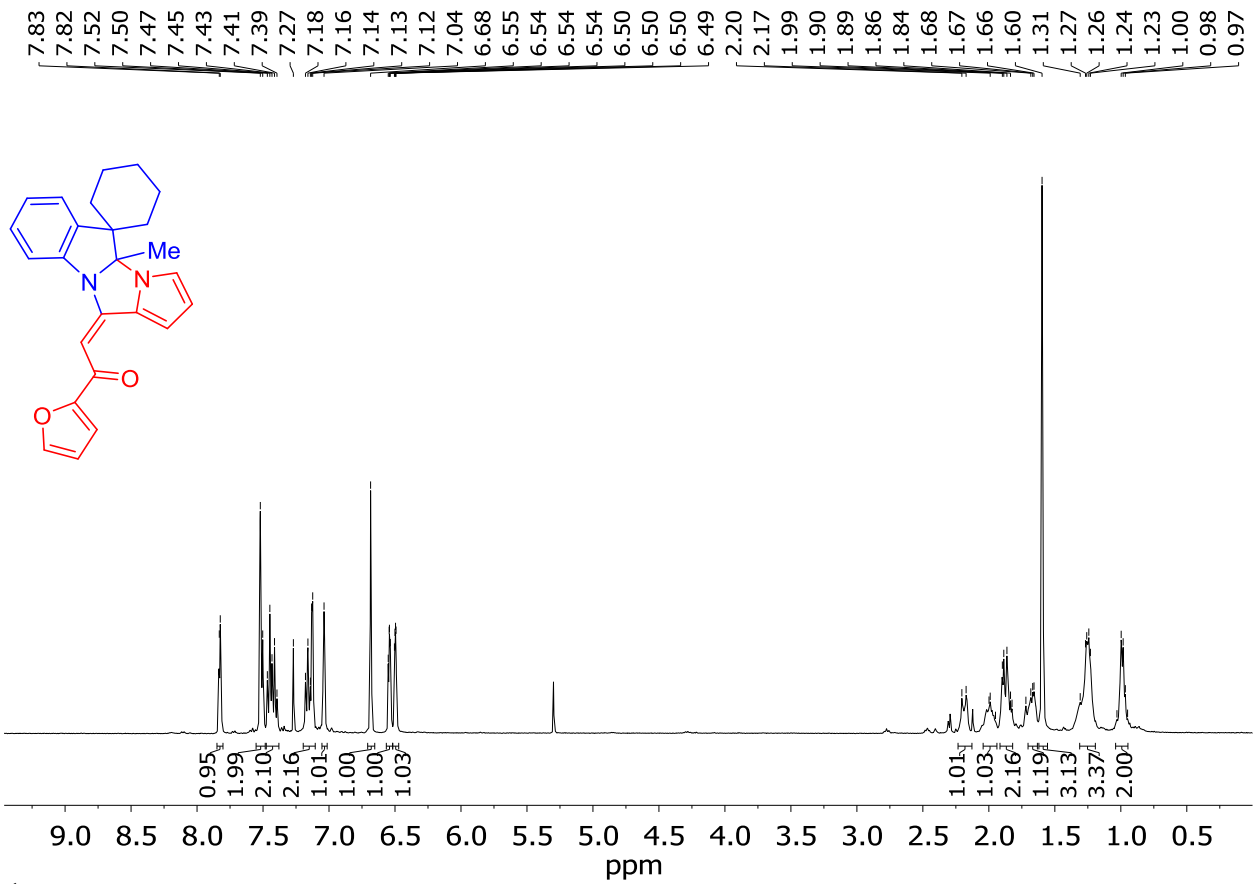
^{19}F NMR Spectrum of **3o** (376.50 MHz, $CDCl_3$)



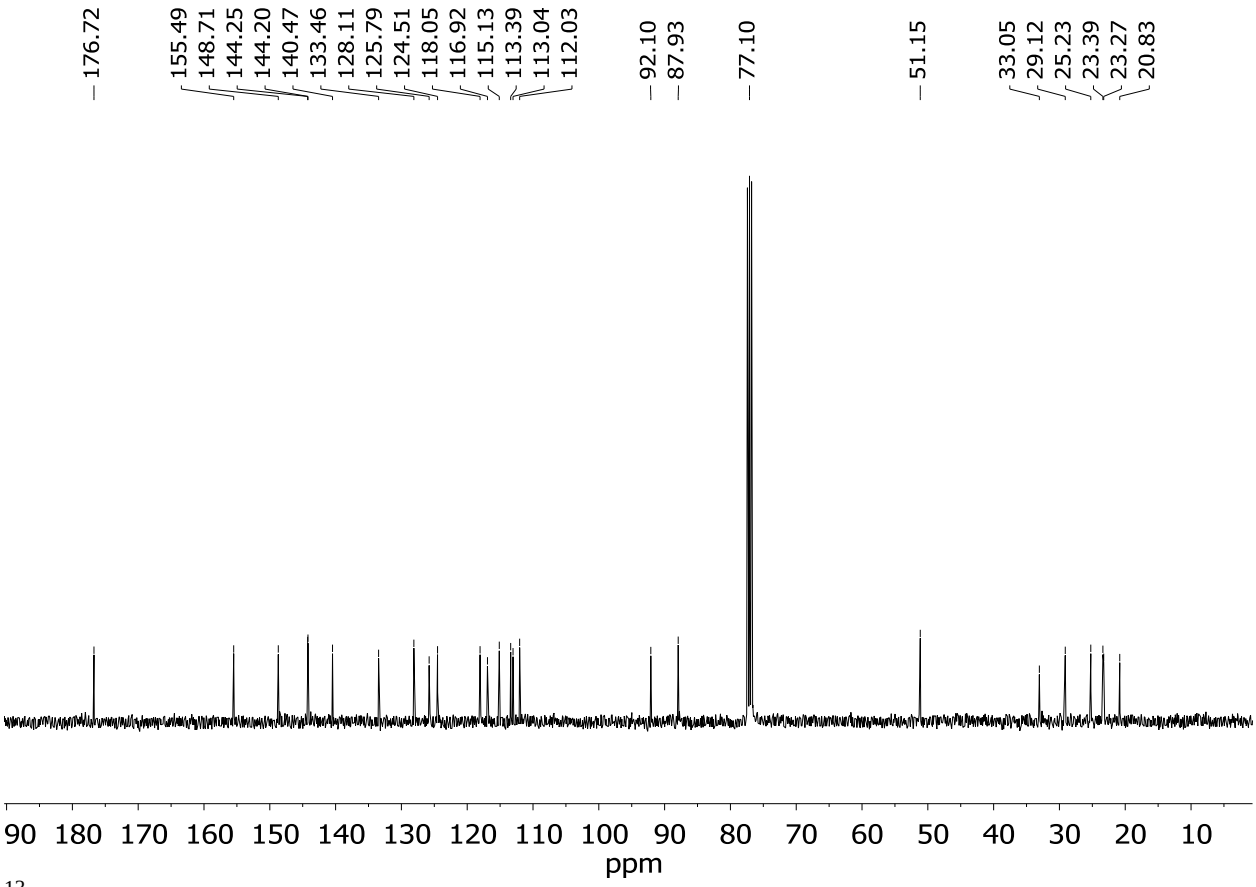
^{1}H NMR Spectrum of **3p** (100.62 MHz, $CDCl_3$)



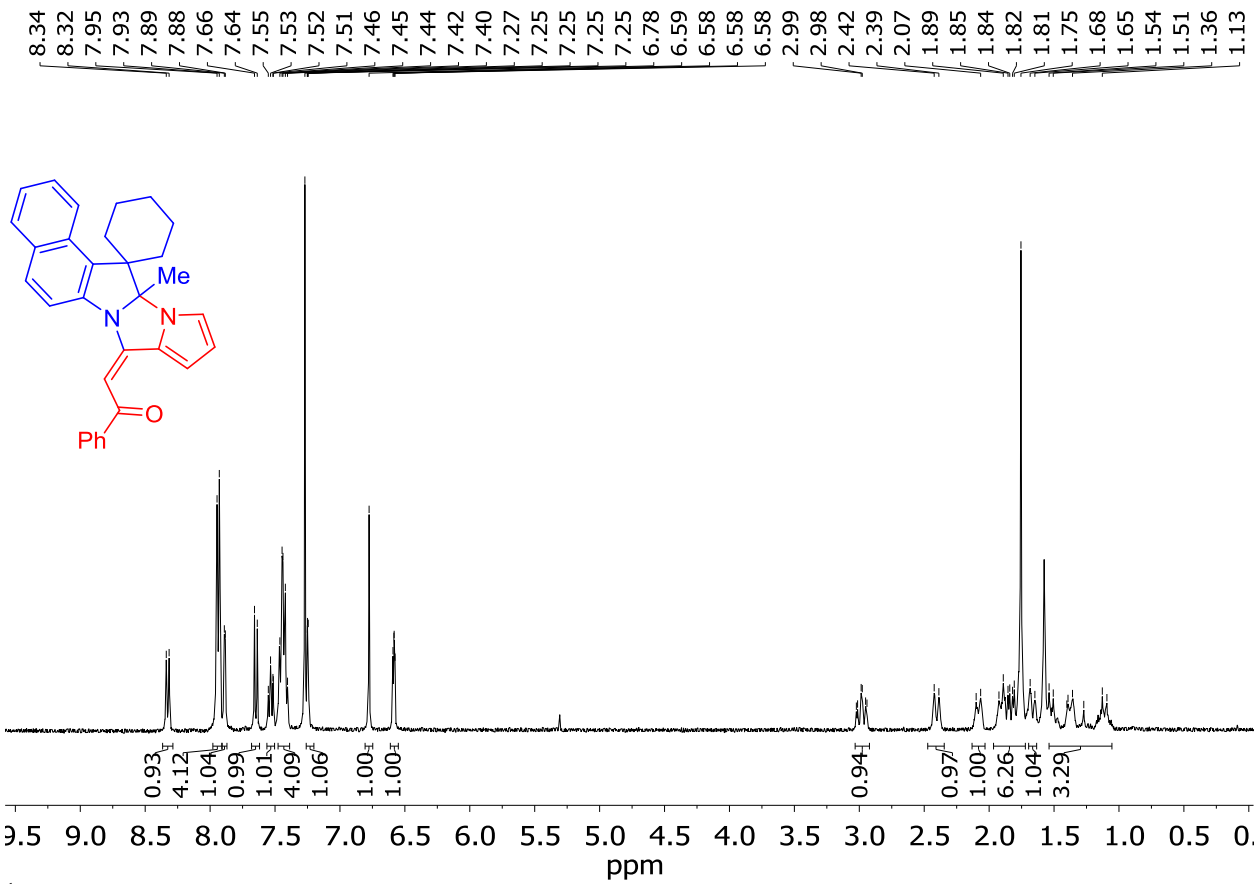
^{13}C NMR Spectrum of **3p** (100.62 MHz, $CDCl_3$)



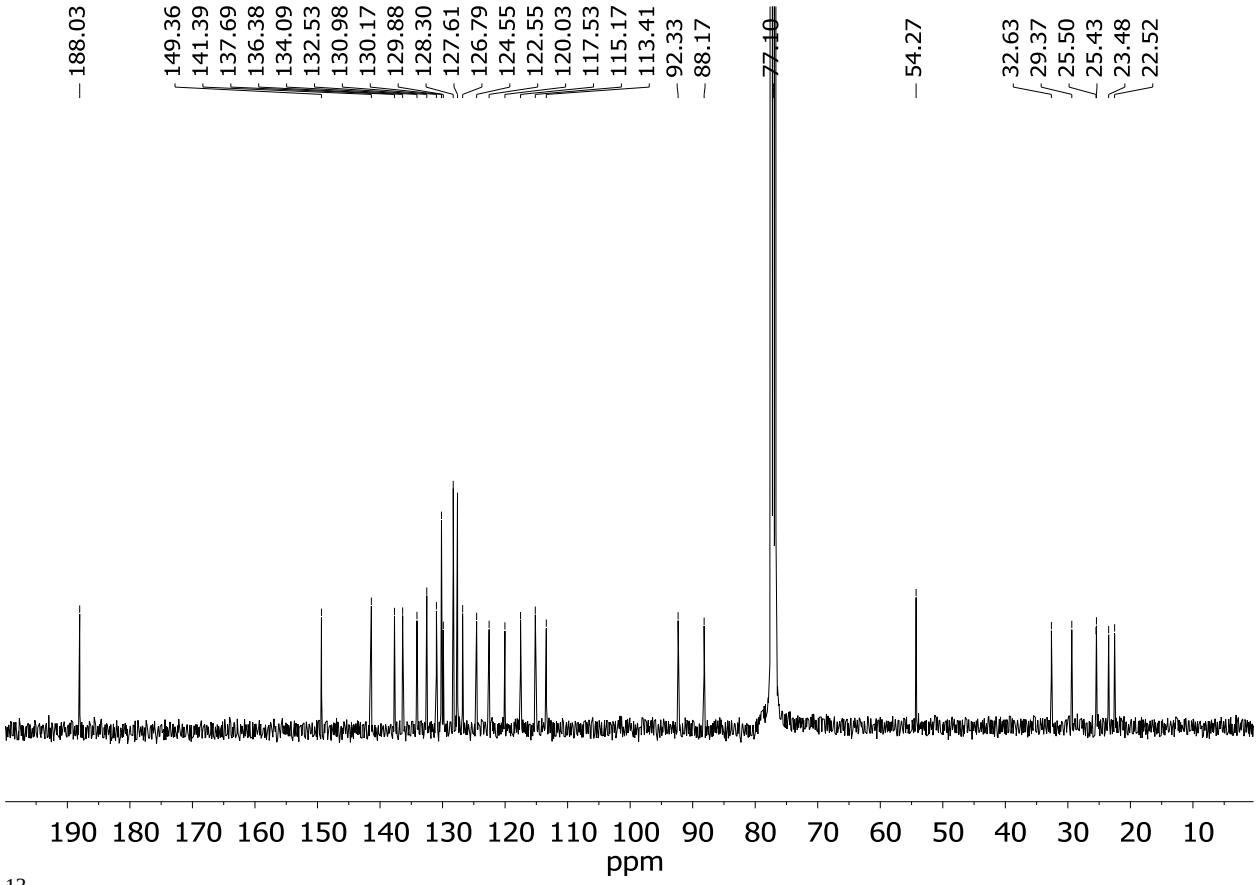
^{1}H NMR Spectrum of **3q** (100.62 MHz, $CDCl_3$)



