Supporting Information

Pd(II)-Catalyzed Regioselective Multiple C−H Arylations of 1-Naphthamides with Cyclic Diaryliodonium Salts: One-Step Access to [4]- and [5]Carbohelicenes

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I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected. Absorption spectra were obtained on a HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. To reduce the fluctuation in the excitation intensity, the xenon lamp was kept on for 1 hour prior to the experiments. The excited state lifetimes were obtained using an HORIBA TEMPRO-01 instrument.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. 1,2-Dichlorobenzene [98%, extra dry, with molecular sieves, water≤50 ppm (by K.F.), Energy Seal] was purchased from Shanghai Energy Chemical CO., Ltd.

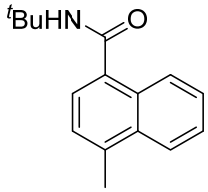
N-(*tert*-butyl)-1-naphthamide (**1a**),[1] *N*-(*tert*-butyl)-4-methyl-1-naphthamide (**1b**),[1] 4-bromo-*N*-(*tert*-butyl)-1-naphthamide (**1c**),[1] *N*-(*tert*-butyl)-4-fluoro-1-naphthamide (**1d**),[1] *N*-(*tert*-butyl)-4-methoxy-1-naphthamide (**1e**),[1] methyl 4-(*tert*-butylcarbamoyl)-1-naphthoate (**1f**),[1] *N*-(*tert*-butyl)-4-pheny1-naphthamide (**1g**),[1,2] *N*-(*tert*-butyl)-4-(*p*-tolyl)-1-naphthamide (**1h**),[1,2] *N*-(*tert*-butyl)-4-(4-methoxyphenyl)-1-naphthamide (**1i**),[1,2] 4-(benzofuran-2-yl)-*N*-(*tert*-butyl)-1-naphthamide (**1j**),[1,2] 4-(benzo[*b*]thiophen-2-yl)-*N*-(*tert*-butyl)-1-naphthamide (**1k**),[1,2] *N*-(*tert*-butyl)phenanthrene-9-carboxamide (**1l**),[1,3] *N*-(*tert*-butyl)pyrene-1-carboxamide (**1m**),[1,3] N^1,N^4-di-*tert*-butylnaphthalene-1,4-dicarboxamidedibenzo (**1n**),[1] dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2a**),[4]

3,7-difluorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2b**),[4] 3,7-dichlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2c**),[4] 2,8-difluorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2d**),[4] 2,8-dichlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2e**),[4] 2,8-dimethoxydibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (**2f**),[4] were prepared according to the corresponding literatures.

II. Synthesis of 1-naphthamide derivatives

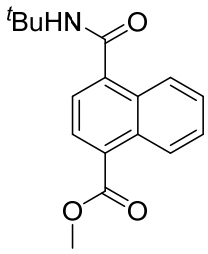
i) General procedure for the synthesis of 1-naphthamides[1]

A Schlenk tube with a magnetic stir bar was charged with corresponding 1-naphthoic acid derivatives (10 mmol), $SOCl_2$ (20.0 mL) and DMF (2 drop) were added. The mixture was stirred for 1 h at room temperature. After removing the volatiles in vacuo, the solids are dissolved with CH_2Cl_2 (20 mL) and then 2-methylpropan-2-amine (12 mmol) and triethylamine (15 mmol) were added at 0 ºC. The resulting mixture was stirred at room temperature for 24 h and then washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 4/1) to provide the desired product.[1]



***N*-(*tert*-butyl)-4-methyl-1-naphthamide (1b)**

Purification via silica gel column chromatography (hexane/EtOAc = 4/1, v/v) afforded the desired product **1b** as a white solid (2.26 g, 94% yield). M.p.: 134-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 9H), 2.70 (s, 3H), 5.80 (br, 1H), 7.26-7.28 (m, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.53-7.57 (m, 2H), 8.00-8.04 (m, 1H), 8.28-8.32 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 29.1, 52.1, 124.3, 124.4, 125.5, 126.0, 126.3, 126.7, 130.2, 132.8, 134.6, 136.8, 169.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{20}NO$: $[M+H]^+$, 242.1539; found: 242.1548.



Methyl-4-(*tert*-butylcarbamoyl)-1-naphthoate (1f)

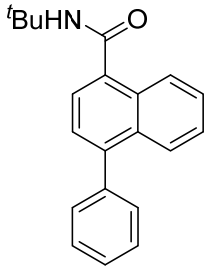
Purification via silica gel column chromatography (hexane/EtOAc = 4/1, v/v) afforded the desired product **1f** as a white solid (2.19 g, 77% yield). M.p.: 182-183 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ =1.53 (s, 9H), 4.00 (s, 3H), 5.86 (br, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.56-7.65 (m, 2H), 8.08 (d, J = 7.6 Hz, 1H), 8.21 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H), 8.87 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.0, 52.5, 122.9, 125.8, 126.1, 127.3, 128.1, 128.8, 129.1, 130.5, 131.6, 140.5, 167.7, 168.7 ppm. HRMS (ESI^+): calcd for $C_{17}H_{19}NNaO_3$: $[M+Na]^+$, 308.1257; found: 308.1256.

ii) General procedure for the synthesis of 4-aryl-1-naphthamides[1,2]

In a 100 mL flask, arylboronic acid (12 mmol), K_2CO_3 (24.0 mmol), $Pd(PPh_3)_4$ (0.2 mmol) and 4-bromo-1-naphthoic acid (10 mmol) were dissolved into the mixed solution of dioxane/water (30/5 mL) under a N_2 atmosphere, and the mixture was stirred magnetically at 100 °C in oil bath for 16 h. The reaction mixture was filtered, and the filtrate was adjusted to pH 2-3 with 2 N hydrochloric acid solutions. A lot of white solid precipitation was filtered and evaporated under reduced pressure to give 4-aryl-1-naphthoic acid as a white solid.[2]

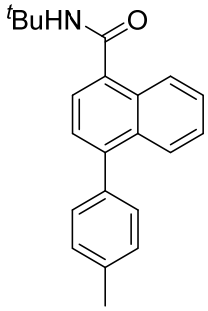
A Schlenk tube with a magnetic stir bar was charged with 4-aryl-1-naphthoic acid, $SOCl_2$ (20.0 mL) and DMF (2 drop) were added. The mixture was stirred for 1 h at room temperature. After removing the volatiles in vacuo, the solids are dissolved with CH_2Cl_2 (20 mL) and then 2-methylpropan-2-amine (12 mmol) and triethylamine (15 mmol) were added at 0 ºC. The resulting mixture was stirred at room temperature for 24 h and then washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel

(hexane/EtOAc = 4/1) to provide the desired product.[1]



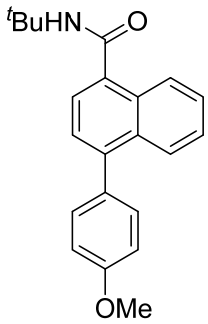
***N*-(*tert*-butyl)-4-phenyl-1-naphthamide (1g)**

Purification via silica gel column chromatography (hexane/EtOAc = 4/1, v/v) afforded the desired product **1g** as a white solid (2.43 g, 80% yield). M.p.: 173-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 9H), 5.88 (br, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.45-7.52 (m, 6H), 7.54-7.60 (m, 2H), 7.90 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.1, 55.2, 124.0, 125.7, 125.9, 126.54, 126.56, 126.9, 127.7, 128.5, 130.1, 130.5, 132.0, 135.6, 140.4, 142.4, 169.4 ppm. HRMS (ESI^+): calcd for $C_{21}H_{22}NO$: $[M+H]^+$, 304.1696; found: 304.1703.



***N*-(*tert*-butyl)-4-(*p*-tolyl)-1-naphthamide (1h)**

Purification via silica gel column chromatography (hexane/EtOAc = 4/1, v/v) afforded the desired product **1h** as a white solid (2.38 g, 75% yield). M.p.: 162-163 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 9H), 2.46 (s, 3H), 5.87 (br, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.34-7.38 (m, 3H), 7.43-7.47 (m, 1H), 7.53-7.56 (m, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 29.1, 52.2, 124.0, 125.7, 125.9, 126.4, 126.6, 126.9, 129.2, 130.0, 130.5, 132.1, 135.4, 137.4, 142.4, 169.4 ppm. HRMS (ESI^+): calcd for $C_{22}H_{24}NO$: $[M+H]^+$, 318.1852; found: 318.1853.



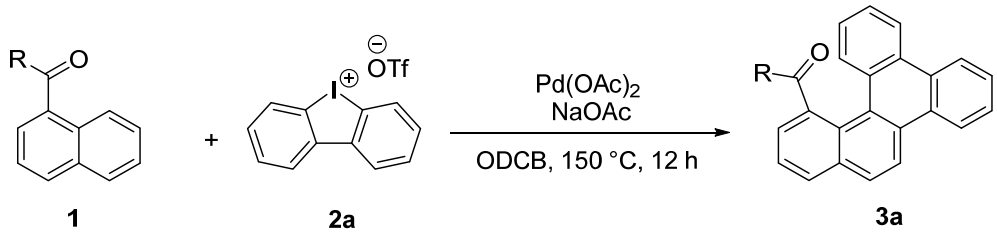
***N*-(*tert*-butyl)-4-(4-methoxyphenyl)-1-naphthamide (1i)**

Purification via silica gel column chromatography (hexane/EtOAc = 4/1, v/v) afforded the desired product **1i** as a white solid (2.23 g, 67% yield). M.p.: 137-138 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 9H), 3.90 (s, 3H), 5.86 (br, 1H), 7.03 (d, J = 8.8 Hz, 2H), 7.35-7.40 (m, 3H), 7.43-7.48 (m, 1H), 7.53-7.58 (m, 2H), 7.93 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.1, 52.2, 55.5, 113.9, 124.0, 125.7, 125.9, 126.4, 126.6, 126.9, 130.5, 131.2, 132.2, 132.7, 135.3, 142.1, 159.3, 169.4 ppm. HRMS (ESI^+): calcd for $C_{22}H_{24}NO_2$: $[M+H]^+$, 334.1802; found: 334.1805.

III. Optimization of the multiple C−H arylation of 1-naphthamides 1 with cyclic diaryliodonium salt 2a

A Schlenk tube with a magnetic stir bar was charged with palladium catalyst (10 mol %), NaOAc (82.0 mg, 5.0 equiv), 1-naphthamides **1** (0.2 mmol, 1.0 equiv), dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate **2a** (0.6 mmol, 3 equiv), and solvent (3.0 mL). The resulting mixture was stirred at corresponding reaction temperature and reaction time, and then removed solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to provide the desired product.

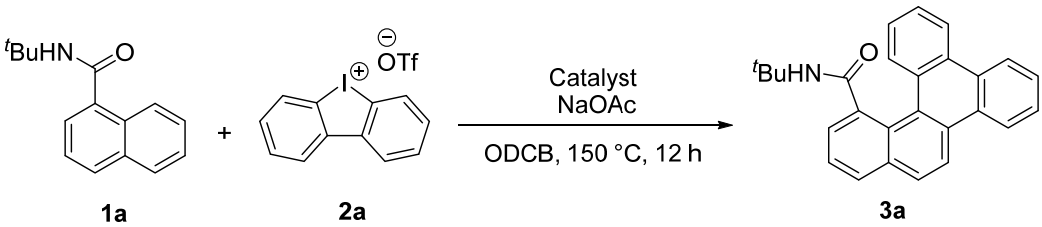
Table S1. Screening of directing groups



Entry	R	Yield(%)[a]
1	NH_2	N.D
2	$NHCH_3$	N.D
3	NH^iPr	13
4	NH^tBu	18

Reaction conditions: 1-naphthamides **1** (0.2 mmol), dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate **2a** (256.8 mg, 3 equiv), $Pd(OAc)_2$ (10 mol %), NaOAc (5.0 equiv) and ODCB (not dry) (3.0 mL) at 150 ºC for 12 h under a N_2 atmosphere. [a]Yield of isolated products. ODCB = 1,2-dichlorobenzene. OTf = trifluoromethanesulfonate. N.D. = not detected.

Table S2. Screening of catalyst

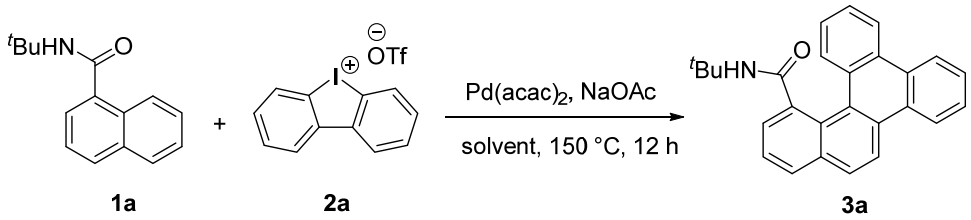


Entry	Catalyst	Yield(%)[a]
1	none	N.D.
2	$Pd(acac)_2$	35
3	$Pd(TFA)_2$	29
4	$Pd_2(dba)_3$	22
5	$Pd(OAc)_2$	18

Reaction conditions: *N*-(*tert*-butyl)-1-naphthamide **1a** (45.4 mg, 0.2 mmol),

dibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate **2a** (256.8 mg, 3 equiv), catalyst (10 mol %), NaOAc (5.0 equiv) and ODCB (not dry) (3.0 mL) at 150 ºC for 12 h under a N_2 atmosphere. [a]Yield of isolated products. ODCB = 1,2-dichlorobenzene. OTf = trifluoromethanesulfonate. dba = dibenzylideneacetone. TFA = 2,2,2-trifluoroacetate. acac = acetylacetone. N.D. = not detected.

Table S3. Screening of solvent

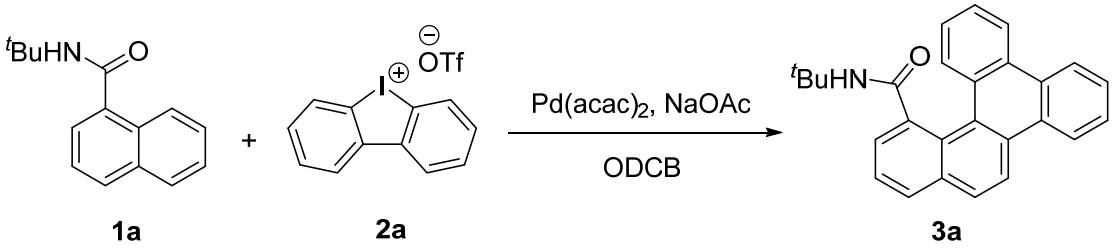


1a **2a** **3a**

Entry	Solvent	Volume(mL)	Yield(%)[a]
1	1,4-dioxane	3	19
2	toluene	3	5
3	ODCB	4	37
4	ODCB (not dry)	3	35
5	ODCB	3	42
6	ODCB	1.5	28

Reaction conditions: *N*-(*tert*-butyl)-1-naphthamide **1a** (45.4 mg, 0.2 mmol), dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate **2a** (256.8 mg, 3 equiv), $Pd(acac)_2$ (10 mol %), NaOAc (5.0 equiv) and solvent (3.0 mL) at 150 ºC for 12 h under a N_2 atmosphere. [a]Yield of isolated products. ODCB = 1,2-dichlorobenzene. OTf = trifluoromethanesulfonate. acac = acetylacetone.

Table S4. Screening of reaction time, temperature and atmosphere



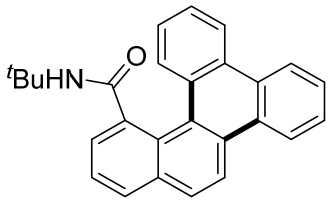
1a **2a** **3a**

Entry	Reaction time	Temperature	Atmosphere	Yield(%)[a]
1	12 h	150 ºC	N_2	42
2	24 h	150 ºC	N_2	58
3	24 h	100 ºC	N_2	trace
4	24 h	160 ºC	N_2	73
5	24 h	160 ºC	Air	25

Reaction conditions: *N*-(*tert*-butyl)-1-naphthamide **1a** (45.4 mg, 0.2 mmol), dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate **2a** (256.8 mg, 3 equiv), $Pd(acac)_2$ (10 mol %), NaOAc (5.0 equiv) and ODCB (3.0 mL). [a]Yield of isolated products. ODCB = 1,2-dichlorobenzene. acac = acetylacetone. OTf = trifluoromethanesulfonate.

IV. General procedure for the double C−H arylations of 1-naphthamides with cyclic diaryliodonium salts

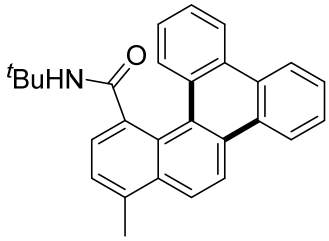
A Schlenk tube with a magnetic stir bar was charged with $Pd(acac)_2$ (6.1 mg, 10 mol %), NaOAc (82.0 mg, 5.0 equiv), 1-naphthamides (**1**, 0.2 mmol, 1.0 equiv), cyclic diaryliodonium salts (**2**, 0.6 mmol, 3 equiv), and ODCB (3.0 mL) under a N_2 atmosphere. The resulting mixture was stirred at 160 ºC in oil bath for 24 h or 48 h and then removed solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to provide the desired product.



***N*-(*tert*-Butyl)-7-methylbenzo[*g*]chrysene-10-carboxamide (3a)**

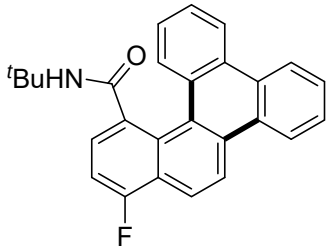
Purification via silica gel column chromatography (hexane/EtOAc = 8/1, v/v) afforded the desired product **3a** as a yellow solid (54.8 mg, 73% yield). M.p.: 180-181 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 9H), 4.77 (br, 1H), 7.57-7.65 (m, 2H), 7.67-7.71

(m, 1H), 7.73-7.76 (m, 2H), 8.02-8.11 (m, 3H), 8.49 (d, J = 8.0 Hz, 1H), 8.58-8.65 (m, 3H), 8.69-8.73 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.9, 51.1, 121.5, 123.3, 123.4, 124.0, 125.5, 126.3, 126.5, 127.3, 127.6, 127.7, 128.1, 128.9, 129.0, 129.2, 129.4, 129.5, 130.0, 130.5, 131.3, 134.1, 137.5, 168.0 ppm. HRMS (ESI^+): calcd for $C_{27}H_{23}NNaO$: $[M+Na]^+$, 400.1672; found: 400.1672.



***N*-(*tert*-Butyl)-7-methylbenzo[*g*]chrysene-10-carboxamide (3b)**

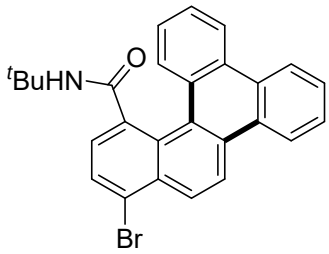
Purification via silica gel column chromatography (hexane/EtOAc = 8/1, v/v) afforded the desired product **3b** as a yellow solid (51.3 mg, 66% yield). M.p.: 171-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 9H), 2.85 (s, 3H), 4.73 (br, 1H), 7.53-7.55 (m, 1H), 7.56-7.64 (m, 2H), 7.72-7.76 (m, 2H), 7.99 (d, J = 7.2 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.44-8.47 (m, 1H), 8.60-8.66 (m, 3H), 8.69-8.73 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 27.8, 51.0, 121.3, 123.3, 123.4, 124.0, 124.1, 125.8, 126.9, 127.2, 127.3, 127.6, 127.7, 128.8, 129.0, 129.10, 129.14, 129.3, 130.5, 131.6, 133.1, 135.7, 136.7, 168.1 ppm. HRMS (ESI^+): calcd for $C_{28}H_{26}NO$: $[M+H]^+$, 392.2009; found: 392.2012.



***N*-(*tert*-Butyl)-7-fluorobenzo[*g*]chrysene-10-carboxamide (3c)**

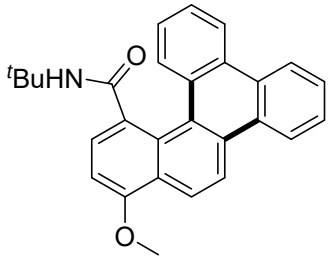
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3c** as a yellow solid (47.3 mg, 60% yield). M.p.: 98-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 9H), 4.73 (br, 1H), 7.36 (dd, J = 9.2 Hz, J = 8.4 Hz, 1H), 7.57-7.66 (m, 2H), 7.73-7.78 (m, 2H), 8.06 (dd, J = 8.0 Hz, J = 6.2 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.43-8.45 (m, 1H), 8.60-8.66 (m, 3H), 8.69-8.73 (m, 1H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.1, 110.3 (d, J_{CF} = 20.4 Hz), 120.16, 120.23, 122.1 (d, J_{CF} = 2.0 Hz), 123.4, 123.9 (d, J_{CF} = 16.1 Hz), 124.1, 126.3(d, J_{CF} = 2.7 Hz), 127.3 (d, J_{CF} = 3.9 Hz), 127.5, 127.77, 127.77(d, J_{CF} = 5.7 Hz), 128.1, 128.9, 129.1 (d, J_{CF} = 7.0 Hz), 129.8 (d, J_{CF} = 9.2 Hz), 130.2, 130.6, 131.1, 133.6 (d, J_{CF} = 3.9 Hz), 159.9 (d, J_{CF} = 255.3 Hz), 167.4 ppm. HRMS (ESI^+): calcd for $C_{27}H_{23}FNO$: $[M+H]^+$, 396.1758; found: 396.1755.



7-Bromo-*N*-(*tert*-butyl)benzo[*g*]chrysene-10-carboxamide (3d)

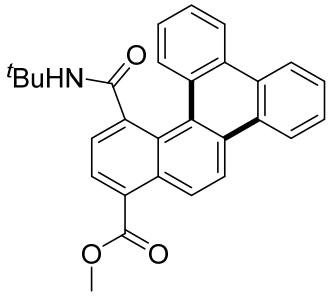
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3d** as a yellow solid (45.8 mg, 50% yield). M.p.: 109-110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 9H), 4.69 (br, 1H), 7.56-7.67 (m, 2H), 7.75-7.78 (m, 2H), 7.92 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 9.2 Hz, 1H), 8.59-8.65 (m, 2H), 8.67-8.72 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.2, 122.9, 123.4, 124.1, 125.2, 126.6, 127.0, 127.1, 127.6, 127.80, 127.84, 128.2, 128.9, 129.1, 129.2, 129.3, 129.9, 130.3, 130.7, 131.2, 132.5, 137.2, 167.3 ppm. HRMS (ESI^+): calcd for $C_{27}H_{23}BrNO$: $[M+H]^+$, 456.0958 (100.0%), 458.0937 (97.3%); found: 456.0958 (100.0 %), 458.0942 (97.3%).



***N*-(*tert*-Butyl)-7-methoxybenzo[*g*]chrysene-10-carboxamide (3e)**

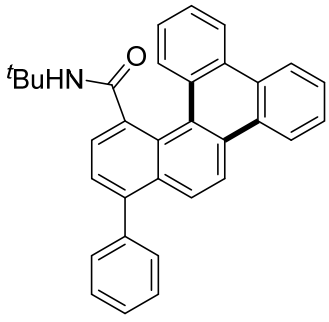
Purification via silica gel column chromatography (hexane/EtOAc = 8/1, v/v) afforded the desired product **3e** as a yellow solid (37.7 mg, 46% yield). M.p.: 240-241 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 9H), 4.12 (s, 3H), 4.74 (br, 1H), 7.04 (d, J = 8.0

Hz, 1H), 7.55-7.63 (m, 2H), 7.71-7.75 (m, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.46-8.51 (m, 2H), 8.56-8.64 (m, 3H), 8.68-8.70 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 50.9, 56.1, 104.6, 120.8, 121.9, 123.3, 124.1, 125.8, 126.2, 126.8, 127.1, 127.5, 127.66, 127.74, 128.9, 129.0, 129.4, 129.8, 129.9, 130.2, 130.5, 131.6, 157.0, 167.9 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{26}NO_2$: $[M+H]^+$, 408.1958; found: 408.1957.



Methyl-10-(*tert*-butylcarbamoyl)benzo[*g*]chrysene-7-carboxylate (3f)

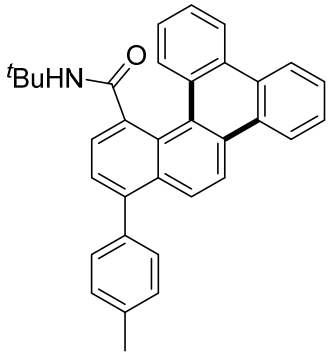
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3f** as a yellow solid (31.8 mg, 37% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.63 (s, 9H), 4.08 (s, 3H), 4.70 (br, 1H), 7.57-7.66 (m, 2H), 7.75-7.77 (m, 2H), 8.09 (d, J = 7.6 Hz, 1H), 8.29 (d, J = 7.6 Hz, 1H), 8.35 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 8.61-8.73 (m, 4H), 9.03-9.07 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7, 51.3, 52.7, 123.0, 123.4, 124.1, 125.3, 126.3, 126.5, 127.5, 127.6, 127.76, 127.79, 128.1, 128.8, 128.9, 129.1, 129.15, 129.19, 129.6, 130.6, 131.2, 132.4, 141.3, 167.3, 167.9 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{25}NNaO_3$: $[M+Na]^+$, 458.1727; found: 458.1726.



***N*-(*tert*-Butyl)-7-phenylbenzo[*g*]chrysene-10-carboxamide (3g)**

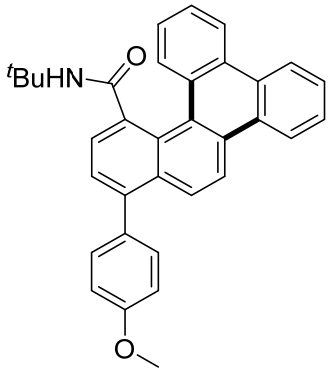
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3g** as a yellow solid (46.9 mg, 52% yield). M.p.: 165-166 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 9H), 4.82 (br, 1H), 7.50-7.67 (m, 8H),

7.73-7.75 (m, 2H), 8.07 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 7.2 Hz, 1H), 8.48-8.54 (m, 2H), 8.58-8.65 (m, 2H), 8.71-8.73 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.1, 121.3, 123.4, 123.9, 126.19, 126.24, 126.5, 127.3, 127.6, 127.8, 127.9, 128.5, 128.6, 128.9, 129.0, 129.1, 130.4, 130.5, 131.6, 132.2, 136.9, 140.3, 142.2, 168.0 ppm. HRMS (ESI$^+$): calcd for $C_{33}H_{28}NO$: $[M+H]^+$, 454.2165; found: 454.2167.



***N*-(*tert*-Butyl)-7-(*p*-tolyl)benzo[*g*]chrysene-10-carboxamide (3h)**

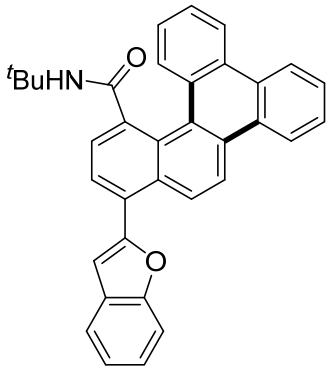
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3h** as a yellow solid (46.0 mg, 49% yield). M.p.: 156-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 9H), 2.50 (s, 3H), 4.81 (br, 1H), 7.37 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.59-7.66 (m, 3H), 7.70-7.76 (m, 2H), 8.09-8.12 (m, 2H), 8.49 (d, J = 9.2 Hz, 1H), 8.51-8.54 (m, 1H), 8.58-8.64 (m, 2H), 8.71-8.73 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 27.8, 51.0, 121.2, 123.3, 123.4, 124.0, 126.2, 126.3, 126.5, 127.2, 127.6, 127.7, 128.5, 128.9, 129.0, 129.1, 129.2, 129.4, 130.3, 130.5, 131.6, 132.3, 136.7, 137.4, 137.7, 142.2, 168.0 ppm. HRMS (ESI$^+$): calcd for $C_{34}H_{30}NO$: $[M+H]^+$, 468.2322; found: 468.2320.



***N*-(*tert*-Butyl)-7-(4-methoxyphenyl)benzo[*g*]chrysene-10-carboxamide (3i)**

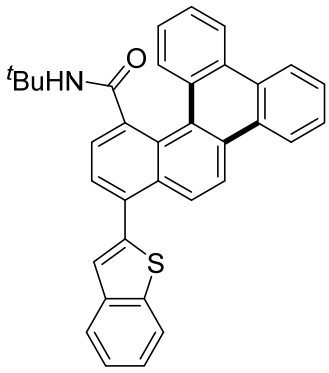
Purification via silica gel column chromatography (hexane/EtOAc = 8/1, v/v) afforded the desired product **3i** as a yellow solid (56.7 mg, 59% yield). M.p.: 130-131 ºC; ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 9H), 3.93 (s, 3H), 4.81 (br, 1H), 7.09 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.59-7.66 (m, 3H), 7.71-7.76 (m, 2H), 8.09-8.12 (m, 2H), 8.49 (d, J = 9.2 Hz, 1H), 8.51-8.54 (m, 1H), 8.57-8.66 (m, 2H), 8,70-8.73 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.0, 55.6, 114.1, 121.2, 123.3, 123.4, 123.9, 126.27, 126.33, 126.5, 127.2, 127.3, 127.6, 127.7, 128.6, 128.9, 129.0, 129.1, 129.2, 130.5, 131.56, 131.58, 132.4, 132.6, 136.6, 141.8, 159.5, 168.0 ppm. HRMS (ESI): calcd for $C_{34}H_{30}NO_2$: $[M+H]^+$, 484.2271; found: 484.2273.



