Supporting Information:

Lewis Acid Promoted Dual Bond Formation: Facile Synthesis of Dihydrocoumarins & Spiro-Tetracyclic Dihydrocoumarins

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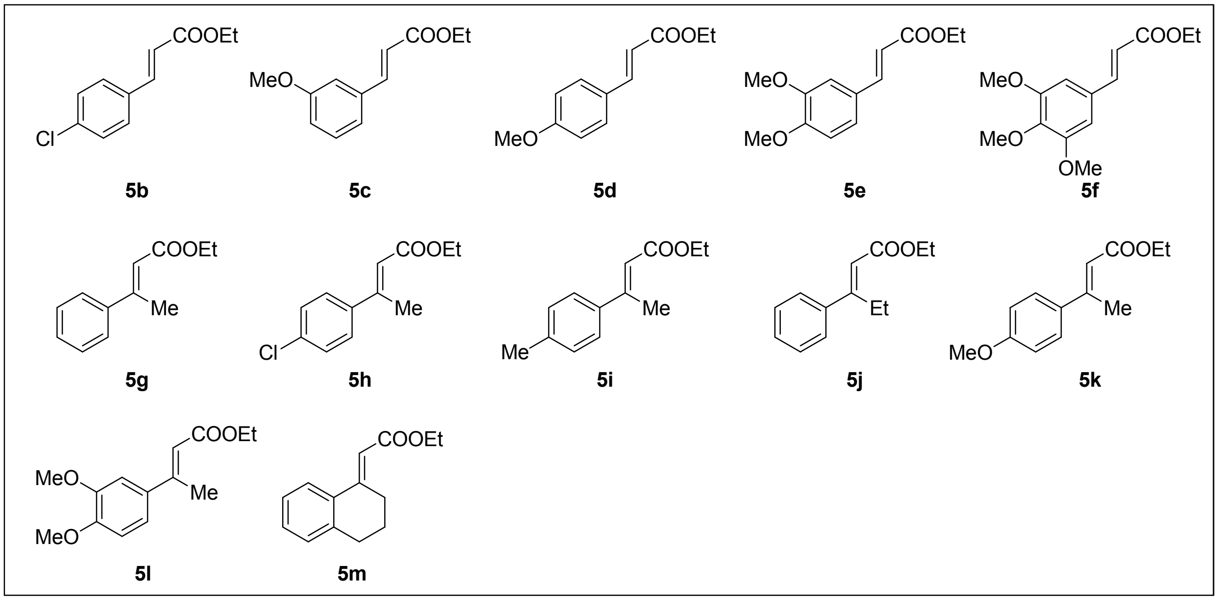
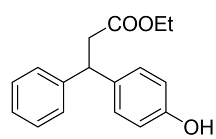
Spectral data for the known compounds S2-S6
^{1}H-NMR and ^{13}C-NMR spectra for all new and known compounds S7-S49

Ethyl cinnamate **5a** is commercially available and the other following cinnamate esters **5b**,[1] **5c**,[2] **5d**,[3] **5e**,[4] **5f**,[4] **5g**,[5] **5h**,[5] **5i**[6] and **5j**[5] are known in the literature.



The following Michael addition ester product **8a**[7] is known in literature



8a

The following 4-aryl-3,4-dihydrocoumarins **7a**,[8] **7b**,[9] **7c**,[7] **7d**,[10] **7f**,[11] **7g**,[4] and **7h**[12] are known in the literature.

[1]M. Tani, S. Sakaguchi and Y. Ishii, *J. Org. Chem*., 2004, **69**, 1221–1226

[2]A. Kubota, M. H. Emmert and M. S. Sanford, *Org. Lett*., 2012, **14**, 1760–1763

[3]T. Hashimoto, T. Shiomi, J. Ito and H. Nishiyama, *Tetrahedron,* 2007, **63**, 12883–12887

[4]S. Aoki, C. Amamoto, J. Oyamada and T. Kitamura, *Tetrahedron,* 2005, **61**, 9291–9297

[5]B. V. Ramulu, A. G. K. Reddy and G. Satyanarayana, *Synlett*, 2013, **24**, 863–872

[6] D. A. Evans, G. C. Andrews, T. T. Fujimoto and D. Wells, *Tetrahedron Lett*., 1973, **16**, 1389–1392

[7] F. Song, S. Lu, J. Gunnet, J. Z. Xu, P. Wines, J. Proost, Y. Liang, C. Baumann, J. Lenhard, W. V. Murray, K. T. Demarest and G.-H. Kuo, *J. Med. Chem.,* 2007, **50***,* 2807–2817

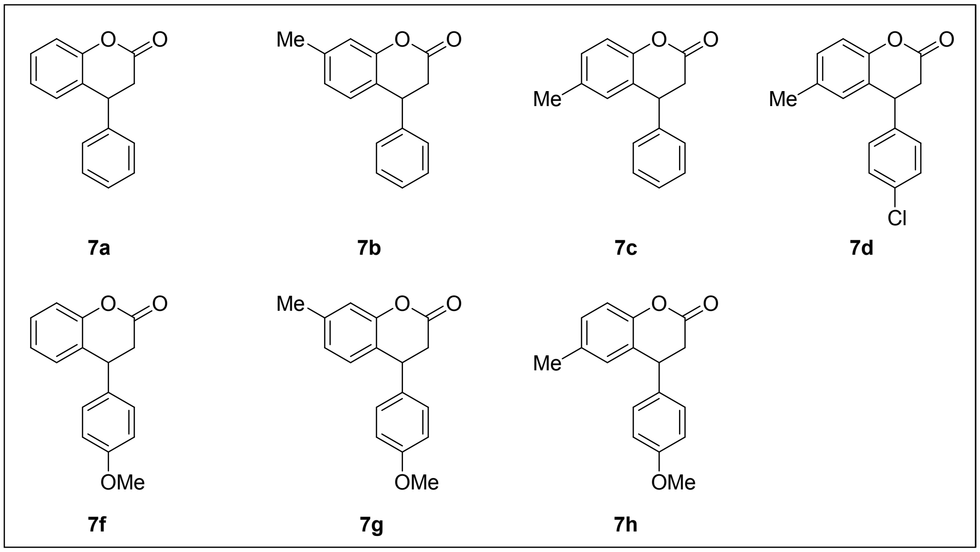
[8]A. R. Jagdale and A. Sudalai, *Tetrahedron Lett*., 2007, **48**, 4895–4898

[9]A. R. Jagdale and A. Sudalai, *Tetrahedron Lett.,* 2008, **49**, 3790–3793

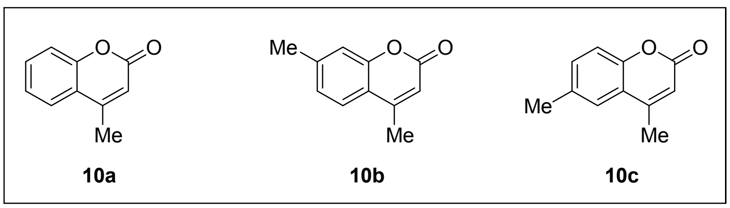
[10]J. O. Park and S. W. Youn, *Org. Lett*., 2010, **12**, 2258–2261

[11]W. H. Dos Santos and L. C. da Silva-Filho, *Synthesis,* 2012, **44**, 3361–3365

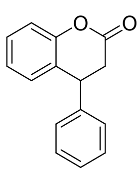
[12]D. P. Kamat, S. G. Tilve and V. P. Kamat, *Tetrahedron Lett*., 2012, **53**, 4469–4472



The following 4-aryl-3,4-dihydrocoumarins **10a**,[13] **10b**,[14] and **10c**[14] are known in the literature.



Data for the reported compounds:

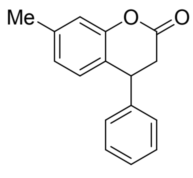


7a

4-phenylchroman-2-one (7a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.20 (m, 4H, ArH), 7.13 (d, 2H, *J*=8.8 Hz, ArH), 7.10 (d, 1H, *J*=7.8 Hz, ArH), 7.05 (ddd, 1H, *J*=7.8, 7.3 and 1.5 Hz, ArH), 6.96 (d, 1H, *J*=7.3 Hz, ArH), 4.31 (dd, 1H, *J*=7.8 and 5.9 Hz, ArC*H*CH_2CO), 3.77 (s, 3H, ArOCH_3), 3.04 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC$H_a$$H_b$CO), 2.98 (dd, 1H, *J*=15.6 and 7.8 Hz, ArCHC$H_a$$H_b$CO) ppm.

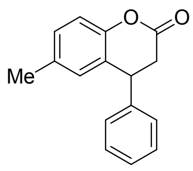
[13] J. Ferguson, F. Zeng and H. Alper, *Org. Lett.*, 2012, **14**, 5602–5605

[14] J. Chang, S. Wang, Z. Shen, G. Huang, Y. Zhang, J. Zhao, C. Li, F. Fan and C. Song, *Tetrahedron Lett.*, 2012, **53**, 6755–6757



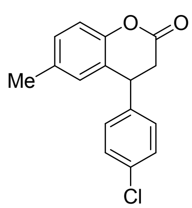
7b

7-methyl-4-phenylchroman-2-one (7b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.31 (dd, 2H, *J*=8.3 and 7.3 Hz, ArH), 7.25 (t, 1H, *J*=7.3 Hz, ArH), 7.13 (d, 2H, *J*=8.3 Hz, ArH), 6.92 (s, 1H, ArH), 6.86 (d, 1H, *J*=7.8 Hz, ArH), 6.84 (d, 1H, *J*=7.8 Hz, ArH), 4.27 (dd, 1H, *J*=7.3 and 5.9 Hz, ArC*H*CH_2CO), 3.03 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC$H_a$$H_b$CO), 2.96 (dd, 1H, *J*=15.6 and 7.3 Hz, ArCHC$H_a$$H_b$CO), 2.33 (s, 3H, Ar$CH_3$) ppm.



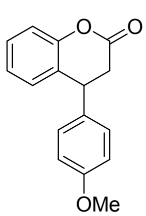
7c

6-methyl-4-phenylchroman-2-one (7c): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.34 (dd, 2H, *J*=8.3 and 7.3 Hz, ArH), 7.28 (t, 1H, *J*=7.3 Hz, ArH), 7.15 (d, 2H, *J*=8.3 Hz, ArH), 7.08 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 7.03 (d, 1H, *J*=8.3 Hz, ArH), 6.78 (br. s, 1H, ArH), 4.29 (dd, 1H, *J*=7.3 and 5.9 Hz, ArC*H*CH_2CO), 3.04 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC$H_a$$H_b$CO), 3.00 (dd, 1H, *J*=15.6 and 7.3 Hz, ArCHC$H_a$$H_b$CO), 2.25 (s, 3H, Ar$CH_3$) ppm.



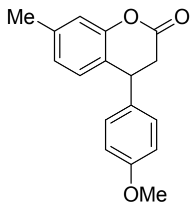
7d

4-(4-chlorophenyl)-6-methylchroman-2-one (7d): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.31 (d, 2H, *J*=8.8 Hz, ArH), 7.19−7.05 (m, 3H, ArH), 7.01 (d, 1H, *J*=8.3 Hz, ArH), 6.76 (br. s, 1H, ArH), 4.27 (dd, 1H, *J*=7.3 and 6.4 Hz, ArC*H*CH_2CO), 3.02 (dd, 1H, *J*=15.6 and 6.4 Hz, ArCHC$H_a$$H_b$CO), 2.95 (dd, 1H, *J*=15.6 and 7.3 Hz, ArCHC$H_a$$H_b$CO), 2.26 (s, 3H, Ar$CH_3$) ppm.



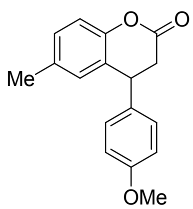
7f

4-(4-methoxyphenyl)chroman-2-one (7f): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.28 (ddd, 1H, *J*=7.8, 7.8 and 1.5 Hz, ArH), 7.11 (dd, 1H, *J*=8.3 and 1.0 Hz, ArH), 7.10−7.03 (m, 3H, ArH), 6.97 (d, 1H, *J*=7.3 Hz, ArH), 6.87 (d, 2H, *J*=8.8 Hz, ArH), 4.29 (dd, 1H, *J*=7.8 and 5.9 Hz, ArC*H*CH$_2$CO), 3.79 (s, 3H, Ar-OCH$_3$), 3.04 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC*H*$_a$H$_b$CO), 2.99 (dd, 1H, *J*=15.6 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO) ppm.



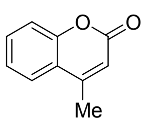
7g

4-(4-methoxyphenyl)-7-methylchroman-2-one (7g): ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.05 (d, 2H, *J*=8.8 Hz, ArH), 6.93 (s, 1H, ArH), 6.91–6.75 (m, 4H, ArH), 4.24 (dd, 1H, *J*=7.8 and 5.9 Hz, ArC*H*CH$_2$CO), 3.78 (s, 3H, Ar-OCH$_3$), 3.01 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC*H*$_a$H$_b$CO), 2.95 (dd, 1H, *J*=15.6 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO), 2.35 (s, 3H, ArCH$_3$) ppm.



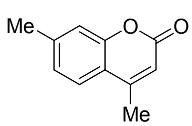
7h

4-(4-methoxyphenyl)-6-methylchroman-2-one (7h): ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.13–7.03 (m, 3H, ArH), 7.00 (d, 1H, *J*=8.3 Hz, ArH), 6.87 (d, 2H, *J*=8.8 Hz, ArH), 6.77 (s, 1H, ArH), 4.24 (dd, 1H, *J*=7.8 and 5.9 Hz, ArC*H*CH$_2$CO), 3.79 (s, 3H, Ar-OCH$_3$), 3.01 (dd, 1H, *J*=15.6 and 5.9 Hz, ArCHC*H*$_a$H$_b$CO), 2.96 (dd, 1H, *J*=15.6 and 7.8 Hz, ArCHCH$_a$*H*$_b$CO), 2.25 (s, 3H, ArCH$_3$) ppm.



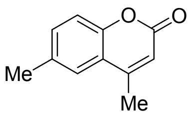
10a

4-methyl-2*H*-chromen-2-one (10a): ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.60 (dd, 1H, *J*=8.8 and 1.5 Hz, ArH), 7.52 (ddd, 1H, *J*=8.8, 7.8 and 1.5 Hz, ArH), 7.32 (dd, 1H, *J*=8.8 and 1.5 Hz, ArH), 7.29 (ddd, 1H, *J*=7.8, 7.8 and 1.5 Hz, ArH), 6.29 (q, 1H, *J*=1.0 Hz, ArC(CH$_3$)=C*H*], 2.43 (d, 3H, *J*=1.0 Hz, ArC(C*H*$_3$)=CH] ppm.



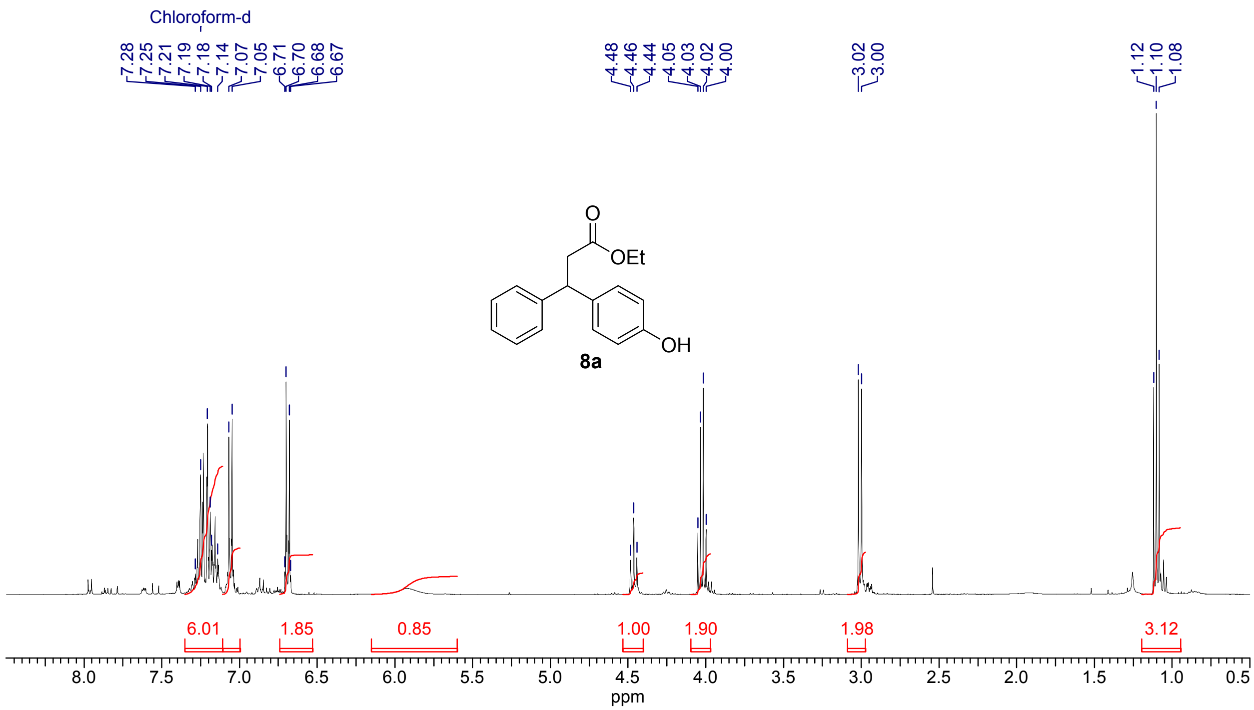
10b

4,7-dimethyl-2*H*-chromen-2-one (10b): ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.43 (d, 1H, *J*=8.8 Hz, ArH), 7.07 (s, 1H, ArH), 7.06 (d, 1H, *J*=8.8 Hz, ArH), 6.17 (q, 1H, *J*=1.0 Hz, ArC(CH$_3$)=C*H*], 2.40 (s, 3H, ArCH$_3$), 2.37 (d, 3H, *J*=1.0 Hz, ArC(C*H*$_3$)=CH] ppm.

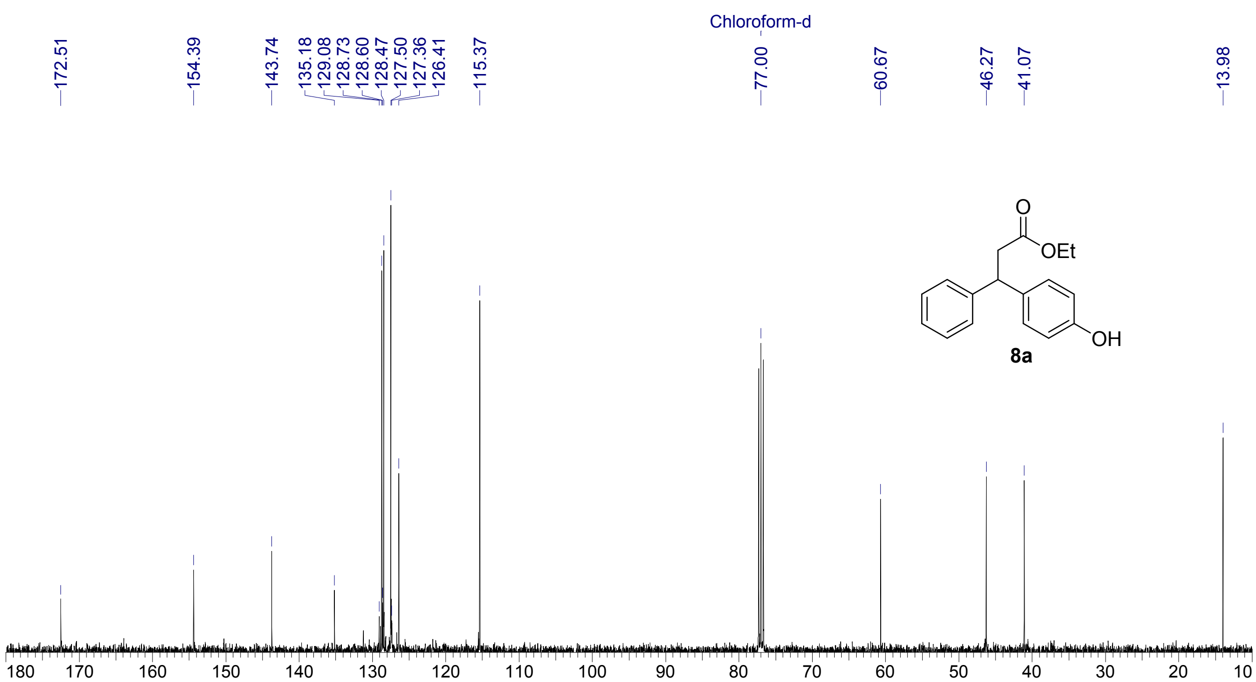


10c

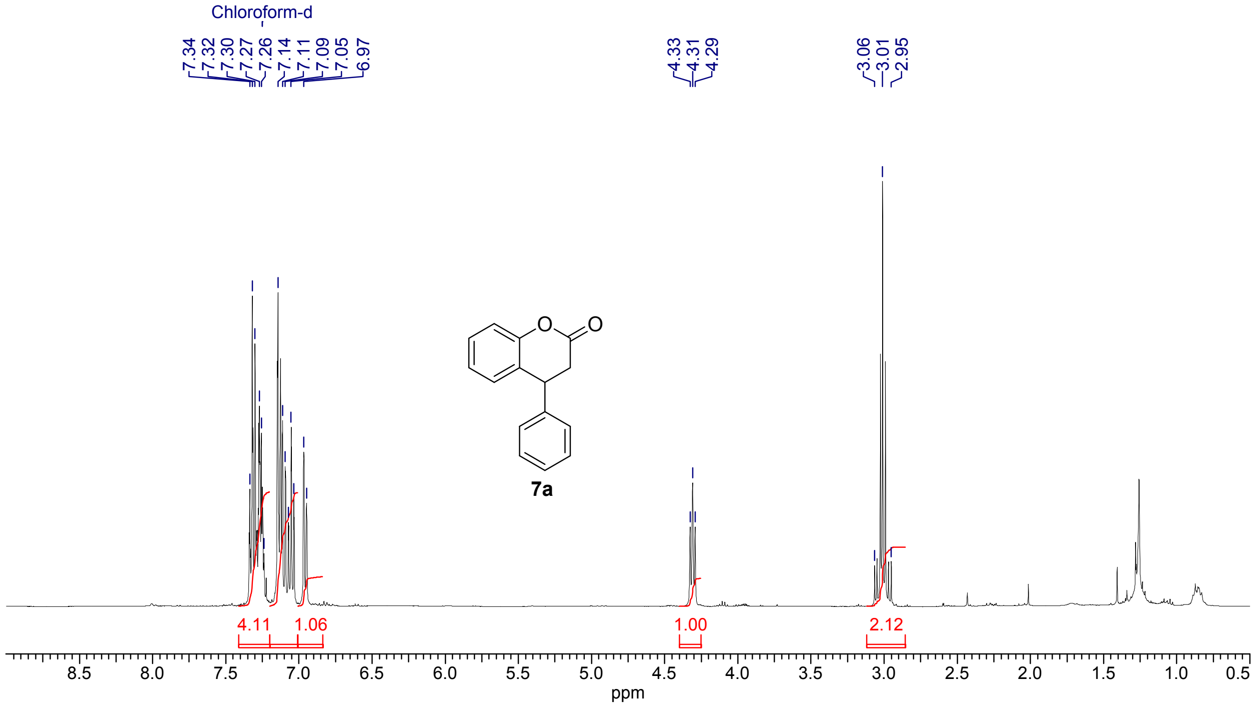
4,6-dimethyl-2*H*-chromen-2-one (10c): ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.35 (s, 1H, ArH), 7.30 (d, 1H, *J*=8.3 Hz, ArH), 7.18 (d, 1H, *J*=8.3 Hz, ArH), 6.23 (s, 1H, ArC(CH_3)=C*H*], 2.40 [s, 6H, $ArCH_3$ and ArC(CH_3)=CH] ppm.



