

Supplementary Information

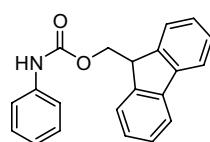
A Greener, Efficient and Catalyst-Free Ultrasonic-Assisted Protocol for the N-Fmoc Protection of Amines

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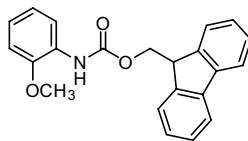
Selected spectral data

N-(9-Fluorenylmethoxycarbonyl) aniline (**1**)



m.p. 191 °C; IR (KBr) ν / cm⁻¹: 3329, 1699, 1596, 1239. ¹H NMR (400 MHz, CDCl₃): δ 4.28 (t, 1H, *J* 8.0 Hz, CH), 4.54 (d, 2H, *J* 8.0 Hz, CH₂), 6.67 (s, 1H, NH), 7.12 (t, 1H, *J* 8.0 Hz, CH_{Ar}), 7.31-7.42 (m, 8H, CH_{Ar}), 7.61 (d, 2H, *J* 12 Hz, CH_{Ar}), 7.78 (d, 2H, *J* 8.0 Hz, CH_{Ar}). ¹³C NMR (100 MHz, CDCl₃): δ 47.3, 66.9, 118.9, 120.2, 123.7, 125.1, 127.3, 127.9, 129.2, 137.8, 141.5, 143.9, 153.5.

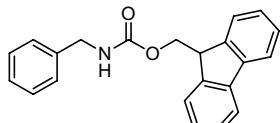
N-(9-Fluorenylmethoxycarbonyl)-2-methoxyaniline (**2**)



m.p. 189 °C; IR (KBr) ν / cm⁻¹: 3450, 1732, 2971, 1226. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 3.90 (s, 3H, CH₃), 4.33 (t, 1H, *J* 8.0 Hz, CH),

4.53 (d, 2H, *J* 8.0 Hz, CH₂), 6.87 (dd, 1H, *J* 4.0, 4.0 Hz, CH_{Ar}), 6.97-7.04 (m, 2H, CH_{Ar}), 7.35 (td, 3H, *J* 8.0, CH_{Ar}), 7.41 (t, 2H, *J* 8.0 Hz, CH_{Ar}), 7.66 (d, 2H, *J* 8.0 Hz, CH_{Ar}), 7.80 (d, 2H, *J* 8.0 Hz, CH_{Ar}), 8.12 (s, 1H, NH). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 47.2, 55.8, 67.1, 110.1, 118.5, 120.1, 121.2, 123.1, 125.2, 127.2, 127.5, 127.9, 141.4, 143.9, 147.7, 153.5.

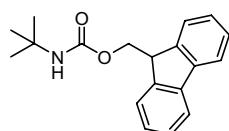
N-(9-Fluorenylmethoxycarbonyl) benzylamine (**8**)



m.p. 192 °C; IR (KBr) ν / cm⁻¹: 3330, 2957, 1695, 1548, 1265. ¹H NMR (400 MHz, CDCl₃): δ 4.23 (t, 1H, *J* 6.8 Hz, CH), 4.38 (d, 2H, *J* 5.6 Hz, CH₂), 4.46 (d, 2H, *J* 6.8 Hz, CH₂), 5.07 (s, 1H, NH), 7.26-7.38 (m, 6H, CH_{Ar}), 7.40 (t, 2H, *J* 7.6 Hz, CH_{Ar}), 7.59 (d, 2H, *J* 7.2 Hz, CH_{Ar}), 7.76 (d, 2H, *J* 7.6 Hz, CH_{Ar}). ¹³C NMR (100 MHz, CDCl₃): δ 45.3, 47.5, 66.8, 120.1,

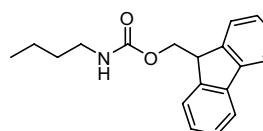
125.1, 127.2, 127.7, 127.8, 128.8, 138.5, 141.5, 144.1, 156.6. MSCI (+) *m/z*, observed: 330 [M + H]⁺; C₂₂H₁₉NO₂; 178 [9-methyl-9H-fluorene-H]⁺, 165 [9H-fluorene-H]⁺.

N-(9-Fluorenylmethoxycarbonyl) *tert*-butylamine (**10**)



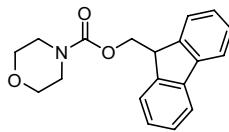
m.p. 137 °C; IR (KBr) ν / cm⁻¹: 3323, 2968, 1692, 1539, 1273. ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 9H, 3CH₃), 4.21 (t, 1H, *J* 6.8 Hz, CH), 4.37 (s, 2H, CH₂), 4.68 (s, 1H, NH), 7.29 (td, 2H, *J* 6.4 Hz, CH_{Ar}), 7.38 (t, 2H, *J* 7.2 Hz, CH_{Ar}), 7.59 (d, 2H, *J* 6.8 Hz, CH_{Ar}), 7.75 (d, 2H, *J* 7.6 Hz, CH_{Ar}). ¹³C NMR (100 MHz, CDCl₃): δ 29.1, 47.6, 50.5, 66.0, 120.1, 125.1, 127.1, 127.7, 141.5, 144.3, 154.9; MSCI(+) *m/z*, observed: 296 [M + H]⁺; C₁₉H₂₁NO; 178 [9-methyl-9H-fluorene-H]⁺, 165 [9H-fluorene-H]⁺.

N-(9-Fluorenylmethoxycarbonyl) butylamine (**12**)



m.p. 102 °C; IR (KBr) ν / cm⁻¹: 3330, 2957, 1695, 1265. ¹H NMR (400 MHz, CDCl₃): δ 0.93 (t, 3H, *J* 8.0 Hz, CH₃), 1.26-1.41 (m, 2H, CH₂), 1.45-1.46 (m, 2H, CH₂), 3.19 (m, 2H, CH₂), 4.22 (t, 1H, *J* 8.0 Hz, CH), 4.39 (d, 2H, *J* 12.0 Hz, CH₂), 4.75 (s, 1H, NH), 7.29-7.34 (td, 2H, *J* 8.0 Hz, CH_{Ar}), 7.38-7.43 (t, 2H, *J* 8.0 Hz, CH_{Ar}), 7.59 (d, 2H, *J* 8.0 Hz, CH_{Ar}), 7.76 (d, 2H, *J* 8.0 Hz, CH_{Ar}). ¹³C NMR (100 MHz, CDCl₃): δ 13.9, 20.0, 32.2, 40.9, 47.4, 66.6, 120.1, 125.2, 127.1, 127.8, 141.4, 144.1, 156.5.

N-(9-Fluorenylmethoxycarbonyl) morpholine (**14**)

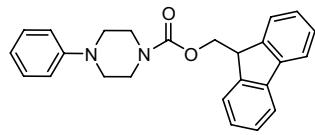


m.p. 112-113 °C; ¹H NMR (400 MHz, CDCl₃): δ 3.43 (s, 4H, 2CH₂), 3.61 (s, 4H, 2CH₂), 4.24 (t, 1H, *J* 6.3 Hz, CH), 4.45 (d, 2H, *J* 6.6 Hz, CH₂), 7.29 (t, 2H, *J* 6.4 Hz, CH_{Ar}), 7.38 (t, 2H, *J* 7.4 Hz, CH_{Ar}), 7.55 (d, 2H, *J* 7.4 Hz, CH_{Ar}), 7.75 (d, 2H, *J* 7.6 Hz, CH_{Ar}). ¹³C NMR

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(100 MHz, CDCl_3): δ 44.1, 47.4, 67.4, 77.4, 120.1, 125.0, 127.1, 127.8, 141.4, 144.0, 150.3.

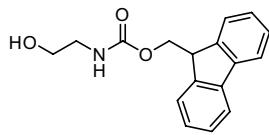
***N*-(9-Fluorenylmethoxycarbonyl) phenyl piperazine (**17**)**



m.p. 117 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 3.12 (s, 4H, 2 CH_2), 3.63 (s, 4H, 2 CH_2), 4.28 (t, 1H, J 6.8 Hz, CH),

4.50 (d, 2H, J 6.4 Hz, CH_2), 6.90-6.95 (m, 3H, CH_{Ar}), 7.28-7.36 (m, 4H, CH_{Ar}), 7.40-7.44 (t, 2H, J 7.2 Hz, CH_{Ar}), 7.60 (d, 2H, J 7.4 Hz, CH_{Ar}), 7.70 (d, 2H, J 7.1 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 43.9, 47.5, 49.5, 67.4, 116.8, 120.1, 120.6, 125.1, 127.2, 127.8, 129.3, 141.5, 144.1, 151.3, 155.2; MSCI (+) m/z 385 [M + H] $^+$ $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2$, 178 [9-methyl-9*H*-fluorene-H] $^+$, 165 [9*H*-fluorene-H] $^+$.

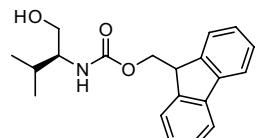
(S)(-)-*N*-(9-Fluorenylmethoxycarbonyl) ethanolamine (18**)**



m.p. 146 °C; IR (KBr) ν / cm $^{-1}$: 3474, 3355, 1673, 1276. ^1H NMR (400 MHz, CDCl_3): δ 2.08 (s, 1H, OH), 3.34 (d, 2H, J 4.0 Hz, CH_2),

3.68 (d, 2H, J 4.0 Hz, CH_2), 4.20 (t, 1H, J 8.0 Hz, CH), 4.41 (d, 2H, J 12.0 Hz, CH_2), 5.24 (s, 1H, NH), 7.33 (t, 2H, J 8.0 Hz, CH_{Ar}), 7.40 (t, 2H, J 8.0 Hz, CH_{Ar}), 7.57 (d, 2H, J 8.0 Hz, CH_{Ar}), 7.75 (d, 2H, J 8.0 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ 44.2, 48.0, 63.0, 67.5, 120.8, 125.8, 127.8, 128.5, 142.1, 144.6, 157.9.

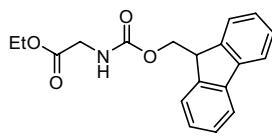
(S)(-)-*N*-(9-Fluorenylmethoxycarbonyl) valinol (20**)**



m.p. 120-123 °C; IR (KBr) ν / cm $^{-1}$: 3468, 3347, 1667, 1699, 1546, 1253. ^1H NMR (400 MHz, CDCl_3): δ 0.92 (t, 3H, J 8.0 Hz, 2 CH_3), 1.87 (m, 1H, CH), 2.10 (s, 1H, OH), 3.43-3.48 (m, 1H, CH), 3.60-

3.72 (m, 2H, CH_2), 4.22 (t, 2H, J 8.0 Hz, CH_2), 4.45 (d, 2H, J 8.0 Hz, CH_2), 4.91 (d, 1H, J 12.0 Hz, NH), 7.29-7.34 (t, 2H, J 8.0 Hz, CH_{Ar}), 7.40 (t, 2H, J 8.0 Hz, CH_{Ar}), 7.59 (d, 2H, J 8.0 Hz, CH_{Ar}), 7.75 (d, 2H, J 12.0, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ 18.8, 29.3, 47.5, 58.7, 63.9, 66.7, 120.1, 125.1, 127.2, 127.8, 141.5, 144.0, 144.0, 157.2.

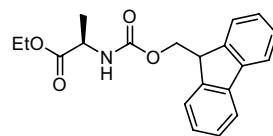
***N*-(9-Fluorenylmethoxycarbonyl) glycine ethyl ester (**23**)**



m.p. 107-108 °C; IR (KBr) ν / cm $^{-1}$: 3330, 1755, 1699, 1538, 1282. ^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, 3H, J 7.2 Hz, CH_3), 3.98 (d, 2H, J 5.6 Hz, CH_2), 4.20-4.26 (m, 3H), 4.40 (d, 2H,

J 7.2 Hz, CH_2), 5.27 (s, 1H, NH) 7.29-7.33 (t, 2H, J 6.4 Hz, CH_{Ar}), 7.38 (t, 2H, J 6.4 Hz, CH_{Ar}), 7.59 (d, 2H, J 7.6 Hz, CH_{Ar}), 7.75 (d, 2H, J 7.6 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ 14.3, 43.0, 47.3, 61.7, 67.4, 120.1, 125.2, 127.2, 127.9, 141.5, 144.0, 156.4, 170.1.

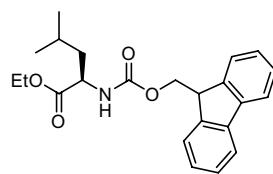
(S)(-)-*N*-(9-Fluorenylmethoxycarbonyl) leucine ethyl ester (26**)**



m.p. 87 °C; IR (KBr)

ν / cm $^{-1}$: 3314, 2959, 1744, 1696, 1541, 1259. ^1H NMR (400 MHz, CDCl_3): δ 0.95 (d, 6H, J 5.6 Hz, 2 CH_3), 1.26 (t, 3H, J 7.2 Hz, CH_3), 1.5 (m, 1H, CH), 1.62 (m, 2H, CH_2), 4.17 (m, 3H), 4.36-4.44 (d, 2H, J 6.8 Hz, CH_2), 5.15 (d, 1H, J 8.4 Hz, NH), 7.29-7.33 (t, 2H, J 5.6 Hz, CH_{Ar}), 7.38 (t, 2H, J 6.8 Hz, CH_{Ar}), 7.58 (d, 2H, J 7.2 Hz, CH_{Ar}), 7.75 (d, 2H, J 6.8 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ 14.3, 22.0, 23.0, 24.9, 42.1, 47.4, 52.7, 61.49, 67.1, 120.1, 125.2, 127.2, 127.9, 141.5, 144.0, 156.1, 173.3.

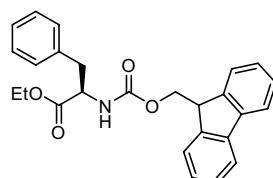
(S)(-)-*N*-(9-Fluorenylmethoxycarbonyl) alanine ethyl ester (24**)**



m.p. 89-90 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, 3H, J 7.2 Hz, CH_3), 1.42 (d, 3H, J 6.8 Hz, CH_3), 4.19-4.25 (m, 3H), 4.34-4.44 (m, 2H, CH_2), 5.34 (d, 1H, J 5.6 Hz,

NH), 7.29 (t, 2H, J 6.4 Hz, CH_{Ar}), 7.38 (t, 2H, J 7.6 Hz, CH_{Ar}), 7.59 (d, 2H, J 7.6 Hz, CH_{Ar}), 7.75 (d, 2H, J 7.2 Hz, CH_{Ar}). ^{13}C NMR (100 MHz, CDCl_3): δ 14.3, 18.9, 47.4, 49.8, 61.7, 67.1, 120.1, 125.2, 127.2, 127.8, 141.5, 144.0, 144.1, 155.8, 173.2.

(S)(-)-*N*-(9-Fluorenylmethoxycarbonyl) phenylalanine ethyl ester (27**)**



m.p. 107 °C; ^1H NMR (400 MHz, CDCl_3): δ 1.24 (t, 3H, J 6.8 Hz, CH_3), 3.12 (m, 2H, CH_2), 4.19 (m, 3H), 4.32-4.46 (m, 2H), 4.63 (d, 1H, J 6.0 Hz, CH), 5.24 (d,

1H, J 8.4 Hz, NH), 7.10 (d, 2H, J 7.2 Hz, CH_{Ar}), 7.24-7.33 (m, 5H, CH_{Ar}), 7.38 (t, 2H, J 7.2 Hz, CH_{Ar}), 7.55 (t, 2H, J 6.8 Hz, CH_{Ar}), 7.76 (d, 2H, J 7.6 Hz, CH_{Ar}); ^{13}C NMR (100 MHz, CDCl_3): δ 14.2, 38.5, 47.4, 55.0, 61.8, 67.1, 120.1, 125.2, 125.3, 127.3, 127.9, 128.7, 129.5, 136.0, 141.5, 143.9, 144.0, 155.7, 171.6.