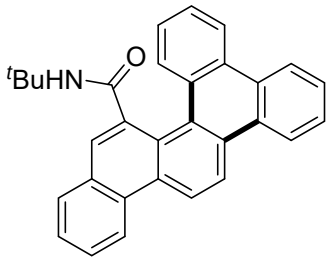
7-(Benzofuran-2-yl)-*N*-(*tert*-butyl)benzo[*g*]chrysene-10-carboxamide (3j)

Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3j** as a yellow solid (49.5 mg, 50% yield). M.p.: 158-159 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 9H), 4.77 (br, 1H), 7.21 (s, 1H), 7.34 (td, J = 7.6 Hz, J =1.2 Hz, 1H), 7.38-7.42 (m, 1H), 7.59-7.68 (m, 3H), 7.72-7.77 (m, 3H), 8.07 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.46-8.48 (m, 1H), 8.62-8.67 (m, 4H), 8.72-8.74 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.2, 107.4, 111.6, 121.4, 122.2, 123.3, 123.36, 123.40, 124.0, 125.0, 125.5, 126.5, 126.7, 127.2, 127.4, 127.7, 127.8, 128.0, 128.5, 128.96, 129.04, 129.07, 129.1, 129.3, 130.0, 130.6, 131.4, 131.7, 138.4, 155.1, 155.4, 167.7 ppm. HRMS (ESI^+): calcd for $C_{35}H_{28}NO_2$: $[M+H]^+$, 494.2115; found: 494.2116.



7-(Benzo[*b*]thiophen-2-yl)-*N*-(*tert*-butyl)benzo[*g*]chrysene-10-carboxamide (3k)

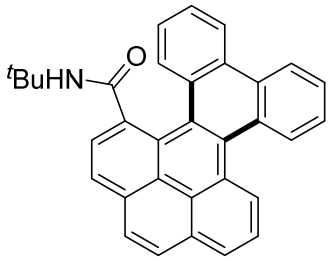
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3k** as a yellow solid (63.0 mg, 62% yield). M.p.: 160-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 9H), 4.79 (br, 1H), 7.42-7.47 (m, 2H), 7.55 (s, 1H), 7.60-7.68 (m, 2H), 7.74-7.76 (m, 2H), 7.85 (d, J = 7.2 Hz, 1H), 7.90 (dd, J = 7.2 Hz, J = 2.0 Hz, 1H), 7.93-7.96 (m, 1H), 8.13 (d, J = 7.2 Hz, 1H), 8.46-8.51 (m, 2H), 8.57 (d, J = 9.2 Hz, 1H), 8.61-8.65 (m, 2H), 8.72-8.74 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.1, 122.0, 122.3, 123.38, 123.39, 123.98, 123.99, 124.78, 124.84, 125.2, 125.8, 126.4, 126.5, 127.4, 127.7, 127.8, 127.9, 128.3, 128.6, 128.99, 129.01, 129.1, 129.4, 130.6, 131.4, 132.6, 134.3, 137.9, 140.3, 140.7, 141.5, 167.7 ppm. HRMS (ESI$^+$): calcd for $C_{35}H_{28}NOS$: $[M+H]^+$, 510.1886; found: 510.1885.



***N*-(*tert*-Butyl)benzo[*f*]picene-9-carboxamide (3l)**

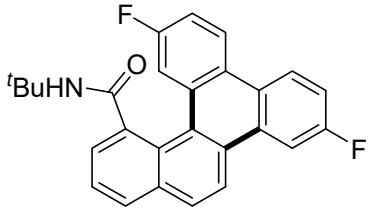
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3l** as a yellow solid (46.4 mg, 54% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 9H), 4.80 (br, 1H), 7.57-7.68 (m, 2H), 7.70-7.79 (m, 4H), 8.08 (d, J = 7.6 Hz, 1H), 8.43 (s, 1H), 8.48 (d, J = 9.2 Hz, 1H), 8.61 (d, J = 7.6 Hz, 1H), 8.65-8.71 (m, 2H), 8.74-8.77 (m, 2H), 8.86 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.1, 121.9, 122.4, 123.1, 123.39, 123.41, 123.8, 123.9, 127.5, 127.7, 127.8, 128.3, 129.2, 129.3, 129.4, 129.6, 130.2, 130.4,

130.8, 131.25, 131.28, 131.37, 131.40, 131.43, 135.1, 167.7 ppm. HRMS (ESI^+): calcd for $C_{31}H_{26}NO$: $[M+H]^+$, 428.2009; found: 428.2010.



***N*-(*tert*-Butyl)tribenzo[*f,ij,no*]tetraphene-1-carboxamide (3m)**

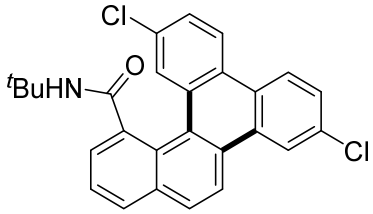
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3m** as a yellow solid (50.6 mg, 56% yield). M.p.: >250 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.61 (s, 9H), 4.92 (br, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.77 (t, J = 7.3 Hz, 1H), 8.05 (t, J = 8.0 Hz, 1H), 8.11-8.16 (m, 2H), 8.22 (d, J = 7.2 Hz, 1H), 8.27 (d, J = 7.6 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.91 (d, J = 8.0 Hz, 1H), 9.07 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7, 51.1, 123.2 123.8, 123.9, 124.4, 124.6, 125.37, 125.43, 126.3, 126.4, 126.8, 126.86, 126.94, 127.1, 127.4, 127.7, 128.0, 128.5, 128.7, 128.8, 128.9, 129.0, 129.1, 130.0, 131.5, 131.7, 132.3, 134.7, 168.4 ppm. HRMS (ESI^+): calcd for $C_{33}H_{26}NO$: $[M+H]^+$, 452.2009; found: 452.2018.



***N*-(*tert*-Butyl)-3,12-difluorobenzo[*g*]chrysene-10-carboxamide (3n)**

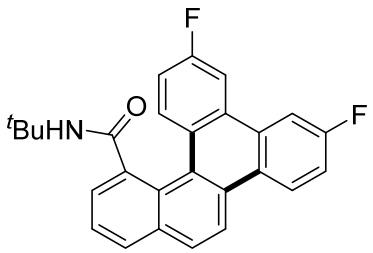
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3n** as a yellow solid (46.6 mg, 56% yield). M.p.: 247-248 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 9H), 4.99 (br, 1H), 7.33-7.37 (m, 1H), 7.43-7.48 (m, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.02-8.07 (m, 3H), 8.12 (dd, J = 10.8 Hz, J = 2.4 Hz, 1H), 8.21 (dd, J = 10.8 Hz, J = 2.4 Hz, 1H), 8.42 (d, J = 8.8 Hz, 1H), 8.51 (dd, J = 8.8 Hz, J = 5.6 Hz, 1H), 8.60 (dd, J = 8.8 Hz, J = 5.6 Hz, 1H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 27.9, 51.3, 109.6 (d, J_{CF}= 22.6 Hz), 114.2 (d, J_{CF} = 23.4 Hz), 115.7 (d, J_{CF} = 23.0 Hz), 116.3 (d, J_{CF} = 23.1 Hz), 121.4, 125.2 (d, J_{CF} = 1.9 Hz), 125.4, 125.5, 125.7, 126.6, 126.8 (d, J_{CF} = 3.2 Hz), 128.8, 129.4 (d, J_{CF} = 3.5 Hz), 129.5, 130.2, 130.9 (d, J_{CF} = 8.1 Hz), 132.5 (d, J_{CF} = 8.6 Hz), 134.3, 137.3, 161.8 (d, J_{CF} = 245.2 Hz), 162.2 (d, J_{CF} = 244.1 Hz), 168.0 ppm. HRMS (ESI^+): calcd for $C_{27}H_{22}F_2NO$: $[M+H]^+$, 414.1664; found: 414.1662.



***N*-(*tert*-Butyl)-3,12-dichlorobenzo[*g*]chrysene-10-carboxamide (3o)**

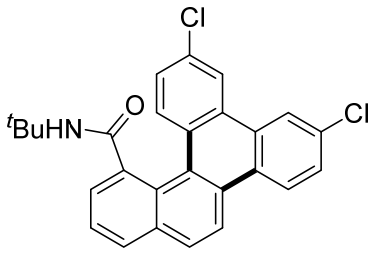
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3o** as a yellow solid (61.3 mg, 69% yield). M.p.: 111-112 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 9H), 4.99 (br, 1H), 7.55 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 7.64-7.67 (m, 1H), 7.70 (d, J = 7.6 Hz, 1H), 8.00-8.06 (m, 3H), 8.38 (d, J = 2.0 Hz, 1H), 8.42-8.46 (m, 2H), 8.52-8.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.3, 121.2, 123.8, 124.8, 124.9, 125.5, 126.4, 126.6, 126.8, 127.6, 128.1, 128.2, 128.3, 128.88, 128.89, 129.4, 130.2, 130.8, 132.2, 133.7, 133.9, 134.4, 137.5, 168.0 ppm. HRMS (ESI^+): calcd for $C_{27}H_{22}Cl_2NO$: $[M+H]^+$, 446.1073 (100.0%), 448.1043 (63.9%); found: 446.1073 (100.0%), 448.1048 (63.9%).



***N*-(*tert*-Butyl)-2,13-difluorobenzo[*g*]chrysene-10-carboxamide (3p)**

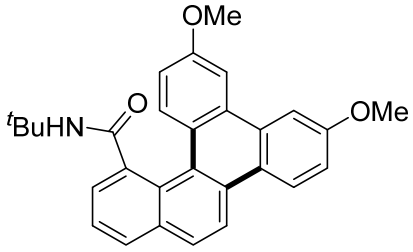
Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3p** as a yellow solid (47.8 mg, 58% yield). M.p.: >250 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.73 (s, 9H), 4.74 (br, 1H), 7.33-7.38 (m, 1H), 7.47-7.52 (m, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 8.04-8.08 (m, 2H),

8.11 (dd, J = 10.4 Hz, J = 2.8 Hz, 1H), 8.19 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 8.46-8.50 (m, 2H), 8.61 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.2, 109.0 (t, J_{CF} = 21.6 Hz), 116.6 (dd, J_{CF} =22.9 Hz, J_{CF} = 15.1 Hz), 121.3, 125.4, 125.5, 126.3 (d, J_{CF} = 2.2 Hz), 126.46, 126.52 (d, J_{CF} = 8.7 Hz), 128.2, 128.4 (d, J_{CF} = 2.2 Hz), 128.50, 129.4, 130.03 (d, J_{CF} = 3.6 Hz), 130.10, 130.13, 131.48 (d, J_{CF} = 8.5 Hz), 131.52 (d, J_{CF} = 8.0 Hz), 134.0, 137.3, 162.0 (d, J_{CF} = 247.7 Hz), 162.4 (d, J_{CF} = 247.6 Hz), 168.1 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{22}F_2NO$: $[M+H]^+$, 414.1664; found: 414.1664.



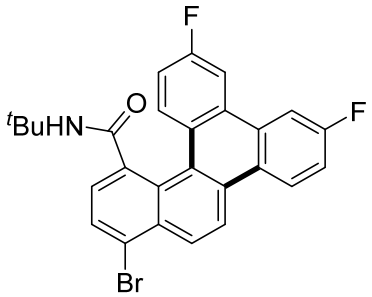
***N*-(*tert*-Butyl)-2,13-dichlorobenzo[*g*]chrysene-10-carboxamide (3q)**

Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3q** as a yellow solid (58.5 mg, 66% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (s, 9H), 4.72 (br, 1H), 7.56 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 7.68-7.72 (m, 2H), 8.02 (d, J = 8.8 Hz, 1H), 8.04-8.08 (m, 2H), 8.39 (d, J = 8.8 Hz, 1H), 8.46-8.49 (m, 2H), 8.53 (d, J = 8.8 Hz, 1H), 8.57 (d, J = 2.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.3, 121.2, 122.9, 123.2, 125.3, 125.7, 125.9, 126.7, 128.2, 128.4, 128.5, 128.7, 128.8, 129.2, 129.5, 130.0, 130.2, 130.57, 130.59, 133.5, 134.16, 134.20, 137.4, 168.0 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{22}Cl_2NO$: $[M+H]^+$, 446.1073 (100.0%), 448.1043 (63.9%); found: 446.1073 (100.0%), 448.1048 (63.9%).



***N*-(*tert*-Butyl)-2,13-dimethoxybenzo[*g*]chrysene-10-carboxamide (3r)**

Purification via silica gel column chromatography (hexane/EtOAc = 8/1, v/v) afforded the desired product **3r** as a yellow solid (44.3 mg, 51% yield). M.p.: 89-90 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (s, 9H), 3.99 (s, 3H), 4.07 (s, 3H), 4.79 (br, 1H), 7.23 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.34 (dd, J = 8.8 Hz, J =2.4 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.91-7.95 (m, 2H), 8.00-8.02 (m, 2H), 8.06 (d, J = 6.8 Hz, 1H), 8.42 (d, J = 9.2 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.0, 55.7, 55.9, 105.8, 106.8, 115.4, 116.4, 121.4, 123.8, 125.0, 125.4, 125.7, 125.8, 126.2, 127.2, 128.3, 129.0, 130.0, 130.2, 130.6, 131.5, 133.7, 137.2, 158.9, 159.2, 168.3 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{28}NO_3$: $[M+H]^+$, 438.2064; found: 438.2062.

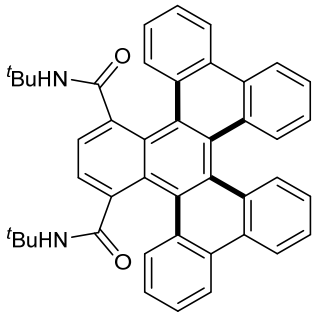


7-Bromo-*N*-(*tert*-butyl)-2,13-difluorobenzo[*g*]chrysene-10-carboxamide (3s)

Purification via silica gel column chromatography (hexane/EtOAc = 10/1, v/v) afforded the desired product **3s** as a yellow solid (57.1mg, 58% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 (s, 9H), 4.65 (br, 1H), 7.33-7.38 (m, 1H), 7.49-7.54 (m, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 8.11 (dd, J = 10.4, 2.4 Hz, 1H), 8.19 (dd, J = 10.2 Hz, J = 2.2 Hz, 1H), 8.38 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H), 8.45 (d, J = 9.2 Hz, 1H), 8.57 (d, J = 9.2 Hz, 1H), 8.61 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.3, 109.1 (dd, J_{CF} = 22.6 Hz, J_{CF} = 13.4 Hz), 116.8 (dd, J_{CF} = 24.9 Hz, J_{CF} = 23.0 Hz), 122.7, 125.3, 125.6, 125.8 (d, J_{CF} = 2.1 Hz), 126.7 (d, J_{CF} = 8.9 Hz), 127.0, 127.1, 128.1 (d, J_{CF} = 2.2 Hz), 128.8, 129.4, 130.26 (d, J_{CF} = 3.6 Hz), 130.34 (d, J_{CF} = 3.7 Hz), 130.5, 131.72 (d, J_{CF} = 8.6 Hz), 131.74 (d, J_{CF} = 8.2 Hz), 132.4, 137.0, 162.1 (d, J_{CF} = 248.5 Hz), 162.7 (d, J_{CF} = 248.3 Hz), 167.3 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{21}BrF_2NO$: $[M+H]^+$, 492.0769 (100.0%), 494.0749 (97.3%); found: 492.0767 (100.0%), 494.0753 (97.3%).

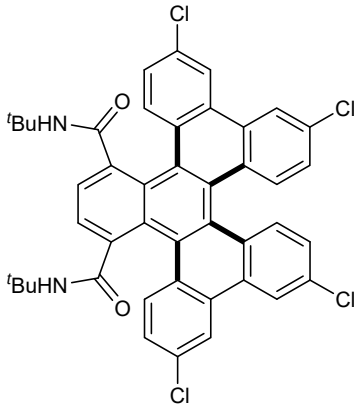
V. General procedure for the quadruple C−H arylations of naphthalene-1,4-dicarboxamide with cyclic diaryliodonium salts

A Schlenk tube with a magnetic stir bar was charged with $Pd(acac)_2$ (12.2 mg, 20 mol %), NaOAc (164.0 mg, 10.0 equiv), N^1,N^4-di-*tert*-butylnaphthalene-1,4-dicarboxamide (**1n**, 0.2 mmol, 1.0 equiv), cyclic diaryliodonium salts (**2**, 1.2 mmol, 6 equiv), and ODCB (4.0 mL) under a N_2 atmosphere. The resulting mixture was stirred at 160 ºC in oil bath for 48 h and then removes solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on Al_2O_3 (hexane/EtOAc = 3/1) to provide the desired product.



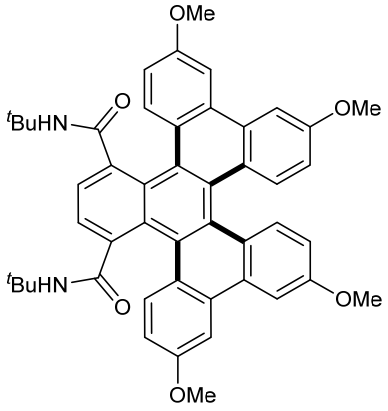
N^{17},N^{20}-Di-*tert*-butyltribenzo[*f,j,s*]picene-17,20-dicarboxamide (4a)

Purification via Al_2O_3 column chromatography (hexane/EtOAc = 3/1, v/v) afforded the desired product **4a** as a yellow solid (52.2 mg, 42% yield). M.p.: 237-238 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.61 (s, 18H), 4.77 (br, 2H), 7.22-7.26 (m, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.61–7.65 (m, 2H), 7.67–7.71 (m, 2H), 8.06 (d, J = 8.4 Hz, 2H), 8.09 (s, 2H), 8.35 (d, J = 8.0 Hz, 2H), 8.55 (d, J = 8.0 Hz, 2H), 8.60 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7, 51.4, 123.0, 123.4, 123.5, 126.08, 126.14, 127.6, 127.8, 128.0, 128.2, 128.8, 129.3, 130.0, 130.5, 131.0, 132.1, 138.6, 167.1 ppm. HRMS (ESI$^+$): calcd for $C_{44}H_{38}N_2NaO_2$: $[M+Na]^+$, 649.2825; found: 649.2834



N^{17},N^{20}-Di-*tert*-butyl-3,6,11,14-tetrachlorotribenzo[*f,j,s*]picene-17,20-dicarboxamide (4b)

Purification via Al_2O_3 column chromatography (hexane/EtOAc = 3/1, v/v) afforded the desired product **4b** as a yellow solid (41.1 mg, 27% yield). M.p.: 235-236 ºC; ^{1}H NMR (400 MHz, DMSO): δ = 0.83 (s, 18H), 7.41 (dd, J = 8.8 Hz, J = 2.0 Hz, 2H), 7.60 (dd, J = 8.8 Hz, J = 2.0 Hz, 2H), 7.80 (s, 2H), 7.85 (br, 2H), 7.89 (d, J = 9.2 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H), 8.88 (d, J = 2.0 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.7, 123.2, 126.1, 126.8, 127.3, 128.2, 128.4, 128.8, 129.3, 129.5, 130.2, 130.5, 130.6, 131.6, 134.18, 134.20, 138.8, 166.9 ppm. HRMS (ESI^+): calcd for $C_{44}H_{34}Cl_4N_2NaO_2$: $[M+Na]^+$, 787.1237 (100.0%), 785.1267 (78.2%); found: 787.1233 (100.0%), 785.1275 (78.2%).

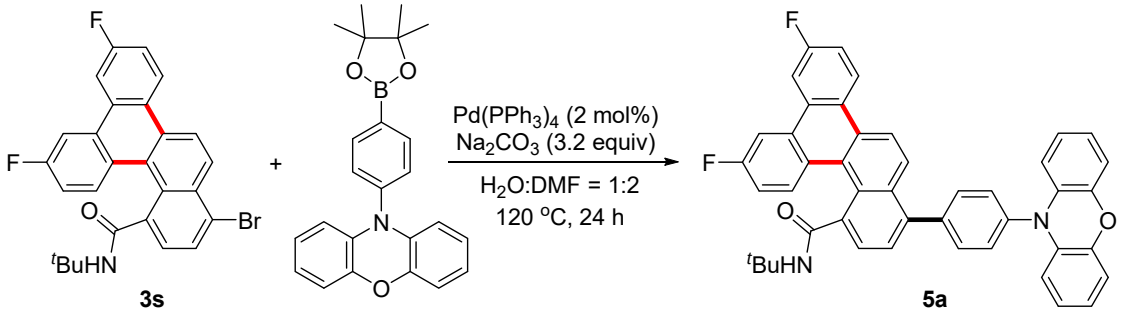


N^{17},N^{20}-Di-*tert*-butyl-2,7,10,15-tetramethyltribenzo[*f,j,s*]picene-17,20-dicarboxamide (4c)

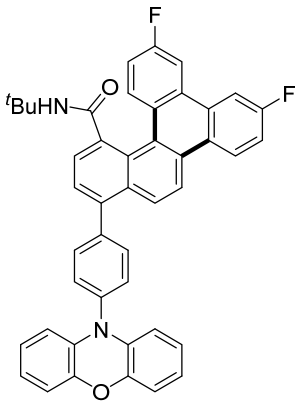
Purification via Al_2O_3 column chromatography (hexane/EtOAc = 2/1, v/v) afforded the desired product **4c** as a yellow solid (51.0 mg, 34% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.65 (s, 18H), 4.01 (s, 6H), 4.02 (s, 6H), 4.80 (br, 2H), 6.87

(dd, J = 9.0 Hz, J = 2.2 Hz, 2H), 7.23-7.26 (m, 2H), 7.84 (s, 2H), 7.94 (s, 2H), 8.01-8.03 (m, 4H), 8.28 (d, J = 9.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8, 51.3, 55.6, 55.9, 105.5, 107.1, 114.7, 115.4, 125.66, 125.67, 125.9, 126.5, 127.0, 127.2, 130.3, 130.5, 131.2, 131.9, 138.2, 158.9, 159.1, 167.4 ppm. HRMS (ESI^+): calcd for $C_{48}H_{46}N_2NaO_6$: $[M+Na]^+$, 769.3248; found: 769.3246.

VI. Preparation of phenoxazine-modified [4]carbohelicene 5a



A Schlenk tube with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (2.3 mg, 2 mol %), Na_2CO_3 (33.8 mg, 3.2 equiv), **3s** (49.1 mg, 0.1 mmol, 1.0 equiv), 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10*H*-phenoxazine (42.4 mg, 0.11 mmol), DMF (1.4 mL) and H_2O (0.7 mL) under a N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then removes solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to provide the desired product.

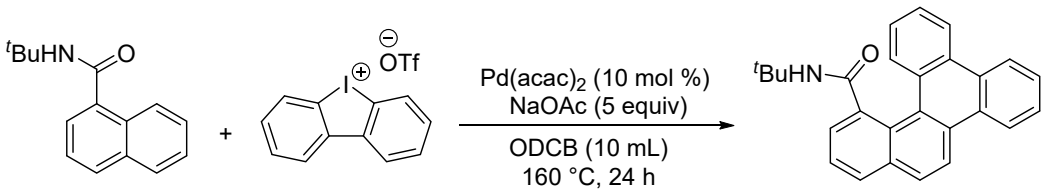


7-(4-(10*H*-Phenoxazin-10-yl)phenyl)-*N*-(*tert*-butyl)-2,13-difluorobenzo[*g*]chrysene-

10-carboxamide (5a)

The desired product **5a** was obtained as a yellow solid (51.7 mg, 77% yield). M.p.: >250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75 (s, 9H), 4.80 (br, 1H), 6.11-6.13 (m, 2H), 6.69-6.76 (m, 6H), 7.38-7.43 (m, 1H), 7.49-7.55 (m, 3H), 7.73 (d, J = 7.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 8.11-8.17 (m, 3H), 8.22 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 8.50-8.56 (m, 2H), 8.61 (dd, J = 9.2 Hz, J = 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 51.3, 109.1 (dd, J_{CF} = 22.3 Hz, J_{CF} = 15.4 Hz), 113.4, 115.7, 116.7 (dd, J_{CF} = 18.6 Hz, J_{CF} = 19.3 Hz), 121.3, 121.5, 121.7, 123.4, 125.7, 126.00, 126.09 (d, J_{CF} = 12.2 Hz), 126.5 (d, J_{CF} = 8.5 Hz). 127.5, 128.2, 128.5 (d, J_{CF} = 2.3 Hz), 128.7, 130.2 (d, J_{CF} = 3.4 Hz), 130.3 (d, J_{CF} = 4.8 Hz), 131.1, 131.62 (d, J_{CF} = 8.3 Hz), 131.65 (d, J_{CF} = 8.3 Hz), 132.0, 133.0, 134.4, 137.2, 138.8, 140.4, 141.1, 144.1, 162.0 (d, J_{CF} = 246.8 Hz), 162.5 (d, J_{CF} = 247.6 Hz), 167.9 ppm. HRMS (ESI^{+}): calcd for $C_{45}H_{32}F_2N_2NaO_2$: $[M+Na]^{+}$, 693.2324; found: 693.2327.

VII. 2 mmol scale synthesis of **3a**



1a (2.0 mmol) **2a** (6.0 mmol) **3a,** 53% (403.0 mg)

A Schlenk tube with a magnetic stir bar was charged with $Pd(acac)_2$ (61.0 mg, 10 mol %), NaOAc (820.0 mg, 5.0 equiv), 1-naphthamide (**1a**, 2.0 mmol, 1.0 equiv), cyclic diaryliodonium salt (**2a**, 6.0 mmol, 3 equiv), and ODCB (10.0 mL) under a N_2 atmosphere. The resulting mixture was stirred at 160 ºC in oil bath for 24 h and then removed solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of CH_2Cl_2. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to to provide **3a** in 53% yield (403.0 mg).

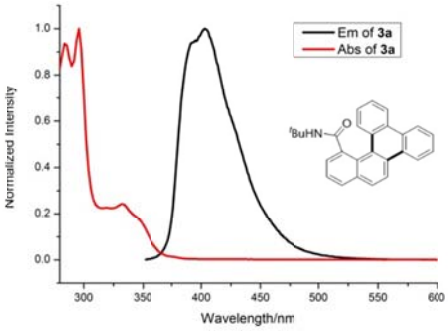
VIII. Photophysical properties

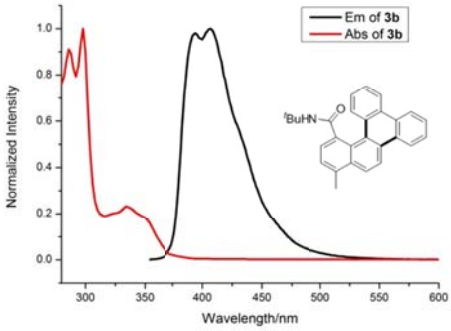
i) Photophysical data and spectra of 3a-3s, 4a-4c and 5a

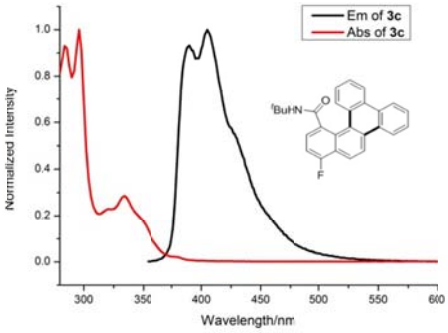
Table S5. **Photophysical data of 3a-3s, 4a-4c and 5a in CH_2Cl_2**

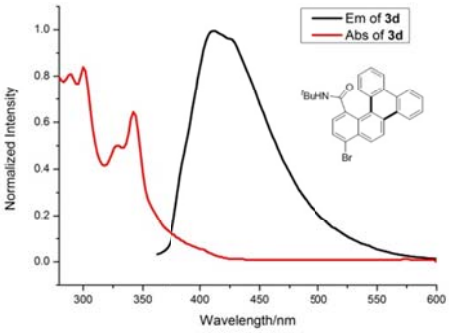
Compounds	λ_{abs} [a] (nm)	λ_{em} [b] (nm)	Stokes shift (cm^{-1})	CIE[c]	Φ_F [d]
3a	285, 296, 332	403	5307	(0.16, 0.01)	0.03
3b	287, 298, 335	394, 407	5281	(0.16, 0.02)	0.04
3c	284, 296, 334	390, 405	5249	(0.15, <0.01)	0.04
3d	288, 301, 328, 343	412	4883	(0.14, 0.06)	<0.01
3e	289, 300, 334	388, 407	5370	(0.16, 0.02)	0.10
3f	301, 336	448	7440	(0.14, 0.12)	0.08
3g	298, 336	413	5549	(0.15, 0.02)	0.08
3h	291, 301, 341	413	5112	(0.16, 0.03)	0.07
3i	301, 339	420	5689	(0.15, 0.04)	0.21
3j	305, 364	441	4797	(0.15, 0.07)	0.44
3k	303, 331, 350	441	5896	(0.15, 0.07)	0.27
3l	305	419	8921	(0.16, 0.02)	0.06
3m	322, 392	425	1981	(0.15, 0.04)	0.23
3n	290, 334	385, 404	5188	(0.16, 0.01)	0.06
3o	287, 296, 335	389, 407	5281	(0.48, <0.01)	0.03
3p	283, 292, 329	388, 404	5643	(0.16, 0.02)	0.05
3q	285, 298, 334	391, 415	5844	(0.16, 0.02)	0.02
3r	304, 342	401, 415	5143	(0.16, 0.03)	0.10
3s	287, 298, 338	394, 409	5136	(0.14, 0.08)	<0.01
4a	336, 388	476	4765	(0.14, 0.28)	0.06
4b	340, 395	476	4308	(0.14, 0.27)	0.07
4c	353, 414	498	4074	(0.23, 0.51)	0.10
5a	298, 331	573	12759	(0.51, 0.50)	0.03

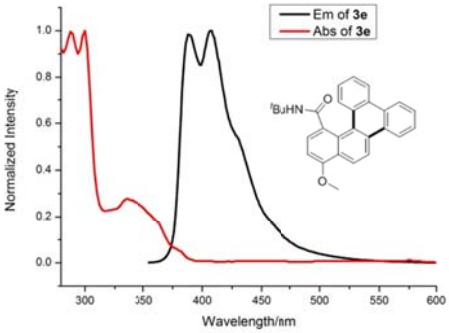
[a]Absorption maxima in CH_2Cl_2 (1.0×10^{-5} mol/L). [b]Emission maxima in CH_2Cl_2 (1.0×10^{-5} mol/L). [c]CIE coordinates measured in CH_2Cl_2 (1.0×10^{-5} mol/L). [d]Absolute quantum yield in CH_2Cl_2 (1.0×10^{-5} mol/L) determined with an integrating sphere system.

