Supporting Information

Asymmetric Synthesis of Axially Chiral *N,N'*-CarbazolePyrrole via Copper-Catalyzed Friedel−Crafts Reaction

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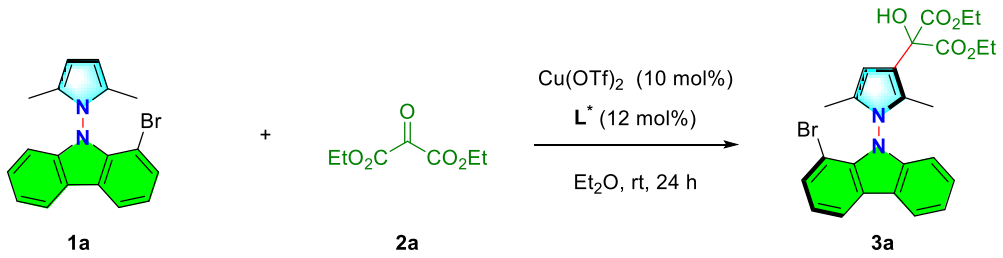
1. General Information

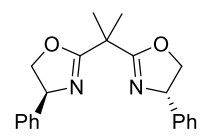
All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H NMR, ^{13}C NMR spectra were measured at 600 MHz and 151 MHz in $CDCl_3$ using TMS signal (δ 0.00 ppm) and the residual signals from $CHCl_3$: (δ = 7.26 ppm for 1H, δ = 77.00 ppm for ^{13}C) as internal references for ^{1}H and ^{13}C NMR respectively. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). X-ray Crystallography was collected at 173 K a on a CCD area detector (Supernova Dual Source, Cu at Zero equipped with an AtlasS2 diffractometer or XtaLAB AFC12 (RINC): Kappa single diffractometer) using Cu Kα radiation. The substrates **1** were synthesized according to published procedures. The spectral data of the substrates were consisted with that reported in the literature. All other chemicals and solvents were purchased from commercial company and used as received.

2. Optimization of Reaction Conditions

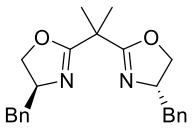
Table S1. The effect of the chiral ligands on the reaction[a]



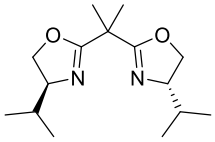
1a **2a** **3a**



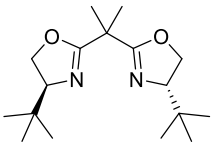
L1, 30% yield, 11% ee



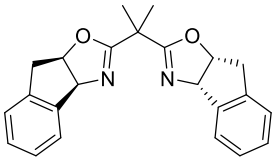
L2, 25% yield, 53% ee



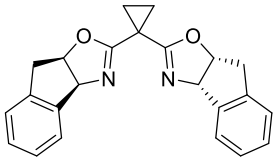
L3, 30% yield, 55% ee



L4, 61% yield, 86% ee



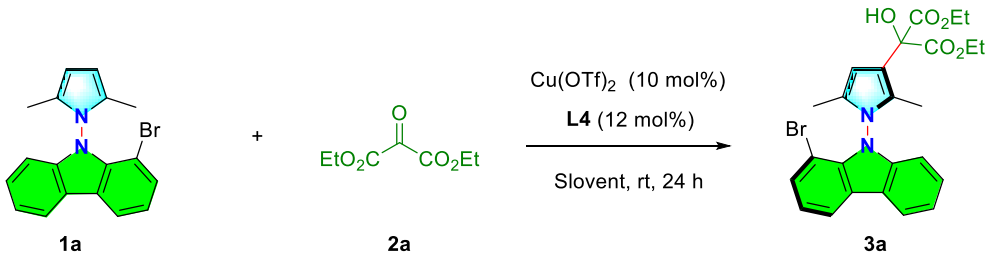
L5, 61% yield, 67% ee



L6, 45% yield, 60% ee

[a] General conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), $Cu(OTf)_2$ (10 mol%), and ligand (12 mol%) in Et_2O (1.0 mL) at rt under Ar atmosphere for 24 h; Isolated yields; Enantiomeric excess of **3a** was determined by HPLC analysis using a chiral stationary phase.

Table S2. The effect of the slovents on the reaction[a]

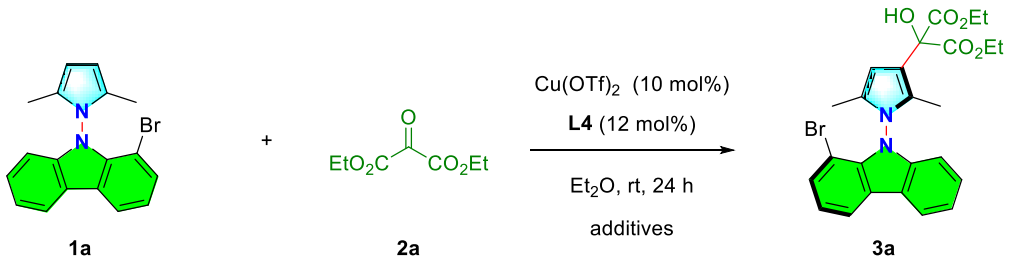


1a **2a** **3a**

entry	slovent	yield	ee
1	**Et_2O**	**61%**	**86%**
2	Diisopropyl ether	37%	86%
3	DCM	27%	75%
4	THF	27%	86%

[a] General conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), $Cu(OTf)_2$ (10 mol%), and **L4** (12 mol%) in solvent (1.0 mL) at rt under Ar atmosphere for 24 h; Isolated yields; Enantiomeric excess of **3a** was determined by HPLC analysis using a chiral stationary phase.

Table S3. The effect of the additives on the reaction[a]

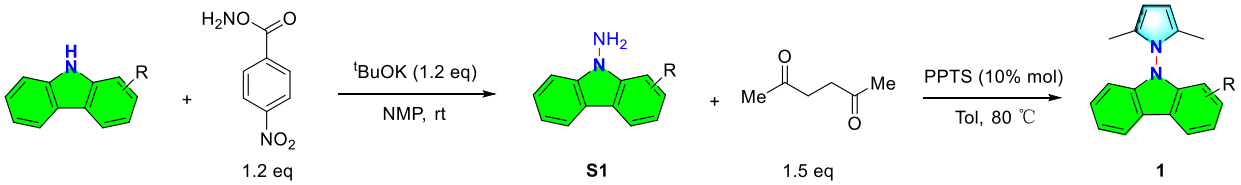


1a **2a** **3a**

entry	additives	yield	ee
1	3Å M.S.	89%	89%
2	4Å M.S.	92%	90%
3	5Å M.S.	88%	90%

[a] General conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), $Cu(OTf)_2$ (10 mol%), **L4** (12 mol%) and additive in Et_2O (1.0 mL) at rt under Ar atmosphere for 24 h; Isolated yields; Enantiomeric excess of **3a** was determined by HPLC analysis using a chiral stationary phase.

3. General Procedure for the Synthesis of carbazole pyrrole ring 1



To a solution of carbazole (10 mmol) in 30 mL NMP was added 12 mL t-BuOK (1M in NMP) and the reaction mixture was stirred at r.t. for 0.5 h. Then, a solution of p-Nitrophenoxyamine (12 mmol) was added to the mixture, which was stirred at r.t. for 2 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was quenched with H_2O and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified through flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford pure product **S1**.

To a solution of 1, 4-diketone (6 mmol, 1.2 equiv.) in toluene was added the 1-amino-heterocycle compound (5 mmol, 1.0 equiv.) and PPTS (0.5 mmol, 10 mol%). The resulting mixture was heated at 80 ℃ for 8-24 h. The solvent was evaporated under reduced pressure and the residue purified by silica gel column chromatography to give the compound **1**.

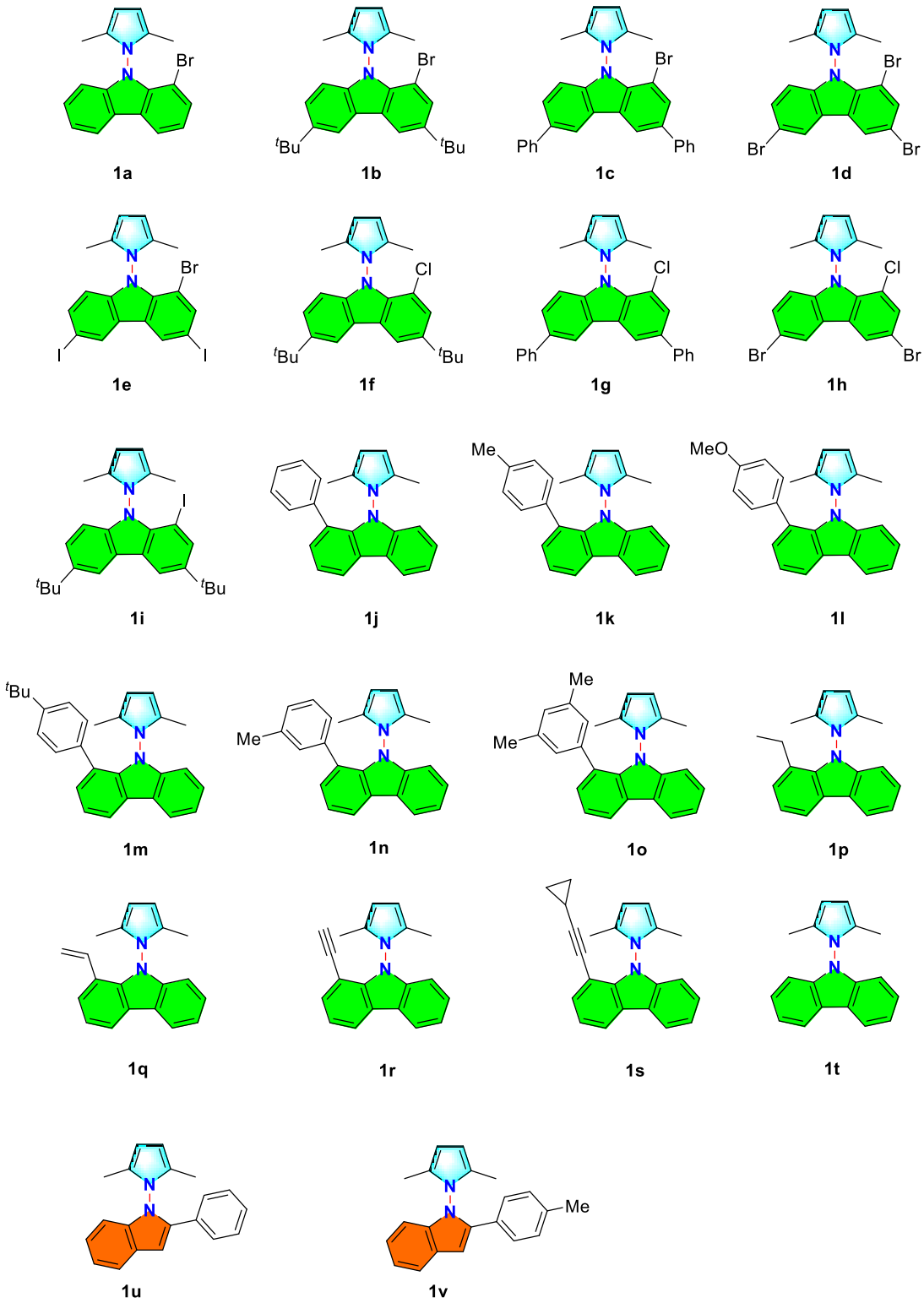
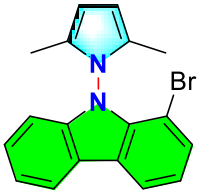


Figure S1. The summary of *N*,*N'*-carbazole-pyrrole rings **1**

4. Characterization data of carbazole pyrrole rings

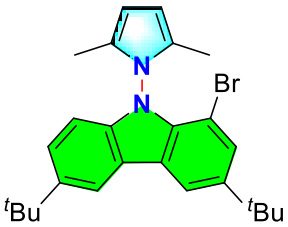
1-bromo-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1a



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1a** (1.1 g, 65% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.61-7.60 (m, 1H), 7.47-7.44 (m, 1H), 7.36-7.33 (m, 1H), 7.19-7.17 (m, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.95 (s, 2H), 1.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.4, 135.9, 131.2, 129.9, 127.5, 124.4, 121.9, 121.7, 120.4, 120.3, 119.5, 109.0, 104.3, 11.0. HRMS (ESI) calcd for $C_{18}H_{16}N_2Br$ [$(M+H^+)$]: 339.0491, found: 339.0491.

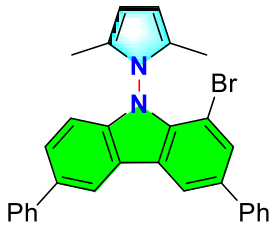
1-bromo-3,6-di-tert-butyl-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1b



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1b** (800 mg, 40% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08-8.07 (m, 2H), 7.62 (s, 1H), 7.49-7.48(m, 1H), 6.91-6.90 (m, 1H), 5.94 (s, 2H), 1.88 (s, 6H), 1.50 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.3, 144.6, 139.9, 134.4, 129.9, 128.7, 125.2, 124.3, 120.3, 116.3, 115.8, 108.5, 104.0, 101.8, 34.82, 34.76, 31.9, 31.8, 11.0. HRMS (ESI) calcd for $C_{26}H_{32}N_2Br$ [$(M+H^+)$]: 451.1743, found: 451.1743.

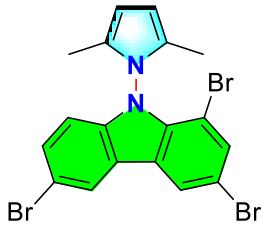
1-bromo-9-(2,5-dimethyl-1H-pyrrol-1-yl)-3,6-diphenyl-9H-carbazole: 1c



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1c** (1.2 g, 49% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35-8.34 (m, 2H), 7.90 (s, 1H), 7.72-7.71 (m, 5H), 7.52-7.49 (m, 4H), 7.41-7.37 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 2H), 1.96 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.4, 141.2, 140.2, 135.9, 135.7, 135.5, 130.6, 129.9, 128.93, 128.86, 127.4, 127.32, 127.30, 127.0, 124.8, 121.0, 119.0, 118.1, 109.4, 104.5, 102.7, 11.0. HRMS (ESI) calcd for $C_{30}H_{24}N_2Br$ [$(M+H^+)$]: 491.1117, found: 491.1118.

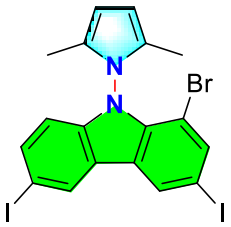
1,3,6-tribromo-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1d



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1d** (930 mg, 38% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18-8.15 (m, 2H), 7.77 (s, 1H), 7.57-7.56 (m, 1H), 6.88-6.86 (m, 1H), 5.95, (s, 1H), 5.94 (s, 1H), 1.842 (s, 3H), 1.837 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.4, 135.2, 133.9, 131.1, 129.6, 124.3, 123.4, 122.6, 121.0, 114.9, 114.1, 110.8, 104.9, 103.2, 10.9. HRMS (ESI) calcd for $C_{18}H_{14}N_2Br_3$ [$(M+H^+)$]: 494.8702, found: 494.8694.

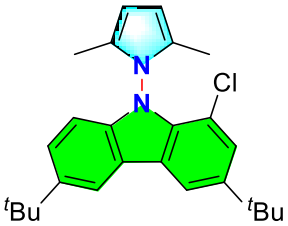
1-bromo-9-(2,5-dimethyl-1H-pyrrol-1-yl)-3,6-dimethyl-9H-carbazole: 1e



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1e** (120 mg, 4% yield). Pink solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37-8.33 (m, 2H), 7.92 (s, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.94 (s, 2H), 1.83 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6, 139.1, 136.6, 135.4, 129.6, 129.5, 128.6, 124.7, 121.3, 111.1, 104.8, 103.5, 10.9. HRMS (ESI) calcd for $C_{18}H_{14}N_2BrI_2$ [$(M+H^+)$]: 590.8424, found: 590.8425.

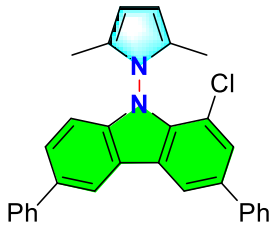
3,6-di-tert-butyl-1-chloro-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1f



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1f** (560 mg, 28% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09-8.02 (m, 2H), 7.51-7.49 (m, 1H), 7.44 (s, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 5.93 (s, 2H), 1.89 (s, 6H), 1.46 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.0, 144.5, 139.8, 133.4, 129.8, 125.5, 125.2, 124.3, 120.5, 116.3, 115.3, 115.2, 108.5, 103.9, 34.82, 34.80, 31.9, 31.8, 10.9. HRMS (ESI) calcd for $C_{26}H_{32}N_2Cl$ [$(M+H^+)$]: 407.2249, found: 407.2249.

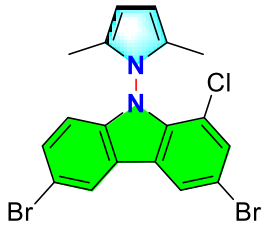
1-chloro-9-(2,5-dimethyl-1H-pyrrol-1-yl)-3,6-diphenyl-9H-carbazole: 1g



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1g** (1.05 g, 47% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36-8.29 (m, 2H), 7.74-7.71 (m, 6H), 7.53-7.50 (m, 4H), 7.42-7.38 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 2H), 1.97 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.4, 141.2, 140.3, 135.6, 135.5, 134.6, 129.7, 128.94, 128.86, 127.4, 127.32, 127.30, 127.28, 127.0, 124.9, 121.3, 119.1, 117.5, 116.4, 109.4, 104.4, 11.0. HRMS (ESI) calcd for $C_{30}H_{24}N_2Cl$ [$(M+H^+)$]: 447.1623, found: 447.1622.

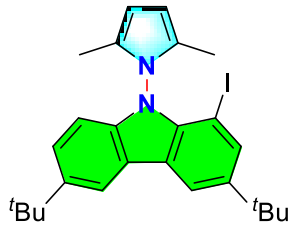
3,6-dibromo-1-chloro-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1h



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1h** (510 mg, 23% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18-8.10 (m, 2H), 7.58-7.57 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.93 (s, 2H), 1.85 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.3, 134.2, 131.1, 130.8, 129.5, 124.3, 123.5, 122.1, 121.1, 117.2, 114.8, 113.7, 110.7, 104.7, 10.8. HRMS (ESI) calcd for $C_{18}H_{14}N_2ClBr_2$ [$(M+H^+)$]: 450.9207, found: 450.9206.

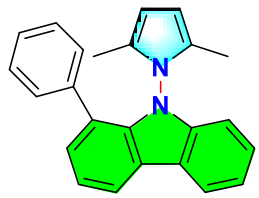
3,6-di-tert-butyl-9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-iodo-9H-carbazole: 1i



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1i** (200 mg, 47% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11-8.08 (m, 2H), 7.899-7.897 (m, 1H), 7.48-7.47 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.96 (s, 2H), 1.87 (s, 6H), 1.456 (s, 9H), 1.455 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 144.6, 139.9, 136.9, 135.6, 130.2, 125.1, 123.6, 120.0, 116.7, 116.1, 108.5, 104.3, 70.4, 34.8, 34.6, 31.9, 31.8, 11.3. HRMS (ESI) calcd for $C_{26}H_{31}N_2NaI$ [$(M+Na^+)$]: 521.1424, found: 521.1420.

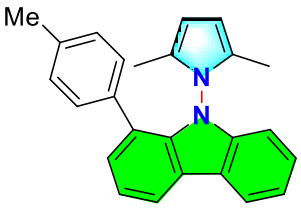
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-phenyl-9H-carbazole: 1j



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1j** (389 mg, 23% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17-8.15 (m, 2H), 7.42-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.20-7.14 (m, 5H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.53 (s, 2H), 1.73 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.3, 137.3, 136.9, 129.4, 128.6, 127.5, 127.3, 126.8, 126.6, 126.5, 122.7, 121.1, 121.0, 120.6, 120.1, 120.0, 108.9, 104.3, 11.0. HRMS (ESI) calcd for $C_{24}H_{21}N_2$ [$(M+H^+)$]: 337.1699, found: 337.1699.

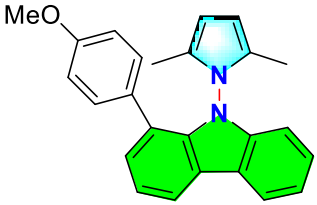
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(p-tolyl)-9H-carbazole: 1k



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1k** (643 mg, 37% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.13 (m, 2H), 7.41-7.38 (m, 1H), 7.37-7.34 (m, 1H), 7.33-7.29 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.53 (s, 2H), 2.32 (s, 3H), 1.71 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.3, 137.0, 136.0, 134.3, 129.5, 128.4, 127.9, 127.5, 126.8, 126.6, 122.6, 121.2, 120.5, 120.1, 119.4, 108.9, 104.3, 21.1, 11.0. HRMS (ESI) calcd for $C_{25}H_{23}N_2$ [$(M+H^+)$]: 351.1856, found: 351.1856.

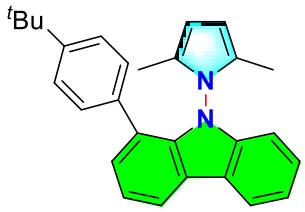
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(4-methoxyphenyl)-9H-carbazole: 1l



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1l** (348 mg, 19% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-8.13 (m, 2H), 7.41-7.40 (m, 1H), 7.37-7.34 (m, 1H), 7.33-7.28 (m, 2H), 7.06-7.04 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.72-6.70 (m, 2H), 5.56 (s, 2H), 3.80 (s, 3H), 1.72 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.4, 141.3, 137.0, 129.7, 129.61, 129.56, 127.5, 126.8, 126.3, 122.6, 121.1, 121.0, 120.6, 119.3, 112.9, 108.9, 104.4, 55.3, 11.0. HRMS (ESI) calcd for $C_{25}H_{23}N_2O$ [$(M+H^+)$]: 367.1805, found: 367.1804.

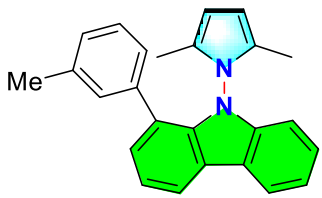
1-(4-(tert-butyl)phenyl)-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1m



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1m** (862 mg, 50% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16-8.14 (m, 2H), 7.42-7.31 (m, 4H), 7.18 (d, *J* = 12.0 Hz, 2H), 7.07 (d, *J* = 6.0 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 5.48 (s, 2H), 1.71 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.2, 141.3, 137.1, 134.0, 129.1, 128.1, 127.4, 126.73, 126.70, 124.1, 122.6, 121.1, 121.0, 120.5, 120.1, 119.4, 108.9, 104.3, 34.4, 31.3, 11.0. HRMS (ESI) calcd for $C_{28}H_{29}N_2$ [$(M+H^+)$]: 393.2325, found: 393.2325.

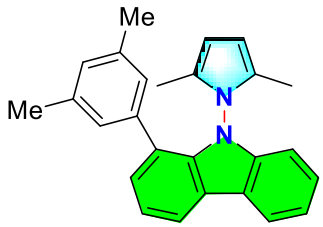
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(m-tolyl)-9H-carbazole: 1n



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1n** (689 mg, 40% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17-8.15 (m, 2H), 7.43-7.40 (m, 1H), 7.39-7.37 (m, 1H), 7.35-7.32 (m, 2H), 7.13-7.11 (m, 1H), 7.02 (d, *J* = 6.0 Hz, 2H), 6.93 (s, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.56 (s, 2H), 2.28 (s, 3H), 1.75 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.3, 137.0, 136.9, 136.7, 129.5, 129.3, 127.5, 127.4, 127.2, 126.8, 126.7, 125.8, 122.6, 121.1, 121.0, 120.6, 120.1, 119.5, 108.9, 104.2, 21.0, 11.0. HRMS (ESI) calcd for $C_{25}H_{23}N_2$ [$(M+H^+)$]: 351.1856, found: 351.1856.

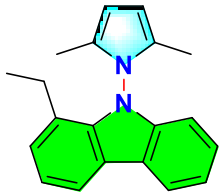
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(3,5-dimethylphenyl)-9H-carbazole: 1o



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1o** (693 mg, 38% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16-8.14 (m, 2H), 7.42-7.40 (m, 1H), 7.38-7.35 (m, 1H), 7.34-7.32 (m, 2H), 6.85-6.84 (m, 2H), 6.77 (s, 2H), 5.56 (s, 2H), 2.25 (s, 6H), 1.74 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.3, 137.0, 136.8, 136.6, 129.2, 128.3, 127.5, 126.9, 126.7, 126.6, 122.6, 121.1, 120.5, 120.1, 119.3, 108.9, 104.1, 108.9, 104.2, 21.0, 10.9. HRMS (ESI) calcd for $C_{26}H_{25}N_2$ [$(M+H^+)$]: 365.2012, found: 365.2012.

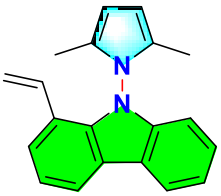
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-ethyl-9H-carbazole: 1p



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1p** (489 mg, 34% yield).White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 8.02-8.01 (m, 1H), 7.44-7.42 (m, 1H), 7.35-7.30 (m, 3H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 2H), 2.36-2.33 (q, *J* = 7.8 Hz, 2H), 1.90 (s, 6H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl3): δ 141.2, 137.4, 129.3, 127.1, 126.63, 126.58, 122.3, 121.3, 121.0, 120.9, 120.1, 118.0, 108.6, 104.6, 20.9, 14.5, 10.9. HRMS (ESI) calcd for $C_{20}H_{21}N_2$ [$(M+H^+)$]: 289.1699, found: 289.1700.

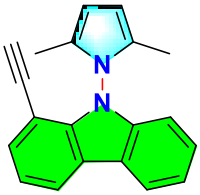
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-vinyl-9H-carbazole: 1q



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1q** (793 mg, 55% yield).White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.07 (m, 2H), 7.63-7.62 (m, 1H), 7.46-7.44 (m, 1H), 7.35-7.31 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.00 (s, 2H), 5.96 (d, *J* = 11.4 Hz, 1H), 5.69 (d, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 1.87 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.9, 136.7, 130.6, 129.1, 126.8, 124.1, 122.6, 122.5, 121.0, 120.2, 119.9, 116.2, 108.6, 104.8, 10.8. HRMS (ESI) calcd for $C_{20}H_{19}N_2$ [$(M+H^+)$]: 287.1543, found: 287.1544.

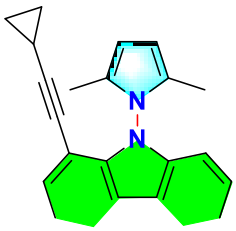
9-(2,5-dimethyl-1H-pyrrol-1-yl)-1-ethynyl-9H-carbazole: 1r



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1r** (762 mg, 53% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03-8.01 (m, 2H), 7.50-7.49 (m, 1H), 7.37-7.35 (m, 1H), 7.26-7.23 (m, 1H), 7.20-7.17 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.81 (s, 2H), 2.84 (s, 1H), 1.78 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.80, 140.77, 131.7, 130.1, 127.2, 122.2, 121.3, 121.2, 120.9, 120.5, 120.4, 108.8, 104.5, 103.8, 80.6, 10.8. HRMS (ESI) calcd for $C_{20}H_{17}N_2$ [$(M+H^+)$]: 285.1386, found: 285.1386.

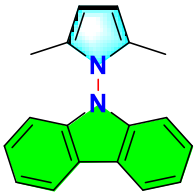
1-(cyclopropylethynyl)-9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1s



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1s** (837 mg, 52% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07-8.01 (m, 2H), 7.47-7.21 (m, 4H), 6.90 (s, 1H), 5.90 (s, 2H), 1.85 (s, 6H), 1.25 (s, 1H), 0.67 (d, *J* = 60.0 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.9, 139.3, 131.3, 129.6, 127.0, 122.1, 121.11, 120.96, 120.6, 120.2, 120.0, 108.7, 106.7, 104.0, 69.6, 10.9, 8.8. HRMS (ESI) calcd for $C_{23}H_{21}N_2$ [$(M+H^+)$]: 325.1699, found: 325.1699.

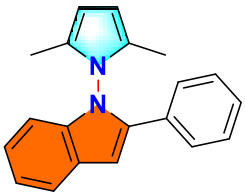
9-(2,5-dimethyl-1H-pyrrol-1-yl)-9H-carbazole: 1t



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1t** (698 mg, 53% yield). White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.44-7.41 (m, 2H), 7.32-7.30 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.98 (s, 2H), 1.84 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.4, 128.8, 126.7, 121.3, 120.8, 120.5, 108.5, 104.7, 10.8. HRMS (ESI) calcd for $C_{18}H_{17}N_2$ [$(M+H^+)$]: 261.1386, found: 261.1386.

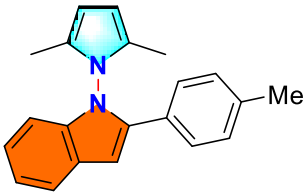
1-(2,5-dimethyl-1H-pyrrol-1-yl)-2-phenyl-1H-indole: 1u



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1u** (437 mg, 30% yield). Yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68-7.67 (m, 1H), 7.33-7.28 (m, 3H), 7.23-7.19 (m, 4H), 6.96-6.94 (m, 1H), 6.90 (s, 1H), 5.91 (s, 2H), 1.85 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.4, 138.3, 130.5, 128.8, 128.5, 128.0, 126.6, 125.7, 123.4, 121.5, 120.7, 109.1, 104.8, 100.9, 10.9. HRMS (ESI) calcd for $C_{20}H_{19}N_2$ [$(M+H^+)$]: 287.1543, found: 287.1542.

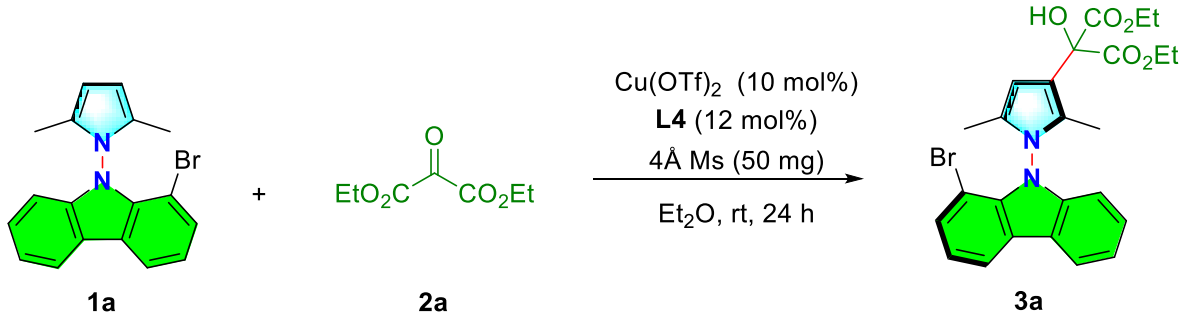
1-(2,5-dimethyl-1H-pyrrol-1-yl)-2-(p-tolyl)-1H-indole: 1v



On a 5 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 40/1) to afford the product **1v** (369 mg, 23% yield). Yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68-7.67 (m, 1H), 7.23-7.22 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.96-6.95 (m, 1H), 6.87 (s, 1H), 5.93 (s, 2H), 2.35 (s, 3H), 1.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.6, 138.2, 137.9, 129.5, 128.5, 127.7, 126.5, 125.8, 123.1, 121.4, 120.6, 109.0, 104.7, 100.4, 21.2, 10.9. HRMS (ESI) calcd for $C_{21}H_{20}N_2Na$ [$(M+Na^+)$]: 323.1519, found: 323.1519.

5. General Procedure for Copper-catalyzed Friedel–Crafts reaction for the asymmetric synthesis of axially chiral *N*,*N*′-carbazolepyrroles

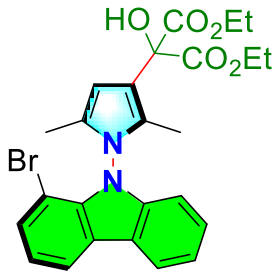


1a **2a** **3a**

To a mixture of $Cu(OTf)_2$ (3.7 mg, 10 mol%), **L4** (3.5mg, 12 mol%), carbazole pyrrole rings **1** (0.10 mmol), diethyl ketomalonates **2a** (0.15 mmol) and 4Å Ms (50 mg, activated under flame dry for 10 min prior to use) was added Et_2O (1.0 mL) at rt under nitrogen atmosphere. Upon complete consumption of carbazole pyrrole rings **1** (TLC monitoring, about 24 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 15:1, v/v) to afford the desired product **3**.

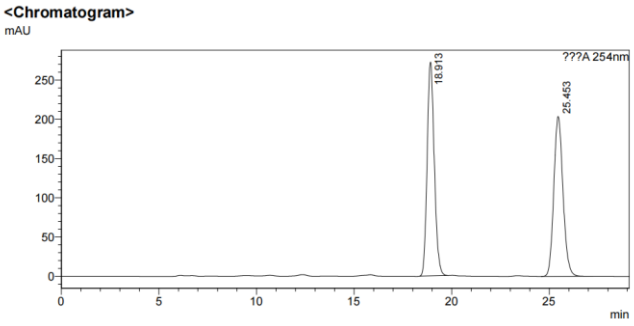
6. Characterization Data of Products

diethyl (S)-2-(1-(1-bromo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3a



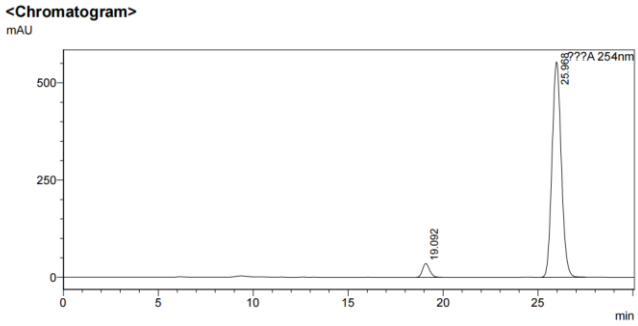
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3a** (41 mg, 92% yield, 90% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09-8.06 (m, 2H), 7.60-7.59 (m, 1H), 7.47-7.44 (m, 1H), 7.36-7.35 (m, 1H), 7.20-7.17 (m, 1H), 7.03-7.02 (m, 1H), 6.127 (s, 1H), 4.38-4.30 (m, 4H), 4.16 (s, 1H), 1.85 (s, 3H), 1.84 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.5, 141.1, 135.7, 131.2, 128.68, 128.66, 127.6, 124.3, 122.1, 121.8, 120.4, 120.3, 119.6, 114.1, 109.0, 104.3, 102.3, 78.0, 62.6, 14.09, 14.07, 10.7, 10.0. HRMS (ESI) calcd for $C_{25}H_{25}N_2NaO_5Br$ [$(M+Na^+)$]: 535.0839, found: 535.0839. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 19.09 min (minor), 25.96 min (major).



<Peak Table>
???A 254nm

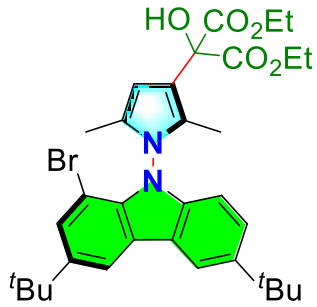
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.913	6926107	272101	50.925		M	
2	25.453	6674449	203689	49.075		M	
Total		13600556	475790				



<Peak Table>
???A 254nm

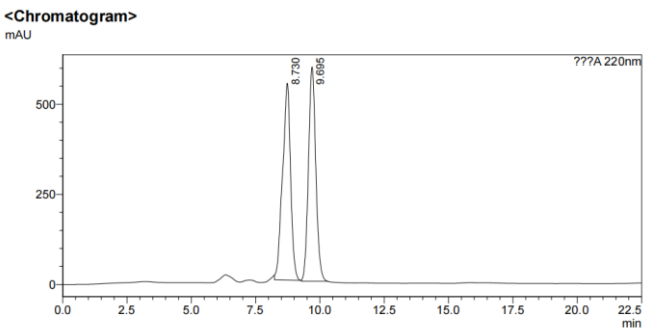
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.092	921582	35609	4.700		M	
2	25.968	18686882	553610	95.300		M	
Total		19608464	589219				

diethyl (S)-2-(1-(1-bromo-3,6-di-tert-butyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3b



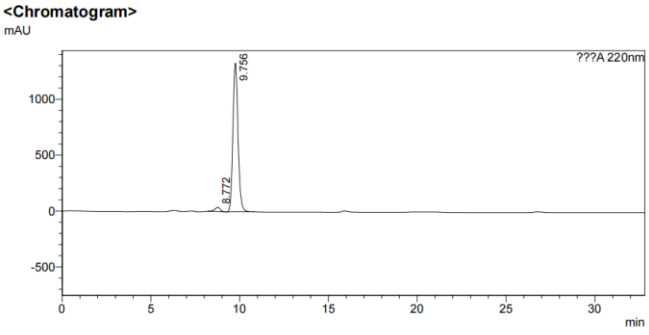
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3b** (60 mg, 96% yield, 94% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07-8.06 (m, 2H), 7.598-7.597 (m, 1H), 7.50-7.48 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 4.38-4.30 (m, 4H), 4.14 (s, 1H), 1.85 (s, 3H), 1.84 (s, 3H), 1.452 (s, 9H), 1.449 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.5, 145.5, 144.7, 139.5, 134.2, 128.8, 128.7, 125.3, 124.3, 120.2, 116.3, 115.8, 113.8, 108.5, 104.0, 101.8, 78.0, 62.57, 62.56, 34.8, 34.7, 31.9, 31.8, 14.10, 14.08, 10.8, 10.1. HRMS (ESI) calcd for $C_{33}H_{42}N_2O_5Br$ [$(M+H^+)$]: 625.2272, found: 625.2273. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 8.77 min (minor), 9.76 min (major).



<Peak Table>
???A 220nm

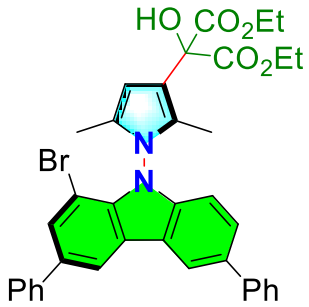
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.730	11906692	545965	50.134		M	
2	9.695	11843202	594560	49.866		M	
Total		23749894	1140525				



<Peak Table>
???A 220nm

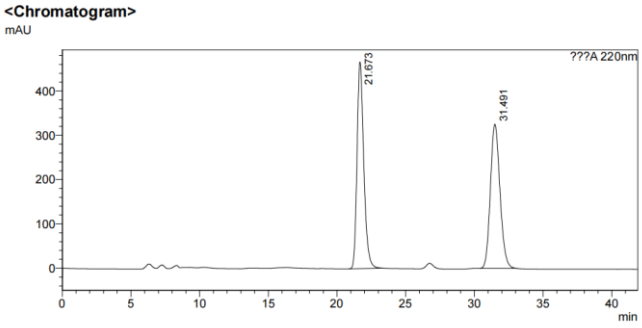
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.772	830825	39117	3.027		M	
2	9.756	26619129	1330360	96.973		M	
Total		27449954	1369478				

diethyl (S)-2-(1-(1-bromo-3,6-diphenyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3c



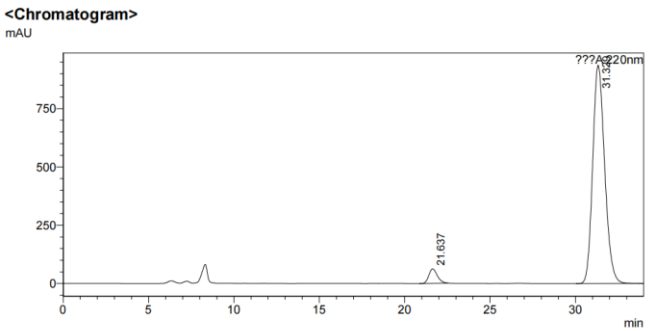
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3c** (57 mg, 86% yield, 91% ee). Yllow oily liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35-8.33 (m, 2H), 7.88 (s, 1H), 7.74-7.70 (m, 5H), 7.52-7.49 (m, 4H), 7.41-7.37 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.18 (s, 1H), 4.42-4.35 (m, 4H), 4.21 (s, 1H), 1.95 (s, 3H), 1.94 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.4, 141.3, 140.9, 140.1, 136.1, 135.5, 135.4, 130.6, 128.9, 128.8, 128.73, 128.70, 127.33, 127.26, 127.0, 124.7, 121.0, 119.0, 118.1, 114.1, 109.4, 104.4, 102.6, 78.0, 62.6, 14.10, 14.09, 10.8, 10.1. HRMS (ESI) calcd for $C_{37}H_{33}N_2NaO_5Br$ [$(M+Na^+)$]: 687.1465, found: 687.1463. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 21.63 min (minor), 31.32 min (major).



<Peak Table>
???A 220nm

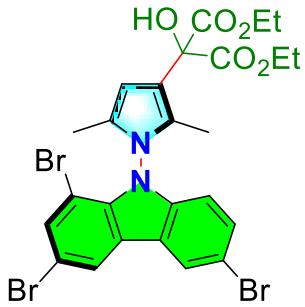
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.673	15904749	466531	50.200		M	
2	31.491	15777766	325469	49.800		M	
Total		31682516	792000				



<Peak Table>
???A 220nm

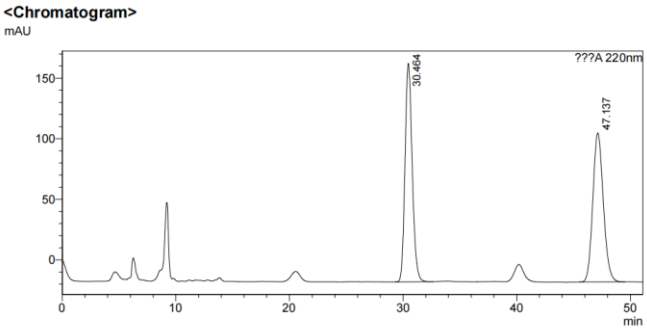
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.637	2149336	62333	4.491		M	
2	31.329	45706302	935999	95.509			
Total		47855638	998333				

diethyl (S)-2-(2,5-dimethyl-1-(1,3,6-tribromo-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3d



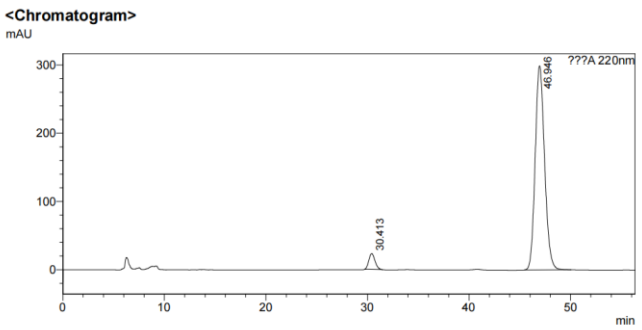
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3d** (52 mg, 77% yield, 90% ee) Yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17-8.14 (m, 2H), 7.75-7.74 (m, 1H), 7.57-7.56 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.12 (s, 1H), 4.37-4.29 (m, 4H), 4.16 (s, 1H), 1.82 (s, 3H), 1.81 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 170.3, 140.0, 135.0, 133.4, 131.2, 128.53, 128.49 124.2, 123.4, 122.6, 120.9, 115.1, 114.4, 114.2, 110.7, 104.8, 103.1, 77.8, 62.7, 14.08, 14.06, 10.6, 10.0. HRMS (ESI) calcd for $C_{25}H_{23}N_2NaO_5Br_3$ [(M+Na$^+$)]: 690.9049, found: 690.9050. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 30.41 min (minor), 46.94 min (major).



<Peak Table>
???A 220nm

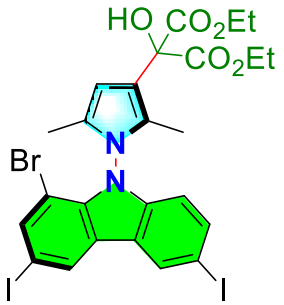
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.464	7912735	180325	50.002			
2	47.137	7911991	122996	49.998			
Total		15824726	303320				



<Peak Table>
???A 220nm

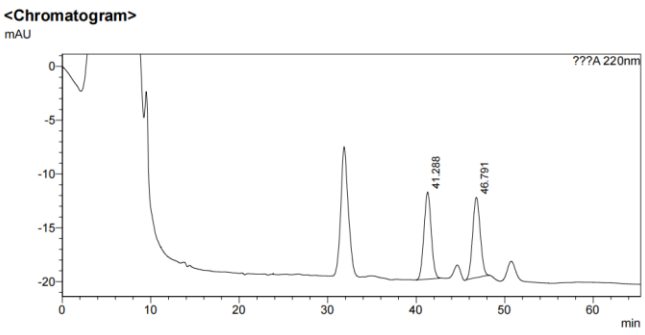
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.413	963871	23123	4.775		M	
2	46.946	19222002	299014	95.225		M	
Total		20185874	322137				

diethyl (S)-2-(1-(1-bromo-3,6-diiodo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3e



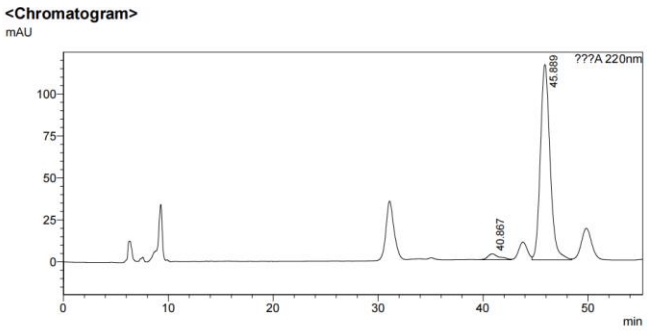
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3e** (54 mg, 71% yield, 93% ee) Colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36-8.32 (m, 2H), 7.90 (s, 1H), 7.74-7.73 (m, 1H), 6.81 (d, *J* = 13.8 Hz, 1H), 6.11 (s, 1H), 4.37-4.29 (m, 4H), 4.14 (s, 1H), 1.810 (s, 3H), 1.805 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 170.3, 140.3, 139.1, 135.2, 129.5, 128.6, 128.52, 128.49, 124.6, 121.3, 114.4, 111.1, 104.8, 103.4, 85.0, 83.9, 77.8, 62.7, 14.08, 14.07, 10.7, 10.0. HRMS (ESI) calcd for $C_{25}H_{23}N_2NaO_5BrI_2$ [(M+Na^+)]: 786.8772, found: 786.8773. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 30.41 min (minor), 46.94 min (major).



<Peak Table>
???A 220nm

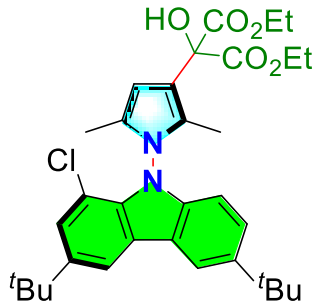
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	41.288	461734	8100	50.972			
2	46.791	444130	7463	49.028		M	
Total		905865	15564				



<Peak Table>
???A 220nm

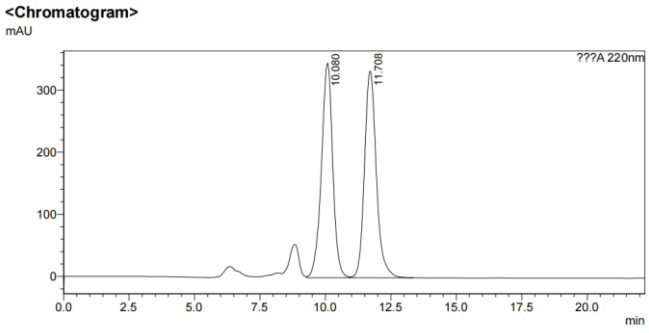
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.867	275606	3537	3.555			
2	45.889	7476959	116384	96.445			
Total		7752565	119921				

diethyl (S)-2-(1-(3,6-di-tert-butyl-1-chloro-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3f



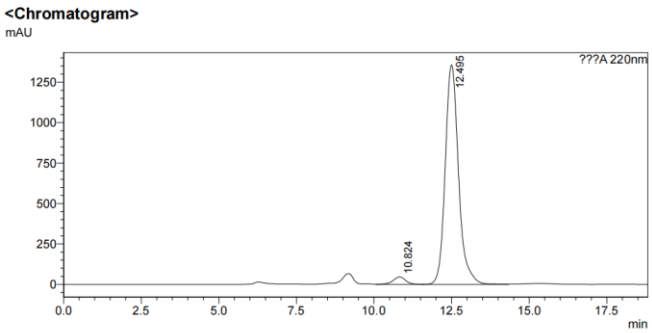
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3f** (51 mg, 88% yield, 94% ee) Yellow oily liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08-8.01 (m, 2H), 7.50-7.49 (m, 1H), 7.41 (s, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 6.09 (s, 1H), 4.38-4.31 (m, 4H), 4.15 (s, 1H), 1.86 (s, 3H), 1.85 (s, 3H), 1.454 (s, 9H), 1.448 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151MHz, $CDCl_3$): δ 170.7, 170.5, 145.2, 144.7, 139.5, 133.2, 128.7, 128.6, 125.5, 125.3, 124.3, 120.5, 116.4, 115.3, 115.2, 113.7, 108.5, 103.9, 78.0, 62.58, 62.55, 34.80, 34.78, 31.9, 31.8, 14.1, 14.0, 10.7, 10.0. HRMS (ESI) calcd for $C_{33}H_{42}N_2O_5Cl$ [$(M+H^+)$]: 581.2777, found: 581.2775. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 10.82 min (minor), 12.49 min (major).



<Peak Table>
???A 220nm

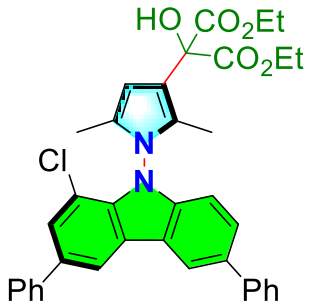
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.080	10393290	345348	49.788			
2	11.708	10481935	332767	50.212		V	
Total		20875225	678116				



<Peak Table>
???A 220nm

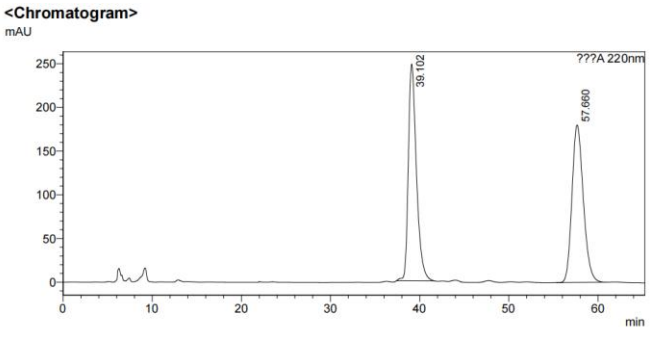
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.824	1318275	45539	3.152			
2	12.495	40506386	1356827	96.848		V	
Total		41824661	1402366				

diethyl (S)-2-(1-(1-chloro-3,6-diphenyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3g



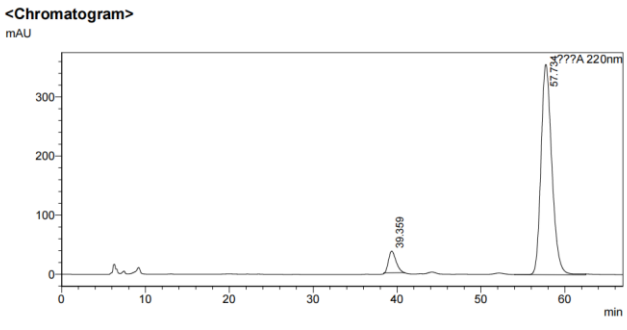
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3g** (38 mg, 61% yield, 87% ee) Colorless oil liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35-8.28 (m, 2H), 7.74-7.69 (m, 6H), 7.52-7.50 (m, 4H), 7.41-7.37 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.16 (s, 1H), 4.41-4.34 (m, 4H), 4.20 (s, 1H), 1.95 (s, 3H), 1.93 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.4, 142.3, 140.9, 140.2, 135.8, 135.6, 134.4, 128.93, 128.85, 128.7, 128.6, 127.4, 127.30, 127.25, 127.0, 124.8, 121.2, 119.1, 117.5, 116.4, 114.0, 109.4, 104.4, 78.0, 70.3, 62.7, 62.6, 14.08, 14.06, 10.7, 10.0. HRMS (ESI) calcd for $C_{37}H_{34}N_2O_5Cl$ [$(M+H^+)$]: 621.2151, found: 5621.2148. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 39.35 min (minor), 57.73 min (major).



<Peak Table>
???A 220nm

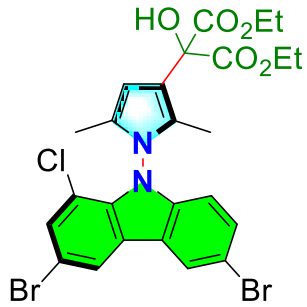
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.102	15688168	248228	49.518		M	
2	57.660	15993596	180289	50.482		V	
Total		31681764	428517				



<Peak Table>
???A 220nm

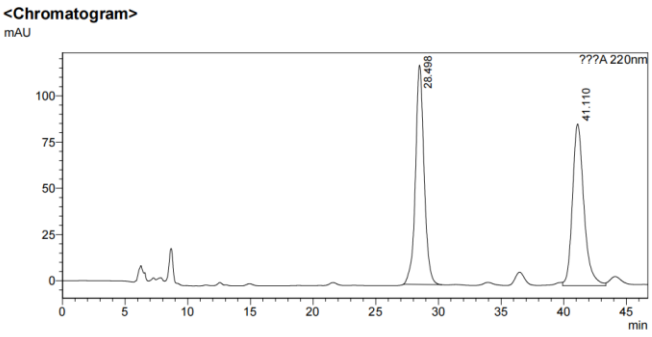
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.359	2273997	36747	6.630		M	
2	57.734	32022136	356148	93.370		M	
Total		34296133	392895				

diethyl (S)-2-(1-(3,6-dibromo-1-chloro-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3h



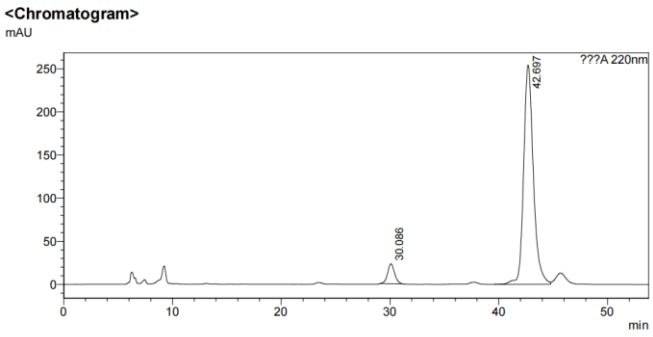
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3h** (34 mg, 54% yield, 88% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.172-8.170 (m, 1H), 8.10-8.09 (m, 1H), 7.59-7.56 (m, 2H), 6.94 (d, *J* = 9.0 Hz, 1H), 6.10 (s, 1H), 4.37-4.30 (m, 4H), 4.14 (s, 1H), 1.83 (s, 3H), 1.82 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 170.3, 142.3, 140.0, 134.0, 130.8, 128.5, 128.4, 124.3, 123.5, 122.1, 121.1, 117.2, 115.0, 114.3, 113.9, 110.7, 104.7, 77.9, 62.69, 62.67, 14.06, 14.04, 10.6, 9.9. HRMS (ESI) calcd for $C_{25}H_{23}N_2NaO_5Br_2Cl$ [(M+Na$^+$)]: 646.9554, found: 646.9554. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 30.08 min (minor), 42.69 min (major).



<Peak Table>
???A 220nm

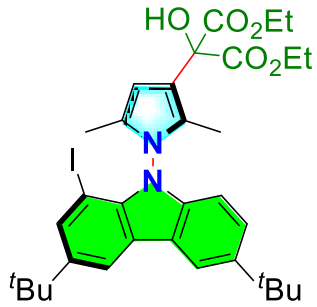
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.498	5674495	118506	50.558		M	
2	41.110	5549279	87342	49.442		M	
Total		11223774	205848				



<Peak Table>
???A 220nm

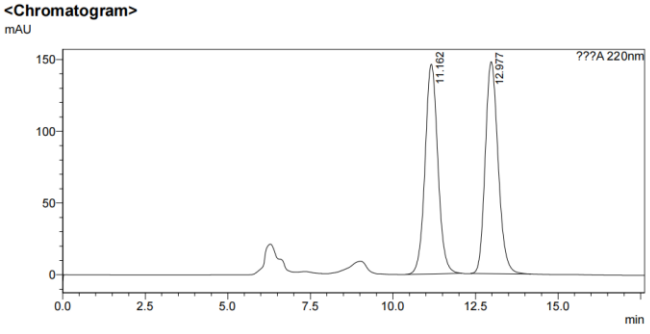
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.086	1029529	23050	6.133		M	
2	42.697	15755843	253989	93.867			
Total		16785371	277039				

diethyl (S)-2-(1-(3,6-di-tert-butyl-1-iodo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3i



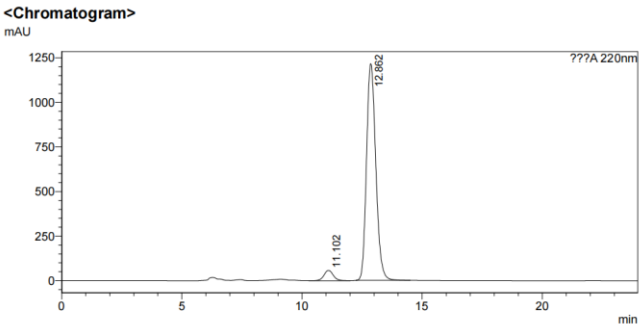
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3i** (44.5 mg, 66% yield, 92% ee) Yellow oily liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.88-7.87 (m, 1H), 7.48-7.46 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.14 (s, 1H), 4.38-4.29 (m, 4H), 4.14 (s, 1H), 1.84 (s, 3H), 1.83 (s, 3H), 1.45 (s, 9H), 1.44 (s, 9H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.5, 144.8, 139.6, 136.7, 140.1, 136.1, 135.7, 128.98, 128.95, 125.2, 123.5, 120.0, 116.7, 116.1, 114.1, 108.5, 104.3, 78.0, 70.3, 62.59, 62.56, 34.8, 34.6, 31.9, 31.8, 14.2, 14.1, 11.1, 10.4. HRMS (ESI) calcd for $C_{33}H_{42}N_2O_5I$ [$(M+H^+)$]: 673.2133, found: 673.2133. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 11.10 min (minor), 12.86 min (major).



<Peak Table>
???A 220nm

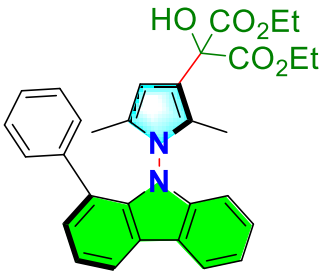
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.162	3942417	146094	49.592		M	
2	12.977	4007244	147675	50.408		M	
Total		7949662	293769				



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.102	1587146	58010	4.638			
2	12.862	32634077	1215079	95.362		M	
Total		34221223	1273090				

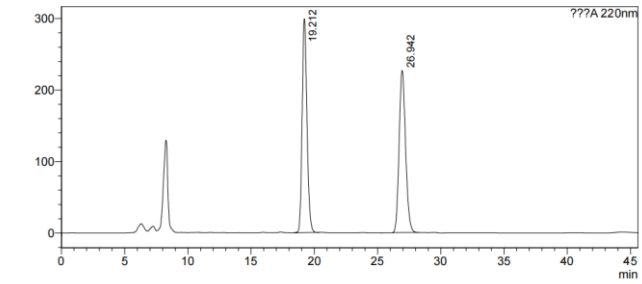
diethyl (S)-2-(2,5-dimethyl-1-(1-phenyl-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3j



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3j** (36 mg, 71% yield, 93% ee) Pink solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16-8.13 (m, 2H), 7.42-7.36 (m, 2H), 7.34-7.30 (m, 2H), 7.21-7.17 (m, 3H), 7.12-7.11 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.63 (s, 1H), 4.41-4.29 (m, 4H), 3.56 (s, 1H), 1.74 (s, 3H), 1.66 (s, 3H), 1.35 (t, *J* = 6.6 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.1, 169.8, 141.0, 137.2, 136.7, 129.4, 128.7, 127.4, 126.9, 126.64, 126.63, 126.5, 122.7, 121.2, 121.1, 120.8, 120.2, 119.7, 114.0, 108.9, 104.2, 77.9, 62.4, 62.3, 14.1, 14.0, 10.7, 10.2. HRMS (ESI) calcd for $C_{31}H_{31}N_2O_5$ [$(M+H^+)$]: 511.2227, found: 511.2226. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 19.52 min (minor), 27.81 min (major).

<Chromatogram>

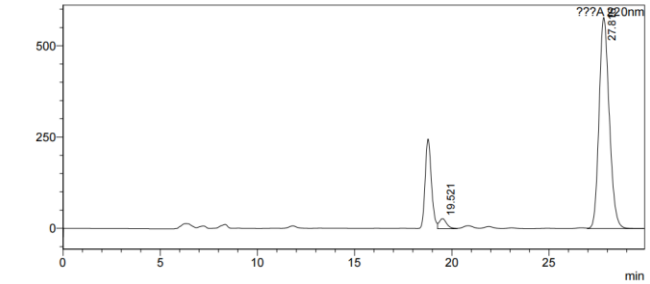


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.212	7954172	299135	49.653		M	
2	26.942	8065431	226867	50.347		M	
Total		16019603	526002				

<Chromatogram>

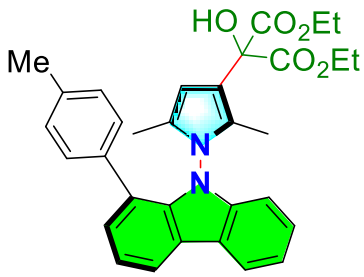


<Peak Table>

???A 220nm

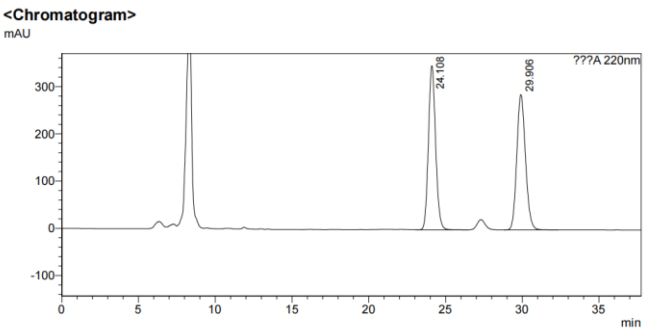
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.521	762281	28001	3.479			
2	27.816	21145509	578362	96.521			
Total		21907790	606363				

diethyl (S)-2-(2,5-dimethyl-1-(1-(p-tolyl)-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3k



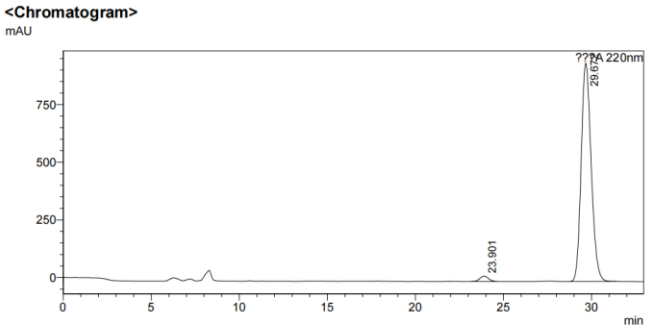
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3k** (43 mg, 82% yield, 96% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.13 (m, 2H), 7.41-7.31 (m, 3H), 7.29-7.28 (m, 1H), 6.99 (s, 4H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.63 (s, 1H), 4.40-4.29 (m, 4H), 3.37 (s, 1H), 2.36 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.1, 169.8, 140.9, 136.7, 136.2, 134.3, 129.5, 128.5, 128.1, 126.88, 126.86, 126.6, 126.5, 122.6, 121.2, 121.1, 120.8, 120.2, 119.5, 114.2, 108.9, 104.1, 78.0, 62.4, 62.3, 21.1, 14.1, 14.0, 10.7, 10.1. HRMS (ESI) calcd for $C_{32}H_{33}N_2O_5$ [$(M+H^+)$]: 525.2384, found: 525.2384. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 23.90 min (minor), 29.67 min (major).



<Peak Table>
???A 220nm

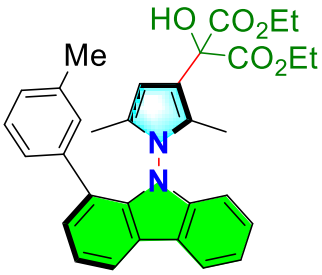
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.108	11310952	347370	50.078			
2	29.906	11275774	286409	49.922			
Total		22586726	633779				



<Peak Table>
???A 220nm

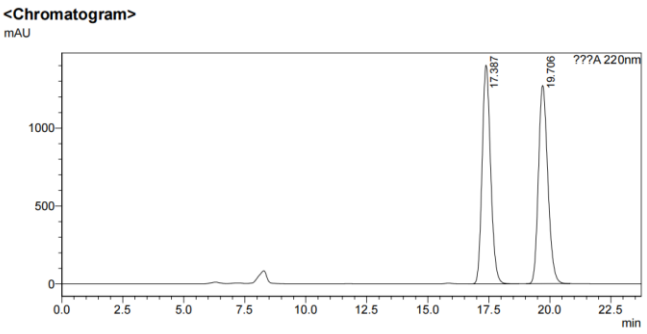
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.901	789497	23639	2.071		M	
2	29.672	37328895	946638	97.929		M	
Total		38118392	970277				

diethyl (S)-2-(2,5-dimethyl-1-(1-(m-tolyl)-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3l



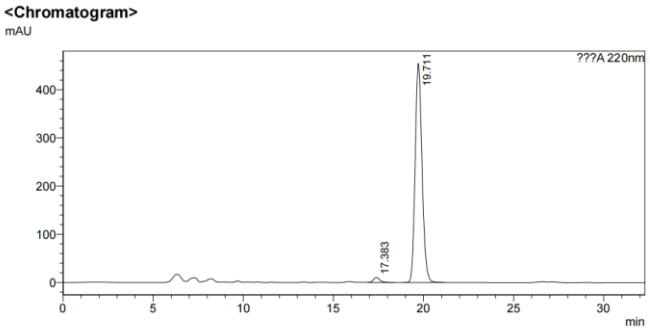
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3l** (26 mg, 50% yield, 96% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-8.13 (m, 2H), 7.41-7.29 (m, 4H), 7.11-7.09 (m, 1H), 7.04-7.03 (m, 1H), 6.95-6.94 (m, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.70 (s, 1H), 4.41-4.25 (m, 4H), 3.31 (s, 1H), 2.28 (s, 3H), 1.76 (s, 3H), 1.68 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.1, 169.6, 140.1, 137.1, 137.0, 136.7, 129.7, 129.4, 128.3, 126.8, 126.7, 126.64, 126.60, 124.3, 122.6, 121.18, 121.16, 120.8, 120.2, 119.4, 114.5, 108.9, 103.5, 62.5, 62.4, 34.4, 31.2, 14.09, 14.06, 10.6, 10.1. HRMS (ESI) calcd for $C_{32}H_{33}N_2O_5$ [$(M+H^+)$]: 525.2384, found: 525.2384. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 17.38 min (minor), 19.71 min (major).



<Peak Table>
???A 220nm

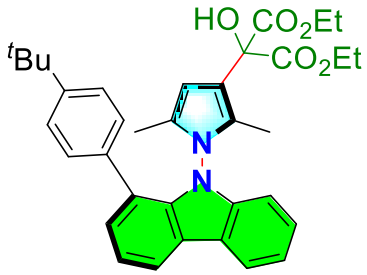
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.387	34090546	1402891	50.044			
2	19.706	34031264	1272384	49.956		M	
Total		68121811	2675275				



<Peak Table>
???A 220nm

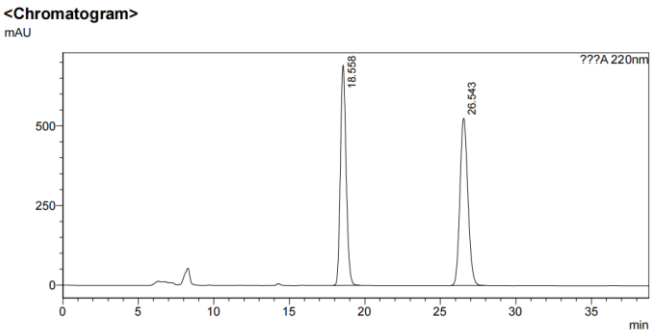
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.383	261572	10445	2.124			
2	19.711	12055115	454502	97.876		M	
Total		12316687	464947				

diethyl (S)-2-(1-(1-(4-(tert-butyl)phenyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3m



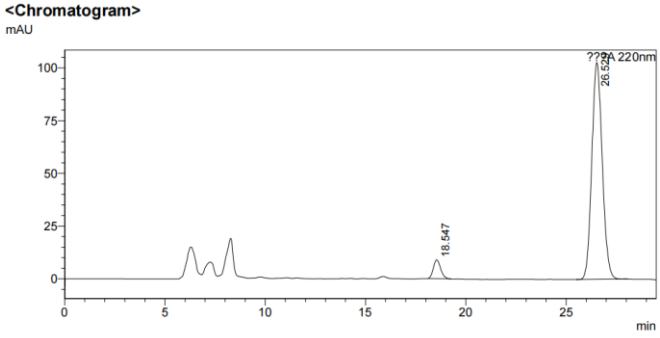
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3m** (20 mg, 35% yield, 89% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20-8.19 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.20-7.18 (m, 2H), 7.03-7.01 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.43 (s, 1H), 4.17-4.10 (m, 4H), 3.40 (s, 1H), 1.37 (s, 3H), 1.23 (s, 3H), 0.94-0.92 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.2, 170.1, 149.5, 141.0, 136.8, 134.0, 129.4, 128.3, 126.8, 126.7, 126.64, 126.60, 124.3, 122.6, 121.18, 121.16, 120.8, 120.2, 119.4, 114.5, 108.9, 103.5, 62.5, 62.4, 34.4, 31.2, 14.09, 14.06, 10.6, 10.1. HRMS (ESI) calcd for $C_{35}H_{39}N_2O_5$ [(M+H$^+$)]: 567.2853, found: 567.2855. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 18.54 min (minor), 26.52 min (major).