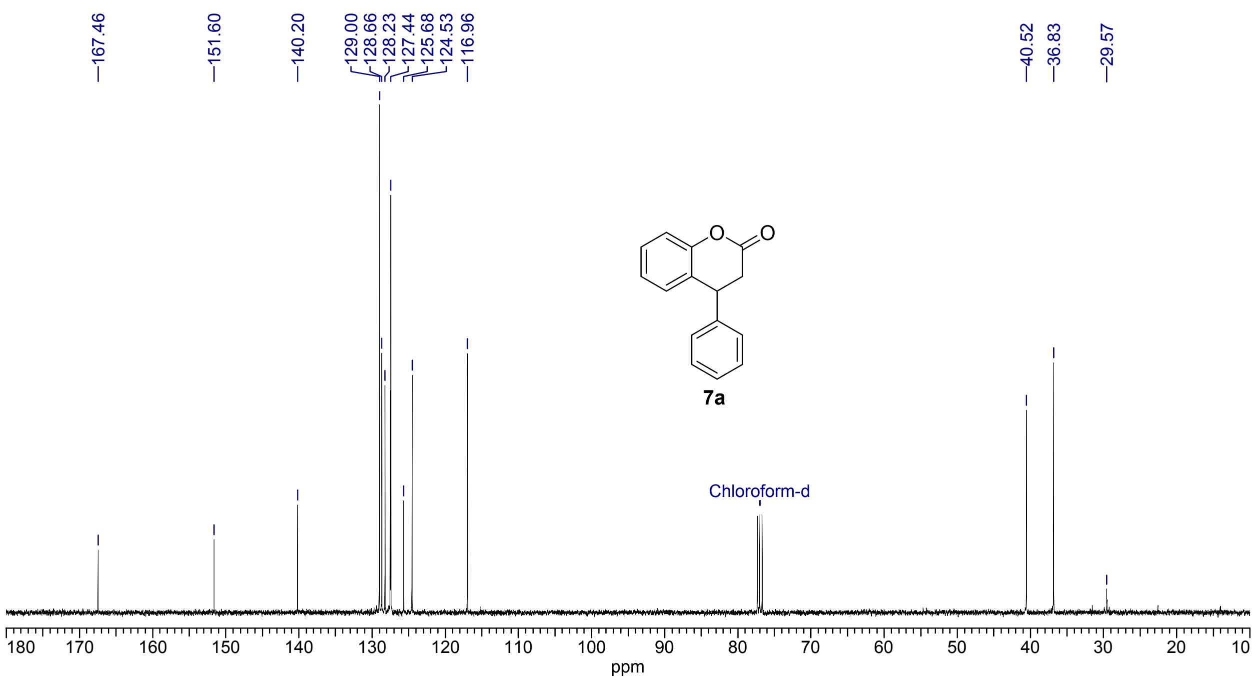
^{1}H NMR (400 MHz) spectrum of **8a** in $CDCl_3$



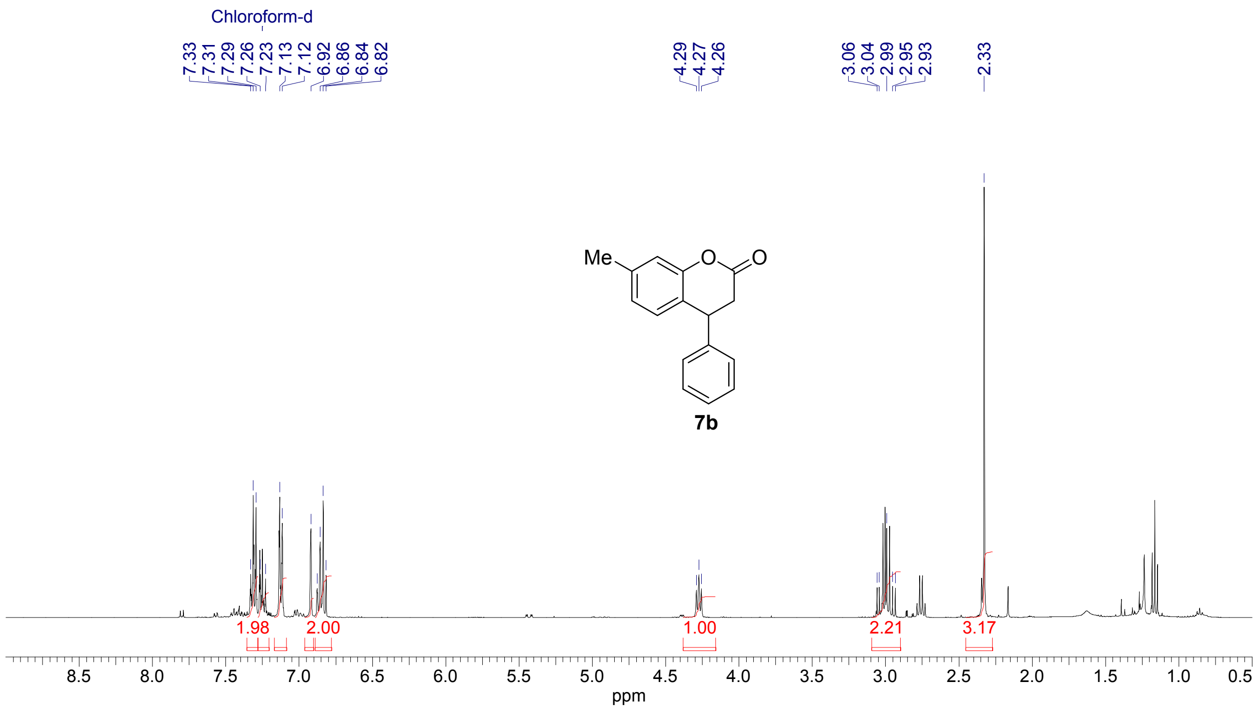
^{13}C NMR (100 MHz) spectrum of **8a** in $CDCl_3$



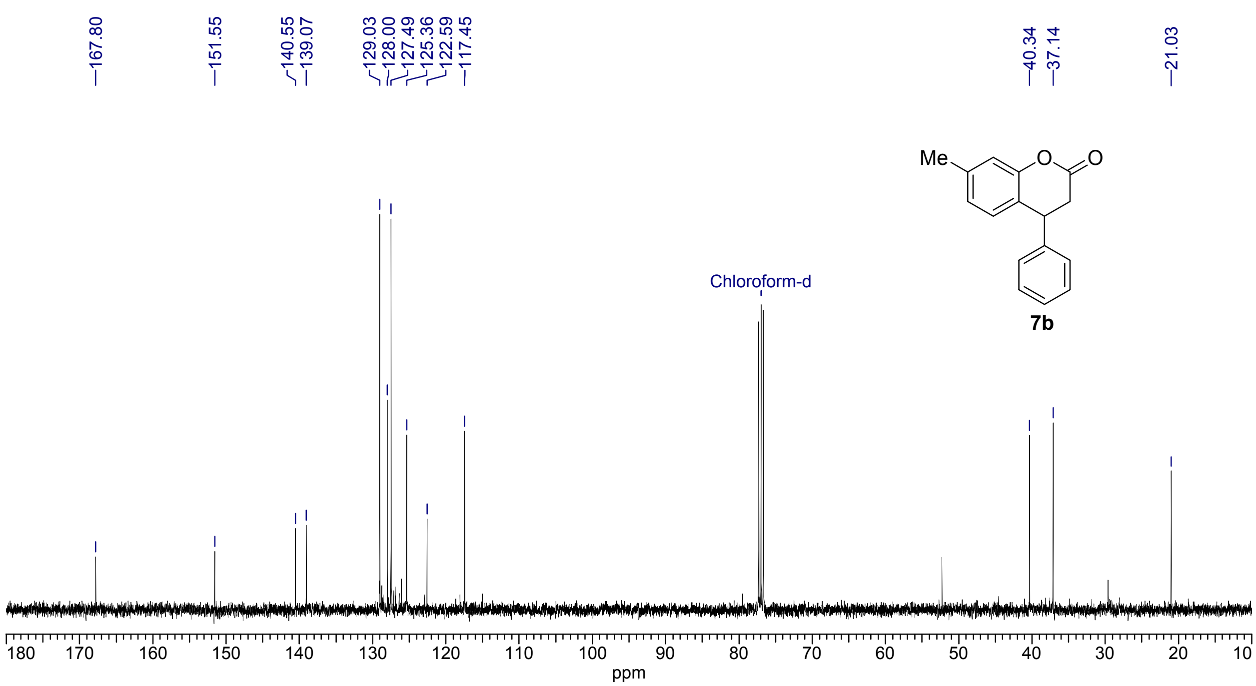
^{1}H NMR (400 MHz) spectrum of **7a** in $CDCl_3$



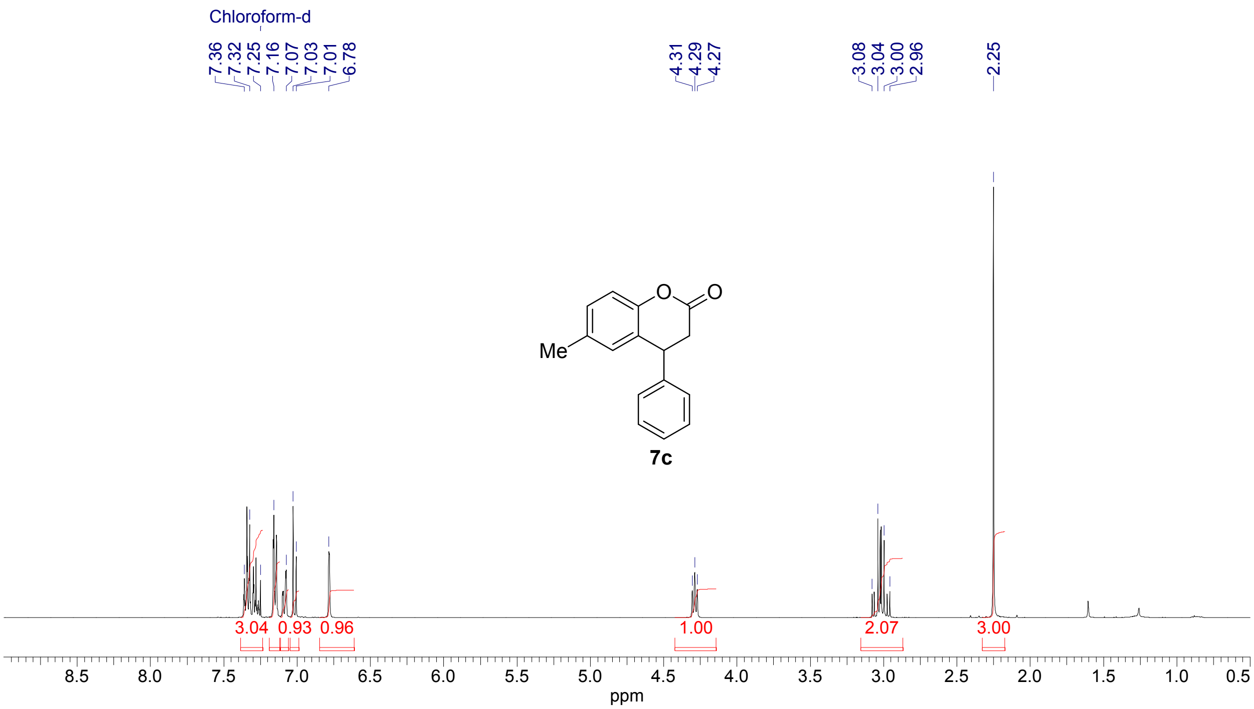
^{13}C NMR (100 MHz) spectrum of **7a** in $CDCl_3$



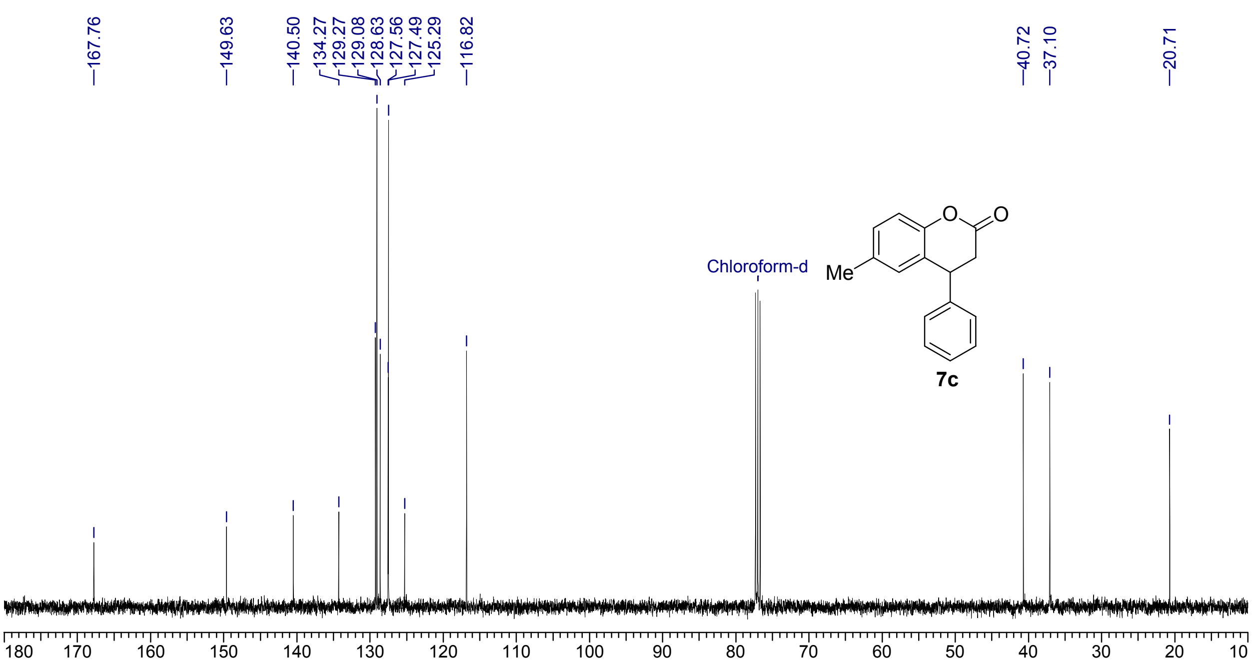
^{1}H NMR (400 MHz) spectrum of **7b** in $CDCl_3$



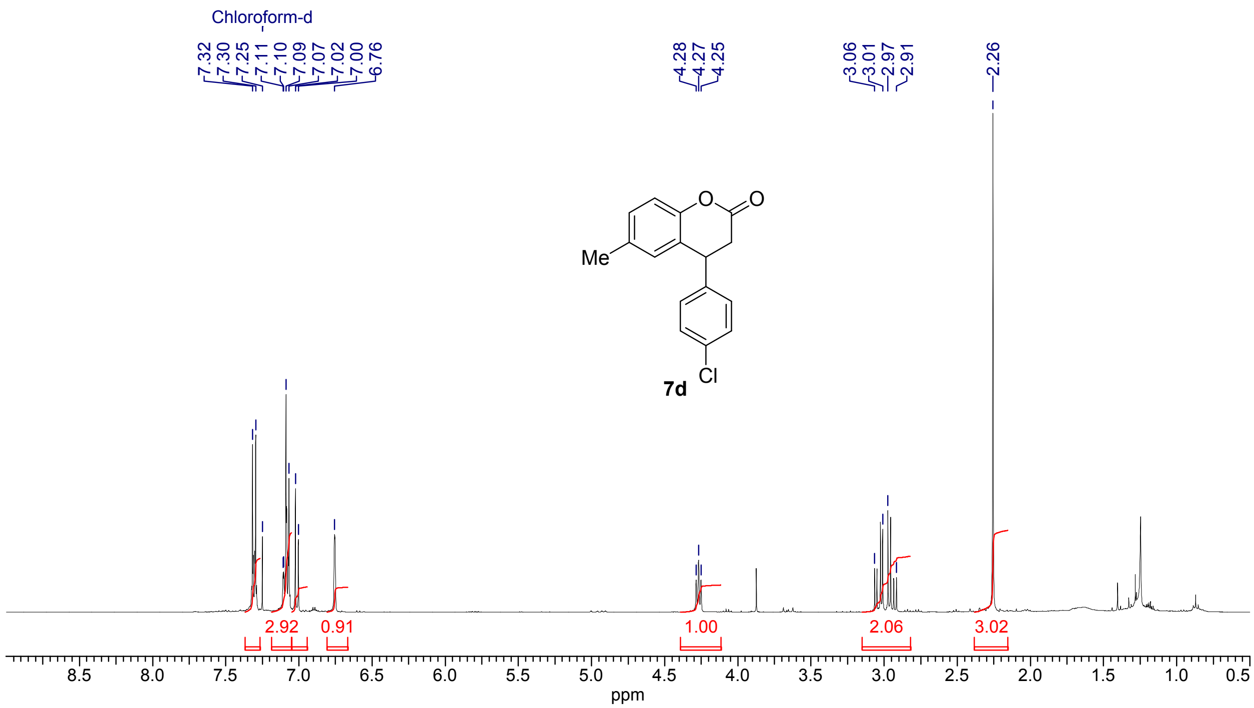
^{13}C NMR (100 MHz) spectrum of **7b** in $CDCl_3$



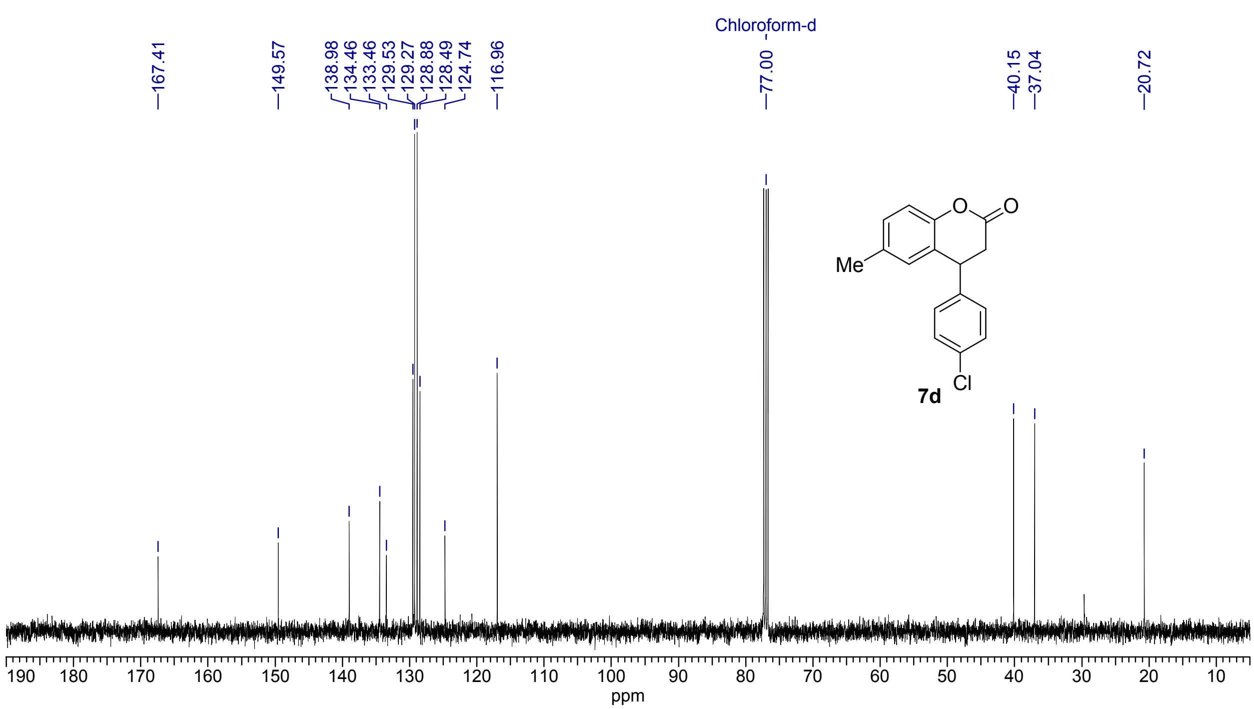
^{1}H NMR (400 MHz) spectrum of **7c** in $CDCl_3$



