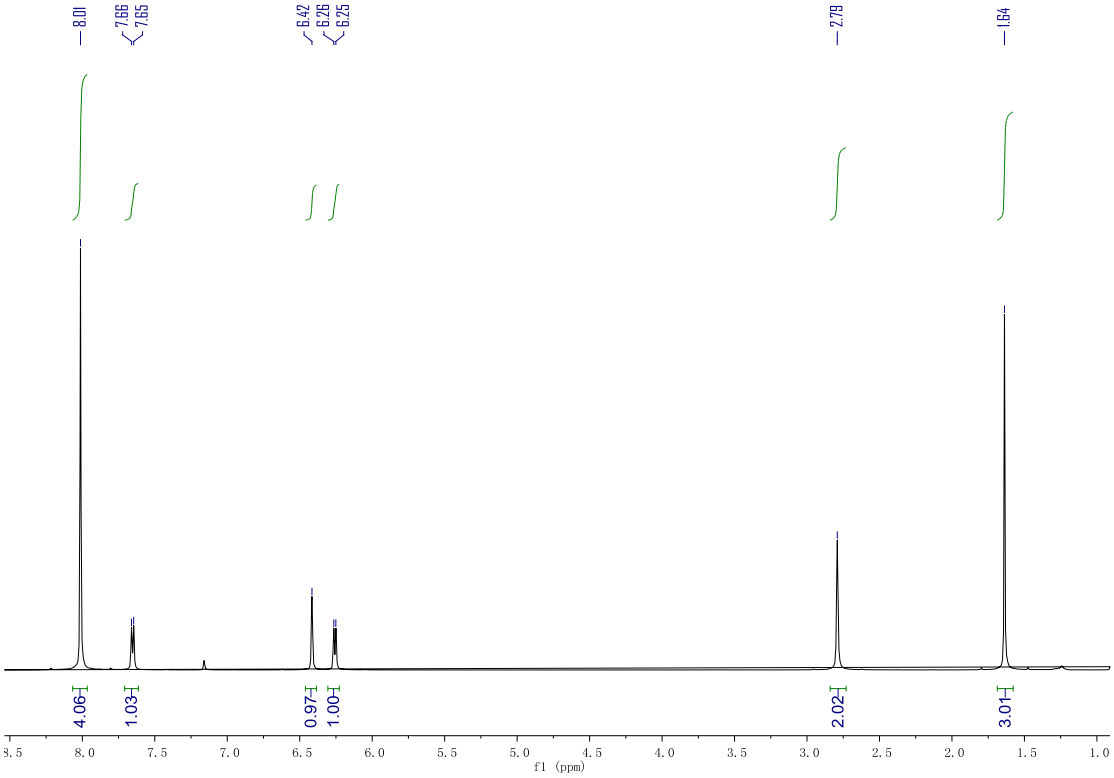

Figure S1: ^{1}H NMR spectrum of **5a** in C_6D_6

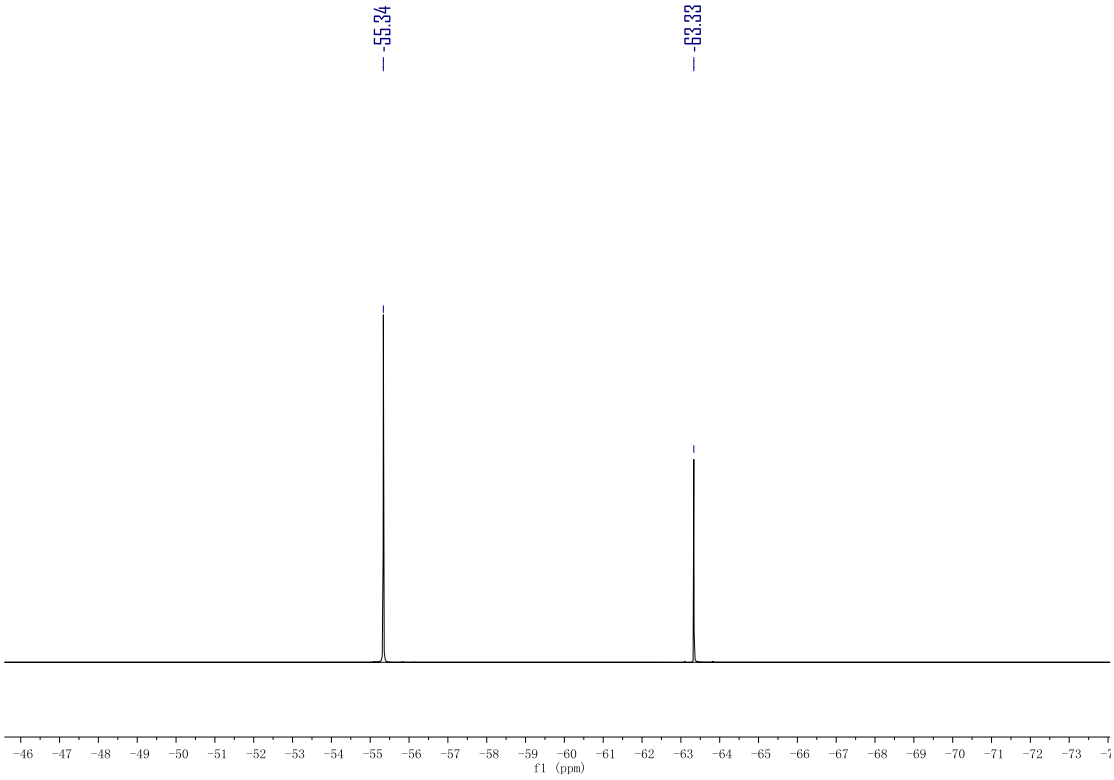

Figure S2: ^{19}F NMR spectrum of **5a** in C_6D_6

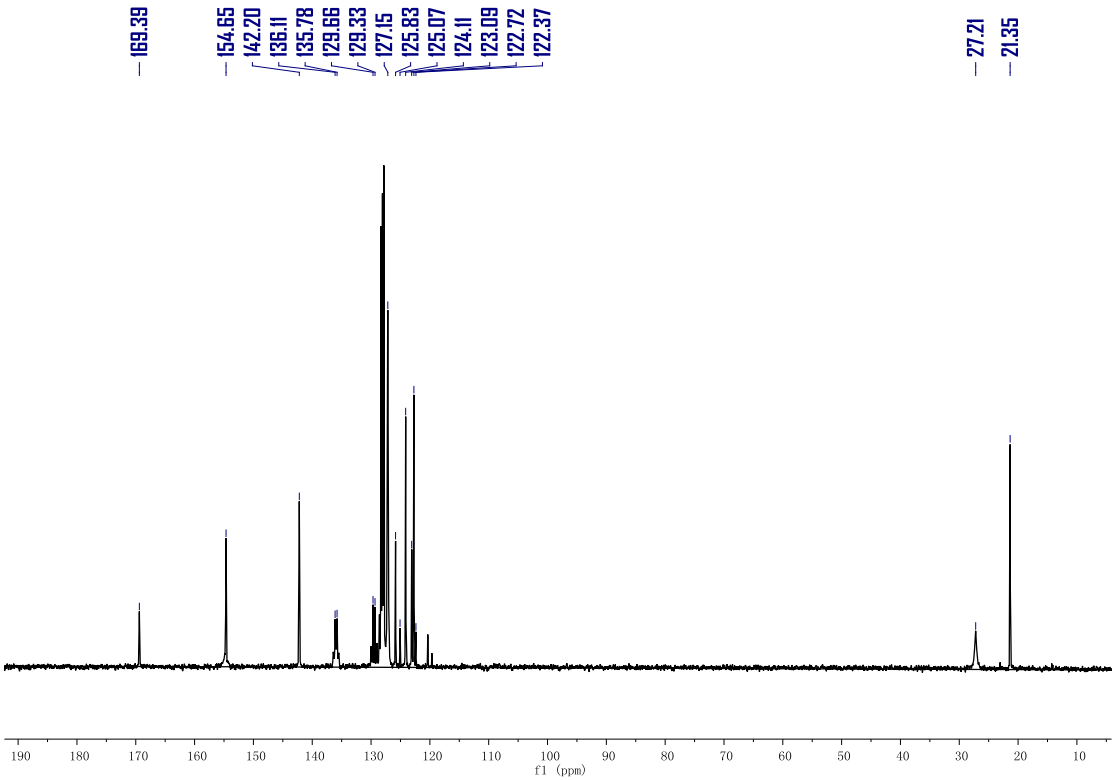

Figure S3: ^{13}C NMR spectrum of **5a** in C_6D_6

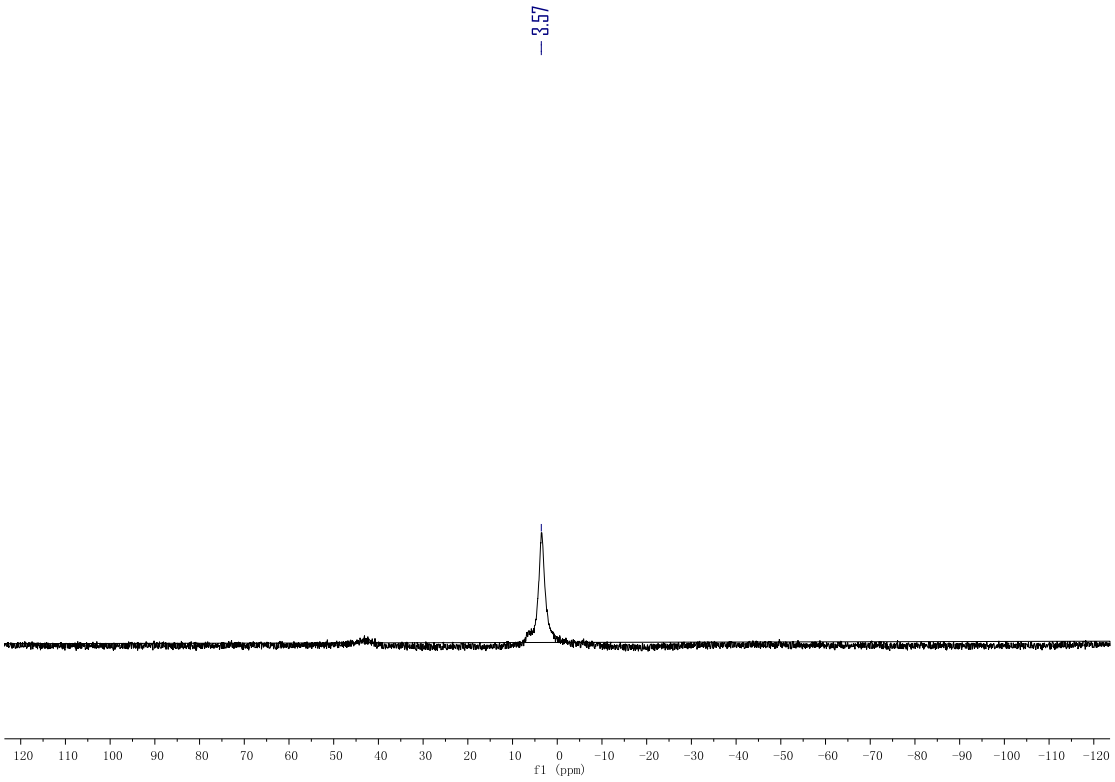

Figure S4: ^{11}B NMR spectrum of **5a** in C_6D_6

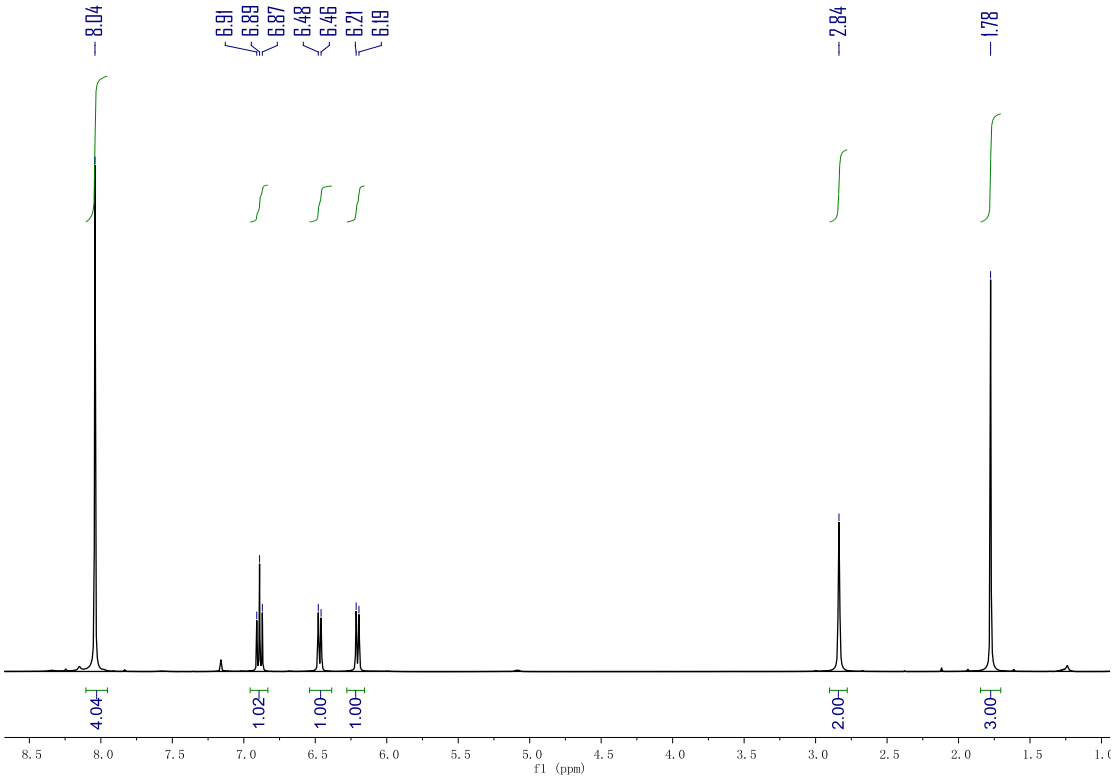

Figure S5: ^{1}H NMR spectrum of **5b** in C_6D_6

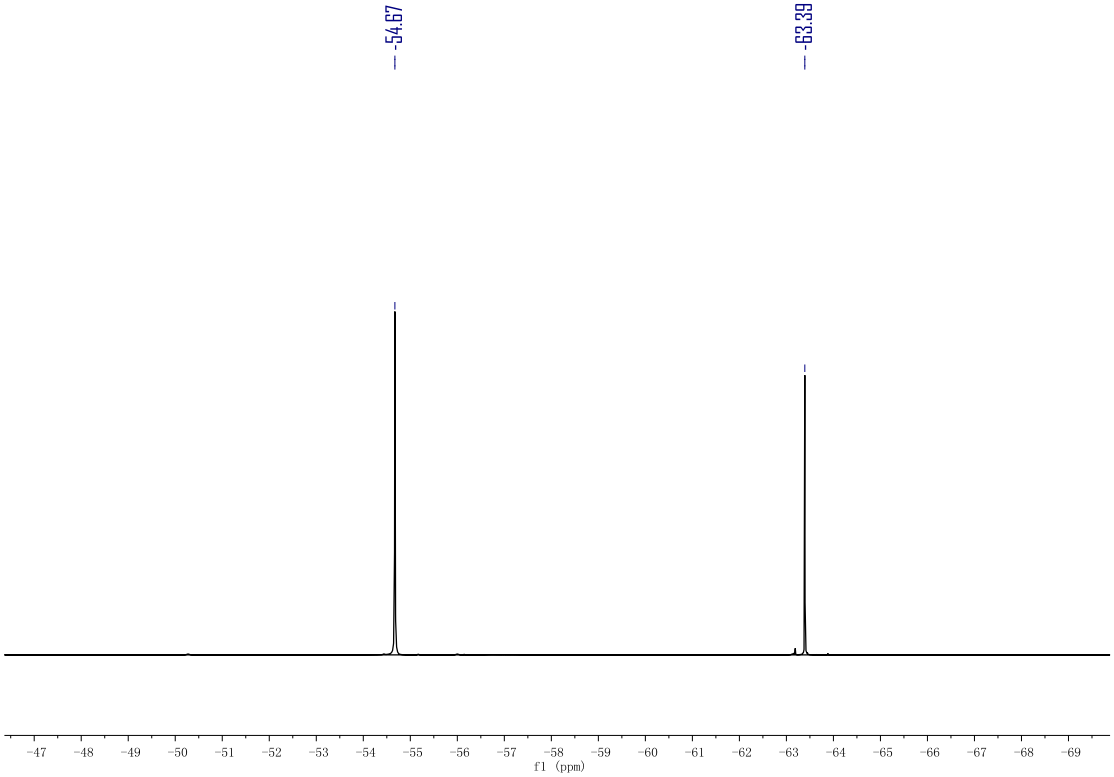

Figure S6: ^{19}F NMR spectrum of **5b** in C_6D_6

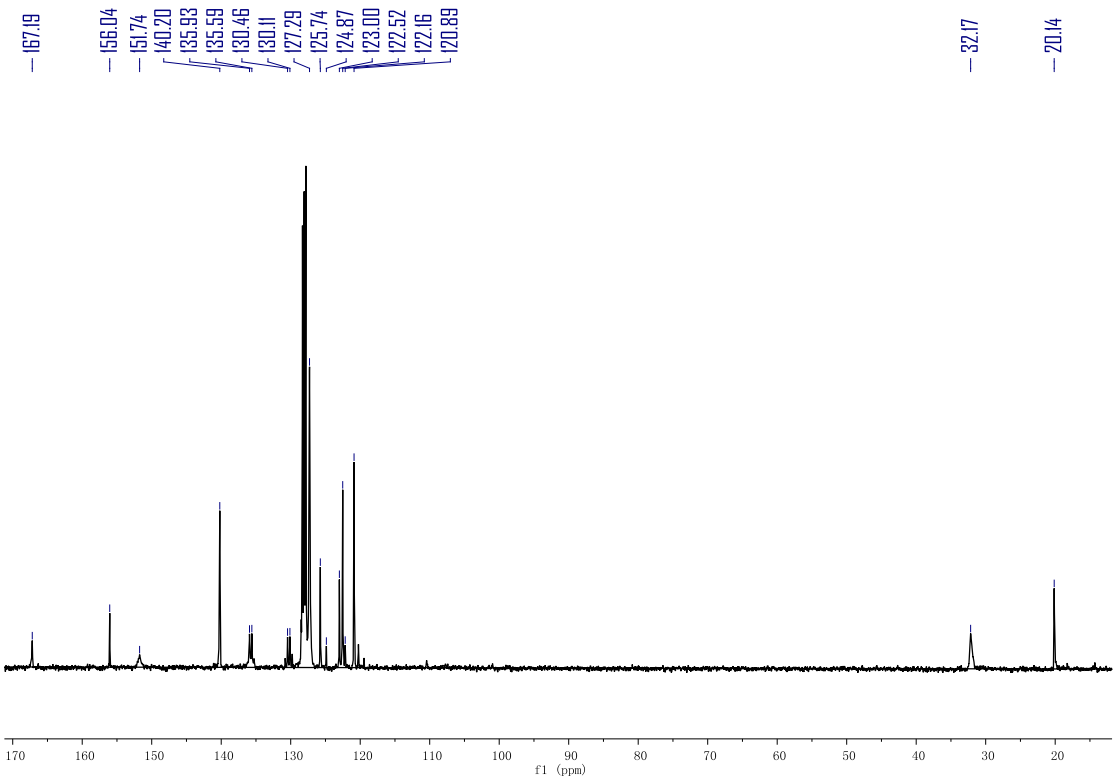

Figure S7: ^{13}C NMR spectrum of **5b** in C_6D_6

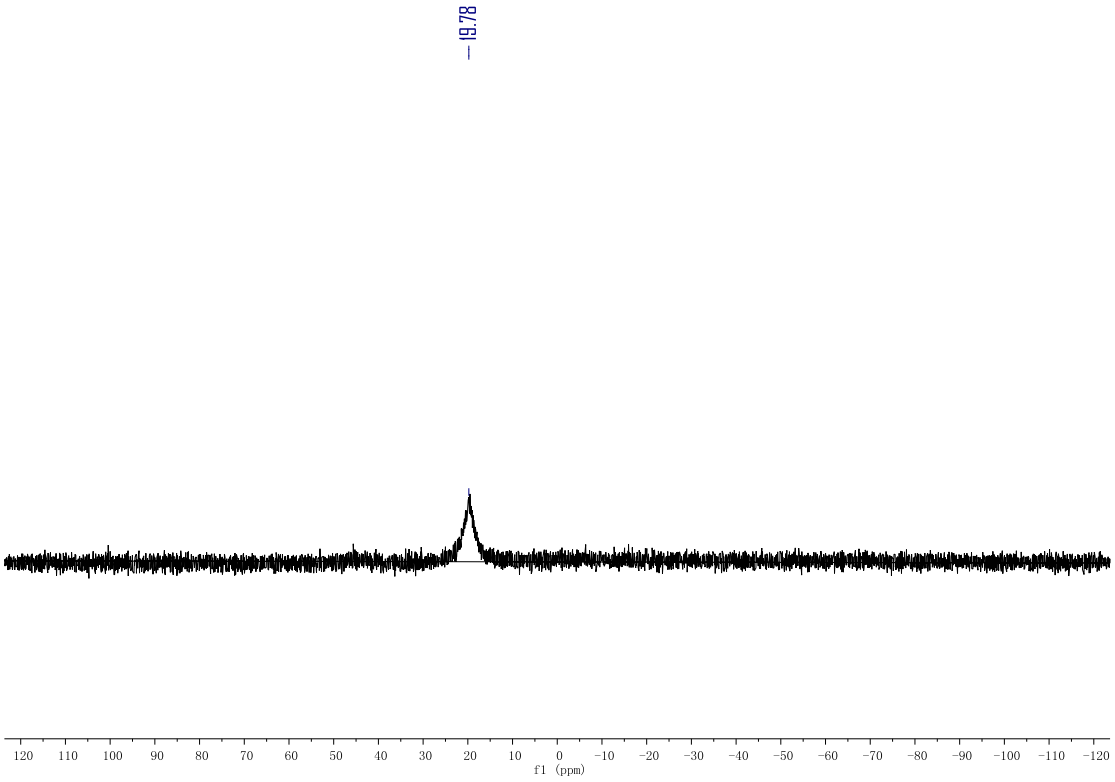

Figure S8: ^{11}B NMR spectrum of **5b** in C_6D_6

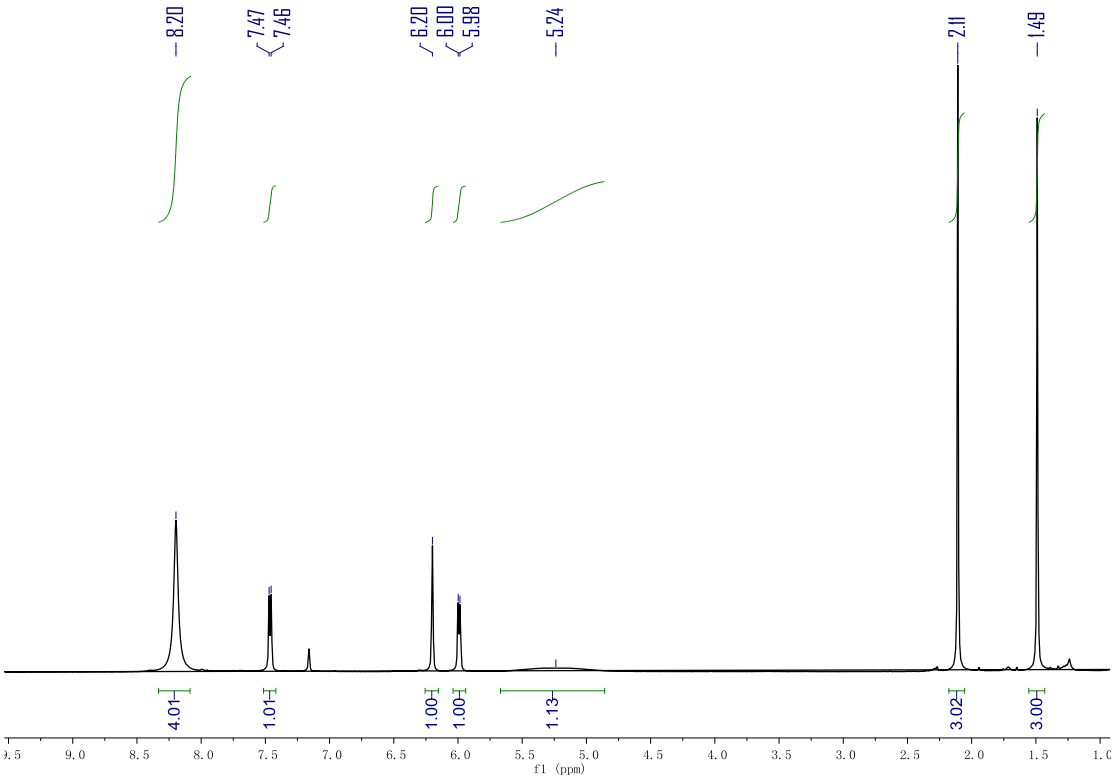

Figure S9: ^{1}H NMR spectrum of **6a** in C_6D_6

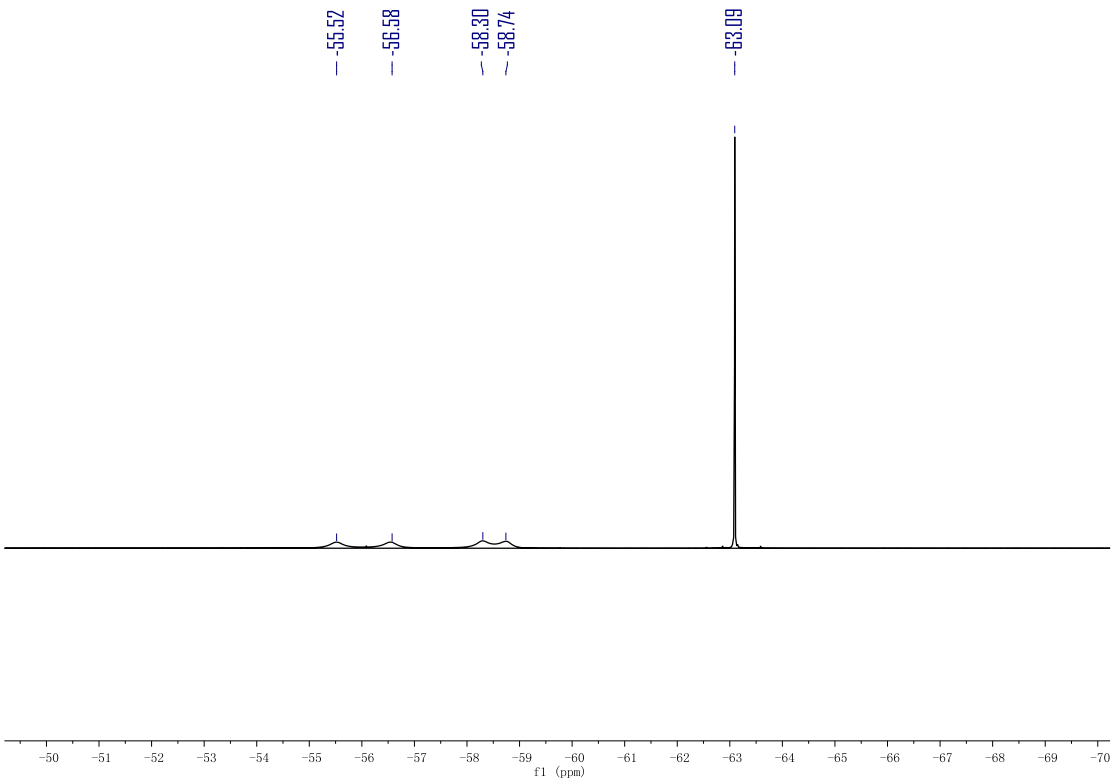

Figure S10: ^{19}F NMR spectrum of **6a** in C_6D_6

