Organic Super-Electron-Donors: Initiators in Transition Metal-Free Haloarene-Arene Coupling

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Supplementary Information

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Experimental Section

NMR spectra were obtained using a Bruker AV 400 spectrometer. ^{1}H-NMR spectra were obtained at 400.03 MHz and ^{13}C-NMR spectra were obtained at 100.59 MHz using broadband decoupled mode. Experiments were carried out using deuterated chloroform ($CDCl_3$) as solvent except where otherwise indicated. Chemical shifts are reported in parts per million (ppm) and coupling constants *J* are reported in Hertz (Hz). The following abbreviations are used to denote peak multiplicities: s, singlet; d, doublet; dd, doublet of doublets t, triplet; td, triplet of doublets; m, multiplet.

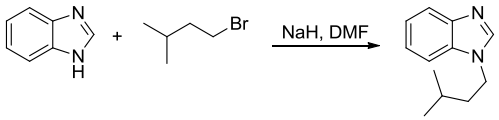
GC-MS data were recorded using an Agilent Technologies 7890A GC System coupled to a 5975C inert XL EI/CI MSD detector. Separation was performed using a DB5MS-UI column (30m x 0.25mm x 0.25µm) at a temperature of 320 ^{o}C with helium as the carrier gas. Positive Chemical Ionisation (PCI+) was used with methane as the ionization gas and a voltage of 952.941V.

High resolution mass spectrometry was performed at the University of Wales, Swansea in the EPSRC National Mass Spectrometry Centre. Accurate mass was obtained using nanospray ionisation (NSI) with a QUATTRO mass spectrometer.

Microwave reactions were carried out using a CEM Discover® SP instrument at 160^{o}C for 10 min. Potassium *tert*-butoxide (97%) and potassium carbonate were purchased from Alfa Aesar; pyridine, benzyl bromide and *N,N*-dimethylformamide were obtained from Sigma Aldrich.

Preparation of 3,3'-(propane-1,3-diyl)bis(1-isopentyl-1H-benzo[d]imidazol-3-ium) iodide 21

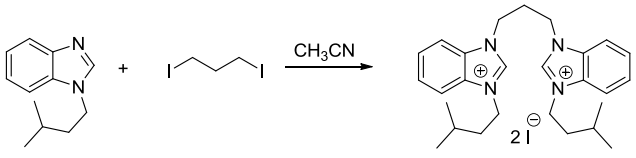
(a) Synthesis of 1-isopentyl-1H-benzo[d]imidazole



Sodium hydride (4.8 g, 60 % in mineral oil, 120 mmol) was washed with dry hexane and the hexane was removed. The remaining solid was suspended in DMF (30 mL). A solution of benzimidazole (11.8 g, 100 mmol) in DMF (60 mL) was added, via a cannula, dropwise under argon, while the reaction vessel was cooled in an ice-water bath. The mixture was stirred at room temperature for 1 h and cooled in an ice water bath. 3-Methyl-1-bromobutane (16.61 g, 110 mmol) was added dropwise via a syringe, and then the mixture was stirred at room temperature for 15 h. The reaction was quenched by adding brine (250 mL) and extracted with ethyl acetate (300 mL). The organic phase was washed with water, dried over sodium sulfate, filtered and concentrated. The product was purified by chromatography using DCM/MeOH (94/6) as the eluent to afford 1-isopentyl-1H-benzo[d]imidazole as a pale yellow oil, (18.15 g, 96 %).

^{1}H NMR($CDCl_3$, 400MHz) δ_H 1.0 (6H, d, J = 6.4 Hz, 2 x CH_3), 1.58-1.68 (1H, m, CH), 1.77-1.82 (2H, m, CH_2), 4.19 (2H, t, J = 7.4 Hz, CH_2), 7.27-7.33 (2H, m, Ar-H), 7.41 (1H, d, J = 8.0 Hz, Ar-H), 7.81-7.84 (1H, m, Ar-H), 7.91 (1H, s, Ar-H); ^{13}C NMR($CDCl_3$, 100MHz) δ_C 21.8, 25.1, 38.1, 42.8, 109.1, 119.9, 121.5, 122.3, 133.3, 142.3, 143.3. Found: (FTMS) 189.1384, $C_{12}H_{17}N_2$ $(M+H)^+$ requires 189.1386.

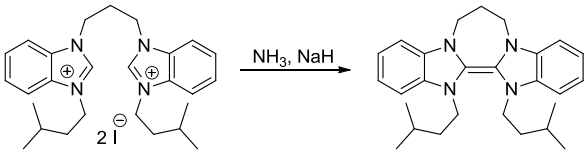
(b) Preparation of 3,3'-(propane-1,3-diyl)bis(1-isopentyl-1H-benzo[d]imidazol-3-ium) iodide 21



A solution of 1-isopentylbenzimidazole (9.0 g, 47.87 mmol) and 1,3-diiodopropane (6.52 g, 22.0 mmol) in acetonitrile 50 mL was refluxed for 15 h. The mixture was cooled

to room temperature, filtered and the solid was dried under vacuum to afford the desired product **21** as a white solid (13.6 g, 92%). M.pt.: >300˚C, (dec.). ^{1}H NMR($CDCl_3$, 400MHz) δ_H 1.0 (12H, d, J = 6.4 Hz, CH_3), 1.58-1.68 (2H, m, CH), 1.77-1.82 (4H, m, CH_2), 4.19 (4H, t, J = 7.4Hz, CH_2), 7.27-7.33 (4H, m, ArH), 7.41 (2H, d, J = 8.0 Hz, ArH), 7.81-7.84 (2H, m, ArH), 7.91 (2H, s, ArH); ^{13}C NMR($CDCl_3$, 125MHz) δ_C 22.7, 25.6, 28.5, 37.5, 44.6, 45.8, 114.1, 114.2, 114.3, 127.1, 131.6, 142.6. Found: (FTMS) 545.2123; $C_{27}H_{38}N_4I$ $(M-I)^+$ requires 545.2136.

Preparation of 14,15-diisopentyl-7,8,14,15-tetrahydro-6H-benzo[4,5]imidazo-[1,2-a]benzo[4,5]-imidazo[2,1-c][1,4]diazepine 22



21 **22**

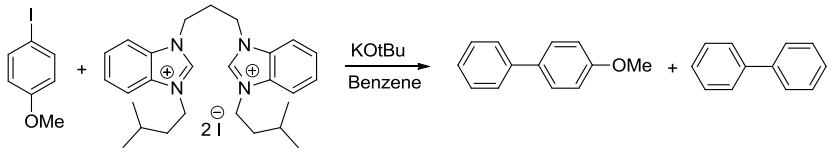
A mixture of 3,3'-(propane-1,3-diyl)bis(1-isopentyl-1H-benzo[d]imidazol-3-ium) iodide **21** (5.0 g, 7.44 mmol) and NaH (oil free, 1.07 g, 44.6 mmol) was stirred at room temperature under argon in a 250 mL Schlenk flask, with a dry ice condenser on top. With a constant flow of argon, ammonia gas was introduced. A total of 150 mL of liquid ammonia was condensed into the flask, and the yellow suspension was stirred at room temperature (with ammonia refluxing) for 5 h. The ammonia was evaporated and the residue was sealed with a septum and transported into glove box. The solid residue was extracted with dry ether, filtered, and concentrated to give product **22** as a yellow solid, (2.25 g, 72 %). ^{1}H NMR (C_6D_6, 500MHz) δ_H 0.83 (12H, d, J = 6.3Hz, CH_3), 1.50-1.61 (8H, m, CH + CH_2), 3.26 (4H, t, J = 5.7 Hz, CH_2), 3.59 (4H, t, J = 7.5 Hz, CH_2), 6.44-6.46 (2H, m, ArH), 6.70-6.72 (2H, m, ArH), 6.85-6.91 (4H, m, ArH); ^{13}C NMR (C_6D_6, 125 MHz) δ 22.4, 26.0, 28.7, 34.4, 44.8, 47.8, 106.3, 109.5, 119.6, 120.8, 128.1, 140.9, 142.1.

Typical procedure for cross coupling of benzene and aryl iodide:

To a 15mL Ace Pressure Tube was added aryl iodide, KOtBu (amounts specified in reactions), some additive (specified in reactions) and dry benzene (dried by refluxing with potassium and distilled under N_2). The mixture was sealed in a glove box, exported to a fumehood and heated to the specified temperature behind a safety shield. After the reaction was finished, the mixture was cooled to room temperature and treated with 1N

HCl (40 mL). The mixture was extracted with a mixture of diethyl ether and hexane (1:1 mixture, 50 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The crude product was purified by chromatography.

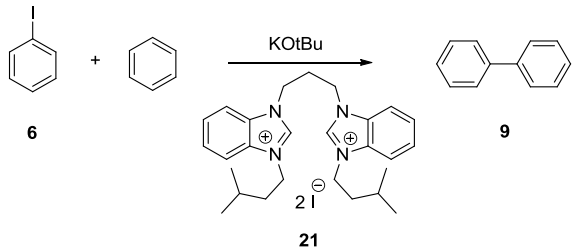
Reactions of *p*-iodoanisole



25 **21** **26** **9**

4-Iodoanisole **25** (234 mg, 1.0 mmol) KOtBu (224 mg, 2.0 mmol), salt **21** [1,1'-(propane-1,3-diyl)bis(3-isopentyl-1H-benzo[d]imidazol-3-ium) diiodide], (40mg, 0.05mmol, 5 mole%) were heated in benzene (10 mL) at 130 ^{o}C for 15 h; Chromatography [hexane → hexane/diethyl ether (100/3)] afforded 4-methoxy-1,1'-biphenyl **26** (146 mg, 79%) and biphenyl **9** (3 mg, 2%).

Reactions of iodobenzene in presence of Salt 21.



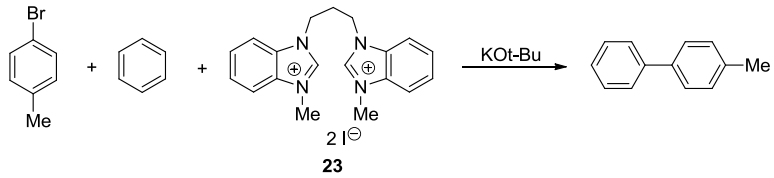
6 **9**

21

(i) Iodobenzene **6**, (204mg, 1.0mmol), KOtBu, (4.0 mmol, 450 mg) and salt **21** [1'-(propane-1,3-diyl)bis(3-isopentyl-1H-benzo[d]imidazol-3-ium) diiodide], (160 mg, 0.2 mmol, 20 mole%) were reacted in benzene, (10 mL), at 180˚C for 5 h. Chromatography (hexane) afforded biphenyl **9** (126 mg, 82%).

(ii) Repeating the reaction (same scale) at 130˚C for 3.5 h, with 5 mole% salt **21** afforded biphenyl **9** (111 mg, 72%).

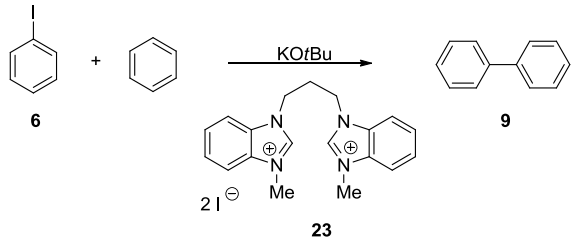
Reaction of 4-bromotoluene with salt 23



23

The mixture of 4-bromotoluene (171mg, 1.0mmol), benzene (10mL), 1,1'-(propane-1,3-diyl)bis(3-methyl-1H-benzo[d]imidazol-3-ium) diiodide **23** (28mg, 0.2mmol) and potassium *tert*-butoxide (224mg, 2.0mmol) was sealed in a 15mL pressure tube inside a glovebox. The mixture was heated to 185˚C for 2.5 h, cooled to room temperature, and quenched with water (30mL). The mixture was extracted with diethyl ether + hexane (15mL + 15mL), the organic layer was dried over sodium sulfate. Filtration and concentration gave a residue, which was purified by column chromatography (hexane). 4-Methyl-1,1'-biphenyl was obtained as solid, (5mg, 3%).

Varying the concentrations of Salt 23.



6 **9**

23

Iodobenzene **6** (204 mg, 1.0 mmol), KO*t*Bu, (3.0 mmol, 336 mg), salt **23**, 1,1'-(propane-1,3-diyl)bis(3-methyl-1H-benzo[d]imidazol-3-ium) diiodide (amounts as below) (*29*) were heated in benzene, (10 mL) at 180˚C for 6 h. Chromatography (hexane) afforded biphenyl **9** in yields as below (three reactions were run with this additive):

- Biphenyl **9** (100 mg, 65%) [when salt **23**, (56 mg, 0.1mmol, 10 mole%) was used]
- Biphenyl **9** (103 mg, 67%) [when salt **23**, (28 mg, 0.05mmol, 5 mole%) was used],
- Biphenyl **9** (113 mg, 73%) [when salt **23**, (5.6 mg, 0.01mmol, 1 mole%) was used].

Varying the temperature

- The mixture of iodobenzene **6** (204mg, 1.0mmol), benzene (10mL), 1,1'-(propane-1,3-diyl)bis(3-isopentyl-1H-benzo[d]imidazol-3-ium) diiodide **21**

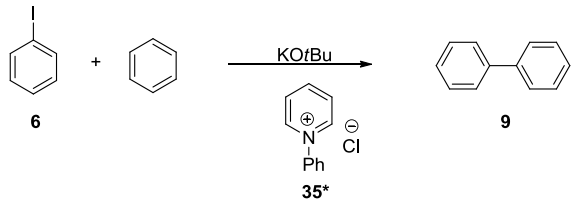
(40mg, 0.05mmol) and KO*t*Bu (224mg, 2.0mmol) was sealed in a 15mL pressure tube inside a glovebox. The mixture was heated to 130˚C for 3.5 h, cooled to room temperature, and quenched with water (30mL). The mixture was extracted with diethyl ether + hexane (15mL +15mL), the organic layer was dried over sodium sulfate. Filtration and concentration gave a residue, which was separated by column (hexane). Biphenyl was obtained as white solid, 123mg, 80%.

- The reaction was repeated in same scale at 110˚C for 3.5 hours. The yield of biphenyl was 72mg, 47%. Iodobenzene was recovered, 53mg, 26%.

Reactions in absence of additives.

- The reaction was run <u>without additives</u>. Iodobenzene **6** (204 mg, 1.0 mmol) and KOtBu, (450 mg, 4.0 mmol), were heated in benzene, 10 mL at, 185˚C for 14 h. Chromatography (hexane) afforded biphenyl **9** (74 mg, 48%).
- When the reaction was conducted at 130 ˚C, it afforded biphenyl **9** (46 mg, 30 %).
- When the reaction was conducted at 110 ˚C, it afforded biphenyl **9** (40 mg, 27 %).

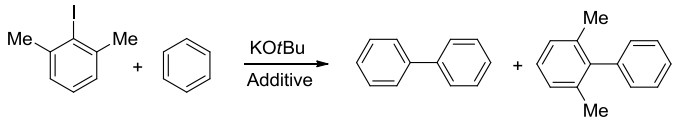
Reactions in presence of *N*-phenylpyridinium chloride (**35***, X = Cl).



6 35* 9

Iodobenzene **6**, (204 mg, 1.0 mmol) and KOtBu, (4.0 mmol, 450 mg) and *N*-phenylpyridinium chloride (**35***, X = Cl). (40 mg, 0.2 mmole) [S1] were reacted in benzene, (10 mL) at 180˚C for 8 h. Chromatography (hexane) afforded biphenyl **9** (104 mg, 68%).

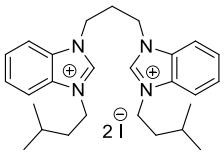
Reactions 2,6-dimethyliodobenzene 44



44 **9** **46**

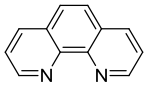
2,6-Dimethyliodobenzene, **44** (116 mg, 0.5 mmol) and KOtBu (224 mg, 2.0 mmol) and the additives indicated below were heated in benzene, (10 mL) at 130˚C for the durations indicated below, affording an inseparable mixture of biphenyl **9** and 2,6-dimethyl-1,1'-biphenyl **46** as listed below. Analysis by ^{1}H NMR indicated that where these products formed, their ratio **9**:**46** was approximately 3.8:1.

High resolution mass analysis on the mixture: Found 154.0778, $C_{12}H_{10}$ requires 154.0777; Found 182.1090, $C_{14}H_{14}$ requires 182.1090.



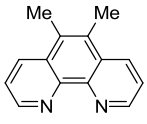
21

- Using salt **21** (79 mg, 20 mole%) as the additive and heating for 22 h led to recovery of **44** (42 mg, 36%) and a mixture of **9** and **46** (19 mg), equating to **9** (14.5 mg, 19%) and **46** (4.5 mg, 5%).



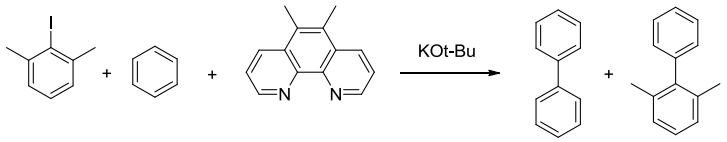
45

- Using phenanthroline **45** (36 mg, 20 mole%) as the additive and heating for 18h led to recovery of **44** (48 mg, 41%) and a mixture of **9** and **46** (19 mg), equating to **9** (14.5 mg, 19%) and **46** (4.5 mg, 5%).



49

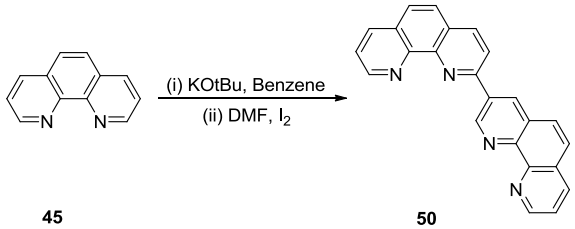
- Using 5,6-dimethylphenanthroline **49** (104 mg, 1 equiv) as the additive and heating for 15 h led to a mixture of **9** and **46** (28 mg), equating to **9** (21 mg, 27%) and **46** (7 mg, 7.7%).



- A mixture of 2,6-dimethyl-1-iodobenzene **44** (232mg, 1.0mmol), benzene (10mL), 5,6-dimethyl-1,10-phenanthroline **49** (42mg, 0.2mmol), and potassium *tert*-butoxide (224mg, 2.0mmol) was sealed in a 15mL pressure tube inside a glove box. The mixture was heated to 130˚C for 18 h, cooled to room temperature, and quenched with 1N HCl (30mL). The mixture was extracted with diethyl ether + hexane (15mL + 15mL), the organic layer was dried over sodium sulfate. Filtration and concentration gave a residue, which was purified by chromatography (hexane). 2,6-Dimethyl-1-iodobenzene **44,** , (71mg, 31%) was isolated as an oil. A mixture of biphenyl **9** and 2,6-dimethyl-1,1'-biphenyl **46**, (35mg) was isolated as a white solid; the molar ratio of biphenyl/2,6-dimethyl-1,1'biphenyl = 3.6/1. Yield of biphenyl is 17%, yield of 2,6-dimethyl-1,1'-biphenyl is 5%.

- When the reactions were repeated (a) with <u>no additive</u> for 22h and (b) with <u>pyridine</u> (1 equiv) as additive for 15h, no reaction was observed.

Preparation of 2,3'-bi(1,10-phenanthroline) 50

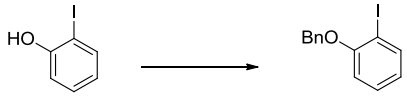


45 50

In a 15 mL Ace Pressure Tube was added 1,10-phenanthroline **45** (180 mg, 1.0 mmol), KOtBu (560 mg, 5.0 mmol) and dry benzene (10 mL). The mixture was sealed in glove box, moved out and heated to 130˚C (oil bath temperature) for 15 h. A deep dark green suspension was obtained. When the mixture was cooled to room temperature, it was

transported into glove box, filtered and washed with benzene. The solid was suspended in dry DMF (8 mL) and iodine (260 mg, 1.0 mmol) was added. The resulting red solution was stirred at room temp. for 2 h in the glove box and quenched with water (150 mL) in a fumehood. The precipitate was filtered, washed with water and dried under vacuum. The dried residue was dissolved in chloroform and purified by chromatography [chloroform/methanol/triethylamine (95/5/2)]. 2,3'-Bi(1,10-phenanthroline) **50** was obtained as a red oil (65mg, 36%). ^{1}HNMR($CDCl_3$, 400MHz) δ_H 7.61 (1H, dd, J = 4.4, 8.3 Hz), 7.64 (1H, dd, J = 4.4, 8.3 Hz), 7.76 (1H, d, J = 8.7 Hz), 7.78 (1H, dd, J = 7.9 Hz), 7.80 (1H, d, J = 8.8 Hz), 7.98 (1H, d, J = 8.8 Hz), 8.22 (1H, dd, J = 1.7, 4.4 Hz), 8.24 (1H, dd, J = 1.72, 4.3 Hz), 8.27 (1H, d, J = 8.4 Hz), 8.35 (1H, d, J = 8.4 Hz), 9.20 (1H, dd, J = 1.7, 4.3 Hz), 9.24 (1H, dd, J = 1.7, 4.3 Hz), 9.42 (1H, d, J = 2.2Hz), 9.84 (1H, d, J = 2.2Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 120.2, 122.6, 125.7, 126.4, 126.7, 127.4, 128.1, 128.5, 128.6, 133.7, 135.12, 135.4, 135.6, 136.7, 145.6, 145.6, 145.8, 145.9, 148.4, 149.8, 149.9, 153.9; Found: 359.1296, $C_{24}H_{15}N_4$ (M+H) requires 359.1297.

Synthesis of 2-(benzyloxy)-iodobenzene 55a:

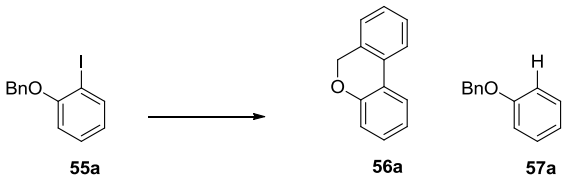


55a

2-Iodophenol (4.0 g, 18.17 mmol) and potassium carbonate (20.09 g, 145.36 mmol) were dissolved in acetone (100 mL). After stirring for 10 min, benzyl bromide (4.0 equiv, 12.43 g, 72.68 mmol) was added and the reaction mixture was stirred at 75 ^{o}C under reflux for 18 h. After cooling to room temperature, the reaction mixture was partitioned between ethyl acetate (50 mL) and water (50 mL). The separated organic phase was washed with two further water portions (2 x 50 mL) and the combined aqueous phases were washed with ethyl acetate (50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous sodium sulfate and concentrated under vacuum to afford the crude product. Purification by chromatography over silica gel using ethyl acetate/petroleum ether (10/90) as the eluent afforded 2-(benzyloxy) iodobenzene **55a** as an orange oil (5.05 g, 16.30 mmol, 89.7%). δ_H (400 MHz, $CDCl_3$): 5.19 (2H, s, CH_2), 6.74-6.78 (1H, td, J = 7.6, 1.3 Hz, ArH), 6.89-6.91 (1H, dd, J = 8.2, 1.2 Hz, ArH), 7.28-7.38 (2H, m, ArH), 7.42-7.46 (2H, m, ArH), 7.53-7.56 (2H, m, ArH), 7.83-7.85 (1H, dd, J = 7.8, 1.6 Hz, ArH). δ_C (100 MHz, $CDCl_3$):

70.4, 86.4, 112.3, 122.4, 126.5, 127.4, 128.1, 128.9, 136.1, 139.1, 156.8 *m/z*: for $C_3H_{11}O^+$ $(M\text{-}I)^+$ expected mass 183.08, observed 183.1

Reaction of 2-(benzyloxy)-iodobenzene 55a under microwave (MW) conditions:



55a **56a** **57a**

2-(benzyloxy)-iodobenzene, **55a** (0.15 g, 0.5 mmol. 1.0 equiv), potassium *tert*-butoxide (0.12 g, 1.0 mmol, 2.0 equiv) and pyridine (4 mL) were added to a microwave tube under argon. The tube was sealed and stirred for 1 min at room temperature to ensure everything was in solution. The reaction mixture was reacted under microwave conditions at 160 ^oC for 10 min and allowed to cool to room temperature. The reaction mixture was partitioned between ethyl acetate (25 mL) and water (25 mL) and acidified with 2N HCl (25 mL) to remove residual pyridine. The organic phase was washed with water (2 x 25mL), brine (25 mL) and dried over anhydrous sodium sulfate and concentrated under vacuum to obtain the crude product. Chromatography over silica gel (pet. ether) afforded a mixture of 6*H*-benzo[c]chromene **56a** and reduced starting material (benzyloxy)benzene **57a**, which co-eluted as a yellow oil. (66 mg): From NMR integrations, this amounts to 6*H*-benzo[c]chromene **56a** (50.3 mg, 56%) and (benzyloxy)benzene **57a** (15.7 mg, 18%) a ratio of 3.23: 1.00 for 6*H*-benzo[c]chromene: (benzyloxy)benzene.

