Cover page for Supporting Information

Title: Cycloaddition Reactions of 1-Lithio-1,3-dienes with Aromatic Nitriles Affording Multiply Substituted Pyridines, Pyrroles and Linear Butadienyl imine

Authors: Congyang Wang,[†] Zhihui Wang,[†] Lantao Liu,[‡] Chao Wang,[†] Guangzhen Liu,[†] and Zhenfeng Xi*[,†,§]

Affiliations: Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China, and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

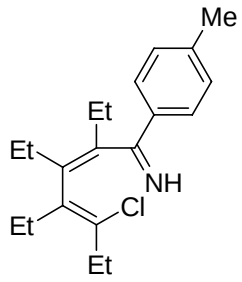
CONTENTS

1) Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds.

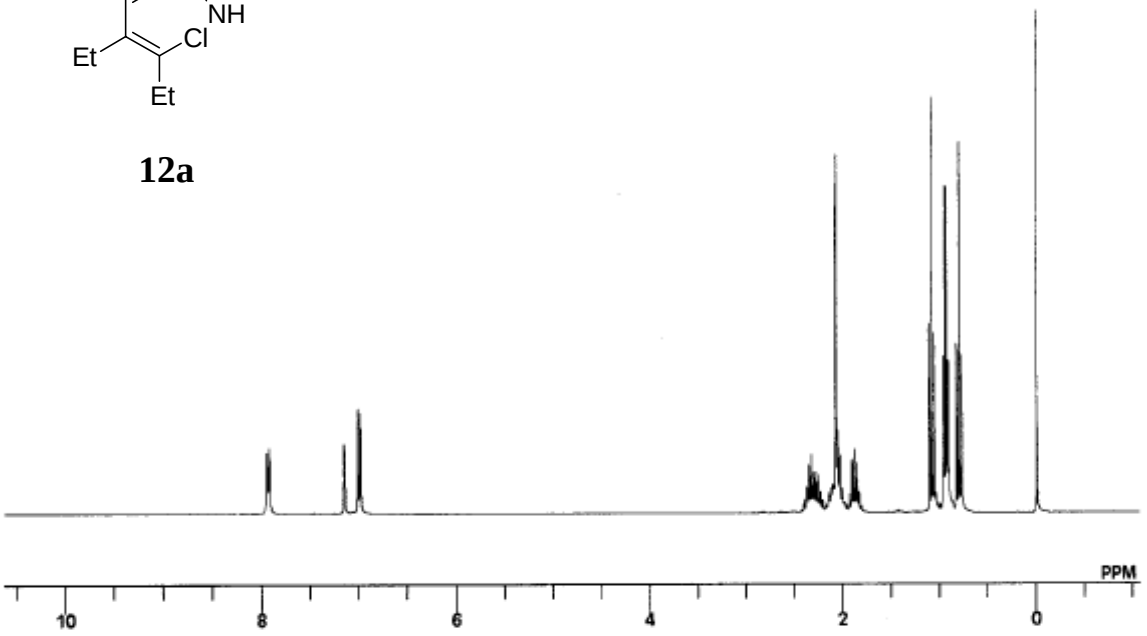
Pages: S1 ~ S23

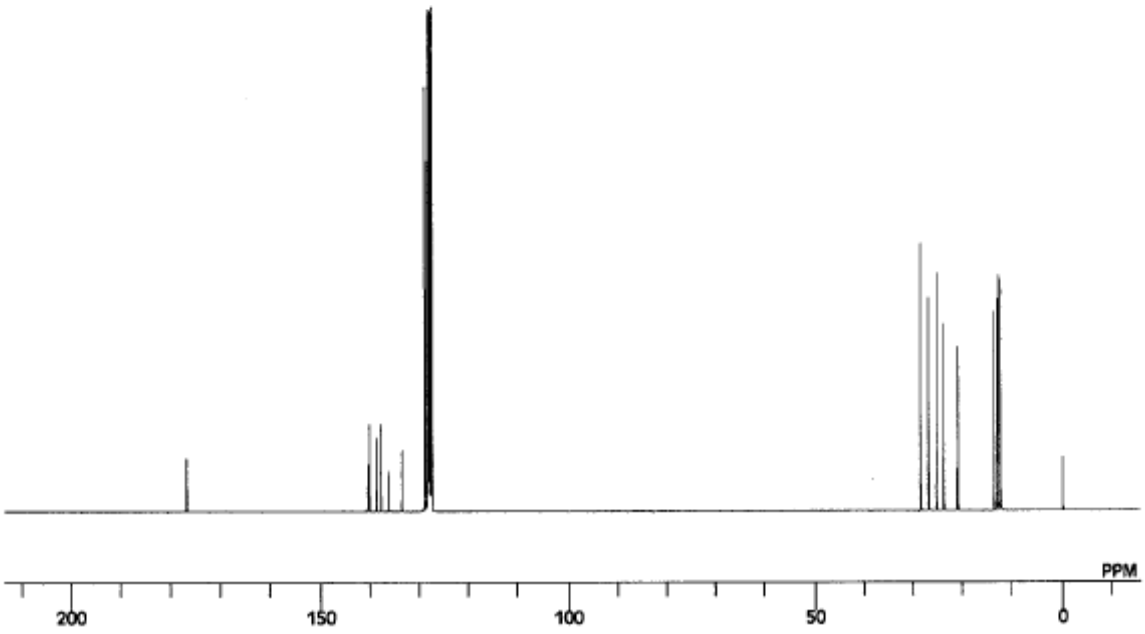
2) General Experimental Methods and Characterization Data.