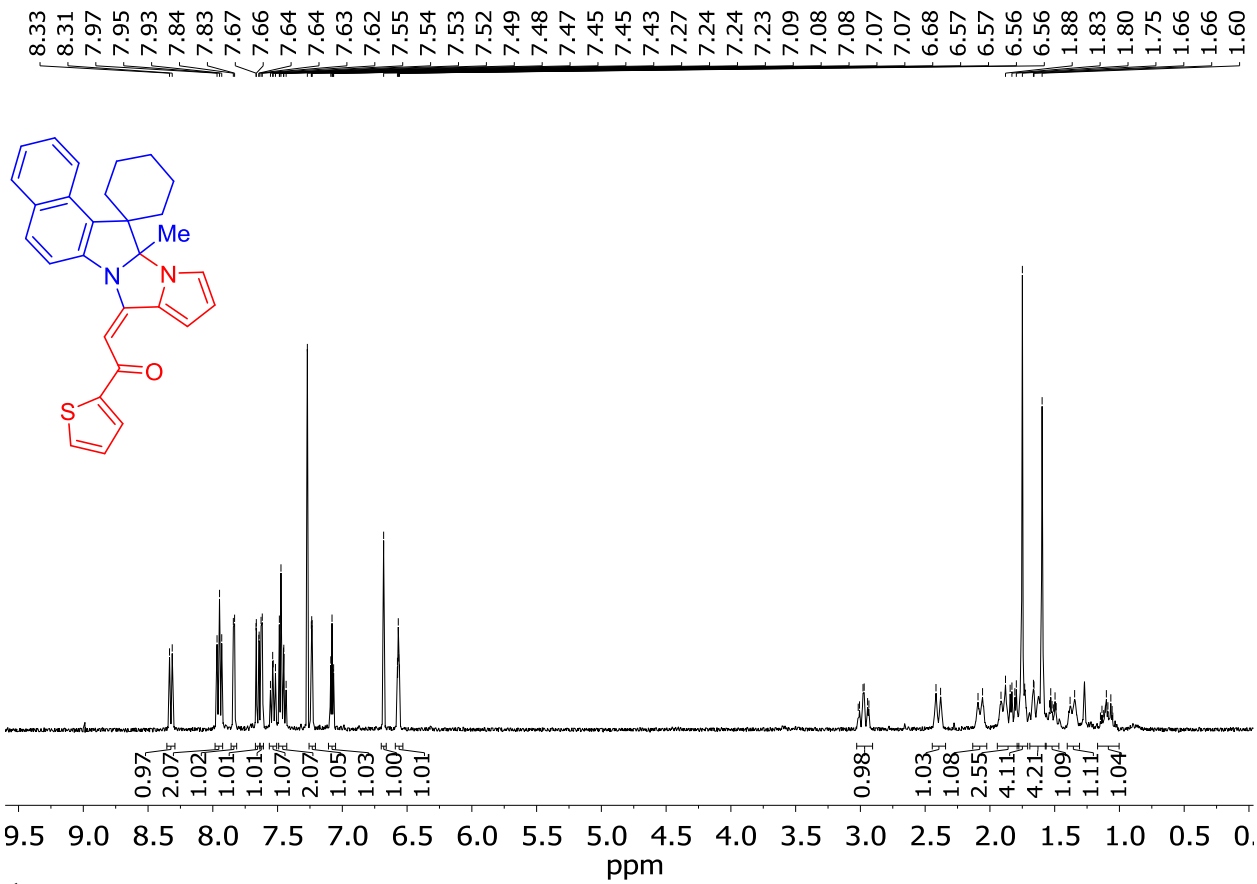
^{13}C NMR Spectrum of **3q** (100.62 MHz, $CDCl_3$)



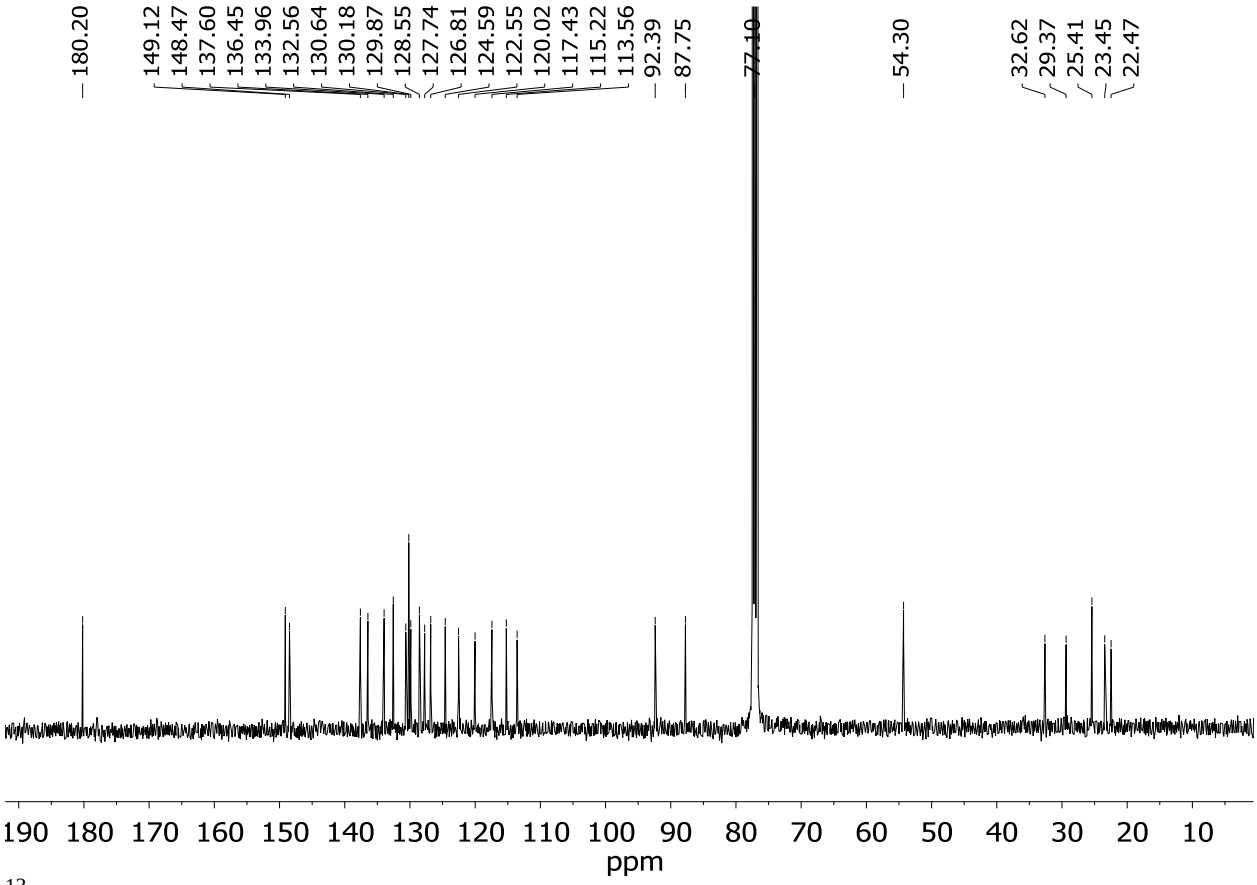
^{1}H NMR Spectrum of **3r** (400.13 MHz, $CDCl_3$)



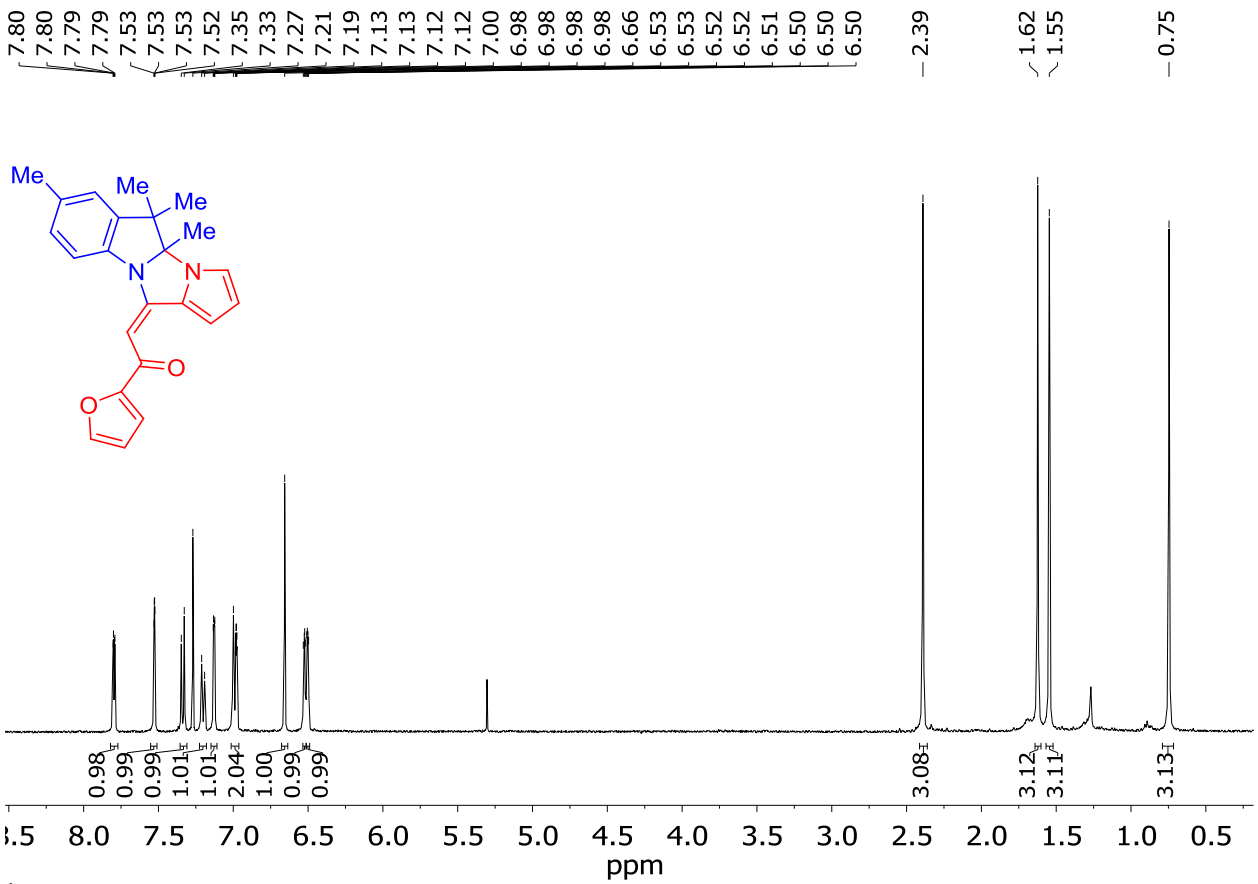
^{13}C NMR Spectrum of **3r** (100.62 MHz, $CDCl_3$)



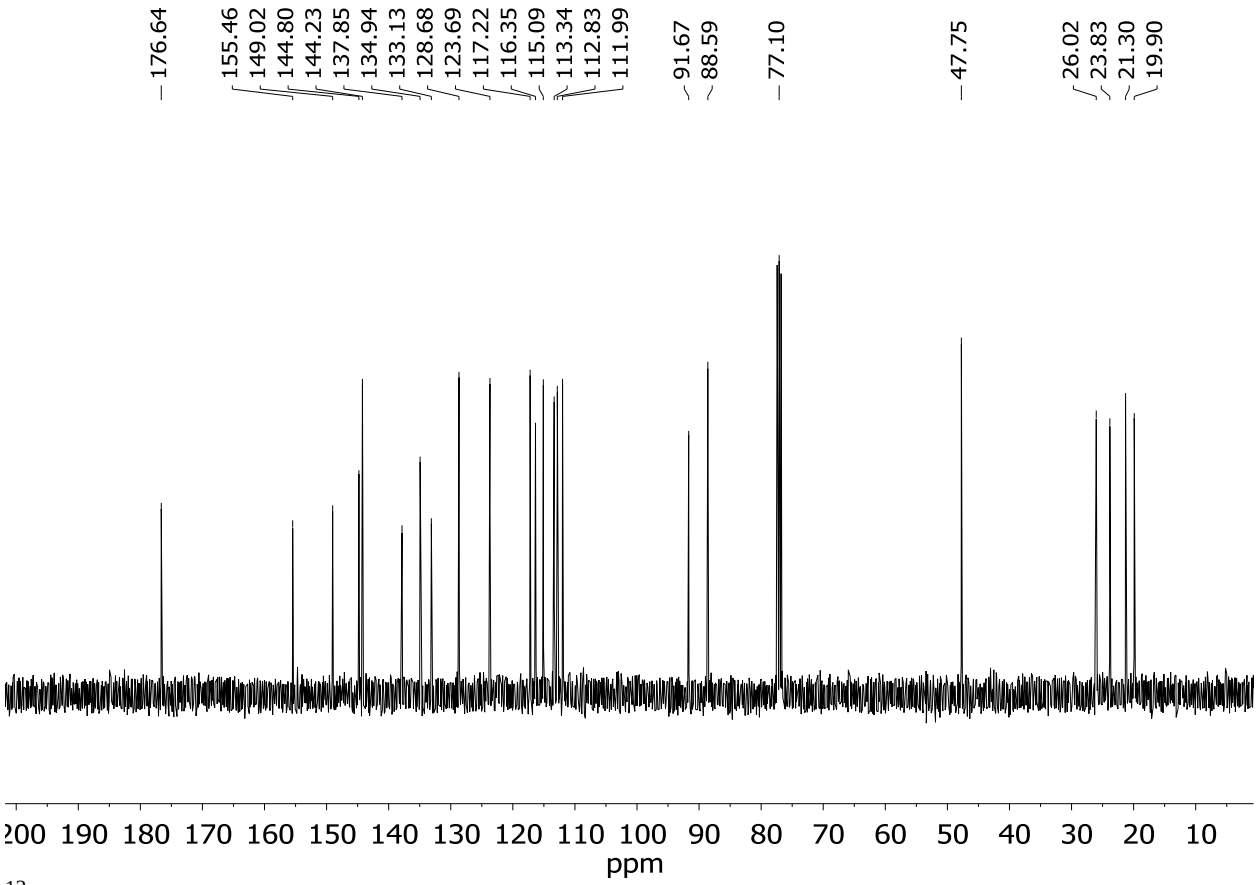
^{1}H NMR Spectrum of **3s** (400.13 MHz, $CDCl_3$)



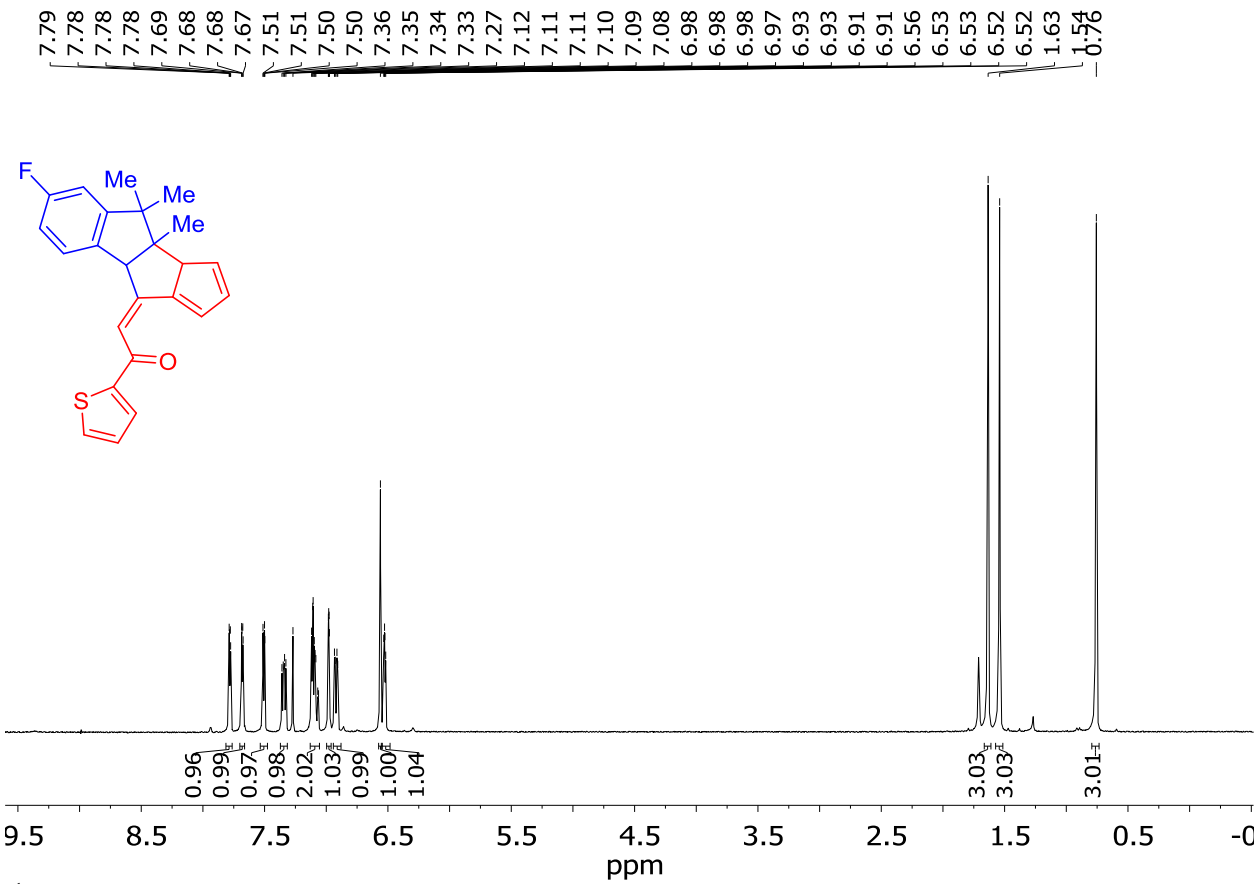
^{13}C NMR Spectrum of **3s** (100.62 MHz, $CDCl_3$)



