

Supplementary Information

Syntheses and Structural Characterization of *o*-Carboranylamides with Direct Cage-Amide Bond

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Figure S1. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2a**

Figure S2. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **3a**

Figure S3. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2b**

Figure S4. IR, NMR (^{11}B { ^1H } and ^1H) spectra of compound **3b**

Figure S5. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2c**

Figure S6. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **3c**

Figure S7. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2d**

Figure S8. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2e**

Figure S9. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2f**

Figure S10. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **2g**

Figure S11. IR, NMR (^{11}B { ^1H } and ^1H) and EI-MS spectra of compound **5**

Figure S12. Hydrogen bond interactions in the crystal of **2a**

Figure S13. Hydrogen bond interactions in the crystal of **3a**

Figure S14. Hydrogen bond interactions in the crystal of **2b**

Figure S15. Hydrogen bond interactions in the crystal of **2c**

Figure S16. Hydrogen bond interactions in the crystal of **2d**

Figure S17. Hydrogen bond interactions in the crystal of **2f**

Table S1. Information on the hydrogen bond interactions in **2a-f**, **3a** and **5**

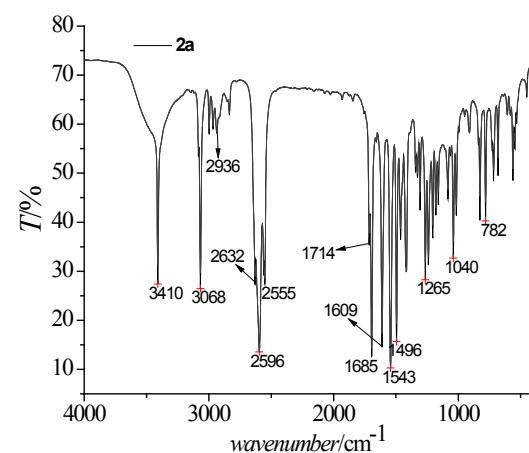


Figure S1 (a). IR spectrum of compound **2a**

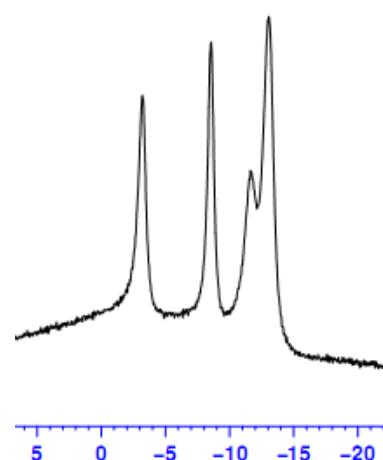


Figure S1 (b). ¹¹B {¹H} NMR spectrum of compound **2a** (in CDCl₃)

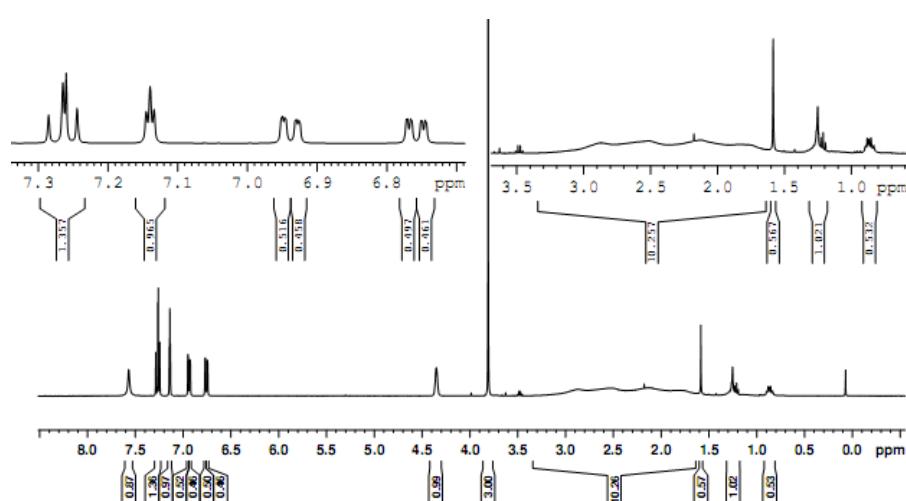


Figure S1 (c). ¹H NMR spectrum of compound **2a** (in CDCl₃)

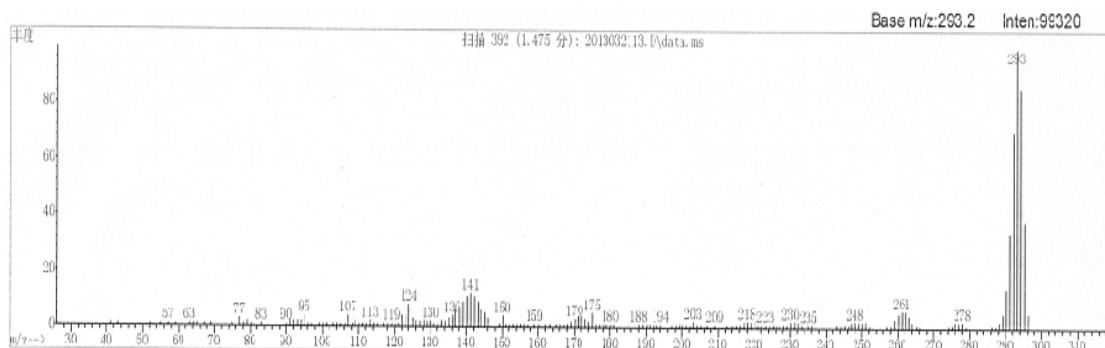


Figure S1 (d). EI-MS spectrum of compound **2a**

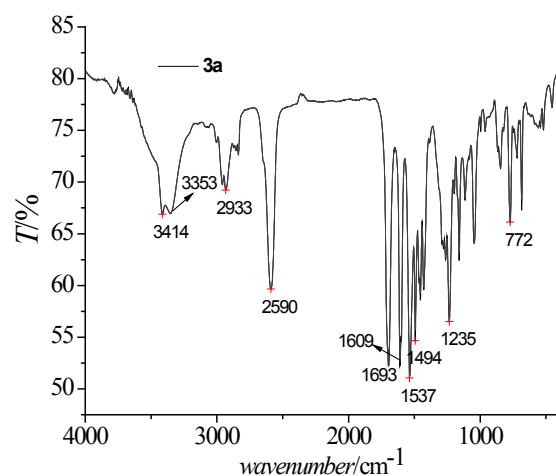


Figure S2 (a). IR spectrum of compound **3a**

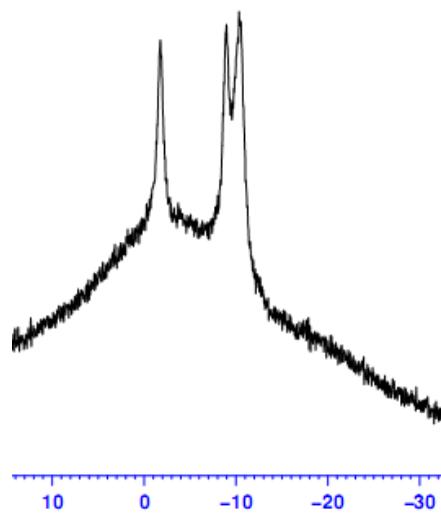


Figure S2 (b). ¹¹B {¹H} NMR spectrum of compound **3a** (in CDCl₃)

