# π-Extension of Heterocycles via a Pd-Catalyzed Heterocyclic Aryne Annulation: π-Extended Donors for TADF Emitters

Katie A. Spence,[§,†] Jason V. Chari,[§,†] Mattia Di Niro,[⊥] Robert B. Susick,[†] Narcisse Ukwitegetse,[⊥] Peter I. Djurovich,[⊥] Mark E. Thompson,*[,⊥] and Neil K. Garg*[,†]

[†]*Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095, United States*

[⊥] *Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States*

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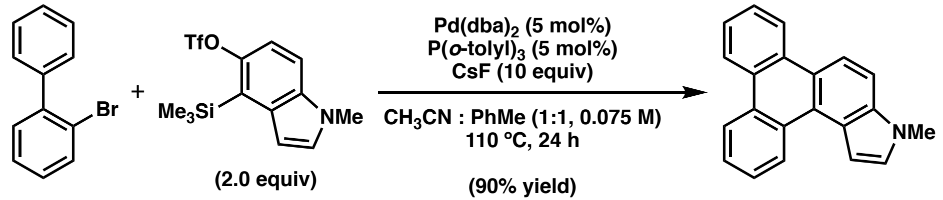
## Materials and Methods

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen or argon and commercially obtained reagents were used as received. Anhydrous solvents were either freshly distilled or passed through activated alumina columns, unless otherwise stated. Reaction temperatures were controlled using an IKAmag temperature modulator and, unless stated otherwise, reactions were performed at room temperature (approximately 23 °C). Cesium Fluoride (CsF) and Bis(dibenzylidenacetone)palladium(0) ($Pd(dba)_2$) were obtained from Strem Chemicals and stored in a desiccator. Tri(*o*-tolyl)phosphine ($P(o\text{-tolyl})_3$), 1,1,1,3,3,3-hexamethyldisilazane (HMDS), *tert*-butyllithium (*t*-BuLi), sodium hydride (NaH), and sodium *ter*-butoxide (NaO*t*-Bu) were obtained from Sigma Aldrich. Methyl iodide (MeI) was acquired from Spectrum Chemical. Triflic anhydride was purchased from Oakwood Chemical and distilled over phosphorous pentoxide prior to use. Di-tert-butyl decarbonate and 4-dimethylaminopyridine (DMAP) were obtained from Oakwood Chemical. Triethylamine was purchased from Fischer Scientific and passed through an activated alumina column prior to use. 2-Bromobiphenyl (**23**) was obtained from Combi-Blocks and purified by flash chromatography (100% Hexanes) prior to use. 3-Bromo-2-phenylpyridine (**43**) was obtained from Combi-Blocks. Bromobiaryls **39**,[1] **41**,[2] **45**,[3] **47,**[4] and **49**,[5] were prepared according to literature procedures. The silyl triflates **14**,[6] **33**,[7] and **24**[7] were prepared following literature procedures. 3-Bromo-2-hydroxycarbazole (**26**) was prepared in one step from 2-hydroxycarbazole following a literature protocol.[8] NHC–Au–Cl complexes **51**[9] and **52**[10] were prepared following literature procedures. Regioisomeric ratios for indolyne annulation products were determined by analysis of the $^1H$ NMR spectra of the crude reaction mixtures. Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm for analytical chromatography and 0.50 mm for preparative chromatography) and visualized using UV(254 nm). Celite® was purchased from Fischer Scientific and used as received. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. $^1H$ NMR spectra were recorded on Bruker spectrometers (at 400, 500 and 600 MHz) and are reported relative to residual solvent signals. Data for $^1H$ NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration. Data for $^{13}C$ NMR are reported in terms of chemical shift (at 101 and 125 MHz). IR spectra were recorded on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency absorption ($cm^{-1}$). DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo

Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using $CH_2Cl_2$ as the solvent. Ionization was accomplished using UHP He plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (–) Ion calibration solutions (Thermo Fisher Scientific). UV-visible absorption spectra were recorded by using Hewlett-Packard 4853 diode array spectrometer. Steady state emission spectra were recorded on Quanta-Master Photon Technology International phosphorescence/fluorescence spectrofluorometer. Emission quantum yields were measured using Hamamatsu C9920 system equipped with a xenon lamp, integrating sphere and model C10027 photonic multichannel analyzer (PMA). Emission lifetimes were acquired on IBH Fluorocube instrument by using time-correlated single photon counting (TCSPC) method.

## Experimental Procedures

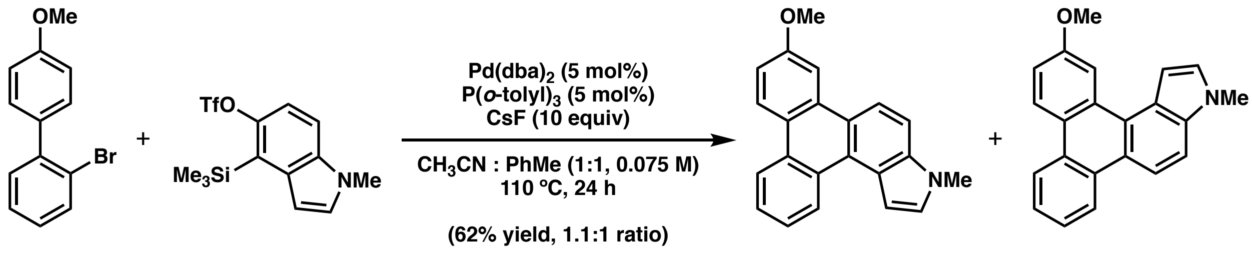
### A. Scope of Pd-Catalyzed Annulation with *N*-Me-4,5-Indolyne



***23*** ***14*** ***16***

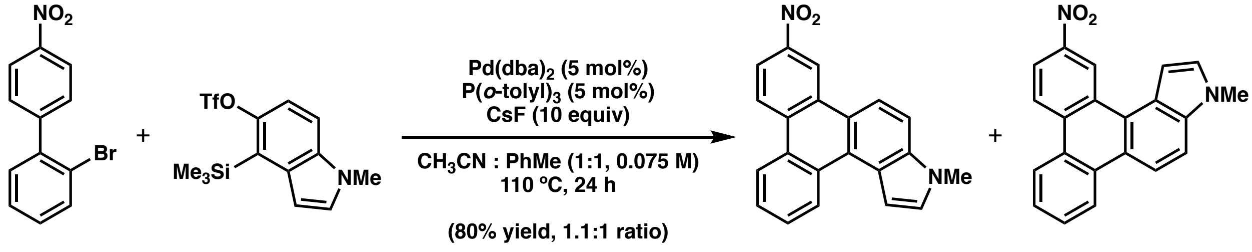
**Representative Procedure A for hetaryne annulations (Figure 3, annulation product 16 used as an example).** A 1-dram vial was charged with Pd(dba)$_2$ (3.7 mg, 0.064 mmol, 5 mol%). Next, toluene (0.86 mL), P(*o*-tolyl)$_3$ (2.0 mg, 0.064 mmol, 5 mol%), 2-bromobiphenyl (**23**) (30.0 mg, 0.129 mmol, 1.0 equiv), silyl triflate **14** (90.5 mg, 0.257 mmol, 2.0 equiv), and acetonitrile (0.86 mL) were added, followed by an oven-dried magnetic stirbar and then CsF (195 mg, 1.29 mmol, 10 equiv). The vial was purged with nitrogen for 3 minutes, then sealed with a Teflon-lined screw cap and stirred at 110 °C for 24 h. Then, after cooling to 23 °C, the mixture was transferred with $CH_2Cl_2$ (10 mL) and $H_2O$ (2 mL) to a 150 mL separatory funnel containing brine (15 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography (100% Hexanes → 200:1 Hexanes:EtOAc) to afford annulation product **16** (90% yield, average of two experiments) as an off-white solid. Indole **16**: mp: 139–144 °C; $R_f$ 0.41 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $CDCl_3$): δ 9.24 (d, *J* = 8.0, 1H), 8.78 (d, *J* = 8.0, 1H), 8.72 (t, *J* = 7.0, 2H), 8.57 (d, *J* = 9.0, 1H), 7.74 (t, *J* = 7.4, 1H), 7.73–7.62 (m, 4H), 7.53 (d, *J* = 2.8, 1H), 7.28 (d, *J* = 3.0, 1H), 3.92 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 136.4, 131.3, 131.2, 130.4, 128.9, 128.8, 127.17, 127.15, 126.7, 126.4, 125.9, 124.6, 124.1, 123.8, 123.6, 123.28, 123.25, 117.7, 110.5, 104.0, 33.3; IR (film): 3069, 2924, 2850, 1514, 1492, 1441, 1417, 1351, 1248, 754, 740, 718 cm$^{-1}$; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{21}H_{16}N^+$, 282.12773; found 282.12717.

*Any modifications of the conditions shown in the representative procedure above are specified in the following schemes, which depict all of the results shown in Figure 3.*



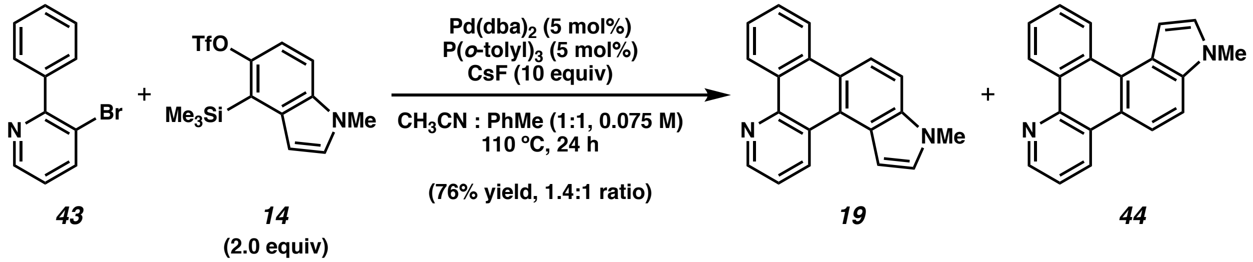
***39*** ***14*** **(2.0 equiv)** ***17*** ***40***

**Indoles 17 and 40**. Followed representative procedure A. Purification by flash chromatography (50:1 Hexanes:EtOAc) afforded an inseparable mixture of indoles **17** and **40** (62% yield, average of two experiments, 1.1:1 ratio, unassigned) as a white solid. Indoles **17** and **40**: $R_f$ 0.27 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$, combined): δ 9.42 (dd, *J* = 8.3, 1.3, 1H), 8.93 (d, *J* = 2.6, 1H), 8.69 (dd, *J* = 7.9, 1.3, 1H), 8.57–8.50 (m, 5H), 8.48 (d, *J* = 9.0, 1H), 8.22 (d, *J* = 2.5, 1H), 7.60–7.47 (m, 6H), 7.30–7.26 (m, 3H), 7.21 (dd, *J* = 9.2, 2.6, 1H), 6.72 (d, *J* = 6.7, 1H), 6.69 (d, *J* = 3.2, 1H), 3.61 (s, 3H), 3.55 (s, 3H), 3.001 (s, 3H), 2.995 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$, combined): δ 159.6, 159.3, 136.8, 136.6, 133.32, 133.31, 131.2, 131.0, 130.8, 129.7, 128.6, 128.5, 127.6, 126.6, 126.4, 126.2, 126.0, 125.8, 125.4, 125.3, 125.2, 125.1, 125.0, 124.6, 124.5, 124.4, 124.0, 123.6, 123.27, 123.25, 118.1, 118.0, 115.5, 115.0, 110.8, 110.5, 110.1, 106.5, 104.5, 104.0, 55.0, 54.9, 32.31, 32.28; IR (film): 2934, 2834, 1614, 1510, 1414, 1246, 1227 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H$^+$] calcd for $C_{22}H_{18}NO^+$, 312.13829; found 312.13897.



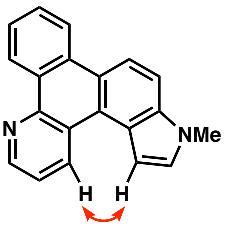
***41*** ***14*** **(2.0 equiv)** ***18*** ***42***

**Indoles 18 and 42**. Followed representative procedure A. Purification by flash chromatography (50:1 Hexanes:EtOAc → 20:1 Hexanes:EtOAc) afforded an inseparable mixture of indoles **18** and **42** (80% yield, average of two experiments, 1.4:1 ratio, unassigned) as a yellow solid. Indoles **18** and **42**: $R_f$ 0.45 (4:1 Hexanes:EtOAc); $^1$H NMR (600 MHz, $CDCl_3$, major): δ 10.10 (d, *J* = 2.4, 1H), 8.79 (d, *J* = 9.1, 1H), 8.71 (d, *J* = 8.3, 1H), 8.66 (d, *J* = 8.2, 1H), 8.55 (d, *J* = 9.2, 1H), 8.41 (dd, *J* = 9.0, 2.3, 1H), 7.78–7.72 (m, 2H), 7.67 (ddd, *J* = 8.1, 7.0, 1.2, 1H), 7.54 (d, *J* = 3.1, 1H), 7.39 (d, *J* = 3.2, 1H), 4.00 (s, 3H); $^1$H NMR (600 MHz, CDCl$_3$, minor): δ 9.54 (d, *J* = 2.3, 1H), 9.21 (d, *J* = 8.3, 1H), 8.75 (d, *J* = 9.1, 1H), 8.70 (d, *J* = 8.3, 1H), 8.55 (d, *J* = 8.9, 1H), 8.35 (dd, *J* = 9.0, 2.3, 1H), 7.82 (ddd, *J* = 8.1, 7.0, 1.3, 1H), 7.76–7.71 (m, 2H), 7.51 (d, *J* = 3.1, 1H), 7.36 (d, *J* = 3.2, 1H), 4.00 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, combined): δ 146.4, 146.0, 136.8, 136.4, 134.8, 133.3, 132.51, 132.48, 131.3, 131.0, 129.9, 129.4, 129.0, 128.7, 128.6, 127.4, 127.3, 126.8, 126.4, 125.2, 124.6, 124.4, 124.21, 124.17, 124.1, 123.8, 123.60, 123.55, 123.5, 123.1, 122.8, 119.9, 119.53, 119.47, 117.5, 117.4, 111.7, 111.1, 104.0, 103.4, 33.4, 33.3; IR (film): 2919, 2852, 1597, 1515, 1346, 854, 747 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H$^+$] calcd for $C_{21}H_{15}N_2O_2^+$, 327.11280; found 327.11387.



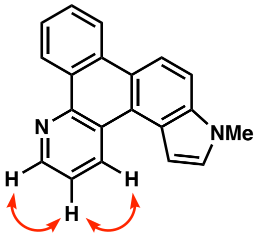
**Indoles 19 and 44**. Followed representative procedure A. Purification by flash chromatography (100% Hexanes → 50:1 Hexanes:EtOAc → 9:1 Hexanes:EtOAc) afforded an inseparable mixture of indoles **19** and **44** (76% yield, 1.4:1 ratio, average of two experiments) as a pale yellow solid. Indole **19**: R$_f$ 0.34 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$): δ 9.40 (ddd, *J* = 8.2, 4.7, 1.4, 2H), 8.99 (dd, *J* = 4.3, 1.6, 1H), 8.66 (d, 8.2, 1H), 8.54 (d, 8.5, 1H), 7.76 (ddd, *J* = 8.1, 6.9, 1.6, 1H), 7.71 (ddd, *J* = 8.3, 6.8, 1.2, 1H), 7.65 (d, *J* = 9.0, 1H), 7.64–7.60 (m, 1H), 7.38 (d, *J* = 2.9, 1H), 7.27 (d, *J* = 3.2, 1H), 3.90 (s, 3H). Indole **44**: R$_f$ 0.34 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$): δ 9.46 (dd, *J* = 8.1, 1.3, 1H), 9.18 (d, *J* = 8.2, 1H), 8.95 (dd, *J* = 4.3, 1.6, 1H), 8.89 (dd, *J* = 8.4, 1.3, 1H), 8.41 (d, *J* = 9.0, 1H), 7.83 (ddd, *J* = 8.2, 7.0, 1.7, 1H), 7.77 (ddd, *J* = 7.2, 5.6, 1.2, 1H), 7.64–7.60 (m, 1H), 7.55 (dd, *J* = 8.3, 4.3, 1H), 7.53 (d, *J* = 3.1, 1H), 7.29 (d, *J* = 3.2, 1H), 3.91 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, combined): 147.69, 147.66, 146.9, 145.6, 136.6, 136.3, 134.2, 132.8, 132.7, 131.4, 131.0, 130.1, 129.3, 129.2, 128.8, 128.4, 126.6, 126.4, 126.2, 126.1, 125.8, 125.4, 125.2, 124.6, 124.2, 124.0, 123.9, 123.2, 122.9, 122.8, 122.1, 121.5, 117.7, 117.3, 111.1, 110.6, 104.0, 103.2, 33.3 (2C); IR (film): 3059, 2920, 1739, 1609, 1579, 1513, 1477, 1444, 1418, 1399, 1349, 1290, 1241 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H$^+$] calcd for $C_{20}H_{15}N_2^+$, 283.12297; found 283.11932.

The structure of **19** was verified by 2D-NOESY and 2D-COSY of the mixture, as the following interactions were observed:

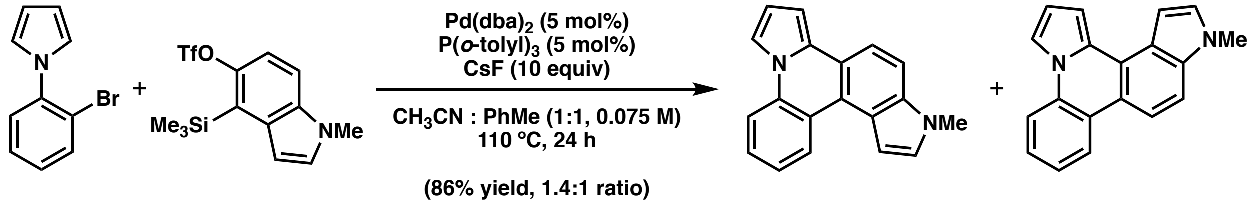


***19***
***2D-NOESY***

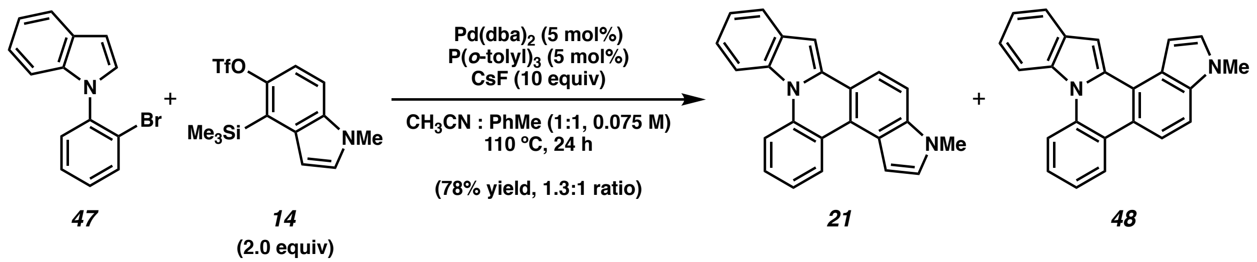
and



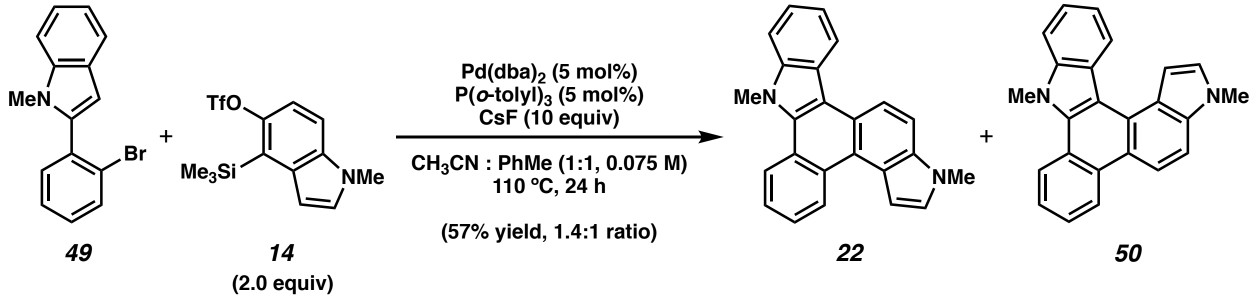
***19***
***2D-COSY***



**Pyrroles 20 and 46**. Followed representative procedure A. Purification by flash chromatography (20:1 Hexanes:Benzene) afforded an inseparable mixture of pyrroles **20** and **46** (86% yield, 1.4:1 ratio, average of two experiments, unassigned) as a yellow solid. Pyrroles **20** and **46**: $R_f$ 0.56 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$, combined): δ 9.01 (dd, *J* = 8.0, 1.5, 1H), 8.33–8.28 (m, 1H), 8.13 (d, *J* = 8.9, 1H), 8.01 (d, *J* = 8.7, 1H), 7.65 (dd, *J* = 3.0, 1.4, 1H), 7.58 (dd, *J* = 3.0, 1.4, 1H), 7.4 (m, 3H), 7.28 (dd, *J* = 3.2, 0.7, 1H), 7.27–7.23 (m, 2H), 7.22–7.19 (m, 1H), 7.19–7.17 (m, 2H), 7.10 (t, *J* = 0.9, 1H), 7.09 (m, 2H), 6.92 (dd, *J* = 4.0, 2.9, 1H), 6.84 (dd, *J* = 3.9, 2.8, 1H), 6.67 (d, *J* = 3.0, 1H), 6.62 (d, *J* = 3.3, 1H), 2.96 (s, 3H), 2.92 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$, combined): δ 136.7, 136.2, 134.0, 132.9, 131.5, 129.6, 128.9, 128.8, 127.60, 127.58, 127.0, 124.3, 124.2, 124.0, 123.7, 123.5, 123.4, 122.9, 121.5, 120.4, 118.9, 118.6, 117.9, 117.0, 115.3, 115.2, 113.0, 112.9, 112.7, 112.2, 111.5, 108.8, 105.6, 102.94, 102.88, 101.0, 32.22, 32.19; IR (film): 3102, 2923, 1500, 1441, 1355 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H$^+$] calcd for $C_{19}H_{15}N_2^+$, 271.12297; found 271.12191.

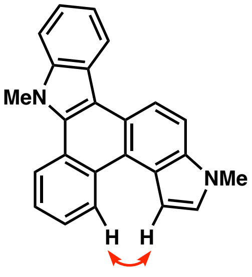


**Indoles 21 and 48**. Followed representative procedure A. Purification by flash chromatography (100% Hexanes → 100:1 Hexanes:EtOAc → 25:1 Hexanes:EtOAc → 9:1 Hexanes:EtOAc, followed by a second column of 9:1 Hexanes:EtOAc) afforded an inseparable mixture of indoles **21** and **48** (78% yield, 1.3:1 ratio, average of two experiments, unassigned) as a bright yellow solid. Indoles **21** and **48**: $R_f$ 0.32 (4:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$, major): δ 8.43 (dd, *J* = 8.2, 1.0, 1H), 8.28 (dd, *J* = 8.0, 1.1, 2H), 8.04 (d, *J* = 9.0, 1H), 7.98 (d, *J* = 8.6, 1H), 7.79 (s, 1H), 7.41 (ddd, *J* = 7.8, 6.8, 0.9, 1H), 7.36–7.31 (m, 1H), 7.30–7.17 (m, 3H), 7.08 (dd, *J* = 8.9, 0.6, 1H), 6.63 (d, *J* = 3.2, 1H), 2.94 (s, 3H); $^1$H NMR (500 MHz, $C_6D_6$, minor): δ 8.95 (dd, *J* = 8.0, 1.6, 1H), 8.41 (dd, *J* = 8.0, 1.1, 1H), 8.23 (d, *J* = 8.4, 1H), 7.98 (d, *J* = 7.6, 1H), 7.91 (d, *J* = 7.9, 1H), 7.41 (ddd, *J* = 7.5, 6.9, 0.9, 1H), 7.36–7.31 (m, 1H), 7.30–7.17 (m, 4H), 7.04 (dd, *J* = 8.7, 0.7, 1H), 6.58 (d, *J* = 3.2, 1H), 2.92 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$, combined; 44 of 46 signals observed): δ 137.6, 137.2, 136.7, 136.5, 135.6, 135.5, 134.1, 133.9, 131.7, 131.6, 129.3, 129.2, 127.6, 127.3, 124.6, 124.3, 124.0, 123.8, 123.7, 123.04, 122.95, 122.3, 122.11, 122.06, 121.6, 121.5, 121.4, 121.1, 121.0, 120.7, 119.9, 118.7, 116.8, 116.7, 116.6, 114.8, 111.3, 110.5, 103.2, 102.9, 99.8, 95.2, 32.21, 32.18; IR (film): 3040, 2923, 1738, 1601, 1550, 1509, 1490, 1447, 1419, 1355; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{17}N_2^+$, 321.13862; found 321.13951.



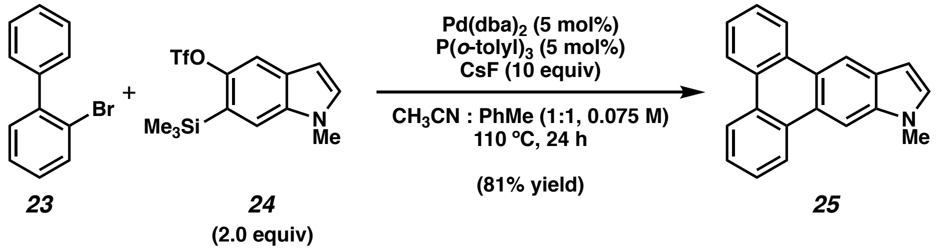
**Indoles 22 and 50**. Followed representative procedure A. Purification by flash chromatography (100% Hexanes → 200:1 Hexanes:EtOAc → 100:1 Hexanes:EtOAc) afforded an inseparable mixture of indoles **22** and **50** (57% yield, 1.4:1 ratio, average of two experiments) as a yellow amorphous solid. Indole **22**: R$_f$ 0.40 (3:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$): δ 9.74 (d, *J* = 8.5, 1H), 9.09 (d, *J* = 8.8, 1H), 8.92–8.88 (m, 1H), 8.48 (dd, *J* = 8.3, 0.9, 1H) 7.70–7.65 (m, 2H), 7.59–7.43 (m, 4H), 7.29 (dd, *J* = 7.5, 1.5, 1H), 6.81 (d, *J* = 3.1, 1H), 3.57 (s, 3H), 3.11 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$; 22 of 24 signals observed): 141.8, 134.8, 134.2, 132.7, 125.7, 125.3, 125.2, 124.4, 123.9, 123.8, 123.6, 123.3, 122.6, 122.1, 120.3, 118.8, 115.7, 111.4, 109.9, 103.9, 34.0, 32.4. Indole **50**: R$_f$ 0.40 (3:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$): δ 9.37 (d, *J* = 8.1, 1H), 8.92–8.88 (m, 1H), 8.68 (d, *J* = 9.1, 1H), 8.38 (dd, *J* = 8.4, 0.9, 1H), 7.95 (d, *J* = 3.1, 1H), 7.59–7.43 (m, 3H), 7.40 (ddd, *J* = 7.9, 7.1, 1.1, 1H), 7.34 (dd, *J* = 9.1, 0.6, 1H), 7.26 (d, *J* = 8.1, 1H), 6.72 (d, *J* = 3.1, 1H), 3.54 (s, 3H), 3.10 (s, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$; 23 of 24 signals observed): 141.5, 136.5, 136.2, 132.8, 126.3, 125.8, 125.1, 124.8, 124.54, 124.51, 124.46, 123.7, 123.6, 123.1, 121.7, 119.2, 118.3, 115.3, 109.7, 108.1, 105.8, 34.0, 32.4; IR (film, entire mixture): 3055, 2923, 2854, 1737, 1509, 1472, 1374, 1342, 1245, 1102 cm$^{-1}$; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{19}N_2^+$, 335.15428; found 335.15396.

The structure of **22** was verified by 2D-NOESY of the mixture, as the following interaction was observed:



***22***

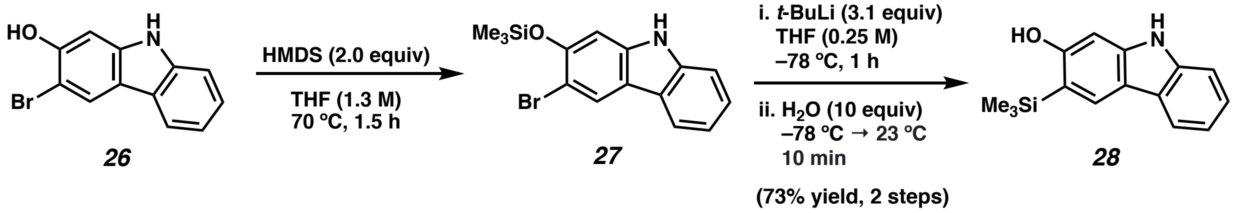
***2D-NOESY***



**Indole 25**. Followed representative Procedure A. Purification by flash chromatography (Hexanes → 1:1 Hexanes:Benzene) afforded indole **25** (81% yield, average of two experiments) as an off-white solid. Indole **25**: mp 169.6–172.0 °C; R$_f$ 0.25 (9:1 Hexanes:EtOAc); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.73 (d, *J* = 8.3, 2H), 8.62 (t, *J* = 7.7, 2H), 8.51 (s, 1H), 7.66–7.56 (m, 4H),

7.27 (d, *J* = 2.6, 1H), 6.70 (dd, *J* = 0.8, 3.1, 1H), 3.99 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$; 27 of 28 signals observed): δ 137.4, 132.0, 131.4, 131.2, 129.6, 129.3, 129.0, 127.3, 127.1, 126.6, 126.1, 125.7, 123.56, 123.55, 123.4, 123.22, 123.15, 115.1, 102.3, 101.1, 33.2; IR (film): 3081, 2928, 2811, 1628, 1601, 1520, 1446, 1218, 1085, 754 cm$^{-1}$; HRMS–APCI (m/z) $[M]^+$ calcd for $C_{21}H_{16}N^+$, 281.11990; found 281.12065.

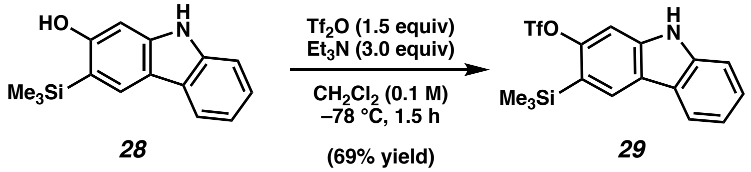
## B. Synthesis of Silyl Triflate Precursor to 2,3-Carbazolyne



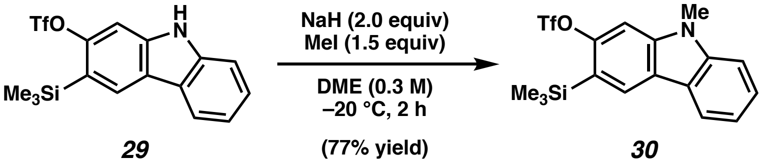
**Silyl alcohol 28**. A 20 mL scintillation vial was charged with 3-bromo-2-hydroxycarbazole (**26**, 4.3 g, 16 mmol, 1.0 equiv) and THF (5.6 mL, 1.3 M). HMDS (6.9 mL, 2.0 equiv, 33 mmol) was added in one portion. The vial was sealed with a Teflon cap, and subsequently placed in an aluminum block preheated to 70 °C, where it was allowed to stir for 1.5 h. After stirring for 1.5 h, the reaction mixture was cooled to 23 °C and concentrated under reduced pressure to afford the intermediate silyl enol ether **27** as a pink solid. This was carried forward without further purification.