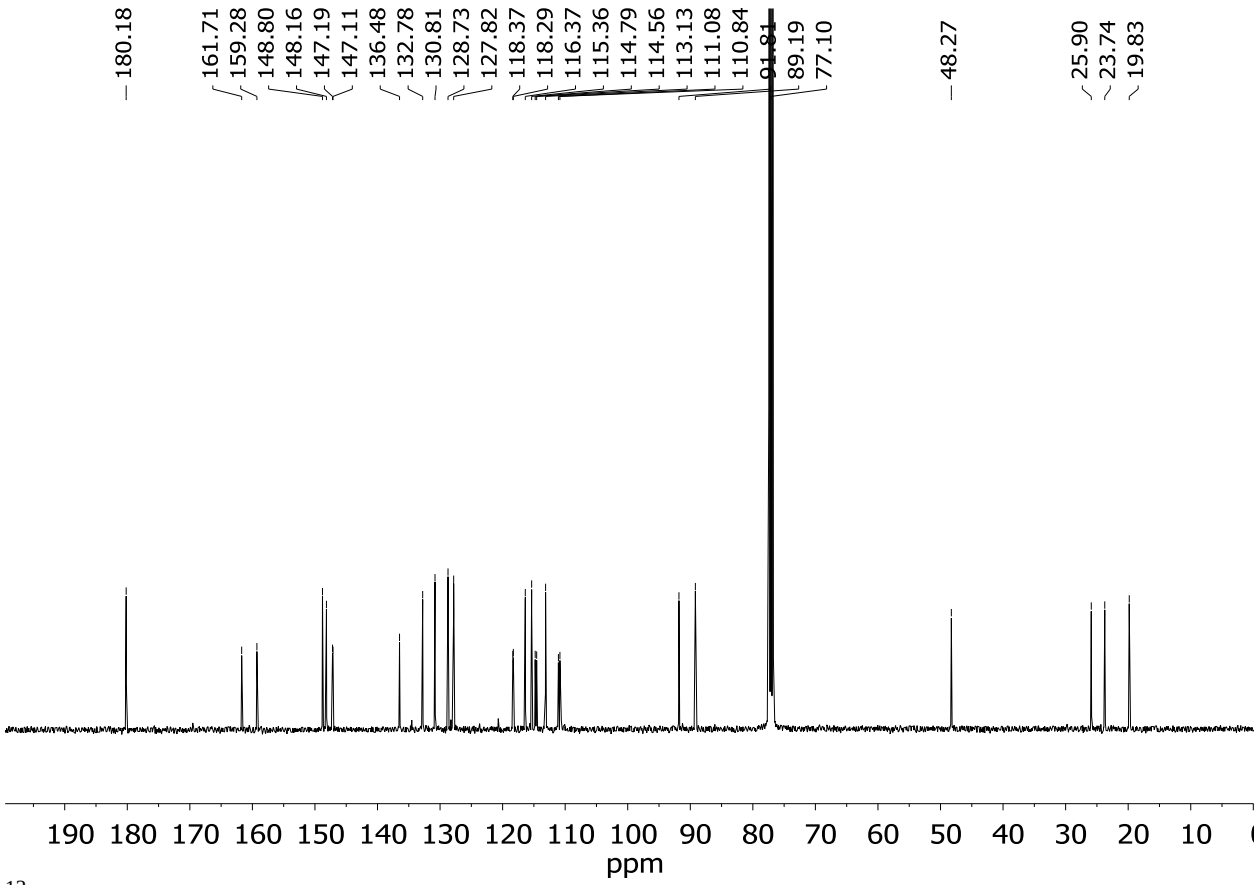
^{1}H NMR Spectrum of **3t** (400.13 MHz, $CDCl_3$)



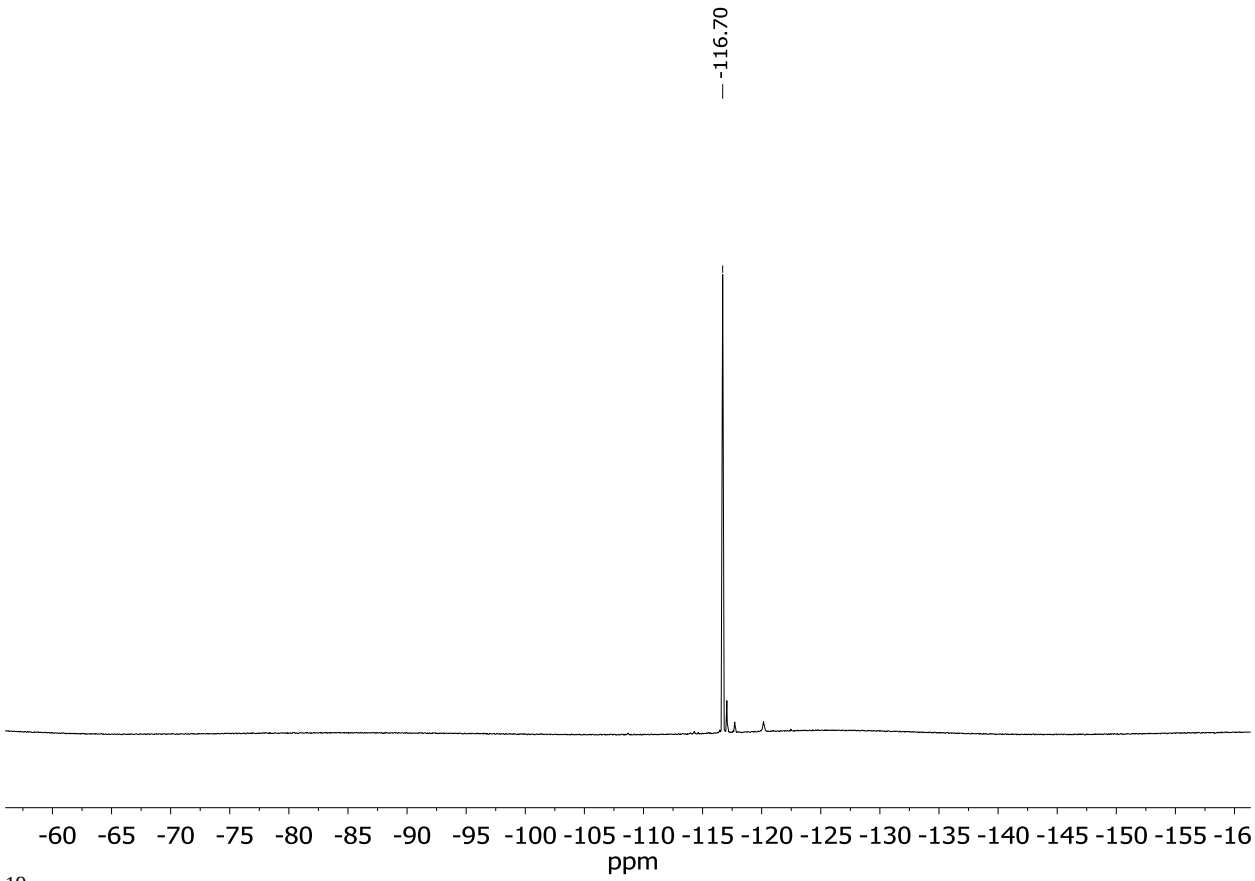
^{13}C NMR Spectrum of **3t** (100.62 MHz, $CDCl_3$)



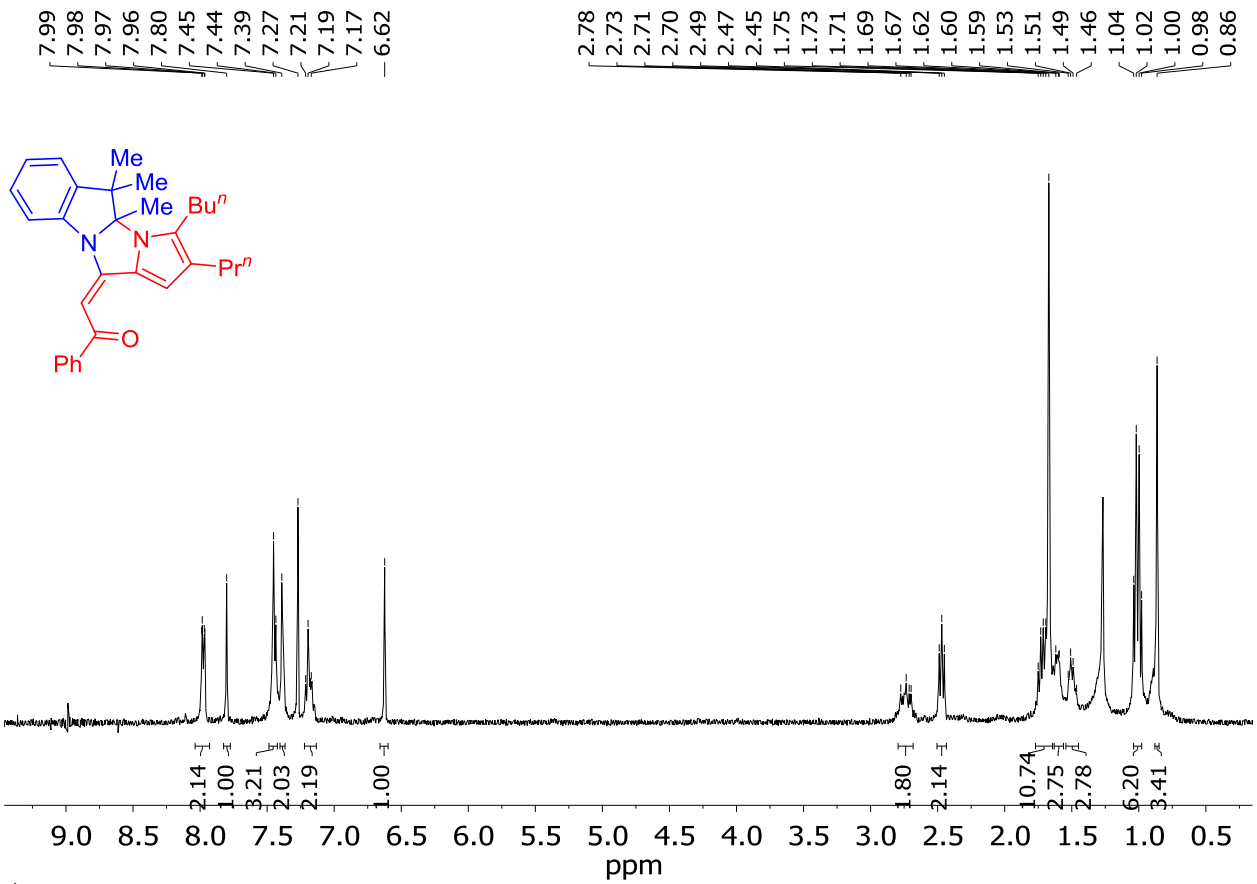
^{1}H NMR Spectrum of **3u** (400.13 MHz, $CDCl_3$)



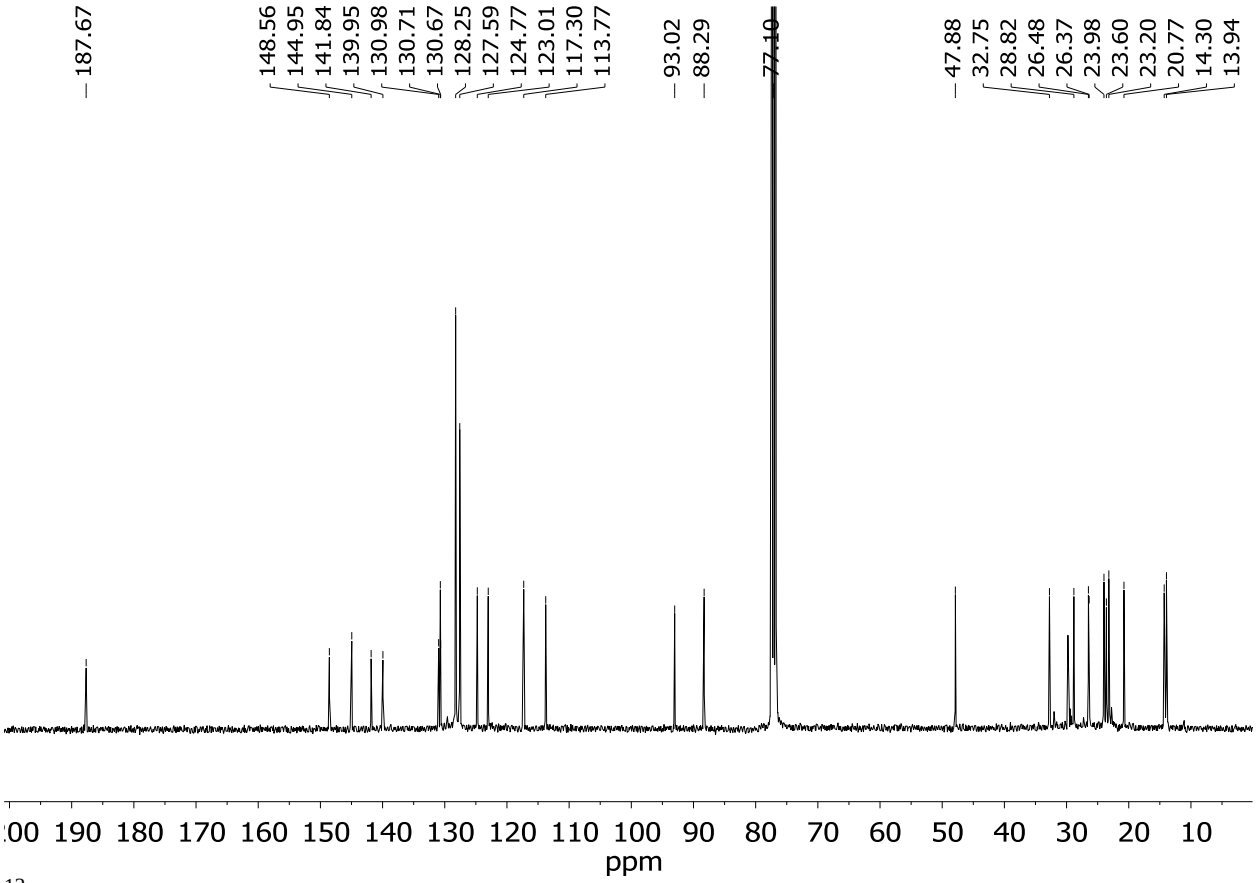
^{13}C NMR Spectrum of **3u** (100.62 MHz, $CDCl_3$)



