Supporting Information

Brønsted acid Mediated Alkenylation and Copper-Catalyzed Aerobic Oxidative Ring Expansion/ Intramolecular Electrophilic Substitution of Indoles with Propargyl Alcohols: A Novel One Pot Approach to Cyclopenta[*c*]quinolines

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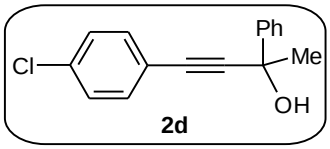
General Methods: All reactions were carried out in air, unless otherwise specified. All Chemicals were procured from Aldrich or local manufacturers and used as purchased without further purification, unless noted. $MeNO_2$ was distilled according to standard procedure.[1] 1,2-substituted indoles were prepared using known literature methods.[2] ^1H and ^{13}C NMR spectra were recorded using 5 mm tubes on a Bruker 400 MHz NMR spectrometer [field strengths: 400, 100 MHz respectively] in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to $SiMe_4$ (^1H, ^{13}C: $\delta = 0$). All *J* values are in Hz. Melting points were determined using a SUPERFIT hot stage apparatus and were uncorrected. IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN or Thermo Finnigan EA1112 CHNS analyzer. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. X-ray data were collected at 293 K on a Bruker AXS-SMART or on an OXFORD diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å). Structures were solved and refined using standard methods.[3]

Synthesis of tertiary propargyl alcohols [2a-e]

Tertiary propargyl alcohols **2a-e** were prepared by Sonogashira cross coupling reaction of aryl halides with terminal acetylinic propargyl alcohols under palladium catalysis.[4] Among these, **2d-e** are new.

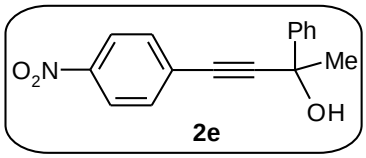


2d

In a round bottomed flask (50 mL) equipped with 1-chloro-4-iodobenzene (2.0 g, 8.39 mmol), $PdCl_2$ (0.05 g, 0.25 mmol), PPh_3 (0.13 g, 0.5 mmol) and CuI (0.10 g, 0.5 mmol) and acetonitrile (20 mL), was added 2-phenylbut-3-yn-2-ol (1.47 g, 10.1 mmol) and Et_3N (1.76 mL, 12.6 mmol). Then the reaction mixture was stirred at room temperature for 6 h and progress of the reaction monitored by TLC. Upon completion of the reaction, the crude mixture was filtered, the solid residue was washed with EtOAc, and washings added to the filtrate and the whole

solution was concentrated under reduced pressure. Purification *via* column chromatography (ethyl acetate: hexane 1:4) yielded the desired product as orange solid.

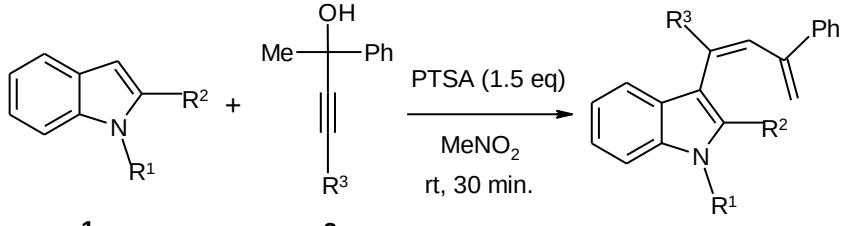
4-(4-chlorophenyl)-2-phenylbut-3-yn-2-ol (2d). Yield 2.4 g (93%); mp 60–62 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.42-7.35 (m, 4H), 7.32-7.30 (m, 3H), 2.55 (qrt, 1H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 134.6, 133.0, 128.7, 128.5, 127.9, 125.0, 121.1, 93.5, 83.8, 70.4, 33.3; IR (KBr) 3375, 3058, 2981, 2230, 1589, 1398, 1085, 827, 762, 707 cm^{-1}; LC-MS: *m/z* 257 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.68; H, 5.18.



2e

4-(4-nitrophenyl)-2-phenylbut-3-yn-2-ol (2e). Procedure was similar to that for compound **2d** using 1-bromo-4-nitrobenzene (2.0 g, 9.9 mmol) and 2-phenylbut-3-yn-2-ol (1.74 g, 11.9 mmol). Orange solid. Yield 2.5 g (93%); mp 68–70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.44-7.40 (m, 2H), 7.35 (dd→t, *J* = 7.2 Hz,1H), 2.65 (qrt, 1H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 144.9, 132.6, 129.5, 128.6, 128.1, 124.9, 123.6, 97.8, 83.0, 70.4, 33.0; IR (KBr) 3567, 3096, 2992, 1595, 1348, 1096, 866, 773 cm^{-1}; LC-MS: *m/z* 268 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.68; H, 4.97; N, 5.32.

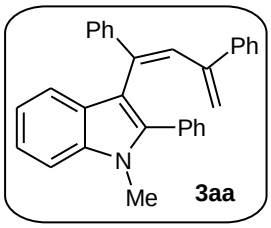
Synthesis of 3-dienylindoles 3aa-3ea



1 **2** **3**

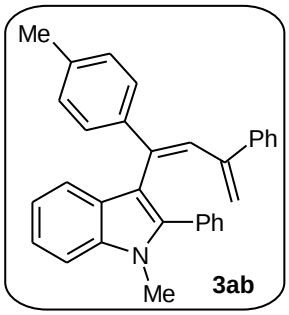
Typical procedure for the synthesis of 3-dienylindole 3aa: An oven dried 25 mL round-bottomed flask was charged with *N*-methyl,2-phenyl indole **1a** (0.3 g, 1.45 mmol), propargyl alcohol **2a** (0.35 g, 1.59 mmol), and PTSA (*p*-toluenesulfonic acid) (0.41 g, 2.17 mmol). To this

was added nitromethane (4 mL) all at once and the mixture was stirred rt (25 ^{o}C) for 30 min. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 2:98) afforded the desired product **3aa** as orange solid. Compounds **3ab-3ea** were prepared by using the same procedure.



3aa

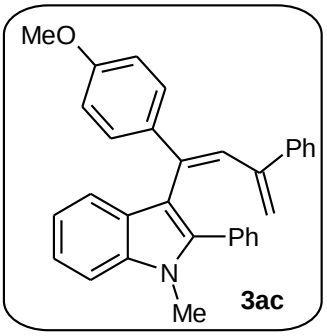
(*Z*)-3-(1,3-diphenylbuta-1,3-dienyl)-1-methyl-2-phenyl-1*H*-indole (3aa). Yield 0.493 g (83%); mp 180–182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 2H), 7.38-7.27 (m, 11H), 7.13-7.00 (m, 6H), 6.83 (s, 1H), 5.20 and 4.98 (2 s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 143.1, 141.0, 138.7, 137.8, 136.9, 131.8, 130.3, 130.0, 128.2, 128.1, 127.7, 127.4, 127.3, 126.8, 126.4, 121.7, 120.5, 119.7, 115.8, 112.9, 109.4, 31.2; IR (KBr) 3047, 3014, 2937, 2915, 1600, 1567, 1485, 1458, 1436, 1370, 1326, 1227, 1151, 1014, 740 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N$ (M^+ + H): *m/z* 412.2066. Found: 412.2066.



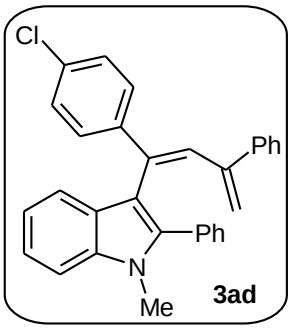
3ab

(*Z*)-1-methyl-2-phenyl-3-(3-phenyl-1-*p*-tolylbuta-1,3-dienyl)-1*H*-indole (3ab). This compound was prepared by following a route similar to that for **3aa** using **1a** (0.35 g, 1.68 mmol) and **2b** (0.44 g, 1.85 mmol). Orange solid. Yield 0.58 g (81%); mp 160–162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.39-7.28 (m, 8H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-6.98 (m, 6H), 6.81 (s, 1H), 5.17 and 4.94 (2 s, 2H), 3.68 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 145.7, 141.0, 140.2, 138.6, 137.8, 137.2, 136.6, 131.8, 130.3, 129.2, 129.0, 128.3, 128.1, 127.6, 127.3, 127.1, 126.7, 126.4, 121.7, 120.5, 119.7, 115.5, 112.9, 109.3, 31.2, 21.2; IR (KBr) 3041, 2926, 1600, 1567, 1468, 1364, 1332, 1184, 1145, 1014, 904, 811, 740 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N$ (M^+ + H): *m/z* 426.2222. Found: 426.2220.

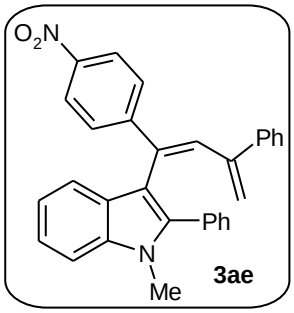


(*Z*)-3-(1-(4-methoxyphenyl)-3-phenylbuta-1,3-dienyl)-1-methyl-2-phenyl-1*H*-indole (3ac). This compound was prepared by following a procedure similar to that for **3aa** using **1a** (0.3 g, 1.45 mmol) and **2c** (0.4 g, 1.59 mmol). White solid. Yield 0.478 g (75%); mp 158–160 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.32-7.22 (m, 8H), 7.05-7.00 (m, 4H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 1H), 5.07 and 4.83 (2 s, 2H), 3.81 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 145.7, 141.1, 138.5, 137.8, 136.2, 135.6, 131.8, 130.3, 128.4, 128.3, 128.1, 127.6, 127.3, 126.7, 126.4, 121.7, 120.5, 119.7, 115.3, 113.6, 113.0, 109.3, 55.3, 31.2; IR (KBr) 3052, 2992, 2942, 2833, 1600, 1507, 1468, 1359, 1255, 1184, 1047, 1014, 904, 833 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}NO$ (M^+ + H): *m/z* 442.2172. Found: 442.2169; X-ray structure has been determined for this compound.



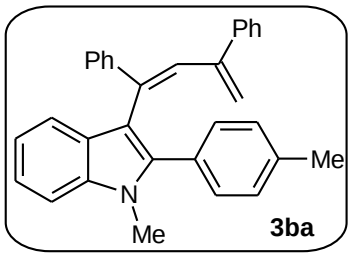
(*Z*)-3-(1-(4-chlorophenyl)-3-phenylbuta-1,3-dienyl)-1-methyl-2-phenyl-1*H*-indole (3ad). Procedure was similar to that for compound **3aa** using **1a** (0.28 g, 1.36 mmol) and **2d** (0.38 g,

1.49 mmol). Orange solid. Yield 0.525 g (87%); mp 164–166 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.31-7.29 (m, 4H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.18-7.10 (m, 8H), 7.07-7.06 (m, 3H), 6.83 (s, 1H), 5.29 and 5.20 (2 s, 2H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.1, 136.9, 136.3, 133.8, 133.3, 131.2, 128.4, 127.2, 125.7, 125.5, 123.9, 123.6, 123.5, 123.4, 123.3, 123.0, 122.9, 122.8, 122.2, 121.8, 117.4, 115.7, 115.6, 111.2, 108.0, 104.9, 25.7; IR (KBr) 3052, 2942, 1611, 1490, 1364, 1310, 1227, 1156, 1090, 1014, 904, 838 cm^{-1}; HRMS (ESI):Calcd. for $C_{31}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 446.1676 and 448.1676. Found: 446.1669 and 448.1653.



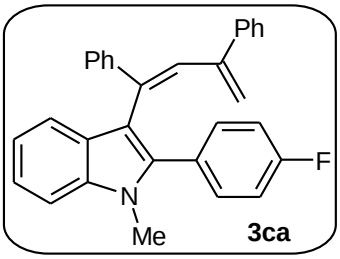
3ae

(*Z*)-1-methyl-3-(1-(4-nitrophenyl)-3-phenylbuta-1,3-dienyl)-2-phenyl-1*H*-indole (3ae). This compound was prepared by following a procedure similar to that for **3aa** using **1a** (0.25 g, 1.21 mmol) and **2e** (0.35 g, 1.33 mmol). Orange solid. Yield 0.472 g (86%); mp 166–168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.28-7.26 (m, 7H), 7.11-7.02 (m, 6H), 6.93 (s, 1H), 5.29 and 5.11 (2 s, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 146.7, 145.2, 140.3, 139.1, 137.7, 135.2, 133.4, 131.3, 130.1, 128.3, 128.0, 127.8, 127.5, 127.4, 127.1, 126.4, 123.5, 122.1, 120.1, 117.5, 111.8, 109.6, 31.2; IR (KBr) 3052, 1584, 1512, 1474, 1348, 1107, 910, 855, 751 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}N_2O_2$ (M^+ + Na): *m/z* 479.1736. Found: 479.1739.

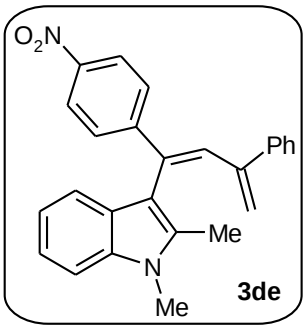


3ba

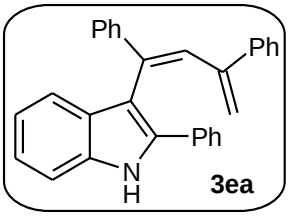
(*Z*)-3-(1,3-diphenylbuta-1,3-dienyl)-1-methyl-2-*p*-tolyl-1*H*-indole (3ba). This compound was prepared by following a procedure similar to that for **3aa** using **1b** (0.24 g, 1.07 mmol) and **2a** (0.26 g, 1.17 mmol). Pale yellow solid. Yield 0.372 g (82%); mp 152–154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.36-7.24 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.13-7.07 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.78 (s, 1H), 5.18 and 4.94 (2 s, 2H), 3.65 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 143.2, 140.9, 138.8, 137.7, 137.5, 137.0, 130.2, 130.0, 128.9, 128.3, 128.2, 127.3_2, 127.2_8, 126.7, 126.4, 121.6, 120.4, 119.6, 115.5, 112.6, 109.3, 31.1, 21.3; IR (KBr) 3047, 3014, 2910, 1600, 1496, 1468, 1370, 1332, 1019, 899, 822 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N$ (M^+ + H): *m/z* 426.2222. Found: 426.2221.



(*Z*)-3-(1,3-diphenylbuta-1,3-dienyl)-2-(4-fluorophenyl)-1-methyl-1*H*-indole (3ca). Procedure was similar to that for compound **3aa** using **1c** (0.22 g, 0.98 mmol) and **2a** (0.24 g, 1.07 mmol). Pale yellow solid. Yield 0.332 g (79%); mp 180–182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.34-7.20 (m, 8H), 7.09-7.04 (m, 4H), 6.99-6.92 (m, 4H), 6.79 (d, *J* = 1.0 Hz, 1H), 5.18 and 4.92 (2 s, 2H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.0 Hz), 145.5, 143.0, 140.6, 137.7 (d, *J* = 16.0 Hz), 136.8, 132.0 (d, *J* = 9.0 Hz), 130.1, 128.3, 128.1, 127.8, 127.5, 127.4, 127.2, 126.9, 126.2, 121.9, 120.5, 119.8, 115.7, 115.2 (d, *J* = 21.0 Hz), 113.1, 109.4, 31.1; IR (KBr) 3052, 1605, 1551, 1468, 1337, 1227, 1162, 904, 849 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}FN$ (M^+ + H): *m/z* 430.1972. Found: 430.1970.



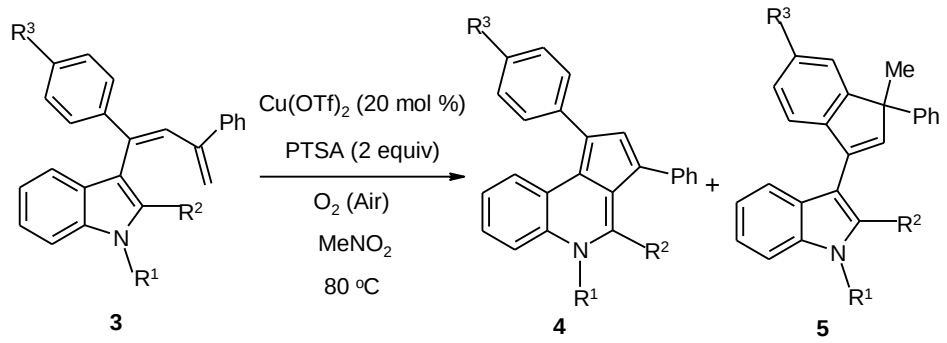
(*Z*)-1,2-dimethyl-3-(1-(4-nitrophenyl)-3-phenylbuta-1,3-dienyl)-1*H*-indole (3de). This compound was prepared by following a procedure similar to that for **3aa** using **1d** (0.19 g, 1.31 mmol) and **2e** (0.39 g, 1.44 mmol). Brown liquid. Yield 0.341 g (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 1H), 7.10-7.03 (m, 4H), 6.95-6.85 (m, 5H), 5.40 (s, 2H), 3.43 (s, 3H), 2.05 (s, 3H). *Note*: For this compound as well as **3ad**, the NMR spectra in $CDCl_3$. indicated isomerism (possibly). While in the case of **3ad**, we could get a better spectrum in C_6D_6 (vide infra), for **3de**, the spectrum still exhibited additional peaks due to (possibly) diene isomerization. However this feature did not affect the isolation of the final product **4de**; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 147.0, 146.9, 140.0, 136.9, 135.5, 132.7, 129.0, 128.0, 127.2, 126.8, 126.6, 126.3, 123.6, 120.8, 119.9, 119.4, 119.3, 110.8, 108.4, 29.3, 11.4; IR (neat) 3058, 2926, 2855, 1600, 1507, 1474, 1342, 1107, 904, 855 cm^{-1}; HRMS (ESI): Calcd. for $C_{26}H_{22}N_2O_2$ (M^+ + H): *m/z* 395.1760. Found: 395.1758.



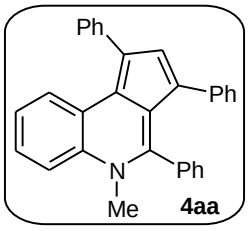
3ea

(*Z*)-3-(1,3-diphenylbuta-1,3-dienyl)-2-phenyl-1*H*-indole (3ea). This compound was prepared by following a procedure similar to that for **3aa** using **1e** (0.2 g, 1.04 mmol) and **2a** (0.25 g, 1.14 mmol). This compound is known,[5] but we could not find the spectroscopic data in the literature. Yellow liquid. Yield 0.374 g (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br 1H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.34-7.23 (m, 8H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06-6.94 (m, 7H), 5.10 and 5.05 (2 s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 142.3, 140.7, 136.5, 135.9, 135.3, 132.4, 130.4, 129.3, 128.5, 128.4, 127.5, 127.4, 127.2, 127.1, 127.0, 126.6, 126.4, 122.3, 120.4, 120.0, 117.1, 112.6, 110.6; IR (neat) 3419, 3052, 3025, 1595, 1496, 1441, 1266, 1074, 1025, 904, 740 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}N$ (M^+ + H): *m/z* 398.1909. Found: 398.1905.

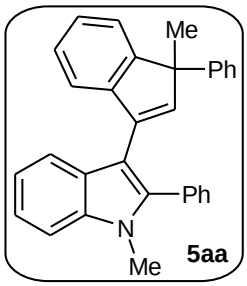
Synthesis of cyclopenta[*c*]quinolines (4) and 3-indenylindoles (5)



Typical procedure for the synthesis of 4aa and 5aa: To an oven dried round-bottomed flask (10 mL), diene **3aa** (0.248 g, 0.60 mmol), $Cu(OTf)_2$ (0.043 g, 0.12 mmol), PTSA (0.23 g, 1.2 mmol) and nitromethane (4 mL) were added. The mixture was stirred at 80 ^oC for 3-5 h in open air. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH solution and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired products **4aa** and **5aa**. Compound 3-indenyl indole (**5aa**) eluted first.

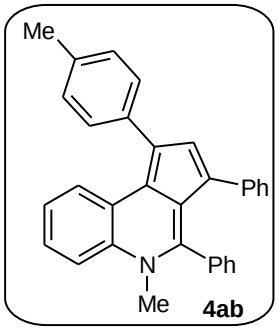


5-methyl-1,3,4-triphenyl-5*H*-cyclopenta[*c*]quinoline (4aa). Red solid. Yield 0.158 g (64%); mp 218–220 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40-7.33 (m, 2H), 7.25-7.21 (m, 4H), 7.14-7.12 (m, 3H), 6.88 (br, 5H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.4, 139.2, 133.7, 133.6, 133.1, 130.4, 129.7, 129.6, 129.2, 128.5, 127.9, 127.3, 126.9, 125.9, 124.7, 124.4, 124.2, 124.1, 124.0, 123.6, 119.8, 119.7, 116.6, 38.5; IR (KBr) 3052, 3013, 2920, 2822, 1599, 1578, 1534, 1462, 1364, 1320, 1238, 1112, 843 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}N$ (M^+ + H): *m/z* 410.1909. Found: 410.1908.



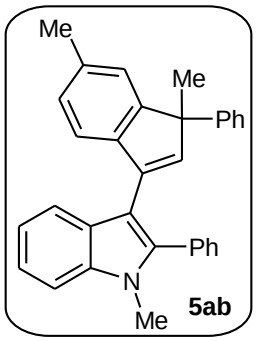
1-methyl-3-(1-methyl-1-phenyl-1*H*-inden-3-yl)-2-phenyl-1*H*-indole (5aa). White solid. Yield 0.055 g (22%); mp 164–166 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 3H), 7.46-7.43 (m, 4H), 7.32-7.27 (m, 7H), 7.23-7.21 (m, 3H), 6.39 (s, 1H), 3.84 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.4, 143.6, 143.4, 138.9, 137.5, 135.2, 132.0, 130.8, 129.4, 128.6, 128.3, 128.2, 128.0, 127.6, 126.4, 126.3, 126.2, 125.4, 122.5, 122.2, 121.7, 120.5, 119.9, 109.7, 109.1, 55.9, 31.2, 22.9; IR (KBr) 3058, 2964, 2921, 1600, 1496, 1463, 1364, 1321, 1266, 1156, 1079, 1019, 751 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N$ (M^+ + H): *m/z* 412.2066. Found: 412.2066.

Compounds 4ab and 5ab: These compounds were prepared by following a procedure similar to that for **4aa** and **5aa** using **3ab** (0.392 g, 0.92 mmol).



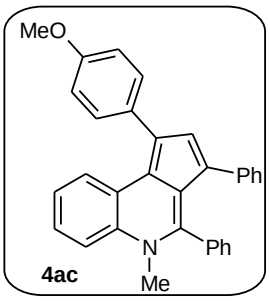
5-methyl-3,4-diphenyl-1-*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4ab). Red solid. Yield 0.238 g (61%); mp 224–226 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26-7.21 (m, 4H), 7.15-7.11 (m, 3H), 6.90-6.88 (m, 5H), 3.73 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 139.2, 137.4, 135.5, 133.8, 133.6, 133.3, 130.4, 129.7, 129.4, 129.3, 129.2, 127.9, 127.2, 126.9, 124.6, 124.3, 124.1, 123.9, 123.6, 119.8, 119.5, 116.5, 38.4, 21.4; IR (KBr) 3046, 3014, 2915, 1605,

1578, 1512, 1463, 1364, 1326, 1238, 1107, 827 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}N$ (M^+ + H): *m/z* 424.2066. Found: 424.2064.



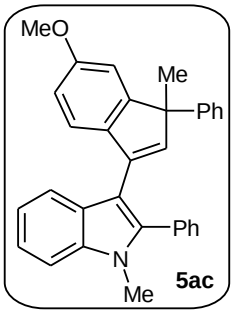
3-(1,6-dimethyl-1-phenyl-1*H*-inden-3-yl)-1-methyl-2-phenyl-1*H*-indole (5ab). White solid. Yield 0.10 g (26%); mp 192–194 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 3H), 7.41-7.34 (m, 4H), 7.27-7.20 (m, 6H), 7.05-6.95 (m, 3H), 6.23 (s, 1H), 3.79 (s, 3H), 2.34 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 144.5, 143.7, 141.1, 138.9, 137.5, 135.1, 132.0, 130.9, 128.3, 128.2, 128.0, 127.6, 127.1, 126.3, 123.4, 122.1, 121.4, 120.6, 119.9, 109.6, 109.3, 55.7, 31.2, 23.0, 21.6; IR (KBr) 3047, 2964, 2915, 1616, 1463, 1436, 1364, 1321, 1233, 1156, 1079, 1019, 816 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N$ (M^+ + H): *m/z* 426.2222. Found: 426.2223. X-ray structure has been determined for this compound.

Compounds 4ac and 5ac: These compounds were prepared by following a procedure similar to that for **4aa** and **5aa** using **3ac** (0.25 g, 0.57 mmol).



1-(4-methoxyphenyl)-5-methyl-3,4-diphenyl-5*H*-cyclopenta[*c*]quinoline (4ac). Red solid. Yield 0.132 g (53%); mp 176–178 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.2 Hz, 1H), 7.66-7.63 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.25-7.20 (m, 4H), 7.14-7.10 (m, 2H), 7.08 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.89-6.87 (m, 5H), 3.92 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz,

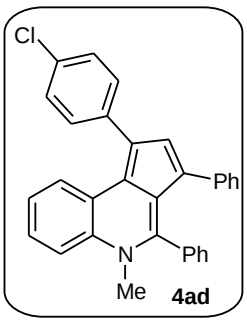
$CDCl_3$) δ 158.1, 148.4, 139.2, 133.8, 133.7, 133.3, 132.8, 130.6, 130.4, 129.7, 129.2, 127.9, 127.5, 127.2, 126.9, 126.5, 124.5, 124.1_1, 124.0_5, 123.9, 123.3, 119.7, 119.4, 116.5, 114.0, 55.4, 38.4; IR (KBr) 3063, 3013, 2926, 2822, 1610, 1578, 1506, 1440, 1369, 1282, 1243, 1156, 1024, 832 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}NO$ (M^+ + H): *m/z* 440.2015. Found: 440.2015. X-ray structure was determined for this compound.



5ac

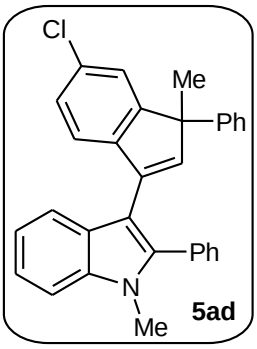
3-(6-methoxy-1-methyl-1-phenyl-1*H*-inden-3-yl)-1-methyl-2-phenyl-1*H*-indole (5ac). White solid. Yield 0.075 g (30%); mp 176–178 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.47-7.43 (m, 3H), 7.38-7.31 (m, 4H), 7.22-7.17 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.16 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 155.8, 143.6, 143.4, 138.8, 137.5, 136.6, 134.7, 132.0, 130.8, 128.3, 128.2, 128.0, 127.6, 126.3, 126.2, 122.1, 120.5, 119.9, 111.3, 109.7, 109.4, 109.3, 55.8, 55.5, 31.3, 23.1; IR (KBr) 3058, 2964, 2921, 2827, 1600, 1463, 1436, 1364, 1288, 1238, 1178, 1079, 1019, 827 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}NO$ (M^+ + H): *m/z* 442.2172. Found: 442.2170.

Compounds 4ad and 5ad: These compounds were prepared by following a procedure similar to that for **4aa** and **5aa** using **3ad** (0.62 g, 1.39 mmol).

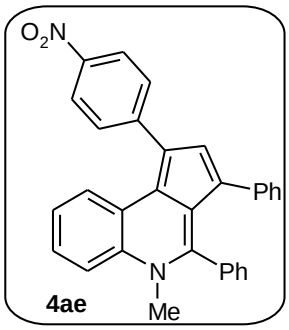


4ad

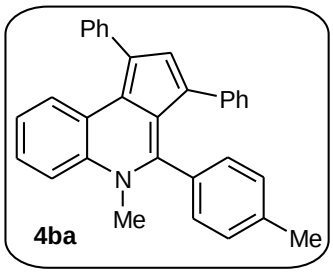
1-(4-chlorophenyl)-5-methyl-3,4-diphenyl-5*H*-cyclopenta[*c*]quinoline (4ad). Red solid. Yield 0.387 g (63%);mp 206–208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.32-7.23 (m, 4H), 7.18-7.13 (m, 3H), 6.95-6.91 (m, 5H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.0, 138.9, 133.7, 133.4, 132.7, 131.5, 130.8, 130.3, 129.6, 129.3, 128.6, 127.9, 127.5, 126.9, 124.8, 124.2, 124.1, 124.0, 122.1, 119.9, 119.8, 116.7, 38.4; IR (KBr) 3047, 1611, 1584, 1512, 1463, 1397, 1370, 1244, 1090, 1003, 827 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{22}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 444.1520 and 446.1520. Found: 444.1517 and 446.1484.