Representative signals due to 6*H*-benzo[c]chromene **56a**:

δ_H (400 MHz, $CDCl_3$): 5.18 (2H, s, CH_2).

m/z for $C_{13}H_9O^+$ $(M\text{-}H)^+$ expected mass 181.06, observed 181.00

Representative signals due to (benzyloxy)benzene **57a**:

δ_H (400 MHz, $CDCl_3$): 5.13 (2H, s, CH_2).

m/z for $C_{13}H_{11}O^+$ $(M\text{-}H)^+$ expected mass 183.08, observed 183.00

Synthesis of 2,6-bis(benzyloxy)-1-iodobenzene 55b:

2-Iodoresorcinol (0.3 g, 1.27 mmol) and potassium carbonate (0.53 g, 3.81 mmol) were dissolved in DMF (15 mL). After stirring for 10 min, benzyl bromide (3.0 equiv, 0.65 g, 3.81 mmol) was added and the reaction mixture was stirred at 80 ^oC for 18 h. After

cooling to room temperature, the reaction mixture was partitioned between ethyl acetate (50 mL) and water (50 mL). The separated organic phase was washed with two further water portions (2 x 50 mL) and the combined aqueous phases were washed with ethyl acetate (50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous sodium sulfate and concentrated under vacuum to afford the crude product. Purification by chromatography over silica gel using ethyl acetate/ pet. ether (90/10) as the eluent afforded 2,6-bis(benzyloxy)-1-iodobenzene **55b** as a white solid (0.392 g, 0.942 mmol, 74.2%) M.Pt. 88-90 ^{o}C (lit. [S2], 90-92 ^{o}C). δ_H (400 MHz, $CDCl_3$): 5.20 (4H, s, CH_2), 6.58 (2H, d, *J* = 8.3 Hz, Ar*H*), 7.21-7.25 (1H, t, *J* = 8.2 Hz, Ar*H*), 7.35-7.39 (2H, m, Ar*H*), 7.45 (4H, td, *J* 7.2, 1.7 Hz, Ar*H*), 7.58 (4H, d, *J* 7.4 Hz, Ar*H*). δ_C (100 MHz, $CDCl_3$): 70.5, 79.0, 105.6, 126.5, 127.4, 128.1, 129.3, 136.3, 158.3. *m/z*: found 417.0346, $C_{20}H_{18}IO_2^+$ $[M+H]^+$ requires 417.0346.

Reaction of 2,6-bis(benzyloxy)-1-iodobenzene 55b under microwave (MW) conditions:

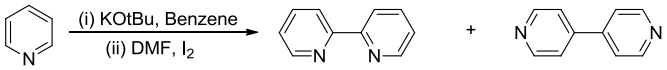
2,6-Bis(benzyloxy)-1-iodobenzene, **55b** (0.21 g, 0.5 mmol. 1.0 equiv), potassium *tert*-butoxide (0.12 g, 1.0 mmol, 2.0 equiv) and pyridine (4 mL) were added to a microwave tube under argon. The tube was sealed and stirred for 1 min at room temperature to ensure everything was in solution. The reaction mixture was reacted under microwave conditions at 160 ^{o}C for 10 min and allowed to cool to room temperature. The reaction mixture was partitioned between ethyl acetate (30 mL) and water (30 mL) and acidified with 2N HCl (10 mL) to remove residual pyridine. The organic phase was washed with water (2 x 30mL), brine (30 mL) and dried over anhydrous sodium sulfate and concentrated under vacuum to obtain the crude product. Chromatography over silica gel (pet. ether) afforded a mixture of 1-(benzyloxy)-6*H*-benzo[c]chromene **56b** and reduced starting material 1,3-bis(benzyloxy)benzene **57b**, which co-eluted as a yellow oil. (34mg): From NMR integrations, this amounts to 1,3-bis(benzyloxy)benzene (21.3mg, 14.6%) **57b** and of 1-(benzyloxy)-6*H*-benzo[c]chromene **56b** (12.7mg, 8.8%), a ratio of 1.67:1.00 for 1,3-bis(benzyloxy)benzene: 1-(benzyloxy)-6*H*-benzo[c]chromene.

Representative signals due to 1-(benzyloxy)-6*H*-benzo[c]chromene **56b**: δ_H (400 MHz, $CDCl_3$): 5.06 (2H, s, C*H*$_2$), 5.25 (2H, s, C*H*$_2$), 6.76 (2H, d, *J* = 8.1 Hz, Ar*H*).

m/z (PCI$^+$) 289.1 [(M+H)$^+$], 317.1 ([M+C_2H_5]$^+$), 329.1 ([M+C_3H_5]$^+$).

Representative signals due to 2,3-dibenzyloxybenzene **57b**: δ_H (400 MHz, $CDCl_3$): 5.09 (4H, s, C*H*$_2$), 6.66 (2H, dd, *J* 8.2, 2.4 Hz, Ar-*H*) 6.70 (1H, t, *J* 2.3 Hz, Ar*H*).
m/z (PCI$^+$) 291.1 ([M_1+H]$^+$), 319.1 ([M+C_2H_5]$^+$), 331.1 ([M+C_3H_5]$^+$).

Synthesis of bipyridines from pyridine.



61 **65**

In an Ace Pressure Tube was added KO*t*Bu (1.0 g, 8.9 mmol) and pyridine (10.0 mL). The mixture was sealed under nitrogen and heated to 180 ˚C for 15 h. The mixture was cooled to room temperature, transported into a glove box, iodine (600 mg, 2.36 mmol) was added and the mixture was stirred for 2 h. The mixture was filtered, and the solid was washed with benzene. The solution was combined and the solvents were removed by rotary evaporator. The residue was washed with $CDCl_3$, the GC-MS showed two peaks with *m/z* 156.
The solution was purified by column chromatography (silica gel), with eluent (DCM → DCM : MeOH :: 100 : 2 → DCM : MeOH : Et_3N :: 100 :3 : 2). Two fractions were obtained with signals due to 2,2'-bipyridine **61** and 4,4'-bipyridine **65** in the aromatic region of the ^{1}HNMR spectrum by comparison with authentic samples. These samples were analysed by GC/MS, with authentic samples as reference and confirmed the formation of bipyridines under the reaction conditions.
First fraction: GC/MS, two peaks at 11.504 min and 12.117 min.
m/z (peak at 11.504 min): 157.0 (M + H, 100 %), 185.0 (M + C_2H_5, 20 %), 197 (M + C_3H_5, 5 %);
m/z (peak at 12.117 min): 157.0 (M+H, 100%), 185.0 (M+C_2H_5, 20%), 197.0 (M+C_3H_5, 5%); High resolution MS of this fraction: [found 156.0680; $C_{10}H_8N_2$ (M) requires 156.0682.

Computational Section

Computational Details

All calculations were performed using Density Functional Theory (DFT) [S3, S4] using the Gaussian 09[S5] software package. All minima (reactants, intermediates, products) and maxima (transition states) were optimized using the M06L [S6, S7] functional with a 6-311G(d,p) [S8-S10] basis set. All reactant and product structures were optimized as their respective complexes. Solvation was modeled implicitly using the Conductor-like Polarizable Continuum Model (CPCM) [S11, S12] for solvents of pyridine (for structures **6**, **33 – 38** and related transition states) and benzene (for structures **6**, **12 – 14**, **33**, **41 – 43**, **51 – 54**, **58 – 60**, **62 – 64** and related transition states). Frequency calculations were performed on all optimized structures in order to characterize minima (zero imaginary frequencies) and maxima (single imaginary frequency). All profiles are plotted using the Gibbs free energy values. GaussView 5.0.8 was used for visualization of structures.

The calculations of the singlet biradical species (see Figure S2) were carried out by initially optimizing the geometries within the triplet state of the electronic structure. Single point calculations using the broken-symmetry formalism of DFT were then carried out on the optimized geometries to obtain the energetics for the reaction on the singlet biradical surface. The calculated S^2 value for each of the singlet states is shown in Figure S2.

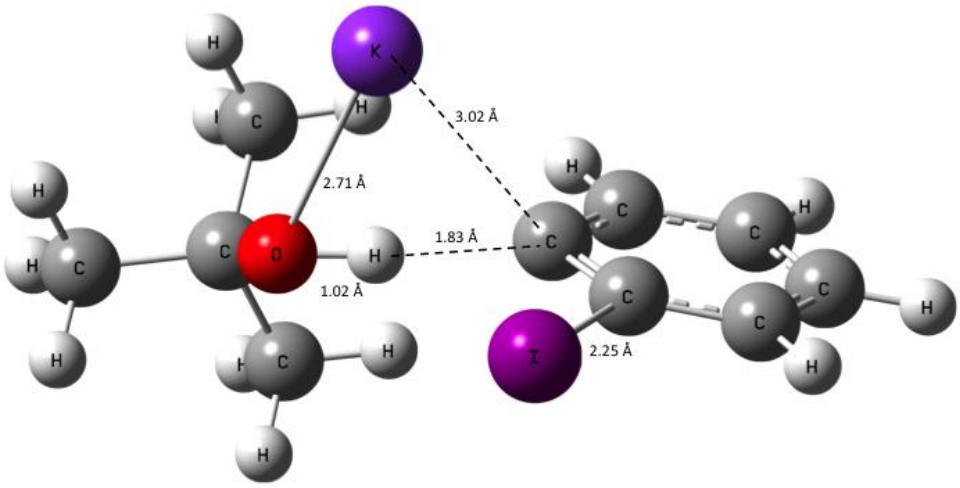


Figure S1: Structure of **I(6-33)**

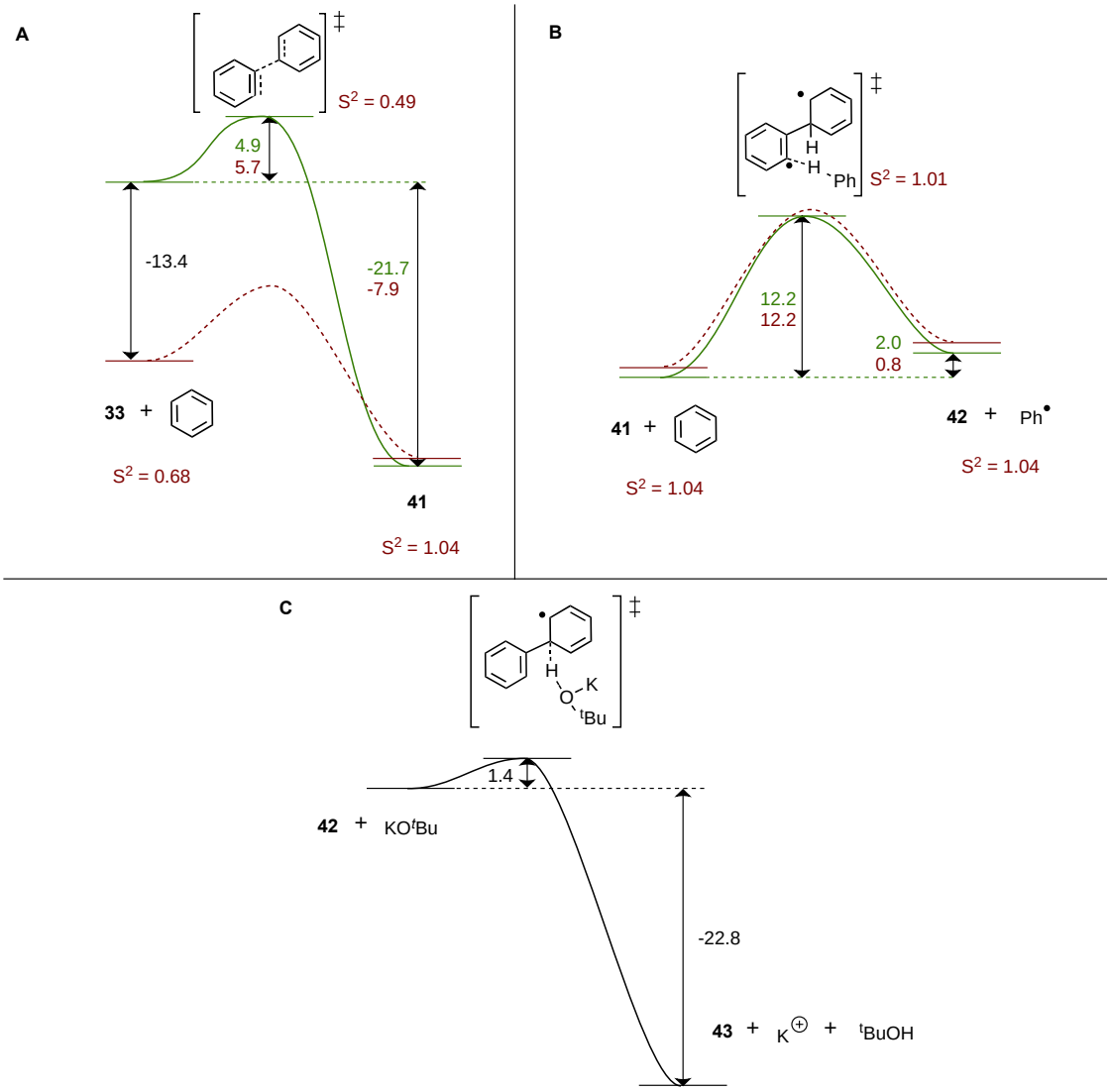


Figure S2: (A) Free energy profile (ΔG, kcal/mole) for the attack of the benzyne triplet (green line) and singlet (red dashed line) biradical on benzene to form the biradical species **41**. **(B)** Free energy profile (ΔG, kcal/mole) for the subsequent reaction of the biradical **41** (singlet energetics shown by the red, dashed line, triplet energetics by the solid green line) with a second molecule of benzene to form the doublet **42** and a phenyl radical. **(C)** Free energy profile (ΔG, kcal/mole) for the formation of the biaryl radical anion **43** from **42**.

Starting from **33**, the singlet biradical state of benzyne is more favourable than the biradical triplet state species by 13.4 kcal/mole (Figure S2A). Reaction of both the biradical singlet and triplet benzyne species proceeds towards via **TS(33-41)** with accessible barriers of 5.7 kcal/mole and 4.9 kcal/mole, respectively. From the transition

state, each reaction pathway leads to the exergonic formation of the biradical **41** (-7.9 kcal/mole for the singlet and -21.7 kcal/mole for the triplet species).

This biradical species **41** is able to abstract a hydrogen atom from a solvent molecule (i.e., benzene). On the singlet and triplet biradical surfaces, the reaction has an equal activation free energy (12.2 kcal/mole, Figure S2B). The resulting biaryl radical (**42**) is formed in an essentially thermoneutral reaction. However, the complex between **42** and the phenyl radical is slightly more stabilized in the singlet configuration than the triplet (ΔΔG = 1.2 kcal/mole, Figure S2B).

The final step of the pathway involves the facile deprotonation of the radical **42** by a molecule of KO^{t}Bu (ΔG* = 1.4 kcal/mole, Figure S2C) in an exergonic reaction (ΔG = -22.8 kcal/mole, Figure S2C) affording the radical anion **43**, complexed to the potassium counterion and *t*BuOH.

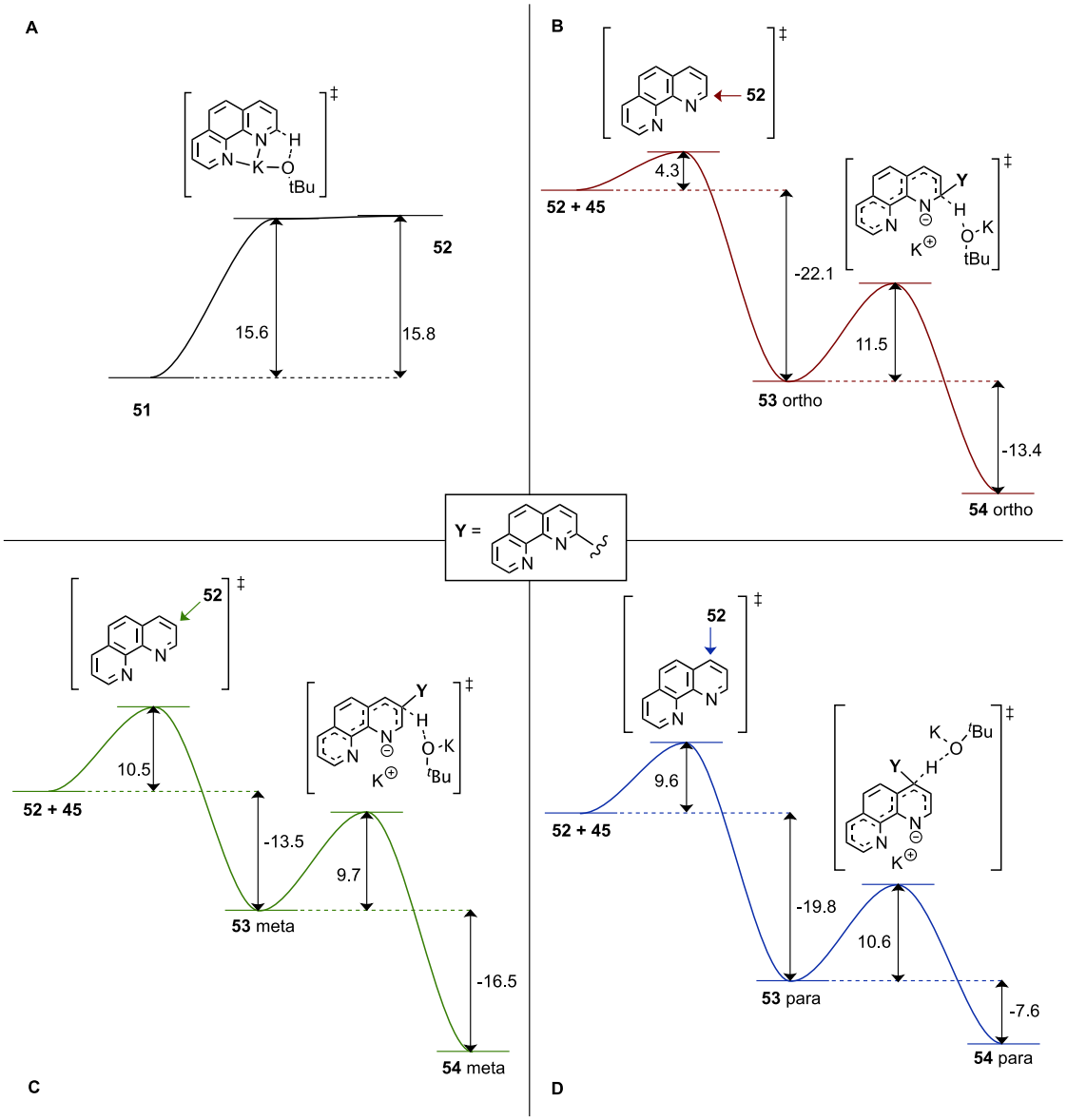


Figure S3: Reaction free energy (ΔG, kcal/mole) profiles for **(A)** the *ortho*-deprotonation of phenanthroline; **(B)** subsequent attack at the *ortho*-position of a second phenathroline molecule; **(C),** subsequent attack at the *meta*-position of a second phenathroline molecule; and **(D)** subsequent attack at the *para*-position of a second phenathroline molecule;

Starting from **51**, an accessible barrier of 15.6 kcal/mole must be overcome to reach the transition state, with **52** being an additional 0.2 kcal/mole uphill from this. As in the case of the formation of benzyne (see main text) **52** is a true minimum on the potential energy surface and is slightly lower in electronic energy (ΔE = 0.01 kcal/mole) than the transition state (**TS(51-52)**). However, the inclusion of the zero-point energy, thermal

contributions and entropy increase the free energy of the intermediate, **52**, to be slightly higher in energy than the transition state. This implies that the reverse reaction, i.e., the formation of **51** from **52**, will occur in a barrierless, exergonic reaction and as such will be strongly favoured. Therefore, the formation of **52**, while kinetically accessible under the reaction conditions, is thermodynamically unfavourable and only trace amounts of **52** will be present *in situ*. However, once **52** is formed it is readily able to interact with a second phenanthroline molecule (**45**) to form the donor **54**.

The nucleophile, **52** is able to add to **45** in any of the *ortho*, *meta* or *para* positions with respect to the nitrogen. For addition to the *ortho* position (Figure S3B) a small barrier of 4.3 kcal/mole must be surpassed in moving towards the *ortho* form of the intermediate **53** which is 22.1 kcal/mole downhill. The subsequent proton abstraction to form the *ortho* donor **54** represents the rate-limiting step in the reaction, with a barrier of 11.5 kcal/mole. The energetics for the addition of the nucleophile (**52**) to **45** in the *para*-position are similar to those for the *ortho*-position. The barrier to the first step is slightly higher (9.6 kcal/mole) than in the *ortho* case, but this step is not rate-limiting. The activation barrier is again the subsequent deprotonation, which occurs with a barrier of 10.6 kcal/mole (ΔG*, Figure 3D).

The formation of the *meta* coupled product is slightly different. The activation barrier for this process is encountered in the initial addition of the **52** to **45**. The free energy barrier for this process is 10.5 kcal/mole (ΔG, Figure S3C), while the relative free energy of the transition state corresponding to the subsequent proton abstraction is lower in energy at 9.7 kcal/mole (Figure S3C). Based on the calculated activation barriers, we would expect that the relative preference of the isomers to be *meta* ~ *para* > *ortho*.

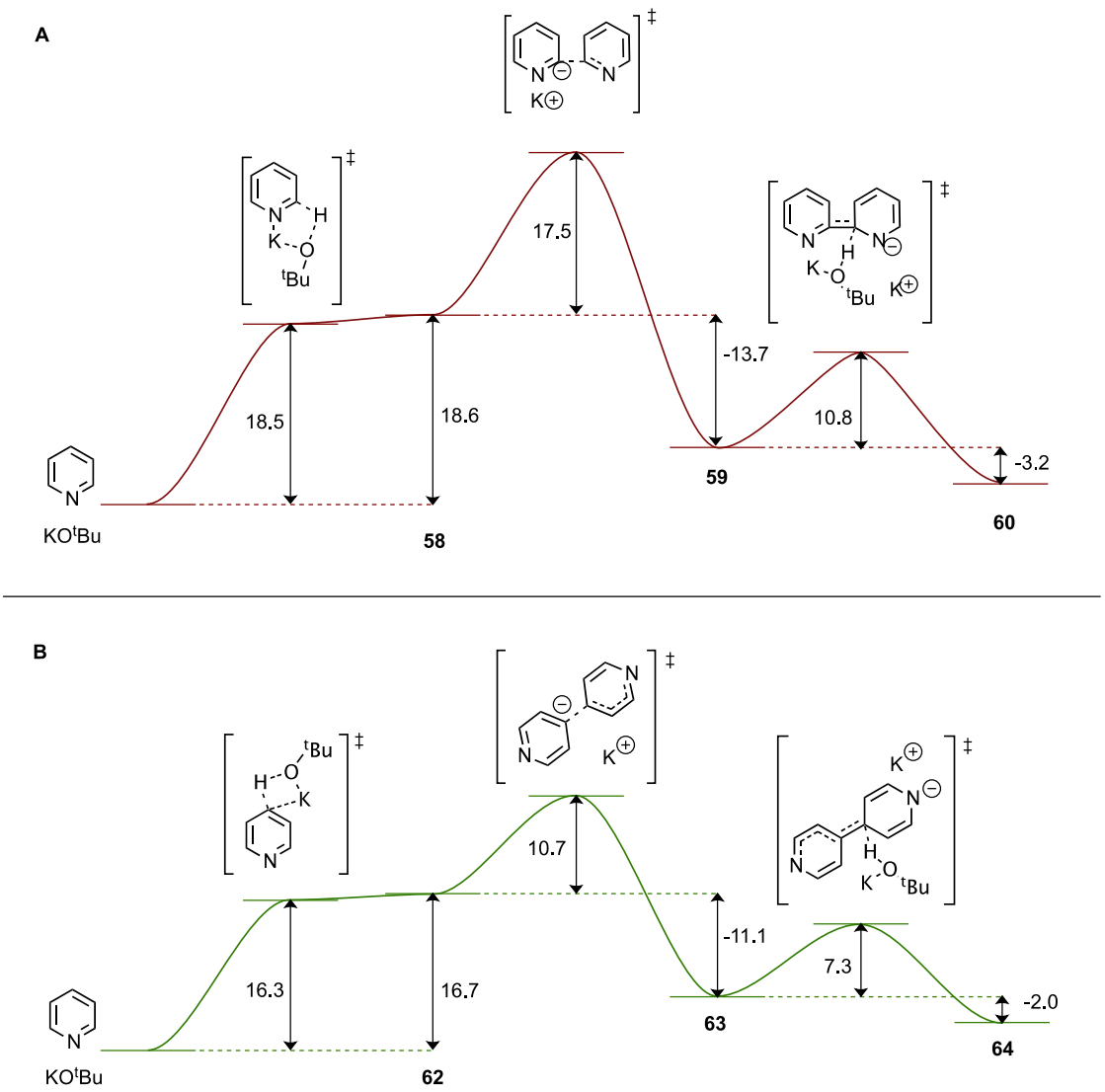


Figure S4: Reaction free energy (ΔG, kcal/mole) profiles for the formation of the donor species **(A) 60;** and **(B) 64** from pyridine and KO*t*Bu.

The deprotonation of pyridine via KO*t*Bu in the *ortho* or *para* positions is shown in Figure S4. The deprotonation step occurs with an activation barrier of 18.5 kcal/mol (*ortho*, Figure S4A) 16.3 kcal/mole (*para*, Figure S4B). As discussed in the case of phenanthroline (**51** → **52**) the products of these reactions (**58** and **62**) are both energetically uphill, relative to their transition states on the free energy surface, 0.1 kcal/mole (*ortho*) and 0.4 kcal/mole (*para*).

Following the initial deprotonation of pyridine to form **58**, nucleophilic attack onto the *ortho*-position of a second pyridine molecule has an activation energy of 17.5 kcal/mole. The intermediate **59** is formed in an exergonic reaction that is 13.7 kcal/mole lower in

energy than **58** (Figure S4A). The analogous step along the *para* pathway results in the formation of **63.** Nucleophilic attack by **62** at the *para*-position of a molecule of pyridine has an activation energy of 10.7 kcal/mol (Figure S4B). The intermediate **63** is 11.1 kcal/mole (ΔG, Figure S4B) below **62**.

The final step for the formation of these bipyridine based donors occurs through abstraction of a proton from structures **59** and **63** by a molecule of KO*t*Bu. Abstraction of the *ortho* proton occurs with a barrier of 10.8 kcal/mole (Figure S4A), while abstraction of the *para* proton has an activation free energy of 7.3 kcal/mole (Figure S4B). In both cases, this step of the reaction is exergonic (ΔG = -3.2 kcal/mole, *ortho*, Figure S4A; ΔG = -2.0 kcal/mole, *para*, Figure S4B) relative to the preceding intermediates. Based on the calculated barriers along these two reaction pathways we would expect the *para,para* > *ortho,ortho* for the bipyridine donors.

