Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Contents

1. NMR spectra for the ligands **L1** – **L5**

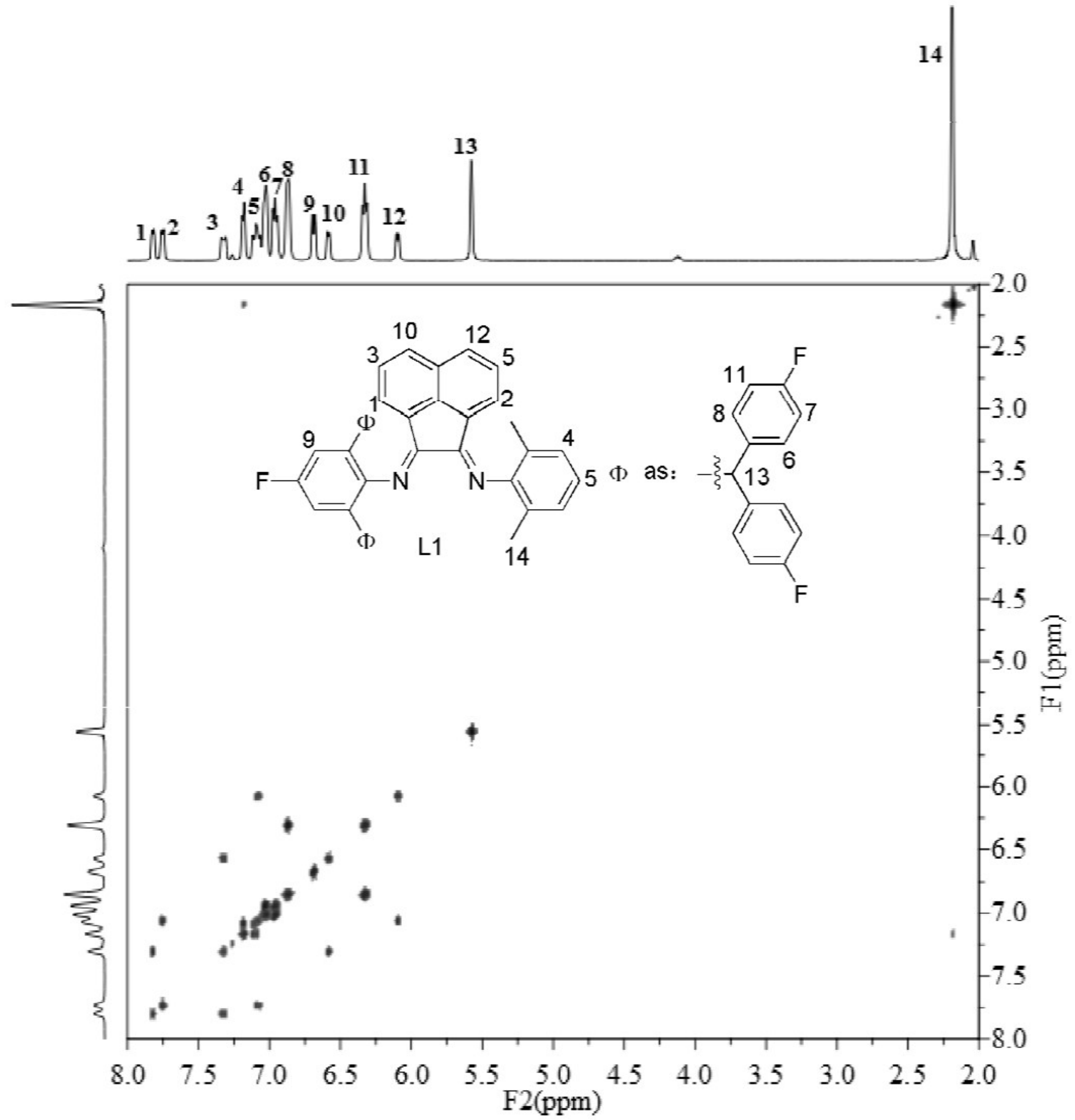

Figure S1. ^1H–^1H COSY spectrum of **L1** in $CDCl_3$ at room temperature

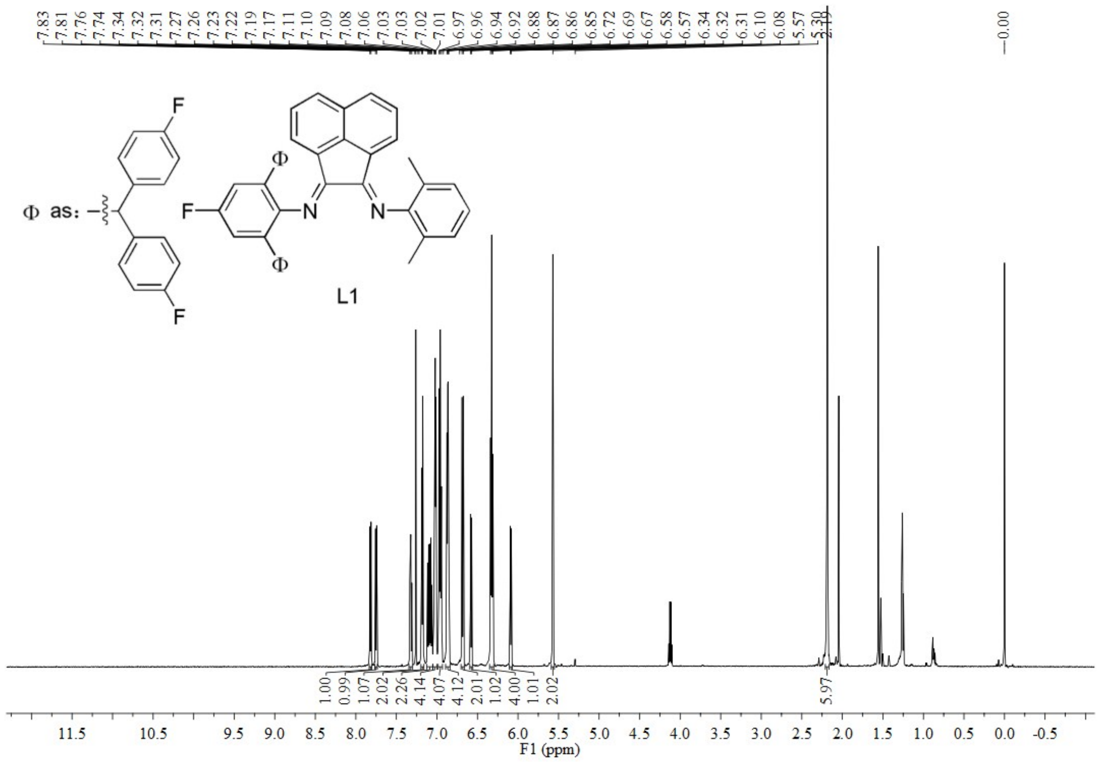

Figure S2. ^{1}H NMR spectrum of **L1** in $CDCl_3$ at room temperature

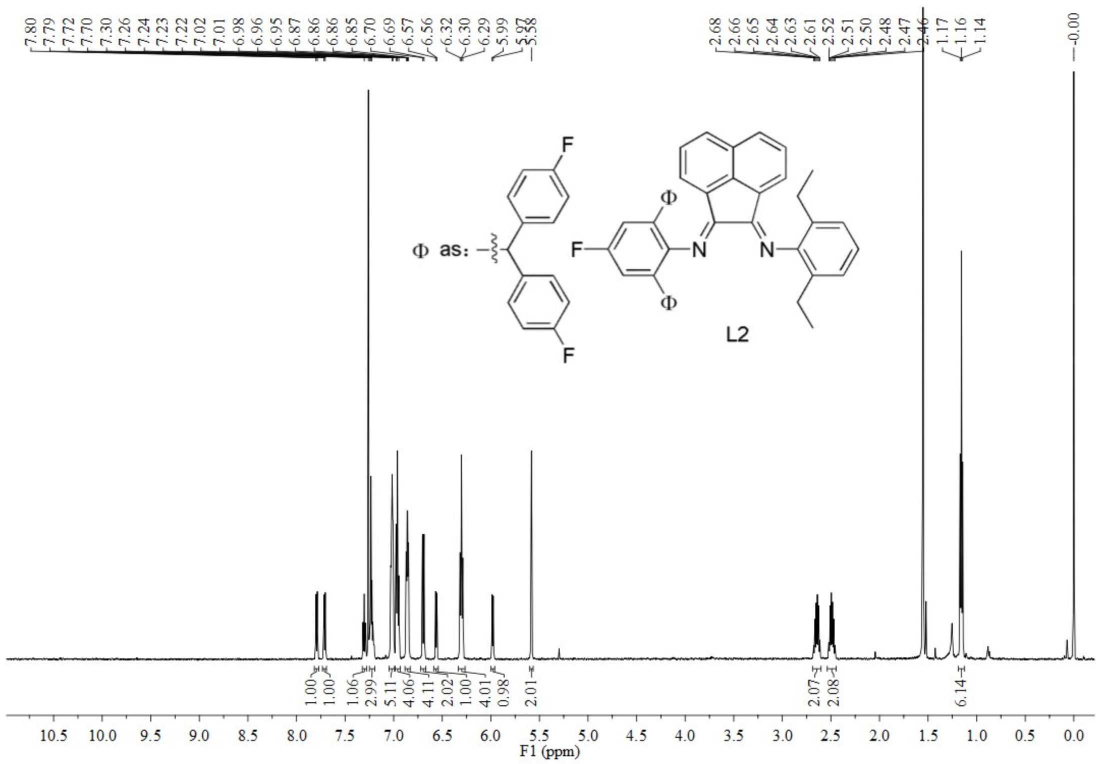

Figure S3. ^{1}H NMR spectrum of **L2** in $CDCl_3$ at room temperature

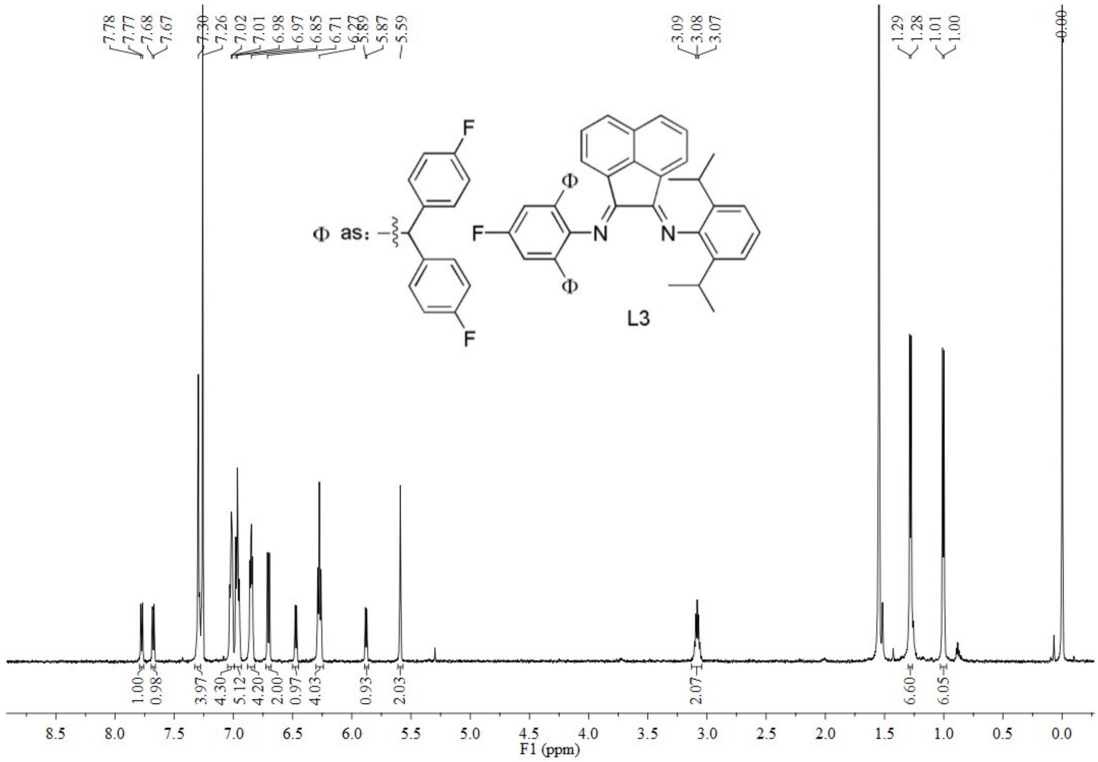

Figure S4. ^{1}H NMR spectrum of **L3** in $CDCl_3$ at room temperature

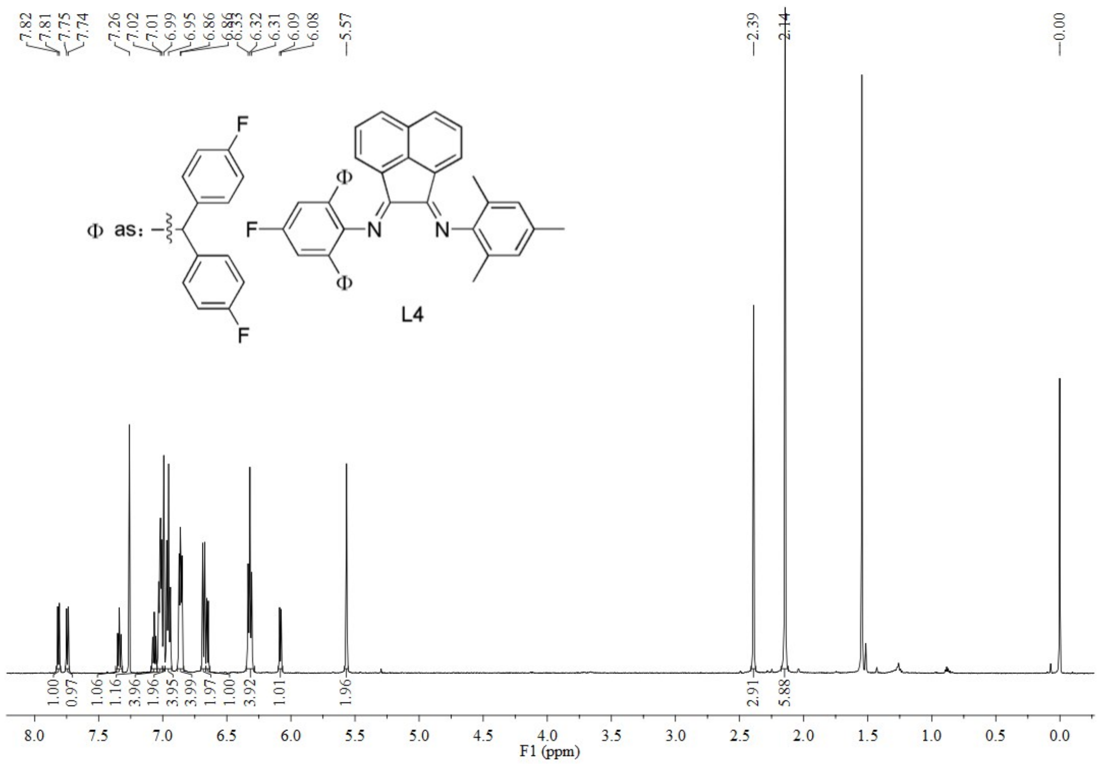

