Supporting information

Metal-Free Dehydrogenative Diels-Alder Reactions of Prenyl Derivatives with Dienophiles via a Thermal Reversible Process

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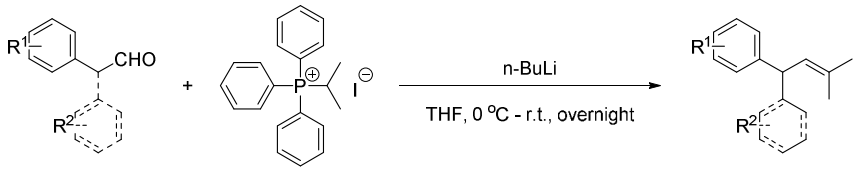
General:

All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on Varian (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^{1}H NMR and to chloroform (δ 77.0), dimethylsulfoxide (δ 39.5) and acetone (δ 206.2) for the ^{13}C NMR measurements. High resolution mass spectra were obtained on a UltiMate 3000 spectrometer. Reactions were followed with TLC (0.254mm silica gel 60-F plates). Visualization was accomplished with UV light. Flash chromatography separations were performed on 200-300 mesh silica gel.

Compound 1r[1], 1s[2] , 2g-2j[3-4] was synthesized according to literature known procedure.

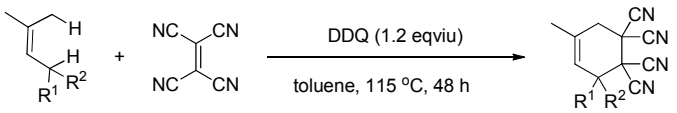
General procedure for the preparation of substrates 1a-1q, 1u-1ac[5-7]:



1

To a stirred solution of isopropyltriphenylphosphonium iodide (4.32 g, 10.0 mmol, 2.0 equiv) in THF (30 mL) at 0 °C was added *n*-BuLi (4.0 mL, 2.5 M solution in hexanes, 2.0 equiv) slowly via syringe. The mixture was stirred for 2 h at 0 °C and then a solution of aldehyde (5.0 mmol, 1 equiv) in THF (8 mL) was added dropwise via syringe, whereupon the mixture was allowed to warm to r.t. and stirred overnight. The mixture was then quenched with H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. After removed the solvent under reduced pressure, the residue was purified on silica gel by flash chromatography to yield the corresponding product.

General procedure for the DDQ-mediated dehydrogenative Diels-Alder reaction.



1 2a 3

In a sealed tube, a mixture of prenyl derivatives **1** (0.2 mmol), tetracyanoethylene (51.2 mg, 0.4 mmol, 2 equiv) and DDQ (54.5 mg, 0.24 mmol, 1.2 equiv) in toluene (2 mL) was stirred at 115 °C for 48 h until the DDQ-adduct **4** was disappeared (monitored by TLC). After removed the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 7:1 to 3:1) to afford the desired product **3**.

Gram-scale reaction of 1a

In a sealed tube, a mixture of prenyl benzene **1a** (1.17 g, 8.0 mmol, 1 equiv), tetracyanoethylene (2.05 g, 16.0 mmol, 2 equiv) and DDQ (2.18 g, 9.6 mmol, 1.2 equiv) in toluene (80.0 mL) was stirred at 115 °C for 48 h until the DDQ-adduct **4** was disappeared (monitored by TLC). After removed the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 7:1 to 3:1) to afford the desired product **3a** (1.96 g, 7.2 mmol) in 90% yield.

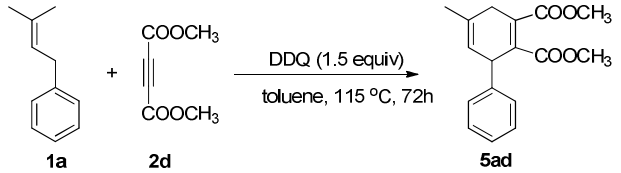
DHDA reaction of quinones 2b-2c with prenyl benzene.

1a 2b-2c 5ab-5ac

In a sealed tube, a mixture of prenyl benzene **1a** (58.5 mg, 0.4 mmol), quinones **2b-2c** (0.2 mmol), LiCl (8.5 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL) was stirred at 115 °C for 72 h until the DDQ-adduct **4** was disappeared (monitored by TLC). After removed the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 15:1) to afford the desired product **5ab-5ac**.

DHDA reaction of DMAD (but-2-ynedioic acid dimethyl ester) 2d with prenyl

benzene.

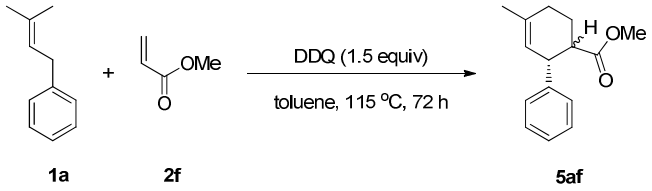


In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), DMAD **2d** (28.5 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL), was stirred at 115 °C until the DMAD **2d** was disappeared nearly, which was determined by TLC analysis (72 h). The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 7:1) to afford the desired product **5ad**.

DHDA reaction of maleic anhydride 2e with prenyl benzene.

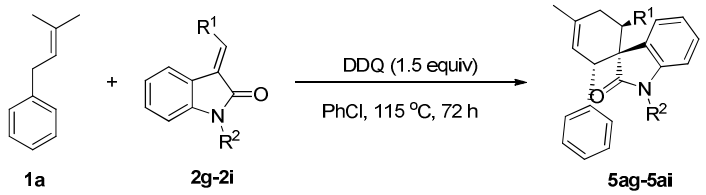
In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), anhydride **2e** (19.7 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL), was stirred at 115 °C until the anhydride **2e** was disappeared nearly, which was determined by TLC analysis (72 h). The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 5:1 to 4:1) to afford the desired product **5ae**.

DHDA reaction of methyl acrylate 2f with prenyl benzene.



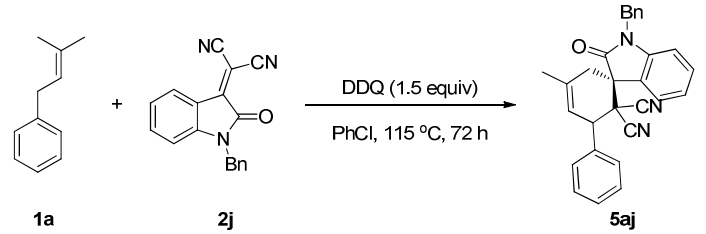
In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), methyl acrylate **2f** (17.3 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL), was stirred at 115 °C until the methyl acrylate **2f** was disappeared nearly, which was determined by TLC analysis (72 h). The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 15:1) to afford the desired product **5af**.

DHDA reaction of 2,3-olefinic oxindoles 2g-2i with prenyl benzene.



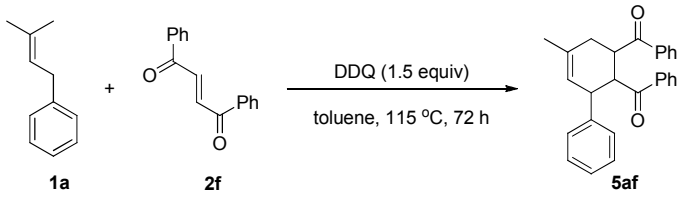
In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), 2,3-olefinic oxindoles **2g-2i** (0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in PhCl (2 mL), was stirred at 115 °C until the 2,3-olefinic oxindoles **2g-2i** was disappeared nearly, which was determined by TLC analysis (72 h). The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 8:1) to afford the desired product **5ag-5ai**.

DHDA reaction of 2,3-olefinic oxindoles 2j with prenyl benzene.



In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), 2,3-olefinic oxindoles **2j** (57.1 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in PhCl (2 mL), was stirred at 115 °C for 72 h. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 8:1) to afford the desired product **5aj**.

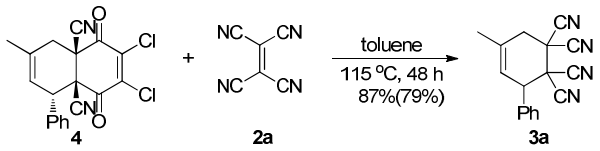
DHDA reaction of trans-dibenzoylethene 2k with prenyl benzene.



In a sealed tube, a mixture of Prenyl benzene **1a** (58.5 mg, 0.4 mmol), trans-dibenzoylethene **2k** (47.3 mg, 0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL), was stirred at 115 °C until the trans-dibenzoylethene **2k** was disappeared nearly, which was determined by TLC analysis (72 h). The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 20:1) to afford the desired product **5ak**.

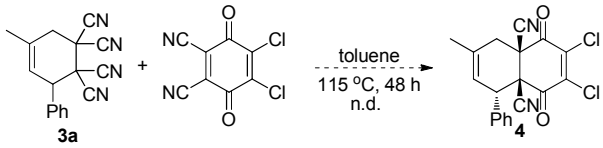
Control experiments

b: a direct thermal reversible process

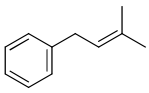


In a sealed tube, a mixture of DDQ-adduct **4** (37.1 mg, 0.1 mmol), tetracyanoethylene **2a** (25.6 mg, 0.2 mmol) in toluene (2 mL), was stirred at 115 °C for 48 h. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 5:1 to 4:1) to provide the desired product **3a** (23.7 mg, 87%). When **2a** was reduced to 1 equiv, the product **3a** was isolated in 79% yield and the DDQ-adduct **4** was recovered in 9% yield.

c: the experiment of thermal stability

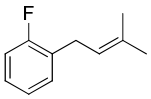


In a sealed tube, a mixture of **3a** (27.2 mg, 0.1 mmol), DDQ (22.7 mg, 0.1 mmol) in toluene (2 mL), was stirred at 115 °C for 48 h. The residue was purified by column chromatography on silica gel (petroleum ether /EtOAc = 7:1) and no product **4** was isolated, recovering **3a** in 91% yield.



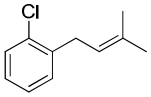
(3-Methylbut-2-en-1-yl)benzene (1a)

Colourless oil, 599 mg, 82% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 5.33 (t, *J* = 7.4 Hz, 1H), 3.35 (d, *J* = 7.3 Hz, 2H), 1.75 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 132.5, 128.3, 128.3, 125.7, 123.2, 34.4, 25.7, 17.8.



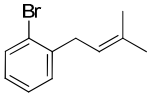
1-Fluoro-2-(3-methylbut-2-en-1-yl)benzene (1b)

Colourless oil, 397 mg, 48% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 1627, 1448, 1226, 1093, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.13 (m, 7.3, 2H), 7.08 – 6.97 (m, 2H), 5.29 (m, 1H), 3.36 (d, *J* = 7.3 Hz, 2H), 1.75 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (d, *J* = 243.0 Hz), 159.7, 133.3, 130.2 (d, *J* = 5.0 Hz), 128.5 (d, *J* = 16.0 Hz), 127.3 (d, *J* = 8.0 Hz), 123.9 (d, *J* = 3.5 Hz), 121.5, 115.1 (d, *J* = 22.0 Hz), 77.3, 77.0, 76.9, 27.3 (d, *J* = 3.0 Hz), 25.7, 17.7. HRMS (EI) calcd for $C_{11}H_{13}F$ *m/z* [M^+]: 164.0996; found: 164.0998.



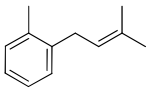
1-Chloro-2-(3-methylbut-2-en-1-yl)benzene (1c)

Colourless oil, 461 mg, 51% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 1625, 1442, 1377, 1041, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.32 (dd, J = 7.8, 1.2 Hz, 1H), 7.24 – 7.10 (m, 3H), 5.29 (m, 1H), 3.44 (d, J = 7.3 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 133.9, 133.5, 129.9, 129.3, 127.1, 126.7, 121.2, 32.1, 25.8, 17.9. HRMS (EI) calcd for $C_{11}H_{13}Cl$ *m/z* [M^+]: 180.0700; found: 180.0705.



1-Bromo-2-(3-methylbut-2-en-1-yl)benzene (1d)

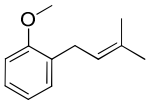
Colourless oil, 554 mg, 49% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.09 – 7.00 (m, 1H), 5.28 (t, *J* = 7.1 Hz, 1H), 3.44 (d, *J* = 7.1 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 133.6, 132.6, 130.0, 127.4, 127.4, 124.5, 121.4, 34.7, 25.8, 18.0.



1-Methyl-2-(3-methylbut-2-en-1-yl)benzene (1e)

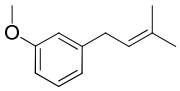
Colourless oil, 417 mg, 52% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.12 (dt, *J* = m, 4H), 5.33 – 5.24 (m, 1H), 3.35 (d, *J* = 7.0 Hz,

2H), 2.34 (s, 3H), 1.79 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 136.1, 132.3, 130.0, 128.6, 125.9, 125.9, 122.5, 32.2, 25.7, 19.4, 17.8.



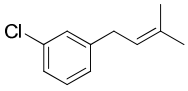
1-Methoxy-2-(3-methylbut-2-en-1-yl)benzene (1f)

Colourless oil, 493 mg, 56% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.11 (m, 2H), 6.89 (td, *J* = 7.4, 0.9 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 5.35 – 5.27 (m, 1H), 3.83 (s, 3H), 3.32 (d, *J* = 7.3 Hz, 2H), 1.74 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 132.4, 130.0, 129.2, 126.8, 122.5, 120.4, 110.1, 55.3, 28.4, 25.8, 17.7.



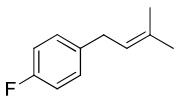
1-Methoxy-3-(3-methylbut-2-en-1-yl)benzene (1g)

Colourless oil, 511 mg, 58% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.1 Hz, 1H), 6.83 – 6.72 (m, 3H), 5.34 (t, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 3.34 (d, *J* = 7.0 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 143.5, 132.6, 129.3, 122.9, 120.7, 114.1, 110.8, 55.1, 34.3, 25.7, 17.8.



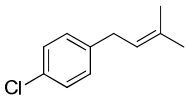
1-Chloro-3-(3-methylbut-2-en-1-yl)benzene (1h)

Colourless oil, 406 mg, 45% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2922, 1630, 1602, 1467, 1371, 775, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.14 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.29 (m, *J* = 1H), 3.32 (d, *J* = 7.3 Hz, 2H), 1.76 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 134.1, 133.4, 129.5, 128.4, 126.5, 125.9, 122.2, 34.0, 25.7, 17.8. HRMS (EI) calcd for $C_{11}H_{13}Cl$ *m/z* [M $^{+}$]: 180.0700; found: 180.0703.



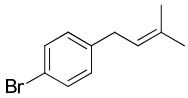
1-Fluoro-4-(3-methylbut-2-en-1-yl)benzene (1i)

Colourless oil, 337 mg, 41% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 1627, 1481, 1371, 1070, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.09 (m, 2H), 7.00 – 6.92 (m, 2H), 5.30 (m, 1H), 3.31 (d, J = 7.3 Hz, 2H), 1.76 (d, J = 0.8 Hz, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, J = 243.1 Hz), 137.3 (d, J = 3.2 Hz), 132.8, 129.6 (d, J = 7.7 Hz), 123.0, 115.0 (d, J = 21.0 Hz), 33.5, 25.7, 17.8. HRMS (EI) calcd for $C_{11}H_{13}F$ *m/z* [M^+]: 164.0996; found: 164.0994.



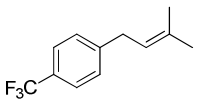
1-Chloro-4-(3-methylbut-2-en-1-yl)benzene (1j)

Colourless oil, 607 mg, 67% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 5.39 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.36 (d, *J* = 7.2 Hz, 2H), 1.82 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 133.1, 131.4, 129.6, 128.4, 122.6, 33.7, 25.7, 17.8.



1-Bromo-4-(3-methylbut-2-en-1-yl)benzene (1k)

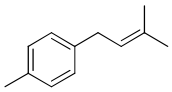
Colourless oil, 599 mg, 53% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 1628, 1483, 1371, 1070, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 5.29 (m, 1H), 3.29 (d, J = 7.3 Hz, 2H), 1.76 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 133.1, 131.3, 130.0, 122.5, 119.4, 33.7, 25.7, 17.8. HRMS (EI) calcd for $C_{11}H_{13}Br$ *m/z* [M^+]: 224.0195; found: 224.0200.



1-(3-Methylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (1l)

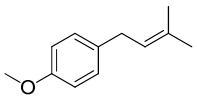
Colourless oil, 225 mg, 21% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.34-5.26 (m, 1H), 3.40 (d, *J* = 7.1 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 133.6, 128.6, 128.1 (q, *J* = 32.6 Hz), 125.2 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.1

Hz), 122.0, 34.2, 25.7, 17.8.



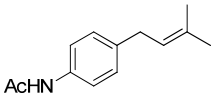
1-Methyl-4-(3-methylbut-2-en-1-yl)benzene (1m)

Colourless oil, 449 mg, 56% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 – 7.06 (m, 4H), 5.33 (t, *J* = 7.3 Hz, 1H), 3.32 (d, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 1.76 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 135.1, 132.3, 129.1, 128.2, 123.5, 33.9, 25.8, 21.0, 17.8.



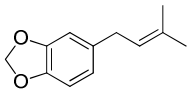
1-Methoxy-4-(3-methylbut-2-en-1-yl)benzene (1n)

Colourless oil, 564 mg, 64% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.32 – 5.25 (m, 1H), 3.31 (d, *J* = 7.3 Hz, 2H), 1.75 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 133.1, 131.4, 129.6, 128.4, 122.6, 33.7, 25.7, 17.8.



N-(4-(3-methylbut-2-en-1-yl)phenyl)acetamide (1o)

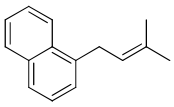
White solid, 347 mg, 34% yield; petroleum ether : EtOAc = 4 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.32 – 5.26 (m, 1H), 3.29 (d, *J* = 7.3 Hz, 2H), 2.15 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 137.9, 135.5, 132.6, 128.7, 123.0, 120.1, 33.7, 25.7, 24.51, 17.8.



5-(3-Methylbut-2-en-1-yl)benzo[d][1,3]dioxole (1p)

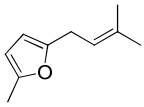
Colourless oil, 580 mg, 61% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 5.28 (t, *J* = 7.3 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 2H), 1.74 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 145.5, 135.7, 132.5, 123.3, 120.8, 108.8, 108.1,

100.7, 34.0, 25.7, 17.8.



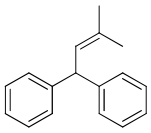
1-(3-Methylbut-2-en-1-yl)naphthalene (1q)

Colourless oil, 658 mg, 67% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 6.9 Hz, 1H), 5.47 – 5.39 (m, 1H), 3.81 (d, *J* = 6.7 Hz, 2H), 1.84 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 133.8, 132.7, 132.0, 128.6, 126.5, 125.7, 125.6, 125.6, 125.4, 124.0, 122.8, 31.8, 25.8, 17.9.



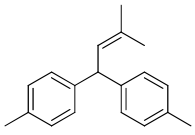
2-Methyl-5-(3-methylbut-2-en-1-yl)furan (1r)

Yellow oil, 320 mg, 67% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 – 5,81 (m, 2H), 5.34 – 5.27 (m, 1H), 3.29 (d, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.74 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 150.4, 133.7, 119.6, 105.8, 105.2, 27.1, 25.7, 17.7, 13.6.



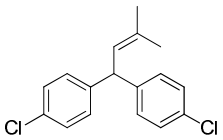
(3-Methylbut-2-ene-1,1-diyl)dibenzene (1u)

Colourless oil, 415 mg, 56% yield; petroleum ether : EtOAc = 20 : 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 4H), 7.24 – 7.18 (m, 6H), 5.69 – 5.63 (m, 1H), 4.92 (d, *J* = 9.5 Hz, 1H), 1.82 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.15, 132.46, 128.33, 128.24, 127.29, 125.97, 77.32, 77.00, 76.68, 49.43, 25.93, 18.06.



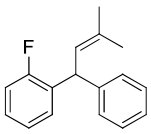
4,4'-(3-Methylbut-2-ene-1,1-diyl)bis(methylbenzene) (1v)

Colourless oil, 488 mg, 39% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2916, 1630, 1506, 1443, 1375, 1024, 802, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 – 7.05 (t, 8H), 5.63 (m, 1H), 4.84 (d, *J* = 9.6 Hz, 1H), 2.33 (s, 6H), 1.80 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 135.4, 132.0, 129.0, 128.1, 127.6, 48.6, 25.9, 21.0, 18.0. HRMS (ESI) calcd for $C_{19}H_{22}Na$ *m/z* $[M + Na]^+$: 273.1614; found: 273.1619.



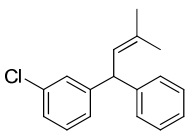
4,4'-(3-Methylbut-2-ene-1,1-diyl)bis(chlorobenzene) (1w)

Colourless oil, 642 mg, 44% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.5 Hz, 4H), 7.08 (d, *J* = 8.5 Hz, 4H), 5.50 (d, *J* = 9.3 Hz, 1H), 4.81 (d, *J* = 9.4 Hz, 1H), 1.79 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 133.6, 132.0, 129.5, 128.6, 126.3, 48.2, 25.9, 18.1.



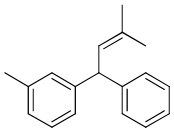
1-Fluoro-2-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1x)

Colourless oil, 505 mg, 42% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2922, 1627, 1483, 1446, 1379, 1028, 744, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 2H), 7.24 – 7.14 (m, 5H), 7.10 – 6.97 (m, 2H), 5.62 (m, 1H), 5.20 (d, *J* = 9.5 Hz, 1H), 1.79 (d, *J* = 1.0 Hz, 3H), 1.71 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, *J* = 245.7 Hz), 133.4, 132.0 (d, *J* = 14.6 Hz), 129.6 (d, *J* = 4.6 Hz), 128.3, 127.8, 127.6 (d, *J* = 8.3 Hz), 126.1, 125.7, 115.4 (d, *J* = 22.4 Hz), 42.4 (d, *J* = 2.5 Hz), 25.9, 18.0. HRMS (ESI) calcd for $C_{17}H_{17}FNa$ *m/z* $[M + Na]^+$: 263.1206; found: 263.1208.



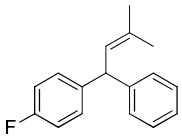
1-Chloro-3-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1y)

Colourless oil, 525 mg, 41% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2918, 1635, 1581, 1375, 1065, 768, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 2H), 7.25 – 7.15 (m, 6H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.60 (m, 1H), 4.87 (d, *J* = 9.5 Hz, 1H), 1.82 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 144.4, 134.2, 133.3, 129.6, 128.5, 128.3, 128.2, 126.6, 126.5, 126.3, 126.2, 49.2, 25.9, 18.1. HRMS (ESI) calcd for $C_{17}H_{17}ClNa$ *m/z* $[M + Na]^+$: 279.0911; found: 279.0919.



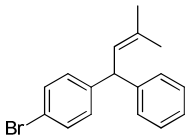
1-Methyl-3-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1z)

Colourless oil, 614 mg, 52% yield; petroleum ether : EtOAc = 20 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 4H), 7.05 – 6.99 (m, 3H), 5.65 (dd, *J* = 9.6, 1.2 Hz, 1H), 4.88 (d, *J* = 9.6 Hz, 1H), 2.33 (s, 3H), 1.82 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.1, 137.9, 132.3, 129.0, 128.3, 128.2, 128.2, 127.3, 126.8, 125.9, 125.3, 49.4, 26.0, 21.5, 18.1.



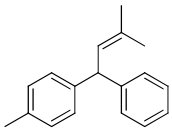
1-Fluoro-4-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1aa)

Colourless oil, 445 mg, 37% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 1633, 1610, 1500, 1377, 1220, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 2H), 7.21 – 7.20 (m, 5H), 6.99 – 6.91 (m, 2H), 5.57 (m, 1H), 4.86 (d, *J* = 9.5 Hz, 1H), 1.79 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (d, *J* = 244.0 Hz), 145.0, 140.8 (d, *J* = 3.1 Hz), 132.8, 129.6 (d, *J* = 7.8 Hz), 128.4, 128.2, 127.1, 126.1, 115.1 (d, *J* = 21.1 Hz), 48.7, 25.9, 18.1. HRMS (ESI) calcd for $C_{17}H_{17}FNa$ *m/z* $[M + Na]^+$: 263.1206; found: 263.1202.



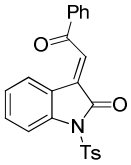
1-Bromo-4-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1ab)

Colourless oil, 528 mg, 35% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2918, 1625, 1483, 1386, 1006, 794, 742, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.56 (m, 1H), 4.83 (d, *J* = 9.4 Hz, 1H), 1.79 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 144.2, 133.1, 131.4, 130.0, 128.5, 128.2, 126.7, 126.2, 119.8, 48.9, 25.9, 18.1. HRMS (EI) calcd for $C_{17}H_{17}Br$ *m/z* [M^+]: 300.0508; found: 300.0512.



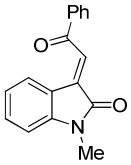
1-Methyl-4-(3-methyl-1-phenylbut-2-en-1-yl)benzene (1ac)

Colourless oil, 613 mg, 52% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2924, 1631, 1500, 1446, 1382, 1028, 734, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (m, 2H), 7.13 – 7.06 (m, 4H), 5.62 (m, 1H), 4.86 (d, *J* = 9.6 Hz, 1H), 2.32 (s, 3H), 1.79 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 142.2, 135.5, 132.2, 129.1, 128.3, 128.2, 128.1, 127.4, 125.9, 49.0, 25.9, 21.0, 18.0. HRMS (ESI) calcd for $C_{18}H_{20}Na$ *m/z* [M + Na]$^+$: 259.1457; found: 259.1464.



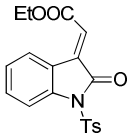
(E)-3-(2-Oxo-2-phenylethylidene)-1-tosylindolin-2-one (2g)

yellow solid; ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.7 Hz, 1H), 8.01 (dd, *J* = 11.9, 5.5 Hz, 5H), 7.77 (s, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.42 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 166.1, 145.9, 141.1, 137.0, 135.2, 134.2, 133.8, 133.2, 129.9, 129.0, 128.8, 128.3, 128.0, 127.4, 124.9, 120.4, 113.6, 21.7.



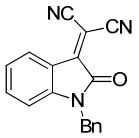
(E)-1-Methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (2h)

red solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.7 Hz, 1H), 8.10 (d, *J* = 7.4 Hz, 2H), 7.88 (s, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 167.9, 146.0, 137.6, 136.5, 133.7, 132.6, 128.9, 128.8, 127.6, 126.2, 122.8, 120.1, 108.2, 26.2.



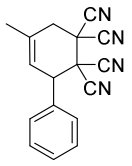
(E)-Ethyl 2-(2-oxo-1-tosylindolin-3-ylidene)acetate (2i)

yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 7.7 Hz, 1H), 8.06 – 7.92 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 164.9, 145.9, 141.1, 135.3, 135.1, 133.1, 129.8, 128.8, 127.9, 125.0, 124.0, 120.3, 113.5, 61.5, 21.7, 14.1.



2-(1-Benzyl-2-oxoindolin-3-ylidene)malononitrile (2j)

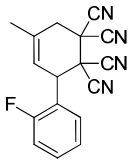
purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 149.2, 146.2, 137.6, 134.1, 129.1, 128.3, 127.5, 126.8, 123.9, 118.3, 112.3, 110.6, 44.2.



5-Methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3a)

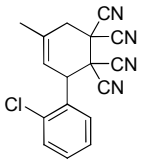
White solid, mp 176-177 °C, 51.2 mg, 94% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2959, 2920, 1626, 1444, 1259, 802, 684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.51 – 7.47 (m, 3H), 7.47 – 7.42 (m, 2H), 5.68 (s, 1H), 4.29 (d, 1H), 3.25 (d, J = 18.2 Hz, 1H), 3.04 (d, J = 18.2 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.1, 130.9, 130.2, 129.4, 129.2, 121.1, 111.0, 110.8, 110.6, 108.9, 47.1, 45.3, 39.2, 36.2, 22.7. HRMS (ESI) calcd for $C_{17}H_{12}N_4Na$ *m/z* $[M + Na]^+$: 295.0954; found: 295.0956.



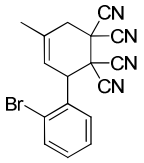
2'-Fluoro-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3b)

Off-white solid, mp 174-175 °C, 50.5 mg, 87% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1628, 1445, 1043, 848, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.45 (m, 1H), 7.44 – 7.38 (m, 1H), 7.31 – 7.20 (m, 2H), 5.57 (s, 1H), 4.81 (s, 1H), 3.26 (d, J = 18.3 Hz, 1H), 3.06 (d, J = 18.3 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (d, J = 250.8 Hz), 132.2 (d, J = 8.6 Hz), 131.1, 130.2 (d, J = 2.2 Hz), 125.2 (d, J = 3.8 Hz), 120.6, 120.5 (d, J = 13.9 Hz), 116.5 (d, J = 21.9 Hz), 110.8, 110.3, 110.2, 109.0, 44.0, 39.6 (d, J = 2.7 Hz), 39.3, 36.2, 22.7. HRMS (ESI) calcd for $C_{17}H_{11}FN_4Na$ *m/z* $[M + Na]^+$: 313.0860; found: 313.0866.



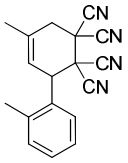
2'-Chloro-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3c)

Off-white solid, mp 165-167 °C, 55.2 mg, 90% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1628, 1445, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 1H), 7.48 – 7.40 (m, 3H), 5.52 (s, 1H), 5.18 (s, 1H), 3.27 (d, J = 18.3 Hz, 1H), 3.07 (d, J = 18.3 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): \δ 135.2, 131.4, 131.1, 130.9, 130.6, 130.3, 127.9, 121.4, 110.8, 110.4, 110.1, 109.2, 43.8, 42.0, 39.6, 36.4, 22.6. HRMS (ESI) calcd for $C_{17}H_{11}ClN_4Na$ *m/z* $[M + Na]^+$: 329.0564; found: 329.0561.



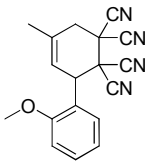
2'-Bromo-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3d)

Off-white solid, mp 176-177 °C, 61.8 mg, 88% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2918, 1628, 1261, 1022, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.39 – 7.32 (m, 1H), 5.52 (s, 1H), 5.21 (s, 1H), 3.27 (d, *J* = 18.4 Hz, 1H), 3.08 (d, *J* = 18.0 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 132.8, 131.6, 130.8, 130.4, 128.5, 125.9, 121.4, 110.9, 110.4, 110.0, 109.2, 44.5, 43.8, 39.6, 36.5, 22.6. HRMS (ESI) calcd for $C_{17}H_{11}BrN_4Na$ *m/z* $[M + Na]^+$: 373.0059; found: 373.0053.



2',5-Dimethyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3e)

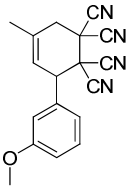
Off-white solid, mp 160-161 °C, 52.7 mg, 92% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2918, 1627, 1373, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 4H), 5.55 (s, 1H), 4.75 (s, 1H), 3.27 (d, *J* = 18.3 Hz, 1H), 3.06 (d, *J* = 18.3 Hz, 1H), 2.56 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 131.6, 131.6, 130.1, 129.9, 128.8, 127.1, 122.5, 111.0, 110.9, 110.7, 109.3, 44.3, 41.8, 39.7, 36.3, 22.6, 19.6. HRMS (ESI) calcd for $C_{18}H_{14}N_4Na$ *m/z* $[M + Na]^+$: 309.1111; found: 309.1117.



2'-Methoxy-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3f)

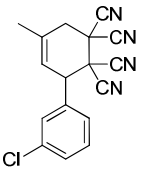
Off-white solid, mp 159-160 °C, 58.7 mg, 97% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1602, 1490, 1375, 1254, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.09 – 6.97 (m, 2H), 5.54 (s, 1H), 5.09 (s, 1H), 3.91 (s, 3H), 3.24 (d, *J* = 17.9 Hz, 1H), 3.02 (d, *J* = 18.2 Hz, 1H), 1.95 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 131.3, 130.0, 129.6, 122.0, 121.6, 121.1, 111.2, 111.1, 110.7, 110.7, 109.5, 55.5, 44.1, 39.5, 38.6, 36.4, 22.7. HRMS (ESI) calcd for $C_{18}H_{14}N_4ONa$ *m/z* $[M + Na]^+$: 325.1060; found: 325.1067.



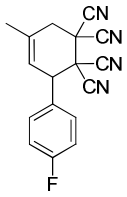
3'-Methoxy-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3g)

Off-white solid, mp 128-130 °C, 56.2 mg, 93% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1630, ,1600, 1440, 1375, 1040, 860, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 8.0 Hz, 1H), 7.05-6.99 (m, 2H), 6.95 (t, *J* = 2.0 Hz, 1H), 5.67 (s, 1H), 4.25 (d, *J* = 1.6 Hz, 1H), 3.85 (s, 3H), 3.24 (d, *J* = 18.2 Hz, 1H), 3.03 (d, *J* = 18.2 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 134.5, 130.8, 130.5, 121.4, 121.1, 115.6, 114.9, 110.9, 110.8, 110.6, 108.9, 55.4, 47.1, 45.1, 39.3, 36.2, 22.8. HRMS (ESI) calcd for $C_{18}H_{14}N_4ONa$ *m/z* $[M + Na]^+$: 325.1060; found: 325.1068.



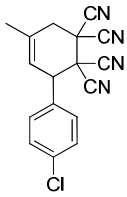
3'-Chloro-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3h)

Off-white solid, mp 132-133 °C, 55.2 mg, 90% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2922, 2361, 1628, 1458, 1373, 860, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.41 (m, 3H), 7.37 – 7.33 (m, 1H), 5.64 (s, 1H), 4.27 (d, *J* = 1.6 Hz, 1H), 3.25 (d, *J* = 18.3 Hz, 1H), 3.05 (d, *J* = 18.3 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 135.0, 131.6, 130.7, 130.6, 129.2, 127.6, 120.3, 110.8, 110.5, 110.4, 108.6, 46.7, 44.9, 39.2, 36.1, 22.8. HRMS (ESI) calcd for $C_{17}H_{11}ClN_4Na$ *m/z* $[M + Na]^+$: 329.0564; found: 329.0571.



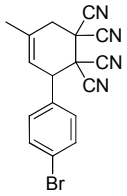
4'-Fluoro-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3i)

Off-white solid, mp 161-162 °C, 51.7 mg, 89% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2916, 1618, 1500, 1226, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.22 – 7.15 (m, 2H), 5.65 (s, 1H), 4.29 (d, *J* = 1.5 Hz, 1H), 3.24 (d, *J* = 17.1 Hz, 1H), 3.04 (d, *J* = 18.3 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7 (d, *J* = 250.8 Hz), 131.3, 131.2 (d, *J* = 8.7 Hz), 128.9 (d, *J* = 3.4 Hz), 120.8, 116.6 (d, *J* = 21.9 Hz), 110.9, 110.7, 110.5, 108.8, 46.5, 45.2, 39.1, 36.2, 22.8. HRMS (ESI) calcd for $C_{17}H_{11}FN_4Na$ *m/z* $[M + Na]^+$: 313.0860; found: 313.0861.



4'-Chloro-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3j)

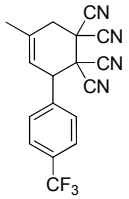
Off-white solid, mp 189-190 °C, 57.7 mg, 94% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1625, 1446, 1259, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 5.63 (s, 1H), 4.28 (d, *J* = 1.6 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.04 (d, *J* = 18.3 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 131.6, 131.5, 130.6, 129.8, 120.6, 110.8, 110.6, 110.4, 108.7, 46.6, 45.1, 39.1, 36.2, 22.8. HRMS (ESI) calcd for $C_{17}H_{11}ClN_4Na$ *m/z* $[M + Na]^+$: 329.0564; found: 329.0565.



4'-Bromo-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3k)

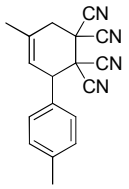
Off-white solid, mp 208-209 °C, 63.9 mg, 91% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1625, 1446, 1259, 802 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 1H), 4.26 (d, *J* = 1.0 Hz, 1H), 3.24

(d, J = 18.4 Hz, 1H), 3.04 (d, J = 18.2 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.7, 132.1, 131.5, 130.8, 124.7, 120.4, 110.8, 110.6, 110.4, 108.7, 46.6, 44.9, 39.1, 36.12, 22.8. HRMS (ESI) calcd for $C_{17}H_{11}BrN_4Na$ *m/z* $[M + Na]^+$: 373.0059; found: 373.0051.



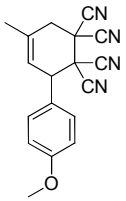
5-Methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3l)

Off-white solid, mp 133-135 °C, 57.2 mg, 84% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1625, 1325, 1126, 846 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 5.65 (s, 1H), 4.36 (d, J = 1.2 Hz, 1H), 3.26 (d, J = 18.3 Hz, 1H), 3.07 (d, J = 18.3 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 132.5 (q, J = 33.0 Hz), 131.9, 129.9, 126.5 (q, J = 3.7 Hz), 123.6 (q, J = 272.5 Hz), 120.1, 110.7, 110.5, 110.4, 108.6, 46.9, 44.9, 39.2, 36.2, 22.9. HRMS (ESI) calcd for $C_{18}H_{11}F_3N_4Na$ *m/z* $[M + Na]^+$: 363.0828; found: 363.0826.



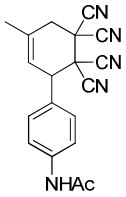
4',5-Dimethyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3m)

Off-white solid, mp 166-167 °C, 54.4 mg, 95% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2956, 2920, 1625, 1431, 1259, 802 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.66 (s, 1H), 4.25 (d, J = 1.6 Hz, 1H), 3.24 (d, J = 19.4 Hz, 1H), 3.02 (d, J = 18.2 Hz, 1H), 2.41 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 130.6, 130.1, 129.1, 121.4, 111.0, 110.9, 110.6, 109.0, 46.8, 45.37, 39.2, 36.2, 22.7, 21.2. HRMS (ESI) calcd for $C_{18}H_{14}N_4Na$ *m/z* $[M + Na]^+$: 309.1111; found: 309.1108.



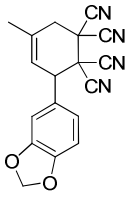
4'-Methoxy-5-methyl-[1,1'-biphenyl]-2,2,3,3(1H,4H)-tetracarbonitrile (3n)

Off-white solid, mp 140-141 °C, 60.7 mg, 96% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2922, 1616, 1512, 1257, 1028, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.65 (s, 1H), 4.25 (d, *J* = 1.6 Hz, 1H), 3.85 (s, 3H), 3.23 (d, *J* = 20.4 Hz, 1H), 3.02 (d, *J* = 18.2 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 130.6, 130.5, 124.8, 121.5, 114.7, 111.0, 110.9, 110.6, 109.0, 55.4, 46.6, 45.5, 39.1, 36.1, 22.7. HRMS (ESI) calcd for $C_{18}H_{14}N_4ONa$ *m/z* $[M + Na]^+$: 325.1060; found: 325.1064.



N-(2',2',3',3'-tetracyano-5'-methyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl)acetamide (3o)

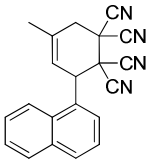
Off-white solid, mp 230-232 °C, 61.9 mg, 94% yield; petroleum ether : EtOAc = 3 : 1. IR (KBr): 2924, 1680, 1604, 1527, 1370, 1317, 837 cm^{-1}; ^1H NMR (400 MHz, Acetone-D_6): δ 9.42 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 5.78 (s, 1H), 4.54 (d, *J* = 1.4 Hz, 1H), 3.63 (d, *J* = 18.6 Hz, 1H), 3.40 (d, *J* = 18.6 Hz, 1H), 2.12 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, Acetone-D_6): δ 169.1, 141.8, 132.6, 130.7, 129.2, 121.1, 120.0, 112.8, 112.6, 111.7, 110.4, 46.8, 46.7, 40.4, 35.6, 24.2, 22.5. HRMS (ESI) calcd for $C_{19}H_{15}N_5ONa$ *m/z* $[M + Na]^+$: 352.1169; found: 352.1175.



3-(Benzo[d][1,3]dioxol-5-yl)-5-methylcyclohex-4-ene-1,1,2,2-tetracarbonitrile

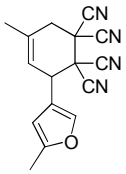
(3p)

Off-white solid, mp 181-182 °C, 61.4 mg, 97% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2918, 1622, 1493, 1445, 1248, 1037, 927, 812, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 – 6.85 (m, 3H), 6.04 (s, 2H), 5.63 (s, 1H), 4.21 (d, *J* = 1.6 Hz, 1H), 3.22 (d, *J* = 18.2 Hz, 1H), 3.01 (d, *J* = 18.2 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.5, 130.8, 126.4, 123.4, 121.3, 110.9, 110.8, 110.5, 109.1, 109.0, 108.9, 101.8, 46.9, 45.3, 39.2, 36.1, 22.7. HRMS (ESI) calcd for $C_{18}H_{12}N_4O_2Na$ *m/z* $[M + Na]^+$: 339.0852; found: 339.0860.



5-Methyl-3-(naphthalen-1-yl)cyclohex-4-ene-1,1,2,2-tetracarbonitrile (3q)

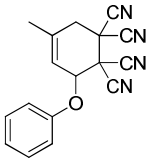
Off-white solid, mp 200-203 °C, 60.0 mg, 93% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1627, 1442, 1257, 856, 785 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.6 Hz, 1H), 7.98 (dd, *J* = 11.1, 8.3 Hz, 2H), 7.71 – 7.55 (m, 4H), 5.66 (s, 1H), 5.42 (s, 1H), 3.34 (d, *J* = 18.3 Hz, 1H), 3.11 (d, *J* = 18.3 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 131.3, 130.9, 130.5, 129.3, 127.9, 127.4, 126.6, 125.3, 122.7, 121.9, 111.0, 110.9, 110.2, 109.2, 44.7, 40.3, 39.9, 36.2, 22.7. HRMS (ESI) calcd for $C_{21}H_{14}N_4Na$ *m/z* $[M + Na]^+$: 345.1111; found: 345.1120.



5-Methyl-3-(5-methylfuran-3-yl)cyclohex-4-ene-1,1,2,2-tetracarbonitrile (3r)

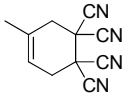
Off-white gum, 40.3 mg, 73% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2922, 2361, 1632, 1448, 1389, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.43 (d, *J* = 3.2 Hz, 1H), 6.04 (dd, *J* = 3.1, 0.9 Hz, 1H), 5.66 (s, 1H), 4.42 (s, 1H), 3.18 (d, *J* = 18.2 Hz, 1H), 3.00 (d, *J* = 18.2 Hz, 1H), 2.33 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 144.2, 130.9, 118.5, 112.2, 110.8, 110.7, 110.4, 108.7, 107.2, 43.4, 41.9, 38.7, 36.1, 22.8, 13.6. HRMS (ESI) calcd for $C_{16}H_{12}N_4ONa$ *m/z* $[M + Na]^+$:

299.0903; found: 299.0897.



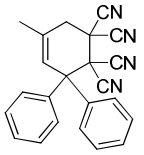
5-Methyl-3-phenoxycyclohex-4-ene-1,1,2,2-tetracarbonitrile (3s)

Off-white gum, 60.7 mg, 75% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 2925, 1619, 1501, 1246, 1044, 843, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 5.80 (s, 1H), 5.35 (s, 1H), 3.20 (d, *J* = 18.4 Hz, 1H), 3.04 (d, *J* = 18.8 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 133.1, 130.2, 124.3, 118.8, 117.1, 110.4, 110.1, 108.2, 74.9, 43.3, 37.9, 36.6, 22.4. HRMS (ESI) calcd for $C_{17}H_{12}N_4ONa$ *m/z* $[M + Na]^+$: 311.0903; found: 311.0905.



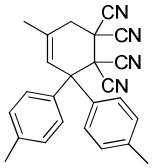
4-Methylcyclohex-4-ene-1,1,2,2-tetracarbonitrile (3t)[8]

Off-white solid, 20.0 mg, 51% yield; petroleum ether : EtOAc = 8 : 1. ^1H NMR (400 MHz, $CDCl_3$): δ 5.62 – 5.56 (m, 1H), 3.12 – 3.08 (m, 2H), 3.01 (d, *J* = 0.8 Hz, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.8, 115.2, 110.7, 110.6, 97.1, 37.8, 37.2, 36.2, 32.4, 22.5.



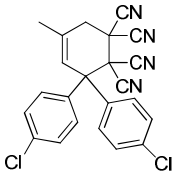
5'-Methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3u)

Off-white solid, mp 198-201 °C, 59.9 mg, 86% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3063, 2922, 1628, 1442, 1263, 1088, 802, 752, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 4H), 7.42 – 7.35 (m, 6H), 6.28 (d, *J* = 1.4 Hz, 1H), 3.23 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 130.2, 129.0, 128.8, 126.8, 111.4, 111.2, 54.9, 46.5, 38.4, 37.2, 23.0. HRMS (ESI) calcd for $C_{23}H_{16}N_4Na$ *m/z* $[M + Na]^+$: 371.1267; found: 371.1266.



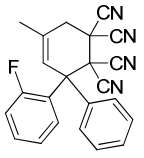
4,4'',5'-Trimethyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3v)

Off-white solid, mp 161-163 °C, 63.9 mg, 85% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3069, 2949, 1648, 1454, 1415, 1115, 1022, 655 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.5 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 4H), 6.24 (d, *J* = 1.5 Hz, 1H), 3.20 (d, *J* = 0.6 Hz, 2H), 2.33 (s, 6H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 136.6, 129.5, 129.4, 128.6, 127.0, 111.5, 111.3, 54.3, 46.7, 38.4, 37.2, 23.0, 20.9. HRMS (ESI) calcd for $C_{25}H_{20}N_4Na$ *m/z* $[M + Na]^+$: 399.1580; found: 399.1576.



4,4''-Dichloro-5'-methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3w)

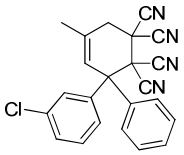
Off-white solid, mp 189-191 °C, 67.6 mg, 81% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3065, 2936, 1668, 1489, 1186, 1097, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.9 Hz, 4H), 7.37 (d, *J* = 8.9 Hz, 4H), 6.18 (d, *J* = 1.5 Hz, 1H), 3.23 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.7, 131.1, 130.1, 129.2, 125.8, 111.0, 111.0, 54.1, 46.3, 38.3, 37.1, 23.2. HRMS (ESI) calcd for $C_{23}H_{14}Cl_2N_4Na$ *m/z* $[M + Na]^+$: 439.0488; found: 439.0490.



2-Fluoro-5'-methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3x)

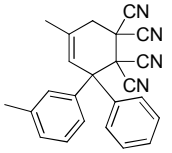
Off-white solid, mp 183-184 °C, 61.6 mg, 84% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3069, 2920, 1628, 1446, 1263, 1082, 802, 750, 698 cm^{-1}; ^{1}H NMR (400

MHz, $CDCl_3$): δ 8.01 (td, *J* = 8.1, 1.5 Hz, 1H), 7.49 – 7.29 (m, 8H), 7.04 (ddd, *J* = 12.7, 8.1, 1.3 Hz, 1H), 6.34 (s, 1H), 3.24 (d, *J* = 0.7 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.8 (d, *J* = 251.3 Hz), 136.5, 131.1 (d, *J* = 4.3 Hz), 131.0, 129.9, 129.7, 128.5, 128.3 (d, *J* = 8.6 Hz), 127.3, 124.5 (d, *J* = 8.3 Hz), 124.0 (d, *J* = 3.6 Hz), 118.0 (d, *J* = 23.1 Hz), 112.4, 111.2, 111.1, 110.0, 54.0 (d, *J* = 3.4 Hz), 46.2, 38.4, 37.0, 22.9. HRMS (ESI) calcd for $C_{23}H_{15}FN_4Na$ *m/z* $[M + Na]^+$: 389.1173; found: 389.1176.



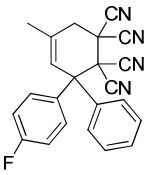
3-Chloro-5'-methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3y)

Off-white solid, mp 175-177 °C, 66.6 mg, 87% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3065, 2920, 1635, 1445, 1263, 1069, 875, 794, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.48 (m, 3H), 7.44 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 6.24 (d, *J* = 1.5 Hz, 1H), 3.23 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.9, 134.9, 130.9, 129.9, 129.4, 129.3, 129.0, 128.5, 126.9, 126.0, 111.2, 111.1, 111.0, 111.0, 54.5, 46.3, 38.4, 37.0, 23.0. HRMS (ESI) calcd for $C_{23}H_{15}ClN_4Na$ *m/z* $[M + Na]^+$: 405.0877; found: 405.0869.



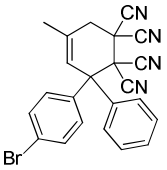
3,5'-Dimethyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3z)

Off-white solid, mp 167-169 °C, 61.6 mg, 85% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3067, 2920, 1626, 1448, 1267, 800, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.41 – 7.33 (m, 4H), 7.27 (dd, *J* = 10.3, 5.1 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 1.4 Hz, 1H), 3.22 (s, 2H), 2.34 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 138.6, 130.0, 129.7, 129.3, 129.0, 128.8, 128.7, 128.6, 126.8, 125.7, 111.4, 111.3, 111.2, 111.1, 54.7, 46.5, 38.4, 37.0, 23.0, 21.7. HRMS (ESI) calcd for $C_{24}H_{18}N_4Na$ *m/z* $[M + Na]^+$: 385.1424; found: 385.1421.



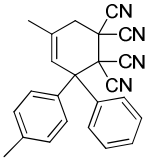
4-Fluoro-5'-methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3aa)

Off-white solid, mp 175-176 °C, 59.7 mg, 85% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 2920, 1632, 1506, 1261, 1059, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ7.56 – 7.48 (m, 4H), 7.44 – 7.36 (m, 3H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.25 (d, *J* = 1.2 Hz, 1H), 3.23 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 251.4 Hz), 139.6, 134.8 (d, *J* = 1.6 Hz), 131.3 (d, *J* = 8.5 Hz), 130.4, 129.0, 128.9, 128.2, 126.5, 115.8 (d, *J* = 21.8 Hz), 111.3, 111.3, 111.2, 110.9, 54.4, 46.5, 38.6, 37.0, 23.0. HRMS (ESI) calcd for $C_{23}H_{15}FN_4Na$ *m/z* $[M + Na]^+$: 389.1173; found: 389.1164.



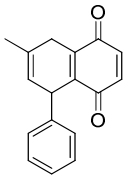
4-Bromo-5'-methyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3ab)

Off-white solid, mp 183-184 °C, 71.8 mg, 84% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3067, 2922, 1636, 1446, 1263, 1014, 804, 754, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 4H), 7.43 – 7.37 (m, 5H), 6.23 (d, *J* = 1.5 Hz, 1H), 3.22 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.4, 131.9, 130.6, 130.5, 129.2, 128.9, 128.5, 126.1, 123.6, 111.2, 111.1, 111.1, 54.5, 46.3, 38.3, 37.1, 23.0. HRMS (ESI) calcd for $C_{23}H_{15}BrN_4Na$ *m/z* $[M + Na]^+$: 449.0372; found: 449.0368.



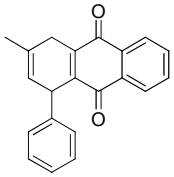
4,5'-Dimethyl-2'H-[1,1':1',1''-terphenyl]-2',2',3',3'(4'H)-tetracarbonitrile (3ac)

Off-white solid, mp 144-146 °C, 62.3 mg, 86% yield; petroleum ether : EtOAc = 7 : 1. IR (KBr): 3064, 2920, 1625, 1442, 1041, 856, 748, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.43 – 7.34 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 1.5 Hz, 1H), 3.22 (d, *J* = 0.7 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 139.2, 136.4, 129.8, 129.4, 128.9, 128.7, 128.7, 126.8, 111.4, 111.2, 111.2, 54.5, 46.5, 38.4, 37.1, 23.0, 21.0. HRMS (ESI) calcd for $C_{24}H_{18}N_4Na$ *m/z* $[M + Na]^+$: 385.1424; found: 385.1421.



7-Methyl-5-phenylnaphthalene-1,4(5H,8H)-dione (5ab)

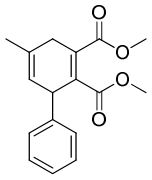
Yellow gum, 25.5 mg, 51% yield; petroleum ether : EtOAc = 15 : 1. IR (KBr): 3010, 2920, 2856, 1647, 1448, 1294, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 3H), 7.23 – 7.16 (m, 3H), 6.72 (d, *J* = 10.1 Hz, 1H), 6.62 (d, *J* = 10.1 Hz, 1H), 5.61 – 5.57 (m, 1H), 4.63 – 4.56 (m, 1H), 3.13 (t, *J* = 4.8 Hz, 2H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 186.1, 142.9, 141.8, 139.2, 136.6, 135.9, 128.9, 128.6, 128.3, 126.8, 122.9, 41.5, 28.9, 22.7. HRMS (ESI) calcd for $C_{17}H_{14}O_2Na$ *m/z* $[M + Na]^+$: 273.0886; found: 273.0882.



3-Methyl-1-phenylanthracene-9,10(1H,4H)-dione (5ac)

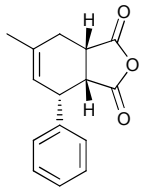
Yellow solid, mp 118-119 °C, 42.6 mg, 71% yield; petroleum ether : EtOAc = 15 : 1. IR (KBr): 3062, 3020, 2920, 1661, 1591, 1445, 1290, 1165, 1078, 754, 698, 577 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.05 (m, 1H), 8.00 – 7.92 (m, 1H), 7.71 – 7.62 (m, 2H), 7.27 (d, *J* = 4.4 Hz, 4H), 7.18 (dq, *J* = 8.7, 4.2 Hz, 1H), 5.68 – 5.61 (m, 1H), 4.84 – 4.76 (m, 1H), 3.40 – 3.20 (m, 2H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 183.7, 144.1, 143.3, 141.6, 133.6, 133.4, 132.1, 131.9, 128.9, 128.6, 128.3, 126.7, 126.4, 126.1, 123.0, 42.0, 29.6, 22.7. HRMS (ESI) calcd for $C_{21}H_{16}O_2Na$ *m/z*

$[M + Na]^+$: 323.1043; found: 323.1050.



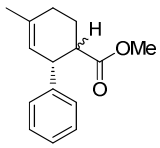
Dimethyl 5-methyl-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (5ad)

Off-white gum, 50.7 mg, 88% yield; petroleum ether : EtAc = 10 : 1. IR (KBr): 3057, 2918, 2852, 1722, 1637, 1431, 1263, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.25 (m, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 5.45 (s, 1H), 4.42 – 4.33 (m, 1H), 3.78 (s, 3H), 3.52 (s, 3H), 3.15 (ddd, *J* = 22.8, 7.6, 0.9 Hz, 1H), 2.88 (dd, *J* = 22.8, 7.3 Hz, 1H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 168.0, 141.7, 137.0, 130.9, 128.7, 128.6, 128.3, 127.0, 122.0, 52.3, 51.9, 45.3, 31.9, 22.5. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ *m/z* $[M + Na]^+$: 309.1097; found: 309.1101.



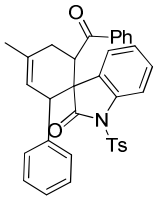
(±)-(3aR,4R,7aS)-6-Methyl-4-phenyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dion e (5ae)

Off-white gum, 29.6 mg, 61% yield; petroleum ether : EtAc = 7 : 1. IR (KBr): 3055, 2920, 2854, 1844, 1774, 1628, 1449, 1263, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 3H), 7.22 – 7.15 (m, 2H), 5.91 – 5.85 (m, 1H), 3.76 (s, 1H), 3.54 – 3.44 (m, 2H), 2.78 (d, *J* = 16.1 Hz, 1H), 2.40 (dd, *J* = 16.3, 5.8 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 170.7, 138.0, 136.7, 128.7, 128.6, 127.8, 123.2, 45.9, 41.0, 40.0, 27.6, 23.5. HRMS (ESI) calcd for $C_{15}H_{14}O_3Na$ *m/z* $[M + Na]^+$: 265.0835; found: 265.0840.



Methyl 5-methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-carboxylate (5af)[9,10]

Off-white gum, 24.9 mg, 54% yield (endo:exo = 1.4:1); petroleum ether : EtAc = 15 : 1. IR (KBr): 3060, 3033, 2954, 1735, 1264, 1167, 765, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.21 (m, 2H, major), 7.28 – 7.21 (m, 2H, minor), 7.20 – 7.10 (m, 3H, major), 7.20 – 7.10 (m, 3H, minor), 5.47 – 5.43 (m, 1H, major), 5.34 (s, 1H, minor), 3.82 (s, 1H, major), 3.73 – 3.67 (m, 1H, minor), 3.53 (s, 3H, minor), 3.46 (s, 3H, major), 2.89 – 2.83 (m, 1H, major), 2.55 – 2.47 (m, 1H, minor), 2.19 – 2.02 (m, 2H, major), 2.19 – 2.02 (m, 2H, minor), 2.01 – 1.94 (m, 1H, minor), 1.92 – 1.81 (m, 1H, major), 1.92 – 1.81 (m, 1H, minor), 1.80 – 1.75 (m, 1H, major), 1.78 (s, 3H, major), 1.73 (s, 3H, minor). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8 (minor), 174.3 (major), 144.6 (minor), 140.8 (major), 135.2 (major), 134.1 (minor), 129.3 (major), 128.3 (minor), 128.0 (major), 127.8 (minor), 126.8 (major), 126.5 (minor), 123.8 (minor), 122.4 (major), 51.4 (minor), 51.0 (major), 48.3 (minor), 44.9 (major), 44.5 (minor), 42.9 (major), 29.4 (major), 29.1 (minor), 25.8 (minor), 23.5 (major), 23.5 (minor), 19.3 (major), 17.2 (major). HRMS (ESI) calcd for $C_{15}H_{19}O_2$ *m/z* $[M + H]^+$: 231.1380; found: 231.1382.

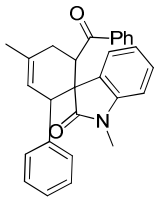


3-Benzoyl-5-methyl-1-phenyl-1'-tosylspiro[cyclohex[5]ene-2,3'-indolin]-2'-one (5ag)

Off-white solid, mp 176-178 °C, 56 mg, 77% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 3058, 2922, 2852, 1755, 1460, 1375, 1176, 1085, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.49 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.20 – 7.07 (m, 7H), 7.04 – 6.97 (m, 2H), 5.64 – 5.57 (m, 1H), 4.17 (dd, *J* = 9.5, 6.7 Hz, 1H), 3.78 (d, *J* = 2.9 Hz, 1H), 2.81 (dd, *J* = 18.4, 6.6 Hz, 1H), 2.35 (s, 3H), 2.27 (dd, *J* = 18.4, 9.6 Hz, 1H), 1.92 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 175.4, 144.8, 138.7, 138.3, 136.0, 134.8, 133.5, 133.0, 132.5, 129.9, 129.3, 128.4, 128.3, 128.3, 128.0, 127.9,

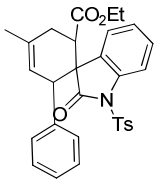
127.3, 124.5, 124.3, 122.3, 113.3, 52.3, 50.1, 44.3, 31.4, 23.1, 21.6. HRMS (ESI) calcd for $C_{33}H_{27}NO_4SNa$ *m/z* $[M + Na]^+$: 556.6260; found: 556.6258.

