Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Hg(II) and Pd(II) complexes with a new selenoether bridged biscarbene ligand: Efficient mono- and bis-arylation of methyl acrylate with a pincer biscarbene Pd(II) precatalyst

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Contents

Heteronuclear NMR spectra and HRMS spectrum of $(LH_2)Br_2$

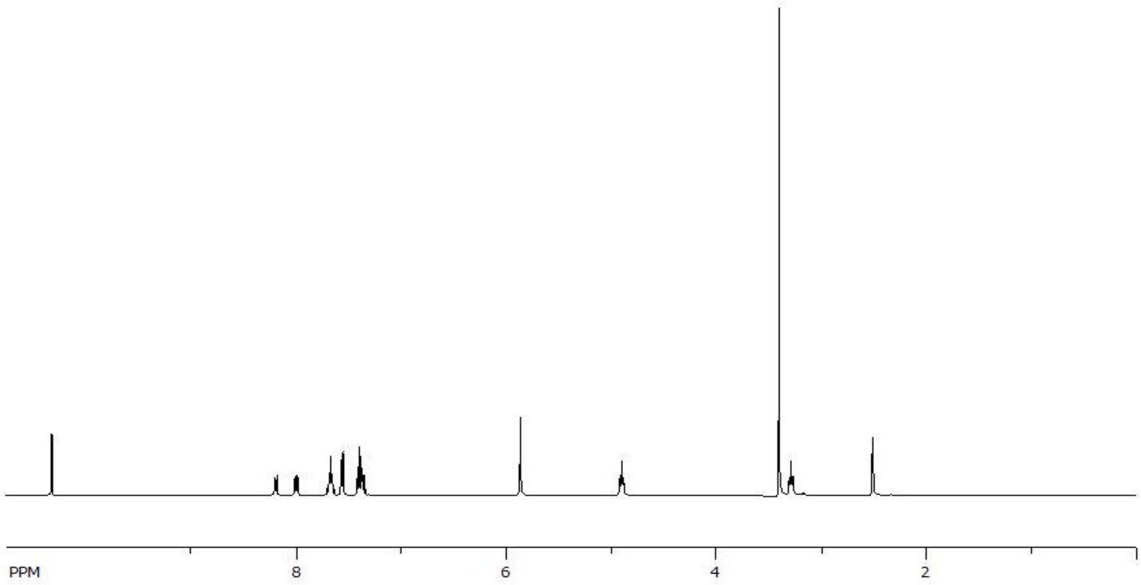


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of (**L**H_2)Br_2

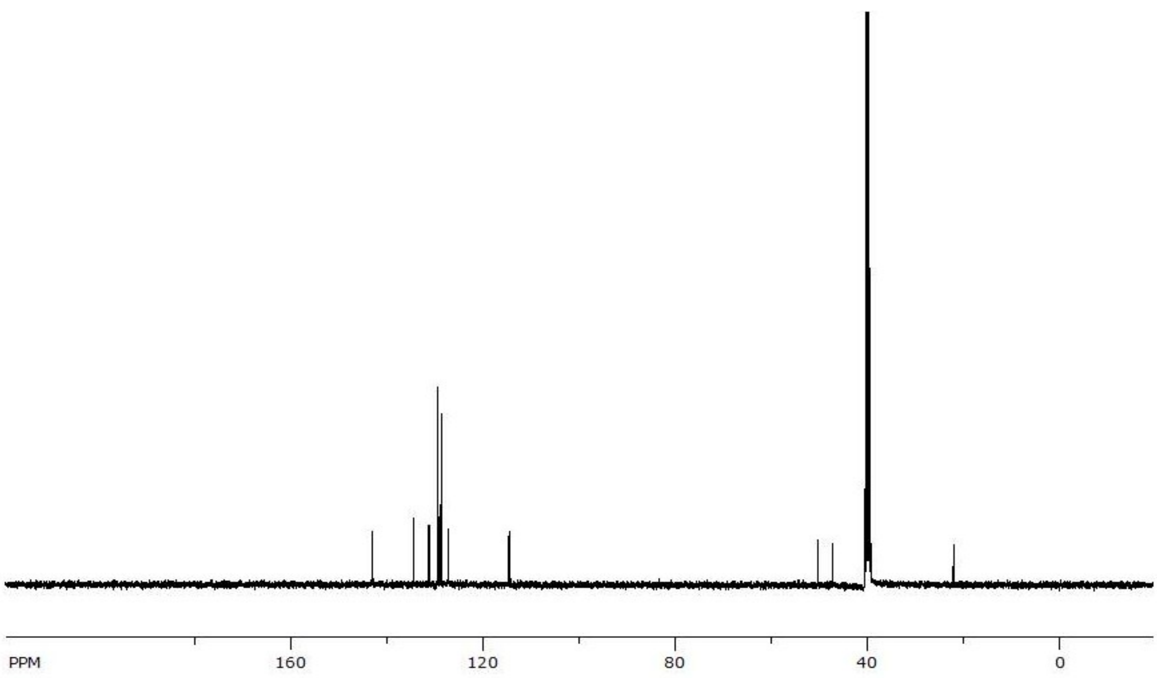


Figure S2. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of (**L**H_2)Br_2

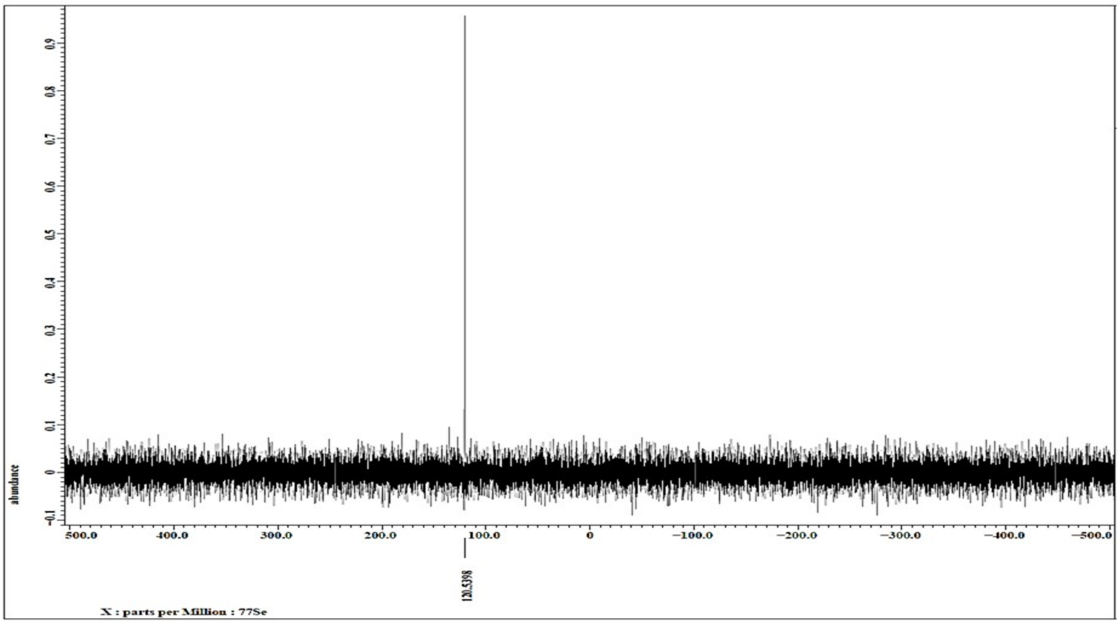


Figure S3. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d$_6$) of (**L**H$_2$)Br$_2$

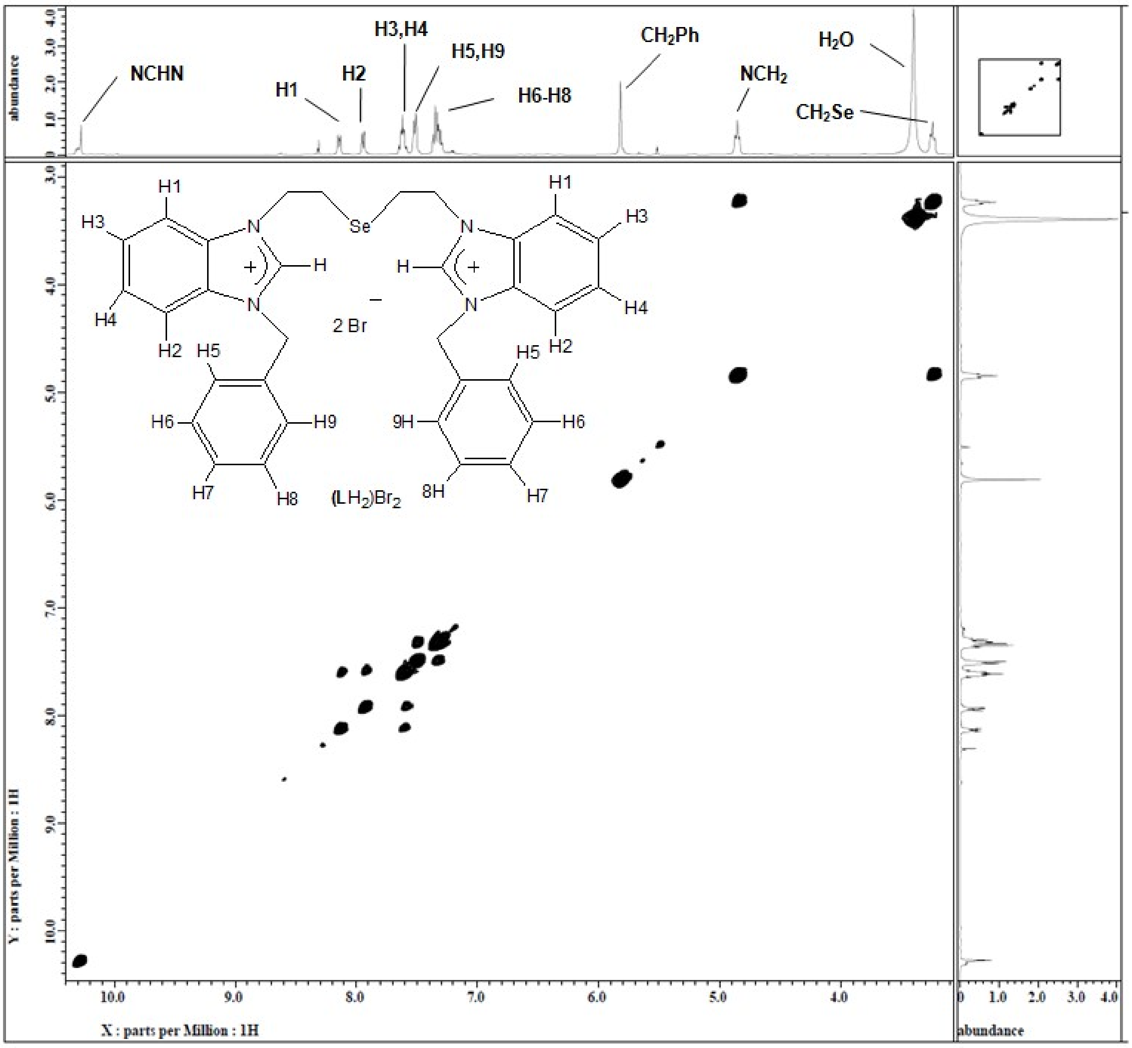


Figure S4. ^{1}H-^{1}H COSY NMR spectrum (DMSO-d$_6$) of (**L**H$_2$)Br$_2$

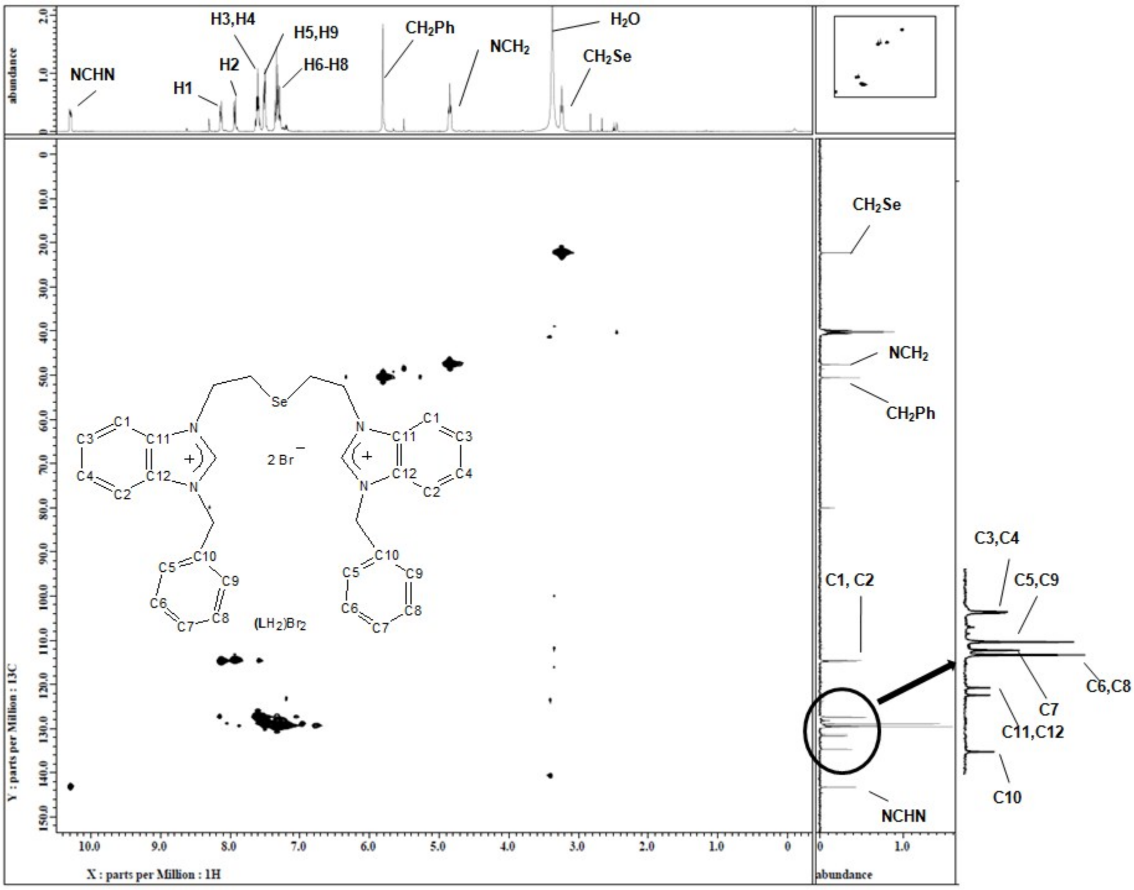


Figure S5. ^{1}H-^{13}C HSQC NMR spectrum (DMSO-d_6) of (**L**H_2)Br_2

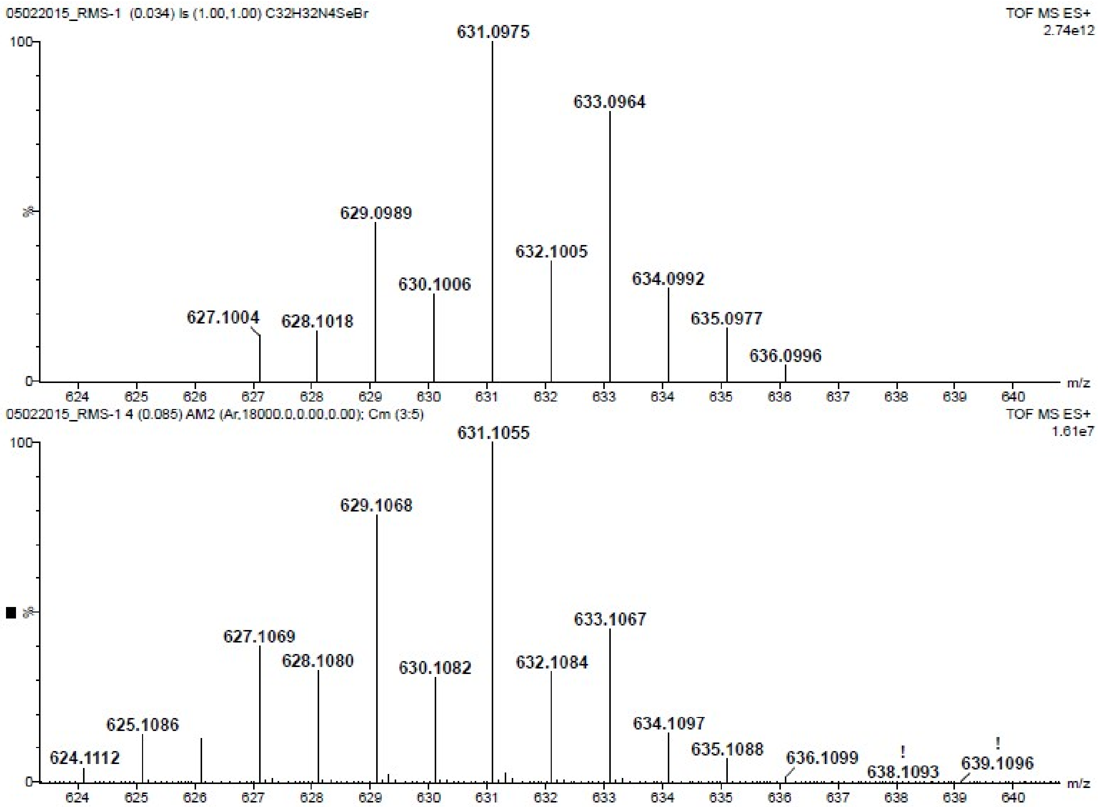


Figure S6. HRMS spectrum (ESI^{+}) of (**L**H_2)Br_2

^{1}H and ^{13}C NMR data for (LH$_2$)Br$_2$: ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 10.33 (s, 2H, NC*H*N), 8.19 (broad d, 2H, $^3J_{H-H}$ = 8 Hz, Ar-*H*), 8.00 (broad d, 2H, $^3J_{H-H}$ = 8 Hz, Ar-*H*), 7.65-7.70 (m, 4H, Ar-*H*), 7.56 (broad d, 4H, $^3J_{H-H}$ = 8 Hz, Ar-*H*), 7.35-7.40 (m, 6H, Ar-*H*), 5.86 (s, 4H, -C*H*$_2$Ph), 4.90 (t, 4H, $^3J_{H,H}$ = 7 Hz, -NC*H*$_2$), 3.28 (t, 4H, $^3J_{H,H}$ = 7 Hz, -C*H*$_2$Se). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 143.1 (N*C*HN), 134.5 (s, C10), 131.5 (s, C11), 131.4 (s, C12), 129.4 (s, C6 & C8), 129.1 (s, C7), 128.7 (s, C5 & C9), 127.3 (s, C3), 127.1 (s, C4), 114.7 (s, C2) 114.5 (s, C1), 50.3 (-*C*H$_2$Ph), 47.3 (-N*C*H$_2$), 22.1 (-*C*H$_2$Se).

Heteronuclear NMR spectra and HRMS spectrum of (LH$_2$)(BF$_4$)$_2$

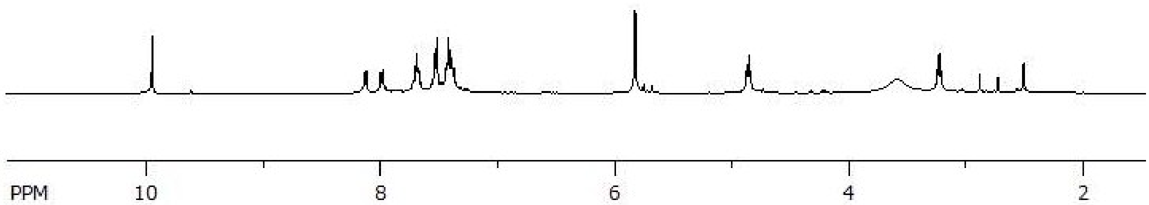


Figure S7. ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$) of (**L**H$_2$)(BF$_4$)$_2$