The crude solid was dissolved in THF (8.5 mL, 0.25 M) and purged with nitrogen for 3 minutes, before being cooled to –78 °C. *tert*-Butyllithium (1.70 M, 4.17 mL, 7.09 mmol, 3.1 equiv) was then added dropwise over 10 min. The solution was allowed to stir for 1 hour at –78 °C. After the allotted time, deionized $H_2O$ (408 μL, 22.5 mmol, 10 equiv) was added dropwise over 2 min. The solution was then allowed to warm to 23 °C over 10 min and the mixture was transferred to a separatory funnel with $H_2O$ (20 mL) and $CH_2Cl_2$ (20 mL). The layers were then separated and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was then purified by flash chromatography (100% Benzene) to afford silyl alcohol **28** as a white solid (3.1 g, 73% yield over two steps). Silyl alcohol **28**: mp: >200 °C; $R_f$ 0.15 (100% Benzene); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.03 (s, 1H), 8.00 (d, *J* = 7.7, 1H), 7.84 (s, 1H), 7.36–7.32 (m, 2H), 7.21 (dd, J = 6.6, 2.2, 1H), 6.72 (d, J= 2.4, 1H), 4.94 (s, 1H), 0.39 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ

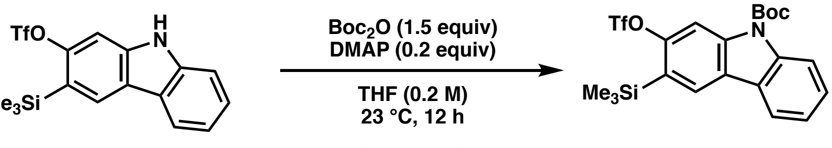
159.4, 141.8, 139.2, 126.9, 124.4, 123.4, 119.6, 119.3, 117.5, 117.2, 110.2, 96.0, –0.7; IR (film): 3416, 3016, 2970, 2926, 2854, 1738, 1366 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{18}NOSi^+$, 256.1152; found 256.1171.



**Silyl triflate 29.** Silyl alcohol **28** (403 mg, 1.58 mmol, 1.00 equiv) was suspended in $CH_2Cl_2$ (15 mL). The solution was purged with nitrogen for 3 minutes, then cooled to –78 °C. Triethylamine (0.66 mL, 4.7 mmol, 3.0 equiv) was then added in one portion followed by trifluoromethanesulfonic anhydride (400 µL, 2.37 mmol, 1.5 equiv), which was added dropwise over 5 min. The solution was allowed to stir for 1.5 h at –78 °C. After the allotted time, saturated aqueous $NaHCO_3$ (20 mL) was added over 1 minute. The solution was then allowed to warm to 23 °C over 10 min and the mixture was transferred to a separatory funnel with $H_2O$ (10 mL) and $CH_2Cl_2$ (20 mL). The layers were then separated and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was then purified by flash chromatography (100% Benzene) to afford silyl triflate **29** as a clear oil (375 mg, 69% yield). Silyl triflate **29**: $R_f = 0.59$ (100% Benzene); $^1$H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.16 (s, 1H), 8.08 (d, J = 7.9, 1H), 7.46 – 7.44 (m, 3H), 7.28 (ddd, J = 7.8, 5.0, 3.1, 1H), 0.44 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 153.3, 140.4, 140.2, 127.5, 126.6, 122.7, 122.3, 121.9, 120.43, 120.41, 110.9, 102.0, 0.40; IR (film): 3443, 3016, 2970, 2948, 1739, 1217 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H]$^+$ calcd for $C_{16}H_{17}NO_3F_3SSi^+$, 388.0645; found 388.0659.



***N*-Me-Carbazole Silyl Triflate 30**. To a 2-dram vial was added carbazole silyl triflate **29** (196 mg, 0.506 mmol, 1.00 equiv) and DME (1.7 mL, 0.3 M). The resulting mixture was stirred under positive nitrogen pressure. The mixture was cooled to –20 °C in a dry ice and water/methanol (7:3) bath for 5 min. To the cooled solution was added iodomethane (48 µL, 0.76 mmol, 1.5 equiv) in a single portion. Next, the septum was removed and NaH (60% dispersion in mineral oil, 40.5 mg, 1.01 mmol, 2.0 equiv) was added in a single portion, then the septum was quickly replaced. The reaction continued to stir under nitrogen at –20 °C for 2 h, at which point the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL) and allowed to stir at 23 °C for 5 min. The mixture was transferred to a separatory funnel containing water (10 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a yellow solid. The crude residue was purified by flash chromatography (16:1 Hexanes:Benzene) to afford *N*-Me-carbazole silyl triflate **30** (156 mg, 77% yield) as a white solid. *N*-Me-carbazole silyl triflate **30**: mp 128.2–130.3 °C; R*f* 0.79 (9:1 Hexanes:EtOAc); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.11 (d, *J* = 7.9, 1H), 7.53–7.50 (m, 1H), 7.43 (d, *J* = 8.3, 1H), 7.38 (s, 1H), 7.30 (td, *J* = 7.5, 0.9, 1H), 3.85 (s, 3H), 0.44 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$; 14 of 15 signals observed): δ 153.5, 142.1, 141.9, 127.4, 126.4, 122.1, 121.9, 121.0, 120.4, 119.9, 108.8, 100.0, 29.3, –0.4; IR (film): 3017, 2955, 1739, 1596, 1414, 1206 cm$^{-1}$; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{17}H_{19}F_3NO_3SSi^+$, 402.0802; found 402.0690.

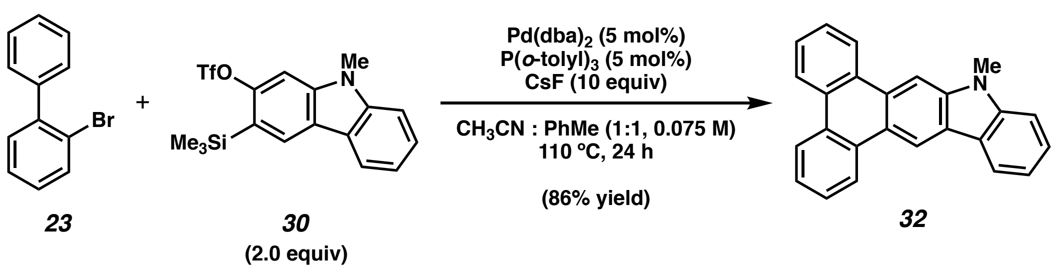


*29* *31*

***N*-Boc-Carbazole Silyl Triflate 31**. To a 50 mL round bottom flask was added carbazole silyl triflate **29** (1.00 g, 2.58 mmol, 1.0 equiv), THF (13 mL, 0.2 M), 4-dimethylaminopyridine (63 mg, 0.51 mmol, 0.2 equiv), and di-*tert*-butyl dicarbonate (839 mg, 3.84 mmol, 1.5 equiv). The resulting mixture was purged with nitrogen for 3 minutes, then allowed to stir under positive nitrogen pressure at 23 °C for 2 h. The mixture was then quenched with deionized water (10 mL). The solution was transferred to a separatory funnel and the layers were separated. The aqueous layer was subsequently extracted with $CH_2Cl_2$ (3 x 10 mL). The organic layers were combined, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure to afford a crude, yellow solid. The crude material was purified by flash chromatography (100:1 Hexanes:EtOAc) to yield *N*-Boc-carbazole silyl triflate **31** (1.17 g, 93% yield) as a white solid. *N*-Boc-carbazole silyl triflate **31**: mp: 170.5–172.3 °C; R*f* 0.57 (9:1 Hexanes:EtOAc); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.36 (d, *J* =

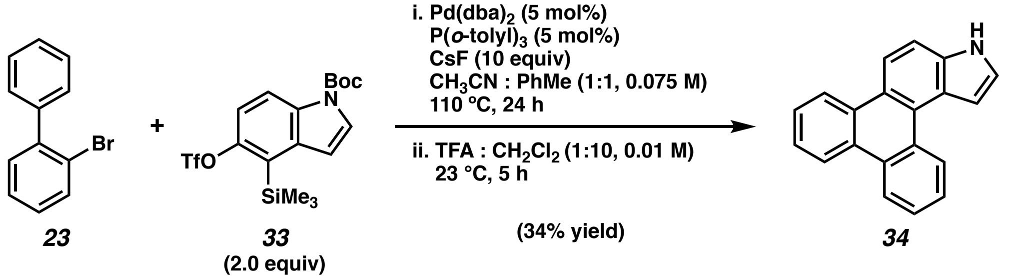
8.6, 1H), 8.35 (s, 1H), 8.08 (s, 1H), 8.00 (d, *J* = 7.9, 1H), 7.51 (td, *J* = 7.6, 1.0, 1H), 7.39 (td, *J* = 7.5, 1.0, 1H), 1.76 (s, 9H), 0.44 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$; 16 of 17 signals observed): δ 153.9, 150.6, 139.6, 127.8, 126.6, 126.4, 124.9, 124.5, 123.6, 119.9, 119.8, 116.5, 108.3, 85.1, 28.4, –0.5; IR (film): 2983, 1728, 1393, 1355, 1212, 1155, 1140 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H]$^+$ calcd for $C_{21}H_{25}F_3NO_5SSi^+$, 488.1169; found 488.1198.

## C. Annulation of *N*-Me-Carbazolyne



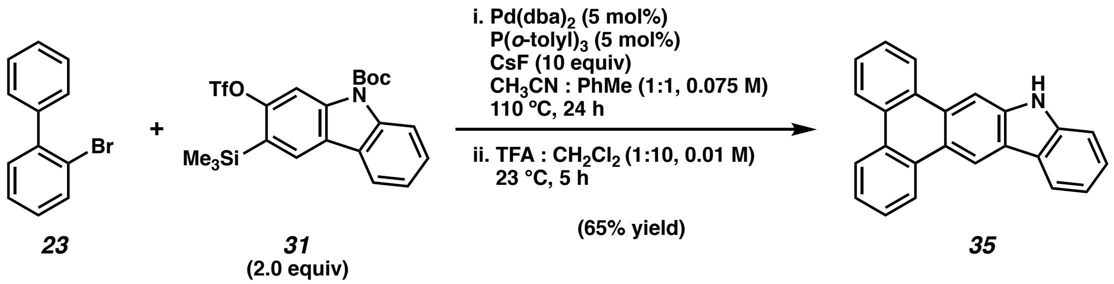
**Carbazole 32**. Followed representative procedure A. Purification by flash chromatography (100% Hexanes → 1:1 Hexanes:Benzene) afforded carbazole **32** (86% yield) as an off-white solid. Carbazole **32**: mp >200 °C; R*f* 0.74 (4:1 Hexanes:EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 8.86 (d, *J* = 8.2, 1H), 8.81 (d, *J* = 7.8, 1H), 8.68 (td, *J* = 8.6, 1.5, 2H), 8.54 (s, 1H), 8.31 (dt, *J* = 7.8, 0.9, 1H), 7.72–7.60 (m, 4H), 7.63 (td, *J* = 7.8, 1.1, 1H), 7.58 (td, *J* = 7.8, 1.1, 1H), 7.47 (d, *J* = 8.1, 1H), 7.33 (td, *J* = 7.4, 0.8, 1H), 4.03 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$; 27 of 28 signals observed): δ 142.9, 141.3, 131.1, 130.6, 130.0, 128.85, 128.78, 127.4, 127.1, 127.0, 126.8, 126.1, 123.9, 123.6, 123.5, 123.4, 123.1, 123.0, 122.9, 120.8, 119.2, 114.8, 108.5, 101.1, 29.3; IR (film): 3049, 2923, 2854, 1638, 1603, 1500, 1443, 1258, 754 cm$^{-1}$; HRMS-APCI (m/z) [M]$^+$ calcd for $C_{25}H_{17}N^+$, 331.13555; found 331.13609.

## D. Synthesis of N–H Annulation Products for Metal Coordination



**Indole 34.** A 2-dram vial was charged with Pd(dba)$_2$ (7.0 mg, 0.012 mmol, 5 mol%). Next, toluene (1.5 mL), P(*o*-tolyl)$_3$ (3.7 mg, 0.012 mmol, 5 mol%), 2-bromobiphenyl (**23**) (56.4 mg, 0.242 mmol, 1.0 equiv), silyl triflate **33** (318 mg, 0.495 mmol, 2.0 equiv), and acetonitrile (1.5 mL) were added sequentially, followed by an oven-dried magnetic stirbar and then CsF (333 mg, 8.26 mmol, 10.0 equiv). The vial was purged with nitrogen for 3 minutes, then sealed with a Teflon-lined screw cap and stirred at 110 °C for 24 h. After allowing to cool to 23 °C, the mixture was transferred with $CH_2Cl_2$ (20 mL) and $H_2O$ (10 mL) to a separatory funnel containing brine (15 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 30 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure to afford a brown residue that was carried forward without further purification.

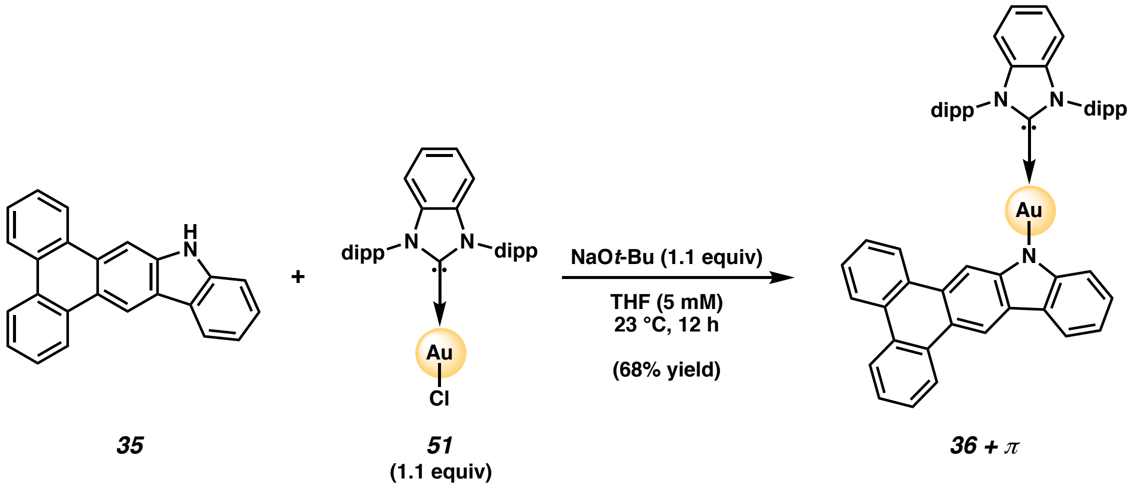
The crude material was dissolved in 10:1 $CH_2Cl_2$:TFA (24.2 mL, 0.01 M) and stirred at 23 °C for 5 h. The reaction was then slowly transferred to a separatory funnel containing sat. aq. sodium bicarbonate (30 mL). The mixture was further diluted with $CH_2Cl_2$ (10 mL) and the layers were separated. The organic phase was dried over $Na_2SO_4$ and filtered. To the filtrate was added silica (500 mg). The resulting mixture was dried under reduced pressure until a free-flowing solid was obtained. The crude material purified by flash chromatography (2:3 $CH_2Cl_2$:Hexanes → 3:1 $CH_2Cl_2$:Hexanes) to afford indole **34** (22.0 mg, 34% yield) as a yellow solid. Indole **34**. mp: >200 °C; R*f* 0.22 (2:3 $CH_2Cl_2$:Hexanes); $^1$H NMR (600 MHz, DMSO-d$_6$): δ 9.23 (dd, *J* = 8.6, 1.4, 1H), 8.77 (dd, *J* = 8.3, 1.7, 1H), 8.74–8.79 (m, 2H), 8.55 (d, *J* = 8.9, 1H), 8.50 (s, 1H), 7.76–7.60 (m, 6H), 7.41 (t, *J* = 3.6, 2.8, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.5, 131.1, 131.0, 130.3, 128.9, 127.1, 127.0, 126.7, 126.3, 125.9, 124.5, 124.4, 124.1, 123.5, 123.19, 123.18, 123.13, 118.1, 112.3, 105.6; IR (film): 3416, 3026, 3073, 2956, 1725, 1350 cm$^{-1}$; HRMS-APCI (*m/z*) [M + H]$^+$ calcd for $C_{20}H_{14}N^+$, 268.1121; found 267.6527.



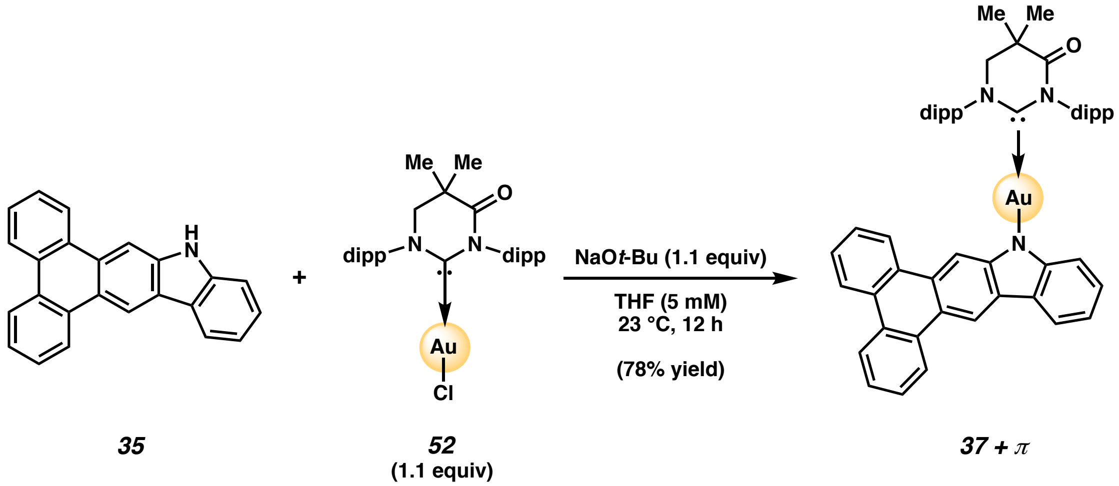
**Carbazole 35.** A 2-dram vial was charged with Pd(dba)$_2$ (7.1 mg, 0.012 mmol, 5 mol%). Next, toluene (1.3 mL), P(*o*-tolyl)$_3$ (3.8 mg, 0.012 mmol, 5 mol%), 2-bromobiphenyl (**23**) (58.0 mg, 0.248 mmol, 1.0 equiv), silyl triflate **31** (241 mg, 0.495 mmol, 2.0 equiv), and acetonitrile (1.6 mL) were added, followed by an oven-dried magnetic stirbar and then CsF (376 mg, 2.48 mmol, 10 equiv). The vial was purged with nitrogen for 3 minutes, then sealed with a Teflon-lined screw cap and stirred at 110 °C for 24 h. After allowing to cool to 23 °C, the mixture was transferred with $CH_2Cl_2$ (20 mL) and $H_2O$ (10 mL) to a separatory funnel containing brine (15 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 30 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure to afford a brown residue that was carried forward without further purification.

The crude material was dissolved in 10:1 $CH_2Cl_2$:TFA (24.2 mL, 0.01 M) and stirred at 23 °C for 5 h. The reaction was then slowly transferred to a separatory funnel containing sat. aq. sodium bicarbonate (30 mL). The mixture was further diluted with $CH_2Cl_2$ (10 mL) and the layers were separated. The organic phase was dried over $Na_2SO_4$ and filtered. To the filtrate was added silica (500 mg). The resulting mixture was dried under reduced pressure until a free-flowing solid was obtained. The crude material purified by flash chromatography (100% Hexanes → 9:1 Hexanes:EtOAc → 1:1 Hexanes:Benzene) to yield carbazole **35** (51 mg, 65% yield) as an off-white solid. Carbazole **35**. mp >200 °C; R$_f$ 0.63 (4:1 Hexanes:EtOAc); $^1$H NMR (600 MHz, $CDCl_3$): δ 11.35 (s, 1H), 9.62 (s, 1H), 9.0 (d, *J* = 8.0, 1H), 8.82 (d, *J* = 8.3, 1H), 8.76 (dd, *J* = 12.5, 8.3, 2H), 8.72 (s, 1H), 8.43 (d, *J* = 7.5, 1H), 7.73–7.69 (m, 2H), 7.67 (t, *J* = 6.9, 1H), 7.62 (t, *J* = 7.5, 1H), 7.55 (d, *J* = 8.0, 1H), 7.46 (t, *J* = 7.5, 1H), 7.24 (t, *J* = 7.5, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$; 22 of 24 signals observed): δ 141.3, 139.8, 131.0, 130.3, 129.9, 129.0, 128.8, 127.3, 127.1, 127.0, 126.9, 126.2, 124.4, 123.5, 123.43, 123.36, 123.0, 120.8, 119.8, 114.8, 110.6, 103.4; IR (film): 3413, 2923, 2852, 1611, 1435, 751 cm$^{-1}$; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{16}N^+$, 318.12773; found 318.12843.

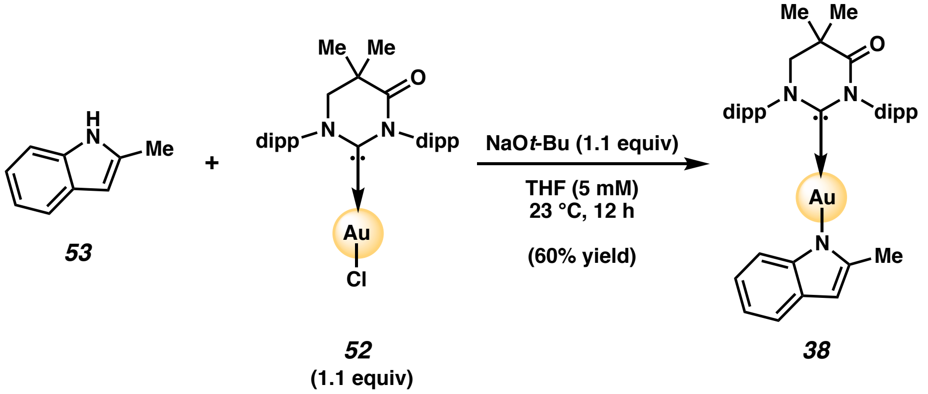
## E. Synthesis of Two-Coordinate Metal Complexes



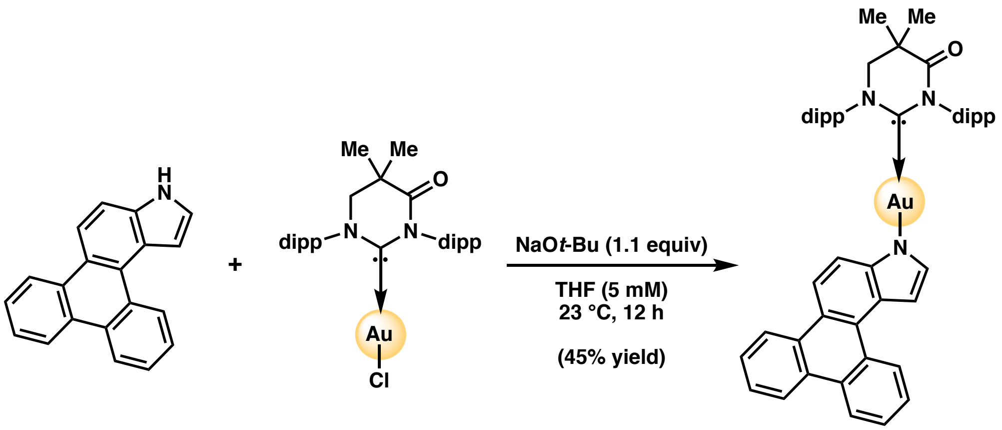
**Representative Procedure B for metal coordination (Figure 7, complex 36+π used as an example).** Sodium *tert*-butoxide (6.4 mg, 67 µmol, 1.1 equiv) was added to a solution of ligand **35** (20 mg, 63 µmol, 1.0 equiv) in THF (10 mL). **51** (44.4 mg, 66.2 µmol, 1.1 equiv) was added to the reaction flask in one portion and the mixture was left stirring under inert gas at 23 ºC for 12 hours. The solution was filtered through a plug of celite (2 cm in a 15 mL fritted funnel), washed with THF (10 mL), and the volatiles were removed under reduced pressure. The resulting product was recrystallized from $CH_2Cl_2$ and hexanes to afford an off-white precipitate (47 mg, 68% yield). Carbazole–Au–BZI **36+π**: $^1$H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.77 (dd, *J* = 8.5, 1.3, 1H), 8.60 (ddd, *J* = 16.7, 8.4, 1.4, 2H), 8.28 (dd, *J* = 8.5, 1.4, 1H), 8.17 (dd, *J* = 7.6, 1.0, 1H), 8.13 (s, 1H), 7.86 (t, *J* = 7.8, 2H), 7.72 (ddd, *J* = 8.2, 6.9, 1.3, 1H), 7.65–7.56 (m, 6H), 7.52–7.47 (m, 3H), 7.29–7.26 (m, 2H), 7.16 (ddd, *J* = 8.2, 7.0, 1.3, 1H), 7.01 (ddd, *J* = 7.9, 7.0, 1.0, 1H), 6.67 (dd, *J* = 8.1, 0.9, 1H), 2.60 (hept, *J* = 6.9, 4H), 1.40 (d, *J* = 6.9, 12H), 1.19 (d, *J* = 6.8, 12H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 207.21, 206.89, 185.66, 151.68, 149.68, 147.17, 146.43, 134.96, 132.19, 131.63, 131.44, 131.04, 129.51, 128.02, 127.23, 126.88, 126.05, 125.74, 125.54, 125.33, 124.75, 124.64, 123.80, 123.73, 123.17, 123.07, 122.78, 120.55, 119.85, 116.11, 113.50, 111.90, 105.58, 30.89, 29.19, 24.64, 24.08. Anal. Calcd for $C_{55}H_{52}AuN_3$: C, 69.39; N, 4.41; H, 5.51. Found: C, 68.05; N, 4.27; H, 5.30. MALDI-TOF (*m/z*) $[M]^+$ calcd for $C_{55}H_{52}AuN_3^+$, 951.38; found, 951.22.



**Annulated Carbazole–Au–MAC 37+π.** Representative procedure B was followed to yield **37+π** (42 mg, 78% yield) as a yellow solid. Annulated Carbazole–Au–MAC **37+π**: $^1$H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.73 (d, *J* = 7.8 Hz, 1H), 8.57 (ddd, *J* = 18.5, 8.3, 1.1 Hz, 2H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 0.7 Hz, 1H), 7.82 – 7.70 (m, 3H), 7.65 – 7.44 (m, 8H), 7.04 – 6.91 (m, 2H), 5.81 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 2H), 3.36 (hept, *J* = 6.5 Hz, 2H), 3.08 (hept, *J* = 6.8 Hz, 2H), 1.56 (s, 6H), 1.45 – 1.33 (m, 18H), 1.26 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 204.87, 171.43, 151.72, 149.54, 146.05, 144.95, 140.12, 135.57, 132.07, 131.35, 130.60, 130.44, 129.45, 127.98, 127.33, 126.87, 125.86, 125.79, 125.65, 125.63, 124.82, 124.73, 124.54, 124.16, 123.54, 123.14, 123.02, 122.80, 120.63, 119.41, 116.24, 114.06, 113.35, 105.48, 77.19, 62.27, 37.95, 29.35, 28.98, 24.70, 24.61, 24.58, 24.13, 23.93. Anal. Calcd for $C_{54}H_{56}AuN_3O$: C, 67.56; N, 4.38; H, 5.88. Found: C, 67.41; N, 4.35; H, 5.93. MALDI-TOF (*m/z*) $[M]^+$ calcd for $C_{54}H_{56}AuN_3O^+$, 959.41; found, 959.16.



**2-Methyl Indole–Au–MAC 38.** Representative procedure B was followed to yield **38** (110 mg, 60% yield) as an off-white solid. 2-Methylindole–Au–MAC **38**: $^1$H NMR (400 MHz, acetone-$D_6$): δ 7.64 (dt, *J* = 17.7, 7.7, 2H), 7.52 (d, *J* = 7.8, 2H), 7.46 (d, *J* = 7.7, 2H), 7.09 (dd, *J* = 7.6, 1.2, 1H), 6.62–6.53 (m, 1H), 6.49 (td, *J* = 7.5, 1.3, 1H), 5.84 (d, *J* = 8.0, 1H), 5.74 (d, *J* = 1.0, 1H), 4.25 (s, 2H), 3.50 (hept, *J* = 6.8, 2H), 3.24 (hept, *J* = 6.8, 2H), 1.69 (s, 6H), 1.48–1.43 (m, 8H), 1.42 (d, *J* = 3.2, 7H), 1.40 (d, *J* = 6.8, 6H), 1.25 (d, *J* = 6.8, 6H). $^{13}$C NMR (101 MHz, acetone-$D_6$): δ 205.18, 171.91, 146.16, 145.94, 144.96, 144.43, 140.69, 136.56, 130.54, 130.07, 129.77, 125.29, 124.30, 117.03, 116.77, 116.13, 113.55, 98.29, 61.12, 37.98, 28.49, 23.94, 23.70, 23.65, 23.25, 15.60. Anal. Calcd for $C_{39}H_{50}AuN_3O$: C, 60.54; N, 5.43; H, 6.51. Found: C, 60.49; N, 5.32; H, 6.67. MALDI-TOF (*m/z*) $[M]^+$ calcd for $C_{39}H_{50}AuN_3O^+$, 773.36; found, 773.45.



***34***

***52***
**(1.1 equiv)**

***38 + π***

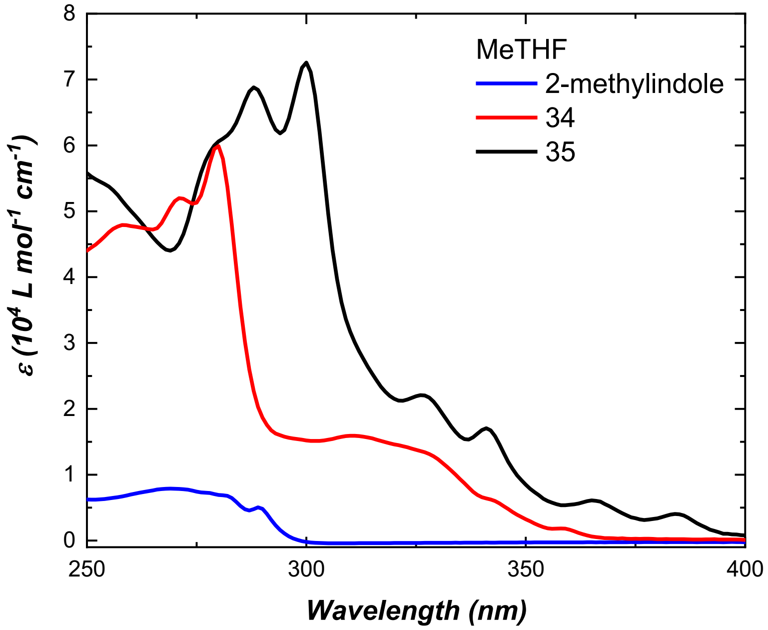
**Annulated Indole–Au–MAC 38+π.** Representative procedure B was followed to yield **38** (120 mg, 45% yield) as an off-white solid. Annulated Indole–Au–MAC **38+π**: $^1$H NMR (400 MHz, acetone-$D_6$): δ 9.18 – 9.11 (m, 1H), 8.77 – 8.62 (m, 3H), 8.05 (d, *J* = 9.1 Hz, 1H), 7.72 (dt, *J* = 20.8, 7.8 Hz, 2H), 7.65 – 7.45 (m, 8H), 7.16 – 7.10 (m, 1H), 6.52 (d, *J* = 2.8 Hz, 1H), 6.49 (dd, *J* = 8.9, 1.0 Hz, 1H), 4.29 (s, 2H), 3.48 (h, *J* = 6.8 Hz, 2H), 3.24 (hept, *J* = 6.8 Hz, 2H), 1.68 (s, 6H), 1.50 – 1.31 (m, 18H), 1.22 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (151 MHz, acetone-$D_6$): δ 205.19, 203.69, 171.81, 146.27, 145.07, 145.00, 140.59, 136.57, 135.92, 132.09, 131.87, 130.31, 129.95, 129.45, 128.12, 126.78, 126.61, 126.17, 125.36, 125.10, 124.71, 124.37, 124.18, 124.05, 123.32, 123.20, 122.94, 122.74, 122.49, 117.26, 113.45, 103.02, 60.96, 38.13, 28.85, 28.35, 24.04, 23.97, 23.92, 23.86, 23.79, 23.72, 23.53, 23.21, 23.07. Anal. Calcd for $C_{50}H_{54}AuN_3O$: C, 66.00; N, 4.62; H, 5.98. Found: C, 65.50; N, 4.49; H, 6.09. MALDI-TOF (*m/z*) $[M]^+$ calcd for $C_{50}H_{54}AuN_3O^+$, 909.39; found, 909.27.

