Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information for

Suzuki-Miyaura Cross-coupling of Bulky Anthracenyl Carboxylates by Using Pincer Nickel N-Heterocyclic Carbene Complexes: An Efficient Protocol to Access Fluorescent Anthracene Derivatives

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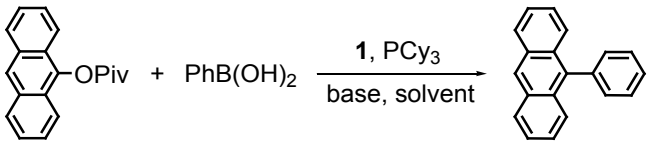
1. General.

Reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents. All commercial reagents were used directly without further purification, unless otherwise stated. The carboxylates were prepared according to literature.[S1] The nickel(II)-pincer complex was prepared according to our reported method.[S2] Toluene, benzene, 1,4-dioxane, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone prior to use. Acetonitrile and *tert*-butanol(*t*-BuOH) were distilled from anhydrous calcium chloride prior to use. Dry N,N-dimethylformamide (DMF) was purchased from Alfa Aesar, stored over 4 Å molecular sieves, and handled under N_2. $K_3PO_4 \cdot H_2O$ was purchased from Alfa Aesar. PCy_3 and PPh_3 are used as purchased without special treatment. All reaction vials (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^1H NMR spectra are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra are referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, dt = doublet of triplets, q = quartet. GC-MS spectra were recorded on Agilent echnologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector. ESI-MS spectra were recorded on a BrukermicrOTOF II instrument. Fluorescence spectra were recorded on Horiba Scientific Fluoromax-4 Spectrofluorometer.

2. General procedure for Ni-catalyzed C-O activation and Suzuki cross-coupling reactions.

Under a nitrogen atmosphere, to a 50 mL Schlenk tube the base (2.25mmol), catalytic amount of nickel(II)-pincer complex (**1, 2** or $NiBr_2$) and additive PCy_3 (or PPh_3), anthracen-9-yl carboxylates (0.5 mmol), (hetero)-aryl boronic acid (2 mmol) and solvent were added. The reaction mixture was heated to 100 °C or 120 °C under stirring and monitored by TLC analysis. After the full conversion of the carboxylates, the reaction mixture was allowed to cool to room temperature. A small amount of silica gel was added and the solvent was removed *in vacuo*. The mixture was ready for purification by flash chromatography to yield the products.

3. Optimization of reaction conditions.[a]

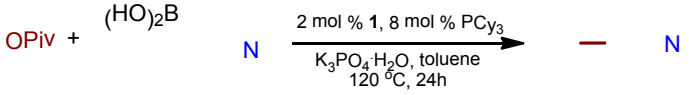


3 4

Entry	Base	Solvent	Yield/%[b]
1	$K_2HPO_4{\cdot}3H_2O$	Toluene (1.5 mL)	6
2	KOAc	Toluene (1.5 mL)	No reaction
3	KF	Toluene (1.5 mL)	trace
4	*t*-BuOK	Toluene (1.5 mL)	13
5	K_2CO_3	Toluene (1.5 mL)	35
6	Cs_2CO_3	Toluene (1.5 mL)	5
7	Na_2CO_3	Toluene (1.5 mL)	4
8	NEt_3	Toluene (1.5 mL)	trace
9	DBU	Toluene (1.5 mL)	trace
10	$K_3PO_4{\cdot}H_2O$	Benzene (1.5 mL)	90
11	$K_3PO_4{\cdot}H_2O$	Dioxane (1.5 mL)	11
12	$K_3PO_4{\cdot}H_2O$	DME (1.5 mL)	42
13	$K_3PO_4{\cdot}H_2O$	*t*-BuOH (1.5 mL)	69
14	$K_3PO_4{\cdot}H_2O$	CH_3CN (1.5 mL)	5
15	$K_3PO_4{\cdot}H_2O$	DMF (1.5 mL)	3
16	$K_3PO_4{\cdot}H_2O$	Toluene (1.5 mL)	70[c]
17	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	93[c]
18	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	61[d]
19	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	94[e]
20	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	91[f]
21	K_3PO_4	Toluene (3 mL)	93[g]
22	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	4[h]
23	$K_3PO_4{\cdot}H_2O$	Toluene (3 mL)	No reaction[i]

[a] The reactions were carried out with **3** (0.5 mmol), $PhB(OH)_2$ (4.0 equiv.), **1** (0.5 mol%), PCy_3 (2mol%), base (4.5 equiv.) in solvent (1.5 mL) at 100 °C for 6h; [b] Isolated yield; [c] 1 mol% PCy_3; [d] Reaction for 1h; [e] 2 mol% **1** and 8 mol% PCy_3, 24h; [f] 5 mol% **1** and 20 mol% PCy_3, 24h; [g] 0.5 mol% $NiCl_2(PCy_3)_2$ instead of **1** and PCy_3, 24h; [h] 2 mol% Zn instead of PCy_3, 24h; [i] PhBpin instead of $PhB(OH)_2$, no PCy_3 used, 24h.

4. Synthesis of 5-(anthracen-9-yl)-1-methyl-1H-indole.

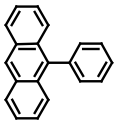


13: 7%

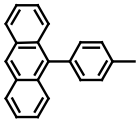
Methyl-1*H*-indol-5-ylboronic acid was synthesized by a literature method.[S3] The cross-coupling of anthracen-9-yl pivalate with 1-methyl-1*H*-indol-5-ylboronic acid was carried

out according to our general procedure with catalyst **1**, and a 7% yield was obtained for product **13** after 24 hours.

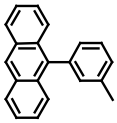
5. Analytical data of the coupling products (Data of all compounds match those in previously reported references).



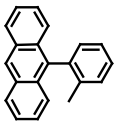
4:[S4] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.51 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.67 (dd, *J* = 8.8 Hz, 0.8 Hz, 2H), 7.62-7.50 (m, 3H), 7.50-7.40 (m, 4H), 7.35 (m, 2H); GC-MS: *m/z* = 254.3 $[M]^+$.



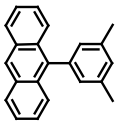
5a:[S5] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.49 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.50-7.29 (m, 8H), 2.53 (s, 3H); GC-MS: *m/z* = 268.3 $[M]^+$, 252.3.



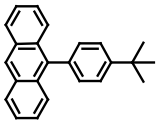
5b:[S6] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.49 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.51-7.41 (m, 3H), 7.40-7.30 (m, 3H), 7.27-7.20 (m, 2H), 2.47 (s, 3H); GC-MS: *m/z* = 268.3 $[M]^+$, 252.3.



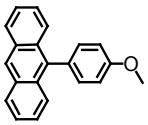
5c:[S7] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.50 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.53-7.41 (m, 6H), 7.41-7.30 (m, 3H), 7.28-7.23 (m, 1H), 1.86 (s, 3H); GC-MS: *m/z* = 268.3 $[M]^+$, 252.3.



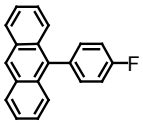
6:[S8] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.48 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.70 (dd, *J* = 8.8 Hz, 0.4 Hz, 2H), 7.50-7.41 (m, 2H), 7.39-7.31 (m, 2H), 7.16 (s, 1H), 7.05 (s, 2H), 2.43 (s, 6H); GC-MS: *m/z* = 282.3 $[M]^+$, 267.3, 252.3.