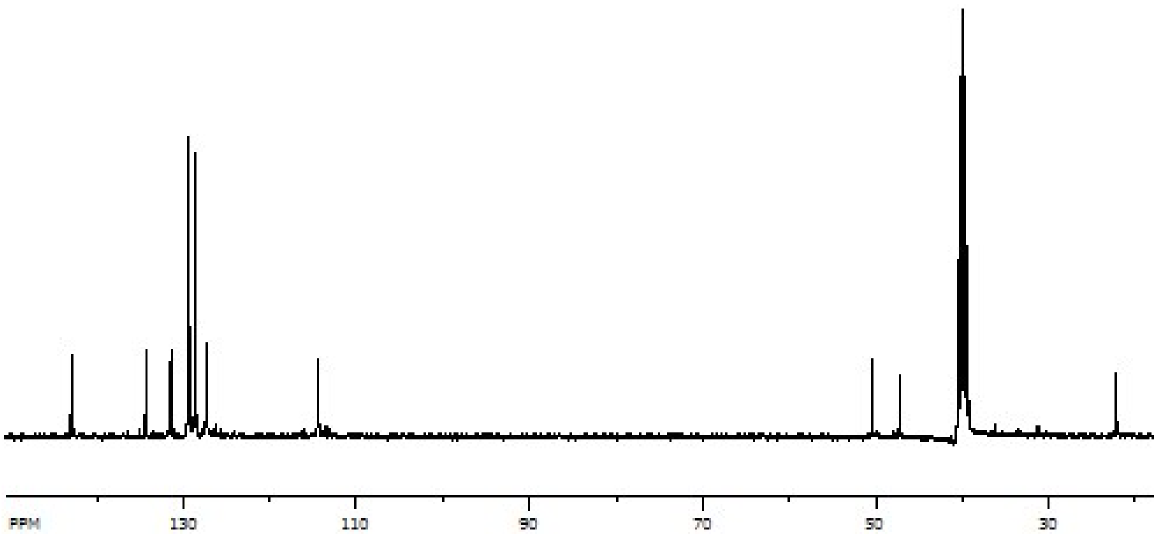


Figure S8. ^{13}C NMR spectrum (100 MHz, DMSO-d$_6$) of (**L**H$_2$)(BF$_4$)$_2$

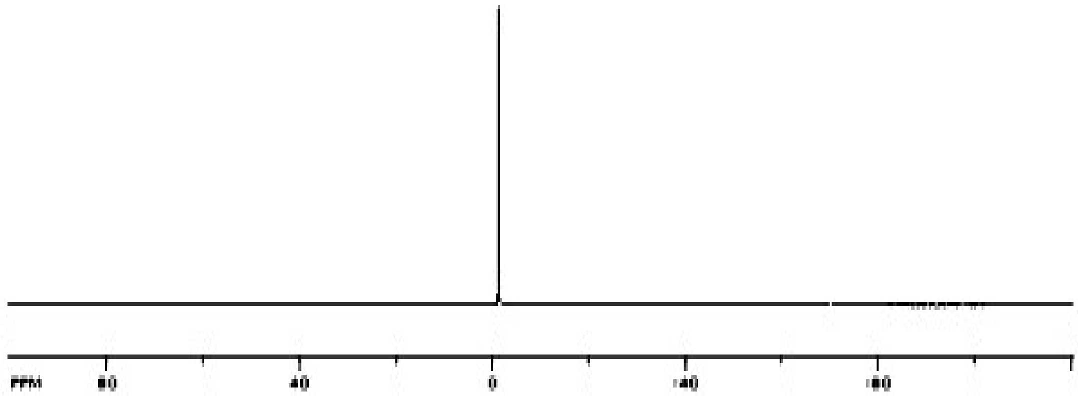


Figure S9. ^{11}B NMR spectrum (128.4 MHz, DMSO-d_6) of (**L**H_2)$(BF_4)_2$

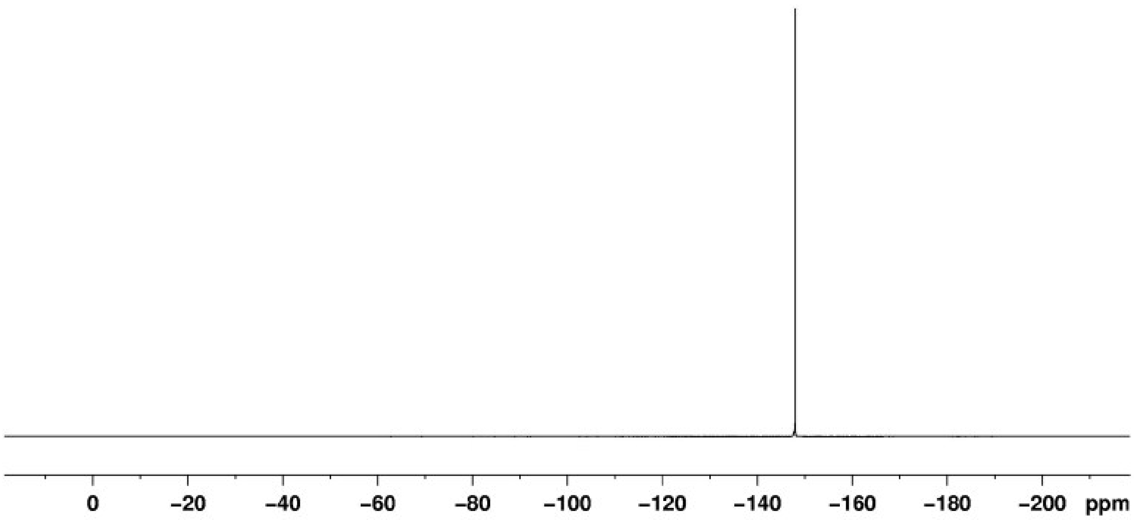


Figure S10. ^{19}F NMR spectrum (376.4 MHz, DMSO-d_6) of (**L**H_2)$(BF_4)_2$

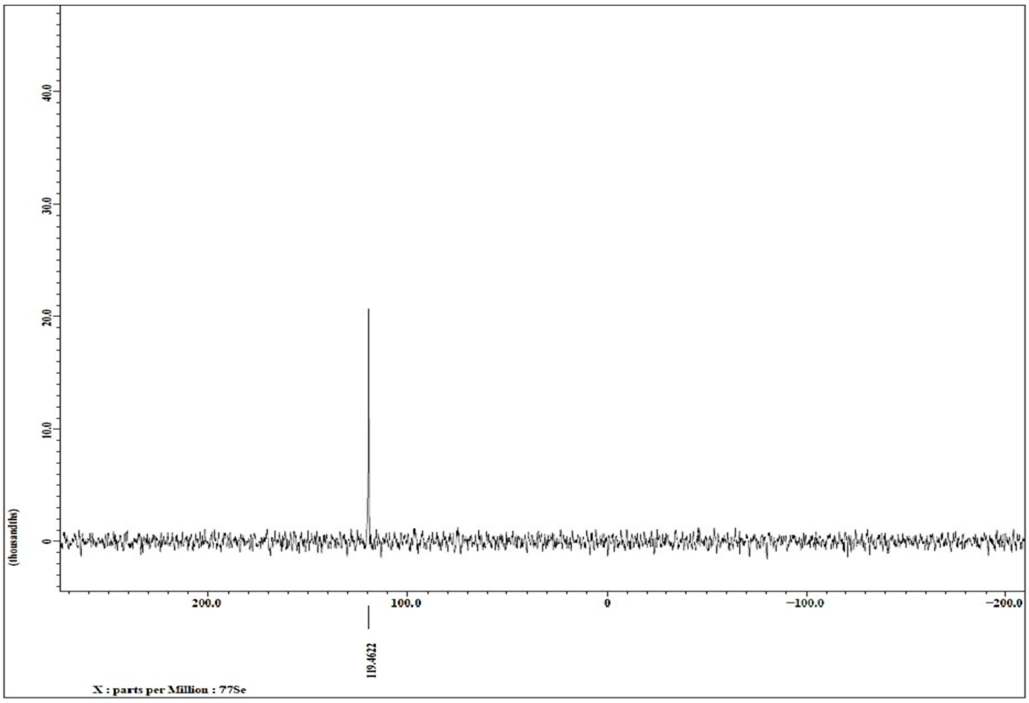


Figure S11. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d_6) of (**L**H_2)(BF_4)$_2$

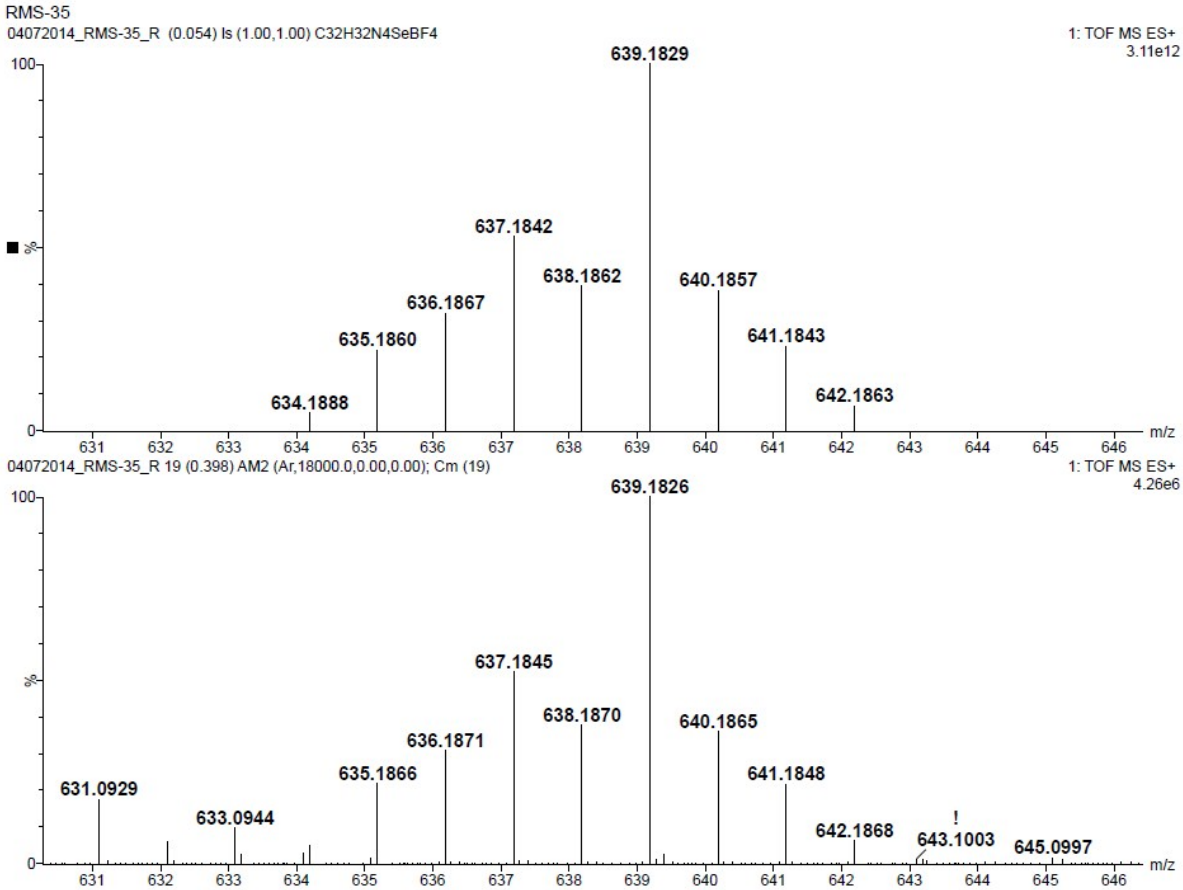


Figure S12. HRMS spectrum (ESI$^+$) of (**L**H_2)(BF_4)$_2$

Heteronuclear NMR spectra and HRMS spectrum of (LH$_2$)(NO$_3$)$_2$

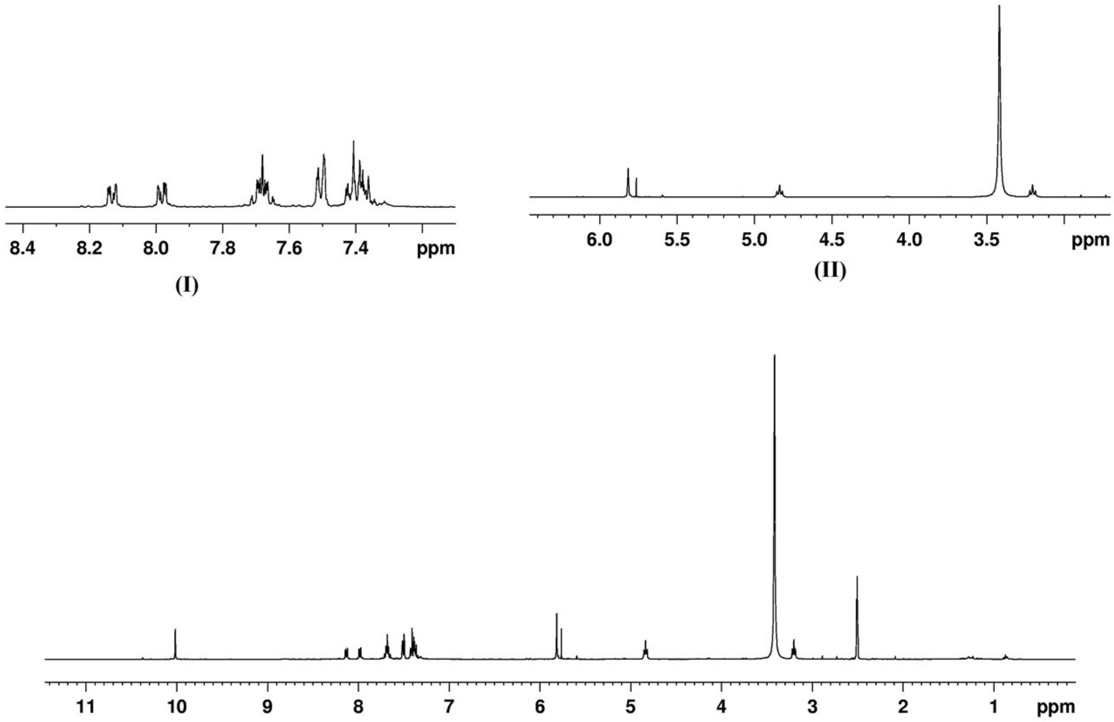


Figure S13. ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$) of (**L**H$_2$)(NO$_3$)$_2$. Insets **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

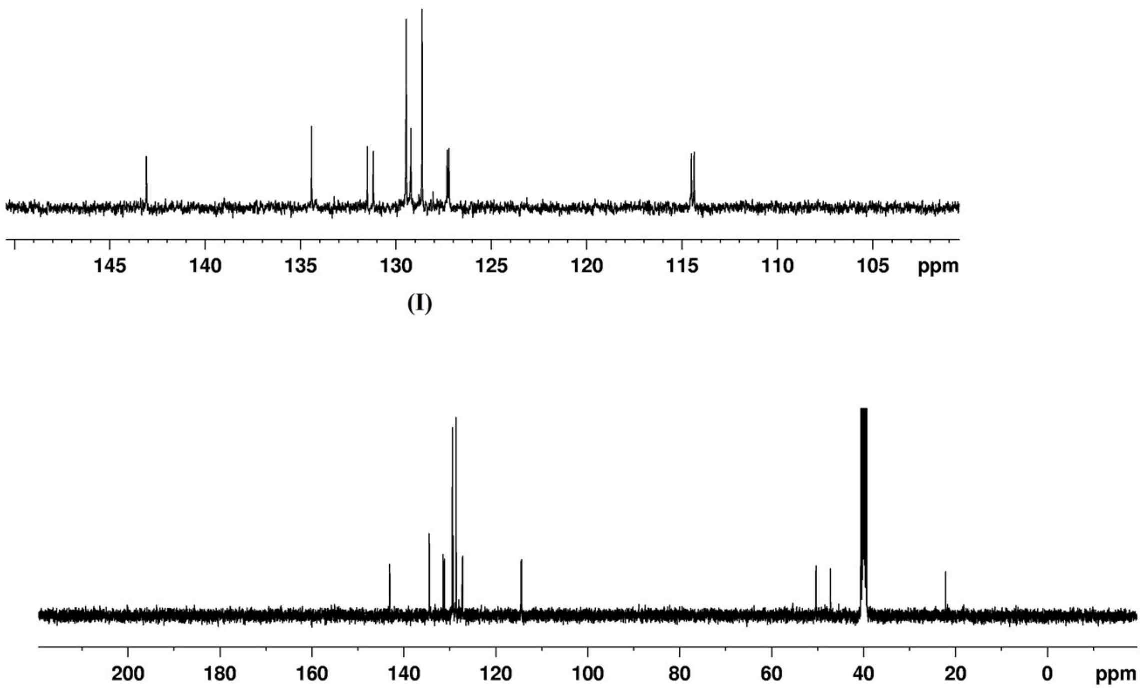


Figure S14. ^{13}C NMR spectrum (100 MHz, DMSO-d$_6$) of (**L**H$_2$)(NO$_3$)$_2$. Inset **(I)** shows expanded aromatic spectral region.

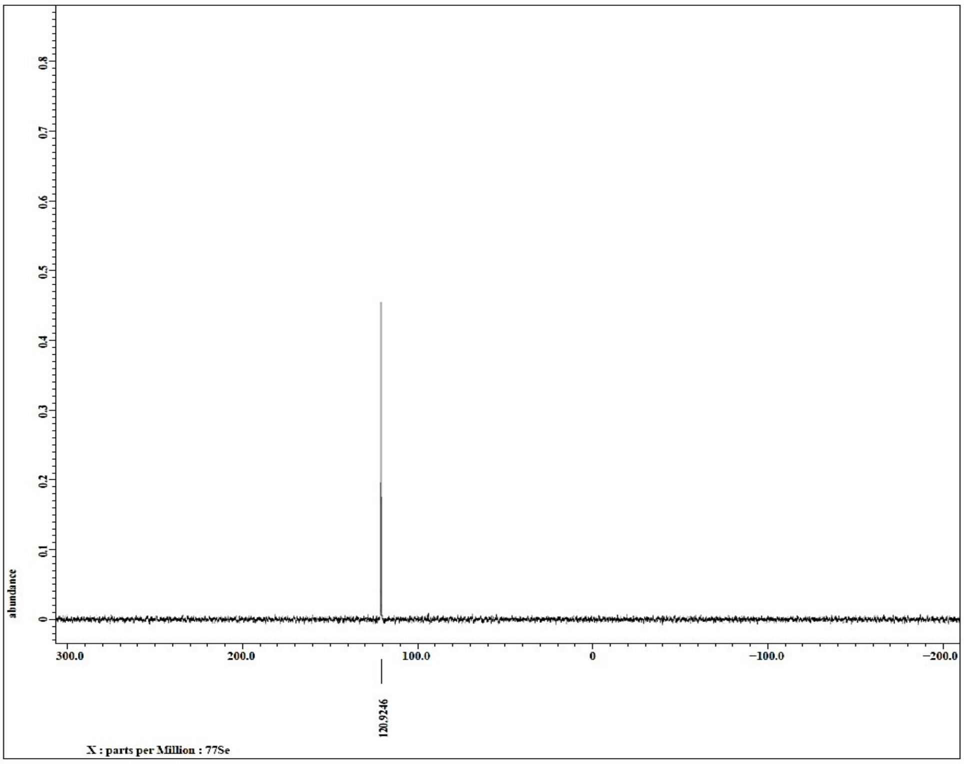


Figure S15. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d_6) of (**L**H_2)(NO_3)$_2$

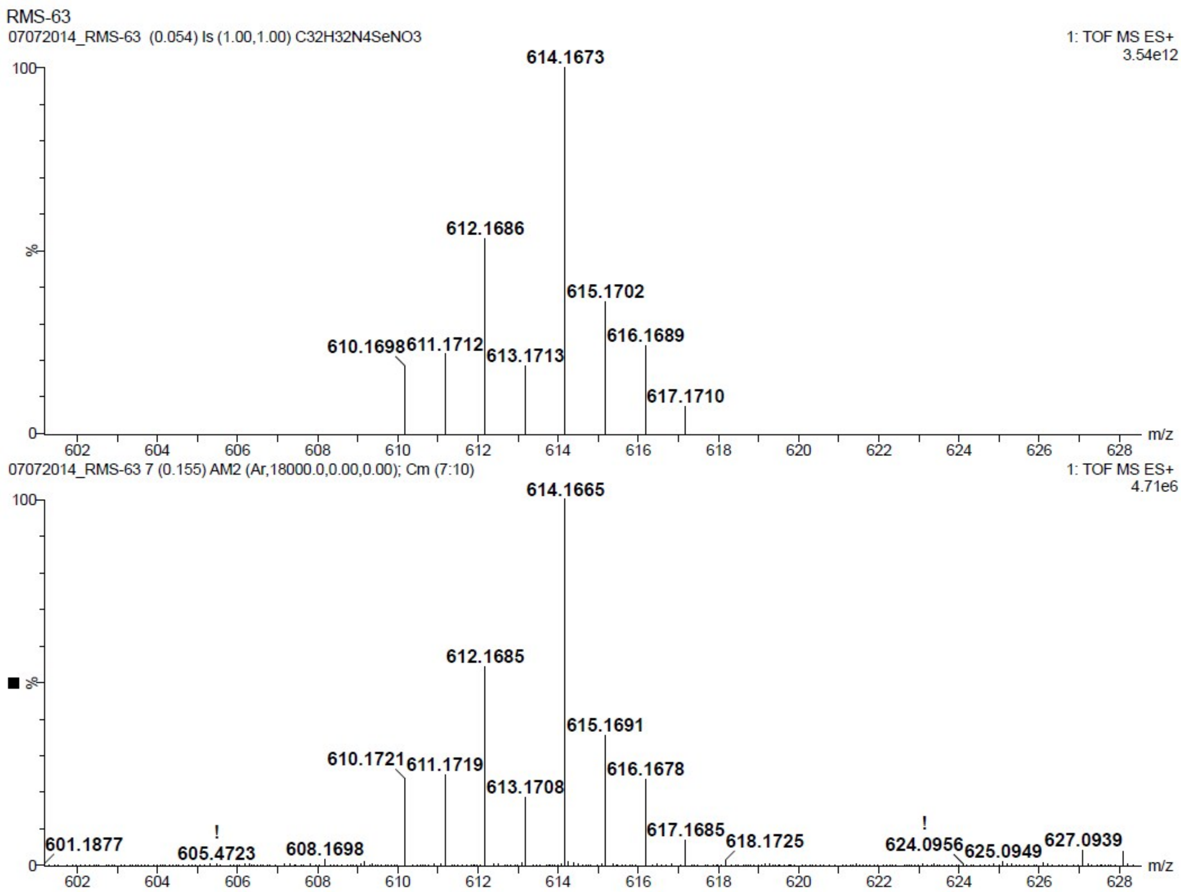


Figure S16. HRMS spectra (ESI$^+$) of (**L**H_2)(NO_3)$_2$.

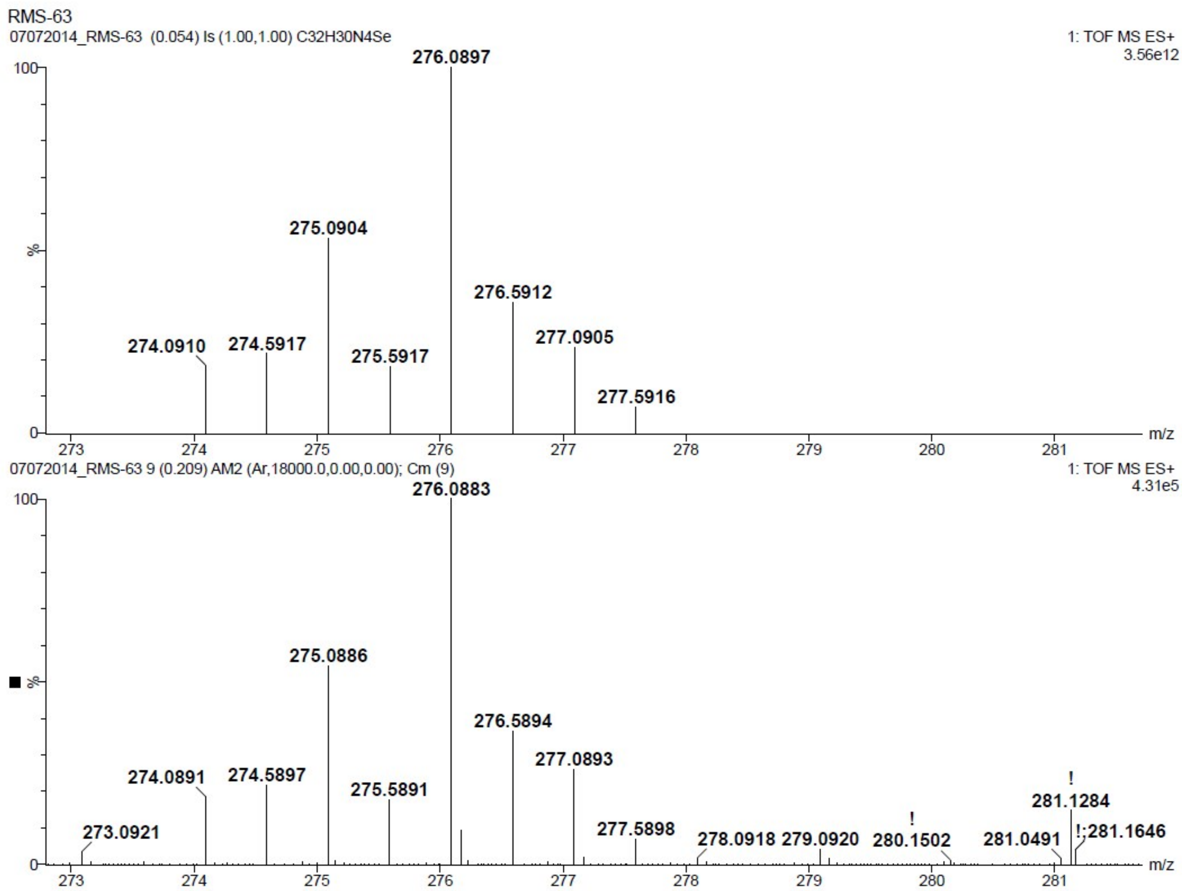


Figure S17. HRMS spectra (ESI^+) of (**L**H_2)$(NO_3)_2$.