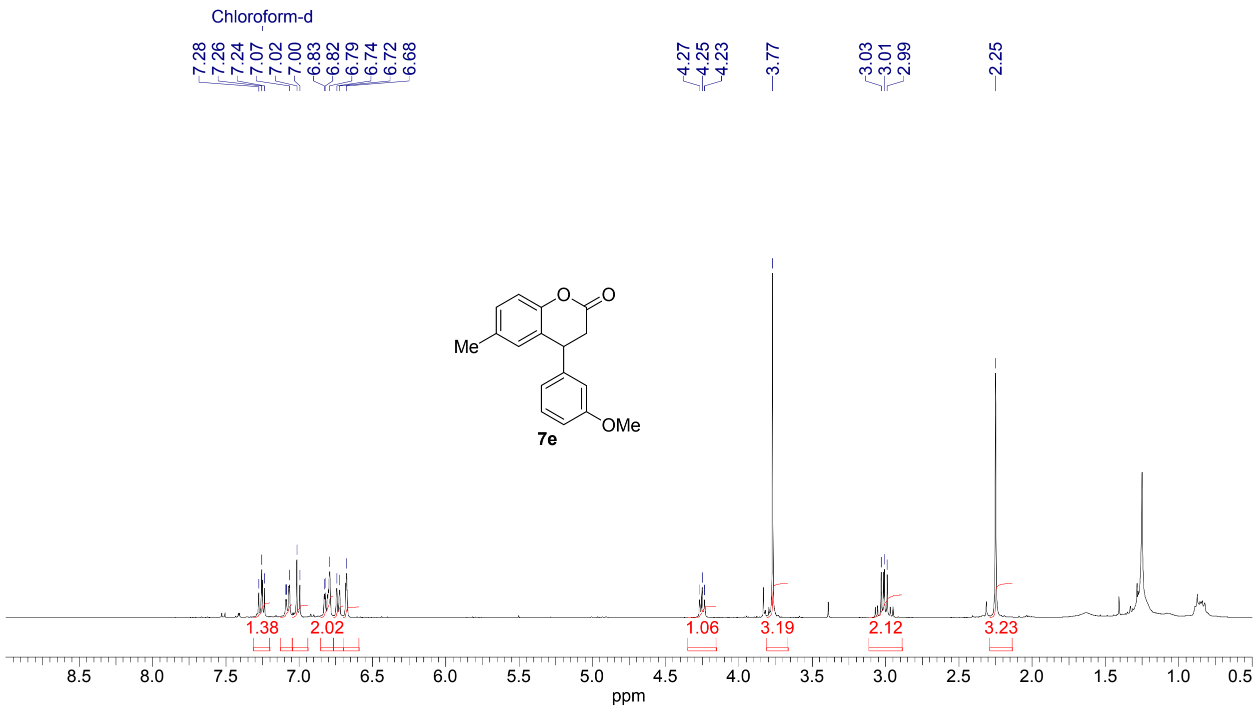
^{13}C NMR (100 MHz) spectrum of **7c** in $CDCl_3$



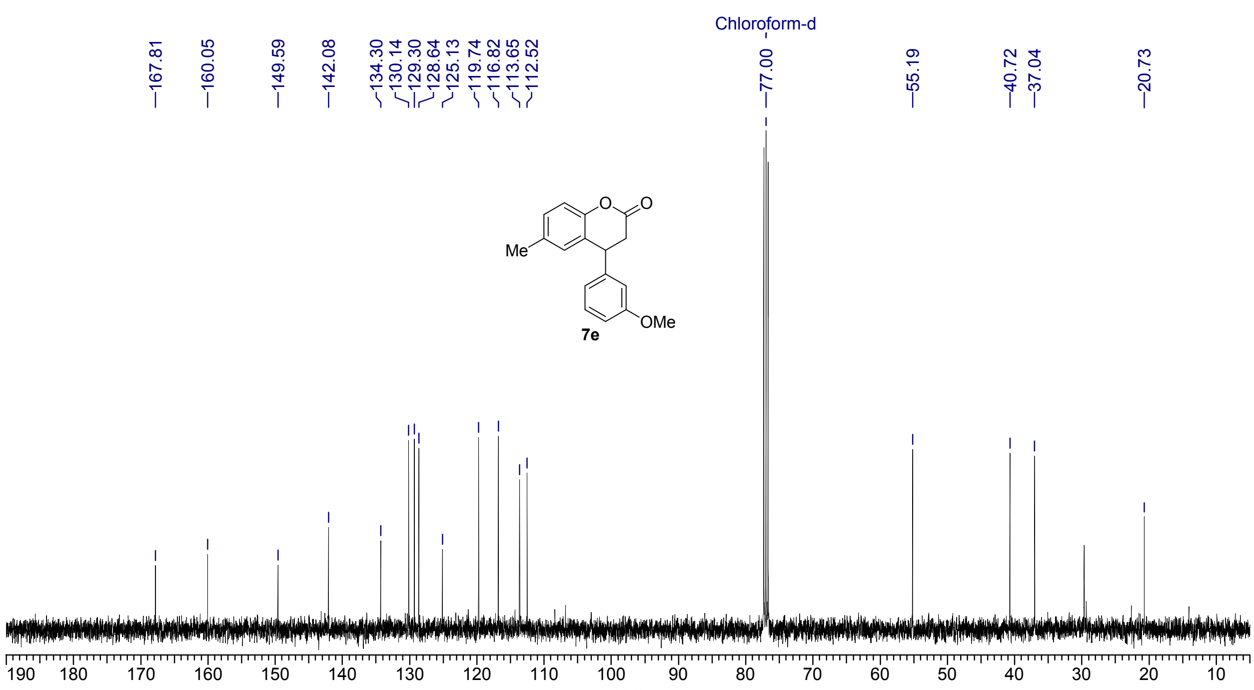
^{1}H NMR (400 MHz) spectrum of **7d** in $CDCl_3$



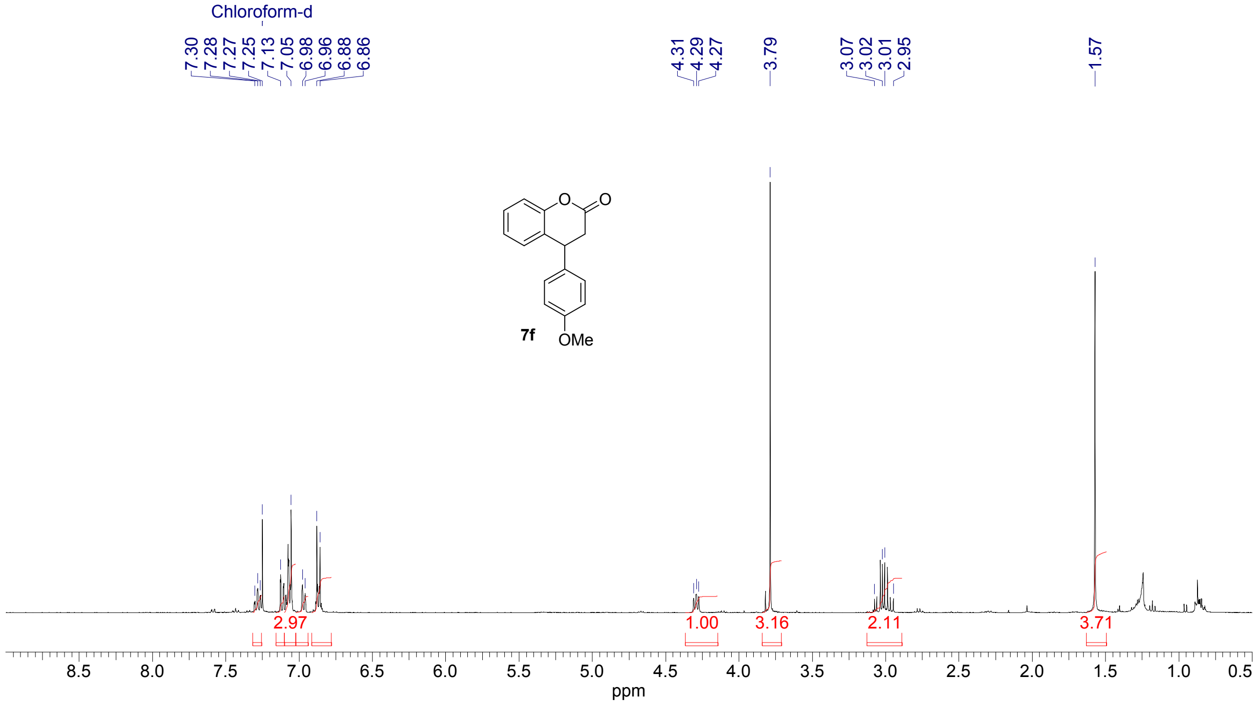
^{13}C NMR (100 MHz) spectrum of **7d** in $CDCl_3$



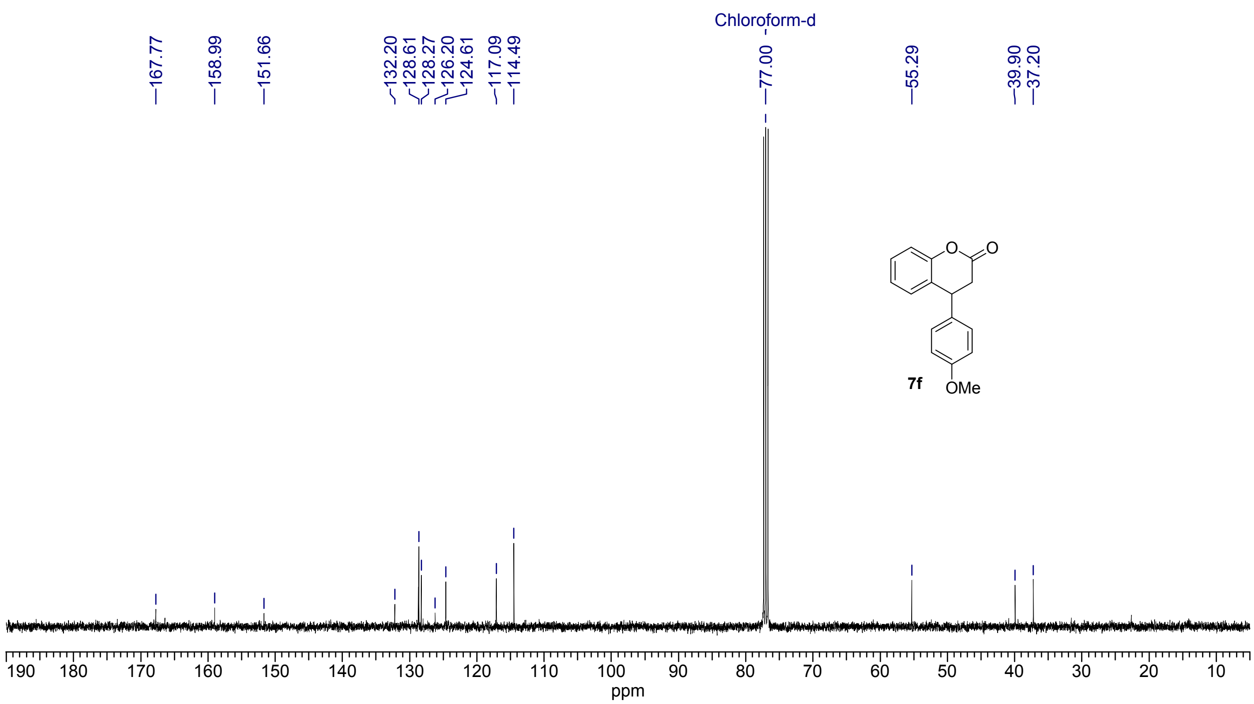
^{1}H NMR (400 MHz) spectrum of **7e** in $CDCl_3$



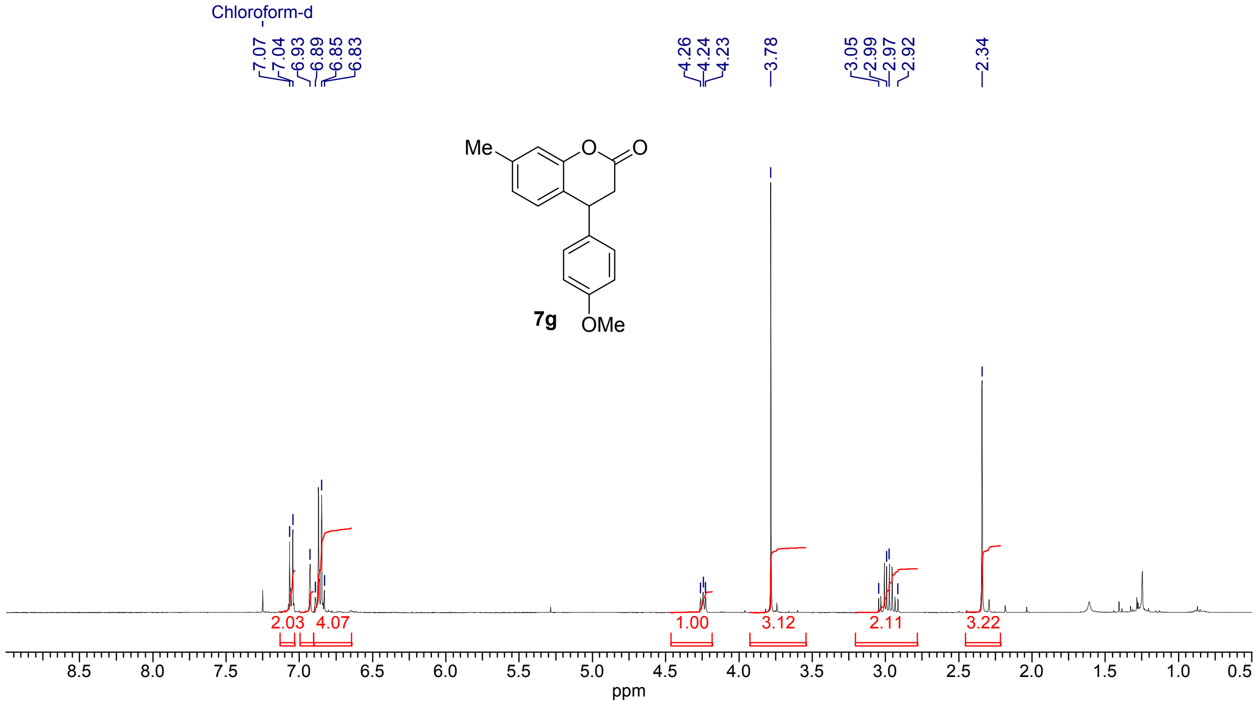
^{13}C NMR (100 MHz) spectrum of **7e** in $CDCl_3$



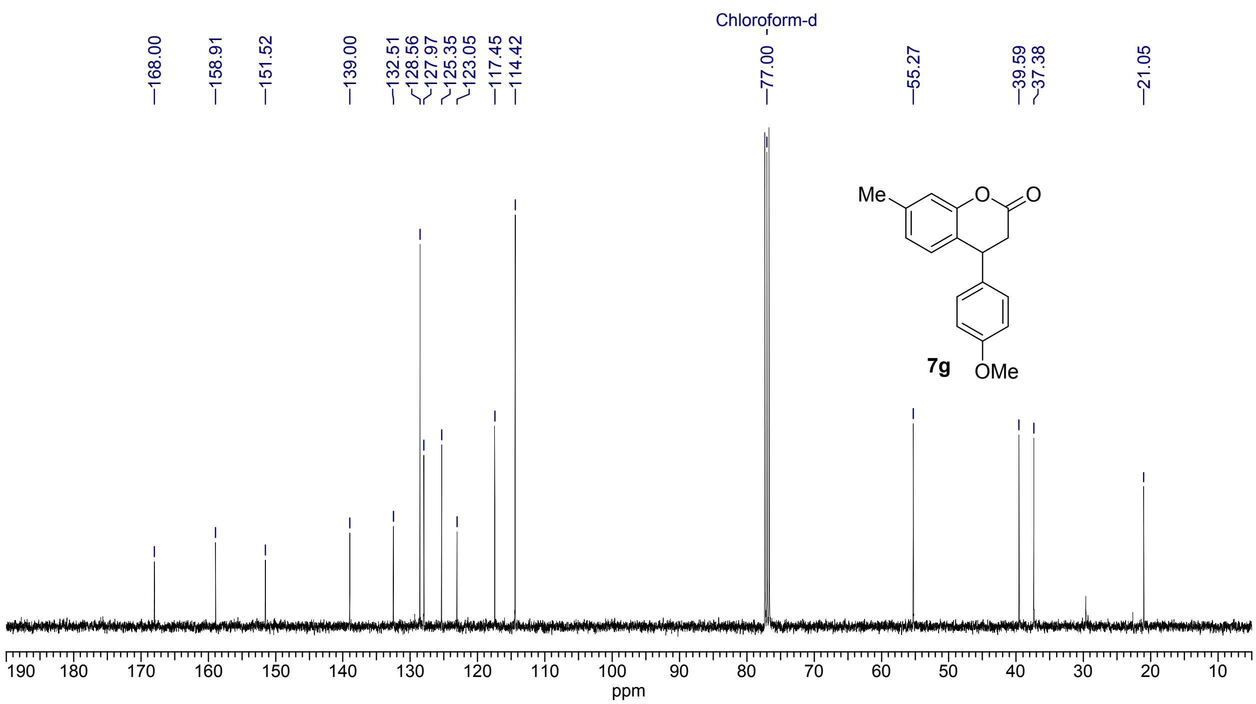
[1]H NMR (400 MHz) spectrum of **7f** in $CDCl_3$



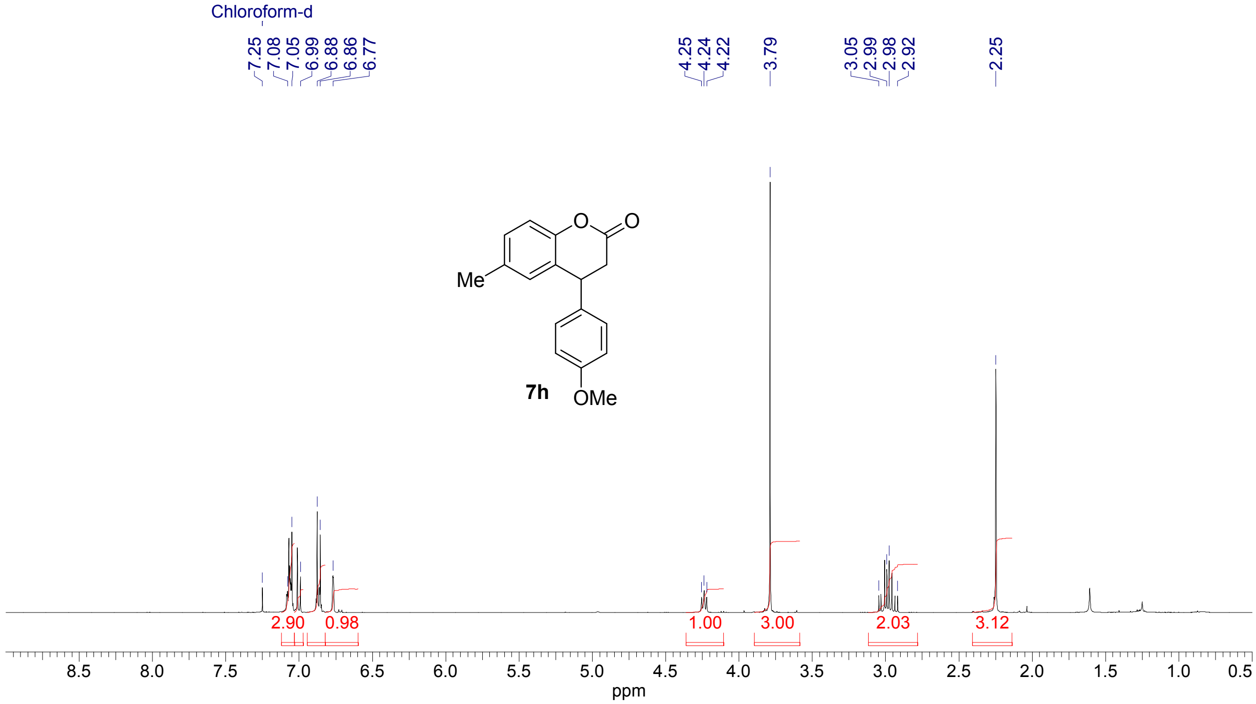
[13]C NMR (100 MHz) spectrum of **7f** in $CDCl_3$