Figure S5. ^{1}H NMR spectrum of **L4** in $CDCl_3$ at room temperature

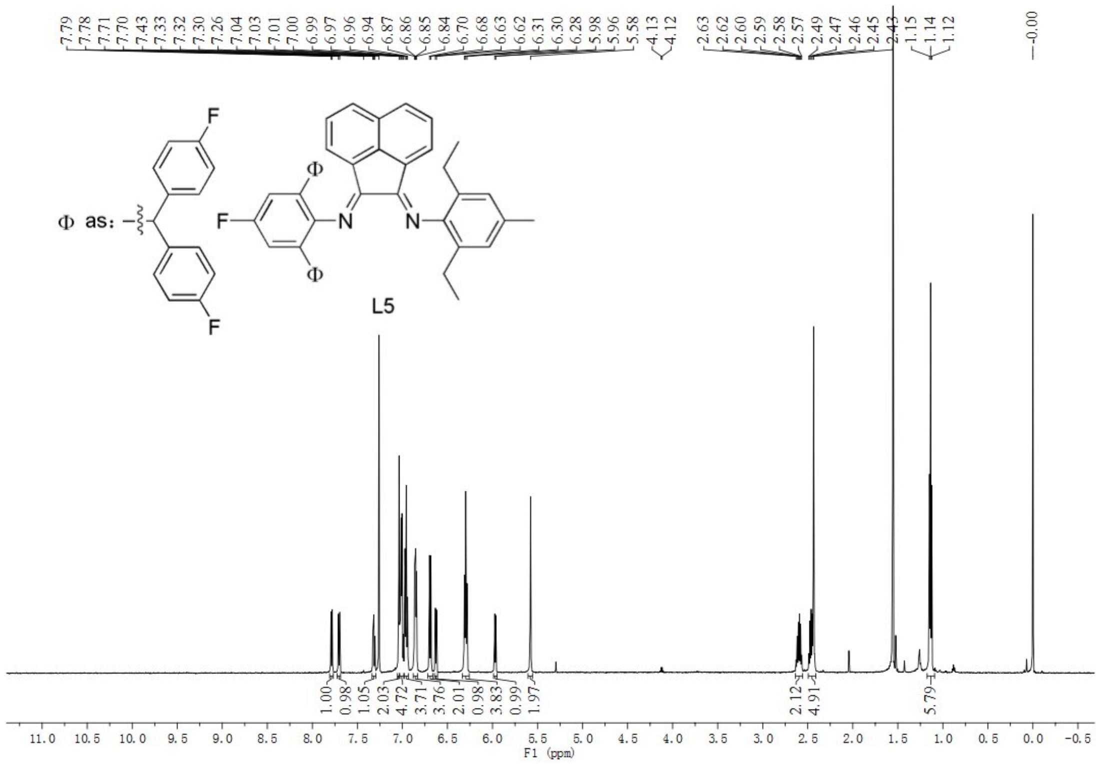

Figure S6. ^{1}H NMR spectrum of **L5** in $CDCl_3$ at room temperature

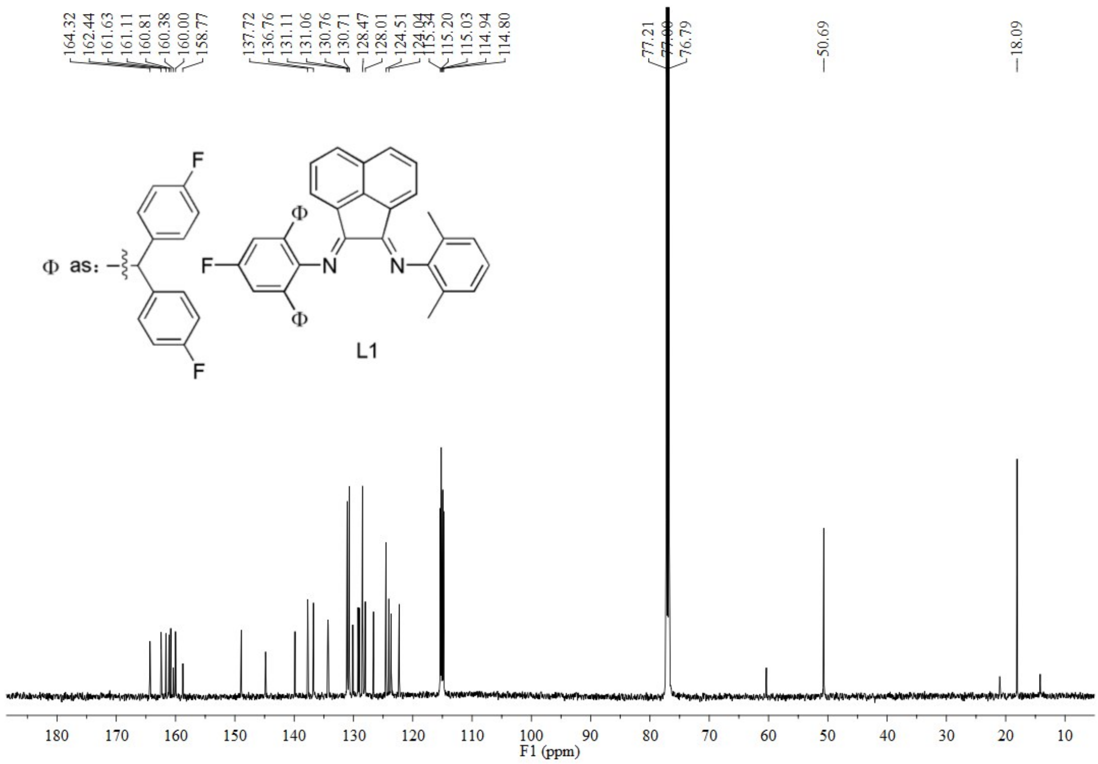

Figure S7. ^{13}C NMR spectrum of **L1** in $CDCl_3$ at room temperature

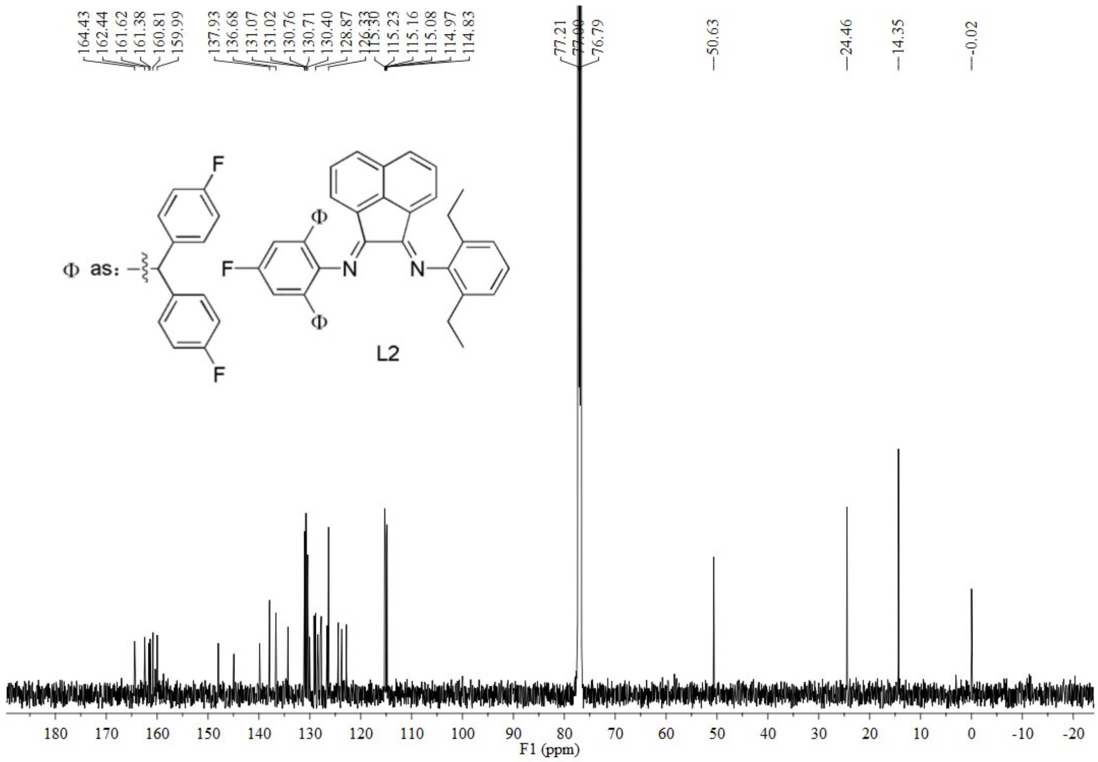

Figure S8. ^{13}C NMR spectrum of **L2** in $CDCl_3$ at room temperature

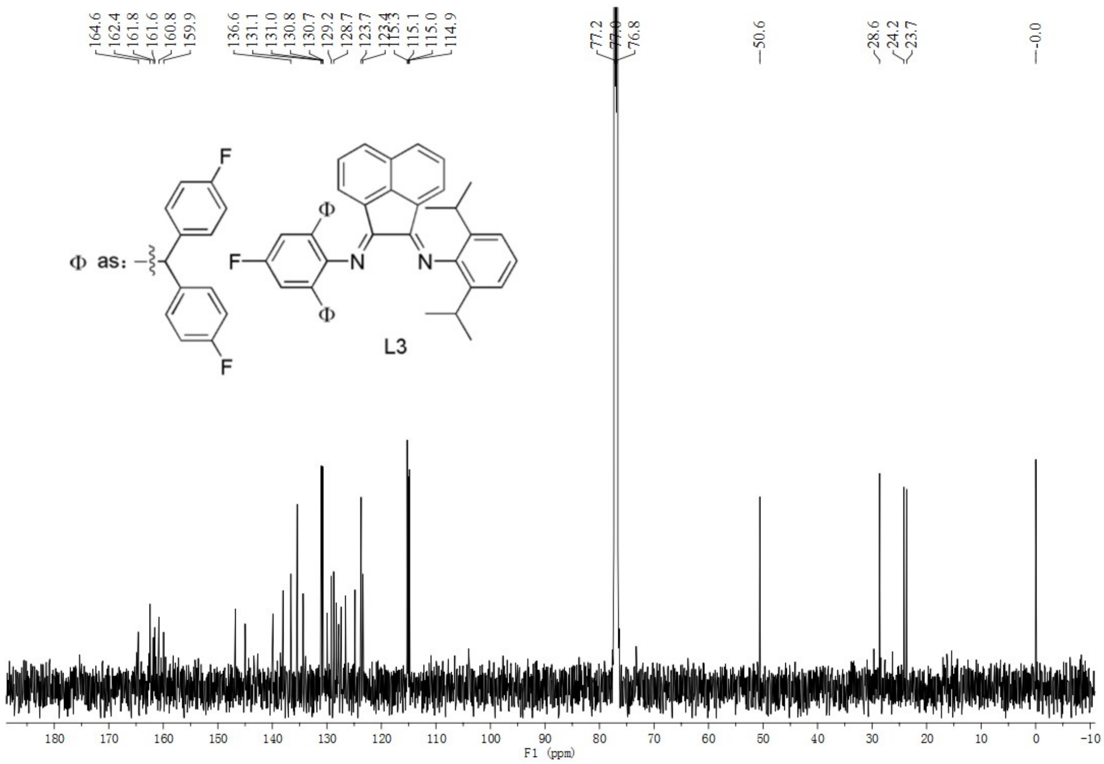

Figure S9. ^{13}C NMR spectrum of **L3** in $CDCl_3$ at room temperature

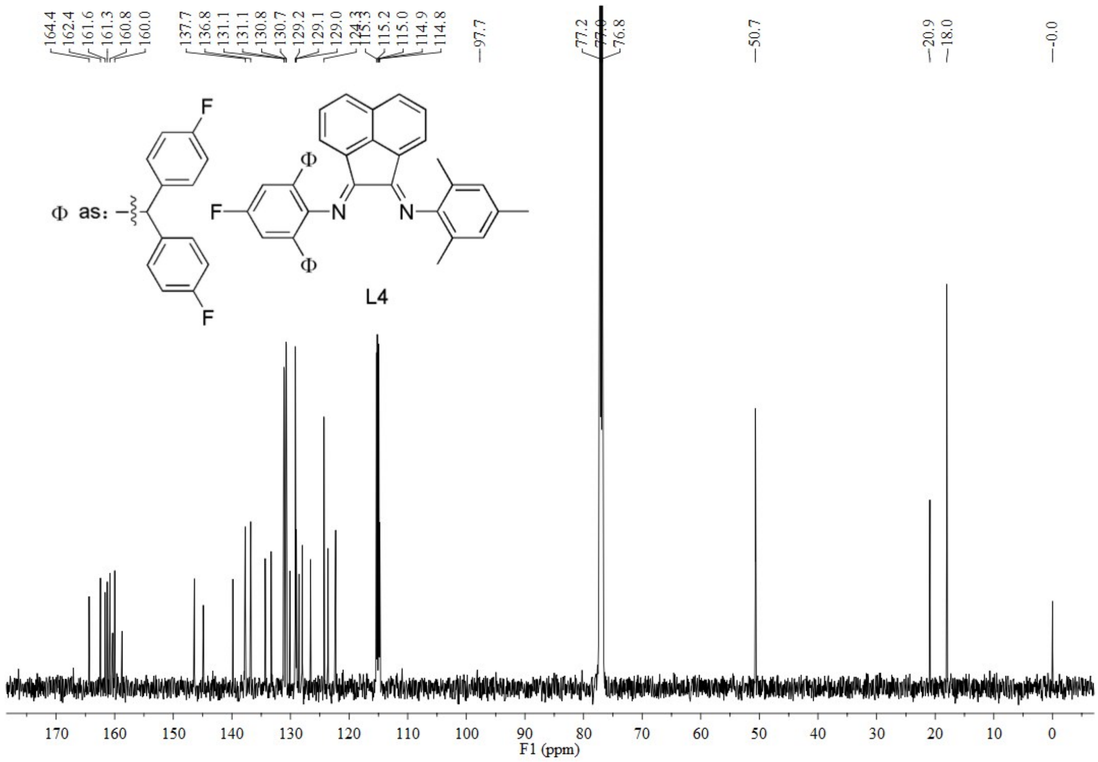