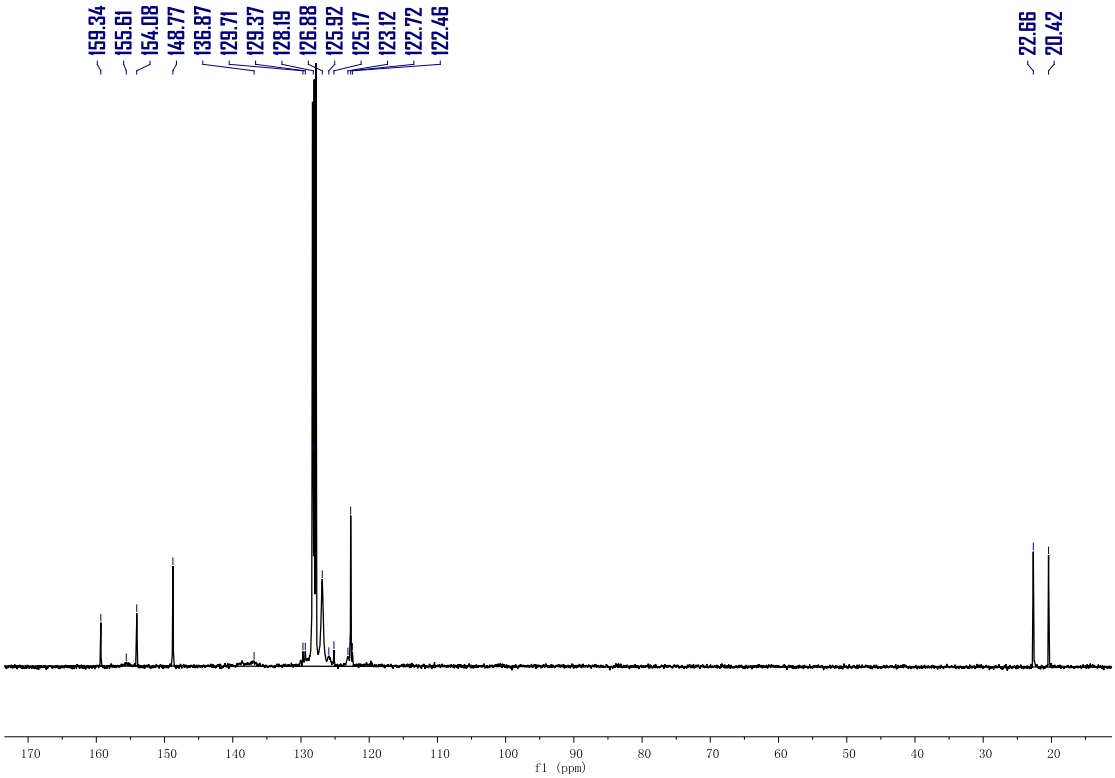

Figure S11: ^{13}C NMR spectrum of **6a** in C_6D_6

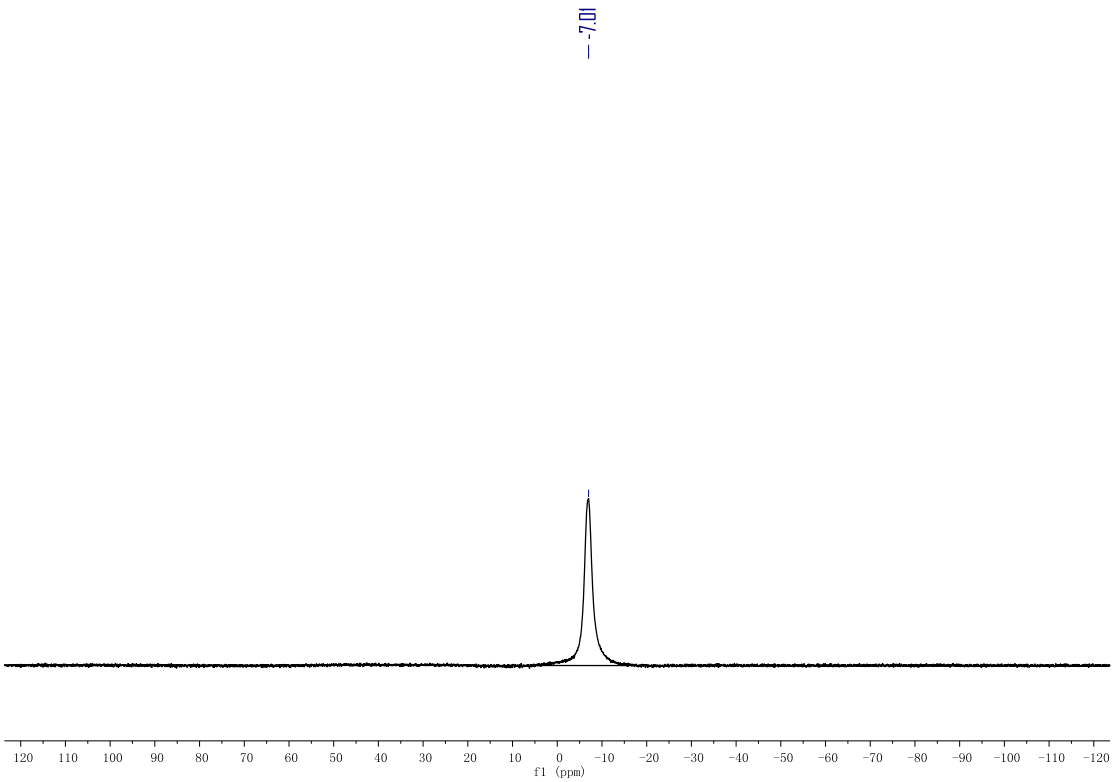

Figure S12: ^{11}B NMR spectrum of **6a** in C_6D_6

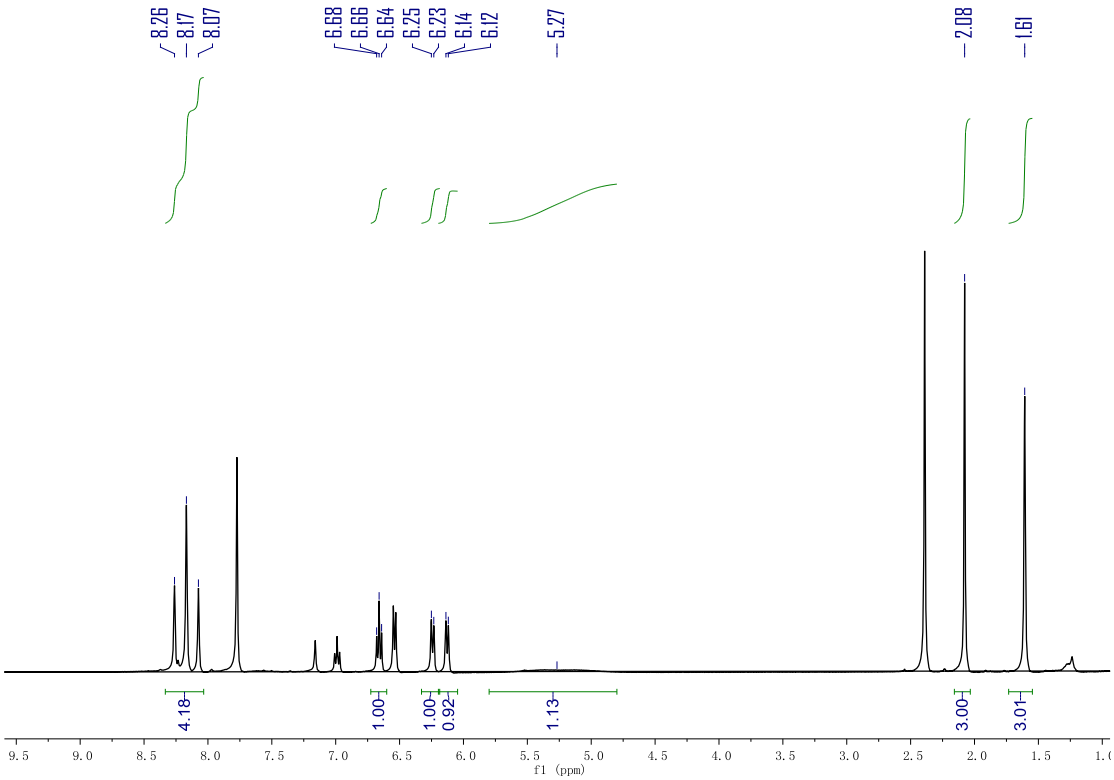

Figure S13: ^{1}H NMR spectrum of **6b** in C_6D_6

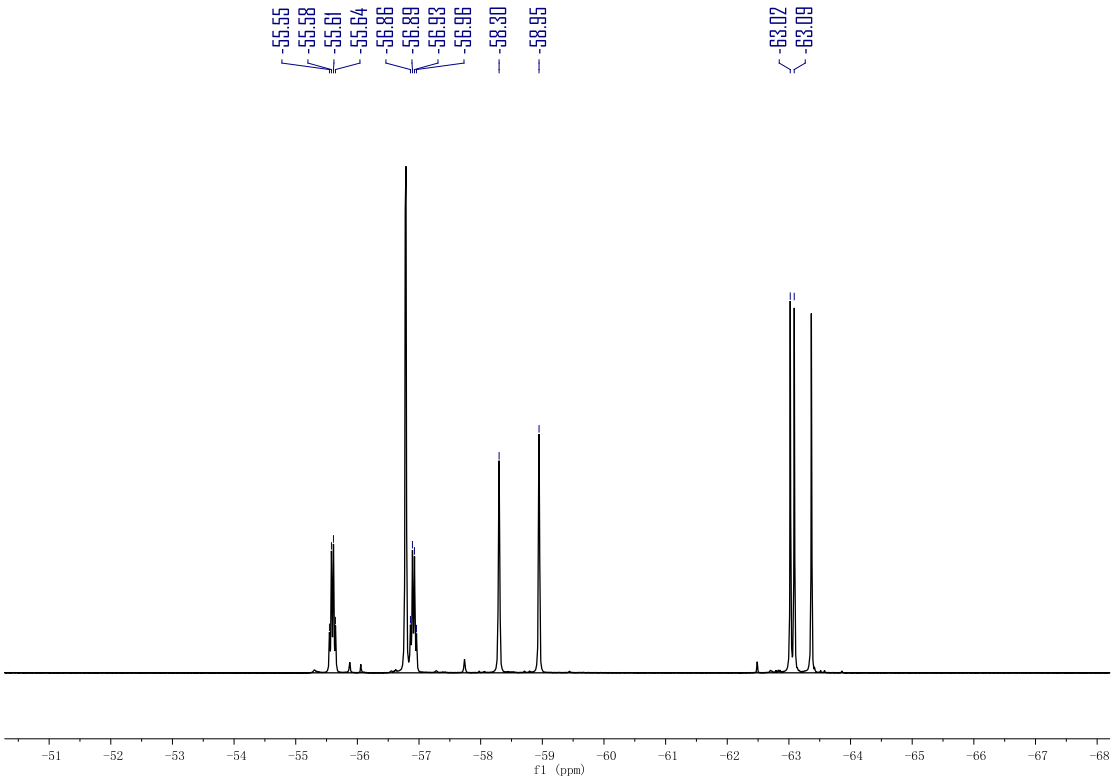

Figure S14: ^{13}C NMR spectrum of **6b** in C_6D_6

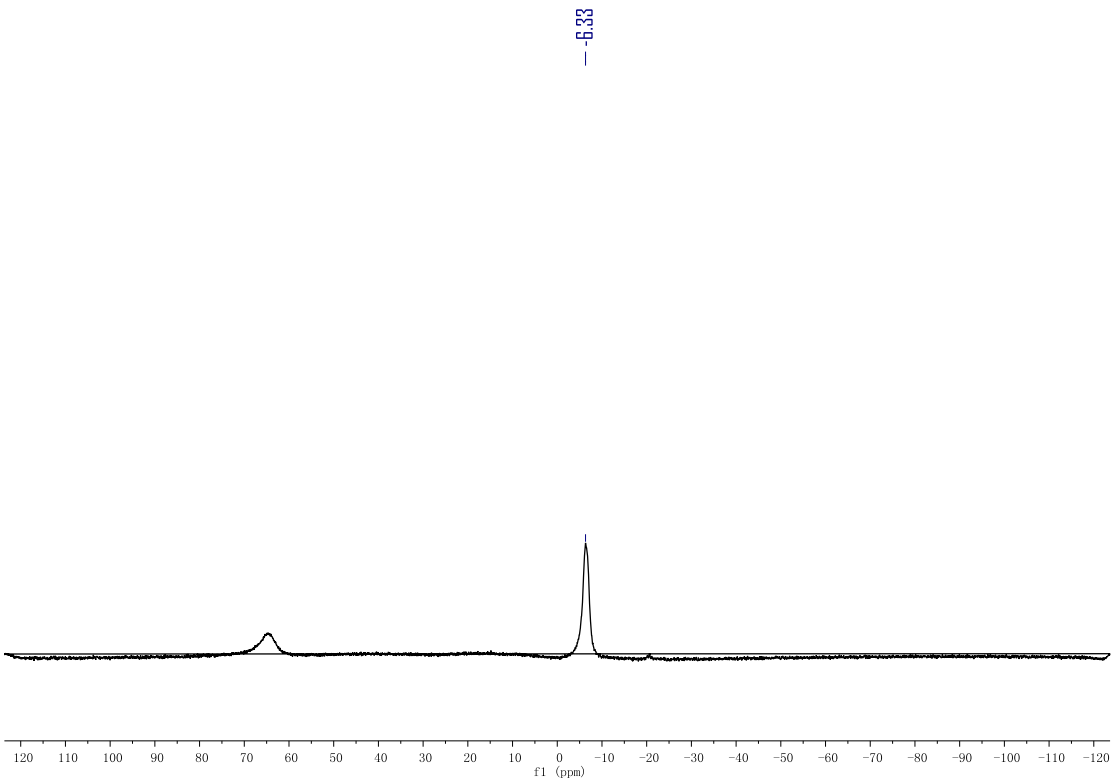

Figure S15: ^{11}B NMR spectrum of **6b** in C_6D_6

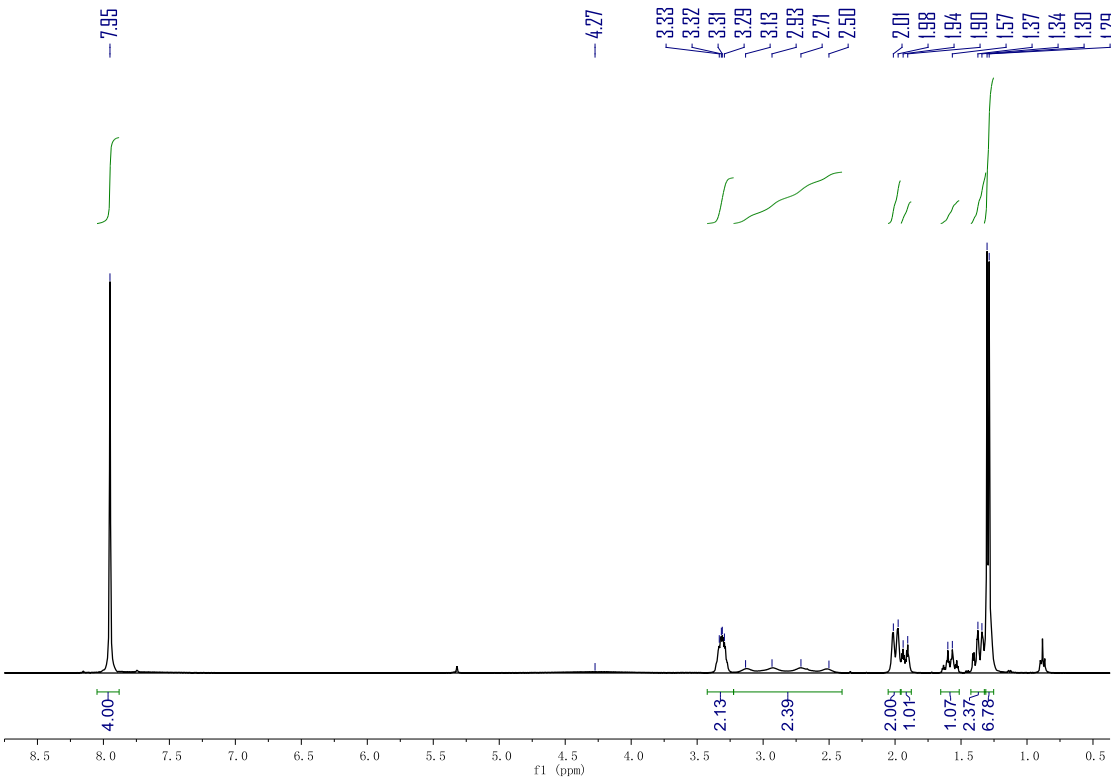

Figure S16: ^{1}H NMR spectrum of **8b** in CD_2Cl_2

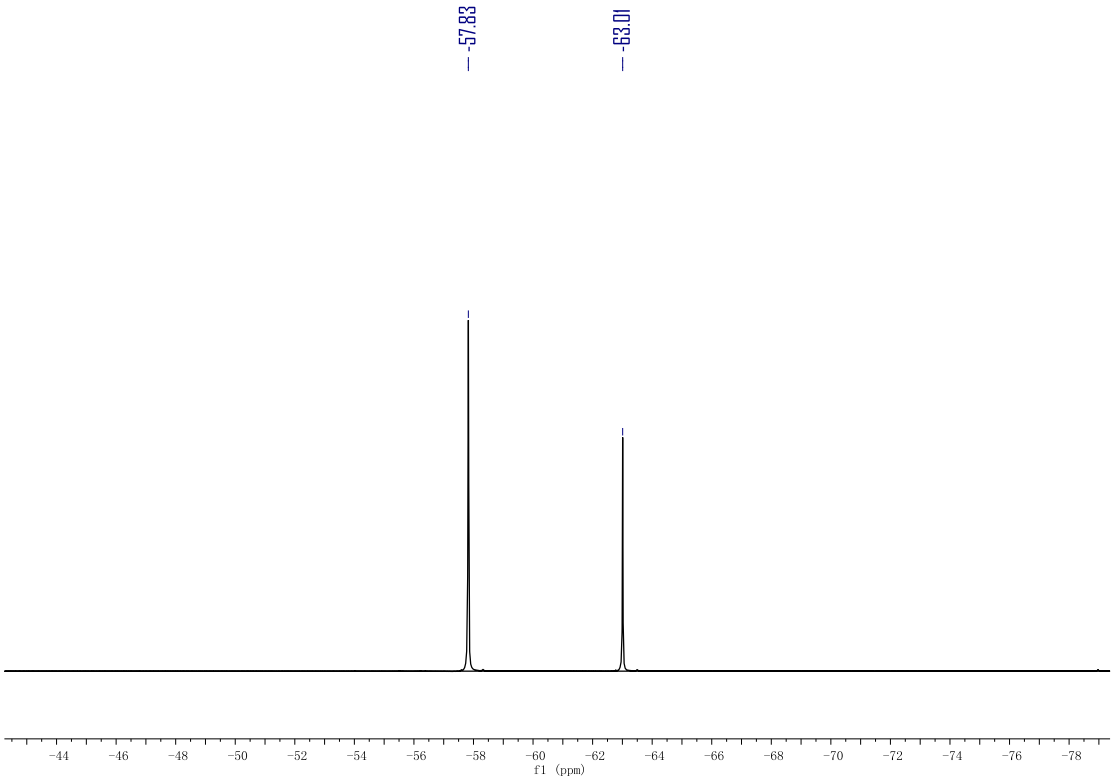

Figure S17: ^{19}F NMR spectrum of **8b** in CD_2Cl_2

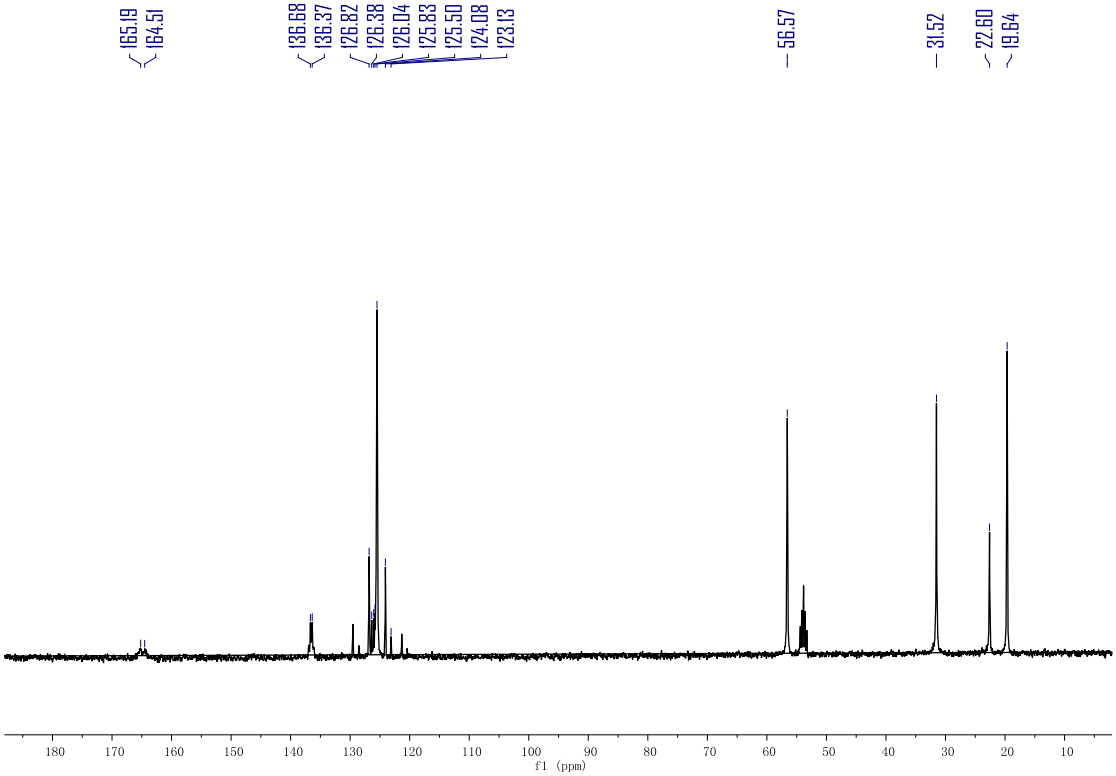

Figure S18: ^{13}C NMR spectrum of **8b** in CD_2Cl_2

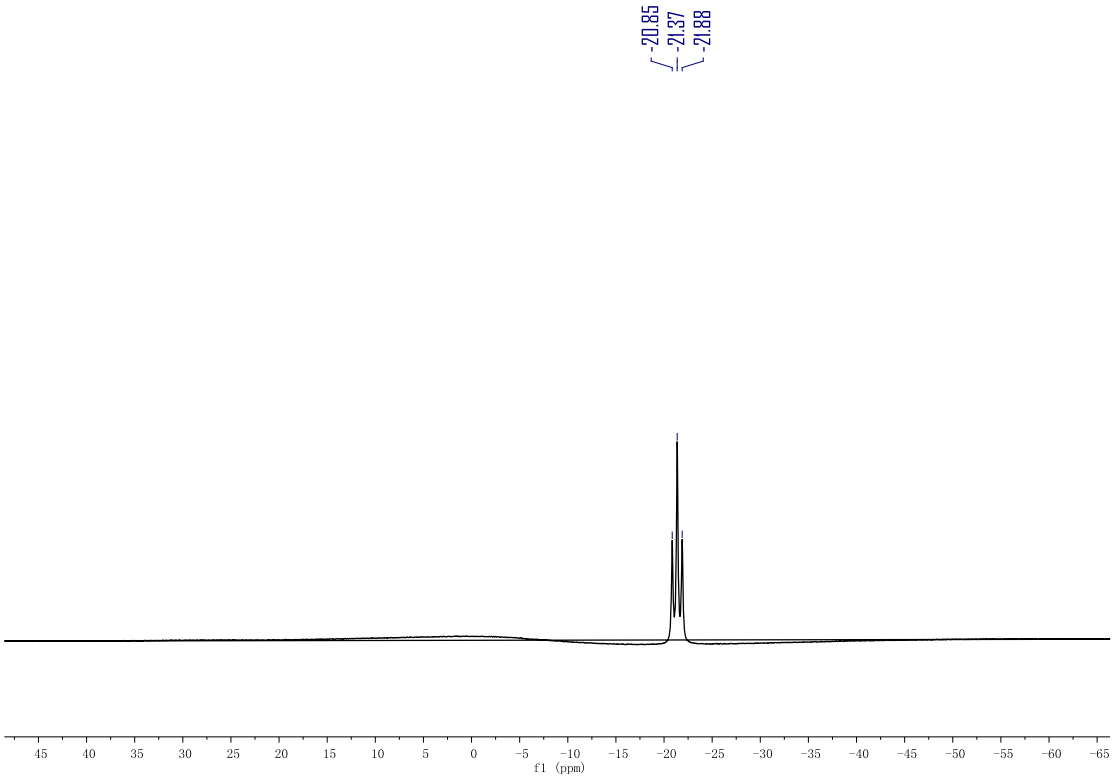

Figure S19: ^{11}B NMR spectrum of **8b** in CD_2Cl_2

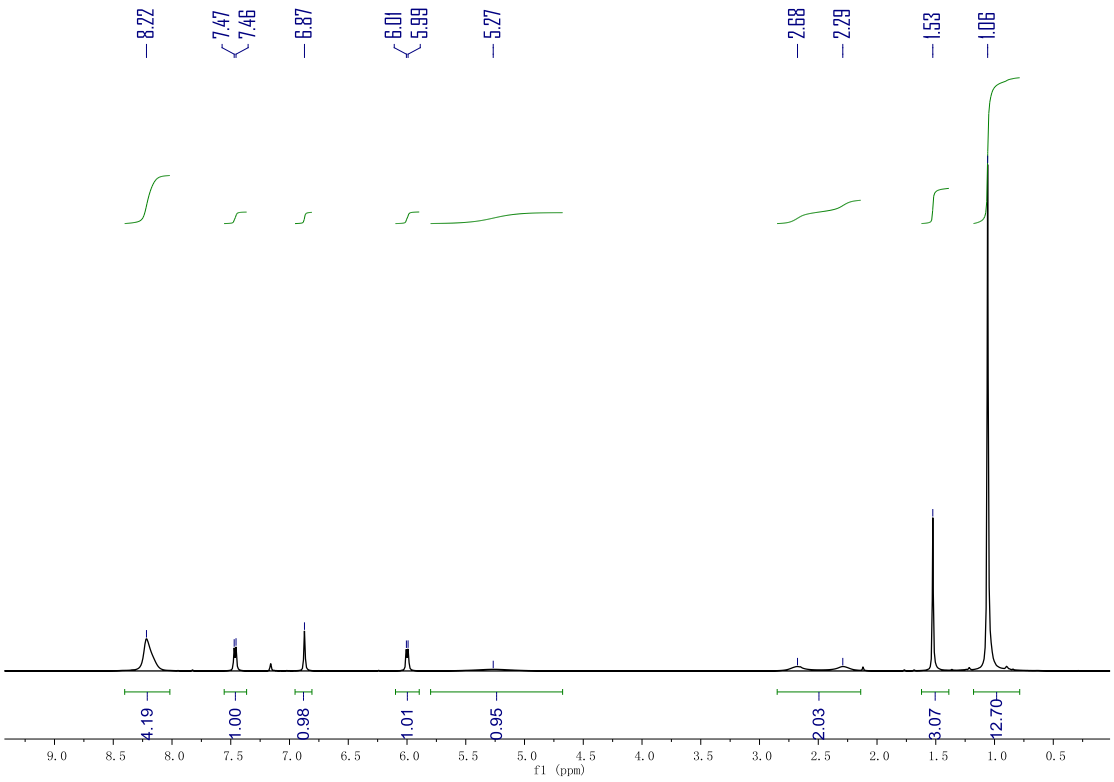