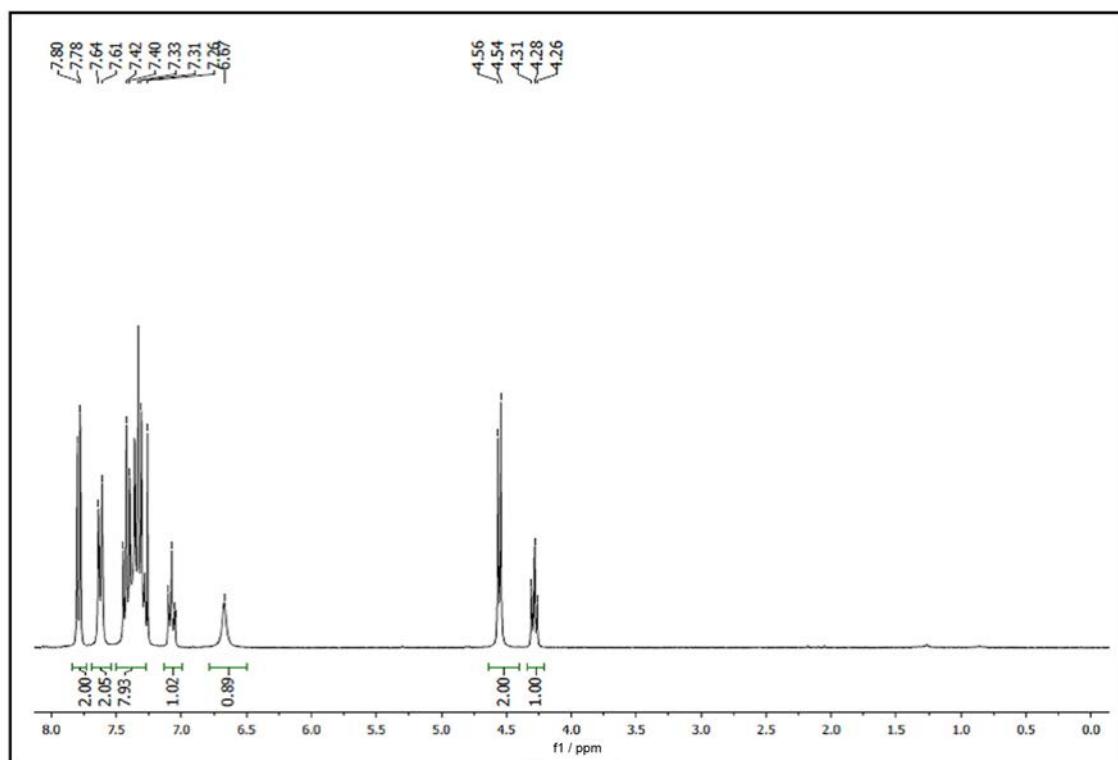


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) aniline (entry 1).

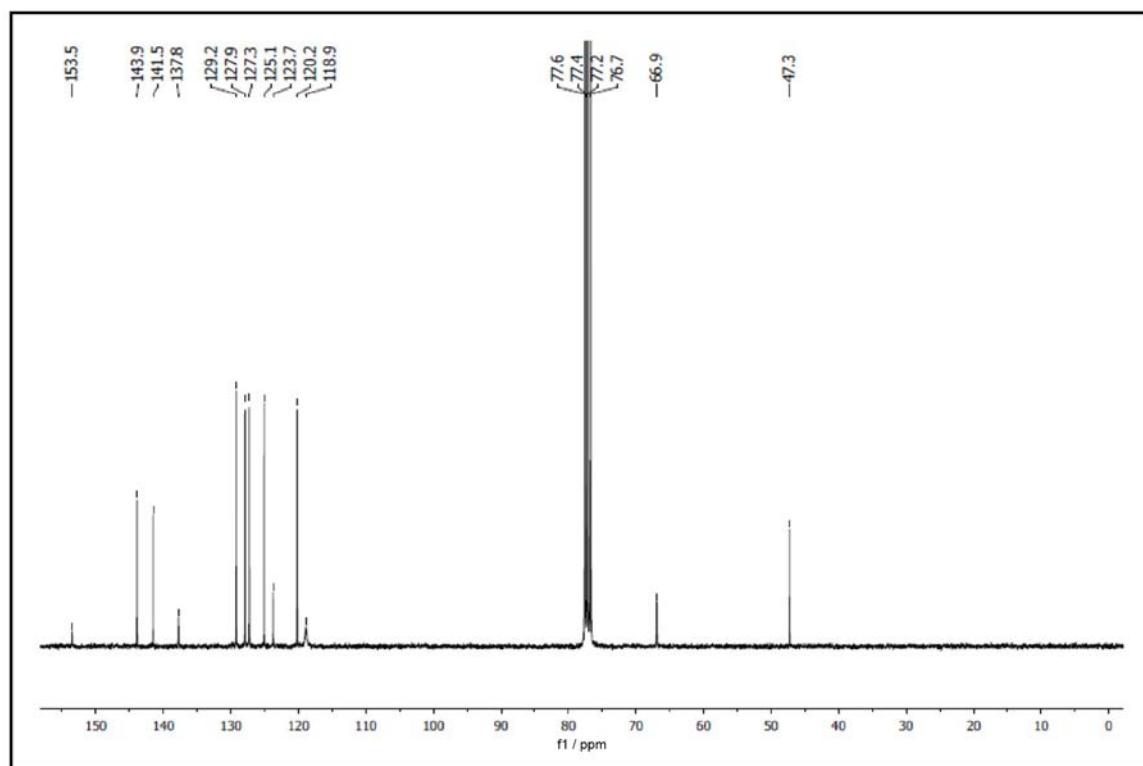


Figure S2. ¹³C NMR spectrum (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) aniline (entry 1).

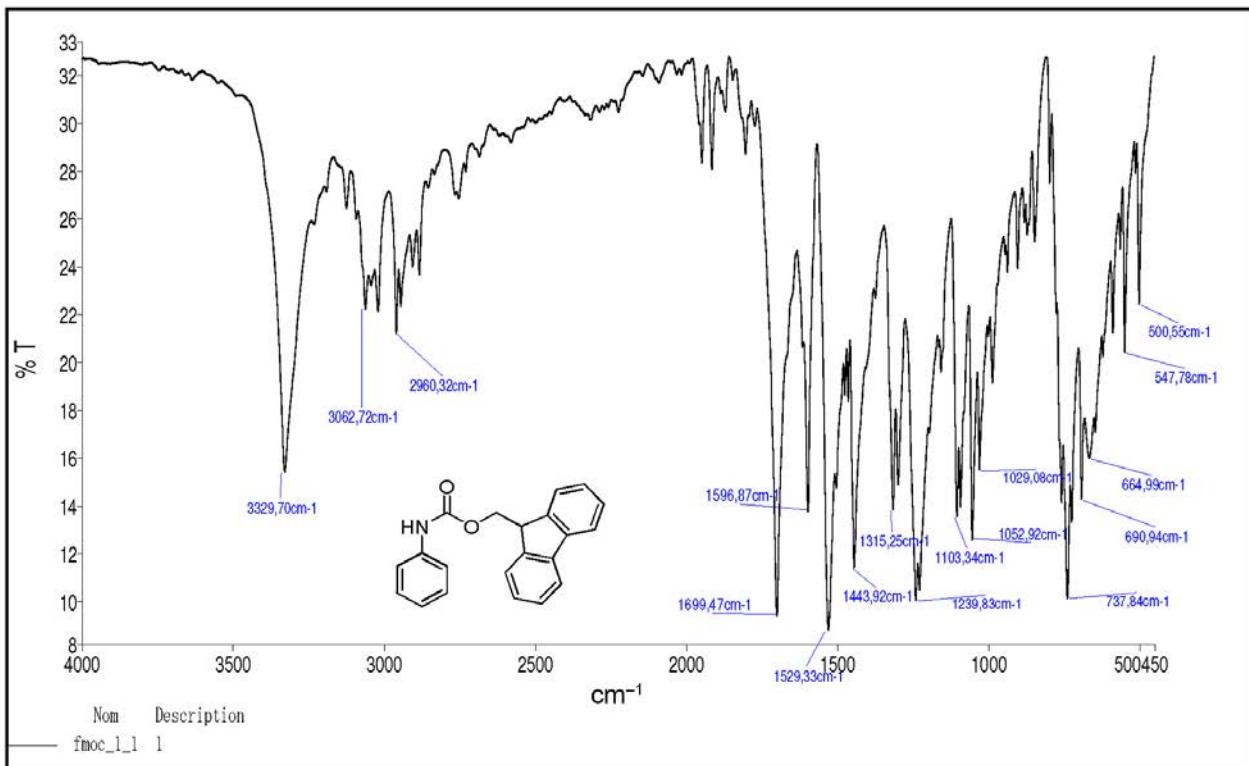


Figure S3. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) aniline (entry 1).

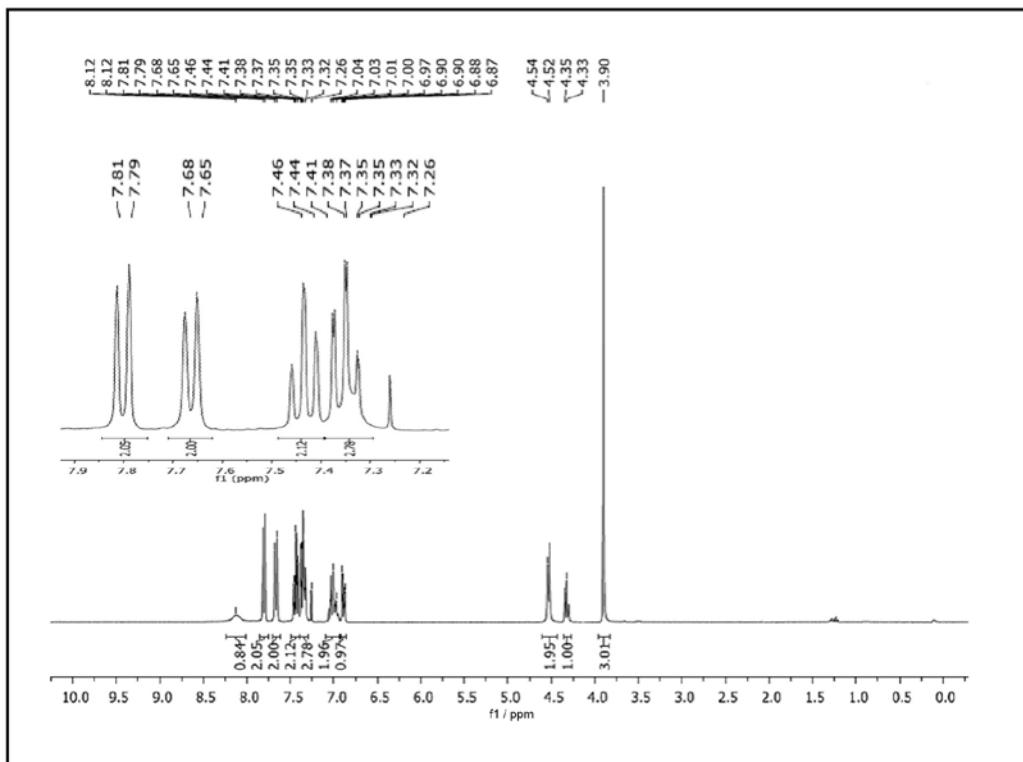


Figure S4. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl)-2-methoxyaniline (entry 2).

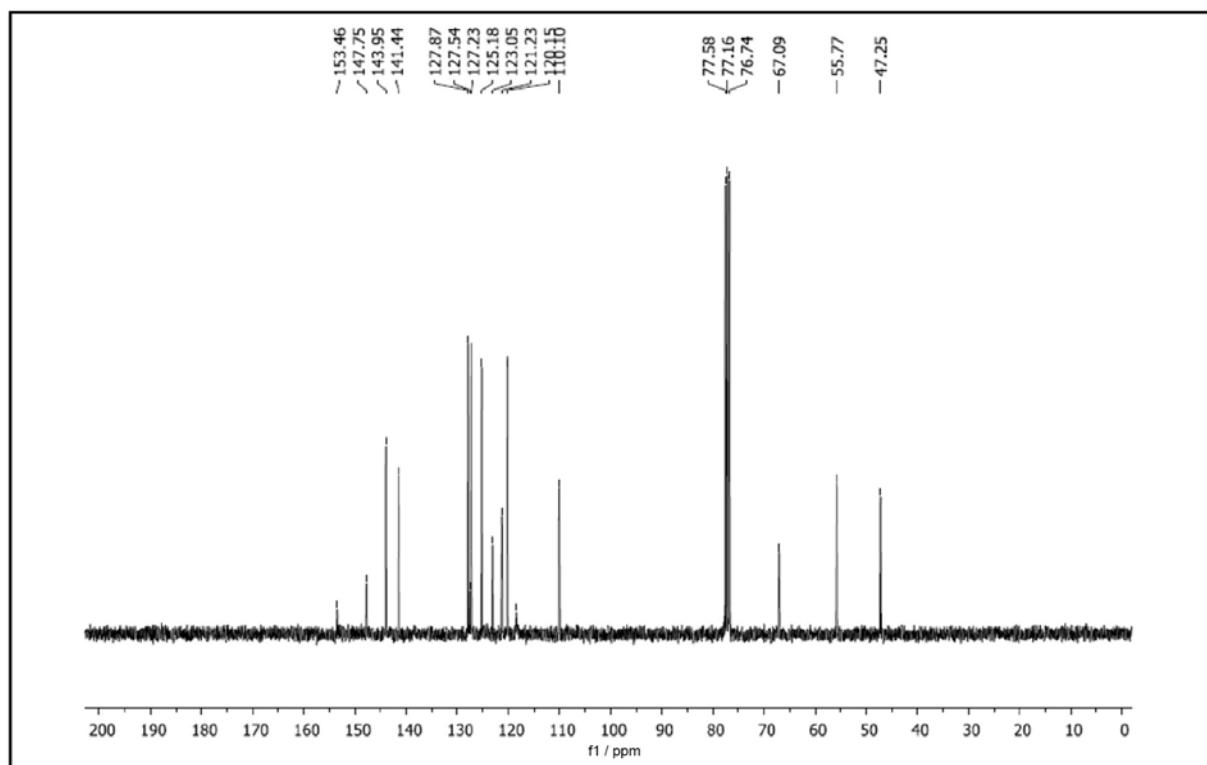


Figure S5. ^{13}C NMR spectrum (100 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl)-2-methoxyaniline (entry 2).

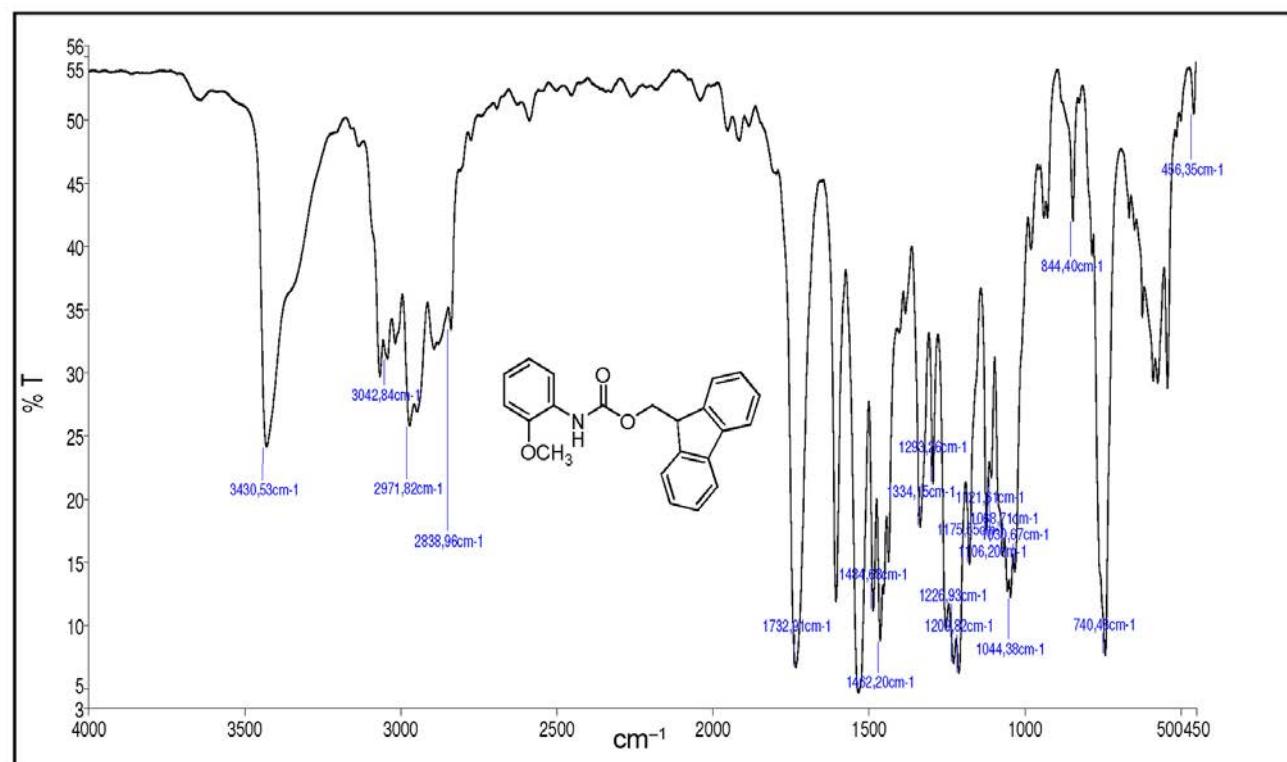


Figure S6. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl)-2-methoxyaniline (entry 2).