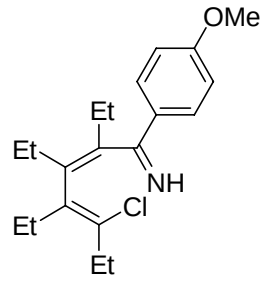
Pages: S24 ~ S27



12a

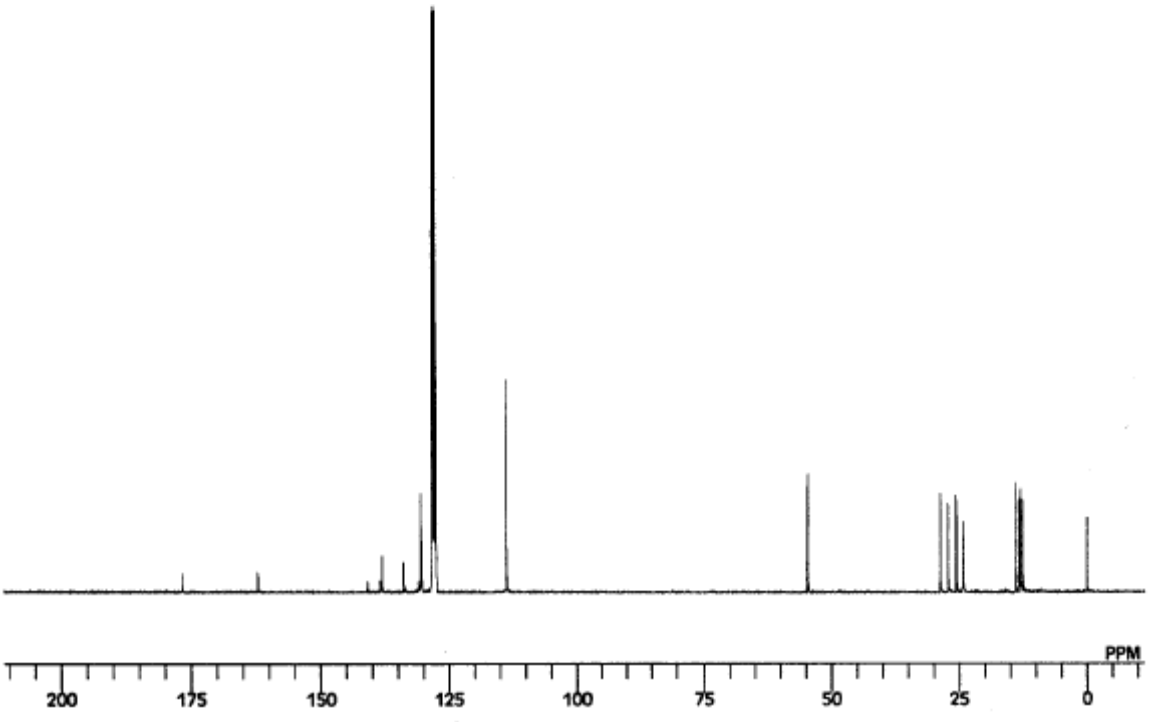


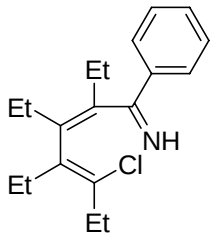



OMe
Et
Et
NH
Cl
Et
Et

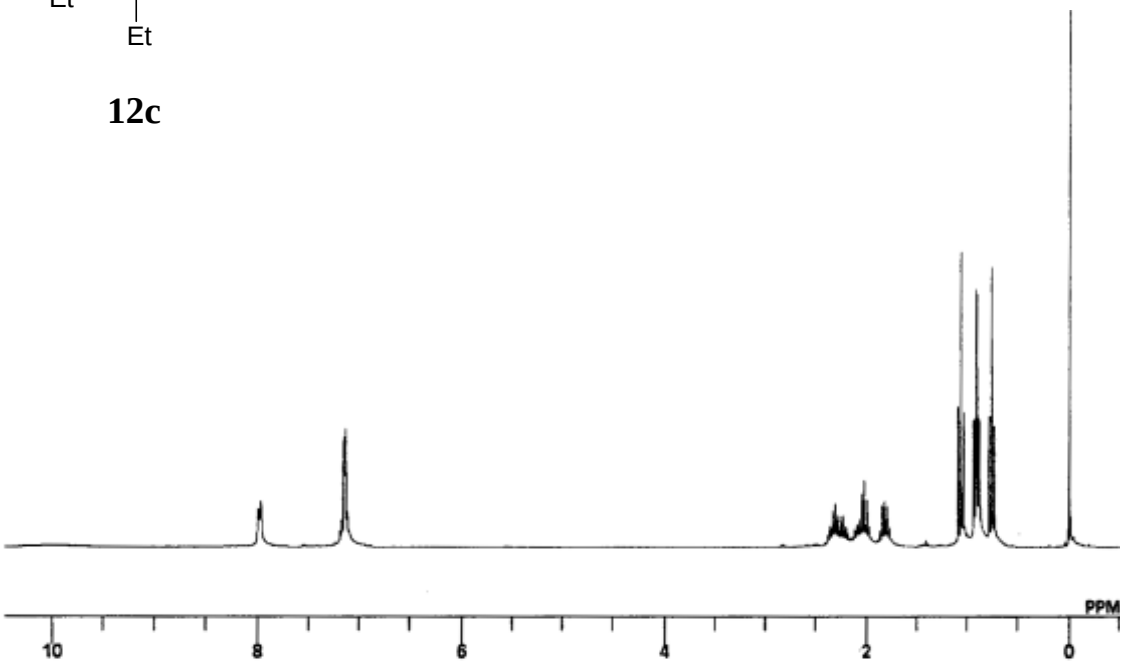
12b

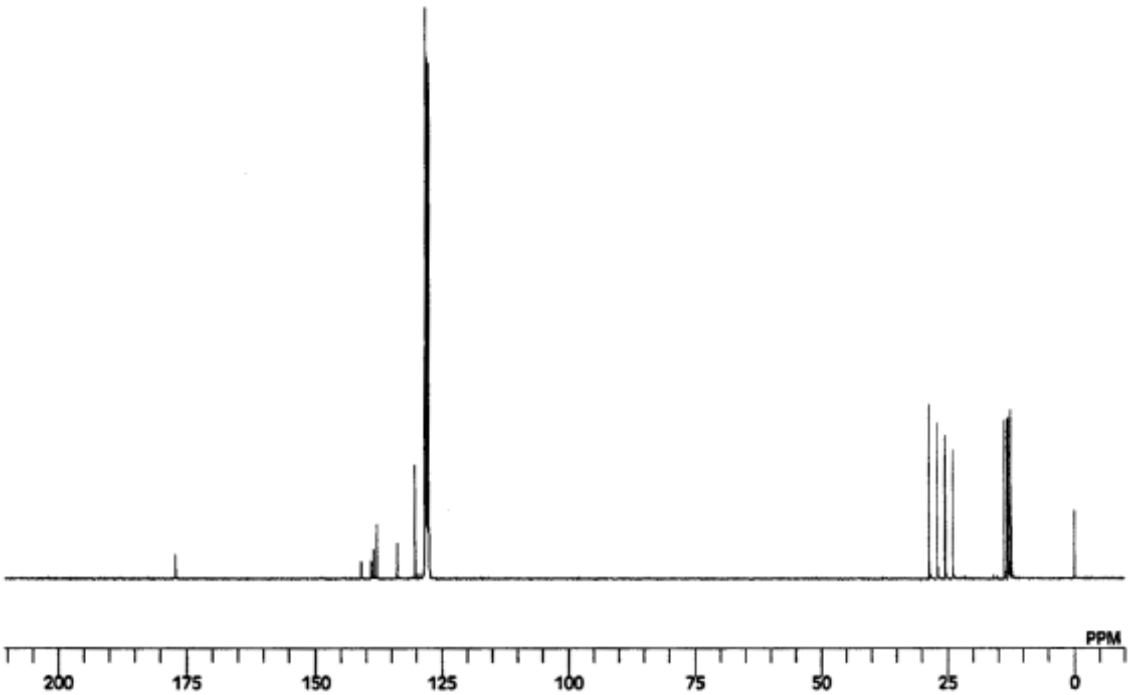
PPM
10
8
6
4
2
0

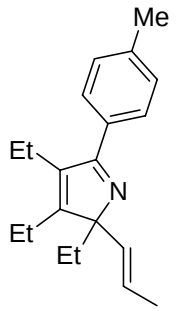

PPM
200
175
150
125
100
75
50
25
0



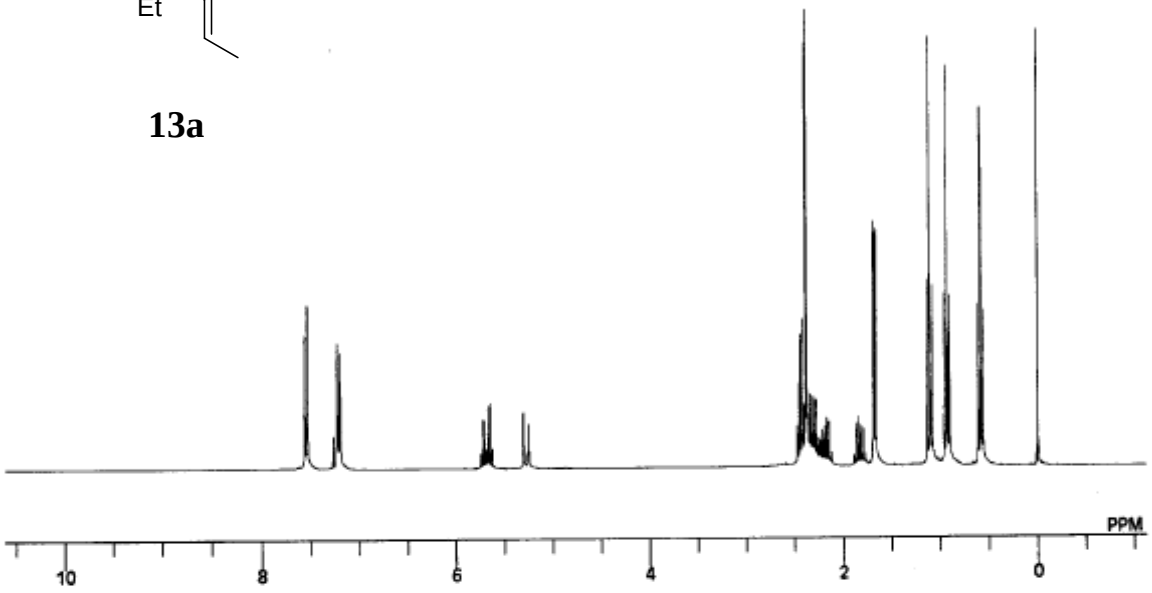
12c

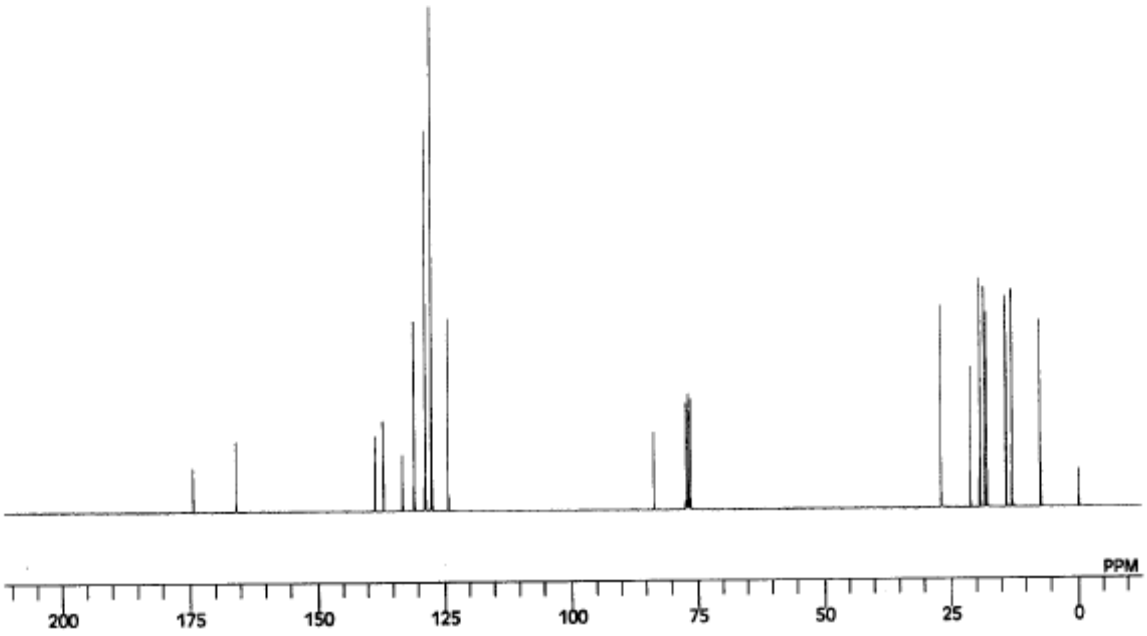


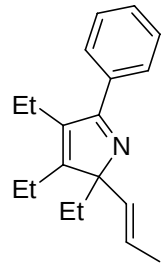




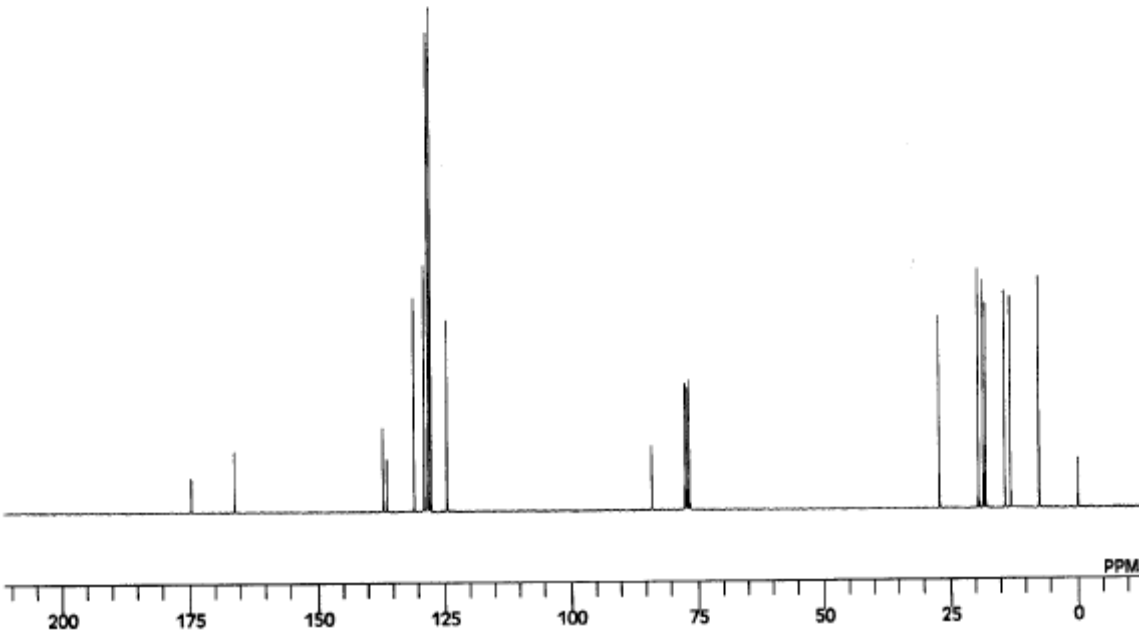
13a

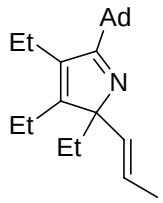




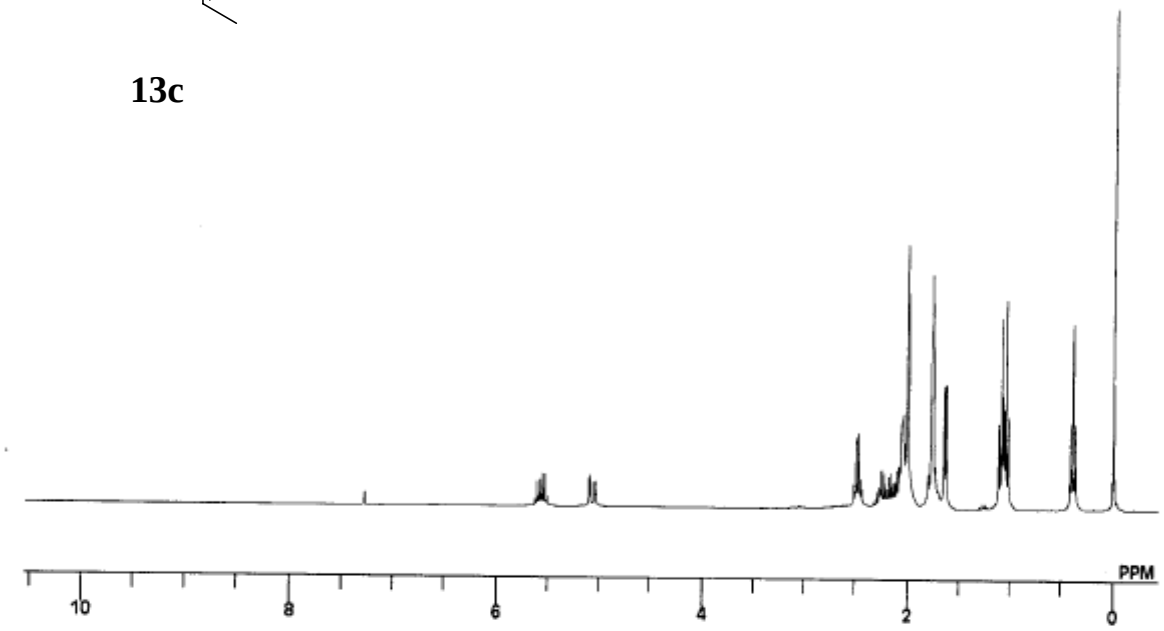


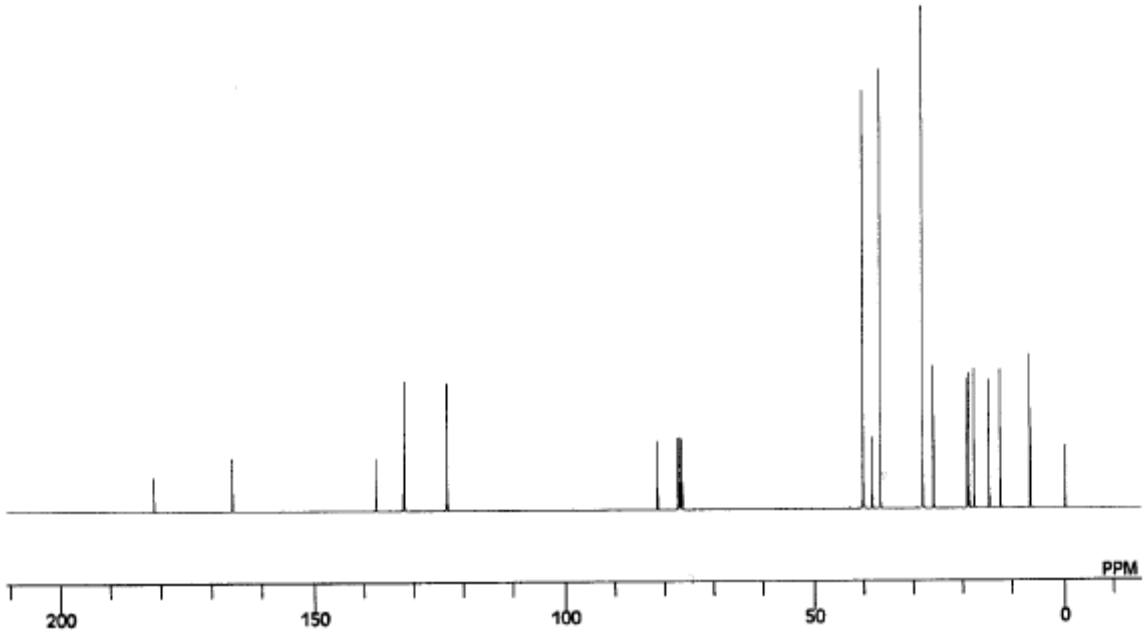
13b

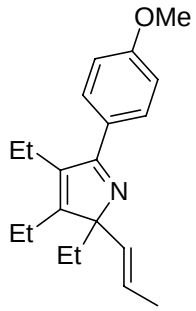




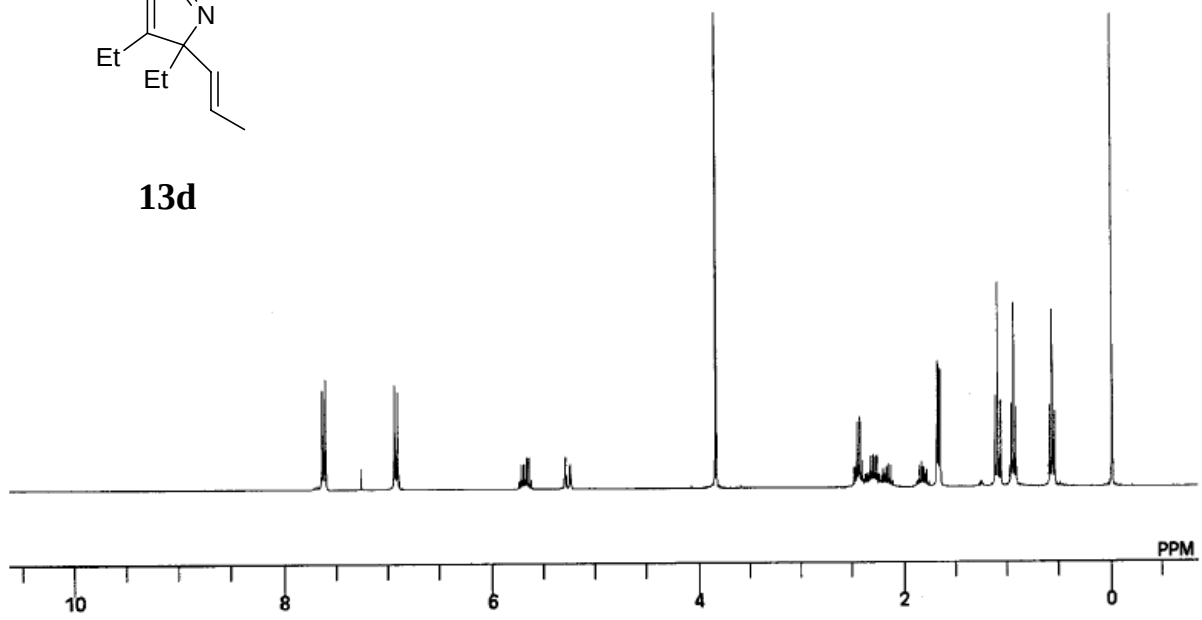
13c

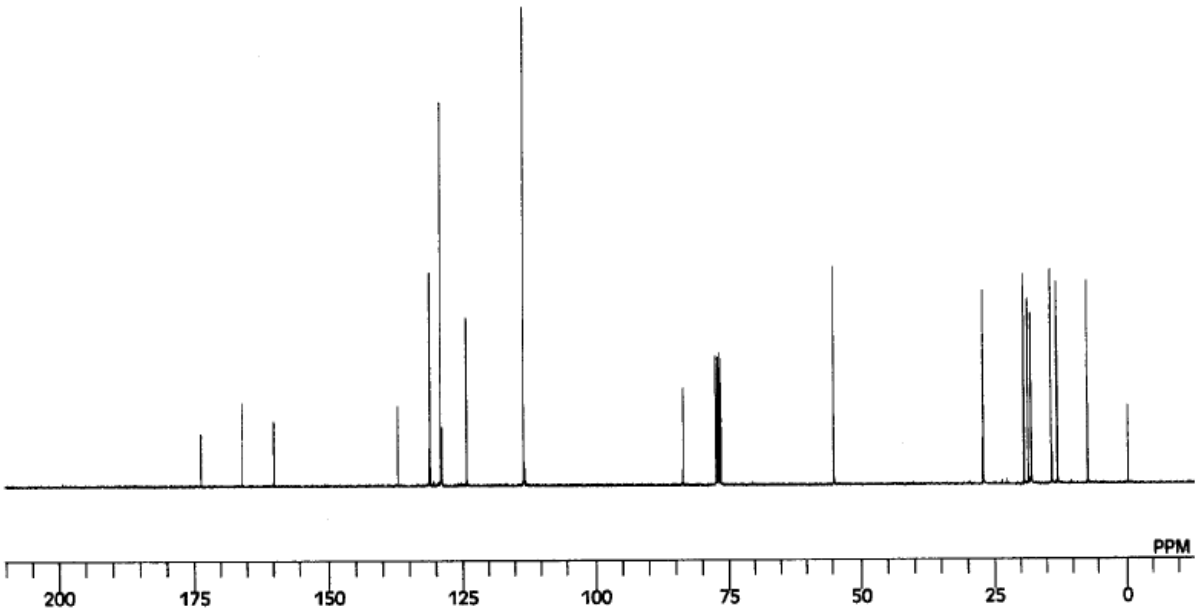


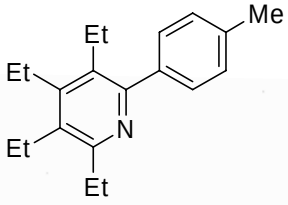




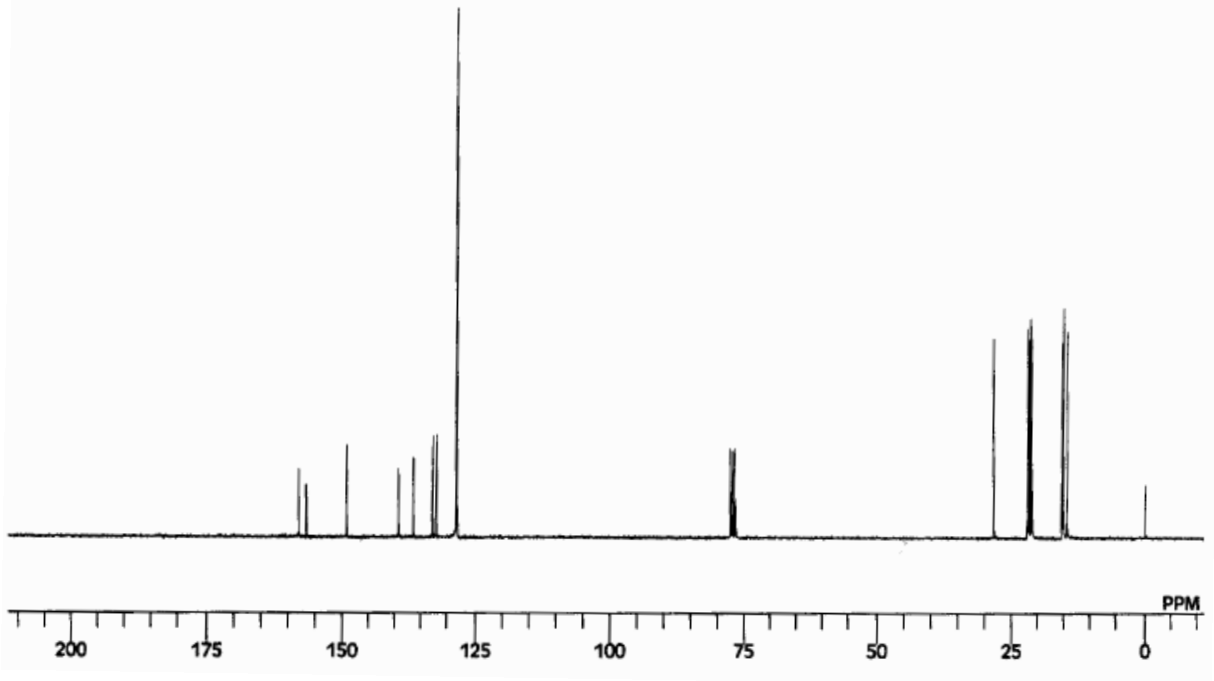
13d

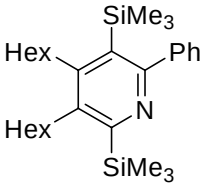




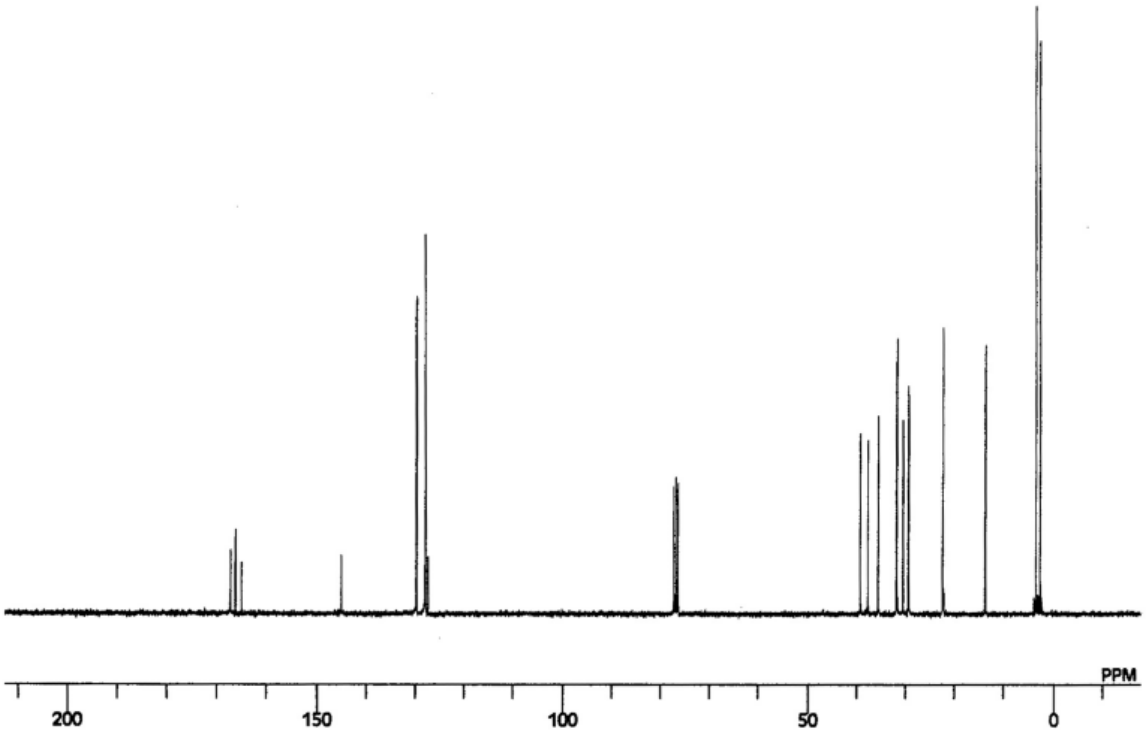


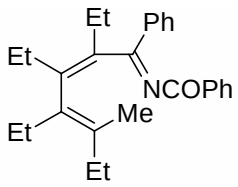
3d





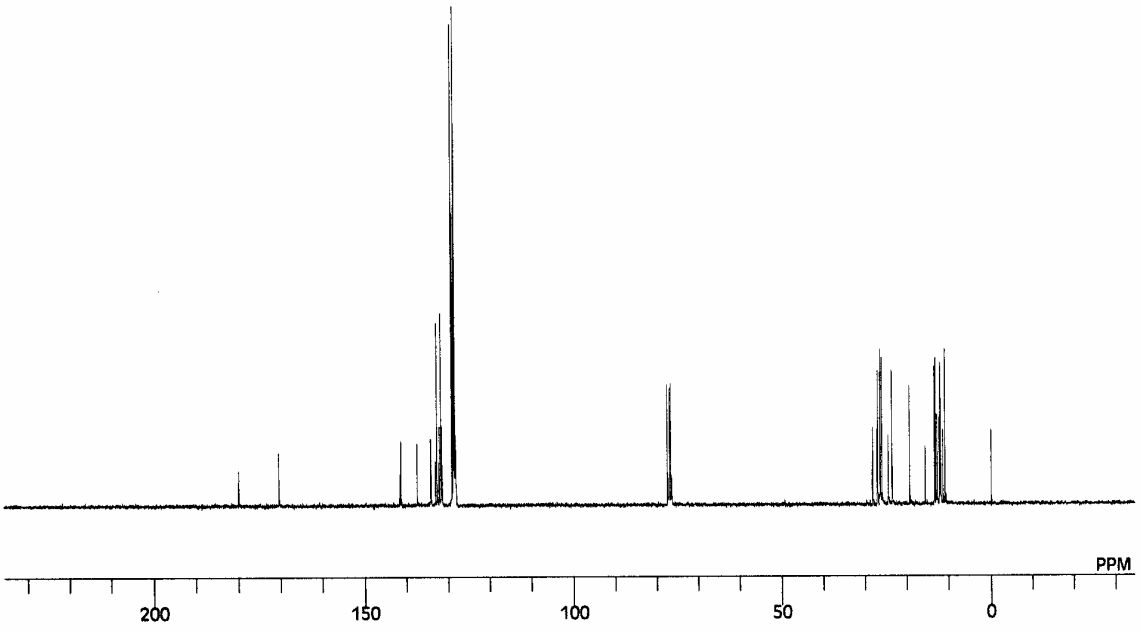
3f

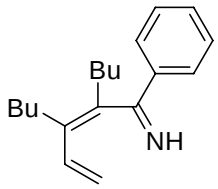



Et
Ph
Et
NCOPh
Me
Et
Et

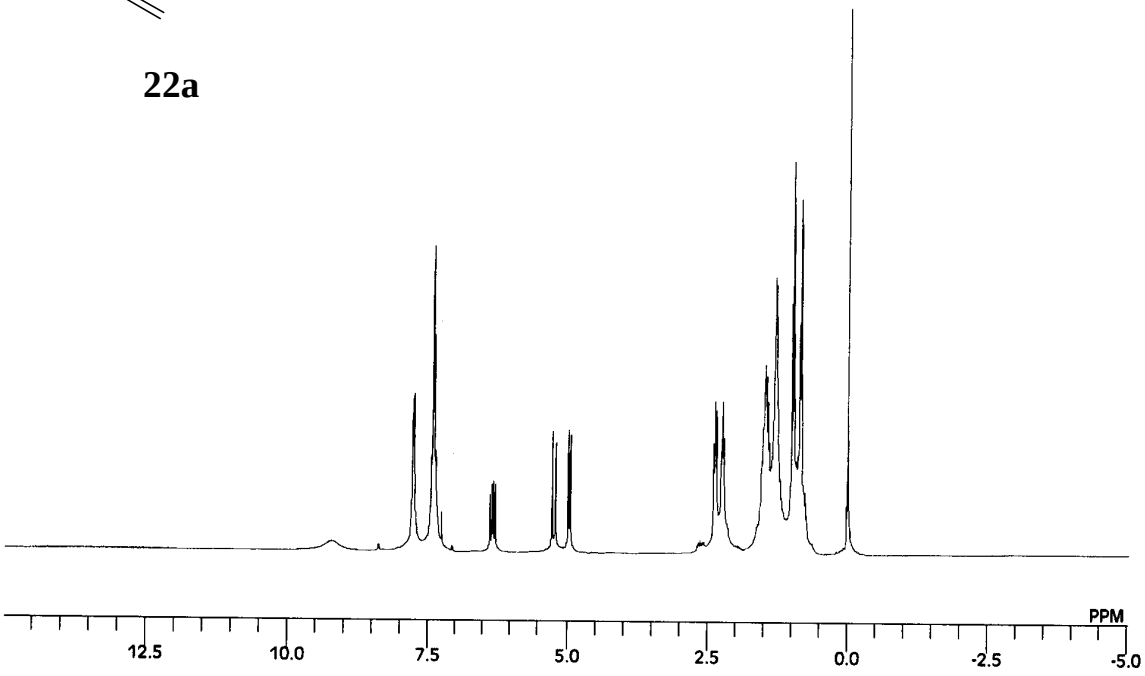
19

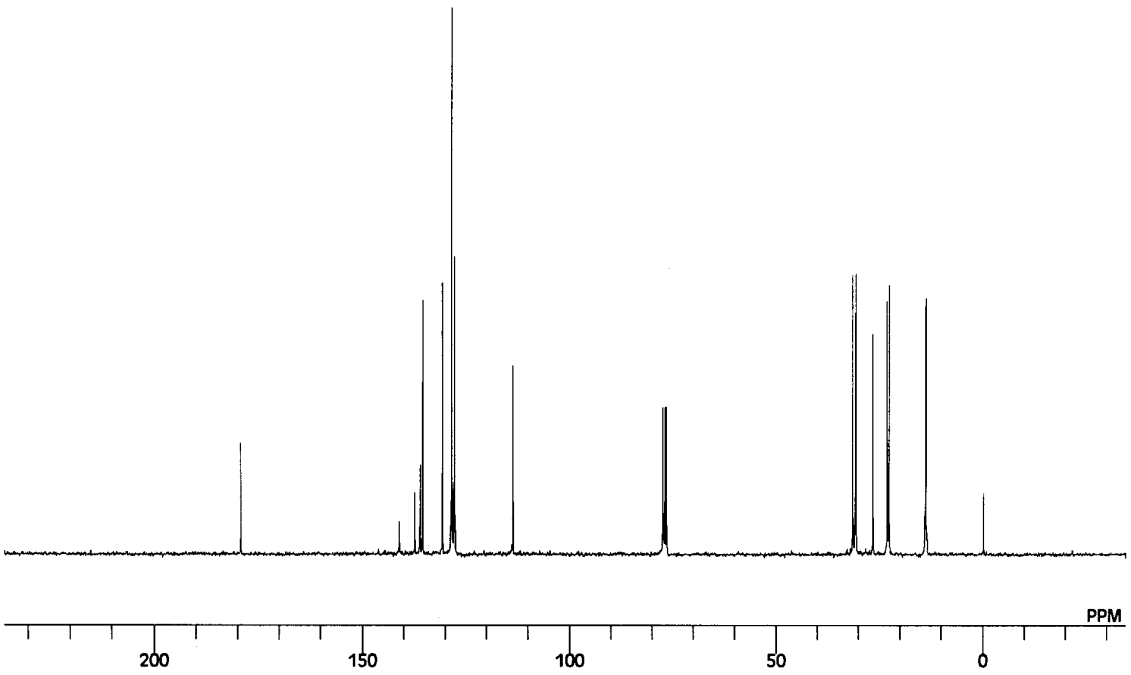
PPM
12.5
10.0
7.5
5.0
2.5
0.0
-2.5
-5.0

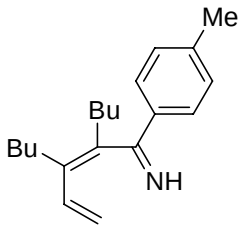

PPM
200
150
100
50
0