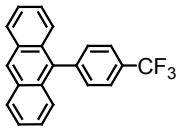
7:[S9] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.48 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.58 (dt, *J* = 8.8 Hz, 2.0 Hz, 2H), 7.49-7.42 (m, 2H), 7.39-7.31 (m, 4H), 1.47 (s, 9H); GC-MS: *m/z* = 310.1 $[M]^+$, 295.1, 279.1, 265.0, 252.1.



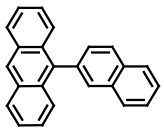
8:[S10] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.48 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.71 (dd, *J* = 8.8 Hz, 0.8 Hz, 2H), 7.49-7.42 (m, 2H), 7.39-7.31 (m, 4H), 7.12 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 3H); GC-MS: *m/z* = 284.3 $[M]^+$, 269.3, 253.3.



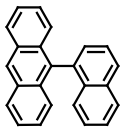
9:[S11] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.51 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 8.8 Hz, 0.4 Hz, 2H), 7.50-7.43 (m, 2H), 7.43-7.33 (m, 4H), 7.28 (t, *J* = 8.8 Hz, 2H); ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = -114.8; GC-MS: *m/z* = 272.3 $[M]^+$.



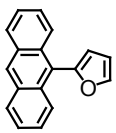
10:[S12] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.54 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.61-7.53 (m, 4H), 7.51-7.44 (m, 2H), 7.41-7.34 (m, 2H); ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = -62.1; GC-MS: *m/z* = 322.3 $[M]^+$, 252.3.



11a:[S13] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.54 (s, 1H), 8.11-7.99 (m, 4H), 7.95-7.88 (m, 2H), 7.68 (dd, *J* = 8.8 Hz, 0.4 Hz, 2H), 7.61-7.54 (m, 3H), 7.50-7.43 (m, 2H), 7.36-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 136.8, 136.3, 133.4, 132.7, 131.4, 130.4, 130.1, 129.5, 128.4, 128.2, 128.1, 127.9, 126.8, 126.7, 126.4, 126.2, 125.4, 125.1.

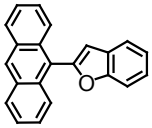


11b:[S7] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.59 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.4Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 8.0 Hz, 7.2 Hz, 1H), 7.53 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.50-7.36 (m, 5H), 7.28-7.15 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 1H); GC-MS: *m/z* = 304.3 $[M]^+$.



12a:[S14] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.51 (s, 1H), 8.05-7.98 (m, 2H), 7.96-7.87 (m,

2H), 7.78-7.72 (m, 1H), 7.51-7.39 (m, 4H), 6.75-6.69 (m, 1H), 6.69-6.65 (m, 1H); GC-MS: *m/z* = 244.3[M]$^+$, 215.3.