Heteronuclear NMR spectra and HRMS spectra of [Hg(L-κ²*C*)][$HgBr_4$] (C1)

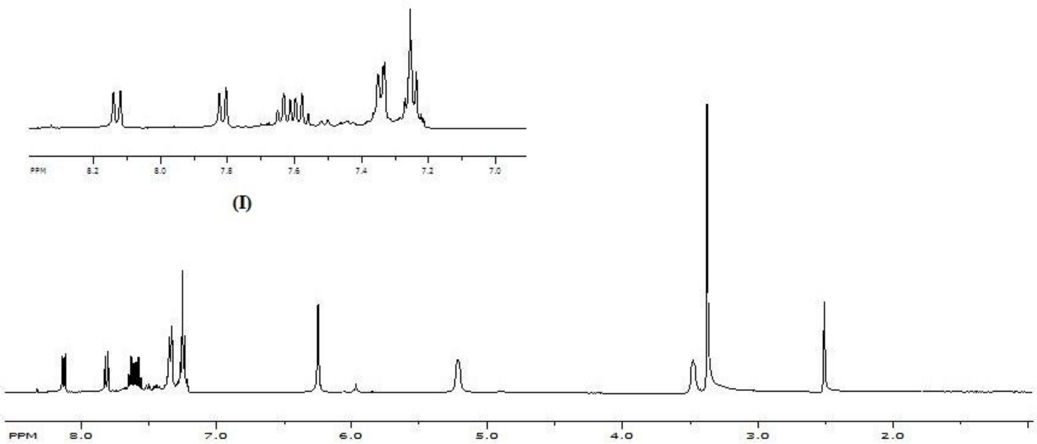


Figure S18. ^1H NMR spectrum (400 MHz, DMSO-d_6) of **C1**. Inset **(I)** shows expanded aromatic spectral region.

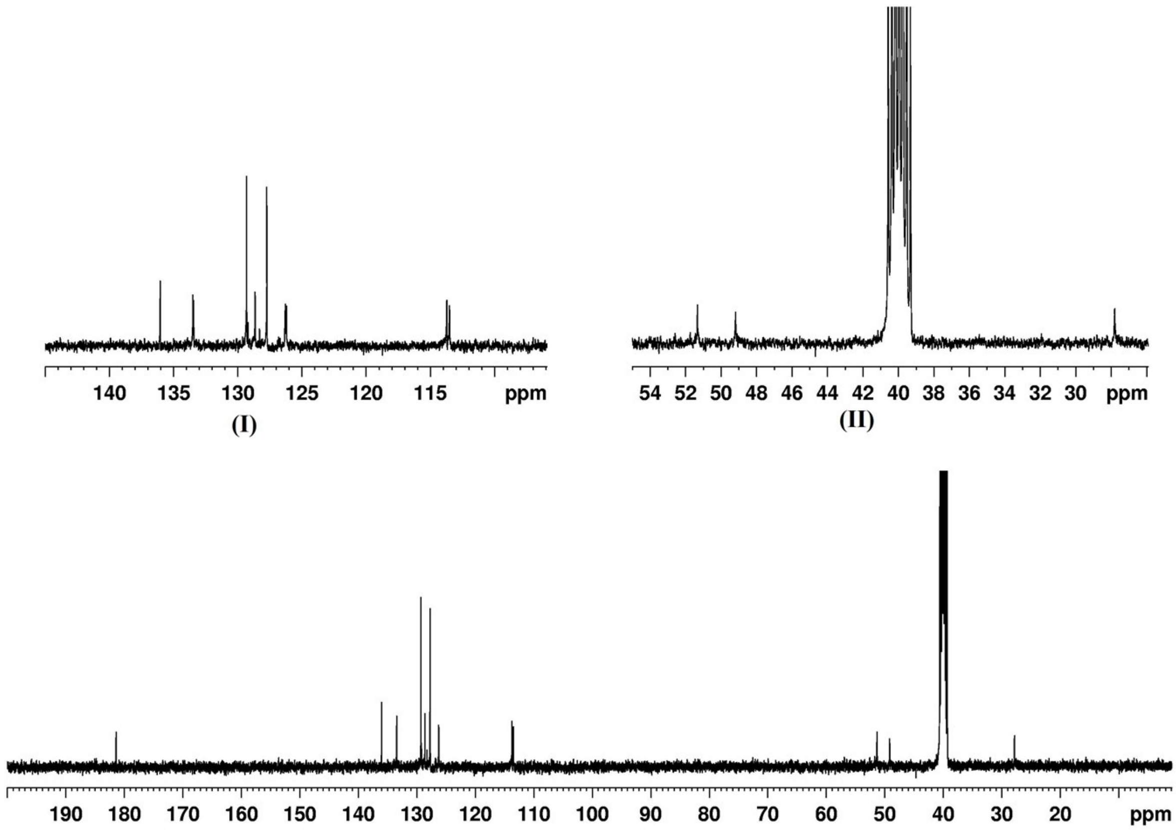


Figure S19. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **C1**. Insets **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

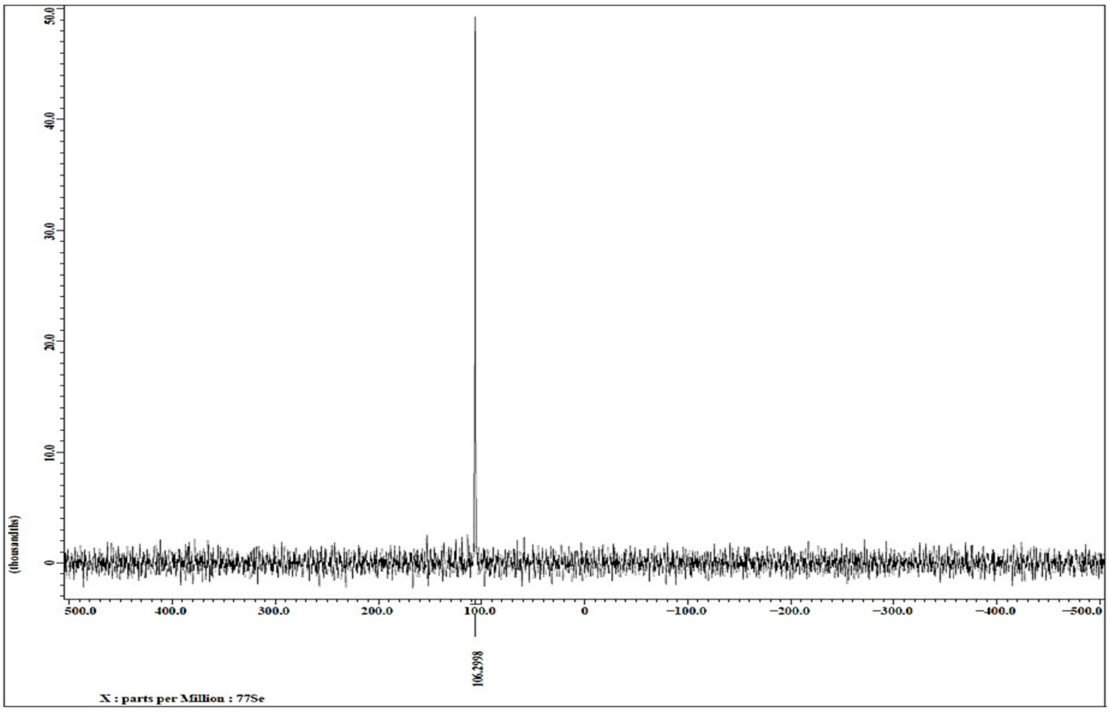


Figure S20. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d_6) of **C1**

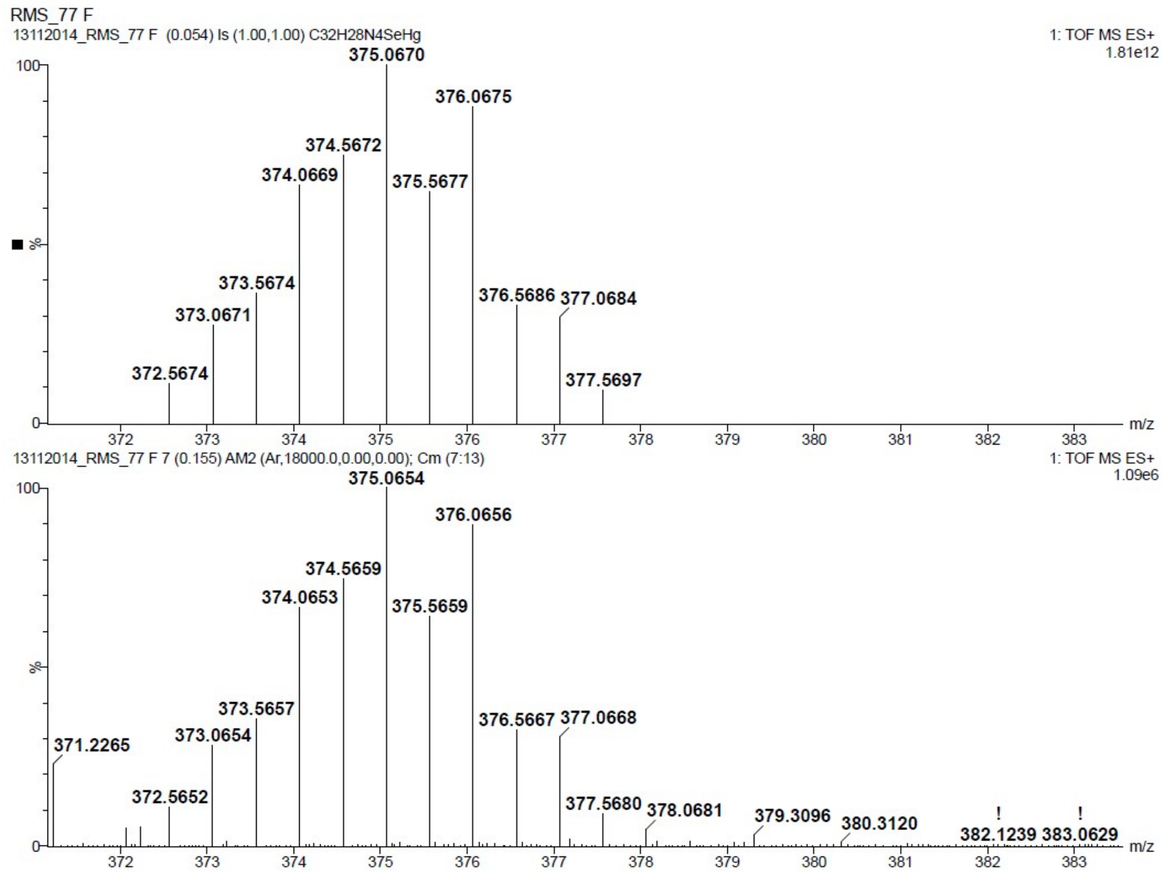


Figure S21. HRMS spectra (ESI^+) of **C1**

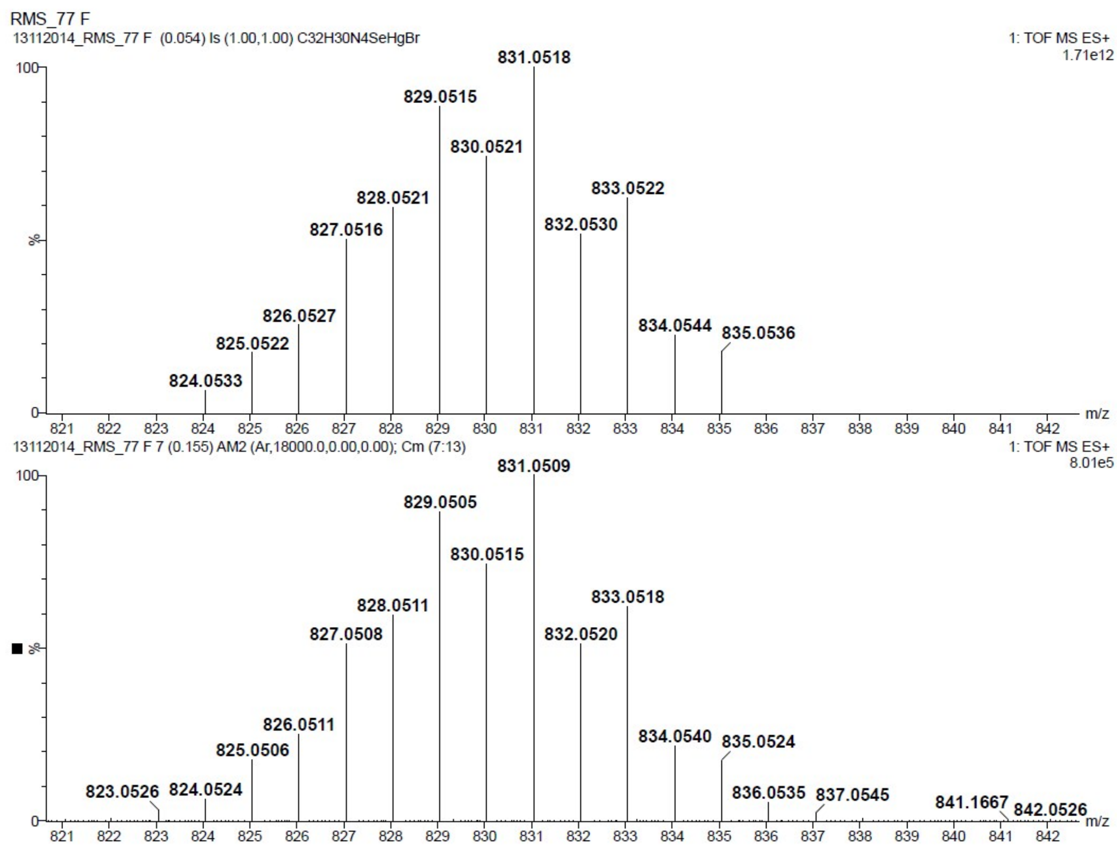


Figure S22. HRMS spectra (ESI^+) of **C1**

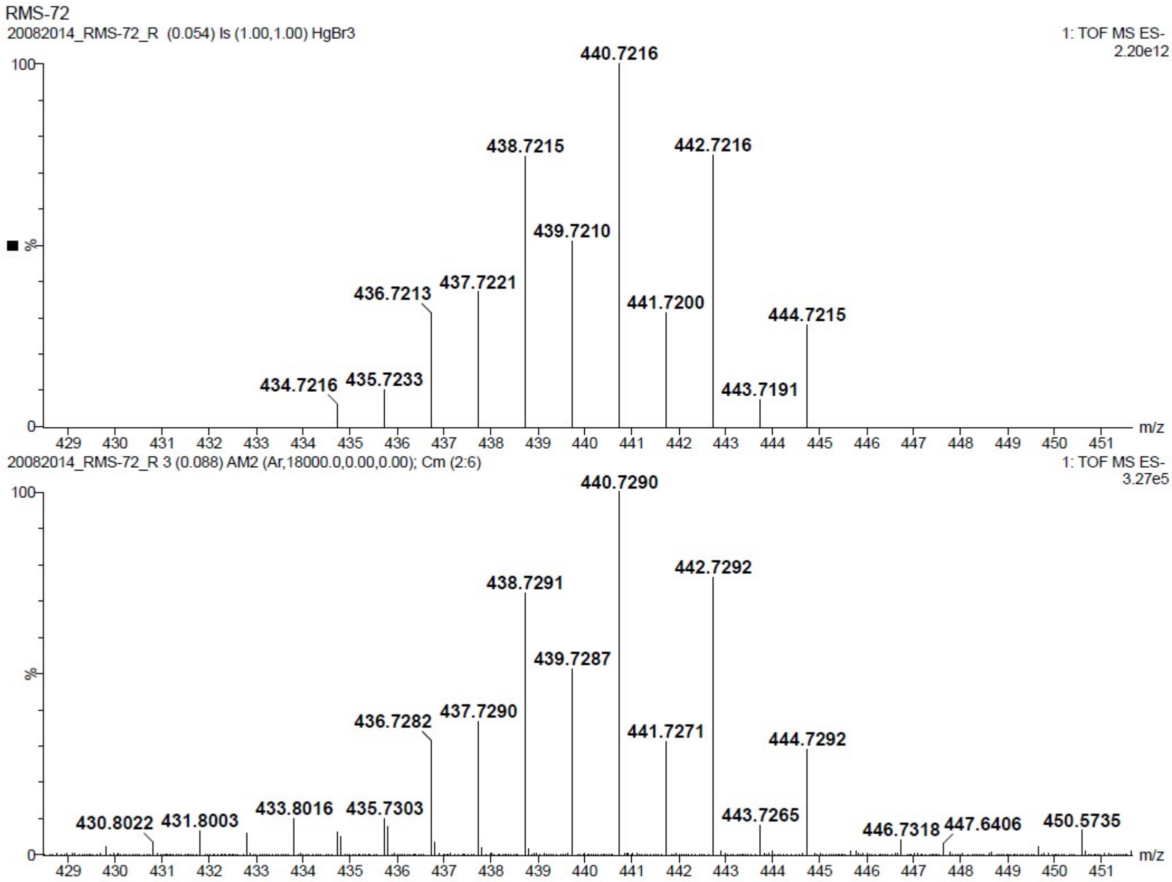


Figure S23. HRMS spectra (ESI⁻) of **C1**

Heteronuclear NMR spectra and HRMS spectrum of [PdBr(L-κ³*CSeC*)]Br (C2)

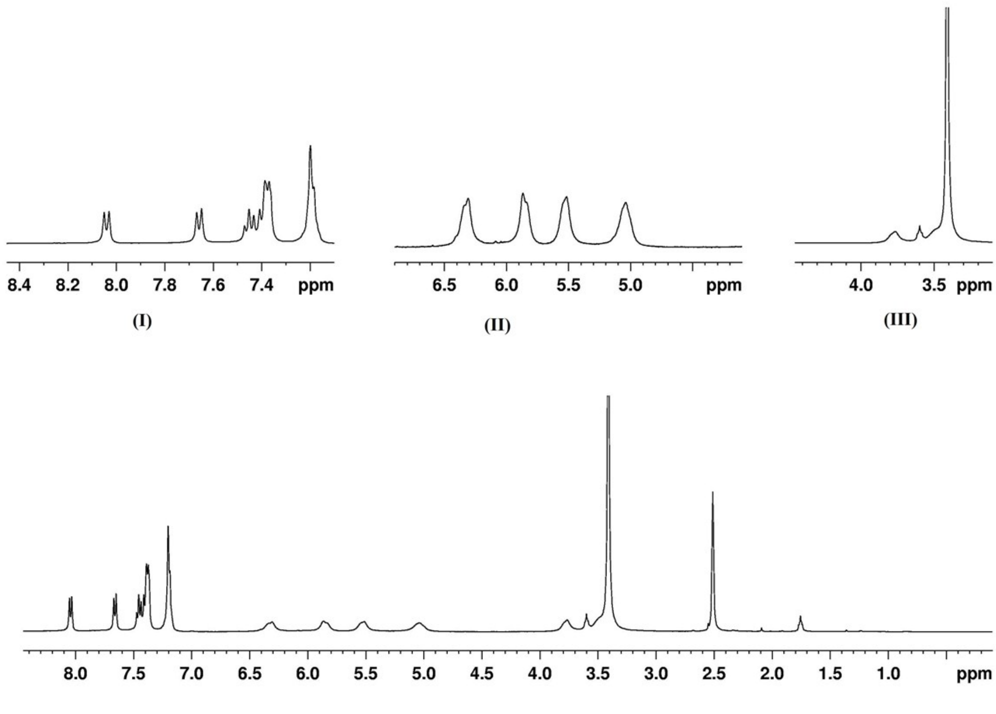


Figure S24. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **C2**. Insets **(I), (II)** and **(III)** show expanded aromatic and aliphatic spectral region.