Figure S20: ^{1}H NMR spectrum of **9a** in C_6D_6

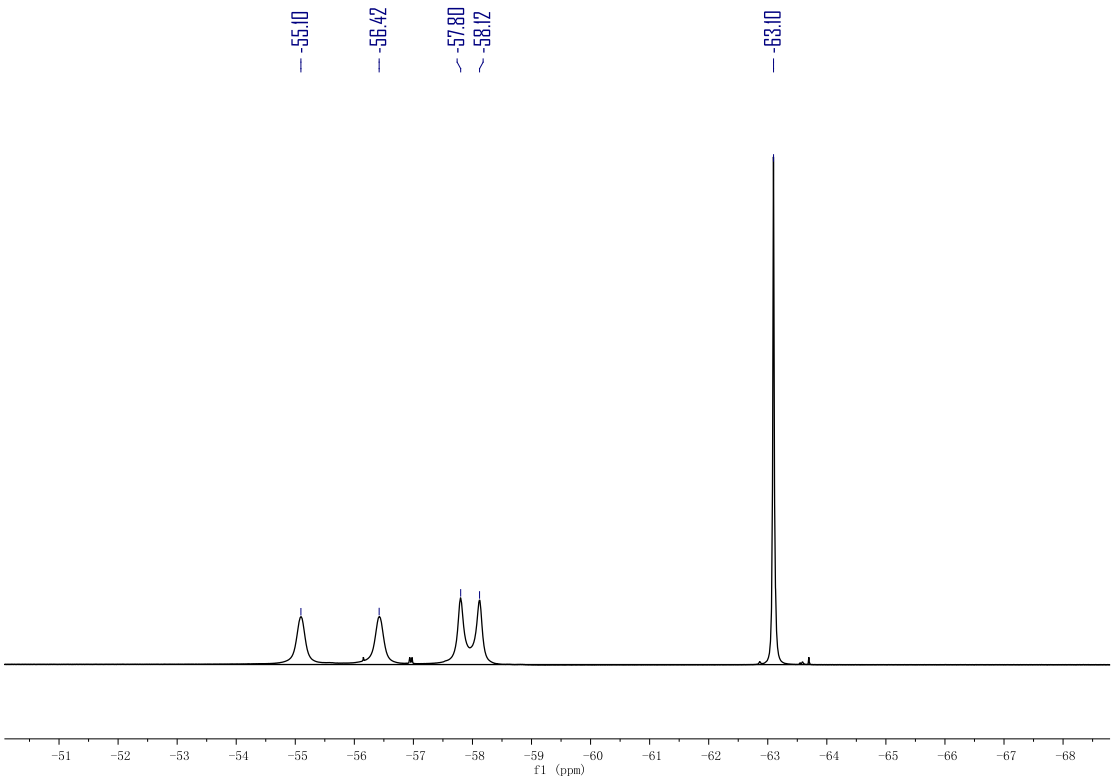

Figure S21: ^{19}F NMR spectrum of **9a** in C_6D_6

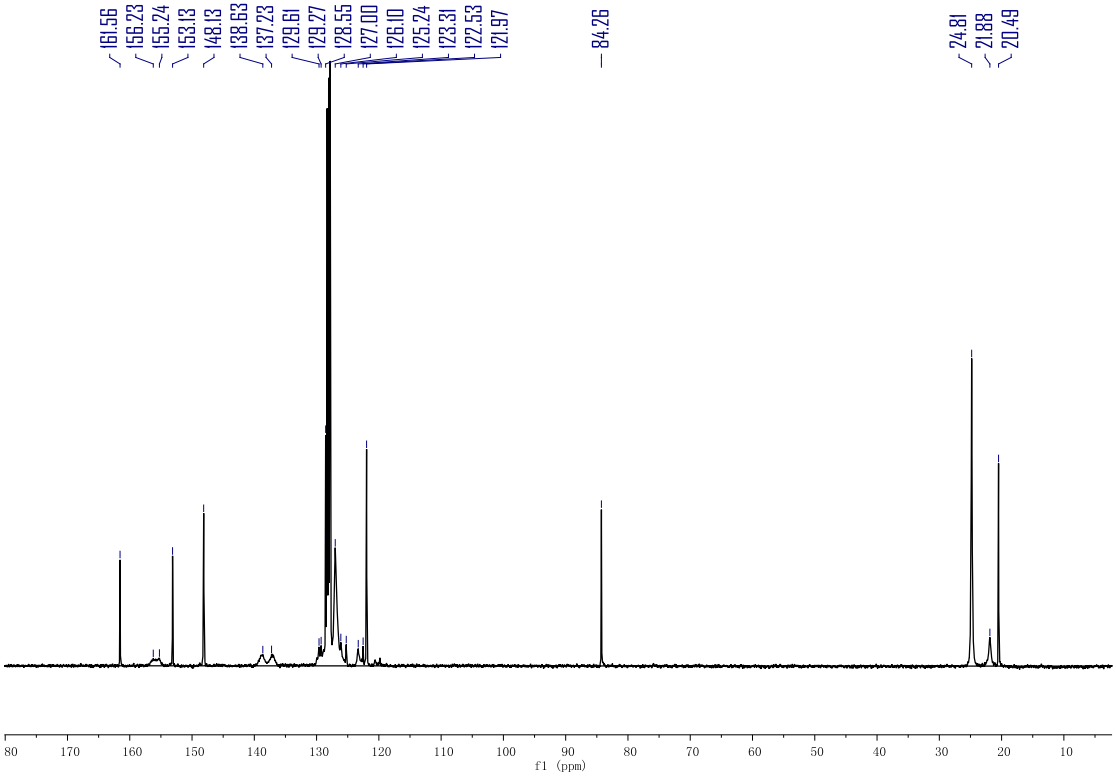

Figure S22: ^{13}C NMR spectrum of **9a** in C_6D_6

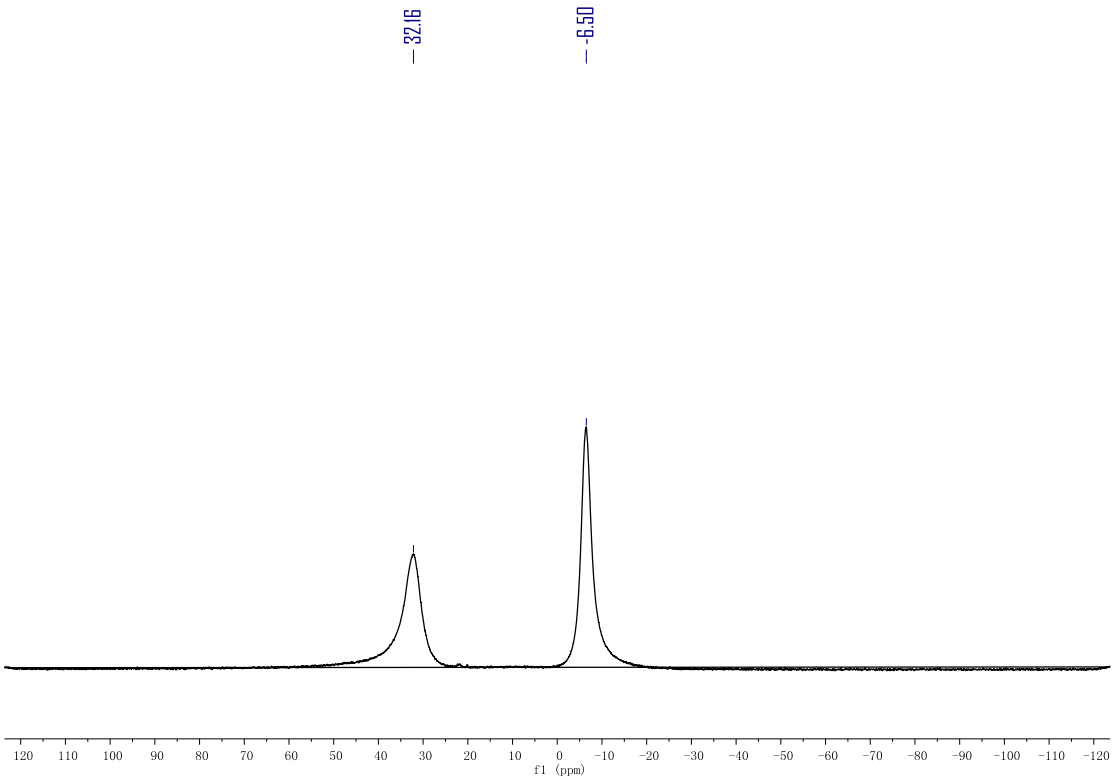

Figure S23: ^{11}B NMR spectrum of **9a** in C_6D_6

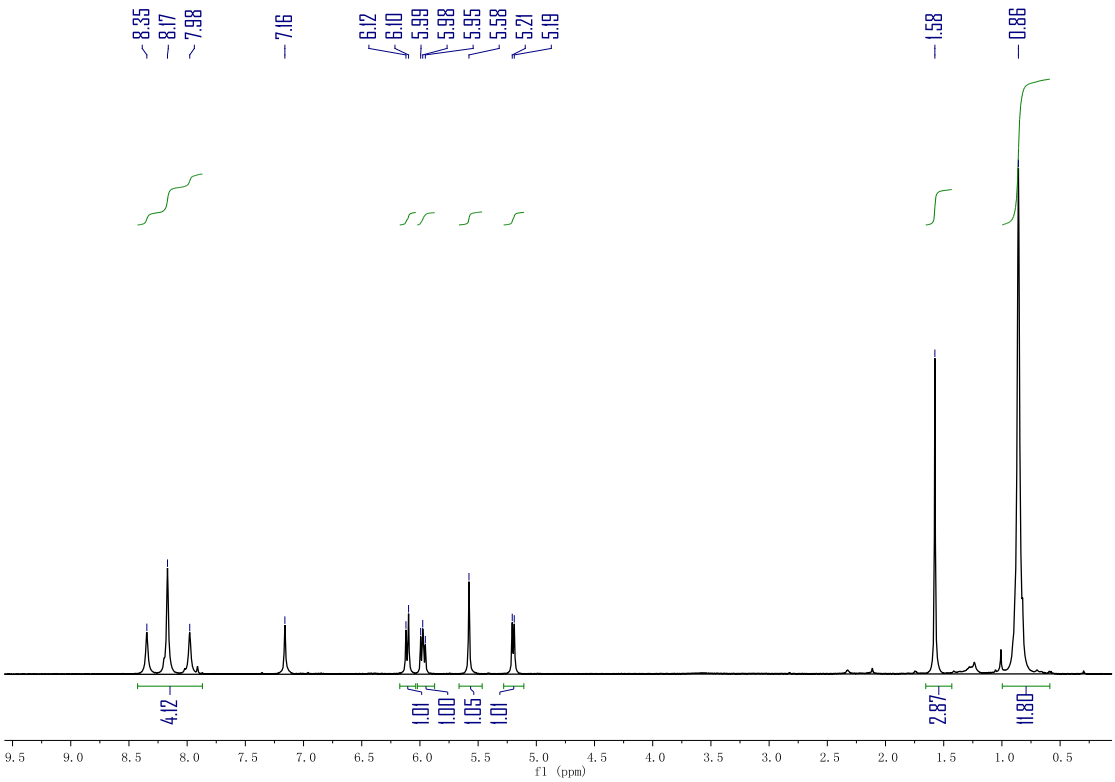

Figure S24: ^{1}H NMR spectrum of **11b** in C_6D_6

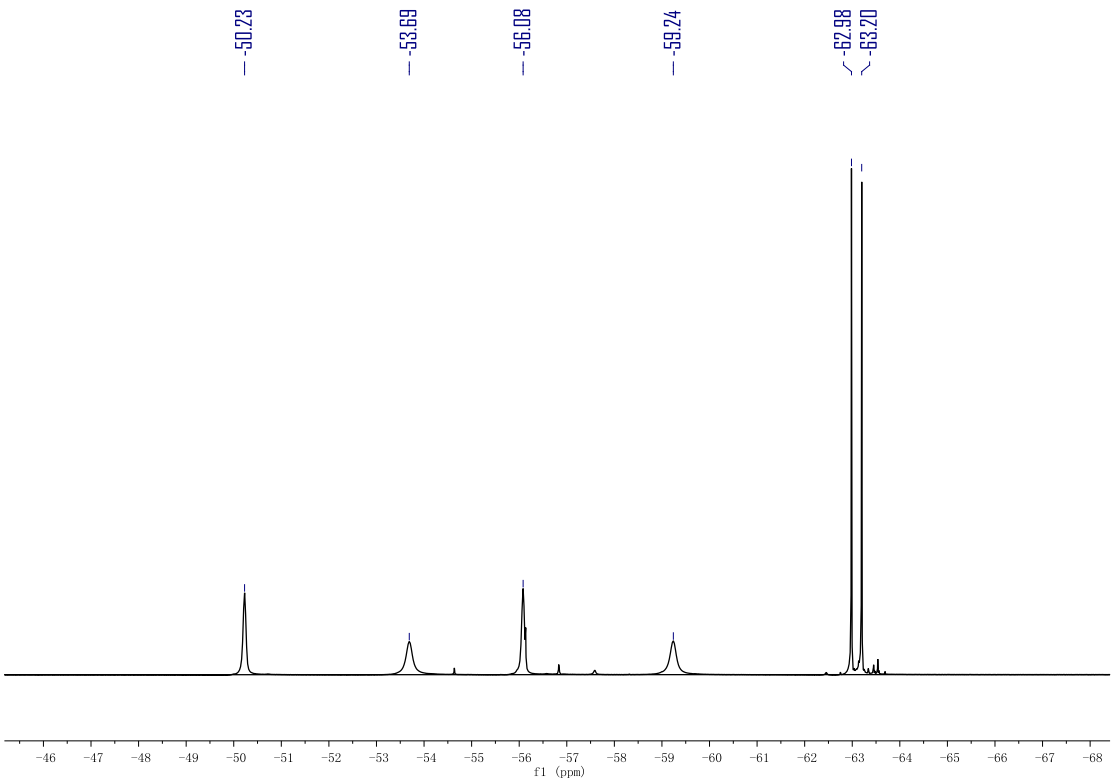

Figure S25: ^{19}F NMR spectrum of **11b** in C_6D_6

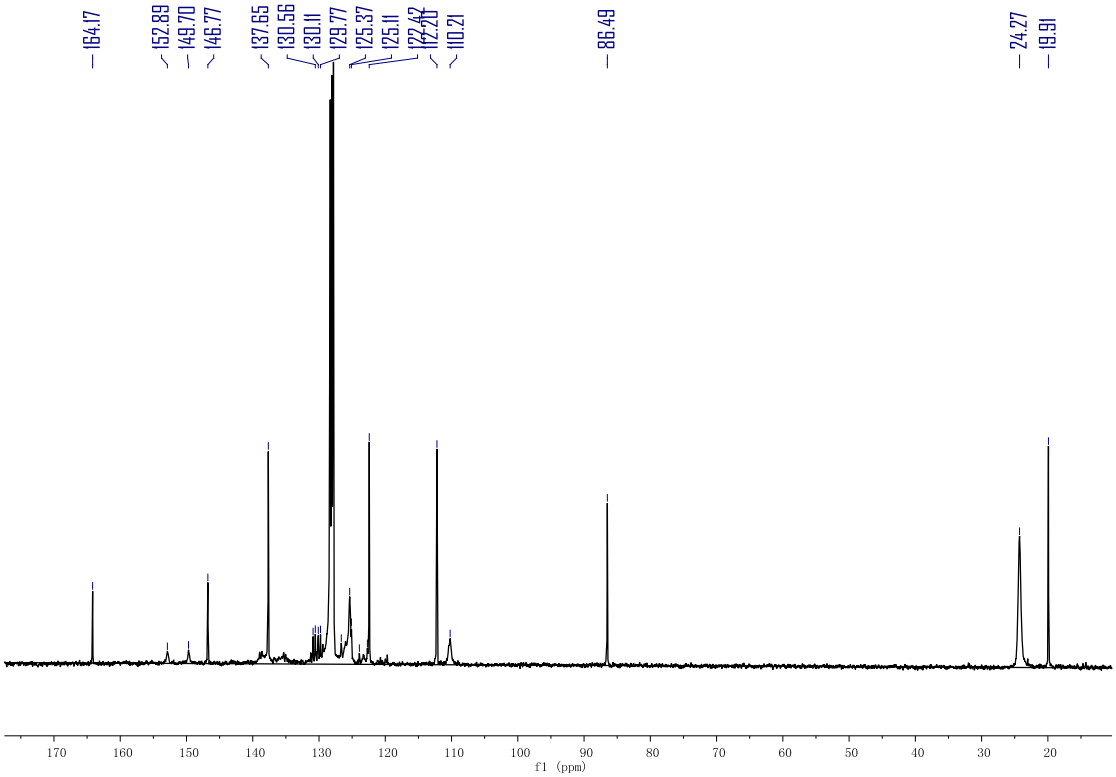

Figure S26: ^{13}C NMR spectrum of **11b** in C_6D_6

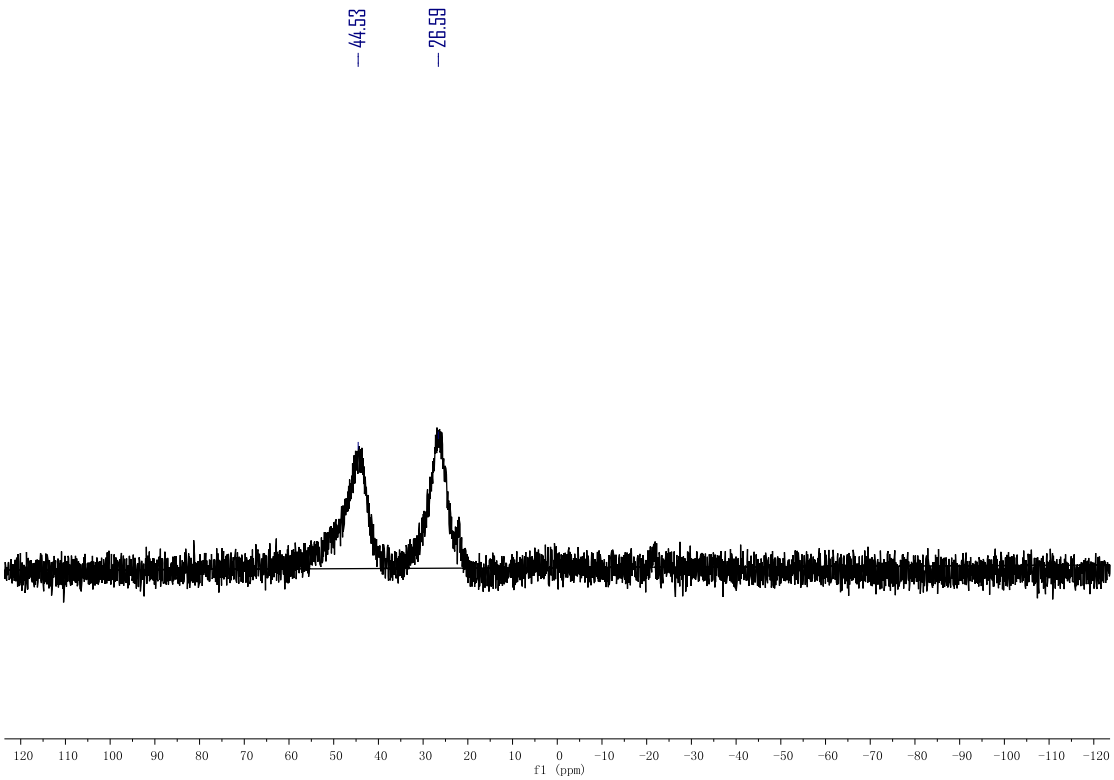

Figure S27: ^{11}B NMR spectrum of **11b** in C_6D_6

Computation details

Quantum chemical calculations were all performed at the density functional theory level using the hybrid meta-GGA M06-2x functional,[1] which has been proven to give reliable results to the structural and energetic properties of non-covalent systems and reaction energy barriers.