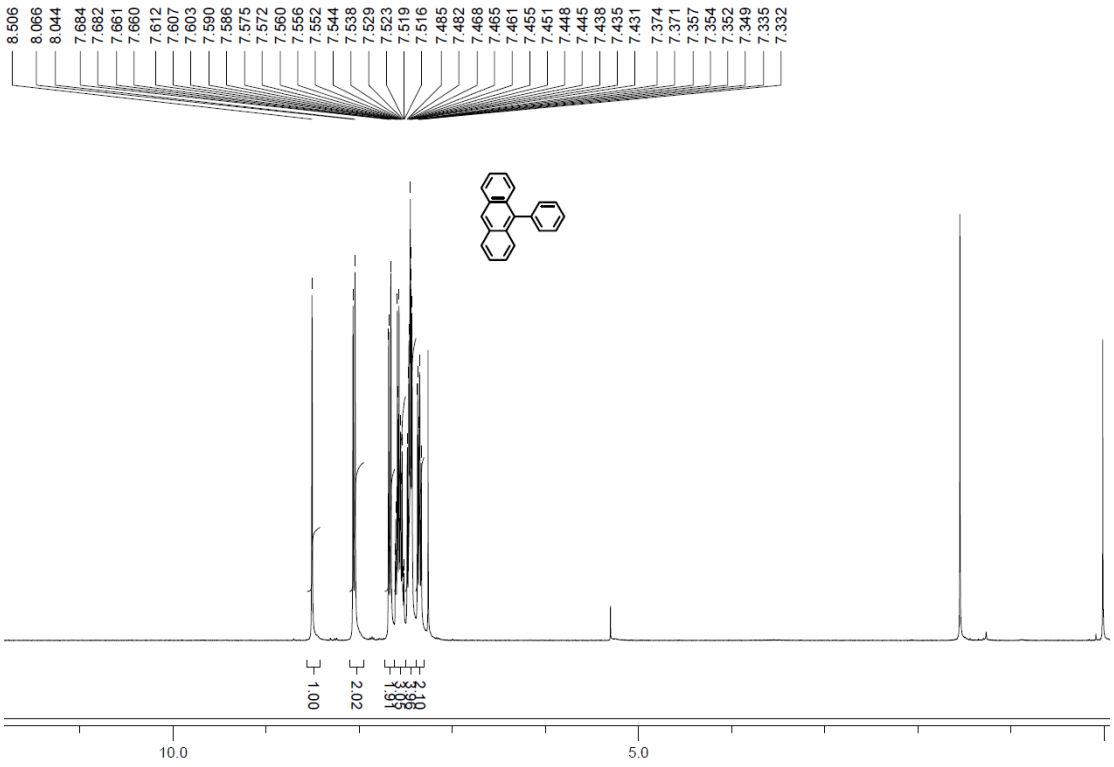


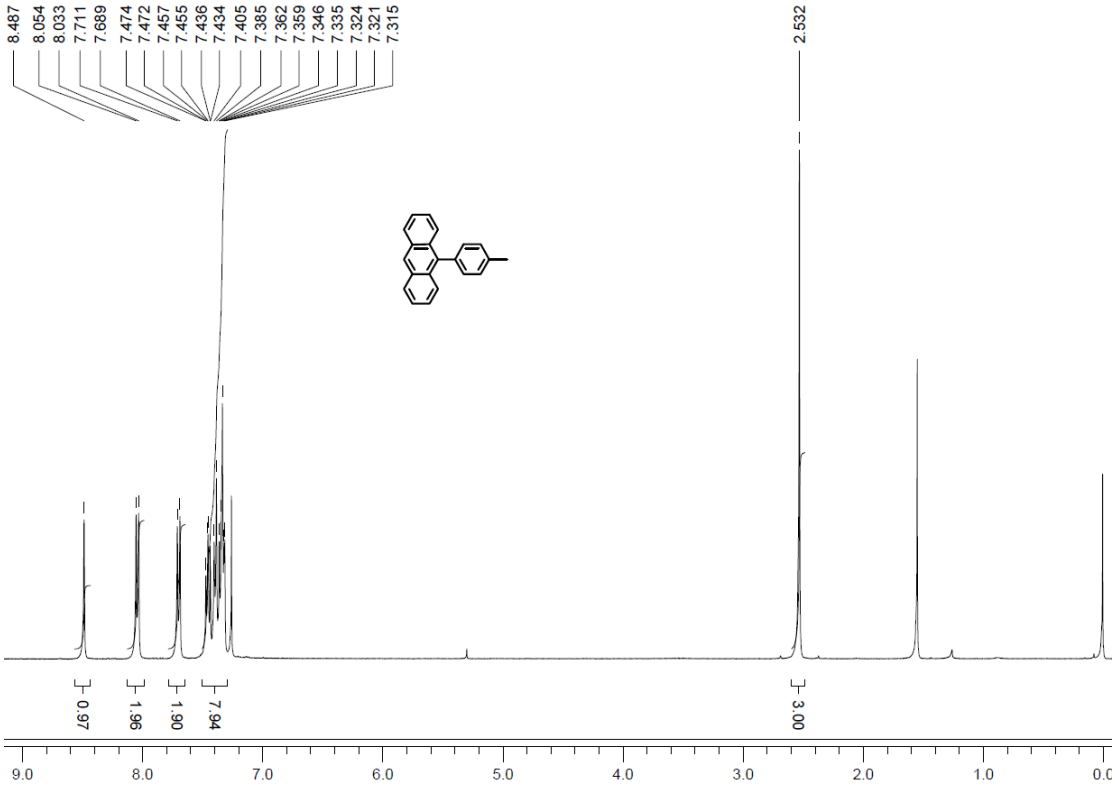
12b:[S15] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.58 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.79-7.71 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.54-7.32 (m, 6H), 7.07 (s, 1H); GC-MS: *m/z* = 294.3 [M]$^+$.

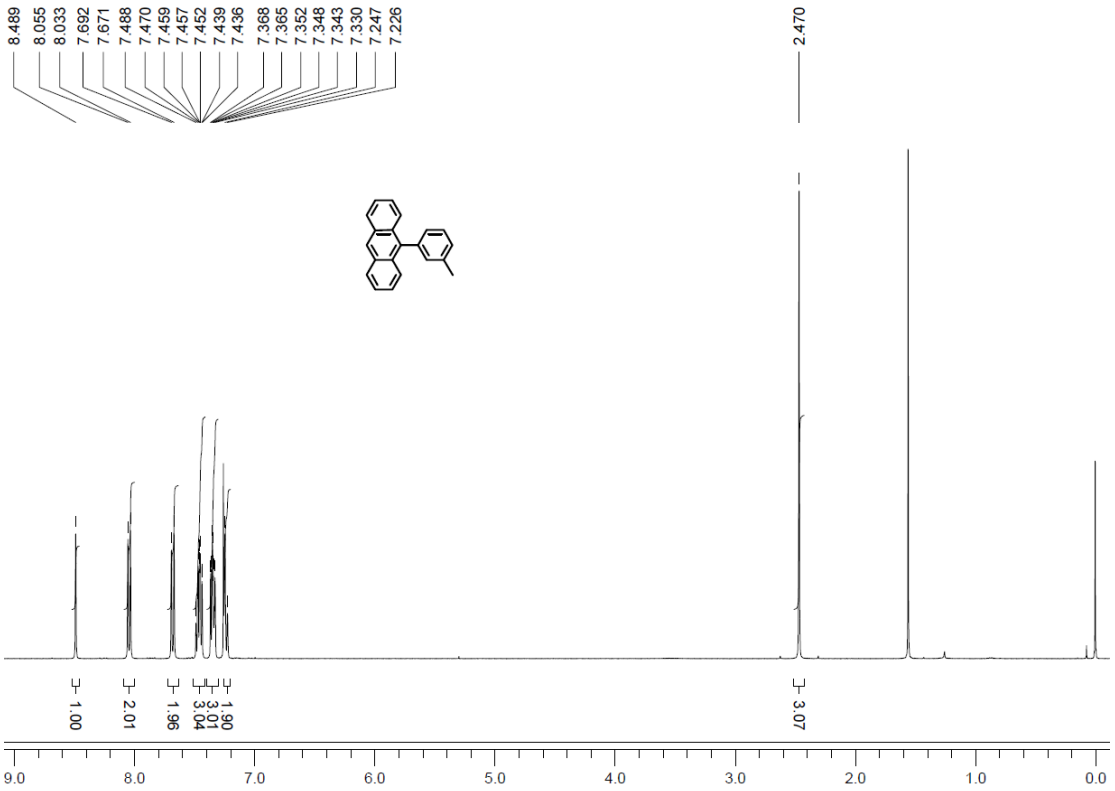
— N

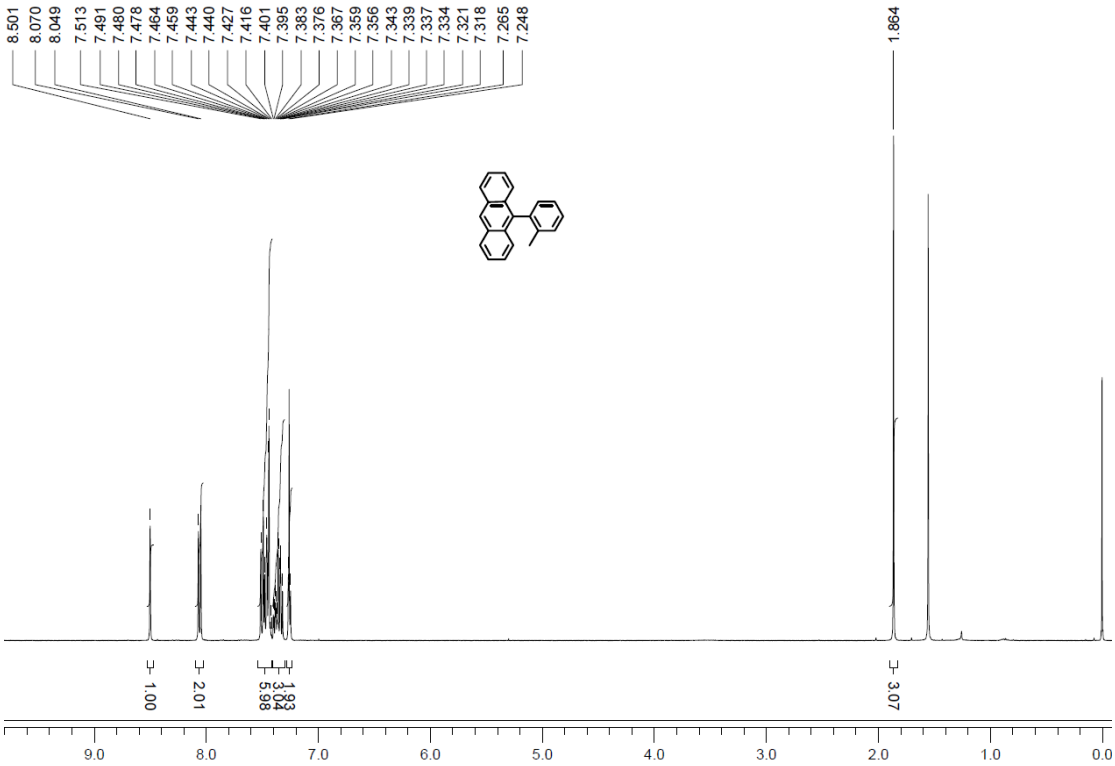
13: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.49 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.69 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.34-7.24 (m, 3H), 7.19 (d, *J* = 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 138.5, 136.1, 131.4, 130.8, 129.5, 129.4, 128.5, 128.2, 127.4, 126.0, 125.1, 124.9, 123.5, 108.9, 101.1, 33.0; HR-MS (ESI): m/z 308.1439 (calcd, [M+H]+); 308.1433 (found, [M+H]+).

