Electronic Supplementary Information (ESI) for

Synthesis of unsymmetrically substituted triarylamines *via* acceptorless dehydrogenative aromatization using a Pd/C and *p*-toluenesulfonic acid hybrid relay catalyst

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Table of Contents

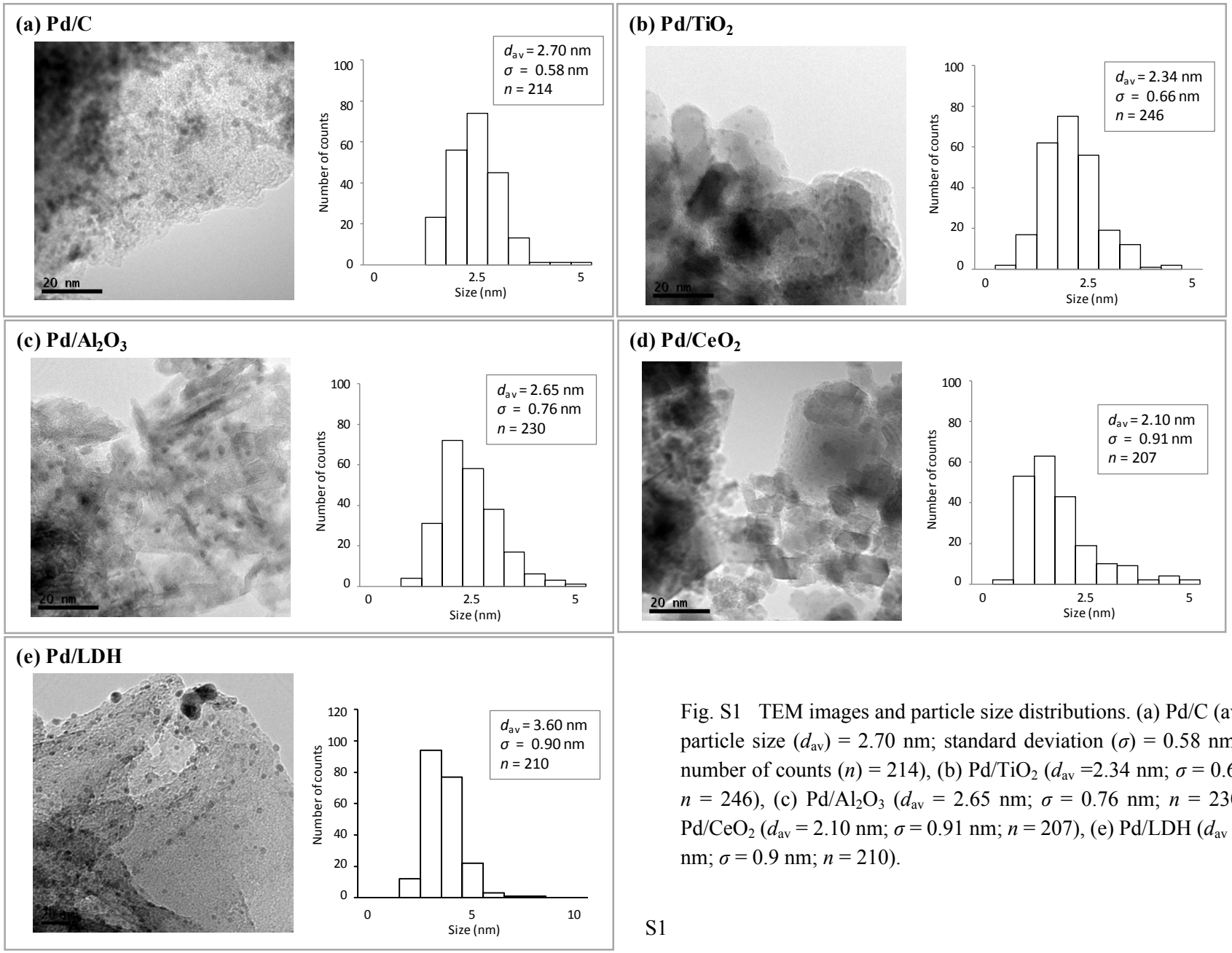
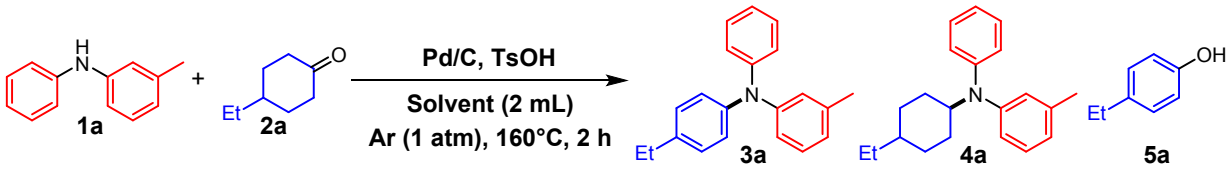


Fig. S1 TEM images and particle size distributions. (a) Pd/C (average particle size (d_{av}) = 2.70 nm; standard deviation (σ) = 0.58 nm; total number of counts (n) = 214), (b) Pd/TiO_2 (d_{av} =2.34 nm; σ = 0.66 nm; n = 246), (c) Pd/Al_2O_3 (d_{av} = 2.65 nm; σ = 0.76 nm; n = 230), (d) Pd/CeO_2 (d_{av} = 2.10 nm; σ = 0.91 nm; n = 207), (e) Pd/LDH (d_{av} = 3.60 nm; σ = 0.9 nm; n = 210).

Table S1 Pd contents and average particle sizes

Catalyst	Pd content (mmol g^{-1})	Average particle size (nm)
Pd/C	0.226	2.70
Pd/TiO_2	0.222	2.34
Pd/Al_2O_3	0.227	2.65
Pd/CeO_2	0.209	2.10
Pd/LDH	0.234	3.60

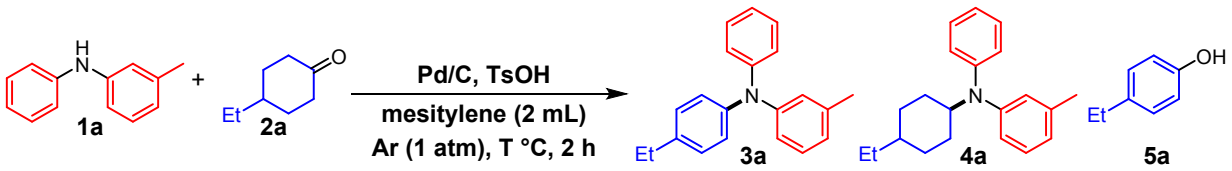
Table S2 Effect of solvents[a]



Entry	Solvent	Yield (%)		
		3a	**4a**	**5a**
1	**Mesitylene**	**85**	**<1**	**<1**
2	Decane	72	<1	<1
3	Diglyme	68	<1	<1
4	DMA	11	<1	2
5	NMP	5	<1	5

[a]Reaction conditions: Pd/C (Pd: 2 mol%), TsOH (10 mol%), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (2 mL), Ar (1 atm), 160°C, 2 h. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

Table S3 Effect of temperatures[a]



Entry	Temperature [°C]	Yield (%)		
		3a	**4a**	**5a**
1	**160**	**85**	**<1**	**<1**
2	150	64	<1	1
3	140	21	<1	1
4	130	7	<1	1

[a]Reaction conditions: Pd/C (Pd: 2 mol%), TsOH (10 mol%), **1a** (0.5 mmol), **2a** (0.5 mmol), mesitylene (2 mL), Ar (1 atm), 2 h. Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

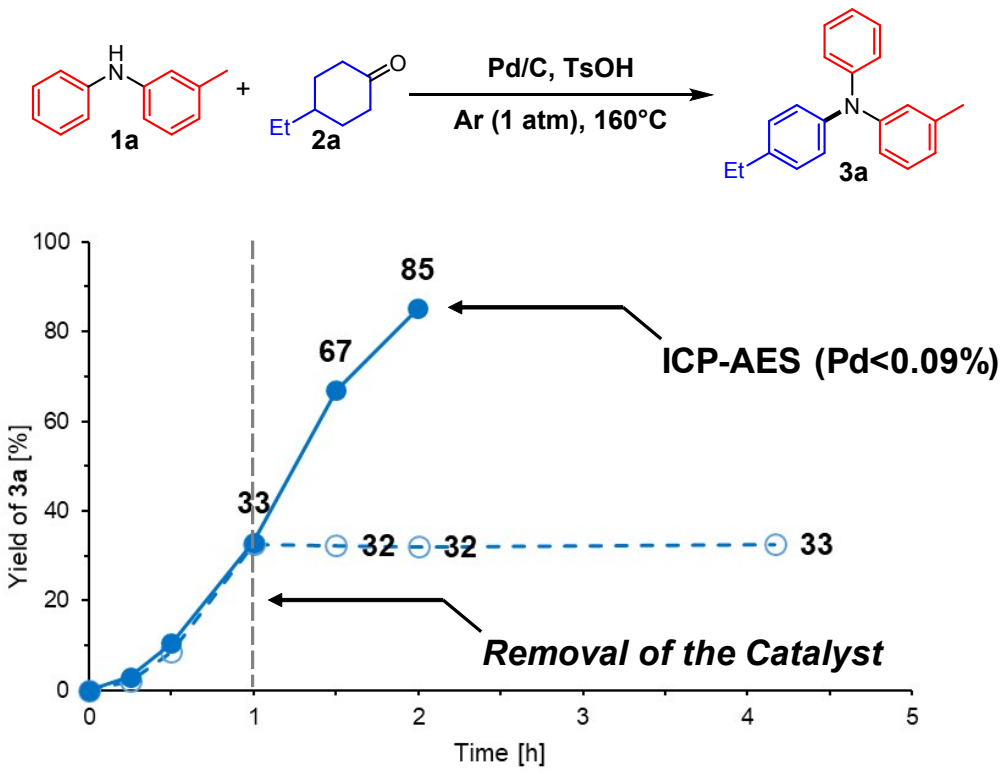


Fig. S2 Effect of removal of Pd/C (verification of heterogeneous catalysis). Reaction conditions: Pd/C (Pd: 2 mol%), TsOH (10 mol%), **1a** (0.5 mmol), **2a** (0.5 mmol), mesitylene (2 mL), 160°C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard. The arrow indicates the removal of Pd/C by hot filtration.

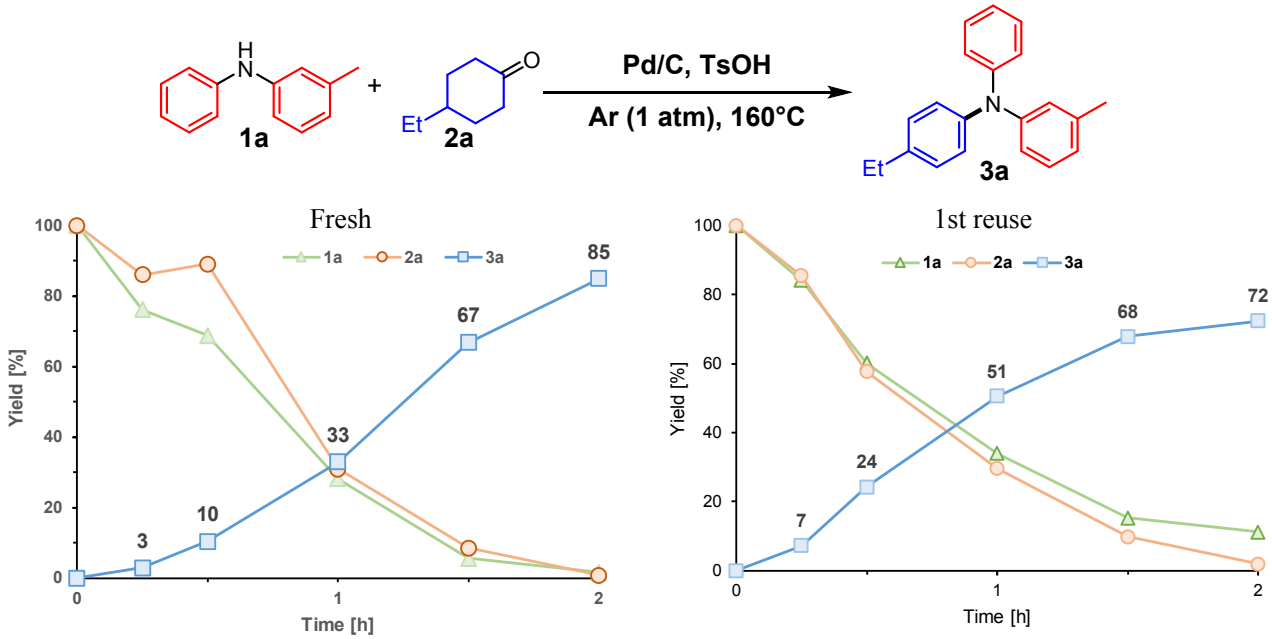
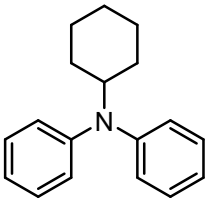
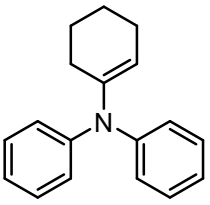


Fig. S3 Reuse test. Reaction conditions: Pd/C (Pd: 2 mol%), TsOH (10 mol%), **1a** (0.5 mmol), **2a** (0.5 mmol), mesitylene (2 mL), 160°C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as an internal standard.

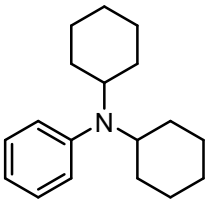
Data of substrates



***N*-cyclohexyldiphenylamine (4b)** (CAS No. 4705-13-9): Isolated as yellow powders (Eluent: hexane/toluene= 1/1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.42–7.23 (m, 4H), 6.99–6.95 (m, 2H), 6.84–6.81 (m, 4H), 3.82 (tt, J = 11.6, 3.4 Hz, 1H, CH), 2.03–2.00 (m, 2H), 1.80–1.76 (m, 2H), 1.63–1.60 (m, 1H), 1.43–1.34 (m, 2H), 1.15–1.07 (m, 2H), 1.04–0.95 (m, 1H). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 146.3, 129.1, 122.7, 121.4, 56.6, 31.7, 26.2, 25.7. MS (70 eV, EI): *m*/*z* (%): 252 (11), 251 (52) [M^+], 209 (17), 208 (100), 194 (8), 193 (6), 182 (5), 169 (21), 168 (14), 167 (12), 104 (13), 91 (8), 77 (17), 55 (8), 51 (6).

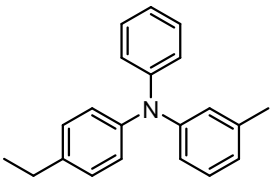


***N*-(1-cyclohexenyl)diphenylamine (9b)**: Isolated as colorless crystals (Eluent: hexane/toluene = 95/5, R_f = 0.56). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.20–7.16 (m, 4H), 7.04–7.02 (m, 4H), 6.91–6.88 (m, 2H), 5.50 (m, 2H), 2.11 (m, 4H), 1.72–1.62 (m, 4H). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 147.3, 143.1, 128.8, 122.5, 122.0, 121.3, 27.8, 25.0, 23.2, 22.3. MS (70 eV, EI): *m*/*z* (%): 250 (16), 249 (89) [M^+], 248 (100), 221 (8), 220 (31), 206 (19), 204 (6), 168 (6), 167 (12), 158 (6), 157 (8), 131 (6), 130 (55), 129 (8), 128 (5), 119 (36), 118 (14), 117 (17), 115 (9), 104 (9), 103 (6), 91 (13), 78 (6), 77 (54), 65 (5), 51 (19).

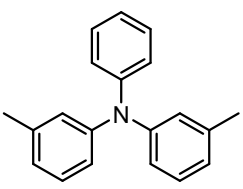


***N,N*-dicyclohexylaniline:** (CAS No. 63302-13-6): Isolated as colorless crystals (Eluent: hexane/toluene = 9/1, R_f = 0.04). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.22–7.12 (m, 2H), 6.98–6.90 (m, 2H), 6.84–6.75 (m, 1H), 3.29–3.18 (m, 2H), 1.79–1.43 (m, 14H), 1.37–1.06 (m, 6H). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 148.5, 128.2, 121.1, 119.0, 57.5, 31.9, 26.3, 26.0. MS (70 eV, EI): *m*/*z* (%): 258 (7), 257 (35) [M^+], 215 (16), 214 (100), 175 (6), 174 (6), 133 (9), 132 (81), 130 (8), 120 (7), 119 (63), 118 (14), 117 (8), 106 (8), 104 (16), 91 (7), 83 (5), 77 (22), 55 (28).