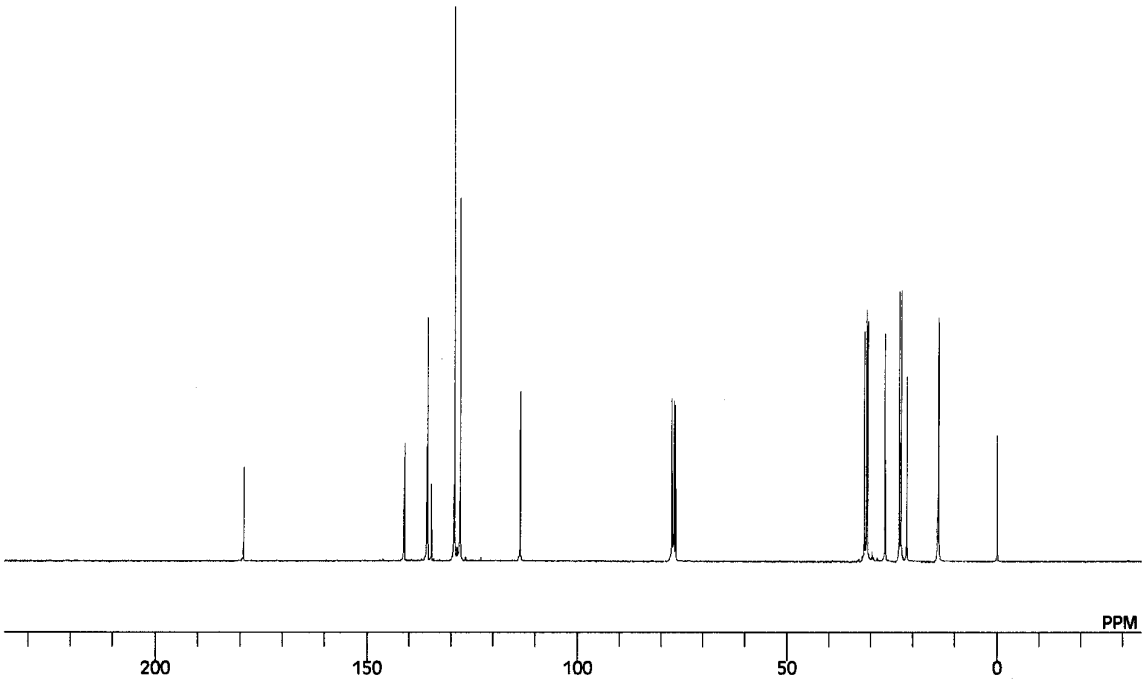
22a

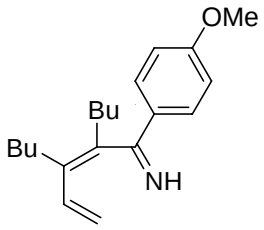




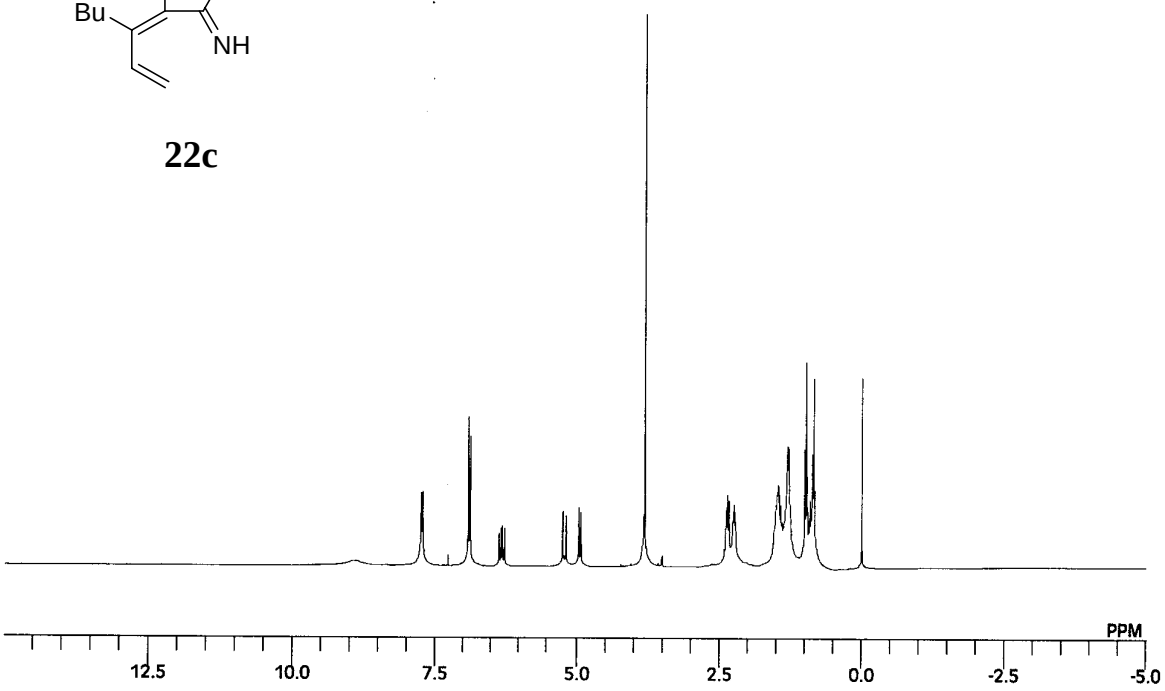


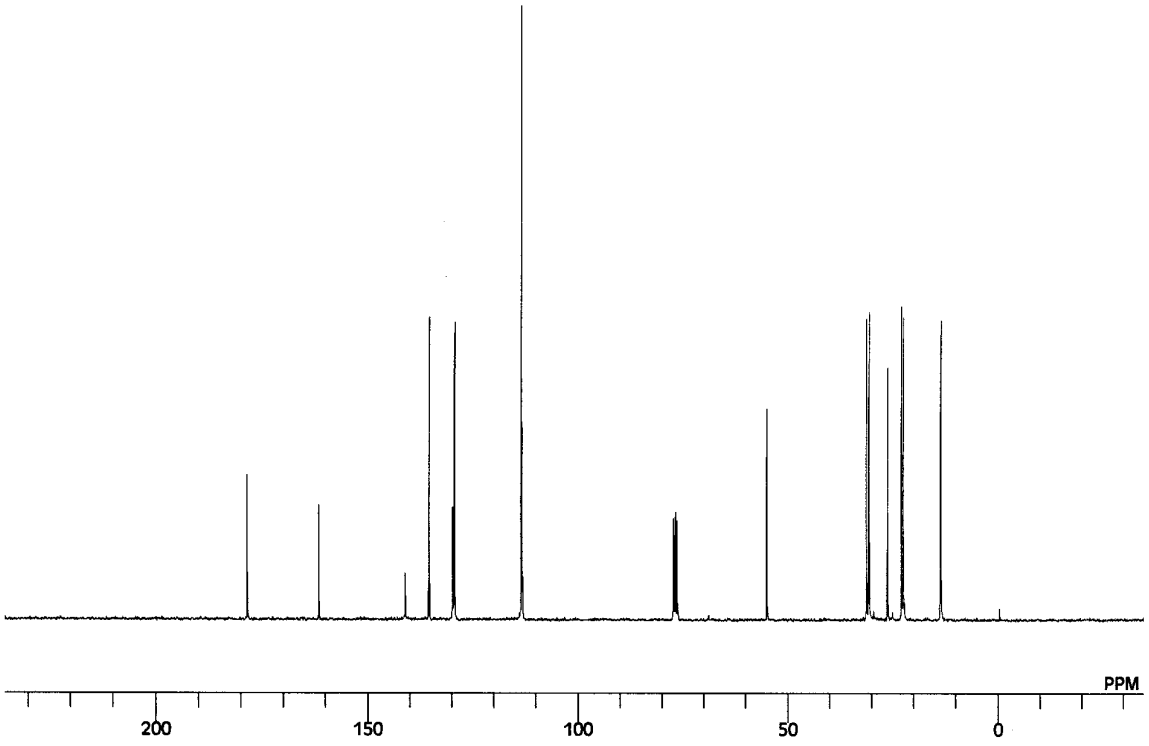
22b

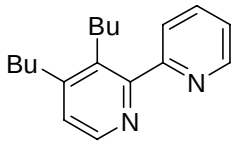




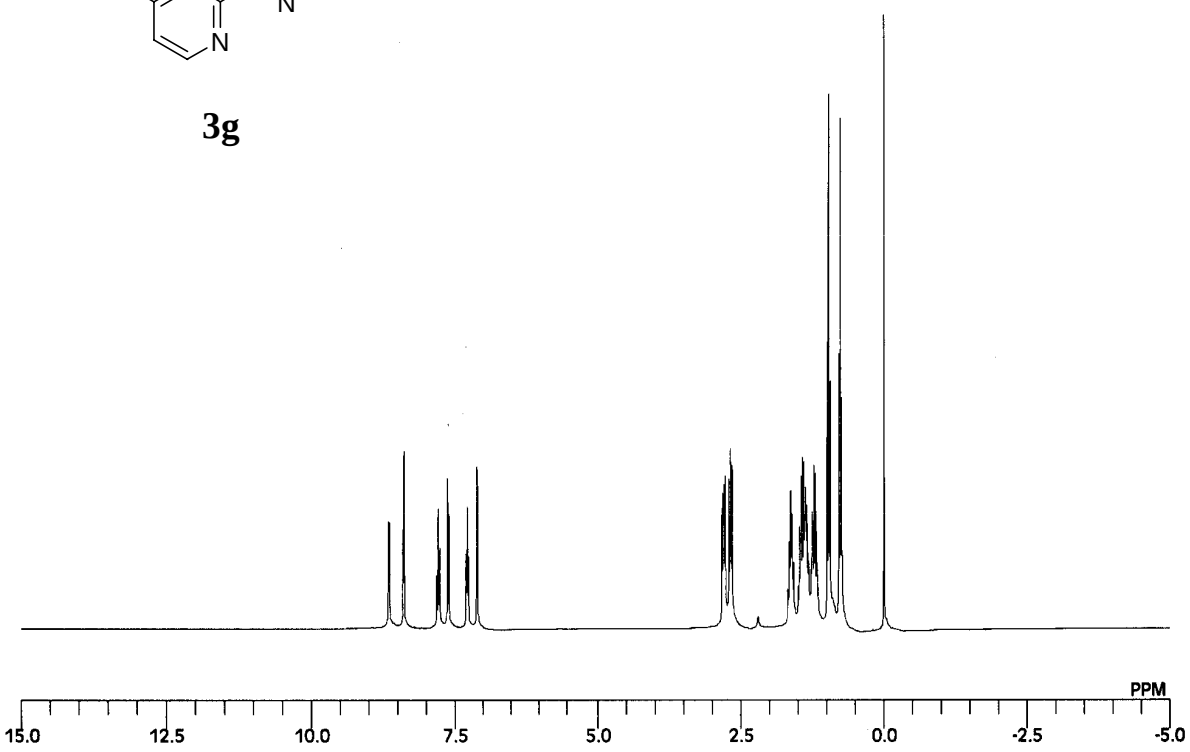
22c

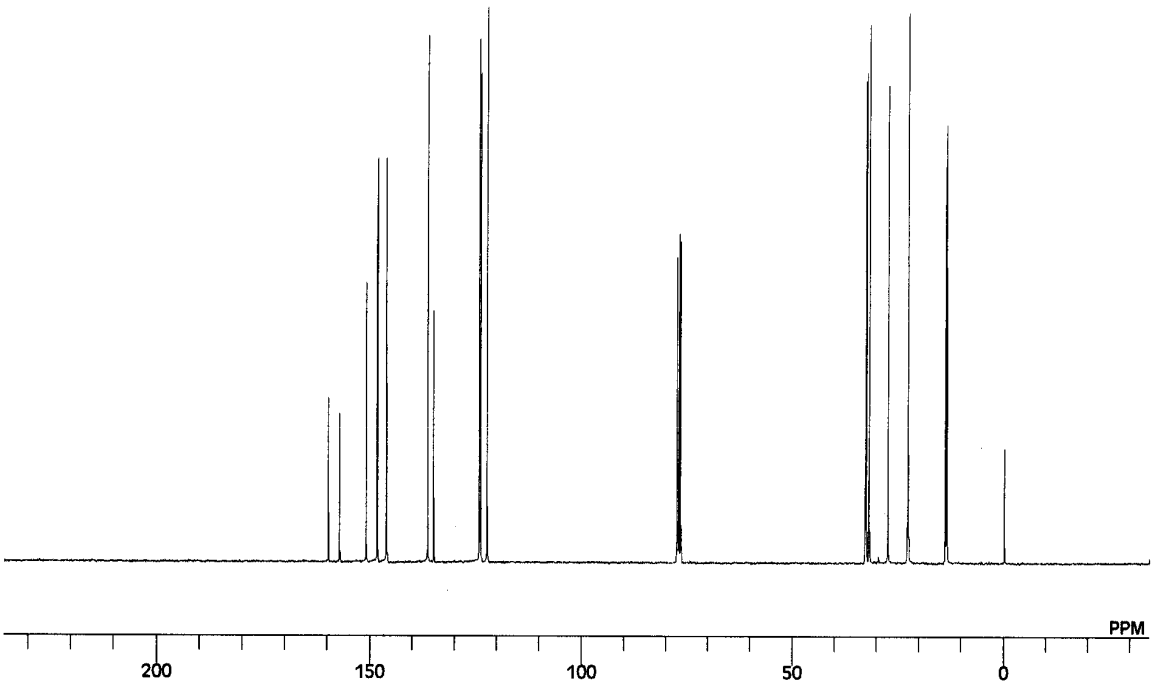


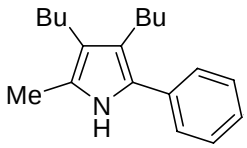




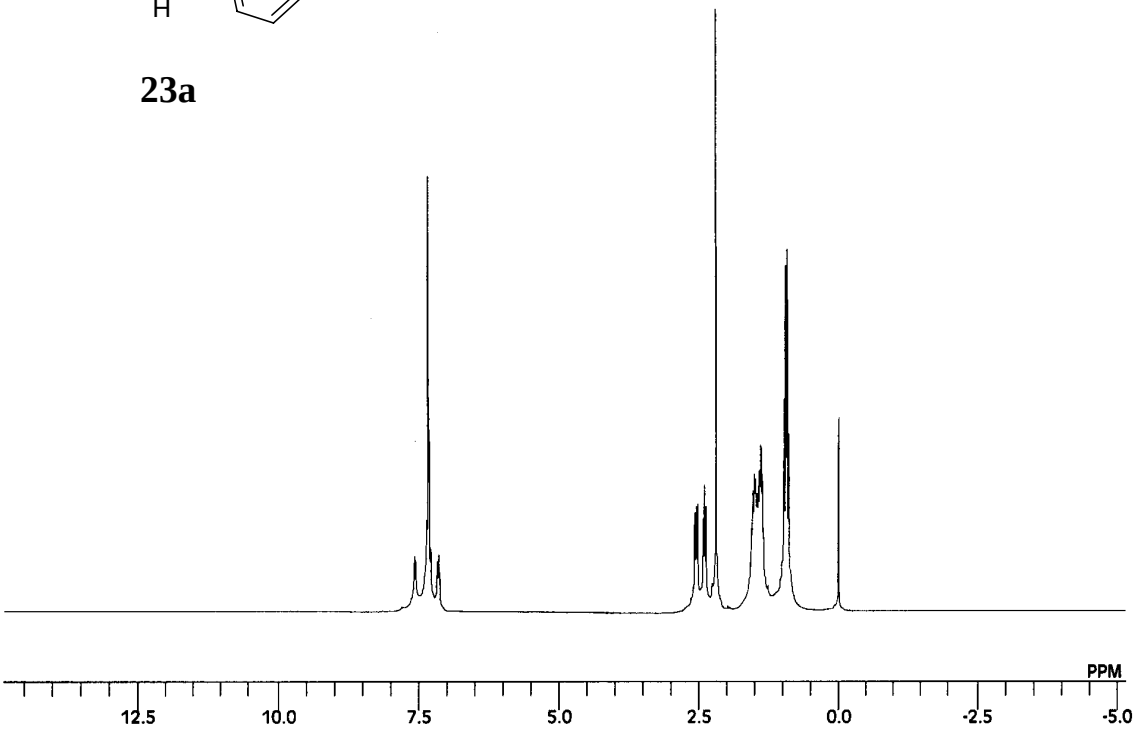
3g

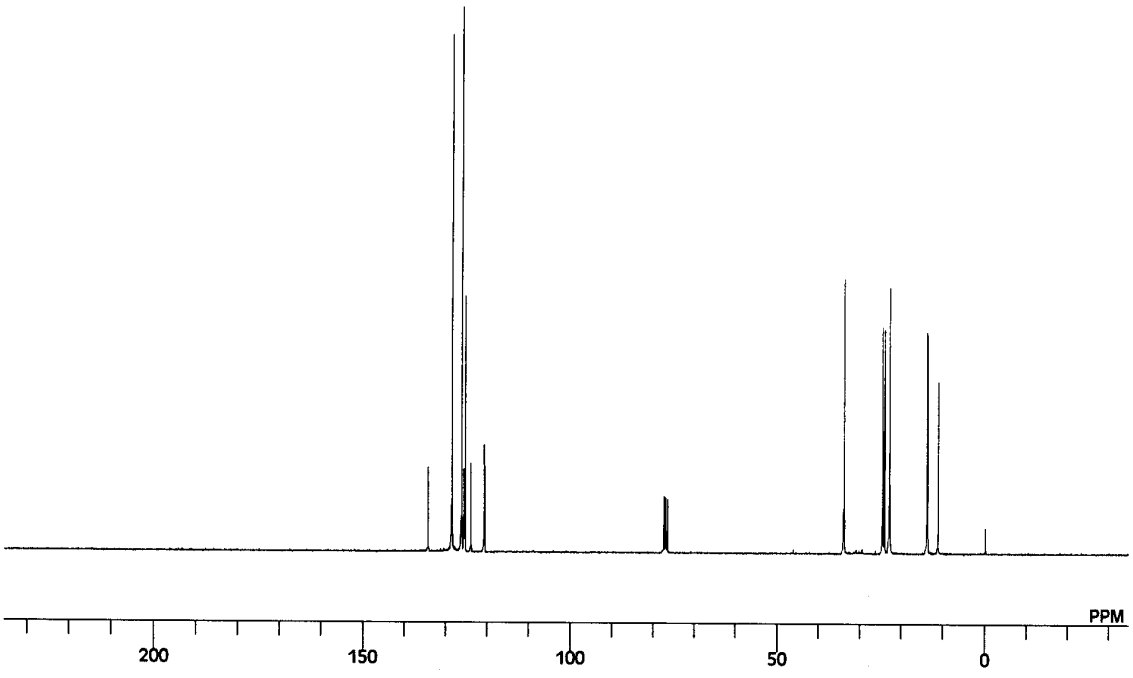


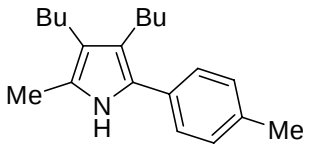




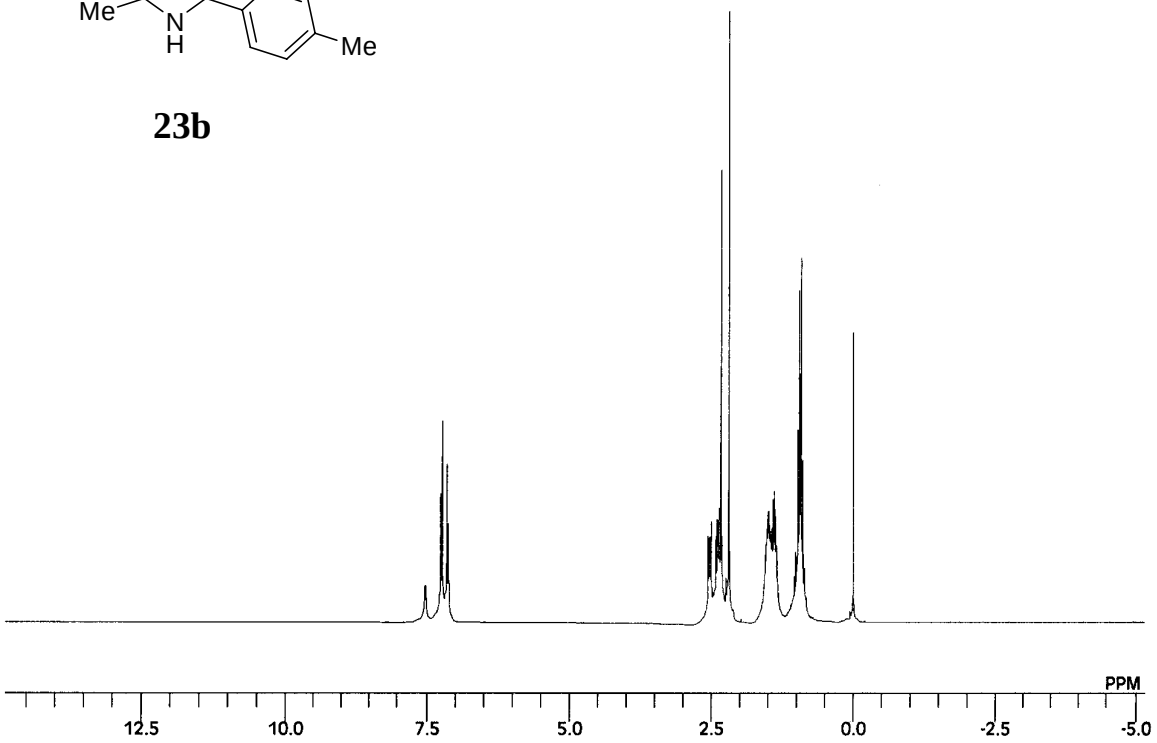
23a

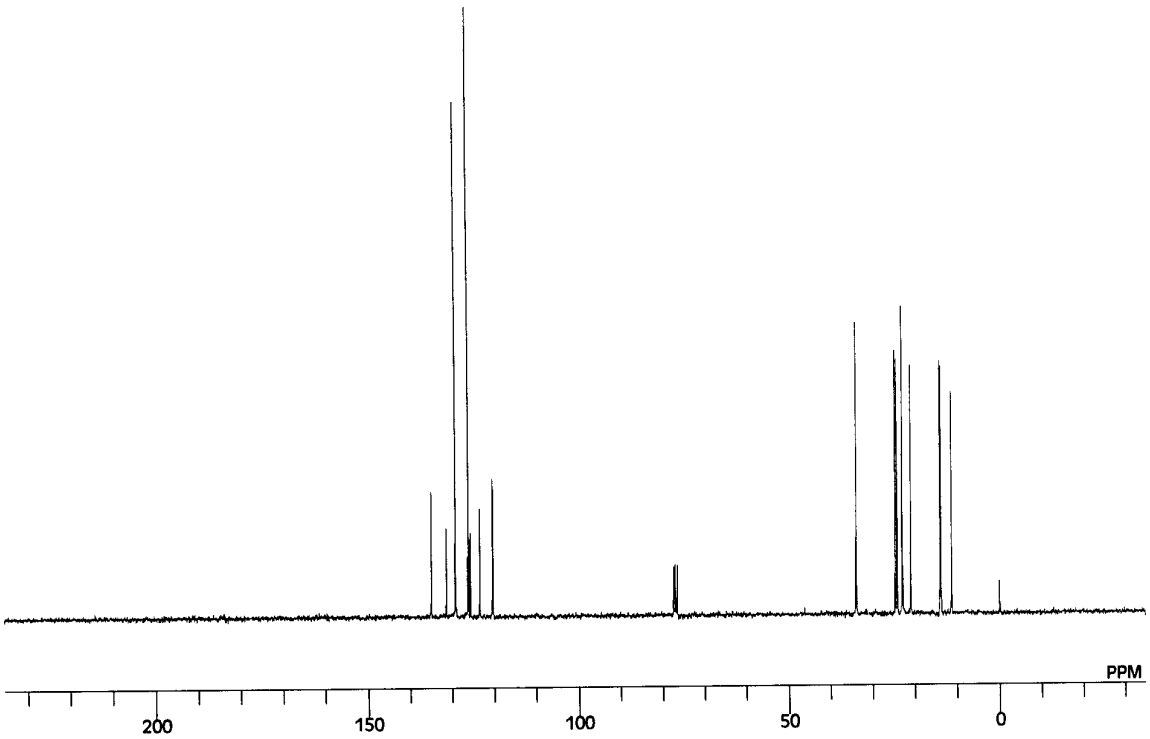


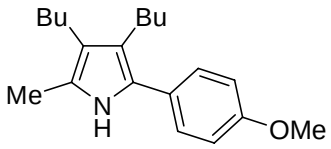




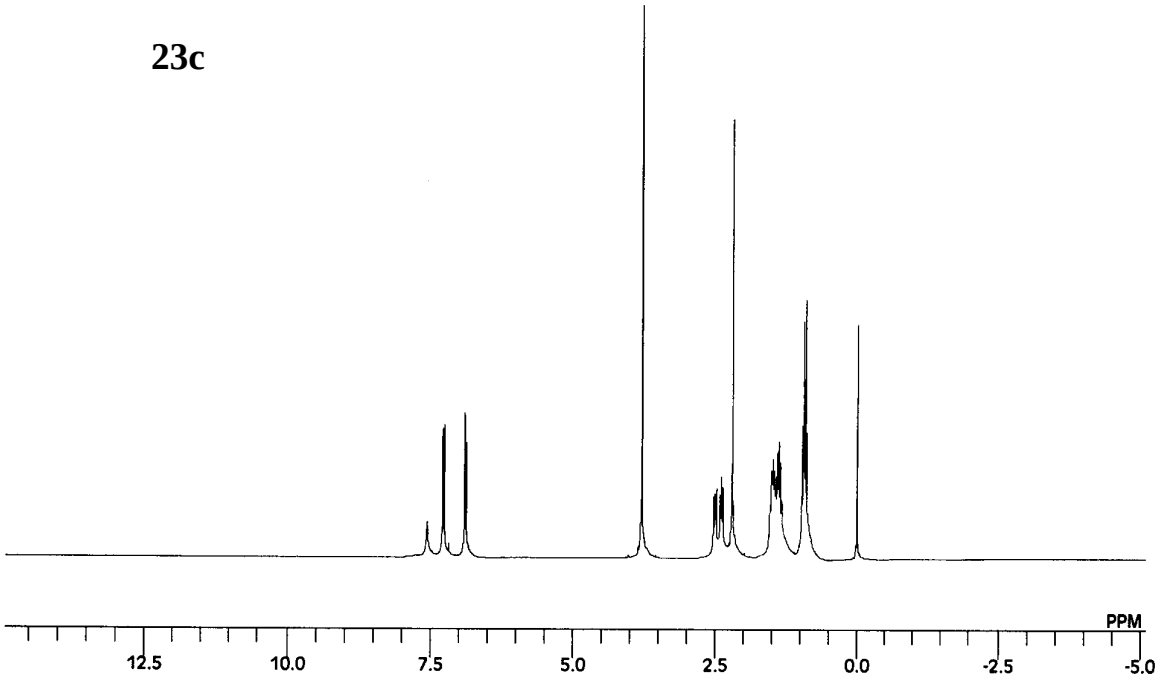
23b

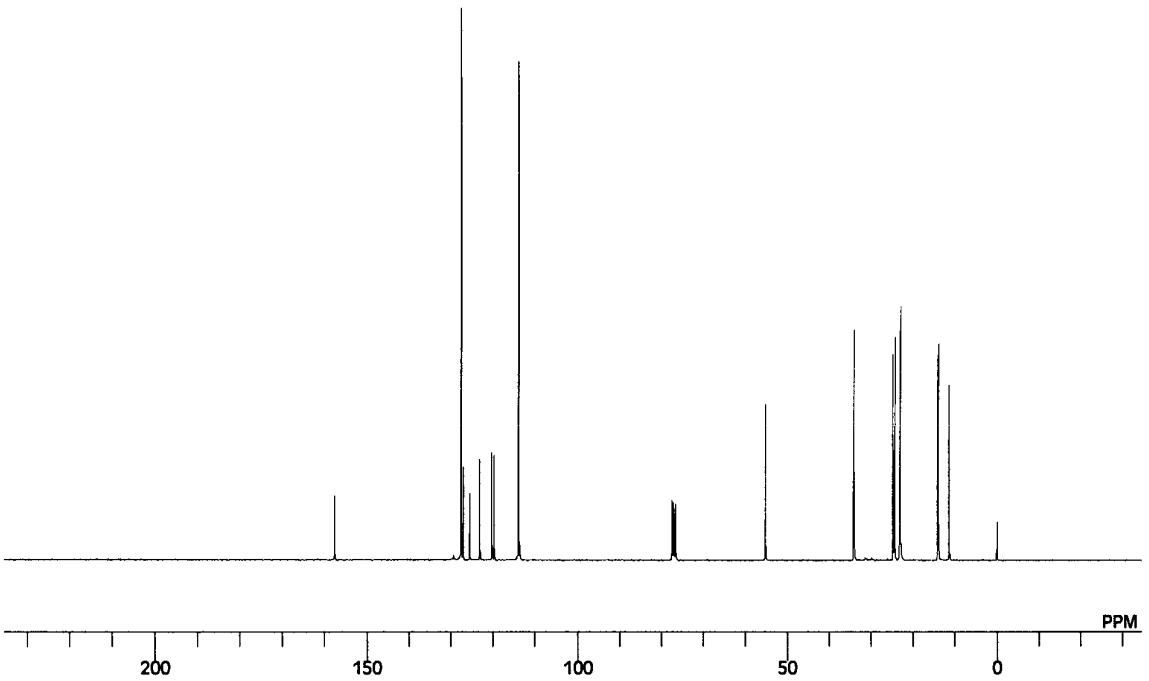


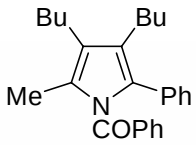




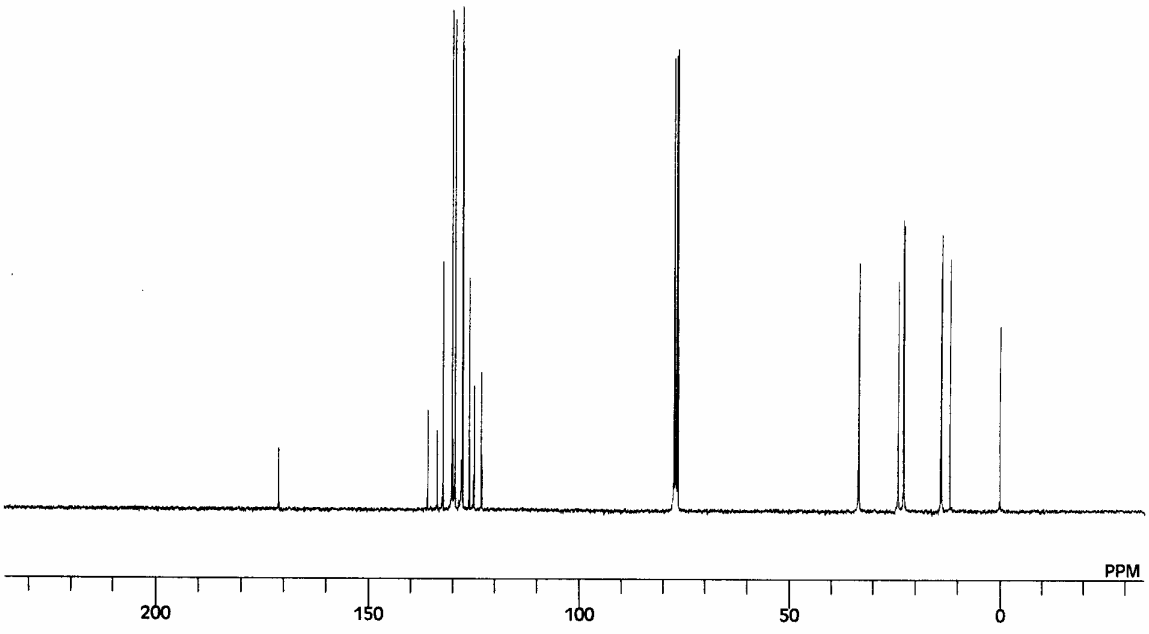
23c

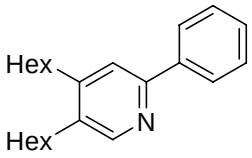




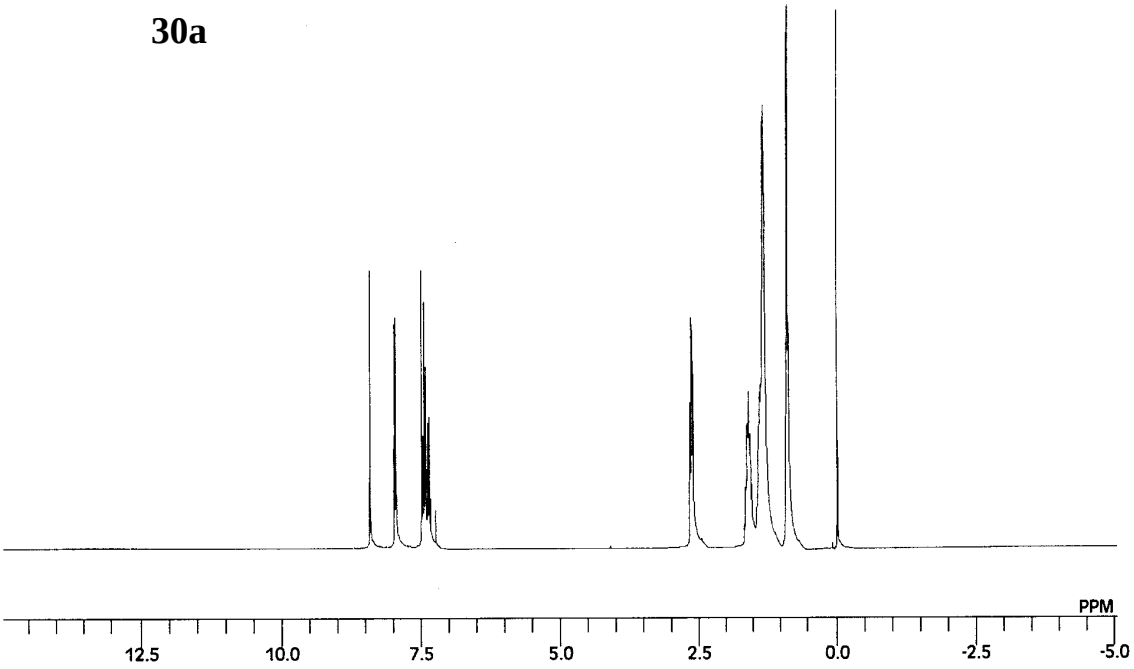


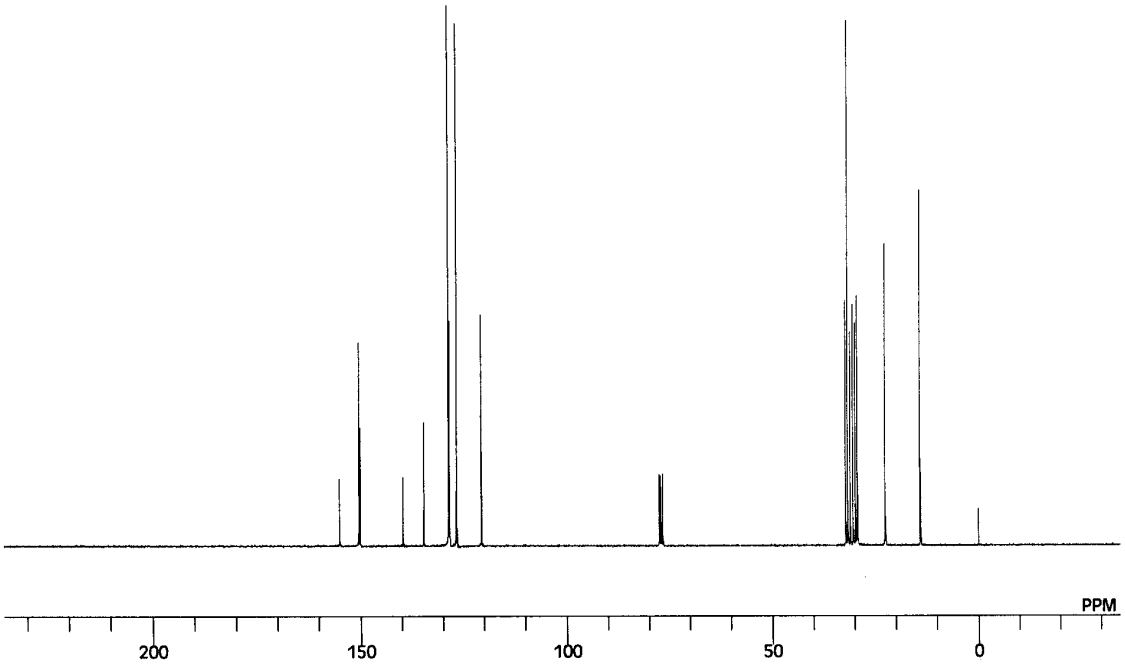
27

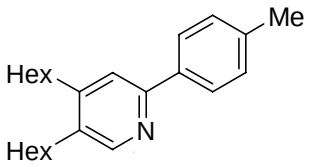




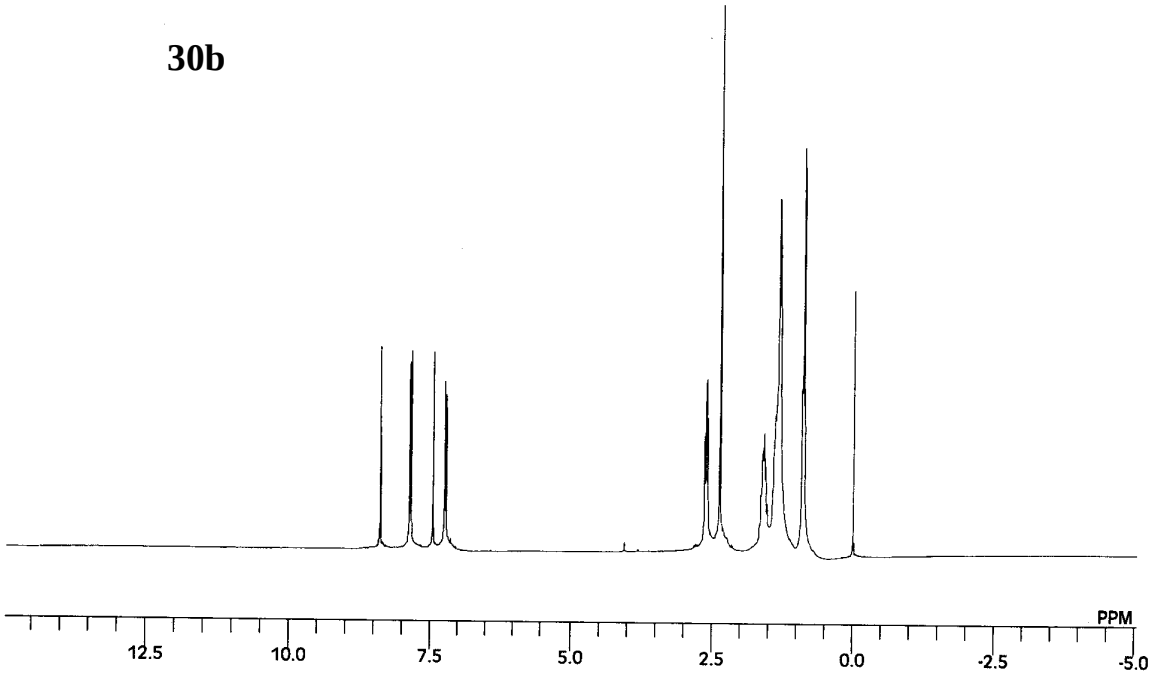
30a

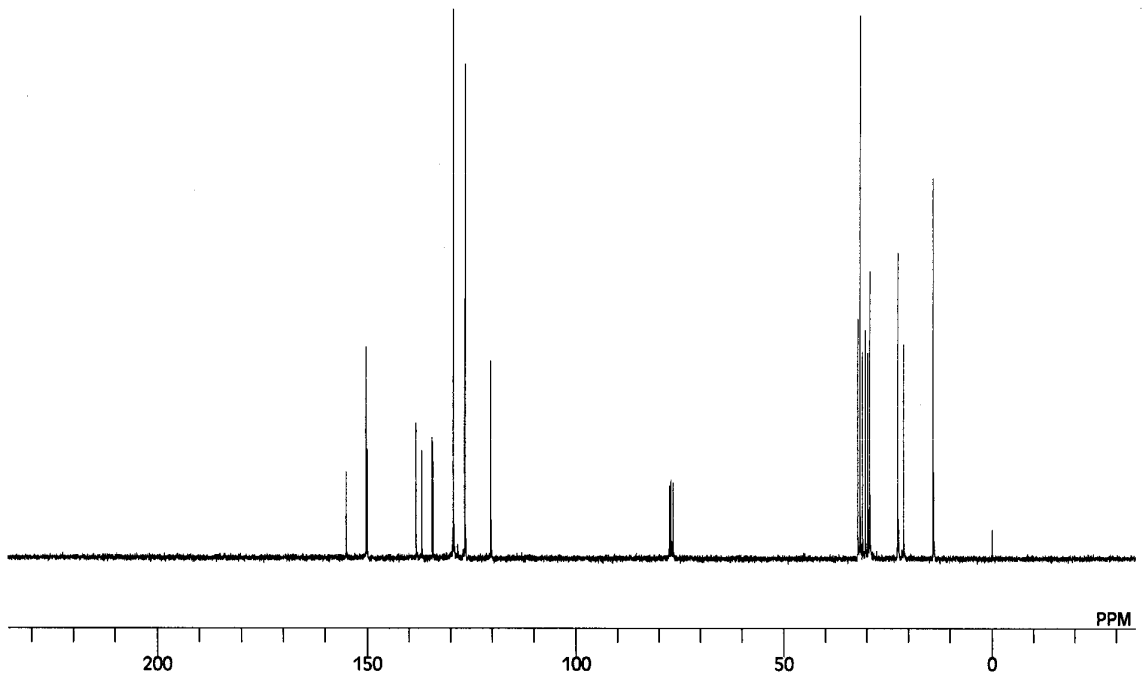


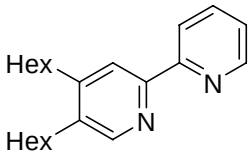




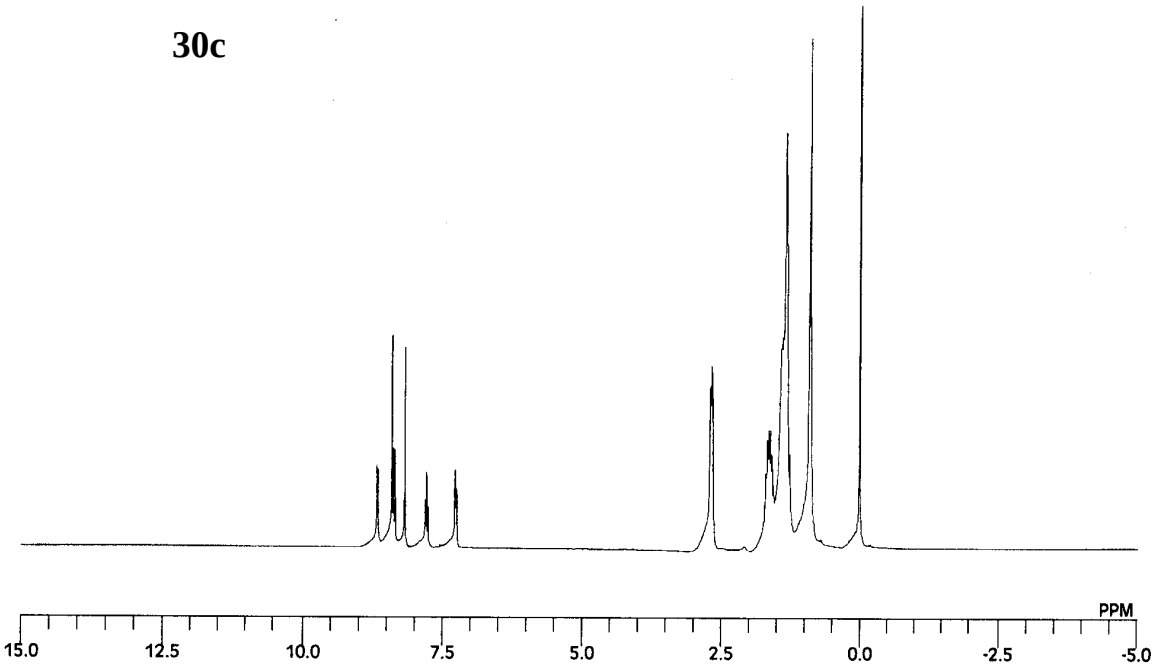
30b

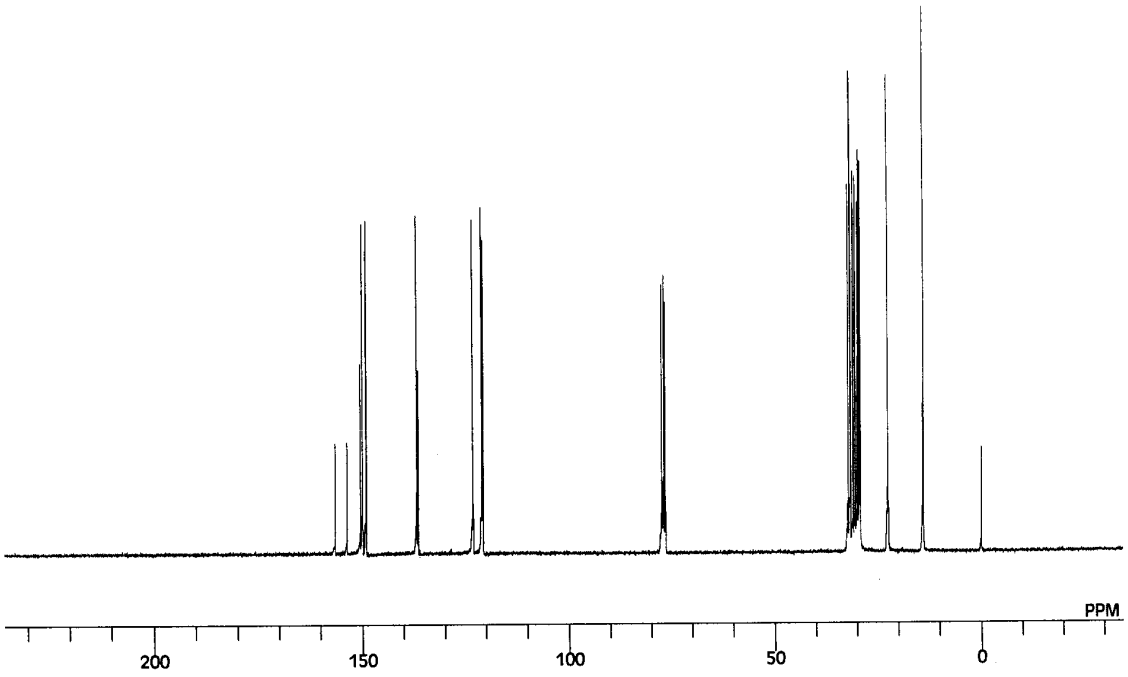


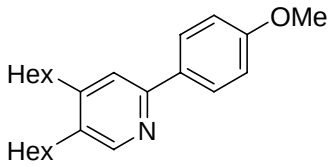




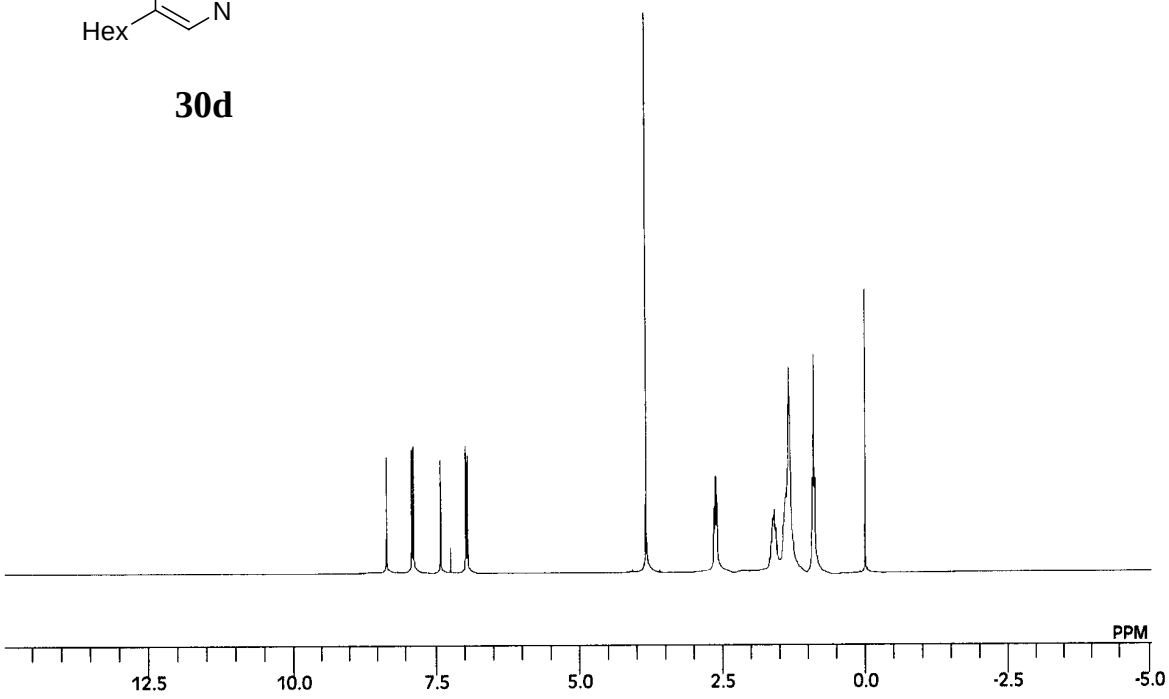
30c

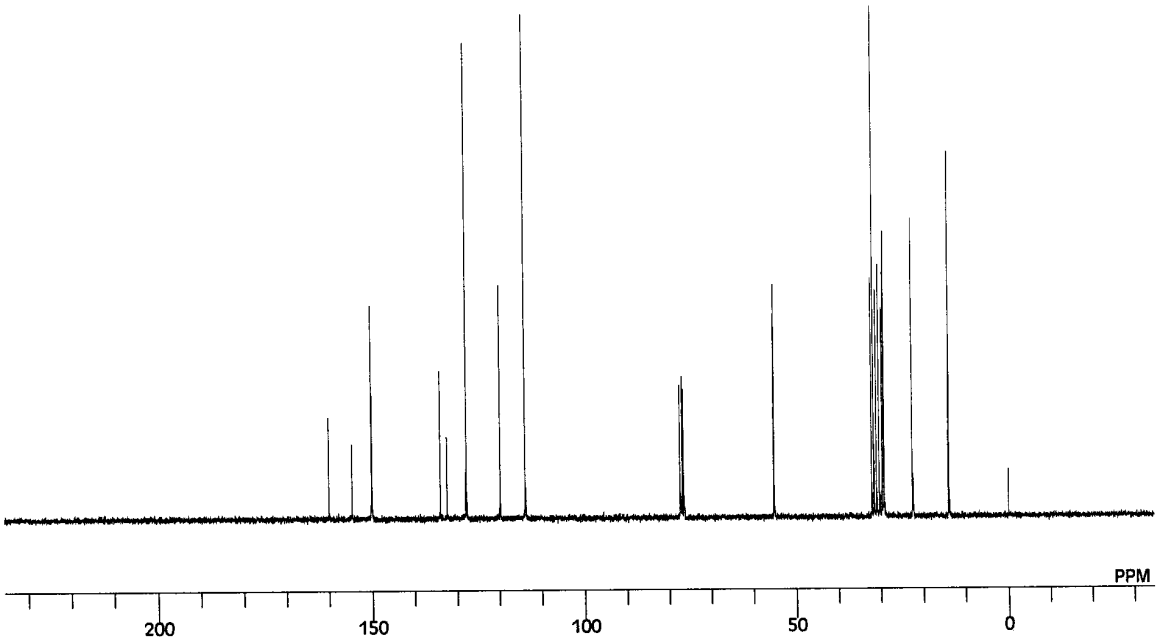






30d





