

Electronic Supplementary Information (ESI)

Fe₃O₄@SiO₂/EDAC-Pd(0) as a novel and efficient inorganic/organic magnetic composite: Sustainable catalyst for the benzylic C-H bond oxidation and reductive amination under mild conditions

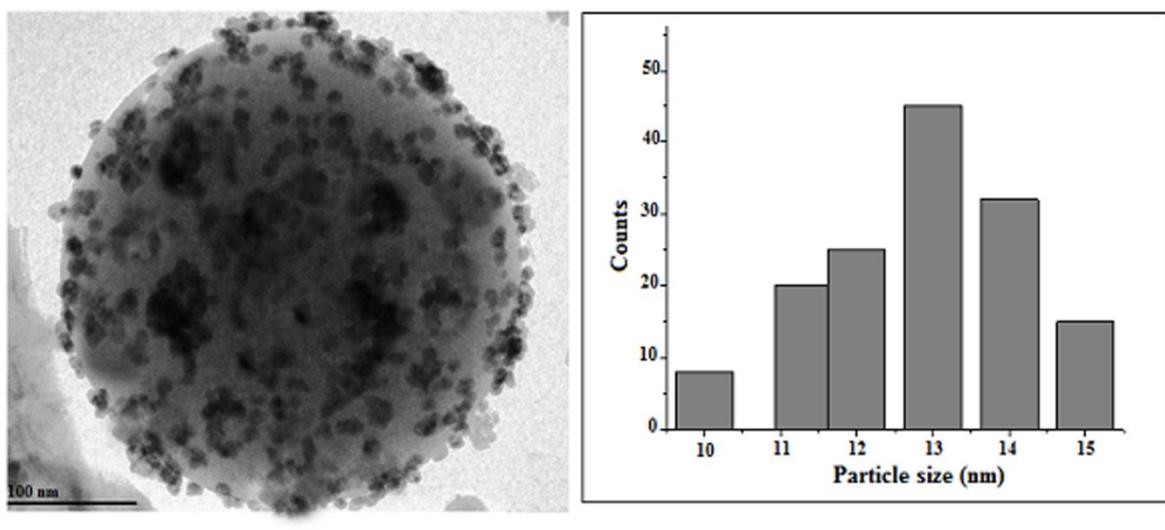
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^bGreen Chemistry Centre of Excellence, Department of Chemistry, University of York, York, UK. Fax: +44 (0)1904 432705; Tel: +44 (0)1904 432567; E-mail: james.clark@york.ac.uk.

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(a)

(b)

Fig. S1 HRTEM (a) and Particle size histogram (b).

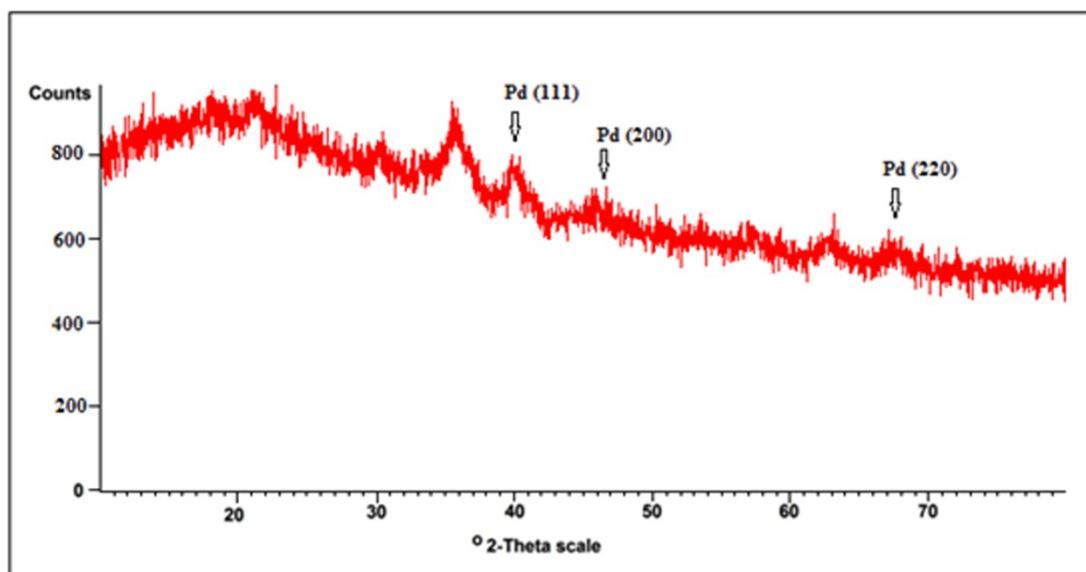
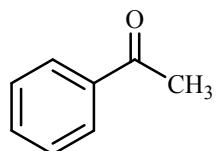


Fig. S2 XRD of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{EDAC-Pd}(0)$.

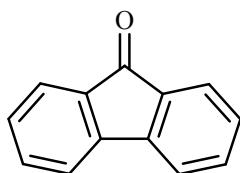
S3. Spectral data of synthesized compounds listed in Table 3

Acetophenone



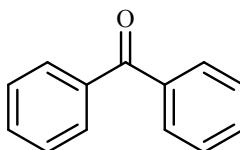
Colourless liquid¹; ¹H NMR (CDCl₃, 400 MHz): δ 2.60 (s, 3H, COCH₃), 7.44-7.47 (t, 1H, J= 8 Hz, H_{arom}), 7.54-7.57 (t, 2H, J= 8 Hz, H_{arom}), 7.94-7.96 (d, 2H, J= 8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 28.62, 127.98, 128.44, 128.56, 133.10, 137.11, 198.14; MS (ESI): 120 (M)⁺.

Fluorenone



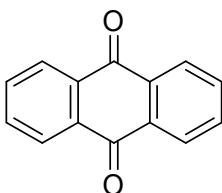
Yellow solid, M.p./Lit. M.p. 80-81/80-83 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.29-7.34 (m, 2H, H_{arom}), 7.49-7.56 (m, 4H, H_{arom}), 7.67-7.69 (d, 2H, J= 8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 120.48, 124.55, 129.34, 134.71, 144.57, 194.15; MS (ESI): 180 (M)⁺.

Benzophenone



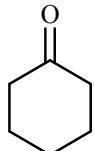
White solid, M.p./Lit. M.p. 48-50/47-51 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.52 (t, 4H, J= 6 Hz, H_{arom}), 7.59-7.63 (t, 2H, J= 8 Hz, H_{arom}), 7.82-7.84 (d, 4H, J= 8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 128.30, 130.08, 132.45, 137.60, 196.79; MS (ESI): 182 (M)⁺.

Anthraquinone



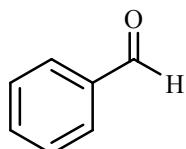
Yellow solid, M.p./Lit. M.p. 285/286 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 6.87-6.89 (m, 1H, H_{arom}), 7.41-7.45 (m, 2H, H_{arom}), 7.81-7.84 (m, 2H, H_{arom}), 7.94-7.96 (m, 1H, H_{arom}), 8.32-8.35 (m, 2H, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 127.25, 134.15, 139.87, 183.35; MS (ESI): 208 (M)⁺.

Cyclohexanone



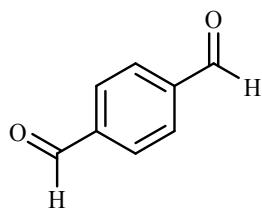
Colourless liquid¹; ¹H NMR (CDCl₃, 400 MHz): δ 1.63-1.69 (m, 2H, CH₂), 1.77-1.83 (m, 4H, 2×CH₂), 2.26-2.29 (t, 4H, J= 8 Hz, 2×CH₂); ¹³C NMR (CDCl₃, 400 MHz): δ 24.90, 26.97, 41.90, 211.48; MS (ESI): 98 (M)⁺.

Benzaldehyde



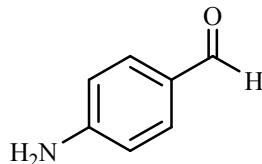
Colourless liquid¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.42 (m, 3H, H_{arom}), 7.75-7.78 (d, 2H, J= 8 Hz, H_{arom}), 9.84 (s, 1H, -CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 129.31, 129.92, 134.62, 136.92, 191.22; MS (ESI): 106 (M)⁺.

Teraphthalaldehyde



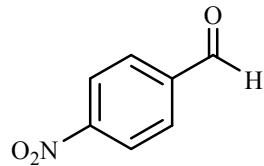
White solid¹, M.p./Lit. M.p. 115-116/114-116 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 8.07 (s, 4H, H_{arom}), 10.15 (s, 2H, -CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 120.14, 140.0, 191.53; MS (ESI): 134 (M)⁺.

4-Aminobenzaldehyde



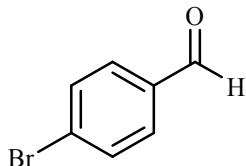
White solid¹, M.p./Lit. M.p. 67-69/68-70 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.85 (bs, 2H, NH₂), 6.63-6.66 (d, 2H, J= 8 Hz, H_{arom}), 7.52-7.55 (d, 2H, J= 12 Hz, H_{arom}), 8.99 (s, 1H, -CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 116.80, 125.95, 130.58, 155.42, 189.74; MS (ESI): 121 (M)⁺.

4-Nitrobenzaldehyde



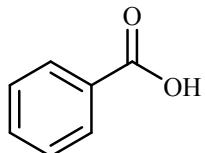
Pale yellow solid¹, M.p./Lit. M.p. 103-104/103-106 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 8.07-8.09 (d, 2H, J= 8 Hz, H_{arom}), 8.35-8.37 (d, 2H, J= 8 Hz, H_{arom}), 9.62 (s, 1H, -CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 123.63, 129.64, 140.94, 152.56, 191.25; MS (ESI): 151 (M)⁺.

4-Bromobenzaldehyde



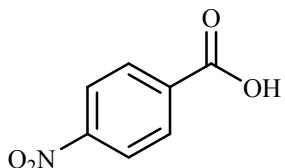
White solid¹, M.p./Lit. M.p. 54-56/55-58 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.86-7.88 (d, 2H, J= 8 Hz, H_{arom}), 8.13-8.15 (d, 2H, J= 8 Hz, H_{arom}), 9.31 (s, 1H, -CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 128.32, 129.36, 132.85, 135.32, 191.20; MS (ESI): 183(M)⁺, 185 (M+2)⁺.

Benzoic acid



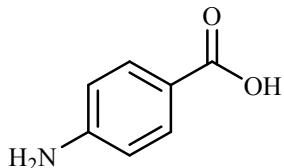
White solid¹, M.p./Lit. M.p. 120-121/121-125 °C¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 7.45-7.64 (m, 3H, H_{arom}), 8.13-8.15 (d, 2H, J= 8 Hz, H_{arom}); ¹³C NMR (DMSO-d₆, 100 MHz): δ 130.09, 131.11, 131.61, 138.22, 166.91; MS (ESI): 122 (M)⁺.

4-Nitrobenzoic acid



Pale yellow solid, M.p./Lit. M.p. 235-236/237-240 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 8.15-8.17 (d, 2H, J= 8 Hz, H_{arom}), 8.30-8.32 (d, 2H, J= 8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 124.22, 131.76, 136.81, 150.42, 166.56; MS (ESI): 167 (M)⁺.

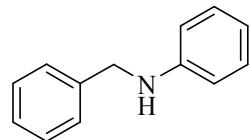
4-Aminobenzoic acid



Greyish white solid¹, M.p./Lit. M.p. 187-188/187-189 °C¹; ¹H NMR (CDCl₃, 400 MHz): δ 5.87 (bs, 2H, NH₂), 6.54-6.56 (d, 2H, J= 8 Hz, H_{arom}), 7.60-7.62 (d, 2H, J= 8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 112.78, 117.29, 131.72, 153.57, 168.10. MS (ESI): 137 (M)⁺.

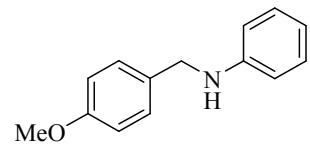
S3. Spectral data of synthesized compounds listed in Table 5

N-Benzylaniline



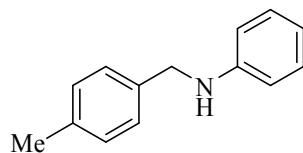
Yellow oil², ¹H NMR (CDCl₃, 400 MHz): δ 4.09 (bs, 1H, NH, exchangeable with D₂O), 4.38 (s, 2H, CH₂), 6.69-6.71 (d, 2H, J=8 Hz, H_{arom}), 6.77-6.80 (t, 1H, J=8 Hz, H_{arom}), 7.22-7.26 (t, 2H, J=8.0 Hz, H_{arom}), 7.32-7.45 (m, 5H, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 48.35, 113.11, 117.60, 127.77, 128.68, 129.34, 129.64, 139.77, 148.36. MS (ESI): 183 (M)⁺.

N-(4-Methoxybenzyl)aniline



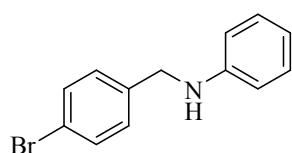
Yellow oil², ¹H NMR (CDCl₃, 400 MHz): δ 3.90 (s, 3H, OCH₃), 4.52 (bs, 1H, NH, exchangeable with D₂O), 4.89 (s, 2H, CH₂), 6.96-6.98 (d, 2H, J=8 Hz, H_{arom}), 7.09-7.13 (m, 5H, H_{arom}), 7.34-7.36 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 47.32, 54.63, 113.52, 115.74, 117.83, 126.46, 130.40, 139.73, 145.02, 149.58; MS (ESI): 213 (M)⁺.