3-(6-chloro-1-methyl-1-phenyl-1*H*-inden-3-yl)-1-methyl-2-phenyl-1*H*-indole (5ad). White solid. Yield 0.173 g (28%); mp 188–190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.52-7.42 (m, 3H), 7.40-7.33 (m, 5H), 7.27-7.20 (m, 7H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.06 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 3.79 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 145.6, 142.5, 142.1, 139.0, 137.5, 134.7, 131.9, 131.3, 130.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.4, 126.6_2, 126.5_7, 126.2, 123.1, 122.6, 122.3, 120.2, 120.1, 109.8, 108.6, 56.0, 31.3, 22.8; IR (KBr) 3058, 3030, 2964, 2926, 2855, 1600, 1496, 1463, 1375, 1255, 1096, 1008, 833 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 446.1676 and 448.1676. Found: 446.1682 and 448.1665.



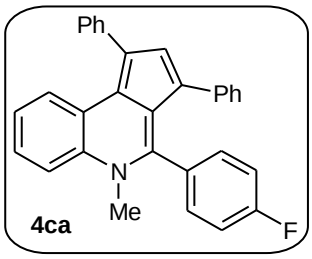
5-methyl-1-(4-nitrophenyl)-3,4-diphenyl-5*H*-cyclopenta[*c*]quinoline (4ae). This compound was prepared by following a procedure similar to that for **4aa** and **5aa** using **3ae** (0.372 g, 0.81 mmol). The corresponding 3-indenyl indole could not be isolated. Brown solid. Yield 0.274 g (74%); mp 206–208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.49-7.46 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25-7.21 (m, 3H), 7.17-7.12 (m, 3H), 6.94-6.85 (m, 5H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 147.6, 145.4, 138.6, 133.8, 133.0, 132.0, 130.3, 129.5, 129.3, 128.3, 128.0, 127.0, 125.6, 124.5, 124.4, 124.0_3, 123.9_5, 123.8, 121.5, 120.9, 120.8, 117.1, 38.7; IR (KBr) 3052, 2915, 1595, 1573, 1512, 1332, 1238, 1112, 855 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{22}N_2O_2$ (M^+ + H): *m/z* 455.1760. Found: 455.1759.



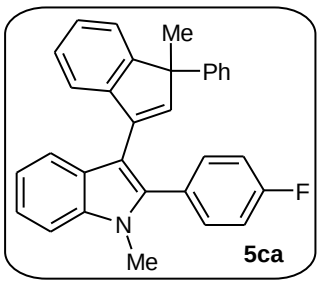
5-methyl-1,3-diphenyl-4-*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4ba). This compound was prepared by following a procedure similar to that for **4aa** and **5aa** using **3ba** (0.35 g, 0.81 mmol). The corresponding 3-indenyl indole could not be isolated. Red solid. Yield 0.191 g (56%); mp 160–162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41-7.34 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.13-7.09 (m, 3H), 6.93-6.88 (m, 7H), 3.79 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 140.5, 139.3, 139.2, 133.8, 132.9, 130.7, 130.3, 129.8, 129.6, 128.4_9, 128.4_8, 127.4, 126.8, 125.9, 124.6, 124.5, 124.2, 123.9, 123.7, 123.5, 120.1, 119.6, 116.6, 38.4, 21.3; IR (KBr) 3058,

2959, 2921, 2849, 1600, 1490, 1463, 1321, 1260, 1112, 1019, 822 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}N$ (M^+ + H): *m/z* 424.2066. Found: 424.2066.

Compounds 4ca and 5ca: These compounds were prepared by following a procedure similar to that for **4aa** and **5aa** using **3ca** (0.273 g, 0.64 mmol).

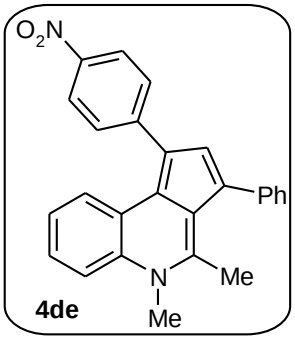


4-(4-fluorophenyl)-5-methyl-1,3-diphenyl-5*H*-cyclopenta[*c*]quinoline (4ca). Red solid. Yield 0.159 g (59%); mp 254–256 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.52-7.49 (m, 2H), 7.42-7.36 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.20-7.16 (m, 3H), 7.01-6.95 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 2H), 6.84-6.80 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0 Hz), 147.3, 140.3, 139.1, 133.7, 133.2, 132.3 (d, *J* = 8.0 Hz), 129.8, 129.5, 128.5, 127.1, 127.0, 126.0, 124.7, 124.4, 124.3, 124.2, 124.1, 123.7, 120.3, 119.6, 116.6, 115.0 (d, *J* = 22.0 Hz), 38.3; IR (KBr) 3052, 2921, 2849, 1710, 1595, 1578, 1501, 1463, 1222, 844 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{22}FN$ (M^+ + H): *m/z* 428.1815. Found: 428.1814.

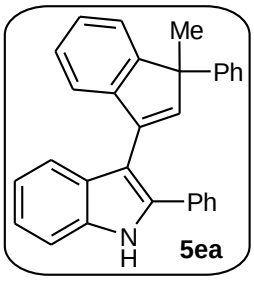


2-(4-fluorophenyl)-1-methyl-3-(1-methyl-1-phenyl-1*H*-inden-3-yl)-1*H*-indole (5ca). White solid. Yield 0.086 g (32%); mp 168–170 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43-7.34 (m, 3H), 7.27-7.23 (m, 7H), 7.21-7.13 (m, 3H), 7.09-7.05 (m, 2H), 6.28 (s, 1H), 3.77 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.0 Hz), 153.9, 145.5, 143.4 (d, *J* = 32.0 Hz), 137.6 (d, *J* = 31.0 Hz), 135.0, 132.5 (d, *J* = 8.0

Hz), 128.3, 128.0, 127.5, 126.4, 126.2, 125.5, 122.7, 122.3, 121.7, 120.5, 120.1, 115.3 (d, *J* = 21.0 Hz), 109.7, 109.4, 56.0, 31.2, 23.0; IR (KBr) 3047, 2959, 1600, 1545, 1501, 1468, 1326, 1216, 1156, 1019, 844 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}FN$ (M^+ + H): *m/z* 430.1972. Found: 430.1971.



4,5-dimethyl-1-(4-nitrophenyl)-3-phenyl-5*H*-cyclopenta[*c*]quinoline (4de). This compound was prepared by following a procedure similar to that for **4aa** and **5aa** using **3de** (0.163 g, 0.41 mmol). The corresponding 3-indenyl indole could not be isolated. Red solid. Yield 0.114 g (70%); mp 154–156 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.48-7.40 (m, 5H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 4.04 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.5, 145.3, 140.1, 133.8, 131.8, 130.3, 129.3, 128.0, 127.4, 126.0, 125.4, 124.1, 123.9, 123.6, 120.9, 120.8, 120.5, 116.3, 35.7, 19.6; IR (KBr) 3052, 2921, 2844, 1578, 1540, 1507, 1370, 1332, 1244, 1107, 855 cm^{-1}; HRMS (ESI): Calcd. for $C_{26}H_{20}N_2O_2$ (M^+ + H): *m/z* 393.1604. Found: 393.1606.



3-(1-methyl-1-phenyl-1*H*-inden-3-yl)-2-phenyl-1*H*-indole (5ea). This compound was prepared by following a procedure similar to that for **4aa** and **5aa** using **3ea** (0.34 g, 0.86 mmol). The corresponding cyclopenta[*c*]quinoline could not be isolated. Pale yellow solid. Yield 0.241 g

(71%); mp 168–170 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (br,s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.23 (m, 8H), 7.20-7.16 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.6, 143.3, 136.1, 135.2, 135.1, 132.8, 129.4, 128.7, 128.5, 127.8, 126.5, 126.3, 125.6, 122.7_9, 122.7_5, 121.9, 120.4, 120.3, 111.0, 108.5, 56.3, 23.0; IR (KBr) 3414, 3052, 2964, 2921, 2860, 1595, 1490, 1441, 1321, 1222, 1025, 838, 740 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}N$ (M^+ + H): *m/z* 398.1909. Found: 398.1910.

One pot synthesis of cyclopenta[*c*]quinolines [4aa-4ga]

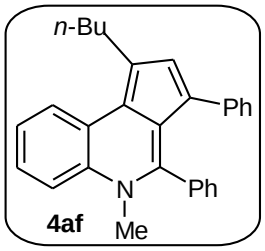
An oven dried 25 mL round-bottomed flask was charged with *N*-methyl-2-phenyl indole **1a** (0.1 g, 0.48 mmol), propargyl alcohol **2a** (0.12 g, 0.53 mmol), PTSA (*p*-toluenesulfonic acid) (0.23 g, 1.21 mmol) and nitromethane (4 mL). The mixture was stirred at rt for 30 min. and then $Cu(OTf)_2$ (0.035 g, 0.097 mmol) was added to the contents. The contents were stirred at 80 ^{o}C for 3-5 h in open air. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH solution and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **4aa** (0.13 g, 65%). Similarly, compounds **4ab**-**4ga** were prepared by using the same procedure.

Compound 4ab: Precursors **1a** (0.2 g, 0.97 mmol) and **2b** (0.25 g, 1.06 mmol) were used. Yield: 0.24 g (58%). Analytical data are given above.

Compound 4ac: Precursors **1a** (0.22 g, 1.06 mmol) and **2c** (0.29 g, 1.17 mmol) were used. Yield: 0.24 g (52%). Analytical data are given above.

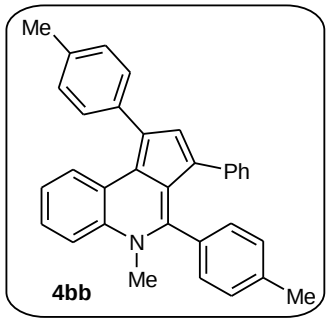
Compound 4ad: Precursors **1a** (0.14 g, 0.69 mmol) and **2d** (0.19 g, 0.76 mmol) were used. Yield: 0.2 g (67%). Analytical data are given above.

Compound 4ae: Precursors **1a** (0.2 g, 0.97 mmol) and **2e** (0.28 g, 1.06 mmol) were used. Yield: 0.34 g (78%). Analytical data are given above.



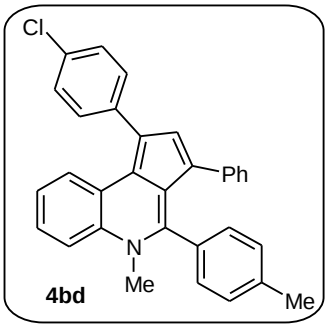
1-butyl-5-methyl-3,4-diphenyl-5*H*-cyclopenta[*c*]quinoline (4af). Precursors **1a** (0.2 g, 0.97 mmol) and **2f** (0.22 g, 1.06 mmol) were used. Red solid. Yield 0.23 g (61%); mp 128–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 6.0 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.50 (t, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 7.20-7.17 (m, 3H), 7.11-7.08 (m, 2H), 7.01 (s, 1H), 6.87-6.81 (m, 5H), 3.67 (s, 3H), 3.19 (t, *J* = 6.2 Hz, 2H), 1.92-1.87 (m, 2H), 1.62-1.56 (m, 2H), 1.04 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 139.6, 133.9, 133.7, 132.7, 130.4, 129.7, 129.0, 127.8, 126.8, 126.5, 125.4, 124.7, 124.3 124.1, 123.8, 123.6, 119.2_1, 119.1_6, 116.3, 38.2, 32.2, 30.2, 23.3 ,14.3; IR (neat) 3052, 2953, 2921, 2860, 1732, 1605, 1584, 1551, 1463, 1370, 1326, 1112, 745 cm^{-1}; HRMS (ESI): Calcd. for $C_{29}H_{27}N$ (M^+ + H): *m/z* 390.2222. Found: 390.2221.

Compound 4ba: Precursors **1b** (0.18 g, 0.83 mmol) and **2a** (0.2 g, 0.91 mmol) were used. Yield: 0.21 g (60%). Analytical data are given above.

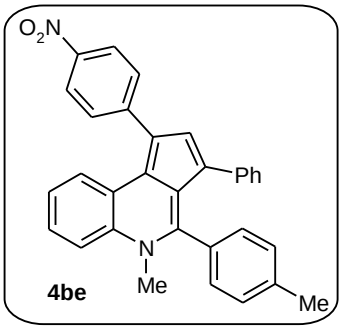


5-methyl-3-phenyl-1,4-di*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4bb). Precursors **1b** (0.225 g, 1.02 mmol) and **2b** (0.264 g, 1.12 mmol) were used. Red solid. Yield 0.237 g (53%); mp 228–230 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.66-7.62 (m, 3H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.29-7.20 (m, 3H), 7.09-7.07 (m, 3H), 6.91-6.83 (m, 7H), 3.76 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.4, 139.2, 137.5, 135.4, 133.8, 133.0, 130.8, 130.3, 129.8, 129.4, 129.2, 128.5, 127.3, 126.8, 124.6, 124.5, 124.2, 123.9, 123.7, 123.5, 120.1, 119.4, 116.5, 38.4, 21.4, 21.3; IR (KBr) 3047, 3014, 2910, 1605, 1578, 1540, 1501, 1397,

1326, 1244, 1178, 1112, 1008, 827 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{27}N$ (M^+ + H): *m/z* 438.2222. Found: 438.2222.



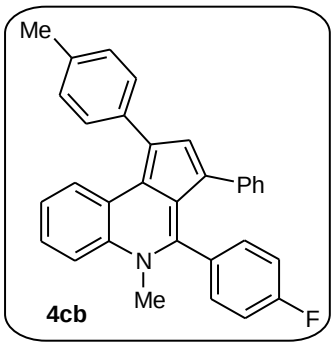
1-(4-chlorophenyl)-5-methyl-3-phenyl-4-*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4bd). Precursors **1b** (0.25 g, 1.13 mmol) and **2d** (0.32 g, 1.24 mmol) were used. Red solid. Yield 0.329 g (64%); mp 216–218 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.70-7.66 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.10-7.07 (m, 3H), 6.94-6.84 (m, 7H), 3.80 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 139.3, 139.2, 139.0, 133.8, 132.4, 131.5, 130.8, 130.5, 130.3, 129.7, 128.6, 128.5, 127.5, 126.8, 124.8, 124.3, 124.1, 123.8, 122.0, 120.2, 119.8, 116.7, 38.5, 21.3; IR (KBr) 3041, 3025, 2921, 2855, 1611, 1573, 1540, 1507, 1392, 1370, 1249, 1085, 1014, 833 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 458.1676 and 460.1676. Found: 458.1675 and 460.1644.



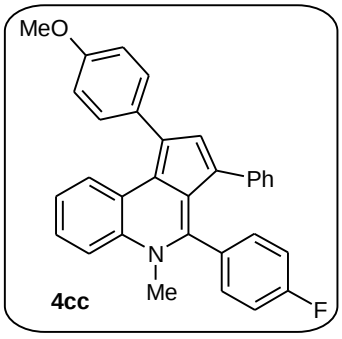
5-methyl-1-(4-nitrophenyl)-3-phenyl-4-*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4be). Precursors **1b** (0.15 g, 0.68 mmol) and **2e** (0.20 g, 0.75 mmol) were used. Red solid. Yield 0.232 g (72%); mp 230–232 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.11 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.95-6.87 (m, 5H), 6.82 (d, *J* = 7.2 Hz, 2H), 3.83

(s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 147.7, 145.4, 139.6, 138.7, 133.9, 131.8, 130.2, 129.6, 129.3, 128.6, 128.3, 126.9, 125.5, 124.3, 124.0_4, 123.9_6, 121.4, 121.1, 120.8, 117.1, 38.7, 21.3; IR (KBr) 3074, 2970, 2921, 1589, 1573, 1540, 1244, 1189, 1107, 1014, 849 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{24}N_2O_2$ (M^+ + H): *m/z* 469.1917. Found: 469.1917.

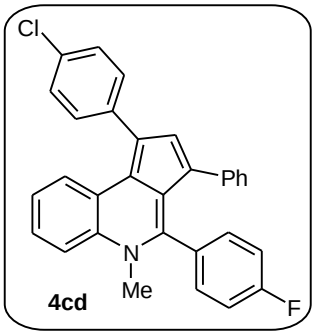
Compound 4ca: Precursors **1c** (0.18 g, 0.8 mmol) and **2a** (0.2 g, 0.88 mmol) were used. Yield: 0.23 g (66%). Analytical data are given above.



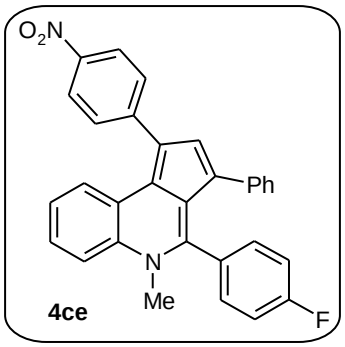
4-(4-fluorophenyl)-5-methyl-3-phenyl-1-*p*-tolyl-5*H*-cyclopenta[*c*]quinoline (4cb). Precursors **1c** (0.228 g, 1.01 mmol) and **2b** (0.263 g, 1.11 mmol) were used. Red solid. Yield 0.251 g (56%); mp 258–260 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.66-7.62 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.27-7.17 (m, 3H), 7.12 (s, 1H), 6.98-6.93 (m, 3H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.83-6.78 (m, 2H), 3.73 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0 Hz), 147.2, 139.1, 137.3, 135.6, 133.7, 133.4, 132.3 (d, *J* = 8.0 Hz), 129.8, 129.7, 129.4, 129.3, 127.1, 127.0, 124.7, 124.5, 124.3_0, 124.2_6, 124.0, 123.8, 120.3, 119.4, 116.5, 115.0 (d, *J* = 22.0 Hz), 38.4, 21.4; IR (KBr) 3063, 3019, 2942, 2921, 1611, 1578, 1507, 1370, 1216, 1003, 855 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{24}FN$ (M^+ + H): *m/z* 442.1972. Found: 442.1972.



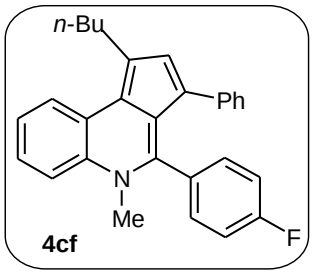
4-(4-fluorophenyl)-1-(4-methoxyphenyl)-5-methyl-3-phenyl-5*H*-cyclopenta[*c*]quinoline (4cc). Precursors **1c** (0.2 g, 0.89 mmol) and **2c** (0.25 g, 0.98 mmol) were used. Red solid. Yield 0.208 g (51%); mp 204–206 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.65-7.63 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.26-7.18 (m, 3H), 7.09-7.03 (m, 3H), 6.97-6.94 (m, 3H), 6.87-6.79 (m, 4H), 3.92 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0 Hz), 158.1, 147.1, 139.1, 133.7, 133.3, 132.7, 132.3 (d, *J* = 9.0 Hz), 130.5, 129.8, 129.7 (d, *J* = 3.0 Hz), 127.0_0, 126.9_7, 124.6, 124.5, 124.3, 124.1, 124.0, 123.5, 120.2, 119.3, 116.5, 115.0 (d, *J* = 22.0 Hz), 114.0, 55.4, 38.4; IR (KBr) 3068, 3025, 2921, 2827, 1616, 1584, 1507, 1364, 1288, 1249, 1167, 1036, 844 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{24}FNO$ (M^+ + H): *m/z* 458.1921. Found: 458.1920.



1-(4-chlorophenyl)-4-(4-fluorophenyl)-5-methyl-3-phenyl-5*H*-cyclopenta[*c*]quinoline (4cd). Precursors **1c** (0.2 g, 0.89 mmol) and **2d** (0.25 g, 0.98 mmol) were used. Red solid. Yield 0.286 g (70%); mp 230–232 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.68-7.66 (m, 3H), 7.46-7.42 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.19-7.16 (m, 2H), 7.10 (s, 1H), 7.01-6.94 (m, 3H), 6.86-6.79 (m, 4H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 249.0 Hz), 147.5, 138.8 (d, *J* = 11.0 Hz), 133.7, 132.7, 132.3 (d, *J* = 8.0 Hz), 131.6, 130.7, 129.7, 129.4_1, 129.3_7, 128.7, 127.3, 127.0, 124.9, 124.4, 124.2, 124.0, 122.2, 120.3, 119.8, 116.7, 115.1 (d, *J* = 22.0 Hz), 38.4; IR (KBr) 3063, 3019, 2926, 1605, 1573, 1501, 1463, 1397, 1364, 1216, 1090, 1008, 827 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{21}ClFN$ (M^+ + H):*m/z* 462.1426. Found: 462.1425.

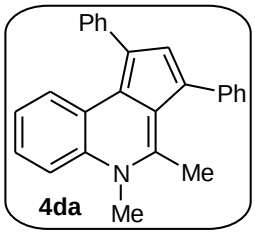


4-(4-fluorophenyl)-5-methyl-1-(4-nitrophenyl)-3-phenyl-5*H*-cyclopenta[*c*]quinoline (4ce). Precursors **1c** (0.25 g, 1.11 mmol) and **2e** (0.326 g, 1.22 mmol) were used. Red solid. Yield 0.393 g (75%); mp 210–212 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.47 (dd→t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.20-7.12 (m, 3H), 7.01-6.94 (m, 3H), 6.85-6.80 (m, 4H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 249.0 Hz), 148.1, 147.5, 145.5, 138.5, 133.9, 132.3 (d, *J* = 8.0 Hz), 132.1, 129.7, 129.3, 129.1, 128.1, 127.1, 125.7, 124.7, 124.5, 124.0_6, 124.9_8, 123.8, 121.4, 121.2, 121.1, 117.1, 115.1 (d, *J* = 22.0 Hz), 38.7; IR (KBr) 3058, 2921, 1595, 1573, 1501, 1370, 1332, 1233, 1112, 1008, 860 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{21}FN_2O_2$ (M^+ + H): *m/z* 473.1666. Found: 473.1664.



1-butyl-4-(4-fluorophenyl)-5-methyl-3-phenyl-5*H*-cyclopenta[*c*]quinoline (4cf). Precursors **1c** (0.213 g, 0.95 mmol) and **2f** (0.21 g, 1.04 mmol) were used. Red solid. Yield 0.251 g (65%); mp 136–138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H), 7.15-7.12 (m, 2H), 7.01 (s, 1H), 6.95-6.89 (m, 3H), 6.82-6.74 (m, 4H), 3.67 (s, 3H), 3.18 (t, *J* = 8.0 Hz, 2H), 1.91-1.85 (m, 2H), 1.61-1.55 (m, 2H), 1.03 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0 Hz), 146.2, 139.6, 133.7, 132.9, 132.3 (d, *J* = 9.0 Hz), 130.0 (d, *J* = 4.0 Hz), 129.9, 126.9, 126.4, 125.4,

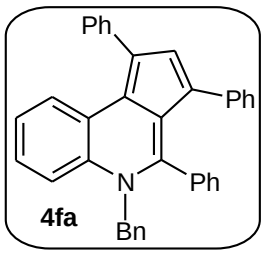
124.8, 124.4, 124.3, 124.1, 123.7, 119.8, 119.1, 116.3, 114.9 (d, J = 22.0 Hz), 38.2, 32.2, 30.1, 23.3, 14.3; IR (KBr) 3052, 2942, 2926, 2860, 1600, 1578, 1551, 1512, 1468, 1375, 1321, 1222, 1156, 1096, 844 cm^{-1}; HRMS (ESI): Calcd. for $C_{29}H_{26}FN$ (M^+ + H): *m/z* 408.2128. Found: 408.2127.



4da

4,5-dimethyl-1,3-diphenyl-5*H*-cyclopenta[*c*]quinoline (4da). Precursors **1d** (0.18 g, 1.24 mmol) and **2a** (0.30 g, 1.36 mmol) were used. Brown solid. Yield 0.185 g (43%); mp 178–180 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.61-7.51 (m, 5H), 7.48-7.45 (m, 2H), 7.42-7.33 (m, 3H), 7.22 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 3.91 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 140.7, 133.5, 132.8, 130.4, 129.6, 128.4, 127.8, 126.4, 125.9, 125.6, 124.4, 124.1, 123.6, 123.1, 119.8, 119.1, 115.8, 35.3, 19.5; IR (KBr) 3063, 3014, 2932, 2849, 1578, 1545, 1507, 1474, 1370, 1326, 1244, 1123, 1052, 915, 833 cm^{-1}; HRMS (ESI): Calcd. for $C_{26}H_{21}N$ (M^+ + H): *m/z* 348.1753. Found: 348.1752.

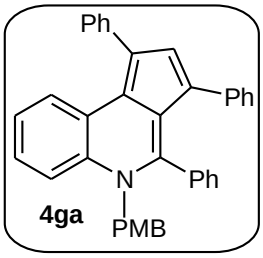
Compound 4de: Precursors **1d** (0.18 g, 1.24 mmol) and **2e** (0.36 g, 1.36 mmol) were used. Yield: 0.283 g (58%). Analytical data are given above.



4fa

5-benzyl-1,3,4-triphenyl-5*H*-cyclopenta[*c*]quinoline (4fa). Precursors **1f**[6] (0.25 g, 0.88 mmol) and **2a** (0.22 g, 0.97 mmol) were used. Red solid. Yield 0.239 g (56%); mp 180–182 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.52-7.46 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.32-7.26 (m, 3H), 7.21-7.11 (m, 6H), 7.03 (d, J = 6.8 Hz, 2H), 6.98 (t, J = 7.6 Hz, 2H), 6.91-6.88 (m, 5H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

148.9, 140.5, 139.1, 137.3, 133.9, 133.2, 132.7, 130.1, 129.8, 129.7, 129.3, 128.9, 128.5, 127.8, 127.7, 127.4, 126.8, 126.0, 125.8, 124.7_0, 124.6_6, 124.4, 124.1, 123.9, 123.8, 120.3, 119.8, 118.0, 53.0; IR (KBr) 3054, 3011, 1606, 1579, 1541, 1471, 1396, 1374, 1282, 1244, 1169, 1028, 963 cm^{-1}; LC-MS: *m/z* 486 $[M+1]^+$; Anal. Calcd. for $C_{37}H_{27}N$: C, 91.51; H, 5.60; N, 2.88. Found: C, 91.43; H, 5.64; N, 2.81.



4ga

5-(4-methoxybenzyl)-1,3,4-triphenyl-5*H*-cyclopenta[*c*]quinoline (4ga). Precursors **1g**[7] (0.25 g, 0.80 mmol) and **2a** (0.20 g, 0.88 mmol) were used. Red solid. Yield 0.201 g (49%); mp 202–204 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.51-7.47 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.23-7.11 (m, 6H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.90-6.87 (m, 5H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 148.9, 140.5, 139.2, 133.9, 133.2, 132.7, 130.1, 129.8, 129.7, 129.3, 129.2, 128.5, 127.7_4, 127.6_7, 127.0, 126.8, 126.0, 124.6_8, 124.6_6, 124.4, 124.1, 123.9, 123.8, 120.2, 119.8, 118.1, 114.3, 55.3, 52.5; IR (KBr) 3071, 3016, 1601, 1579, 1541, 1514, 1433, 1396, 1293, 1244, 1163, 1039, 758 cm^{-1}; LC-MS: *m/z* 516 $[M+1]^+$; Anal. Calcd. for $C_{38}H_{29}NO$: C, 88.51; H, 5.67; N, 2.72. Found: C, 88.36; H, 5.62; N, 2.79.

References:

(1) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1986.

(2) (a) Yu, X.; Park, E.-J.; Kondratyuk, T. P.; Pezzuto, J. M.; Sun, D. *Org. Biomol. Chem.***2012**, *10*, 8835. (b) Yu, L.; Jiang, X.; Wang, L.; Li, Z.; Wu, D.; Zhou, X. *Eur. J. Org. Chem.***2010**, 5560.

(3) (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, **1996**. (b) Sheldrick, G. M., SHELX-97- *A program for crystal structure solution and refinement*, University of Göttingen, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10.

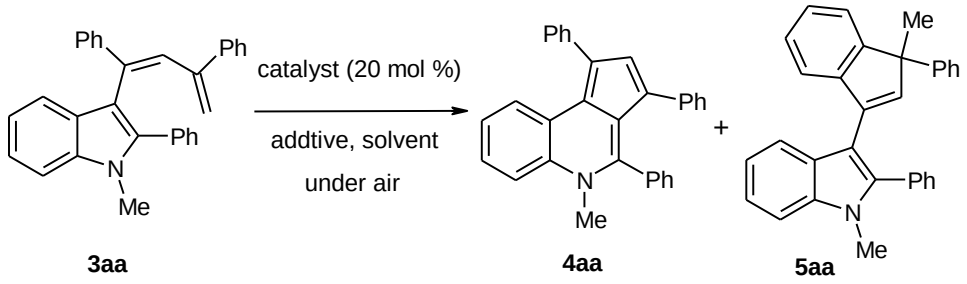
(4) (a) Shao, Y.; Zhu, K.; Qin, Z.; Li, E.; Li, Y.*J. Org. Chem.***2013**, *78*, 5731. (b) Hussain, M. K.; Ansari, M. I. Kant, R.; Hajela, K. *Org. Lett*. **2014**, *16*, 560.

