# Supporting Information

## Au(III)/TPPMS-catalyzed Friedel–Crafts Benzylation of Deactivated N-alkylanilines in Water

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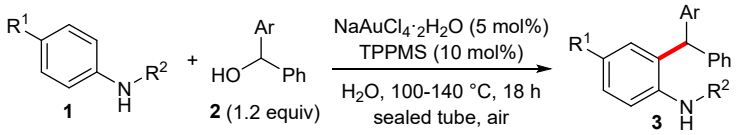
**General Methods.**

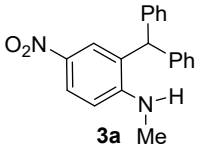
All of the starting materials and solvents were purchased from Sigma–Aldrich Japan, FUJIFILM Wako Pure Chemical Co., Nacalai Tesque, Inc., and TCI Co., Ltd. All commercially available reagents and solvents (guaranteed reagents) were used without further purification. CHROMATOREX Q-PACK SI50 (Fuji Silysia Chemical Ltd, Japan) was used for flash column chromatography. All melting points were determined using a Yanako micro melting point apparatus without correction. $^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a JEOL ECS400 spectrometer. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Mass spectra were obtained using a JEOL the JMS-700 MStation Mass Spectrometer.

**Scheme S1.** Substrate scope.




**General procedure**: A mixture of anilines **1** (1 mmol), alcohols **2** (1.2 mmol), $NaAuCl_4{\cdot}2H_2O$ (5 mol%) and TPPMS (10 mol%) in water (4 mL) was stired at 90-140 °C for 18 h in a sealed tube under air. After cooling, the reaction mixture was extracted with EtOAc. The organic layer was dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give desired product **3**.

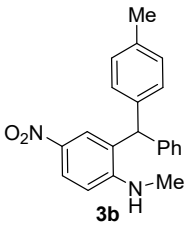
**2-Benzhydryl-*N*-methyl-4-nitroaniline 3a**




Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (152.2 mg, 1.0 mmol) and benzhydrol (221.1 mg, 1.2 mmol) in 4 mL of water at 100 °C for 18 h. The desired product **3a** was obtained in 80% yield (255.8 mg) as a yellow solid.

mp: 160−162 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 2.83 (d, *J*=5.0 Hz, 3H), 4.32 (brq, *J*=5.0 Hz, 1H), 5.30 (s, 1H), 6.59 (d, *J*=9.2 Hz, 1H), 7.05-7.11 (m, 4H), 7.24-7.40 (m, 7H), 7.56 (dd, *J*=2.6, 0.7 Hz, 1H), 8.12 (dd, *J*=9.0, 2.6 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 30.7, 49.5, 109.3, 125.5, 125.8, 126.7, 127.2, 127.3, 127.6, 128.6, 129.1, 129.7, 136.1, 142.3, 152.9; MS (FAB): *m/z* 319 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80, Found: C, 75.46; H, 5.62; N, 8.77.

***N*-Methyl-4-nitro-2-[phenyl(*p*-tolyl)methyl]aniline 3b**

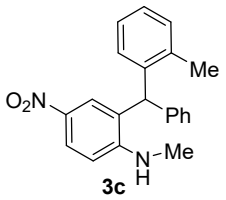


**3b**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (154.1 mg, 1.0 mmol) and 4-methylbenzhydrol (238.2 mg, 1.2 mmol) in 4 mL of water at 100 °C for 18 h. The desired product **3b** was obtained in 74% yield (244.9 mg) as a yellow solid.

mp: 140−141 °C; FT–IR (KBr, $cm^{-1}$): 3450, 1586; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.84 (s, 3H), 4.36 (brs, 1H), 5.27 (s, 1H), 6.59 (d, *J*=9.2 Hz, 1H), 6.97 (d, *J*=8.0 Hz, 2H), 7.08 (d, *J*=6.6 Hz, 2H), 7.13 (d, *J*=8.2 Hz, 2H), 7.27-7.35 (m, 3H), 7.58 (d, *J*=2.5 Hz, 1H), 8.13 (dd, *J*=9.0, 2.6 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 21.1, 30.6, 51.6, 108.6, 125.0, 126.1, 127.3, 127.6, 128.9, 129.1, 129.2, 129.7, 137.0, 137.7, 137.9, 141.0, 151.7; MS (FAB): *m/z* 319 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43, Found: C, 75.83; H, 5.97; N, 8.41.

***N*-Methyl-4-nitro-2-[phenyl(*o*-tolyl)methyl]aniline 3c**

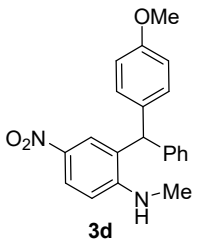


**3c**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (156.3 mg, 1.0 mmol) and 2-methylbenzhydrol (231.2 mg, 1.2 mmol) in 4 mL of water at 120 °C for 18 h. The desired product **3c** was obtained in 57% yield (187.8 mg) as a yellow solid.

mp: 134−136 °C; FT–IR (KBr, $cm^{-1}$): 3417, 3056, 2923, 1587; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.84 (s, 3H), 4.22 (brs, 1H), 5.36 (s, 1H), 6.62 (d, *J*=9.2 Hz, 1H), 6.79 (d, *J*=7.6 Hz, 1H), 7.06 (d, *J*=7.6 Hz, 2H), 7.11−7.16 (m, 1H), 7.21 (d, *J*=3.9 Hz, 2H), 7.27−7.36 (m, 4H), 7.49 (dd, *J*=2.5, 0.5 Hz, 1H), 8.13 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 19.6, 30.7, 48.6, 108.7, 125.0, 125.8, 126.5, 127.3, 127.4, 127.5, 128.7, 129.0, 129.5, 131.0, 136.5, 138.0, 139.0, 140.1, 151.7; MS (FAB): *m/z* 333 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43, Found: C, 75.88; H, 5.96; N, 8.41.

**2-[(4-Methoxyphenyl)(phenyl)methyl]-*N*-methyl-4-nitroaniline 3d**



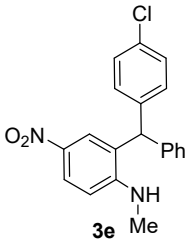
**3d**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (153.1 mg, 1.0 mmol) and 4-methoxybenzhydrol (257.7 mg, 1.2 mmol) in 4 mL of water at 100 °C for 18 h. The desired product **3d** was obtained in 70% yield (245.2 mg) as a yellow solid.

mp: 115−117 °C; FT–IR (KBr, $cm^{-1}$): 3447, 3000, 2834, 1586; $^1H$ NMR (400 MHz, $CDCl_3$): δ 2.84 (s, 3H), 3.79 (s, 3H), 4.36 (brs, 1H), 5.25 (s, 1H), 6.59 (d, *J*=8.9 Hz, 1H), 6.86 (d, *J*=8.7 Hz, 2H), 7.00 (d, *J*=8.7 Hz, 2H), 7.08 (d, *J*=6.9 Hz, 2H), 7.28−7.35 (m, 3H), 7.57 (d, *J*=2.5 Hz, 1H), 8.13 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 30.6, 51.1, 55.3, 108.6, 114.4, 125.0, 126.0, 127.3, 127.8, 129.0, 129.1, 130.2, 132.7, 137.9, 141.2, 151.7, 158.8; MS (FAB): *m/z* 349 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04, Found: C, 72.29; H, 5.68; N,

7.82.

**2-[(4-Chlorophenyl)(phenyl)methyl]-*N*-methyl-4-nitroaniline 3e**

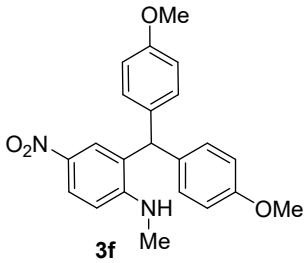


**3e**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (152.9 mg, 1.0 mmol) and 4-chlorobenzhydrol (538.3 mg, 2.4 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3e** was obtained in 50% yield (177.1 mg) as a yellow solid.

mp: 133−135 °C; FT–IR (KBr, $cm^{-1}$): 3433, 3024, 2921, 1587; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.85 (s, 3H), 4.30 (s, 1H), 5.28 (s, 1H), 6.62 (d, *J*=9.2 Hz, 1H), 7.02 (d, *J*=8.2 Hz, 2H), 7.06−7.08 (m, 2H), 7.30−7.36 (m, 5H), 7.55 (dd, *J*=2.8, 0.7 Hz, 1H), 8.14 (dd, *J*=9.2, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.6, 51.2, 108.8, 125.2, 126.0, 126.8, 127.6, 129.1, 129.2, 130.6, 133.3, 137.9, 139.4, 140.3, 151.6; MS (FAB): *m/z* 353 $[M+H]^+$; Anal. Calcd. for $C_{20}H_{17}ClN_2O_2$: C, 68.09; H, 4.86; N, 7.94, Found: C, 67.99; H, 4.81; N, 7.98.

**2-[Bis(4-methoxyphenyl)methyl]-*N*-methyl-4-nitroaniline 3f**

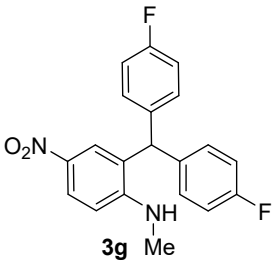


**3f**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (154.1 mg, 1.0 mmol) and 4-4'-dimethoxybenzhydrol (293.4 mg, 1.2 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3f** was obtained in 54% yield (203.6 mg) as a yellow solid.

mp: 152−153 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.83 (s, 3H), 3.80 (s, 6H), 4.38 (brs, 1H), 5.19 (s, 1H), 6.58 (d, *J*=9.2 Hz, 1H), 6.85 (d, *J*=8.7 Hz, 4H), 6.98 (d, *J*=8.7 Hz, 4H), 7.57 (dd, *J*=2.6, 0.7 Hz, 1H), 8.12 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.6, 50.3, 55.3, 108.5, 114.3, 124.9, 125.9, 128.1, 130.1, 133.1, 137.9, 151.7, 158.7; MS (FAB): *m/z* 379 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{22}N_2O_4$: C, 69.83; H, 5.86; N, 7.40, Found: C, 69.58; H, 5.78; N, 7.44.

**2-[Bis(4-fluorophenyl)methyl]-*N*-methyl-4-nitroaniline 3g**



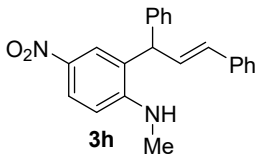
**3g**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (153.7 mg, 1.0 mmol) and 4,4'-difluorobenzhydrol (526.3 mg, 2.4 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3g** was obtained in 83% yield (294.5 mg) as a yellow solid.

mp: 148−150 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.86 (d, *J*=5.0 Hz, 3H), 4.24 (brq, *J*=5.0 Hz, 1H), 5.28 (s, 1H), 6.62 (d, *J*=9.2 Hz, 1H), 7.04 (d, *J*=6.9 Hz, 8H), 7.51 (d, *J*=2.8 Hz, 1H), 8.15 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.7, 50.5, 109.0, 116.2 (d, $J_{CF}$ = 22.0 Hz), 125.4, 126.0, 127.1, 130.8 (d, $J_{CF}$=7.7 Hz), 136.5 (d, $J_{CF}$=3.8 Hz), 138.1, 151.6,

162.2 (d, $J_{CF}$=247.3 Hz); MS (FAB): *m/z* 355 $[M+H]^+$. Anal. Calcd. for $C_{20}H_{16}F_2N_2O_2$: C, 67.79; H, 4.55; N, 7.91, Found: C, 67.80; H, 4.57; N, 7.91.

**(*E*)-2-(1,3-Diphenylallyl)-*N*-methyl-4-nitroaniline 3h** [1]

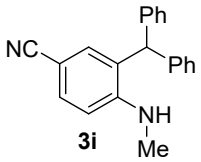


**3h**

Prepared according to the general procedure by using *N*-methyl-4-nitroaniline (156.8 mg, 1.0 mmol) and *trans*-1,3-diphenyl-2-propen-1-ol (257.1 mg, 1.2 mmol) in 4 mL of water at 100 °C for 18 h. The desired product **3h** was obtained in 82% yield (290.4 mg) as a yellow solid.

mp: 101−103 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.88 (s, 3H), 4.48 (s, 1H), 4.76 (d, *J*=6.9 Hz, 1H), 6.29 (dd, *J*=15.9, 1.1 Hz, 1H), 6.59−6.64 (m, 2H), 7.20−7.38 (m, 10H), 8.02 (dd, *J*=2.8, 0.5 Hz, 1H), 8.16 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.6, 49.3, 108.8, 125.2, 125.3, 126.4, 126.5, 127.6, 127.8, 128.5, 128.6, 129.2, 129.5, 132.7, 136.5, 137.9, 140.0, 151.8; MS (FAB): *m/z* 345 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13, Found: C, 76.36; H, 5.87; N, 8.05.

**3-Benzhydryl-4-(methylamino)benzonitrile 3i**

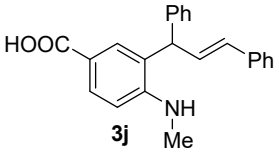


**3i**

Prepared according to the general procedure by using 4-(Methylamino)benzonitrile (134.4 mg, 1.0 mmol) and benzhydrol (440.9 mg, 2.4 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3i** was obtained in 98% yield (291.6 mg) as a white solid.

mp: 150-152 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.78 (d, *J*=4.6 Hz, 3H), 4.06 (brd, *J*=4.4 Hz, 1H), 5.29 (s, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 7.05−7.10 (m, 4H), 7.27−7.40 (m, 6H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.4, 51.7, 98.4, 109.7, 120.8, 126.5, 127.2, 127.3, 128.3, 128.5, 128.6, 128.9, 129.3, 129.4, 132.5, 133.5, 141.0, 149.8; MS (FAB): *m/z* 299 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39, Found: C, 84.58; H, 6.07; N, 8.31.

**(*E*)-3-(1,3-Diphenylallyl)-4-(methylamino)benzoic acid 3j**

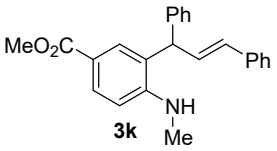


**3j**

Prepared according to the general procedure by using 4-(methylamino)benzoic acid (152.8 mg, 1.0 mmol) and *trans*-1,3-diphenyl-2-propen-1-ol (252.9 mg, 1.2 mmol) in 4 mL of water at 120 °C for 18 h. The desired product **3j** was obtained in 58% yield (201.7 mg) as a white solid.

mp: 194−195 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.81 (s, 3H), 4.78 (d, *J*=6.9 Hz, 1H), 6.28 (d, *J*=16 Hz, 1H), 6.63−6.68 (m, 2H), 7.22−7.38 (m, 10H), 7.85 (d, *J*=1.8 Hz, 1H), 7.99 (dd, *J*=8.7, 2.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.5, 49.5, 109.3, 116.9, 126.2, 126.5, 127.2, 127.5, 128.6, 128.9, 130.5, 131.2, 131.3, 132.1,136.9, 140.9, 151.0, 171.9; MS (FAB): *m/z* 344 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08, Found: C, 79.91; H, 6.19; N, 4.01.

**Methyl (*E*)-3-(1,3-diphenylallyl)-4-(methylamino)benzoate 3k**

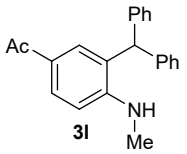


**3k**

Prepared according to the general procedure by using methyl 4-(methylamino)benzoate (165.2 mg, 1.0 mmol) and *trans*-1,3-diphenyl-2-propen-1-ol (252.9 mg, 1.2 mmol) in 4 mL of water at 120 °C for 18 h. The desired product **3k** was obtained in 67% yield (239.9 mg) as a white solid.

mp: 56−58 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.80 (s, 3H), 3.83 (s, 3H), 4.08 (s, 1H), 4.78 (d, *J*=6.9 Hz, 1H), 6.27 (d, *J*=16.0 Hz, 1H), 6.63 (d, *J*=8.5 Hz, 1H), 6.66 (d, *J*=16.0, 7.1 Hz, 1H), 7.18−7.40 (m, 10H), 7.81 (d, *J*=1.8 Hz, 1H), 7.93 (dd, *J*=8.5, 2.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 30.5, 49.5, 51.6, 109.3, 118.0, 126.2, 126.5, 127.1, 127.5, 128.5, 128.6, 128.9, 130.4, 130.6, 130.7, 132.0, 137.0, 141.0, 150.4, 167.6; MS (EI): *m/z* (%): 357 ($M^+$, 39.6), 266 (100); HRMS (EI): *m/z* ($M^+$) calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1729.