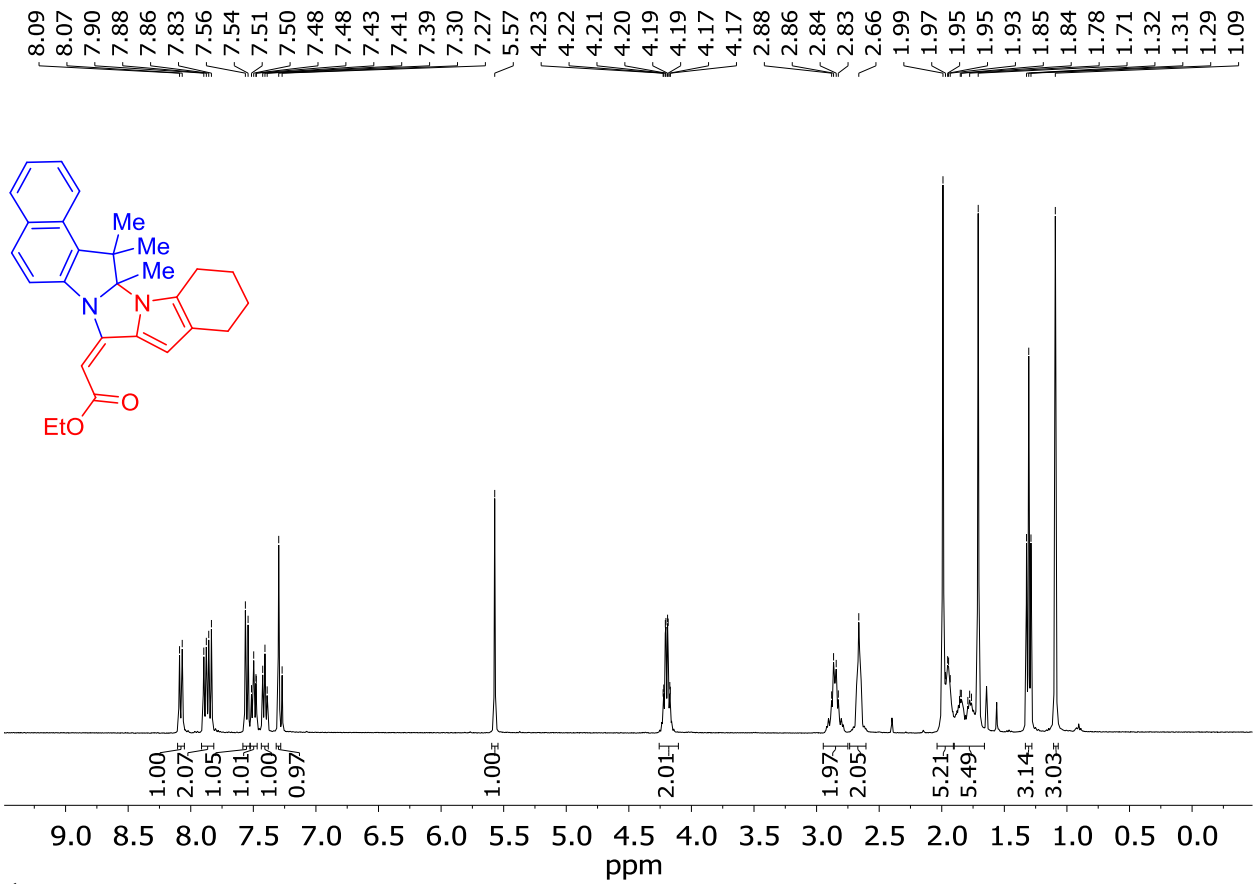
^{19}F NMR Spectrum of **3u** (376.50 MHz, $CDCl_3$)



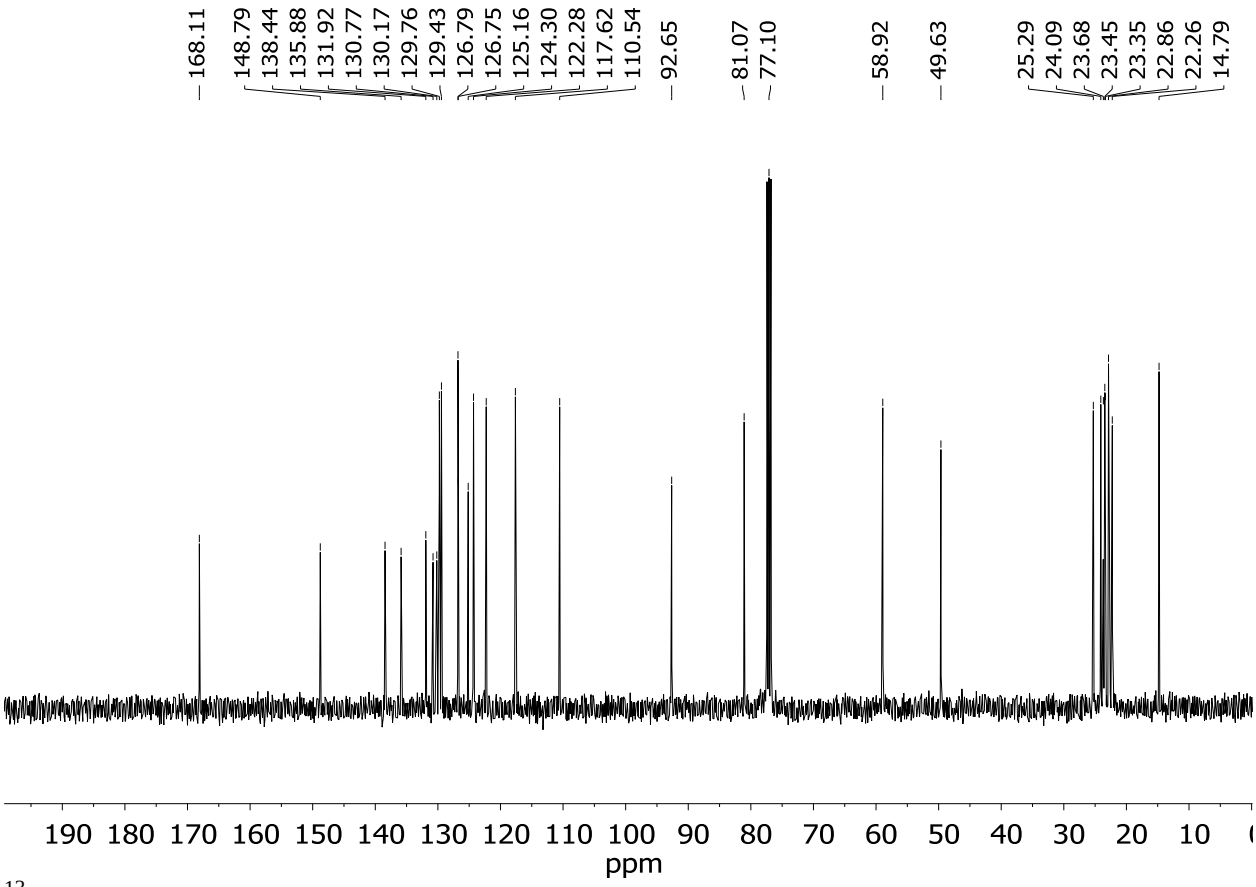
^{1}H NMR Spectrum of **3v** (400.13 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3v** (100.62 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3w** (100.62 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3w** (100.62 MHz, $CDCl_3$)

6. Computational details

All calculations were performed using the Gaussian09 suite of programs.[7] Based on general recommendations,[8] geometry optimization was performed using Head-Gordon's long-range corrected DFT-D2 hybrid functional (ωB97XD)[9] and balanced split valence triple-ξ with two sets of polarization functions Def2-TZVPP basis set. To achieve an accurate total energy, Grimme's B2PLYP-D3BJ double hybrid density functional and the same basis set with an additional diffuse function set on all atoms, Def2-TZVPPD, single point energy refinement step was performed utilizing optimized geometry.[10] Tight SCF convergence threshold and ultrafine DFT integration grid were applied at all calculation steps. Solvation effect on the mechanism was performed for water, using Truhlar's universal solvation model density (SMD) throughout the manuscript.[11] For each stationary point, second derivatives of the energy with respect to the Cartesian nuclear coordinates were calculated to confirm whether these structures were local minima or transition states. All transition state calculations were accompanied by intrinsic reaction coordinate (IRC) calculations at ωB97XD/DGDZVP level of theory to verify that each transition state connected the corresponding reactant and product.[12] For structure visualization, ChemCraft 1.8 was employed.[13] Charge model 5 (CM5) charges proposed by Truhlar et al.[14] were performed using Multiwfn 3.8 and the B2PLYP-D3BJ/Def2-TZVPPD "relaxed correlated" wavefunction.[15] Both DFT functionals predict comparable relative total energies of intermediates, the RMSE and MAD are ca. 1.5 and 1.3 kcal/mol, respectively.

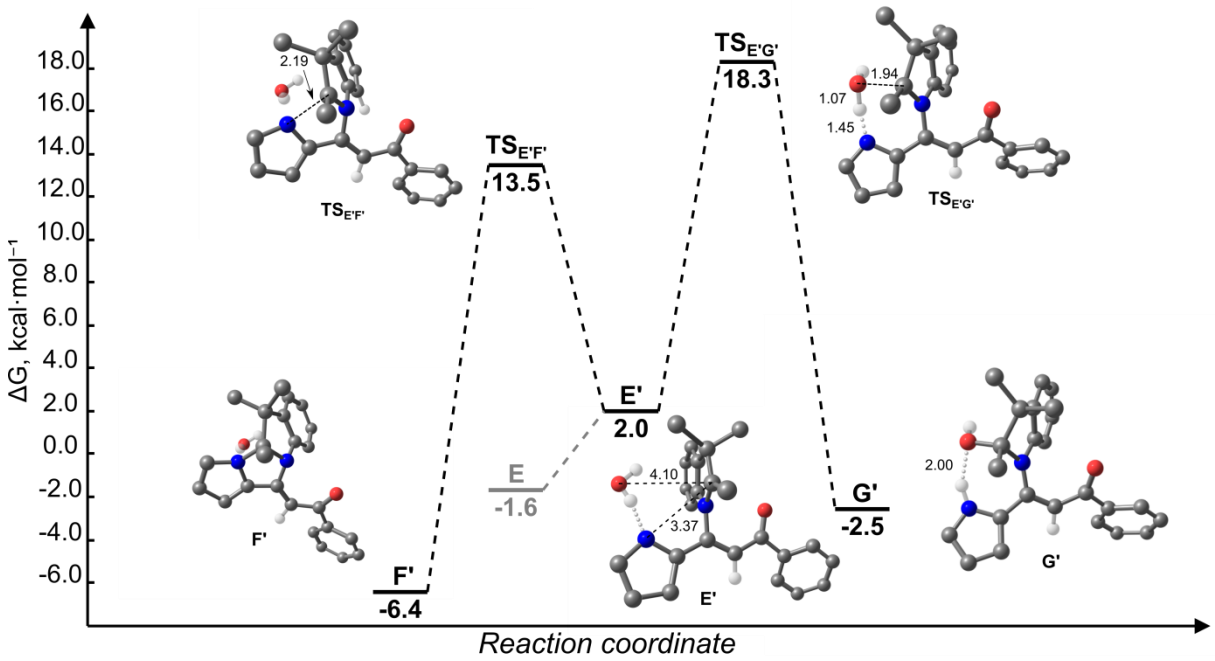


Fig. S1. Free energy profile for competitive intermediate **F′** and intermediate **G′** formation.

Cartesian coordinates, the number of imaginary frequencies, and computed total energies of target and optimized structures

H_2O; E_B2PLYP-D3BJ = -76.42788065349; E_wB97XD = -76.45353003570; ZPE = 0.021470; Qcorr = 0.024306; Hcorr = 0.025250; Gcorr = 0.003835;

O	-0.16698501	0.00000000	-0.74674174
H	-0.16698501	0.75734120	-0.15889386
H	-0.16698501	-0.75734120	-0.15889386

1a (isomer 1); E_B2PLYP-D3BJ = -630.4646802491; E_wB97XD = -630.73367765; ZPE = 0.185198 Qcorr = 0.197436; Hcorr = 0.198381; Gcorr = 0.143683;

C	-0.05084386	0.04069298	-0.48247833
C	-1.29953088	-0.06148905	0.12963796
C	1.09924149	0.10657712	0.30099306
C	-1.39397905	-0.09719064	1.50876598
C	1.00132107	0.07036815	1.68214842
C	-0.24374478	-0.03139058	2.28598359
H	-2.19035245	-0.11195915	-0.48111227
H	2.07109875	0.18613717	-0.16795960
H	-2.36375273	-0.17665584	1.98111579
H	1.89640157	0.12115389	2.28706288
H	-0.31965000	-0.05955369	3.36500721
C	0.02120128	0.07619268	-1.96505982
O	-0.97804473	0.01525694	-2.67106896
C	1.31824182	0.18566792	-2.56668256
C	2.39645954	0.27608255	-3.10408986
C	3.64514370	0.38104422	-3.72759125
C	3.96578027	0.43008159	-5.07475426
H	3.25411132	0.39151225	-5.88282024
C	5.36335181	0.53650160	-5.16685931
H	5.95079354	0.59664931	-6.06764630
C	5.85808031	0.54941056	-3.87879816
H	6.87049354	0.61830766	-3.51876297
N	4.82192530	0.45590204	-3.02054964
H	4.89183118	0.44136518	-2.01679638

1a (isomer 2); E_B2PLYP-D3BJ = -630.46476419972; E_wB97XD = -630.733752219; ZPE = 0.185344; Qcorr = 0.197534; Hcorr = 0.198478; Gcorr = 0.144237;

C	-0.06524803	0.02663542	-0.52591235
C	-1.31072531	-0.01140701	0.10005191
C	1.09485384	0.05454331	0.24506448
C	-1.39204051	-0.02124510	1.48044451
C	1.00999487	0.04431515	1.62753561
C	-0.23187685	0.00655634	2.24514707
H	-2.20948565	-0.03272049	-0.50068045
H	2.06424163	0.08408041	-0.23467557
H	-2.35932252	-0.05066483	1.96354327
H	1.91275337	0.06569127	2.22270411
H	-0.29760921	-0.00125493	3.32518164
C	-0.00679920	0.03628620	-2.00952929
O	-1.01467045	0.00858779	-2.70531387
C	1.28805382	0.07994741	-2.62423938
C	2.36627908	0.11556088	-3.16804482
C	3.62504652	0.15705813	-3.77874117
C	4.88685581	0.19091855	-3.20678639
H	5.08692366	0.19011093	-2.14803538
C	5.81934205	0.22555621	-4.25654830
H	6.89248318	0.25687367	-4.16960004
C	5.10563356	0.21201272	-5.43762268
H	5.44386010	0.22872012	-6.45969414
N	3.79013524	0.17083499	-5.14333895

H 3.03927489 0.15211232 -5.81312887

1a' (isomer 1); E_B2PLYP-D3BJ = -706.89862707126; E_wB97XD = -707.19362383; ZPE = 0.20922; Qcorr = 0.224971; Hcorr = 0.225915; Gcorr = 0.163656;

C -3.63651604 -0.16443788 1.68359257
C -4.89003753 -0.24436974 2.28891152
C -2.48765634 -0.16929124 2.47134874
C -4.98999937 -0.32793185 3.66574421
C -2.59088014 -0.25291649 3.84997874
C -3.84073898 -0.33205329 4.44731765
H -5.78012620 -0.24071273 1.67494531
H -1.51182749 -0.10756470 2.00841392
H -5.96352586 -0.39022045 4.13296338
H -1.69578450 -0.25622962 4.45714930
H -3.92135485 -0.39733581 5.52441479
C -3.55645377 -0.07483508 0.20321081
O -4.55525826 -0.06484335 -0.50668229
C -2.25301767 0.00193116 -0.38720673
C -1.16430020 0.06669827 -0.90796639
C 0.09891418 0.14274194 -1.50585683
C 0.44515128 0.24260817 -2.84537776
H -0.25187628 0.27698290 -3.66645485
C 1.84662224 0.28906988 -2.90723414
H 2.45459279 0.36605764 -3.79318538
C 2.31340164 0.21600242 -1.60867543
H 3.32157046 0.22010779 -1.22966309
N 1.26085424 0.12880488 -0.77259786
H 1.30732183 0.05671391 0.24546991
O 1.30995360 -0.09771538 2.09006377
H 1.67708120 0.70122608 2.47404540
H 1.91950242 -0.79434962 2.34249671

1a' (isomer 2); E_B2PLYP-D3BJ = -706.89872387234; E_wB97XD = -707.19390106; ZPE = 0.209174; Qcorr = 0.224984; Hcorr = 0.225928; Gcorr = 0.162930;

C -3.55069065 -0.19472263 1.54058890
C -4.82598141 -0.24072244 2.10250395
C -2.43224152 -0.13079298 2.36878437
C -4.97802218 -0.22276225 3.47683899
C -2.58784609 -0.11351594 3.74500367
C -3.85919611 -0.15928978 4.29891722
H -5.69191521 -0.28965295 1.45675791
H -1.43992741 -0.09483986 1.93883445
H -5.96827729 -0.25824934 3.91044724
H -1.71735184 -0.06463017 4.38493808
H -3.98030957 -0.14552410 5.37407564
C -3.41453271 -0.21488735 0.06290757
O -4.38382811 -0.27704528 -0.68483284
C -2.09392235 -0.15841694 -0.49015609
C -1.00413561 -0.11292654 -1.01043109
C 0.24199792 -0.06102272 -1.64543259
C 1.52209648 0.00643461 -1.11681200
H 1.76081200 0.03029854 -0.06632783

C	2.41390785	0.03579330	-2.20096333
H	3.48893412	0.08761297	-2.15483494
C	1.65579687	-0.01389915	-3.35556580
H	1.95912205	-0.01151258	-4.38888735
N	0.35434793	-0.07251981	-3.01469806
H	-0.44977128	-0.11604589	-3.63837273
O	-2.27439664	-0.20666023	-4.25153172
H	-2.69123869	-0.39102643	-3.40541636
H	-2.50754843	0.70527120	-4.43824865