(5) Sanz, R.; Gohain, M.; Miguel, D.; Martinez, A.; Rodriguez, F. *Synlett* **2009**, *12*, 1985.

(6) Yu, X.; Park, E.-J.; Kondratyuk, T. P.; Pezzuto, J. M.; Sun, D. *Org. Biomol. Chem.* **2012**, *10*, 8835.

(7) Higuchi, K.; Sato, Y.; Kojima, S.; Tsuchimochi, M.; Sugiura, K.; Hatori, M.; Kawasaki T. *Tetrahedron* **2010**, *66*, 1236.

Table-S1. Optimization Studies for the Ring-expansion/ Intramolecular Electrophilic Substitution Reaction of 3-Dienylindole **3aa**[a]



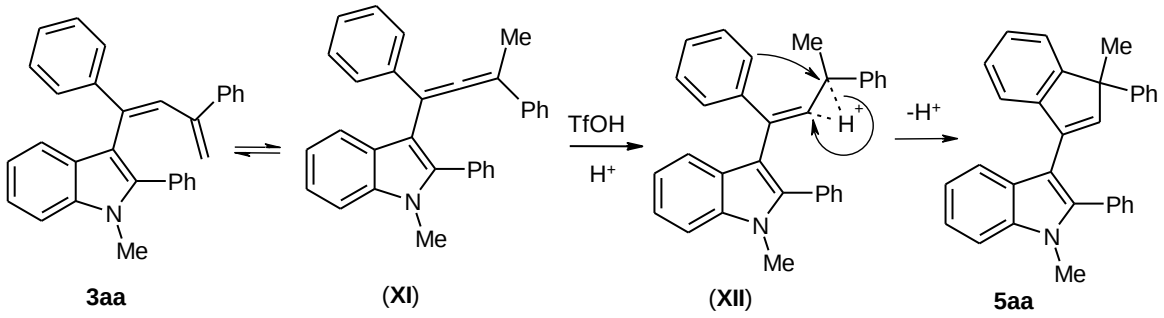
3aa **4aa** **5aa**

Entry	catalyst	solvent	temp(^{o}C) /time (h)	Yield(%)[b]	
				4aa	**5aa**
1	$Cu(OTf)_2$	$MeNO_2$	100/8	43	37
2[c]	$Cu(OTf)_2$	$MeNO_2$	rt/12	n.d	24
3	$Cu(OTf)_2$	$MeNO_2$	80/5	55	33
4[d]	$Cu(OTf)_2$	$MeNO_2$	80/5	56	34
5[e]	$Cu(OTf)_2$	$MeNO_2$	80/5	42	40
6[f]	-	$MeNO_2$	80/15	n.d	n.d
7	$Cu(OAc)_2$	$MeNO_2$	80/15	trace	trace
8	$Cu(Br)_2$	$MeNO_2$	80/12	n.d	n.d
9	$Cu(SO_4)_2.5H_2O$	$MeNO_2$	80/12	n.d	n.d
10	$Pd(OAc)_2$	$MeNO_2$	80/8	n.d	trace
11	$Zn(OTf)_2$	$MeNO_2$	80/5	25	40
12	AgOTf	$MeNO_2$	80/4	31	45
13	TfOH	$MeNO_2$	80/8	n.d	82
14	$Cu(OTf)_2$	CH_3CN	80/5	trace	68
15	$Cu(OTf)_2$	DCE	80/4	30	28
16	$Cu(OTf)_2$	toluene	80/4	n.d	35
17	$Cu(OTf)_2$	DMF	80/4	26	57
18[g]	$Cu(OTf)_2$	$MeNO_2$	80/5	28	40

19[h]	$Cu(OTf)_2$	$MeNO_2$	80/5	23	34
20[i]	$Cu(OTf)_2$	$MeNO_2$	80/5	64	22
21[j]	$Cu(OTf)_2$	$MeNO_2$	80/5	47	35
22[k]	$Cu(OTf)_2$	$MeNO_2$	80/3	75	trace

[a]Reaction conditions: **3aa** (0.3 mmol), catalyst (0.06 mmol), additive (2 equiv) and solvent (2.0 mL) at the specified temperature and time in air unless otherwise noted. [b]Isolated yields. [c]3-dienylindole was recovered in 52% yield. [d]under oxygen. [e]under nitrogen. [f]3-dienylindole was completely recovered. [g]AcOH, [h]pivOH, [i]PTSA and [j]TFA are used as additive. [k]Stoichiometric amount of catalyst was used. n.d = not detected.

Scheme S1. Plausible Mechanism for the Formation of Indenyl Indoles **5aa**



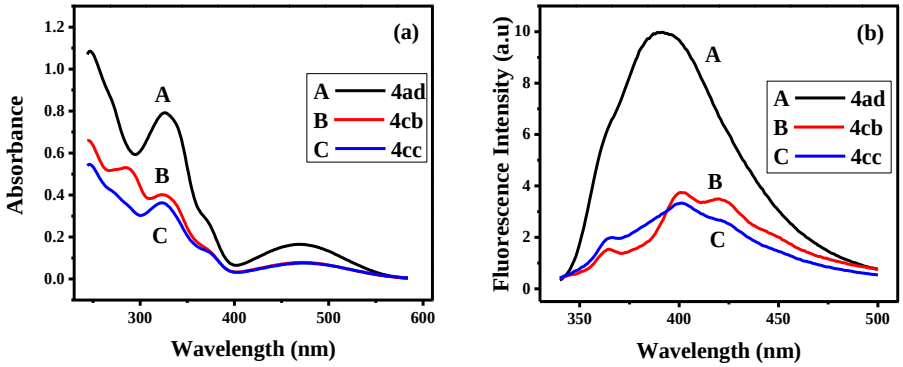


Figure S1. The absorption (a) and fluorescence emission spectra (b) of compounds **4ad** (A), **4cb** (B) and **4cc** (C) with c = 1.3 x 10^{-5} mol/L in THF, upon excitation at 330 nm.

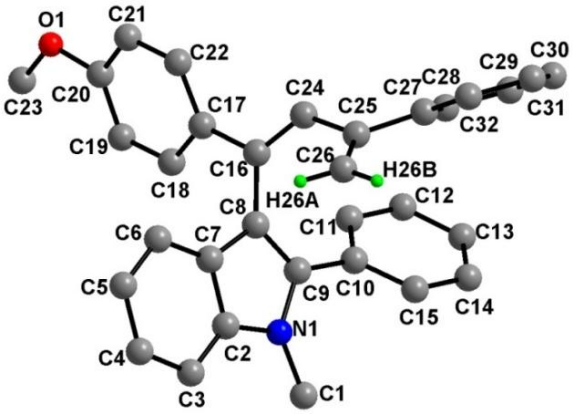


Figure S2. Molecular structure of compound **3ac** (CCDC No. 1025010). Hydrogen atoms (except $=CH_2$) are omitted for clarity. Selected bond parameters: N1-C9 1.390(3), C9-C8 1.372(3), C8-C16 1.481(2), C16-C17 1.484(3), C16-C24 1.334(3), C24-C25 1.473(3), C25-C26 1.322(3), C25-C27 1.484(3) (Å).

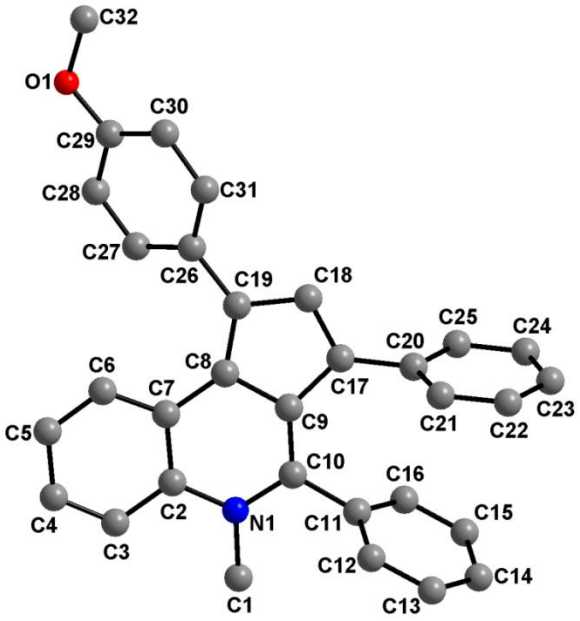


Figure S3. Molecular structure of compound **4ac** (CCDC No. 1025011). Hydrogen atoms omitted for clarity. Selected bond parameters: N1-C10 1.364(2), C9-C10 1.370(2), C8-C9 1.449(2), C9-C17 1.437(2), C17-C20 1.472(2), C17-C18 1.364(2), C18-C19 1.428(2), C8-C19 1.383(2), C19-C26 1.468(2) (Å).

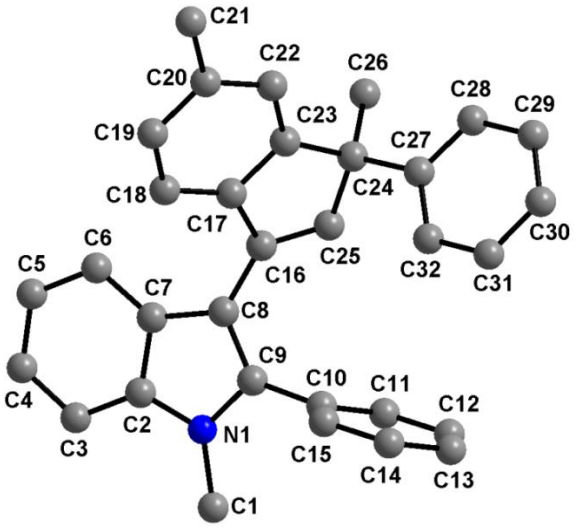


Figure S4. Molecular structure of compound **5ab** (CCDC No. 1025012). Hydrogen atoms omitted for clarity. Selected bond parameters: N1-C9 1.384(4), C9-C8 1.365(4), C8-C16 1.468(4), C16-C17 1.475(4), C16-C25 1.328(4), C25-C24 1.515(4), C24-C23 1.514(4), C24-C26 1.540(4), C24-C27 1.522(4) (Å).