**1-[3-Benzhydryl-4-(methylamino)phenyl]ethan-1-one 3l**

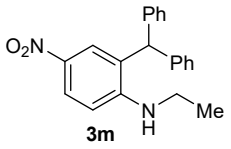


**3l**

Prepared according to the general procedure by using 1-[4-(methylamino)phenyl]ethan-1-one (149.2 mg, 1.0 mmol) and benzhydrol (221.1 mg, 1.2 mmol) in 4 mL of water at 120 °C for 18 h. The desired product **3l** was obtained in 61% yield (193.6 mg) as a white solid.

mp: 159−162 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.80 (s, 3H), 4.06 (brs, 1H), 5.35 (s, 1H), 6.63 (d, *J*=8.5 Hz, 1H), 7.08-7.12 (m, 4H), 7.23-7.35 (m, 7H), 7.86 (dd, *J*=8.7, 2.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 25.9, 30.5, 52.0, 109.0, 126.2, 127.0, 128.7, 129.3, 130.8, 141.7, 150.6, 196.7; MS (EI): *m/z* (%): 315 ($M^+$, 100); HRMS (EI): *m/z* ($M^+$) calcd for $C_{22}H_{21}NO$ 315.1623, found 315.1623.

**2-Benzhydryl-*N*-ethyl-4-nitroaniline 3m**

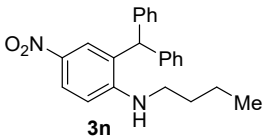


**3m**

Prepared according to the general procedure by using *N*-ethyl-4-nitroaniline (166.2 mg, 1.0 mmol) and benzhydrol (221.1 mg, 1.2 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3m** was obtained in 70% yield (238.0 mg) as a yellow solid.

mp: 164−165 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, *J*=7.1 Hz, 3H), 3.12 (q, *J*=7.1 Hz, 3H), 4.15 (brs, 1H), 5.28 (s, 1H), 6.57 (d, *J*=8.9 Hz, 1H), 7.08-7.13 (m, 4H), 7.25-7.36 (m, 6H), 7.57 (dd, *J*=2.5, 0.9 Hz, 1H), 8.09 (dd, *J*=9.2, 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.1, 38.2, 52.3, 109.0, 125.1, 126.1, 127.3, 127.4, 129.0, 129.2, 137.7, 140.7, 151.0; MS (FAB): *m/z* 333 $[M+H]^+$; Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43, Found: C, 75.78; H, 6.00; N, 8.41.

**2-Benzhydryl-*N*-butyl-4-nitroaniline 3n**

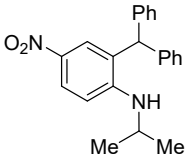


3n

Prepared according to the general procedure by using *N*-butyl-4-nitroaniline (198.2 mg, 1.0 mmol) and benzhydrol (226.6 mg, 1.2 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3n** was obtained in 76% yield (273.1 mg) as a yellow solid.

mp: 93−95 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.79 (t, *J*=7.6 Hz, 3H), 1.04 (sext, *J*=7.6 Hz, 2H), 1.38 (quin, *J*=7.3 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 4.28 (brs, 1H), 5.28 (s, 1H), 6.58 (d, *J* = 8.9 Hz, 1H), 7.12−7.14 (m, 4H), 7.26−7.38 (m, 6H), 7.58 (dd, *J* = 2.8, 0.7 Hz, 1H), 8.11 (dd, *J* = 9.2, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.6, 19.6, 30.6, 43.0, 52.4, 108.9, 125.1, 126.2, 127.3, 127.4, 129.0, 129.2, 137.6, 140.7, 151.0; MS (FAB): *m/z* 361 $[M+H]^+$; Anal. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77, Found: C, 76.75; H, 6.68; N, 7.79.

**2-Benzhydryl-*N*-isopropyl-4-nitroaniline 3o**



3o

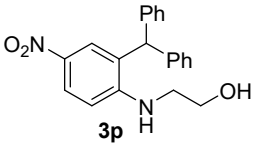
Prepared according to the general procedure by using *N*-Isopropyl-4-nitroaniline (181.4 mg, 1.0 mmol) and benzhydrol (227.2 mg, 1.2 mmol) in 4 mL of water at 140 °C for 18 h. The desired product **3o** was obtained in 95% yield (328.1 mg) as a yellow solid.

mp: 169−170 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.98 (d, *J*=6.2 Hz, 6H), 3.61 (sep, *J*=6.2 Hz, 1H), 4.14 (brs, 1H), 5.25 (s, 1H), 6.58 (d, *J*=9.4 Hz, 1H), 7.09−7.14 (m, 4H), 7.30−7.37 (m, 6H), 7.58 (dd, *J*=2.8, 0.7 Hz, 1H), 8.09 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 22.3, 44.3, 52.5, 109.3, 125.1, 126.3, 127.3, 127.4, 129.0, 129.2, 137.3, 140.6, 150.2; MS (FAB): *m/z* 347 $[M+H]^+$; Anal. Calcd. for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09, Found: C, 76.36; H, 6.4; N, 8.09.

**2-[(2-Benzhydryl-4-nitrophenyl)amino]ethan-1-ol 3p and**
**2-Benzhydryl-*N*-[2-(2,2-diphenylethoxy)ethyl]-4-nitroaniline 3p'**

Prepared according to the general procedure by using 2-[(4-nitrophenyl)amino]ethanol **1p** (183.4 mg, 1.0 mmol) and benzhydrol (222.0 mg, 1.2 mmol) in 4 mL of water at 120 °C for 18 h. The desired products **3p** and **3p'** were obtained in 54% yield (186.3 mg) and 26% yield (132.1 mg), respectively.

**2-[(2-Benzhydryl-4-nitrophenyl)amino]ethan-1-ol 3p**

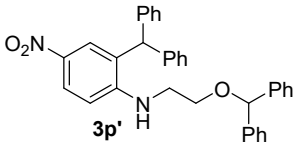


3p

Yield: 186.3 mg (0.54 mmol); yellow solid; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.09 (brs, 1H), 3.28 (t, *J*=5.0 Hz, 2H), 3.63 (t, *J*=5.5 Hz, 2H), 4.68 (brs, 1H), 5.35 (s, 1H), 6.62 (d, *J*=9.2 Hz, 1H), 7.12−7.15 (m, 4H), 7.26−7.37 (m, 6H), 7.60 (dd, *J* = 2.8, 0.9 Hz, 1H), 8.10 (dd, *J*=8.7, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 45.3, 52.2, 60.6, 109.2, 125.0, 126.2, 127.5, 128.0, 129.0, 129.2, 138.0, 140.6, 150.7; MS (FAB): *m/z* 349

$[M+H]^+$.

**2-Benzhydryl-N-(2-(benzhydryloxy)ethyl)-4-nitroaniline 3p'**



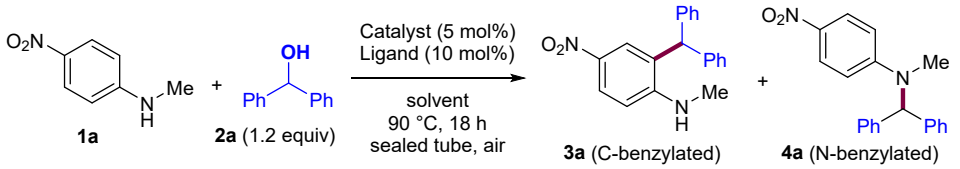
**3p'**

Yield: 132.1 mg (0.26 mmol), 26%; yellow solid; mp: 153-155 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.35 (t, *J*=5.0 Hz, 2H), 3.52 (t, *J*=4.8 Hz, 2H), 4.81 (brs, 1H), 5.25 (s, 1H), 5.31 (s, 1H), 6.59 (d, *J*=9.2 Hz, 1H), 7.02−7.09 (m, 4H), 7.19−7.34 (m, 16H), 7.59 (d, *J*=2.8, 0.7 Hz, 1H), 8.08 (dd, *J*=9.0, 2.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 43.4, 52.0, 66.9, 84.2, 109.2, 124.9, 126.2, 126.8, 127.3, 127.7, 127.7, 128.5, 128.9, 129.2, 137.9, 140.1, 141.6, 150.8; MS (FAB): *m/z* 515 $[M+H]^+$; Anal. Calcd. for $C_{35}H_{32}N_2O_3$: C, 79.52; H, 6.10; N, 5.30, Found: C, 79.33; H, 5.93; N, 5.41.

**References**

1. R. Nallagonda, M. Rehan, P. Ghorai, *Org. Lett.* **2014**, *16*, 4786−4789.

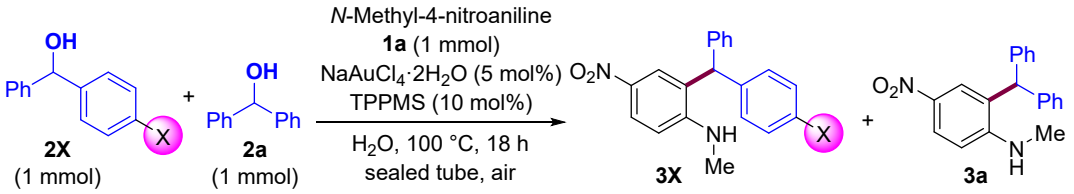
**Table S1.** Optimization of catalytic dehydrative Friedel−Crafts benzylation.[a]




| Entry | Catalyst | Ligand | Solvent | NMR Yields (%) | |
|---|---|---|---|---|---|
| | | | | **3a** | **4a** |
| 1 | $Re_2O_7$ | TPPMS | $H_2O$ | 8 | 45 |
| 2 | $FeCl_2$ | TPPMS | $H_2O$ | 2 | 60 |
| 3 | $CuCl_2$ | TPPMS | $H_2O$ | 3 | 55 |
| 4 | HCl | none | $H_2O$ | 7 | 54 |
| 5 | $ZnCl_2$, $CoCl_2$ or $MnCl_2$ | TPPMS | $H_2O$ | 0 | 0 |
| 6 | none | none | $H_2O$ | 0 | 0 |
| **7** | **$NaAuCl_4{\cdot}2H_2O$** | **TPPMS** | **$H_2O$** | **87** | **5** |
| 8 | $AuBr_3$ | TPPMS | $H_2O$ | 79 | 11 |
| 9 | $HAuCl_4{\cdot}4H_2O$ | TPPMS | $H_2O$ | 79 | 18 |
| 10 [b] | $NH_4AuCl_4$ | TPPMS | $H_2O$ | 30 | 27 |
| 11 | $AuCl_3$ | TPPMS | $H_2O$ | 23 | 26 |
| 12 | AuCl | TPPMS | $H_2O$ | 31 | 30 |
| 13 | $NaAuCl_4{\cdot}2H_2O$ | none | $H_2O$ | 0 | 34 |
| 14 | $NaAuCl_4{\cdot}2H_2O$ | TPPMS [c] | $H_2O$ | 17 | 13 |
| 15 | $NaAuCl_4{\cdot}2H_2O$ | TPPTS [d] | $H_2O$ | 0 | 54 |
| 16 | $NaAuCl_4{\cdot}2H_2O$ | TPPMS | Toluene | 20 | 43 |
| 17 | $NaAuCl_4{\cdot}2H_2O$ | TPPMS | 1-Propanol | 0 | 0 |
| 18 | $NaAuCl_4{\cdot}2H_2O$ | TPPMS | DMF | 0 | 11 |
| 19 | $NaAuCl_4{\cdot}2H_2O$ | TPPMS | DMF | 10 | 14 |
| **20 [d]** | **$NaAuCl_4{\cdot}2H_2O$** | **TPPMS** | **$H_2O$** | **96** | **4** |

[a] **1a** (1 mmol), catalysts (5 mol%), ligand (10 mol%), **2a** (1.2 mmol), and solvent (4 mL) were used at 90 °C for 18 h. All the reactions were performed in a sealed tube under air. [b] 10 mol% was used. [c] 5 mol% was used. [d] $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$. [e] at 100 °C.

**Scheme S2.** Hammett study.




A mixture of *N*-methyl-4-nitroaniline **1a** (152.9 mg, 1.0 mmol), benzhydrol **2a** (184 mg, 1 mmol), $NaAuCl_4{\cdot}2H_2O$ (5 mol%) and TPPMS (10 mol%) in water (4 mL) was heated at 100 °C for 18 h in a sealed tube under air. After the reaction mixture was cooled, 1,3,5-trimethoxybenzene (168 mg, 1 mmol, internal standard) was added to the reaction mixture, which was extracted with EtOAc. The organic layer was concentrated in vacuo. The residue was analyzed by $^1$H-NMR spectroscopy.

**Table S2.**

| | sigma | log ($k_X/k_H$) |
|---|---|---|
| OMe | -0.27 | 0.602 |
| Me | -0.17 | 0.3505 |
| H | 0 | 0 |
| F | 0.06 | -0.237 |
| Cl | 0.23 | -0.3631 |

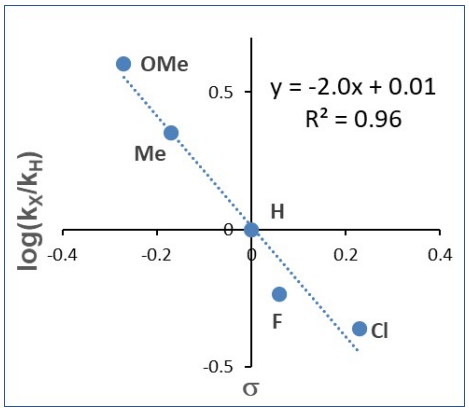
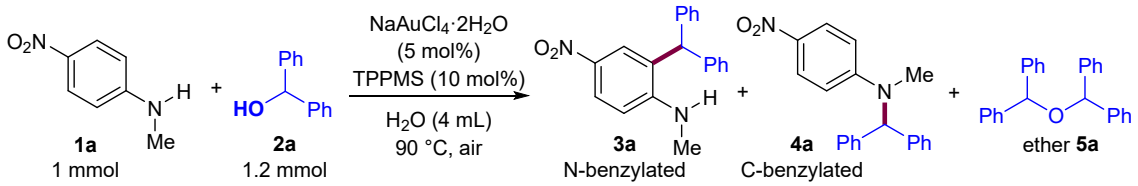



**Figure S1.** Hammett plot for the dehydrative Friedel–Crafts benzylation using 4-substituted benzhydrols **2**.

**Scheme S3.** Reaction progress.




A mixture of *N*-methyl-4-nitroaniline **1a** (152.9 mg, 1.0 mmol), benzhydrol **2a** (184 mg, 1 mmol), $NaAuCl_4{\cdot}2H_2O$ (5 mol%), TPPMS (10 mol%) and 1,3,5-trimethoxybenzene (168 mg, 1 mmol, internal standard) in water (4 mL) was heated at 90 °C in a sealed tube under air. Every hour, a few drops of the reaction mixture were transferred into a test tube. The sample was extracted with $CDCl_3$, which was analyzed by $^1$H-NMR spectroscopy.