Off-white solid, mp 172-174 ℃, 15 mg, 20% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 2920, 2850, 1744, 1460, 1377, 1176, 1089, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.14 – 6.99 (m, 5H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.2 Hz, 2H), 5.62 (s, 1H), 4.43 (dd, *J* = 12.4, 6.1 Hz, 1H), 4.19 (s, 1H), 2.61 (dd, *J* = 18.3, 6.0 Hz, 1H), 2.49 (dd, *J* = 21.2, 9.4 Hz, 1H), 2.32 (s, 3H), 1.90 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 178.2, 144.7, 139.7, 137.4, 135.9, 135.1, 134.6, 133.0, 129.2, 128.7, 128.4, 128.4, 128.3, 128.1, 127.9, 127.5, 127.0, 125.0, 124.7, 123.8, 112.9, 53.7, 51.1, 50.1, 32.2, 23.0, 21.6. HRMS (ESI) calcd for $C_{33}H_{27}NO_4SNa$ *m/z* $[M + Na]^+$: 556.6260; found: 556.6263.



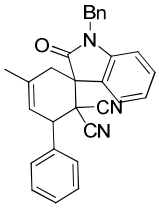
3-Benzoyl-1',5-dimethyl-1-phenylspiro[cyclohex[5]ene-2,3'-indolin]-2'-one (5ah)

Off-white solid, mp 156-159 ℃, 78 mg, 96% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 2922, 2852, 1708, 1612, 1492, 1469, 1377, 1348, 1263, 1026, 752, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.74 (m, 2H), 7.56 – 7.35 (m, 3H), 7.30 – 7.24 (m, 2H), 7.24 – 7.10 (m, 3H), 7.06 – 6.77 (m, 4H), 6.59 (dd, *J* = 103.3, 7.7 Hz, 1H), 5.71 – 5.65 (m, 1H), 4.64 – 3.93 (m, 2H), 3.05 – 2.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 200.0,* 178.4,* 176.7, 143.9,* 143.6, 139.4, 138.5,* 136.8, 136.5,* 134.5,* 133.0, 132.9,* 132.8, 132.7, 129.7, 128.9,* 128.8,* 128.5, 128.5,* 128.4, 127.8,* 127.5, 126.9, 126.9,* 126.5,* 124.9,* 124.7,* 124.4, 122.8, 122.0, 121.6,* 107.6, 107.4,* 53.8,* 52.1, 50.3,* 49.2, 48.6,* 43.7, 32.2,* 31.2, 25.9, 25.7,* 23.3, 23.0.* HRMS (ESI) calcd for $C_{28}H_{25}NO_2Na$ *m/z* $[M + Na]^+$: 430.1778; found: 430.1782.



Ethyl 5-methyl-2'-oxo-1-phenyl-1'-tosylspiro[cyclohex[5]ene-2,3'-indoline]-3-carboxylate (5ai)

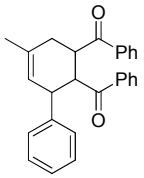
Off-white solid, mp 165-168 ℃, 94 mg, 91% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 2979, 2920, 2854, 1759, 1730, 1458, 1375, 1178, 1087, 750,694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.56 (m, 3H), 7.37 – 7.21 (m, 3H), 7.21 – 7.03 (m, 4H), 6.96 – 6.53 (m, 3H), 5.57 – 5.46 (m, 1H), 4.07 – 3.26 (m, 4H), 2.86 – 2.37 (m, 5H), 2.00 – 1.88 (m, 3H), 0.90 (dt, *J* = 17.2, 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 175.0, 171.8, 171.0, 144.9, 139.7, 138.8, 138.1, 137.7, 135.5, 135.2, 134.0, 133.7, 131.9, 129.8, 129.4, 129.3, 128.7, 128.4, 128.3, 128.2, 127.8, 127.4, 127.3, 127.2, 126.6, 125.2, 124.3, 123.9, 123.9, 123.8, 121.5, 113.1, 112.7, 60.91, 60.53, 53.2, 51.7, 50.6, 50.4, 46.1, 41.4, 30.2, 30.1, 23.0, 22.9, 21.6, 21.6, 13.7, 13.7. HRMS (ESI) calcd for $C_{30}H_{29}NO_5SK$ *m/z* $[M + K]^+$: 554.1398; found: 554.1393.



1'-Benzyl-4-methyl-2'-oxo-6-phenylspiro[cyclohex[4]ene-2,3'-indoline]-1,1-dicarbonitrile (5aj)

Off-white solid, mp 148-151 ℃, 61 mg, 71% yield; petroleum ether : EtOAc = 8 : 1. IR (KBr): 2923, 2853, 1713, 1489, 1468, 1366, 1175, 832, 783, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 6.7 Hz, 2H), 7.34 (m, 10H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.73 (s, 1H), 5.09 (d, *J* = 15.7 Hz, 1H), 4.99 (s, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 2.96 (d, *J* = 18.9 Hz, 1H), 2.37 (d, *J* = 18.8 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 142.5, 136.5, 134.8, 132.7, 130.5, 130.0, 128.9, 128.7, 127.9, 127.3, 127.2, 124.3, 123.8, 121.3,

113.1, 112.8, 110.0, 50.4, 45.3, 45.3, 44.3, 35.5, 23.2. HRMS (ESI) calcd for $C_{29}H_{23}N_3ONa$ *m/z* $[M + Na]^+$: 452.1733; found: 452.1725.

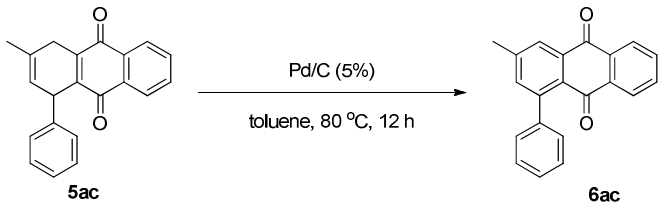


(5-Methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2,3-diyl)bis(phenylmethanone) (5ak)

Off-white solid, mp 135-138 ℃, 47 mg, 62% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2924, 2850, 1666, 1631, 1448, 1380,1259, 1209, 756, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.46 (dd, *J* = 18.1, 7.8 Hz, 4H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.09 – 6.95 (m, 5H), 5.53 (s, 1H), 4.42 (td, *J* = 11.3, 5.3 Hz, 1H), 4.03 (t, *J* = 10.6 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 2.44 (dd, *J* = 17.3, 4.0 Hz, 1H), 2.29 (t, *J* = 14.6 Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 202.8, 143.1, 138.2, 136.1, 133.2, 132.9, 132.2, 128.6, 128.6, 128.3, 128.1, 127.7, 126.7, 125.4, 50.9, 47.9, 46.8, 34.5, 23.1. HRMS (ESI) calcd for $C_{27}H_{24}O_2Na$ *m/z* $[M + Na]^+$: 403.1669; found: 403.1667.

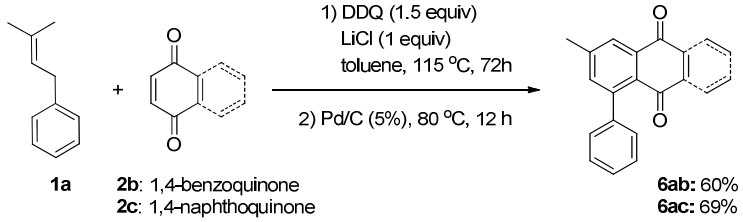
Off-white solid, mp 141-143 ℃, 25 mg, 33% yield; petroleum ether : EtOAc = 20 : 1. IR (KBr): 2920, 2854, 1676, 1632, 1446, 1382,1274, 750, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.42 (m, 6H), 7.21 – 7.14 (m, 3H), 6.90 – 6.78 (m, 2H), 5.58 (s, 1H), 4.48 (dd, *J* = 11.0, 5.8 Hz, 1H), 4.28 (td, *J* = 11.4, 5.8 Hz, 1H), 4.09 (s, 1H), 2.52 (dd, *J* = 17.6, 5.6 Hz, 1H), 2.29 – 2.13 (m, 1H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 200.9, 139.8, 137.4, 136.7, 133.6, 132.9, 129.2, 128.7, 128.6, 128.5, 128.4, 127.9, 127.1, 123.0, 49.2, 44.1, 38.8, 34.5, 23.1. HRMS (ESI) calcd for $C_{27}H_{24}O_2Na$ *m/z* $[M + Na]^+$: 403.1669; found: 403.1665.

Reaction of 5ac[11,12]

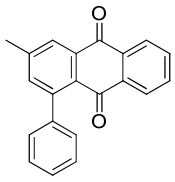


A solution of 1,4-dihydro-9,10-anthraquinone **5ac** (30.2 mg, 0.1 mmol) and 5% Pd/C (10.6 mg, 0.005 mmol, 5 mol%) in dry toluene (5 mL) was stirred at 80 °C for 12 h. After removed the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 15:1) to afford the desired product **6ac** in 87% yield.

One-pot reaction of 1,4-quinones and prenyl benzene.



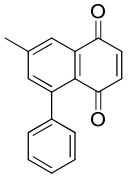
In a sealed tube, a mixture of prenyl benzene **1a** (58.5 mg, 0.4 mmol), 1,4-quinones **2b-2c** (0.2 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL), was stirred at 115 °C for 72 h. Then to the mixture was added 5% Pd/C (21.2 mg, 0.01 mmol, 5 mol%), the reaction was further stirred at 80 °C for 12 h. After removed the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 15:1) to afford the desired product **6ab-6ac**.



3-Methyl-1-phenylanthracene-9,10-dione (6ac)

Yellow solid, mp 179-181 °C, 41.4 mg, 69% yield; petroleum ether : EtOAc = 15 : 1. IR (KBr): 3065, 2922, 1630, 1456, 1330, 1269, 1097, 802, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.25 (m, 1H), 8.21 (d, *J* = 1.2 Hz, 1H), 8.14 – 8.10 (m, 1H), 7.78 – 7.70 (m, 2H), 7.49 – 7.42 (m, 3H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.32 – 7.27 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 183.1, 144.6, 143.9, 142.1,

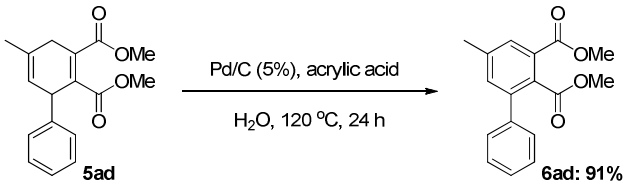
138.5, 134.7, 134.6, 134.2, 133.5, 132.9, 128.5, 128.0, 128.0, 127.6, 127.3, 127.1, 126.7, 21.7. HRMS (ESI) calcd for $C_{21}H_{14}O_2Na$ *m/z* [M + Na]$^+$: 321.0886; found: 321.0887.



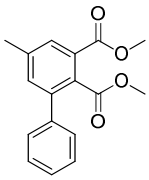
7-Methyl-5-phenylnaphthalene-1,4-dione (6ab)

Yellow solid, mp 113-115 °C, 19.5 mg, 60% yield; petroleum ether : EtOAc = 15 : 1. IR (KBr): 2918, 1651, 1454, 1332, 1269, 1033, 842, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 1.2 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 (d, *J* = 1.1 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.91 (d, *J* = 10.2 Hz, 1H), 6.79 (d, *J* = 10.2 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.5, 185.0, 143.8, 141.0, 140.3, 138.1, 136.9, 133.2 128.1, 128.0, 127.3, 126.9, 126.8, 21.6. HRMS (ESI) calcd for $C_{21}H_{14}O_2Na$ *m/z* [M + Na]$^+$: 271.0730; found: 271.0739.

Reaction of 5ad[13]



To a solution of 1,4-cyclohexadiene derivative **5ad** (28.6 mg, 0.1 mmol) in H_2O (1 mL) were added 5% Pd/C (10.6 mg, 0.005 mmol, 5 mol%) and acrylic acid (34.3 μL, 0.5 mmol) under N_2. The reaction mixture was refluxed at 120 °C. After 24 hours, the reaction mixture was cooled to room temperature and filtered over Celite® to remove Pd/C. The filtrate was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed satd $NaHCO_3$ (3 × 10 mL), dried over $NaSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/EtOAc = 15:1) to afford the desired product **6ad**.



Dimethyl 5-methyl-[1,1'-biphenyl]-2,3-dicarboxylate (6ad)

Off-white gum, 25.8 mg, 91% yield; petroleum ether : EtOAc = 15 : 1. IR (KBr): 3033, 2952, 2850, 1728, 1600, 1487, 1237, 1120, 985, 844, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 0.9 Hz, 1H), 7.42 – 7.32 (m, 6H), 3.90 (s, 3H), 3.65 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 166.4, 140.6, 139.4, 139.3, 134.8, 132.0, 129.4, 128.5, 128.2, 127.8, 52.5, 52.2, 21.1. HRMS (ESI) calcd for $C_{17}H_{16}O_4Na$ *m/z* $[M + Na]^+$: 307.0941; found: 307.0946.

References

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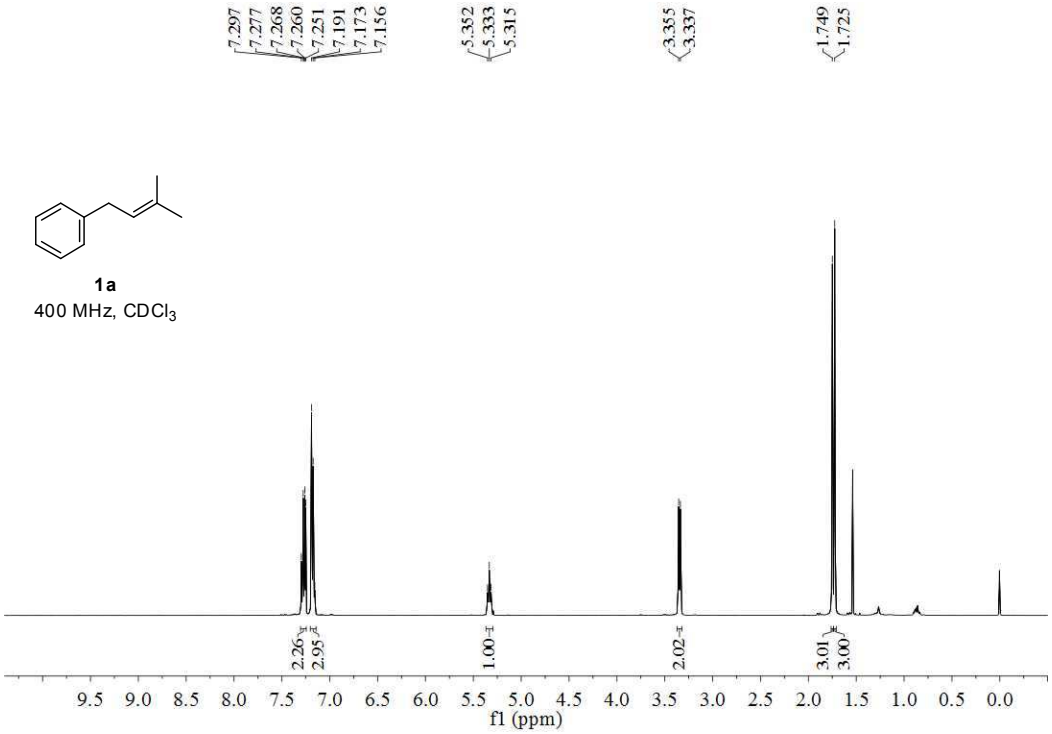
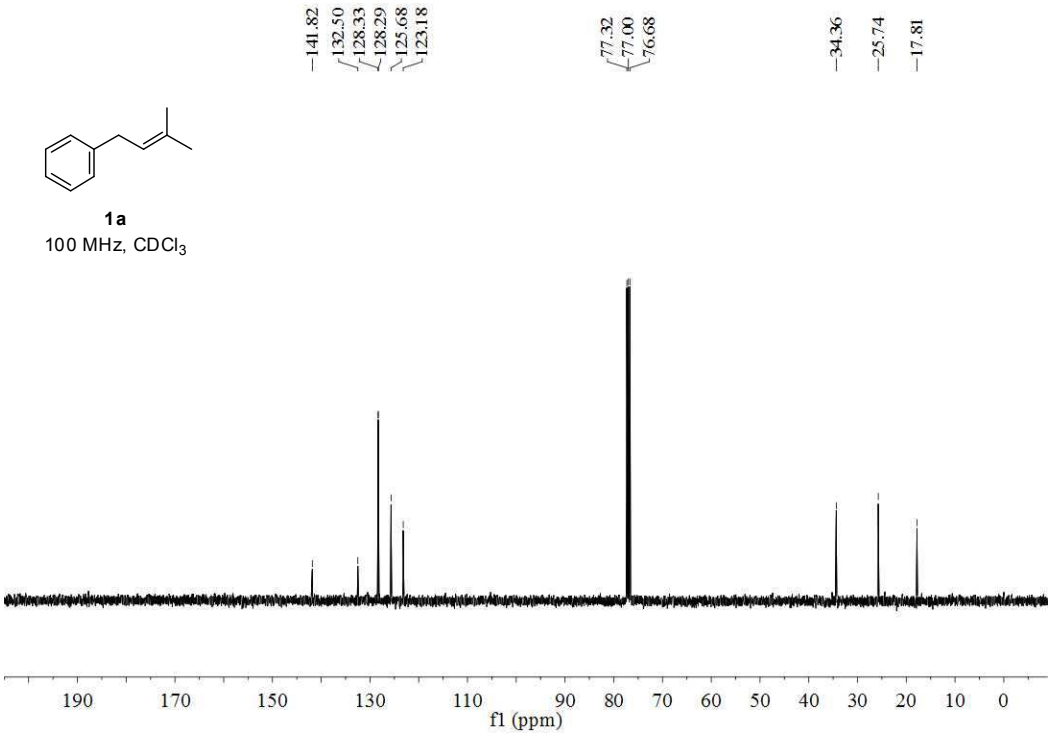
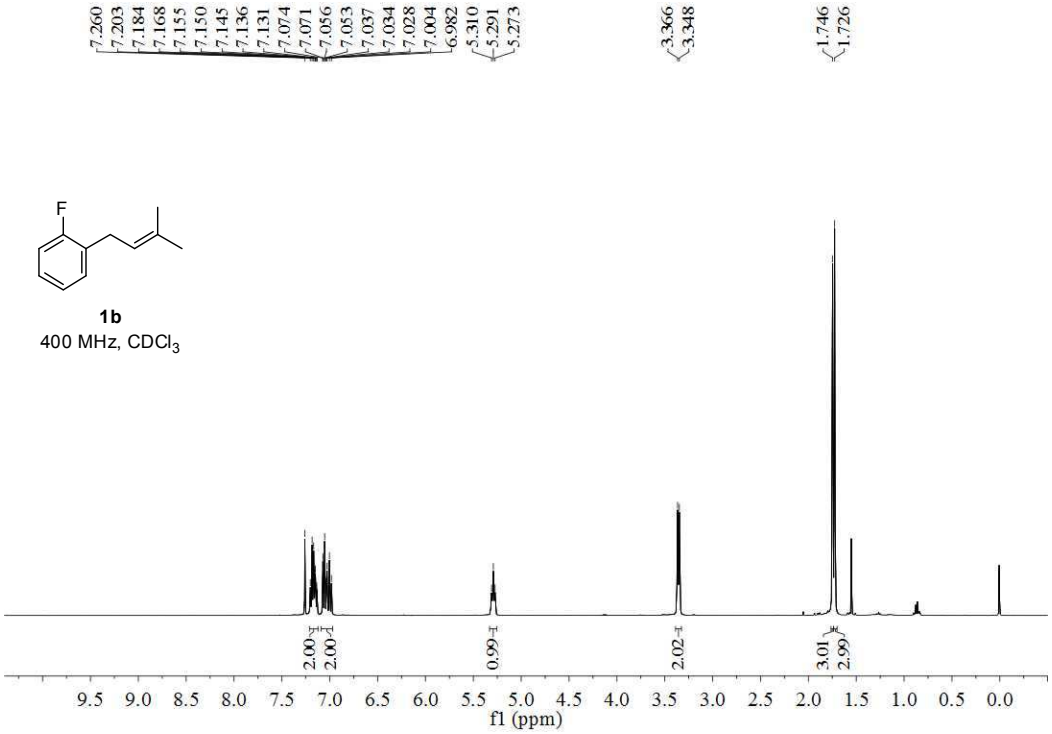
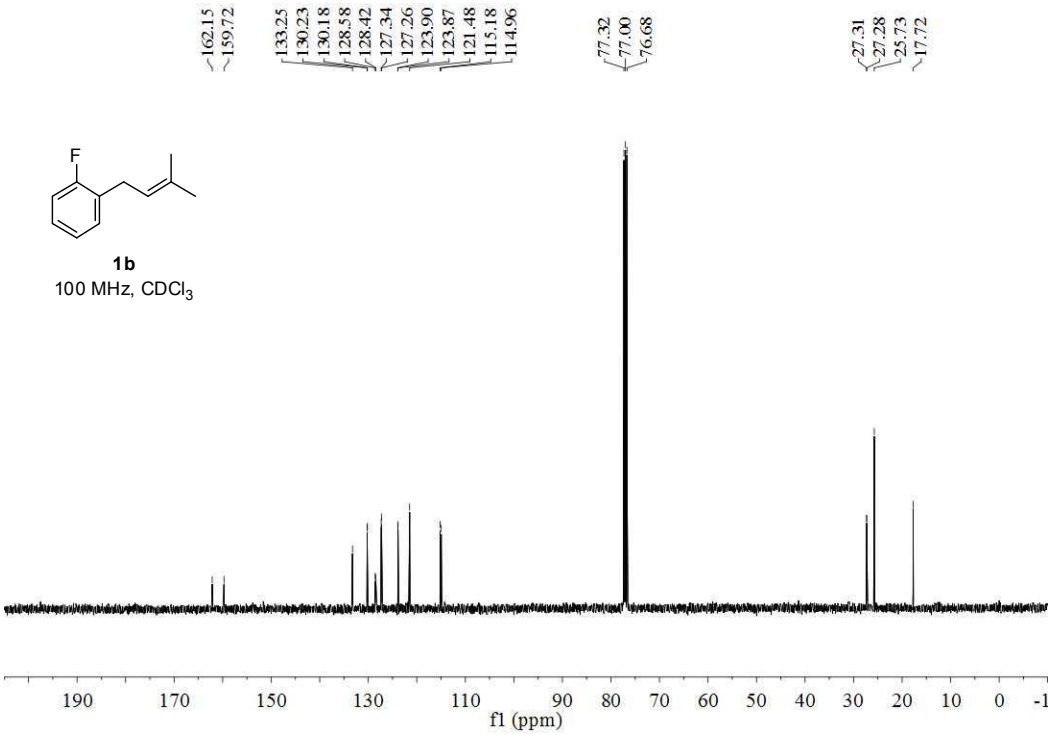


1a
400 MHz, $CDCl_3$



1a
100 MHz, $CDCl_3$


7.260
7.203
7.184
7.168
7.155
7.150
7.145
7.136
7.131
7.074
7.071
7.056
7.053
7.037
7.034
7.028
7.004
6.982
5.310
5.291
5.273
3.366
3.348
1.746
1.726
F
1b
400 MHz, CDCl3
2.00
2.00
0.99
2.02
3.01
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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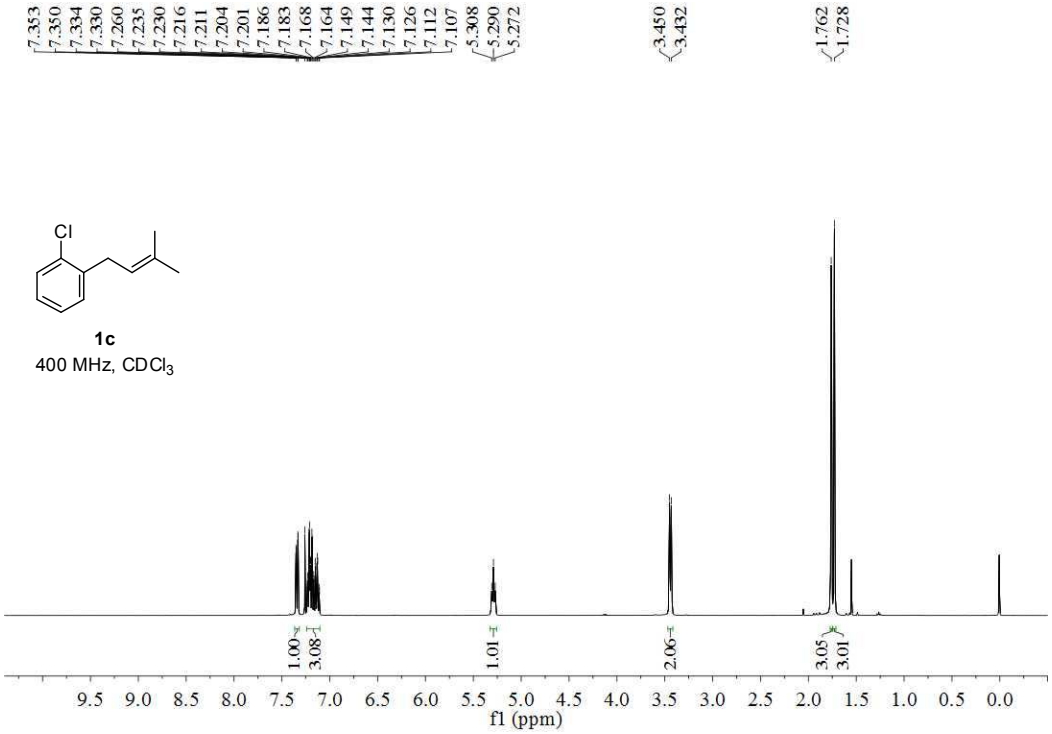
159.72
133.25
130.23
130.18
128.58
128.42
127.34
127.26
123.90
123.87
121.48
115.18
114.96
77.32
77.00
76.68
27.31
27.28
25.73
17.72
F
1b
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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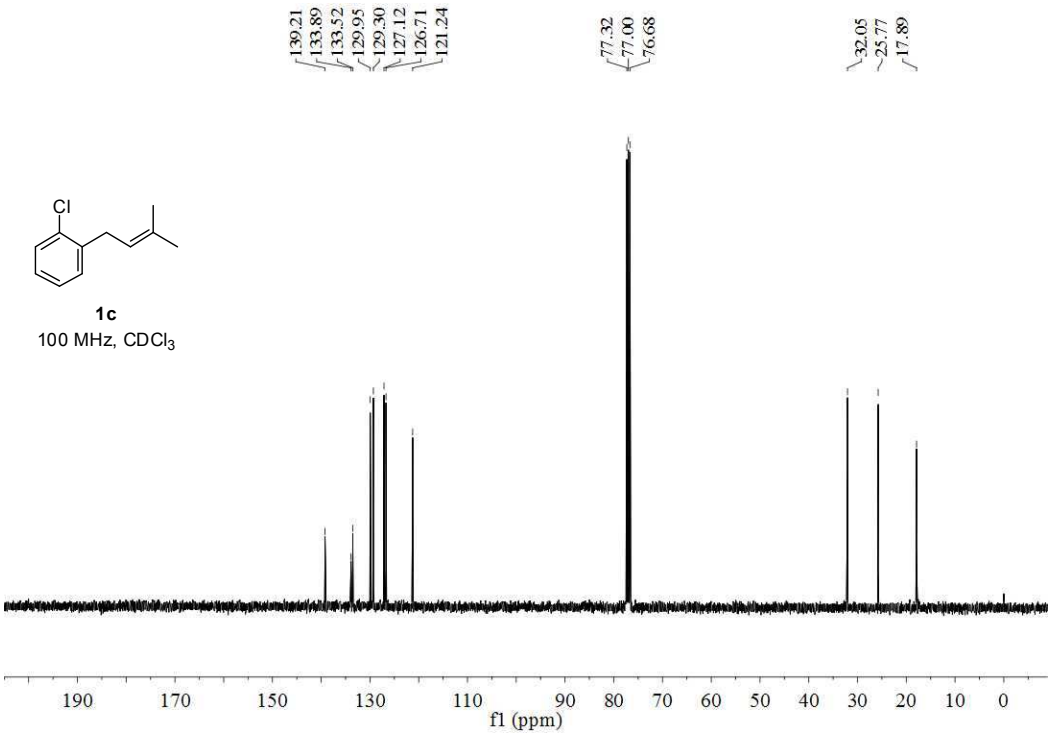
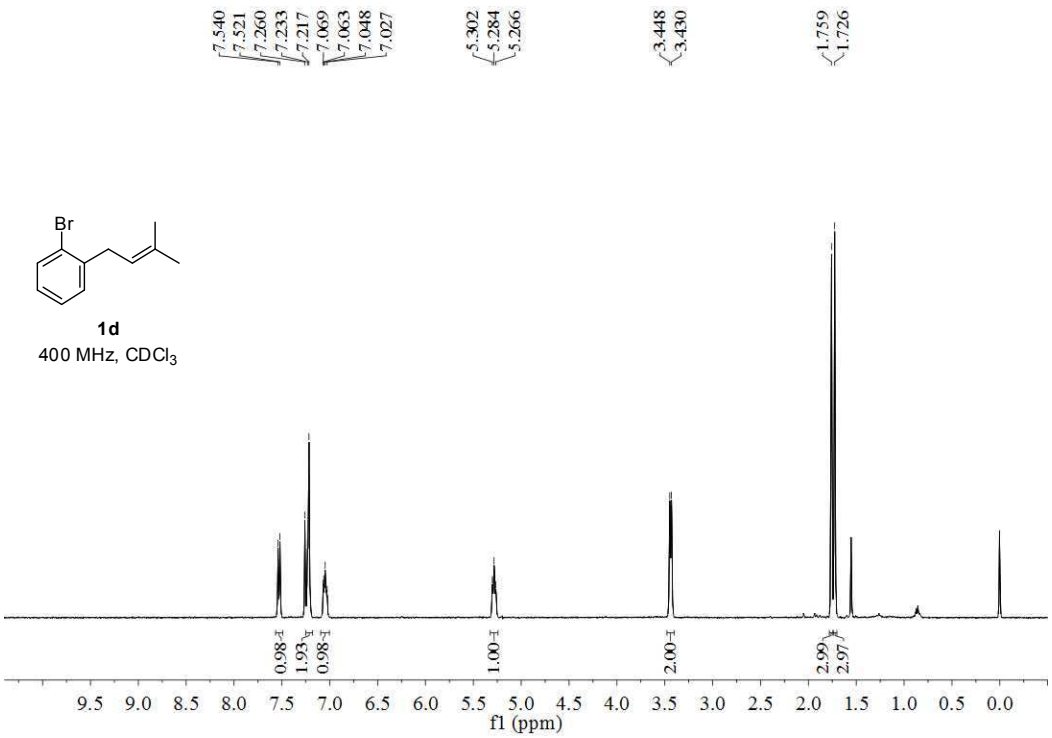
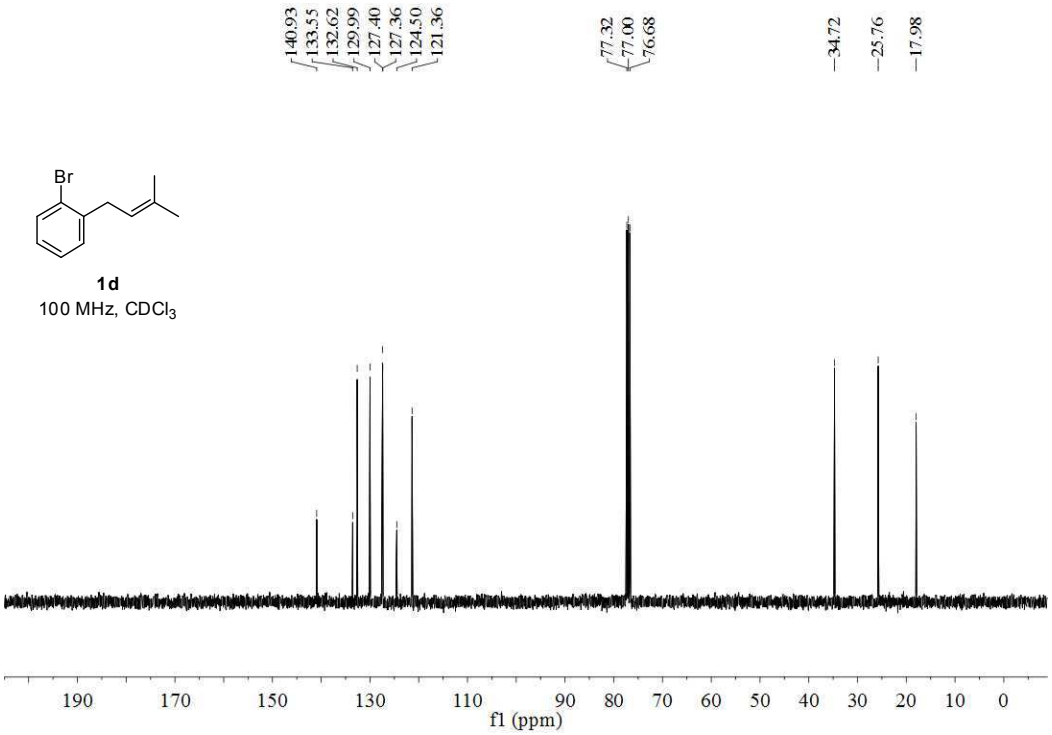
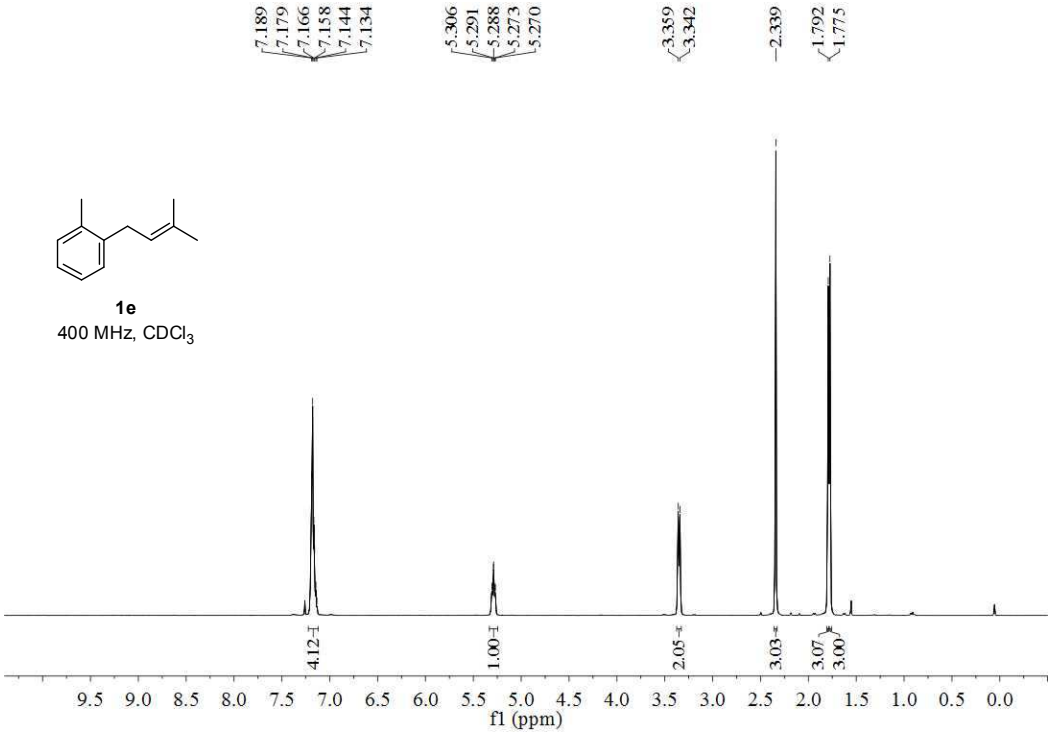
7.350
7.334
7.330
7.260
7.235
7.230
7.216
7.211
7.204
7.201
7.186
7.183
7.168
7.164
7.149
7.144
7.130
7.126
7.112
7.107
5.308
5.290
5.272
3.450
3.432
1.762
1.728
Cl
1c
400 MHz, CDCl3
1.00
3.08
1.01
2.06
3.05
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

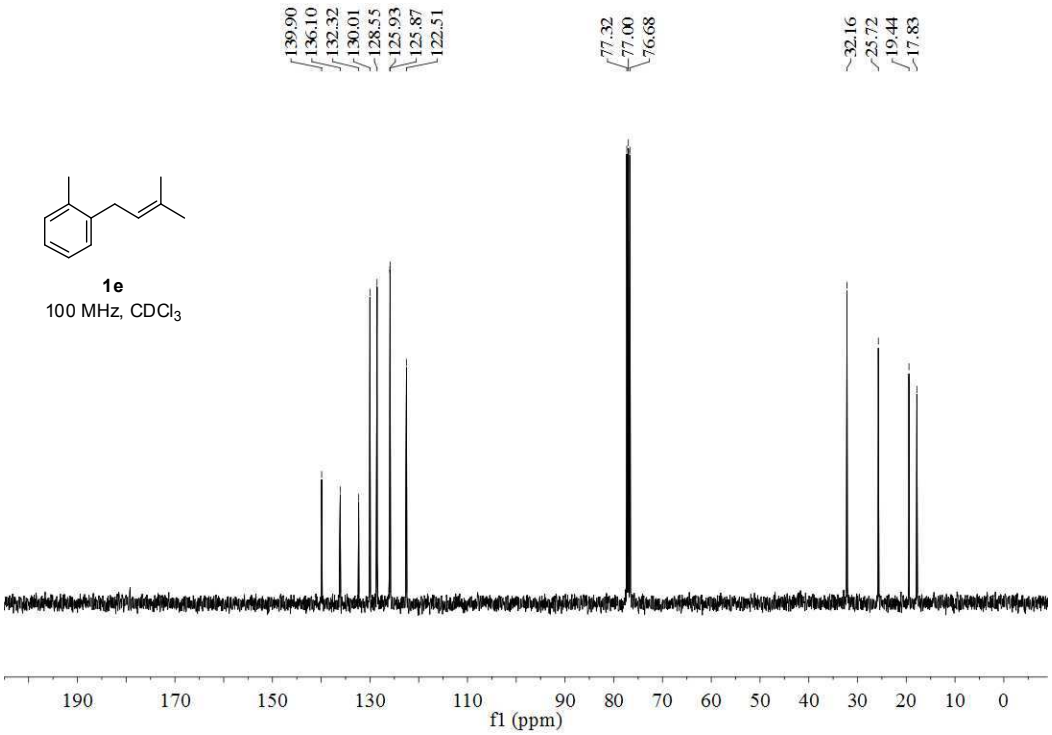

139.21
133.89
133.52
129.95
129.30
127.12
126.71
121.24
77.32
77.00
76.68
32.05
25.77
17.89
Cl
1c
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.540
7.521
7.260
7.233
7.217
7.069
7.063
7.048
7.027
5.302
5.284
5.266
3.448
3.430
1.759
1.726
Br
1d
400 MHz, CDCl3
0.98
1.93
0.98
1.00
2.00
2.99
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

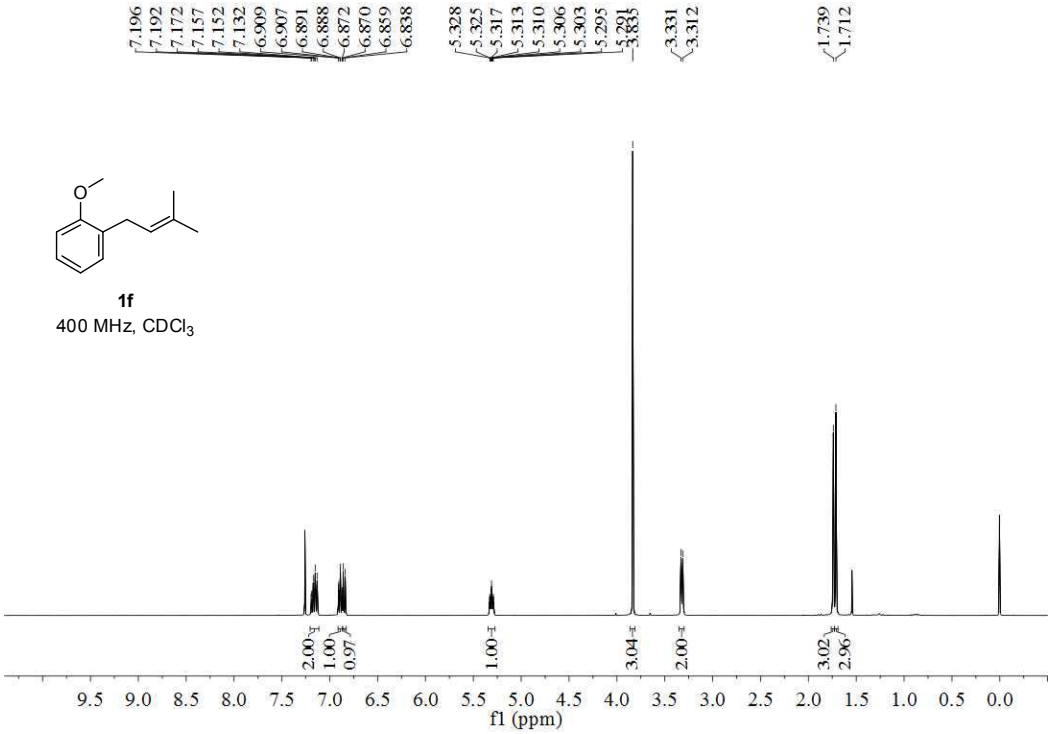

140.93
133.55
132.62
129.99
127.40
127.36
124.50
121.36
77.32
77.00
76.68
34.72
25.76
17.98
Br
1d
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

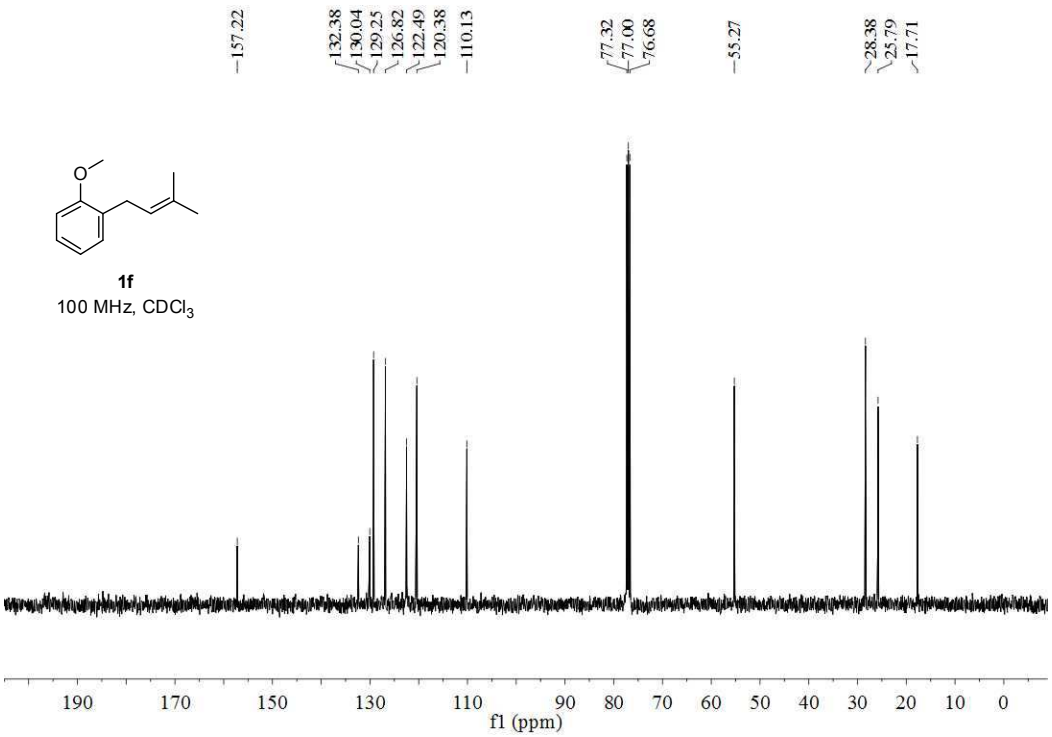


1e
400 MHz, $CDCl_3$



1e
100 MHz, $CDCl_3$


7.196
7.192
7.172
7.157
7.152
7.132
6.909
6.907
6.891
6.888
6.872
6.870
6.859
6.838
5.328
5.325
5.317
5.313
5.310
5.306
5.303
5.295
3.835
3.331
3.312
1.739
1.712
1f
400 MHz, CDCl3
2.00
1.00
0.97
1.00
3.04
2.00
3.02
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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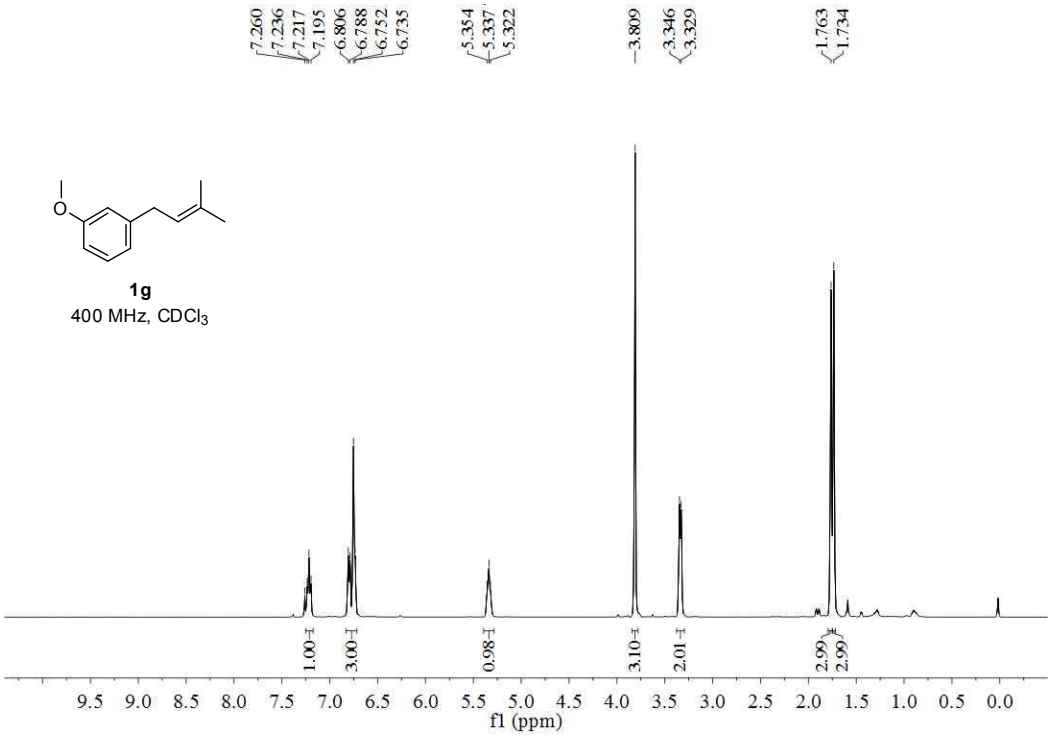
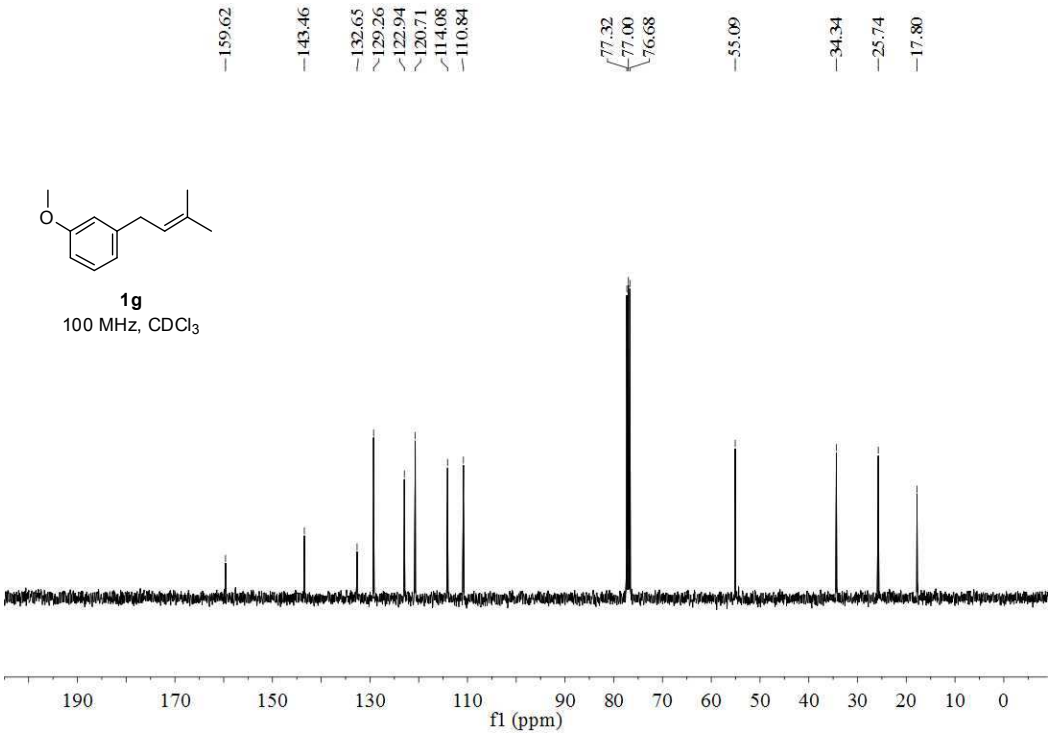
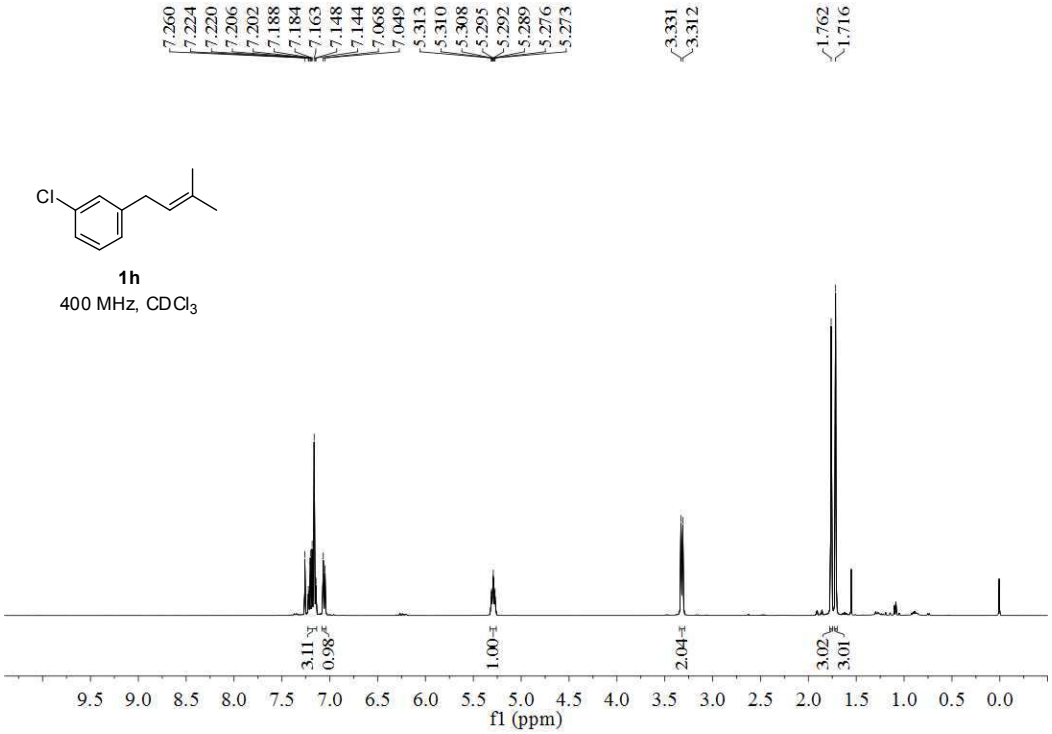
132.38
130.04
129.25
126.82
122.49
120.38
110.13
77.32
77.00
76.68
55.27
28.38
25.79
17.71
1f
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
7.236
7.217
7.195
6.806
6.788
6.752
6.735
5.354
5.337
5.322
3.809
3.346
3.329
1.763
1.734
1g
400 MHz, CDCl3
1.00
3.00
0.98
3.10
2.01
2.99
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.62
143.46
132.65
129.26
122.94
120.71
114.08
110.84
77.32
77.00
76.68
55.09
34.34
25.74
17.80
1g
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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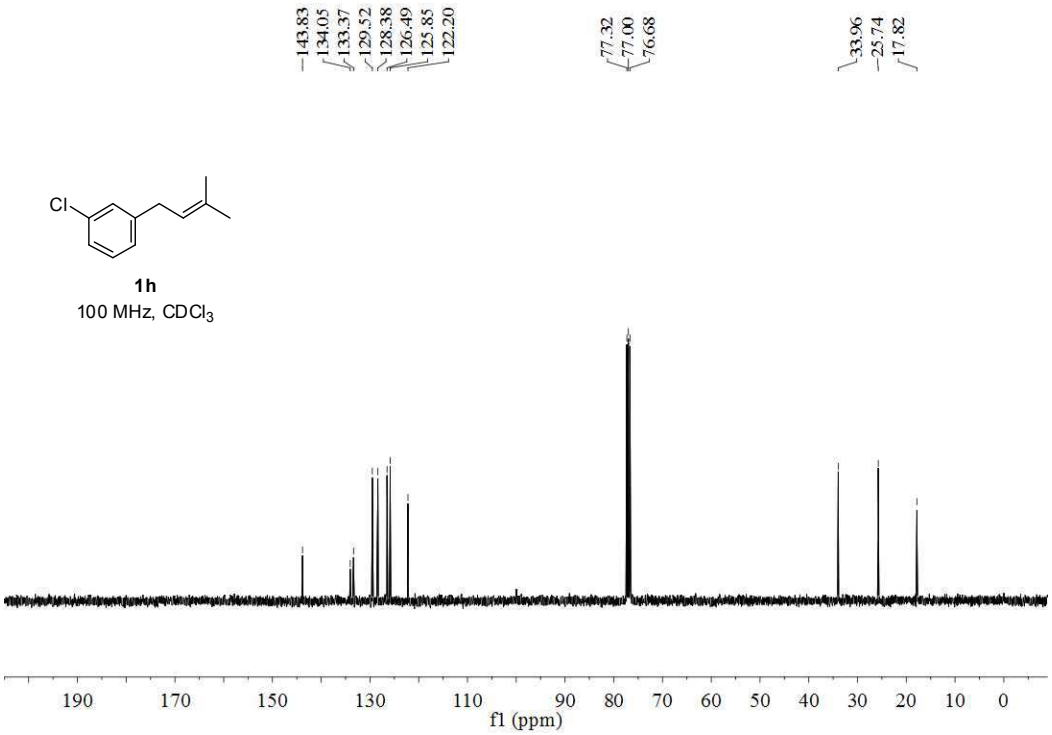
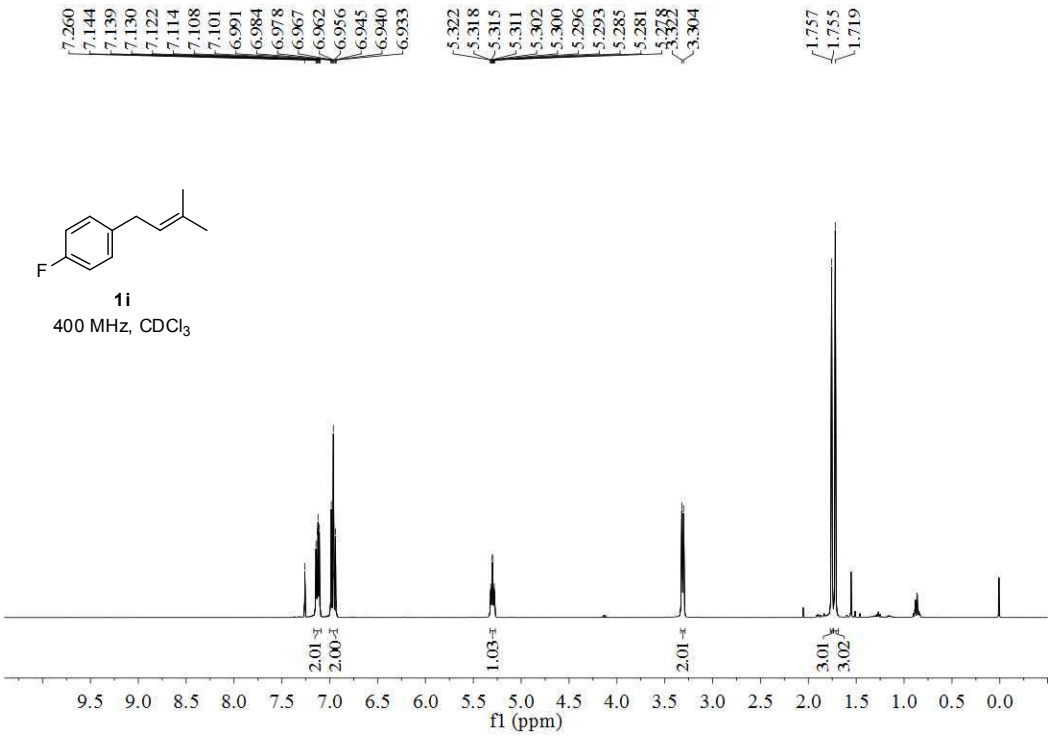
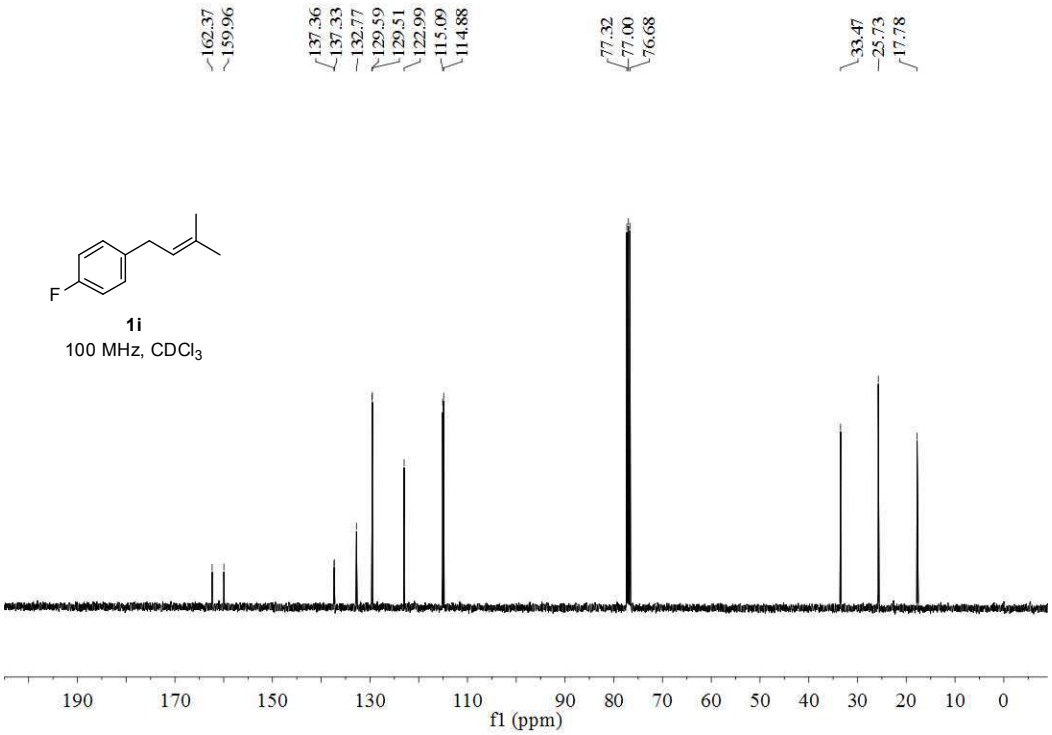
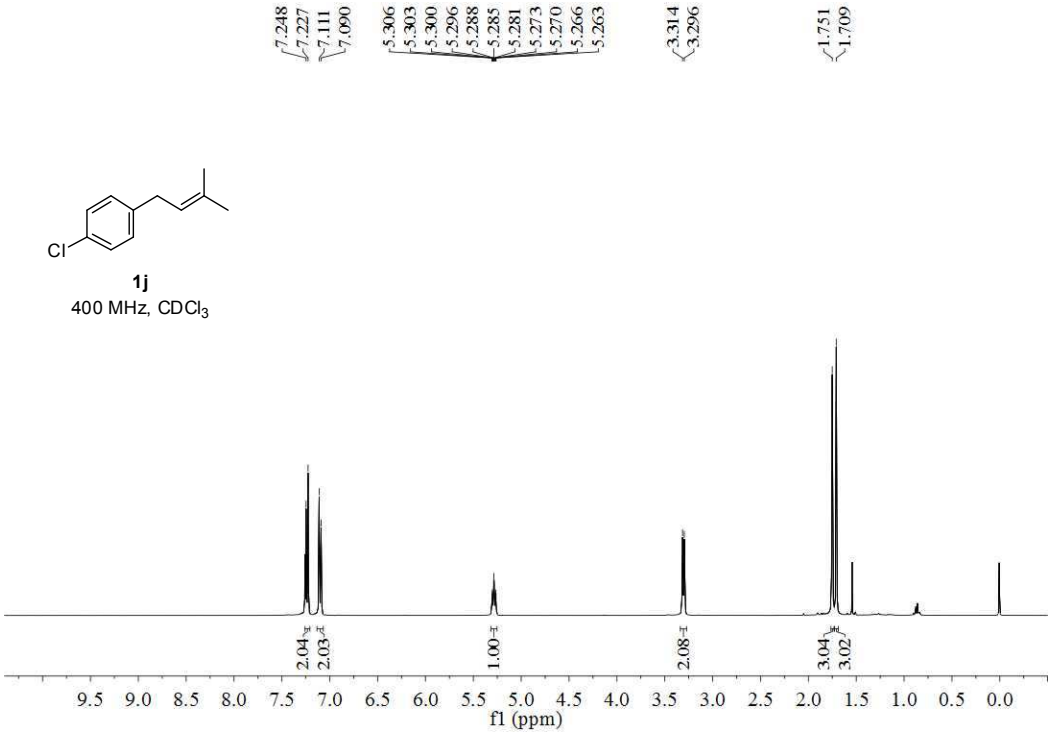
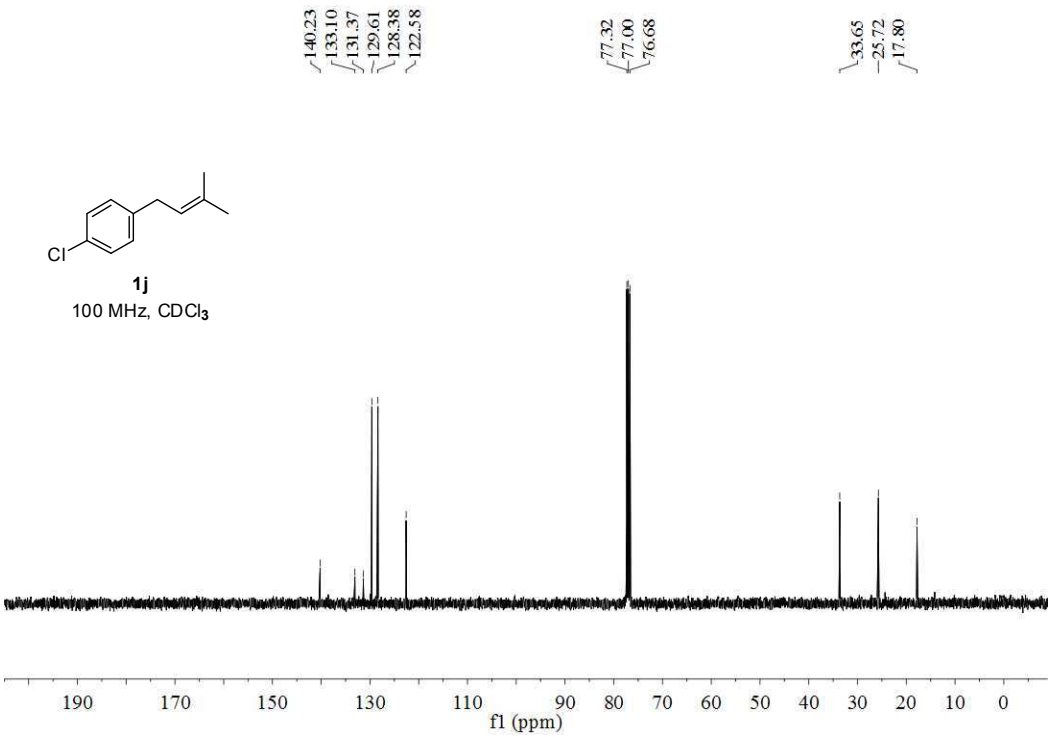
7.224
7.220
7.206
7.202
7.188
7.184
7.163
7.148
7.144
7.068
7.049
5.313
5.310
5.308
5.295
5.292
5.289
5.276
5.273
3.331
3.312
1.762
1.716
Cl
1h
400 MHz, CDCl3
3.11
0.98
1.00
2.04
3.02
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