2) General Experimental Methods and Characterization Data.

General. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. *t*-BuLi was obtained from Kanto Chemicals Co. Ltd.

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ unless stated otherwise. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector using a capillary column (CBP1-M25-25). GLC yields were determined using suitable hydrocarbons as internal standards.

Experimental procedures of **2a-c** and characterization data for **3a-c** have been described in Supplementary Information of Ref. 1.

12b. colorless liquid, isolated yield 87% (290 mg). ^{1}H NMR (C_6D_6, TMS): δ 0.82 (t, J = 7.8 Hz, 3H), 0.91-0.98 (m, 6H), 1.10 (t, J = 7.5 Hz, 3H), 1.87-2.40 (m, 8H), 3.23 (s, 3H), 6.75 (d, J = 9.0 Hz, 2H), 7.16 (s, 1H), 8.03 (d, J = 8.7 Hz, 2H). ^{13}C NMR (C_6D_6, TMS): δ 12.6, 13.1, 13.3, 14.0, 24.3, 25.6, 27.2, 28.8, 54.8, 113.8, 130.5, 130.9, 133.8, 138.0, 138.4, 140.9, 162.2, 176.8. HRMS calcd for $C_{20}H_{28}ON^{35}Cl$ 333.1859, found 333.1863.

12c. colorless liquid, isolated yield 91% (276 mg). ^{1}H NMR (C_6D_6, TMS): δ 0.77 (t, J = 7.5 Hz, 3H), 0.89-0.95 (m, 6H), 1.07 (t, J = 7.5 Hz, 3H), 1.78-2.36 (m, 8H), 7.13-8.00 (m, 6H). ^{13}C NMR (C_6D_6, TMS): δ 12.6, 13.1, 13.3, 13.9, 24.1, 25.5, 27.1, 28.8, 128.3, 128.5, 130.3, 133.9, 137.9, 138.5, 139.0, 140.9, 177.2. HRMS calcd for $C_{19}H_{26}N^{35}Cl$ 303.1754, found 303.1749.