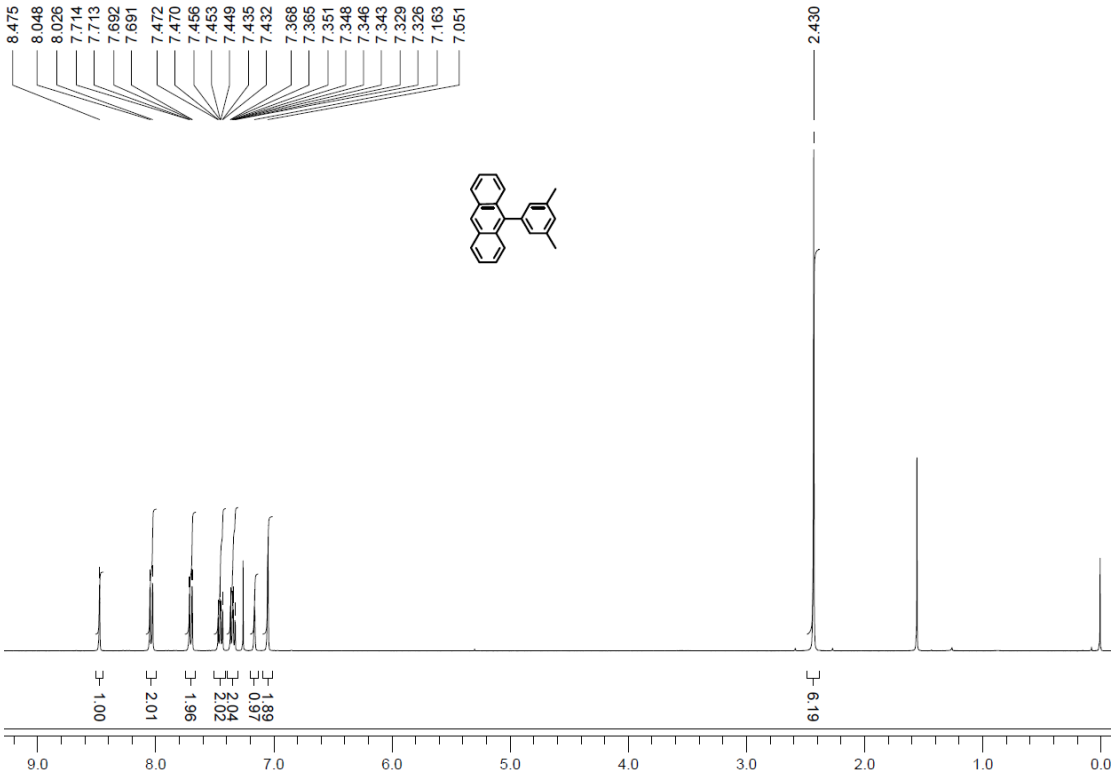
6. NMR spectra of the coupling products.