[2] The M06-2x functional has a mean absolute error in energy barriers for the fluorine and carbon atoms on the ArF group, the 6-31G and 6-31G(d) basis sets were used, respectively. For all other atoms the 6-31+G(d,p) basis set was used.

Full geometry optimization were carried out in the benzene solution which was modelled by the polarizable continuum solvation model (IEFPCM)[4] with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.[5] All the calculations were performed by using the Gaussian 09 program. [6]

References:

1. (a) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101; (b) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 5121.
2. Zhao, Y.; Truhlar, D. G. *Theo. Chem. Acc.* **2008**, *120*, 215.
3. (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639-5648. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-654.
4. Scalmani, G.; Frisch, M. J.; Map, V. *J. Chem. Phys.* **2010**, *132*, 114110.
5. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
6. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

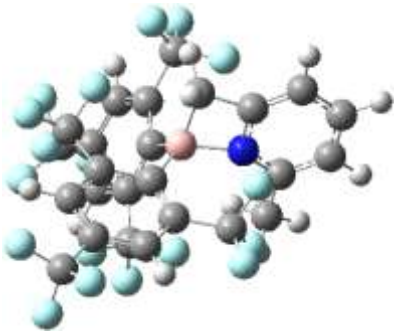

Figure S28: simulated structure of **5b**

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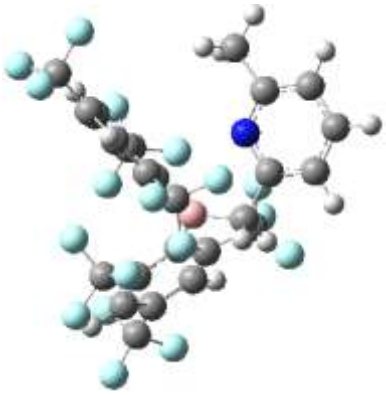

Figure S29: simulated structure of **5b'**

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C,0,1.6378195204,5.4516443373,-0.5751478562
H,0,-0.1006890778,4.7957696813,-1.6810164595
C,0,2.6553454274,3.7326007909,0.7532900784
C,0,2.6411172722,5.0537618595,0.3065078108
H,0,3.3999107772,5.752551336,0.6435004796
C,0,-0.1998084893,2.1511027089,-0.9341584749
H,0,-1.220235069,2.4920832052,-0.7432473364

H,0,-0.1663064414,2.0572053352,-2.0265891181
C,0,3.7106718652,3.2092146159,1.6877750445