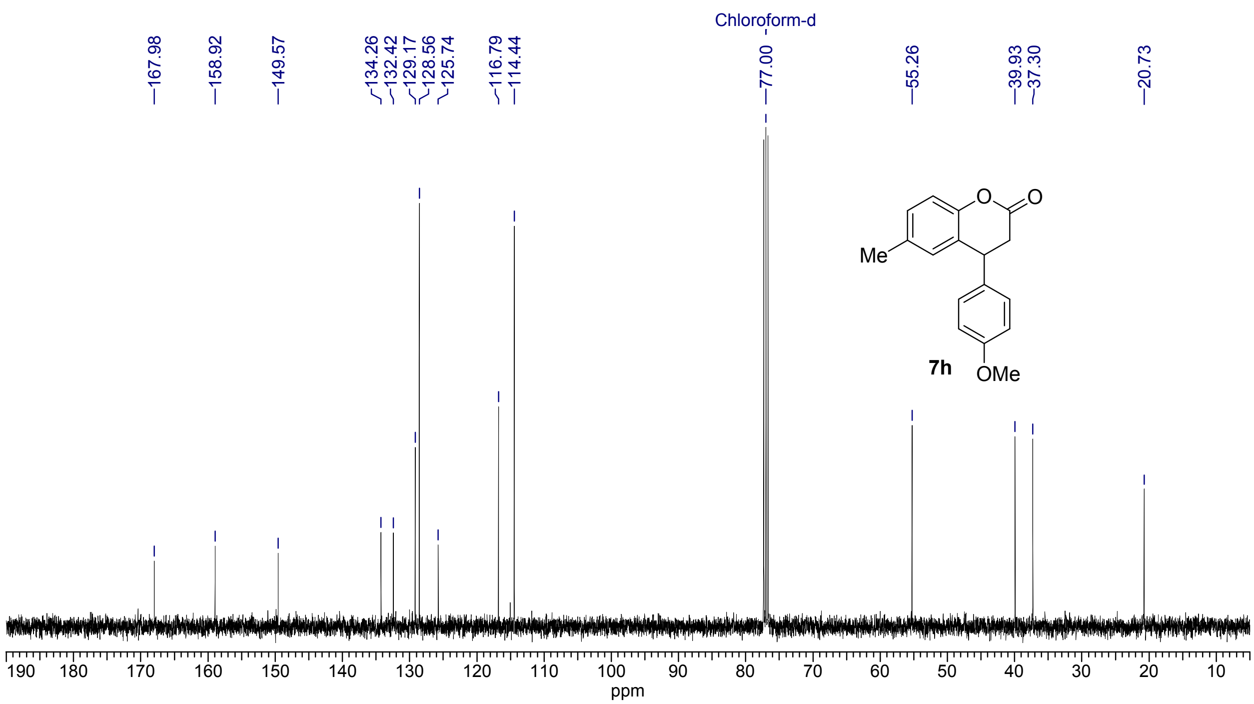
^{1}H NMR (400 MHz) spectrum of **7g** in $CDCl_3$



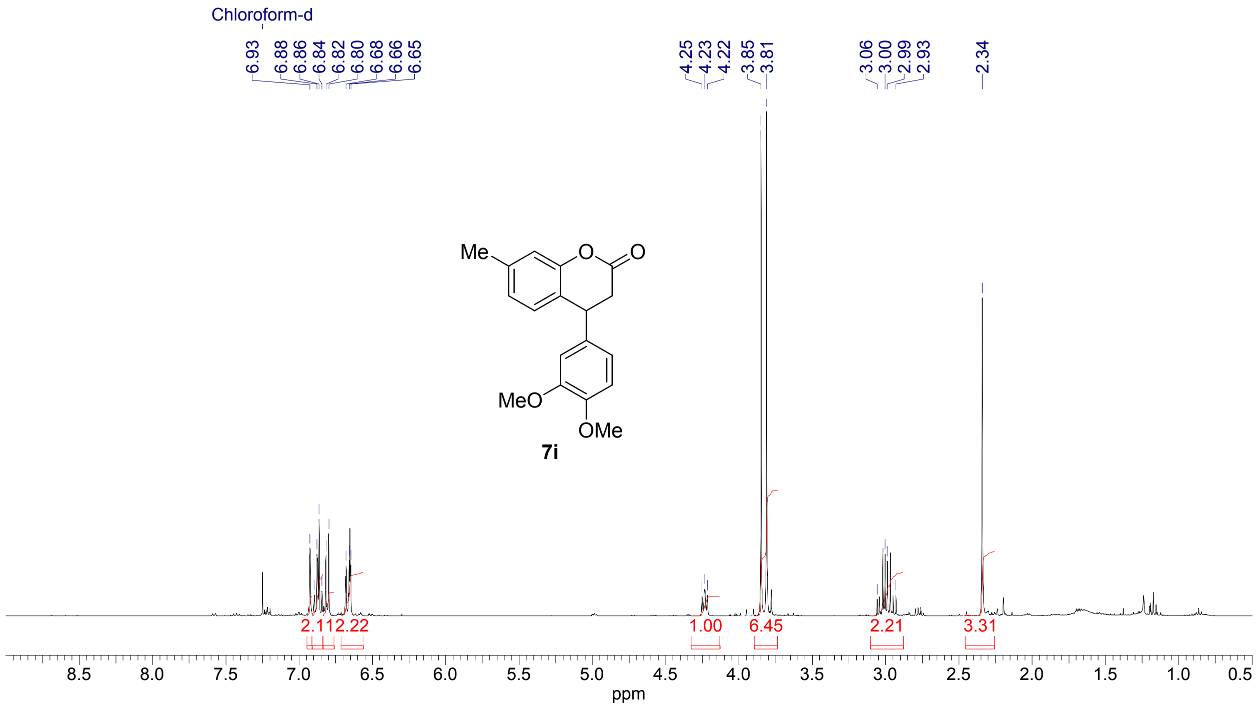
^{13}C NMR (100 MHz) spectrum of **7g** in $CDCl_3$



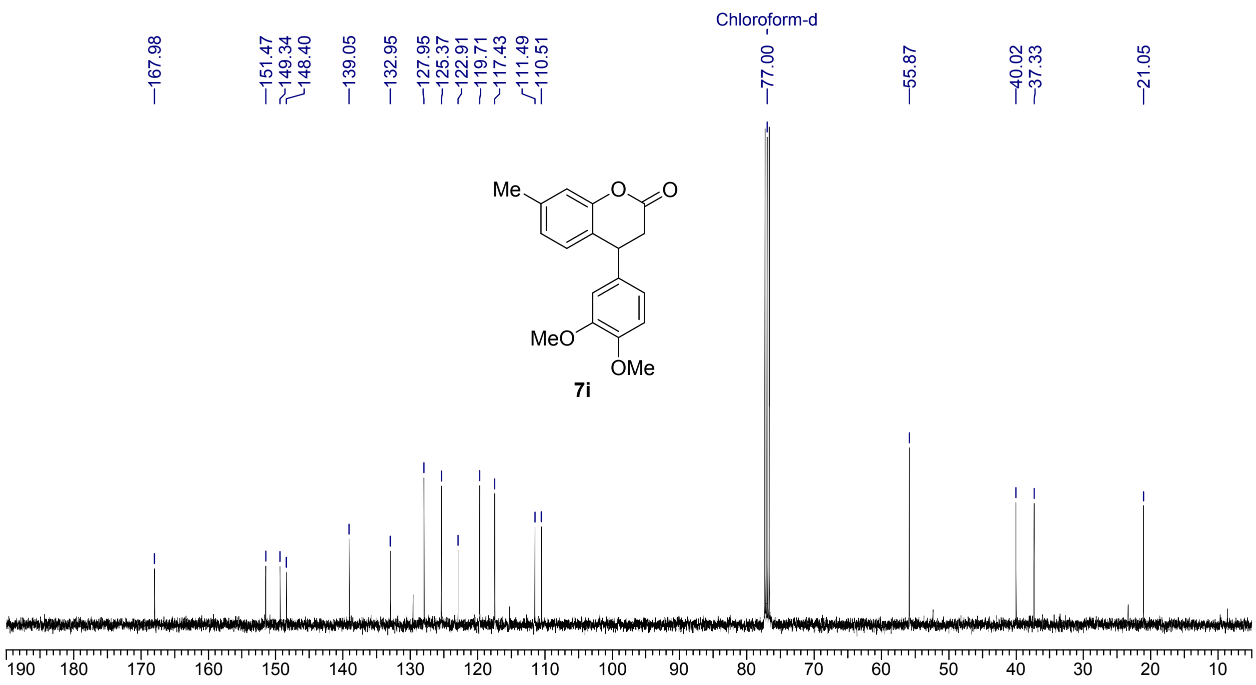
^{1}H NMR (400 MHz) spectrum of **7h** in $CDCl_3$



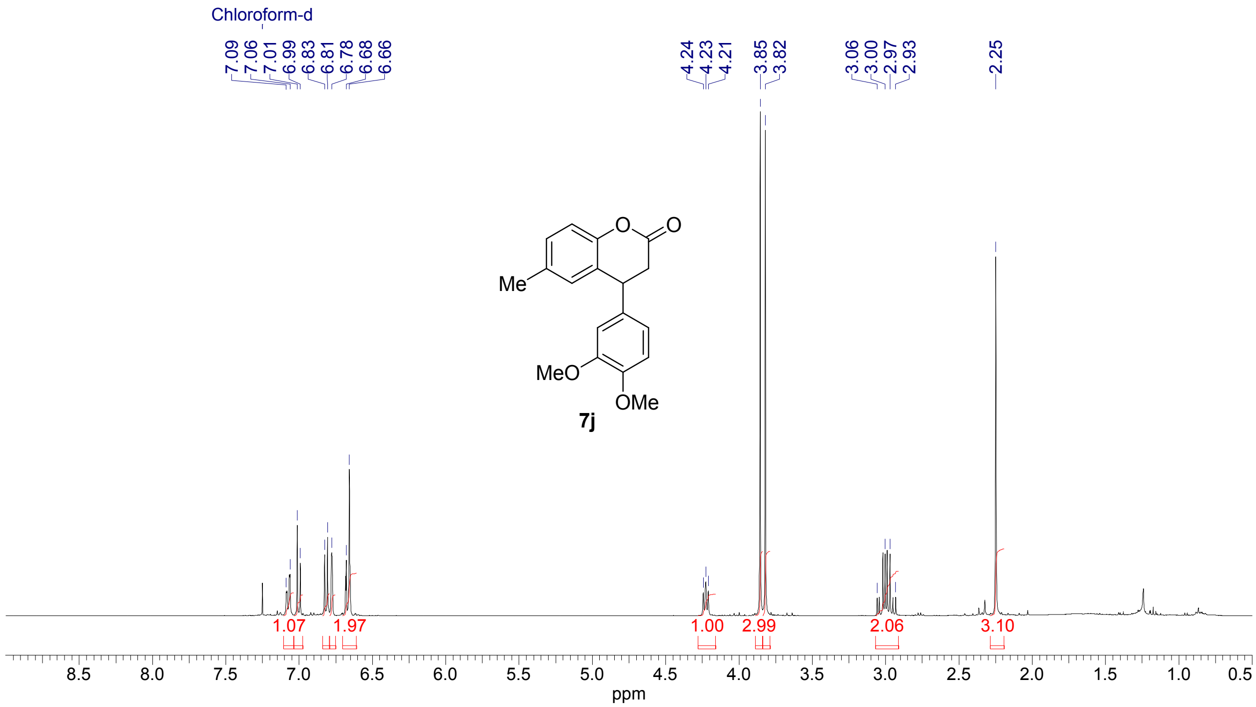
^{13}C NMR (100 MHz) spectrum of **7h** in $CDCl_3$



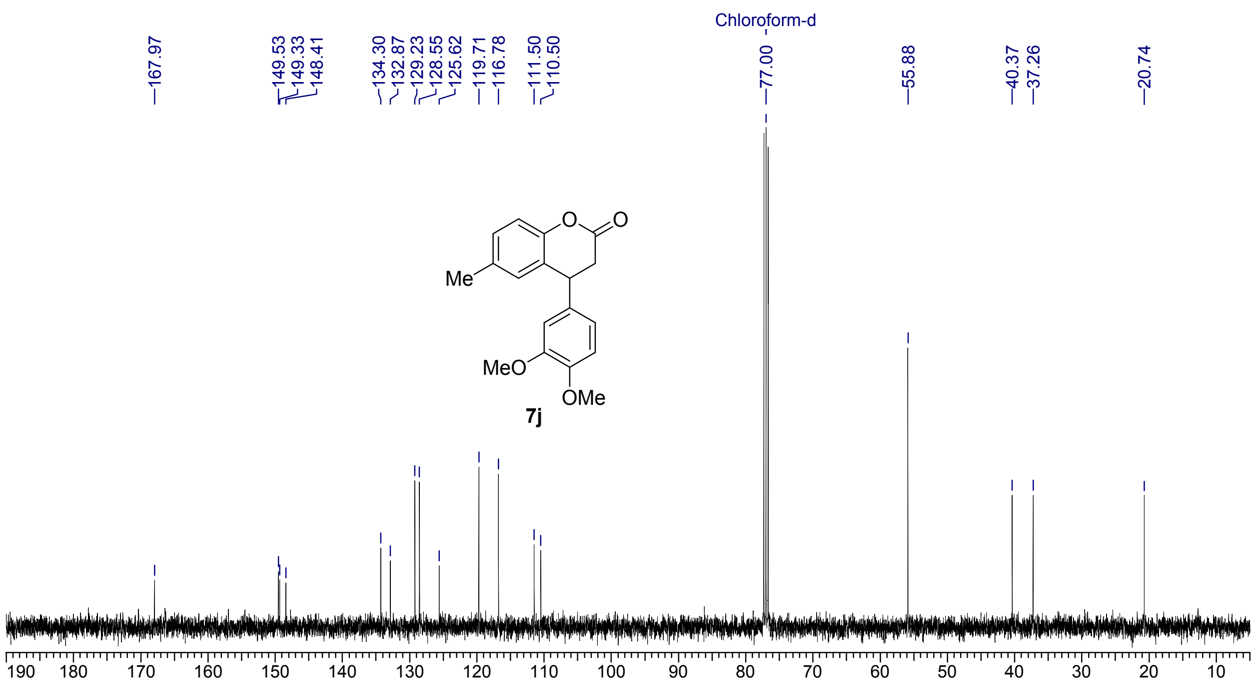
^{1}H NMR (400 MHz) spectrum of **7i** in $CDCl_3$



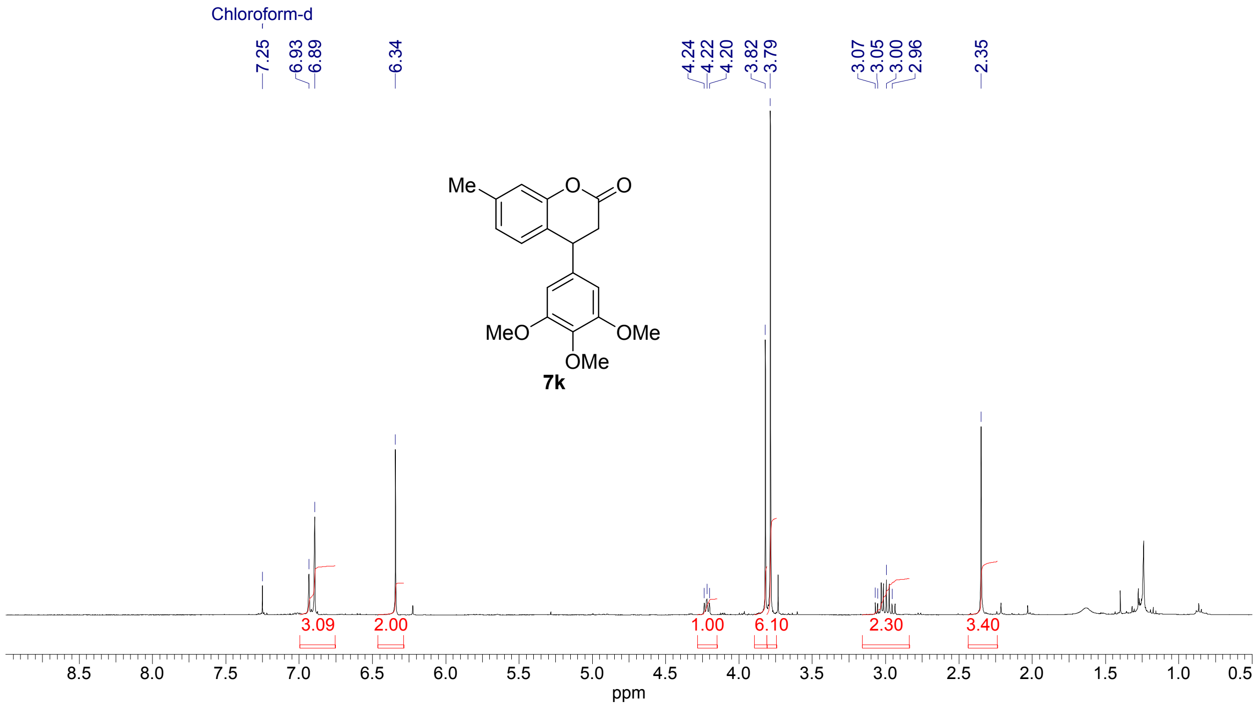
^{13}C NMR (100 MHz) spectrum of **7i** in $CDCl_3$



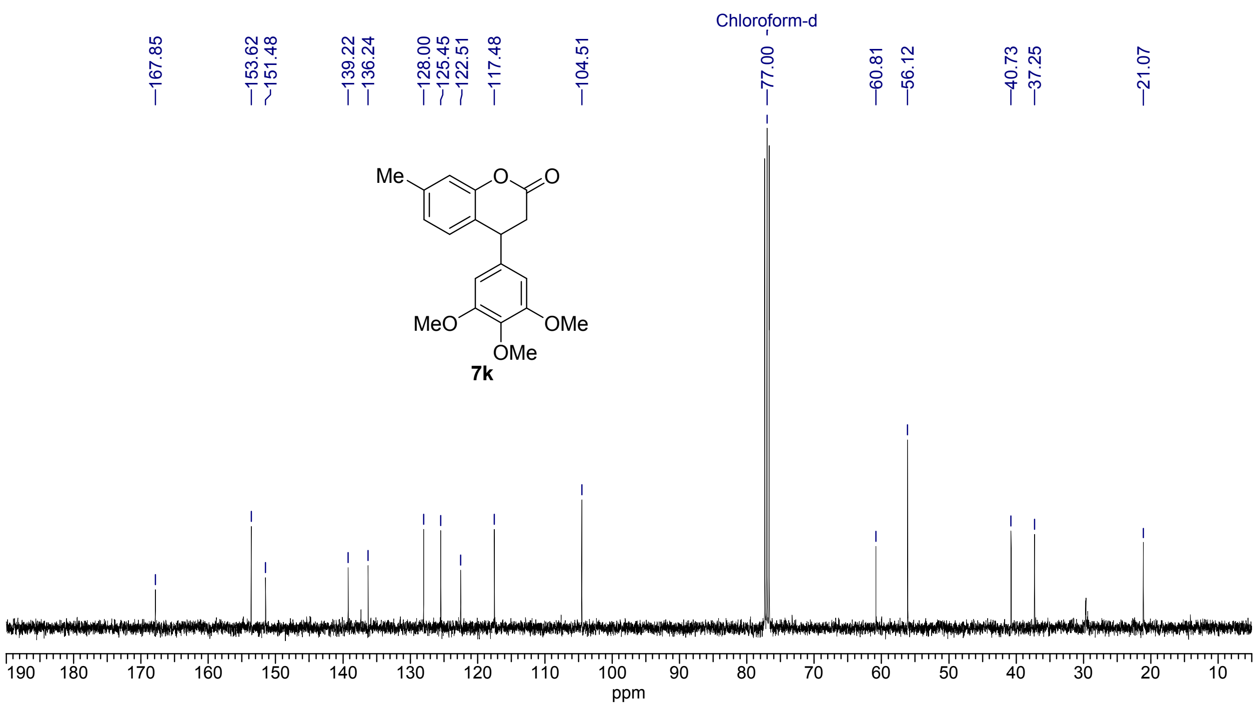
^{1}H NMR (400 MHz) spectrum of **7j** in $CDCl_3$



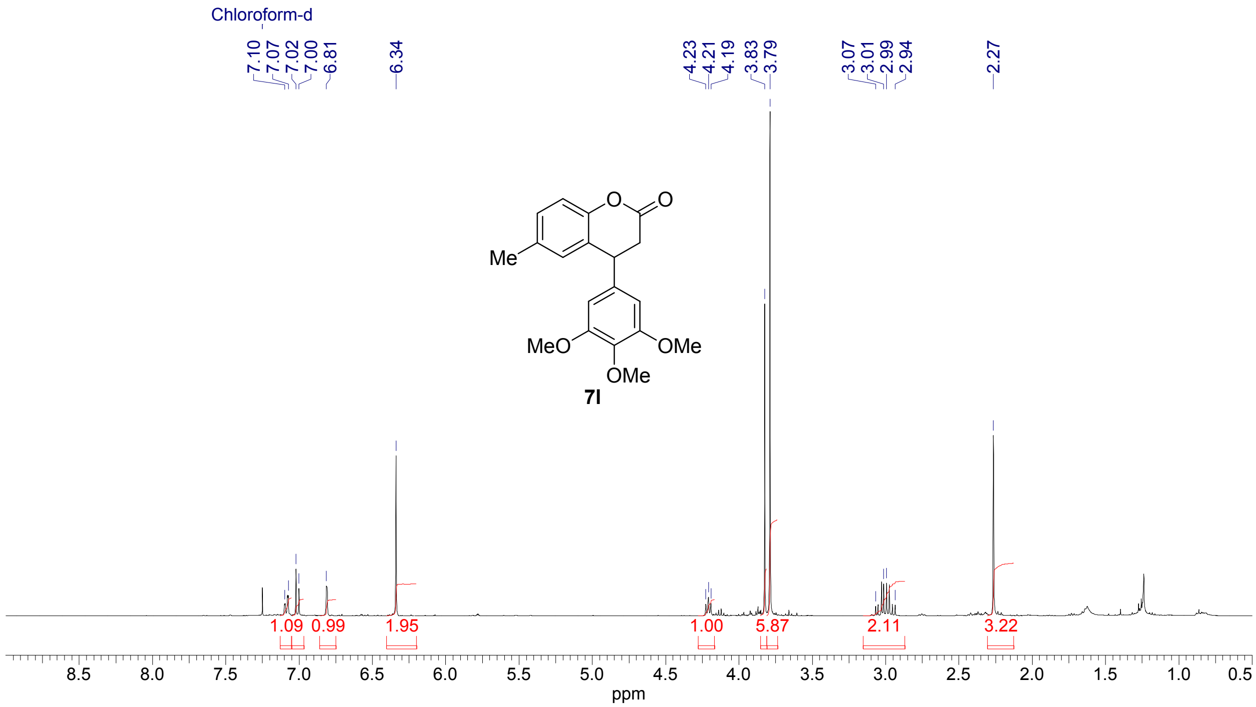
^{13}C NMR (100 MHz) spectrum of **7j** in $CDCl_3$