3e.[2] colorless liquid, isolated yield 56% (150 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.99 (t, J = 7.5 Hz, 3H), 1.19-1.31 (m, 9H), 2.57 (q, J = 7.2 Hz, 2H), 2.71 (q, J = 7.5 Hz, 4H), 2.83 (q, J = 7.5 Hz, 2H), 7.33-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, TMS): δ 14.6, 15.3, 15.4, 15.5, 21.4, 21.7, 21.9, 28.3, 127.1, 127.9, 128.8, 132.4, 133.3, 142.3, 149.2, 156.6, 158.2.

13b. colorless liquid, isolated yield 19% (51 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.60 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H), 1.12 (t, J = 7.8 Hz, 3H), 1.68 (dd, J = 6.3, 1.5 Hz, 3H), 1.80-2.47 (m, 6H), 5.29 (dq, J = 15.3, 1.5 Hz, 1H), 5.70 (dq, J = 15.0, 6.3 Hz, 1H), 7.38-7.65 (m, 5H). ^{13}C NMR ($CDCl_3$, TMS): δ 7.6, 13.3, 14.4, 18.2, 18.6, 19.6, 27.2, 84.1, 124.5, 127.7, 128.2, 129.0, 131.0, 136.4, 137.1, 166.3, 174.7. HRMS calcd for $C_{19}H_{25}N$ 267.1987, found 267.1989.

13c. colorless liquid, isolated yield 67% (218 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.40 (t, J = 7.5 Hz, 3H), 1.03-1.12 (m, 9H), 1.64 (dd, J = 6.6, 1.8 Hz, 3H), 1.74-2.53 (m, 21H), 5.08 (dd, J = 15.3, 1.5 Hz, 1H), 5.57 (dq, J = 15.6, 6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ 6.9, 12.8, 15.1, 18.1, 19.1, 19.5, 26.2, 28.4, 36.9, 38.5, 40.3, 81.5, 123.6, 132.1, 137.7, 166.2, 181.6. HRMS calcd for $C_{23}H_{35}N$ 325.2770, found 325.2769.