<Peak Table>
???A 220nm

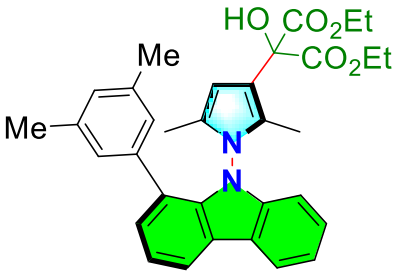
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.558	18190789	691618	48.669		M	
2	26.543	19185916	525298	51.331		M	
Total		37376705	1216916				



<Peak Table>
???A 220nm

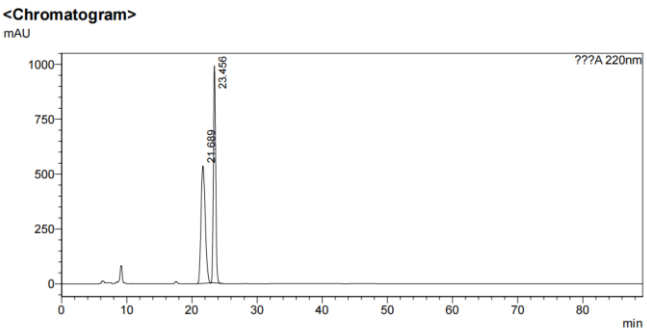
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.547	227242	8918	5.743		M	
2	26.529	3729359	102771	94.257		M	
Total		3956601	111688				

diethyl (S)-2-(1-(1-(3,5-dimethylphenyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3n



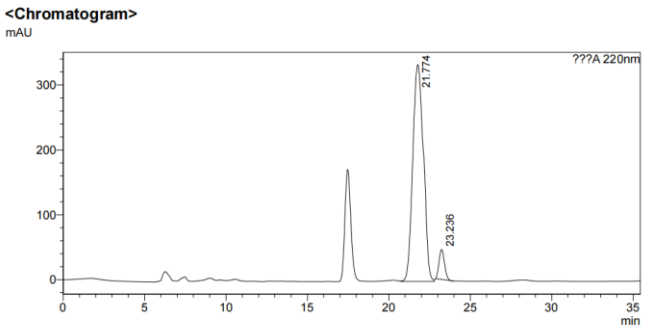
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3n** (25 mg, 46% yield, 87% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.12 (m, 2H), 7.4-7.38 (m, 1H), 7.36-7.31 (m, 2H), 7.29-7.27 (m, 1H), 6.87-6.86 (m, 2H), 6.73 (s, 2H), 5.71 (s, 1H), 4.41-4.21 (m, 4H), 3.09 (s, 1H), 2.25 (s, 6H), 1.80 (s, 3H), 1.64 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.1, 169.4, 140.1, 137.1, 137.0, 136.7, 129.2, 128.2, 127.2, 126.9, 126.8, 126.7, 126.5, 122.6, 121.21, 121.17, 120.8, 120.2, 119.5, 113.8, 108.9, 104.4, 78.1, 62.4, 62.2, 21.0, 14.1, 14.0, 10.9, 10.0. HRMS (ESI) calcd for $C_{33}H_{35}N_2O_5$ [(M+H$^+$)]: 539.2540, found: 539.2540. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 21,77 min (major), 23.24 min (minor).



<Peak Table>
???A 220nm

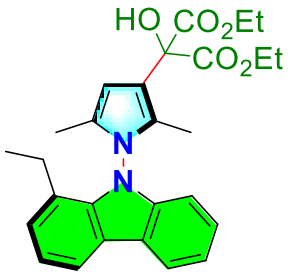
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.689	24259298	536014	50.152		M	
2	23.456	24112709	990966	49.848		M	
Total		48372007	1526979				



<Peak Table>
???A 220nm

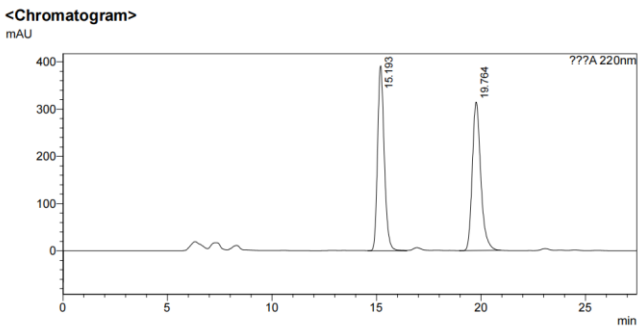
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.774	15238462	334172	93.435			
2	23.236	1070613	46198	6.565		M	
Total		16309075	380370				

diethyl (S)-2-(1-(1-ethyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3o



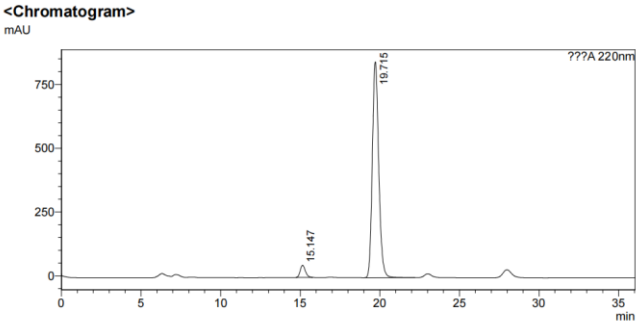
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3o** (21 mg, 45% yield, 91% ee) Colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09-8.08 (m, 1H), 7.90-7.97 (m, 1H), 7.42-7.39 (m, 1H), 7.32-7.28 (m, 3H), 6.93 (d, *J* = 8.4 Hz 1H), 6.13 (s, 1H), 4.39-4.31 (m, 4H), 4.16 (s, 1H), 2.32 (q, *J* = 12.0 Hz, 2H), 1.85 (s, 6H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.5, 170.4, 140.9, 137.3, 128.2, 128.1, 127.0, 126.74, 126.65, 122.3, 121.3, 121.2, 121.1, 120.1, 118.1, 114.1, 108.6, 104.5, 78.0, 62.6, 21.0, 14.5, 14.04, 14.02, 10.7, 10.0. HRMS (ESI) calcd for $C_{27}H_{30}N_2KO_5$ [(M+K^+)]: 501.1786, found: 501.1788. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 15.14 min (minor), 19.71 min (major).



<Peak Table>
???A 220nm

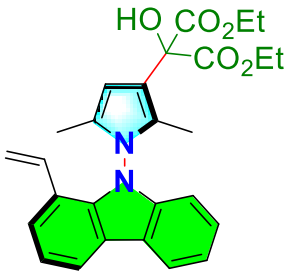
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.193	8767276	391595	49.635			
2	19.764	8896313	314408	50.365		M	
Total		17663589	706003				



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.147	1074996	47794	4.356		M	
2	19.715	23604337	846249	95.644			
Total		24679333	894043				

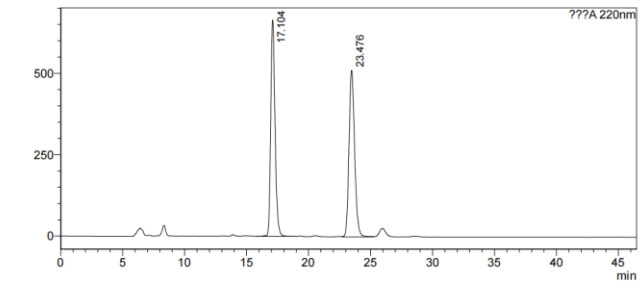
diethyl (S)-2-(2,5-dimethyl-1-(1-vinyl-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3p



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3p** (36 mg, 78% yield, 85% ee) Colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 8.06-8.05 (m, 1H), 7.59-7.58 (m, 1H), 7.45-7.42 (m, 1H), 7.35-7.29 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.16 (s, 1H), 5.98 (dd, *J* = 10.2 Hz, and 10.8 Hz, 1H), 5.65 (d, *J* = 18.6 Hz, 1H), 5.10 (d, *J* = 11.4 Hz, 1H), 4.40-4.32 (m, 4H), 4.18 (s, 1H), 1.85 (s, 3H), 1.83 (s, 3H), 1.35 (t, *J* = 7.2 Hz 3H), 1.34 (t, *J* = 7.2 Hz 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.5, 170.4, 140.6, 136.4, 130.5, 128.1, 127.9, 126.9, 124.3, 122.6, 121.2, 121.0, 120.2, 119.9, 116.4, 114.3, 108.5, 104.7, 77.9, 62.6, 14.0, 10.6, 9.9. HRMS (ESI) calcd for $C_{27}H_{28}N_2NaO_5$ [(M+Na$^+$)]: 483.1890, found: 483.1889. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 17.06 min (minor), 23.44 min (major).

<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.104	16029223	664463	50.028			
2	23.476	16011270	511425	49.972			
Total		32040493	1175888				

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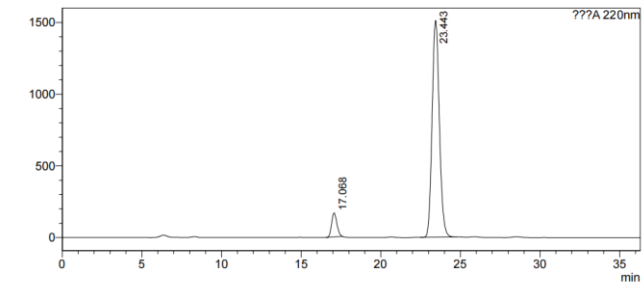
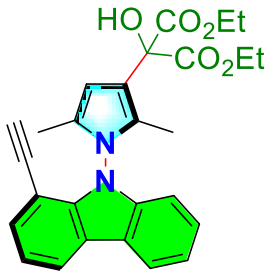


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.068	3858875	167367	7.443		M	
2	23.443	47986537	1512352	92.557		M	
Total		51845413	1679720				

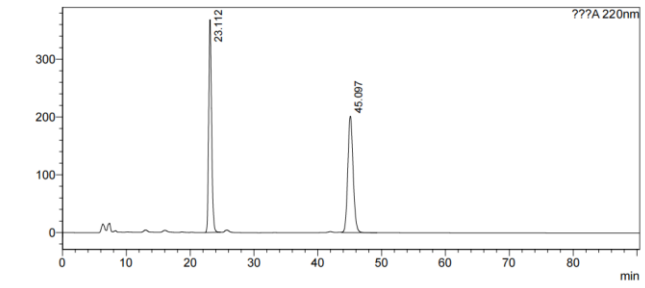
diethyl (S)-2-(1-(1-ethynyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3q



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3q** (32 mg, 70% yield, 95% ee) Colorless oil liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11-8.10 (m, 2H), 7.57-7.56 (m, 1H), 7.47-7.45 (m, 1H), 7.36-7.33 (m, 1H), 7.29-7.27 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.06 (s, 1H), 4.39-4.31 (m, 4H), 4.13 (s, 1H), 2.98 (s, 1H), 1.88 (s, 3H), 1.83 (s, 3H), 1.36 (t, *J* = 7.8 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.4, 140.5, 140.4, 131.4, 129.1, 129.0, 127.3, 122.2, 121.4, 121.1, 120.9, 120.7, 120.4, 113.4, 108.8, 104.6, 103.8, 81.4, 78.1, 62.6, 62.5, 14.1, 10.6, 10.0. HRMS (ESI) calcd for $C_{27}H_{27}N_2O_5$ [$(M+H^+)$]: 459.1914, found: 459.1916. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 22.82 min (minor), 44.55 min (major).

<Chromatogram>

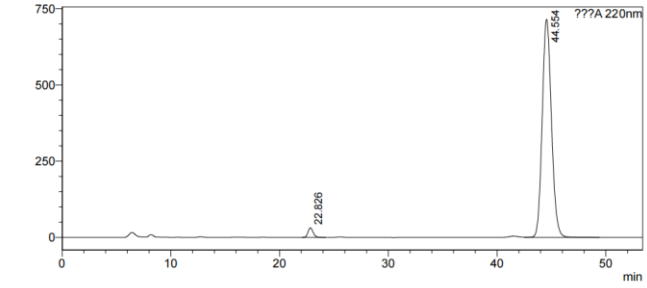


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.112	11591809	368363	49.831			
2	45.097	11670283	201775	50.169			
Total		23262092	570139				

<Chromatogram>

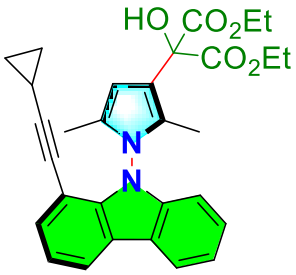


<Peak Table>

???A 220nm

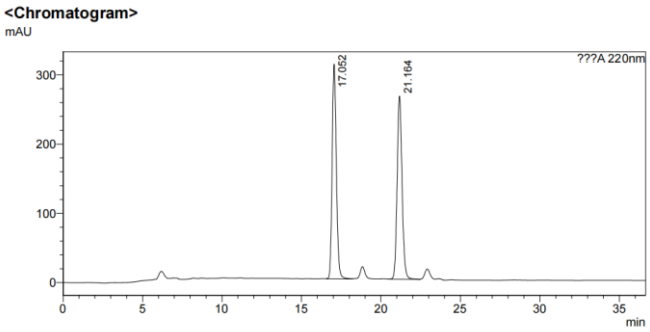
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.826	1057543	31464	2.437			
2	44.554	42338653	715237	97.563			
Total		43396196	746701				

diethyl (S)-2-(1-(1-(cyclopropylethynyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 3r



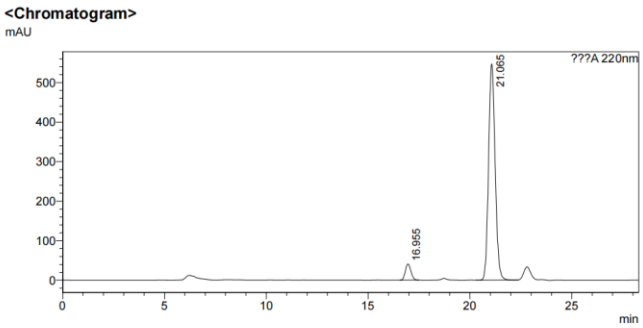
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3r** (25 mg, 50% yield, 88% ee) White solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.46-7.45 (m, 1H), 7.42-7.40 (m, 1H), 7.32-7.30 (m, 1H), 7.24-7.21 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.07 (s, 1H), 4.38-4.31 (m, 4H), 4.08 (s, 1H), 1.92 (s, 3H), 1.76 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 6.6 Hz, 3H), 1.26 (s, 1H), 0.75-0.73 (m, 2H), 0.62-0.61 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.5, 140.6, 139.0, 131.2, 128.7, 128.5, 127.0, 122.0, 121.3, 121.0, 120.7, 120.3, 119.7, 113.6, 108.7, 106.7, 103.8, 98.0, 78.0, 69.2, 62.6, 62.5, 14.1, 14.0, 10.8, 9.9, 8.83, 8.75. HRMS (ESI) calcd for $C_{30}H_{31}N_2O_5$ [$(M+H^+)$]: 499.2227, found: 499.2229. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 16.95 min (minor), 21.06 min (major).



<Peak Table>
???A 220nm

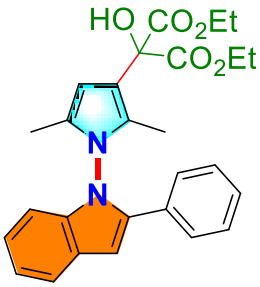
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.052	5726040	310288	50.172			
2	21.164	5686817	264294	49.828			
Total		11412858	574581				



<Peak Table>
???A 220nm

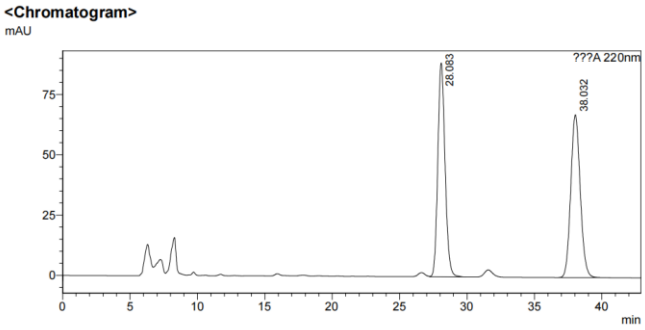
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.955	785745	40931	6.022		M	
2	21.065	12262894	546709	93.978		M	
Total		13048639	587641				

diethyl-2-(2,5-dimethyl-1-(2-phenyl-1H-indol-1-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3s



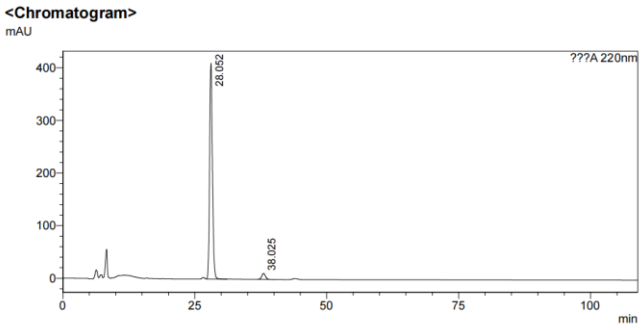
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3s** (41 mg, 89% yield, 93% ee) Yellow oily liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68-7.67 (m, 1H), 7.32-7.27 (m, 3H), 7.25-7.19 (m, 4H), 6.97-6.96 (m, 1H), 6.91 (s, 1H), 6.10 (s, 1H), 4.35-4.28 (m, 4H), 4.15 (s, 1H), 1.85 (s, 3H), 1.82 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 139.2, 138.0, 130.3, 128.8, 128.0, 127.4, 126.6, 125.6, 123.5, 121.6, 120.8, 114.3, 109.1, 104.6, 101.1, 77.9, 62.6, 13.99, 13.96, 10.7, 10.0. HRMS (ESI) calcd for $C_{27}H_{28}KN_2O_5$ [$(M+K^+)$]: 499.1630, found: 499.1630. 93% ee. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 28.05 min (major), 38.02 min (minor).



<Peak Table>
???A 220nm

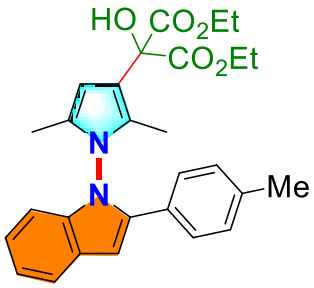
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.083	3307872	88633	50.017			
2	38.032	3305597	67453	49.983			
Total		6613469	156086				



<Peak Table>
???A 220nm

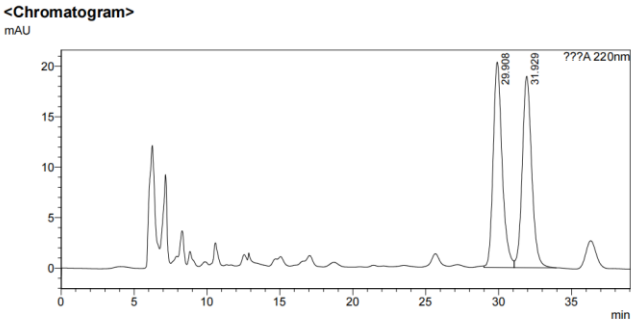
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.052	15227799	409719	96.477			
2	38.025	555985	11387	3.523			
Total		15783783	421105				

diethyl-2-(2,5-dimethyl-1-(2-(p-tolyl)-1H-indol-1-yl)-1H-pyrrol-3-yl)-2-hydroxymalonate: 3t



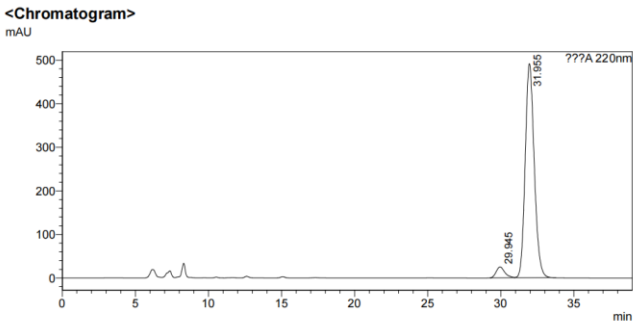
On a 0.1 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **3t** (41 mg, 86% yield, 91% ee) Yellow oily liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.65 (m, 1H), 7.23-7.19 (m, 2H), 7.12-7.07 (m, 4H), 6.96-6.94 (m, 1H), 6.86 (s, 1H), 6.09 (s, 1H), 4.35-4.28 (m, 4H), 4.14 (s, 1H), 2.33 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 8.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.42, 170.41, 139.4, 137.92, 137.89, 129.5, 127.5, 127.4, 126.5, 125.7, 123.2, 121.5, 120.6, 114.2, 109.0, 104.5, 100.5, 77.9, 62.6, 21.1, 14.0, 13.9, 10.7, 10.0. HRMS (ESI) calcd for $C_{28}H_{30}N_2KO_5$ [$(M+K^+)$]: 513.1786, found: 513.1786. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 29.94 min (minor), 31.95 min (major).



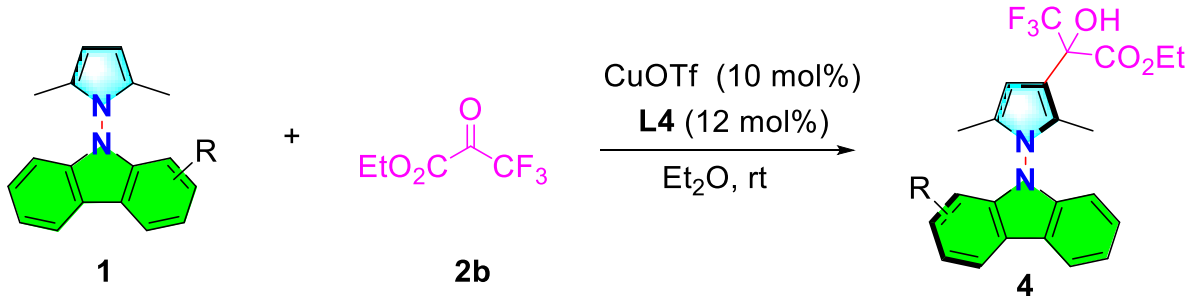
<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.908	874853	20370	50.580			
2	31.929	854781	18976	49.420		V	
Total		1729634	39345				



<Peak Table>
???A 220nm

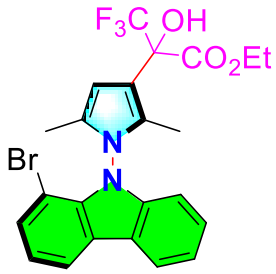
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.945	1024012	25160	4.632		M	
2	31.955	21081104	491005	95.368		V M	
Total		22105116	516165				



General Procedure A: To a mixture of CuOTf (2.1 mg, 10 mol%), **L4** (3.5mg, 12 mol%), carbazole pyrrole rings **1** (0.10 mmol) and ethyl trifluoropyruvate **2b** (0.15 mmol) was added Et_2O (1.0 mL) at rt under nitrogen atmosphere. Upon complete consumption of carbazole pyrrole rings **1** (TLC monitoring, about 24 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 15:1, v/v) to afford the desired product **4**.

General Procedure B: To a mixture of CuOTf (2.1 mg, 10 mol%), **L4** (3.5mg, 12 mol%), carbazole pyrrole rings **1** (0.10 mmol) and ethyl trifluoropyruvate **2b** (0.15 mmol) was added Et_2O (1.0 mL) at 0 ℃ under nitrogen atmosphere. Upon complete consumption of carbazole pyrrole rings **1** (TLC monitoring, about 24 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 15:1, v/v) to afford the desired product **4**.

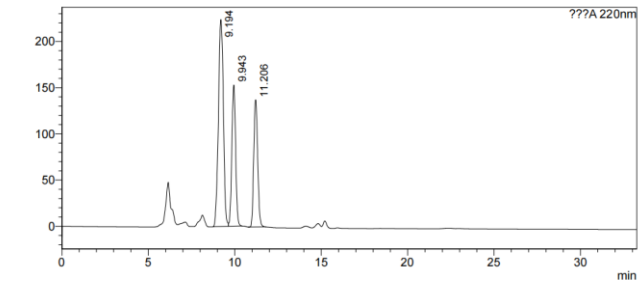
Ethyl -2-((S)-1-(1-bromo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4a



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4a** (21 mg, 41% yield, 97% ee, 92:8 dr). colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.60-7.58 (m, 1H), 7.49-7.47 (m, 1H), 7.38-7.35 (m, 1H), 7.20-7.18 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 0.92H), 6.99 (d, *J* = 8.4 Hz, 0.08H), 6.19 (s, 1H), 4.46-4.35 (m, 2H), 4.20 (s, 0.92H), 4.13 (s, 0.08H), 1.96 (s, 0.24H), 1.88 (s, 2.76H), 1.85 (s, 3H), 1.44 (t, *J* = 6.6 Hz, 0.24H), 1.37 (t, *J* = 7.2 Hz, 2.76H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8, 141.0, 135.6, 131.2, 130.1, 129.4, 127.7, 124.4, 122.2, 121.9, 120.43, 120.38, 119.7, 110.5, 109.0, 104.39, 104.37, 102.1, 63.9, 14.0, 10.7, 9.8. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.4 (major), -77.1 (minor). HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3BrF_3$ [$(M+H^+)$]: 509.0682, found: 509.0682. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 9.24 min (minor), 11.39 min (major).

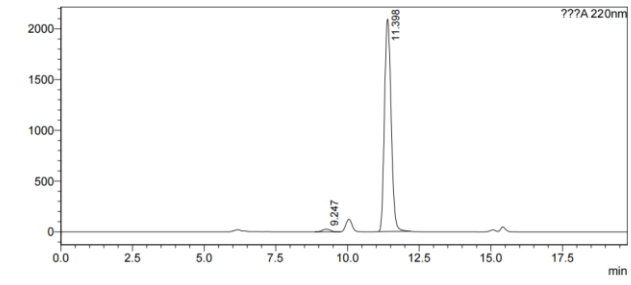
<Chromatogram>



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.194	4463673	224013	49.745		M	
2	9.943	2321534	152731	25.872		V M	
3	11.206	2187855	137700	24.382		M	
Total		8973061	514445				

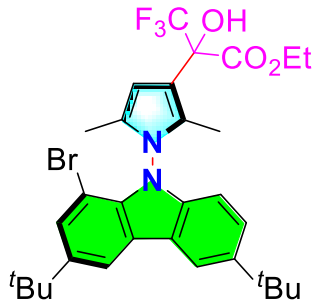
<Chromatogram>



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.247	521560	26626	1.520		M	
2	11.398	33794570	2091651	98.480		M	
Total		34316130	2118277				

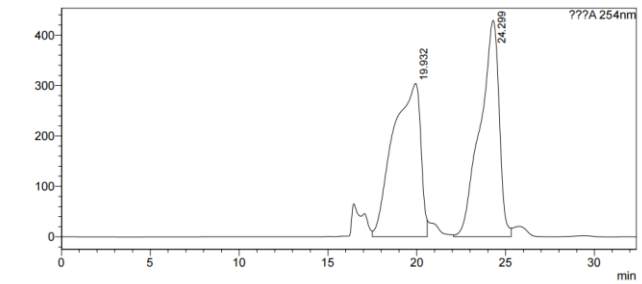
ethyl -3,3,3-trifluoro-2-hydroxy-2-((S)-1-(1-(4-methoxyphenyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)propanoate: 4b



On a 0.1 mmol scale, Prepared following general procedure B and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4b** (35 mg, 56% yield, 93% ee, 94:6 dr). colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.592-7.589 (m, 1H), 7.52-7.50 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 0.94H), 6.90 (d, *J* = 8.4 Hz, 0.06H), 6.16 (s, 1H), 4.48-4.35 (m, 2H), 4.20 (s, 0.94H), 4.13 (s, 0.06H), 1.95 (s, 0.18H), 1.88 (s, 2.82H), 1.86 (s, 2.82H), 1.454 (s, 9H), 1.451 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8, 145.7, 144.9, 139.5, 134.1, 130.2, 129.4, 128.7, 125.4, 124.4, 120.3, 116.3, 115.9, 110.3, 108.5 (major), 108.4 (minor), 104.1, 101.6, 63.9, 34.9, 34.8, 31.9, 31.8, 14.0, 10.8, 9.9. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.4 (major), -77.0 (minor). HRMS (ESI) calcd for $C_{31}H_{37}N_2O_3BrF_3$ [$(M+H^+)$]: 621.1934, found: 621.1934. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 97/3, 0.2 mL/min. Retention times: 19.69 min (minor), 24.32 min (major).

<Chromatogram>

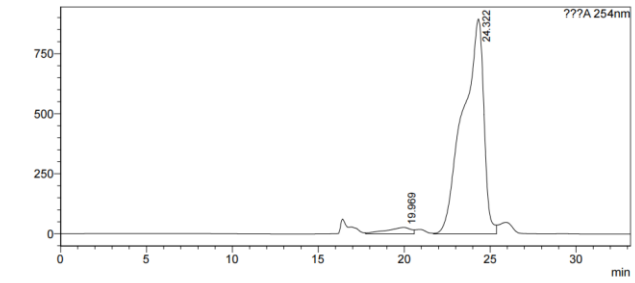


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.932	32815248	303640	50.556		M	
2	24.299	32093453	428881	49.444		M	
Total		64908701	732521				

<Chromatogram>

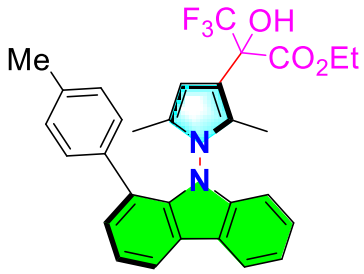


<Peak Table>

???A 254nm

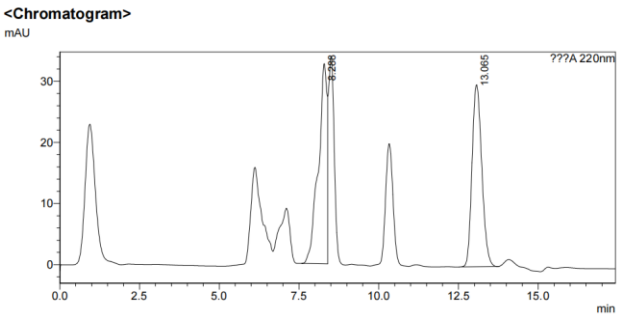
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.969	2774473	27120	3.544			
2	24.322	75508023	894641	96.456			
Total		78282497	921761				

ethyl -2-((S)-2,5-dimethyl-1-(1-(p-tolyl)-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4c



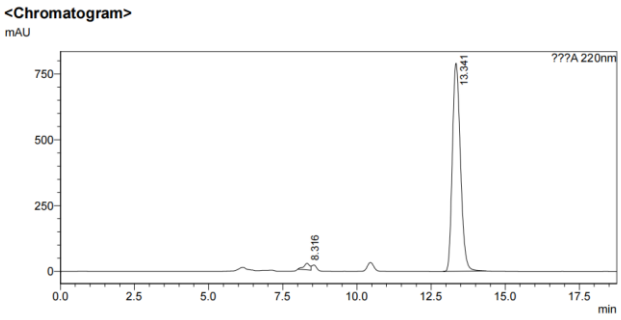
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4c** (32 mg, 62% yield, 95% ee, 95:5 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.11 (m, 2H), 7.42-7.39 (m, 1H), 7.36-7.31 (m, 2H), 7.25-7.24 (m, 1H), 7.00 (, *J* = 6.0 Hz, 0.20H), 6.97-6.93 (m, 3.8H), 6.79 (d, *J* = 7.8 Hz, 0.95H), 6.72 (d, *J* = 8.4 Hz, 0.05H), 5.77 (s, 0.05H), 5.72 (s, 0.95H), 4.52-4.37 (m, 2H), 3.79 (s, 0.95H), 3.65 (s, 0.05H), 2.32 (s, 3H), 1.84 (s, 2.85H), 1.81 (s, 0.15H), 1.69 (s, 0.15H), 1.65 (s, 2.84H), 1.42 (t, *J* = 6.6 Hz, 2.85H), 1.36 (t, *J* = 7.8 Hz, 0.15H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.4, 140.9, 136.8 (major), 136.7 (minor), 136.3, 134.1, 129.63 (minor), 129.57 (major), 128.4 (major), 128,3 (minor), 128.2 (minor), 128.0 (major), 127.3 (minor), 127.2 (major), 127.0 (major), 126.9 (minor), 126.5 (major), 126.4 (minor), 122.7 (major), 122.6 (minor), 121.3, 121.2, 120.9, 120.2, 119.5, 109.8, 108.8 (major), 108.7 (minor), 104.3, 63.6, 21.0, 14.05 (major), 13.97 (minor), 10.8 (minor), 10.7 (major), 10.2 (major), 10.1 (minor). ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.8 (minor), -77.0 (major). HRMS (ESI) calcd for $C_{30}H_{28}N_2O_3F_3$ [$(M+H^+)$]: 521.2047, found: 521.2047. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 8.3 min (minor), 13.34 min (major).



<Peak Table>
???A 220nm

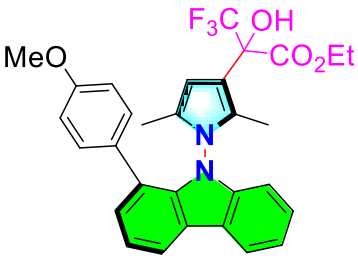
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.288	626310	32740	49.679		M	
2	13.065	634398	29749	50.321		M	
Total		1260708	62489				



<Peak Table>
???A 220nm

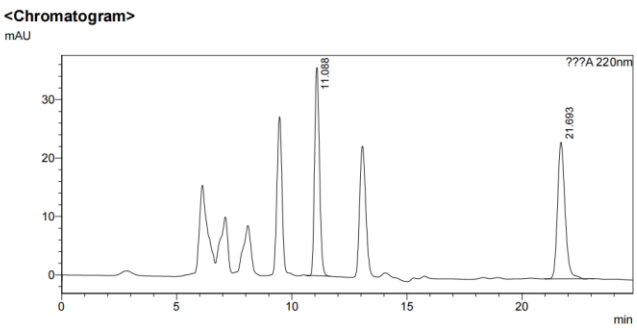
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.316	358258	25118	2.328		M	
2	13.341	15027669	790742	97.672		M	
Total		15385927	815861				

ethyl -3,3,3-trifluoro-2-hydroxy-2-((S)-1-(1-(4-methoxyphenyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)propanoate: 4d



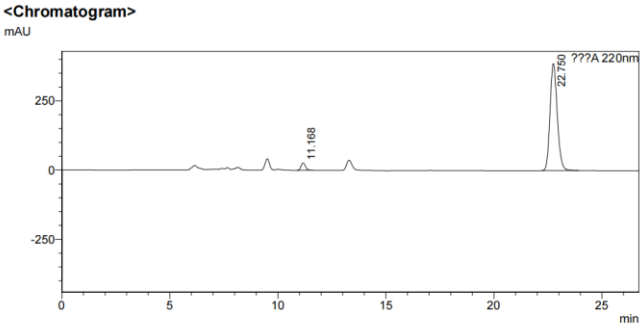
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product 4d (22 mg, 41% yield, 92% ee, 87:13 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.11 (m, 2H), 7.42-7.40 (m, 1H), 7.36-7.31 (m, 2H), 7.25-7.24 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 0.26H), 6.99 (d, *J* = 8.4 Hz, 1.74H), 6.80 (d, *J* = 8.4 Hz, 0.87H), 6.73 (d, *J* = 8.4 Hz, 0.26H), 6.70 (d, *J* = 7.8 Hz, 0.13H), 6.66 (d, *J* = 7.8 Hz 1.74H), 5.79 (s, 0.13H), 5.75 (s, 0.87H), 4.52-4.39 (m, 2H), 3.92 (s, 0.87H), 3.82 (s, 0.13H), 3.80 (s, 3H), 1.85 (s, 2.61H), 1.81 (s, 0.39H), 1.68 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 2.63H), 1.35 (t, *J* = 6.6 Hz, 0.37H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.4, 158.6 (minor), 158.4 (major), 141.0 (minor), 140.9 (major), 136.82 (major), 136.80 (minor), 129.8 (minor), 129.7 (major), 129.55 (major), 128.52 (minor), 129.43 (major), 128.28, 127.4 (minor), 127.3 (major), 127.0 (major), 126.9 (minor), 126.4 (minor), 126.2 (major), 122.64 (major), 122.57 (minor), 121.3, 121.2, 120.9 (minor), 120.8 (major), 120.24 (minor), 120.21 (major), 119.5 (major), 119.4 (minor), 113.0 (minor), 112.7 (major), 108.7 (minor), 109.6, 108.8 (major), 108.7 (minor), 104.4 (major), 104.3 (minor), 63.74 (major), 63.66 (minor), 55.00 (major), 54.96 (minor), 14.0, 10.8 (minor), 10.7 (major), 10.2 (major), 10.0 (minor). ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.6 (minor), -77.2 (major). HRMS (ESI) calcd for $C_{30}H_{28}N_2O_4F_3$ [$(M+H^+)$]: 537.1996, found: 537.1998. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 11.16 min (minor), 22.75 min (major).



<Peak Table>
???A 220nm

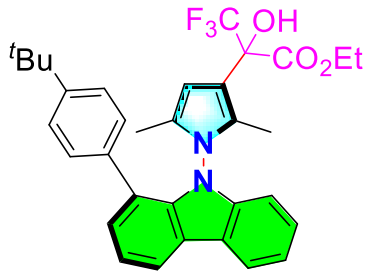
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.088	524426	35652	49.721		M	
2	21.693	530303	23376	50.279		M	
Total		1054729	59029				



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.168	374645	26390	4.007		M	
2	22.750	8976101	386760	95.993		M	
Total		9350746	413149				

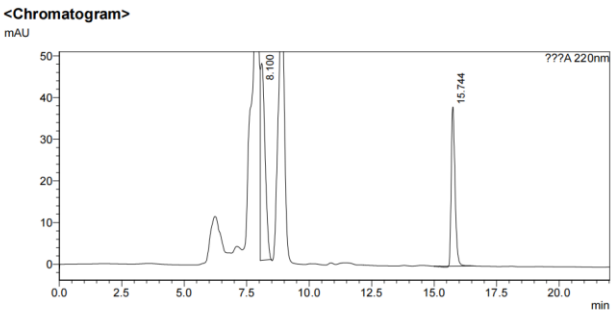
ethyl -2-((S)-1-(1-(4-(tert-butyl)phenyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4e



On a 0.1 mmol scale, Prepared following general procedure B and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4e** (19 mg, 34% yield, 95% ee, > 20:1 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.12 (m, 2H), 7.41-7.31 (m, 4H), 7.18-7.17 (m, 2H), 7.02-7.01 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 4.54-4.35 (m, 2H), 3.97 (s, 1H), 1.81 (s, 3H), 1.60 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.6, 149.6, 141.2, 137.0, 134.1, 129.6, 128.3, 128.2, 127.5, 127.0, 126.8, 124.2, 122.8, 121.4, 121.3, 121.0, 120.2, 119.5, 110.4, 108.9, 103.8, 63.7, 34.4, 31.2, 14.0, 10.6, 10.0. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.2 (minor), -76.6 (major). HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 11.16 min (minor), 22.75 min (major). HRMS (ESI) calcd for $C_{33}H_{33}N_2KO_3F_3$ [(M+K$^+$)]: 601.2075, found: 601.2076. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 8.01 min (minor), 15.42 min (major).

<Chromatogram>

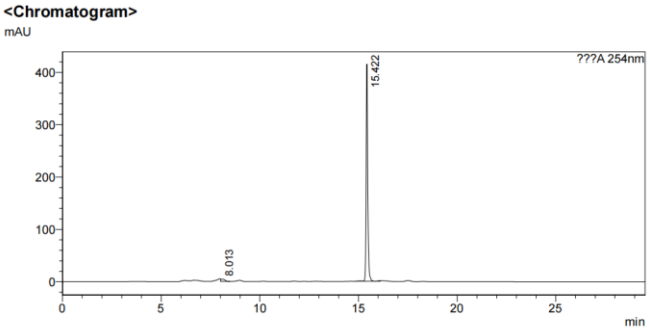


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.100	594427	47284	59.835		M	
2	15.744	399019	38218	40.165		M	
Total		993446	85501				

<Chromatogram>

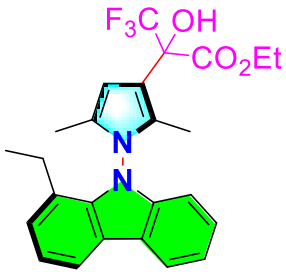


<Peak Table>

???A 254nm

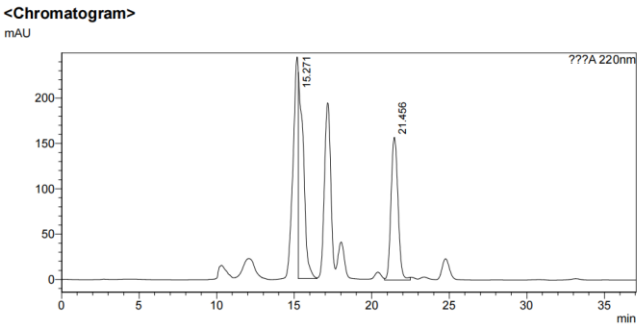
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.013	64651	4725	2.620		M	
2	15.422	2402718	414839	97.380		M	
Total		2467368	419563				

ethyl -2-((S)-1-(1-ethyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4f



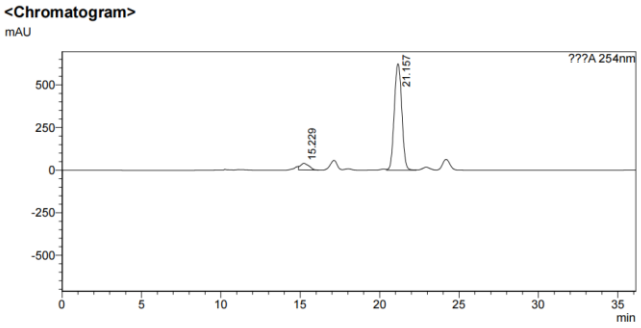
On a 0.1 mmol scale, Prepared following general procedure B and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4f** (17 mg, 37% yield, 87% ee, 91:9 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10-8.08 (m, 1H), 8.00-7.97 (m, 1H), 7.44-7.41 (m, 1H), 7.33-7.29 (m, 3H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.21 (s, 0.91H), 6.18 (s, 0.09H), 4.51-4.36 (m, 2H), 4.18 (s, 0.91H), 4.16 (s, 0.09H), 2.27-2.19 (m, 2H), 1.91 (s, 3H), 1.85 (s, 3H), 1.39 (t, *J* = 6.6 Hz, 3H), 1.13 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.7, 140.8, 137.2, 129.5, 128.9, 127.0 (minor), 126.9 (major), 126.8 (major), 126.7 (minor), 122.4, 121.4, 121.3, 121.2, 120.23 (minor), 120.17 (major), 118.2 (major), 118.1 (minor), 110.6, 108.6 (major), 108.4 (minor), 104.62, 104.60, 64.0 (minor), 63.9 (major), 20.9 (major), 20.8 (minor), 14.5, 14.0, 10.7, 9.9. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.6 (major), -77.4 (minor). HRMS (ESI) calcd for $C_{25}H_{26}N_2O_3F_3$ [$(M+H^+)$]: 459.1890, found: 459.1888. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 15.22 min (minor), 21.15 min (major).



<Peak Table>
???A 220nm

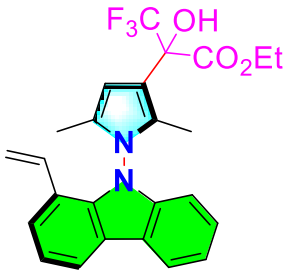
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.271	5030943	227508	50.380		M	
2	21.456	4954987	157441	49.620		M	
Total		9985930	384949				



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.229	1420229	38685	6.462		M	
2	21.157	20556586	624393	93.538			
Total		21976815	663078				

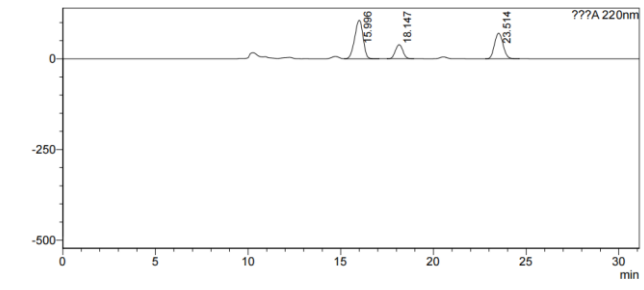
ethyl -2-((S)-2,5-dimethyl-1-(1-vinyl-9H-carbazol-9-yl)-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4g



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4g** (25 mg, 56% yield, 90% ee, 87:13 dr), colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11-8.05 (m, 2H), 7.57 (d, *J* = 7.8 Hz 1H), 7.47-7.44 (m, 1H), 7.35-7.30 (m, 2H), 7.02 (d, *J* = 8.4 Hz 1H), 6.24 (s, 0.87H), 6.22 (s, 0.13H), 5.84 (dd, *J* = 16.8 Hz, and10.8 Hz, 1H), 5.63 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.8 Hz, 0.13H), 5.06 (d, *J* = 10.2 Hz, 0.87H), 4.52-4.37 (m, 2H), 4.20 (s, 0.86H), 4.17 (s, 0.13H), 1.97 (s, 0.39H), 1.89 (s, 2.61H), 1.84 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 0.41H), 1.40 (t, *J* = 6.6 Hz, 2.62H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8 (major), 169.6 (minor), 140.5 (major), 140.4 (minor), 136.4, 130.4 (major), 130.2 (minor), 130.0 (minor), 129.4 (major), 128.8, 127.1 (major), 126.9 (minor), 124.5 (minor), 124.4 (major), 122.63 (minor), 122.55 (major), 122.5 (major), 122.4 (minor), 121.34, 121.30 (major), 121.27 (minor), 121.12 (minor), 121.06 (major), 120.4 (minor), 120.3 (major), 120.0 (major), 119.9 (minor), 116.8 (minor), 116.5 (major), 110.9 (major), 110.4 (minor), 108.6 (major), 108.4 (minor), 104.9 (minor), 104.8 (major), 64.0 (minor), 63.9 (major), 14.03 (minor), 13.97 (major), 10.6, 9.9 (minor), 9.7 (major). ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.6 (major), -77.3 (minor). HRMS (ESI) calcd for $C_{25}H_{23}N_2NaO_3F_3$ [$(M+Na^+)$]: 479.1553, found: 479.1552. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 16.02 min (minor), 23.52 min (major).

<Chromatogram>

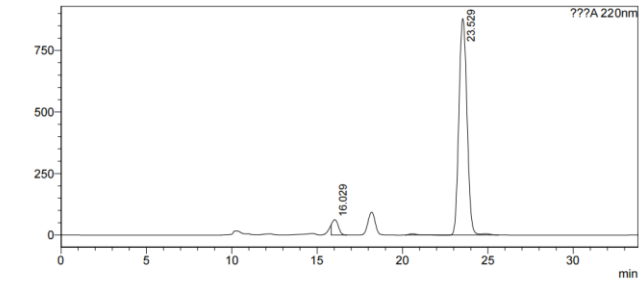


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.996	3351821	106194	50.033			
2	18.147	1078832	38453	16.104		M	
3	23.514	2268537	70340	33.863		M	
Total		6699190	214987				

<Chromatogram>

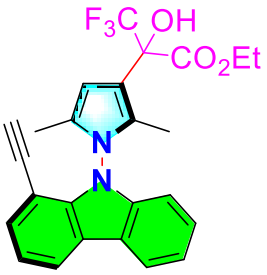


<Peak Table>

???A 220nm

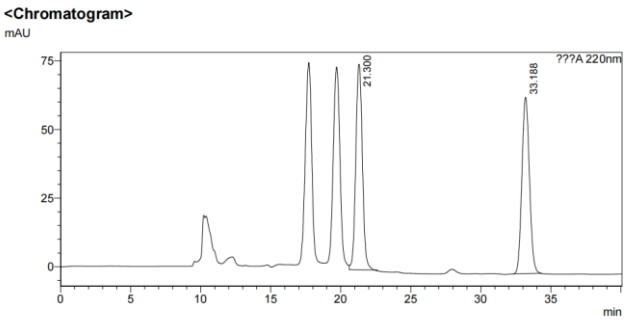
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.029	1598512	62344	5.176		M	
2	23.529	29283559	879695	94.824		M	
Total		30882072	942039				

Ethyl -2-((S)-1-(1-ethynyl-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4h



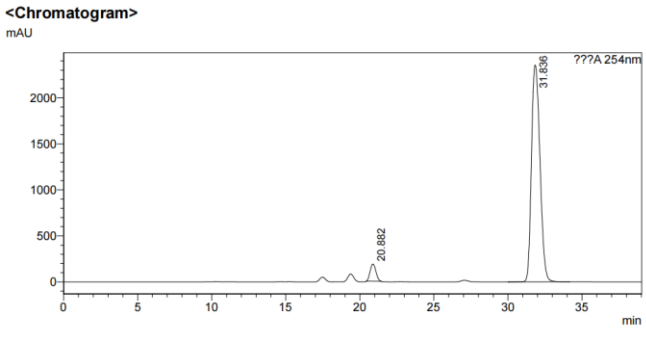
On a 0.1 mmol scale, Prepared following general procedure B and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4h** (26 mg, 57% yield, 90% ee, 94:6 dr), colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09-8.07 (m, 2H), 7.54-7.53 (m, 1H), 7.46-7.43 (m, 1H), 7.34-7.31 (m, 1H), 7.25-7.23 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 0.94H), 6.98 (d, *J* = 8.4 Hz, 0.06H), 6.10 (s, 1H), 4.48-4.32 (m, 2H), 4.11 (s, 0.06H), 4.09 (s, 0.94H), 2.86 (s, 0.06H), 2.79 (s, 0.94H), 1.98 (s, 0.18H), 1.88 (s, 2.83H), 1.80 (s, 2.82H), 1.78 (s, 0.18H), 1.42 (t, *J* = 7.2 Hz, 0.19H), 1.37 (t, *J* = 7.2 Hz, 2.84H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8 (major), 169.7 (minor), 140.4 (major), 140.32 (minor), 140.31 (major), 131.7 (minor), 131.6 (major), 130.9 (minor), 130.3 (major), 129.8 (major), 129.7 (minor), 127.4 (major), 127.3 (minor), 122.3 (major), 122.2 (minor), 121.63 (major), 121.55 (minor), 121.3 (major), 121.2 (minor), 121.0 (minor), 120.9 (major), 120.8, 120.49 (minor), 120.47 (major), 110.0 (major), 109.4 (minor), 108.7 (major), 108.6 (minor), 104.6 (minor), 104.4 (major), 103.9 (minor), 103.8 (major), 81.2 (minor), 80.7 (major), 76.8 (major), 76.6 (minor), 63.9 (minor), 63.8 (major), 64.0 (minor), 63.9 (major), 14.04 (minor), 14.01 (major), 10.6, 10.0 (minor), 9.7 (major). ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.4 (major), -76.9 (minor). HRMS (ESI) calcd for $C_{25}H_{21}N_2KO_3F_3$ [(M+K^+)]: 493.1136, found: 493.1134. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 20.88 min (minor), 31.83 min (major).



<Peak Table>
???A 220nm

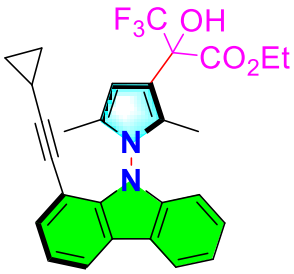
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.300	2442545	74848	50.430		M	
2	33.188	2400894	64157	49.570		M	
Total		4843439	139005				



<Peak Table>
???A 254nm

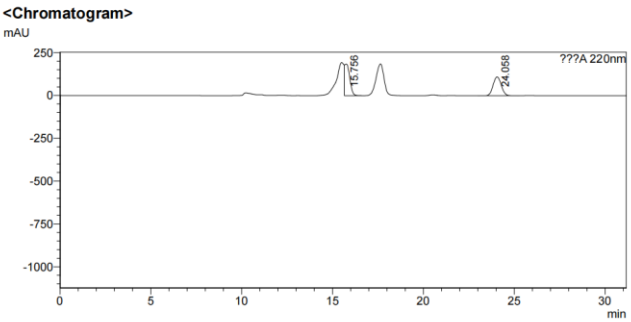
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.882	5047474	186643	5.097		M	
2	31.836	93989277	2356636	94.903		M	
Total		99036751	2543280				

ethyl -2-((S)-1-(1-(cyclopropylethynyl)-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4i



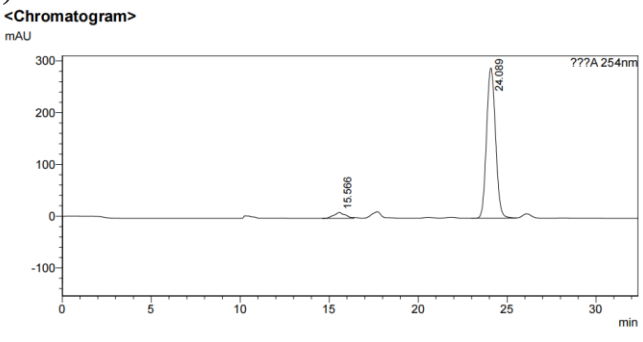
On a 0.1 mmol scale, Prepared following general procedure B and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4i** (33 mg, 66% yield, 90% ee, 95:5 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08-8.07 (m, 1H), 8.03-8.01 (m, 1H), 7.46-7.42 (m, 2H), 7.34-7.31 (m, 1H), 7.25-7.22 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 0.95H), 6.80 (d, *J* = 8.4 Hz, 0.05H), 6.19 (s, 0.95H), 6.17 (s, 0.05H), 4.53-4.41 (m, 2H), 4.20 (s, 0.95H), 4.15 (s, 0.05H), 1.92 (s, 0.15H), 1.90 (s, 2.86H), 1.89 (s, 2.86H), 1.85 (s, 0.15H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.22-1.18 (m, 1H), 0.76-0.69 (m, 2H), 0.60-0.53 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8, 140.6, 139.0, 131.3 (minor), 131.2 (major), 130.3, 129.1, 127.2 (major), 127.0 (minor), 126.8 (major), 126.7 (minor), 122.2, 121.5 (major), 121.4 (minor), 121.0, 120.1, 120.3, 119.8, 110.6, 109.5, 108.6 (major), 108.5 (minor), 105.6, 104.0, 97.8, 69.3, 63.9 (major), 63.8 (minor), 14.0, 10.8, 9.8 (major), 9.6 (minor), 8.8, 8.7. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.4 (minor), -76.9 (major). HRMS (ESI) calcd for $C_{28}H_{25}N_2KO_3F_3$ [(M+K$^+$)]: 533.1449, found: 533.1449. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 15.56 min (minor), 24.08 min (major).



<Peak Table>
???A 220nm

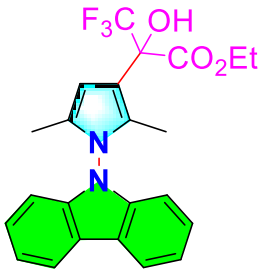
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.756	3502929	184186	50.423			
2	24.058	3444173	110001	49.577			
Total		6947103	294187				



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.566	507357	11359	4.741			
2	24.089	10193165	290277	95.259			
Total		10700522	301636				

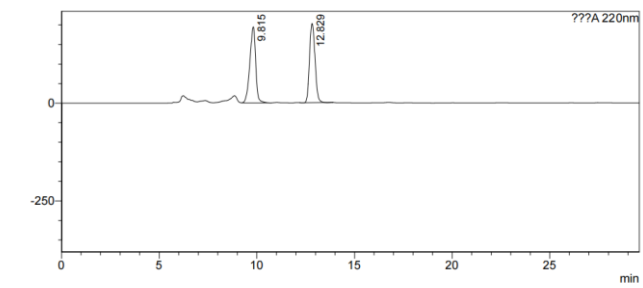
ethyl -2-(1-(9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4j



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4j** (18 mg, 41% yield, 92% ee) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.50-7.42 (m, 2H), 7.35-7.32 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.22 (s, 1H), 4.53-4.44 (m, 2H), 4.20 (s, 1H), 1.91 (s, 3H), 1.82 (s, 3H), 1.43 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.7, 140.0, 129.2, 128.3, 126.9, 126.7, 123.59 (q, *J* = 286.6 Hz), 121.4, 121.3, 121.10, 121.06, 120.61, 120.55, 110.3, 108.5, 108.3, 104.8, 64.0, 14.0, 10.6, 9.7. ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.9. HRMS (ESI) calcd for $C_{23}H_{22}N_2O_3F_3$ [$(M+H^+)$]: 431.1577, found: 431.1576. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 9.89 min (minor), 12.97 min (major).

<Chromatogram>

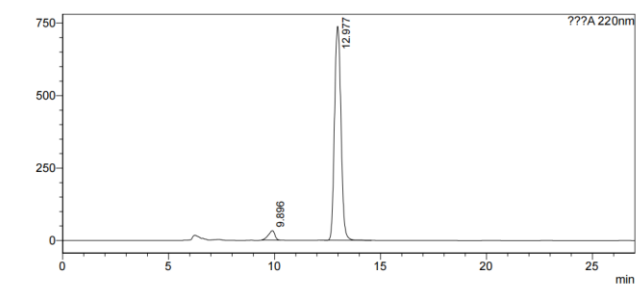


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.815	4038147	194311	50.541			
2	12.829	3951677	202255	49.459		M	
Total		7989824	396566				

<Chromatogram>

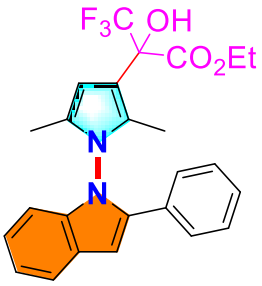


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.896	696273	32908	4.250		M	
2	12.977	15687276	738325	95.750		M	
Total		16383549	771233				

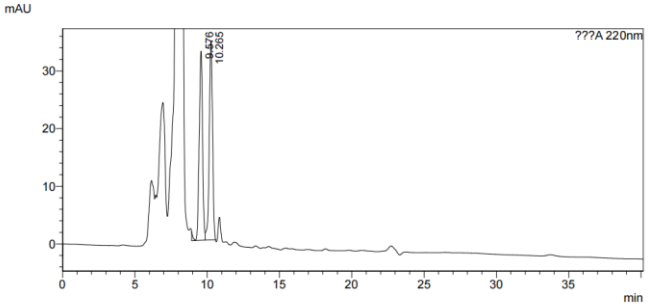
ethyl -2-((R)-2,5-dimethyl-1-(2-phenyl-1H-indol-1-yl)-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4k



On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4k** (17 mg, 37% yield, 94% ee, 95:5 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.66 (m, 1H), 7.28-7.20 (m, 5H), 7.14-7.12 (m, 2H), 6.95-6.93 (m, 1H), 6.89 (s, 1H), 6.15 (s, 0.95H), 6.12 (s, 0.05H), 4.44-4.28 (m, 2H), 4.14 (s, 1H),1.97 (s, 0.15H), 1.86 (s, 2.86H), 1.83 (s, 2.85H), 1.77 (s, 0.15H), 1.40 (t, *J* = 6.6 Hz, 0.15H), 1.31 (t, *J* = 7.2 Hz, 2.85H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.7, 139.33, 138.0, 130.3, 128.9, 128.8, 128.1, 128.0, 126.6 (major), 126.5 (minor), 125.7, 123.7, 121.8, 120.8, 110.7, 109.1, 104.8, 101.4 (major), 101.2 (minor), 64.0 (minor), 63.9 (major), 13.9, 10.7, 9.8. ^{19}F NMR (566 MHz, CDCl3): δ -76.6 (major), -77.4 (minor). HRMS (ESI) calcd for $C_{25}H_{23}N_2NaO_3F_3$ [$(M+Na^+)$]: 479.1553, found: 479.1554. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 9.60 min (minor), 10.33 min (major).

<Chromatogram>

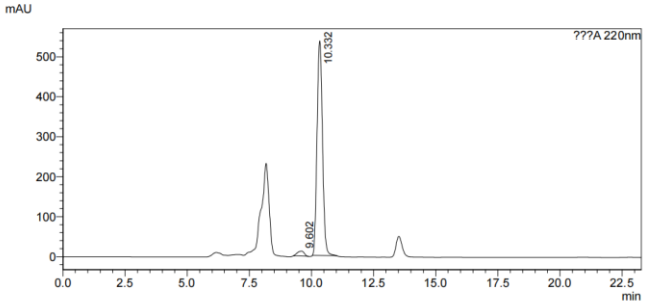


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.576	528707	32791	49.156		M	
2	10.265	546869	34508	50.844		V M	
Total		1075576	67299				

<Chromatogram>

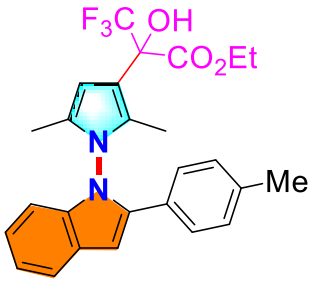


<Peak Table>

???A 220nm

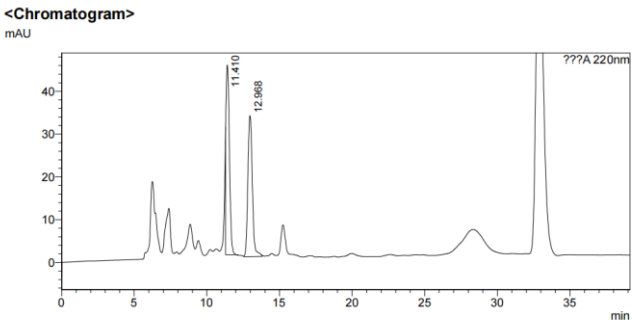
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.602	233171	12130	2.767		M	
2	10.332	8193131	536786	97.233		M	
Total		8426302	548915				

ethyl -2-((R)-2,5-dimethyl-1-(2-(p-tolyl)-1H-indol-1-yl)-1H-pyrrol-3-yl)-3,3,3-trifluoro-2-hydroxypropanoate: 4l



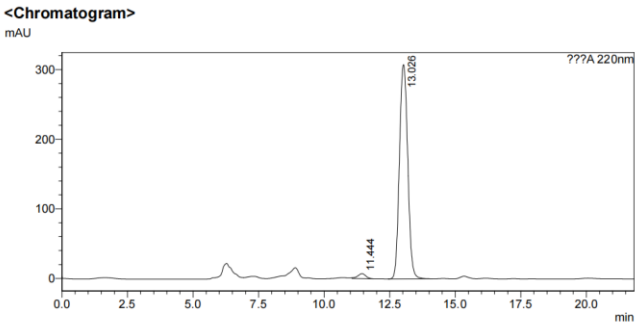
On a 0.1 mmol scale, Prepared following general procedure A and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 15/1) to afford the product **4l** (20 mg, 42% yield, 96% ee, 90:10 dr) colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.65 (m, 1H), 7.25-7.20 (m, 2H), 7.10-7.09 (m, 2H), 7.03-7.02 (m, 2H), 6.94-6.93 (m, 1H), 6.87 (s, 0.10H), 6.85 (s, 0.90H), 6.16 (s, 0.90H), 6.13 (s, 0.10H), 4.48-4.31 (m, 2H), 4.14 (s, 1H), 2.33 (s, 3H), 1.99 (s, 0.30H), 1.87 (s, 2.71H), 1.83 (s, 2.70H), 1.77 (s, 0.31H), 1.41 (t, *J* = 7.2 Hz, 0.31H), 1.33 (t, *J* = 7.2 Hz, 2.71H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.7 (major), 169.6 (minor), 138.0, 137.9, 129.6 (minor), 129.5 (major), 128.9, 128.21 (minor), 128.15 (major), 127.5 (major), 127.2 (minor), 126.5 (major), 126.3 (minor), 125.79 (minor), 125.77 (major), 123.5, 121.7 (major), 121.6 (minor), 120.73 (minor), 121.70 (major), 110.7, 109.0 (major), 108.9 (minor), 104.8 (minor), 104.7 (major), 100.8 (major), 100.6 (minor), 64.0 (minor), 63.8 (major), 21.2 14.0 (minor), 13.9 (major), 10.75 (major), 10.67 (minor), 10.1 (minor), 9.8 (major). ^{19}F NMR (566 MHz, $CDCl_3$): δ -76.6 (major), -77.4 (minor). HRMS (ESI) calcd for $C_{26}H_{25}N_2KO_3F_3$ [$(M+K^+)$]: 509.1449, found: 509.1449. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 11.44 min (minor), 13.02 min (major).



<Peak Table>
???A 220nm

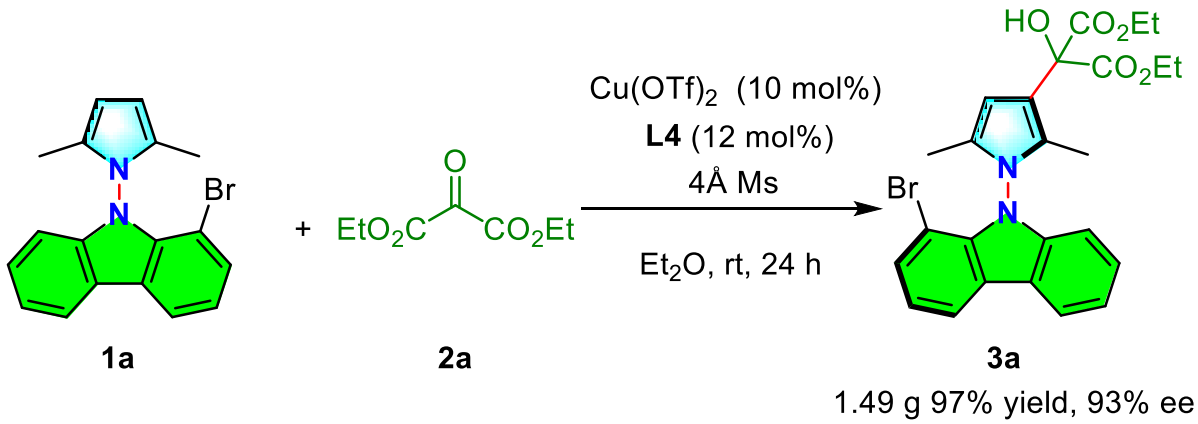
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.410	721916	44337	50.506		M	
2	12.968	707437	32953	49.494		M	
Total		1429353	77290				



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.444	152049	6992	2.193		M	
2	13.026	6780554	307919	97.807		M	
Total		6932603	314911				

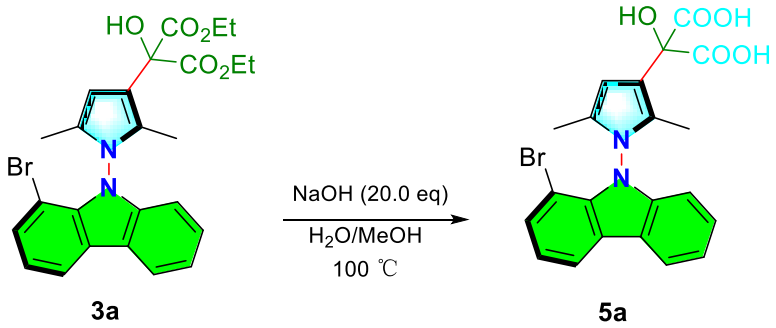
Gram-scale reaction



1a **2a** **3a**

1.49 g 97% yield, 93% ee

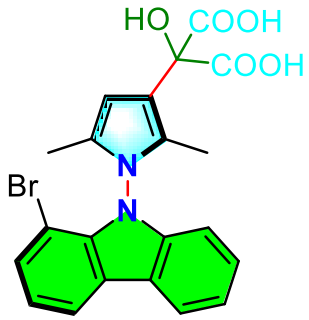
To a mixture of $Cu(OTf)_2$ (108.5 mg, 10 mol%), **L4** (105.99 mg, 12 mol%), carbazole pyrrole rings **1a** (3 mmol), diethyl ketomalonates **2a** (4.5 mmol) and 4Å Ms (1.5 g, activated under flame dry for 30 min prior to use) was added Et_2O (30.0 mL) at rt under nitrogen atmosphere. Upon complete consumption of carbazole pyrrole rings **1a** (TLC monitoring, about 24 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 5:1, v/v) to afford the desired product **3a**.



3a 5a

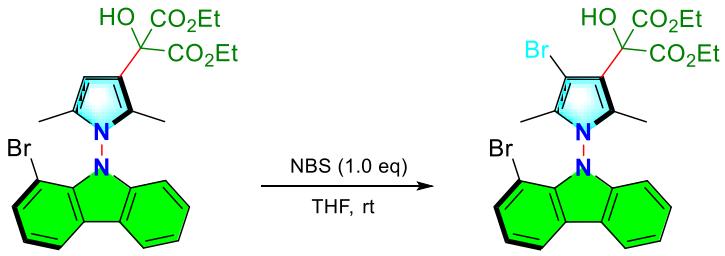
Procedure: **3a** (51.3 mg, 0.1 mmol) and NaOH (20 eq) were dissolved in H_2O/MeOH at 100 ℃ (oil bath heating) under nitrogen atmosphere. After stirring for 2 h at room temperature. When the reaction was completed as monitored by TLC. After dilute with a 1M aqueous solution of NaOH, then pour into a separating funnel. The aqueous phase is acidified with 4M HCl, and extracted five times with dichloromethane. The combined organic phase is dried over Na_2SO_4 and filtered to afford the product **5a**.