## F. General Procedure for Photophysical Property Analyses

**General Procedure for 1% Polystyrene Films**. A mixture of polystyrene pellets (99 mg) and toluene (2 mL) was sonicated for 1 h, until all pellets are dissolved. Two-coordinate metal complex (1 mg) was dissolved in the solution. Using a pipet, ~0.5 mL of the solution was drop-casted onto a glass substrate (2 cm x 2 cm) to achieve an even surface. The film was left to air-dry for 30 min and then placed in the vacuum chamber for further drying overnight. The resulting film was used to acquire the photophysical data.

## G. Absorption Spectra of Donor Ligands

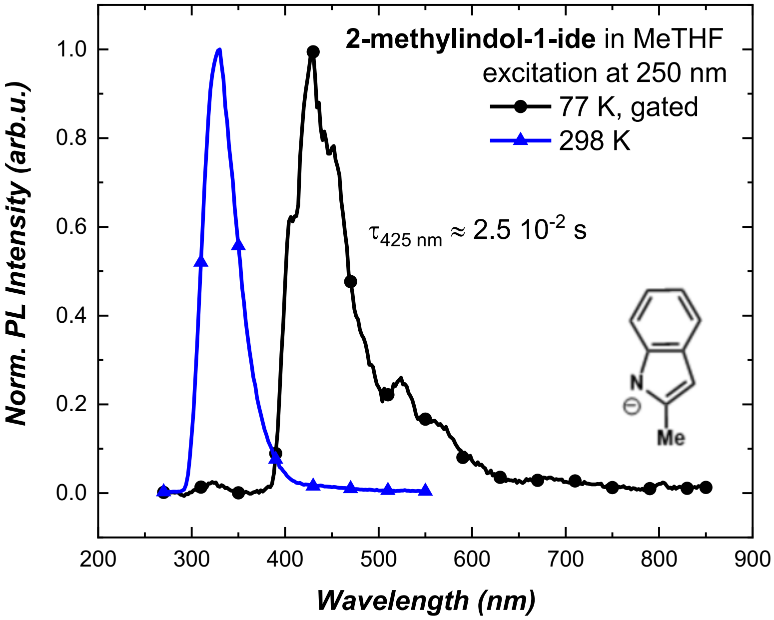
The extinction coefficient for the donor ligands was measured in 2-MeTHF. The molar absorptivity values for the donor ligands are comparable in magnitude to the molar absorptivity values for the transitions localized on the donor ligands in the metal complexes.



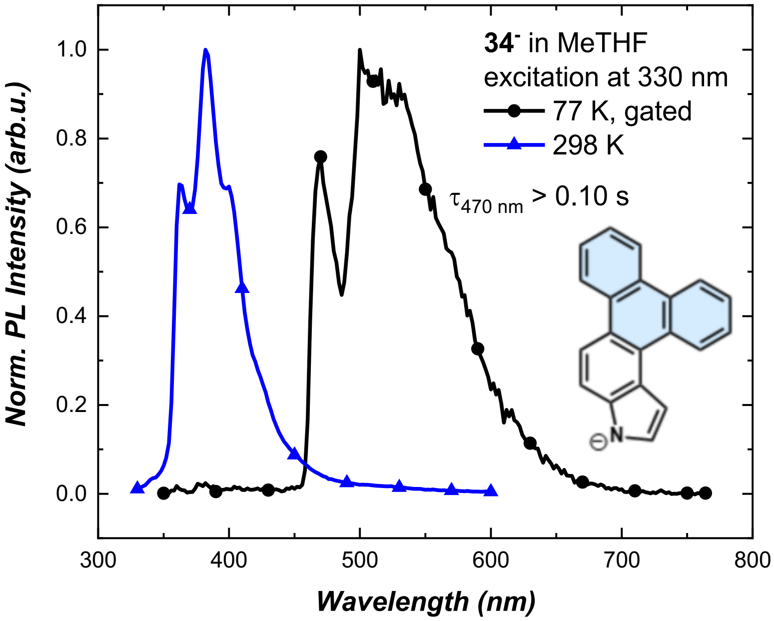
**Supplementary Figure 1.** Extinction coefficients for the donor ligands in 2-MeTHF.

## H. Emission Spectra of Deprotonated Donor Ligands

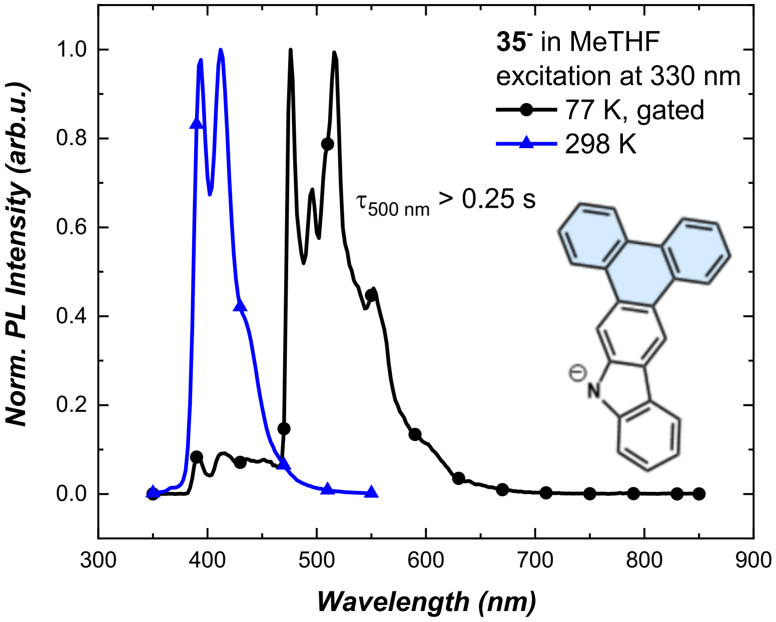
A few milligrams of donor ligand (1–3 mg) were dissolved in THF (10 mL). The solution was cooled in an ice bath. Once completely dissolved, a solution containing 1.2 equivalents of *n*-BuLi diluted in THF was added. Although a color change was immediately observable, the reaction was allowed to stir for 1 h. The solvent was then evaporated under reduced pressure, and the solid obtained was dissolved in 2-MeTHF.



**Supplementary Figure 2.** Emission spectra of 2-methylindol-1-ide in 2-MeTHF.



**Supplementary Figure 3.** Emission spectra of ligand **34**$^-$ in 2-MeTHF.



**Supplementary Figure 4.** Emission spectra of ligand **35**⁻ in 2-MeTHF.

## Computational Methods

### A. Complete Citation of Q-Chem 5.1

Density functional theory (DFT) calculations were executed using Q-Chem 5.1 program[11] at the B3LYP/6-31G** level for ground state geometry optimization of the organic ligands and at the B3LYP/LACVP level for the metal complexes. Time-dependent density functional theory (TD-DFT) calculations were performed on the ground state optimized geometries at the CAM-B3LYP/LACVP** level for a balanced description of both charge-transfer and locally excited (LE) states (Supplementary Table 1).

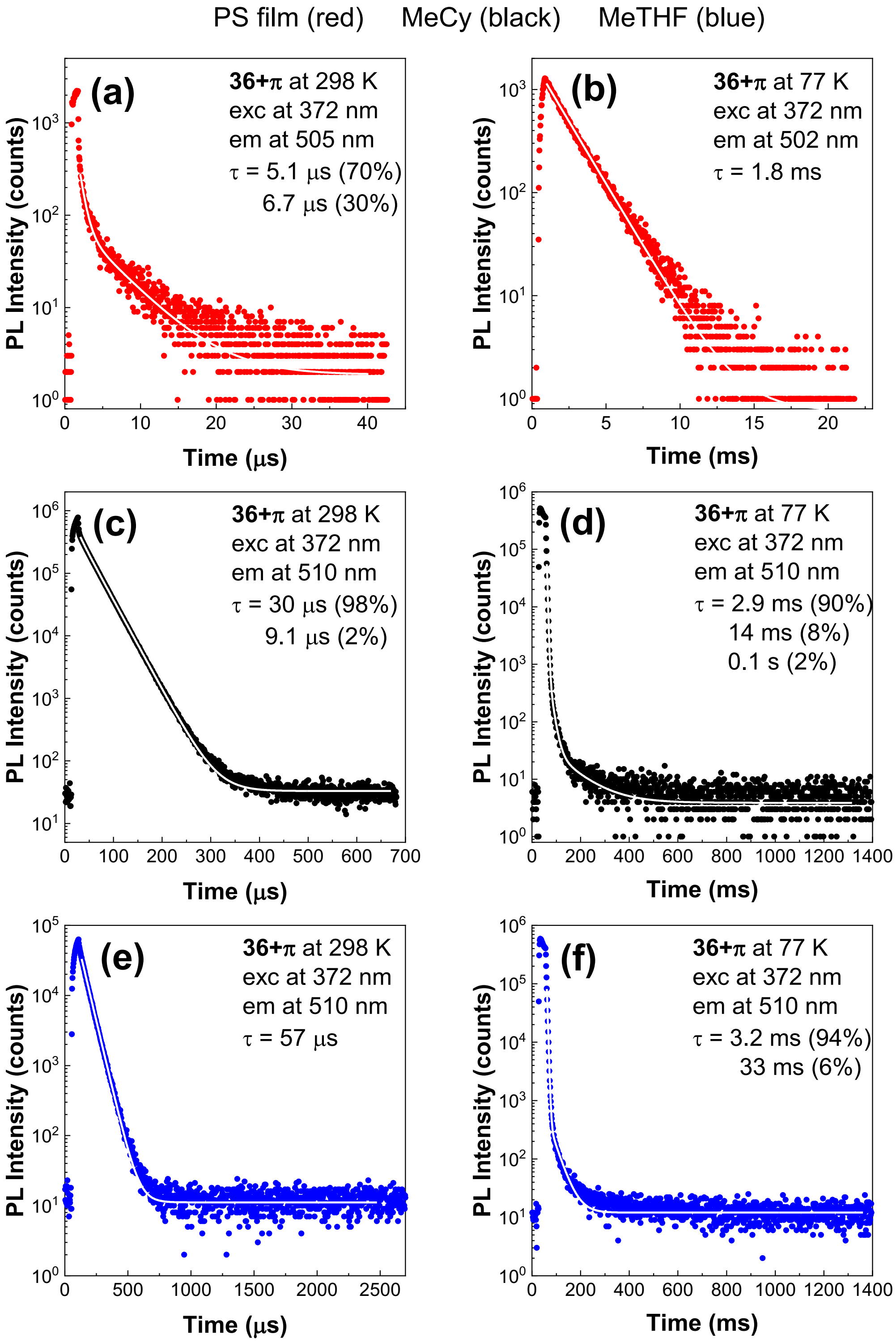
## B. Calculated Frontier Molecular Orbital Energies

**Supplementary Table 1**. Calculated frontier molecular orbital, singlet ($S_1$), and triplet ($T_1$) energies. CT = Charge Transfer state, LE = Locally Excited state.

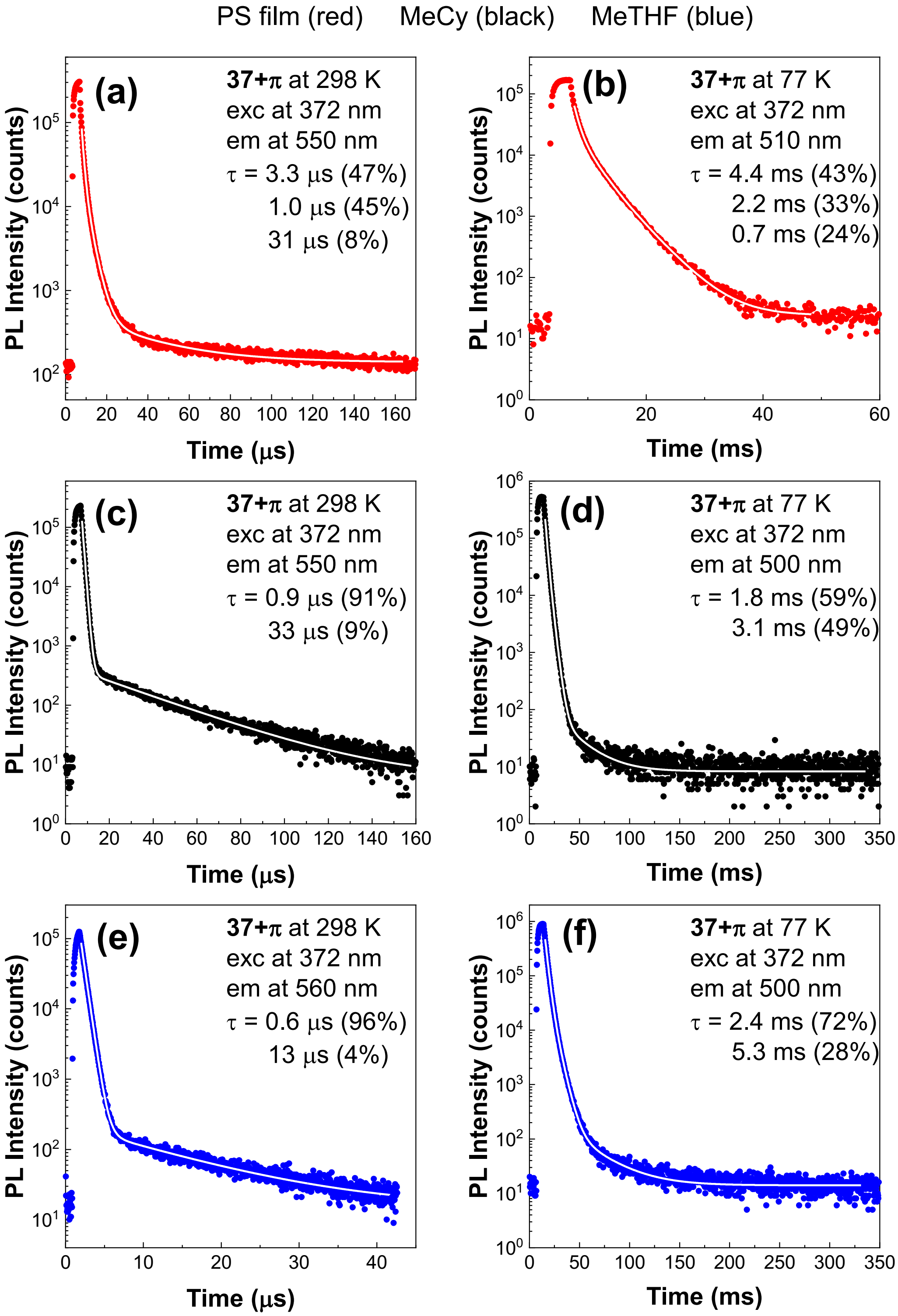
| | HOMO (eV) | LUMO (eV) | $\Delta E_{\text{HOMO-LUMO}}$ (eV) | $S_1$ (eV) | Nature of $S_1$ transition | $T_1$ (eV) | Nature of $T_1$ transition |
|---|---|---|---|---|---|---|---|
| **2-methylindole** | -5.28 | 0.00 | 5.28 | 5.21 | - | 3.16 | - |
| **34** | -5.28 | -0.90 | 4.38 | 4.24 | - | 2.55 | - |
| **carbazole** | -5.47 | -0.65 | 4.82 | 4.58 | - | 3.09 | - |
| **35** | -5.28 | -1.20 | 4.08 | 4.04 | - | 2.53 | - |
| **36** | -4.22 | -1.44 | 2.78 | 3.50 | CT | 3.07 | LE |
| **36+π** | -4.27 | -1.52 | 2.75 | 3.46 | CT | 2.48 | LE |
| **37** | -4.30 | -1.96 | 2.34 | 3.10 | CT | 2.85 | CT |
| **37+π** | -4.35 | -2.07 | 2.29 | 3.07 | CT | 2.48 | LE |
| **38** | -4.16 | -1.96 | 2.20 | 3.11 | CT | 2.87 | CT |
| **38+π** | -4.38 | -2.10 | 2.29 | 3.27 | CT | 2.51 | LE |

## Photoluminescence (PL) Decay Lifetime Data

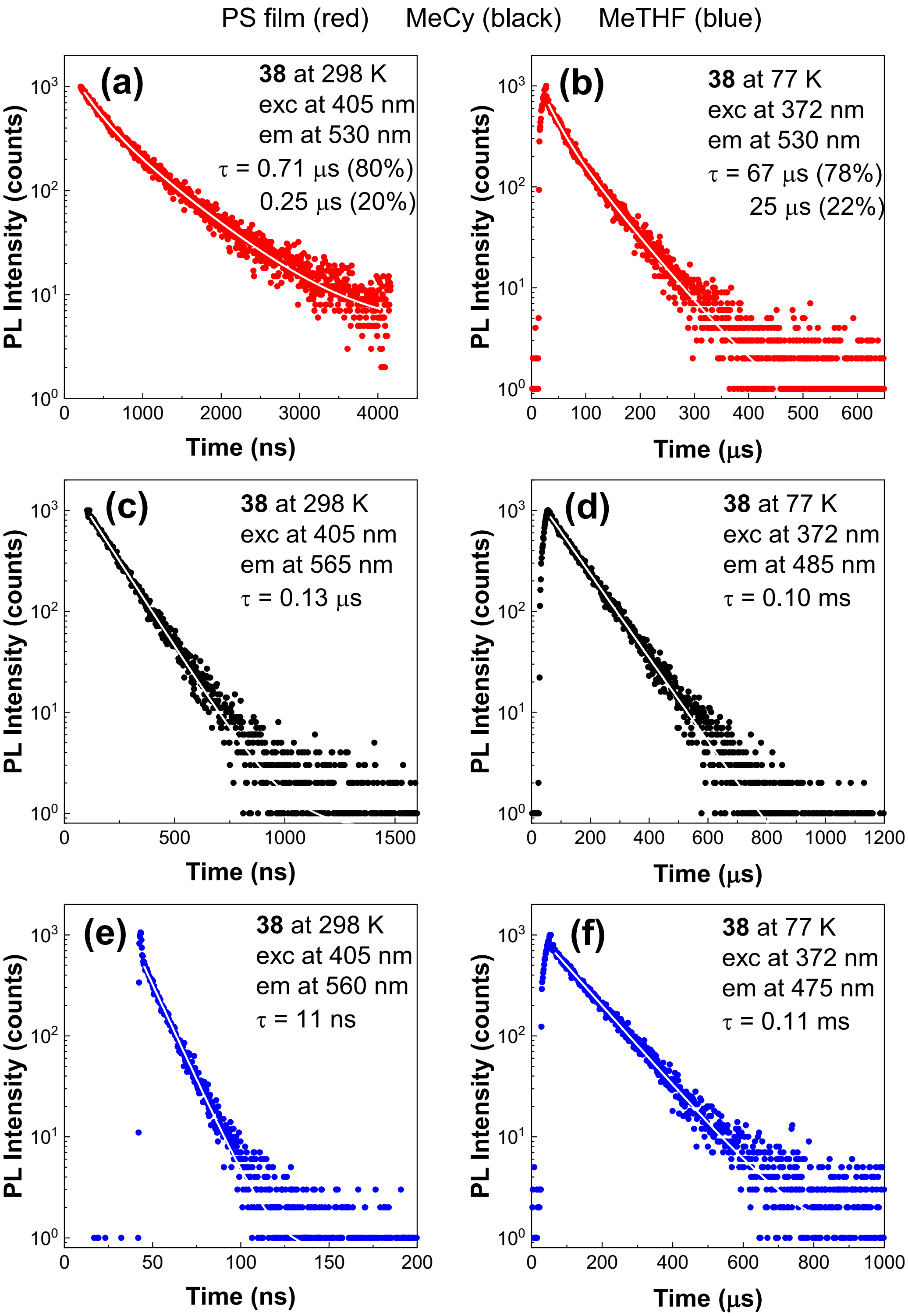
## A. Lifetime Plots



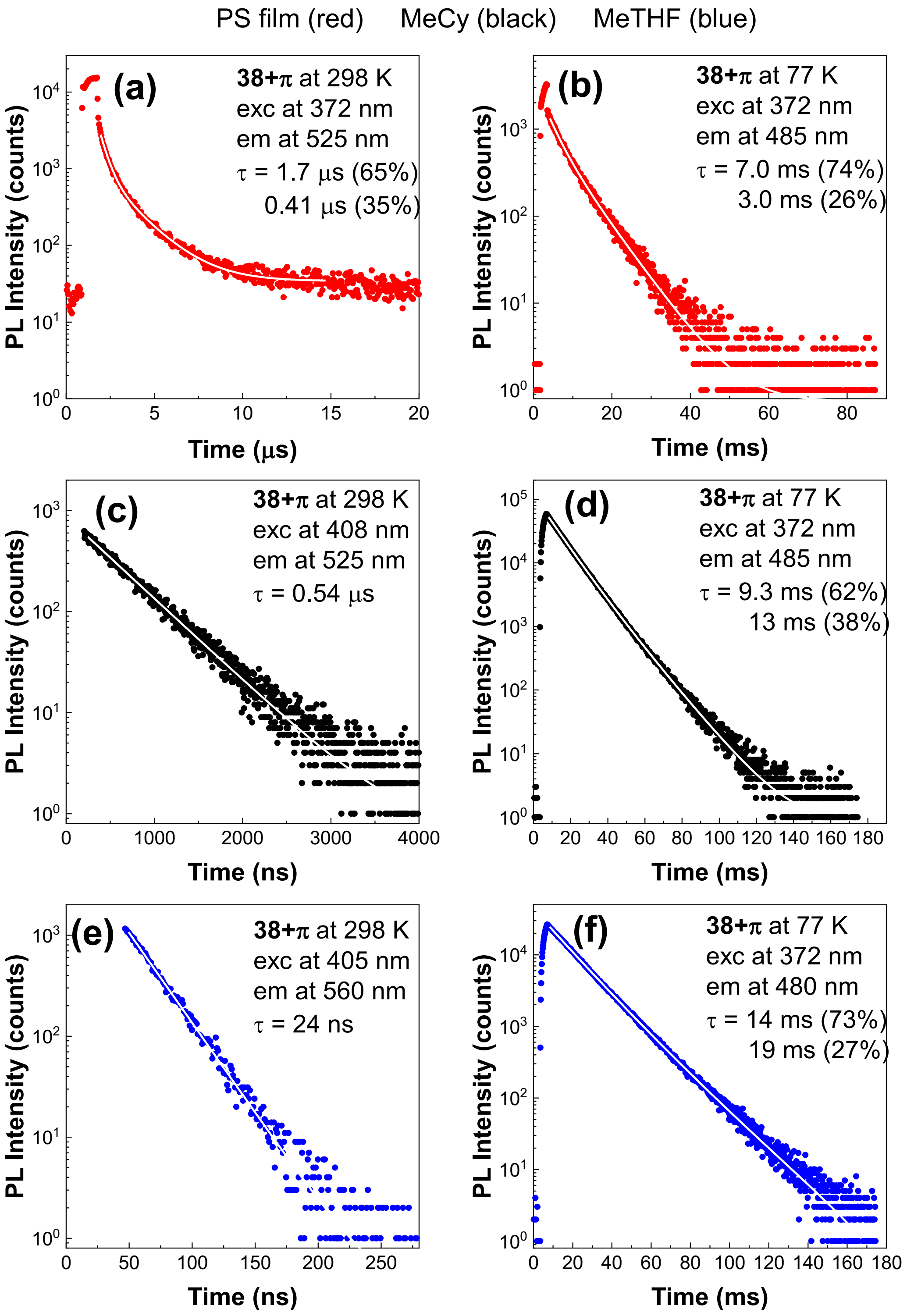
**Supplementary Figure 5.** Emission lifetime decay for **36+π** in (a-b) PS film, (c-d) MeCy, and (e-f) MeTHF at 298 K (left side) and 77 K (right side).



**Supplementary Figure 6.** Emission lifetime decay for **37+π** in (a-b) PS film, (c-d) MeCy, and (e-f) MeTHF at 298 K (left side) and 77 K (right side).



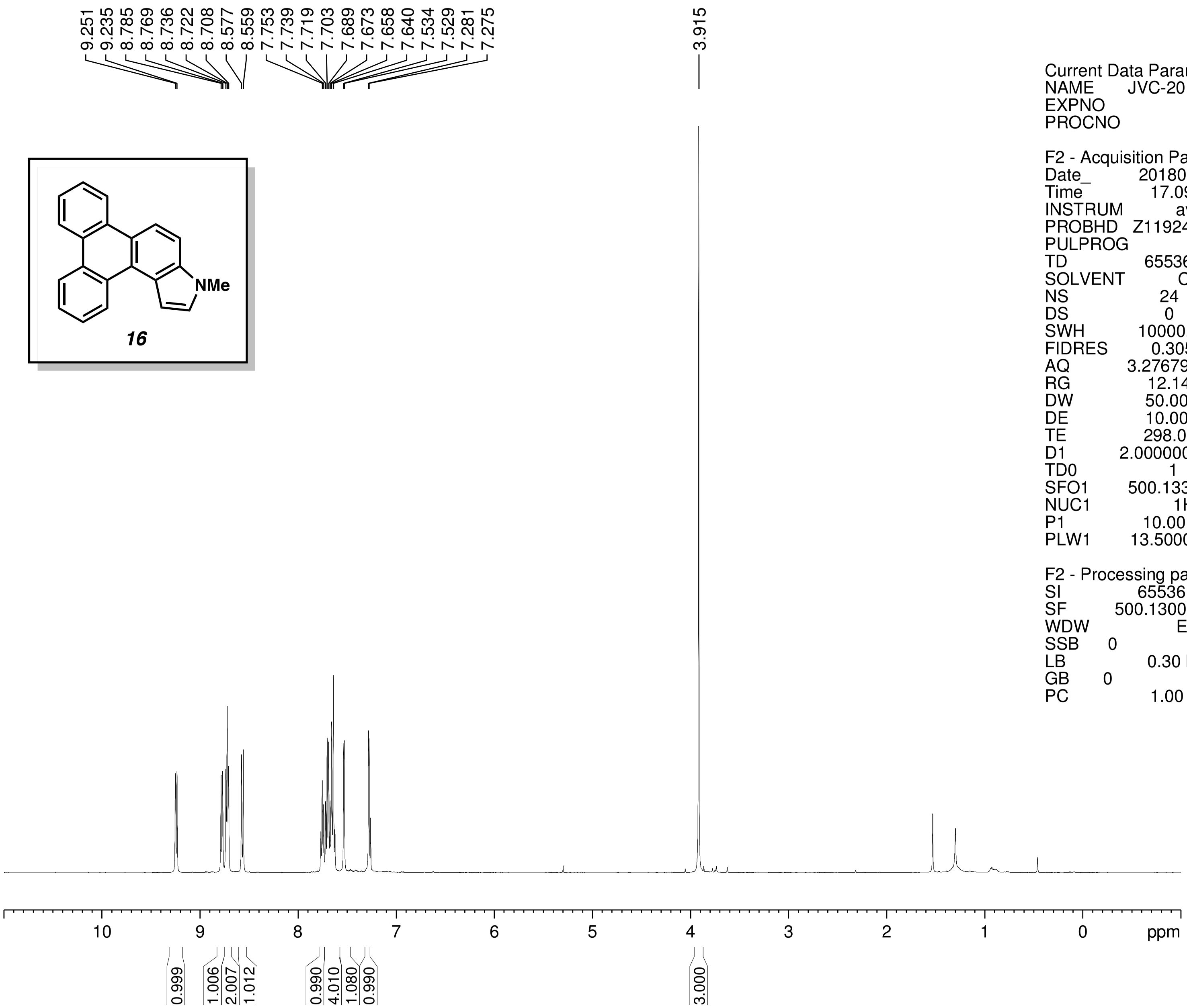
**Supplementary Figure 7.** Emission lifetime decay for **38** in (a-b) PS film, (c-d) MeCy, and (e-f) MeTHF at 298 K (left side) and 77 K (right side).



**Supplementary Figure 8.** Emission lifetime decay for **38+π** in (a-b) PS film, (c-d) MeCy, and (e-f) MeTHF at 298 K (left side) and 77 K (right side). In **37+π**, in both MeCy and MeTHF at 298 K a biexponential decay is observed. The slow lifetime is in the range of tens of microseconds. It is assigned to p-type delayed fluorescence caused by a bimolecular triplet-triplet annihilation.