***N*-(4-Methylbenzyl)aniline**



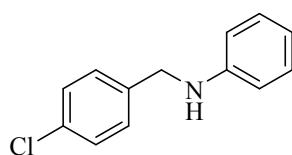
Yellow oil³, ¹H NMR (CDCl₃, 400 MHz): δ 2.39 (s, 3H, CH₃), 3.79 (bs, 1H, NH, exchangeable with D₂O), 4.34 (s, 2H, CH₂), 6.57-6.59 (d, 2H, J=8 Hz, H_{arom}), 6.78-6.80 (d, 2H, J=8 Hz, H_{arom}), 7.03-7.17 (m, 5H, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 26.72, 46.74, 115.75, 118.53, 128.41, 130.58, 133.56, 137.54, 140.72, 147.23. MS (ESI): 197 (M)⁺.

***N*-(4-Bromobenzyl)aniline**



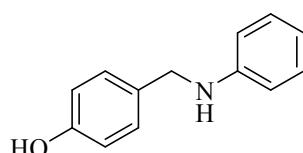
Yellow oil⁴, ¹H NMR (CDCl₃, 400 MHz): δ 4.32 (bs, 1H, NH, exchangeable with D₂O), 4.68 (s, 2H, CH₂), 7.23-7.30 (m, 3H, H_{arom}), 7.41-7.45 (t, 2H, J=8 Hz, H_{arom}), 7.63-7.65 (d, 2H, J=8 Hz, H_{arom}), 7.79 -7.81 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 45.83, 120.86, 125.92, 126.26, 129.23, 130.17, 132.06, 135.10, 151.65, 159.0; MS (ESI): 261 (M)⁺.

***N*-(4-Chlorobenzyl)aniline**



Yellow oil², ¹H NMR (CDCl₃, 400 MHz): δ 3.54 (bs, 1H, NH, exchangeable with D₂O), 4.34 (s, 2H, CH₂), 6.07-6.21 (m, 3H, H_{arom}), 6.70-6.72 (d, 2H, J=8 Hz, H_{arom}), 7.09-7.11 (d, 2H, J=8 Hz, H_{arom}), 7.19-7.21 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 56.75, 113.54, 114.82, 128.43, 129.56, 133.28, 134.85, 145.06, 148.64. MS (ESI): 217 (M)⁺.

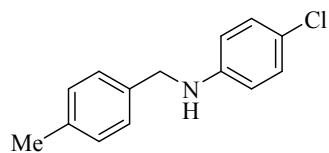
***N*-(4-Hydroxybenzyl)aniline**



M.Pt./Lit. M.Pt. 85-87/88-89 °C⁵; ¹H NMR (CDCl₃, 400 MHz): δ 3.11 (bs, 1H, NH, exchangeable with D₂O), 4.42-4.43 (d, 2H, J=5.4 Hz, CH₂), 5.43 (s, 1H, OH), 6.54-6.56 (d, 2H, J= 8 Hz, H_{arom}), 6.99-7.11 (d, 2H, J=8 Hz, H_{arom}), 7.34-7.41 (m, 5H, H_{arom}); ¹³C NMR

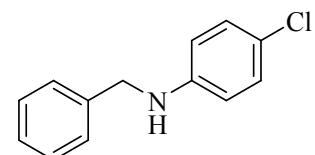
(CDCl₃, 100 MHz): δ 49.77, 113.43, 117.24, 127.26, 127.65, 128.54, 138.58, 143.35, 147.52; MS (ESI): 199 (M)⁺.

N-(4-Methylbenzyl)-4-chloroaniline



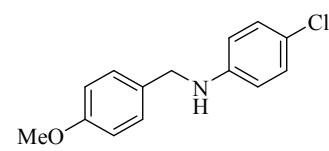
M.Pt./Lit. M.Pt. 72-73/71-73⁶; ¹H NMR (CDCl₃, 400 MHz): δ 2.37 (s, 3H, CH₃), 4.05 (bs, 1H, NH, exchangeable with D₂O), 4.28 (s, 2H, CH₂), 6.56-6.58 (d, 2H, J=8 Hz, H_{arom}), 7.12-7.14 (d, 2H, J=8 Hz, H_{arom}), 7.17-7.19 (d, 2H, J=8 Hz, H_{arom}), 7.25-7.29 (t, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 21.11, 48.10, 113.90, 122.24, 127.43, 129.05, 129.38, 129.5, 135.85, 137.06, 146.93; MS (ESI): 231 (M)⁺.

N-Benzyl-4-chloroaniline



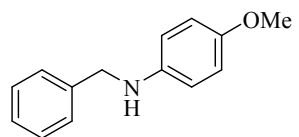
Yellow oil⁷, ¹H NMR (CDCl₃, 400 MHz): δ 3.84 (bs, 1H, NH, exchangeable with D₂O), 4.13 (s, 2H, CH₂), 6.56-6.58 (d, 2H, J=8 Hz, H_{arom}), 6.82-6.84 (d, 2H, J=8 Hz, H_{arom}), 7.12-7.14 (d, 2H, J=8 Hz, H_{arom}), 7.20-7.22 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 46.81, 113.84, 123.62, 124.75, 127.63, 128.92, 129.31, 130.56, 149.72; MS (ESI): 217 (M)⁺.

N-(4-Methoxybenzyl)-4-chloroaniline



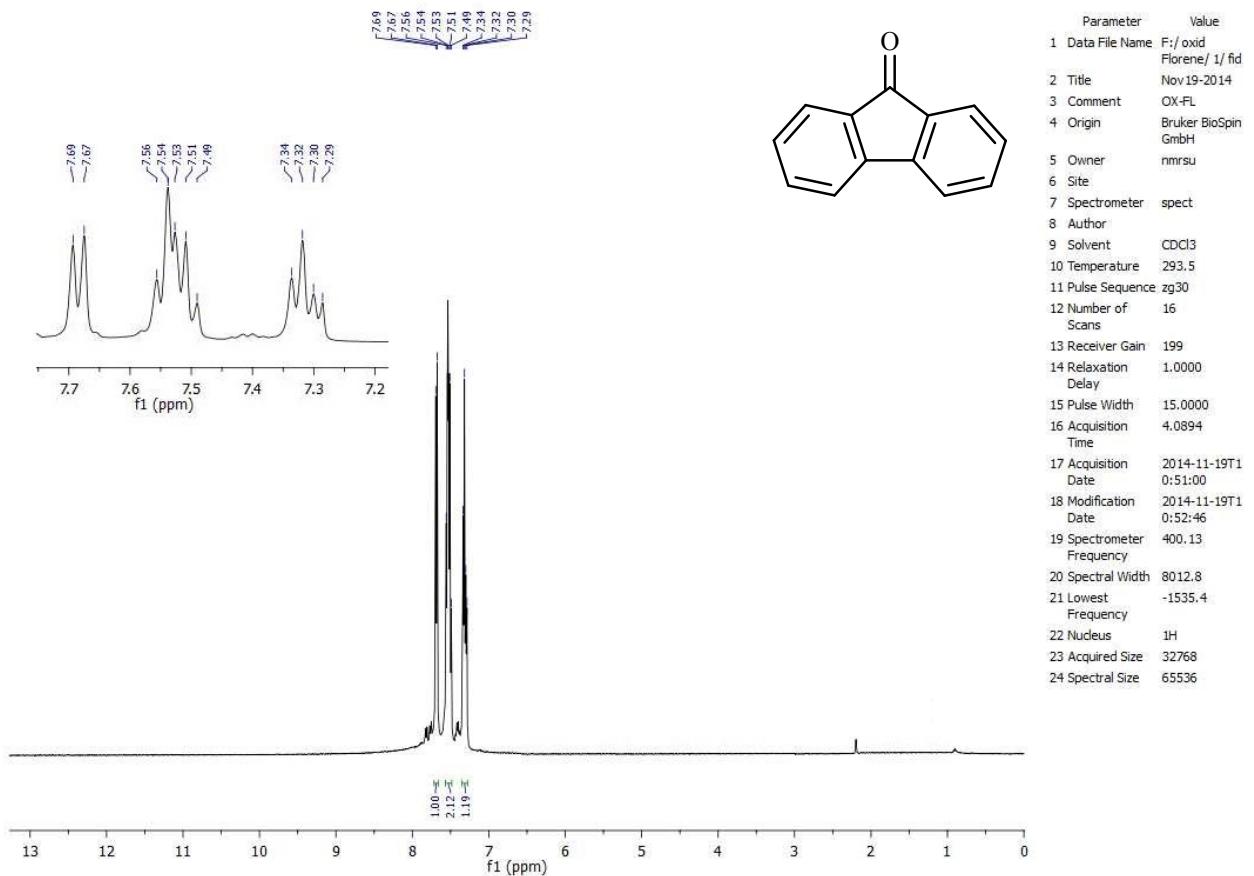
M.Pt./Lit. M.Pt. 77-78/78-81 °C⁶; ¹H NMR (CDCl₃, 400 MHz): δ 3.84 (s, 3H, OCH₃), 4.38 (s, 2H, CH₂), 4.81 (bs, 1H, NH, exchangeable with D₂O), 6.58-6.60 (d, 2H, J=8 Hz, H_{arom}), 6.92-6.94 (d, 2H, J=8 Hz, H_{arom}), 7.27-7.29 (d, 2H, J=8 Hz, H_{arom}), 8.10-8.12 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 47.20, 55.34, 111.29, 114.35, 126.41, 128.78, 129.27, 137.30, 153.01, 159.33; MS (ESI): 247 (M)⁺.

N-Benzyl-4-methoxyaniline

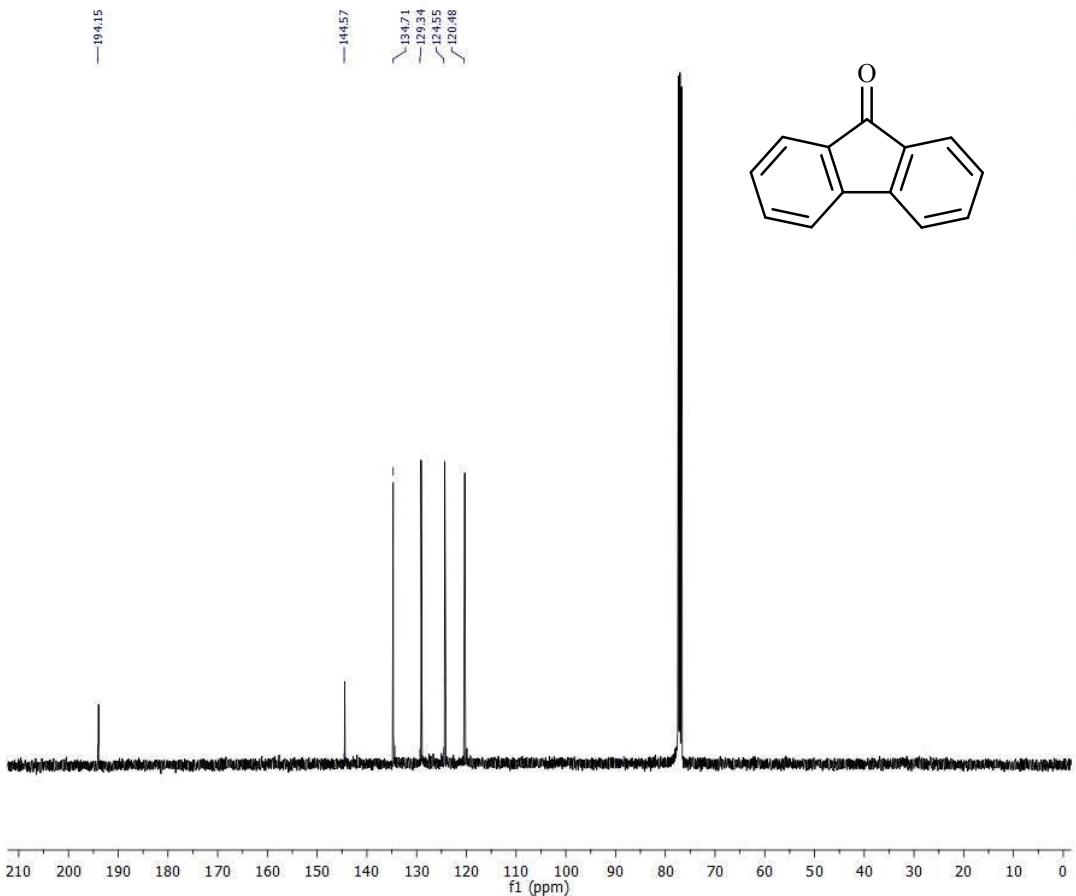


Yellow oil²; ¹H NMR (CDCl₃, 400 MHz): δ 3.89 (s, 3H, OCH₃), 4.06 (bs, 1H, NH, exchangeable with D₂O), 4.32 (s, 2H, CH₂), 6.78-6.80 (d, 2H, J=8 Hz, H_{arom}), 6.94-6.96 (d, 2H, J=8 Hz, H_{arom}), 7.21-7.25 (t, 1H, J=8.0 Hz, H_{arom}), 7.28-7.30 (d, 2H, J=8 Hz, H_{arom}), 7.60-7.62 (d, 2H, J=8 Hz, H_{arom}); ¹³C NMR (CDCl₃, 100 MHz): δ 43.52, 57.84, 113.21, 115.54, 126.46, 127.31, 128.92, 129.48, 140.51, 1523; MS (ESI): 213 (M)⁺.