Data of triarylamines

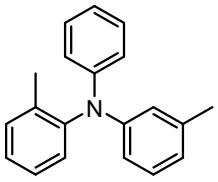


***N*-(4-ethylphenyl)-3-methyl-*N*-phenylaniline (3a):** 85% GC yield, 70% isolated yield (Fig. 3). Isolated as colorless crystals (Eluent: hexane/toluene = 19/1, R_f = 0.27). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.20–7.17 (m, 2H, Ar), 7.10–7.04 (m, 5H, Ar), 7.01–6.99 (m, 2H, Ar), 6.95–6.92 (m, 1H, Ar), 6.90 (s, 1H, Ar), 6.87–6.85 (m, 1H, Ar), 6.79–6.77 (m, 1H, Ar), 2.59 (q, J = 7.6 Hz, 2H, CH_2), 1.22 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 148.1, 147.9, 145.4, 138.9, 138.8, 129.0, 128.9. 128.6, 124.7, 124.5, 123.5, 123.2, 122.0, 121.1, 28.2, 21.4, 15.5. MS (70 eV, EI): *m*/*z* (%): 288 (20), 287 (89) [M^+], 273 (23), 272 (100), 258 (6), 257 (5), 256 (7), 180 (8), 167 (6), 154 (6), 153 (6), 128 (7), 127 (5), 115 (5), 91 (6), 77 (10), 65 (6), 51 (5). Anal. Calc. for $C_{21}H_{21}N$: C, 87.76; H, 7.37; N, 4.87. Found: C, 87.84; H, 7.61; N, 4.76.

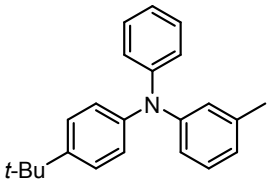


3-methyl-*N*-phenyl-*N*-(*m*-tolyl) aniline (3b) (CAS No. 13511-11-0)[S1]: 80% GC yield, 70% isolated yield (Fig. 3). Isolated as white powder (Eluent: hexane/toluene = 23/2, R_f

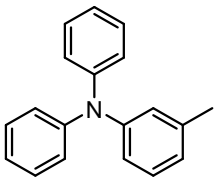
= 0.43). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.22–7.19 (m, 2H, Ar), 7.12–7.09 (m, 2H, Ar), 7.06–7.05 (m, 2H, Ar), 6.98–6.94 (m, 1H, Ar), 6.90 (s, 2H, Ar), 6.88–6.86 (m, 2H, Ar), 6.82–6.80 (m, 2H, Ar), 2.24 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 148.0, 147.8, 139.0, 129.1, 128.9, 124.9, 123.9, 123.5, 122.3, 121.4, 21.4. These NMR spectral data accord with those previously reported.[S1] MS (70 eV, EI): *m*/*z* (%): 274 (22), 273 (100) [M^+], 272 (19), 258 (12), 257 (22), 256 (6), 243 (5), 180 (10), 167 (7), 166 (5), 155 (5), 136 (5), 128 (7), 127 (5), 115 (6), 91 (6), 77 (9), 65 (9), 51 (5).



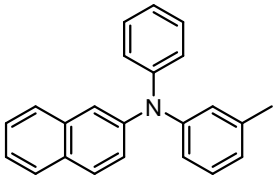
2-methyl-*N*-phenyl-*N*-(*m*-tolyl) aniline (3c) (CAS No. 1648726-23-1): 79% GC yield, 62% isolated yield (Fig. 4). Isolated as colorless crystals (Eluent: hexane/toluene = 97/3, R_f = 0.43). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.22–7.04 (m, 7H, Ar), 6.95–6.93 (m, 2H, Ar), 6.89–6.86 (m, 1H, Ar), 6.80–6.71 (m, 3H, Ar), 2.21 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 147.6, 147.4, 145.4, 138.7, 136.4, 131.6, 129.6, 128.9, 128.8, 127.3, 125.8, 122.3, 122.2, 121.4, 121.1, 118.9, 21.5, 18.6. MS (70 eV, EI): *m*/*z* (%): 274 (21), 273 (100) [M^+], 272 (12), 258 (16), 257 (8), 256 (7), 243 (9), 196 (7), 194 (5), 182 (11), 181 (8), 180 (26), 167 (10), 166 (7), 165 (6), 137 (5), 136 (6), 128 (6), 115 (5), 91 (6), 77 (10), 65 (10), 51(7).



***N*-(4-(tert-butyl) phenyl)-3-methyl-*N*-phenylaniline (3d)**: 73% GC yield, 76% isolated yield. Isolated as colorless crystals (Eluent: hexane/toluene = 19/1, R_f = 0.35). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.24–7.18 (m, 4H, Ar), 7.11–7.08 (m, 1H, Ar), 7.06–7.05 (m, 2H, Ar), 7.00–6.99 (m, 2H, Ar), 6.96–6.93 (m, 1H, Ar), 6.91 (s, 1H, Ar), 6.87–6.86 (m, 1H, Ar), 6.80–6.78 (m, 1H, Ar), 2.23 (s, 3H, CH_3), 1.30 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 148.1, 147.9, 145.5, 145.1, 138.9, 129.0, 128.9, 126.0, 124.6, 123.8, 123.7, 123.3, 122.1, 121.2, 34.2, 31.4, 21.4. MS (70 eV, EI): *m*/*z* (%): 316 (14), 315 (52) [M^+], 301 (24), 300 (100), 285 (10), 167 (12), 150 (5), 136 (6), 135 (5), 128 (13), 77 (6). Anal. Calc. for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.17; H, 7.92; N, 4.28.

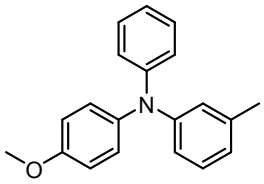


3-methyl-*N*, *N*-diphenylaniline (3e) (CAS No. 4316-54-5)[S2]: 78% GC yield, 66% isolated yield (Fig. 3). Isolated as white powder (Eluent: hexane/toluene =19/1, R_f = 0.36). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.23–7.20 (m, 4H, Ar), 7.13–7.10 (m, 1H, Ar), 7.07–7.06 (m, 4H), 6.99–6.96 (m, 2H, Ar), 6.91 (s, 1H, Ar), 6.89–6.87 (m, 1H, Ar), 6.83–6.81 (m, 1H, Ar), 2.24 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125MHz, $CDCl_3$, TMS): δ 147.9, 147.7, 139.0, 129.1, 129.0, 125.0, 124.0, 123.7, 122.5, 121.5, 21.4. These NMR spectral data accord with those previously reported.[S2] MS (70 eV, EI): *m*/*z* (%): 260 (21), 259 (100) [M^+], 258 (25), 244 (12), 243 (21), 242 (5), 180 (7), 167 (14), 166 (11), 141 (8), 129 (5), 128 (7), 115 (8), 77 (14), 65 (7), 51 (11).

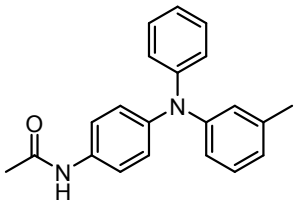


***N*-phenyl-*N*-(*m*-tolyl) naphthalen-2-amine (3f)**: 84% GC yield, 84% isolated yield (Fig. 3). Isolated as colorless crystals (Eluent: hexane/toluene = 19/1, R_f = 0.34). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.72–7.70 (m, 1H, Ar), 7.68–7.66 (m, 1H, Ar),

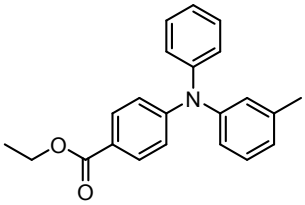
7.55–7.53 (m, 1H, Ar), 7.41–7.40 (m, 1H, Ar), 7.36–7.21 (m, 5H, Ar), 7.14–7.10 (m, 3H, Ar), 7.01–6.98 (m, 1H, Ar), 6.95 (s, 1H, Ar), 6.93–6.92 (m, 1H, Ar), 6.85–6.83 (m, 1H, Ar), 2.24 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 147.9, 147.7, 145.6, 139.1, 134.4, 129.9, 129.2, 128.7, 127.5, 126.9, 126.2, 125.2, 125.1, 124.3, 123.8, 122.8, 122.6, 121.8, 121.6, 120.0, 21.4. MS (70 eV, EI): *m*/*z* (%): 310 (25), 309 (100) [M^+], 308 (22), 294 (7), 293 (11), 217 (9), 216 (7), 192 (6), 191 (8), 155 (6), 146 (5), 115 (5), 77 (5). Anal. Calc. for $C_{23}H_{19}N \cdot 0.3\ H_2O$: C, 87.75; H, 6.28; N, 4.45. Found: C, 87.87; H, 6.41; N, 4.48.



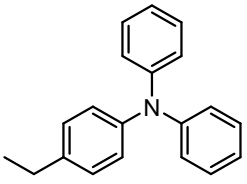
***N*-(4-methoxyphenyl)-3-methyl-*N*-phenylaniline (3g)** (CAS No. 1648726-90-2): 86% GC yield, 74% isolated yield (Fig. 4). Isolated as colorless crystals (Eluent: hexane/toluene = 4/1, R_f = 0.33). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.18–7.15 (m, 2H, Ar), 7.09–7.00 (m, 5H, Ar), 6.92–6.74 (m, 6H, Ar), 3.76 (s, 3H, CH_3 methoxy), 2.22 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 156.0, 148.2, 148.0, 140.8, 138.8, 129.0, 128.8, 127.2, 123.6, 122.8, 122.7, 121.6, 120.2, 114.6, 55.3, 21.4. MS (70 eV, EI): *m*/*z* (%): 290 (23), 289 (100) [M^+], 275 (21), 274 (93), 230 (6), 145 (6), 128 (9), 91 (5), 77 (7), 65 (5).



***N*-(4-(phenyl (*m*-tolyl) amino) phenyl) acetamide (3h)**: 31% GC yield, 32% isolated yield (Fig. 3). Isolated as white powder (Eluent: hexane/EtOAc = 2/3, R_f = 0.37). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.61 (s, 1H, NH), 7.38–7.35 (m, 2H, Ar), 7.22–7.19 (m, 2H, Ar), 7.12–7.09 (m, 1H, Ar), 7.03–7.01 (m, 4H, Ar), 6.98–6.95 (m, 1H, Ar), 6.87–6.80 (m, 3H, Ar), 2.23 (s, 3H, CH_3), 2.14 (s, 3H, CH_3 amide). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 168.4 (CO), 147.8, 147.6, 144.2, 139.0, 132.8, 129.1, 129.0, 124.8, 124.5, 123.6, 123.5, 122.3, 121.2, 121.1, 24.3, 21.4. MS (70 eV, EI): *m*/*z* (%): 317 (24), 316 (100) [M^+], 275 (15), 274 (52), 273 (59), 182 (5), 181 (5), 167 (5), 129 (6), 128 (9), 91 (5), 77 (7), 65 (6). Anal. Calc. for $C_{21}H_{20}N_2O \cdot 0.7\ H_2O$: C, 76.66; H, 6.56; N, 8.51. Found: C, 76.42; H, 6.14; N, 8.42.

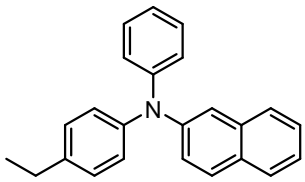


ethyl 4-(phenyl (*m*-tolyl) amino) benzoate (3i) (CAS No. 1344716-76-2)[S3]: 54% GC yield, 58% isolated yield (Fig. 3). Isolated as colorless crystals (Eluent: hexane/toluene =1/4, R_f = 0.39). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.88–7.87 (m, 2H, Ar), 7.32–7.29 (m, 2H, Ar), 7.21–7.18 (m, 1H, Ar), 7.16–7.10 (m, 3H, Ar), 7.00–6.94 (m, 5H, Ar), 4.33 (q, J = 7.2 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.36 (t, J = 7.2 Hz, 3H, CH_3), $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 166.4 (CO), 152.0, 146.7, 146.6, 139.4, 130.7, 129.4, 129.3, 126.4, 125.6, 125.3, 124.2, 123.0, 122.3, 120.0, 60.4, 21.2, 14.4. MS (70 eV, EI): *m*/*z* (%): 332 (24), 331(100) [M^+], 304 (9), 303 (42), 302 (5), 286 (18), 259 (5), 258 (15), 257 (9), 256 (7), 244 (5), 243 (16), 242 (8), 241 (6), 180 (5), 167 (9), 166 (8), 143 (6), 115 (5), 77 (7), 65 (6).

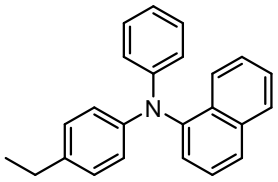


4-ethyl-*N*, *N*-diphenylaniline (3j) (CAS No. 36809-22-0)[S4]: 67% GC yield, 63% isolated yield (Fig. 3). Isolated as colorless crystals (Eluent: hexane/toluene =19/1, R_f = 0.39). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.22–7.18 (m, 4H, Ar), 7.08–7.00 (m, 8H,

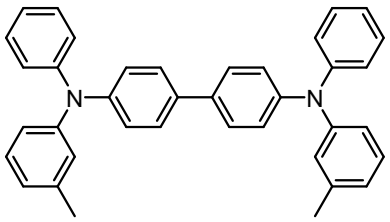
Ar), 6.96–6.93 (m, 2H, Ar), 2.60 (q, J = 7.6 Hz, 2H, CH_2), 1.22 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 148.0, 145.4, 139.0, 129.1, 128.6, 124.8, 123.6, 122.2, 28.2, 15.5. These NMR spectral data accord with those previously reported.[S4] MS (70 eV, EI): m/z (%): 324 (27), 323 (100) [M^+], 309 (19), 308 (74), 294 (9), 293 (7), 292 (5), 230 (7), 217 (8), 216 (7), 136 (5), 77 (6).



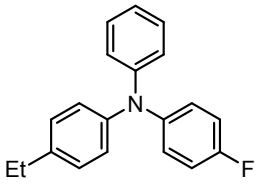
***N*-(4-ethylphenyl)-*N*-phenylnaphthalen-2-amine (3k):** 73% GC yield, 76% isolated yield (Fig. 3). Isolated as colorless crystals (Eluent: hexane/toluene =19/1, R_f = 0.32). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.70–7.69 (m, 1H, Ar), 7.66–7.64 (m, 1H, Ar), 7.53–7.52 (m, 1H, Ar), 7.39–7.39 (m, 1H, Ar), 7.34–7.19 (m, 5H, Ar), 7.15–7.04 (m, 6H, Ar), 6.99–6.96 (m, 1H, Ar), 2.60 (q, J = 7.6 Hz, 2H, CH_2), 1.23 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 147.9, 145.6, 145.3, 139.2, 134.4, 129.8, 129.2, 128.7, 127.5, 126.8, 126.2, 124.9, 124.2, 124.2, 123.9, 122.5, 119.5, 28.2, 15.5. MS (70 eV, EI): m/z (%): 324 (27), 323 (100) [M^+], 322 (5), 309 (17), 308 (69), 294 (7), 293 (6), 230 (5), 217 (6), 127 (5), 115 (5), 77 (6). Anal. Calc. for $C_{24}H_{21}N \cdot 0.3\ H_2O$: C, 87.86; H, 6.62; N, 4.26. Found: C, 87.76; H, 6.48; N, 4.29.



***N*-(4-ethylphenyl)-*N*-phenylnaphthalen-1-amine (3l):** 62% GC yield, 62% isolated yield. Isolated as colorless crystals (Eluent: hexane/toluene =19/1, R_f = 0.34). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.95–7.94 (m, 1H, Ar), 7.85–7.83 (m, 1H, Ar), 7.72–7.71 (m, 1H, Ar), 7.43–7.39 (m, 2H, Ar), 7.33–7.29 (m, 2H, Ar), 7.15–7.12 (m, 2H, Ar), 7.02–6.94 (m, 6H, Ar), 6.87–6.84 (m, 1H, Ar), 2.56 (q, J = 7.6 Hz, 2H, CH_2), 1.19 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 148.8, 146.0, 143.7, 137.9, 135.2, 131.3, 128.9, 128.5, 128.3, 127.1, 126.3, 126.24, 126.18, 126.0, 124.3, 122.5, 121.0, 120.9, 28.1, 15.5. MS (70 eV, EI): m/z (%): 324 (27), 323 (100) [M^+], 309 (19), 308 (74), 294 (9), 293 (7), 292 (5), 230 (7), 217 (8), 216 (7), 136 (5), 77 (6). Anal. Calc. for $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33. Found: C, 89.15; H, 6.51; N, 4.22.