# $^1$H NMR Spectra

Purified Product, 1H NMR



**16**

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DE 10.00 usec
TE 298.0 K
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TD0 1
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F2 - Processing parameters
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WDW EM
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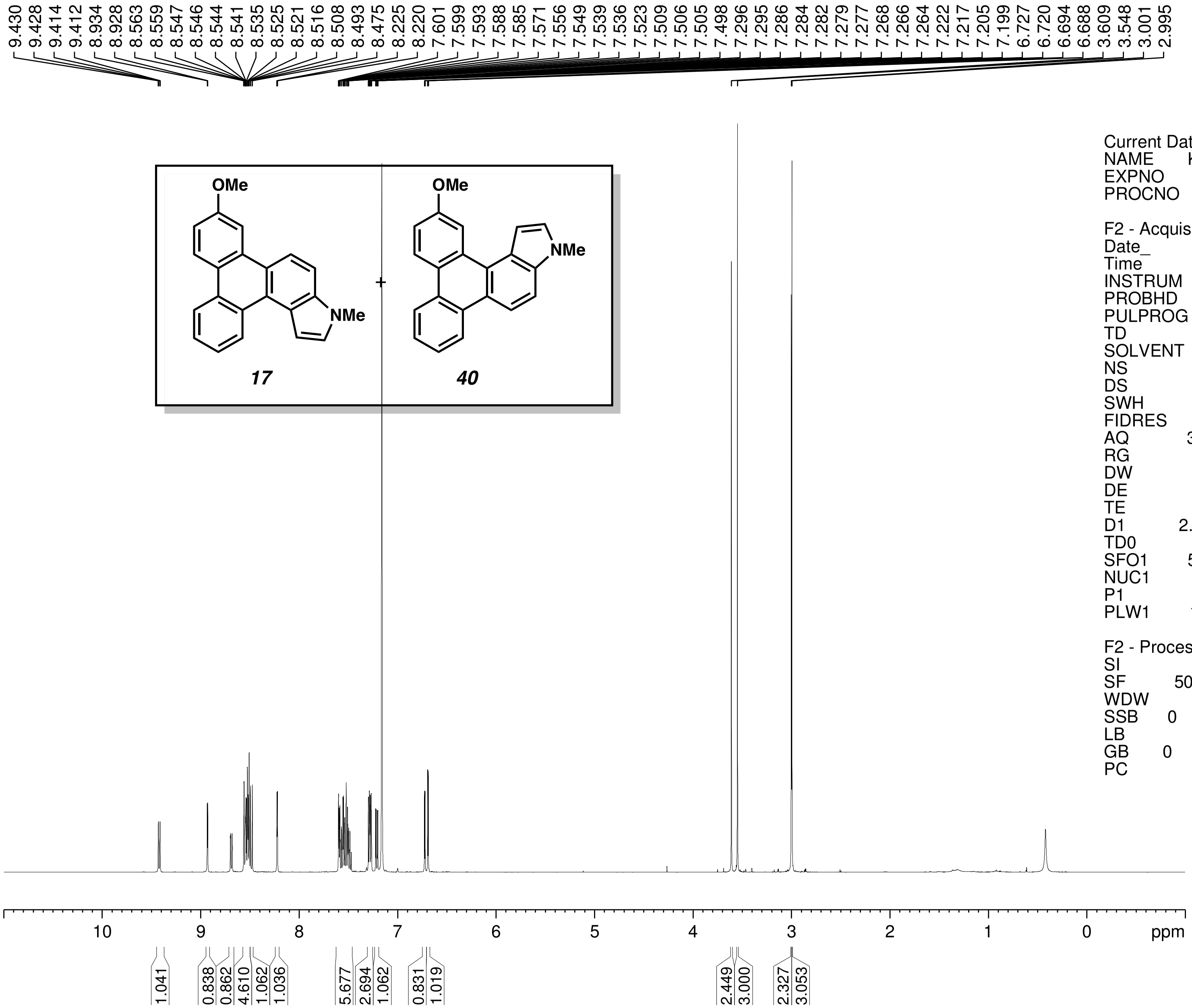
PC 1.00

Purified Product, 1H NMR



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TD0                   1
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P1                10.00 usec
PLW1        13.50000000 W

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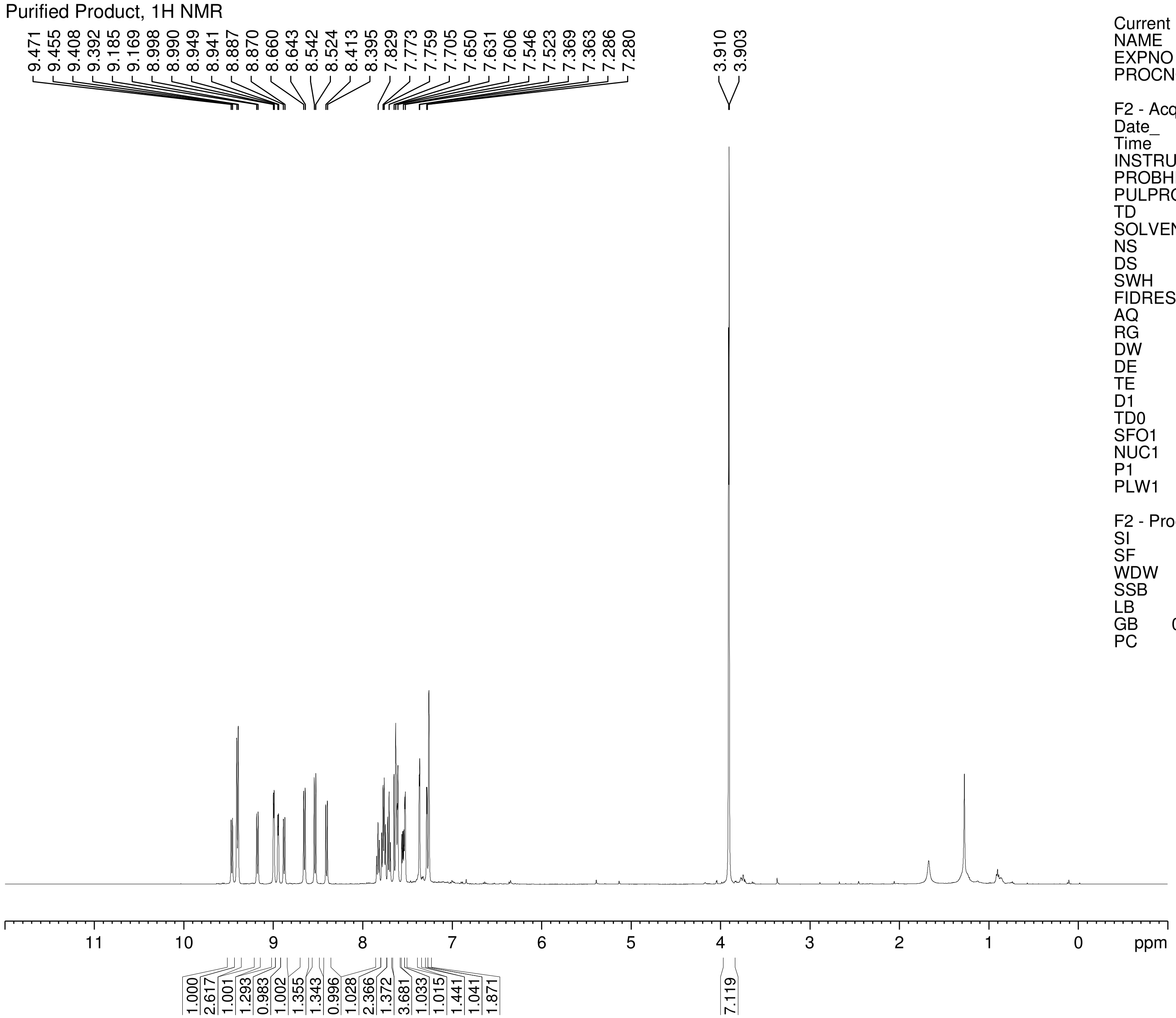

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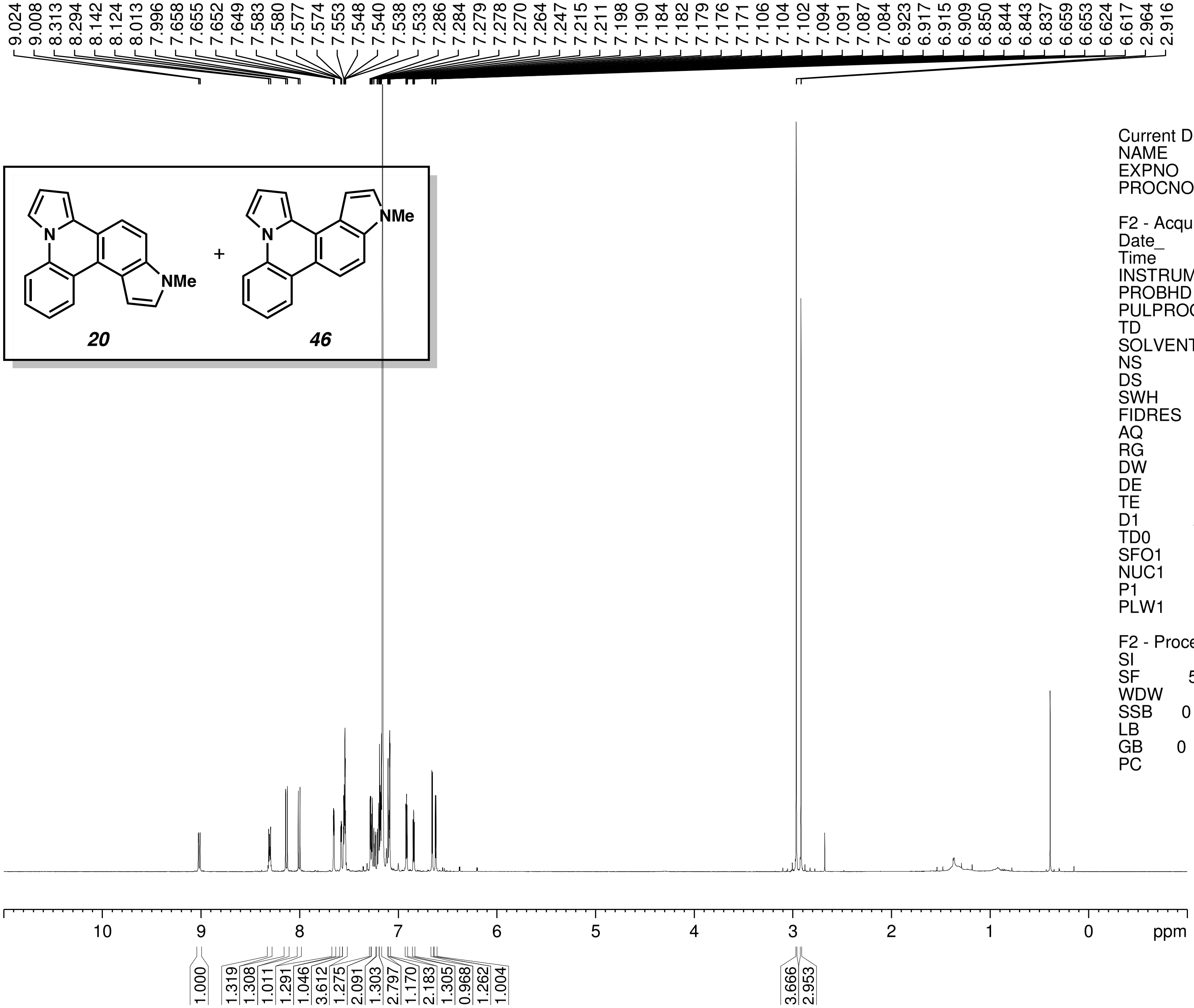
Purified Product, 1H NMR



**20** + **46**

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TE               298.0 K
D1          2.00000000 sec
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P1               10.00 usec
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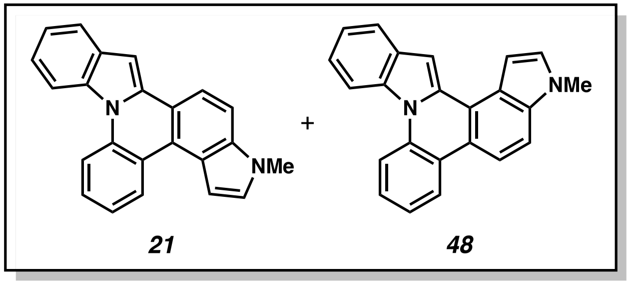
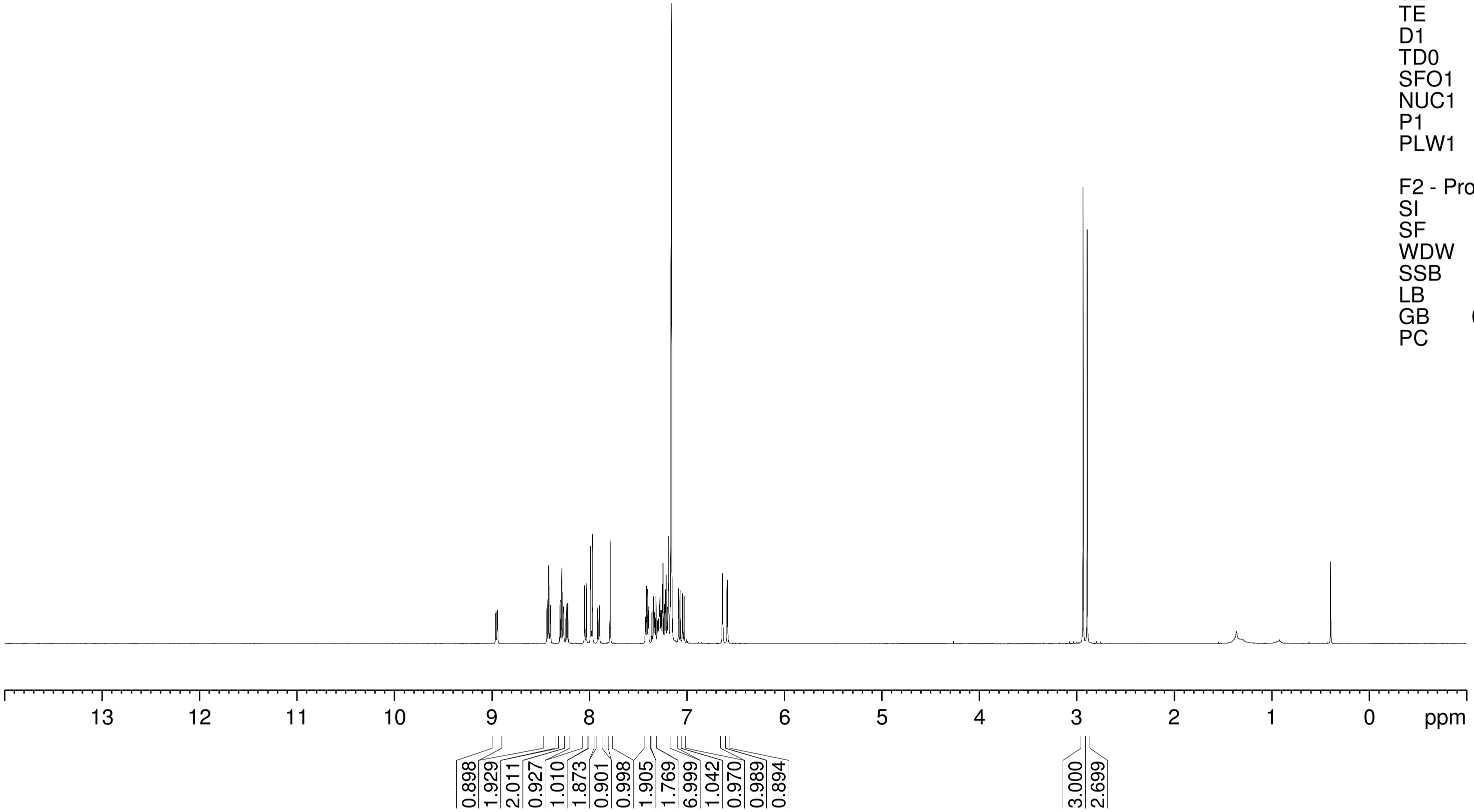
Purified Product, 1H NMR



**21** + **48**



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| PLW1 | 13.50000000 W |

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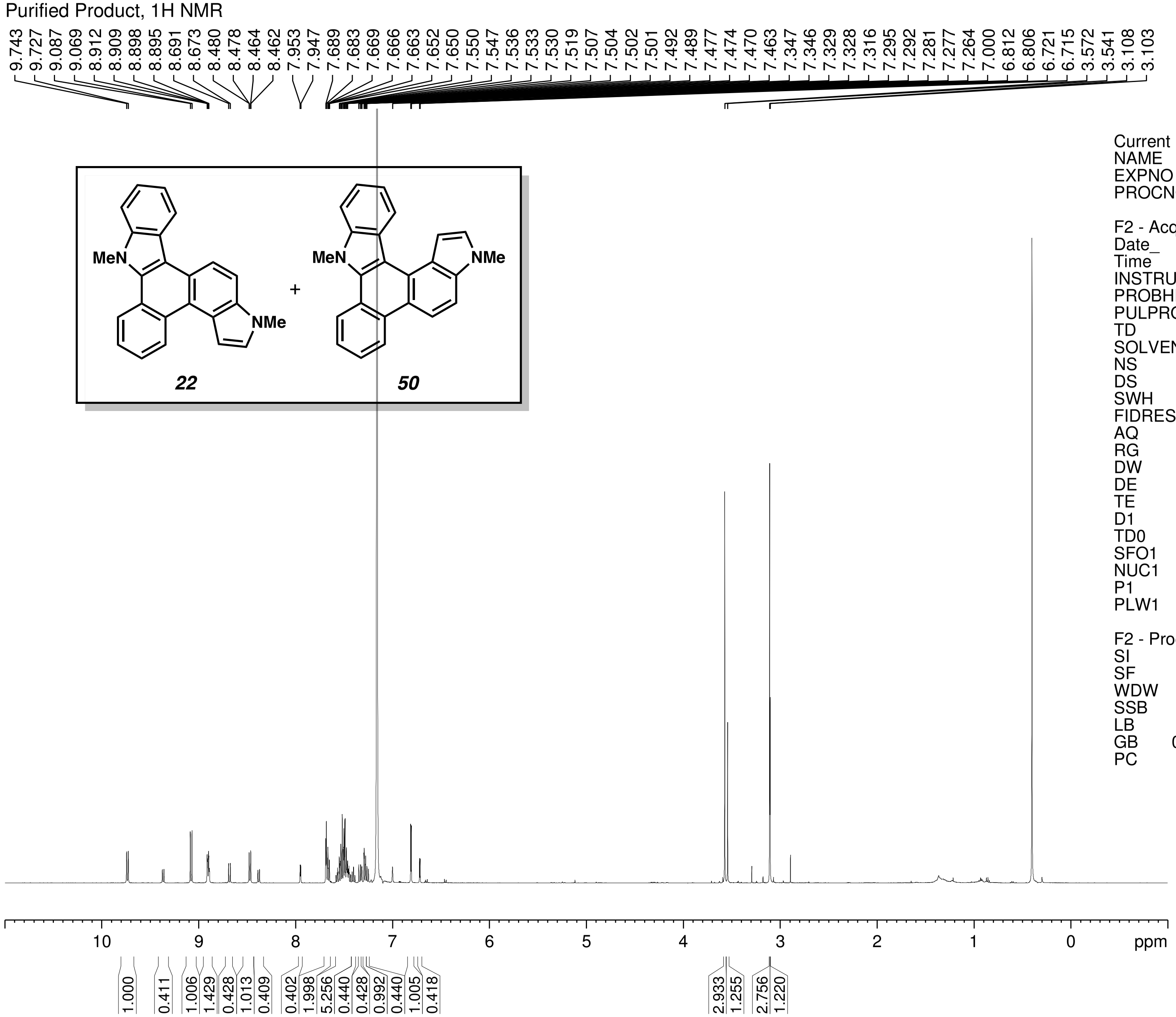

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| PROCNO | 1 |

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| PULPROG | zg30 |
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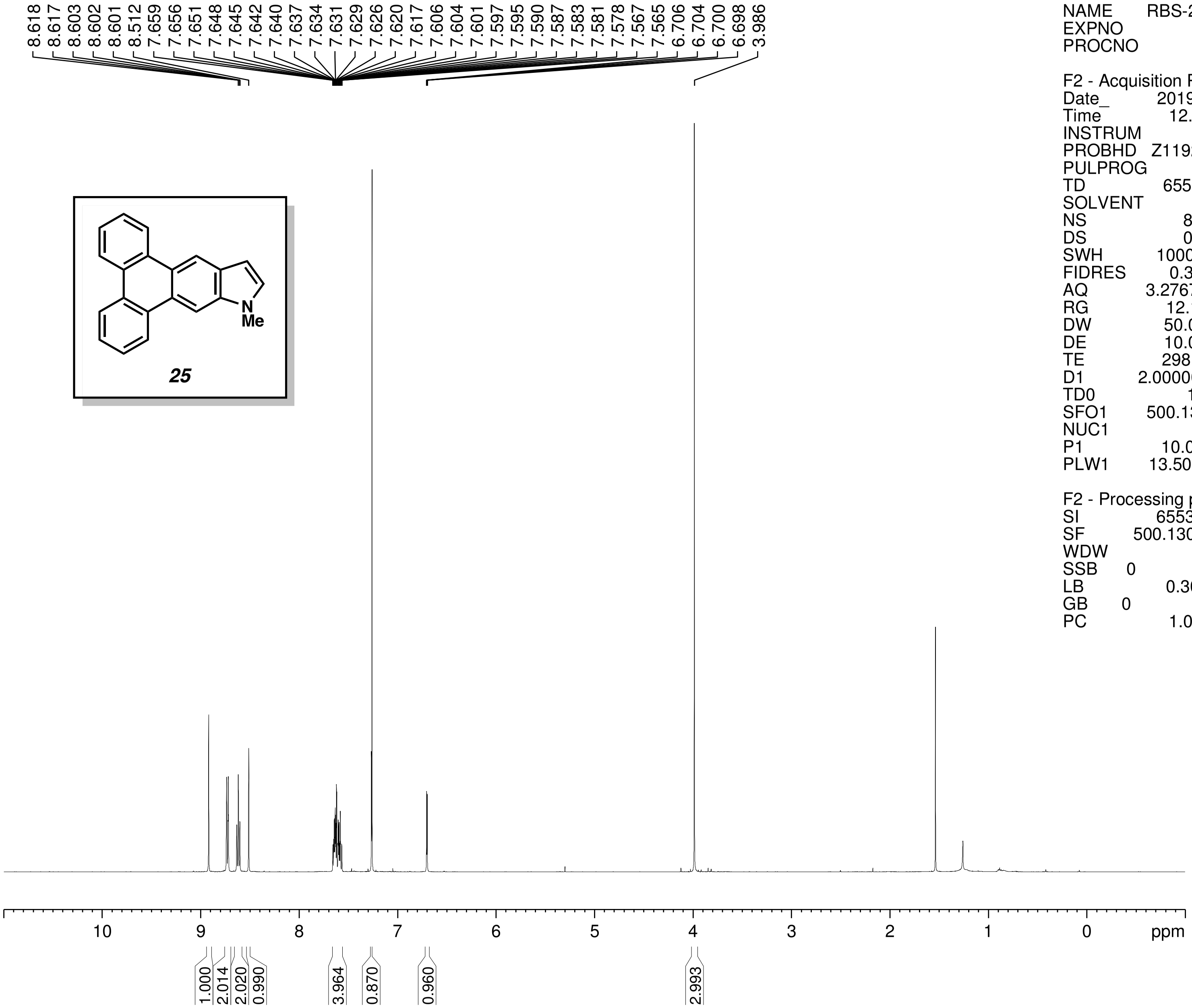
Purified Product, 1H NMR



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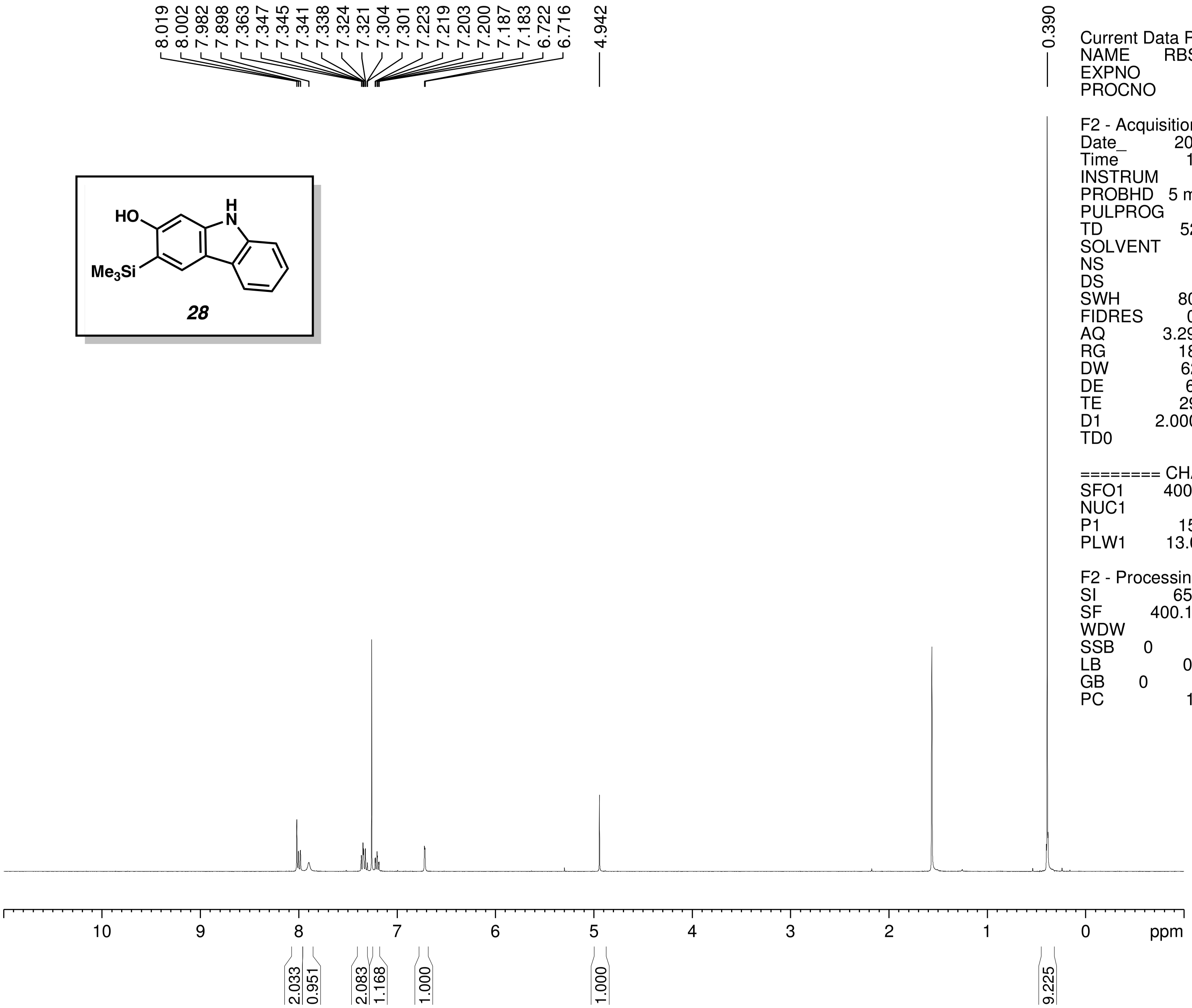
Purified Product, 1H NMR



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TD0 1

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NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

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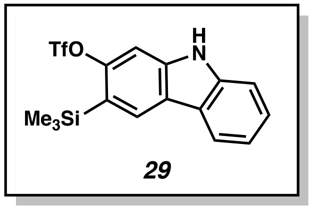
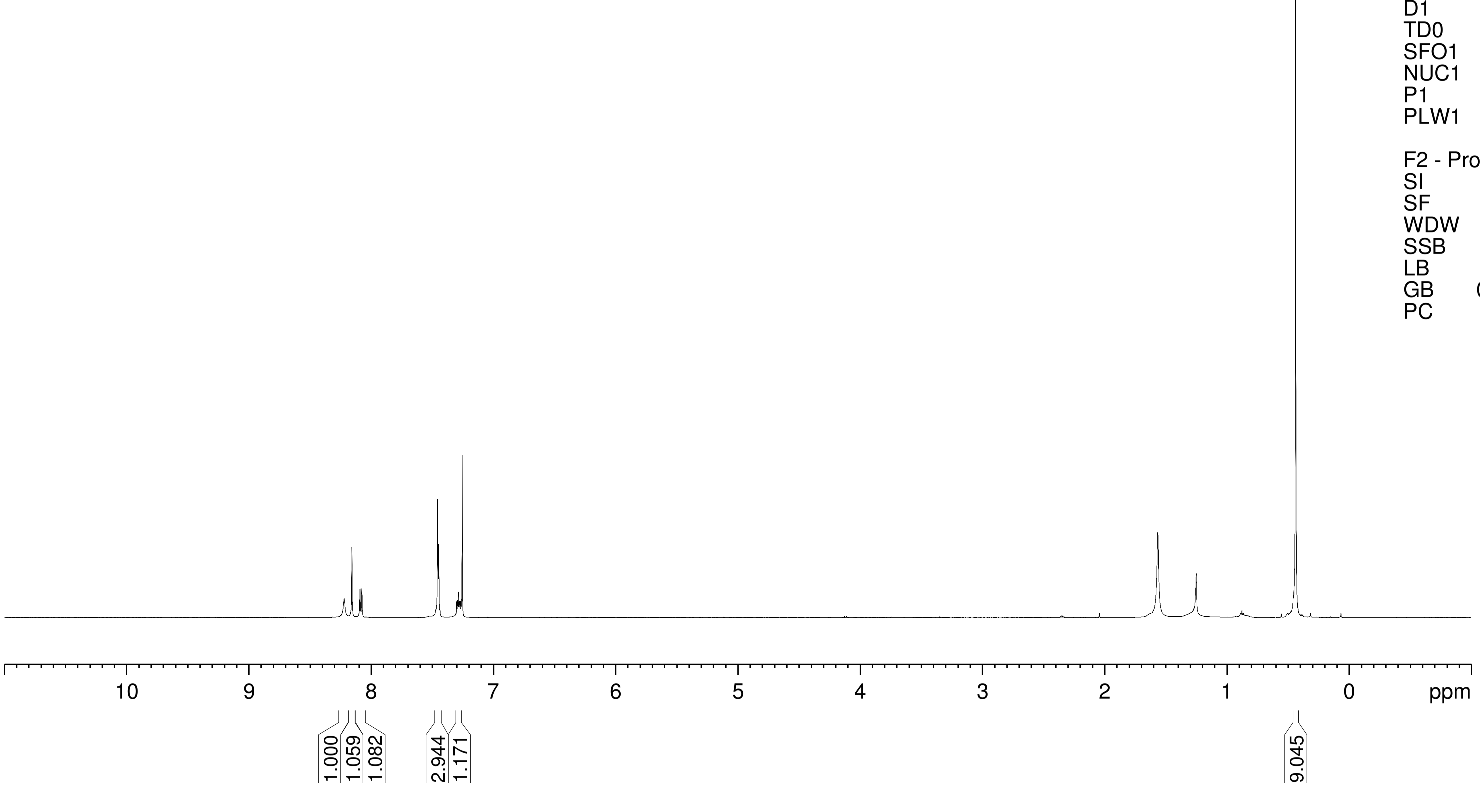
Purified Product, 1H NMR



**29**



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DE 10.00 usec
TE 298.0 K
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TD0 1
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NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

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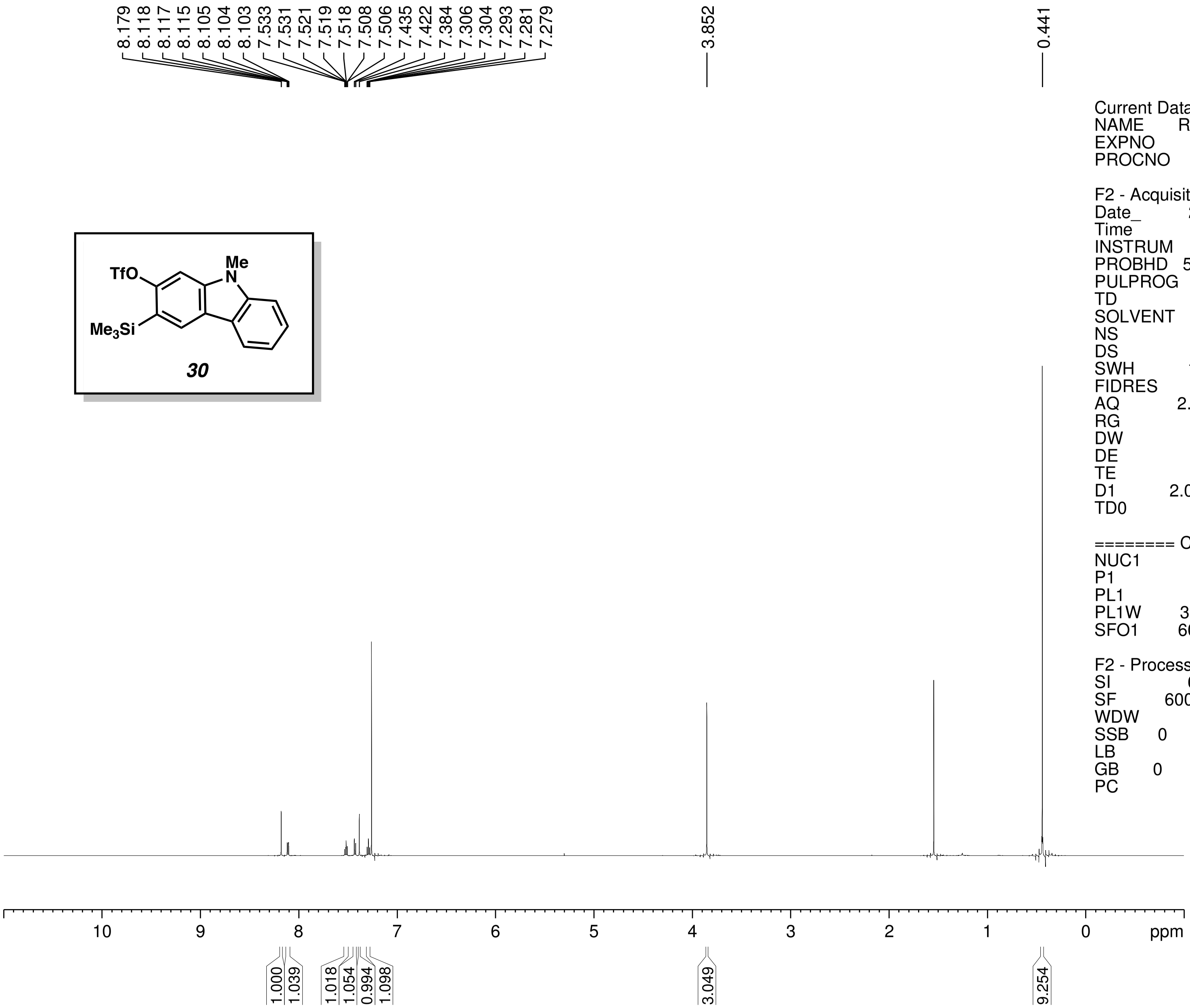
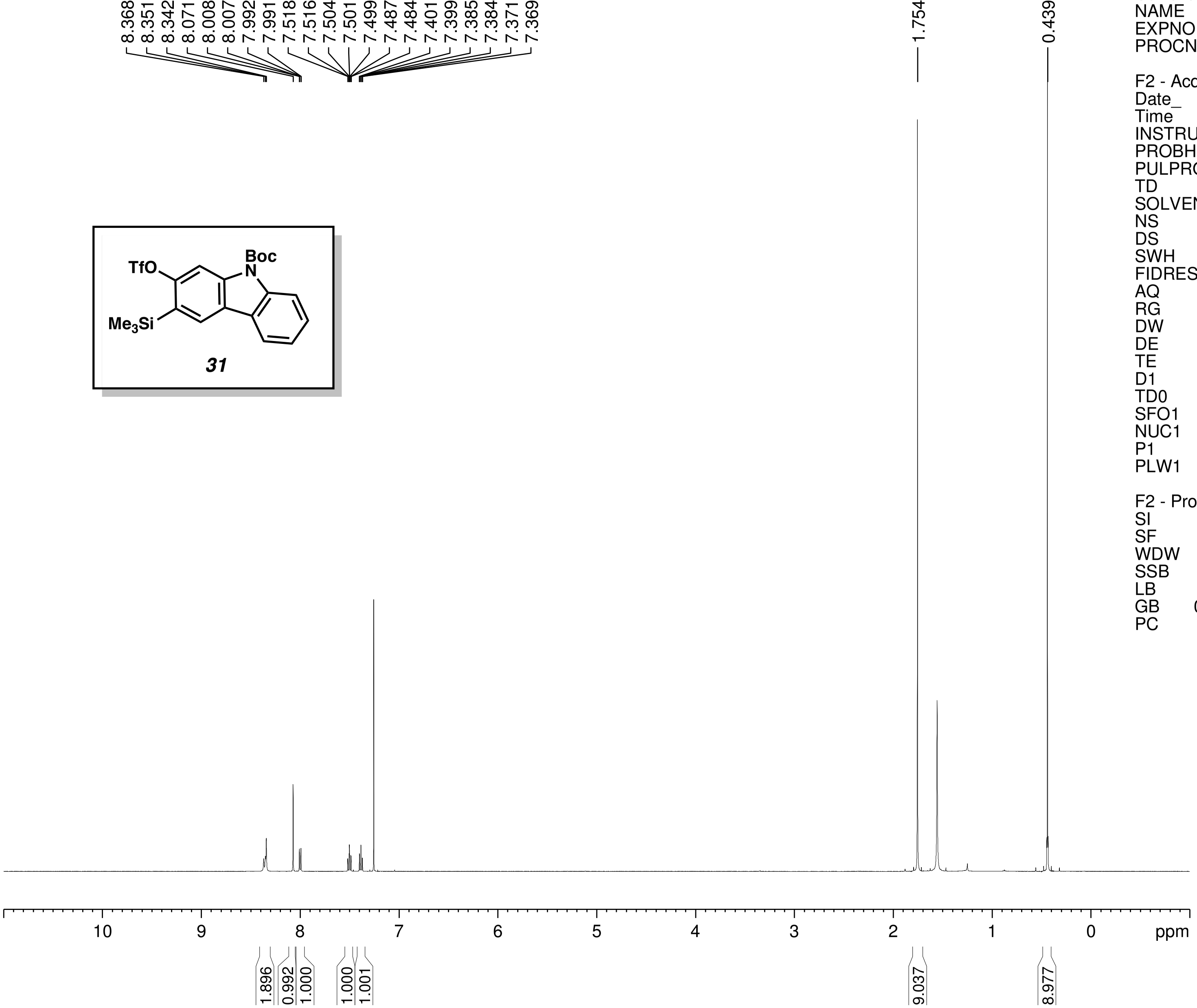
Purified Material, 1H NMR