13d. colorless liquid, isolated yield 40% (119 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.58 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.8 Hz, 3H), 1.11 (t, J = 7.8 Hz, 3H), 1.68 (dd, J = 6.3, 1.5 Hz, 3H), 1.79-2.49 (m, 6H), 3.84 (s, 3H), 5.27 (dq, J = 15.6, 1.8 Hz, 1H), 5.68 (dq, J = 15.3, 6.6 Hz, 1H), 6.92-6.95 (m, 2H), 7.62-7.64 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS): δ 7.5, 13.2, 14.3, 18.1, 18.7, 19.5, 27.1, 55.2, 83.7, 113.5, 124.3, 128.8, 129.1, 131.2, 137.1, 160.2, 166.1, 173.7. HRMS calcd for $C_{20}H_{27}NO$ 297.2093, found 297.2098.

22b. colorless liquid, isolated yield 65% (184 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.83-1.01 (m, 6H), 1.26-1.51 (m, 8H), 2.22-2.38 (m, 7H), 4.94-4.98 (m, 1H), 5.21-5.26 (m, 1H), 6.28-6.38 (m, 1H), 7.19-7.21 (m, 2H), 7.65-7.67 (m, 2H), 9.09 (br, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ 13.9, 14.0, 21.5, 22.8, 23.2, 26.6, 30.8, 31.0, 31.6, 113.6, 127.9, 129.2, 134.7, 135.6, 135.9, 141.1, 141.3, 179.2. HRMS calcd for $C_{20}H_{29}N$ 283.2300, found 283.2293.

22c. colorless liquid, isolated yield 62% (186 mg). ^{1}H NMR ($CDCl_3$, TMS): δ 0.83-1.01 (m, 6H), 1.30-1.54 (m, 8H), 2.23-2.39 (m, 4H), 3.83 (s, 3H), 4.94-4.98 (m, 1H), 5.20-5.26 (m, 1H), 6.28-6.38 (m, 1H), 6.89-6.92 (m, 2H), 7.72-7.75 (m, 2H), 8.91 (br, 1H). ^{13}C NMR