Coordinates for optimised geometries of all species mentioned in the text in XYZ format.

6

C	-1.246813	-1.211676	-0.000010
C	-0.564881	0.000006	0.000017
C	-1.246821	1.211685	-0.000007
C	-2.638144	1.203309	0.000003
C	-3.334931	-0.000007	-0.000011
C	-2.638141	-1.203313	0.000008
H	-0.704216	-2.148210	-0.000027
H	-0.704225	2.148220	-0.000018
H	-3.174723	2.144416	0.000037
H	-4.417860	-0.000002	-0.000023
H	-3.174703	-2.144431	0.000041
I	1.550832	0.000000	0.000000

12a

C	1.763775	3.457125	0.007938
C	3.009784	2.882251	-0.016306
C	3.125930	1.478640	-0.017305
C	1.936001	0.723147	0.007867
C	0.638562	2.615228	0.032460
C	4.400770	0.818584	-0.043167
C	2.021777	-0.728832	0.006996
C	3.292903	-1.337881	-0.019508
C	4.480752	-0.531103	-0.044325
C	3.344619	-2.745481	-0.020216
H	4.308120	-3.242997	-0.040723
C	2.175666	-3.464076	0.004568
C	0.958766	-2.761892	0.029996
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H	1.633789	4.531123	0.008893
H	3.907540	3.490512	-0.034635
H	-0.360387	3.039657	0.052730
H	5.442054	-1.031642	-0.064383
H	2.174223	-4.545832	0.004827
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N	0.876887	-1.445634	0.031426
N	0.715059	1.298701	0.033128
Na	-1.398134	-0.146128	0.081599
O	-3.255196	0.648213	-0.026455
C	-4.489489	1.216540	-0.158635
C	-5.334532	0.989680	1.113528
H	-6.335326	1.430874	1.046624
H	-5.436866	-0.085028	1.290451

H	-4.815770	1.426468	1.971965
C	-5.243625	0.604135	-1.358410
H	-4.653246	0.756807	-2.266615
H	-5.352201	-0.473205	-1.202544
H	-6.238197	1.039095	-1.507997
C	-4.366827	2.738200	-0.390669
H	-3.836085	3.187322	0.453835
H	-3.779161	2.918763	-1.295567
H	-5.337876	3.234542	-0.498642

12b

C	1.663473	3.474215	0.010126
C	2.909482	2.899341	-0.014118
C	3.025628	1.495730	-0.015117
C	1.835699	0.740237	0.010055
C	0.538260	2.632318	0.034648
C	4.300468	0.835674	-0.040979
C	1.921475	-0.711742	0.009184
C	3.192601	-1.320791	-0.017320
C	4.380450	-0.514013	-0.042137
C	3.244317	-2.728391	-0.018028
H	4.207818	-3.225907	-0.038535
C	2.075364	-3.446986	0.006756
C	0.858464	-2.744802	0.032184
H	5.196312	1.445972	-0.059150
H	1.533487	4.548213	0.011081
H	3.807238	3.507602	-0.032447
H	-0.460689	3.056747	0.054918
H	5.341752	-1.014552	-0.062195
H	2.073921	-4.528742	0.007015
H	-0.081855	-3.286776	0.052081
N	0.776585	-1.428544	0.033614
N	0.614757	1.315791	0.035316
O	-4.662346	-0.024733	0.091493
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C	-6.669611	-0.464676	1.323214
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H	-6.358863	-1.498777	1.498828
H	-6.313513	0.142909	2.160381
C	-6.547762	-0.817227	-1.152315
H	-6.095236	-0.467108	-2.084693
H	-6.242728	-1.856325	-0.997479
H	-7.638106	-0.783262	-1.255926
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H	-6.121560	2.123988	0.610030
H	-6.043793	1.875728	-1.141566
H	-7.573096	1.600833	-0.275503

K	-1.973296	-0.089660	0.121372

13a

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C	3.352832	-2.673348	0.061556
C	3.247421	-1.268786	0.059655
C	1.957925	-0.704059	-0.020354
C	0.976162	-2.780703	-0.080913
C	4.406042	-0.424962	0.135495
C	1.823766	0.744200	-0.029720
C	2.987169	1.536581	0.052151
C	4.281239	0.920647	0.133965
C	2.831722	2.936388	0.048857
H	3.710364	3.568913	0.110484
C	1.573119	3.477148	-0.032317
C	0.477348	2.604155	-0.116674
H	5.380821	-0.894303	0.197338
H	2.253612	-4.517502	-0.011530
H	4.333200	-3.132918	0.121145
H	0.061825	-3.362833	-0.134658
H	5.153181	1.561450	0.192406
H	1.413014	4.546819	-0.035180
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N	0.587313	1.288063	-0.118249
N	0.841509	-1.466764	-0.086206
Na	-1.190425	-0.262158	-0.267570
O	-3.436450	-0.241754	-0.055773
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C	-5.199213	0.674176	-1.193765
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H	-4.695570	1.638818	-1.246706
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H	-4.770047	0.267766	2.238645
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H	-6.171059	0.958907	1.408696
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H	-5.246190	-2.029676	-0.730582
H	-5.174099	-1.995133	1.044644
H	-6.574705	-1.313067	0.206062

13b

C	2.214788	-3.436627	-0.010121
C	3.352832	-2.673348	0.061556
C	3.247421	-1.268786	0.059655

C	1.957925	-0.704059	-0.020354
C	0.976162	-2.780703	-0.080913
C	4.406042	-0.424962	0.135495
C	1.823766	0.744200	-0.029720
C	2.987169	1.536581	0.052151
C	4.281239	0.920647	0.133965
C	2.831722	2.936388	0.048857
H	3.710364	3.568913	0.110484
C	1.573119	3.477148	-0.032317
C	0.477348	2.604155	-0.116674
H	5.380821	-0.894303	0.197338
H	2.253612	-4.517502	-0.011530
H	4.333200	-3.132918	0.121145
H	0.061825	-3.362833	-0.134658
H	5.153181	1.561450	0.192406
H	1.413014	4.546819	-0.035180
H	-0.528414	3.006492	-0.188865
N	0.587313	1.288063	-0.118249
N	0.841509	-1.466764	-0.086206
O	-3.436450	-0.241754	-0.055773
C	-4.796710	-0.085430	0.105970
C	-5.199213	0.674176	-1.193765
H	-6.278022	0.831592	-1.145526
H	-4.695570	1.638818	-1.246706
H	-4.960388	0.079186	-2.074809
C	-5.097839	0.778602	1.331259
H	-4.770047	0.267766	2.238645
H	-4.582524	1.737390	1.256826
H	-6.171059	0.958907	1.408696
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H	-5.246190	-2.029676	-0.730582
H	-5.174099	-1.995133	1.044644
H	-6.574705	-1.313067	0.206062
K	-1.190425	-0.262158	-0.267570

14

C	0.000000	-1.396897	0.000000
C	-1.221142	-0.767891	-0.000027
C	-1.209612	0.630138	0.000022
C	0.000000	1.319901	0.000000
C	1.209612	0.630139	-0.000022
C	1.221142	-0.767891	0.000027
H	-2.153920	-1.319352	-0.000015
H	-2.146565	1.175336	0.000032
H	0.000000	2.403046	0.000000
H	2.146565	1.175335	-0.000032
H	2.153921	-1.319351	0.000015

TS(6-33)

C	0.723293	2.729081	0.342213
C	0.880212	1.346628	0.217242
C	-0.285212	0.569154	0.139425
C	-1.570285	1.052928	0.148113
C	-1.676930	2.453651	0.268083
C	-0.560019	3.274018	0.370220
H	1.589744	3.375521	0.417249
H	-2.755138	0.201688	-0.188132
H	-2.664990	2.917950	0.272194
H	-0.668751	4.351993	0.467870
I	0.029050	-1.608923	-0.006844
C	-4.724532	0.170799	-0.966521
C	-5.746920	-0.874173	-1.405351
H	-6.080382	-1.467822	-0.548656
H	-6.629158	-0.412180	-1.861746
H	-5.303122	-1.556682	-2.135824
C	-5.366948	1.119476	0.053156
H	-5.756102	0.558286	0.909823
H	-4.631160	1.840212	0.425267
H	-6.201407	1.684723	-0.376050
C	-4.256134	0.973067	-2.184632
H	-3.535907	1.742633	-1.890014
H	-3.765666	0.313361	-2.906981
H	-5.092783	1.468352	-2.688934
O	-3.639858	-0.515410	-0.378469
K	-3.158750	-0.823738	2.163322
H	1.829720	0.854832	0.178875

I(6-33)

C	0.711761	2.728611	0.405607
C	0.878576	1.349696	0.255453
C	-0.285908	0.568828	0.228740
C	-1.575070	1.014088	0.322270
C	-1.686322	2.417066	0.468255
C	-0.576448	3.253259	0.511856
H	1.572580	3.386124	0.438009
H	-3.004772	0.032611	-0.299153
H	-2.675230	2.876048	0.540498
H	-0.694626	4.329302	0.625181
I	0.088920	-1.631891	-0.002019
C	-4.864605	0.246980	-0.983996
C	-5.943505	-0.699889	-1.484782
H	-6.267960	-1.371886	-0.685122
H	-6.817754	-0.147452	-1.841049
H	-5.565203	-1.310332	-2.309221

C	-5.388347	1.084322	0.182404
H	-5.751814	0.438840	0.988482
H	-4.594490	1.722209	0.584421
H	-6.215945	1.731988	-0.123525
C	-4.383543	1.157200	-2.111257
H	-3.589720	1.821907	-1.755977
H	-3.983945	0.562360	-2.937512
H	-5.198400	1.776802	-2.498593
O	-3.782555	-0.576462	-0.536664
K	-3.037743	-0.993221	2.048454
H	1.830485	0.869863	0.163099

TS(I(6-33)-33)

C	-0.931701	2.800838	-1.139498
C	0.107995	1.864911	-1.249251
C	0.591860	1.495689	-0.017362
C	0.282189	1.842724	1.196018
C	-0.755021	2.792966	1.288759
C	-1.358519	3.252492	0.112273
H	-1.404461	3.169659	-2.045508
H	-1.918567	0.532989	0.167021
H	-1.113598	3.164390	2.248538
H	-2.173678	3.969989	0.167856
I	2.330184	-0.546471	-0.422600
C	-2.537374	-1.218323	-0.500855
C	-1.869694	-0.970795	-1.845912
H	-0.787431	-1.111957	-1.770508
H	-2.258415	-1.654896	-2.605481
H	-2.055829	0.051022	-2.191565
C	-2.287341	-2.637561	-0.021046
H	-1.215648	-2.856960	0.007568
H	-2.698441	-2.784754	0.981743
H	-2.759842	-3.360192	-0.690103
C	-4.027790	-0.911596	-0.565923
H	-4.499111	-1.077252	0.406096
H	-4.193500	0.131966	-0.852347
H	-4.529994	-1.543887	-1.303835
O	-1.929175	-0.371928	0.505190
K	-0.010250	-0.844800	2.342193
H	0.449300	1.491430	-2.208103

33

C	-3.042591	1.367943	-0.001315
C	-1.647431	1.367943	-0.001315
C	-0.949893	2.575694	-0.001315

C	-1.647547	3.784203	-0.002514
C	-3.042372	3.784125	-0.002993
C	-3.739973	2.575919	-0.001997
H	-3.592350	0.415626	-0.000865
H	-1.097347	4.736346	-0.002573
H	-3.592494	4.736406	-0.003946
H	-4.839577	2.576102	-0.002177

TS(33-34)

C	-3.754662	-0.046378	-0.041861
C	-3.036185	-1.242822	-0.006391
C	-1.604428	-1.278110	0.014317
C	-1.042195	-0.061796	0.021195
C	-1.693056	1.176391	0.037042
C	-3.080357	1.174637	-0.005106
H	-4.842604	-0.054617	-0.082977
H	-1.154278	2.117790	0.123958
H	-3.626022	2.112610	0.013081
C	1.626535	-1.180083	0.016369
C	3.005579	-1.206733	-0.004248
C	3.716381	-0.012850	-0.014334
C	3.012538	1.187067	-0.017625
C	1.634187	1.164656	-0.008602
N	0.956981	-0.004559	0.017154
H	4.800046	-0.015027	-0.021517
H	0.976645	-2.046797	0.001107
H	3.511551	-2.164001	0.003490
H	3.520981	2.142104	-0.047027
H	1.031733	2.061355	-0.047500
H	-3.622939	-2.165373	-0.007249

34

C	-0.124133	2.619296	-0.269451
C	0.146672	1.245781	-0.209175
C	-0.823582	0.242688	-0.113396
C	-2.102926	0.777182	-0.094851
C	-2.474984	2.123896	-0.185436
C	-1.444901	3.052591	-0.271783
H	0.693803	3.334023	-0.324221
H	-3.509913	2.449151	-0.239049
H	-1.672123	4.110815	-0.352071
C	-3.076728	-1.405218	-0.559412
C	-4.082139	-2.346359	-0.484297
C	-5.256832	-2.043965	0.193890
C	-5.382956	-0.796319	0.794549

C	-4.347498	0.109214	0.699443
N	-3.218411	-0.193158	0.021780
H	-6.059464	-2.769324	0.258168
H	-2.115556	-1.543386	-1.040218
H	-3.941199	-3.304279	-0.968488
H	-6.268253	-0.522980	1.353532
H	-4.370675	1.080706	1.173302
H	1.193041	1.023613	-0.234745

TS(34-35)

C	-3.485775	-0.029672	-0.042267
C	-2.764628	-1.181180	-0.363074
C	-1.355499	-1.262645	-0.377005
C	-0.772907	-0.052008	-0.003085
C	-1.426164	1.124660	0.378600
C	-2.813720	1.129765	0.346272
H	-4.573960	-0.029870	-0.077339
H	-0.888711	2.001508	0.734059
H	-3.361157	2.019116	0.641646
C	1.375618	-1.128584	0.337922
C	2.754856	-1.152964	0.340099
C	3.463426	-0.007619	-0.001678
C	2.757355	1.138229	-0.353392
C	1.379037	1.112282	-0.352724
N	0.703836	-0.004788	-0.002589
H	4.547104	-0.006223	0.003341
H	0.727616	-1.967165	0.562995
H	3.262551	-2.065926	0.625010
H	3.264260	2.048066	-0.647873
H	0.775341	1.957825	-0.651289
H	-3.349490	-2.065395	-0.630437
H	-0.572926	-2.510663	-0.751746
C	-0.931338	-4.484090	-1.674727
C	-1.990341	-4.915159	-0.643081
H	-2.936835	-4.490168	-0.904675
H	-2.068138	-5.982306	-0.636428
H	-1.701849	-4.572512	0.328652
C	-1.629189	-3.850908	-2.892794
H	-1.752934	-4.589681	-3.656863
H	-2.587863	-3.476641	-2.599933
H	-1.031639	-3.046466	-3.267904
C	-0.124976	-5.715404	-2.127766
H	0.378997	-6.141354	-1.285462
H	-0.788590	-6.440539	-2.550490
H	0.594930	-5.419841	-2.862122
O	0.019152	-3.454887	-1.035266

TS(34-36)

C	-0.001455	2.316267	0.128659
C	-0.091777	0.921998	0.013900
C	1.044696	0.115992	-0.034313
C	2.248722	0.779080	0.039269
C	2.419241	2.156222	0.162742
C	1.256627	2.915904	0.205225
H	-0.882761	2.947445	0.159527
H	3.385538	2.643245	0.229935
H	1.324644	3.994955	0.299266
C	3.019780	-1.468393	-0.088248
C	4.036157	-2.413389	-0.152978
C	5.375508	-2.038367	-0.147974
C	5.700958	-0.685854	-0.080938
C	4.685792	0.243813	-0.018182
N	3.400018	-0.164008	-0.021359
H	6.163404	-2.783786	-0.197315
H	1.668278	-1.176996	-0.094151
H	3.770901	-3.464824	-0.207107
H	6.728783	-0.346962	-0.078719
H	4.873680	1.307786	0.030934
H	-1.027336	0.406108	-0.045151

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C	0.003646	3.574578	-0.107616
C	-0.695691	2.474820	-0.598988
C	-0.186139	1.167377	-0.600012
C	1.098213	1.062346	-0.062642
C	1.816947	2.122743	0.498162
C	1.260326	3.392923	0.465885
H	-0.432044	4.569704	-0.149005
H	2.774129	1.972548	0.988421
H	1.799381	4.228314	0.900092
C	1.008491	-1.380185	-0.007259
C	1.613781	-2.620347	0.019871
C	2.997278	-2.723979	-0.015956
C	3.748813	-1.558013	-0.111782
C	3.109200	-0.339617	-0.148340
N	1.757828	-0.251177	-0.070885
H	3.482901	-3.692384	0.014980
H	-0.074128	-1.251098	-0.034369
H	0.982832	-3.498721	0.074157
H	4.828743	-1.581564	-0.176504
H	3.642757	0.592641	-0.260623
H	-1.693698	2.645315	-1.005366
H	-0.889020	0.351928	-0.770605

C	-3.160362	-1.152481	0.028098
C	-2.600510	-1.007801	1.451758
H	-2.017863	-0.084961	1.546067
H	-3.394389	-0.981451	2.206916
H	-1.941501	-1.849523	1.691649
C	-4.111462	0.015488	-0.259500
H	-4.966109	0.034760	0.426767
H	-3.584524	0.970185	-0.164896
H	-4.496541	-0.056200	-1.281459
C	-3.929787	-2.469374	-0.076029
H	-3.263123	-3.313733	0.127263
H	-4.766078	-2.518341	0.630847
H	-4.329478	-2.594914	-1.086937
O	-2.124647	-1.188185	-0.917832

TS(35-36)

C	-1.225809	3.494852	-0.703900
C	-0.744123	2.960397	0.494533
C	-0.857965	1.604841	0.880445
C	-1.513008	0.851273	-0.098080
C	-2.020041	1.318904	-1.312851
C	-1.869983	2.666915	-1.619924
H	-1.099378	4.552386	-0.931167
H	-2.493409	0.644597	-2.025267
H	-2.239469	3.057123	-2.563298
C	-0.599025	-1.341054	0.465045
C	-0.847042	-2.702004	0.686838
C	-2.111178	-3.261636	0.597136
C	-3.187102	-2.439641	0.262867
C	-2.947203	-1.104219	0.040890
N	-1.694205	-0.592488	0.144494
H	-2.271076	-4.320133	0.780037
H	0.713277	-0.845224	0.410326
H	0.004466	-3.334096	0.927418
H	-4.197966	-2.819778	0.185829
H	-3.731517	-0.397592	-0.203775
H	-0.244430	3.663969	1.170356
C	2.467190	-0.776525	-0.853991
C	1.715302	-0.037653	-1.970659
H	2.154358	-0.221600	-2.958154
H	0.667642	-0.355496	-2.001926
H	1.728038	1.042680	-1.789577
C	3.916780	-0.293515	-0.813460
H	4.469276	-0.815965	-0.026233
H	4.436624	-0.462754	-1.763334
H	3.952962	0.778739	-0.593537
C	2.442485	-2.283595	-1.147469

H	2.939743	-2.833451	-0.342086
H	1.411058	-2.645479	-1.213009
H	2.943825	-2.530569	-2.090465
O	1.882484	-0.508813	0.391109
H	-0.489983	1.206897	1.803012

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C	0.000989	2.246086	-0.371677
C	0.154985	0.883271	-0.102088
C	-0.968761	0.063361	0.022573
C	-2.232590	0.607769	-0.124576
C	-2.406257	1.963890	-0.401073
C	-1.280822	2.766926	-0.522817
H	0.858853	2.899549	-0.466879
H	-3.397860	2.374920	-0.550538
H	-1.399238	3.821086	-0.750296
C	-3.307063	-1.511209	-0.574674
C	-4.503007	-2.246312	-0.392641
C	-5.625616	-1.774563	0.263141
C	-5.591265	-0.500294	0.837844
C	-4.446938	0.239254	0.705820
N	-3.381077	-0.260599	0.009131
H	-6.523951	-2.380584	0.348716
H	-0.857703	-0.995558	0.219856
H	-4.535324	-3.248086	-0.816015
H	-6.428412	-0.094957	1.392204
H	-4.326763	1.218411	1.153379
H	1.097025	0.393075	0.028936

TS(36-37)

C	-0.365588	-2.505199	-3.220017
C	0.585517	-3.069591	-2.375100
C	0.734678	-2.619479	-1.070708
C	-0.085607	-1.593709	-0.572081
C	-1.046756	-1.023777	-1.424220
C	-1.174763	-1.484436	-2.729712
H	-0.472824	-2.855121	-4.241247
H	-1.745460	-0.273829	-1.047158
H	-1.934600	-1.040494	-3.366766
C	-0.425333	0.109128	1.027380
C	-0.366334	0.509713	2.334989
C	0.162351	-0.259806	3.305224
C	0.712974	-1.543403	3.025140
C	0.617647	-1.908745	1.718083
N	0.072499	-1.113495	0.744794

H	0.179390	0.029660	4.351367
H	1.516790	-3.047157	-0.455042
H	-0.811367	1.461255	2.609905
H	1.142568	-2.222734	3.748879
H	0.953177	-2.884096	1.393809
C	4.666945	-0.822682	0.741426
C	4.196851	-0.869142	-0.567885
C	3.155084	-0.040066	-0.965061
C	2.586109	0.814888	-0.028458
C	3.052773	0.889150	1.276870
C	4.098789	0.056617	1.657864
H	5.481968	-1.469712	1.046727
H	2.608641	1.588229	1.975729
H	4.471416	0.102467	2.675148
C	1.984571	2.724737	-1.318037
C	1.132920	3.700218	-1.766713
C	-0.196979	3.670868	-1.351504
C	-0.608559	2.624651	-0.516218
C	0.257729	1.655714	-0.083082
N	1.557101	1.742356	-0.475160
H	-0.892959	4.427699	-1.695777
H	2.769687	-0.066129	-1.979168
H	1.512529	4.466281	-2.429963
H	-1.655735	2.492708	-0.238073
H	-1.518239	0.154272	0.771976
H	3.033164	2.681947	-1.580709
H	1.236793	-3.859754	-2.736283
H	4.638638	-1.552111	-1.285283

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C	4.197301	-0.071235	1.236707
C	3.058582	0.327974	1.927992
C	1.800870	-0.082010	1.500665
C	1.695264	-0.902229	0.381257
C	2.829812	-1.317337	-0.310215
C	4.080391	-0.896146	0.121848
H	5.176356	0.253343	1.571072
H	2.736274	-1.979791	-1.164338
H	4.966917	-1.225197	-0.408819
C	0.080911	-1.059313	-1.413109
C	-1.150086	-1.565240	-1.891891
C	-2.075656	-2.066913	-1.020507
C	-1.791029	-2.112945	0.362932
C	-0.558738	-1.724842	0.792978
N	0.397034	-1.296567	-0.091407
H	-3.025765	-2.438121	-1.388620
H	0.907492	0.238917	2.027242

H	-1.342449	-1.508741	-2.955859
H	-2.511839	-2.482564	1.079389
H	-0.238789	-1.787331	1.825082
C	-4.119496	0.023752	1.096734
C	-3.103460	0.396599	1.971777
C	-1.874384	0.814072	1.476473
C	-1.672073	0.841753	0.099168
C	-2.679612	0.476209	-0.784232
C	-3.907545	0.068802	-0.277594
H	-5.079641	-0.295429	1.487234
H	-2.490989	0.519178	-1.851720
H	-4.702529	-0.208752	-0.961499
C	0.157695	2.404355	0.093312
C	1.371225	2.850880	-0.360705
C	2.014168	2.133768	-1.371886
C	1.410551	0.996256	-1.880667
C	0.173700	0.527946	-1.423180
N	-0.397423	1.270883	-0.429983
H	2.974863	2.470900	-1.748953
H	-1.077158	1.104836	2.153775
H	1.796799	3.752930	0.059650
H	1.916550	0.425992	-2.656229
H	0.928545	-0.964075	-2.076066
H	-0.422126	2.923110	0.846764
H	3.144825	0.968503	2.798863
H	-3.265302	0.363550	3.043490

TS(37-38)

C	1.443370	-1.885496	-3.006782
C	1.923797	-2.593199	-1.907668
C	1.469487	-2.305853	-0.629586
C	0.504778	-1.310909	-0.431274
C	0.015299	-0.606862	-1.534148
C	0.487412	-0.894012	-2.808686
H	1.811693	-2.102464	-4.003949
H	-0.749444	0.150145	-1.394453
H	0.096166	-0.336243	-3.654415
C	-0.474377	0.277218	1.230529
C	-1.493839	0.264273	2.248469
C	-1.749627	-0.823732	3.016986
C	-1.001420	-2.025669	2.805160
C	-0.165060	-2.086755	1.748484
N	0.035260	-1.017611	0.882191
H	-2.511724	-0.779728	3.786917
H	1.902287	-2.825842	0.217616
H	-2.040760	1.178116	2.441855
H	-1.123636	-2.895098	3.437469

H	0.351912	-2.997035	1.478942
C	4.679917	-0.666618	0.840255
C	4.488684	-0.170073	-0.446989
C	3.372314	0.592135	-0.753581
C	2.423611	0.885806	0.234895
C	2.620198	0.393490	1.528831
C	3.738410	-0.376960	1.822290
H	5.548846	-1.272658	1.072664
H	1.895856	0.616766	2.304489
H	3.872628	-0.749363	2.833382
C	1.406186	2.696263	-0.997809
C	0.580167	3.762403	-1.009925
C	-0.432999	3.857633	-0.002579
C	-0.653467	2.803627	0.822015
C	0.073884	1.567652	0.697435
N	1.273549	1.662421	-0.076546
H	-1.024546	4.760732	0.095440
H	3.218869	0.915539	-1.776410
H	0.730163	4.543482	-1.743479
H	-1.445316	2.870645	1.556755
H	-1.807147	0.566161	0.393727
H	2.251271	2.618907	-1.666832
O	-3.099603	0.802169	-0.782376
C	-4.045453	-0.285274	-0.687976
C	-3.298232	-1.610571	-0.599408
H	-2.652391	-1.752129	-1.470375
H	-2.672545	-1.643523	0.299532
H	-3.994814	-2.452724	-0.547622
C	-4.924966	-0.080541	0.540324
H	-4.322500	-0.107173	1.454179
H	-5.431591	0.886958	0.491868
H	-5.685943	-0.862785	0.619057
C	-4.863809	-0.204283	-1.964136
H	-4.222198	-0.328671	-2.840495
H	-5.629064	-0.984041	-1.985259
H	-5.361578	0.765977	-2.039929
H	5.203482	-0.398404	-1.231472
H	2.681590	-3.358740	-2.040473