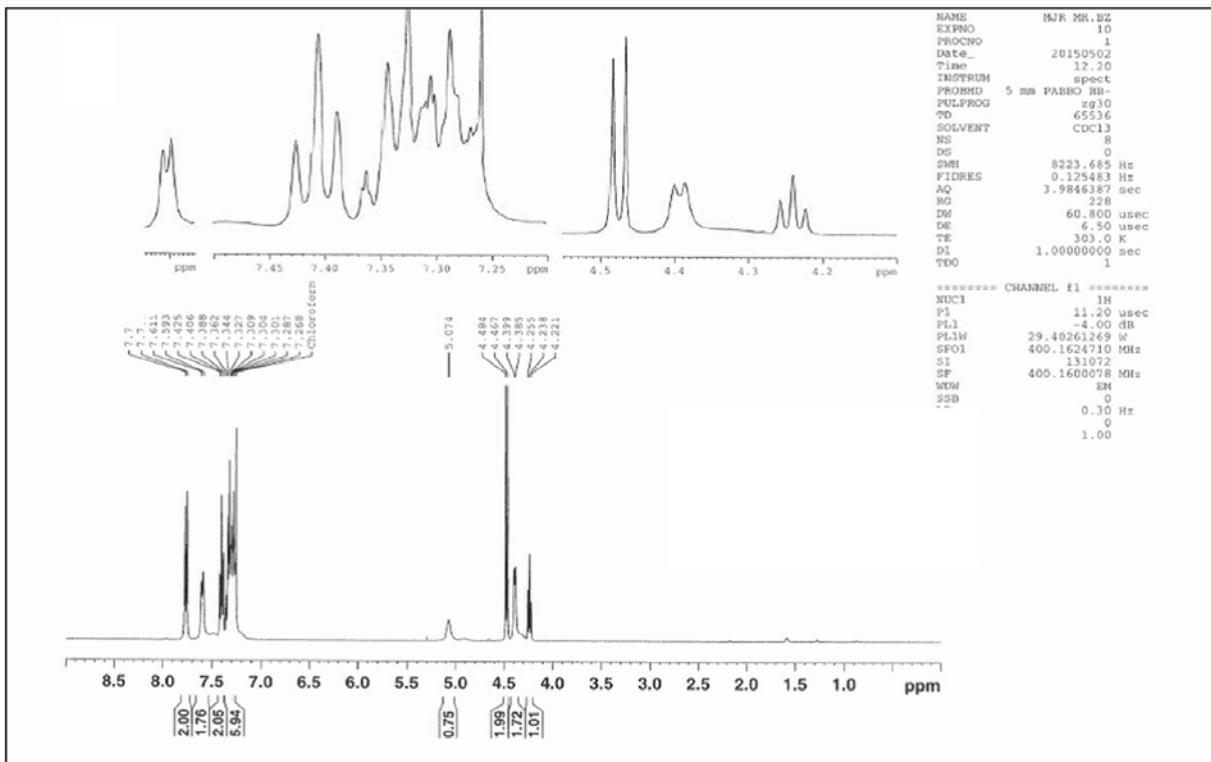


Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) benzylamine (entry 8).

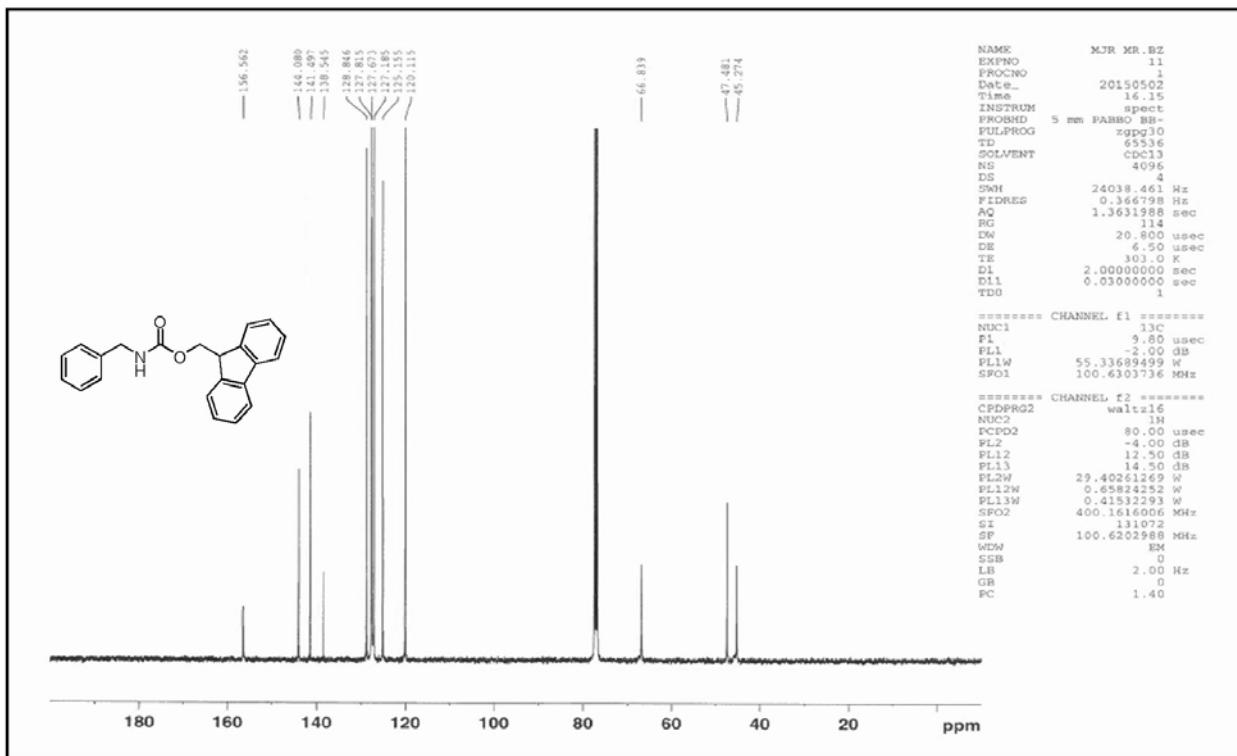


Figure S8. ¹³C NMR of Spectrum: (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) benzylamine (entry 8).

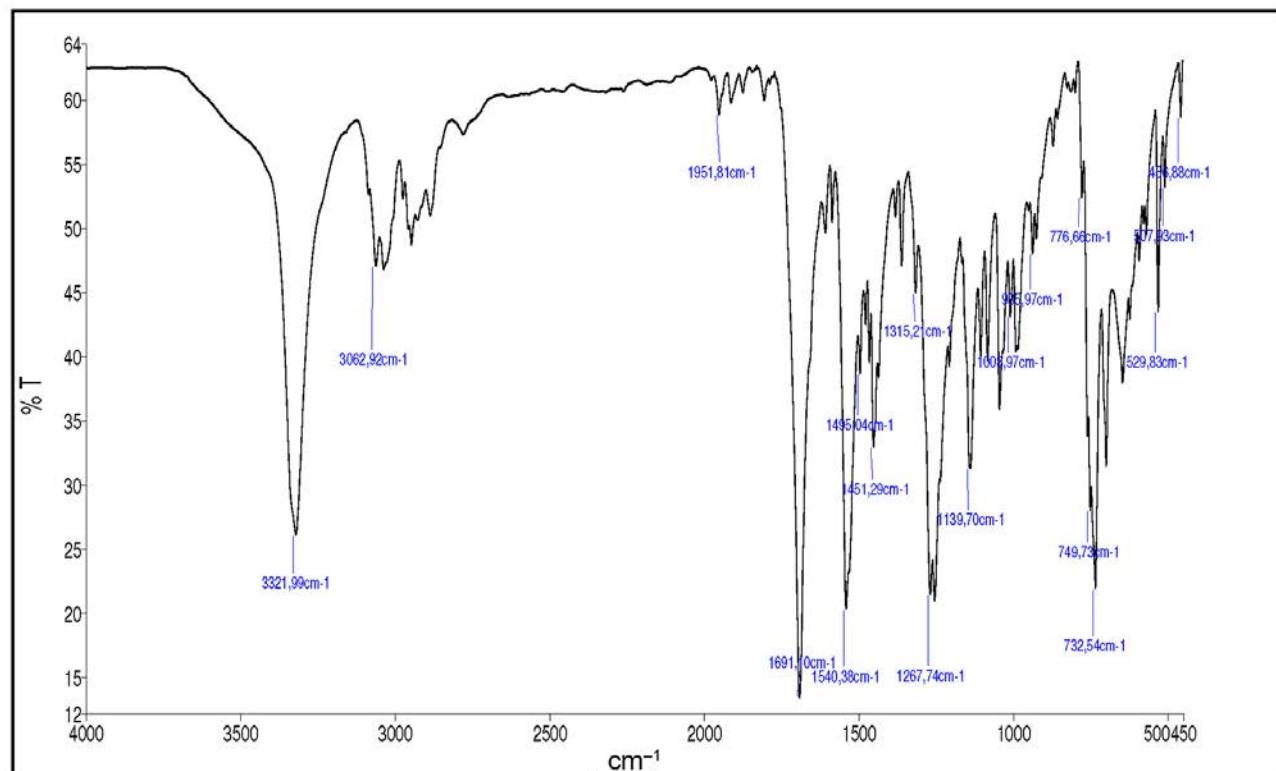


Figure S9. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) benzylamine (entry 8).

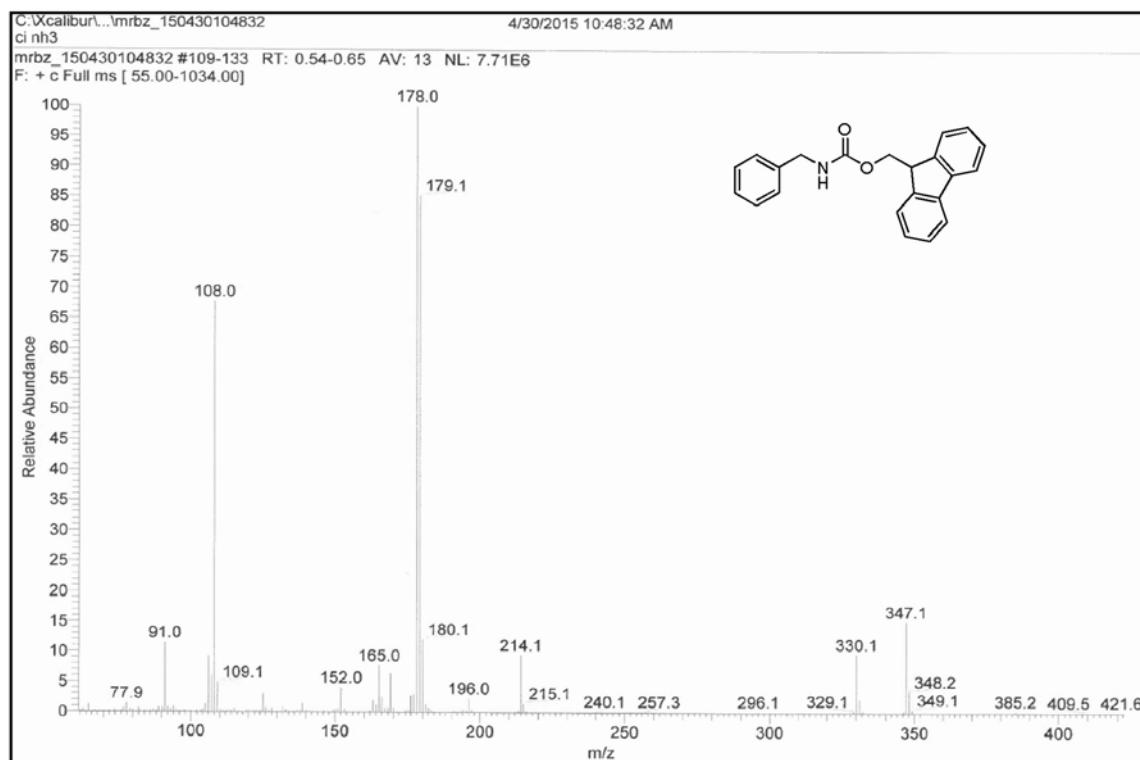


Figure S10. Mass spectrum of *N*-(9-fluorenylmethoxycarbonyl) benzylamine (entry 8).

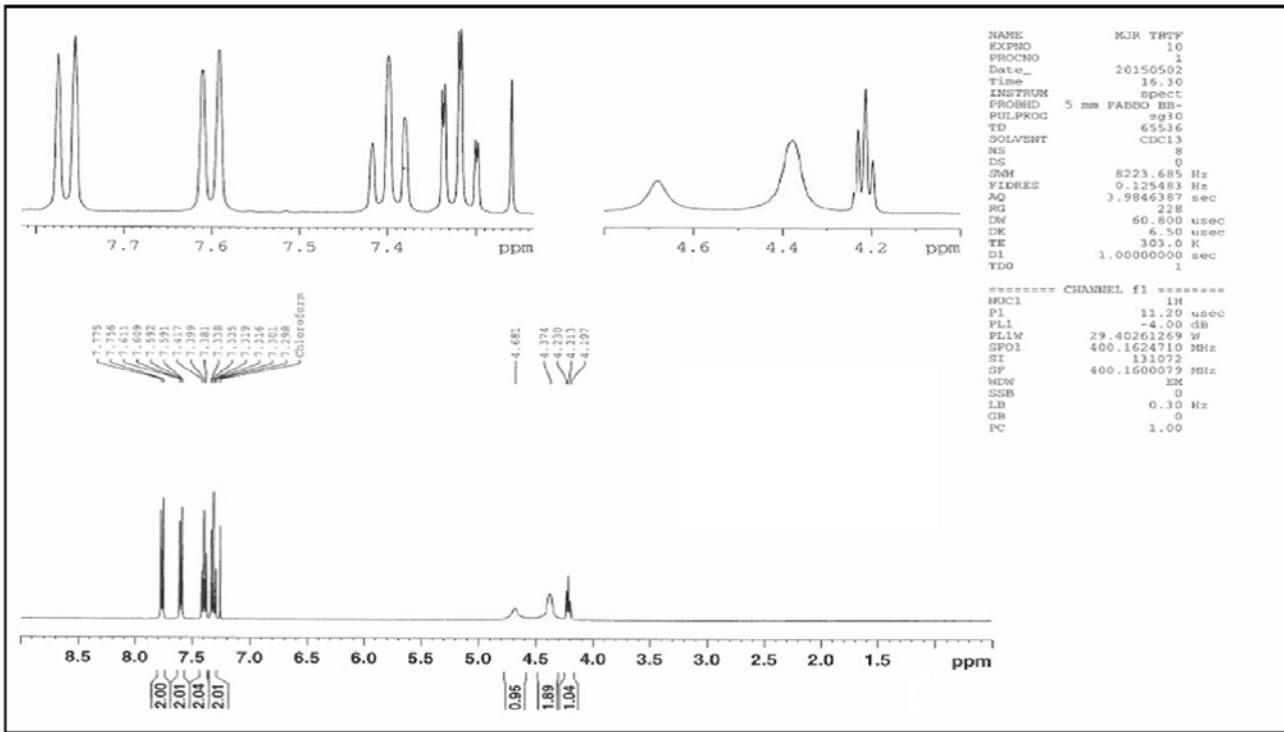


Figure S11. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) *tert*-butylamine (entry 10).