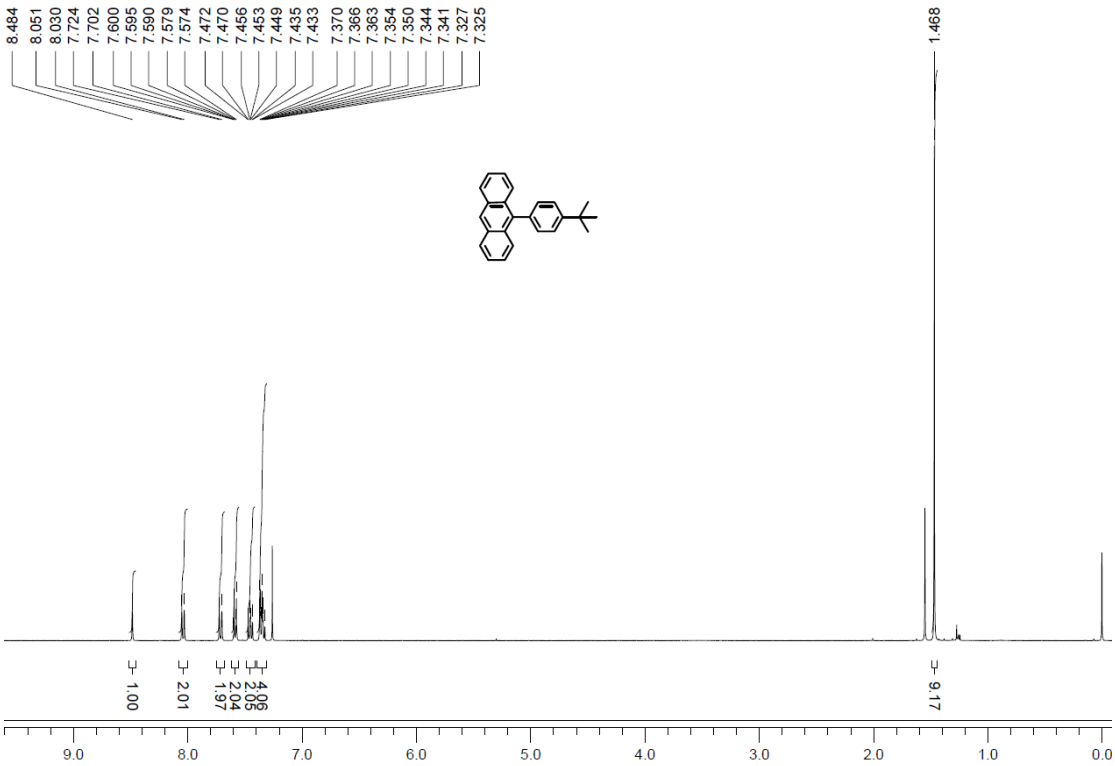


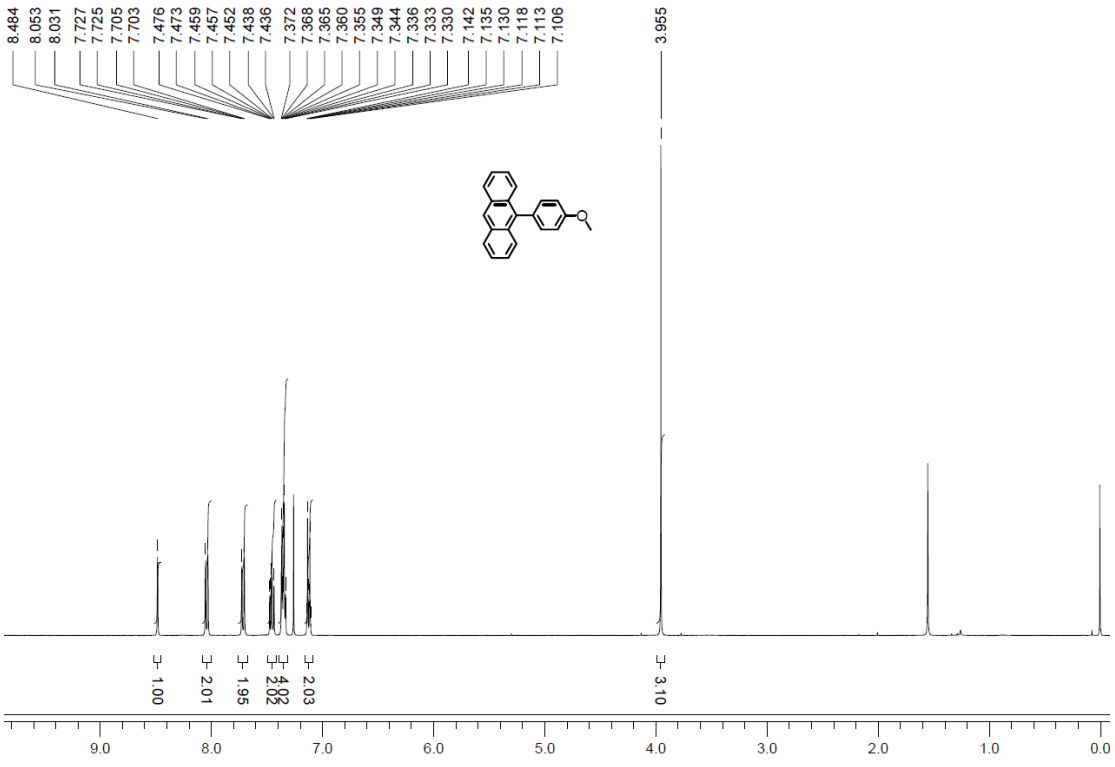


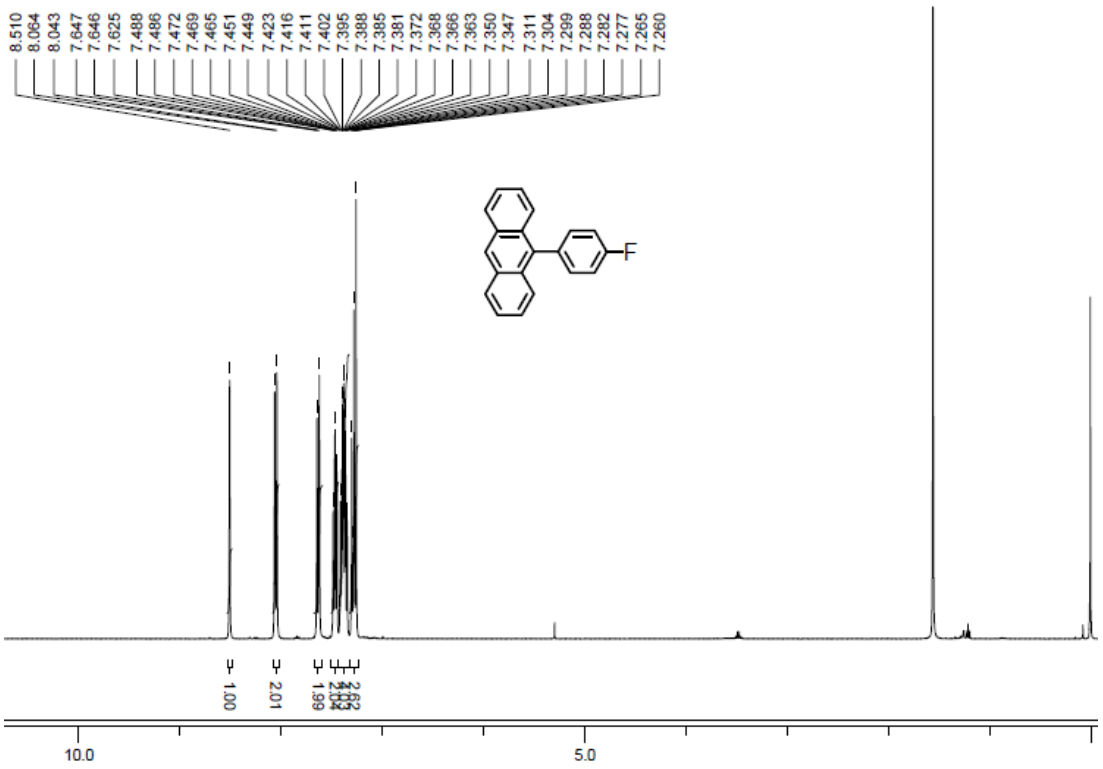


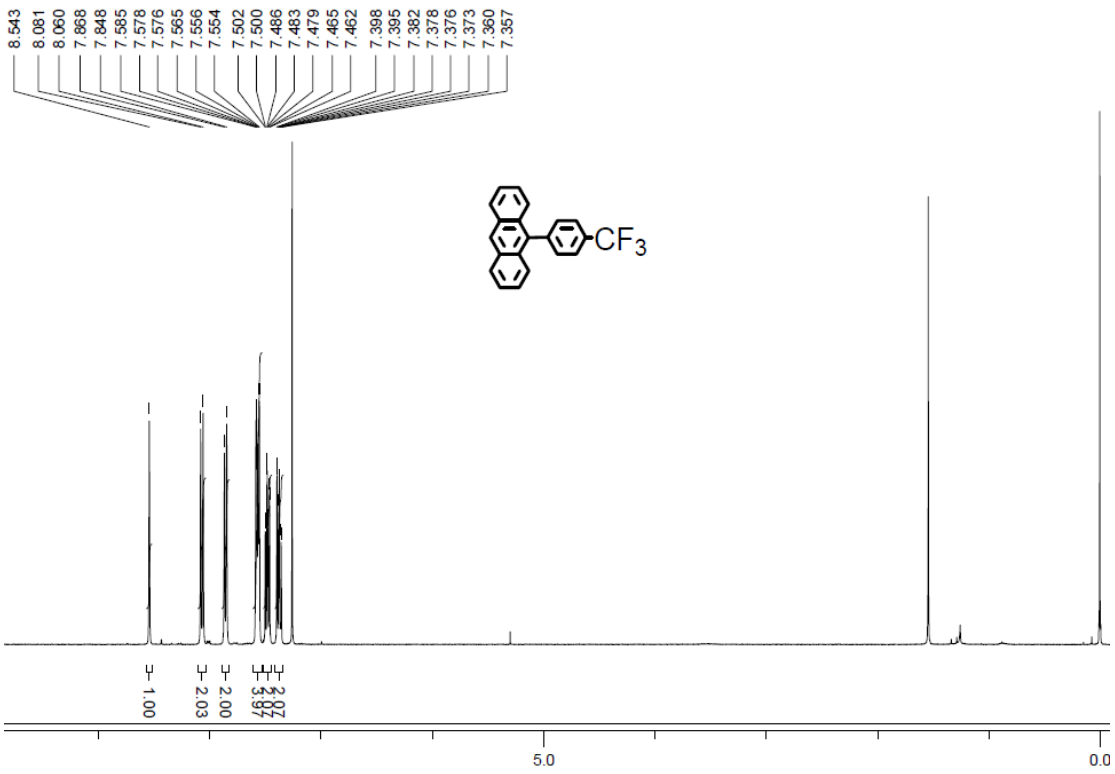