**Table S3.** Reaction time course (conversion % or concentration M).

| Time (min) | C-benzyl **3a** (%) | N-benzyl **4a** (%) | Aniline **1a** (%) | Alcohol **2a** (M) | Dimer **5a** (M) |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 100 | 0.3 | 0 |
| 60 | 15 | 32 | 50 | 0.045 | 0.0575 |
| 80 | 18 | 34 | 48 | 0.0425 | 0.06 |
| 120 | 27 | 26 | 45 | 0.04 | 0.0575 |
| 180 | 40 | 23 | 42 | 0.0375 | 0.0575 |
| 240 | 48 | 21 | 36 | 0.0375 | 0.0575 |
| 300 | 50 | 19 | 35 | 0.035 | 0.0475 |

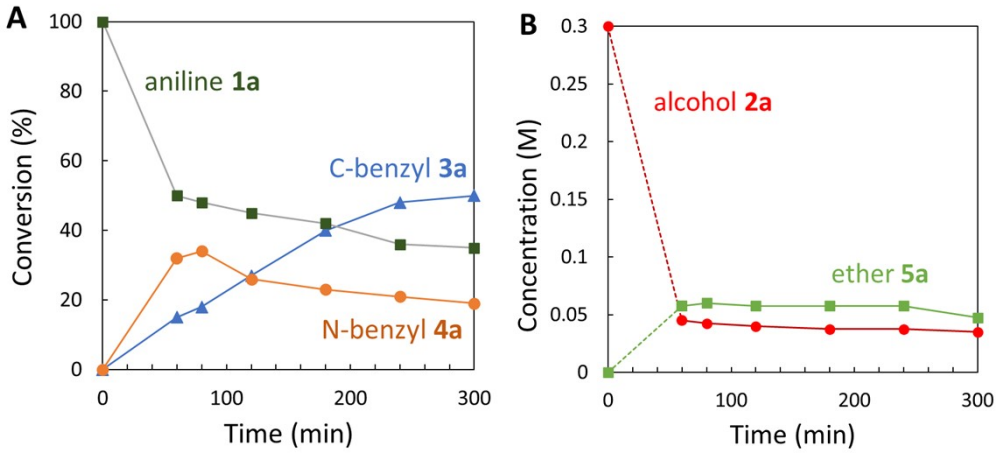



**Figure S2.** (A) and (B) The reaction profile for the dehydrative coupling of aniline **1a** with alcohol **2a**.

**Table S4.** Reaction time course (Concentration M).

| Time (min) | C-benzyl **3a** | N-benzyl **4a** |
|---|---|---|
| 0 | 0 | 0 |
| 60 | 0.0425 | 0.0775 |
| 80 | 0.0525 | 0.0825 |
| 120 | 0.07 | 0.075 |
| 180 | 0.0925 | 0.0575 |
| 240 | 0.1125 | 0.0525 |
| 300 | 0.1275 | 0.05 |

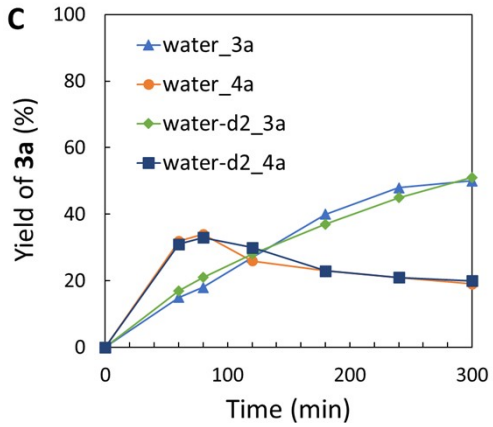



**Figure S3.** (C) The solvent isotope effect studies in $H_2O$ or in $D_2O$.

**X-ray structure of 3a.**

Single crystal of **3a** was obtained by slow evaporation of toluene solution at room temperature as a colorless crystal. Single crystal was mounted on a loop for X-ray measurements. Diffraction data were collected on an X-ray diffractometer (Rigaku XtaLAB P200) equipped with a rotating anode X-ray source (Mo-$K\alpha$, $\alpha$ = 0.71075 Å) and a hybrid photon counting detector (PILATUS 200K) at 93 K. The frame data were integrated, and the absorption correction was calculated using the Rigaku CrystalClear, CrysAlisPro program package. The structures were solved by SHELXT Version 2018/2, and refined by full-matrix least-squares fitting on $F^2$ (SHELXL Version 2018/3)[1-2]. All non-hydrogen atoms were refined anisotropically. All N−H hydrogen atoms were found by difference Fourier synthesis. The other hydrogens were located at the calculated positions. The crystal data and the structure refinements are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 2358605. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**Table S5.** Crystallographic data and refinement parameters.

| Compound | **3a** |
|---|---|
| Formula | $C_{20}H_{18}N_2O_2$ |
| $M_r$ | 318.36 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| $a$ / Å | 14.4437(5) |
| $b$ / Å | 5.5419(2) |
| $c$ / Å | 20.4328(6) |
| $\alpha$ / deg | 90 |
| $\beta$ / deg | 95.219(3) |
| $\gamma$ / deg | 90 |
| $V$ / Å$^3$ | 1628.77(9) |
| $Z$ | 4 |
| Z' | 1 |
| Temperature / $K$ | 93.15 |
| Goodness-of-fit on $F^2$ | 1.028 |
| $R_1$ [$I > 2\sigma(I)$] on $F$ | 0.0471 |
| $wR_2$ (all data) on $F^2$ | 0.1124 |
| Reflection collected (all data) | 24796 |
| No. of reflections [$I > 2\sigma(I)$] | 2825 |
| $R_{int}$ | 0.0651 |
| Abs. corr. | multi-scan |

| | |
|---|---|
| Radiation type | Mo$K\alpha$ ($\lambda$ = 0.71075Å) |
| $T_{min}$ | 0.78362 |
| $T_{max}$ | 1.00000 |
| $\theta_{max}$ | 27.497 |
| $\mu$ /mm$^{-1}$ | 0.085 |
| CCDC No. | 2358605 |

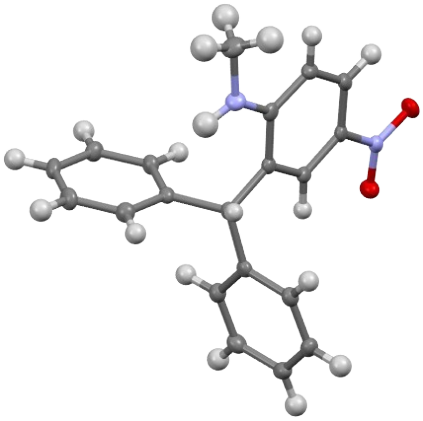
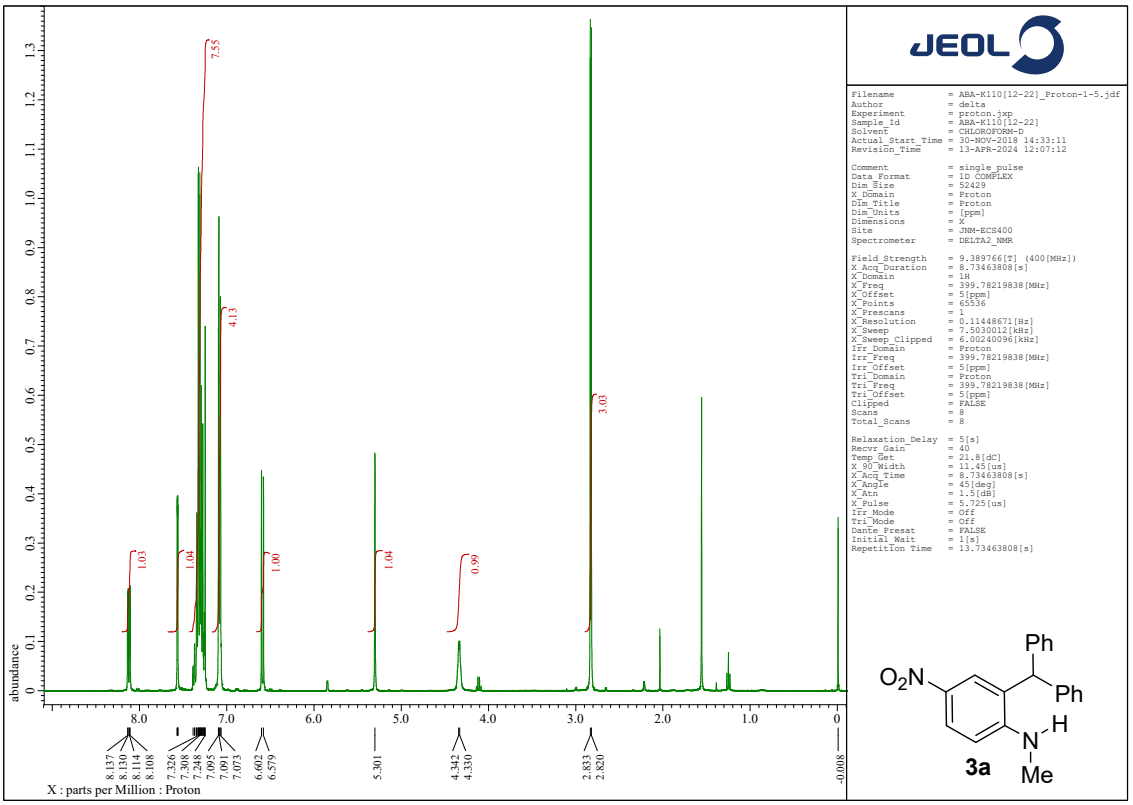


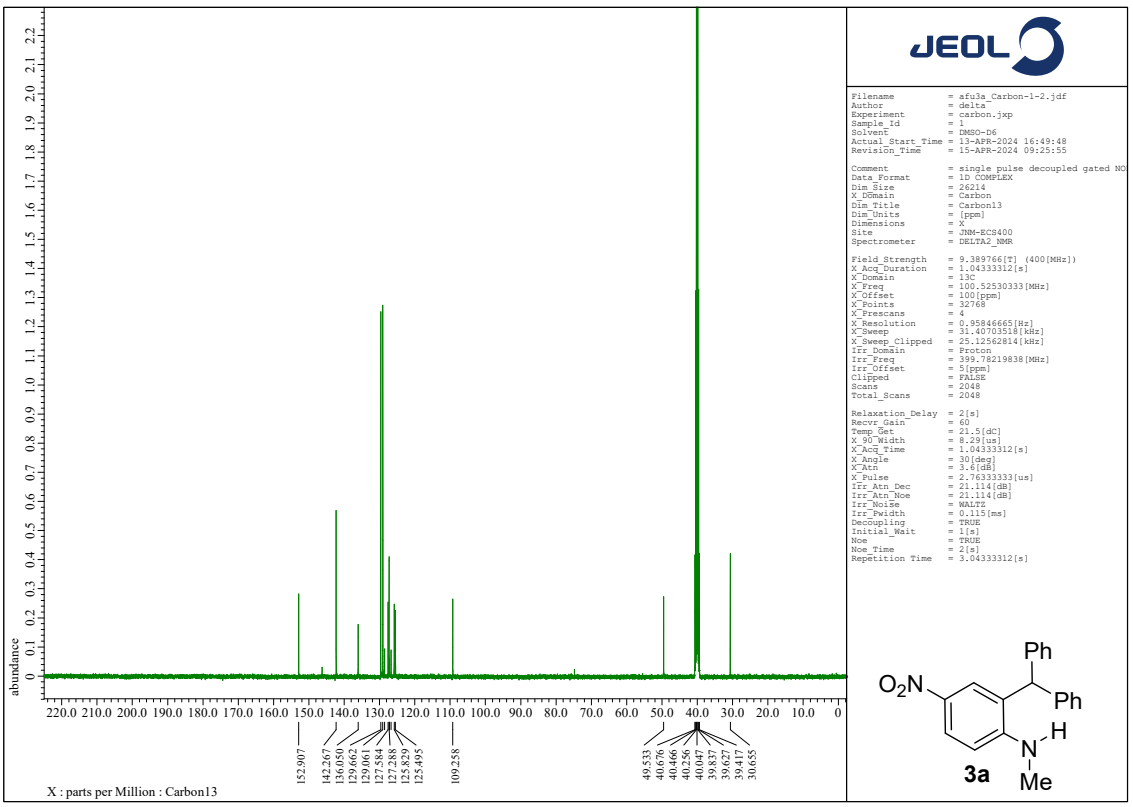
**Figure S4**. Crystal structure of the compound **3a**. The ORTEP drawings are shown with thermal ellipsoids at the 50% probability level.

**References**

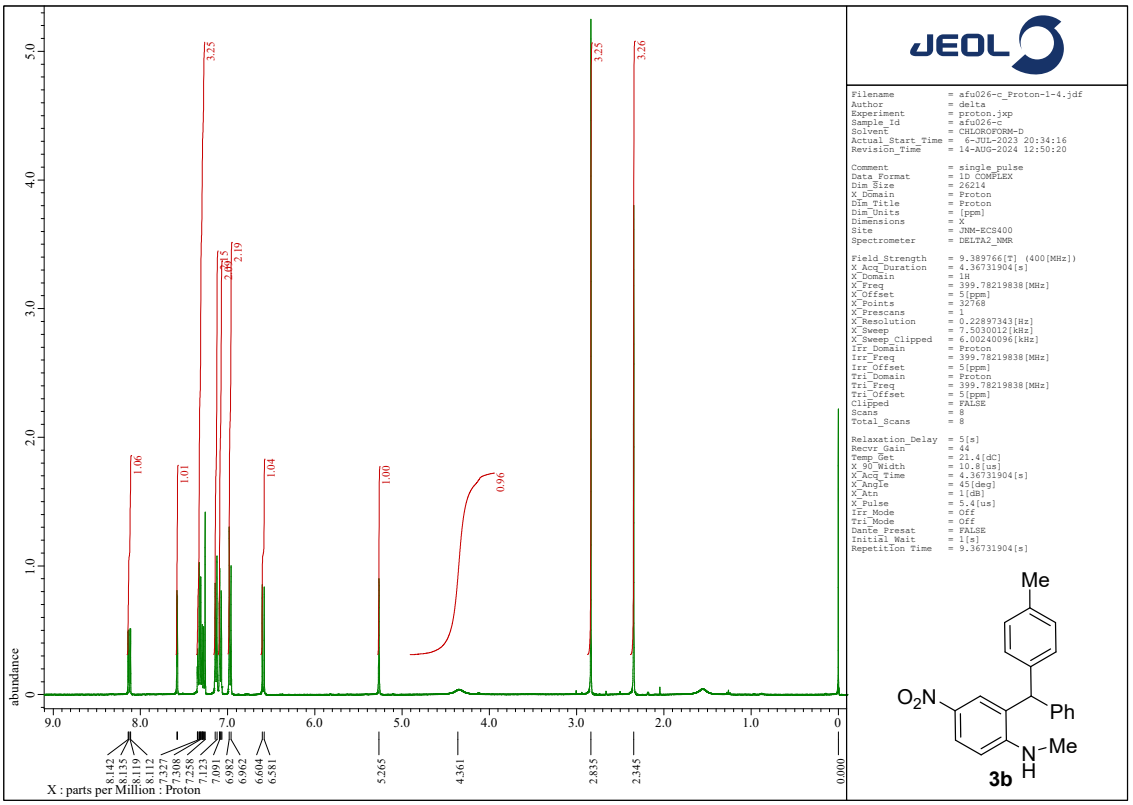

1. G. M. Sheldrick, A short history of SHELX, *Acta Cryst.* **2008**, *A64,* 112–122. https//doi.org/10.1107/S0108767307043930.
2. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.* **2015**, *C71*, 3-8. https//doi.org/10.1107/S2053229614024218.

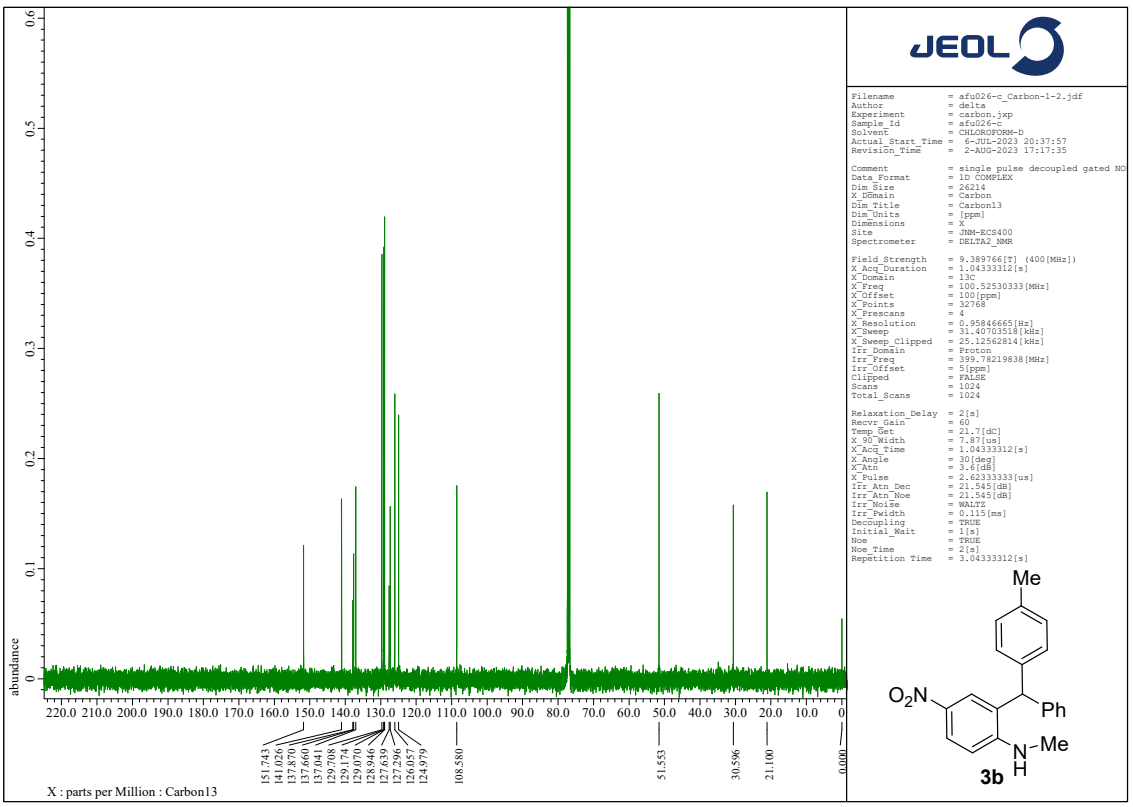
2-Benzhydryl-*N*-methyl-4-nitroaniline **3a**