Figure S10. ^{13}C NMR spectrum of **L4** in $CDCl_3$ at room temperature

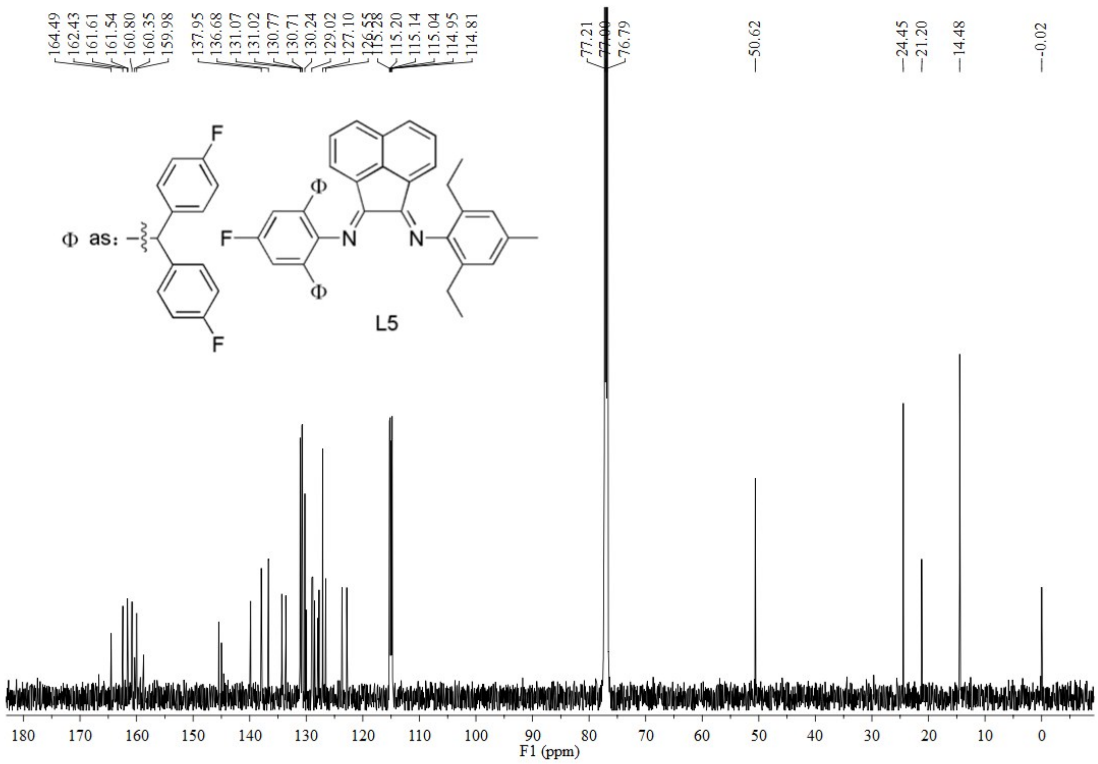

Figure S11. ^{13}C NMR spectrum of **L5** in $CDCl_3$ at room temperature

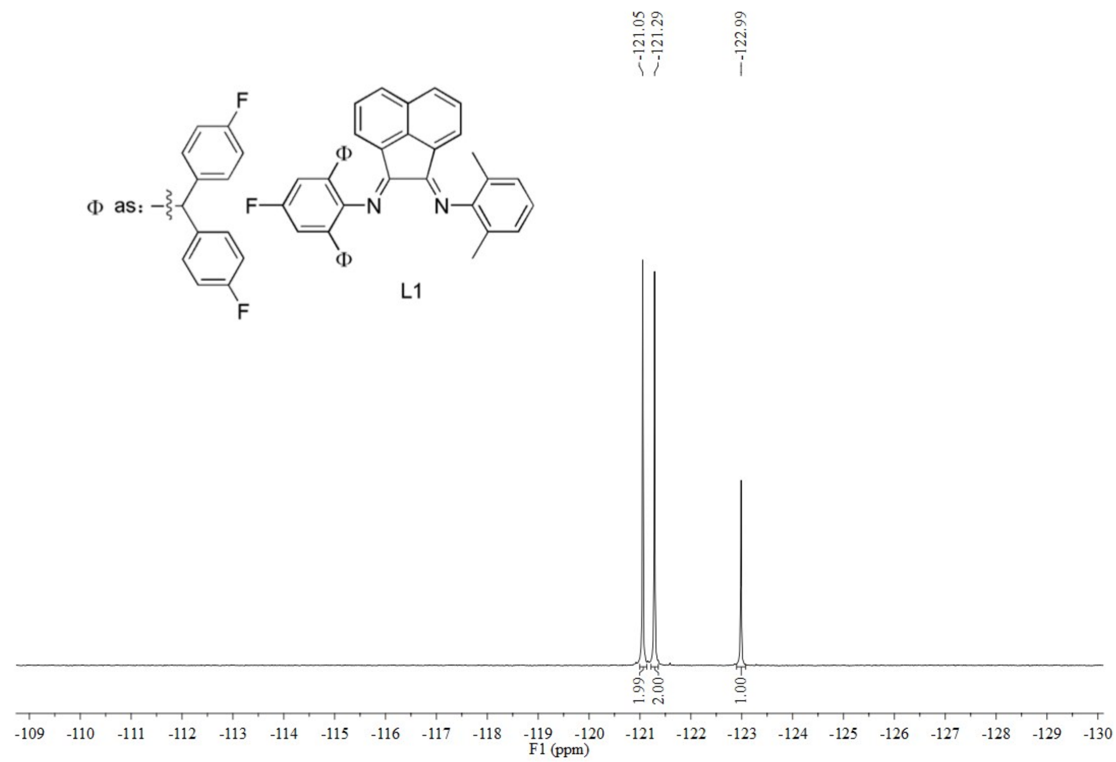

Figure S12. ^{19}F NMR spectrum of **L1** in $CDCl_3$ at room temperature

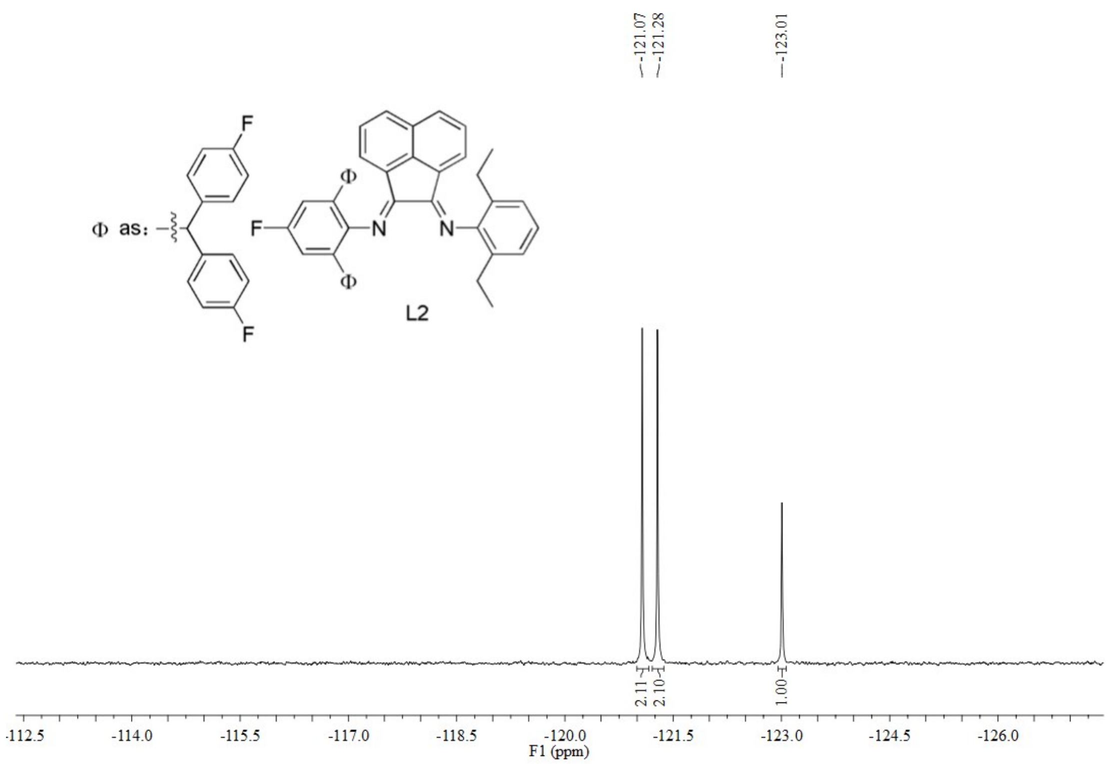

Figure S13. ^{19}F NMR spectrum of **L2** in $CDCl_3$ at room temperature

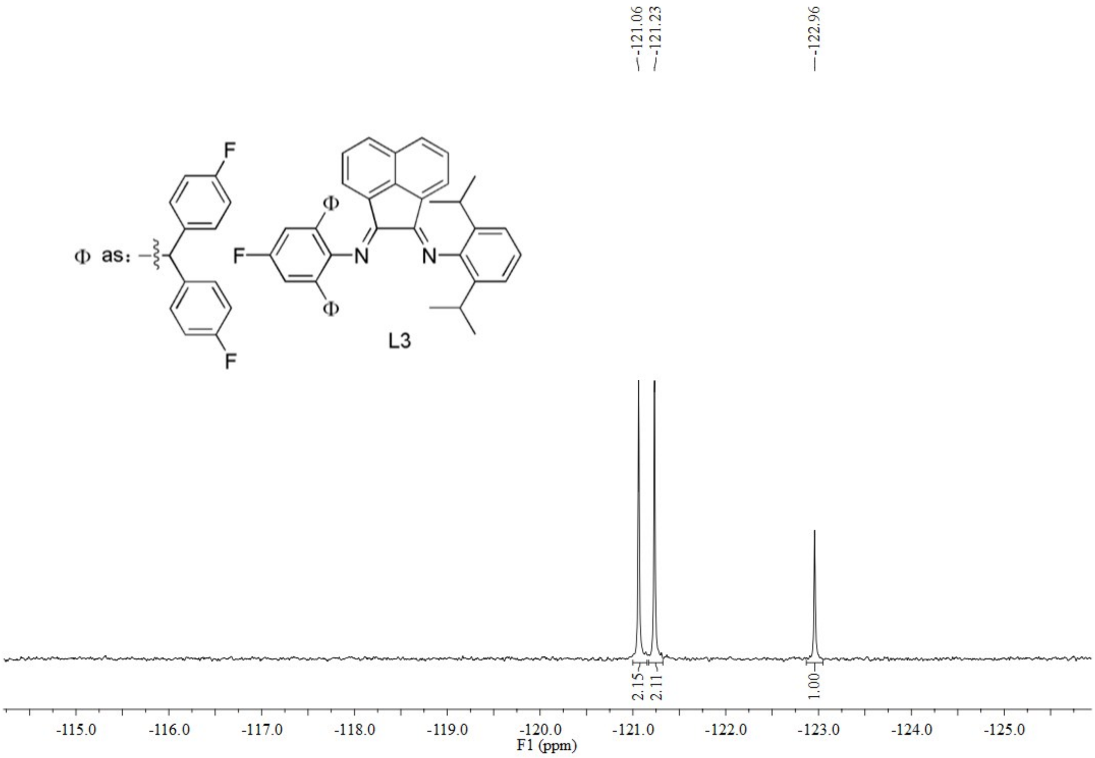

Figure S14. ^{19}F NMR spectrum of **L3** in $CDCl_3$ at room temperature

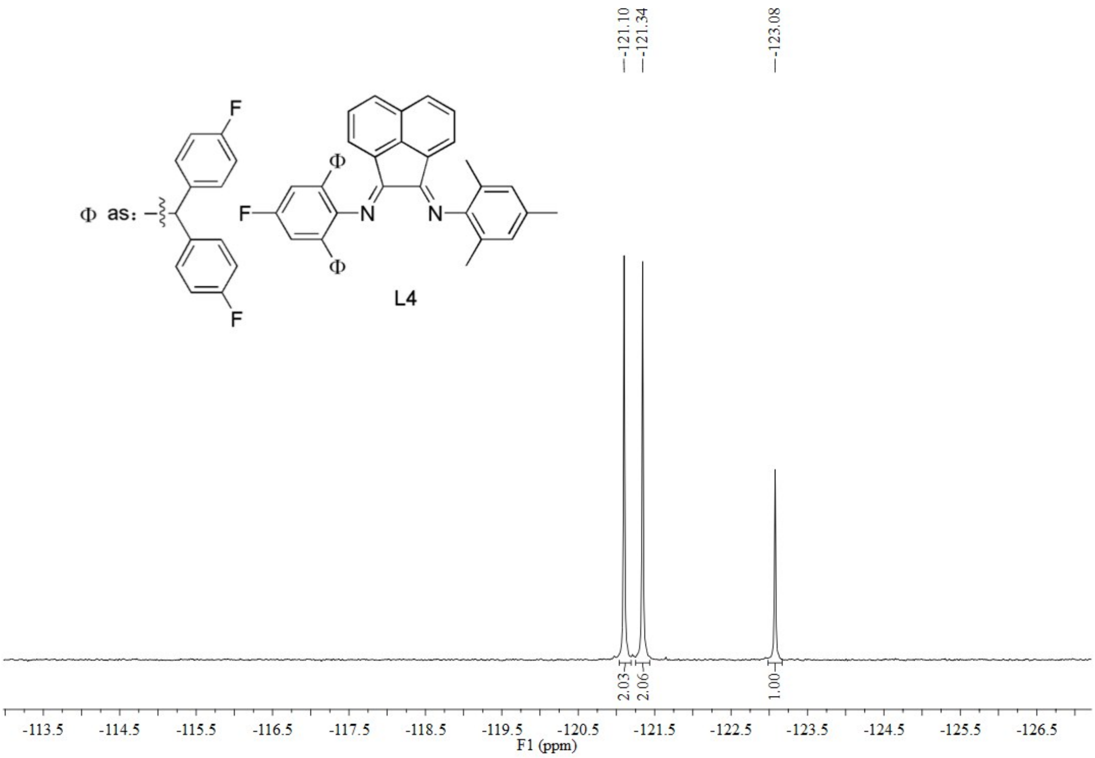