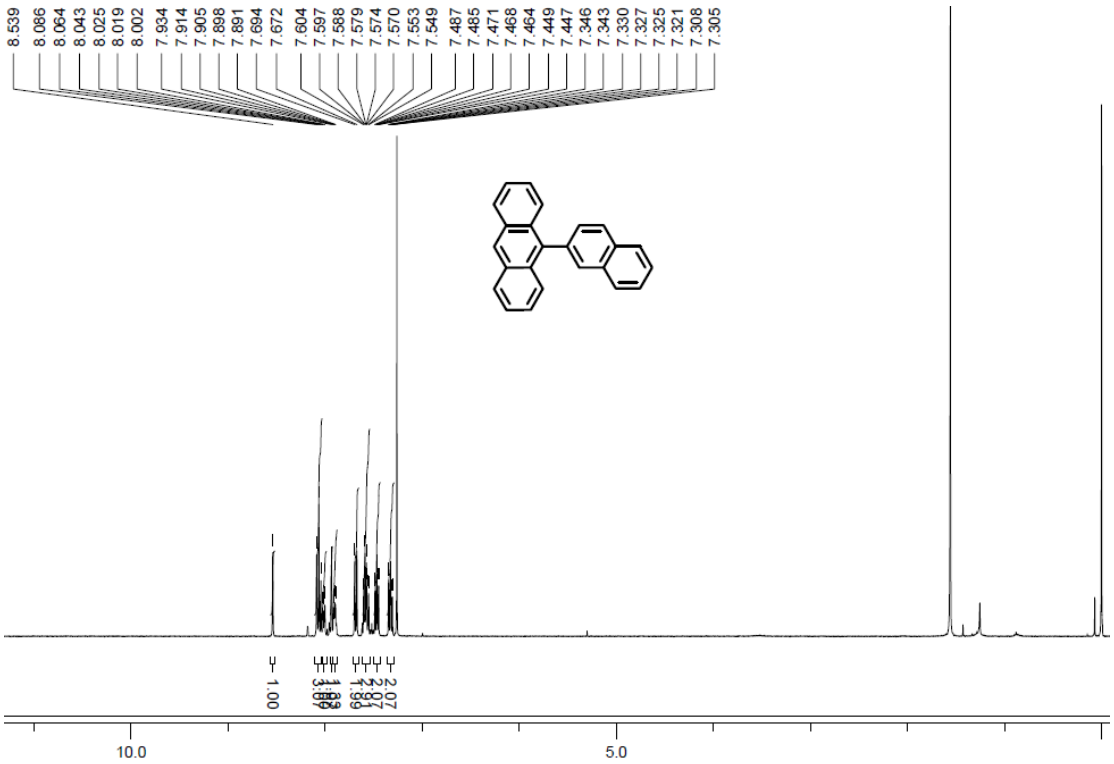


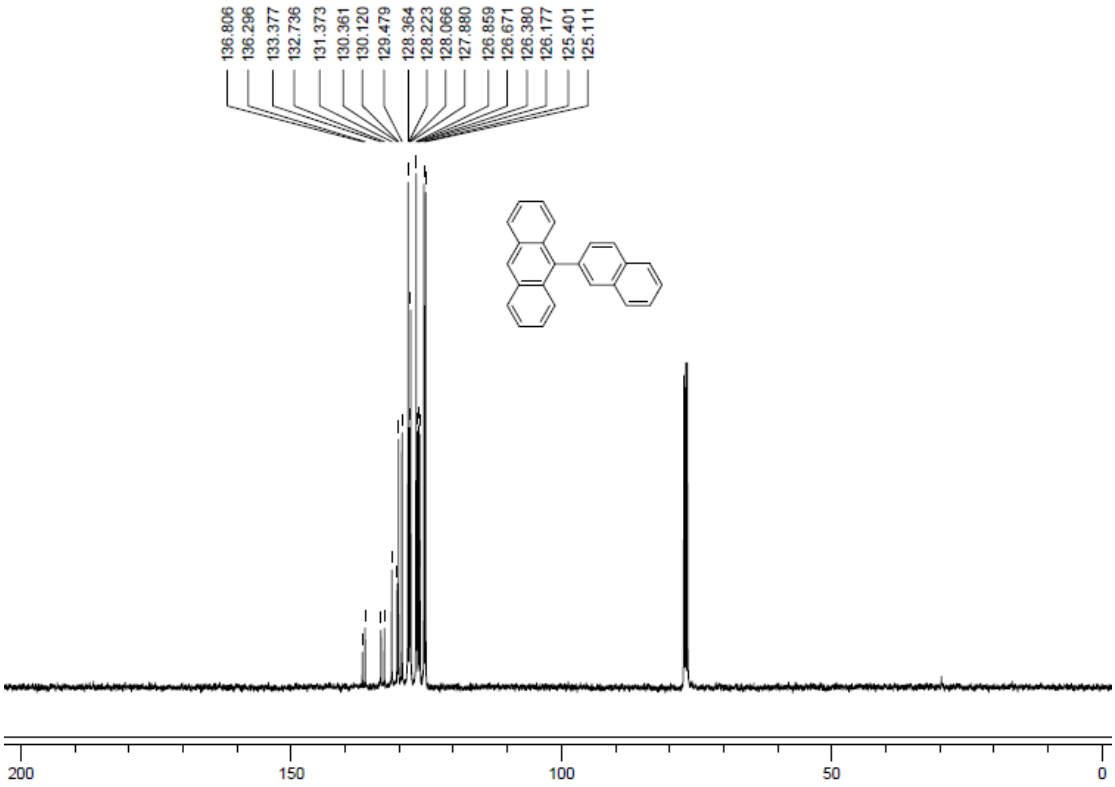


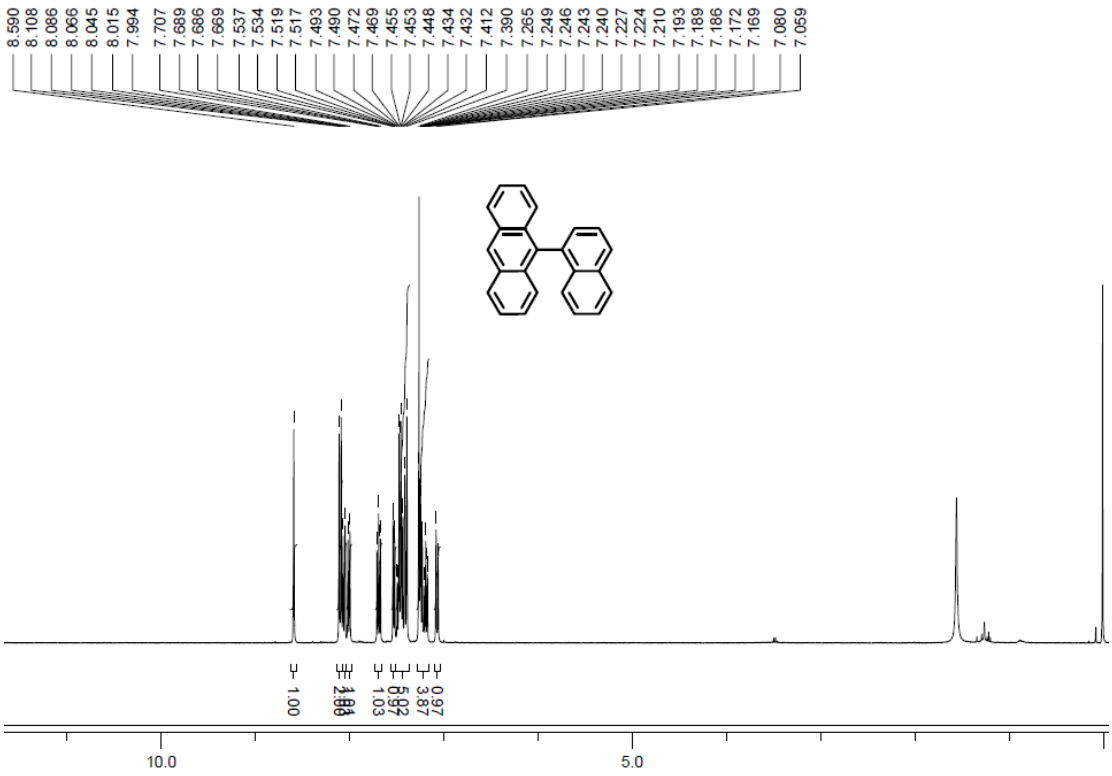