***30***



```
Current Data Parameters
NAME       RBS-2019-153
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20190929
Time            20.34
INSTRUM         av600
PROBHD   5 mm TBI5
PULPROG          zg30
TD             65536
SOLVENT          CDCl3
NS                 16
DS                  0
SWH        12376.237 Hz
FIDRES      0.188846 Hz
AQ         2.6476543 sec
RG                181
DW             40.400 usec
DE               6.50 usec
TE              294.5 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 =====
NUC1               1H
P1              11.55 usec
PL1             -2.00 dB
PL1W      39.81071854 W
SFO1      600.1336008 MHz

F2 - Processing parameters
SI             65536
SF        600.1300282 MHz
WDW               EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

Purified Material, 1H NMR

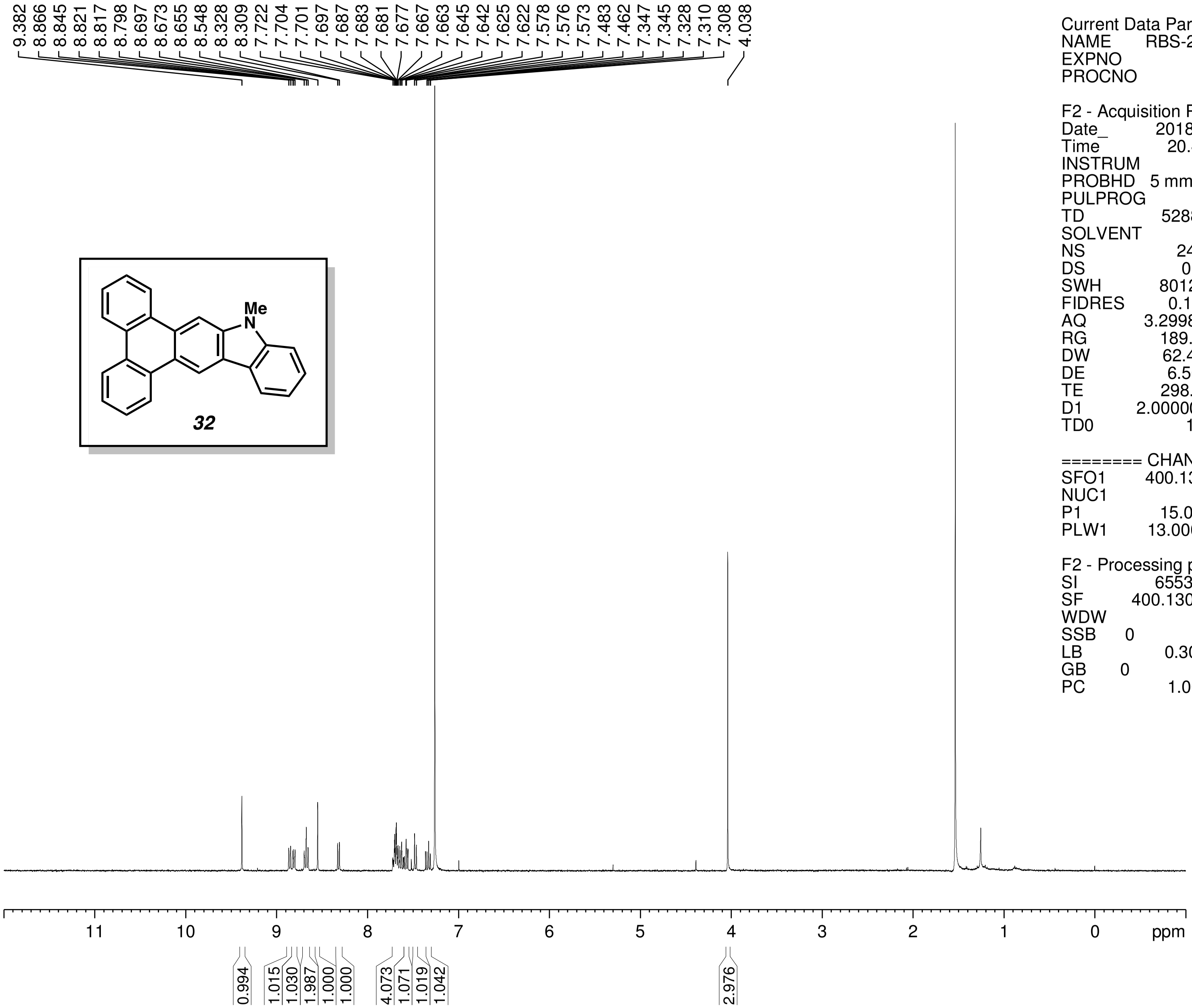


Current Data Parameters
NAME KAS-2021-000
EXPNO 110
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210722
Time 16.19 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

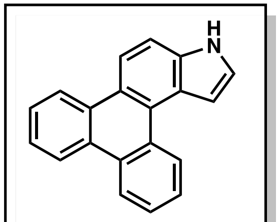
Purified Product, 1H NMR



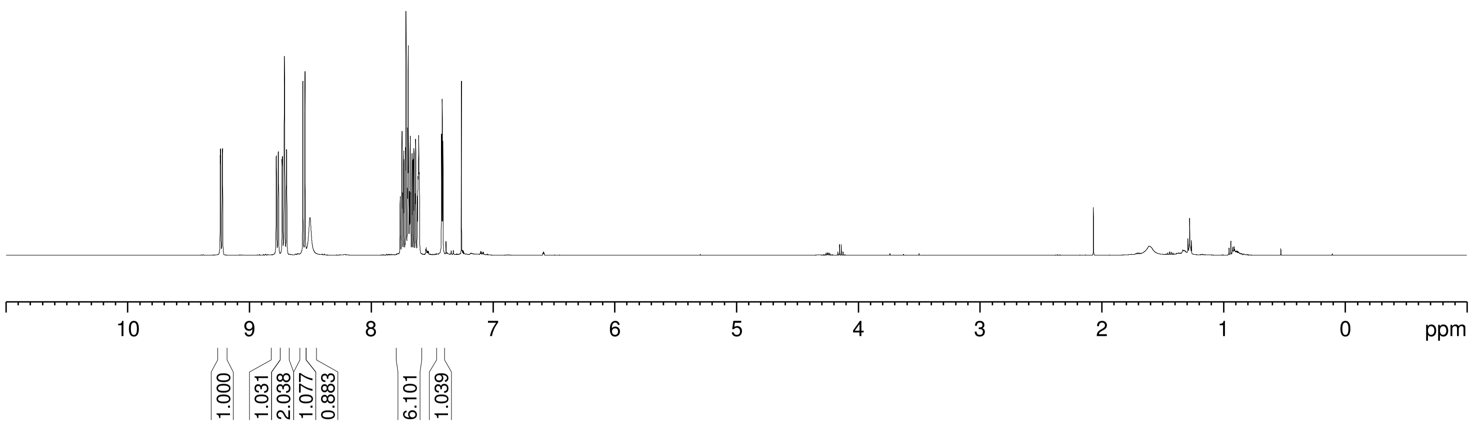
**32**

```
Current Data Parameters
NAME       RBS-2018-171
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_        20181023
Time            20.40
INSTRUM         av400
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              52882
SOLVENT         CDCl3
NS                 24
DS                  0
SWH         8012.820 Hz
FIDRES      0.151523 Hz
AQ         3.2998369 sec
RG            189.85
DW            62.400 usec
DE              6.50 usec
TE             298.3 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 ======
SFO1      400.1324008 MHz
NUC1               1H
P1              15.00 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI              65536
SF        400.1300177 MHz
WDW                EM
SSB     0
LB               0.30 Hz
GB      0
PC               1.00
```

Purified Product, 1H NMR



***34***

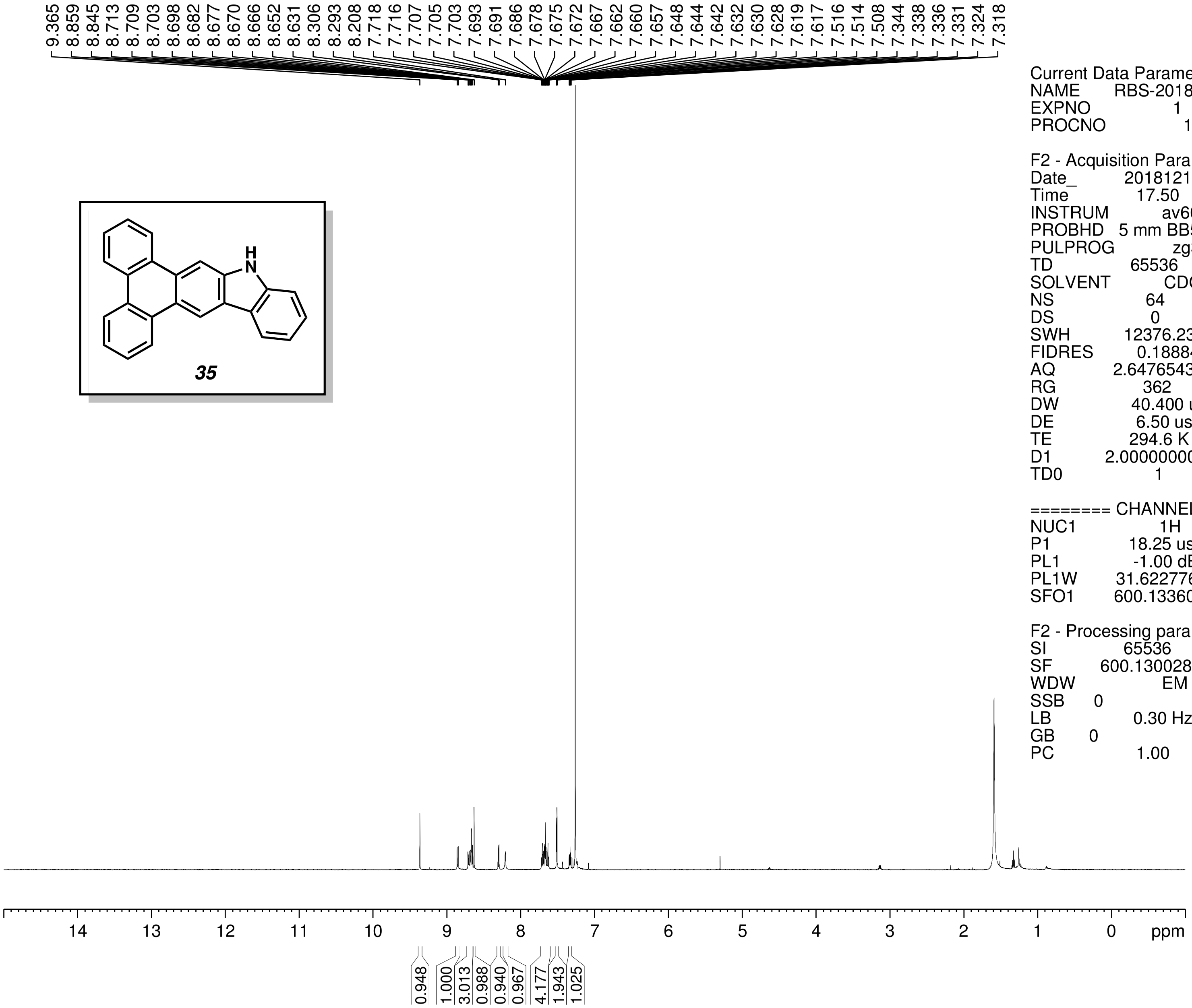


Current Data Parameters
NAME KAS-2021-000
EXPNO 32
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210714
Time 13.56 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 26.59
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

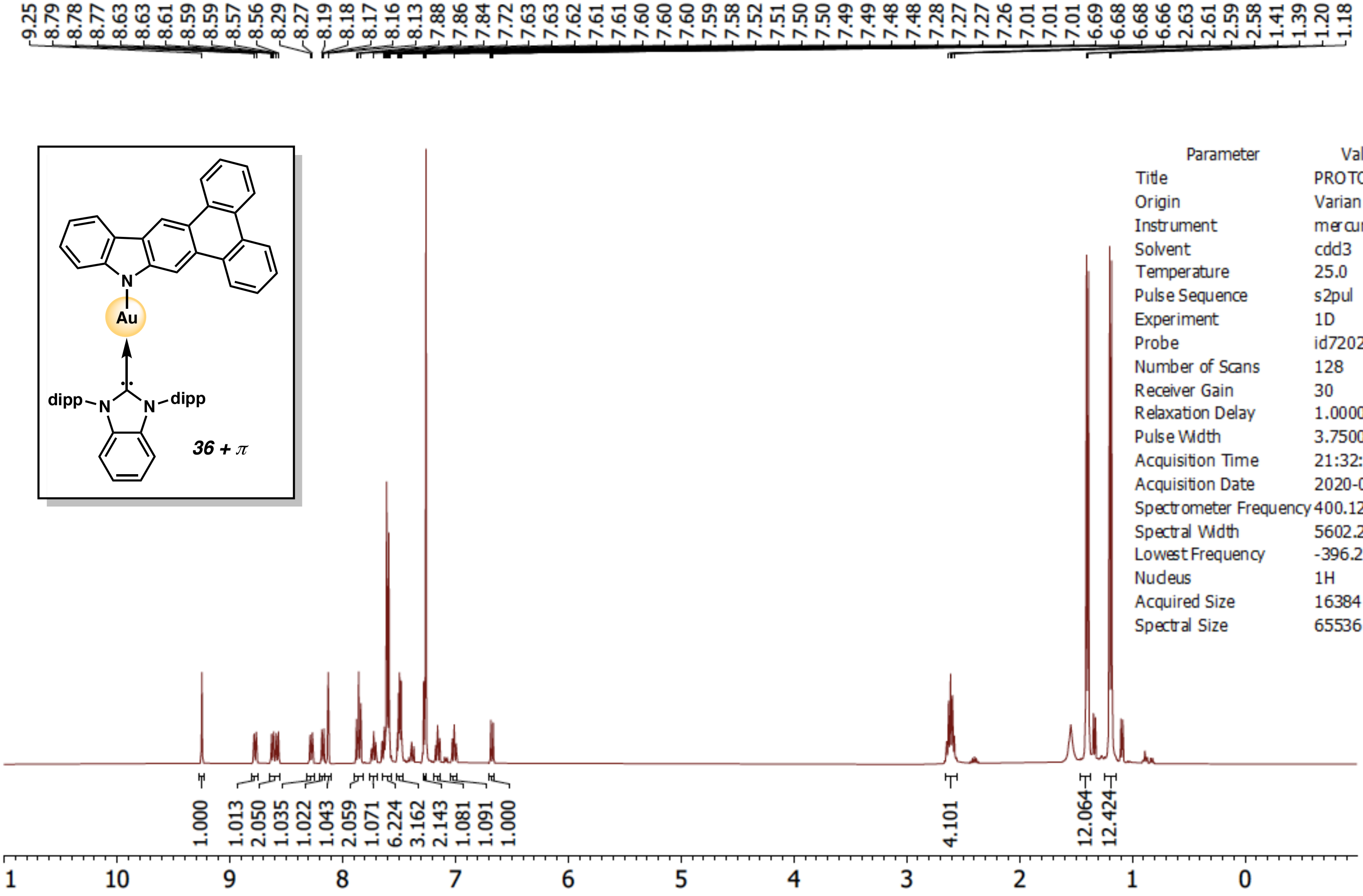
F2 - Processing parameters
SI 65536
SF 500.1300127 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified Product, 1H NMR



```
Current Data Parameters
NAME       RBS-2018-202
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20181217
Time              17.50
INSTRUM           av600
PROBHD    5 mm BB5
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    0
SWH          12376.237 Hz
FIDRES        0.188846 Hz
AQ           2.6476543 sec
RG                  362
DW               40.400 usec
DE                 6.50 usec
TE                294.6 K
D1          2.00000000 sec
TD0                   1

======== CHANNEL f1 =====
NUC1                 1H
P1                18.25 usec
PL1               -1.00 dB
PL1W        31.62277603 W
SFO1        600.1336008 MHz

F2 - Processing parameters
SI                65536
SF          600.1300286 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

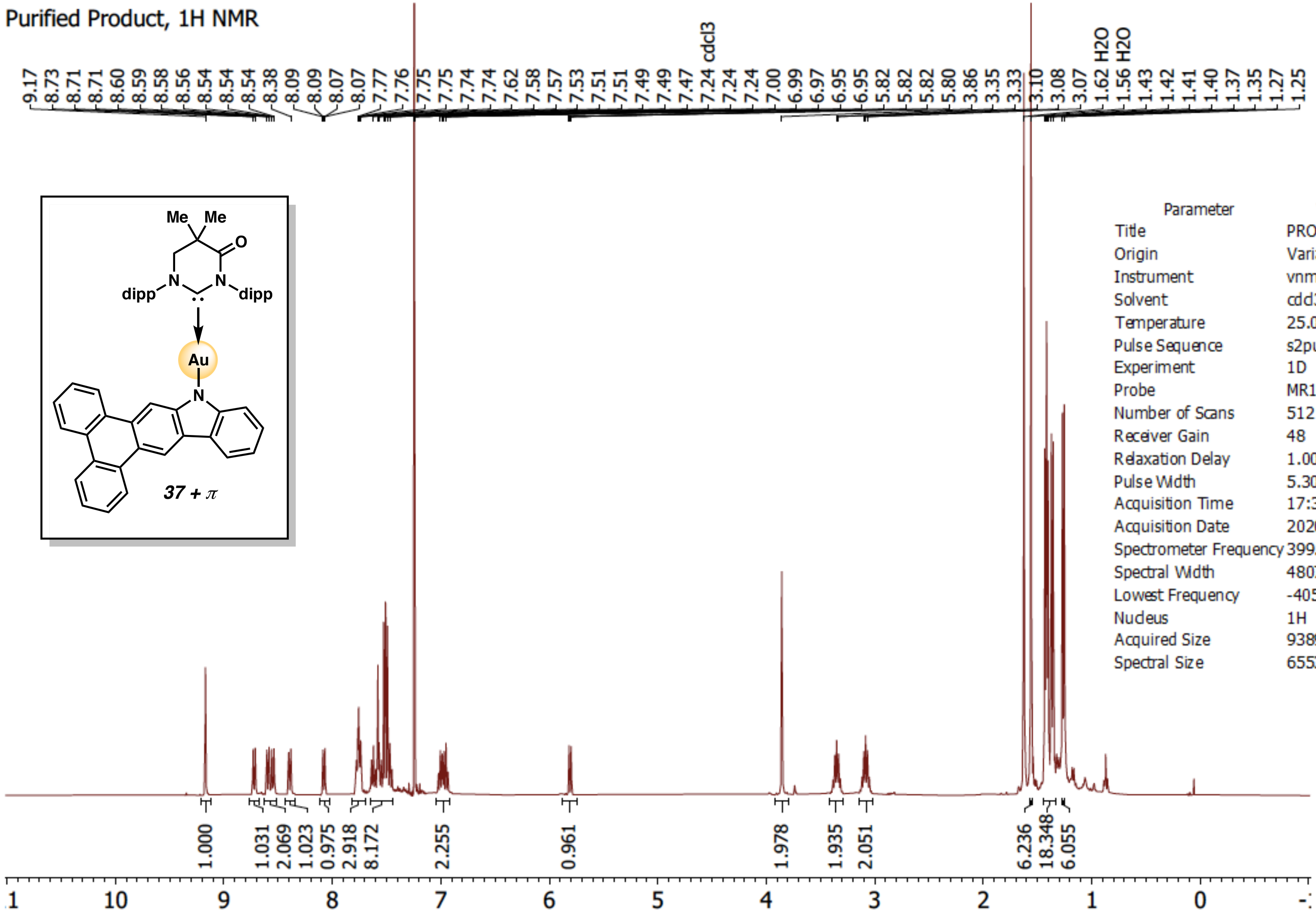
Purified Product, 1H NMR



36 + π

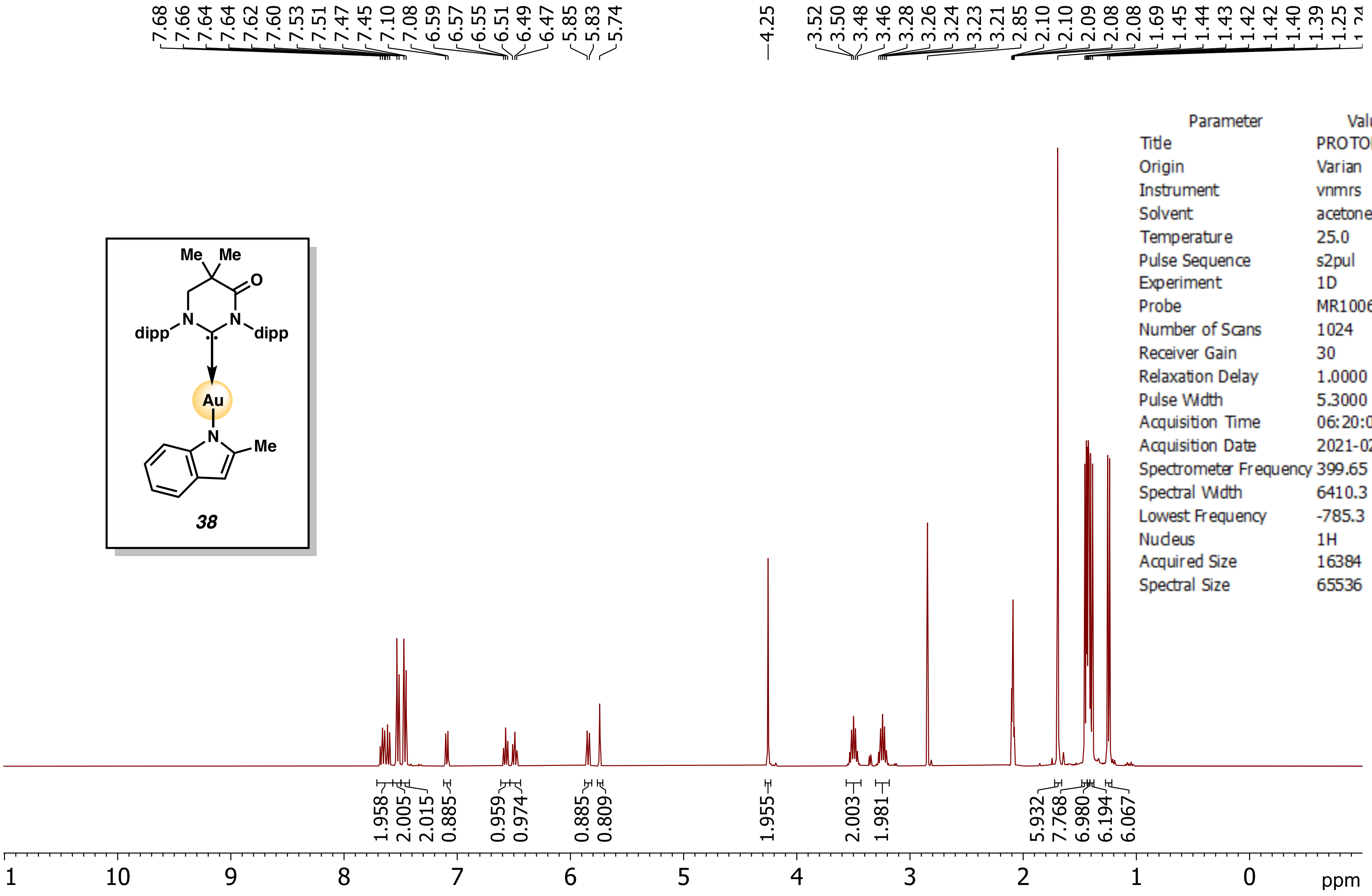
| Parameter | Value |
|---|---|
| Title | PROTON_01 |
| Origin | Varian |
| Instrument | mercury |
| Solvent | cdcl3 |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | id7202 |
| Number of Scans | 128 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 3.7500 |
| Acquisition Time | 21:32:55 |
| Acquisition Date | 2020-02-28 |
| Spectrometer Frequency | 400.12 |
| Spectral Width | 5602.2 |
| Lowest Frequency | -396.2 |
| Nucleus | 1H |
| Acquired Size | 16384 |
| Spectral Size | 65536 |

Purified Product, 1H NMR



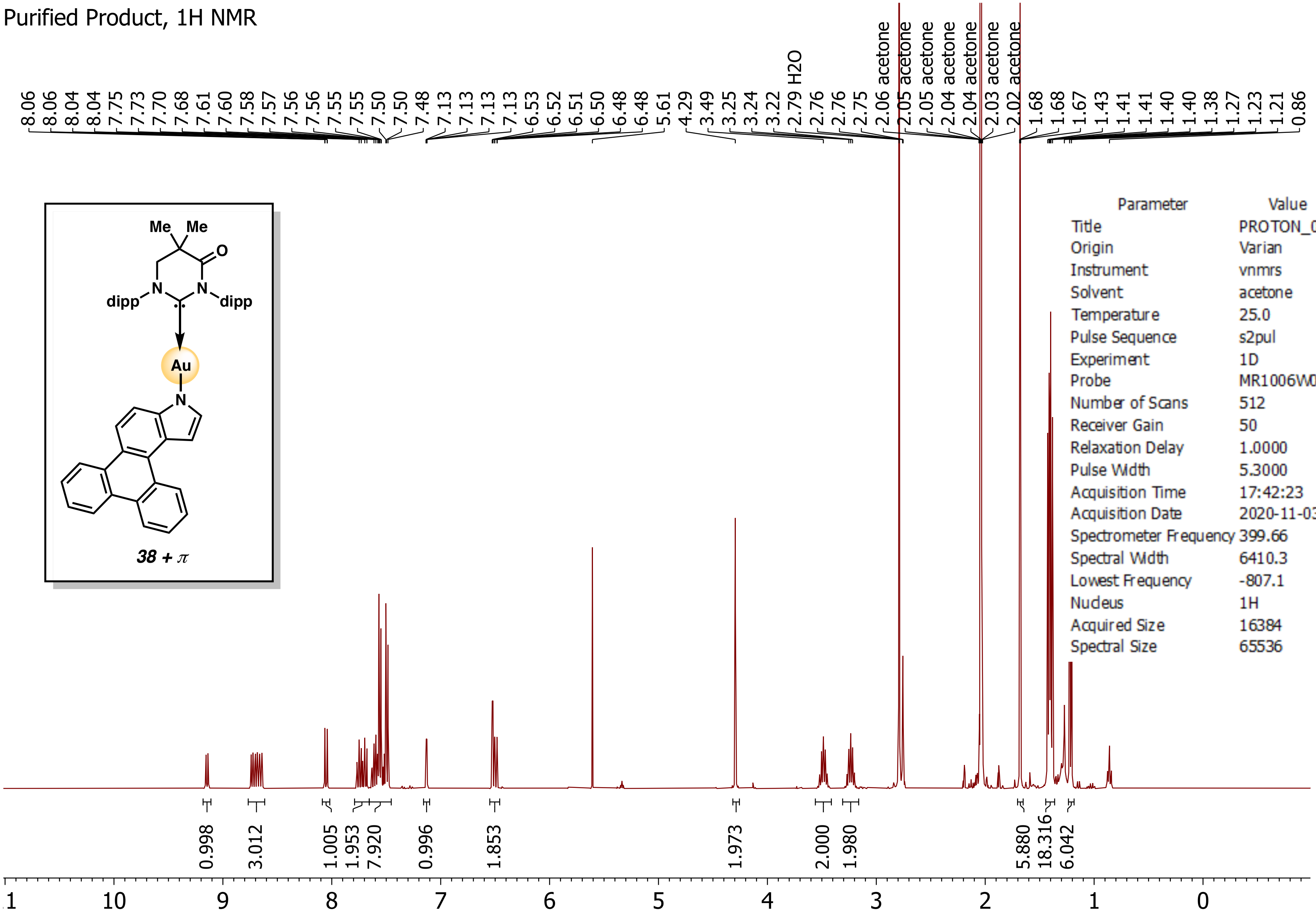
| Parameter | Value |
|---|---|
| Title | PROTON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | cdcl3 |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR1006W029 |
| Number of Scans | 512 |
| Receiver Gain | 48 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 5.3000 |
| Acquisition Time | 17:37:45 |
| Acquisition Date | 2020-03-06 |
| Spectrometer Frequency | 399.66 |
| Spectral Width | 4807.7 |
| Lowest Frequency | -405.5 |
| Nucleus | 1H |
| Acquired Size | 9389 |
| Spectral Size | 65536 |

Purified Product, 1H NMR



| Parameter | Value |
|---|---|
| Title | PROTON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | acetone |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR1006W029 |
| Number of Scans | 1024 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 5.3000 |
| Acquisition Time | 06:20:03 |
| Acquisition Date | 2021-02-13 |
| Spectrometer Frequency | 399.65 |
| Spectral Width | 6410.3 |
| Lowest Frequency | -785.3 |
| Nucleus | 1H |
| Acquired Size | 16384 |
| Spectral Size | 65536 |