Figure S15. ^{19}F NMR spectrum of **L4** in $CDCl_3$ at room temperature

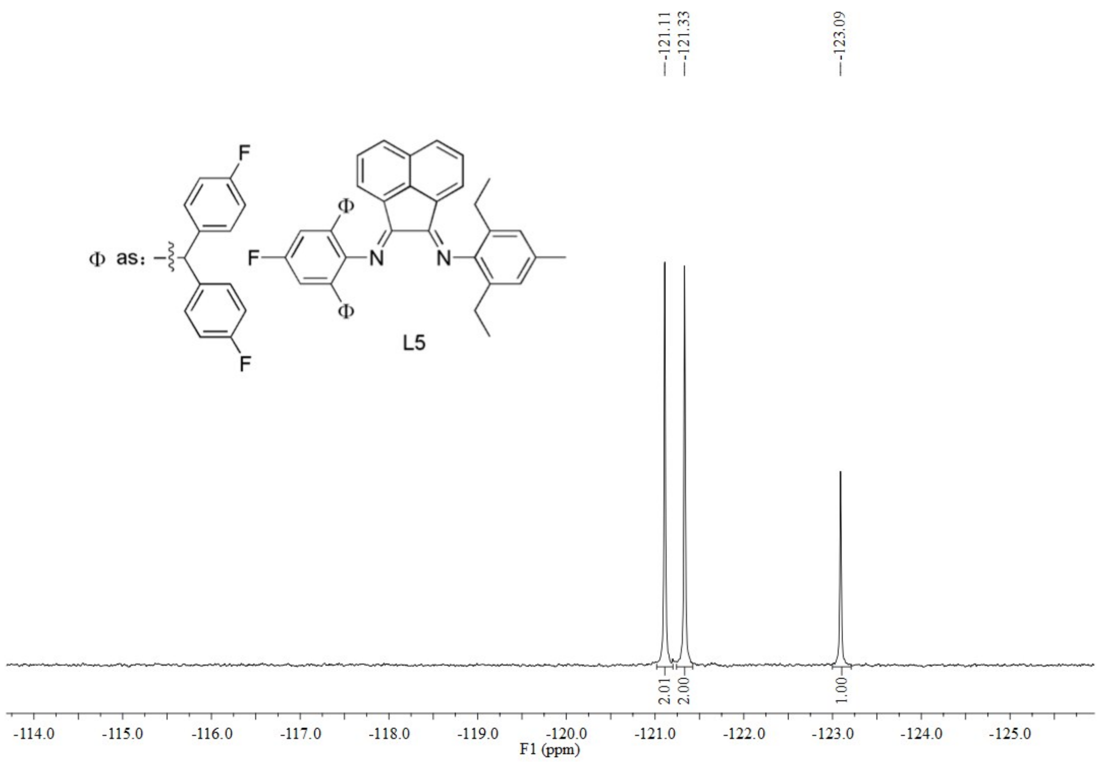

Figure S16. ^{19}F NMR spectrum of **L5** in $CDCl_3$ at room temperature

2. ^{1}H NMR spectra for **Ni1 – Ni10**

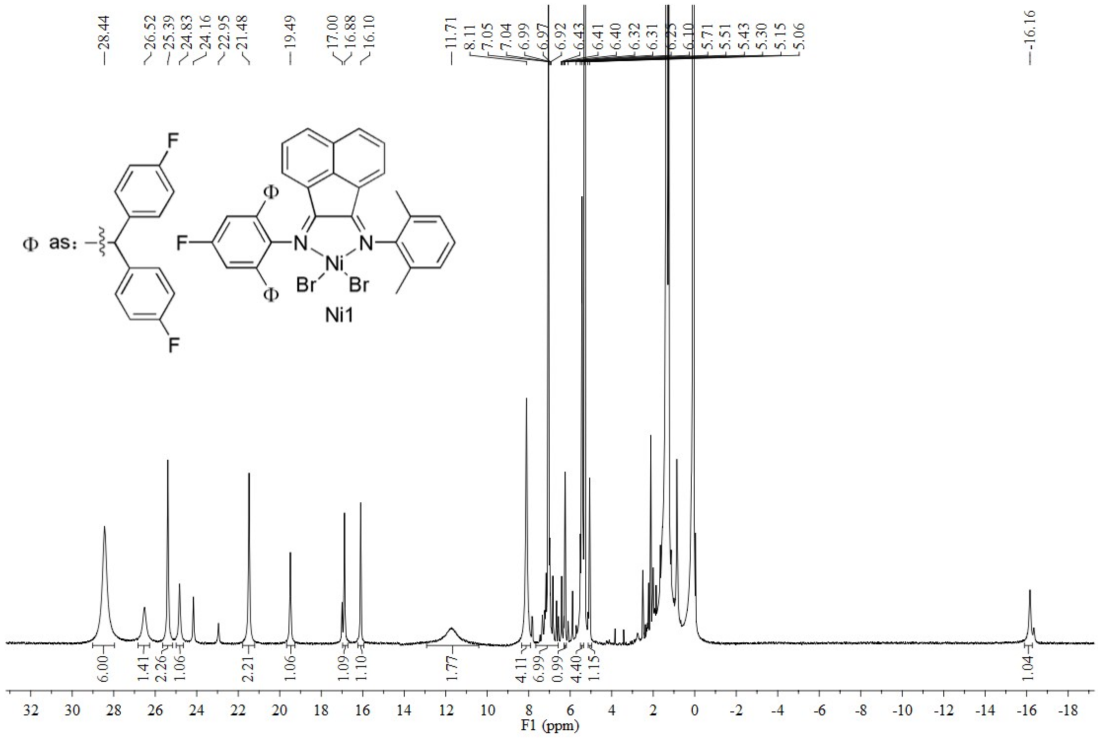

Figure S17. ^{1}H NMR spectrum of **Ni1** in CD_2Cl_2 at room temperature

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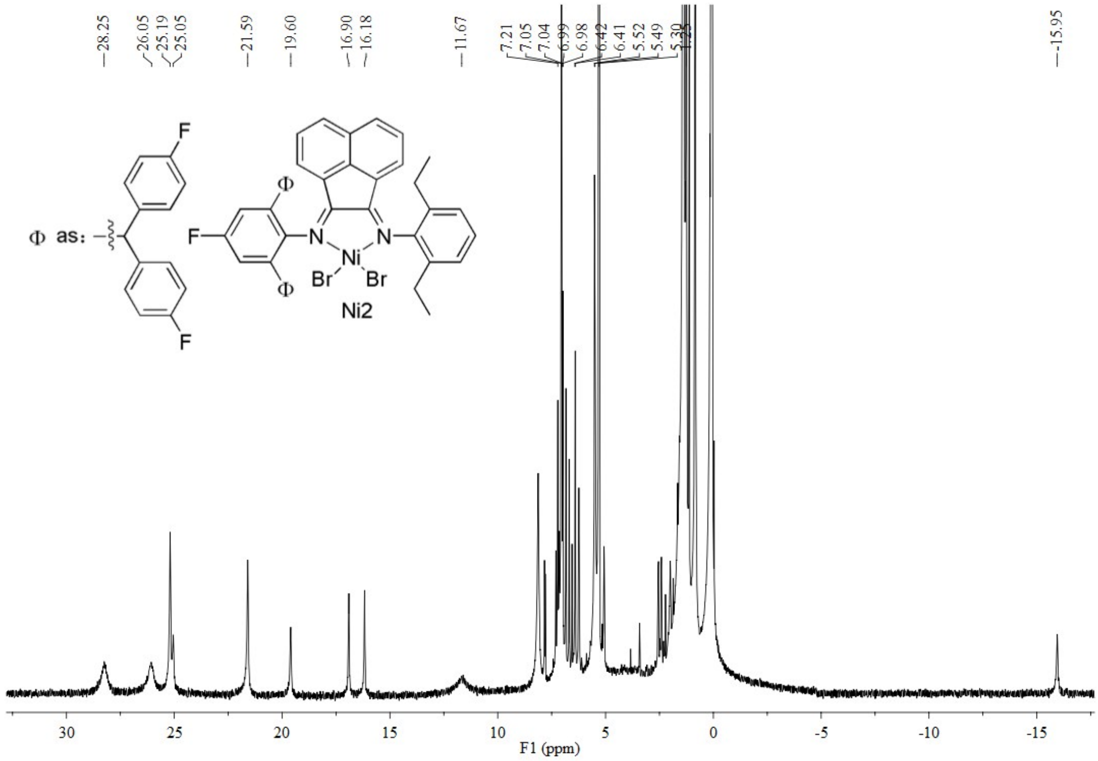

Figure S18. ^{1}H NMR spectrum of **Ni2** in CD_2Cl_2 at room temperature

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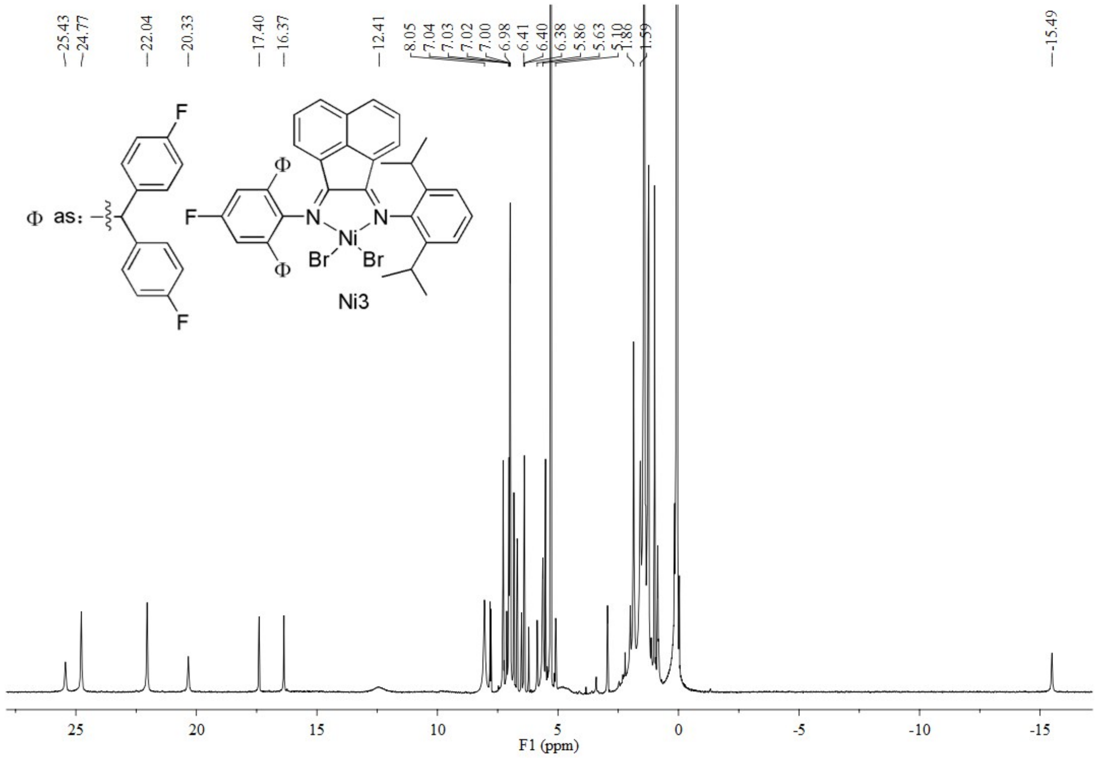