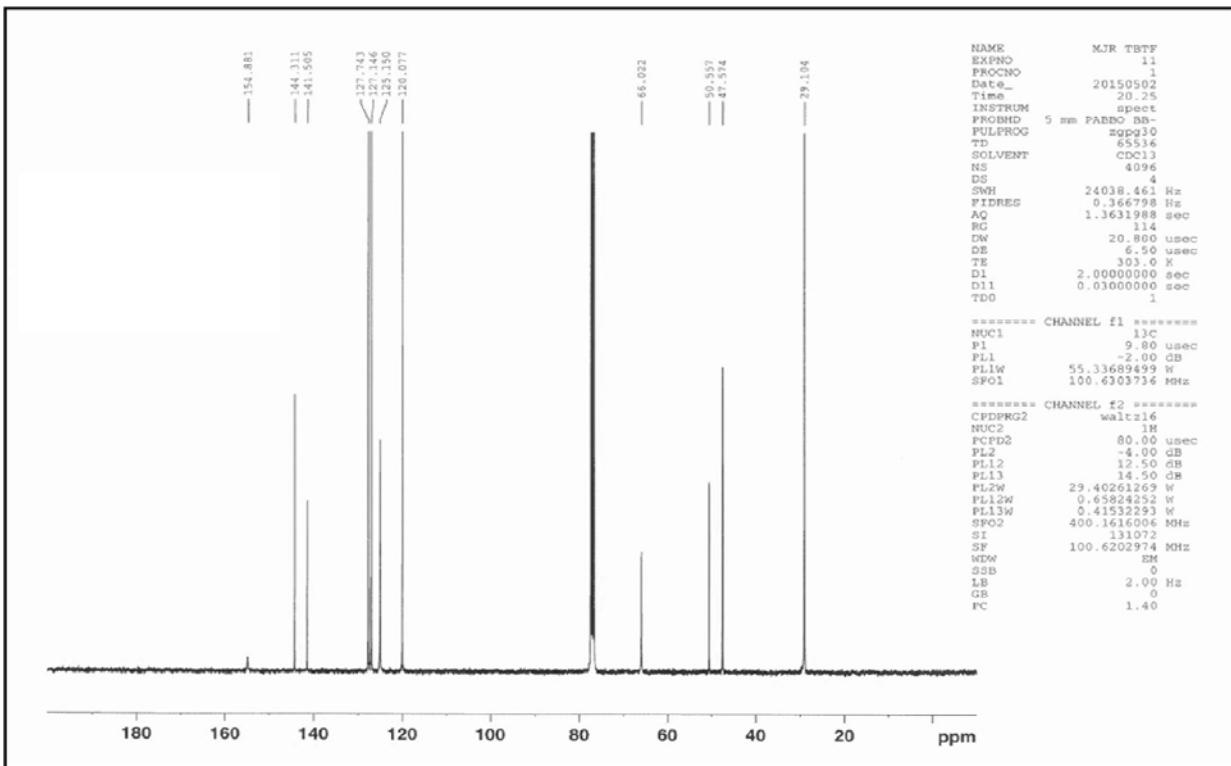


Figure S12. ^{13}C NMR spectrum (100 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) *tert*-butylamine (entry 10).

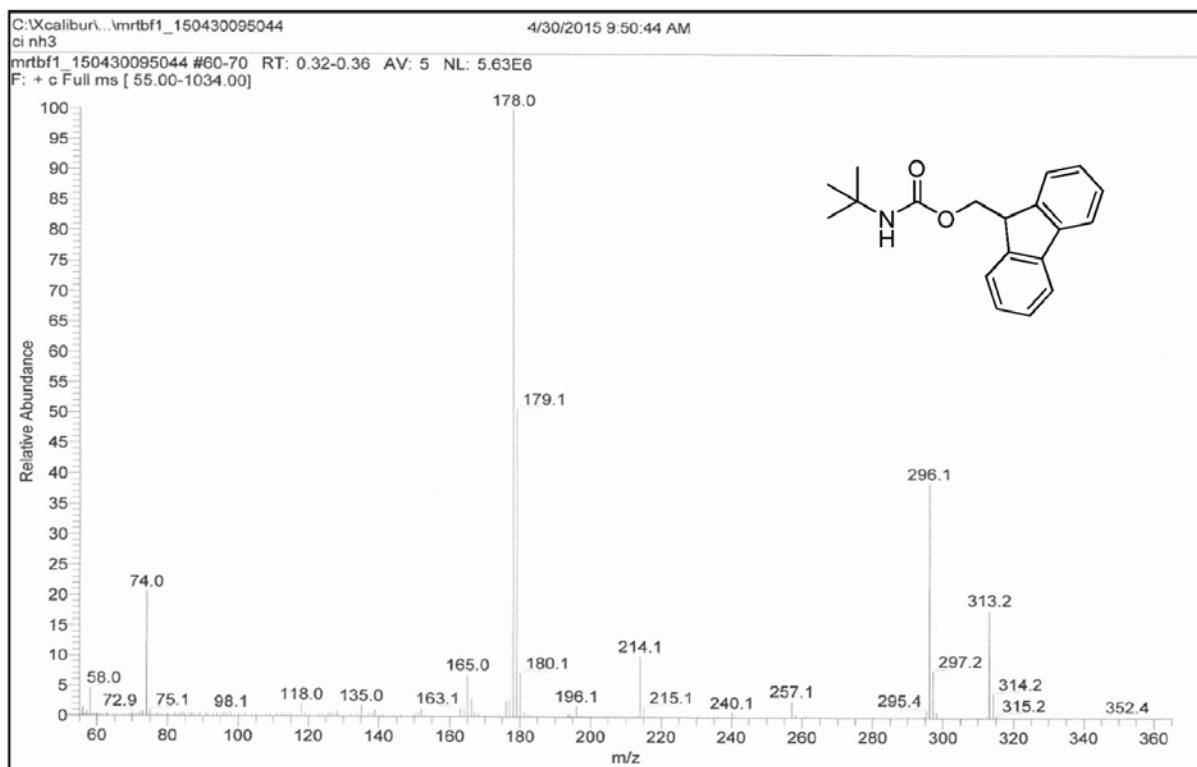


Figure S13. Mass spectrum of *N*-(9-fluorenylmethoxycarbonyl) *tert*-butylamine (entry 10).

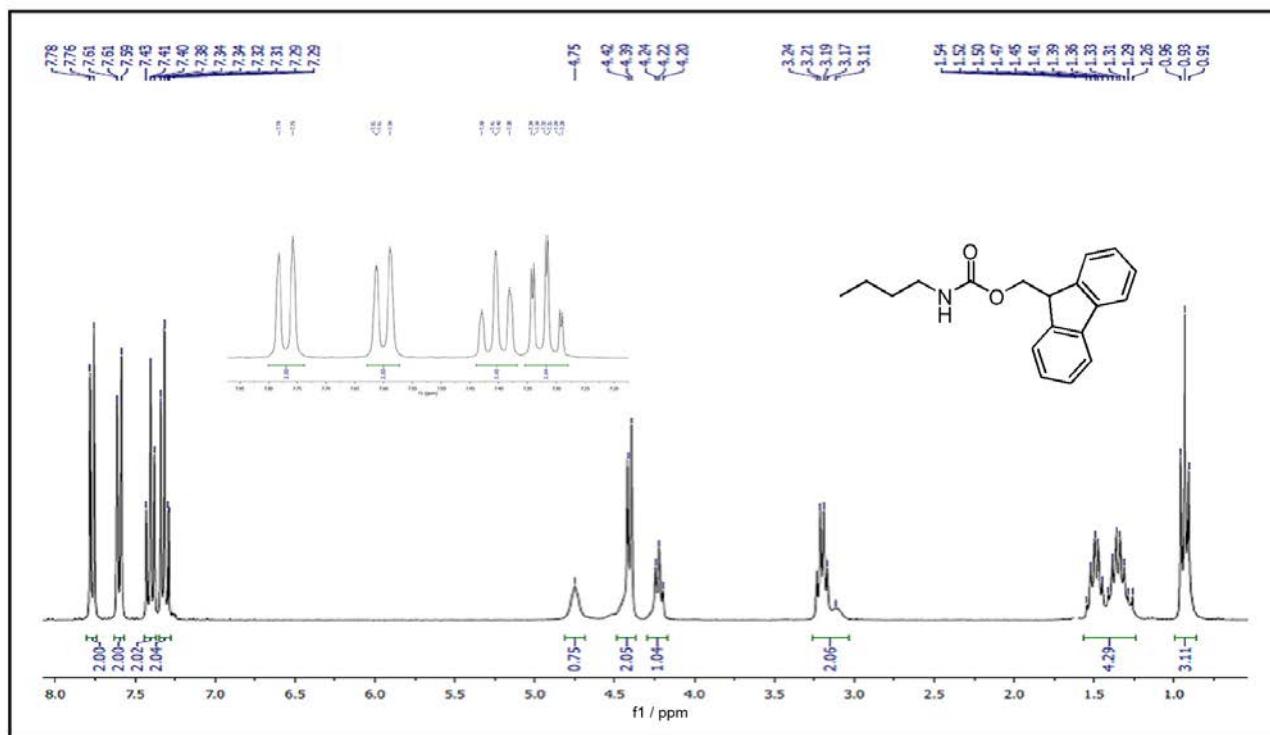


Figure S14. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) butylamine (entry 12).

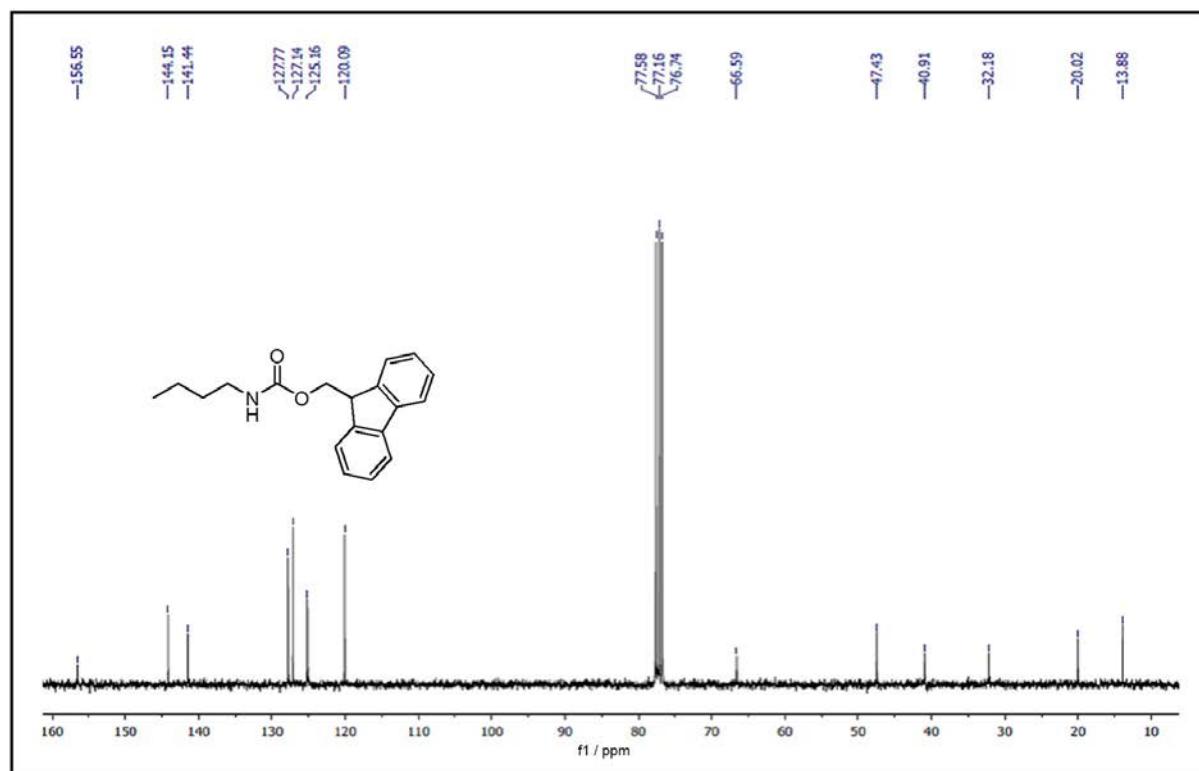


Figure S15. ¹³C NMR spectrum (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) butylamine (entry 12).