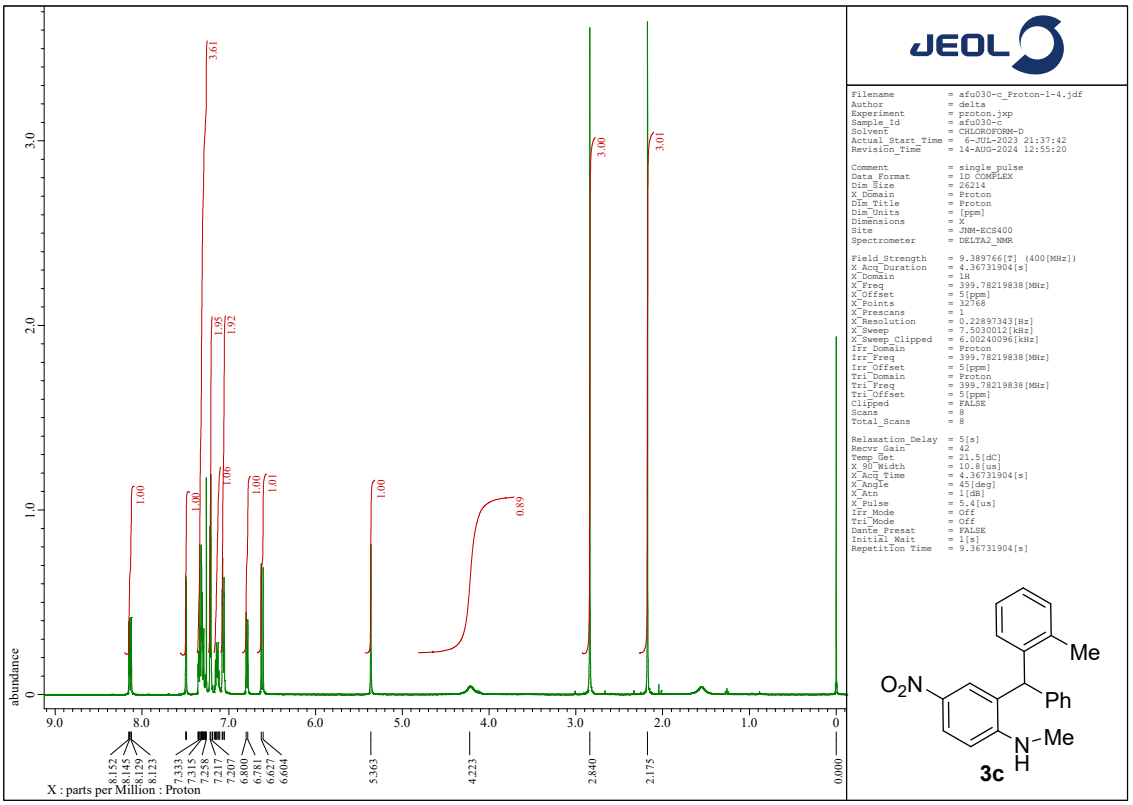



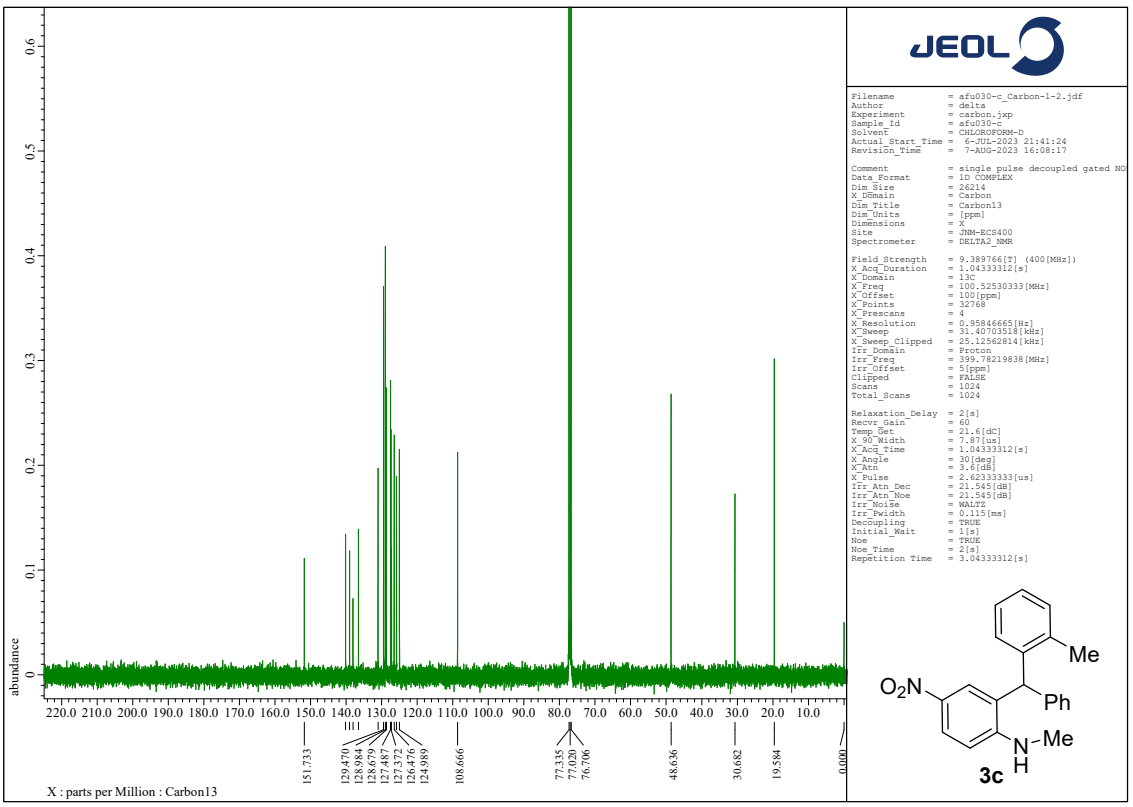
*N*-Methyl-4-nitro-2-(phenylmethyl)aniline **3b**



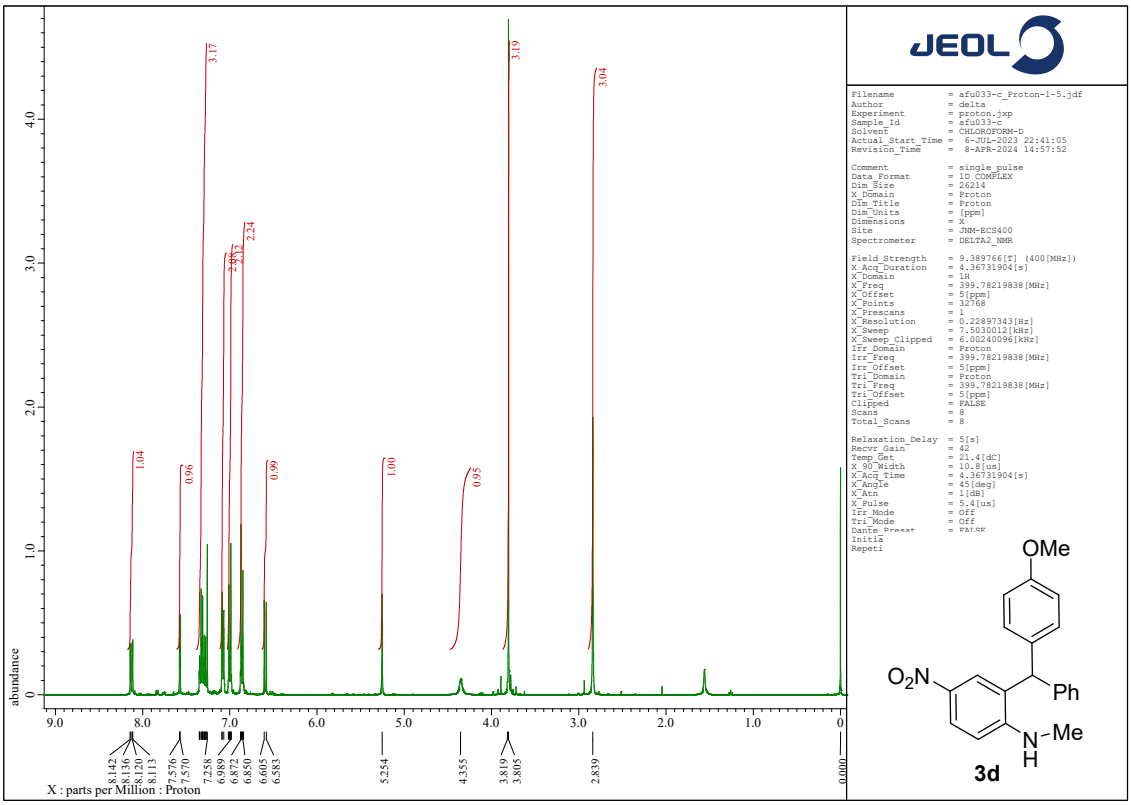



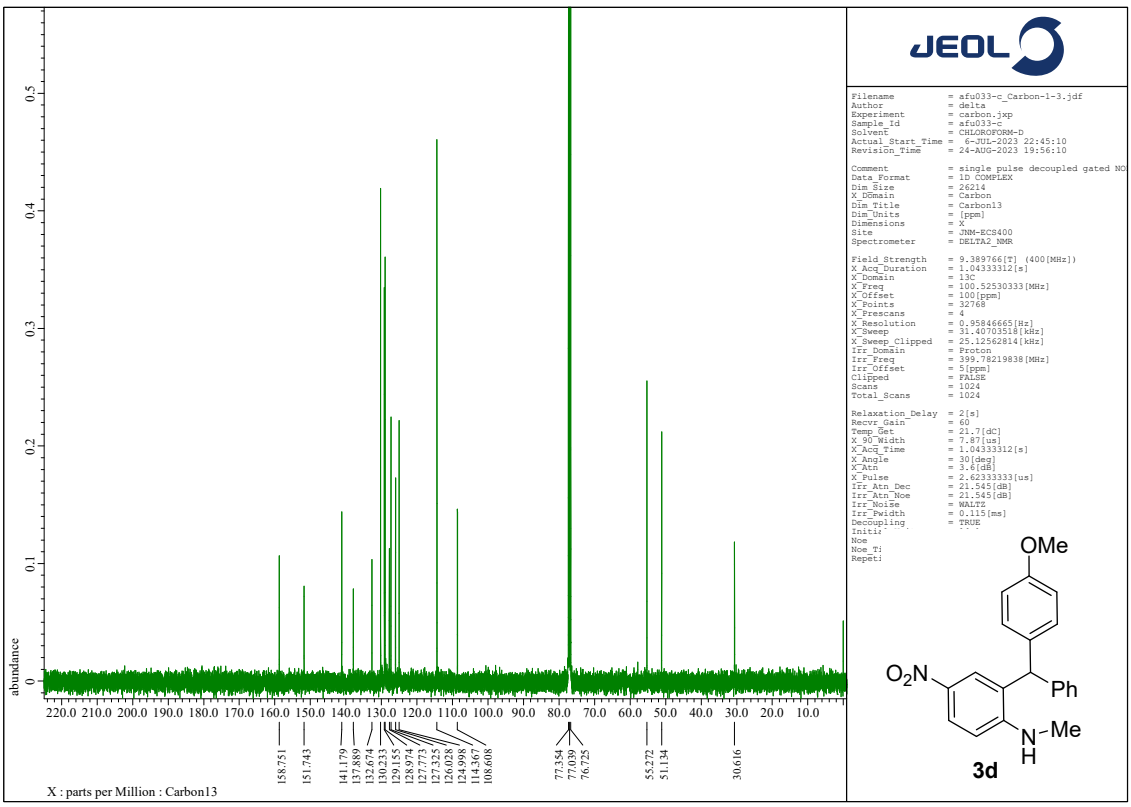
*N*-Methyl-4-nitro-2-(phenylmethyl)aniline **3c**



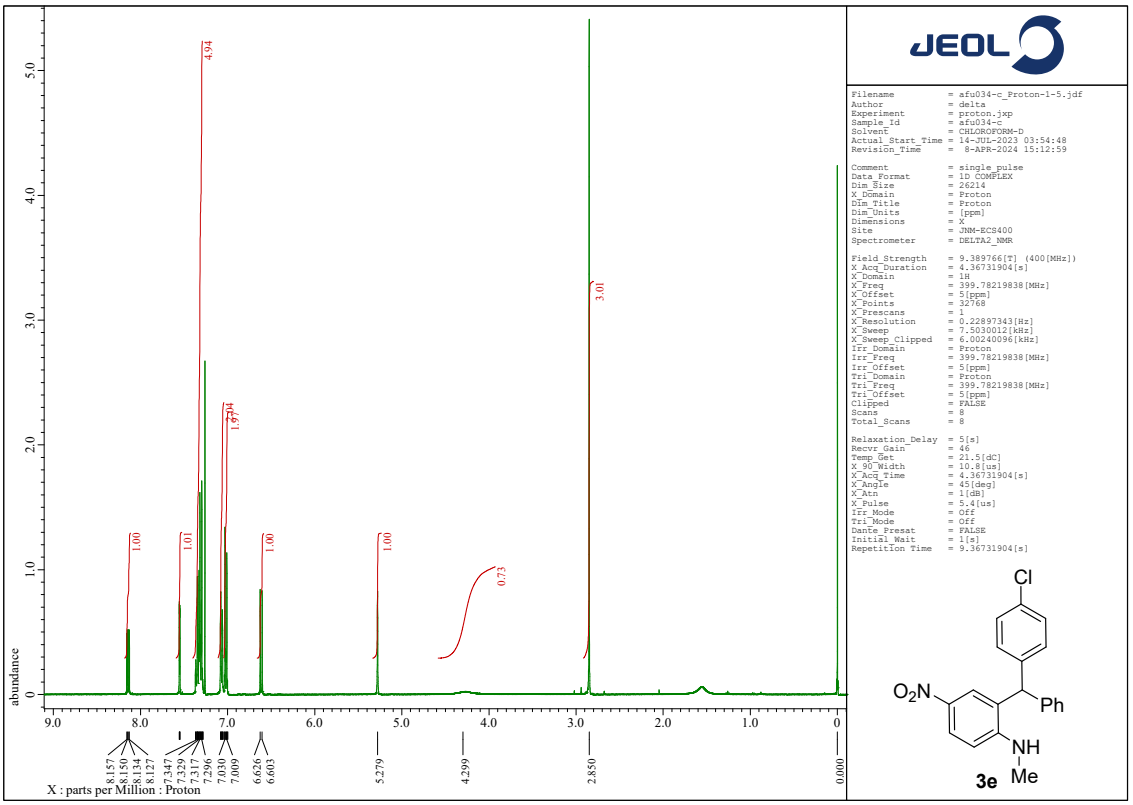



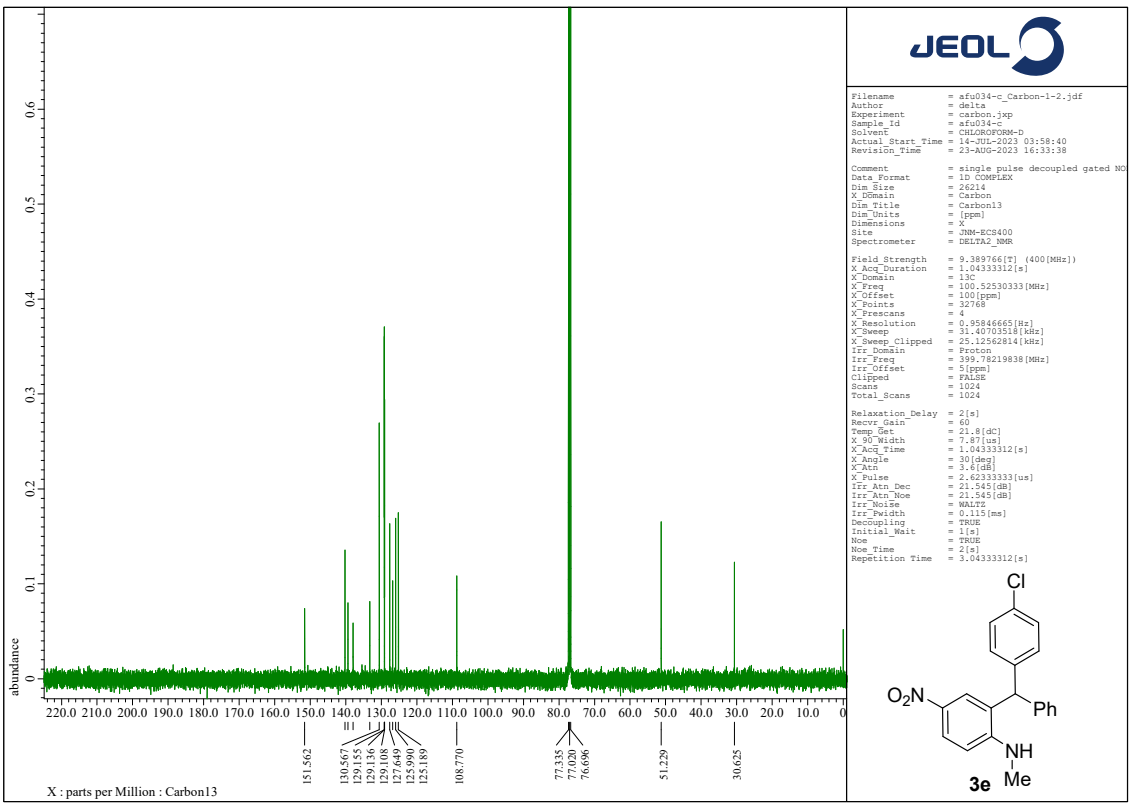
2-[(4-Methoxyphenyl)(phenyl)methyl]-*N*-methyl-4-nitroaniline **3d**