2a; E_B2PLYP-D3BJ = -481.53565071948; E_wB97XD = -481.782716556; ZPE = 0.214254; Qcorr = 0.224940; Hcorr = 0.225884; Gcorr = 0.178668;

C	0.28832640	0.85327981	-3.44417620
C	-0.99008985	0.82629003	-2.89561547
C	1.40337768	0.83837486	-2.63229769
C	-1.18831394	0.78396046	-1.52799234
C	1.21713203	0.79574944	-1.25169199
C	-0.06297779	0.76909025	-0.70897034
H	2.40136043	0.85929338	-3.05278367
H	-2.18578585	0.76322651	-1.10847683
H	2.07674190	0.78352666	-0.59443654
H	-0.18625760	0.73635218	0.36576018
C	0.13620976	0.89684318	-4.93916415
C	0.74067353	-0.33747972	-5.61773567
C	0.72028978	2.17917674	-5.54222705
H	0.27659823	3.06628063	-5.08889864
H	1.79700952	2.20593110	-5.37153924
H	0.54347999	2.21222347	-6.61783654
H	1.81787270	-0.35667360	-5.44908826
H	0.56317869	-0.30937624	-6.69337998
H	0.31207585	-1.25713146	-5.21790296
C	-1.38263469	0.88718552	-5.03303926
N	-1.98941172	0.84821454	-3.90091443
C	-2.09361067	0.91954736	-6.33325512
H	-1.80603665	0.06008084	-6.94240889
H	-3.17165701	0.91074271	-6.19038880
H	-1.81379005	1.81292855	-6.89530735

2a'; E_B2PLYP-D3BJ = -557.97109021666; E_wB97XD = -558.244361218; ZPE = 0.238210; Qcorr = 0.252335; Hcorr = 0.253279; Gcorr = 0.196648;

C	-0.80180042	-0.44855652	0.11302305
C	-2.09095800	-0.46849275	0.63382851
C	0.29230456	-0.46642399	0.95295794
C	-2.32782714	-0.50605768	1.99472704
C	0.07018894	-0.50456802	2.32831249
C	-1.22282172	-0.52388059	2.84048026
H	1.30067350	-0.45114258	0.55816555
H	-3.33687329	-0.52048256	2.38562938
H	0.91311290	-0.51902088	3.00673471
H	-1.37191188	-0.55301894	3.91194368
C	-0.91803067	-0.40751633	-1.38624940
C	-0.30542873	-1.64671364	-2.04863452

C	-0.31517435	0.87131513	-1.97846864
H	-0.76448668	1.76108532	-1.53626780
H	0.75740789	0.89215697	-1.78351229
H	-0.46831321	0.90250472	-3.05765186
H	0.76749149	-1.66958622	-1.85581020
H	-0.45958430	-1.61957430	-3.12780121
H	-0.74711582	-2.56306468	-1.65582957
C	-2.43280100	-0.40985419	-1.52000413
N	-3.06003220	-0.44449306	-0.39896973
C	-3.12451326	-0.37502834	-2.82906069
H	-2.83089386	-1.23610265	-3.43270543
H	-4.20431216	-0.37947317	-2.69840783
H	-2.83233930	0.51746437	-3.38591873
O	-5.85766623	-0.41418842	-0.04912332
H	-6.09970645	0.51291652	-0.05214361
H	-4.88460939	-0.41701630	-0.17187488

A; E_B2PLYP-D3BJ = -1112.01935430200; E_wB97XD = -1112.535393960; ZPE = 0.400747; Qcorr = 0.425214; Hcorr = 0.426159; Gcorr = 0.345503;

C	-0.28401159	-1.76846912	-2.72373209
C	-1.38399055	-2.35411730	-2.09846441
C	0.31036434	-2.40144385	-3.81304531
C	-1.87634925	-3.56319501	-2.55572566
C	-0.19629220	-3.60320906	-4.27886294
C	-1.28468441	-4.18676300	-3.64804915
H	-1.83844011	-1.86372992	-1.24847229
H	1.16616871	-1.95414577	-4.30027722
H	-2.72085306	-4.02323780	-2.06067530
H	0.26920811	-4.09037430	-5.12520061
H	-1.67104908	-5.13269620	-4.00412488
C	0.22761581	-0.46976778	-2.21460418
O	-0.43341000	0.24854454	-1.47467802
C	1.54633884	-0.09103742	-2.62552545
C	2.66617364	0.18954966	-2.98174325
C	3.96921168	0.45179555	-3.42223987
C	4.69042757	1.63493076	-3.47191181
H	4.33074593	2.59837085	-3.15007831
C	5.94297574	1.32807151	-4.02820041
H	6.75296947	2.01262518	-4.21777432
C	5.95067431	-0.02870939	-4.29246214
H	6.72704015	-0.65364957	-4.70125816
N	4.75840397	-0.54655048	-3.93972057
H	4.49179753	-1.53874602	-3.90703565
C	2.69238715	-5.28163612	-3.38479813
C	3.23771078	-4.28173664	-4.18286609
C	2.10567226	-6.39117823	-3.95561093
C	3.21349375	-4.35644052	-5.56227419
C	2.07040313	-6.47982865	-5.34593484
C	2.61787487	-5.47536011	-6.13696815
H	1.67395817	-7.17268979	-3.34259915
H	3.63536956	-3.56856666	-6.17252050
H	1.60898958	-7.33788548	-5.81682650

H	2.57706008	-5.56346151	-7.21476451
C	2.88784020	-4.87464713	-1.95052347
C	3.85622741	-5.82463329	-1.23046073
C	1.57863960	-4.76097646	-1.16653549
H	0.89830183	-4.04633181	-1.62709043
H	1.08749048	-5.73386685	-1.13145652
H	1.77634406	-4.44091885	-0.14291882
H	3.41329302	-6.81953256	-1.17710800
H	4.04765224	-5.47943091	-0.21405816
H	4.80648558	-5.89707384	-1.76049278
C	3.54496069	-3.51975887	-2.16408254
N	3.75956462	-3.22572826	-3.39728534
C	3.89311920	-2.62060889	-1.03928428
H	4.46755253	-3.15719129	-0.28256560
H	4.45922594	-1.75688239	-1.37886069
H	2.97619701	-2.27346716	-0.55656981

A'; E_B2PLYP-D3BJ = -1188.45194524010; E_wB97XD = -1188.993922800; ZPE = 0.425365; Qcorr = 0.453345; Hcorr = 0.454289; Gcorr = 0.364344;

C	-0.69637243	-1.97106720	-3.43067434
C	-1.50601581	-2.96895052	-2.88960812
C	-0.86040162	-1.59516281	-4.76126094
C	-2.45904922	-3.58840985	-3.67721449
C	-1.82459717	-2.20753844	-5.54410675
C	-2.62011262	-3.20731474	-5.00418307
H	-1.37644740	-3.26092665	-1.85694888
H	-0.23801041	-0.81709815	-5.18184927
H	-3.07826178	-4.37038422	-3.25888821
H	-1.94844402	-1.90943874	-6.57639217
H	-3.36731245	-3.69328876	-5.61769085
C	0.32746312	-1.32352471	-2.57319032
O	0.35983734	-1.48042531	-1.35813016
C	1.30660905	-0.50123668	-3.21845236
C	2.18120155	0.14496521	-3.74568582
C	3.19957377	0.88769218	-4.35357651
C	4.28136797	1.54539796	-3.78682286
H	4.50289255	1.58262201	-2.73296799
C	5.00318945	2.13324855	-4.83745542
H	5.90263047	2.72068678	-4.75768977
C	4.34410626	1.81855529	-6.01054008
H	4.57572946	2.07580132	-7.03041779
N	3.26256269	1.07270655	-5.71344177
H	2.59400873	0.67886009	-6.37630004
C	1.86112739	-4.75206357	-3.63490533
C	2.69843636	-3.73690130	-4.08440527
C	0.87511653	-5.26673666	-4.45169167
C	2.58505872	-3.22069553	-5.36283401
C	0.74826273	-4.75376882	-5.73982845
C	1.59809582	-3.74834969	-6.18939628
H	0.21455570	-6.05132473	-4.10360642
H	3.24167202	-2.43233677	-5.70802051
H	-0.02052119	-5.13716214	-6.39767563

H	1.48506060	-3.36950695	-7.19748386
C	2.28449354	-5.09986426	-2.23501842
C	2.83786572	-6.52960126	-2.15914806
C	1.16920186	-4.90818624	-1.20490349
H	0.81132641	-3.87961971	-1.19651647
H	0.33233935	-5.56560076	-1.44377342
H	1.52631419	-5.15971768	-0.20545725
H	2.04258425	-7.24002251	-2.38726085
H	3.21065789	-6.74321604	-1.15676989
H	3.64935178	-6.67823747	-2.87246333
C	3.40357372	-4.08406194	-2.05747887
N	3.63060398	-3.35130626	-3.08861871
C	4.16680442	-3.96170227	-0.79274447
H	4.62190555	-4.91816964	-0.52776849
H	4.94399115	-3.20561317	-0.87641662
H	3.49448598	-3.69337495	0.02511593
O	1.31550253	-0.22958154	-7.40219179
H	0.46599155	0.17433644	-7.21002345
H	1.29591626	-1.06308114	-6.92451725

TS_{AB}; E_B2PLYP-D3BJ = -1111.98232796550; E_wB97XD = -1112.496715910; ZPE = 0.400279; Qcorr = 0.424006; Hcorr = 0.424950; Gcorr = 0.346395;
imaginary frequency -367.8574 cm^{-1};

C	-0.24247406	-2.17677778	-3.32526756
C	-0.82882331	-3.35930998	-2.88234891
C	-0.42600929	-1.76872005	-4.64337913
C	-1.57782771	-4.13260274	-3.75398729
C	-1.19682550	-2.53075787	-5.50641006
C	-1.76648932	-3.71708005	-5.06541315
H	-0.67450613	-3.68179376	-1.86122037
H	0.03164143	-0.85176740	-4.99092033
H	-2.01222107	-5.06228822	-3.41122556
H	-1.34581318	-2.20342463	-6.52675471
H	-2.35494137	-4.32010023	-5.74438922
C	0.63230523	-1.41290059	-2.38663341
O	0.40808282	-1.41108719	-1.16925116
C	1.73248496	-0.73745413	-2.96072048
C	2.93786699	-0.93801384	-3.23838710
C	4.17584416	-0.38435449	-3.69117621
C	4.74068722	0.83778909	-3.39311528
H	4.32518324	1.56521171	-2.71532430
C	5.93906559	0.93742134	-4.13724350
H	6.63215729	1.76243049	-4.14045655
C	6.06948773	-0.22775293	-4.85421091
H	6.84002971	-0.55588474	-5.53079048
N	4.99948935	-1.01638459	-4.58033520
H	4.83677509	-1.93486991	-4.95737390
C	2.62111810	-4.96398163	-2.75138787
C	2.78801681	-3.84481501	-3.55434874
C	2.02025450	-6.09726297	-3.25997053
C	2.37765679	-3.80752477	-4.87134810
C	1.59036370	-6.07807755	-4.58434790

C	1.76769493	-4.94911411	-5.37829128
H	1.87701899	-6.97718409	-2.64564177
H	2.50655485	-2.91875121	-5.47461365
H	1.10744045	-6.95137310	-5.00244254
H	1.41938267	-4.95667610	-6.40246870
C	3.16855329	-4.64319967	-1.38632120
C	4.36116136	-5.53292343	-1.01833733
C	2.08889513	-4.70856409	-0.29916830
H	1.24905845	-4.05656229	-0.53965046
H	1.72319466	-5.73223079	-0.21624957
H	2.50001844	-4.40972316	0.66534177
H	4.02975256	-6.56913922	-0.95046432
H	4.77332428	-5.23955597	-0.05268687
H	5.14805569	-5.46874476	-1.77021754
C	3.60813822	-3.20754564	-1.61133849
N	3.39958309	-2.80394538	-2.81397931
C	4.16204621	-2.34330572	-0.54822791
H	4.93665725	-2.87200293	0.00782857
H	4.56815546	-1.42115756	-0.95679232
H	3.36697453	-2.09700486	0.15967517

$TS_{A'B'}$; E_B2PLYP-D3BJ = -1188.41872381550; E_wB97XD = -1188.957993700; ZPE = 0.424367; Qcorr = 0.451501; Hcorr = 0.452446; Gcorr = 0.365401;
imaginary frequency -329.4695 cm^{-1};

C	-0.92582631	-2.05738123	-4.08071533
C	-1.57332552	-3.23602949	-3.72042162
C	-1.06294832	-1.56044863	-5.37376348
C	-2.34330948	-3.91559028	-4.64975553
C	-1.85326037	-2.22911448	-6.29391397
C	-2.48803652	-3.41037665	-5.93507565
H	-1.44944114	-3.62855014	-2.71975344
H	-0.55379445	-0.64849435	-5.65748869
H	-2.82787338	-4.84251101	-4.37337034
H	-1.96686662	-1.83391276	-7.29447877
H	-3.09220021	-3.94089095	-6.65925524
C	-0.03916704	-1.39169867	-3.08472115
O	-0.24559035	-1.49640115	-1.87446268
C	1.07974982	-0.68065800	-3.59944087
C	2.28099089	-0.81781016	-3.89564382
C	3.48901300	-0.26803286	-4.43072801
C	4.78759461	-0.72733325	-4.47455860
H	5.12857966	-1.67261775	-4.08971349
C	5.56116144	0.27007045	-5.11172727
H	6.61913149	0.23538507	-5.31317935
C	4.71209325	1.30117906	-5.43426463
H	4.89920259	2.24009298	-5.92723605
N	3.46299001	0.96865147	-5.02142931
H	2.62451435	1.53029818	-5.12348790
C	1.92108061	-4.86830874	-3.46113752
C	2.13940277	-3.74335275	-4.24399288
C	1.25129135	-5.95702285	-3.98131976
C	1.71178910	-3.66023070	-5.55401400

C	0.80412857	-5.88909385	-5.29827253
C	1.03240342	-4.75601324	-6.07305438
H	1.06725483	-6.83898257	-3.38079165
H	1.87927506	-2.76824136	-6.14262648
H	0.26699787	-6.72587898	-5.72492084
H	0.66851685	-4.72353476	-7.09140187
C	2.49933669	-4.60296192	-2.09724121
C	3.66105025	-5.54799789	-1.76885605
C	1.43305714	-4.65679510	-0.99747488
H	0.60697807	-3.98025360	-1.21661840
H	1.04151692	-5.67187686	-0.92551943
H	1.86336633	-4.38546053	-0.03315182
H	3.29096562	-6.57215193	-1.71892717
H	4.09960379	-5.29321699	-0.80371053
H	4.43862585	-5.49691990	-2.53148266
C	3.00122839	-3.18305532	-2.30107390
N	2.81012366	-2.74597233	-3.49414950
C	3.60913138	-2.36902907	-1.22758181
H	4.41565216	-2.92093910	-0.74277217
H	3.99227441	-1.42799564	-1.61486470
H	2.85739433	-2.16115538	-0.46274927
O	0.66089955	2.06161600	-5.02412146
H	0.62327696	2.73648902	-4.34313201
H	0.57696243	1.22649155	-4.54053905

B, E_B2PLYP-D3BJ = -1111.99775568960; E_wB97XD = -1112.518461660; ZPE = 0.402766; Qcorr = 0.426275; Hcorr = 0.427220; Gcorr = 0.349205;

C	-0.26805383	-1.96672219	-3.18546970
C	-0.80215580	-3.18874147	-2.78185315
C	-0.49733658	-1.51759280	-4.48343466
C	-1.53200964	-3.96132238	-3.67109998
C	-1.24819007	-2.28071968	-5.36453643
C	-1.75736816	-3.50816918	-4.96423749
H	-0.61582068	-3.54549613	-1.77719461
H	-0.08706533	-0.56889005	-4.80290648
H	-1.92205638	-4.92032515	-3.35613486
H	-1.42875814	-1.92027297	-6.36873916
H	-2.32936605	-4.11048042	-5.65780778
C	0.64820748	-1.25034679	-2.24007774
O	0.38124399	-1.22091579	-1.01745353
C	1.78367307	-0.65736850	-2.81462140
C	2.94152670	-1.24708035	-3.04407570
C	4.13233957	-0.70406248	-3.69399219
C	4.30981365	0.48603947	-4.36592151
H	3.54612015	1.22864545	-4.52950745
C	5.65936229	0.53580056	-4.79349704
H	6.13275717	1.32867497	-5.34947186
C	6.26322587	-0.62289632	-4.37533684
H	7.27145231	-0.98047345	-4.49575076
N	5.33154566	-1.36414546	-3.71277998
H	5.50900689	-2.26017784	-3.29122927
C	2.72274099	-4.90564491	-2.85830740