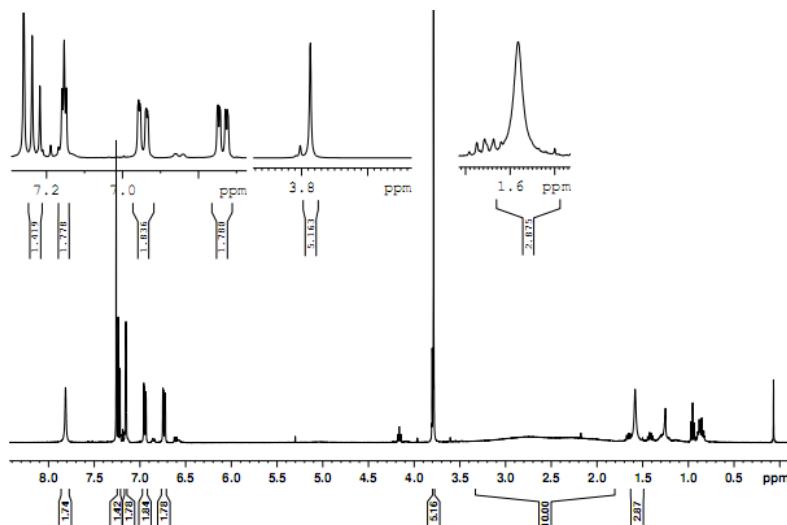


Figure S2 (c). ¹H NMR spectrum of compound 3a (in CDCl₃)

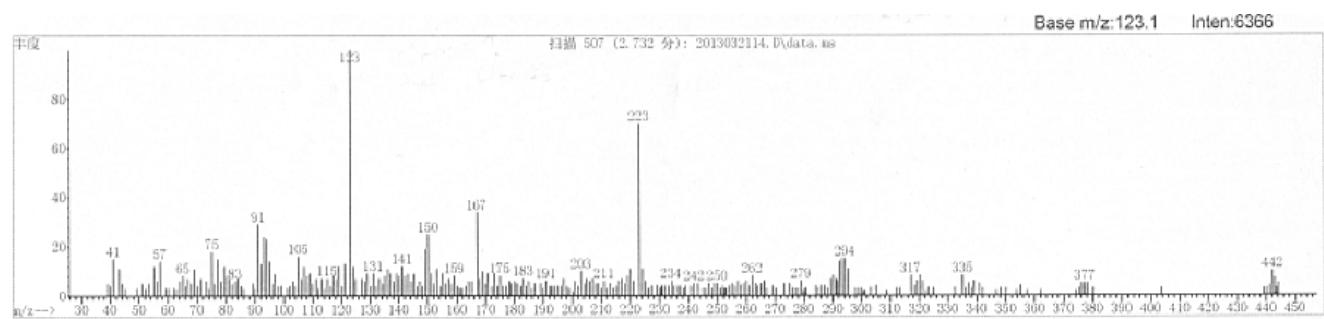


Figure S2 (d). EI-MS spectrum of compound 3a

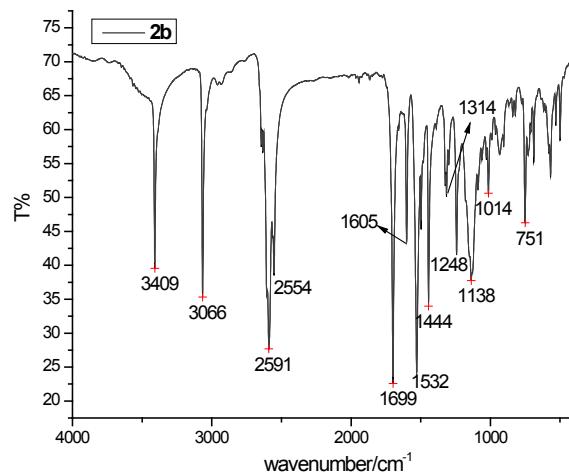


Figure S3 (a). IR spectrum of compound 2b

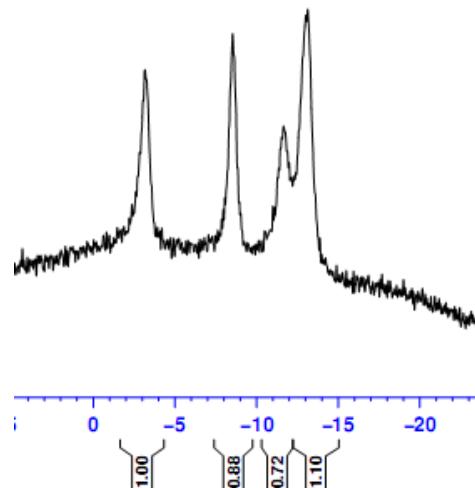


Figure S3 (b). ^{11}B { ^1H } NMR spectrum of compound **2b** (in CDCl_3)

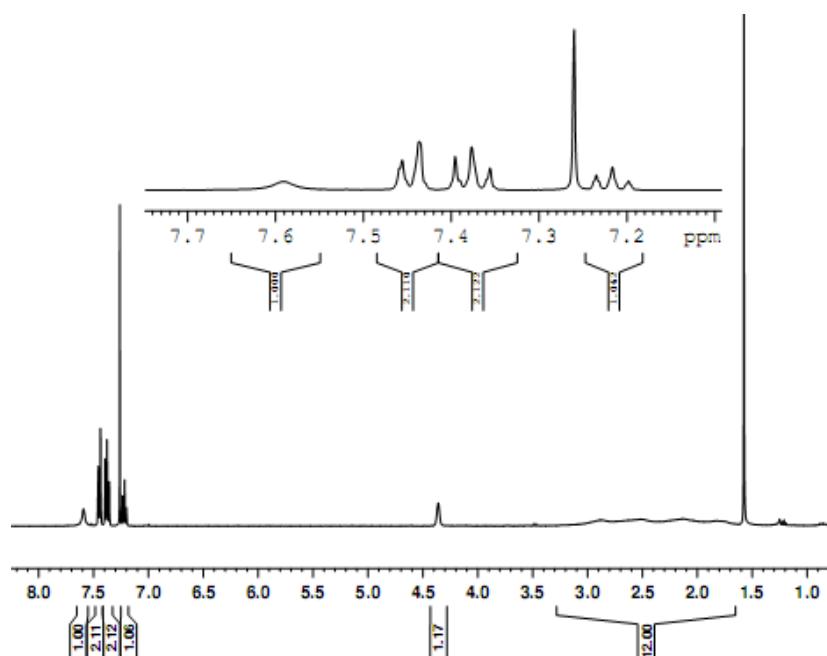


Figure S3 (c). ^1H NMR spectrum of compound **2b** (in CDCl_3)

