SUPPORTING INFORMATION

Raising the pK_a Limit of "Soft" Nucleophiles in Palladium-Catalyzed Allylic Substitutions. Application of Diarylmethane Pronucleophiles

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General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. The solvents (DME and THF) were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with neutral alumina. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI America, Strem Chemicals or Matrix Scientific, and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wavelength ultraviolet light as well as by treatment potassium permanganate ($KMnO_4$) stain or iodine. Silica gel (230−400 mesh, Silicycle) was used for flash chromatography. The ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained using a Brüker AM-500 Fourier transform NMR spectrometer at 500 and 126 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC−TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of Diarylmethanes.

Compounds **1e**[1], **1f**[2], **1g**[3], **4f**[4], **8a**[5] were prepared according to literature procedures.

Preparation of Allylic Electrophiles.

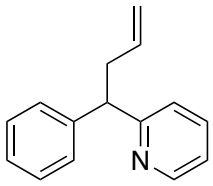
Compounds **2a**[6], **2b**[7], **2c**[8], **2d**[7], **2e**[9], **2f**[10], **2g**[11], **2h**[12], **2i**[12], and **2j**[13] were prepared according to literature procedures.

General Procedure A: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(COD)Cl_2$ (1.43 mg, 0.0050 mmol) and Xantphos (4.34 mg, 0.0075 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, **1a** (16 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by **2a** (34 μL, 0.2 mmol, 2 equiv). Note that the diarylmethanes or allyl OBoc in a solid form was added to the reaction vial prior to $NaN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 24 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was

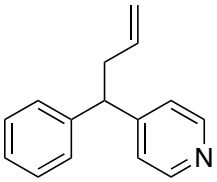
rinsed with additional ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes.

General Procedure B: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (160 mg, 0.80 mmol, 8 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(COD)Cl_2$ (1.43 mg, 0.0050 mmol) and Xantphos (4.34 mg, 0.0075 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, **4g** (18.5 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by **2a** (51 μL, 0.3 mmol, 3 equiv). The reaction mixture was stirred for 12 h at 50 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes.

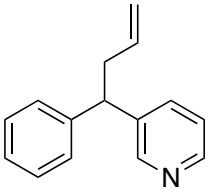
General Procedure C: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $LiN(SiMe_3)_2$ (51 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(COD)Cl_2$ (1.43 mg, 0.0050 mmol) and Xantphos (4.34 mg, 0.0075 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 0 °C, **1b** (16 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by **2g** (46 μL, 0.2 mmol, 2 equiv). The reaction mixture was stirred for 12 h at 0 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes



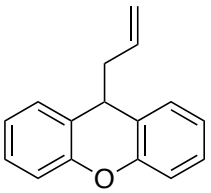
2-(1-phenylbut-3-en-1-yl)pyridine (3aa): The reaction was performed following General Procedure A with **1a** (16 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 10:90) to give the product (21 mg, 99% yield) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (dt, J = 4.8, 0.9 Hz, 1H), 7.54 (td, J = 7.7, 1.8 Hz, 1H), 7.34-7.06 (m, 7H), 5.73 (dd, J = 17.1, 10.2 Hz, 1H), 5.04-4.91 (m, 2H), 4.15 (t, J = 7.8 Hz, 1H), 3.06-2.82 (m, 2H) ppm; ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.5, 149.5, 143.5, 136.9, 136.5, 128.7, 128.3, 126.7, 123.1, 121.5, 116.5, 53.8, 39.4 ppm; IR (thin film): 3063, 3025, 3005, 2975, 2917, 1639, 1589, 1568, 1493, 1471, 1432, 994, 913, 800, 746, 699 cm^{-1}; HRMS calc'd for $C_{15}H_{16}N^+$ 210.1283, observed 210.1287 $[MH]^+$.



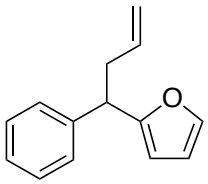
4-(1-phenylbut-3-en-1-yl)pyridine (3ba): The reaction was performed following General Procedure A with **1b** (16 μL, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 30:70) to give the product (21 mg, 99% yield) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 40:60); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (dd, J = 4.5, 1.6 Hz, 2H), 7.30-7.12 (m, 7H), 5.67 (d, J = 6.8 Hz, 1H), 5.04-4.95 (m, 2H), 3.97 (t, J = 7.9 Hz, 1H), 2.79 (ddd, J = 7.9, 6.7, 1.2 Hz, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.2, 149.8, 142.5, 135.7, 128.6, 127.9, 126.7, 123.2, 117.0, 50.5, 39.1 ppm; IR (thin film): 3064, 3026, 2977, 2923, 1640, 1595, 1557, 1494, 1452, 1413, 994, 916, 813, 746, 700 cm^{-1}; HRMS calc'd for $C_{15}H_{16}N^+$ 210.1283, observed 210.1292 $[MH]^+$.



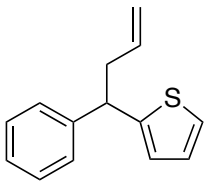
3-(1-phenylbut-3-en-1-yl)pyridine (3ca): The reaction was performed following General Procedure A with **1c** (17 mg, 0.1 mmol), $KN(SiMe_3)_2$ (60 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 30:70) to give the product (19 mg, 91% yield) as a yellow oil. R_f = 0.40 (EtOAc:hexanes = 40:60); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 2.3 Hz, 1H), 8.40 (dd, J = 4.8, 1.6 Hz, 1H), 7.48 (dt, J = 7.9, 2.0 Hz, 1H), 7.48 (dt, J = 7.9, 2.0 Hz, 1H), 7.28-7.15 (m, 6H), 5.67 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H), 5.03-4.93 (m, 2H), 4.00 (t, J = 7.9 Hz, 1H), 2.86-2.74 (m, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.7, 147.7, 143.3, 139.8, 136.0, 135.3, 128.7, 127.9, 126.6, 123.4, 117.0, 48.8, 39.6 ppm; IR (thin film): 3061, 3027, 2977, 2925, 1640, 1601, 1574, 1494, 1478, 1452, 1423, 1025, 994, 916, 813, 750, 714, 700 cm^{-1}; HRMS calc'd for $C_{15}H_{16}N^+$ 210.1283, observed 210.1286 $[MH]^+$.



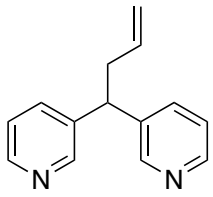
9-allyl-9*H*-xanthene (3da): The reaction was performed following General Procedure A with **1d** (18.2 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (18 mg, 82% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[14]



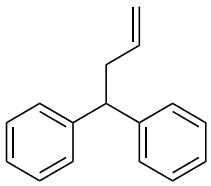
2-(1-phenylbut-3-en-1-yl)furan (3ea): The reaction was performed following General Procedure A with **1e** (15 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (45 mg, 0.25 mmol), 15-Crown-5 (50 μL, 0.25 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (15.8 mg, 80% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[15]



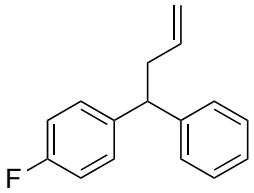
2-(1-phenylbut-3-en-1-yl)thiophene (3fa): The reaction was performed following General Procedure A with **1f** (16 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (20 mg, 93% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[16]



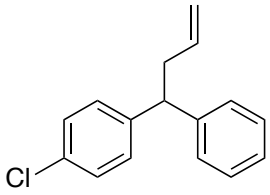
3,3'-(but-3-ene-1,1-diyl)dipyridine (3ga): The reaction was performed following General Procedure A with **1g** (17 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.30 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (18 mg, 85% yield) as a yellow oil. R_f = 0.30 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54-8.44 (m, 4H), 7.49 (dt, J = 7.9, 1.8 Hz, 2H), 7.24-7.20 (m, 2H), 5.69-5.61 (m, 1H), 5.03-4.97 (m, 2H), 4.04 (dd, J = 10.1, 5.7 Hz, 1H), 2.81 (t, J = 7.3 Hz, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.5, 148.1, 138.5, 135.14, 135.02, 123.5, 117.7, 46.2, 39.2.; IR (thin film): 3078, 3032, 3001, 2978, 2852, 1641, 1589, 1575, 1479, 1423, 1178, 1132, 1047, 1025, 994, 917, 803, 775, 715 cm^{-1}; HRMS calc'd for $C_{14}H_{15}N_2^+$ 211.1235, observed 211.1238 $[MH]^+$



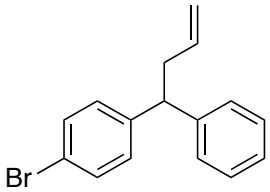
but-3-ene-1,1-diyldibenzene (5aa): The reaction was performed following General Procedure A with 4a (17 µL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and 2a (51 µL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (20 mg, 95% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[17]



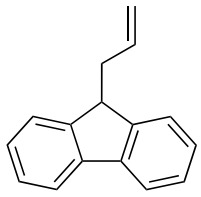
1-fluoro-4-(1-phenylbut-3-en-1-yl)benzene (5ba): The reaction was performed following General Procedure A with **4b** (17 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (19 mg, 84% yield) as a colorless oil. R_f = 0.25 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.16 (m, 9H), 6.97-6.93 (m, 2H), 5.69 (dd, J = 17.1, 10.2 Hz, 1H), 5.03-4.93 (m, 2H), 3.98 (t, J = 7.8 Hz, 1H), 2.80-2.76 (m, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.3 (J = 244 Hz), 144.3, 140.1 (J = 3.4 Hz), 136.5, 129.26 (J = 7.6 Hz), 128.4, 127.8, 126.3, 116.4, 115.09 (J = 21.3 Hz), 50.4, 40.0 ppm; IR (thin film): 3063, 3027, 3003, 2977, 2924, 2850, 1640, 1603, 1508, 1494, 994, 915, 833, 771, 698 cm^{-1}; HRMS calc'd for $C_{16}H_{16}F^+$ 227.1236, observed 227.1232 $[MH]^+$.



1-chloro-4-(1-phenylbut-3-en-1-yl)benzene (5ca): The reaction was performed following General Procedure A with **4c** (18 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (23 mg, 95% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[17]

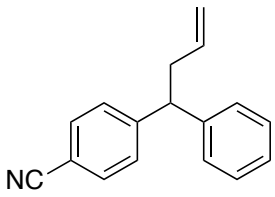


1-bromo-4-(1-phenylbut-3-en-1-yl)benzene (5da): The reaction was performed following General Procedure A with **4d** (18.5 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (21 mg, 73% yield) as a colorless oil. R_f = 0.25 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.10 (m, 9H), 5.71 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H), 5.06-4.96 (m, 2H), 3.99 (t, J = 7.9 Hz, 1H), 2.82-2.78 (m, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.9, 143.5, 136.4, 131.5, 129.8, 128.5, 127.9, 126.4, 120.0, 116.7, 50.7, 39.8 ppm; IR (thin film): 3076, 3062, 3025, 3002, 2976, 2924, 2850, 1640, 1599, 1487, 1451, 1402, 1114, 1073, 1009, 915, 815, 747, 699 cm^{-1}; HRMS calc'd for $C_{13}H_{10}Br^+$ 246.0044, observed 246.0163 $[M\text{-}C_3H_5]^+$.

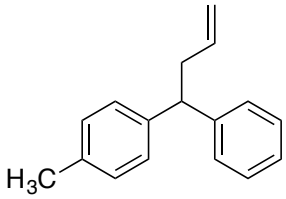


9-allyl-9*H*-fluorene (5ea): The reaction was performed following General Procedure A with **4e** (16.7 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (25 mg, 0.15 mmol) and **2a** (19 μL, 0.11 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give

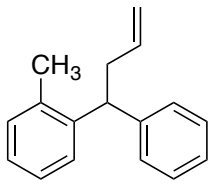
the product (18 mg, 87% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[18]



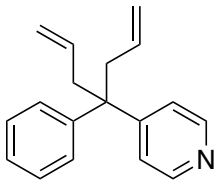
4-(1-phenylbut-3-en-1-yl)benzonitrile (5fa): The reaction was performed following General Procedure A with **4f** (19 mg, 0.1 mmol), $KN(SiMe_3)_2$ (30 mg, 0.15 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (21 mg, 90% yield) as a colorless oil. R_f = 0.25 (EtOAc:hexanes = 5:95); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.58 (m, 2H), 7.37-7.22 (m, 7H), 5.73-5.66 (m, 1H), 5.08-4.99 (m, 2H), 4.09 (t, J = 7.9 Hz, 1H), 2.88-2.80 (m, 2H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.0, 142.9, 135.7, 132.2, 128.75, 128.67, 127.8, 126.7, 118.9, 117.1, 110.0, 51.1, 39.4 ppm; IR (thin film): 3063, 3027, 3003, 2977, 2925, 2227, 1641, 1605, 1502, 1492, 1451, 1414, 1020, 994, 916, 862, 826, 765, 730, 700 cm^{-1}; HRMS calc'd for $C_{17}H_{15}NNa^+$ 256.1102, observed 256.1111 $[M+Na]^+$



1-methyl-4-(1-phenylbut-3-en-1-yl)benzene (5ga):The reaction was performed following General Procedure B with **4g** (18.5 μL, 0.1 mmol), $KN(SiMe_3)_2$ (160 mg, 0.8 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (15 mg, 68% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[17]

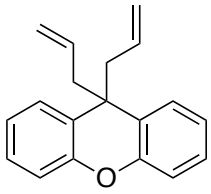


1-methyl-2-(1-phenylbut-3-en-1-yl)benzene (5ha):The reaction was performed following General Procedure B with **4h** (18.5 μL, 0.1 mmol), $KN(SiMe_3)_2$ (200 mg, 1.0 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (15.5 mg, 70% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[19]

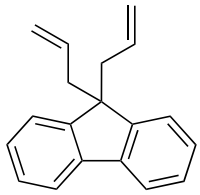


4-(4-phenylhepta-1,6-dien-4-yl)pyridine (6ba): The reaction was performed following General Procedure B with **1b** (16 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2a** (51 μL, 0.3 mmol) at 0.066 M. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 40:60) to give the product (21 mg, 85% yield) as a colorless oil. R_f = 0.25 (EtOAc:hexanes = 40:60); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (dd, J = 4.9, 1.2

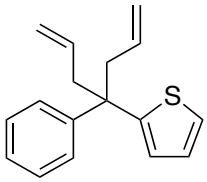
Hz, 2H), 7.28-7.05 (m, 7H), 5.32-5.27 (m, 2H), 5.00-4.95 (m, 4H), 2.83 (dd, J = 6.7, 3.4 Hz, 4H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 156.9, 149.4, 145.9, 133.4, 128.1, 127.7, 126.3, 123.2, 118.6, 48.8, 41.3 ppm; IR (thin film): 3074, 3024, 2978, 2931, 2853, 1638, 1594, 1551, 1494, 1445, 1411, 996, 916, 819, 773, 749, 700, 664 cm^{-1}; HRMS calc'd for $C_{18}H_{20}N^+$ 250.1595, observed 250.1595 $[MH]^+$.



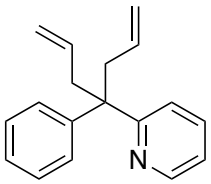
9,9-diallyl-9*H*-xanthene (6da): The reaction was performed following General Procedure A with **1b** (18.2 mg, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (17 mg, 65% yield) as a colorless oil. R_f = 0.25 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-6.98 (m, 9H), 5.39-5.34 (m, 2H), 4.80-4.76 (m, 4H), 2.74 (dd, J = 8.1, 1.0 Hz, 4H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.7, 134.0, 127.5, 126.8, 124.7, 122.9, 117.9, 116.2, 48.0, 42.2 ppm; IR (thin film): 3074, 3005, 2978, 2923, 2852, 1639, 1599, 1572, 1480, 1447, 1326, 1303, 1266, 1232, 1130, 1098, 1042, 994, 916, 886, 749, 700, 665 cm^{-1}; HRMS calc'd for $C_{16}H_{13}^+$ 221.0967, observed 221.0963 $[M-C_3H_5]^+$.



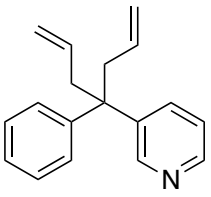
9,9-diallyl-9*H*-fluorene (7ea): The reaction was performed following General Procedure A with **4e** (16.7 mg, 0.1 mmol), $KN(SiMe_3)_2$ (60 mg, 0.3 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (21 mg, 85% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[20]



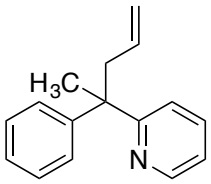
2-(4-phenylhepta-1,6-dien-4-yl)thiophene (6fa): The reaction was performed following General Procedure A with **1f** (16 μL, 0.1 mmol), $KN(SiMe_3)_2$ (160 mg, 0.8 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (18 mg, 70% yield) as a colorless oil. R_f = 0.30 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.24 (m, 4H), 7.20-7.15 (m, 2H), 6.91 (dd, J = 5.1, 3.6 Hz, 1H), 6.84 (dd, J = 3.6, 1.2 Hz, 1H), 5.44 (ddt, J = 17.2, 10.1, 7.0 Hz, 2H), 5.04-4.97 (m, 4H), 2.90-2.87 (m, 4H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.7, 147.0, 134.1, 127.9, 127.3, 126.3, 126.0, 124.3, 123.8, 118.2, 47.6, 43.5 ppm; IR (thin film): 3073, 3007, 2977, 2929, 2853, 1638, 1597, 1494, 1443, 1414, 1234, 997, 915, 849, 826, 771, 743, 695, 665 cm^{-1}; HRMS calc'd for $C_{14}H_{14}S^+$ 214.0816, observed 214.0850 $[M-C_3H_5]^+$.



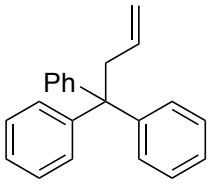
2-(4-phenylhepta-1,6-dien-4-yl)pyridine (6aa): The reaction was performed following General Procedure B with **3aa** (21 μL, 0.1 mmol), $KN(SiMe_3)_2$ (60 mg, 0.3 mmol) and **2a** (34 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (21 mg, 84% yield) as a colorless oil. R_f = 0.30 (EtOAc:hexanes = 5:95); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61-8.53 (m, 1H), 7.52 (ddd, J = 8.0, 7.5, 1.9 Hz, 1H), 7.28-7.02 (m, 8H), 5.36 (ddt, J = 17.2, 10.1, 7.1 Hz, 2H), 4.99-4.91 (m, 4H), 3.04-2.93 (m, 4H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.3, 148.2, 146.7, 135.7, 134.4, 128.0, 127.6, 125.9, 123.1, 120.9, 117.8, 51.4, 41.4 ppm; IR (thin film): 3073, 3005, 2977, 2926, 2854, 1638, 1586, 1566, 1495, 1468, 1444, 1428, 1152, 994, 913, 798, 762, 748, 700, 666 cm^{-1}; HRMS calc'd for $C_{18}H_{19}N^+$ 249.1517, observed 249.1514 $[M]^+$.



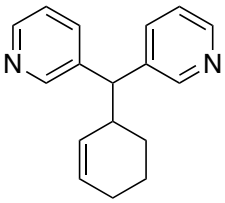
3-(4-phenylhepta-1,6-dien-4-yl)pyridine (6ca): The reaction was performed following General Procedure A with **3ca** (20 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 20:80) to give the product (20 mg, 80% yield) as a colorless oil. R_f = 0.20 (EtOAc:hexanes = 20:80); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45-8.41 (m, 2H), 7.41 (ddt, J = 8.0, 2.5, 1.3 Hz, 1H), 7.28-7.24 (m, 2H), 7.20-7.13 (m, 4H), 5.36-5.29 (m, 2H), 4.99-4.96 (m, 4H), 2.87 (d, J = 7.0 Hz, 4H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.5, 147.2, 146.4, 143.0, 135.5, 133.6, 128.1, 127.8, 126.2, 122.7, 118.5, 47.8, 41.7 ppm; IR (thin film): 3074, 3029, 3007, 2977, 2930, 2853, 1638, 1597, 1572, 1477, 1445, 1414, 1136, 1023, 997, 916, 809, 769, 740, 714, 700, 666 cm^{-1}; HRMS calc'd for $C_{18}H_{20}N^+$ 250.1595, observed 210.1606 $[MH]^+$



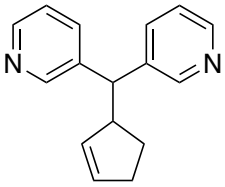
2-(2-phenylpent-4-en-2-yl)pyridine (8aa): The reaction was performed following General Procedure A with **8a** (18 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (20 mg, 90% yield) as a colorless oil. R_f = 0.20 (EtOAc:hexanes = 5:95); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51-8.49 (m, 1H), 7.46-7.42 (m, 1H), 7.21-7.08 (m, 5H), 7.01-6.95 (m, 2H), 5.44-5.37 (m, 1H), 4.97-4.85 (m, 2H), 3.04-2.85 (m, 2H), 1.60 (s, 3H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.6, 148.3, 147.9, 135.9, 135.2, 128.0, 127.1, 125.9, 122.4, 120.8, 117.5, 48.4, 45.4, 26.1 ppm; IR (thin film): 3061, 3028, 2974, 2924, 1638, 1586, 1567, 1494, 1469, 1444, 1427, 1374, 1152, 1091, 1028, 993, 913, 788, 759, 747, 700, 665 cm^{-1}; HRMS calc'd for $C_{16}H_{18}N^+$ 224.1439, observed 224.1436 $[MH]^+$.



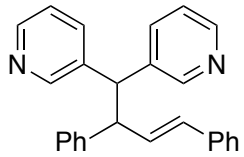
but-3-ene-1,1,1-triyltribenzene (9aa): The reaction was performed following General Procedure A with **9a** (24.4 mg, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2a** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (25.5 mg, 90% yield) as white solid. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data. [21]



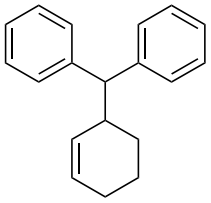
3,3'-(cyclohex-2-en-1-ylmethylene)dipyridine (10a): The reaction was performed following General Procedure A with **1g** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and **2b** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (22 mg, 89% yield) as a yellow oil. R_f = 0.25 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (dd, J = 14.6, 2.2, 2H), 8.49 (ddd, J = 6.5, 4.8, 1.6, 2H), 7.68-7.59 (m, 2H), 7.31-7.24 (m, 2H), 5.78-5.75 (m, 1H), 5.44-5.41 (m, 1H), 3.72 (d, J = 11.1 Hz, 1H), 3.06-3.02 (m, 1H), 2.05-2.02 (m, 2H), 1.79-1.74 (m, 1H), 1.68-1.54 (m, 2H), 1.33-1.23 (m, 1H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.0, 148.04, 138.0, 135.0, 129.4, 128.2, 123.6, 52.8, 38.4, 28.0, 25.2, 21.1 ppm; IR (thin film): 3082, 3024, 2927, 2857, 2836, 1719, 1587, 1574, 1478, 1174, 1138, 1045, 1024, 902, 860, 792, 721, 680, 665 cm^{-1}; HRMS calc'd for $C_{17}H_{19}N_2^+$ 251.1548, observed 251.1548 $[MH]^+$.



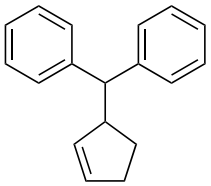
3,3'-(cyclopent-2-en-1-ylmethylene)dipyridine (10b): The reaction was performed following General Procedure A with **1g** (17 mg, 0.1 mmol), $KN(SiMe_3)_2$ (60 mg, 0.3 mmol) and **2d** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (21.2 mg, 90% yield) as a yellow oil. R_f = 0.25 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (dd, J = 10.8, 2.3 Hz, 2H), 8.41 (s, 2H), 7.55 (ddt, J = 12.5, 8.0, 2.1 Hz, 2H), 7.26-7.18 (m, 2H), 5.78 (dq, J = 5.9, 2.1 Hz, 1H), 5.42 (dq, J = 5.8, 2.0 Hz, 1H), 3.68 (d, J = 10.8 Hz, 1H), 3.56 (dtd, J = 8.4, 4.2, 2.2 Hz, 1H), 2.32-2.27 (m, 2H), 1.98 (dtd, J = 13.3, 8.1, 5.3 Hz, 1H), 1.44 (ddt, J = 13.2, 8.7, 6.5 Hz, 1H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.8, 148.1, 138.9, 135.4, 132.8, 132.3, 123.6, 52.9, 49.7, 32.0, 29.1 ppm; IR (thin film): 3051, 2928, 2849, 1574, 1478, 1421, 1177, 1105, 1025, 918, 862, 797, 718, 665 cm^{-1}; HRMS calc'd for $C_{16}H_{17}N_2^+$ 237.1391, observed 237.1391 $[MH]^+$.



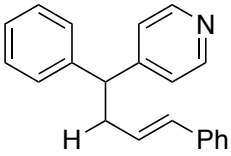
(*E*)-3,3'-(2,4-diphenylbut-3-ene-1,1-diyl)dipyridine (10c): The reaction was performed following General Procedure A with **1g** (17 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.3 mmol) and **2e** (62 mg, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (31.5 mg, 87% yield *trans*:*cis*= 10:1) as a yellow oil. R_f = 0.20 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J = 2.2 Hz, 1H), 8.44 (d, J = 1.3 Hz, 1H), 8.39 (d, J = 2.2 Hz, 1H), 8.29 (dd, J = 4.8, 1.4 Hz, 1H), 7.69 (dt, J = 8.0, 1.9 Hz, 1H), 7.46 (dt, J = 8.0, 1.9 Hz, 1H), 7.26-7.04 (m, 12H), 6.29-6.22 (m, 2H), 4.45 (d, J = 11.5 Hz, 1H), 4.29 (dd, J = 11.5, 6.2 Hz, 1H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.2, 148.3, 147.8, 141.5, 137.5, 136.9, 135.9, 132.3, 131.2, 128.8, 128.2, 127.5, 126.8, 126.2, 123.6, 53.6, 52.6 ppm; IR (thin film): 3081, 3026, 2926, 1575, 1479, 1423, 1372, 1175, 1129, 1105, 1076, 1025, 966, 912, 789, 761, 664 cm^{-1}; HRMS calc'd for $C_{26}H_{23}N_2^+$ 363.1861, observed 363.1861 $[MH]^+$.