(S)-2-(1-(1-bromo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonic acid: 5a



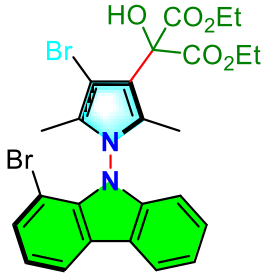
On a 0.1 mmol scale, Prepared following general procedure and the reaction mixture was dried over Na_2SO_4 and filtered to afford the product **5a** (40 mg, 88% yield) White solid.

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 8.30-8.27 (m, 2H), 7.67-7.66 (m, 1H), 7.53-7.25 (m, 4H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.95 (s, 1H), 4.06 (s, 2H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 174.0, 173.9, 140.7, 135.3, 131.1, 128.0, 126.92, 126.87, 123.9, 122.6, 121.9, 121.0, 120.4, 119.8, 108.5, 104.9, 101.4, 75.5, 10.4, 9.3. HRMS (ESI) calcd for $C_{21}H_{18}N_2O_5Br$ [$(M+H^+)$]: 457.0394, found: 457.0390.



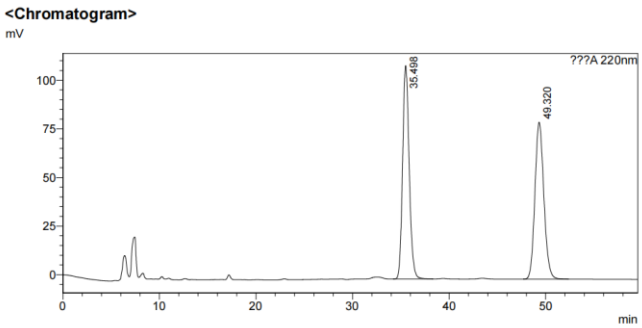
Procedure: **3a** (51.3 mg, 0.1 mmol) and NBS (1.0 eq) were dissolved in THF at rt under nitrogen atmosphere. After stirring for 24 h at room temperature. When the reaction was completed as monitored by TLC. After filtration and evaporation in vacuo, the residuewas purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 5:1) to afford the product **6a**.

diethyl (R)-2-(4-bromo-1-(1-bromo-9H-carbazol-9-yl)-2,5-dimethyl-1H-pyrrol-3-yl)-2-hydroxymalonate: 6a



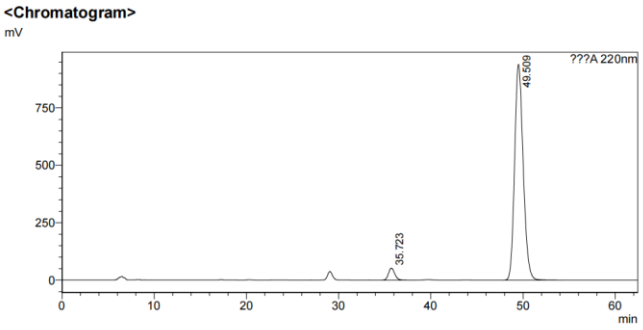
On a 0.1 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 5/1) to afford the product **6a** (56 mg, 95% yield, 92% ee) White solid.

^{1}H NMR (600 MHz, ($CDCl_3$): δ 8.09-8.06 (m, 2H), 7.60-7.59 (m, 1H), 7.49-7.47 (m, 1H), 7.38-7.36 (m, 1H), 7.21-7.18 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.41-4.37 (m, 1H), 4.30-4.26 (m, 4H), 1.832 (s, 3H), 1.826 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, ($CDCl_3$): δ 170.3, 170.2, 140.7, 135.6, 131.3, 129.6, 128.7, 127.8, 124.4, 122.5, 122.1, 120.5, 120.4, 119.7, 113.6, 109.1, 102.2, 94.4, 77.9, 62.9, 13.91, 13.89, 9.9, 9.8. HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_5Br$ [(M+Na^+)]: 591.0125, found: 591.0125. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 35.72 min (minor), 49.50 min (major).



<Peak Table>
???A 220nm

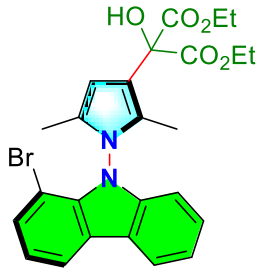
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.498	5191183	109763	50.032			
2	49.320	5184574	80695	49.968			
Total		10375757	190458				



<Peak Table>
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.723	2506895	52831	3.953			
2	49.509	60904214	939896	96.047			
Total		63411110	992727				

7. Crystal Structure of (*S*)-3a



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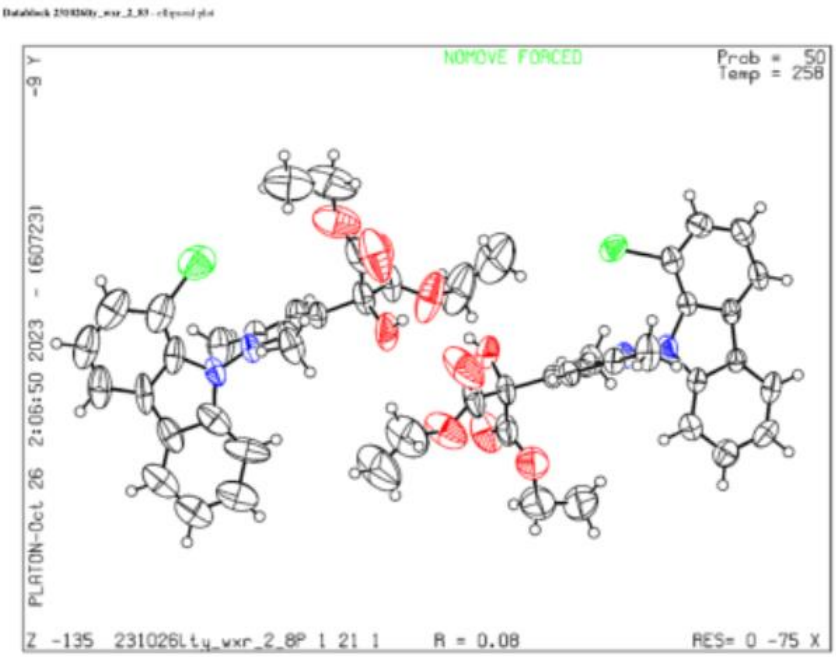


Method for single crystals cultivation: **3a** (50.0 mg) was dissolved in n-hexane/ dichloromethane (v/v =80:20, 2.0 mL) in a vial at room temperature. The vial was properly sealed with parafilm and kept at 25 ^{o}C to allow the slow evaporation of the solvents until a single crystal was obtained. The absolute configuration of compound **3a** is determined by anomalous dispersion with Ga Kα radiation (λ =1.34139 Å) as X-ray source for X-ray diffraction experiment, and a Flack parameter of -0.01(2) is obtained as result. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2405517.

Table S4. Crystal data and structure refinement for 231026lty_wxr_2_83.

Identification code	231026lty_wxr_2_83	
Empirical formula	C25 H25 Br N2 O5	
Formula weight	513.38	
Temperature	258.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.9596(5) Å	α= 90 °.
	b = 7.6809(3) Å	β= 103.416(2) °.
	c = 24.4062(10) Å	γ = 90 °.
Volume	2363.13(16) $Å^3$	
Z	4	
Density (calculated)	1.443 Mg/m^3	
Absorption coefficient	1.772 mm^{-1}	
F(000)	1056	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	3.239 to 55.640 °.	
Index ranges	-15<=h<=15, -8<=k<=9, -29<=l<=29	
Reflections collected	25114	
Independent reflections	8578 [R(int) = 0.0828]	
Completeness to theta = 53.594 °	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4349	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8578 / 185 / 593	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0767, wR2 = 0.2132	
R indices (all data)	R1 = 0.0880, wR2 = 0.2269	
Absolute structure parameter	0.082(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.464 and -0.812 e.$Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 231026lty_wxr_2_83. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	4784(1)	4063(1)	4987(1)	66(1)
C(1)	2853(5)	2285(9)	5002(2)	37(1)
N(1)	2541(4)	3976(9)	4115(2)	41(1)
O(1)	4379(5)	4016(15)	2900(3)	89(2)
C(2)	3886(6)	2582(10)	5286(3)	48(2)
N(2)	2222(5)	2883(9)	4486(2)	45(1)
O(2)	2907(8)	2741(12)	2064(3)	102(3)
C(3)	4269(7)	1754(12)	5785(3)	56(2)
O(3)	1621(7)	4159(17)	2314(3)	106(3)
C(4)	3643(7)	604(14)	6011(3)	62(2)
O(4)	4159(13)	7618(19)	2849(4)	169(6)
C(5)	2612(7)	271(11)	5737(3)	54(2)
O(5)	3208(10)	6809(12)	2048(4)	121(3)
C(6)	2205(6)	1129(10)	5235(3)	43(2)
C(7)	1185(5)	1060(9)	4833(3)	40(1)
C(8)	254(6)	107(11)	4821(4)	56(2)
C(9)	-578(6)	282(14)	4371(4)	64(2)
C(10)	-526(7)	1376(14)	3921(4)	64(2)
C(11)	393(6)	2308(12)	3924(3)	54(2)
C(12)	1231(5)	2135(10)	4385(3)	42(1)
C(13)	2461(6)	5758(9)	4115(3)	43(2)
C(14)	2754(6)	6340(10)	3643(3)	44(2)
C(15)	3005(5)	4840(10)	3344(3)	42(1)
C(16)	2880(5)	3404(10)	3644(3)	43(2)
C(17)	3039(8)	1537(11)	3564(3)	55(2)
C(18)	2129(10)	6700(13)	4577(4)	73(3)
C(19)	3349(7)	4861(11)	2797(3)	55(2)
C(20)	2626(8)	3792(15)	2352(3)	73(3)
C(21)	829(14)	3220(30)	1922(6)	127(4)
C(22)	354(12)	1950(30)	2207(6)	122(6)
C(23)	3486(11)	6650(15)	2578(4)	81(3)
C(24)	3491(19)	8470(20)	1784(8)	140(5)
C(25)	3260(20)	8240(30)	1225(8)	182(8)
Br(1A)	9682(1)	7578(3)	1379(1)	116(1)

C(1A)	8144(9)	7849(11)	356(4)	68(2)
N(1A)	7413(5)	5872(9)	948(2)	53(2)
O(1A)	5995(6)	5536(15)	2303(4)	112(4)
C(2A)	9123(9)	8271(15)	643(6)	84(3)
N(2A)	7344(6)	6939(10)	500(2)	58(2)
O(2A)	7538(13)	7139(14)	3023(5)	142(4)
C(3A)	9746(10)	9389(17)	343(7)	102(3)
O(3A)	8795(11)	5529(17)	2842(5)	132(3)
C(4A)	9316(12)	9889(18)	-195(8)	103(3)
O(4A)	7846(9)	2109(15)	2639(5)	127(4)
C(5A)	8382(12)	9485(15)	-470(7)	96(3)
O(5A)	6298(8)	2531(13)	2746(6)	130(3)
C(6A)	7741(9)	8442(12)	-212(4)	73(2)
C(12A)	6437(5)	6864(9)	52(2)	80(2)
C(7A)	6639(5)	7777(9)	-403(2)	75(2)
C(8A)	5859(7)	7909(10)	-900(2)	94(3)
C(9A)	4877(6)	7128(11)	-941(2)	95(3)
C(10A)	4674(5)	6215(10)	-485(3)	101(3)
C(11A)	5454(6)	6083(9)	11(2)	99(3)
C(13A)	7719(6)	4130(13)	964(3)	53(2)
C(14A)	7640(7)	3539(11)	1487(3)	55(2)
C(15A)	7262(6)	4880(11)	1771(3)	49(2)
C(16A)	7152(7)	6348(11)	1450(3)	52(2)
C(17A)	6791(10)	8135(13)	1528(4)	75(3)
C(18A)	8019(10)	3294(16)	484(5)	80(3)
C(19A)	7001(9)	4833(14)	2342(4)	71(2)
C(20A)	7812(12)	6020(20)	2788(5)	93(3)
C(21A)	9558(19)	6640(30)	3235(8)	153(6)
C(22A)	10015(16)	7960(30)	2953(8)	140(6)
C(23A)	7056(10)	2995(14)	2567(4)	80(3)
C(24A)	6197(15)	740(20)	2938(12)	149(5)
C(25A)	6315(17)	880(20)	3558(11)	164(8)

Table S6. Bond lengths [Å] and angles [°] for 231026lty_wxr_2_83.

Br(1)-C(2)	1.890(8)
C(1)-C(2)	1.376(10)
C(1)-N(2)	1.411(9)
C(1)-C(6)	1.427(9)
N(1)-N(2)	1.366(8)
N(1)-C(13)	1.373(10)
N(1)-C(16)	1.395(8)
O(1)-H(1)	0.8200
O(1)-C(19)	1.452(12)
C(2)-C(3)	1.362(11)
N(2)-C(12)	1.376(9)
O(2)-C(20)	1.182(13)
C(3)-H(3)	0.9300
C(3)-C(4)	1.396(13)
O(3)-C(20)	1.315(14)
O(3)-C(21)	1.427(16)
C(4)-H(4)	0.9300
C(4)-C(5)	1.372(13)
O(4)-C(23)	1.219(15)
C(5)-H(5)	0.9300
C(5)-C(6)	1.384(10)
O(5)-C(23)	1.265(13)
O(5)-C(24)	1.512(17)
C(6)-C(7)	1.452(10)
C(7)-C(8)	1.406(10)
C(7)-C(12)	1.382(10)
C(8)-H(8)	0.9300
C(8)-C(9)	1.356(13)
C(9)-H(9)	0.9300
C(9)-C(10)	1.398(14)
C(10)-H(10)	0.9300
C(10)-C(11)	1.388(12)
C(11)-H(11)	0.9300
C(11)-C(12)	1.376(11)
C(13)-C(14)	1.370(9)
C(13)-C(18)	1.484(10)
C(14)-H(14)	0.9300

C(14)-C(15)	1.440(10)
C(15)-C(16)	1.354(11)
C(15)-C(19)	1.502(9)
C(16)-C(17)	1.468(12)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-C(20)	1.504(12)
C(19)-C(23)	1.500(13)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(21)-C(22)	1.42(2)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(24)-C(25)	1.34(3)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
Br(1A)-C(2A)	1.852(14)
C(1A)-C(2A)	1.339(17)
C(1A)-N(2A)	1.362(11)
C(1A)-C(6A)	1.437(15)
N(1A)-N(2A)	1.351(9)
N(1A)-C(13A)	1.393(13)
N(1A)-C(16A)	1.395(8)
O(1A)-H(1A)	0.8200
O(1A)-C(19A)	1.394(12)
C(2A)-C(3A)	1.483(17)
N(2A)-C(12A)	1.409(9)
O(2A)-C(20A)	1.138(17)
C(3A)-H(3A)	0.9300
C(3A)-C(4A)	1.36(2)
O(3A)-C(20A)	1.305(18)

O(3A)-C(21A)	1.481(18)
C(4A)-H(4A)	0.9300
C(4A)-C(5A)	1.28(2)
O(4A)-C(23A)	1.208(14)
C(5A)-H(5A)	0.9300
C(5A)-C(6A)	1.404(13)
O(5A)-C(23A)	1.218(12)
O(5A)-C(24A)	1.470(17)
C(6A)-C(7A)	1.486(14)
C(12A)-C(7A)	1.3900
C(12A)-C(11A)	1.3900
C(7A)-C(8A)	1.3900
C(8A)-H(8A)	0.9300
C(8A)-C(9A)	1.3900
C(9A)-H(9A)	0.9300
C(9A)-C(10A)	1.3900
C(10A)-H(10A)	0.9300
C(10A)-C(11A)	1.3900
C(11A)-H(11A)	0.9300
C(13A)-C(14A)	1.379(11)
C(13A)-C(18A)	1.466(12)
C(14A)-H(14A)	0.9300
C(14A)-C(15A)	1.393(12)
C(15A)-C(16A)	1.361(11)
C(15A)-C(19A)	1.509(10)
C(16A)-C(17A)	1.476(13)
C(17A)-H(17D)	0.9600
C(17A)-H(17E)	0.9600
C(17A)-H(17F)	0.9600
C(18A)-H(18D)	0.9600
C(18A)-H(18E)	0.9600
C(18A)-H(18F)	0.9600
C(19A)-C(20A)	1.61(2)
C(19A)-C(23A)	1.511(14)
C(21A)-H(21C)	0.9700
C(21A)-H(21D)	0.9700
C(21A)-C(22A)	1.43(3)
C(22A)-H(22D)	0.9600
C(22A)-H(22E)	0.9600

C(22A)-H(22F)	0.9600
C(24A)-H(24C)	0.9700
C(24A)-H(24D)	0.9700
C(24A)-C(25A)	1.49(3)
C(25A)-H(25D)	0.9600
C(25A)-H(25E)	0.9600
C(25A)-H(25F)	0.9600

C(2)-C(1)-N(2)	133.6(6)
C(2)-C(1)-C(6)	119.8(6)
N(2)-C(1)-C(6)	106.6(6)
N(2)-N(1)-C(13)	125.3(5)
N(2)-N(1)-C(16)	123.7(7)
C(13)-N(1)-C(16)	110.6(6)
C(19)-O(1)-H(1)	109.5
C(1)-C(2)-Br(1)	121.3(5)
C(3)-C(2)-Br(1)	119.8(6)
C(3)-C(2)-C(1)	118.9(7)
N(1)-N(2)-C(1)	126.1(6)
N(1)-N(2)-C(12)	123.5(6)
C(12)-N(2)-C(1)	110.3(5)
C(2)-C(3)-H(3)	119.2
C(2)-C(3)-C(4)	121.6(8)
C(4)-C(3)-H(3)	119.2
C(20)-O(3)-C(21)	119.0(13)
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-C(3)	121.0(7)
C(5)-C(4)-H(4)	119.5
C(4)-C(5)-H(5)	121.0
C(4)-C(5)-C(6)	118.1(7)
C(6)-C(5)-H(5)	121.0
C(23)-O(5)-C(24)	118.6(11)
C(1)-C(6)-C(7)	106.3(6)
C(5)-C(6)-C(1)	120.6(7)
C(5)-C(6)-C(7)	132.9(7)
C(8)-C(7)-C(6)	132.4(7)
C(12)-C(7)-C(6)	108.2(6)
C(12)-C(7)-C(8)	119.3(7)
C(7)-C(8)-H(8)	120.6

C(9)-C(8)-C(7)	118.8(7)
C(9)-C(8)-H(8)	120.6
C(8)-C(9)-H(9)	119.2
C(8)-C(9)-C(10)	121.5(8)
C(10)-C(9)-H(9)	119.2
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-C(9)	120.2(8)
C(11)-C(10)-H(10)	119.9
C(10)-C(11)-H(11)	121.0
C(12)-C(11)-C(10)	118.0(7)
C(12)-C(11)-H(11)	121.0
N(2)-C(12)-C(7)	108.5(6)
N(2)-C(12)-C(11)	129.2(6)
C(11)-C(12)-C(7)	122.2(7)
N(1)-C(13)-C(18)	121.5(7)
C(14)-C(13)-N(1)	106.8(6)
C(14)-C(13)-C(18)	131.7(7)
C(13)-C(14)-H(14)	126.1
C(13)-C(14)-C(15)	107.7(6)
C(15)-C(14)-H(14)	126.1
C(14)-C(15)-C(19)	126.1(7)
C(16)-C(15)-C(14)	107.9(5)
C(16)-C(15)-C(19)	125.9(7)
N(1)-C(16)-C(17)	119.8(6)
C(15)-C(16)-N(1)	106.8(6)
C(15)-C(16)-C(17)	133.3(6)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(1)-C(19)-C(15)	106.9(6)

O(1)-C(19)-C(20)	105.9(8)
O(1)-C(19)-C(23)	107.0(8)
C(15)-C(19)-C(20)	111.9(6)
C(23)-C(19)-C(15)	114.3(7)
C(23)-C(19)-C(20)	110.3(8)
O(2)-C(20)-O(3)	122.8(10)
O(2)-C(20)-C(19)	125.2(10)
O(3)-C(20)-C(19)	112.0(9)
O(3)-C(21)-H(21A)	109.6
O(3)-C(21)-H(21B)	109.6
H(21A)-C(21)-H(21B)	108.1
C(22)-C(21)-O(3)	110.3(12)
C(22)-C(21)-H(21A)	109.6
C(22)-C(21)-H(21B)	109.6
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(4)-C(23)-O(5)	119.6(9)
O(4)-C(23)-C(19)	119.6(11)
O(5)-C(23)-C(19)	115.2(9)
O(5)-C(24)-H(24A)	110.1
O(5)-C(24)-H(24B)	110.1
H(24A)-C(24)-H(24B)	108.4
C(25)-C(24)-O(5)	107.9(14)
C(25)-C(24)-H(24A)	110.1
C(25)-C(24)-H(24B)	110.1
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(2A)-C(1A)-N(2A)	132.4(10)
C(2A)-C(1A)-C(6A)	121.0(9)
N(2A)-C(1A)-C(6A)	106.5(10)
N(2A)-N(1A)-C(13A)	124.8(6)

N(2A)-N(1A)-C(16A)	124.6(7)
C(13A)-N(1A)-C(16A)	110.6(6)
C(19A)-O(1A)-H(1A)	109.5
C(1A)-C(2A)-Br(1A)	123.2(8)
C(1A)-C(2A)-C(3A)	116.2(12)
C(3A)-C(2A)-Br(1A)	120.7(10)
C(1A)-N(2A)-C(12A)	111.6(7)
N(1A)-N(2A)-C(1A)	127.5(8)
N(1A)-N(2A)-C(12A)	119.3(7)
C(2A)-C(3A)-H(3A)	120.2
C(4A)-C(3A)-C(2A)	119.5(13)
C(4A)-C(3A)-H(3A)	120.2
C(20A)-O(3A)-C(21A)	112.9(15)
C(3A)-C(4A)-H(4A)	117.8
C(5A)-C(4A)-C(3A)	124.4(12)
C(5A)-C(4A)-H(4A)	117.8
C(4A)-C(5A)-H(5A)	120.3
C(4A)-C(5A)-C(6A)	119.4(14)
C(6A)-C(5A)-H(5A)	120.3
C(23A)-O(5A)-C(24A)	121.9(11)
C(1A)-C(6A)-C(7A)	107.6(7)
C(5A)-C(6A)-C(1A)	119.5(12)
C(5A)-C(6A)-C(7A)	132.9(11)
C(7A)-C(12A)-N(2A)	108.8(5)
C(7A)-C(12A)-C(11A)	120.0
C(11A)-C(12A)-N(2A)	131.2(5)
C(12A)-C(7A)-C(6A)	105.5(5)
C(12A)-C(7A)-C(8A)	120.0
C(8A)-C(7A)-C(6A)	134.5(5)
C(7A)-C(8A)-H(8A)	120.0
C(9A)-C(8A)-C(7A)	120.0
C(9A)-C(8A)-H(8A)	120.0
C(8A)-C(9A)-H(9A)	120.0
C(10A)-C(9A)-C(8A)	120.0
C(10A)-C(9A)-H(9A)	120.0
C(9A)-C(10A)-H(10A)	120.0
C(11A)-C(10A)-C(9A)	120.0
C(11A)-C(10A)-H(10A)	120.0
C(12A)-C(11A)-H(11A)	120.0

C(10A)-C(11A)-C(12A)	120.0
C(10A)-C(11A)-H(11A)	120.0
N(1A)-C(13A)-C(18A)	121.6(8)
C(14A)-C(13A)-N(1A)	105.2(6)
C(14A)-C(13A)-C(18A)	133.2(10)
C(13A)-C(14A)-H(14A)	125.5
C(13A)-C(14A)-C(15A)	109.1(8)
C(15A)-C(14A)-H(14A)	125.5
C(14A)-C(15A)-C(19A)	128.5(7)
C(16A)-C(15A)-C(14A)	109.2(6)
C(16A)-C(15A)-C(19A)	122.3(7)
N(1A)-C(16A)-C(17A)	120.3(7)
C(15A)-C(16A)-N(1A)	105.9(7)
C(15A)-C(16A)-C(17A)	133.7(6)
C(16A)-C(17A)-H(17D)	109.5
C(16A)-C(17A)-H(17E)	109.5
C(16A)-C(17A)-H(17F)	109.5
H(17D)-C(17A)-H(17E)	109.5
H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5
C(13A)-C(18A)-H(18D)	109.5
C(13A)-C(18A)-H(18E)	109.5
C(13A)-C(18A)-H(18F)	109.5
H(18D)-C(18A)-H(18E)	109.5
H(18D)-C(18A)-H(18F)	109.5
H(18E)-C(18A)-H(18F)	109.5
O(1A)-C(19A)-C(15A)	109.5(8)
O(1A)-C(19A)-C(20A)	106.4(10)
O(1A)-C(19A)-C(23A)	110.6(9)
C(15A)-C(19A)-C(20A)	111.1(8)
C(15A)-C(19A)-C(23A)	110.9(7)
C(23A)-C(19A)-C(20A)	108.3(9)
O(2A)-C(20A)-O(3A)	125.3(16)
O(2A)-C(20A)-C(19A)	122.6(15)
O(3A)-C(20A)-C(19A)	112.1(11)
O(3A)-C(21A)-H(21C)	109.1
O(3A)-C(21A)-H(21D)	109.1
H(21C)-C(21A)-H(21D)	107.8
C(22A)-C(21A)-O(3A)	112.7(15)

C(22A)-C(21A)-H(21C)	109.1
C(22A)-C(21A)-H(21D)	109.1
C(21A)-C(22A)-H(22D)	109.5
C(21A)-C(22A)-H(22E)	109.5
C(21A)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5
O(4A)-C(23A)-O(5A)	120.6(10)
O(4A)-C(23A)-C(19A)	123.2(10)
O(5A)-C(23A)-C(19A)	115.5(10)
O(5A)-C(24A)-H(24C)	110.8
O(5A)-C(24A)-H(24D)	110.8
O(5A)-C(24A)-C(25A)	104.9(17)
H(24C)-C(24A)-H(24D)	108.8
C(25A)-C(24A)-H(24C)	110.8
C(25A)-C(24A)-H(24D)	110.8
C(24A)-C(25A)-H(25D)	109.5
C(24A)-C(25A)-H(25E)	109.5
C(24A)-C(25A)-H(25F)	109.5
H(25D)-C(25A)-H(25E)	109.5
H(25D)-C(25A)-H(25F)	109.5
H(25E)-C(25A)-H(25F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 231026lty_wxr_2_83. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	53(1)	57(1)	86(1)	9(1)	14(1)	-11(1)
C(1)	46(3)	30(3)	39(3)	2(2)	18(3)	5(3)
N(1)	53(3)	32(3)	43(2)	4(3)	22(2)	6(3)
O(1)	69(4)	133(7)	79(4)	-1(5)	43(3)	-8(5)
C(2)	63(4)	40(4)	48(3)	-1(3)	24(3)	10(3)
N(2)	50(3)	46(4)	43(3)	12(3)	16(2)	0(3)
O(2)	165(8)	74(5)	75(4)	-34(4)	45(5)	-15(5)
C(3)	55(5)	60(5)	54(4)	-4(4)	12(4)	17(4)
O(3)	104(5)	132(7)	78(4)	-18(5)	13(4)	-40(6)
C(4)	75(5)	70(6)	47(4)	13(4)	23(4)	14(5)
O(4)	254(13)	137(9)	91(5)	42(6)	-13(7)	-120(10)
C(5)	69(5)	53(5)	48(4)	10(3)	32(3)	10(4)
O(5)	188(8)	59(5)	96(5)	23(4)	-10(5)	-23(5)
C(6)	50(4)	41(4)	45(3)	3(3)	26(3)	10(3)
C(7)	42(3)	40(4)	44(3)	1(3)	19(3)	5(3)
C(8)	61(5)	41(5)	80(5)	6(4)	43(4)	0(3)
C(9)	42(4)	72(6)	83(6)	-12(5)	24(4)	-9(4)
C(10)	60(5)	66(6)	68(5)	-3(5)	21(4)	1(4)
C(11)	64(4)	49(4)	51(4)	4(3)	21(3)	6(4)
C(12)	44(3)	38(4)	48(3)	2(3)	21(3)	1(3)
C(13)	55(4)	26(3)	54(4)	0(3)	21(3)	2(3)
C(14)	57(4)	33(4)	44(3)	0(3)	17(3)	-4(3)
C(15)	43(3)	45(4)	41(3)	0(3)	15(3)	-5(3)
C(16)	44(3)	44(4)	47(3)	-10(3)	22(3)	-2(3)
C(17)	78(6)	36(4)	57(4)	-5(3)	31(4)	-3(4)
C(18)	106(8)	44(5)	87(6)	-13(5)	57(6)	6(5)
C(19)	78(5)	51(4)	46(3)	1(3)	32(3)	-19(4)
C(20)	92(5)	83(7)	52(4)	-5(4)	29(4)	-40(5)
C(21)	122(8)	156(11)	92(7)	-5(8)	5(6)	-58(8)
C(22)	112(10)	147(14)	104(8)	-25(9)	18(7)	-65(10)
C(23)	139(7)	60(5)	57(4)	-4(4)	49(4)	-41(5)
C(24)	211(12)	65(7)	130(8)	29(7)	8(9)	-41(8)
C(25)	270(20)	121(13)	132(8)	54(10)	9(14)	-76(14)
Br(1A)	99(1)	138(2)	107(1)	-42(1)	16(1)	-22(1)

C(1A)	91(5)	37(4)	97(5)	2(4)	66(5)	-2(4)
N(1A)	71(4)	53(4)	42(3)	1(3)	29(3)	0(3)
O(1A)	93(5)	153(9)	114(6)	63(6)	75(5)	60(6)
C(2A)	91(6)	54(5)	125(7)	-15(5)	62(5)	0(5)
N(2A)	79(5)	57(5)	41(3)	6(3)	23(3)	-10(3)
O(2A)	267(13)	84(6)	107(6)	-10(5)	105(8)	-14(8)
C(3A)	87(6)	62(6)	175(9)	-12(6)	65(6)	10(5)
O(3A)	155(7)	105(7)	110(6)	-30(5)	-23(6)	3(6)
C(4A)	109(7)	65(6)	161(9)	20(6)	87(7)	4(6)
O(4A)	126(8)	109(8)	160(8)	81(7)	62(7)	30(6)
C(5A)	126(7)	60(6)	131(7)	36(5)	88(6)	26(5)
O(5A)	130(6)	64(5)	239(9)	36(6)	127(6)	15(4)
C(6A)	121(6)	40(4)	88(5)	19(4)	83(5)	23(4)
C(12A)	125(6)	58(5)	53(4)	-7(4)	13(5)	21(5)
C(7A)	124(7)	57(5)	54(4)	5(4)	42(4)	22(5)
C(8A)	143(8)	77(6)	59(4)	-1(4)	18(5)	49(6)
C(9A)	130(8)	75(7)	72(5)	-5(5)	9(6)	33(6)
C(10A)	125(7)	70(7)	90(6)	-8(5)	-11(6)	23(6)
C(11A)	125(6)	58(6)	82(5)	-22(4)	-42(6)	25(5)
C(13A)	68(4)	42(4)	56(4)	-6(4)	26(3)	-7(4)
C(14A)	67(5)	45(5)	59(4)	11(3)	24(4)	5(3)
C(15A)	57(4)	45(4)	50(4)	13(3)	25(3)	3(3)
C(16A)	72(5)	45(4)	46(3)	6(3)	29(3)	9(4)
C(17A)	119(8)	54(6)	66(5)	4(4)	48(5)	24(5)
C(18A)	104(8)	65(6)	85(6)	-6(5)	48(6)	3(6)
C(19A)	96(6)	66(5)	63(4)	19(4)	48(4)	23(5)
C(20A)	127(7)	99(7)	63(5)	13(5)	41(5)	17(6)
C(21A)	202(12)	93(9)	120(9)	-28(8)	-49(9)	-23(9)
C(22A)	152(13)	107(12)	138(12)	-38(10)	-16(10)	17(11)
C(23A)	113(7)	63(6)	85(5)	26(5)	67(5)	24(5)
C(24A)	143(9)	68(7)	269(13)	46(9)	116(10)	-4(7)
C(25A)	160(14)	77(10)	270(20)	49(13)	84(15)	-22(10)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 231026lty_wxr_2_83.

	x	y	z	U(eq)
H(1)	4844	4754	2924	134
H(3)	4964	1961	5981	68
H(4)	3929	56	6352	75
H(5)	2199	-510	5885	64
H(8)	210	-631	5117	67
H(9)	-1197	-341	4361	77
H(10)	-1109	1480	3617	77
H(11)	442	3028	3625	64
H(14)	2786	7496	3535	52
H(17A)	3471	1056	3904	82
H(17B)	3386	1376	3261	82
H(17C)	2365	957	3476	82
H(18A)	1529	6124	4663	110
H(18B)	1940	7875	4461	110
H(18C)	2704	6712	4906	110
H(21A)	290	4015	1724	152
H(21B)	1148	2651	1647	152
H(22A)	-399	1937	2056	183
H(22B)	499	2221	2602	183
H(22C)	640	820	2158	183
H(24A)	3086	9438	1880	168
H(24B)	4240	8722	1921	168
H(25A)	3401	9301	1046	273
H(25B)	2528	7937	1096	273
H(25C)	3696	7325	1132	273
H(1A)	5985	6063	2594	167
H(3A)	10427	9745	522	123
H(4A)	9729	10572	-376	123
H(5A)	8130	9878	-837	116
H(8A)	5995	8520	-1205	113
H(9A)	4355	7216	-1273	114
H(10A)	4017	5692	-513	121
H(11A)	5319	5472	316	119

H(14A)	7811	2424	1627	67
H(17D)	7018	8904	1269	113
H(17E)	7090	8510	1907	113
H(17F)	6031	8154	1459	113
H(18D)	7453	3419	154	121
H(18E)	8152	2079	563	121
H(18F)	8648	3835	420	121
H(21C)	9196	7194	3496	183
H(21D)	10120	5921	3453	183
H(22D)	10281	7442	2655	211
H(22E)	10586	8516	3216	211
H(22F)	9485	8812	2797	211
H(24C)	6746	0	2852	178
H(24D)	5510	256	2759	178
H(25D)	5630	1036	3638	246
H(25E)	6755	1866	3698	246
H(25F)	6637	-158	3738	246

Table S9. Torsion angles [°] for 231026lty_wxr_2_83.

Br(1)-C(2)-C(3)-C(4)	-177.8(6)
C(1)-C(2)-C(3)-C(4)	0.7(11)
C(1)-N(2)-C(12)-C(7)	0.9(8)
C(1)-N(2)-C(12)-C(11)	-177.3(7)
C(1)-C(6)-C(7)-C(8)	177.4(7)
C(1)-C(6)-C(7)-C(12)	-0.2(7)
N(1)-N(2)-C(12)-C(7)	177.8(6)
N(1)-N(2)-C(12)-C(11)	-0.4(12)
N(1)-C(13)-C(14)-C(15)	0.8(9)
O(1)-C(19)-C(20)-O(2)	-15.3(12)
O(1)-C(19)-C(20)-O(3)	164.8(8)
O(1)-C(19)-C(23)-O(4)	-54.9(15)
O(1)-C(19)-C(23)-O(5)	98.5(13)
C(2)-C(1)-N(2)-N(1)	1.3(12)
C(2)-C(1)-N(2)-C(12)	178.0(7)
C(2)-C(1)-C(6)-C(5)	-1.4(10)
C(2)-C(1)-C(6)-C(7)	-178.5(6)
C(2)-C(3)-C(4)-C(5)	-0.3(13)
N(2)-C(1)-C(2)-Br(1)	-0.3(11)
N(2)-C(1)-C(2)-C(3)	-178.8(7)
N(2)-C(1)-C(6)-C(5)	177.8(6)
N(2)-C(1)-C(6)-C(7)	0.8(7)
N(2)-N(1)-C(13)-C(14)	-173.3(6)
N(2)-N(1)-C(13)-C(18)	7.8(12)
N(2)-N(1)-C(16)-C(15)	172.7(6)
N(2)-N(1)-C(16)-C(17)	-7.9(11)
C(3)-C(4)-C(5)-C(6)	-1.0(12)
C(4)-C(5)-C(6)-C(1)	1.9(11)
C(4)-C(5)-C(6)-C(7)	177.9(8)
C(5)-C(6)-C(7)-C(8)	0.9(13)
C(5)-C(6)-C(7)-C(12)	-176.7(7)
C(6)-C(1)-C(2)-Br(1)	178.6(5)
C(6)-C(1)-C(2)-C(3)	0.1(10)
C(6)-C(1)-N(2)-N(1)	-177.8(6)
C(6)-C(1)-N(2)-C(12)	-1.0(7)
C(6)-C(7)-C(8)-C(9)	-177.9(8)
C(6)-C(7)-C(12)-N(2)	-0.4(8)

C(6)-C(7)-C(12)-C(11)	177.9(7)
C(7)-C(8)-C(9)-C(10)	0.3(13)
C(8)-C(7)-C(12)-N(2)	-178.4(6)
C(8)-C(7)-C(12)-C(11)	-0.1(10)
C(8)-C(9)-C(10)-C(11)	0.4(14)
C(9)-C(10)-C(11)-C(12)	-1.0(13)
C(10)-C(11)-C(12)-N(2)	178.7(8)
C(10)-C(11)-C(12)-C(7)	0.8(11)
C(12)-C(7)-C(8)-C(9)	-0.5(11)
C(13)-N(1)-N(2)-C(1)	-91.1(9)
C(13)-N(1)-N(2)-C(12)	92.6(9)
C(13)-N(1)-C(16)-C(15)	-0.5(8)
C(13)-N(1)-C(16)-C(17)	178.8(7)
C(13)-C(14)-C(15)-C(16)	-1.2(9)
C(13)-C(14)-C(15)-C(19)	179.0(7)
C(14)-C(15)-C(16)-N(1)	1.0(8)
C(14)-C(15)-C(16)-C(17)	-178.2(9)
C(14)-C(15)-C(19)-O(1)	121.6(9)
C(14)-C(15)-C(19)-C(20)	-122.9(9)
C(14)-C(15)-C(19)-C(23)	3.4(13)
C(15)-C(19)-C(20)-O(2)	-131.5(10)
C(15)-C(19)-C(20)-O(3)	48.6(12)
C(15)-C(19)-C(23)-O(4)	63.2(17)
C(15)-C(19)-C(23)-O(5)	-143.3(11)
C(16)-N(1)-N(2)-C(1)	96.7(9)
C(16)-N(1)-N(2)-C(12)	-79.6(9)
C(16)-N(1)-C(13)-C(14)	-0.3(9)
C(16)-N(1)-C(13)-C(18)	-179.1(8)
C(16)-C(15)-C(19)-O(1)	-58.2(10)
C(16)-C(15)-C(19)-C(20)	57.3(11)
C(16)-C(15)-C(19)-C(23)	-176.4(9)
C(18)-C(13)-C(14)-C(15)	179.5(9)
C(19)-C(15)-C(16)-N(1)	-179.2(7)
C(19)-C(15)-C(16)-C(17)	1.6(14)
C(20)-O(3)-C(21)-C(22)	103.1(17)
C(20)-C(19)-C(23)-O(4)	-169.7(13)
C(20)-C(19)-C(23)-O(5)	-16.2(15)
C(21)-O(3)-C(20)-O(2)	2.0(18)
C(21)-O(3)-C(20)-C(19)	-178.1(11)

C(23)-O(5)-C(24)-C(25)	171(2)
C(23)-C(19)-C(20)-O(2)	100.1(13)
C(23)-C(19)-C(20)-O(3)	-79.8(10)
C(24)-O(5)-C(23)-O(4)	-16(3)
C(24)-O(5)-C(23)-C(19)	-169.6(14)
Br(1A)-C(2A)-C(3A)-C(4A)	-179.6(9)
C(1A)-C(2A)-C(3A)-C(4A)	-1.2(16)
C(1A)-N(2A)-C(12A)-C(7A)	-0.7(8)
C(1A)-N(2A)-C(12A)-C(11A)	179.8(6)
C(1A)-C(6A)-C(7A)-C(12A)	0.9(7)
C(1A)-C(6A)-C(7A)-C(8A)	-179.9(6)
N(1A)-N(2A)-C(12A)-C(7A)	-167.3(6)
N(1A)-N(2A)-C(12A)-C(11A)	13.3(10)
N(1A)-C(13A)-C(14A)-C(15A)	1.8(9)
O(1A)-C(19A)-C(20A)-O(2A)	2.9(14)
O(1A)-C(19A)-C(20A)-O(3A)	-177.1(10)
O(1A)-C(19A)-C(23A)-O(4A)	-180.0(13)
O(1A)-C(19A)-C(23A)-O(5A)	-9.7(16)
C(2A)-C(1A)-N(2A)-N(1A)	-16.1(16)
C(2A)-C(1A)-N(2A)-C(12A)	178.7(10)
C(2A)-C(1A)-C(6A)-C(5A)	-0.2(13)
C(2A)-C(1A)-C(6A)-C(7A)	-179.1(8)
C(2A)-C(3A)-C(4A)-C(5A)	1(2)
N(2A)-C(1A)-C(2A)-Br(1A)	1.9(16)
N(2A)-C(1A)-C(2A)-C(3A)	-176.4(9)
N(2A)-C(1A)-C(6A)-C(5A)	177.6(8)
N(2A)-C(1A)-C(6A)-C(7A)	-1.3(9)
N(2A)-N(1A)-C(13A)-C(14A)	-177.9(7)
N(2A)-N(1A)-C(13A)-C(18A)	1.1(13)
N(2A)-N(1A)-C(16A)-C(15A)	176.0(8)
N(2A)-N(1A)-C(16A)-C(17A)	-1.3(14)
N(2A)-C(12A)-C(7A)-C(6A)	-0.1(6)
N(2A)-C(12A)-C(7A)-C(8A)	-179.5(6)
N(2A)-C(12A)-C(11A)-C(10A)	179.4(8)
C(3A)-C(4A)-C(5A)-C(6A)	-1(2)
C(4A)-C(5A)-C(6A)-C(1A)	0.1(16)
C(4A)-C(5A)-C(6A)-C(7A)	178.7(10)
C(5A)-C(6A)-C(7A)-C(12A)	-177.8(10)
C(5A)-C(6A)-C(7A)-C(8A)	1.4(14)

C(6A)-C(1A)-C(2A)-Br(1A)	179.1(7)
C(6A)-C(1A)-C(2A)-C(3A)	0.7(14)
C(6A)-C(1A)-N(2A)-N(1A)	166.4(7)
C(6A)-C(1A)-N(2A)-C(12A)	1.3(9)
C(6A)-C(7A)-C(8A)-C(9A)	-179.2(8)
C(12A)-C(7A)-C(8A)-C(9A)	0.0
C(7A)-C(12A)-C(11A)-C(10A)	0.0
C(7A)-C(8A)-C(9A)-C(10A)	0.0
C(8A)-C(9A)-C(10A)-C(11A)	0.0
C(9A)-C(10A)-C(11A)-C(12A)	0.0
C(11A)-C(12A)-C(7A)-C(6A)	179.4(6)
C(11A)-C(12A)-C(7A)-C(8A)	0.0
C(13A)-N(1A)-N(2A)-C(1A)	-83.4(11)
C(13A)-N(1A)-N(2A)-C(12A)	80.8(10)
C(13A)-N(1A)-C(16A)-C(15A)	-2.0(10)
C(13A)-N(1A)-C(16A)-C(17A)	-179.3(9)
C(13A)-C(14A)-C(15A)-C(16A)	-3.2(10)
C(13A)-C(14A)-C(15A)-C(19A)	177.1(9)
C(14A)-C(15A)-C(16A)-N(1A)	3.1(10)
C(14A)-C(15A)-C(16A)-C(17A)	179.9(11)
C(14A)-C(15A)-C(19A)-O(1A)	-130.1(10)
C(14A)-C(15A)-C(19A)-C(20A)	112.6(11)
C(14A)-C(15A)-C(19A)-C(23A)	-7.9(15)
C(15A)-C(19A)-C(20A)-O(2A)	122.1(11)
C(15A)-C(19A)-C(20A)-O(3A)	-58.0(13)
C(15A)-C(19A)-C(23A)-O(4A)	58.4(17)
C(15A)-C(19A)-C(23A)-O(5A)	-131.4(12)
C(16A)-N(1A)-N(2A)-C(1A)	98.9(11)
C(16A)-N(1A)-N(2A)-C(12A)	-96.9(9)
C(16A)-N(1A)-C(13A)-C(14A)	0.1(9)
C(16A)-N(1A)-C(13A)-C(18A)	179.0(9)
C(16A)-C(15A)-C(19A)-O(1A)	50.1(14)
C(16A)-C(15A)-C(19A)-C(20A)	-67.1(12)
C(16A)-C(15A)-C(19A)-C(23A)	172.4(9)
C(18A)-C(13A)-C(14A)-C(15A)	-176.9(10)
C(19A)-C(15A)-C(16A)-N(1A)	-177.1(8)
C(19A)-C(15A)-C(16A)-C(17A)	-0.3(17)
C(20A)-O(3A)-C(21A)-C(22A)	-97(2)
C(20A)-C(19A)-C(23A)-O(4A)	-63.8(14)

C(20A)-C(19A)-C(23A)-O(5A)	106.5(14)
C(21A)-O(3A)-C(20A)-O(2A)	-2(2)
C(21A)-O(3A)-C(20A)-C(19A)	177.9(13)
C(23A)-O(5A)-C(24A)-C(25A)	111.8(18)
C(23A)-C(19A)-C(20A)-O(2A)	-115.9(12)
C(23A)-C(19A)-C(20A)-O(3A)	64.0(12)
C(24A)-O(5A)-C(23A)-O(4A)	-14(3)
C(24A)-O(5A)-C(23A)-C(19A)	175.2(17)

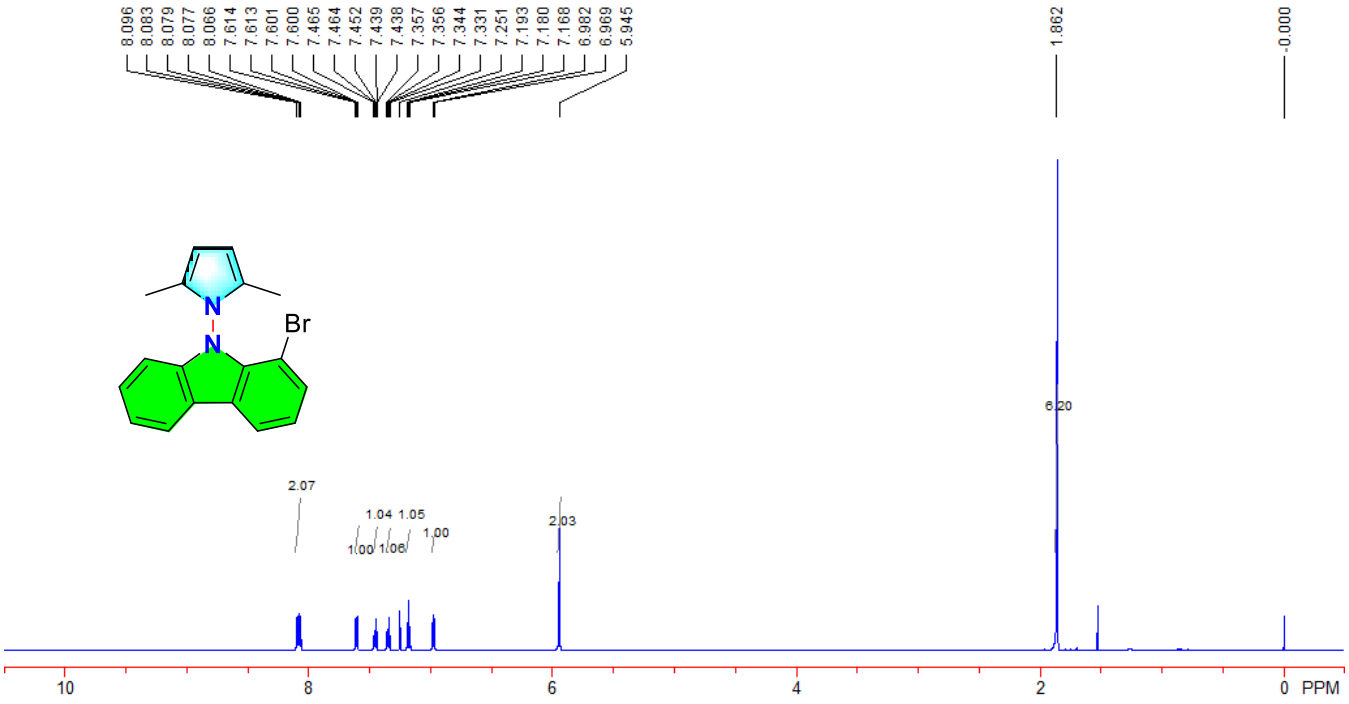
Symmetry transformations used to generate equivalent atoms:

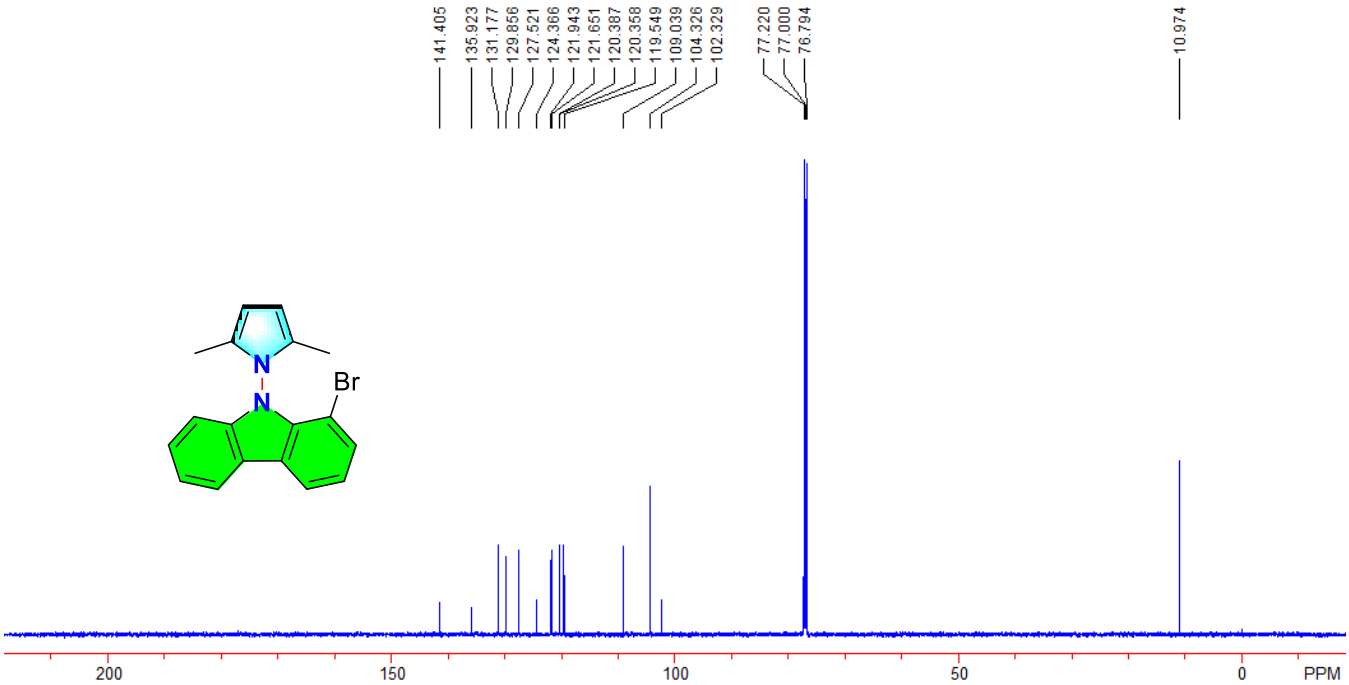
Table S10. Hydrogen bonds for 231026lty_wxr_2_83 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

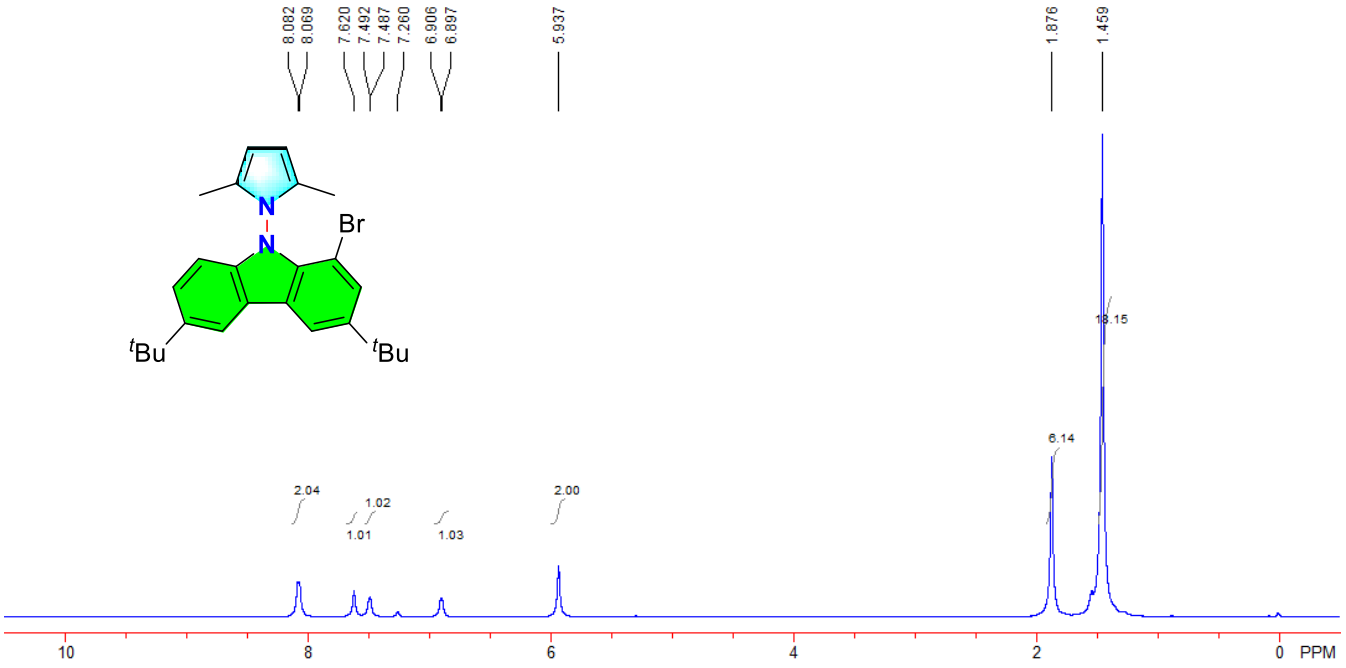
8. ^{1}H and ^{13}C NMR Spectra for New Compounds

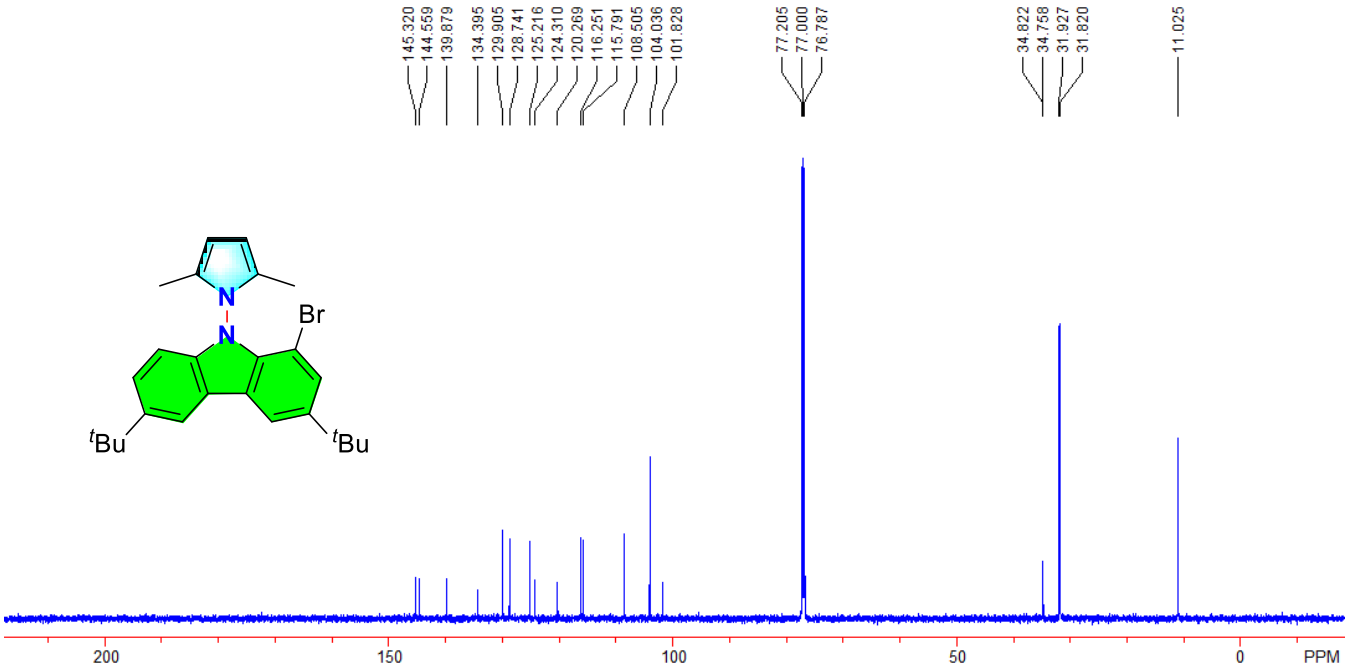
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1a**



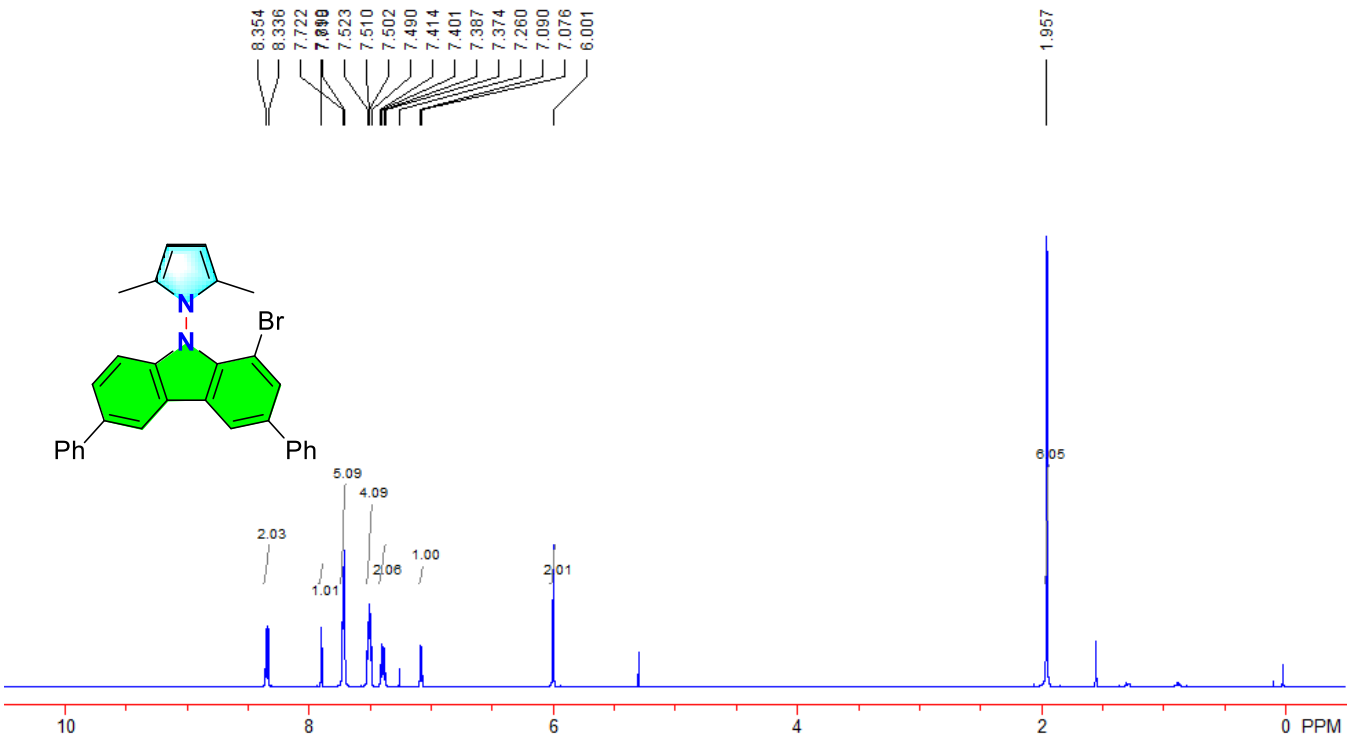


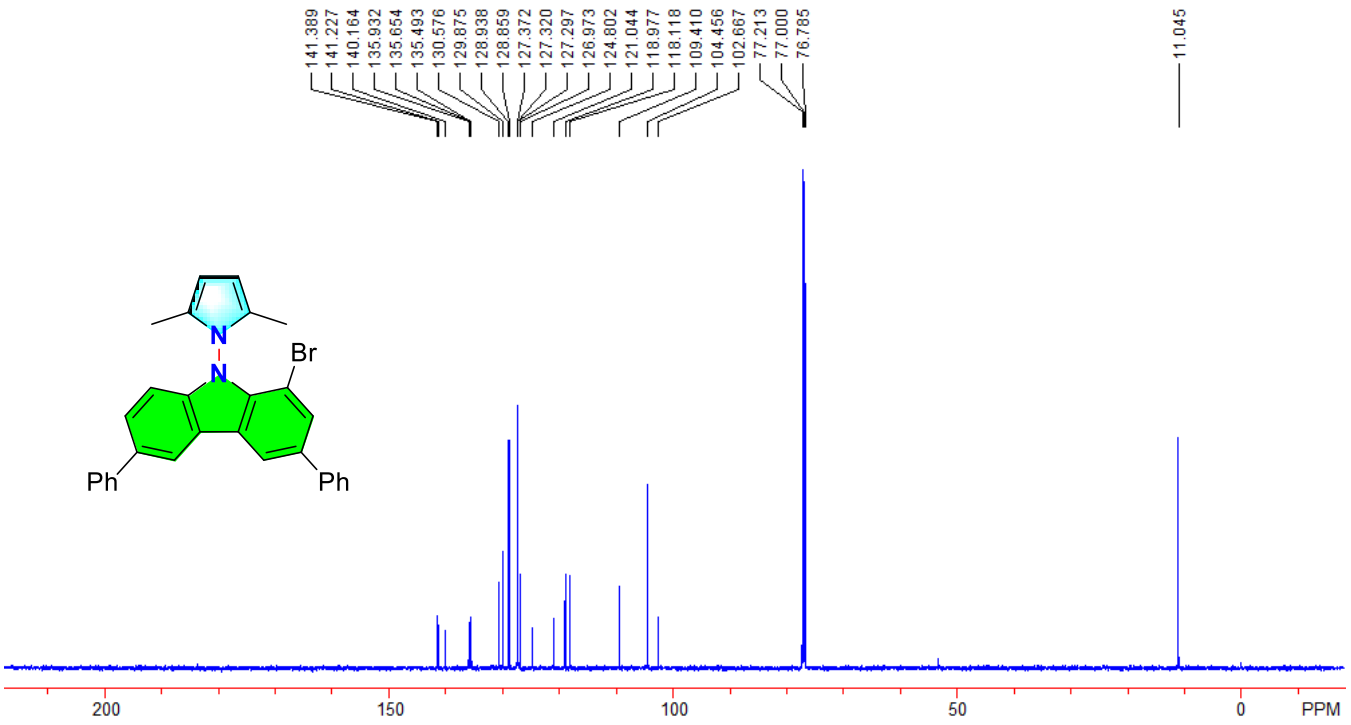
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1b**



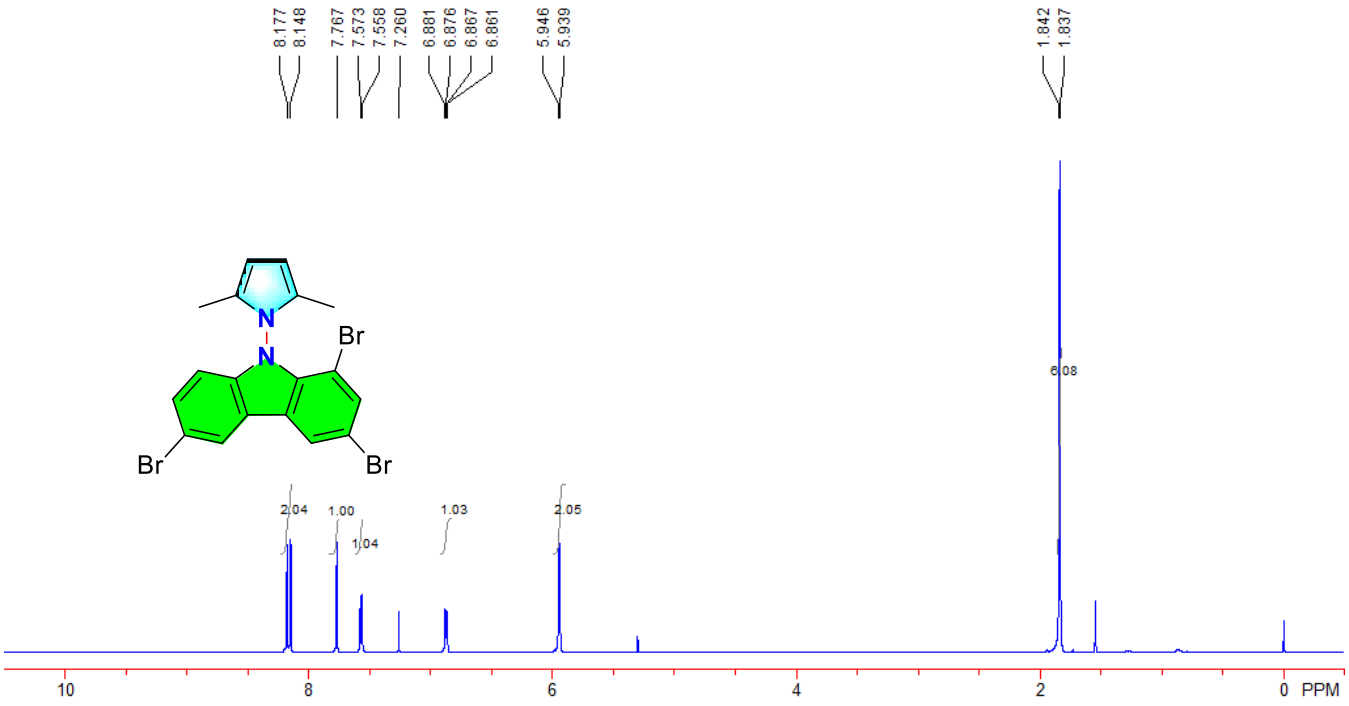


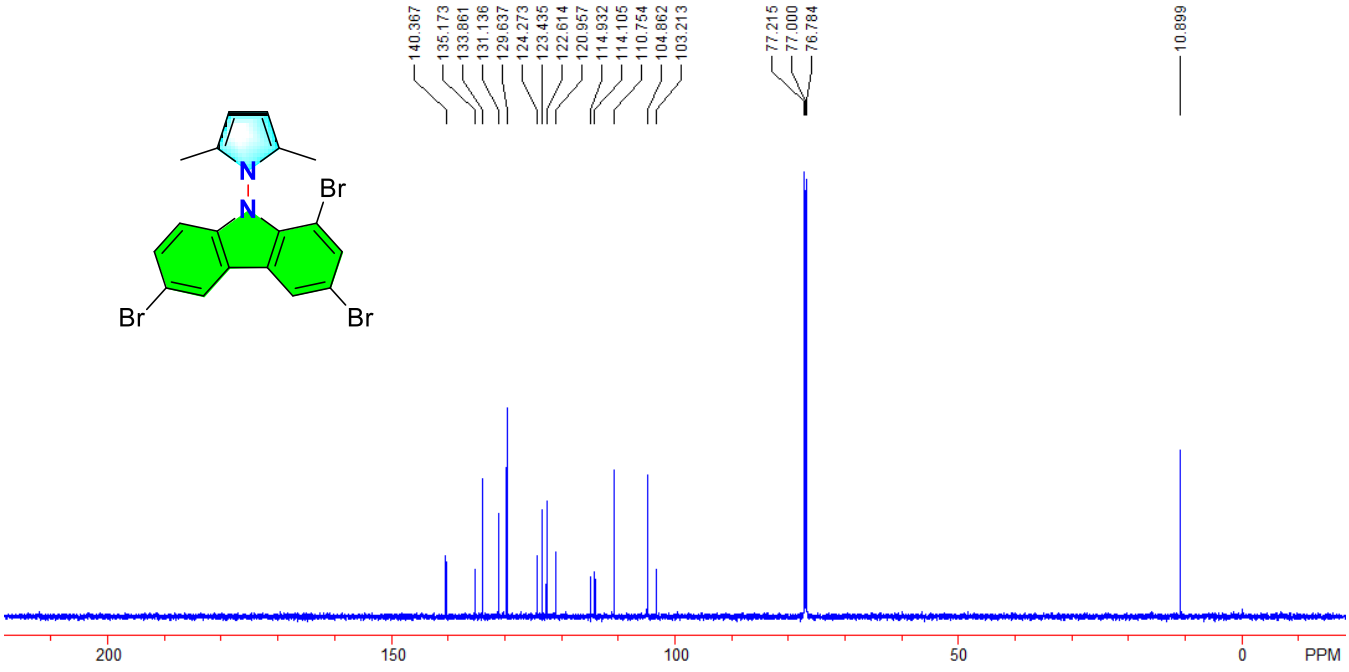
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1c**