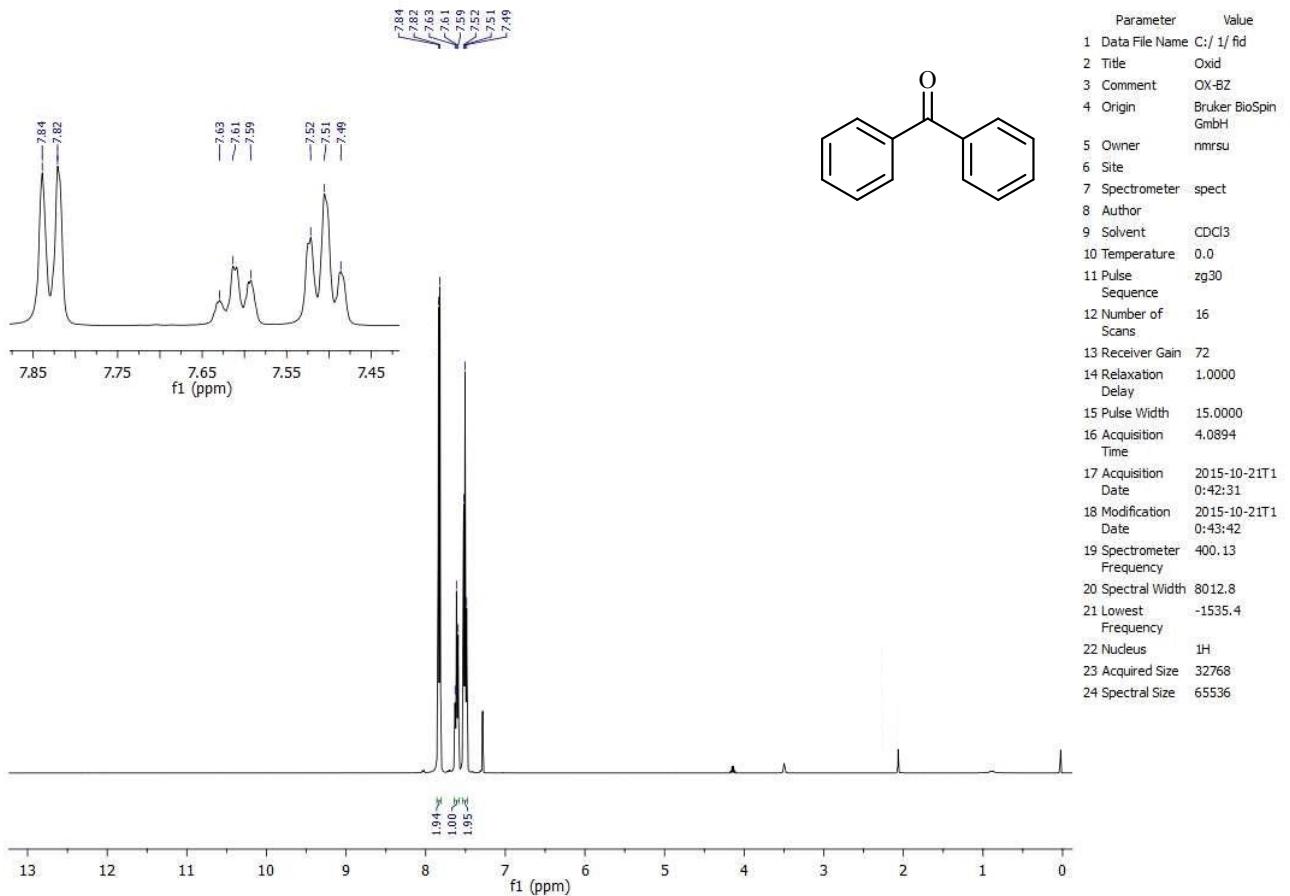
S4. Copies of ^1H , D_2O , ^{13}C and DEPT NMR spectra of selected compounds.