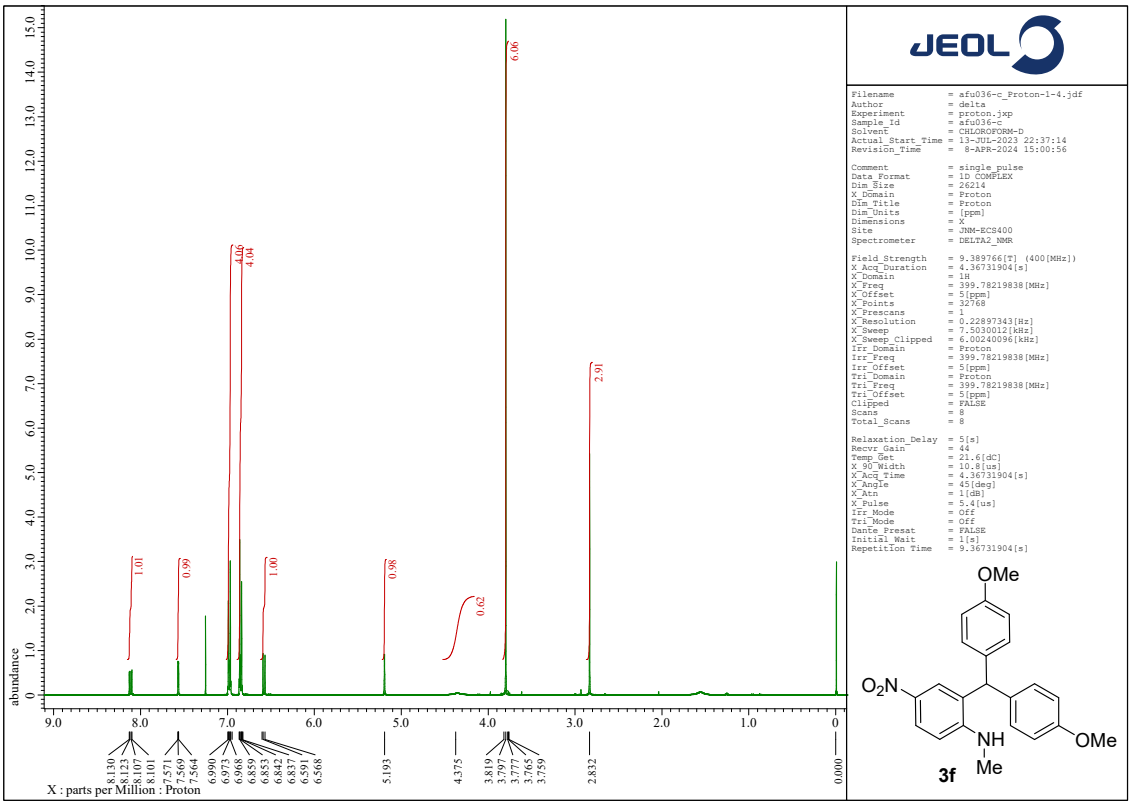



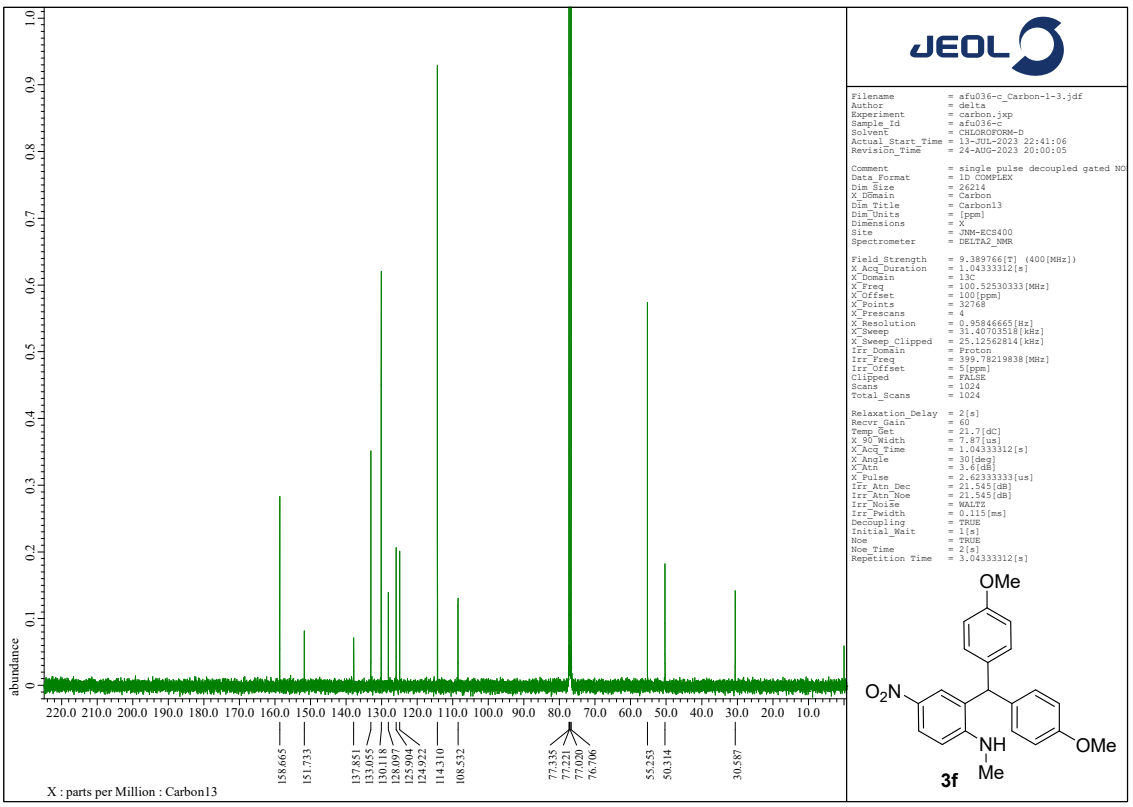
2-[(4-Chlorophenyl)(phenyl)methyl]-*N*-methyl-4-nitroaniline **3e**



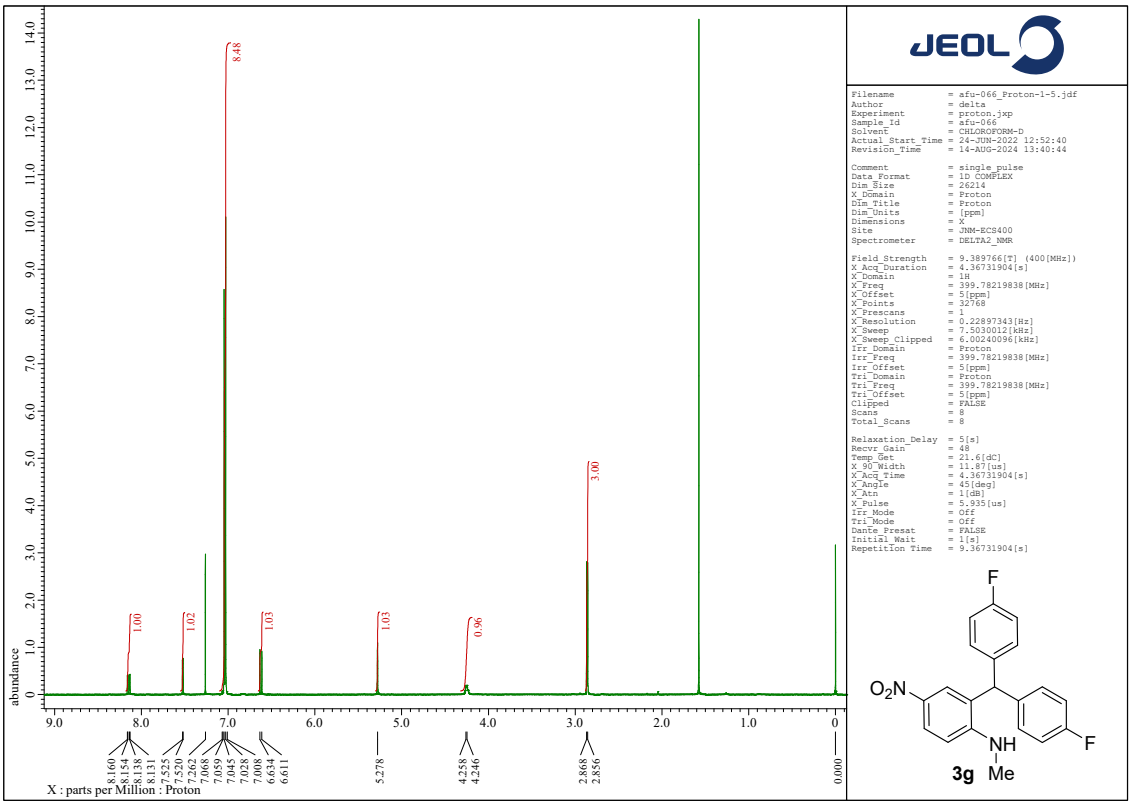



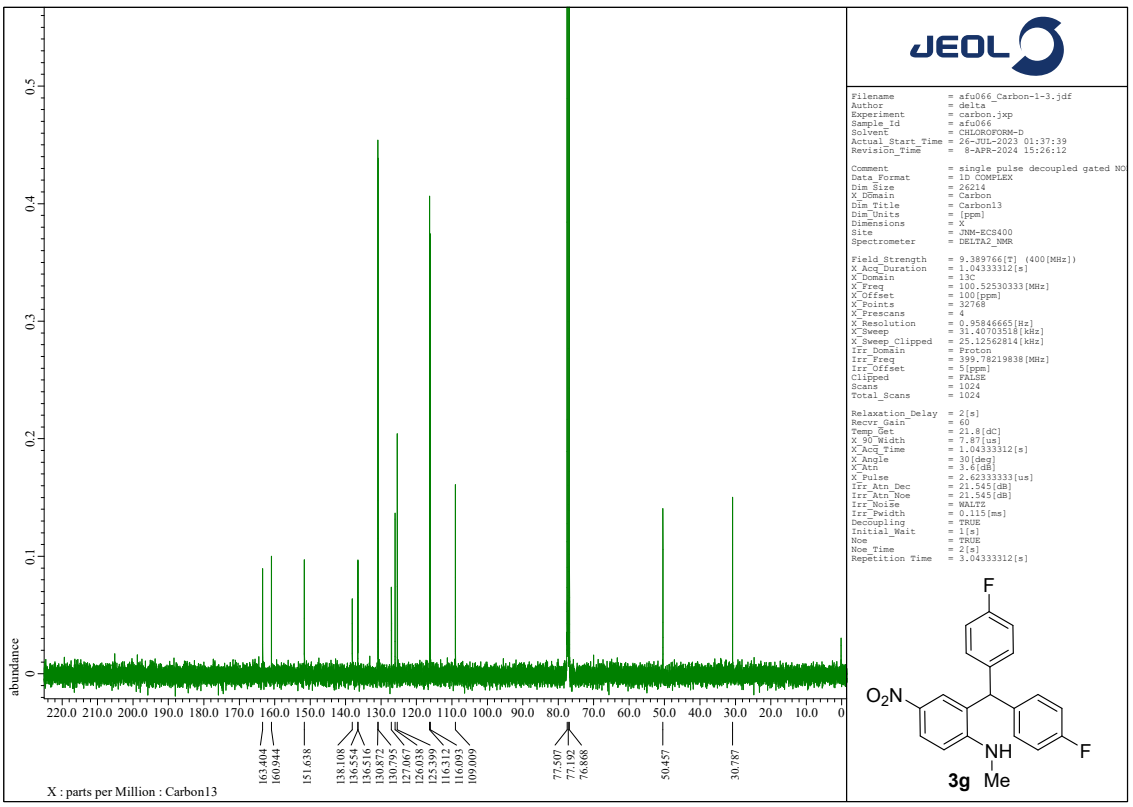
2-[Bis(4-methoxyphenyl)methyl]-*N*-methyl-4-nitroaniline **3f**



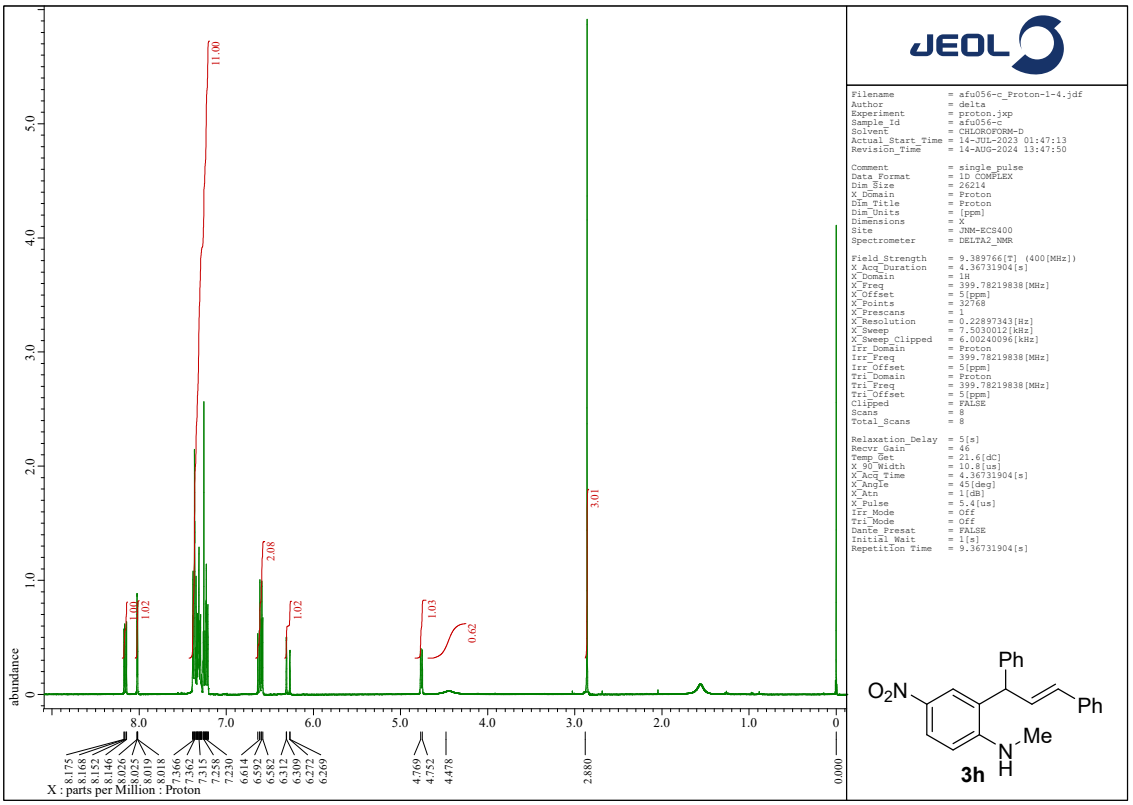



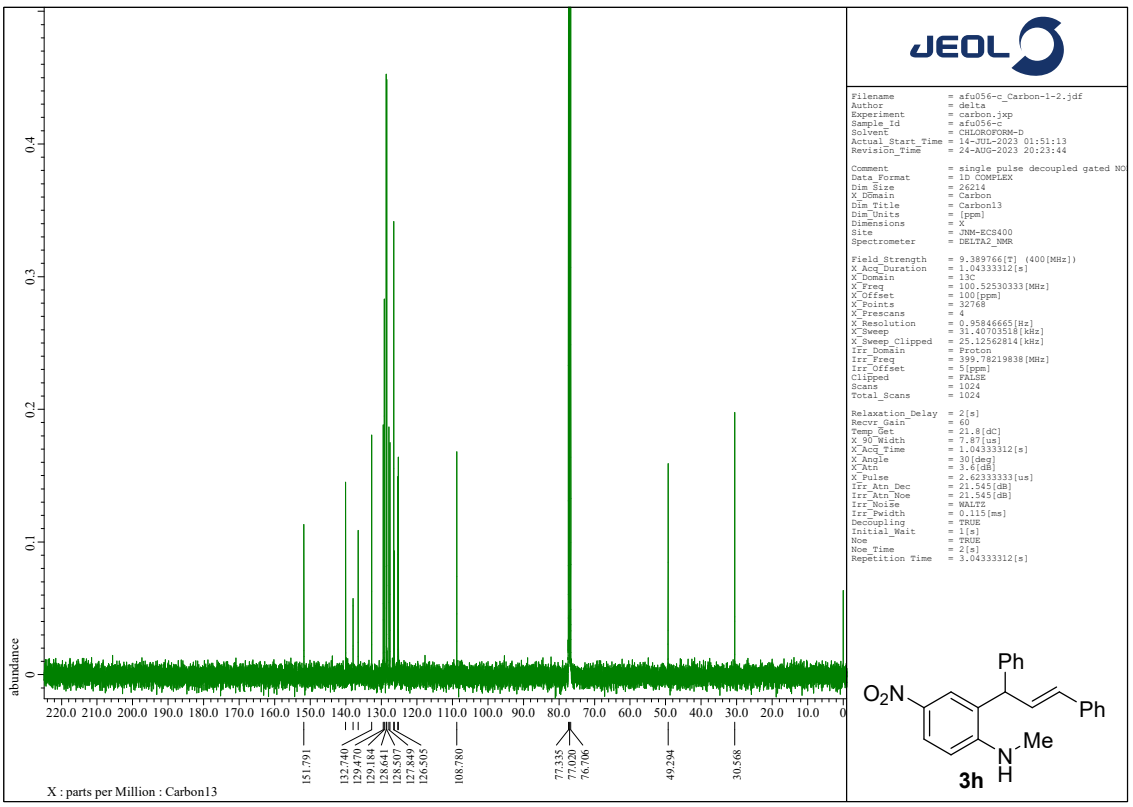
2-[Bis(4-fluorophenyl)methyl]-*N*-methyl-4-nitroaniline **3g**