(cyclohex-2-en-1-ylmethylene)dibenzene (10d): The reaction was performed following General Procedure A with **4a** (17 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2b** (60 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (21 mg, 85% yield) as white solid. R_f = 0.20 (hexanes), $KMnO_4$ stained; The NMR spectral data match the previously published data.[22]

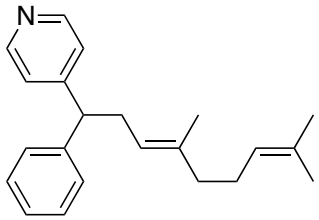


(cyclopent-2-en-1-ylmethylene)dibenzene (10e): The reaction was performed following General Procedure B with **4a** (17 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2d** (60 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (22 mg, 94% yield) as white solid. R_f = 0.20 (hexanes), $KMnO_4$ stained; The NMR spectral data match the previously published data.[13]

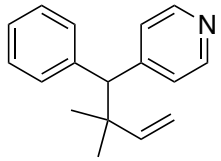


(*E*)-4-(1,4-diphenylbut-3-en-1-yl)pyridine (10f): The reaction was performed following General Procedure C with **1b** (16 μL, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.3 mmol) and **2g** (46 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 40:60) to give the product (26 mg, 91% yield linear:branched= 2.6:1) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 40:60); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 4.8 Hz, 2H), 7.34-7.08 (m, 12H), 6.39 (dd, J = 15.8, 0.9 Hz, 1H), 6.05 (dtd, J = 15.7, 7.1, 1.1 Hz, 1H), 4.06-4.03 (m, 1H), 2.98-2.90 (m, 2H)

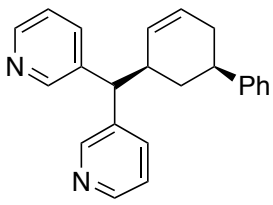
ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.2, 149.7, 142.5, 137.2, 132.2, 128.68, 128.55, 128.43, 128.29, 128.16, 127.9, 127.4, 126.8, 126.0, 123.3, 50.9, 38.4 ppm; IR (thin film): 3059, 3025, 2922, 2851, 1945, 1878, 1805, 1594, 1557, 1493, 1451, 1413, 1279, 1072, 1029, 993, 967, 916, 810, 749, 699, 640 cm^{-1}; HRMS calc'd for $C_{21}H_{20}N^+$ 286.1595, observed 286.1591 $[MH]^+$



(*E*)-4-(4,8-dimethyl-1-phenylnona-3,7-dien-1-yl)pyridine (10g): The reaction was performed following General Procedure C with **1b** (16 μL, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.3 mmol) and **2h** (56 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 40:60) to give the product (27 mg, 88% yield linear:branched= 1.9:1) as a yellow oil. R_f = 0.25 (EtOAc:hexanes = 40:60); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49-8.46 (m, 2H), 7.39-7.14 (m, 7H), 5.03-4.97 (m, 2H), 3.92 (t, J = 7.8 Hz, 1H), 2.75-2.72 (m, 2H), 1.95 (td, J = 17.4, 10.3 Hz, 4H), 1.65 (d, J = 7.5 Hz, 3H), 1.55 (d, J = 9.8 Hz, 6H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.8, 149.7, 143.2, 137.2, 131.4, 130.1, 128.6, 126.7, 125.2, 124.1, 123.5, 62.6, 51.0, 39.7, 33.6, 26.5, 25.7, 16.2 ppm; IR (thin film): 3058, 2917, 1593, 1493, 1451, 1413, 1028, 993, 699, 665 cm^{-1}; HRMS calc'd for $C_{22}H_{28}N^+$ 306.2221, observed 306.2220 $[MH]^+$.



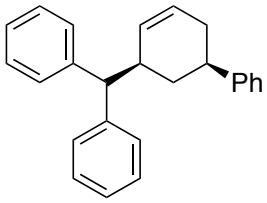
4-(2,2-dimethyl-1-phenylbut-3-en-1-yl)pyridine (10h'): The reaction was performed following General Procedure C with **1b** (16 μL, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.3 mmol) and **2i** (41 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 30:70) to give the product (22 mg, 93% yield linear:branched= 1:4.5) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 30:70); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 5.8 Hz, 2H), 7.33-7.18 (m, 7H), 5.99 (dd, J = 17.5, 10.8 Hz, 1H), 5.11-4.98 (m, 2H), 3.74 (s, 1H), 1.06 (s, 6H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.3, 149.3, 144.8, 140.6, 129.8, 128.0, 126.7, 125.0, 113.0, 63.0, 40.2, 27.34, 27.26 ppm; IR (thin film): 3059, 3026, 2964, 2925, 2868, 1636, 1593, 1556, 1494, 1453, 1415, 1379, 1363, 1221, 1166, 1072, 1012, 994, 916, 822, 746, 701, 640 cm^{-1}; HRMS calc'd for $C_{17}H_{19}N^+$ 237.1517, observed 237.1525 $[M]^+$.



3,3'-(((1*R*,3*R*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)methylene)dipyridine (11a): The reaction was performed following General Procedure A with **1g** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and **2j** (54 μL, 0.2 mmol). The crude material was

purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (29.4 mg, 90% yield) as a white solid (m.p. = 104-105 °C). R_f = 0.20 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (d, J = 2.1Hz, 1H), 8.56 (d, J = 2.1Hz, 1H), 8.49 (dd, J = 4.8, 1.6 Hz, 1H), 8.41 (dd, J = 4.8, 1.6 Hz, 1H), 7.67 (dt, J = 7.9, 2.0 Hz, 1H), 7.56 (dt, J = 8.0, 2.0 Hz, 1H), 7.28-7.25 (m, 3H), 7.19-7.13 (m, 3H), 5.83 (dq, J = 7.6, 2.6 Hz, 1H), 5.49 (ddd, J = 10.2, 2.5, 1.3 Hz, 1H), 3.70 (d, J = 11.0 Hz, 1H), 3.29-3.23 (m, 1H), 2.90-2.84 (m, 1H), 2.34-2.28 (m, 1H), 2.18-2.11 (m, 1H), 1.80-1.76 (m, 1H), 1.42 (td, J = 12.6, 10.9 Hz, 1H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.1, 149.6, 148.2, 146.3, 138.0, 135.5, 135.1, 129.1, 128.5, 128.1, 126.8, 126.3, 123.7, 53.2, 40.57, 40.45, 36.2, 34.0 ppm; IR (thin film): 3026, 2906, 2852, 2836, 1733, 1649, 1574, 1492, 1452, 1243, 1175, 1142, 1045, 1024, 909, 849, 794, 721, 701, 666 cm^{-1}; HRMS calc'd for $C_{23}H_{23}N_2^+$ 327.1861, observed 327.1867 $[MH]^+$.

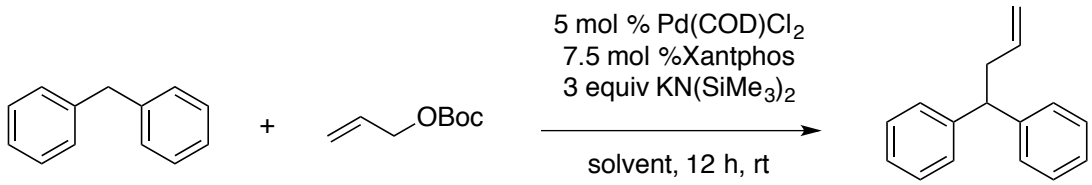
Stereochemistry was assigned by ^{1}H NMR analysis.[13]



(1*R*,3*R*)-3-benzhydryl-1,2,3,6-tetrahydro-1,1'-biphenyl (11b): The reaction was performed following General Procedure A with **4a** (17 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and **2j** (81 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (28.5 mg, 88% yield) as a white solid (m.p = 124-125 °C). R_f = 0.25 (EtOAc:hexanes = 2:98); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.06 (m, 17H), 5.74-5.71 (m, 1H), 5.52-5.50 (m, 1H), 3.58 (d, J = 11.3, 1H), 3.24-3.18 (m, 1H), 2.86-2.79 (m, 1H), 2.27-2.22 (m, 1H), 2.13-2.05 (m, 1H), 1.80-1.76 (m, 1H), 1.40-1.33 (m, 1H) ppm;^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 147.0, 143.83, 143.72, 129.8, 128.59, 128.53, 128.38, 128.35, 127.89, 127.73, 126.9, 126.23, 126.17, 126.06, 58.4, 40.8, 36.2, 34.3 ppm; IR (thin film): 3083, 3060, 3024, 2905, 1648, 1596, 1492, 1450, 1072, 1028, 960, 906, 758, 745, 726, 698 cm^{-1}; HRMS calc'd for $C_{13}H_{11}^+$ 167.0860, observed 167.0863 [M-$C_{12}H_{13}$]$^+$

Stereochemistry was assigned by X-Ray structure determination and by ^{1}H NMR analysis.[13]

Screening Results of Ethereal Solvents[a]



4a + **2a** → **5aa**

entry	(**4a**:base:**2a**)	solvent	yield (%)[b]
1	1:3:2	THF	10%
2	1:3:2	CPME	9%
3	1:3:2	Dioxane	trace
4	1:3:2	2-Me THF	7%
5	1:3:2	DME	55%

[a] Reaction conducted on a 0.1 mmol scale with 1 equiv of **4a** and 2 equiv of **2a** at 0.1M . [b] Yield determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

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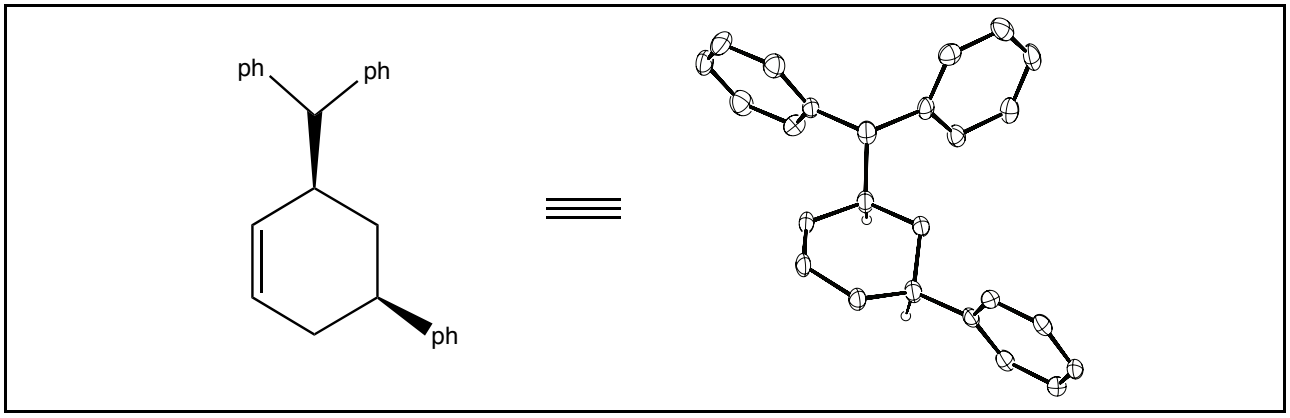
X-ray Structure Determination



Compound **11b**, $C_{25}H_{24}$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=18.8031(14)Å, b=5.8211(5)Å, c=17.3207(13)Å, b=103.022(4)°, V=1847.1(3)Å^3, Z=4, and d_{calc}=1.167 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l=0.71073 Å) at a temperature of 143(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2591 frames were collected with a crystal to detector distance of 37.6 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2q	w	f	c	frames
f	-15.50	258.48	8.28	19.46	739
w	-18.00	243.20	310.97	36.30	208
f	-23.00	315.83	12.48	28.88	346
f	-13.00	335.42	31.84	64.29	739
f	19.50	59.55	348.71	-26.26	559

Rotation frames were integrated using SAINT[1], producing a listing of unaveraged F^2 and $s(F^2)$ values which were then passed to the SHELXTL[2] program package for further processing and structure solution. A total of 38765 reflections were measured over the ranges 2.22 £ q £ 25.42°, -22 £ h £ 22, -7 £ k £ 7, -14 £ l £ 20 yielding 3315 unique reflections (Rint = 0.0633). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[3] (minimum and maximum transmission 0.6194, 0.7452).

The structure was solved by direct methods (SHELXS-97[4]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[5] All reflections were used during refinement. The weighting scheme used was $w=1/[s^2(F_o^2)+ (0.0781P)^2 + 1.2783P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0597 and wR2=0.1474 for 2336 observed reflections for which F > 4s(F) and R1=0.0922 and wR2=0.1680 and GOF =1.029 for all 3315

unique, non-zero reflections and 226 variables.[6] The maximum D/s in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.647 and -0.268 e/Å^3.

Table S1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S2. and S3. Anisotropic thermal parameters are in Table S4. Tables S5. and S6. list bond distances and bond angles. Figure S1. is an ORTEP[7] representation of the molecule with 30% probability thermal ellipsoids displayed.

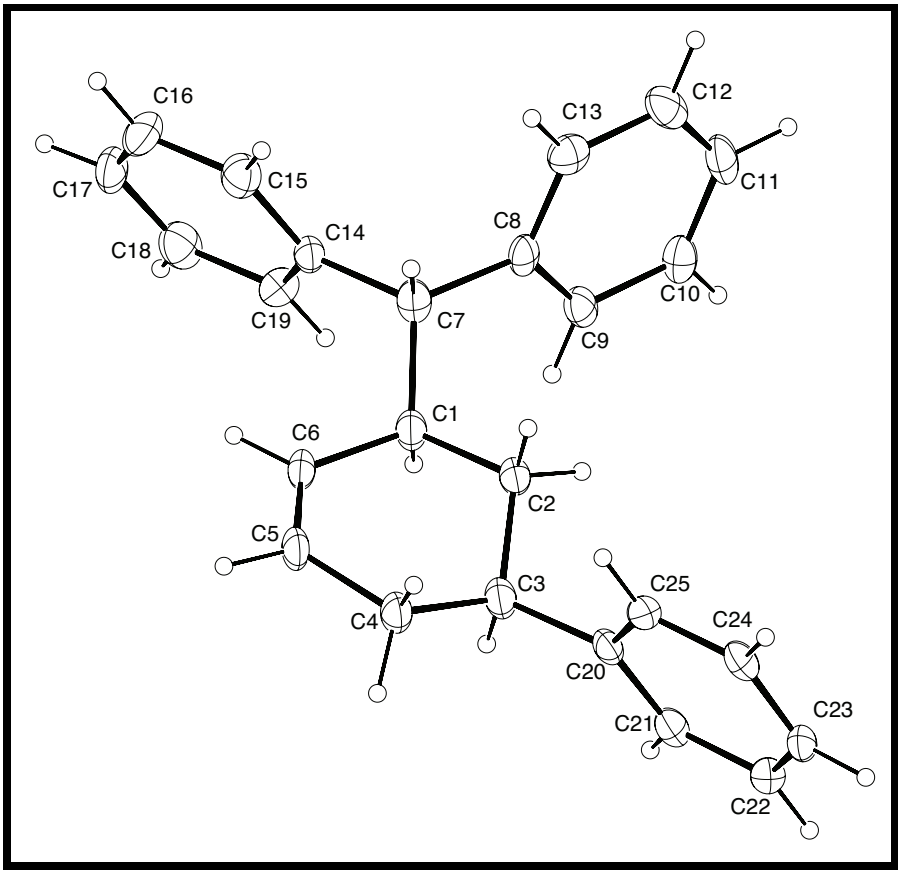


Figure S1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound 11b

Empirical formula	$C_{25}H_{24}$
Formula weight	324.44
Temperature	143(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants:	
a	18.8031(14) Å
b	5.8211(5) Å
c	17.3207(13) Å
b	103.022(4)°
Volume	1847.1(3) $Å^3$
Z	4
Density (calculated)	1.167 Mg/m^3
Absorption coefficient	0.066 mm^{-1}
F(000)	696
Crystal size	0.38 x 0.08 x 0.02 mm^3
Theta range for data collection	2.22 to 25.42°
Index ranges	-22 £ h £ 22, -7 £ k £ 7, -14 £ l £ 20
Reflections collected	38765
Independent reflections	3315 [R(int) = 0.0633]
Completeness to theta = 25.42°	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6194
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3315 / 0 / 226
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1474
R indices (all data)	R1 = 0.0922, wR2 = 0.1680
Largest diff. peak and hole	0.647 and -0.268 $e.Å^{-3}$

Table S2. Refined Positional Parameters for Compound 11b

Atom	x	y	z	U_{eq}, Å^2
C1	0.25836(12)	0.5999(5)	0.37321(14)	0.0373(6)
C2	0.32754(12)	0.6628(4)	0.34482(13)	0.0323(5)
C3	0.39163(13)	0.7204(5)	0.41133(15)	0.0392(6)
C4	0.37472(13)	0.9183(5)	0.46128(15)	0.0394(6)
C5	0.30031(13)	0.8965(5)	0.47782(15)	0.0419(7)
C6	0.24952(13)	0.7568(4)	0.43987(14)	0.0364(6)
C7	0.19031(13)	0.5970(4)	0.30647(15)	0.0378(6)
C8	0.19607(12)	0.4448(4)	0.23636(14)	0.0331(6)
C9	0.22874(13)	0.2295(4)	0.24320(14)	0.0354(6)
C10	0.23135(13)	0.1019(4)	0.17631(16)	0.0392(6)
C11	0.20071(14)	0.1864(5)	0.10251(16)	0.0450(7)
C12	0.16823(14)	0.3986(5)	0.09499(16)	0.0463(7)
C13	0.16575(13)	0.5275(4)	0.16086(16)	0.0398(6)
C14	0.12092(12)	0.5408(4)	0.33504(14)	0.0324(6)
C15	0.06520(14)	0.7006(5)	0.32197(16)	0.0449(7)
C16	0.00226(15)	0.6631(6)	0.34928(19)	0.0568(8)
C17	-0.00550(14)	0.4669(6)	0.38946(17)	0.0525(8)
C18	0.04834(15)	0.3032(5)	0.40079(17)	0.0497(7)
C19	0.11123(13)	0.3392(5)	0.37348(16)	0.0413(6)
C20	0.46183(12)	0.7607(4)	0.38311(13)	0.0326(6)
C21	0.51697(13)	0.6006(4)	0.39917(13)	0.0344(6)
C22	0.58197(13)	0.6338(4)	0.37662(14)	0.0368(6)
C23	0.59312(12)	0.8305(4)	0.33675(14)	0.0348(6)
C24	0.53837(13)	0.9925(4)	0.31791(13)	0.0358(6)
C25	0.47286(13)	0.9589(4)	0.34133(14)	0.0358(6)

$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos g+2U_{13}aa^*cc^*\cos b+2U_{23}bb^*cc^*\cos a]$

Table S3. Positional Parameters for Hydrogens in Compound 11b

Atom	x	y	z	U_{iso}, Å^2
H1	0.2652	0.4438	0.3948	0.045
H2a	0.3407	0.5349	0.3149	0.039
H2b	0.3170	0.7935	0.3094	0.039
H3	0.4002	0.5856	0.4461	0.047
H4a	0.4109	0.9223	0.5110	0.047
H4b	0.3778	1.0618	0.4338	0.047
H5	0.2893	0.9879	0.5176	0.050
H6	0.2051	0.7542	0.4550	0.044
H7	0.1841	0.7543	0.2859	0.045
H9	0.2491	0.1703	0.2932	0.042
H10	0.2539	-0.0412	0.1816	0.047
H11	0.2019	0.1001	0.0576	0.054
H12	0.1477	0.4560	0.0448	0.056
H13	0.1436	0.6713	0.1548	0.048
H15	0.0699	0.8350	0.2945	0.054
H16	-0.0348	0.7723	0.3401	0.068
H17	-0.0471	0.4441	0.4091	0.063
H18	0.0426	0.1673	0.4269	0.060
H19	0.1472	0.2266	0.3811	0.050
H21	0.5102	0.4666	0.4259	0.041
H22	0.6184	0.5230	0.3884	0.044
H23	0.6374	0.8541	0.3226	0.042
H24	0.5451	1.1236	0.2897	0.043
H25	0.4362	1.0689	0.3291	0.043

Table S4. Refined Thermal Parameters (U's) for Compound 11b

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0308(13)	0.0504(15)	0.0339(14)	-0.0132(11)	0.0139(10)	-0.0064(11)
C2	0.0319(12)	0.0391(13)	0.0278(13)	-0.0056(10)	0.0107(10)	-0.0005(10)
C3	0.0346(13)	0.0546(16)	0.0317(14)	-0.0105(11)	0.0143(11)	-0.0058(12)
C4	0.0321(13)	0.0528(16)	0.0357(14)	-0.0171(12)	0.0128(10)	-0.0058(11)
C5	0.0348(13)	0.0594(17)	0.0358(15)	-0.0215(12)	0.0168(11)	-0.0019(12)
C6	0.0294(12)	0.0522(15)	0.0317(14)	-0.0090(11)	0.0156(10)	0.0002(11)
C7	0.0393(14)	0.0399(14)	0.0377(15)	-0.0058(11)	0.0163(11)	-0.0040(11)
C8	0.0271(12)	0.0393(13)	0.0373(14)	-0.0090(11)	0.0168(10)	-0.0114(10)
C9	0.0353(13)	0.0433(14)	0.0307(14)	-0.0011(11)	0.0142(10)	-0.0074(11)
C10	0.0408(14)	0.0358(14)	0.0468(17)	-0.0084(12)	0.0220(12)	-0.0072(11)
C11	0.0466(15)	0.0586(18)	0.0369(16)	-0.0155(13)	0.0241(12)	-0.0196(14)
C12	0.0449(15)	0.0647(19)	0.0308(15)	0.0031(13)	0.0116(11)	-0.0188(14)
C13	0.0325(13)	0.0413(14)	0.0462(16)	0.0038(12)	0.0103(11)	-0.0060(11)
C14	0.0283(12)	0.0413(14)	0.0291(13)	-0.0093(10)	0.0096(10)	-0.0014(10)
C15	0.0487(15)	0.0437(15)	0.0438(16)	-0.0022(12)	0.0137(12)	0.0059(12)
C16	0.0355(15)	0.074(2)	0.061(2)	-0.0176(17)	0.0107(13)	0.0166(15)
C17	0.0318(14)	0.085(2)	0.0463(17)	-0.0207(16)	0.0206(12)	-0.0116(14)
C18	0.0496(16)	0.0591(18)	0.0433(17)	0.0001(13)	0.0165(13)	-0.0145(14)
C19	0.0330(13)	0.0474(15)	0.0431(16)	-0.0003(12)	0.0078(11)	0.0051(12)
C20	0.0306(12)	0.0468(14)	0.0215(12)	-0.0102(10)	0.0081(9)	-0.0086(11)
C21	0.0405(13)	0.0392(13)	0.0248(13)	-0.0018(10)	0.0101(10)	-0.0039(11)
C22	0.0342(13)	0.0457(15)	0.0303(14)	-0.0016(11)	0.0072(10)	0.0075(11)
C23	0.0271(12)	0.0536(15)	0.0262(13)	-0.0058(11)	0.0112(10)	-0.0033(11)
C24	0.0446(14)	0.0418(14)	0.0228(13)	0.0014(10)	0.0111(10)	-0.0026(11)
C25	0.0313(12)	0.0464(15)	0.0283(13)	-0.0071(11)	0.0036(10)	0.0085(11)

The form of the anisotropic displacement parameter is:
$\exp[-2p^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table S5. Bond Distances in Compound 11b, Å

C1-C6	1.510(3)	C1-C7	1.519(3)	C1-C2	1.535(3)
C2-C3	1.505(3)	C3-C4	1.517(3)	C3-C20	1.525(3)
C4-C5	1.495(3)	C5-C6	1.312(3)	C7-C8	1.527(3)
C7-C14	1.531(3)	C8-C9	1.389(3)	C8-C13	1.390(4)
C9-C10	1.386(3)	C10-C11	1.370(4)	C11-C12	1.372(4)
C12-C13	1.375(4)	C14-C15	1.381(3)	C14-C19	1.382(4)
C15-C16	1.387(4)	C16-C17	1.362(4)	C17-C18	1.372(4)
C18-C19	1.385(4)	C20-C21	1.375(3)	C20-C25	1.402(4)
C21-C22	1.378(3)	C22-C23	1.378(3)	C23-C24	1.380(3)
C24-C25	1.395(3)				

Table S6. Bond Angles in Compound 11b, °

C6-C1-C7	111.7(2)	C6-C1-C2	110.34(19)	C7-C1-C2	112.8(2)
C3-C2-C1	113.46(19)	C2-C3-C4	111.8(2)	C2-C3-C20	112.98(19)
C4-C3-C20	112.0(2)	C5-C4-C3	111.7(2)	C6-C5-C4	124.3(2)
C5-C6-C1	124.4(2)	C1-C7-C8	114.4(2)	C1-C7-C14	112.9(2)
C8-C7-C14	110.59(19)	C9-C8-C13	118.2(2)	C9-C8-C7	124.4(2)
C13-C8-C7	117.4(2)	C10-C9-C8	120.7(2)	C11-C10-C9	120.1(2)
C10-C11-C12	119.8(2)	C11-C12-C13	120.7(3)	C12-C13-C8	120.5(2)
C15-C14-C19	118.3(2)	C15-C14-C7	118.3(2)	C19-C14-C7	123.5(2)
C14-C15-C16	120.8(3)	C17-C16-C15	120.3(3)	C16-C17-C18	119.7(2)
C17-C18-C19	120.4(3)	C14-C19-C18	120.6(2)	C21-C20-C25	118.0(2)
C21-C20-C3	119.9(2)	C25-C20-C3	122.1(2)	C20-C21-C22	121.6(2)
C23-C22-C21	120.2(2)	C22-C23-C24	119.8(2)	C23-C24-C25	119.7(2)
C24-C25-C20	120.6(2)				

[1]Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[2]Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[3]Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[4]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

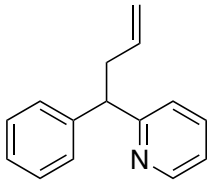
[5]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

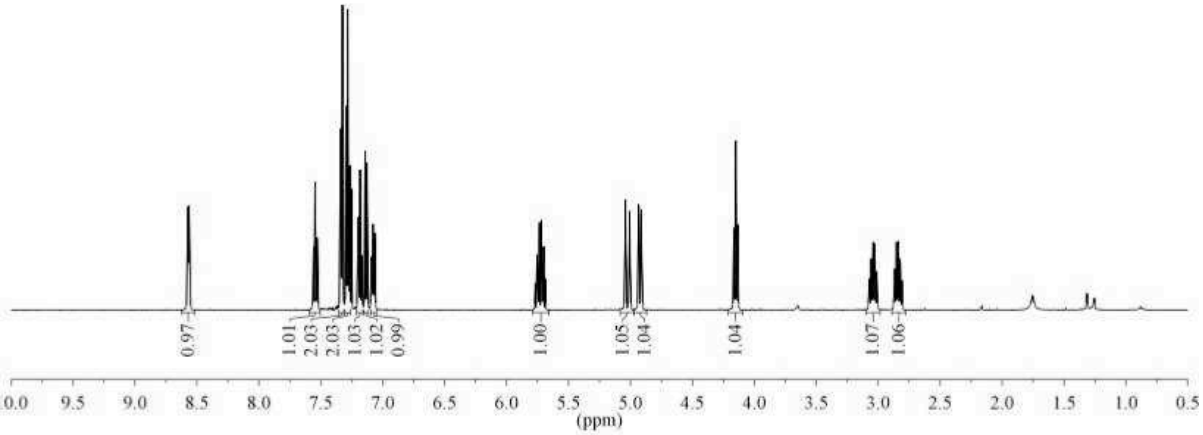
[6]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined.