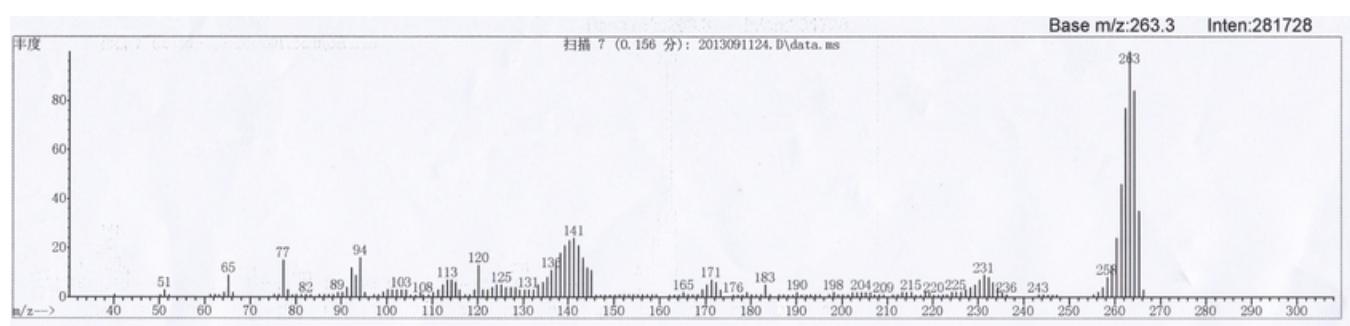


Figure S3 (d). EI-MS spectrum of compound **2b**

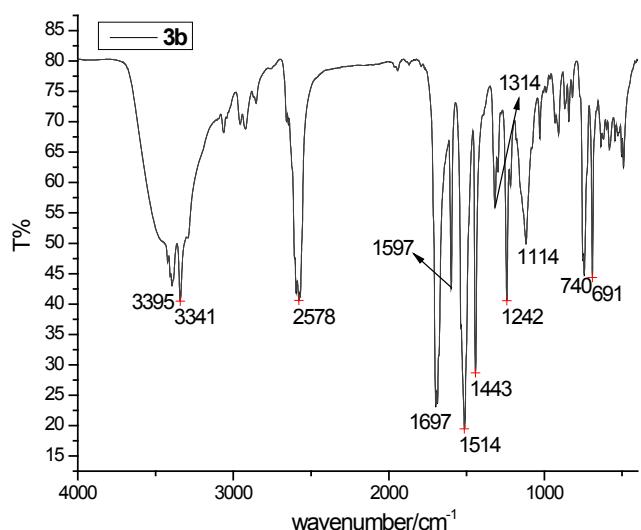


Figure S4 (a). IR spectrum of compound 3b

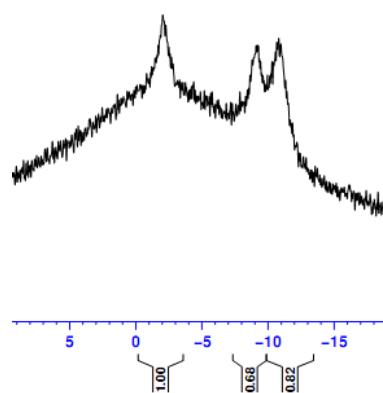


Figure S4 (b). ¹¹B-¹H NMR spectrum of compound 3b (in CDCl₃)

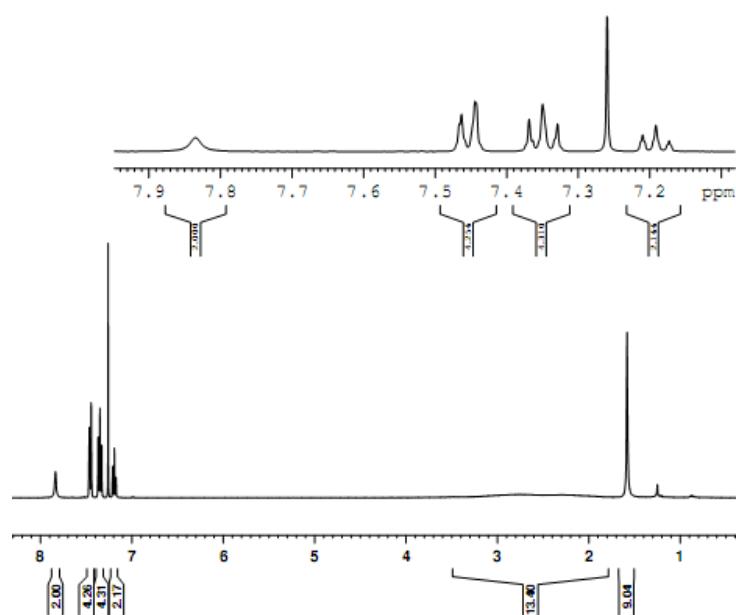


Figure S4 (c). ¹H NMR spectrum of compound 3b (in CDCl₃)

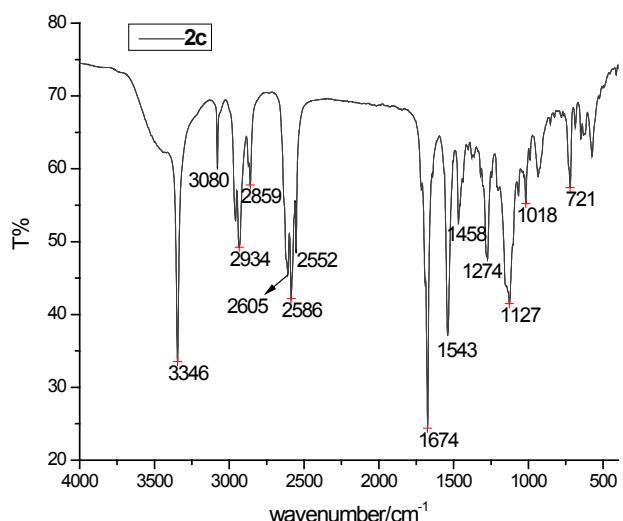


Figure S5 (a). IR spectrum of compound **2c**

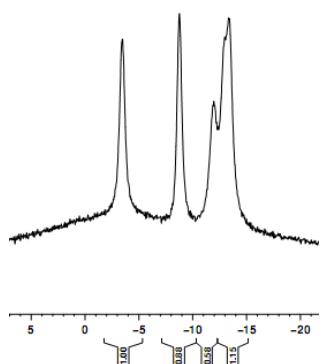


Figure S5 (b). ^{11}B { ^1H } NMR spectrum of compound **2c** (in CDCl_3)

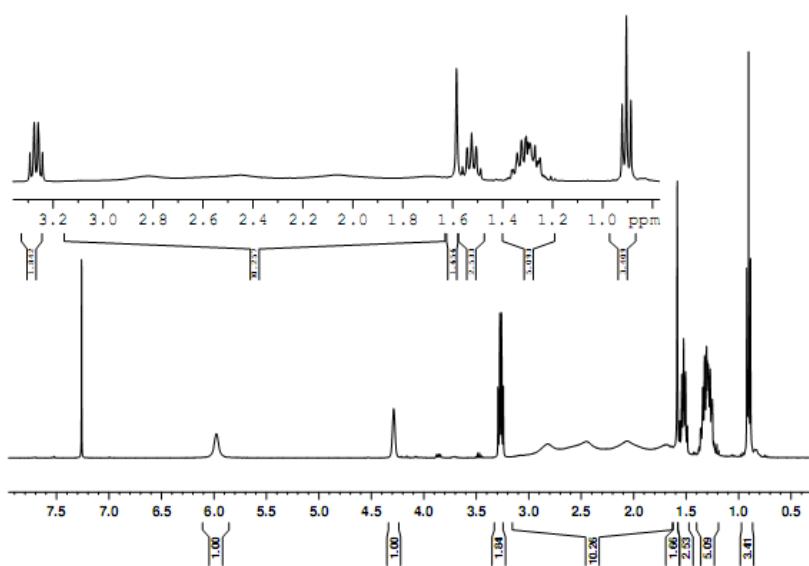


Figure S5 (c). ^1H NMR spectrum of compound **2c** (in CDCl_3)