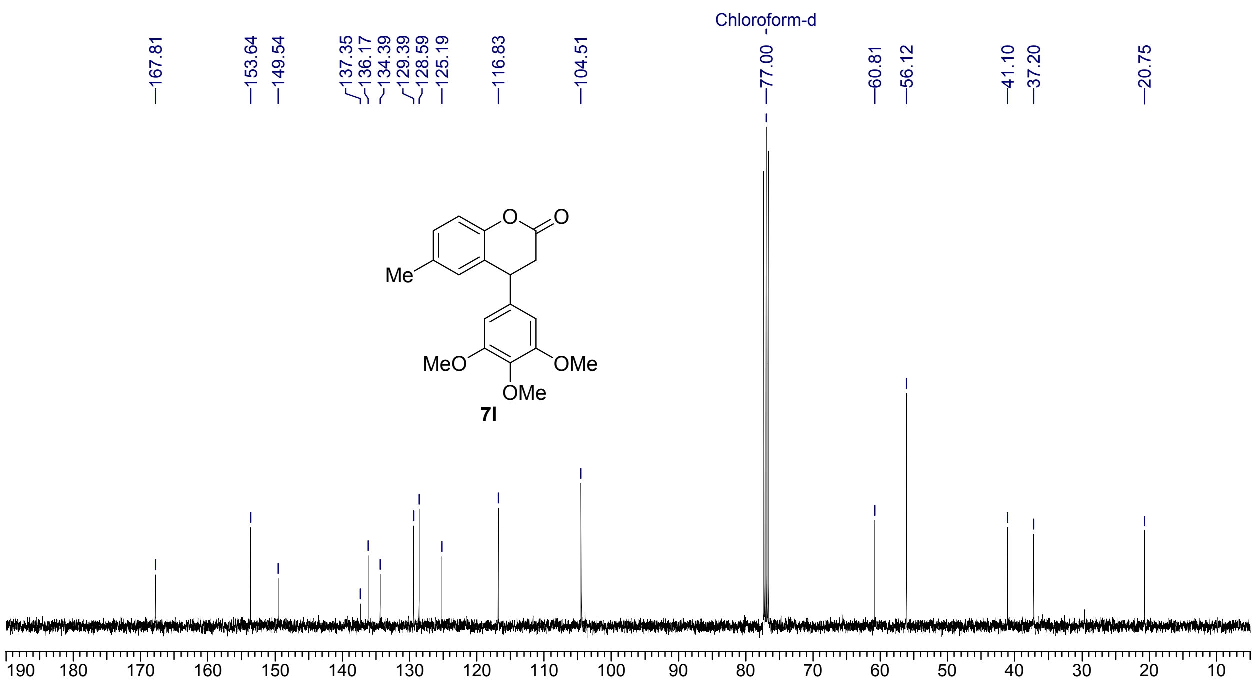
^{1}H NMR (400 MHz) spectrum of **7k** in $CDCl_3$



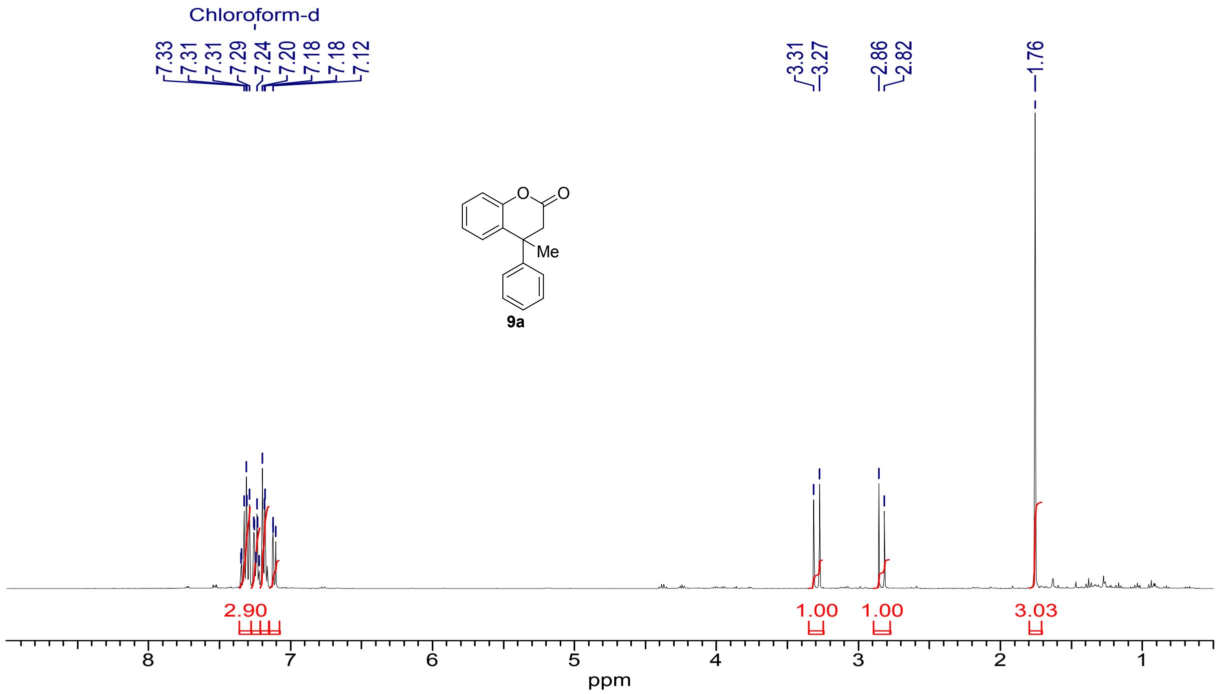
^{13}C NMR (100 MHz) spectrum of **7k** in $CDCl_3$



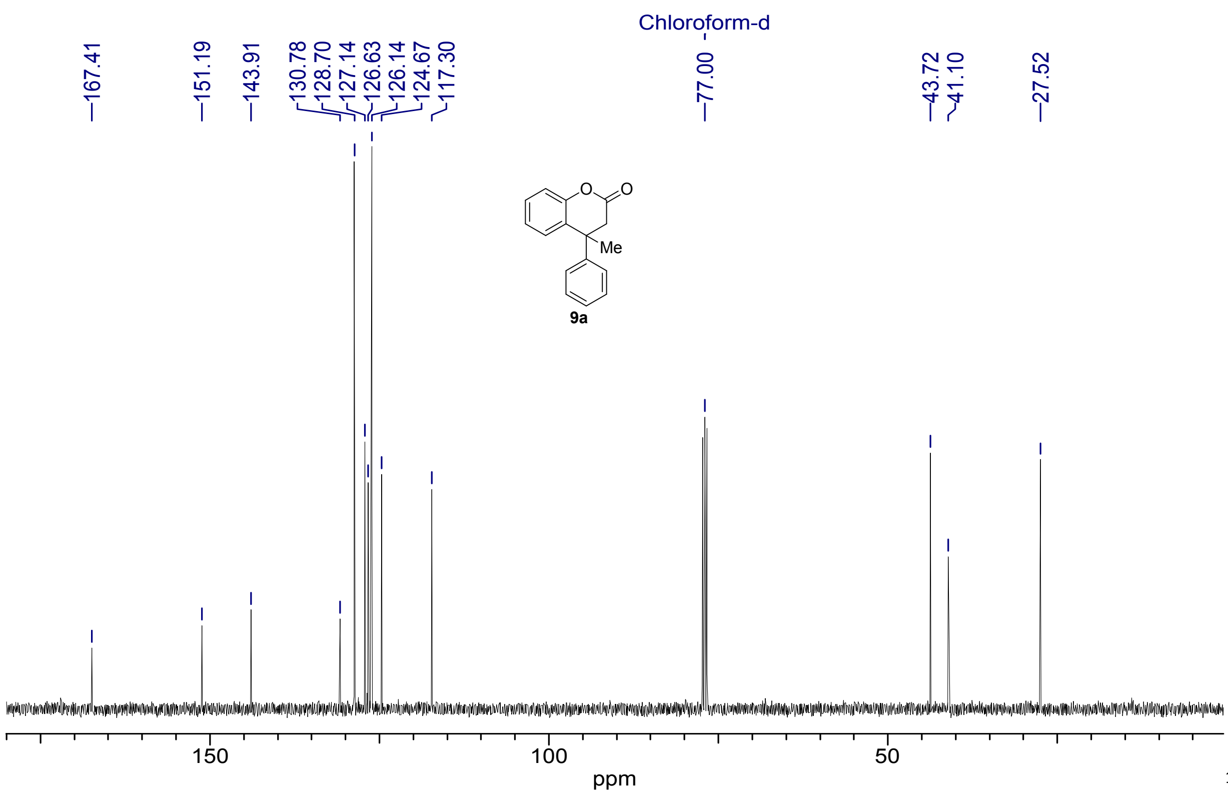
^{1}H NMR (400 MHz) spectrum of **7l** in $CDCl_3$



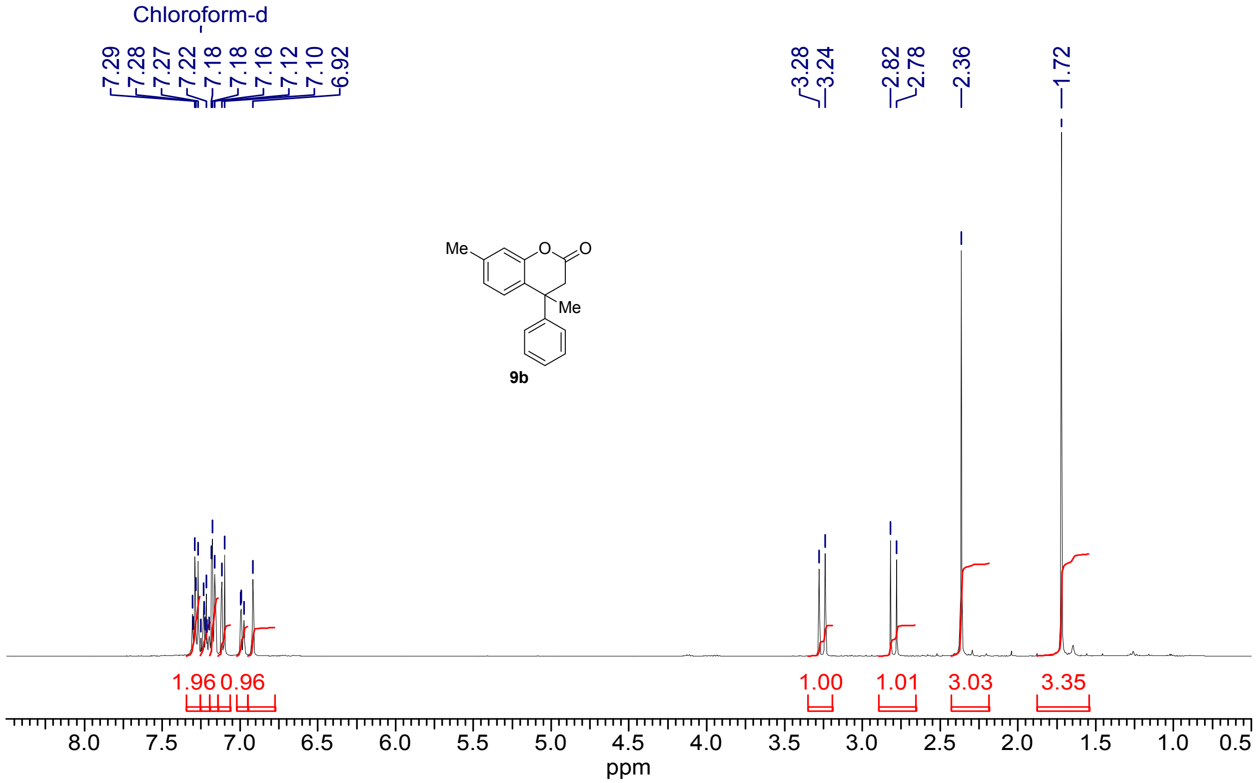
^{13}C NMR (100 MHz) spectrum of **7l** in $CDCl_3$



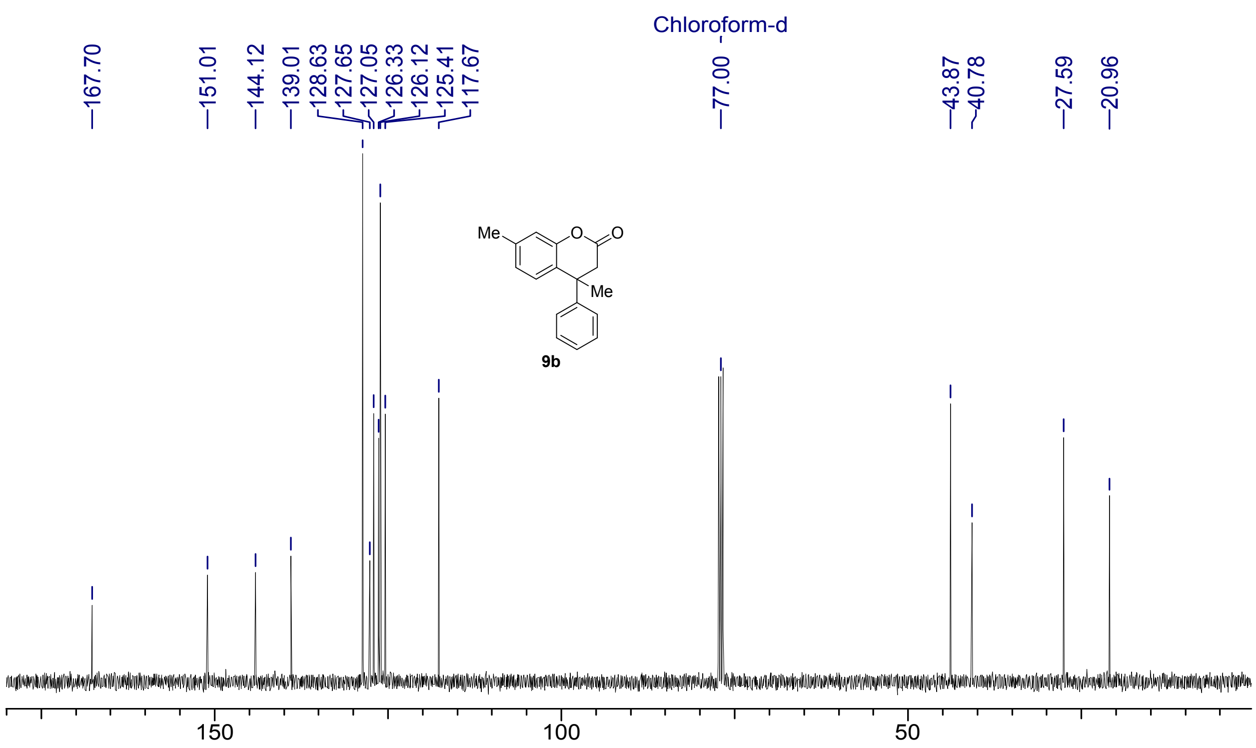
[1]H NMR (400 MHz) spectrum of **9a** in $CDCl_3$



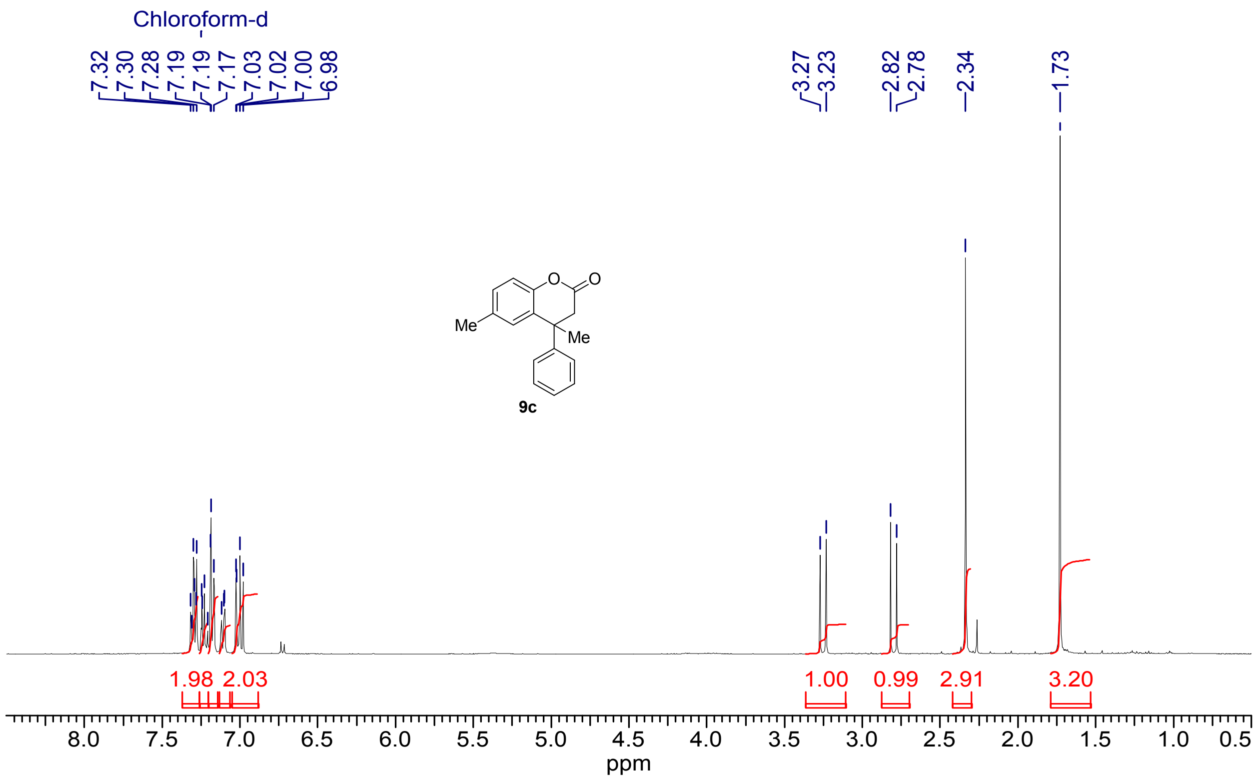
[13]C NMR (100 MHz) spectrum of **9a** in $CDCl_3$



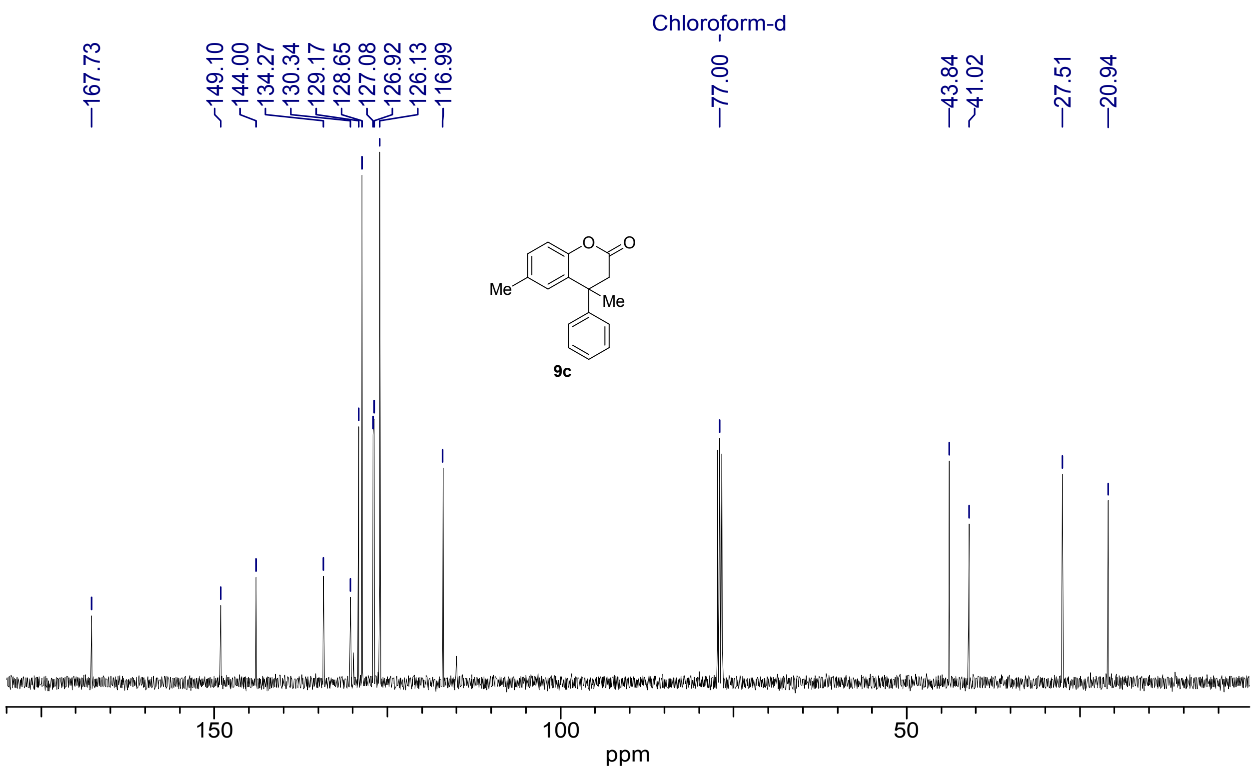
[1]H NMR (400 MHz) spectrum of **9b** in $CDCl_3$