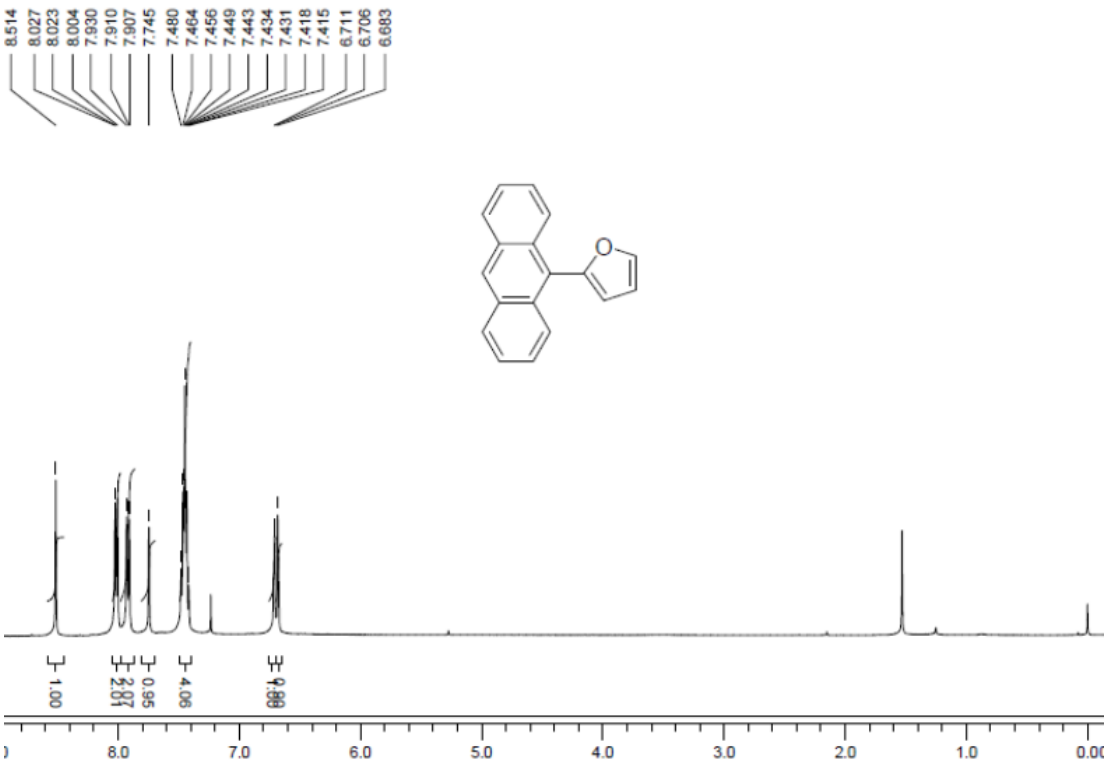


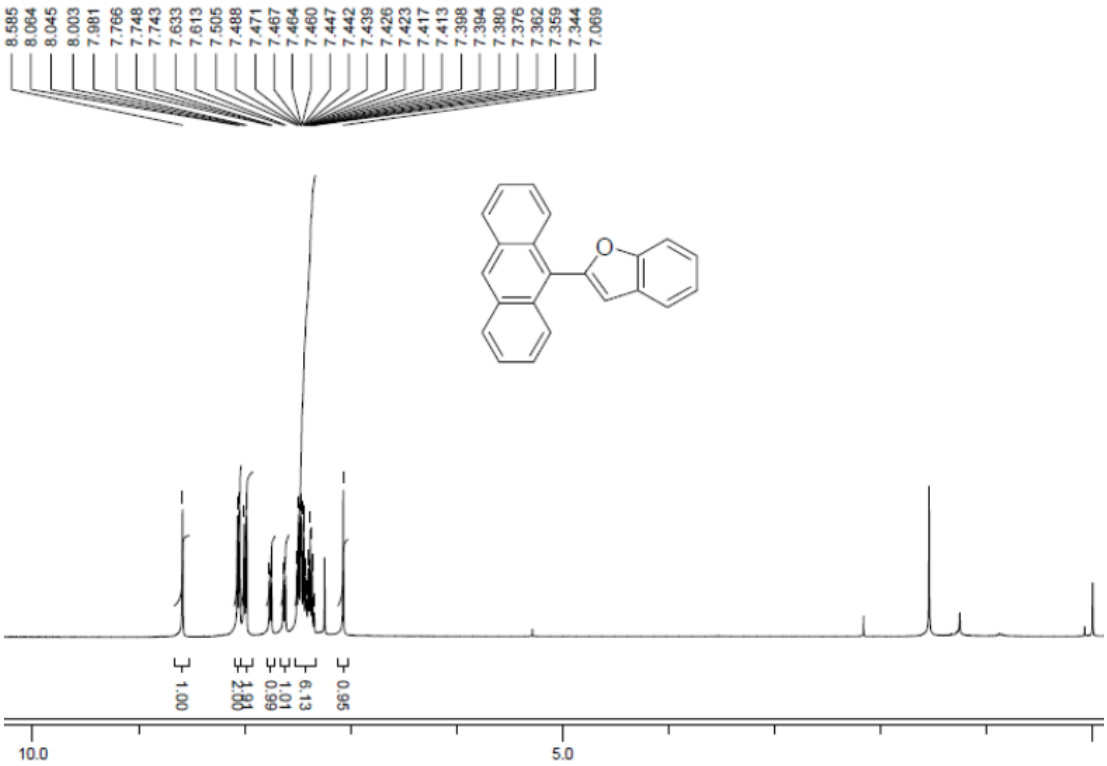


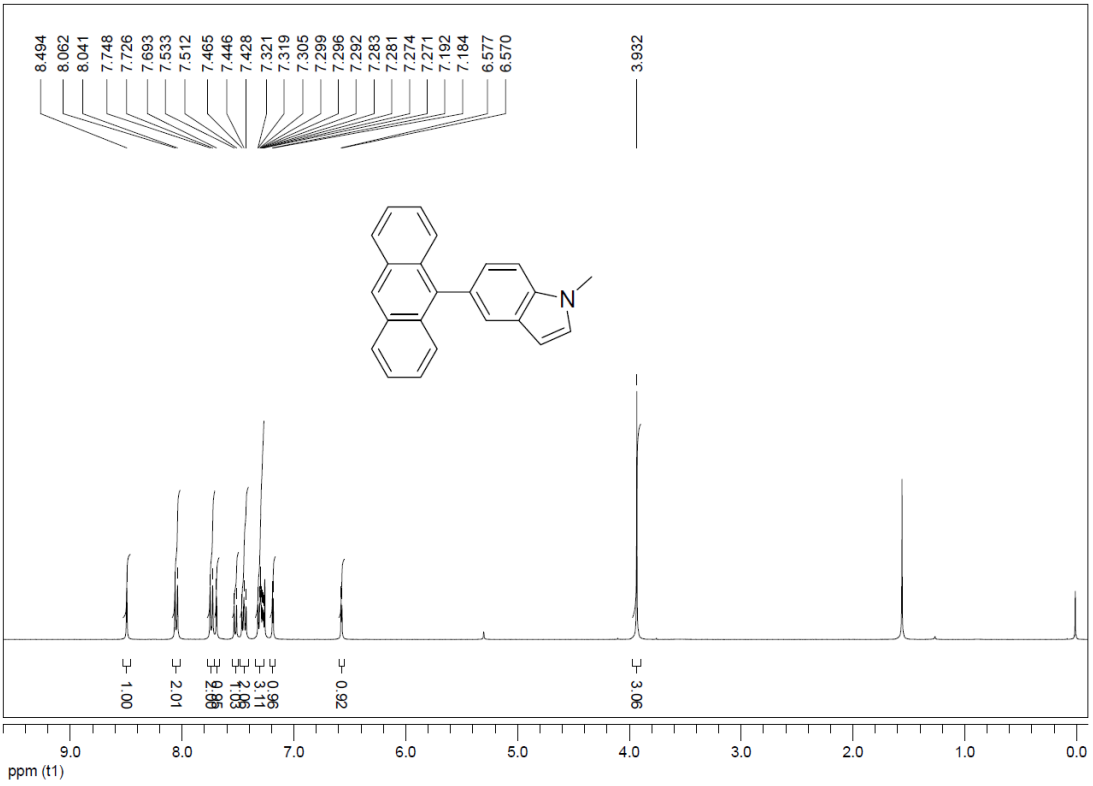


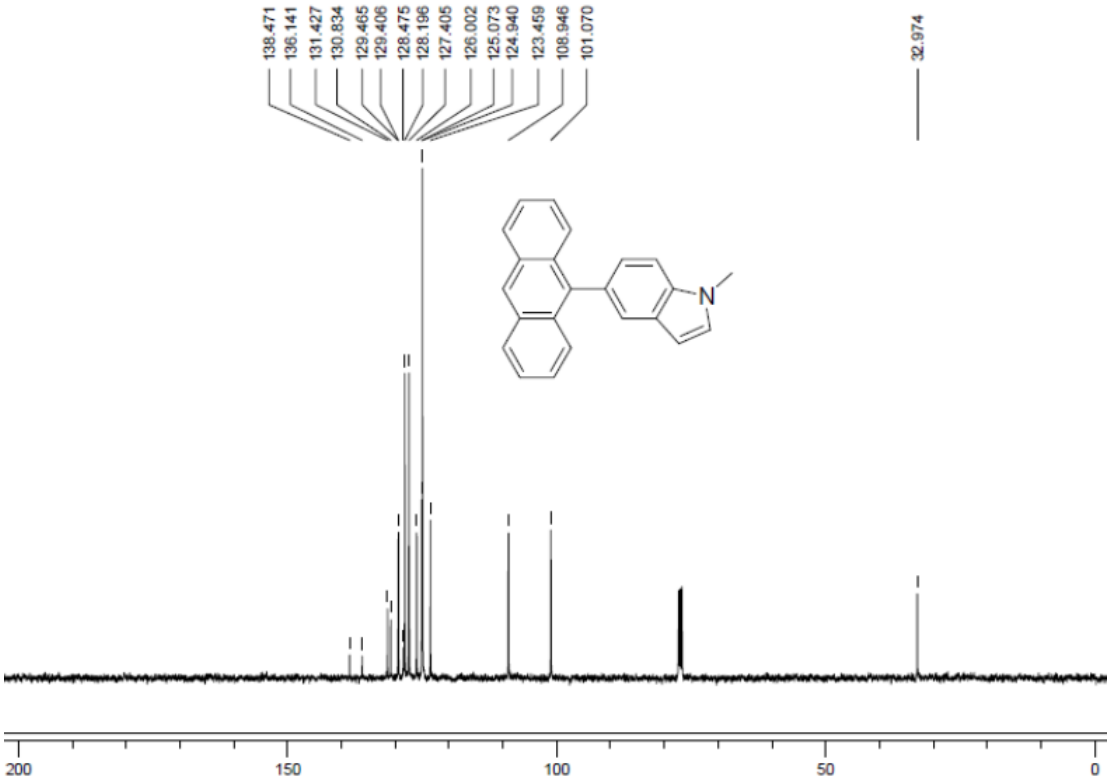