***N*^{4},*N*$^{4'}$-diphenyl-*N*^{4},*N*$^{4'}$-di-*m*-tolyl-[1,1'-biphenyl]-4,4'-diamine (TPD) (3m)** (CAS No. 65181-78-4)[S5]: 51% isolated yield. Isolated as colorless crystals (Eluent: hexane/toluene = 60/40, R_f = 0.49). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.40–7.39 (m, 4H, Ar), 7.21–7.18 (m, 4H, Ar), 7.14–7.07 (m, 10H, Ar), 6.97–6.89 (m, 6H, Ar), 6.81–6.80 (m, 2H, Ar), 2.22 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 147.7, 147.6, 146.7, 139.0, 134.5, 129.1, 129.0, 127.2, 125.0, 124.1, 124.0, 123.8, 122.6, 121.6, 21.4. These NMR spectral data accord with those previously reported.[S5]



4-ethyl-*N*-(4-fluorophenyl)-*N*-phenylaniline (3n): 63% GC yield. Isolated as colorless crystals (Eluent: hexane/toluene = 19/1, R_f = 0.52). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.26–7.20 (m, 3H, Ar), 7.09–6.92 (m, 10H, Ar), 2.61 (q, J = 7.6 Hz, 2H, CH_2), 1.23 (t, J = 7.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$, TMS): δ 158.7 (d, J = 242 Hz, Ar), 148.1, 145.4, 144.1, 138.9, 129.1, 128.7, 126.0 (d, J = 8.4 Hz, Ar), 124.2, 122.9,

122.0, 115.9 (d, J = 22.8 Hz, Ar), 28.2, 15.5. MS (70 eV, EI): m/z (%): 292 (17), 291 (78) [M^+], 277 (22), 276 (100), 185 (5), 77 (8), 51 (5). Anal. Calc. for $C_{18}H_{21}FN$: C, 82.45; H, 6.23; F, 6.52; N, 4.81. Found: C, 82.26; H, 6.45; N, 4.46.

Additional references

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S2 Y. Hirai and Y. Uozumi, *Chem. Commun.*, 2010, **46**, 1103.

S3 M. Kurt, S. Okur, S. Demic, J. Karpagam and N. Sunderganes, *J. Raman Spectrosc.*, 2011, **42**, 1682.