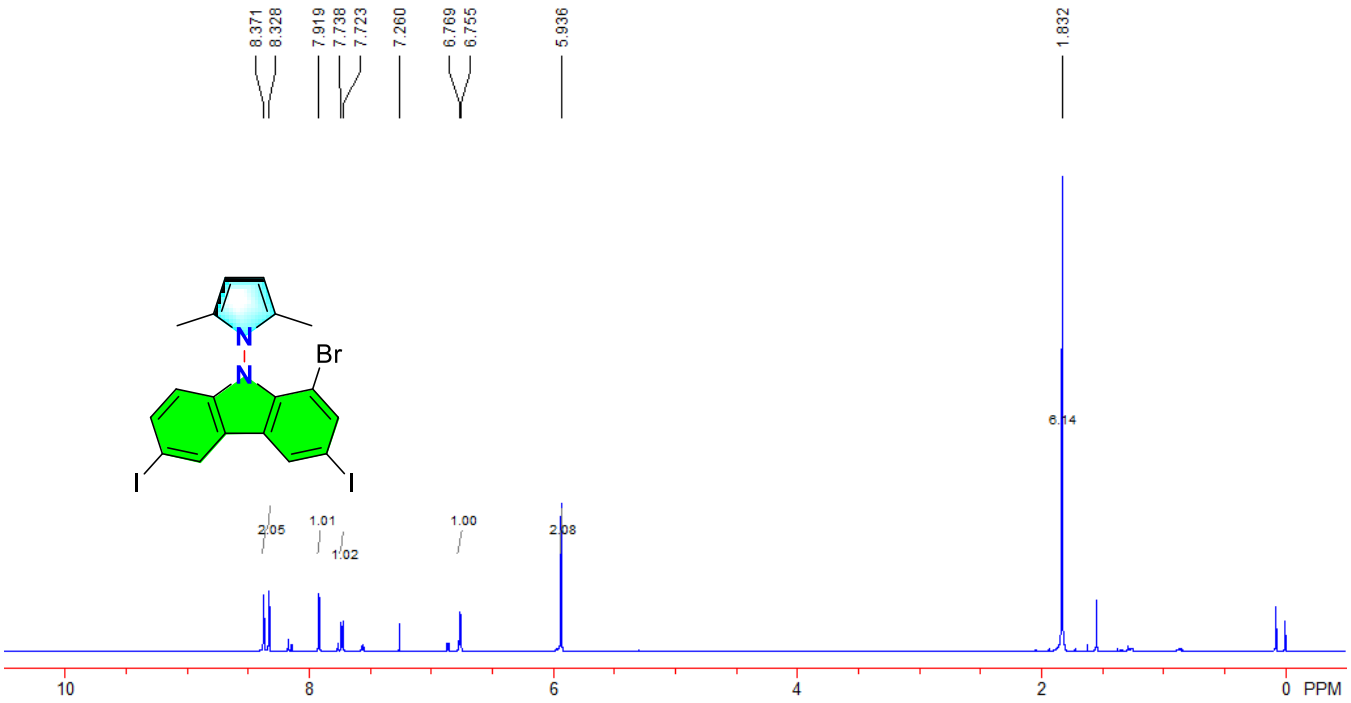


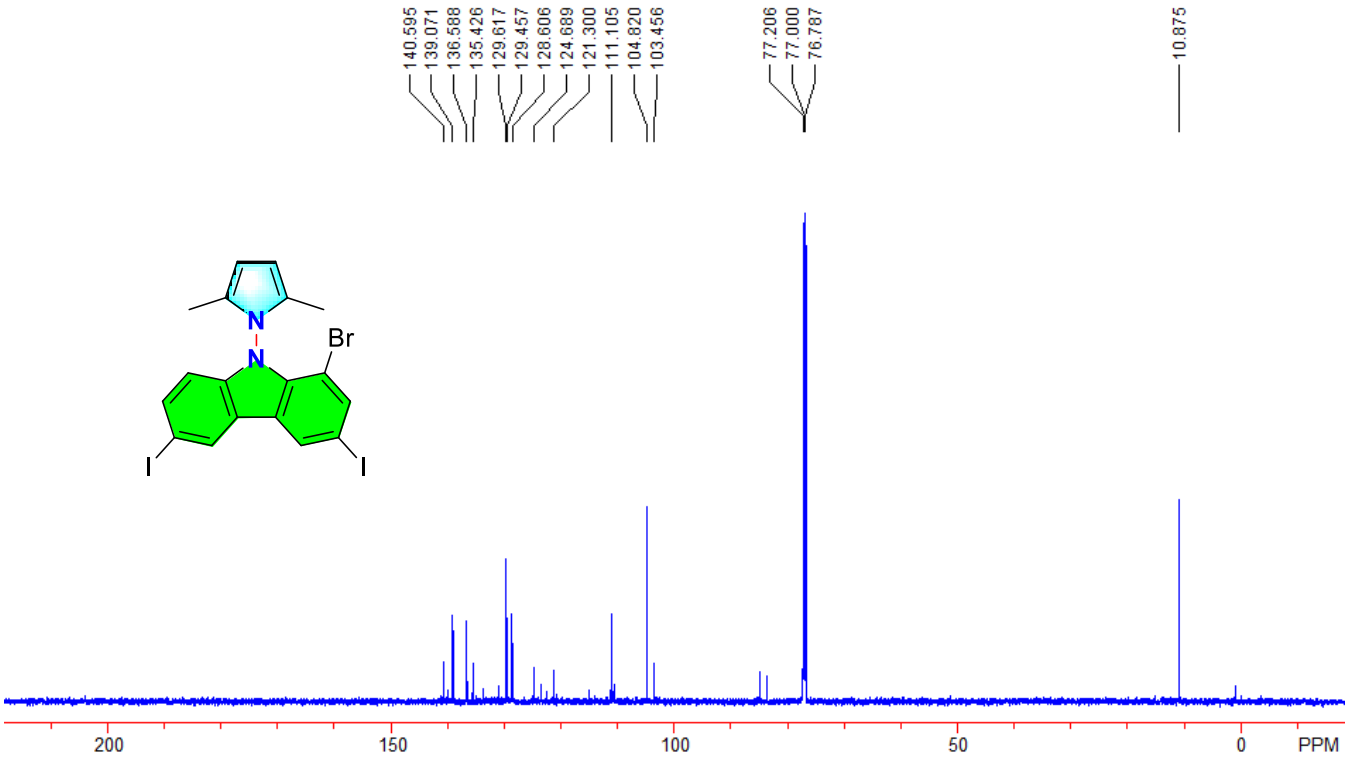
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1d**



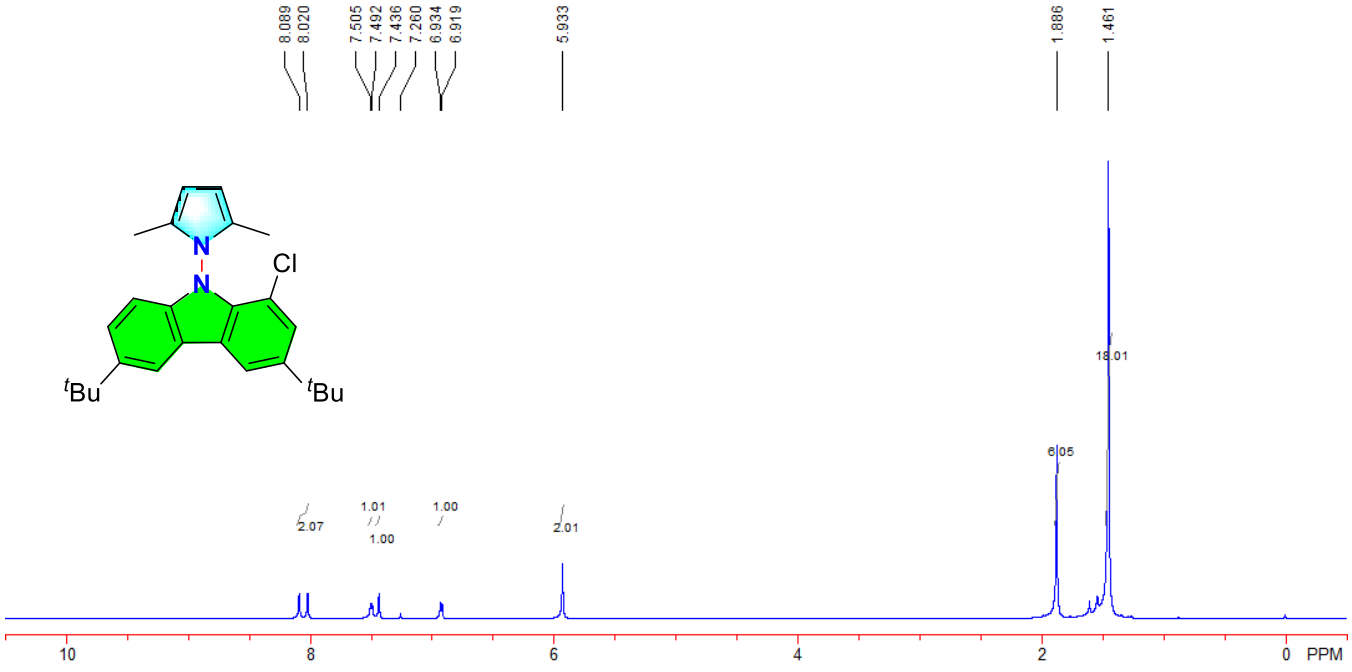


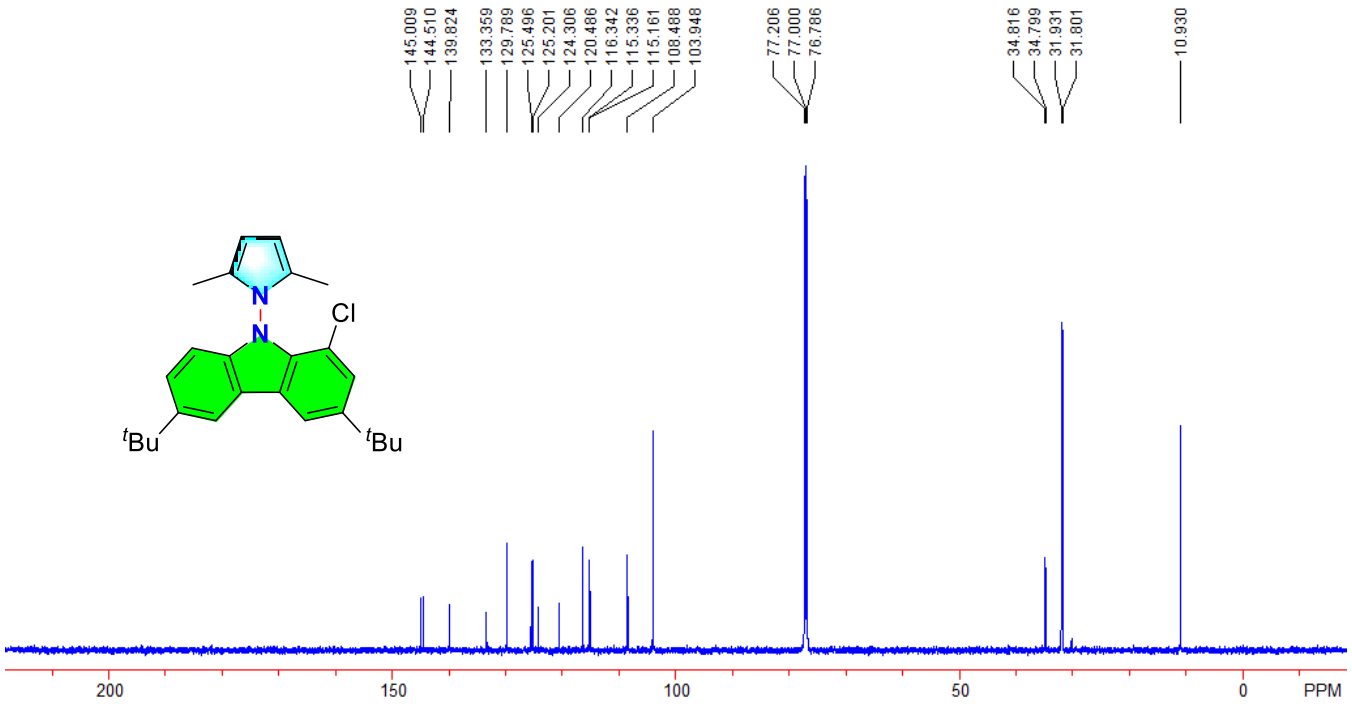
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1e**



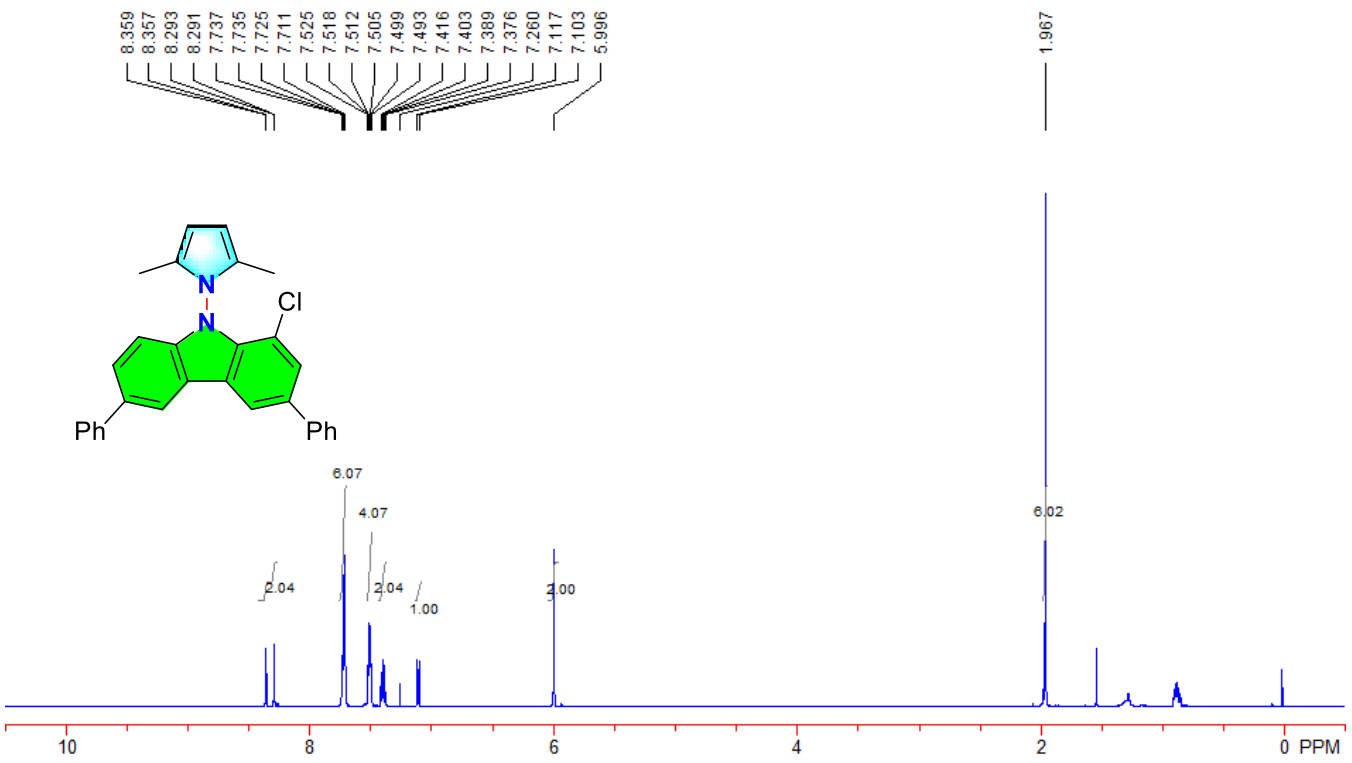


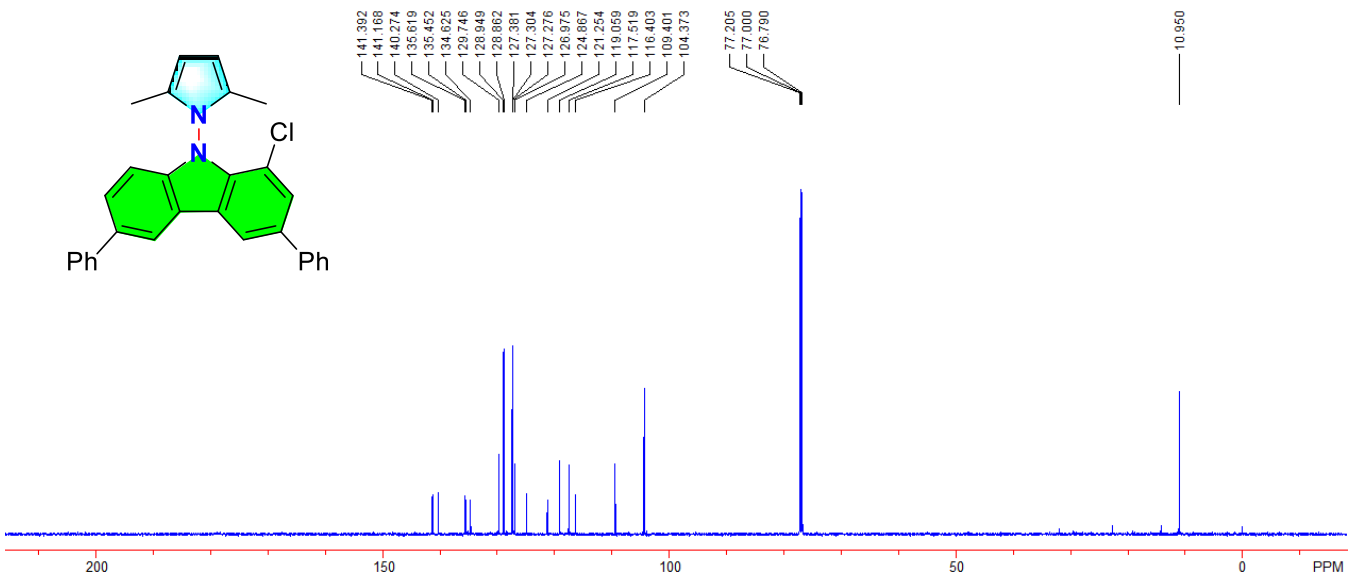
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1f**



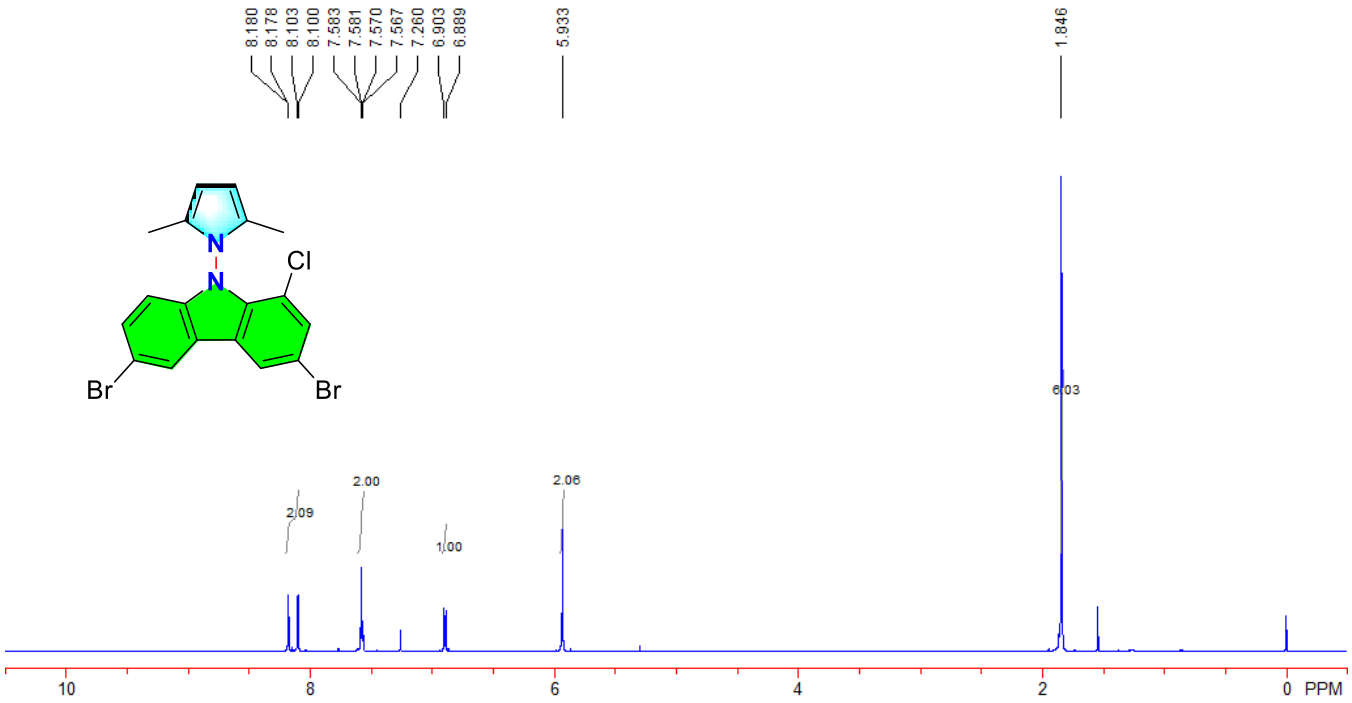


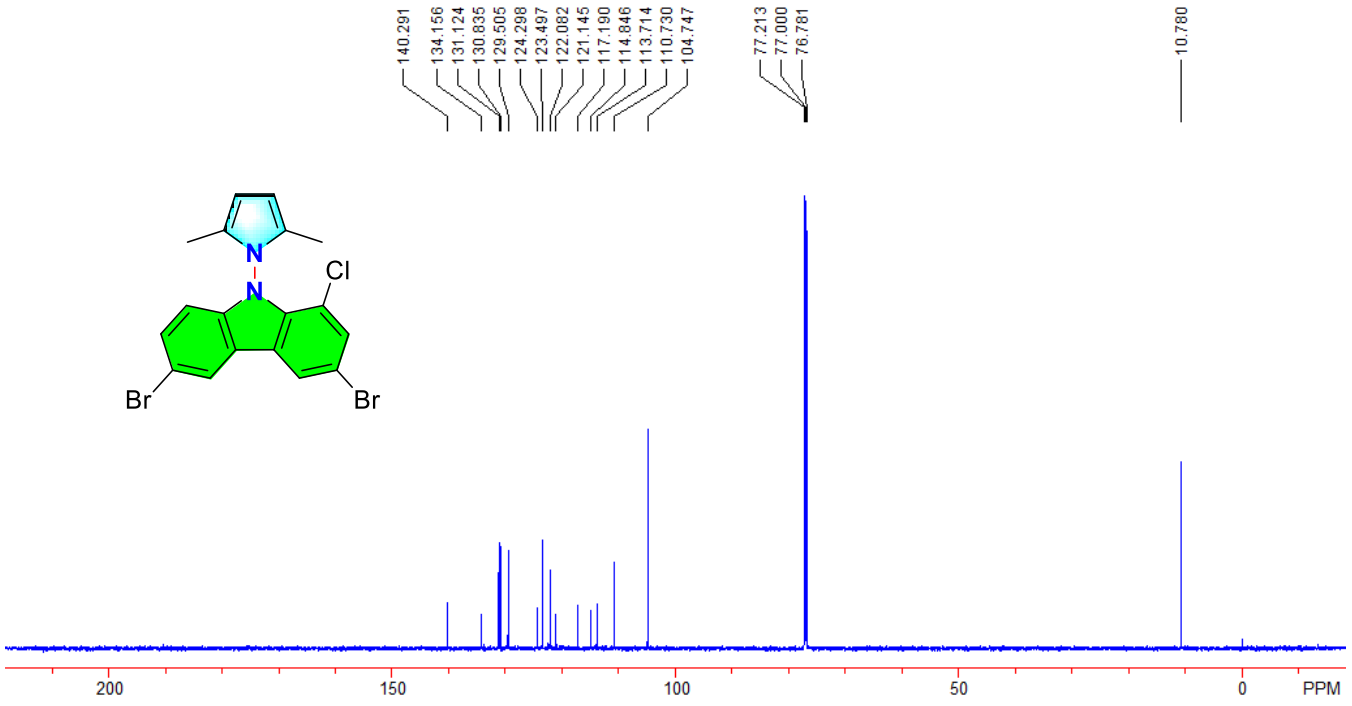
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1g**



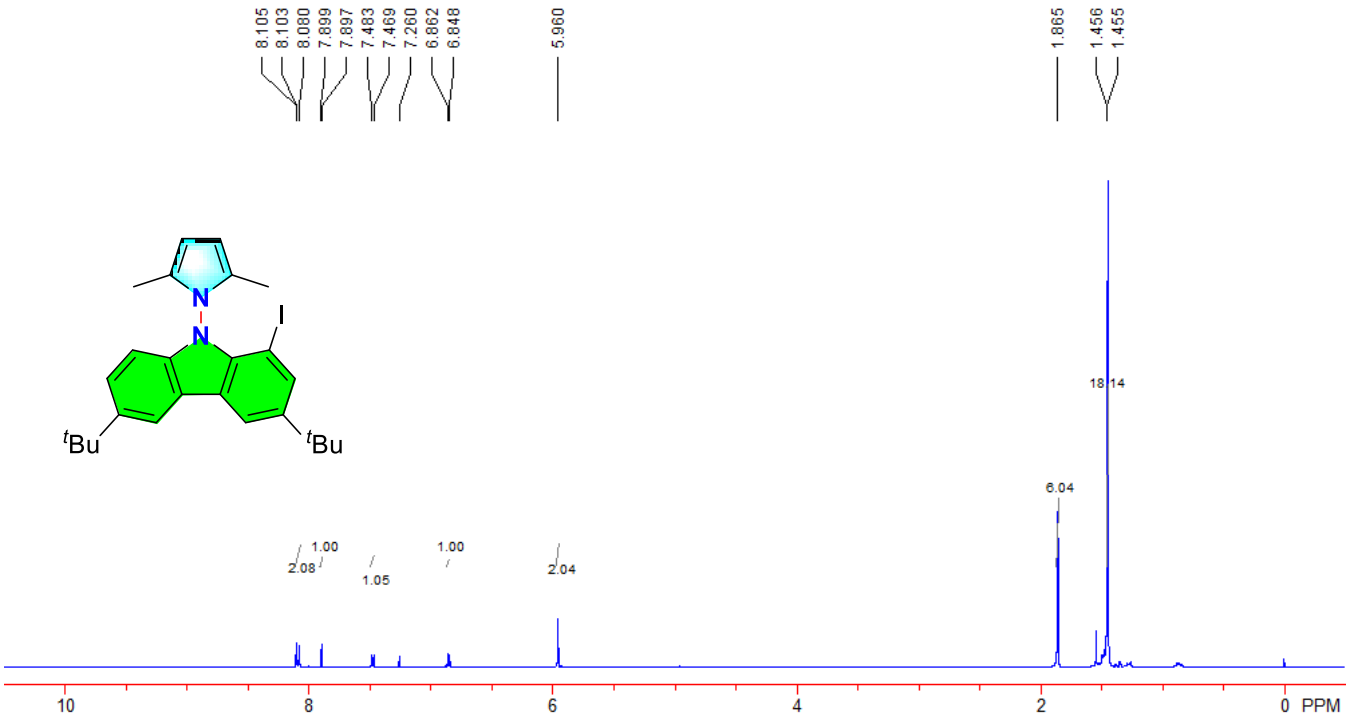


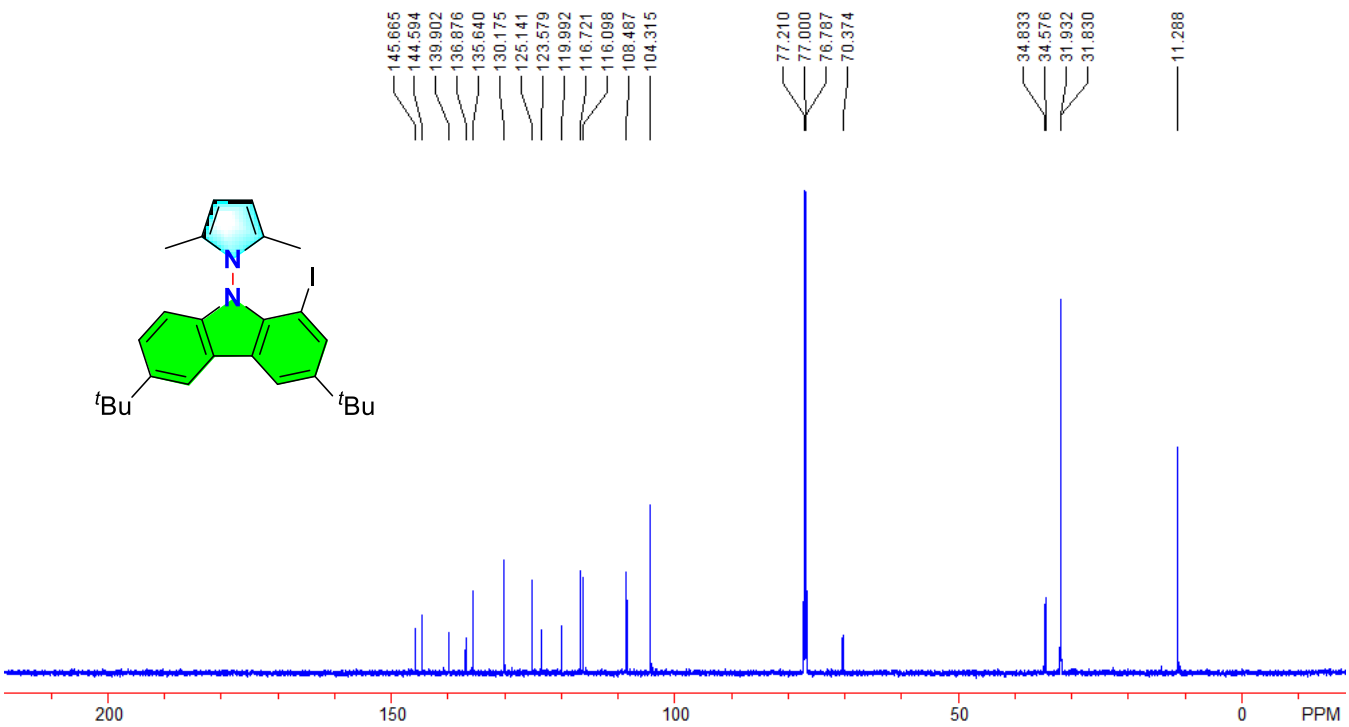
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1h**



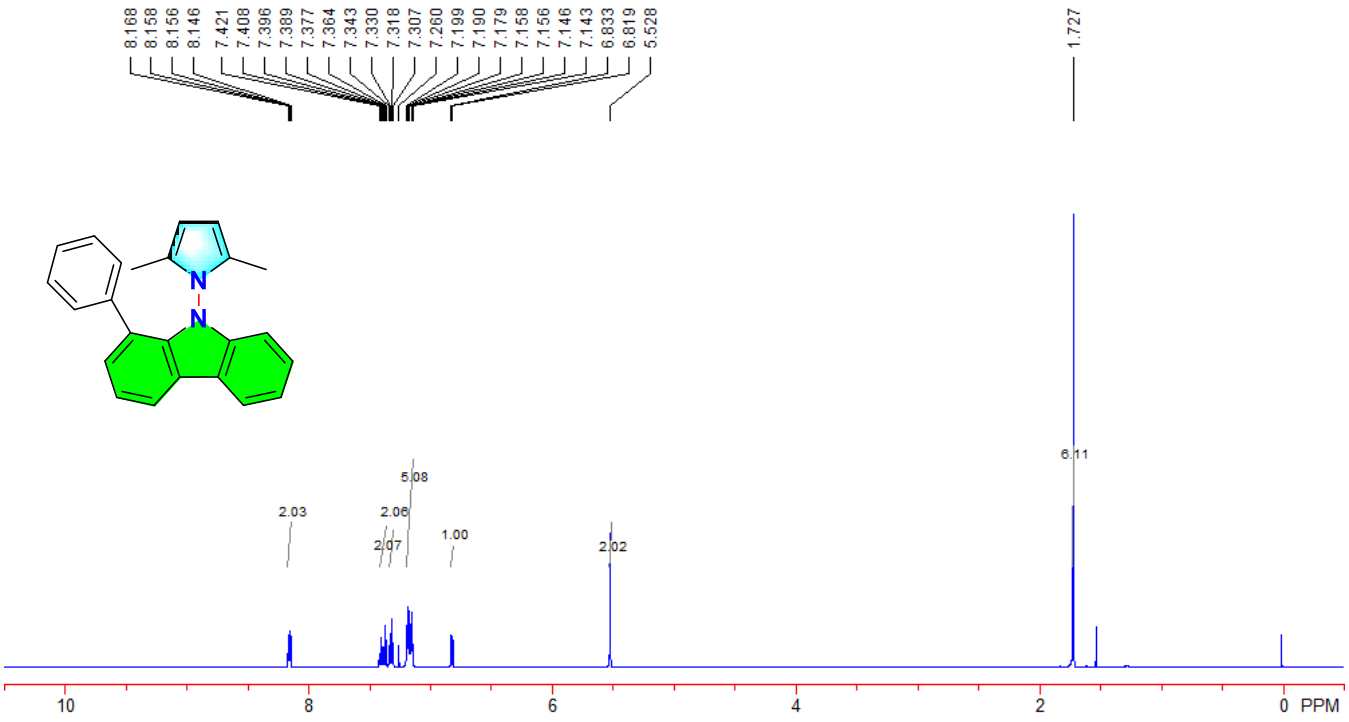


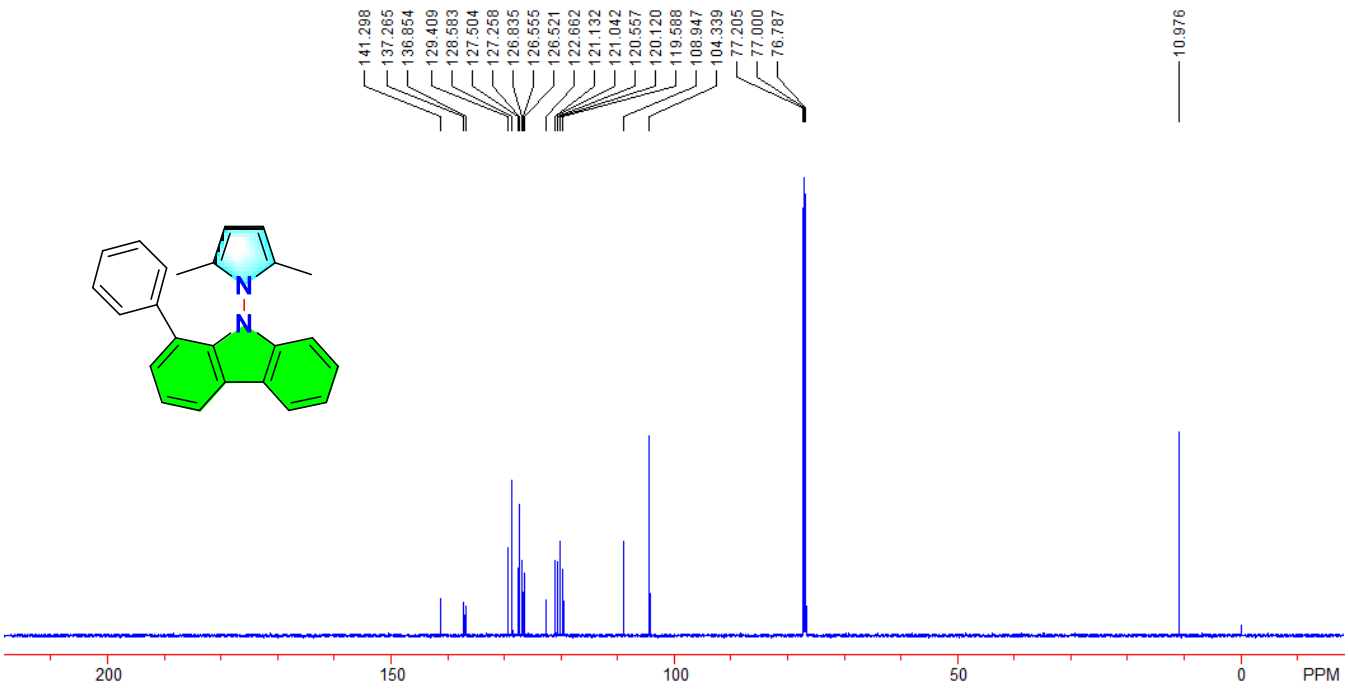
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1i**



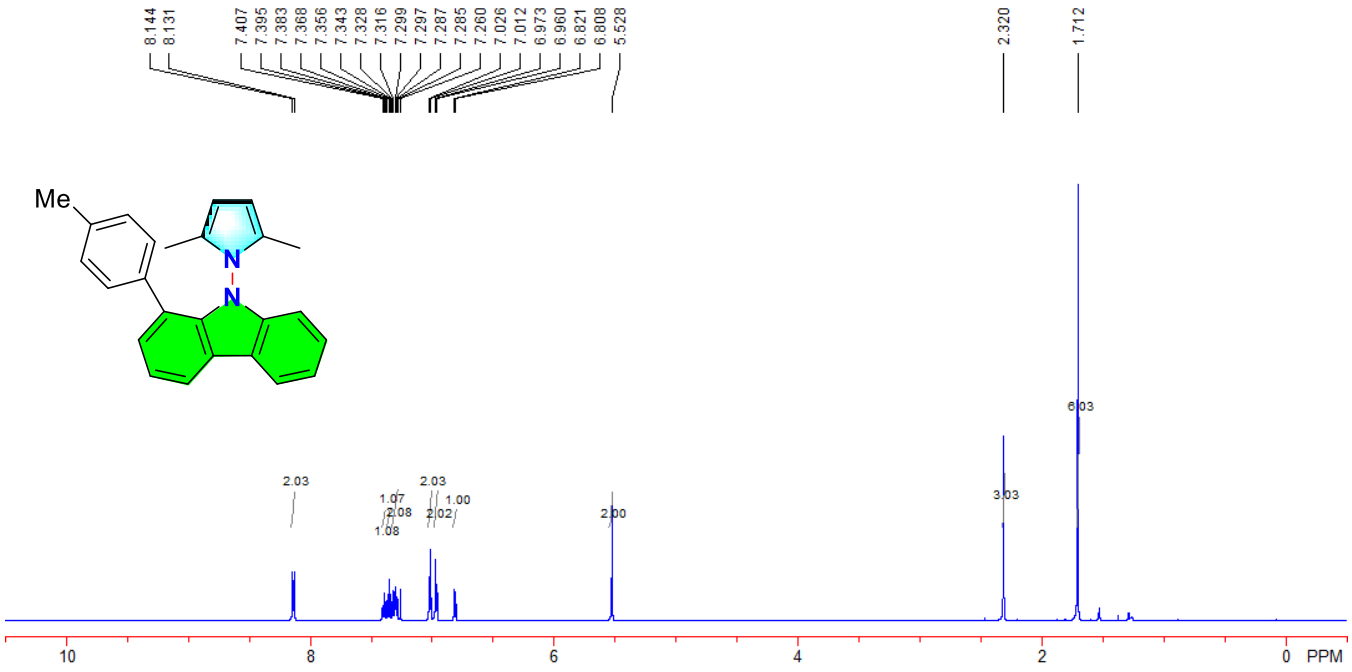


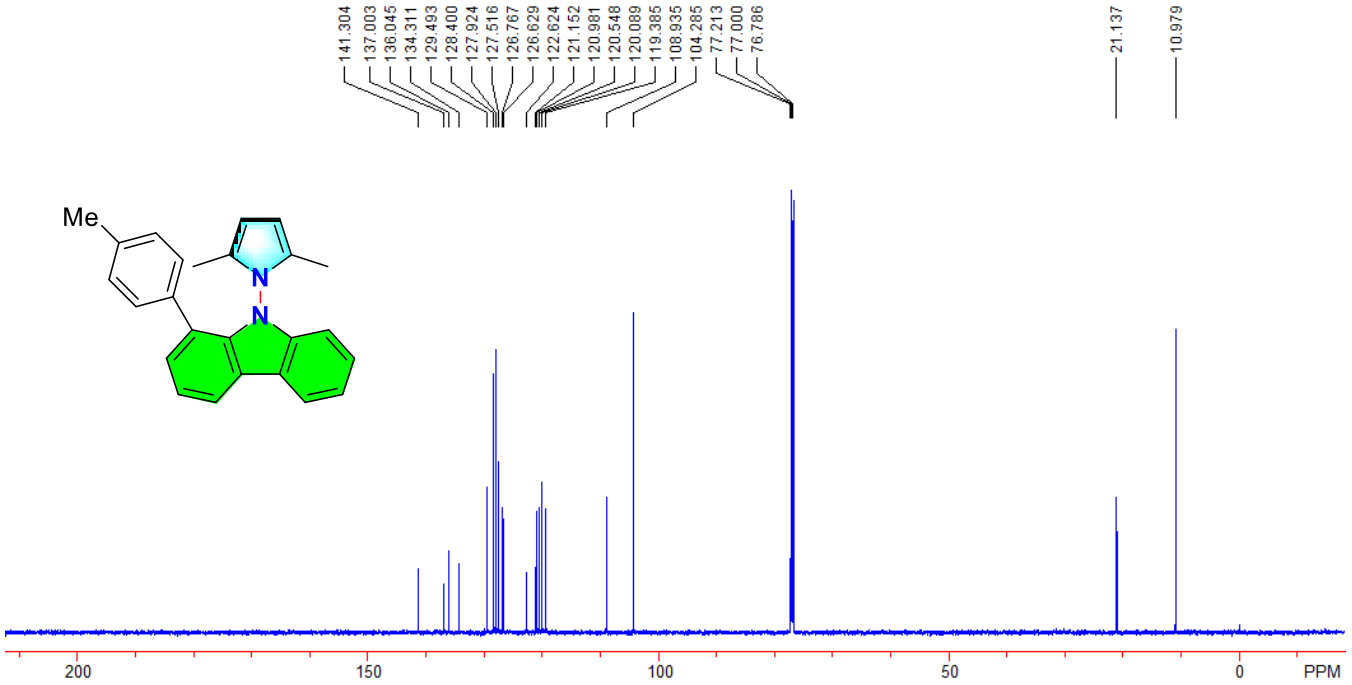
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1j**



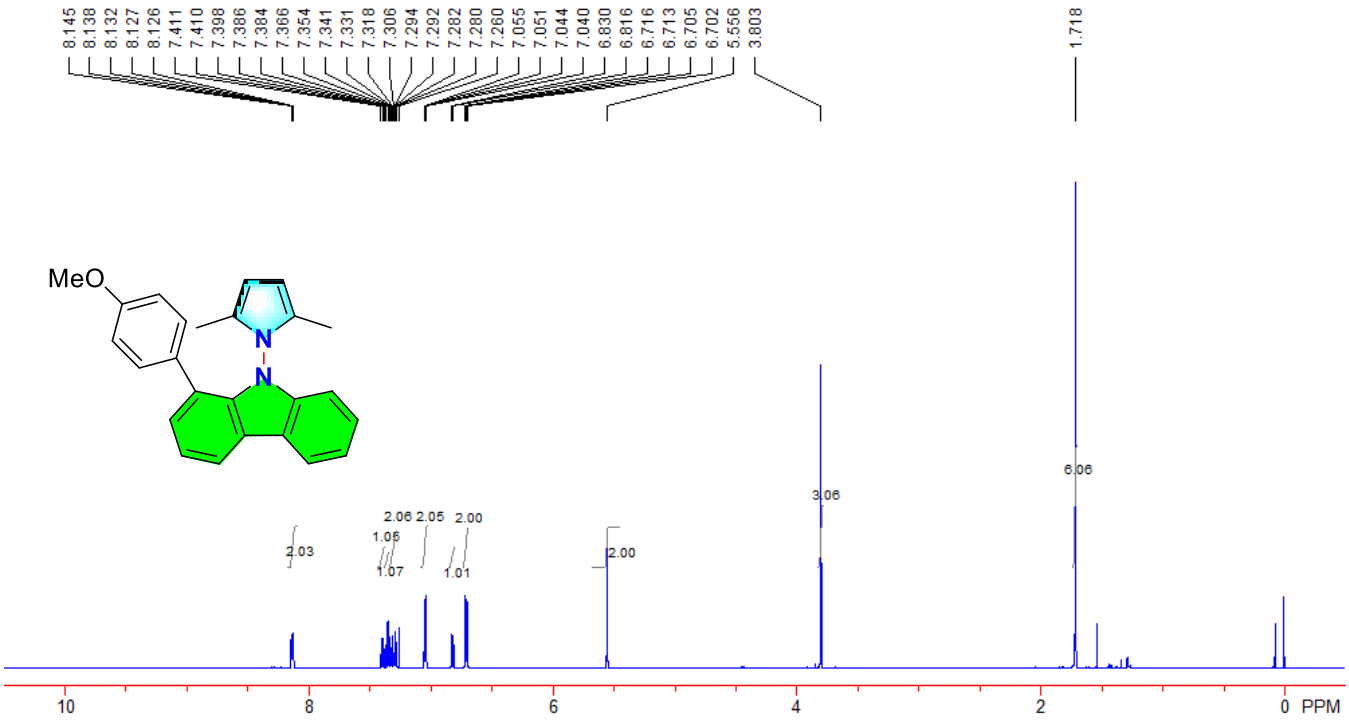


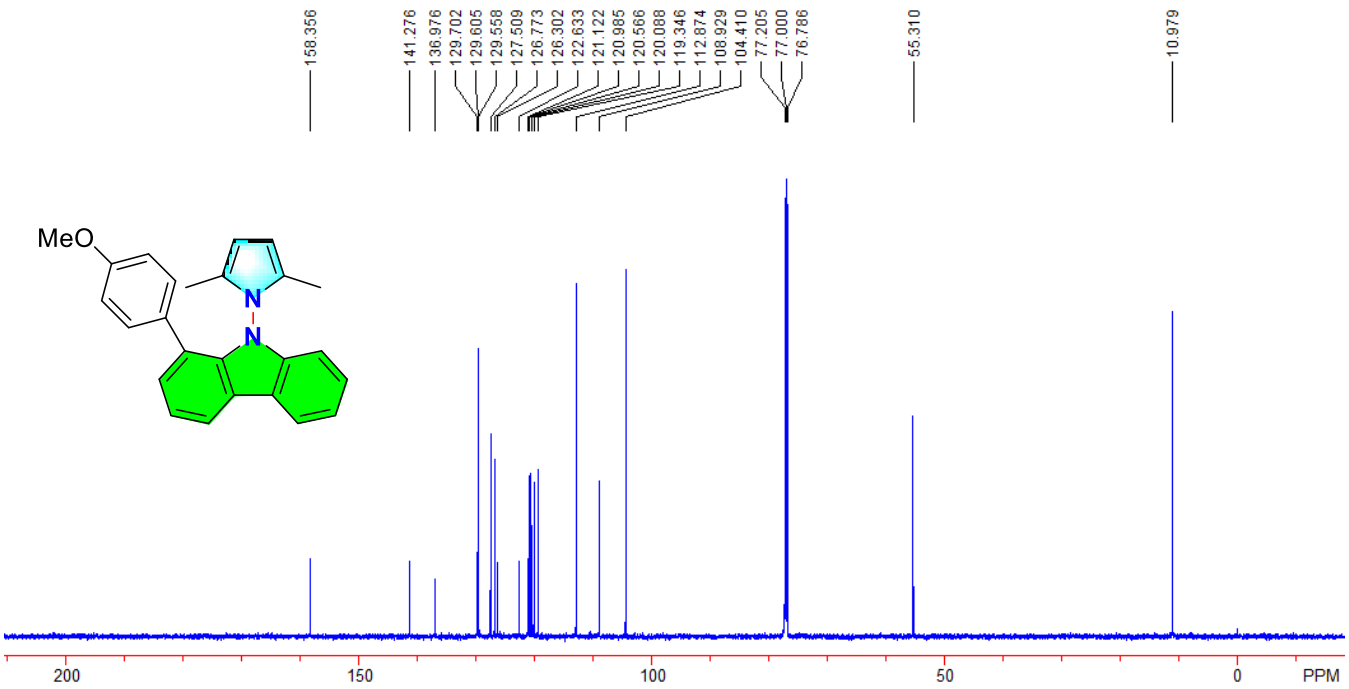
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1k**



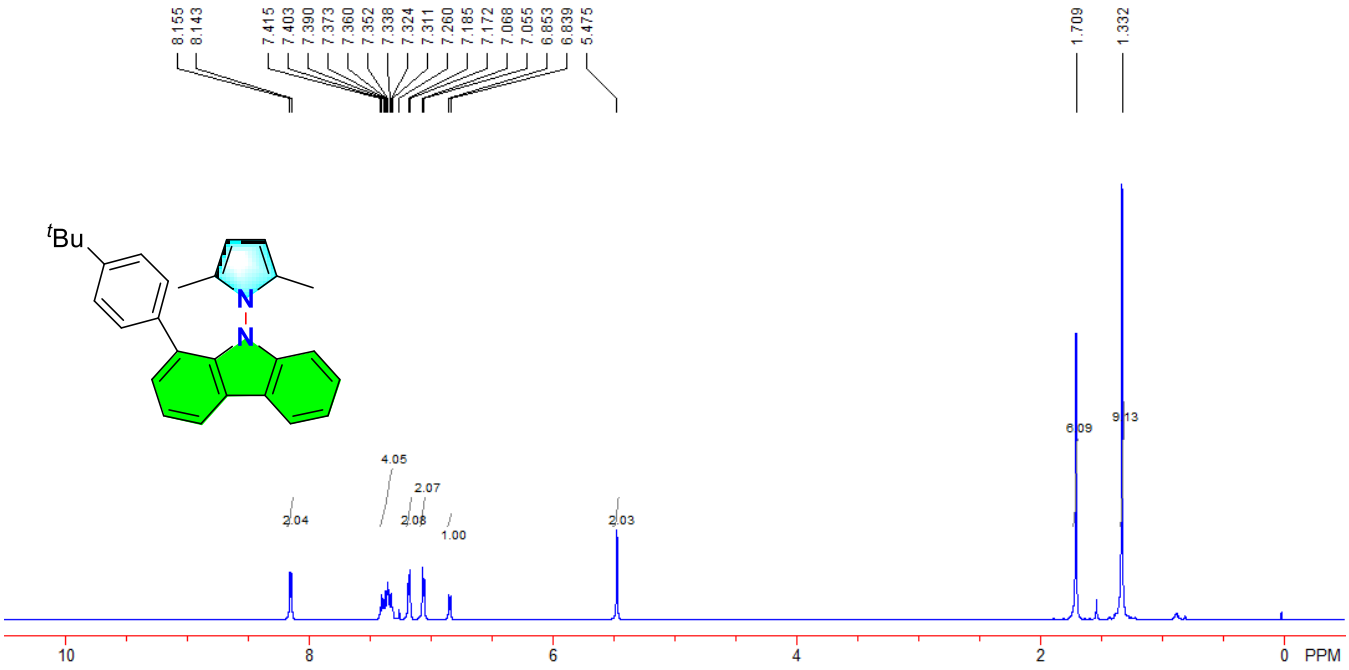


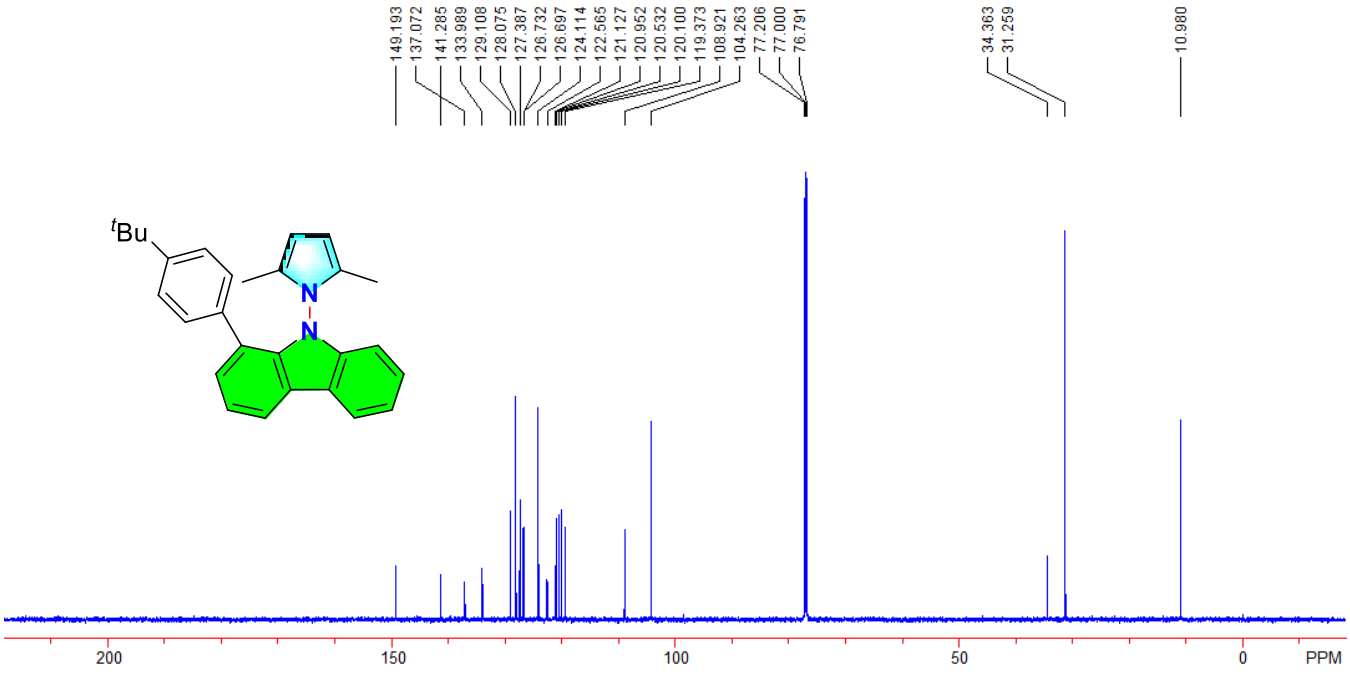
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1l**



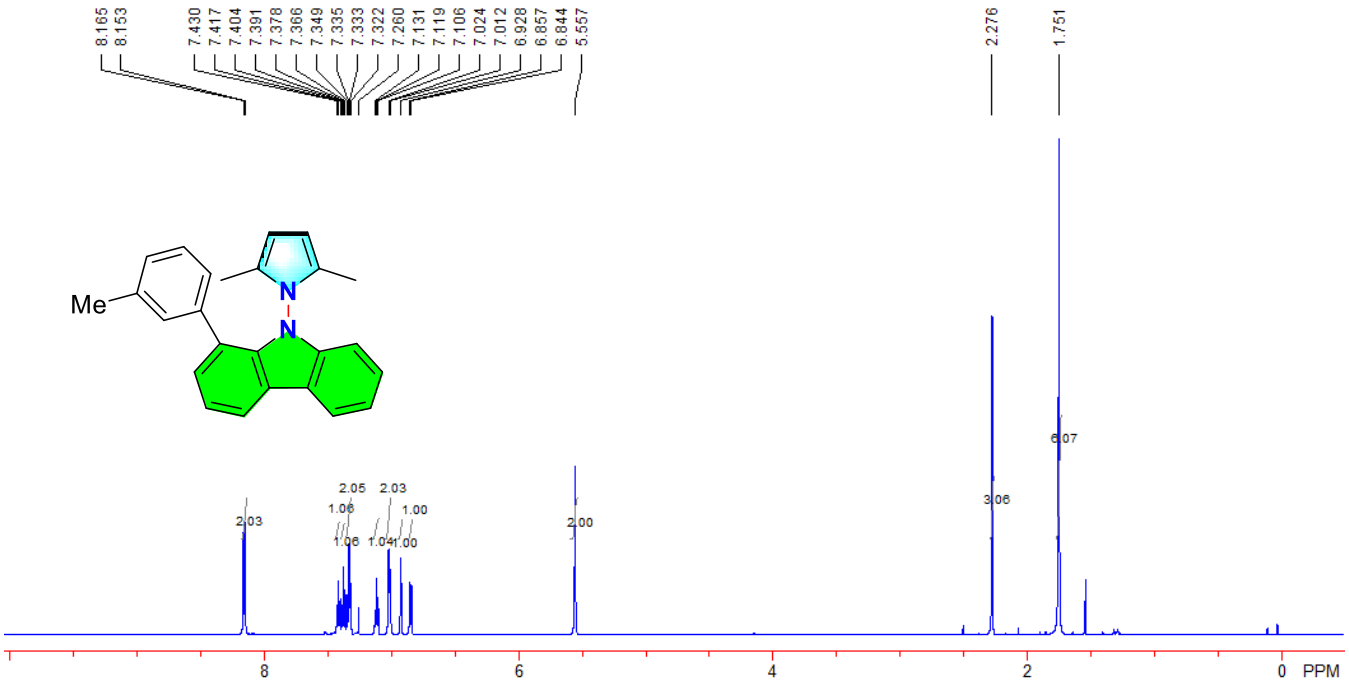


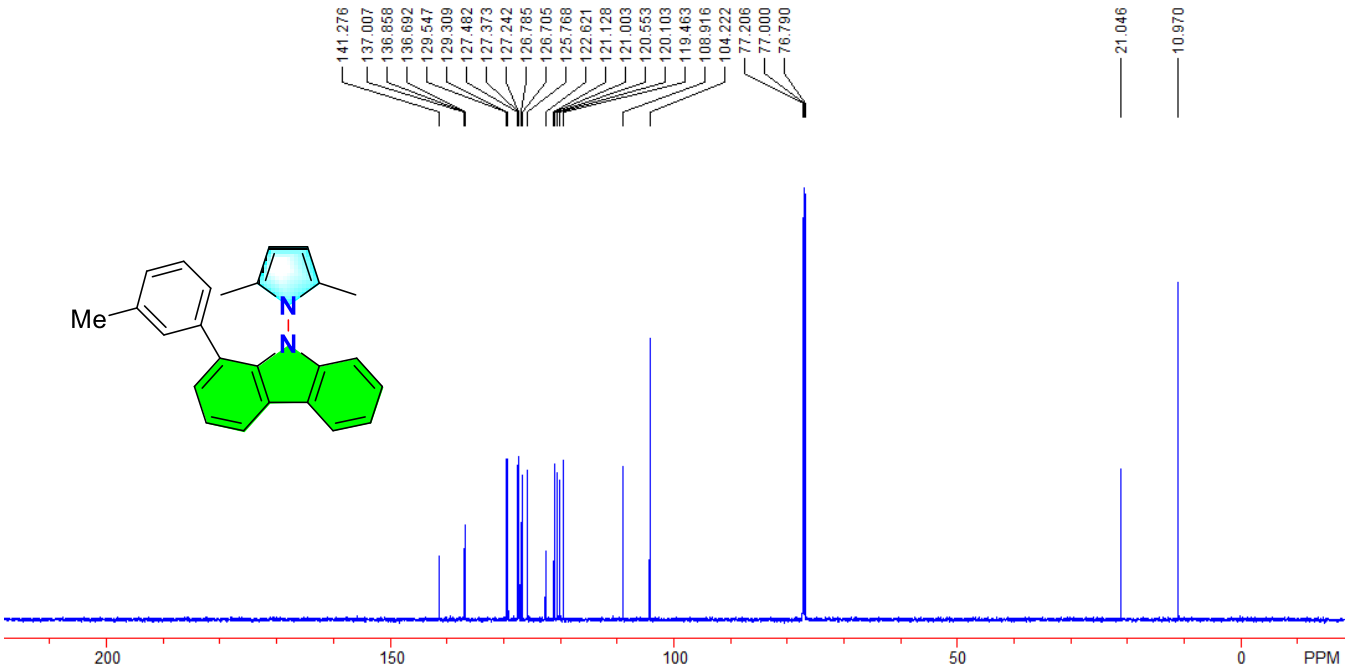
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1m**



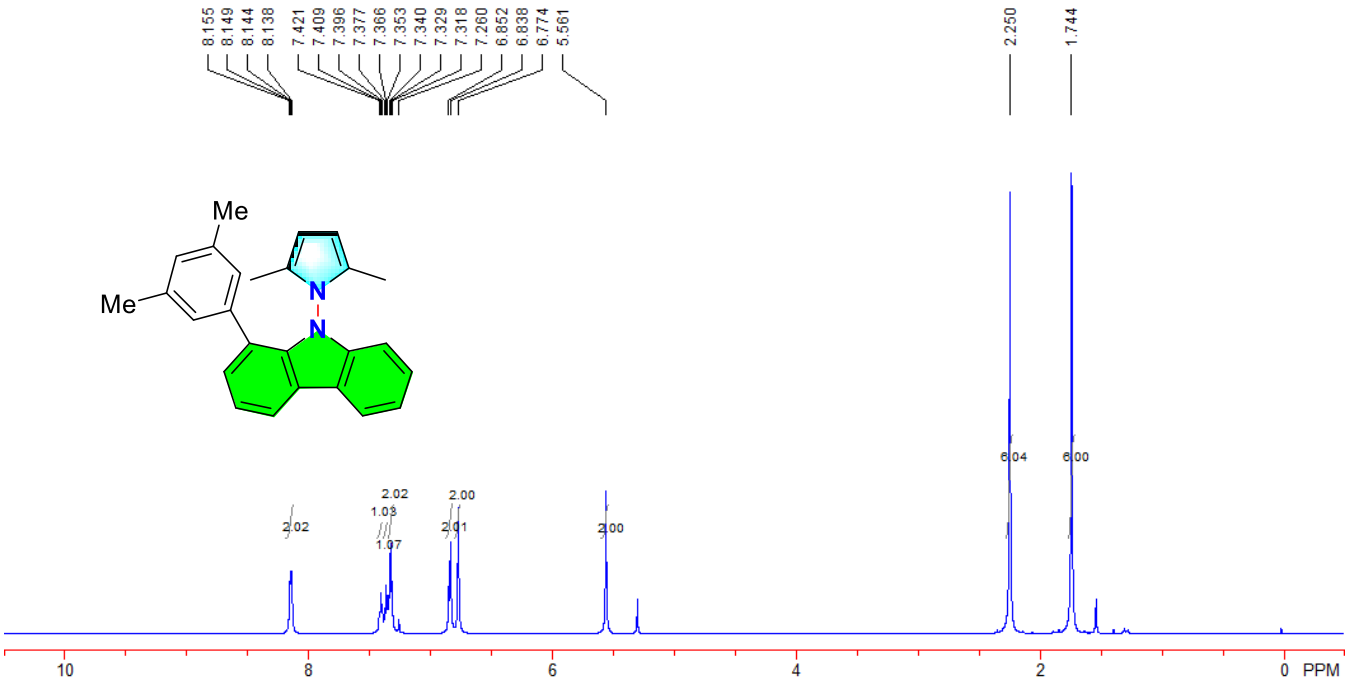


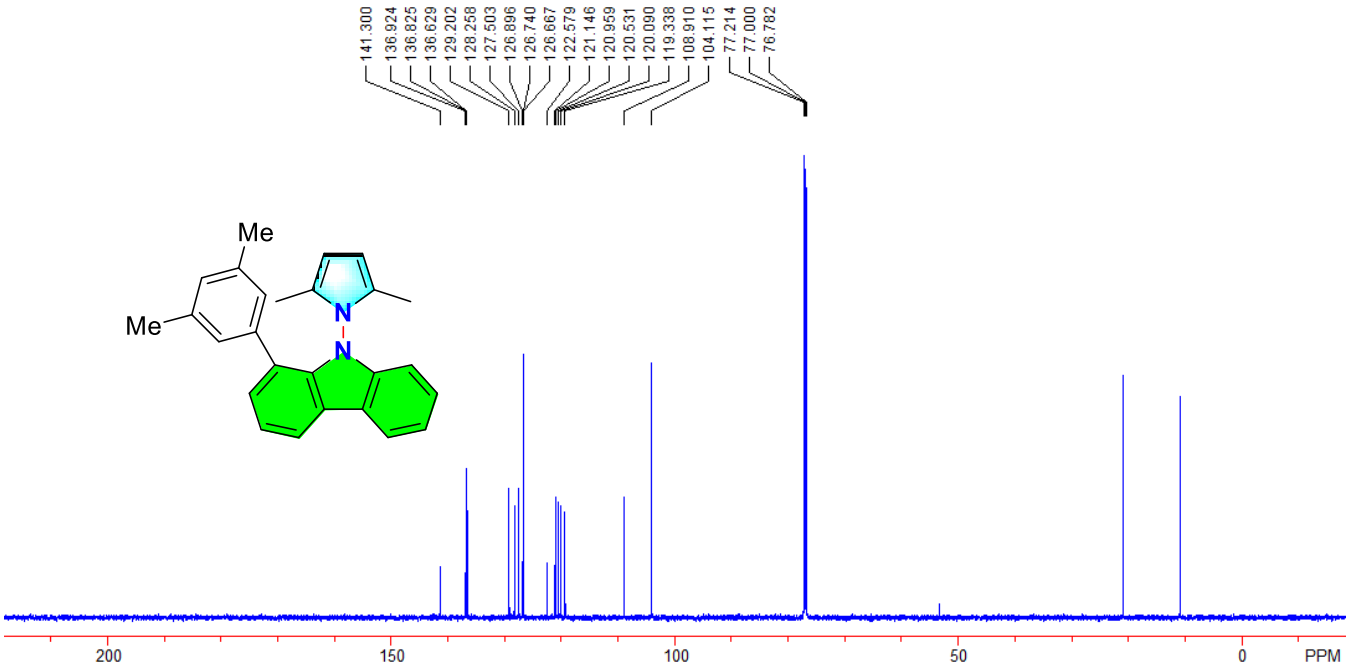
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1n**



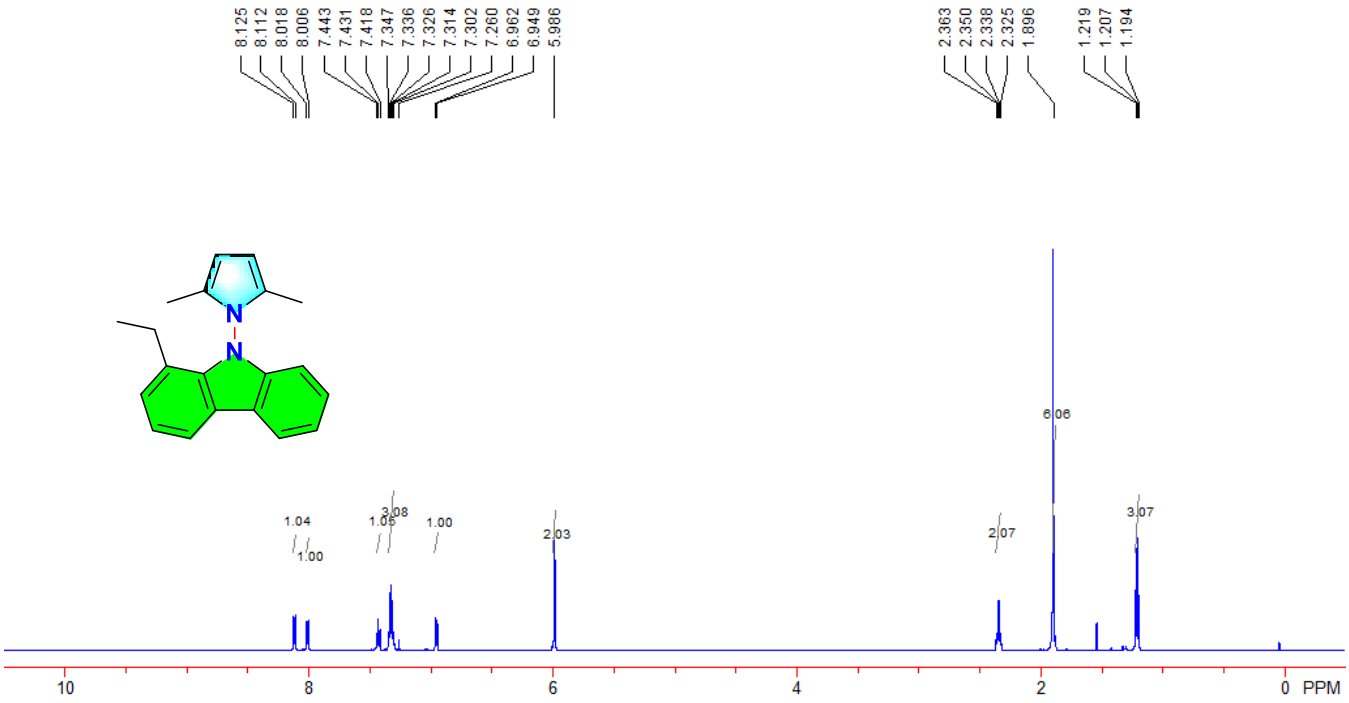


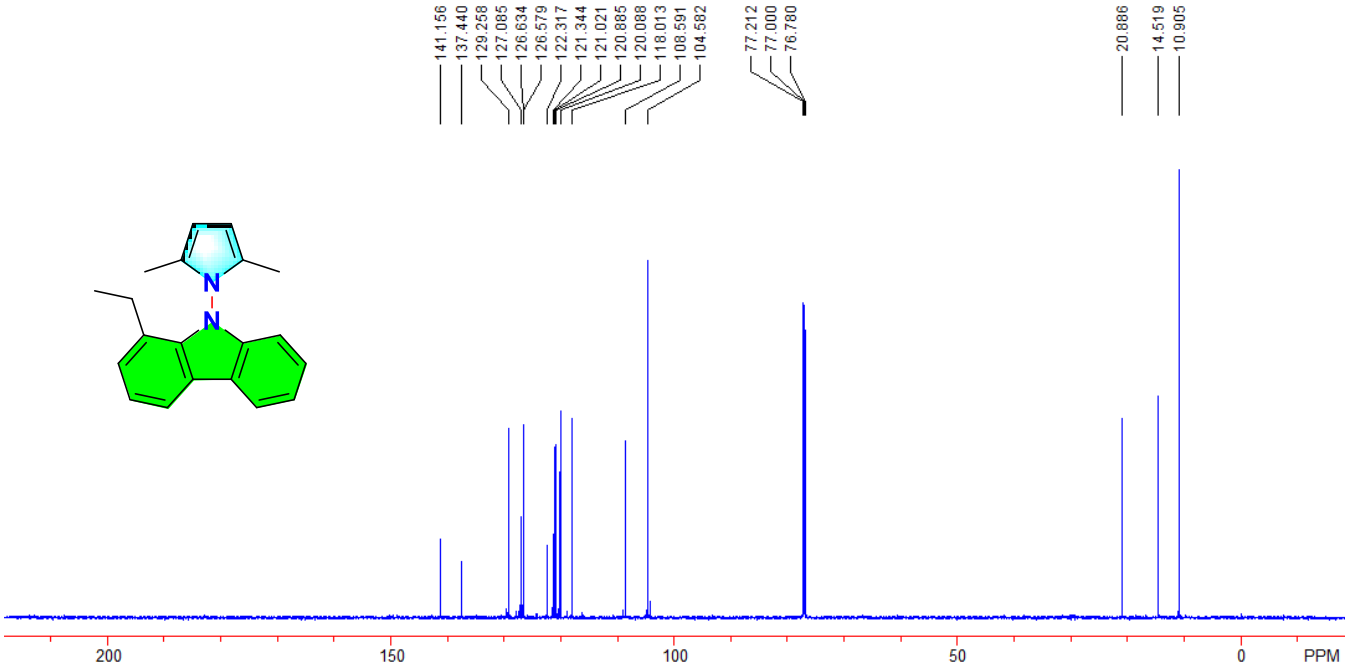
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1o**