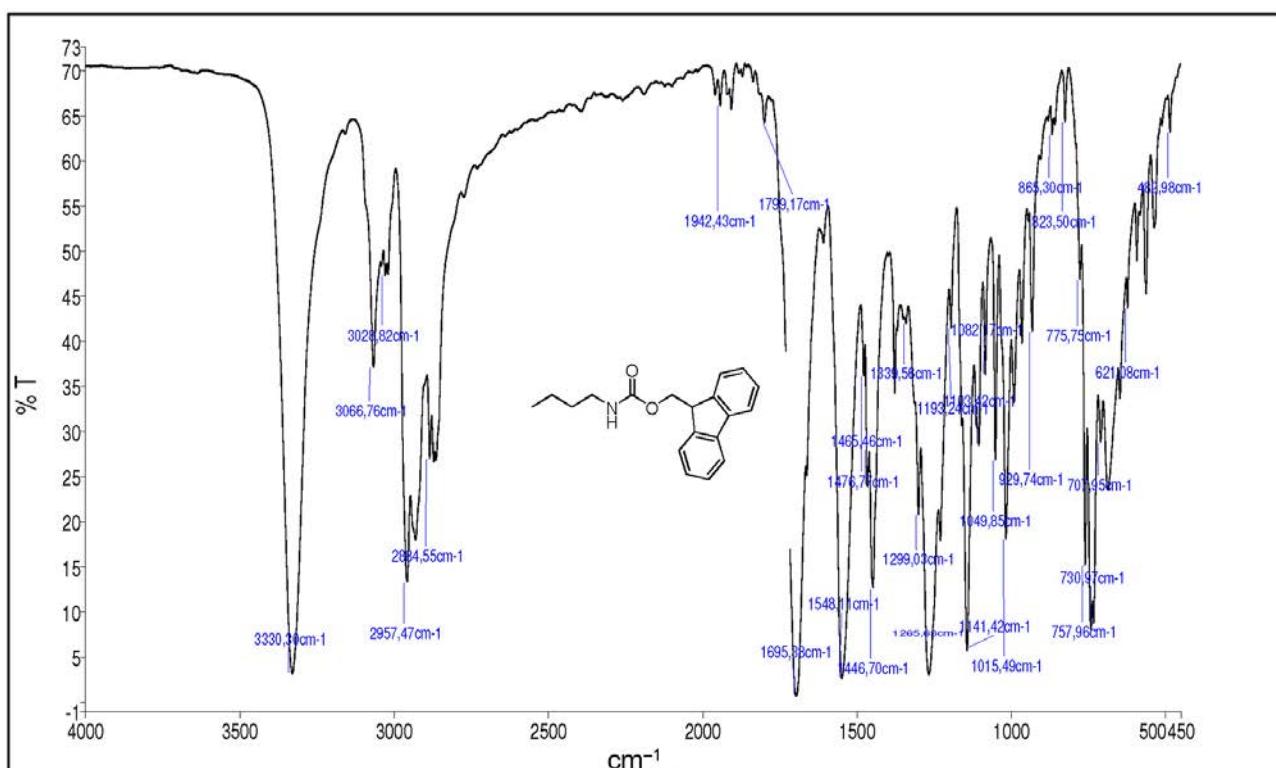
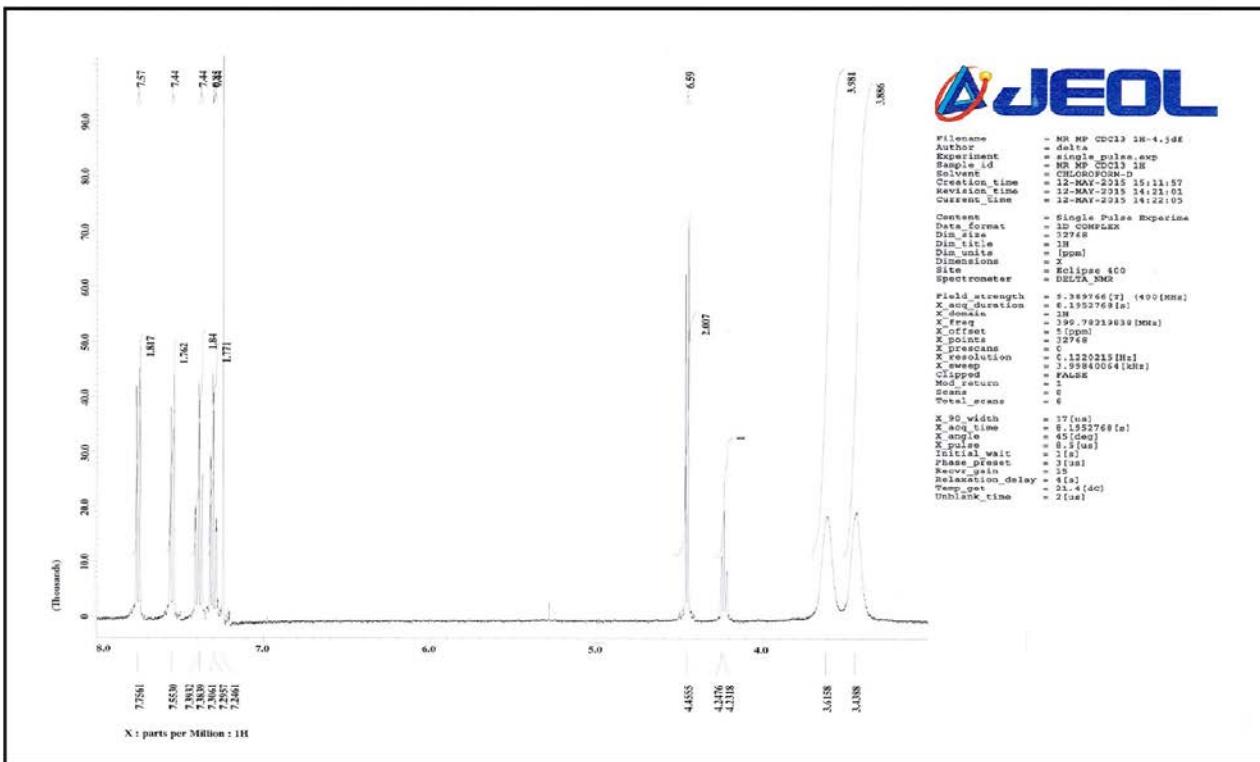
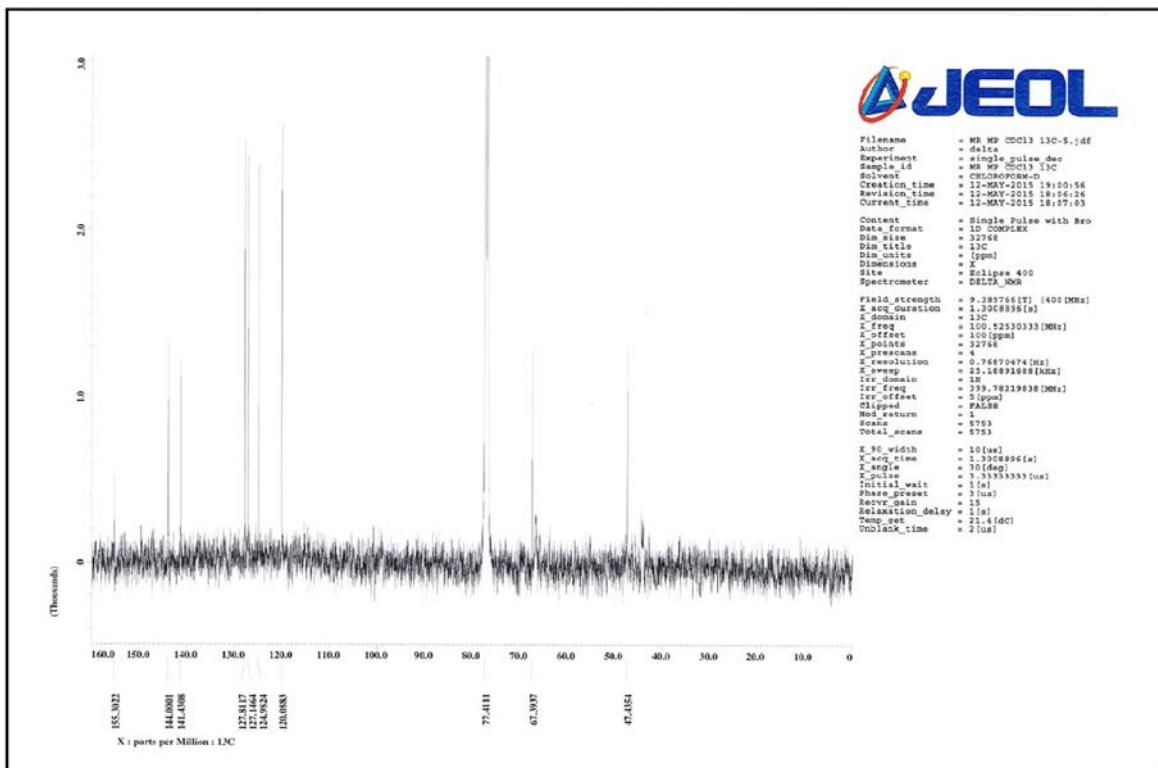


Figure S16. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) butylamine (entry 12).

**Figure S17.** ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) morpholine (entry 14).**Figure S18.** ^{13}C NMR spectrum (100 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) morpholine (entry 14).

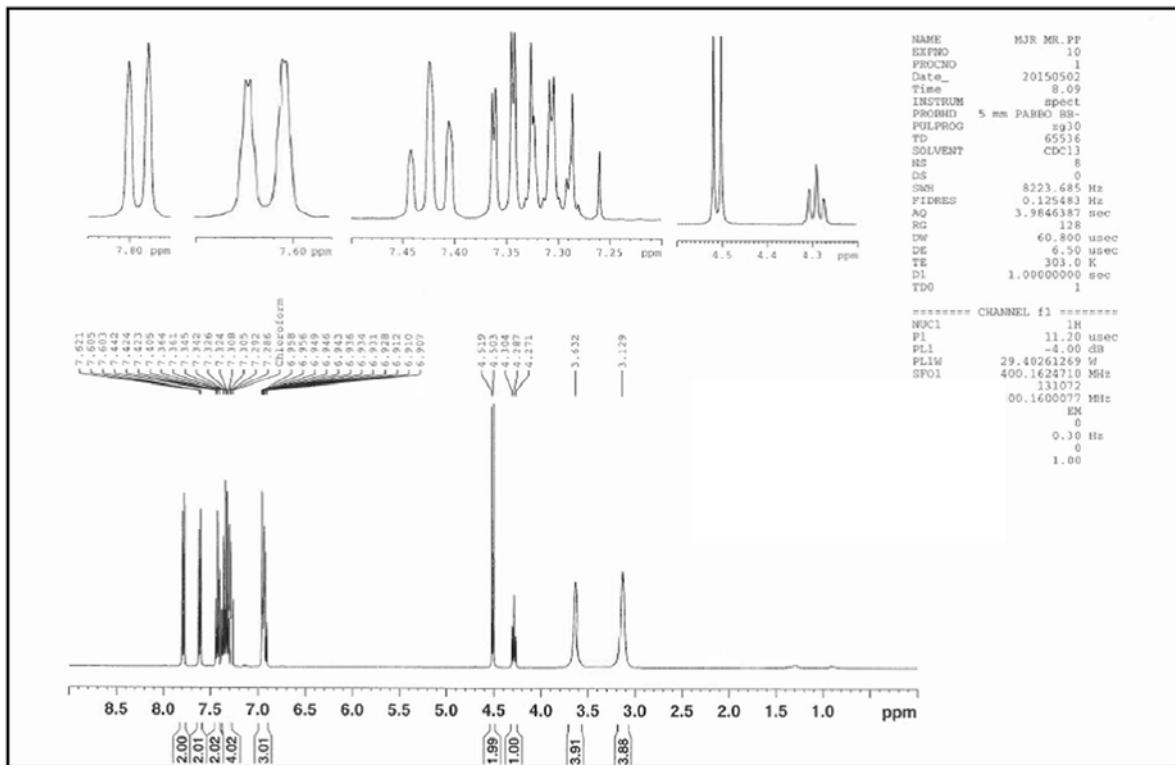


Figure S19. ¹H NMR spectrum (400 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) phenylpiperazine (entry 17).

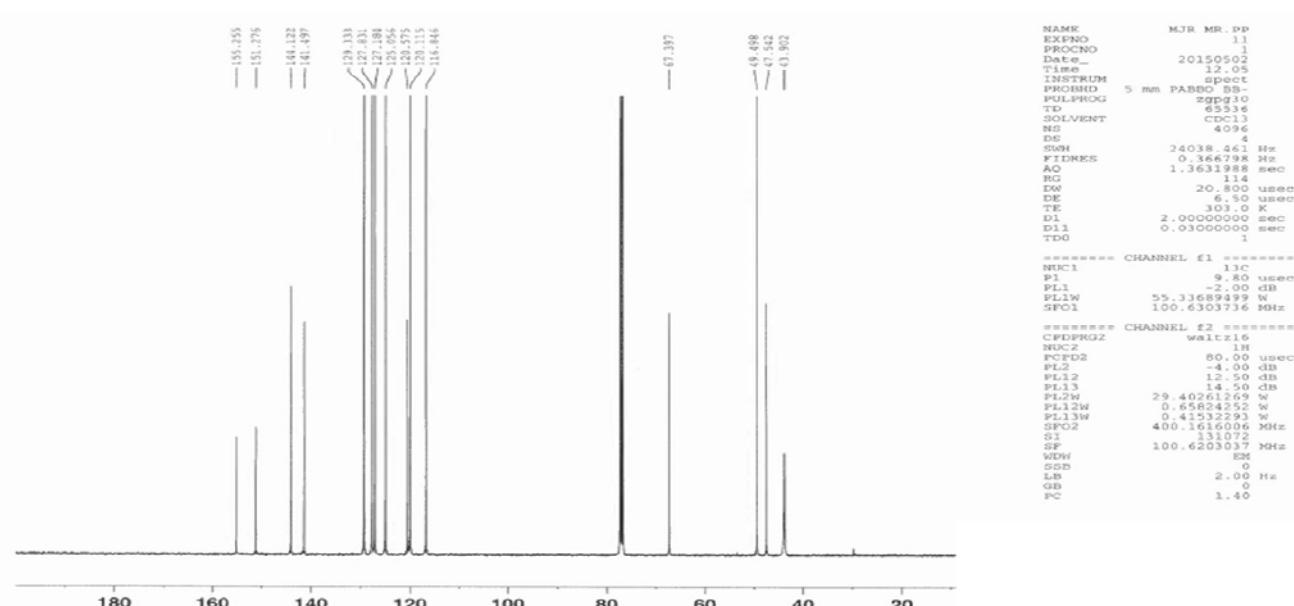


Figure S20. ¹³C NMR spectrum (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) phenylpiperazine (entry 17).

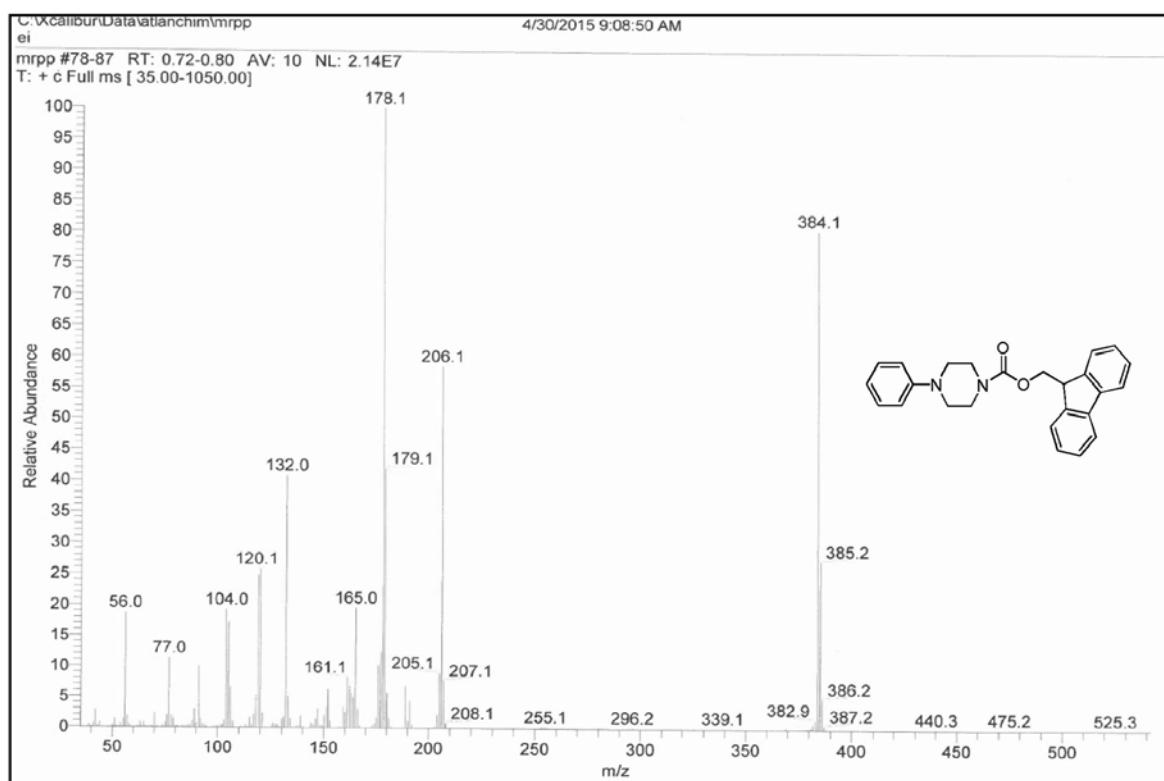


Figure S21. Mass spectrum of *N*-(9-fluorenylmethoxycarbonyl) phenylpiperazine (entry 17).