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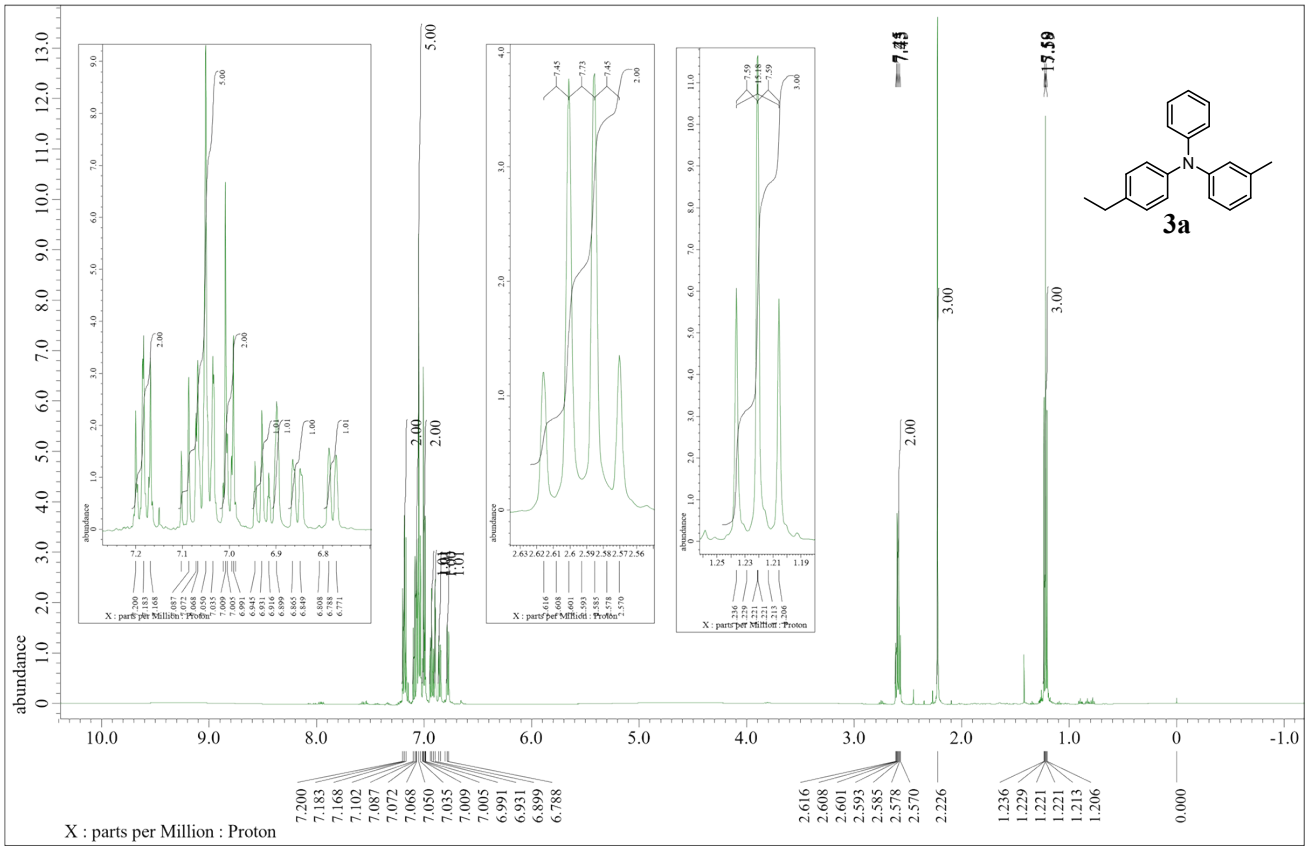
S5 D. S. Surry and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 10354.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7.102
7.087
7.072
7.068
7.050
7.035
7.009
7.005
6.991
6.931
6.899
6.788
2.616
2.608
2.601
2.593
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2.578
2.570
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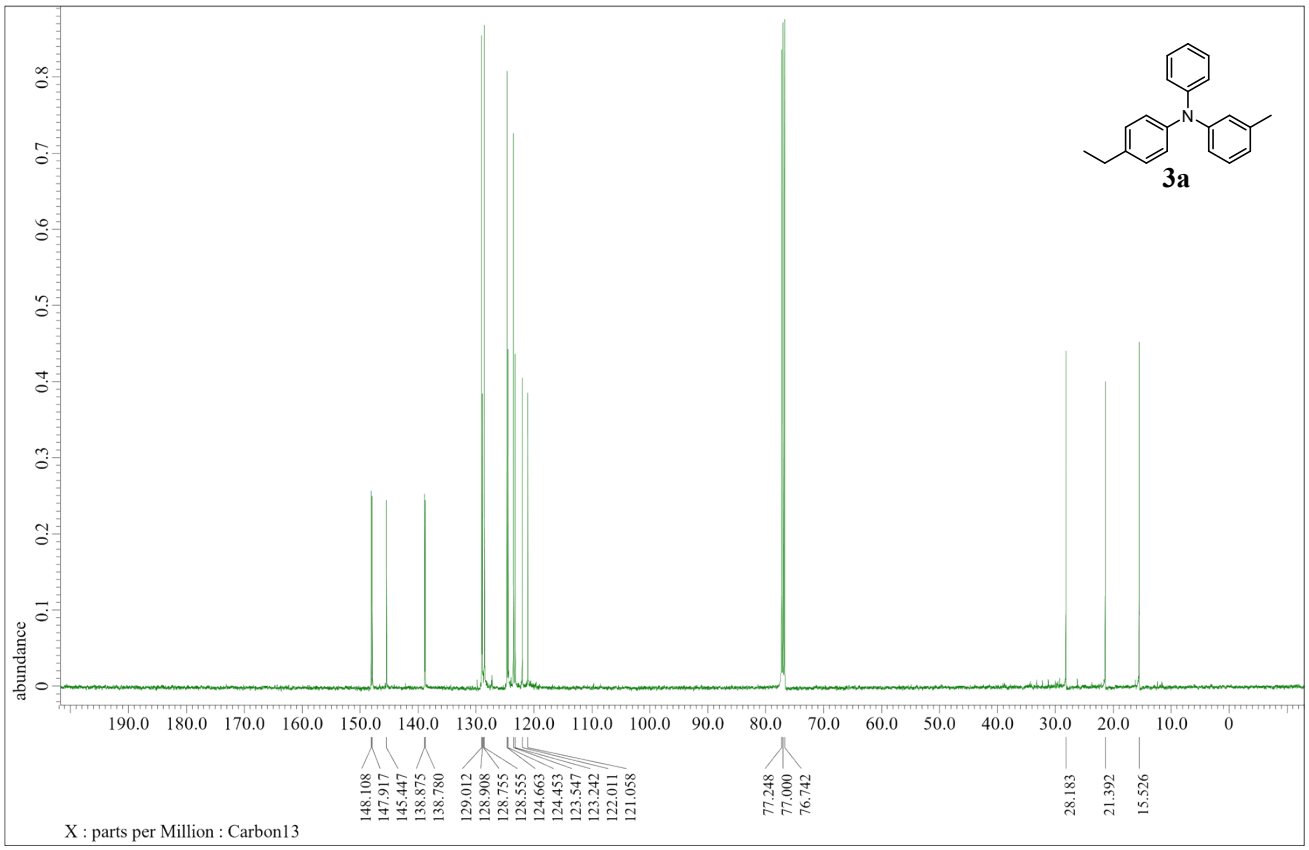
1.229
1.221
1.221
1.213
1.206
0.000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128.555
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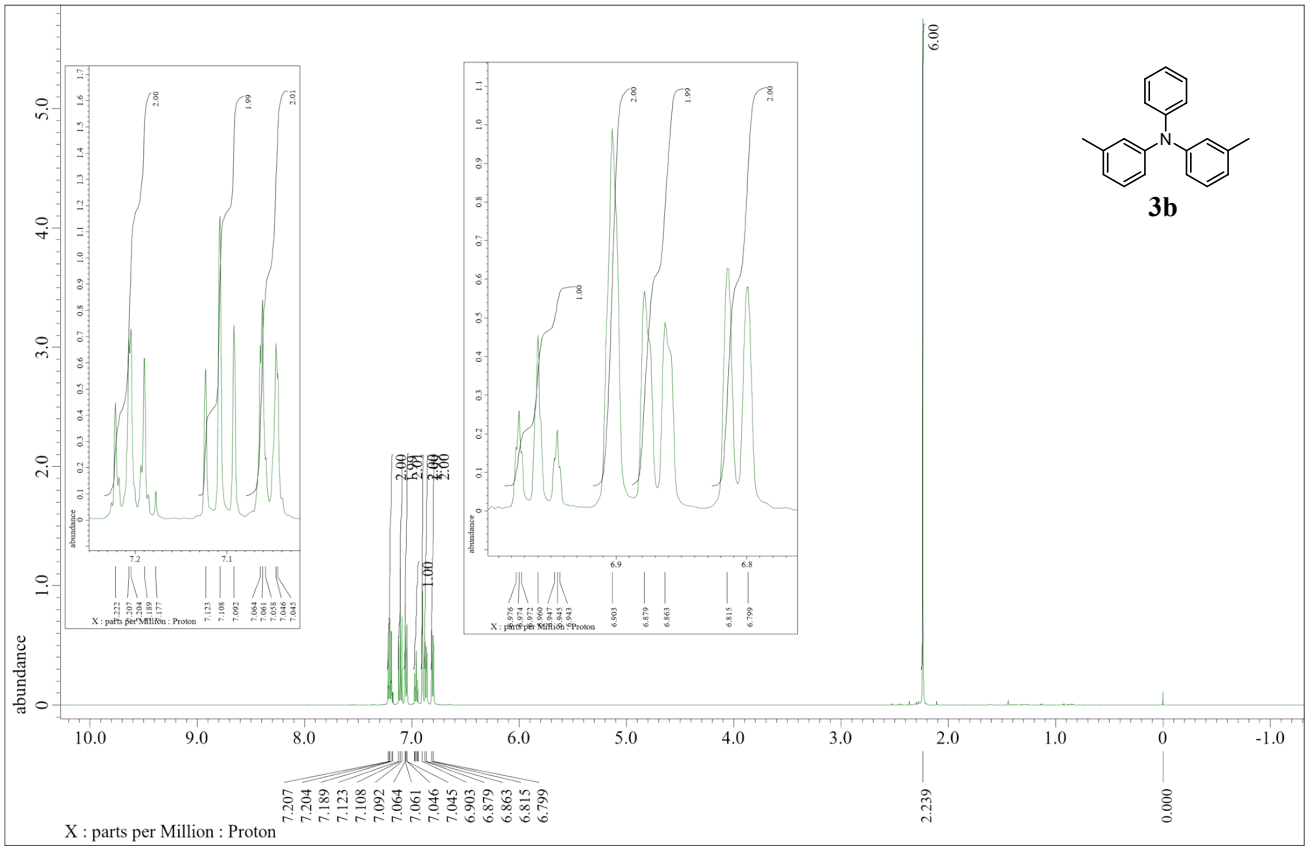
15.526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abundance
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7.123