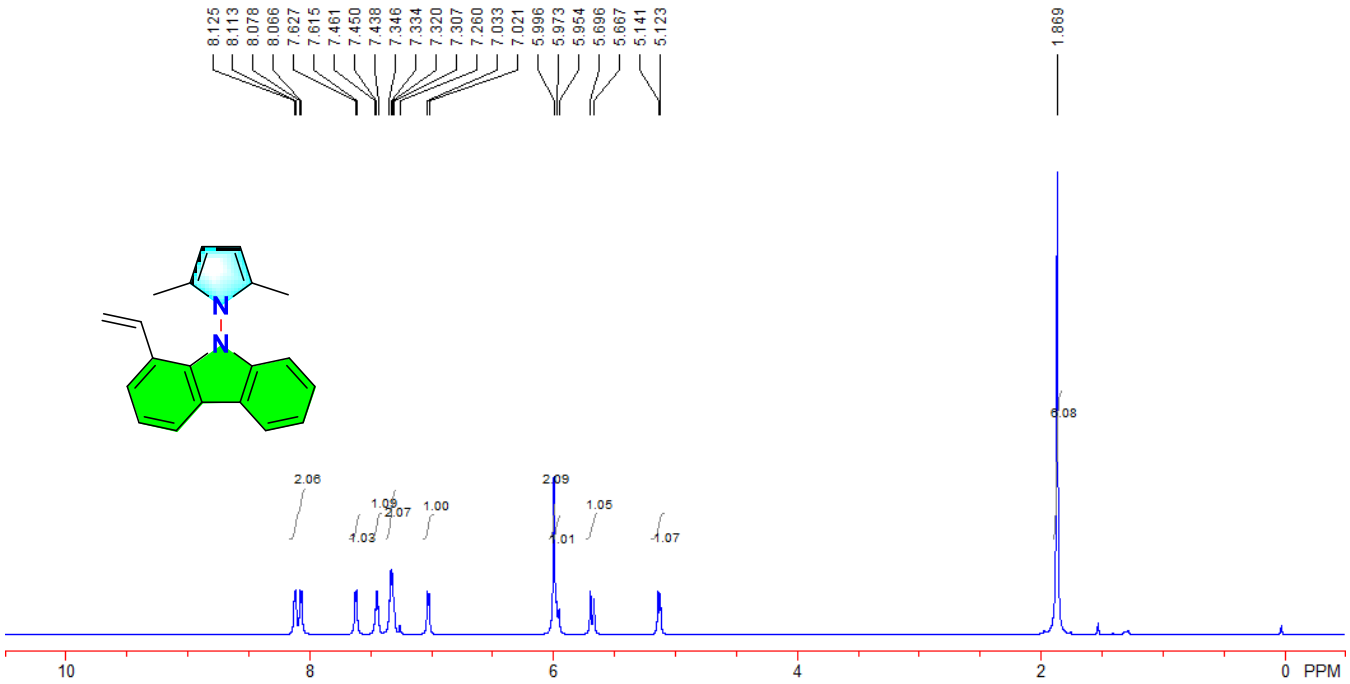


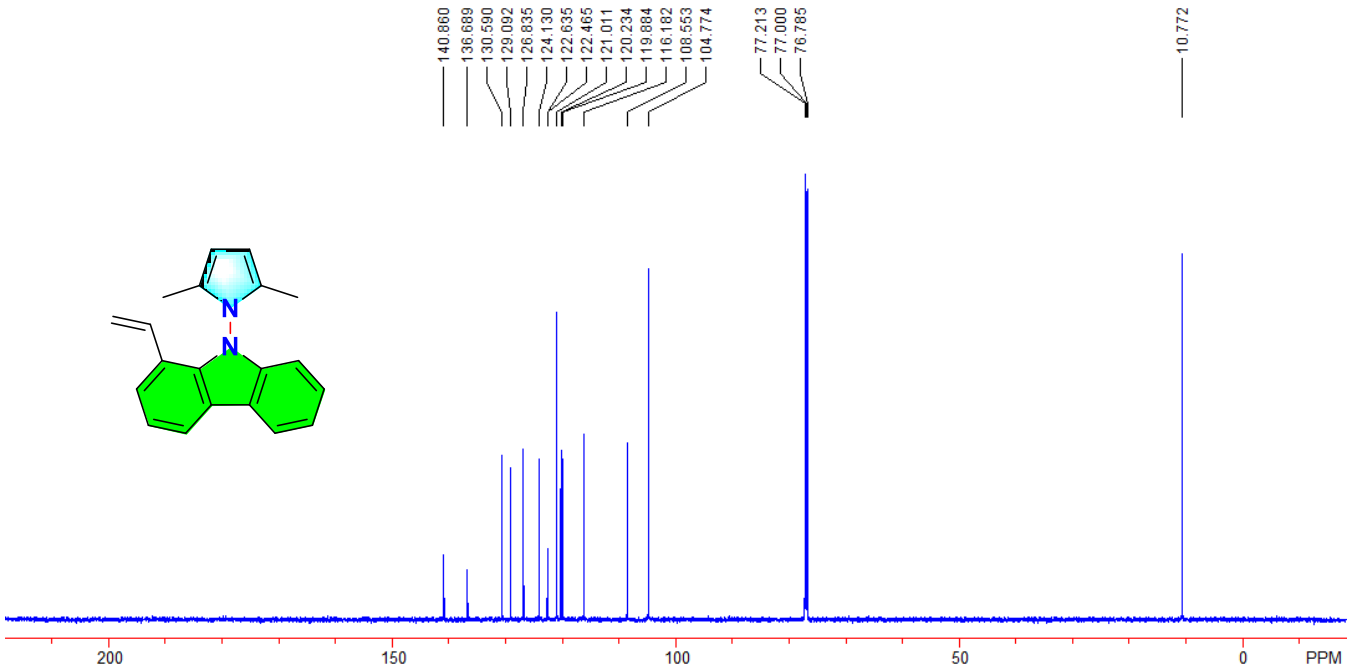
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1p**



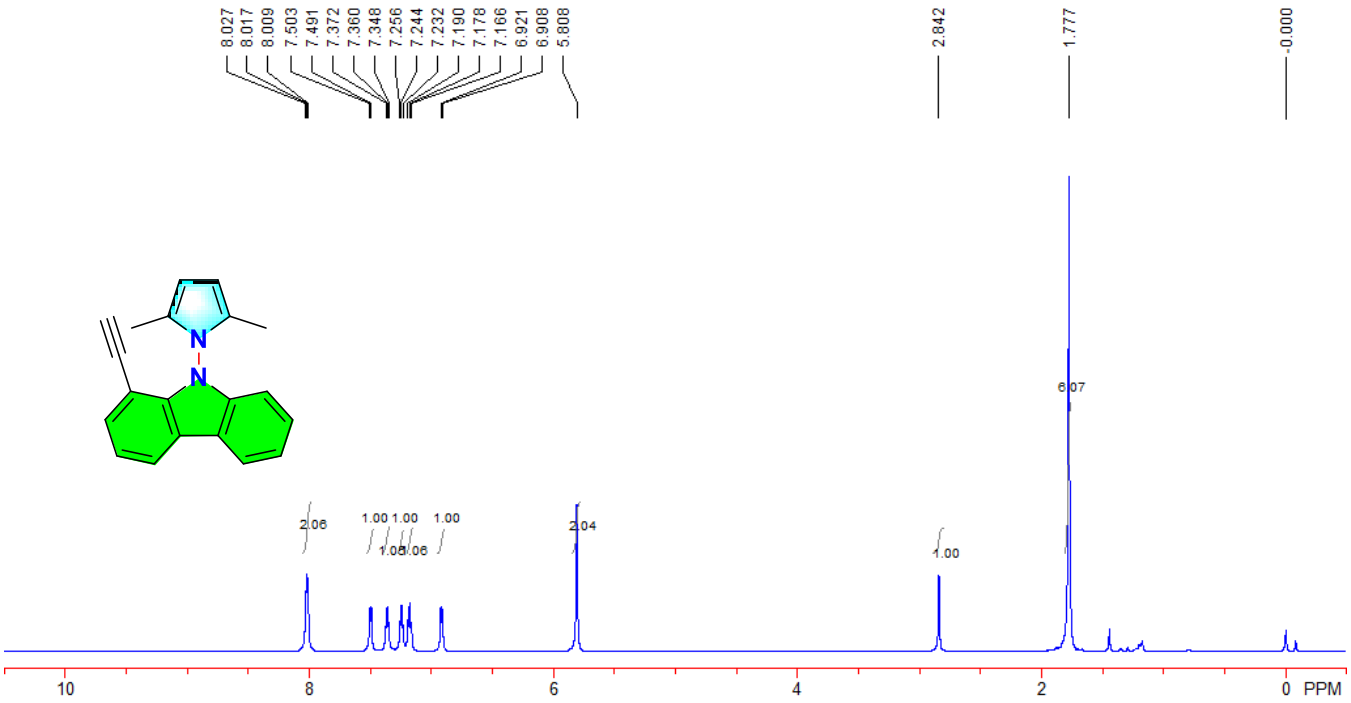


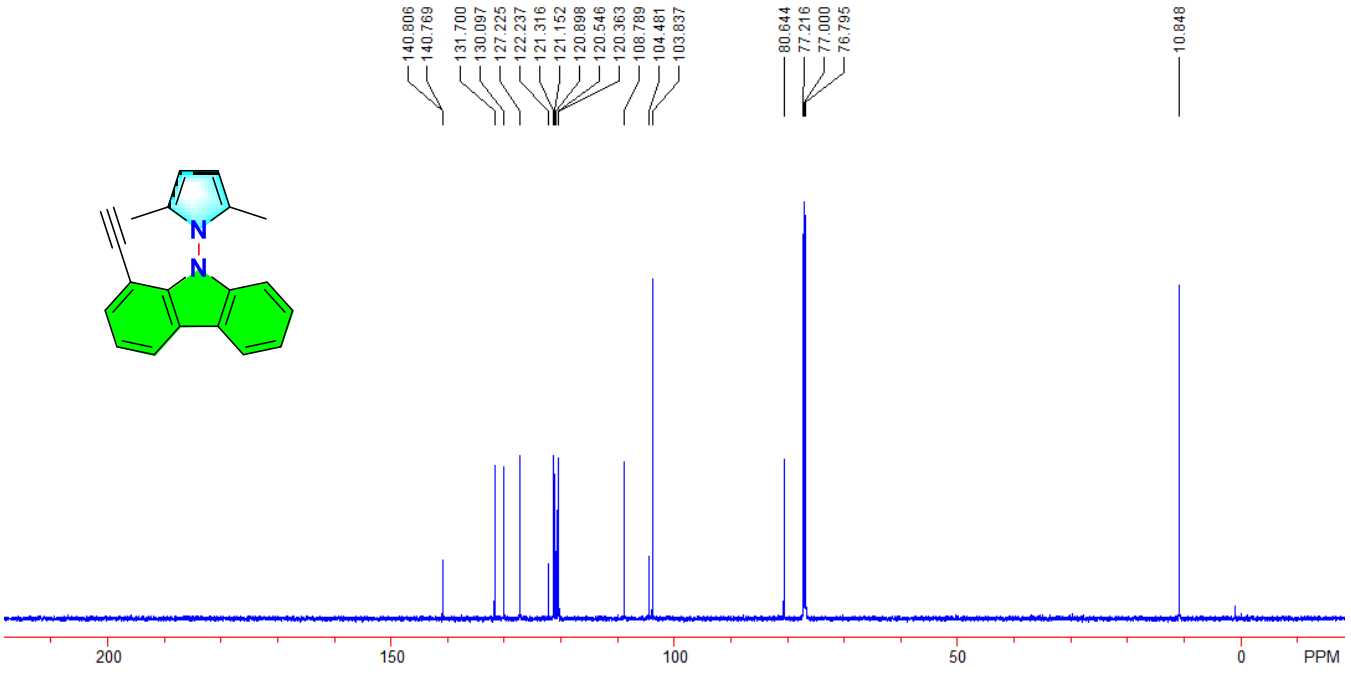
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1q**



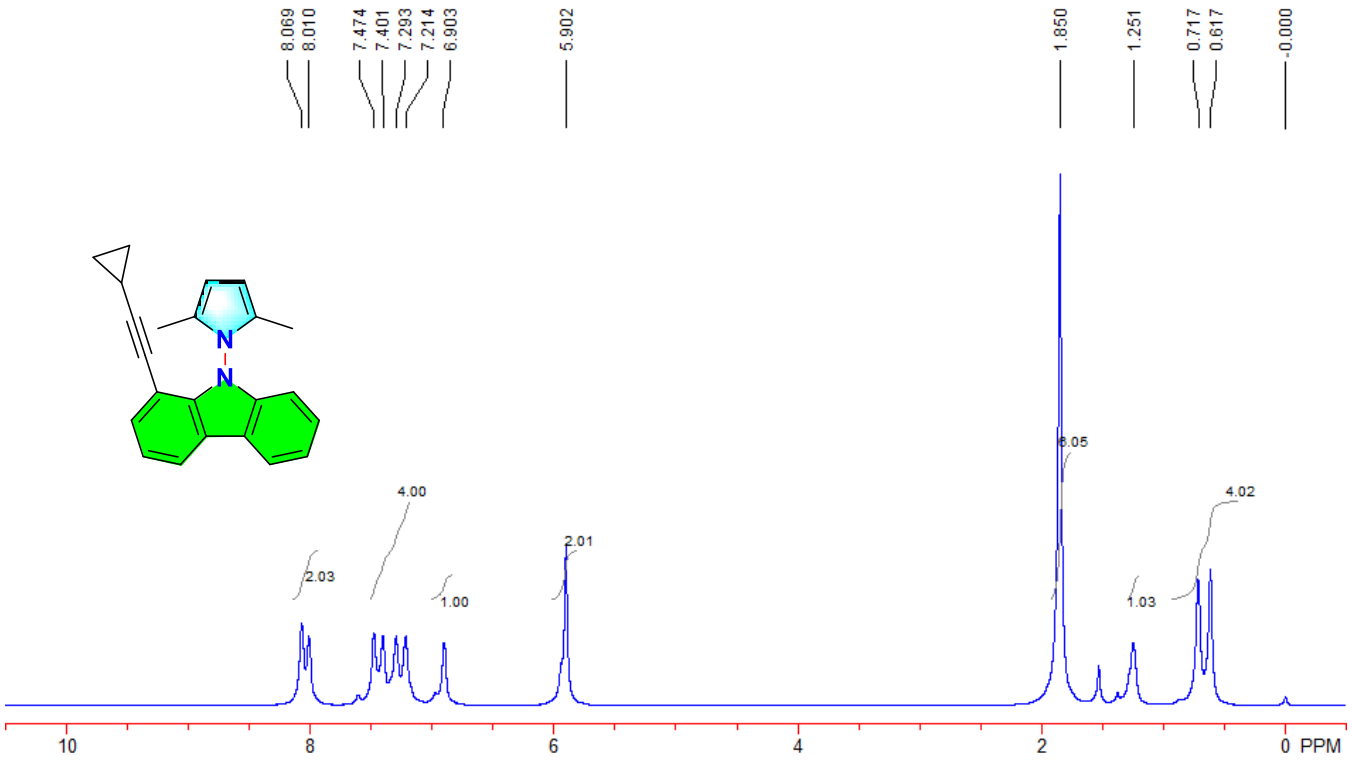


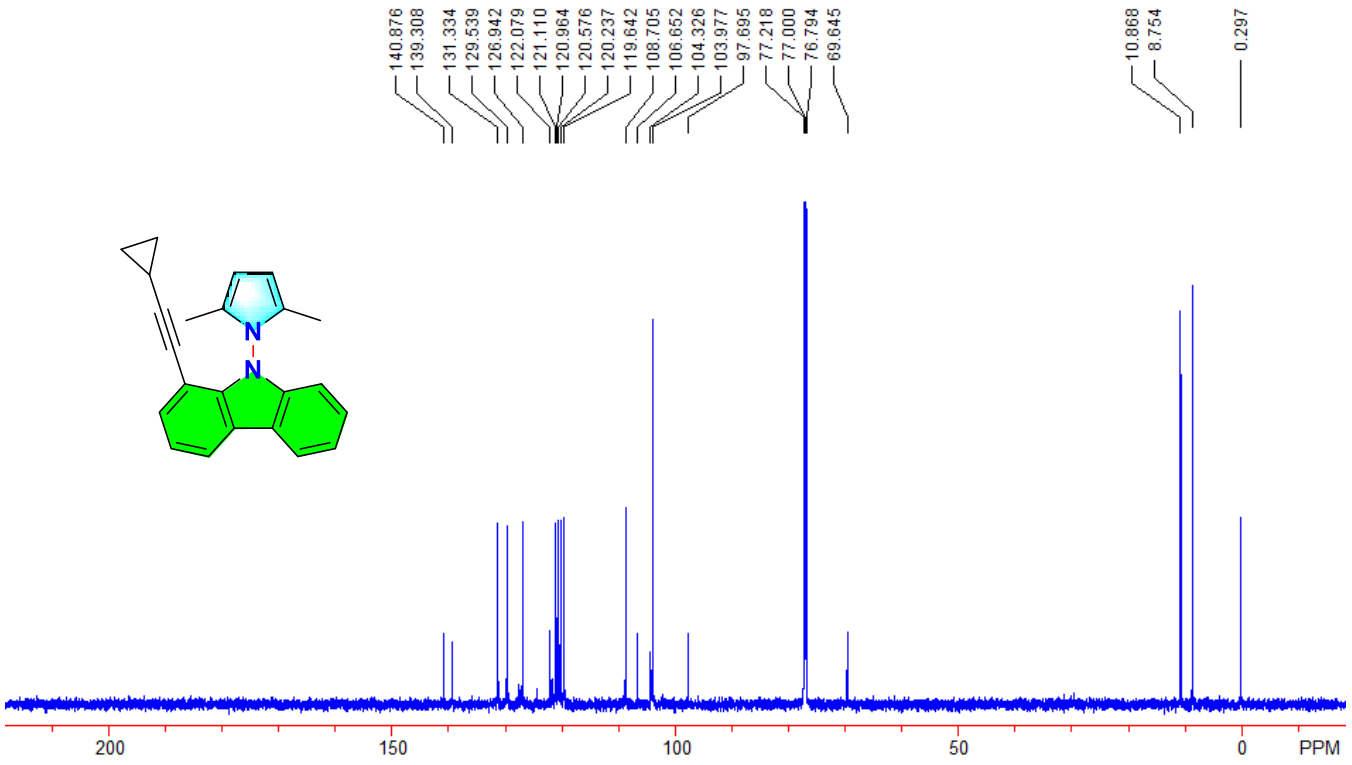
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1r**



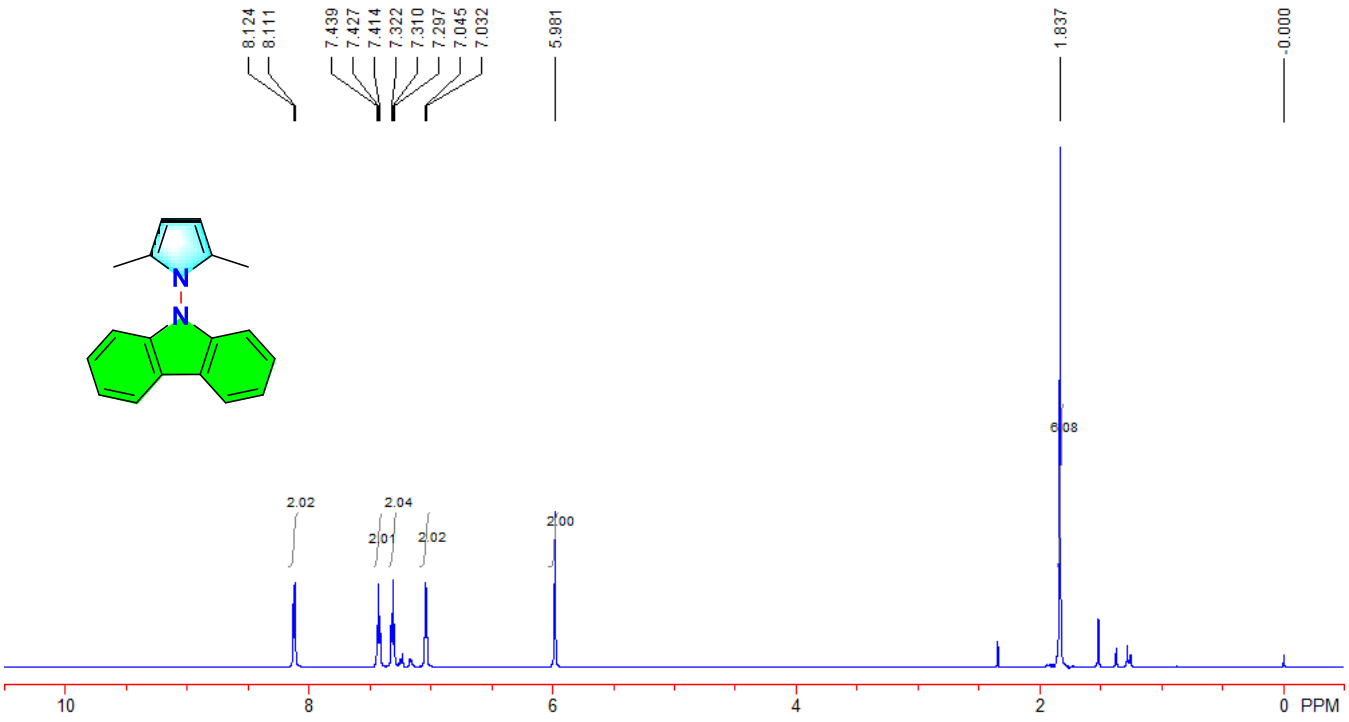


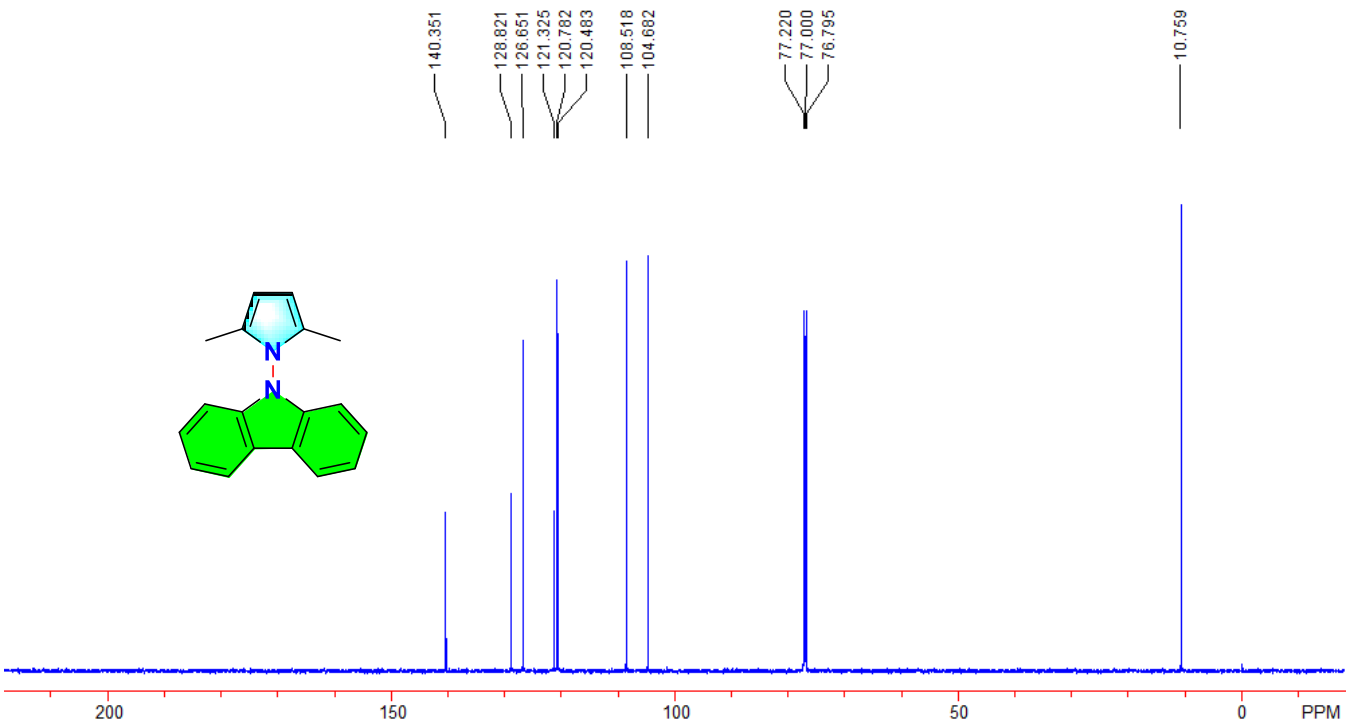
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1s**



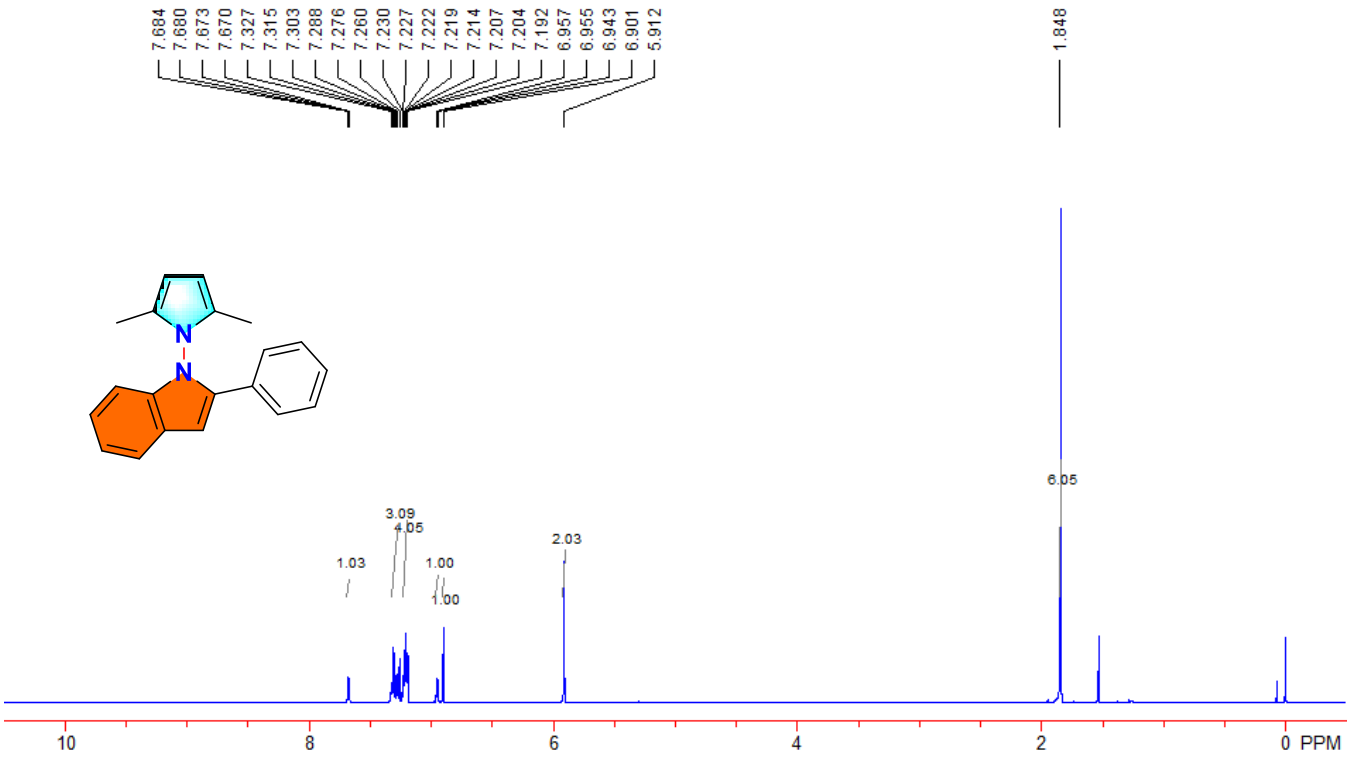


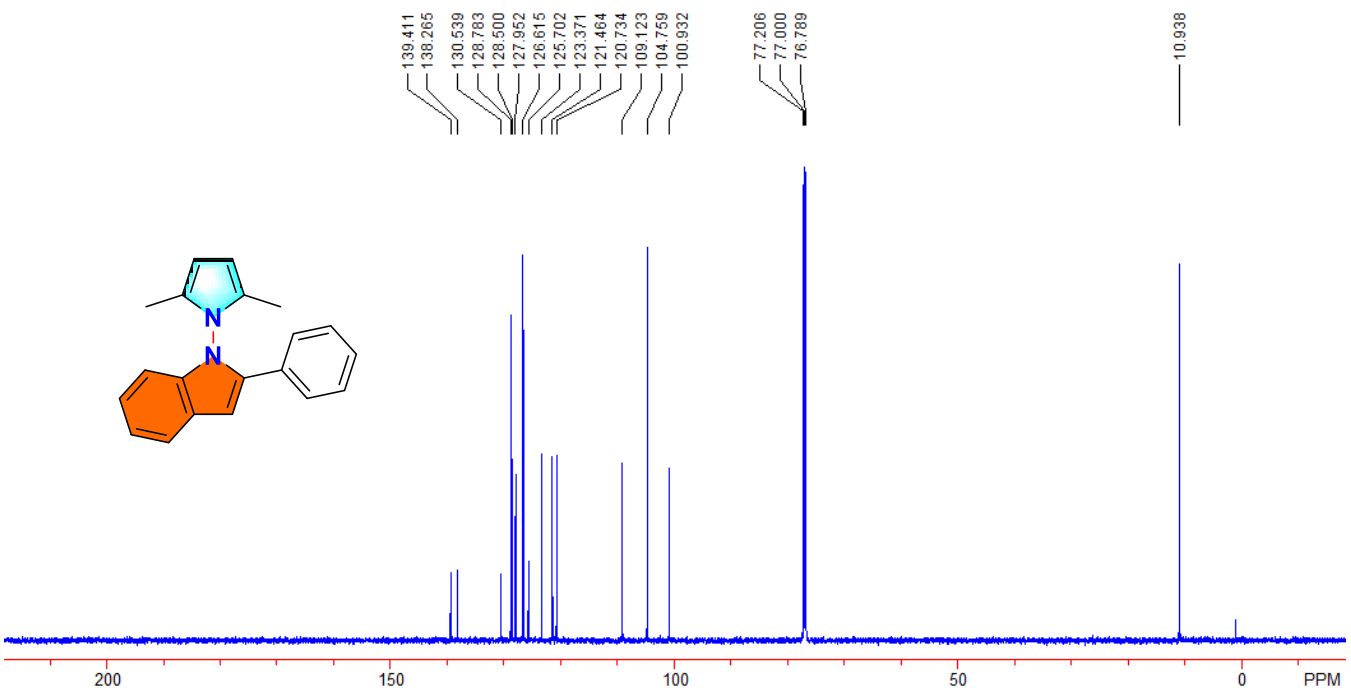
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1t**



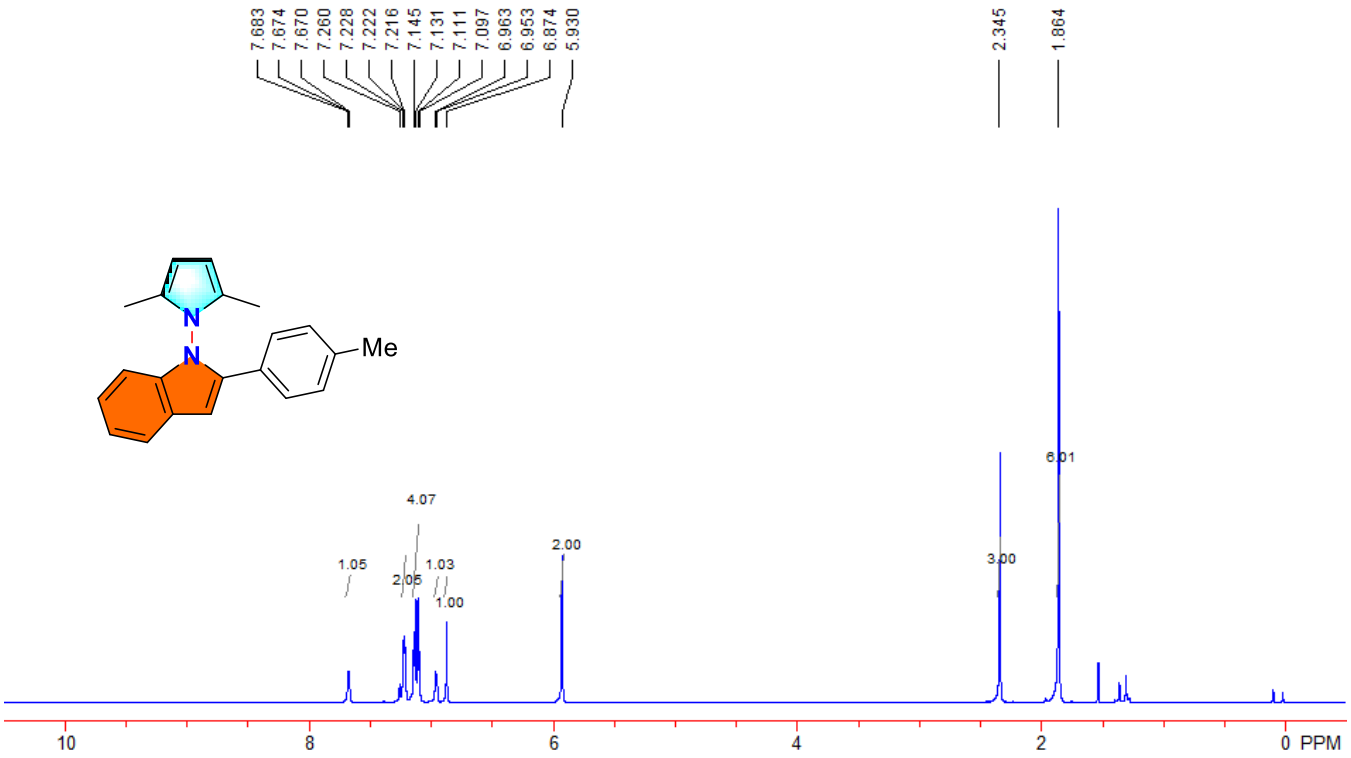


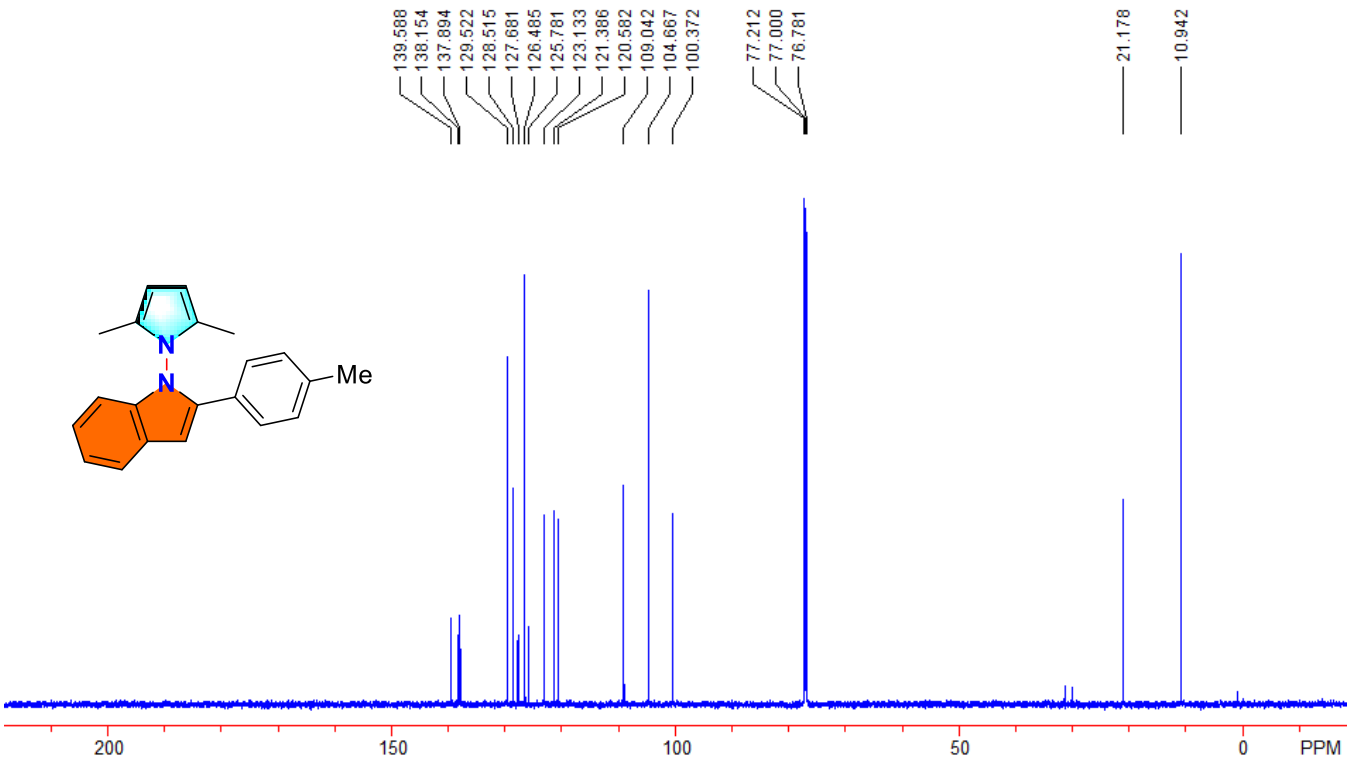
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1u**



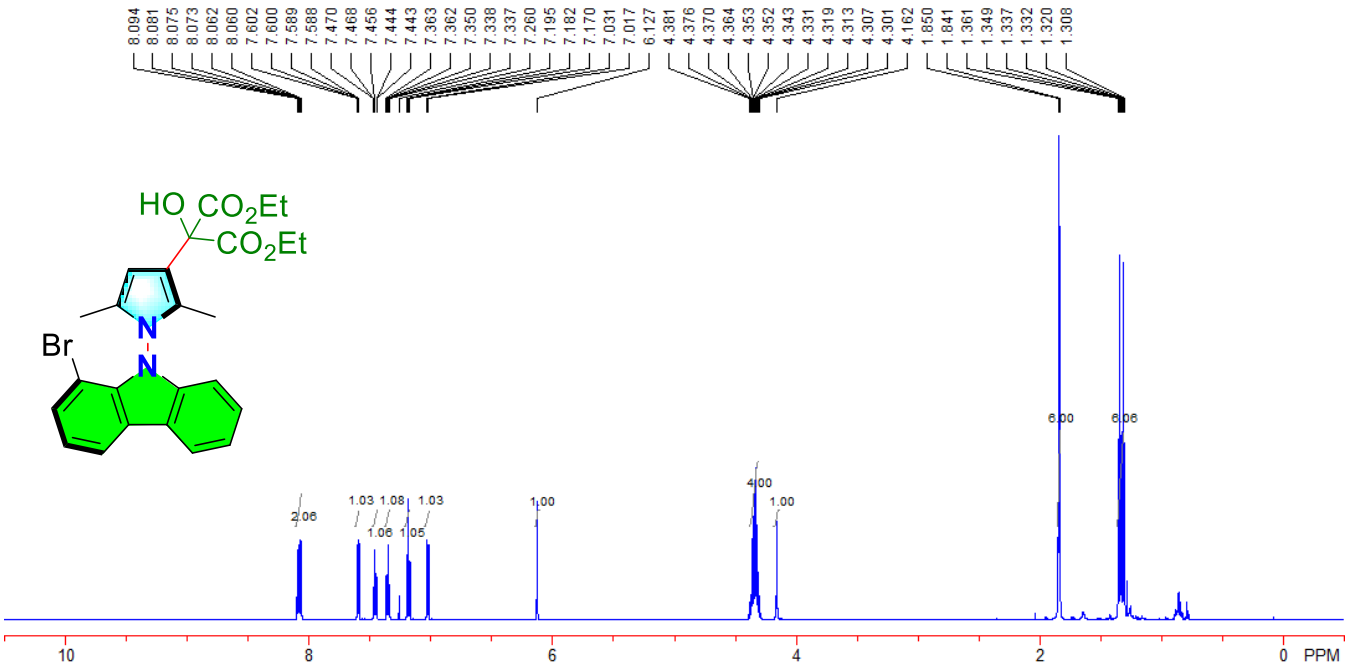


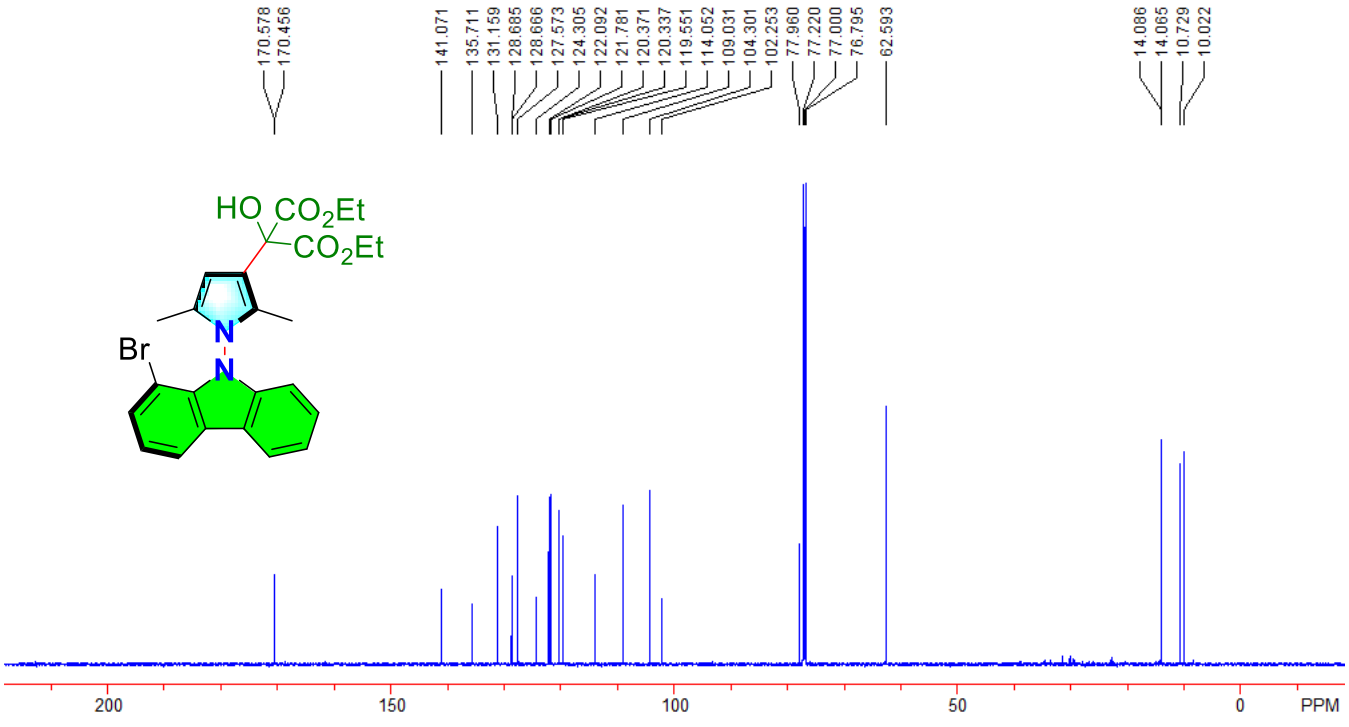
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **1v**



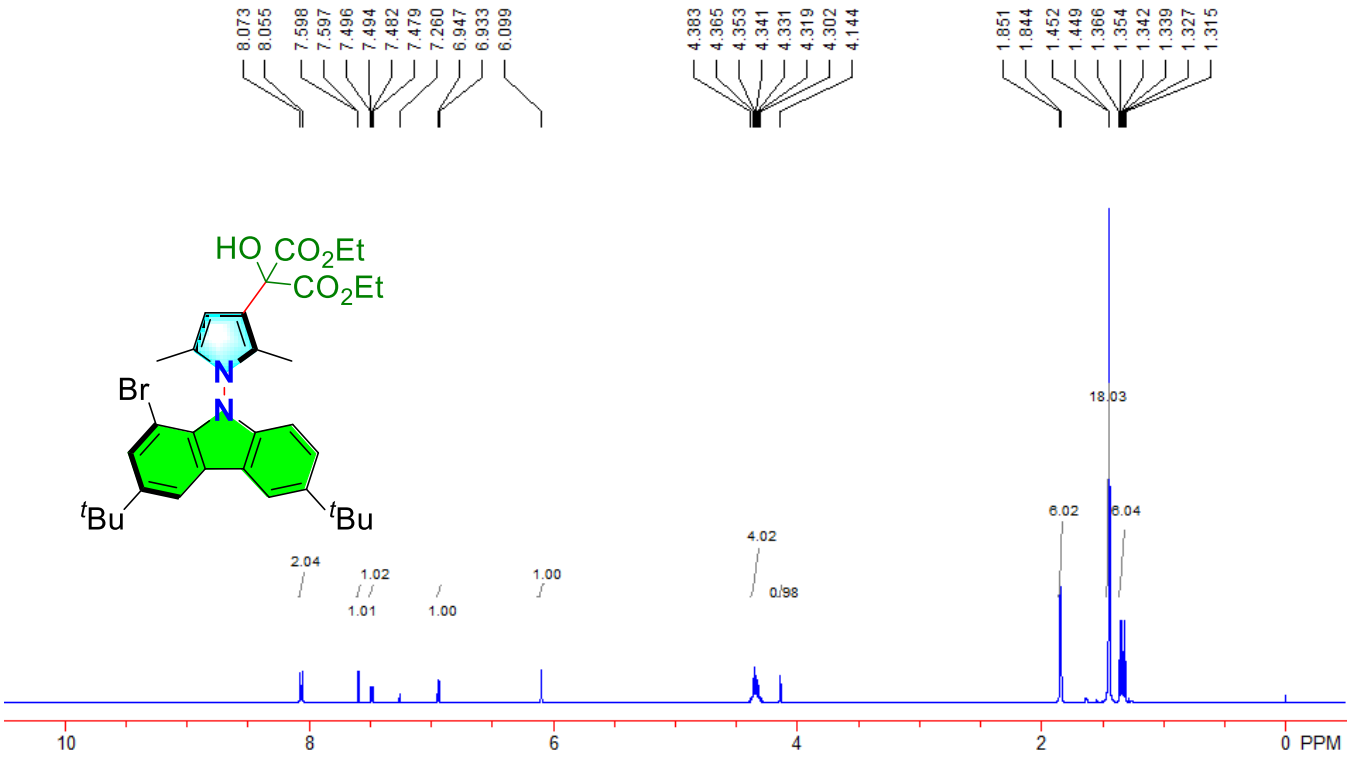


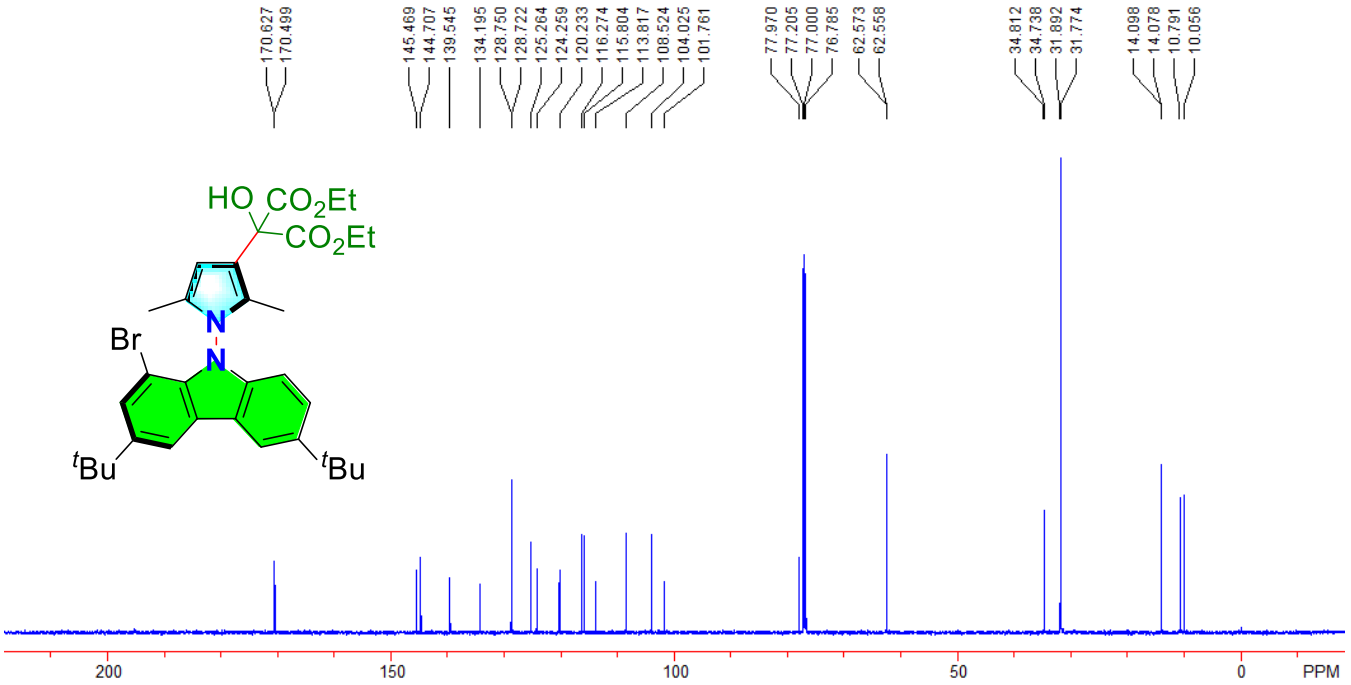
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3a**



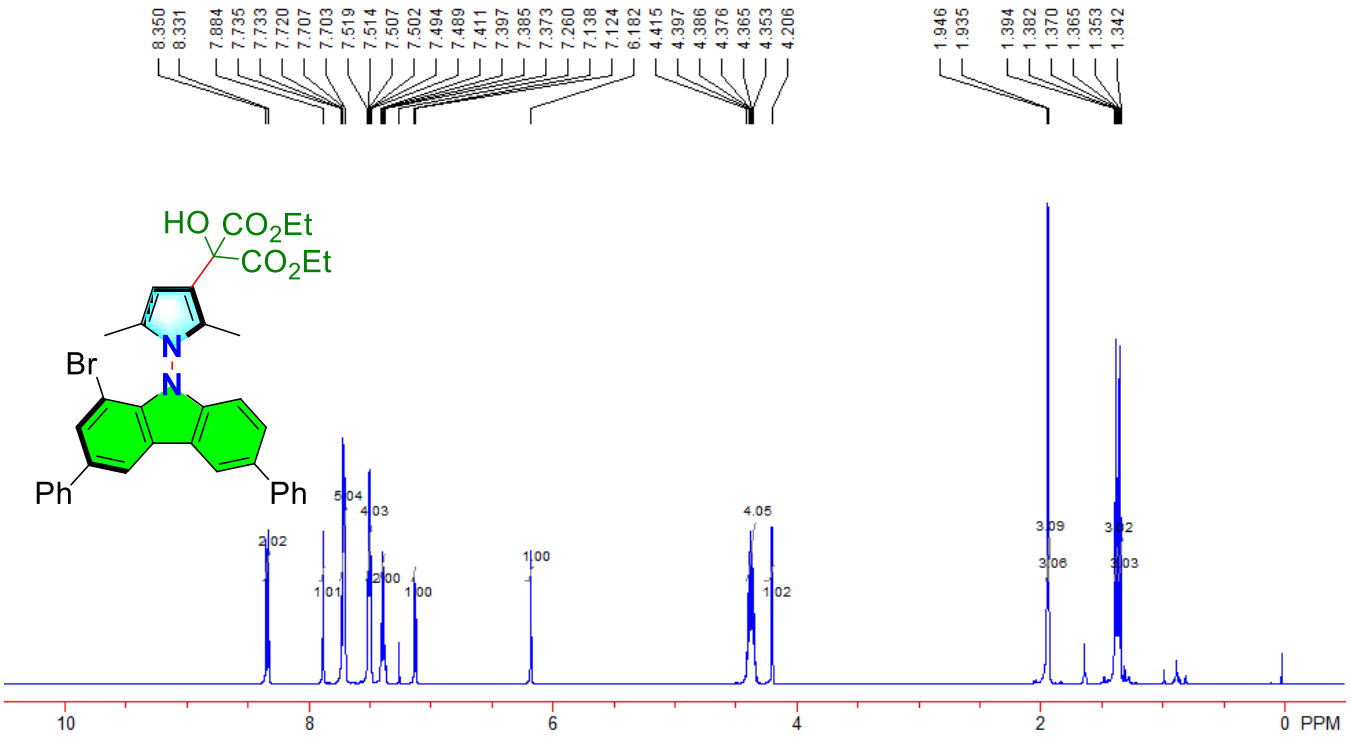


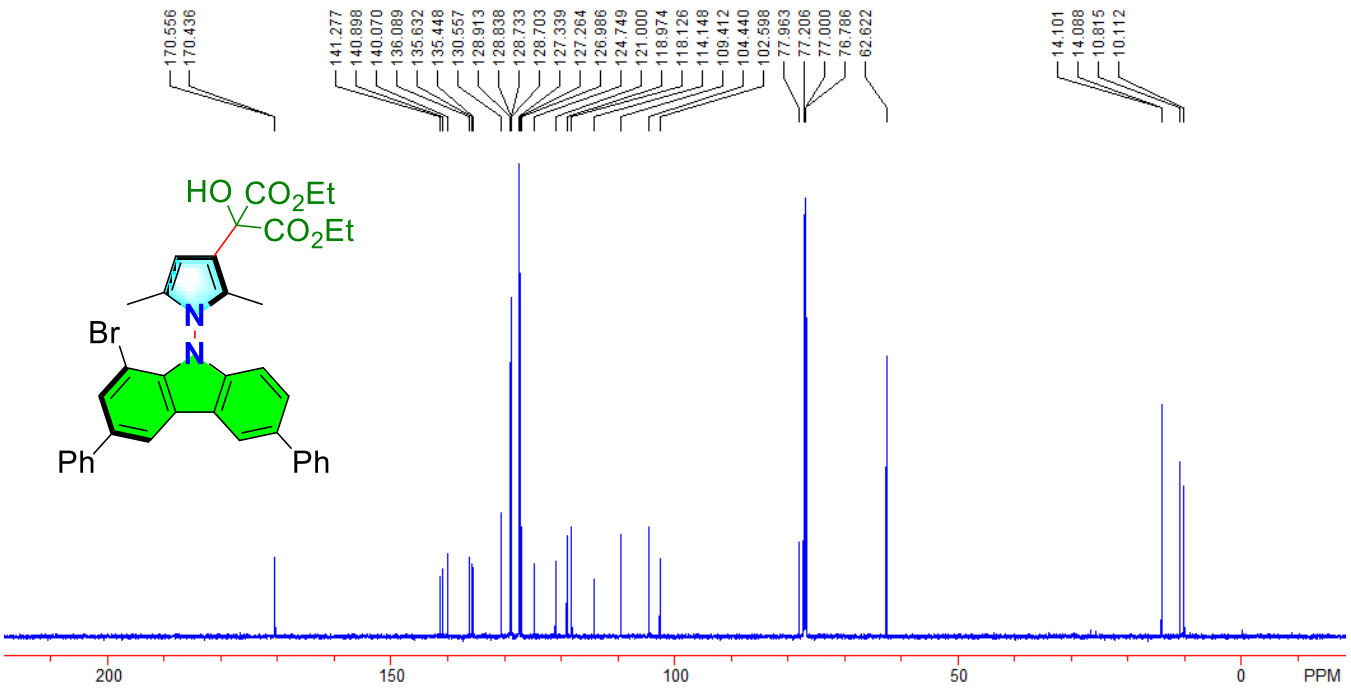
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3b**



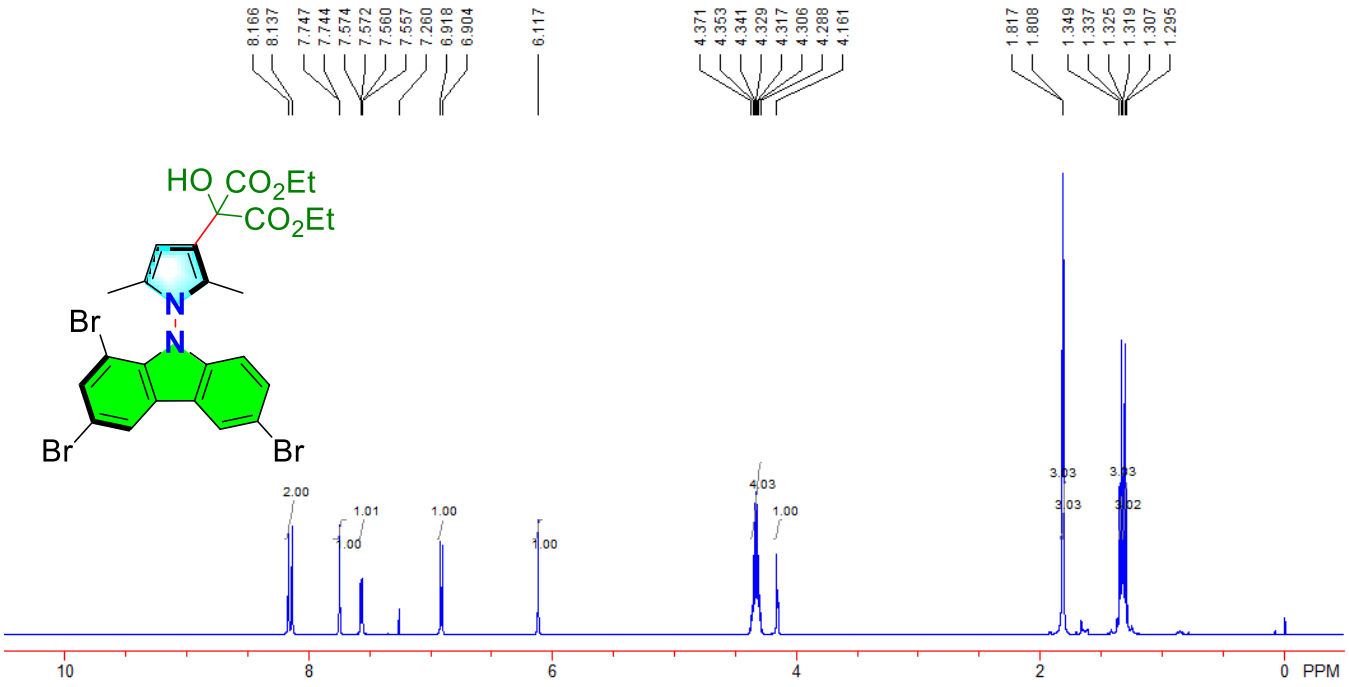


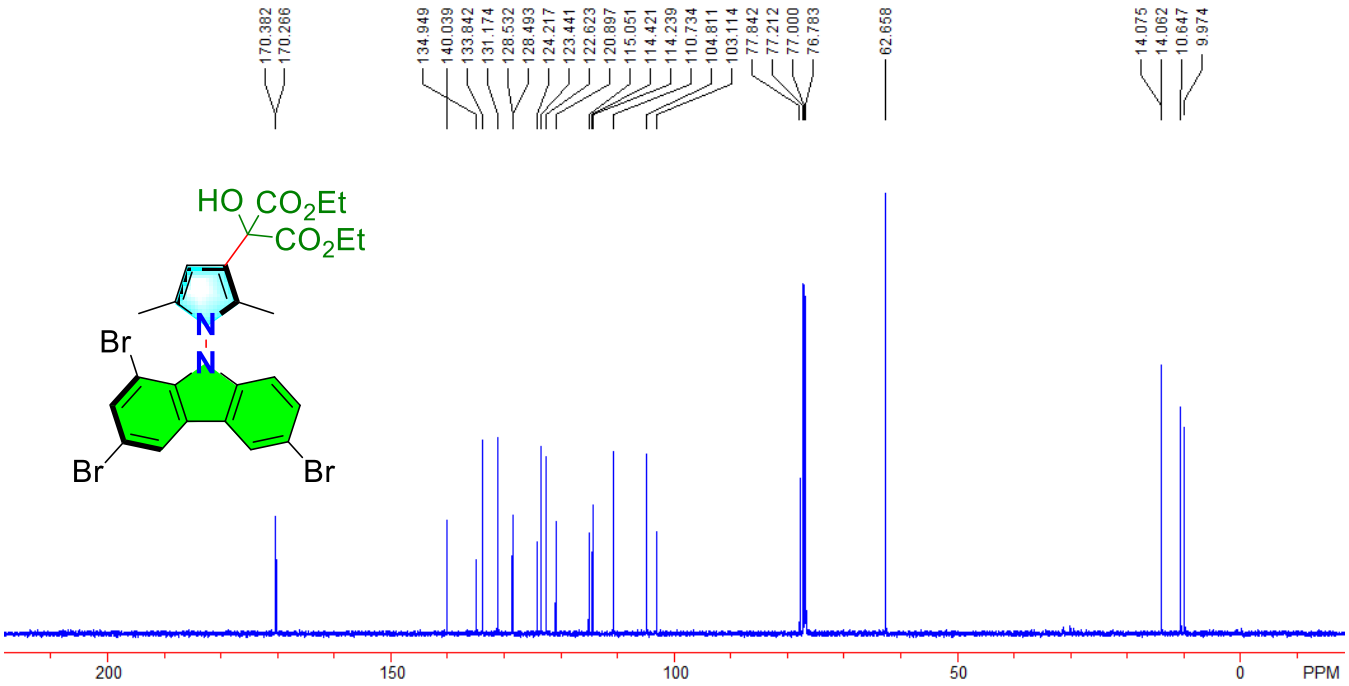
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3c**



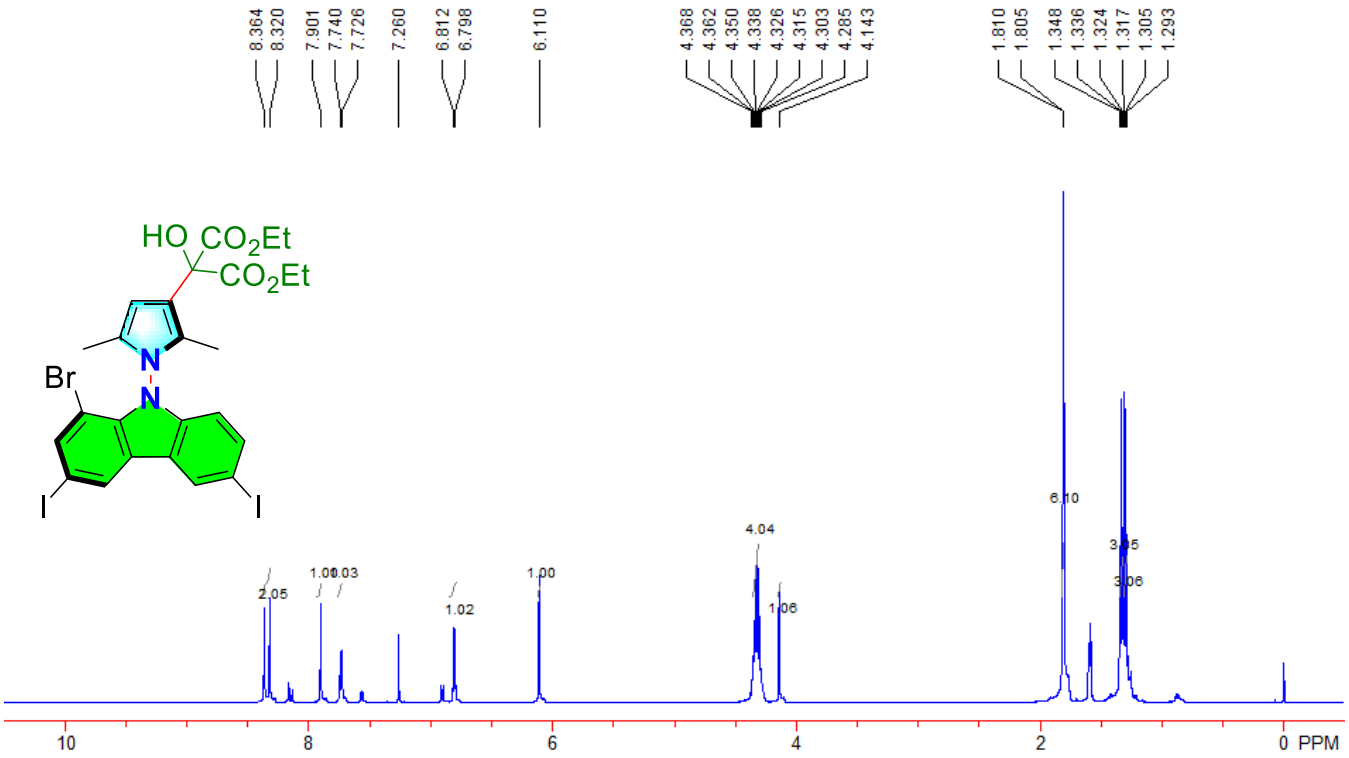


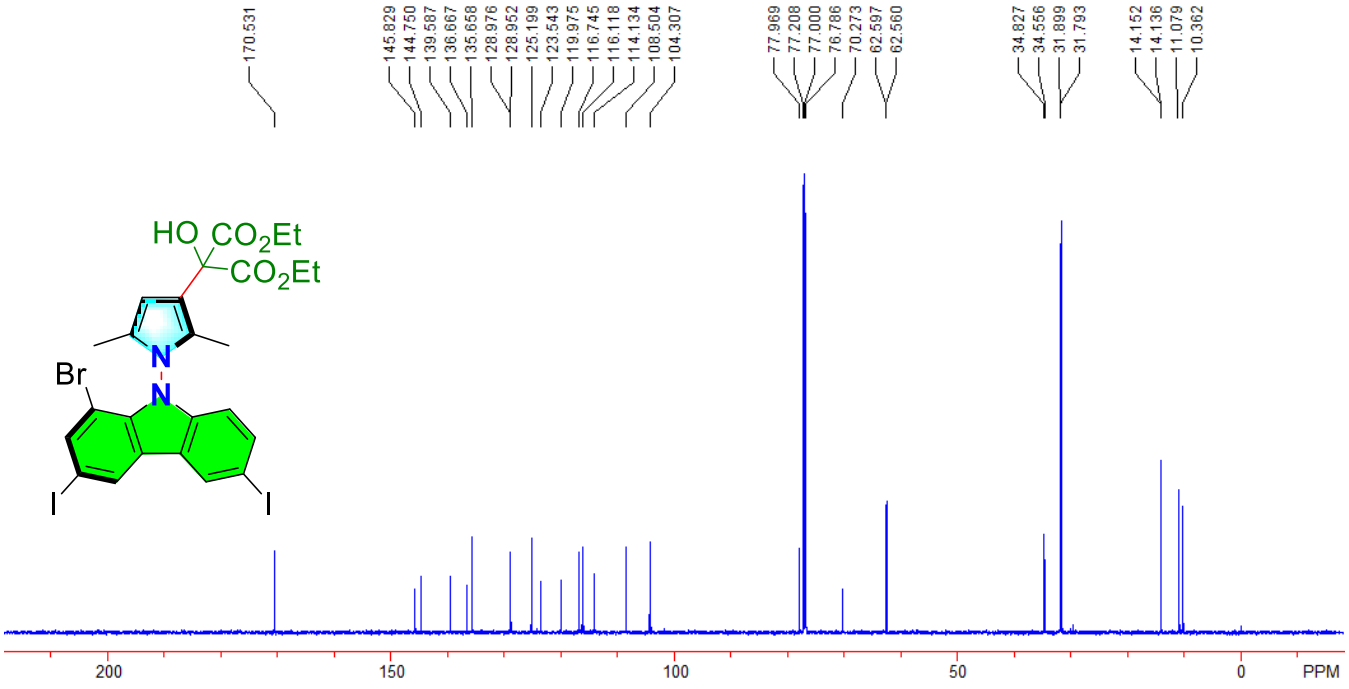
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3d**