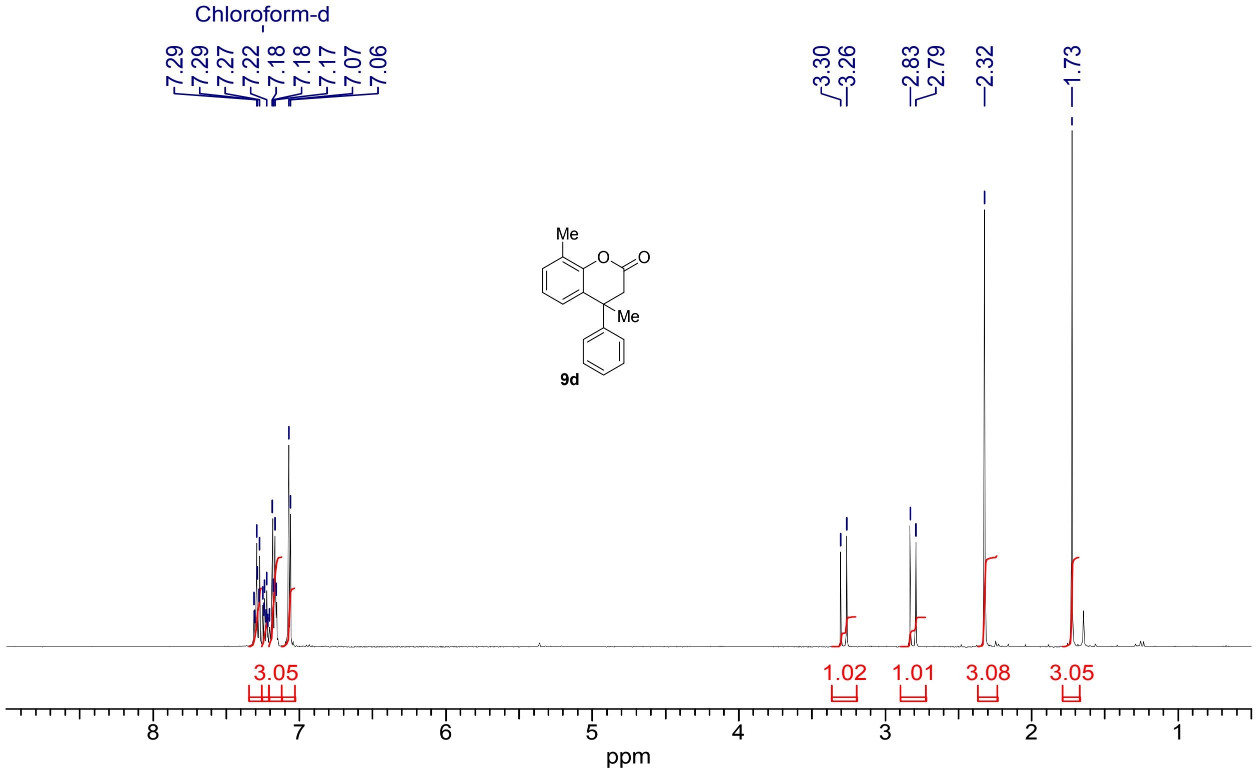
[13]C NMR (100 MHz) spectrum of **9b** in $CDCl_3$



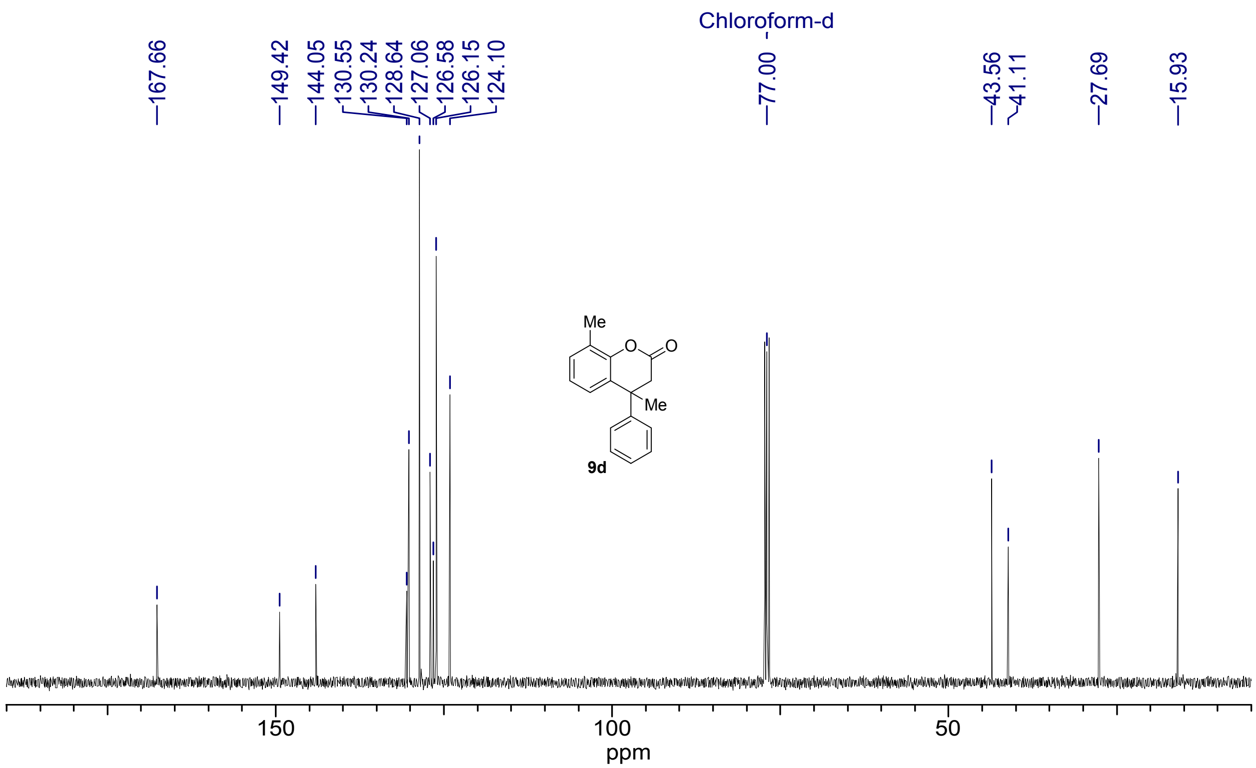
^{1}H NMR (400 MHz) spectrum of **9c** in $CDCl_3$



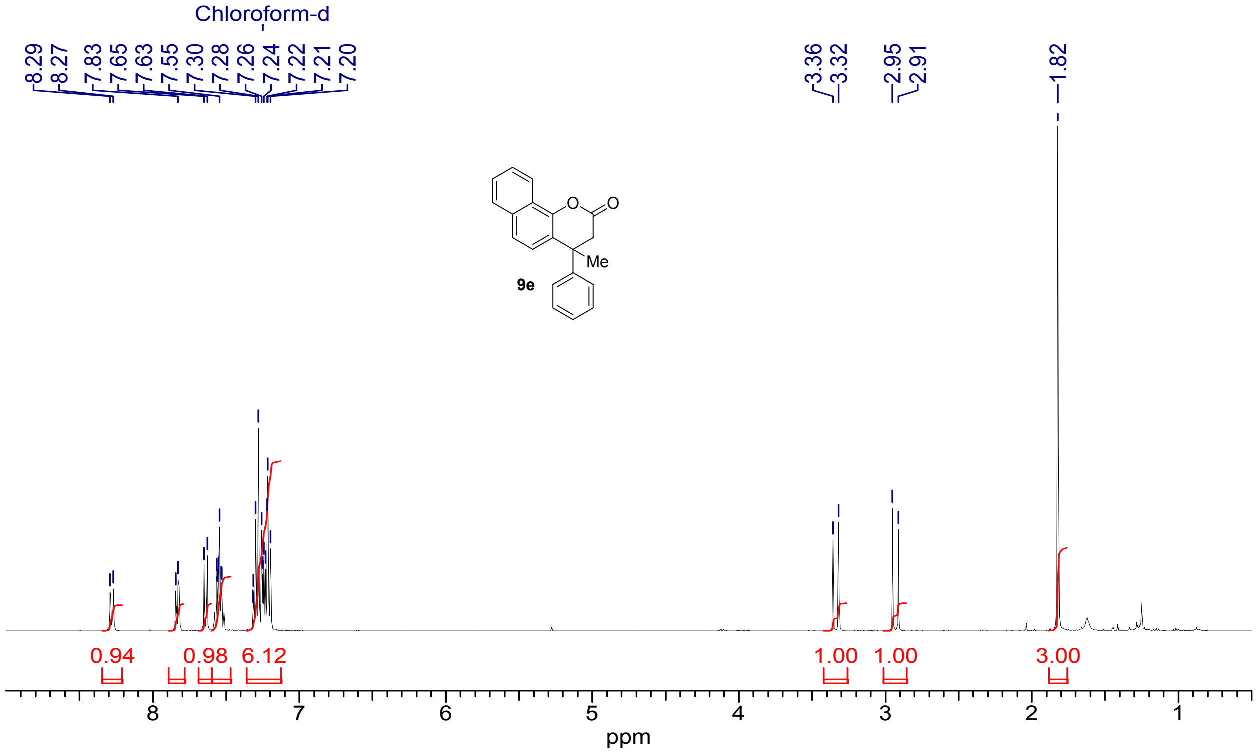
^{13}C NMR (100 MHz) spectrum of **9c** in $CDCl_3$



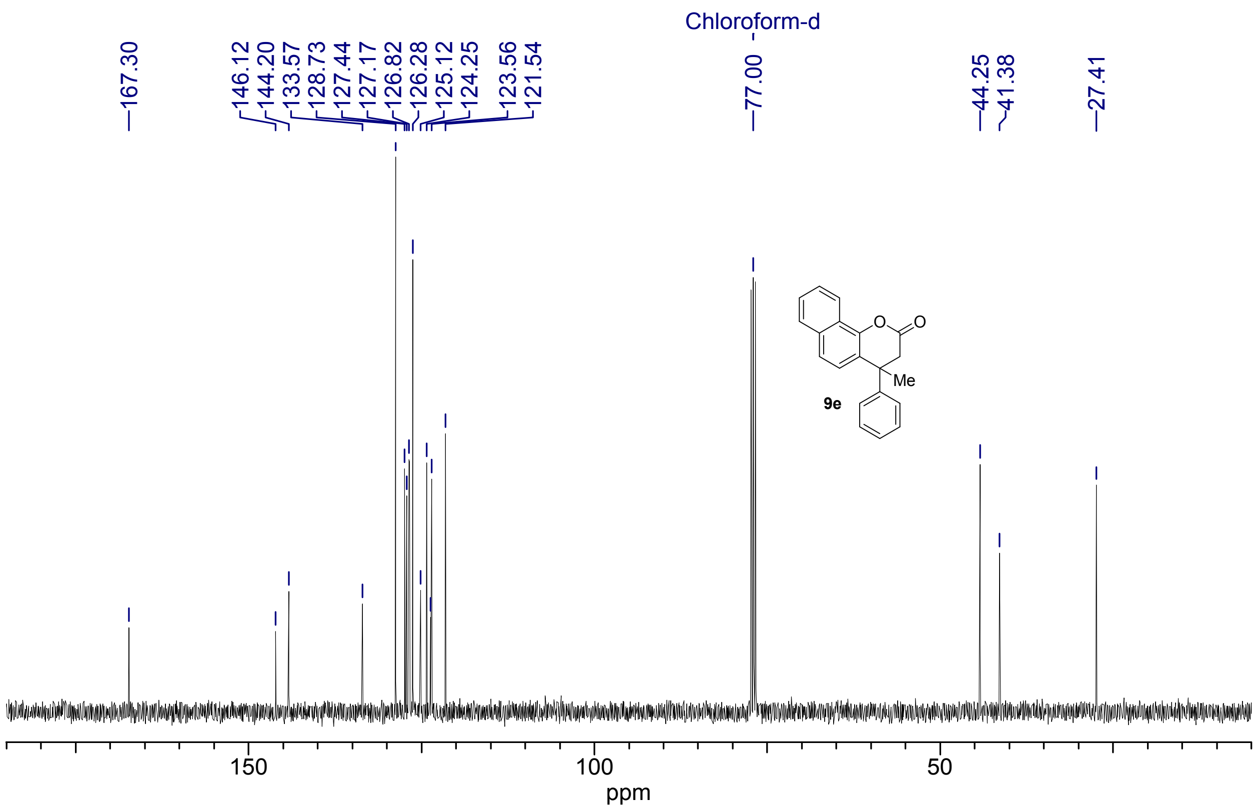
^{1}H NMR (400 MHz) spectrum of **9d** in $CDCl_3$



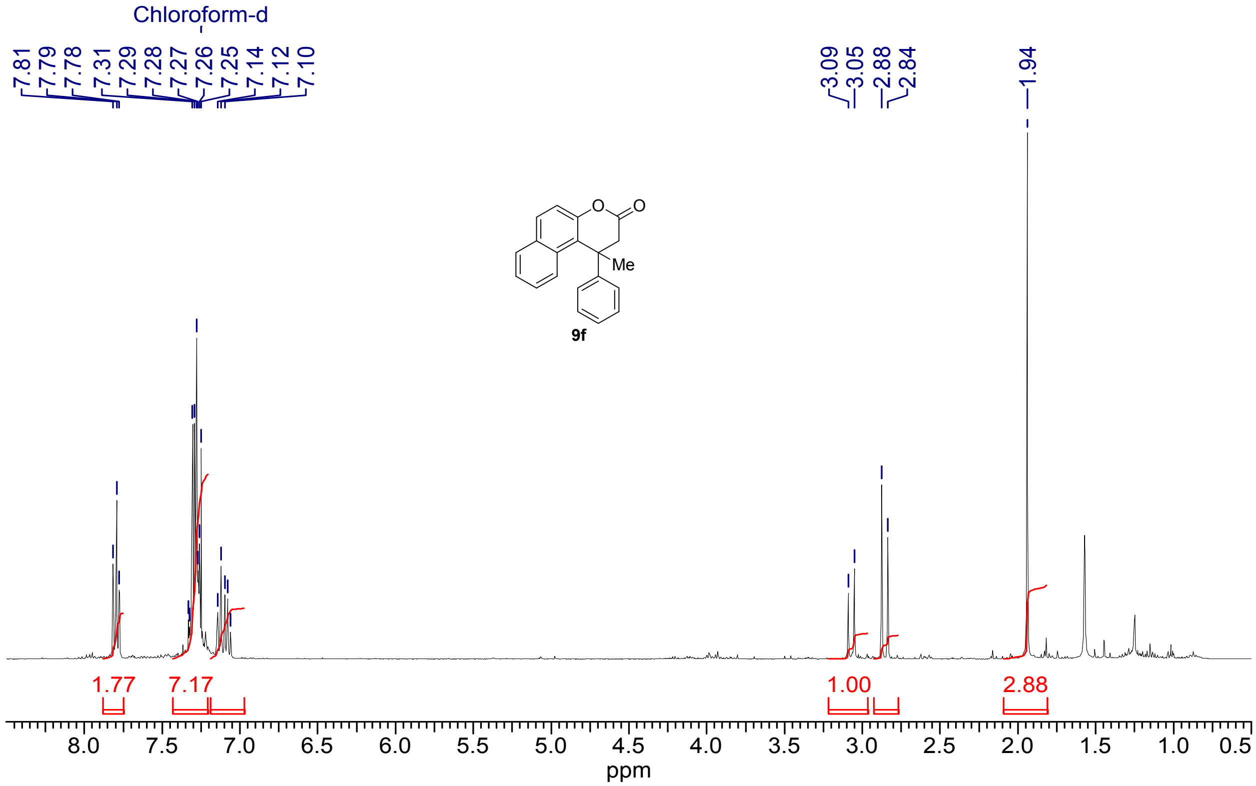
^{13}C NMR (100 MHz) spectrum of **9d** in $CDCl_3$



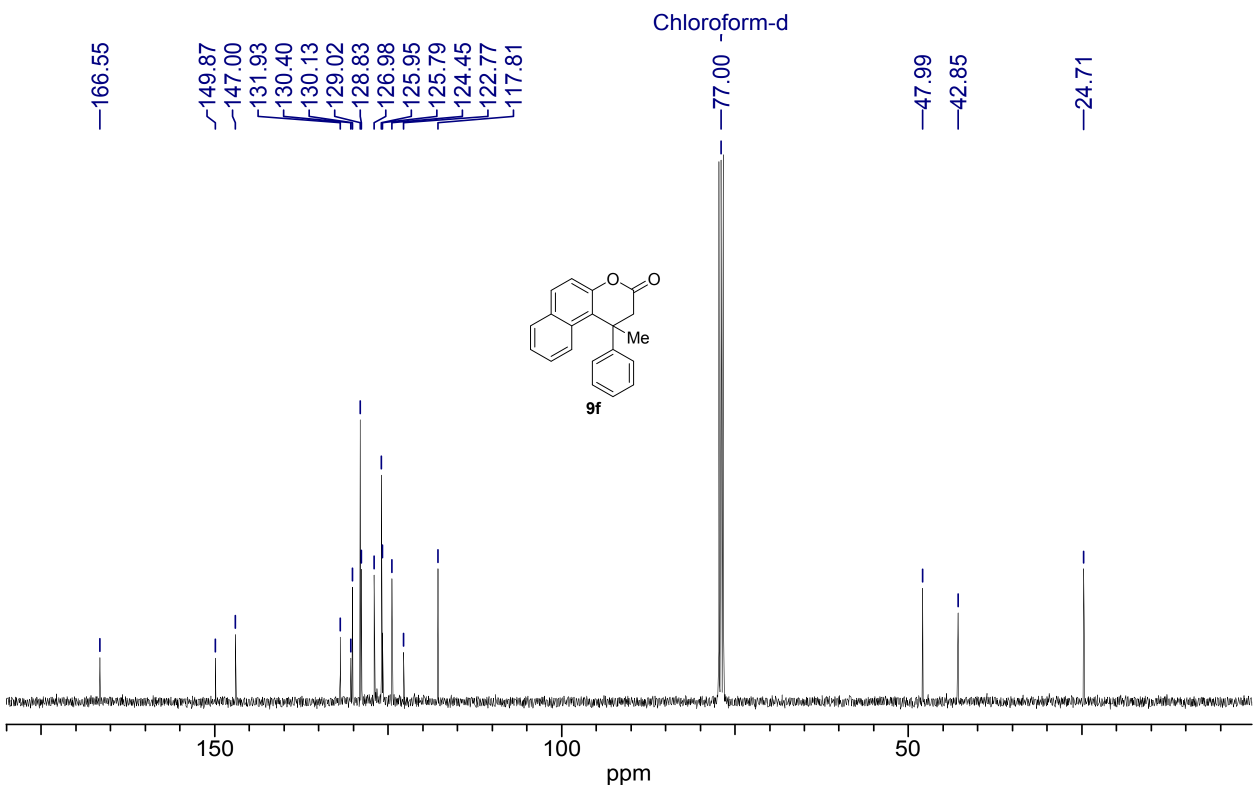
^{1}H NMR (400 MHz) spectrum of **9e** in $CDCl_3$



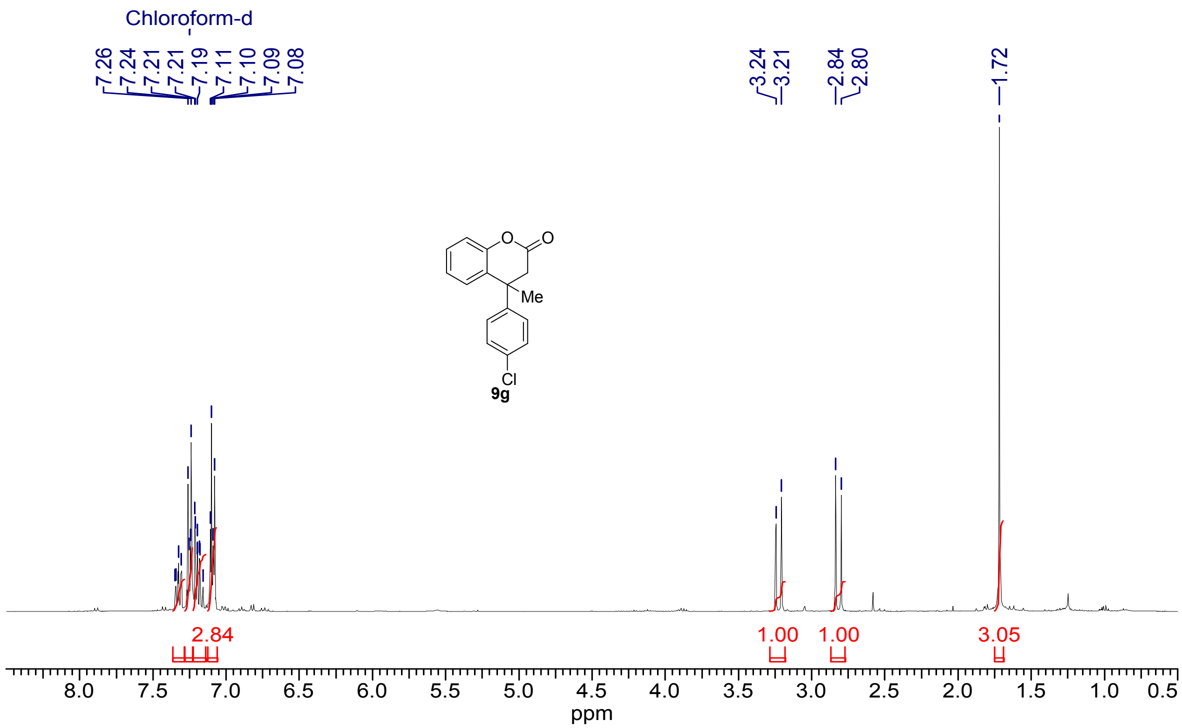
^{13}C NMR (100 MHz) spectrum of **9e** in $CDCl_3$