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C	1.496270	-2.553529	-2.494854
C	1.967028	-3.008434	-1.265515
C	1.580798	-2.384114	-0.088712
C	0.696427	-1.301376	-0.127162
C	0.213410	-0.852095	-1.356085
C	0.618505	-1.474628	-2.530095
H	1.812306	-3.034142	-3.414755

H	-0.488723	-0.025404	-1.391623
H	0.236992	-1.111862	-3.479859
C	-0.029484	0.731247	1.140692
C	-0.991869	1.080827	2.156250
C	-1.349607	0.232507	3.151527
C	-0.788058	-1.082020	3.193502
C	-0.021777	-1.484729	2.157571
N	0.294727	-0.662032	1.085986
H	-2.064105	0.547474	3.903697
H	2.001865	-2.711270	0.855452
H	-1.413054	2.077207	2.142315
H	-1.008132	-1.774697	3.994868
H	0.340700	-2.499953	2.069783
C	4.982217	-0.880516	0.783451
C	4.763698	-0.646904	-0.572034
C	3.696457	0.128142	-0.998055
C	2.817754	0.697804	-0.064909
C	3.045050	0.470415	1.298168
C	4.116337	-0.311065	1.711253
H	5.814855	-1.494201	1.109845
H	2.383326	0.915514	2.032839
H	4.273590	-0.470238	2.773840
C	1.798991	2.210497	-1.667441
C	1.112888	3.359263	-1.842666
C	0.326899	3.865165	-0.756519
C	0.093100	3.072709	0.318871
C	0.595620	1.720472	0.377648
N	1.710422	1.475978	-0.487627
H	-0.079401	4.869393	-0.797399
H	3.530056	0.249584	-2.061236
H	1.212458	3.901804	-2.773910
H	-0.519924	3.447371	1.129115
H	-3.597941	0.441345	-0.109202
H	2.486953	1.834501	-2.411810
O	-4.185981	0.412175	-0.875065
C	-5.352408	-0.351850	-0.497116
C	-4.934640	-1.748819	-0.052285
H	-4.410613	-2.273340	-0.855713
H	-4.267293	-1.697404	0.815524
H	-5.805402	-2.345718	0.235132
C	-6.087778	0.372004	0.624304
H	-5.463906	0.429338	1.522416
H	-6.346145	1.389619	0.319911
H	-7.010192	-0.150553	0.894552
C	-6.200585	-0.411629	-1.754966
H	-5.653691	-0.903628	-2.563438
H	-7.123017	-0.969349	-1.576209
H	-6.467588	0.595335	-2.086053
H	5.421882	-1.088974	-1.313778

H	2.664486	-3.838832	-1.221237

TS(33-41)

C	2.435792	1.382228	-0.361426
C	1.132226	1.031571	0.004319
C	0.863664	-0.274172	0.366256
C	1.878399	-1.214795	0.342665
C	3.169004	-0.898643	-0.017774
C	3.447655	0.427104	-0.370703
H	2.658623	2.408160	-0.639788
H	0.336676	1.774733	0.008259
H	3.952708	-1.652057	-0.027349
H	4.458077	0.706843	-0.653088
C	-1.249267	-0.921762	0.821291
C	-1.798445	0.274587	1.332974
C	-1.651807	-1.362201	-0.460609
C	-2.599964	1.068682	0.531904
H	-1.553352	0.584947	2.343690
C	-2.454941	-0.558737	-1.251634
H	-1.292514	-2.316232	-0.832672
C	-2.922422	0.665128	-0.767372
H	-2.994585	2.002763	0.919866
H	-2.733088	-0.887287	-2.248267
H	-3.554010	1.290560	-1.389526
H	-0.777898	-1.626374	1.499522

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C	2.304952	1.379956	-0.413365
C	0.993116	0.951605	-0.244448
C	0.716481	-0.364543	0.154531
C	1.810922	-1.173552	0.354888
C	3.125607	-0.805869	0.201864
C	3.372740	0.511437	-0.193316
H	2.499403	2.402818	-0.719905
H	0.163913	1.634609	-0.418939
H	3.942025	-1.499714	0.378508
H	4.394496	0.854146	-0.327642
C	-0.719928	-0.850350	0.333216
C	-1.455340	-0.014180	1.337960
C	-1.423864	-0.911881	-0.990561
C	-2.618089	0.632760	1.042841
H	-1.011575	0.070690	2.326024
C	-2.585816	-0.242809	-1.234686
H	-0.954832	-1.507259	-1.769054
C	-3.209018	0.542884	-0.238173

H	-3.101826	1.233067	1.808527
H	-3.043956	-0.313120	-2.217397
H	-4.131377	1.070812	-0.454023
H	-0.626847	-1.878793	0.729398

TS(41-42)

C	0.195235	2.910971	-0.176037
C	0.145340	1.546377	0.034045
C	1.280276	0.763517	0.207246
C	2.522150	1.402726	0.130112
C	2.598894	2.776626	-0.079876
C	1.441949	3.536072	-0.223656
H	-0.715403	3.486912	-0.318165
H	3.429240	0.811662	0.236413
H	3.570180	3.258473	-0.110313
H	1.503053	4.608557	-0.379147
C	1.179712	-0.750945	0.390023
C	1.087252	-1.422743	-0.949777
C	2.272569	-1.312560	1.246947
C	1.945738	-2.410726	-1.332165
H	0.271034	-1.111380	-1.597024
C	3.117494	-2.288221	0.808988
H	2.335493	-0.941208	2.269649
C	3.011187	-2.822479	-0.496890
H	1.826805	-2.877576	-2.306610
H	3.871803	-2.687535	1.484109
H	3.725827	-3.560599	-0.847120
H	0.219455	-0.920958	0.913863
C	-2.728136	-0.107709	1.262523
C	-2.233980	0.341671	0.051699
C	-2.929941	0.188576	-1.133188
C	-4.169786	-0.450511	-1.102842
C	-4.688116	-0.910107	0.104666
C	-3.975015	-0.734607	1.288029
H	-2.157718	0.024918	2.179471
H	-1.044431	0.943967	0.042873
H	-2.521070	0.539052	-2.075226
H	-4.731295	-0.583474	-2.024798
H	-5.648210	-1.415351	0.126187
H	-4.371696	-1.111026	2.226749

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C	0.358058	3.176914	0.844186
C	0.589864	1.857218	1.217180
C	0.963411	0.904126	0.269391

C	1.115894	1.299136	-1.059724
C	0.880365	2.616704	-1.437280
C	0.498015	3.559225	-0.486794
H	0.058582	3.905757	1.591189
H	1.409557	0.560692	-1.801945
H	0.993197	2.909120	-2.476893
H	0.310881	4.586864	-0.781785
C	1.223584	-0.542942	0.682462
C	0.679664	-1.530363	-0.306316
C	2.687068	-0.745154	0.951123
C	1.456530	-2.485569	-0.891413
H	-0.377012	-1.451999	-0.551007
C	3.422449	-1.706821	0.325572
H	3.154355	-0.066539	1.659857
C	2.835210	-2.597742	-0.601332
H	1.007243	-3.174867	-1.601022
H	4.483157	-1.792841	0.545190
H	3.437024	-3.358731	-1.085953
H	0.671978	-0.671575	1.634721
C	-2.350663	0.716710	-0.111521
C	-2.206510	0.097877	1.107087
C	-2.617925	-1.177579	1.405291
C	-3.239714	-1.897596	0.378786
C	-3.414280	-1.316046	-0.874745
C	-2.975892	-0.016901	-1.123539
H	-1.979901	1.721966	-0.293057
H	0.459791	1.552249	2.253392
H	-2.469725	-1.619742	2.385861
H	-3.582881	-2.911642	0.562872
H	-3.894852	-1.881977	-1.666106
H	-3.112156	0.426086	-2.105807

TS(42-43)

C	3.543086	0.261525	-1.273750
C	2.201991	-0.088518	-1.211331
C	1.659410	-0.682900	-0.063810
C	2.511151	-0.911809	1.020695
C	3.854018	-0.547913	0.965833
C	4.378341	0.038510	-0.180202
H	3.937987	0.724686	-2.173445
H	2.120141	-1.389562	1.914935
H	4.495463	-0.733887	1.822608
H	5.425346	0.321017	-0.222692
C	0.190360	-1.002595	-0.021088
C	-0.273322	-1.902173	-1.101294
C	-0.403089	-1.337120	1.288627
C	-1.287587	-2.807506	-0.927415

H	0.217951	-1.826298	-2.068186
C	-1.431977	-2.233829	1.426075
H	-0.055451	-0.787188	2.160550
C	-1.925441	-2.975550	0.326439
H	-1.590403	-3.429491	-1.767015
H	-1.865849	-2.393705	2.410720
H	-2.698939	-3.723365	0.461846
H	-0.290406	0.130159	-0.297173
O	-0.984302	1.313995	-0.685251
C	-0.810081	2.405653	0.171178
C	-1.895434	2.399854	1.263287
H	-2.893294	2.489727	0.815641
H	-1.853188	1.462078	1.831910
H	-1.788650	3.223985	1.977813
C	-0.932335	3.693238	-0.650328
H	-1.906599	3.735716	-1.148136
H	-0.826314	4.592572	-0.032202
H	-0.160063	3.717057	-1.424522
C	0.565023	2.377767	0.851351
H	0.670757	1.494548	1.490187
H	1.362949	2.339872	0.103951
H	0.722068	3.262581	1.478192
K	-2.966284	-0.209113	-0.584673
H	1.570458	0.098687	-2.054552

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C	3.543191	0.261436	-1.273734
C	2.202092	-0.088606	-1.211361
C	1.659447	-0.682892	-0.063824
C	2.511131	-0.911703	1.020749
C	3.854001	-0.547816	0.965930
C	4.378389	0.038511	-0.180125
H	3.938139	0.724515	-2.173450
H	2.120075	-1.389387	1.915006
H	4.495400	-0.733719	1.822756
H	5.425397	0.321010	-0.222582
C	0.190388	-1.002574	-0.021137
C	-0.273266	-1.902192	-1.101324
C	-0.403089	-1.337057	1.288578
C	-1.287497	-2.807560	-0.927422
H	0.218015	-1.826338	-2.068213
C	-1.431940	-2.233806	1.426049
H	-0.055526	-0.787037	2.160475
C	-1.925350	-2.975594	0.326434
H	-1.590287	-3.429582	-1.767004
H	-1.865827	-2.393651	2.410692
H	-2.698808	-3.723445	0.461865

H	-0.444210	0.392534	-0.383222
O	-0.984464	1.313963	-0.685206
C	-0.810097	2.405675	0.171115
C	-1.895393	2.400045	1.263274
H	-2.893267	2.489993	0.815674
H	-1.853189	1.462271	1.831902
H	-1.788484	3.224188	1.977768
C	-0.932262	3.693201	-0.650505
H	-1.906549	3.735732	-1.148265
H	-0.826115	4.592588	-0.032476
H	-0.160031	3.716863	-1.424746
C	0.565033	2.377742	0.851243
H	0.670685	1.494629	1.490238
H	1.362939	2.339628	0.103829
H	0.722188	3.262640	1.477938
K	-2.966482	-0.209176	-0.584541
H	1.545820	0.130714	-2.049885

TS(51-52)

C	-2.727092	-2.547416	0.078871
C	-2.230671	-0.304185	0.010567
C	-3.599657	0.042727	0.189901
C	-4.530481	-1.005313	0.313057
C	-4.097616	-2.309751	0.259655
H	-2.362455	-3.573316	0.032095
H	-5.582221	-0.768286	0.449966
H	-4.787249	-3.141311	0.352259
C	-1.247549	0.751412	-0.118467
C	-1.678339	2.099042	-0.059775
C	-0.682086	3.090335	-0.189874
C	1.018340	1.342153	-0.437167
C	0.626109	2.712896	-0.375373
H	-0.977248	4.138054	-0.144605
H	2.264163	0.543660	-0.598921
H	1.390217	3.481862	-0.480605
C	-3.987935	1.415268	0.240521
H	-5.039509	1.650065	0.378094
C	-3.059878	2.403544	0.121298
H	-3.358377	3.448154	0.161177
N	-1.814290	-1.596201	-0.044981
N	0.048549	0.410372	-0.293599
C	4.041230	-0.124994	0.262189
C	3.495937	-0.280008	1.688958
H	3.095502	-1.289081	1.840629
H	4.266156	-0.114721	2.450819
H	2.685113	0.433436	1.864265
C	5.117215	-1.176975	0.007740

H	4.703780	-2.184722	0.123739
H	5.500374	-1.087943	-1.012740
H	5.959778	-1.076515	0.701101
C	4.644283	1.275312	0.099175
H	5.023783	1.404539	-0.918667
H	3.884255	2.042657	0.273195
H	5.470342	1.449713	0.797373
O	3.008813	-0.323977	-0.673492
K	1.028549	-2.040416	-0.582044

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C	-2.681599	-2.562049	0.036656
C	-2.218835	-0.309338	-0.004666
C	-3.587724	0.011890	0.223300
C	-4.497937	-1.052796	0.358150
C	-4.048399	-2.349601	0.266326
H	-2.303314	-3.581235	-0.041886
H	-5.547870	-0.834126	0.533866
H	-4.722385	-3.193148	0.365591
C	-1.254424	0.762693	-0.145099
C	-1.708483	2.101604	-0.056171
C	-0.733331	3.111590	-0.201631
C	1.003522	1.394214	-0.510522
C	0.575017	2.757544	-0.424918
H	-1.045748	4.153725	-0.135804
H	2.636701	0.311010	-0.711265
H	1.320284	3.544115	-0.540588
C	-3.996636	1.376409	0.307209
H	-5.046804	1.591985	0.481453
C	-3.087945	2.380458	0.171379
H	-3.401030	3.419951	0.234173
N	-1.787402	-1.594724	-0.096568
N	0.044513	0.445470	-0.355353
C	4.298107	-0.288647	0.264822
C	3.642724	-0.397507	1.645771
H	3.211921	-1.394647	1.792567
H	4.361156	-0.228464	2.455203
H	2.838311	0.337521	1.742422
C	5.359186	-1.369173	0.103843
H	4.913665	-2.364577	0.202651
H	5.822811	-1.305050	-0.884367
H	6.145911	-1.275120	0.859279
C	4.926675	1.096368	0.100800
H	5.378878	1.191594	-0.890328
H	4.163160	1.873631	0.198830
H	5.702604	1.280062	0.851482
O	3.326711	-0.500276	-0.747928

K	1.013263	-2.006143	-0.600587

TS(52-53 ortho)

C	-3.355018	1.645994	-0.440566
C	-1.698362	0.209633	-1.138977
C	-2.567778	-0.912746	-1.004590
C	-3.884675	-0.673496	-0.570917
C	-4.290631	0.611732	-0.294293
H	-3.646854	2.671212	-0.211618
H	-4.567066	-1.512976	-0.461330
H	-5.301312	0.830706	0.033169
C	-0.341972	0.005623	-1.611113
C	0.073038	-1.313330	-1.919570
C	1.395936	-1.462262	-2.390964
C	1.982692	1.053802	-1.805482
C	2.194624	-0.352726	-2.514890
H	1.752231	-2.464851	-2.635070
H	3.217509	-0.486495	-2.869955
C	-2.093848	-2.223818	-1.306874
H	-2.773769	-3.062332	-1.183088
C	-0.819039	-2.410571	-1.748475
H	-0.457121	-3.409992	-1.982631
N	-2.104963	1.470382	-0.837793
N	0.477390	1.079515	-1.738951
K	0.165984	3.046720	-0.046303
C	3.139176	1.462485	0.092707
C	4.246927	0.484817	0.186924
C	1.721934	0.120638	1.193496
C	3.832421	-0.796957	0.441505
C	2.530091	-1.018316	0.938371
H	4.475883	-1.649099	0.240787
C	0.368023	-0.077256	1.670466
C	-0.107798	-1.403796	1.866682
C	-1.437550	-1.561932	2.300905
C	-1.647850	0.812329	2.309135
C	-2.214076	-0.451428	2.530018
H	-1.833433	-2.564122	2.441889
H	-2.248599	1.706867	2.471072
H	-3.244183	-0.535924	2.858240
C	2.017375	-2.327697	1.165927
H	2.663791	-3.176399	0.959692
C	0.745096	-2.516694	1.610350
H	0.351242	-3.516702	1.767048
N	2.155019	1.382955	0.983105
N	-0.409299	1.010091	1.887947
H	3.671641	2.564997	0.260784
H	5.226895	0.692671	-0.228032

TS(52-53 meta)

C	2.667974	3.121258	0.132313
C	3.259259	0.903148	0.044248
C	4.640609	1.227940	0.129929
C	4.989925	2.588954	0.208805
C	4.002318	3.544801	0.208099
H	1.867869	3.860390	0.138283
H	6.038717	2.864852	0.269806
H	4.235786	4.601628	0.266972
C	2.870936	-0.489090	-0.055785
C	3.884104	-1.483761	-0.037973
C	3.470814	-2.826284	-0.133168
C	1.194996	-2.067338	-0.265854
C	2.134635	-3.117991	-0.251772
H	4.218998	-3.614313	-0.117174
H	1.785718	-4.142410	-0.337246
C	5.624403	0.193281	0.136983
H	6.670605	0.475416	0.205170
C	5.257708	-1.112895	0.062188
H	6.005785	-1.900435	0.071034
N	2.292795	1.853791	0.052277
N	1.560785	-0.792332	-0.163663
K	-0.447394	1.133851	-0.048357
C	-1.137987	-1.347083	-1.538854
C	-0.622865	-2.225161	-0.405042
C	-2.877115	-0.361885	-0.356498
C	-1.307806	-1.799753	0.863300
C	-2.416979	-0.987852	0.859742
H	-0.970585	-2.238786	1.799433
C	-3.988980	0.526333	-0.357027
C	-4.687817	0.767285	0.876586
C	-5.790166	1.621331	0.861234
C	-5.421558	1.951975	-1.465980
C	-6.180844	2.226829	-0.323796
H	-6.329271	1.804953	1.788579
H	-5.691245	2.425345	-2.411953
H	-7.033158	2.895194	-0.372120
C	-3.134247	-0.677286	2.073962
H	-2.793929	-1.137810	2.999120
C	-4.216610	0.139745	2.075102
H	-4.752172	0.339521	3.001178
N	-2.152509	-0.547680	-1.515143
N	-4.369924	1.146127	-1.512070
H	-0.589123	-1.411293	-2.483127
H	-0.807285	-3.294113	-0.649487

TS(52-53 para)

C	2.803275	2.924075	0.668970
C	3.234908	0.762222	0.000027
C	4.597038	1.085017	-0.270412
C	5.017877	2.407381	-0.038529
C	4.121843	3.337391	0.434192
H	2.073507	3.641982	1.042566
H	6.051609	2.676485	-0.238891
H	4.414455	4.364219	0.622715
C	2.765568	-0.588411	-0.229234
C	3.685027	-1.546214	-0.721096
C	3.189166	-2.850217	-0.937484
C	0.955455	-2.127401	-0.178609
C	1.868443	-3.119026	-0.675900
H	3.872583	-3.612717	-1.312847
H	1.494401	-4.127584	-0.852782
C	5.484685	0.083044	-0.762156
H	6.517093	0.356127	-0.959895
C	5.039726	-1.184480	-0.978135
H	5.714507	-1.949697	-1.354933
N	2.361261	1.692728	0.465505
N	1.465006	-0.891885	0.030000
K	-0.279858	0.902801	0.914362
C	-1.207375	-0.975511	2.405832
C	-0.688685	-2.167286	1.899745
C	-2.018110	-0.319166	0.363339
C	-0.736815	-2.409428	0.513621
C	-1.552603	-1.512512	-0.247872
H	-1.050969	-3.484910	0.335100
C	-2.684275	0.670141	-0.462314
C	-2.925435	0.375994	-1.835442
C	-3.591162	1.349074	-2.604625
C	-3.647082	2.740618	-0.668047
C	-3.962824	2.537283	-2.021749
H	-3.796344	1.147493	-3.652429
H	-3.910600	3.683310	-0.189305
H	-4.476421	3.308797	-2.584643
C	-1.801419	-1.756155	-1.629731
H	-1.421434	-2.677241	-2.061697
C	-2.476396	-0.856275	-2.393739
H	-2.667715	-1.049397	-3.445333
N	-1.827561	-0.044965	1.681061
N	-3.033653	1.853770	0.095372
H	-1.103302	-0.751654	3.467724
H	-0.167811	-2.856097	2.555614

53 ortho

C	3.073259	0.233078	-1.165636
C	1.325560	1.540830	-0.446385
C	2.185459	2.286193	0.409620
C	3.547037	1.929650	0.440195
C	3.998655	0.895135	-0.345151
H	3.408048	-0.587302	-1.800976
H	4.224284	2.478027	1.089690
H	5.039350	0.591106	-0.340666
C	-0.087432	1.847871	-0.466380
C	-0.569209	2.906005	0.341625
C	-1.960438	3.154824	0.306073
C	-2.337136	1.011346	-1.190813
C	-2.773848	2.339951	-0.440886
H	-2.360639	3.976731	0.899267
H	-3.850886	2.500734	-0.430270
C	1.657010	3.347217	1.203386
H	2.335961	3.904120	1.842570
C	0.329639	3.647130	1.162391
H	-0.072212	4.453254	1.771550
N	1.786973	0.532854	-1.230228
N	-0.916775	1.082392	-1.217983
K	-0.065693	-0.948475	-2.803328
C	-2.994204	-0.606327	-1.072942
C	-3.920147	-0.569240	0.080385
C	-1.370324	-1.575988	0.287511
C	-3.378481	-0.671939	1.321551
C	-2.024143	-1.100041	1.460108
H	-3.946833	-0.418854	2.212722
C	-0.022036	-2.097980	0.432951
C	0.619352	-2.045801	1.708923
C	1.944513	-2.522185	1.790407
C	1.842276	-3.047770	-0.530935
C	2.561824	-3.031932	0.674188
H	2.459332	-2.483780	2.747085
H	2.309031	-3.442003	-1.434180
H	3.578097	-3.409798	0.709406
C	-1.358017	-1.090742	2.707982
H	-1.897365	-0.712188	3.573328
C	-0.067311	-1.526957	2.837479
H	0.443680	-1.498137	3.795032
N	-1.941874	-1.554350	-0.933189
N	0.607180	-2.594092	-0.661706
H	-3.566967	-0.900093	-2.032127
H	-4.934397	-0.212400	-0.071318

53 meta

C	-2.174453	1.680083	-1.347202
C	0.006545	1.851202	-0.624834
C	-0.270743	3.099276	0.008582
C	-1.586238	3.596257	-0.063861
C	-2.550598	2.885928	-0.737679
H	-2.915689	1.100406	-1.898003
H	-1.820809	4.540843	0.419923
H	-3.574209	3.237035	-0.805879
C	1.336896	1.286042	-0.536180
C	2.326745	2.022654	0.162972
C	3.617211	1.451420	0.270903
C	2.769266	-0.697065	-0.806874
C	3.812794	0.177936	-0.185513
H	4.408705	2.027396	0.748910
H	4.767976	-0.320254	-0.024297
C	0.761321	3.801495	0.691715
H	0.523363	4.752590	1.159097
C	2.017095	3.280479	0.752992
H	2.809726	3.809842	1.275676
N	-0.953811	1.174107	-1.302196
N	1.597579	0.070245	-1.105315
K	-0.441488	-1.212455	-2.564647
C	1.582927	-3.077107	-0.734505
C	2.632358	-2.316054	-0.032194
C	-0.060717	-2.071179	0.516231
C	2.223594	-2.040036	1.328685
C	0.875149	-1.733544	1.536523
H	2.961987	-1.781187	2.081294
C	-1.410717	-1.611892	0.601783
C	-1.825577	-0.883991	1.762314
C	-3.150363	-0.431658	1.815595
C	-3.501065	-1.393563	-0.338052
C	-4.007849	-0.692030	0.764486
H	-3.485632	0.124296	2.687646
H	-4.151252	-1.592320	-1.191013
H	-5.039671	-0.359360	0.774579
C	0.405682	-1.047499	2.701642
H	1.119956	-0.825176	3.490464
C	-0.886665	-0.636757	2.807829
H	-1.225268	-0.093635	3.686283
N	0.309467	-2.847104	-0.556497
N	-2.259256	-1.839439	-0.442828
H	1.853215	-3.693244	-1.594254
H	3.657811	-2.615896	-0.213393