Purified Product, 1H NMR

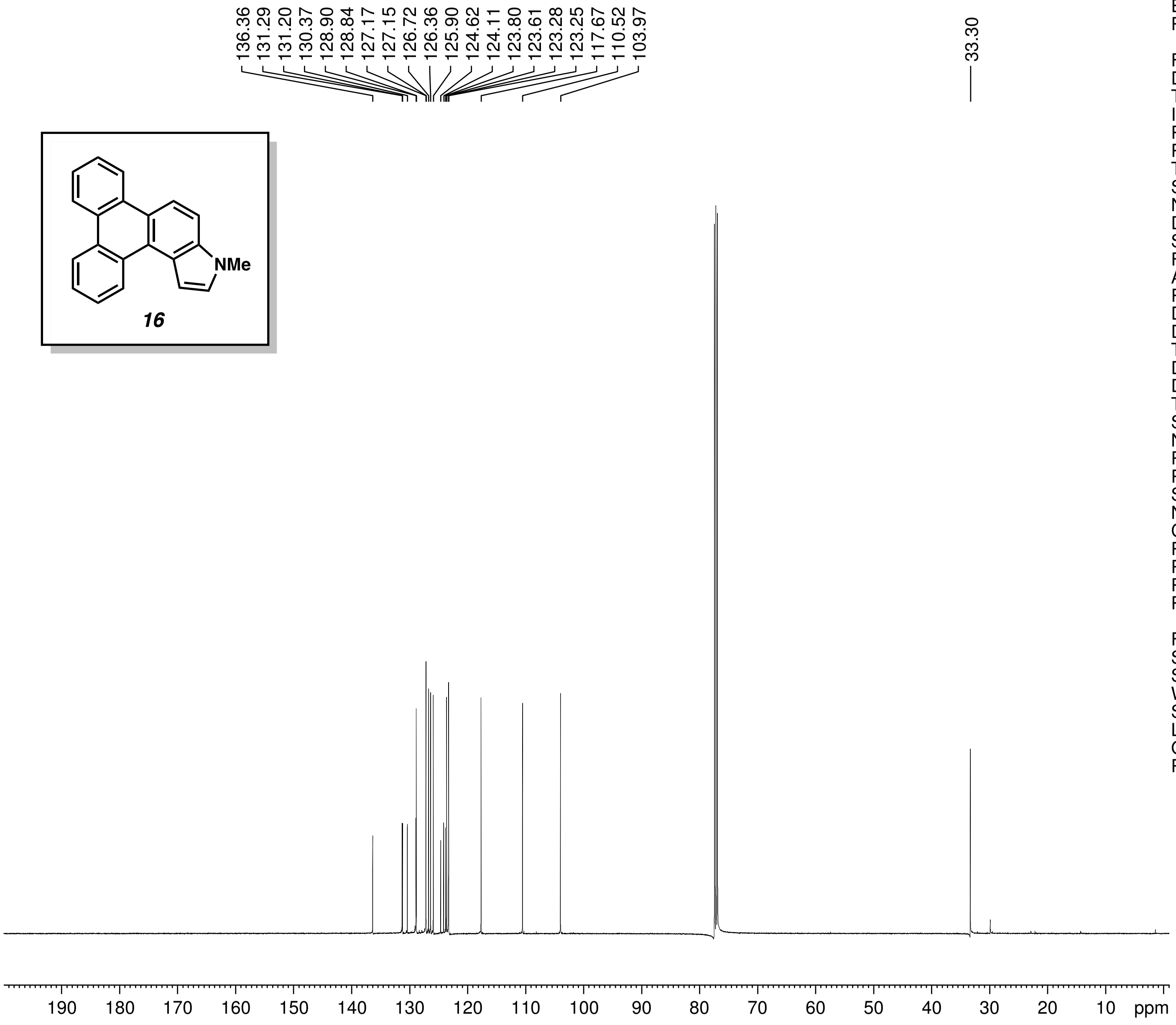


**38 + π**

| Parameter | Value |
|---|---|
| Title | PROTON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | acetone |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR1006W029 |
| Number of Scans | 512 |
| Receiver Gain | 50 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 5.3000 |
| Acquisition Time | 17:42:23 |
| Acquisition Date | 2020-11-03 |
| Spectrometer Frequency | 399.66 |
| Spectral Width | 6410.3 |
| Lowest Frequency | -807.1 |
| Nucleus | 1H |
| Acquired Size | 16384 |
| Spectral Size | 65536 |

# $^{13}$C NMR Spectra

Purified Product, 13C NMR

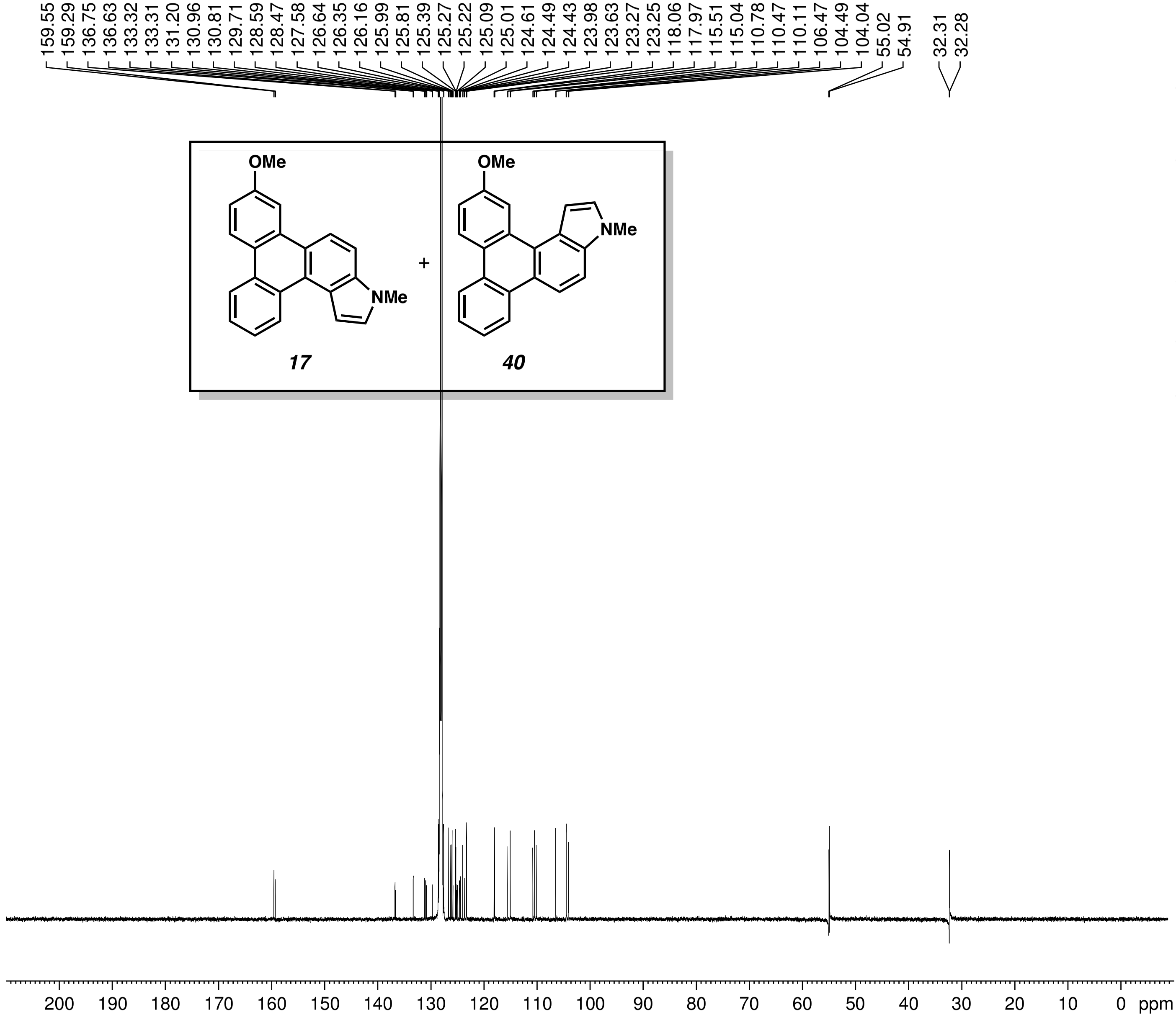


Current Data Parameters
NAME JVC-2018-087
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180624
Time 18.05 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 368
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577785 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified Product, 13C NMR



Current Data Parameters

| | |
|---|---|
| NAME | KAS-2018-052 |
| EXPNO | 2 |
| PROCNO | 1 |

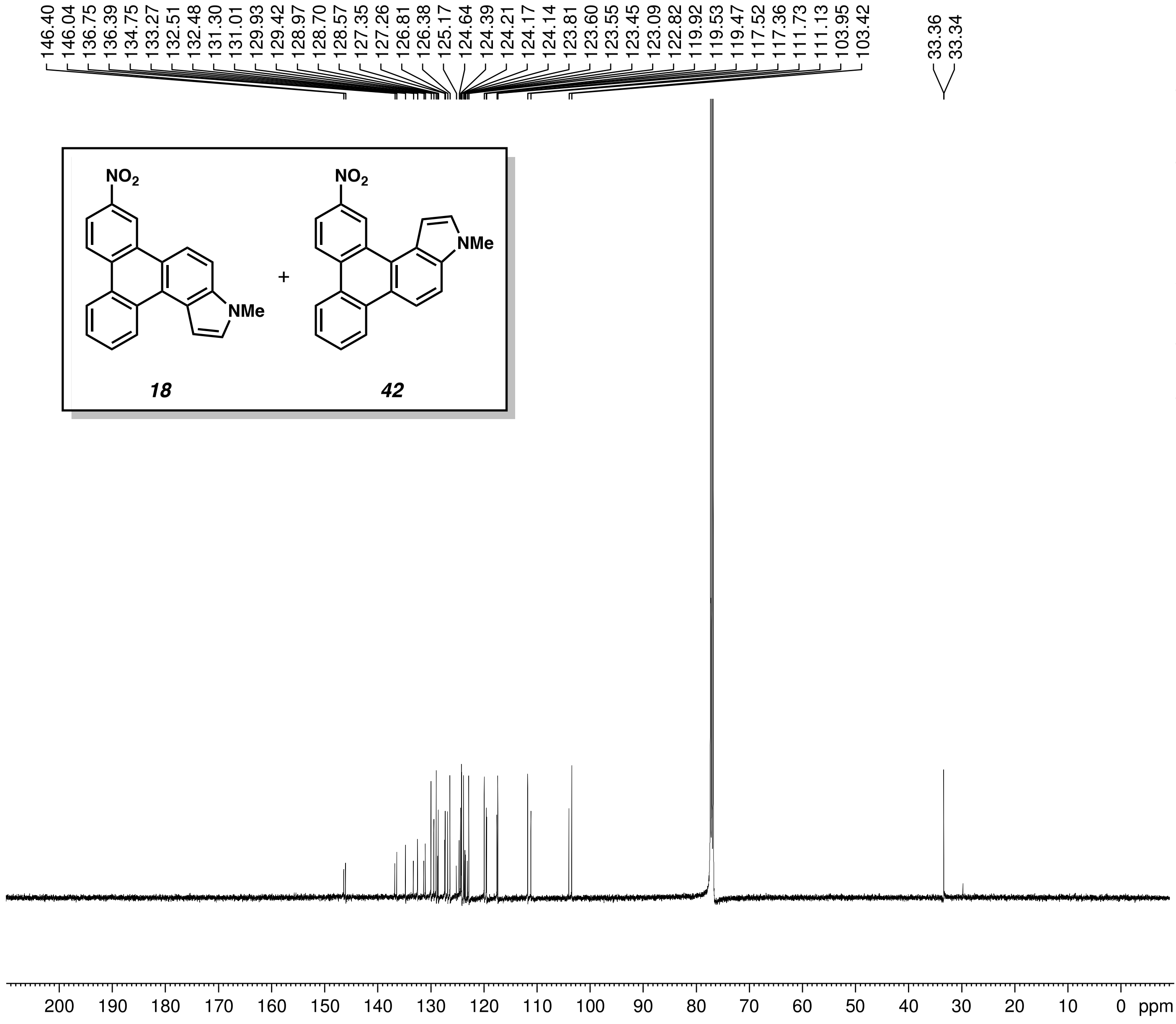
F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20180923 |
| Time | 17.42 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | C6D6 |
| NS | 92 |
| DS | 2 |
| SWH | 31250.000 Hz |
| FIDRES | 0.953674 Hz |
| AQ | 1.0485760 sec |
| RG | 14.67 |
| DW | 16.000 usec |
| DE | 18.00 usec |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 125.7722511 MHz |
| NUC1 | 13C |
| P1 | 9.63 usec |
| PLW1 | 23.00000000 W |
| SFO2 | 500.1330008 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 13.50000000 W |
| PLW12 | 0.21094000 W |
| PLW13 | 0.13500001 W |

F2 - Processing parameters

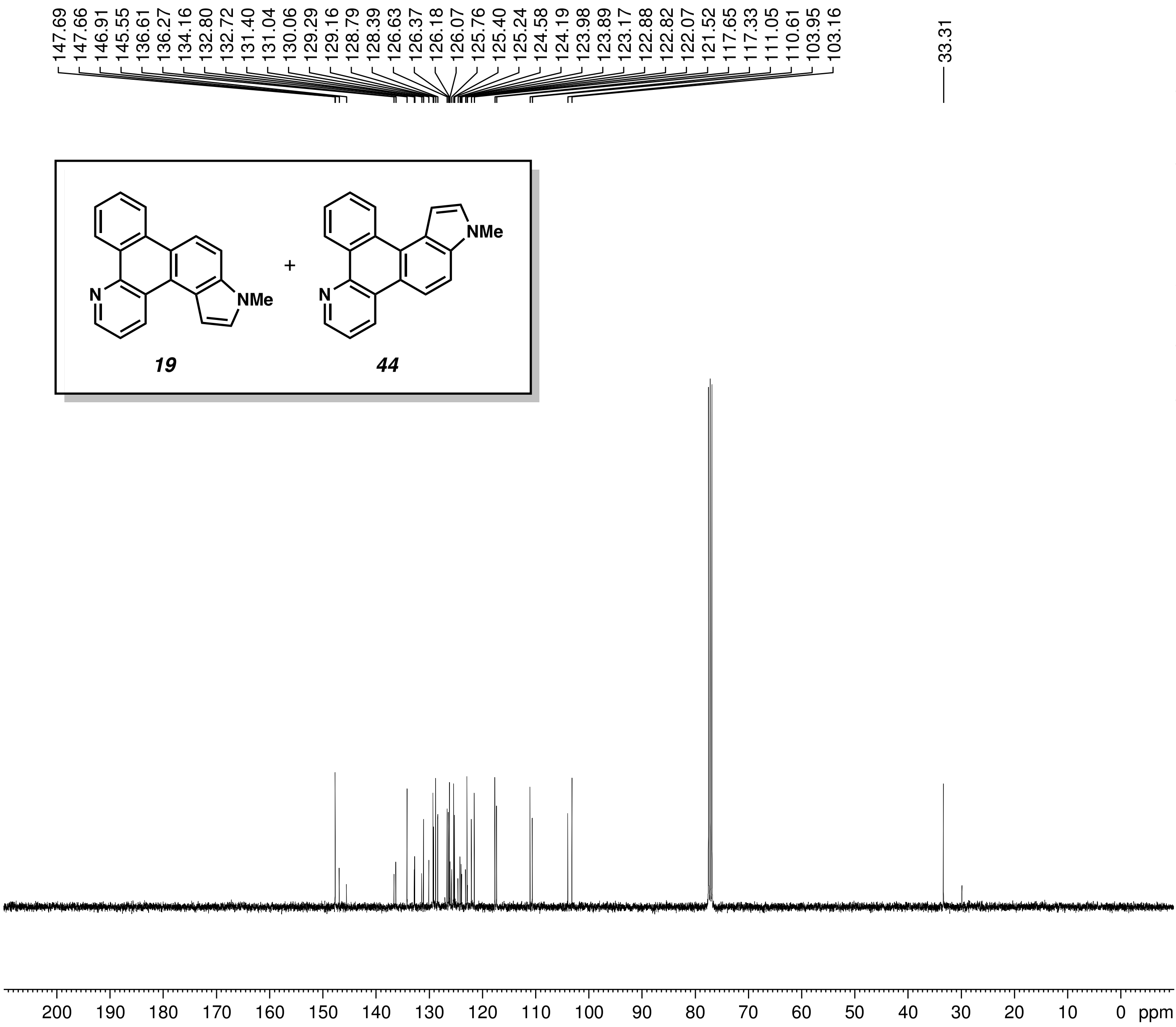
| | |
|---|---|
| SI | 131072 |
| SF | 125.7577435 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |
]

Purified Product, 13C NMR



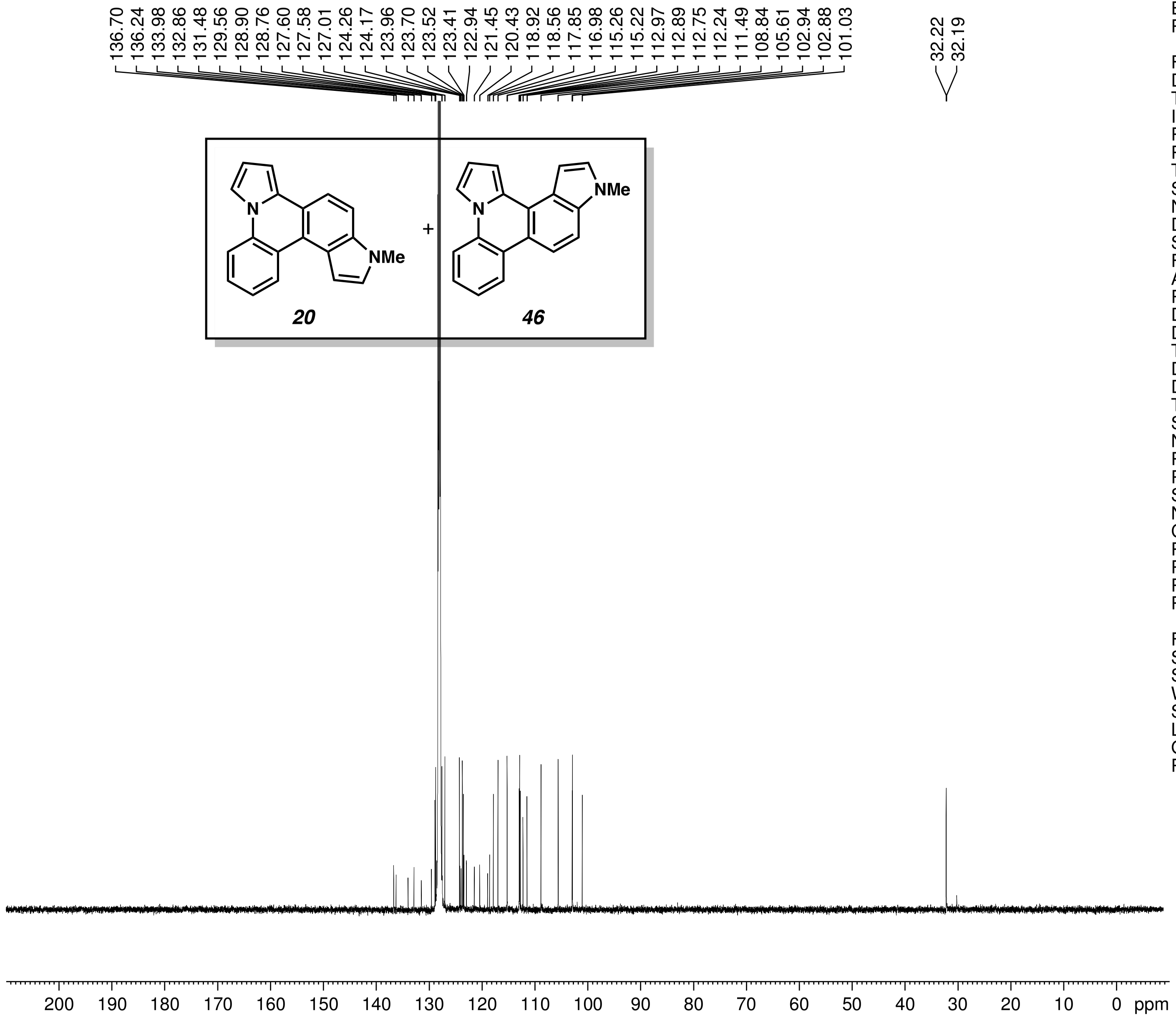
```
Current Data Parameters
NAME      KAS-2019-014
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20190122
Time            16.27 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD            65536
SOLVENT         CDCl3
NS              529
DS                2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE             28.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1
SFO1     125.7722511 MHz
NUC1             13C
P1             10.50 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2      waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.10610000 W

F2 - Processing parameters
SI            131072
SF       125.7577892 MHz
WDW               EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```

Purified Product, 13C NMR



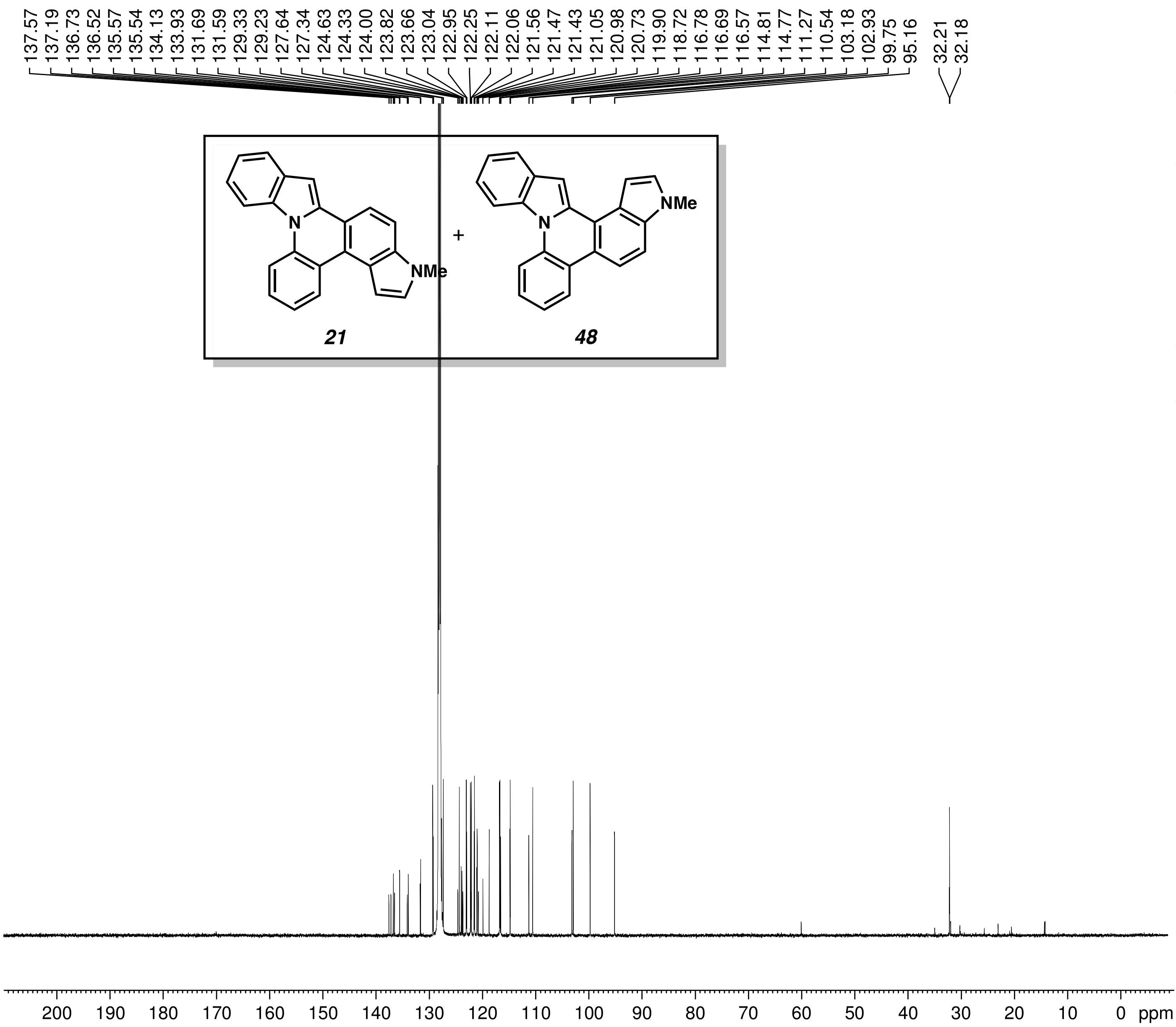
```
Current Data Parameters
NAME      JVC-2018-105
EXPNO              4
PROCNO             1

F2 - Acquisition Parameters
Date_        20180725
Time           23.55
INSTRUM        av400
PROBHD   5 mm PABBO BB/
PULPROG       zgpg30
TD           65536
SOLVENT        CDCl3
NS             352
DS               0
SWH        25252.525 Hz
FIDRES      0.385323 Hz
AQ         1.2976128 sec
RG           189.85
DW           19.800 usec
DE            6.50 usec
TE           299.1 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0              1

======== CHANNEL f1 =====
SFO1      100.6243395 MHz
NUC1            13C
P1            10.00 usec
PLW1       52.00000000 W

======== CHANNEL f2 =====
SFO2      400.1324008 MHz
NUC2             1H
CPDPRG[2       waltz16
PCPD2          90.00 usec
PLW2       13.00000000 W
PLW12       0.36111000 W
PLW13       0.29249999 W

F2 - Processing parameters
SI           65536
SF        100.6127603 MHz
WDW             EM
SSB     0
LB             1.00 Hz
GB      0
PC             1.40
```

Purified Product, 13C NMR



```
Current Data Parameters
NAME        KAS-2019-015
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20190122
Time             20.13 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                  147
DS                    2
SWH          31250.000 Hz
FIDRES        0.953674 Hz
AQ          1.0485760 sec
RG               204.54
DW             16.000 usec
DE              28.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                   1
SFO1      125.7722511 MHz
NUC1                13C
P1              10.50 usec
PLW1      23.00000000 W
SFO2      500.1330008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2           80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.10610000 W

F2 - Processing parameters
SI               131072
SF        125.7577434 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Purified Product, 13C NMR



Current Data Parameters

| | |
|---|---|
| NAME | JVC-2019-010 |
| EXPNO | 16 |
| PROCNO | 1 |

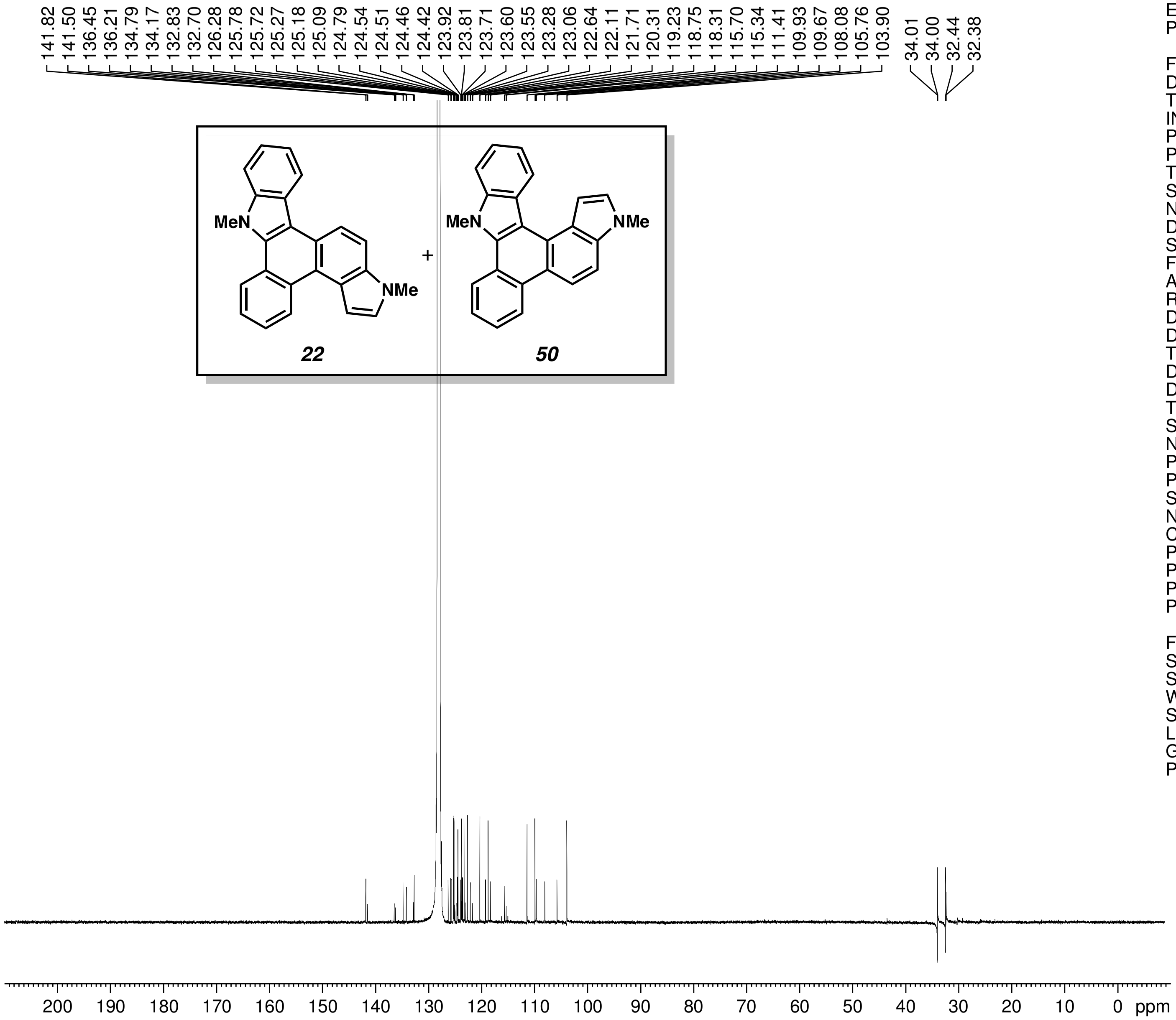
F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20190125 |
| Time | 15.05 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | C6D6 |
| NS | 234 |
| DS | 2 |
| SWH | 31250.000 Hz |
| FIDRES | 0.953674 Hz |
| AQ | 1.0485760 sec |
| RG | 204.54 |
| DW | 16.000 usec |
| DE | 28.00 usec |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 125.7722511 MHz |
| NUC1 | 13C |
| P1 | 10.50 usec |
| PLW1 | 23.00000000 W |
| SFO2 | 500.1330008 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 13.50000000 W |
| PLW12 | 0.21094000 W |
| PLW13 | 0.10610000 W |

F2 - Processing parameters

| | |
|---|---|
| SI | 131072 |
| SF | 125.7577432 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

Purified Product, 13C NMR

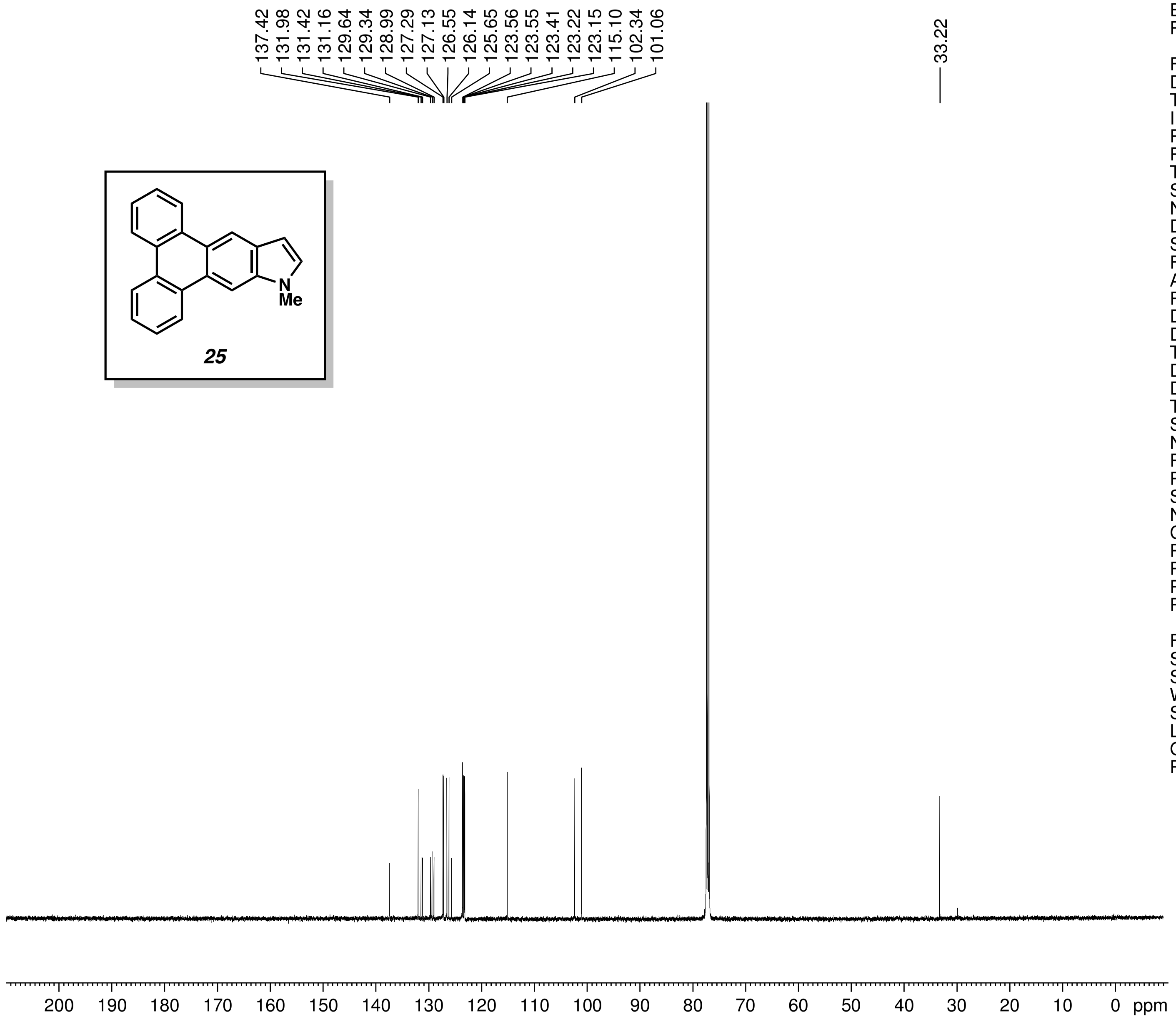


Current Data Parameters
NAME JVC-2018-107-3-2D
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180820
Time 2.52 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 4600
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577430 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified Product, 13C NMR