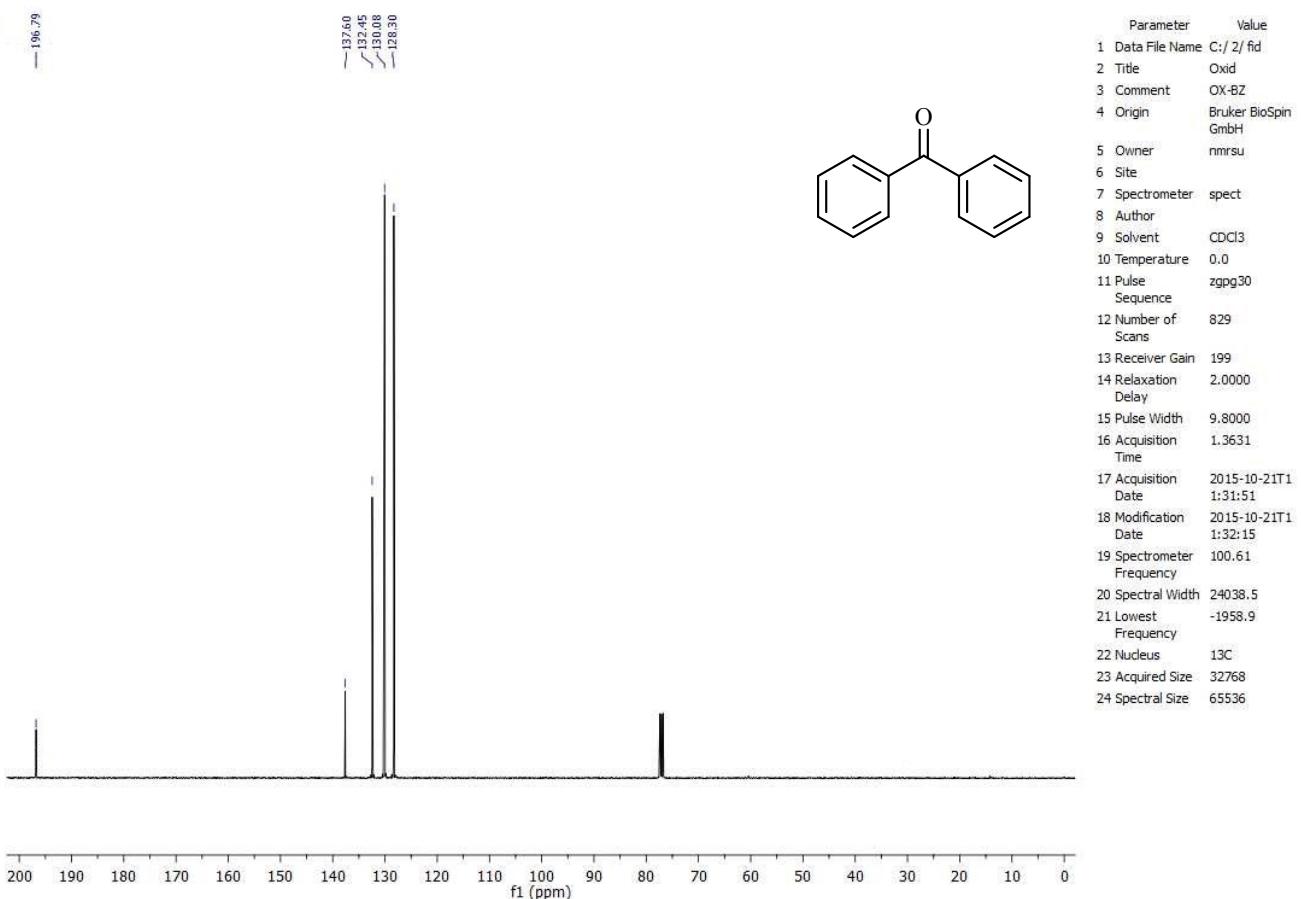
^1H spectra of fluorenone



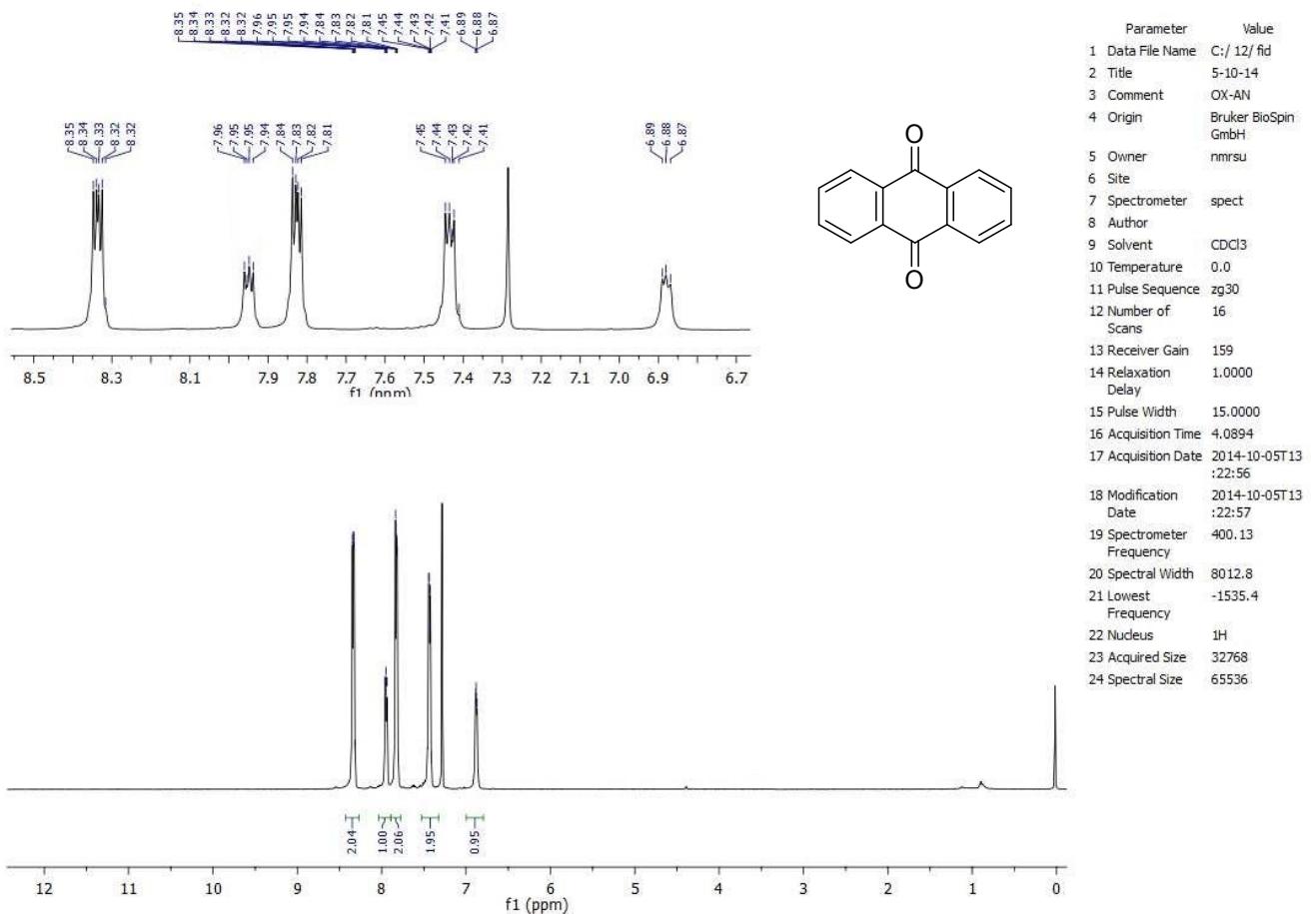
¹³C spectra of fluorenone



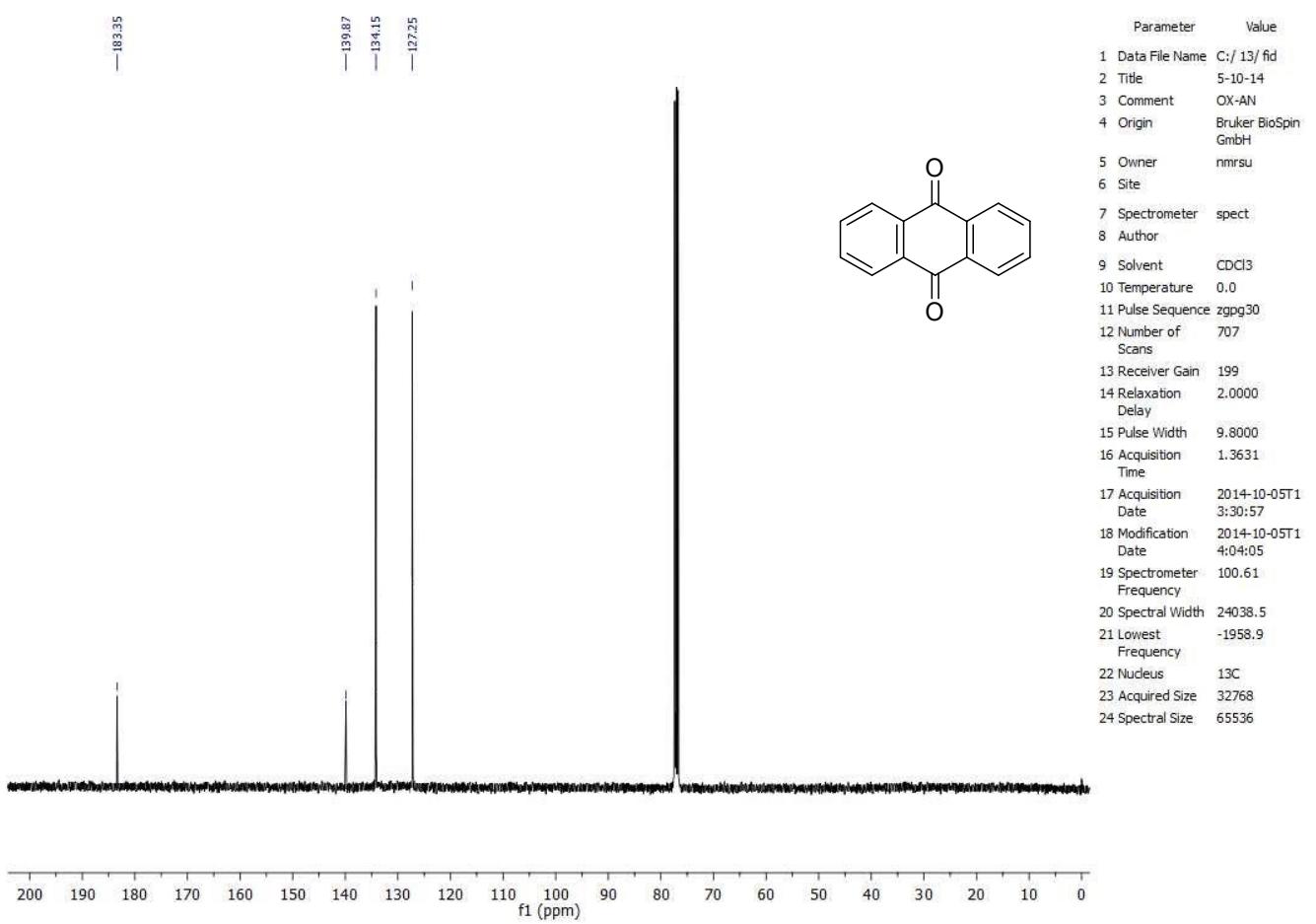
¹H spectra of benzophenone

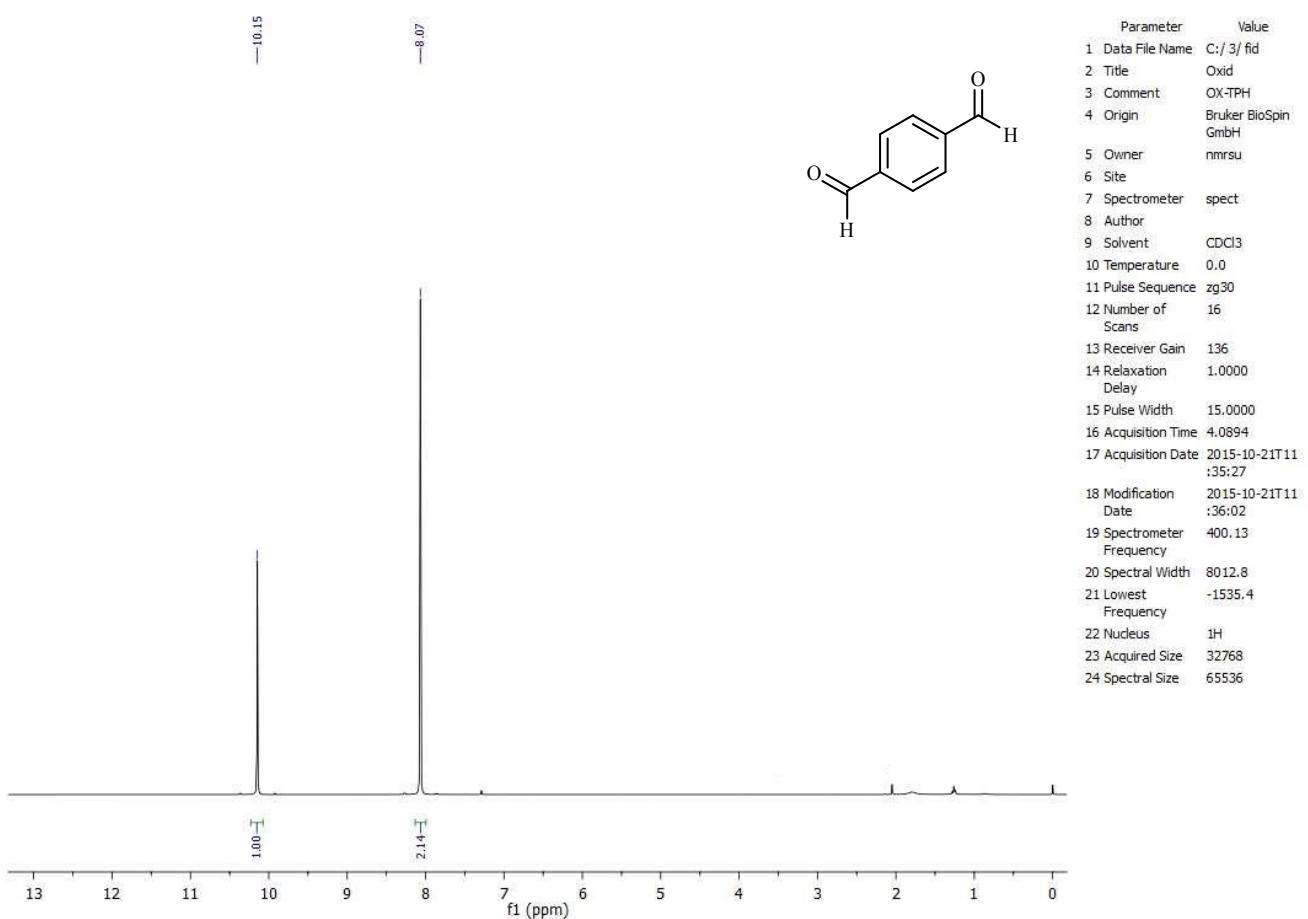


¹³C spectra of benzophenone

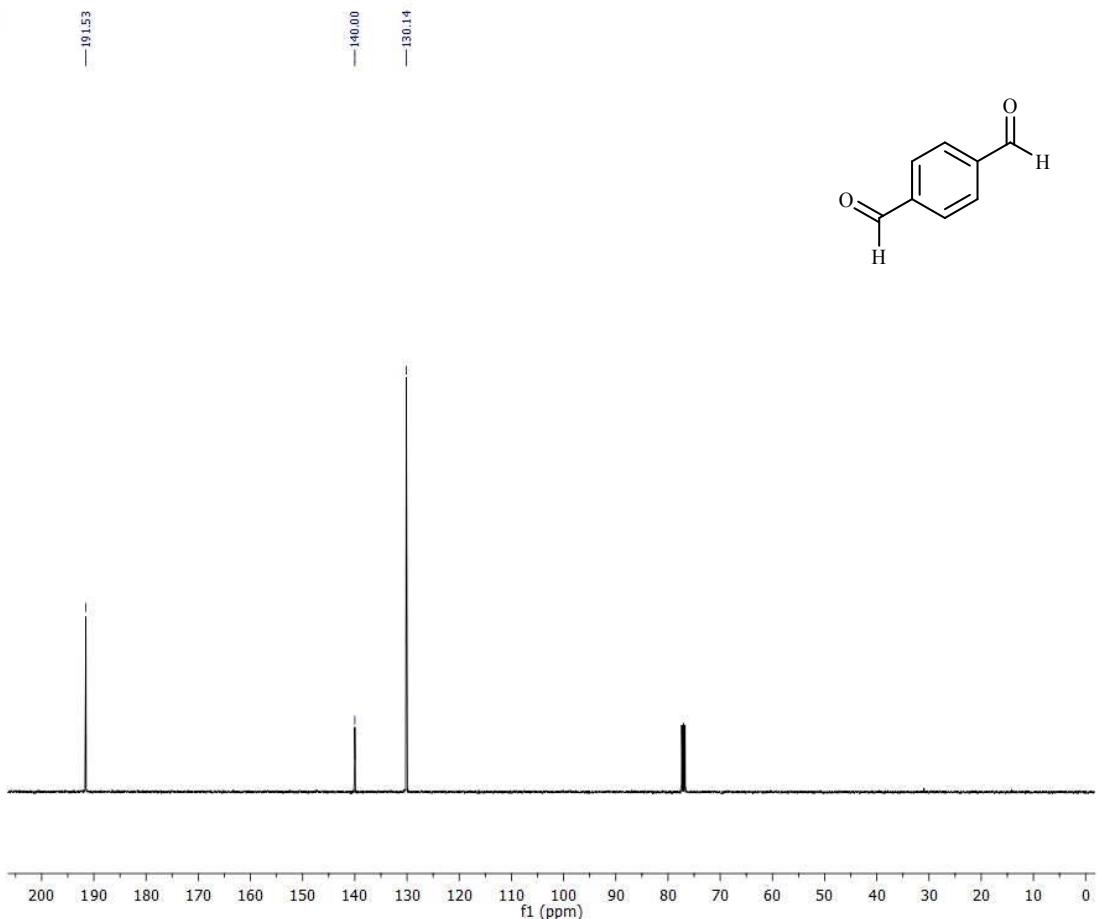


¹H spectra of anthraquinone