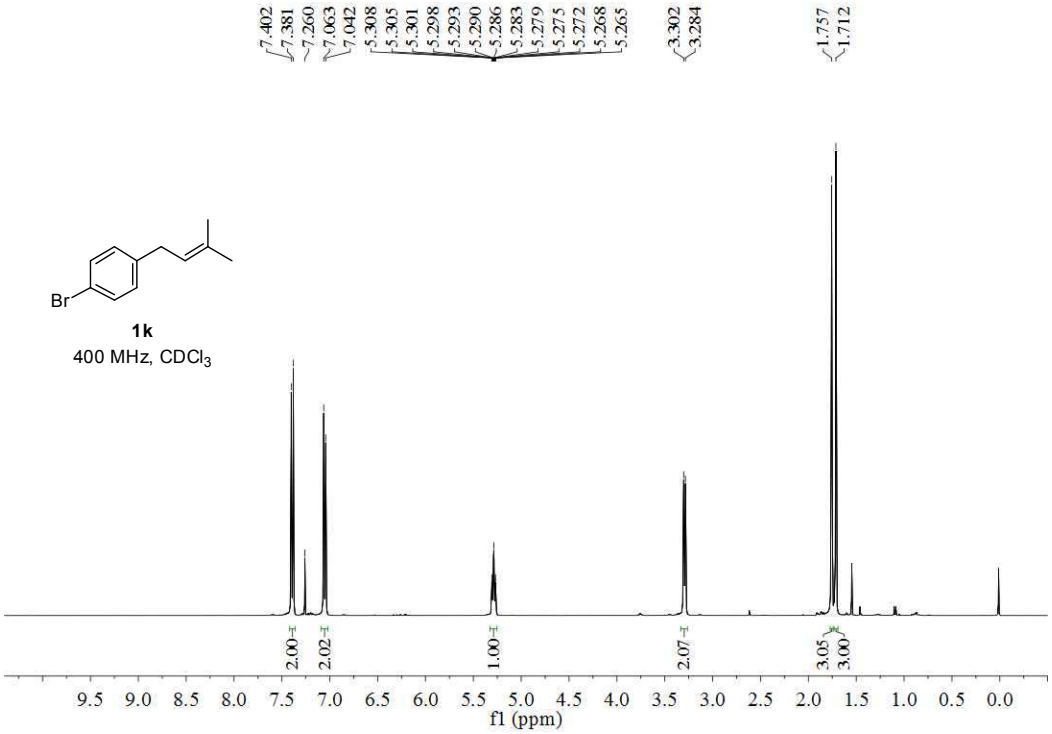

143.83
134.05
133.37
129.52
128.38
126.49
125.85
122.20
77.32
77.00
76.68
33.96
25.74
17.82
Cl
1h
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

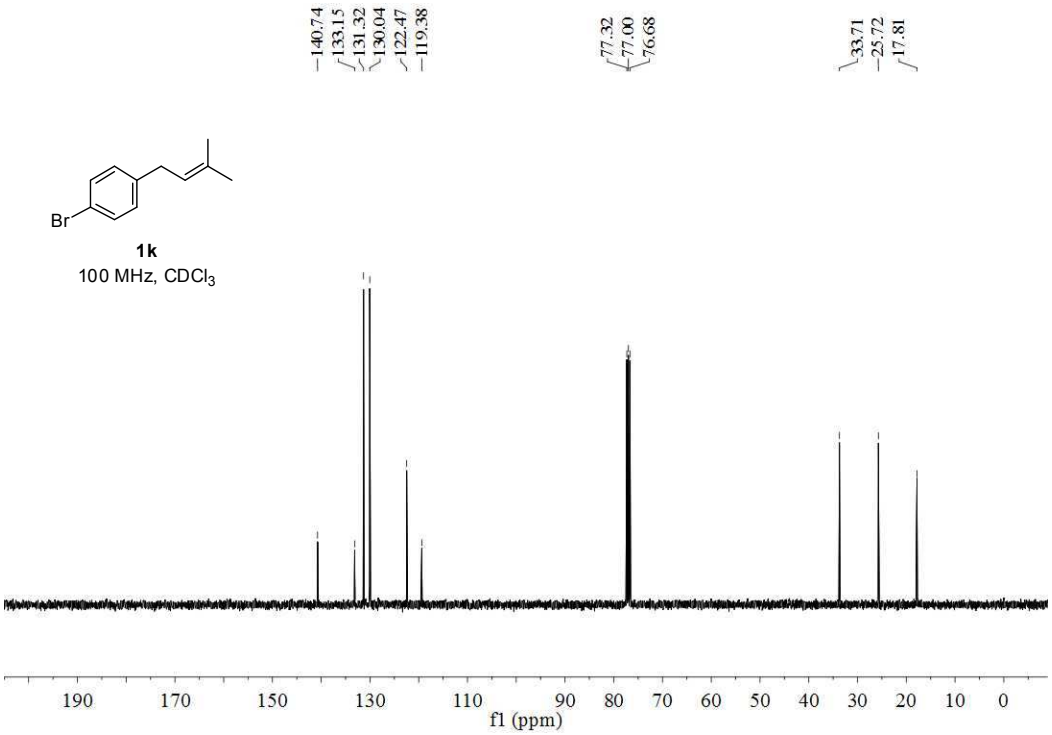

7.260
7.144
7.139
7.130
7.122
7.114
7.108
7.101
6.991
6.984
6.978
6.967
6.962
6.956
6.945
6.940
6.933
5.322
5.318
5.315
5.311
5.302
5.300
5.296
5.293
5.285
5.281
3.304
1.757
1.755
1.719
F
1i
400 MHz, CDCl3
2.01
2.00
1.03
2.01
3.01
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

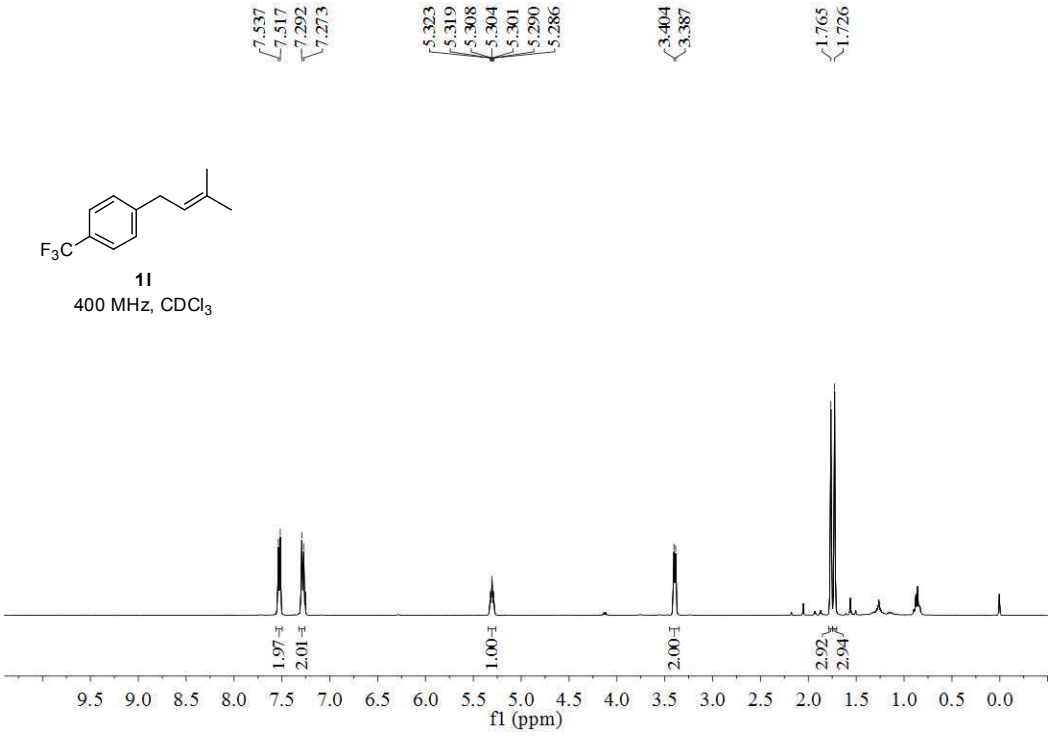

162.37
159.96
137.36
137.33
132.77
129.59
129.51
122.99
115.09
114.88
77.32
77.00
76.68
33.47
25.73
17.78
F
1i
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

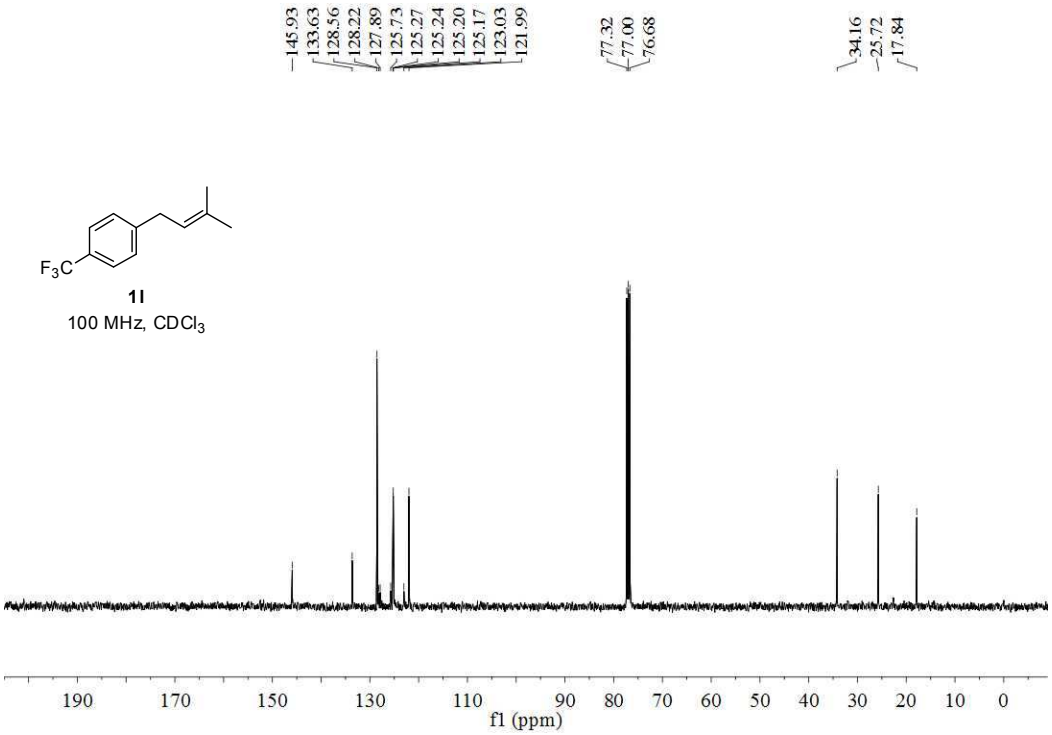

7.248
7.227
7.111
7.090
5.306
5.303
5.300
5.296
5.288
5.285
5.281
5.273
5.270
5.266
5.263
3.314
3.296
1.751
1.709
Cl
1j
400 MHz, CDCl3
2.04
2.03
1.00
2.08
3.04
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

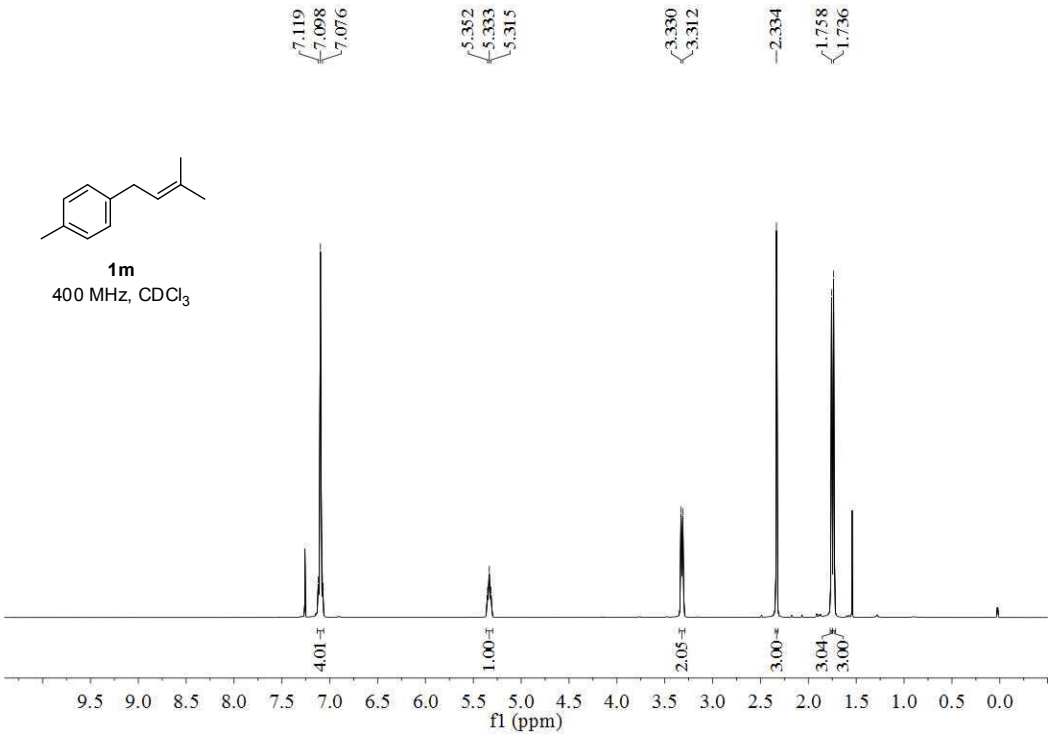

140.23
133.10
131.37
129.61
128.38
122.58
77.32
77.00
76.68
33.65
25.72
17.80
Cl
1j
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.402
7.381
7.260
7.063
7.042
5.308
5.305
5.301
5.298
5.293
5.290
5.286
5.283
5.279
5.275
5.272
5.268
5.265
3.302
3.284
1.757
1.712
Br
1k
400 MHz, CDCl3
2.00
2.02
1.00
2.07
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

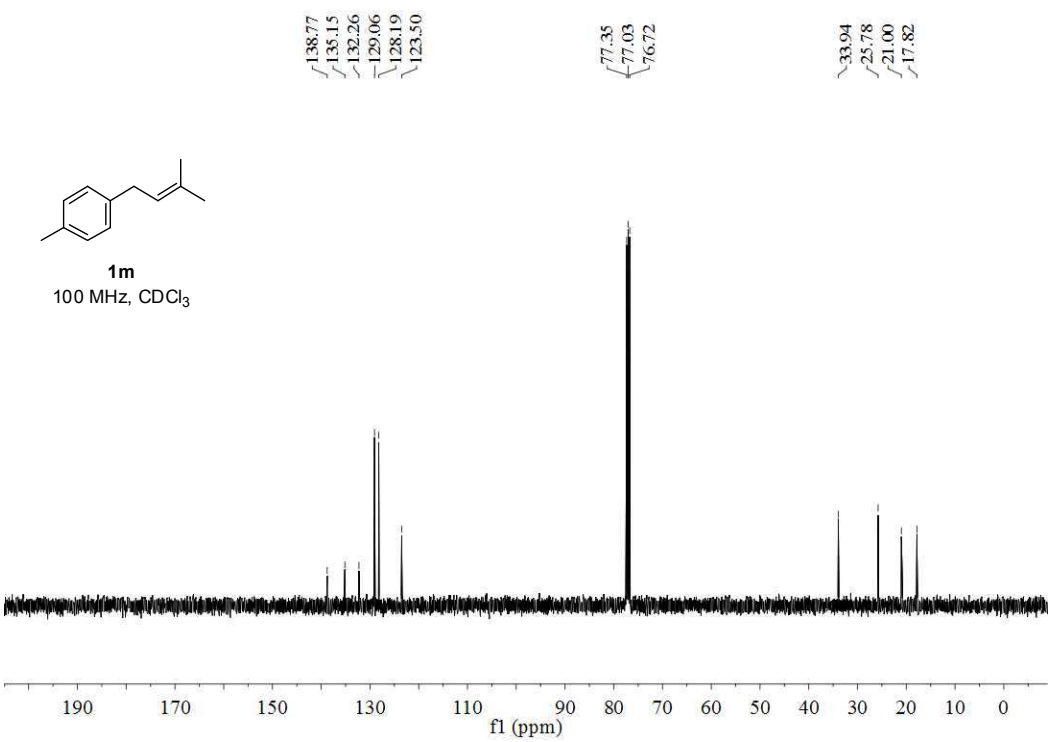

140.74
133.15
131.32
130.04
122.47
119.38
77.32
77.00
76.68
33.71
25.72
17.81
Br
1k
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.537
7.517
7.292
7.273
5.323
5.319
5.308
5.304
5.301
5.290
5.286
3.404
3.387
1.765
1.726
F3C
1l
400 MHz, CDCl3
1.97
2.01
1.00
2.00
2.92
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

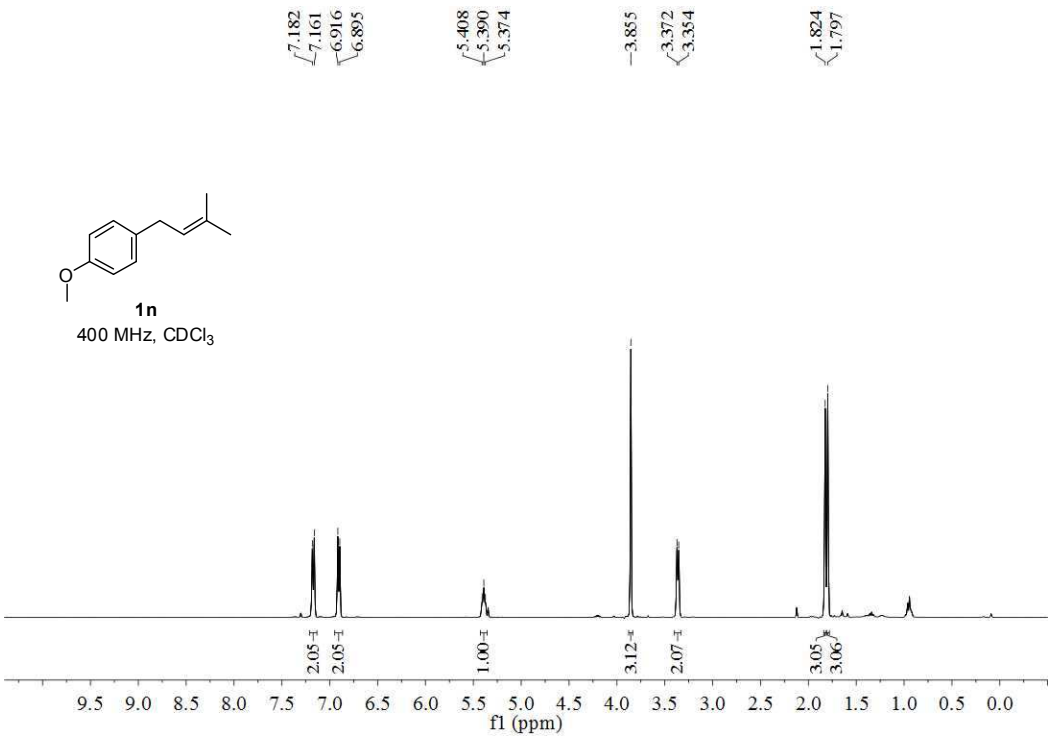

145.93
133.63
128.56
128.22
127.89
125.73
125.27
125.24
125.20
125.17
123.03
121.99
77.32
77.00
76.68
34.16
25.72
17.84
F3C
1l
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

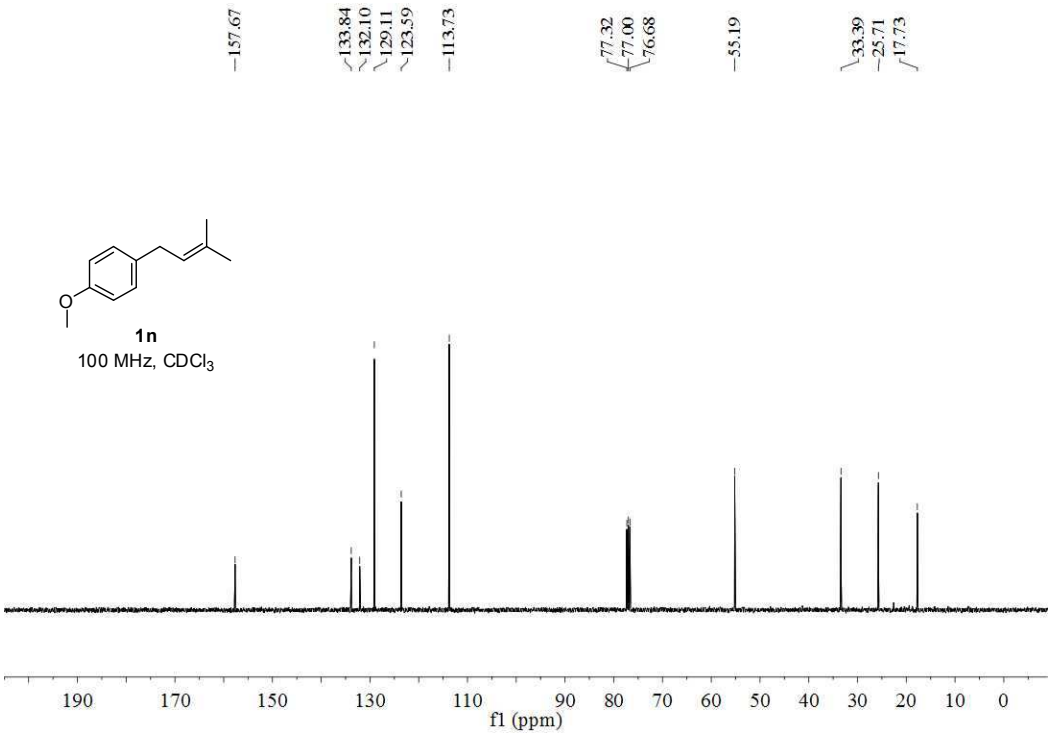


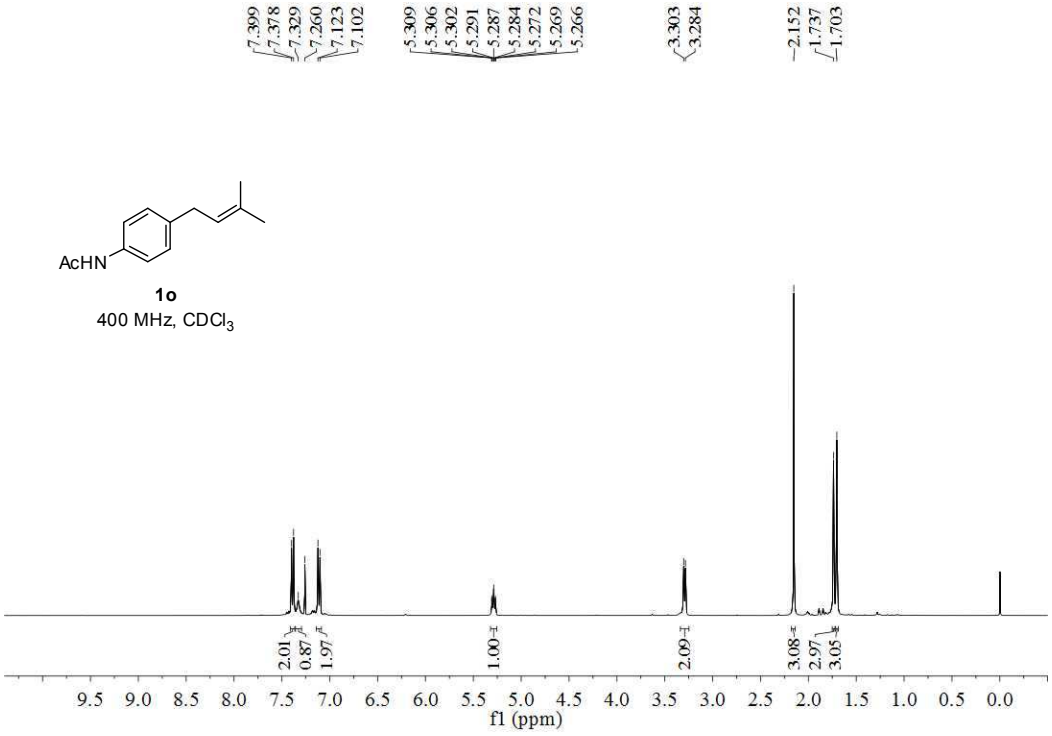
1m
400 MHz, $CDCl_3$

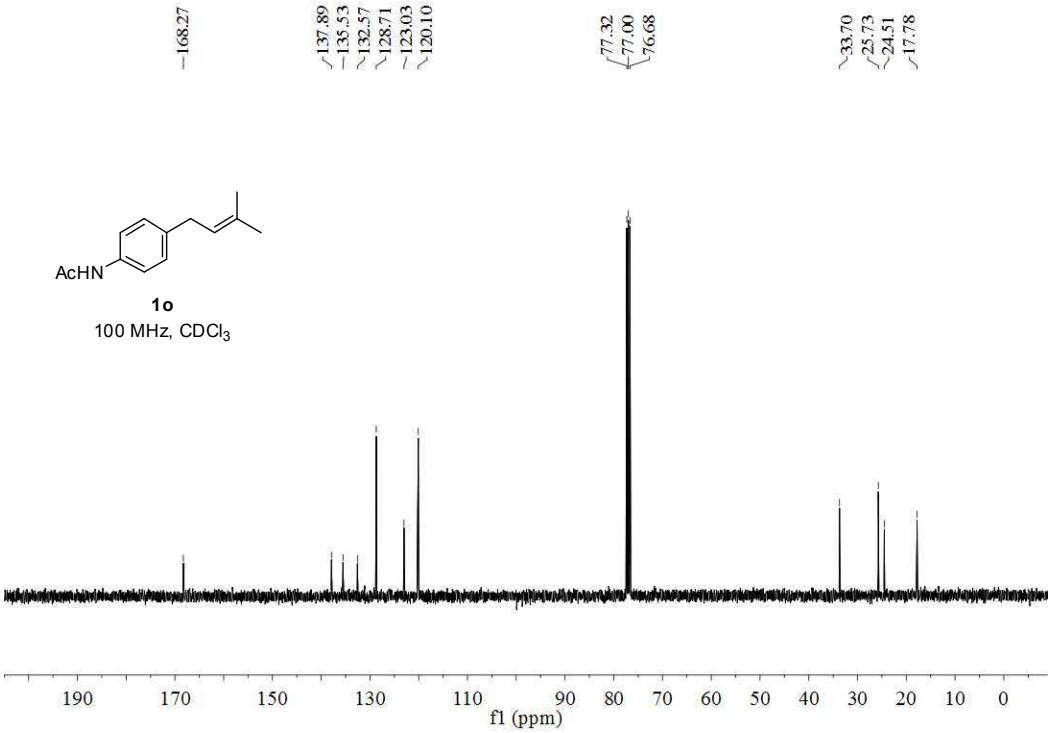


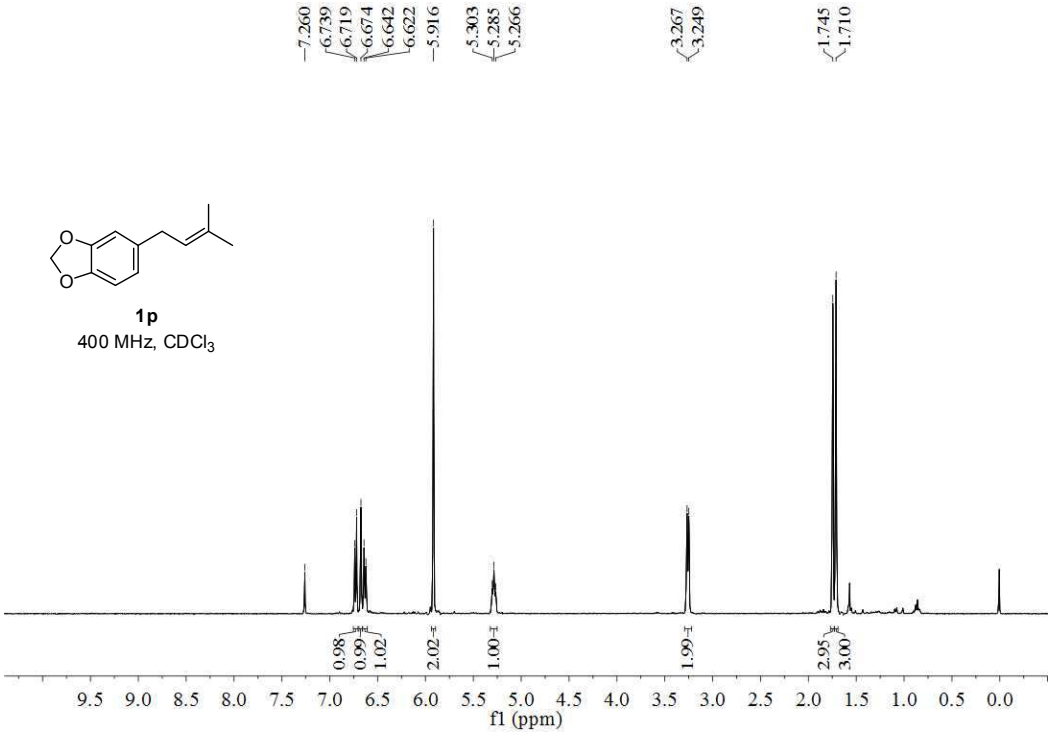
1m
100 MHz, $CDCl_3$

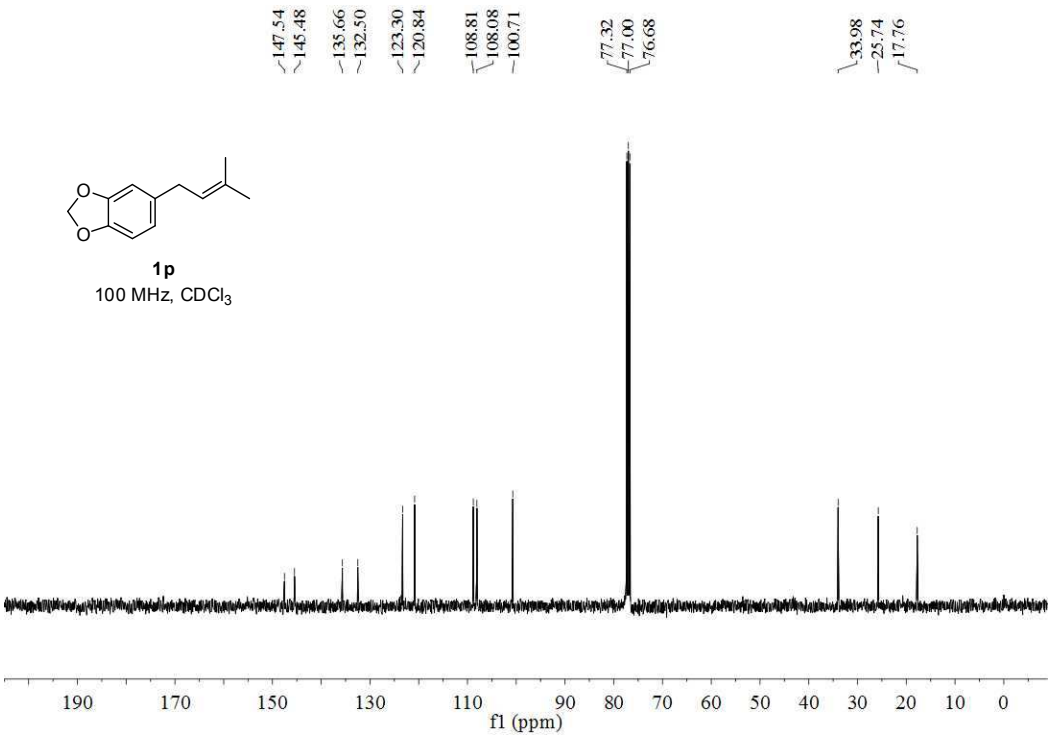

7.182
7.161
6.916
6.895
5.408
5.390
5.374
3.855
3.372
3.354
1.824
1.797
1n
400 MHz, CDCl3
2.05
2.05
1.00
3.12
2.07
3.05
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

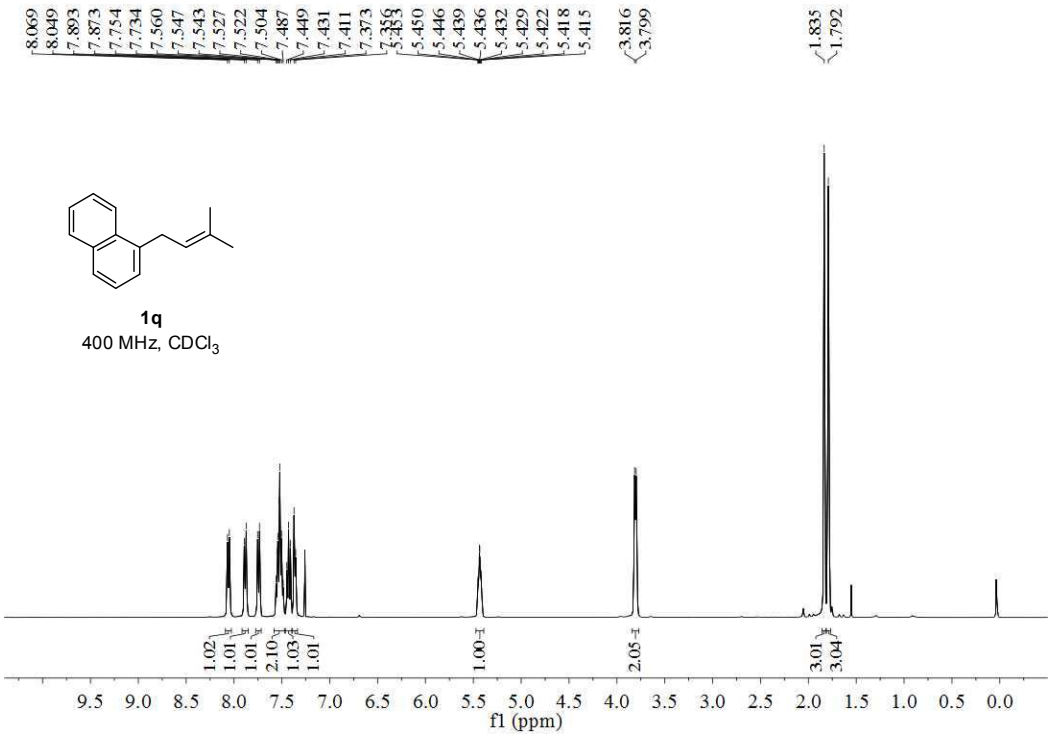

157.67
133.84
132.10
129.11
123.59
113.73
77.32
77.00
76.68
55.19
33.39
25.71
17.73
1n
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.399
7.378
7.329
7.260
7.123
7.102
5.309
5.306
5.302
5.291
5.287
5.284
5.272
5.269
5.266
3.303
3.284
2.152
1.737
1.703
AcHN
1o
400 MHz, CDCl3
2.01
0.87
1.97
1.00
2.09
3.08
2.97
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

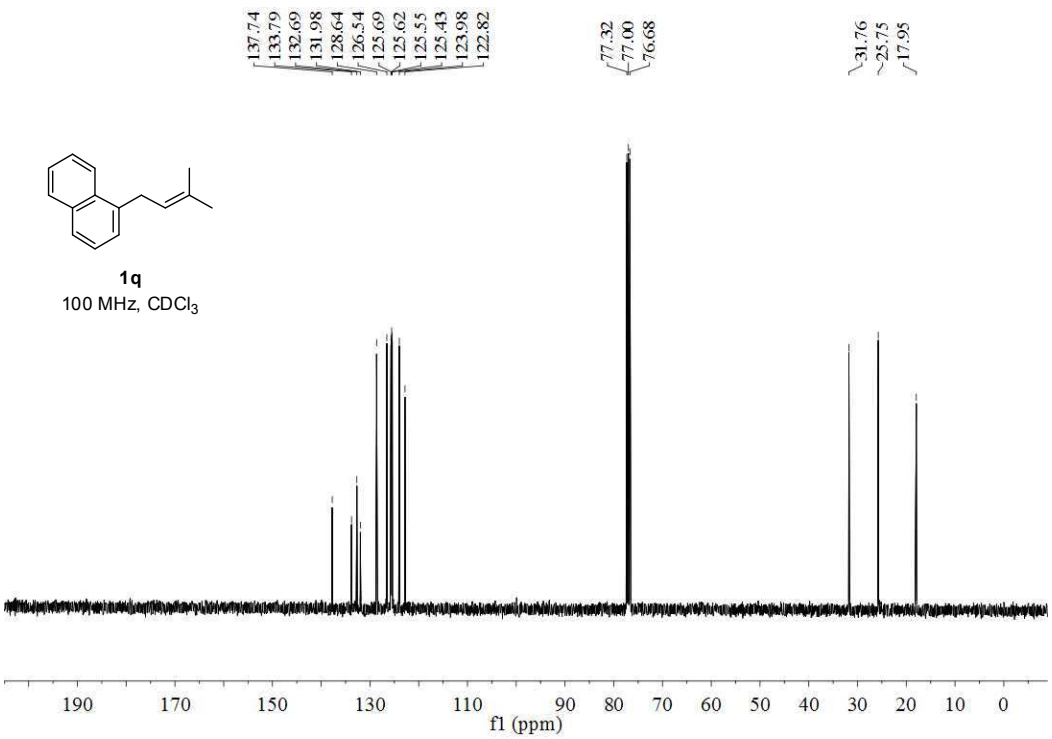

168.27
137.89
135.53
132.57
128.71
123.03
120.10
77.32
77.00
76.68
33.70
25.73
24.51
17.78
AcHN
1o
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
6.739
6.719
6.674
6.642
6.622
5.916
5.303
5.285
5.266
3.267
3.249
1.745
1.710
1p
400 MHz, CDCl3
0.98
0.99
1.02
2.02
1.00
1.99
2.95
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

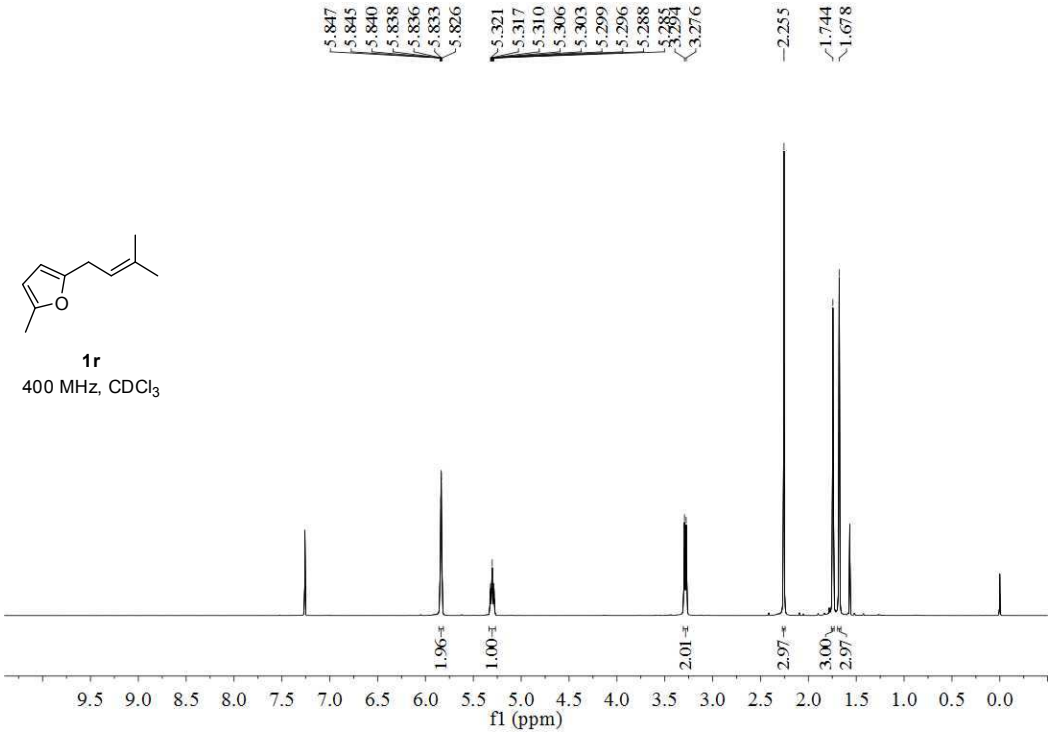

147.54
145.48
135.66
132.50
123.30
120.84
108.81
108.08
100.71
77.32
77.00
76.68
33.98
25.74
17.76
1p
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



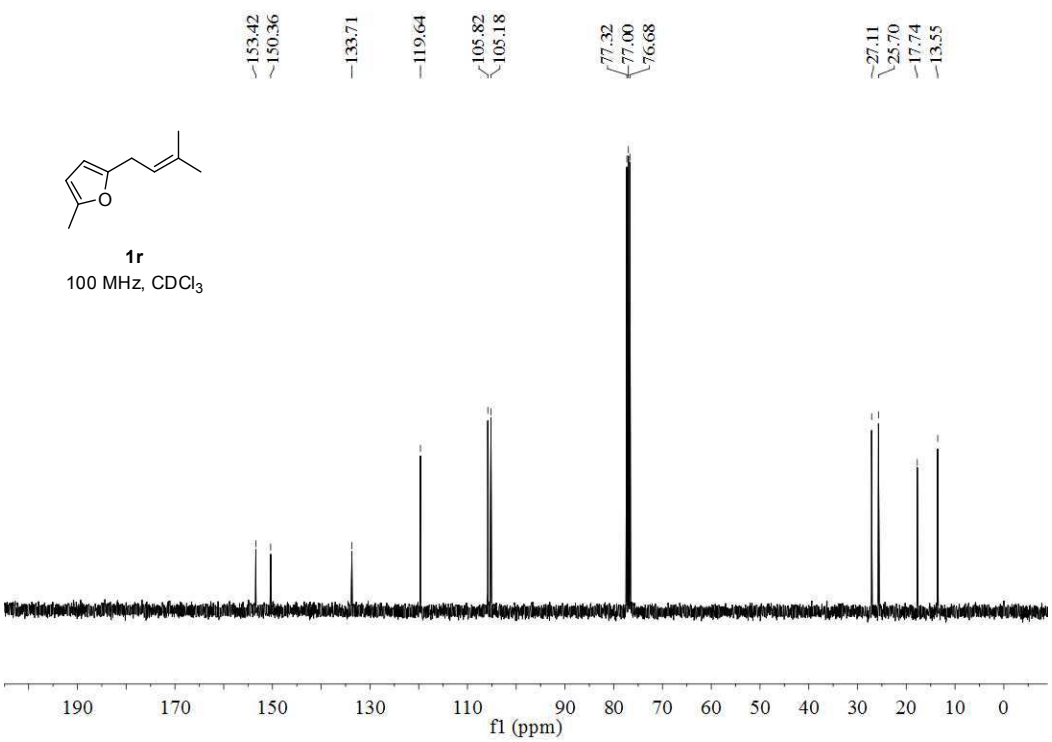
1q
400 MHz, $CDCl_3$



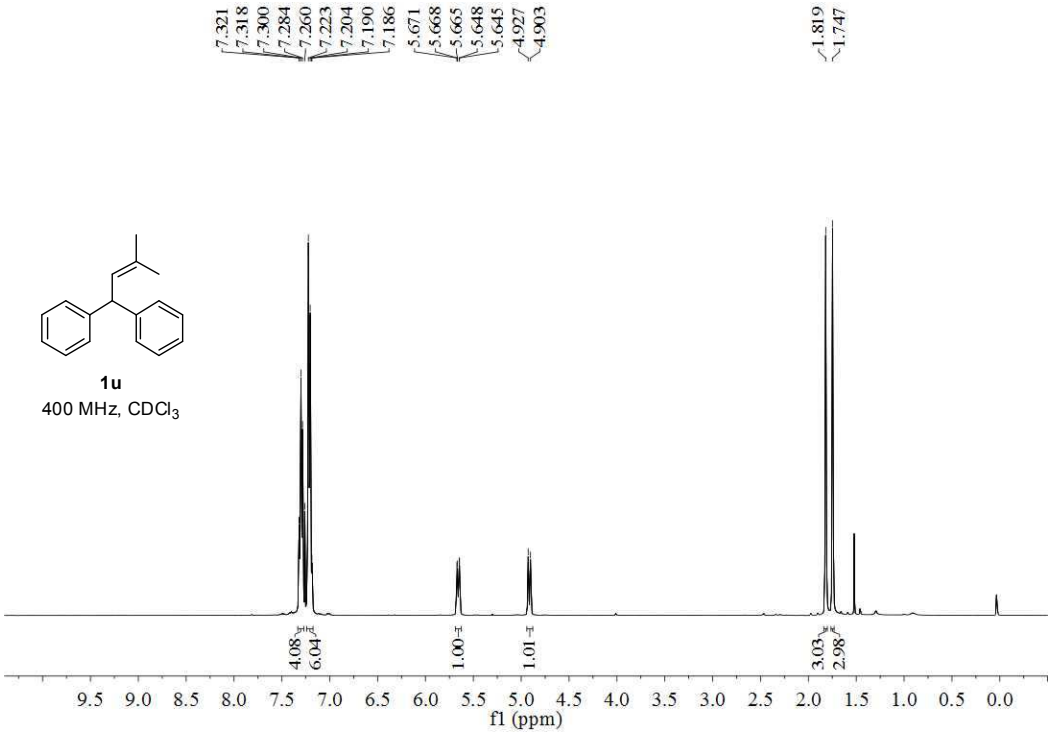
1q
100 MHz, $CDCl_3$

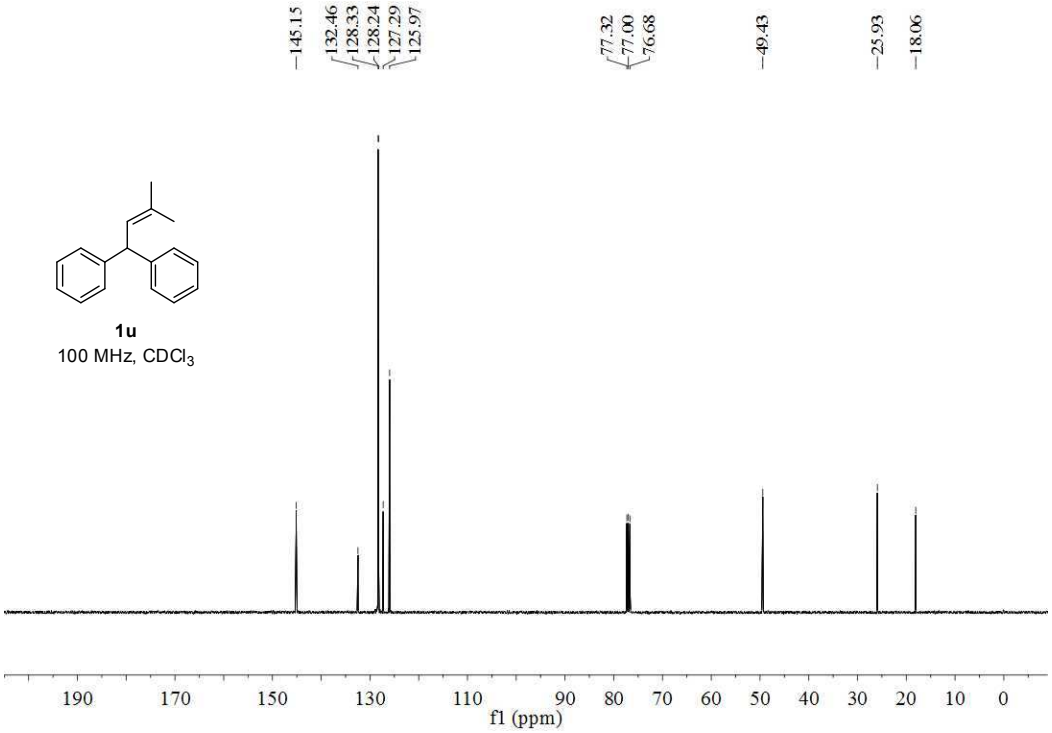


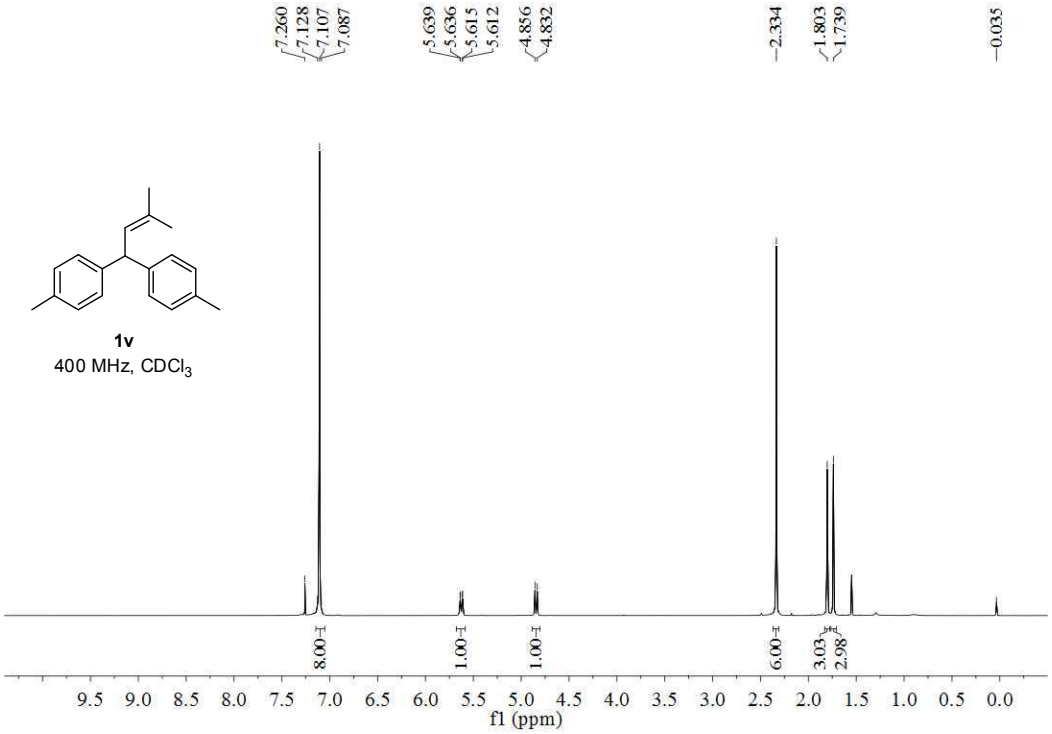
1r
400 MHz, $CDCl_3$



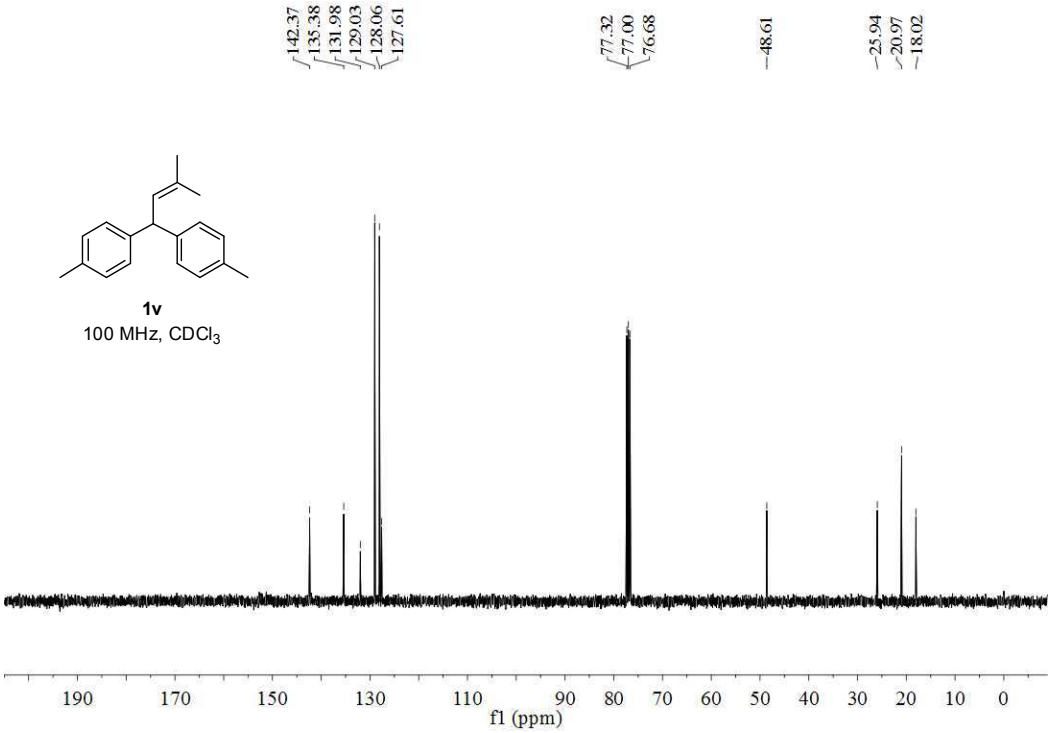
1r
100 MHz, $CDCl_3$


7.321
7.318
7.300
7.284
7.260
7.223
7.204
7.190
7.186
5.671
5.668
5.665
5.648
5.645
4.927
4.903
1.819
1.747
1u
400 MHz, CDCl3
4.08
6.04
1.00
1.01
3.03
2.98
f1 (ppm)