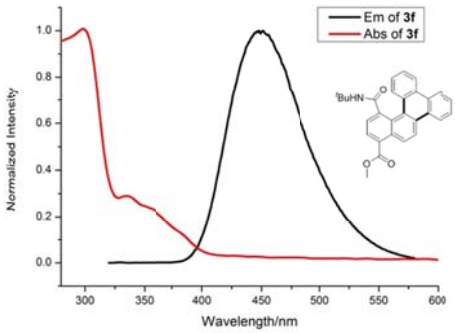


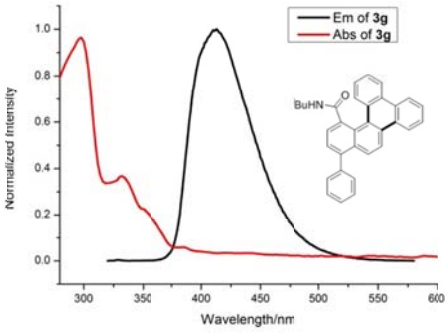


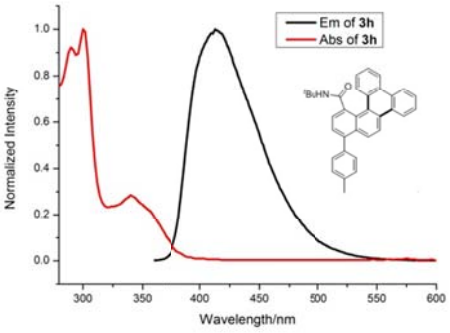

Em of 3c
Abs of 3c
Normalized Intensity
Wavelength/nm

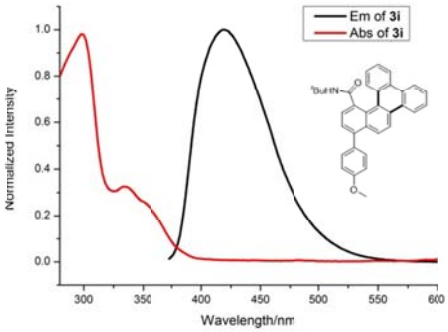

Em of 3d
Abs of 3d
Normalized Intensity
Wavelength/nm

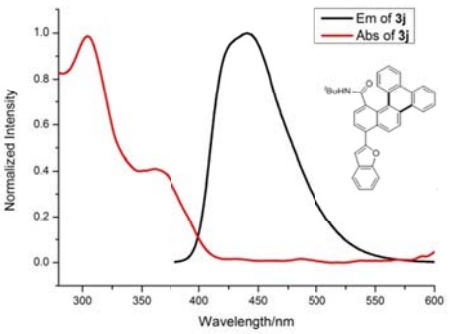

Em of 3e
Abs of 3e
Normalized Intensity
Wavelength/nm

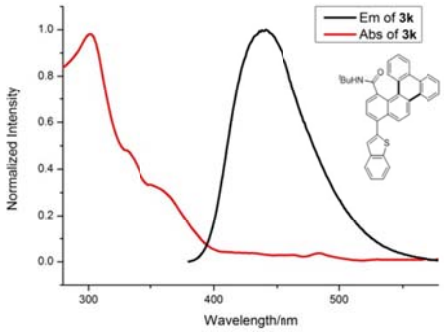

Em of 3f
Abs of 3f
Normalized Intensity
Wavelength/nm

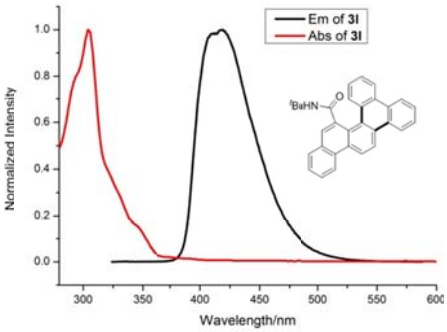

Em of 3g
Abs of 3g
Normalized Intensity
Wavelength/nm

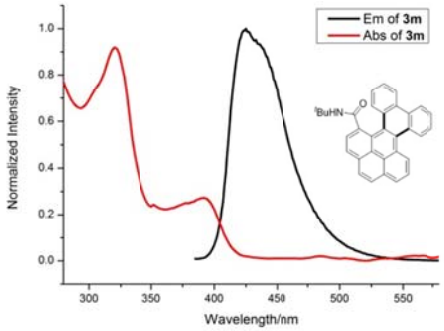

Em of 3h
Abs of 3h
Normalized Intensity
Wavelength/nm


Em of 3i
Abs of 3i
Normalized Intensity
Wavelength/nm


Em of 3j
Abs of 3j
Normalized Intensity
Wavelength/nm


Em of 3k
Abs of 3k
Normalized Intensity
Wavelength/nm


Em of 3l
Abs of 3l
Normalized Intensity
Wavelength/nm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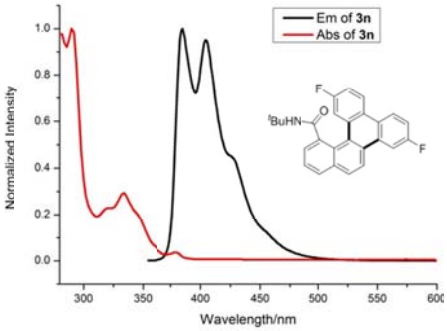
Wavelength/nm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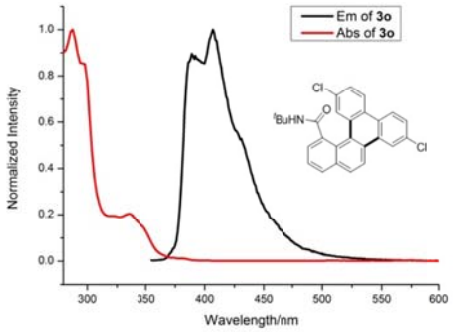
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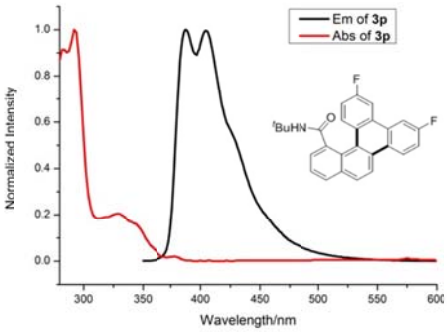
Normalized Intensity
Wavelength/nm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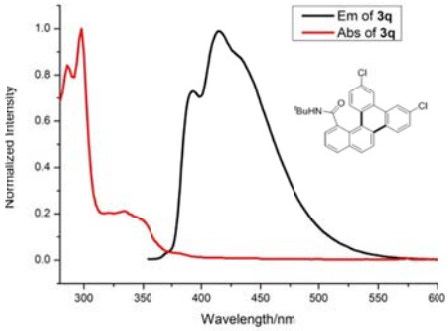
Abs of 3p
Normalized Intensity
Wavelength/nm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Abs of 3q
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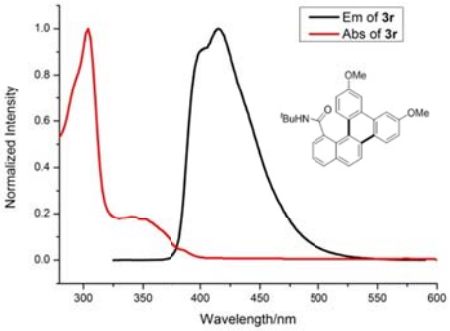
Wavelength/nm


Em of 3r
Abs of 3r
Normalized Intensity
Wavelength/nm

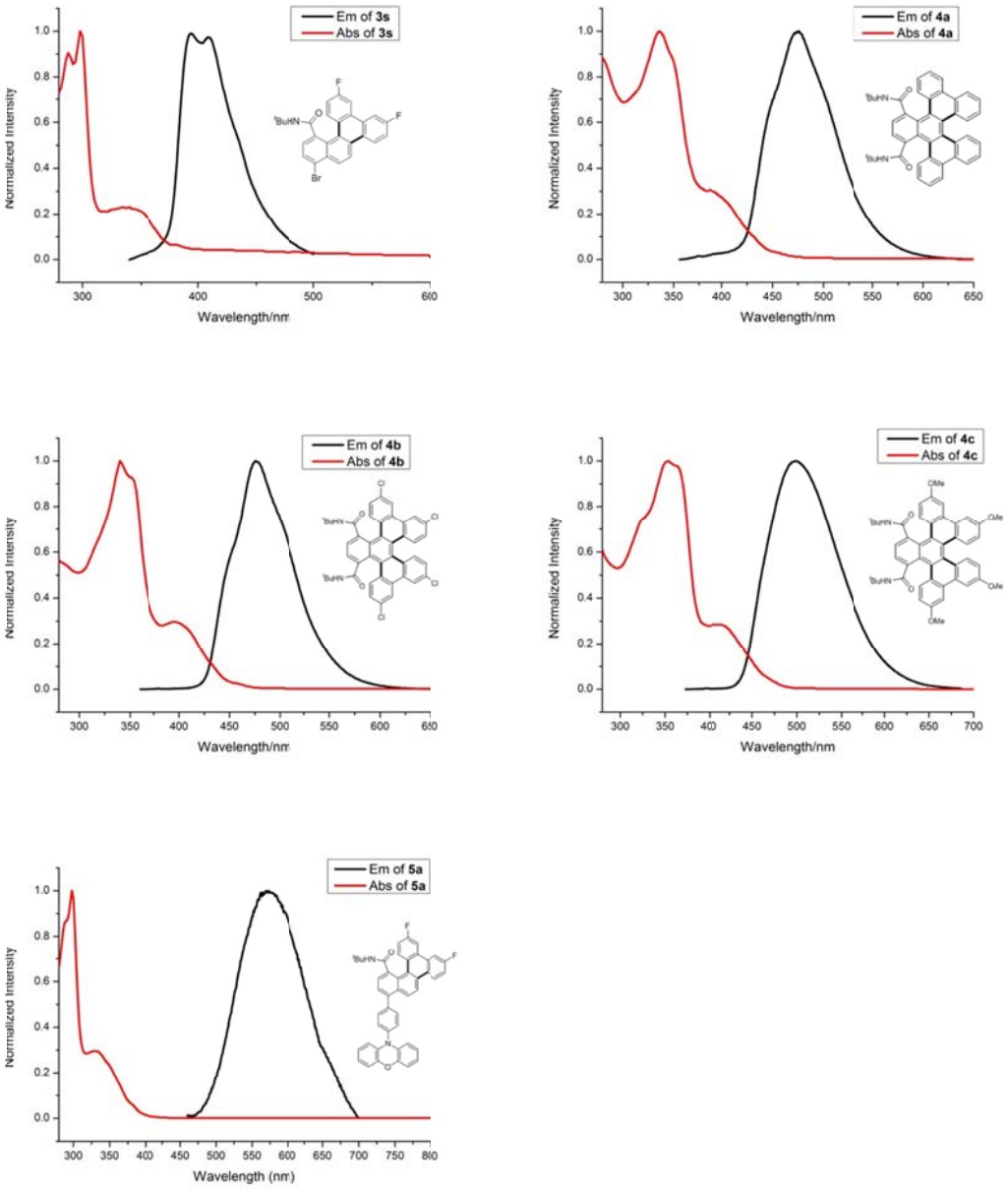


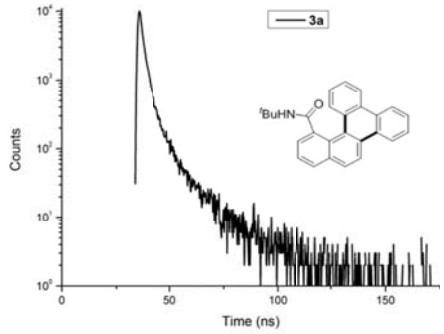
Figure S1. Absorption and fluorescence emission spectra in CH_2Cl_2 at 1×10^{-5} mol/L.

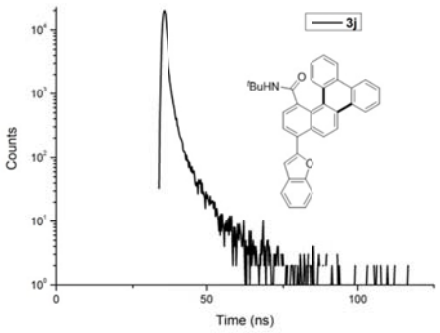
ii) The room temperature transient decay data and spectra of 3a, 3j, 3k, 3l, 3m, 4c and 5a

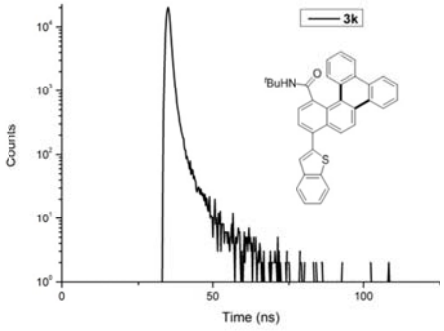
Table S6. **Photoluminescence lifetime of 3a-3s, 4a-4c and 5a in neat film**

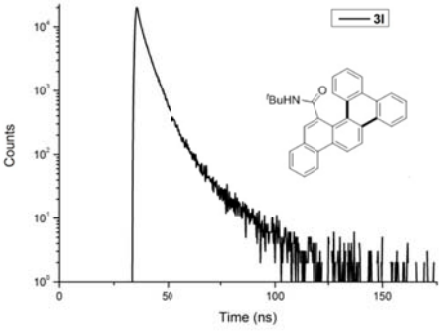
Compounds	τ_1 (ns)	τ_2 (ns)	$\chi2$
3a	1.74 (75%)	8.73 (25%)	0.97
3j	0.85 (85%)	4.18 (15%)	1.06
3j	0.69 (88%)	3.72 (12%)	0.91
3l	3.28 (75%)	9.31 (25%)	0.98

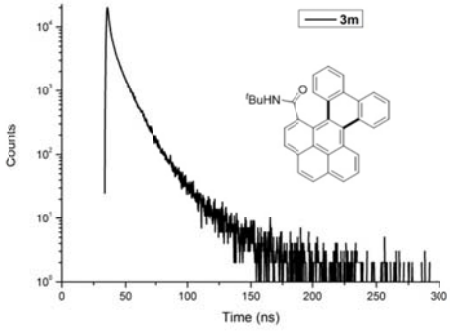
3m	2.41 (38%)	11.86 (62%)	1.03
4c	0.85 (86%)	4.51 (14%)	1.08
5a	89.33 (30%)	7211.13 (70%)	0.92

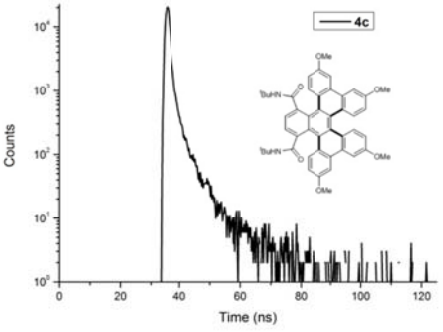












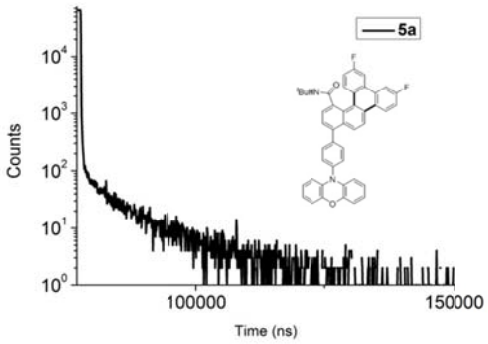


Figure S2. Photoluminescence transient decay curves of **3a**, **3j**, **3k**, **3l**, **3m** and **4c**, and **5a** in neat film.

IX. References

(1) Ryu, J.; Kwak, J.; Shin, K.; Lee, D.; Chang, S. *J. Am. Chem. Soc.* **2013**, *135*, 12861-12868.

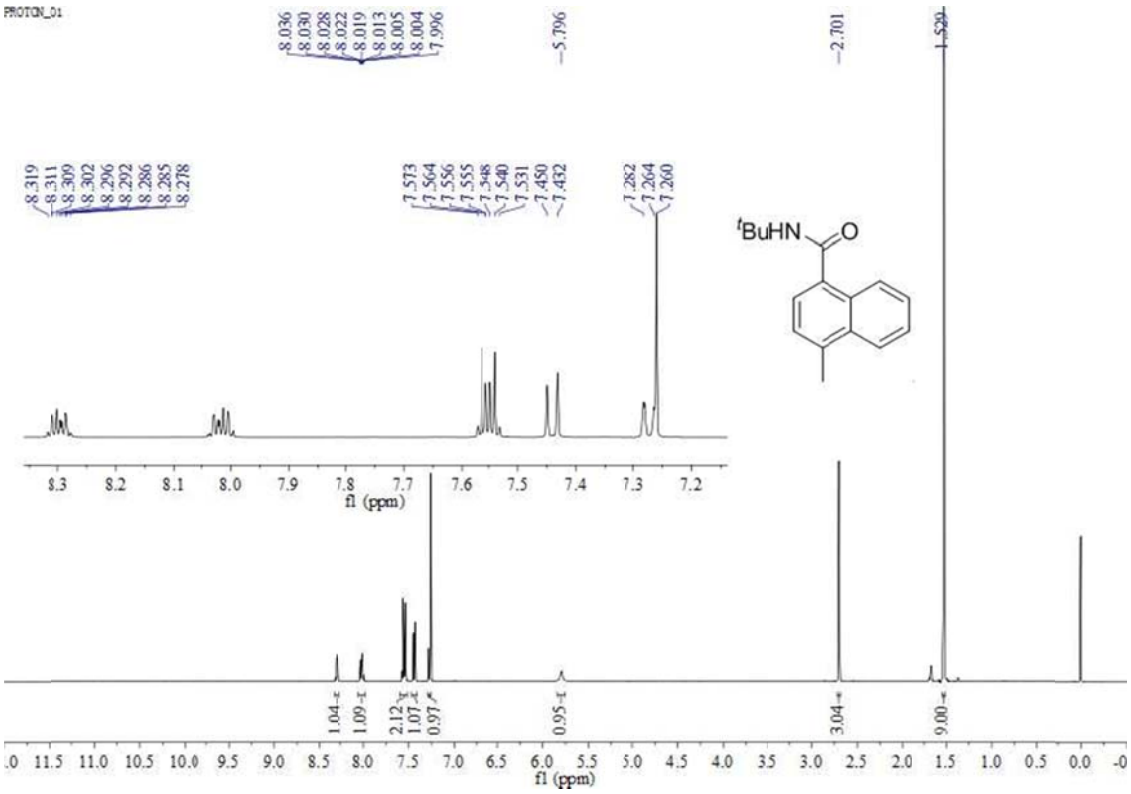
(2) Johnson, S. M.; Connelly, S.; Wilson, I. A.; Kelly, J. W. *J. Med. Chem.* **2008**, *51*, 6348-6358.

(3) Das, R.; Chakraborty, D. *Appl. Organometal. Chem.* **2011**, *25*, 437–442.

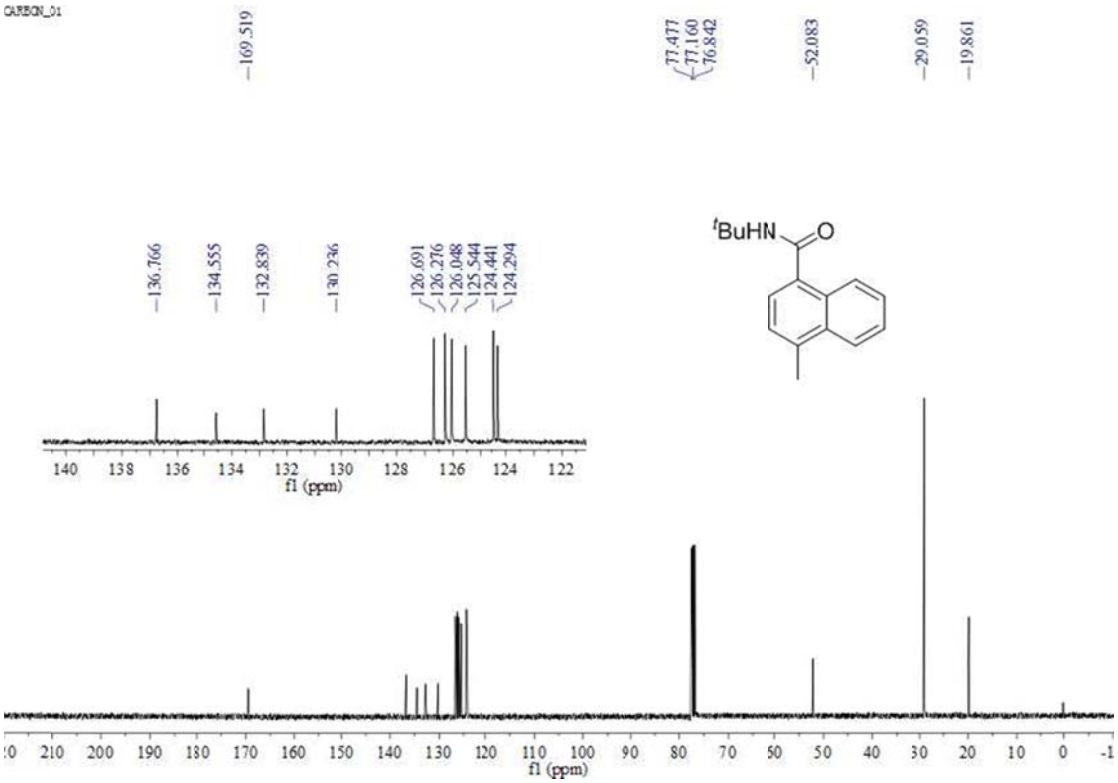
(4) Mathew, B. P.; Yang, H. J.; Kim, J.; Lee, J. B.; Kim, Y.-T.; Lee, S.; Lee, C. Y.; Choe, W.; Myung, K.; Park, J.-U.; Hong, S. Y. *Angew. Chem., Int. Ed*. **2017**, *56*, 5007–5011.

X. Copies of ^{1}H and ^{13}C NMR spectra

^{1}H NMR spectrum of **1b** in $CDCl_3$



^{13}C NMR spectrum of **1b** in $CDCl_3$



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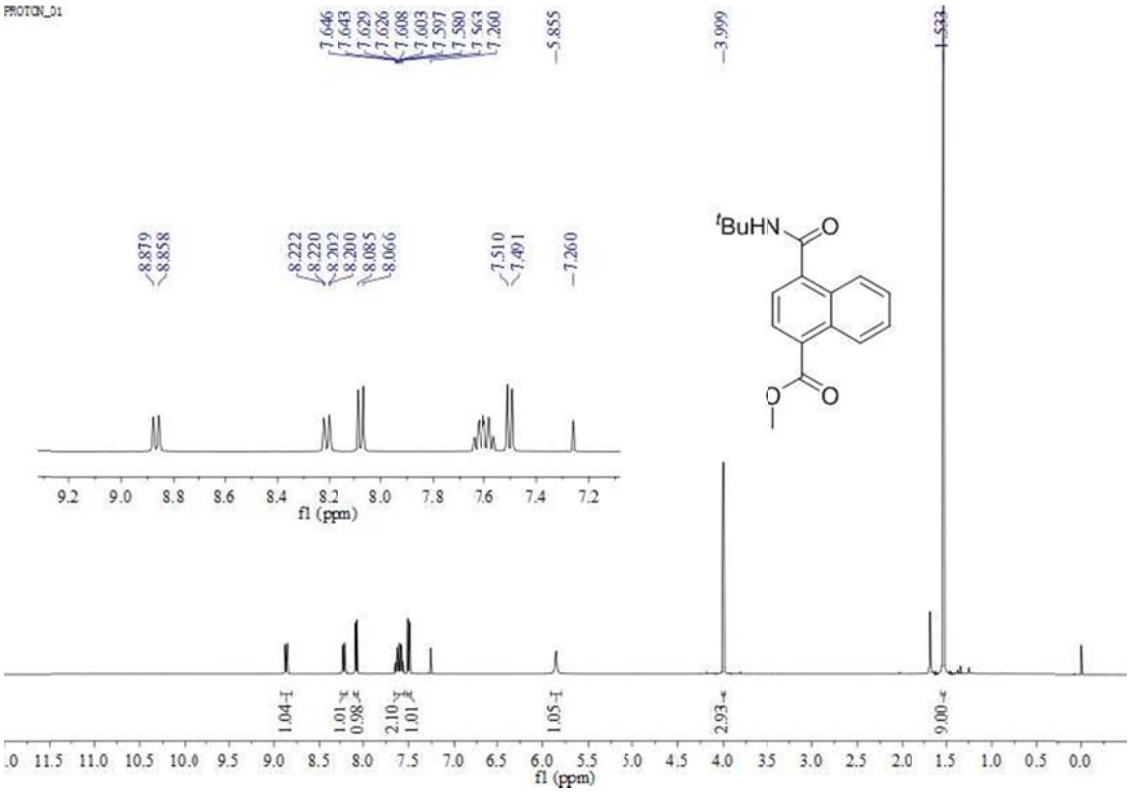
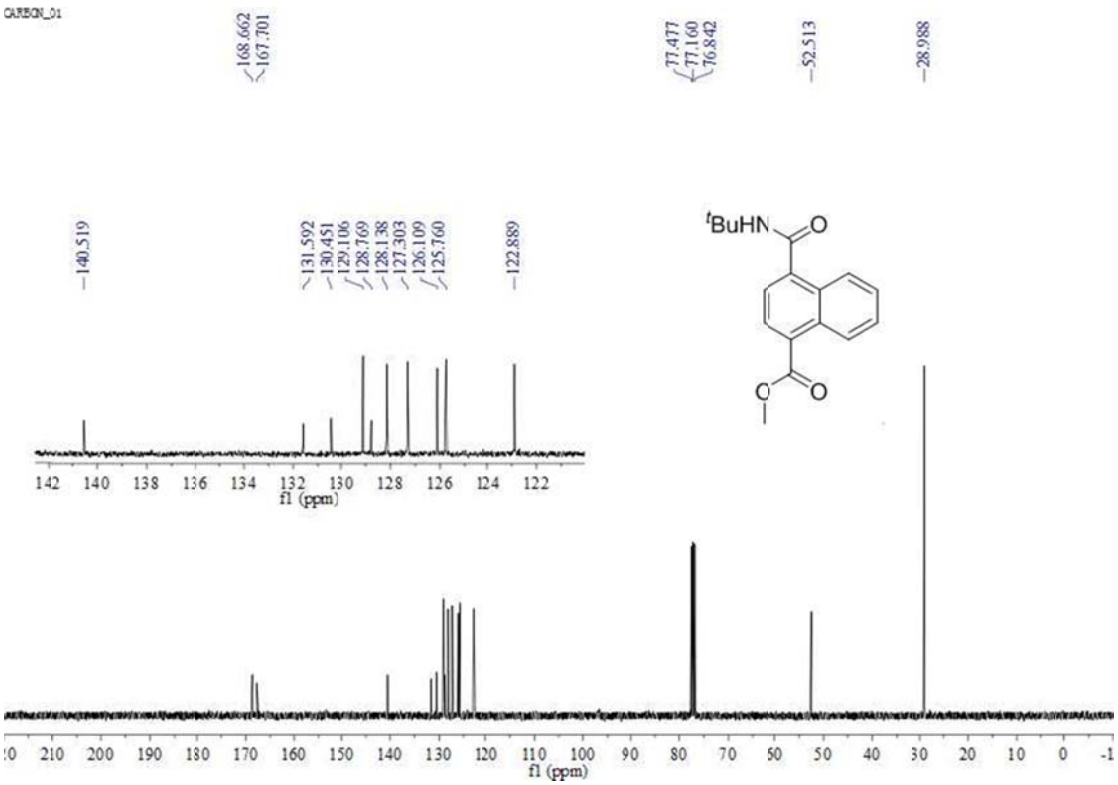