Figure S19. ^{1}H NMR spectrum of **Ni3** in CD_2Cl_2 at room temperature

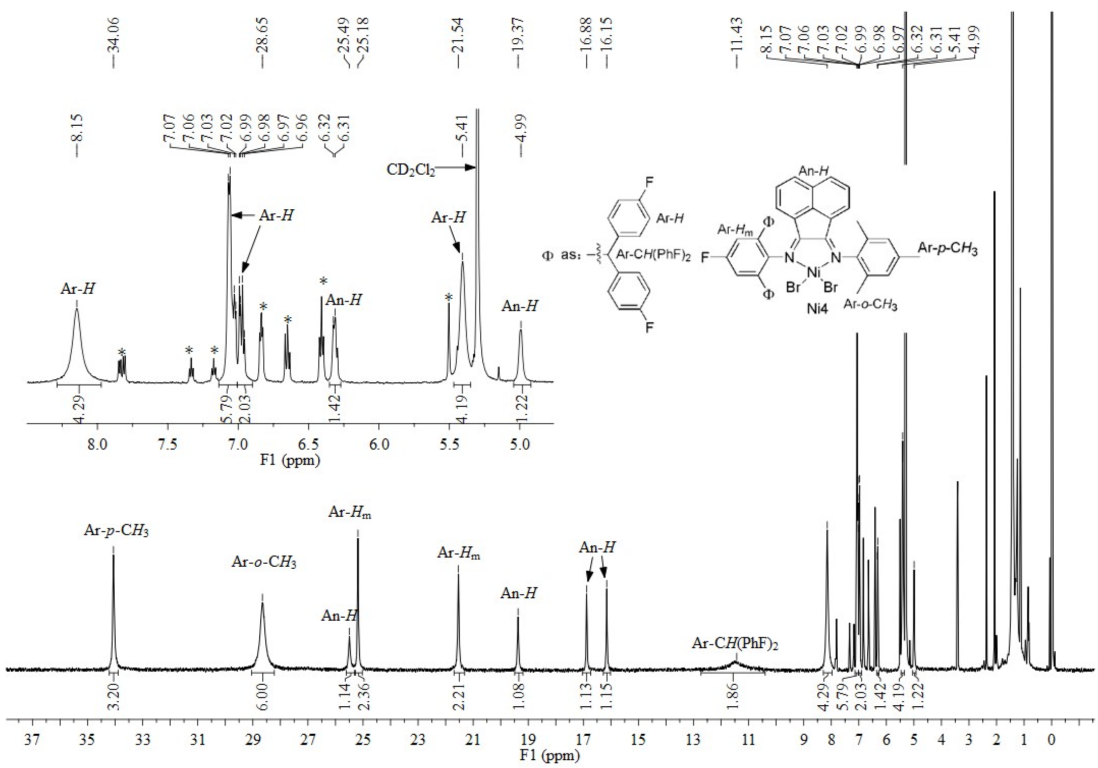

Figure S20. ^{1}H NMR spectrum of **Ni4** in CD_2Cl_2 at room temperature

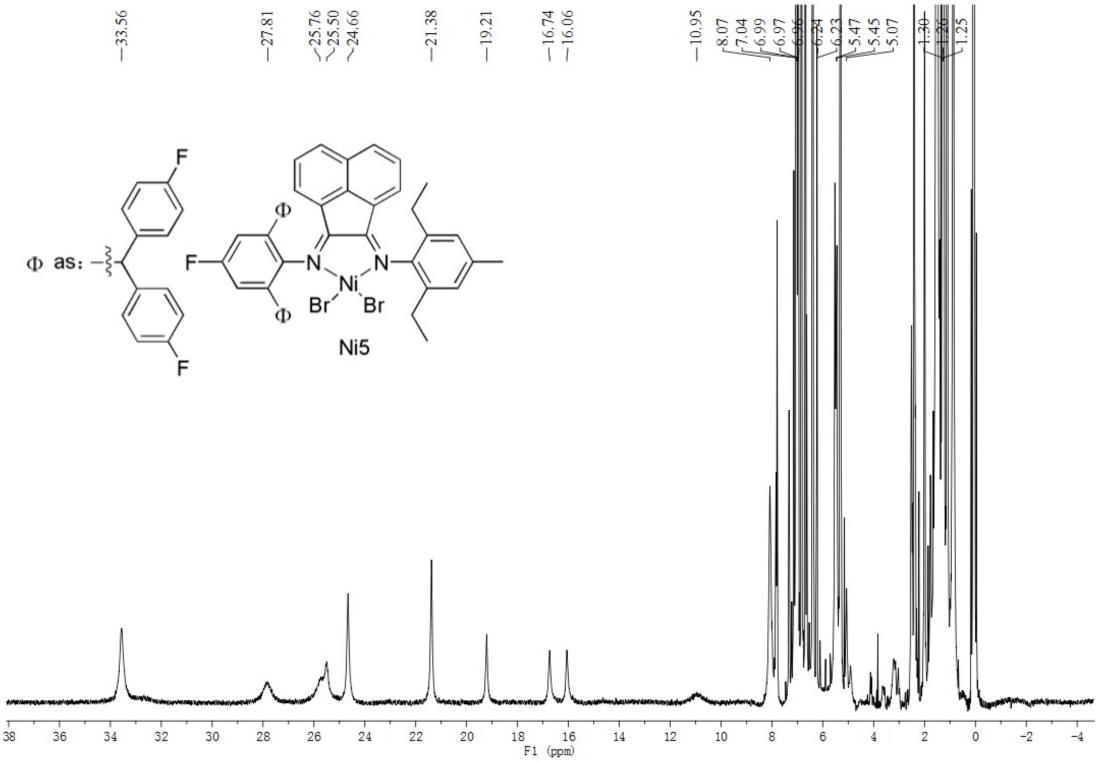

Figure S21. ^{1}H NMR spectrum of **Ni5** in CD_2Cl_2 at room temperature

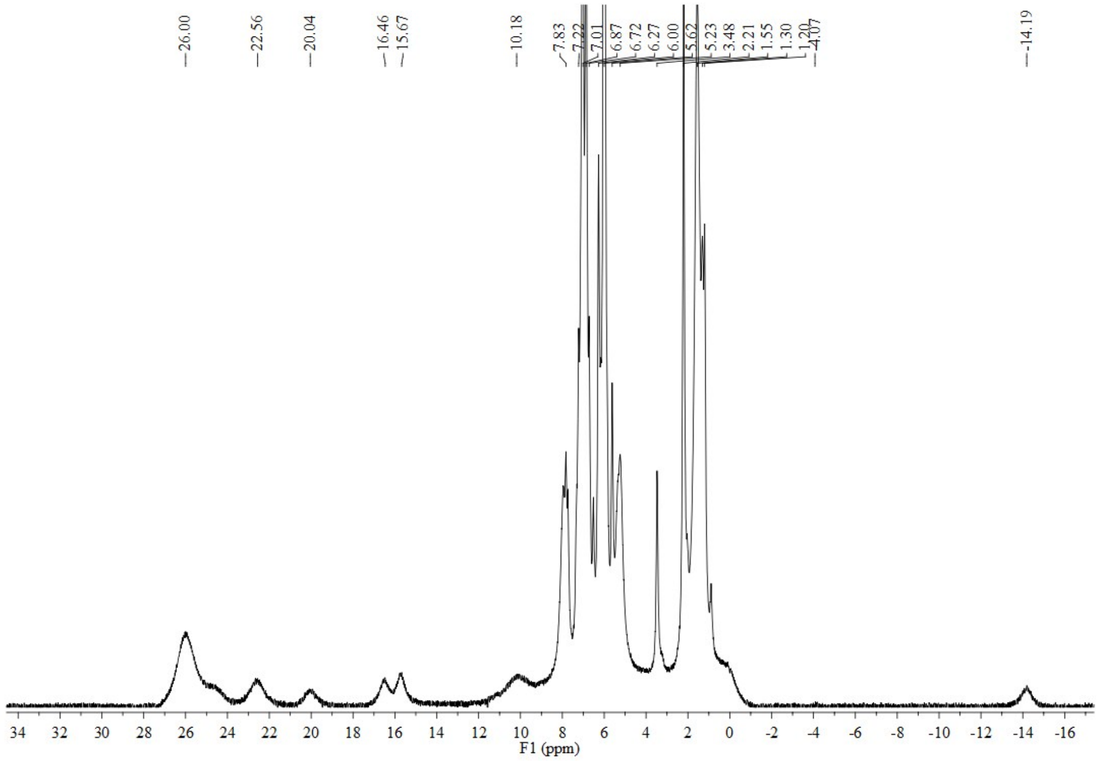

Figure S22. ^{1}H NMR spectrum of **Ni6** in CD_2Cl_2 at room temperature

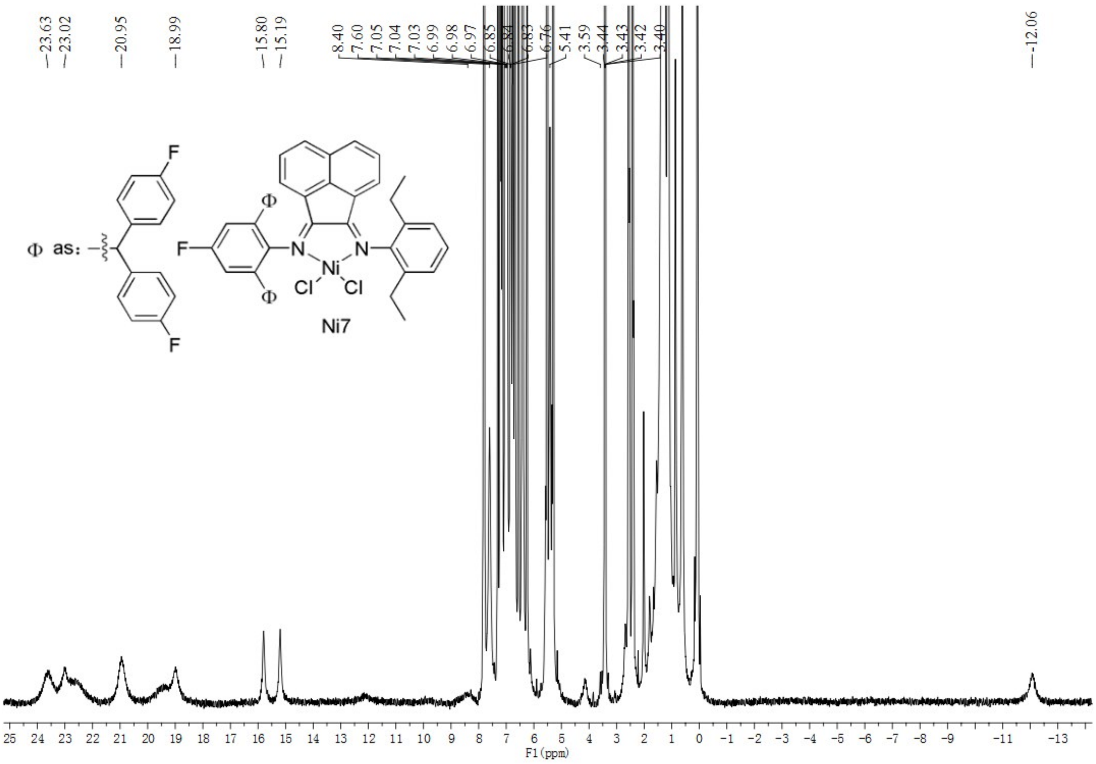

Figure S23. ^{1}H NMR spectrum of **Ni7** in CD_2Cl_2 at room temperature

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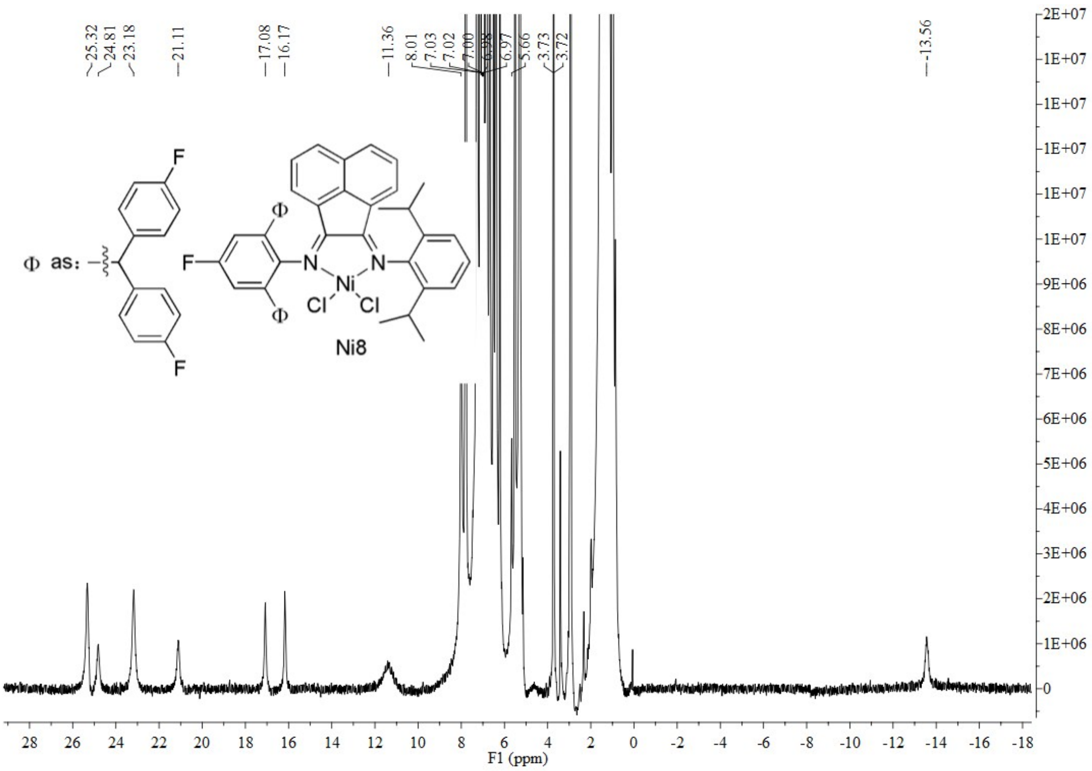

Figure S24. ^{1}H NMR spectrum of **Ni8** in CD_2Cl_2 at room temperature

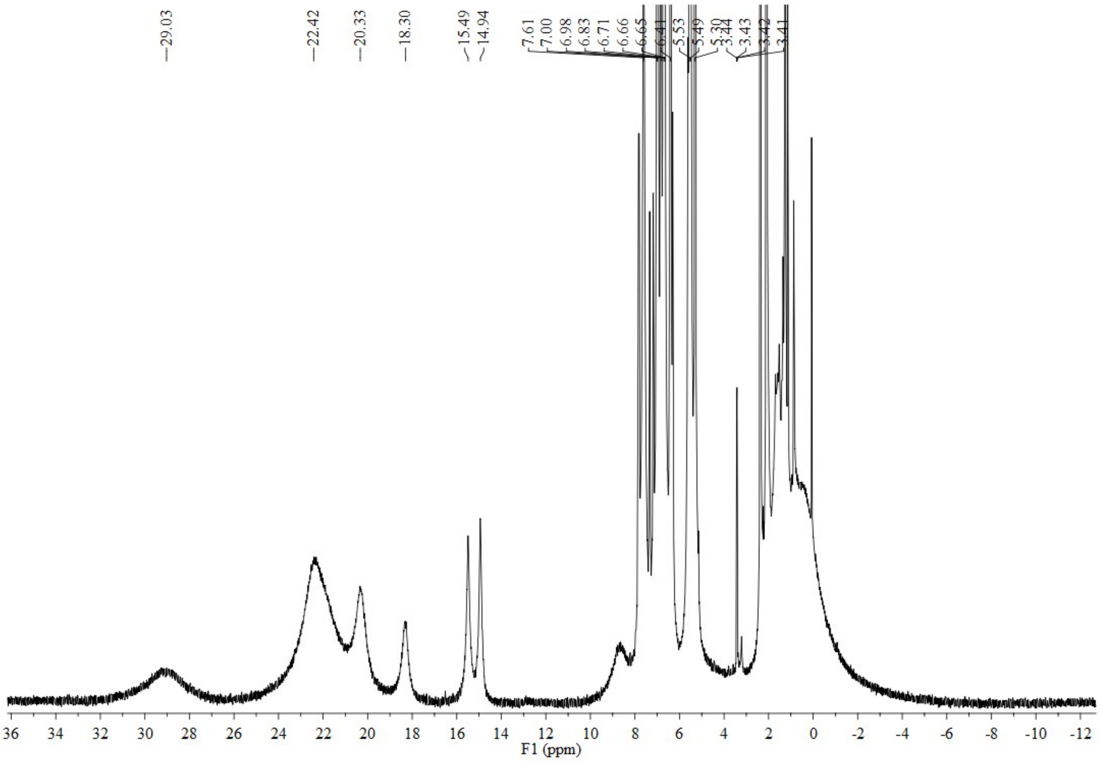

Figure S25. ^{1}H NMR spectrum of **Ni9** in CD_2Cl_2 at room temperature

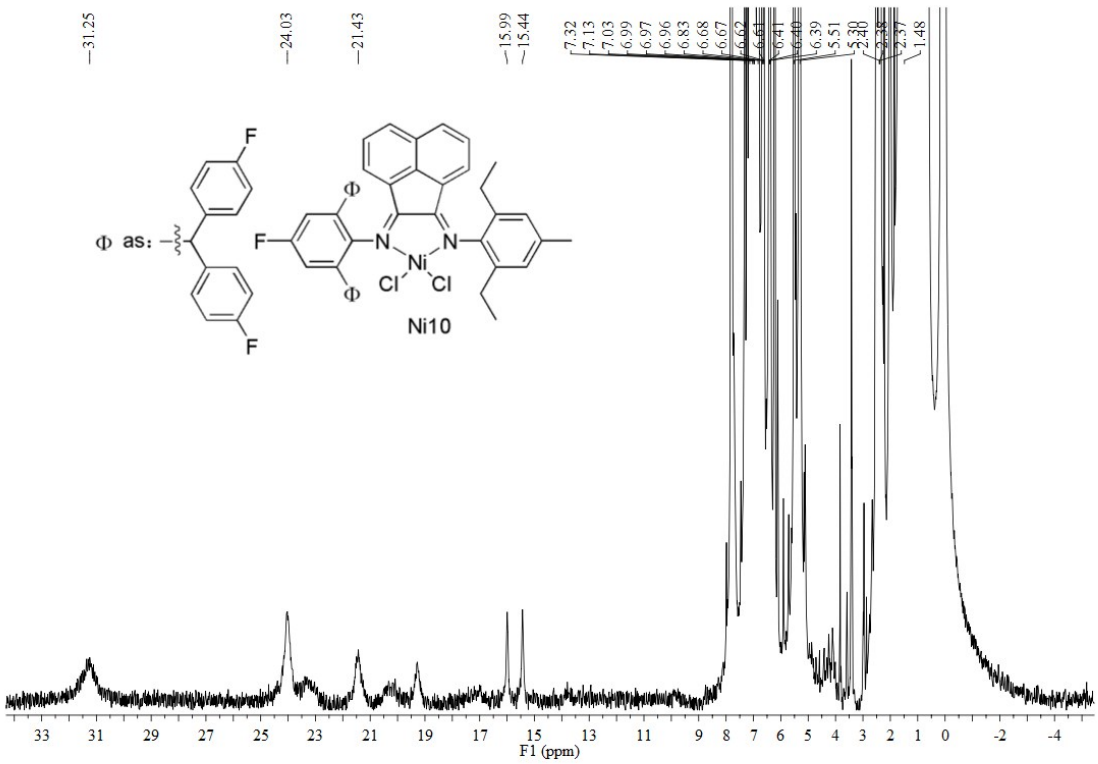

Figure S26. ^{1}H NMR spectrum of **Ni10** in CD_2Cl_2 at room temperature

3.[1]H NMR spectra for $[1,2\text{-}(ArN)_2C_2C_{10}H_6]NiBr_2$ (Ar = $2,6\text{-}Me_2C_6H_3$,[1] $2,6\text{-}Et_2C_6H_3$,[2] $2,6\text{-}i\text{Pr}_2C_6H_3$,[1,3] $2,4,6\text{-}Me_3C_6H_2$[4])

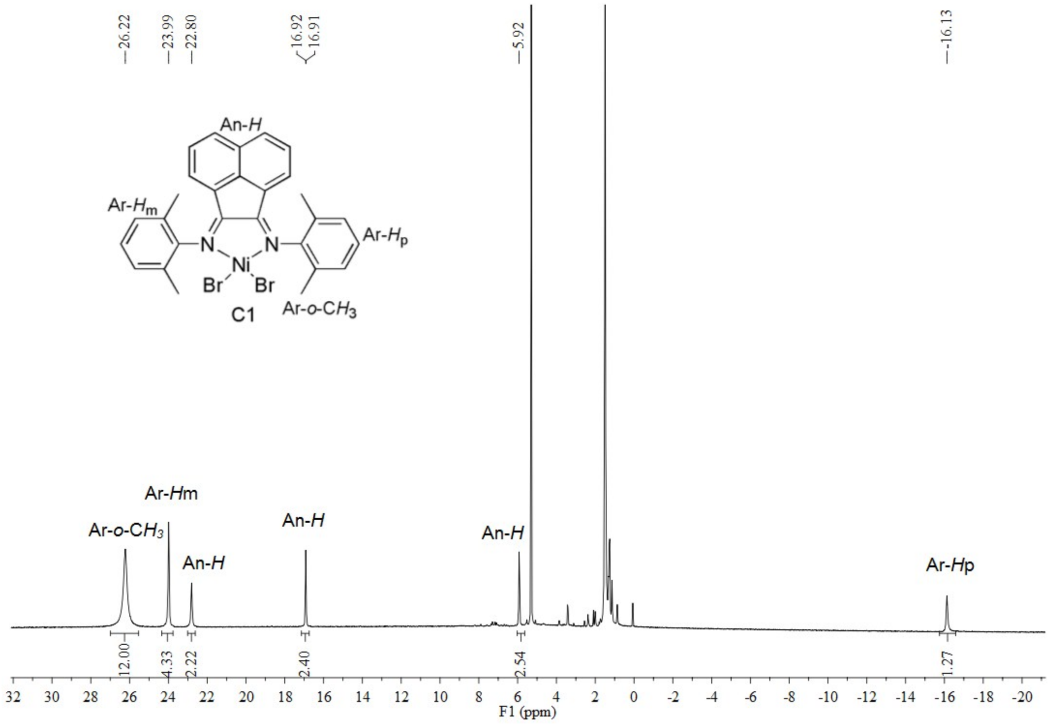

Figure S27. ^{1}H NMR spectrum of $[1,2\text{-}(2,6\text{-}Me_2C_6H_3N)_2C_2C_{10}H_6]NiBr_2$ (**C1**) in CD_2Cl_2 at room temperature