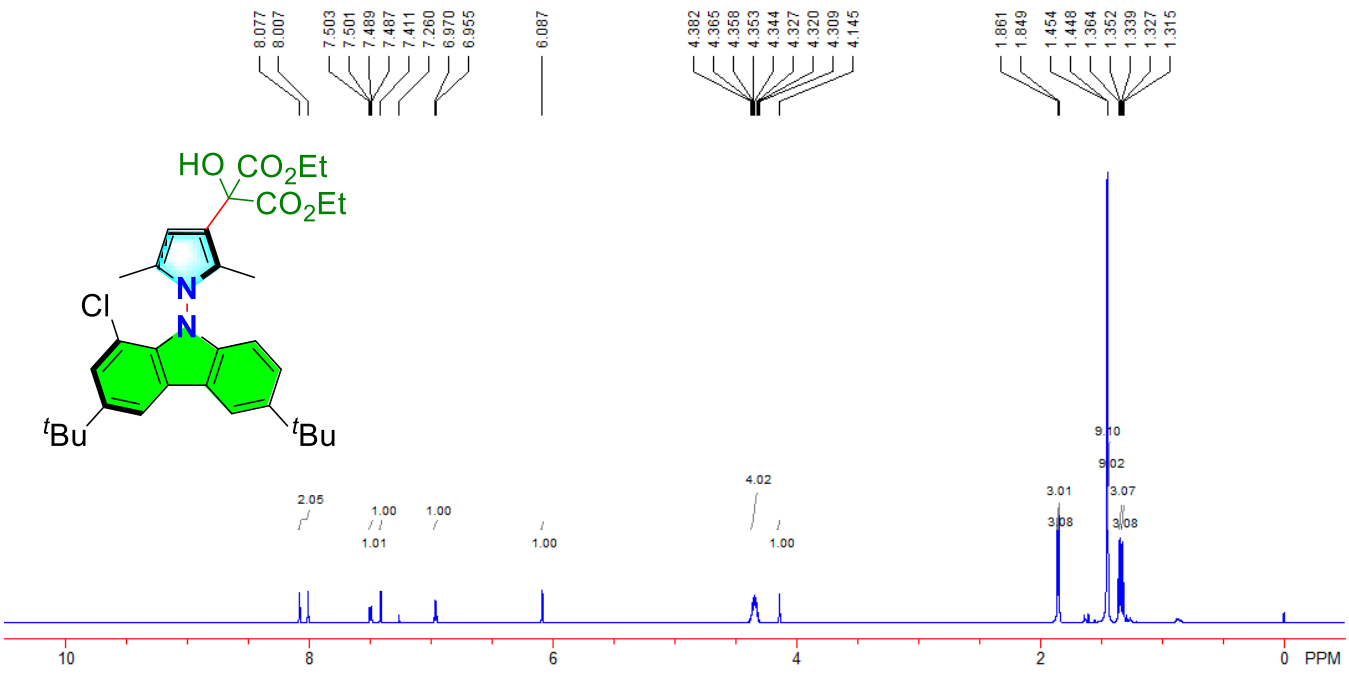


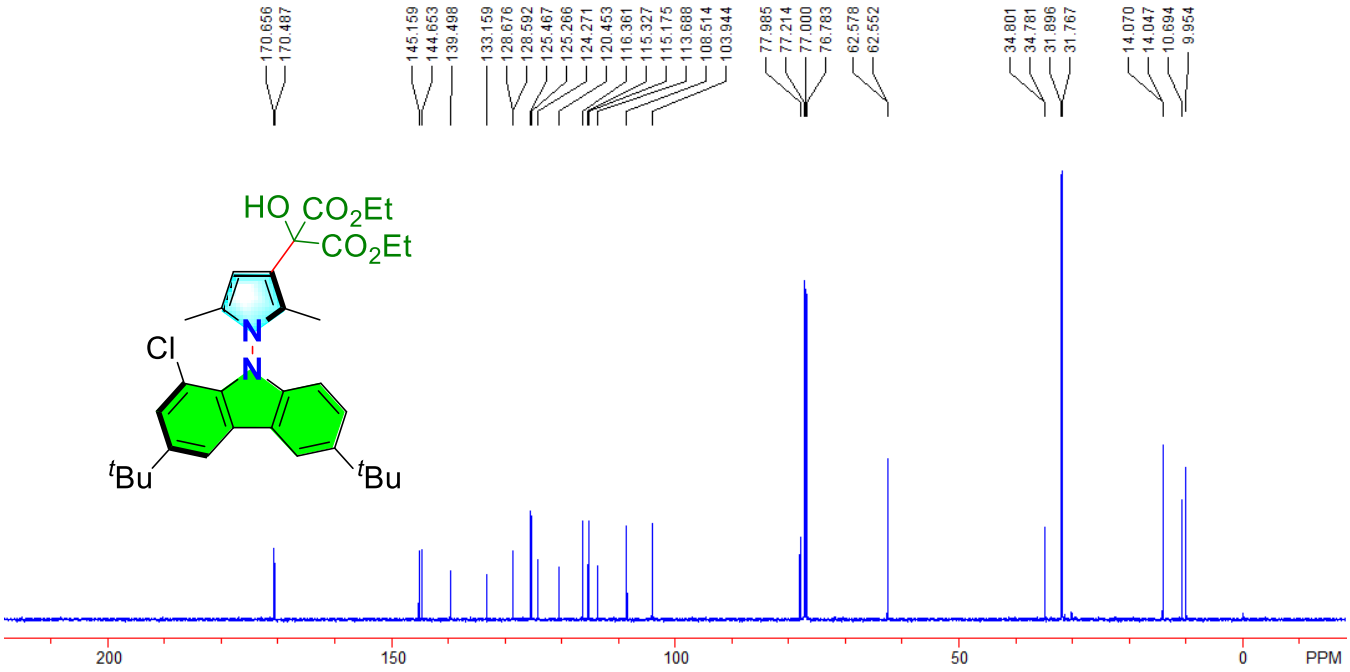
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3e**



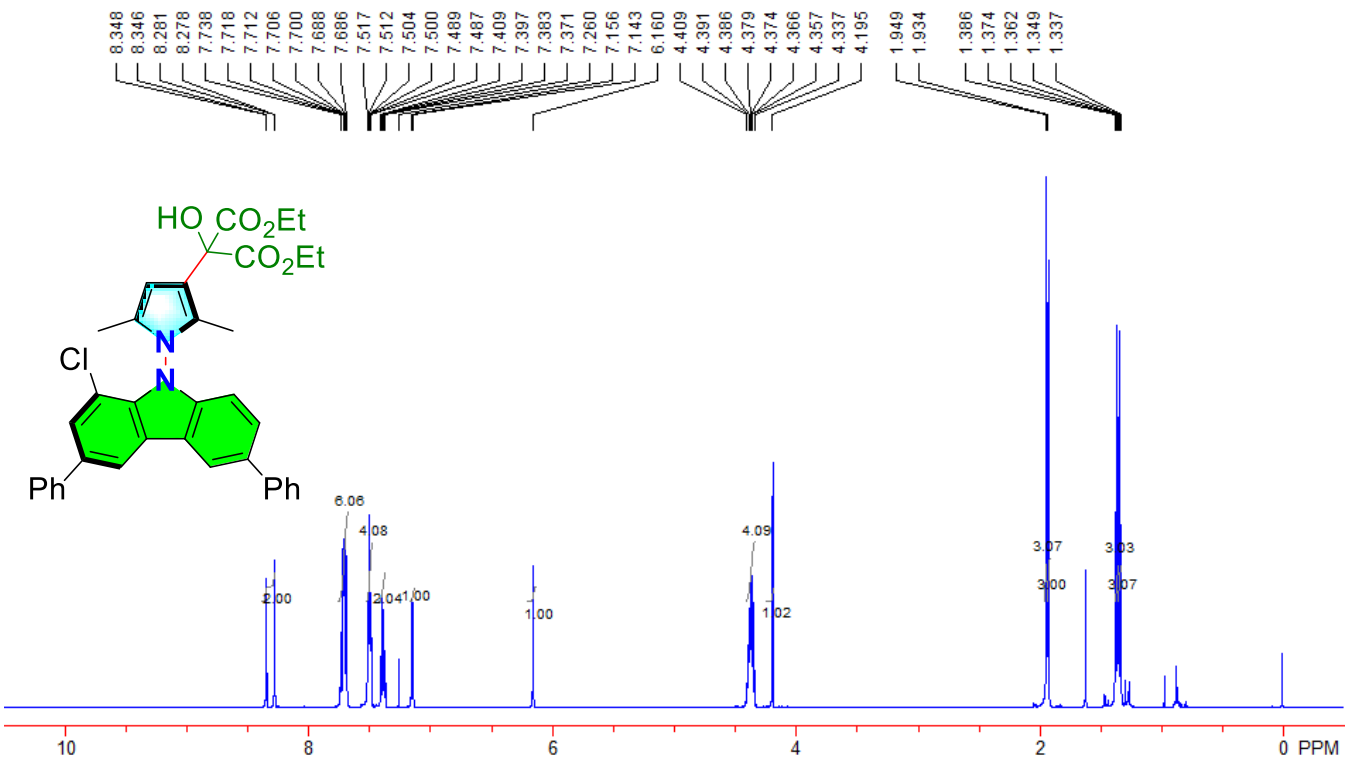


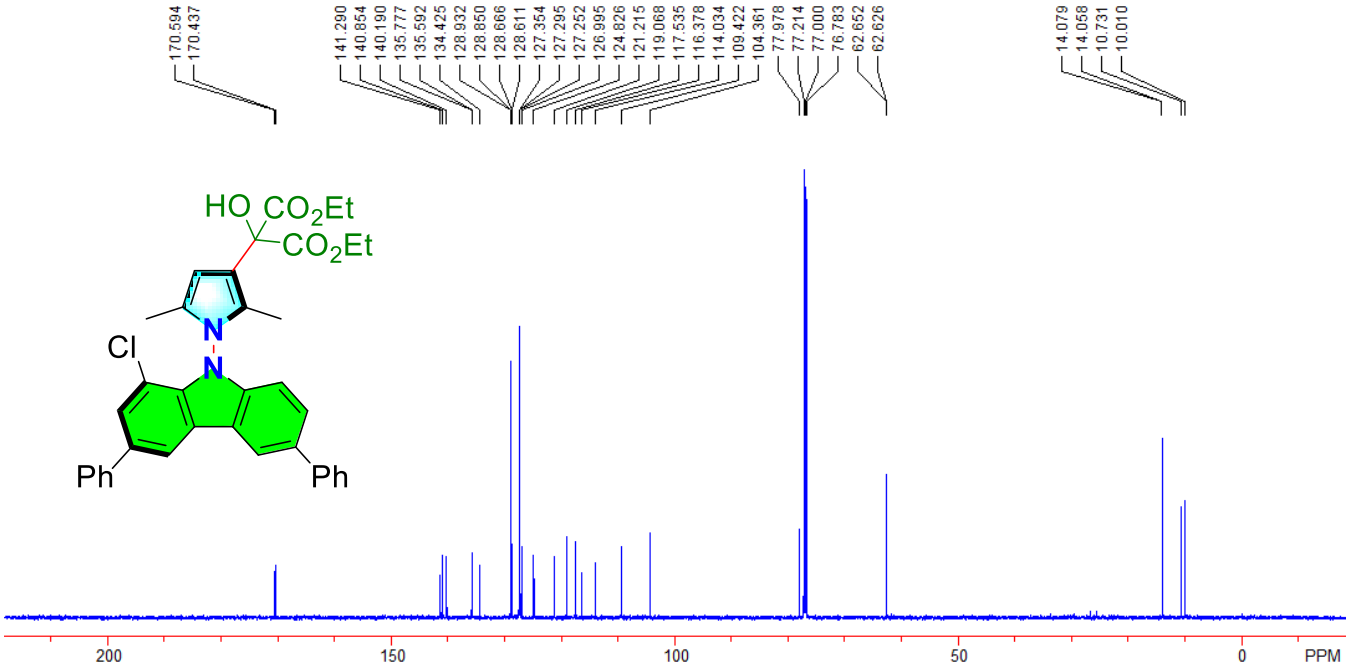
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3f**



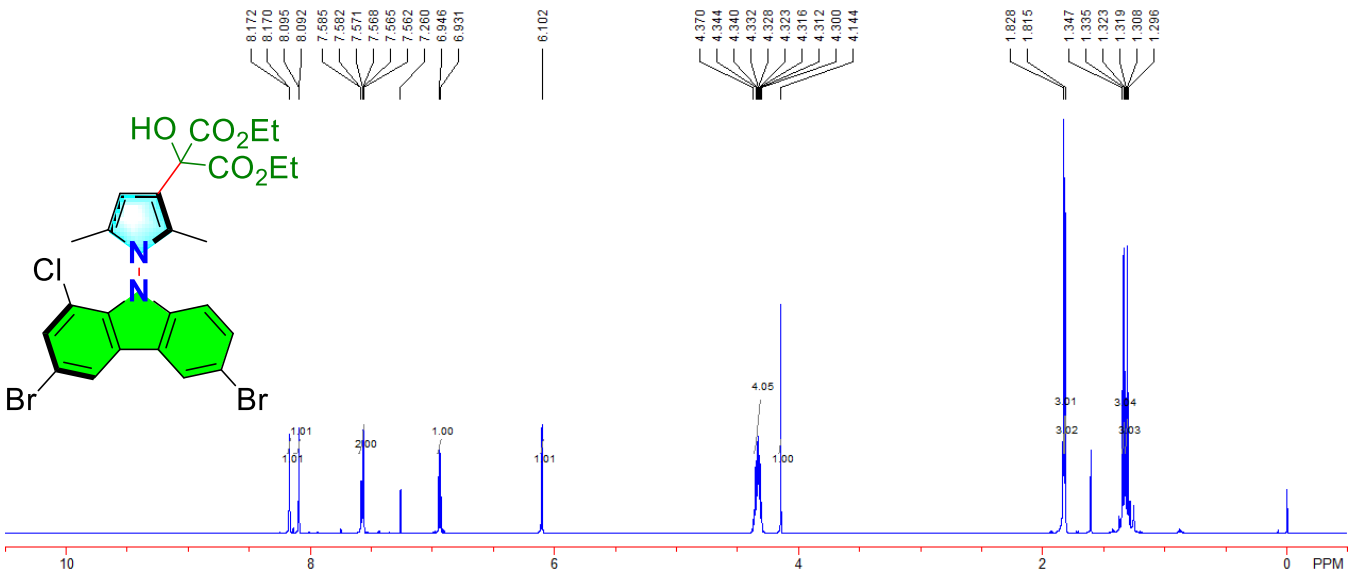


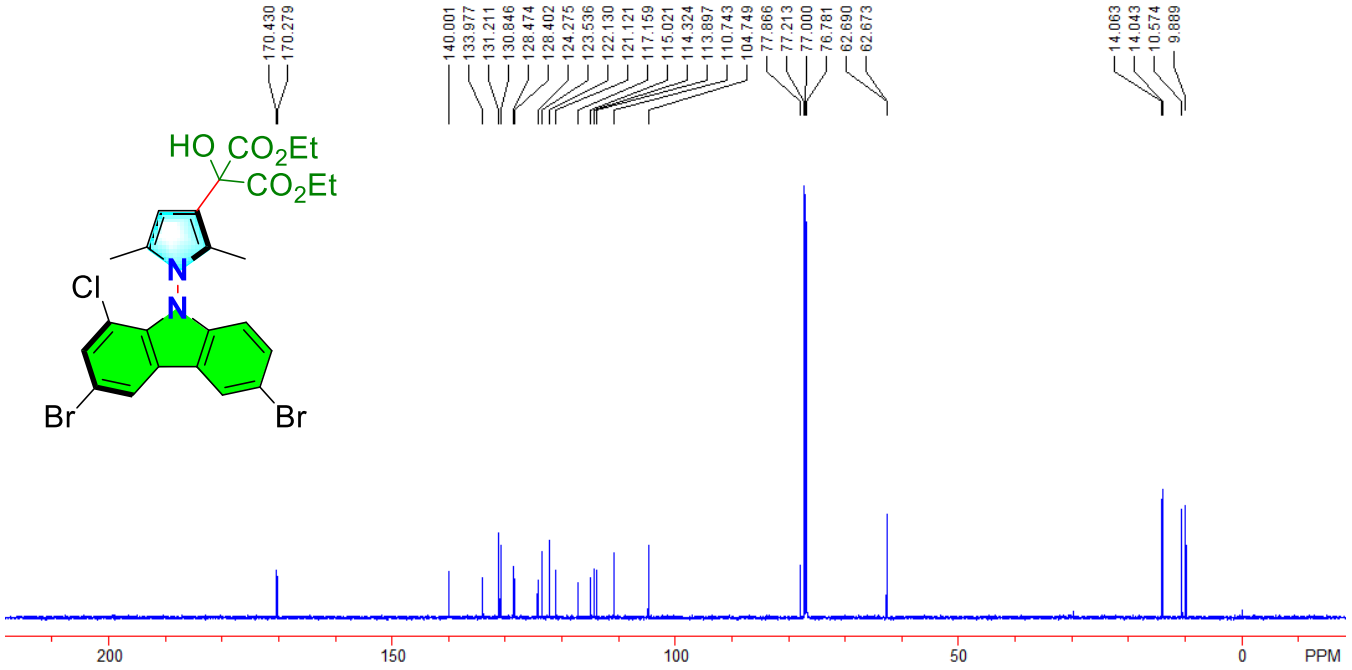
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3g**



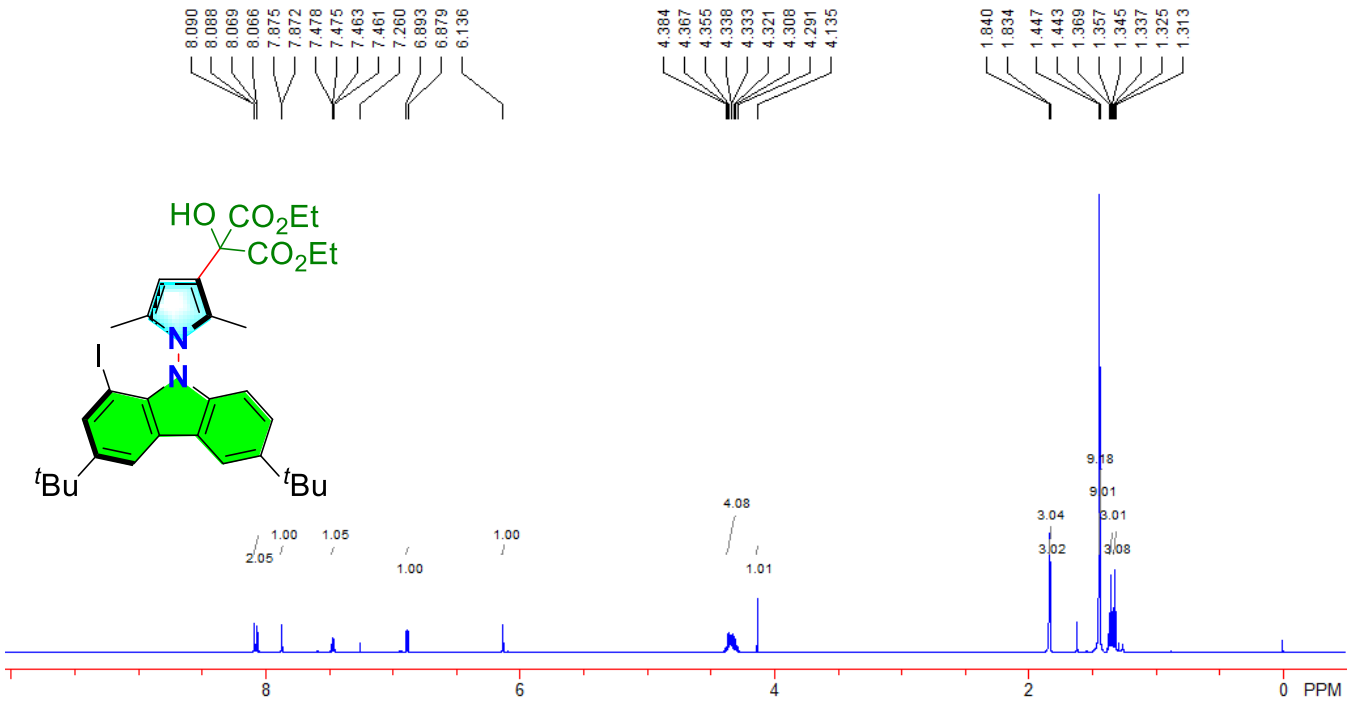


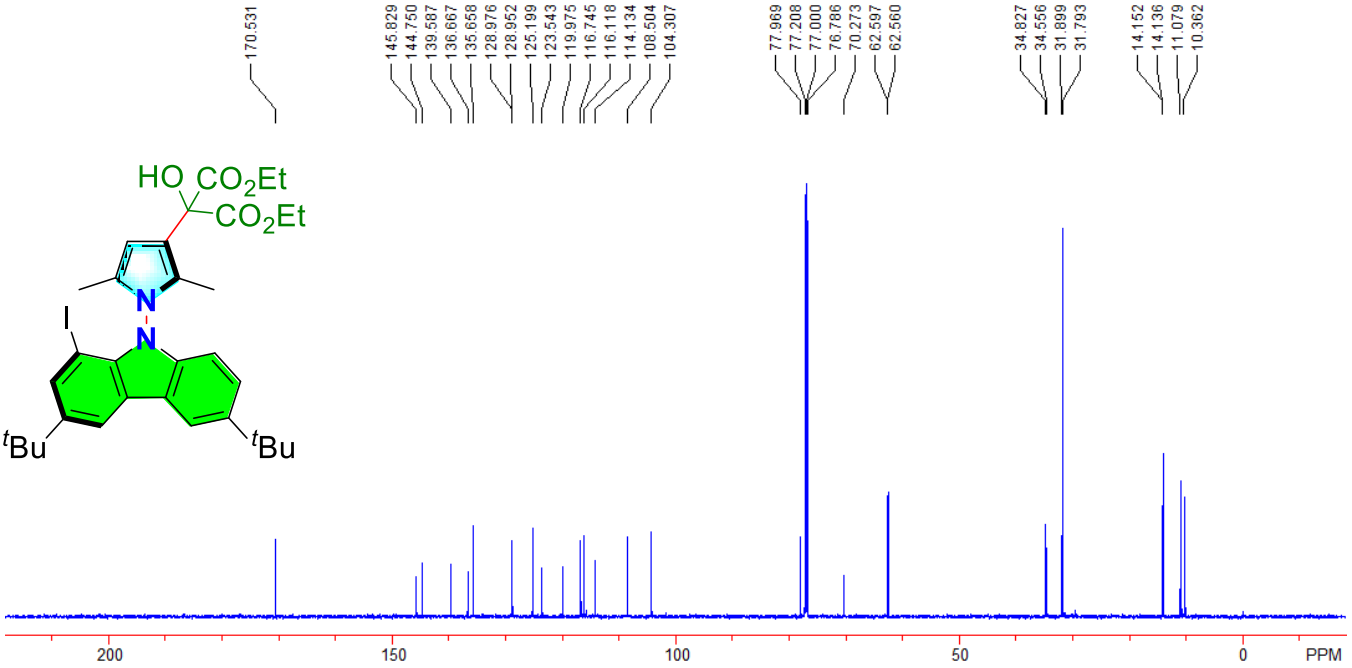
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3h**



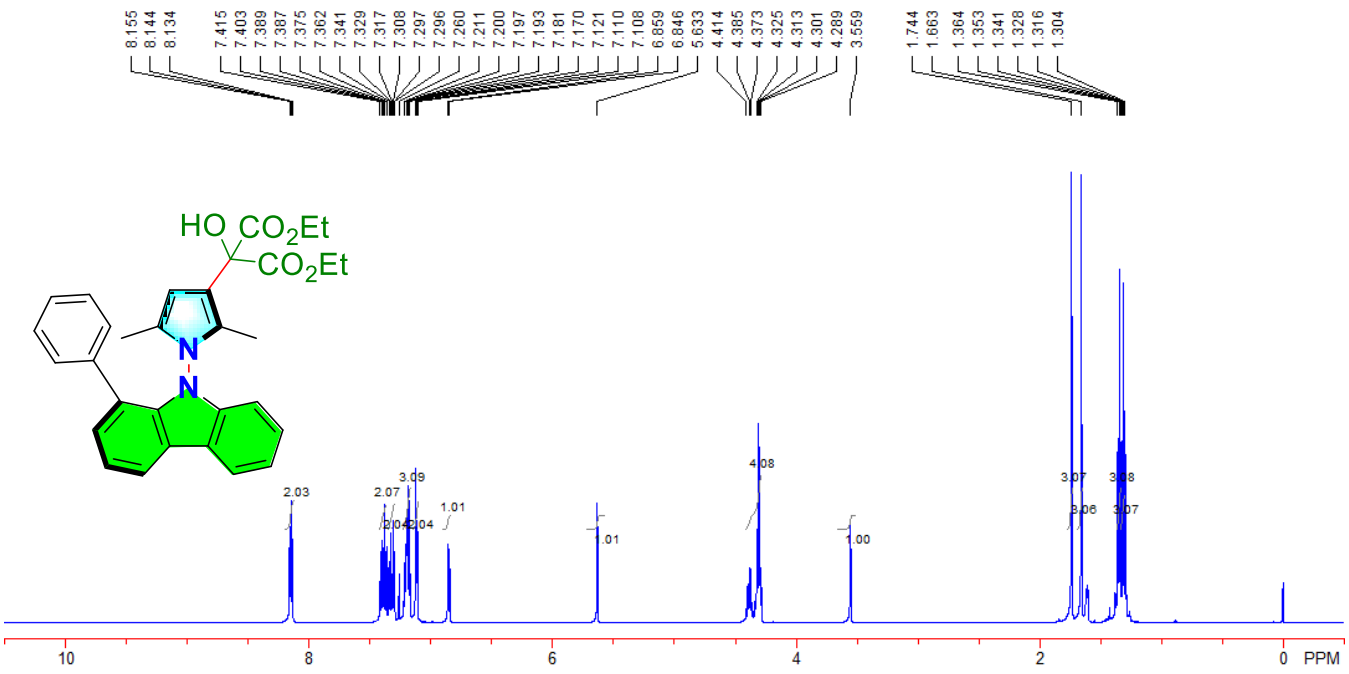


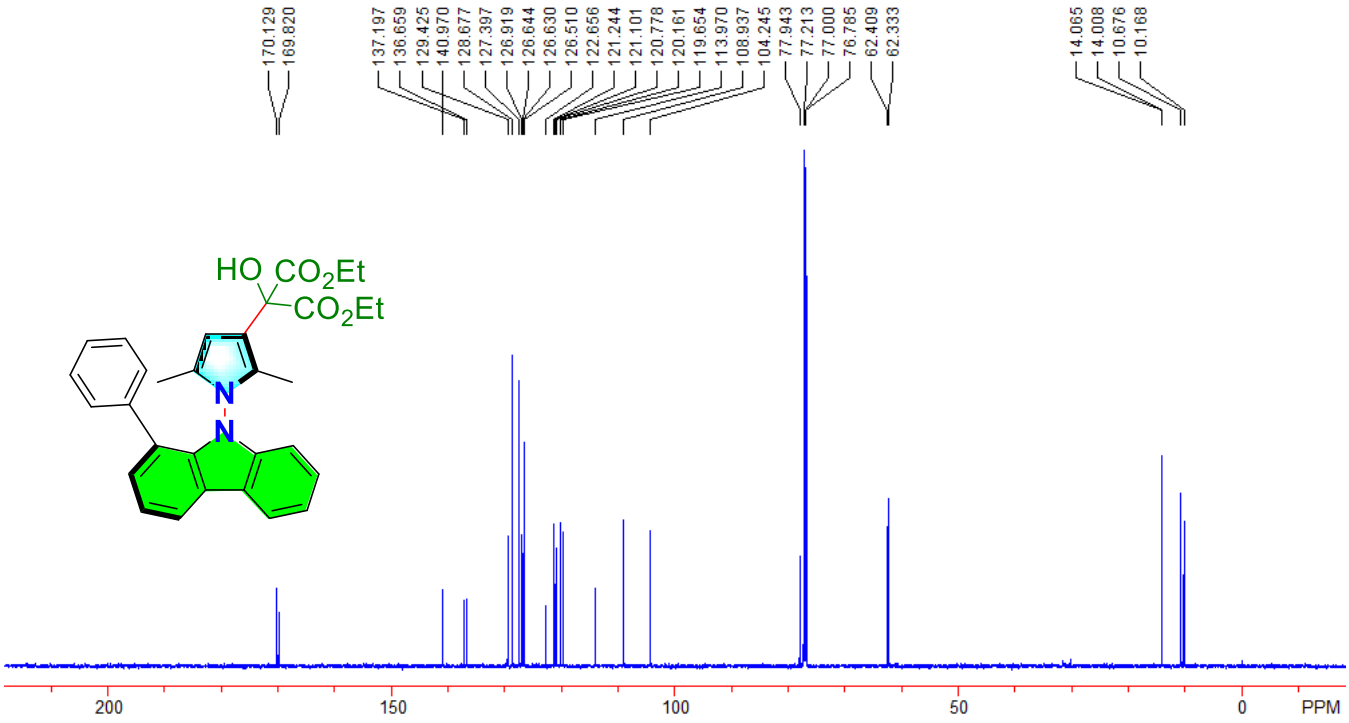
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3i**



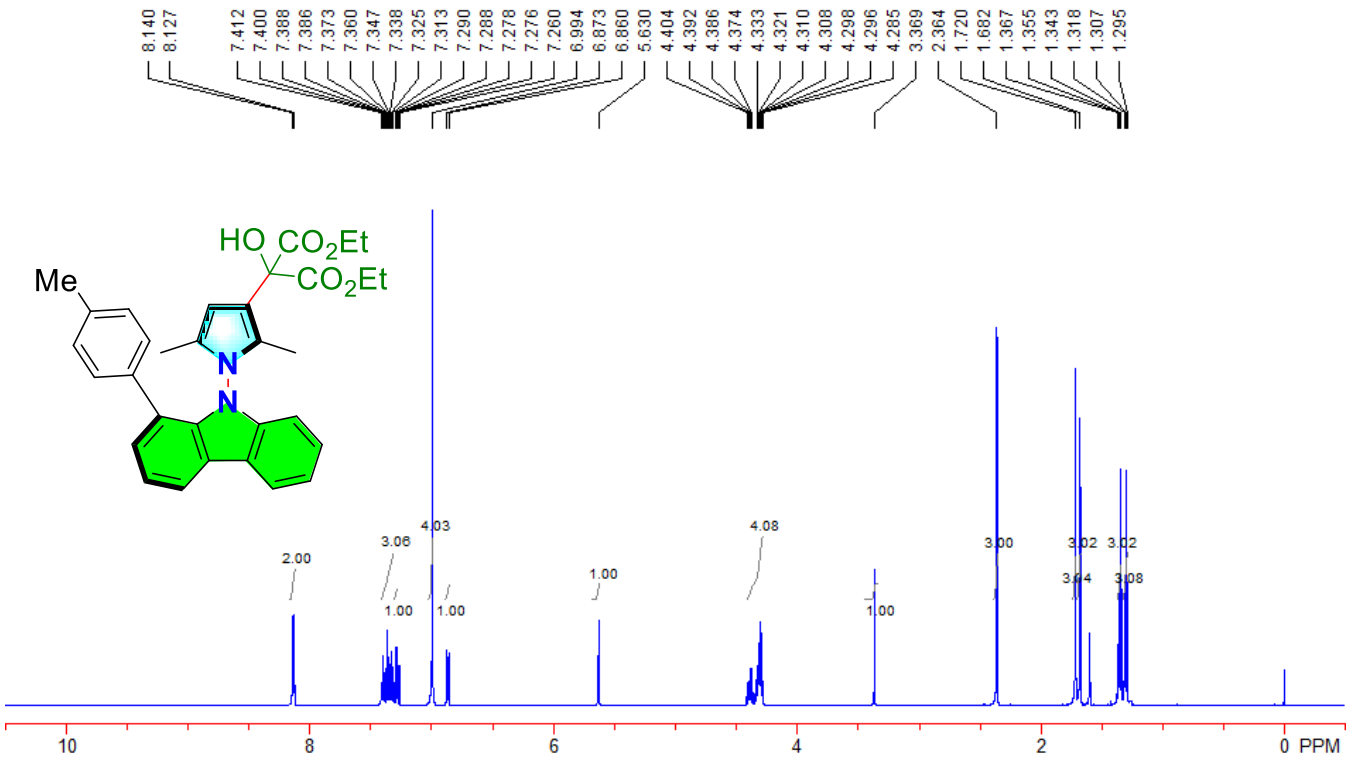


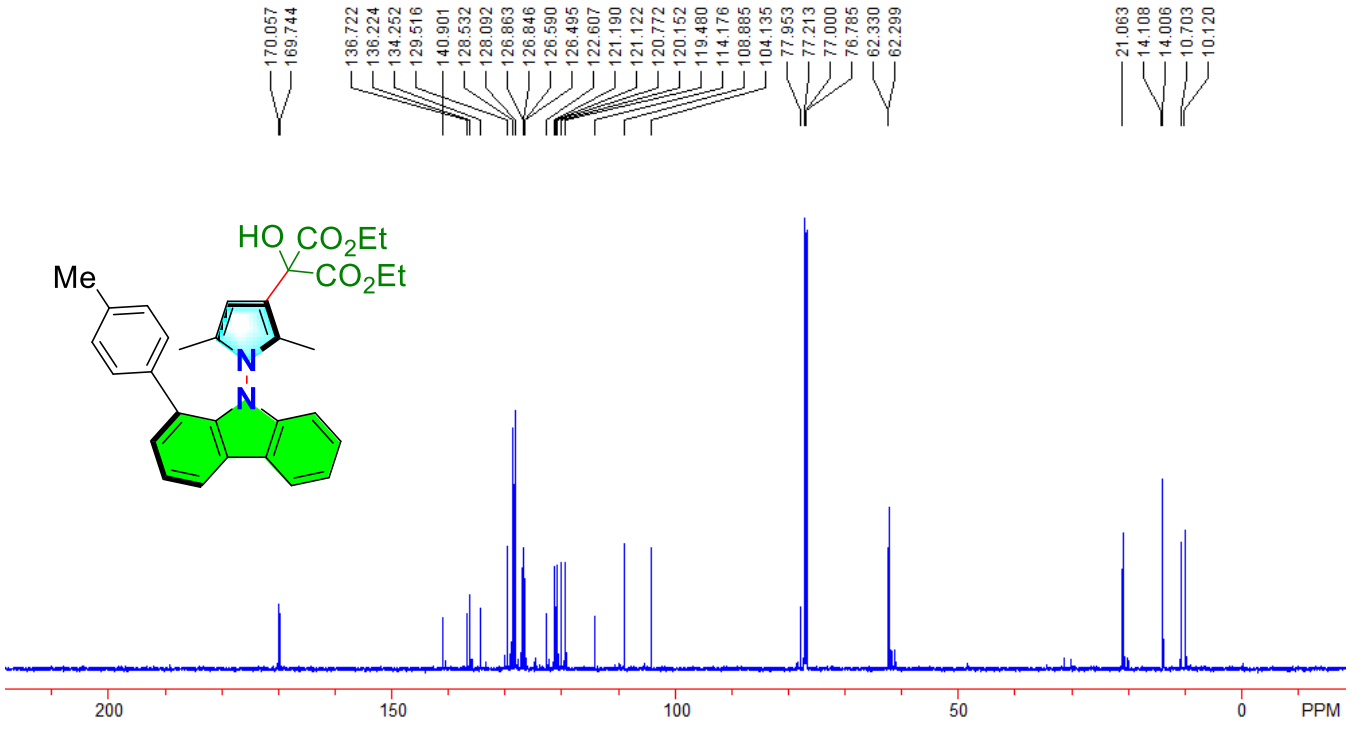
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3j**



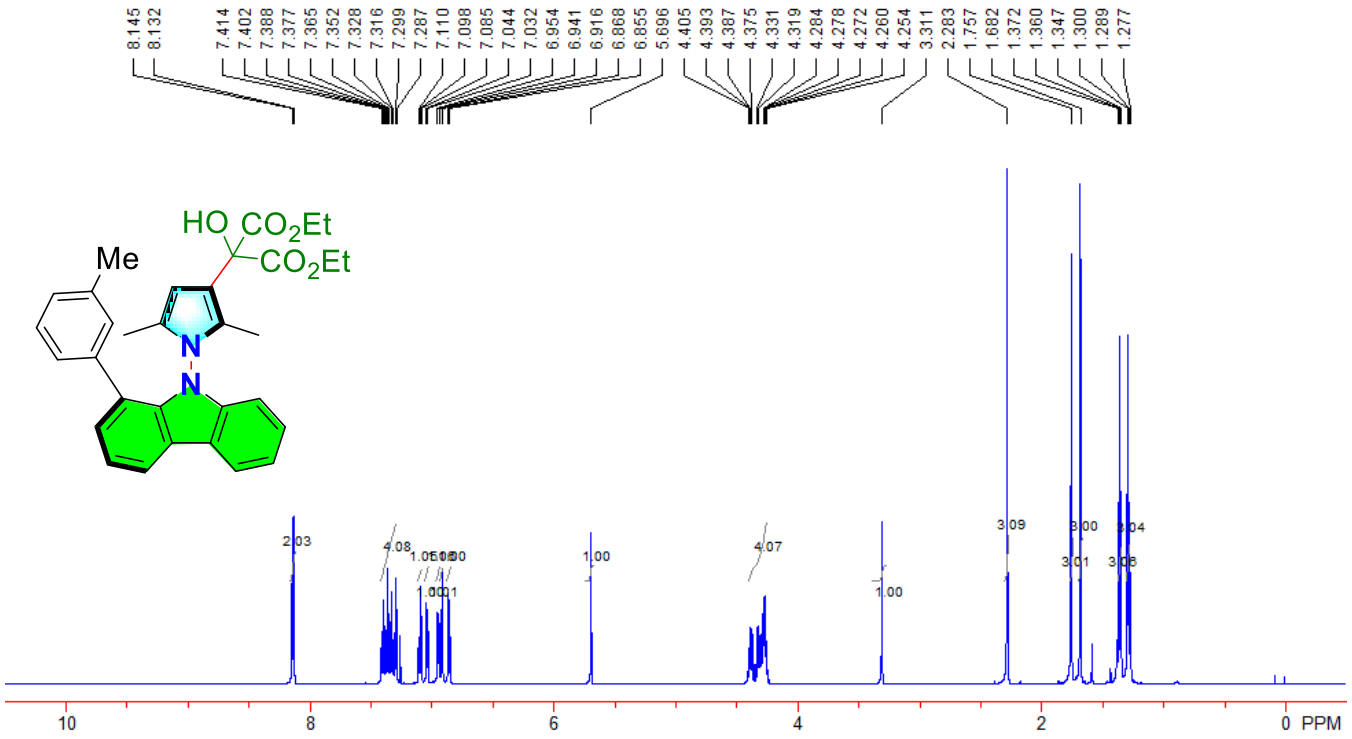


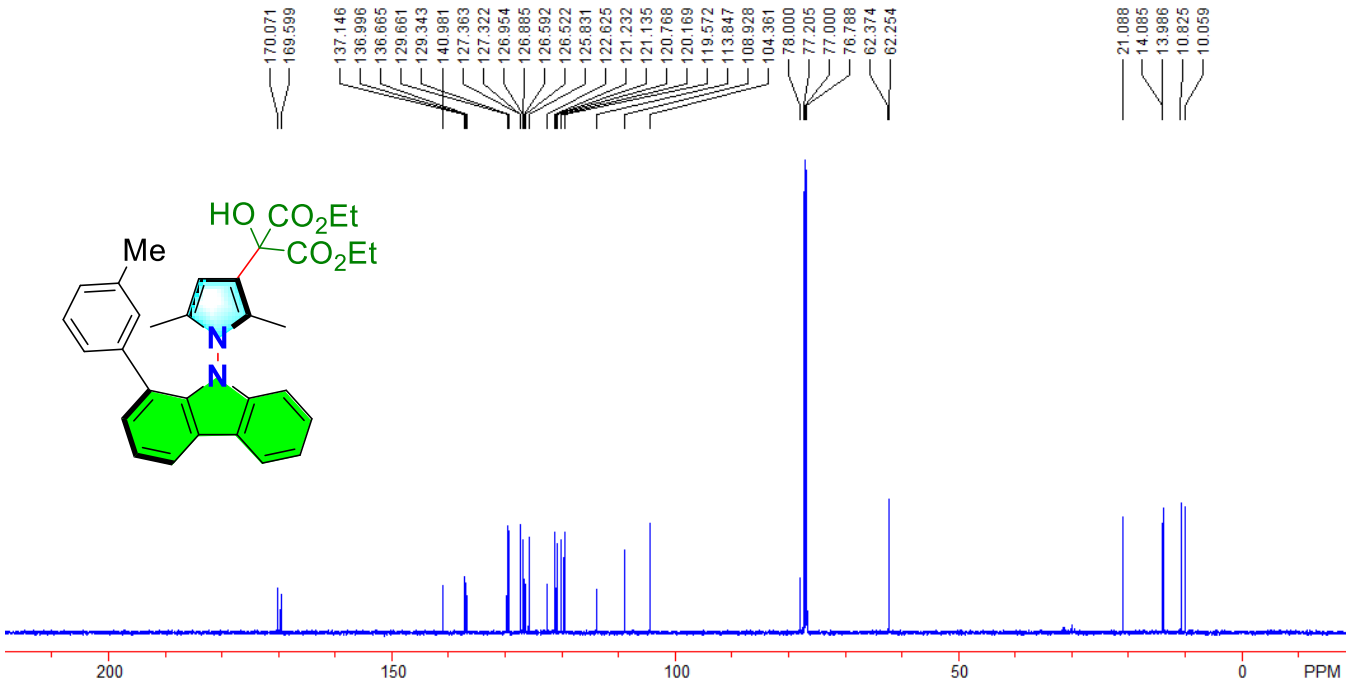
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3k**



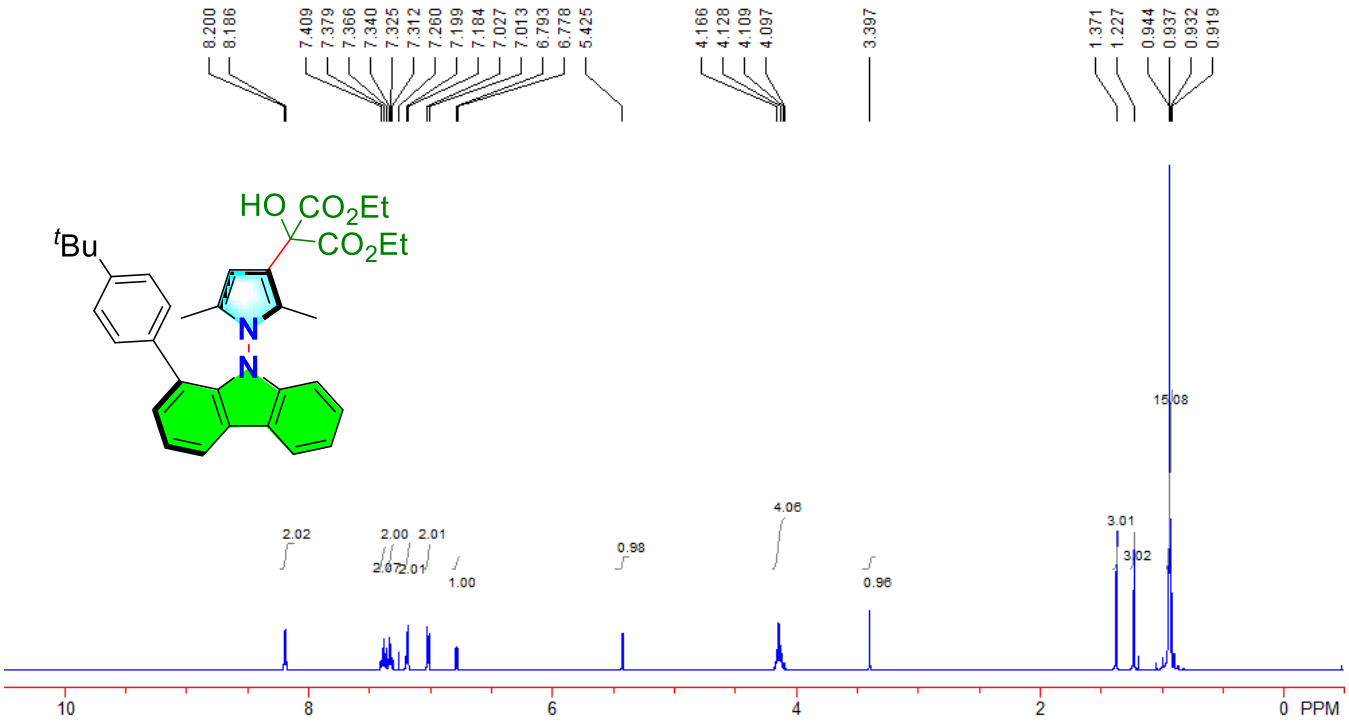


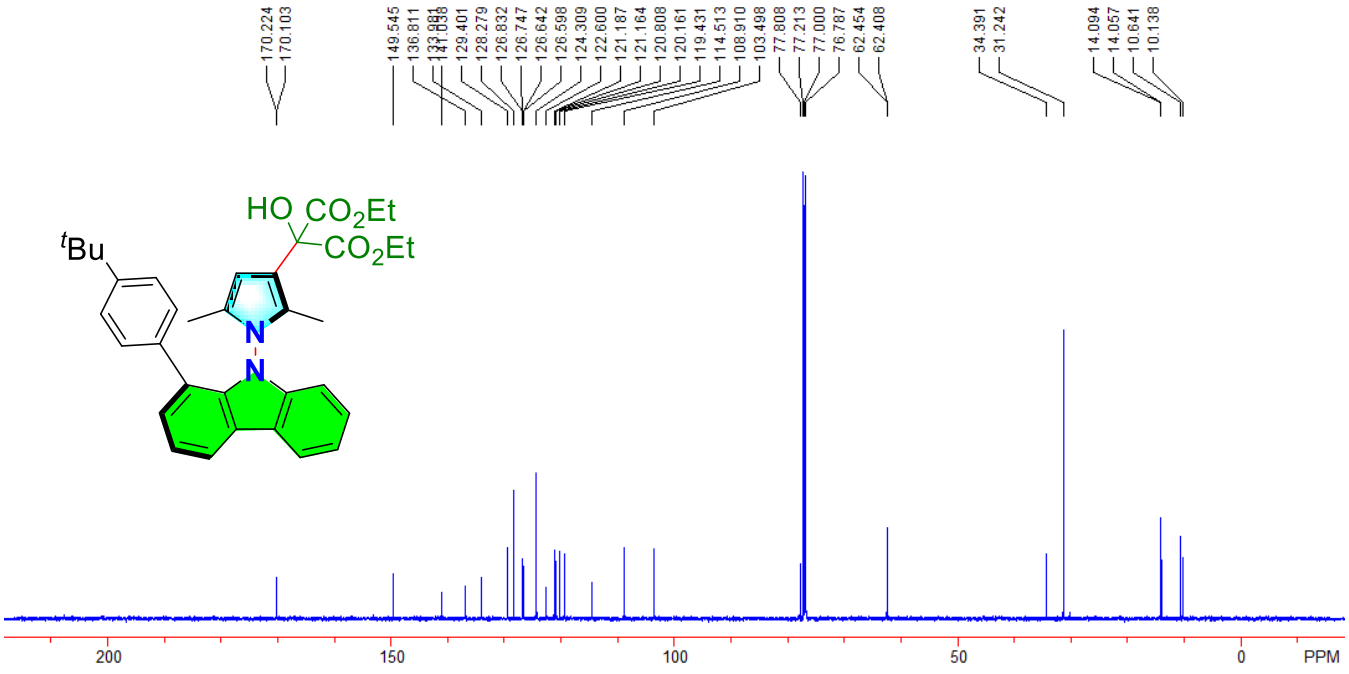
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3l**



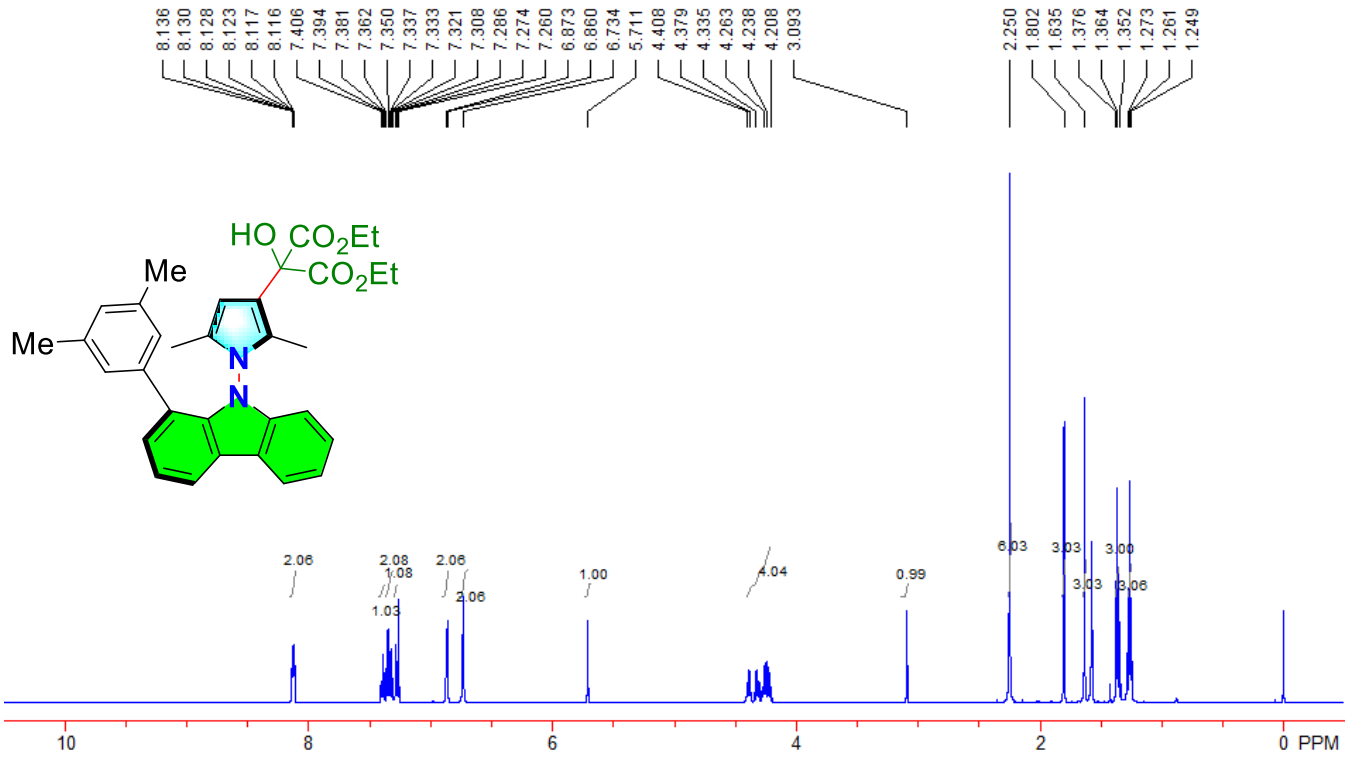


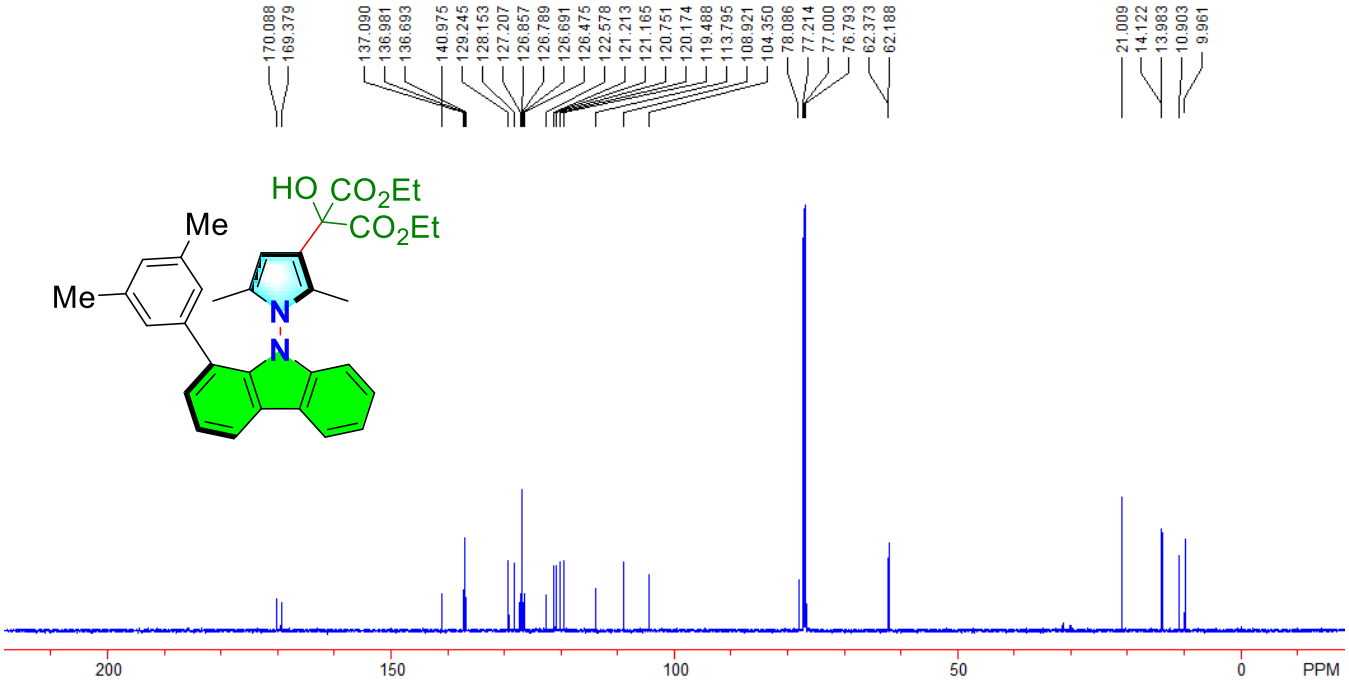
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3m**



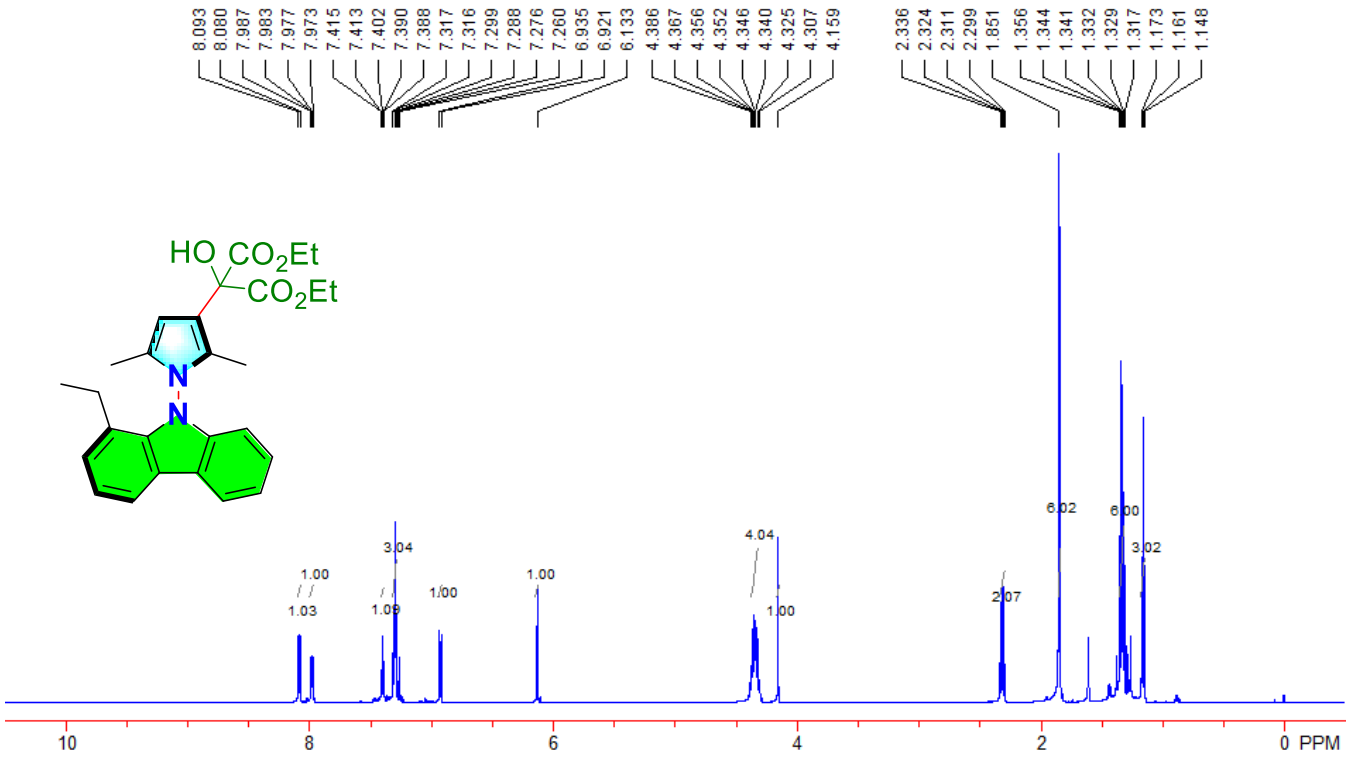


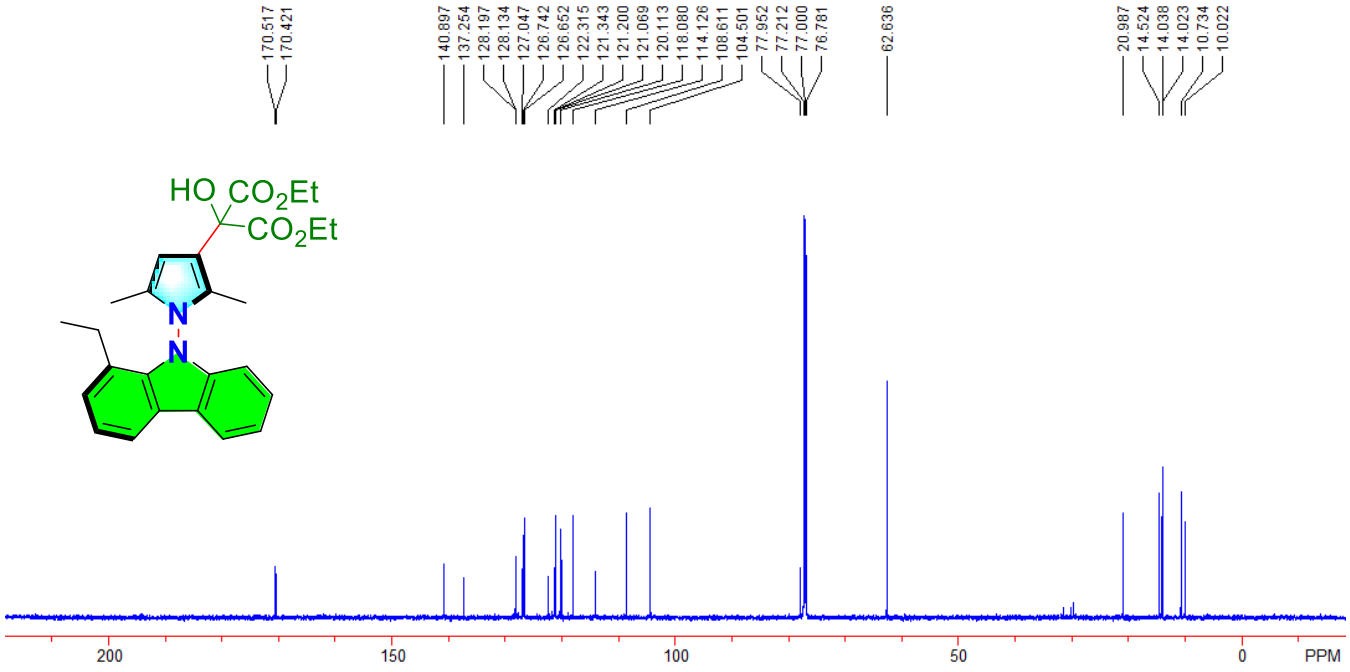
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3n**



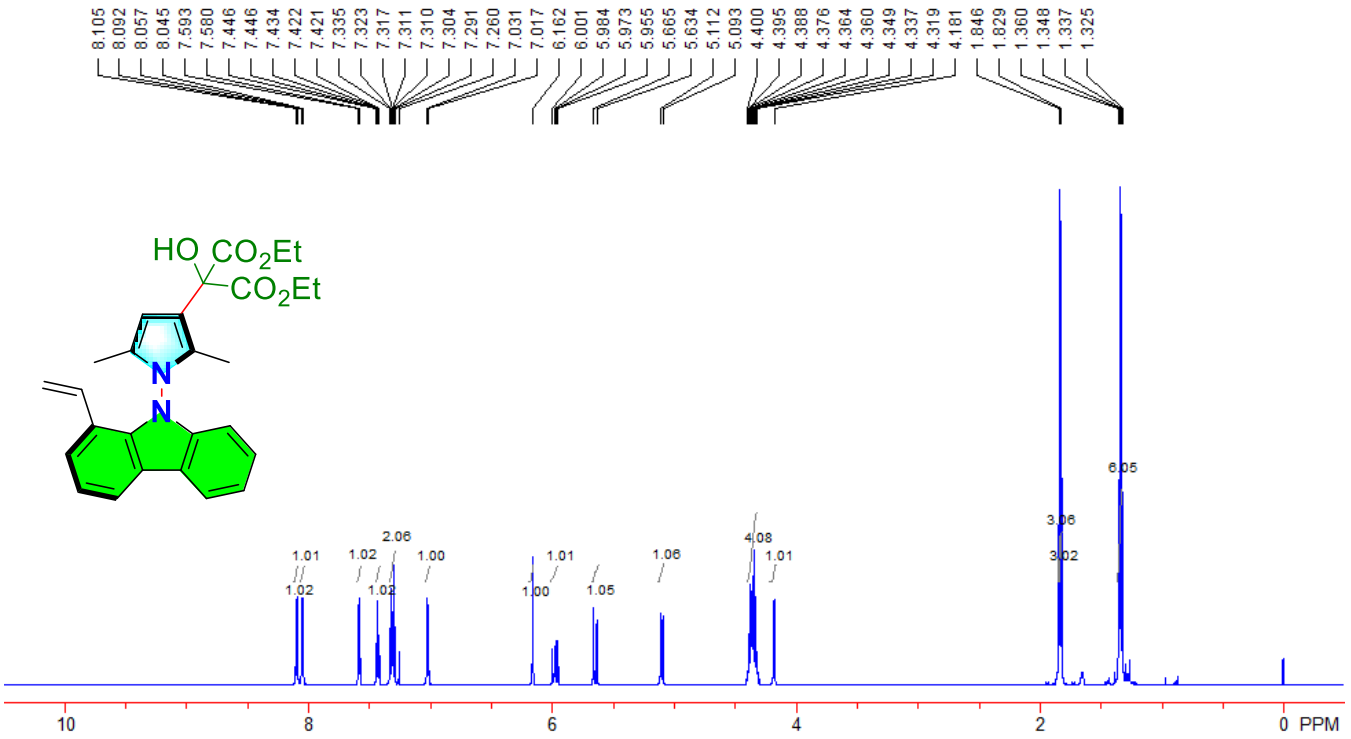


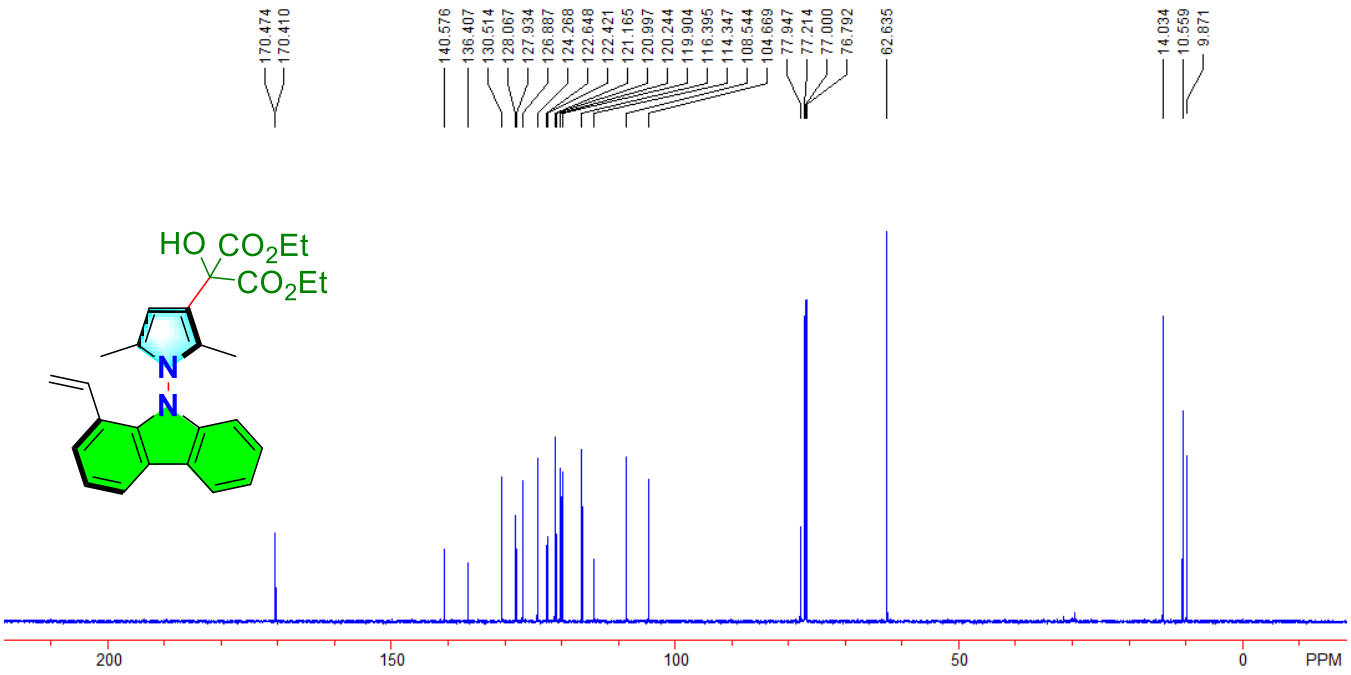
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3o**