^{13}C NMR spectrum of **1f** in $CDCl_3$



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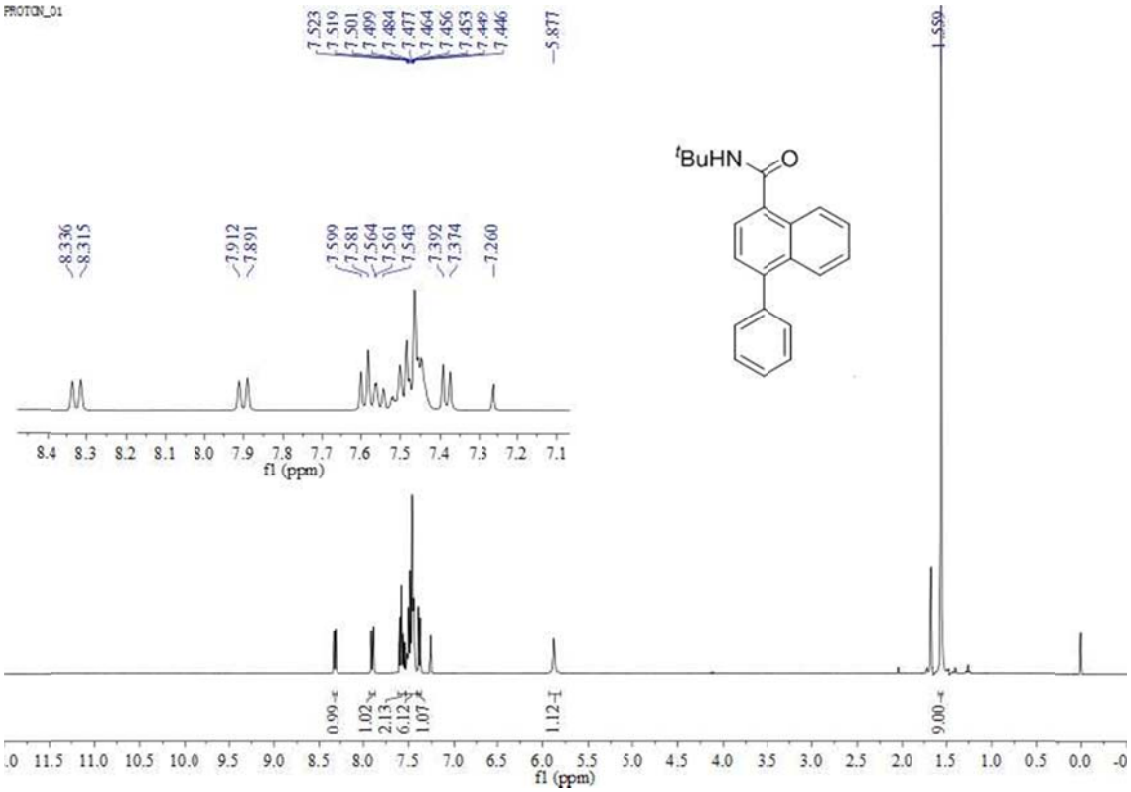

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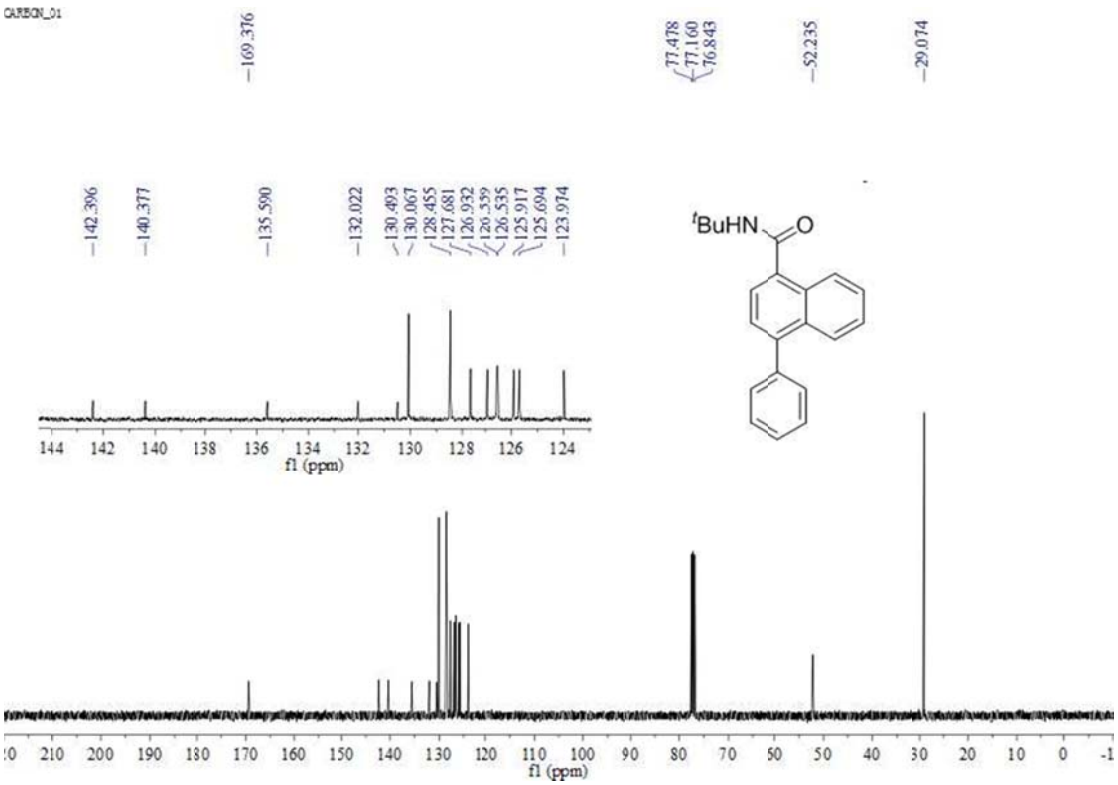

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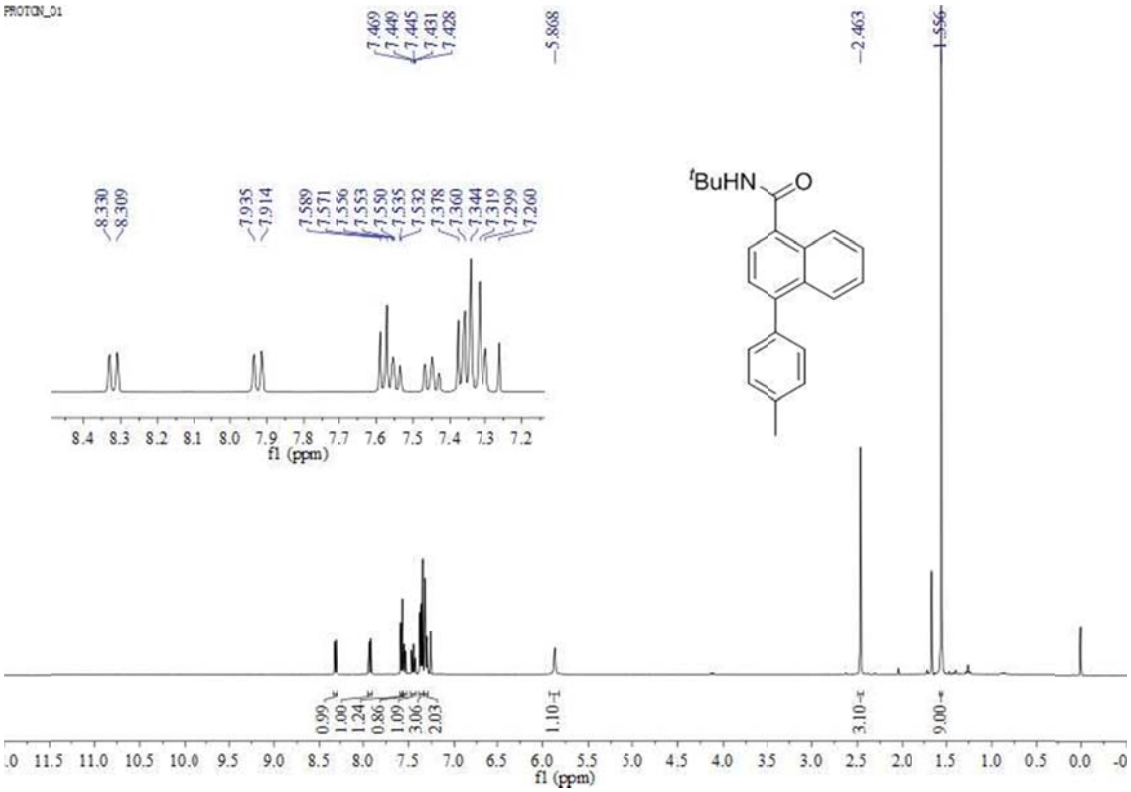
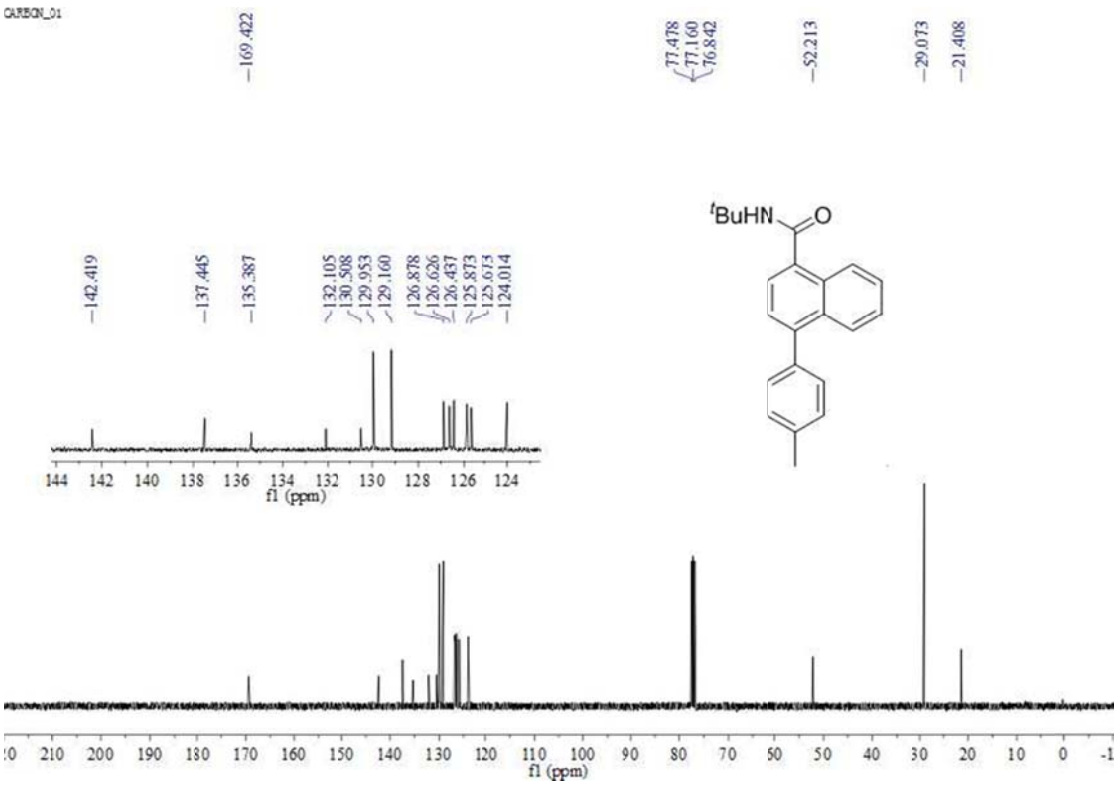
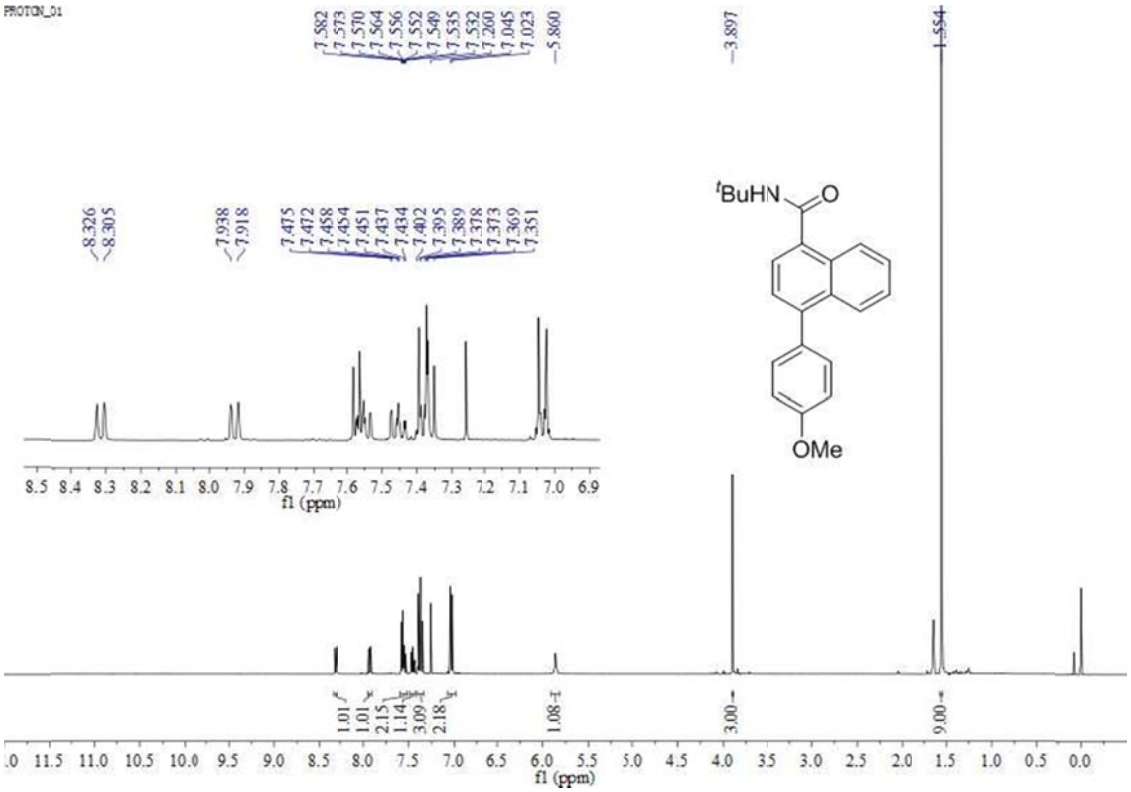


^{13}C NMR spectrum of **1h** in $CDCl_3$



^{1}H NMR spectrum of **1i** in $CDCl_3$



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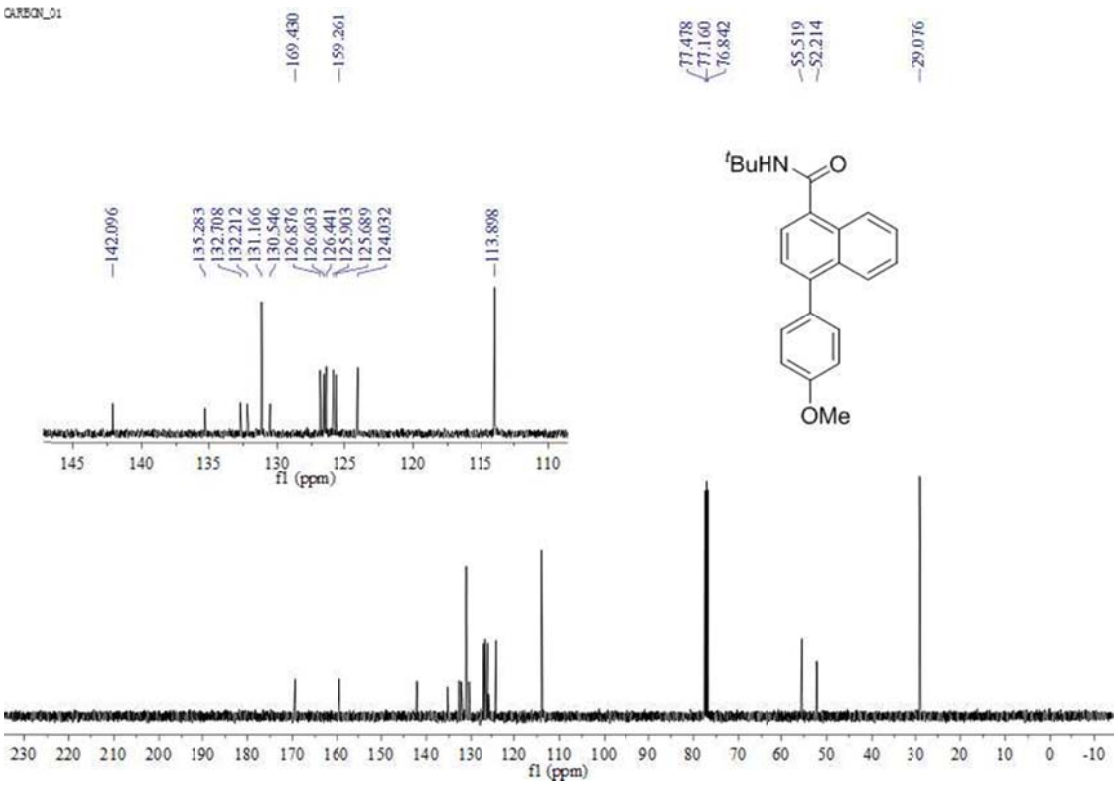
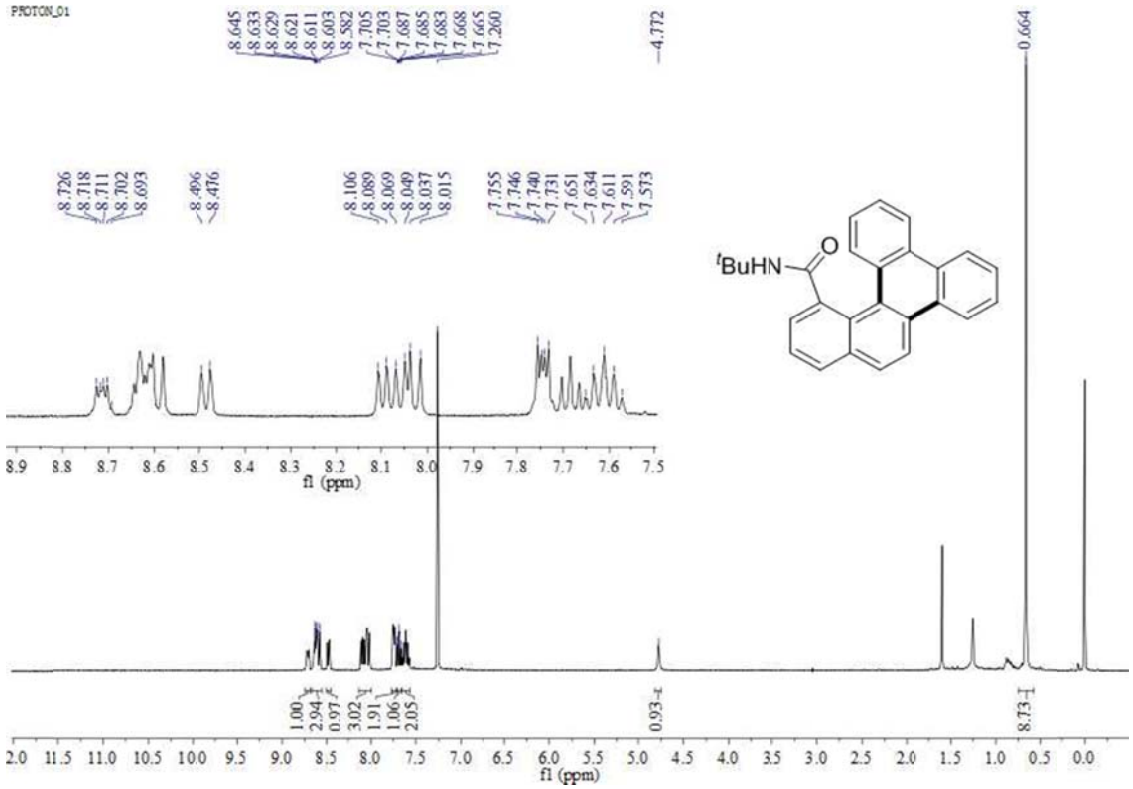


^{1}H NMR spectrum of **3a** in $CDCl_3$



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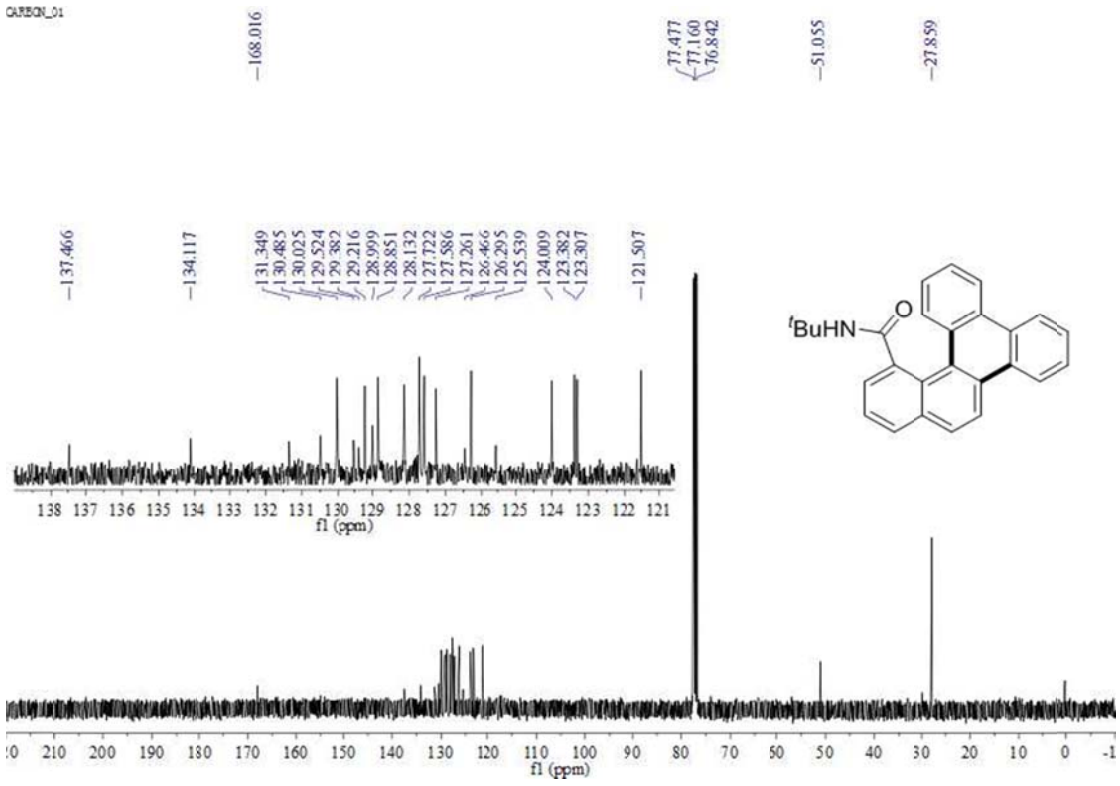

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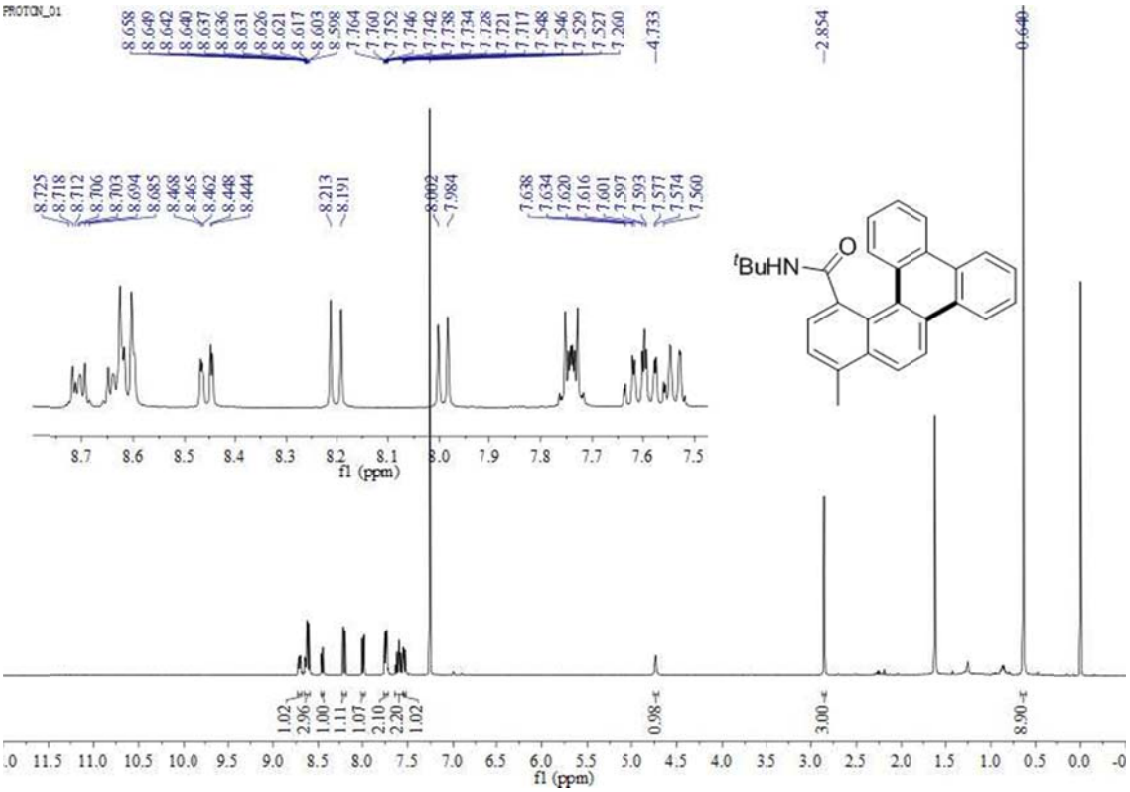

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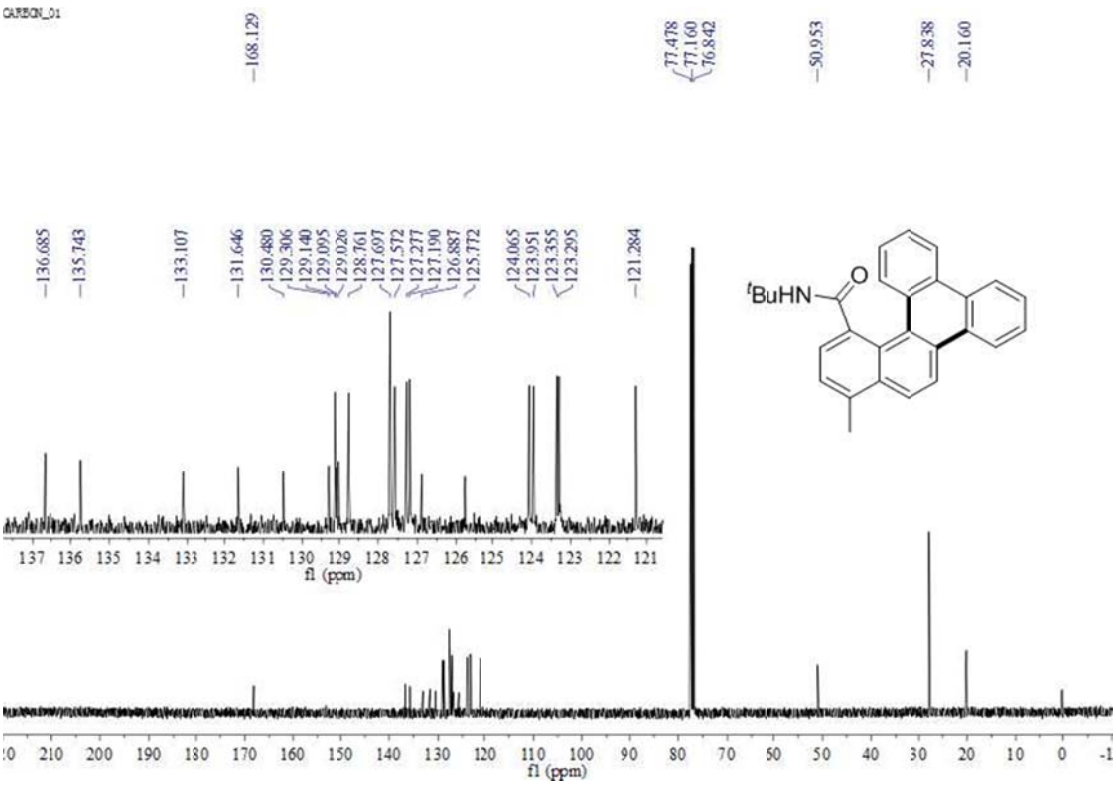