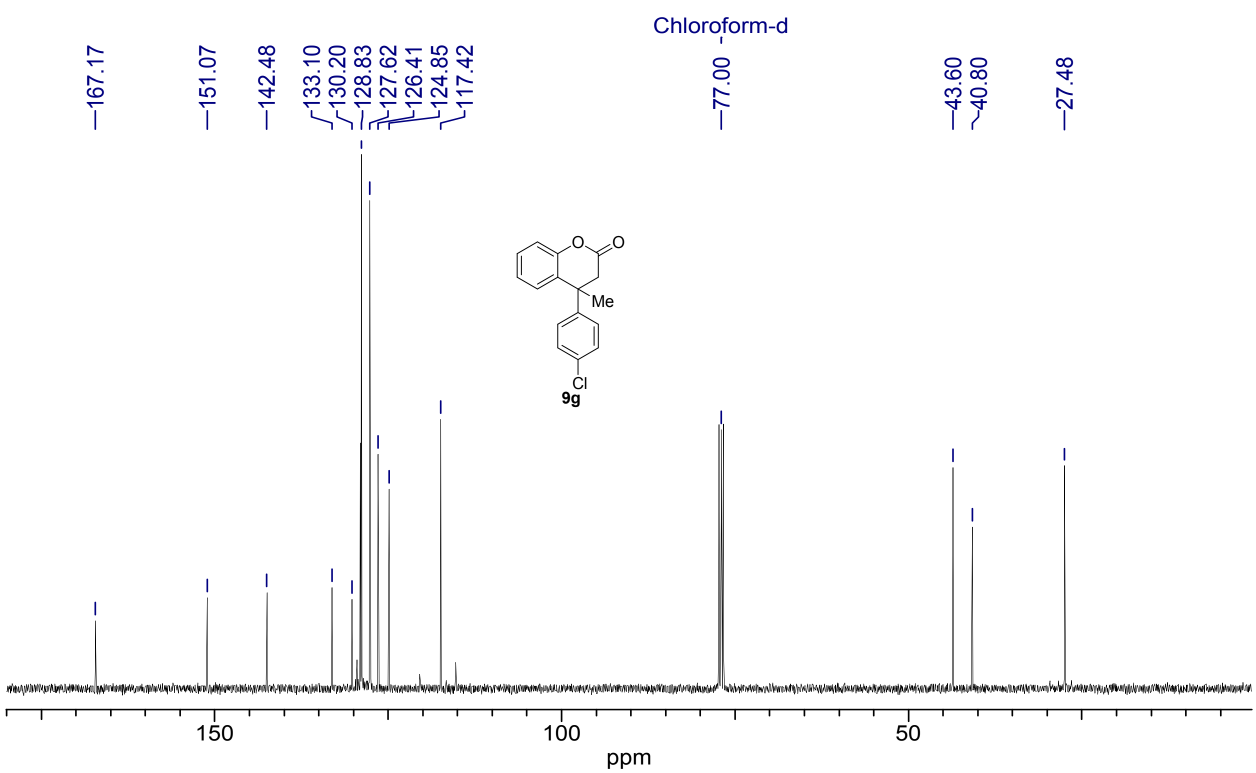
[1]H NMR (400 MHz) spectrum of **9f** in $CDCl_3$



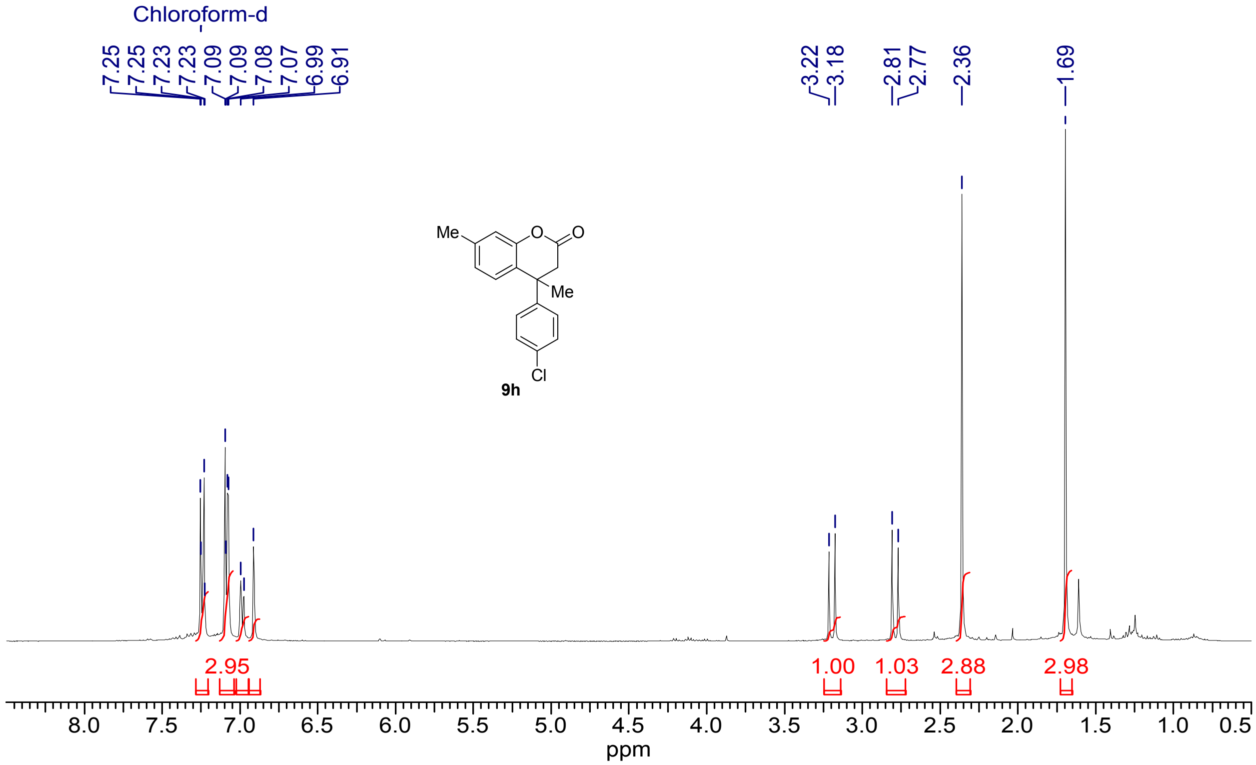
[13]C NMR (100 MHz) spectrum of **9f** in $CDCl_3$



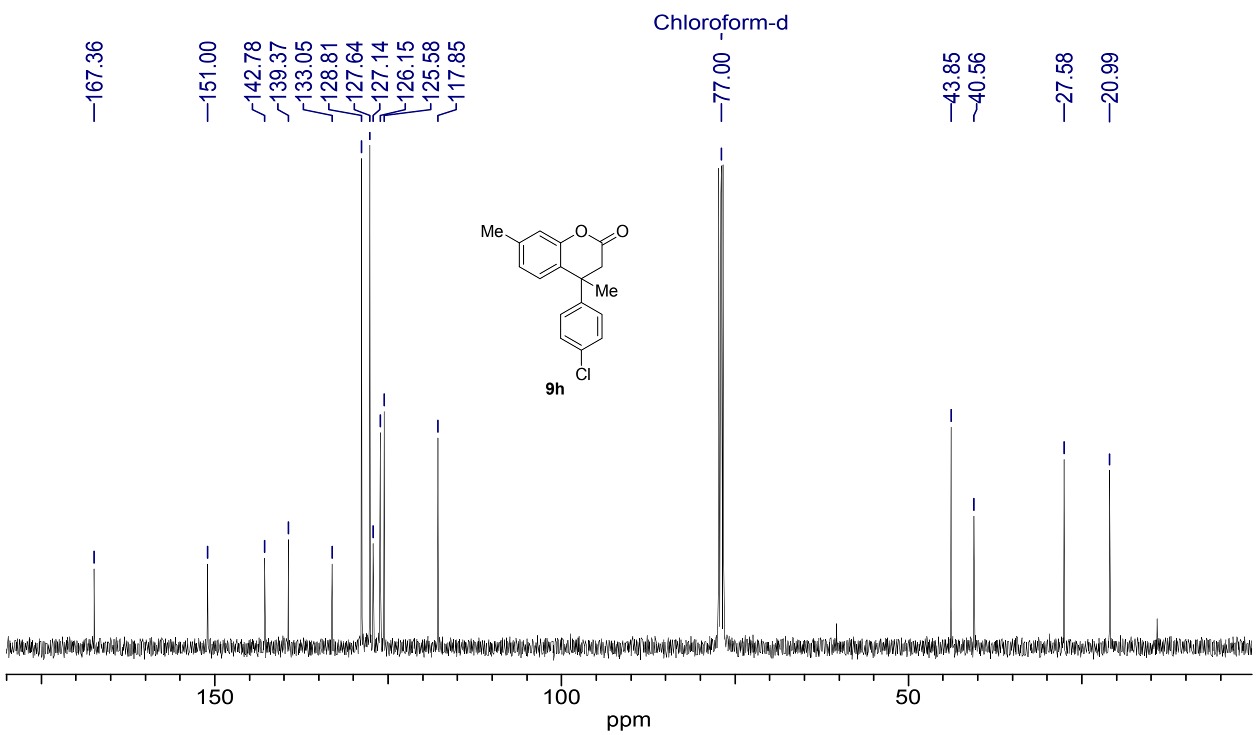
[1]H NMR (400 MHz) spectrum of **9g** in $CDCl_3$



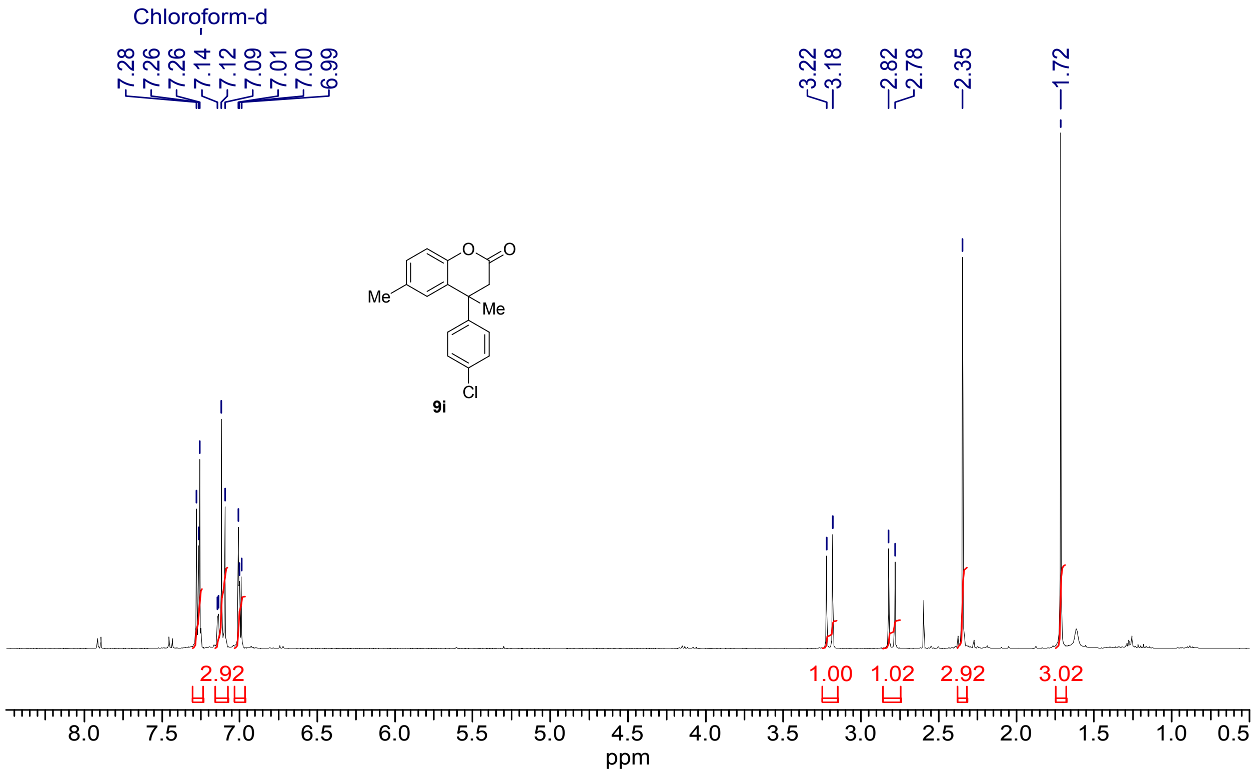
[13]C NMR (100 MHz) spectrum of **9g** in $CDCl_3$



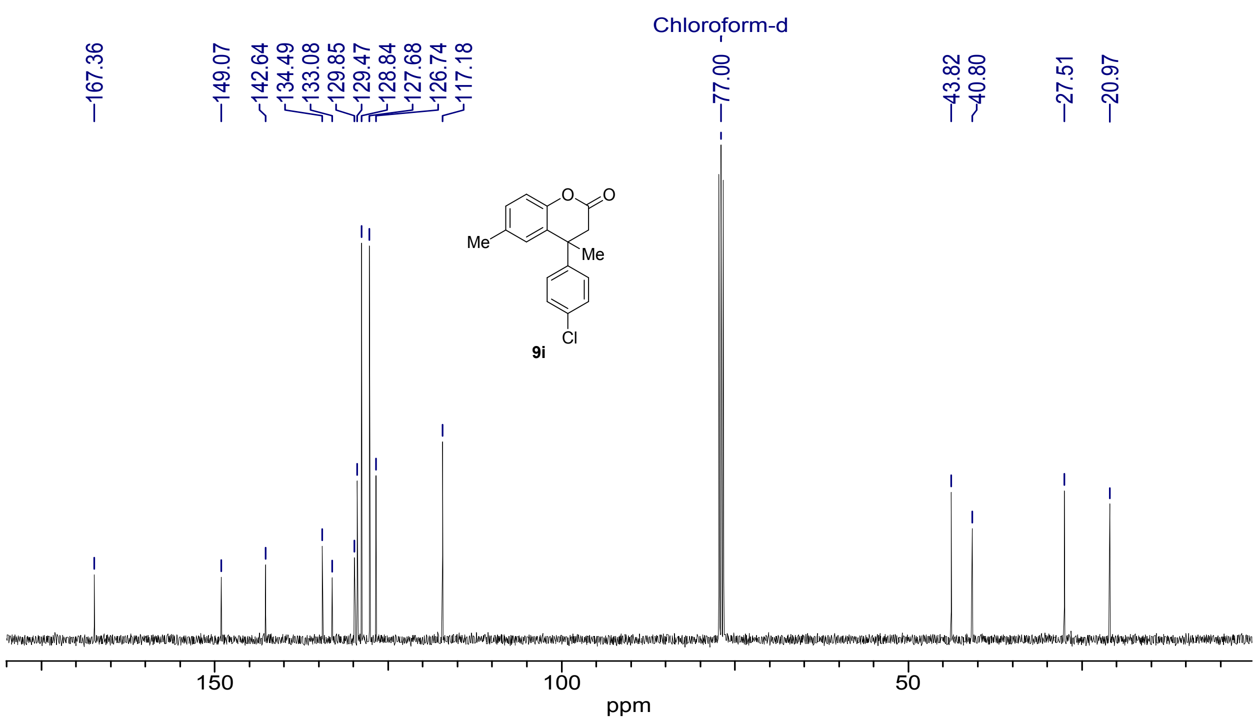
[1]H NMR (400 MHz) spectrum of **9h** in $CDCl_3$



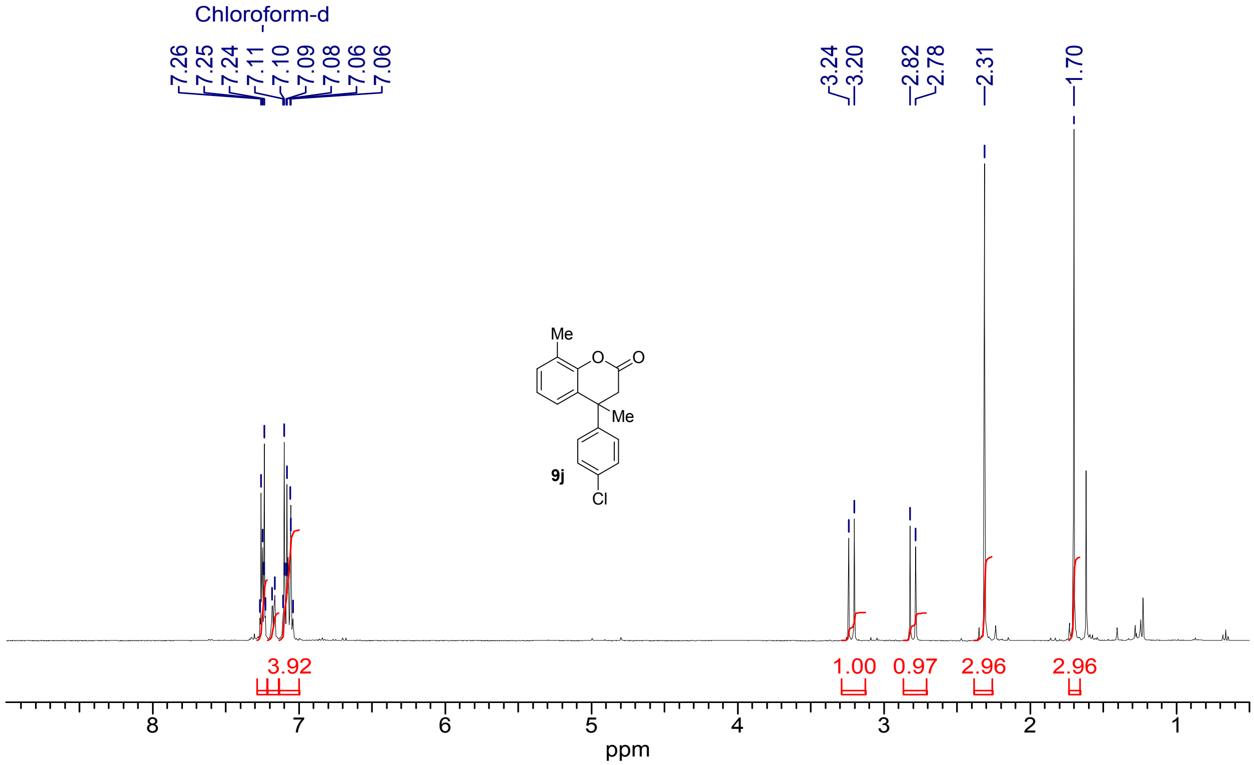
[13]C NMR (100 MHz) spectrum of **9h** in $CDCl_3$



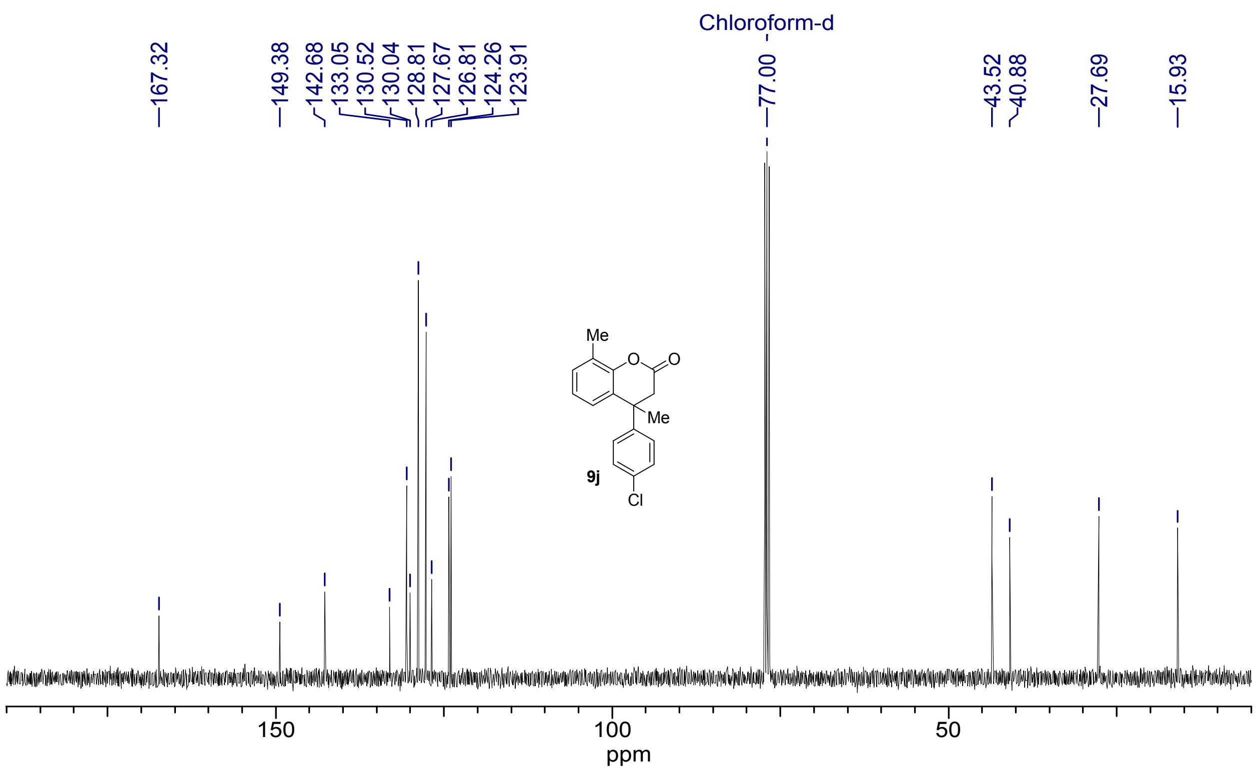
^{1}H NMR (400 MHz) spectrum of **9i** in $CDCl_3$