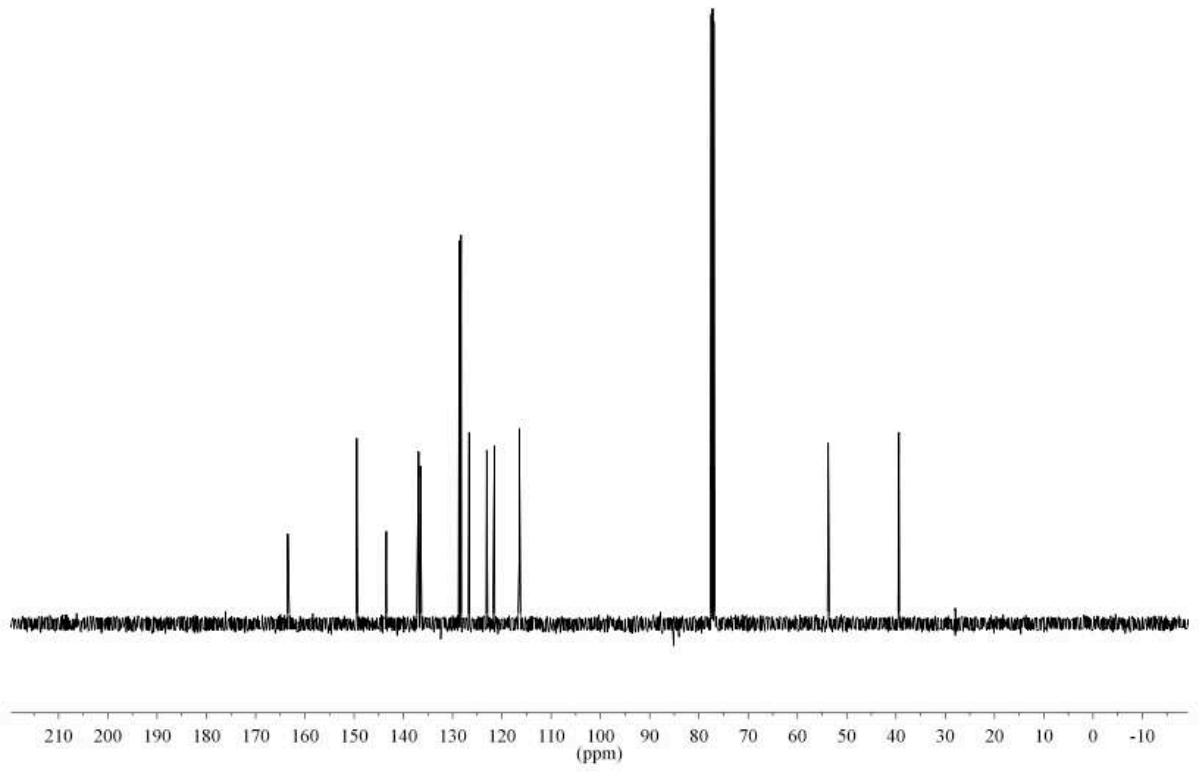
[7]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.

NMR Spectra

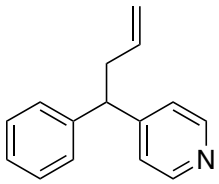
2-(1-phenylbut-3-en-1-yl)pyridine (3aa)

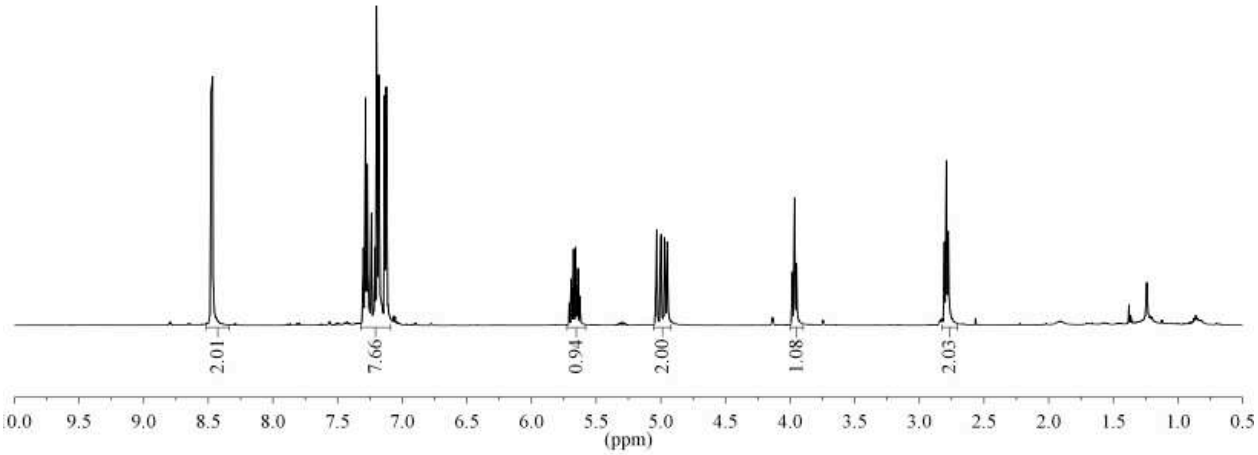


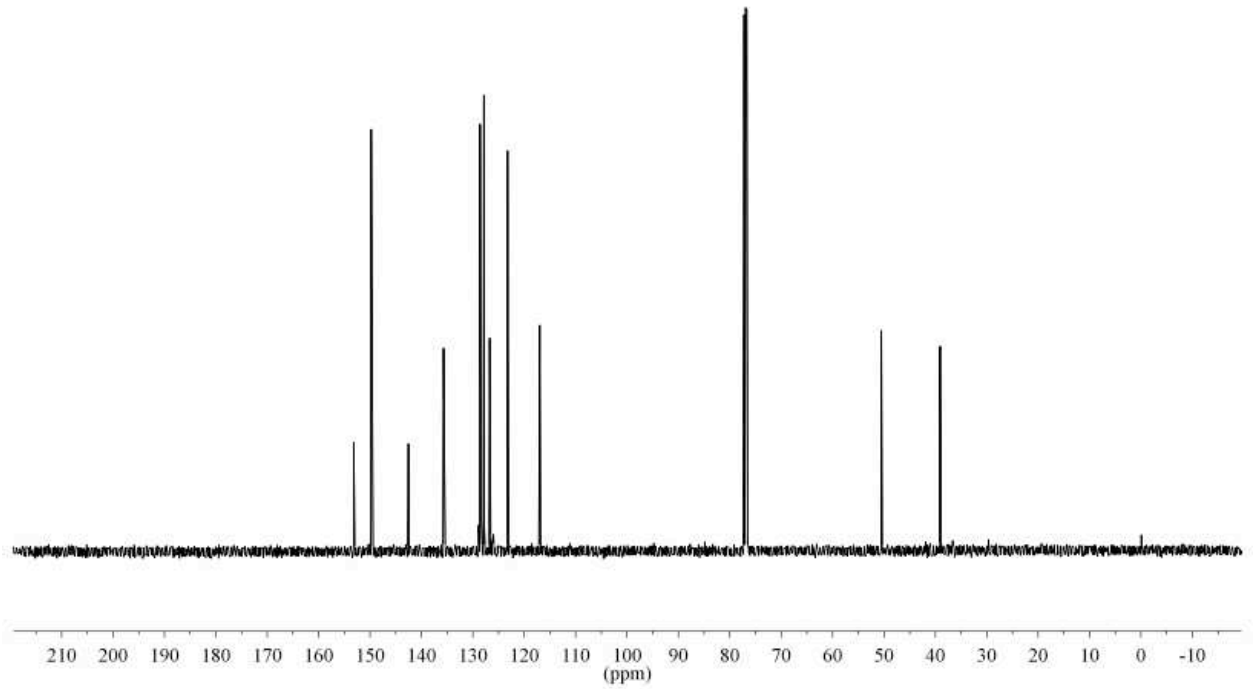




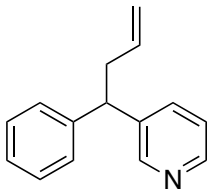
4-(1-phenylbut-3-en-1-yl)pyridine (3ba)

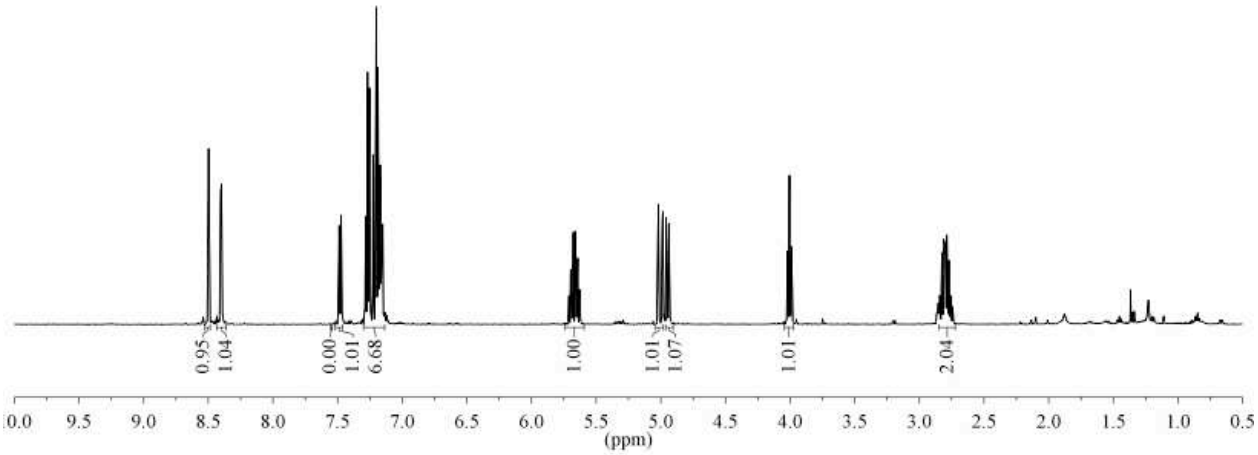


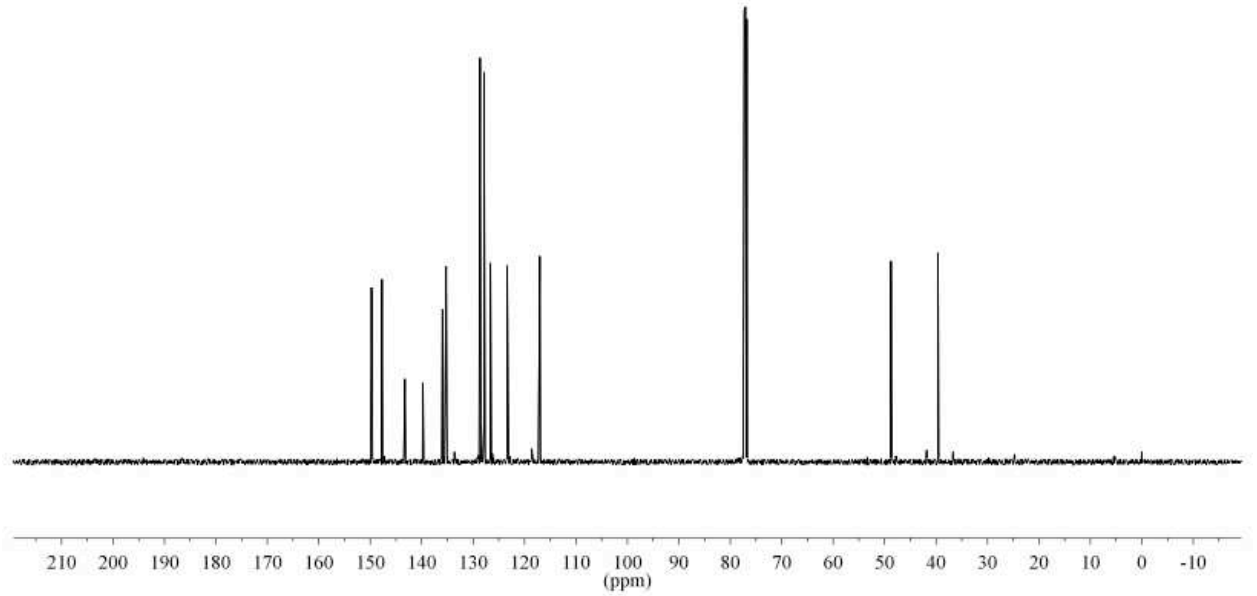




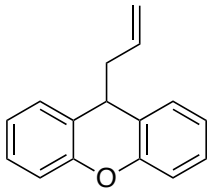
3-(1-phenylbut-3-en-1-yl)pyridine (3ca)

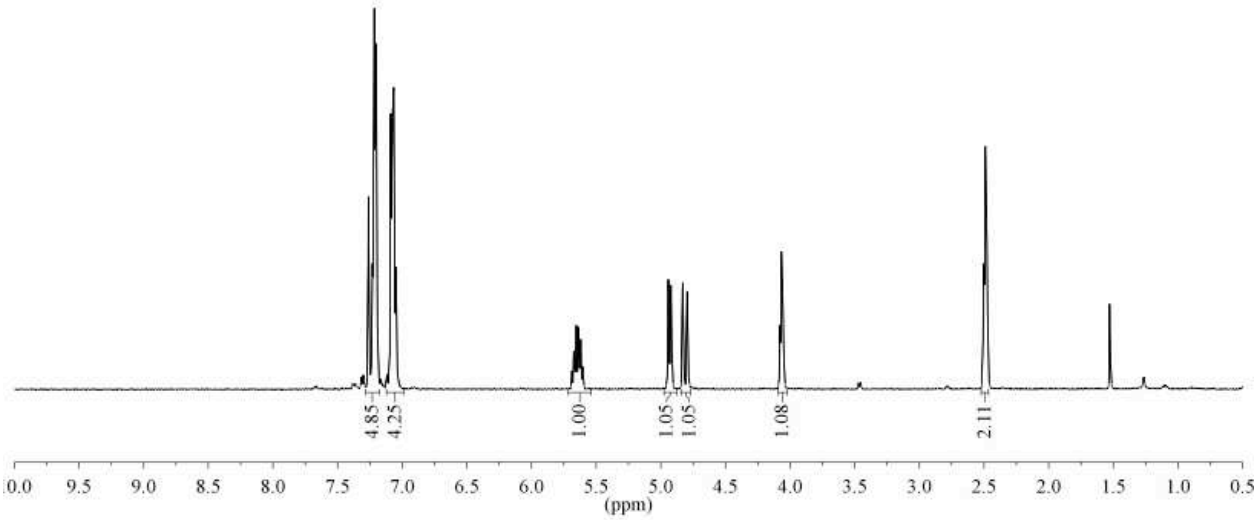


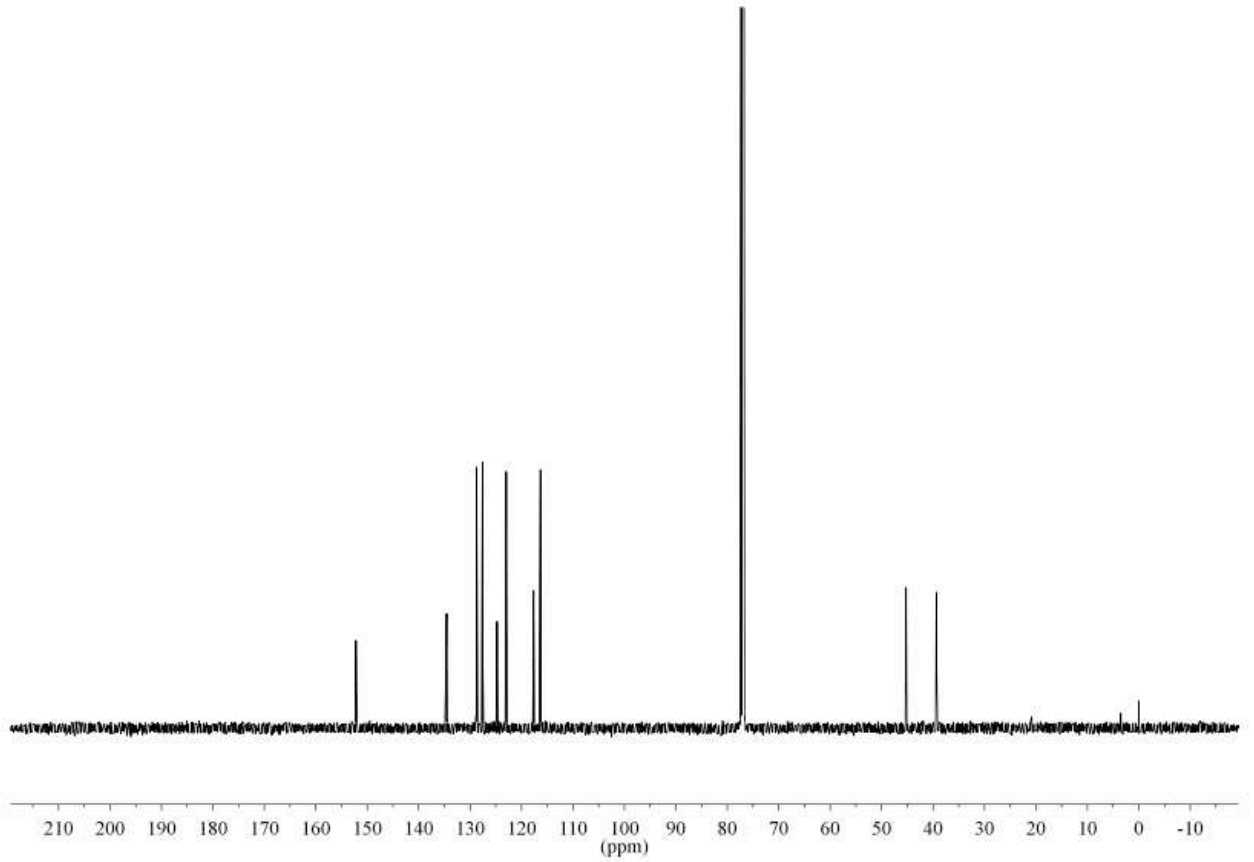




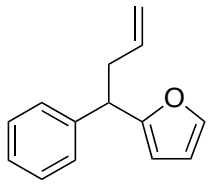
9-allyl-9*H*-xanthene (3da)

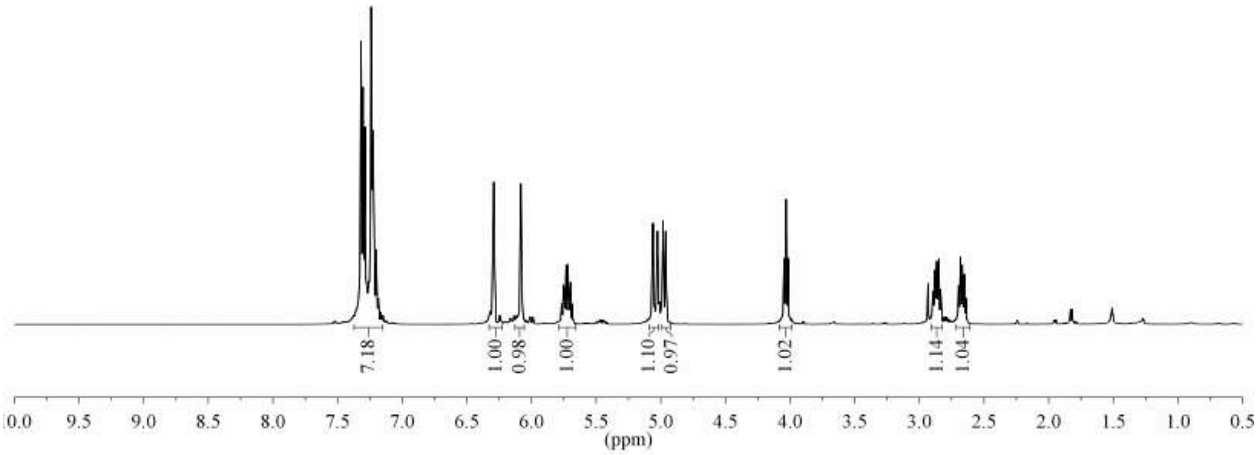


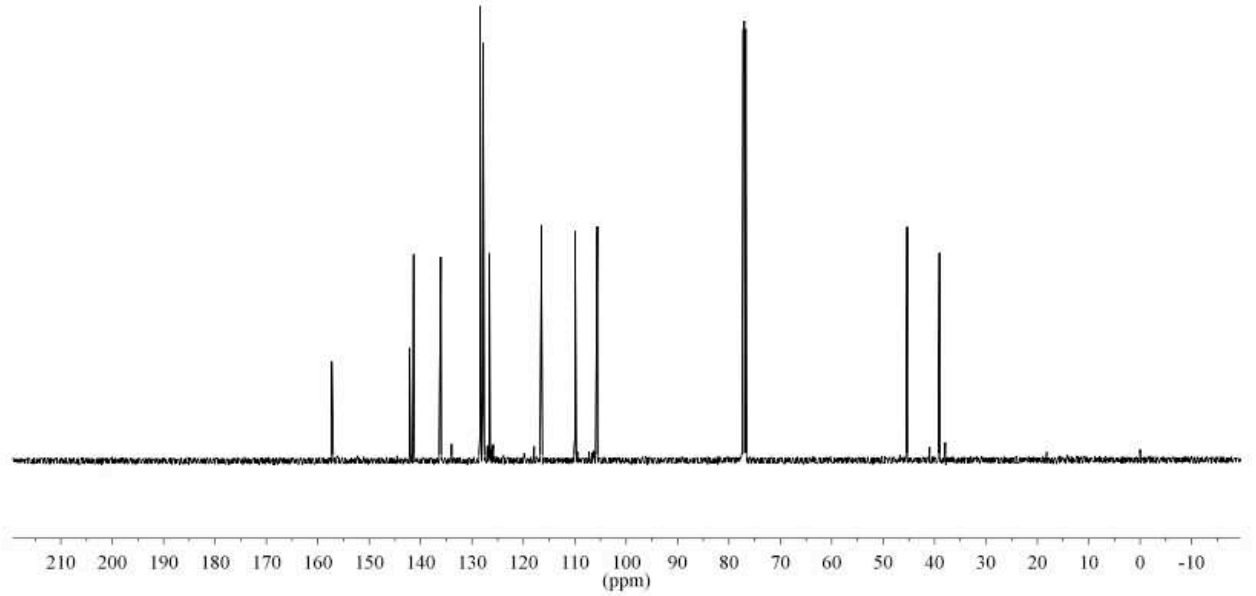




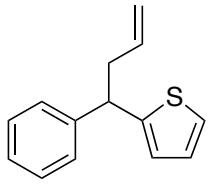
2-(1-phenylbut-3-en-1-yl)furan (3ea)