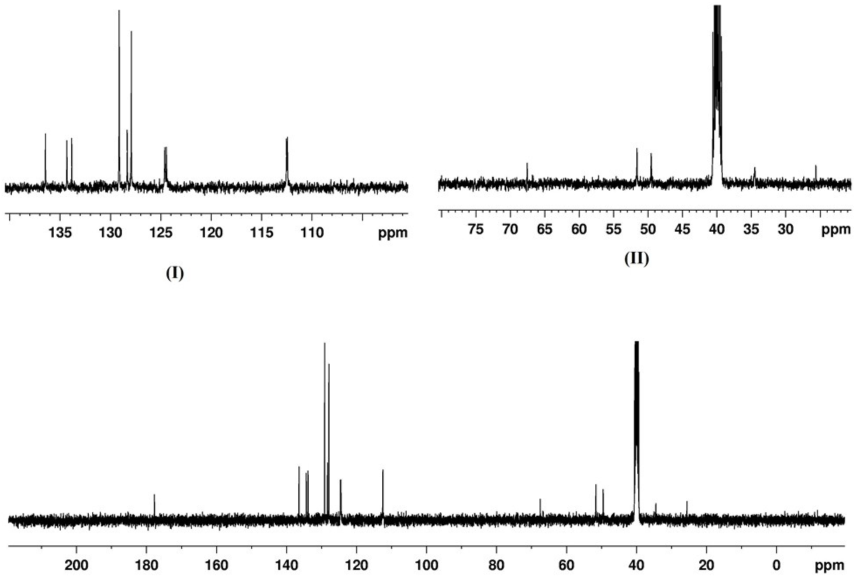


Figure S25. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **C2**. Insets **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

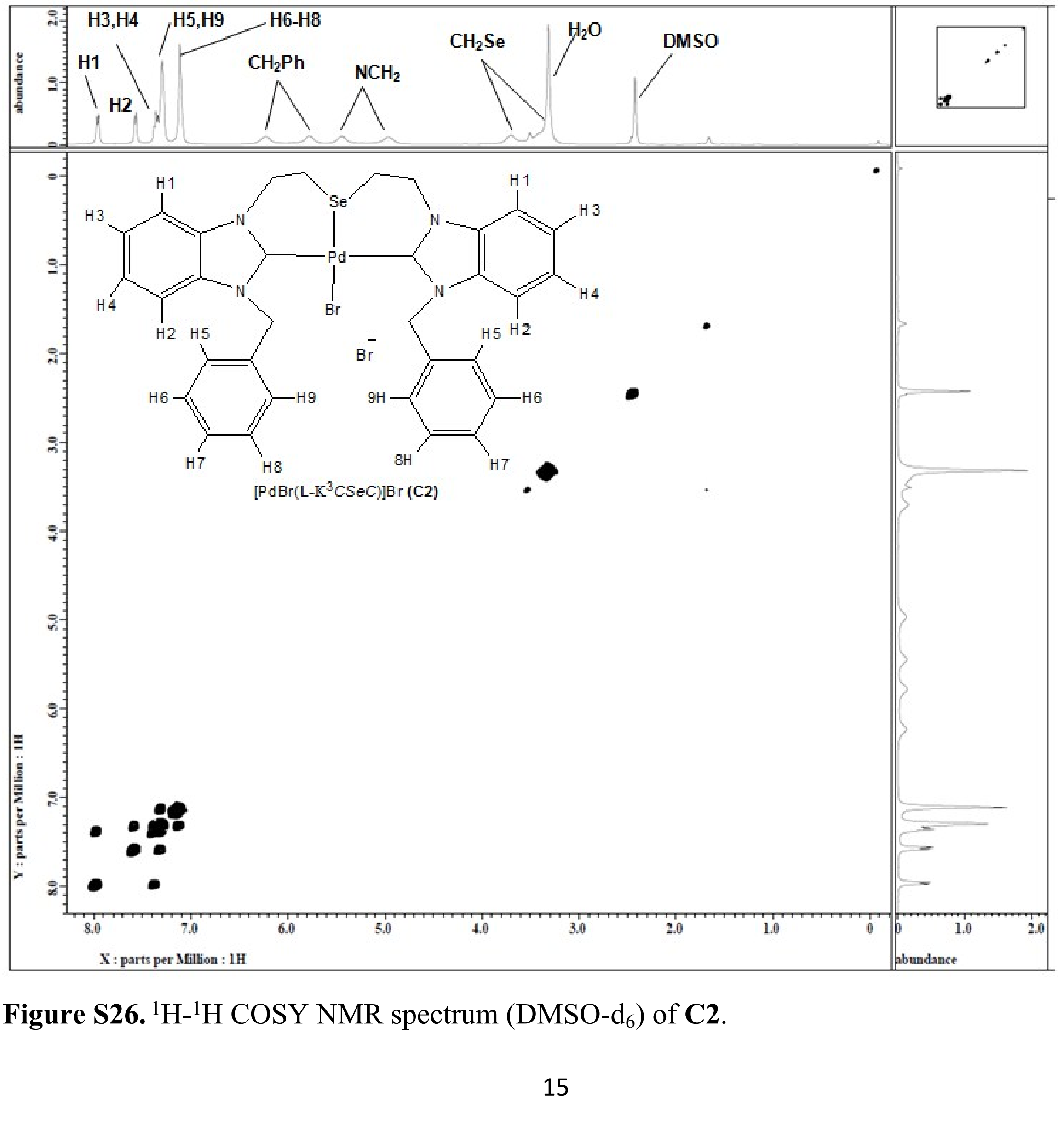


Figure S26. ^{1}H-^{1}H COSY NMR spectrum (DMSO-d_6) of **C2**.

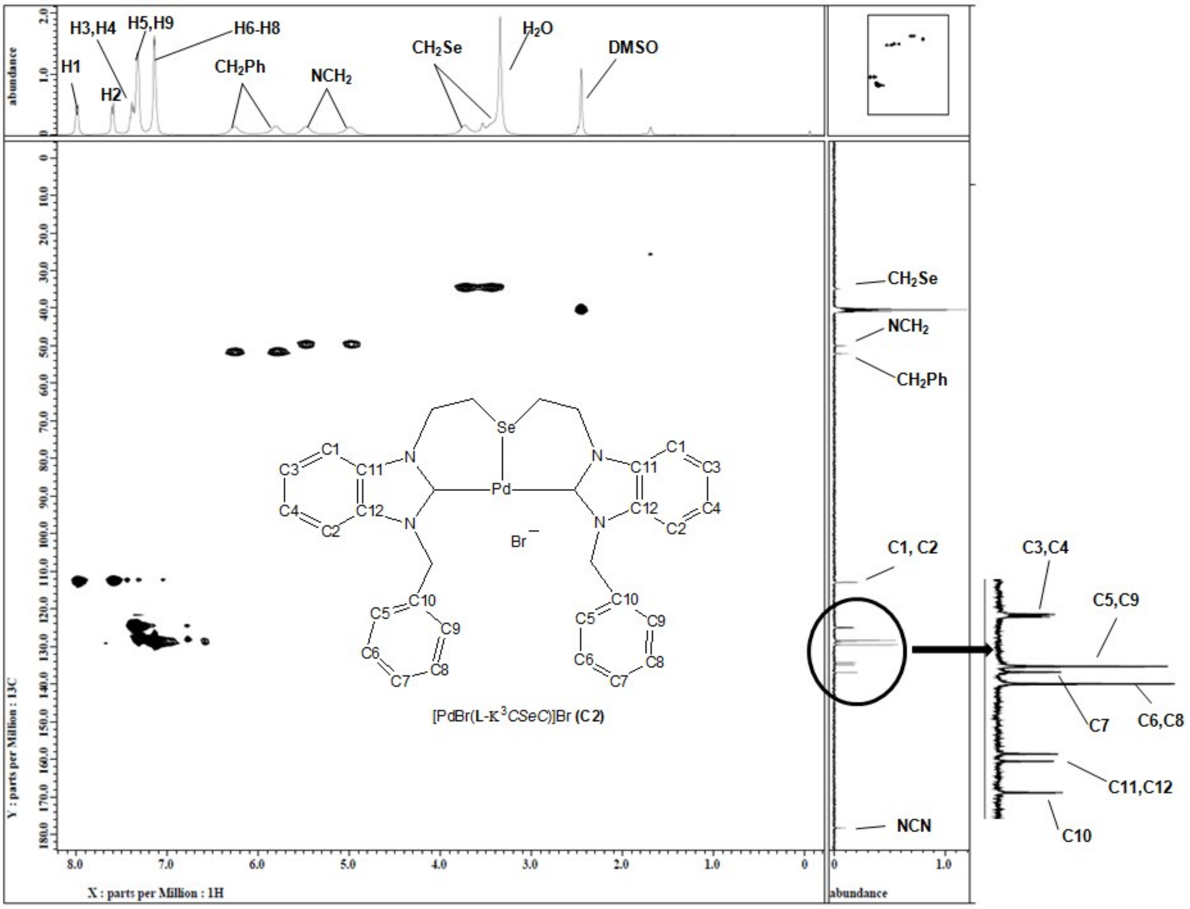


Figure S27. ^{1}H-^{13}C HSQC NMR spectrum (DMSO-d_6) of **C2**.

^{1}H and ^{13}C NMR data for C2: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.04 (d, 2H, $^{3}J_{H,H}$ = 8 Hz, Ar-*H*), 7.67 (d, 2H, $^{3}J_{H,H}$ = 8 Hz, Ar-*H*), 7.47-7.38 (m, 8H, Ar-*H*), 7.17-7.20 (m, 6H, Ar-*H*), 6.33 (broad, 2H, -CH_2Ph), 5.87 (broad, 2H, -CH_2Ph), 5.53 (broad, 2H, -NCH_2), 5.06 (broad, 2H, -CH_2Se), 3.78 (broad, 2H, -NCH_2), 3.48 (broad, 2H, -CH_2Se) the signal overlaps with the signal of residual water in DMSO-d_6. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ = 177.7 (N*C*N), 136.4 (s, C10), 134.3 (s, C11), 133.8 (s, C12), 129.1 (s, C6 & C8), 128.3 (s, C7), 127.9 (s, C5 & C9), 124.6 (s, C3), 124.4 (s, C4), 112.5 (s, C2), 112.4 (s, C1), 51.6 (-*C*H_2Ph), 49.5 (-N*C*H_2), 34.5 (-*C*H_2Se).

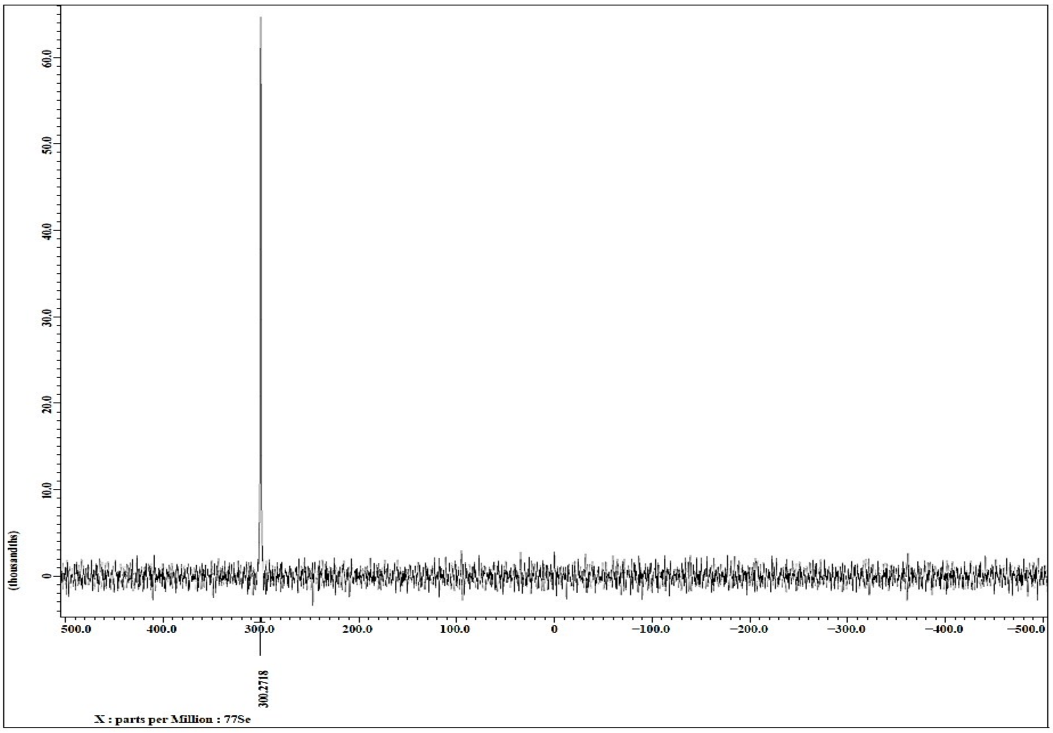


Figure S28. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d_6) of **C2**

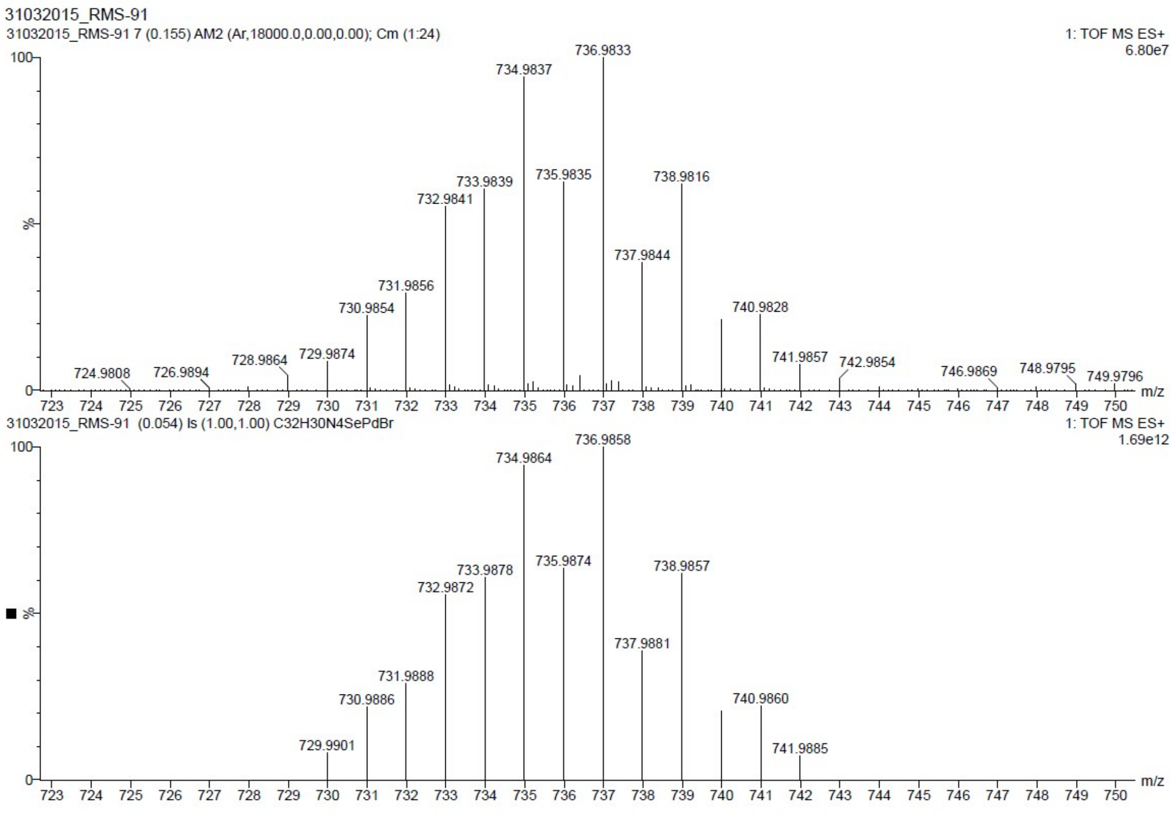


Figure S29. HRMS spectrum (ESI$^+$) of **C2**

Heteronuclear NMR spectra and HRMS spectrum of *cis*-[PdBr$_2$(L-κ^2*C*)] (C3)

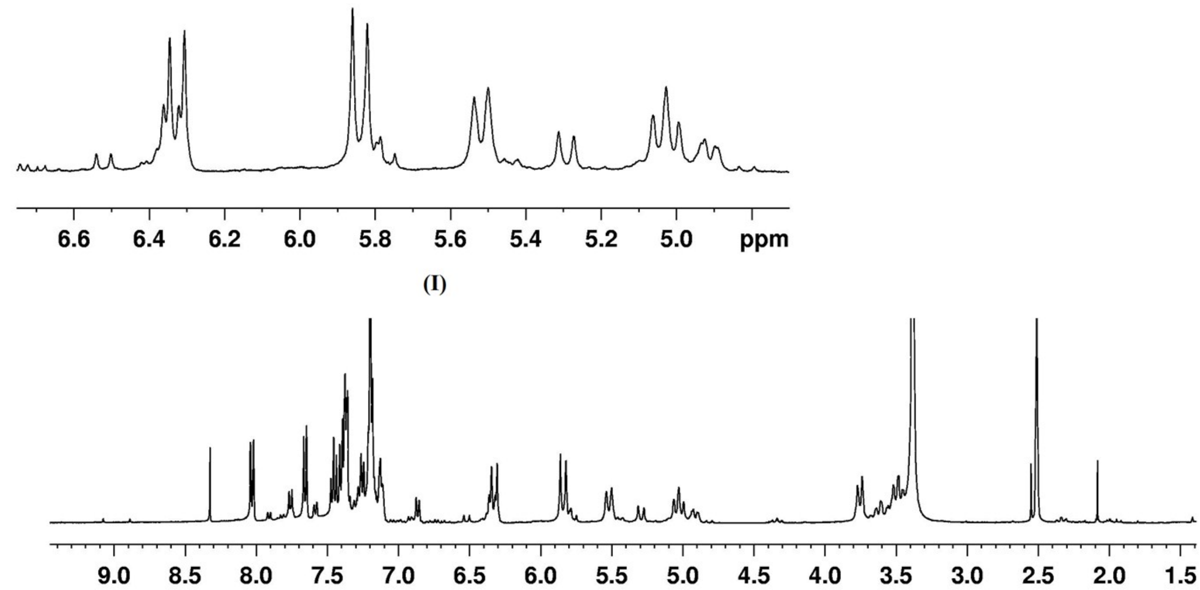


Figure S30. ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$) of **C3**. Inset **(I)** shows expanded aliphatic spectral region.

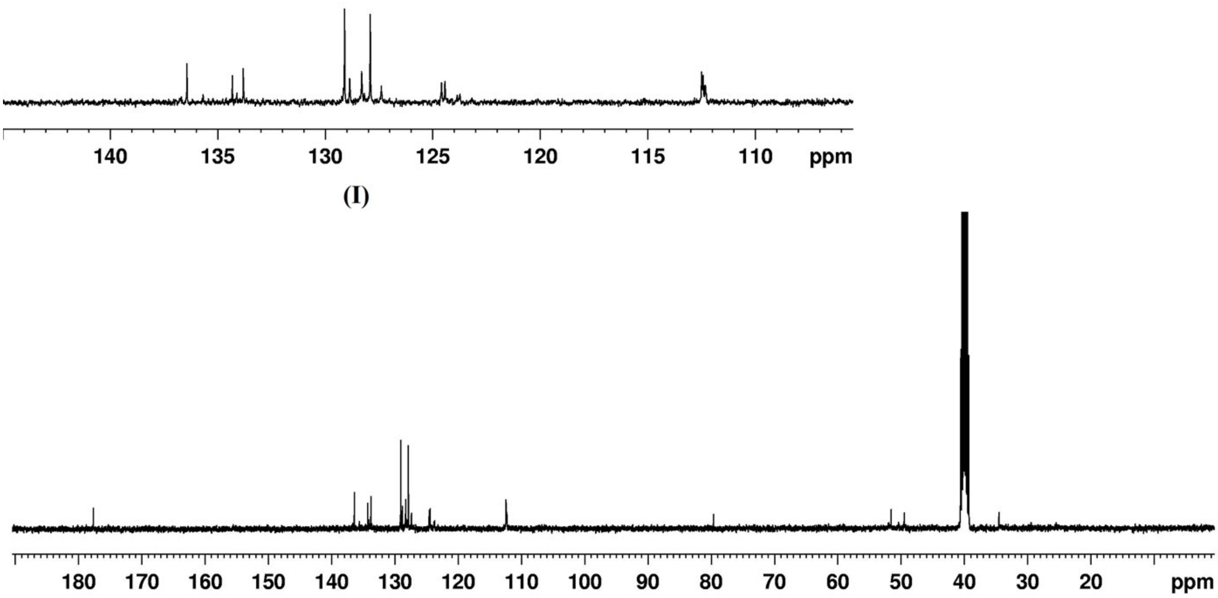


Figure S31. ^{13}C NMR spectrum (100 MHz, DMSO-d$_6$) of **C3**. Inset **(I)** shows expanded aromatic spectral region.