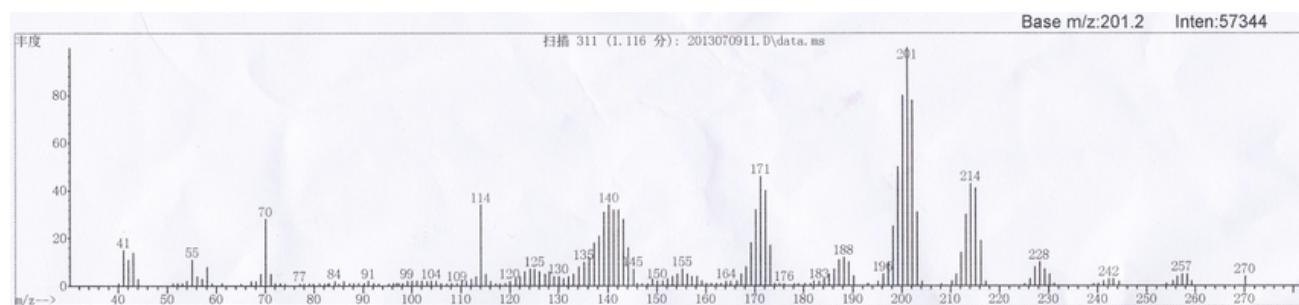


Figure S5 (d). EI-MS spectrum of compound **2c**

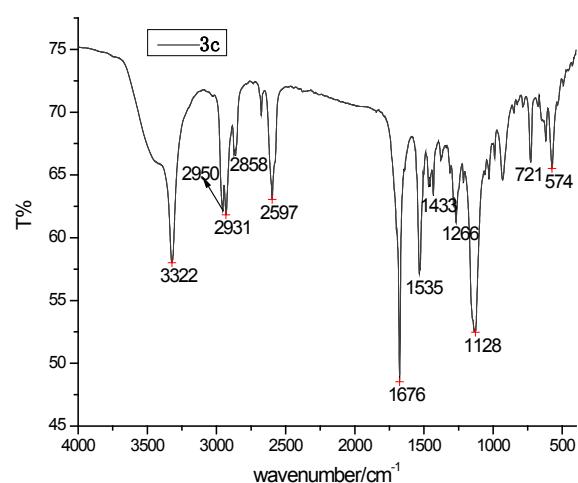


Figure S6 (a). IR spectrum of compound **3c**

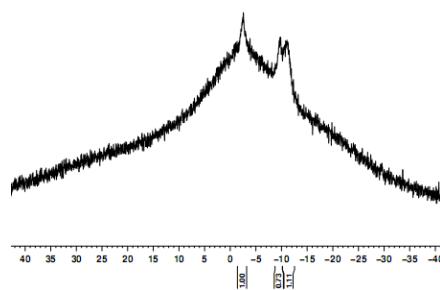


Figure S6 (b). ^{11}B { ^1H } NMR spectrum of compound **3c** (in CDCl_3)

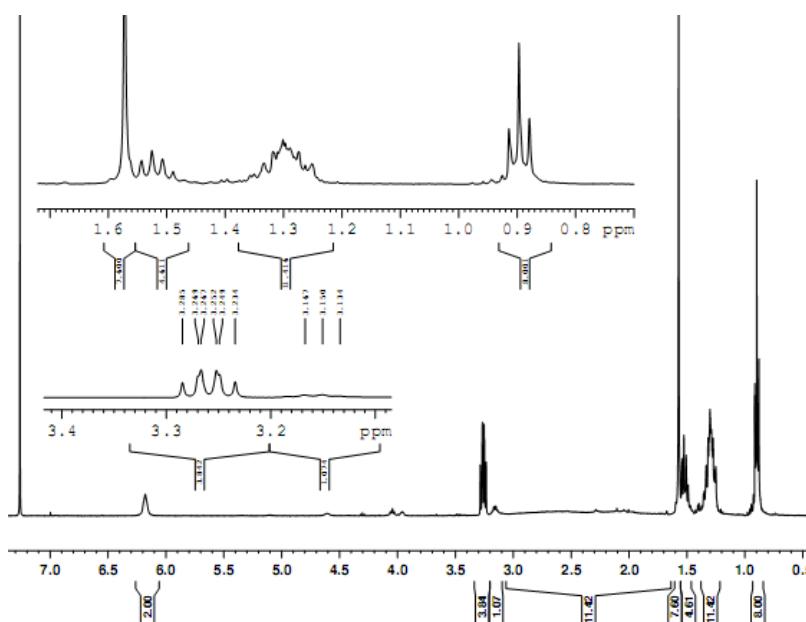


Figure S6 (c). ¹H NMR spectrum of compound 3c (in CDCl₃)

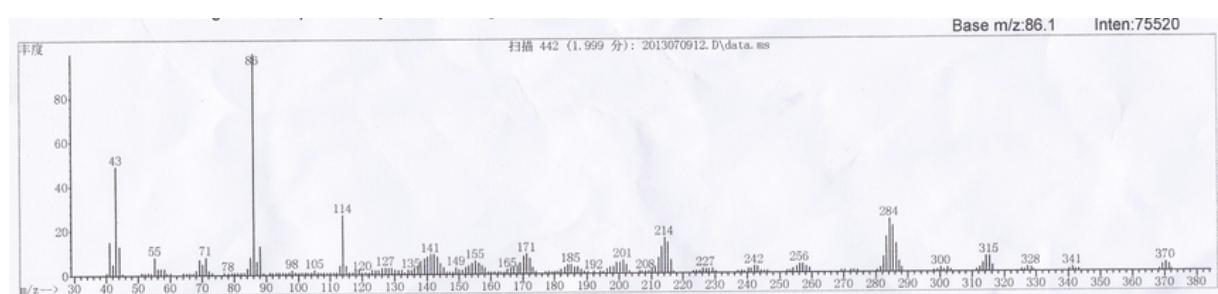


Figure S6 (d). EI-MS spectrum of compound 3c

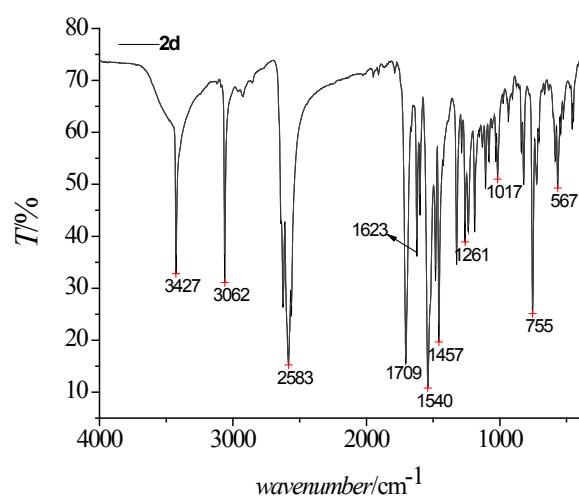


Figure S7 (a). IR spectrum of compound 2d

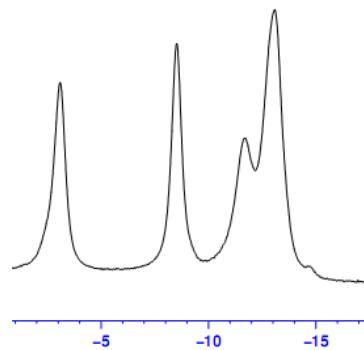


Figure S7 (b). ^{11}B { ^1H } NMR spectrum of compound **2d** (in CDCl_3)