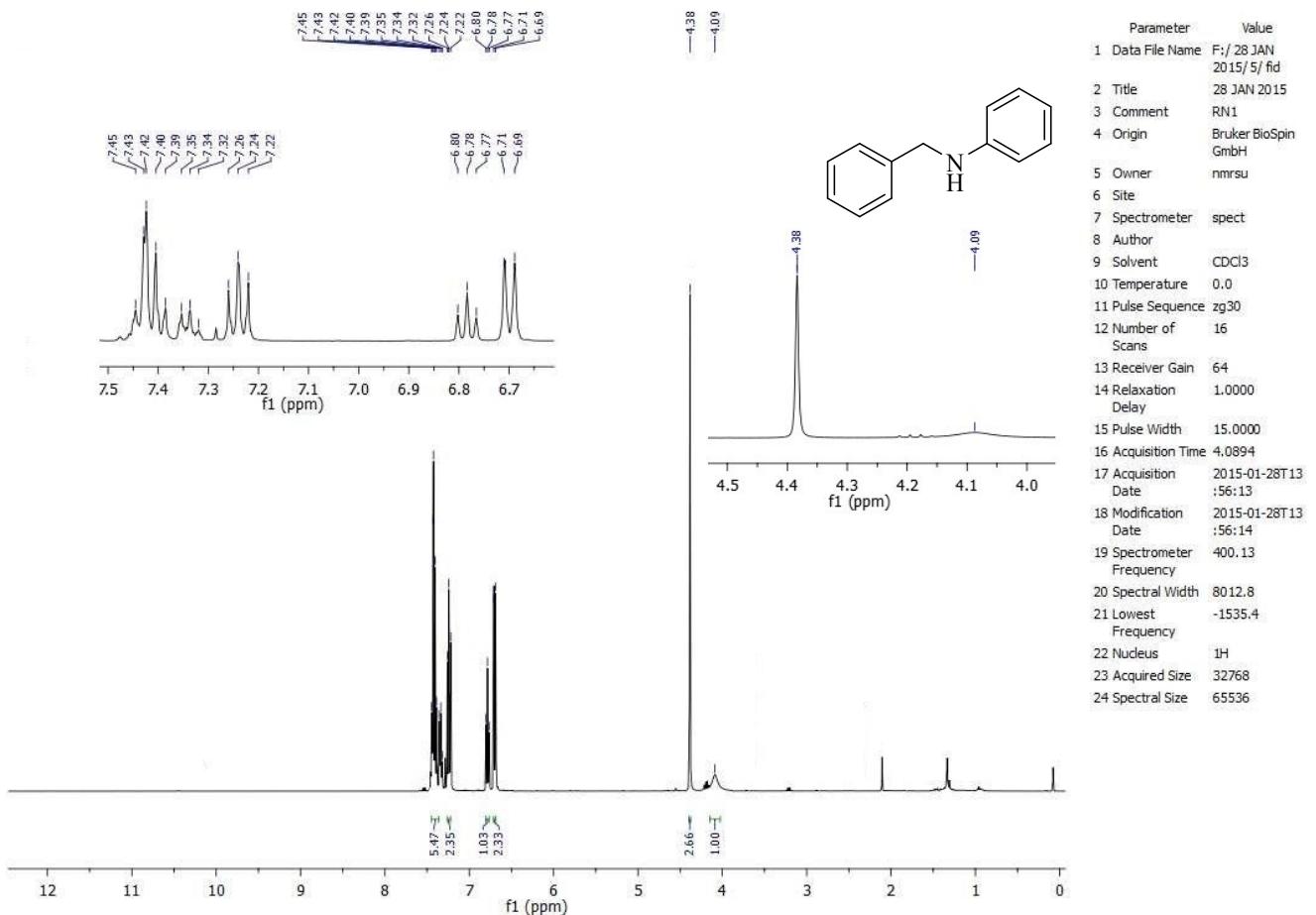




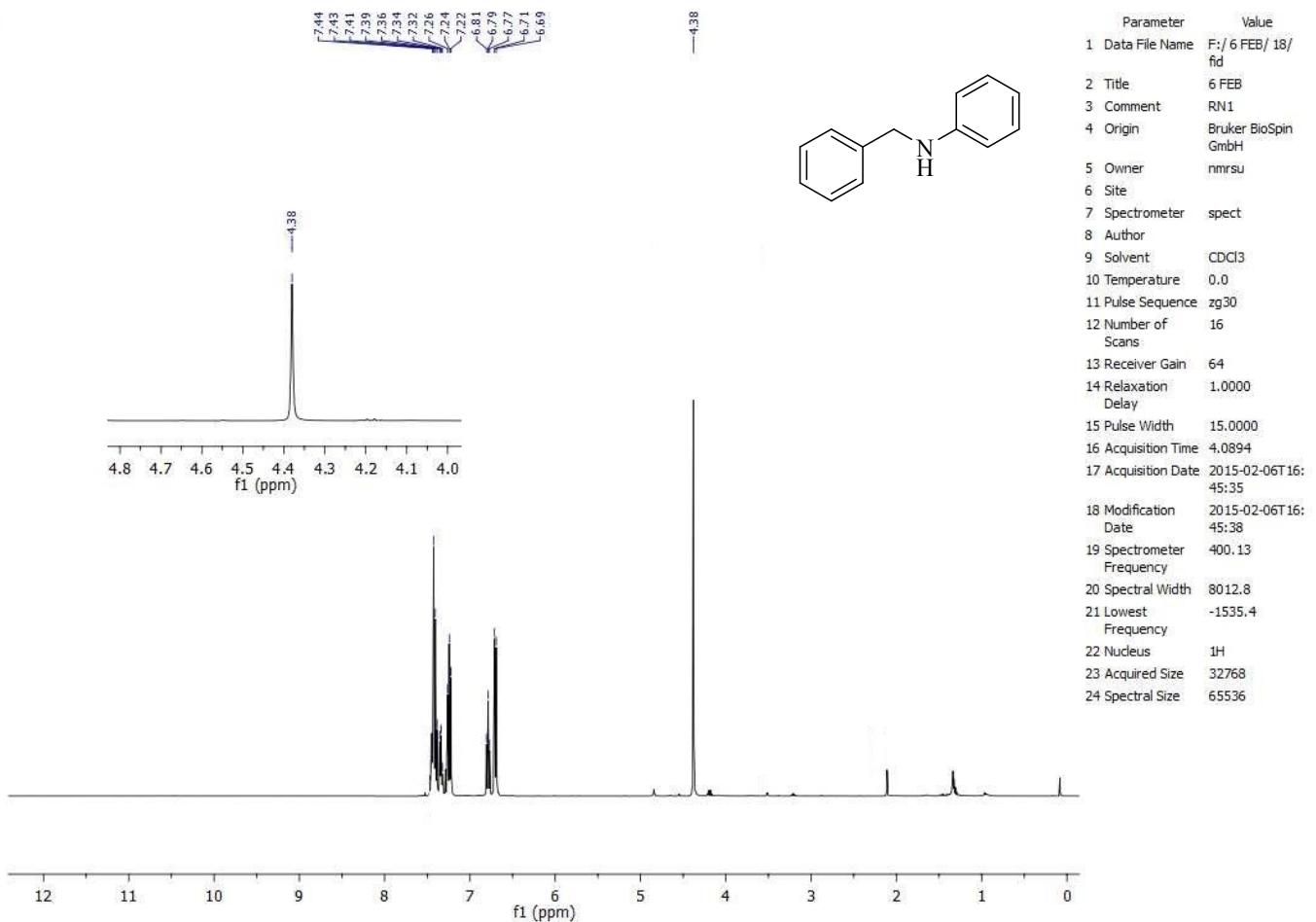
¹H spectra of teraphthalaldehyde



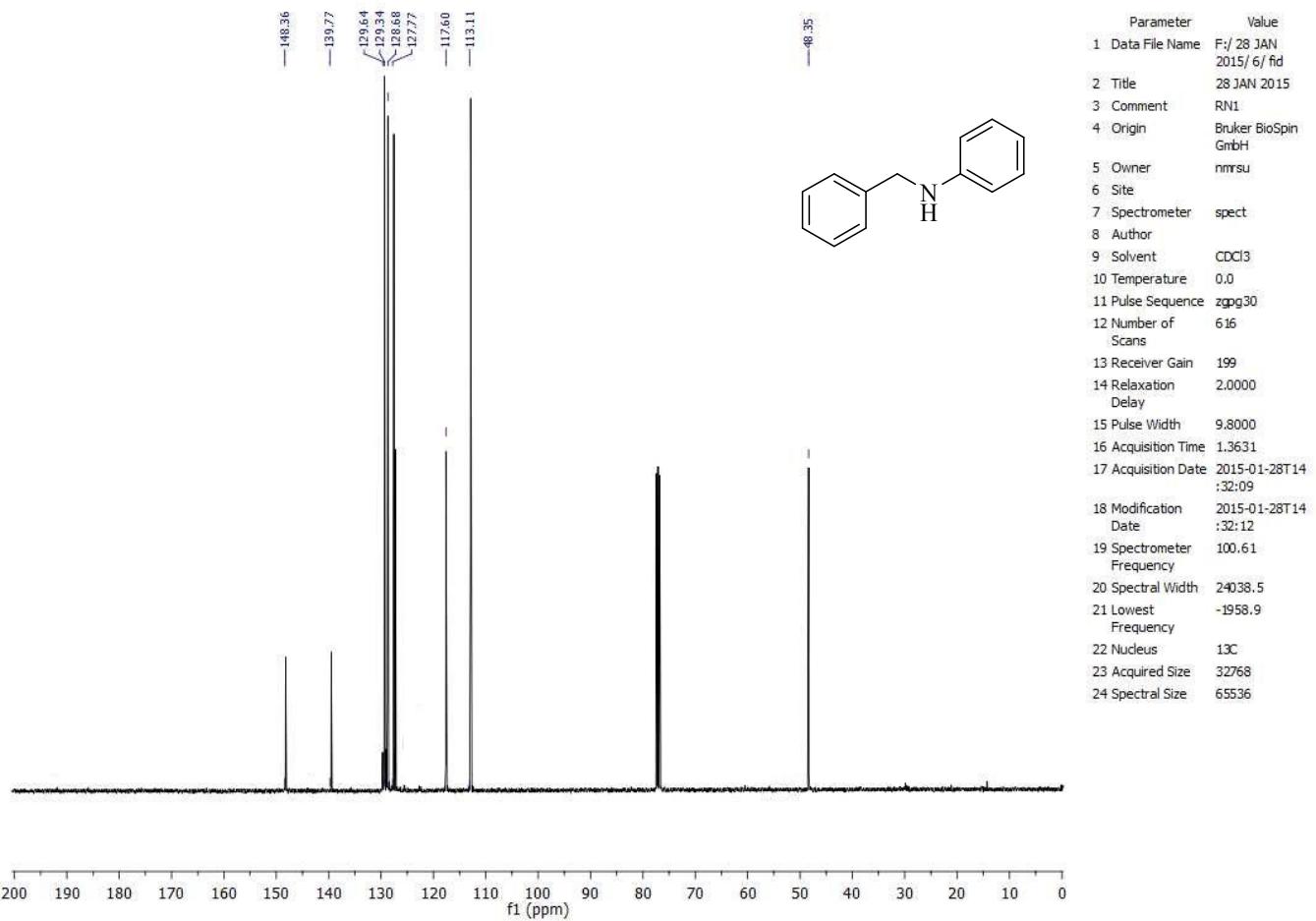
¹³C spectra of teraphthalaldehyde



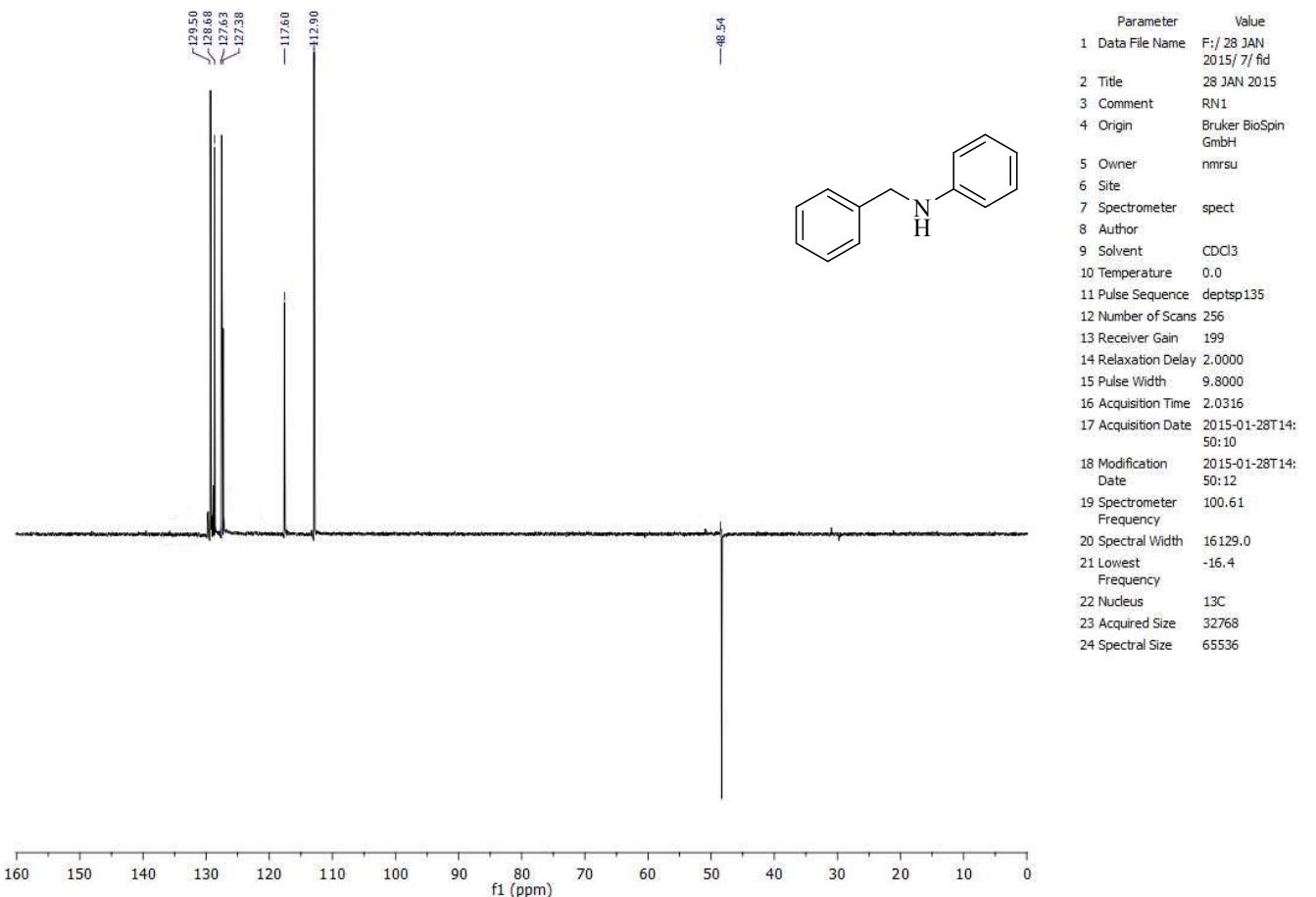
¹H spectra of N-Benzylaniline



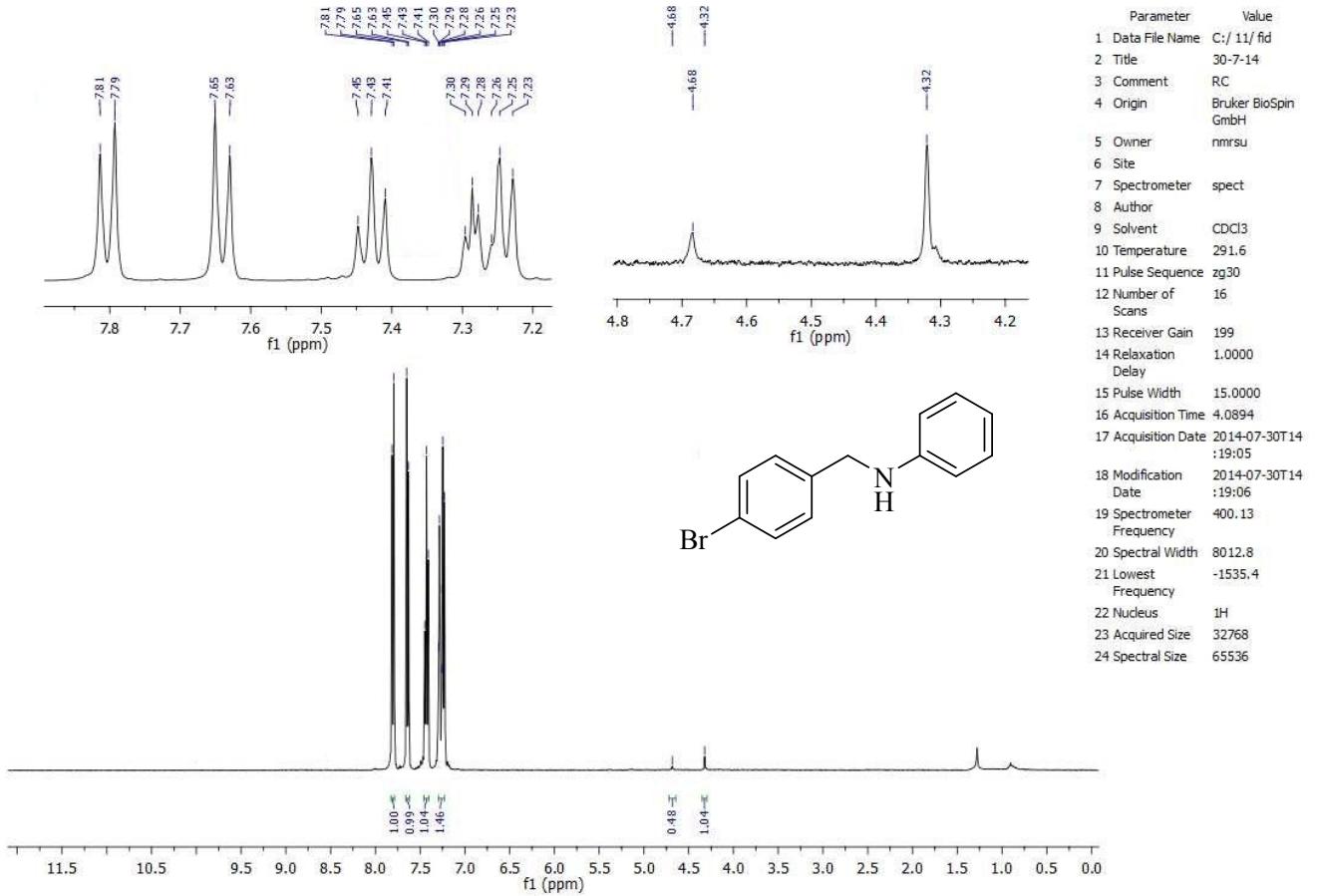
D₂O spectra of N-Benzylaniline