^{1}H and ^{13}C NMR spectra

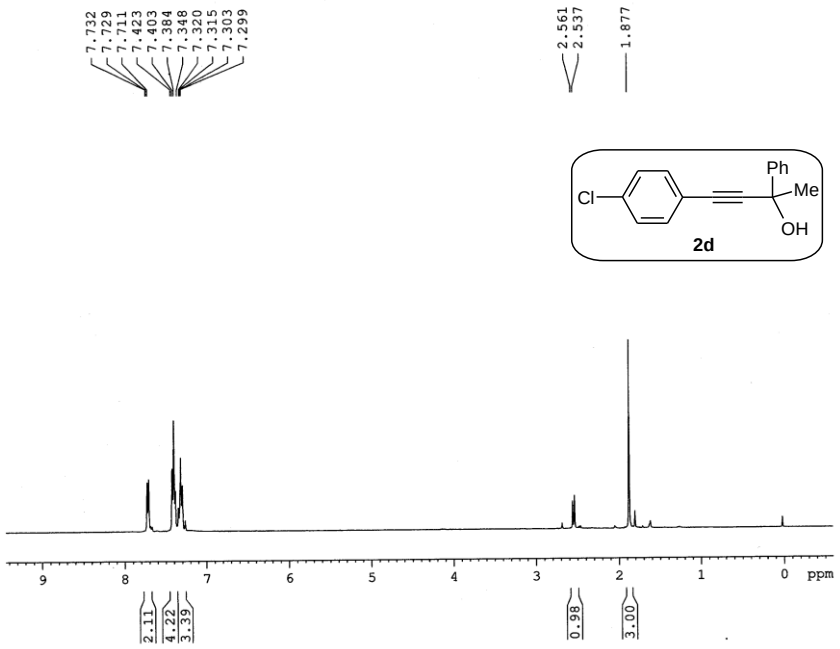


Figure S5. ^{1}H NMR spectrum of compound **2d**

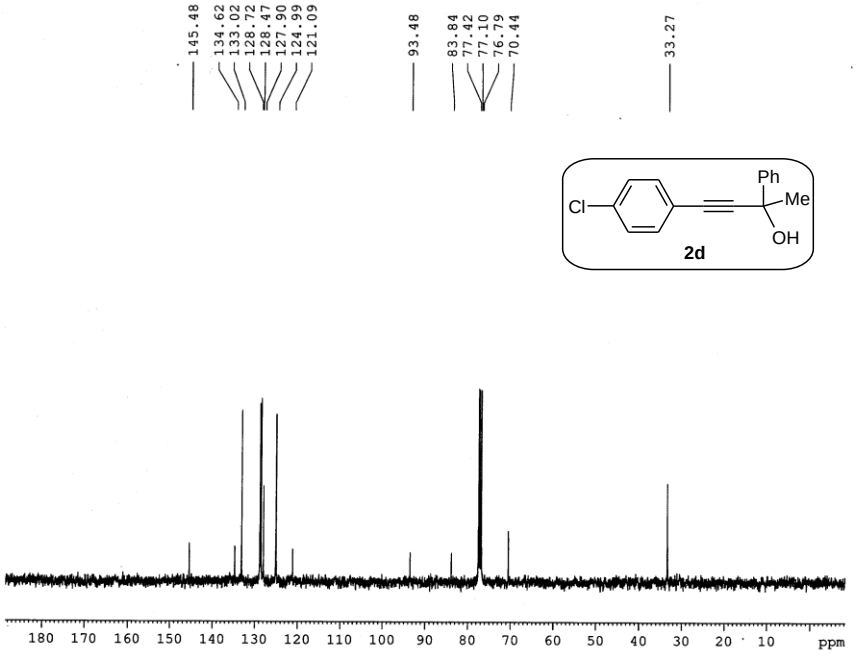


Figure S6. ^{13}C NMR spectrum of compound **2d**

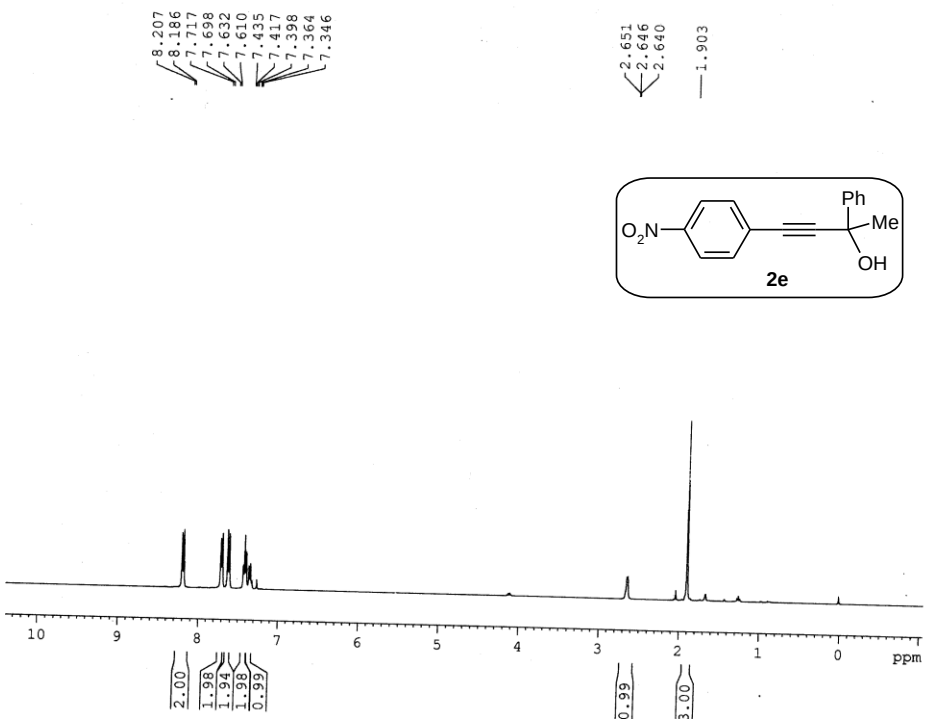


Figure S7. ^{1}H NMR spectrum of compound **2e**

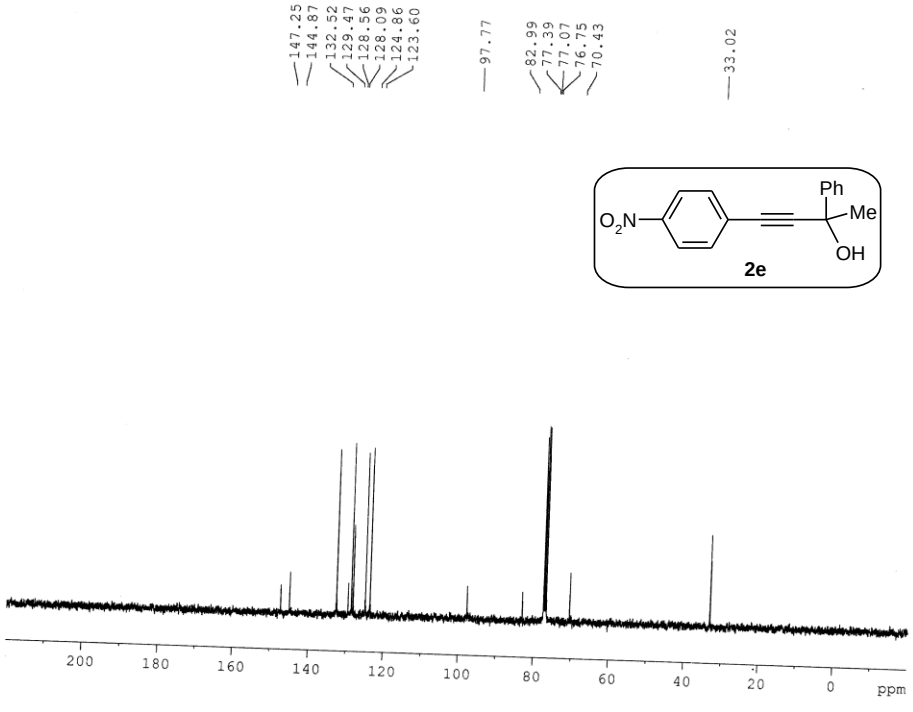


Figure S8. ^{13}C NMR spectrum of compound **2e**

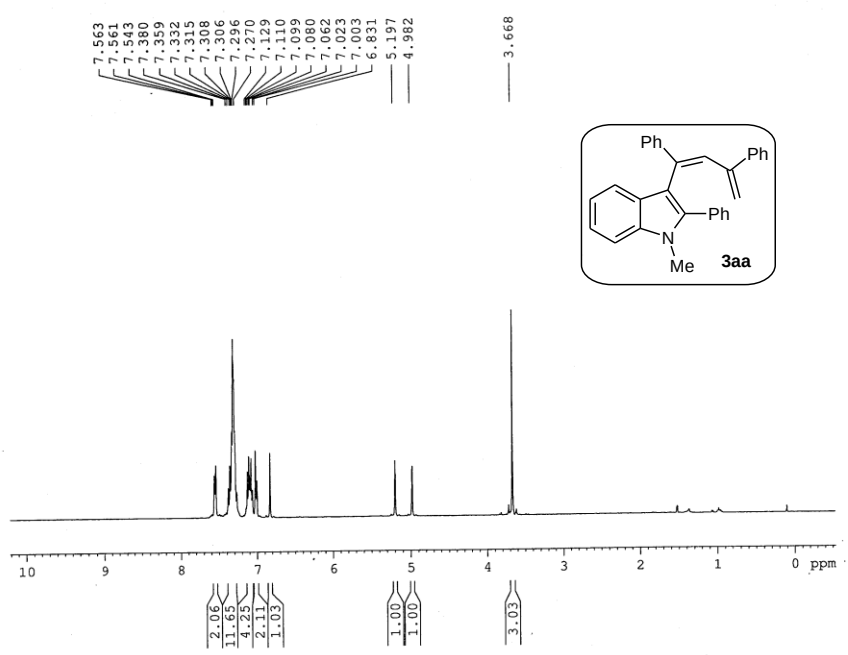


Figure S9. ^{1}H NMR spectrum of compound **3aa**

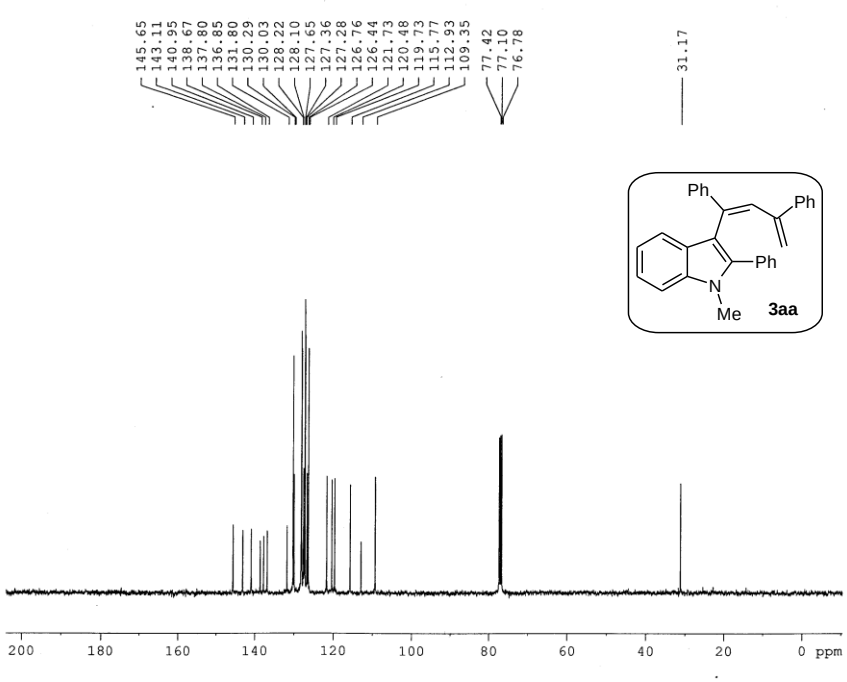


Figure S10. ^{13}C NMR spectrum of compound **3aa**

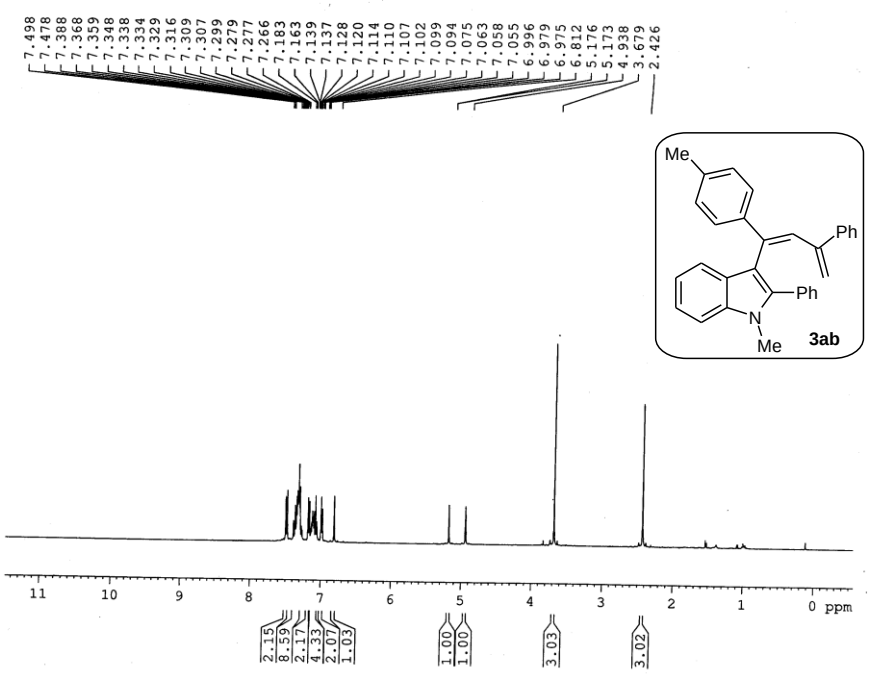


Figure S11. ^{1}H NMR spectrum of compound **3ab**

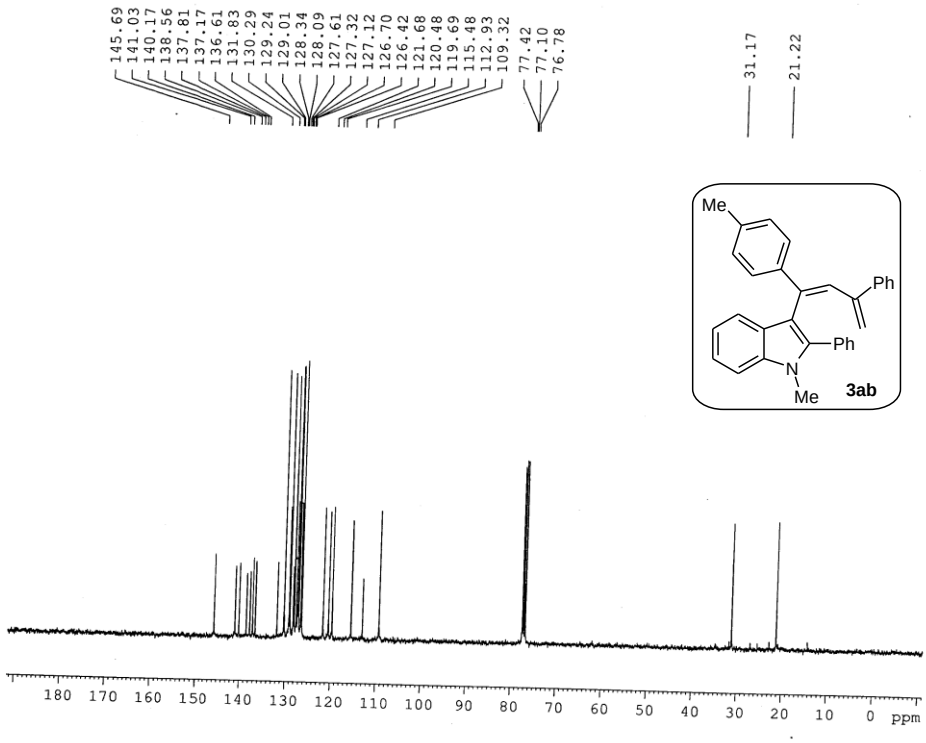


Figure S12. ^{13}C NMR spectrum of compound **3ab**

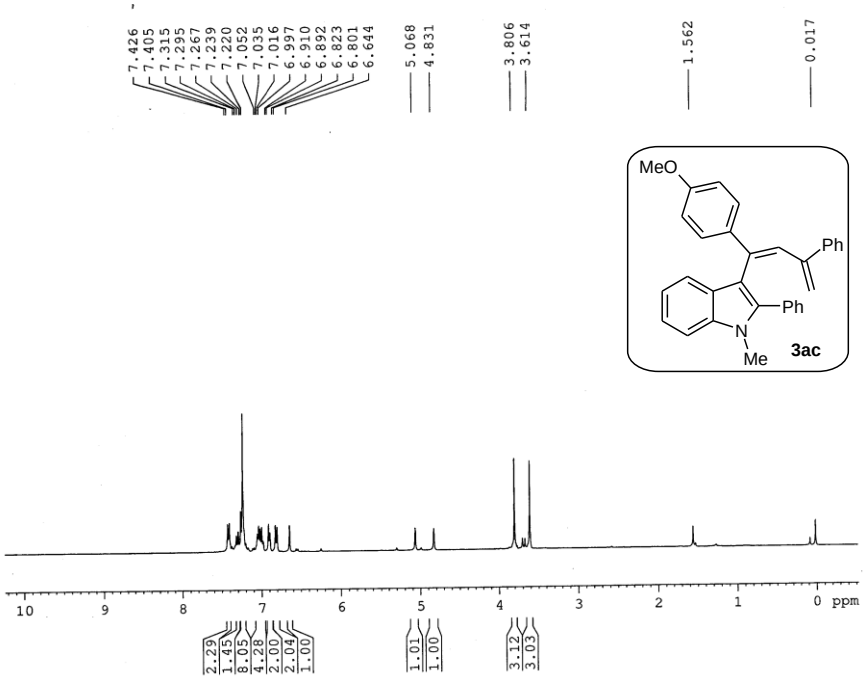


Figure S13.[1]H NMR spectrum of compound **3ac**

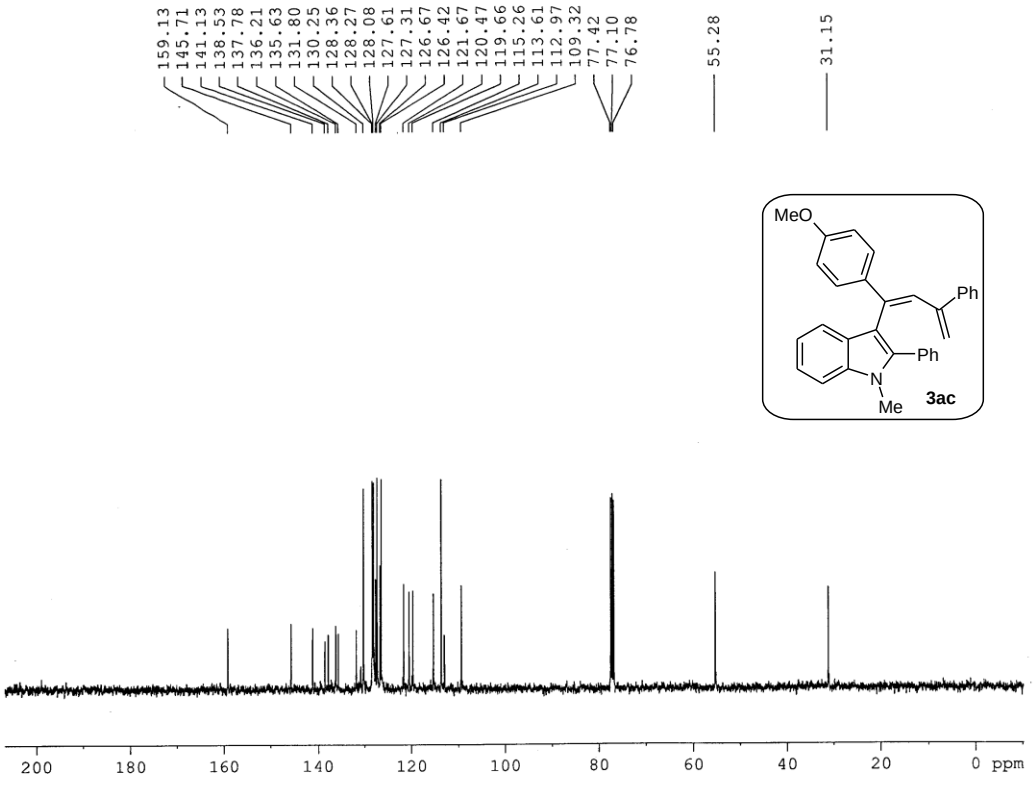


Figure S14.[13]C NMR spectrum of compound **3ac**

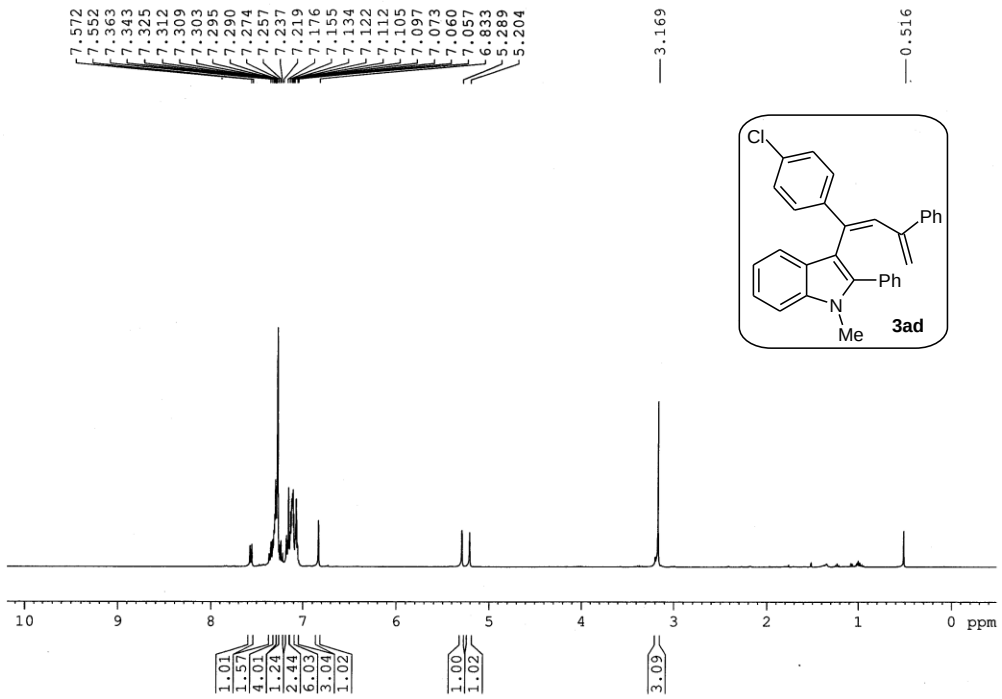


Figure S15. ^{1}H NMR (C_6D_6) spectrum of compound **3ad**

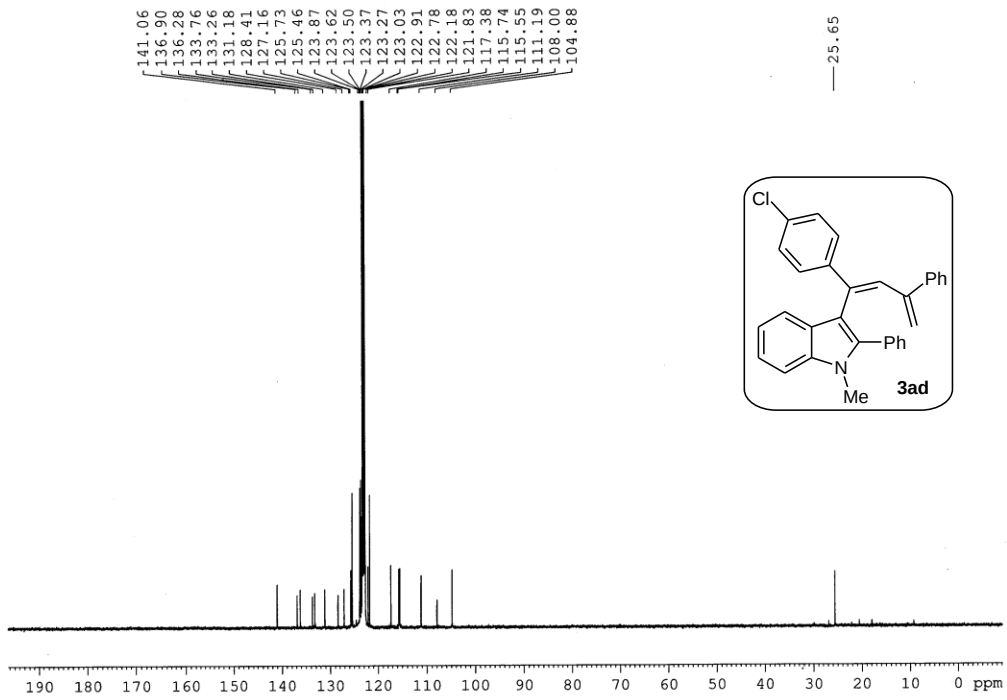


Figure S16. ^{13}C NMR (C_6D_6) spectrum of compound **3ad**

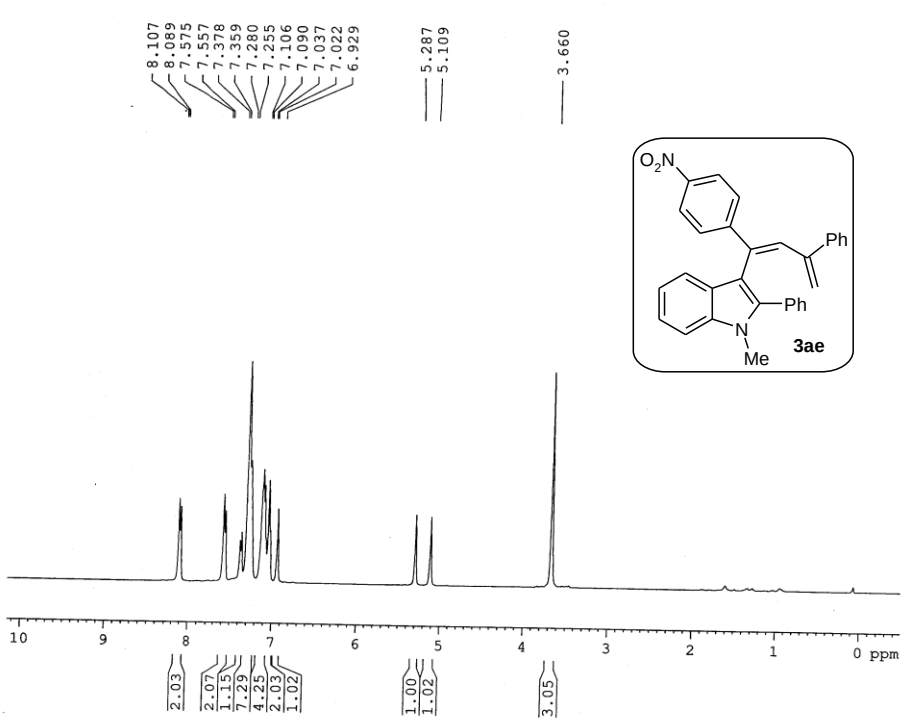


Figure S17. ^{1}H NMR spectrum of compound **3ae**

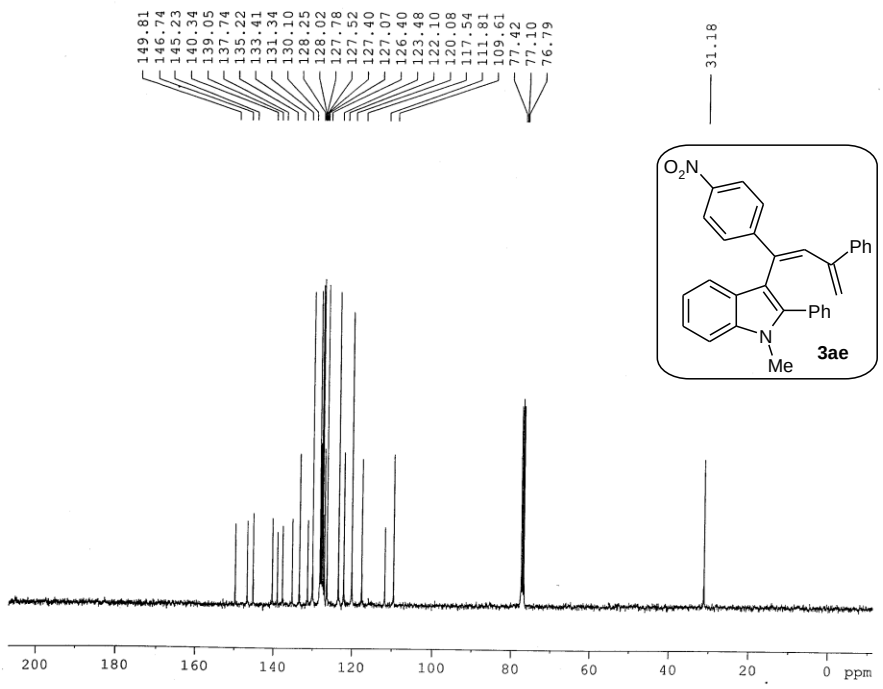


Figure S18. ^{13}C NMR spectrum of compound **3ae**

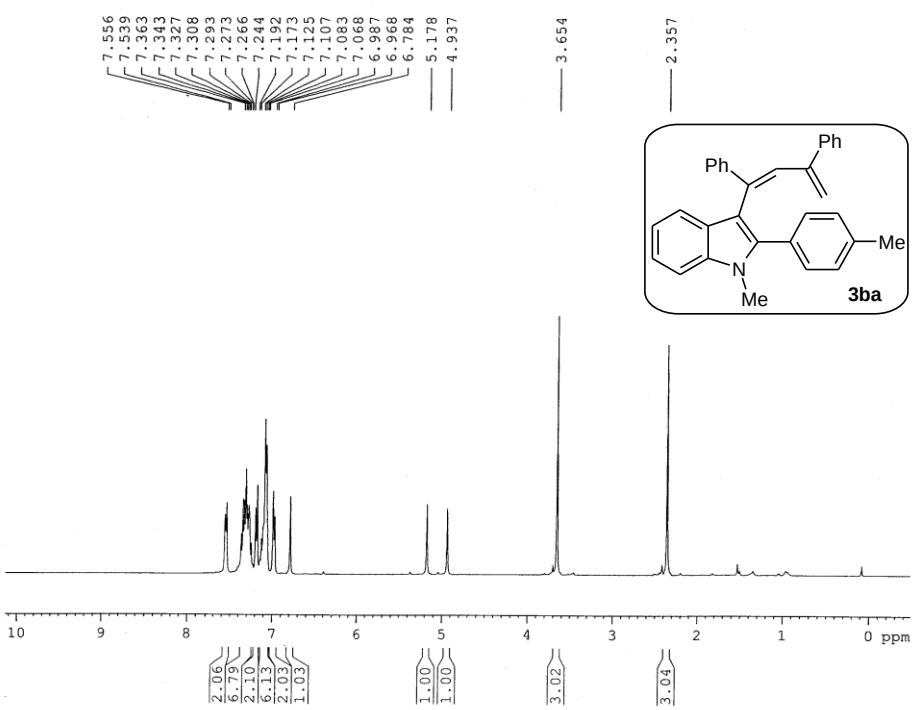


Figure S19.[1]H NMR spectrum of compound **3ba**

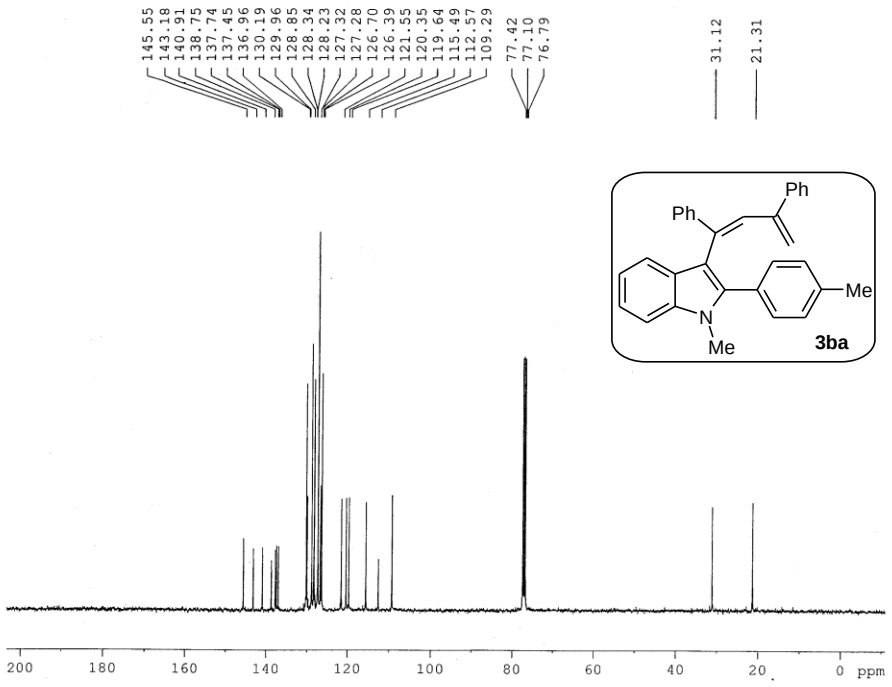


Figure S20.[13]C NMR spectrum of compound **3ba**

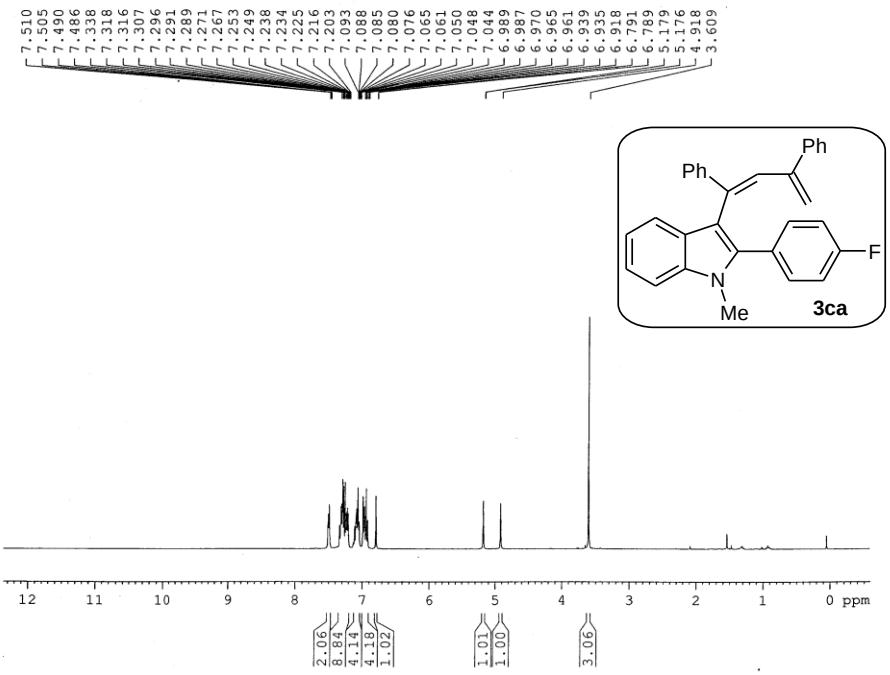


Figure S21. ^{1}H NMR spectrum of compound **3ca**

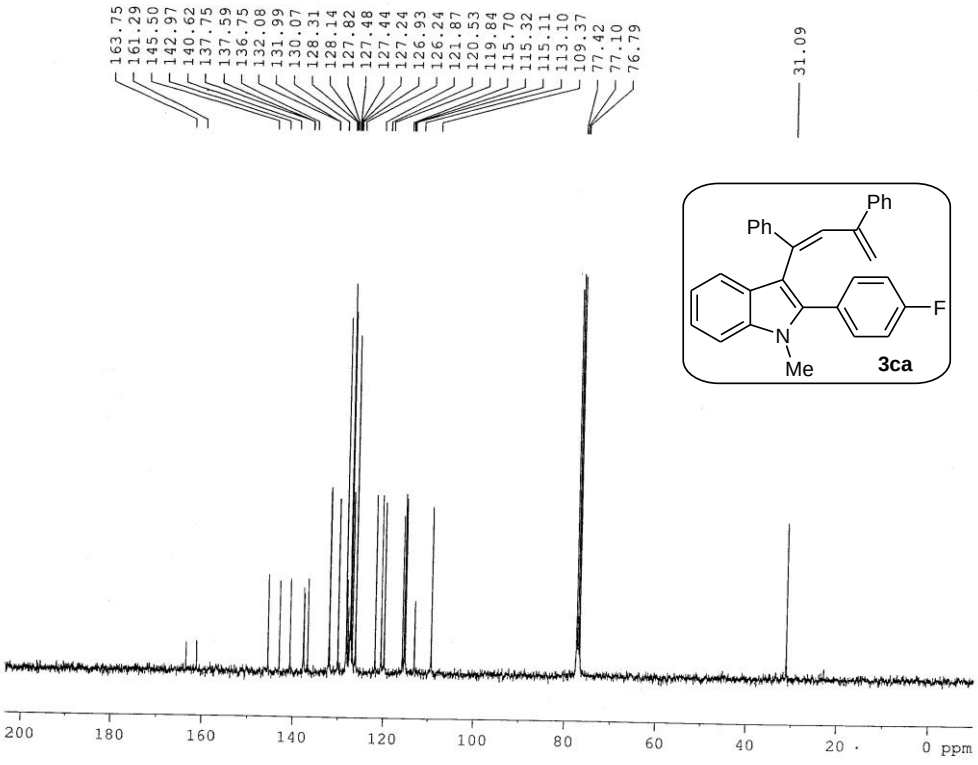


Figure S22. ^{13}C NMR spectrum of compound **3ca**

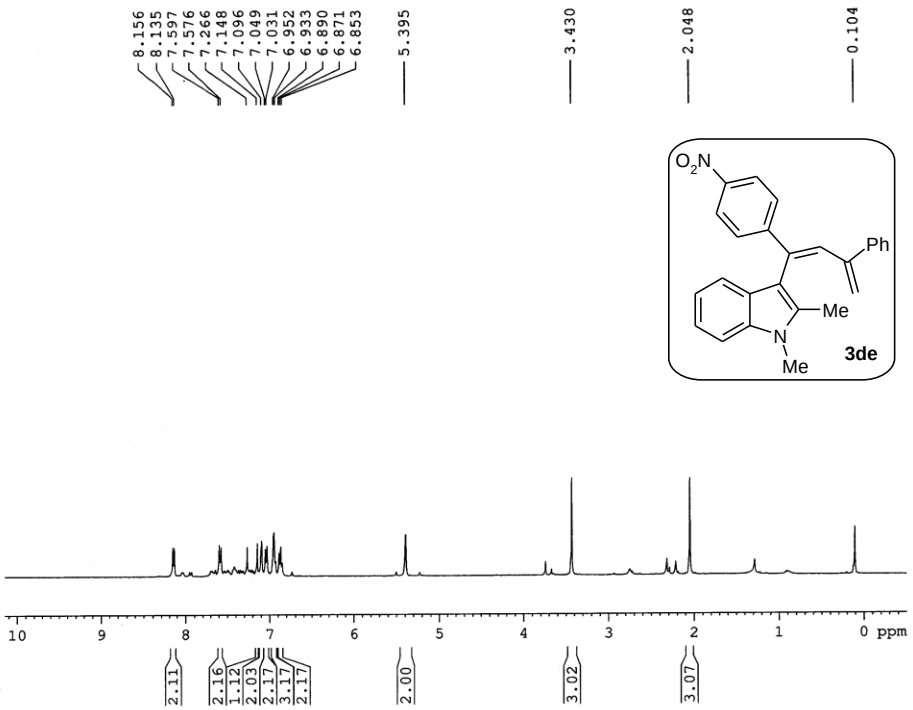


Figure S23. ^{1}H NMR spectrum of compound **3de**. (For minor peaks see experimental section)