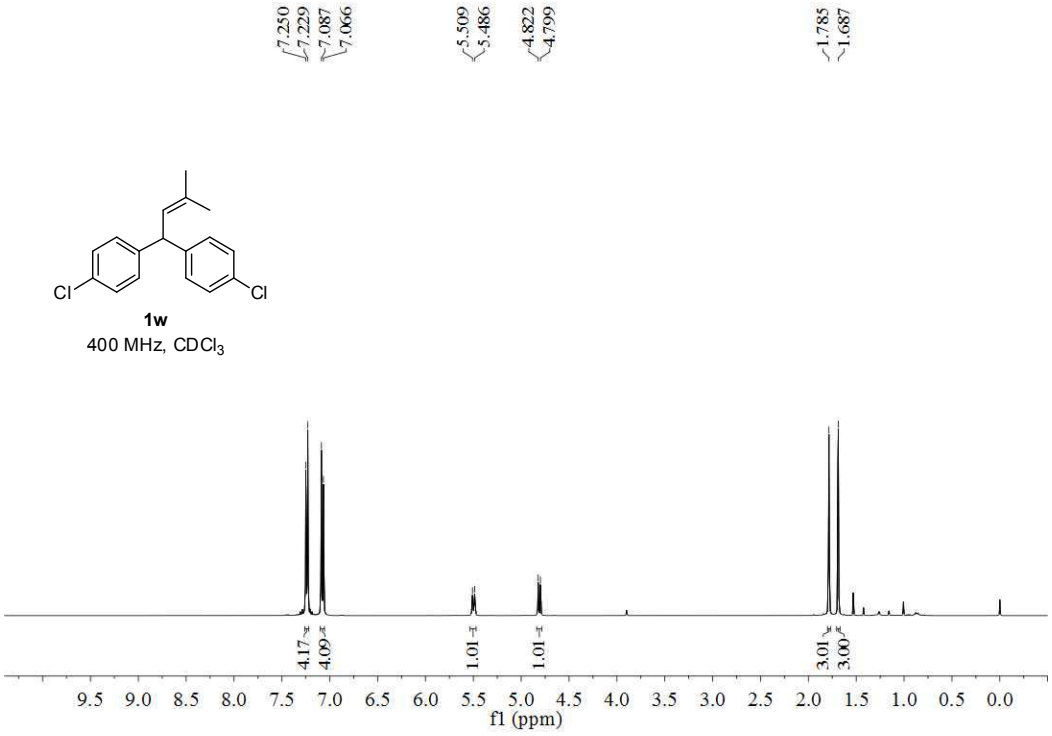

145.15
132.46
128.33
128.24
127.29
125.97
77.32
77.00
76.68
49.43
25.93
18.06
1u
100 MHz, CDCl3
f1 (ppm)

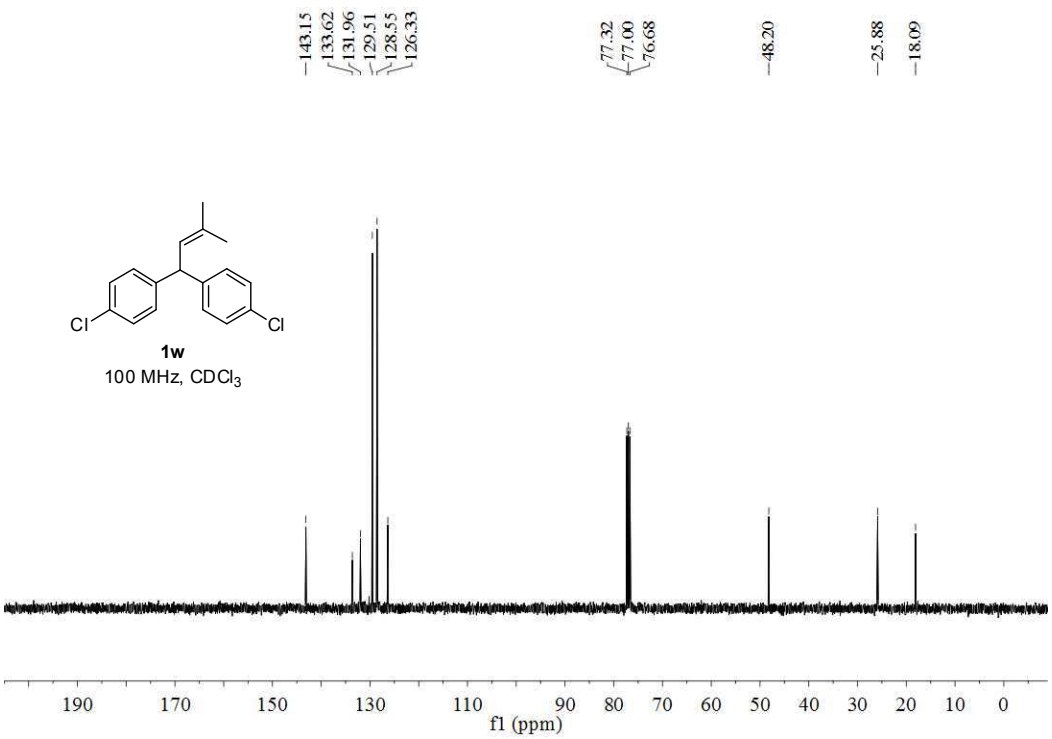


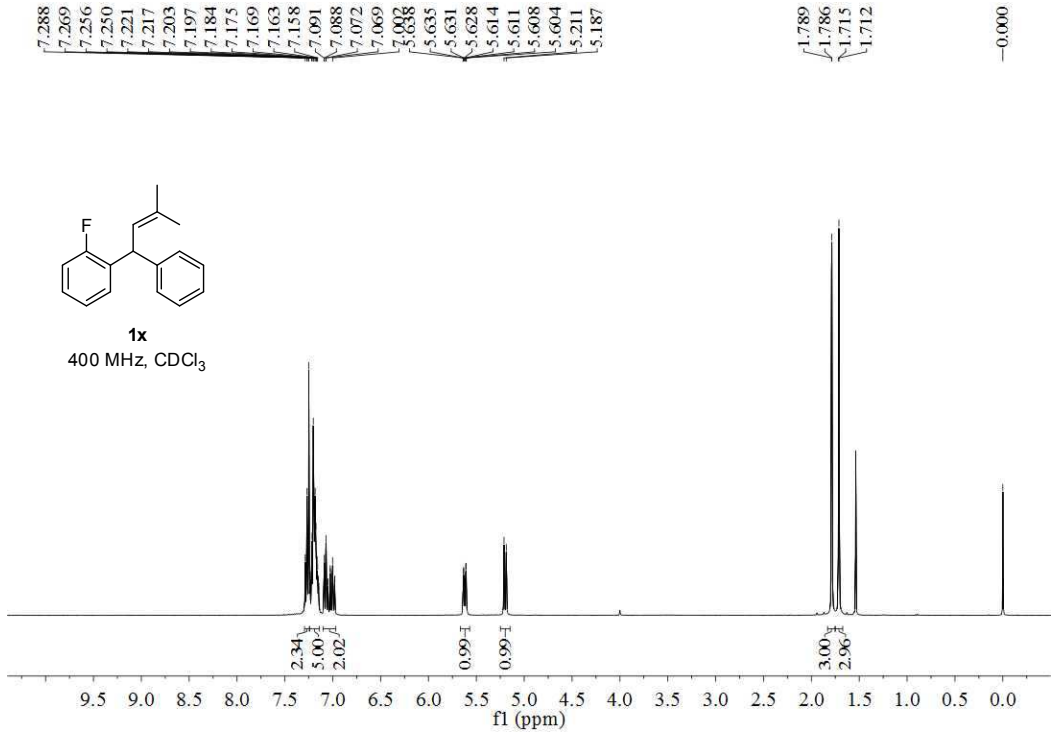
1v
400 MHz, $CDCl_3$

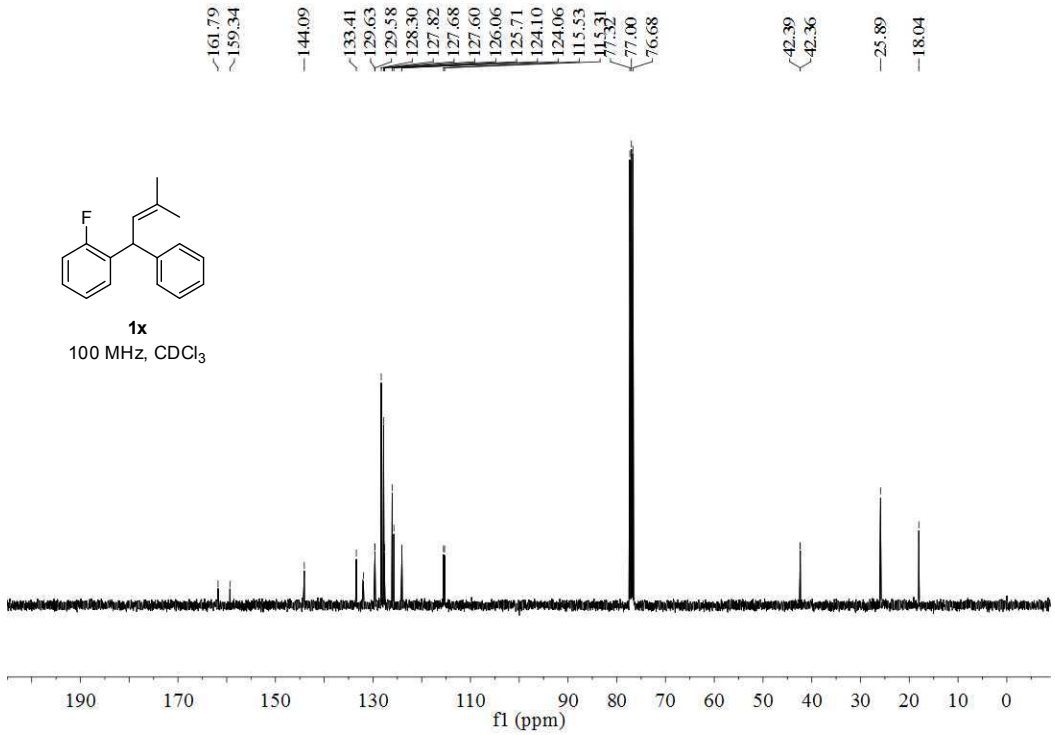


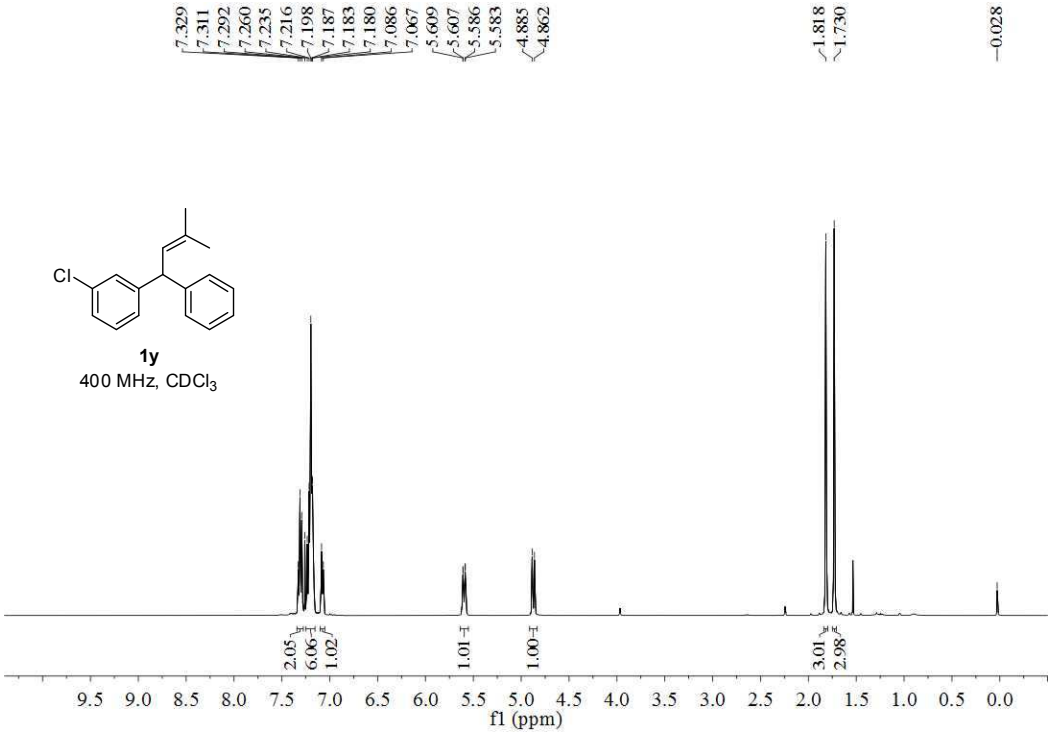
1v
100 MHz, $CDCl_3$

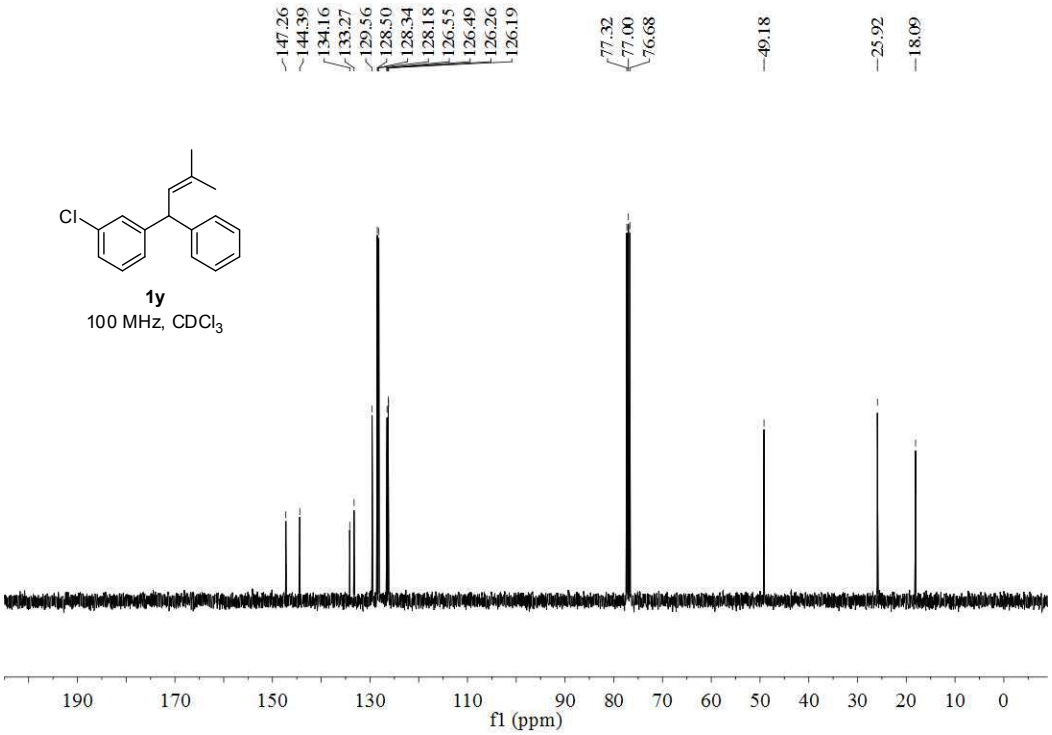

7.250
7.229
7.087
7.066
5.509
5.486
4.822
4.799
1.785
1.687
Cl
Cl
1w
400 MHz, CDCl3
4.17
4.09
1.01
1.01
3.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

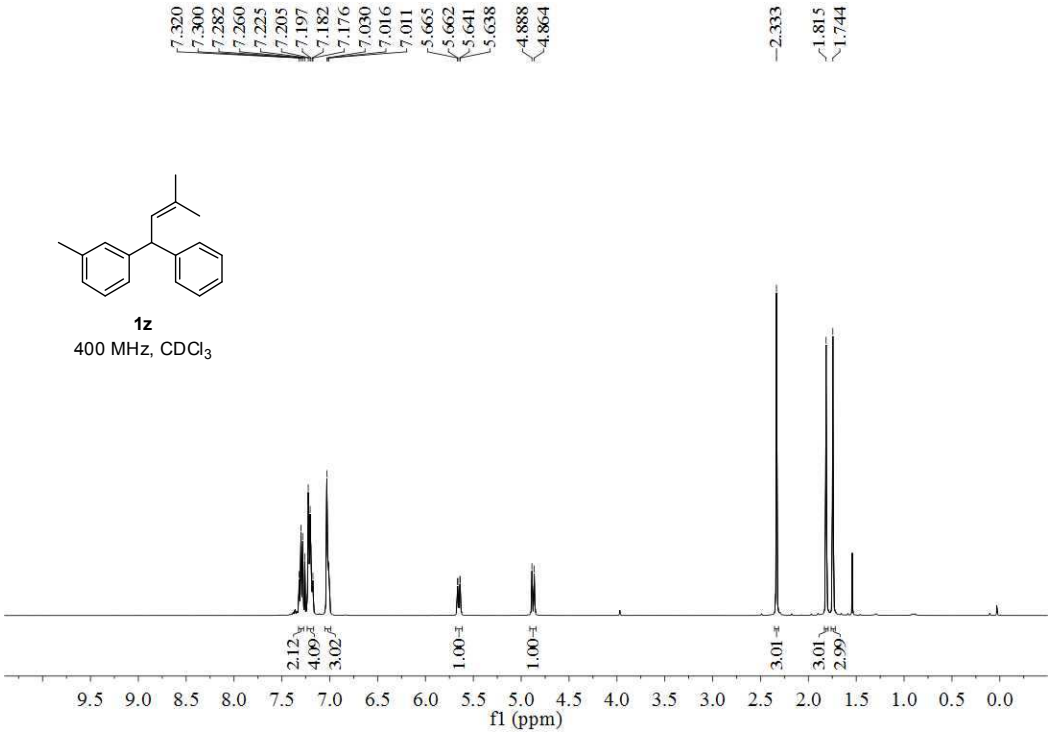

143.15
133.62
131.96
129.51
128.55
126.33
77.32
77.00
76.68
48.20
25.88
18.09
Cl
Cl
1w
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.288
7.269
7.256
7.250
7.221
7.217
7.203
7.197
7.184
7.175
7.169
7.163
7.158
7.091
7.088
7.072
7.069
7.002
5.635
5.631
5.628
5.614
5.611
5.608
5.604
5.211
5.187
1.789
1.786
1.715
1.712
0.000
F
1x
400 MHz, CDCl3
2.34
5.00
2.02
0.99
0.99
3.00
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

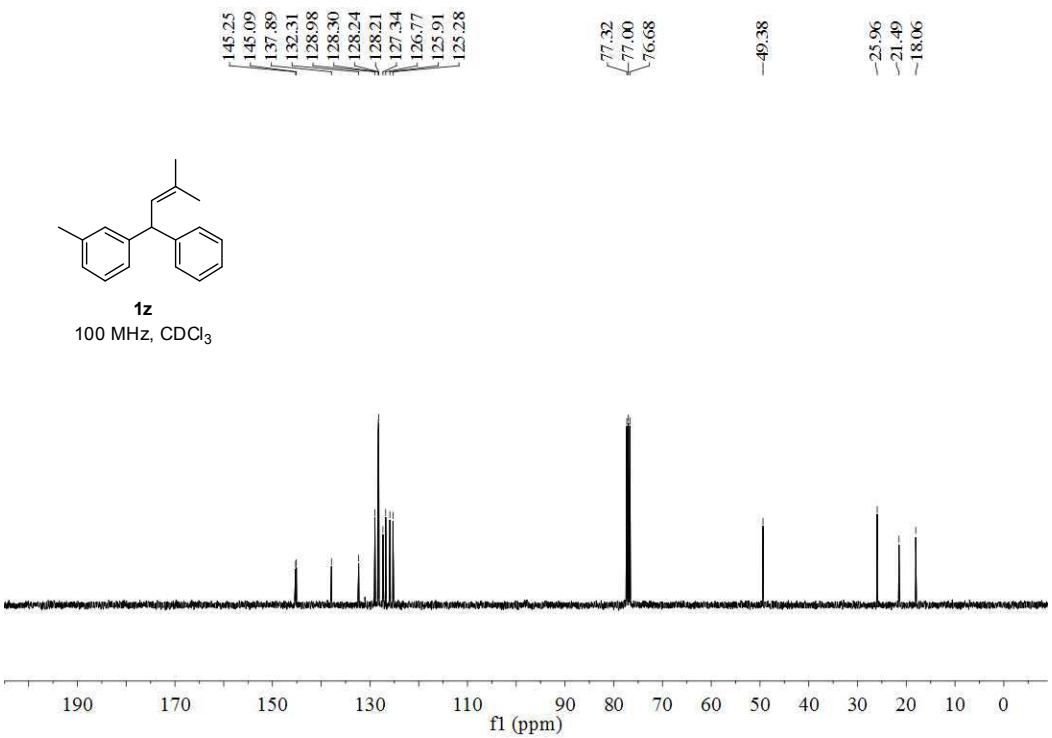

161.79
159.34
144.09
133.41
129.63
129.58
128.30
127.82
127.68
127.60
126.06
125.71
124.10
124.06
115.53
115.31
77.32
77.00
76.68
42.39
42.36
25.89
18.04
F
1x
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.329
7.311
7.292
7.260
7.235
7.216
7.198
7.187
7.183
7.180
7.086
7.067
5.609
5.607
5.586
5.583
4.885
4.862
1.818
1.730
0.028
Cl
1y
400 MHz, CDCl3
2.05
6.06
1.02
1.01
1.00
3.01
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

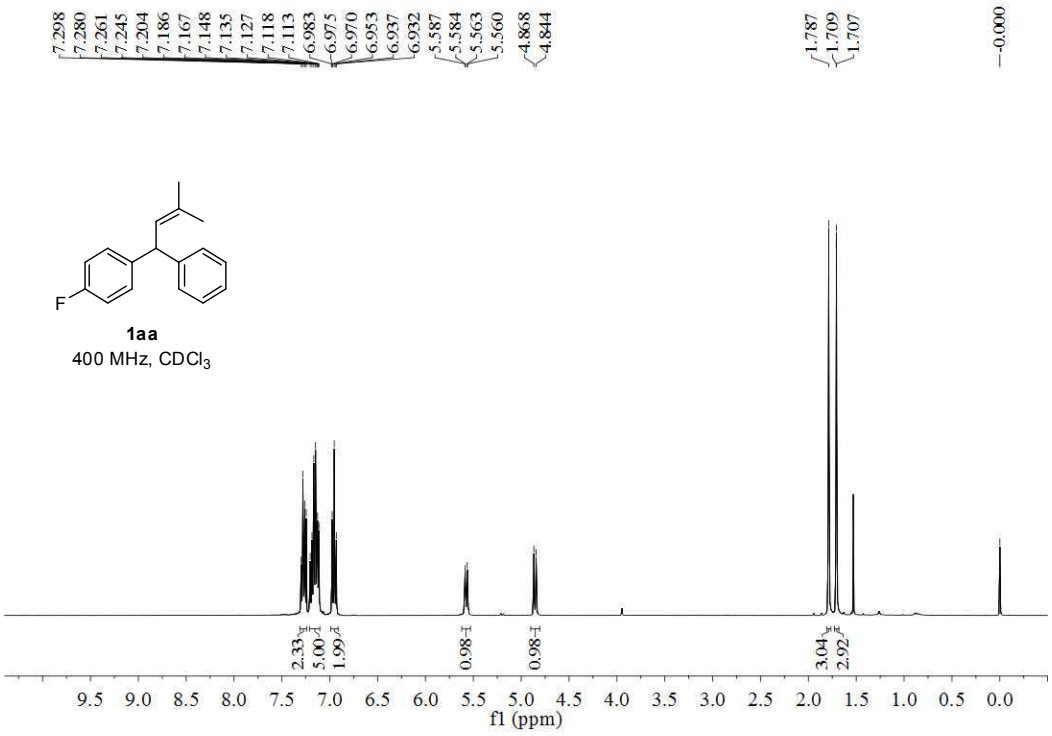

147.26
144.39
134.16
133.27
129.56
128.50
128.34
128.18
126.55
126.49
126.26
126.19
77.32
77.00
76.68
49.18
25.92
18.09
Cl
1y
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

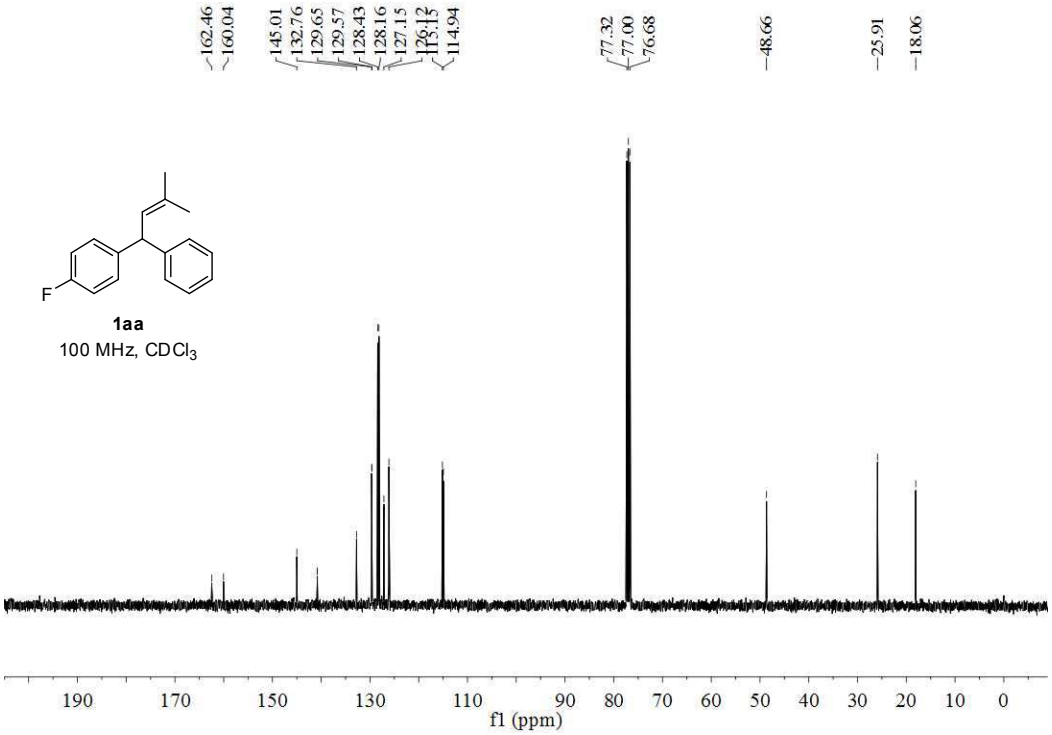


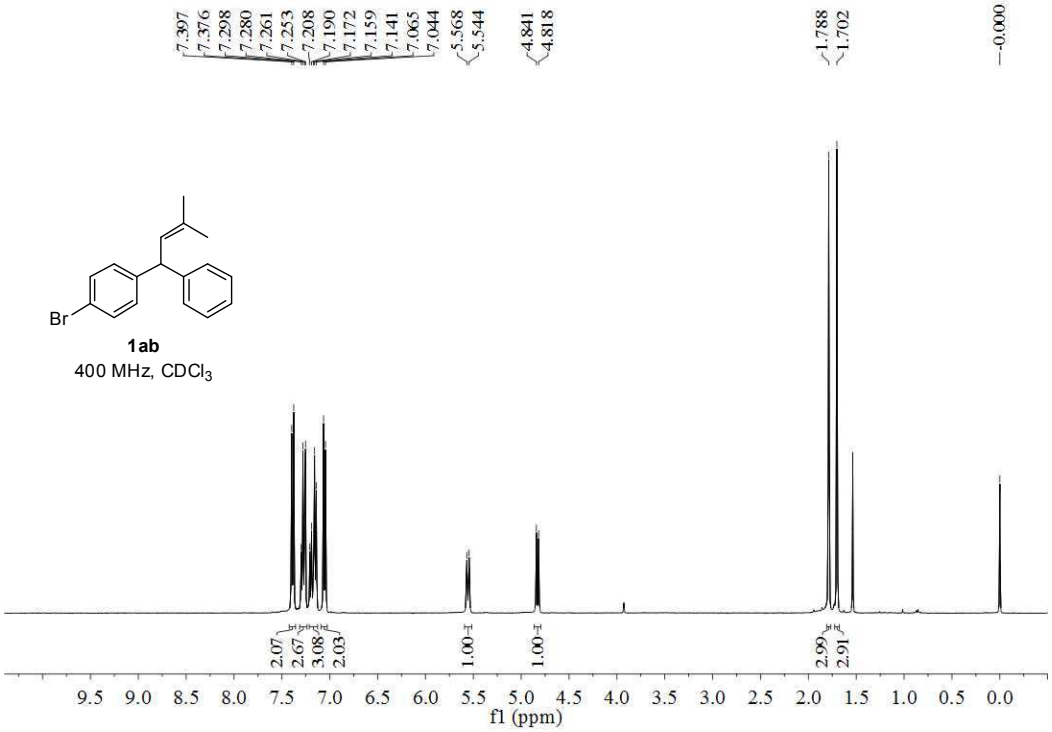
1z
400 MHz, $CDCl_3$

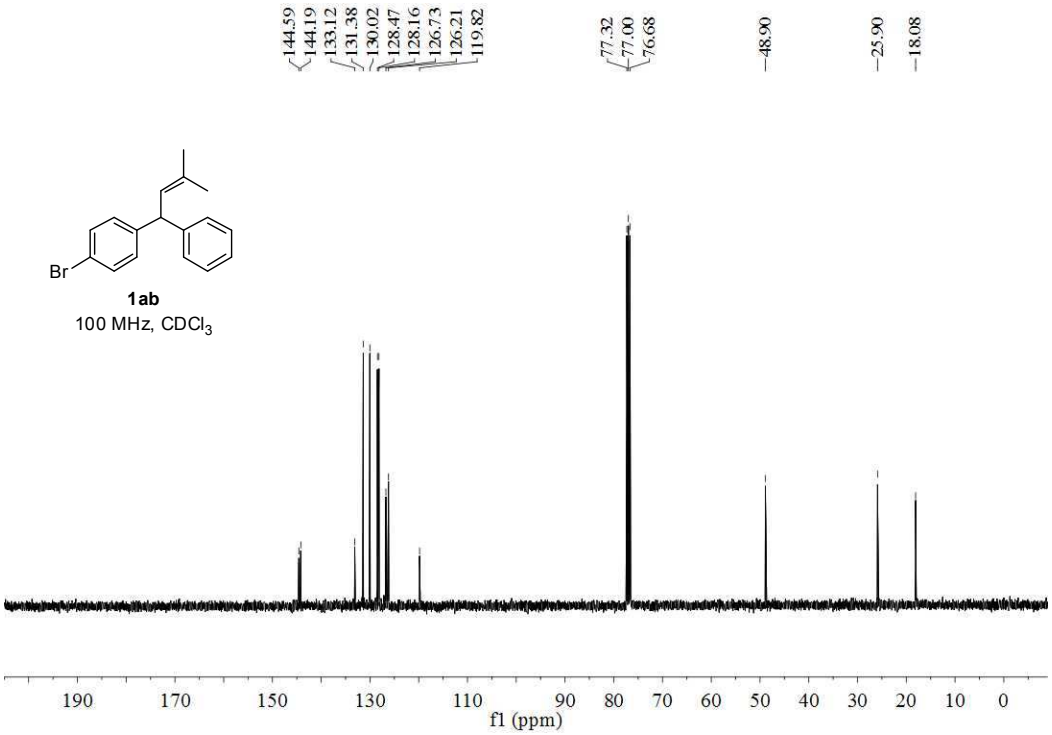


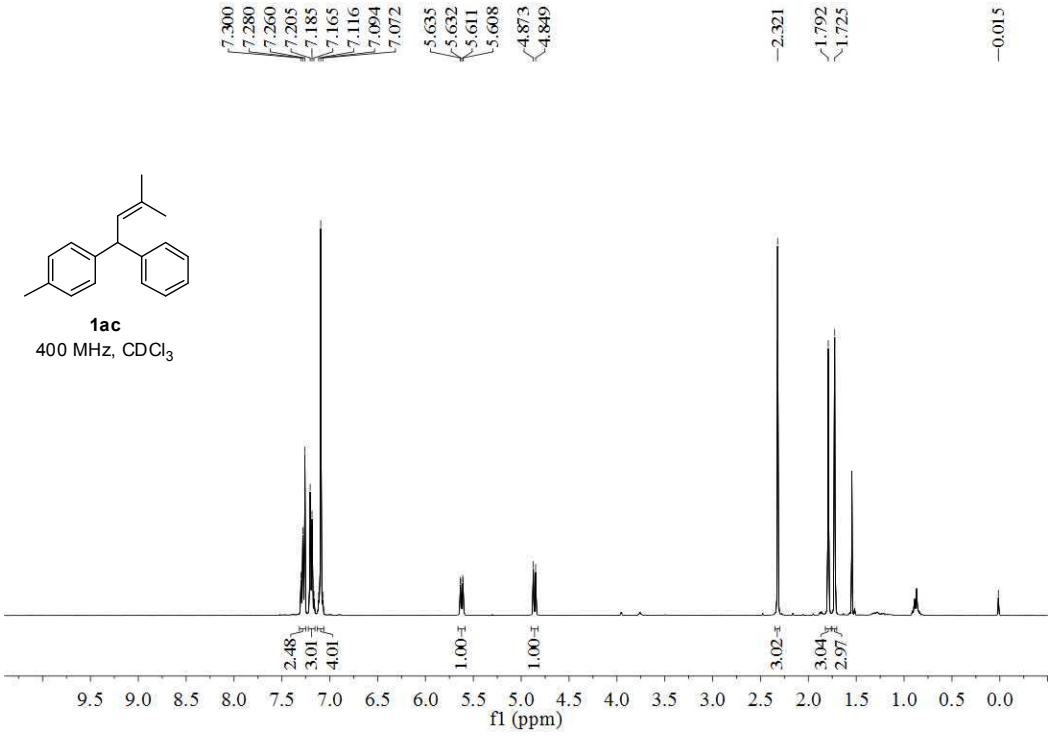
1z
100 MHz, $CDCl_3$

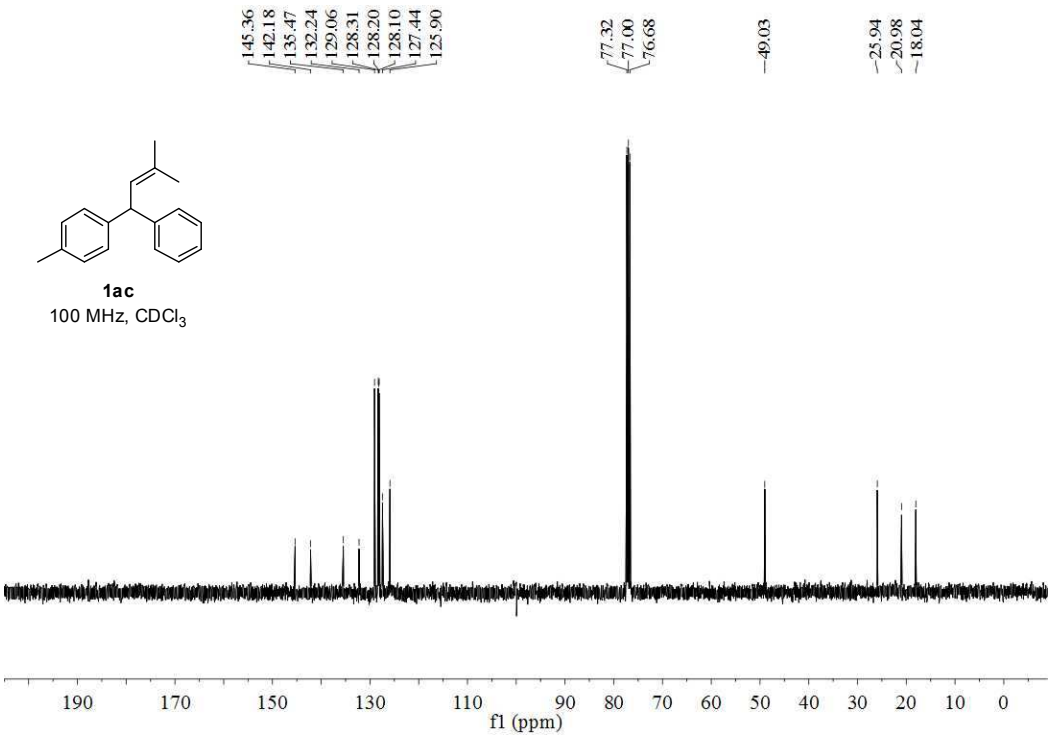

7.298
7.280
7.261
7.245
7.204
7.186
7.167
7.148
7.135
7.127
7.118
7.113
6.983
6.975
6.970
6.953
6.937
6.932
5.587
5.584
5.563
5.560
4.868
4.844
1.787
1.709
1.707
0.000
F
1aa
400 MHz, CDCl3
2.33
5.00
1.99
0.98
0.98
3.04
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.46
160.04
145.01
132.76
129.65
129.57
128.43
128.16
127.15
126.12
115.15
114.94
77.32
77.00
76.68
48.66
25.91
18.06
F
1aa
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

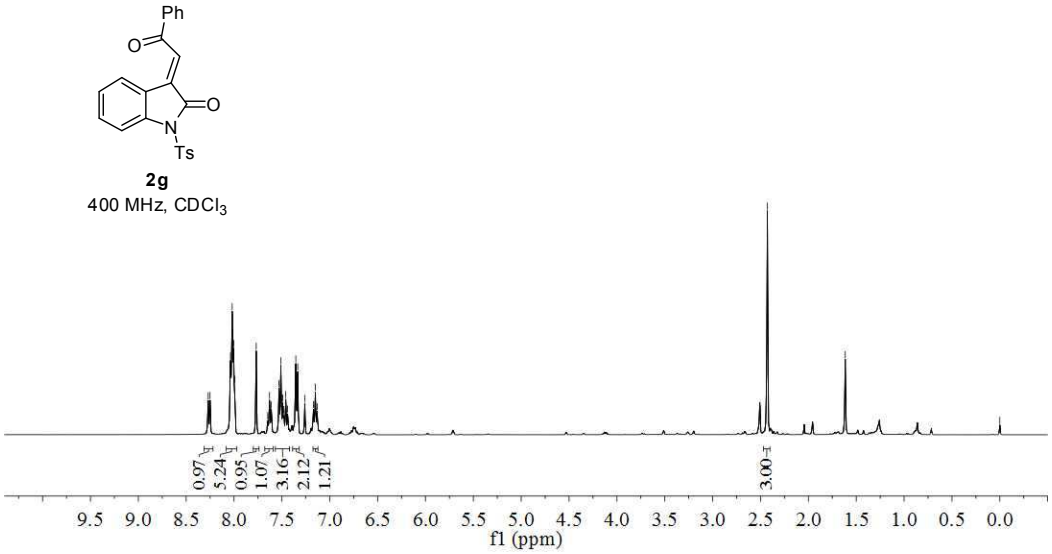

7.397
7.376
7.298
7.280
7.261
7.253
7.208
7.190
7.172
7.159
7.141
7.065
7.044
5.568
5.544
4.841
4.818
1.788
1.702
0.000
Br
1ab
400 MHz, CDCl3
2.07
2.67
3.08
2.03
1.00
1.00
2.99
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

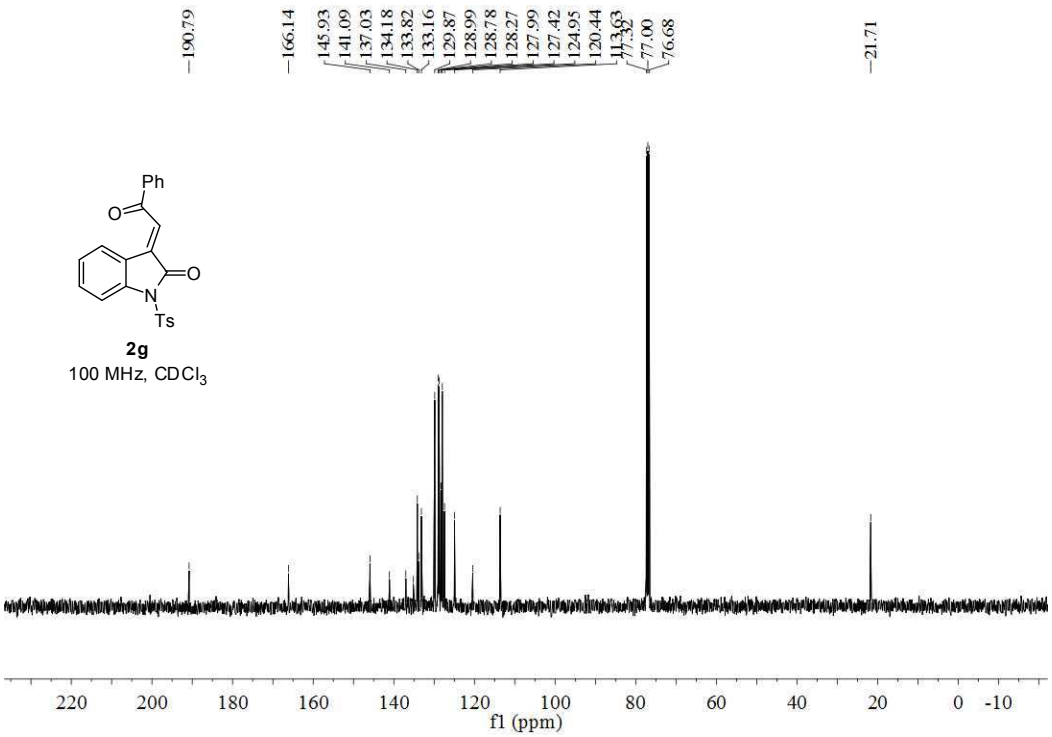

144.59
144.19
133.12
131.38
130.02
128.47
128.16
126.73
126.21
119.82
77.32
77.00
76.68
48.90
25.90
18.08
Br
1ab
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

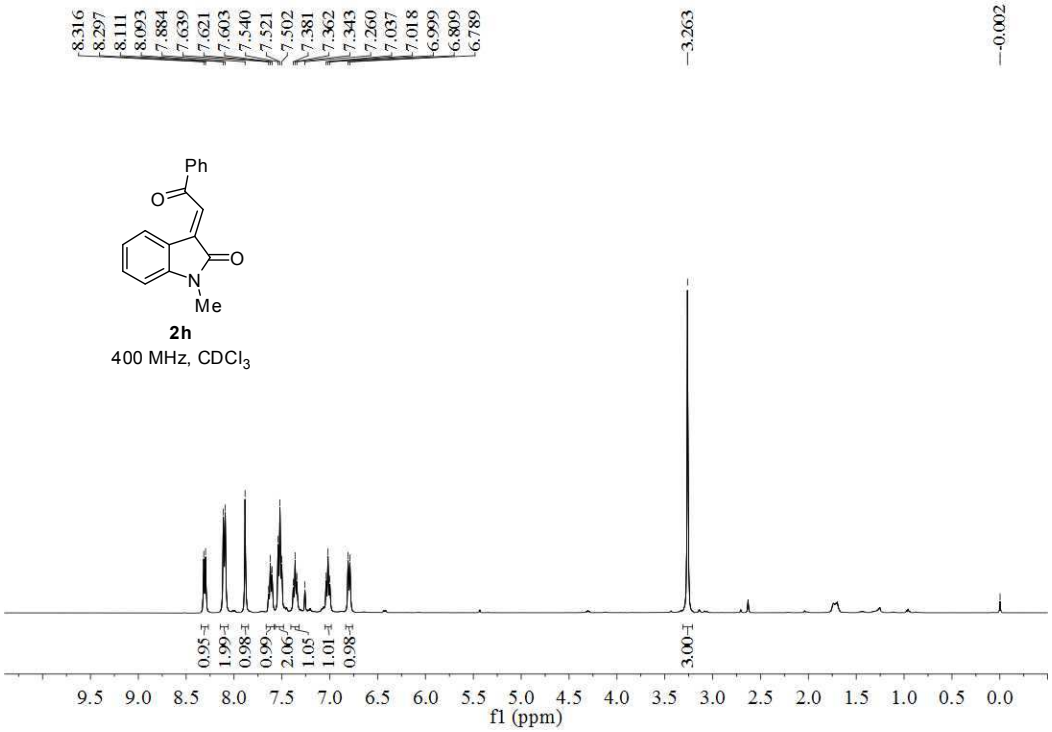

7.300
7.280
7.260
7.205
7.185
7.165
7.116
7.094
7.072
5.635
5.632
5.611
5.608
4.873
4.849
2.321
1.792
1.725
0.015
1ac
400 MHz, CDCl3
2.48
3.01
4.01
1.00
1.00
3.02
3.04
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

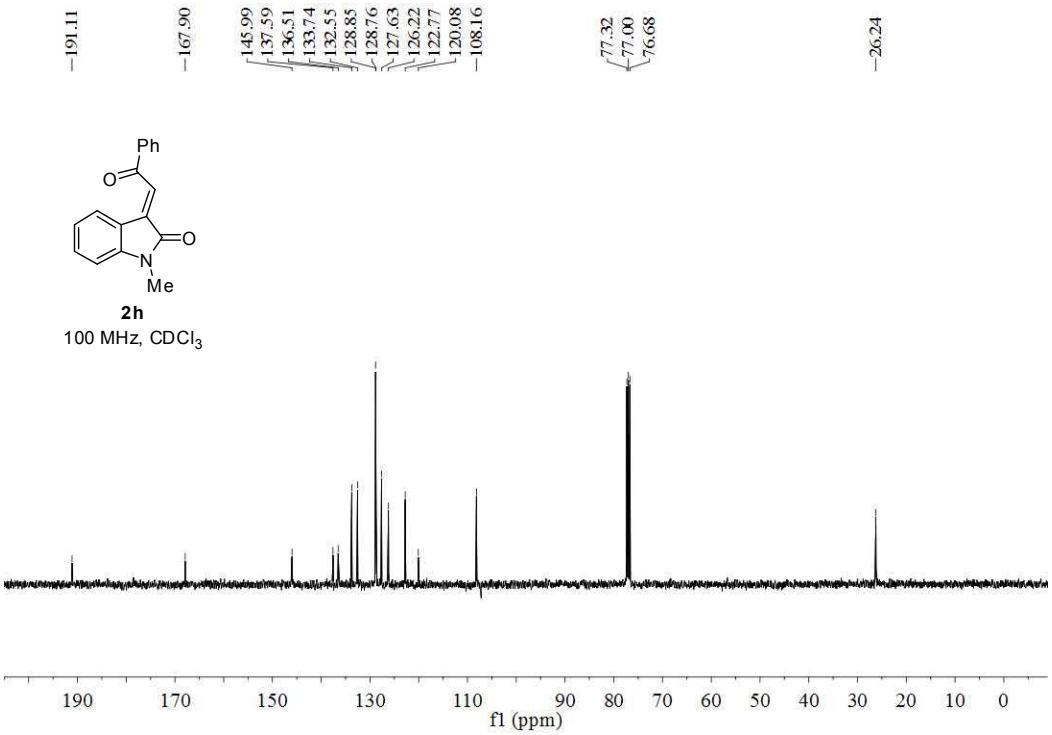

145.36
142.18
135.47
132.24
129.06
128.31
128.20
128.10
127.44
125.90
77.32
77.00
76.68
49.03
25.94
20.98
18.04
1ac
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

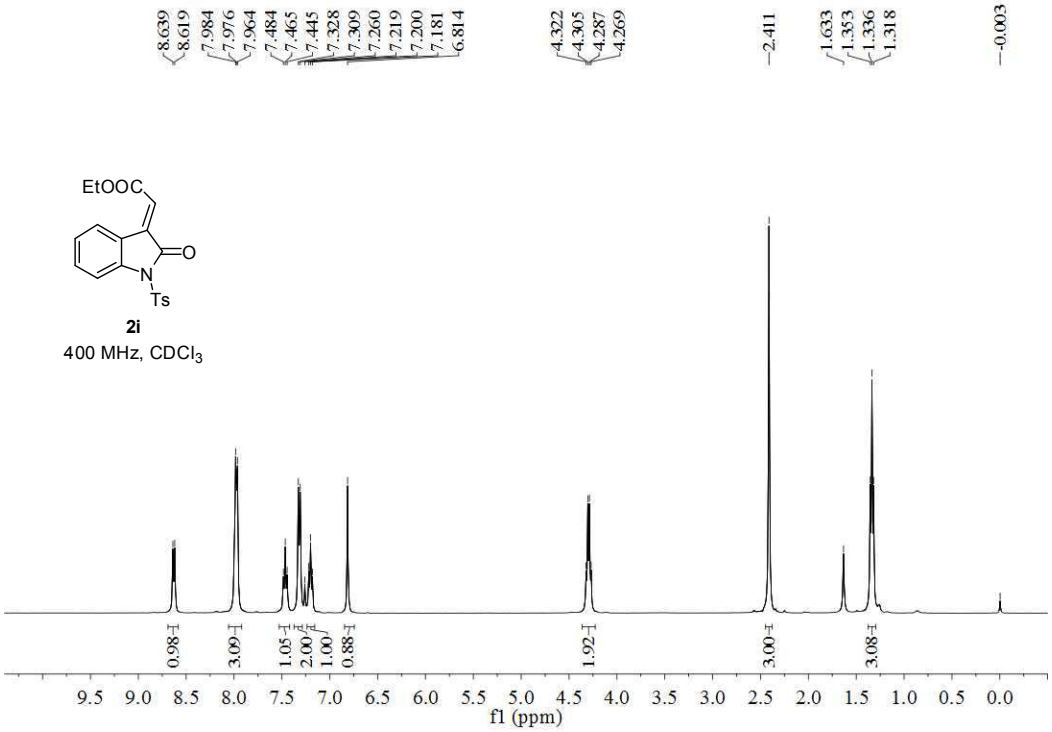
8.270
8.251
8.037
8.019
8.003
7.993
7.768
7.648
7.629
7.611
7.530
7.511
7.492
7.481
7.460
7.441
7.355
7.334
7.260
7.169
7.150
7.132
2.428
1.615
0.000

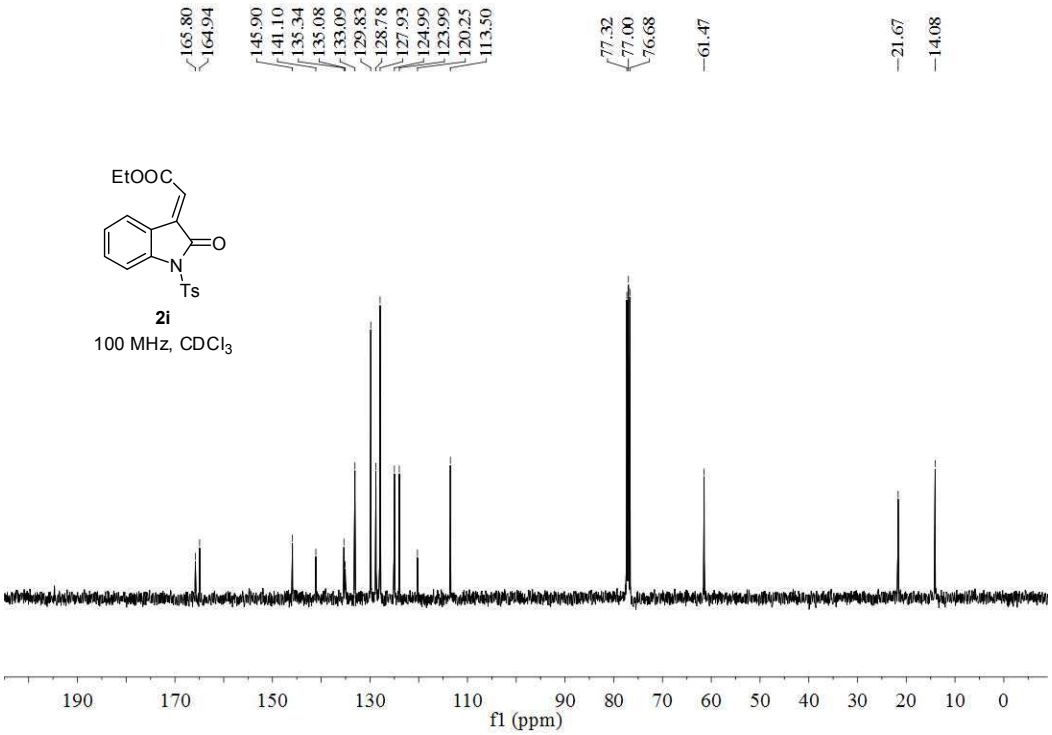

Ph
O
O
N
Ts
2g
400 MHz, CDCl3
0.97
5.24
0.95
1.07
3.16
2.12
1.21
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

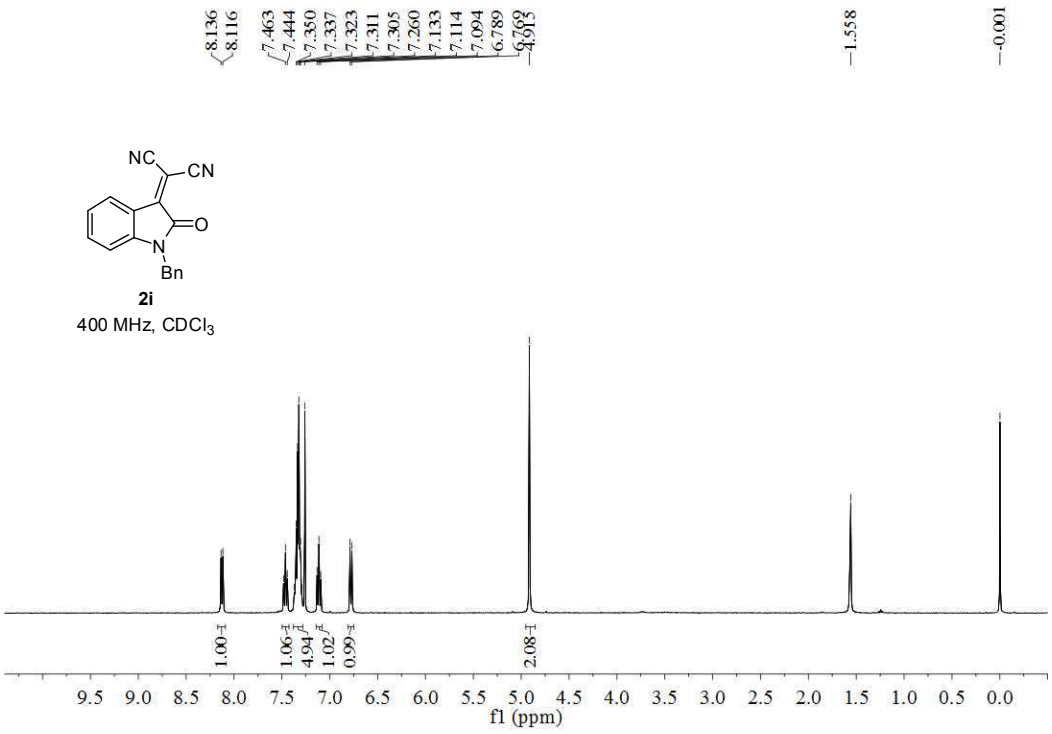

190.79
166.14
145.93
141.09
137.03
134.18
133.82
133.16
129.87
128.99
128.78
128.27
127.99
127.42
124.95
120.44
113.63
77.32
77.00
76.68
21.71
Ph
O
O
N
Ts
2g
100 MHz, CDCl3
220 200 180 160 140 120 100 80 60 40 20 0 -10
f1 (ppm)

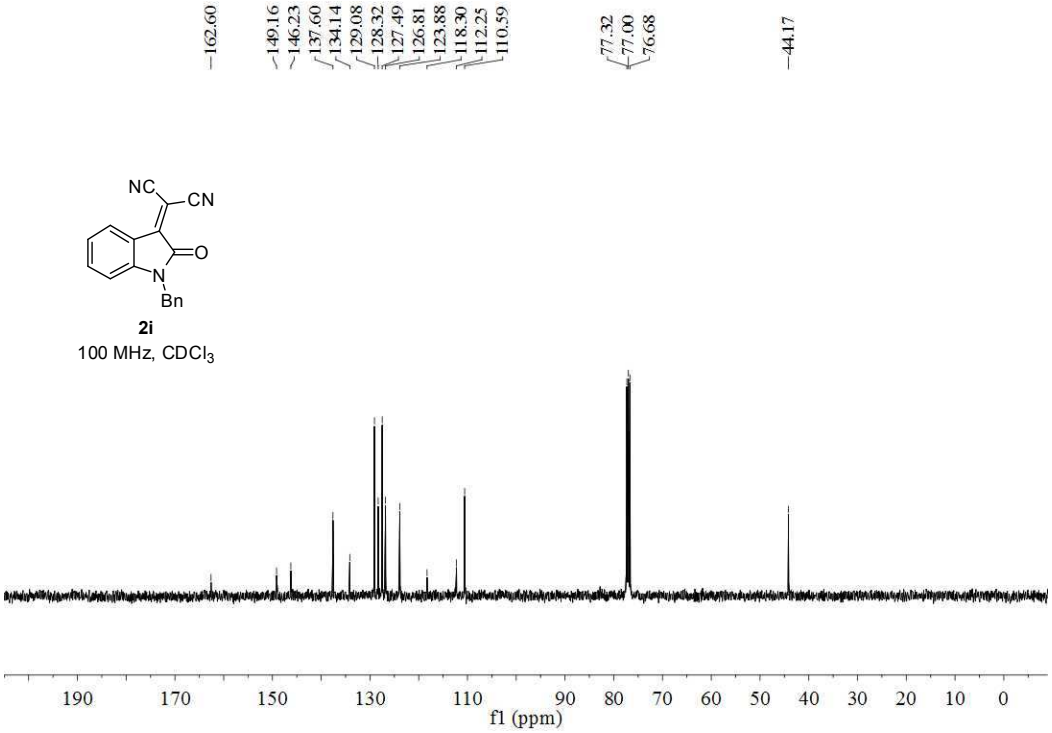

8.316
8.297
8.111
8.093
7.884
7.639
7.621
7.603
7.540
7.521
7.502
7.381
7.362
7.343
7.260
7.037
7.018
6.999
6.809
6.789
3.263
-0.002
Ph
O
O
N
Me
2h
400 MHz, CDCl3
0.95
1.99
0.98
0.99
2.06
1.05
1.01
0.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