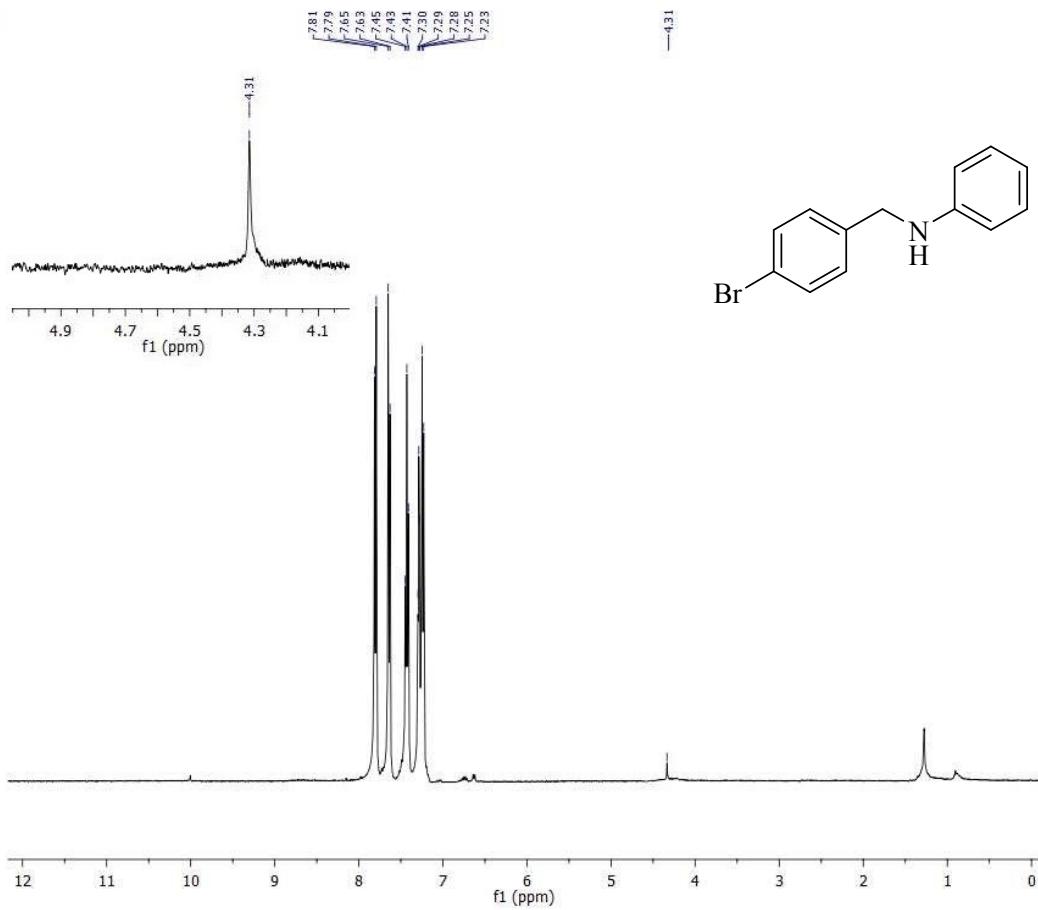
¹³C spectra of *N*-Benzylaniline



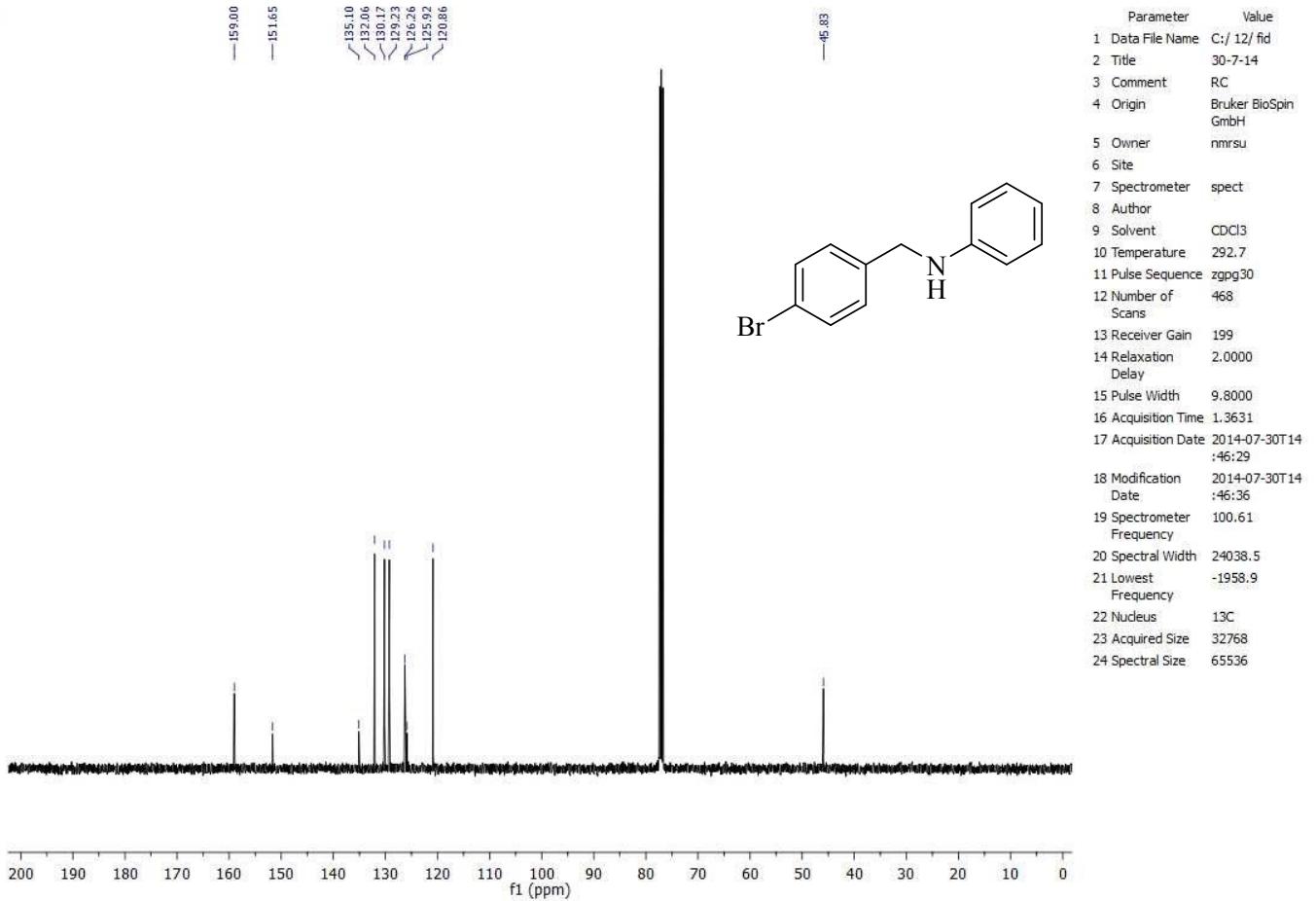
DEPT spectra of *N*-Benzylaniline



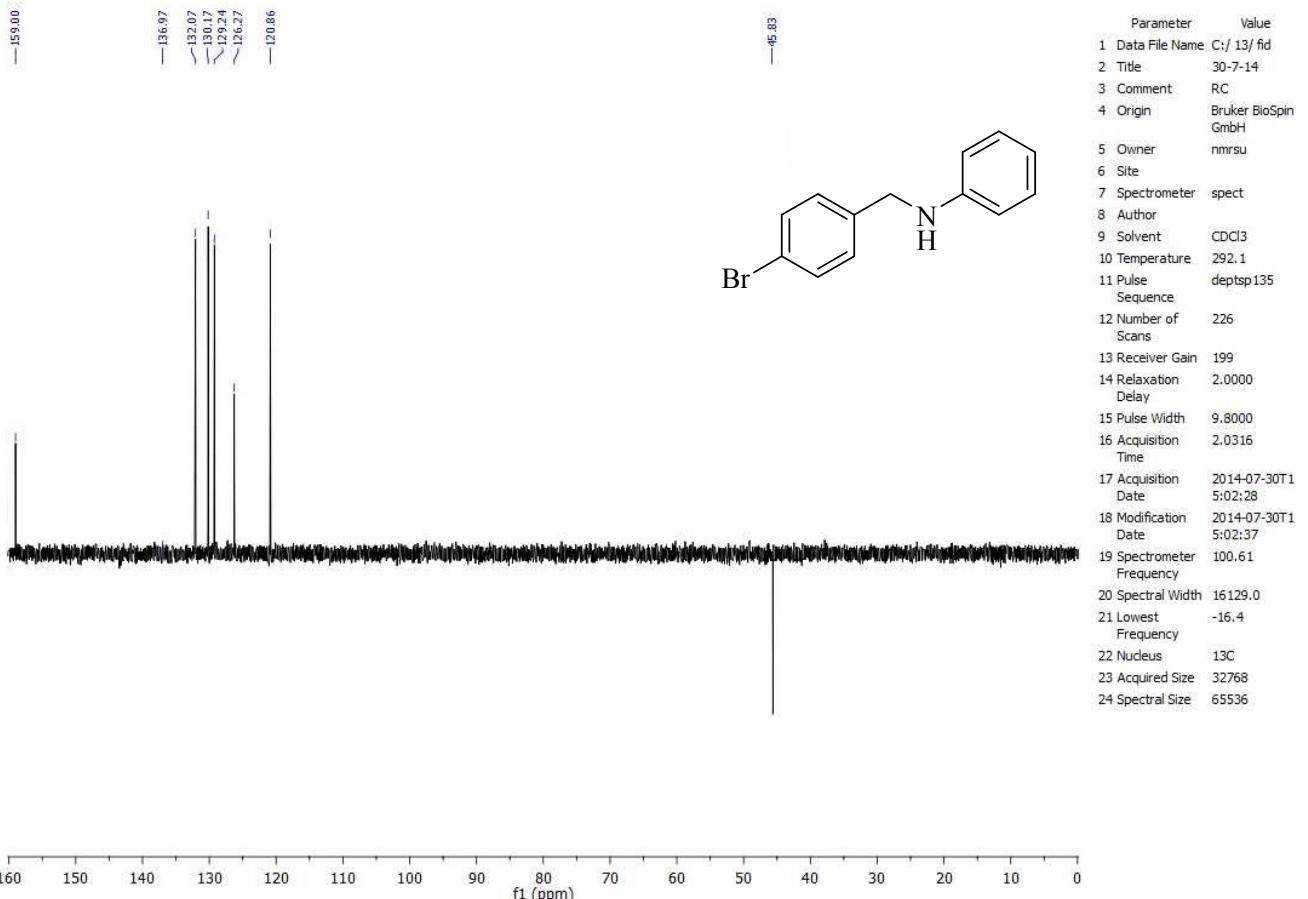
¹H spectra of N-(4-Bromobenzyl)aniline



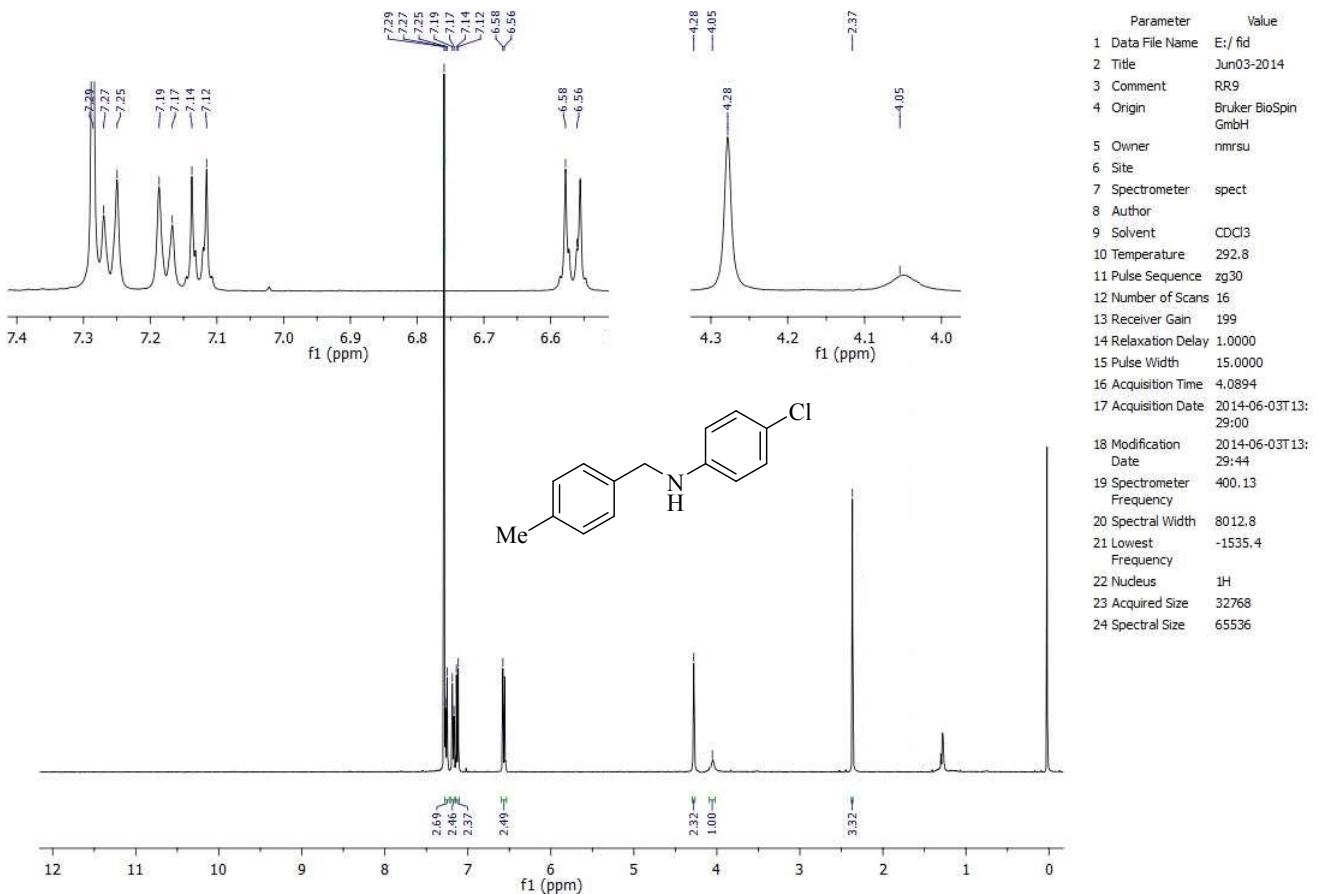
D₂O spectra of N-(4-Bromobenzyl)aniline