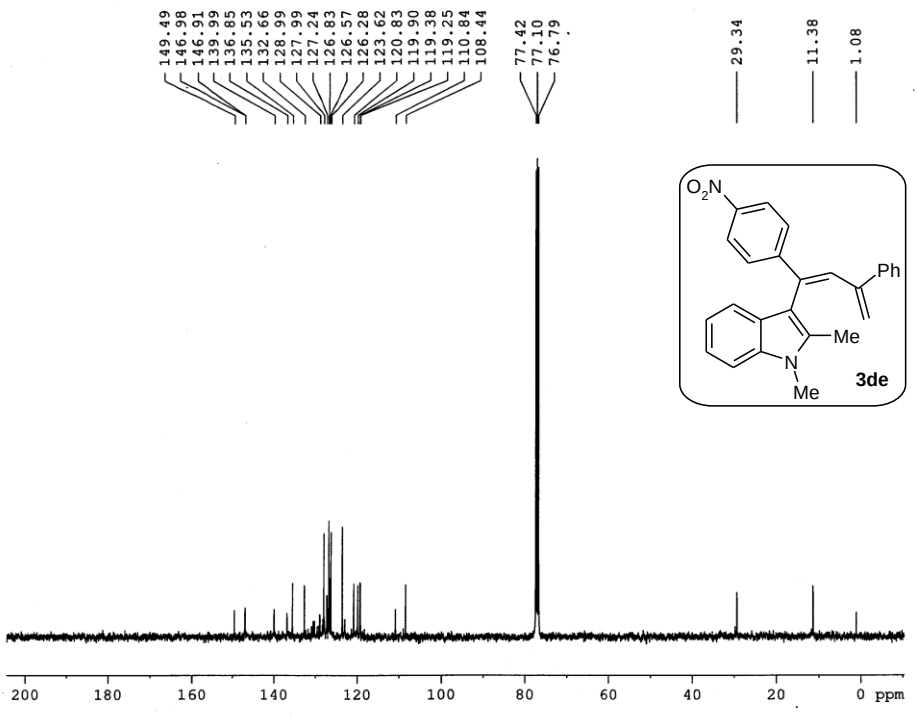


Figure S24. ^{13}C NMR spectrum of compound **3de**

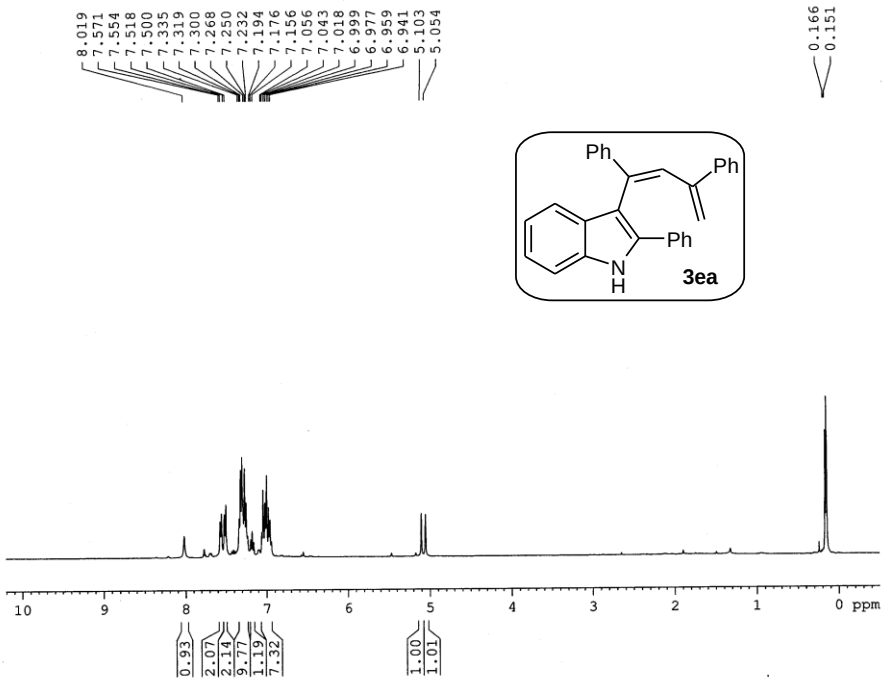


Figure S25. ^{1}H NMR spectrum of compound **3ea**

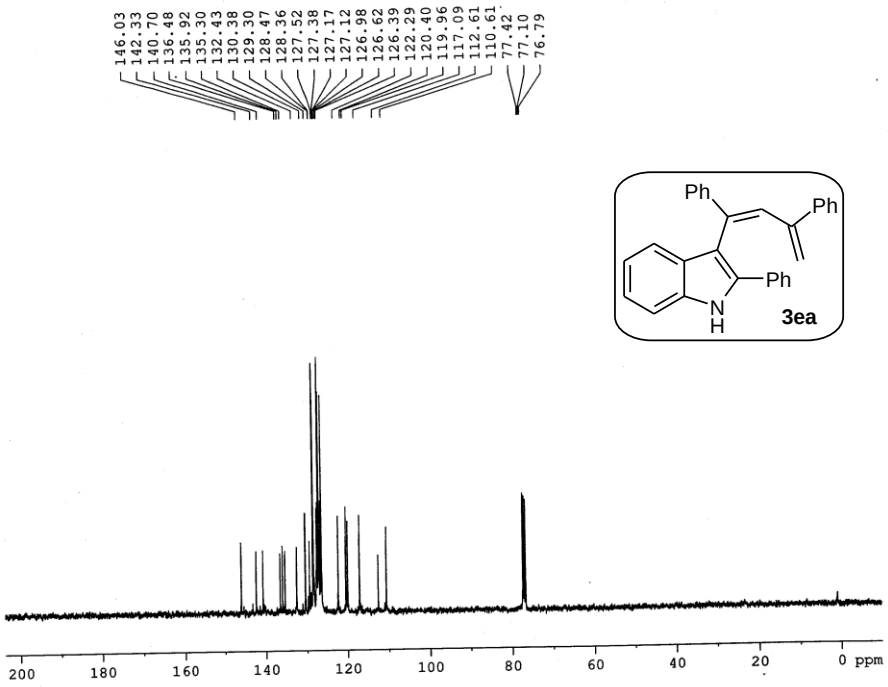


Figure S26. ^{13}C NMR spectrum of compound **3ea**

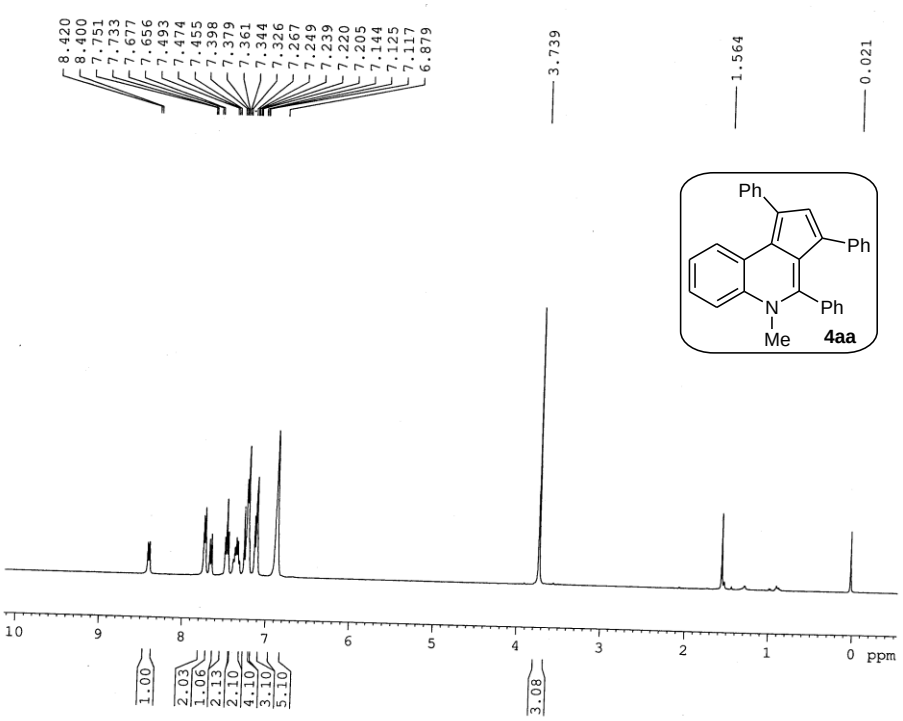


Figure S27.[1]H NMR spectrum of compound **4aa**

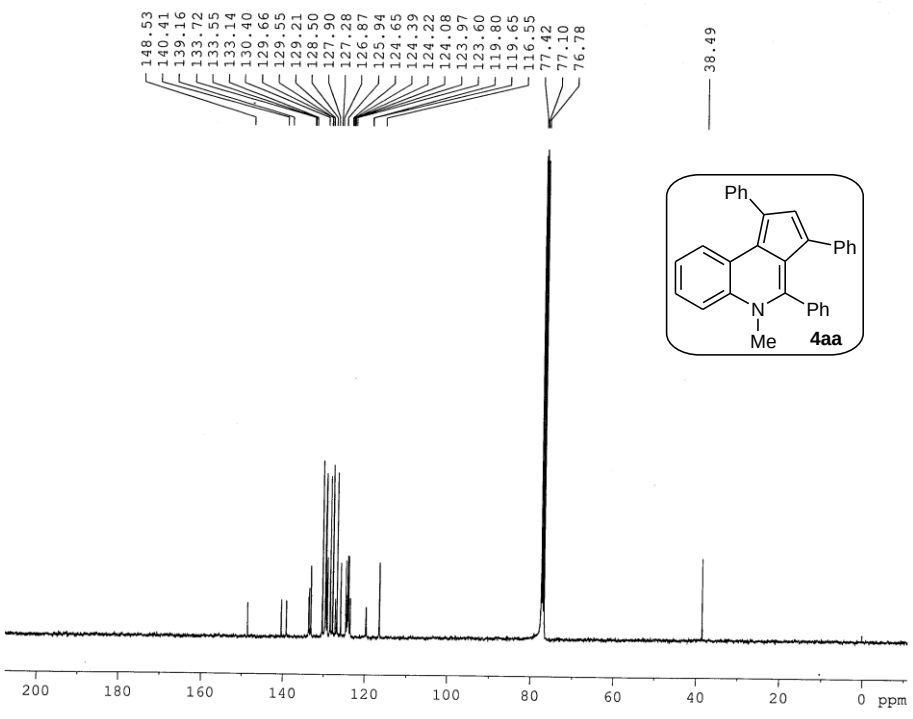


Figure S28.[13]C NMR spectrum of compound **4aa**

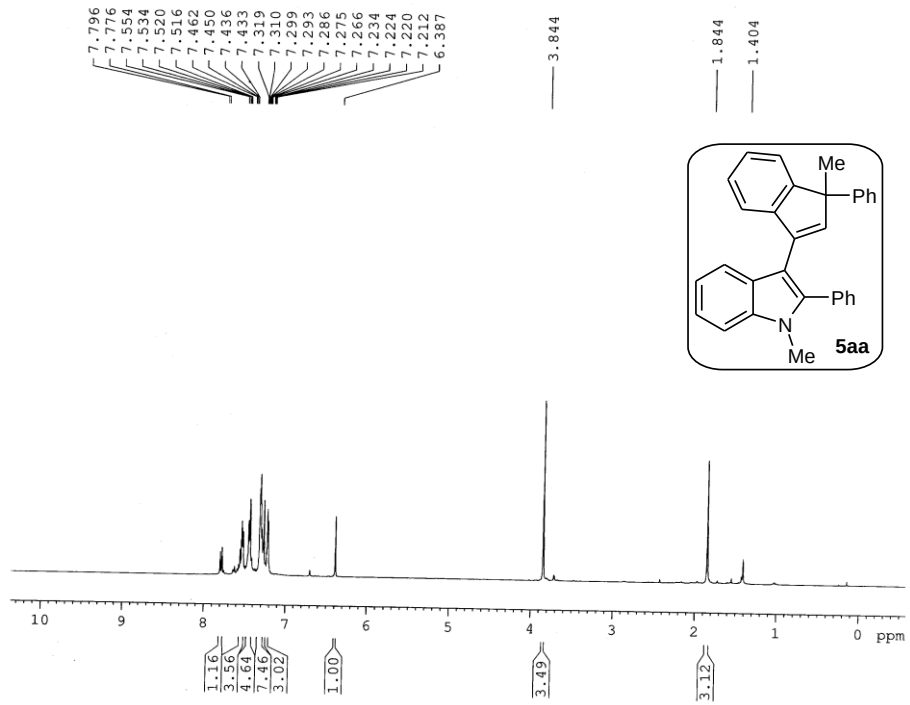


Figure S29.[1]H NMR spectrum of compound **5aa**

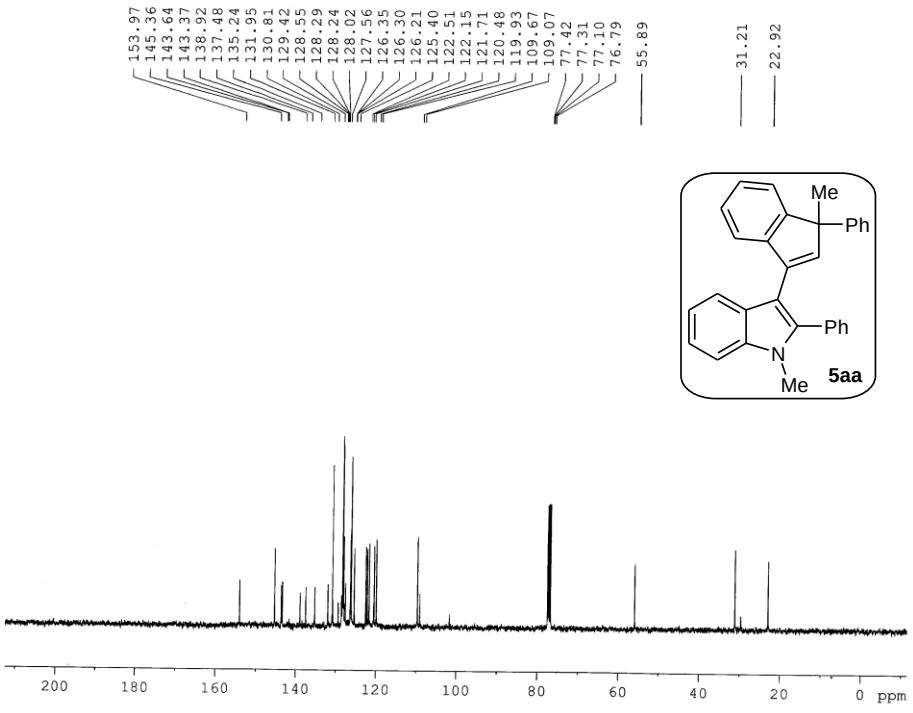


Figure S30.[13]C NMR spectrum of compound **5aa**

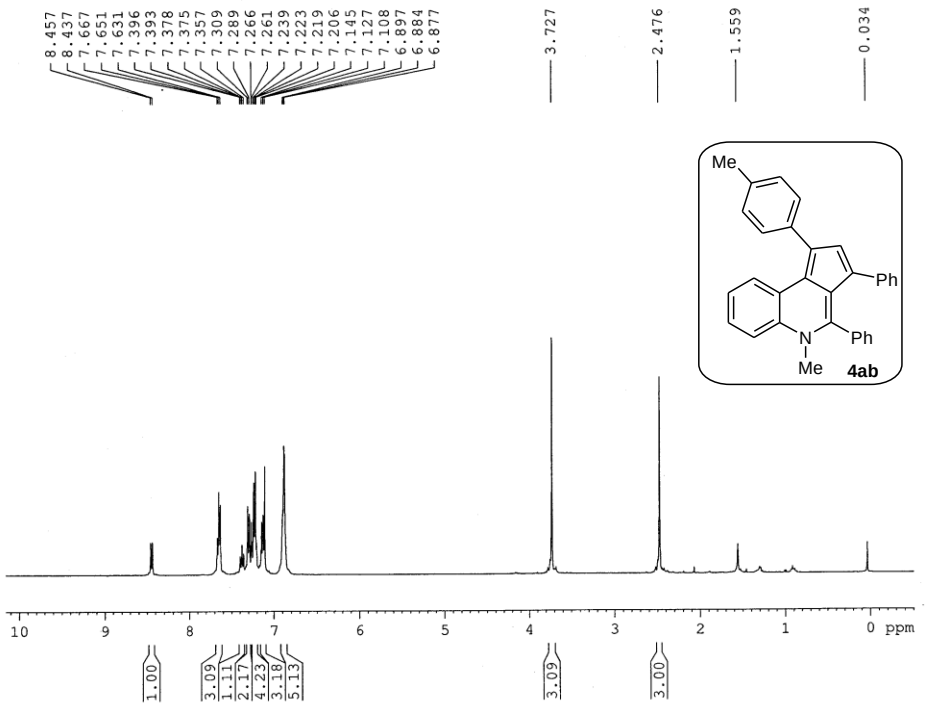


Figure S31. ^{1}H NMR spectrum of compound **4ab**

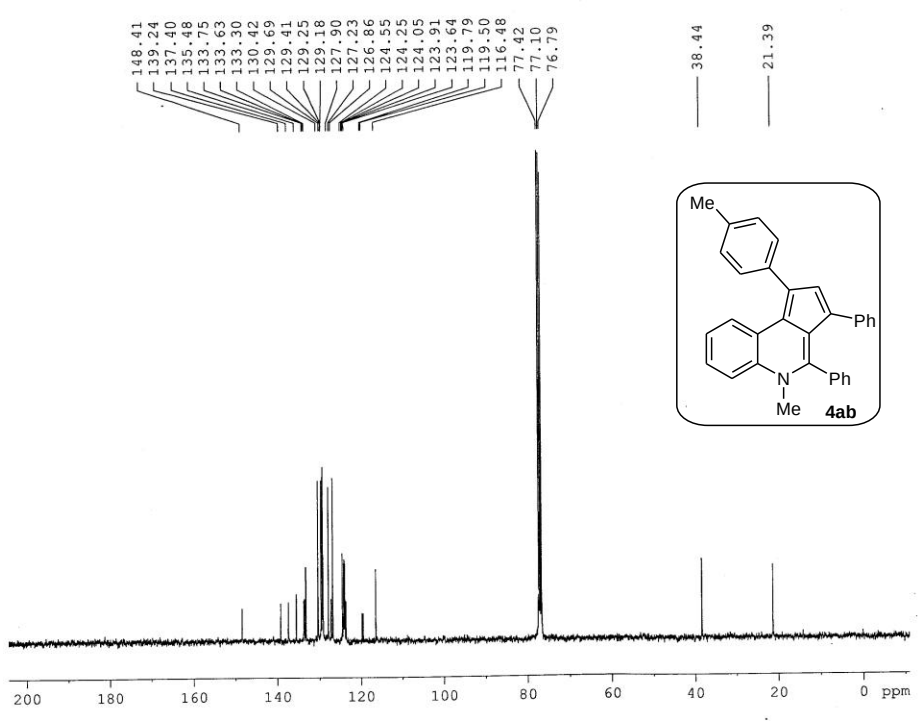


Figure S32. ^{13}C NMR spectrum of compound **4ab**

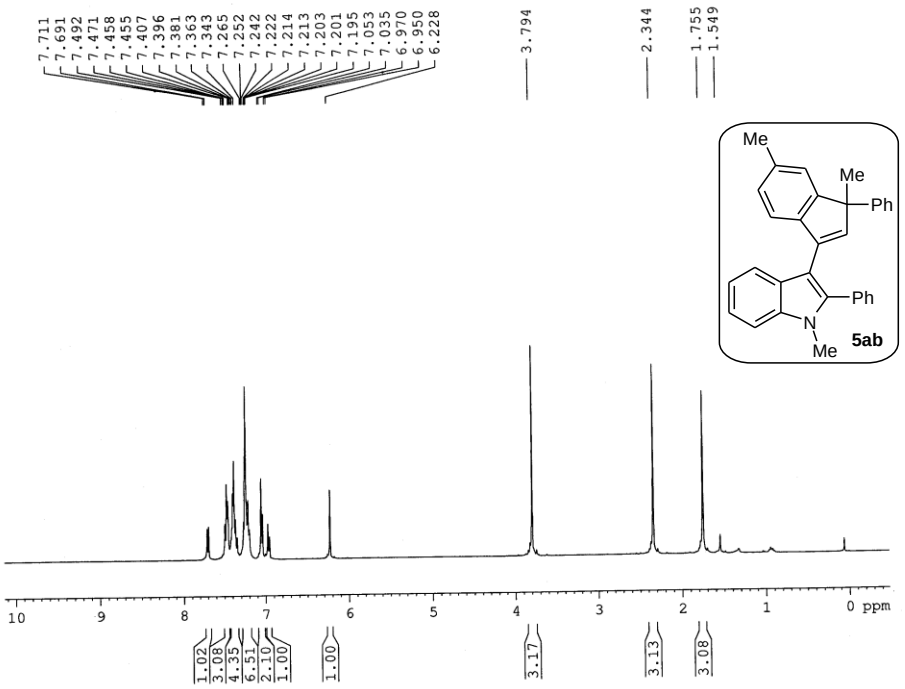


Figure S33.[1]H NMR spectrum of compound **5ab**

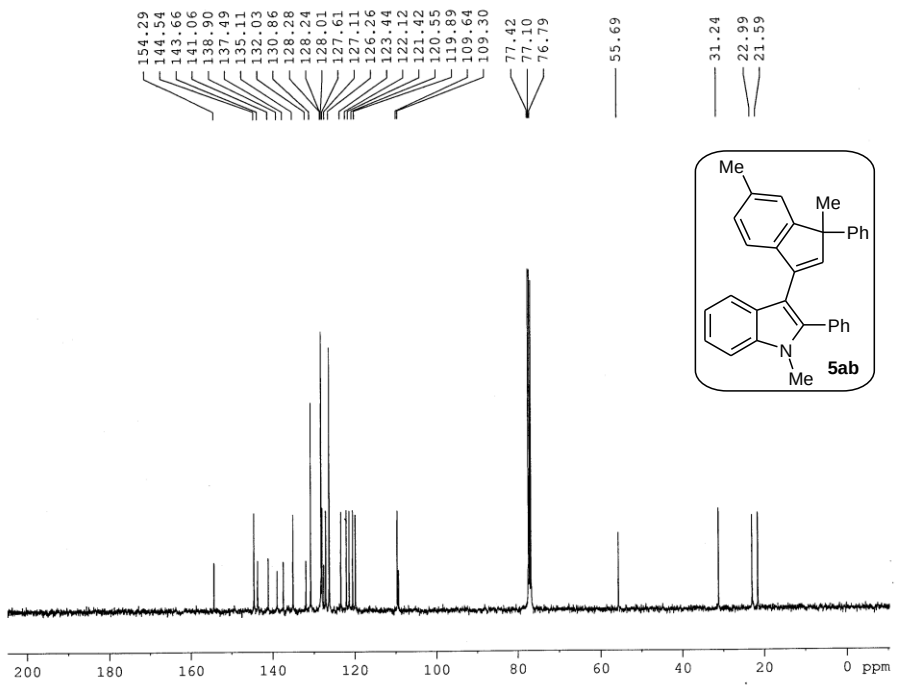


Figure S34.[13]C NMR spectrum of compound **5ab**

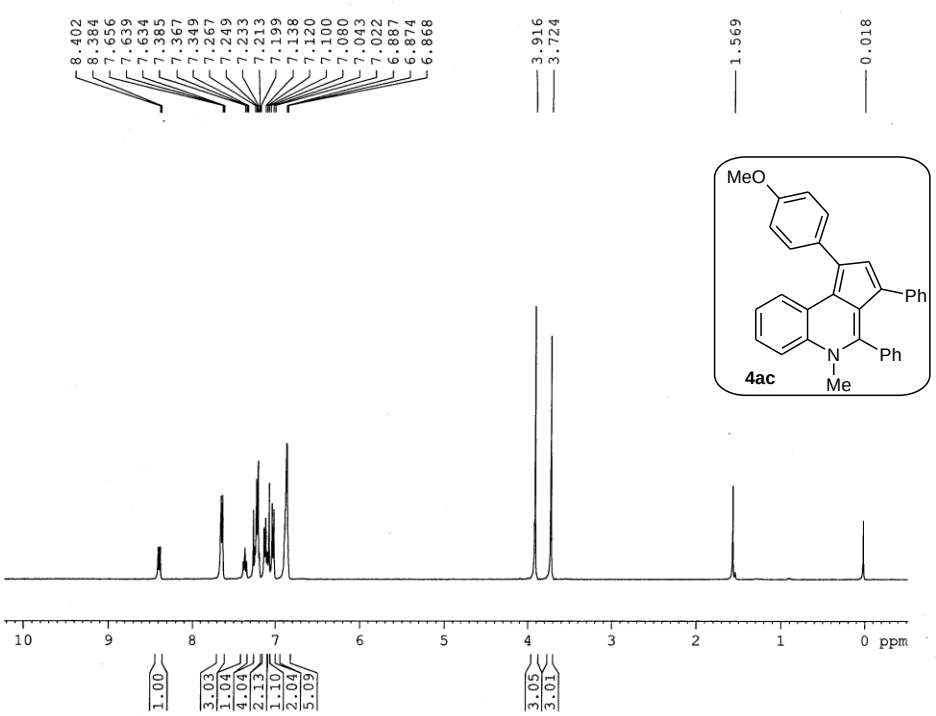


Figure S35. ^{1}H NMR spectrum of compound **4ac**

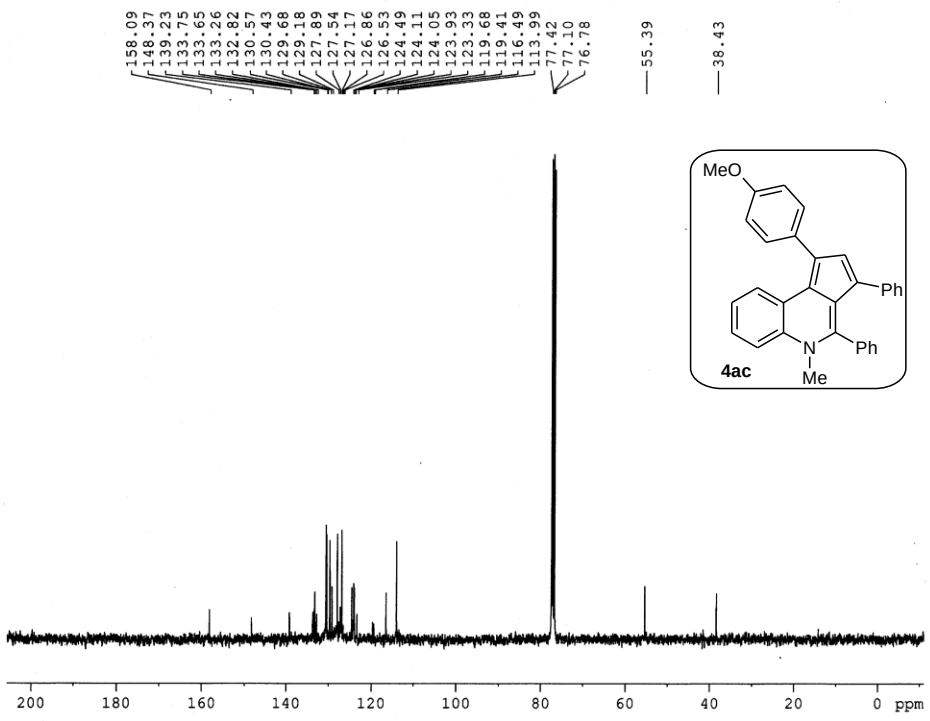


Figure S36. ^{13}C NMR spectrum of compound **4ac**

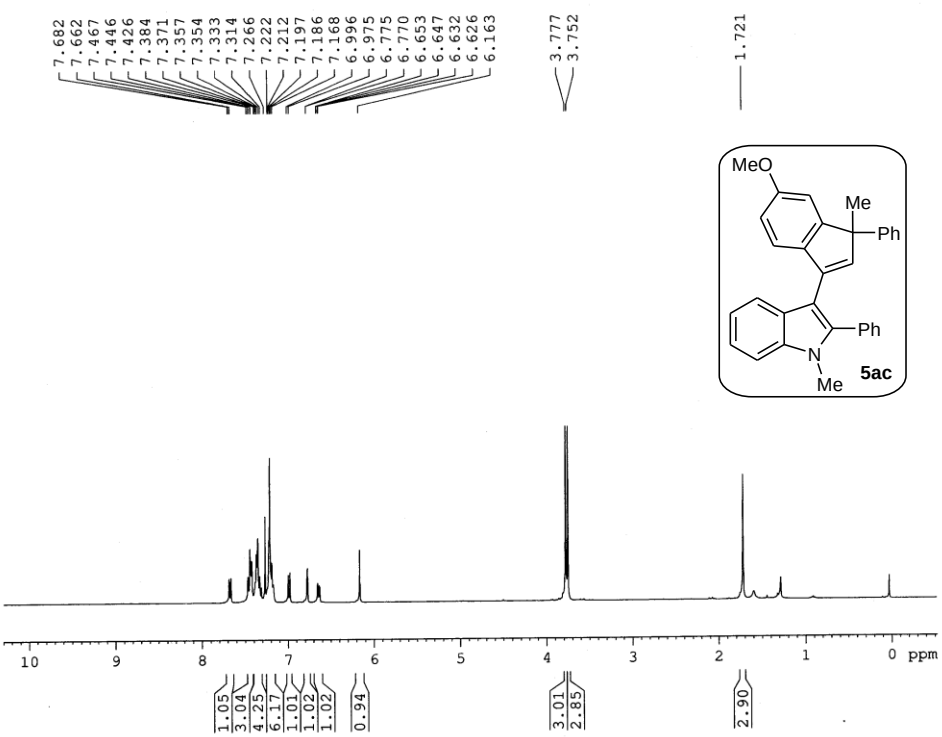


Figure S37.[1]H NMR spectrum of compound **5ac**

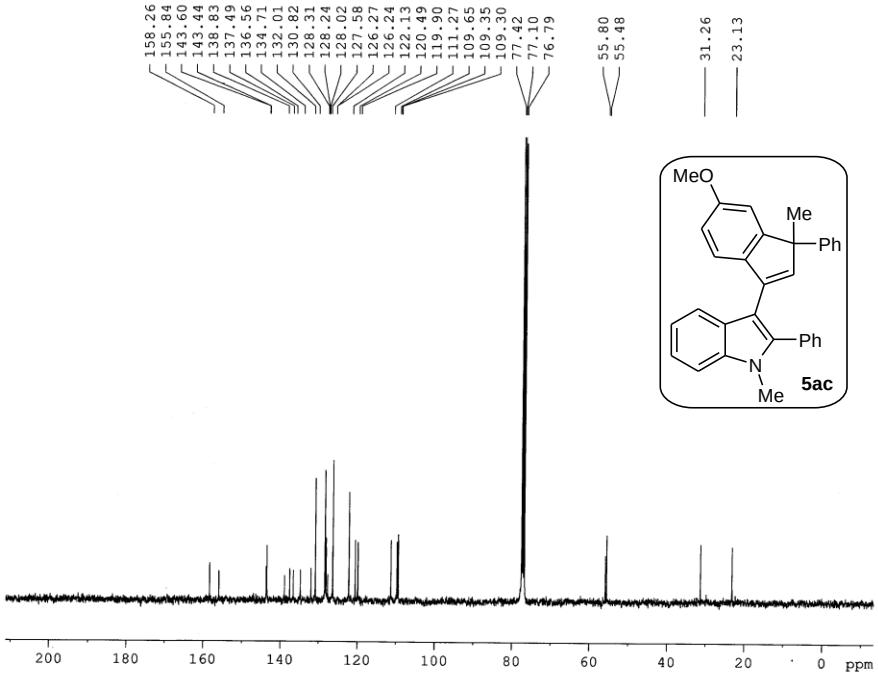


Figure S38.[13]C NMR spectrum of compound **5ac**

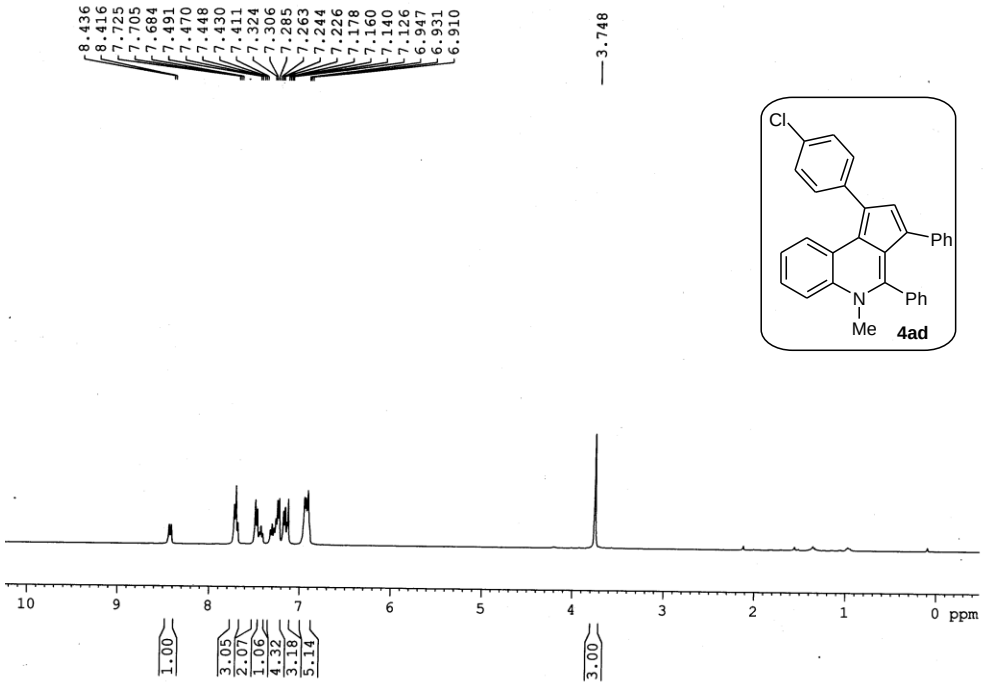


Figure S39.[1]H NMR spectrum of compound **4ad**

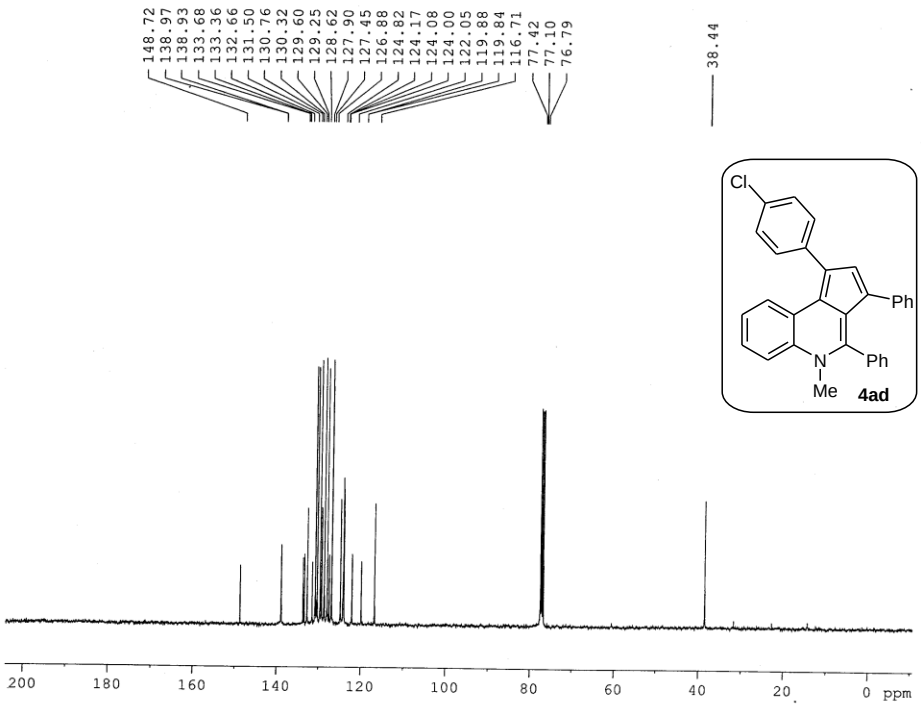


Figure S40.[13]C NMR spectrum of compound **4ad**

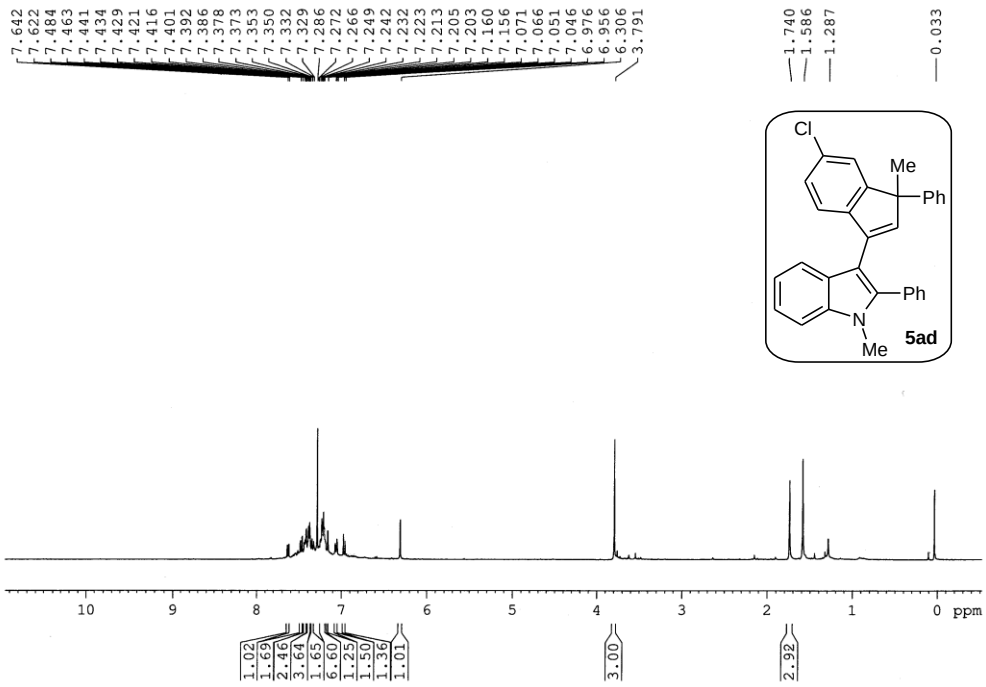


Figure S41.[1]H NMR spectrum of compound **5ad**. (Additional peak is due to grease)