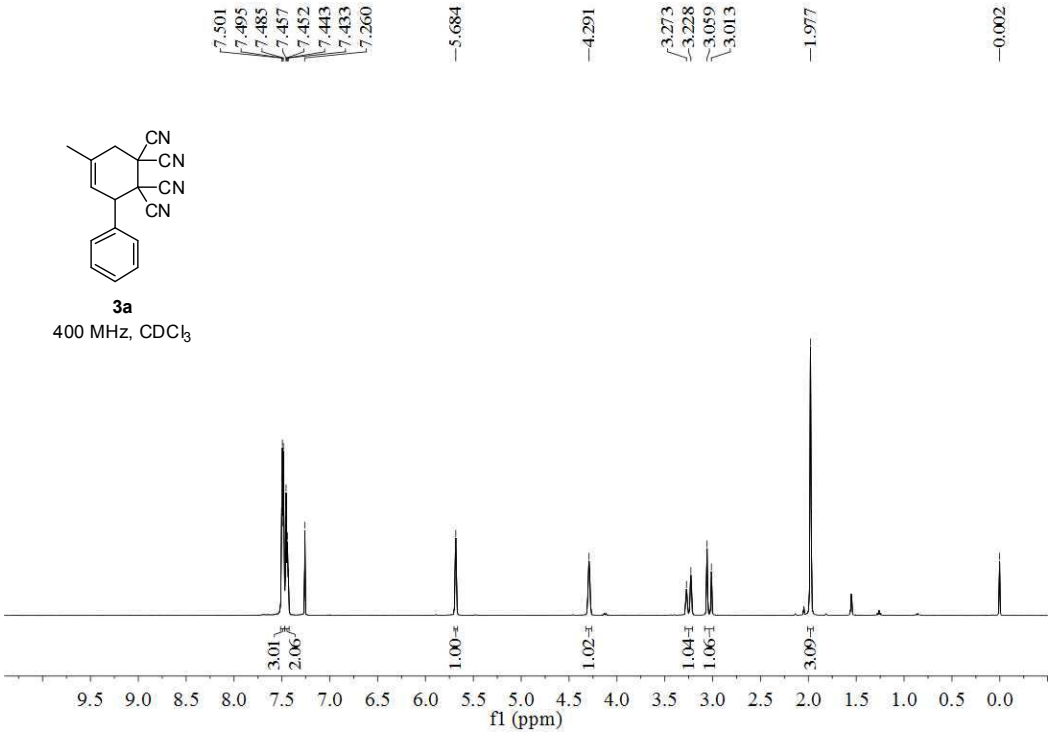

191.11
167.90
145.99
137.59
136.51
133.74
132.55
128.85
128.76
127.63
126.22
122.77
120.08
108.16
77.32
77.00
76.68
26.24
Ph
O
O
N
Me
2h
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

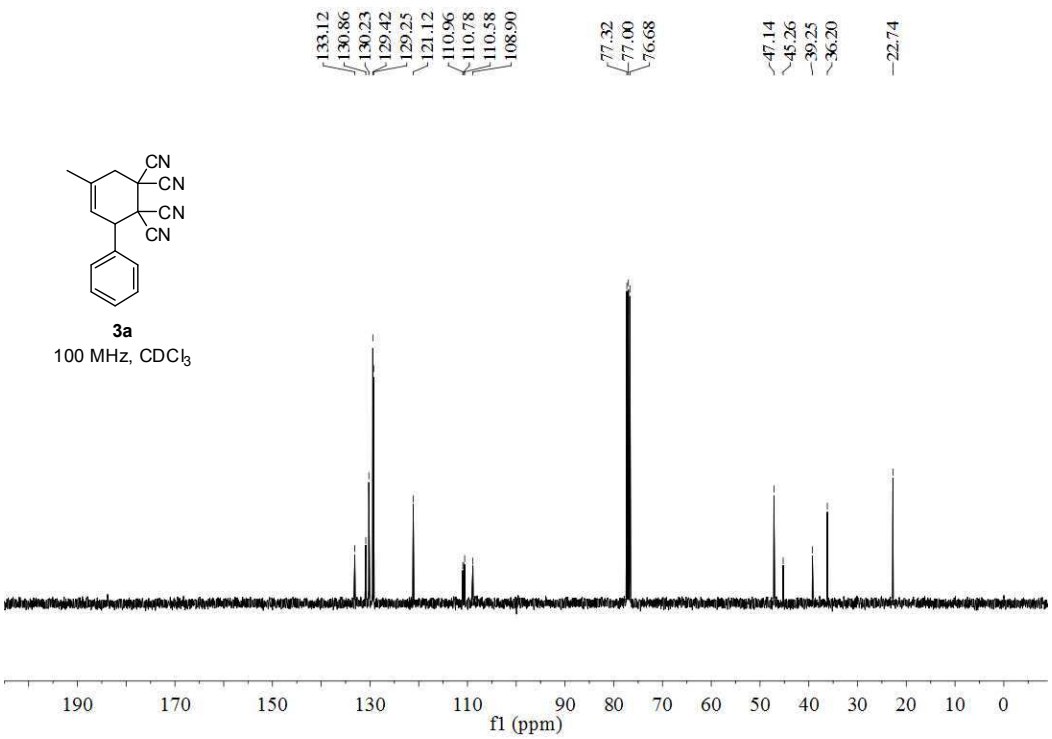

8.639
8.619
7.984
7.976
7.964
7.484
7.465
7.445
7.328
7.309
7.260
7.219
7.200
7.181
6.814
4.322
4.305
4.287
4.269
2.411
1.633
1.353
1.336
1.318
-0.003
EtOOC
O
N
Ts
2i
400 MHz, CDCl3
0.98
3.09
1.05
2.00
1.00
0.88
1.92
3.00
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

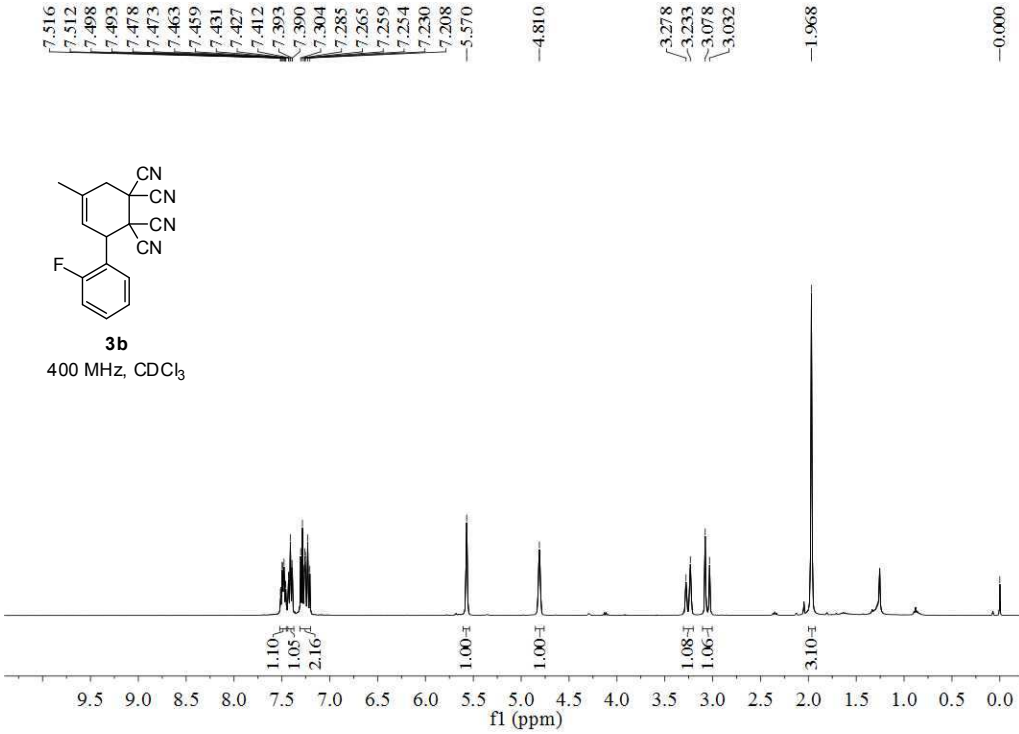

165.80
164.94
145.90
141.10
135.34
135.08
133.09
129.83
128.78
127.93
124.99
123.99
120.25
113.50
77.32
77.00
76.68
61.47
21.67
14.08
EtOOC
O
N
Ts
2i
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.136
8.116
7.463
7.444
7.350
7.337
7.323
7.311
7.305
7.260
7.133
7.114
7.094
6.789
6.769
4.915
1.558
0.001
NC
CN
O
N
Bn
2i
400 MHz, CDCl3
1.00
1.06
4.94
1.02
0.99
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

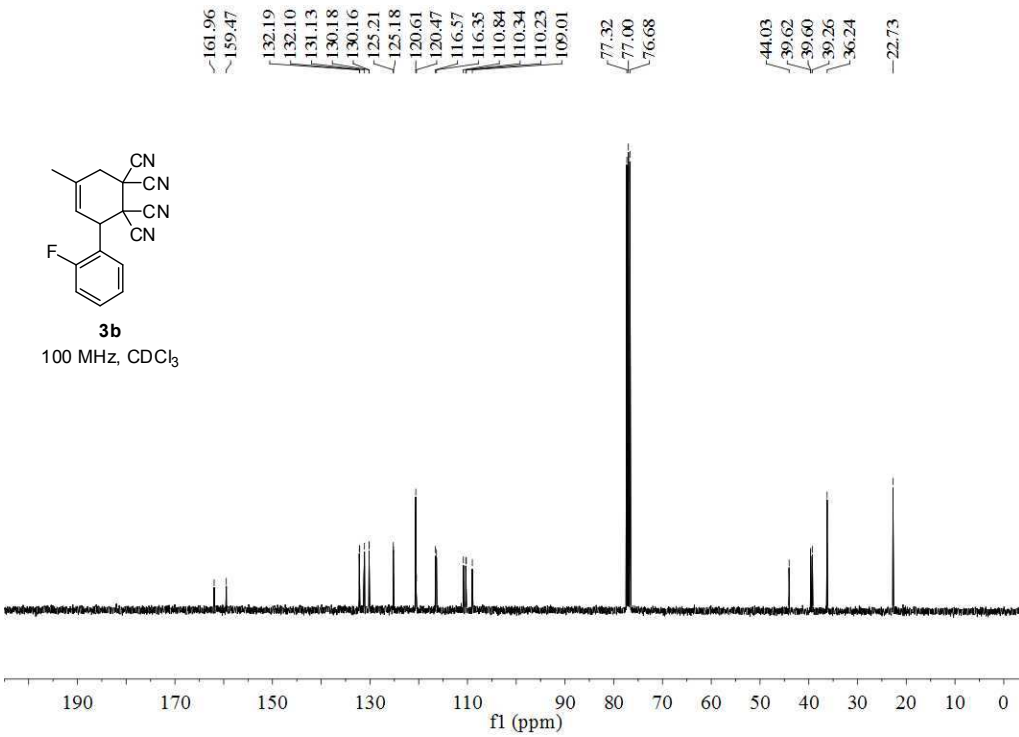

162.60
149.16
146.23
137.60
134.14
129.08
128.32
127.49
126.81
123.88
118.30
112.25
110.59
77.32
77.00
76.68
44.17
NC
CN
O
N
Bn
2i
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.501
7.495
7.485
7.457
7.452
7.443
7.433
7.260
5.684
4.291
3.273
3.228
3.059
3.013
1.977
0.002
CN
CN
CN
CN
3a
400 MHz, CDCl3
3.01
2.06
1.00
1.02
1.04
1.06
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

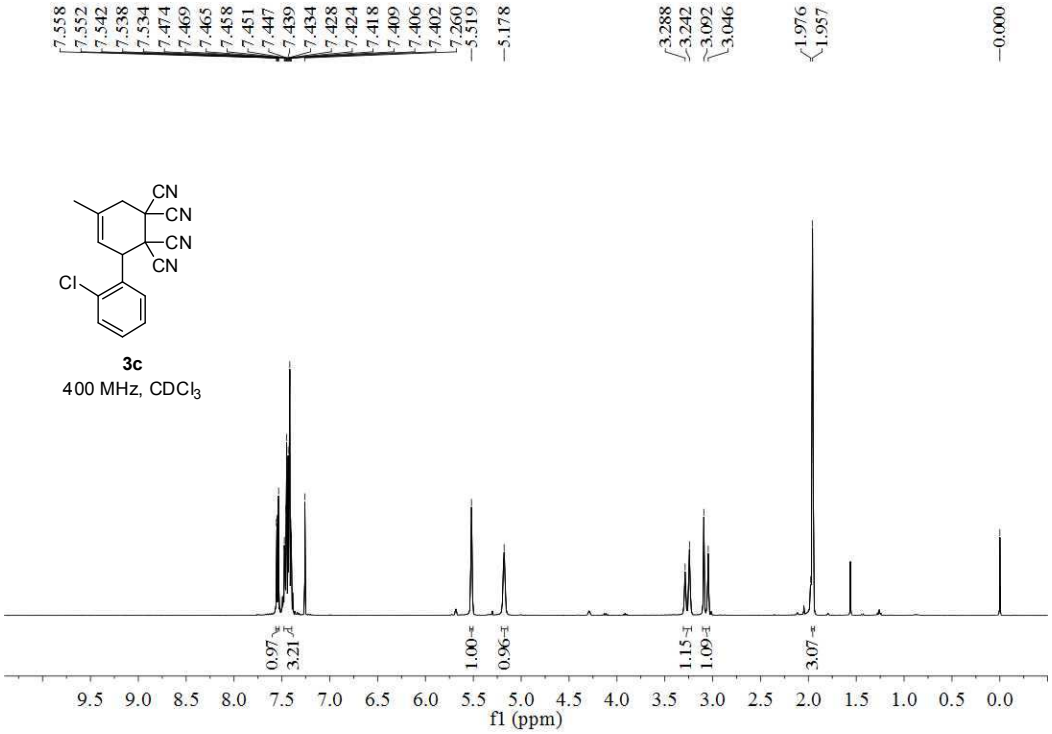

133.12
130.86
130.23
129.42
129.25
121.12
110.96
110.78
110.58
108.90
77.32
77.00
76.68
47.14
45.26
39.25
36.20
22.74
CN
CN
CN
CN
3a
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

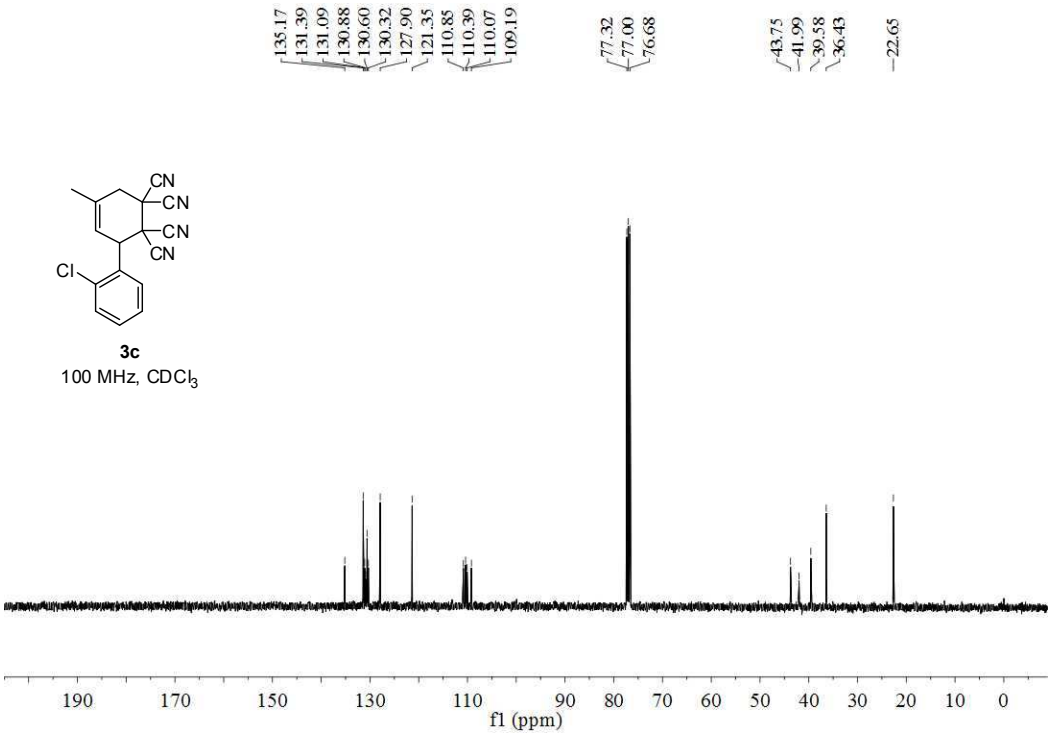


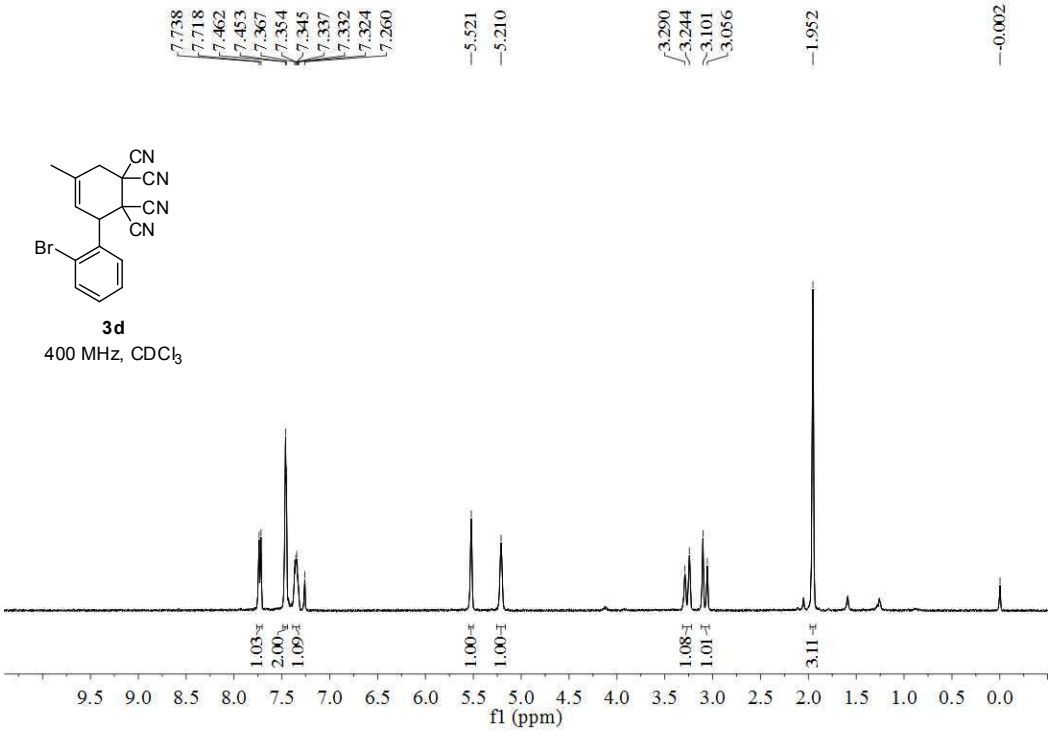
3b
400 MHz, $CDCl_3$

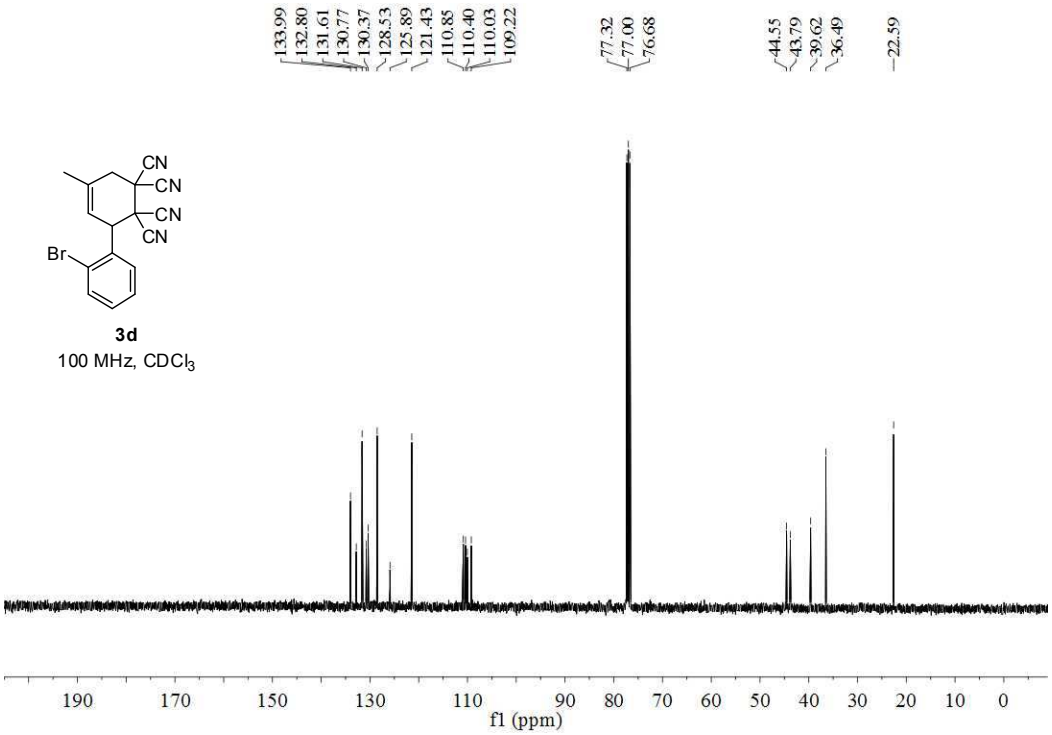


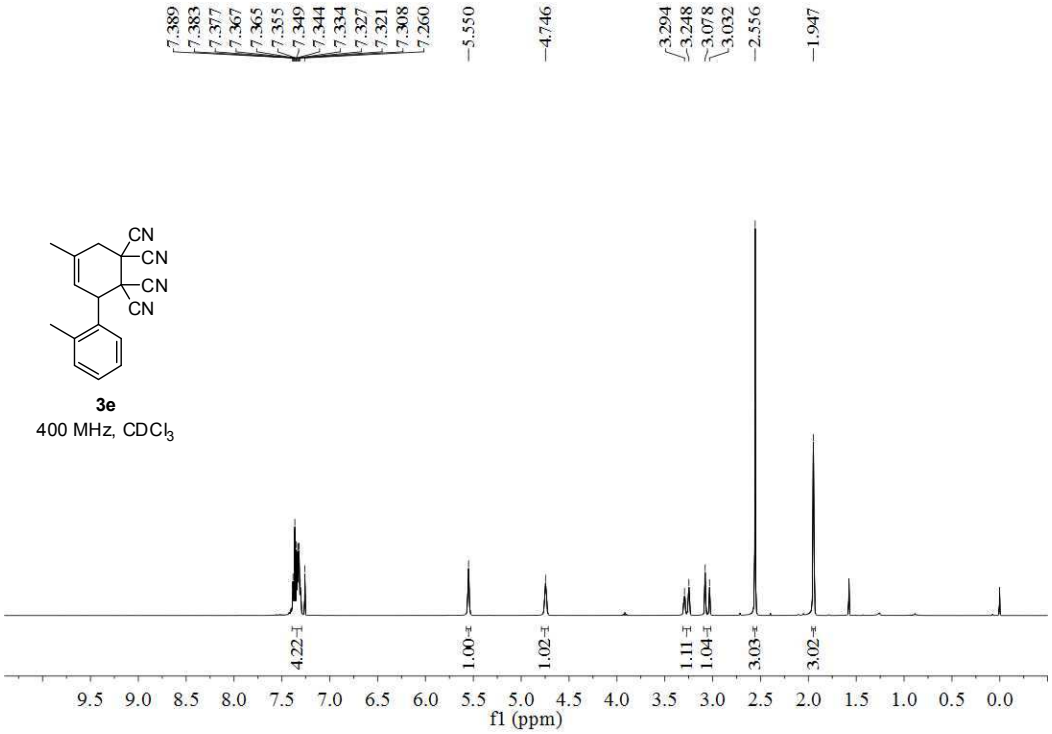
3b
100 MHz, $CDCl_3$


7.558
7.552
7.542
7.538
7.534
7.474
7.469
7.465
7.458
7.451
7.447
7.439
7.434
7.428
7.424
7.418
7.409
7.406
7.402
7.260
5.519
5.178
3.288
3.242
3.092
3.046
1.976
1.957
0.000
CN
CN
CN
CN
Cl
3c
400 MHz, CDCl3
0.97
3.21
1.00
0.96
1.15
1.09
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

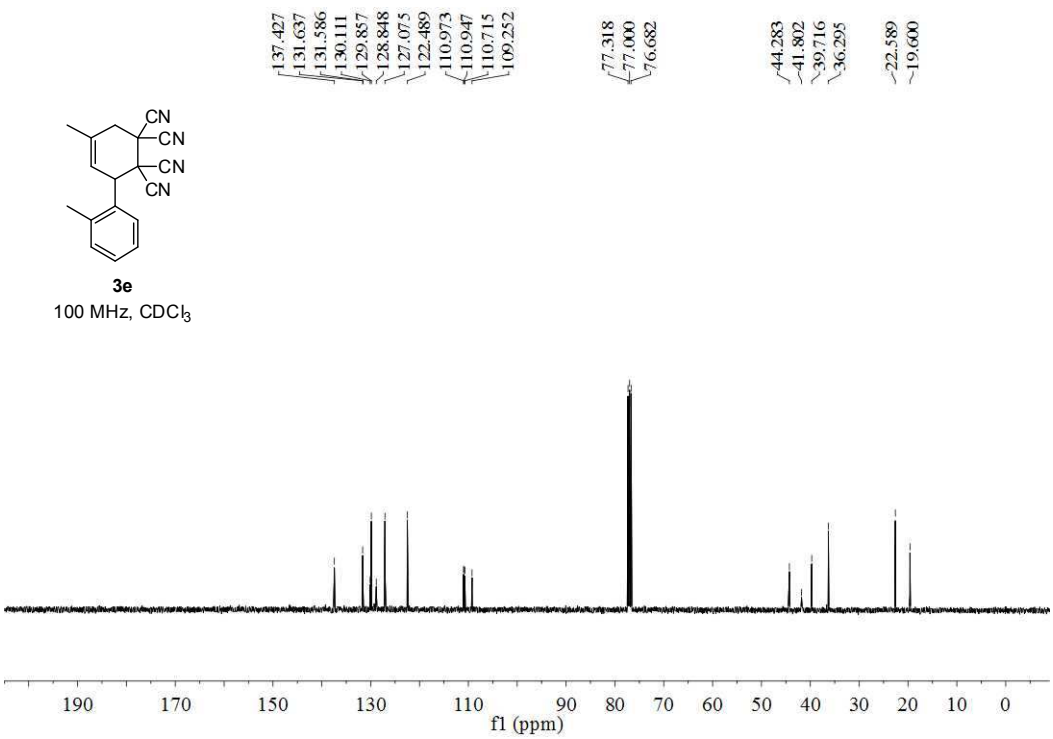

135.17
131.39
131.09
130.88
130.60
130.32
127.90
121.35
110.85
110.39
110.07
109.19
77.32
77.00
76.68
43.75
41.99
39.58
36.43
22.65
CN
CN
CN
CN
Cl
3c
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.738
7.718
7.462
7.453
7.367
7.354
7.345
7.337
7.332
7.324
7.260
5.521
5.210
3.290
3.244
3.101
3.056
1.952
0.002
CN
CN
CN
CN
Br
3d
400 MHz, CDCl3
1.03
2.00
1.09
1.00
1.00
1.08
1.01
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

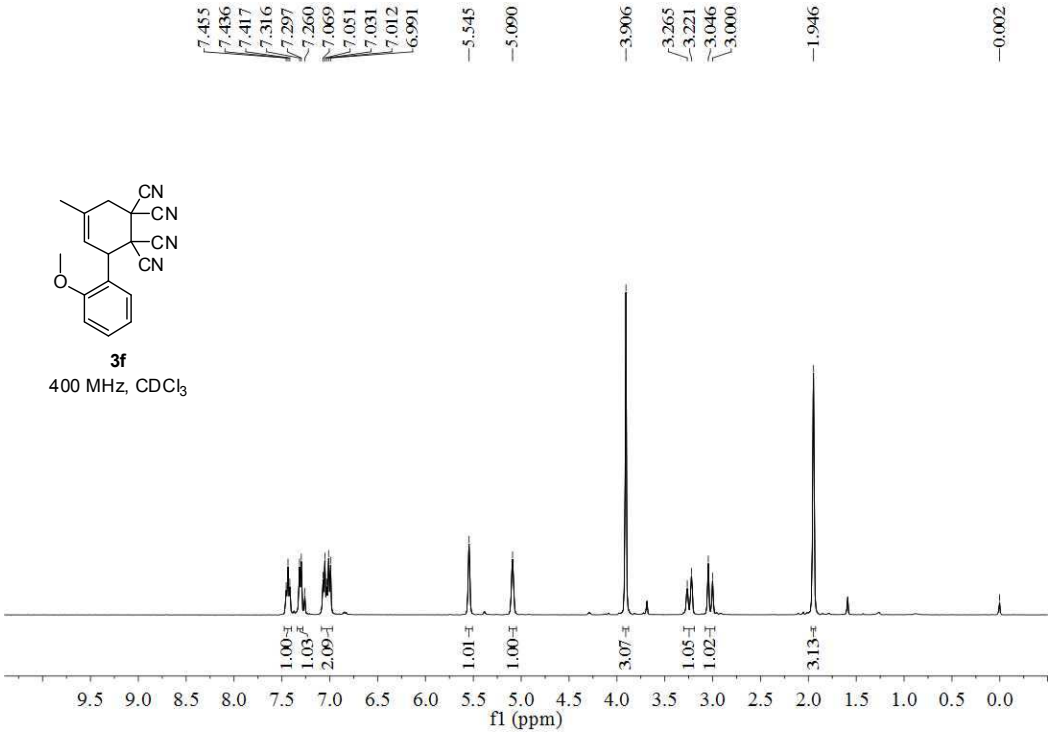

133.99
132.80
131.61
130.77
130.37
128.53
125.89
121.43
110.85
110.40
110.03
109.22
77.32
77.00
76.68
44.55
43.79
39.62
36.49
22.59
CN
CN
CN
CN
Br
3d
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



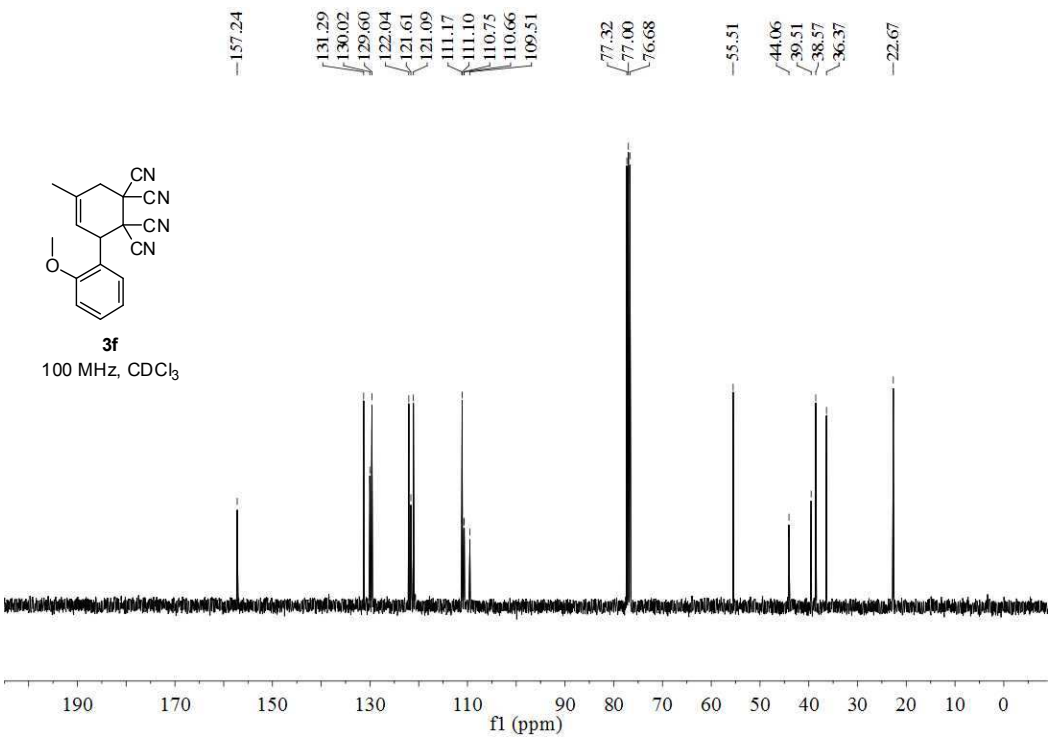
3e
400 MHz, $CDCl_3$



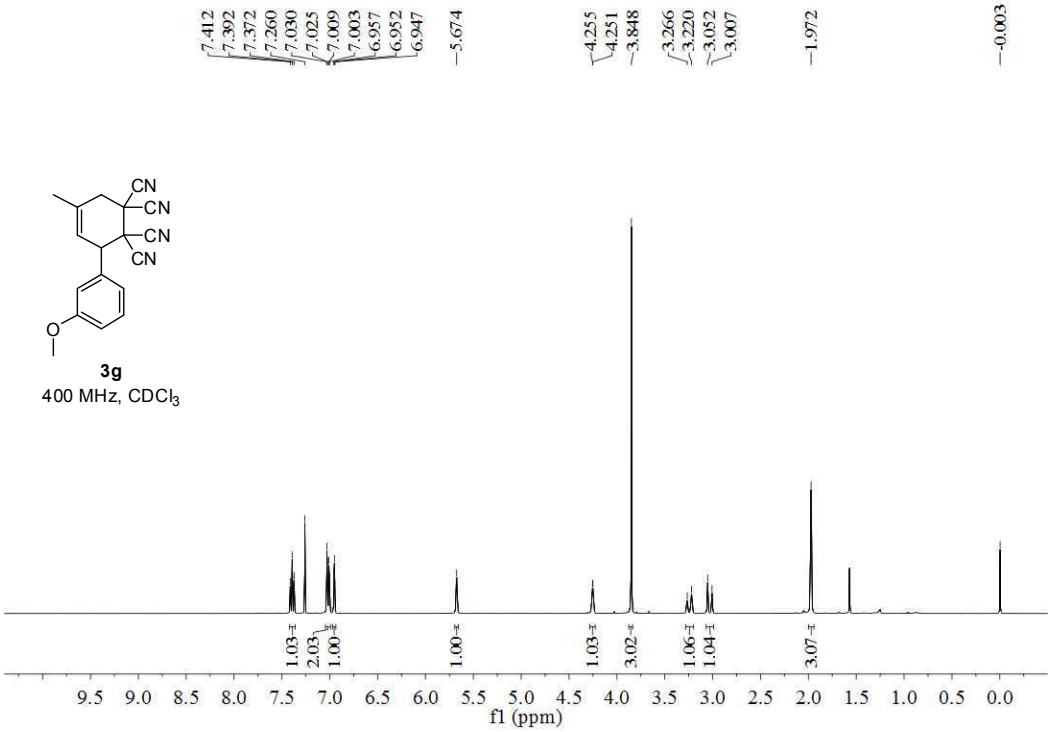
3e
100 MHz, $CDCl_3$

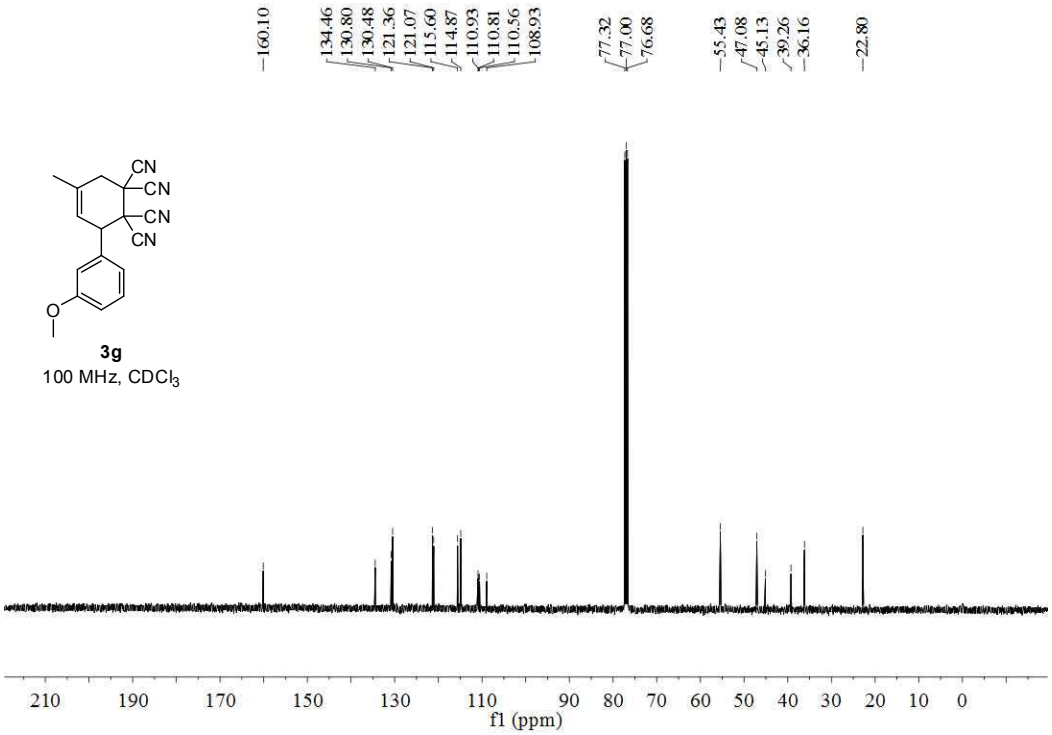


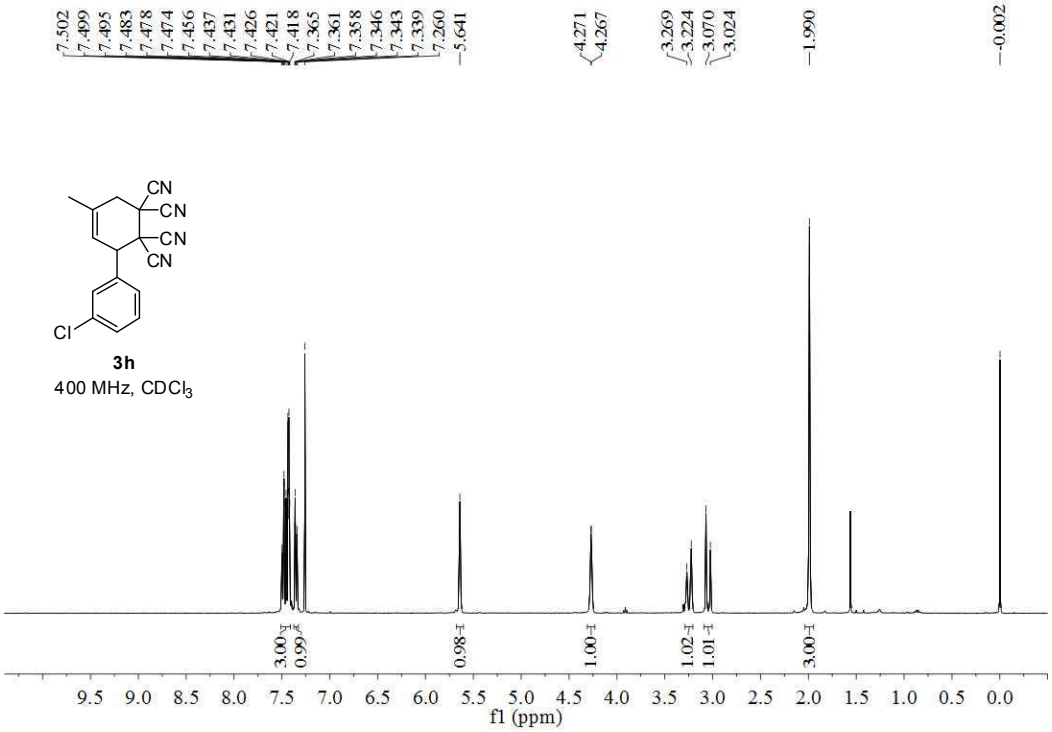
3f
400 MHz, $CDCl_3$



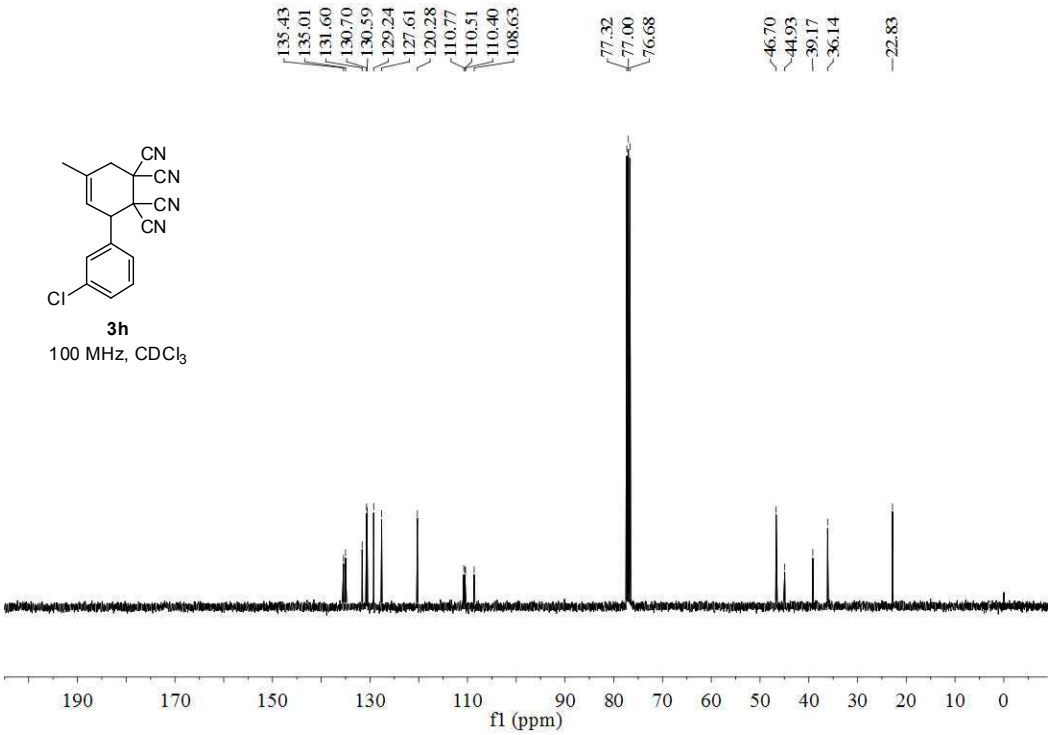
3f
100 MHz, $CDCl_3$


7.412
7.392
7.372
7.260
7.030
7.025
7.009
7.003
6.957
6.952
6.947
5.674
4.255
4.251
3.848
3.266
3.220
3.052
3.007
1.972
0.003
CN
CN
CN
CN
O
3g
400 MHz, CDCl3
1.03
2.03
1.00
1.00
1.03
3.02
1.06
1.04
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

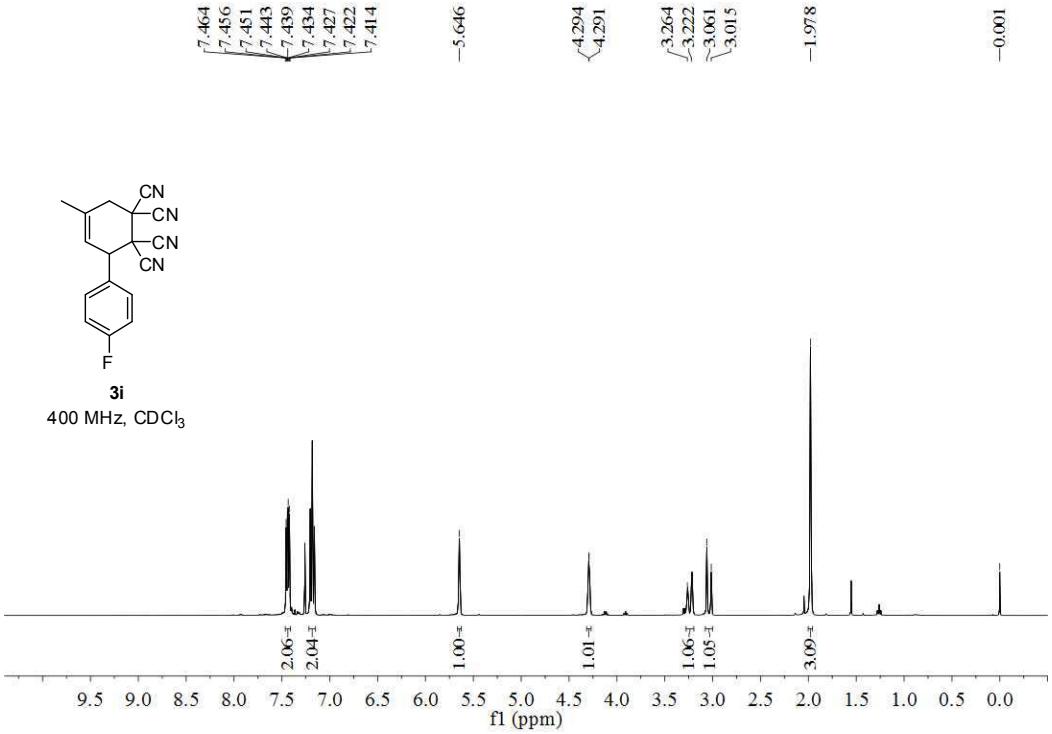

160.10
134.46
130.80
130.48
121.36
121.07
115.60
114.87
110.93
110.81
110.56
108.93
77.32
77.00
76.68
55.43
47.08
45.13
39.26
36.16
22.80
CN
CN
CN
CN
O
3g
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

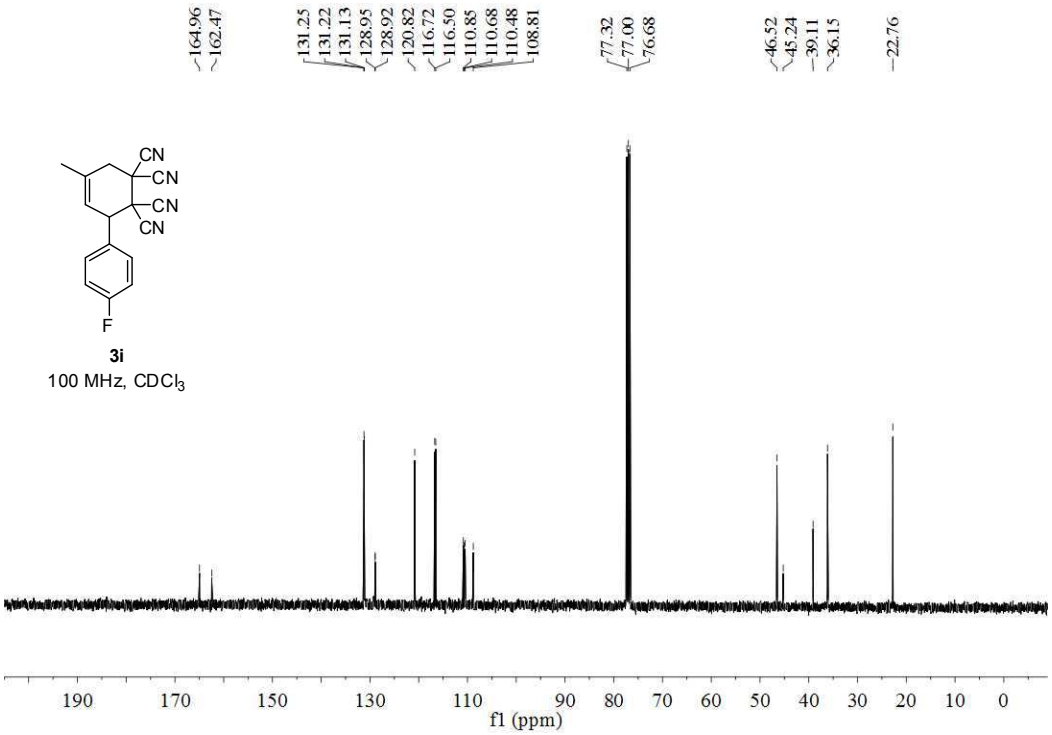


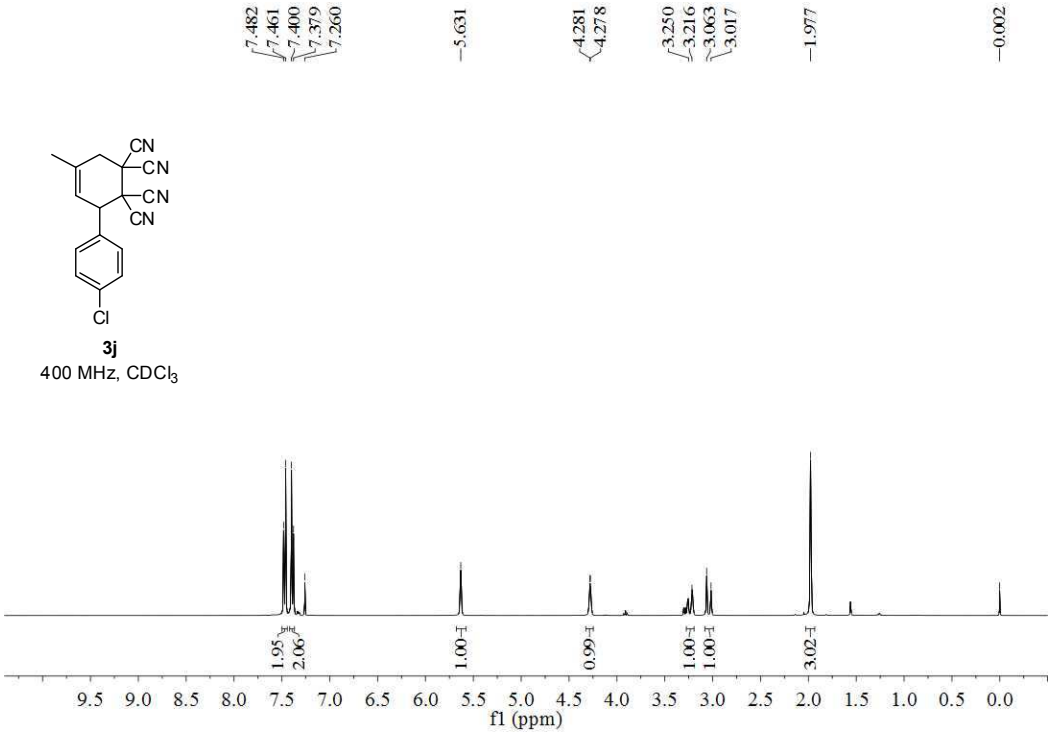
3h
400 MHz, $CDCl_3$



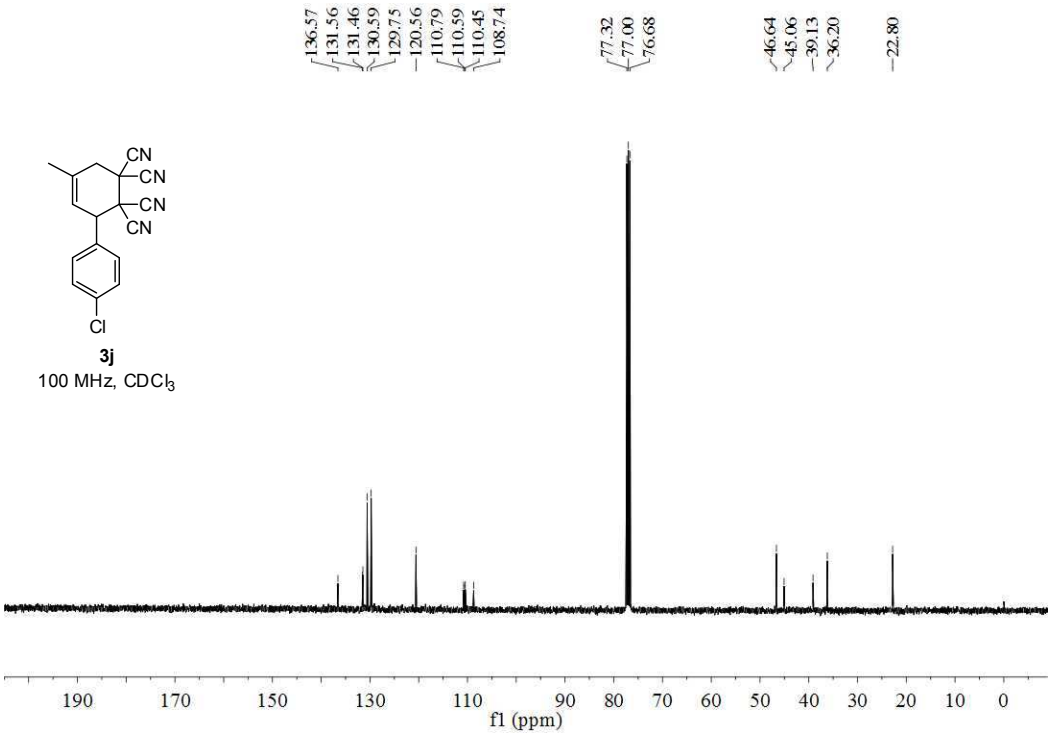
3h
100 MHz, $CDCl_3$


7.464
7.456
7.451
7.443
7.439
7.434
7.427
7.422
7.414
5.646
4.294
4.291
3.264
3.222
3.061
3.015
1.978
0.001
CN
CN
CN
CN
F
3i
400 MHz, CDCl3
2.06
2.04
1.00
1.01
1.06
1.05
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

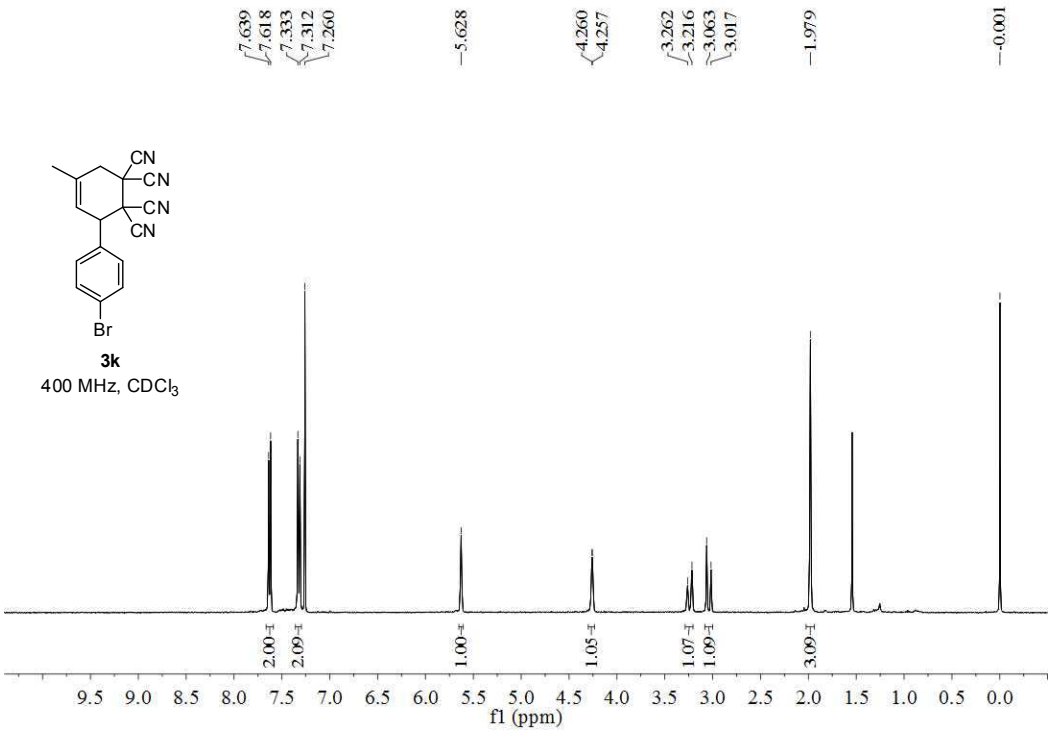

164.96
162.47
131.25
131.22
131.13
128.95
128.92
120.82
116.72
116.50
110.85
110.68
110.48
108.81
77.32
77.00
76.68
46.52
45.24
39.11
36.15
22.76
CN
CN
CN
CN
F
3i
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