C	2.66941178	-3.71403135	-3.55373559
C	2.32793160	-6.07319049	-3.47985905
C	2.24409256	-3.60545590	-4.85881445
C	1.88550561	-5.99863005	-4.79656161
C	1.84583910	-4.78418241	-5.47593475
H	2.35275214	-7.01912927	-2.95518737
H	2.20411707	-2.65255353	-5.36698149
H	1.56377042	-6.89916029	-5.30211462
H	1.49421794	-4.75442849	-6.49811511
C	3.21337529	-4.63059126	-1.46230224
C	4.55373289	-5.32048438	-1.17709447
C	2.16772027	-4.99712855	-0.39941599
H	1.22958941	-4.47035255	-0.57642044
H	1.98238602	-6.06967374	-0.44423877
H	2.53372075	-4.74655762	0.59574160
H	4.41396605	-6.39854348	-1.24671025
H	4.90172966	-5.07900314	-0.17339114
H	5.31229928	-5.01828746	-1.89919738
C	3.38706857	-3.13381020	-1.50690430
N	3.07795458	-2.66719508	-2.67587992
C	3.81712142	-2.30428361	-0.37369649
H	4.70933170	-2.73940682	0.07709628
H	4.00704239	-1.27576020	-0.66647913
H	3.03224916	-2.32076768	0.38602711

C; E_B2PLYP-D3BJ = -1112.00141144090; E_wB97XD = -1112.522084410; ZPE = 0.402523; Qcorr = 0.425361; Hcorr = 0.426305; Gcorr = 0.349576;

C	-0.32274145	-1.98491401	-3.19624786
C	-0.83278436	-3.21540087	-2.78739007
C	-0.56079411	-1.54543331	-4.49584883
C	-1.54793084	-4.00546749	-3.67323678
C	-1.29736151	-2.32625954	-5.37344438
C	-1.78257172	-3.56171313	-4.96797583
H	-0.63861254	-3.56449473	-1.78147888
H	-0.16851838	-0.59050980	-4.81934666
H	-1.91910829	-4.97067935	-3.35451886
H	-1.48521976	-1.97346964	-6.37902975
H	-2.34302598	-4.17766070	-5.65898700
C	0.57844976	-1.24640093	-2.25381222
O	0.30802268	-1.21341789	-1.03291625
C	1.70788026	-0.63625645	-2.82722479
C	2.87479920	-1.21601203	-3.04014131
C	4.07550050	-0.66785715	-3.65438501
C	5.32860545	-1.21560456	-3.82876481
H	5.63307922	-2.20181853	-3.51670154
C	6.12557364	-0.24179825	-4.48460772
H	7.15907173	-0.33922222	-4.77445732
C	5.33454959	0.86050356	-4.68572035
H	5.54964173	1.80994105	-5.14565594
N	4.09821300	0.58948262	-4.18047493
H	3.30808767	1.21222753	-4.18417201
C	2.74168421	-4.87538967	-2.85947292

C	2.64990704	-3.68402607	-3.55145706
C	2.37601213	-6.05229328	-3.48144472
C	2.21420363	-3.58513383	-4.85394228
C	1.92374974	-5.98755987	-4.79533545
C	1.84564469	-4.77312992	-5.47151119
H	2.43177807	-6.99853073	-2.95966928
H	2.14584194	-2.63283869	-5.36007599
H	1.62552896	-6.89582885	-5.30147818
H	1.48824291	-4.75114338	-6.49190627
C	3.23236794	-4.58909703	-1.46553380
C	4.57920756	-5.26133757	-1.17411763
C	2.18806381	-4.96547873	-0.40348170
H	1.24312056	-4.45274948	-0.58613314
H	2.01784036	-6.04069059	-0.44414017
H	2.54716345	-4.70512246	0.59168704
H	4.45228190	-6.34143372	-1.23730519
H	4.92235606	-5.01028881	-0.17102821
H	5.33615517	-4.95530049	-1.89600798
C	3.37754931	-3.08877049	-1.51342781
N	3.03834730	-2.62957749	-2.67545494
C	3.80448000	-2.24871451	-0.38663169
H	4.71019841	-2.66528658	0.05443983
H	3.97205250	-1.21782325	-0.68474119
H	3.02915755	-2.27843654	0.38253401

C'; E_B2PLYP-D3BJ = -1188.44050469770; E_wB97XD = -1188.987126310; ZPE = 0.427041; Qcorr = 0.453625; Hcorr = 0.454569; Gcorr = 0.369200;

C	-1.03438362	-1.88580381	-3.98159315
C	-1.55884878	-3.10856812	-3.56926662
C	-1.26339901	-1.44558617	-5.28265346
C	-2.28207163	-3.89183219	-4.45450517
C	-2.00932292	-2.21865994	-6.15865605
C	-2.50964634	-3.44729963	-5.75020943
H	-1.36975426	-3.45697025	-2.56217650
H	-0.85760385	-0.49674709	-5.60780011
H	-2.66512667	-4.85197996	-4.13477708
H	-2.19176898	-1.86638267	-7.16533047
H	-3.07644822	-4.05806966	-6.44062916
C	-0.12854281	-1.15026363	-3.04392997
O	-0.37977731	-1.12494008	-1.82482038
C	0.99542748	-0.51760038	-3.63020616
C	2.16225958	-1.10703894	-3.83168058
C	3.37292661	-0.58097312	-4.44814777
C	4.62170249	-1.15258043	-4.57973247
H	4.90688149	-2.13088661	-4.22697731
C	5.44397493	-0.21550896	-5.25491071
H	6.48104031	-0.33760792	-5.52174678
C	4.67082943	0.88912319	-5.50987453
H	4.90852461	1.81753850	-6.00097647
N	3.42185394	0.65730490	-5.01959704
H	2.63704124	1.29640841	-5.06661277
C	2.02871321	-4.76330717	-3.61384320

C	1.93635570	-3.57871480	-4.31714382
C	1.67147225	-5.94711697	-4.22764267
C	1.50802492	-3.49265507	-5.62298950
C	1.22720486	-5.89569518	-5.54481680
C	1.14803698	-4.68756191	-6.23216158
H	1.72763303	-6.88845795	-3.69715699
H	1.43909373	-2.54516089	-6.13802402
H	0.93595301	-6.80958016	-6.04486522
H	0.79697472	-4.67607395	-7.25491144
C	2.50756999	-4.46255159	-2.21885082
C	3.85613039	-5.12392192	-1.91057910
C	1.45653123	-4.83631310	-1.16264544
H	0.51050871	-4.32983973	-1.35665044
H	1.29202967	-5.91261075	-1.19723914
H	1.80611510	-4.56731522	-0.16642038
H	3.73628426	-6.20531467	-1.96429561
H	4.18971927	-4.86059239	-0.90738475
H	4.61673672	-4.81999493	-2.62955793
C	2.64726678	-2.96213834	-2.27878575
N	2.31438980	-2.51499453	-3.44747497
C	3.07279248	-2.11188623	-1.15957466
H	4.01147006	-2.49267656	-0.75543540
H	3.18711588	-1.07289435	-1.45425610
H	2.32883506	-2.18246299	-0.36308677
O	0.75283696	2.09520021	-4.85164452
H	0.87132237	2.74950035	-4.16041569
H	0.72438549	1.22871189	-4.37393088

TS_{CD}; E_B2PLYP-D3BJ = -1111.96263840720; E_wB97XD = -1112.482063940; ZPE = 0.397576; Qcorr = 0.420900; Hcorr = 0.421844; Gcorr = 0.342439;
imaginary frequency -1766.3307 cm^{-1};

C	-0.57937248	-1.81068684	-3.59900391
C	-1.70457337	-2.55058961	-3.24301747
C	-0.40064368	-1.43452260	-4.92874814
C	-2.63323352	-2.91480505	-4.20331584
C	-1.33451057	-1.79176726	-5.88770418
C	-2.44987187	-2.53490595	-5.52671332
H	-1.84033457	-2.84925660	-2.21236091
H	0.47059952	-0.85842280	-5.21175129
H	-3.50018423	-3.49768673	-3.92196193
H	-1.19151998	-1.49206069	-6.91729594
H	-3.17647150	-2.81899411	-6.27658664
C	0.43957774	-1.47694713	-2.55815951
O	0.16929691	-1.59846687	-1.35862676
C	1.71276684	-0.98201652	-3.00489324
C	2.88134987	-1.60630496	-2.99030807
C	4.00345898	-0.82894567	-3.52308943
C	5.37600904	-0.90463782	-3.63446322
H	6.00711202	-1.72990800	-3.34272881
C	5.77724520	0.34182706	-4.18477222
H	6.78362529	0.64984281	-4.42597443
C	4.62616551	1.09100274	-4.36981397

H	4.52008040	2.08424090	-4.77764766
N	3.54948780	0.36431002	-3.97576515
H	2.31894352	0.17116530	-3.63899605
C	3.01069715	-5.23283571	-2.61824723
C	2.67001072	-4.09365645	-3.32165610
C	2.70013411	-6.47144902	-3.14140287
C	2.03591313	-4.10678768	-4.54368457
C	2.05175291	-6.52165852	-4.37148356
C	1.72692388	-5.35828563	-5.06230297
H	2.95366174	-7.37915046	-2.60994463
H	1.79032350	-3.19534279	-5.06925736
H	1.79721427	-7.48146926	-4.80042564
H	1.22592742	-5.42557141	-6.01826940
C	3.69556942	-4.82991083	-1.34025605
C	5.14720866	-5.32510267	-1.27040161
C	2.90562694	-5.27779206	-0.10189515
H	1.89164305	-4.87897785	-0.11589672
H	2.85366578	-6.36585636	-0.09970968
H	3.40505699	-4.95225448	0.80961824
H	5.14442173	-6.41427078	-1.25362280
H	5.62734093	-4.96256185	-0.36206291
H	5.71946312	-4.98868422	-2.13453572
C	3.67256486	-3.32958504	-1.45905370
N	3.09618071	-2.96324149	-2.56217321
C	4.24190413	-2.39545031	-0.48085706
H	5.32314677	-2.35473721	-0.63971229
H	3.83420788	-1.39372183	-0.59022056
H	4.07421174	-2.76590663	0.52880698

$TS_{C'D'}$; E_B2PLYP-D3BJ = -1188.43259350480; E_wB97XD = -1188.977826450; ZPE = 0.422564; Qcorr = 0.448277; Hcorr = 0.449221; Gcorr = 0.366318;
imaginary frequency -1363.7184 cm^{-1};

C	-1.03501429	-1.81603058	-4.03693988
C	-1.59161042	-3.01014821	-3.58628680
C	-1.23518252	-1.41276437	-5.35471347
C	-2.32553899	-3.80326589	-4.45286266
C	-1.99784531	-2.19149169	-6.20941246
C	-2.53232555	-3.39255778	-5.76323963
H	-1.41956383	-3.32792967	-2.56630959
H	-0.79552567	-0.48968457	-5.70912501
H	-2.73443506	-4.74344882	-4.10761187
H	-2.16269126	-1.86954012	-7.22891656
H	-3.10870176	-4.01127857	-6.43840767
C	-0.14062053	-1.05020648	-3.12319685
O	-0.35407027	-1.01019464	-1.91380009
C	0.99618602	-0.37686498	-3.73456513
C	2.15151068	-1.00737350	-3.91237596
C	3.36856513	-0.48895717	-4.51517506
C	4.60208034	-1.08559159	-4.68147471
H	4.86745950	-2.08462915	-4.37390664
C	5.43499204	-0.14010726	-5.32726605
H	6.46596770	-0.27283350	-5.61197738

C	4.68056434	0.99151442	-5.52754265
H	4.93733986	1.93383113	-5.98162631
N	3.43362940	0.77046942	-5.03588530
H	2.64101145	1.42337920	-5.01700697
C	2.02235455	-4.65440510	-3.67080789
C	1.92136010	-3.47703088	-4.38463345
C	1.69363613	-5.84793635	-4.28148043
C	1.51303047	-3.40580704	-5.69744914
C	1.26857903	-5.81245263	-5.60538161
C	1.18076504	-4.61070529	-6.30268180
H	1.75769555	-6.78451235	-3.74366989
H	1.44054844	-2.46370844	-6.22166868
H	0.99979124	-6.73427755	-6.10336259
H	0.84594397	-4.61200600	-7.33086722
C	2.47816491	-4.33798623	-2.27188729
C	3.83356552	-4.97612914	-1.94246224
C	1.42011342	-4.72077364	-1.22563572
H	0.46964173	-4.22781987	-1.43179770
H	1.27081170	-5.79921442	-1.25854203
H	1.75558077	-4.44341671	-0.22695618
H	3.73045941	-6.05928551	-1.99336803
H	4.14867740	-4.70315702	-0.93596680
H	4.59860251	-4.66328061	-2.65277316
C	2.59679483	-2.83729275	-2.33738313
N	2.27032373	-2.40245160	-3.51429270
C	2.99572103	-1.97399276	-1.21999085
H	3.93199799	-2.34199209	-0.79896597
H	3.10204077	-0.93544483	-1.51894141
H	2.23987379	-2.04969673	-0.43494184
O	0.94379008	2.04796959	-4.67496422
H	1.02923677	2.63786020	-3.92383671
H	0.89720255	0.88083301	-4.17021697

D; E_B2PLYP-D3BJ = -1112.02955619330; E_wB97XD = -1112.545101630; ZPE = 0.402605; Qcorr = 0.426022; Hcorr = 0.426966; Gcorr = 0.348071;

C	-0.98454511	-1.92108123	-3.76706205
C	-2.10237812	-2.28537590	-3.01816938
C	-1.16199286	-1.17713637	-4.93206324
C	-3.37132026	-1.90118743	-3.41664230
C	-2.43475861	-0.80880424	-5.34057353
C	-3.54022169	-1.16411234	-4.58149390
H	-1.96879967	-2.86400666	-2.11411568
H	-0.31169027	-0.90106155	-5.54080135
H	-4.23056241	-2.17744532	-2.81995705
H	-2.56221959	-0.24409268	-6.25452879
H	-4.53221598	-0.86888148	-4.89736753
C	0.36614176	-2.37989676	-3.30588688
O	0.44149276	-3.41300073	-2.63190961
C	1.49717143	-1.56234297	-3.67094102
C	2.80782310	-1.84242706	-3.43224582
C	3.92918324	-1.04973389	-3.75915535
C	5.29113155	-1.37161072	-3.54271881

H	5.68100014	-2.27300018	-3.09374064
C	6.01211465	-0.29653664	-4.02857482
H	7.08446552	-0.17452904	-4.03930022
C	5.05169918	0.61840710	-4.51374437
H	5.24903912	1.58079007	-4.96750285
N	3.80533365	0.18067394	-4.36017162
H	1.30637174	-0.62439796	-4.16754259
C	3.65259063	-5.30792377	-2.69081664
C	3.27705026	-4.30605315	-3.56378996
C	3.84645569	-6.58692947	-3.17159441
C	3.07728999	-4.49387024	-4.91280504
C	3.65305867	-6.81436890	-4.53032433
C	3.27463045	-5.78486721	-5.38696947
H	4.14039260	-7.39125724	-2.51037575
H	2.78247273	-3.68411462	-5.56550763
H	3.79896023	-7.80898558	-4.92956206
H	3.13106230	-5.99011606	-6.43890436
C	3.77311722	-4.72951428	-1.30678907
C	5.20614210	-4.81707151	-0.76183571
C	2.77644014	-5.36750119	-0.32877977
H	1.75164080	-5.25879671	-0.68223016
H	3.00708362	-6.42867525	-0.24403229
H	2.86487310	-4.91250555	0.65694029
H	5.47649001	-5.86733361	-0.66010644
H	5.26891820	-4.34305814	0.21705540
H	5.91395857	-4.33618482	-1.43676314
C	3.41436086	-3.28924004	-1.56232465
N	3.15190492	-3.10084845	-2.81572893
C	3.38365691	-2.23193750	-0.54551582
H	4.41328615	-2.00660351	-0.25558642
H	2.90854445	-1.32431497	-0.90693824
H	2.87092524	-2.59579581	0.34443128