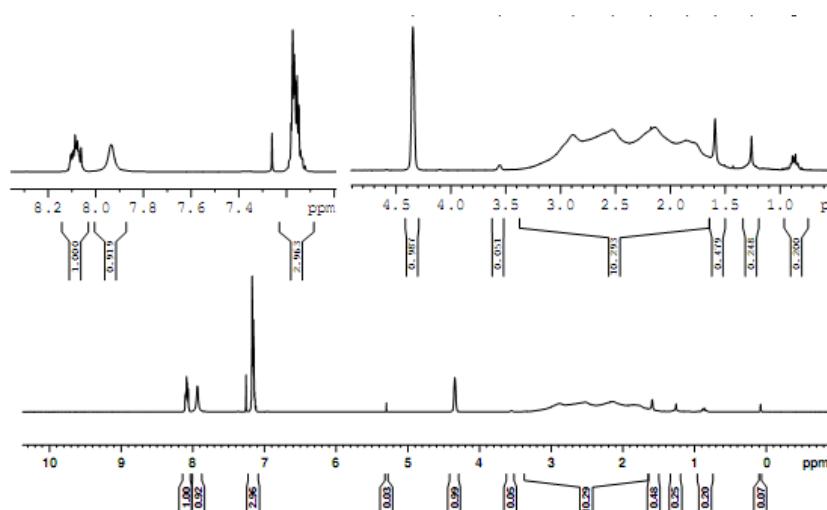


Figure S7 (c). ^1H NMR spectrum of compound **2d** (in CDCl_3)

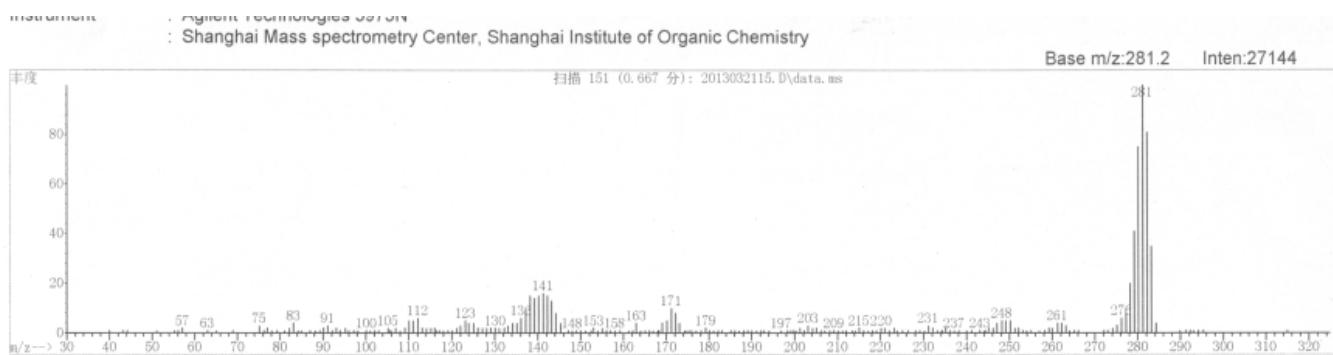


Figure S7 (d). EI-MS spectrum of compound **2d**

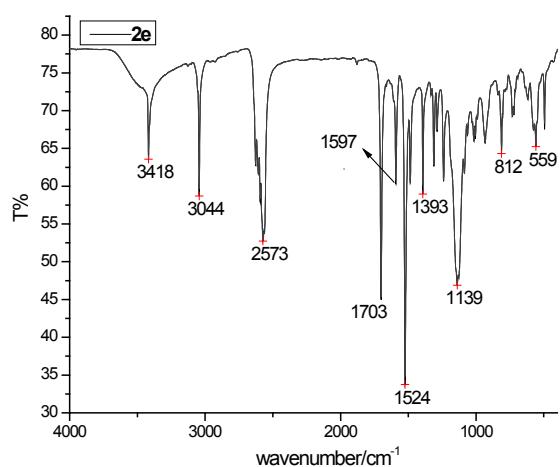


Figure S8 (a). IR spectrum of compound **2e**

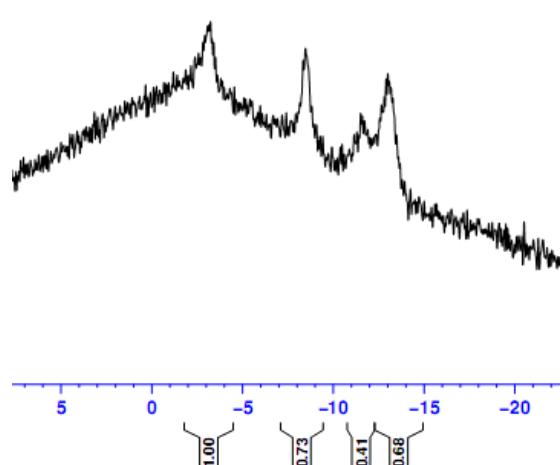


Figure S8 (b). $^{11}\text{B} \{^1\text{H}\}$ NMR spectrum of compound **2e** (in CDCl_3)

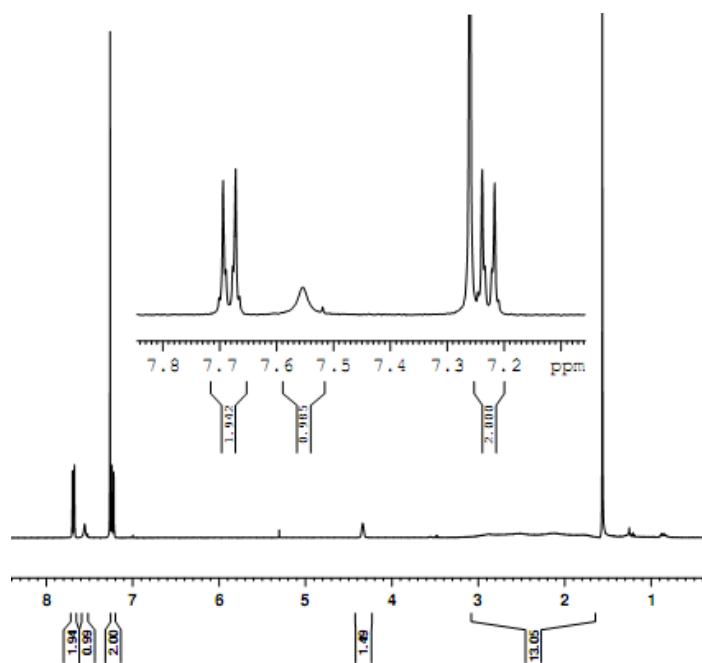


Figure S8 (c). ¹H NMR spectrum of compound 2e (in CDCl₃)