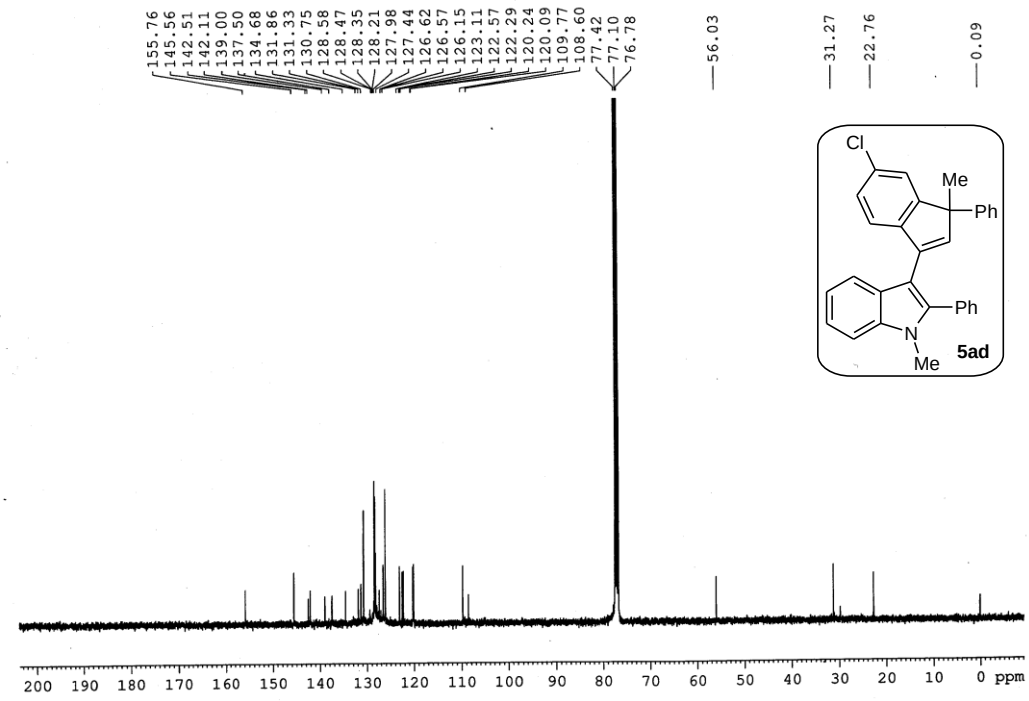


Figure S42.[13]C NMR spectrum of compound **5ad**. (Additional peak is due to grease)

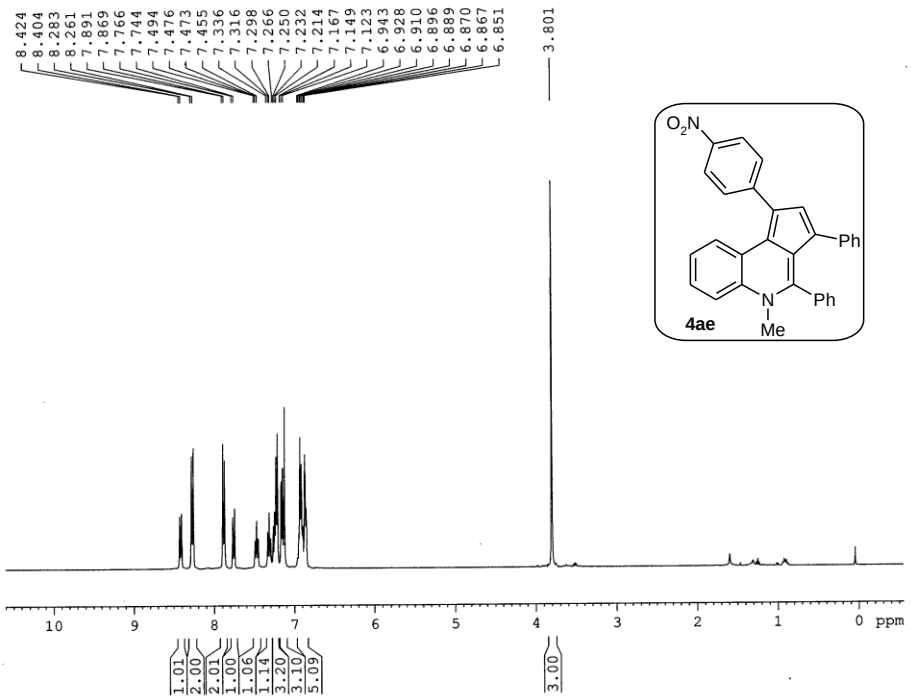


Figure S43. ^{1}H NMR spectrum of compound **4ae**

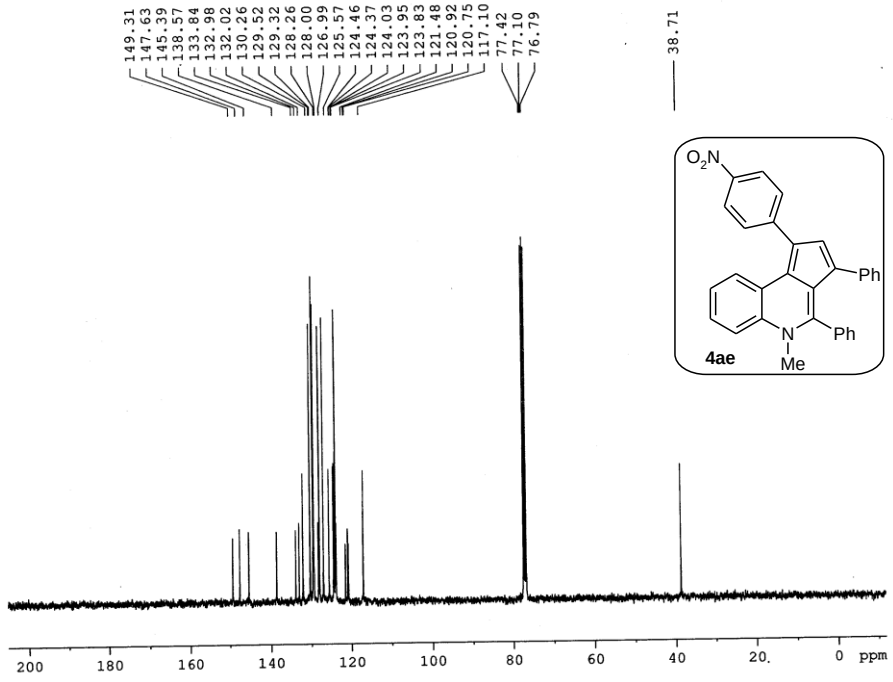


Figure S44. ^{13}C NMR spectrum of compound **4ae**

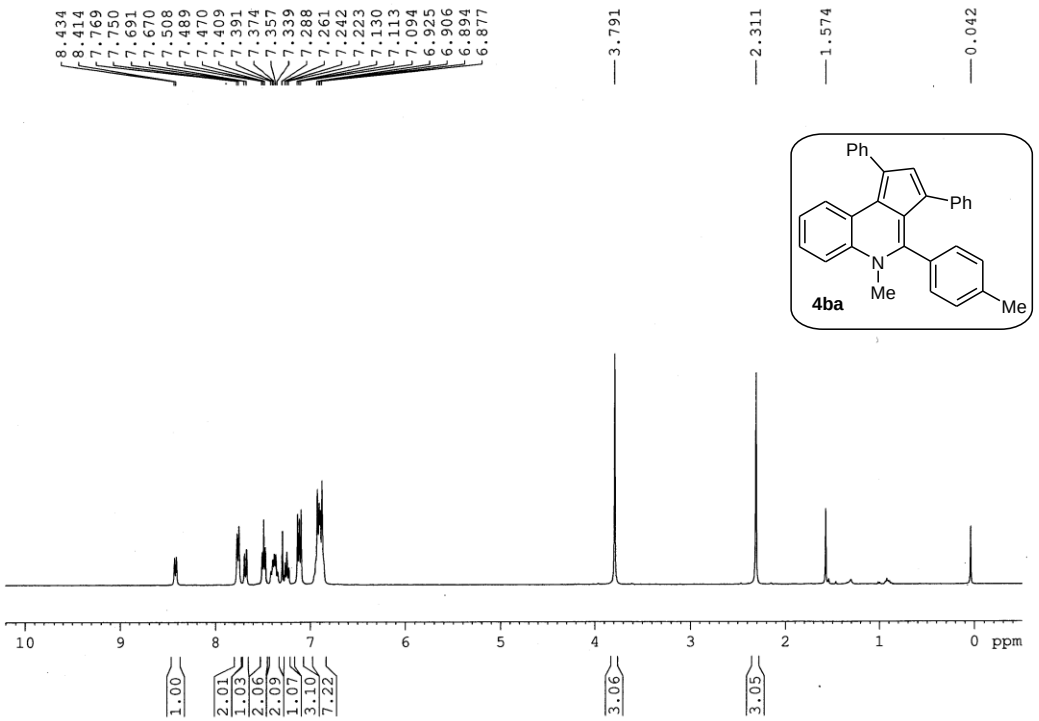


Figure S45. ^{1}H NMR spectrum of compound **4ba**.

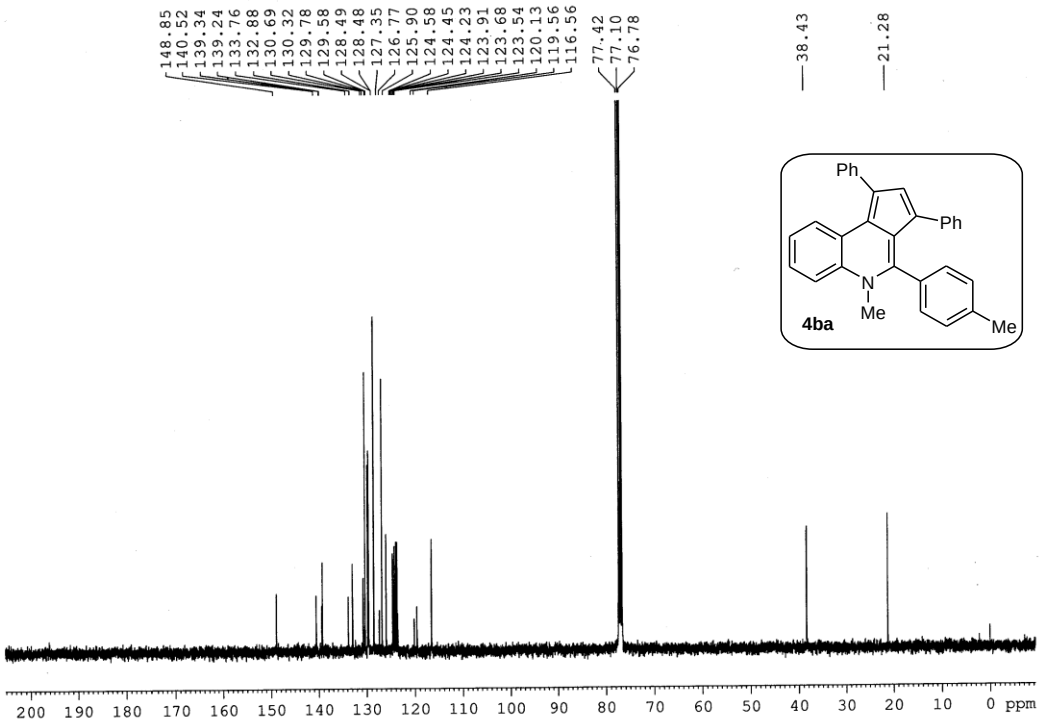


Figure S46. ^{13}C NMR spectrum of compound **4ba**.