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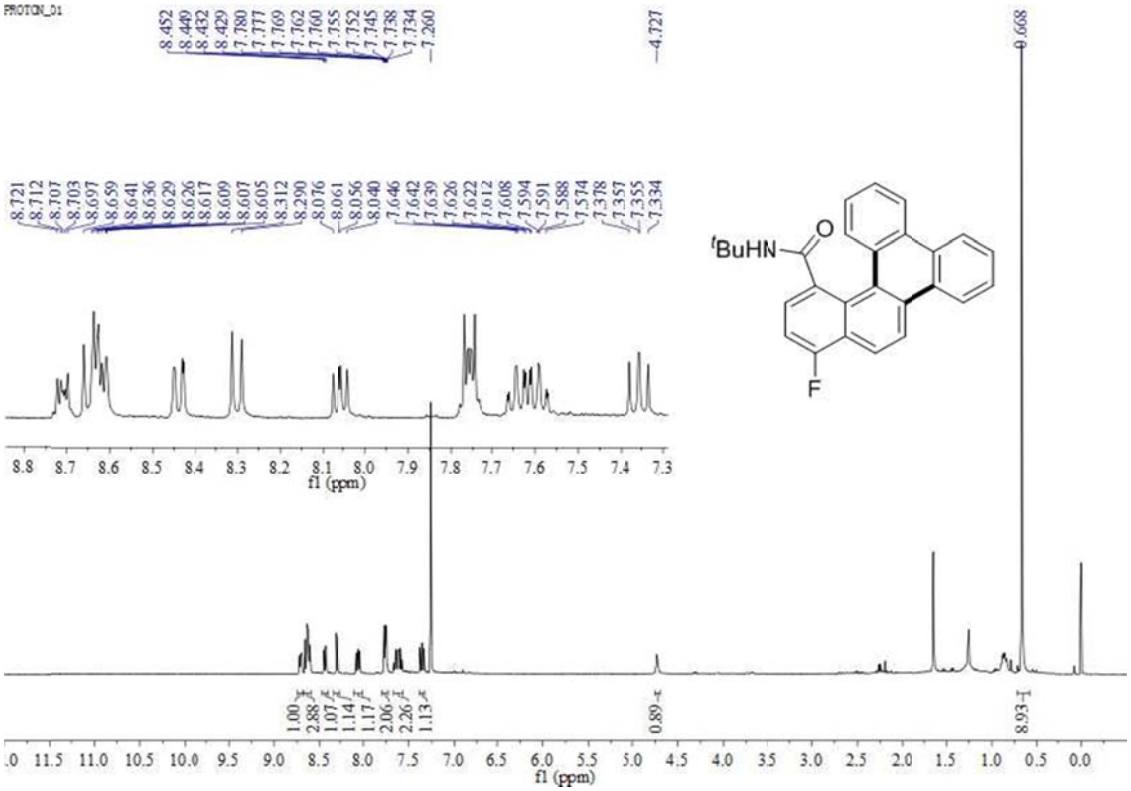

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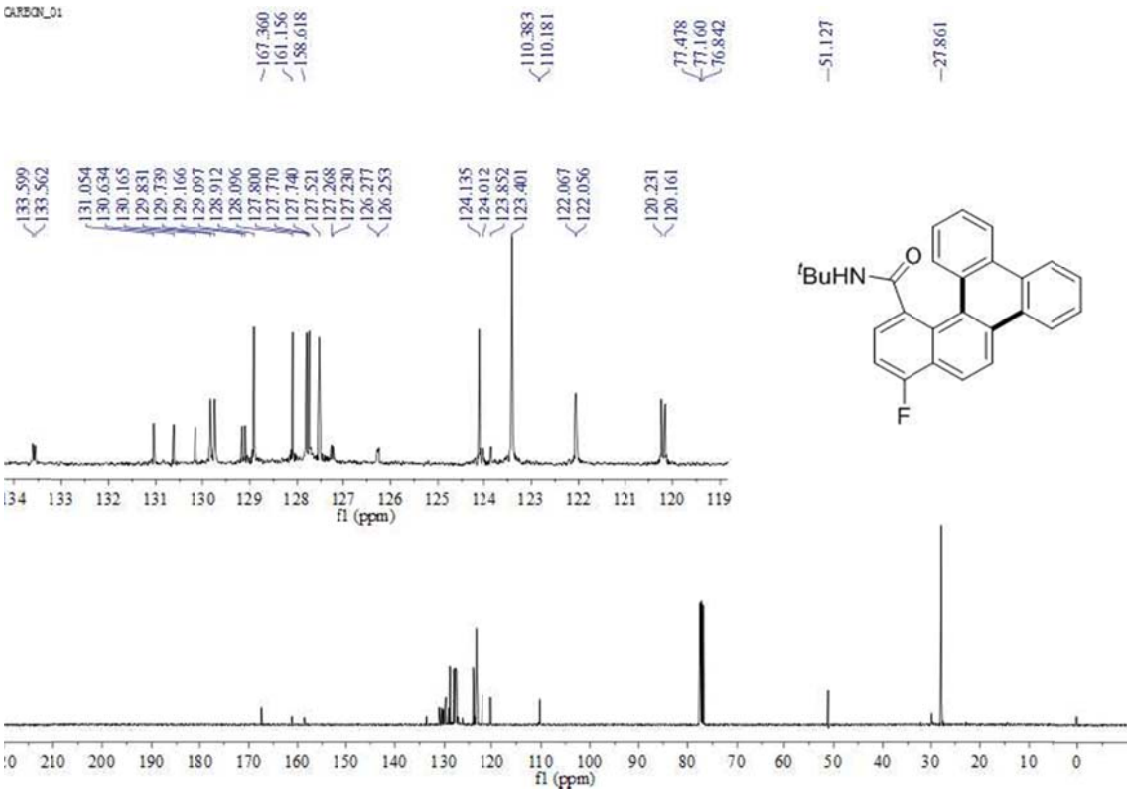

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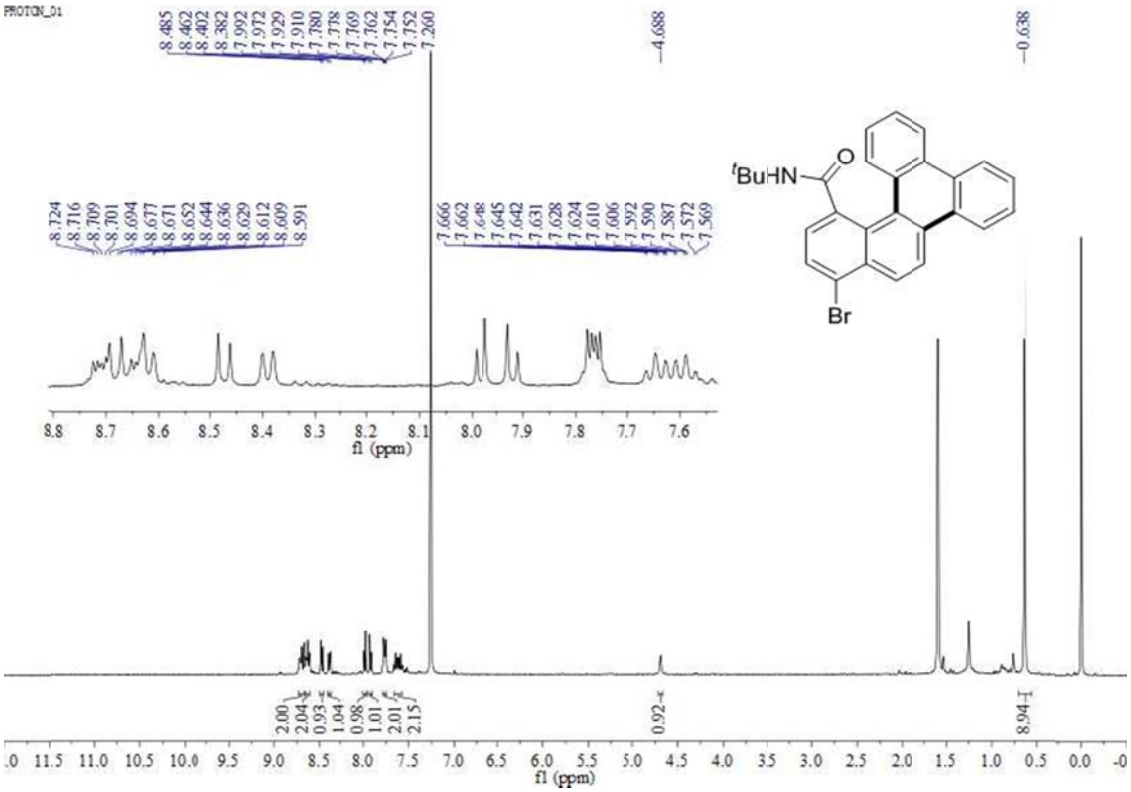

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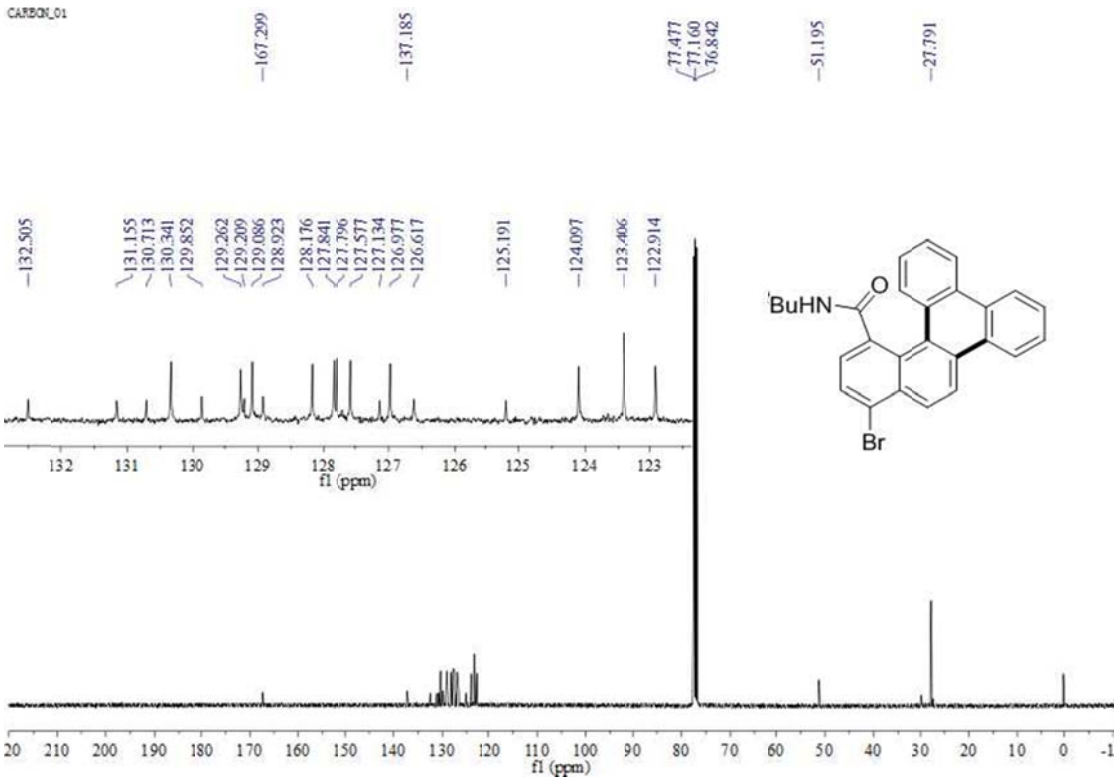

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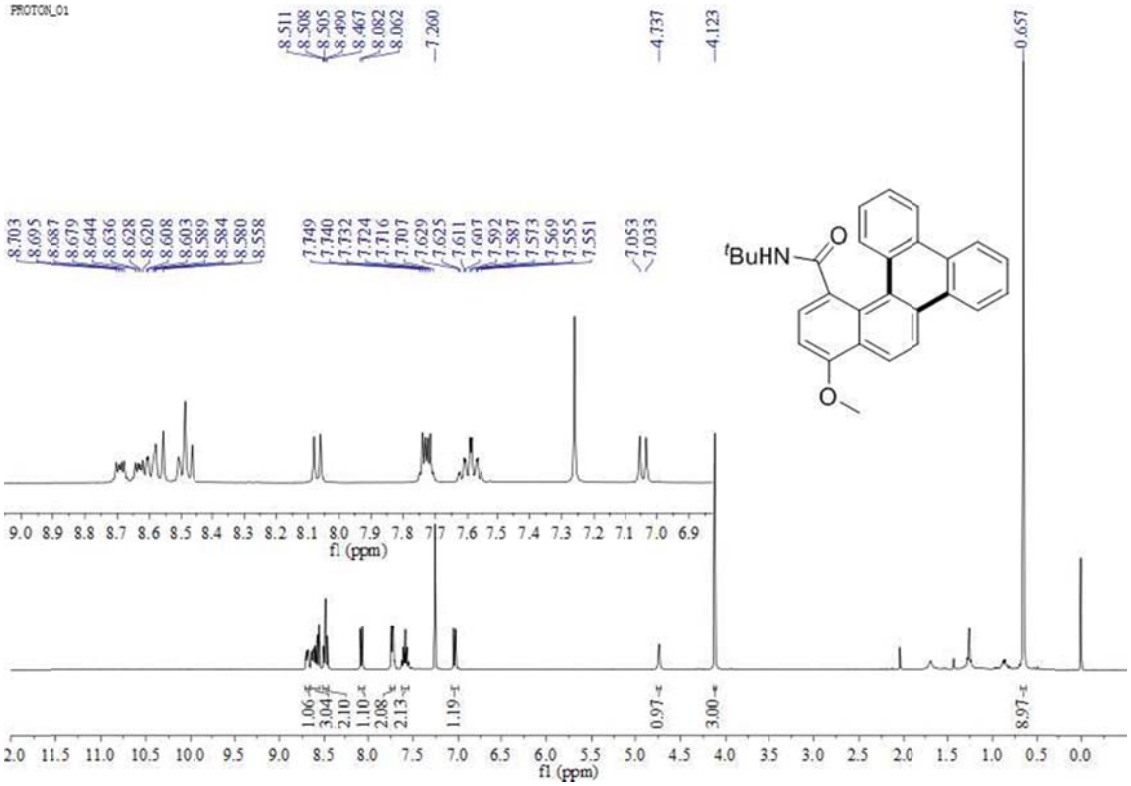

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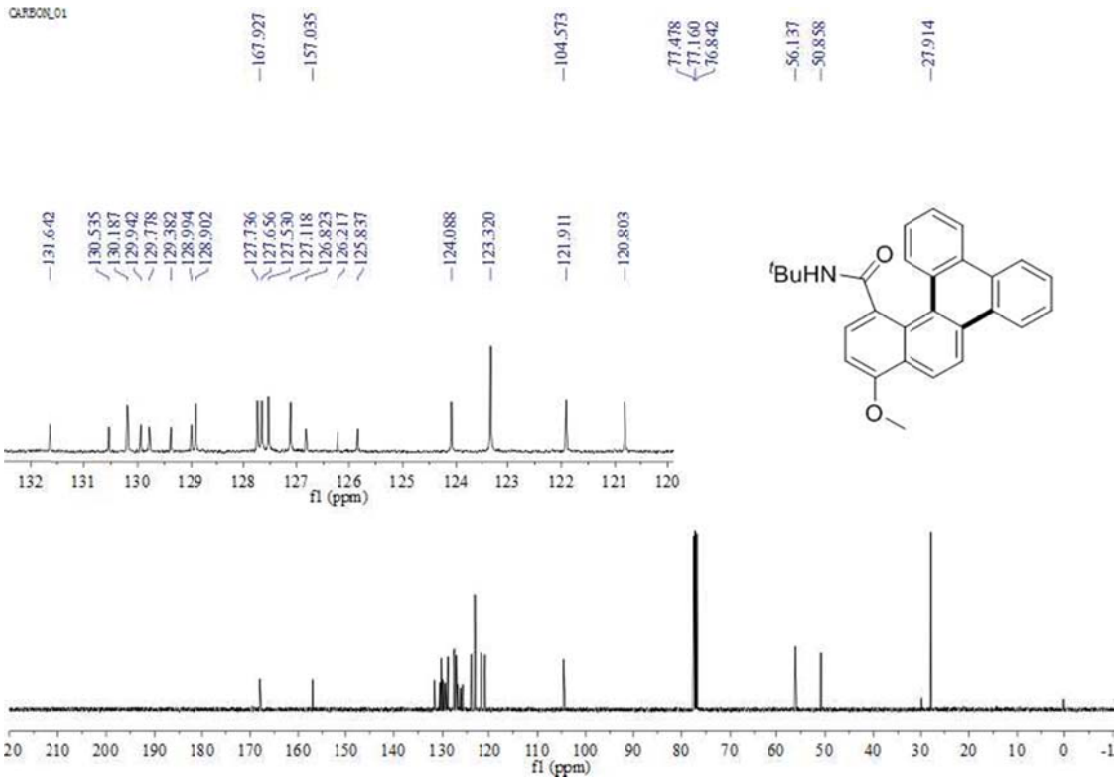

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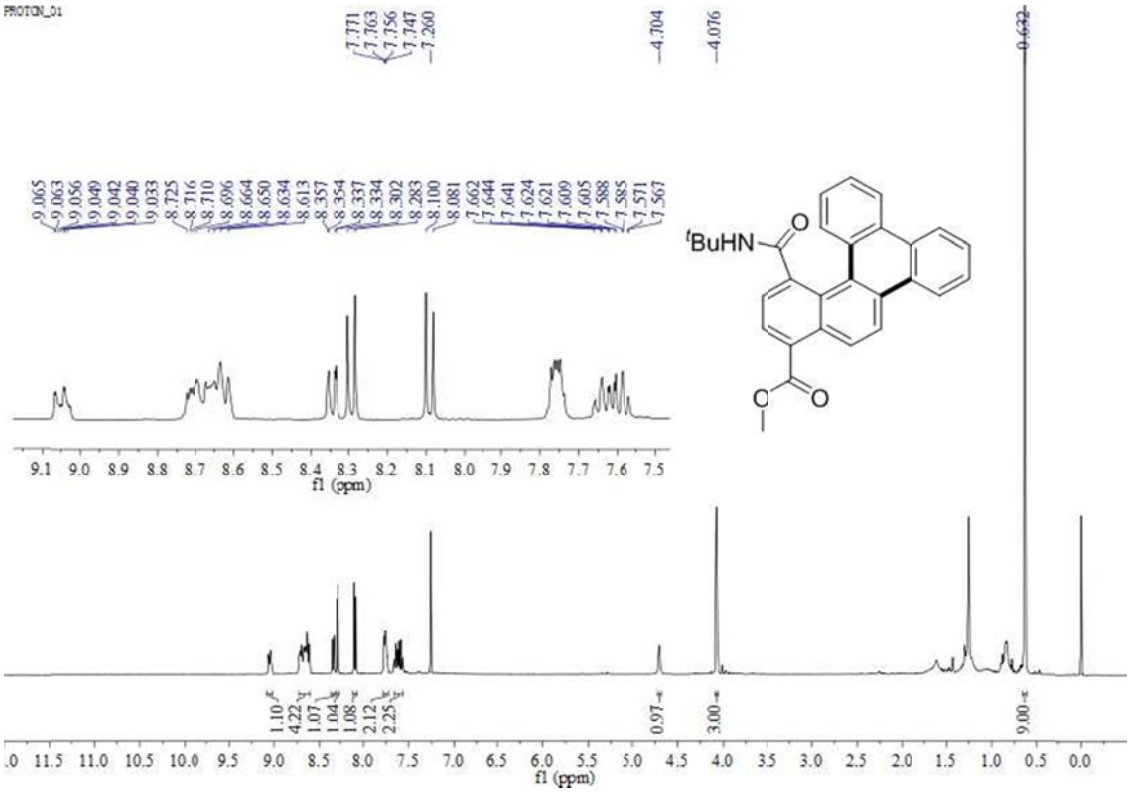

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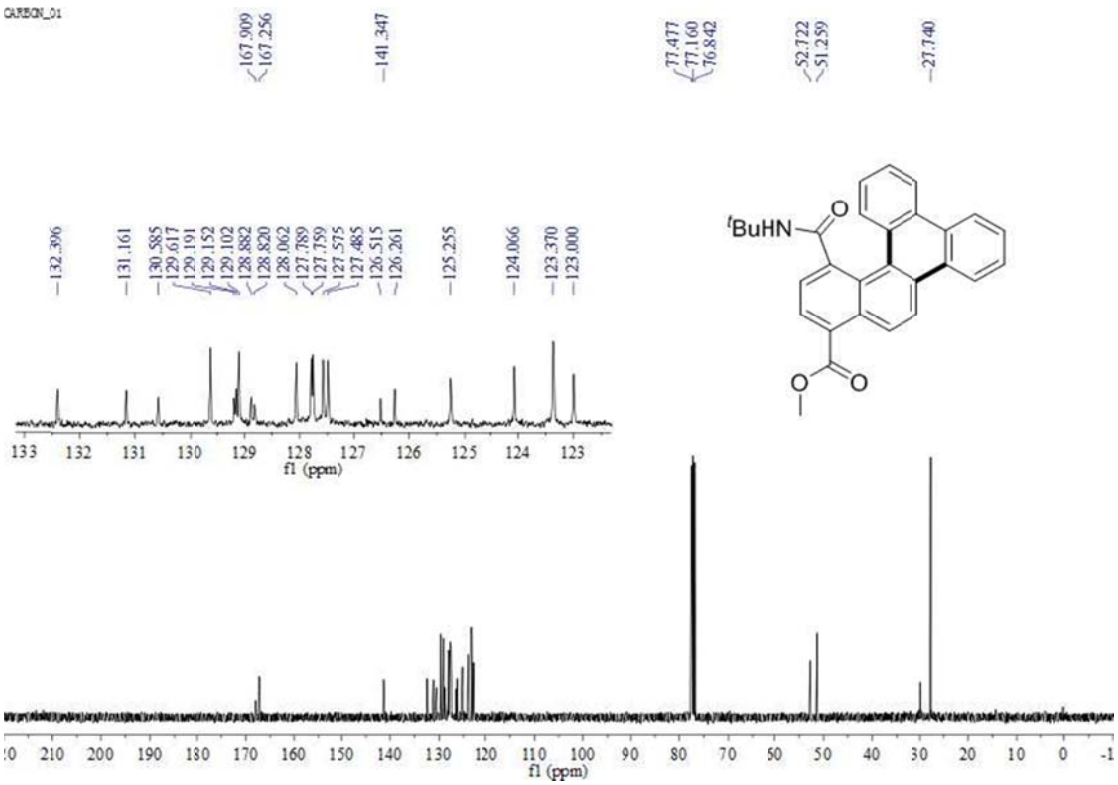
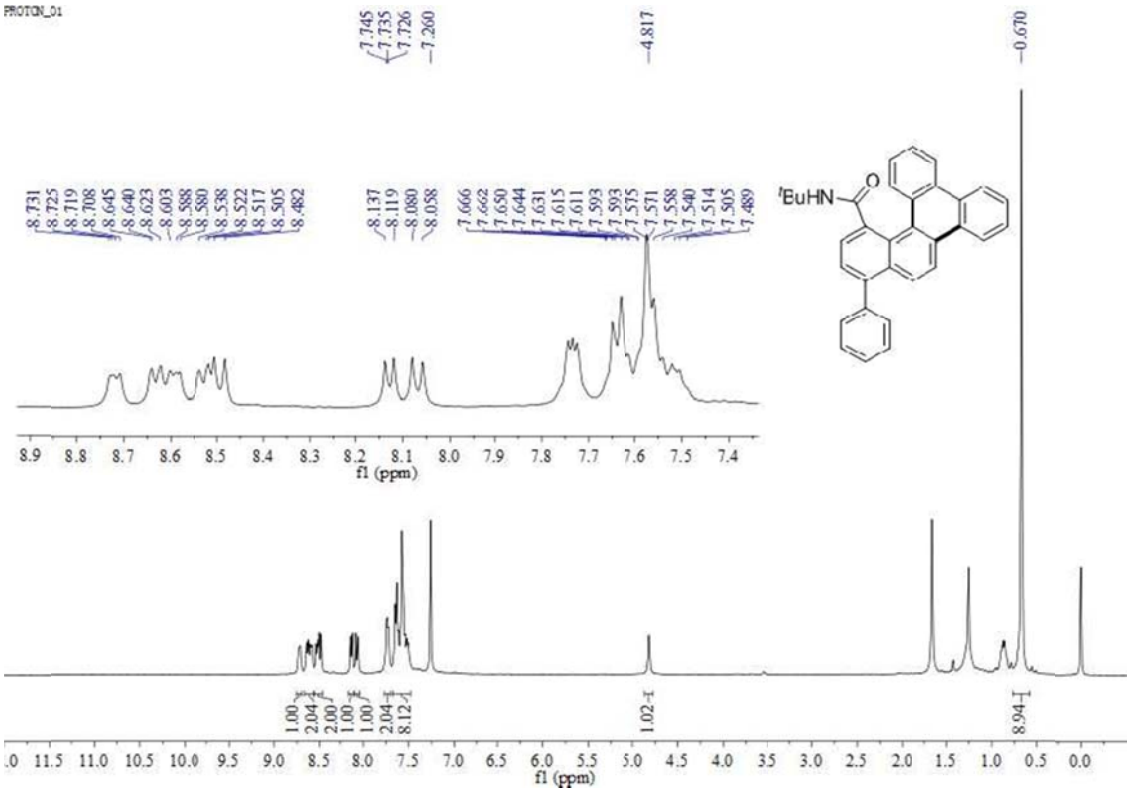


^{1}H NMR spectrum of **3g** in $CDCl_3$



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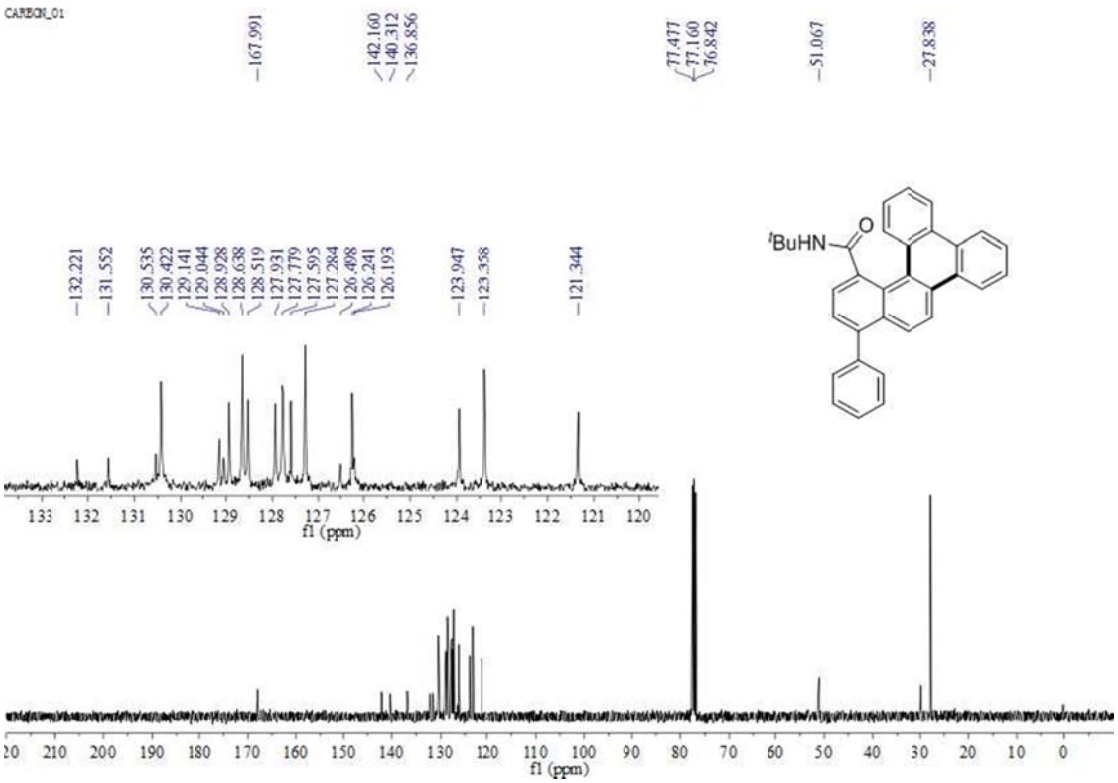

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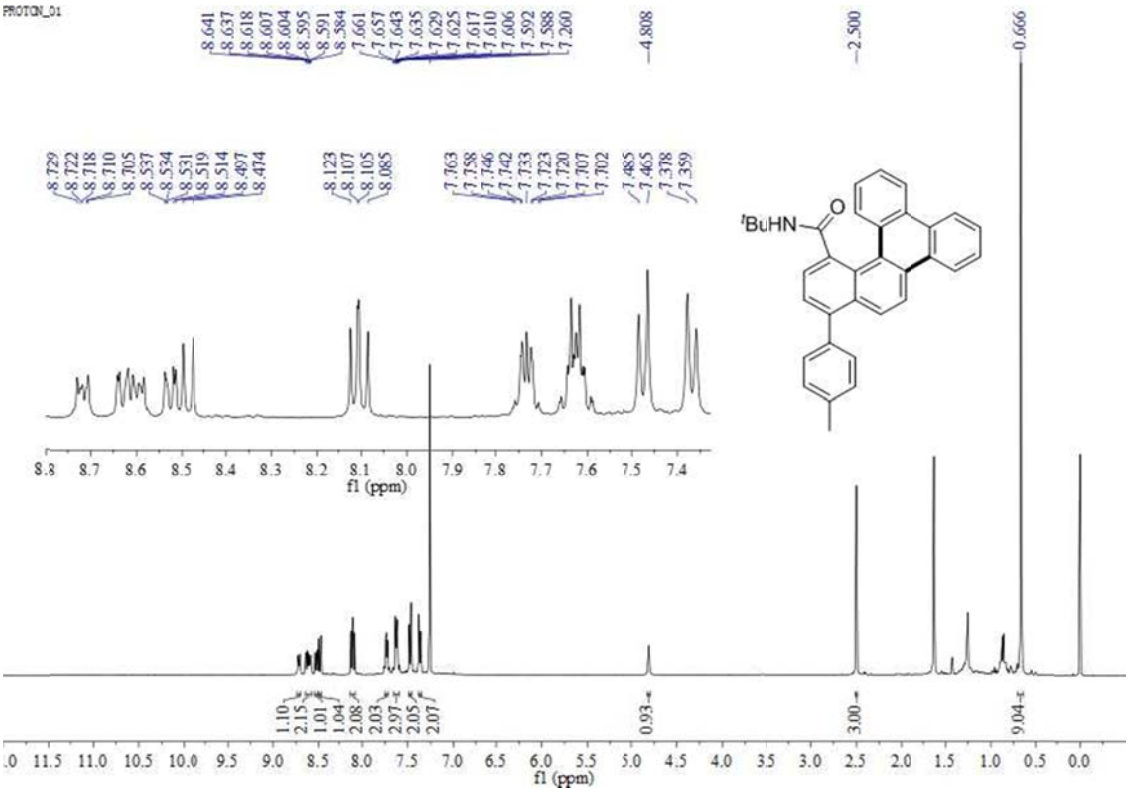