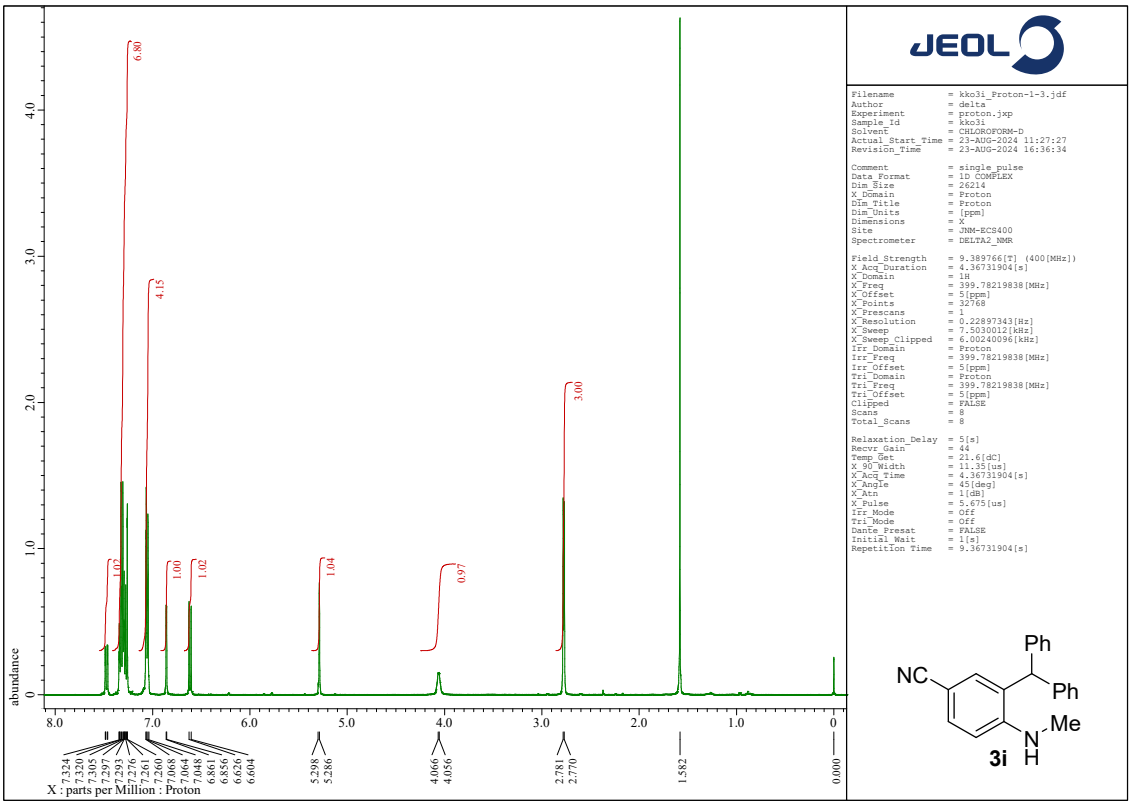



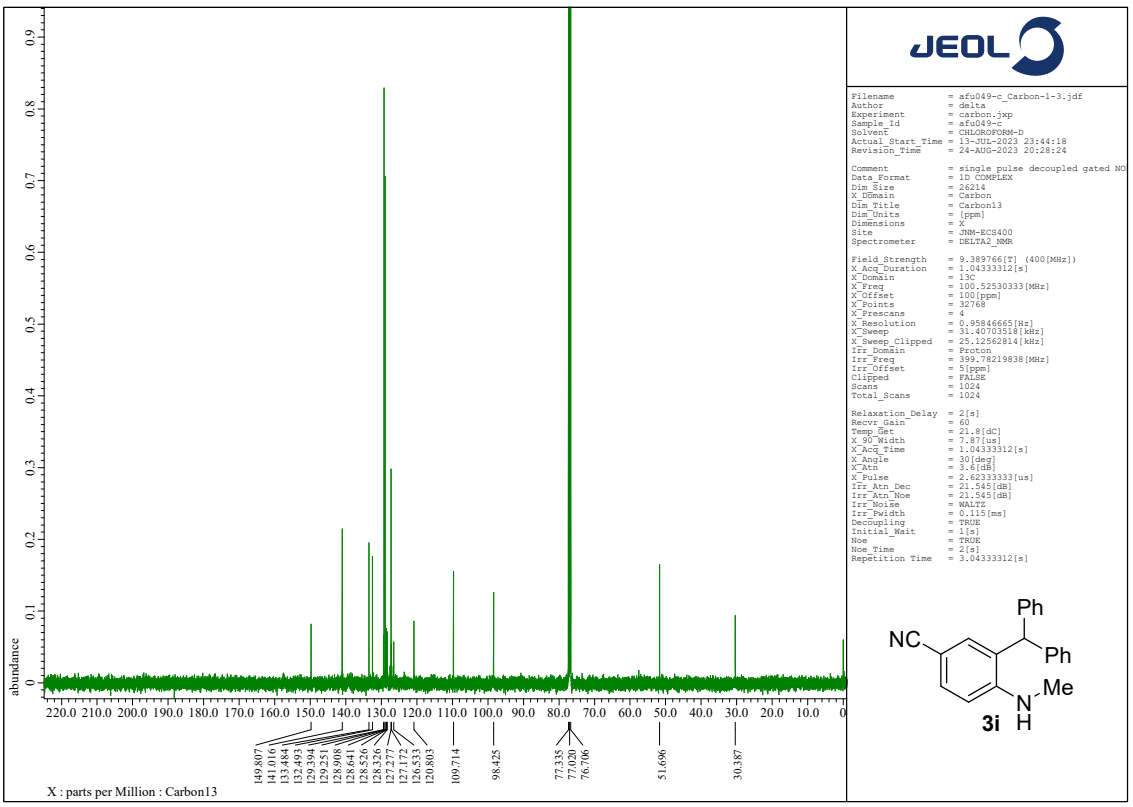
(*E*)-2-(1,3-Diphenylallyl)-*N*-methyl-4-nitroaniline **3h**



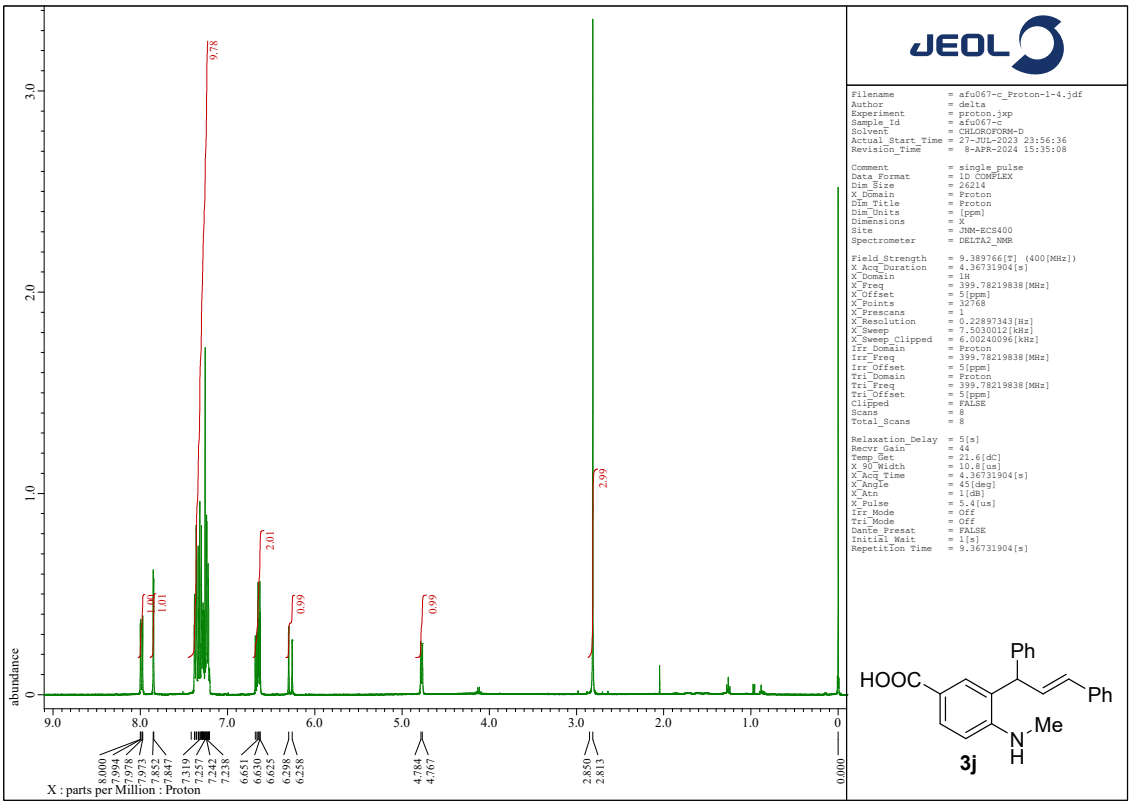



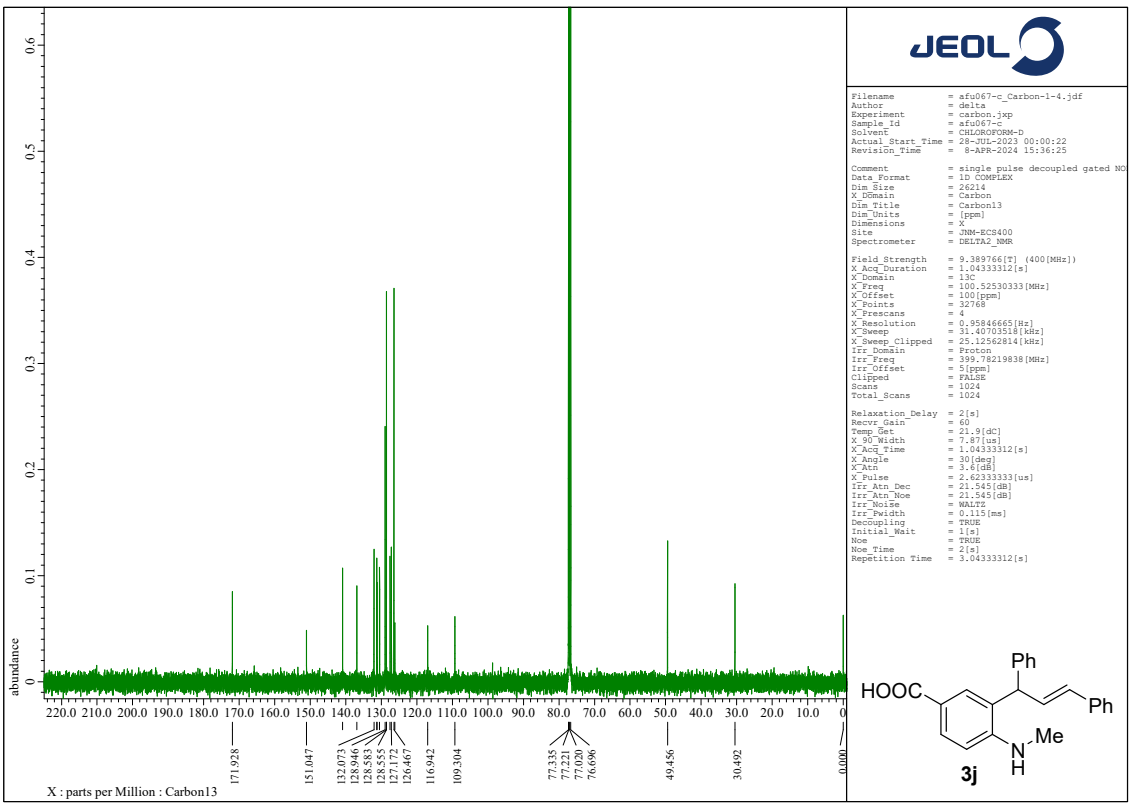
3-Benzhydryl-4-(methylamino)benzonitrile **3i**



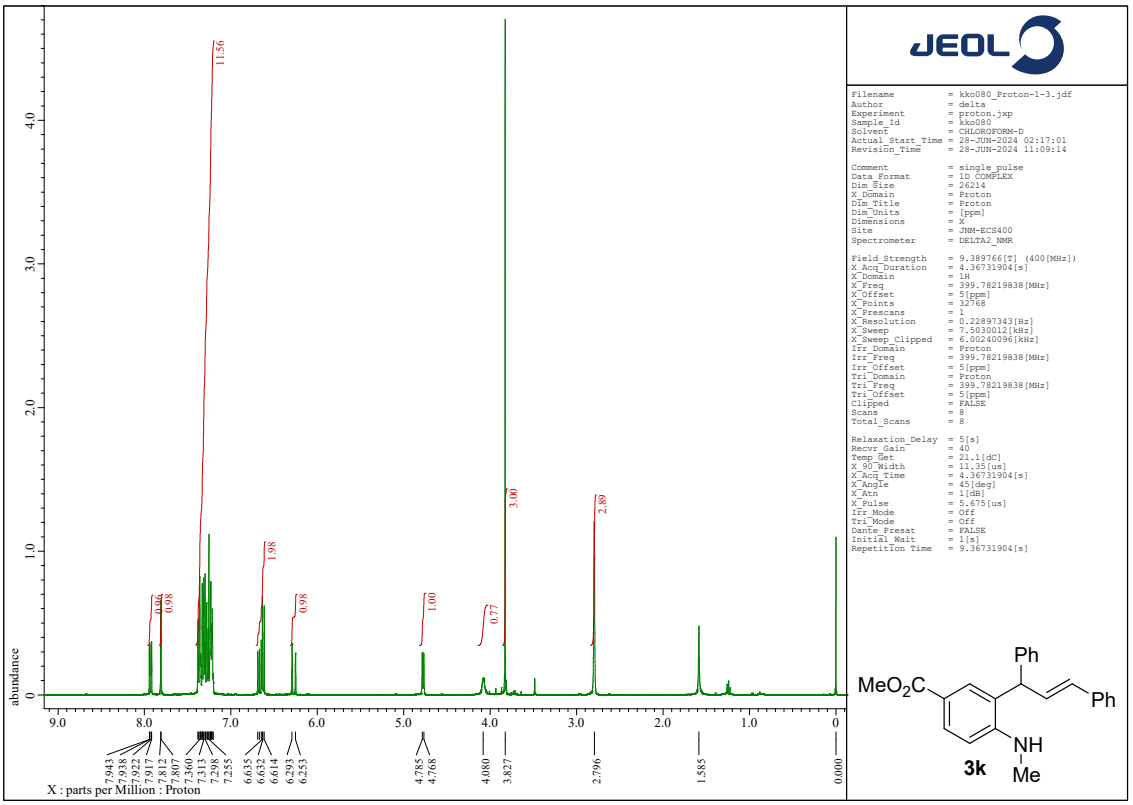



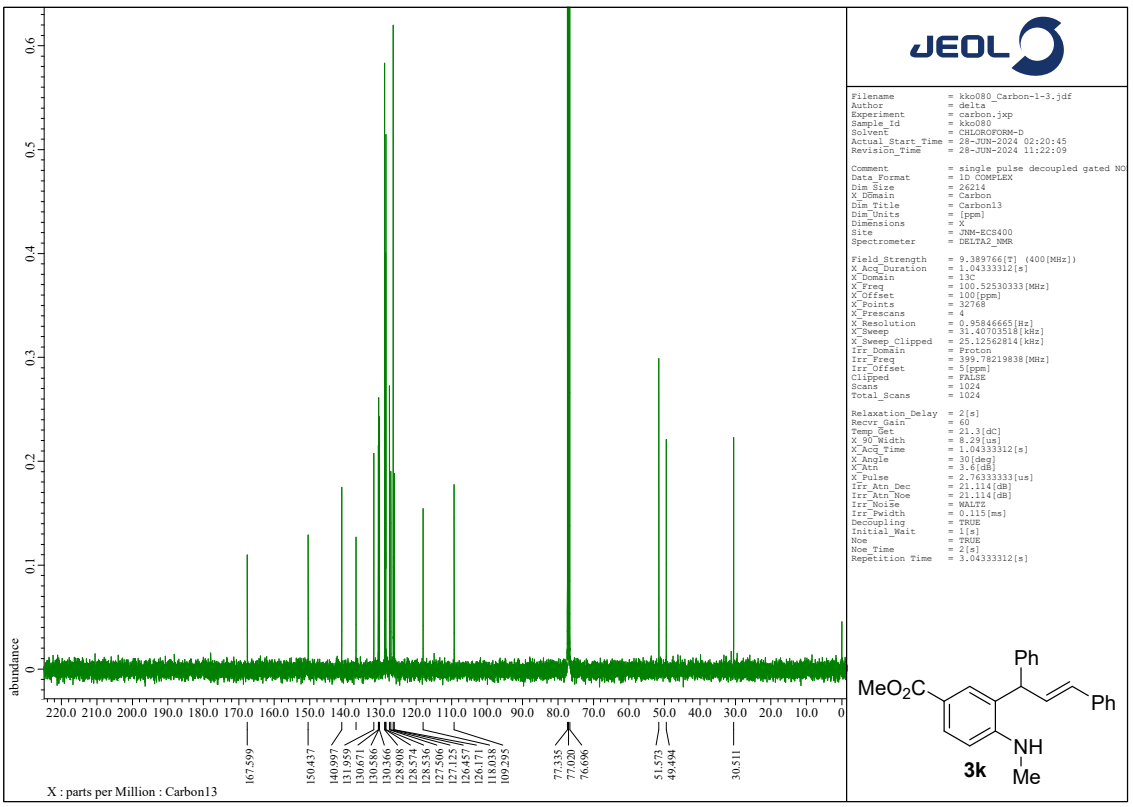
(*E*)-3-(1,3-Diphenylallyl)-4-(methylamino)benzoic acid **3j**