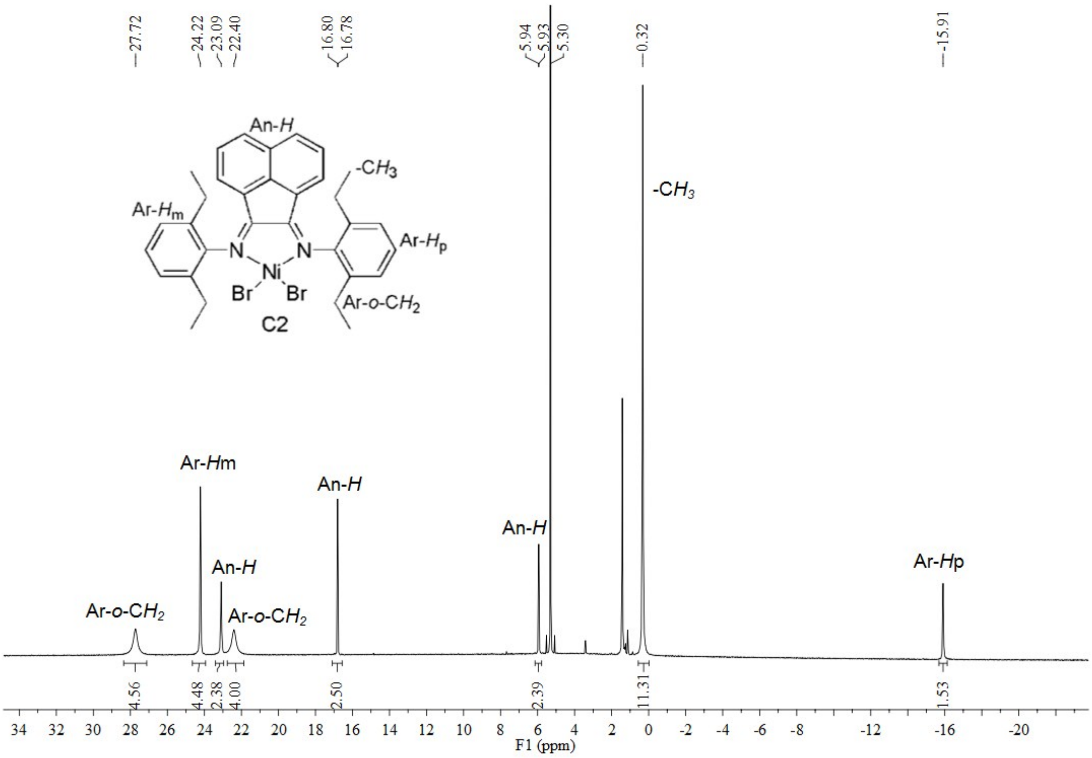

Figure S28. ^{1}H NMR spectrum of $[1,2\text{-}(2,6\text{-}Et_2C_6H_3N)_2C_2C_{10}H_6]NiBr_2$ (**C2**) in CD_2Cl_2 at room temperature

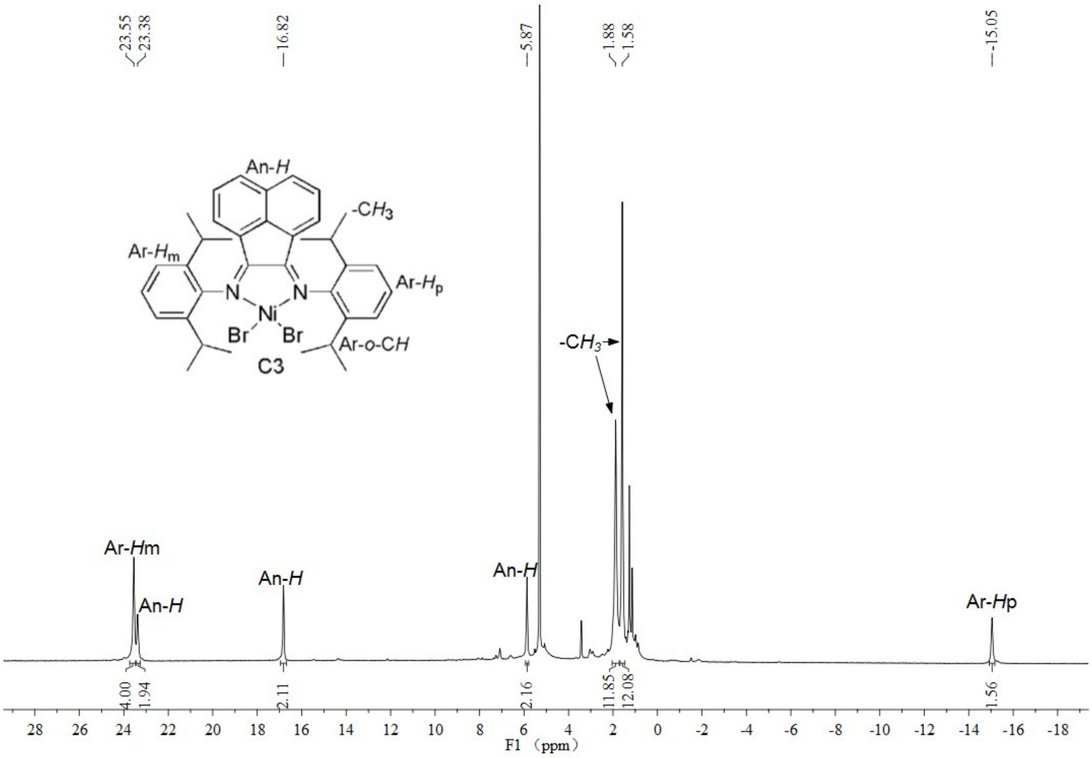

Figure S29. [1]H NMR spectrum of $[1,2\text{-}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{C}_2\text{C}_{10}\text{H}_6]\text{NiBr}_2$ (**C3**) in CD_2Cl_2 at room temperature (the peak for the Ar-*o*-C*H* proton was not visible)

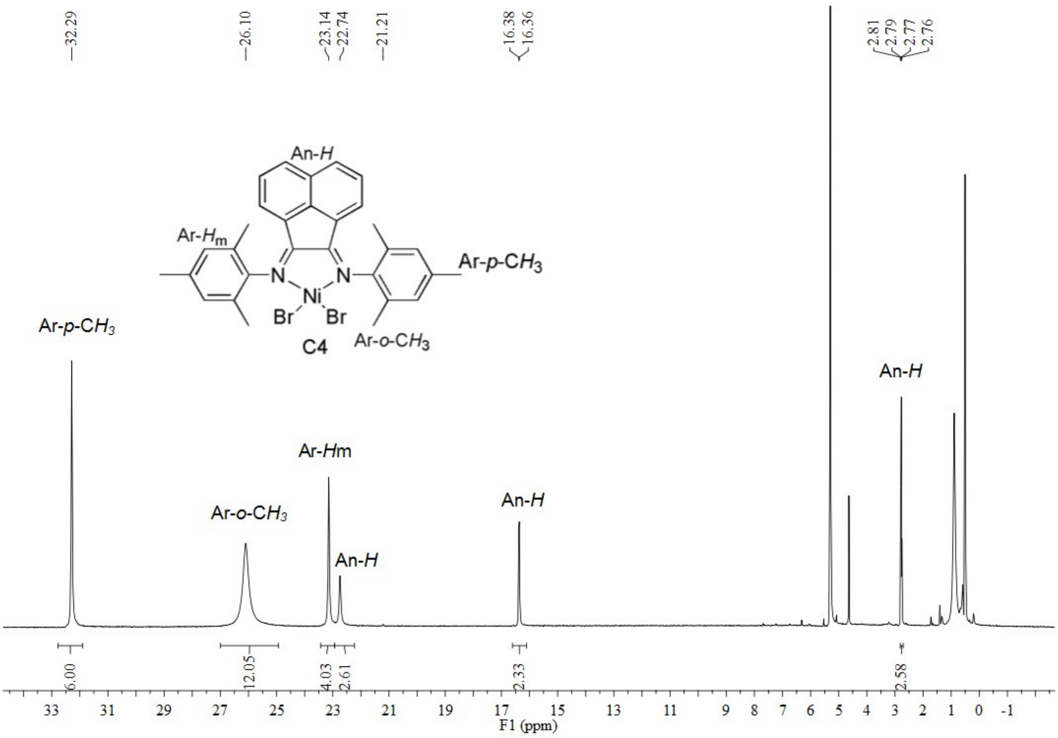

Figure S30. [1]H NMR spectrum of $[1,2\text{-}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N})_2\text{C}_2\text{C}_{10}\text{H}_6]\text{NiBr}_2$ (**C4**) in CD_2Cl_2 at room temperature