($CDCl_3$, TMS): δ 13.8, 13.9, 22.8, 23.1, 26.5, 30.8, 31.0, 31.5, 55.2, 113.4, 113.7, 129.5, 130.0, 135.5, 135.6, 141.2, 161.7, 178.5. HRMS calcd for $C_{20}H_{29}NO$ 299.2249, found 299.2236.

23b. colorless liquid, isolated yield 71% (201 mg). ^1H NMR ($CDCl_3$, TMS): δ 0.85-1.04 (m, 6H), 1.31-1.57 (m, 8H), 2.19 (s, 3H), 2.33-2.56 (m, 7H), 7.13－7.26 (m, 4H), 7.53 (br, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ 11.4, 14.0, 14.1, 21.1, 23.0, 23.1, 24.3, 24.6, 34.0, 34.1, 120.3, 120.5, 123.5, 125.8, 126.2, 129.3, 131.5, 135.0. HRMS calcd for $C_{20}H_{29}N$ 283.2300, found 283.2296.

23c. colorless liquid, isolated yield 65% (194 mg). ^1H NMR ($CDCl_3$, TMS): δ 0.89-0.97 (m, 6H), 1.31-1.56 (m, 8H), 2.20 (s, 3H), 2.37-2.42 (m, 2H), 2.48-2.53 (m, 2H), 3.79 (s, 3H), 6.88-6.91 (m, 2H), 7.27-7.30 (m, 2H), 7.57 (br, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ 11.4, 14.0, 14.1, 23.0, 23.1, 24.3, 24.7, 34.0, 34.1, 55.2, 114.0, 119.8, 120.3, 123.2, 125.7, 127.2, 127.7, 157.7. HRMS calcd for $C_{20}H_{29}NO$ 299.2249, found 299.2250.

30b. colorless liquid, isolated yield 62% (209 mg). ^1H NMR ($CDCl_3$, TMS): δ 0.87-0.92 (m, 6H), 1.32-1.67 (m, 16H), 2.37 (s, 3H), 2.59-2.65 (m, 4H), 7.23-7.25 (m, 2H), 7.46 (s, 1H), 7.85-7.88 (m, 2H), 8.39 