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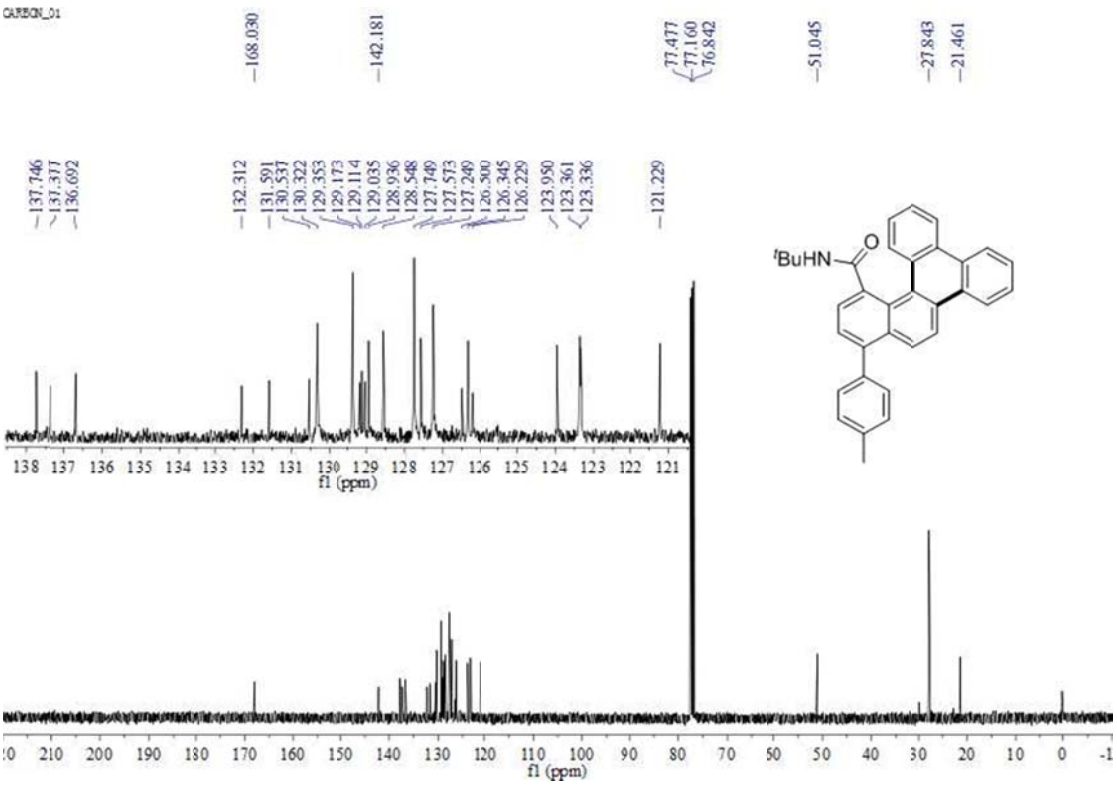

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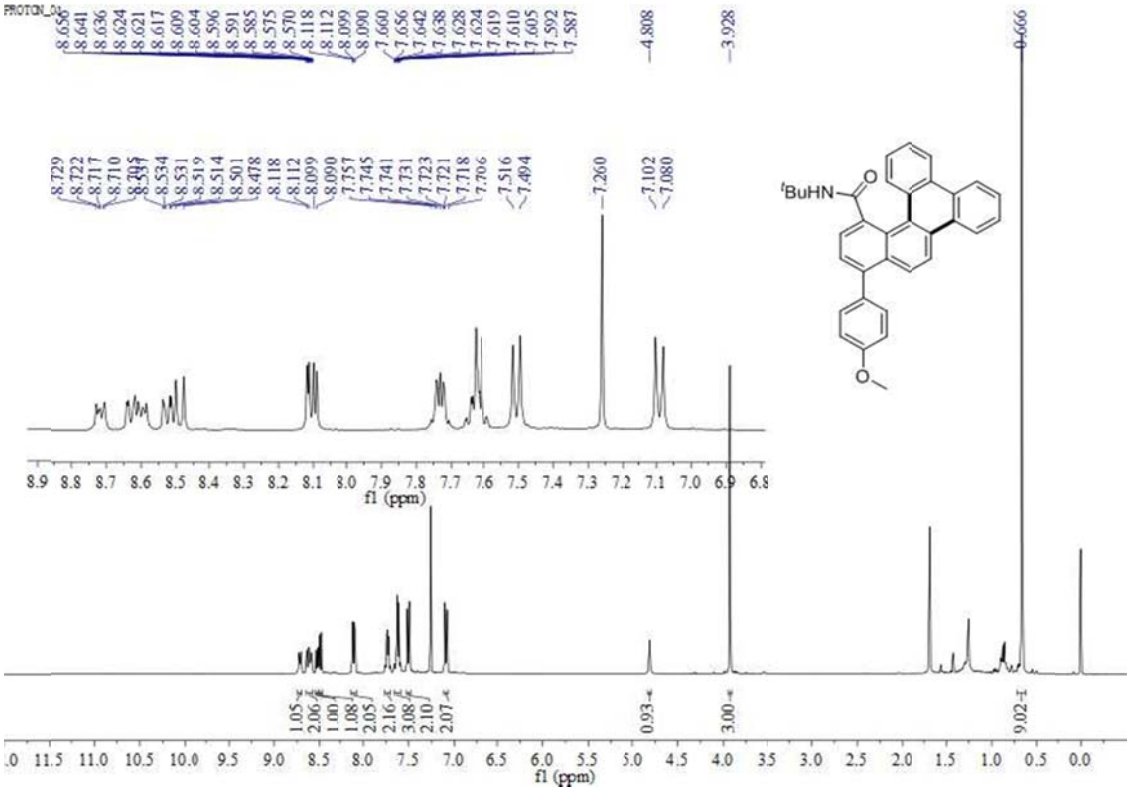

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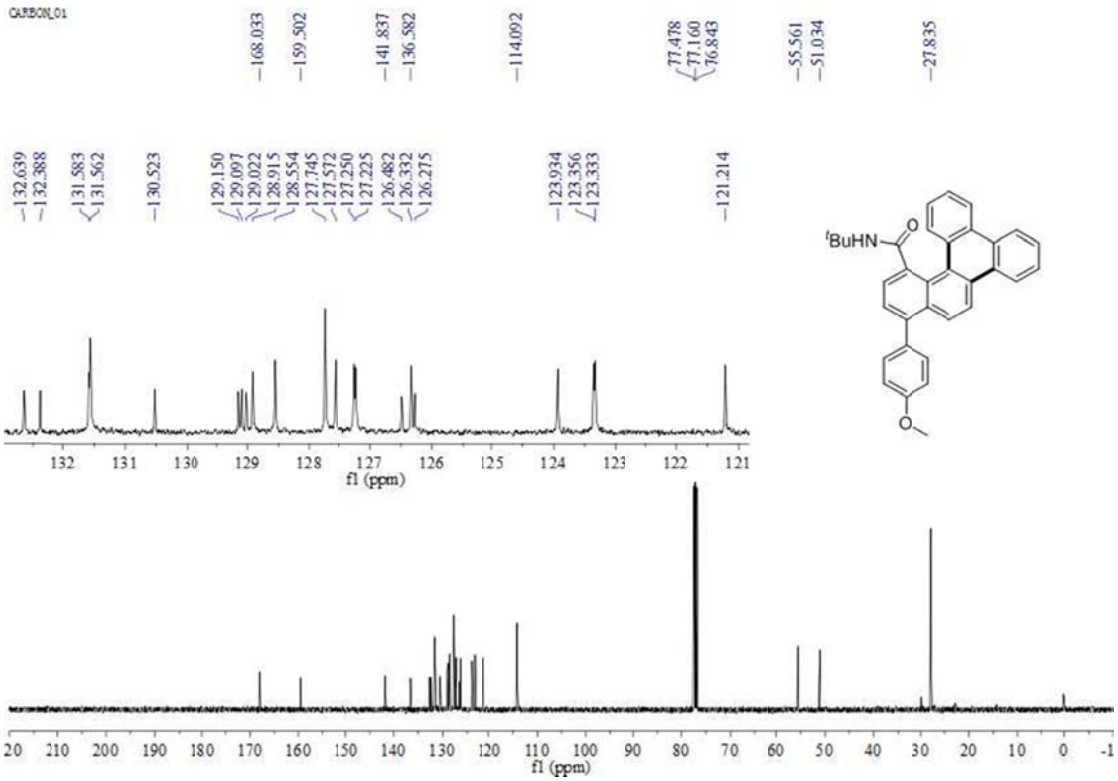

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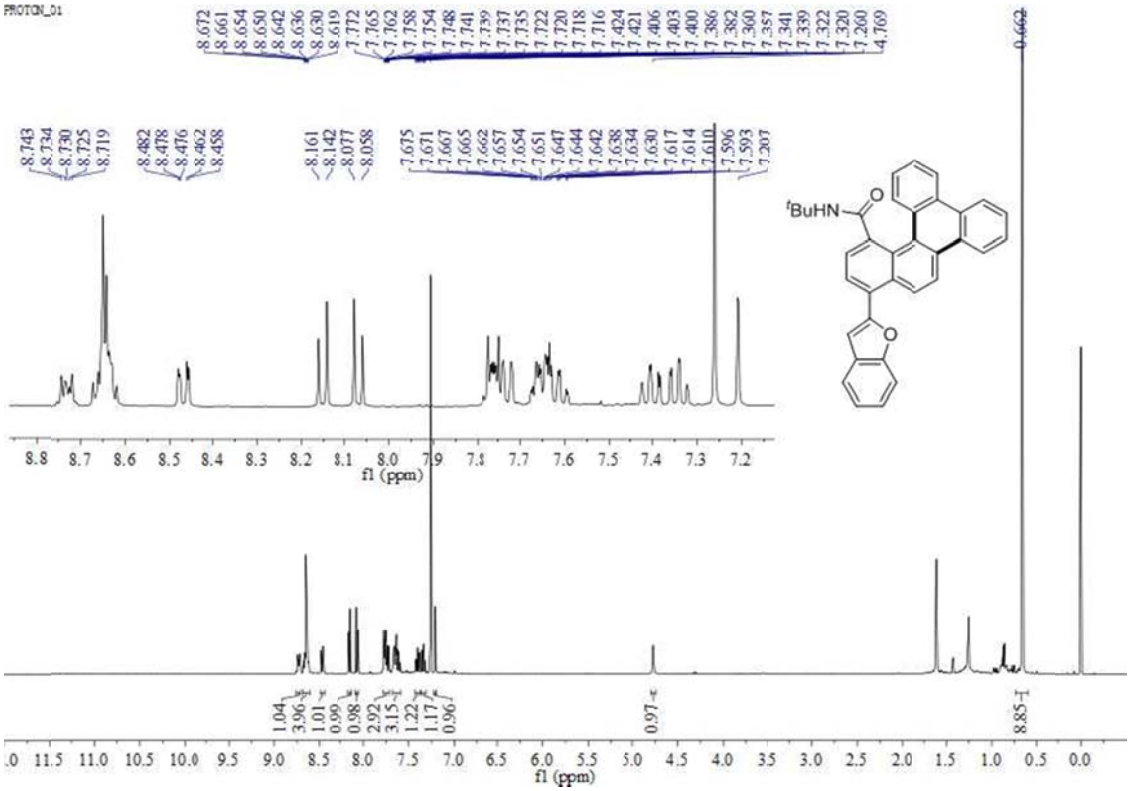

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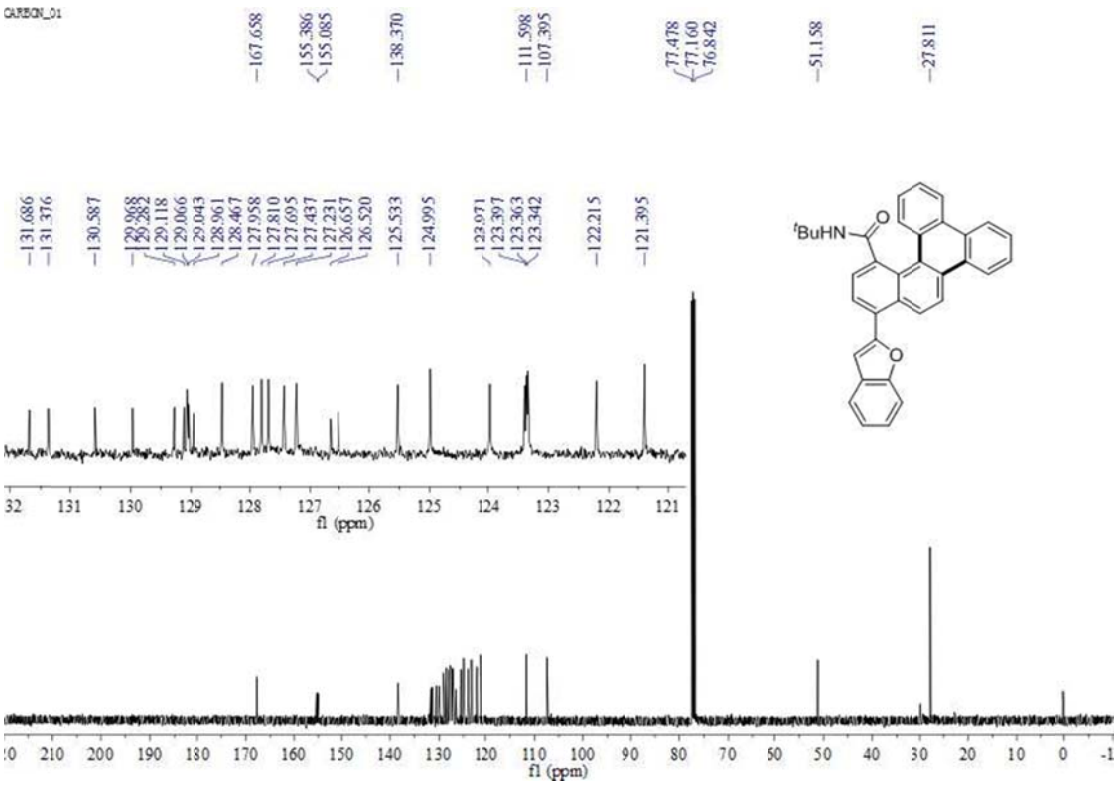

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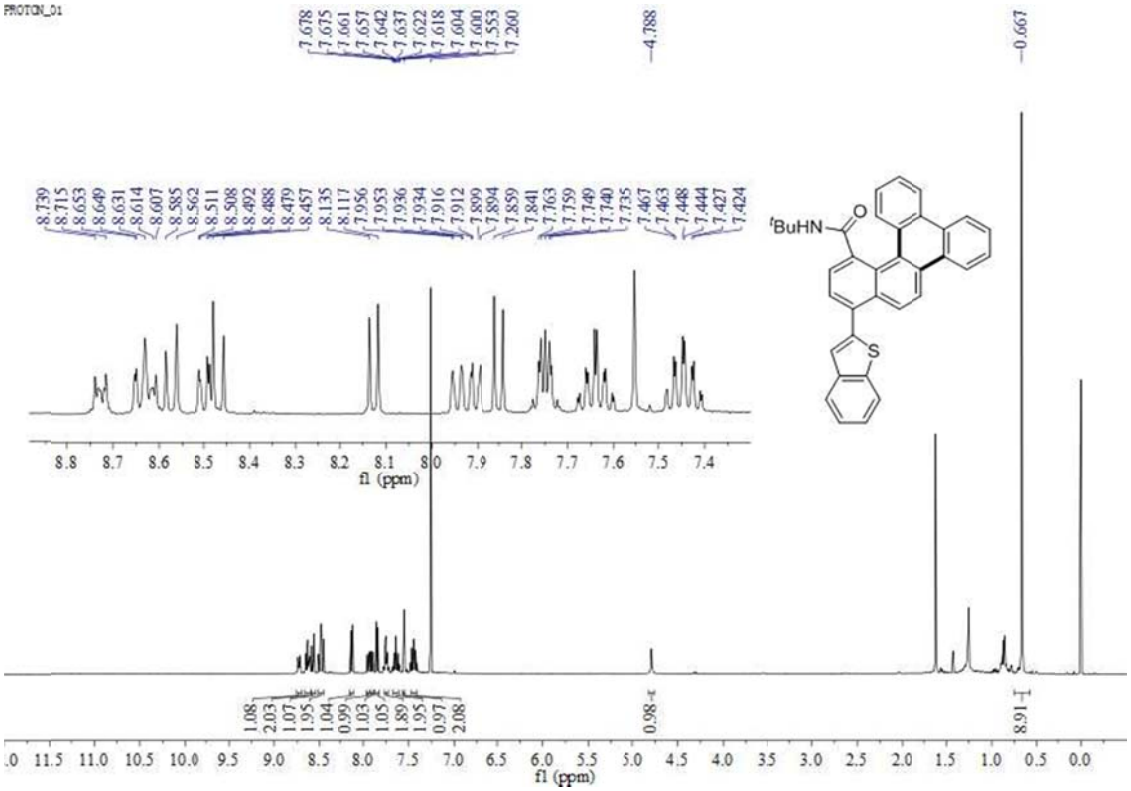

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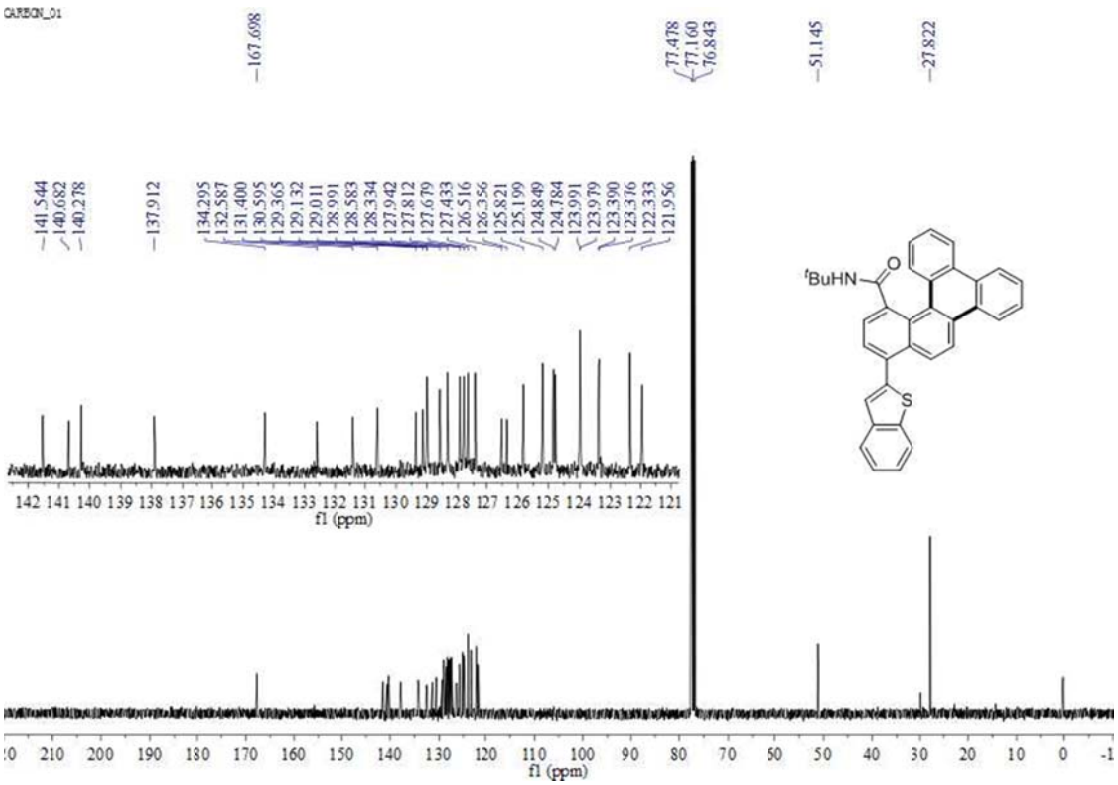

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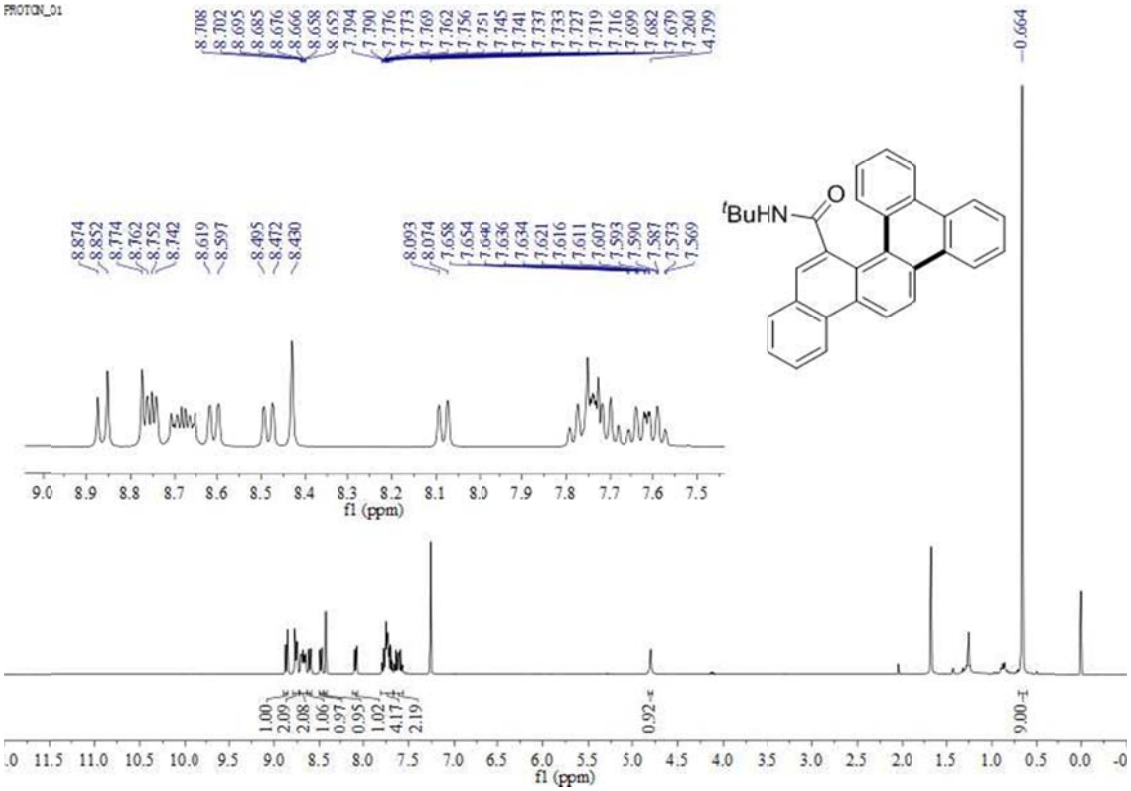

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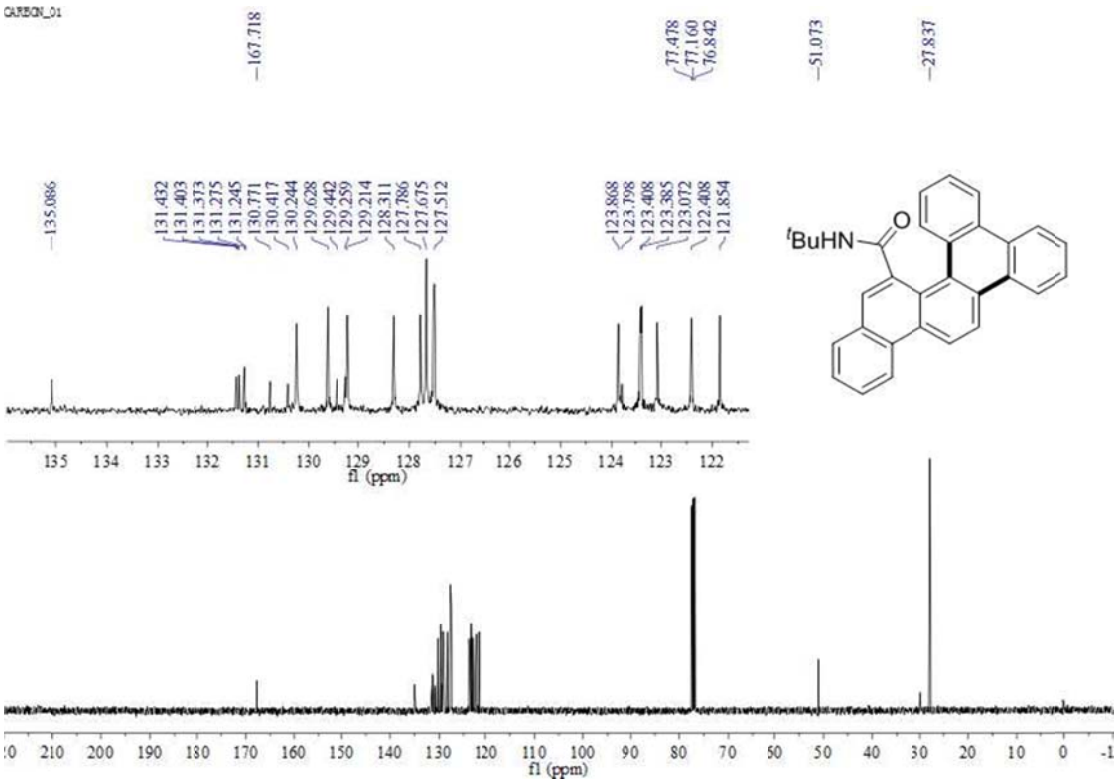

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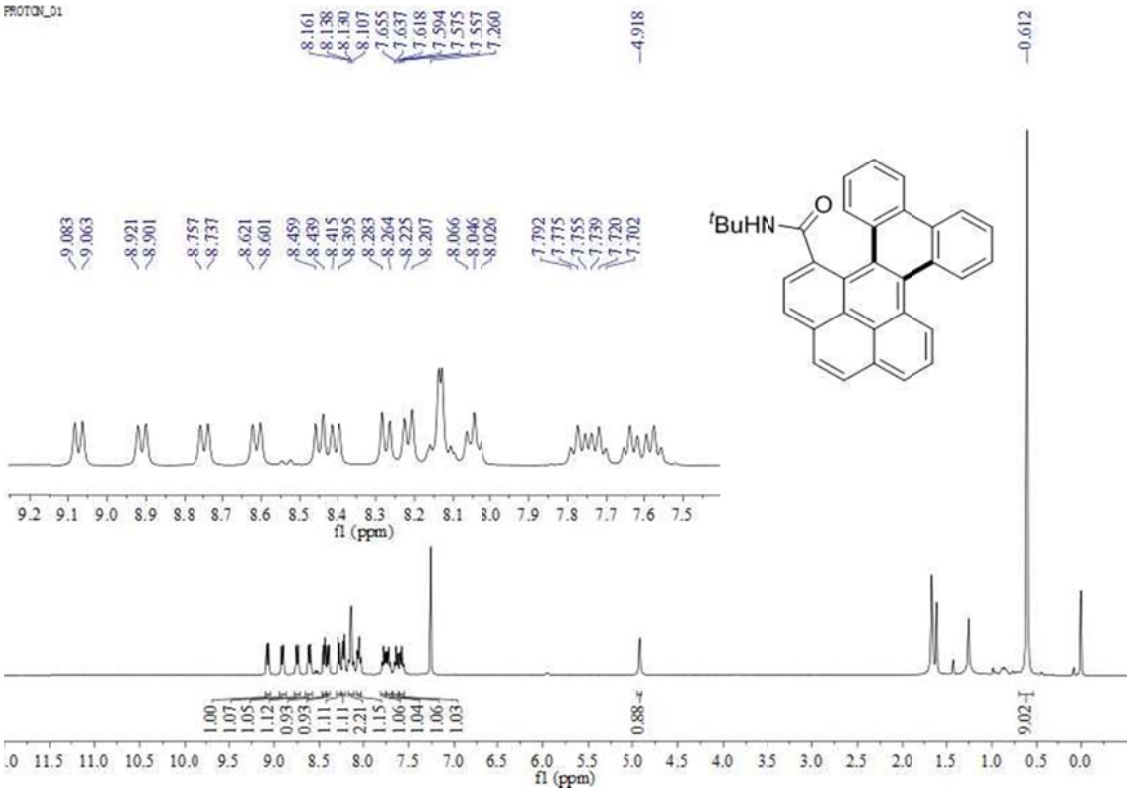