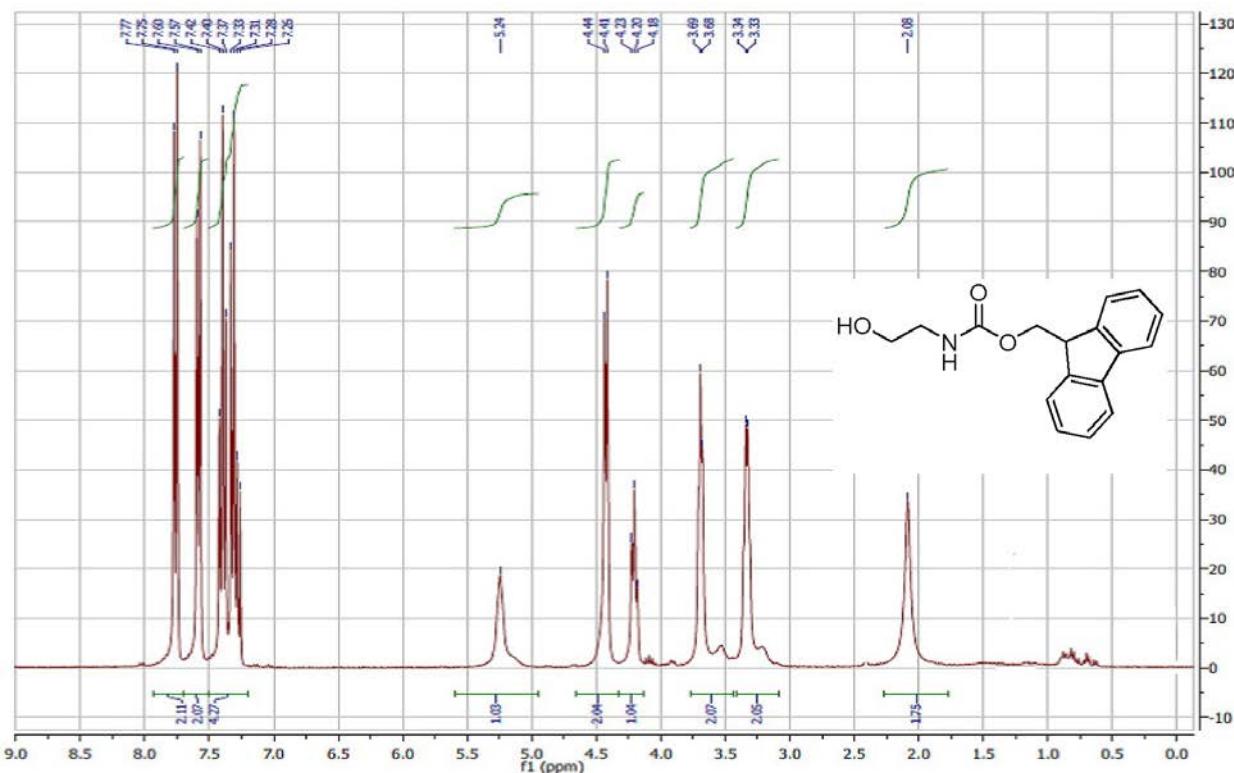


Figure S22. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) ethanolamine (entry 18).

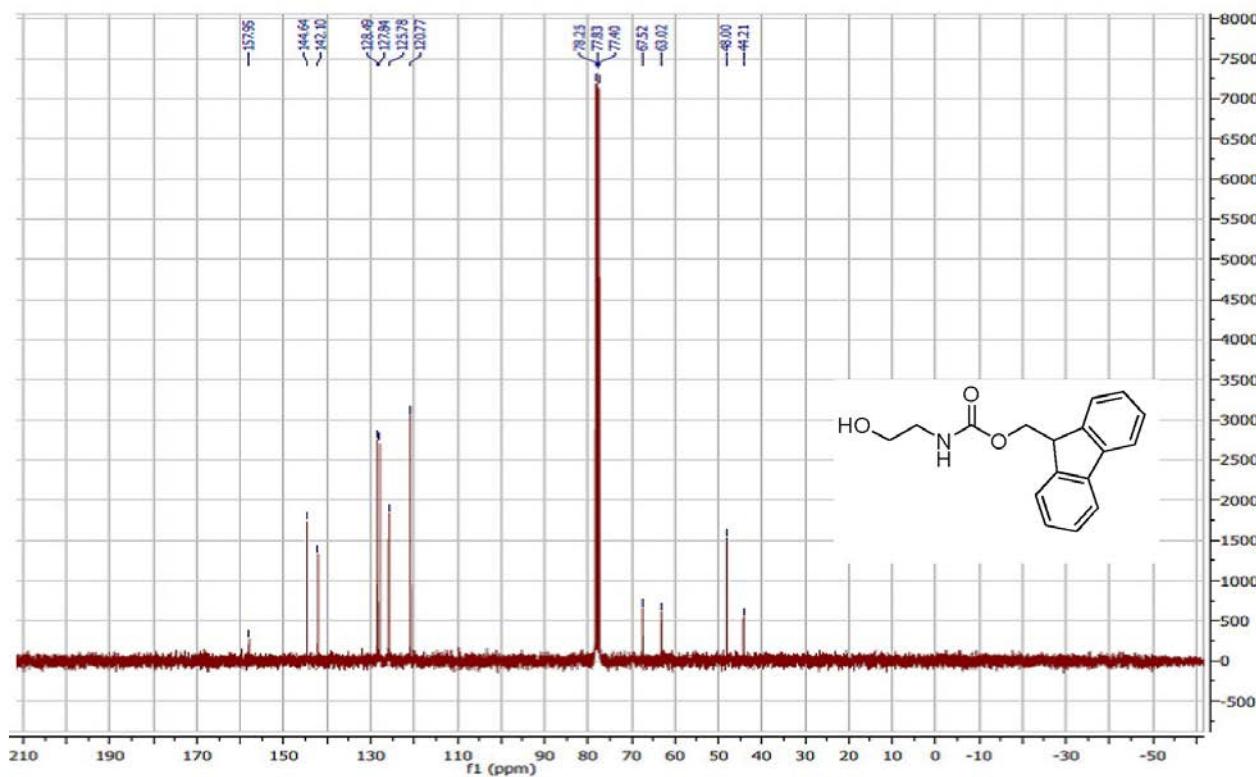


Figure S23. ¹³C NMR spectrum (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) ethanolamine (entry 18).

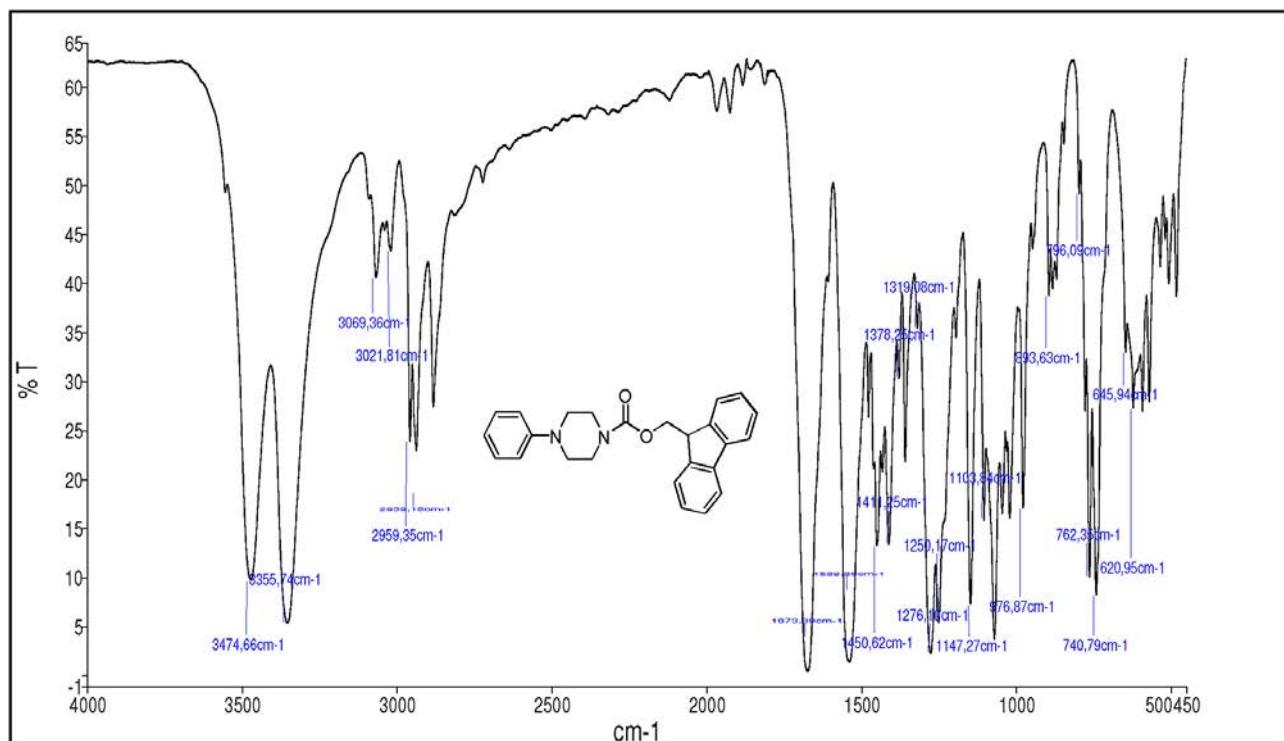


Figure S24. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) ethanolamine (entry 18).

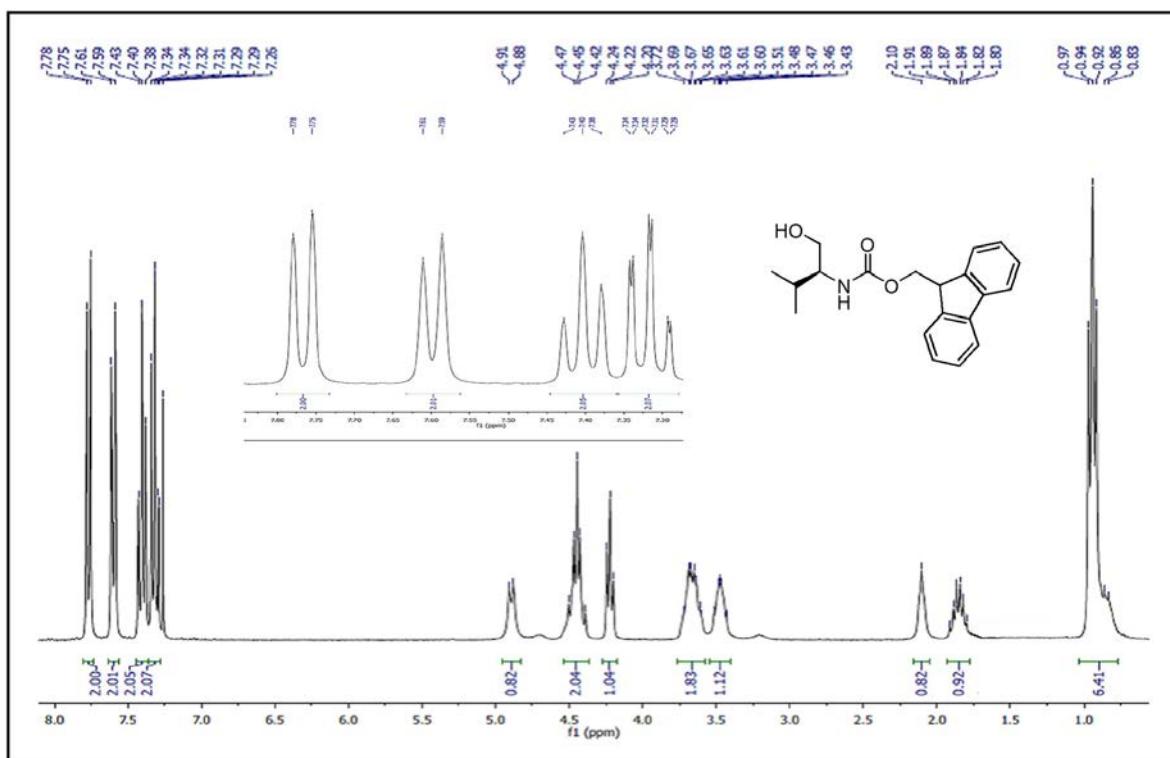


Figure S25. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) valinol (entry 20).

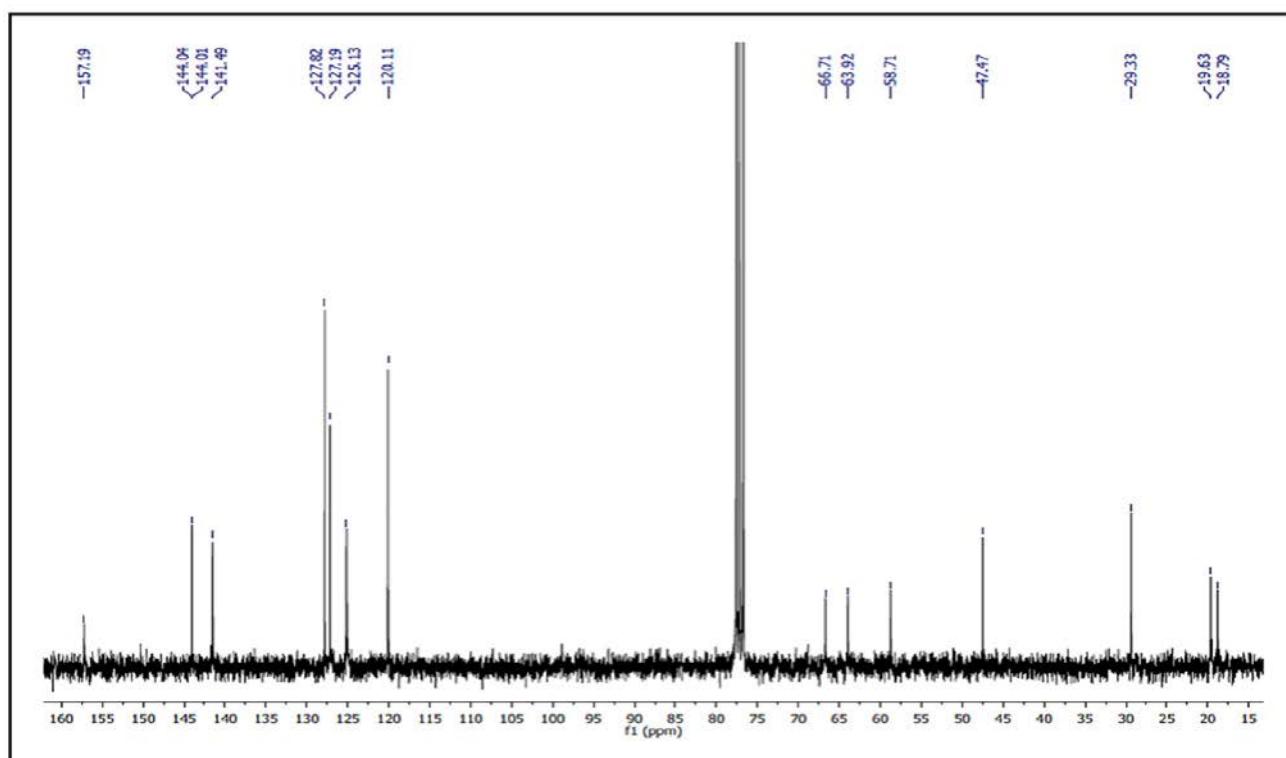


Figure S26. ^{13}C NMR spectrum (100 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) valinol (entry 20).

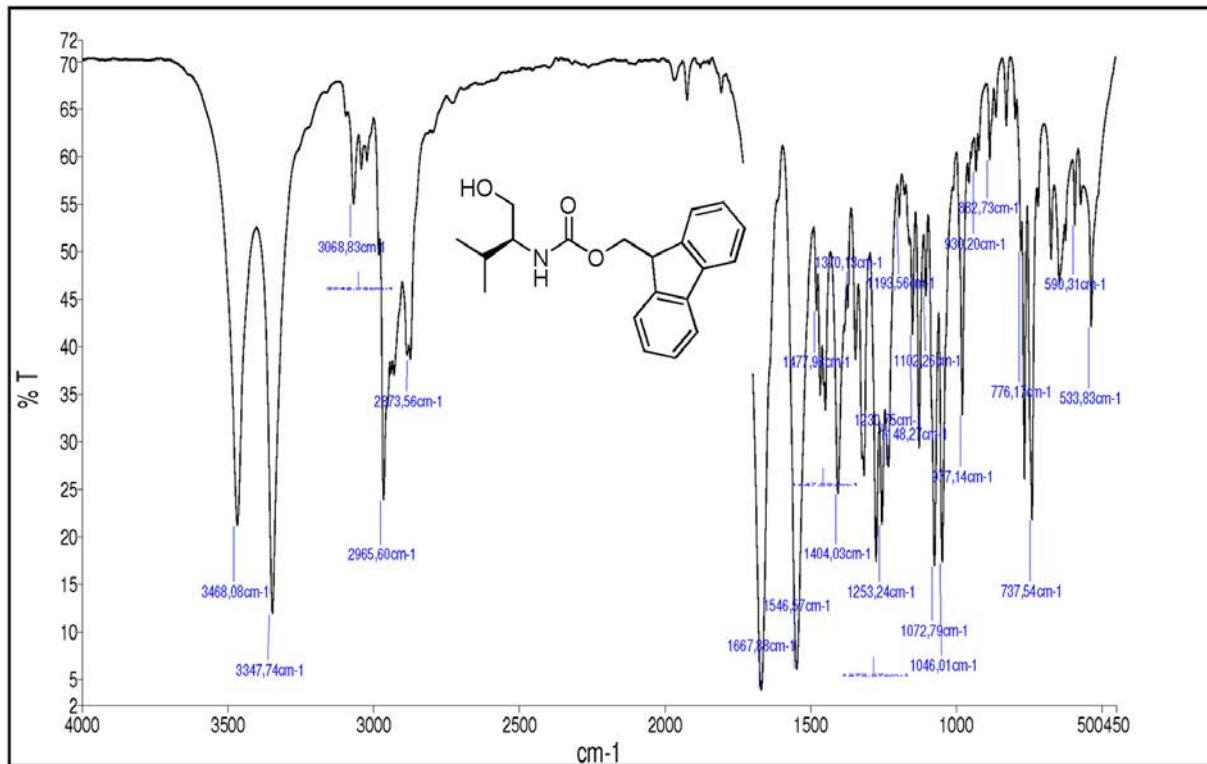


Figure S27. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) valinol (entry 20).