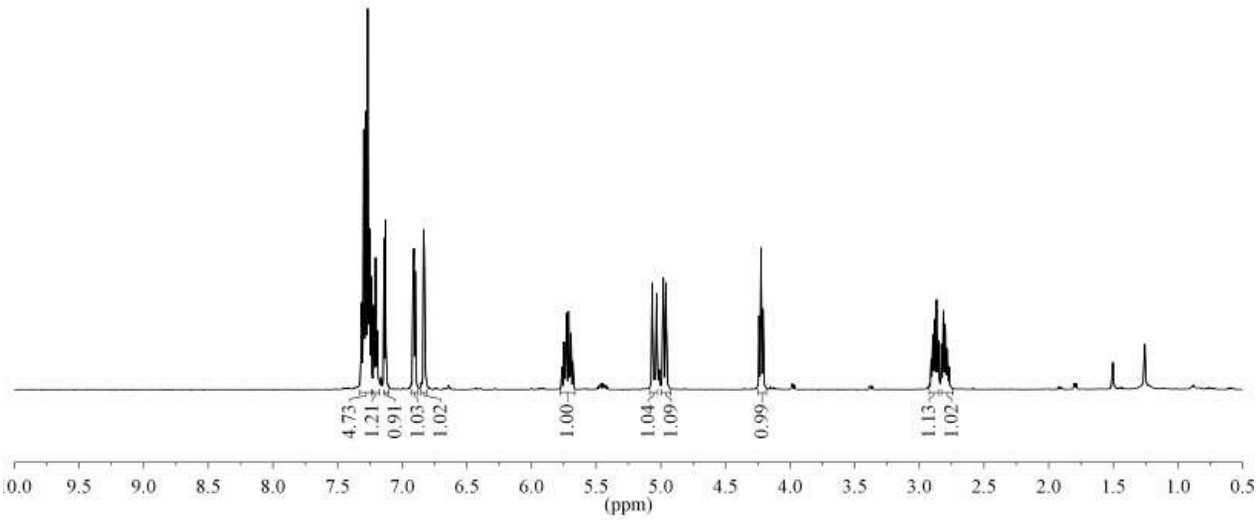


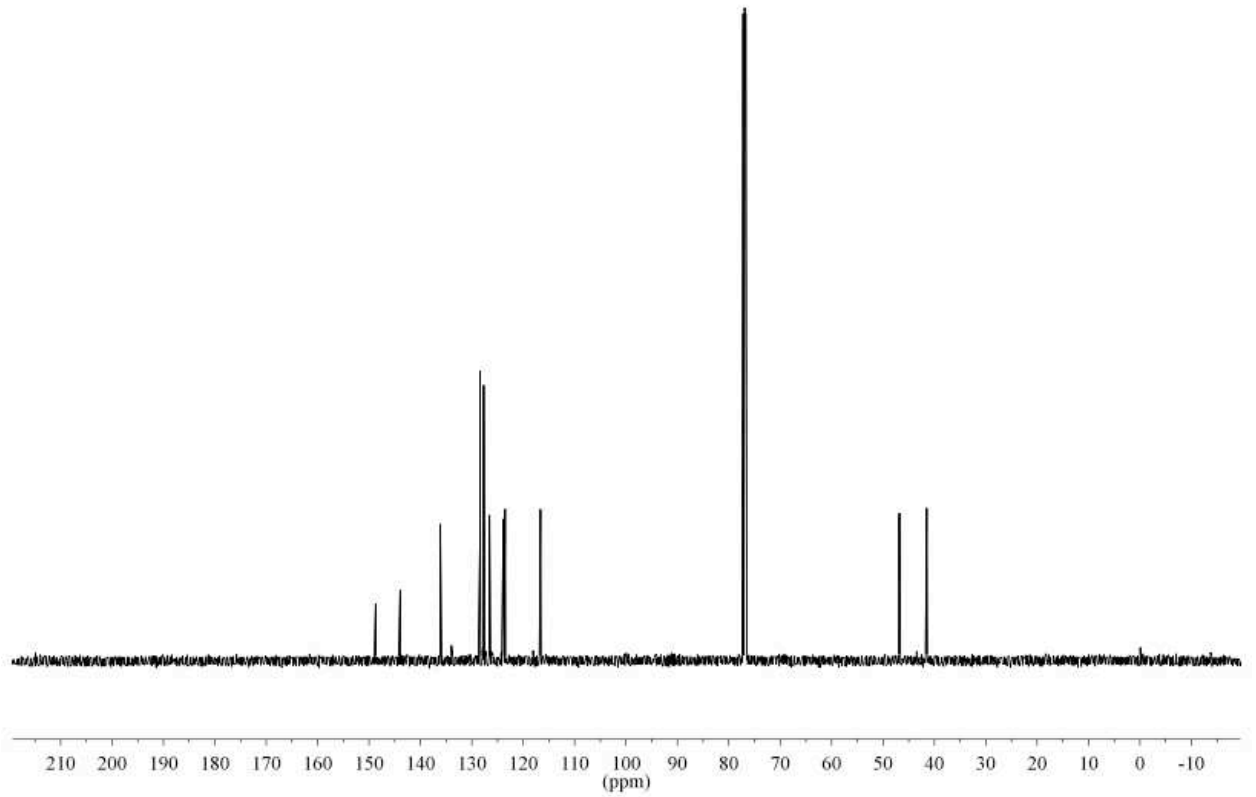




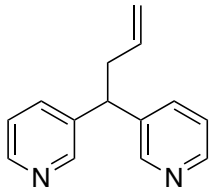
2-(1-phenylbut-3-en-1-yl)thiophene (3fa)

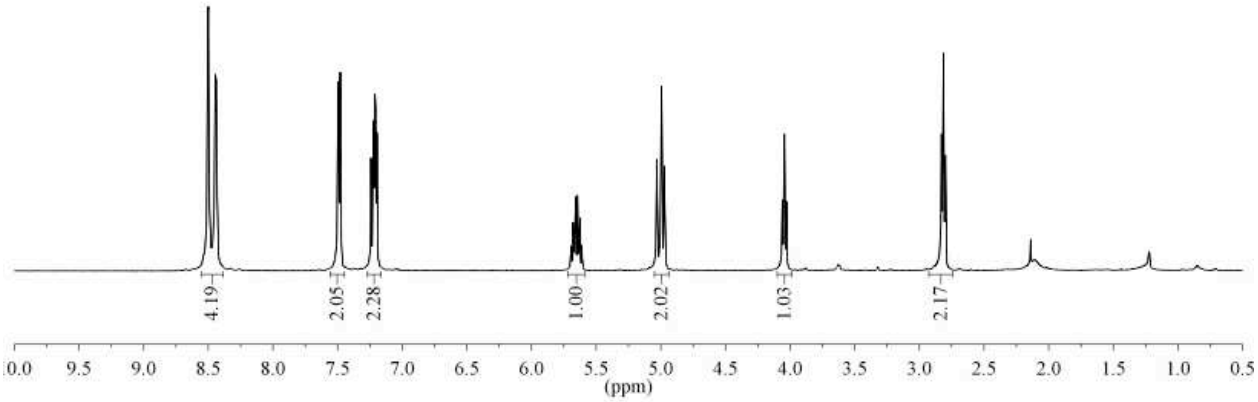


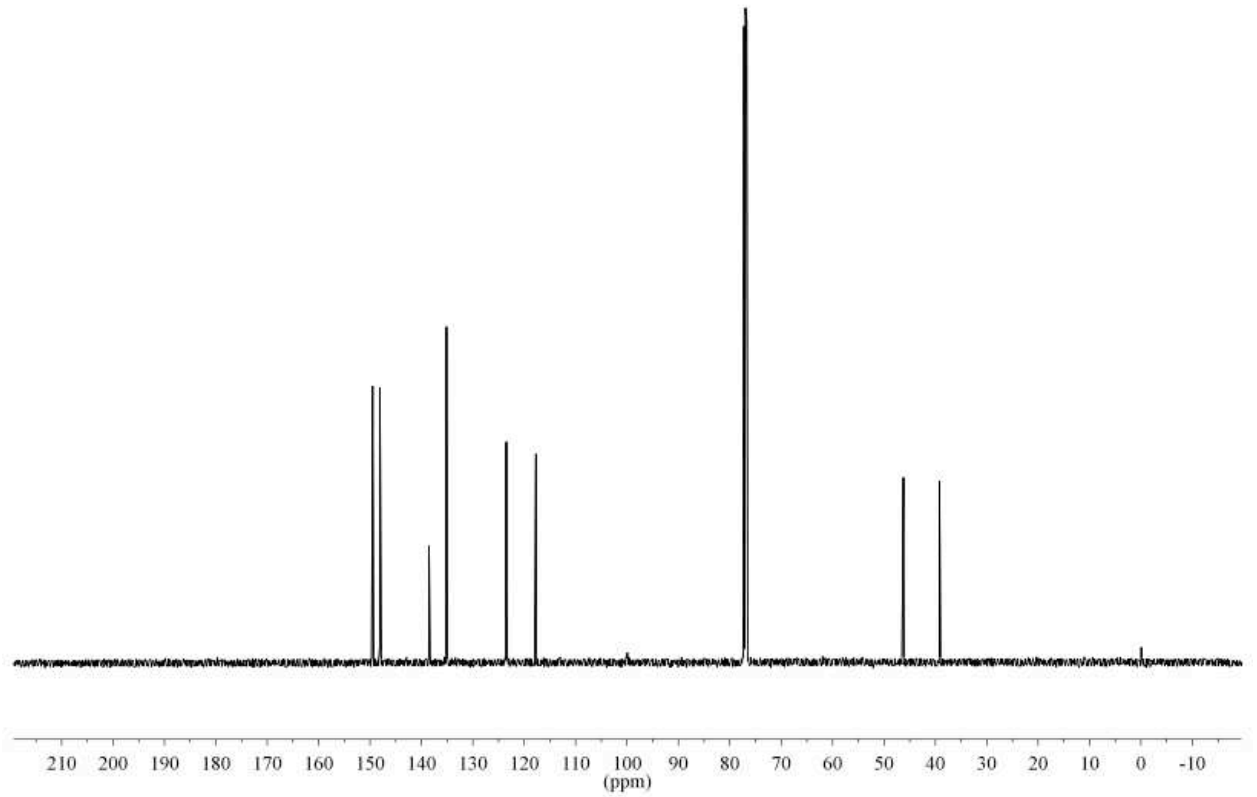




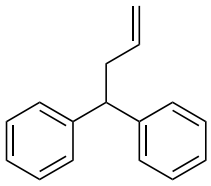
3,3'-(but-3-ene-1,1-diyl)dipyridine (3ga)

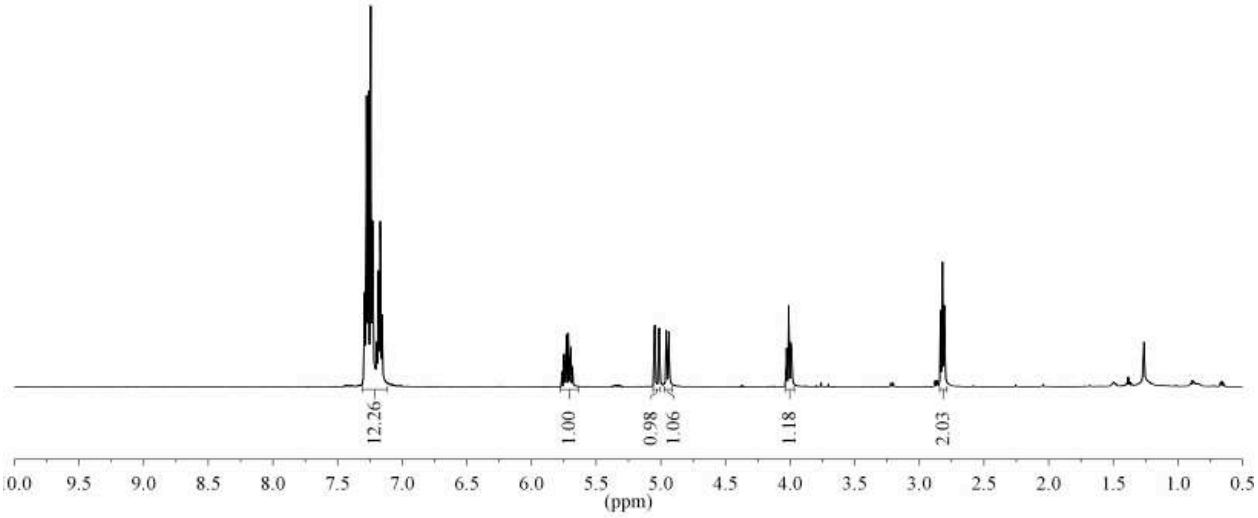


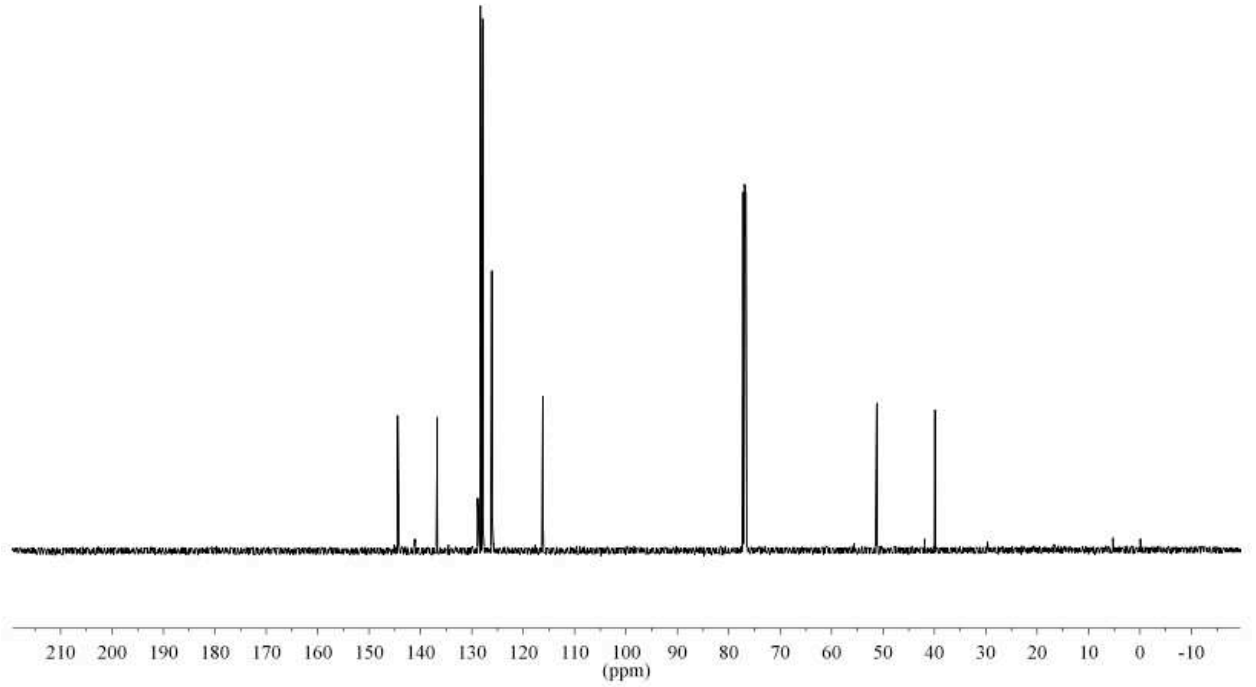




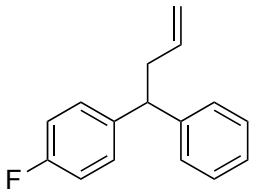
but-3-ene-1,1-diyldibenzene (5aa)

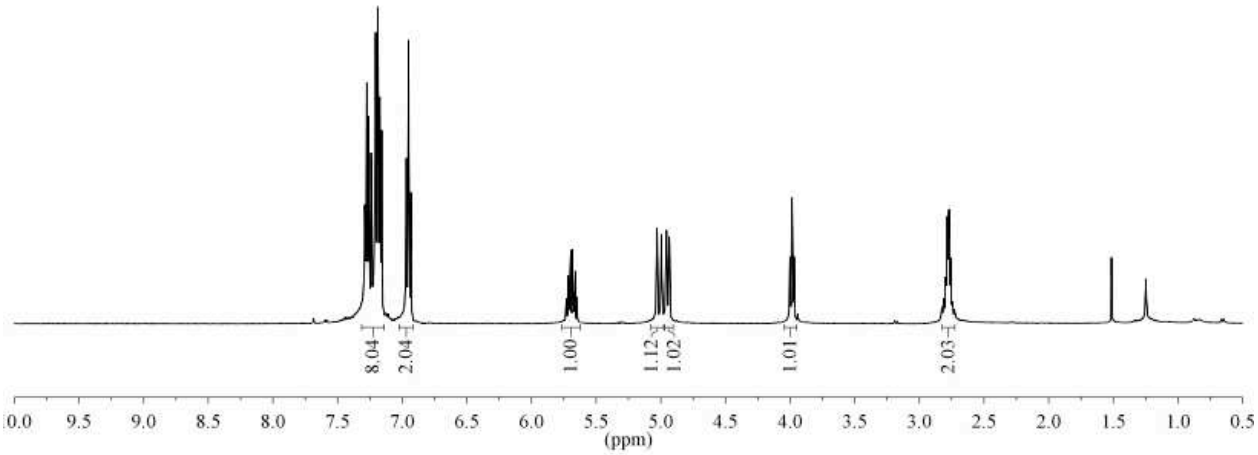


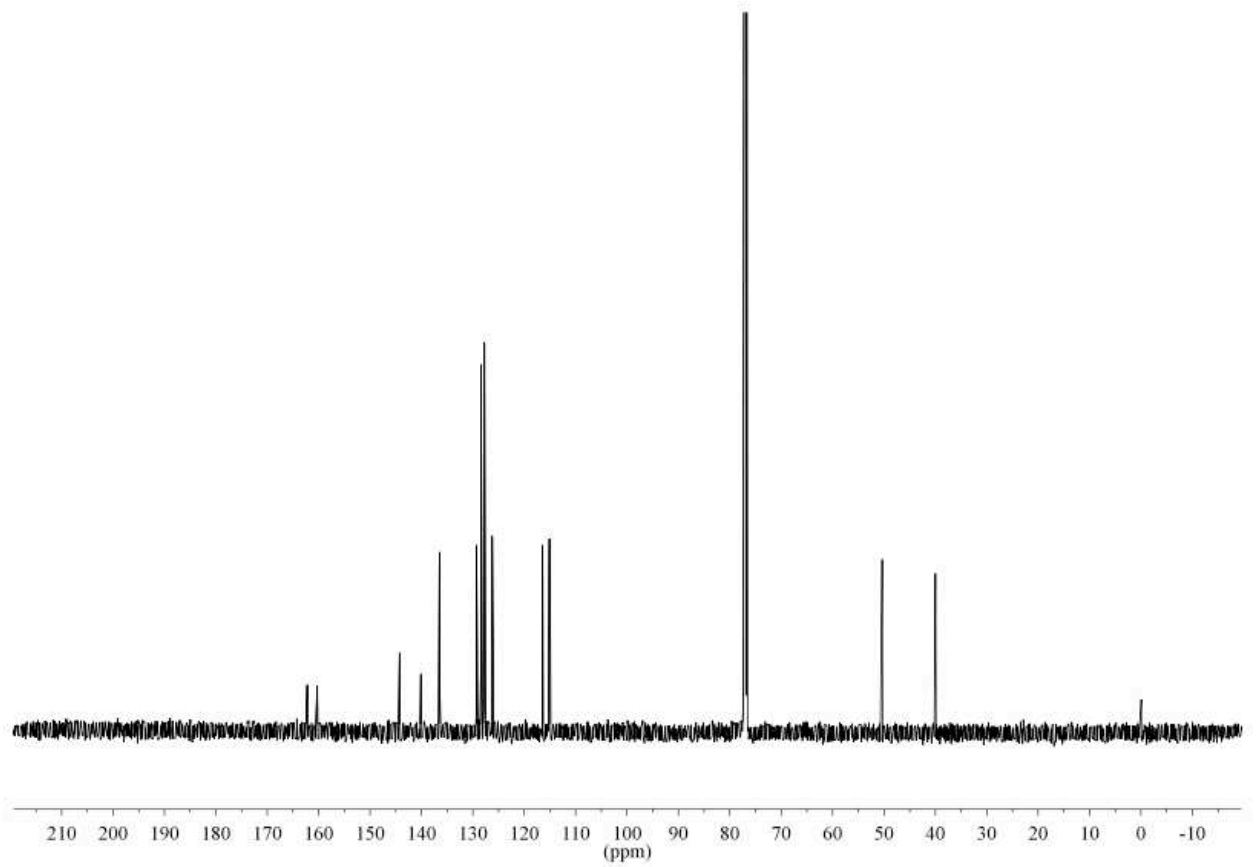




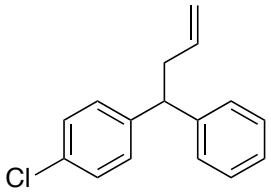
1-fluoro-4-(1-phenylbut-3-en-1-yl)benzene (5ba)

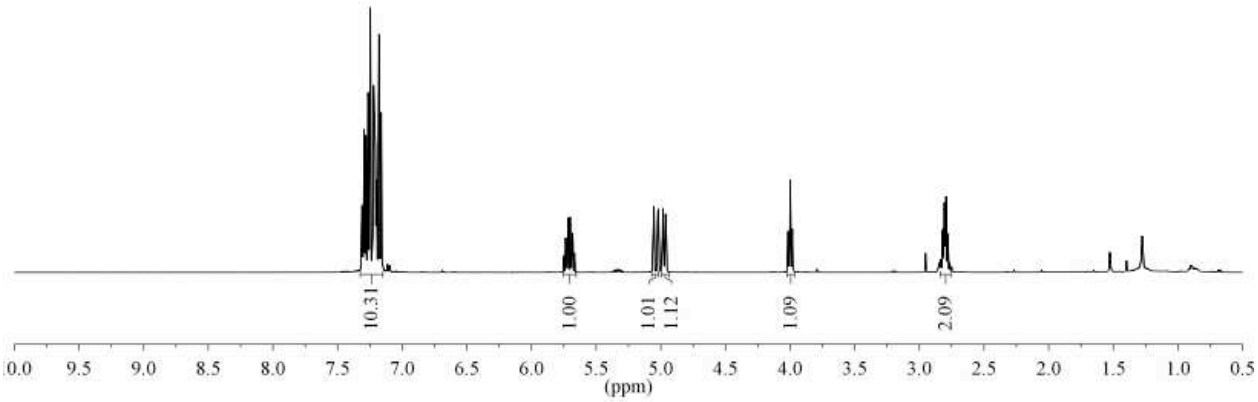


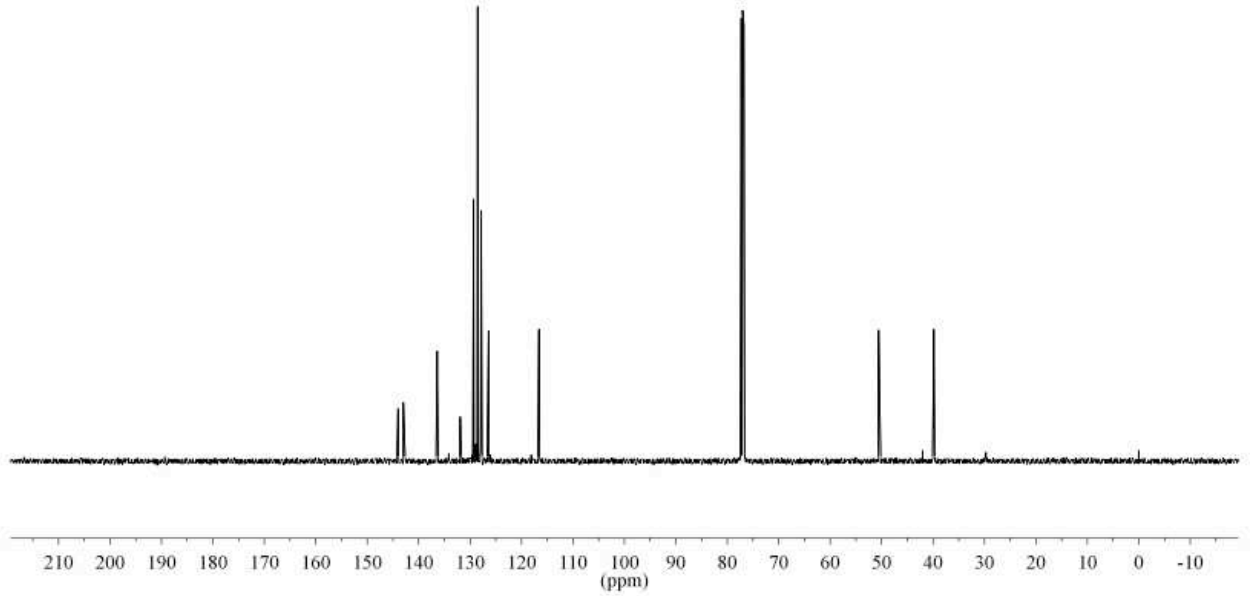




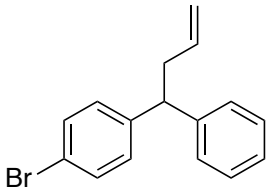
1-chloro-4-(1-phenylbut-3-en-1-yl)benzene (5ca)