H,0,3.2434819044,2.6971148233,2.5342428503
H,0,4.3418113351,2.4790279807,1.1695180496
H,0,4.3494490875,4.0102380316,2.0666969005
H,0,1.6016047767,6.4747692121,-0.937989809

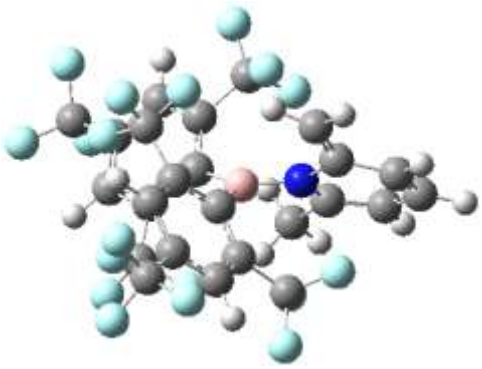

Figure S30: simulated structure of **5b''**

0 1
C,0,4.041189181,1.0513379084,-0.7970207744
C,0,4.2706599713,-0.315267453,-0.834186151
C,0,3.2243316313,-1.1980611927,-0.6339092431
C,0,1.9478571942,-0.7002634755,-0.3915675041
C,0,1.6587163732,0.6785129123,-0.3336161545
C,0,2.7596905922,1.5394800417,-0.5586765665
C,0,-1.0018127275,0.6743233843,-1.1108285694
C,0,-0.8745545585,0.4557016019,-2.4980023197
C,0,-2.2204478894,0.2474796902,-0.5351812379
C,0,-1.8768615613,-0.1303307724,-3.263431807
C,0,-3.2291231672,-0.3450670468,-1.291545492
C,0,-3.0535636881,-0.5313984897,-2.6527551668
C,0,2.6818400189,3.0543929341,-0.5036316526
C,0,0.8786181851,-1.7494005484,-0.2193869678
C,0,5.6484746311,-0.8207644713,-1.1488060414