D'; E_B2PLYP-D3BJ = -1188.46818971560; E_wB97XD = -1189.010207930; ZPE = 0.427453; Qcorr = 0.453787; Hcorr = 0.454732; Gcorr = 0.368959;

C	-3.51535888	0.85647798	-1.27748881
C	-4.60294505	0.39338236	-0.53860581
C	-3.73749021	1.75152831	-2.32314166
C	-5.88535289	0.82697182	-0.82794733
C	-5.02420891	2.17114491	-2.62348379
C	-6.09876039	1.71559884	-1.87361692
H	-4.43495165	-0.30201710	0.27253739
H	-2.91394360	2.11084961	-2.92554686
H	-6.72020921	0.47181497	-0.23851036
H	-5.18650662	2.85533218	-3.44561739
H	-7.10152021	2.05060072	-2.10423691
C	-2.14888962	0.34649282	-0.93301215
O	-2.04363666	-0.75060688	-0.37826936
C	-1.03112176	1.20109532	-1.26481385
C	0.28599766	0.91725562	-1.09994507
C	1.38863629	1.73590447	-1.44060340
C	2.75531403	1.45939711	-1.21869934

H	3.16778670	0.57604192	-0.75481628
C	3.44884396	2.55300514	-1.71182492
H	4.51700616	2.70548734	-1.71777806
C	2.47023474	3.43410946	-2.20991146
H	2.63421793	4.39424076	-2.68060849
N	1.23604144	2.95646848	-2.05240997
H	-0.13665281	3.75347612	-2.88098734
C	1.23504219	-2.55627604	-0.55575961
C	0.88451586	-1.50381751	-1.37862346
C	1.50058233	-3.79065041	-1.11265809
C	0.77507312	-1.59787375	-2.74760528
C	1.39768887	-3.92401560	-2.49372634
C	1.04121896	-2.84564367	-3.29798823
H	1.77895072	-4.63252132	-0.49274122
H	0.49716597	-0.75095546	-3.35947818
H	1.59784656	-4.88302975	-2.95220508
H	0.96901512	-2.97826160	-4.36871406
C	1.26305092	-2.07222214	0.86893621
C	2.68255644	-2.13374496	1.45560748
C	0.26644363	-2.80987825	1.77156158
H	-0.74668221	-2.74440779	1.37678713
H	0.55548976	-3.85870514	1.82554583
H	0.28500297	-2.39103908	2.77716261
H	3.00119033	-3.17503742	1.47903257
H	2.69344307	-1.74280286	2.47220838
H	3.38574382	-1.56584752	0.84654094
C	0.84758497	-0.63590959	0.69600902
N	0.66660401	-0.36242917	-0.55608926
C	0.61861708	0.31768060	1.78648635
H	1.35103925	0.16864470	2.57745588
H	0.63465535	1.34892304	1.44412779
H	-0.36838374	0.10086587	2.20692293
O	-0.82894539	4.22945856	-3.40137839
H	-1.63505382	4.13073215	-2.89240180
H	-1.24944862	2.17279357	-1.67518471

E; E_B2PLYP-D3BJ = -1112.02828102590; E_wB97XD = -1112.543806900; ZPE = 0.402640; Qcorr = 0.426086; Hcorr = 0.427031; Gcorr = 0.347705;

C	-3.58191744	1.17566194	-3.05094108
C	-4.71381790	0.91979411	-2.27862651
C	-3.72073672	1.88563072	-4.24207956
C	-5.95740799	1.37686766	-2.68015003
C	-4.96928264	2.32724765	-4.65279337
C	-6.08806032	2.07937719	-3.87092770
H	-4.61053297	0.36731122	-1.35444039
H	-2.86093065	2.07814334	-4.86938791
H	-6.82671360	1.18383811	-2.06557995
H	-5.06756013	2.86467873	-5.58657359
H	-7.06056623	2.43125909	-4.18929471
C	-2.26102577	0.63969024	-2.58492281
O	-2.25100298	-0.37458829	-1.87843331
C	-1.08239396	1.36685321	-2.98503213

C	0.21162666	1.01335452	-2.74365902
C	1.37461523	1.72668844	-3.10742170
C	1.44816848	2.97217281	-3.77427096
H	0.61795020	3.57593096	-4.10718990
C	2.79551321	3.24928125	-3.90398450
H	3.24625405	4.11731656	-4.36100597
C	3.47214265	2.15887227	-3.31169178
H	4.54314001	2.02963062	-3.22920127
N	2.63594015	1.24382890	-2.83319011
H	-1.22597317	2.29647797	-3.51370542
C	0.82648654	-2.46961748	-1.87719094
C	0.52270432	-1.47565322	-2.78665512
C	0.93359677	-3.77494590	-2.31189639
C	0.31450821	-1.69713937	-4.12926601
C	0.72871690	-4.03672875	-3.66292842
C	0.42439918	-3.01466047	-4.55700753
H	1.16975605	-4.57366418	-1.62136095
H	0.07752629	-0.89278286	-4.81161803
H	0.80716335	-5.05253312	-4.02616655
H	0.27020341	-3.24661342	-5.60188152
C	0.98206546	-1.85185211	-0.51371742
C	2.40469221	-2.01915992	0.03980064
C	-0.05675587	-2.38547977	0.48262457
H	-1.07143978	-2.22553143	0.11971557
H	0.10454435	-3.45500108	0.61161104
H	0.05768755	-1.89742338	1.44978096
H	2.60201212	-3.08149969	0.17794638
H	2.49843643	-1.51804842	1.00264544
H	3.14514962	-1.61104591	-0.64760049
C	0.72028620	-0.40024904	-0.82260628
N	0.47434186	-0.24043066	-2.08174082
C	0.74252530	0.68924547	0.15952670
H	1.76731106	0.81037211	0.51854571
H	0.39277907	1.62979509	-0.25627254
H	0.13227103	0.41207469	1.01956442

E'; E_B2PLYP-D3BJ = -1188.46808371630; E_wB97XD = -1189.010618770; ZPE = 0.427194; Qcorr = 0.453533; Hcorr = 0.454477; Gcorr = 0.369270;

C	-3.49361199	0.78580631	-1.36682943
C	-4.58398915	0.36864444	-0.60518243
C	-3.71352164	1.59147427	-2.48250159
C	-5.86784971	0.76195749	-0.94207089
C	-5.00159205	1.96801872	-2.83082065
C	-6.07946595	1.56046797	-2.05845116
H	-4.41747814	-0.25762212	0.26081058
H	-2.88538956	1.90934035	-3.10143253
H	-6.70543220	0.44500435	-0.33495672
H	-5.16267071	2.58065979	-3.70782563
H	-7.08336017	1.86253253	-2.32654468
C	-2.12570843	0.31795431	-0.97165305
O	-2.01640294	-0.75905212	-0.37836161
C	-1.01724822	1.18281617	-1.30474039

C	0.30201737	0.93130970	-1.09112910
C	1.39276951	1.77515766	-1.40907085
C	1.34633185	3.07992772	-1.94531827
H	0.45922790	3.64332451	-2.19013148
C	2.66376918	3.48405850	-2.07606915
H	3.02570410	4.43032694	-2.44809153
C	3.44597189	2.40511957	-1.61850083
H	4.52558156	2.34889194	-1.58079713
N	2.69735084	1.38066668	-1.21403902
H	3.64359336	-0.18043771	-1.24514704
C	1.30010086	-2.50478996	-0.40701835
C	0.97351263	-1.48238693	-1.27742032
C	1.65513080	-3.73778260	-0.91535907
C	0.96774952	-1.60862707	-2.64780815
C	1.66173743	-3.90160426	-2.29721621
C	1.32157324	-2.85528849	-3.14906233
H	1.92237730	-4.55452536	-0.25814068
H	0.70927736	-0.78406050	-3.29746926
H	1.93635226	-4.85939539	-2.71803930
H	1.33582330	-3.01124915	-4.21894417
C	1.21323660	-1.98971553	1.00419814
C	2.57573853	-2.02265765	1.71356996
C	0.15049945	-2.72025319	1.83665581
H	-0.82412587	-2.68527993	1.35201199
H	0.45116098	-3.76136020	1.94716637
H	0.07272338	-2.27273767	2.82698385
H	2.90902000	-3.05792938	1.77410845
H	2.48841633	-1.62586320	2.72411705
H	3.32071550	-1.44575518	1.16674129
C	0.79250713	-0.56506506	0.76591171
N	0.68348927	-0.32721314	-0.50097773
C	0.48439679	0.41461002	1.81342055
H	1.10812852	0.24361826	2.68784553
H	0.59324293	1.43812367	1.46288825
H	-0.55710553	0.25797001	2.11159092
O	4.28403300	-0.92142446	-1.34394686
H	3.77913348	-1.71149209	-1.14153400
H	-1.24679502	2.13265628	-1.76231481

TS_{EF}; E_B2PLYP-D3BJ = -1112.01575315790; E_wB97XD = -1112.530148560; ZPE = 0.402808; Qcorr = 0.424895; Hcorr = 0.425839; Gcorr = 0.351200;
imaginary frequency -191.2968 cm^{-1};

C	-3.26329301	2.60225479	-0.77241085
C	-4.22880448	3.09170285	0.10581987
C	-3.28079320	3.01907868	-2.10198310
C	-5.18437855	3.99235552	-0.33216013
C	-4.25030582	3.90602377	-2.54436476
C	-5.19862707	4.39906872	-1.66010949
H	-4.21890031	2.76897009	1.13811702
H	-2.55449460	2.63643332	-2.80604858
H	-5.92015920	4.37746457	0.36129961
H	-4.26411506	4.21201225	-3.58191981

H	-5.94906879	5.09817515	-2.00508339
C	-2.26226586	1.61330490	-0.25855752
O	-2.56516851	0.90275729	0.70231121
C	-0.97537165	1.57135949	-0.91851398
C	0.04530463	0.73538139	-0.61516685
C	1.35795083	0.71244097	-1.17691746
C	2.01091374	1.54307368	-2.09729118
H	1.57669764	2.36997480	-2.63751361
C	3.32751010	1.09084586	-2.14578582
H	4.12862117	1.47784683	-2.75747870
C	3.40825595	0.00796232	-1.25223930
H	4.26912040	-0.60551078	-1.02719614
N	2.22256733	-0.23077920	-0.69054937
H	-0.77758464	2.29844948	-1.69182881
C	-0.06951944	-2.60731062	0.61455163
C	-0.68060245	-1.57008518	-0.06798652
C	-0.48770064	-3.90604183	0.40766018
C	-1.70312427	-1.76743252	-0.97151860
C	-1.52106763	-4.13512183	-0.49511995
C	-2.11702622	-3.07920222	-1.17498284
H	-0.01794264	-4.72763846	0.93273771
H	-2.16149807	-0.94631973	-1.50392456
H	-1.86326437	-5.14576970	-0.67272803
H	-2.91643689	-3.27673136	-1.87631944
C	0.99658028	-2.04866840	1.51785578
C	2.36646999	-2.70264335	1.33753321
C	0.56148464	-2.15505744	2.99262921
H	-0.38642556	-1.64576635	3.16586154
H	0.44115937	-3.20868652	3.24121413
H	1.31982007	-1.72797793	3.64785492
H	2.31197993	-3.73572063	1.68055222
H	3.11558491	-2.18250116	1.93470731
H	2.67439104	-2.68835640	0.29502829
C	0.98591688	-0.59230104	1.10561189
N	-0.06149898	-0.34504092	0.31467166
C	1.64531249	0.46211893	1.90684686
H	2.66768486	0.17533596	2.13954352
H	1.63259428	1.42856629	1.41231274
H	1.09329154	0.54599996	2.84693332

TS_E (rotation of C(O)Ph group); E_B2PLYP-D3BJ = -1111.99300750870; E_wB97XD = -1112.510921320; ZPE = 0.401800; Qcorr = 0.424533; Hcorr = 0.425477; Gcorr = 0.348614; ***imaginary frequency*** -95.7179 cm^{-1};

C	-3.44713574	1.26138009	-1.30777863
C	-4.35729755	2.23500601	-0.90090232
C	-3.86867099	0.29949883	-2.22427189
C	-5.64665516	2.26104504	-1.41044631
C	-5.16138779	0.31687402	-2.72757797
C	-6.05416350	1.30061232	-2.32612830
H	-4.04665630	2.98254647	-0.18281471
H	-3.18737969	-0.48202832	-2.53495227
H	-6.33553122	3.03248618	-1.09099496

H	-5.47378507	-0.44490079	-3.43023225
H	-7.06231537	1.31505737	-2.71927793
C	-2.05279358	1.26899786	-0.73284784
O	-1.92230271	1.66466429	0.47882709
C	-1.02574423	0.87575783	-1.55460347
C	0.35105251	0.81402753	-1.07318892
C	1.25418288	1.80257450	-1.06775150
C	1.02338509	3.17503574	-1.50291680
H	0.09181560	3.55349471	-1.89072956
C	2.18234160	3.82546778	-1.30665092
H	2.40992107	4.86099680	-1.50367096
C	3.10831849	2.83892649	-0.76403013
H	4.14061044	3.03142670	-0.50116164
N	2.58652101	1.66371147	-0.62009341
C	1.26573247	-2.69213537	-0.63138003
C	0.92907907	-1.60763890	-1.41704448
C	1.48555010	-3.91957687	-1.22283687
C	0.81083981	-1.66381595	-2.78883901
C	1.35995739	-4.01528662	-2.60447511
C	1.03119296	-2.90421198	-3.37475330
H	1.75182843	-4.78314438	-0.62789553
H	0.56625135	-0.79584567	-3.38408892
H	1.52616469	-4.96719944	-3.09047453
H	0.94785745	-3.00330248	-4.44832166
C	1.34101013	-2.25194127	0.80418737
C	2.75186168	-2.42092452	1.38635117
C	0.30098264	-2.96561919	1.67945067
H	-0.70927282	-2.79988892	1.30598477
H	0.50914122	-4.03470184	1.66242534
H	0.36291375	-2.61573699	2.70900067
H	3.00423821	-3.48054141	1.38639970
H	2.78557431	-2.05407880	2.41151496
H	3.49013019	-1.88385109	0.79129544
C	1.00580835	-0.78701813	0.67950590
N	0.78292844	-0.47355571	-0.56057002
C	0.93831511	0.14125822	1.81397773
H	1.94309645	0.24770153	2.22954342
H	0.55700916	1.11758650	1.53526806
H	0.31426981	-0.29466367	2.59463467
H	-1.21154121	0.56881951	-2.57392669

$TS_{E'}$ (rotation of C(O)Ph group); E_B2PLYP-D3BJ = -1188.43023993050; E_wB97XD = -1188.974814000; ZPE = 0.427157; Qcorr = 0.452613; Hcorr = 0.453557; Gcorr = 0.371397; ***imaginary frequency*** -96.9836 cm^{-1};

C	-3.44267568	1.25358909	-1.27450729
C	-4.35771111	2.22161576	-0.86536093
C	-3.86381926	0.28184914	-2.18066545
C	-5.65201795	2.23246127	-1.36271238
C	-5.16132422	0.28412107	-2.67173460
C	-6.05926492	1.26226784	-2.26814450
H	-4.04708453	2.97674417	-0.15525264
H	-3.17841296	-0.49546271	-2.49280223