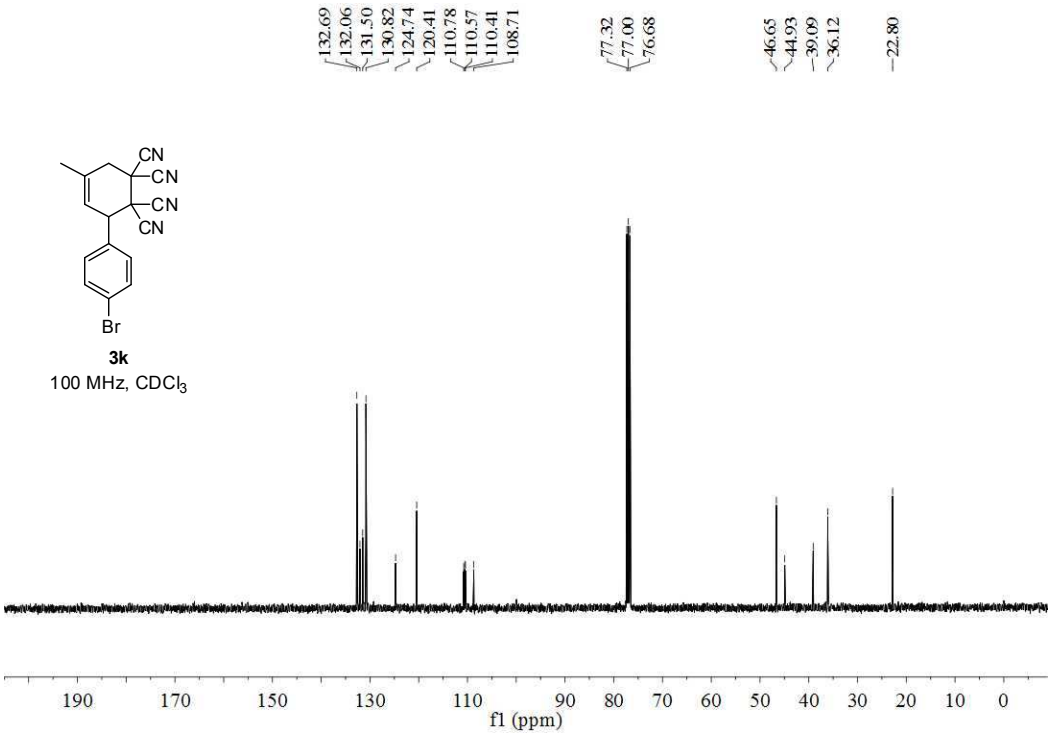
3j
400 MHz, $CDCl_3$



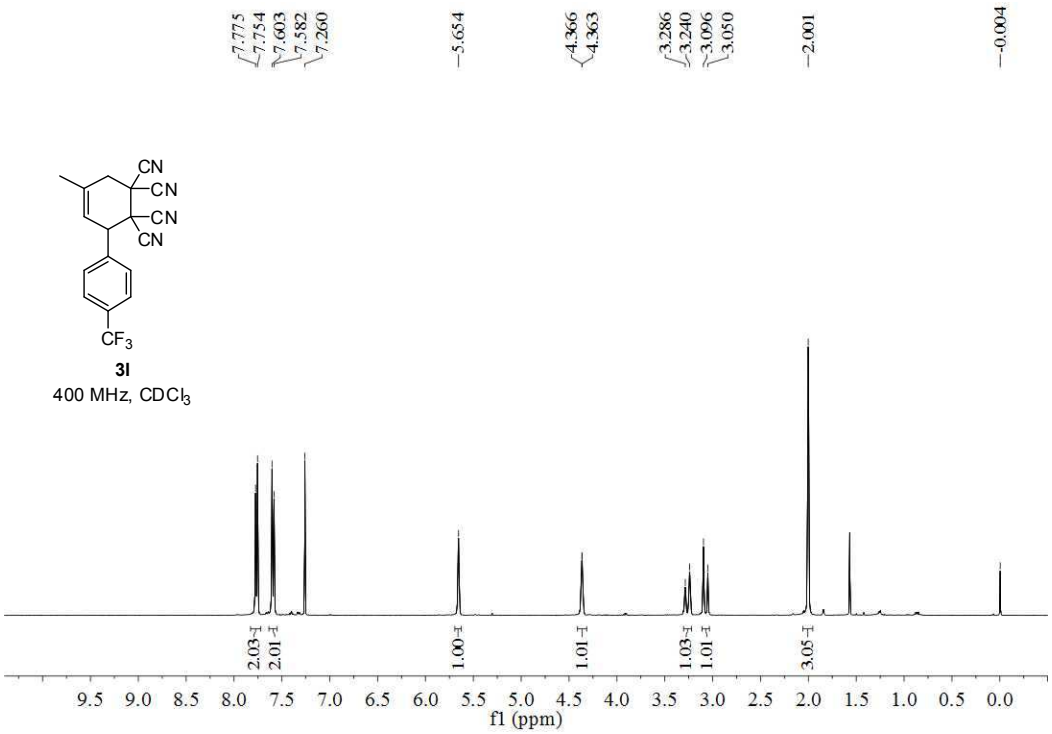
3j
100 MHz, $CDCl_3$

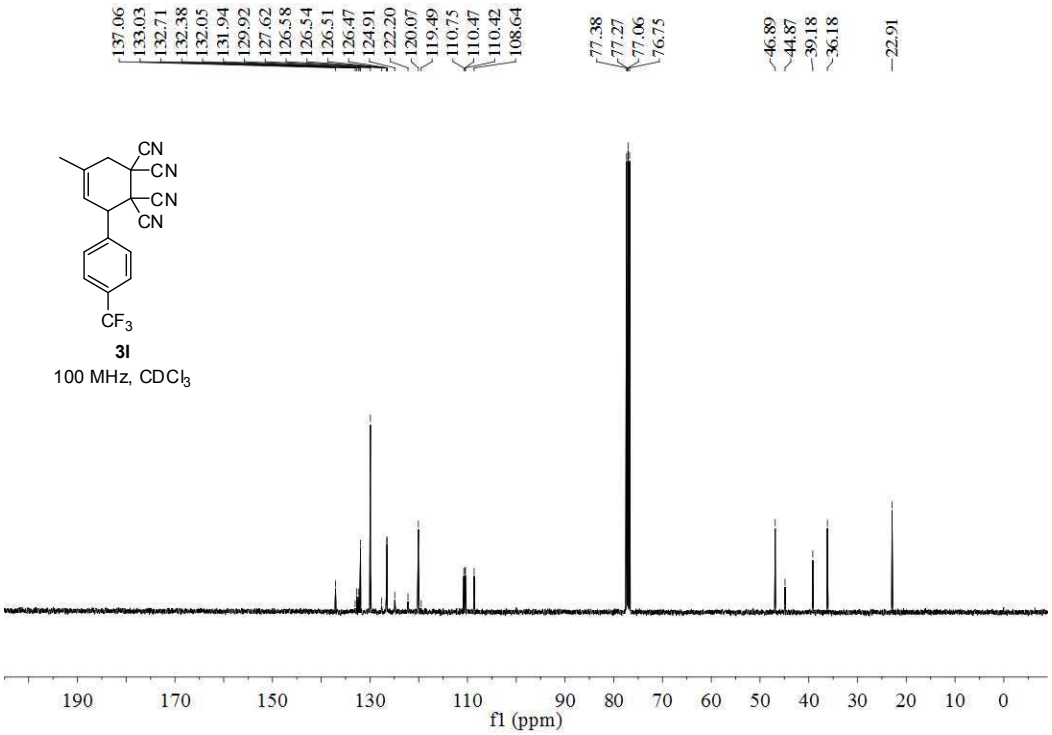


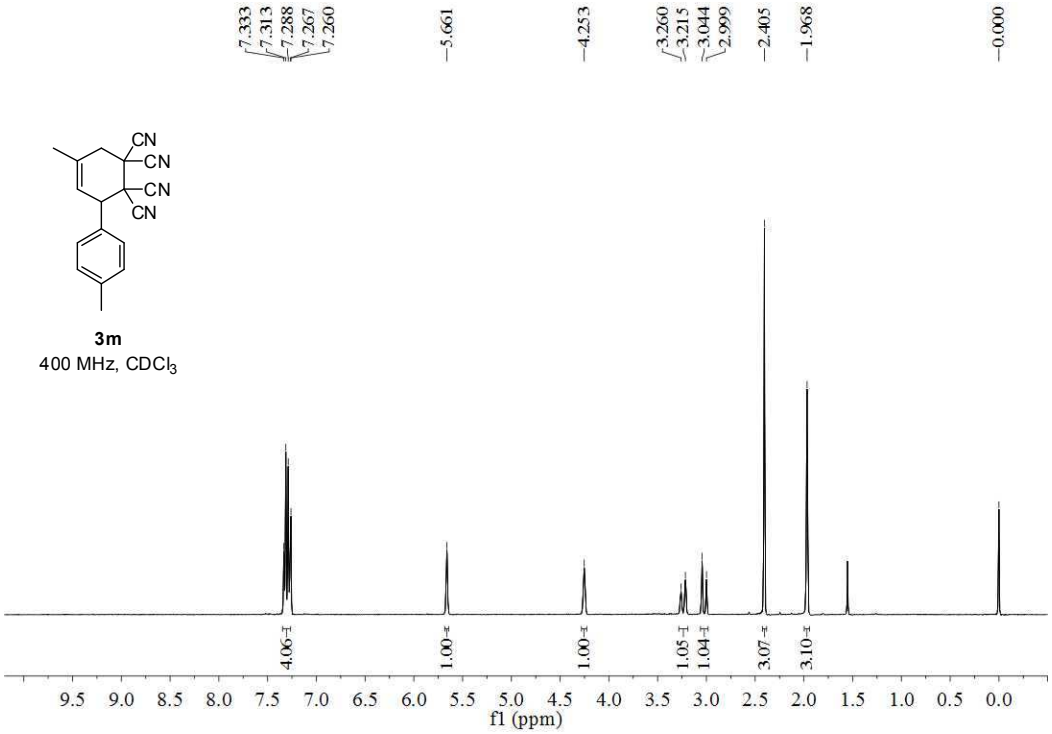
3k
400 MHz, $CDCl_3$



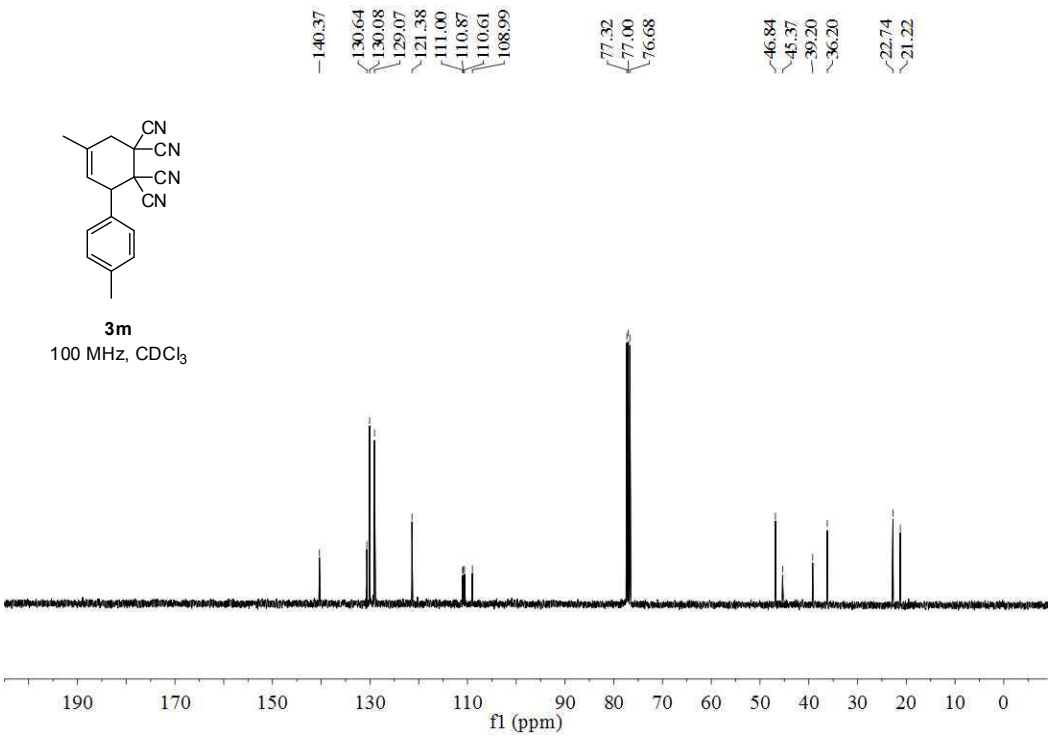
3k
100 MHz, $CDCl_3$


7.775
7.754
7.603
7.582
7.260
5.654
4.366
4.363
3.286
3.240
3.096
3.050
2.001
0.004
CN
CN
CN
CN
CF3
3l
400 MHz, CDCl3
2.03
2.01
1.00
1.01
1.03
1.01
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

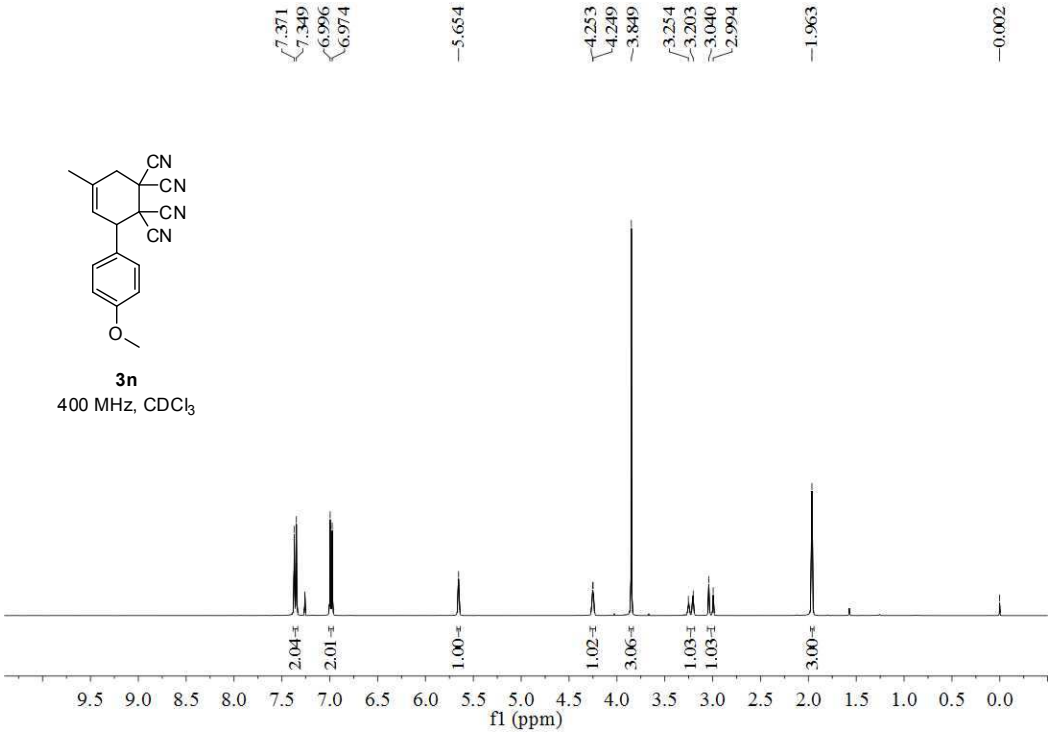

137.06
133.03
132.71
132.38
132.05
131.94
129.92
127.62
126.58
126.54
126.51
126.47
124.91
122.20
120.07
119.49
110.75
110.47
110.42
108.64
77.38
77.27
77.06
76.75
46.89
44.87
39.18
36.18
22.91
CN
CN
CN
CN
CF3
3l
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



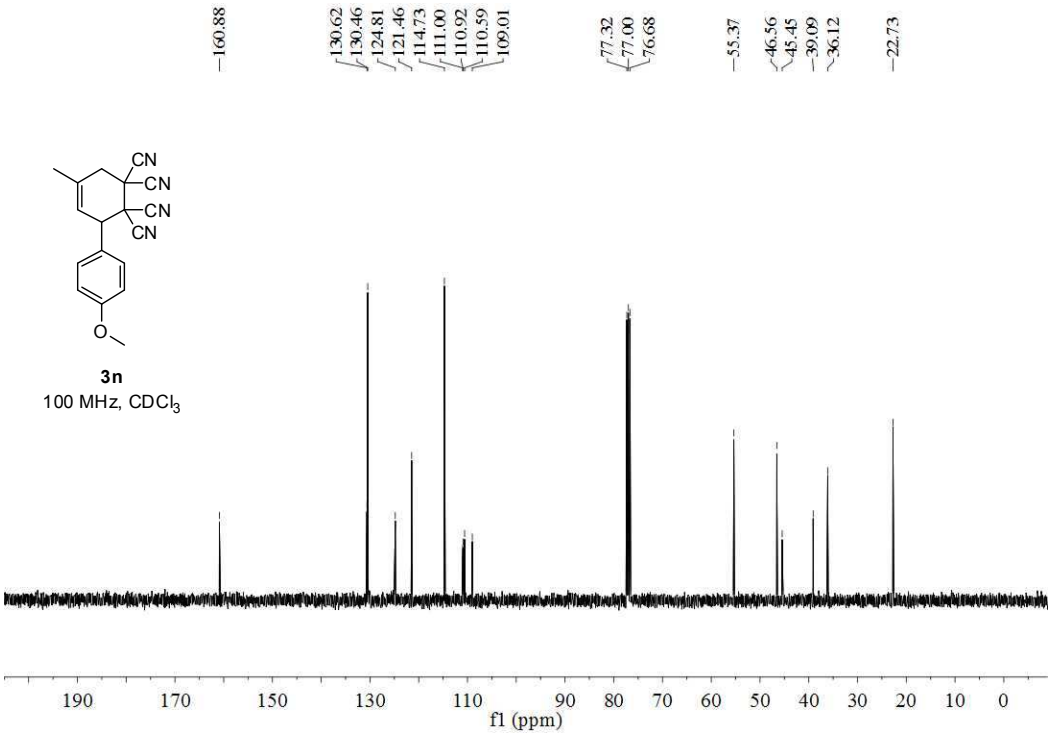
3m
400 MHz, $CDCl_3$



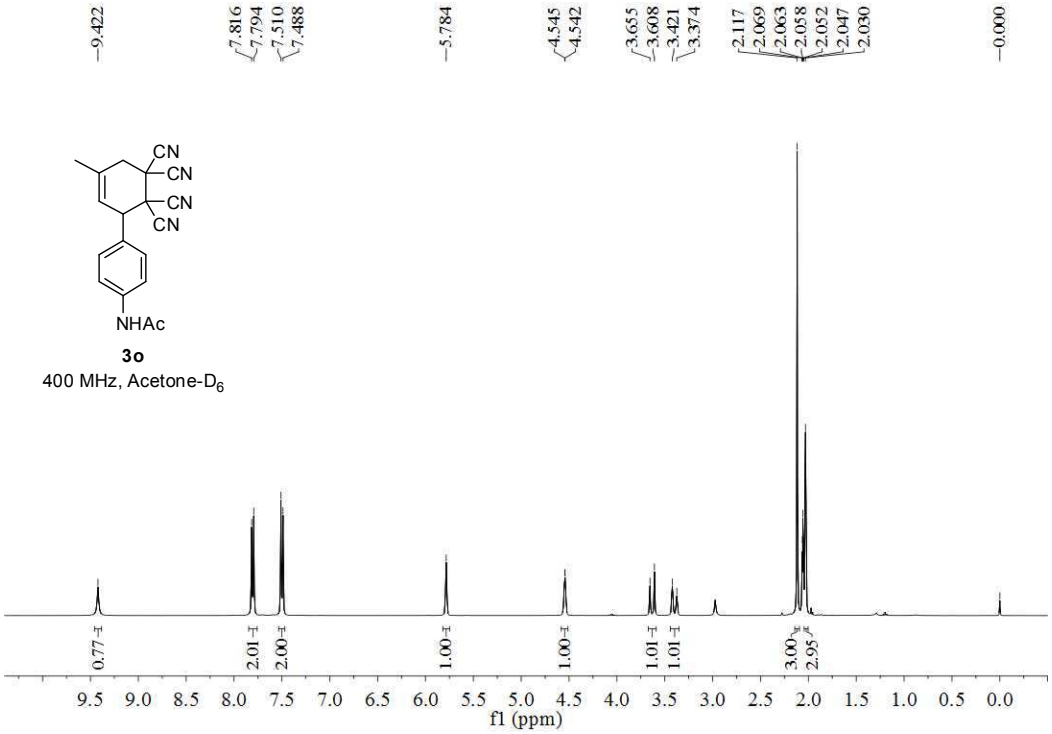
3m
100 MHz, $CDCl_3$



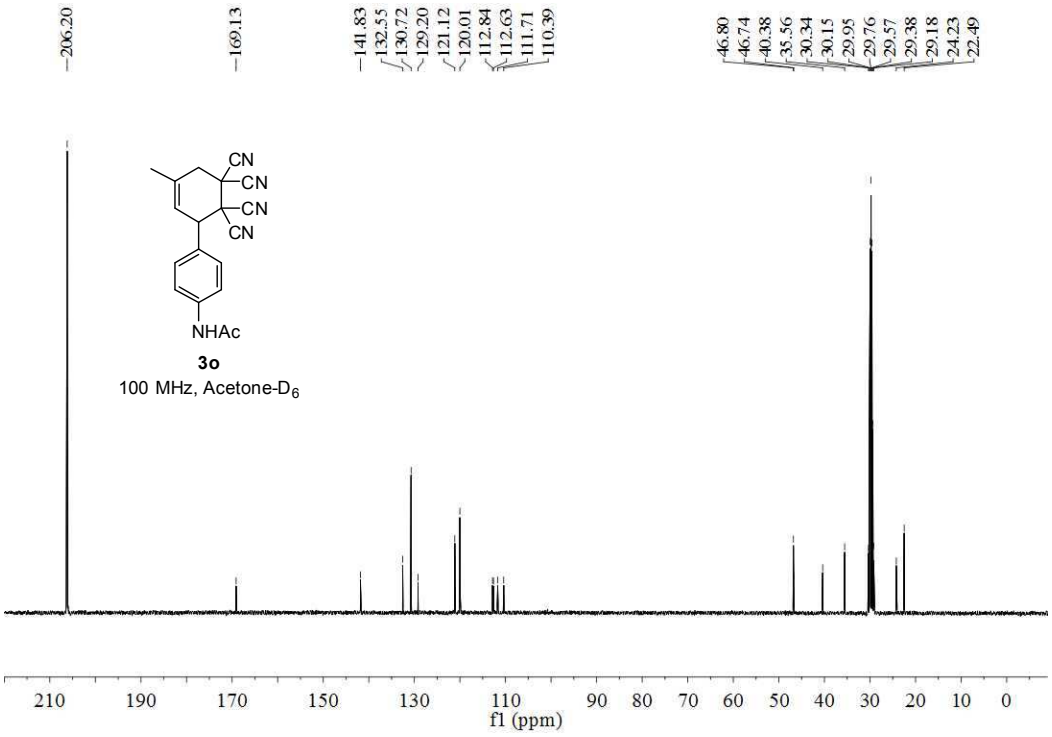
3n
400 MHz, $CDCl_3$



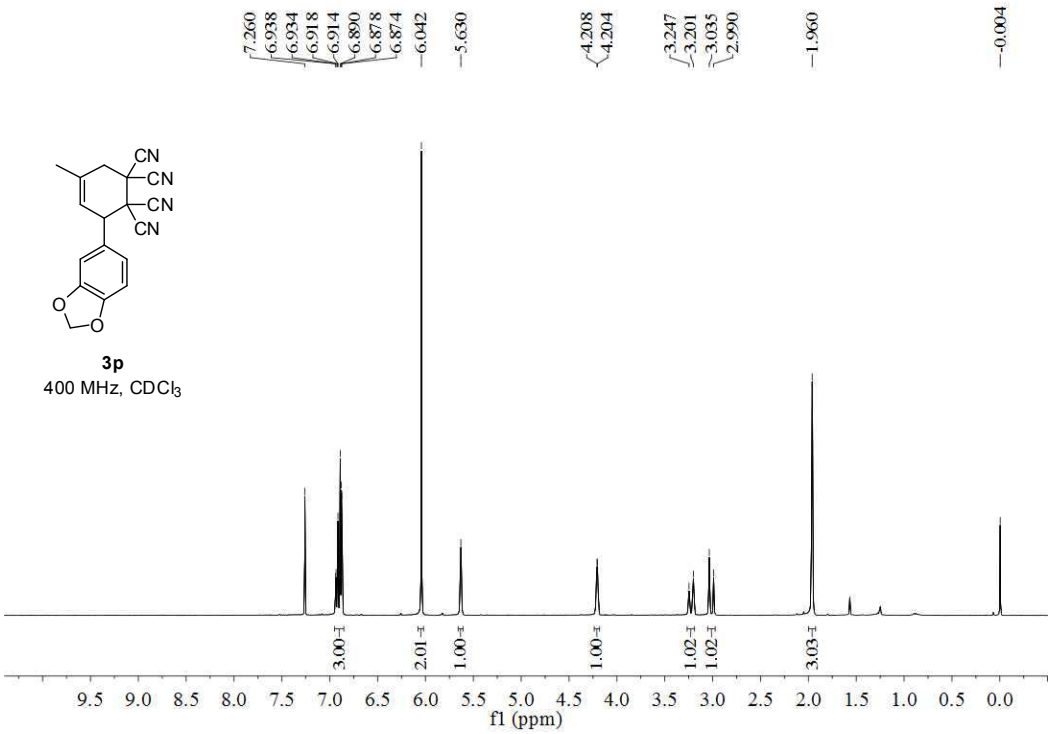
3n
100 MHz, $CDCl_3$

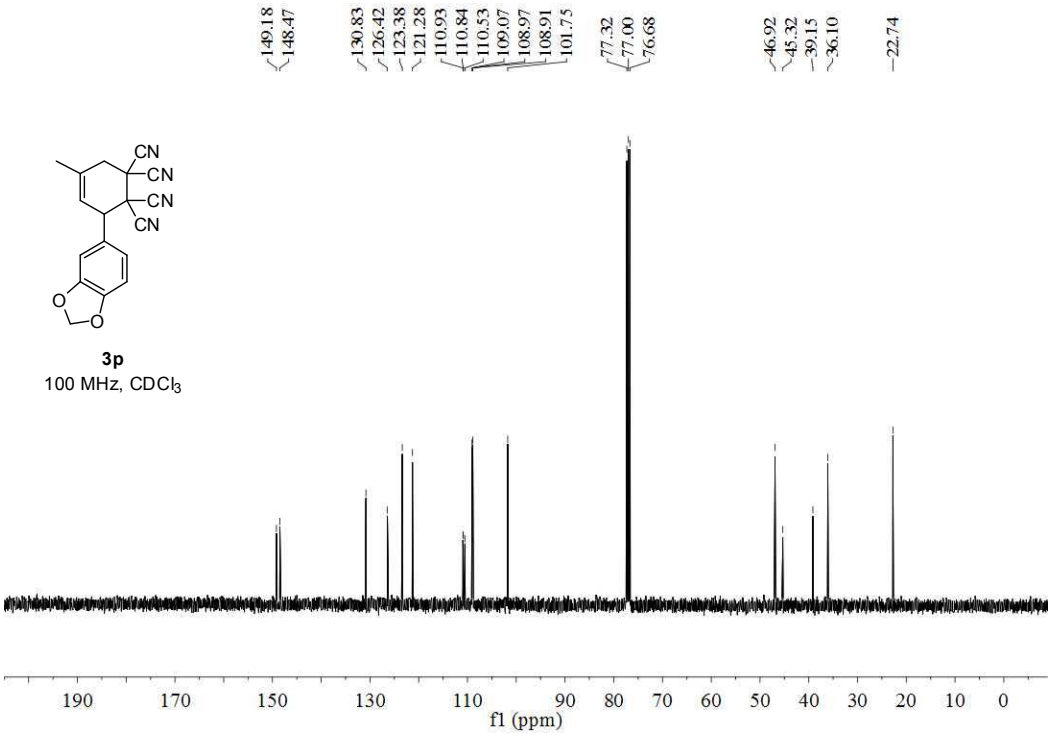


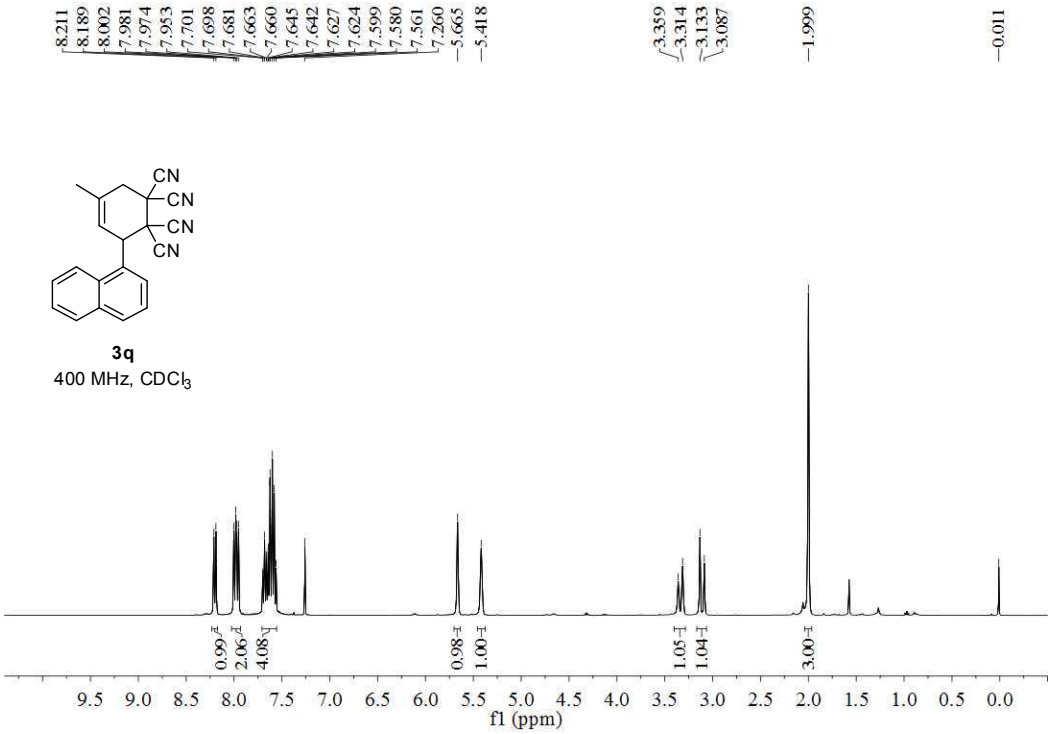
3o
400 MHz, Acetone-D_6

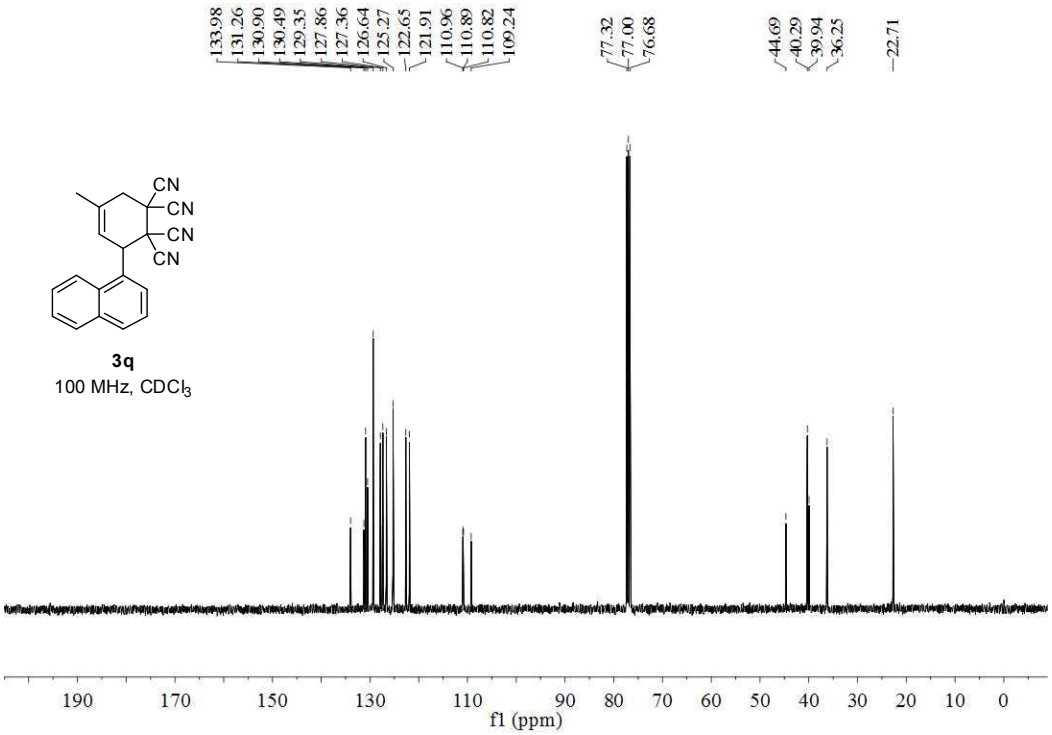


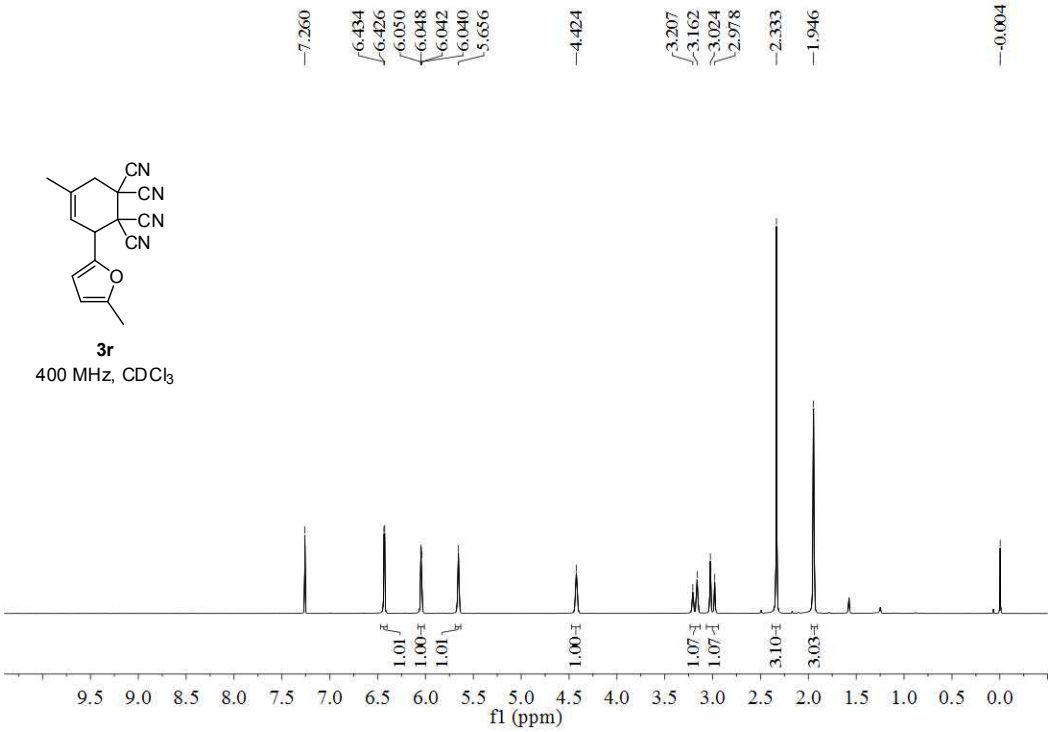
3o
100 MHz, Acetone-D_6

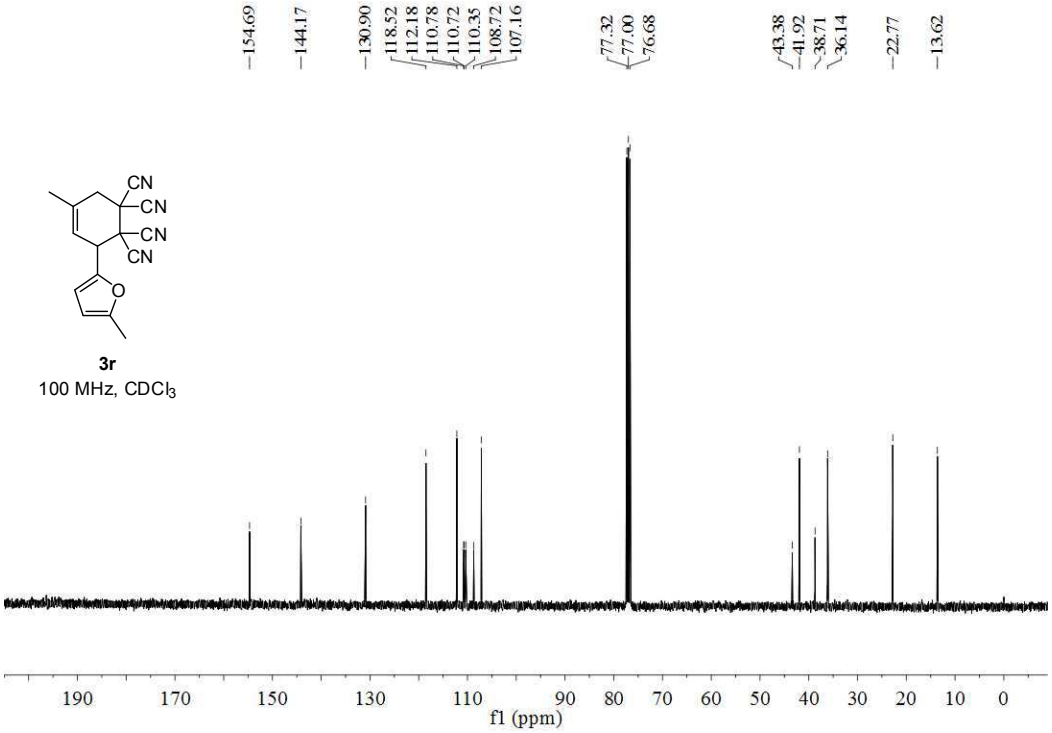

7.260
6.938
6.934
6.918
6.914
6.890
6.878
6.874
6.042
5.630
4.208
4.204
3.247
3.201
3.035
2.990
1.960
0.004
CN
CN
CN
CN
O
O
3p
400 MHz, CDCl3
3.00
2.01
1.00
1.00
1.02
1.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

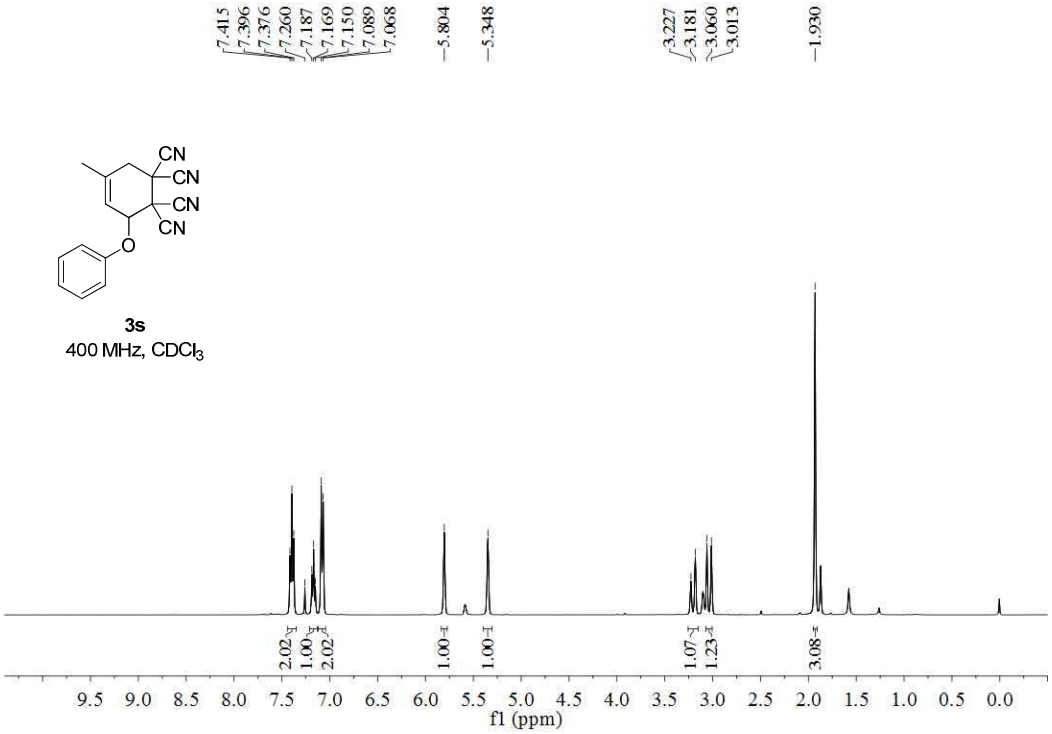

149.18
148.47
130.83
126.42
123.38
121.28
110.93
110.84
110.53
109.07
108.97
108.91
101.75
77.32
77.00
76.68
46.92
45.32
39.15
36.10
22.74
CN
CN
CN
CN
O
O
3p
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.211
8.189
8.002
7.981
7.974
7.953
7.701
7.698
7.681
7.663
7.660
7.645
7.642
7.627
7.624
7.599
7.580
7.561
7.260
5.665
5.418
3.359
3.314
3.133
3.087
1.999
0.011
CN
CN
CN
CN
3q
400 MHz, CDCl3
0.99
2.06
4.08
0.98
1.00
1.05
1.04
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

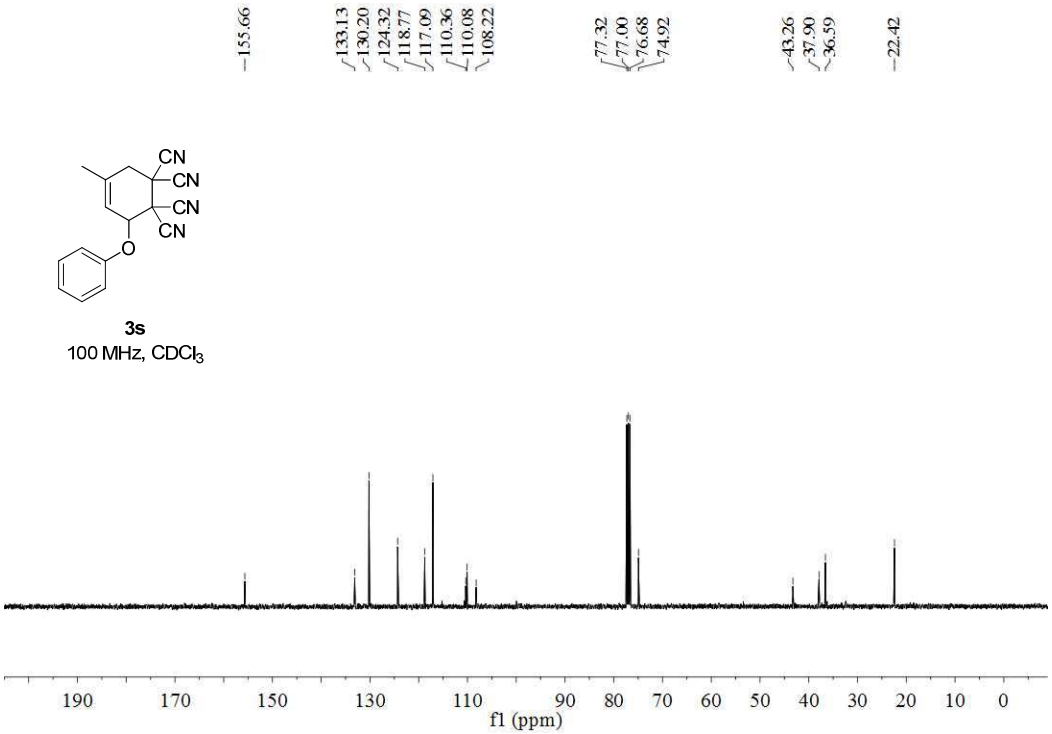

133.98
131.26
130.90
130.49
129.35
127.86
127.36
126.64
125.27
122.65
121.91
110.96
110.89
110.82
109.24
77.32
77.00
76.68
44.69
40.29
39.94
36.25
22.71
CN
CN
CN
CN
3q
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
6.434
6.426
6.050
6.048
6.042
6.040
5.656
4.424
3.207
3.162
3.024
2.978
2.333
1.946
0.004
CN
CN
CN
CN
O
3r
400 MHz, CDCl3
1.01
1.00
1.01
1.00
1.07
1.07
3.10
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

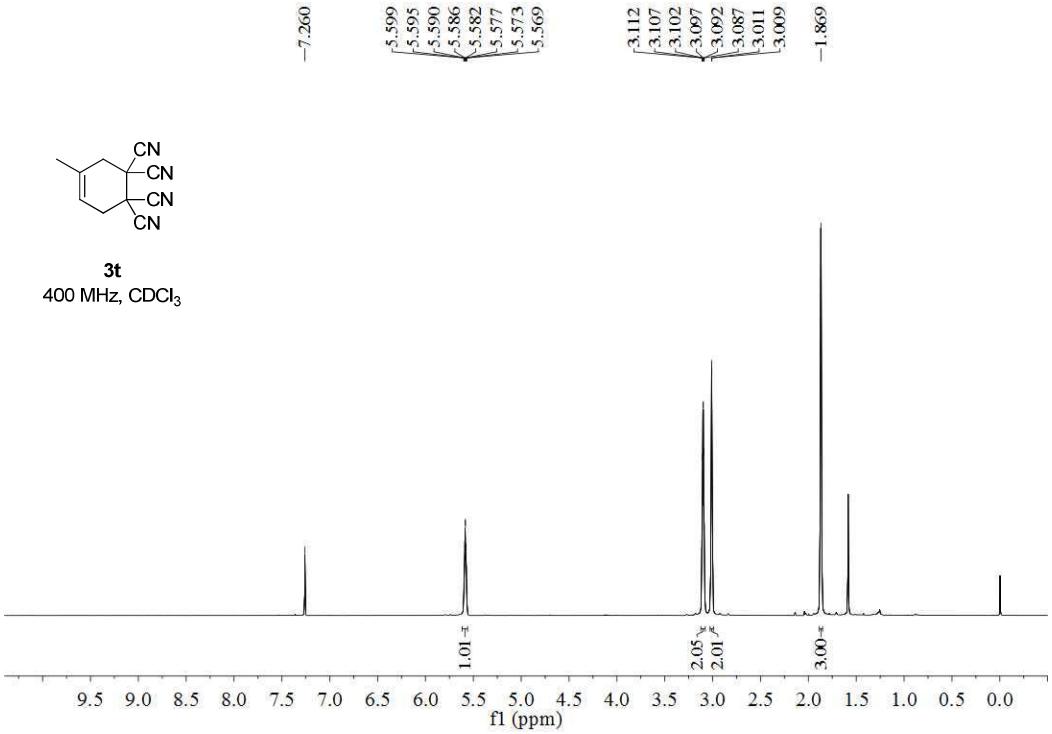

154.69
144.17
130.90
118.52
112.18
110.78
110.72
110.35
108.72
107.16
77.32
77.00
76.68
43.38
41.92
38.71
36.14
22.77
13.62
CN
CN
CN
CN
O
3r
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



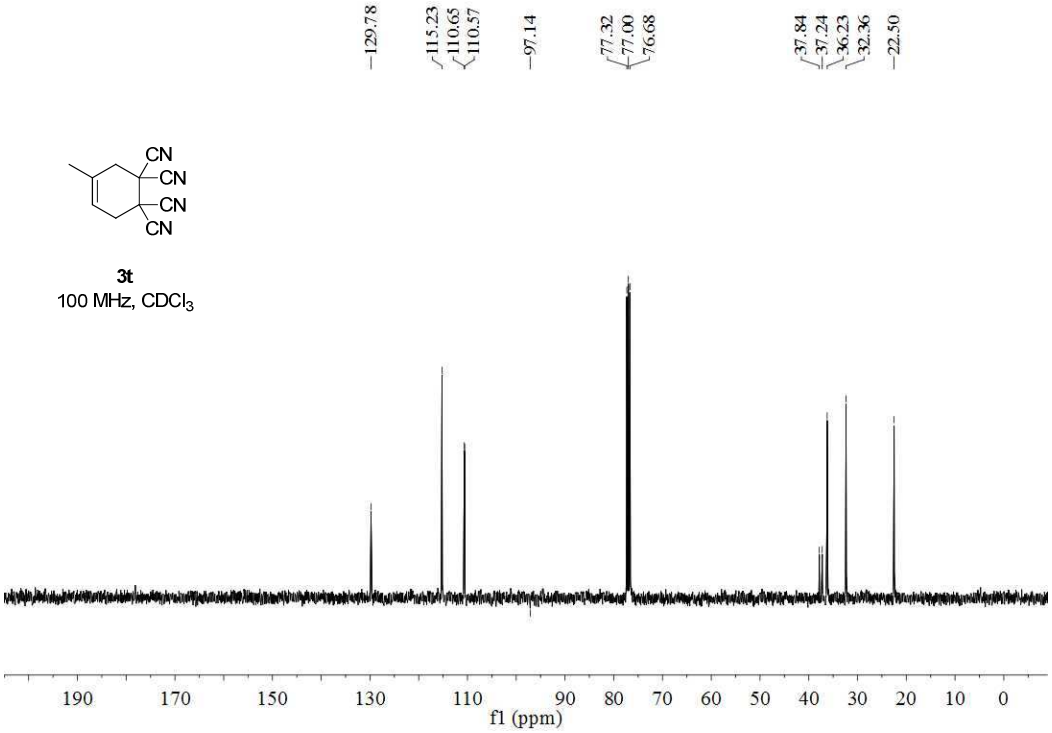
3s
400 MHz, $CDCl_3$



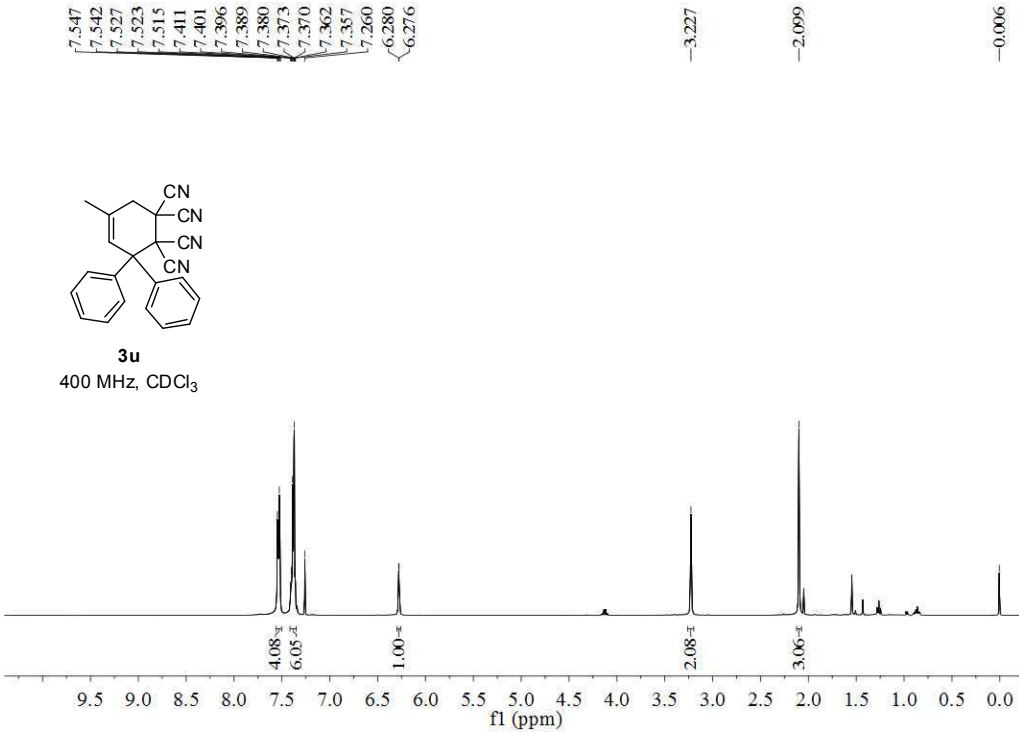
3s
100 MHz, $CDCl_3$



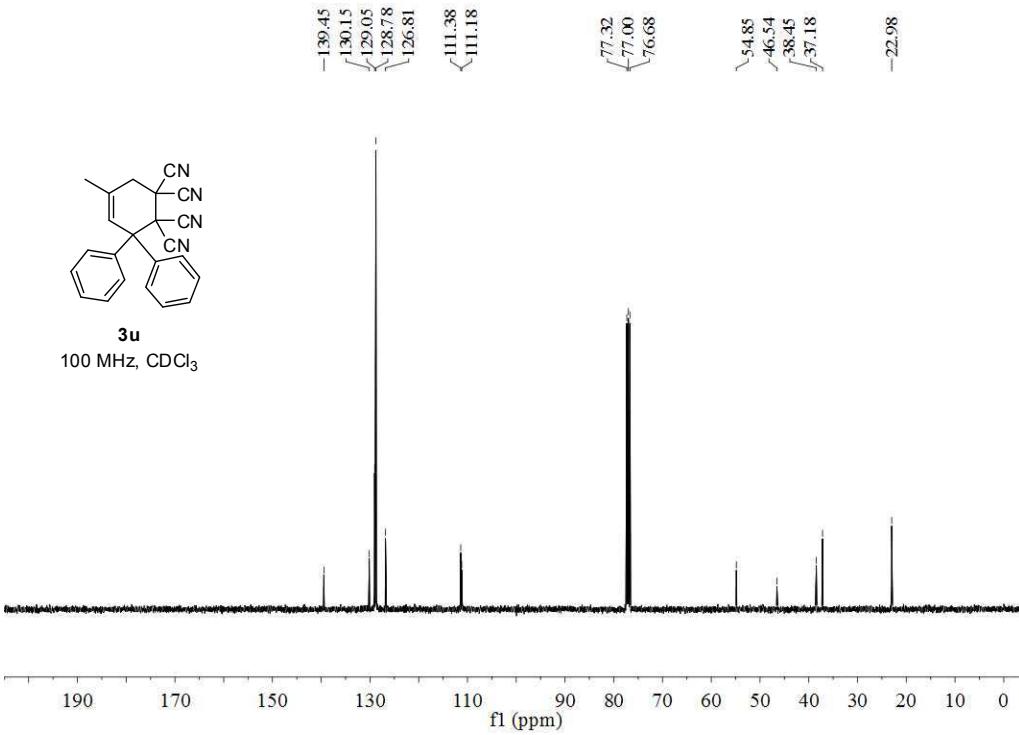
3t
400 MHz, $CDCl_3$



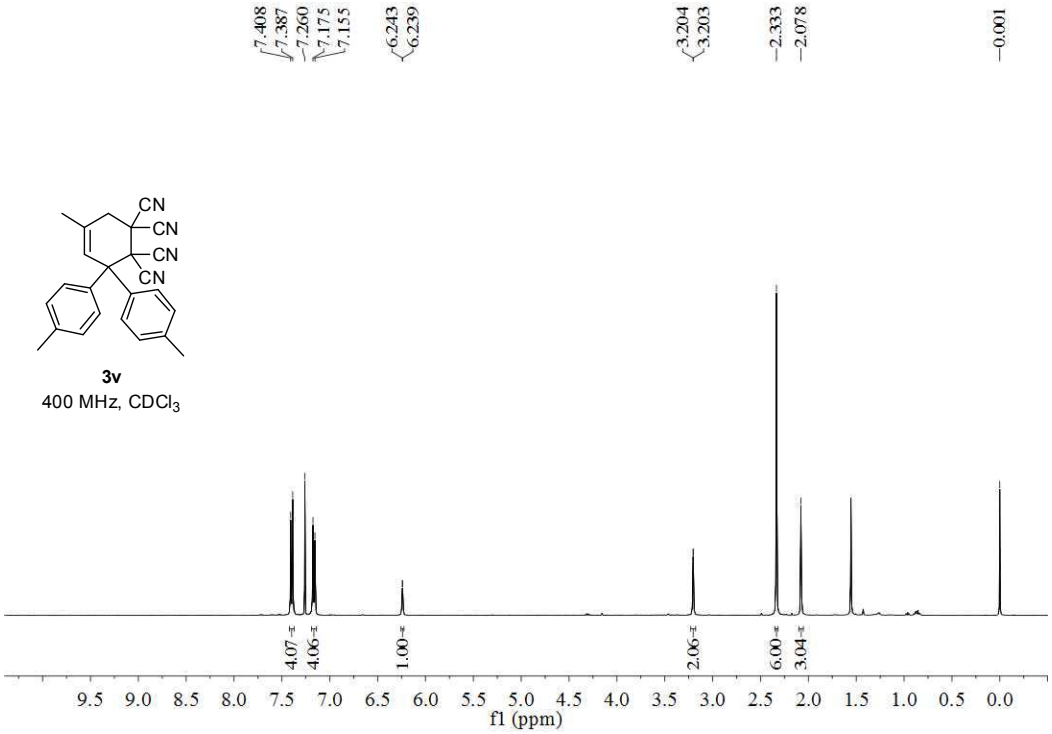
3t
100 MHz, $CDCl_3$

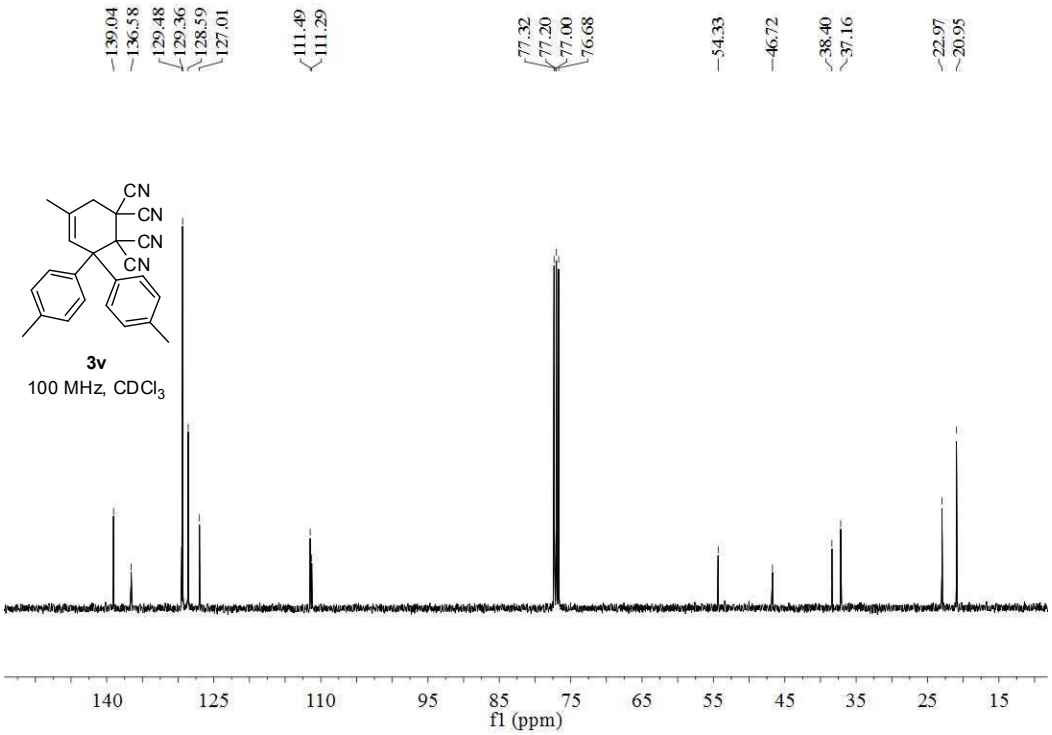


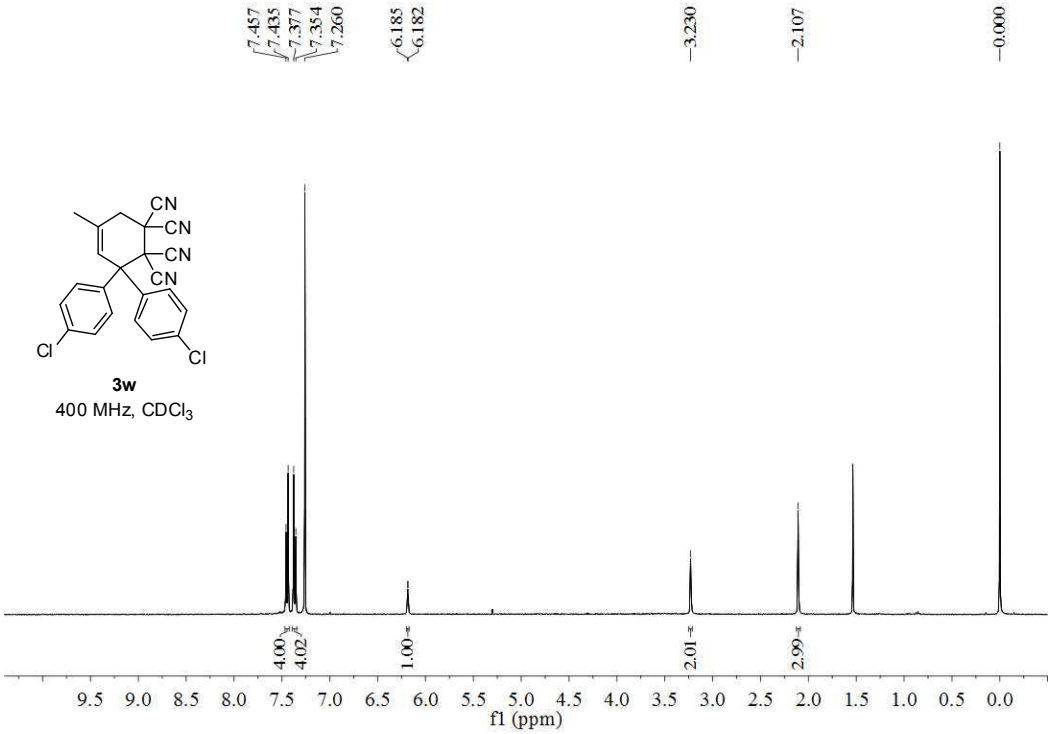
3u
400 MHz, $CDCl_3$



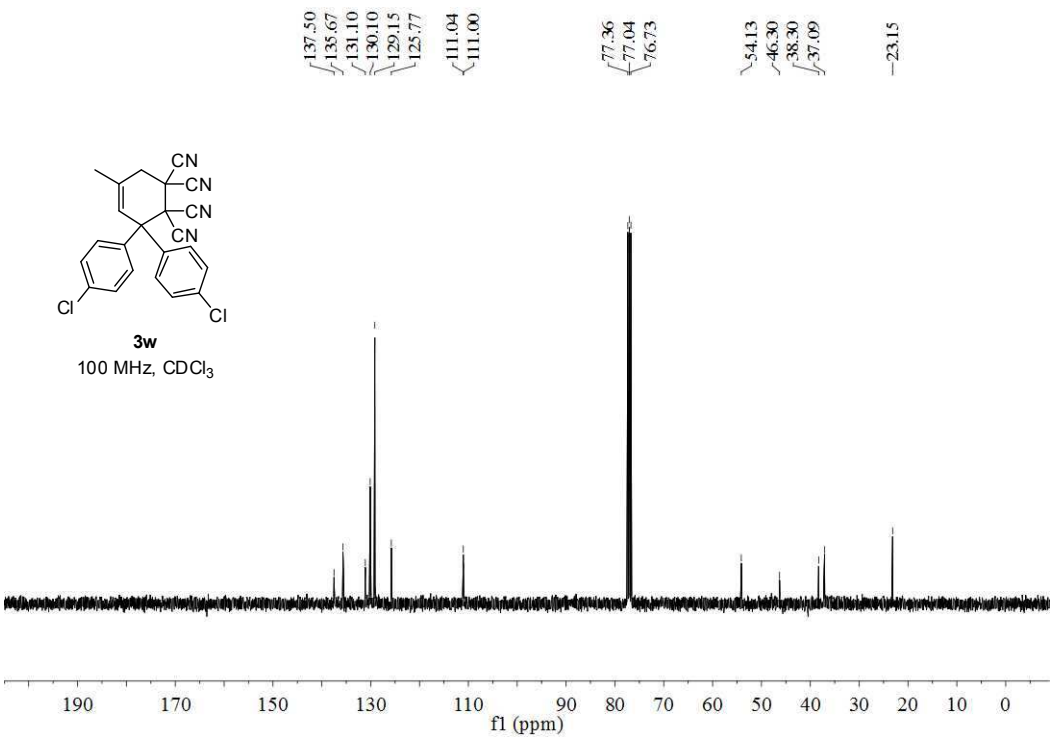
3u
100 MHz, $CDCl_3$


7.408
7.387
7.260
7.175
7.155
6.243
6.239
3.204
3.203
2.333
2.078
0.001
CN
CN
CN
CN
3v
400 MHz, CDCl3
4.07
4.06
1.00
2.06
6.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