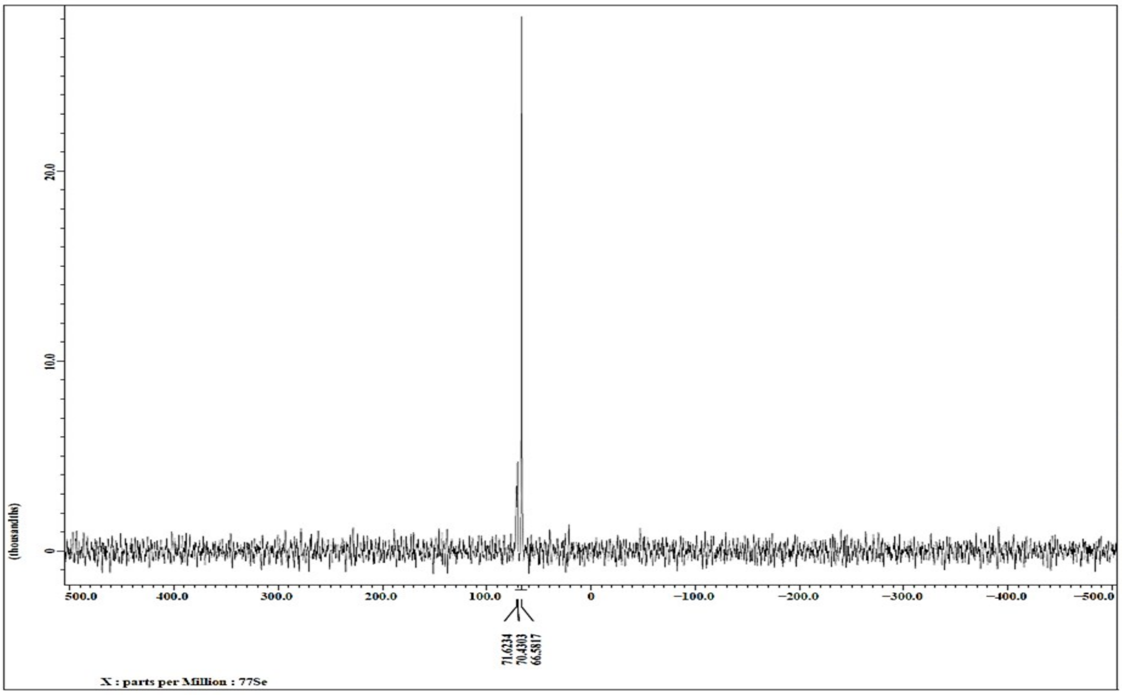


Figure S32. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d_6) of **C3.**

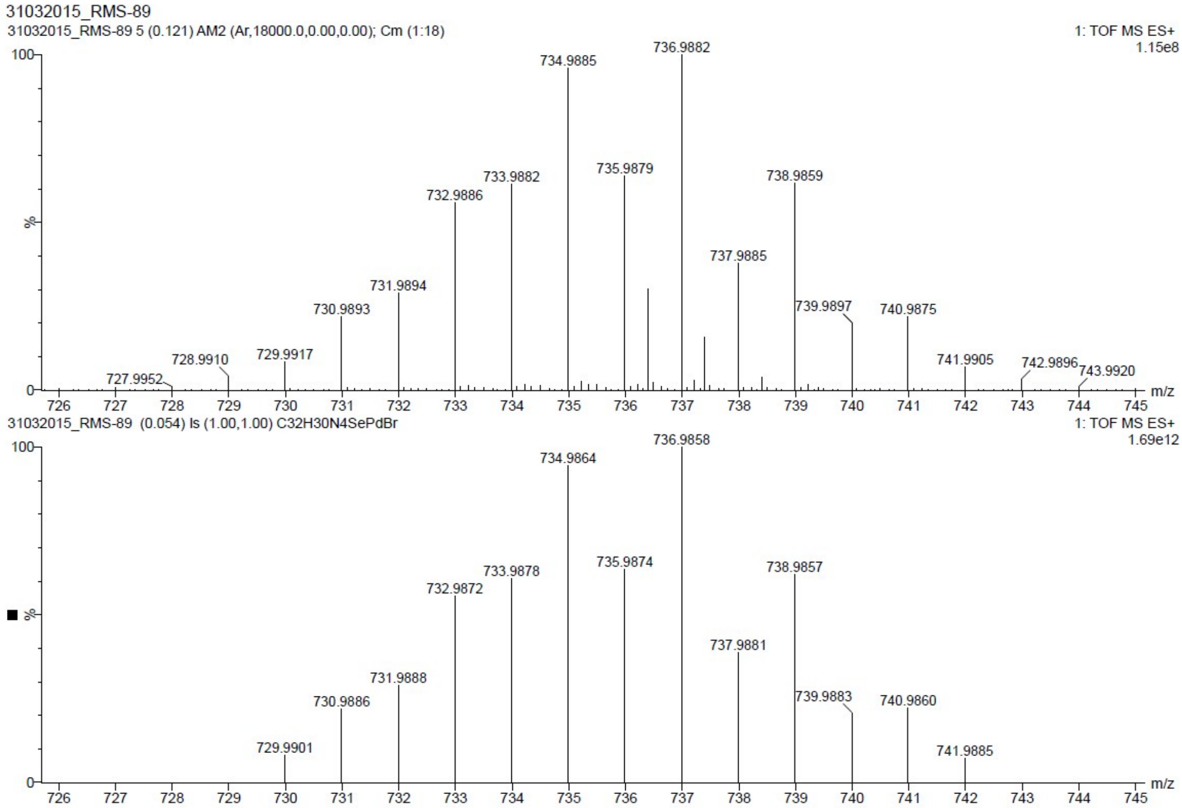


Figure S33. HRMS spectrum (ESI$^+$) of **C3**

Heteronuclear NMR spectra and HRMS spectrum of [Pd(L-κ^4$C_{Bz}$$CSeC$)]$NO_3$ (C4)

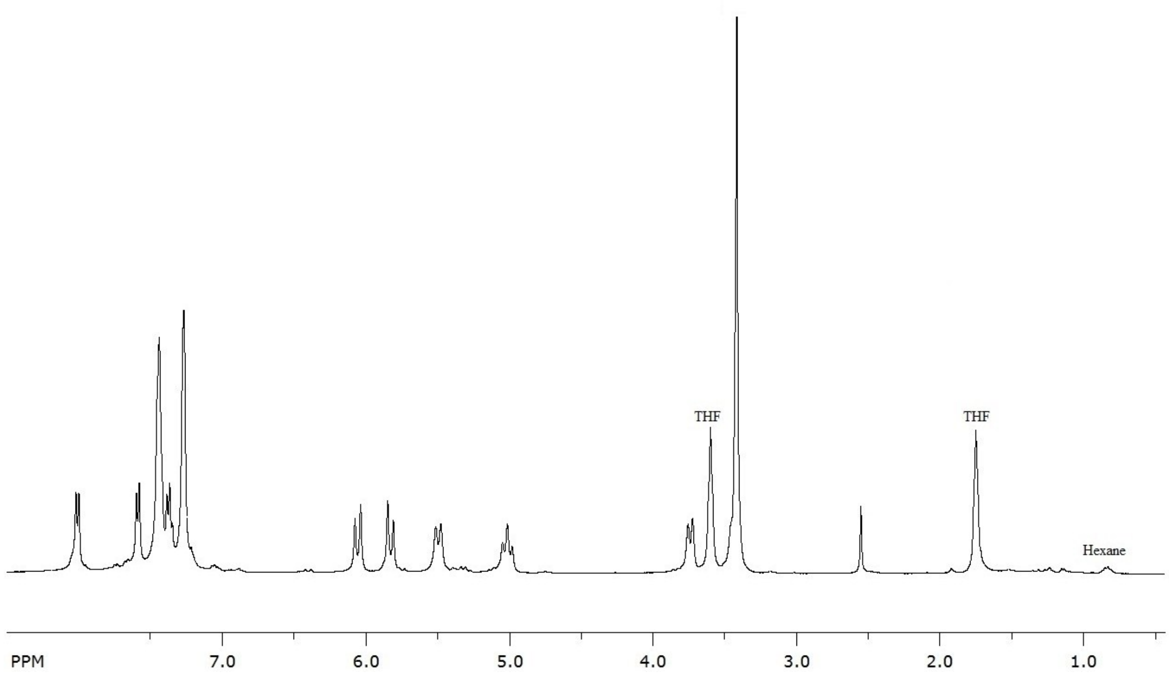


Figure S34. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **C4**.

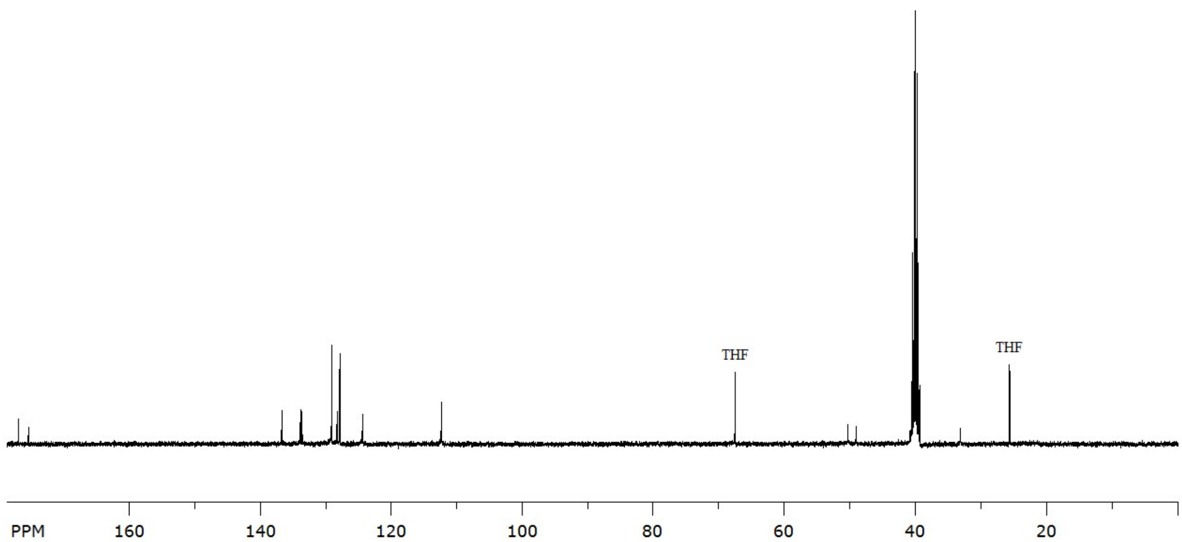


Figure S35. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **C4.**

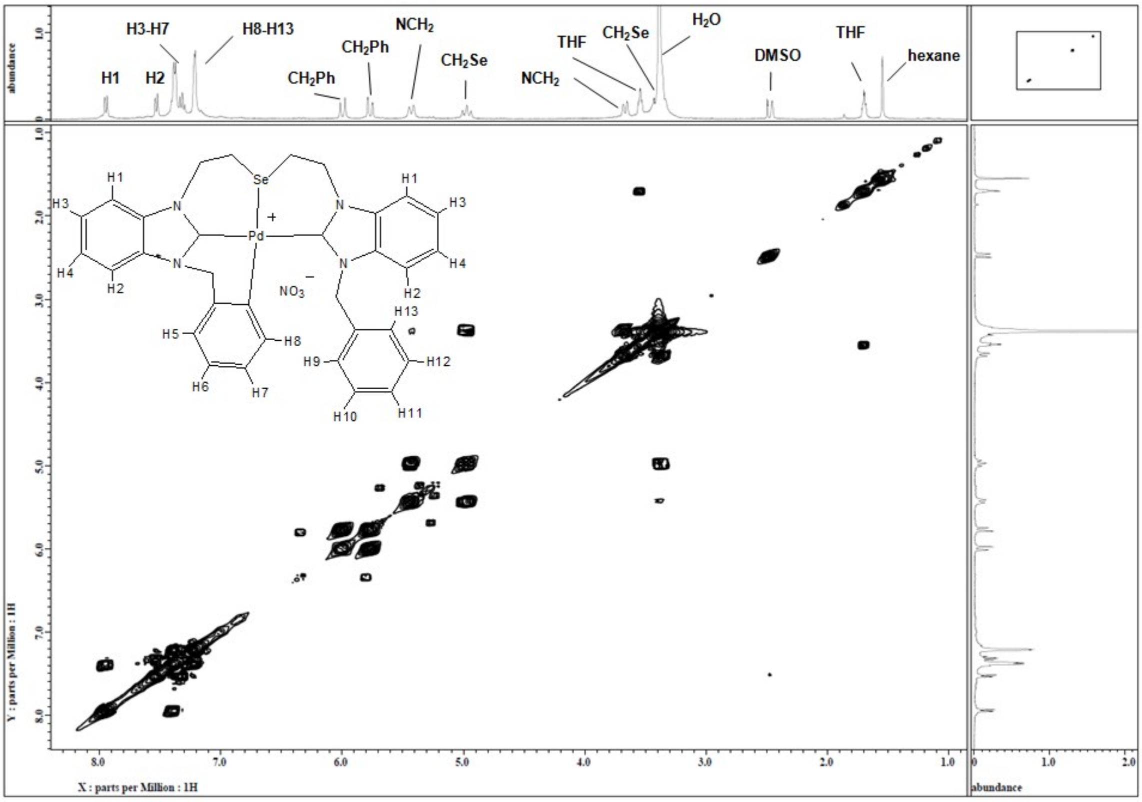


Figure S36. ${}^{1}H$-${}^{1}H$ COSY NMR spectrum (DMSO-d_6) of **C4.**

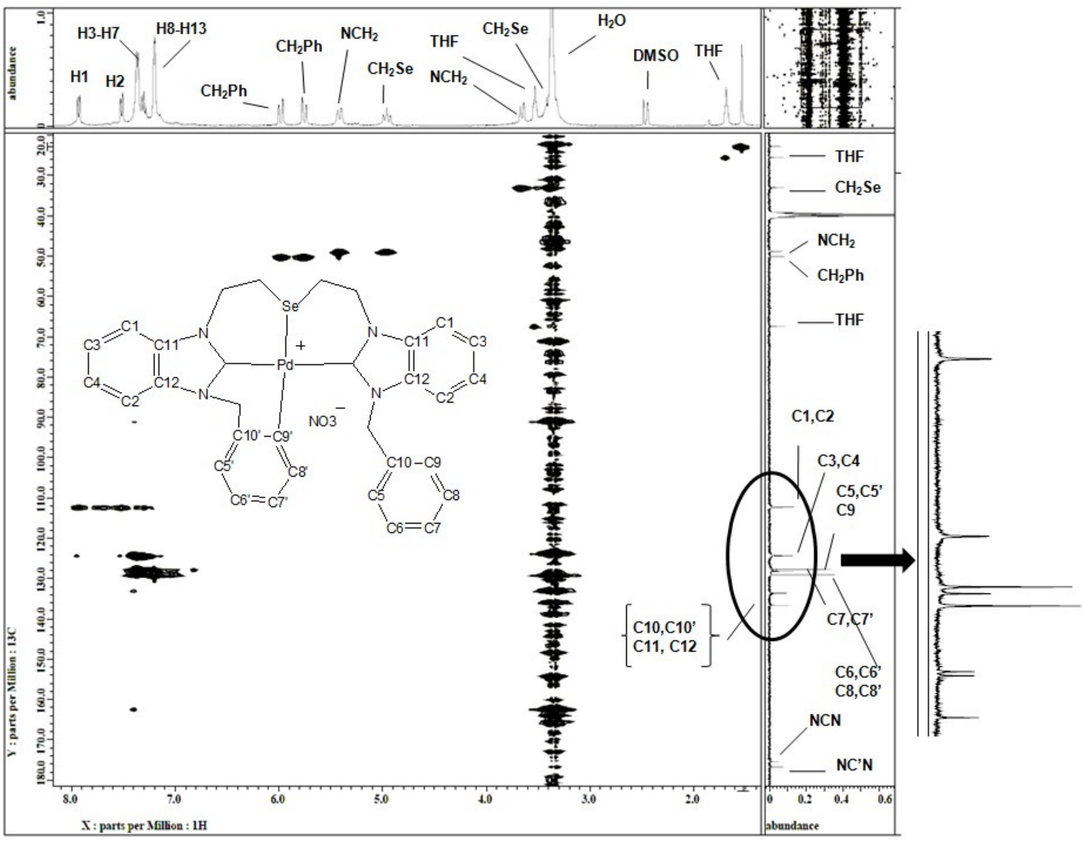


Figure S37. ${}^{1}H$-${}^{13}C$ HSQC NMR spectrum (DMSO-d_6) of **C4.**

^{1}H and ^{13}C NMR data for C4: ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 8.00 (d, 2H, $^{3}J_{H,H}$ = 8 Hz, Ar-*H*), 7.59 (d, 2H, $^{3}J_{H,H}$ = 8 Hz, Ar-*H*), 7.44 (m, 7H, $^{3}J_{H,H}$ = 8 Hz, Ar-*H*), 7.27 (m, 6H, Ar-*H*), 6.06 (d, 2H, $^{2}J_{H,H}$ = 16 Hz, -C*H*HPh), 5.83 (d, 2H, $^{2}J_{H,H}$ = 16 Hz, -C*H*HPh), 5.50 (d, 2H, $^{2}J_{H,H}$ = 12 Hz, NC*H*H), 5.02 (ps t, 2H, $^{2}J_{H,H}$ = 12 Hz, -C*H*HSe), 3.73 (d, 2H, $^{2}J_{H,H}$ = 12 Hz, -NCH*H*), 3.53 (ps t, 2H, $^{2}J_{H,H}$ = 12 Hz, -CH*H*Se). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 176.9 (N*C*N), 175.4 (N*C*N), 136.8 (s, C10, C10'), 133.9 & 133.6 (s, C11 & C12), 129.1 (s, C6, C6', C8 & C8'), 128.3 (s, C7 &C7'), 127.9 (s, C5, C5', C9), 124.4 (s, C3 & C4), 112.4 (s, C1 & C2), 50.3 (-*C*H$_2$Ph), 49.0 (-N*C*H$_2$), 33.1 (-*C*H$_2$Se).

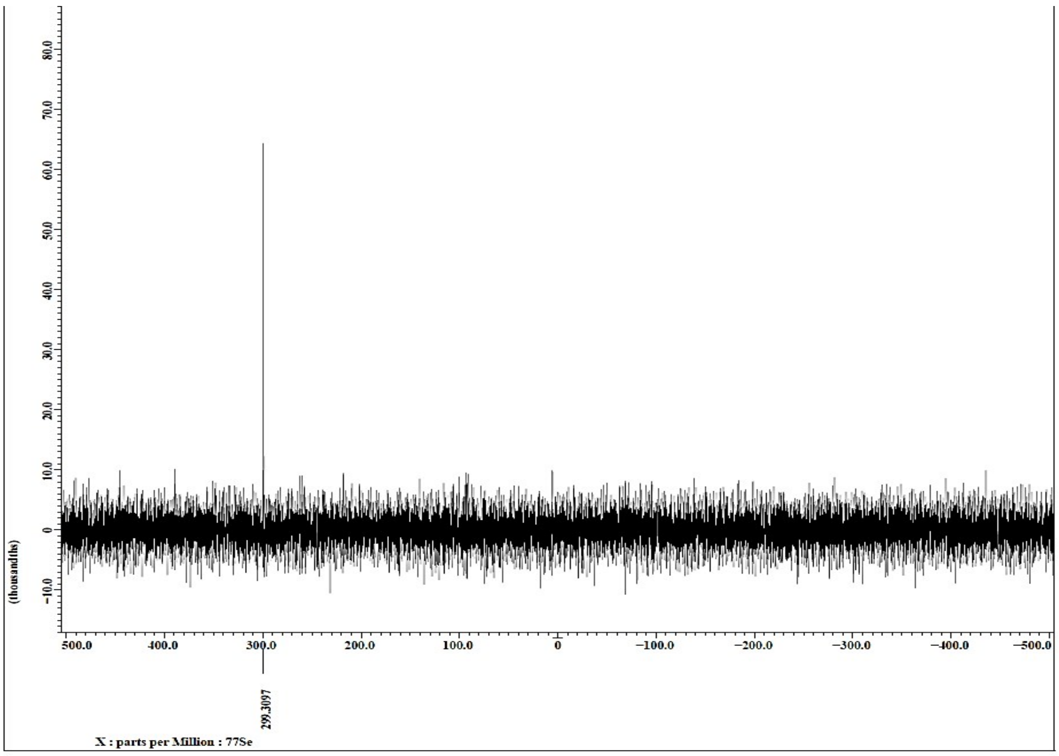


Figure S38. ^{77}Se NMR spectrum (76.2 MHz, DMSO-d$_6$) of **C4**

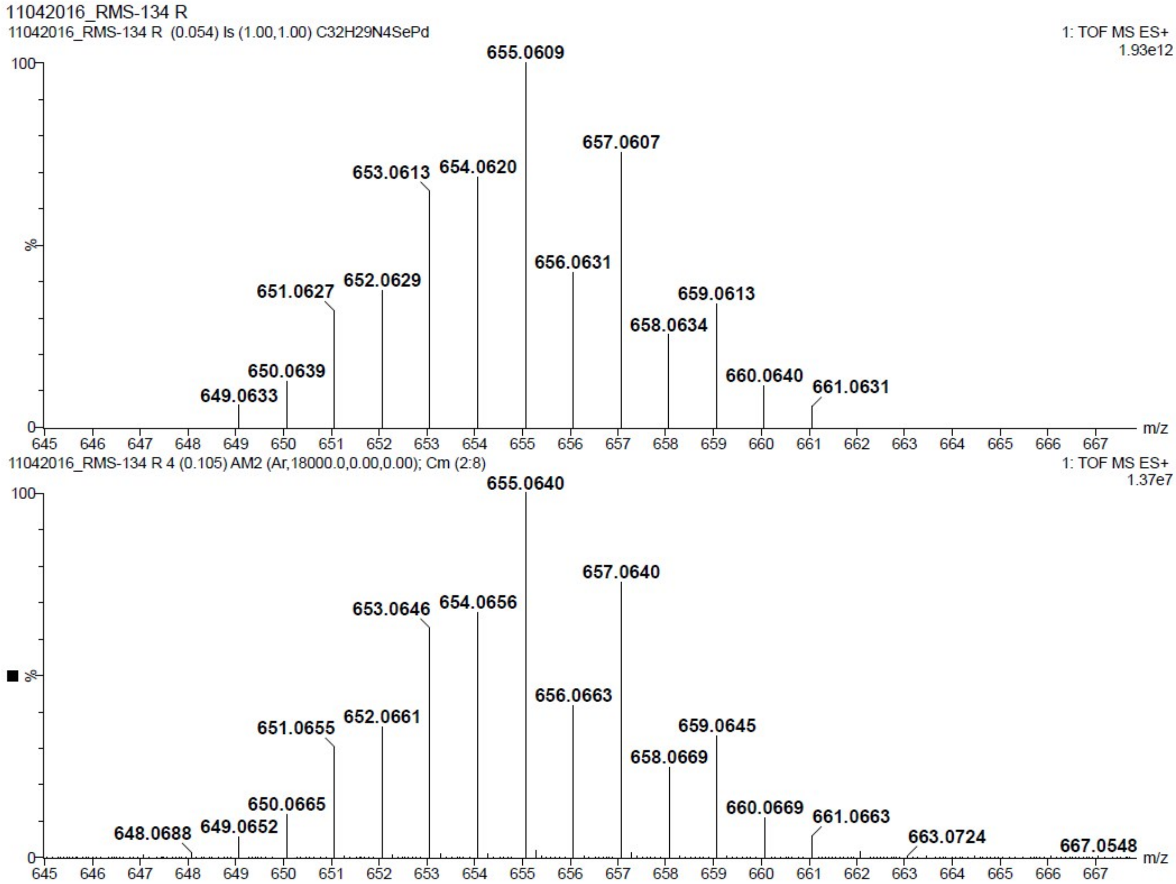
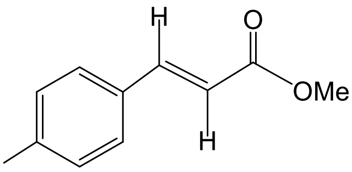


Figure S39. HRMS spectrum (ESI$^+$) of **C4**

Characterization of Heck coupled products

Heteronuclear NMR spectra of 1a and 1b

***trans*-4-methylcinnamic acid methyl ester (1a)**



M.pt. 57-58ºC. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 7.45 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.22(d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 6.42 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 3.82 (s, 3H, OC*H*$_3$), 2.40 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 167.7, 144.9, 140.8, 131.7, 129.6, 128.1, 116.7, 51.7, 21.5. MS (ESI): calcd (found) *m/z* = 178.0993 (178.0732) [M+2H]$^+$