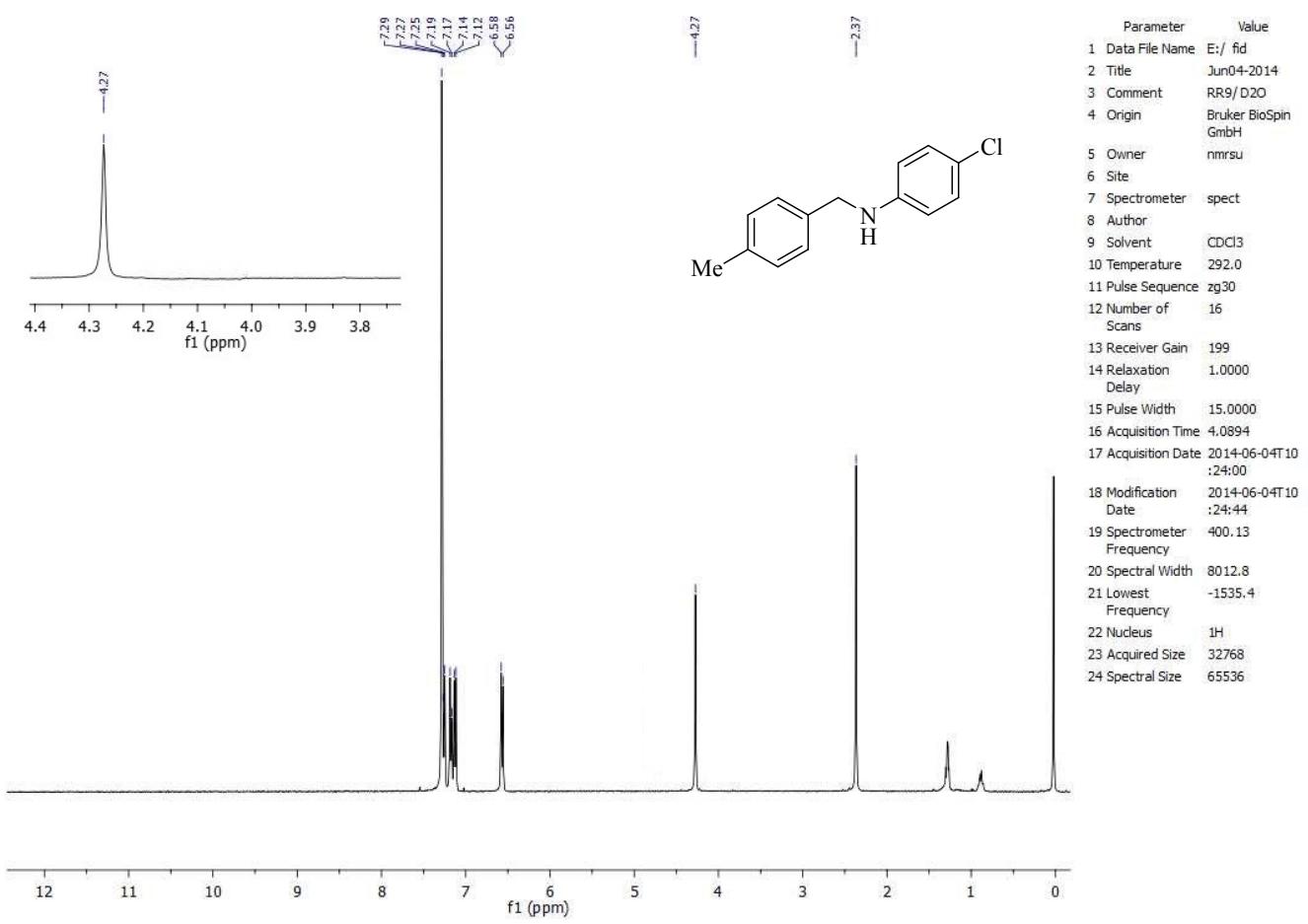
¹³C spectra of N-(4-Bromobenzyl)aniline



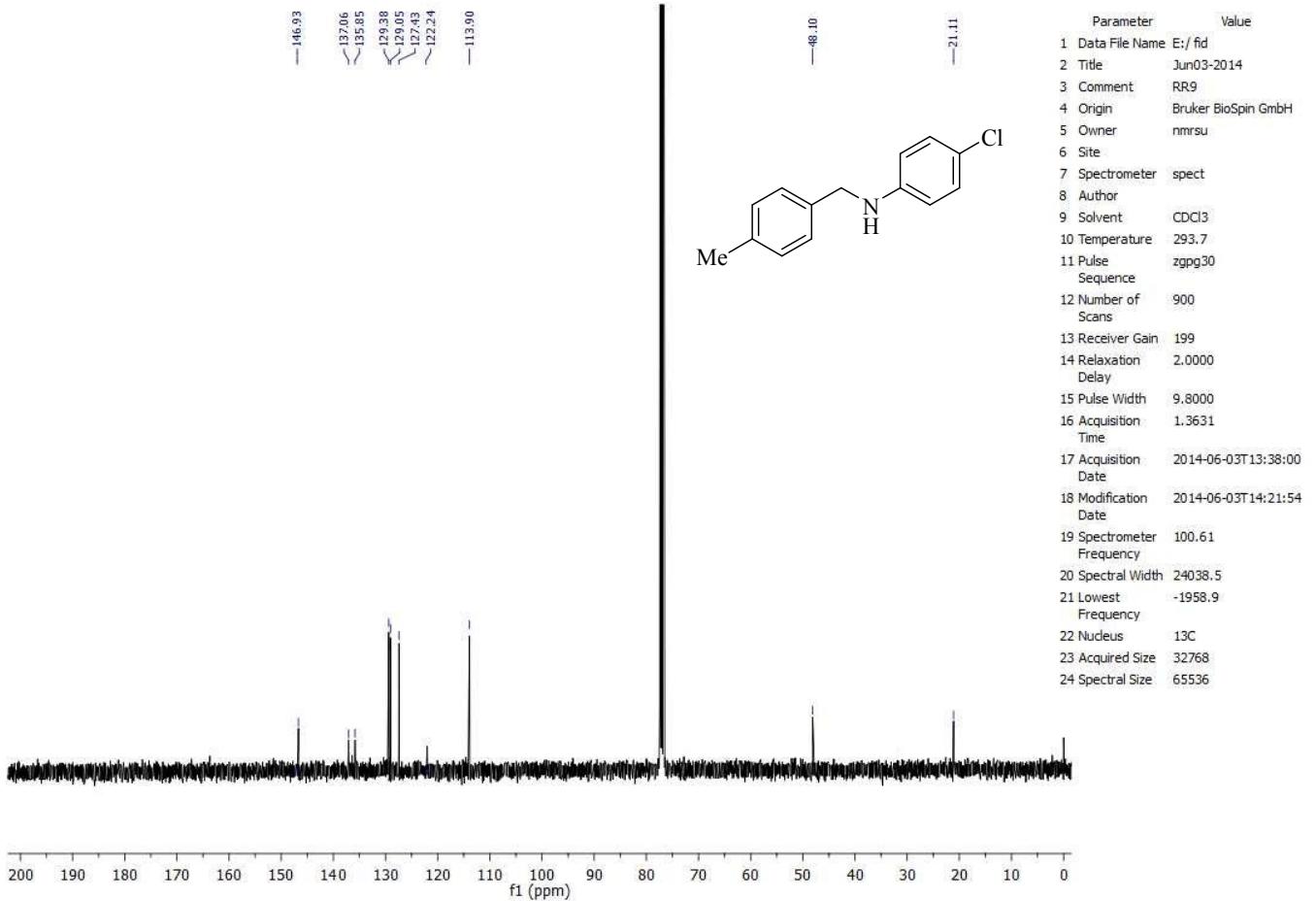
DEPT spectra of *N*-(4-Bromobenzyl)aniline



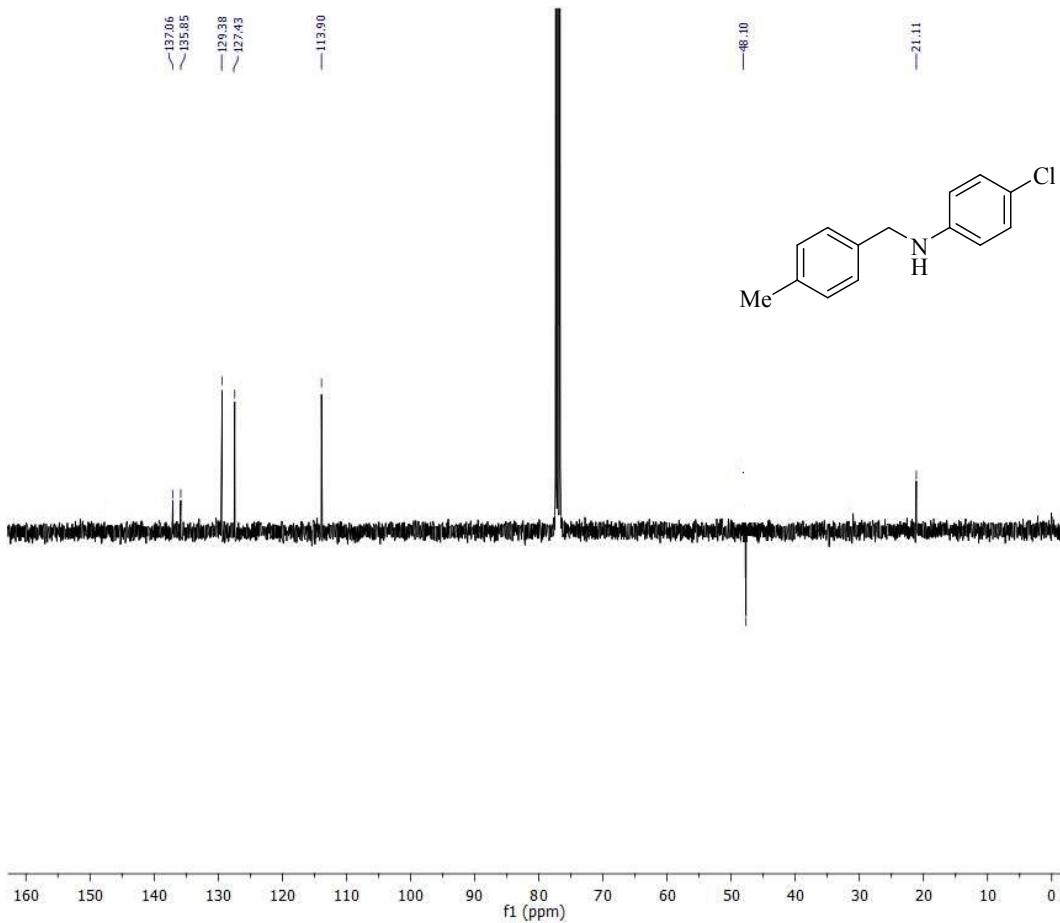
¹H spectra of *N*-(4-methylbenzyl)-4-chloroaniline



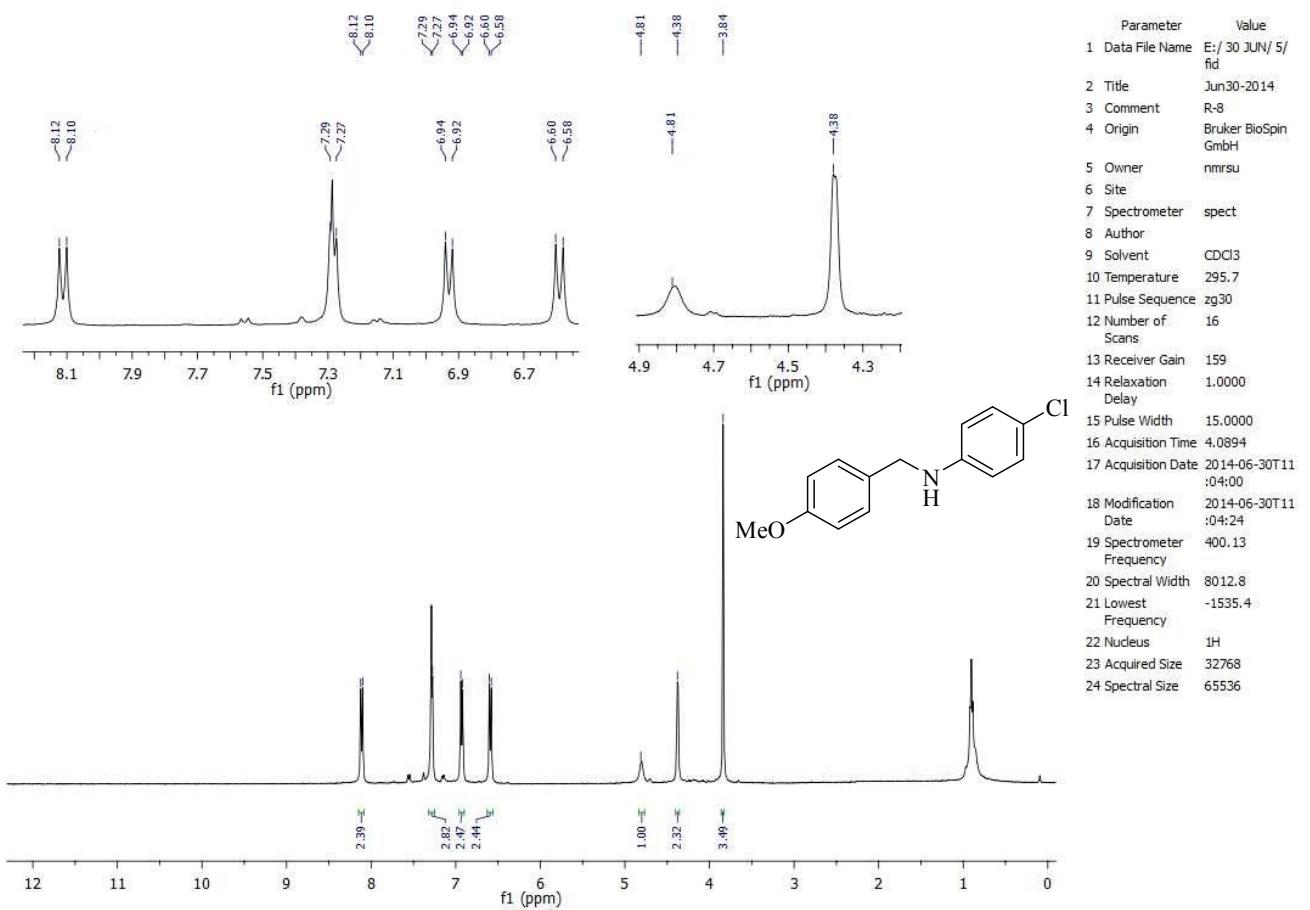
D₂O spectra of N-(4-methylbenzyl)-4-chloroaniline