4. ^{19}F NMR spectra for **Ni1 – Ni10**

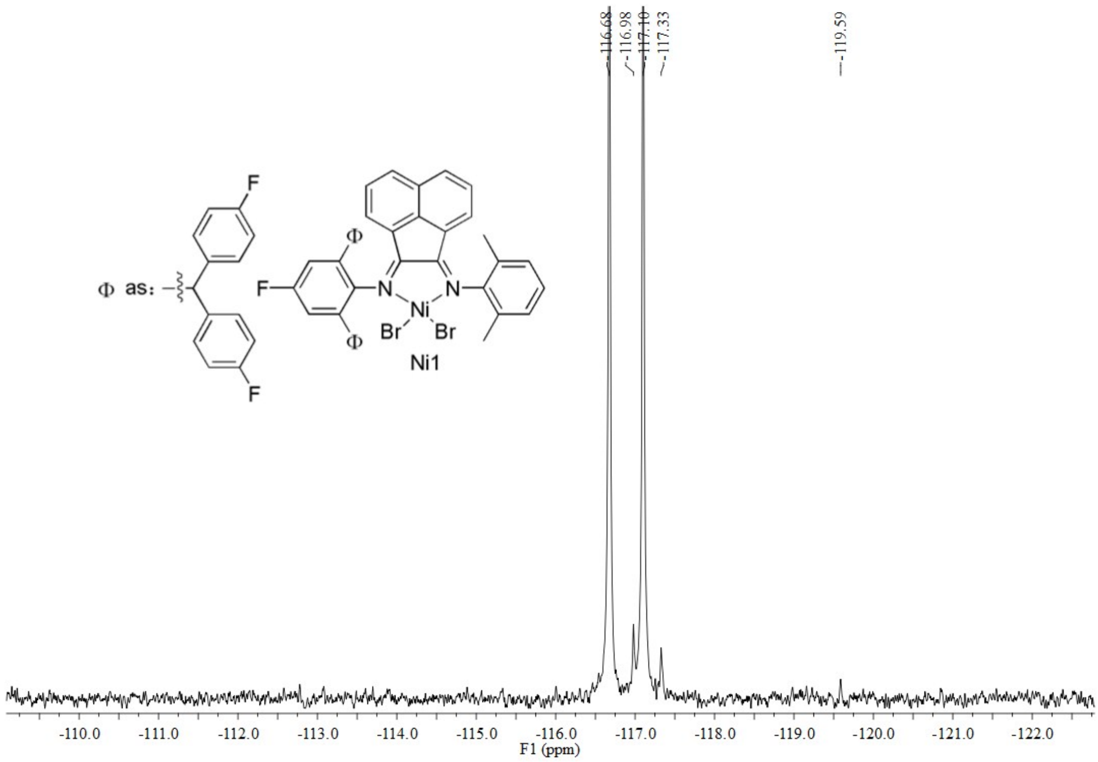

Figure S31. ^{19}F NMR spectrum of **Ni1** in CD_2Cl_2 at room temperature

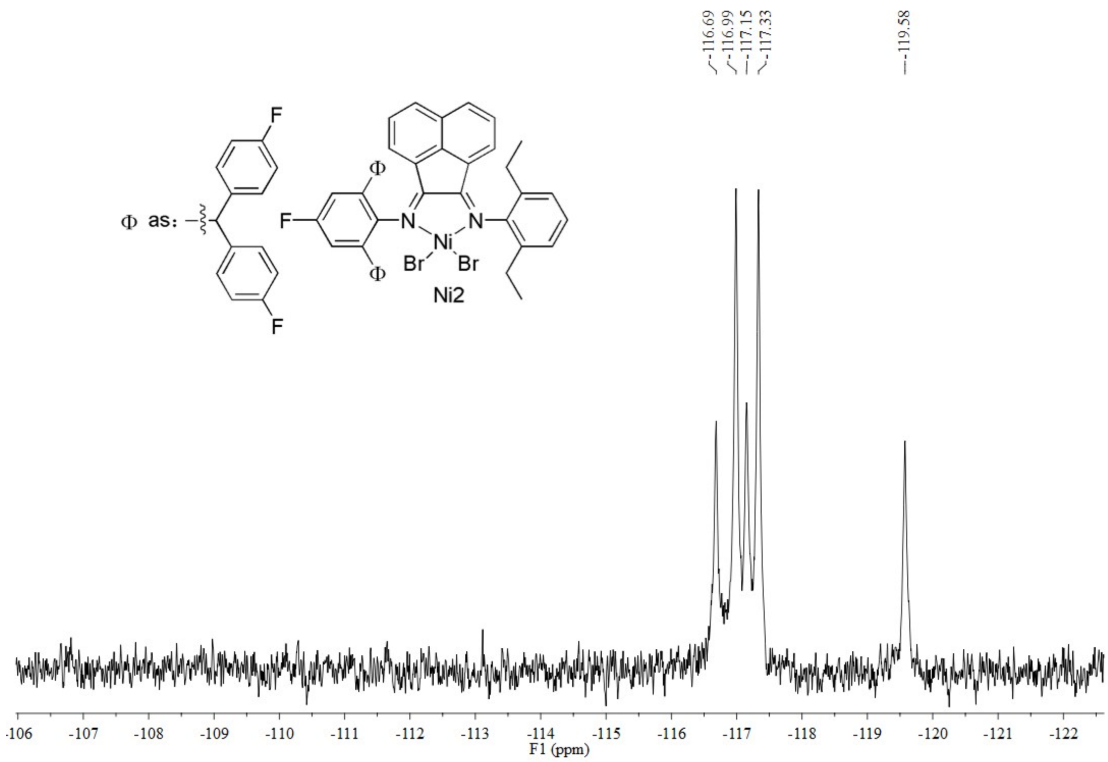

Figure S32. ^{19}F NMR spectrum of **Ni2** in CD_2Cl_2 at room temperature

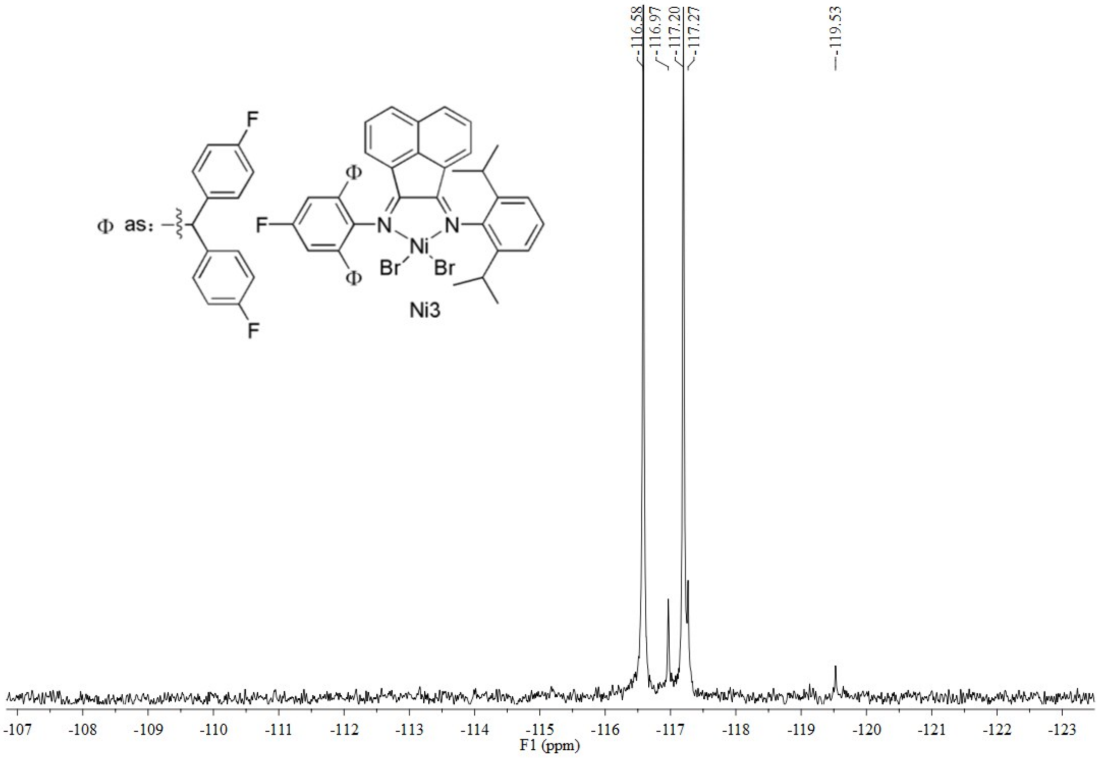

Figure S33. ^{19}F NMR spectrum of **Ni3** in CD_2Cl_2 at room temperature

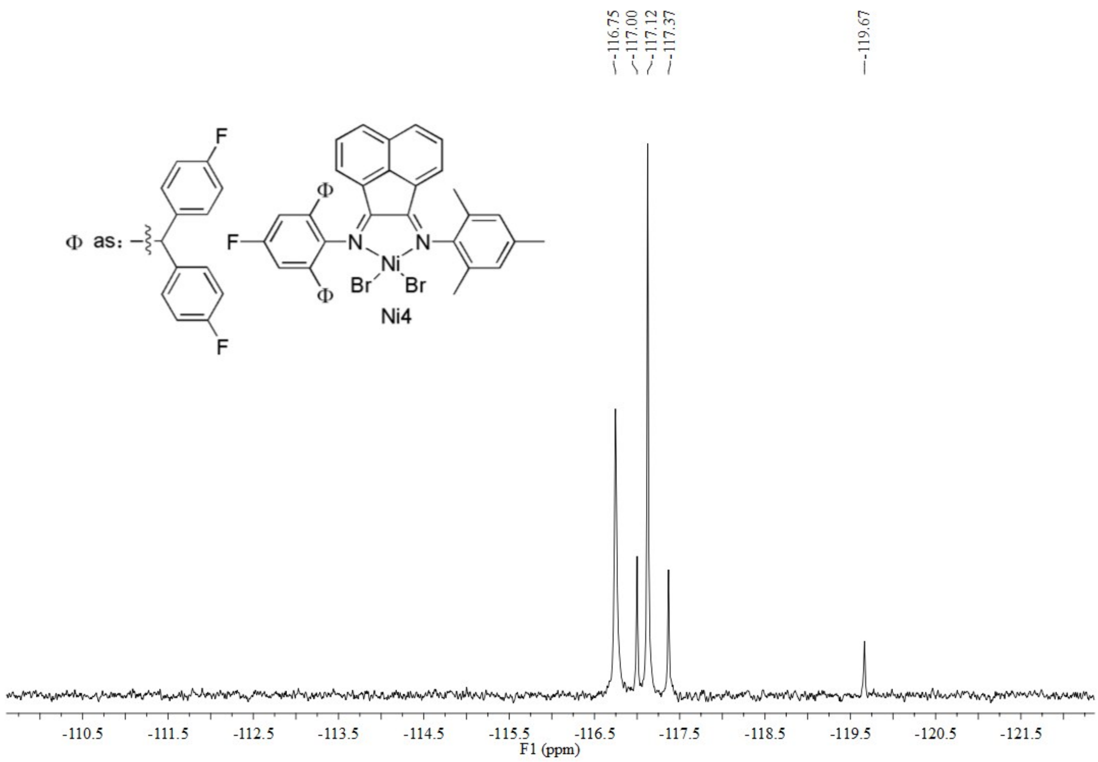

Figure S34. ^{19}F NMR spectrum of **Ni4** in CD_2Cl_2 at room temperature

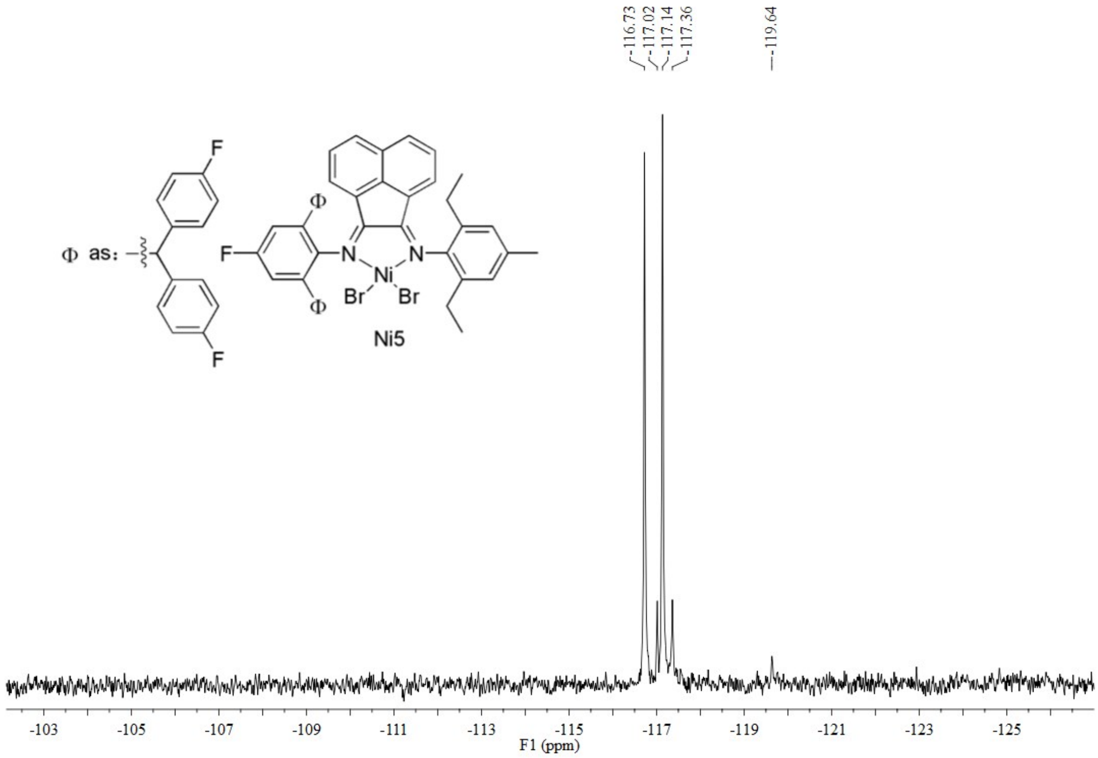

Figure S35. ^{19}F NMR spectrum of **Ni5** in CD_2Cl_2 at room temperature

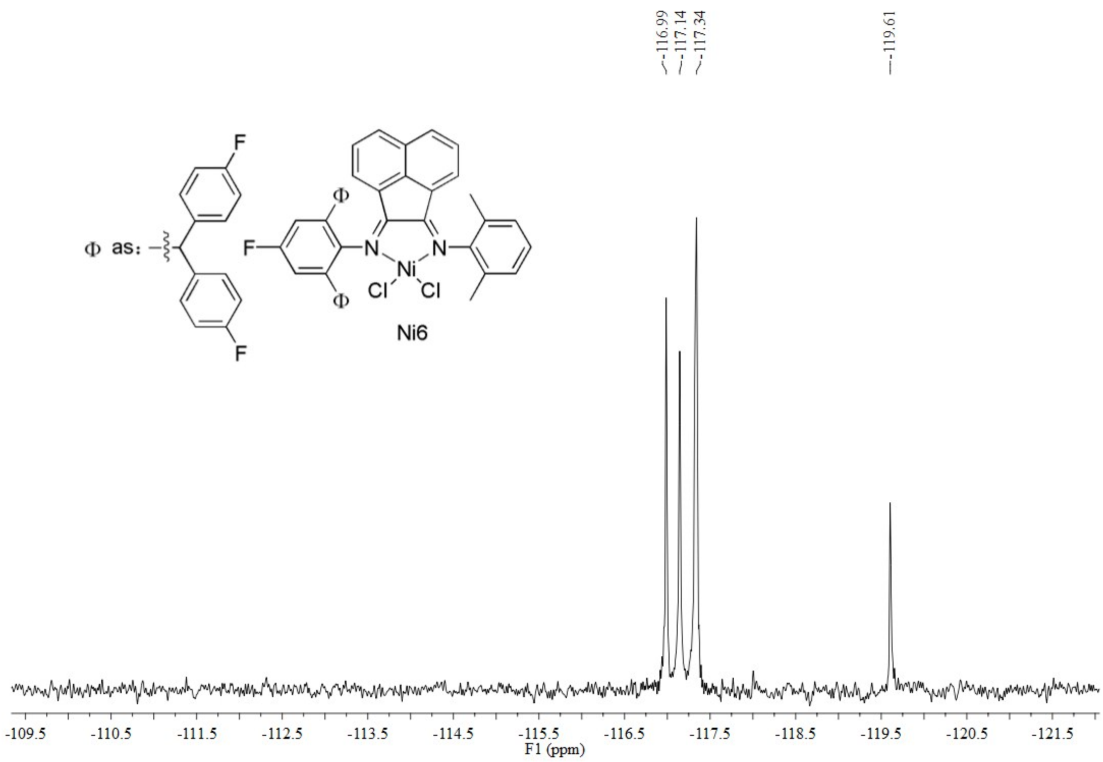

Figure S36. ^{19}F NMR spectrum of **Ni6** in CD_2Cl_2 at room temperature

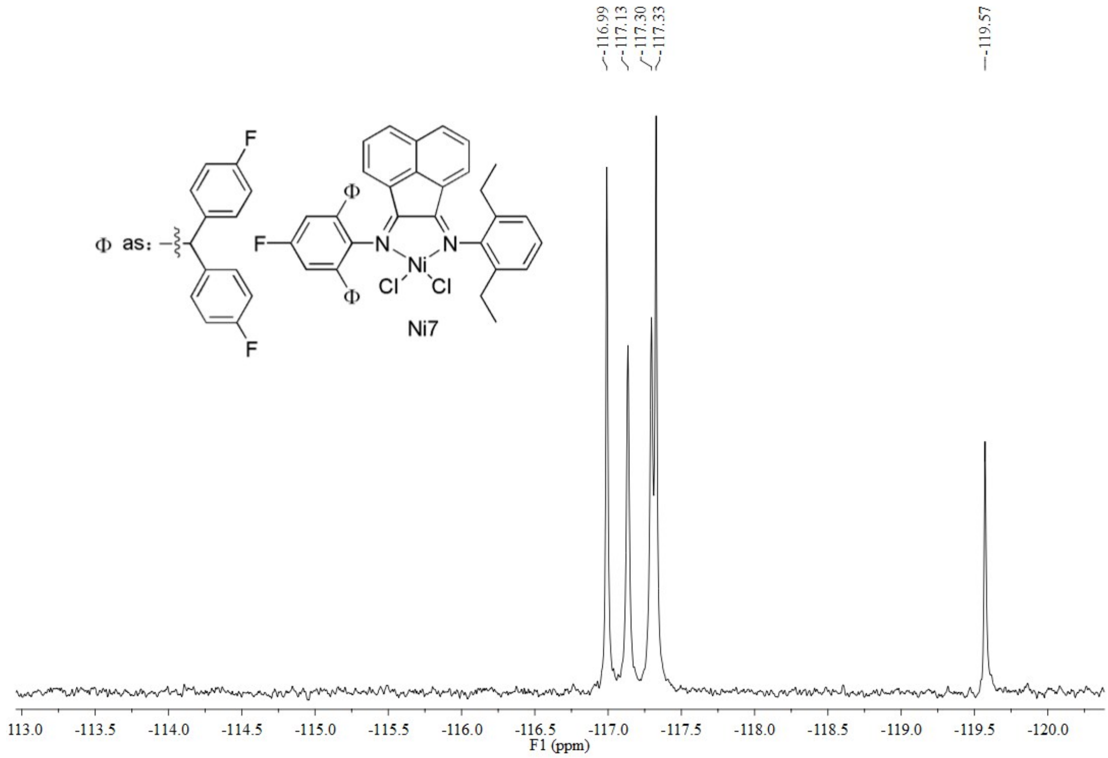

Figure S37. ^{19}F NMR spectrum of **Ni7** in CD_2Cl_2 at room temperature

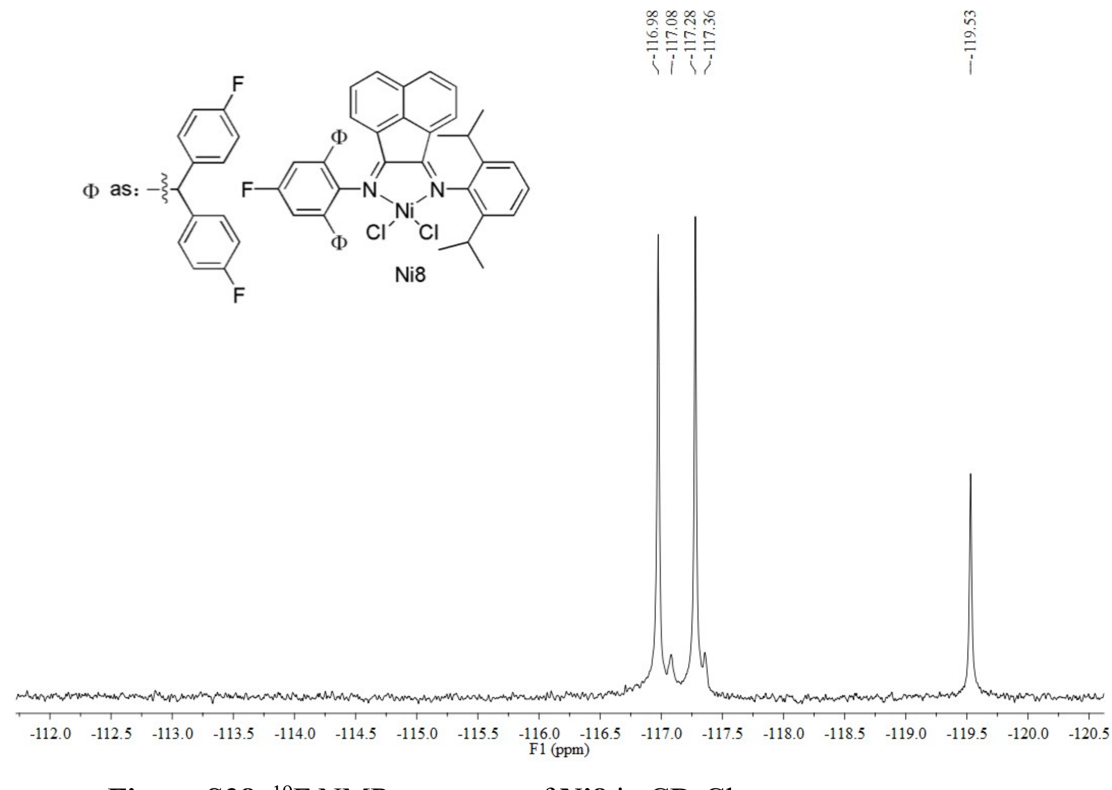

Figure S38. ^{19}F NMR spectrum of **Ni8** in CD_2Cl_2 at room temperature

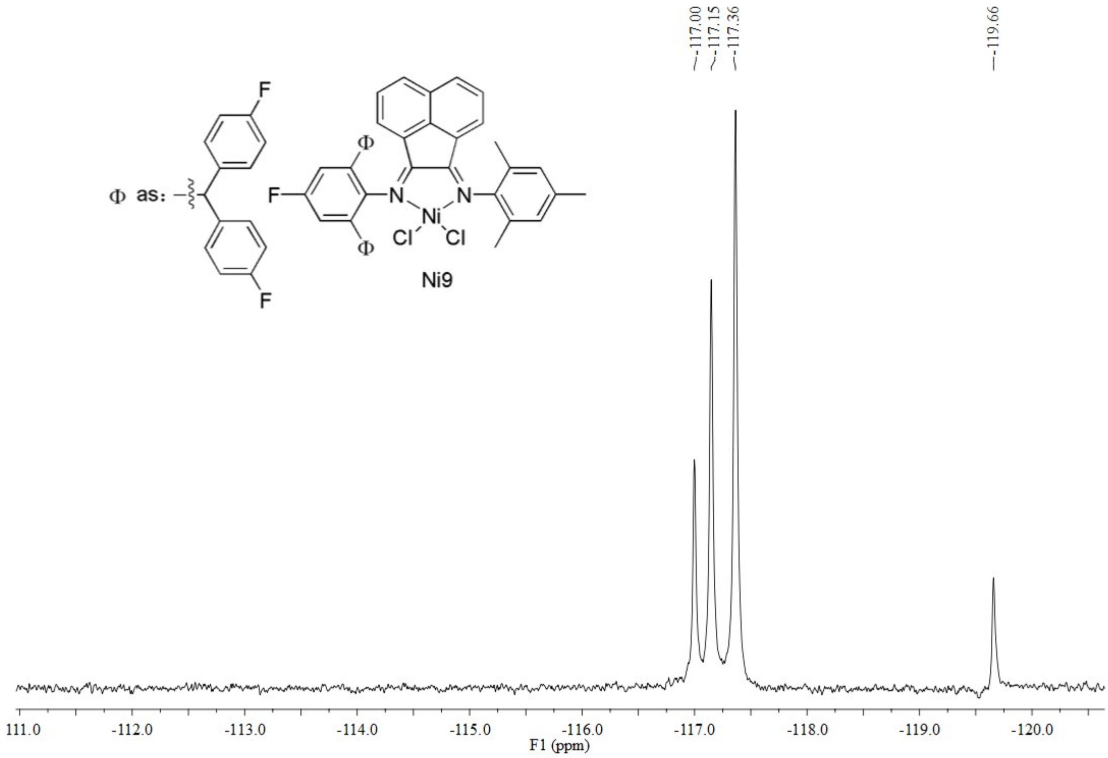

Figure S39. ^{19}F NMR spectrum of **Ni9** in CD_2Cl_2 at room temperature

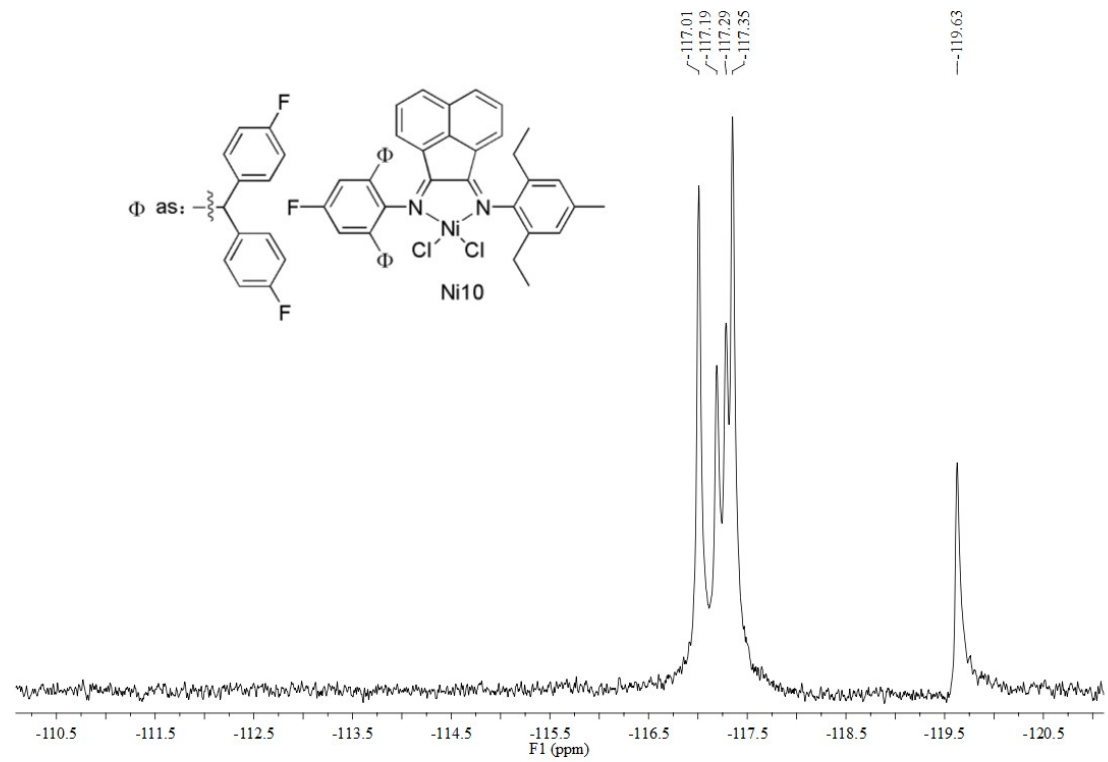

Figure S40. ^{19}F NMR spectrum of **Ni10** in CD_2Cl_2 at room temperature

5. ^{19}F NMR spectra for the species formed on treating **Ni2** with 10, 50 and 100 equivalents of EASC

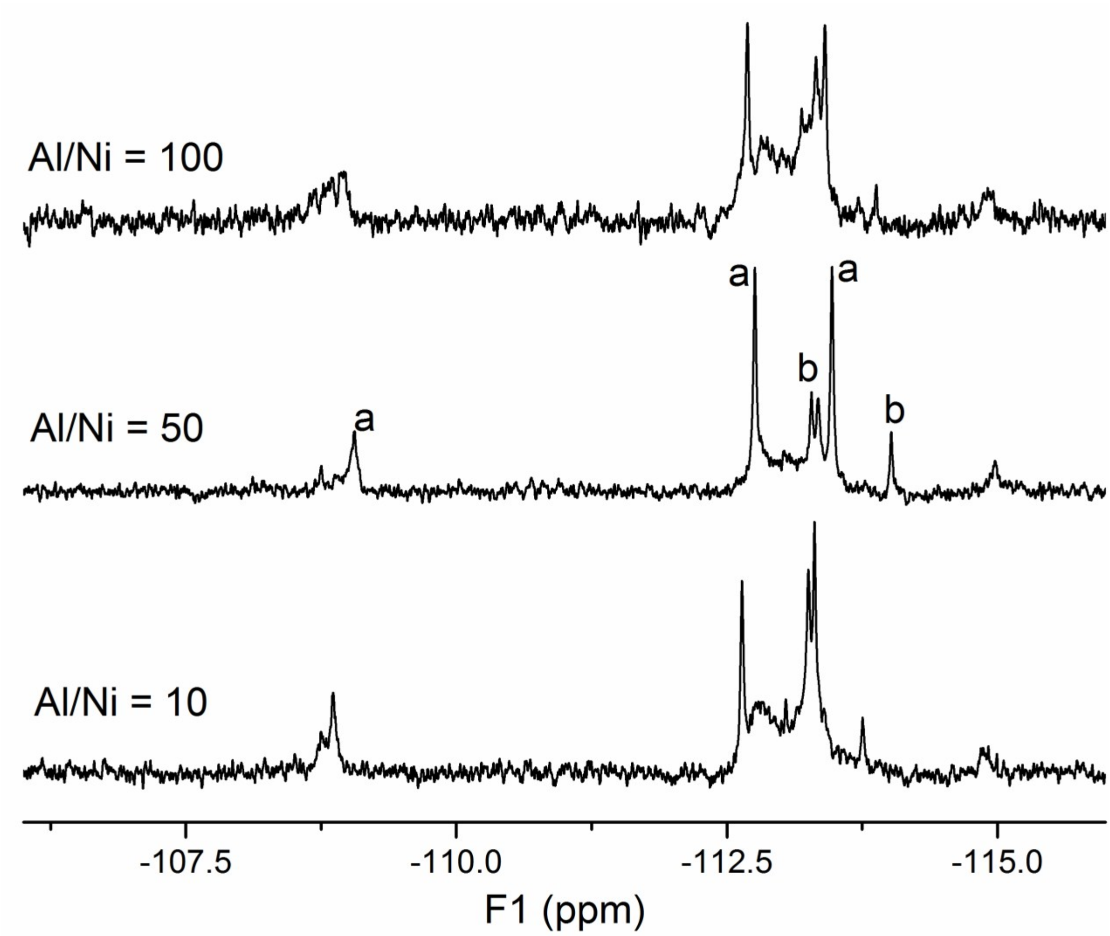

Figure S41. ^{19}F NMR spectra of **Ni2**/EASC with different Al/Ni ratios. At a ratio of Al/**Ni2** = 50, two species **a** and **b** have been identified

6. Polyethylene microstructures

Table S1. Carbon-13 NMR: Chemical shift, integral and assignments of the polyethylenes obtained using **Ni4**/EASC (entry 4 in Table 4)

Peak No.	Chem.Shift(ppm)	Integral	Assignments
1	11.29	0.21	$1B_2$-I_1
2	14.28	0.44	$1B_4$-I_2
3	20.11	1	$1B_1$- I_4
4	22.91	0.39	$2B_n$- I_7
5	26.79	0.35	$2B_2$- I_{10}
6	27.25	0.88	βB_2- I_{11}； (n-1)B_n- I_{11}
7	27.44	0.86	βB_1- I_{12}

8	30	7.91	$\delta B_{1\text{-}n}$- I_{16}
9	30.39	1.28	γB_1- I_{17}
10	32.2	0.16	$3B_n$- I_{20}
11	33.21	0.45	brB_1- I_{22}
12	33.8	0.21	αB_2- I_{24}
13	34.5	0.62	n-B_n- I_{26}
14	37.54	1.02	αB_1- I_{29}
15	38.23	0.2	brB_n- I_{31}
16	39.6	0.1	brB_2- I_{33}

Table S2. Carbon-13 NMR: Chemical shift, integral and assignments of the polyethylene obtained using **Ni6**/EASC (entry 3 in Table 5)