C,0,-2.5808966748,0.4627350467,0.9243719097
C,0,0.372893276,0.837216175,-3.2578432838
C,0,-4.1731267565,-1.0951269379,-3.4799919046
H,0,-1.7415430855,-0.2728191112,-4.3300329641
H,0,-4.1524634444,-0.6628201314,-0.8207900374
H,0,3.4017411623,-2.2675951074,-0.6575282456
H,0,4.8659890396,1.7374640849,-0.9547093569
F,0,-4.9361409593,-1.9410067688,-2.77192261
F,0,-4.9834860553,-0.1226466164,-3.9340491469
F,0,-3.7147112259,-1.7554372678,-4.5535893233
F,0,0.1280915857,1.0007498102,-4.5660763132

F,0,0.897159103,1.9955121591,-2.816143099
F,0,1.3439643431,-0.0893323845,-3.1633314846
F,0,1.5596524189,3.5844419267,-1.0170824266
F,0,3.6966582475,3.615616814,-1.1853450018
F,0,2.7834516216,3.5089518971,0.7612887679
F,0,5.8055713757,-2.101373727,-0.7816821579
F,0,6.5933469758,-0.0987660744,-0.52455064
F,0,5.9145780712,-0.7505583283,-2.4645541146
F,0,-3.5749047109,-0.3572715903,1.3051763683
F,0,-3.0258959943,1.719319018,1.1406509288