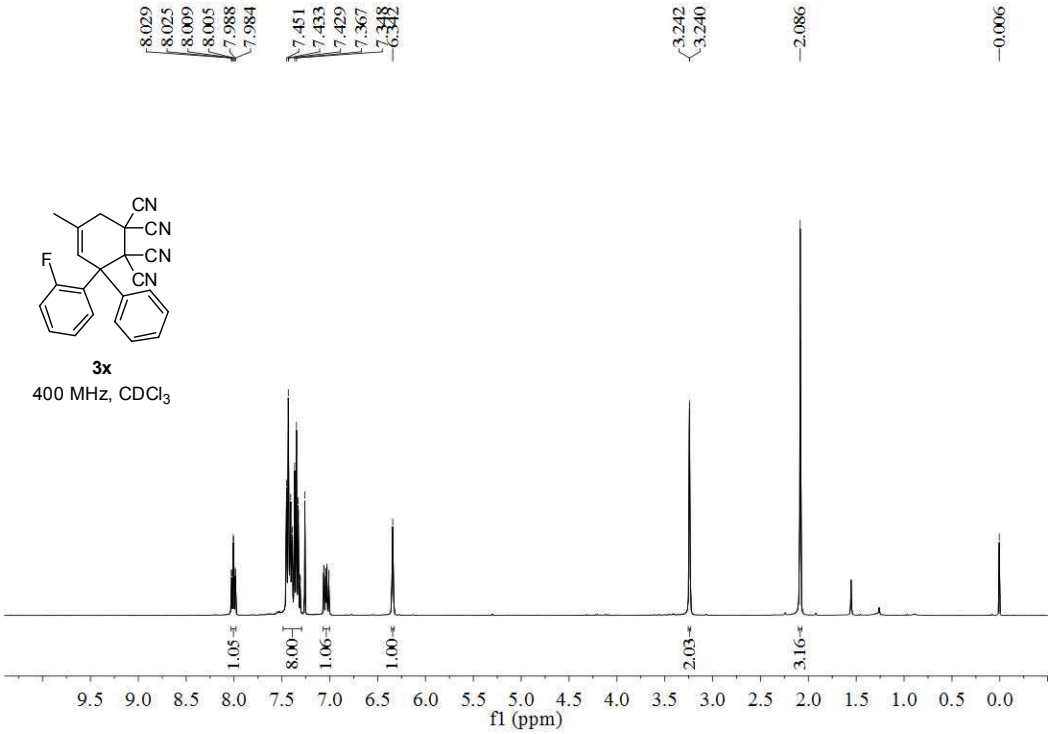

139.04
136.58
129.48
129.36
128.59
127.01
111.49
111.29
77.32
77.20
77.00
76.68
54.33
46.72
38.40
37.16
22.97
20.95
CN
CN
CN
CN
3v
100 MHz, CDCl3
140 125 110 95 85 75 65 55 45 35 25 15
f1 (ppm)

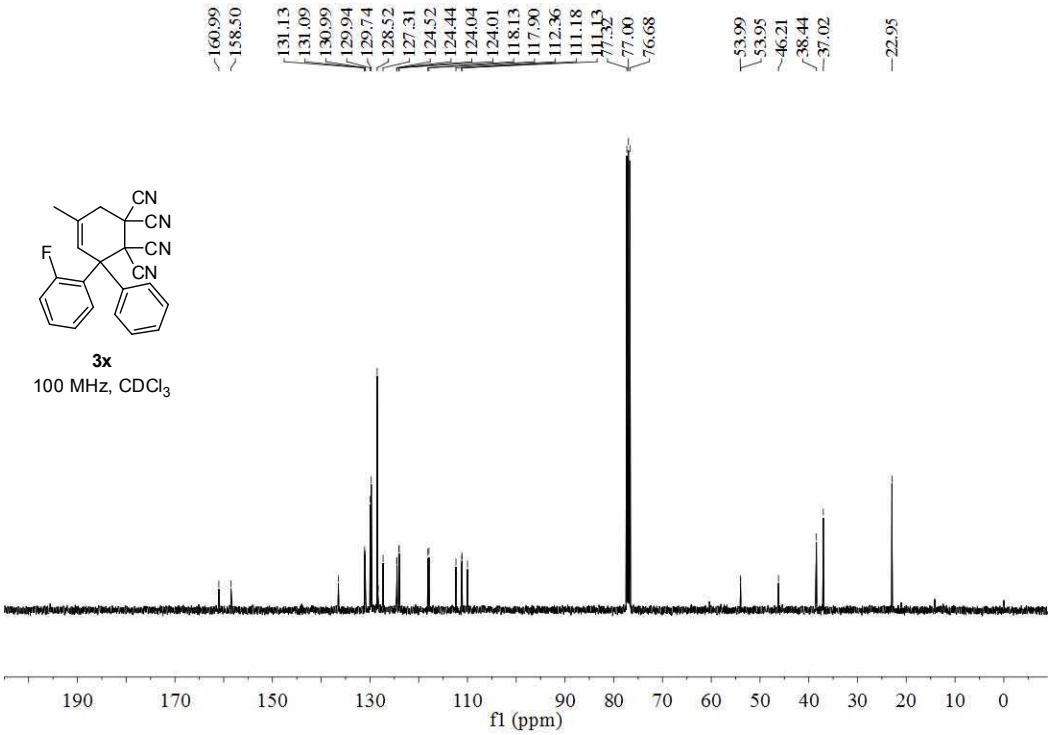


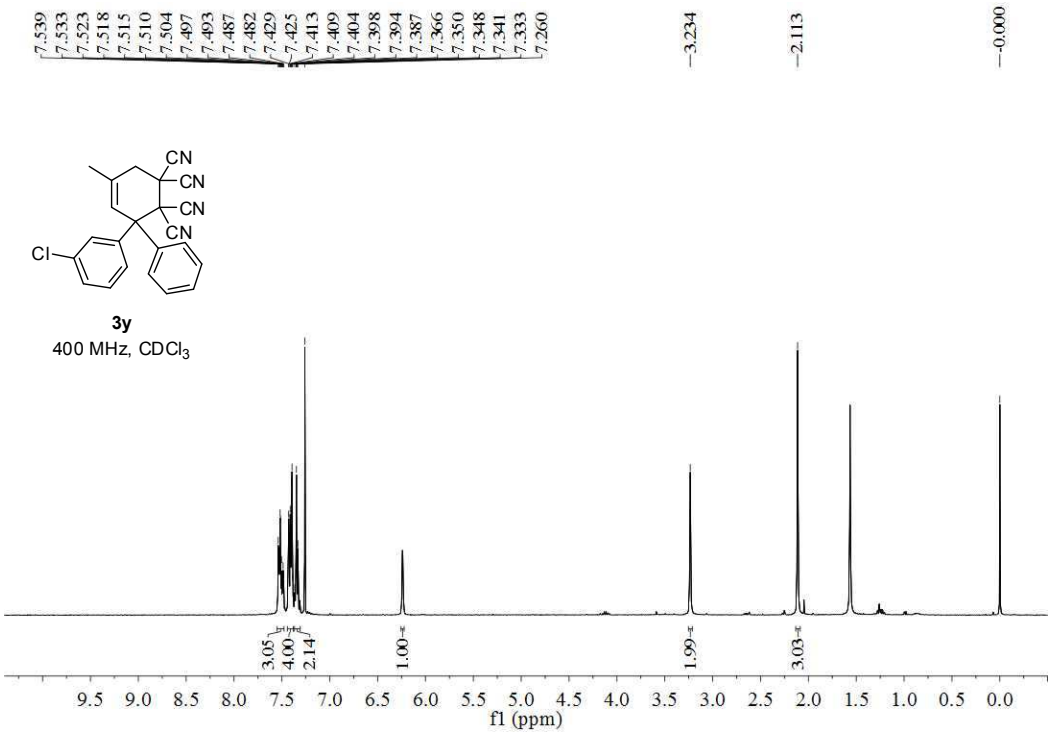
3w
400 MHz, $CDCl_3$

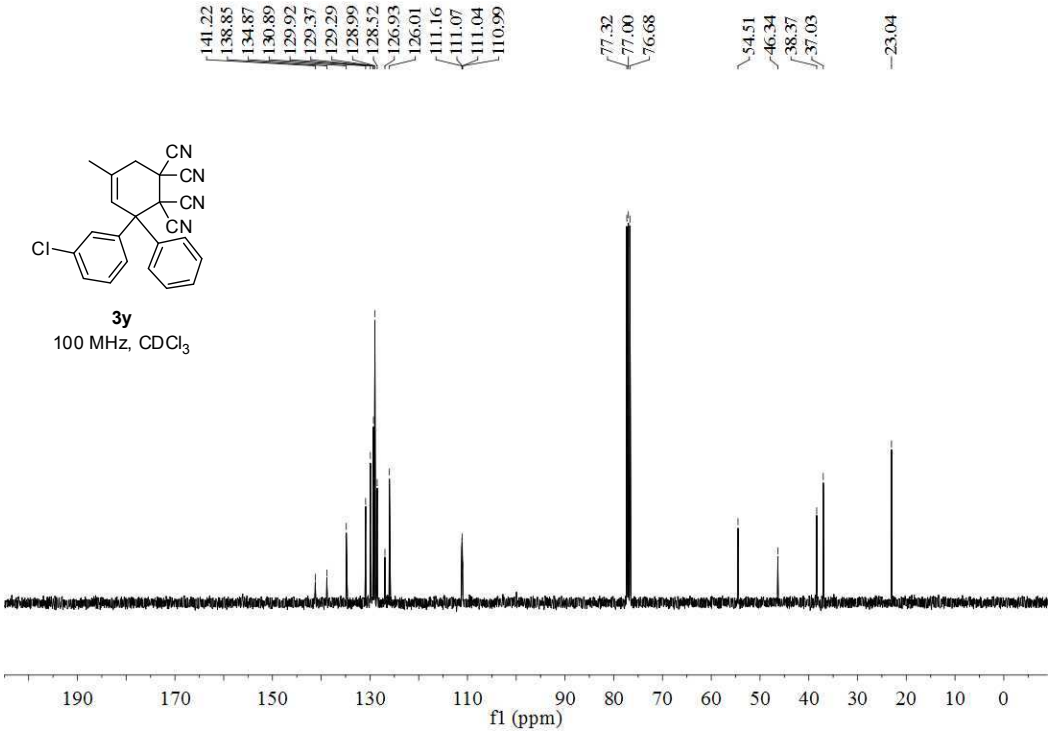


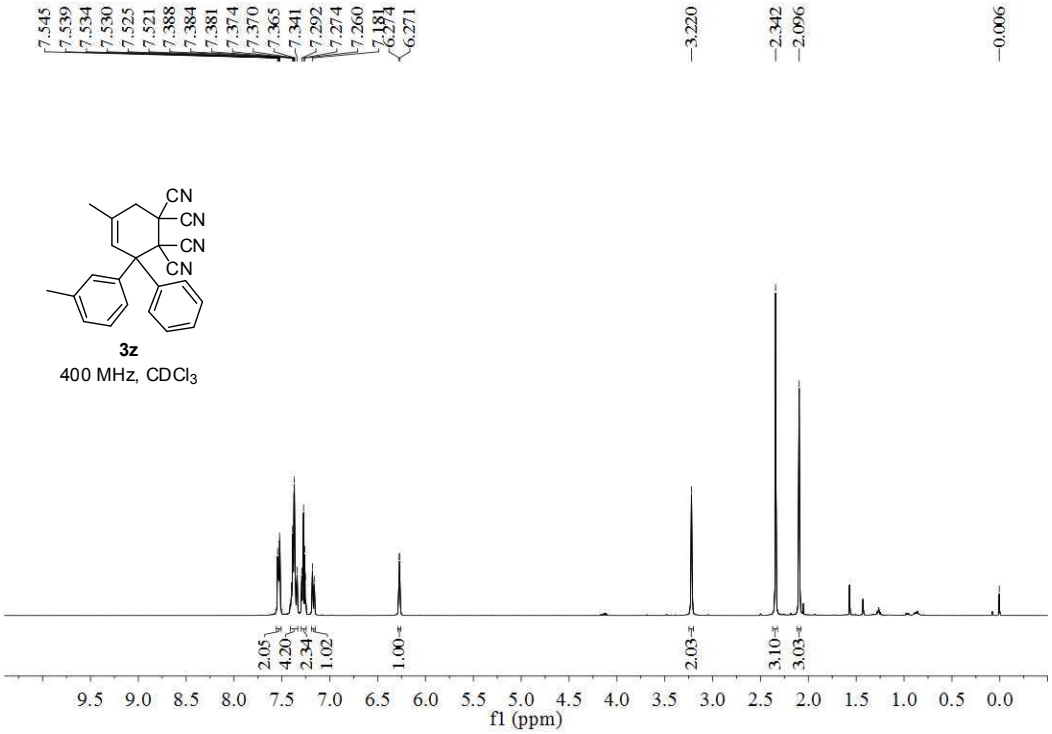
3w
100 MHz, $CDCl_3$

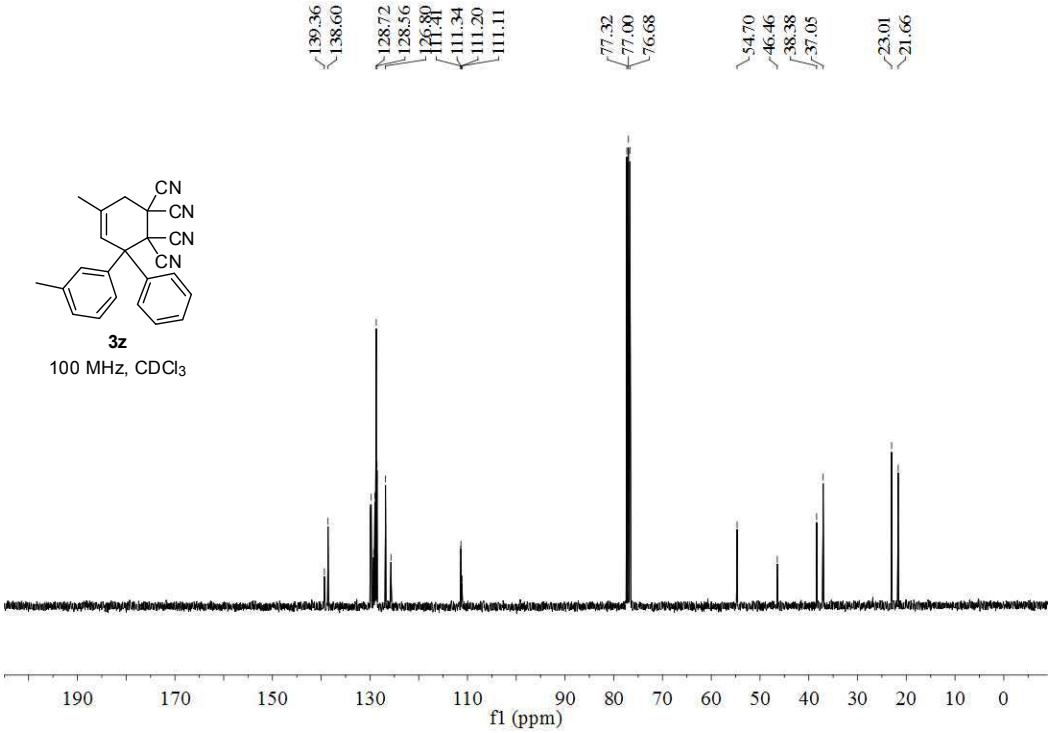

8.029
8.025
8.009
8.005
7.988
7.984
7.451
7.433
7.429
7.367
3.242
3.240
2.086
0.006
CN
CN
CN
CN
F
3x
400 MHz, CDCl3
1.05
8.00
1.06
1.00
2.03
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

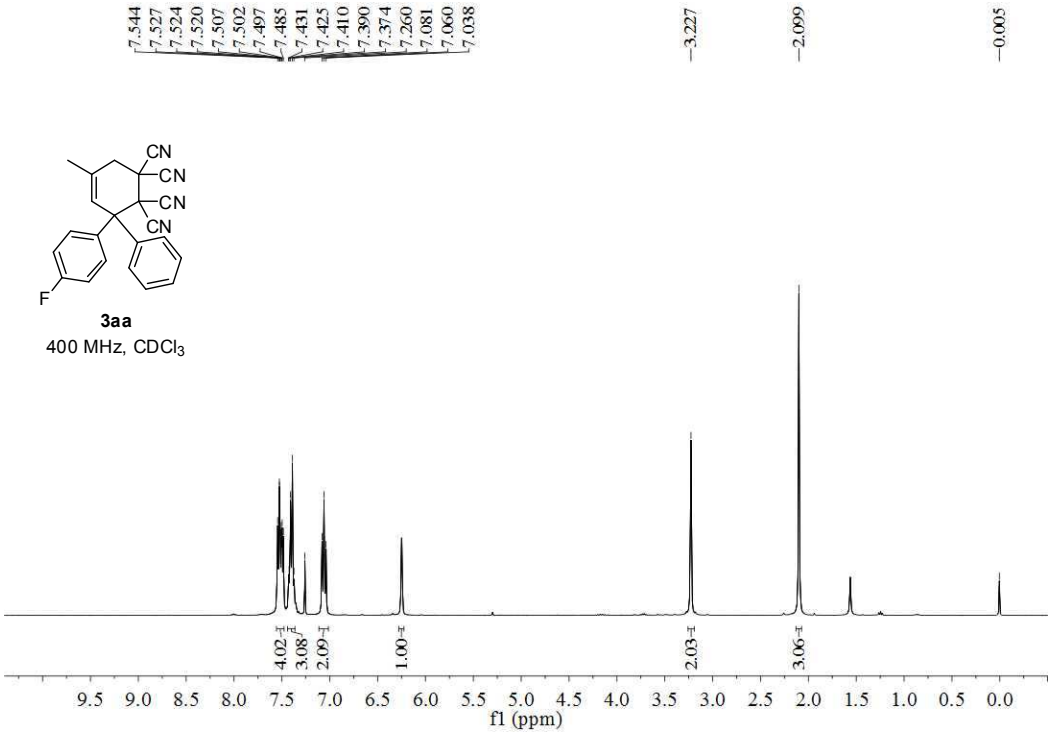

160.99
158.50
131.13
131.09
130.99
129.94
129.74
128.52
127.31
124.52
124.44
124.04
124.01
118.13
117.90
112.36
111.18
77.32
77.00
76.68
53.99
53.95
46.21
38.44
37.02
22.95
CN
CN
CN
CN
F
3x
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.539
7.533
7.523
7.518
7.515
7.510
7.504
7.497
7.493
7.487
7.482
7.429
7.425
7.413
7.409
7.404
7.398
7.394
7.387
7.366
7.350
7.348
7.341
7.333
7.260
3.234
2.113
0.000
CN
CN
CN
CN
Cl
3y
400 MHz, CDCl3
3.05
4.00
2.14
1.00
1.99
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

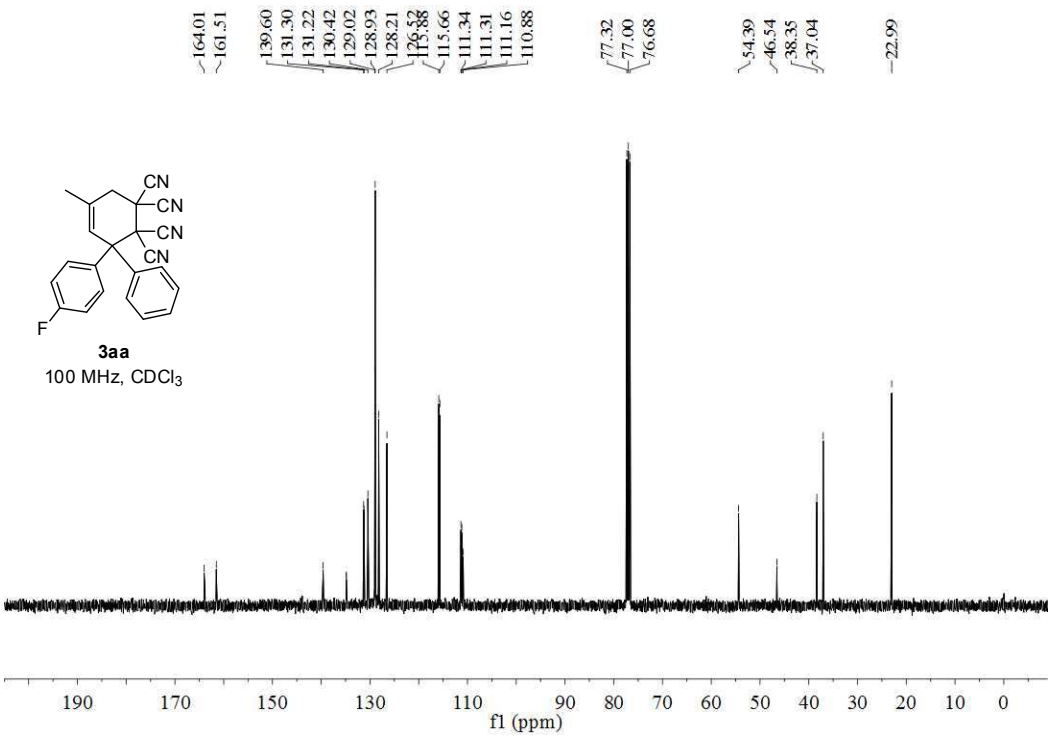

141.22
138.85
134.87
130.89
129.92
129.37
129.29
128.99
128.52
126.93
126.01
111.16
111.07
111.04
110.99
77.32
77.00
76.68
54.51
46.34
38.37
37.03
23.04
CN
CN
CN
CN
Cl
3y
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.545
7.539
7.534
7.530
7.525
7.521
7.388
7.384
7.381
7.374
7.370
7.365
7.341
7.292
7.274
7.260
7.181
6.274
6.271
3.220
2.342
2.096
0.006
CN
CN
CN
CN
3z
400 MHz, CDCl3
2.05
4.20
2.34
1.02
1.00
2.03
3.10
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

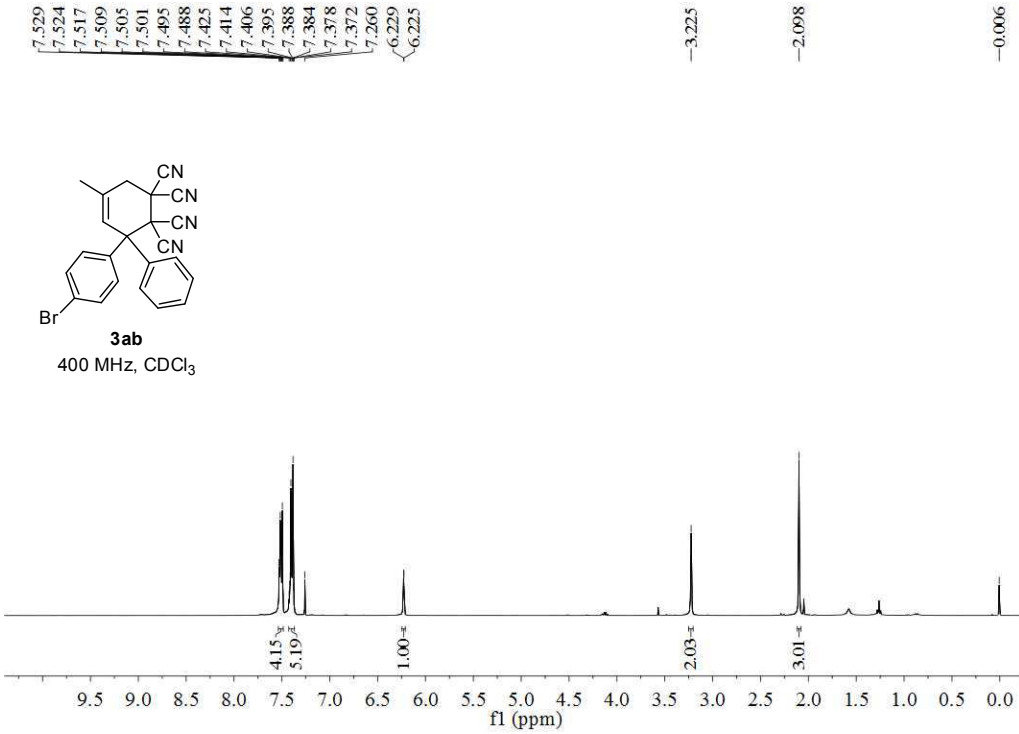

139.36
138.60
128.72
128.56
126.80
111.41
111.34
111.20
111.11
77.32
77.00
76.68
54.70
46.46
38.38
37.05
23.01
21.66
CN
CN
CN
CN
3z
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

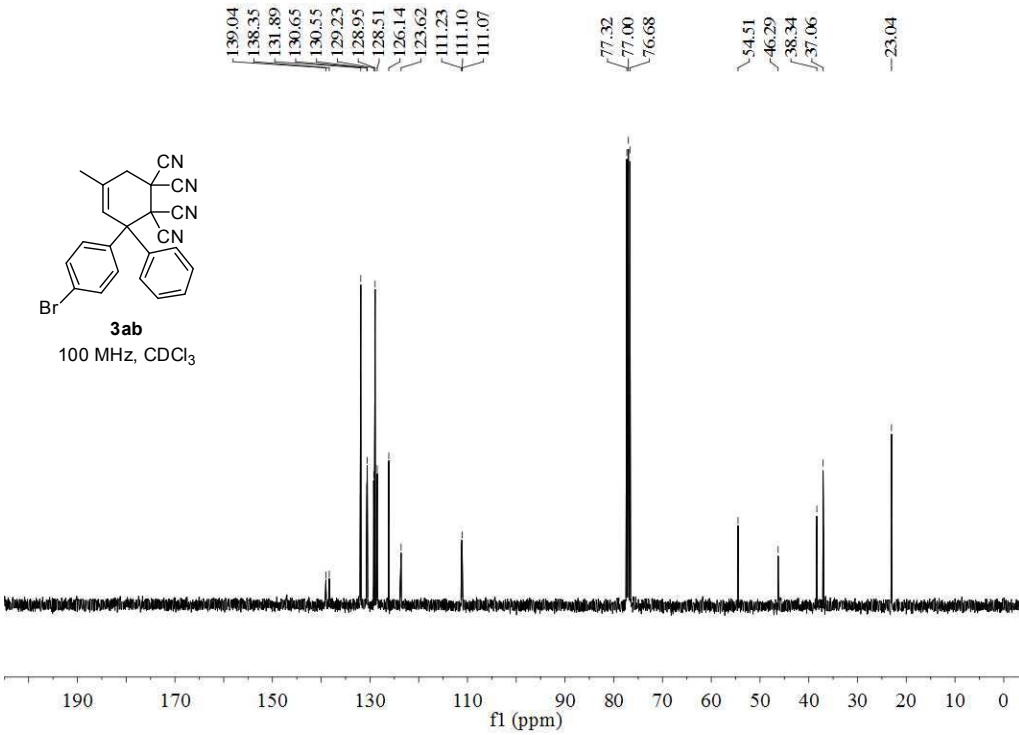


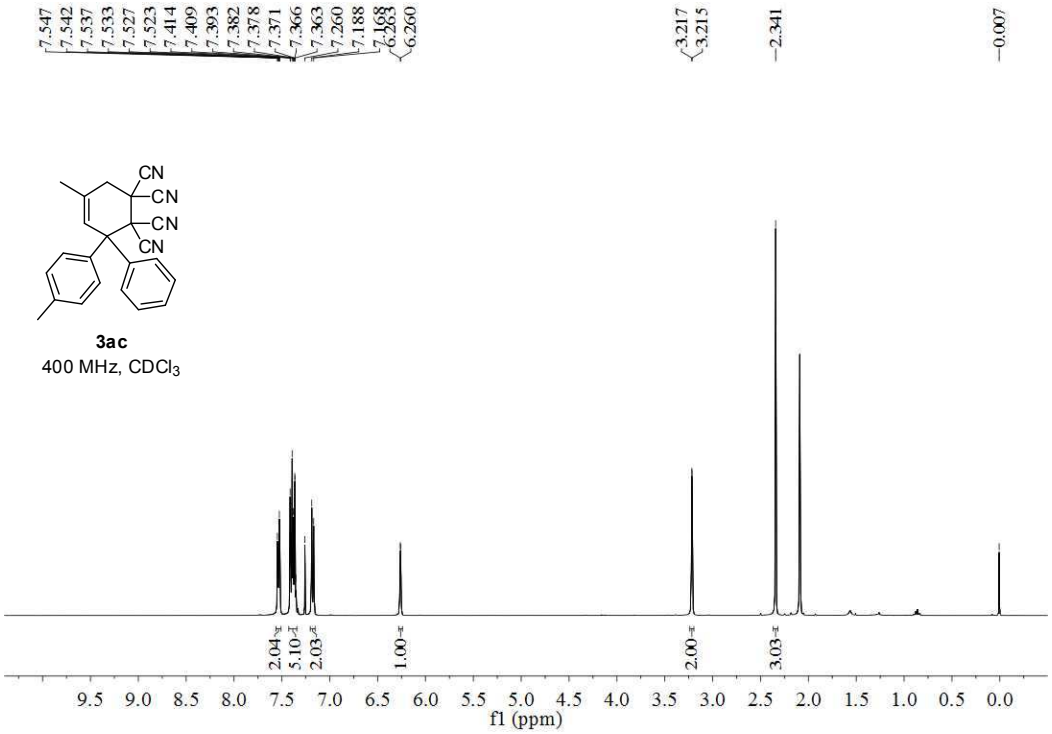
3aa
400 MHz, $CDCl_3$



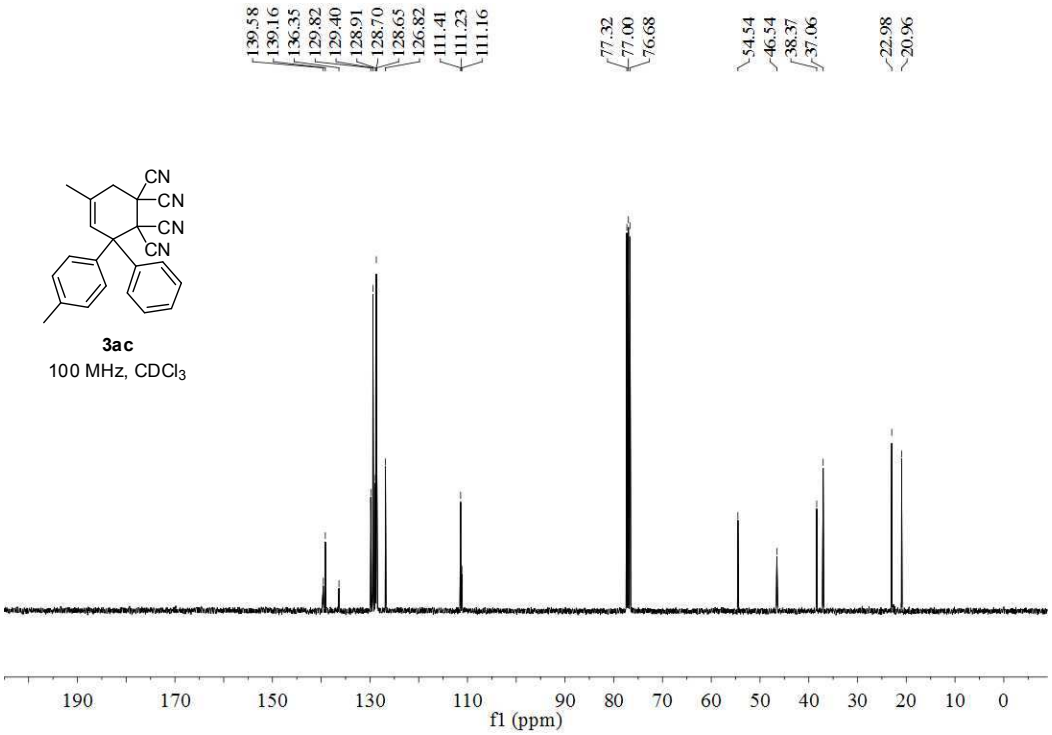
3aa
100 MHz, $CDCl_3$


7.529
7.524
7.517
7.509
7.505
7.501
7.495
7.488
7.425
7.414
7.406
7.395
7.388
7.384
7.378
7.372
7.260
6.229
6.225
3.225
2.098
0.006
CN
CN
CN
CN
Br
3ab
400 MHz, CDCl3
4.15
5.19
1.00
2.03
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

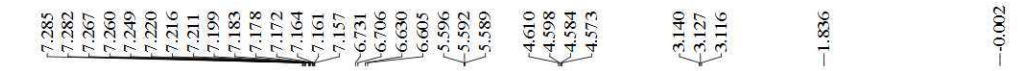

139.04
138.35
131.89
130.65
130.55
129.23
128.95
128.51
126.14
123.62
111.23
111.10
111.07
77.32
77.00
76.68
54.51
46.29
38.34
37.06
23.04
CN
CN
CN
CN
Br
3ab
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

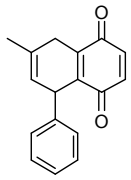


3ac
400 MHz, $CDCl_3$

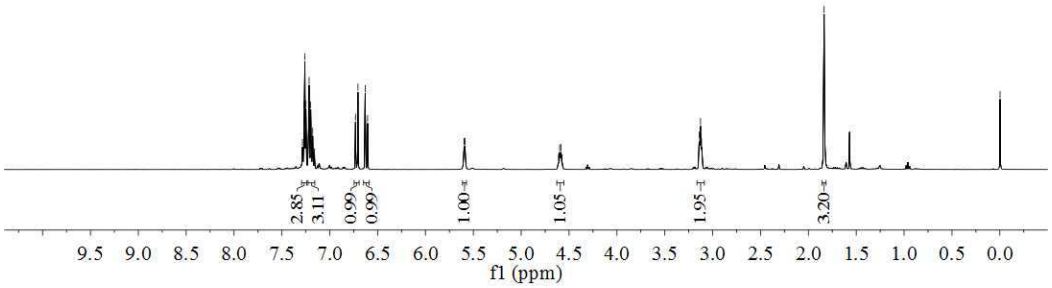


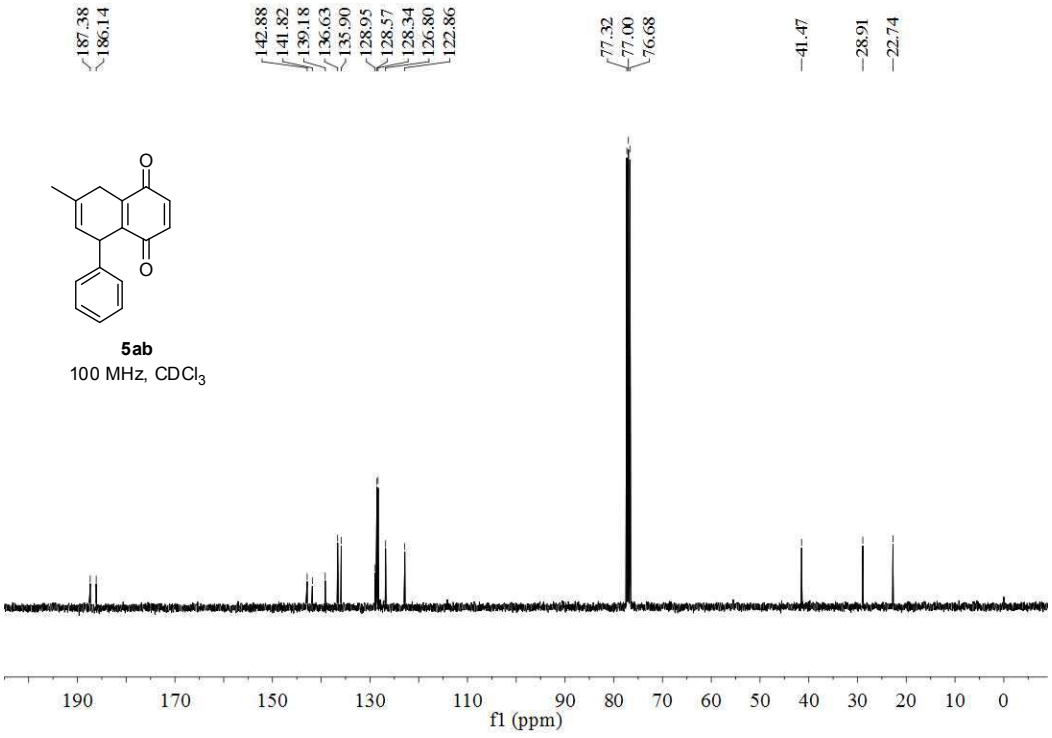
3ac
100 MHz, $CDCl_3$



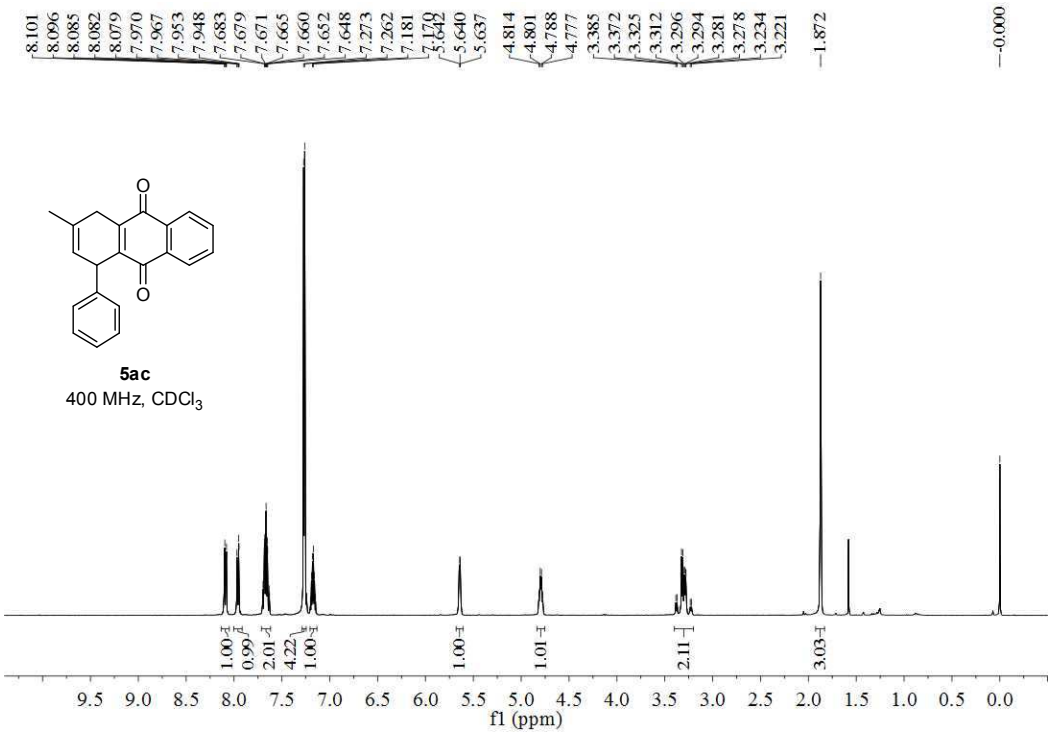


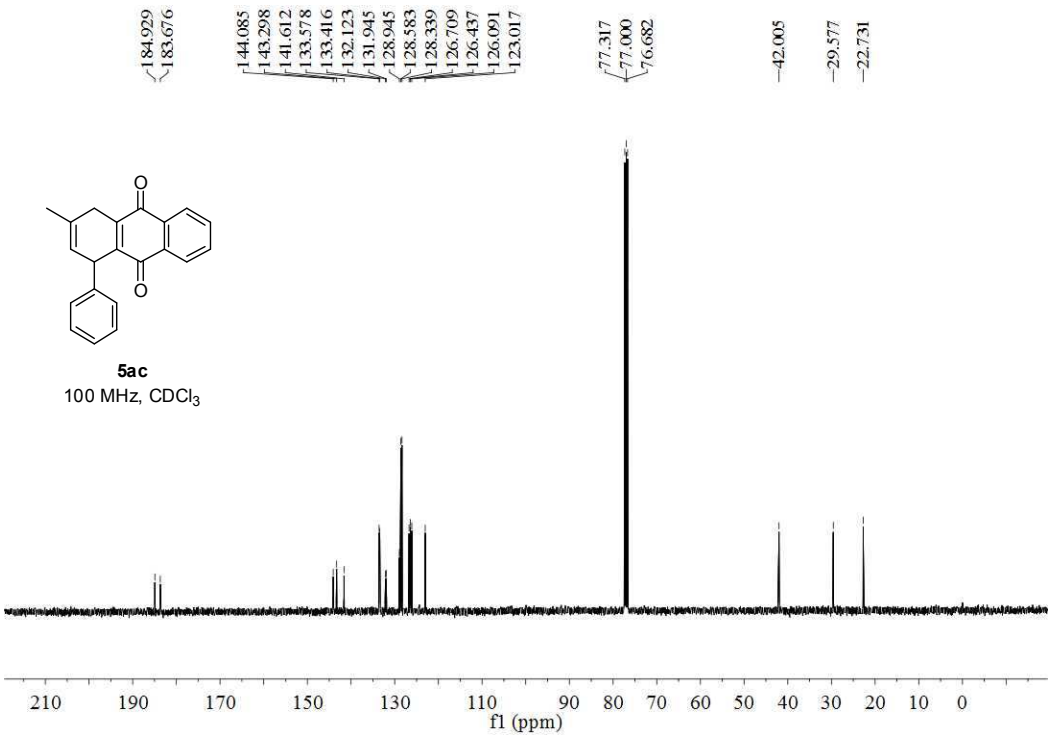
5ab
400 MHz, $CDCl_3$

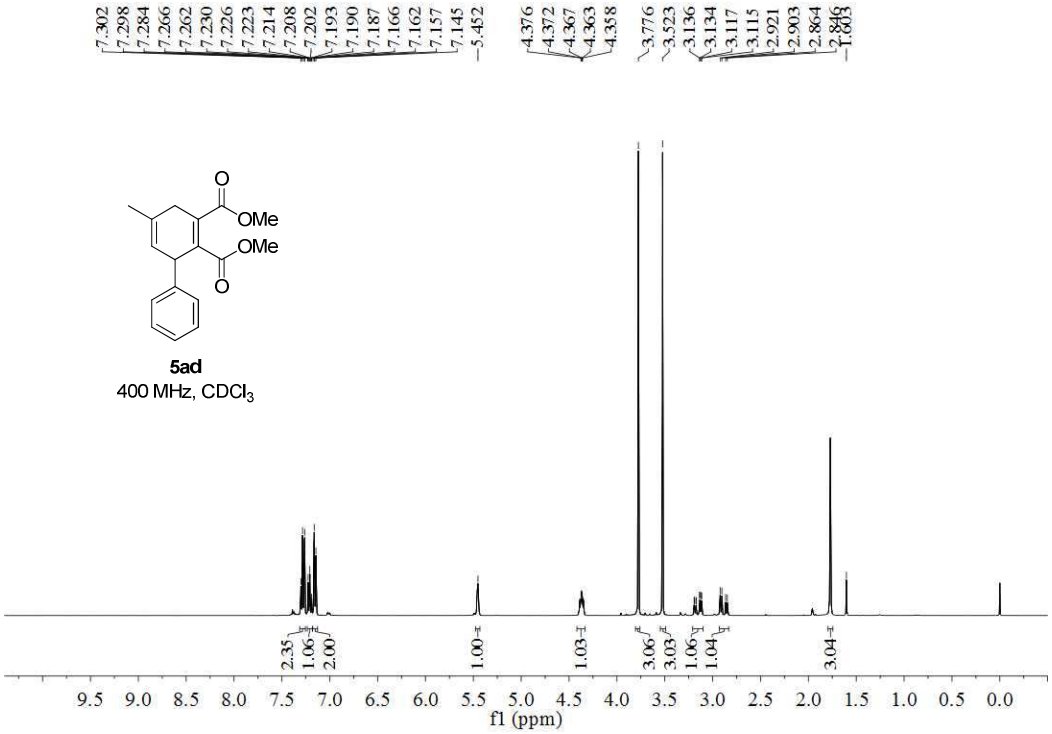


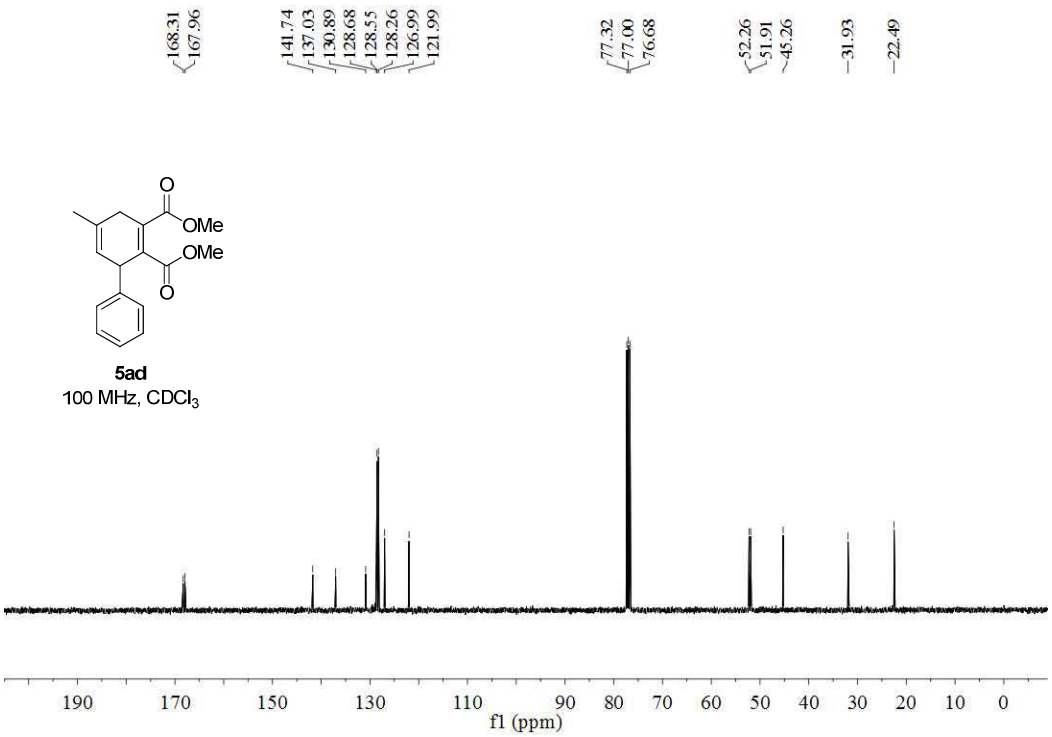


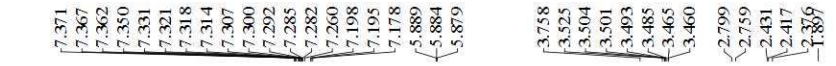
5ab
100 MHz, $CDCl_3$

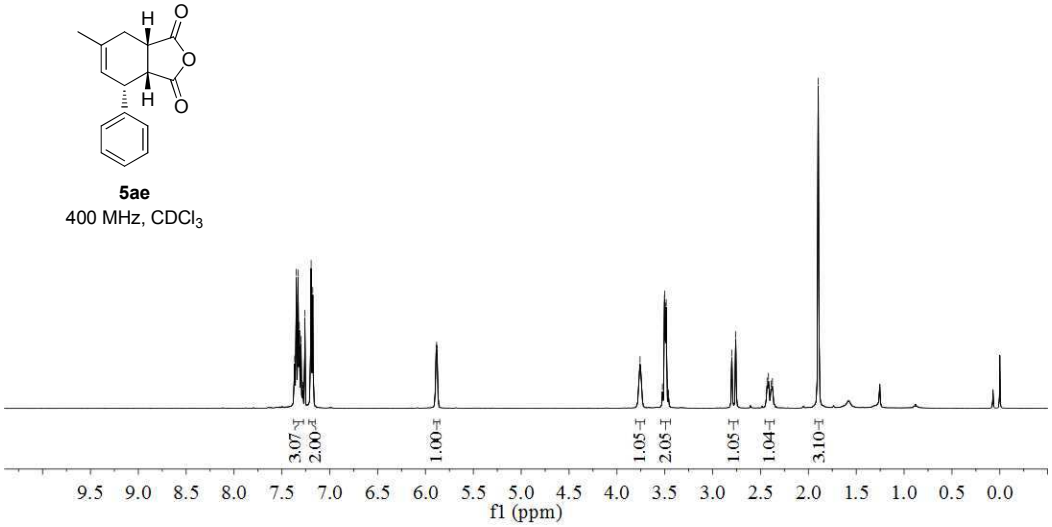

8.101
8.096
8.085
8.082
8.079
7.970
7.967
7.953
7.948
7.683
7.679
7.671
7.665
7.660
7.652
7.648
7.273
7.262
7.181
7.170
5.642
5.640
5.637
4.814
4.801
4.788
4.777
3.385
3.372
3.325
3.312
3.296
3.294
3.281
3.278
3.234
3.221
1.872
0.000
O
O
5ac
400 MHz, CDCl3
1.00
0.99
2.01
4.22
1.00
1.00
1.01
2.11
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


184.929
183.676
144.085
143.298
141.612
133.578
133.416
132.123
131.945
128.945
128.583
128.339
126.709
126.437
126.091
123.017
77.317
77.000
76.682
42.005
29.577
22.731
O
O
5ac
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

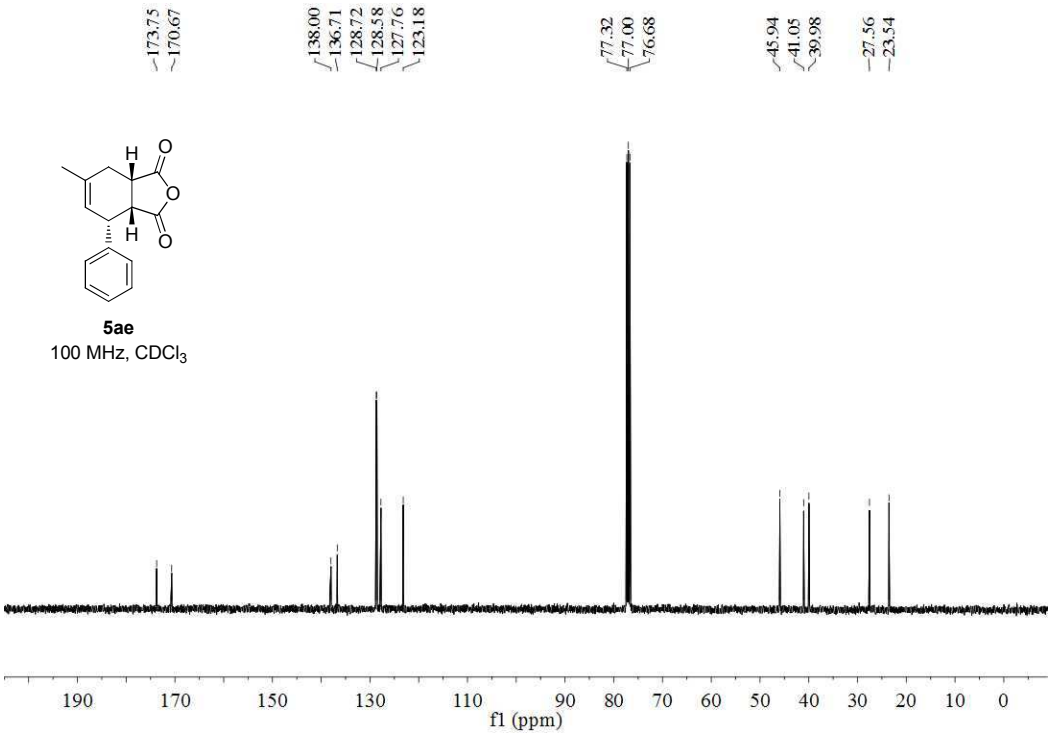

7.302
7.298
7.284
7.266
7.262
7.230
7.226
7.223
7.214
7.208
7.202
7.193
7.190
7.187
7.166
7.162
7.157
7.145
5.452
4.376
4.372
4.367
4.363
4.358
3.776
3.523
3.136
3.134
3.117
3.115
2.921
2.903
2.864
2.846
1.603
O
OMe
OMe
O
5ad
400 MHz, CDCl3
2.35
1.06
2.00
1.00
1.03
3.06
3.03
1.06
1.04
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.31
167.96
141.74
137.03
130.89
128.68
128.55
128.26
126.99
121.99
77.32
77.00
76.68
52.26
51.91
45.26
31.93
22.49
O
OMe
OMe
O
5ad
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