53 para

C	2.338765	-1.747725	-1.433169
C	1.941611	0.401120	-0.706619
C	3.280278	0.523051	-0.235393
C	4.136222	-0.583973	-0.393619
C	3.667845	-1.731362	-0.988569
H	1.941468	-2.641133	-1.915875
H	5.161282	-0.514463	-0.039646
H	4.299599	-2.602619	-1.121034
C	1.018166	1.502900	-0.518468
C	1.502674	2.685826	0.098176
C	0.580717	3.735666	0.293424
C	-1.347881	2.253869	-0.552830
C	-0.729515	3.556672	-0.073559
H	0.929160	4.660149	0.753427
H	-1.451611	4.353752	0.097434
C	3.718546	1.734928	0.375396
H	4.747601	1.801835	0.715872
C	2.858797	2.777587	0.526803
H	3.188480	3.702111	0.994408
N	1.501426	-0.731668	-1.307450
N	-0.284300	1.357922	-0.877802
K	-1.055945	-0.948269	-2.284706
C	-4.041223	-0.302177	-0.918982
C	-4.088447	1.022167	-0.541173
C	-2.267041	-0.771478	0.459617
C	-2.921584	1.583533	0.251040
C	-2.334448	0.519389	1.040293
H	-3.036784	2.560833	0.708731
C	-1.180381	-1.637693	0.871625
C	-0.359860	-1.254676	1.974484
C	0.690171	-2.120390	2.336235
C	0.082317	-3.524724	0.507671
C	0.911924	-3.266610	1.611076
H	1.325030	-1.857766	3.178565
H	0.264403	-4.403217	-0.111537
H	1.719128	-3.948058	1.858023
C	-1.521363	0.851591	2.151766
H	-1.632849	1.839333	2.593288
C	-0.581695	-0.015720	2.633384
H	0.043339	0.244798	3.482620
N	-3.113153	-1.193513	-0.513764
N	-0.928844	-2.754654	0.141897
H	-4.783041	-0.689690	-1.618105
H	-4.829109	1.689239	-0.968791

TS(53-54 ortho)

C	2.878614	-3.123059	-1.535716
C	2.506141	-1.944359	0.400470
C	3.475707	-2.714052	1.100638
C	4.157513	-3.715675	0.385713
C	3.865462	-3.922005	-0.942088
H	2.618018	-3.278077	-2.581836
H	4.904849	-4.316437	0.896168
H	4.371726	-4.684897	-1.522291
C	1.797198	-0.896345	1.109036
C	2.066863	-0.705223	2.490095
C	1.337076	0.297034	3.153602
C	0.234742	0.806415	1.081747
C	0.421054	1.047771	2.456885
H	1.506615	0.462320	4.214444
H	-0.164215	1.822589	2.940493
C	3.725754	-2.471713	2.485333
H	4.469446	-3.080424	2.990468
C	3.039226	-1.509374	3.154892
H	3.220528	-1.332222	4.211136
N	2.213728	-2.167625	-0.903652
N	0.905403	-0.143944	0.434198
K	-0.271151	-1.122356	-1.912683
C	-0.769838	1.598991	0.230691
C	-1.527839	2.636634	1.007111
C	-2.763753	0.315664	0.129806
C	-2.732160	2.318591	1.517968
C	-3.359969	1.063508	1.202678
H	-3.289878	3.037126	2.116894
C	-3.524301	-0.832797	-0.364791
C	-4.773010	-1.185815	0.245393
C	-5.444480	-2.313394	-0.275756
C	-3.670898	-2.602900	-1.841459
C	-4.904343	-3.022879	-1.321442
H	-6.395491	-2.605637	0.163397
H	-3.211789	-3.153593	-2.663035
H	-5.406627	-3.890446	-1.736956
C	-4.590213	0.678205	1.757978
H	-5.001436	1.294500	2.556701
C	-5.290473	-0.424039	1.320039
H	-6.237192	-0.710039	1.767236
N	-1.623710	0.635891	-0.466829
N	-2.997836	-1.556747	-1.383289
H	-0.002000	2.214149	-0.708248
H	-1.087802	3.619409	1.155835
C	2.120415	2.114504	-1.722329
C	3.065352	2.936128	-2.618783
H	2.637422	3.031889	-3.594798

H	3.204904	3.908054	-2.193597
H	4.010275	2.439307	-2.690815
C	1.933993	0.709514	-2.324698
H	1.605806	0.034985	-1.561675
H	1.201964	0.749845	-3.104061
H	2.864682	0.367518	-2.726888
C	2.727768	1.992116	-0.312456
H	1.992437	2.260144	0.417167
H	3.043708	0.983377	-0.146539
H	3.569152	2.647791	-0.228408
O	0.754546	2.820260	-1.633379
K	1.010406	5.093671	-0.218375

TS(53-54 meta)

C	-4.460005	1.122099	-1.123162
C	-2.587919	2.125566	-0.231400
C	-3.378091	3.187011	0.300091
C	-4.767242	3.153229	0.074537
C	-5.321416	2.114752	-0.633944
H	-4.868994	0.285587	-1.691530
H	-5.384746	3.953050	0.474057
H	-6.387980	2.053789	-0.816973
C	-1.159196	2.108135	0.007507
C	-0.605383	3.167618	0.773007
C	0.781035	3.130510	1.038923
C	0.885713	1.048270	-0.161817
C	1.509021	2.056805	0.609496
H	1.239426	3.943468	1.595076
H	2.567240	1.964616	0.835535
C	-2.766966	4.236658	1.041339
H	-3.392865	5.035795	1.427110
C	-1.425890	4.223087	1.264607
H	-0.951579	5.015100	1.837670
N	-3.150797	1.118851	-0.942500
N	-0.406306	1.087111	-0.494467
K	-1.857402	-0.746066	-2.460912
C	1.157559	-1.104391	-1.507457
C	1.728654	-0.181628	-0.474036
C	-0.258167	-2.058067	0.031356
C	1.766005	-0.972708	0.809617
C	0.668410	-1.754798	1.093516
H	2.578061	-0.834996	1.516481
C	-1.496856	-2.694064	0.309489
C	-1.751755	-3.175643	1.637512
C	-2.973818	-3.799559	1.887533
C	-3.576132	-3.422942	-0.387278
C	-3.906291	-3.935126	0.868675

H	-3.180180	-4.178629	2.885930
H	-4.294155	-3.502935	-1.204904
H	-4.865136	-4.413507	1.033011
C	0.412719	-2.346748	2.378650
H	1.153159	-2.209129	3.163497
C	-0.741299	-3.014322	2.639549
H	-0.930390	-3.423723	3.628873
N	0.159224	-1.899587	-1.269824
N	-2.429799	-2.818537	-0.683142
H	1.600643	-1.134471	-2.505124
H	2.944700	0.229493	-0.822046
C	4.940872	1.142305	0.072123
C	6.435472	0.794905	-0.058579
H	6.822198	1.217612	-0.962273
H	6.968954	1.193988	0.778696
H	6.553721	-0.268261	-0.082973
C	4.777934	2.668180	0.201568
H	4.141583	3.026536	-0.580440
H	4.342391	2.901117	1.150748
H	5.736619	3.137071	0.124336
C	4.361905	0.456245	1.323411
H	3.382865	0.840560	1.520086
H	4.303982	-0.599135	1.156924
H	4.996600	0.650632	2.162622
O	4.188176	0.649888	-1.177907
K	4.632086	-1.998663	-1.022277

TS(53-54 para)

C	4.901778	0.693645	0.092269
C	3.528526	-1.132001	-0.193088
C	4.641758	-1.943611	-0.557490
C	5.915537	-1.345520	-0.587749
C	6.054308	-0.016820	-0.268601
H	4.983749	1.747288	0.361057
H	6.774509	-1.949243	-0.866760
H	7.019243	0.476564	-0.286636
C	2.196872	-1.715288	-0.180106
C	2.077879	-3.092751	-0.514352
C	0.788181	-3.656172	-0.506874
C	-0.083689	-1.499077	0.105946
C	-0.283345	-2.865036	-0.196879
H	0.664520	-4.705853	-0.759646
H	-1.293230	-3.263741	-0.188190
C	4.461775	-3.319786	-0.880970
H	5.333787	-3.909118	-1.147616
C	3.221596	-3.871243	-0.855180
H	3.073732	-4.919448	-1.099300

N	3.686171	0.172076	0.135470
N	1.127028	-0.940718	0.126473
K	2.009057	1.798251	1.623405
C	-0.974733	0.422637	2.677075
C	-1.415261	-0.663114	1.996256
C	-0.784327	1.753964	0.818149
C	-1.311663	-0.680745	0.492938
C	-1.299851	0.737196	-0.017452
H	-2.347247	-1.327656	-0.034293
C	-0.491327	3.026954	0.185340
C	-0.972894	3.296623	-1.137757
C	-0.724723	4.584685	-1.662158
C	0.502033	5.104980	0.316997
C	-0.003869	5.499268	-0.934187
H	-1.101394	4.829902	-2.652264
H	1.129733	5.788577	0.888287
H	0.200204	6.493872	-1.316779
C	-1.755047	1.030562	-1.308420
H	-2.203135	0.225395	-1.890046
C	-1.642932	2.289206	-1.863782
H	-2.014907	2.504289	-2.860664
N	-0.547122	1.610407	2.147527
N	0.271551	3.923477	0.865818
H	-0.981754	0.393922	3.768858
H	-1.775440	-1.546685	2.514487
O	-3.398403	-1.984294	-0.569453
C	-4.403339	-2.171884	0.430453
C	-4.850737	-0.801442	0.972046
H	-4.317272	-0.582709	1.873418
H	-4.644852	-0.045456	0.243351
H	-5.900942	-0.823971	1.175671
C	-5.612167	-2.899426	-0.186813
H	-5.300486	-3.849898	-0.566759
H	-6.362438	-3.043414	0.562360
H	-6.013477	-2.310466	-0.984921
C	-3.829351	-3.016806	1.582949
H	-2.903983	-3.457432	1.275635
H	-3.661037	-2.391083	2.434443
H	-4.524223	-3.788958	1.839529
K	-3.351991	0.279591	-2.021615

54 ortho

C	3.488476	3.002849	0.882127
C	3.511234	1.105643	-0.418766
C	4.914239	1.230848	-0.649392
C	5.571571	2.333115	-0.064608
C	4.862264	3.226265	0.701390

H	2.905909	3.689954	1.495330
H	6.639063	2.457806	-0.226271
H	5.341814	4.081609	1.164818
C	2.789814	-0.011491	-1.007047
C	3.534454	-0.968499	-1.751512
C	2.803492	-2.067412	-2.270874
C	0.785898	-1.159762	-1.294480
C	1.462619	-2.173650	-2.031258
H	3.322172	-2.812085	-2.869696
H	0.904894	-3.009631	-2.439240
C	5.602784	0.263709	-1.431494
H	6.669648	0.385530	-1.592055
C	4.927012	-0.804176	-1.954419
H	5.453754	-1.553854	-2.539966
N	2.826701	1.987820	0.349206
N	1.465915	-0.097383	-0.809918
K	0.106643	1.402615	1.035135
C	-0.614618	-1.293883	-0.889762
C	-1.425503	-2.401050	-1.430455
C	-2.601350	0.045526	-0.887082
C	-2.745488	-2.258159	-1.682369
C	-3.422185	-1.001950	-1.443055
H	-3.329502	-3.100758	-2.049259
C	-3.301592	1.273240	-0.479208
C	-4.695205	1.437410	-0.784775
C	-5.284111	2.668116	-0.403474
C	-3.200970	3.331485	0.558148
C	-4.543159	3.616726	0.257595
H	-6.331412	2.842979	-0.638139
H	-2.600202	4.052711	1.111456
H	-4.979159	4.564493	0.557499
C	-4.781336	-0.797265	-1.694397
H	-5.346041	-1.615200	-2.140680
C	-5.422198	0.399251	-1.406313
H	-6.474191	0.543772	-1.630038
N	-1.308324	-0.049174	-0.653224
N	-2.597098	2.204194	0.203620
H	-0.305955	-1.510172	0.609988
H	-0.959902	-3.373701	-1.573790
C	0.759130	-1.990215	2.400646
C	0.217975	-2.541016	3.723847
H	-0.225710	-1.735064	4.317908
H	-0.558507	-3.291334	3.536045
H	0.999069	-3.014629	4.329233
C	1.875600	-0.978699	2.687562
H	2.233555	-0.541909	1.749203
H	1.503619	-0.168260	3.325712
H	2.731496	-1.433408	3.198382
C	1.333167	-3.144087	1.570287

H	1.791001	-2.771533	0.649163
H	2.097865	-3.700118	2.123114
H	0.539730	-3.847350	1.292267
O	-0.293310	-1.356302	1.719296
K	-2.780273	-1.648134	1.492006

54 meta

C	-3.372612	-3.065200	-1.941685
C	-3.249371	-1.651936	-0.126493
C	-4.522645	-2.090657	0.346384
C	-5.211824	-3.045762	-0.427402
C	-4.645947	-3.531439	-1.581400
H	-2.887978	-3.454082	-2.837051
H	-6.186620	-3.390766	-0.093108
H	-5.153133	-4.265746	-2.197545
C	-2.521745	-0.642245	0.622746
C	-3.073122	-0.210494	1.860067
C	-2.294323	0.693765	2.628191
C	-0.657646	0.737101	0.848871
C	-1.104082	1.143747	2.143523
H	-2.665839	1.015789	3.598179
H	-0.489608	1.838142	2.709879
C	-5.051856	-1.584937	1.564954
H	-6.021348	-1.939692	1.900938
C	-4.332979	-0.687235	2.301346
H	-4.719724	-0.316878	3.247420
N	-2.689910	-2.164077	-1.251760
N	-1.353329	-0.176248	0.133231
K	0.139487	-2.226911	-1.223218
C	0.918324	0.800499	-1.053534
C	0.506583	1.375864	0.258590
C	2.543613	-0.483858	-0.065155
C	1.745812	1.499842	1.095966
C	2.666297	0.475943	1.011526
H	1.884171	2.324268	1.796635
C	3.299618	-1.680158	-0.061558
C	4.334624	-1.852602	0.920784
C	5.076259	-3.030745	0.895623
C	3.759255	-3.762761	-0.953232
C	4.801933	-4.005392	-0.058226
H	5.872024	-3.172573	1.623736
H	3.504510	-4.520184	-1.696359
H	5.362314	-4.932261	-0.103771
C	3.785827	0.309410	1.903224
H	3.959632	1.074242	2.658016
C	4.570047	-0.799795	1.865735
H	5.383097	-0.923991	2.577717

N	1.818157	-0.130567	-1.190711
N	3.010057	-2.662859	-0.973346
H	0.440710	1.159367	-1.973137
H	0.210828	2.831803	-0.131300
C	-1.017521	4.380199	-0.682856
C	-0.882623	5.738985	-1.369300
H	-0.400310	5.627397	-2.345703
H	-1.855981	6.217028	-1.525840
H	-0.268254	6.412056	-0.763322
C	-1.872169	3.449158	-1.552755
H	-1.980617	2.466981	-1.080283
H	-2.876564	3.852899	-1.721877
H	-1.397025	3.300369	-2.527847
C	-1.690339	4.561487	0.682553
H	-1.799351	3.595336	1.185545
H	-1.079914	5.206879	1.321565
H	-2.686883	5.009441	0.597038
O	0.271726	3.848412	-0.519754
K	2.657298	3.378934	-1.068480

54 para

C	3.552986	-3.095119	1.029543
C	3.550982	-1.000078	0.072228
C	4.972892	-0.914196	0.166748
C	5.652223	-2.001192	0.754192
C	4.945881	-3.093093	1.197109
H	2.971659	-3.958549	1.351241
H	6.734223	-1.959095	0.844713
H	5.441491	-3.941448	1.655810
C	2.807417	0.110998	-0.494916
C	3.546937	1.208689	-1.013437
C	2.796646	2.233734	-1.645694
C	0.757076	1.067257	-1.059110
C	1.436445	2.159560	-1.680906
H	3.322425	3.070153	-2.099264
H	0.858411	2.938708	-2.165863
C	5.658802	0.227204	-0.328838
H	6.740421	0.264296	-0.245611
C	4.959368	1.245581	-0.914030
H	5.480600	2.110742	-1.316223
N	2.870556	-2.096868	0.488997
N	1.461879	0.050510	-0.520213
K	0.337713	-2.473257	-0.610068
C	-2.568410	0.934612	-2.526980
C	-1.493983	1.620608	-2.066707
C	-2.471024	-0.711192	-0.923333
C	-0.697876	1.113443	-0.914142

C	-1.387907	-0.053464	-0.259094
H	-1.024972	2.190453	0.135781
C	-2.985666	-1.932487	-0.300429
C	-2.533584	-2.316962	1.007570
C	-3.085299	-3.497701	1.559429
C	-4.375683	-3.763898	-0.430311
C	-4.007937	-4.222880	0.848825
H	-2.768515	-3.810801	2.551844
H	-5.099212	-4.326892	-1.019824
H	-4.447369	-5.129387	1.252962
C	-1.046313	-0.417183	1.053912
H	-0.294435	0.182965	1.560016
C	-1.582667	-1.523871	1.691857
H	-1.292336	-1.788239	2.704526
N	-3.072661	-0.250293	-2.035649
N	-3.893495	-2.667035	-0.987012
H	-3.134324	1.347357	-3.364605
H	-1.234579	2.571755	-2.525114
O	-1.568421	2.840175	0.853155
C	-0.734536	3.782180	1.457968
C	-1.540439	4.512430	2.535517
H	-2.406561	5.010984	2.087821
H	-1.908805	3.800104	3.280269
H	-0.944958	5.271829	3.055400
C	0.474224	3.094268	2.109059
H	1.066685	2.562875	1.355467
H	1.136568	3.808401	2.611974
H	0.138315	2.361780	2.850053
C	-0.237257	4.801101	0.423375
H	0.359206	4.299506	-0.345435
H	-1.087592	5.281832	-0.070945
H	0.385921	5.584308	0.871136
K	-3.716063	1.782240	0.159513

Pyridine + KO^{t}Bu ortho complex

C	-1.528144	-1.530067	-0.000003
C	-2.872325	-1.877050	0.000139
C	-3.821048	-0.858387	0.000207
C	-3.359519	0.449295	0.000140
H	-0.782841	-2.326917	-0.000055
H	-4.885950	-1.069527	0.000311
H	-4.073781	1.275222	0.000199
H	-3.186310	-2.919158	0.000193
C	2.465195	-0.535156	-0.000146
C	2.258986	-1.389606	1.253265
H	2.963924	-2.226986	1.297670
H	2.393898	-0.782078	2.153114

H	1.244445	-1.799140	1.275419
C	2.259362	-1.390863	-1.252758
H	2.394532	-0.784234	-2.153171
H	2.964313	-2.228288	-1.296119
H	1.244828	-1.800421	-1.274801
C	3.868003	0.059089	-0.000240
H	4.635414	-0.721962	0.000190
H	4.018545	0.683505	-0.885890
H	4.018347	0.684279	0.884899
O	1.547583	0.541631	-0.000840
C	-1.088847	-0.189143	-0.000084
H	-0.022425	0.036342	-0.000392
N	-2.060491	0.786379	0.000003
K	-0.027617	2.505082	0.000114

TS (Pyridine + KO^{t}Bu-58)

C	-1.542107	-1.526679	-0.002601
C	-2.881768	-1.890910	-0.001733
C	-3.843842	-0.884623	0.001058
C	-3.398249	0.428527	0.002764
H	-0.788037	-2.315667	-0.004787
H	-4.905996	-1.109471	0.001809
H	-4.122944	1.245615	0.005004
H	-3.182784	-2.937035	-0.003127
C	2.516108	-0.520723	0.000601
C	2.313761	-1.372373	1.254896
H	3.022028	-2.206714	1.297944
H	2.448090	-0.763956	2.154006
H	1.300937	-1.786005	1.278342
C	2.313984	-1.375527	-1.251559
H	2.443412	-0.767907	-2.151912
H	3.025591	-2.206975	-1.295140
H	1.302810	-1.793400	-1.271806
C	3.908912	0.092939	0.000026
H	4.684612	-0.679229	0.002486
H	4.052242	0.716941	-0.886869
H	4.050938	0.721226	0.884105
O	1.401490	0.487548	-0.001211
C	-1.114971	-0.180225	-0.000948
H	0.307118	0.102905	-0.001049
N	-2.103407	0.781394	0.001936
K	-0.081572	2.484382	-0.001455

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C	-1.528144	-1.530067	-0.000003
C	-2.872325	-1.877050	0.000139
C	-3.821048	-0.858387	0.000207
C	-3.359519	0.449295	0.000140
H	-0.782841	-2.326917	-0.000055
H	-4.885950	-1.069527	0.000311
H	-4.073781	1.275222	0.000199
H	-3.186310	-2.919158	0.000193
C	2.792249	-0.234538	-0.000204
C	2.683720	-1.106848	1.253168
H	3.478622	-1.859361	1.297558
H	2.749219	-0.488016	2.153045
H	1.721854	-1.628218	1.275281
C	2.684286	-1.107950	-1.252855
H	2.750178	-0.489907	-2.153240
H	3.479207	-1.860503	-1.296231
H	1.722430	-1.629341	-1.274939
C	4.119066	0.514163	-0.000240
H	4.969688	-0.175331	0.000178
H	4.198225	1.151613	-0.885862
H	4.197906	1.152286	0.884927
O	1.759023	0.731861	-0.000878
C	-1.088847	-0.189143	-0.000084
H	0.751966	0.217164	-0.000619
N	-2.060491	0.786379	0.000003
K	-0.027617	2.505082	0.000114

TS(58-59)

C	-0.925472	-0.234017	-0.909522
C	-1.240906	1.084642	-0.513840
C	-2.342985	1.374462	0.279272
C	-3.143946	0.316363	0.709321
H	-2.584925	2.398519	0.569694
H	-4.017334	0.477884	1.336481
H	-0.585931	1.894985	-0.841849
C	-2.776371	-0.965248	0.317690
H	-3.375559	-1.819263	0.650179
N	-1.717162	-1.248914	-0.456486
C	1.500501	-0.507374	-1.139877
C	1.675010	-1.408255	-0.057761
N	1.969527	0.769237	-1.092320
C	2.132440	-0.929192	1.144883
H	1.379396	-2.446564	-0.176448
C	2.381280	1.205537	0.101617
C	2.465776	0.435190	1.254096

H	2.242111	-1.594180	1.998689
H	2.701193	2.250256	0.133682
H	2.829584	0.861131	2.183558
H	1.292954	-0.897672	-2.127618
K	0.547902	-2.211633	-2.235494

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C	0.712585	-0.038190	-0.523379
C	0.988700	-1.312294	-1.039997
C	2.022199	-2.078690	-0.524409
C	2.761221	-1.577348	0.547548
H	2.252132	-3.060019	-0.934920
H	3.564952	-2.148006	1.001066
H	0.361405	-1.697088	-1.841234
C	2.433145	-0.320378	1.028058
H	2.985271	0.109003	1.865234
N	1.449565	0.434801	0.509635
C	-0.780094	0.349095	-0.679645
C	-1.185927	0.730673	0.648186
N	-1.283855	-0.809980	-1.232220
C	-1.613217	-0.255371	1.504314
H	-1.144012	1.766176	0.982702
C	-1.680853	-1.735212	-0.363212
C	-1.781675	-1.561804	1.016528
H	-1.873989	-0.015941	2.532462
H	-2.003028	-2.681634	-0.803663
H	-2.129503	-2.366800	1.653948
H	-0.668686	1.145731	-1.419164
K	0.558062	2.739502	-0.269033

TS(59-60)

C	-1.286060	-1.139531	-0.209799
C	-1.920390	-1.171708	1.076009
C	-3.250656	-0.853130	1.206274
C	-3.999355	-0.477632	0.063508
H	-3.733328	-0.917898	2.179466
H	-5.061237	-0.266157	0.113871
H	-1.341704	-1.521613	1.925648
C	-3.324437	-0.519210	-1.160314
H	-3.875028	-0.288921	-2.077027
N	-2.035826	-0.799126	-1.331200
C	0.130742	-1.323902	-0.365795
C	0.679614	-1.628292	-1.706419
N	0.845407	-1.867794	0.779121
C	1.916962	-2.169291	-1.839691

H	0.055019	-1.414262	-2.567209
C	2.056187	-2.367655	0.538881
C	2.694139	-2.508736	-0.687332
H	2.302867	-2.381735	-2.835891
H	2.580505	-2.728209	1.435133
H	3.666329	-2.980837	-0.763273
H	0.309648	0.037144	-0.147511
C	1.504635	1.920220	-0.485496
C	1.082591	1.929982	-1.958213
H	0.122829	2.445019	-2.087302
H	1.813935	2.446542	-2.589046
H	0.975758	0.905704	-2.329059
C	1.618939	3.355408	0.027400
H	0.661864	3.881375	-0.067102
H	1.902938	3.366437	1.085188
H	2.369298	3.930128	-0.526801
C	2.854976	1.210959	-0.354033
H	3.228564	1.271625	0.675972
H	2.763861	0.153975	-0.624668
H	3.619888	1.663427	-0.994310
O	0.529113	1.254051	0.294992
K	0.872122	1.025417	2.832835
K	0.275395	-4.345573	-0.433224

60

C	1.335800	-0.659240	-0.308003
C	1.958906	-1.272523	0.815256
C	2.767947	-2.378983	0.639519
C	2.964865	-2.889296	-0.647110
H	3.259681	-2.837525	1.495032
H	3.579717	-3.762574	-0.832270
H	1.823468	-0.826234	1.796936
C	2.370723	-2.191641	-1.699690
H	2.545643	-2.523637	-2.725285
N	1.603710	-1.114741	-1.573700
C	0.334531	0.392940	-0.167640
C	0.180661	1.366773	-1.297766
N	0.242678	0.961105	1.199922
C	0.034986	2.694531	-1.066687
H	0.124290	0.959247	-2.301778
C	0.079357	2.275326	1.304303
C	0.064860	3.223682	0.275788
H	-0.122346	3.367989	-1.908455
H	-0.026744	2.635695	2.335467
H	-0.171310	4.260786	0.483694
H	-1.087947	-0.616093	-0.289594
C	-3.146294	-0.637379	-0.545758

C	-3.168127	-0.476674	-2.070877
H	-2.949519	-1.436766	-2.547713
H	-4.138551	-0.122405	-2.438061
H	-2.403135	0.239964	-2.386548
C	-4.310625	-1.534774	-0.116878
H	-4.212066	-2.526919	-0.567641
H	-4.315278	-1.661282	0.972188
H	-5.282923	-1.121459	-0.409597
C	-3.304695	0.744093	0.107395
H	-3.338917	0.653336	1.200862
H	-2.459816	1.390128	-0.151155
H	-4.227270	1.246549	-0.206884
O	-1.952542	-1.244534	-0.134875
K	-1.028495	-1.248987	2.191496
K	2.689858	1.961855	0.057530