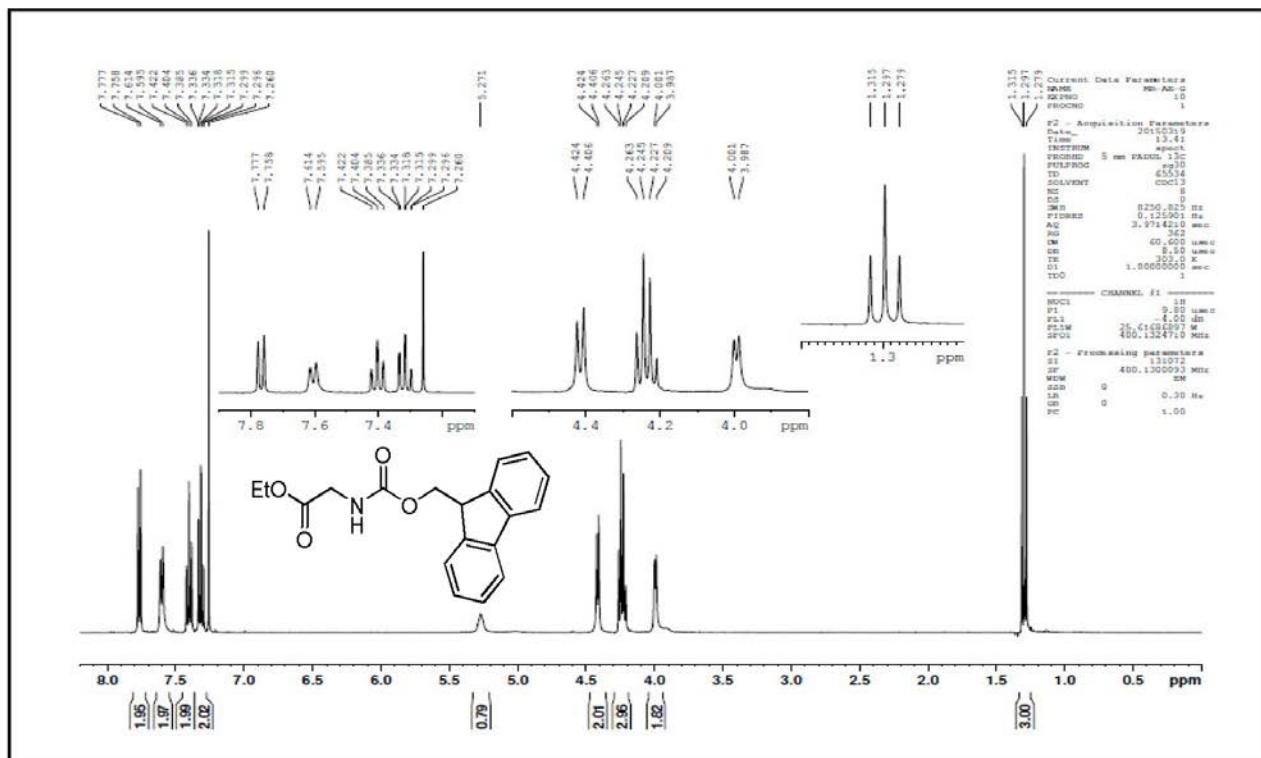


Figure S28. ^1H NMR spectrum (400 MHz, CDCl_3) of *N*-(9-fluorenylmethoxycarbonyl) glycine ethyl ester (entry 23).

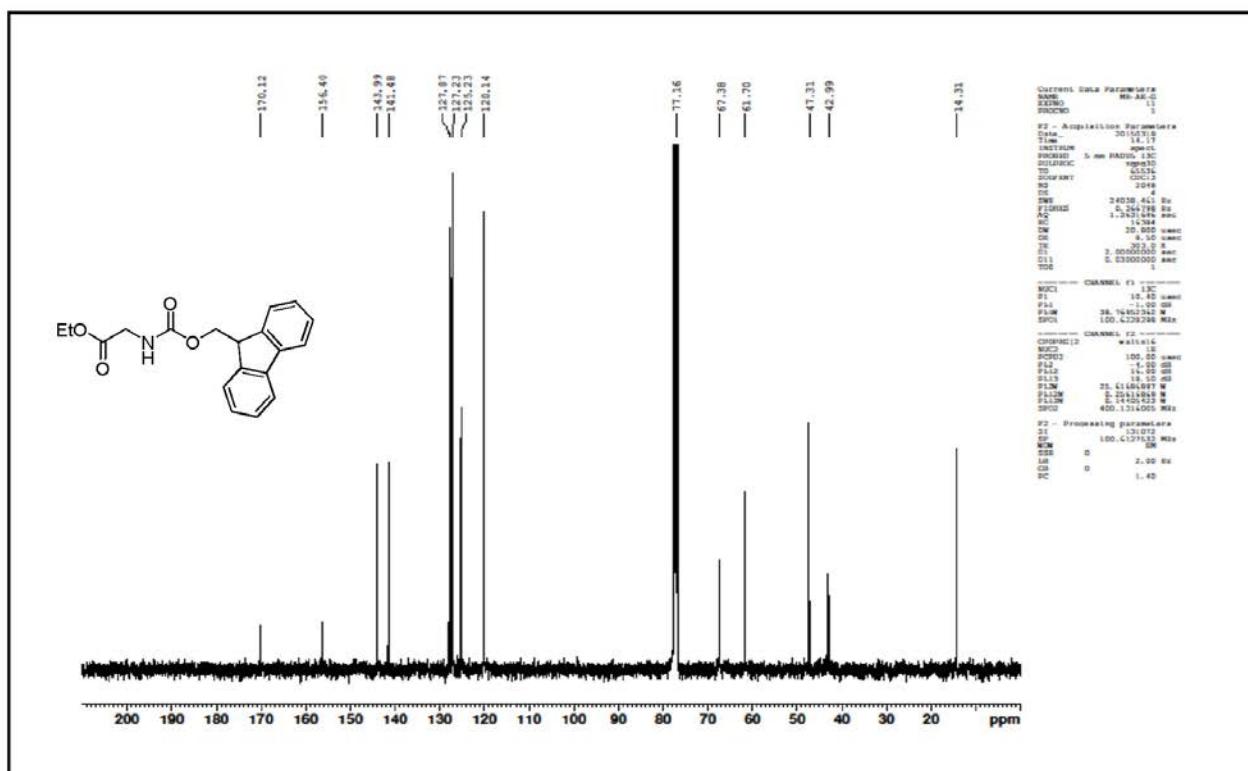


Figure S29. ¹³C NMR spectrum (100 MHz, CDCl₃) of *N*-(9-fluorenylmethoxycarbonyl) glycine ethyl ester (entry 23).

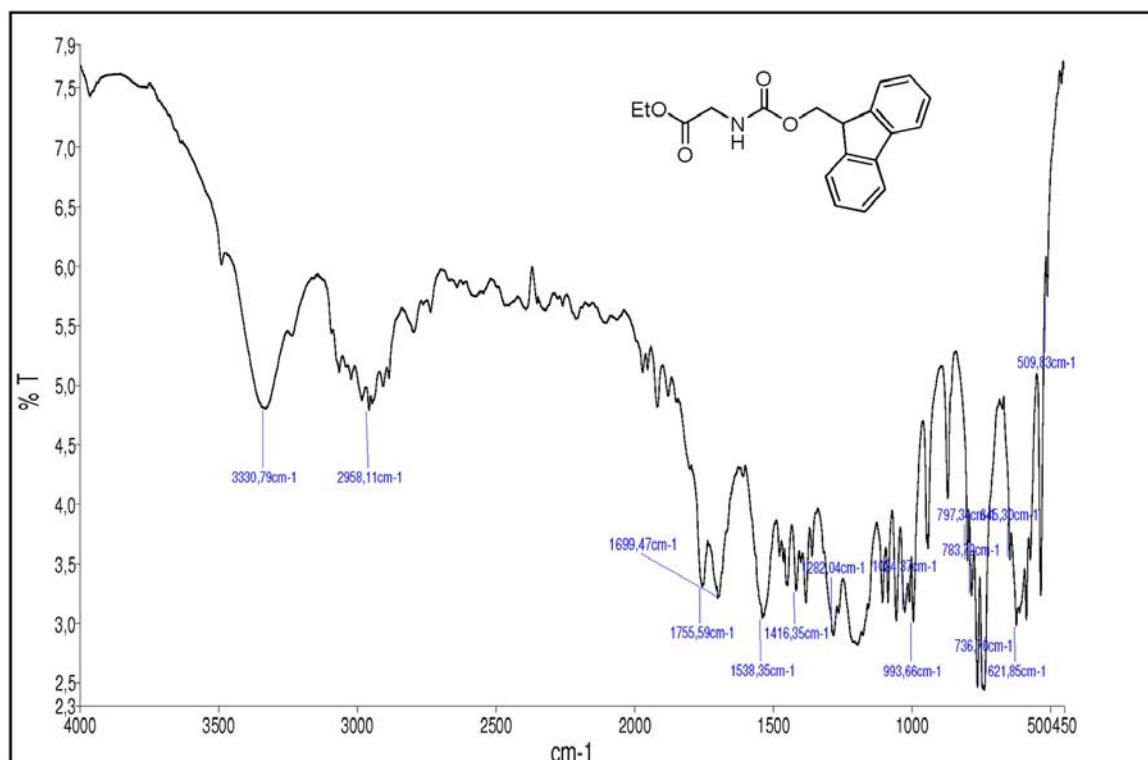


Figure S30. FTIR (KBr) spectrum of *N*-(9-fluorenylmethoxycarbonyl) glycine ethyl ester (entry 23).

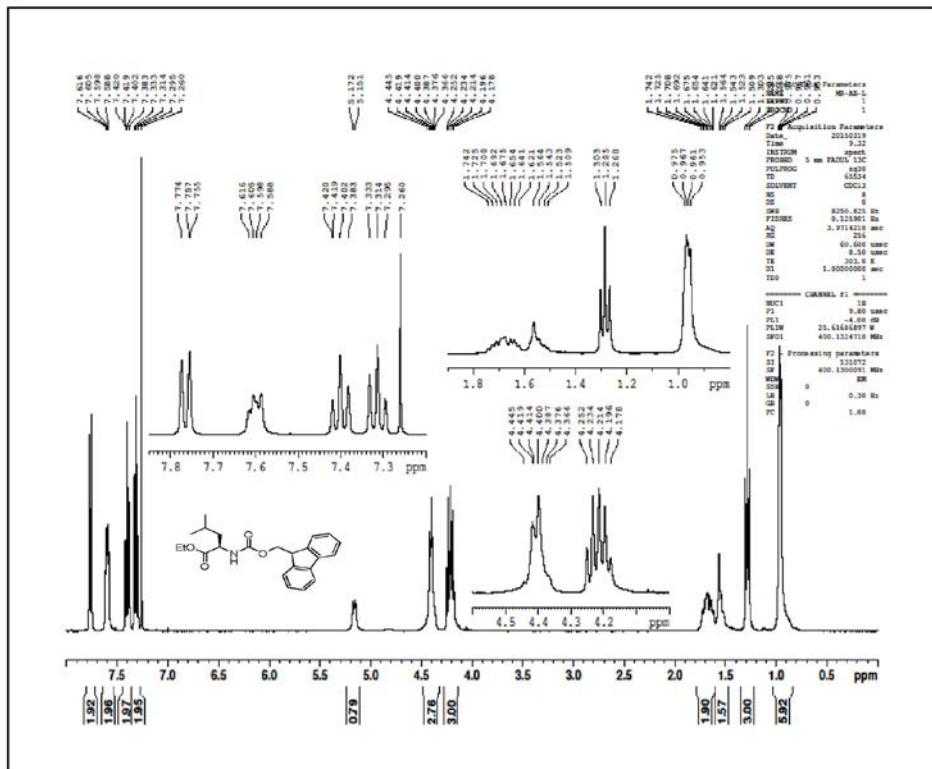


Figure S31. ^1H NMR spectrum (400 MHz, CDCl_3) of (S)(-)N-(9-fluorenylmethoxycarbonyl) leucine ethyl ester (entry 26).

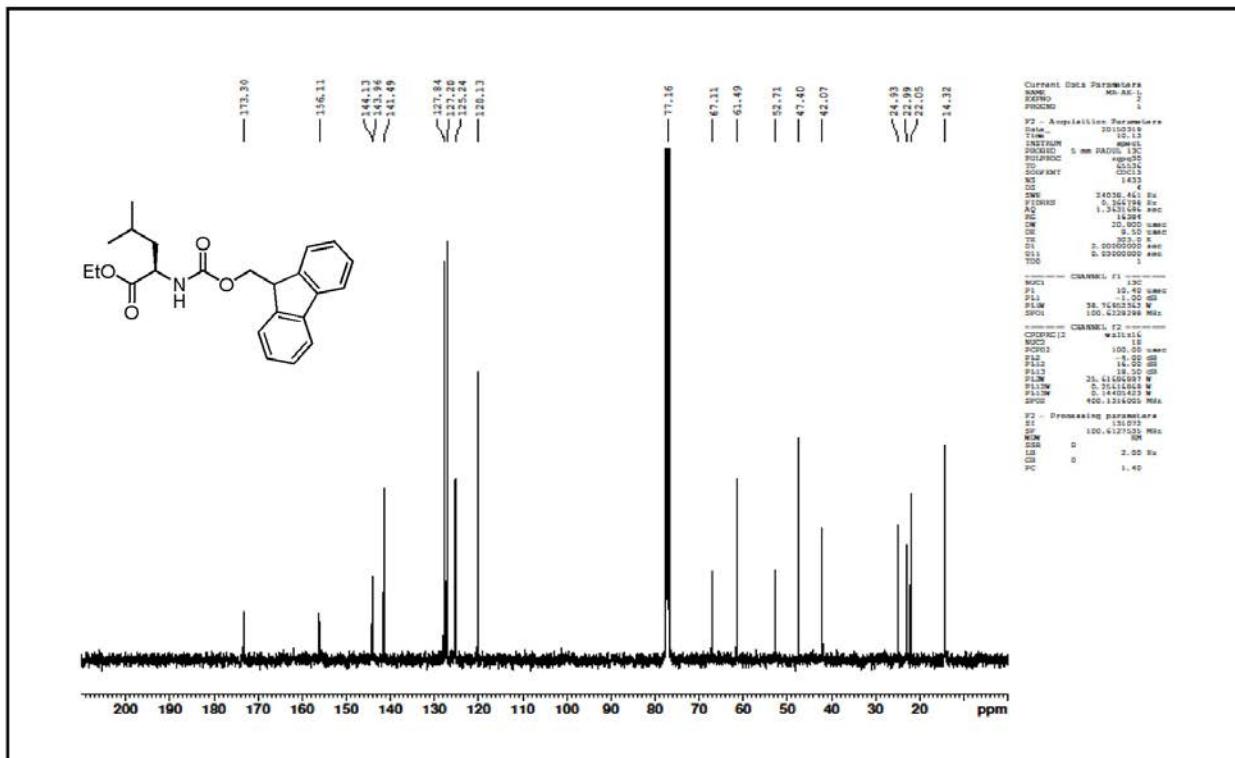


Figure S32. ^{13}C NMR spectrum (100 MHz, CDCl_3) of (S)(-)N-(9-fluorenylmethoxycarbonyl) leucine ethyl ester (entry 26).