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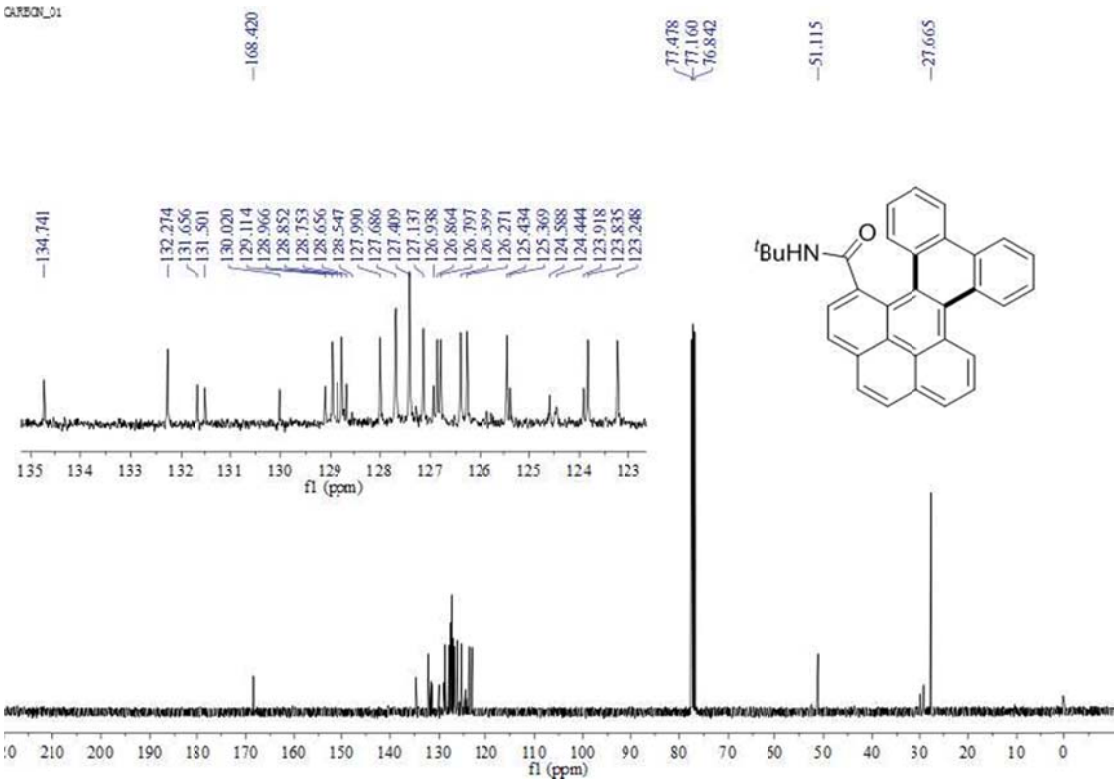
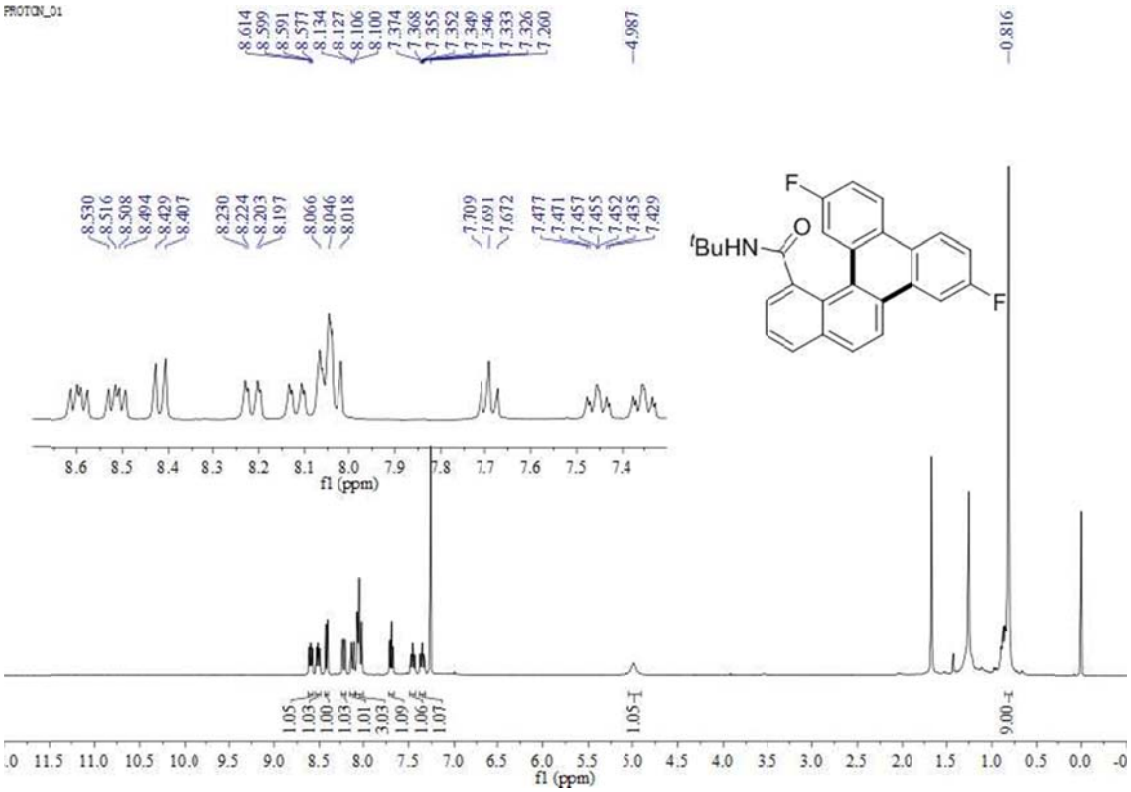
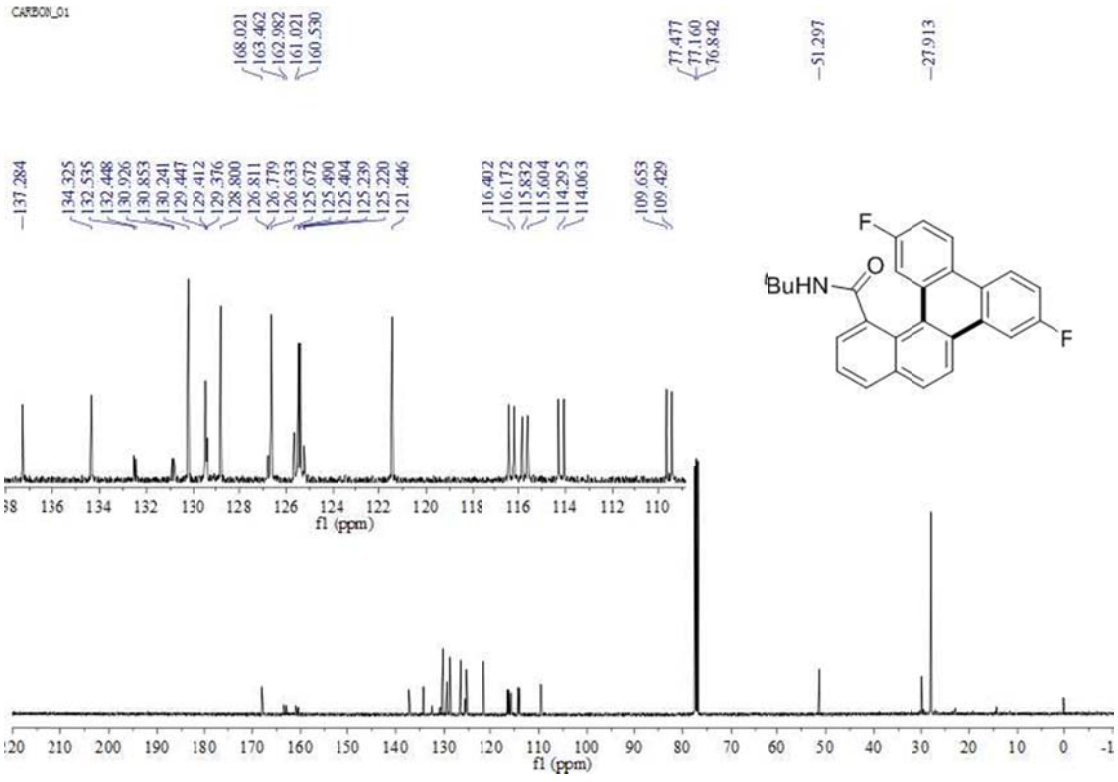


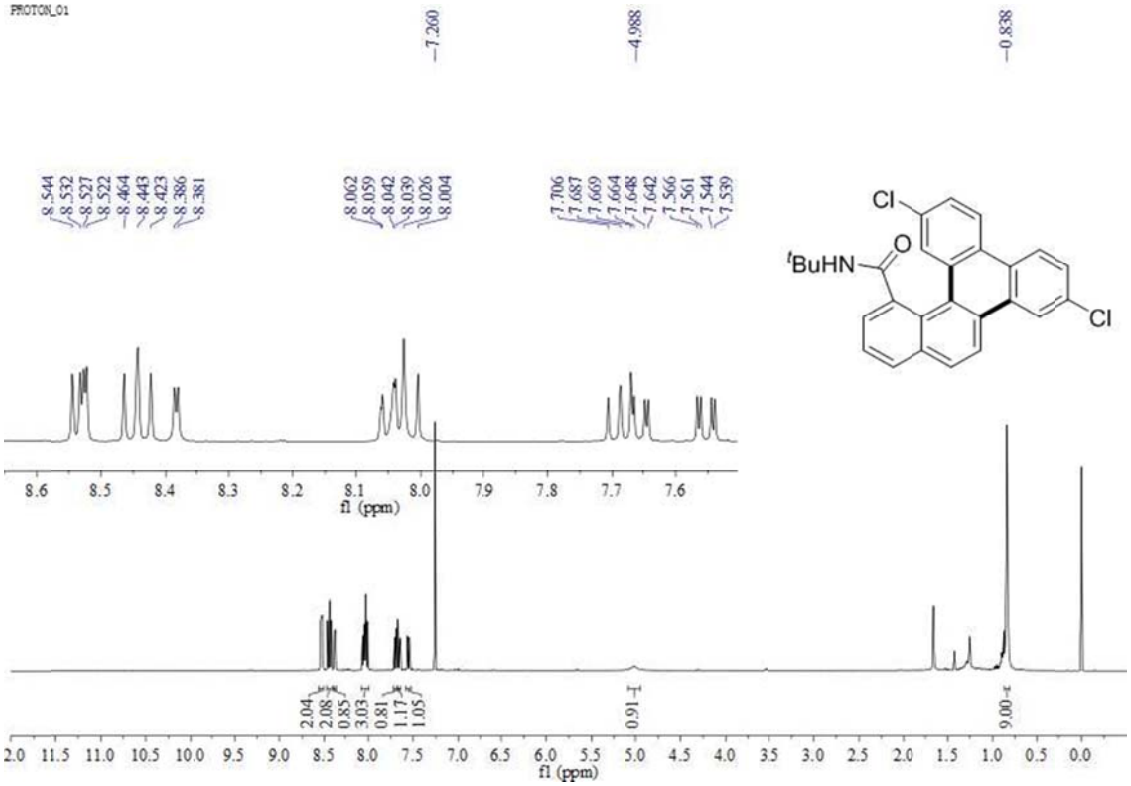
^{1}H NMR spectrum of **3n** in $CDCl_3$



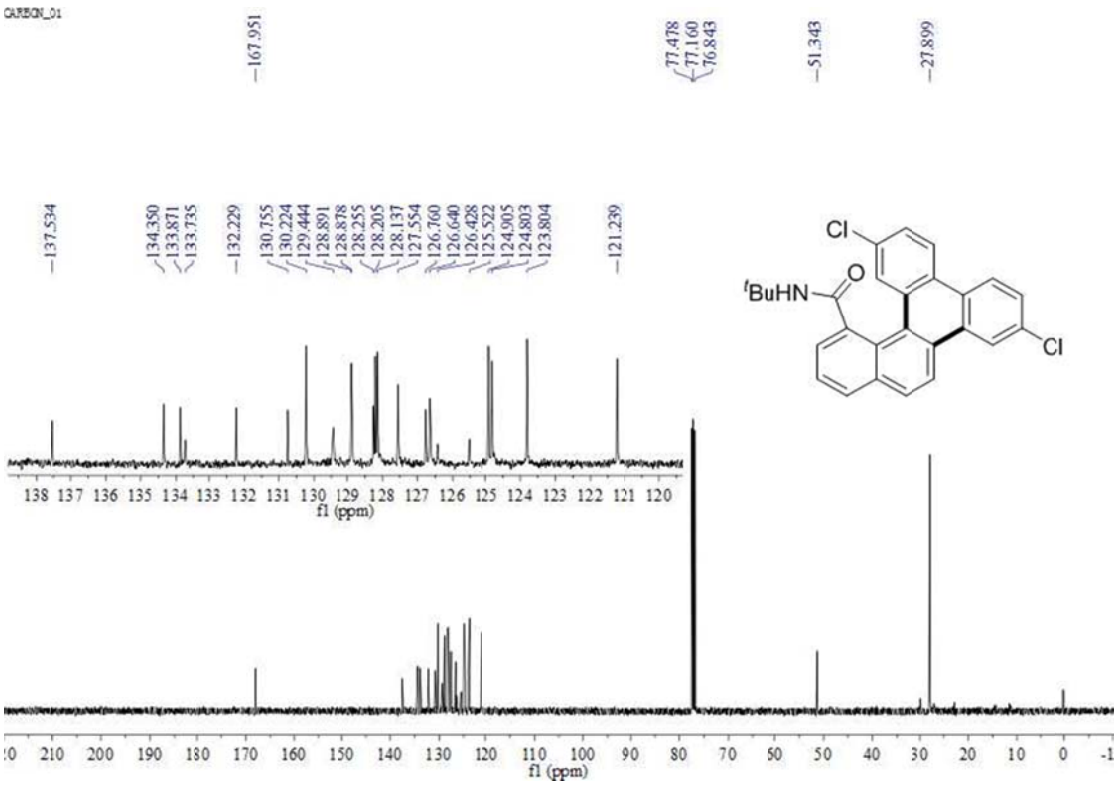
^{13}C NMR spectrum of **3n** in $CDCl_3$



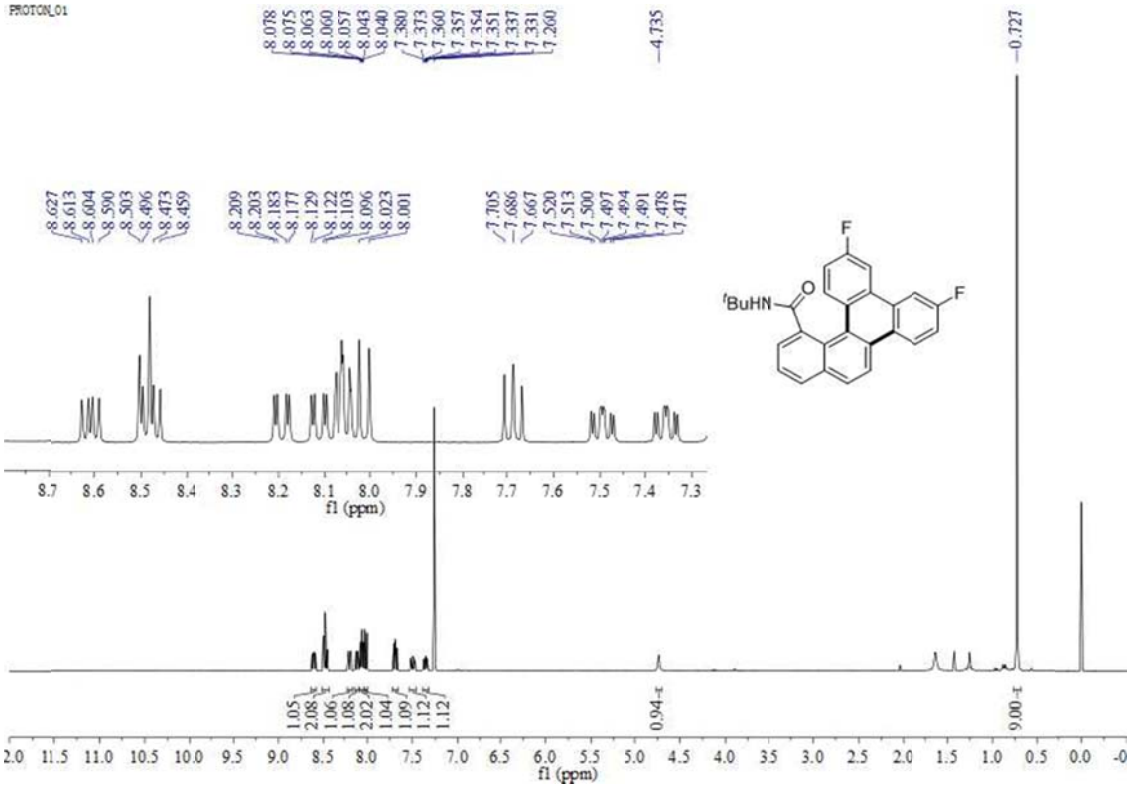
^{1}H NMR spectrum of **3o** in $CDCl_3$



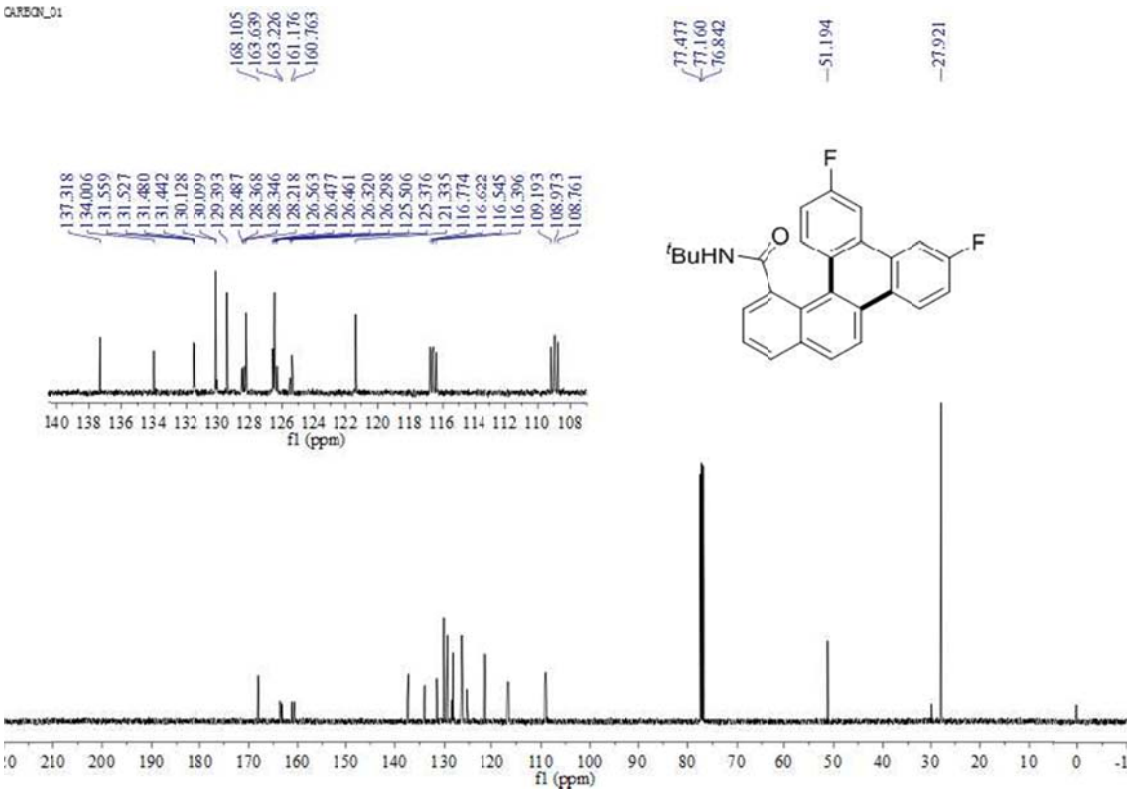
^{13}C NMR spectrum of **3o** in $CDCl_3$



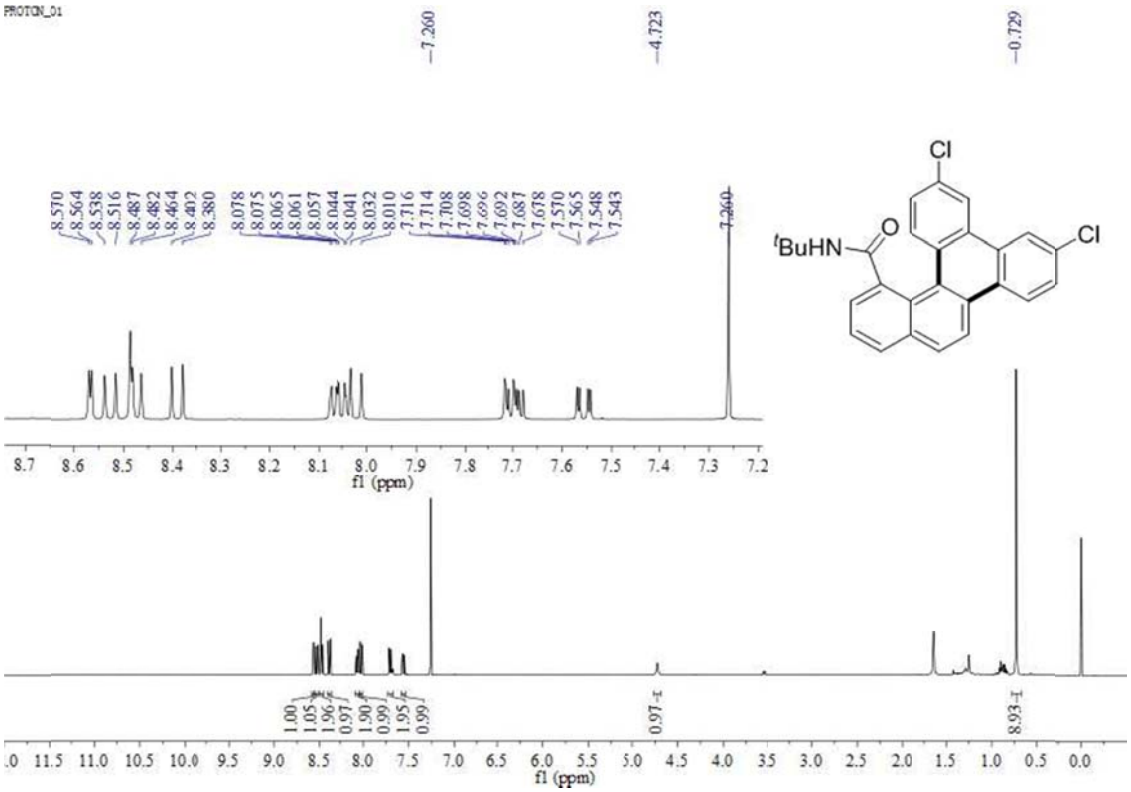
^{1}H NMR spectrum of **3p** in $CDCl_3$



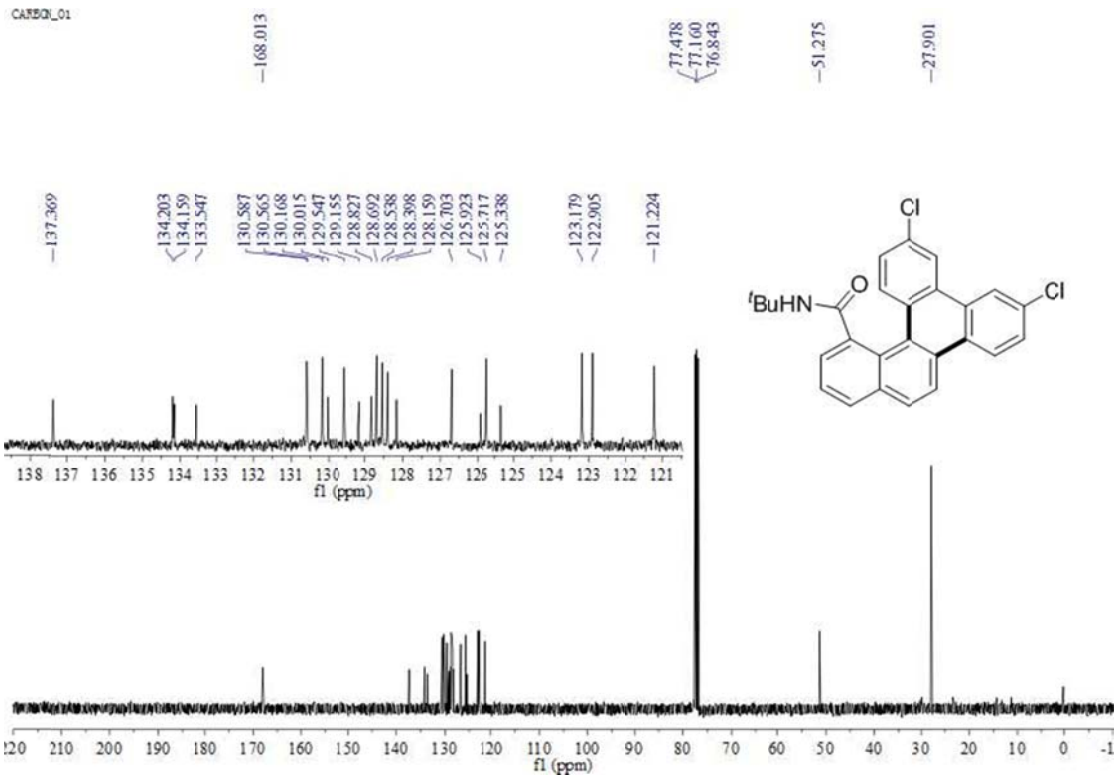
^{13}C NMR spectrum of **3p** in $CDCl_3$



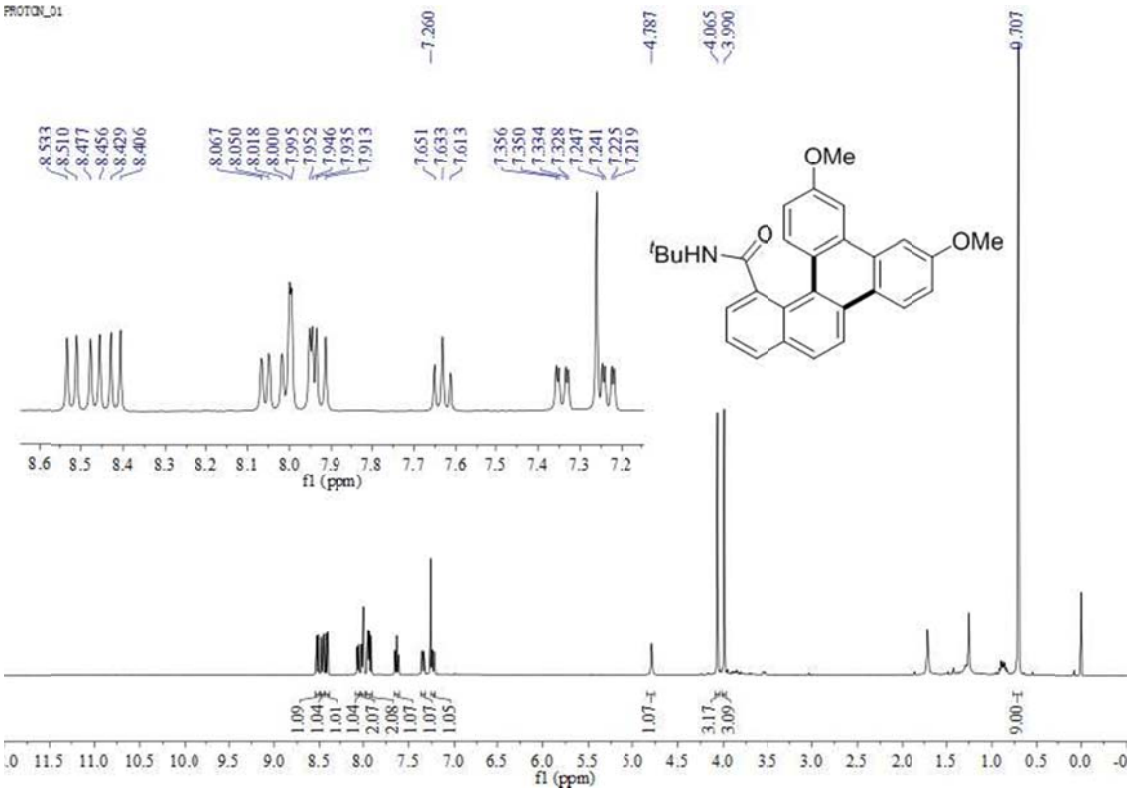
^{1}H NMR spectrum of **3q** in $CDCl_3$