F,0,-1.5743982841,0.2569114164,1.7818319292
F,0,1.3864265044,-2.9173092214,0.1994818524
F,0,-0.0512549097,-1.3872345731,0.6866523831
F,0,0.2161362578,-2.0097009512,-1.3634870913
B,0,0.1697576441,1.2731780615,-0.1873713659
C,0,0.5740941764,2.2938232823,2.023947652
C,0,0.6991314156,3.5410330528,2.7602747228
N,0,-0.0904640323,2.3335723077,0.7514393586
C,0,-0.0238141386,4.6189974631,2.411932398
H,0,1.3503667526,3.5349096359,3.6280513878
C,0,-0.8750469964,3.473793362,0.4298700835
C,0,-0.8553254705,4.5584908049,1.2359932772
H,0,-1.420782249,5.4315899119,0.9327216636
C,0,1.0169011864,1.1350541746,2.5534093417
H,0,1.5845725439,1.1685172679,3.4766633065
H,0,0.8052217281,0.1630107892,2.1335952162
C,0,-1.5762943031,3.5436302733,-0.8969570804
H,0,-0.881962334,3.3480935638,-1.7204035756
H,0,-2.4169785999,2.8527991855,-0.9831976307
H,0,-1.9666151242,4.5543694897,-1.0247795028
H,0,0.025930523,5.5386034938,2.985745548