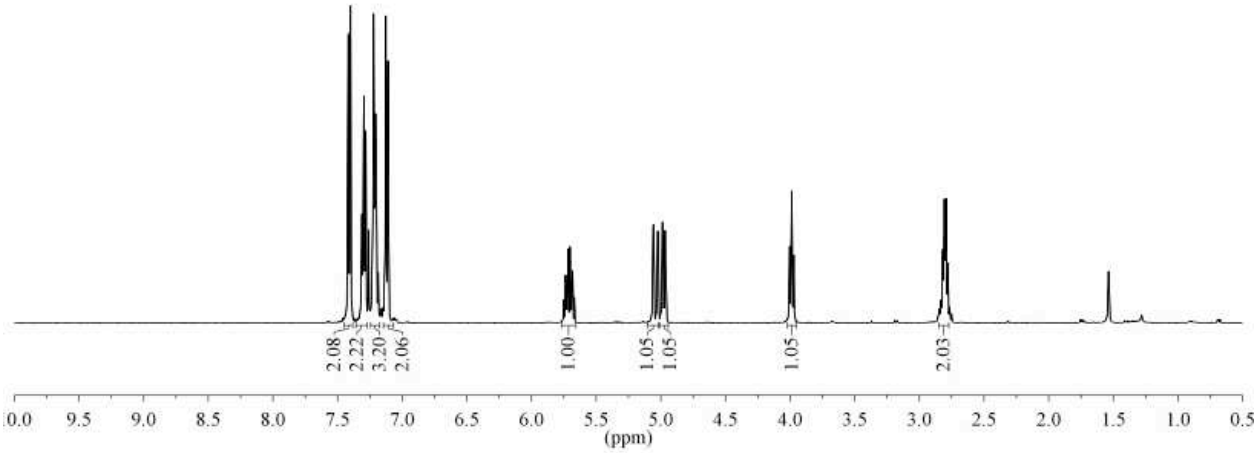


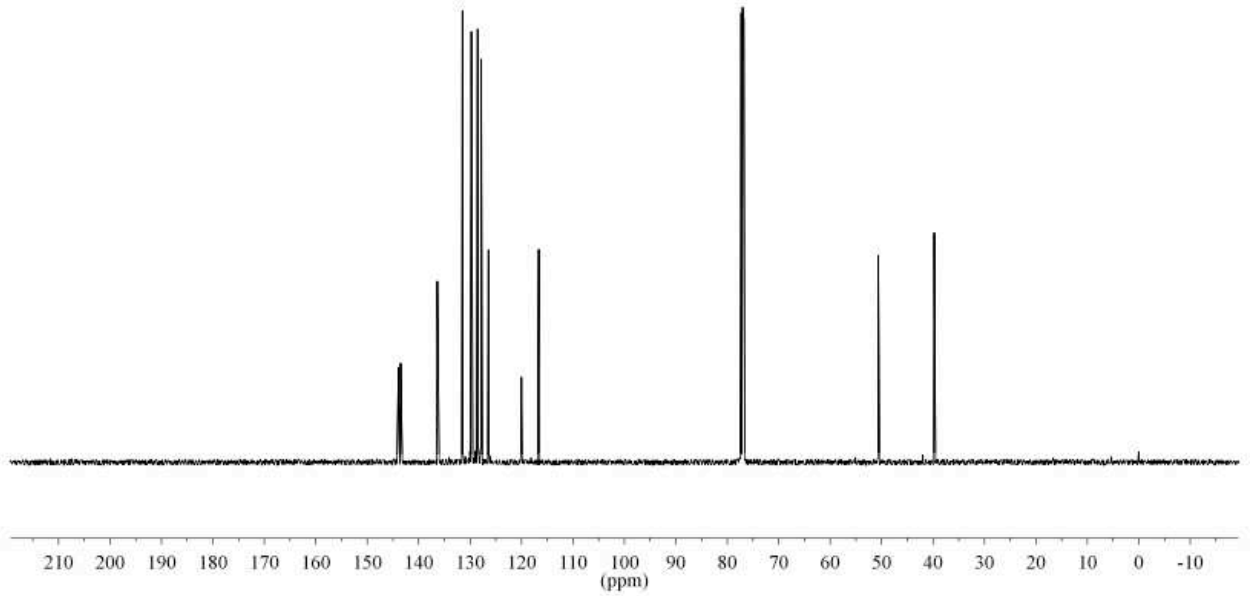




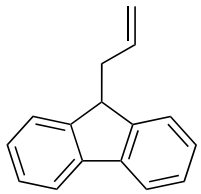
1-bromo-4-(1-phenylbut-3-en-1-yl)benzene (5da)

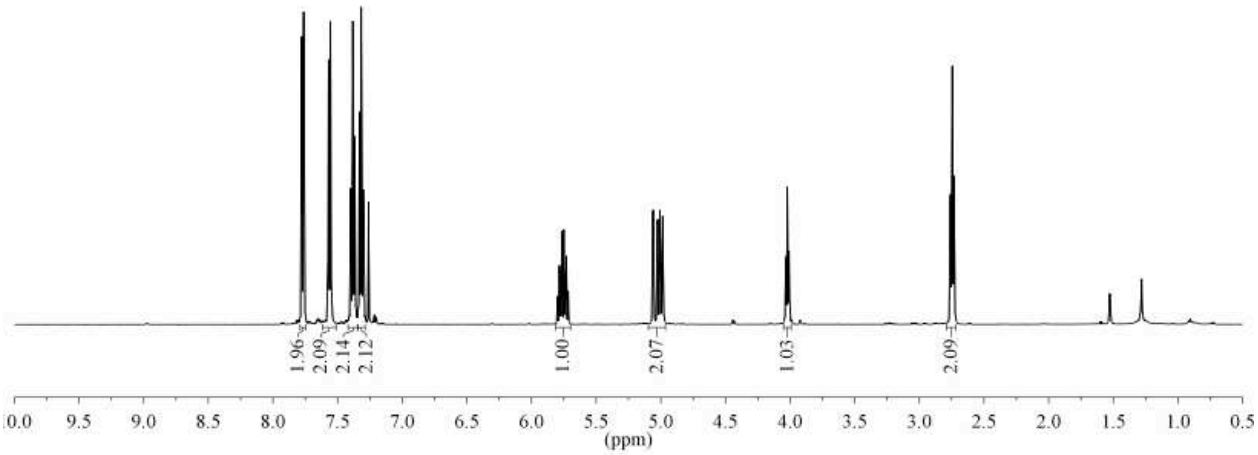


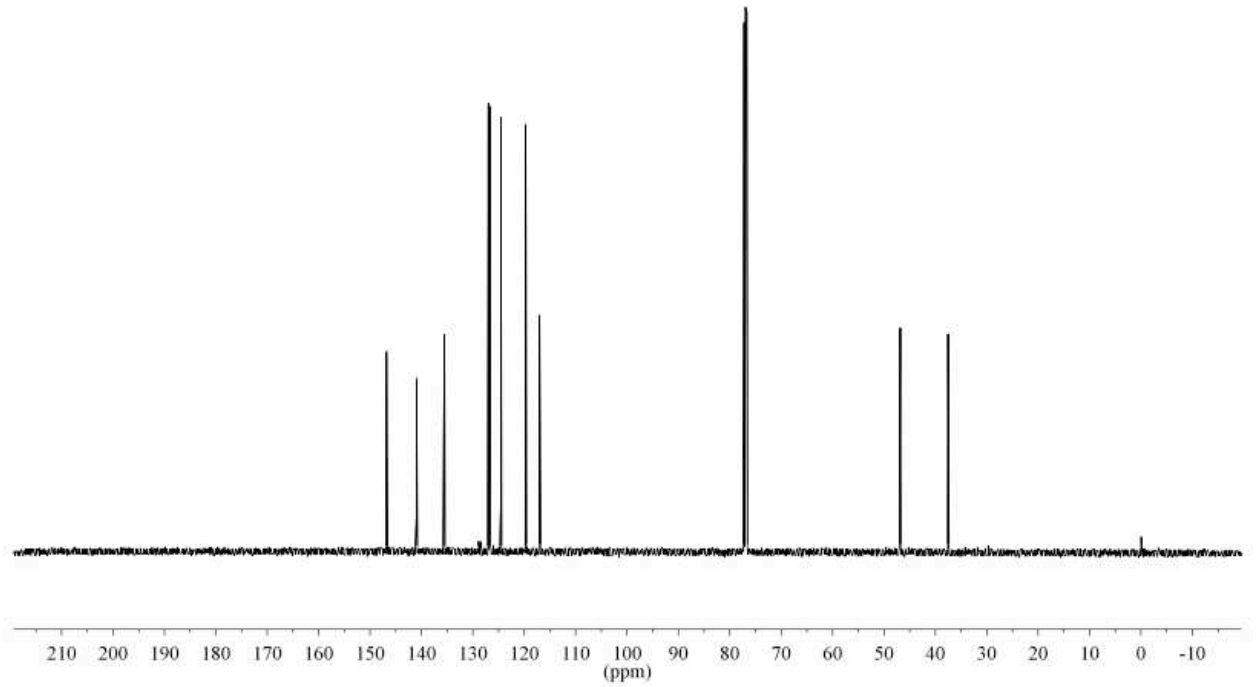




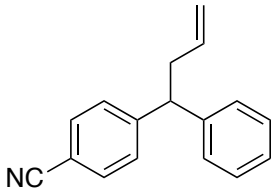
9-allyl-9*H*-fluorene (5ea)

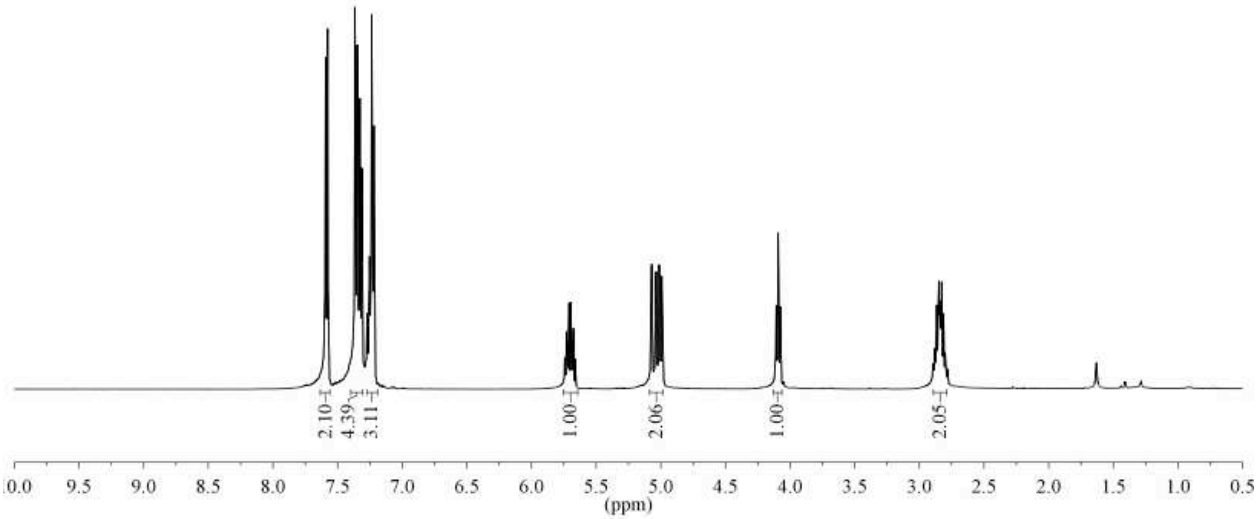


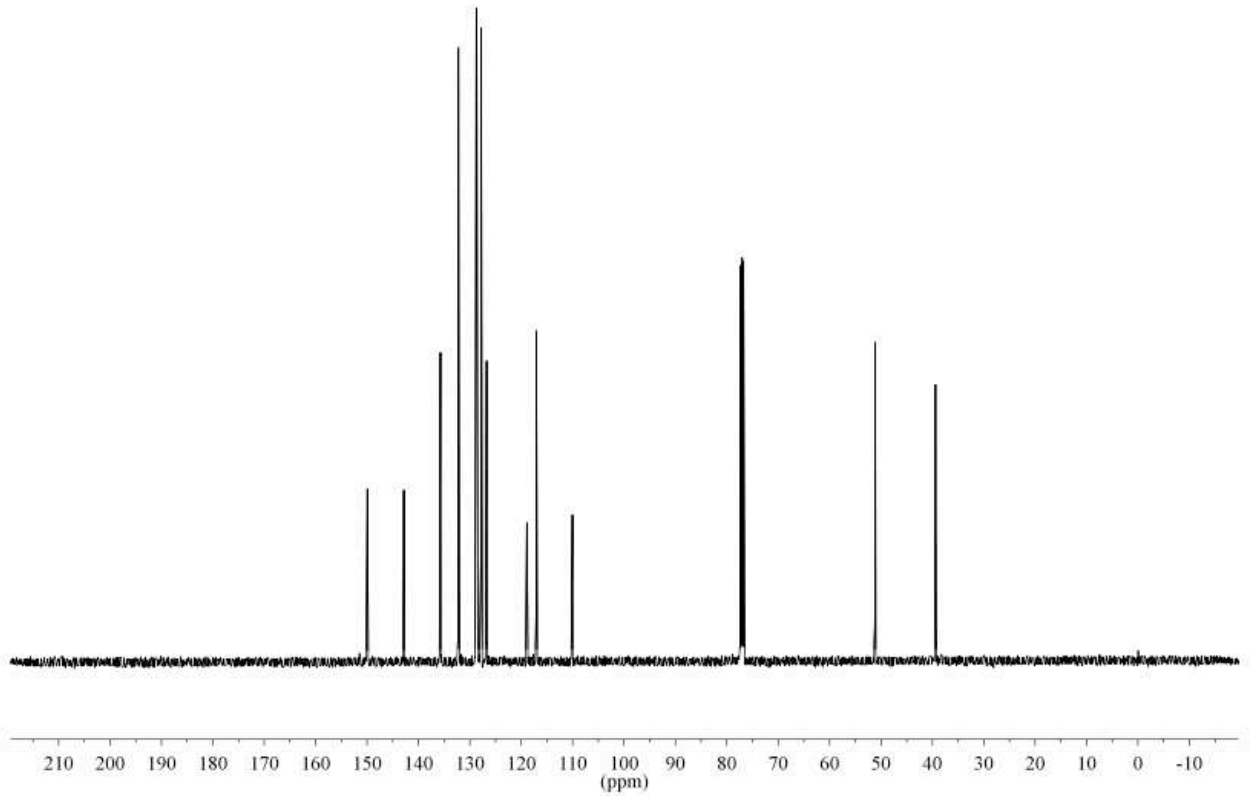




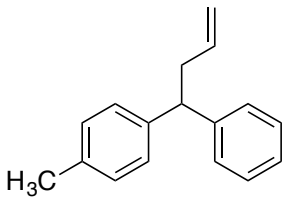
4-(1-phenylbut-3-en-1-yl)benzonitrile (5fa)

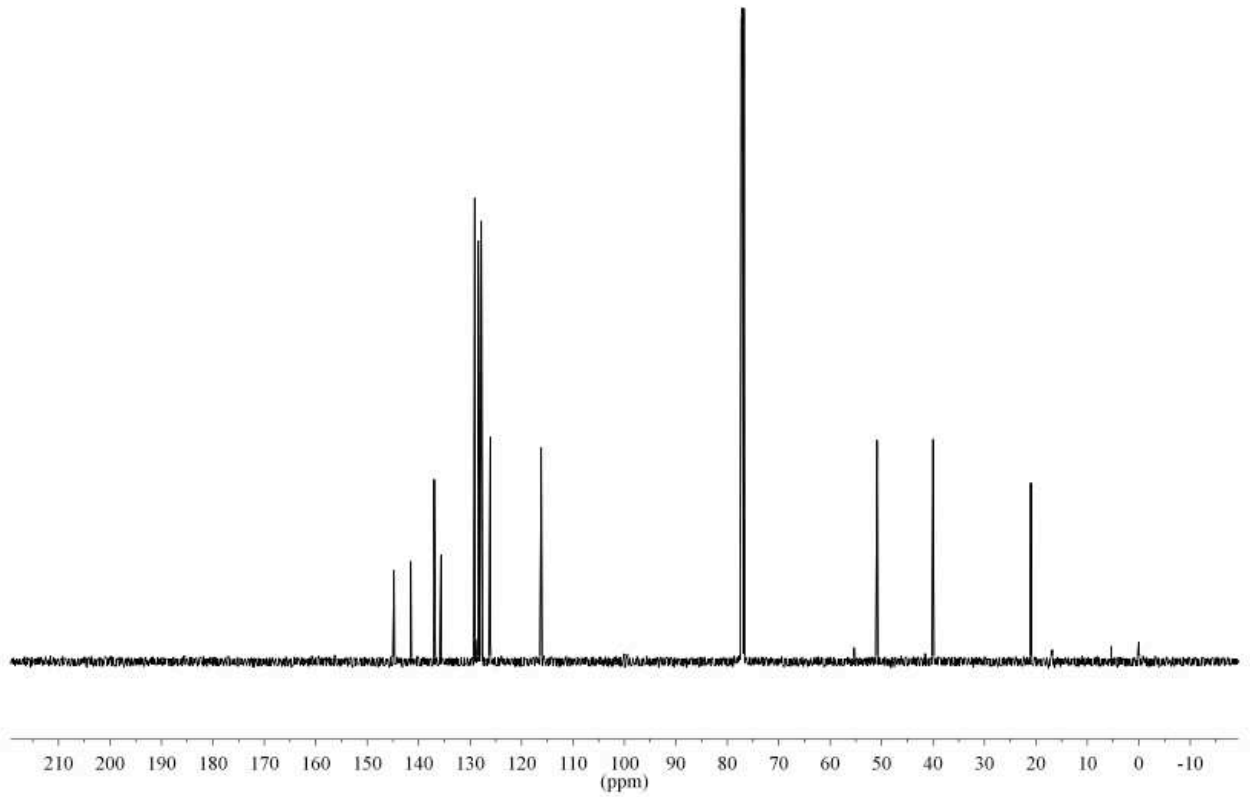




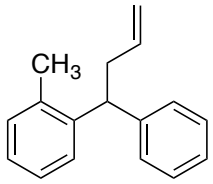


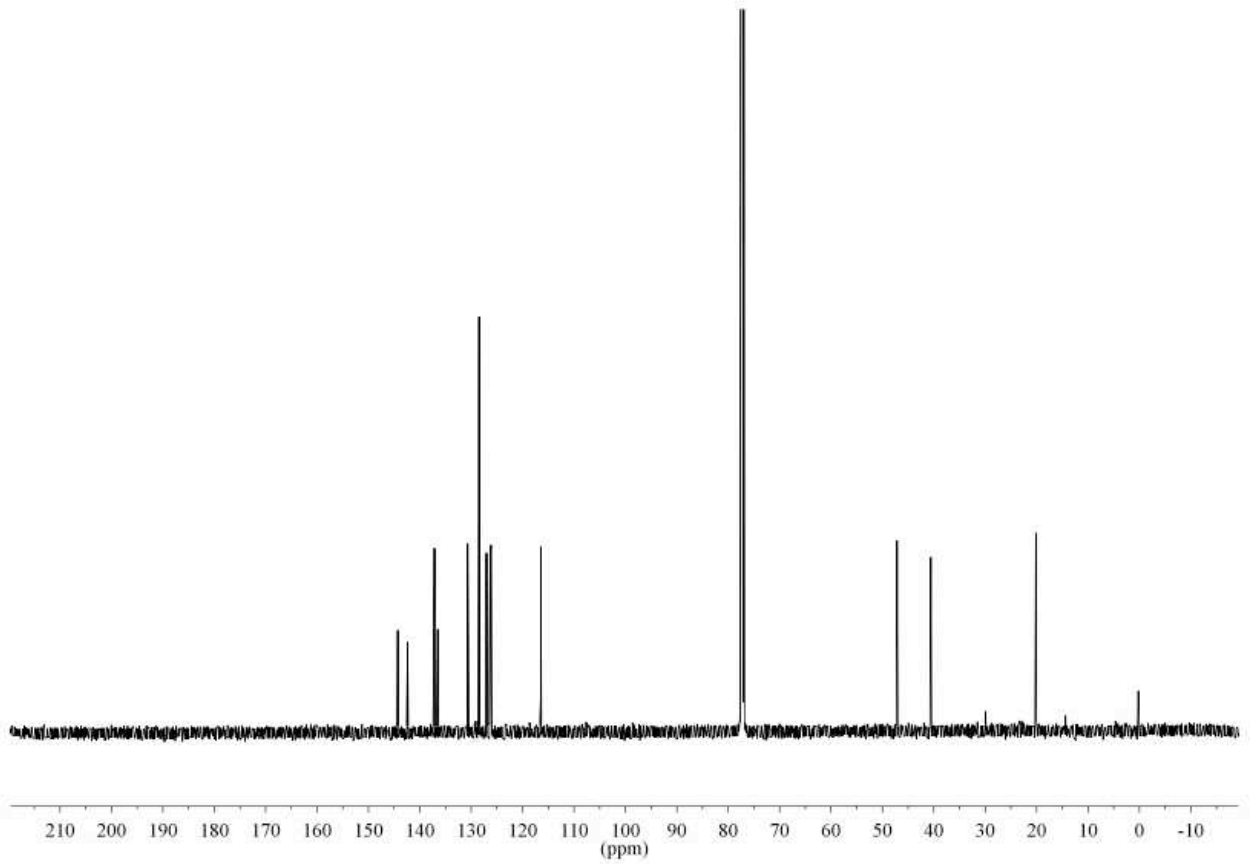
1-methyl-4-(1-phenylbut-3-en-1-yl)benzene (5ga)



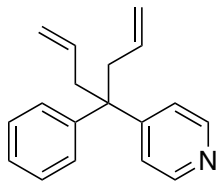


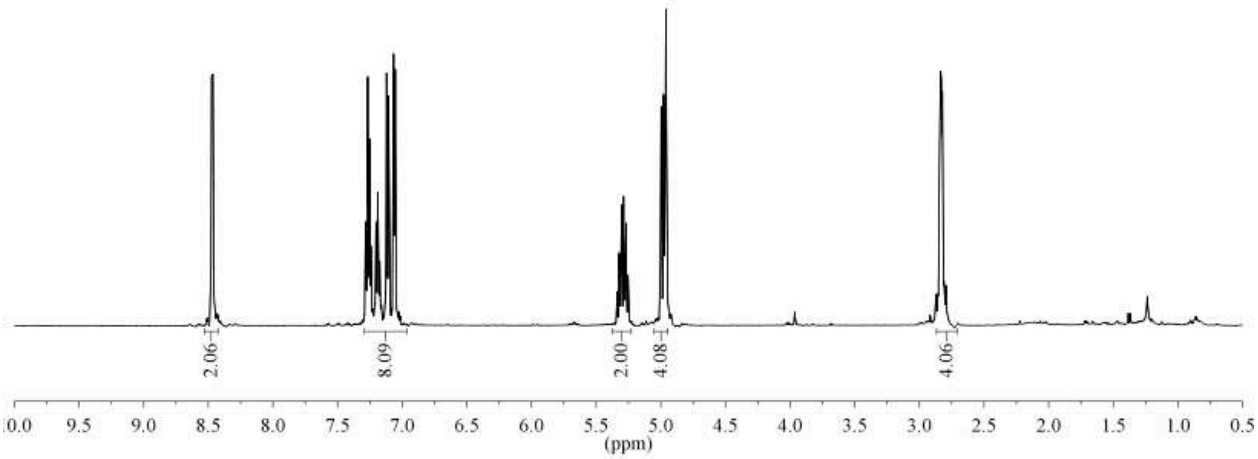
1-methyl-2-(1-phenylbut-3-en-1-yl)benzene (5ha)

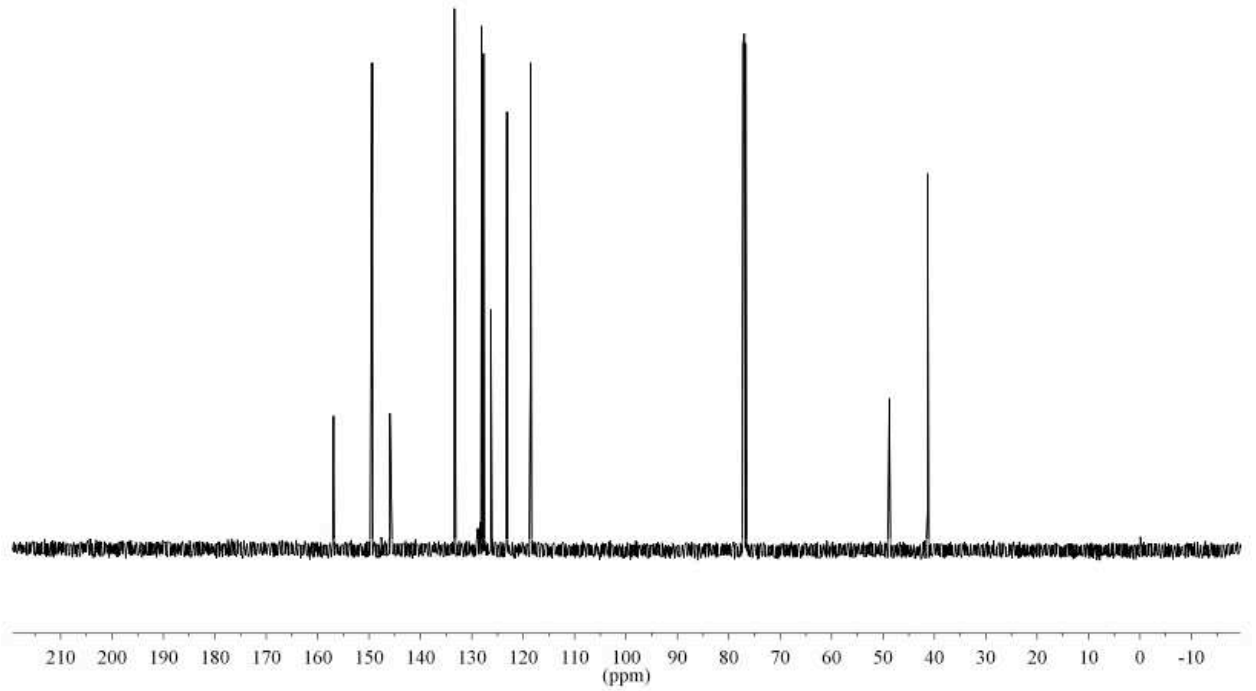




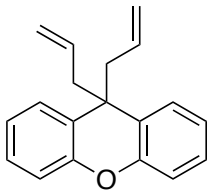
4-(4-phenylhepta-1,6-dien-4-yl)pyridine (6ba)