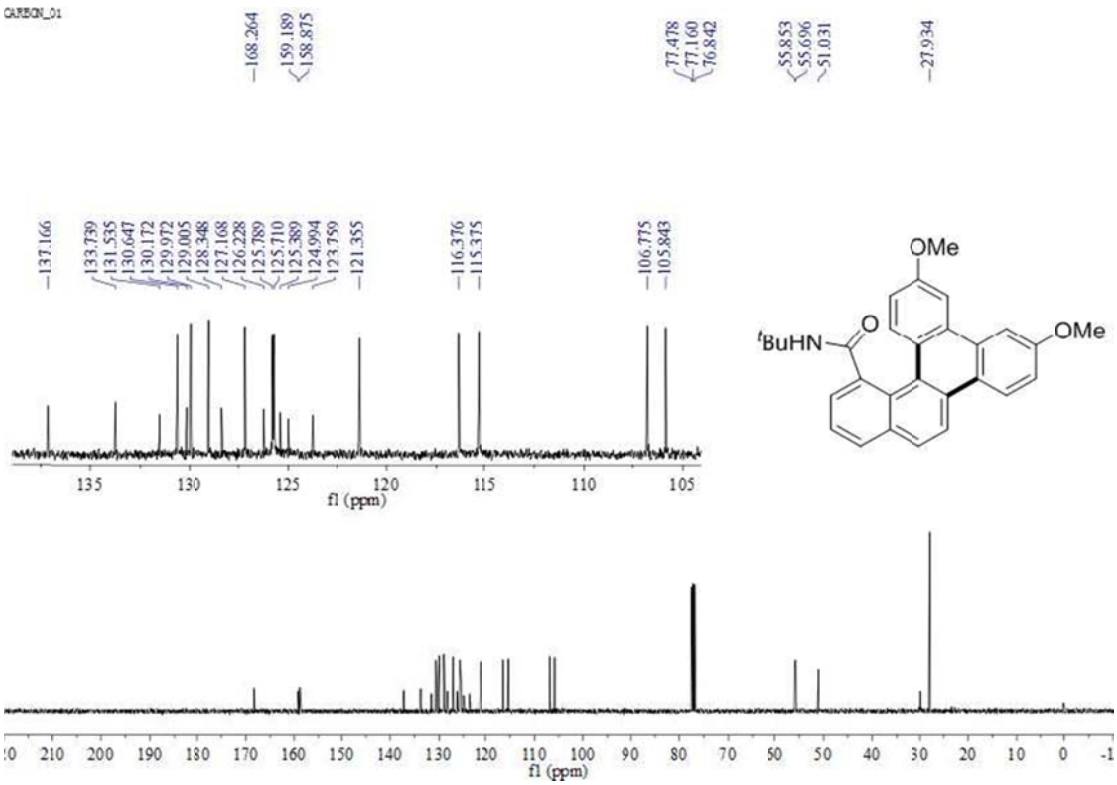
^{13}C NMR spectrum of **3q** in $CDCl_3$



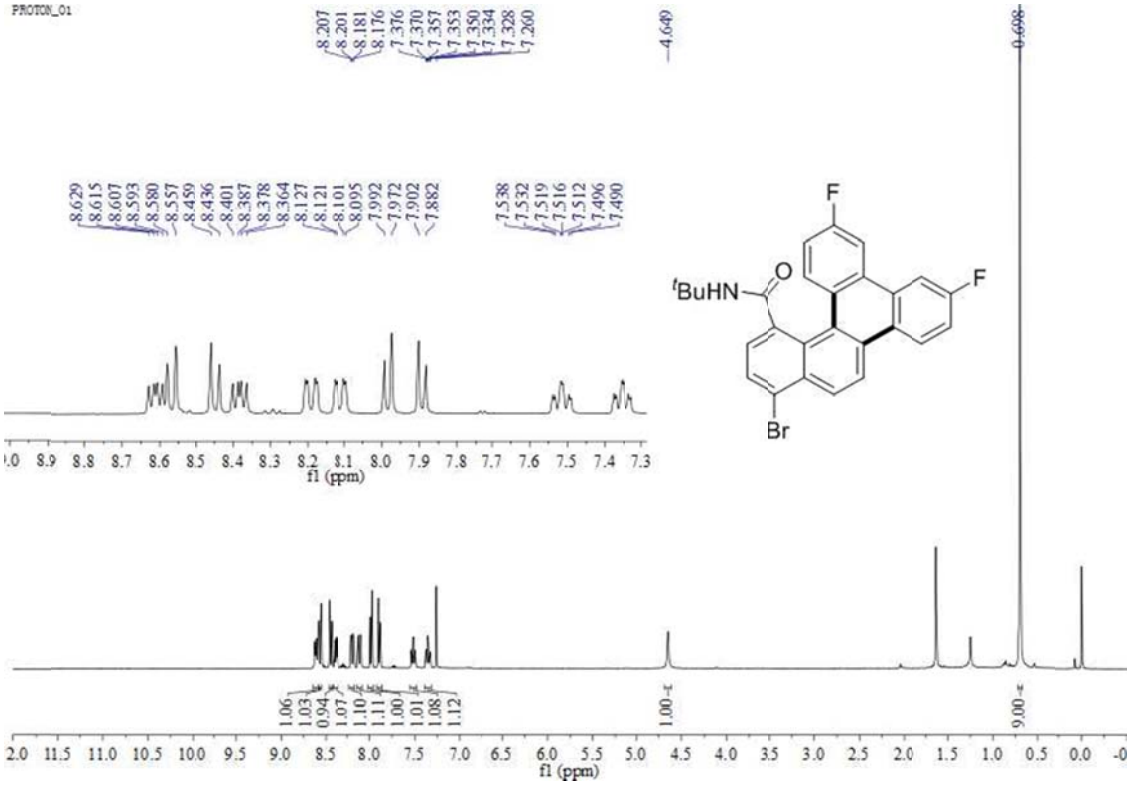
^{1}H NMR spectrum of **3r** in $CDCl_3$



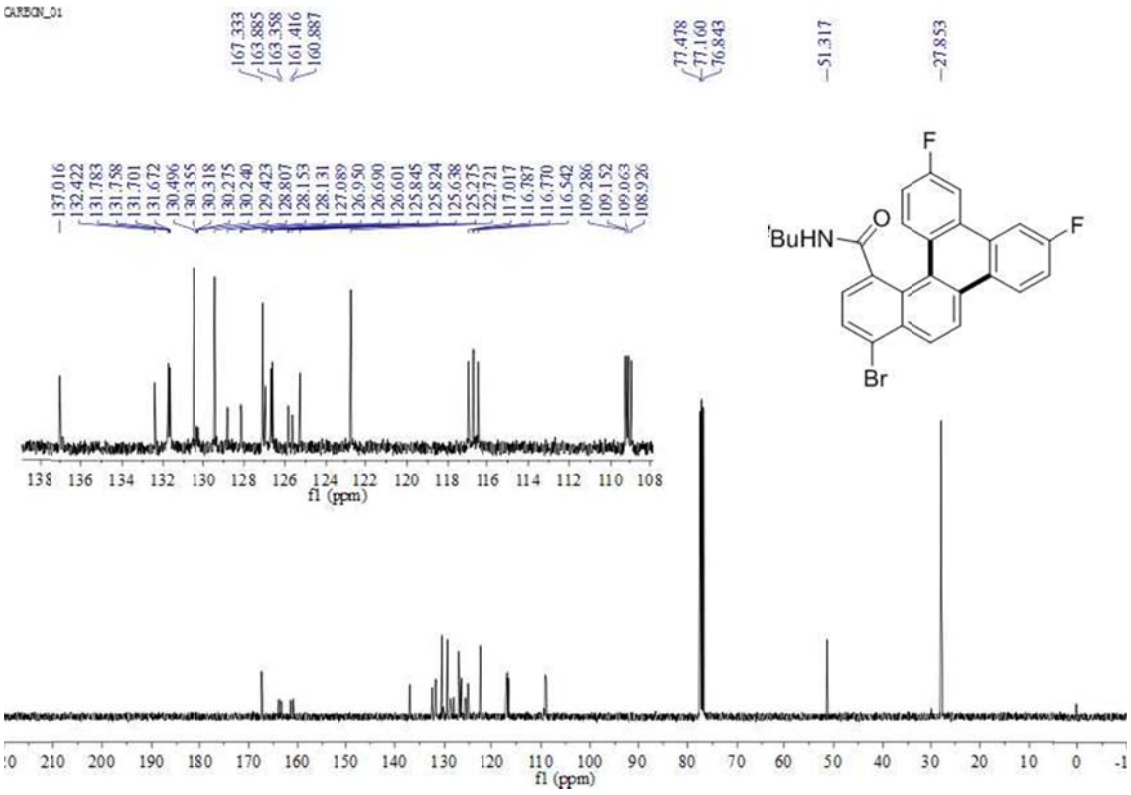
^{13}C NMR spectrum of **3r** in $CDCl_3$



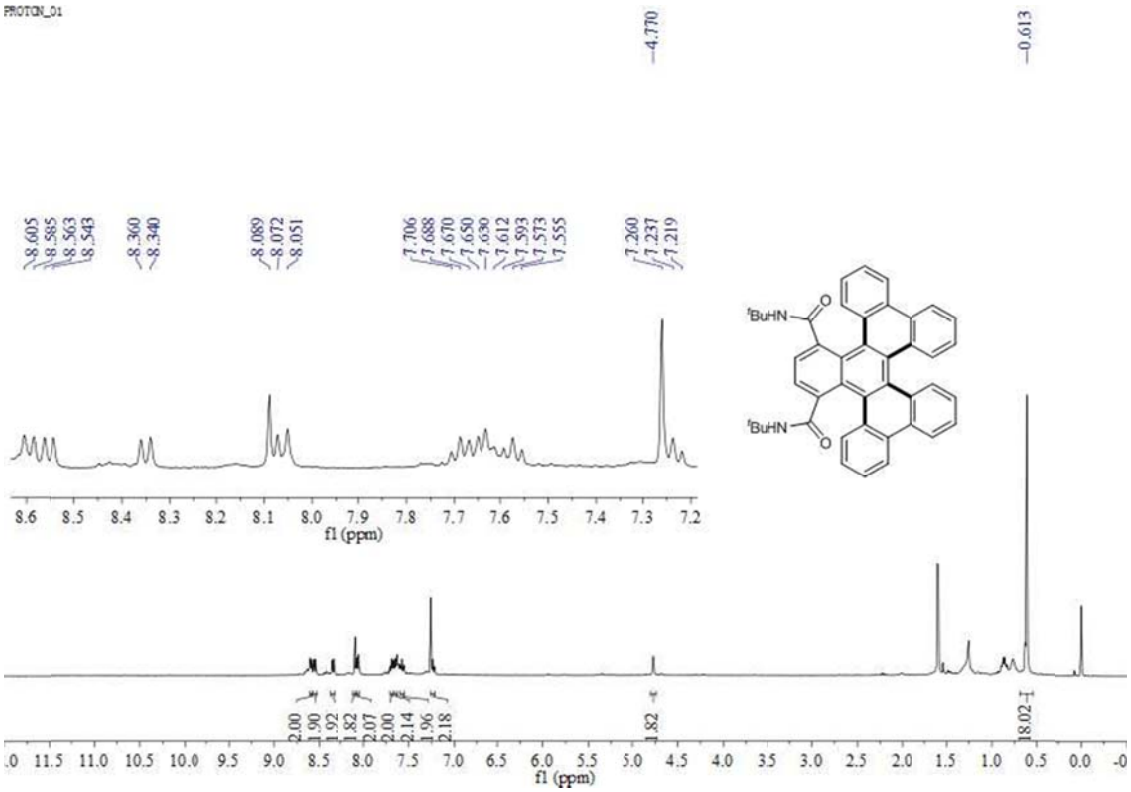
^{1}H NMR spectrum of **3s** in $CDCl_3$



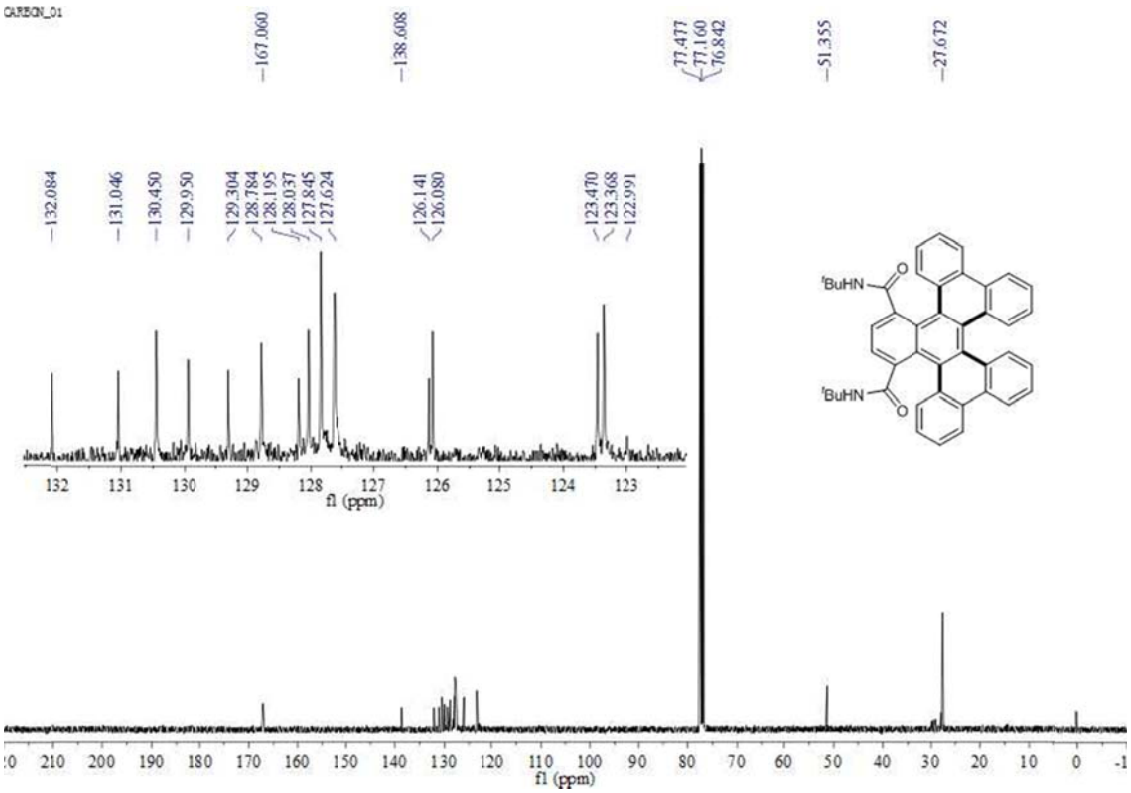
^{13}C NMR spectrum of **3s** in $CDCl_3$



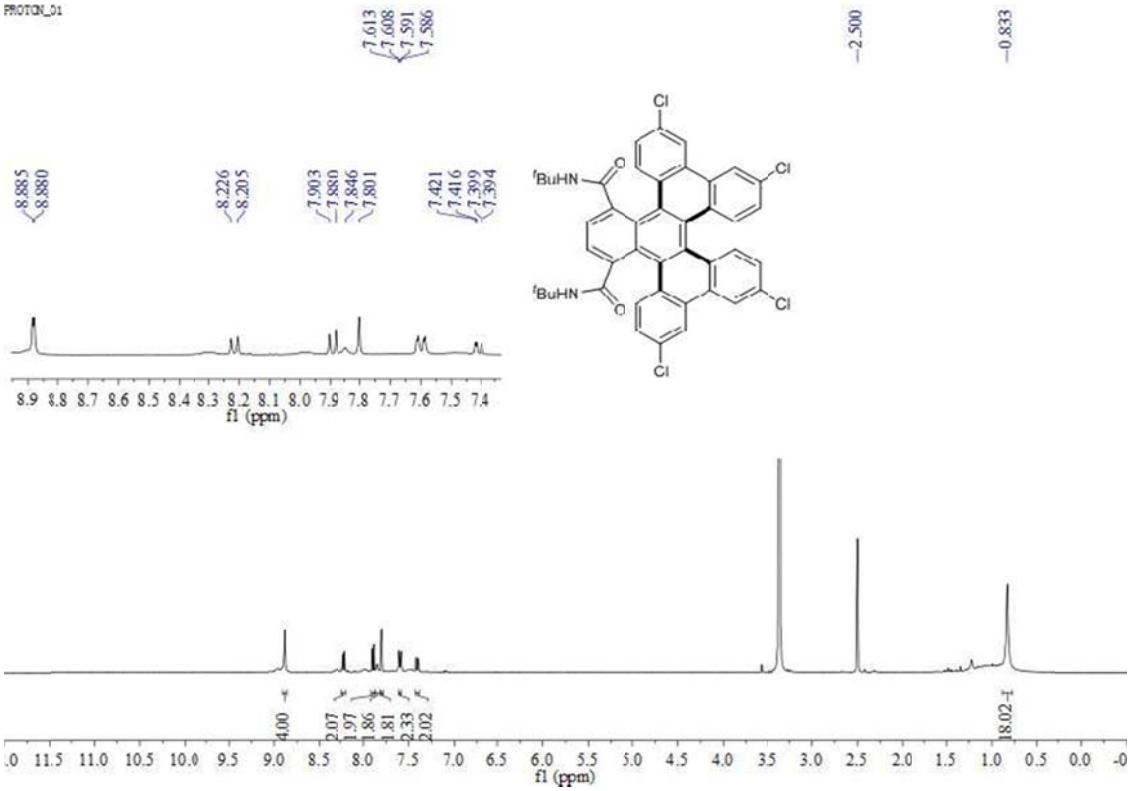
^{1}H NMR spectrum of **4a** in $CDCl_3$



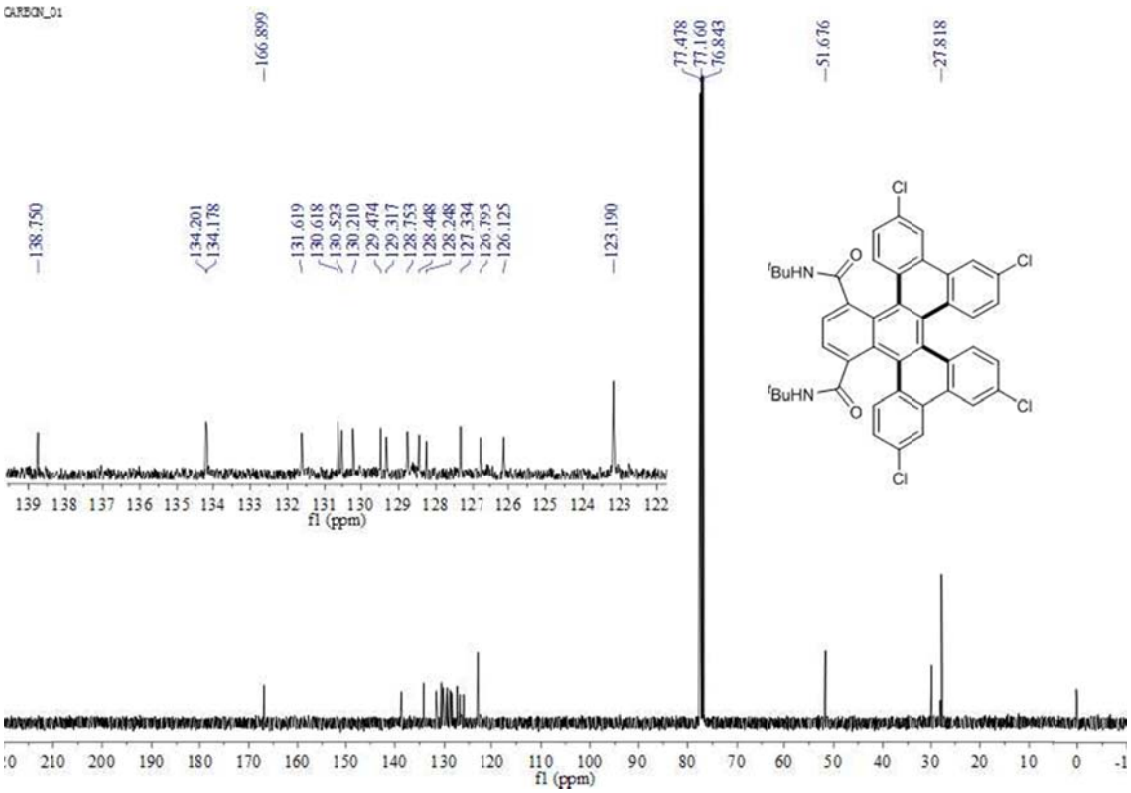
^{13}C NMR spectrum of **4a** in $CDCl_3$



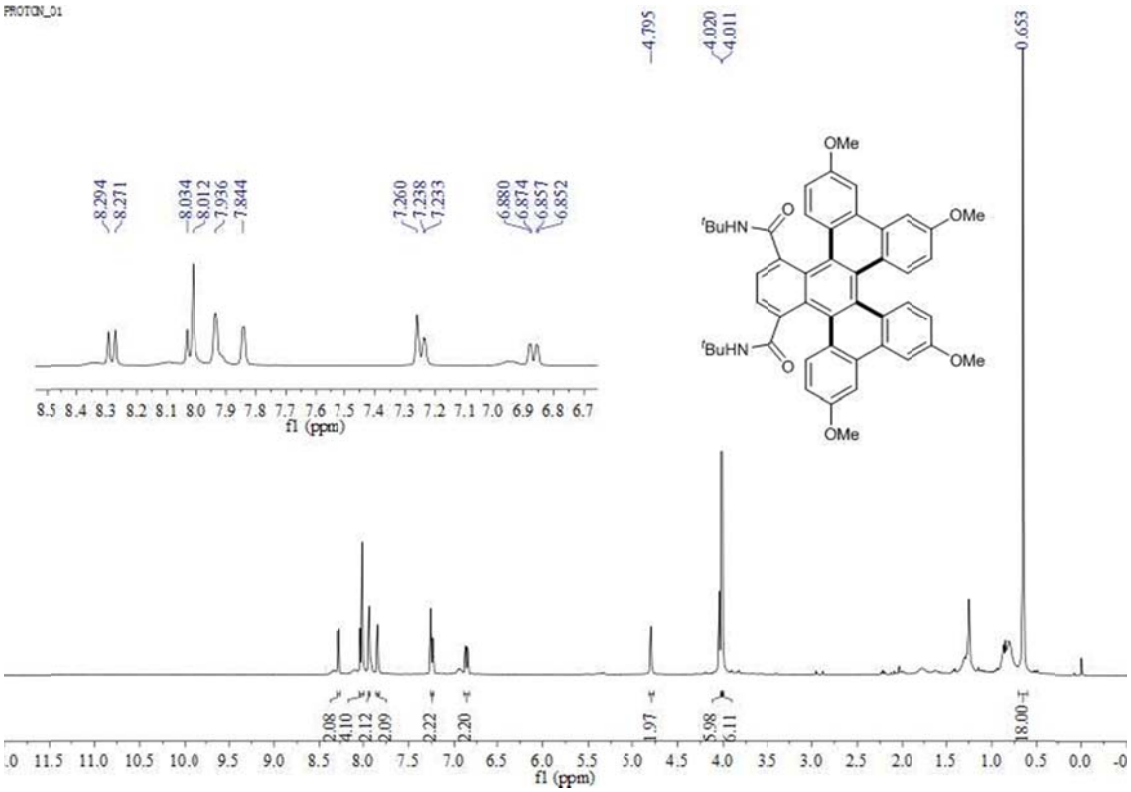
^{1}H NMR spectrum of **4b** in DMSO



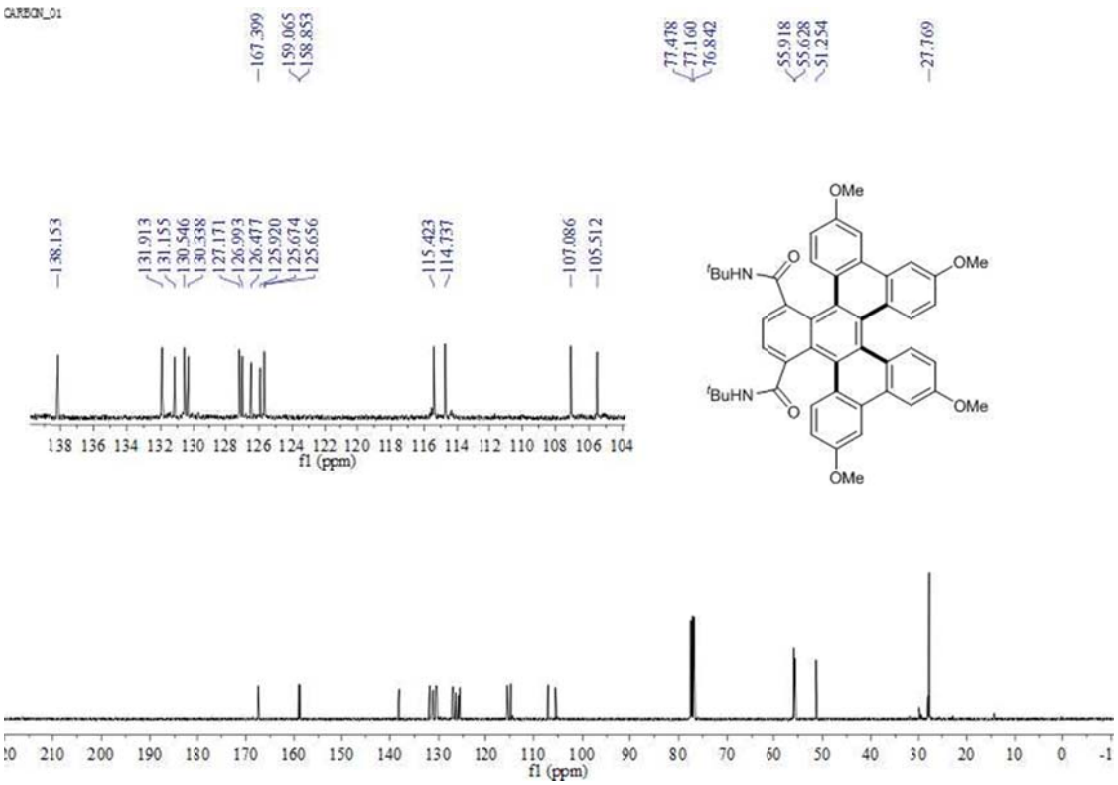
^{13}C NMR spectrum of **4b** in $CDCl_3$



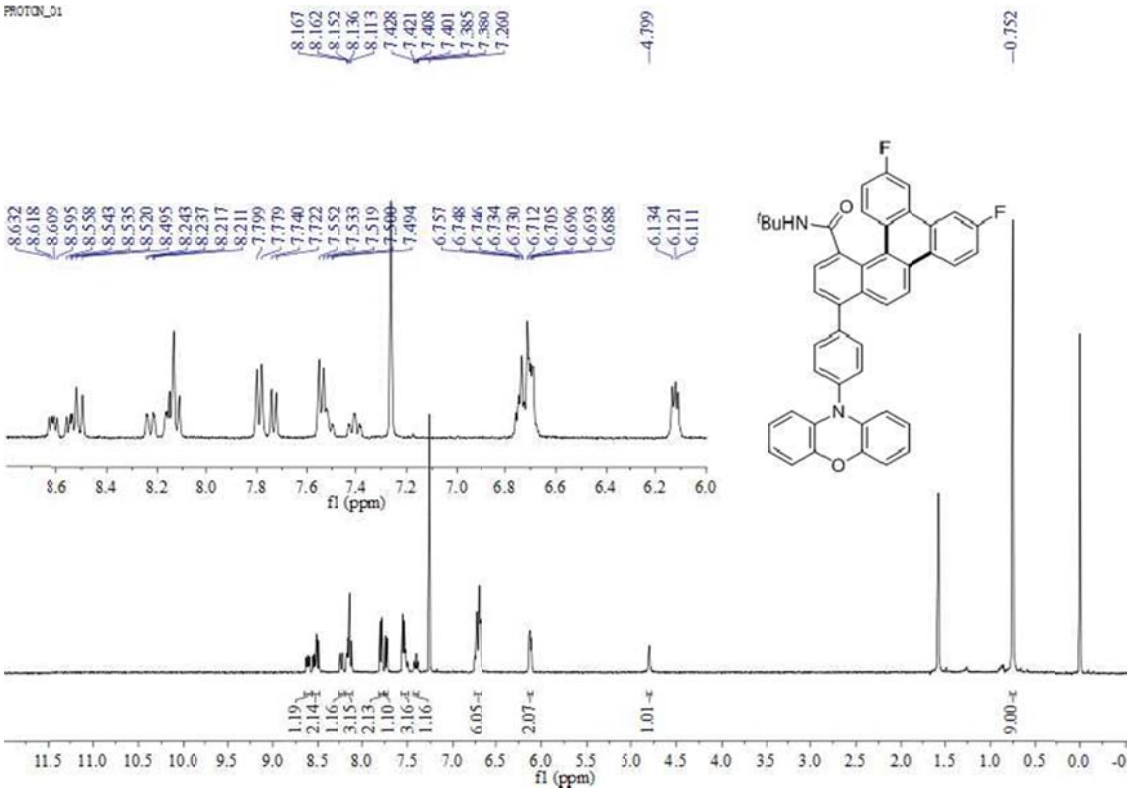
^{1}H NMR spectrum of **4c** in $CDCl_3$



^{13}C NMR spectrum of **4c** in $CDCl_3$



^{1}H NMR spectrum of **5a** in $CDCl_3$



^{13}C NMR spectrum of **5a** in $CDCl_3$