Pyridine + KO^{t}Bu para complex

C	-0.306837	-2.461034	1.141459
C	-0.254182	-1.096605	1.152011
C	-0.357811	-0.281576	-0.108529
C	-0.410106	-1.212613	-1.292945
C	-0.461395	-2.566336	-1.142943
N	-0.456163	-3.280747	0.043986
H	-0.201956	-2.993088	2.091945
H	-0.063203	-0.588056	2.095166
H	-0.362875	-0.796099	-2.296908
H	-0.491489	-3.185541	-2.043390
H	0.672400	0.183382	-0.257118
C	-1.267258	0.861515	-0.104856
C	-1.483218	1.656267	-1.258593
C	-1.943226	1.317161	1.053669
C	-2.277693	2.783066	-1.191238
H	-1.004011	1.395963	-2.199073
C	-2.725737	2.460566	1.004400
H	-1.856726	0.763545	1.987021
N	-2.914395	3.219067	-0.085100
H	-2.423816	3.389416	-2.085409
H	-3.250671	2.787054	1.903536
K	-2.943995	-1.670437	0.165988
C	3.119444	1.367970	0.271997
C	2.457858	1.620590	1.635017
H	1.451731	2.033439	1.509451
H	2.370180	0.682879	2.195457
H	3.034410	2.326860	2.243275
C	3.198390	2.695510	-0.510885
H	3.187131	2.478686	-1.581585
H	2.343323	3.343288	-0.293058

H	4.108055	3.264224	-0.289056
C	4.534168	0.823560	0.501814
H	5.026997	0.631137	-0.457070
H	5.164274	1.512060	1.075414
H	4.484682	-0.124997	1.049546
K	2.307657	-2.109632	-0.247290
O	2.406771	0.412308	-0.450779

TS(Pyridine + KO^{t}Bu-62)

C	-1.864724	1.264194	-0.141799
C	-0.503780	1.306374	-0.407046
C	0.242161	0.139036	-0.633794
C	-0.518255	-1.038018	-0.552678
C	-1.877917	-1.010563	-0.284074
N	-2.573766	0.122882	-0.077593
H	-2.431904	2.182325	0.028487
H	-0.018001	2.283475	-0.435944
H	-0.040823	-2.008288	-0.700650
H	-2.455645	-1.938266	-0.229219
H	1.609495	0.096745	-0.860999
C	3.422234	-0.890426	-0.218174
C	3.239319	-0.463496	1.252181
H	3.744499	-1.133742	1.960064
H	3.635781	0.547285	1.394256
H	2.174670	-0.441775	1.510091
C	2.828319	-2.302195	-0.396721
H	2.923882	-2.611875	-1.442942
H	3.319852	-3.056324	0.231942
H	1.761379	-2.298786	-0.147790
C	4.920590	-0.942626	-0.535022
H	5.466989	-1.644310	0.108282
H	5.070015	-1.243801	-1.576867
H	5.362062	0.051518	-0.412520
O	2.822189	0.014050	-1.076040
K	3.057449	2.538285	-0.176602

62

C	-3.573038	0.244491	-0.700611
C	-2.227817	0.566084	-0.864539
C	-1.199639	-0.130731	-0.200612
C	-1.694252	-1.166355	0.613400
C	-3.054814	-1.435469	0.725639
N	-4.009609	-0.744999	0.087093
H	-4.347885	0.805461	-1.227875
H	-1.994941	1.386996	-1.552225

H	-1.008405	-1.799622	1.183026
H	-3.409466	-2.247977	1.363474
H	0.555498	0.098256	-0.527806
C	2.442755	-0.596357	-0.149185
C	2.290595	-0.642910	1.375776
H	2.935831	-1.400192	1.833754
H	2.555287	0.325089	1.817634
H	1.255940	-0.872457	1.650348
C	2.101507	-1.964186	-0.743421
H	2.188174	-1.933947	-1.833088
H	2.769307	-2.746697	-0.367869
H	1.073490	-2.246380	-0.497155
C	3.870214	-0.209825	-0.516229
H	4.596087	-0.935445	-0.135018
H	3.980338	-0.153894	-1.602536
H	4.122408	0.771238	-0.101252
O	1.582699	0.391950	-0.685926
K	0.217121	2.349760	0.422988

TS(62-63)

C	-2.457077	0.684734	-1.163815
C	-1.768330	1.398273	-0.208777
C	-1.353080	0.755013	0.988731
C	-1.891802	-0.543180	1.179317
C	-2.577401	-1.156164	0.149801
N	-2.872625	-0.595883	-1.039757
H	-2.728987	1.173852	-2.101576
H	-1.488961	2.430463	-0.403398
H	-1.719490	-1.081477	2.107761
H	-2.946266	-2.174656	0.291441
H	-1.047155	1.346144	1.839403
C	0.944852	0.357129	0.656634
C	1.999569	1.219421	0.325410
C	1.175140	-0.973472	0.298000
C	3.158880	0.746601	-0.287018
H	1.943433	2.292269	0.539525
C	2.366285	-1.374960	-0.298838
H	0.400409	-1.729482	0.477767
N	3.371864	-0.539170	-0.601570
H	3.973432	1.432622	-0.540988
H	2.536698	-2.424729	-0.557324
K	0.705351	0.235441	3.443717

63

C	-2.480438	-0.023635	1.126489
C	-1.259001	-0.498285	1.505990
C	-0.365675	-1.282503	0.575734
C	-1.100422	-1.439116	-0.738327
C	-2.328530	-0.890300	-0.960046
N	-3.067641	-0.115168	-0.106652
H	-3.069465	0.516091	1.874090
H	-0.950444	-0.382201	2.543112
H	-0.650835	-2.063751	-1.506431
H	-2.788763	-1.062495	-1.936168
H	-0.120827	-2.275541	1.010186
C	1.011759	-0.649039	0.353823
C	1.956728	-1.270348	-0.468017
C	1.395215	0.566498	0.922711
C	3.181822	-0.659602	-0.691920
H	1.735318	-2.228212	-0.931166
C	2.652696	1.094381	0.642980
H	0.717896	1.084958	1.598723
N	3.548459	0.514161	-0.158195
H	3.917975	-1.137034	-1.336588
H	2.957967	2.039054	1.093089
K	-1.110499	1.738309	-0.745864

TS(63-64)

C	-2.464977	-0.182799	1.151936
C	-1.209171	-0.604556	1.477657
C	-0.305133	-1.307185	0.496435
C	-1.034203	-1.362308	-0.832151
C	-2.301920	-0.887113	-0.994311
N	-3.077690	-0.237887	-0.071820
H	-3.062965	0.283118	1.940036
H	-0.877141	-0.517493	2.510191
H	-0.546764	-1.873750	-1.659126
H	-2.760218	-0.998801	-1.980886
H	-0.000604	-2.593093	0.927485
C	1.059450	-0.645263	0.316676
C	2.063926	-1.272650	-0.426173
C	1.371581	0.611299	0.835151
C	3.275369	-0.628425	-0.628262
H	1.897055	-2.262227	-0.844246
C	2.621090	1.171917	0.586379
H	0.648486	1.133625	1.459499
N	3.573931	0.584435	-0.141634
H	4.057749	-1.110501	-1.212438
H	2.872642	2.148071	1.000746

K	-1.268264	1.776323	-0.655830
C	1.357485	-3.736029	2.438089
C	1.149950	-2.460410	3.275541
H	1.640900	-1.637441	2.799526
H	0.103335	-2.253086	3.356252
H	1.561420	-2.604396	4.252711
C	2.756532	-3.706046	1.795152
H	2.668871	-3.874974	0.742213
H	3.207564	-2.751062	1.966836
H	3.365225	-4.471271	2.229690
C	1.237058	-4.972667	3.347936
H	1.330673	-5.860216	2.757687
H	2.013010	-4.950578	4.084354
H	0.283817	-4.966431	3.833934
K	-2.022970	-5.020811	2.347926
O	0.286398	-3.804991	1.333726

64

C	-0.306837	-2.461034	1.141459
C	-0.254182	-1.096605	1.152011
C	-0.357811	-0.281576	-0.108529
C	-0.410106	-1.212613	-1.292945
C	-0.461395	-2.566336	-1.142943
N	-0.456163	-3.280747	0.043986
H	-0.201956	-2.993088	2.091945
H	-0.063203	-0.588056	2.095166
H	-0.362875	-0.796099	-2.296908
H	-0.491489	-3.185541	-2.043390
H	1.277284	0.375385	-0.360061
C	-1.267258	0.861515	-0.104856
C	-1.483218	1.656267	-1.258593
C	-1.943226	1.317161	1.053669
C	-2.277693	2.783066	-1.191238
H	-1.004011	1.395963	-2.199073
C	-2.725737	2.460566	1.004400
H	-1.856726	0.763545	1.987021
N	-2.914395	3.219067	-0.085100
H	-2.423816	3.389416	-2.085409
H	-3.250671	2.787054	1.903536
K	-2.943995	-1.670437	0.165988
C	2.950837	1.551167	0.090314
C	2.276166	1.779787	1.451154
H	1.227898	2.068252	1.322997
H	2.302680	0.861327	2.048491
H	2.772110	2.571649	2.024043
C	2.868516	2.846652	-0.744217
H	2.873273	2.587455	-1.805505

H	1.945985	3.399436	-0.540328
H	3.707944	3.525077	-0.556510
C	4.421087	1.183508	0.322335
H	4.924642	1.011246	-0.634809
H	4.971985	1.962540	0.860576
H	4.486683	0.258191	0.906890
K	2.307657	-2.109632	-0.247290
O	2.347640	0.491486	-0.585576

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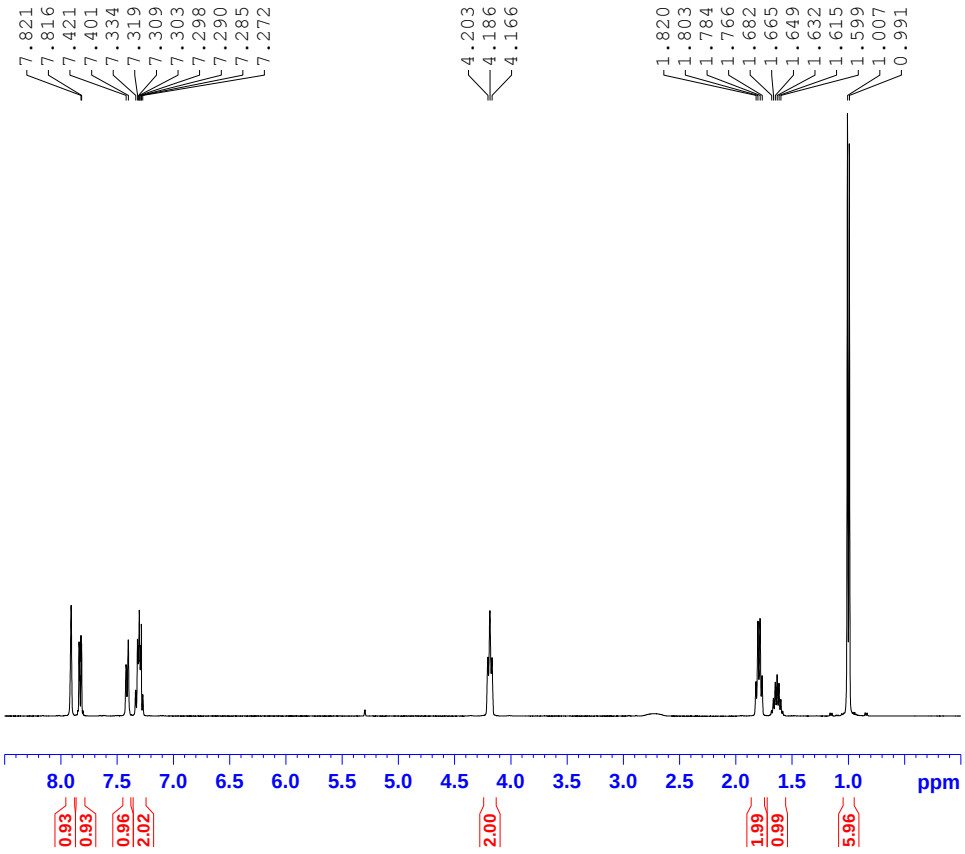

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TD	32564
SOLVENT	CDC13
NS	16
DS	2
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FIDRES	0.252539 Hz
AQ	1.9799412 sec
RG	90.5
DW	60.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
TD0	1
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NUC1	1H
P1	9.40 usec
PL1	-4.00 dB
PL1W	19.93825150 W
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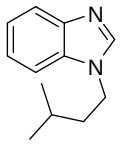

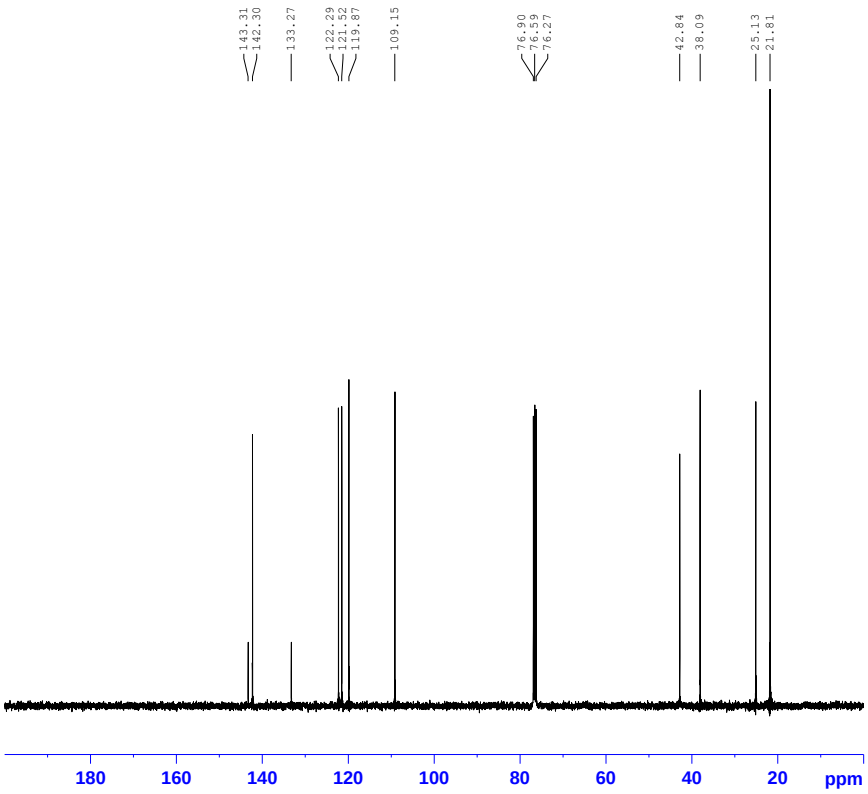

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AQ	0.3714207 sec
RG	2050
DW	22.667 usec
DE	6.50 usec
TE	294.2 K
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D11	0.03000000 sec
TD0	1
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NUC1	13C
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PL1	-2.60 dB
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CPDPRG2	waltz16
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PL12	14.06 dB
PL13	120.00 dB
PL2W	19.93825150 W
PL12W	0.31166428 W
PL13W	0.00000000 W
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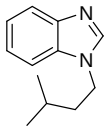
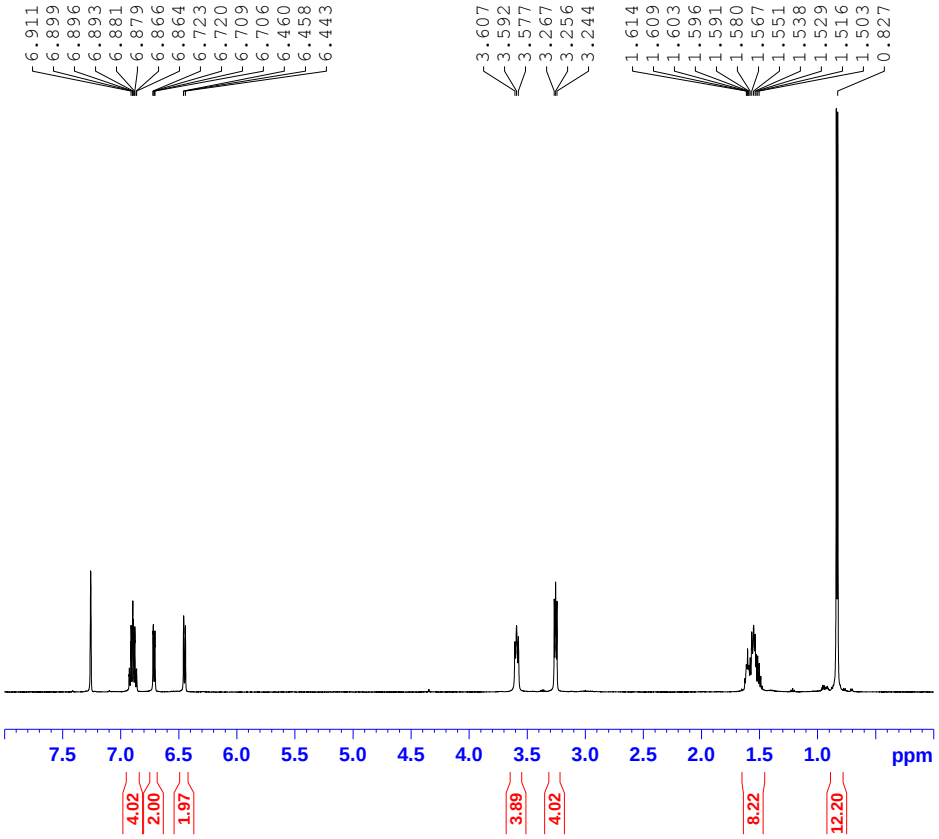


Spectra of **22**

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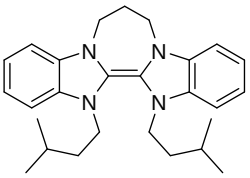
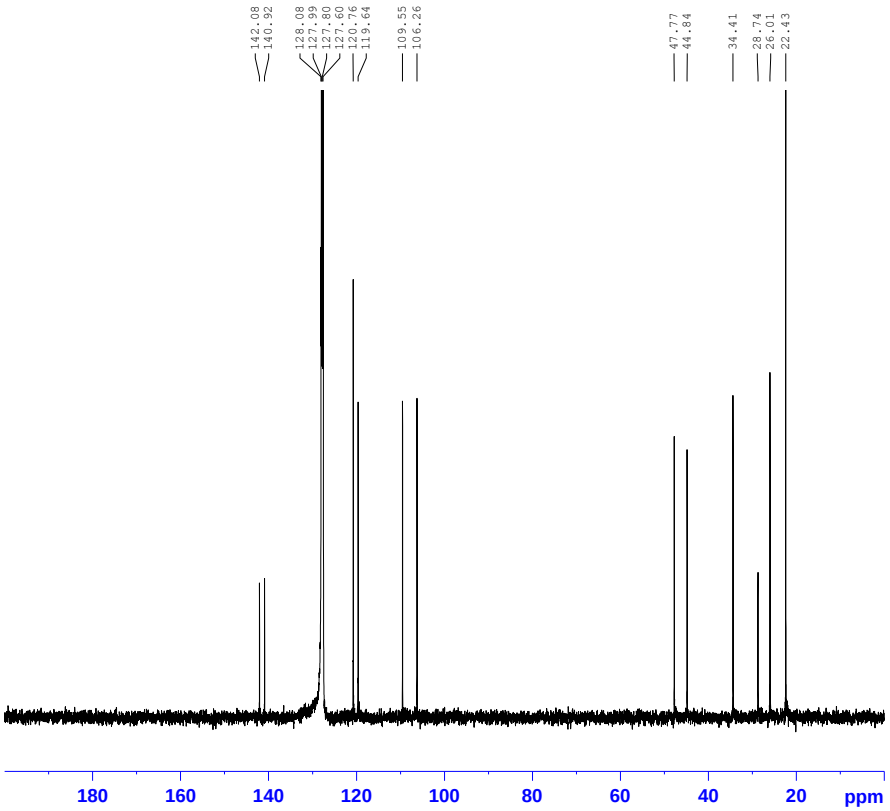
NS                      16
DS                       2
SWH              10288.065 Hz
FIDRES           0.156983 Hz
AQ               3.1850996 sec
RG                   322.5
DW                  48.600 usec
DE                   6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -2.70 dB
SFO1          500.1330885 MHz
SI                   32768
SF            500.1300084 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



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NAME                A33378
EXPNO                    2
PROCNO                   1
Date_             20130605
Time                 11.26
INSTRUM             DRX500
PROBHD    5 mm DUL 13C-1
PULPROG           zgpg30
TD                   16384
SOLVENT               C6D6
NS                    1500
DS                       4
SWH              30120.482 Hz
FIDRES           1.838408 Hz
AQ               0.2720244 sec
RG                  5160.6
DW                  16.600 usec
DE                   6.00 usec
TE                  300.0 K
D1              0.69999999 sec
d11             0.03000000 sec
DELTA           0.59999996 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   8.00 usec
PL1                  -2.30 dB
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.30 dB
PL12                 12.84 dB
PL13                120.00 dB
SFO2          500.1320005 MHz
SI                   32768
SF            125.7577890 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```
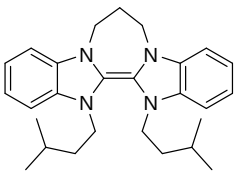
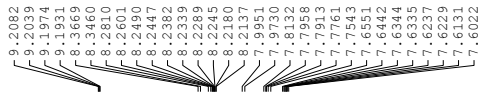
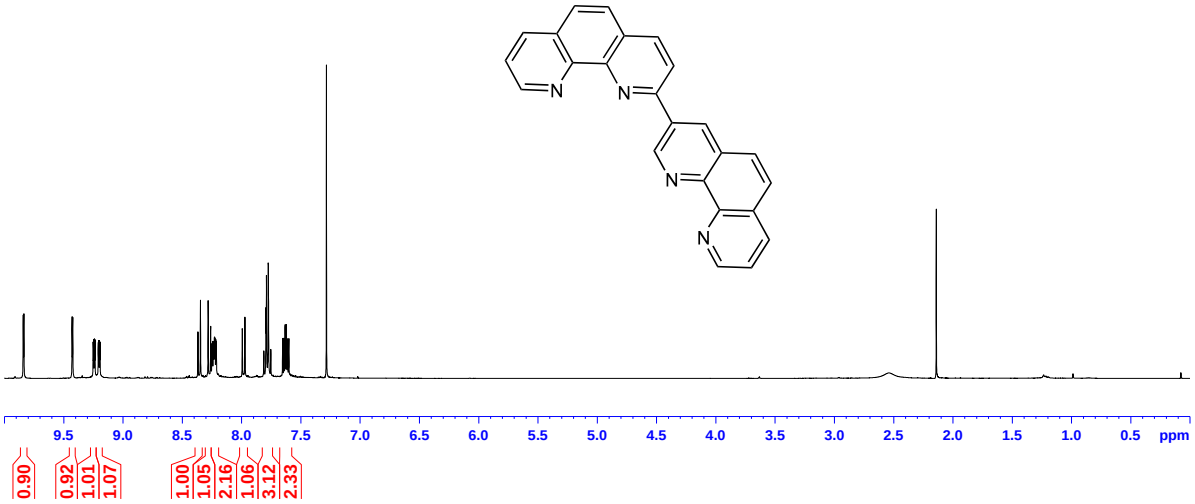
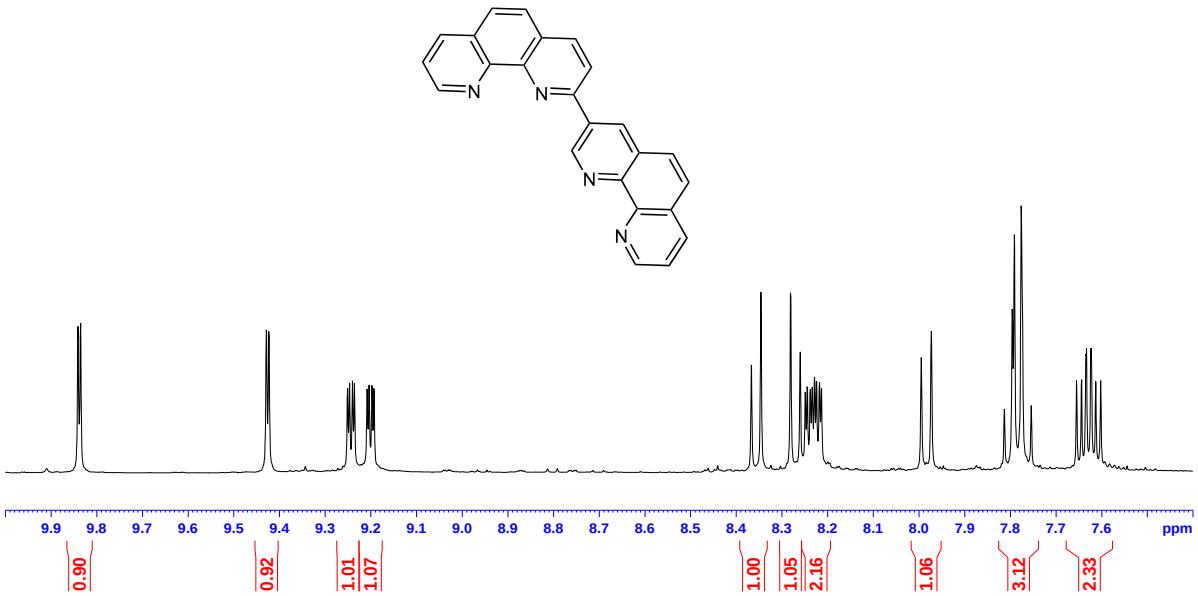
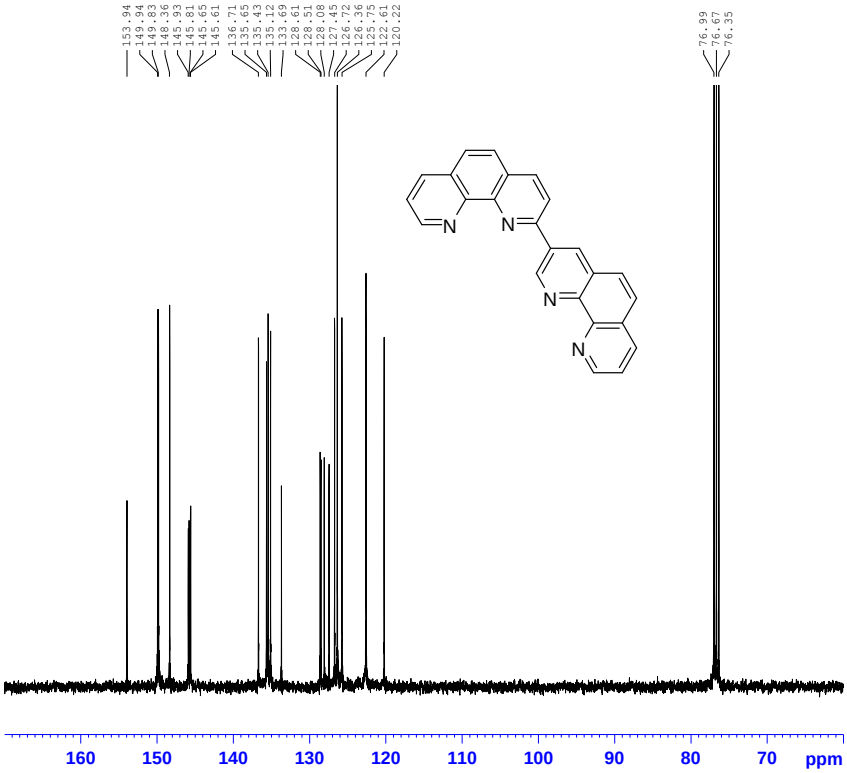