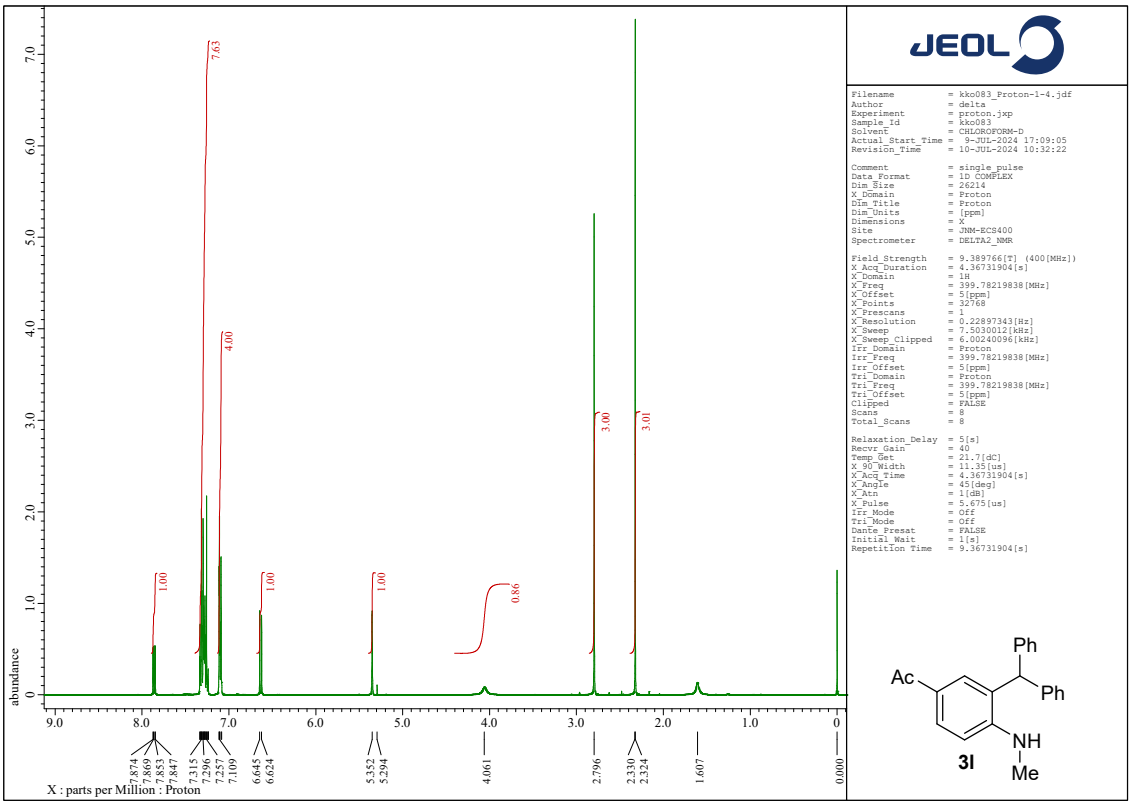


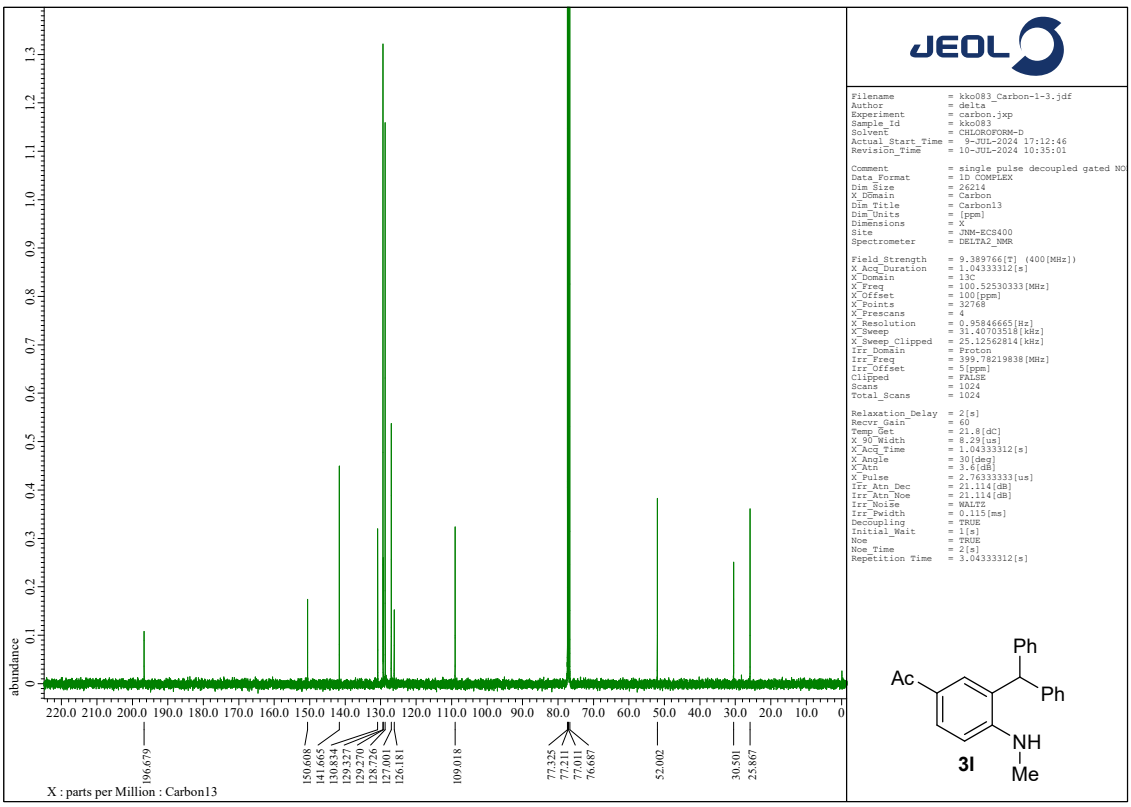



**Methyl (*E*)-3-(1,3-diphenylallyl)-4-(methylamino)benzoate 3k**

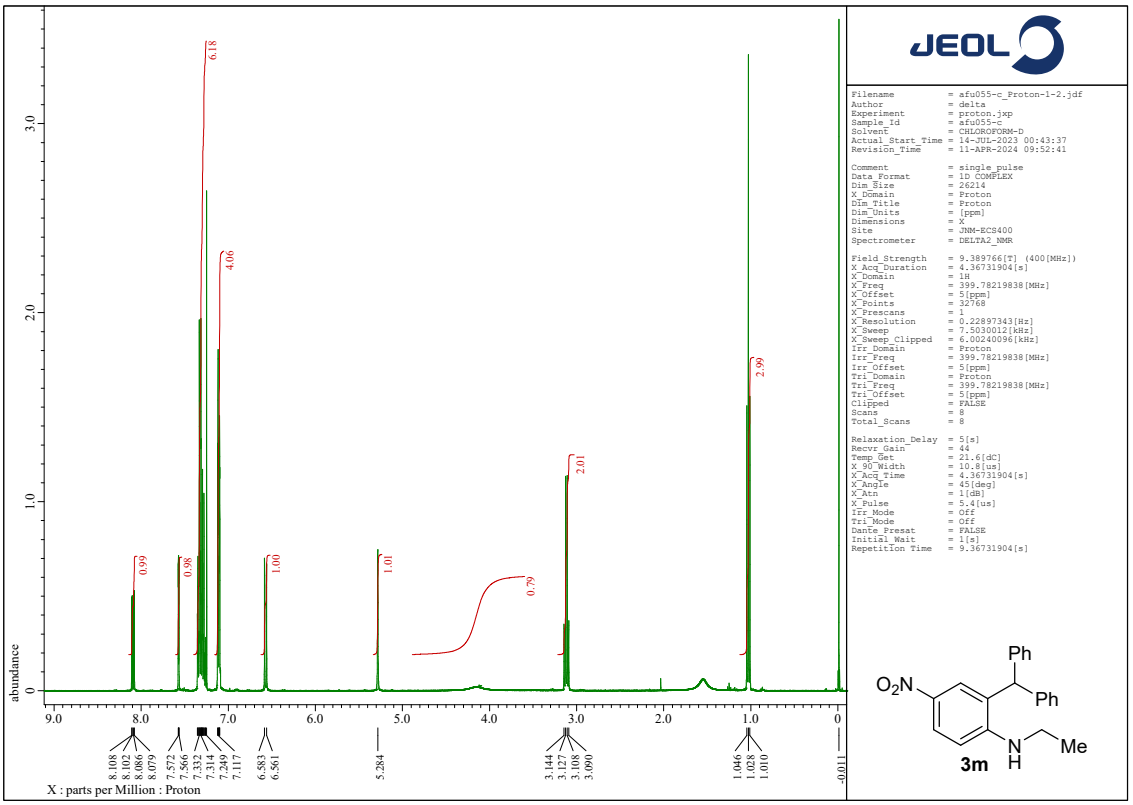


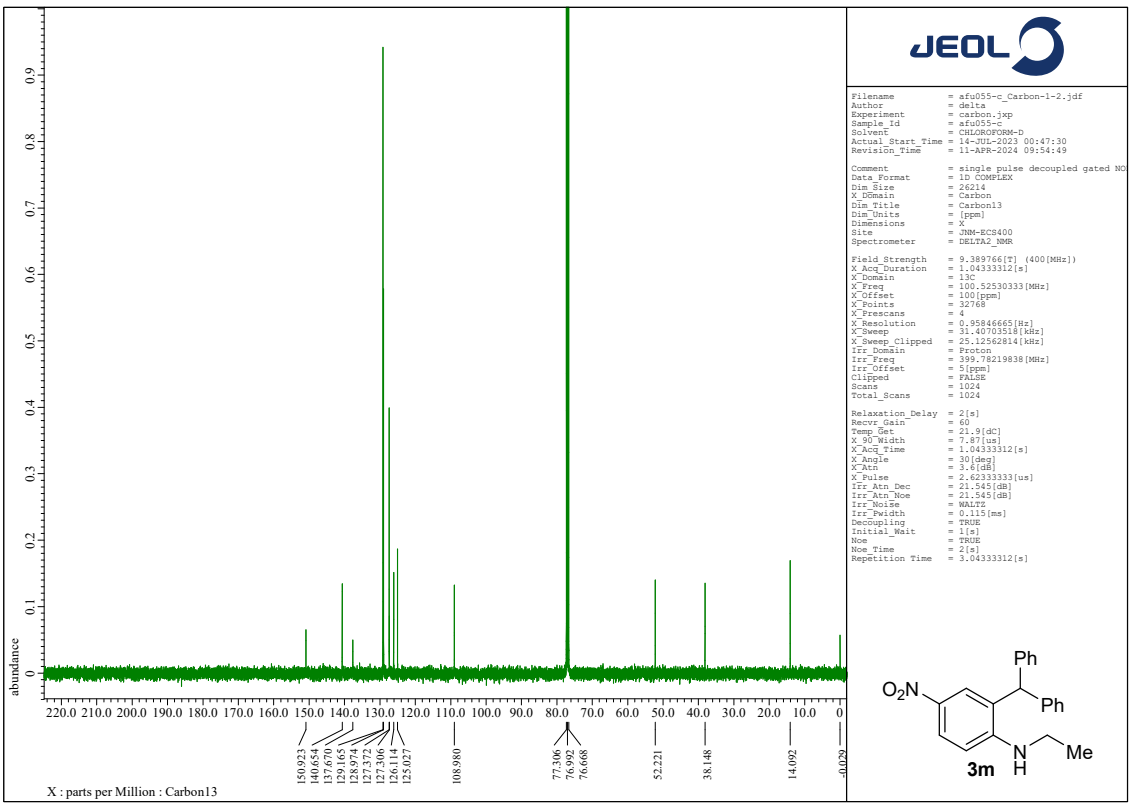




JEOL
Filename = kko083_Proton-1-4.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = kko083
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-JUL-2024 17:09:05
Revision_Time = 10-JUL-2024 10:32:22
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 4.36731904[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22897343[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 40
Temp_Get = 21.7[dC]
X_90_Width = 11.35[us]
X_Acq_Time = 4.36731904[s]
X_Angle = 45[deg]
X_Atn = 1[dB]
X_Pulse = 5.675[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 9.36731904[s]
abundance
X : parts per Million : Proton
7.63
4.00
3.00
3.01
1.00
1.00
1.00
0.86
7.874
7.869
7.853
7.847
7.315
7.296
7.257
7.109
6.645
6.624
5.352
5.294
4.061
2.796
2.330
2.324
1.607
0.000
Ph
Ac
Ph
NH
Me
3l