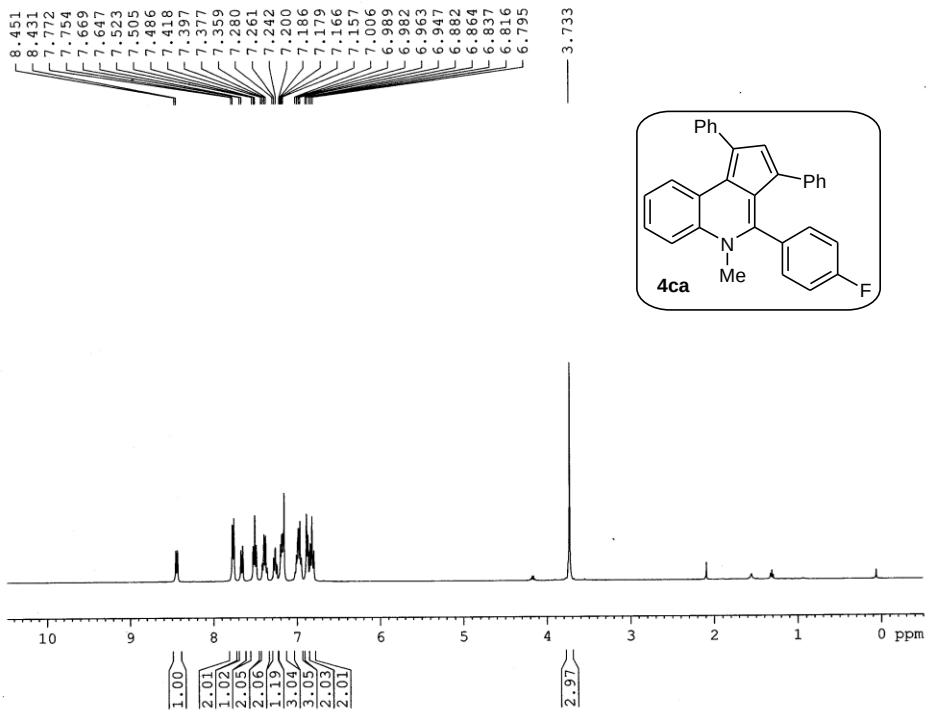


Figure S47.[1]H NMR spectrum of compound **4ca**

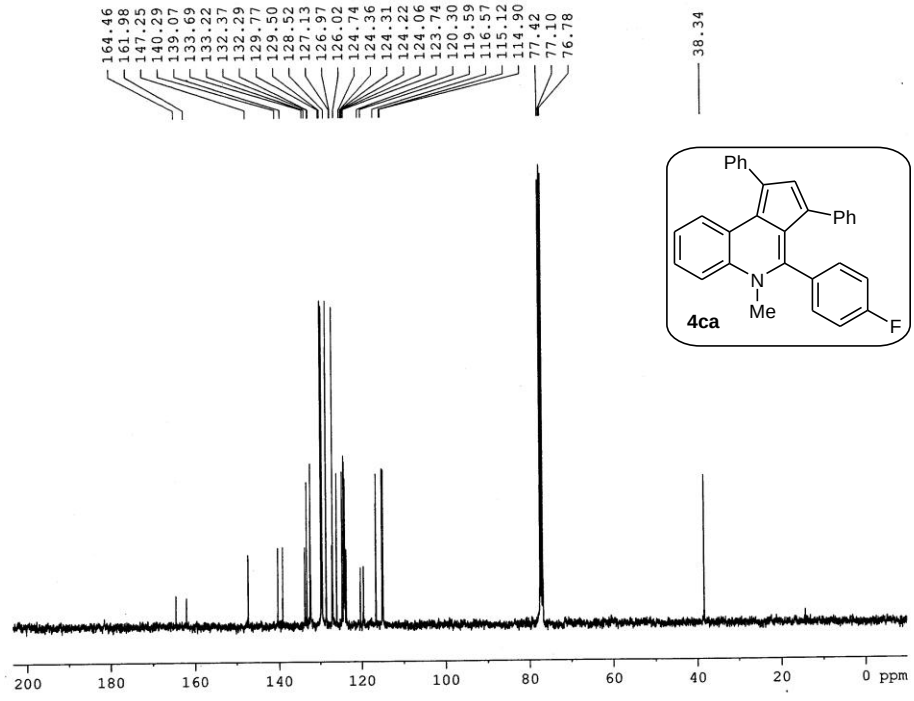


Figure S48.[13]C NMR spectrum of compound **4ca**

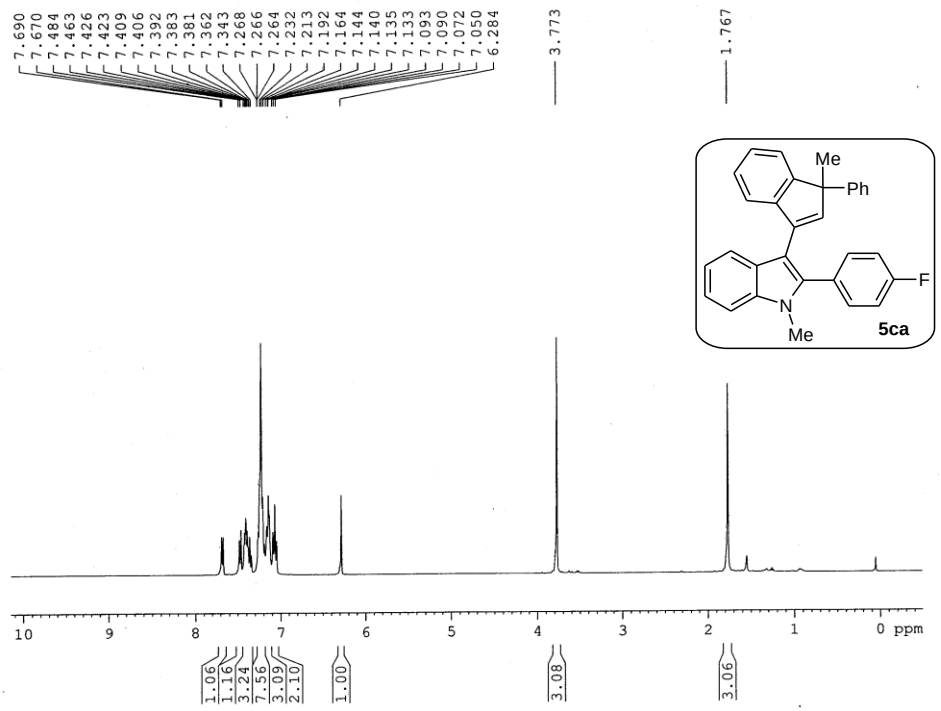


Figure S49.[1]H NMR spectrum of compound **5ca**

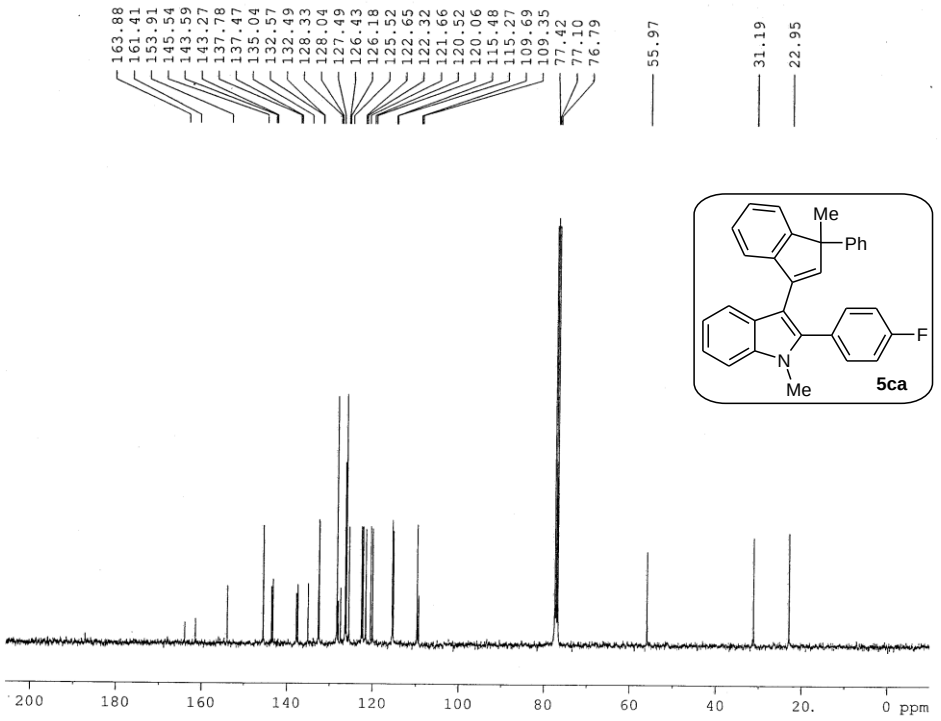


Figure S50.[13]C NMR spectrum of compound **5ca**

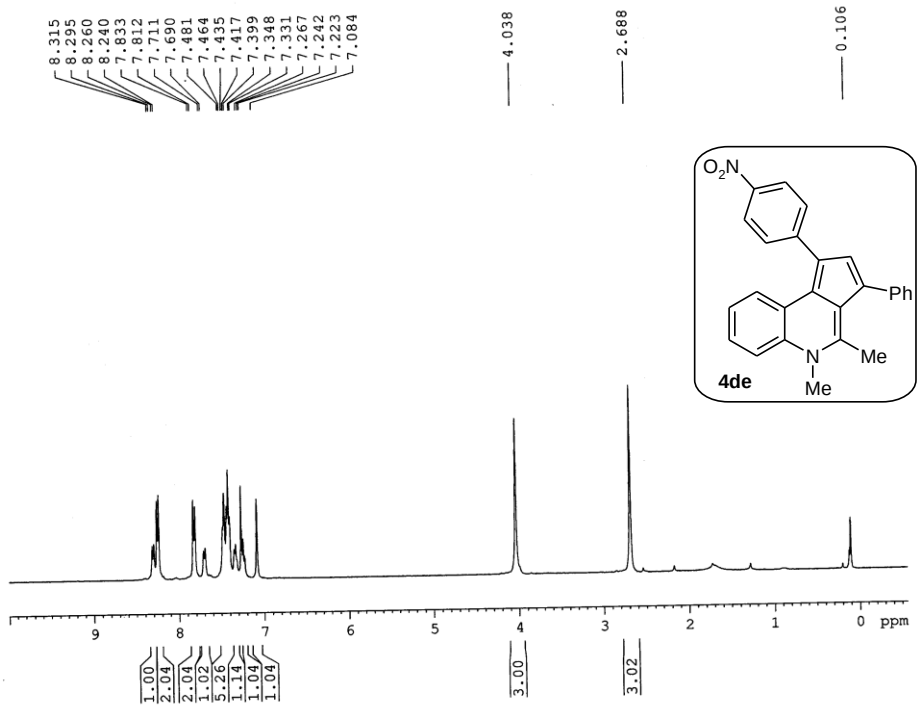


Figure S51. ^{1}H NMR spectrum of compound **4de**

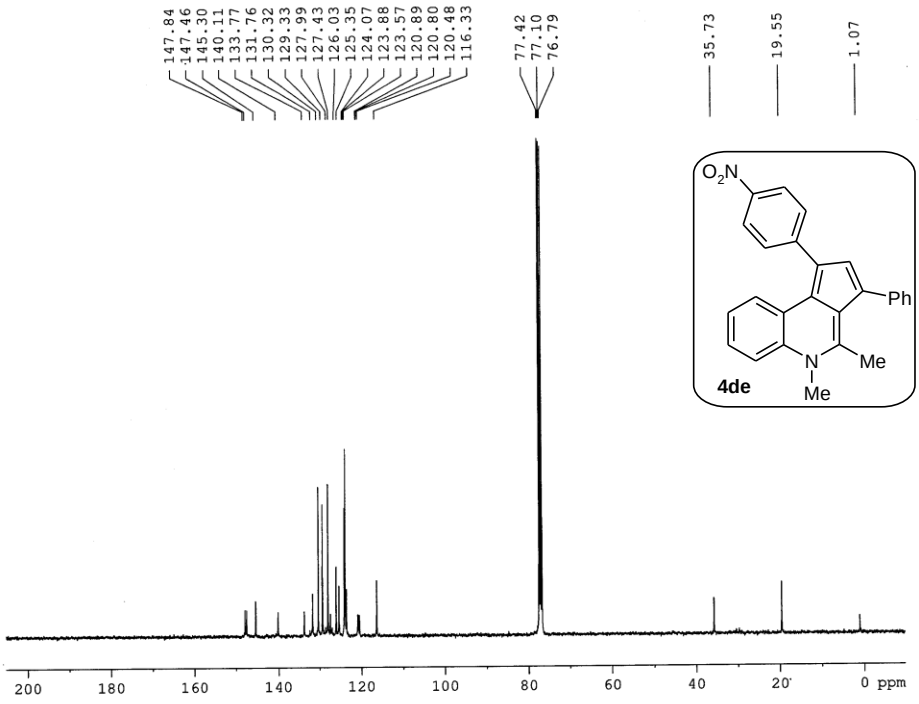


Figure S52. ^{13}C NMR spectrum of compound **4de**

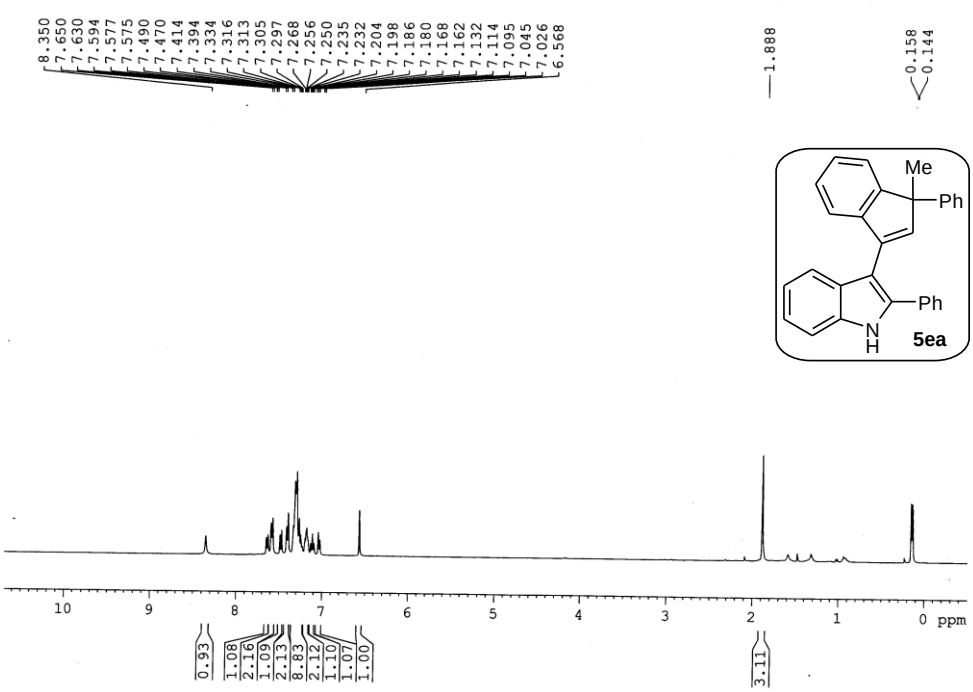


Figure S53.[1]H NMR spectrum of compound **5ea**

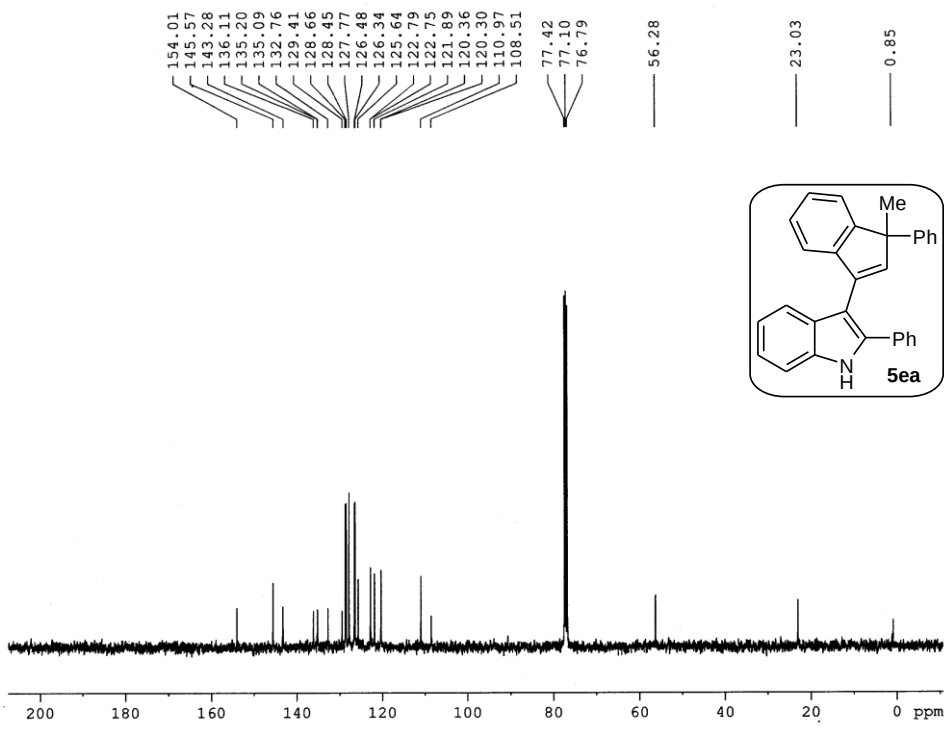


Figure S54.[13]C NMR spectrum of compound **5ea**

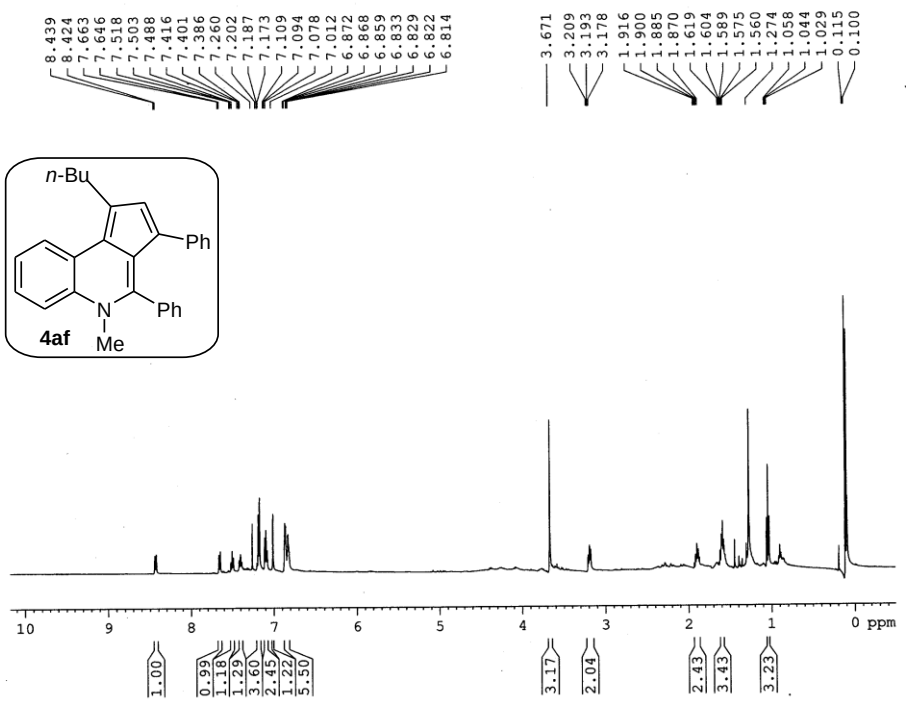


Figure S55. ^{1}H NMR spectrum of compound **4af**. Additional peak is due to grease.

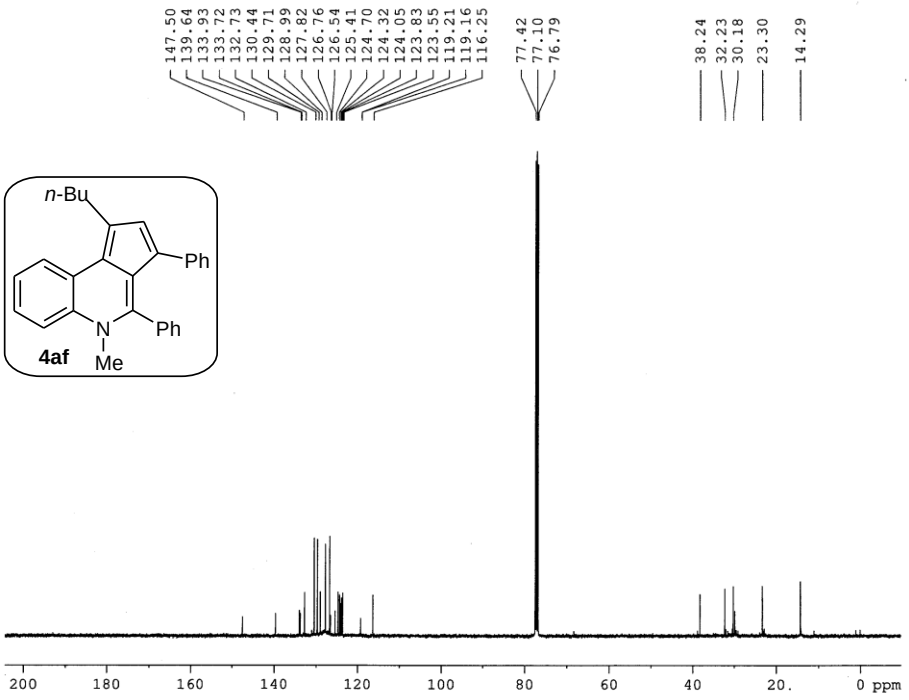


Figure S56. ^{13}C NMR spectrum of compound **4af**. Additional peak is due to grease.

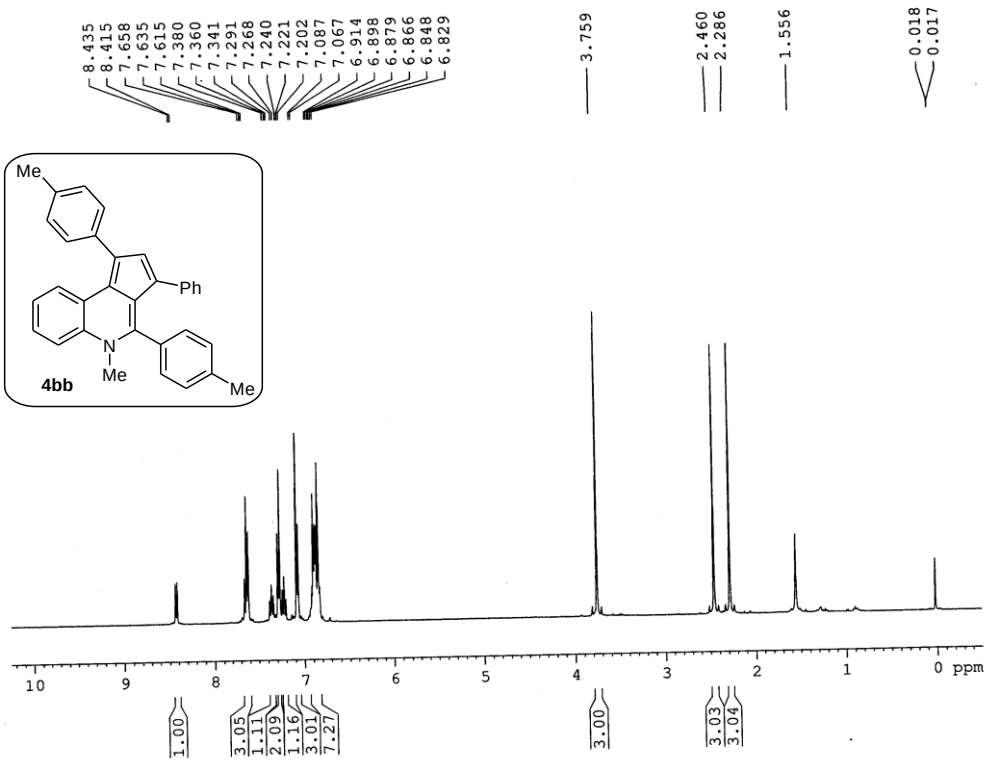


Figure S57.[1]H NMR spectrum of compound **4bb**

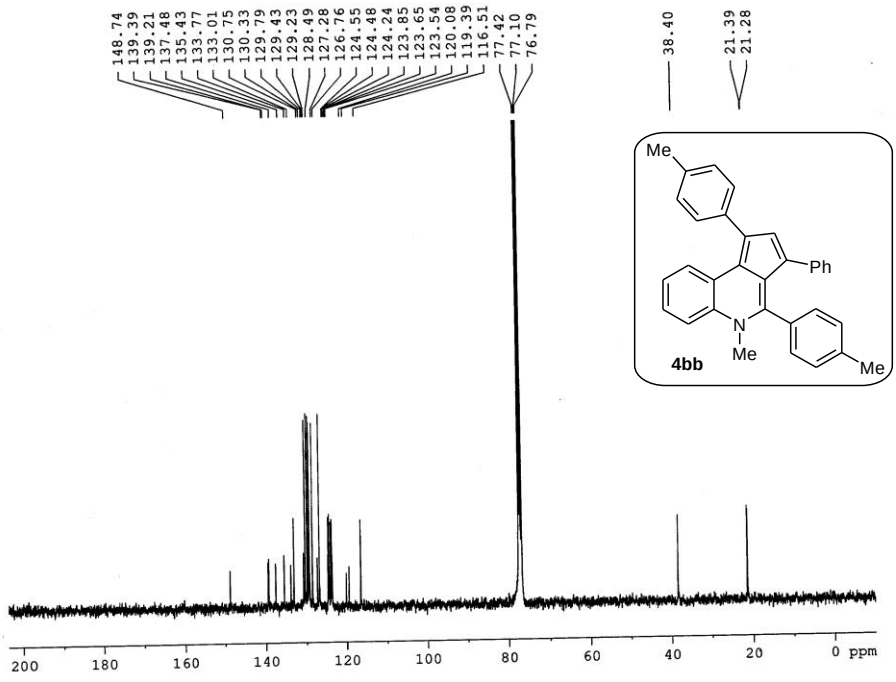


Figure S58.[13]C NMR spectrum of compound **4bb**

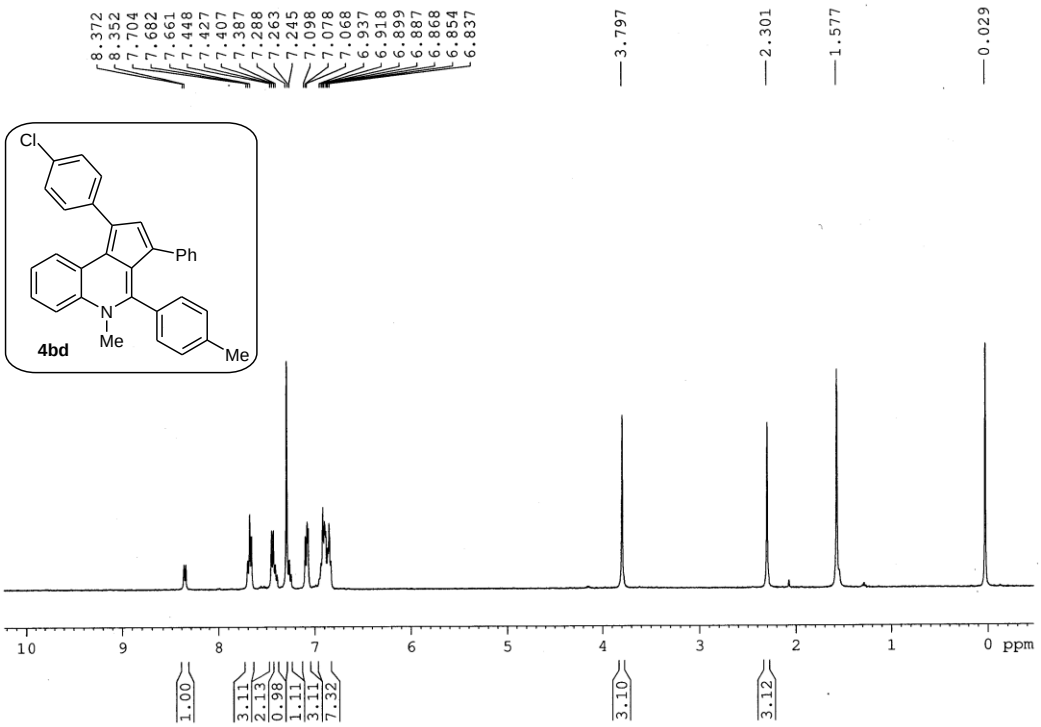


Figure S59.[1]H NMR spectrum of compound **4bd**

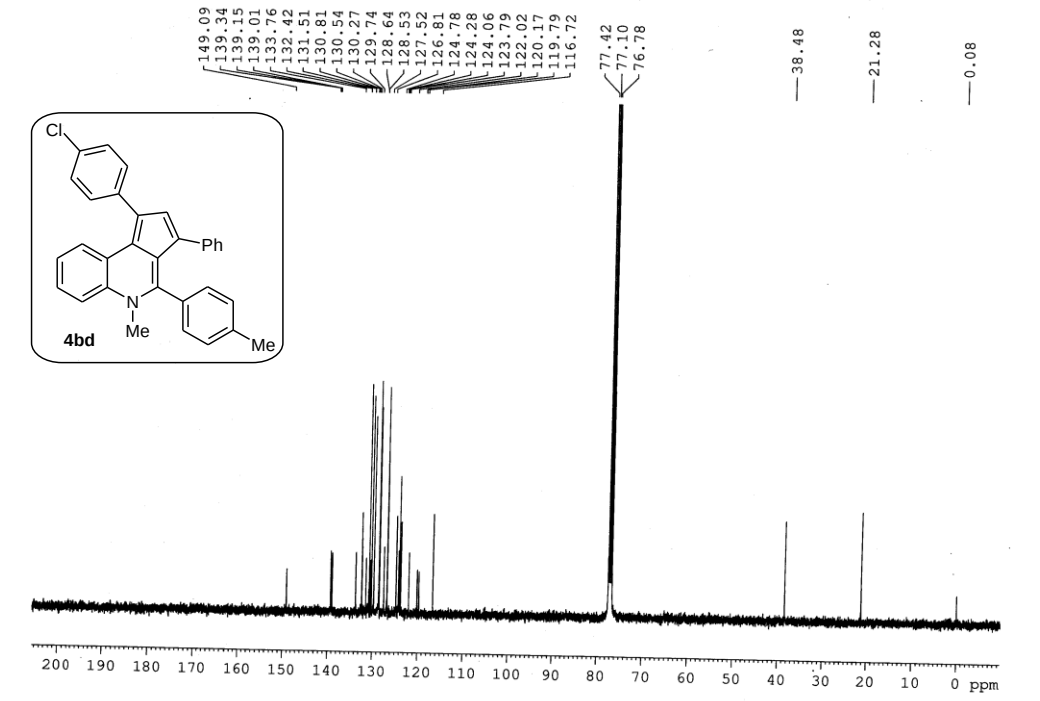


Figure S60.[13]C NMR spectrum of compound **4bd**.