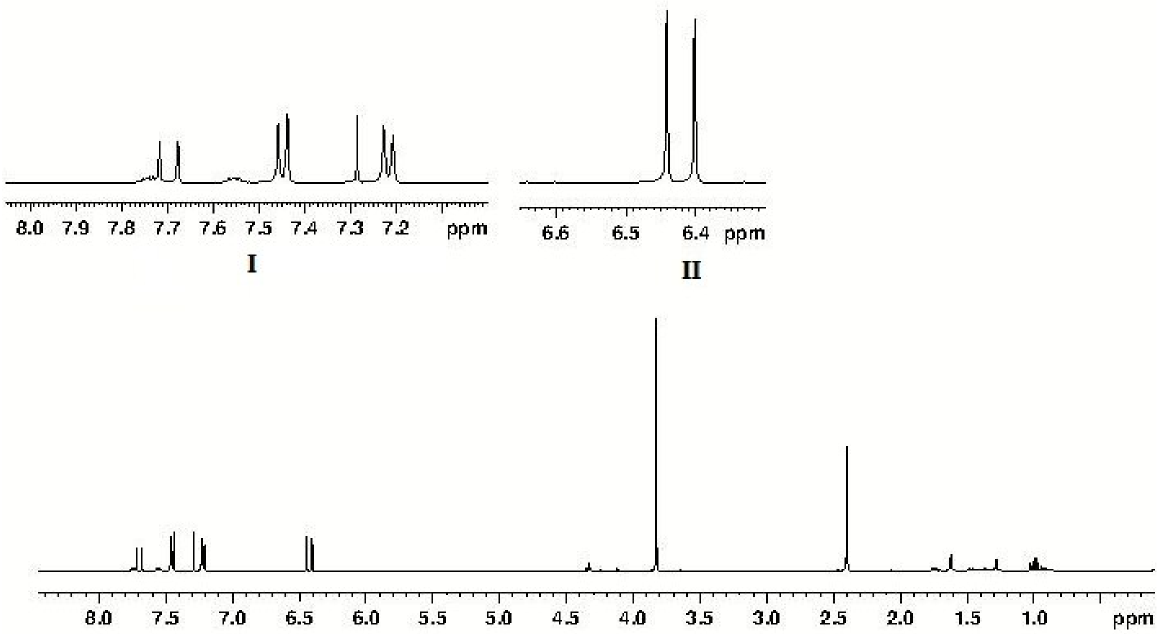


Figure S40. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**. Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

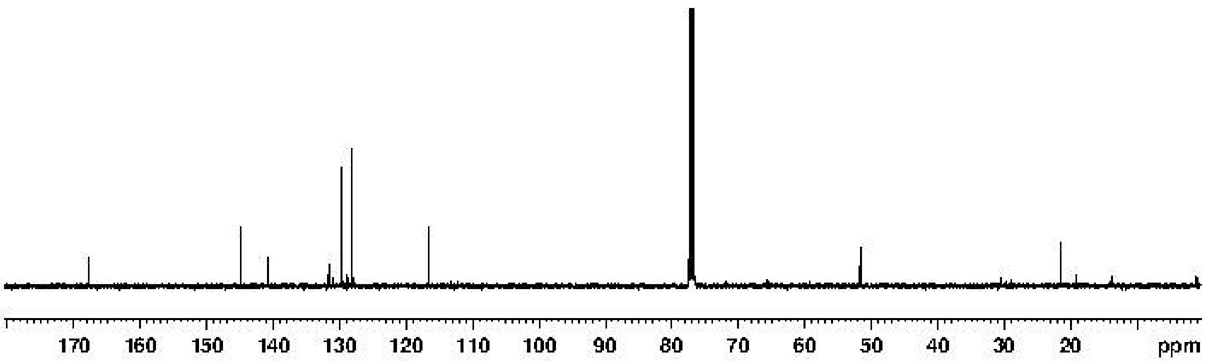
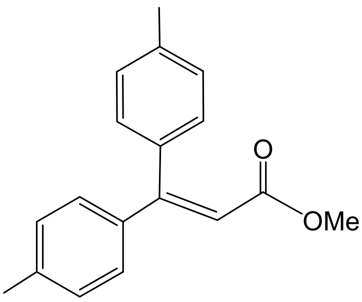


Figure S41. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1a**

***bis*(4-methylphenyl)cinnamic acid methyl ester (1b)**



M.pt. 84.8-86.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, 4H, ^{3}J(H,H) = 12 Hz, Ar-*H*), 7.18 (d, 4H, ^{3}J(H,H) = 12 Hz, Ar-*H*), 6.39 (s, 1H, Alkene), 3.69 (s, 3H, OCH_3), 2.47 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 157.5, 139.7, 138.3, 138.1, 136.0, 129.2, 129.1, 128.7, 128.4, 115.6, 51.2, 21.5, 21.3. MS (ESI): calcd (found) *m/z* = 266.1385 (267.1393) $[M+H]^+$.

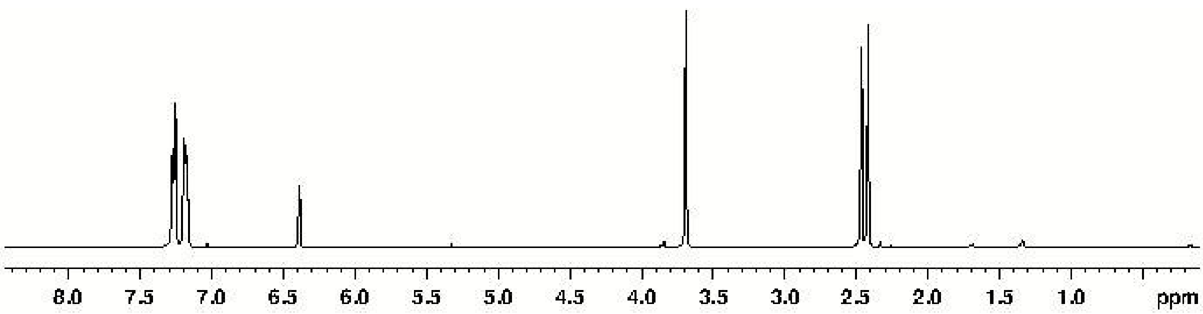


Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**

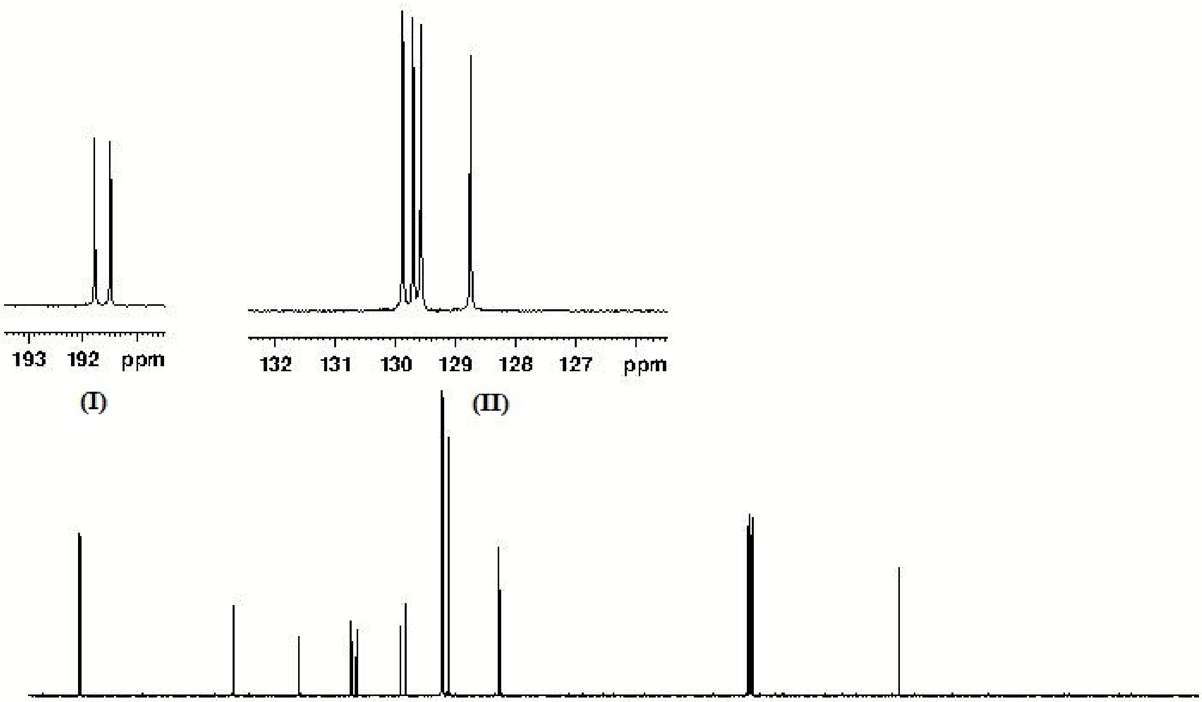
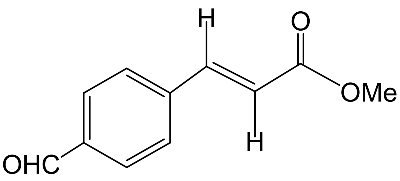


Figure S43. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1b.** Inset **(I)** and **(II)** show expanded aromatic spectral region.

Heteronuclear NMR spectra of 2a and 2b

***trans*-4-formylcinnamic methyl ester (2a)**



M.pt. 75.6-78.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H, C*H*O), 7.89 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.66 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.70 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 6.54 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 3.82 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 166.8, 143.1, 140.0, 137.2, 130.2, 128.5, 120.9, 52.0. MS (ESI): calcd (found) *m/z* = 191.0708 (191.0990) $[M]^+$.

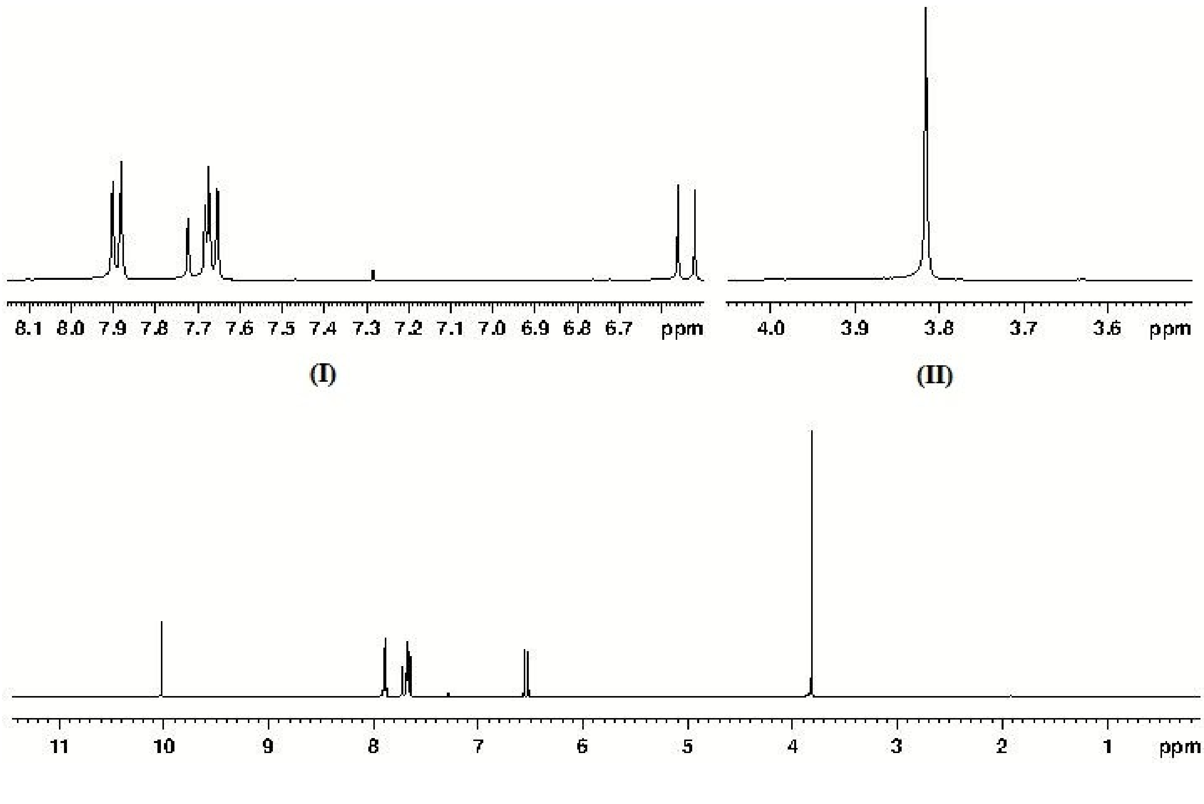


Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a.** Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

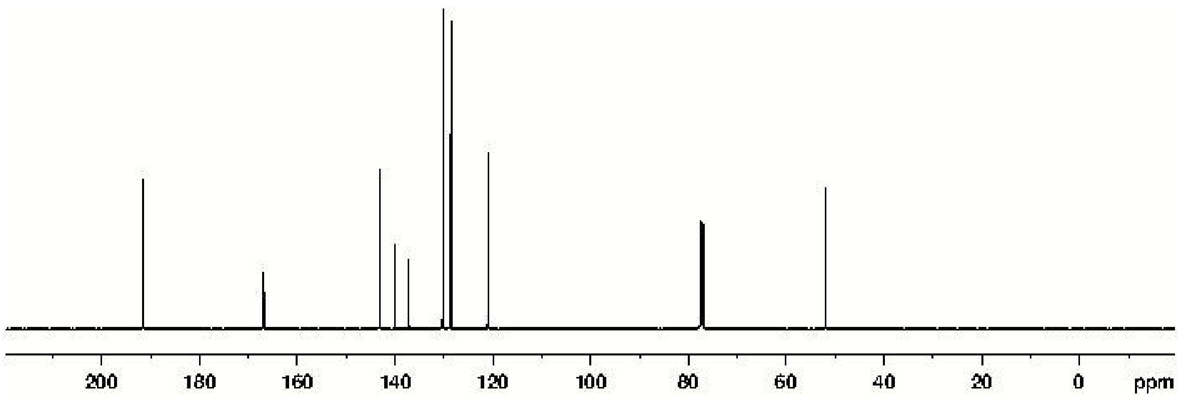
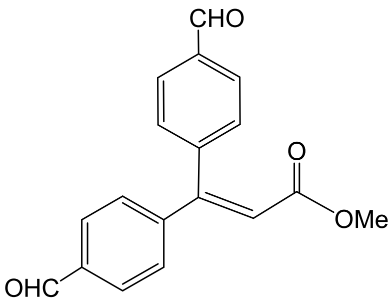


Figure S45. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2a**

***bis*(4-formylphenyl)cinnamic methyl ester (2b)**



M.pt. 113.0-113.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1H, C*H*O), 10.04 (s, 1H, C*H*O), 7.96 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.87 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.45 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.40 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 6.54 (s, 1H, Alkene), 3.65(s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 191.5, 165.6, 154.2, 145.3, 144.4, 136.9, 136.1, 129.9, 129.7, 129.6, 128.8, 120.0, 51.7. MS (ESI): calcd (found) *m/z* = 295.0970 (295.1320) $[M]^+$.

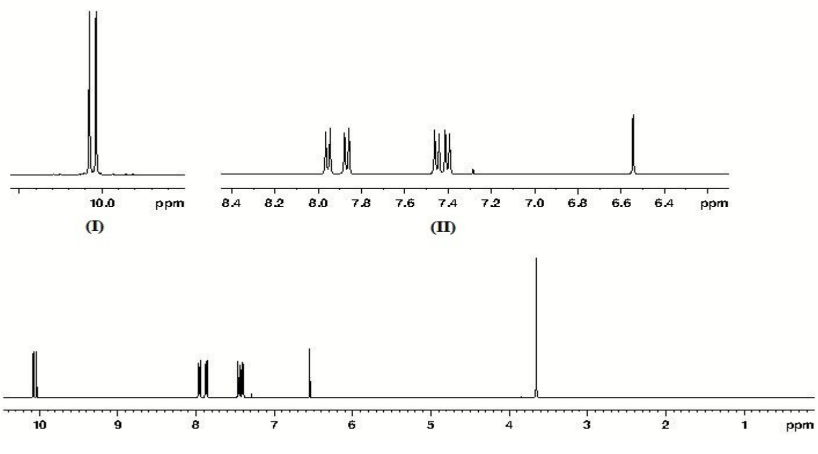


Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(2b)**. Inset **(I)** and **(II)** show expanded aromatic spectral region.

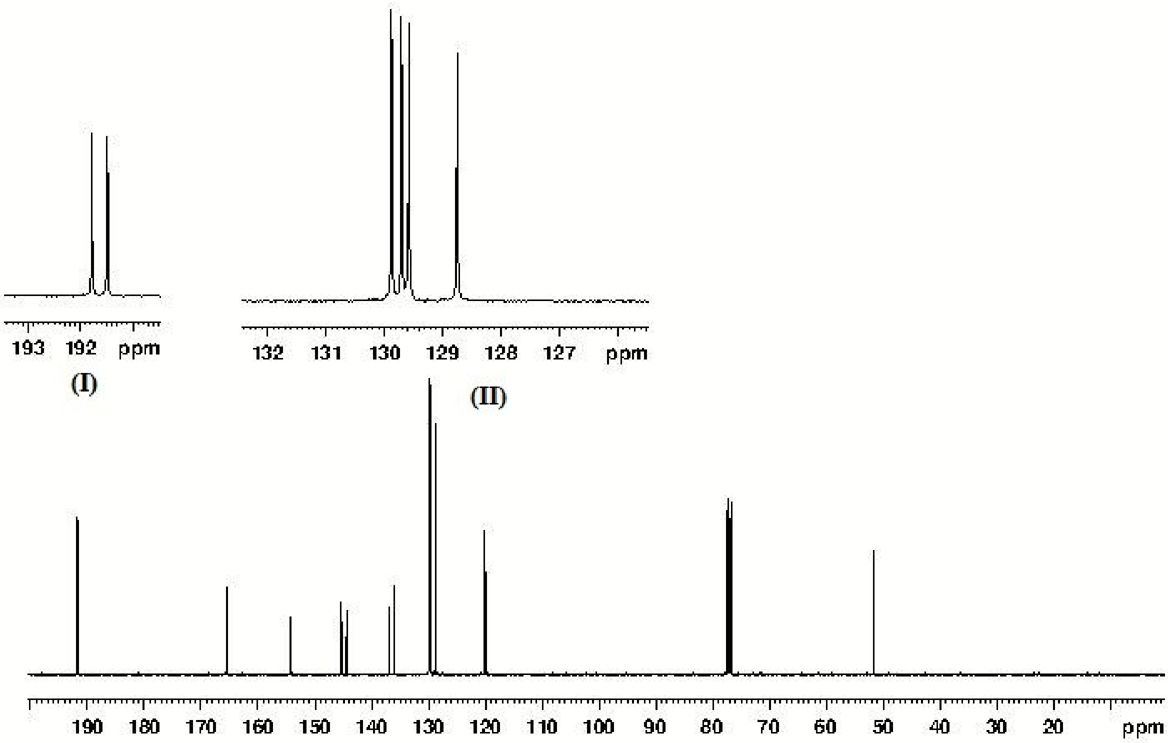
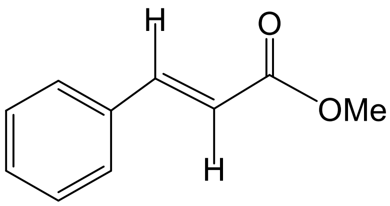


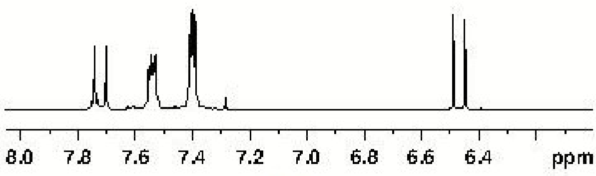
Figure S47. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(2b)**. Inset **(I)** and **(II)** show expanded aromatic spectral region.

Heteronuclear NMR spectra of 3a

***trans*-cinnamic acid methyl ester (3a)**



M.pt. 36-37 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 7.53-7.55 (m, 2H, Ar-*H*), 7.39-7.40 (m, 3H, Ar-*H*), 6.47 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 3.82 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 144.9, 134.4, 131.0, 130.3, 128.9, 128.8, 128.1, 117.8, 51.7. MS (ESI): calcd (found) *m/z* =163.0769 (163.0701) [M+H]$^{+}$.



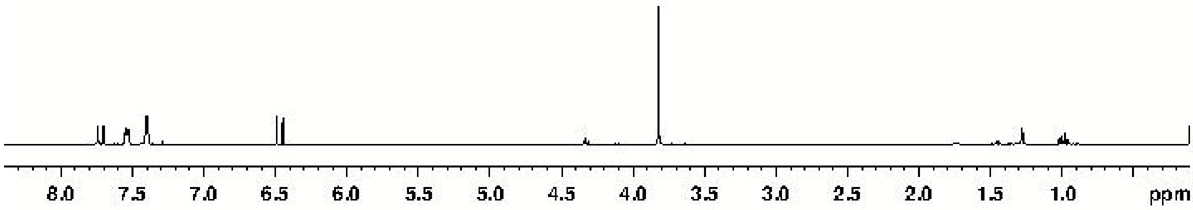


Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(3a)**. Inset **(I)** show expanded aromatic and aliphatic spectral region.

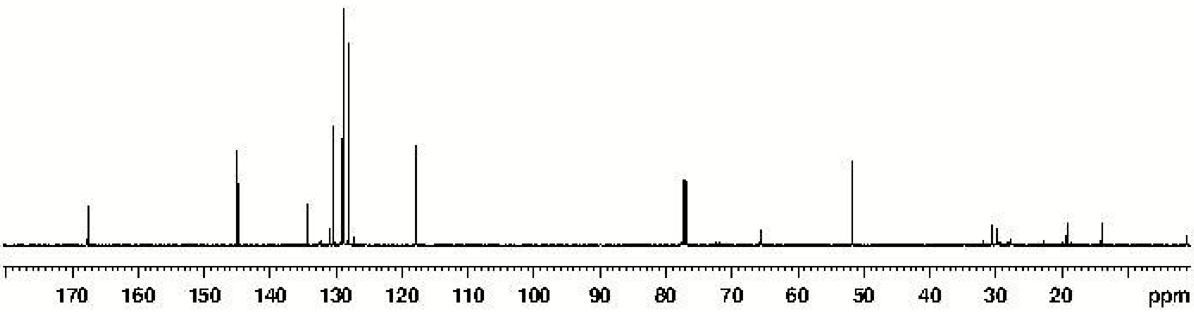
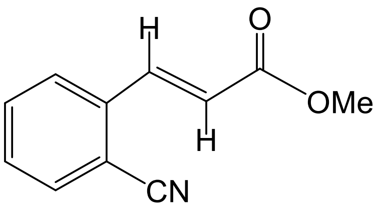


Figure S49. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(3a)**

Heteronuclear NMR spectra of 4a

***trans*-2-cyanocinnamic acid methyl ester (4a)**



M.pt. 61-62 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 7.62-7.77 (m, 3H, Ar-*H*), 7.54 (t, 1H, ^{3}J(H,H) = 24 Hz, Ar-*H*), 6.64 (d, 1H, ^{3}J(H,H) = 16 Hz, Alkene), 3.87 (s, 3H, OCH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 139.6, 137.3, 133.6, 133.0, 130.2, 126.9 122.7, 117.2, 112.8, 51.1. MS (ESI): calcd (found) m/z = 188.0711 (188.0178) $[M+H]^+$.