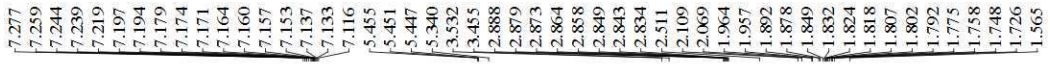


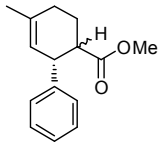


5ae
400 MHz, $CDCl_3$

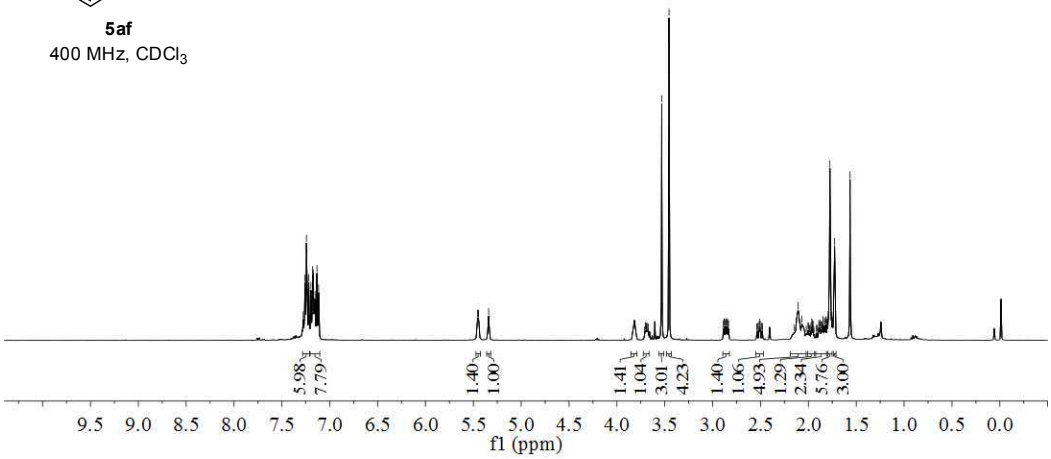


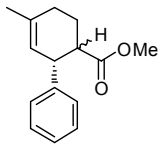
5ae
100 MHz, $CDCl_3$



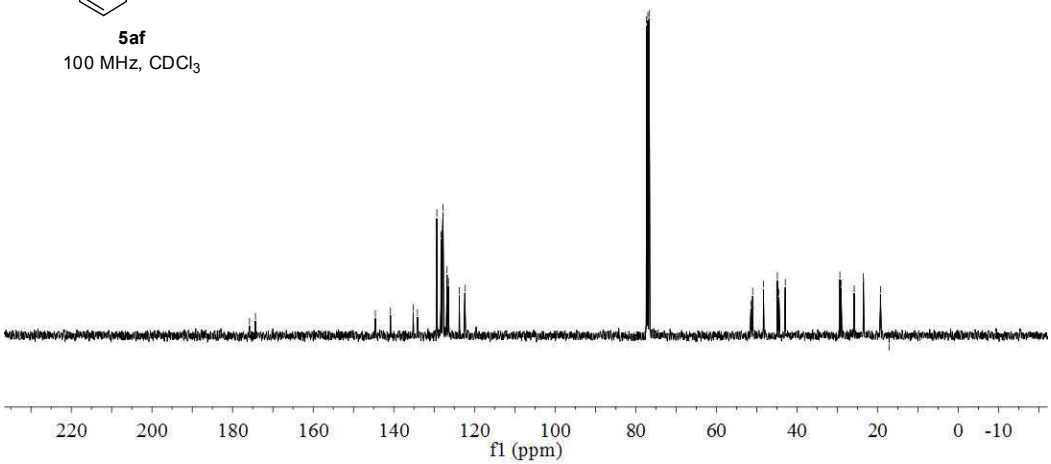


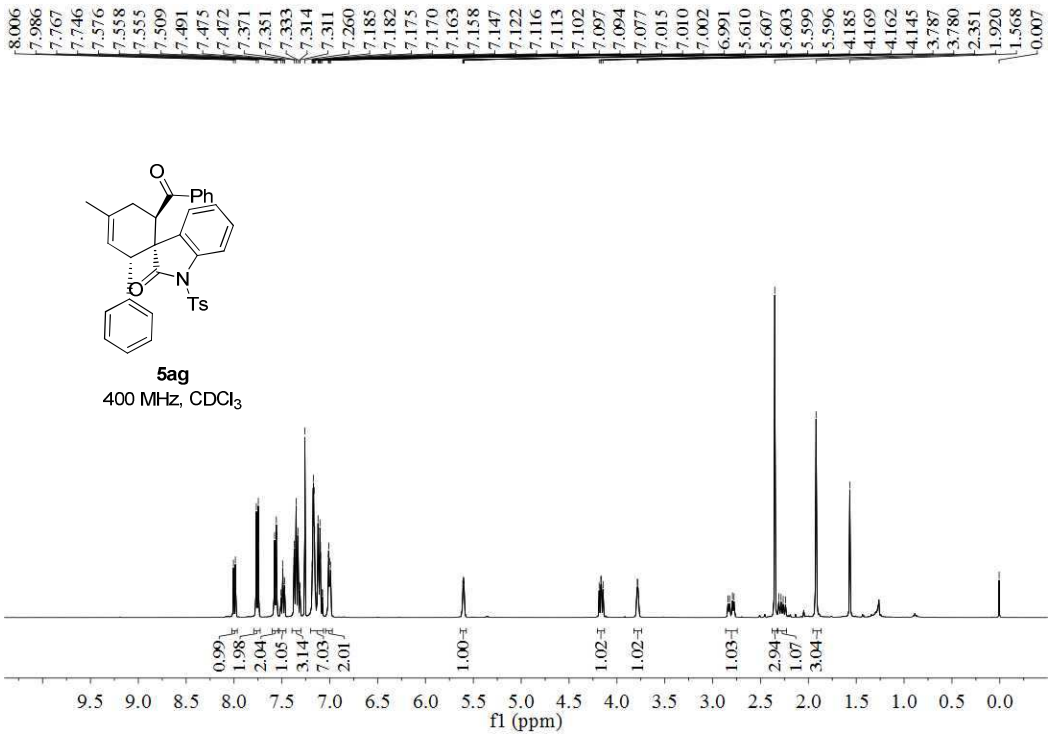
5af
400 MHz, $CDCl_3$

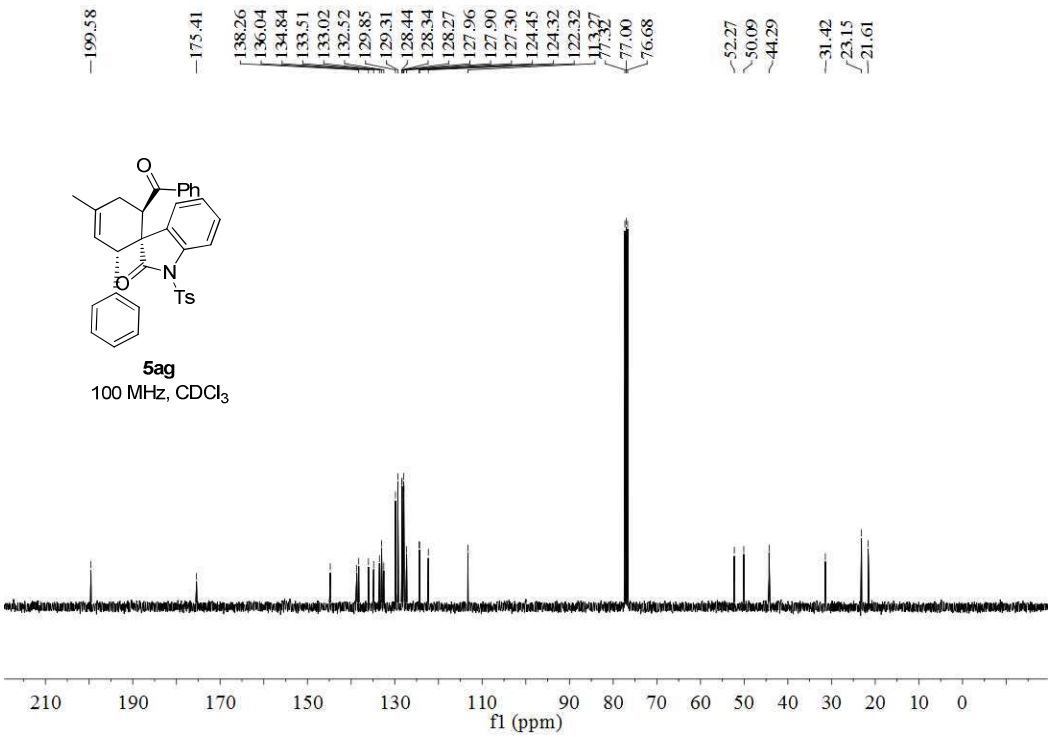


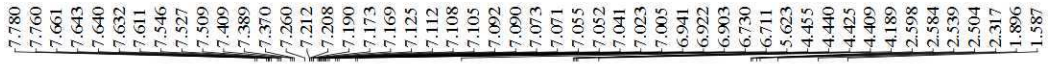


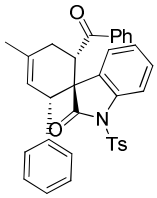
5af
100 MHz, $CDCl_3$



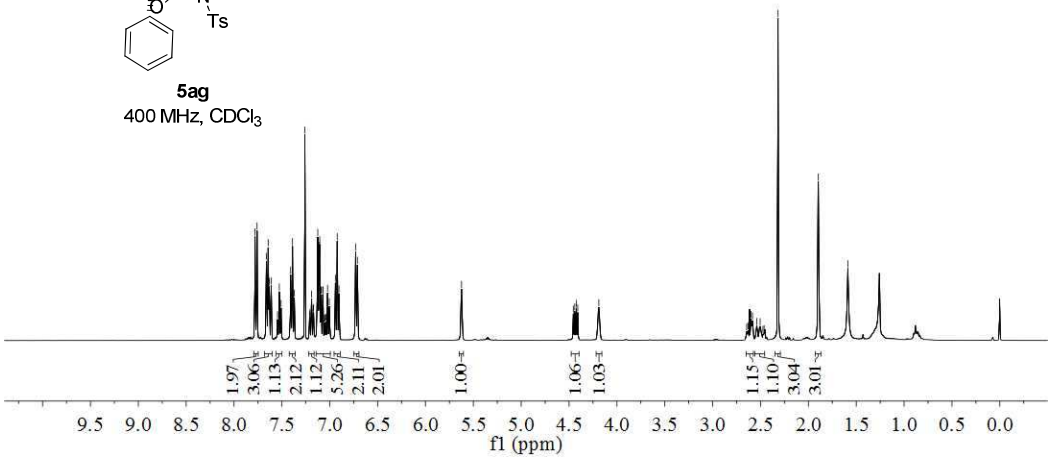

8.006
7.986
7.767
7.746
7.576
7.558
7.555
7.509
7.491
7.475
7.472
7.371
7.351
7.333
7.314
7.311
7.260
7.185
7.182
7.175
7.170
7.163
7.158
7.147
7.122
7.116
7.113
7.102
7.097
7.094
7.077
7.015
7.010
7.002
6.991
5.610
5.607
5.603
5.599
5.596
4.185
4.169
4.162
4.145
3.787
3.780
2.351
1.920
1.568
0.007
O
Ph
O
N
Ts
5ag
400 MHz, CDCl3
0.99
1.98
2.04
1.05
3.14
7.03
2.01
1.00
1.02
1.02
1.03
2.94
1.07
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

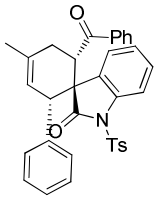

199.58
175.41
138.26
136.04
134.84
133.51
133.02
132.52
129.85
129.31
128.44
128.34
128.27
127.96
127.90
127.30
124.45
124.32
122.32
77.32
77.00
76.68
52.27
50.09
44.29
31.42
23.15
21.61
O
Ph
O
N
Ts
5ag
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



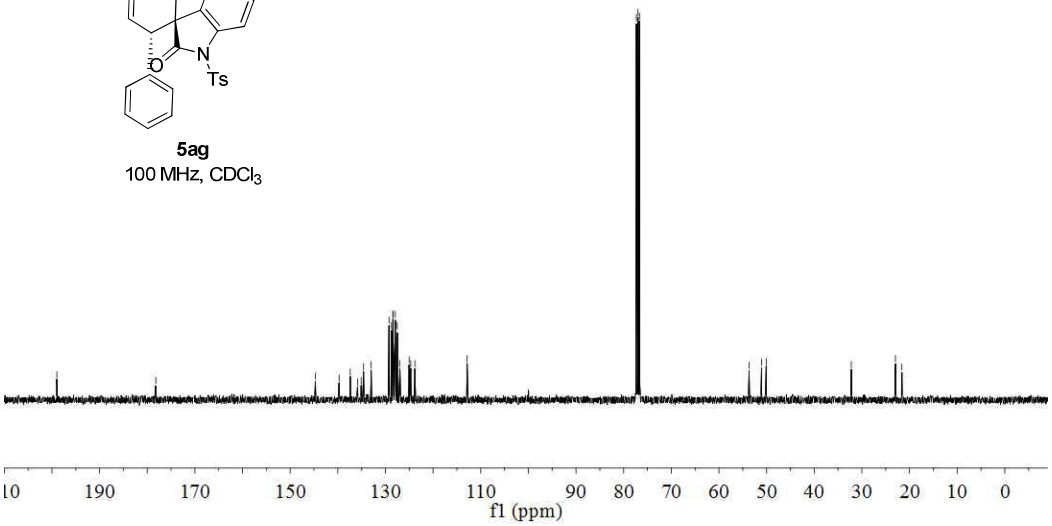


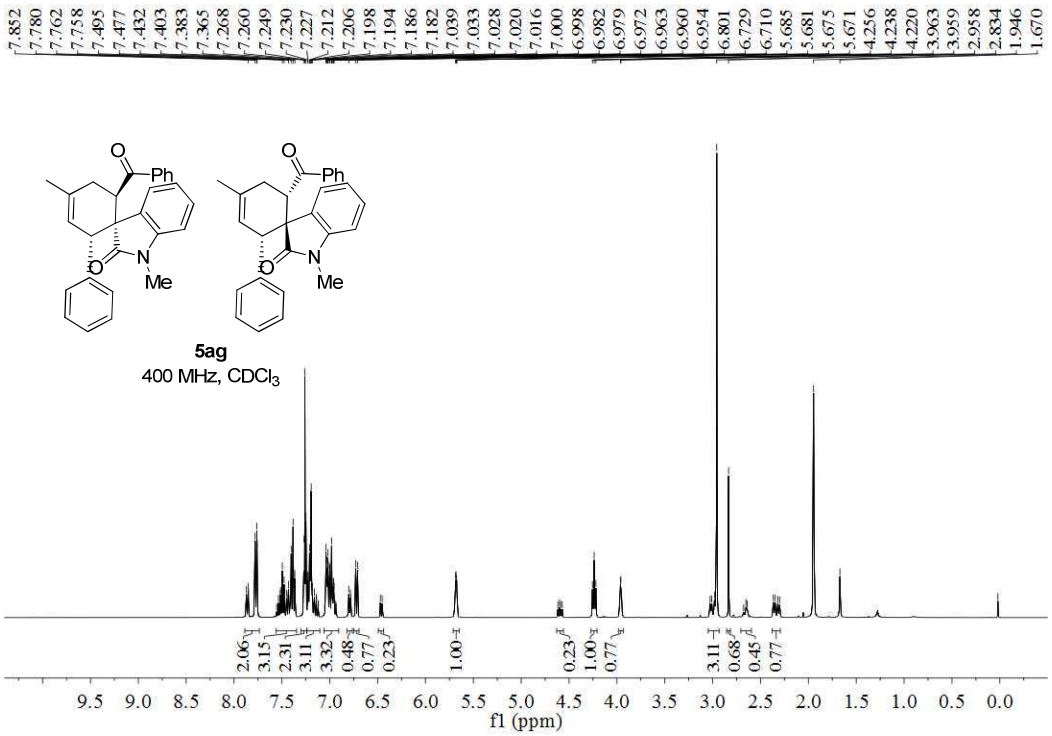
5ag
400 MHz, $CDCl_3$

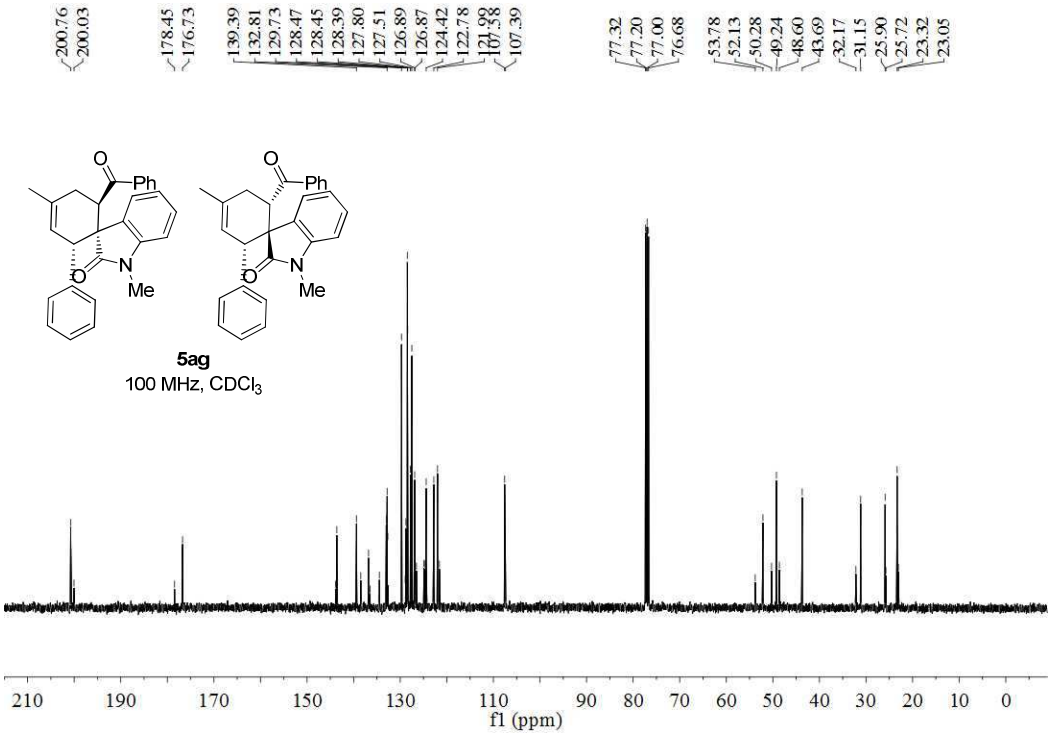


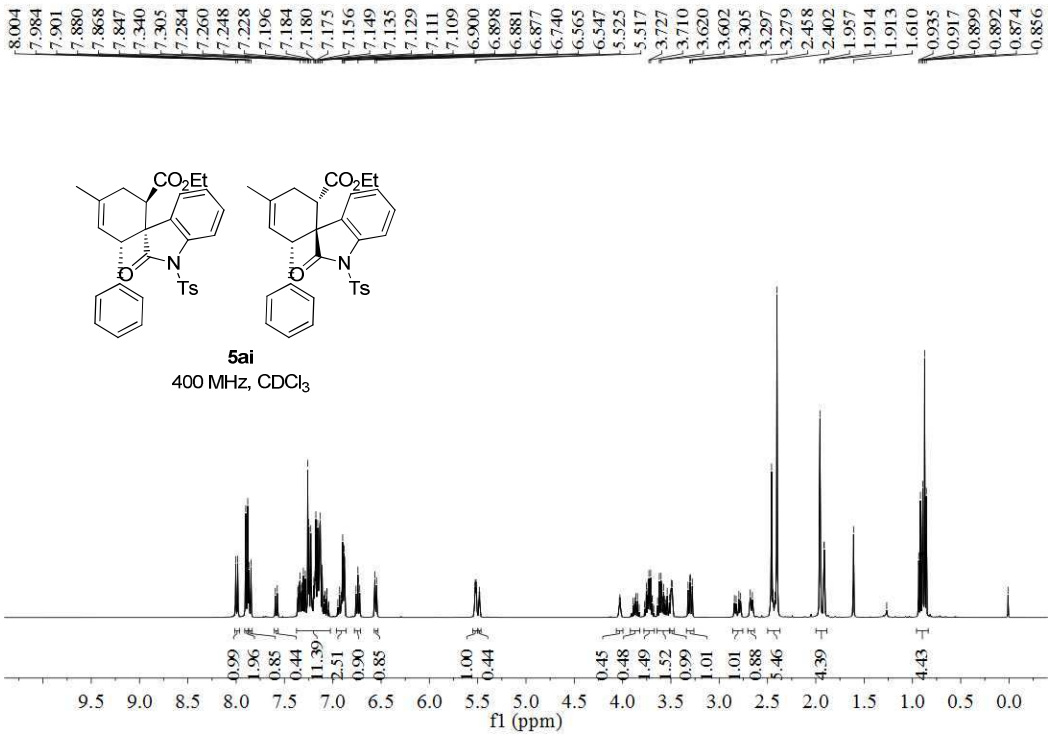


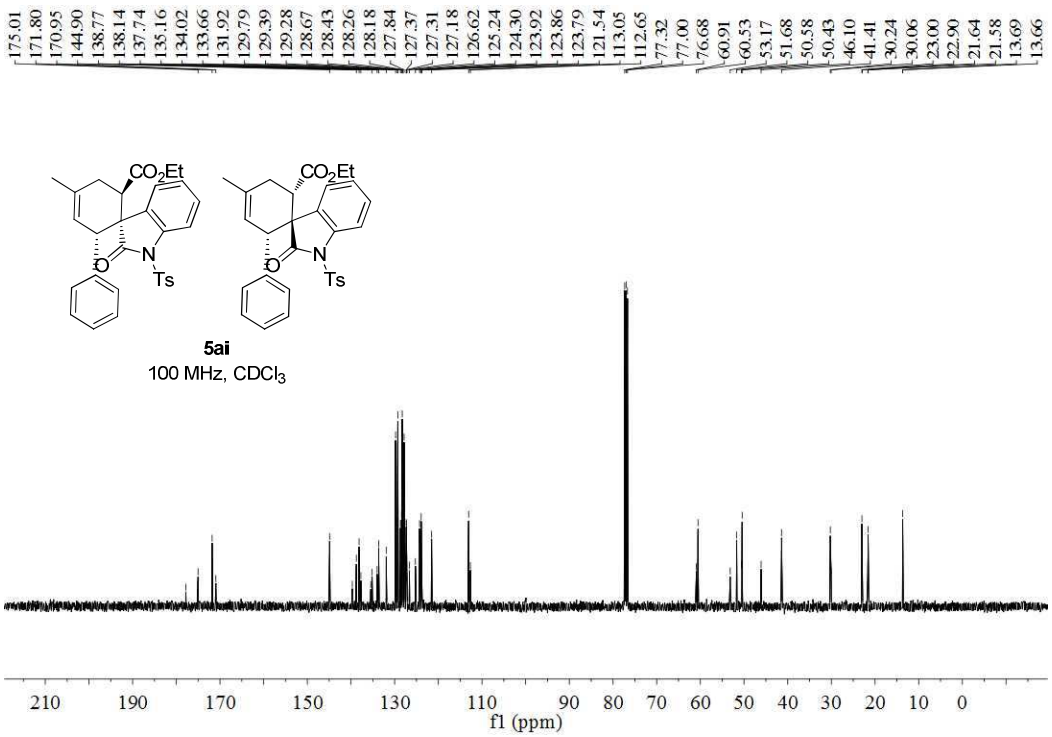
5ag
100 MHz, $CDCl_3$

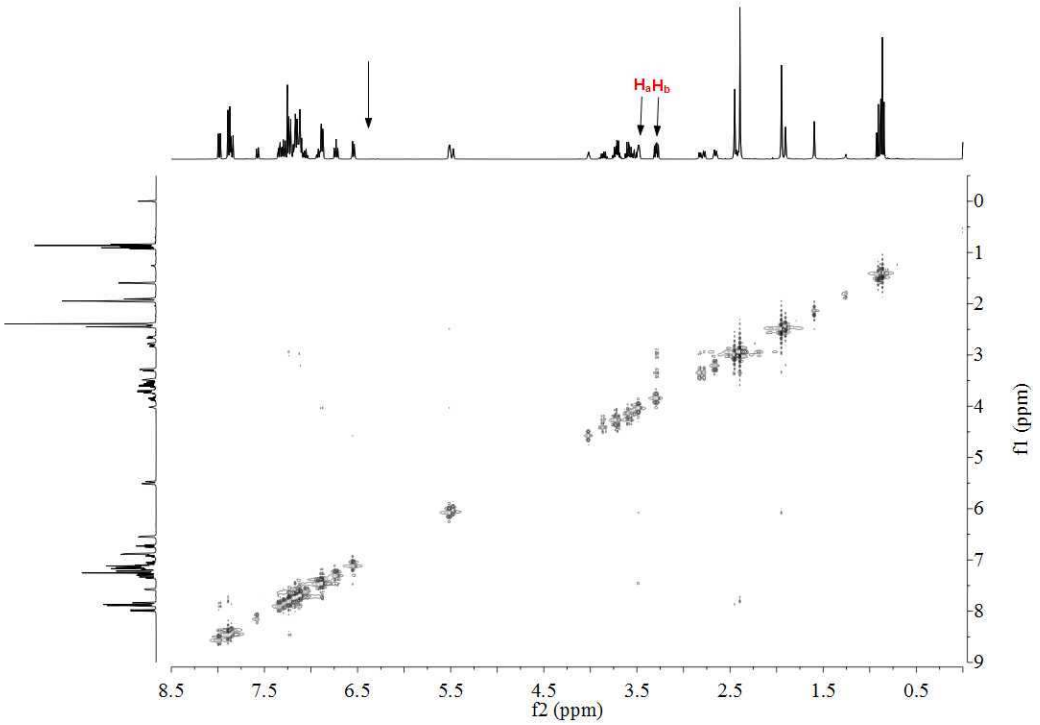


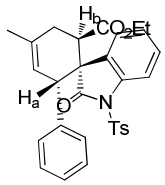

7.852
7.780
7.762
7.758
7.495
7.477
7.432
7.403
7.383
7.365
7.268
7.260
7.249
7.230
7.227
7.212
7.206
7.198
7.194
7.186
7.182
7.039
7.033
7.028
7.020
7.016
7.000
6.998
6.982
6.979
6.972
6.963
6.960
6.954
6.801
6.729
6.710
5.685
5.681
5.675
5.671
4.256
4.238
4.220
3.963
3.959
2.958
2.834
1.946
1.670
Ph
O
N
Me
5ag
400 MHz, CDCl3
2.06
3.15
2.31
3.11
3.32
0.48
0.77
0.23
1.00
0.23
1.00
0.77
3.11
0.68
0.45
0.77
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.76
200.03
178.45
176.73
139.39
132.81
129.73
128.47
128.45
128.39
127.80
127.51
126.89
126.87
124.42
122.78
107.39
77.32
77.20
77.00
76.68
53.78
52.13
50.28
49.24
48.60
43.69
32.17
31.15
25.90
25.72
23.32
23.05
Ph
O
N
Me
5ag
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

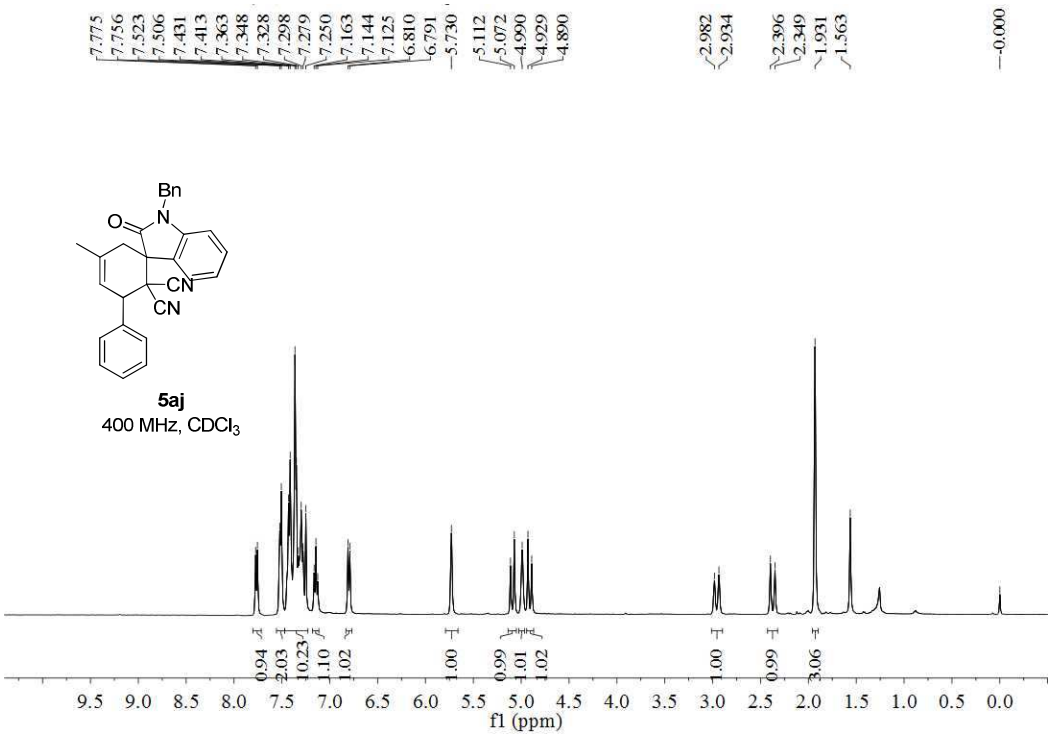

8.004
7.984
7.901
7.880
7.868
7.847
7.340
7.305
7.284
7.260
7.248
7.228
7.196
7.184
7.180
7.175
7.156
7.149
7.135
7.129
7.111
7.109
6.900
6.898
6.881
6.877
6.740
6.565
6.547
5.525
5.517
3.727
3.710
3.620
3.602
3.305
3.297
3.279
2.458
2.402
1.957
1.914
1.913
1.610
0.935
0.917
0.899
0.892
0.874
0.856
CO2Et
N
Ts
O
5ai
400 MHz, CDCl3
0.99
1.96
0.85
0.44
11.39
2.51
0.90
0.85
1.00
0.44
0.45
0.48
1.49
1.52
0.99
1.01
1.01
0.88
5.46
4.39
4.43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

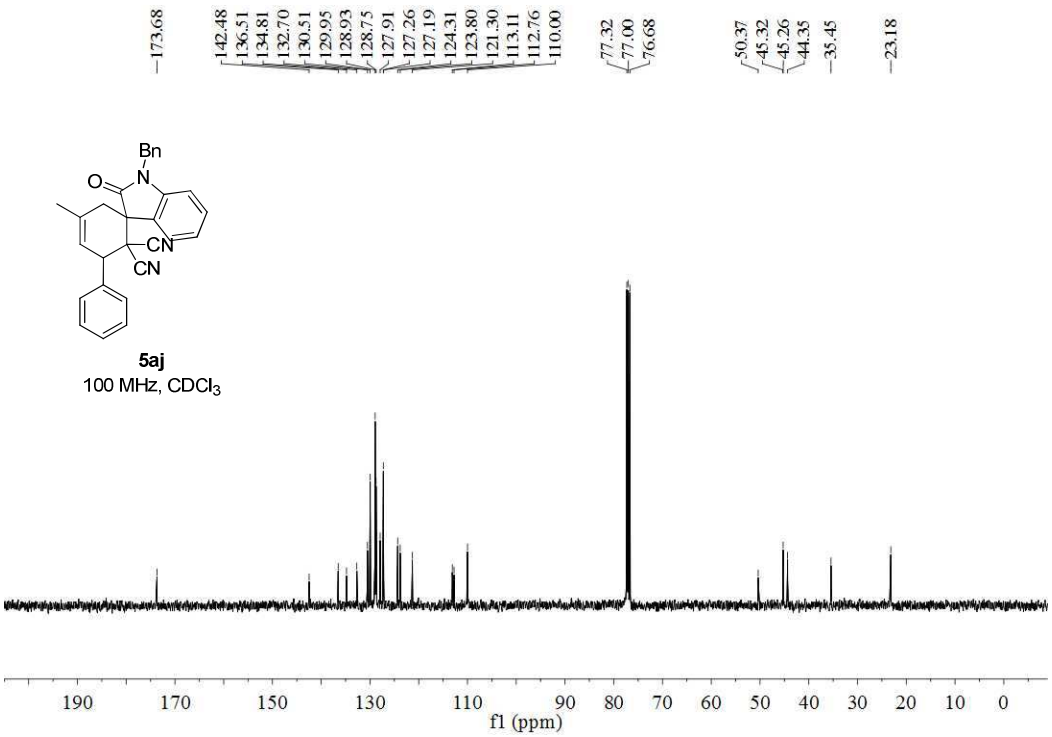

175.01
171.80
170.95
144.90
138.77
138.14
137.74
135.16
134.02
133.66
131.92
129.79
129.39
129.28
128.67
128.43
128.26
128.18
127.84
127.37
127.31
127.18
126.62
125.24
124.30
123.92
123.86
123.79
121.54
113.05
112.65
77.32
77.00
76.68
60.91
60.53
53.17
51.68
50.58
50.43
46.10
41.41
30.24
30.06
23.00
22.90
21.64
21.58
13.69
13.66
CO2Et
N
Ts
O
5ai
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

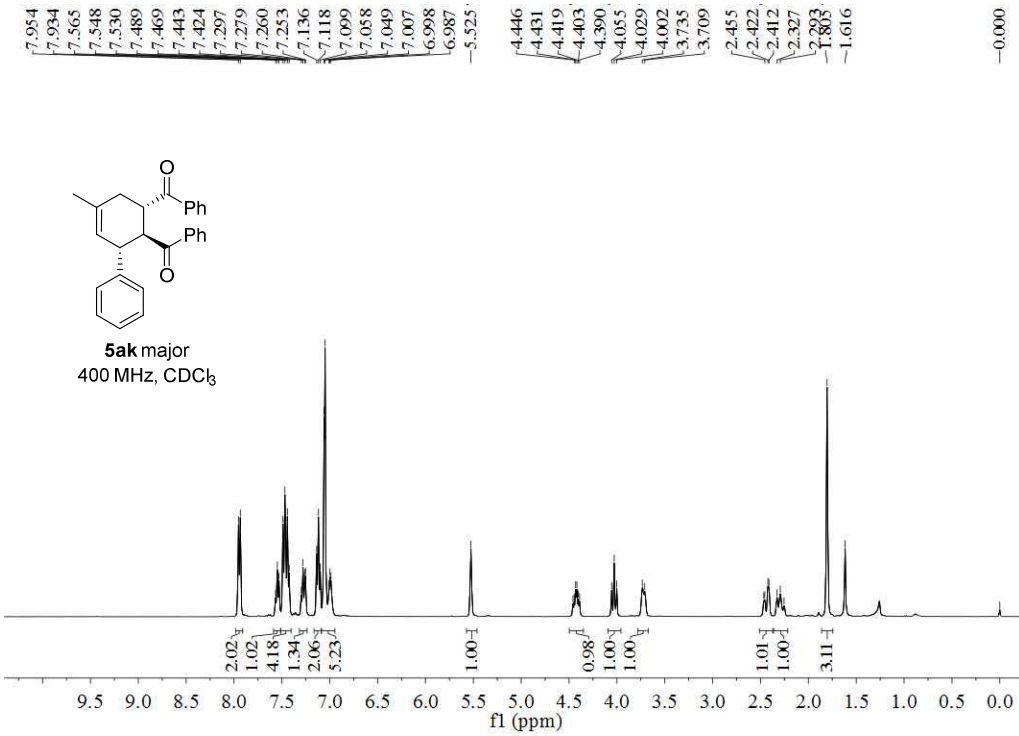

HaHb
0
1
2
3
4
5
6
7
8
9
f1 (ppm)
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f2 (ppm)

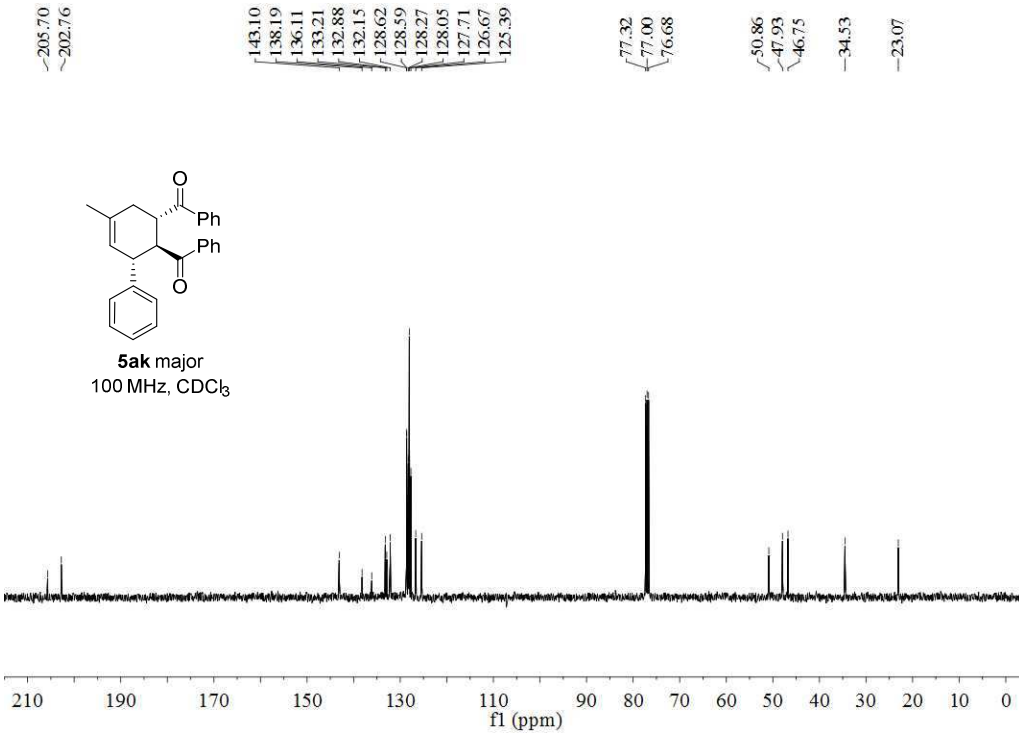

Hb
CO2Et
Ha
O
N
Ts

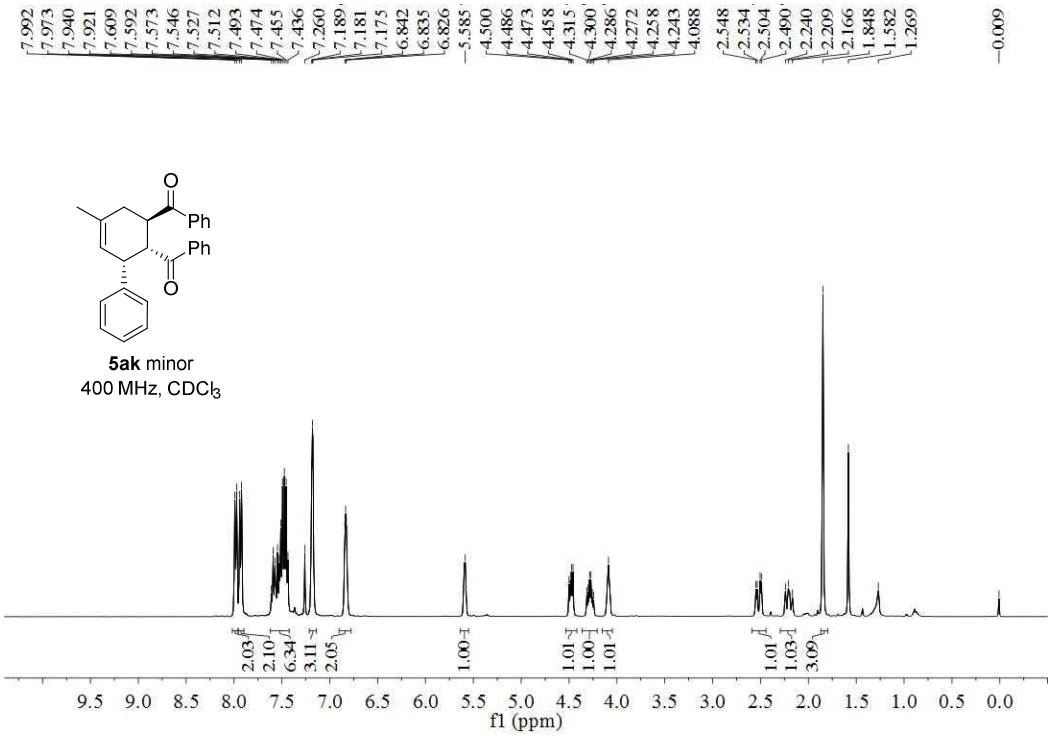
NOESY of **5ai**

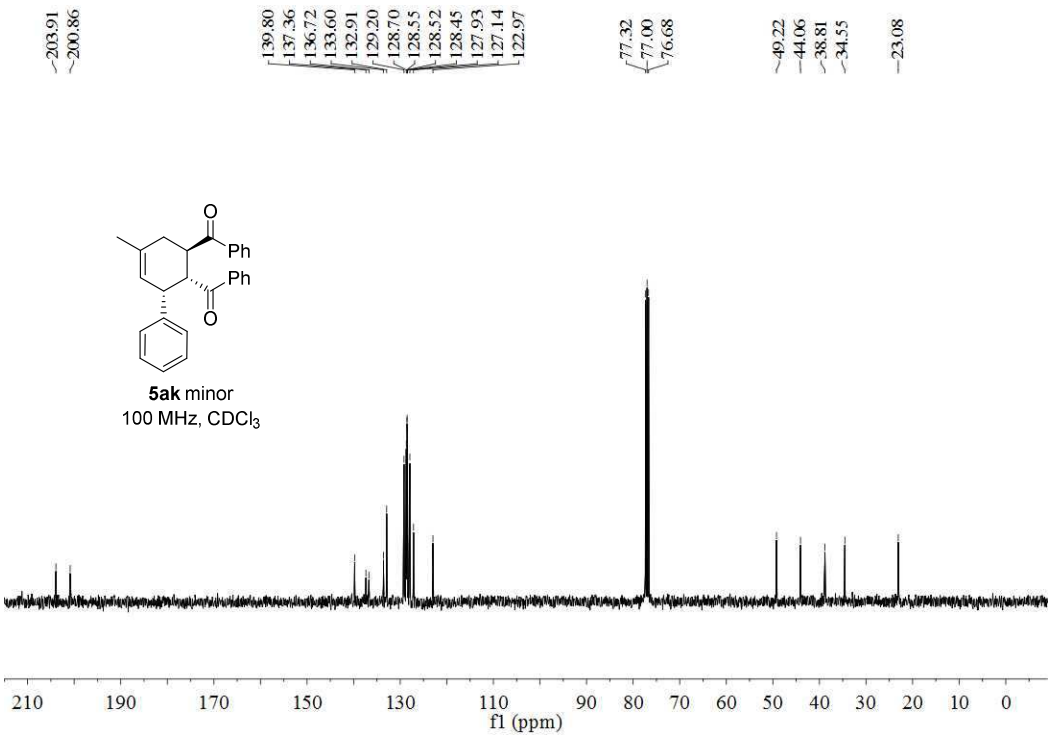

7.775
7.756
7.523
7.506
7.431
7.413
7.363
7.348
7.328
7.298
7.279
7.250
7.163
7.144
7.125
6.810
6.791
5.730
5.112
5.072
4.990
4.929
4.890
2.982
2.934
2.396
2.349
1.931
1.563
0.000
Bn
O
N
CN
CN
5aj
400 MHz, CDCl3
0.94
2.03
10.23
1.10
1.02
1.00
0.99
1.01
1.02
1.00
0.99
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

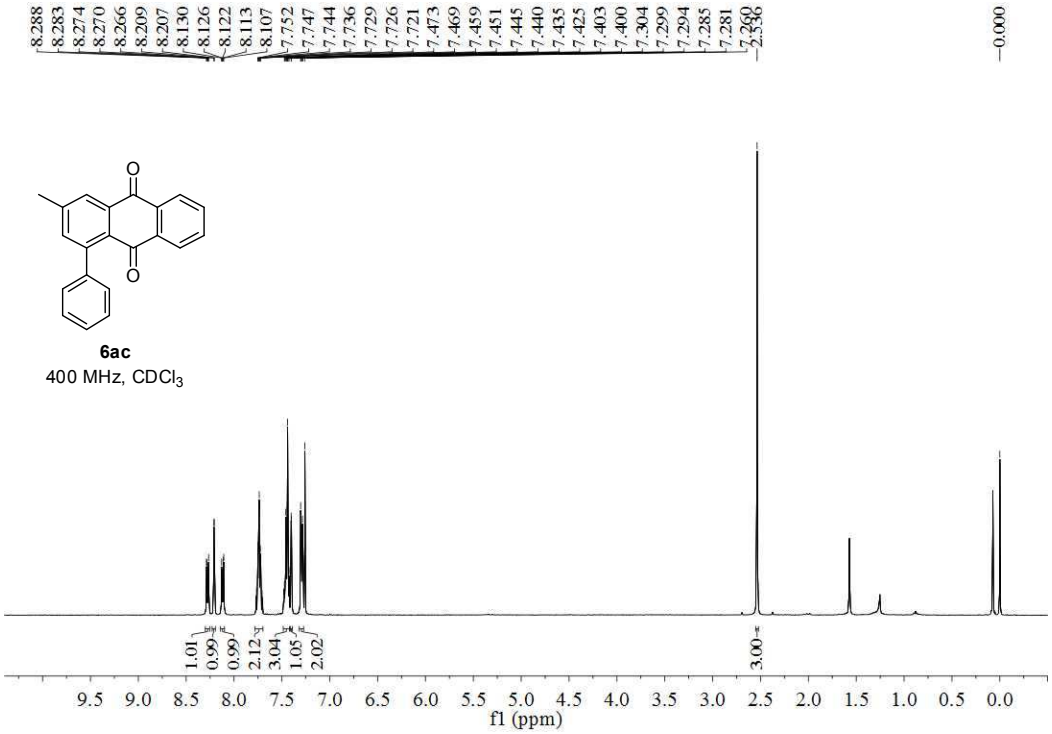

173.68
142.48
136.51
134.81
132.70
130.51
129.95
128.93
128.75
127.91
127.26
127.19
124.31
123.80
121.30
113.11
112.76
110.00
77.32
77.00
76.68
50.37
45.32
45.26
44.35
35.45
23.18
Bn
O
N
CN
CN
5aj
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

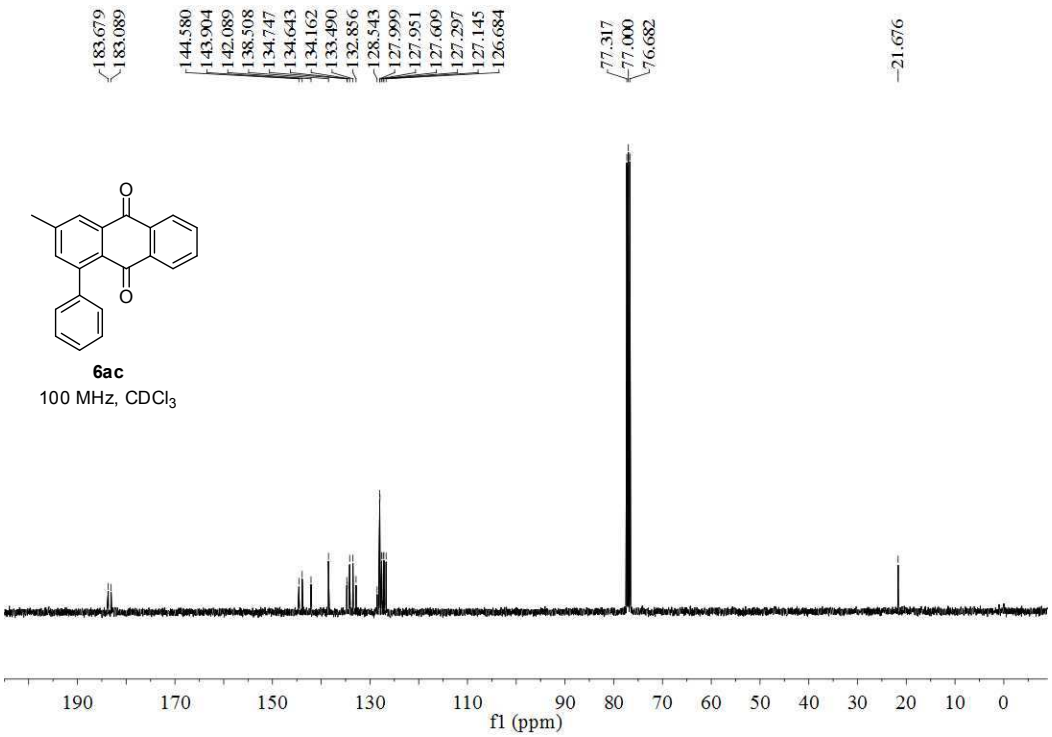

7.954
7.934
7.565
7.548
7.530
7.489
7.469
7.443
7.424
7.297
7.279
7.260
7.253
7.136
7.118
7.099
7.058
7.049
7.007
6.998
6.987
5.525
4.446
4.431
4.419
4.403
4.390
4.055
4.029
4.002
3.735
3.709
2.455
2.422
2.412
2.327
2.293
1.805
1.616
0.000
Ph
Ph
O
O
5ak major
400 MHz, CDCl3
2.02
1.02
4.18
1.34
2.06
5.23
1.00
0.98
1.00
1.00
1.01
1.00
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

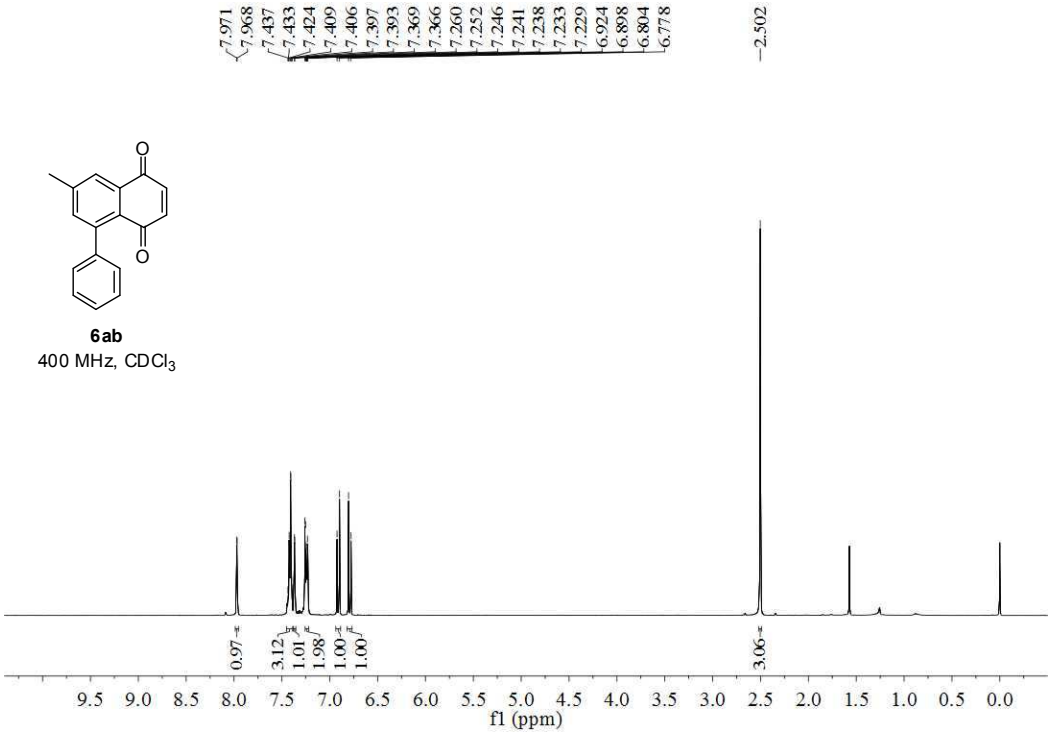

205.70
202.76
143.10
138.19
136.11
133.21
132.88
132.15
128.62
128.59
128.27
128.05
127.71
126.67
125.39
77.32
77.00
76.68
50.86
47.93
46.75
34.53
23.07
Ph
Ph
O
O
5ak major
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.992
7.973
7.940
7.921
7.609
7.592
7.573
7.546
7.527
7.512
7.493
7.474
7.455
7.436
7.260
7.189
7.181
7.175
6.842
6.835
6.826
5.585
4.500
4.486
4.473
4.458
4.315
4.300
4.286
4.272
4.258
4.243
4.088
2.548
2.534
2.504
2.490
2.240
2.209
2.166
1.848
1.582
1.269
0.009
O
Ph
Ph
O
5ak minor
400 MHz, CDCl3
2.03
2.10
6.34
3.11
2.05
1.00
1.01
1.00
1.01
1.01
1.03
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

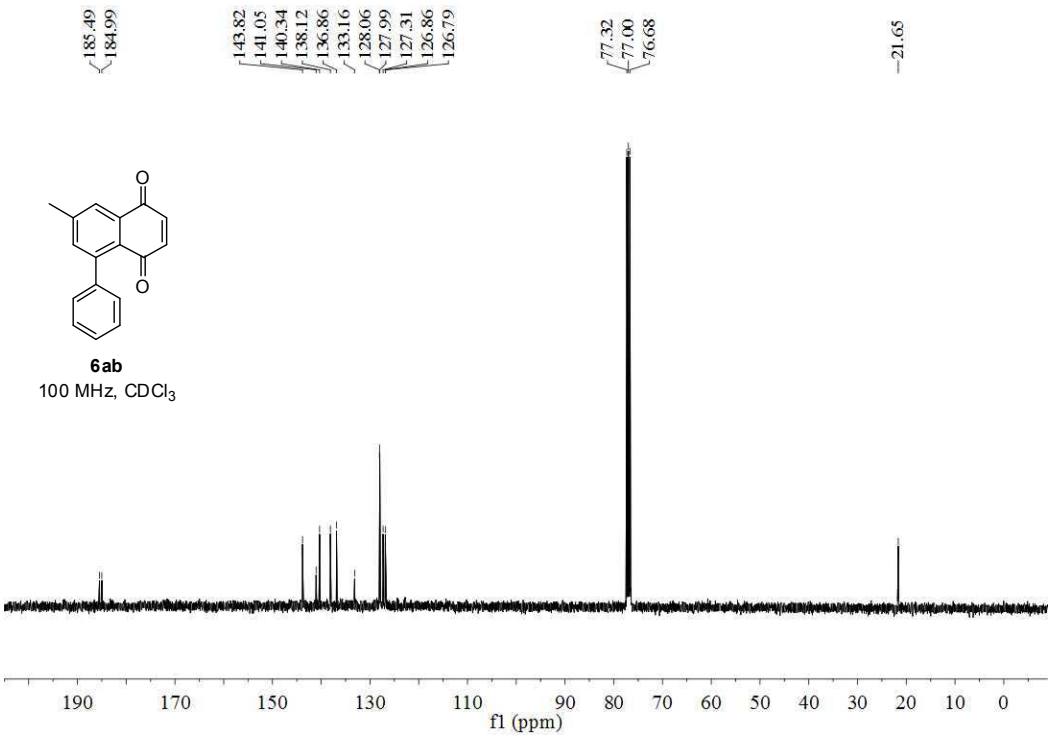

203.91
200.86
139.80
137.36
136.72
133.60
132.91
129.20
128.70
128.55
128.52
128.45
127.93
127.14
122.97
77.32
77.00
76.68
49.22
44.06
38.81
34.55
23.08
O
Ph
Ph
O
5ak minor
100 MHz, CDCl3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.288
8.283
8.274
8.270
8.266
8.209
8.207
8.130
8.126
8.122
8.113
8.107
7.752
7.747
7.744
7.736
7.729
7.726
7.721
7.473
7.469
7.459
7.451
7.445
7.440
7.435
7.425
7.403
7.400
7.304
7.299
7.294
7.285
7.281
7.260
2.506
0.000
O
O
6ac
400 MHz, CDCl3
1.01
0.99
0.99
2.12
3.04
1.05
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

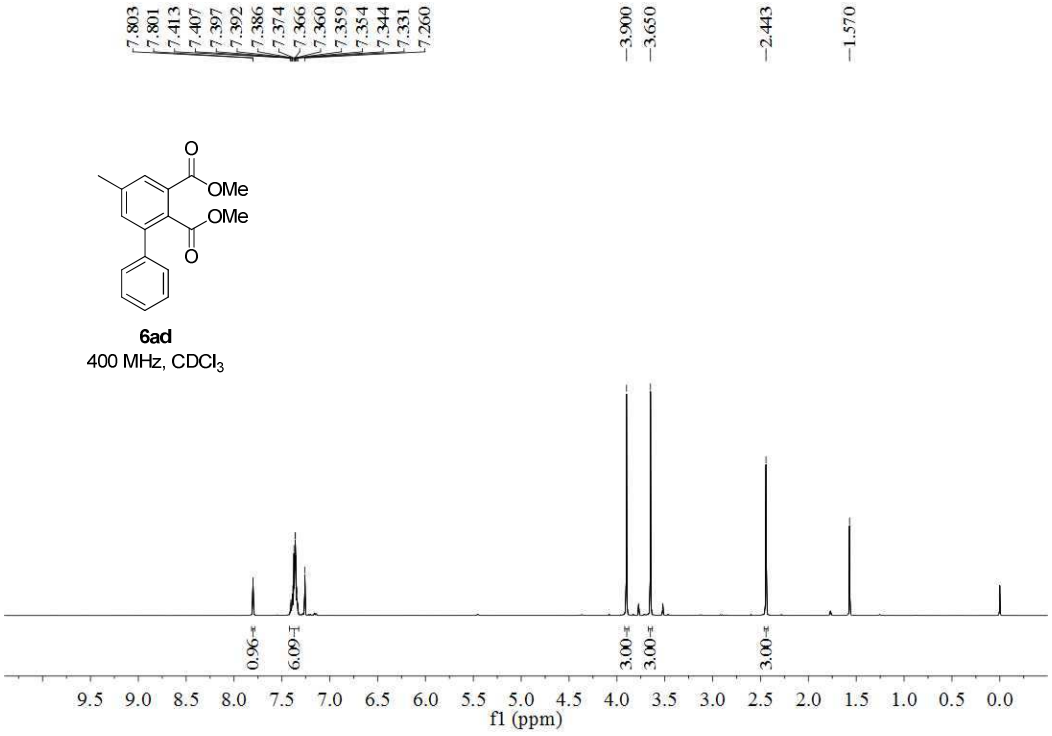

183.679
183.089
144.580
143.904
142.089
138.508
134.747
134.643
134.162
133.490
132.856
128.543
127.999
127.951
127.609
127.297
127.145
126.684
77.317
77.000
76.682
21.676
O
O
6ac
100 MHz, CDCl3
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



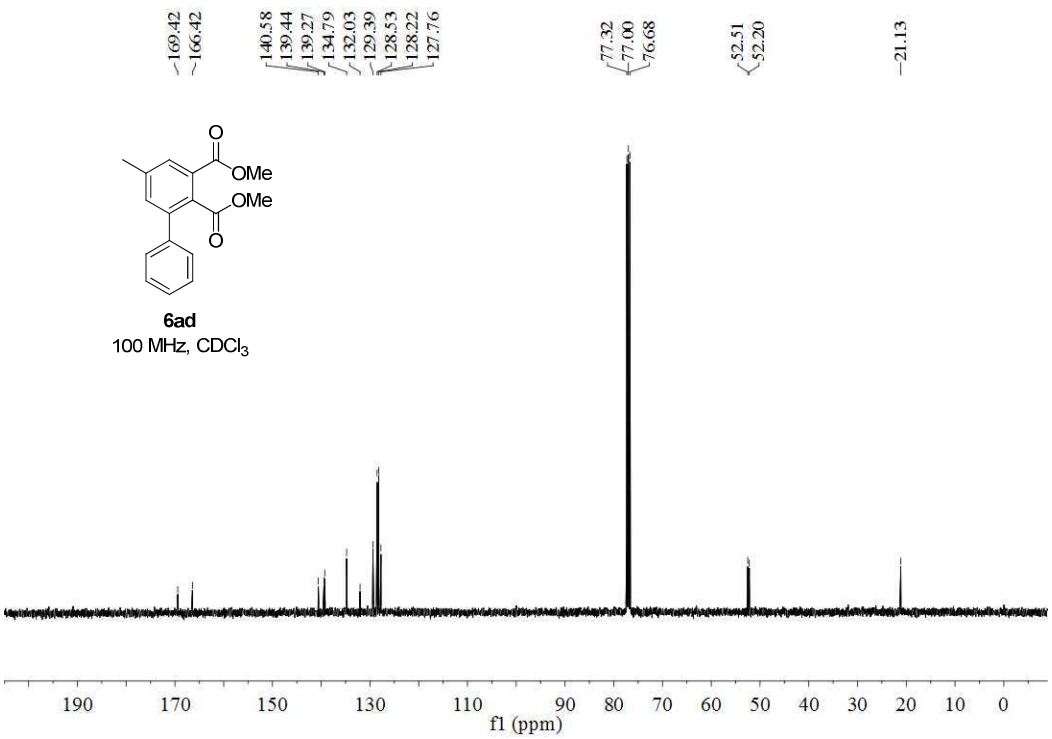
6ab
400 MHz, $CDCl_3$



6ab
100 MHz, $CDCl_3$

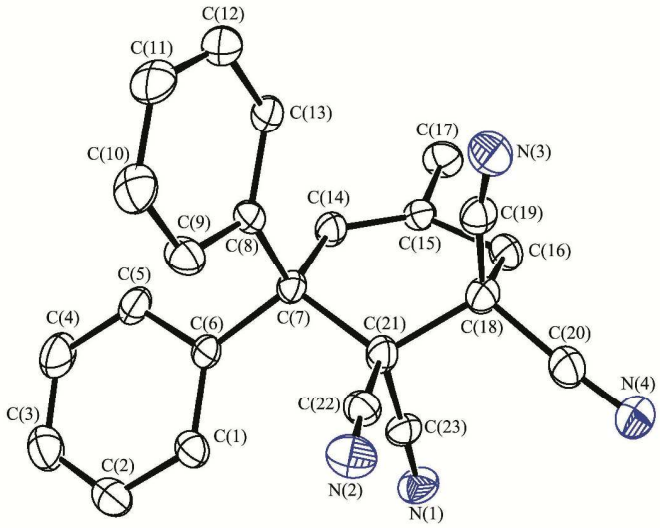


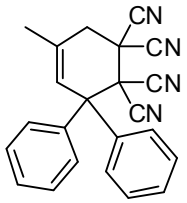
6ad
400 MHz, $CDCl_3$



6ad
100 MHz, $CDCl_3$

Figure S1. X-ray structure of 3u





3u