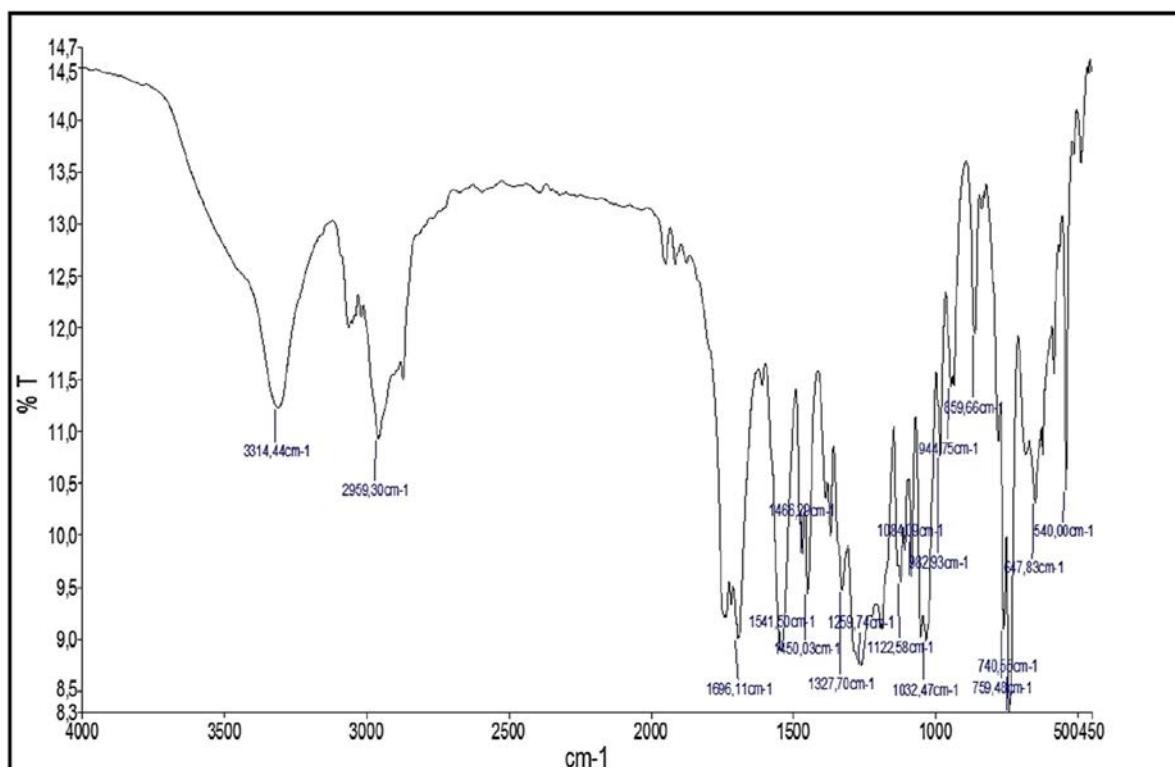


Figure S33. FTIR (KBr) spectrum of (S)(-)N-(9-fluorenylmethoxycarbonyl) leucine ethyl ester (entry 26).

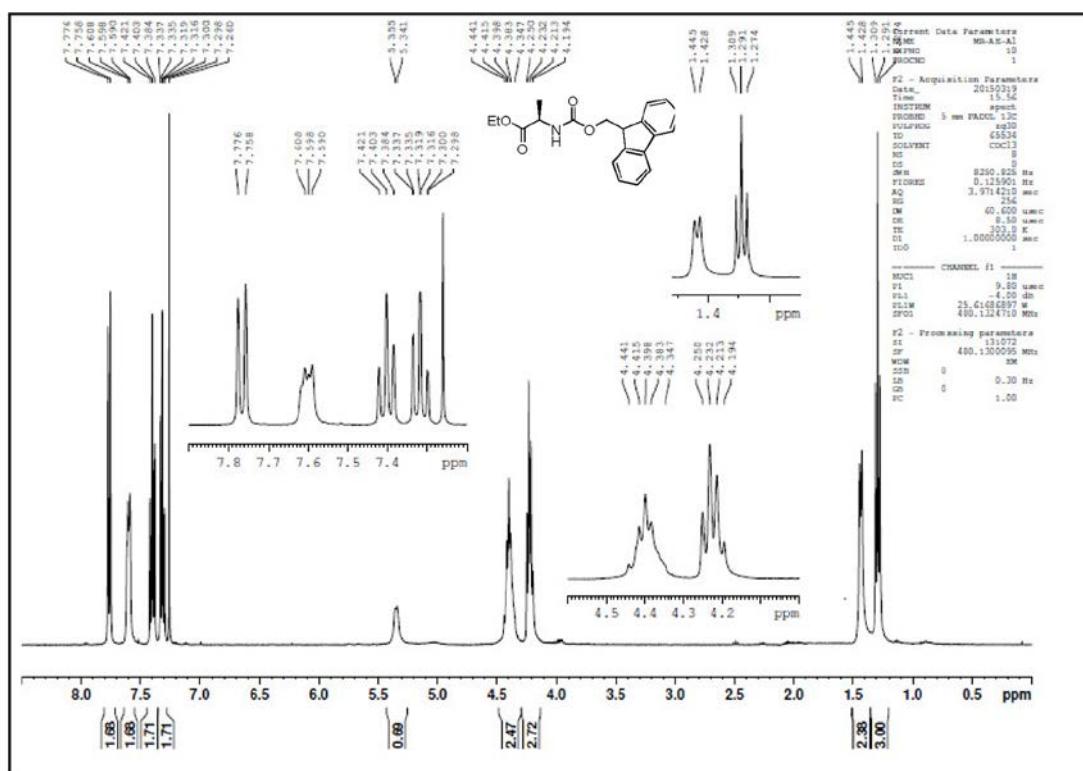


Figure S34. ^1H NMR spectrum (400 MHz, CDCl_3) of (S)(-)N-(9-fluorenylmethoxycarbonyl) alanine ethyl ester (entry 24).

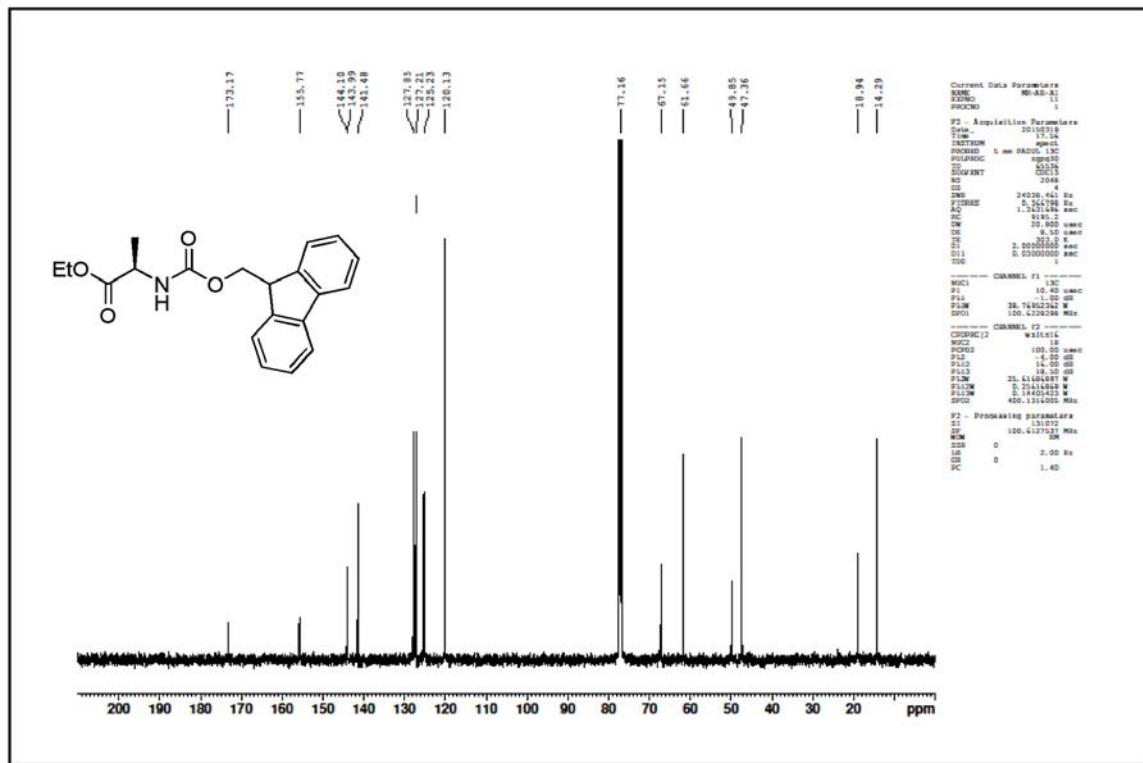


Figure S35. ¹³C NMR spectrum (100 MHz, CDCl₃) of (S)(-)N-(9-fluorenylmethoxycarbonyl) alanine ethyl ester (entry 24).

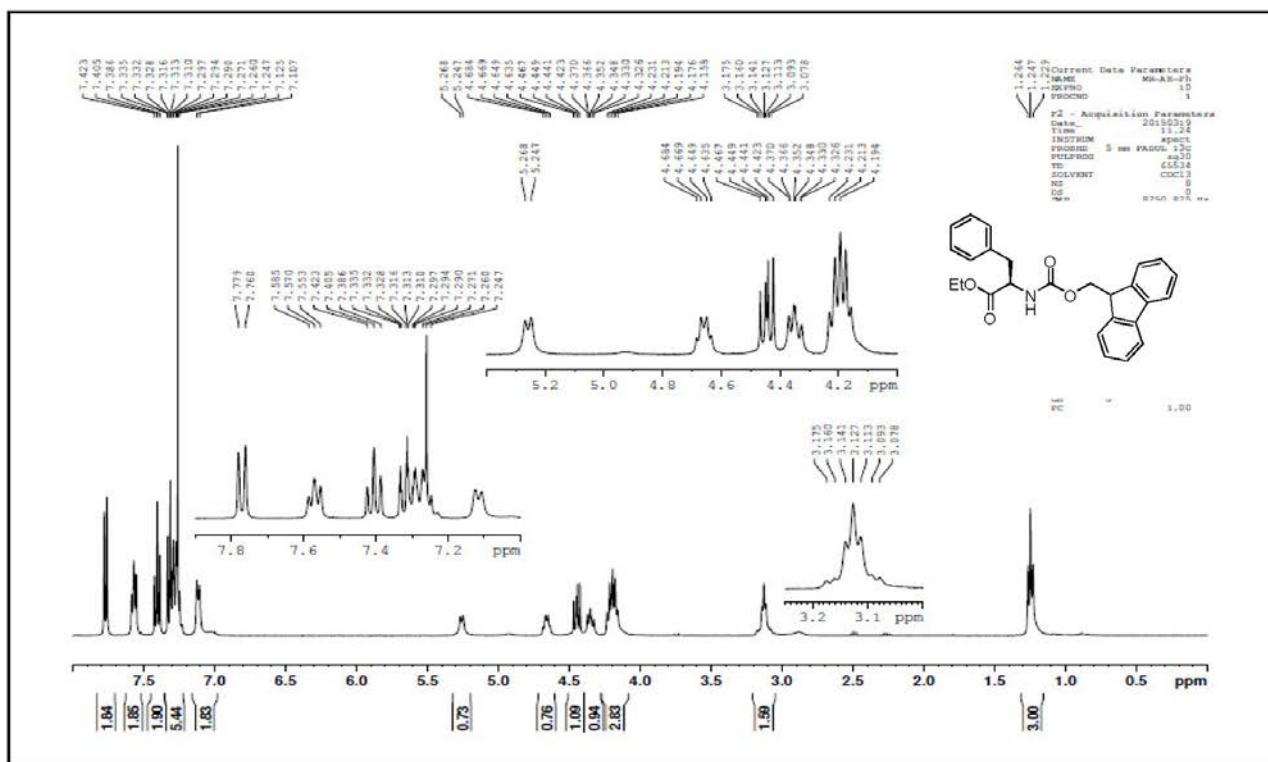


Figure S36. ¹H NMR spectrum (400 MHz, CDCl₃) of (S)(-)N-(9-fluorenylmethoxycarbonyl) phenylalanine ethyl ester (entry 27).

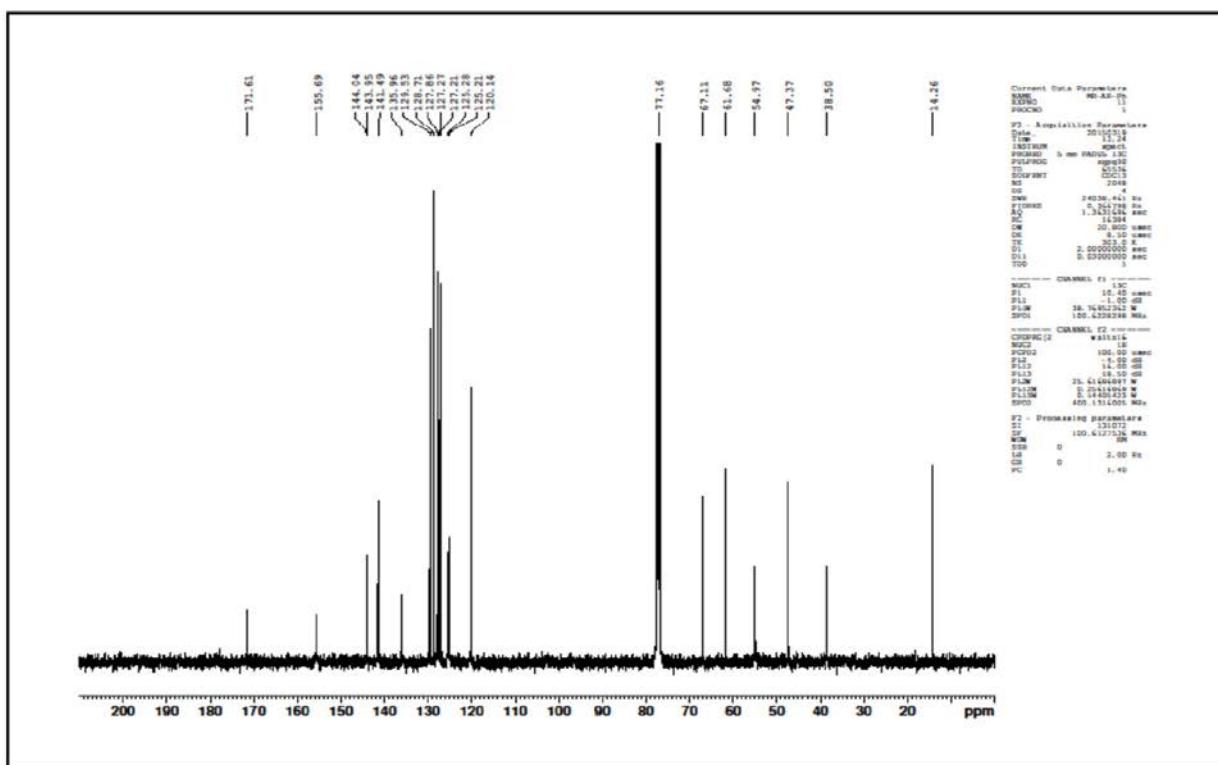


Figure S37. ^{13}C NMR spectrum (100 MHz, CDCl_3) of (S)(-)-*N*-(9-fluorenylmethoxycarbonyl) phenylalanine ethyl ester (entry 27).