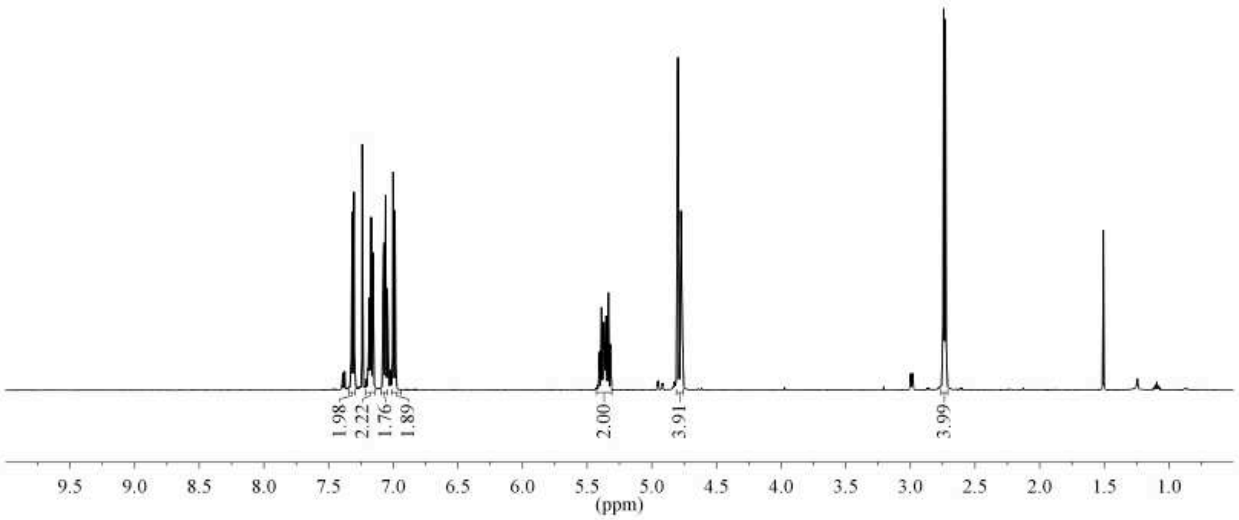


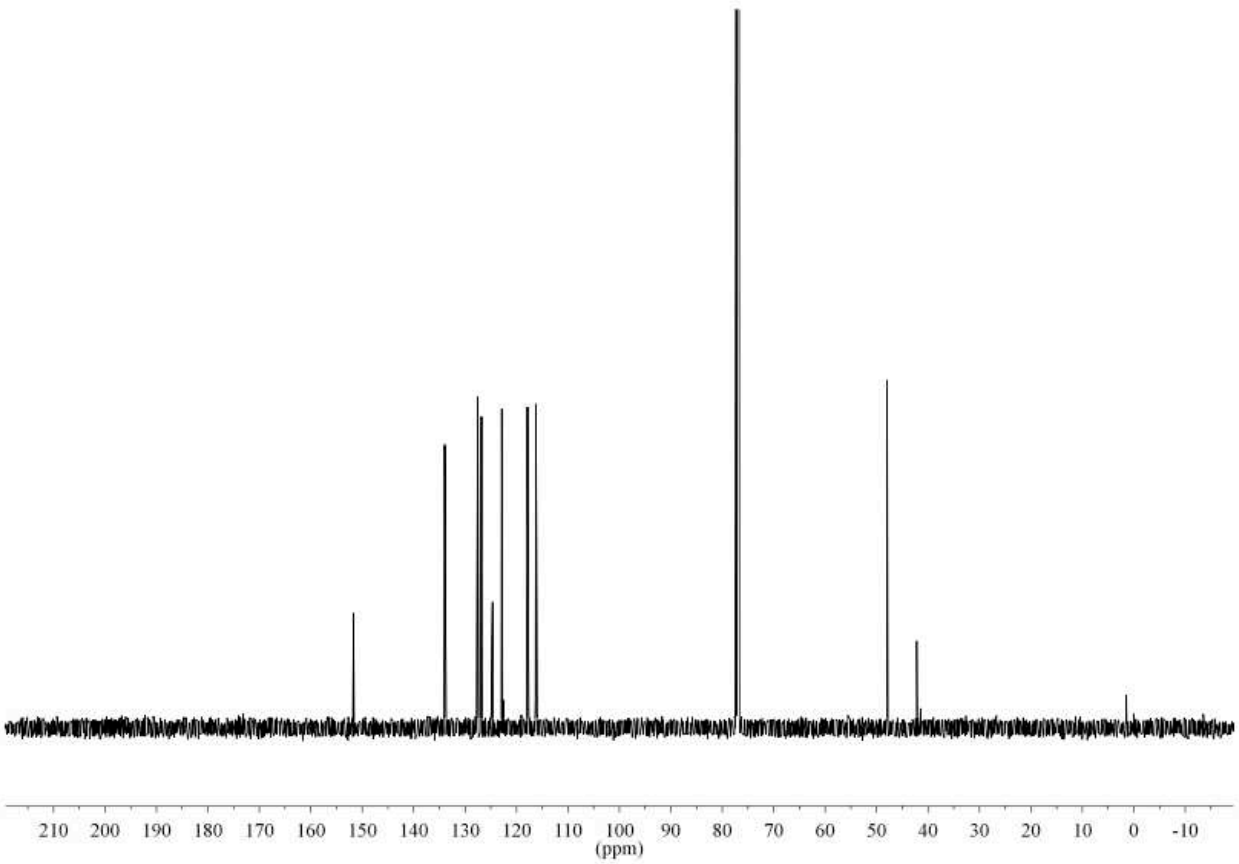




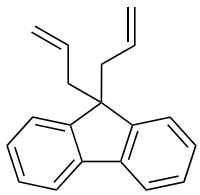
9,9-diallyl-9*H*-xanthene (6da)

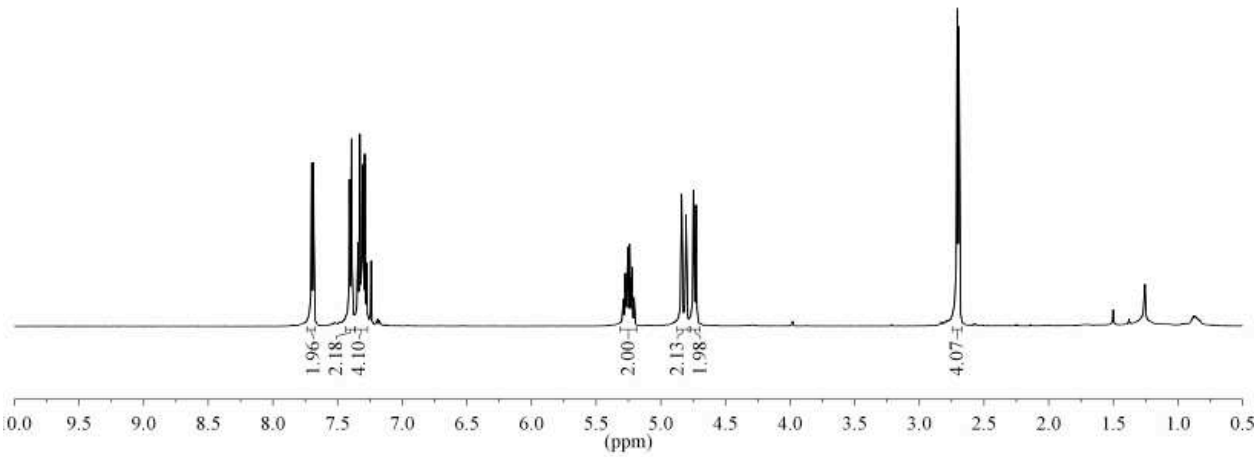


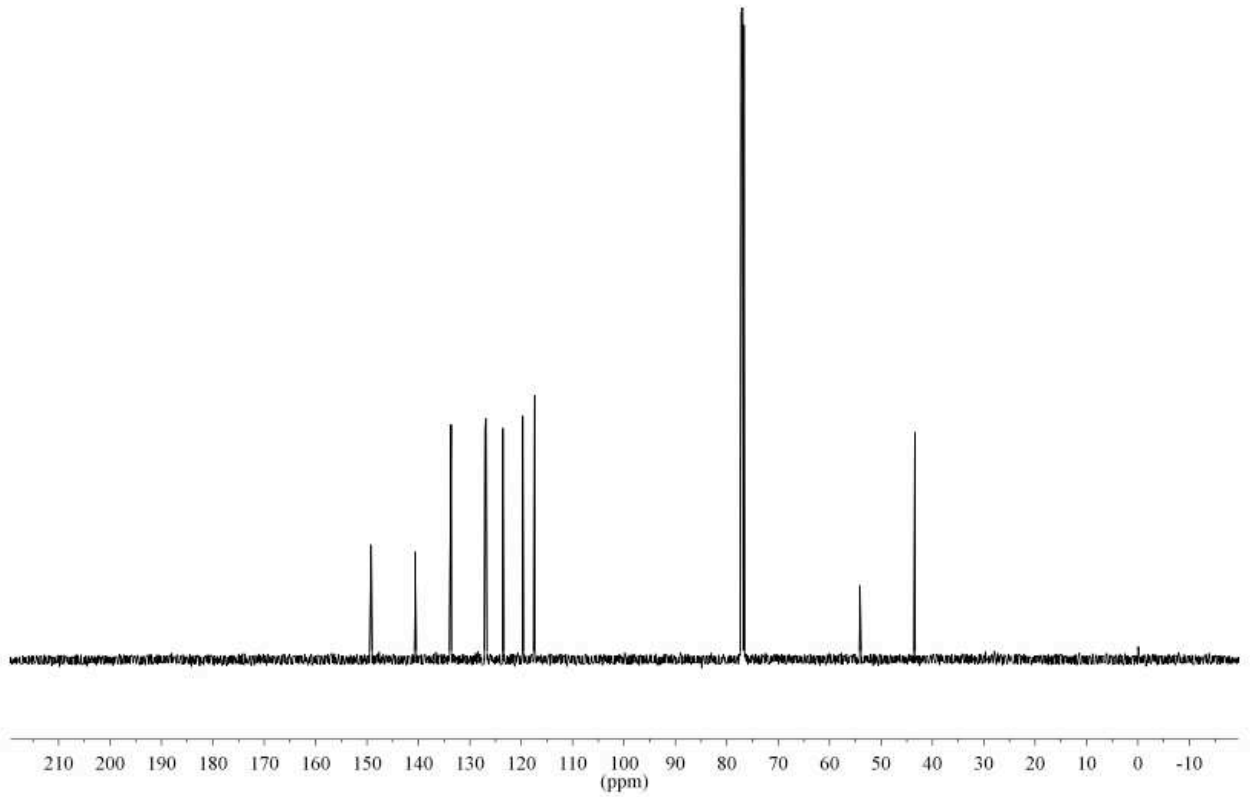




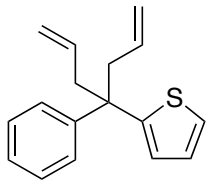
9,9-diallyl-9*H*-fluorene (7ea)

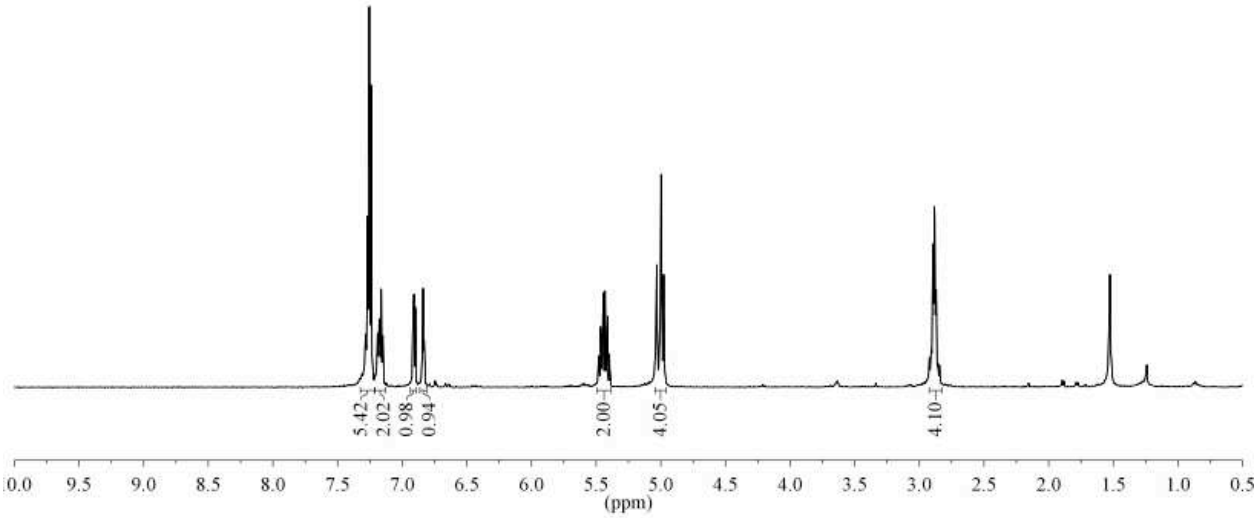


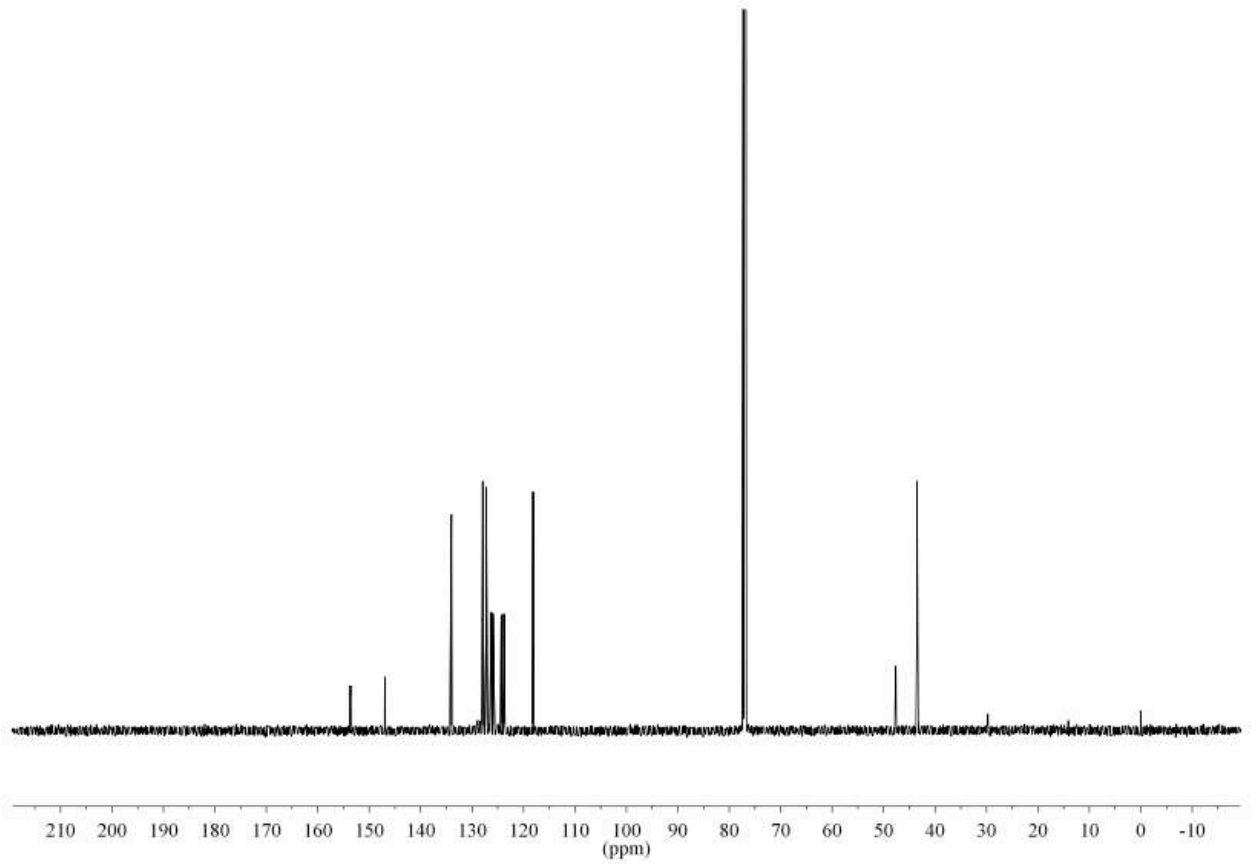




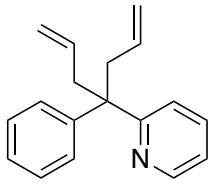
2-(4-phenylhepta-1,6-dien-4-yl)thiophene (6fa)

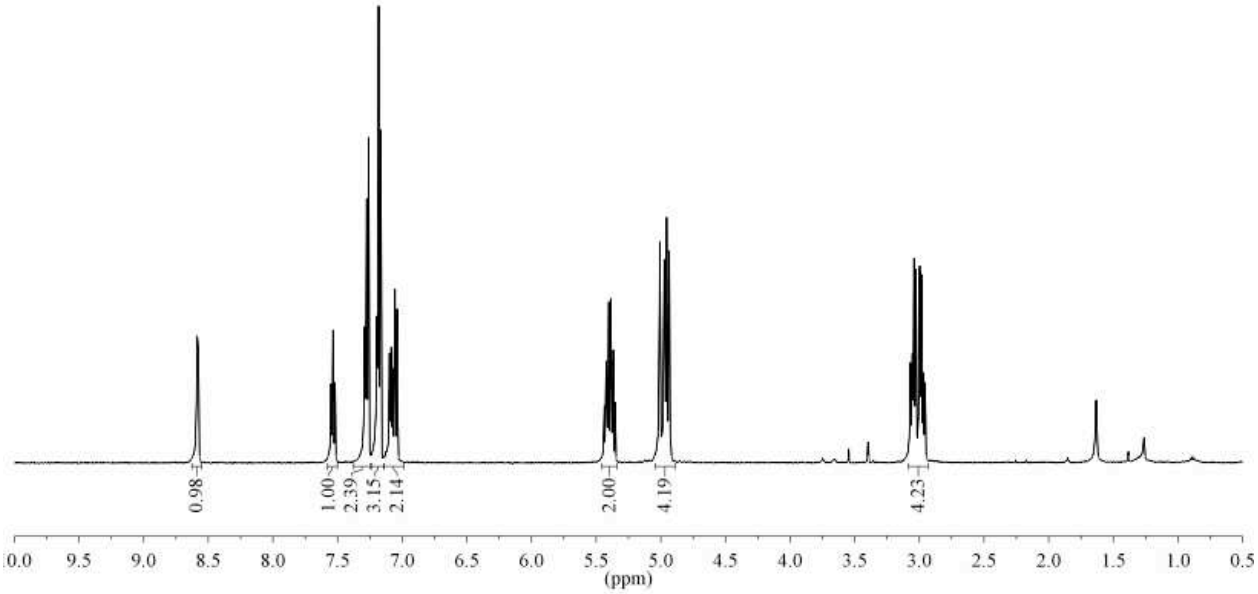


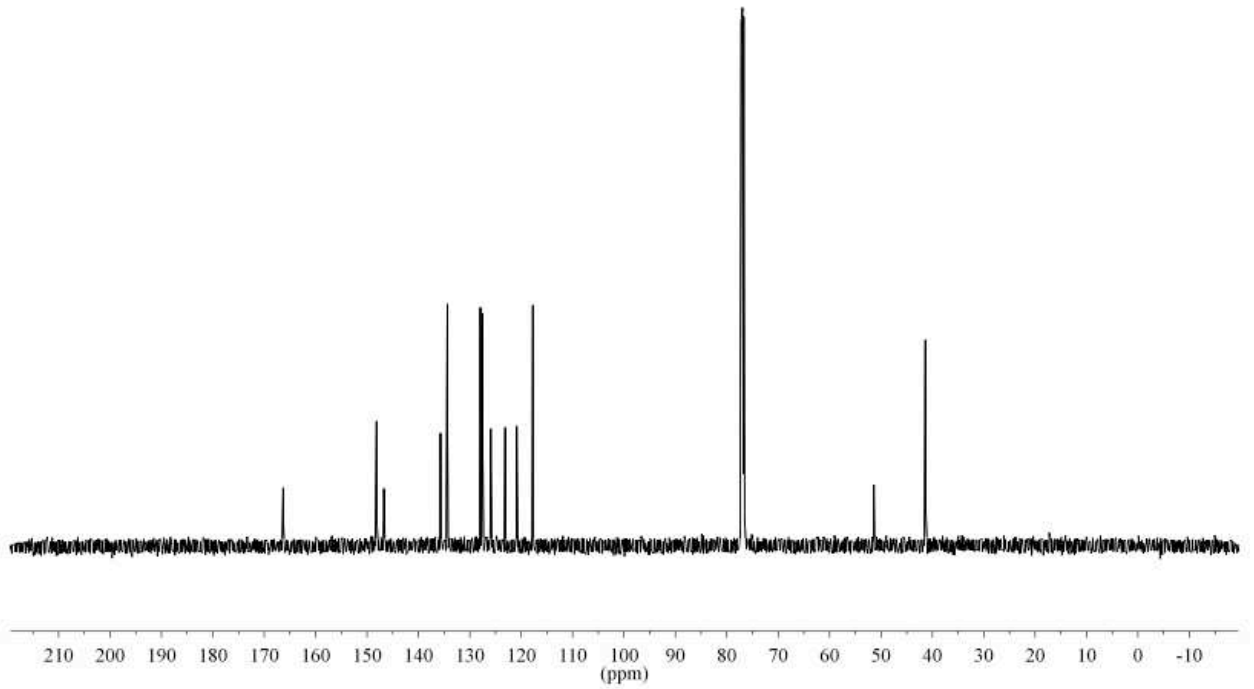




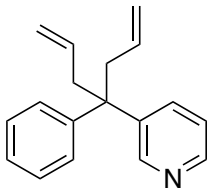
2-(4-phenylhepta-1,6-dien-4-yl)pyridine (6aa)

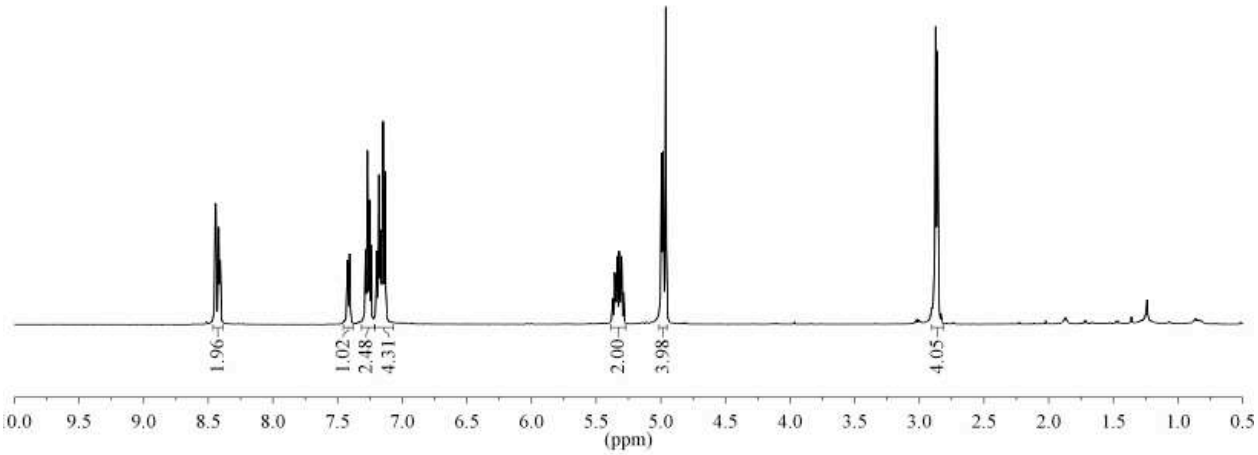


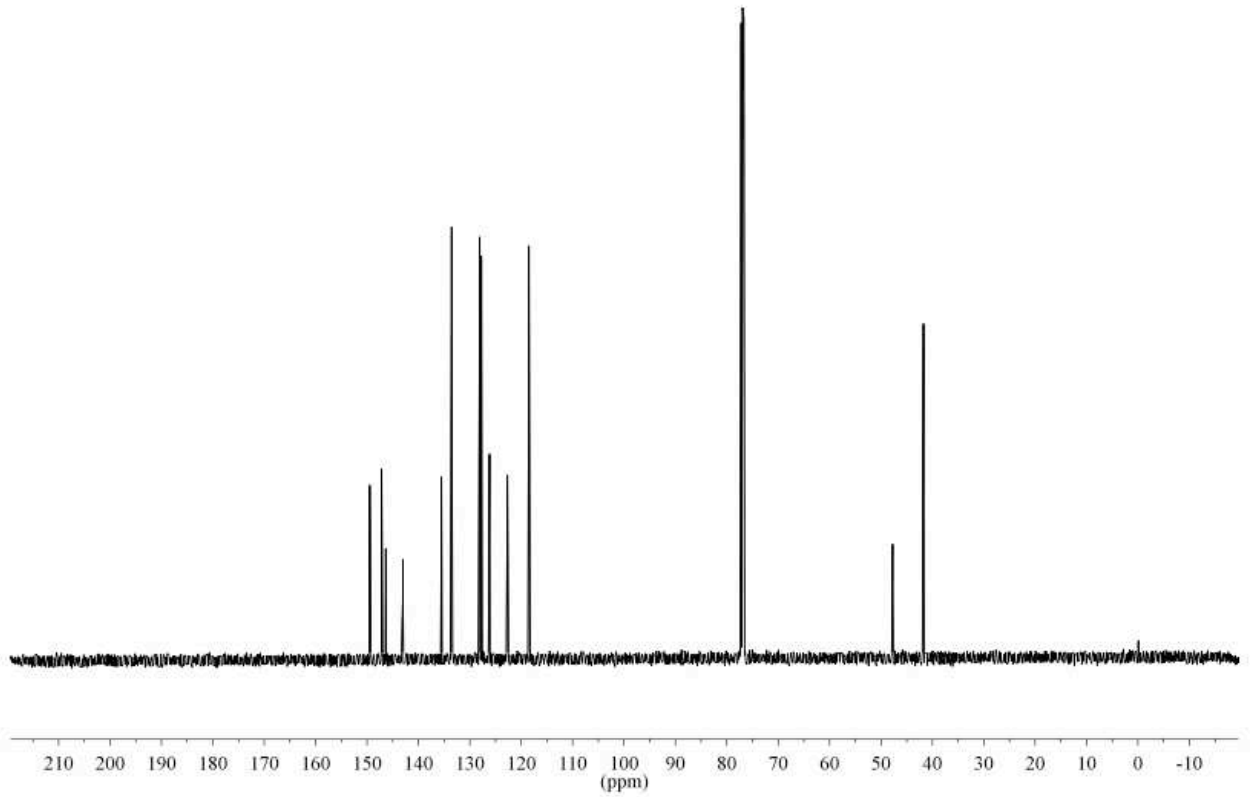




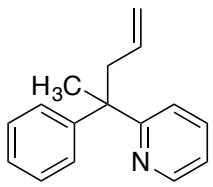
3-(4-phenylhepta-1,6-dien-4-yl)pyridine (6ca)