Spectra of **50**

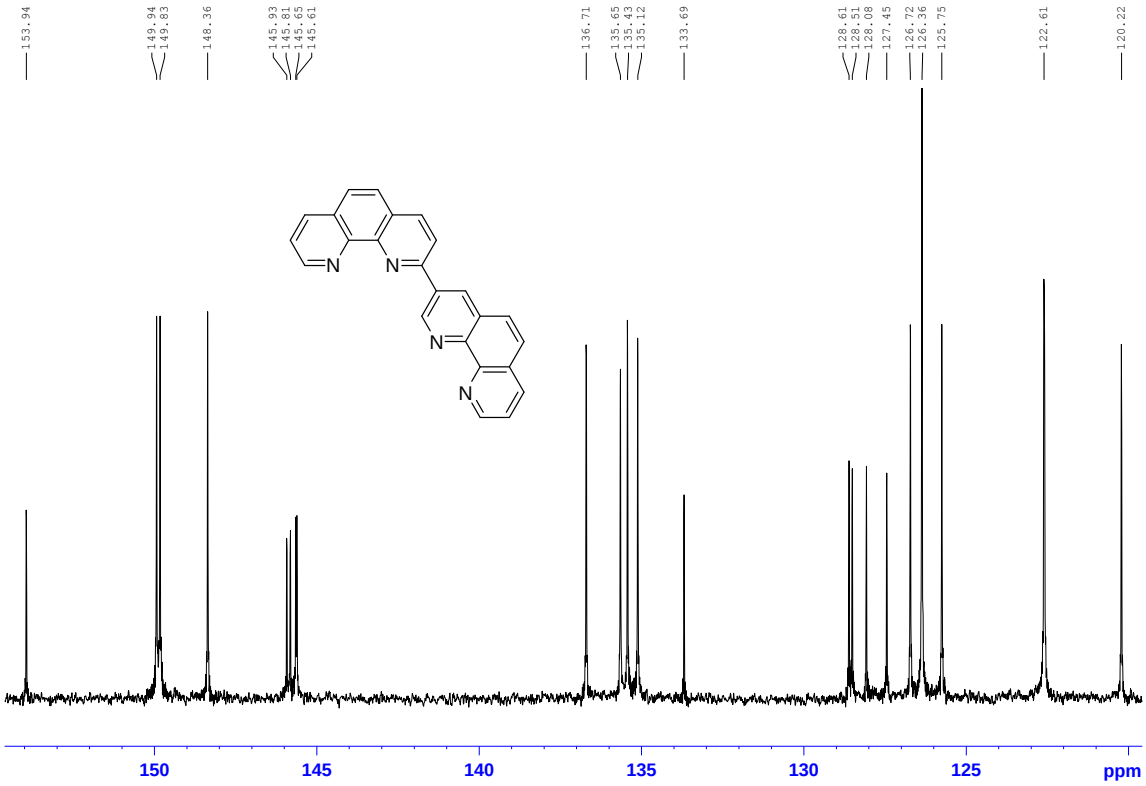




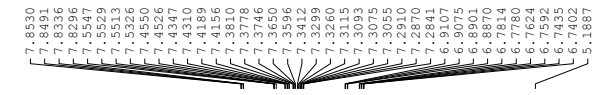


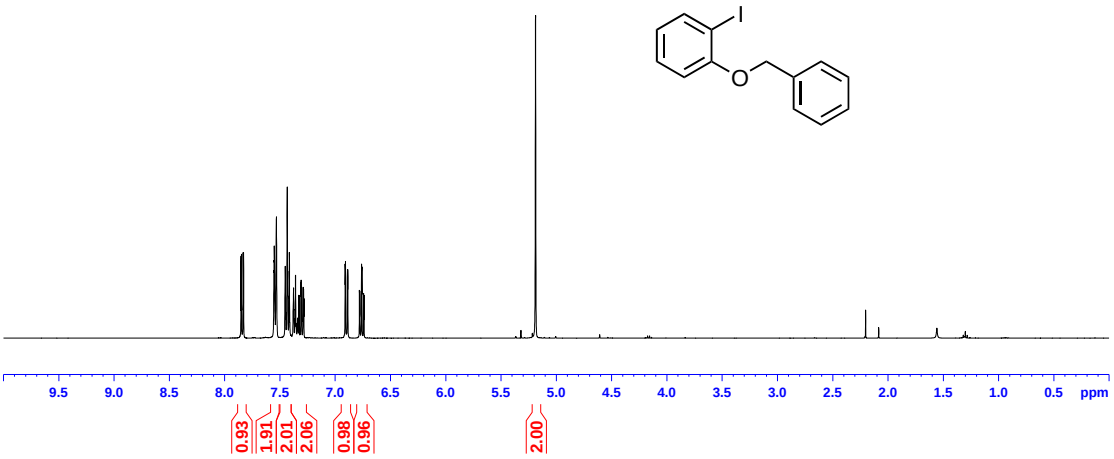


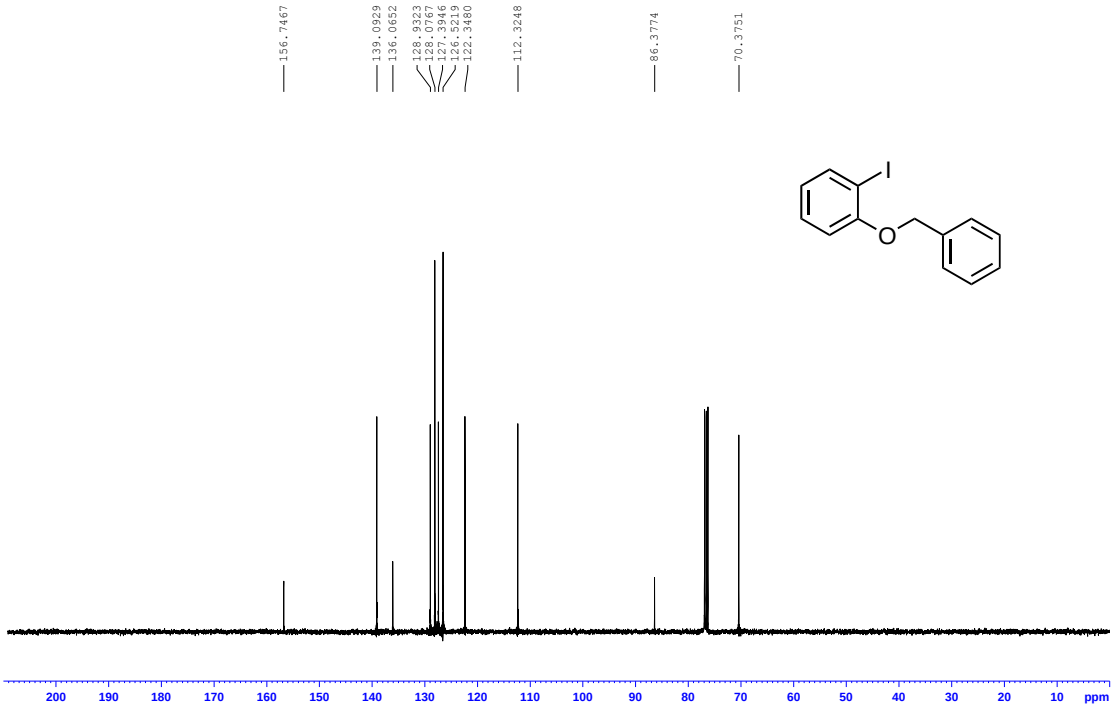

```
NAME              D182131
EXPNO                   2
PROCNO                  1
Date_            20130604
Time                 1.25
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  16384
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             22058.824 Hz
FIDRES           1.346364 Hz
AQ               0.3714207 sec
RG                   2050
DW                 22.667 usec
DE                   6.50 usec
TE                  300.0 K
D1              0.69999999 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.00 usec
PL1                 -2.60 dB
PL1W         61.34123230 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.06 dB
PL13              120.00 dB
PL2W         19.93825150 W
PL12W         0.31166428 W
PL13W         0.00000000 W
SFO2        400.1316005 MHz
SI                 32768
SF          100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



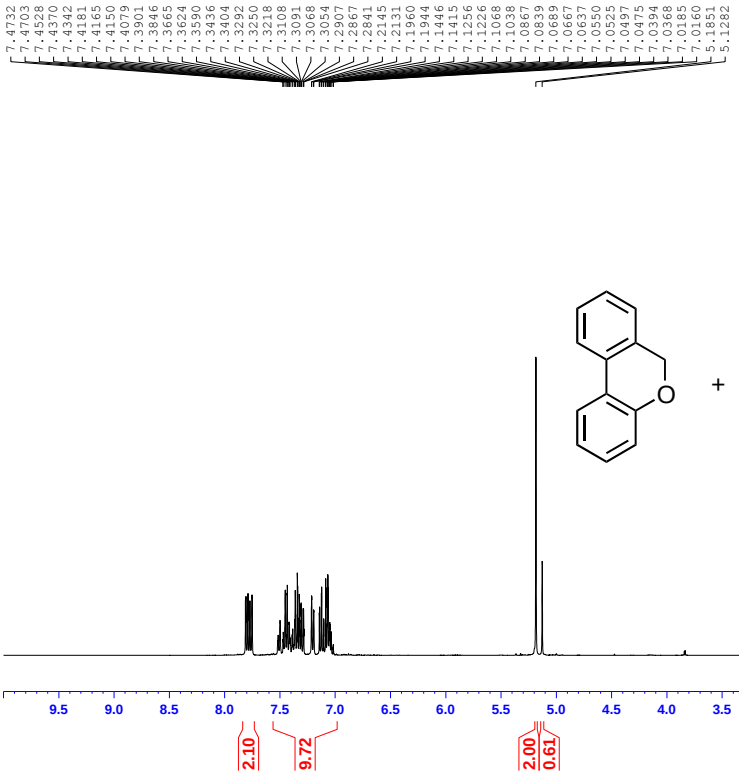
Spectra of **55a**

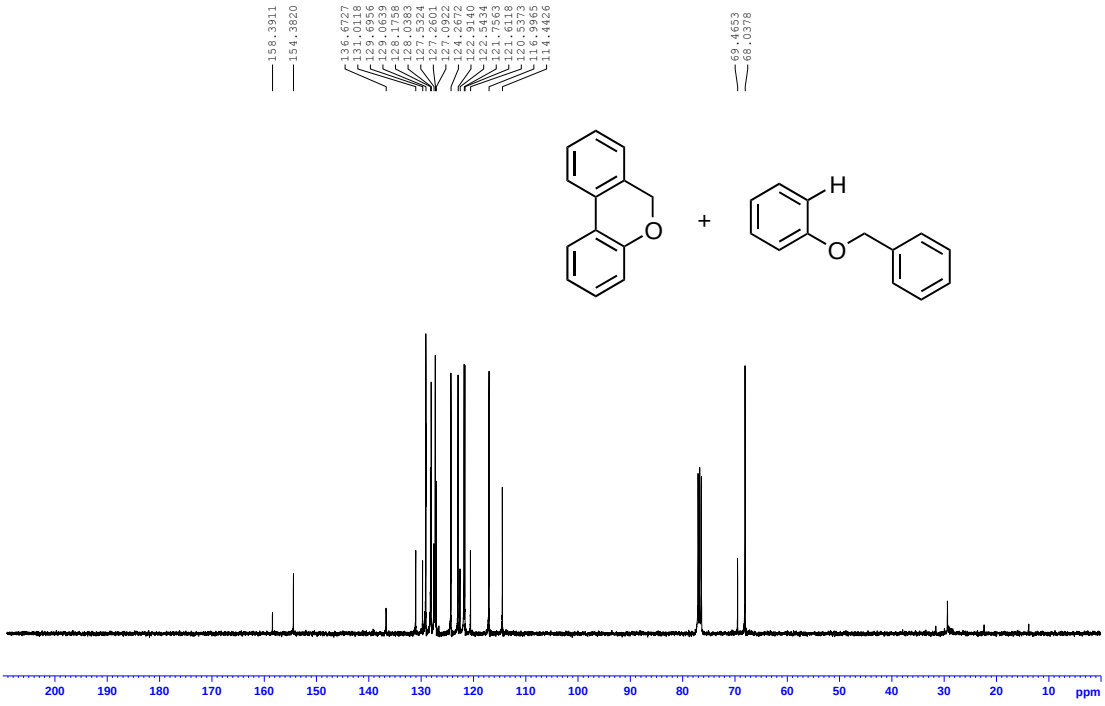




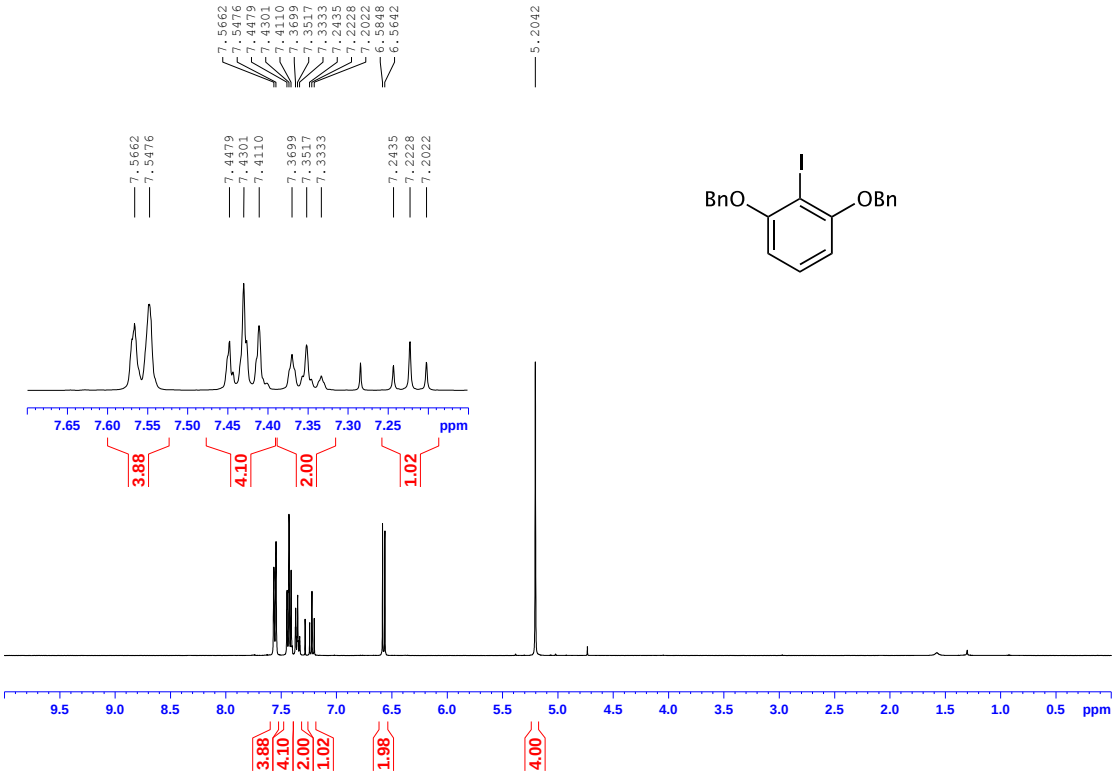


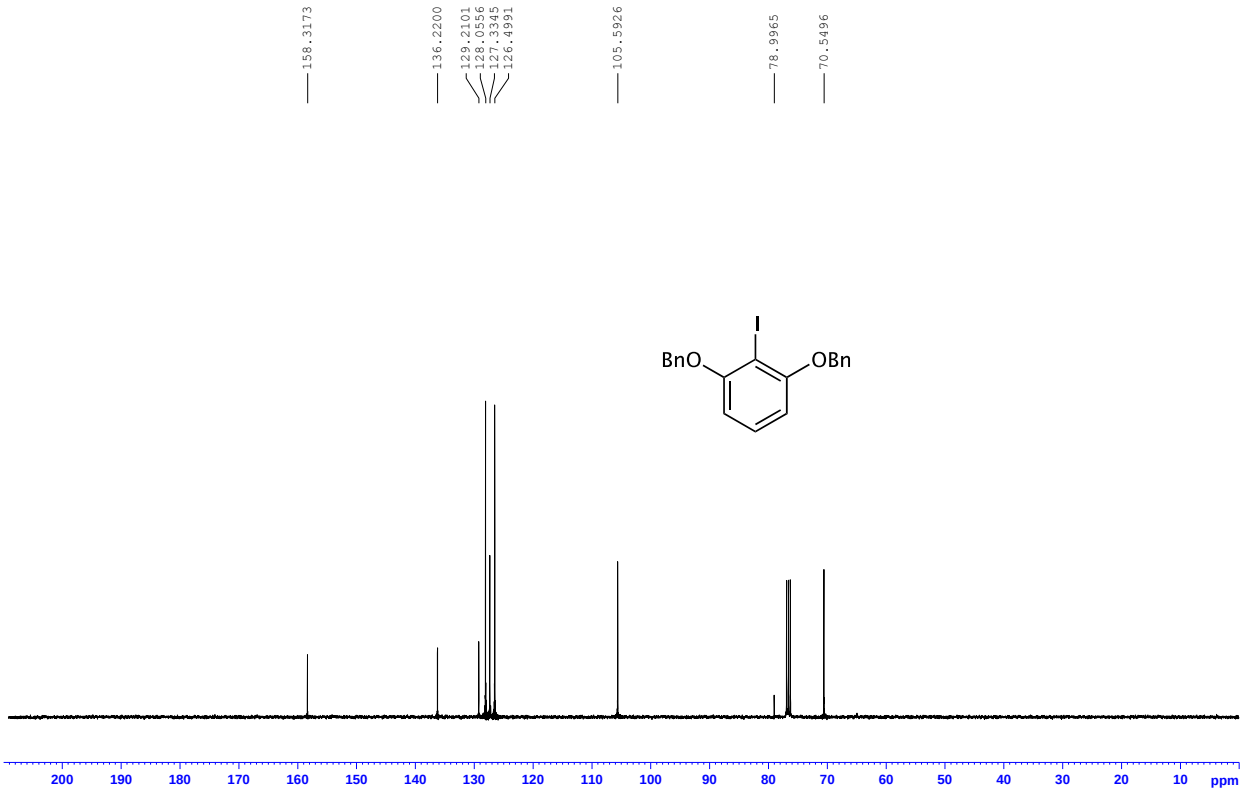
Spectra of **56a** + **57a**



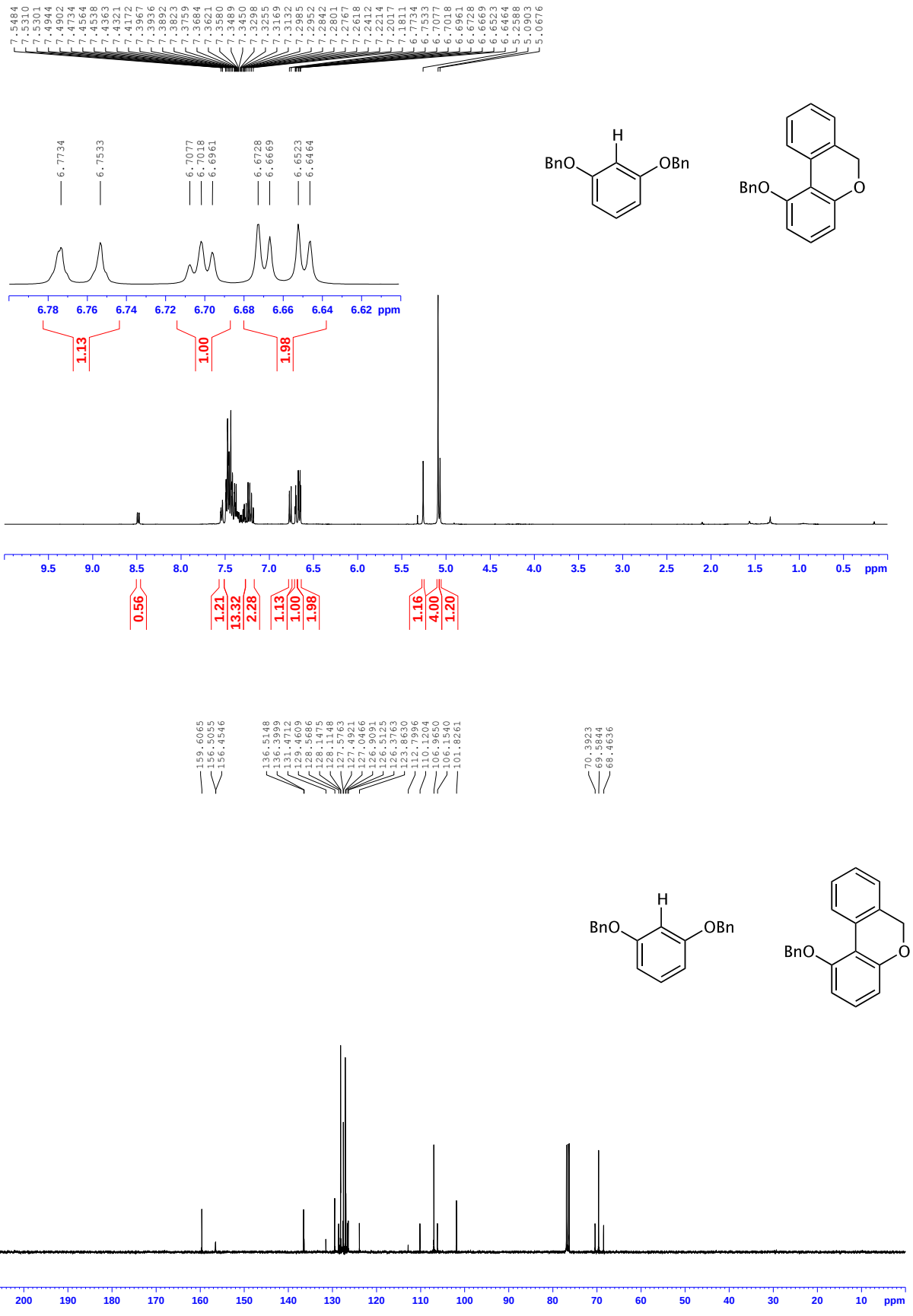


Spectra of **55b**

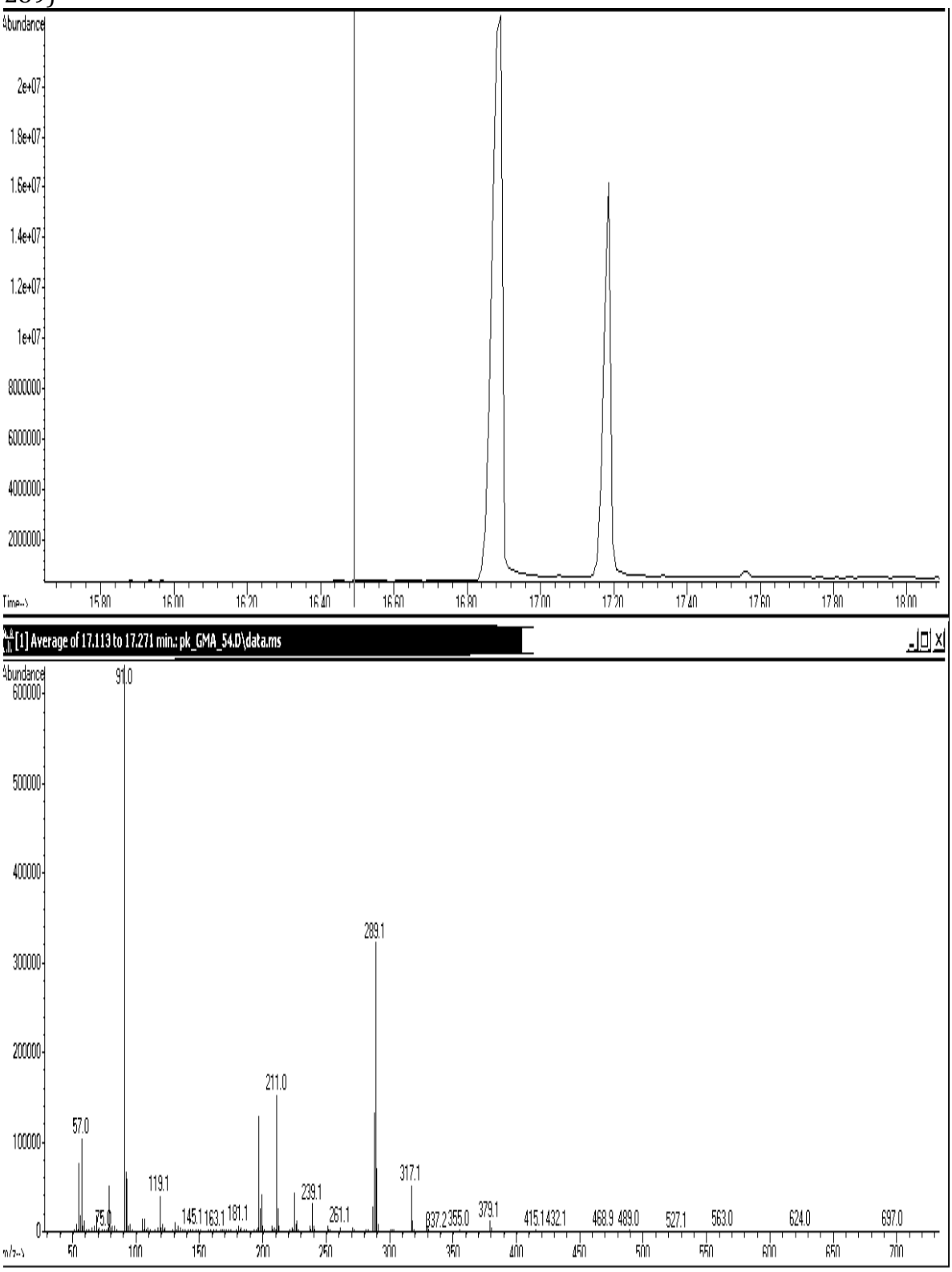




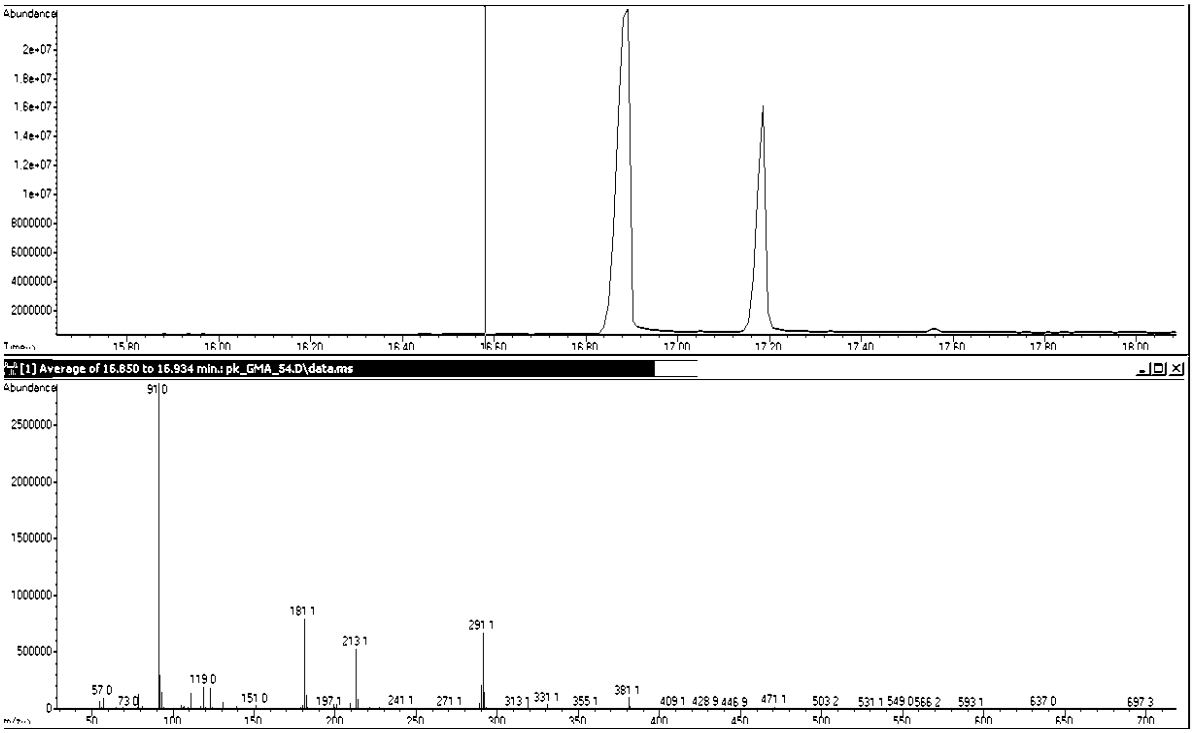
Spectra of **56b** + **57b**



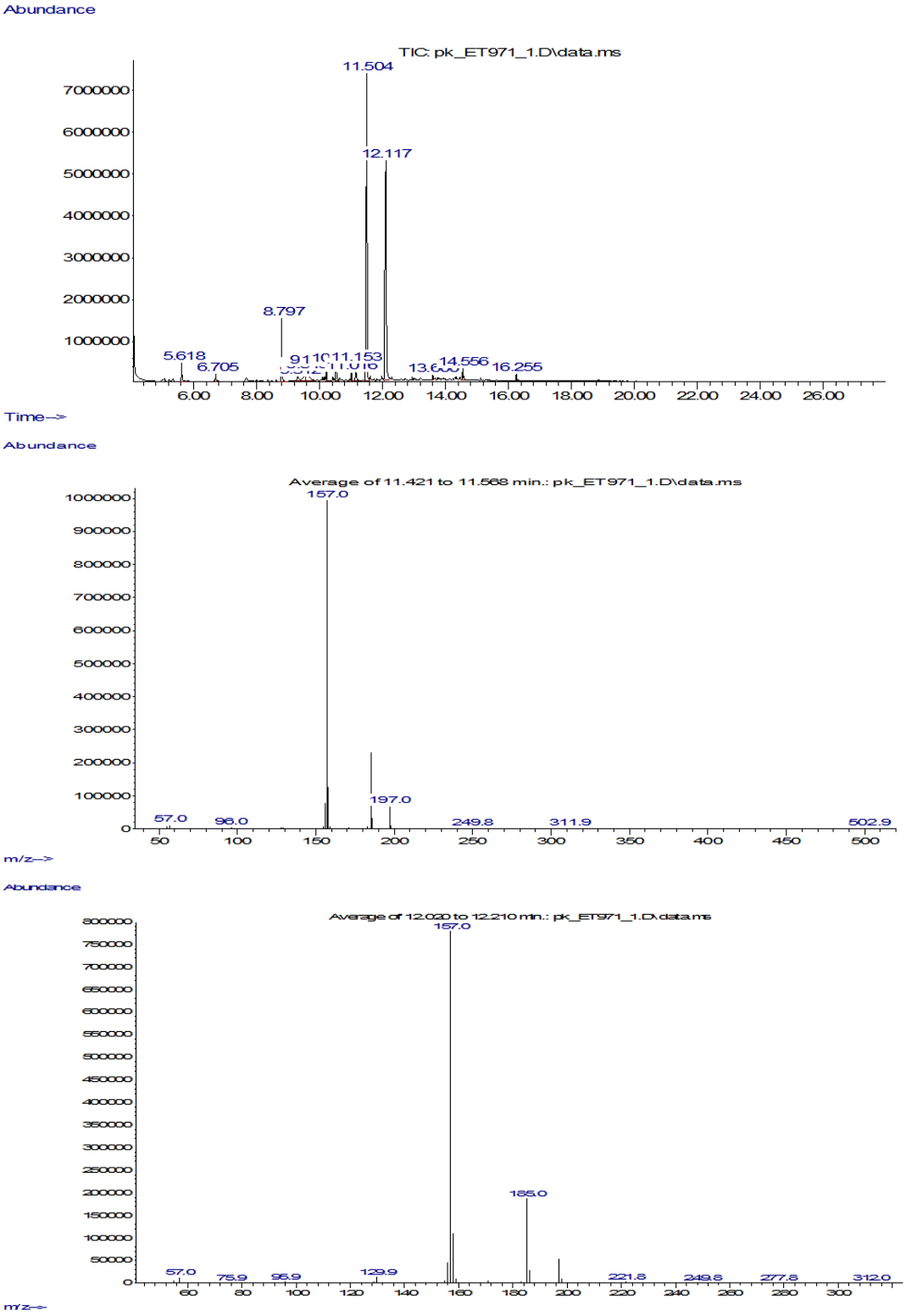
See below:
Top trace: GCMS of mixture of **56b** and **57b**.
Lower trace: mass spectrum of peak at 17.2 min corresponding to **56b** (*m/z* = 289)