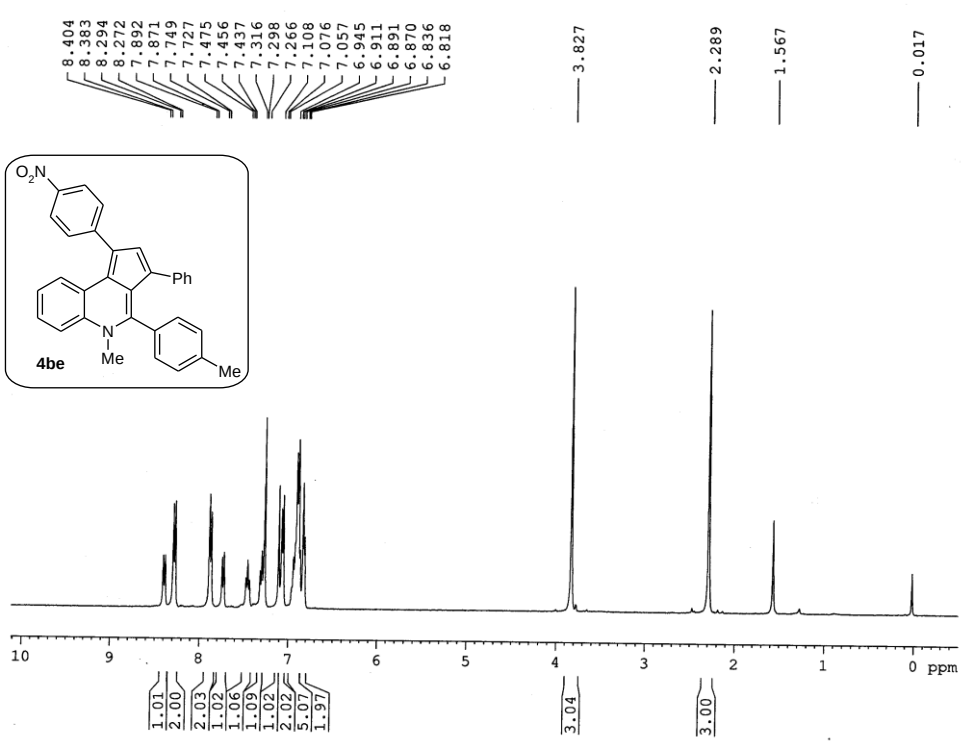


Figure S61. ^{1}H NMR spectrum of compound **4be**

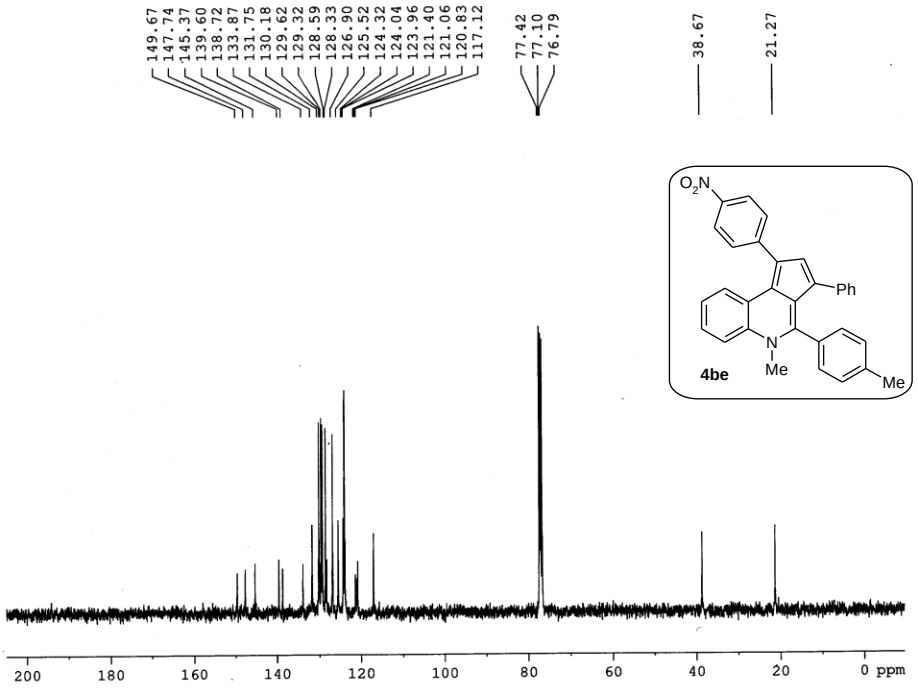


Figure S62. ^{13}C NMR spectrum of compound **4be**

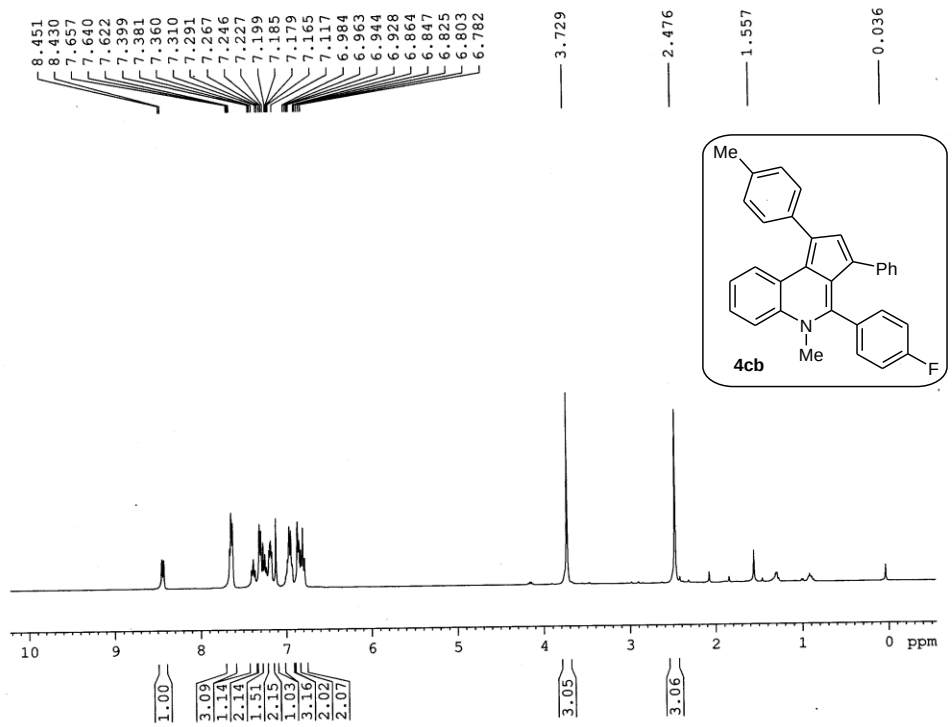


Figure S63. ^{1}H NMR spectrum of compound **4cb**

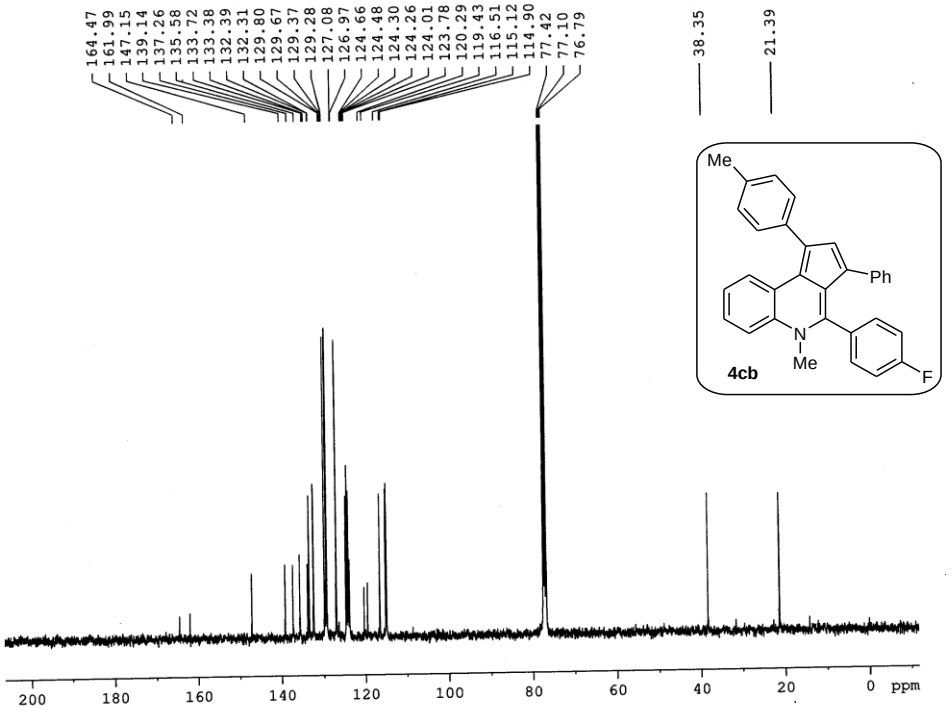


Figure S64. ^{13}C NMR spectrum of compound **4cb**

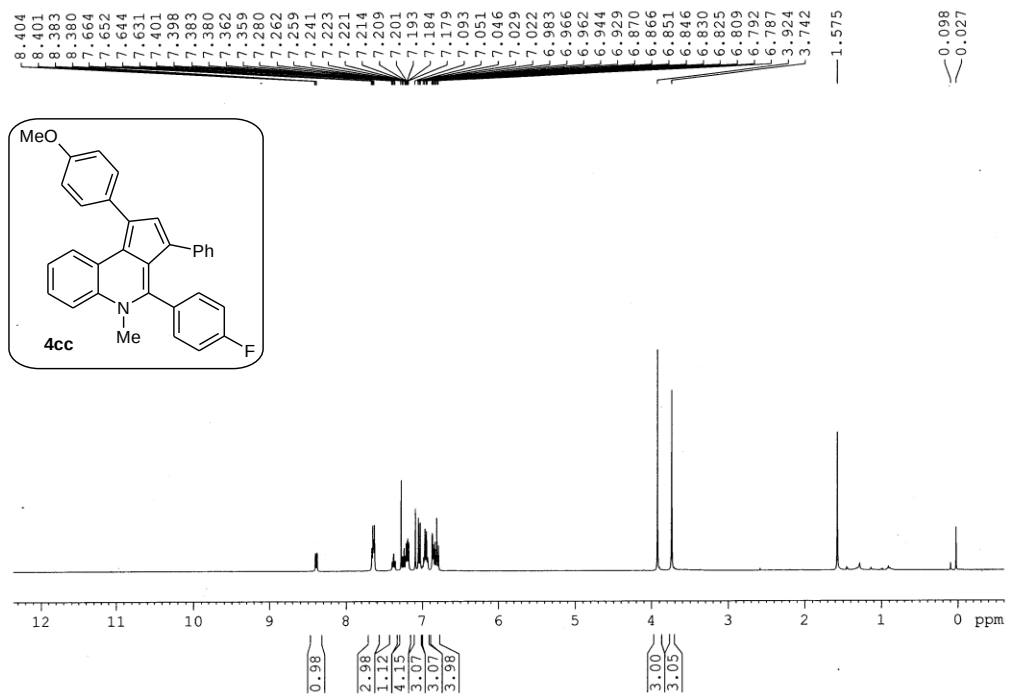


Figure S65. ^{1}H NMR spectrum of compound **4cc**

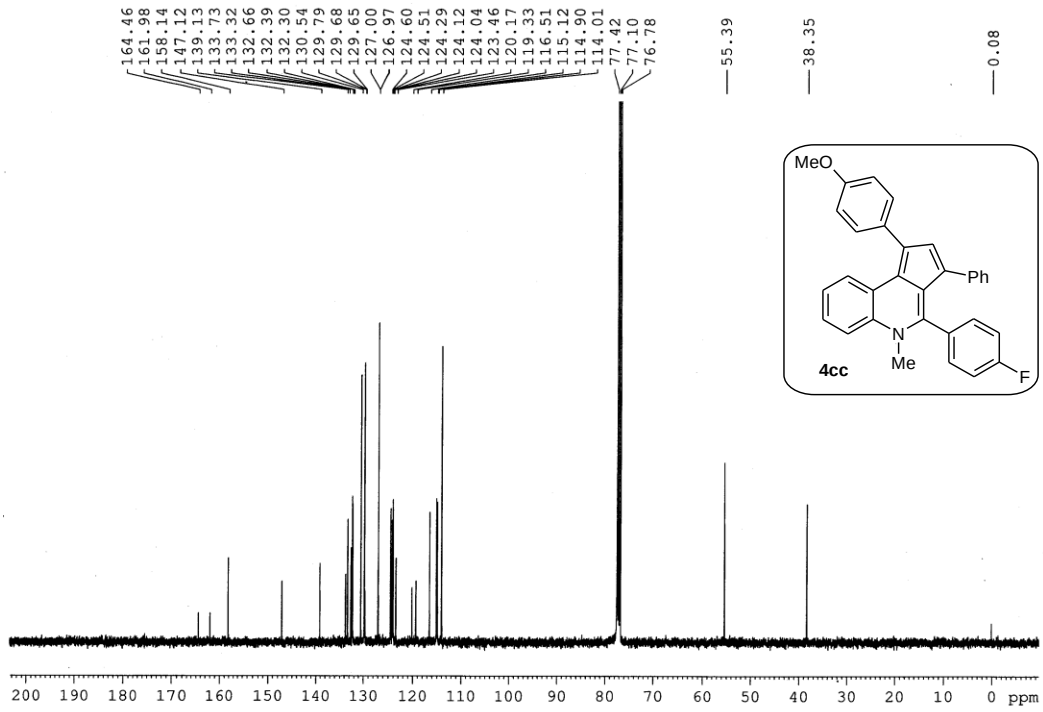


Figure S66. ^{13}C NMR spectrum of compound **4cc**

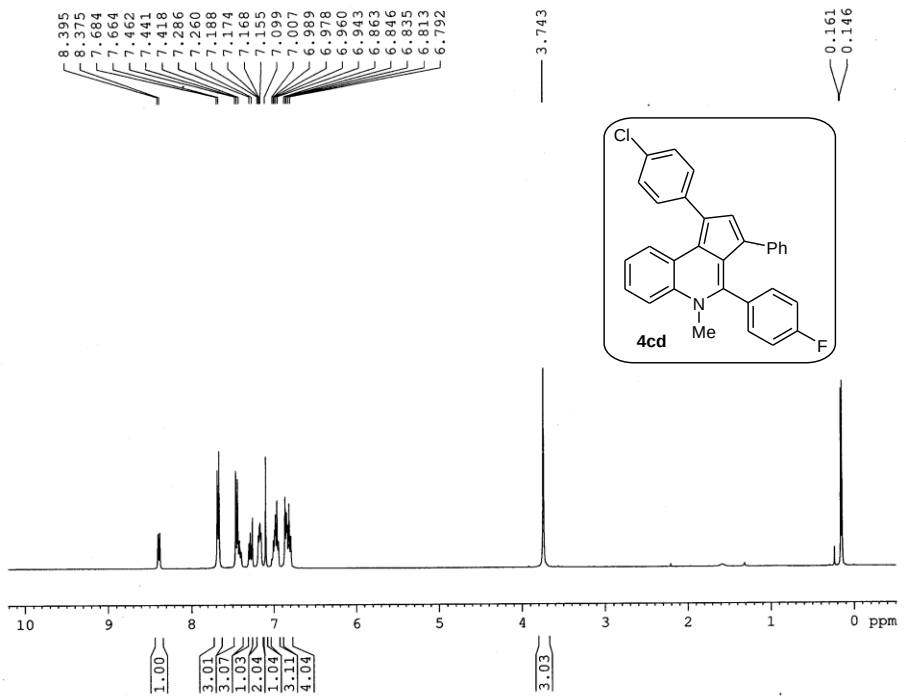


Figure S67. ^{1}H NMR spectrum of compound **4cd**

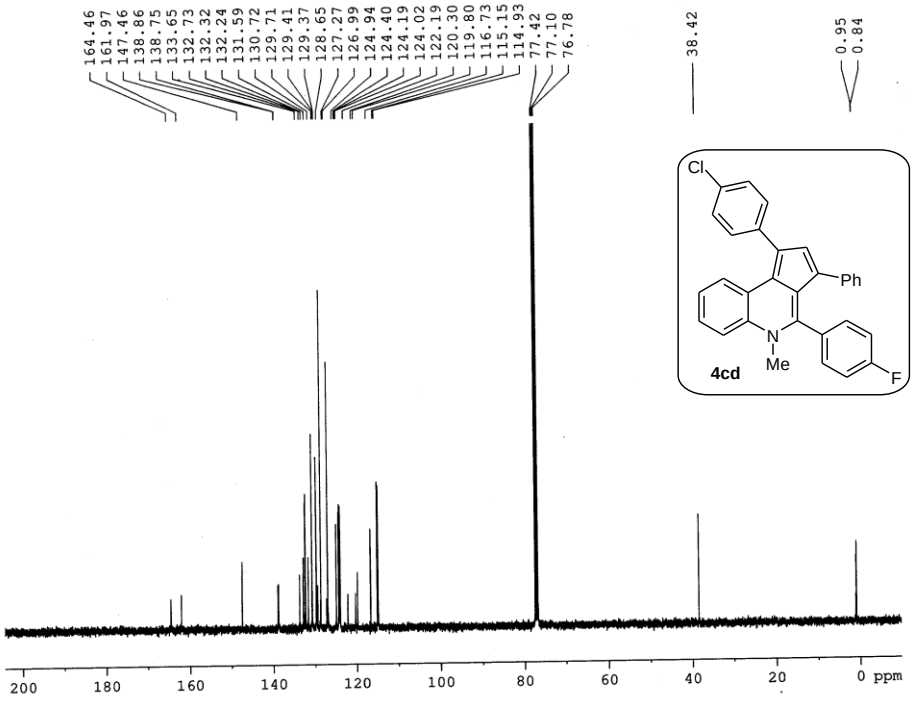


Figure S68. ^{13}C NMR spectrum of compound **4cd**

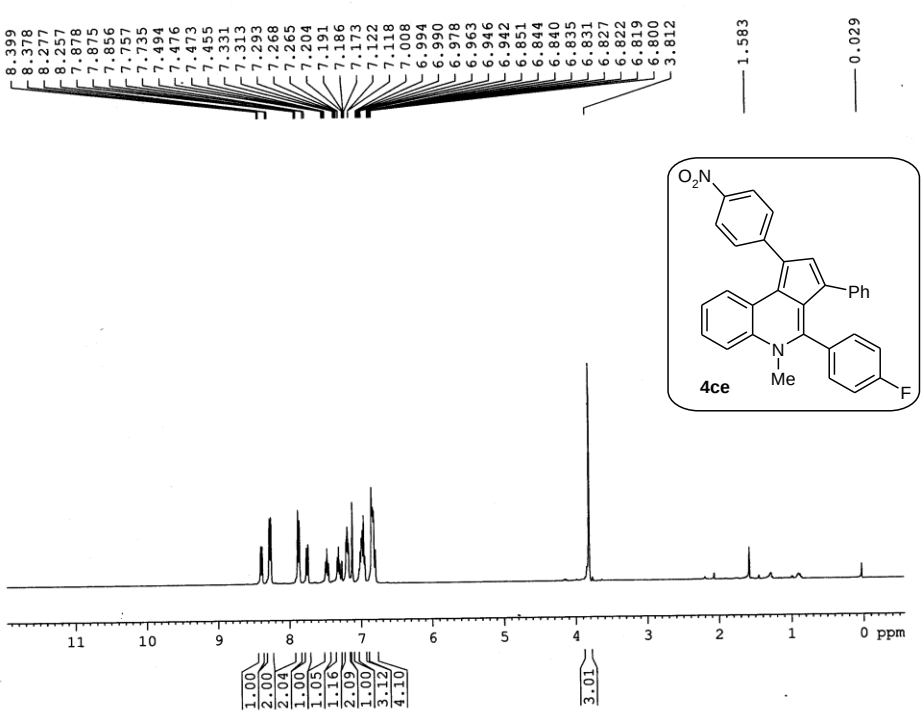


Figure S69.[1]H NMR spectrum of compound **4ce**

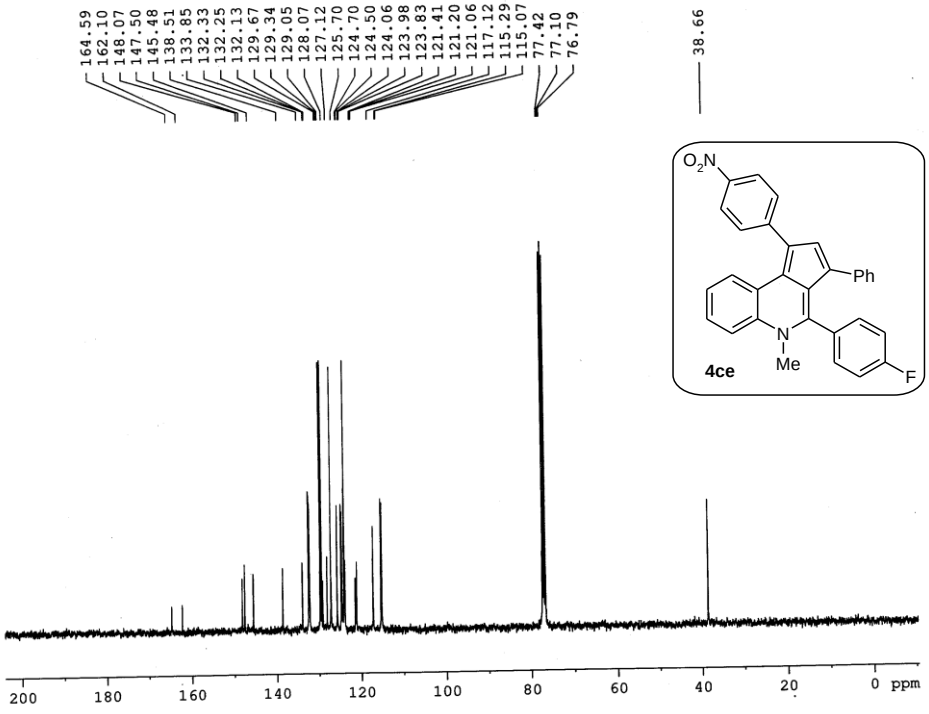


Figure S70.[13]C NMR spectrum of compound **4ce**

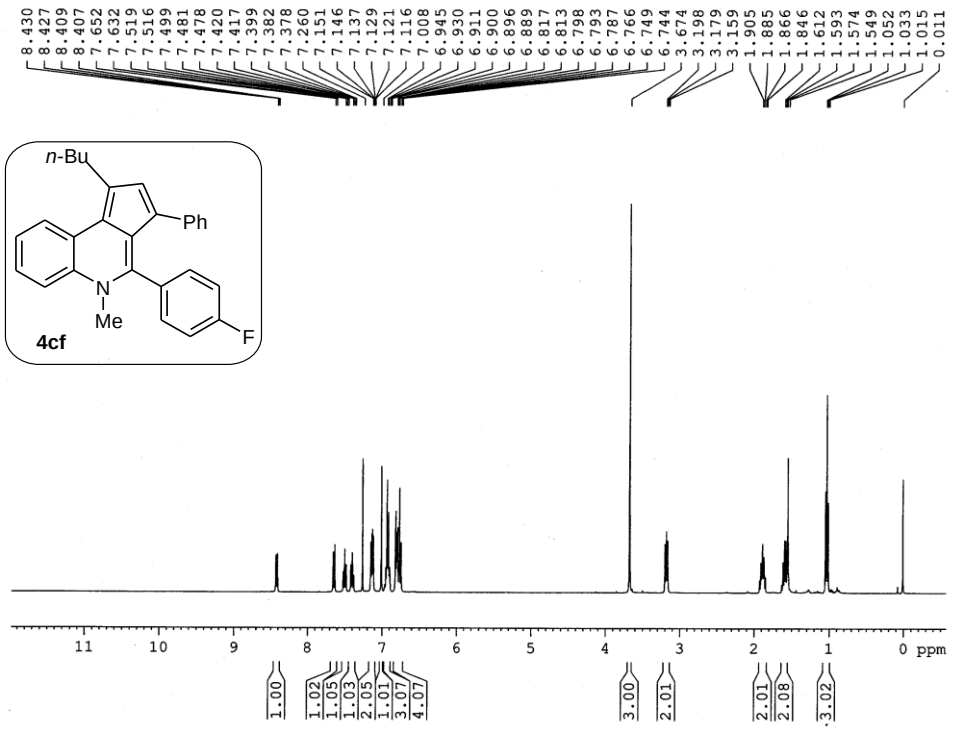


Figure S71. ^{1}H NMR spectrum of compound **4cf**

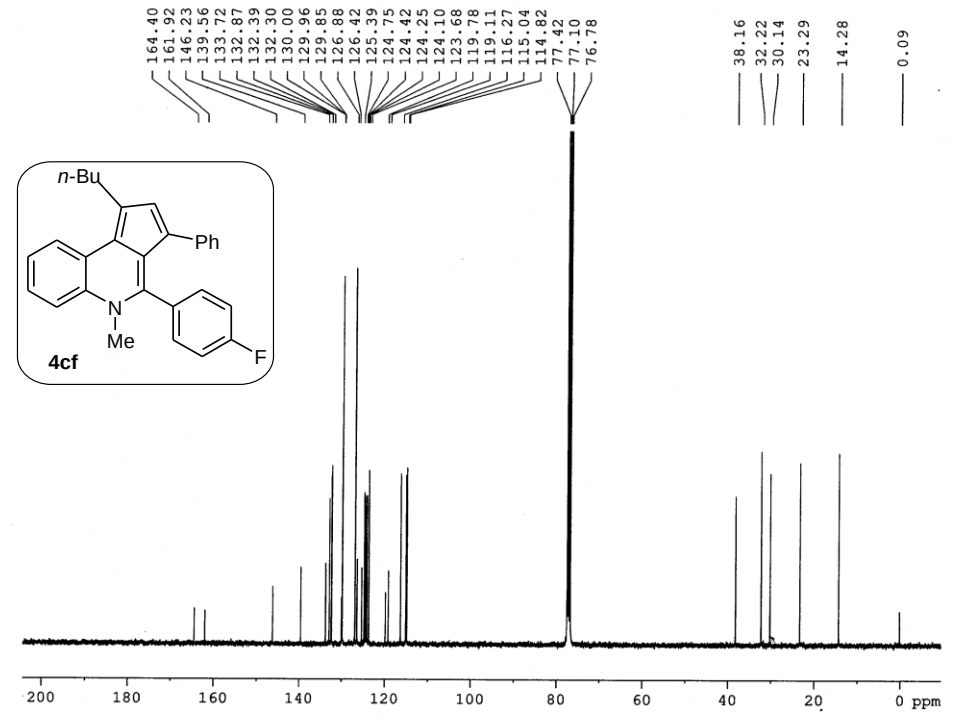


Figure S72. ^{13}C NMR spectrum of compound **4cf**

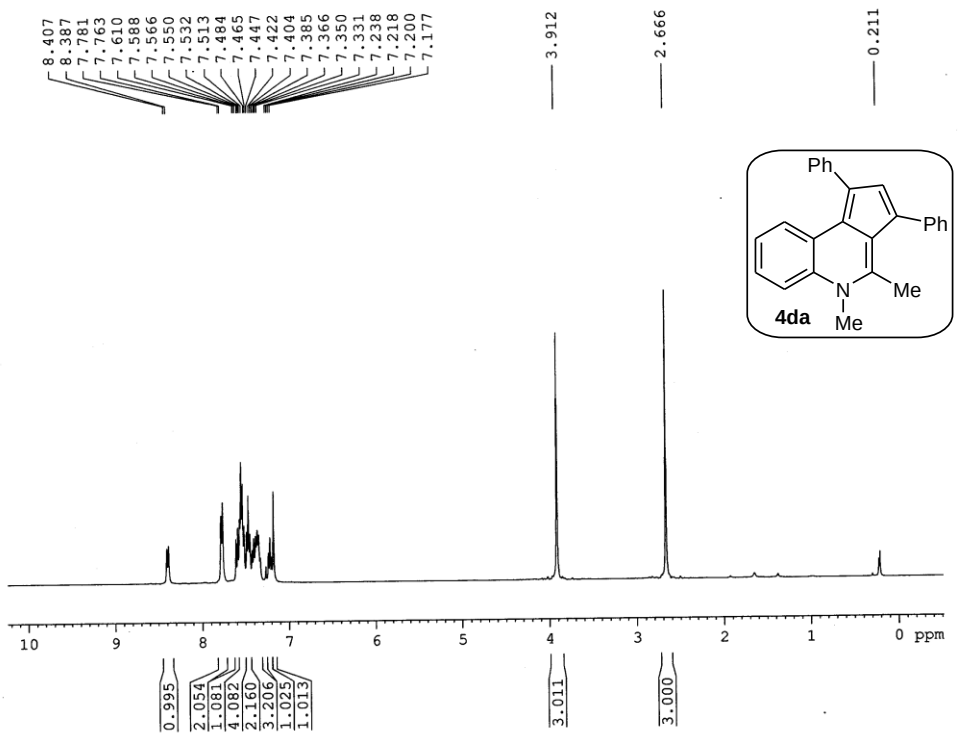


Figure S73. ^{1}H NMR spectrum of compound **4da**

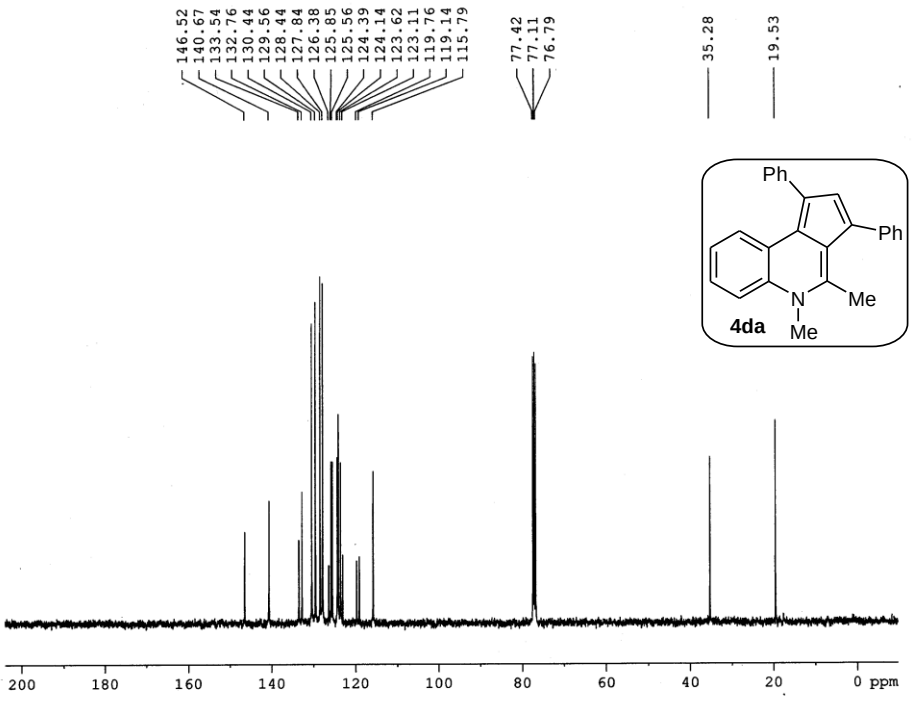


Figure S74. ^{13}C NMR spectrum of compound **4da**

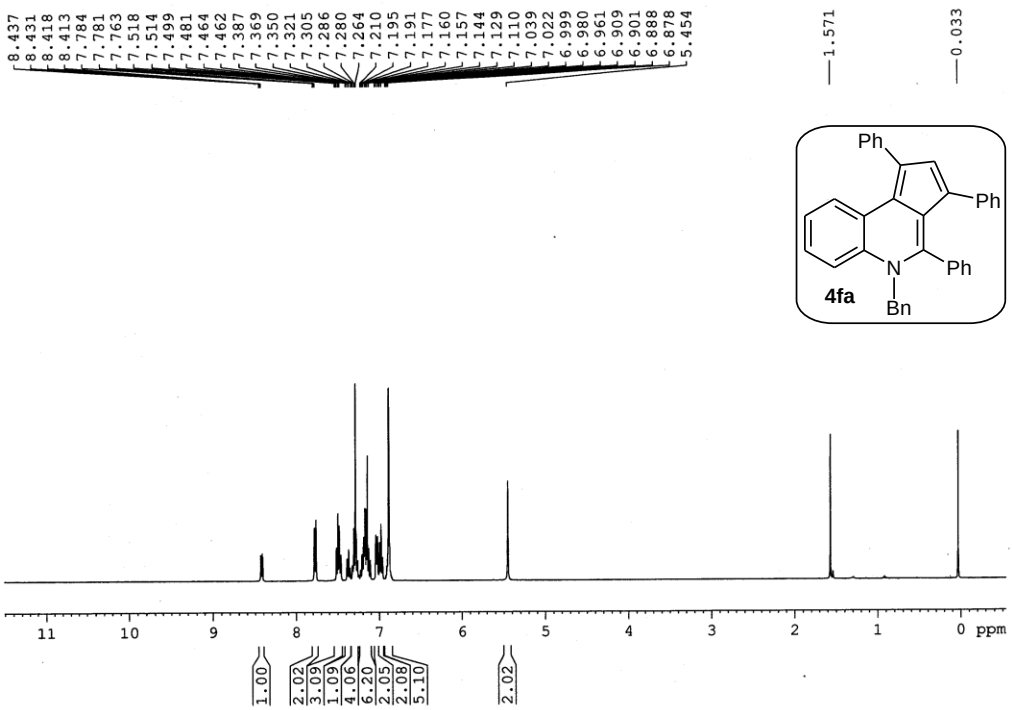


Figure S75. ^{1}H NMR spectrum of compound **4fa**

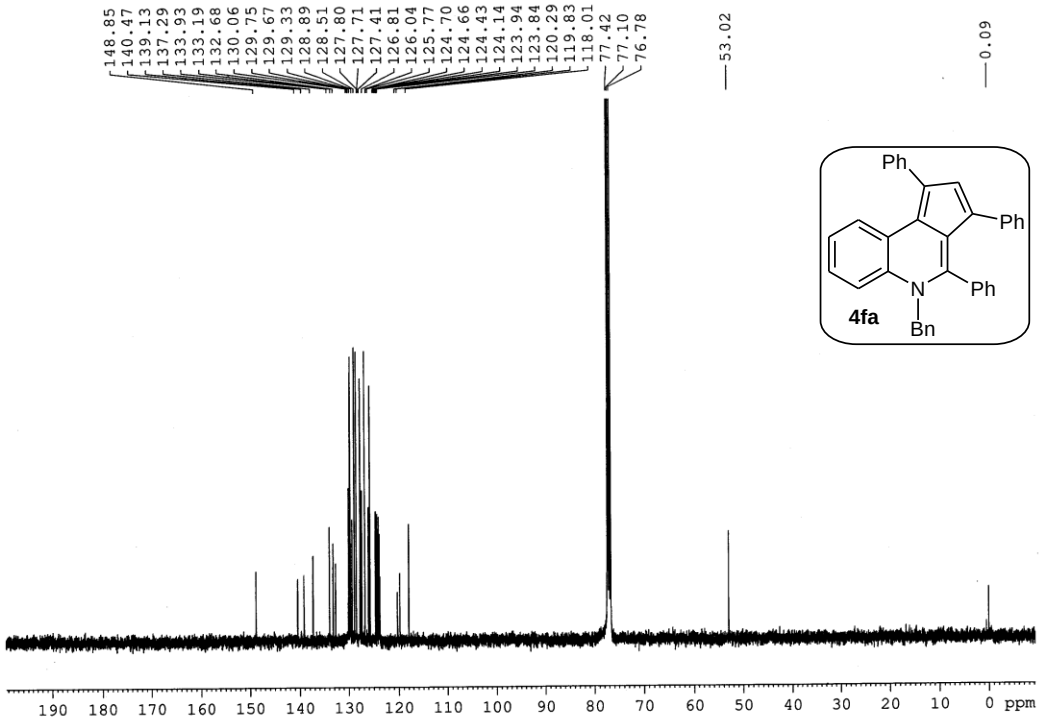


Figure S76. ^{13}C NMR spectrum of compound **4fa**

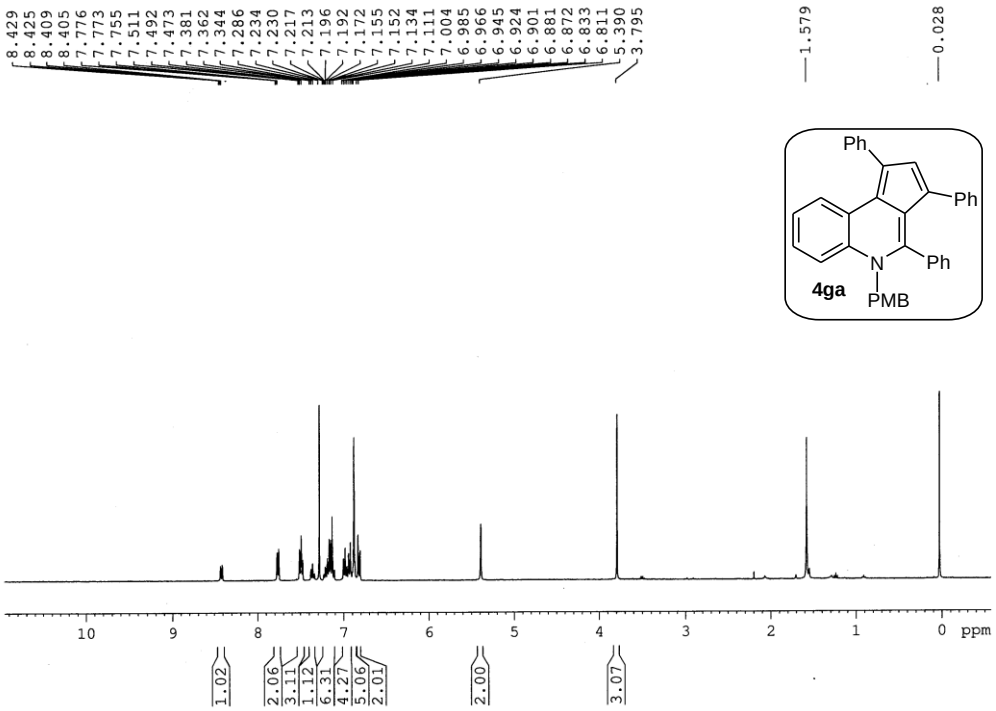


Figure S77. ^{1}H NMR spectrum of compound **4ga**

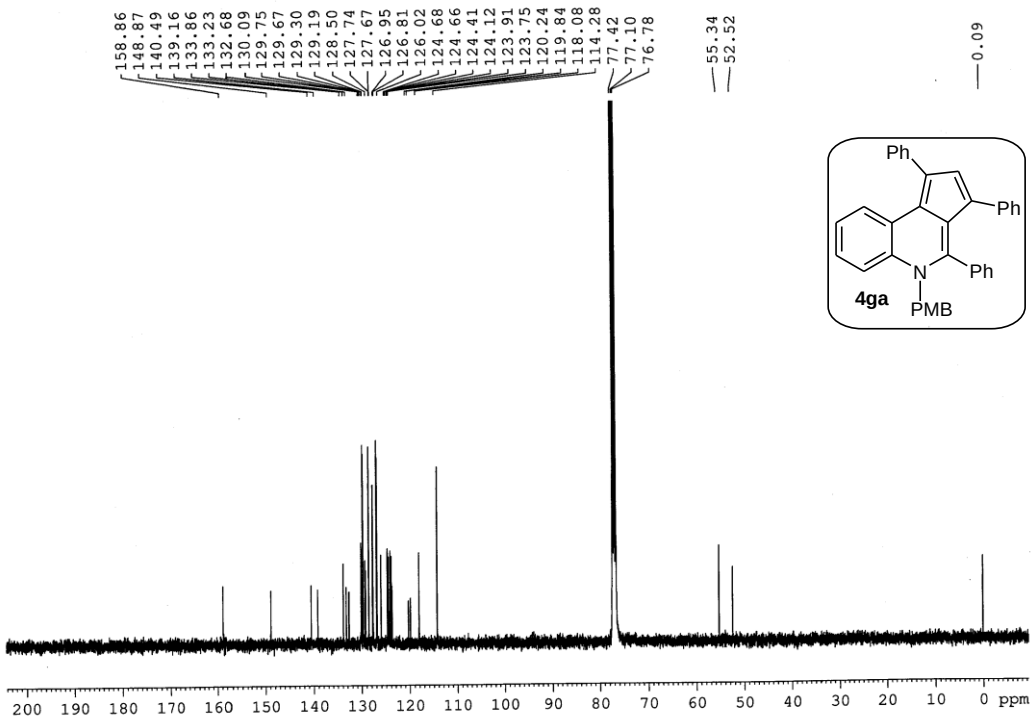


Figure S78. ^{13}C NMR spectrum of compound **4ga**