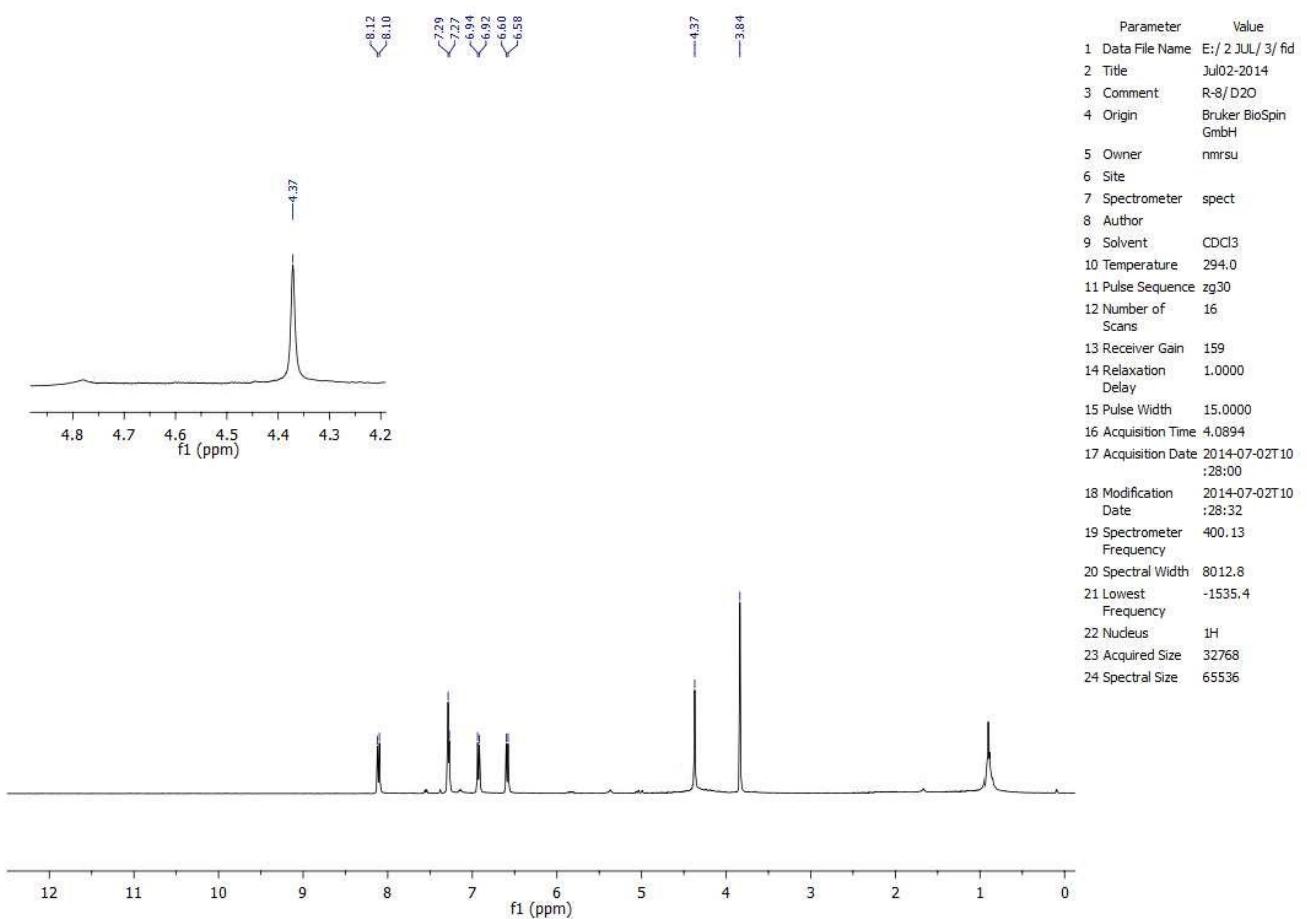
¹³C spectra of N-(4-methylbenzyl)-4-chloroaniline



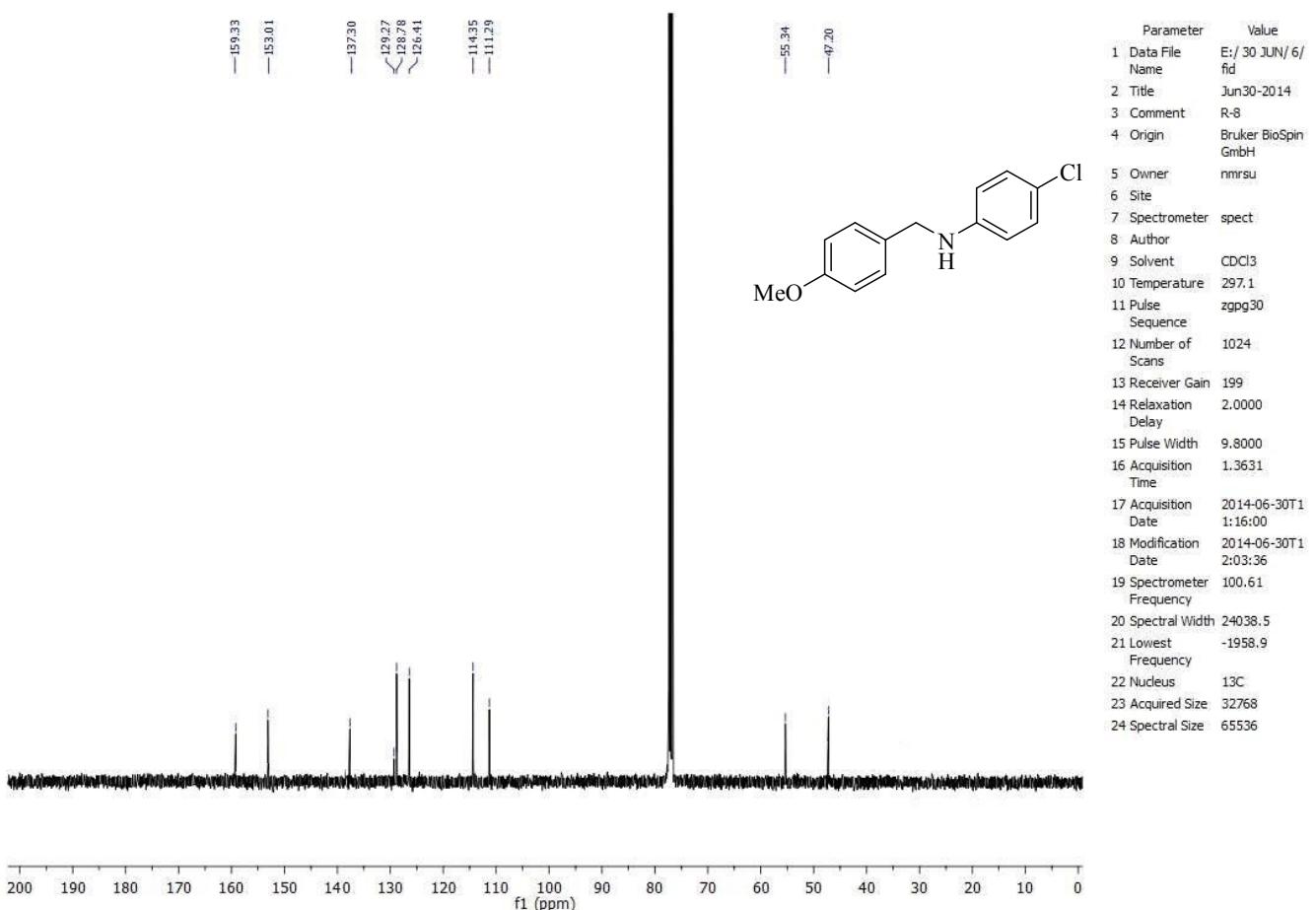
DEPT spectra of *N*-(4-methylbenzyl)-4-chloroaniline



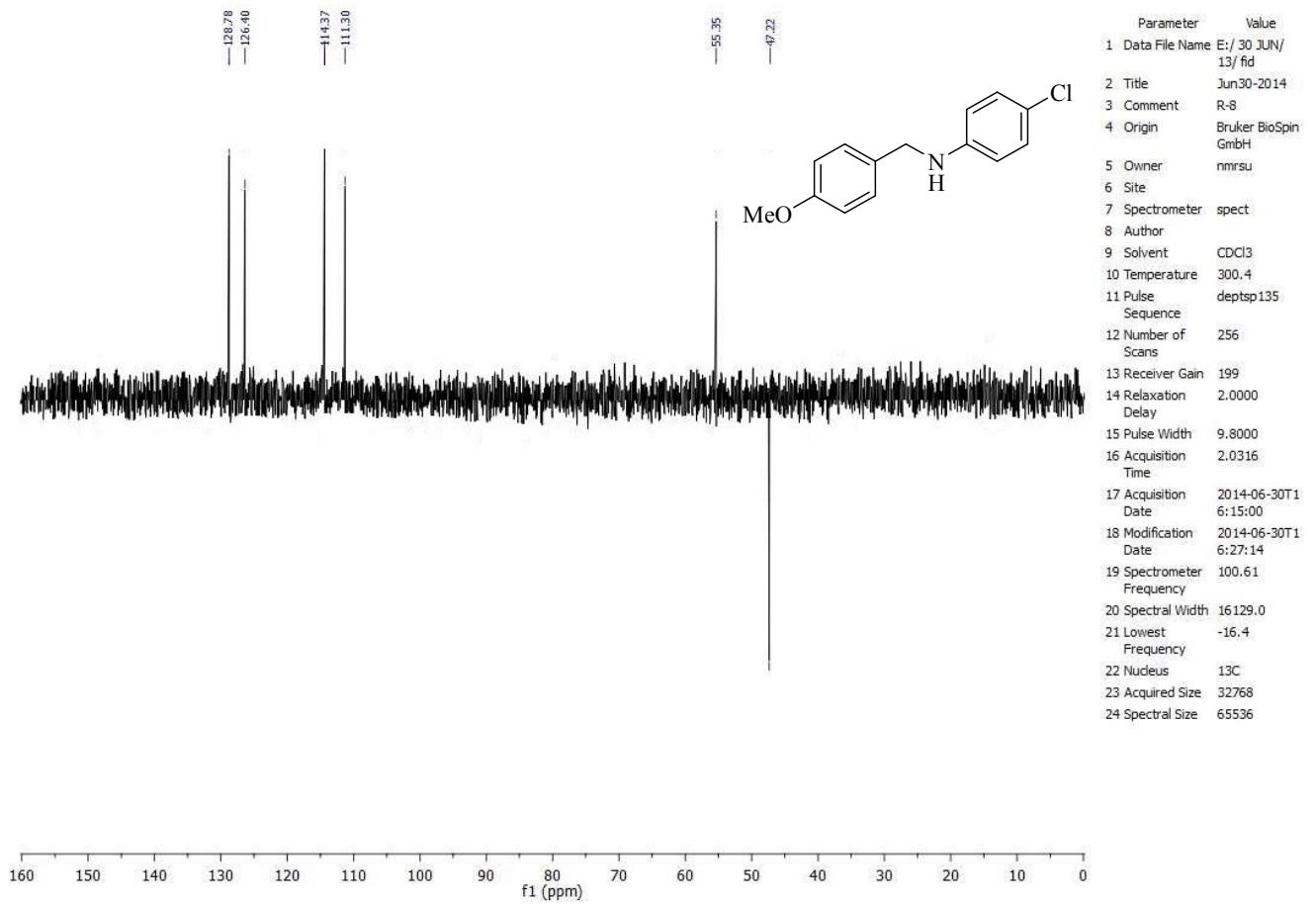
¹H spectra of *N*-(4-methoxylbenzyl)-4-chloroaniline



D₂O spectra of N-(4-methoxylbenzyl)-4-chloroaniline



¹³C spectra of *N*-(4-methoxybenzyl)-4-chloroaniline



DEPT spectra of *N*-(4-methoxybenzyl)-4-chloroaniline

S5. References

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