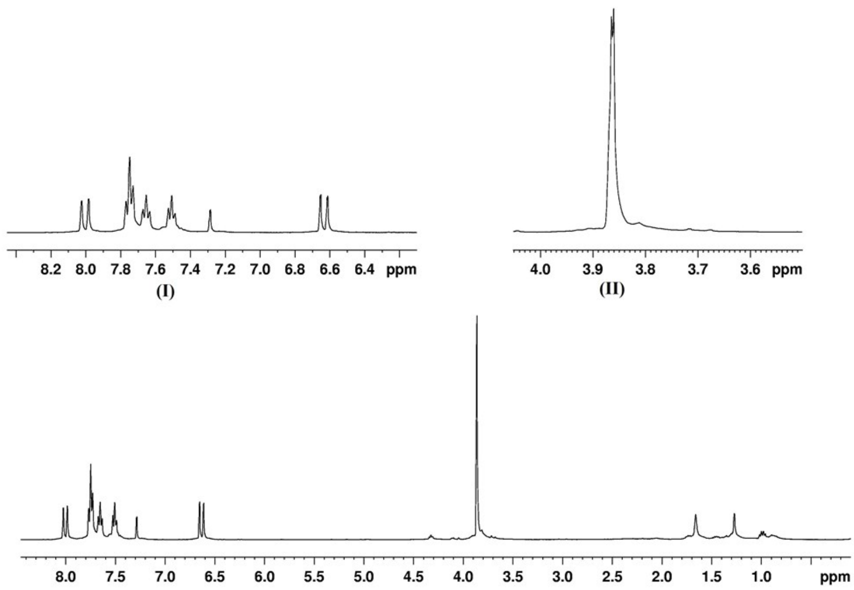


Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(4a)**. Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

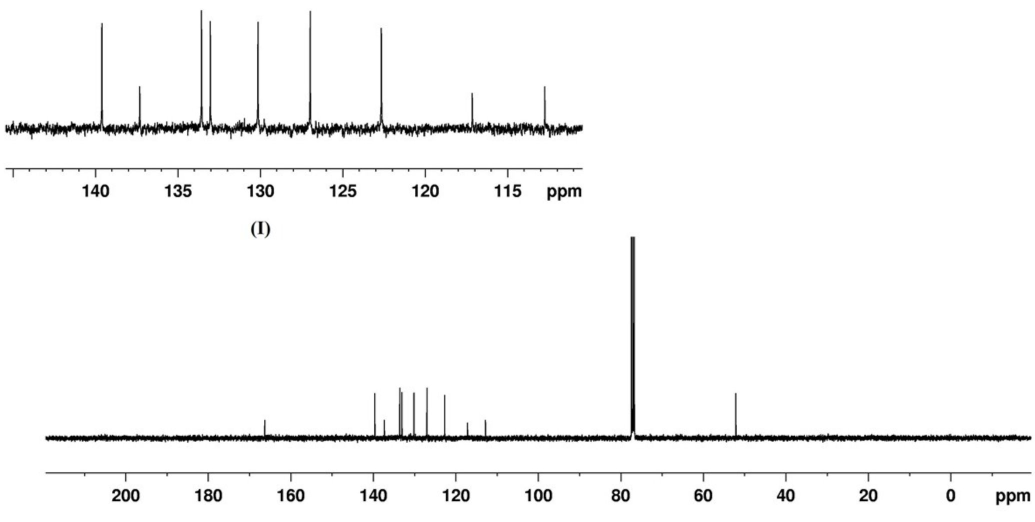
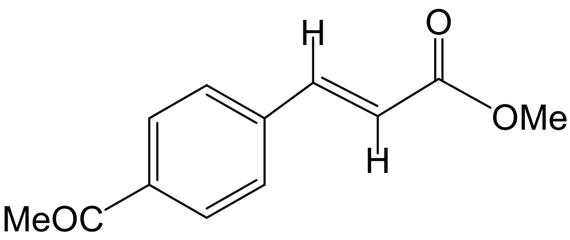


Figure S51. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(4a)**. Inset **(I)** shows expanded aromatic spectral region.

Heteronuclear NMR spectra of 5a and 5b

***trans*-4-acylcinnamic acid methyl ester (5a)**



M.pt. 104-105 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, 4H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 7.73 (d, 1H, ^{3}J(H,H) = 16 Hz, alkene), 7.63 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 6.55 (d, 1H, ^{3}J(H,H) = 16 Hz, alkene), 3.84(s, 3H, OCH_3). 2.64 (s, 3H, -COCH_3) ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 166.1, 143.3, 138.7, 138.0, 128.8, 128.2, 120.3, 52.0, 26.8. MS (ESI): calcd (found) *m/z* =205.0864 (205.0865) $[M+H]^{+}$.

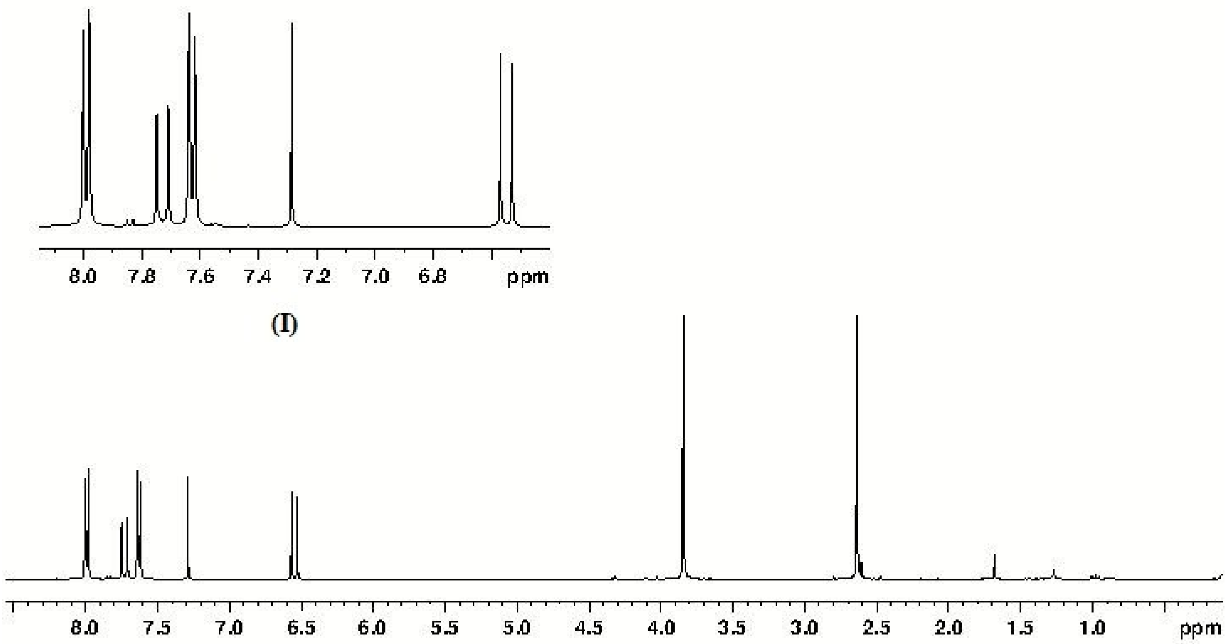


Figure S52. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(5a)**. Inset **(I)** shows expanded aromatic spectral region.

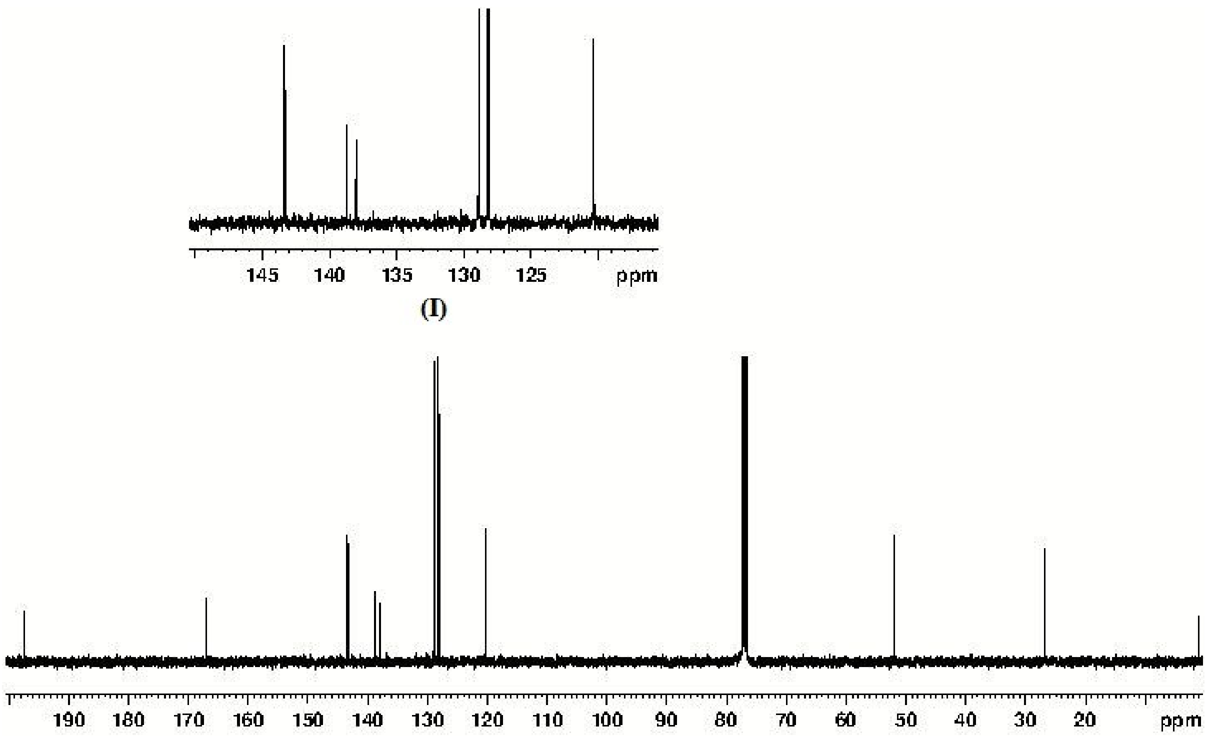
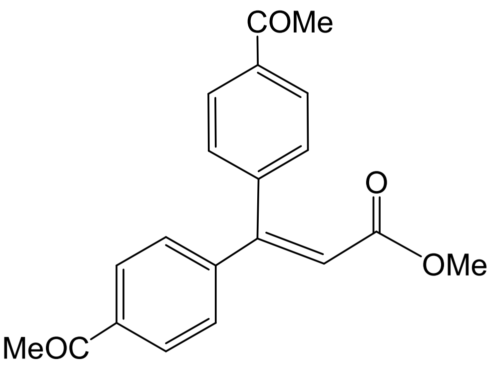


Figure S53. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(5a)**. Inset **(I)** shows expanded aromatic spectral region.

***bis*(4-acyl phenyl) cinnamic acid methyl ester (5b)**



M.pt. 126.0-129.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, 2H, ^3J(H,H) = 4 Hz, Ar-*H*),7.93 (d, 2H, ^3J(H,H) = 4 Hz, Ar-*H*), 7.38 (d, 2H, ^3J(H,H) = 4 Hz, Ar-*H*), 7.33 (d, 2H, ^3J(H,H) = 4 Hz, Ar-*H*), 6.51 (s, 1H, alkene), 3.66 (s, 3H, -OCH_3), 2.66 (s, 3H, -COCH_3), 2.62 (s, 3H, -COCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.6, 197.4, 165.7, 154.6, 144.2, 143.2, 137.7, 136.8, 129.3, 128.5, 128.4, 128.2, 119.3, 51.6, 26.8, 26.7. MS (ESI): calcd (found) *m/z* = 323.1283 (323.1277) $[M+H]^+$.

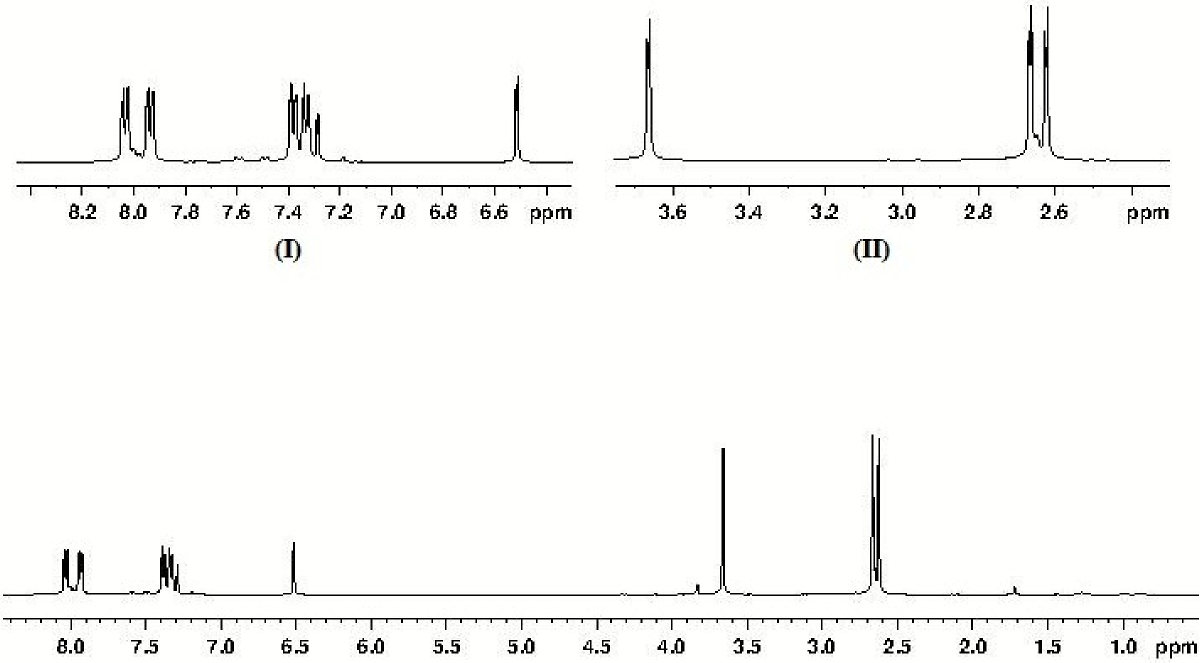


Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(5b)**. Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

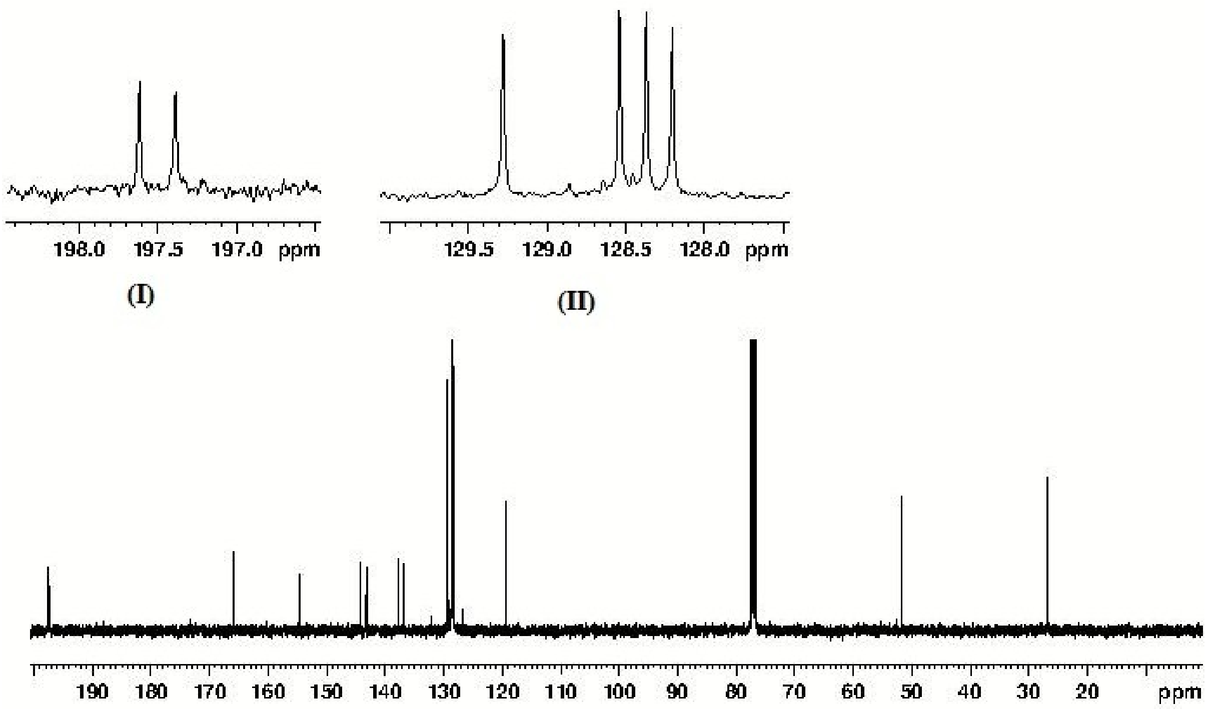
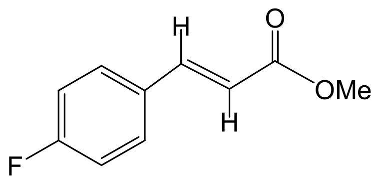


Figure S55. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(5b)**. Inset **(I)** and **(II)** show expanded aromatic spectral region.

Heteronuclear NMR spectra of 6a

***trans*-4-fluorocinnamic acid methyl ester (6a)**



M.pt. 45-47 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, 1H, ^{3}J(H,H) = 16 Hz, alkene), 7.50-7.54 (m, 2H, Ar-*H*), 7.06-7.11 (m, 2H, Ar-*H*), 6.37 (d, 1H, ^{3}J(H,H) = 16 Hz, alkene), 3.81 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 162.6, 143.6, 129.9, 130.0, 117.5, 116.0, 51.6. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ = -109.6. MS (ESI): calcd (found) *m/z* = 181.0664 (181.0617) $[M+H]^+$.

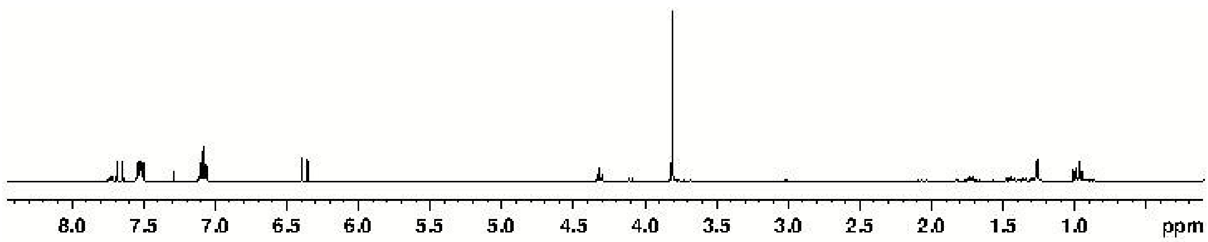


Figure S56. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(6a)**

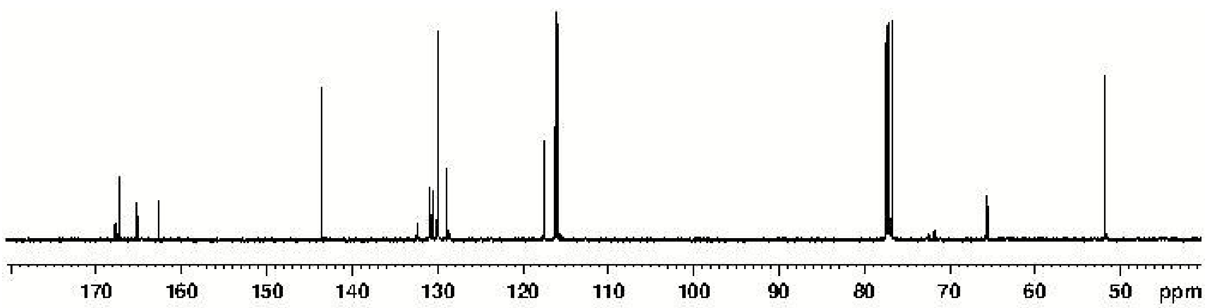


Figure S57. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(6a)**

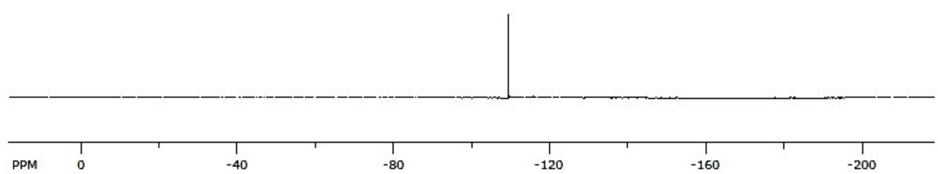
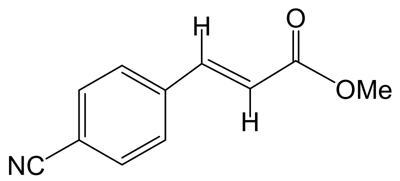


Figure S58. ^{19}F NMR spectrum (376.4 MHz, $CDCl_3$) of **(6a)**

Heteronuclear NMR spectra of 7a and 7b

***trans*-4-cyanocinnamic acid methyl ester (7a)**



M.pt. 100-102 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.72* (m, 5H, alkene & Ar-*H*), 6.54 (d, 1H, ^{3}J(H,H) = 16 Hz, alkene), 3.85(s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 142.5, 138.6, 132.7, 128.4, 121.4, 118.4, 113.4, 52.1. MS (ESI): calcd (found) *m/z* = 188.0711 (188.0767) $[M+H]^{+}$.