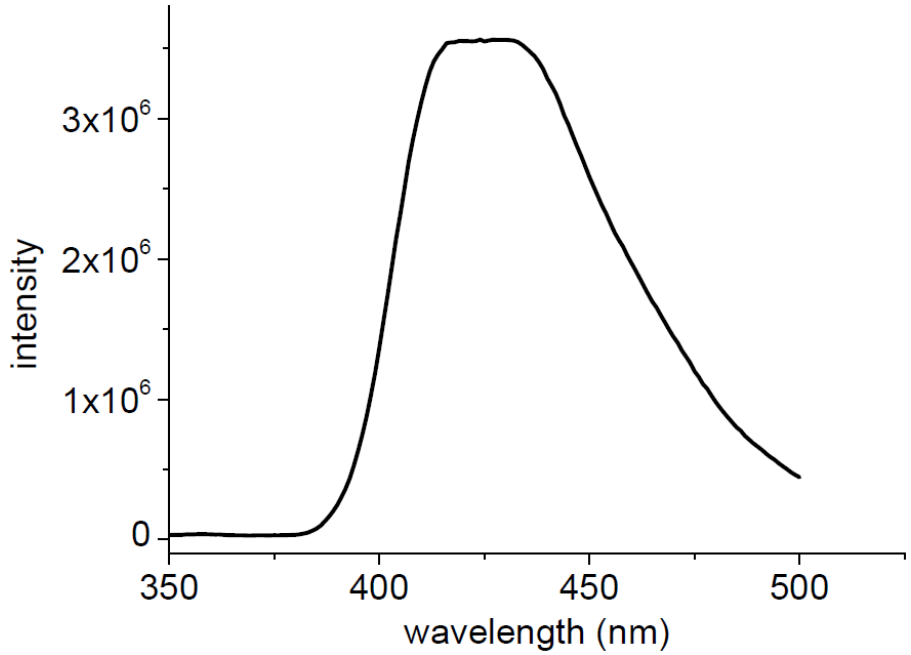








Fluorescence spectrum for 13.



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