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ 14.1, 21.2, 22.62, 22.64, 29.3, 29.4, 29.8, 30.4, 31.1, 31.7, 32.2, 120.3, 126.5, 129.3, 134.3, 136.9, 138.3, 149.9, 150.2, 155.0. HRMS calcd for $C_{24}H_{35}N$ 337.2770, found 337.2768.

30c. colorless liquid, isolated yield 53%(172 mg). ^1H NMR ($CDCl_3$, TMS): δ 0.87-0.92 (m, 6H), 1.26-1.71 (m, 16H), 2.64-2.71 (m, 4H), 7.24-7.28 (m, 1H), 7.75-7.81 (m, 1H), 8.18 (br, 1H), 8.35-8.41 (m, 2H), 8.65-8.68 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ 14.1, 22.60, 22.62, 29.3, 29.5, 30.0, 30.5, 31.0, 31.7, 32.3, 120.8, 121.1, 123.3, 136.5, 136.8, 149.1, 150.0, 150.5, 153.7, 156.6. HRMS calcd for $C_{22}H_{32}N_2$ 324.2566, found 324.2570.

30d. colorless liquid, isolated yield 51%(180 mg). ^1H NMR ($CDCl_3$, TMS): δ 0.88-0.92

(m, 6H), 1.33-1.63 (m, 16H), 2.59-2.65 (m, 4H), 3.84 (s, 3H), 6.96-6.99 (m, 2H), 7.43 (s, 1H), 7.89-7.93 (m, 2H), 8.37 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ 14.1, 22.61, 22.64, 29.3, 29.4, 29.8, 30.4, 31.1, 31.7, 32.2, 55.3, 114.0, 120.0, 127.9, 132.4, 134.0, 150.0, 150.2, 154.7, 160.1. HRMS calcd for $C_{24}H_{35}NO$ 353.2719, found 353.2718.

References:

(1) Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc*. **2002**, *124*, 6238-6239.

(2) McCormick, M. M.; Duong, H. A.; Zuo, G.; Louie, J. *J. Am. Chem. Soc*. **2005**, *127*, 5030-5031.