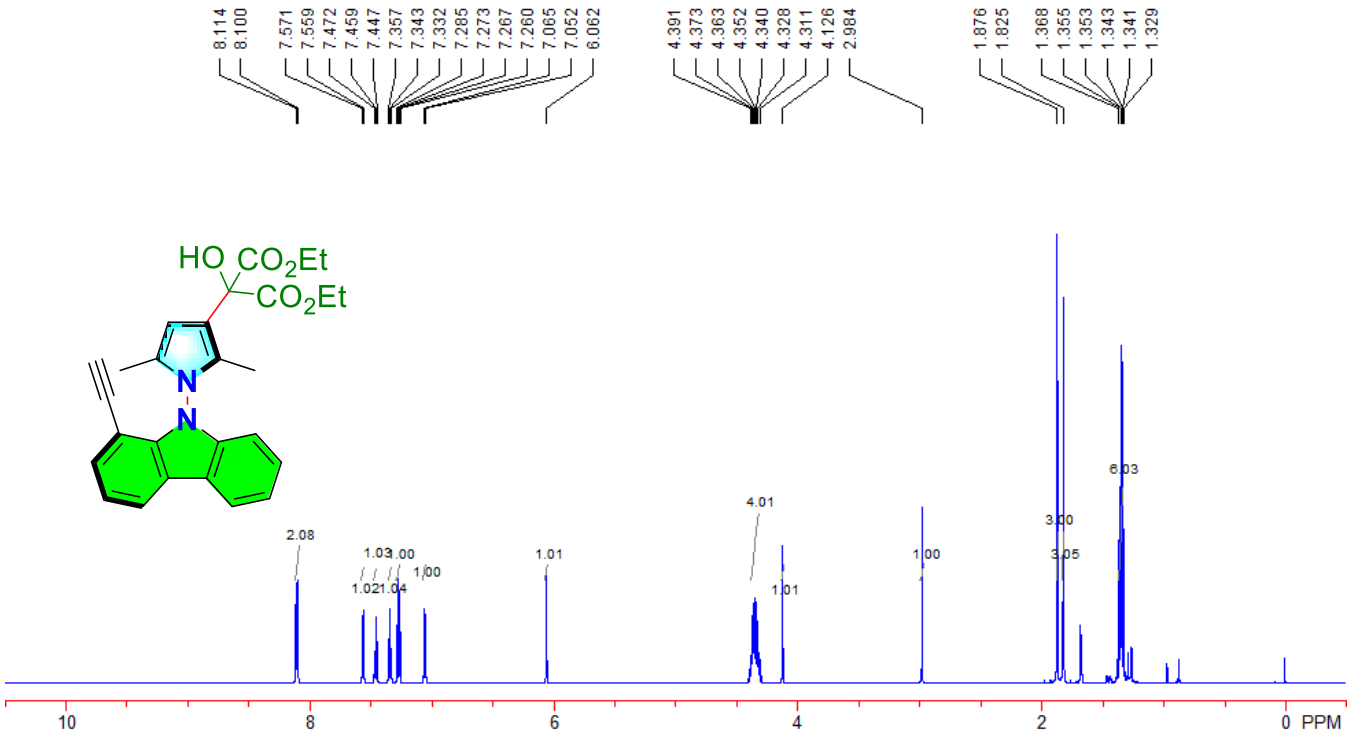


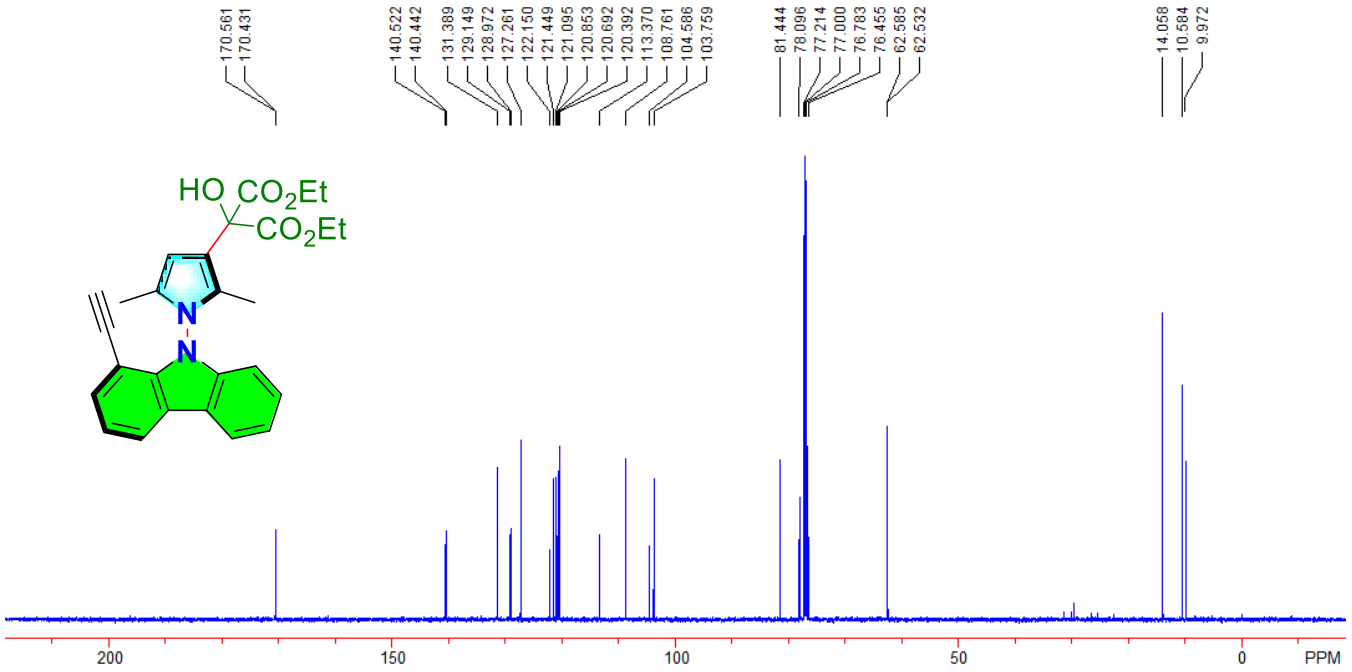
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3p**



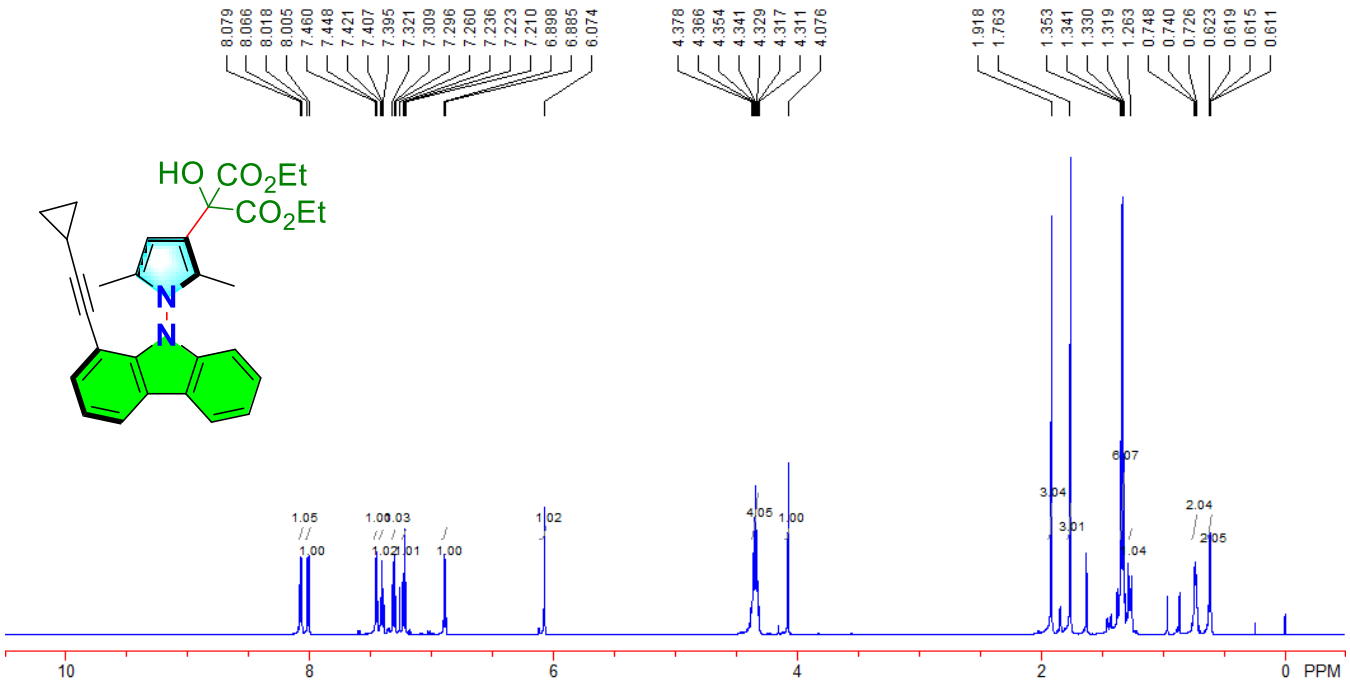


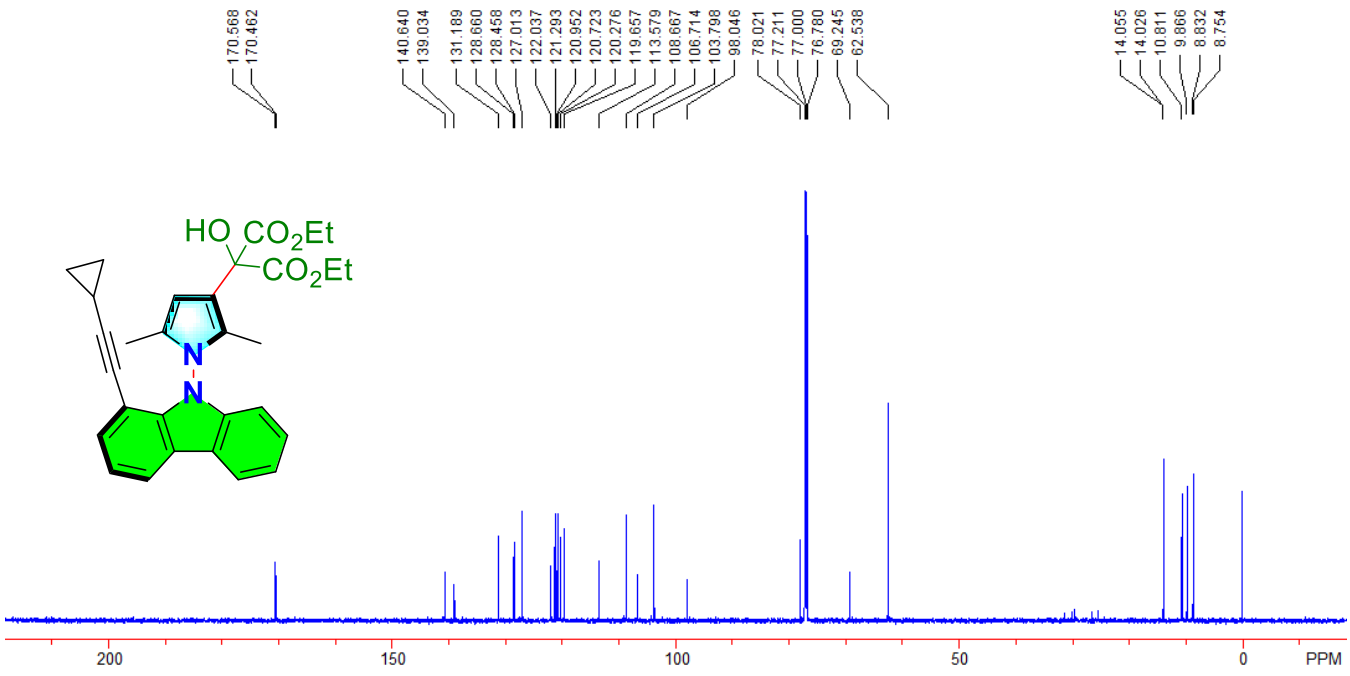
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3q**



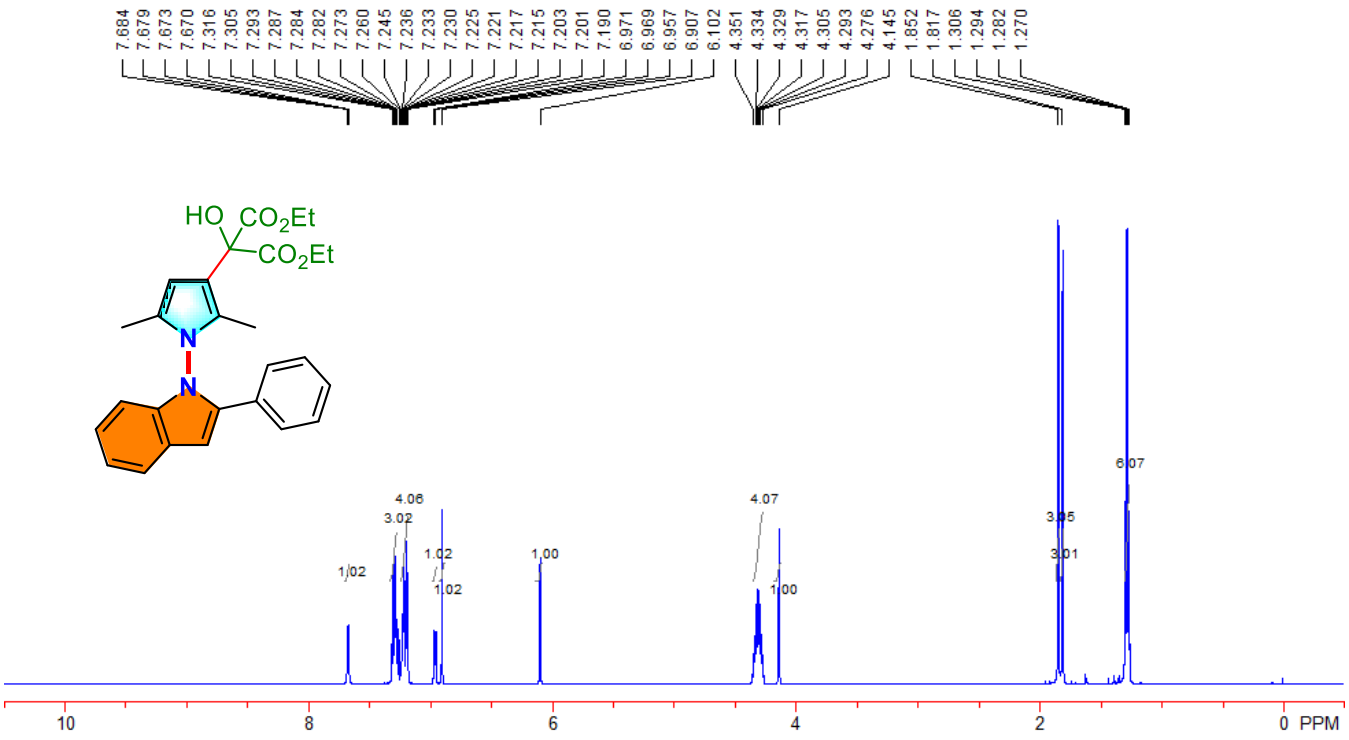


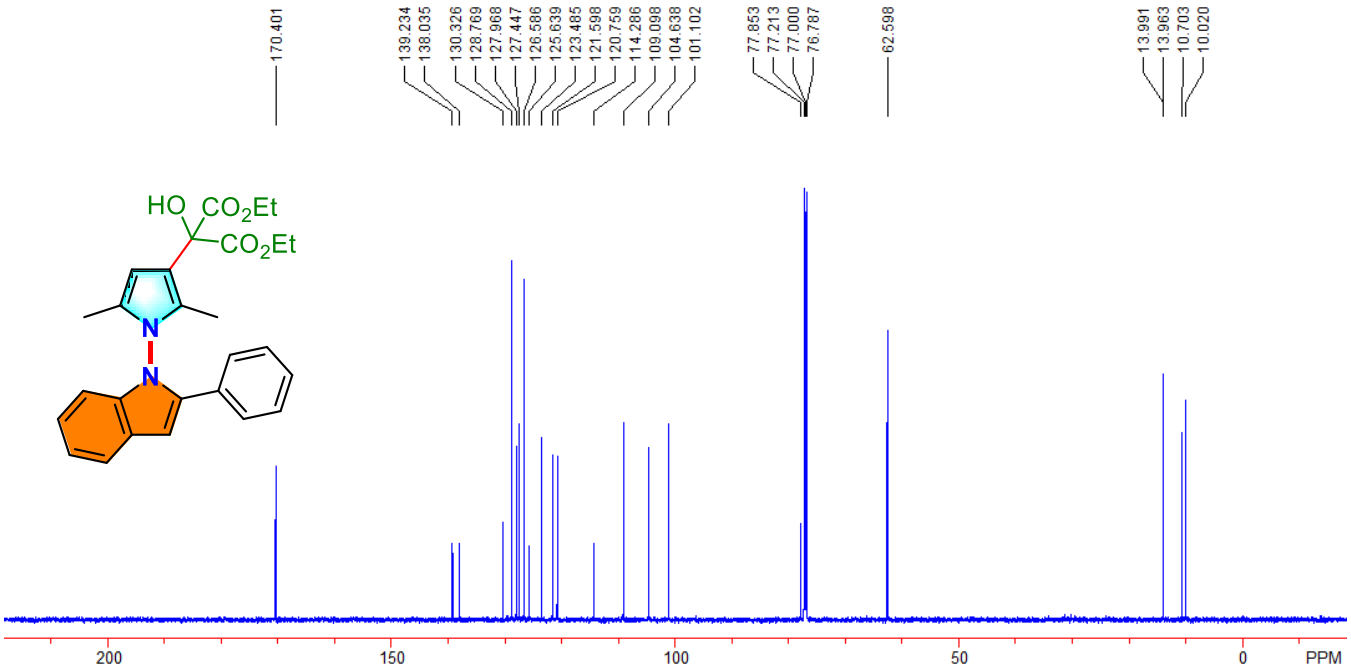
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(S)-3r**



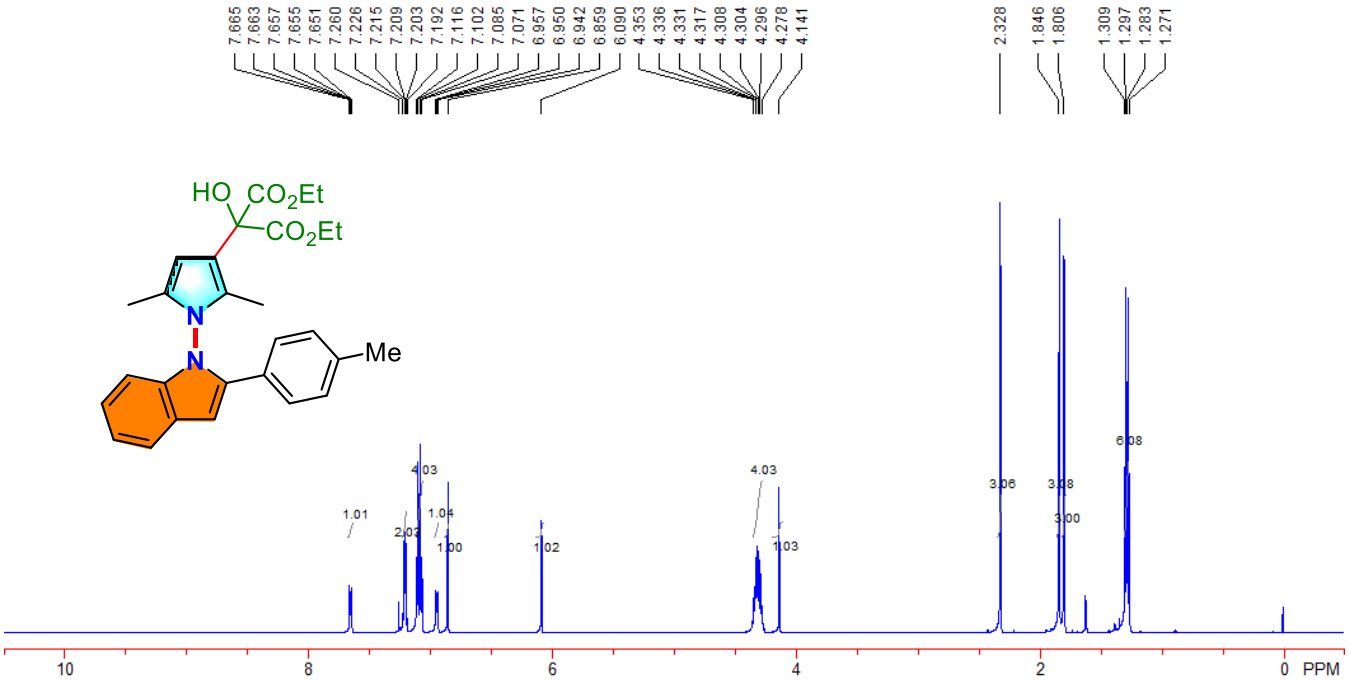


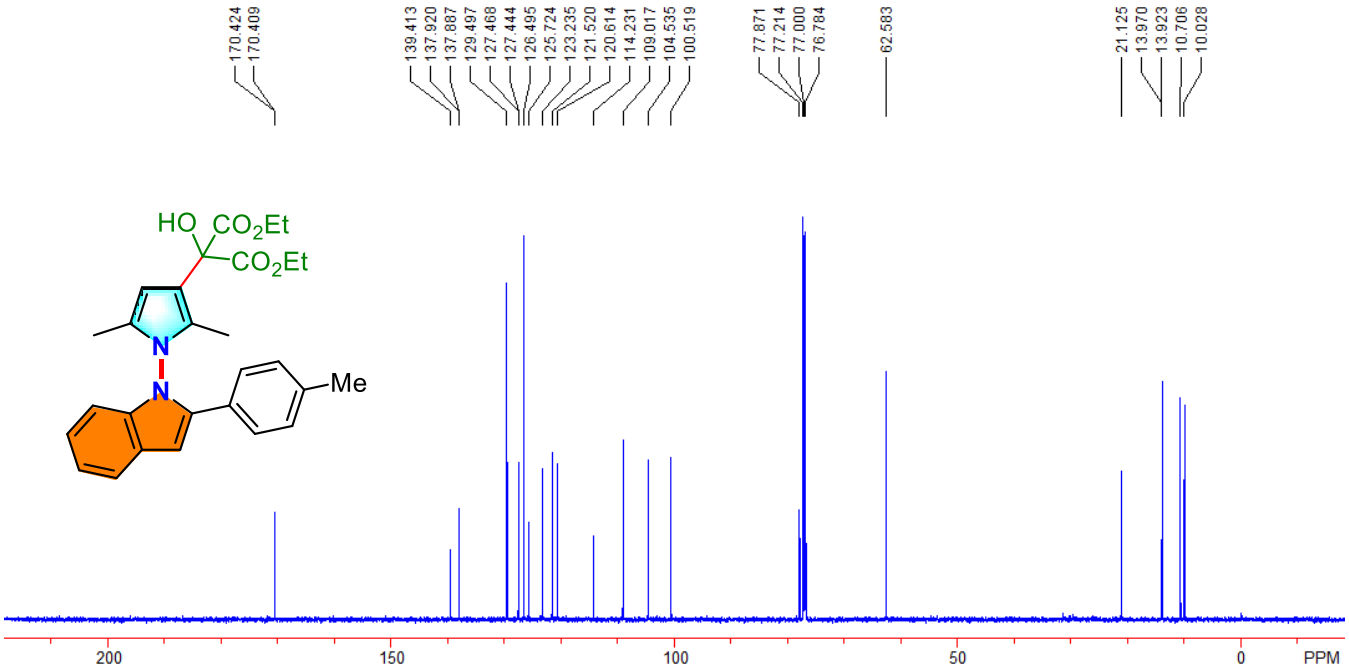
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(R)-3s**



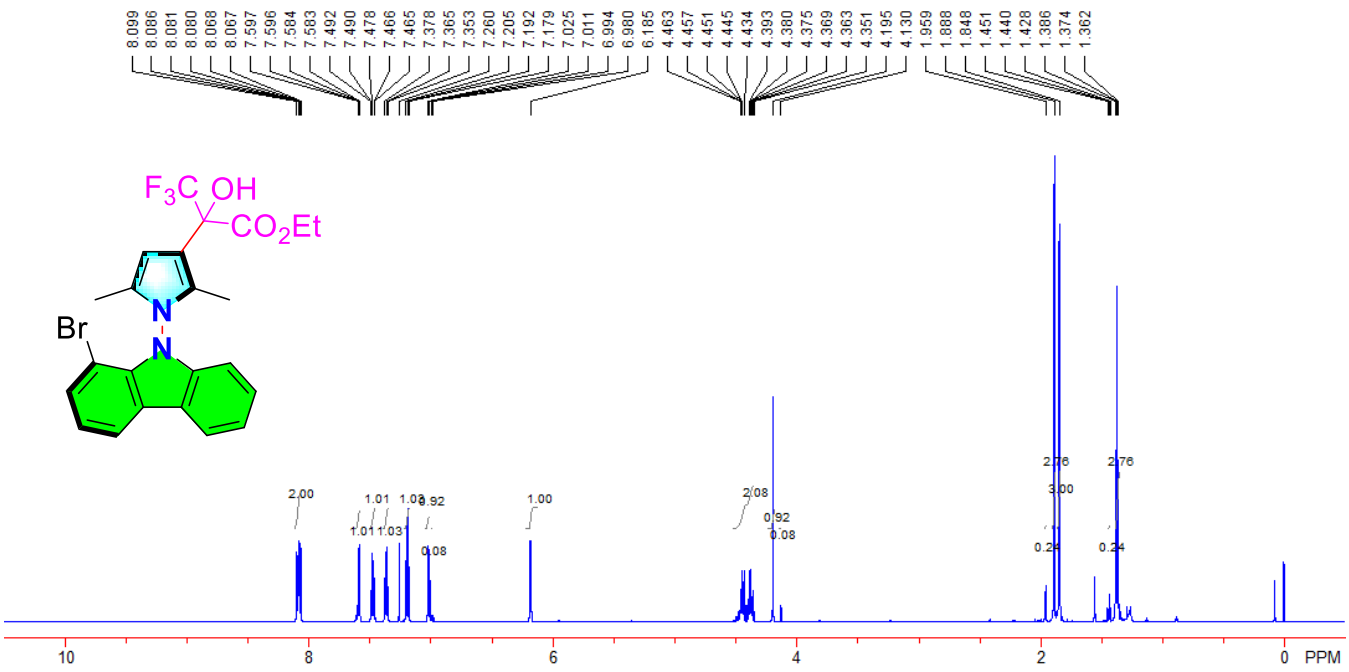


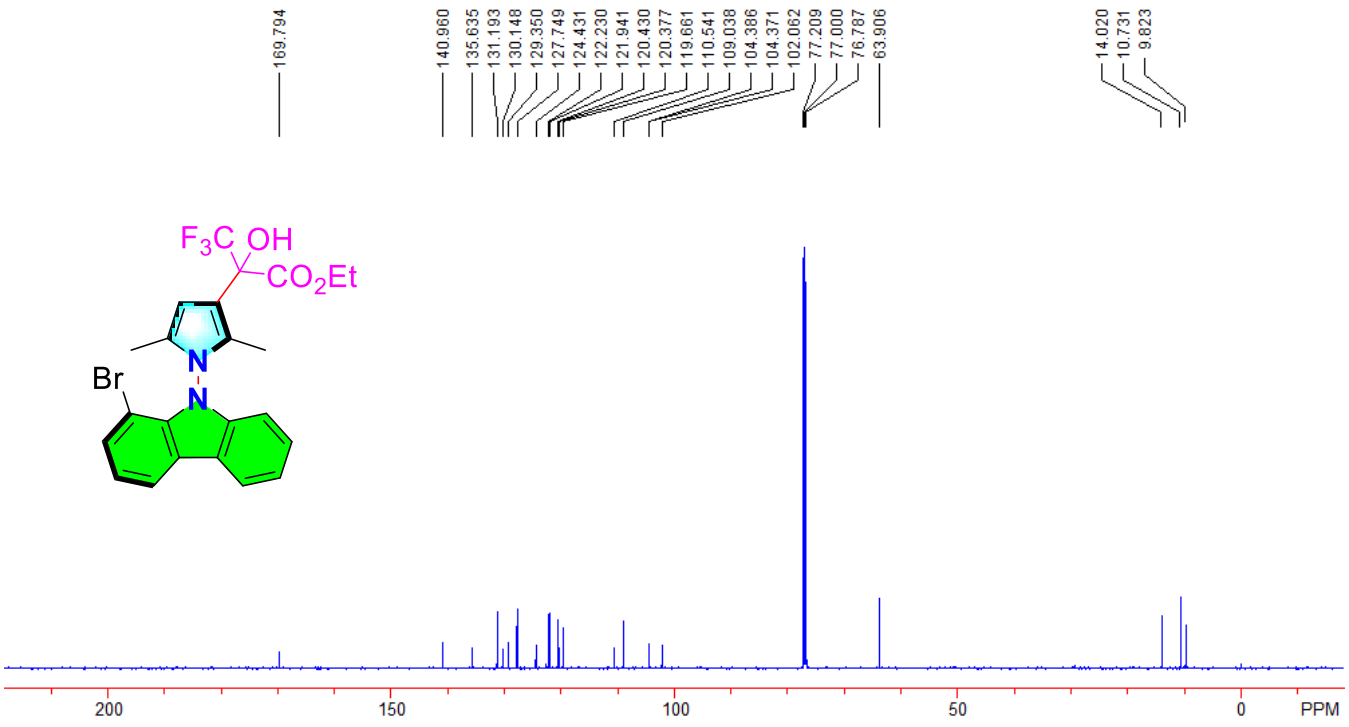
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(R)-3t**

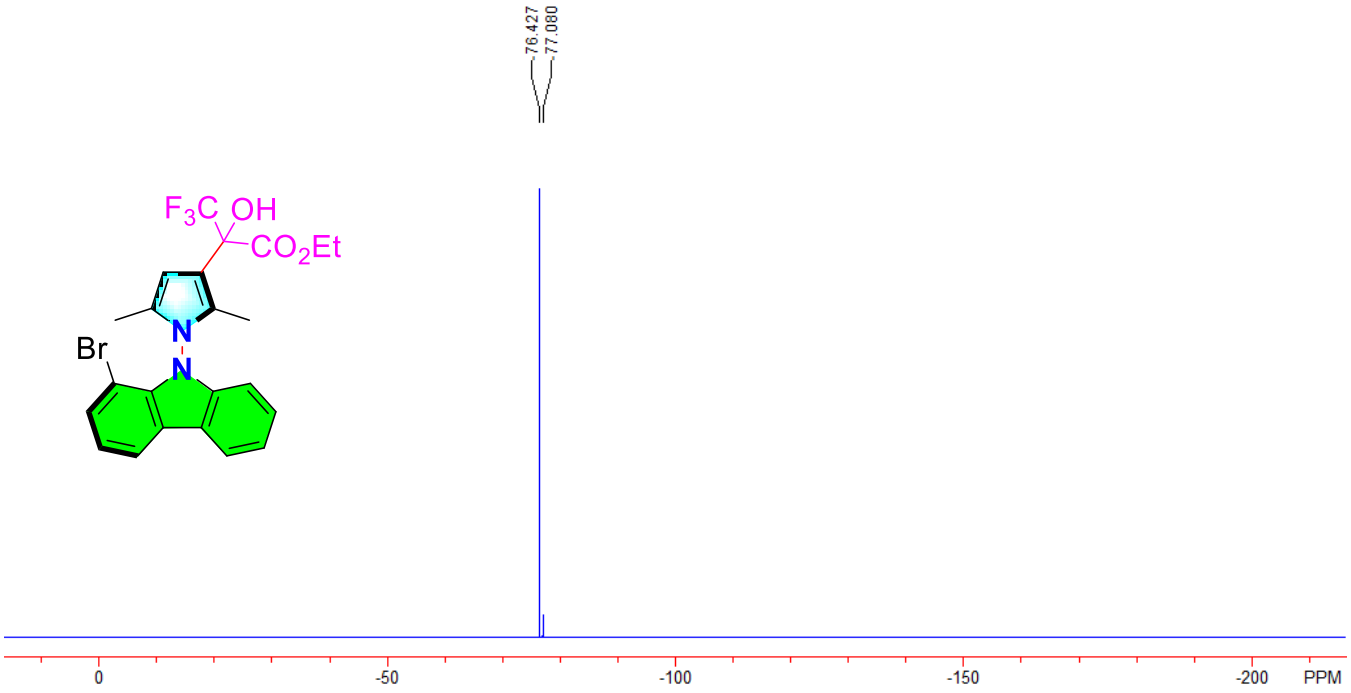




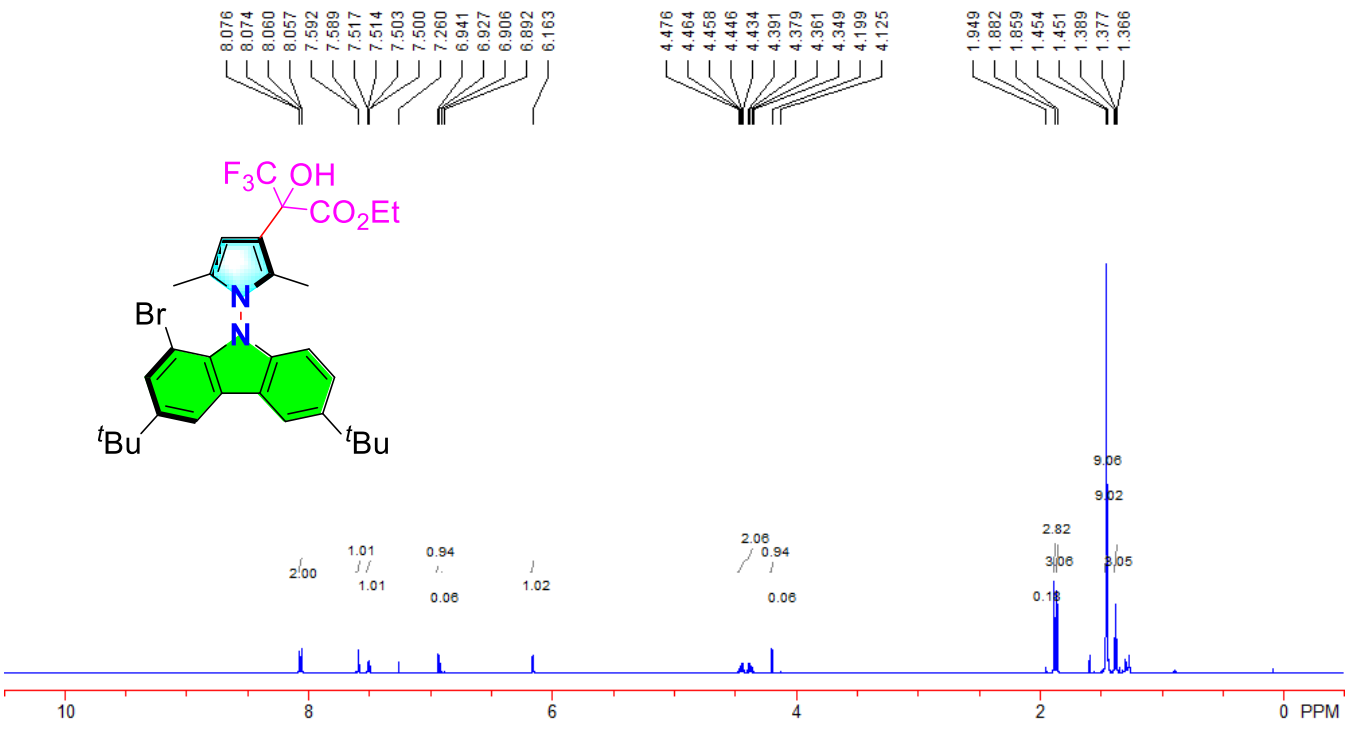
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4a**

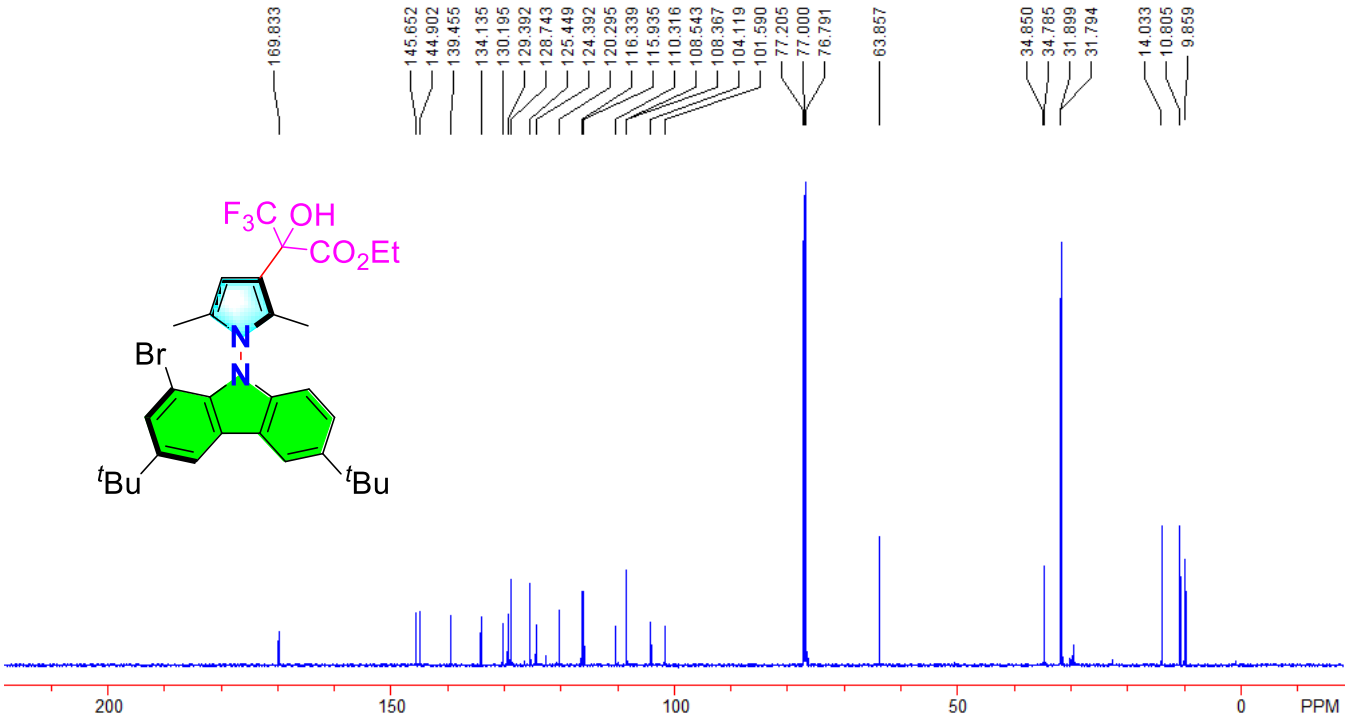


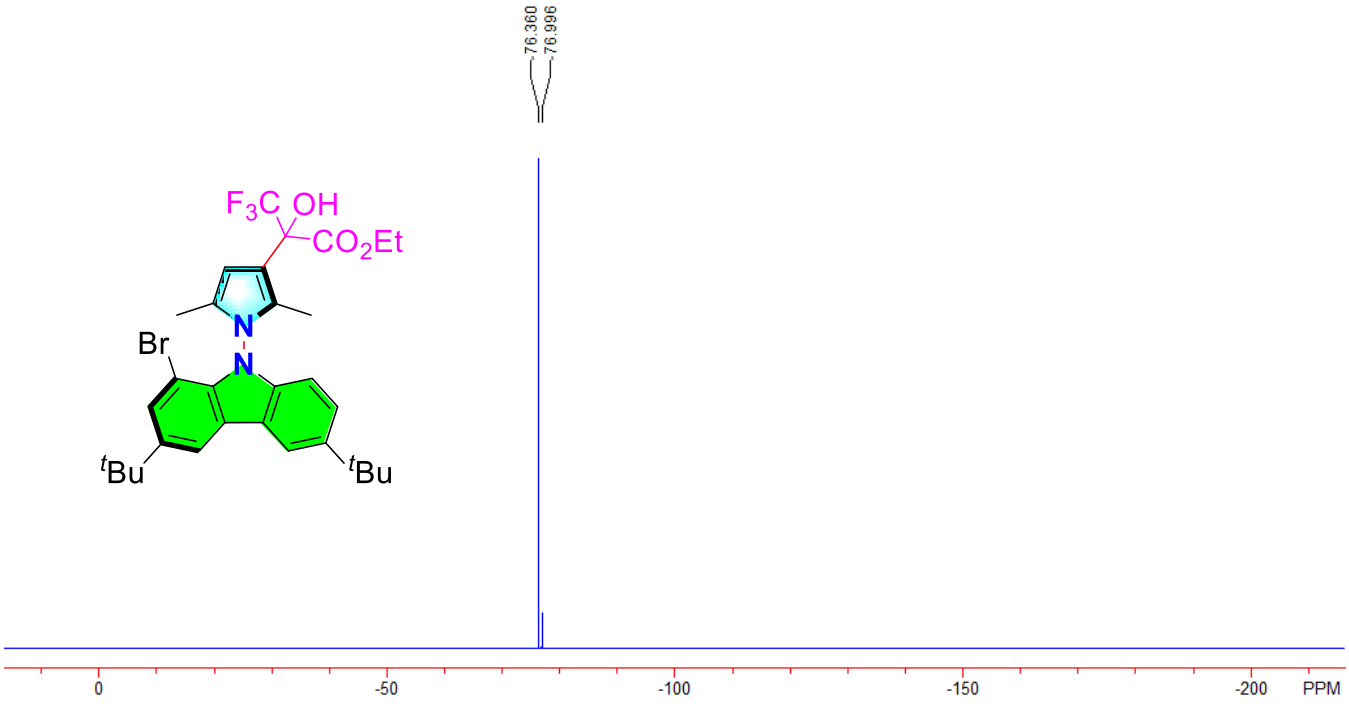



76.427
77.080
F3C OH
CO2Et
Br
N
N
0
-50
-100
-150
-200
PPM

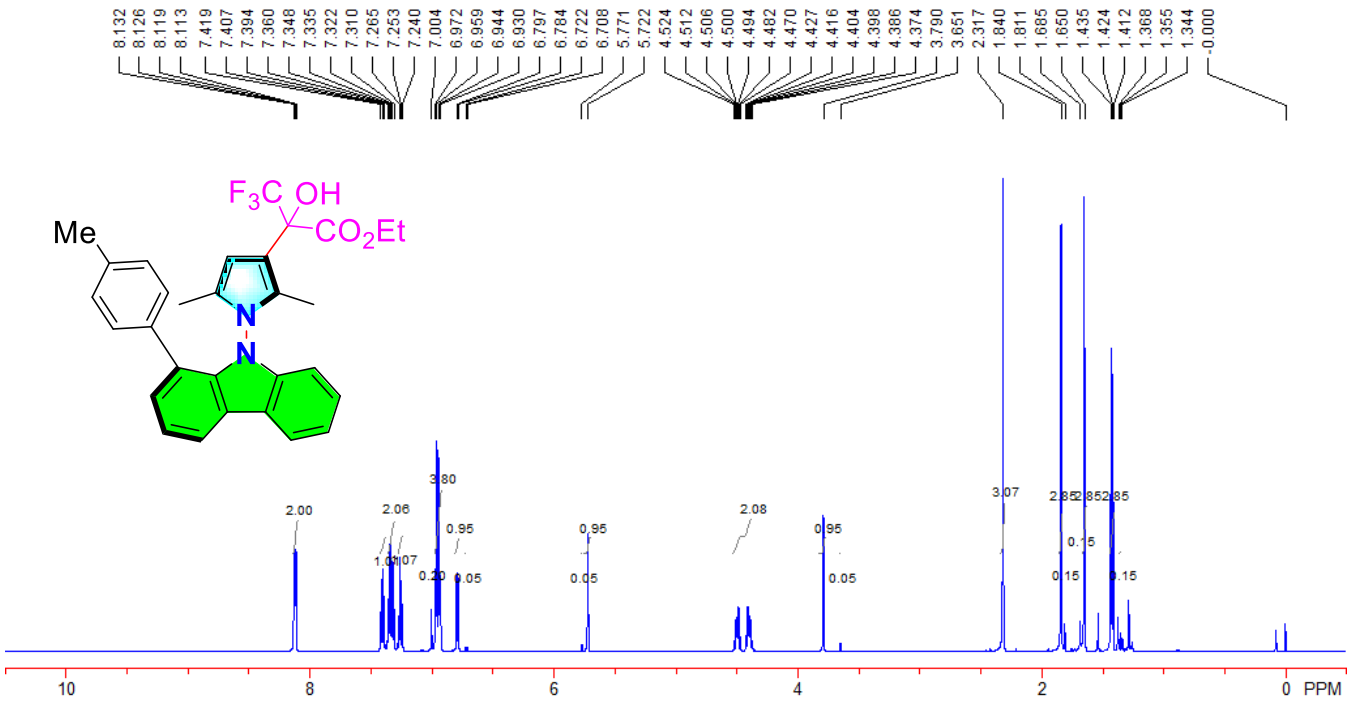
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4b**

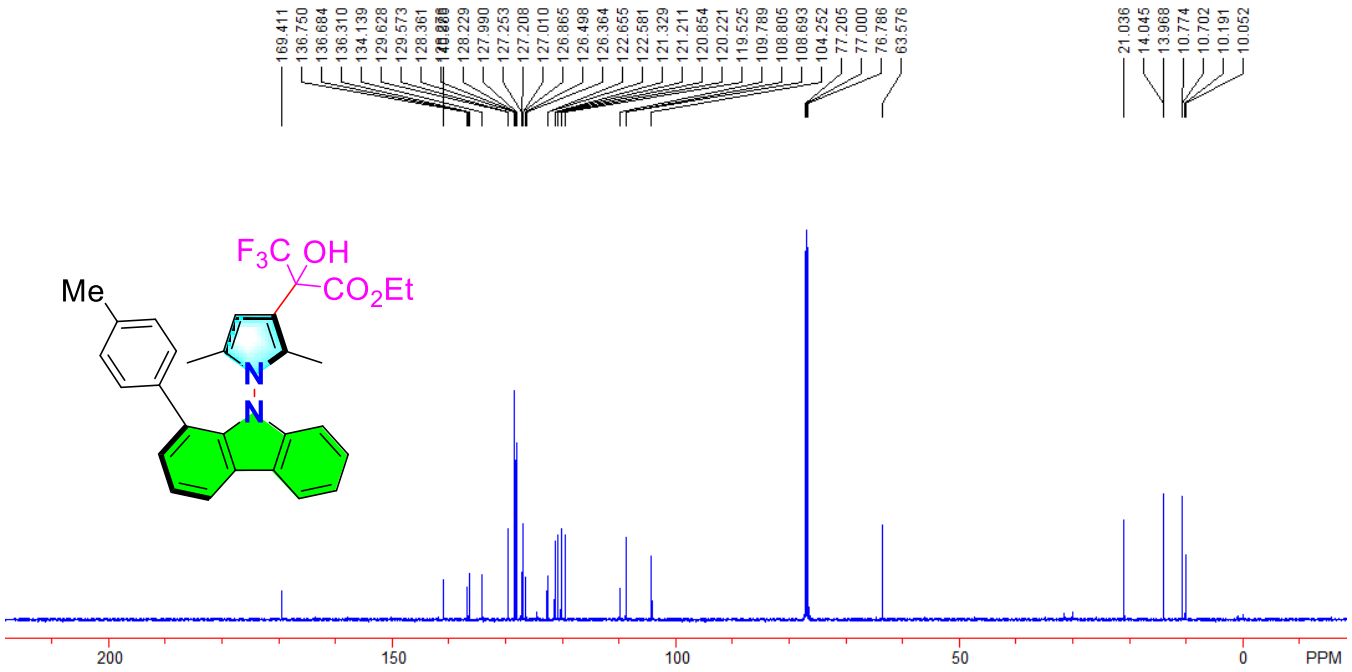


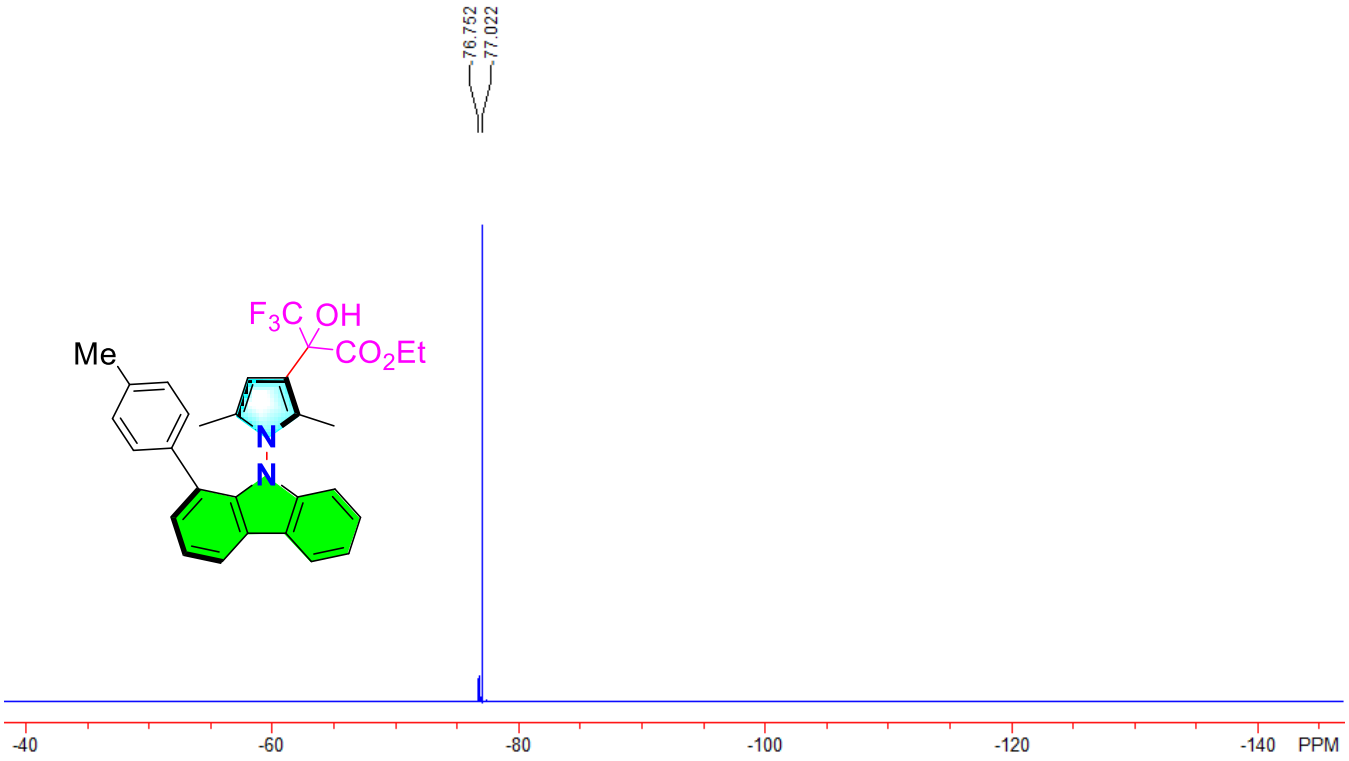



76.360
76.996
F3C OH
CO2Et
N
N
Br
tBu
tBu
0
-50
-100
-150
-200
PPM

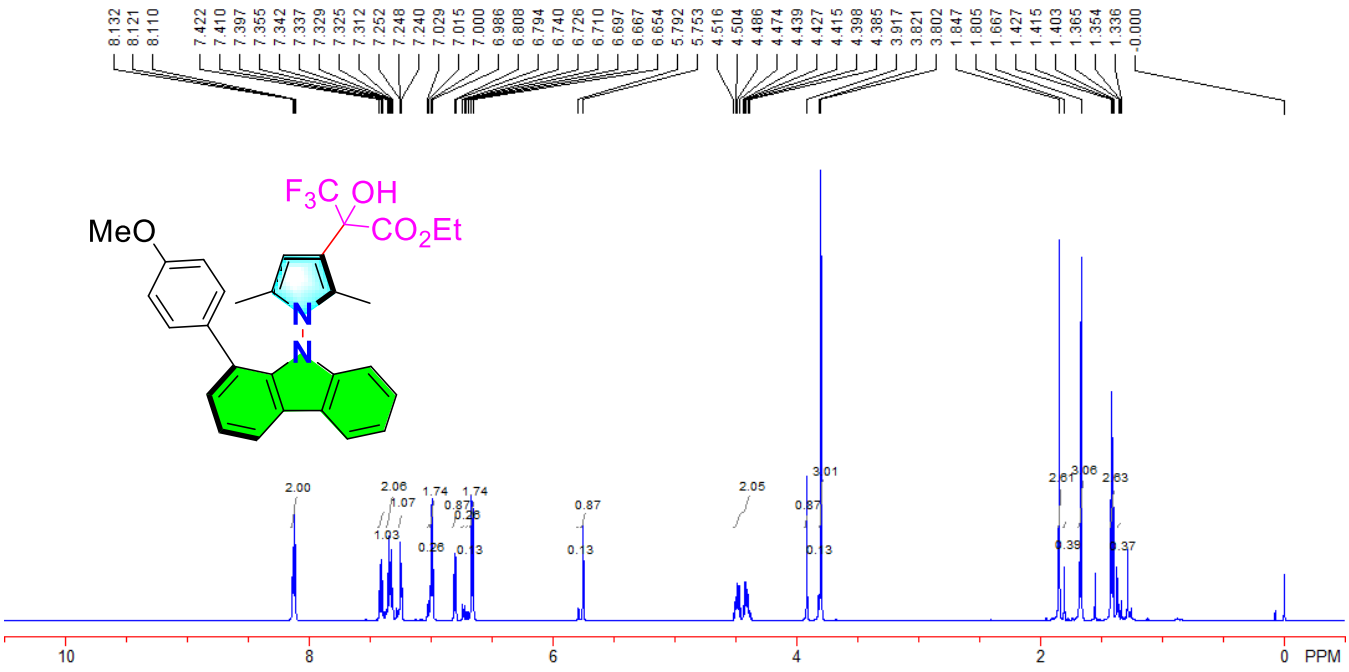
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4c**

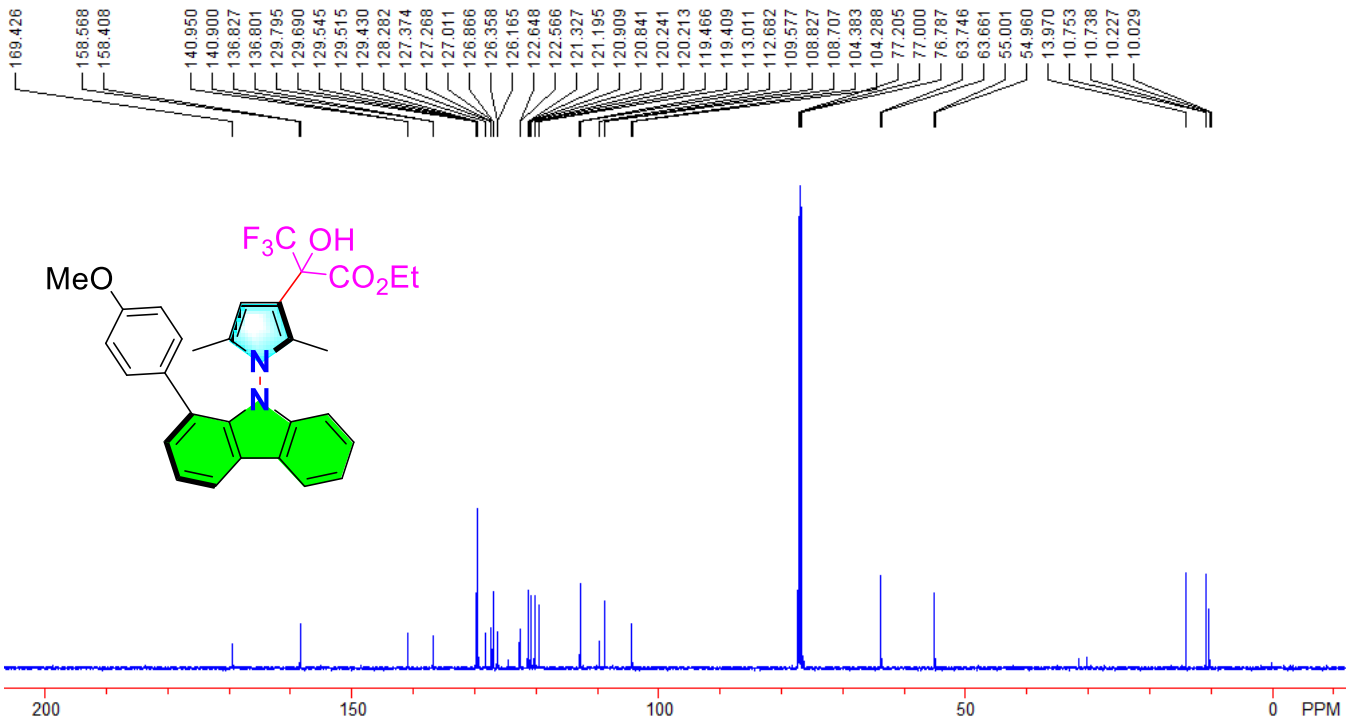


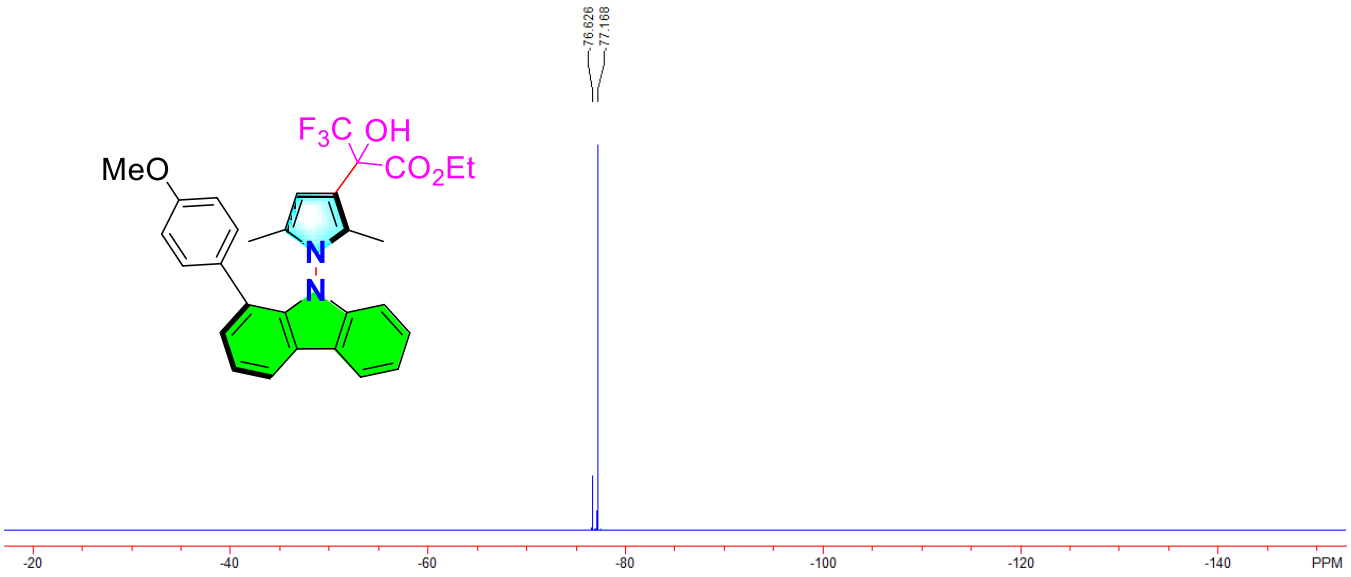



76.752
77.022
F3C OH
CO2Et
Me
N
N
-40
-60
-80
-100
-120
-140
PPM

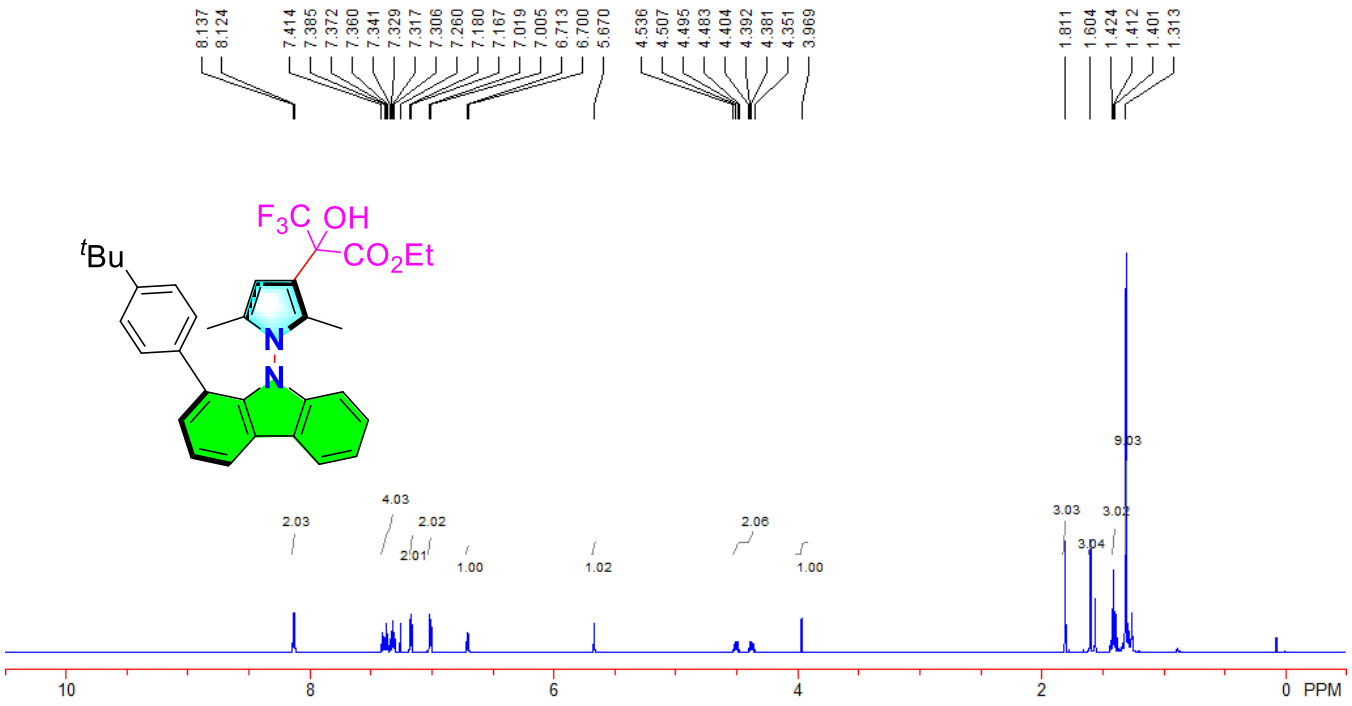
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4d**

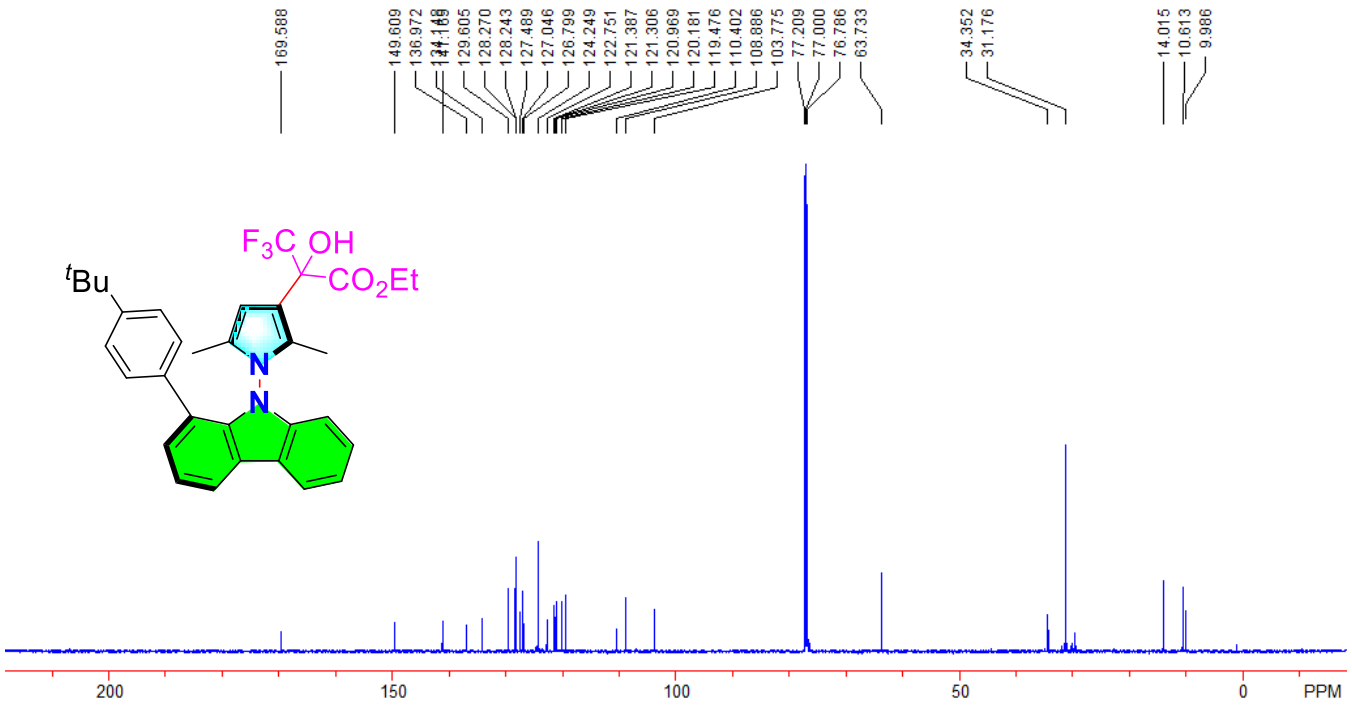


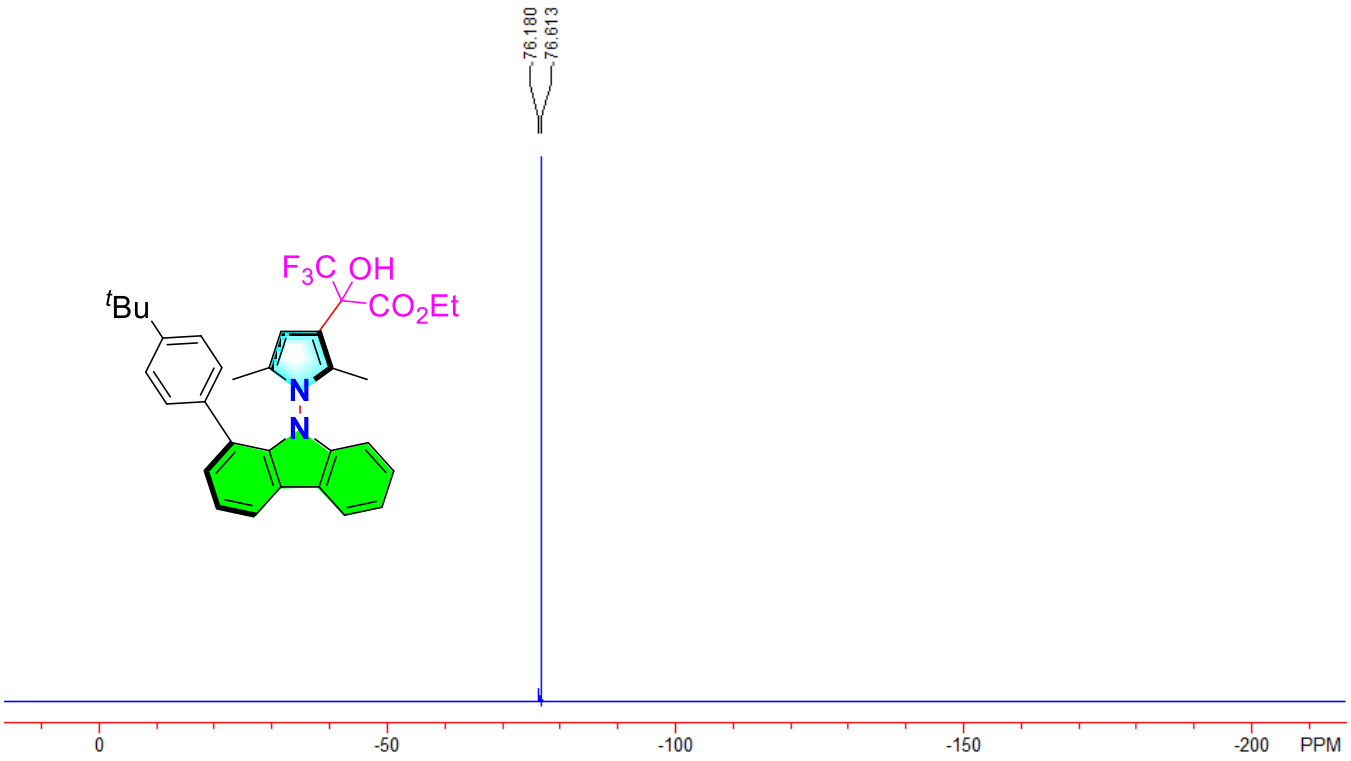



76.626
77.168
F3C OH
CO2Et
MeO
N
N
-20
-40
-60
-80
-100
-120
-140
PPM

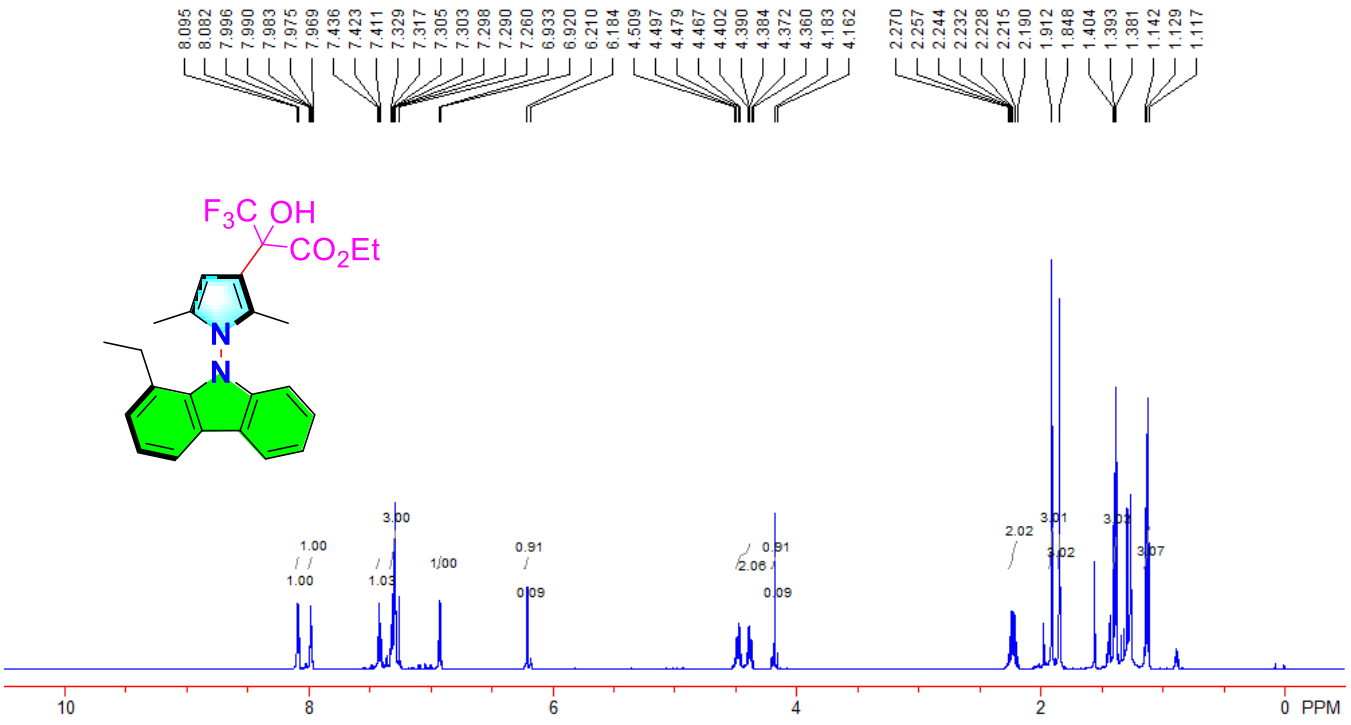
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4e**