**25**

Current Data Parameters

| | |
|---|---|
| NAME | RBS-2019-012 |
| EXPNO | 4 |
| PROCNO | 1 |

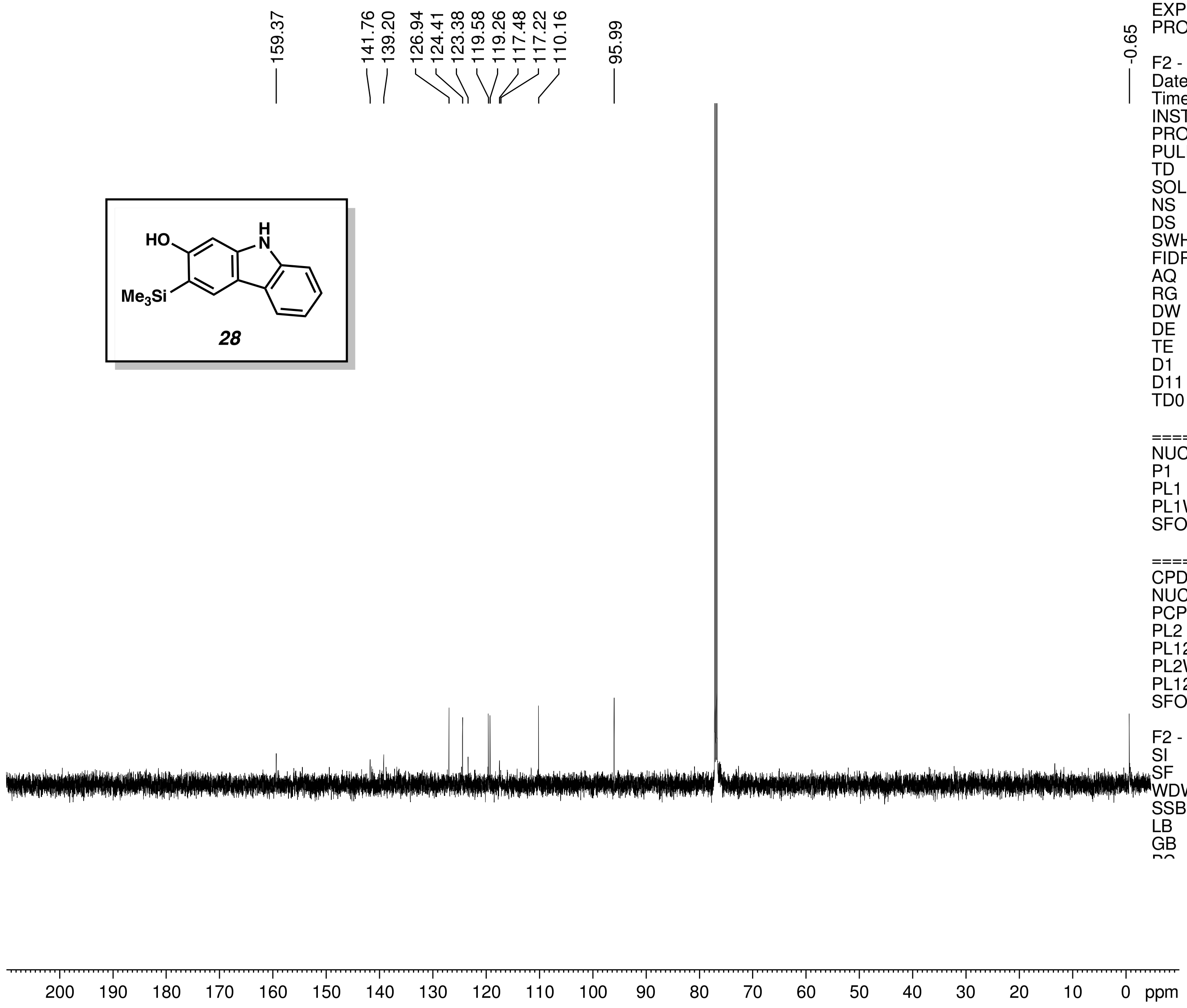
F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20190127 |
| Time | 12.59 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 240 |
| DS | 2 |
| SWH | 31250.000 Hz |
| FIDRES | 0.953674 Hz |
| AQ | 1.0485760 sec |
| RG | 204.54 |
| DW | 16.000 usec |
| DE | 28.00 usec |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 125.7722511 MHz |
| NUC1 | 13C |
| P1 | 10.50 usec |
| PLW1 | 23.00000000 W |
| SFO2 | 500.1330008 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 13.50000000 W |
| PLW12 | 0.21094000 W |
| PLW13 | 0.10610000 W |

F2 - Processing parameters

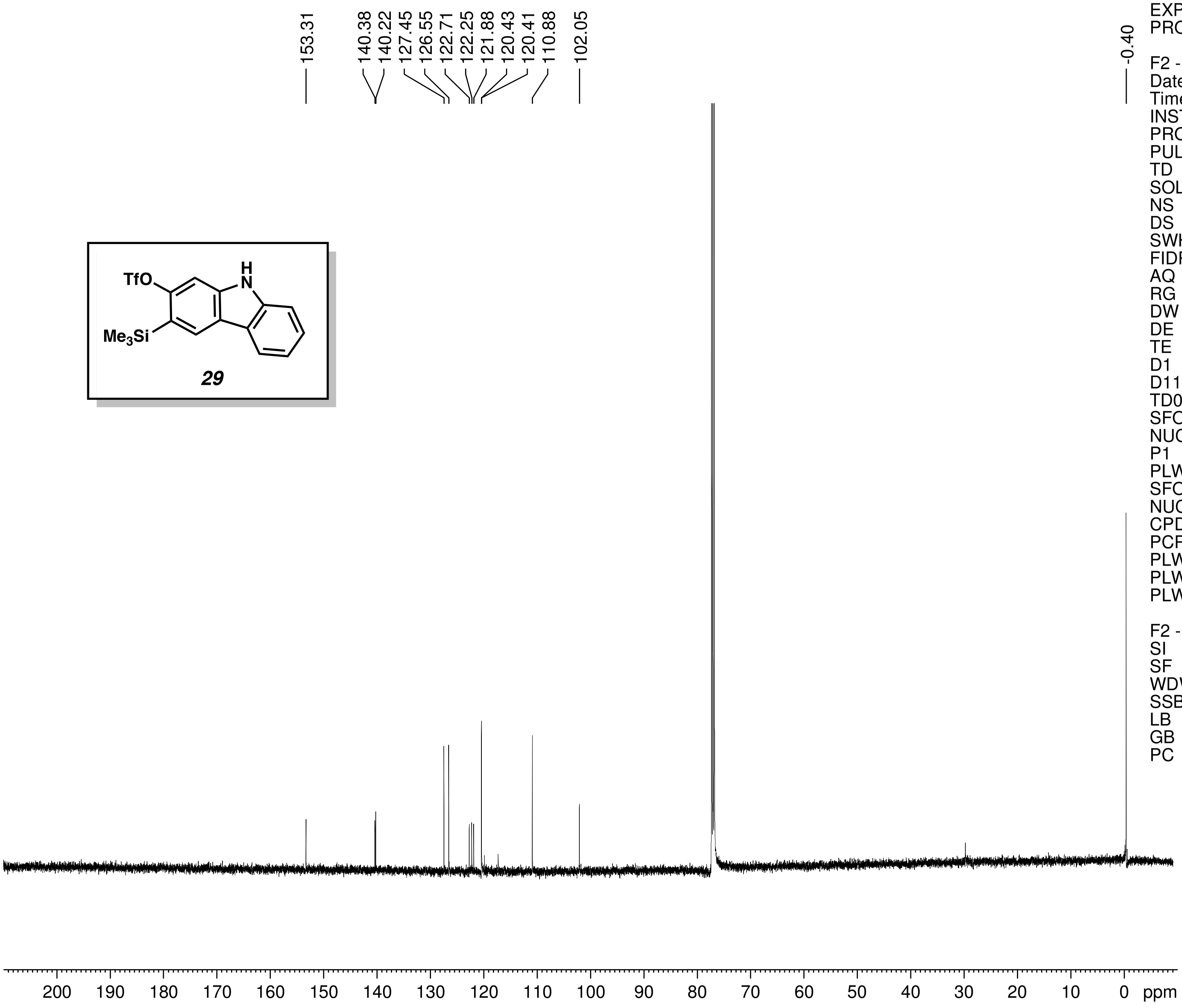
| | |
|---|---|
| SI | 131072 |
| SF | 125.7577725 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

Purified Product, 13C NMR



```
Current Data Parameters
NAME      KAS-2020-017
EXPNO              3
PROCNO           999

F2 - Acquisition Parameters
Date_         20200121
Time             10.32
INSTRUM          av600
PROBHD   5 mm BB5
PULPROG        zgdc30
TD             65536
SOLVENT          CDCl3
NS               181
DS                 0
SWH        37593.984 Hz
FIDRES      0.573639 Hz
AQ         0.8716288 sec
RG           18390.4
DW            13.300 usec
DE              6.50 usec
TE             295.9 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ====
NUC1             13C
P1             10.50 usec
PL1     0 dB
PL1W      75.35659027 W
SFO1      150.9209173 MHz

======== CHANNEL f2 ====
CPDPRG[2        waltz16
NUC2                1H
PCPD2          100.00 usec
PL2             -1.00 dB
PL12            14.65 dB
PL2W      31.62277603 W
PL12W      0.86099380 W
SFO2      600.1336008 MHz

F2 - Processing parameters
SI             65536
SF        150.9028319 MHz
WDW                EM
SSB     0
LB              1.00 Hz
GB      0
```

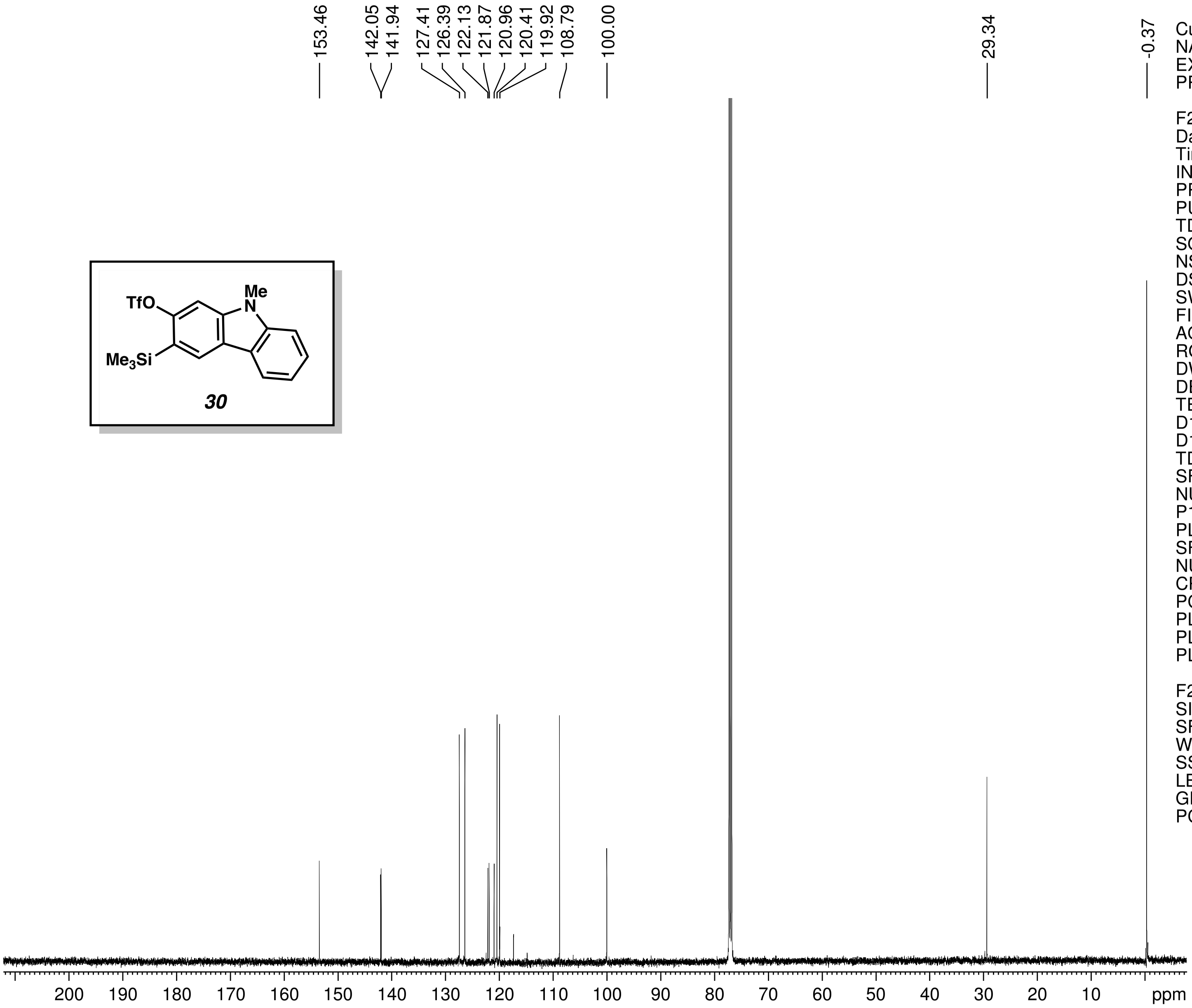
Purified Product, 13C NMR



**29**

```
Current Data Parameters
NAME        KAS-2021-000
EXPNO              201
PROCNO               1

F2 - Acquisition Parameters
Date_         20210728
Time            15.26 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD            65536
SOLVENT         CDCl3
NS               193
DS                 2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE             28.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1
SFO1      125.7722511 MHz
NUC1             13C
P1             10.50 usec
PLW1       23.00000000 W
SFO2      500.1330008 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2          80.00 usec
PLW2       13.50000000 W
PLW12       0.21094000 W
PLW13       0.10610000 W

F2 - Processing parameters
SI            131072
SF       125.7577892 MHz
WDW               EM
SSB      0
LB              1.00 Hz
GB       0
PC              1.40
```

Purified Product, 13C NMR



**30**

Current Data Parameters

| | |
|---|---|
| NAME | KAS-2021-000 |
| EXPNO | 21 |
| PROCNO | 1 |

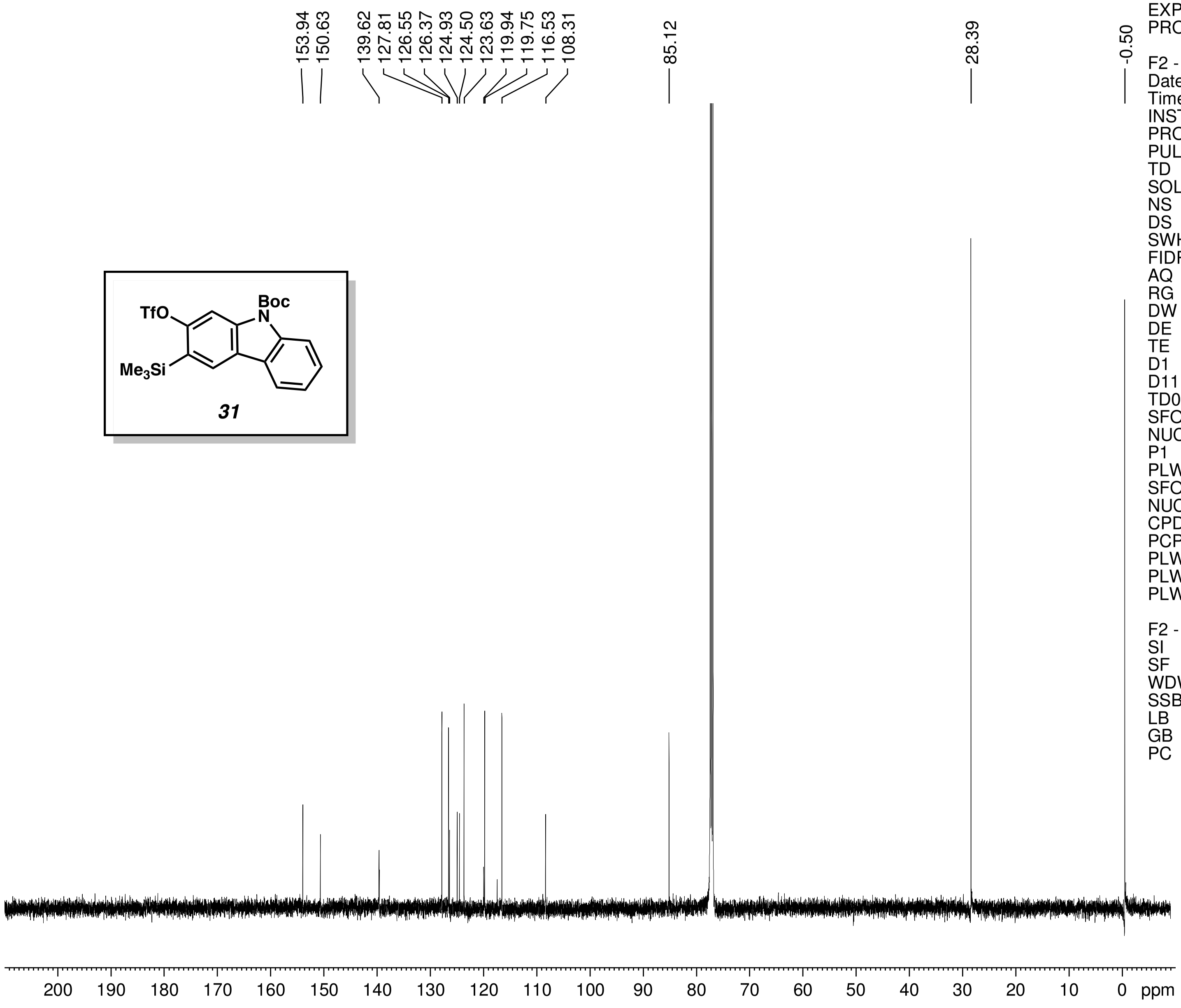
F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20210713 |
| Time | 18.47 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 46 |
| DS | 2 |
| SWH | 31250.000 Hz |
| FIDRES | 0.953674 Hz |
| AQ | 1.0485760 sec |
| RG | 204.54 |
| DW | 16.000 usec |
| DE | 28.00 usec |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 125.7722511 MHz |
| NUC1 | 13C |
| P1 | 10.50 usec |
| PLW1 | 23.00000000 W |
| SFO2 | 500.1330008 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 13.50000000 W |
| PLW12 | 0.21094000 W |
| PLW13 | 0.10610000 W |

F2 - Processing parameters

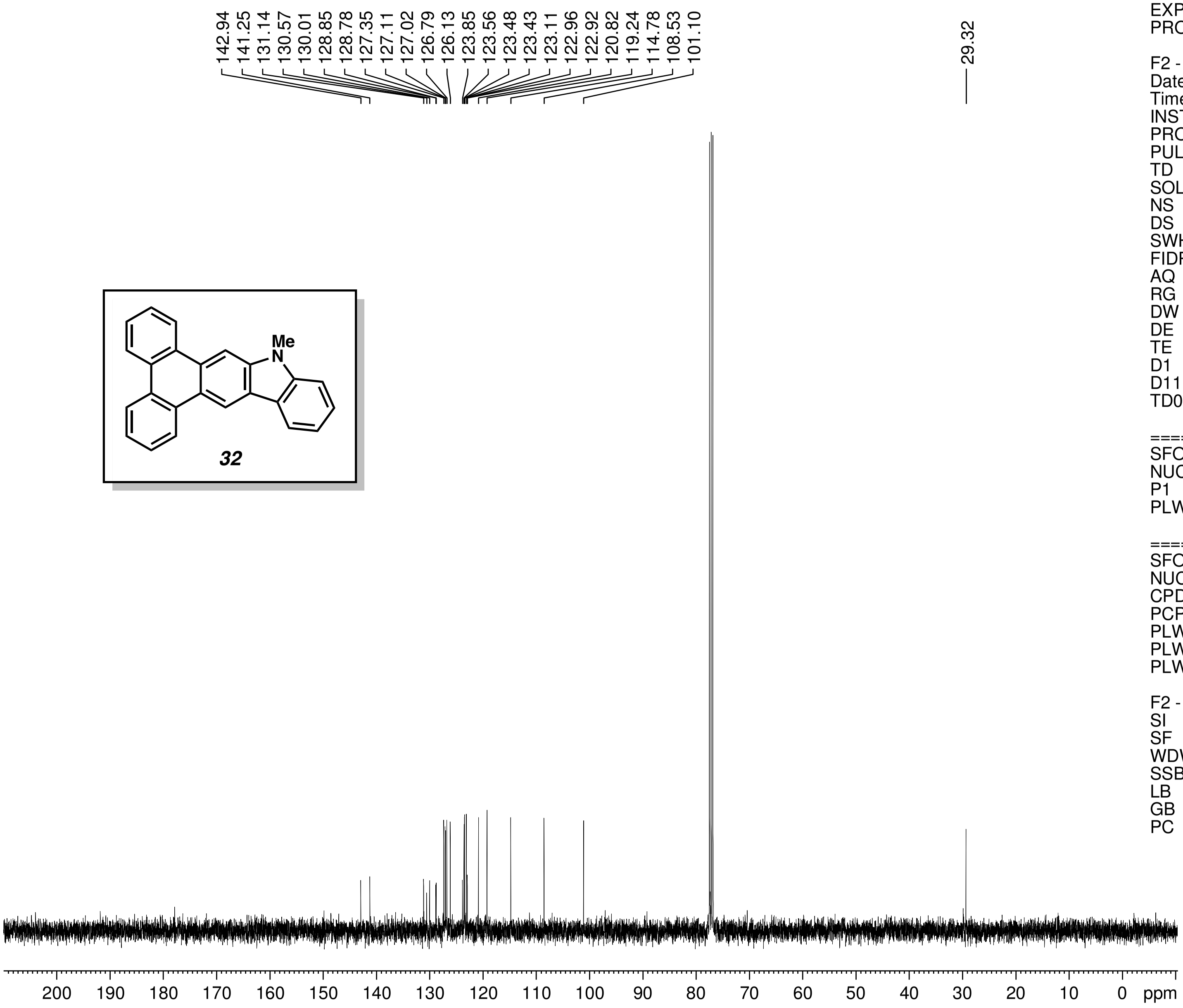
| | |
|---|---|
| SI | 131072 |
| SF | 125.7577892 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

Purified Product, 13C NMR



```
Current Data Parameters
NAME       KAS-2021-000
EXPNO               111
PROCNO                1

F2 - Acquisition Parameters
Date_          20210722
Time            16.27 h
INSTRUM           av500
PROBHD   Z119248_0002 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   85
DS                    2
SWH        31250.000 Hz
FIDRES      0.953674 Hz
AQ        1.0485760 sec
RG               204.54
DW           16.000 usec
DE            28.00 usec
TE              298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                   1
SFO1     125.7722511 MHz
NUC1                13C
P1           10.50 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2        80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.10610000 W

F2 - Processing parameters
SI               131072
SF       125.7577769 MHz
WDW                  EM
SSB      0
LB              1.00 Hz
GB       0
PC                 1.40
```

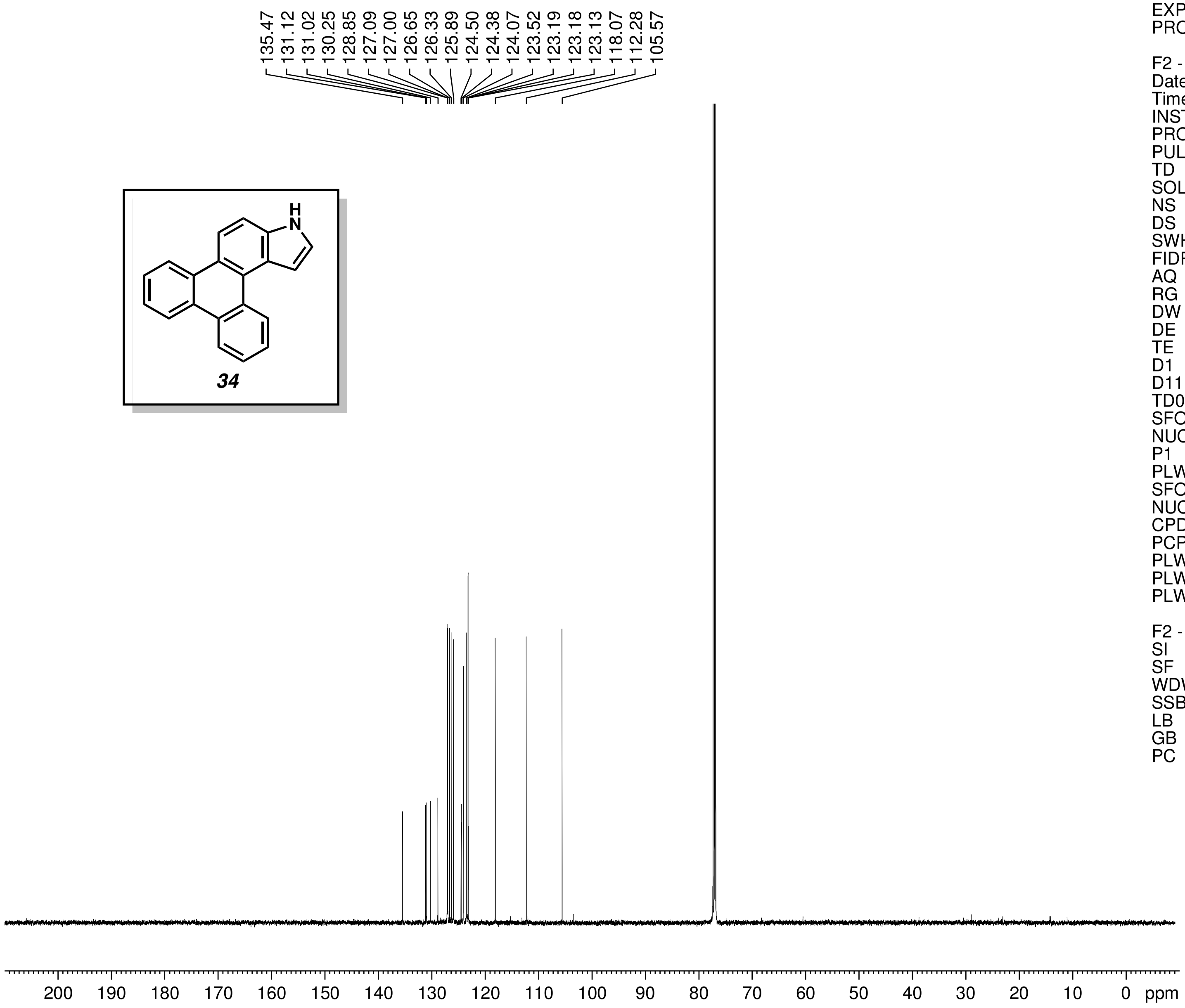
Purified Product, 13C NMR



**32**

```
Current Data Parameters
NAME       RBS-2018-171
EXPNO              5
PROCNO             1

F2 - Acquisition Parameters
Date_         20181106
Time             16.21
INSTRUM          av400
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD             65536
SOLVENT          CDCl3
NS                  88
DS                   0
SWH        25252.525 Hz
FIDRES      0.385323 Hz
AQ        1.2976128 sec
RG             189.85
DW          19.800 usec
DE           6.50 usec
TE             299.2 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

======== CHANNEL f1 =====
SFO1     100.6243395 MHz
NUC1                13C
P1           10.00 usec
PLW1     52.00000000 W

======== CHANNEL f2 =====
SFO2     400.1324008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2        90.00 usec
PLW2     13.00000000 W
PLW12     0.36111000 W
PLW13     0.29249999 W

F2 - Processing parameters
SI             65536
SF       100.6127581 MHz
WDW               EM
SSB      0
LB              1.00 Hz
GB      0
PC              1.40
```

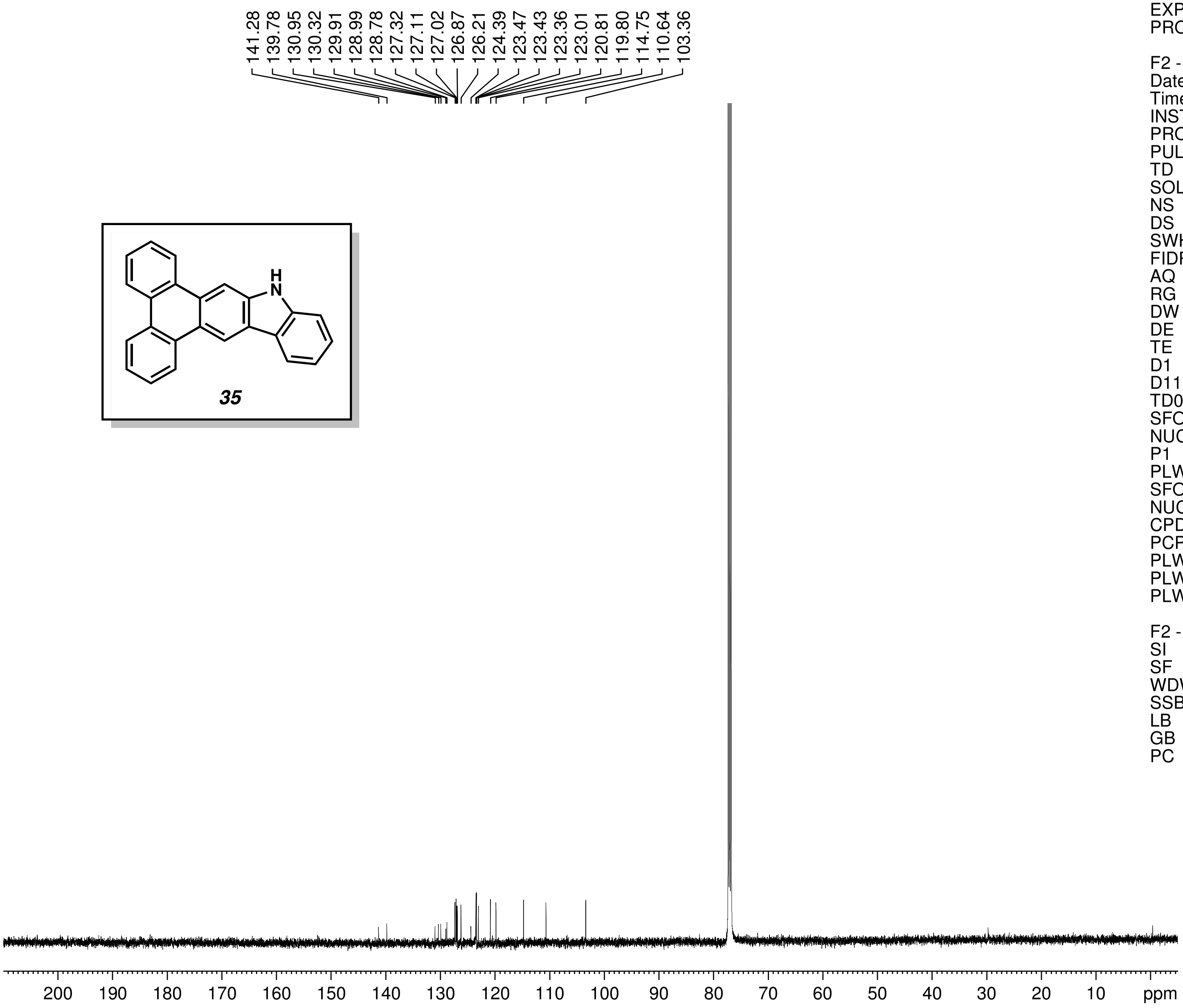
Purified Product, 13C NMR



**34**

|  |  |
|---|---|
| Current Data Parameters | |
| NAME | KAS-2021-000 |
| EXPNO | 33 |
| PROCNO | 1 |
| F2 - Acquisition Parameters | |
| Date_ | 20210714 |
| Time | 14.01 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 32 |
| DS | 2 |
| SWH | 31250.000 Hz |
| FIDRES | 0.953674 Hz |
| AQ | 1.0485760 sec |
| RG | 204.54 |
| DW | 16.000 usec |
| DE | 28.00 usec |
| TE | 298.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| SFO1 | 125.7722511 MHz |
| NUC1 | 13C |
| P1 | 10.50 usec |
| PLW1 | 23.00000000 W |
| SFO2 | 500.1330008 MHz |
| NUC2 | 1H |
| CPDPRG[2 | waltz16 |
| PCPD2 | 80.00 usec |
| PLW2 | 13.50000000 W |
| PLW12 | 0.21094000 W |
| PLW13 | 0.10610000 W |
| F2 - Processing parameters | |
| SI | 131072 |
| SF | 125.7577907 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