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6.799
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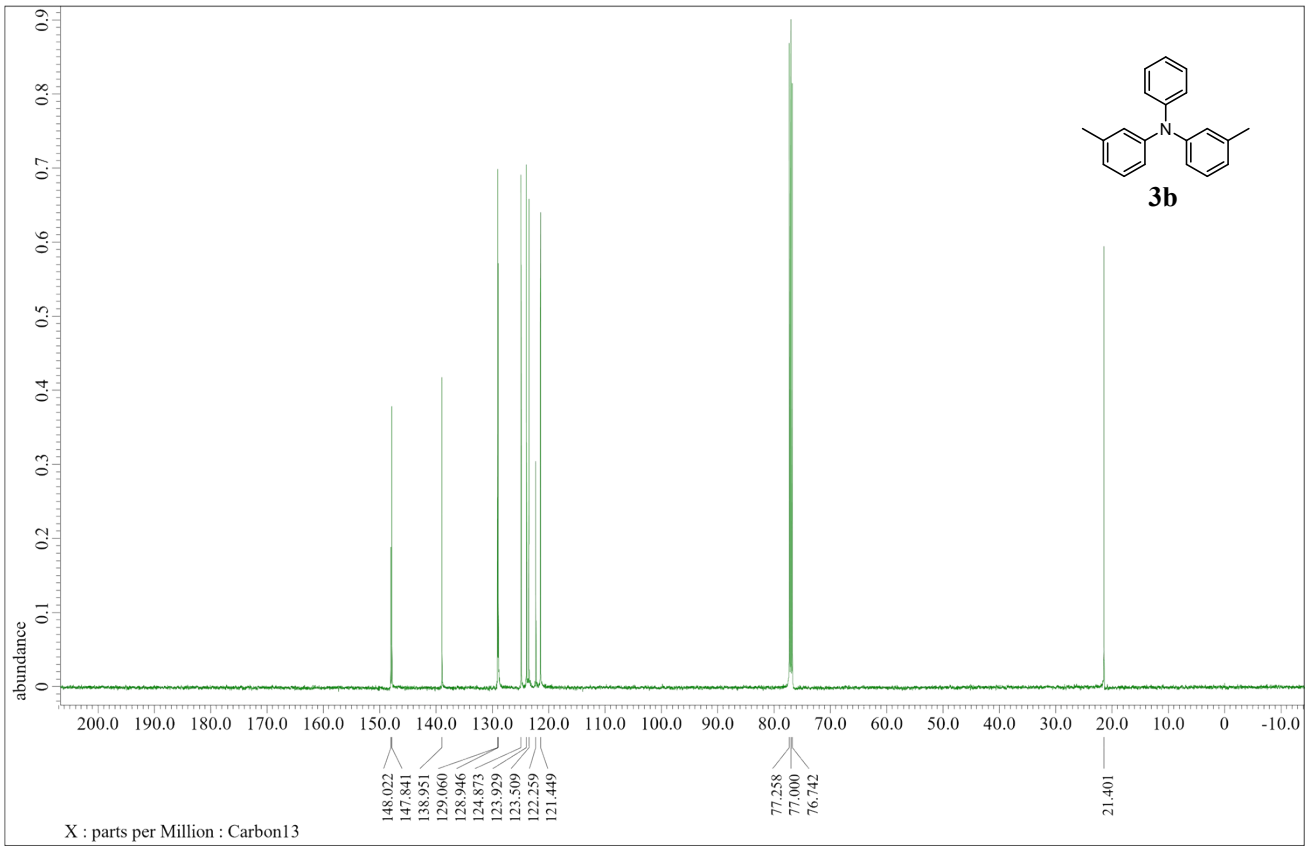
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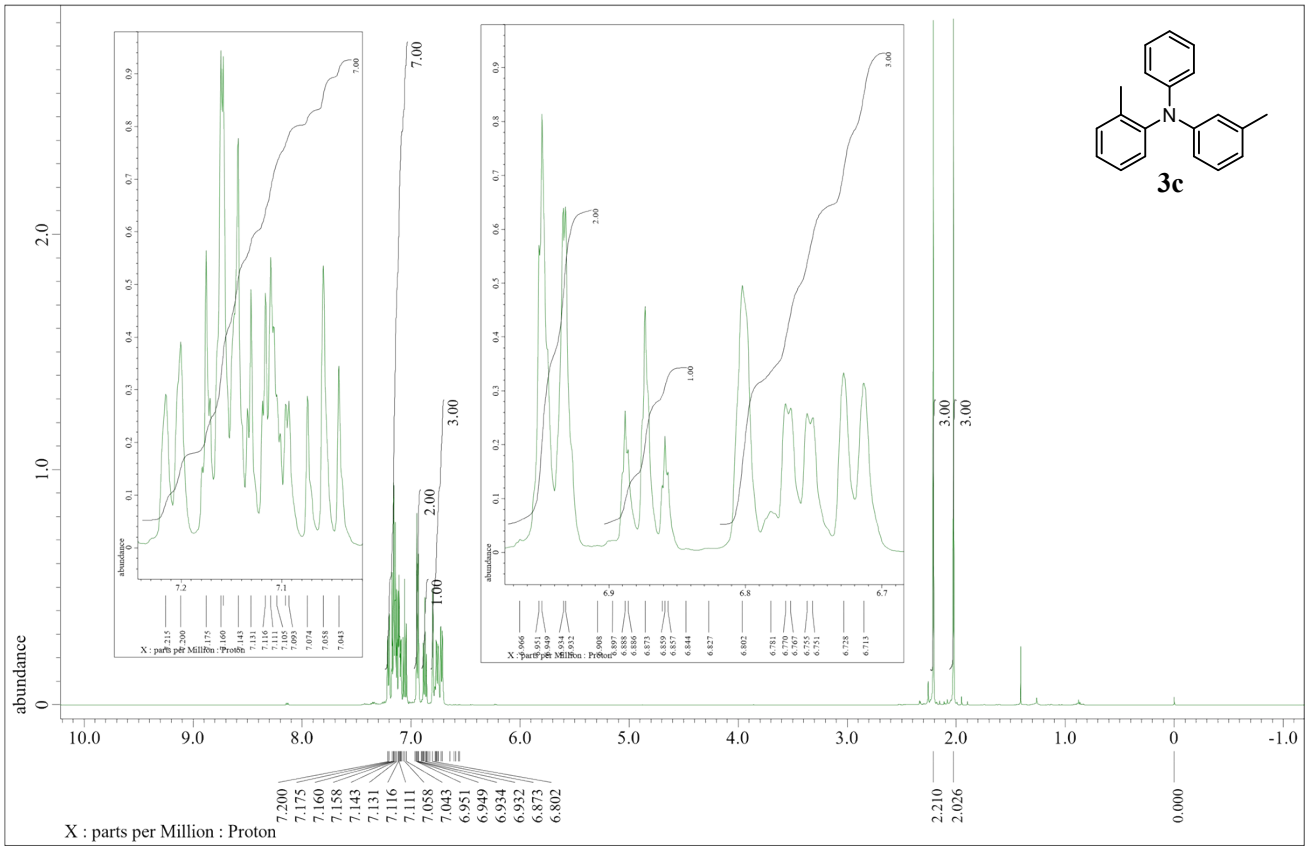
76.742
21.401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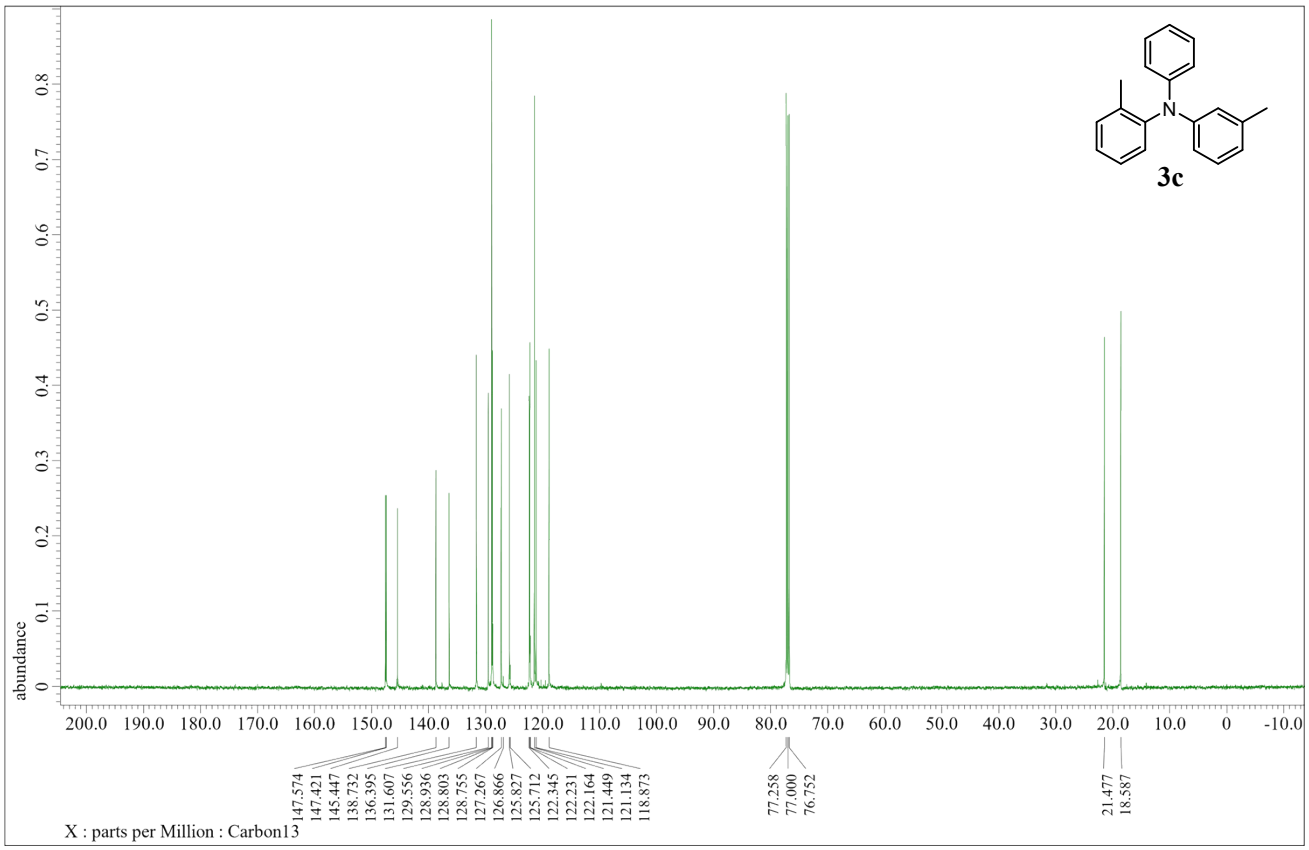
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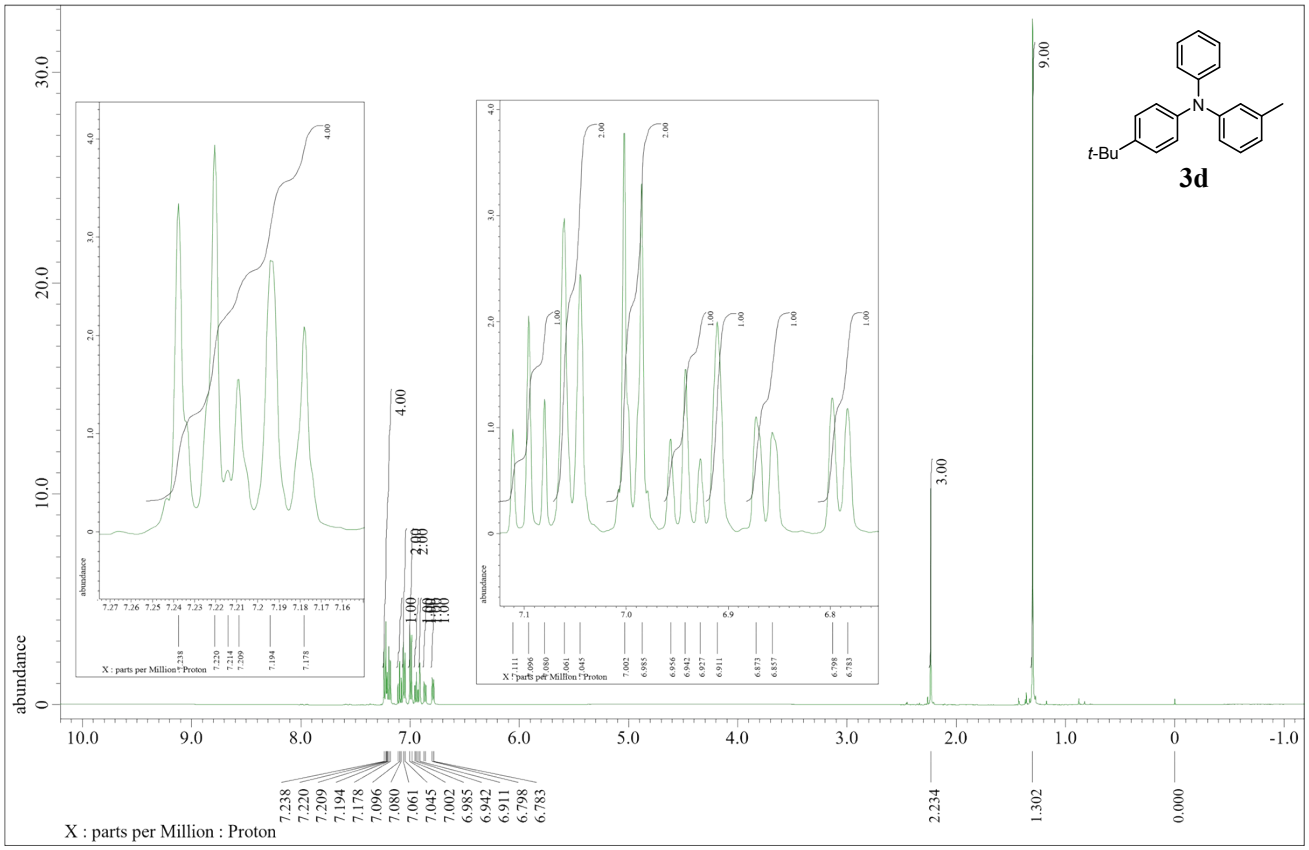
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7.002
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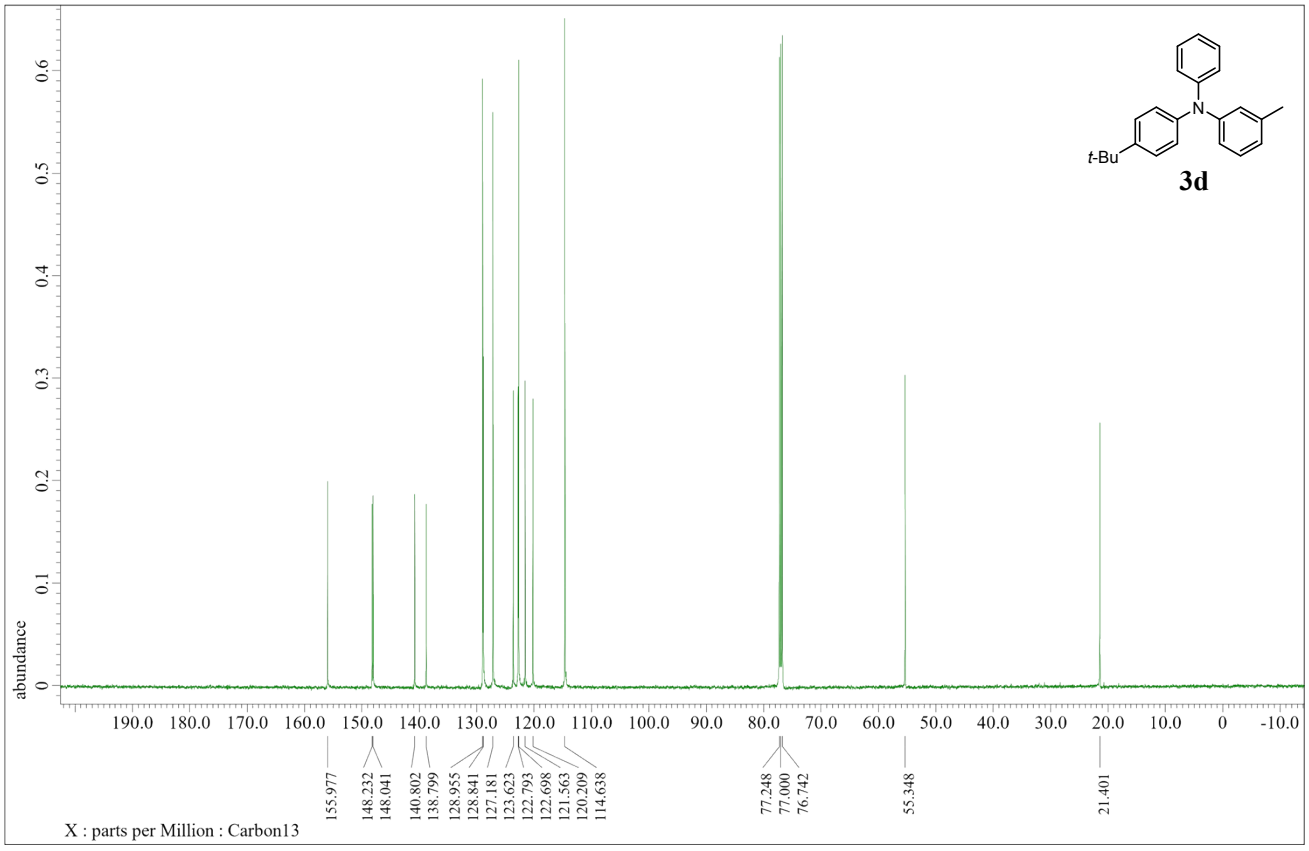
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t-Bu
abundance
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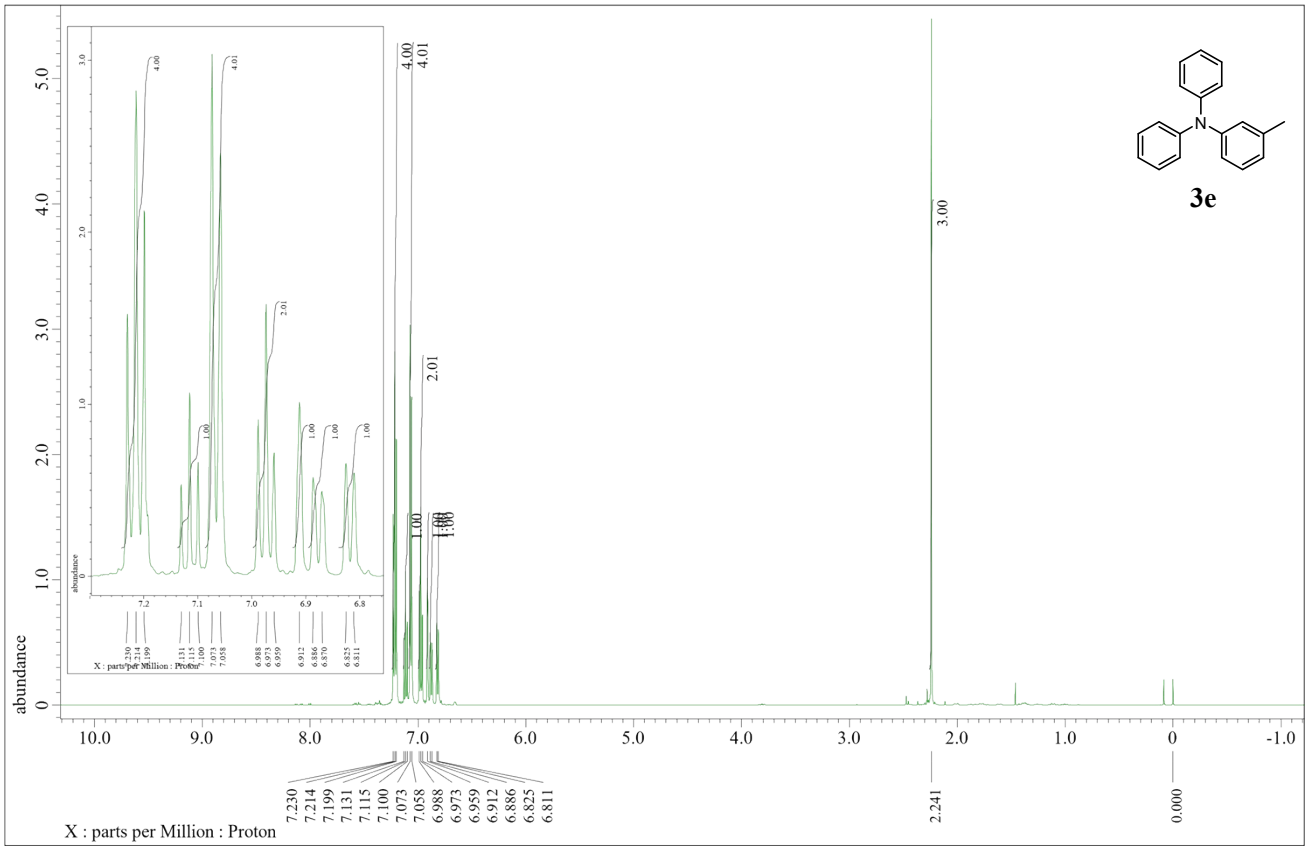
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abundance