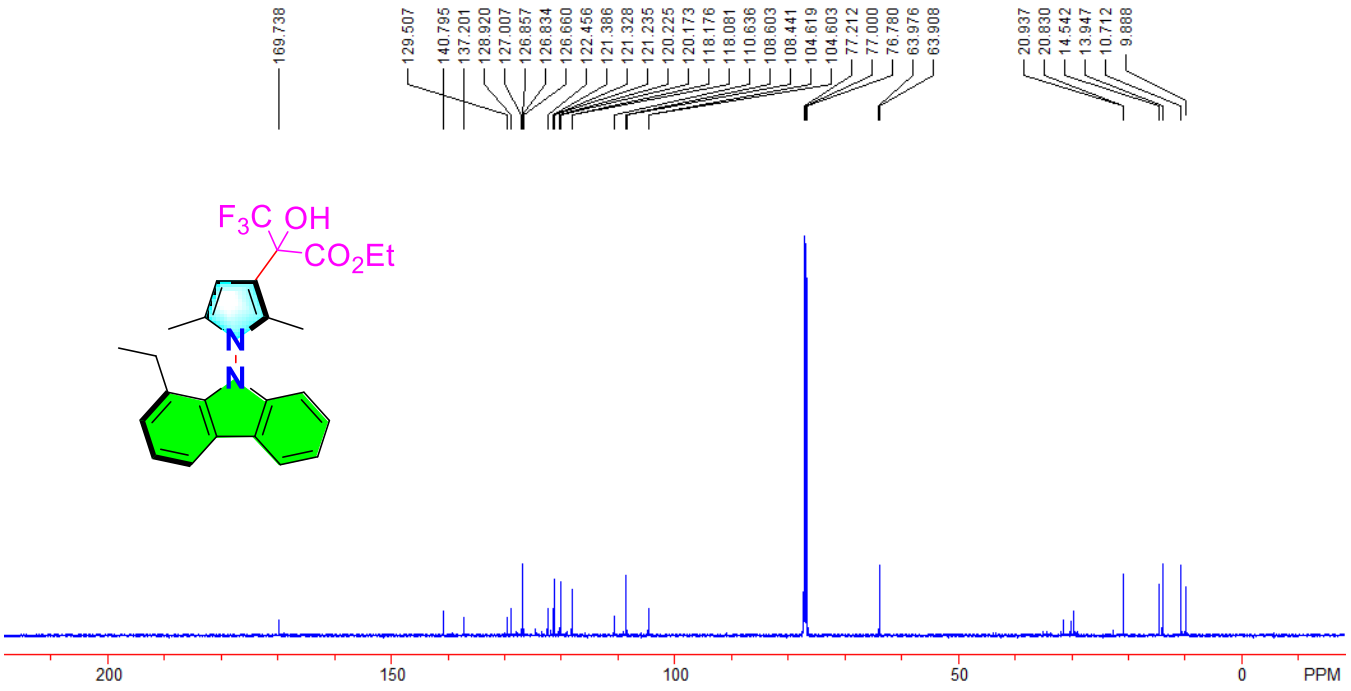


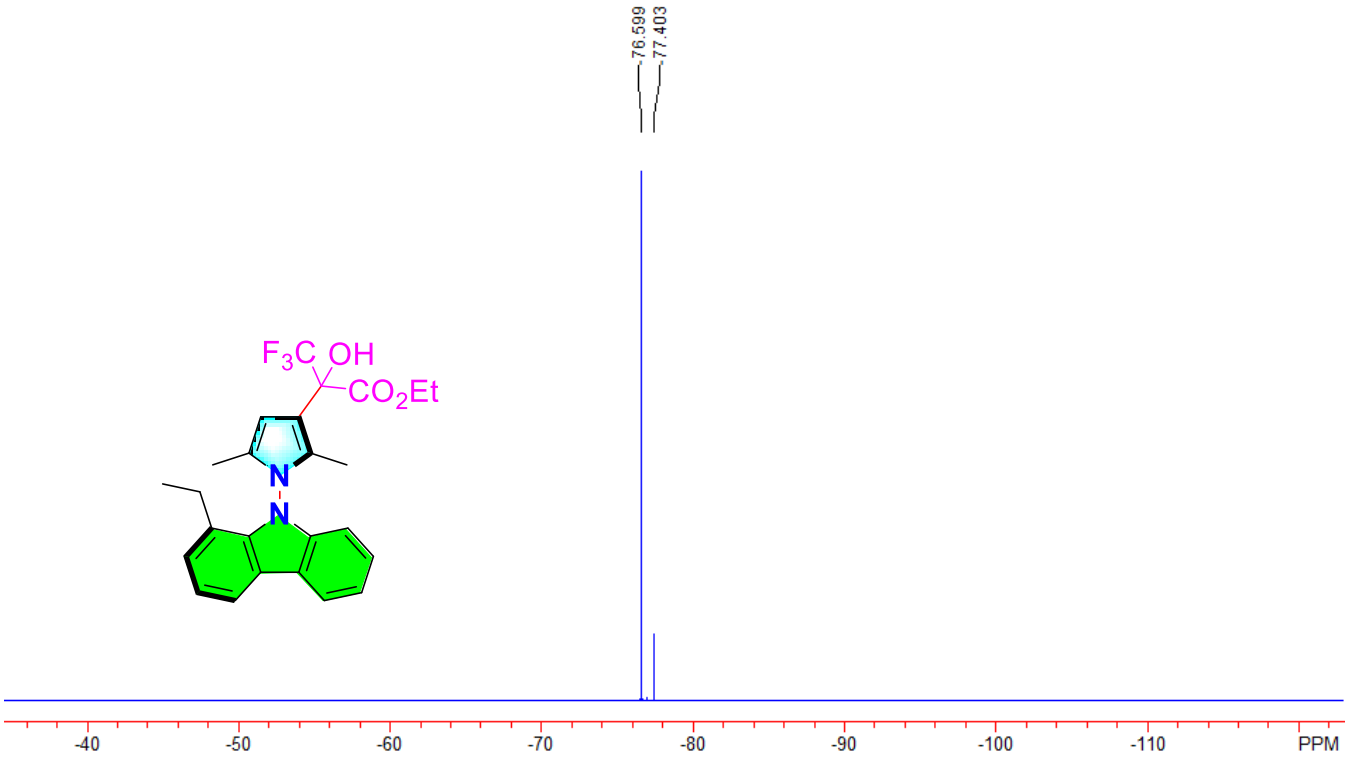



76.180
76.613
F3C OH
CO2Et
tBu
N
N
0
-50
-100
-150
-200
PPM

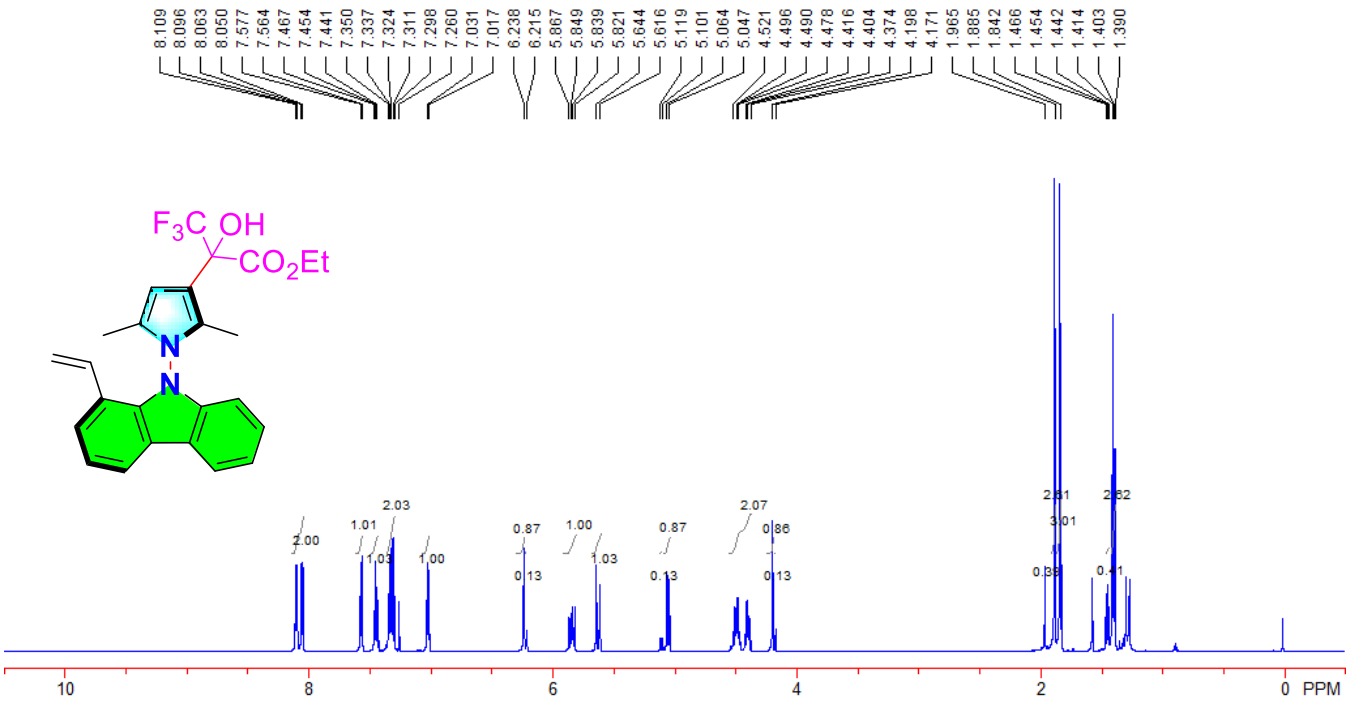
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4f**

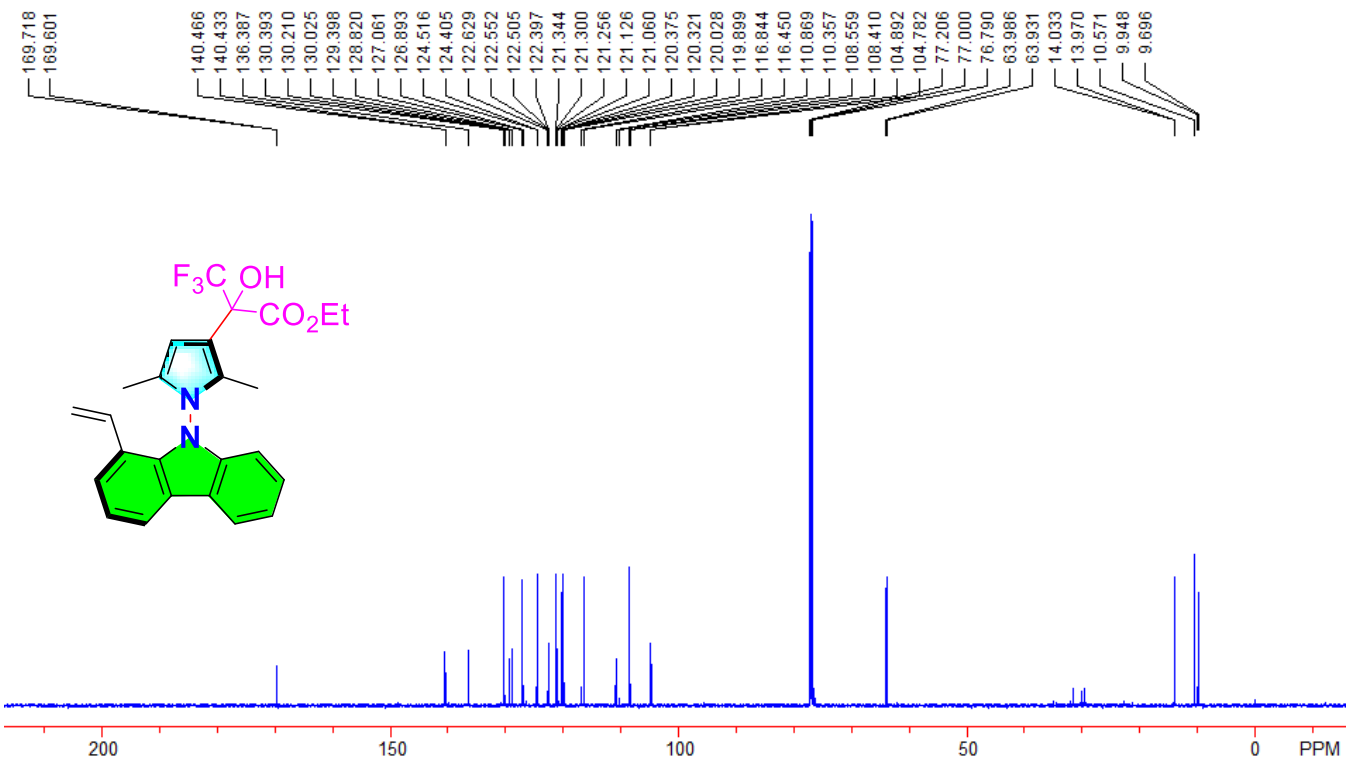


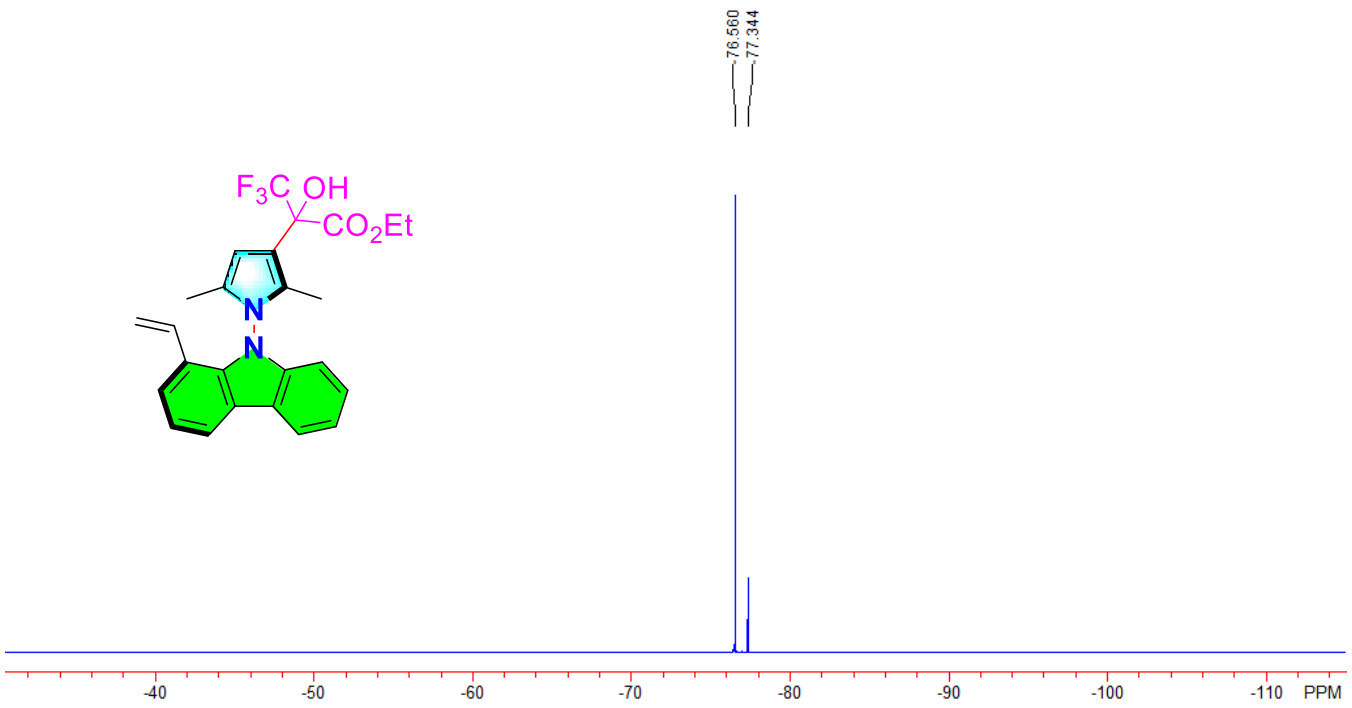



76.599
77.403
F3C OH
CO2Et
N
N
-40
-50
-60
-70
-80
-90
-100
-110
PPM

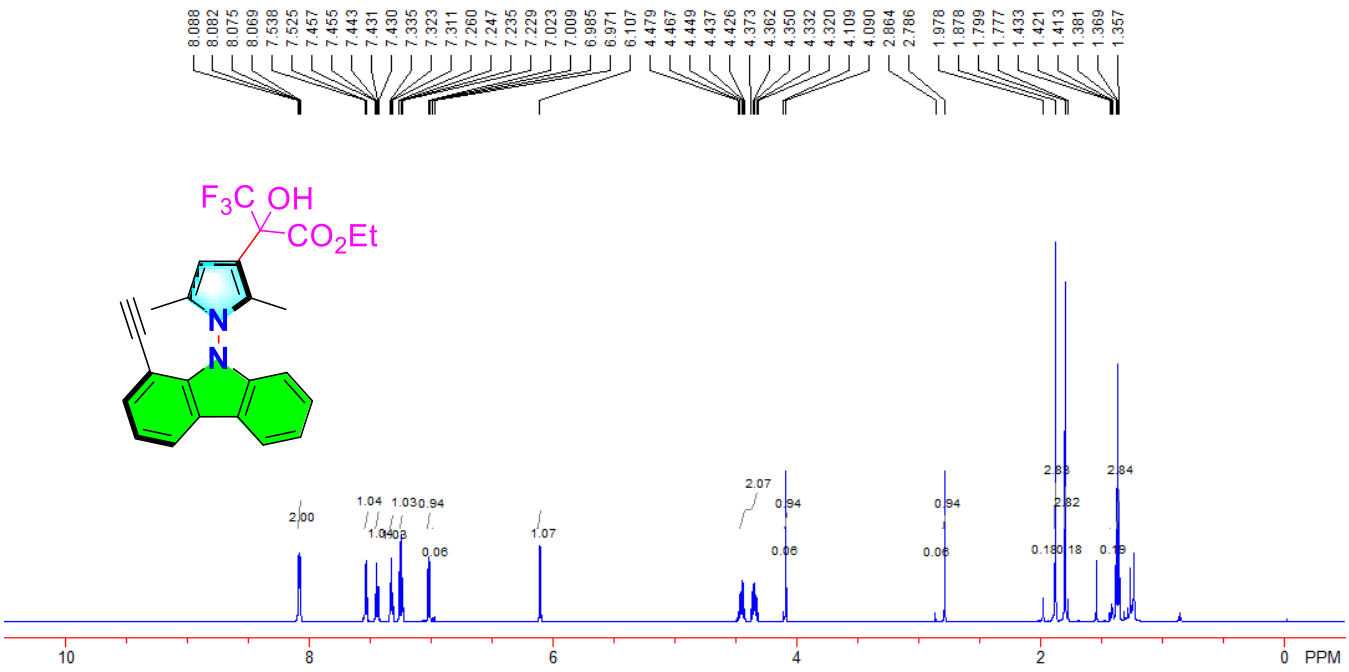
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4g**

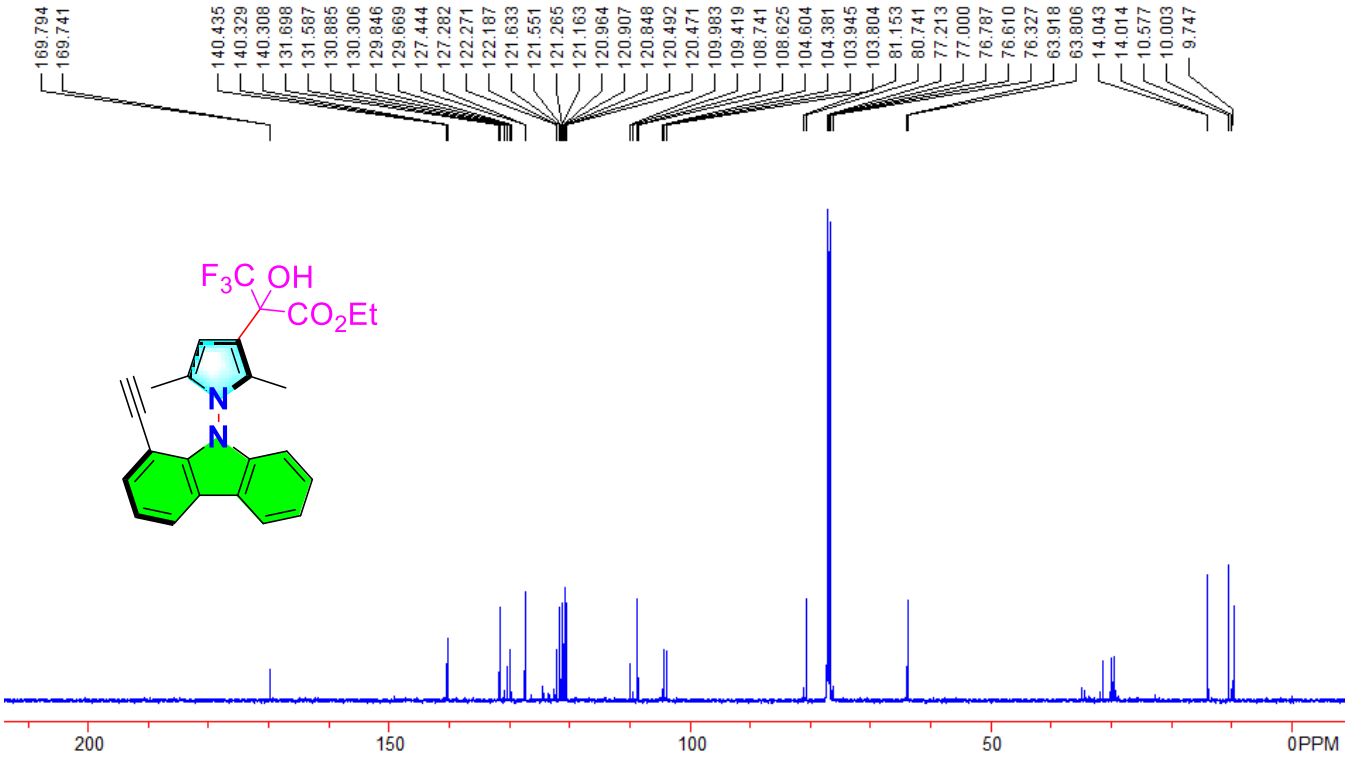


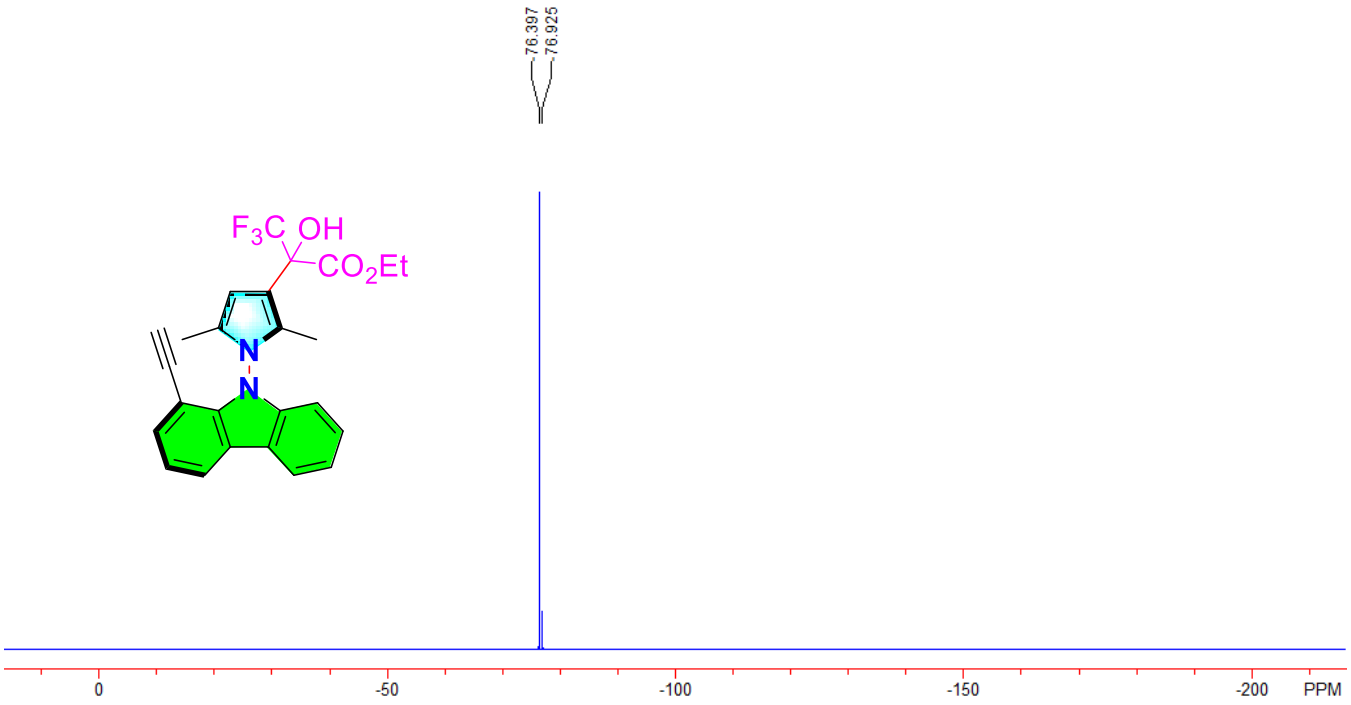



-76.560
-77.344
F3C OH
CO2Et
N
N
-40
-50
-60
-70
-80
-90
-100
-110
PPM

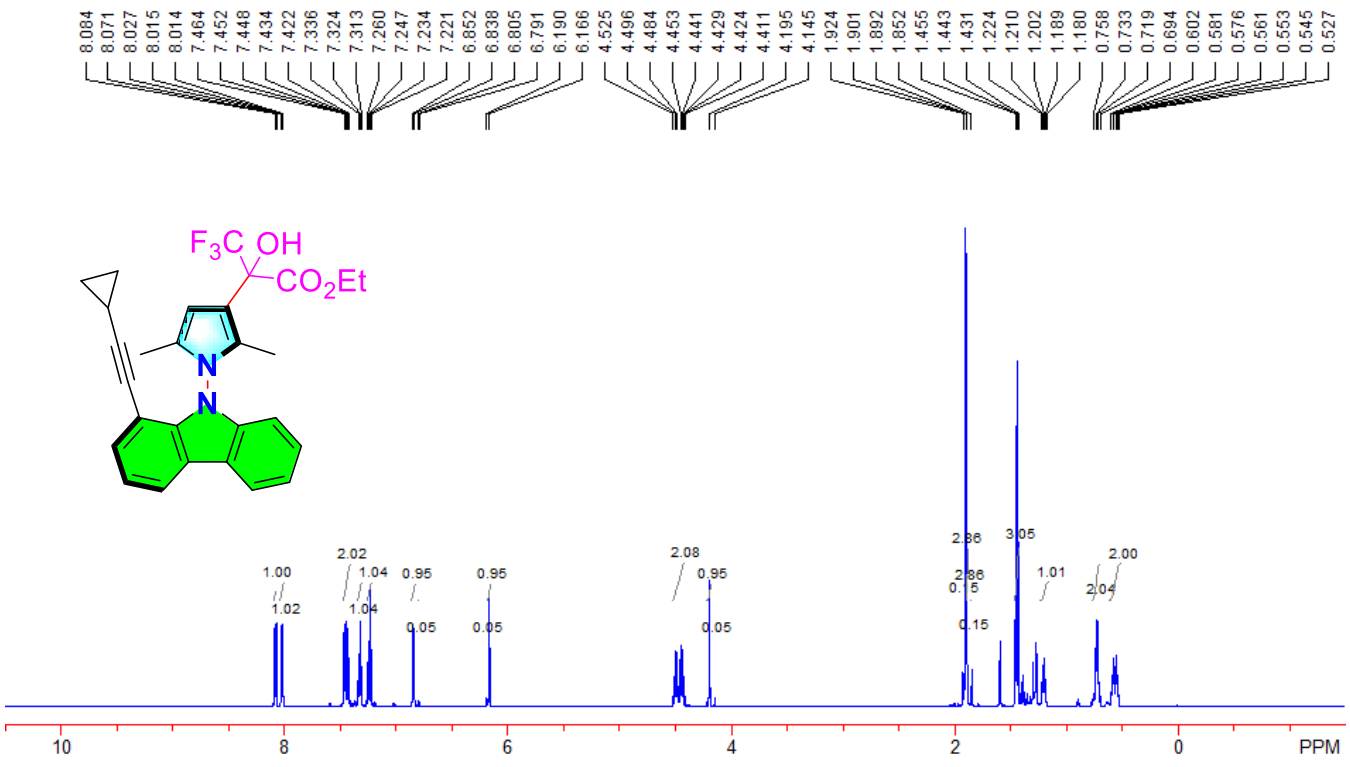
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4h**

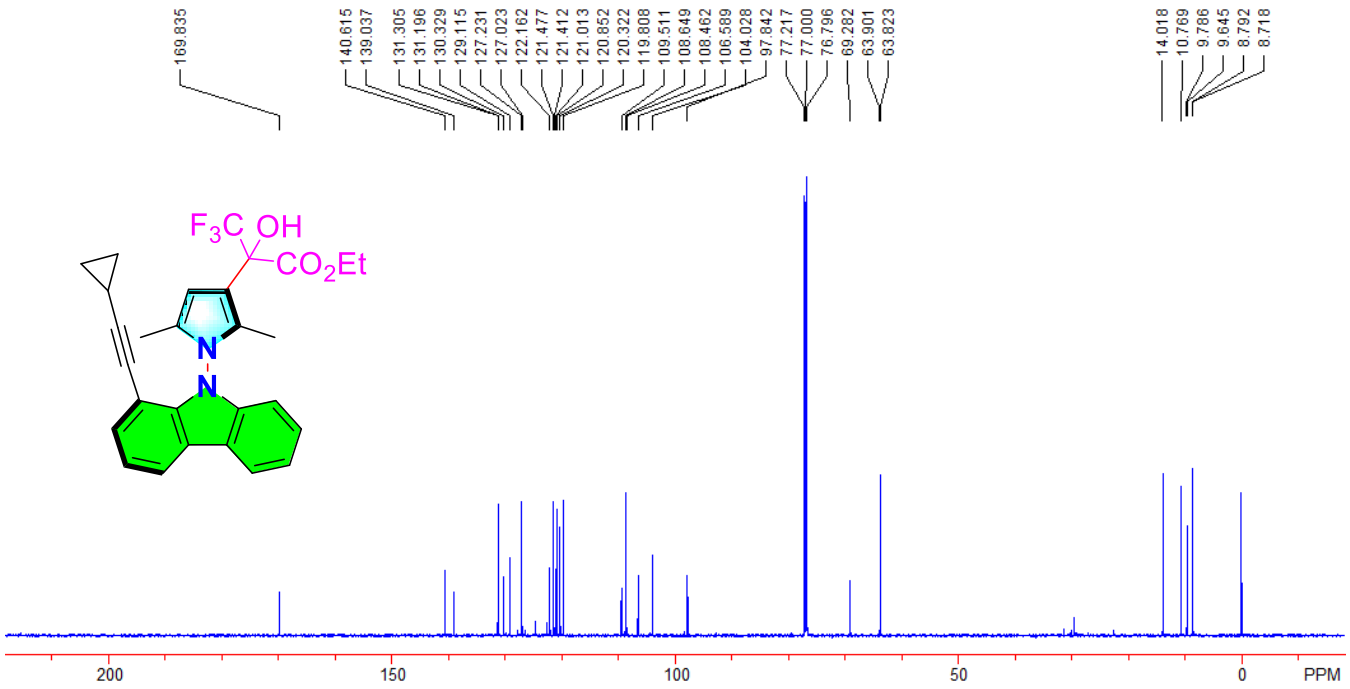


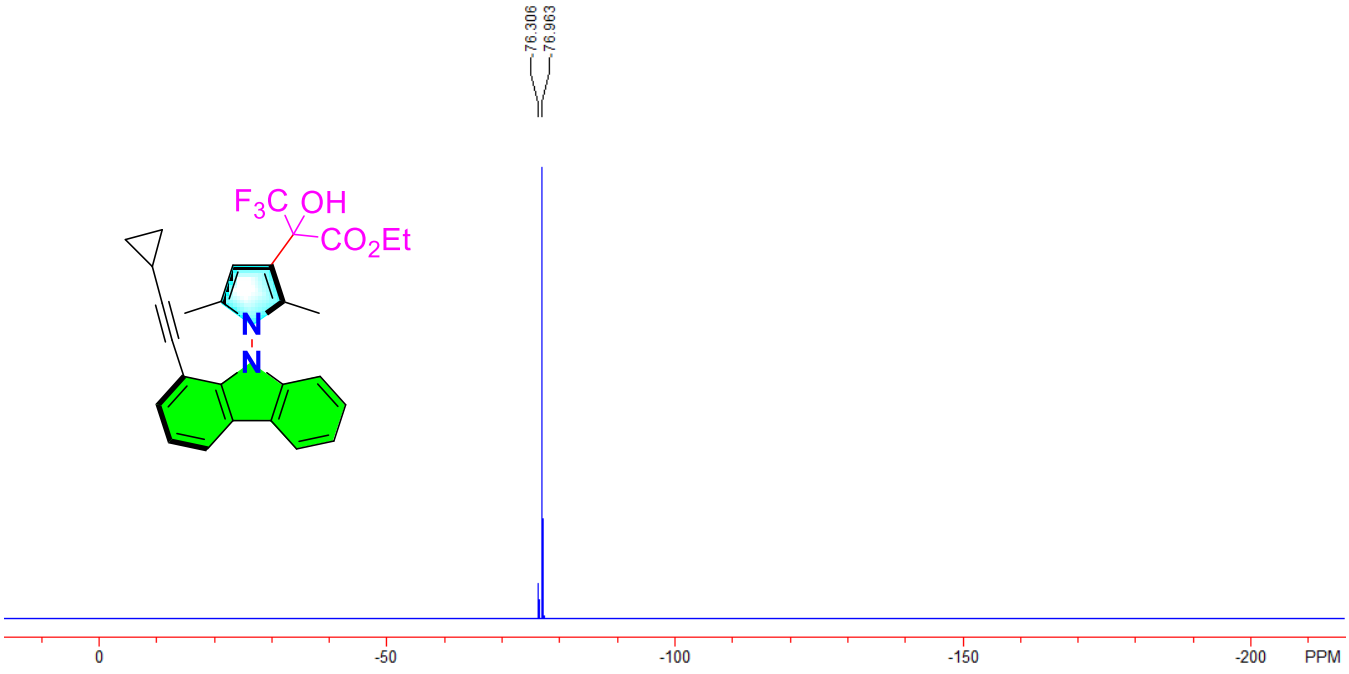



-76.397
-76.925
F3C OH
CO2Et
N
N
0
-50
-100
-150
-200
PPM

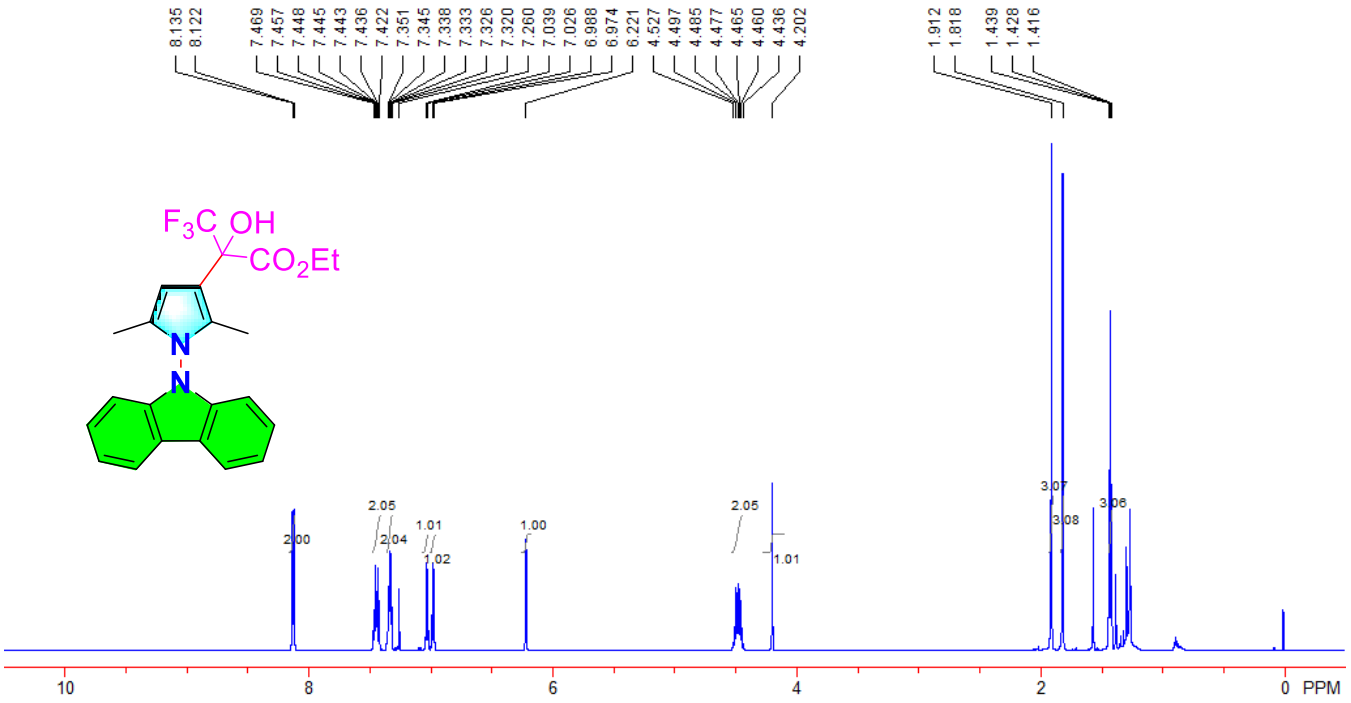
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(S)-4i**

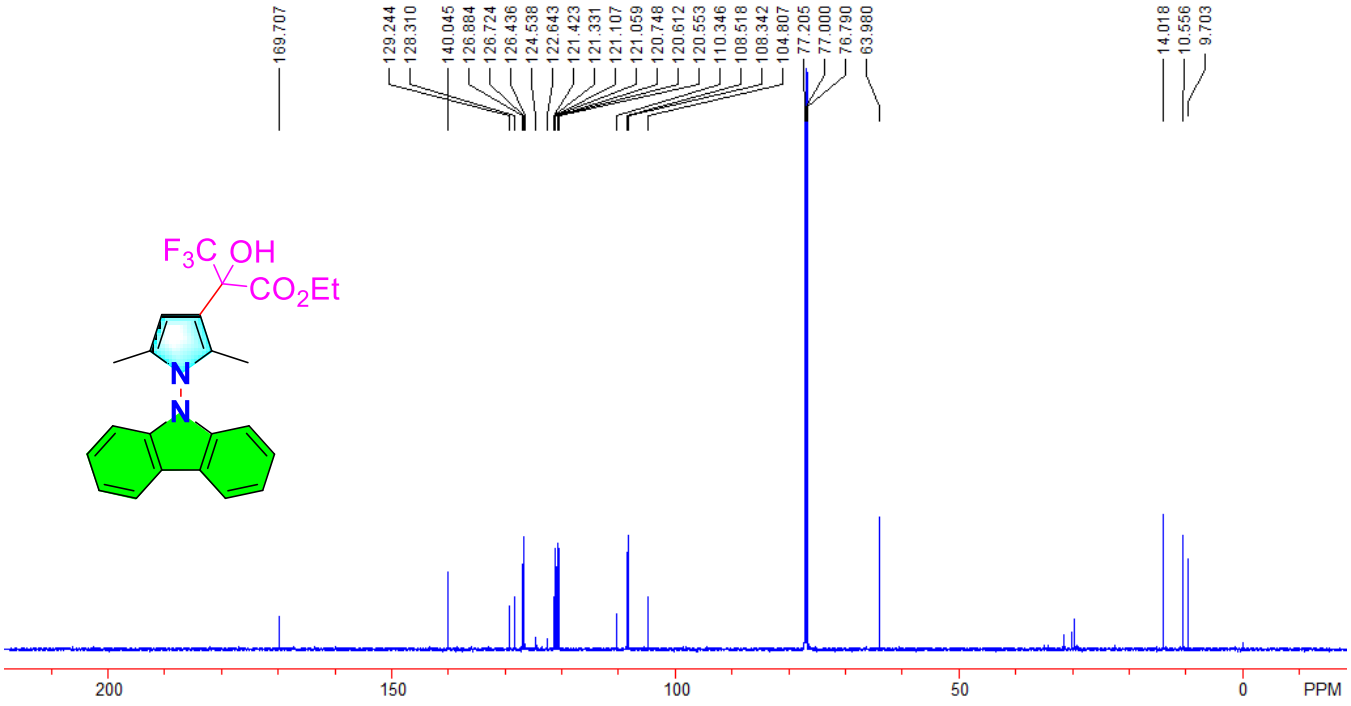


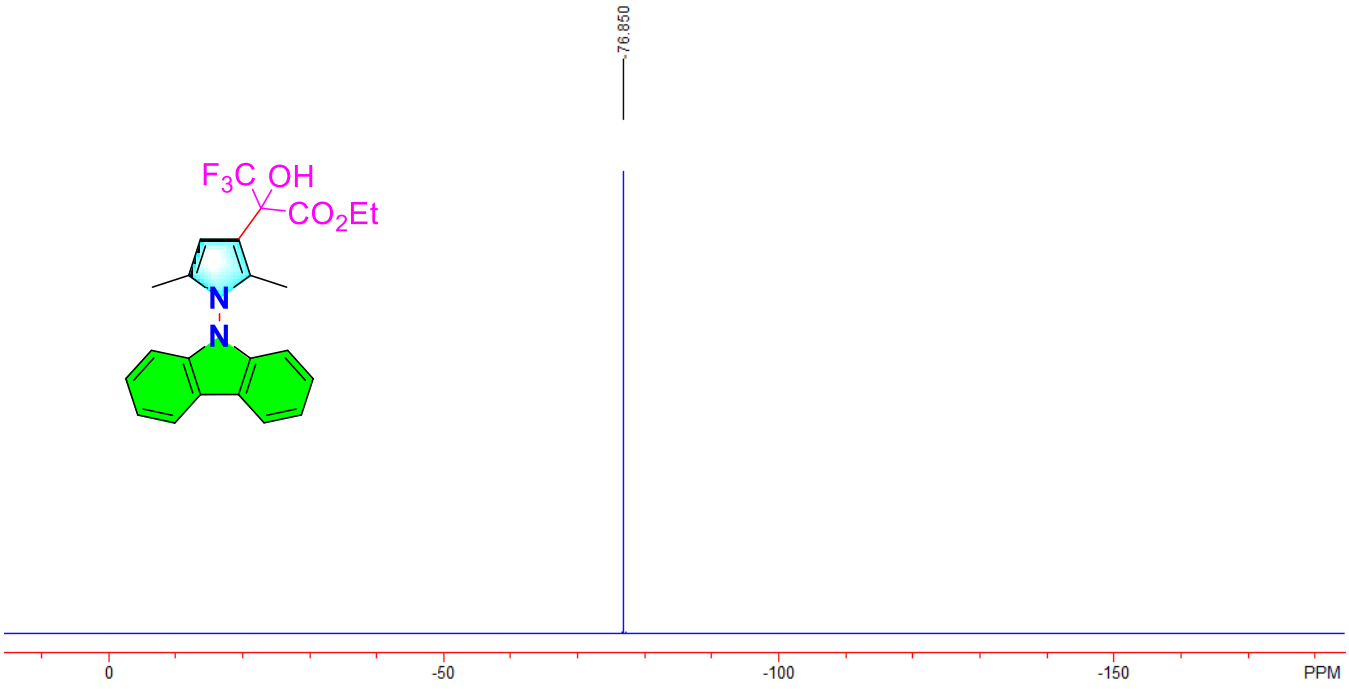



76.306
76.963
F3C OH
CO2Et
N
N
0
-50
-100
-150
-200
PPM

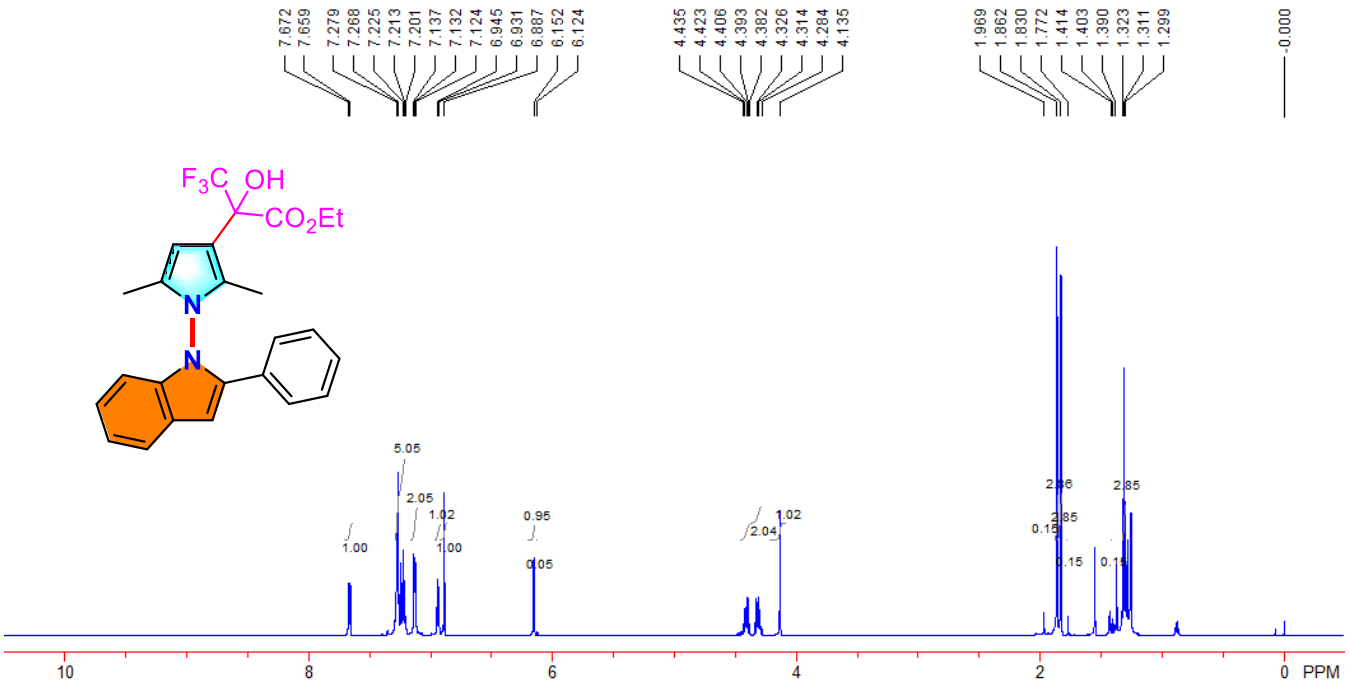
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound -**4j**

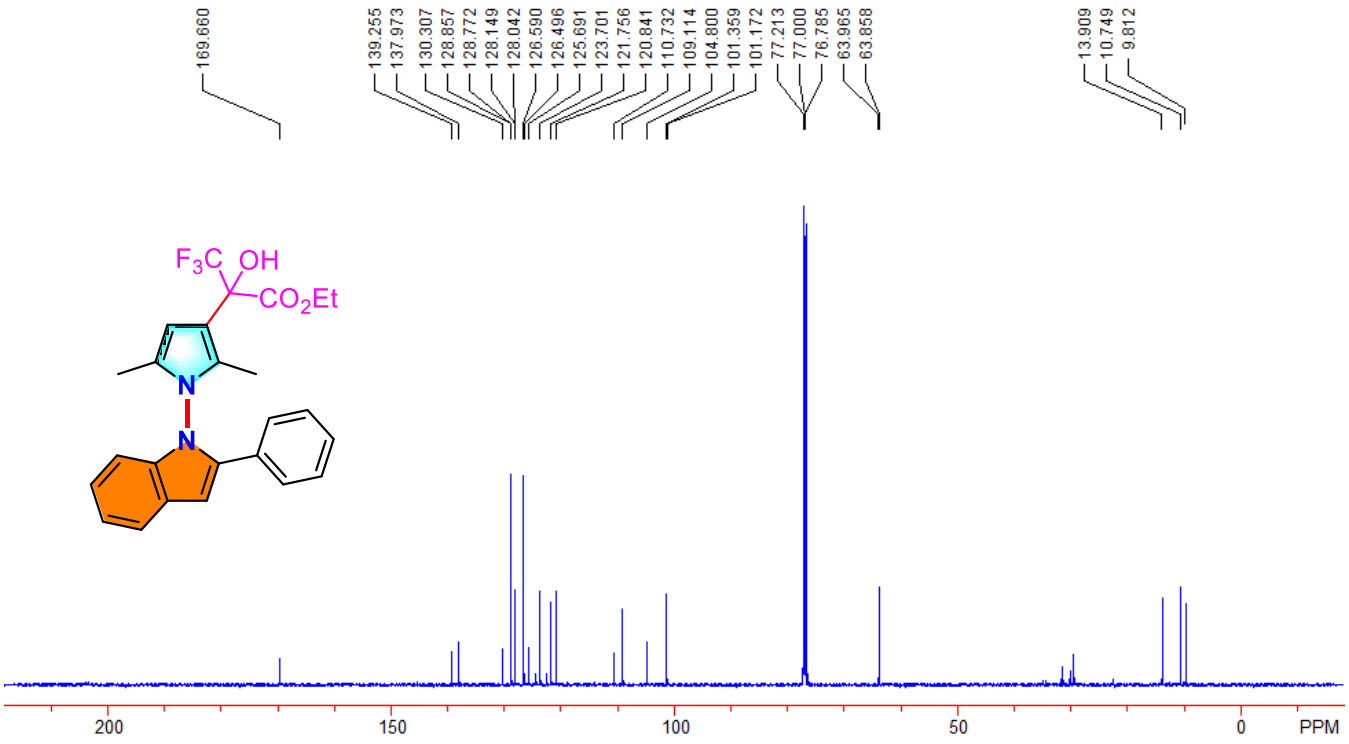


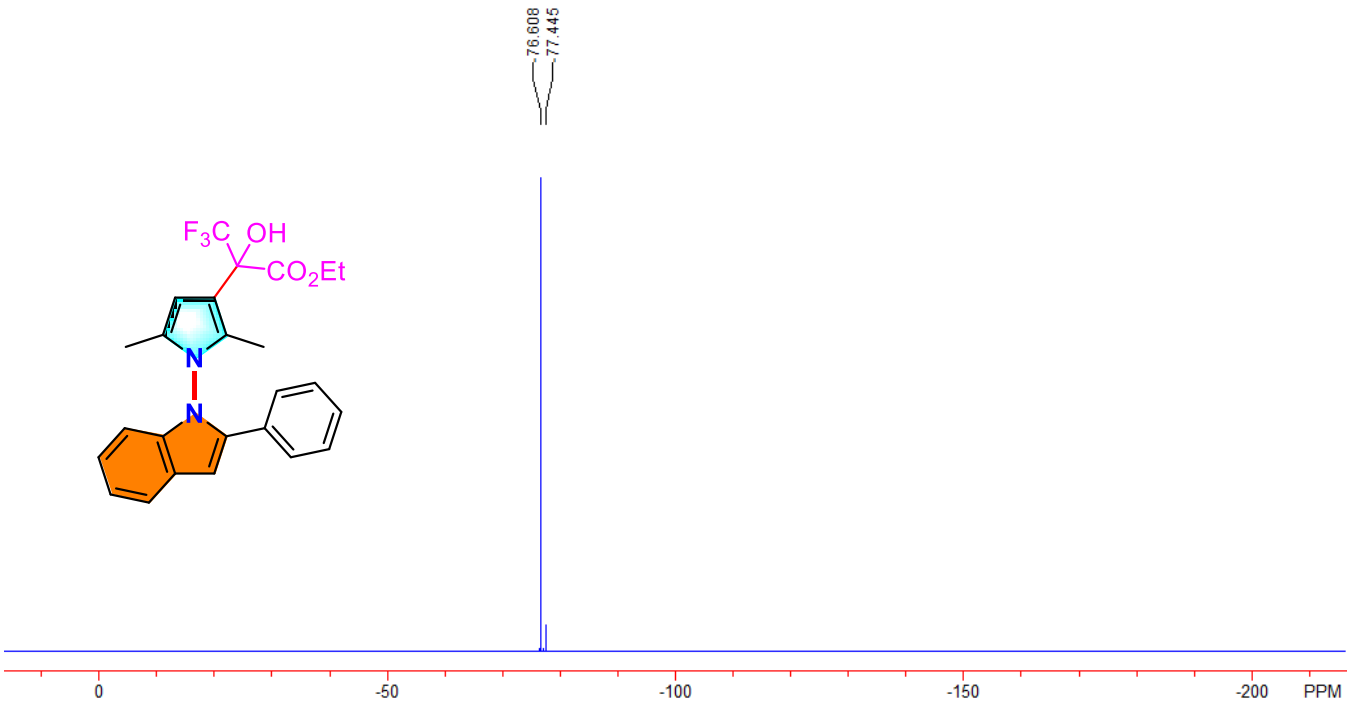



76.850
F3C OH
CO2Et
N
N
0
-50
-100
-150
PPM

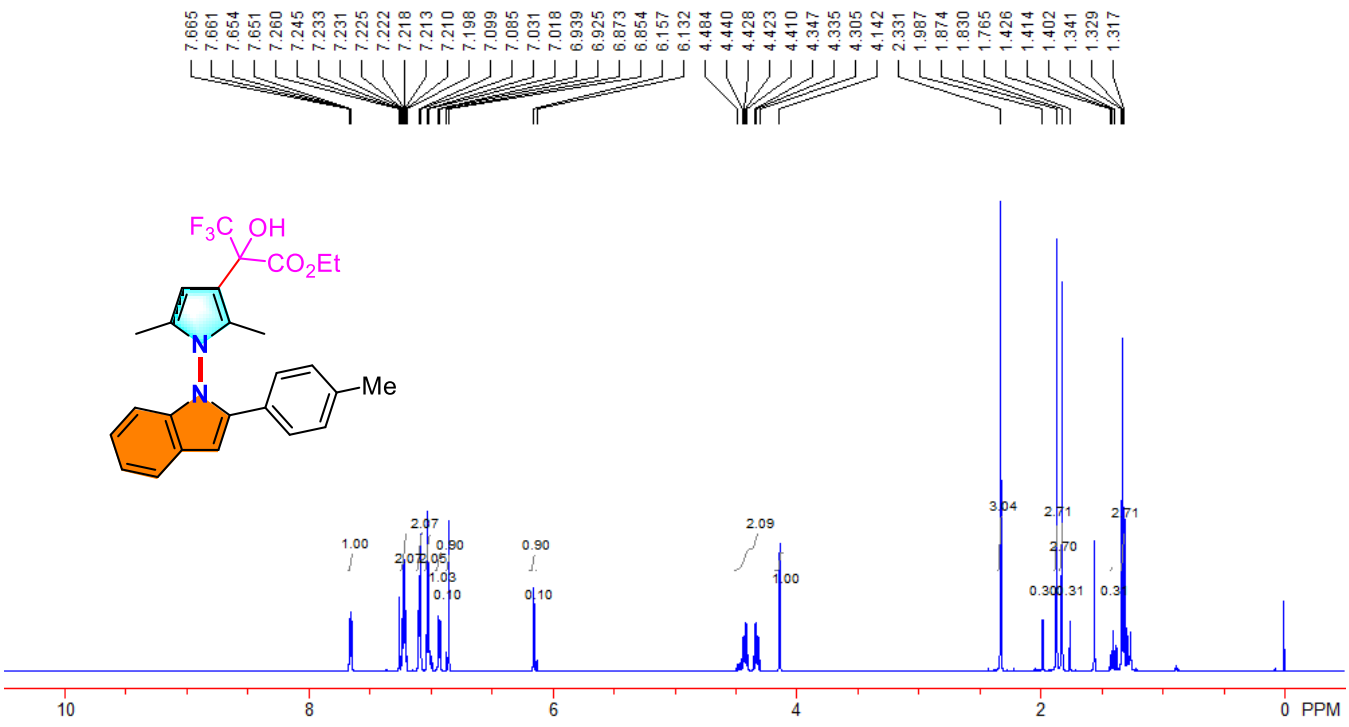
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(R)-4k**

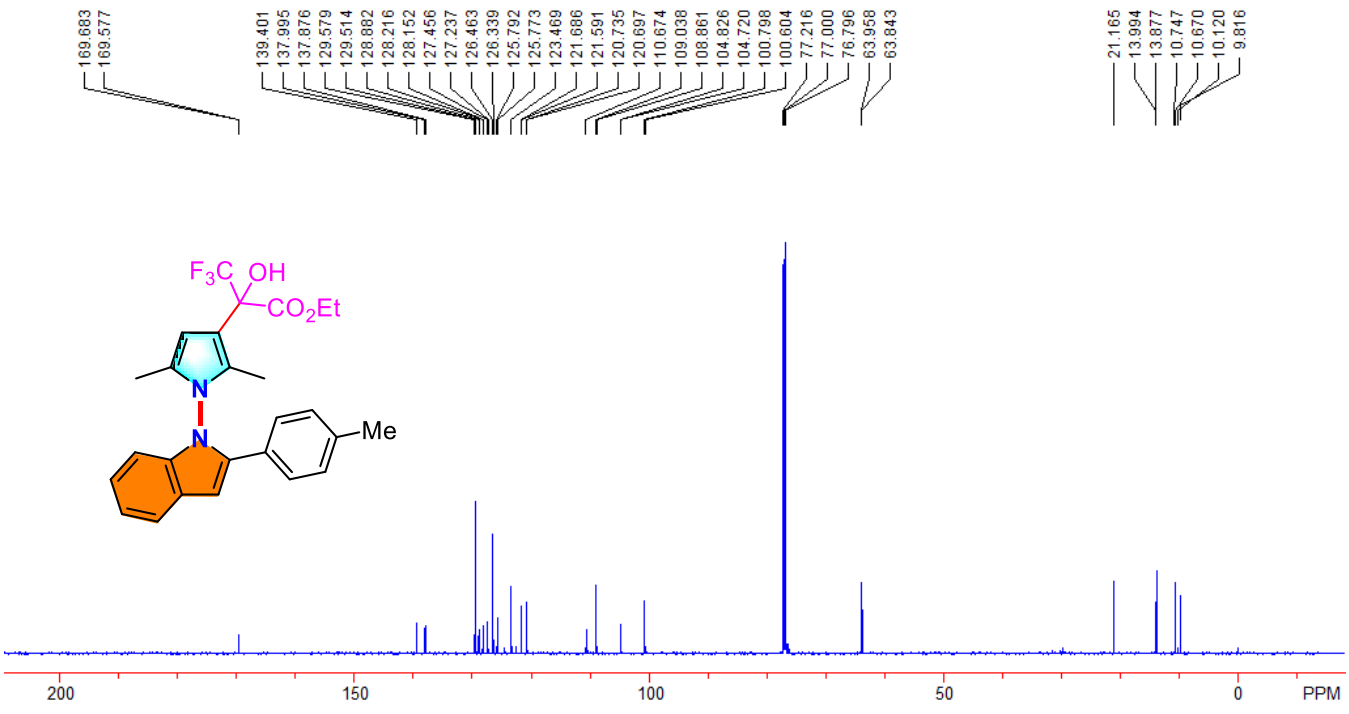


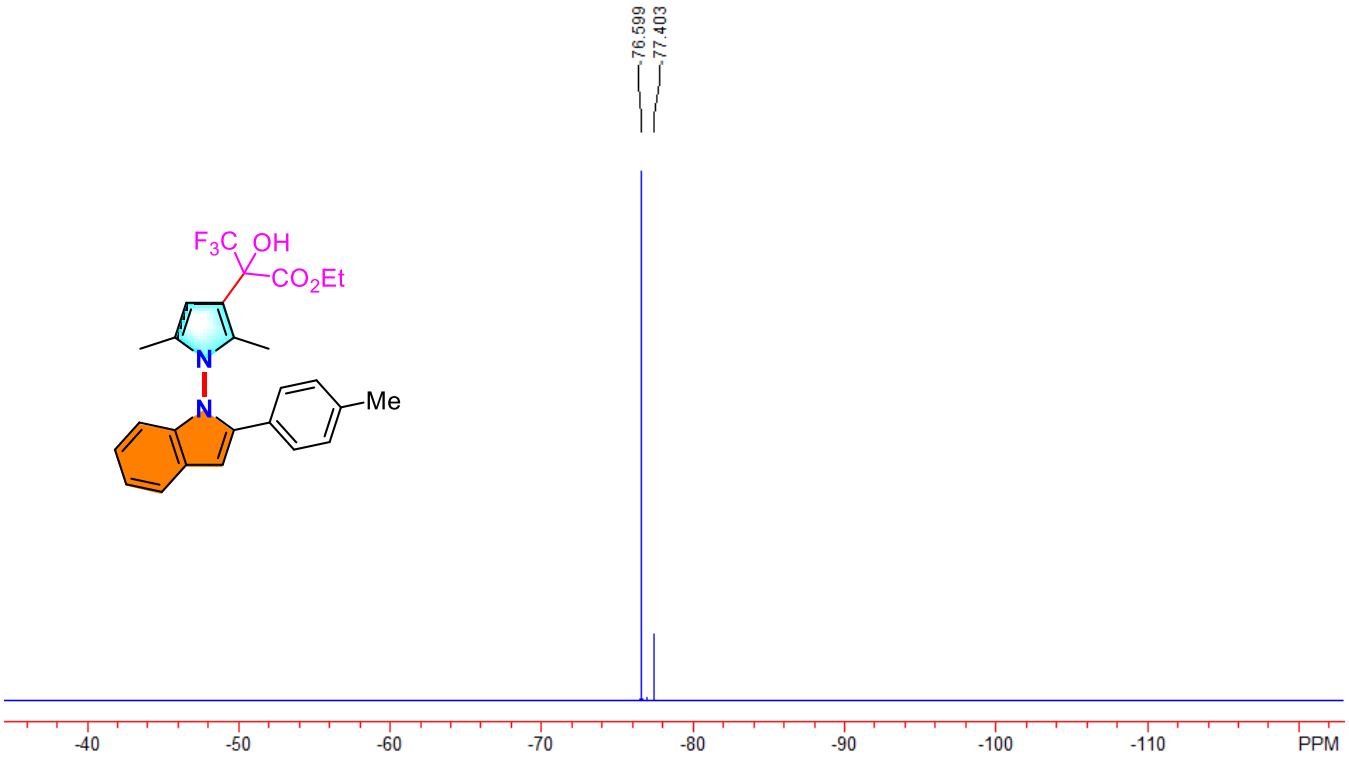



76.608
77.445
F3C
OH
CO2Et
N
N
0
-50
-100
-150
-200
PPM

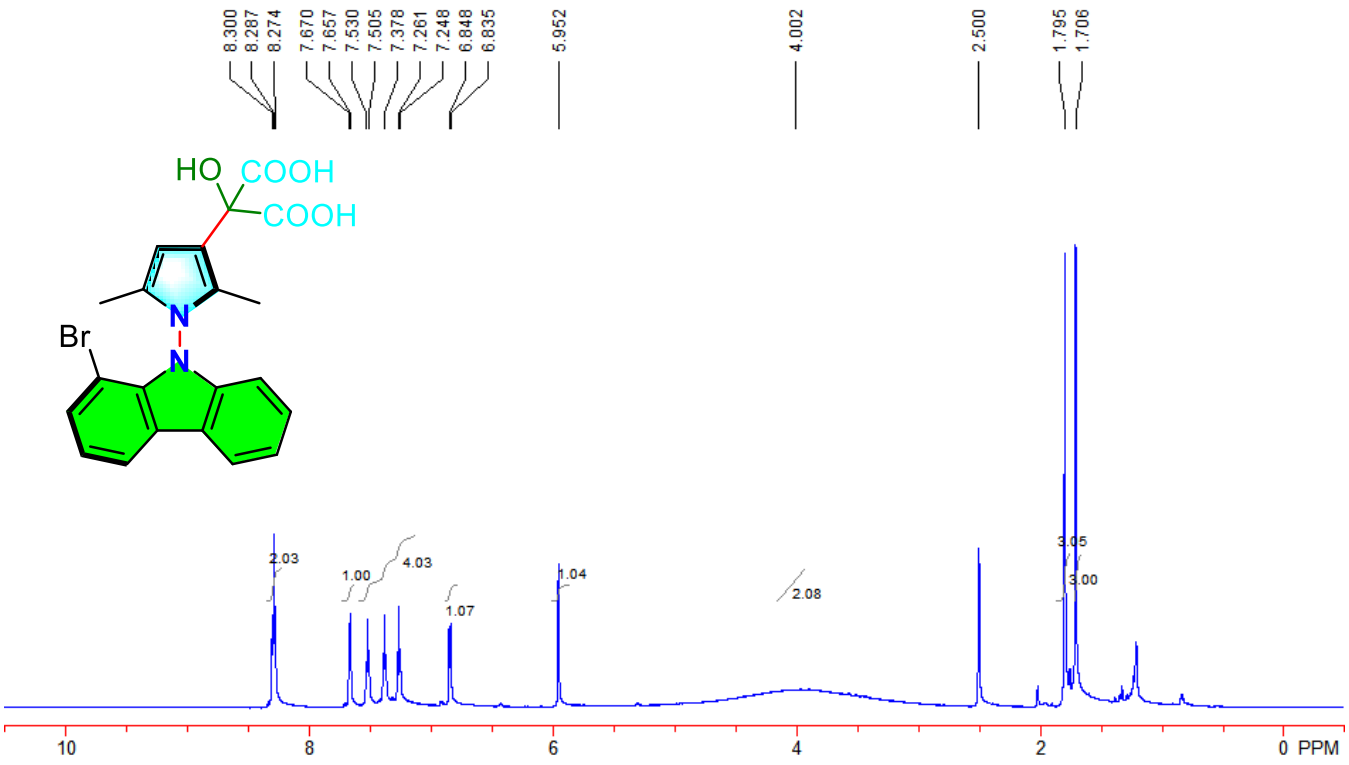
^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **(R)-4l**

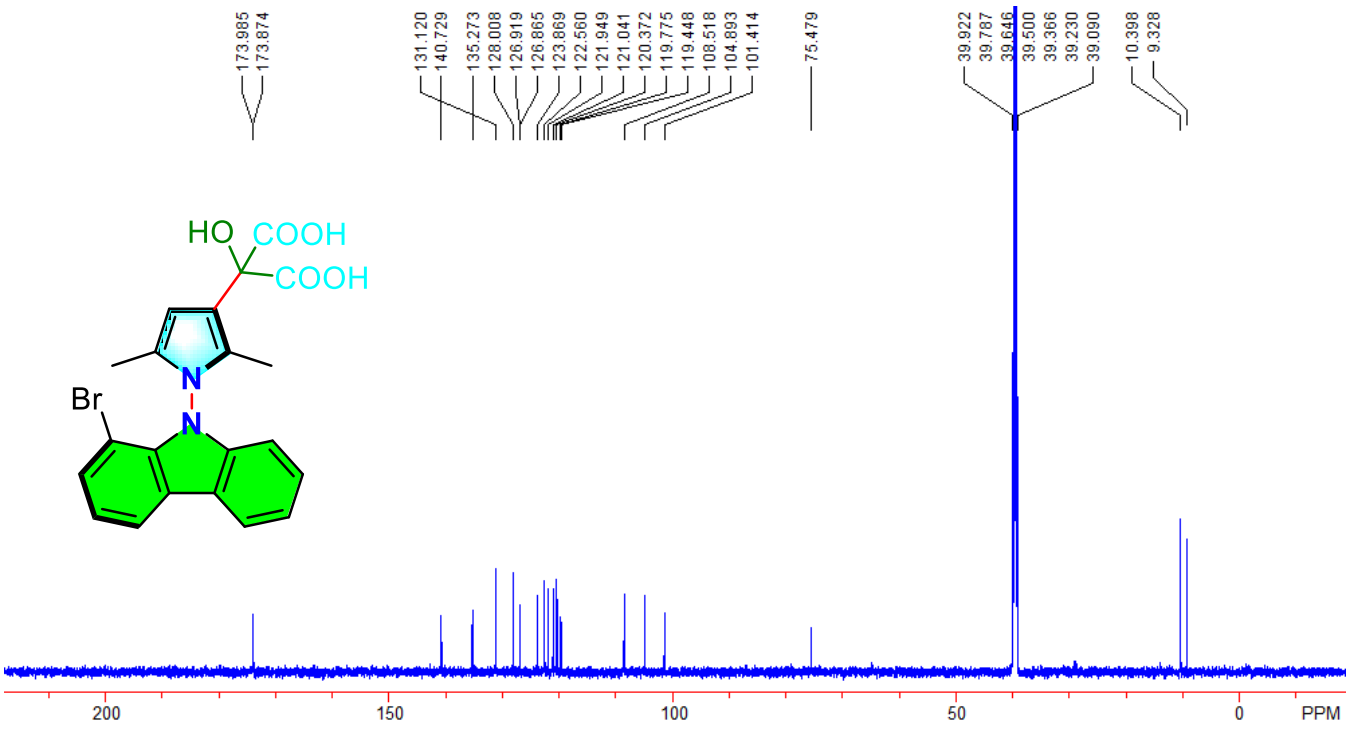





76.599
77.403
F3C
OH
CO2Et
N
N
Me
-40
-50
-60
-70
-80
-90
-100
-110
PPM

^{1}H and ^{13}C NMR $(CD_3)_2SO$) Spectra for Compound **(S)-5a**





^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **(R)-6a**