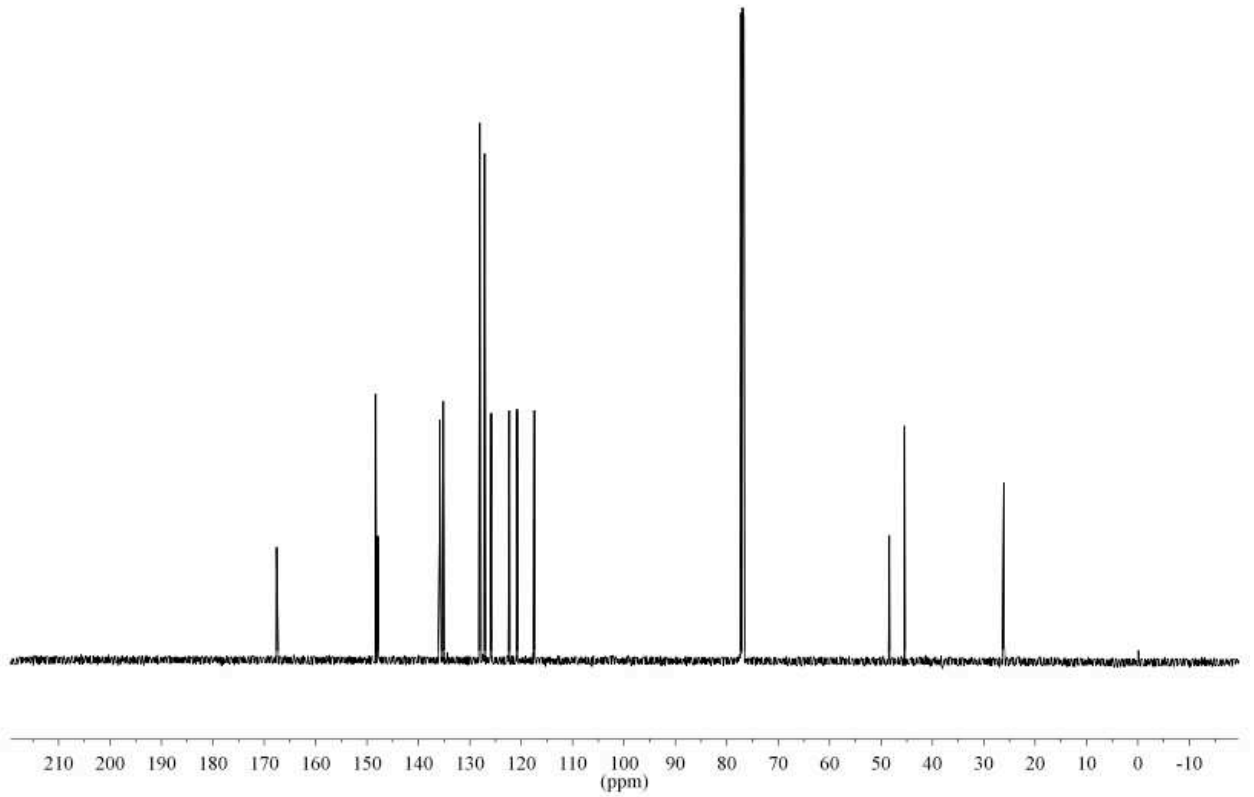




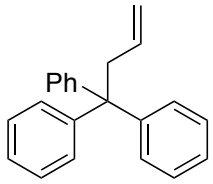


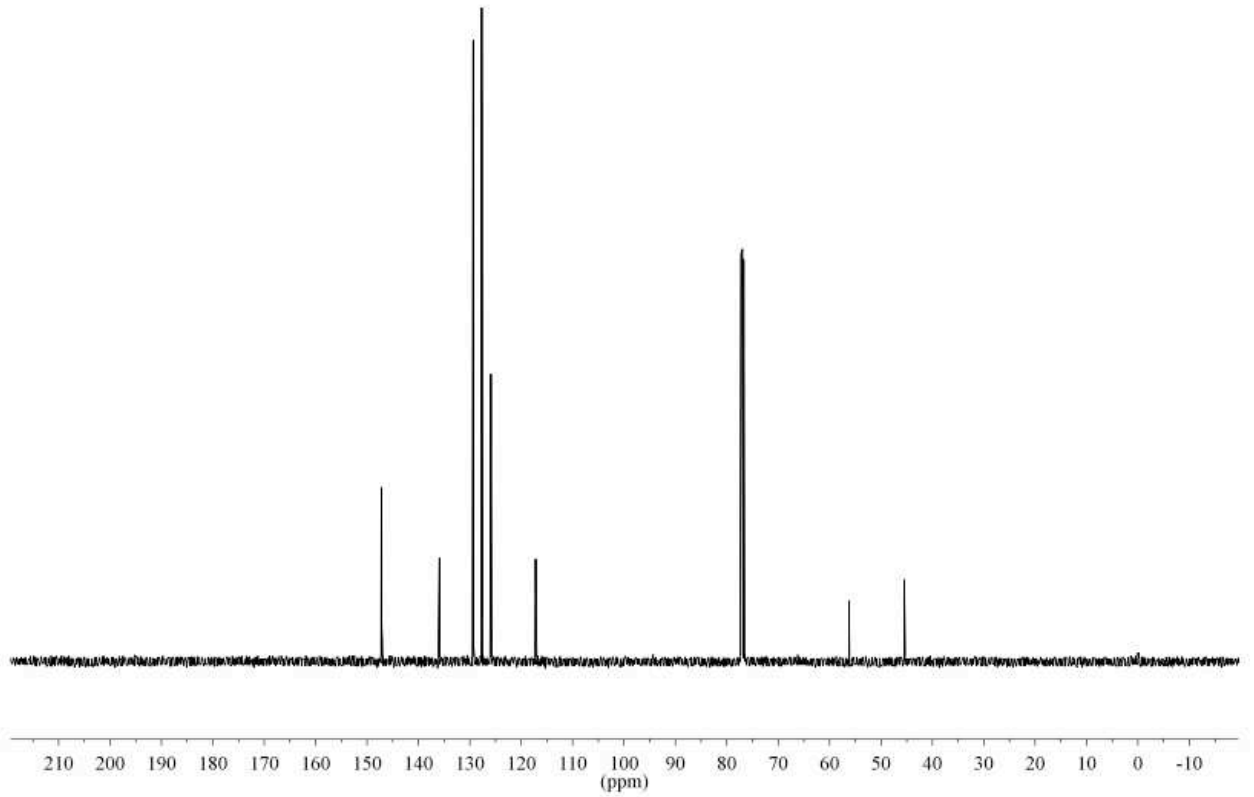
2-(2-phenylpent-4-en-2-yl)pyridine (8aa)



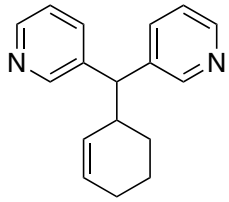


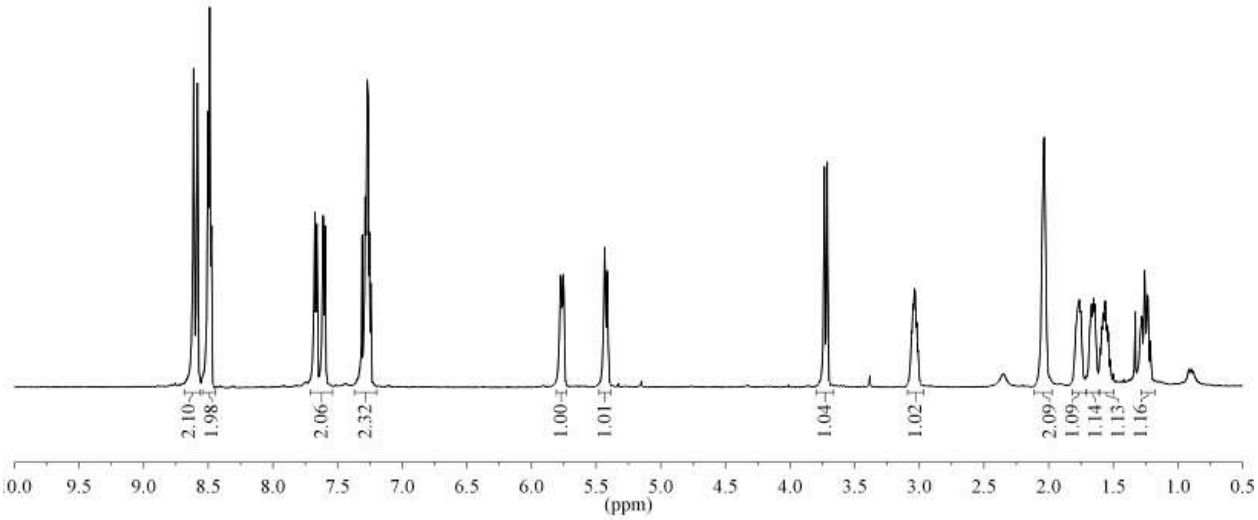
but-3-ene-1,1,1-triyltribenzene (9aa)

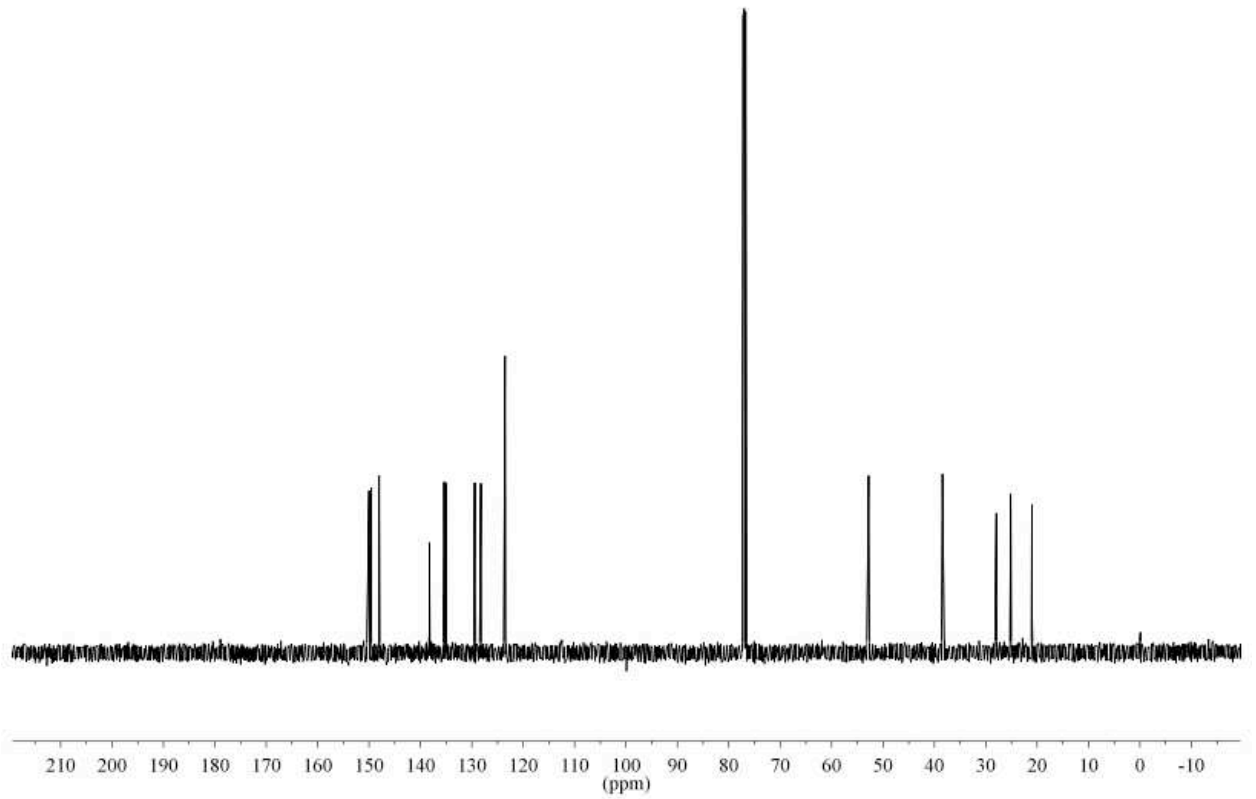




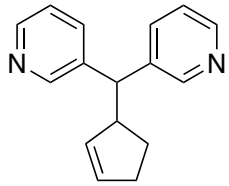
3,3'-(cyclohex-2-en-1-ylmethylene)dipyridine (10a)

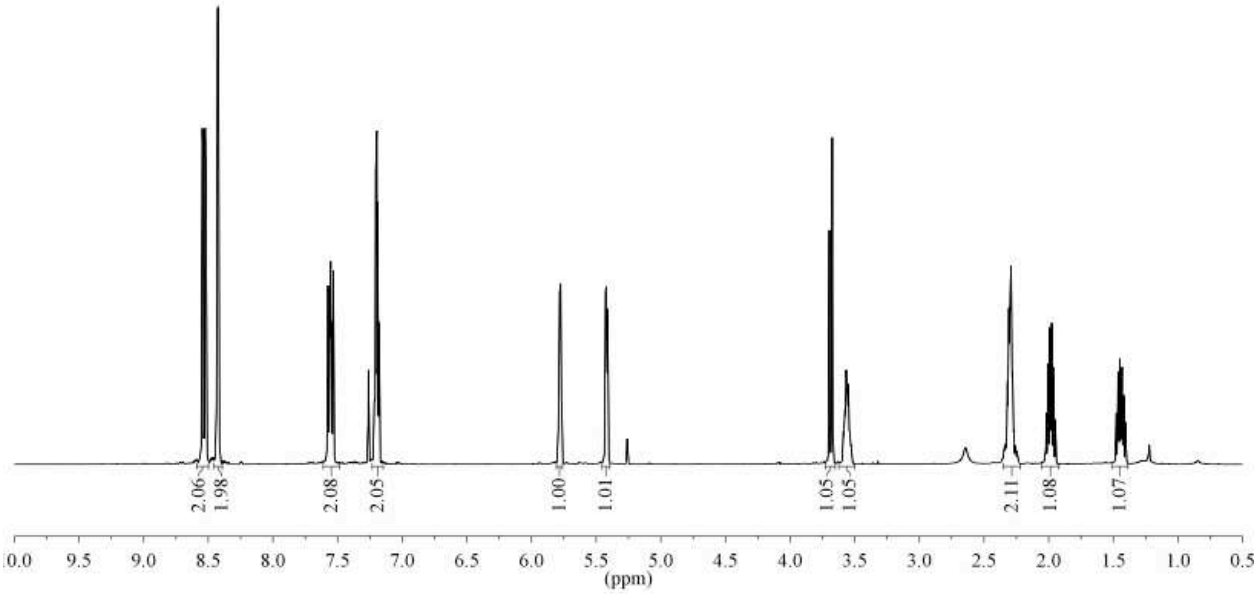


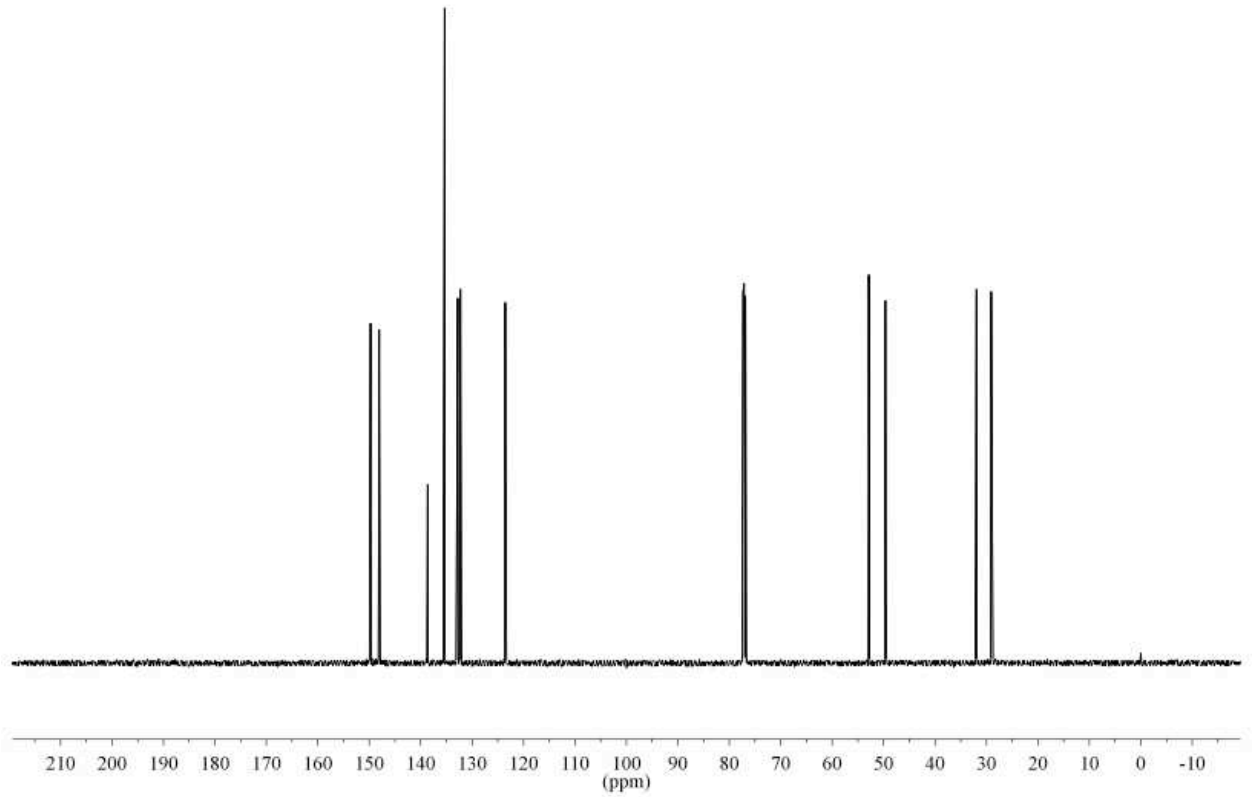




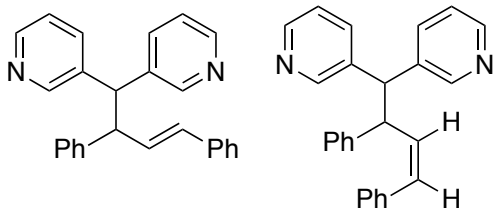
3,3'-(cyclopent-2-en-1-ylmethylene)dipyridine (10b)



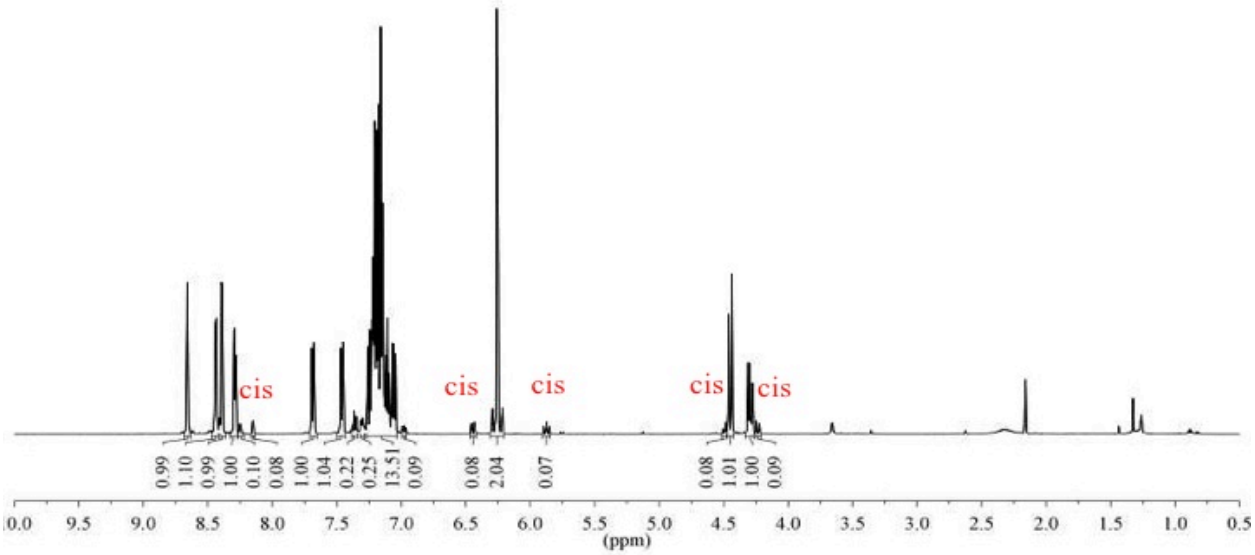


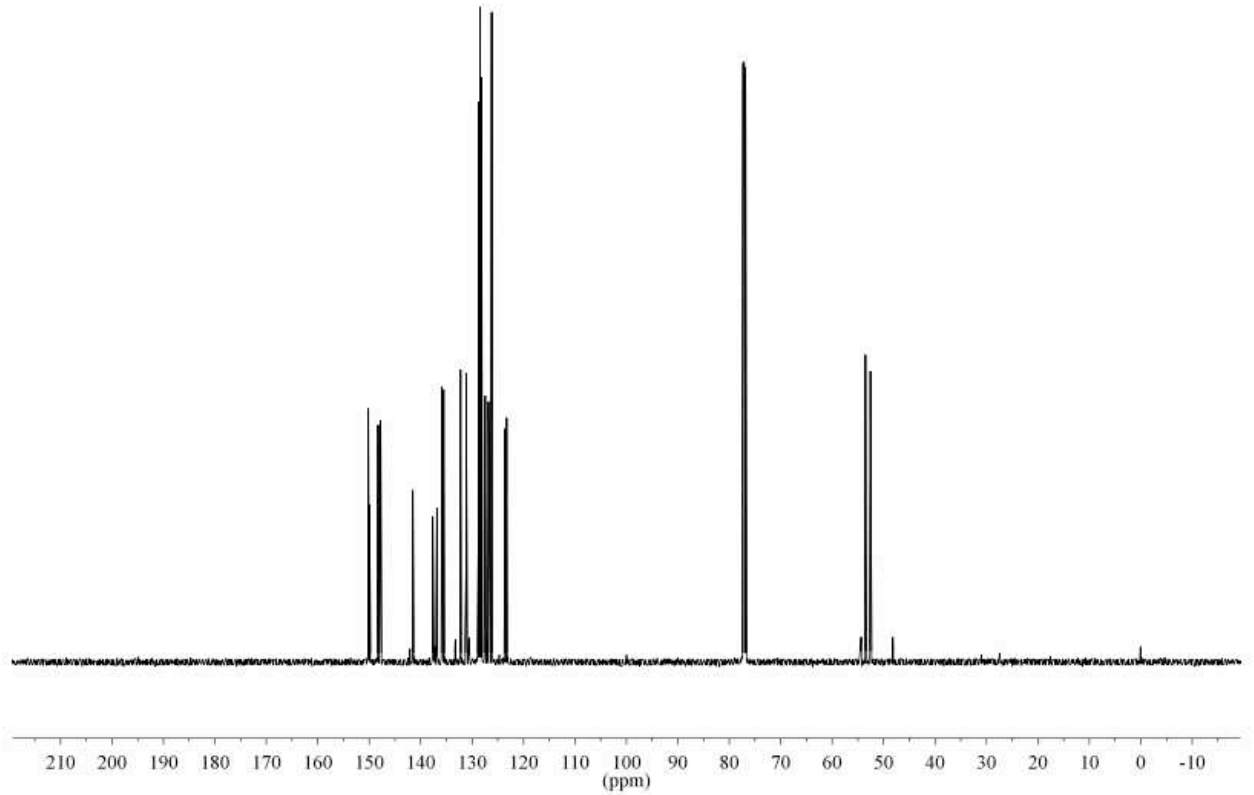


(*E*)-3,3'-(2,4-diphenylbut-3-ene-1,1-diyl)dipyridine (10c)