* one of the olefinic proton merged in the aromatic region

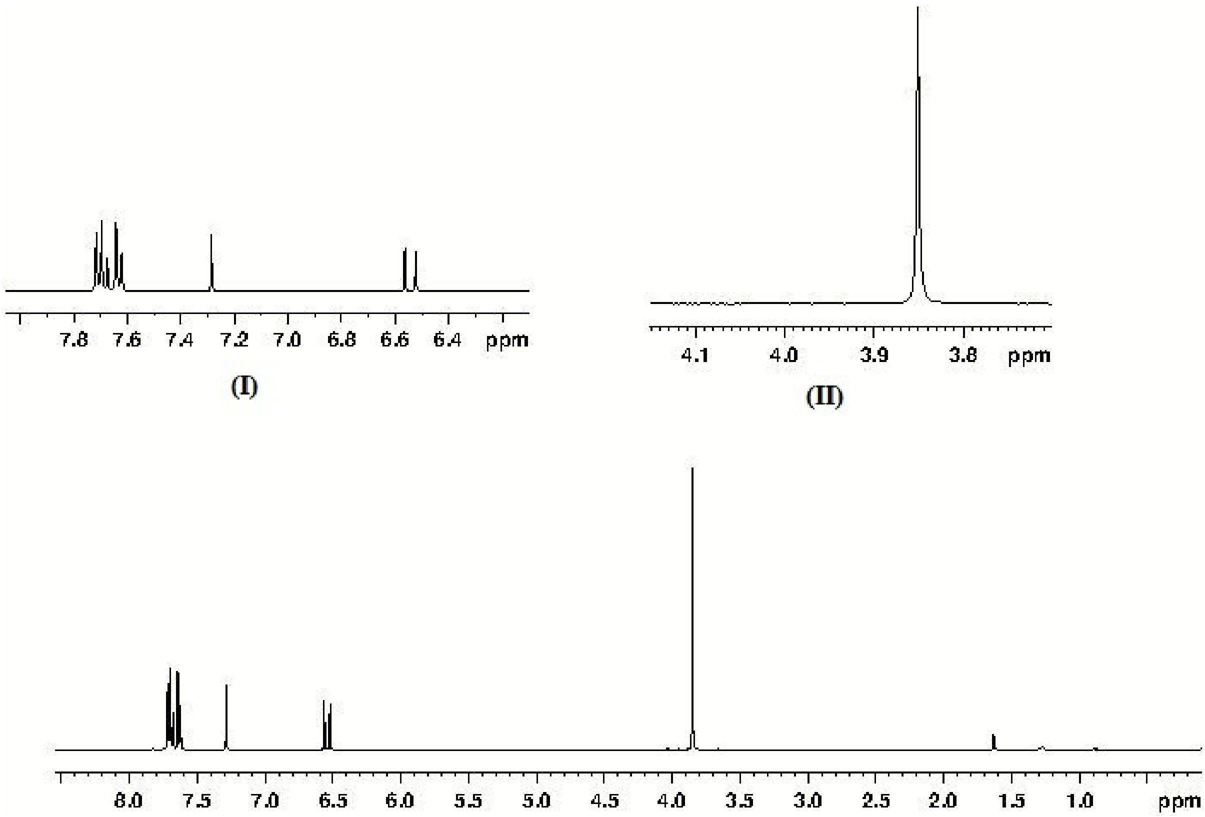


Figure S59. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(7a)**. Insets **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

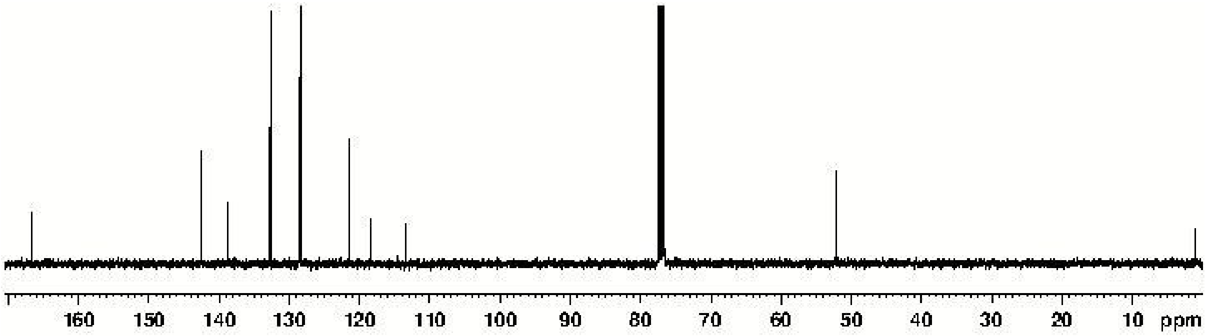
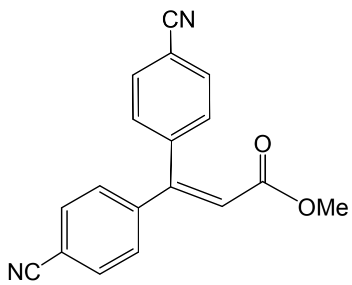
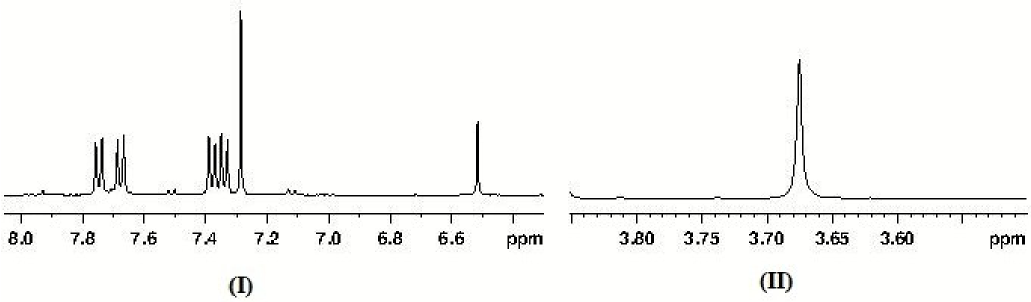


Figure S60. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(7a)**

***bis*(4-cyanophenyl)cinnamic acid methyl ester (7b)**



M.pt. 100-102 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.75 (m, 4H Ar-*H*), 7.33-7.39 (m, 4H, Ar-*H*), 6.52 (s, 1H, alkene) 3.68 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 152.9, 143.6, 142.4, 132.5, 132.1, 129.8, 128.6, 120.6, 118.5, 118.1, 113.5, 112.6, 51.9. MS (ESI): calcd (found) m/z = 289.0977 (289.0771) $[M+H]^+$.



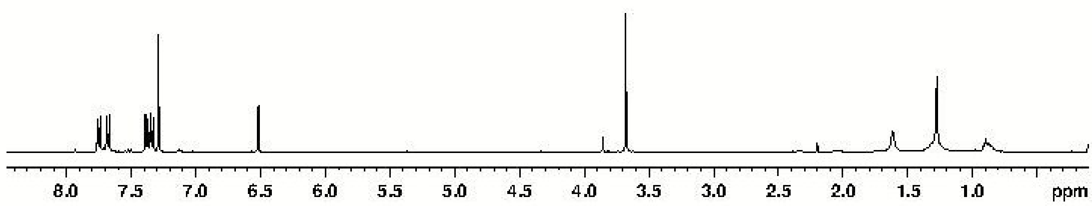


Figure S61. ^1H NMR spectrum (400 MHz, $CDCl_3$) of **(7b)**. Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region.

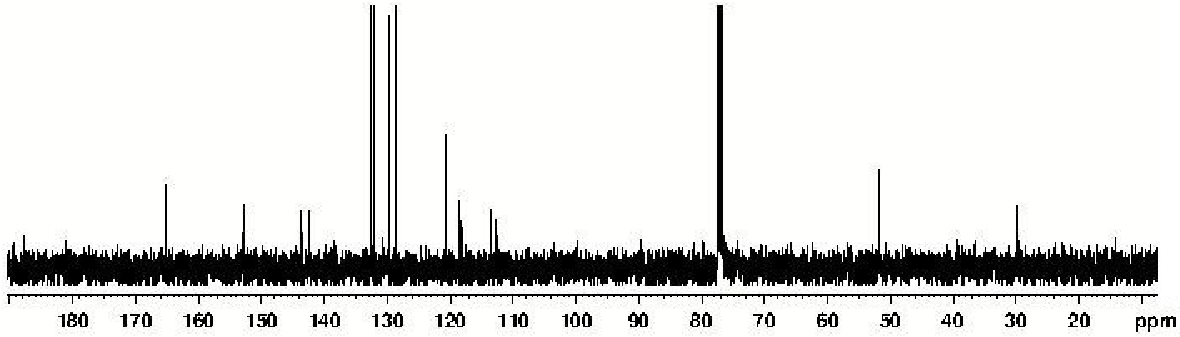
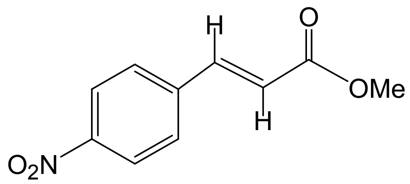


Figure S62. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(7b)**

Heteronuclear NMR spectra of 8a and 8b

***trans*-4-nitrocinnamic acid methyl ester (8a)**



M.pt. 132-133 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, 2H, ^3J(H,H) = 8 Hz, Ar-*H*), 7.74 (d, 1H, ^3J(H,H) = 16 Hz, alkene), 7.70 (d, 2H, ^3J(H,H) = 8 Hz, Ar-*H*), 6.59 (d, 1H, ^3J(H,H) = 16 Hz, alkene), 3.86 (s, 3H, OCH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 148.5, 141.9, 140.5, 128.7, 124.2, 122.1, 52.1. MS (ESI): calcd (found) m/z = 208.0609 (208.0657) $[M+H]^+$.

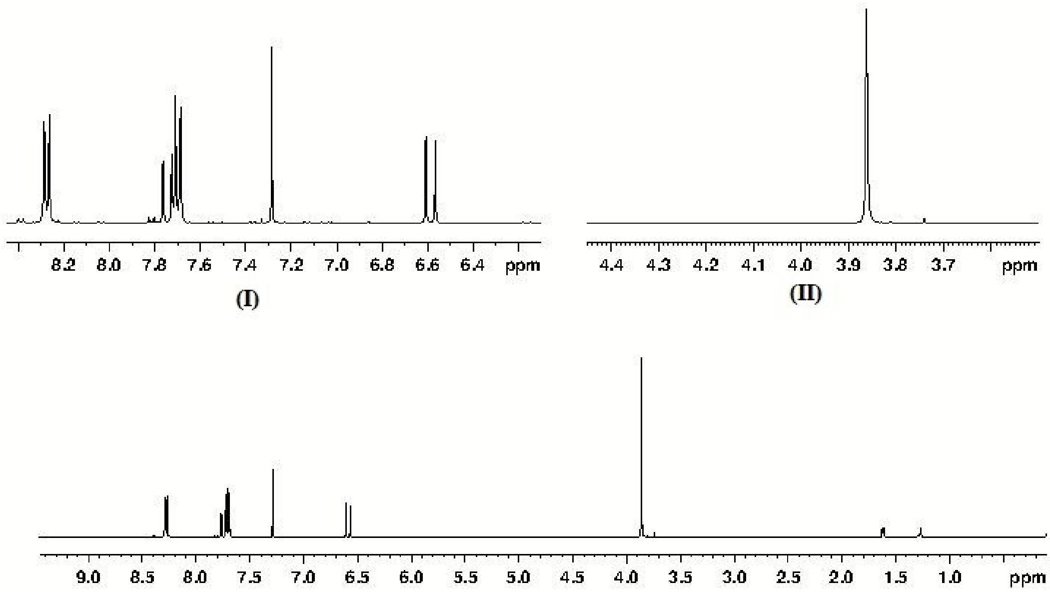


Figure S63. ^1H NMR spectrum (400 MHz, $CDCl_3$) of **(8a)**. Inset **(I)** and **(II** show expanded aromatic and aliphatic spectral region.

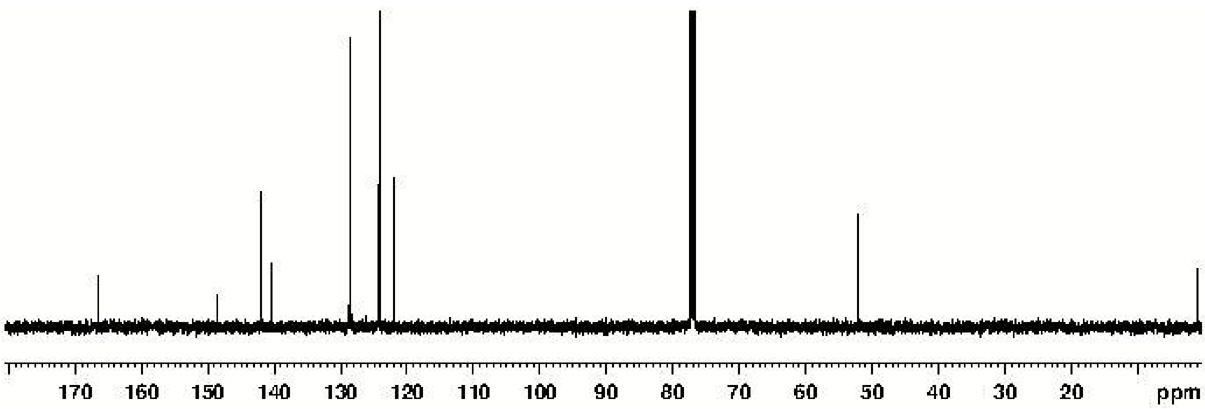
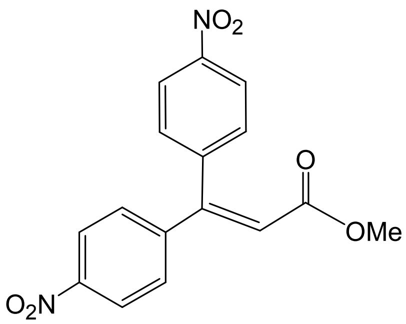
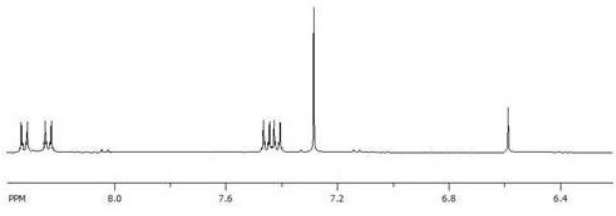


Figure S64. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **(8a)**

***bis*(4-nitrophenyl)cinnamic acid methyl ester (8b)**



M.Pt. 155-157 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, 2H,^{3}J(H,H) = 16 Hz, Ar-*H*), 8.23 (d, 2H, ^{3}J(H,H) = 16 Hz, Ar-*H*), 7.46 (d, 2H, ^{3}J(H,H) = 12 Hz, Ar-*H*), 7.42 (d, 2H, ^{3}J(H,H) = 8 Hz, Ar-*H*), 6.59 (s, 1H, alkene), 3.69 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 152.2, 148.0, 145.2, 144.3, 130.0, 128.9, 124.0, 123.7, 121.4, 51.9. MS (ESI): calcd (found) *m/z* =329.0773 (329.1685) $[M+H]^{+}$.



(I)

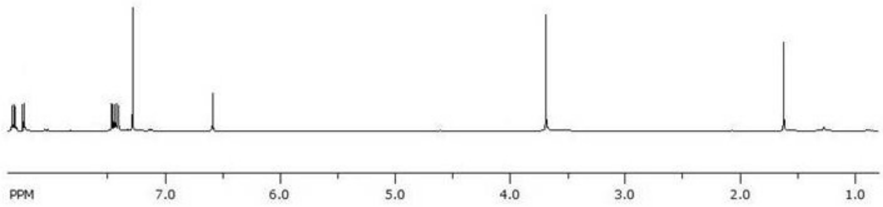


Figure S65. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **(8b)**. Inset **(I)** shows expanded aromatic spectral region.

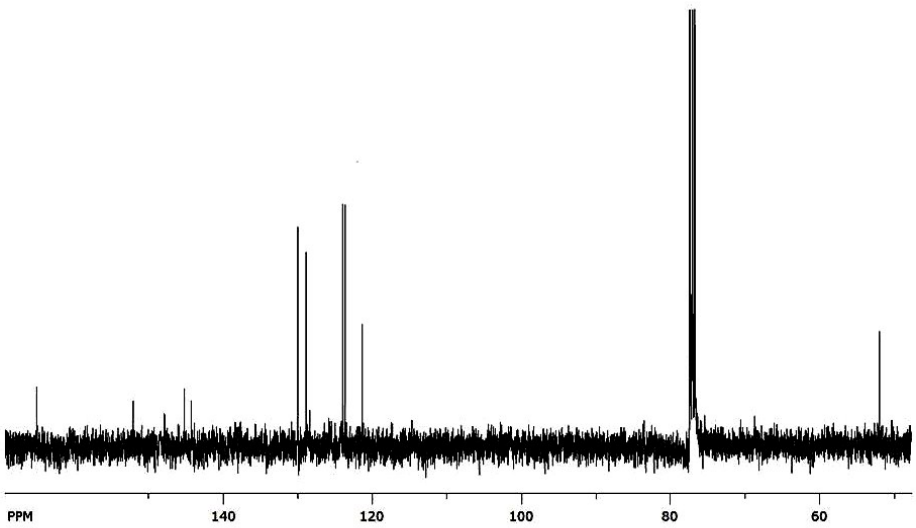


Figure S66. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **(8b)**

Structural description and X-ray data for (LH$_2$)(BF$_4$)$_2$ and compound 2b.

Crystals of (**L**H_2)(BF_4)$_2$ suitable for X-ray diffraction were grown by slow evaporation of its methanol solution. The salt (**L**H_2)(BF_4)$_2$ crystallizes in the triclinic system with $P\bar{1}$ space group (Figure S52, Table S1). The arrangement of atoms in the backbone of (**L**H_2)(BF_4)$_2$ and the orientation of benzimidazole rings and its substituents closely resembles to that of (**L**H_2)Br_2 with similar metric parameters. The average B–F distance in the BF_4^- anion is 1.350 Å for (**L**H_2)(BF_4)$_2$.

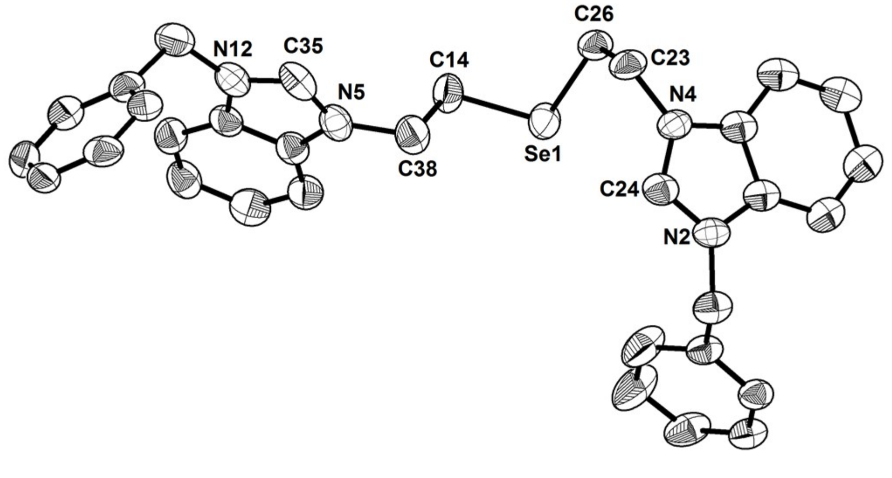


Figure S67 Solid state structure of (**L**H_2)(BF_4)$_2$. Ellipsoids are set at the 50% probability level. Two BF_4^- anions and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: C(14)–Se(1) 1.955(7), C(26)–Se(1) 1.956(7), C(24)–N(2) 1.329(9), C(24)–N(4) 1.344(9), C(23)-N(4) 1.464(8), C(38)-N(5) 1.489(9), C(35)-N(5) 1.343(10), C(35)-N(12) 1.319(10), C(14)-Se(1)-C(26) 102.0(3), C(23)–N(4)–C(24), 125.5(6), N(2)–C(24)–N(4) 110.8(6), N(5)–C(35)–N(12) 110.2(7), C(35)–N(5)–C(38) 127.2(7).

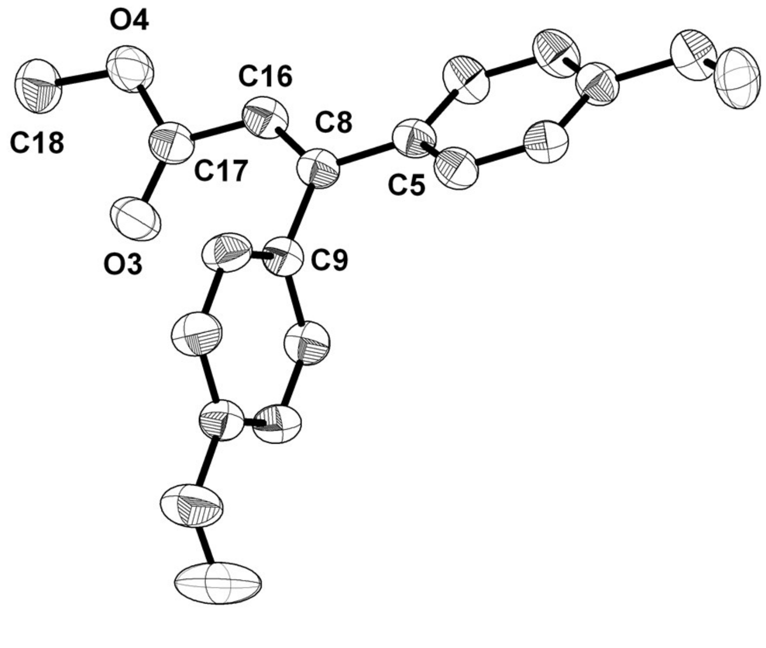


Figure S68 Single crystal X-ray structure of **2b**.

Table S1: Crystallographic parameters for compounds (**L**H_2)$(BF_4)_2$ and **2b.**

Compound[a]	(**L**H_2)$(BF_4)_2$	*bis*(4-formylphenyl) cinnamic acid methyl ester **(2b)**
Chemical formula	$C_{32}H_{32}N_4B_2F_8Se$	$C_{18}H_{14}O_4$
Molar mass	725.19	294.29
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	C_2/c
T [K]	100.0(2)	296.0(2)
a [Å]	11.7285(8)	25.424(8)
b [Å]	11.8807(7)	8.1347(17)
c [Å]	12.3142(8)	15.680(4)
α[°]	96.183(5)	90.0
β [°]	98.868(6)	113.947(13)
γ[°]	101.395(5)	90.0
V [Å^3]	1644.96(19)	2963.7(14)
Z	2	8
D(calcd.) [g·cm^{-3}]	1.464	1.319
μ(Mo-K_α) [mm^{-1}]	1.216	0.093
Index range	$-13 \leq h \leq 13$	$-30 \leq h \leq 27$
	$-14 \leq k \leq 14$	$0 \leq k \leq 9$
	$-13 \leq l \leq 14$	$0 \leq l \leq 18$
Reflections collected	10901	12921
Independent reflections	5803	2713
Data/restraints/parameters	5803/393/486	2713/0/200
$R1, wR2[I>2\sigma(I)]$[a]	0.081, 0.212	0.0781, 0.231
R1, wR2 (all data)[a]	0.114, 0.239	0.094, 0.243
GOF	1.036	1.096

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |FC3|)^2/\Sigma w|Fo^2|^2]^{1/2}$