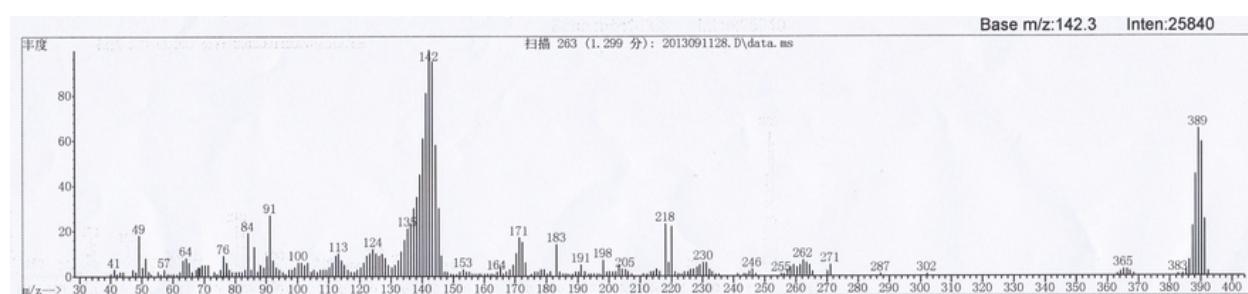


Figure S8 (d). EI-MS spectrum of compound 2e

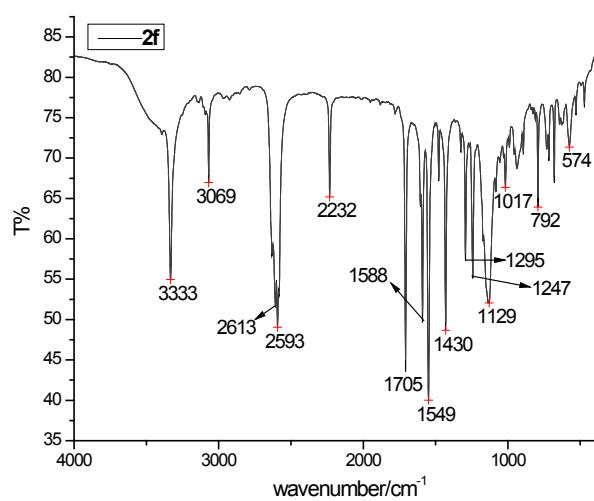


Figure S9 (a). IR spectrum of compound 2f

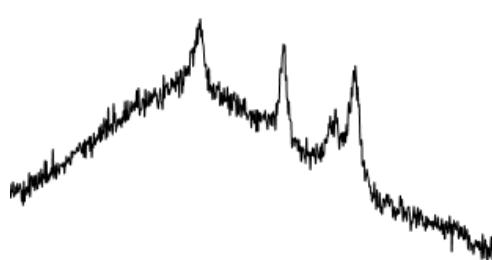


Figure S9 (b). ^{11}B { ^1H } NMR spectrum of compound **2f** (in CDCl_3)

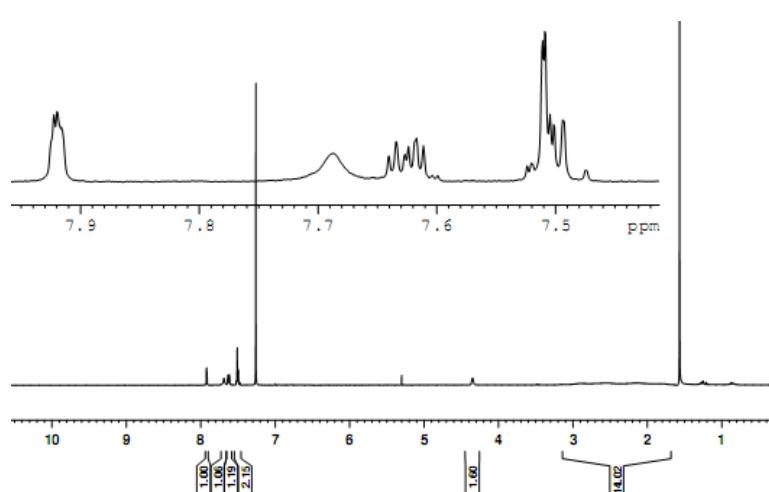


Figure S9 (c). ^1H NMR spectrum of compound **2f** (in CDCl_3)

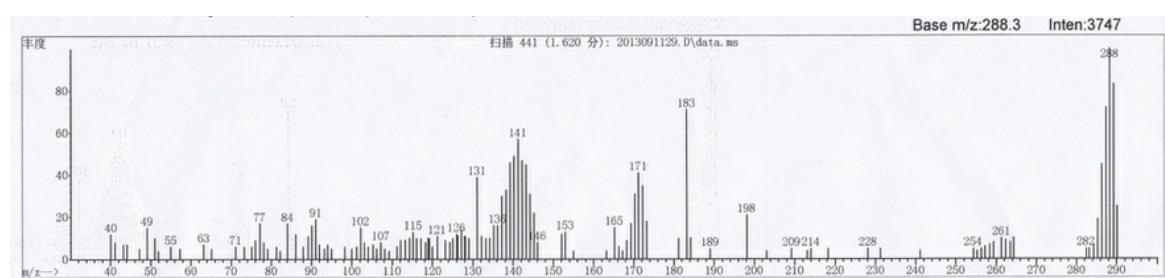


Figure S9 (d). EI-MS spectrum of compound **2f**

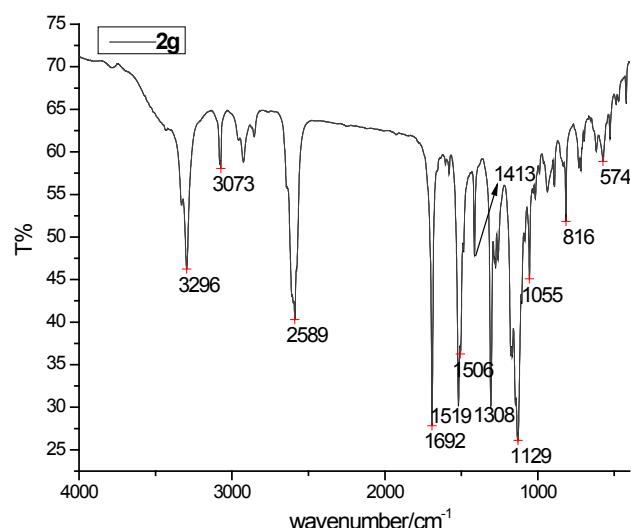


Figure S10 (a). IR spectrum of compound **2g**

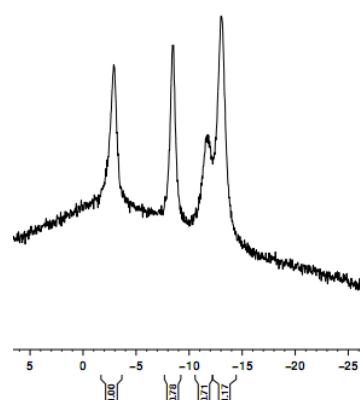


Figure S10 (b). ¹¹B {¹H} NMR spectrum of compound **2g** (in CDCl₃)

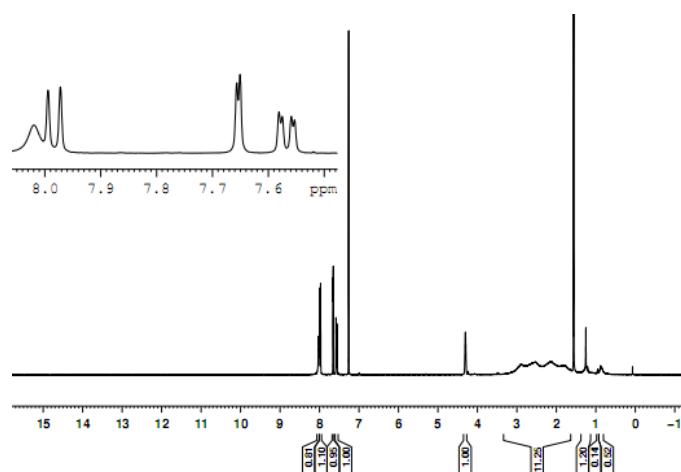


Figure S10 (c). ¹H NMR spectrum of compound **2g** (in CDCl₃)