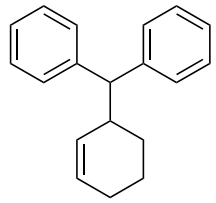


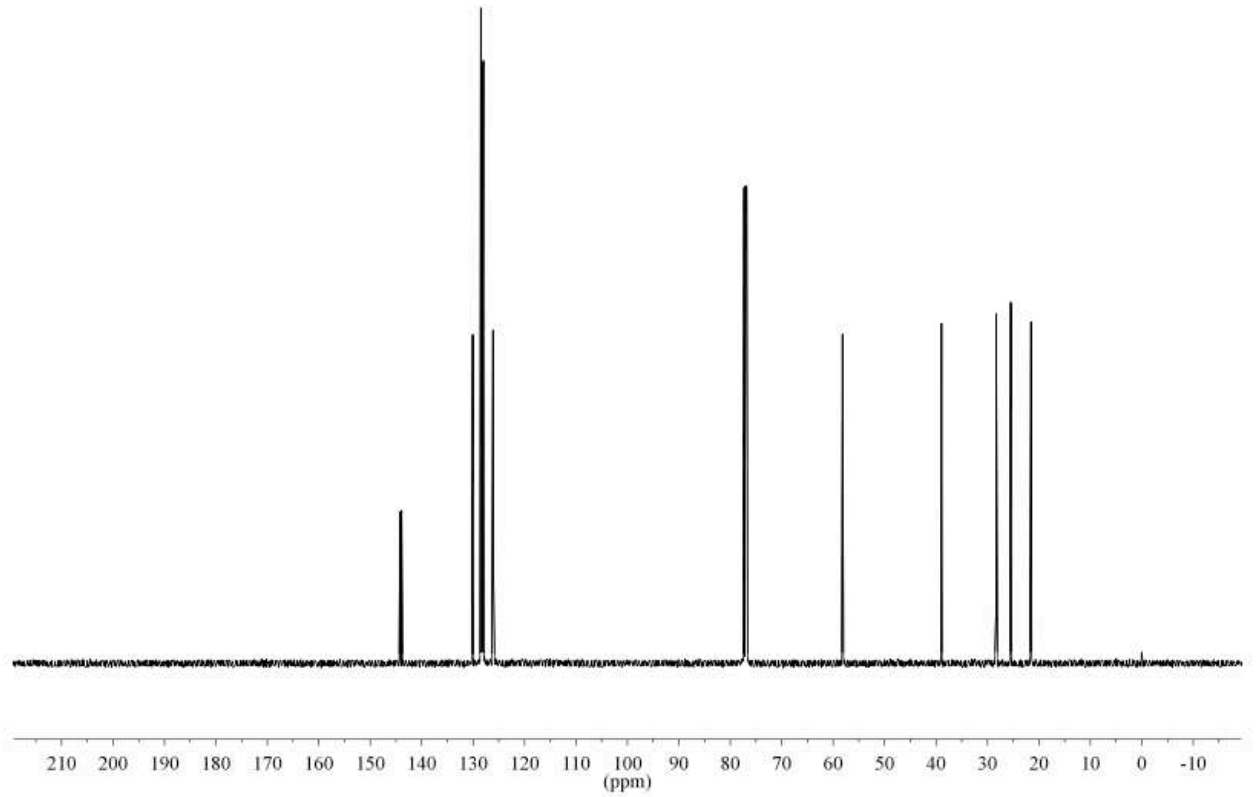
(*trans*:*cis*=10:1)



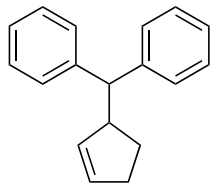


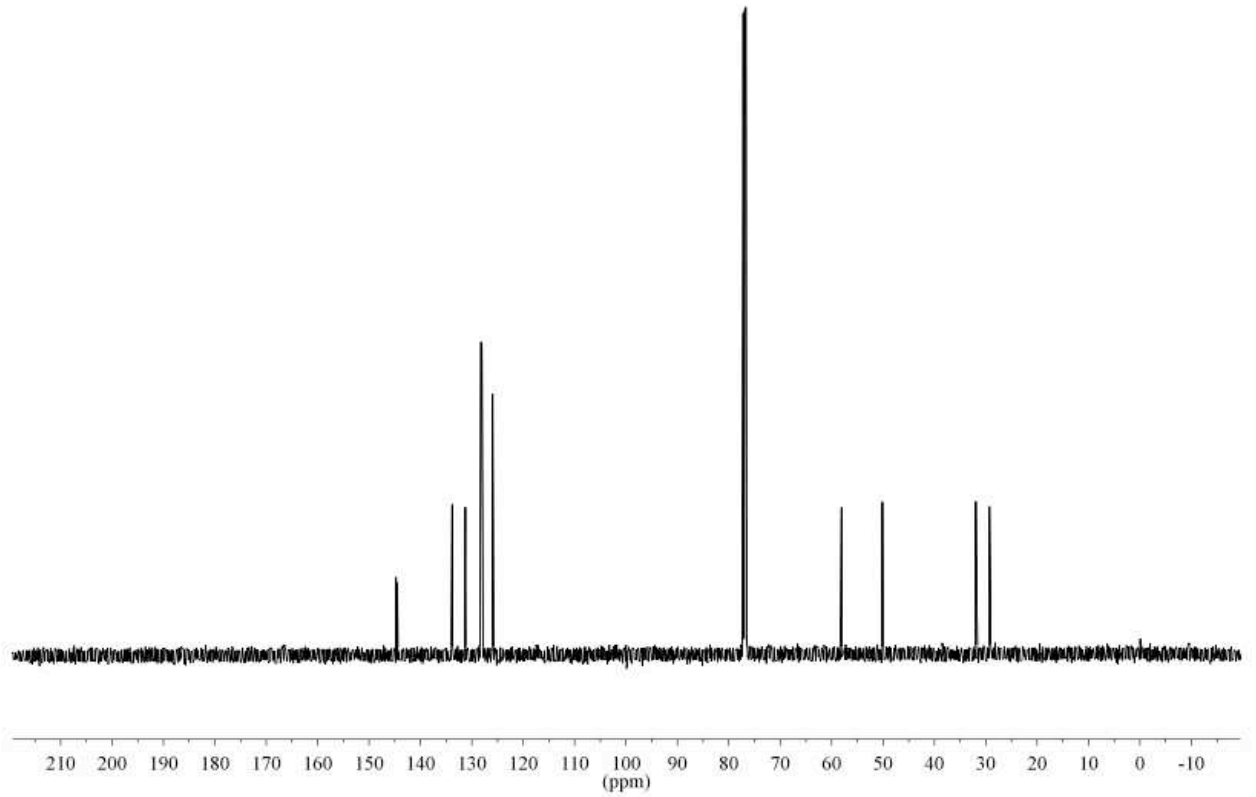
(cyclohex-2-en-1-ylmethylene)dibenzene (10d)



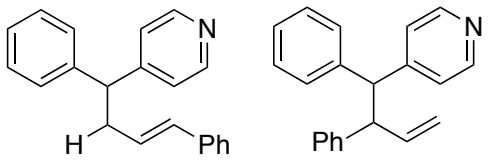


(cyclopent-2-en-1-ylmethylene)dibenzene (10e)



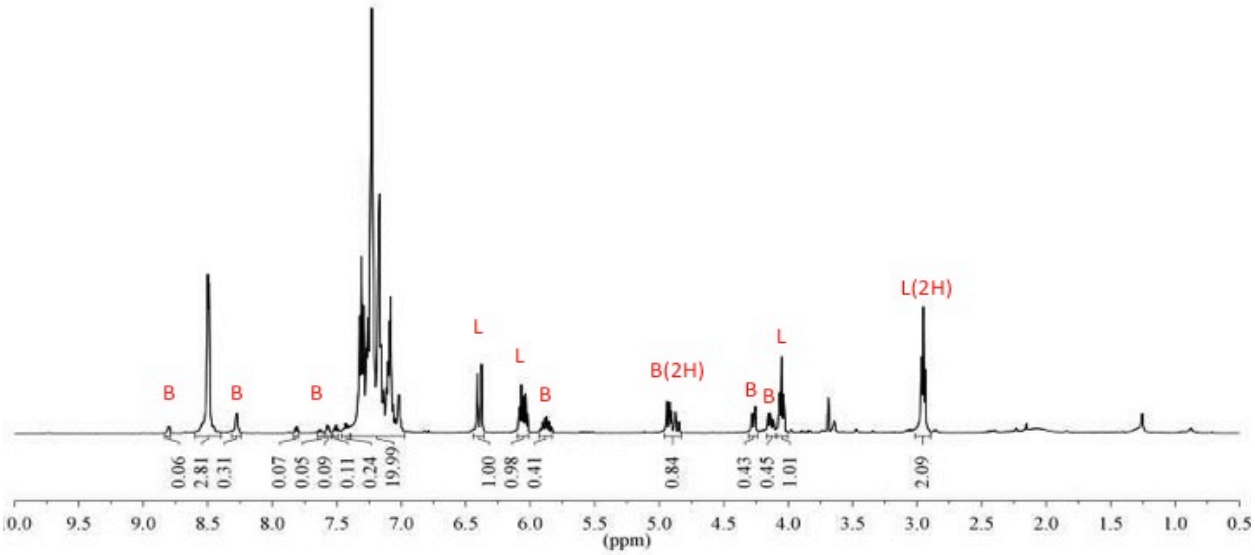


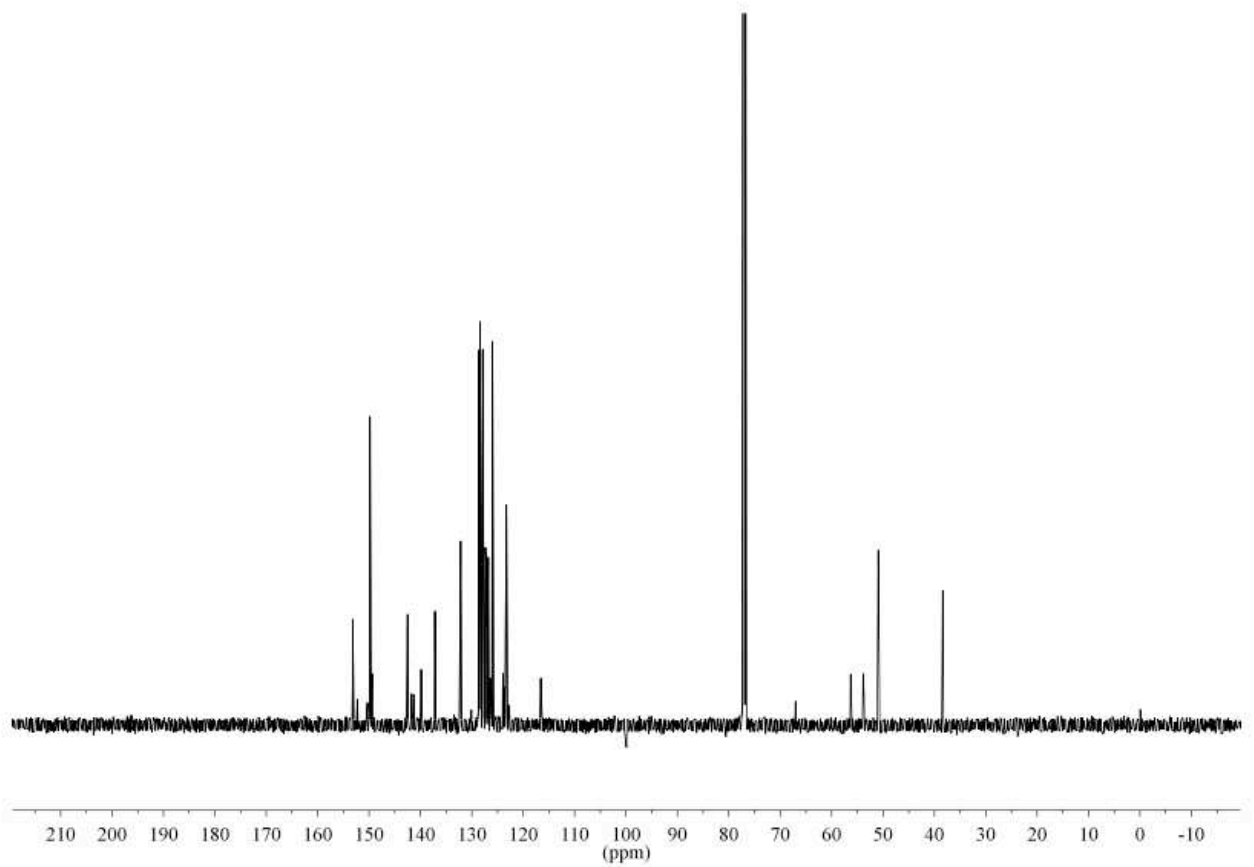
(*E*)-4-(1,4-diphenylbut-3-en-1-yl)pyridine (10f)



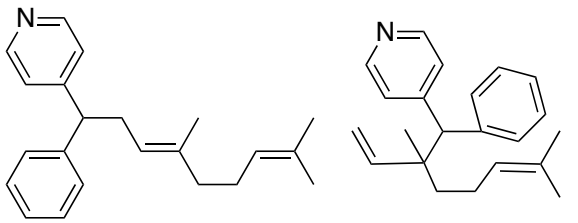
L=linear B=branched (diastereomers)

(linear:branched = 2.6:1)



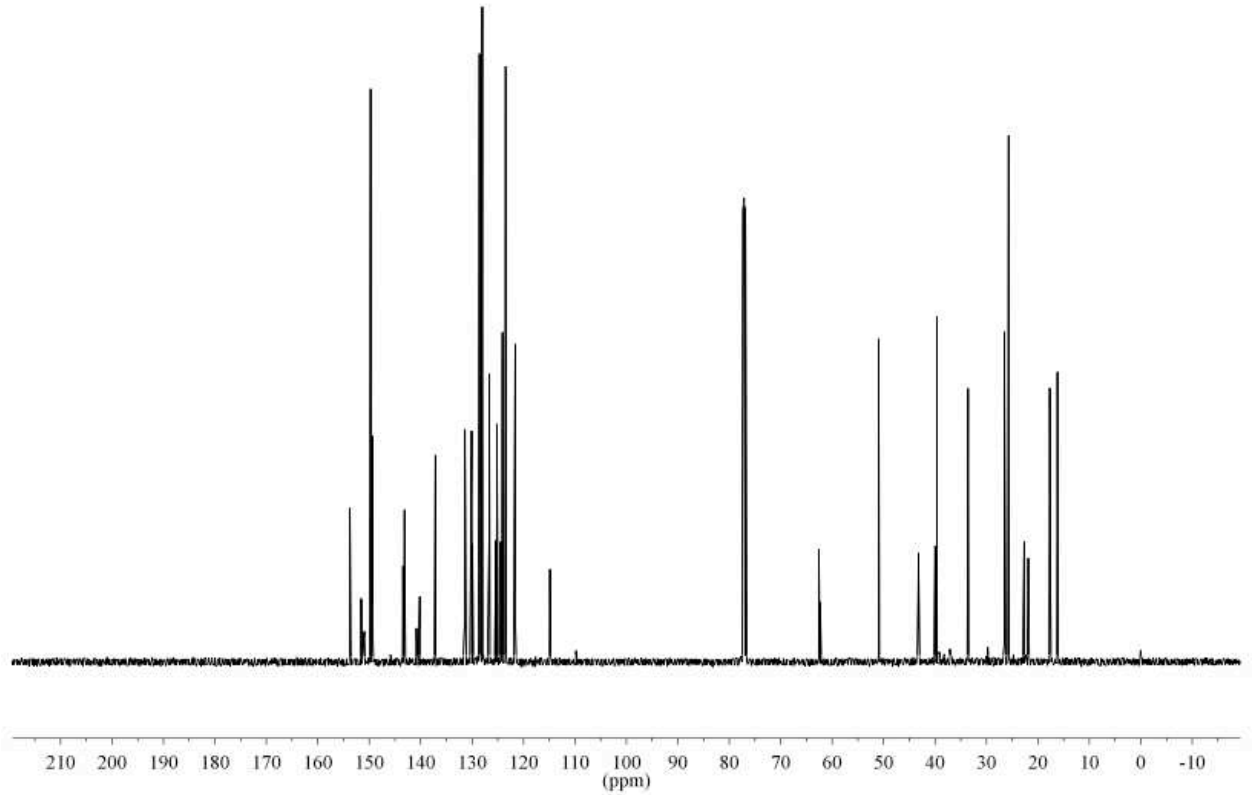


(*E*)-4-(4,8-dimethyl-1-phenylnona-3,7-dien-1-yl)pyridine (10g)

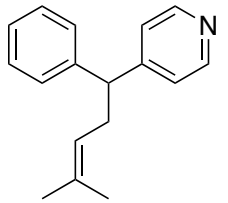


L=linear B=branched (diastereomers)

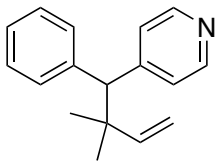
(linear:branched = 1.9:1)



4-(2,2-dimethyl-1-phenylbut-3-en-1-yl)pyridine (10h')

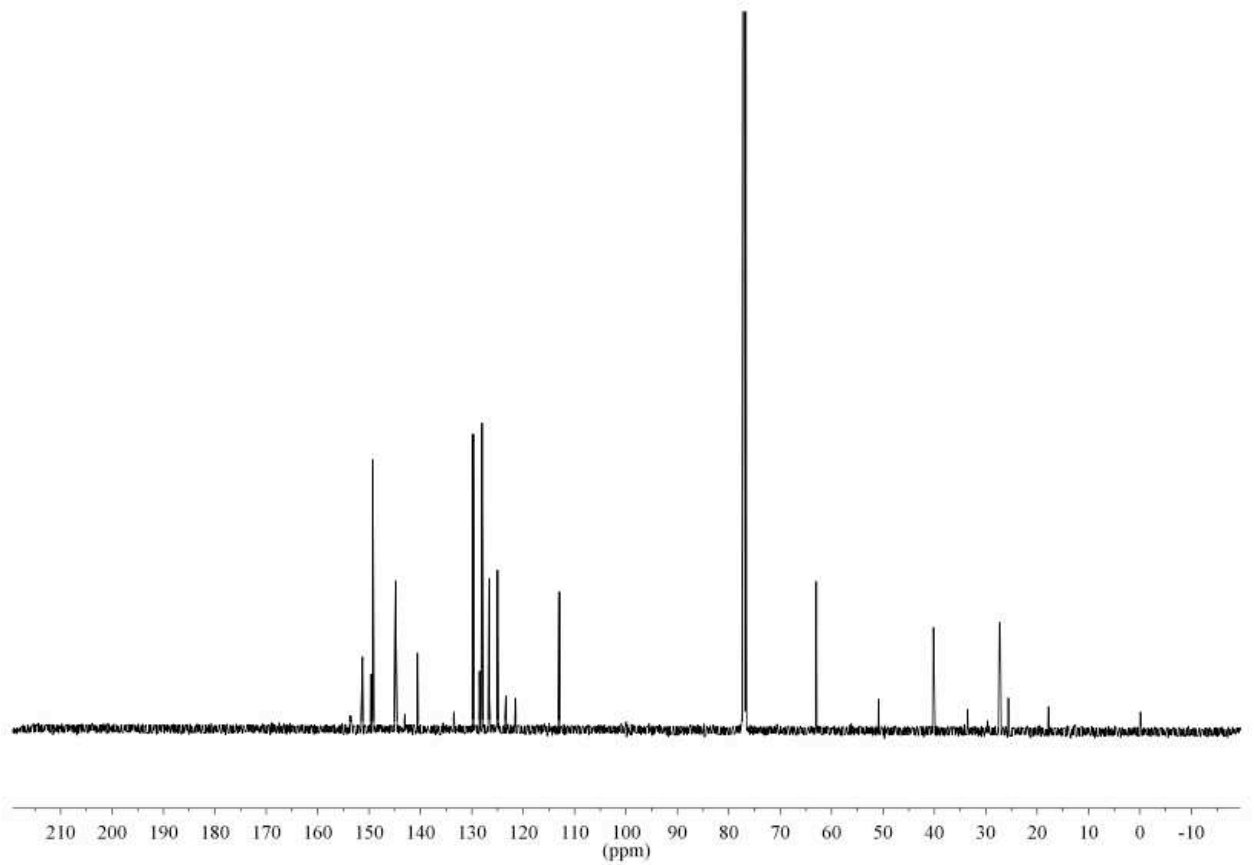


L=linear

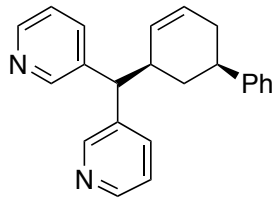


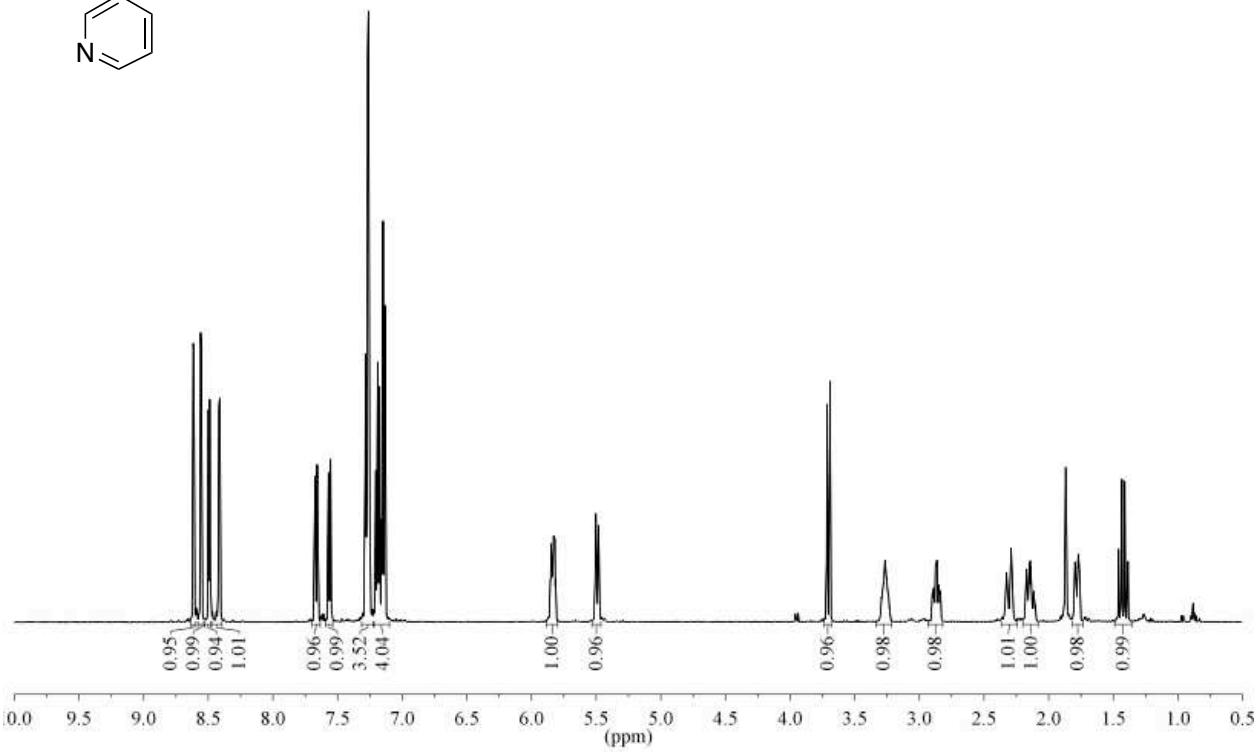
B=branched

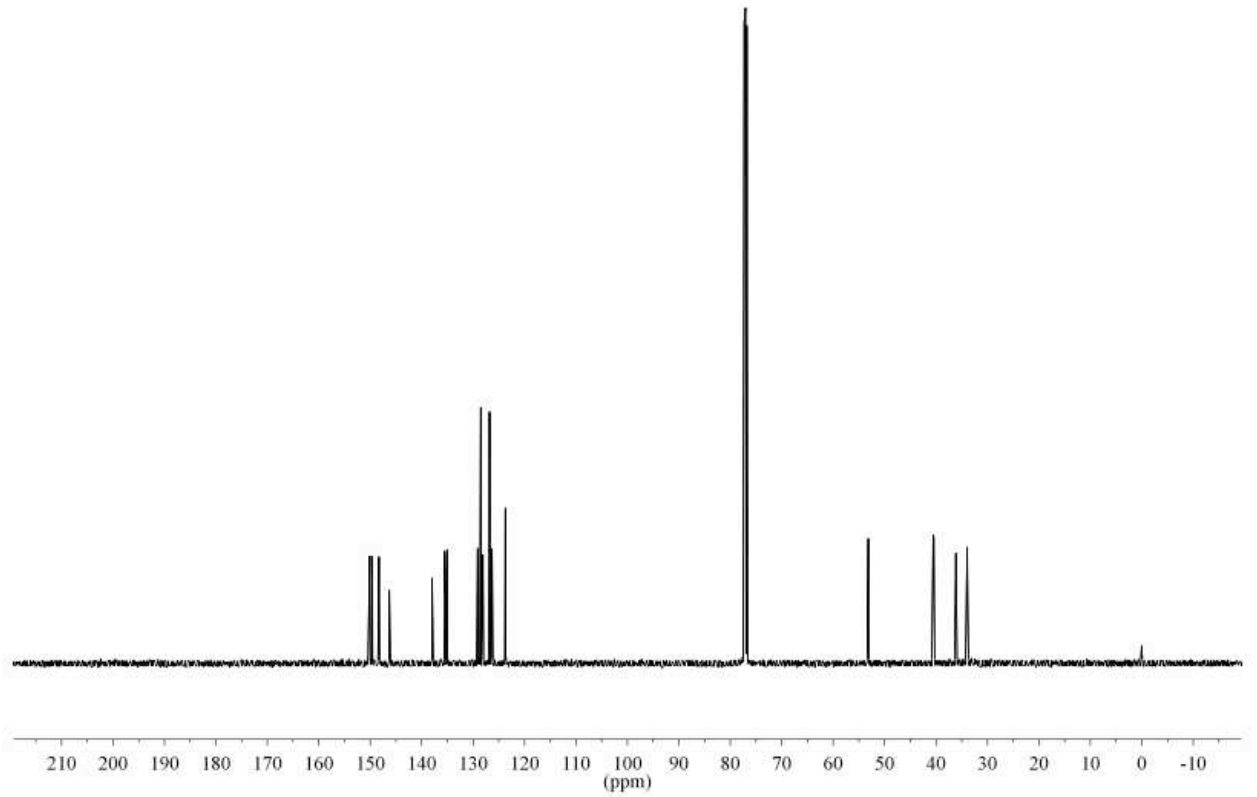
(linear:branch = 1:4.5)



3,3'-(((1*R*,3*R*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)methylene)dipyridine (11a)







(1*R*,3*R*)-3-benzhydryl-1,2,3,6-tetrahydro-1,1'-biphenyl (11b)