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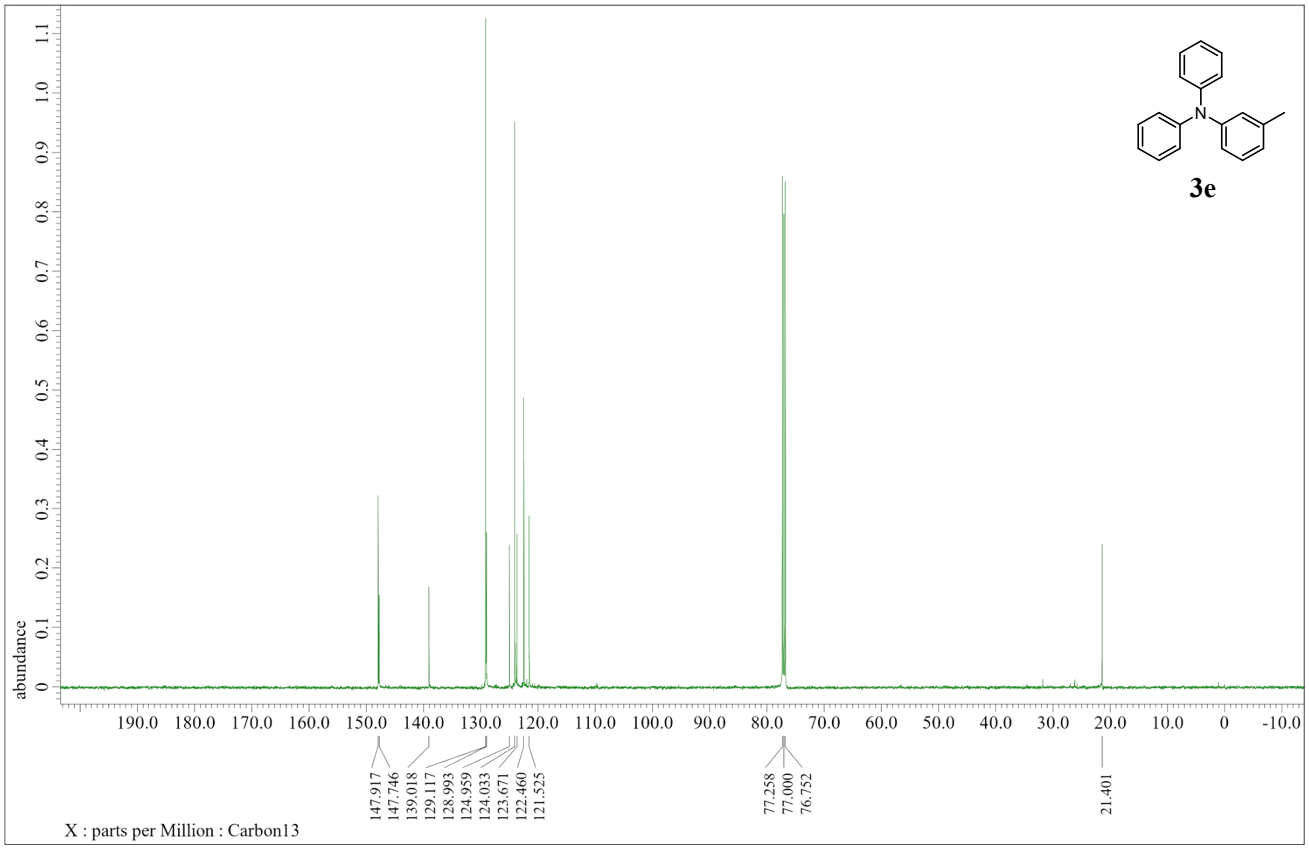
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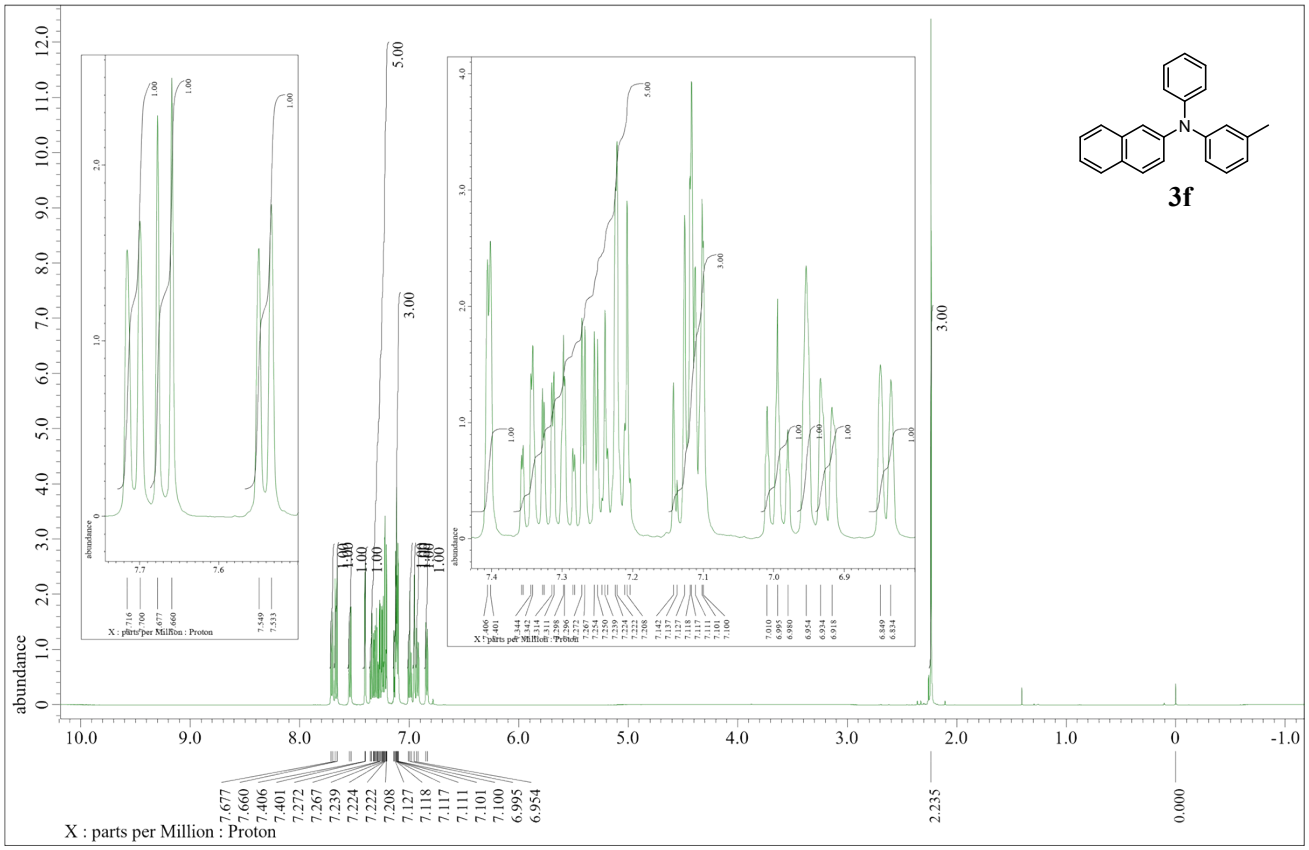
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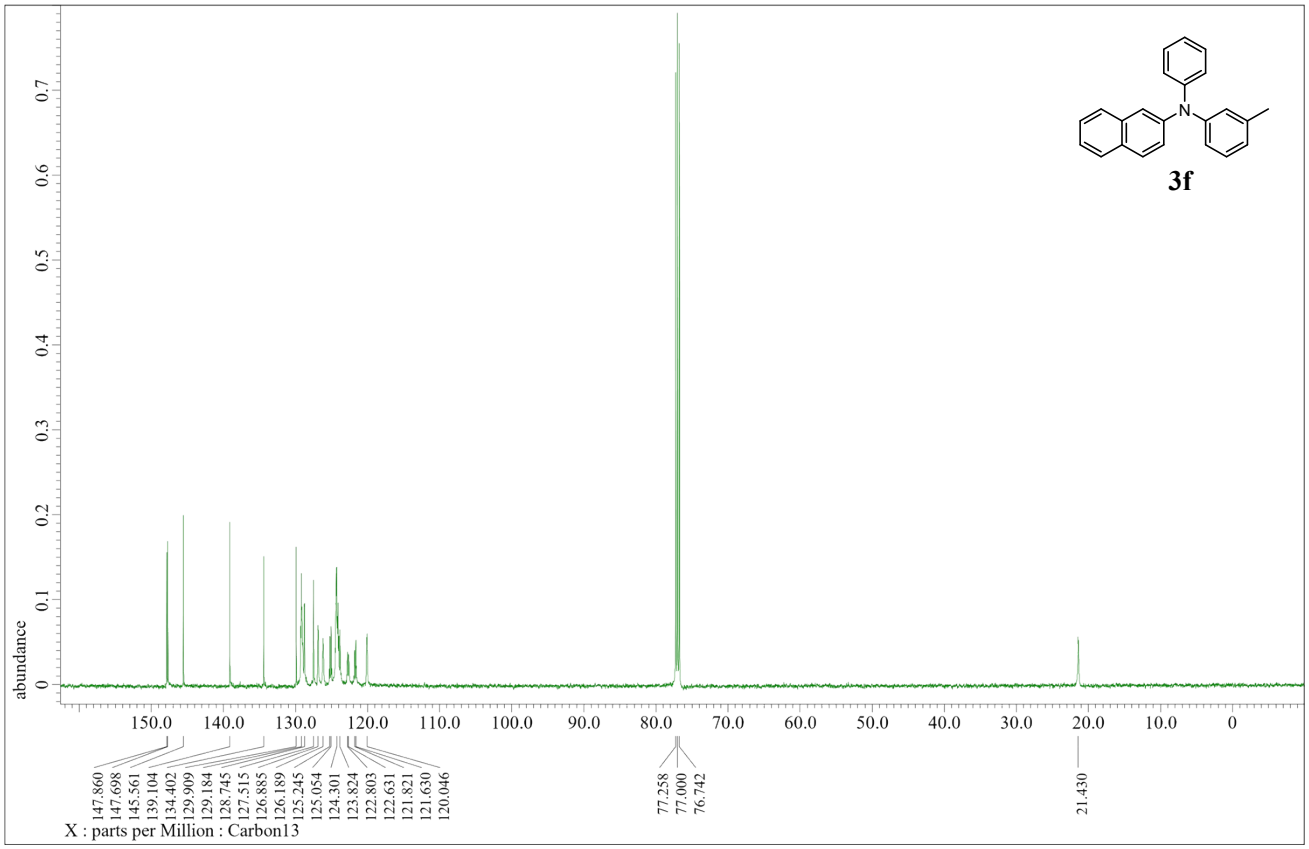
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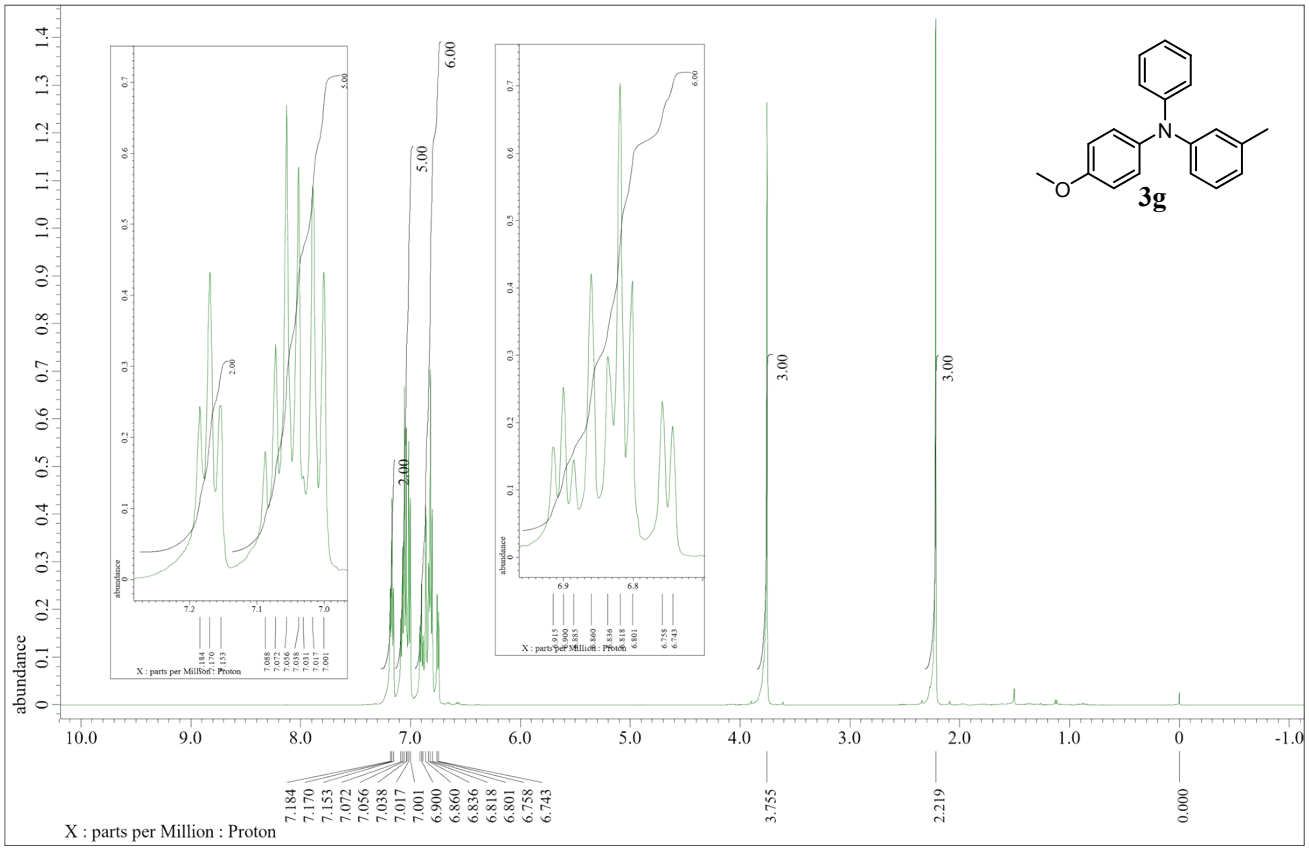
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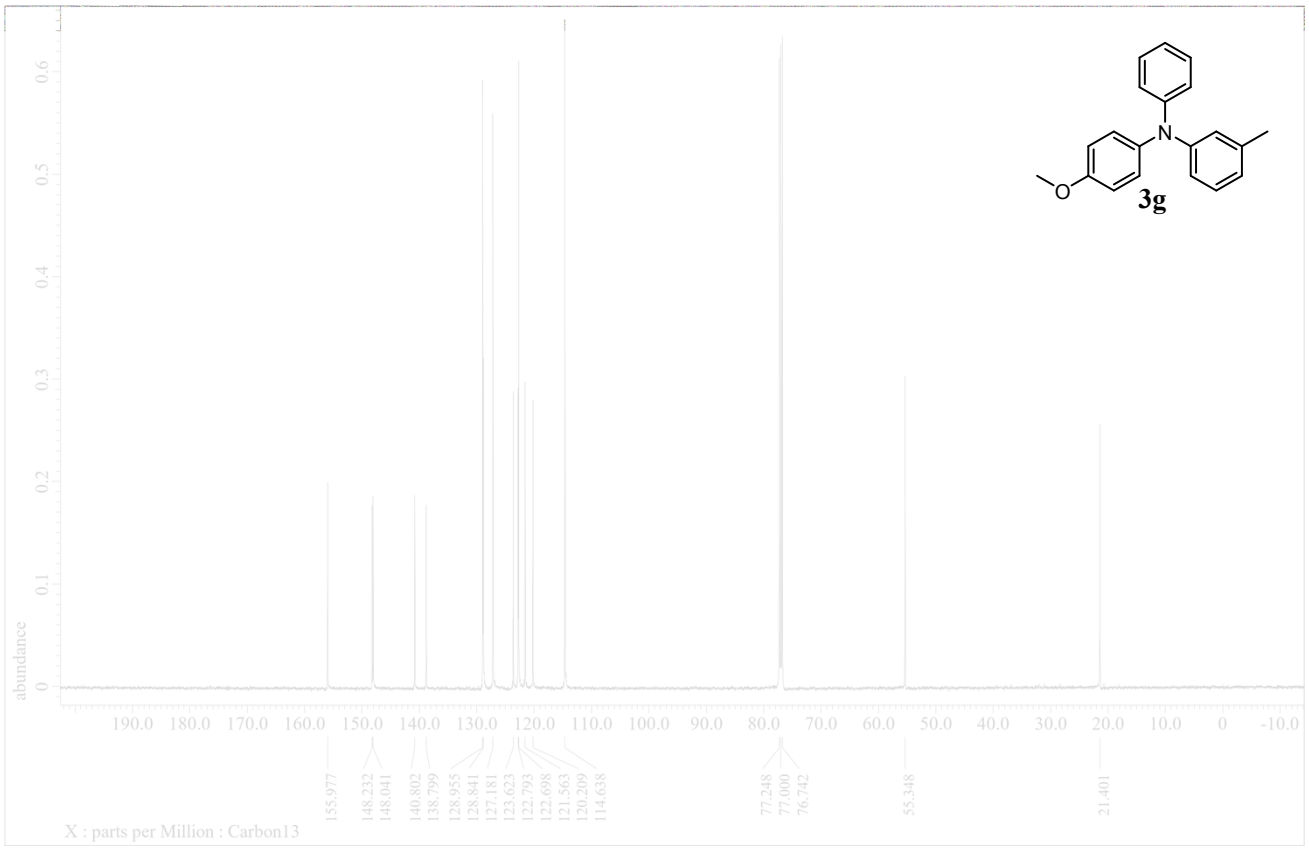
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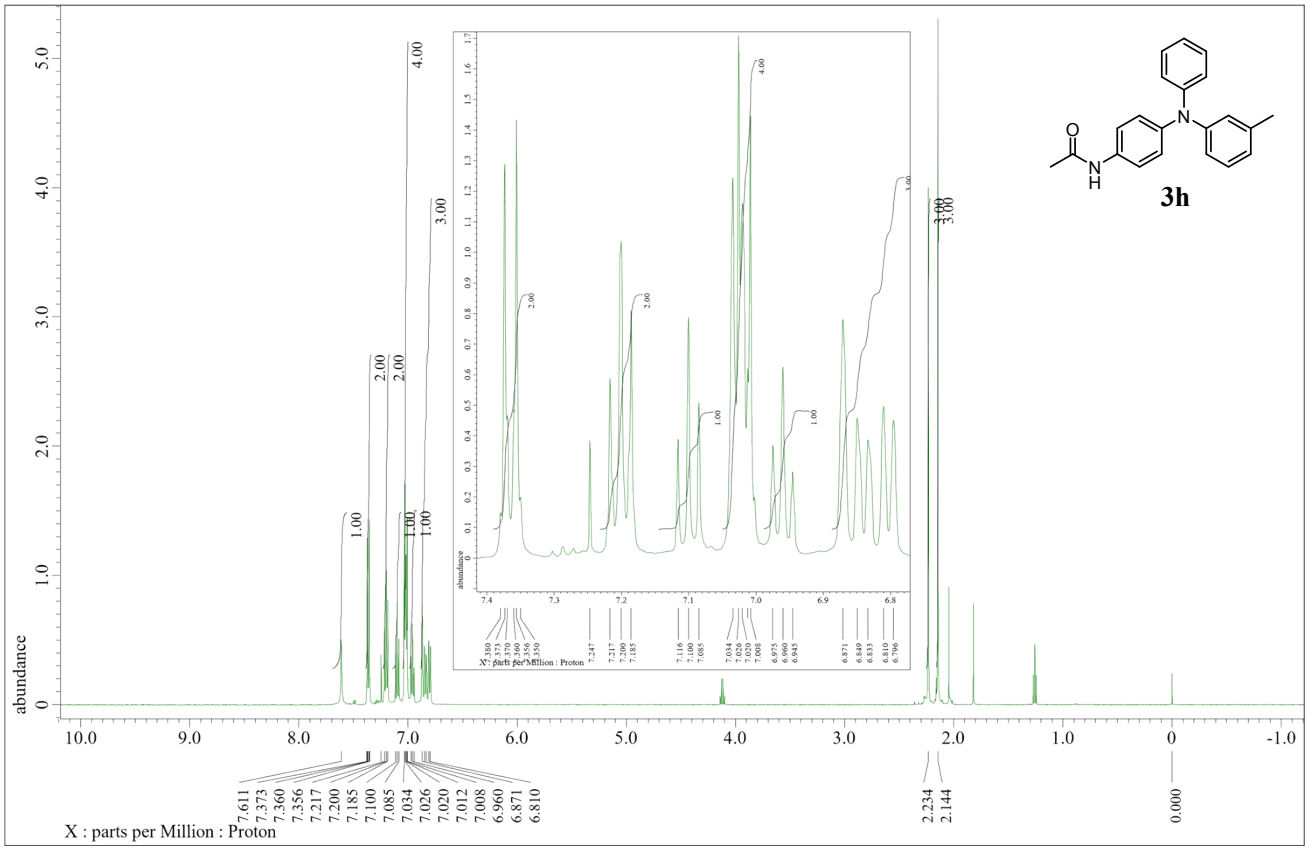
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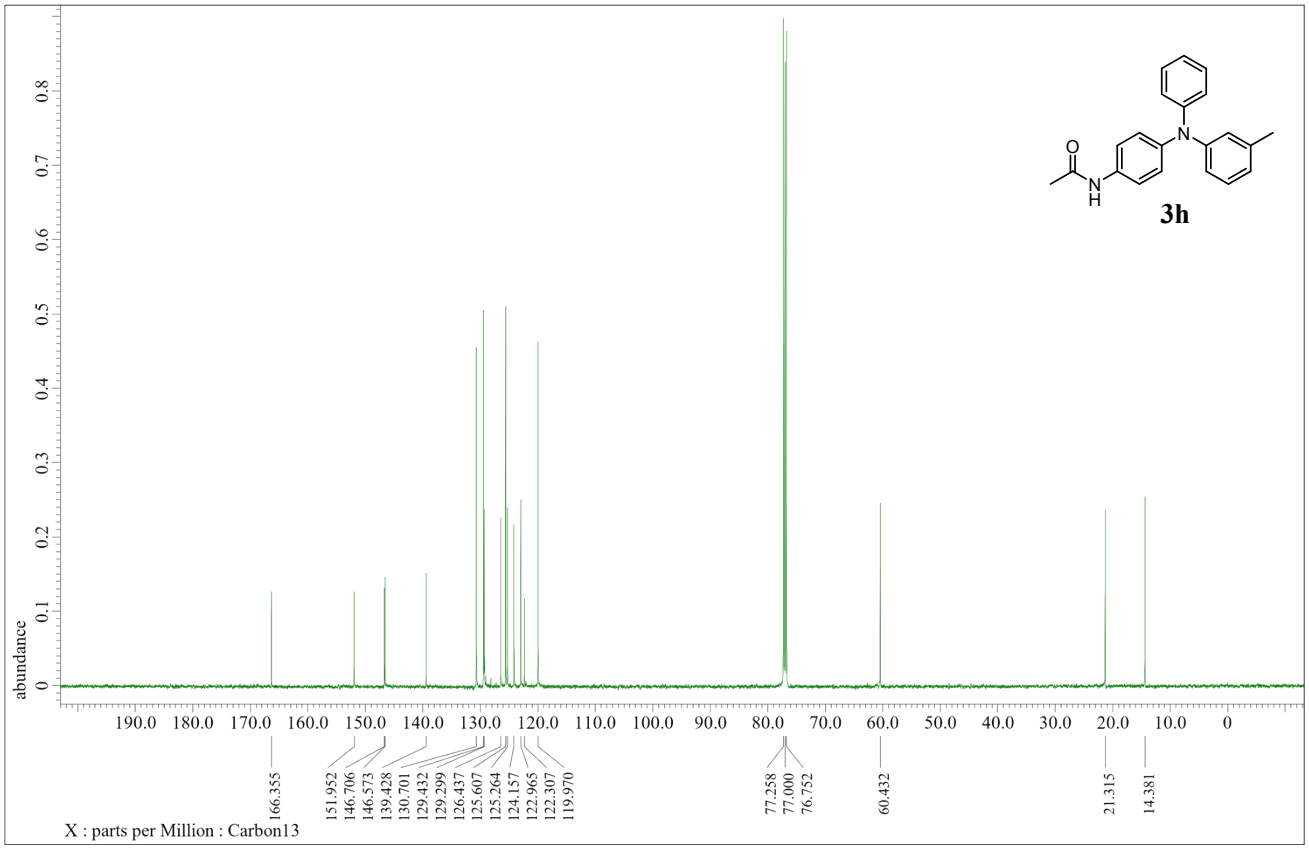
abundance
X : parts per Million : Proton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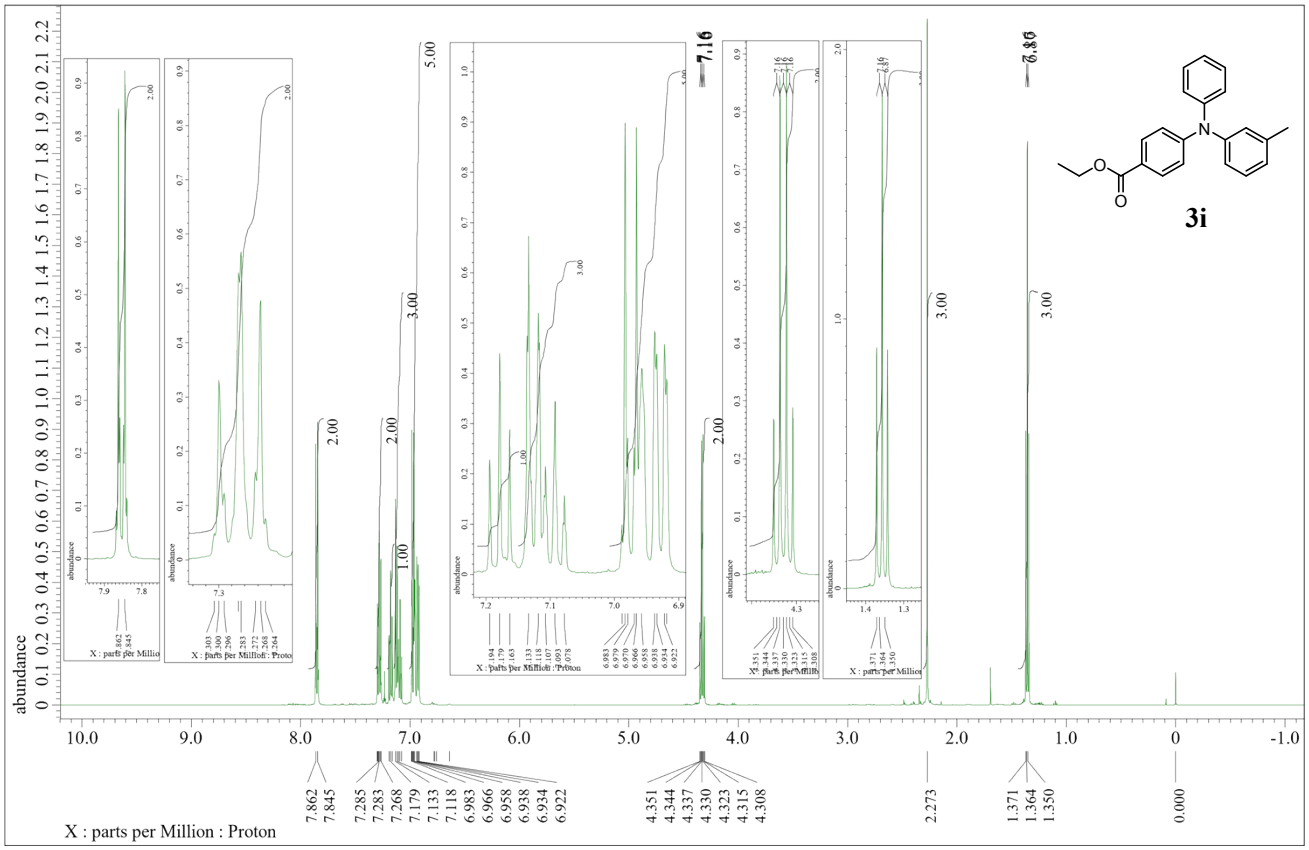