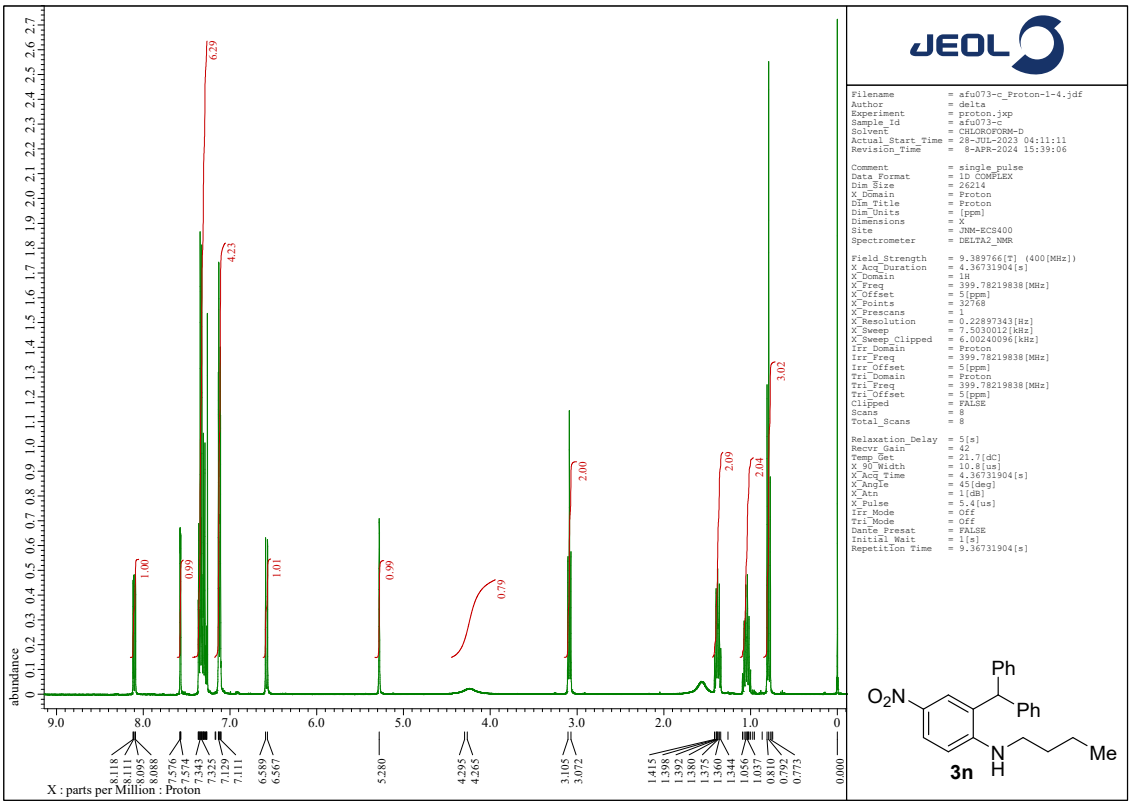

JEOL
Filename = kko083_Carbon-1-3.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = kko083
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-JUL-2024 17:12:46
Revision_Time = 10-JUL-2024 10:35:01
Comment = single_pulse decoupled gated NO
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Carbon
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 21.8[dC]
X_90_Width = 8.29[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 3.6[dB]
X_Pulse = 2.76333333[us]
Irr_Atn_Dec = 21.114[dB]
Irr_Atn_Noe = 21.114[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.04333312[s]
abundance
X : parts per Million : Carbon13
196.679
150.608
141.665
130.834
129.327
129.270
128.726
127.001
126.181
109.018
77.325
77.211
77.011
76.687
52.002
30.501
25.867
Ph
Ac
Ph
NH
Me
3l

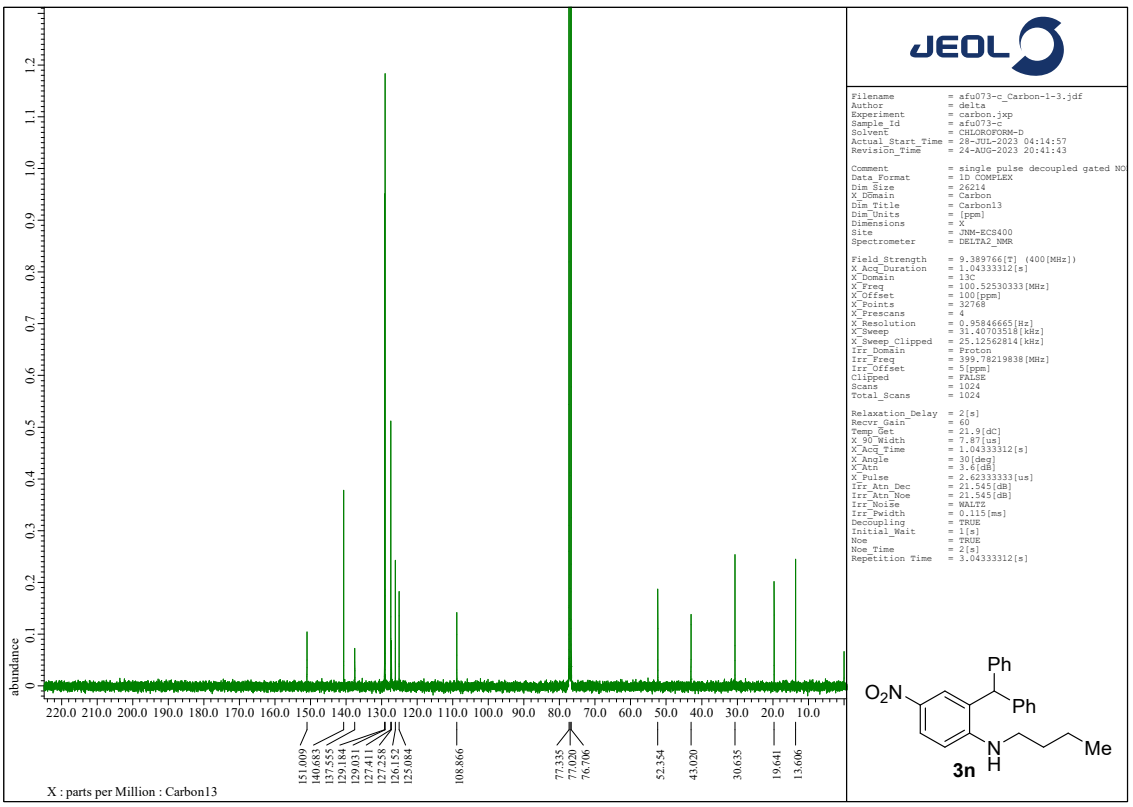
2-Benzhydryl-*N*-ethyl-4-nitroaniline **3m**



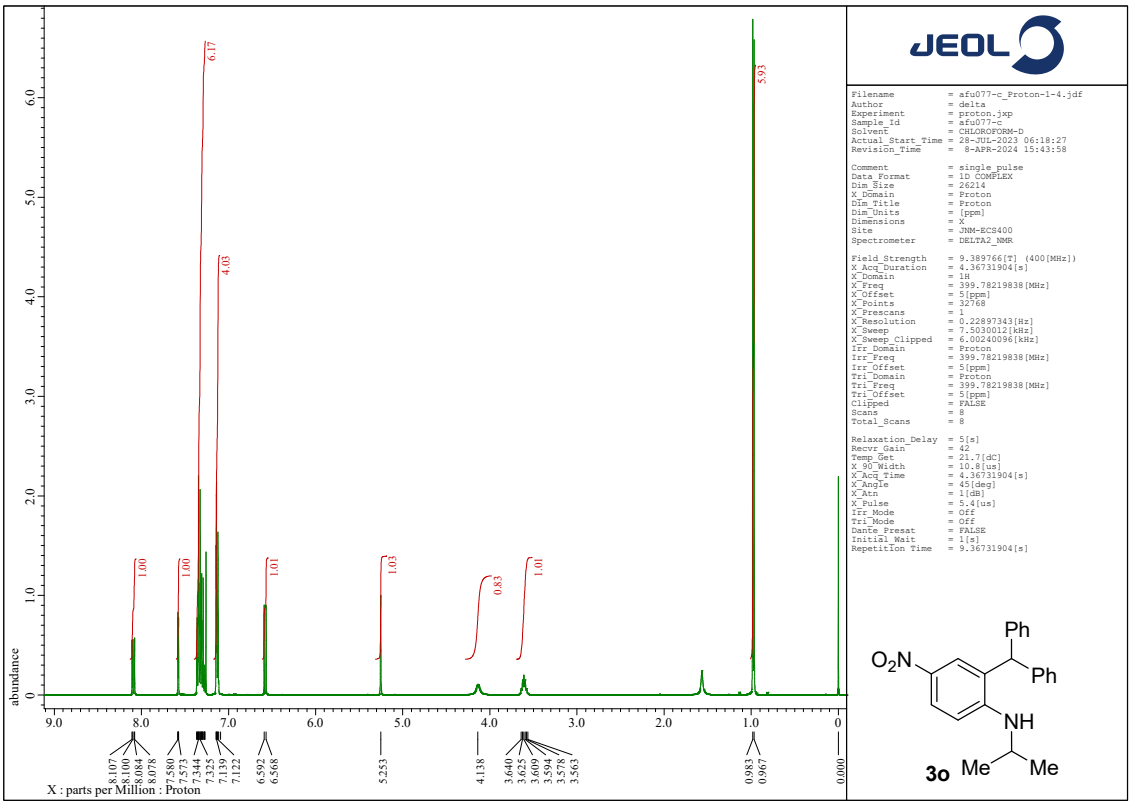



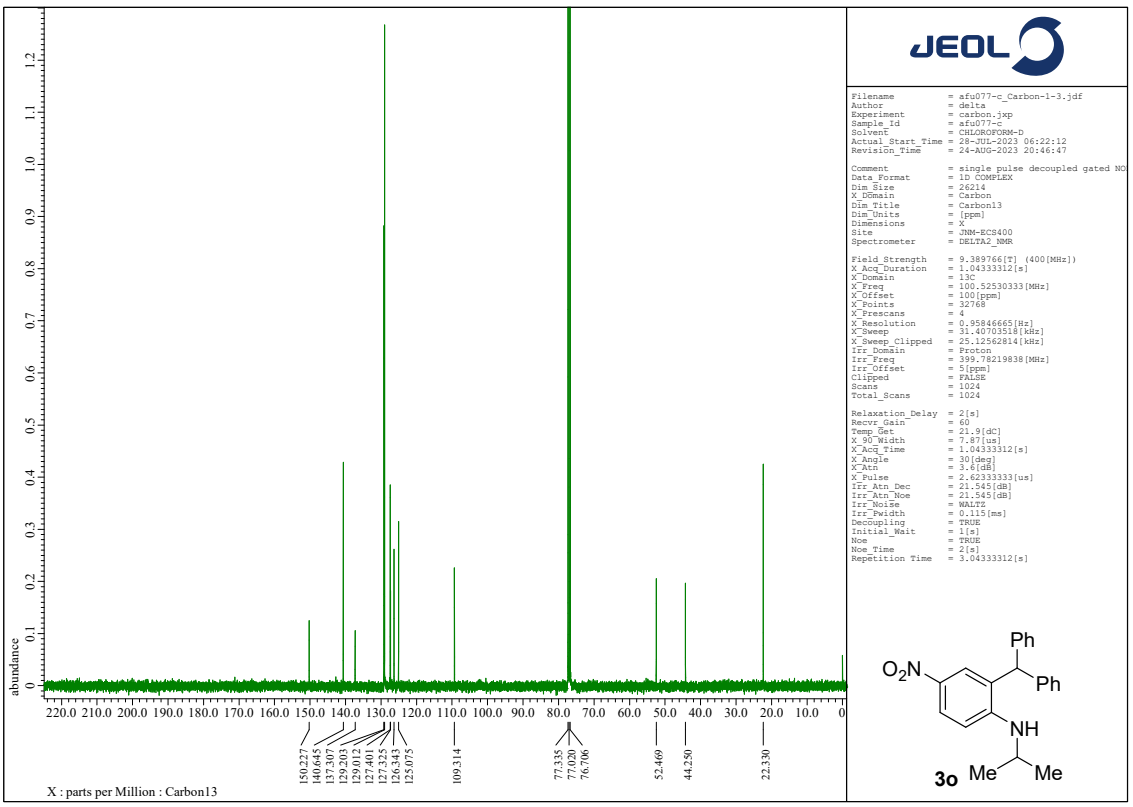
2-Benzhydryl-*N*-butyl-4-nitroaniline **3n**



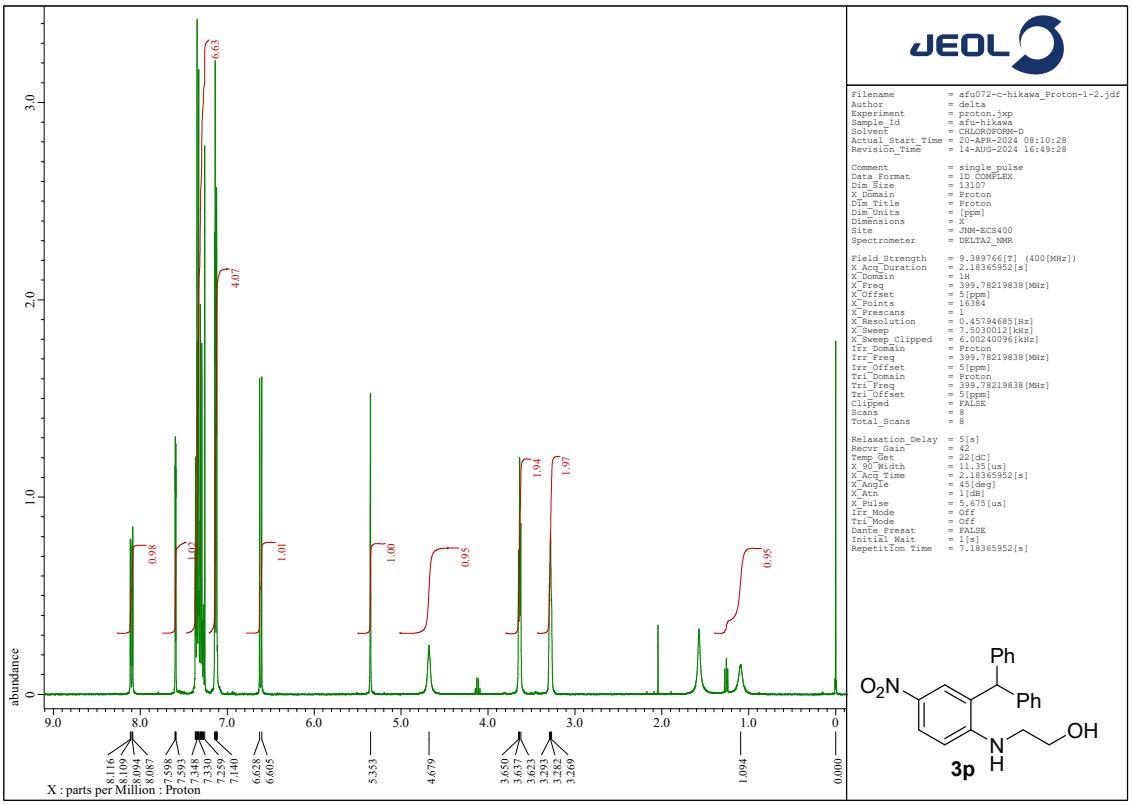



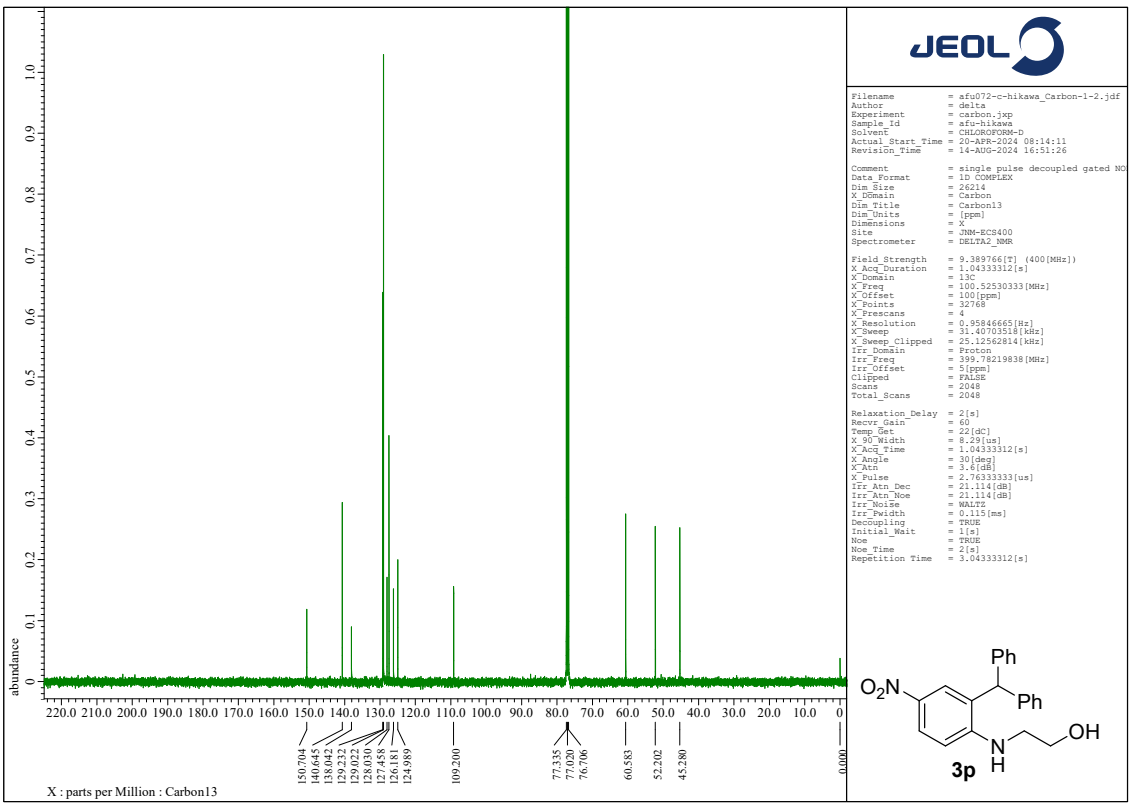
2-Benzhydryl-*N*-isopropyl-4-nitroaniline **3o**



2-[(2-Benzhydryl-4-nitrophenyl)amino]ethan-1-ol **3p**



2-Benzhydryl-*N*-(2-(benzhydryloxy)ethyl)-4-nitroaniline **3p'**