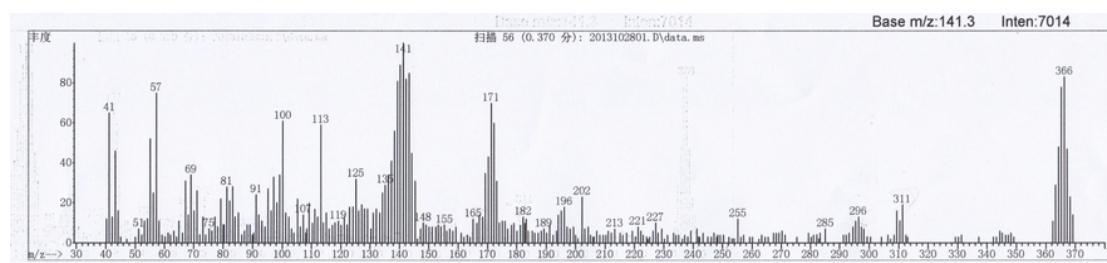


Figure S10 (d). EI-MS spectrum of compound **2g**

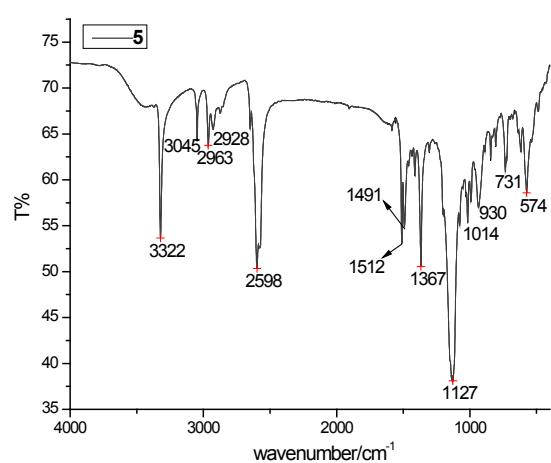


Figure S11 (a). IR spectrum of compound **5**

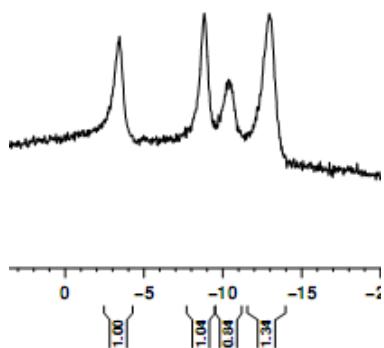


Figure S11 (b). ^{11}B { ^1H } NMR spectrum of compound **5** (in CDCl_3)

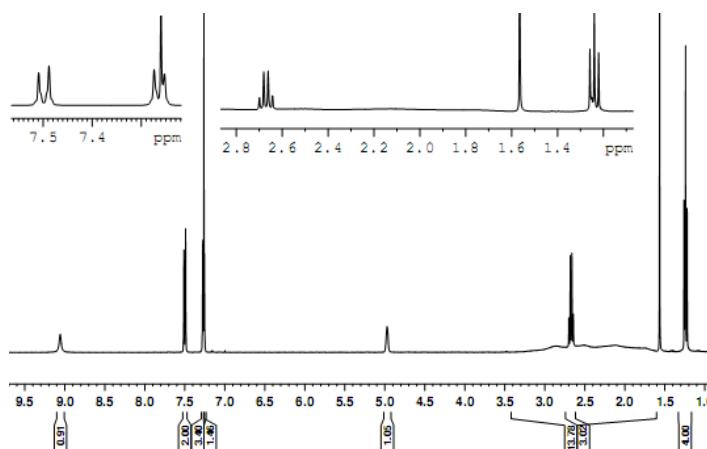


Figure S11 (c). ^1H NMR spectrum of compound 5 (in CDCl_3)

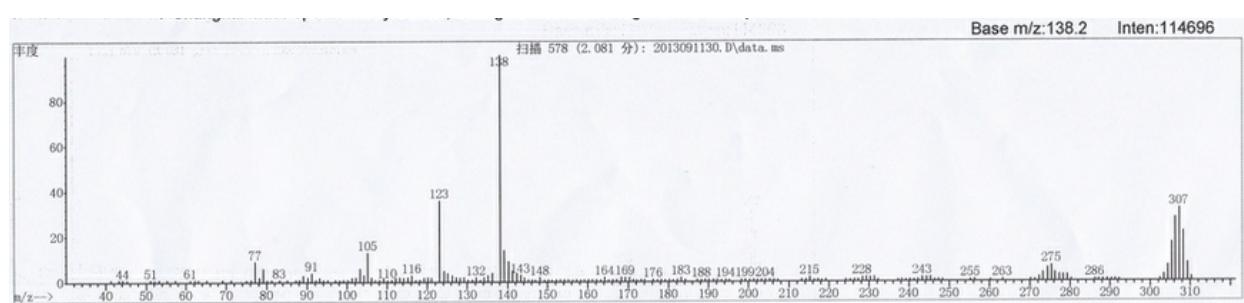


Figure S11 (d). EI-MS spectrum of compound 5

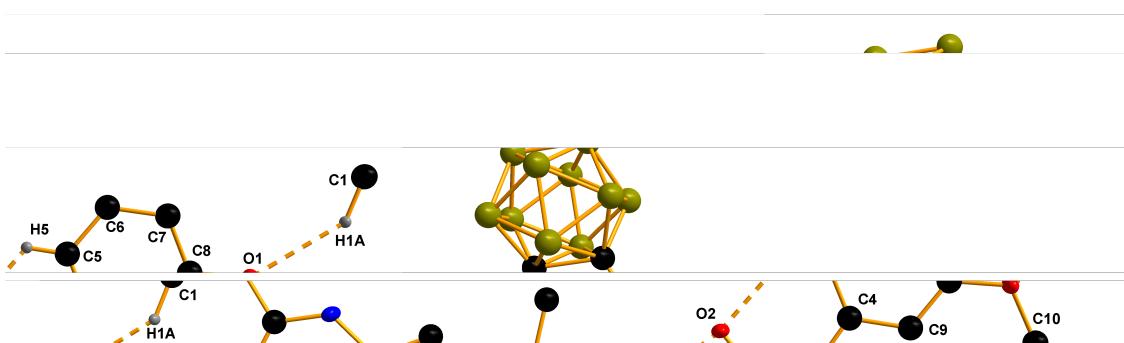


Fig. S12 Hydrogen bond interactions in the crystal of 2a (only the hydrogen atoms involved are shown).

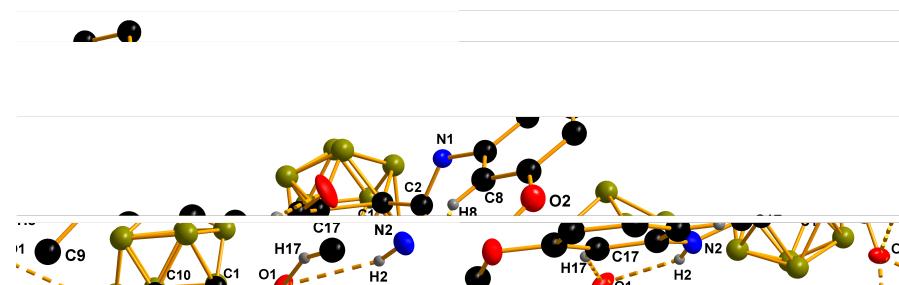


Fig. S13 Hydrogen bond interactions in the crystal of **3a** (only the hydrogen atoms involved are shown).