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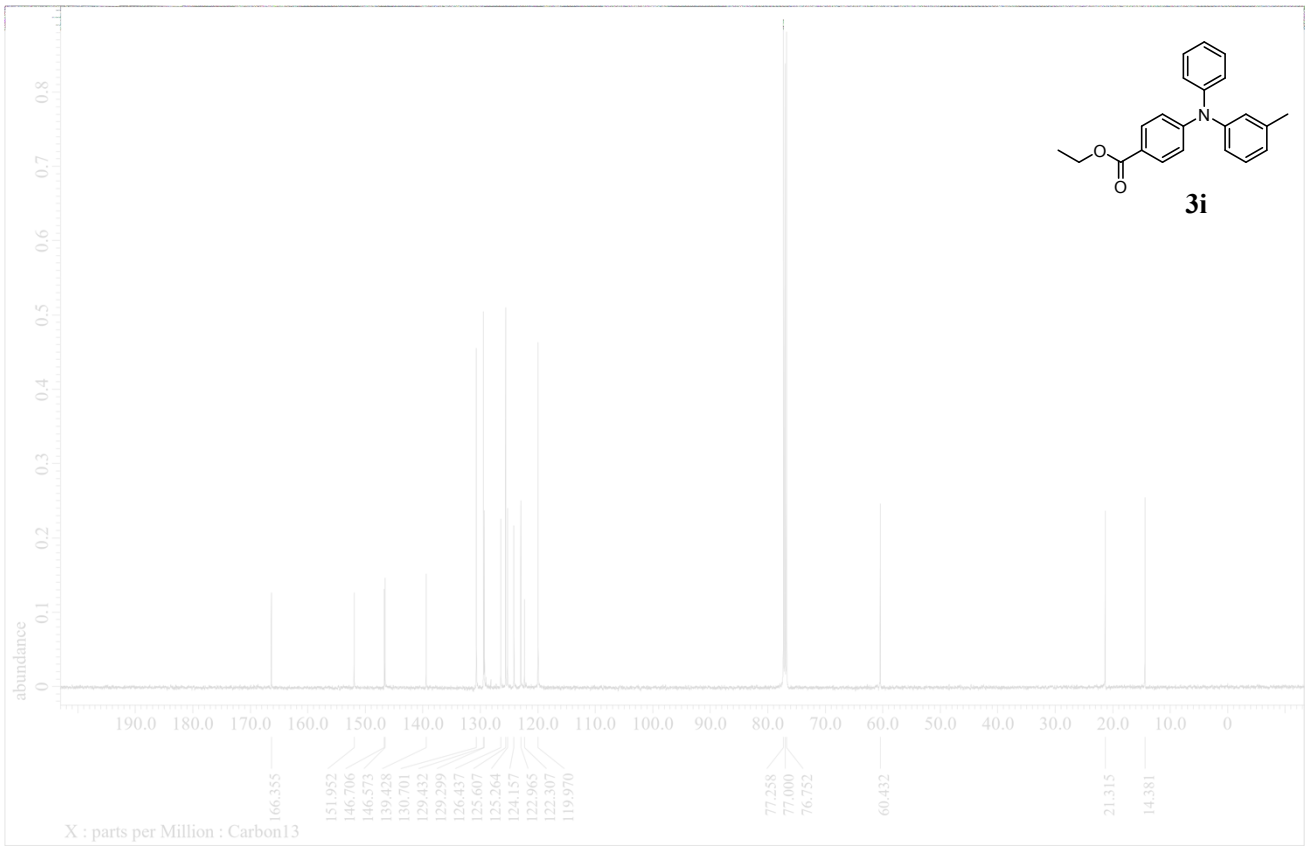
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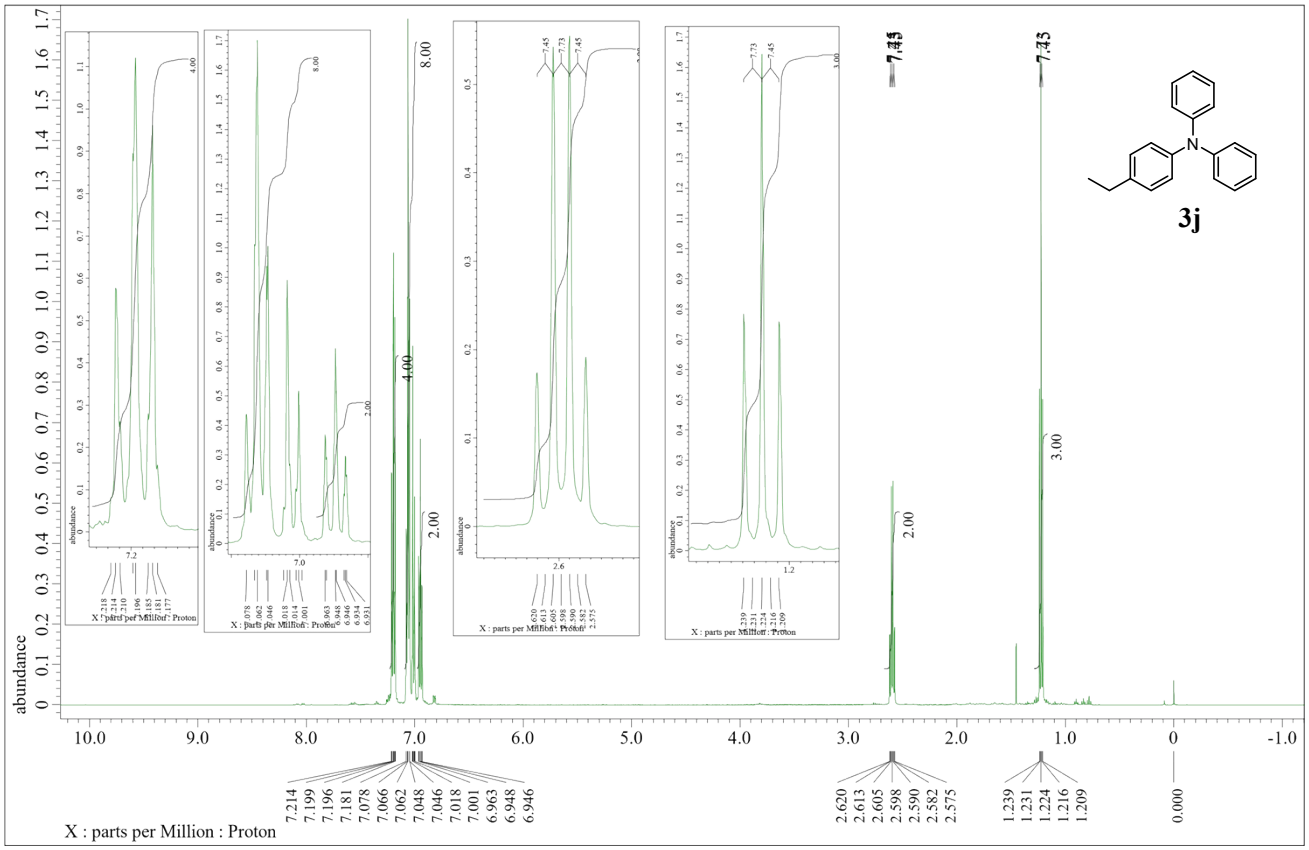
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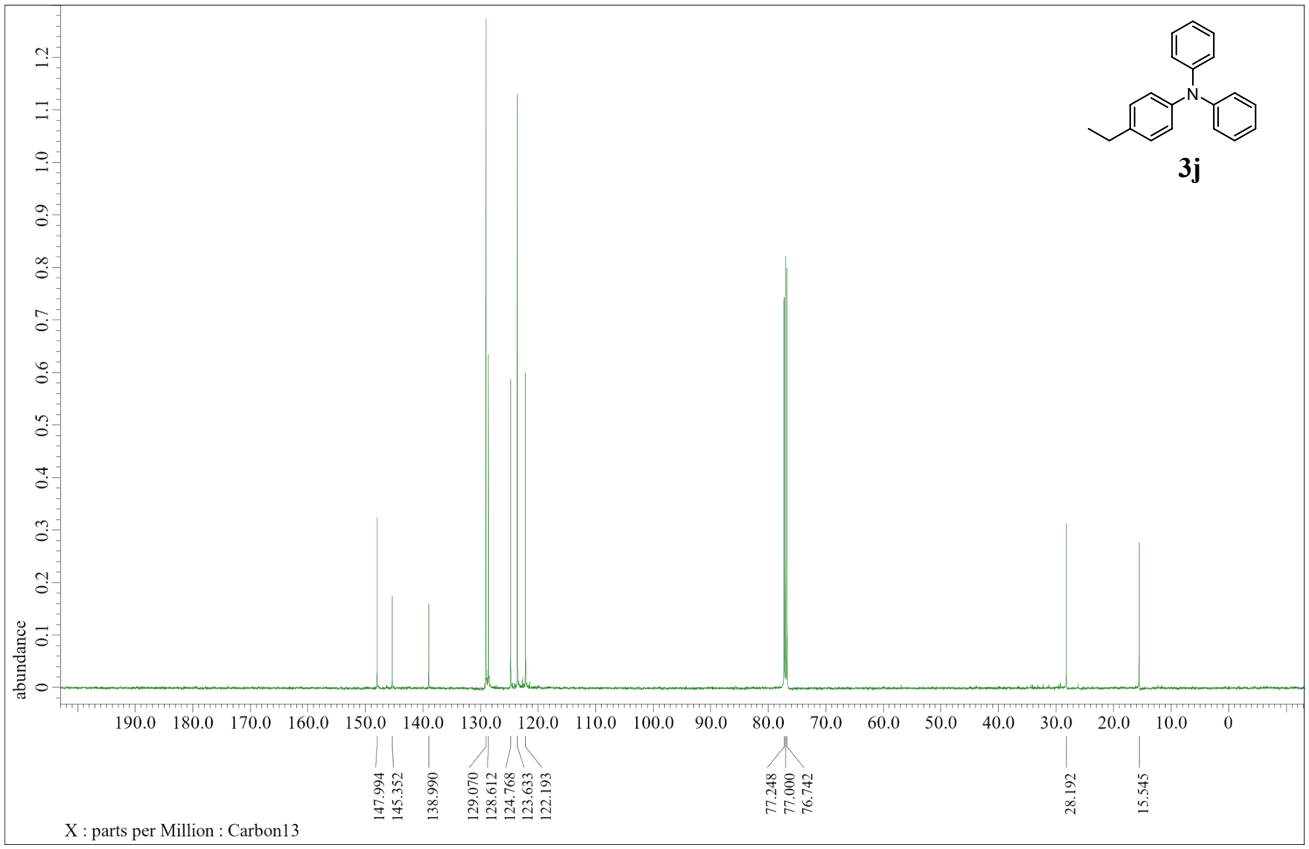
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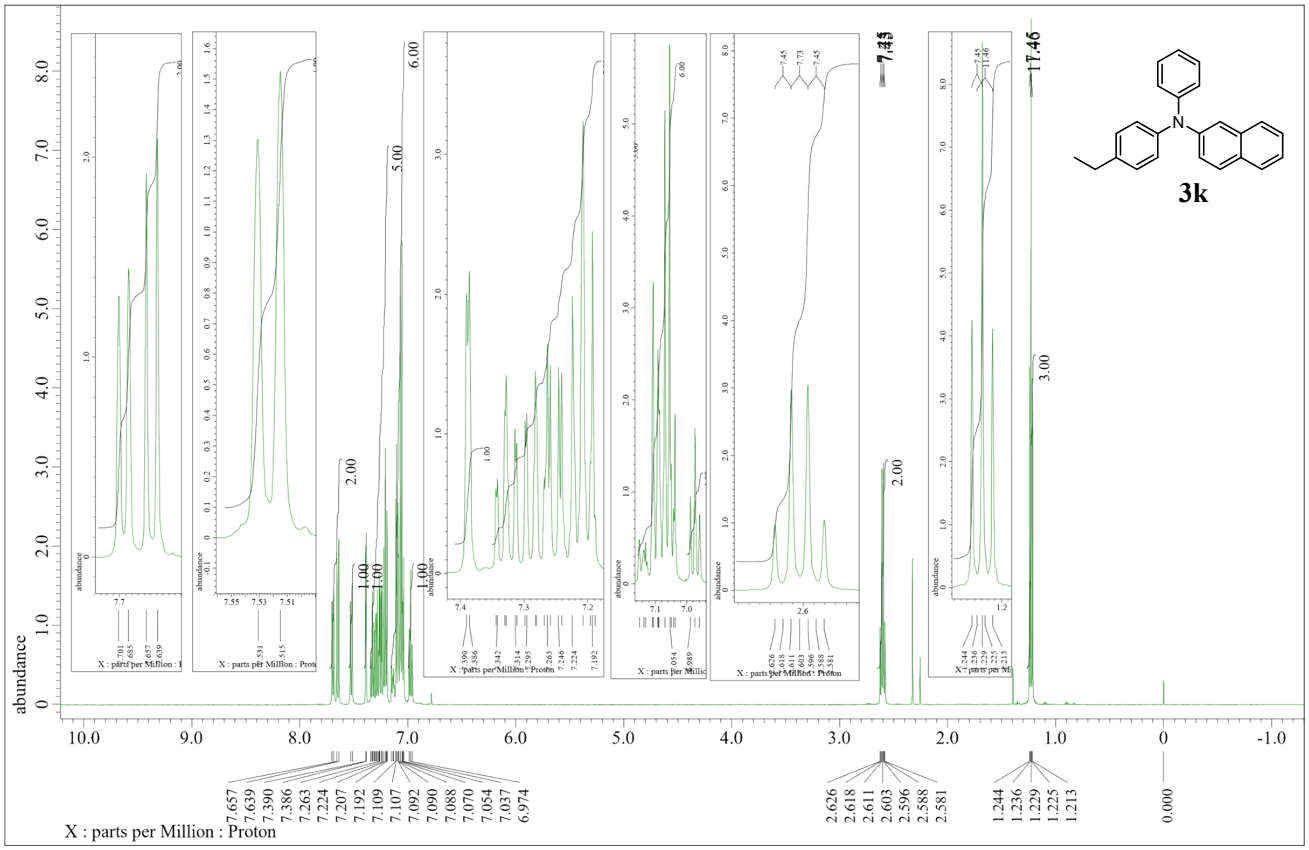
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abundance
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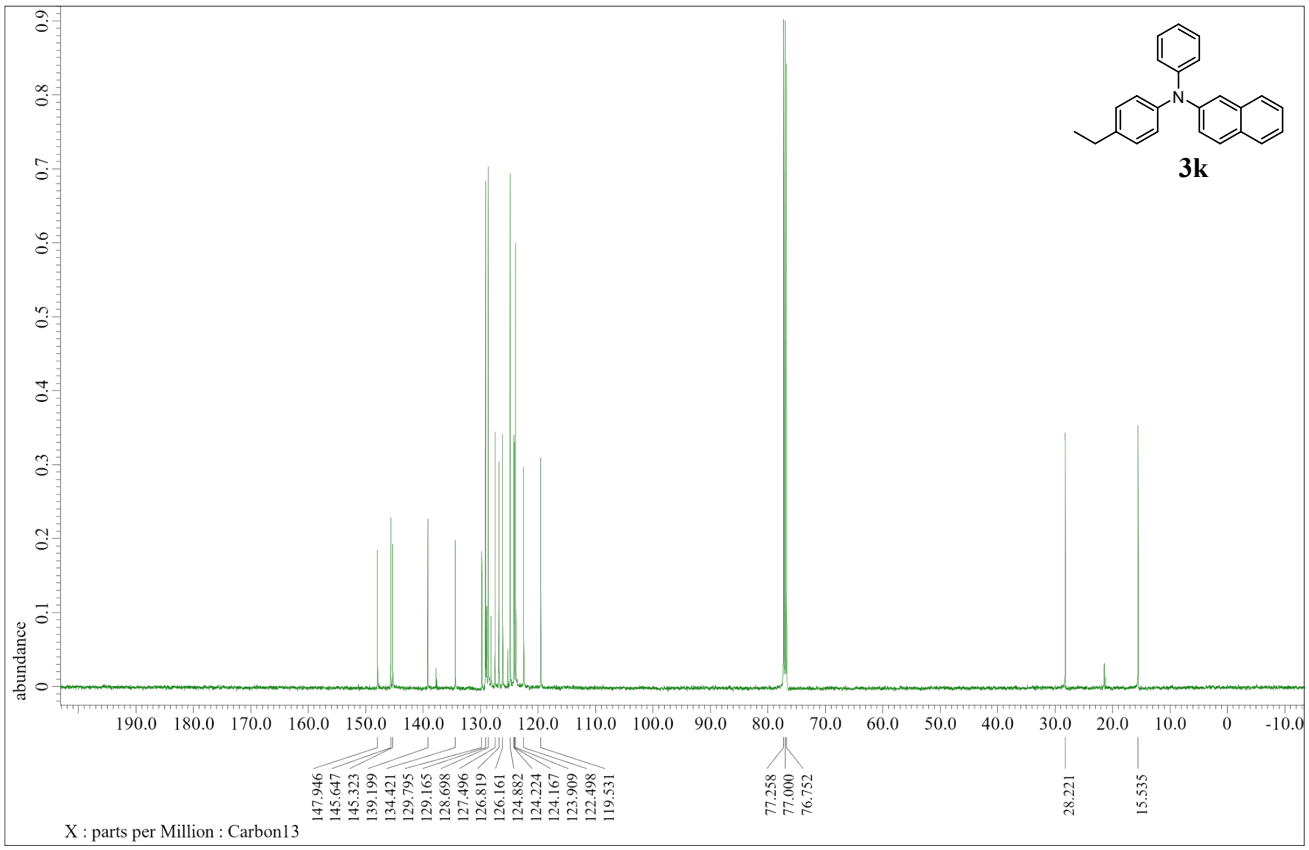
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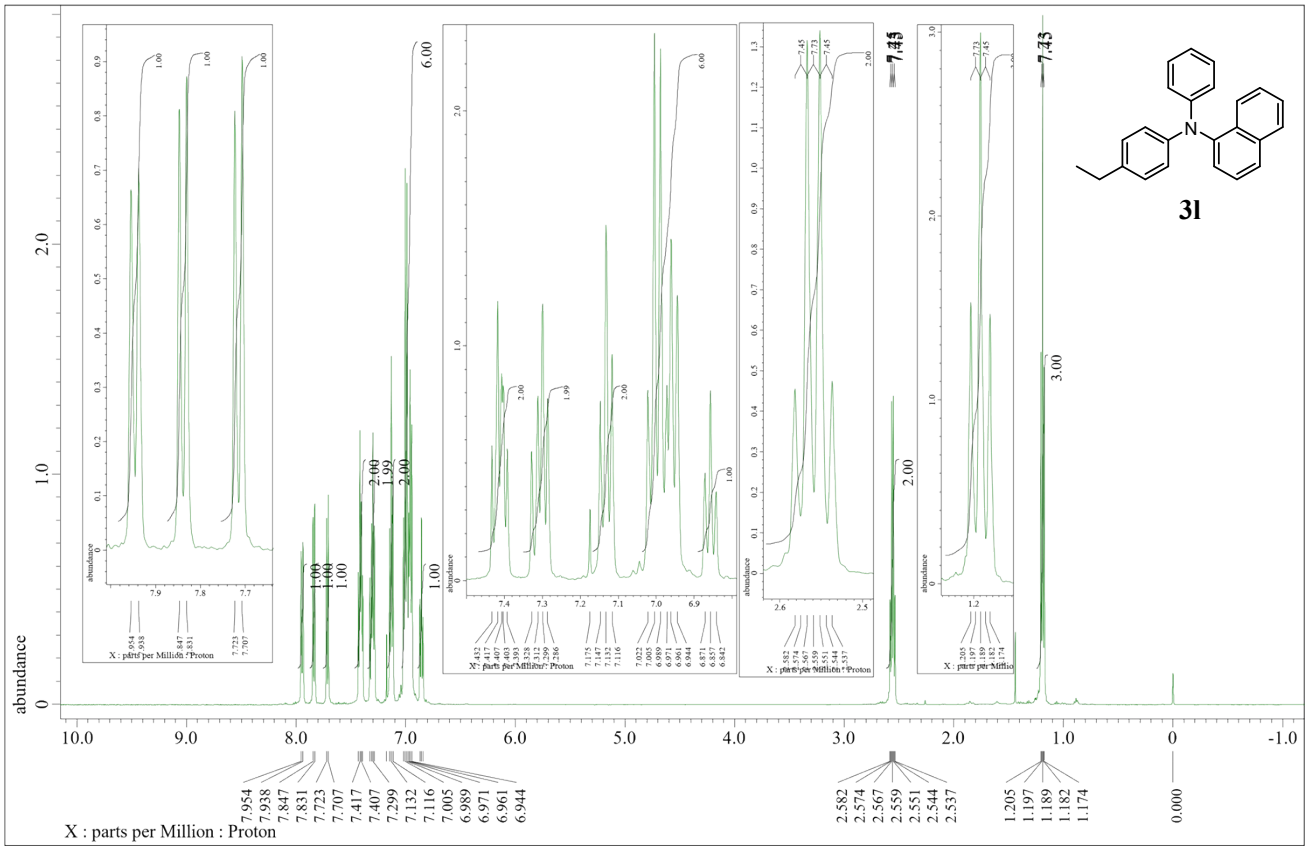
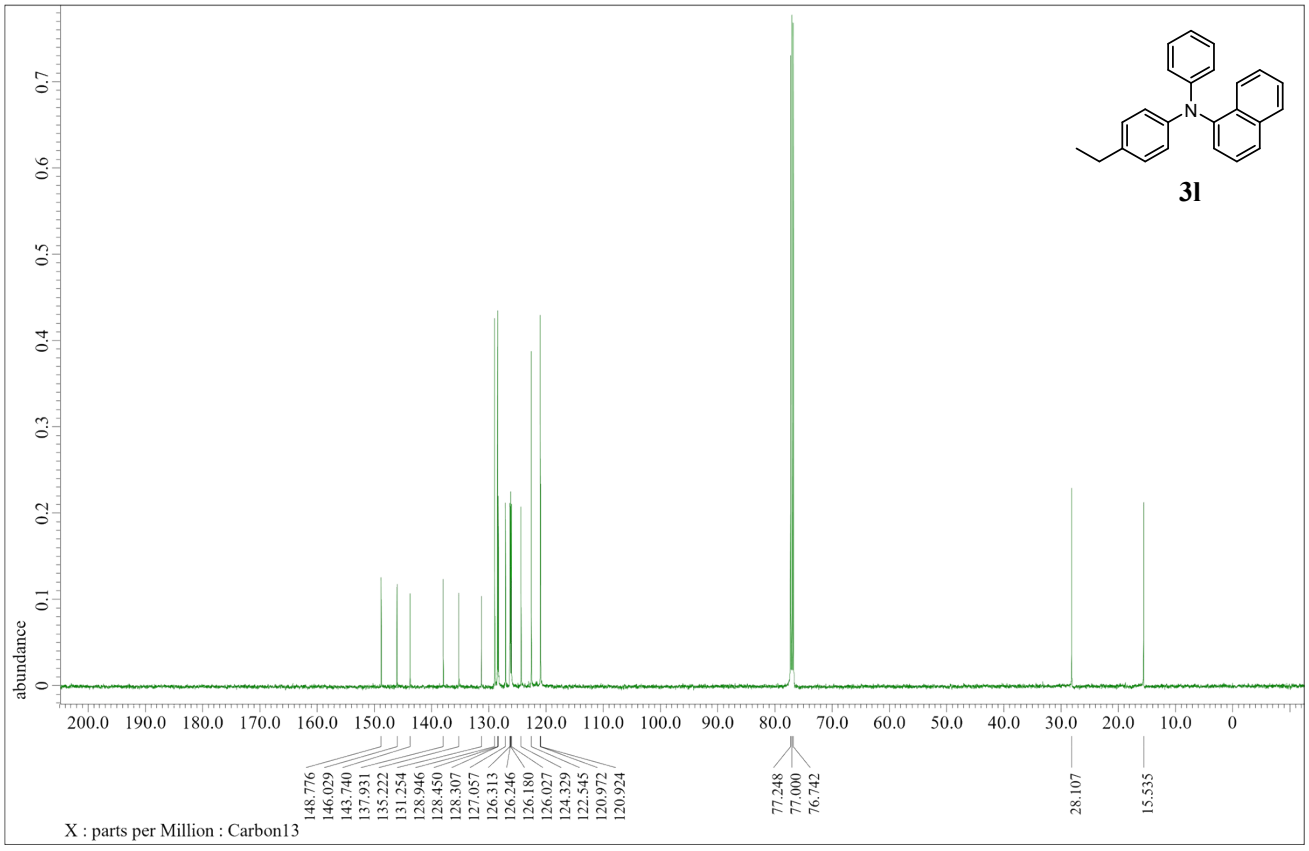
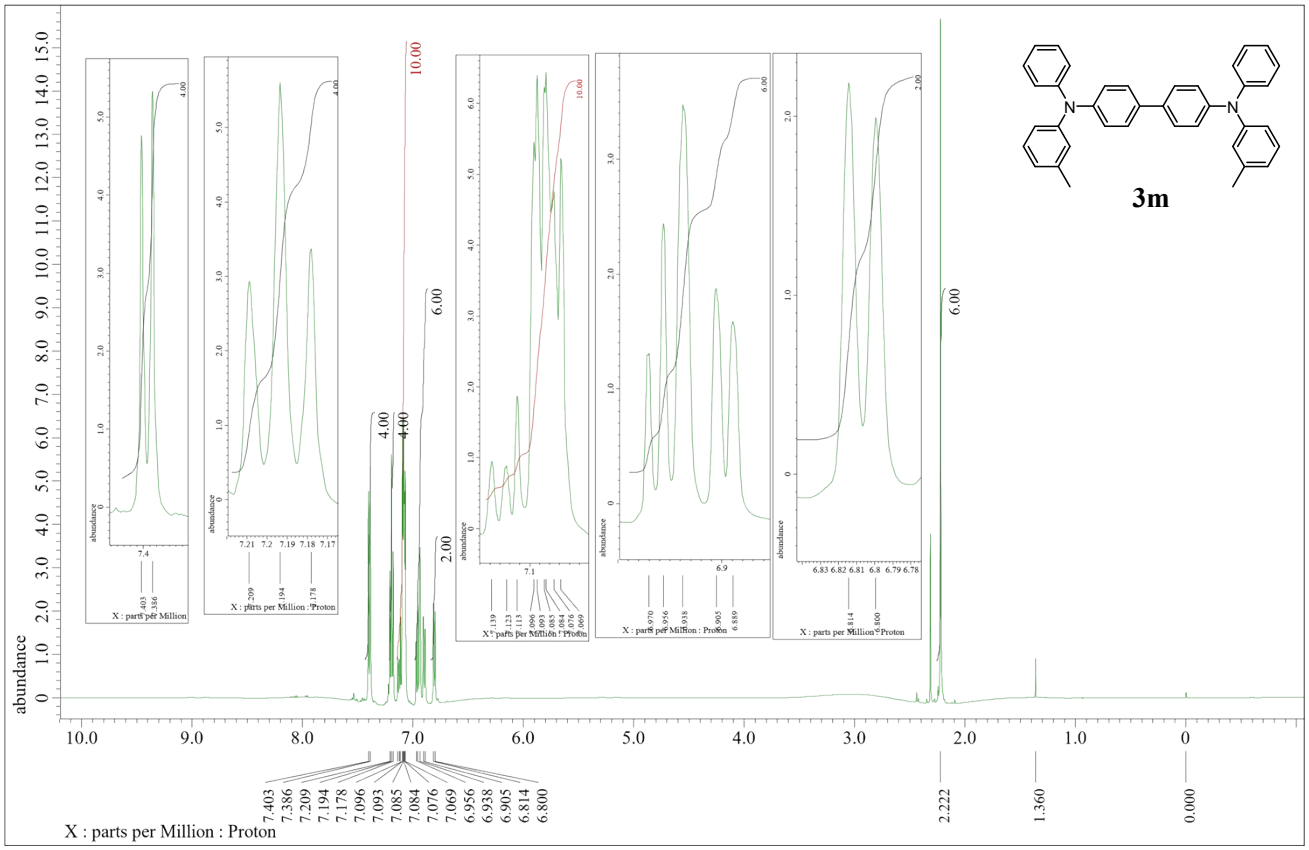
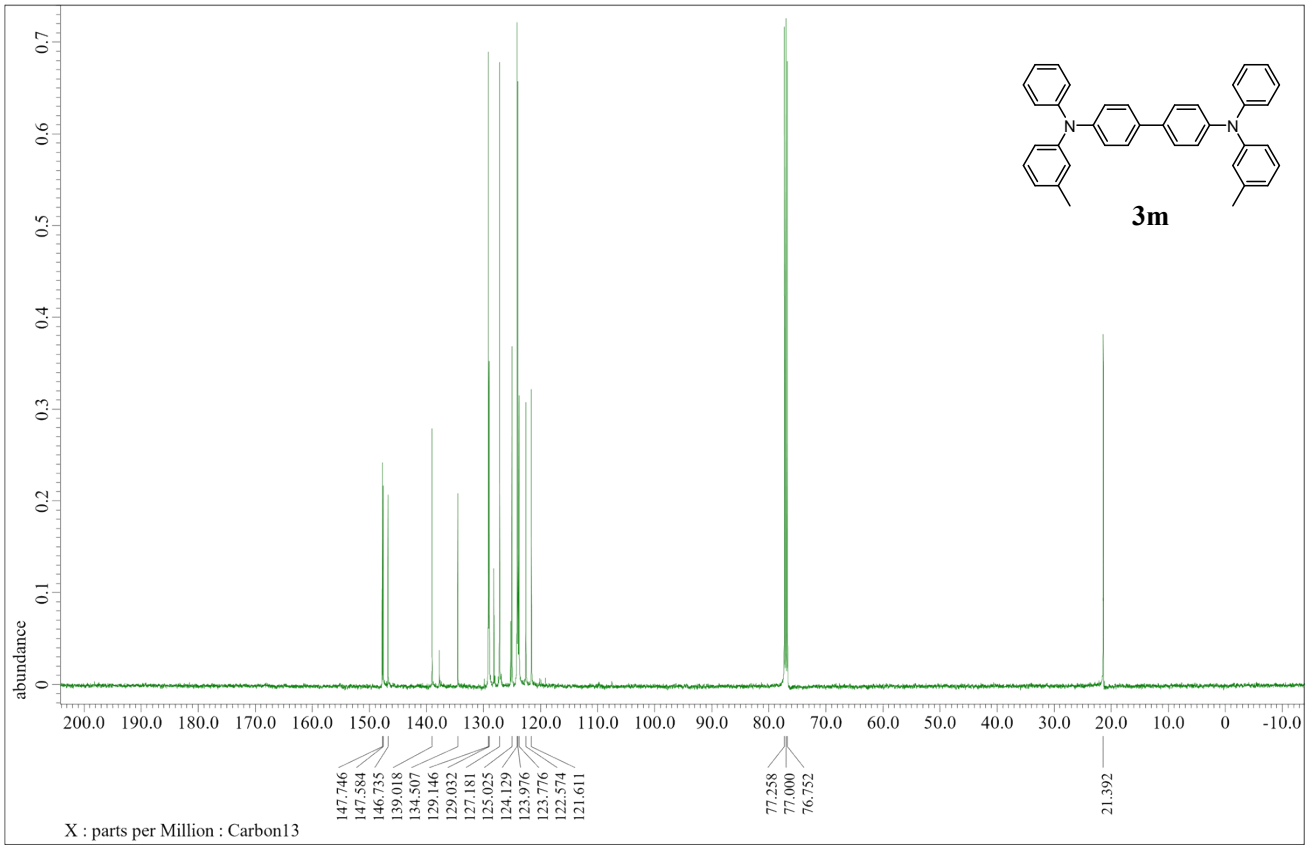
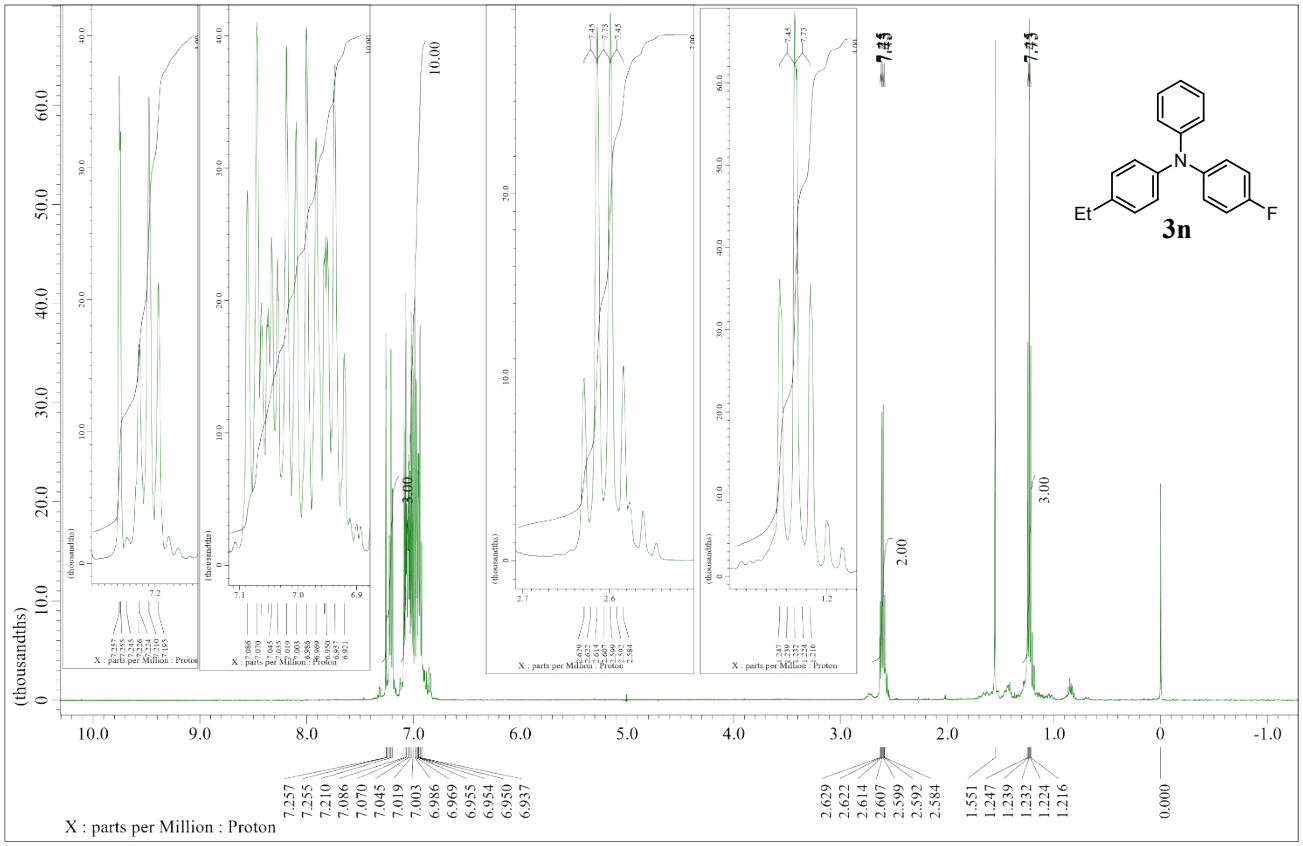
abundance
X : parts per Million : Carbon13