Top trace: GCMS of mixture of **56b** and **57b**.
Lower trace: mass spectrum of peak at 16.9 min corresponding to **57b** (*m/z* = 291)

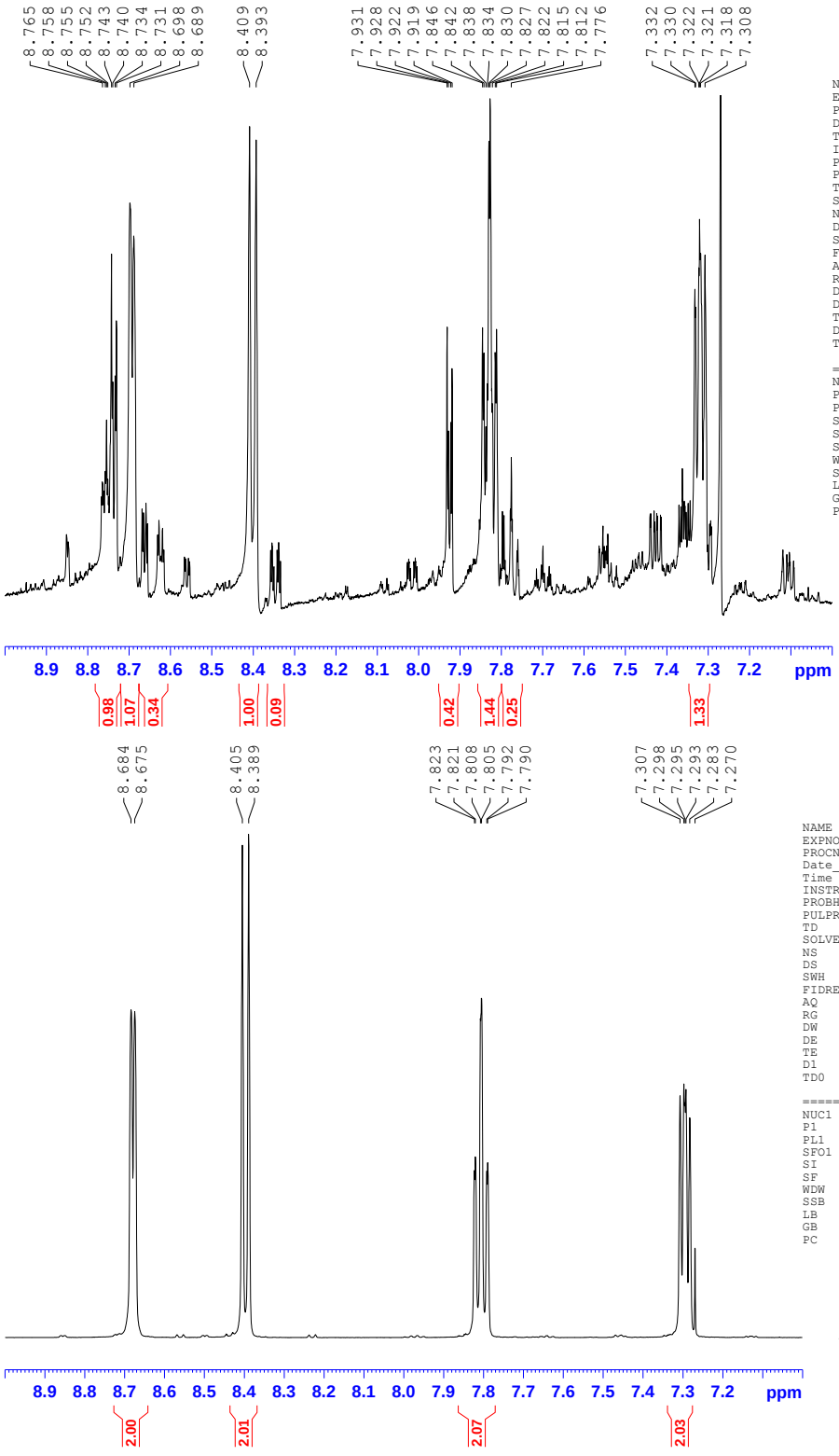


See below: GCMS of reaction of KOtBu with Pyridine, showing two fractions at 11.504 and 12.117 mins, with their mass spectra below confirming M+H = 157, each corresponding to a bipyridine.



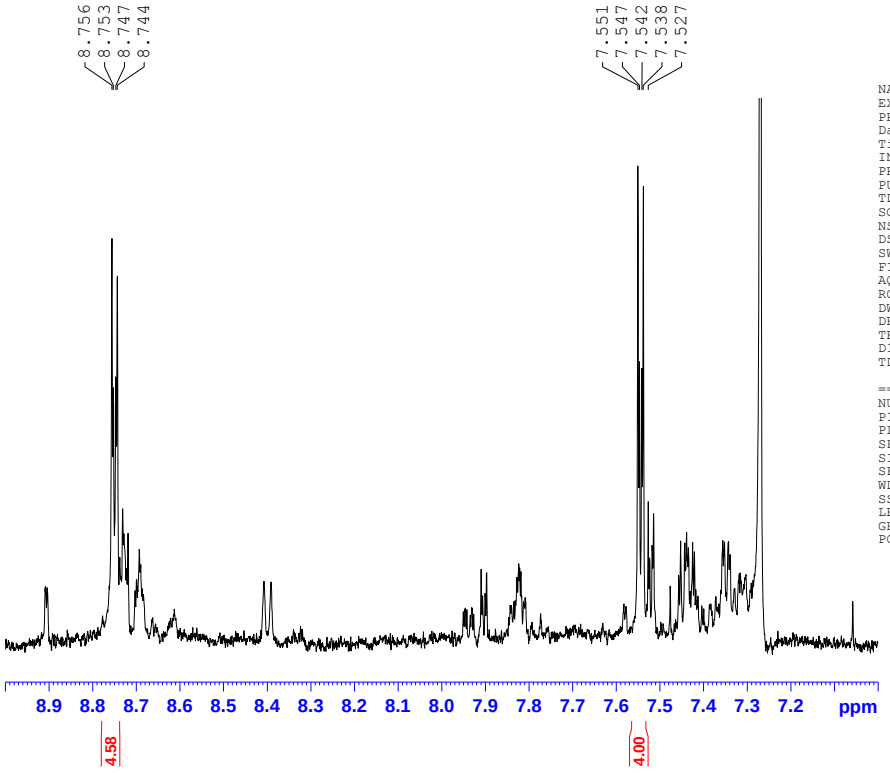
See below: fractions emerging from chromatography of products from reaction of KOtBu and pyridine, Top trace: ^{1}H NMR spectrum in $CDCl_3$ of the 1st fraction enriched in 2,2-bipyridine **61**.

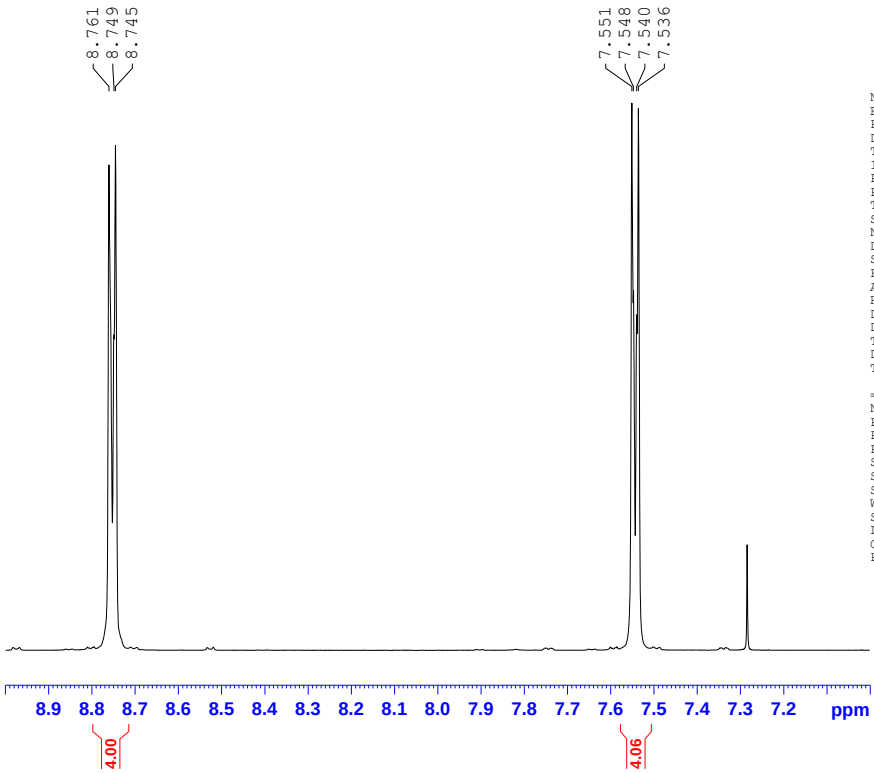
Lower trace: authentic 2,2-bipyridine **61** in $CDCl_3$.



See below 2nd fraction from chromatography: Top trace ^{1}H NMR of second fraction, enriched in 4,4'-bipyridine **65**;

Lower trace ^{1}H NMR spectrum of authentic 4,4'-bipyridine **65**:

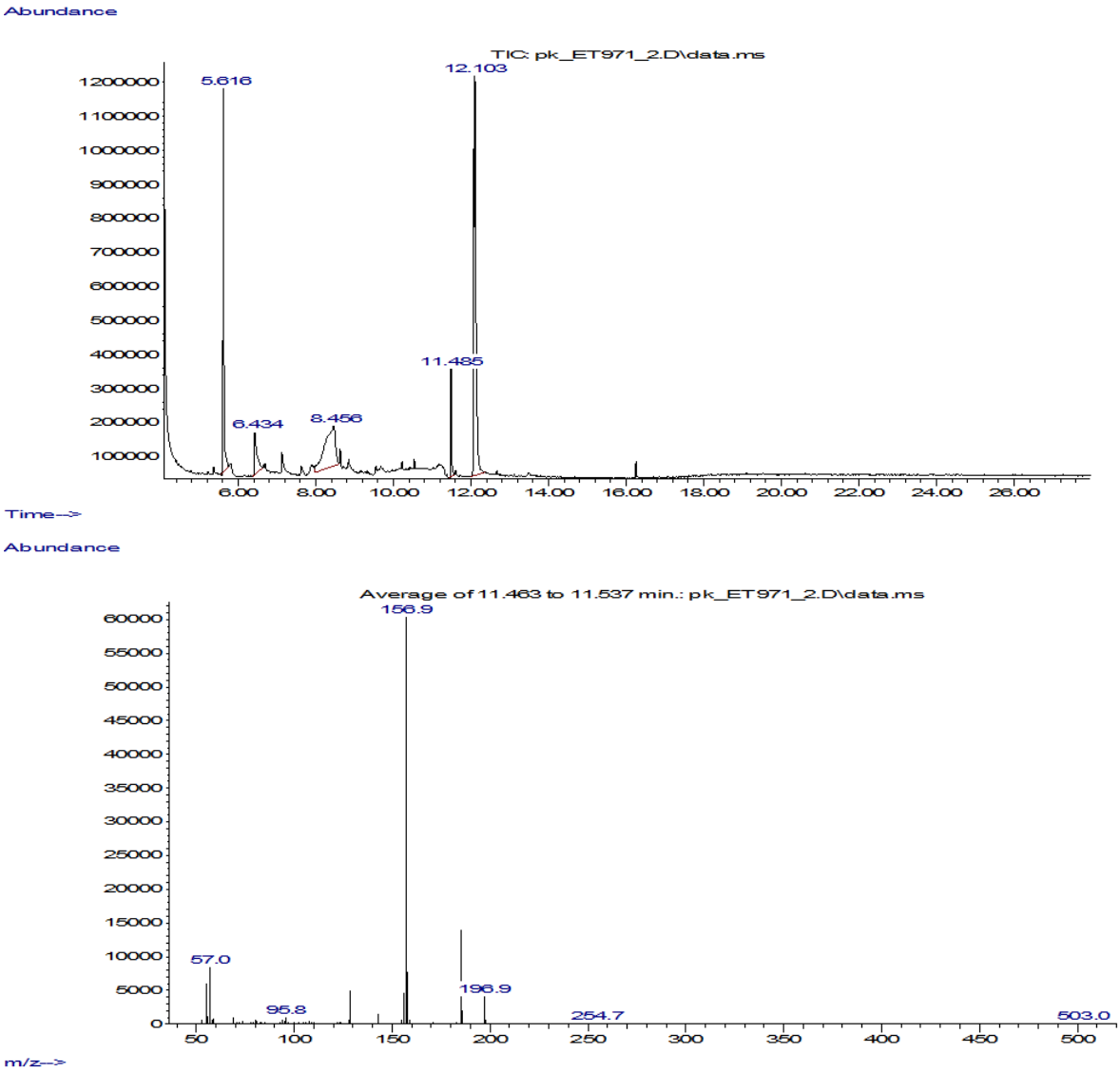




See below:

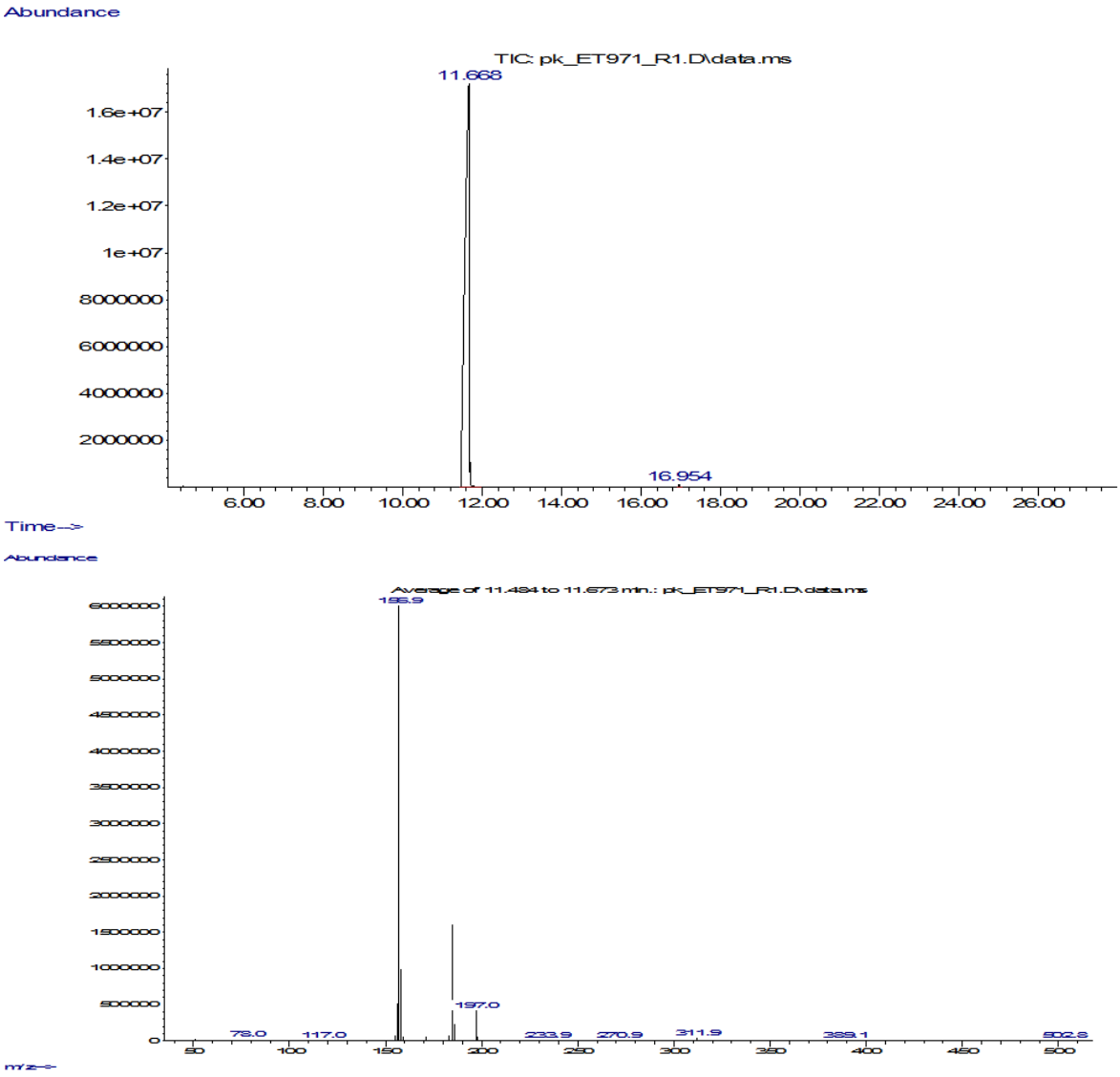
Top trace GC/MS of fraction 2 from column chromatography, mainly one peak at 12.103 minute.

Lower trace: MS of the peak: 156.9 (M+H, 100%), 185.0 (M+C_2H_5, 20%), 197 (M+C_3H_5, 5%); High resolution *m/z* of this fraction: Found 156.0684; $C_{10}H_8N_2$ (M) requires 156.0682.



See below:

GC/MS of authentic reference sample of 2,2'-bipyridine: Upper trace: one peak at 11.668 minute, Lower trace: *m/z* of that peak: 156.9 (M+H, 100%), 185.0 ($M+C_2H_5$, 20%), 197 ($M+C_3H_5$).



See below:

GC/MS of authentic reference sample of 4,4'-bipyridine: Upper trace, one peak at 12.170 min,

Lower trace: 157.0 (M+H, 100%), 185.0 ($M+C_2H_5$, 20%), 197.0 ($M+C_3H_5$).