H	-6.34493528	2.99960290	-1.04169568
H	-5.47328045	-0.48502347	-3.36650149
H	-7.07115703	1.26488793	-2.65181681
C	-2.04332452	1.27712577	-0.71238347
O	-1.90398422	1.68466083	0.49357826
C	-1.02056038	0.88520842	-1.54052918
C	0.36061581	0.83153276	-1.07500983
C	1.26312462	1.82023041	-1.08700810
C	1.02604875	3.20133000	-1.48433708
H	0.08230424	3.59171477	-1.82834200
C	2.19247637	3.84605909	-1.30806815
H	2.41493999	4.88623619	-1.48389104
C	3.13492370	2.84756929	-0.82615813
H	4.18005319	3.02363586	-0.60637963
N	2.60898053	1.67209560	-0.68876001
H	3.65327884	0.11464943	-0.97511010
C	1.30526189	-2.66716257	-0.63474919
C	0.97577171	-1.58084593	-1.42209550
C	1.57193916	-3.88252845	-1.23207640
C	0.90409943	-1.62305771	-2.79728888
C	1.49897634	-3.96339705	-2.61853180
C	1.17138860	-2.85152687	-3.38830372
H	1.83637055	-4.74734083	-0.63823691
H	0.66212472	-0.75159456	-3.38891429
H	1.70661284	-4.90478710	-3.10902375
H	1.12926873	-2.94015429	-4.46512839
C	1.31266113	-2.24090616	0.80723991
C	2.65918558	-2.47289041	1.50043556
C	0.17566981	-2.92298078	1.59013210
H	-0.79385889	-2.71990698	1.13579204
H	0.34940165	-3.99816808	1.57892303
H	0.16536323	-2.58169427	2.62425675
H	2.87151267	-3.54127891	1.50380979
H	2.61820434	-2.12382531	2.53162039
H	3.46531511	-1.95566604	0.98187512
C	1.01479555	-0.76868998	0.67809243
N	0.80319697	-0.45325798	-0.56392077
C	0.97286569	0.16704415	1.80726570
H	2.00041519	0.32429184	2.14629226
H	0.53219698	1.12333010	1.54506607
H	0.42868963	-0.28505606	2.63571146
O	4.26607647	-0.60002625	-1.23196286
H	3.72065188	-1.38733411	-1.28354573
H	-1.21070155	0.56758032	-2.55603905

$TS_{E'F'}$; E_B2PLYP-D3BJ = -1188.45315393860; E_wB97XD = -1188.994409930; ZPE = 0.427615; Qcorr = 0.452819; Hcorr = 0.453763; Gcorr = 0.372670;
imaginary frequency -208.6989 cm^{-1};

C	-3.72847799	0.83178462	-1.76868629
C	-4.95378856	0.50010256	-1.19248630
C	-3.70901521	1.61671488	-2.91994048
C	-6.13667758	0.95744973	-1.74696532

C	-4.89541236	2.05743033	-3.48596554
C	-6.10951814	1.73519837	-2.89736851
H	-4.97259191	-0.10960597	-0.29932933
H	-2.77088246	1.86891434	-3.39537964
H	-7.08153133	0.70716648	-1.28311776
H	-4.87052876	2.65418462	-4.38795584
H	-7.03413864	2.08835666	-3.33468808
C	-2.47523541	0.30090785	-1.14402763
O	-2.52684935	-0.74309083	-0.49245505
C	-1.26474611	1.07651952	-1.32822970
C	-0.04285230	0.76531483	-0.84137717
C	1.15623513	1.54304045	-0.91519724
C	1.42556752	2.83506895	-1.37336809
H	0.73245883	3.49999848	-1.86463823
C	2.75625166	3.08840364	-1.03612946
H	3.32160817	3.98459238	-1.24245548
C	3.22888703	1.93772216	-0.39018307
H	4.21842606	1.75009910	0.00111184
N	2.27495216	1.00019883	-0.33826355
H	3.05753442	-0.24582074	-1.77887535
C	1.43774559	-2.42730849	-0.28930313
C	0.50987849	-1.64730332	-0.95723667
C	1.86256887	-3.61692075	-0.84464195
C	-0.01923066	-1.99645405	-2.18141324
C	1.34221789	-3.99727829	-2.07778287
C	0.41665519	-3.19501721	-2.73552025
H	2.59283027	-4.23361538	-0.33704045
H	-0.72929382	-1.36648648	-2.69763005
H	1.66498393	-4.92376825	-2.53311692
H	0.02852140	-3.50339143	-3.69682495
C	1.82531107	-1.74951710	0.99670515
C	3.33453056	-1.58999489	1.17877942
C	1.23269832	-2.50271076	2.20392537
H	0.14798688	-2.58078385	2.13122218
H	1.65356682	-3.50711291	2.22311407
H	1.49182401	-1.99922356	3.13462032
H	3.77900839	-2.57546641	1.31705435
H	3.54879306	-0.99087863	2.06388109
H	3.78680195	-1.11492918	0.31164585
C	1.11050761	-0.42372852	0.84728952
N	0.27015406	-0.46877917	-0.19342695
C	0.91658481	0.50062568	1.98629038
H	1.86018026	0.66975351	2.49875069
H	0.48302684	1.44867214	1.68267384
H	0.23142541	0.01338815	2.68513231
O	3.43978076	-0.71525081	-2.53488766
H	2.93174249	-1.52763900	-2.59059669
H	-1.33982340	2.01733482	-1.85258658

F; E_B2PLYP-D3BJ = -1112.05502967320; E_wB97XD = -1112.576645380; ZPE = 0.405781; Qcorr = 0.427560; Hcorr = 0.428505; Gcorr = 0.354775;

C	-3.28888725	2.60837820	-1.20588009

C	-4.28739733	3.37041726	-0.60301105
C	-3.23230625	2.54198219	-2.59617820
C	-5.20481140	4.06337731	-1.37489210
C	-4.15973232	3.22374625	-3.36906826
C	-5.14397240	3.98924431	-2.76036021
H	-4.33595433	3.42286426	0.47629404
H	-2.47423119	1.94068115	-3.08035823
H	-5.96929548	4.66138036	-0.89668107
H	-4.11429931	3.15557824	-4.44789134
H	-5.86407647	4.52593734	-3.36407226
C	-2.32805218	1.84896614	-0.34000803
O	-2.67199420	1.55418512	0.81328606
C	-1.02656108	1.58628112	-0.88048406
C	-0.01935100	0.86473807	-0.29670002
C	1.38651711	1.10408409	-0.52523404
C	2.26596117	1.94231315	-1.17707009
H	2.01289315	2.73140621	-1.86509414
C	3.55676227	1.55255612	-0.75584406
H	4.49216834	1.98080415	-1.07716108
C	3.42352426	0.51133204	0.14688301
H	4.16317032	-0.04825300	0.69387105
N	2.10447716	0.24804502	0.25387402
H	-0.71293805	2.20502717	-1.70962013
C	-0.14964001	-2.45508819	0.80042506
C	-0.92248807	-1.31329610	0.58792405
C	-0.74329606	-3.69640228	0.87160007
C	-2.28725917	-1.40393211	0.38444403
C	-2.12206716	-3.79942729	0.70435505
C	-2.87490922	-2.66573220	0.44660803
H	-0.14102501	-4.58162435	1.03212708
H	-2.89284522	-0.53402204	0.20288702
H	-2.60226320	-4.76716936	0.76015706
H	-3.94316630	-2.75157221	0.29750602
C	1.32638710	-2.12180616	0.77371106
C	1.84068614	-2.38148118	-0.64890905
C	2.16265316	-2.91820622	1.76634614
H	1.77182813	-2.85660322	2.78051921
H	2.17013216	-3.96792531	1.47197312
H	3.19486124	-2.56535519	1.76643513
H	1.70565313	-3.43613526	-0.88856307
H	2.90180122	-2.14403316	-0.72820806
H	1.29608310	-1.79357714	-1.38905510
C	1.26344709	-0.59207905	1.07670808
N	-0.08421401	-0.17550501	0.59567205
C	1.42877111	-0.23265602	2.54244920
H	2.44302019	-0.45475003	2.87087422
H	1.23824410	0.83117106	2.67621620
H	0.72776606	-0.79957006	3.15315624

F'; E_B2PLYP-D3BJ = -1188.48670819090; E_wB97XD = -1189.035185520; ZPE = 0.429964; Qcorr = 0.455357; Hcorr = 0.456301; Gcorr = 0.374470;

C	-3.77673334	0.86460428	-1.93304872

C	-5.07070535	0.70768236	-1.43992668
C	-3.59058522	1.45537749	-3.18092853
C	-6.15888513	1.14620372	-2.17449684
C	-4.68236284	1.87652785	-3.92466793
C	-5.96634320	1.72881447	-3.42059937
H	-5.21721108	0.24692796	-0.47227746
H	-2.59546556	1.56824898	-3.58965560
H	-7.15883778	1.03255415	-1.77735026
H	-4.52910906	2.32055567	-4.89920305
H	-6.81708130	2.06548697	-3.99839416
C	-2.62817414	0.34754553	-1.12263654
O	-2.82155554	-0.58033138	-0.33661360
C	-1.35257780	1.01465979	-1.28650182
C	-0.19069299	0.70453962	-0.66583679
C	0.99328403	1.52134845	-0.64739358
C	1.48089221	2.74430806	-1.05239848
H	0.97924963	3.45814558	-1.68416776
C	2.76589720	2.85870890	-0.48047307
H	3.45508503	3.67783259	-0.60711410
C	3.00996182	1.71993373	0.26464185
H	3.86334555	1.45106256	0.86171987
N	1.94459526	0.89768575	0.11545983
H	2.52764548	-0.02549070	-2.13066163
C	1.48213434	-2.29755865	-0.28448117
C	0.31521119	-1.65817101	-0.67712599
C	1.88553999	-3.46148896	-0.90856662
C	-0.46032929	-2.15699750	-1.71046834
C	1.11474244	-3.98036298	-1.94346315
C	-0.04385151	-3.32651738	-2.33757791
H	2.79976509	-3.95476932	-0.60323235
H	-1.35605030	-1.65850122	-2.04321029
H	1.42190354	-4.88802436	-2.44527488
H	-0.63729623	-3.72533783	-3.14969390
C	2.15454922	-1.56334005	0.84790969
C	3.65034161	-1.37087439	0.61282353
C	1.96040610	-2.37251509	2.13778984
H	0.90705194	-2.55742966	2.34721409
H	2.45330093	-3.33747023	2.01797499
H	2.40696672	-1.86845552	2.99471437
H	4.13766638	-2.34581537	0.60019937
H	4.09692217	-0.78787034	1.41929750
H	3.85690588	-0.87872863	-0.33634202
C	1.35099337	-0.21929455	0.87352231
N	0.12469744	-0.45916889	0.06189040
C	1.00980646	0.30880537	2.25706099
H	1.92946672	0.50503136	2.80843745
H	0.45494447	1.24245637	2.16441270
H	0.40609351	-0.40133889	2.81480573
O	2.62116965	-0.47560123	-2.97456657
H	2.24321306	-1.34412535	-2.81407341
H	-1.33925285	1.92740207	-1.86434903

TS_{F3a}; E_B2PLYP-D3BJ = -1112.02765936350; E_wB97XD = -1112.548976560; ZPE = 0.404076; Qcorr = 0.425570; Hcorr = 0.426514; Gcorr = 0.353497;
imaginary frequency -148.9563 cm^{-1};

C	-3.95374093	2.75554524	-1.93307894
C	-4.36195025	4.08319458	-1.82411353
C	-4.64963459	1.91312075	-2.79825814
C	-5.42360811	4.56352777	-2.57577764
C	-5.71863289	2.38892270	-3.54332464
C	-6.10671762	3.71722229	-3.43835893
H	-3.83651245	4.74585375	-1.14918166
H	-4.36730733	0.87134189	-2.87841744
H	-5.71919118	5.60103214	-2.48719530
H	-6.25392489	1.71789752	-4.20268626
H	-6.93978644	4.08893470	-4.02058401
C	-2.79715943	2.26847521	-1.10041288
O	-2.62846092	2.80316512	0.05160020
C	-1.99275428	1.29111927	-1.62663213
C	-0.89395580	0.75518515	-0.84603464
C	0.45142899	1.19410130	-0.78778971
C	1.31840558	2.18716951	-1.21292097
H	1.06223408	3.04715013	-1.80849132
C	2.57931506	1.83920847	-0.71013184
H	3.49962187	2.38049283	-0.85408890
C	2.45659996	0.65144567	0.00851664
H	3.19668802	0.07208146	0.53461021
N	1.17446364	0.27394597	-0.06344082
H	-2.14957917	0.85528560	-2.60289422
C	-1.01912596	-2.59133769	-0.04303653
C	-1.81980018	-1.45927290	-0.14520888
C	-1.61027361	-3.83776911	-0.05632739
C	-3.19181903	-1.51009723	-0.26452566
C	-2.99478162	-3.91963359	-0.18067903
C	-3.77270012	-2.77347187	-0.28636185
H	-1.00999616	-4.73478891	0.02102348
H	-3.78563941	-0.60995380	-0.32725196
H	-3.47241046	-4.89015624	-0.19246985
H	-4.84691864	-2.86056618	-0.37644971
C	0.45398584	-2.21112529	-0.00031545
C	1.01586939	-2.23708133	-1.42599874
C	1.29661010	-3.09644116	0.90478665
H	0.87242103	-3.18966490	1.90287638
H	1.36429308	-4.09445836	0.47175152
H	2.30860337	-2.69816485	0.98866317
H	0.95010658	-3.25221743	-1.81618128
H	2.06291611	-1.93312115	-1.43036183
H	0.45974611	-1.58151634	-2.09751547
C	0.31774168	-0.73805633	0.51156924
N	-0.97466705	-0.32773701	-0.08744619
C	0.27932980	-0.59784185	2.02276927
H	1.26951332	-0.80578636	2.42466696
H	-0.00413114	0.41950000	2.28699405
H	-0.43388308	-1.29560022	2.45714318

3a; E_B2PLYP-D3BJ = -1112.06181082590; E_wB97XD = -1112.583696180; ZPE = 0.406190; Qcorr = 0.427942; Hcorr = 0.428886; Gcorr = 0.355463;

C	-0.93853432	4.68396285	1.39486245
C	-1.06682674	5.82127450	0.59979039
C	-1.85181343	4.47531380	2.42661877
C	-2.09398401	6.72374576	0.81986432
C	-2.86977817	5.38797093	2.65828354
C	-2.99726644	6.50999313	1.85246151
H	-0.35874903	5.98947370	-0.20043253
H	-1.76313987	3.61188947	3.07199764
H	-2.18985492	7.59563306	0.18630626
H	-3.56416949	5.22165030	3.47115253
H	-3.79682350	7.21731970	2.02945704
C	0.20361403	3.74499954	1.12057780
O	1.22856002	4.20308847	0.60080289
C	0.01472483	2.37067811	1.46864852
C	0.91606579	1.35972012	1.27674853
C	2.24592315	1.34334616	0.70243920
C	3.27968979	2.12251798	0.21306297
H	3.29591989	3.19398398	0.15445069
C	4.29827032	1.23245509	-0.18529859
H	5.24841629	1.50067166	-0.61738847
C	3.86986282	-0.05787487	0.06860299
H	4.34881184	-1.00838008	-0.09570976
N	2.63561781	0.03373270	0.59762905
H	-0.93729022	2.09862331	1.89117567
C	-0.50276227	-1.69367725	0.64812057
C	-0.61495860	-0.60710036	1.51178977
C	-1.58705025	-2.51695209	0.43045007
C	-1.78981245	-0.32696345	2.18179115
C	-2.78595597	-2.23860388	1.08341877
C	-2.88310593	-1.15628307	1.94525649
H	-1.51024670	-3.36290987	-0.24070897
H	-1.86241366	0.48901917	2.88622062
H	-3.64532796	-2.87581129	0.92284914
H	-3.81562709	-0.95815066	2.45666248
C	0.88049441	-1.73225340	0.02706186
C	0.83381502	-0.99364856	-1.31612041
C	1.42824981	-3.13638711	-0.18270287
H	1.37981546	-3.73915026	0.72258038
H	0.84810231	-3.64217277	-0.95499268
H	2.46530236	-3.09354760	-0.51927913
H	0.15938390	-1.52206584	-1.98986181
H	1.82280543	-0.96147308	-1.77466089
H	0.46694597	0.02798953	-1.20903522
C	1.66059923	-0.89725101	1.10120863
N	0.63673589	0.04721155	1.60503910
C	2.24161869	-1.72990924	2.22862967
H	3.05075080	-2.35441502	1.85305616
H	2.63403438	-1.07139373	3.00157656
H	1.47755326	-2.37312885	2.66273916

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