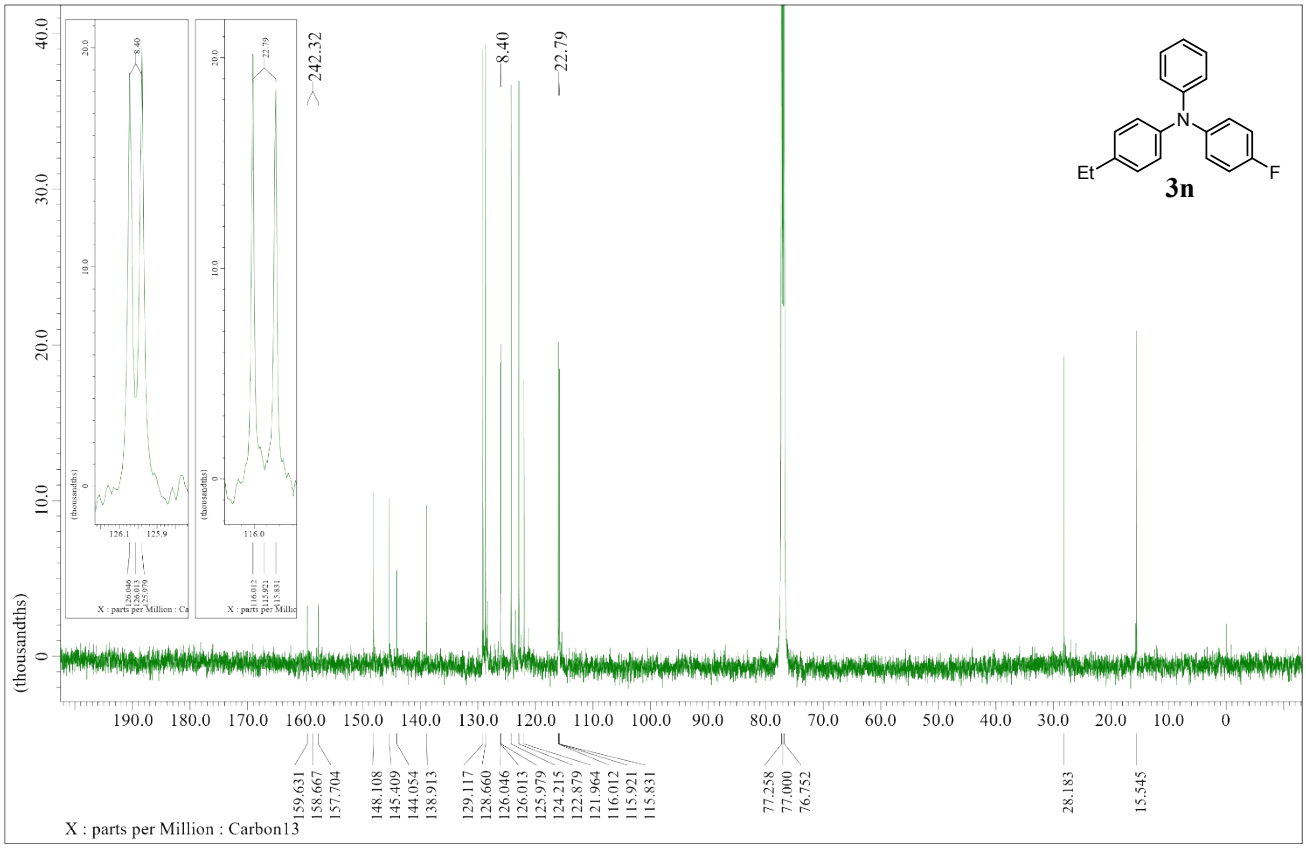

3l
abundance
X : parts per Million : Proton


3l
abundance
X : parts per Million : Carbon13


3m
abundance
X : parts per Million : Proton
7.403
7.386
7.209
7.194
7.178
7.096
7.093
7.085
7.084
7.076
7.069
6.956
6.938
6.905
6.814
6.800
2.222
1.360
0.000
10.00
6.00
4.00
4.00
2.00


3m
abundance
X : parts per Million : Carbon13
147.746
147.584
146.735
139.018
134.507
129.146
129.032
127.181
125.025
124.129
123.976
123.776
122.574
121.611
77.258
77.000
76.752
21.392


3n
Et
F
X : parts per Million : Proton


3n
Et
F
X : parts per Million : Carbon13