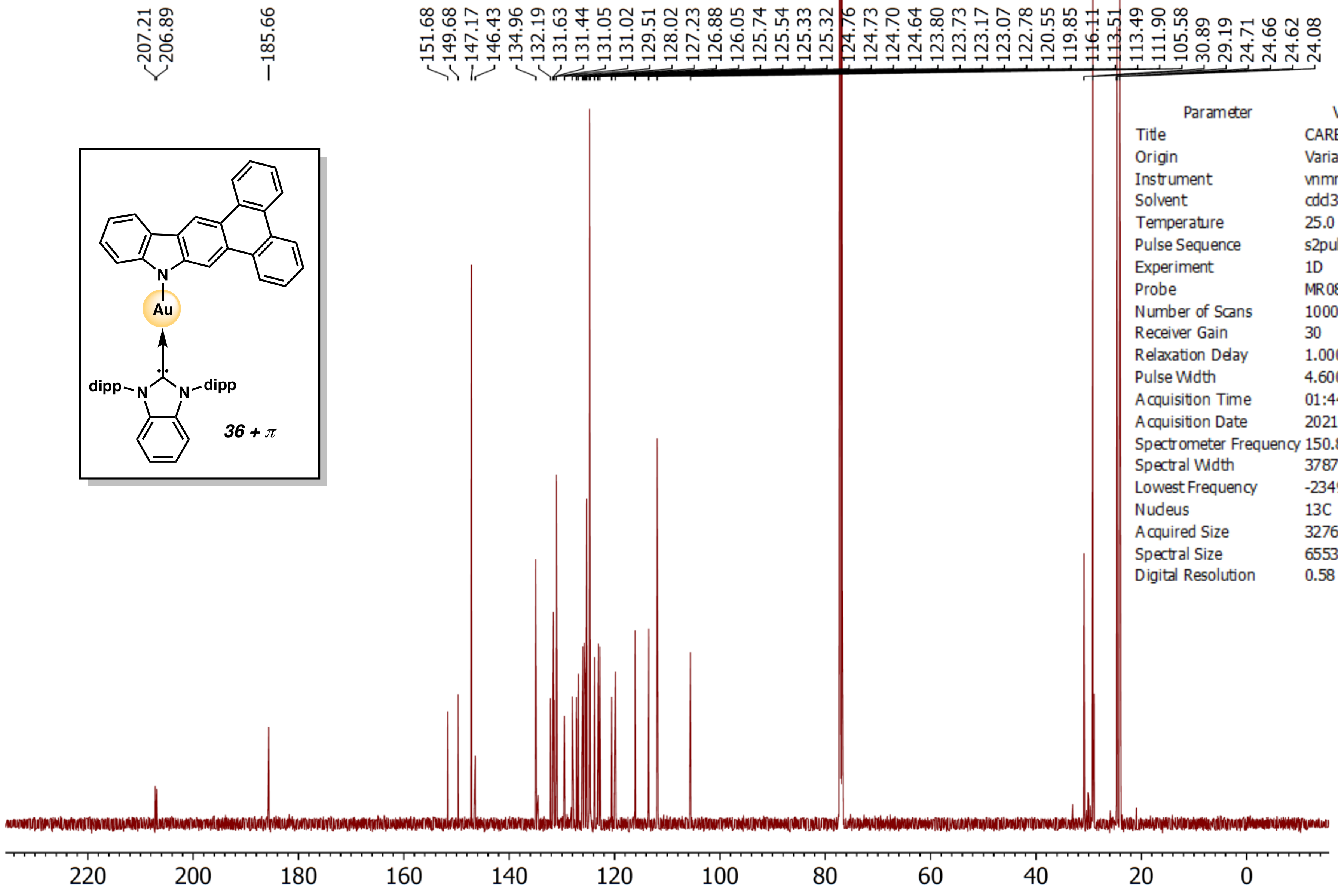
Purified Material, 13C NMR



**35**

```
Current Data Parameters
NAME      KAS-2021-000
EXPNO              6
PROCNO             1

F2 - Acquisition Parameters
Date_        20210405
Time           11.06 h
INSTRUM         av500
PROBHD   Z119248_0002 (
PULPROG        zgpg30
TD            65536
SOLVENT         CDCl3
NS              193
DS                2
SWH         31250.000 Hz
FIDRES       0.953674 Hz
AQ         1.0485760 sec
RG            204.54
DW            16.000 usec
DE             28.00 usec
TE             298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                1
SFO1     125.7722511 MHz
NUC1             13C
P1             10.50 usec
PLW1     23.00000000 W
SFO2     500.1330008 MHz
NUC2              1H
CPDPRG[2       waltz16
PCPD2          80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.10610000 W

F2 - Processing parameters
SI            131072
SF       125.7577892 MHz
WDW               EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```

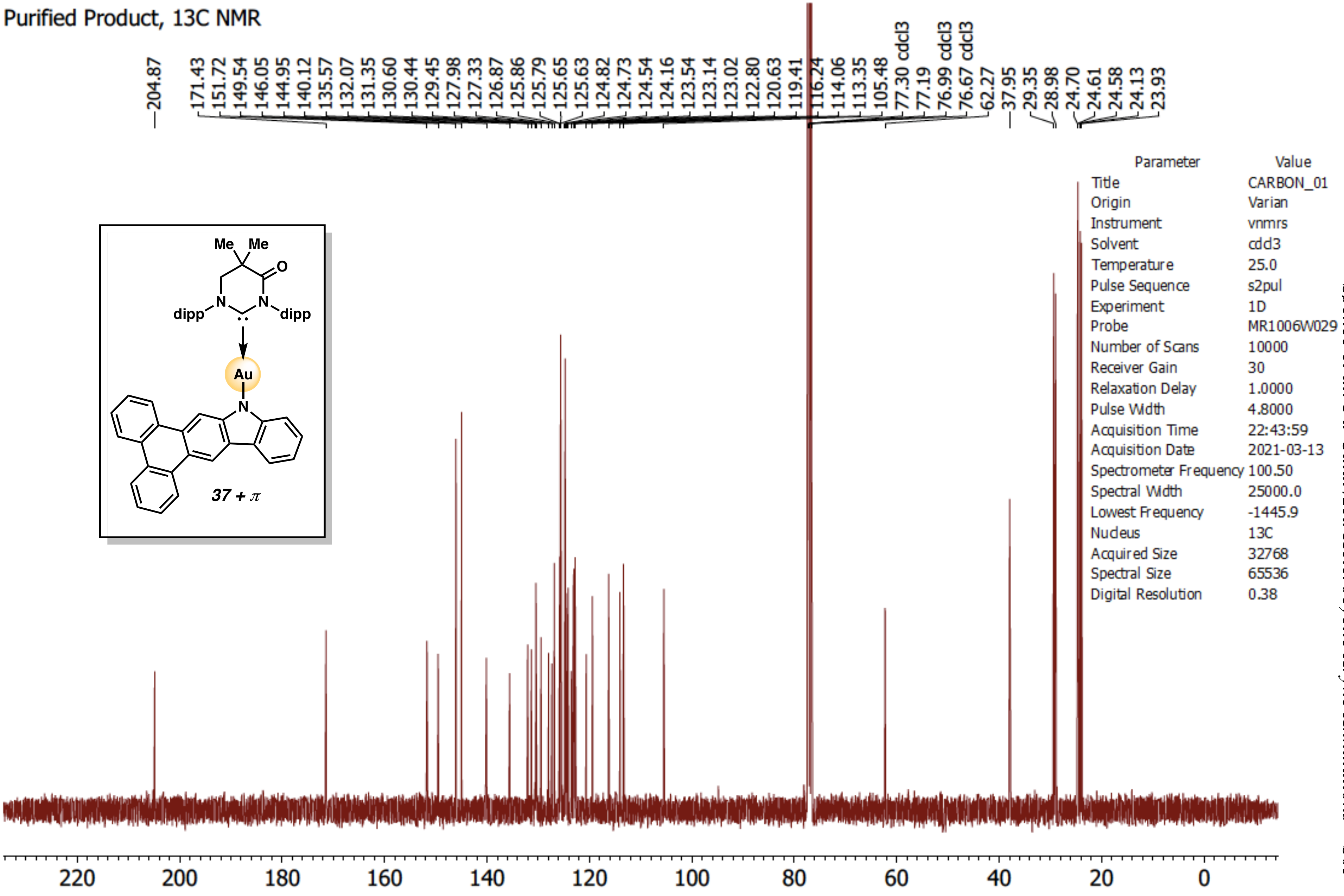
Purified Product, 13C NMR



36 + π

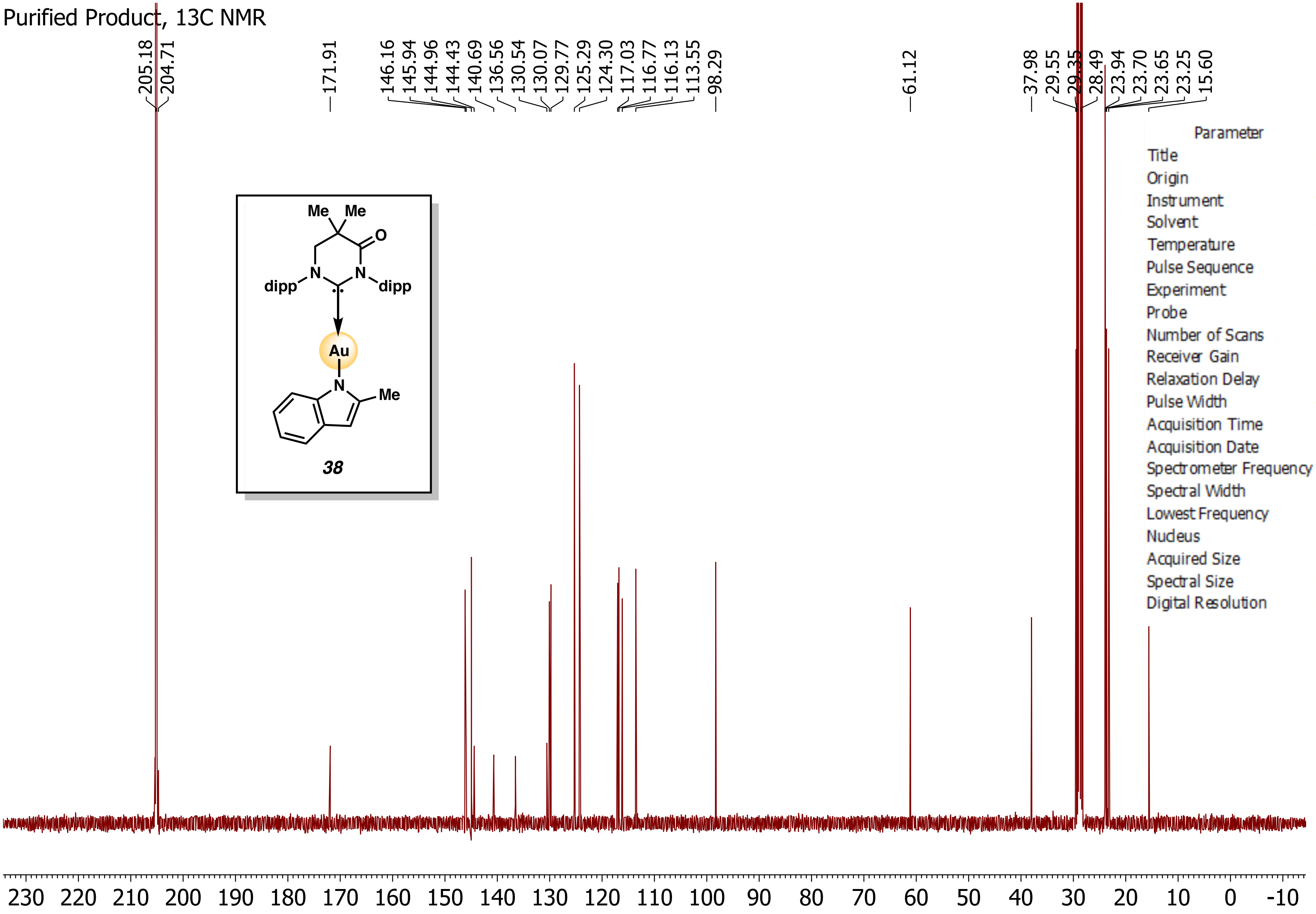
| Parameter | Value |
|---|---|
| Title | CARBON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | cdcl3 |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR0808W005 |
| Number of Scans | 10000 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 4.6000 |
| Acquisition Time | 01:44:46 |
| Acquisition Date | 2021-03-14 |
| Spectrometer Frequency | 150.84 |
| Spectral Width | 37878.8 |
| Lowest Frequency | -2349.3 |
| Nucleus | 13C |
| Acquired Size | 32768 |
| Spectral Size | 65536 |
| Digital Resolution | 0.58 |

Purified Product, 13C NMR



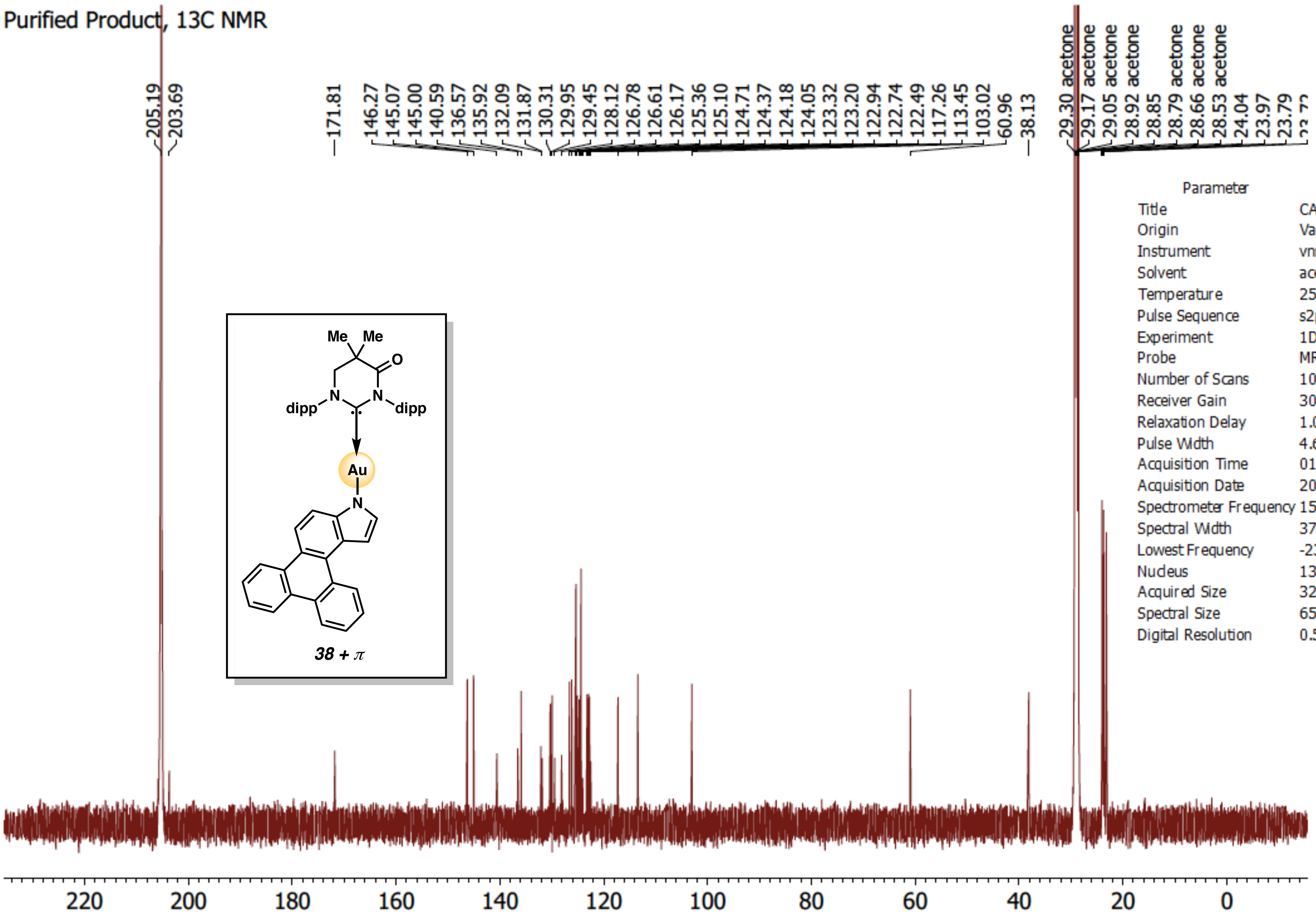
| Parameter | Value |
|---|---|
| Title | CARBON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | cdcl3 |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR1006W029 |
| Number of Scans | 10000 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 4.8000 |
| Acquisition Time | 22:43:59 |
| Acquisition Date | 2021-03-13 |
| Spectrometer Frequency | 100.50 |
| Spectral Width | 25000.0 |
| Lowest Frequency | -1445.9 |
| Nucleus | 13C |
| Acquired Size | 32768 |
| Spectral Size | 65536 |
| Digital Resolution | 0.38 |

Purified Product, 13C NMR



| Parameter | Value |
|---|---|
| Title | CARBON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | acetone |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR1006W029 |
| Number of Scans | 5000 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 4.8000 |
| Acquisition Time | 02:11:47 |
| Acquisition Date | 2021-02-14 |
| Spectrometer Frequency | 100.50 |
| Spectral Width | 25000.0 |
| Lowest Frequency | -1445.9 |
| Nucleus | 13C |
| Acquired Size | 32768 |
| Spectral Size | 65536 |
| Digital Resolution | 0.38 |

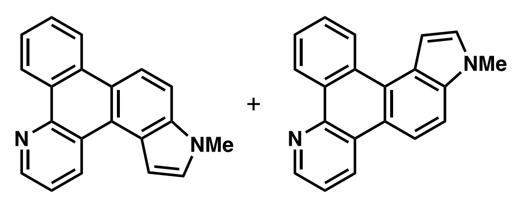
Purified Product, 13C NMR



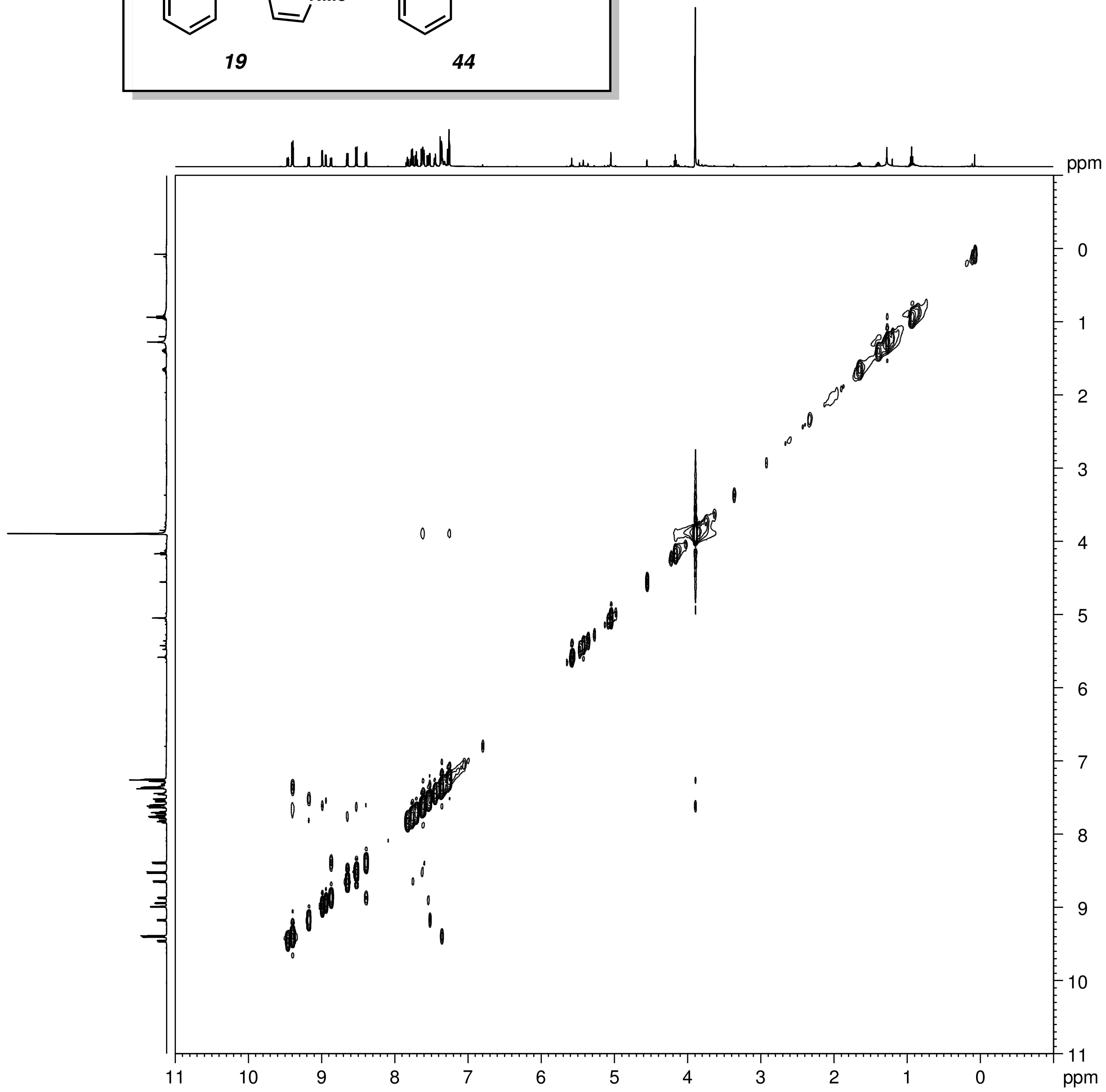
| Parameter | Value |
|---|---|
| Title | CARBON_01 |
| Origin | Varian |
| Instrument | vnmrs |
| Solvent | acetone |
| Temperature | 25.0 |
| Pulse Sequence | s2pul |
| Experiment | 1D |
| Probe | MR0808W005 |
| Number of Scans | 10000 |
| Receiver Gain | 30 |
| Relaxation Delay | 1.0000 |
| Pulse Width | 4.6000 |
| Acquisition Time | 01:07:53 |
| Acquisition Date | 2021-03-16 |
| Spectrometer Frequency | 150.84 |
| Spectral Width | 37878.8 |
| Lowest Frequency | -2349.1 |
| Nucleus | 13C |
| Acquired Size | 32768 |
| Spectral Size | 65536 |
| Digital Resolution | 0.58 |

# NOESY Spectra

NOESY

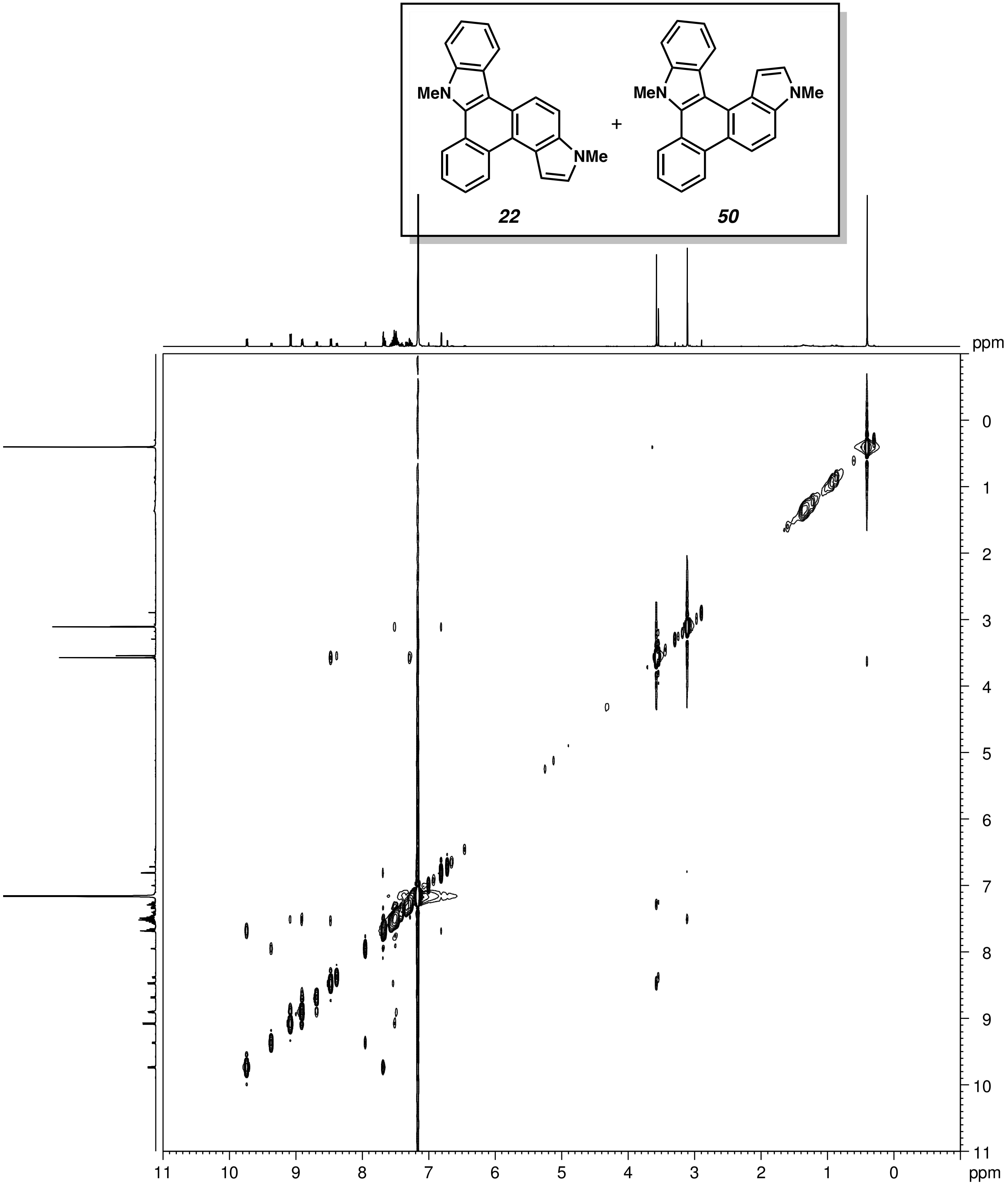


**19** **44**



```
Current Data Parameters
NAME       JVC-2018-097
EXPNO               6
PROCNO              1

F2 - Acquisition Parameters
Date_         20180719
Time            11.16 h
INSTRUM          av500
PROBHD   Z119248_0002 (
PULPROG      noesygpph
TD                2048
SOLVENT          CDCl3
NS                   6
DS                   8
SWH       10000.000 Hz
FIDRES     9.765625 Hz
AQ        0.1024000 sec
RG               12.14
DW          50.000 usec
DE          10.00 usec
TE             298.0 K
D0       0.00003727 sec
D1       2.00000000 sec
D8       0.75000000 sec
D16      0.00020000 sec
IN0      0.00010000 sec
TDav                 1
SFO1    500.1330008 MHz
NUC1                1H
P1          10.00 usec
P2          20.00 usec
PLW1     13.50000000 W
GPNAM[1]     SINE.100
GPZ1           40.00 %
P16       1000.00 usec

F1 - Acquisition parameters
TD                 256
SFO1       500.133 MHz
FIDRES    78.125000 Hz
SW          19.995 ppm
FnMODE     States-TPPI

F2 - Processing parameters
SI                2048
SF      500.1300124 MHz
WDW              QSINE
SSB                  2
LB                0 Hz
GB                   0
PC                1.40

F1 - Processing parameters
SI                2048
MC2        States-TPPI
SF      500.1300128 MHz
WDW              QSINE
SSB                  2
LB                0 Hz
GB                   0
```

NOESY



**22** + **50**

| Current Data Parameters | |
|---|---|
| NAME | JVC-2018-107-3-2D |
| EXPNO | 3 |
| PROCNO | 1 |

| F2 - Acquisition Parameters | |
|---|---|
| Date_ | 20180819 |
| Time | 21.40 h |
| INSTRUM | av500 |
| PROBHD | Z119248_0002 ( |
| PULPROG | noesygpph |
| TD | 2048 |
| SOLVENT | C6D6 |
| NS | 6 |
| DS | 8 |
| SWH | 10000.000 Hz |
| FIDRES | 9.765625 Hz |
| AQ | 0.1024000 sec |
| RG | 12.14 |
| DW | 50.000 usec |
| DE | 10.00 usec |
| TE | 298.0 K |
| D0 | 0.00003727 sec |
| D1 | 2.00000000 sec |
| D8 | 0.75000000 sec |
| D16 | 0.00020000 sec |
| IN0 | 0.00010000 sec |
| TDav | 1 |
| SFO1 | 500.1330008 MHz |
| NUC1 | 1H |
| P1 | 10.00 usec |
| P2 | 20.00 usec |
| PLW1 | 13.50000000 W |
| GPNAM[1] | SINE.100 |
| GPZ1 | 40.00 % |
| P16 | 1000.00 usec |

| F1 - Acquisition parameters | |
|---|---|
| TD | 256 |
| SFO1 | 500.133 MHz |
| FIDRES | 78.125000 Hz |
| SW | 19.995 ppm |
| FnMODE | States-TPPI |

| F2 - Processing parameters | |
|---|---|
| SI | 2048 |
| SF | 500.1299963 MHz |
| WDW | QSINE |
| SSB | 2 |
| LB | 0 Hz |
| GB | 0 |
| PC | 1.40 |

| F1 - Processing parameters | |
|---|---|
| SI | 2048 |
| MC2 | States-TPPI |
| SF | 500.1299969 MHz |
| WDW | QSINE |
| SSB | 2 |
| LB | 0 Hz |
| GB | 0 |

**Supplementary References**

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Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C. M.; Chen, Y. Q.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; DiStasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T. C.; Ji, H. J.; Kaduk, B.; Khistyaev, K.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S. P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; Oana, C. M.; Olivares-Amaya, R.; O'Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.; Sodt, A.; Stein, T.; Stuck, D.; Su, Y. C.; Thom, A. J. W.; Tsuchimochi, T.; Vanovschi, V.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Yang, J.; Yeganeh, S.; Yost, S. R.; You, Z. Q.; Zhang, I. Y.; Zhang, X.; Zhao, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A.; Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer, H. F.; Schmidt, M. W.; Sherrill, C. D.; Truhlar, D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai, J. D.; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C. P.; Jung, Y. S.; Kong, J.; Lambrecht, D. S.; Liang, W. Z.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.; Subotnik, J. E.; Van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Mol. Phys.* **2015,** *113*, 184–215.