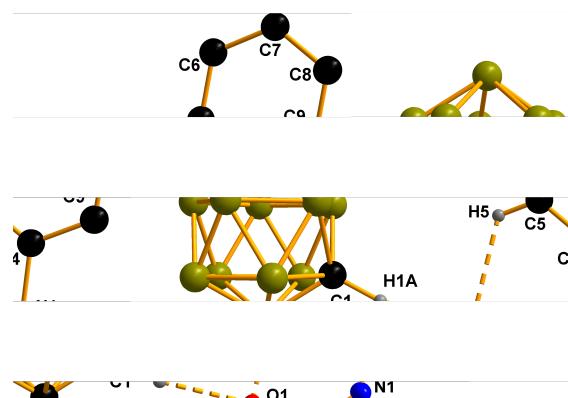


Fig. S14 Hydrogen bond interactions in the crystal of **2b** (only the hydrogen atoms involved are shown).

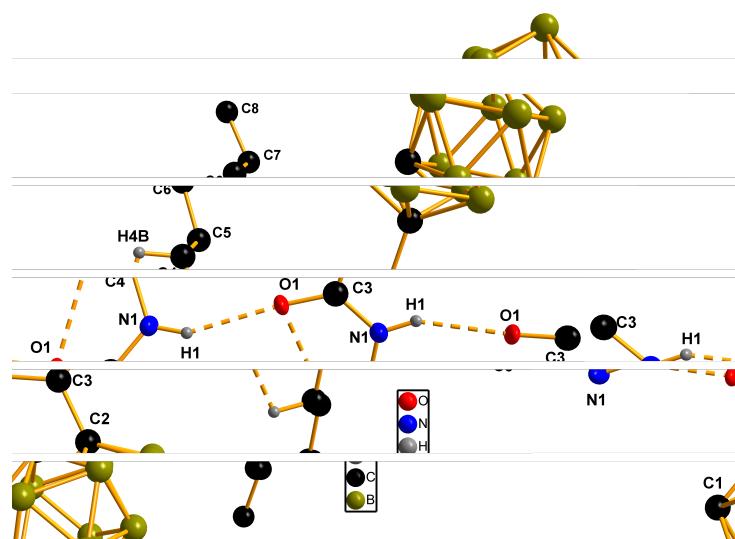


Fig. S15 Hydrogen bond interactions in the crystal of **2c** (only the hydrogen atoms involved are shown).

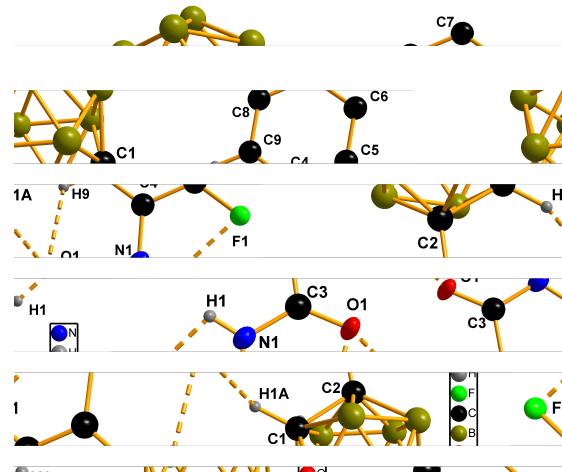


Fig. S16 Hydrogen bond interactions in the crystal of **2d** (only the hydrogen atoms involved are shown).

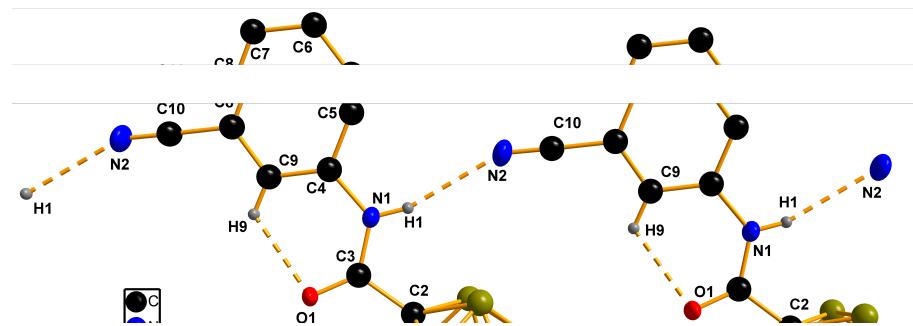


Fig. S17 Hydrogen bond interactions in the crystal of **2f** (only the hydrogen atoms involved are shown).

Table S1 Information on the hydrogen bond interactions in **2a-f**, **3a** and **5**

| Compounds | D-H···A | d(H···A)/ Å | d(D-A)/Å | $\angle(D\text{-}H\cdots A)^\circ$ |
|-----------|----------------------------------|-------------|----------|------------------------------------|
| 2a | C(5)-H(5)···O(2) | 2.28 | 2.879(3) | 122 |
| | C(1)-H(1A)···O(1) ⁱ | 2.44 | 3.381(3) | 143 |
| 3a | N(2)-H(2)···O(1) ⁱⁱ | 2.42 | 3.177(3) | 148 |
| | C(8)-H(8)···O(1) | 2.59 | 2.947(4) | 103 |
| | C(13)-H(13)···O(3) | 2.28 | 2.814(4) | 116 |
| | C(17)-H(17)···O(1) ⁱⁱ | 2.25 | 3.100(4) | 152 |
| 2b | C(5)-H(5)···O(1) | 2.32 | 2.877(3) | 118 |
| | C(1)-H(1A)···O(1) ⁱⁱⁱ | 2.12 | 3.104(3) | 147 |
| 2c | N(1)-H(1)···O(1) ^{iv} | 2.18 | 2.969(2) | 152 |
| | C(4)-H(4B)···O(1) | 2.48 | 2.836(3) | 102 |
| 2d | C(1)-H(1A)···O(1) ^v | 2.40 | 3.287(3) | 137 |

| | | | | |
|-----------|------------------------------|------|----------|-----|
| | C(9)-H(9)…O(1) | 2.39 | 2.917(3) | 116 |
| | N(1)-H(1)…F(1) | 2.29 | 2.628(3) | 104 |
| 2e | C(9)-H(9)…O(1) | 2.28 | 2.859(5) | 119 |
| 2f | N(1)-H(1)…N(2) ^{vi} | 2.50 | 3.327(3) | 163 |
| | C(9)-H(9)…O(1) | 2.30 | 2.874(3) | 119 |
| 5 | N(1)-H(1)…H(4)-B(4) | 2.21 | 2.92 | 139 |
| | C(1)-H(1A)…S(1) | 2.75 | 3.134(3) | 100 |

Symmetry codes: (i) $1 - x, 1/2 + y, 3/2 - z$; (ii) $x, 1/2 - y, 1/2 + z$; (iii) $-x, 1 - y, -z$; (iv) $3/2 - x, -1/2 + y, z$; (v) $-x, 1 - y, 2 - z$; (vi) $x, -1 + y, z$.