Peak No.	Chem.Shift(ppm)	Integral	Assignments
1	11.3	0.06	$1B_2$- I_1
2	14.25	0.3	$1B_4$- I_2
3	14.73	0.07	
4	20.12	1	$1B_1$- I_4
5	22.92	0.26	$2B_n$- I_7
6	26.73	0.15	$2B_2$- I_{10}
7	27.28	1.08	βB_2- I_{11}； (n-1)B_n- I_{11}
8	27.44	1.62	βB_1- I_{12}
9	29.62	0.64	$4B_n$- I_{15}
10	30	10.59	$\delta B_{1\text{-}n}$- I_{16}
11	30.4	2.61	γB_1- I_{17}
12	32.24	0.29	$3B_n$- I_{20}
13	33.24	0.82	brB_1- I_{22}
14	34.12	0.29	αb_2- I_{24}
15	34.53	1.11	n-B_n- I_{26}
16	37.56	1.47	αB_1- I_{29}
17	38.14	0.35	brB_n- I_{31}

Based on assignments listed in the literature,[5] the branching content of the polyethylenes could be calculated using the following equations:

$$N_E = (I_{10} + I_{24}/2 + I_{33})/3$$

$$N_B = (I_8 + I_{25})/2$$

$$N_A = I_{21}$$

$$N_{M(1,4)} = (I_{23}/2 + I_{27}/2)/2$$

$$N_{L(1,4)} = (I_{19}/2 + I_{32}/2)/2$$

$$N_L = I_{20} - (I_{23}/2 + I_{27}/2)$$

$$N_M = I_{12} - (I_{23}/2 + I_{27}/2 + I_{13} + I_{21} + 2I_9)/2$$

Total methyl branches = $N_{\mathrm{M}} + N_{\mathrm{M(1,4)}} + N_{\mathrm{M(1,5)}} + N_{\mathrm{M(1,6)}}$

Total longer chain branches = $N_{\mathrm{L}} + N_{\mathrm{L(1,4)}}$

The polyethylene produced using **Ni4**/EASC possessed 85 branches per 1000 carbons including methyl (56.6%), ethyl (23.3%) and longer chains (20.1%). By contrast, the polyethylene obtained using **Ni6**/EASC contained 116 branches per 1000 carbons, including methyl (52.6%), ethyl (6.4%) and longer chains (41.0%).

7. References

1 (a) M. D. Leatherman, M. Brookhart, *Macromolecules,* 2001, ***34***, 2748-2750; (b) J. Liu, Yanguo Li, Y. Li, N. Hu, *J. Appl Polym. Sci*., 2008, ***109***, 700-707.

2 S. D. Ittel, S. D. Arthur, J. D. Citron, PCT Int. Appl., 1999, WO 9950273 A1 Oct 07, 1999.

3 (a) C. S. B. Gomes, P. T. Gomes, M. T. Duarte, *J. Organomet. Chem.,* 2014, ***760***, 101-107; (b) J.-C. Buffet, Z. R. Turner, R. T. Cooper, D. O'Hare, *Polym. Chem.,* 2015, ***6***, 2493-2503; (c) F. Wang, R. Tanaka, Q. Li, Y. Nakayama, J. Yuan, T. Shiono, *J. Mol. Cat. A: Chem*., 2015, ***398***, 231-240; (d) W. Zou, C. Chen, *Organometallics,* 2016, ***35***, 1794-1801.

4 J. Liu, Y. Li, Y. Li, N. Hu, *J. Appl. Polym. Sci*., 2008, ***109***, 700-707.

5 G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules,* 1999, ***32***, 1620-1625.