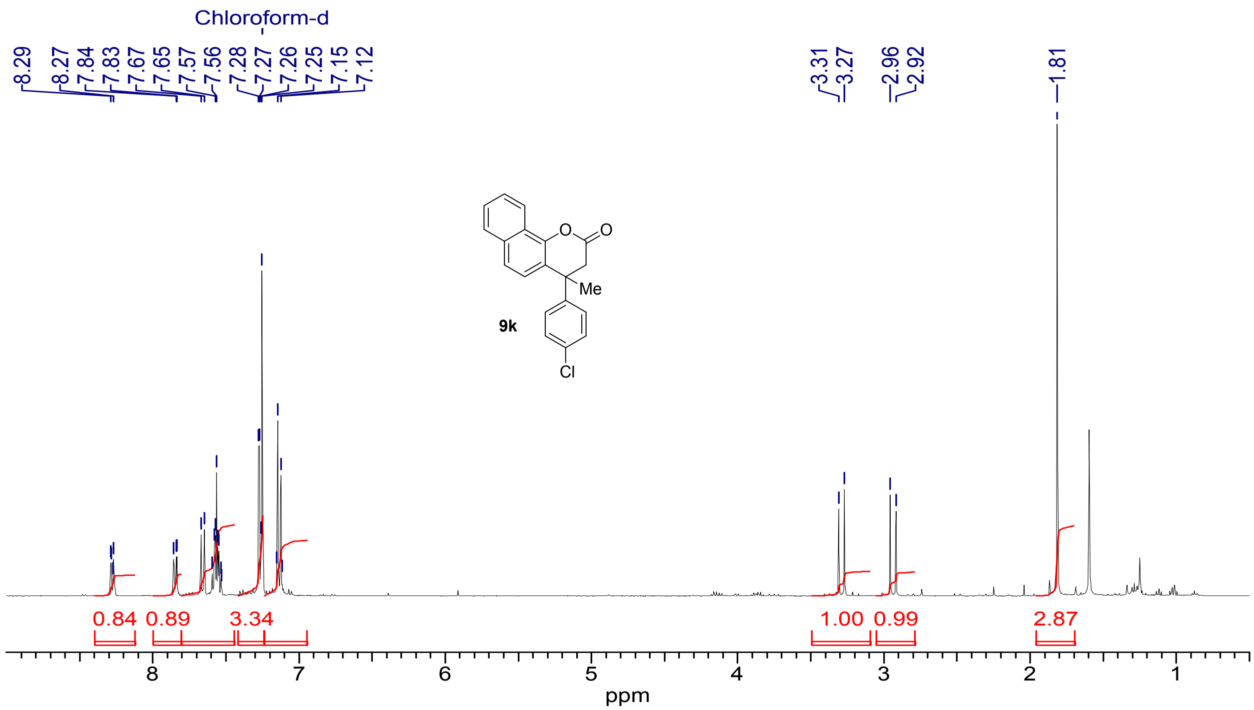
^{13}C NMR (100 MHz) spectrum of **9i** in $CDCl_3$



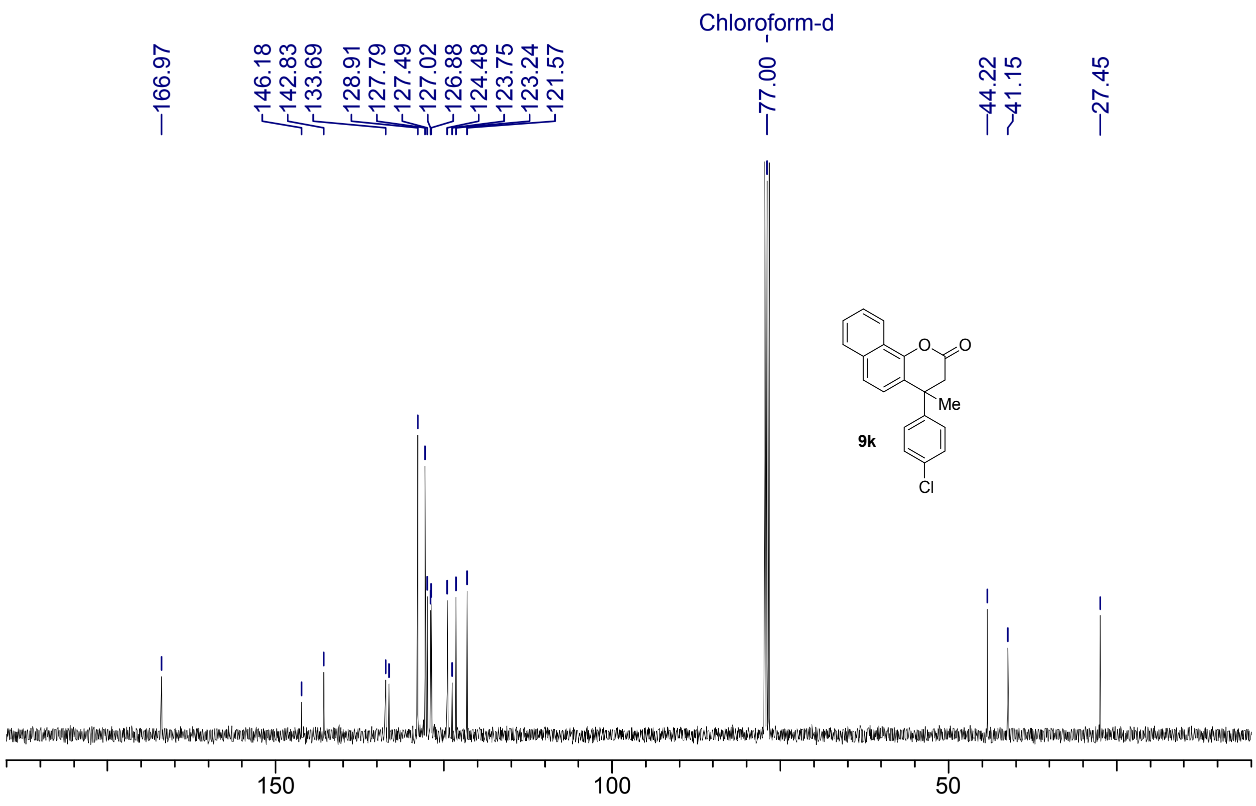
^{1}H NMR (400 MHz) spectrum of **9j** in $CDCl_3$



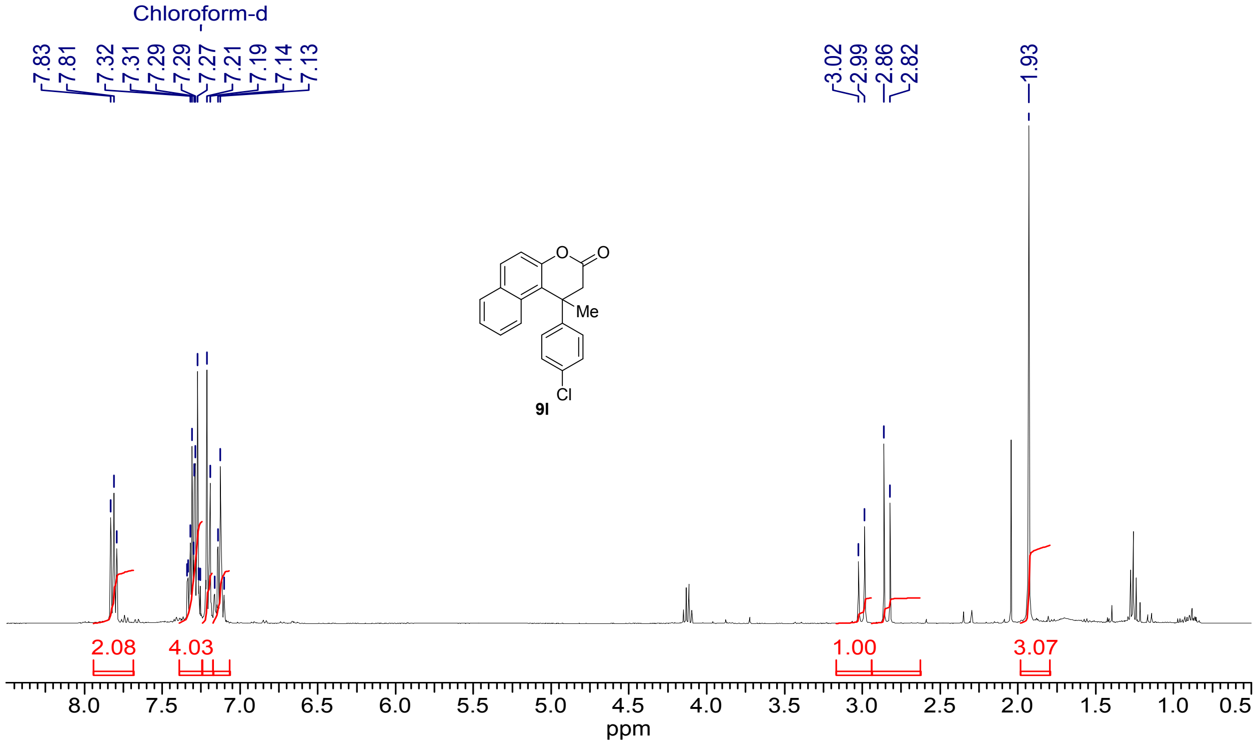
^{13}C NMR (100 MHz) spectrum of **9j** in $CDCl_3$



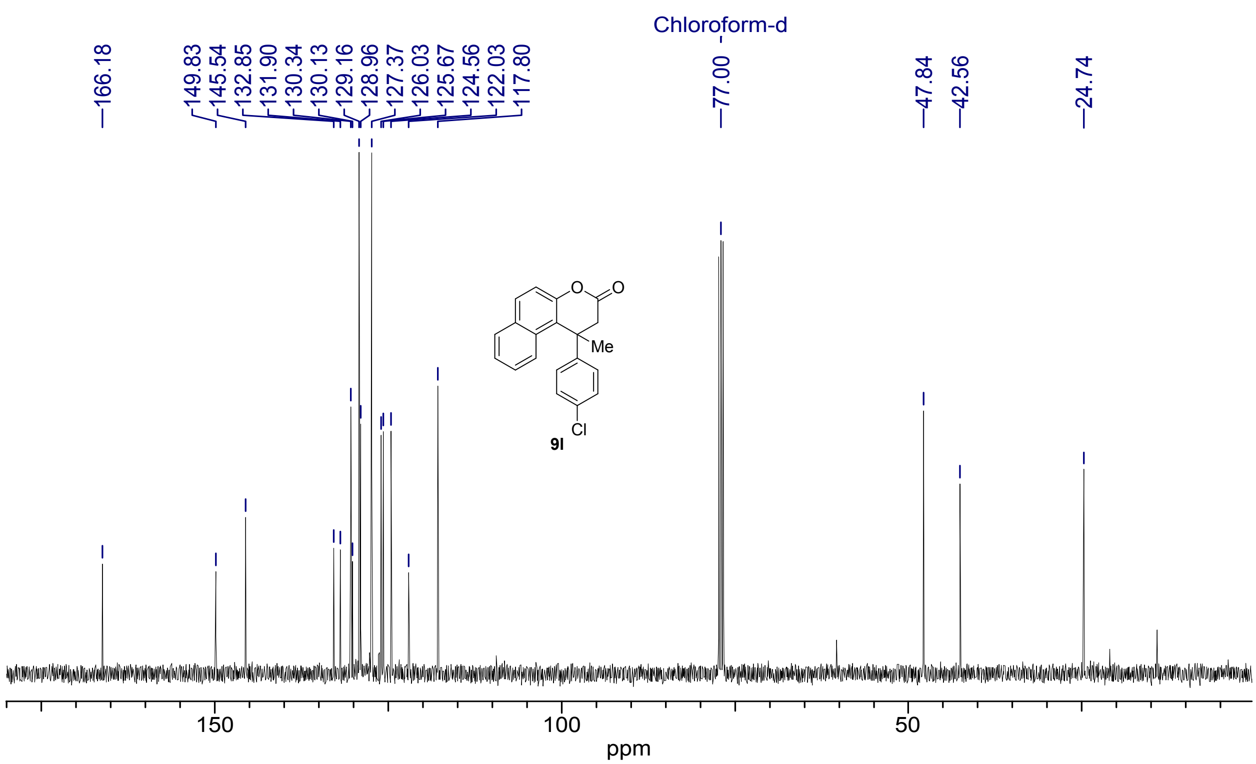
^{1}H NMR (400 MHz) spectrum of **9k** in $CDCl_3$



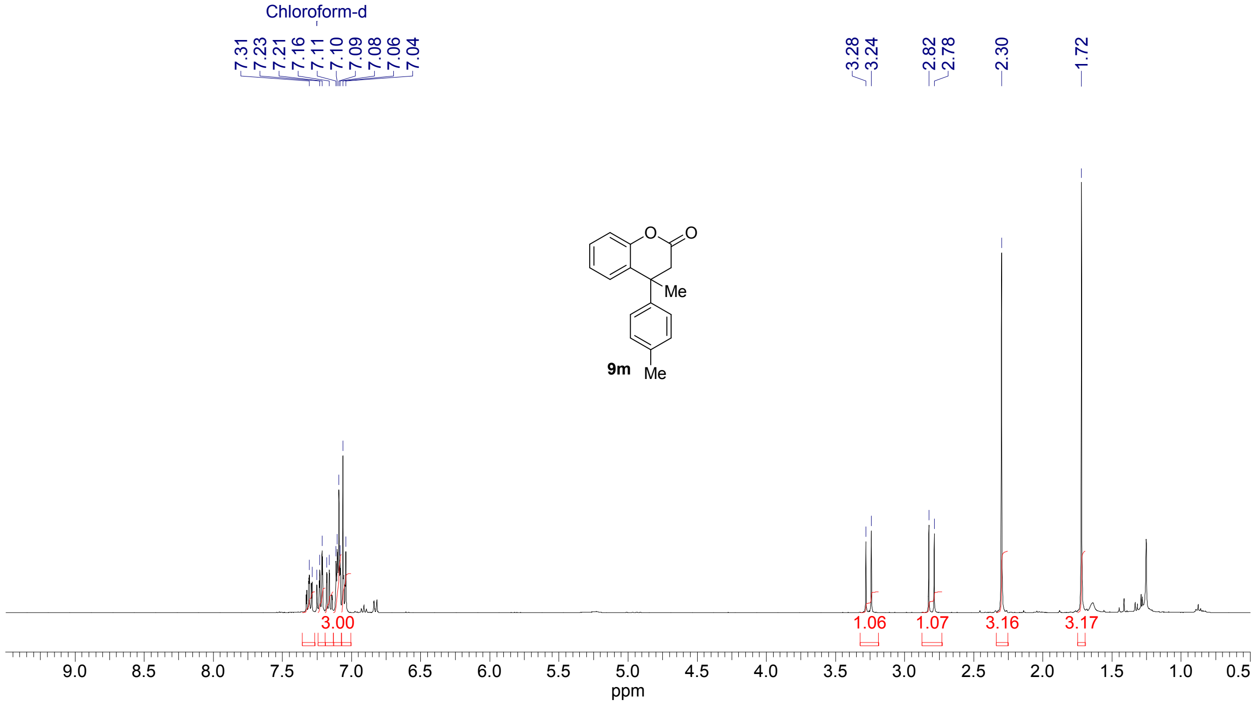
^{13}C NMR (100 MHz) spectrum of **9k** in $CDCl_3$



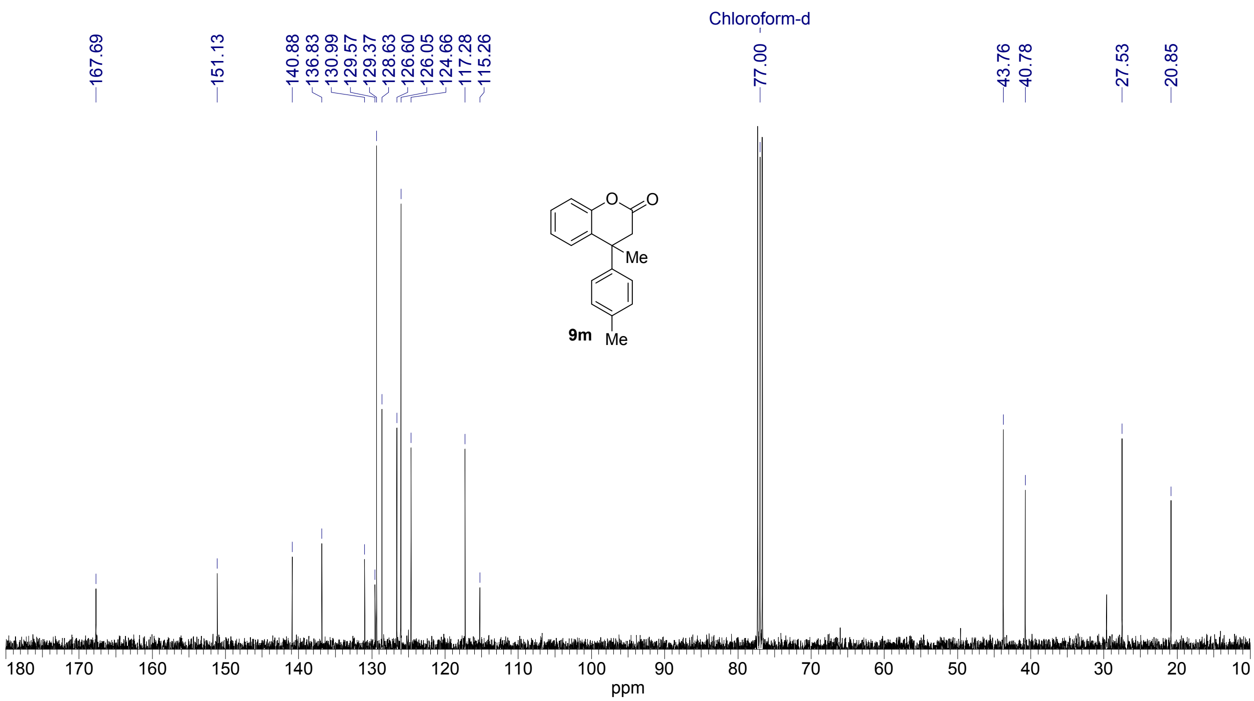
^{1}H NMR (400 MHz) spectrum of **9l** in $CDCl_3$



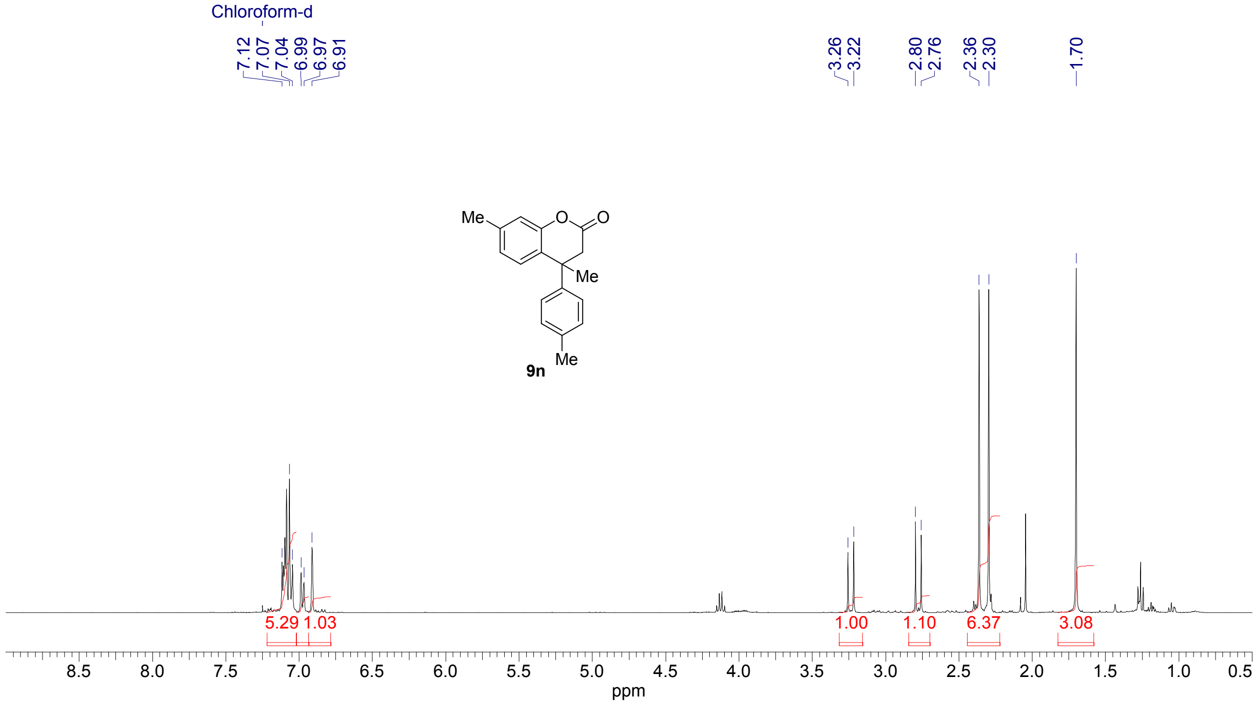
^{13}C NMR (100 MHz) spectrum of **9l** in $CDCl_3$



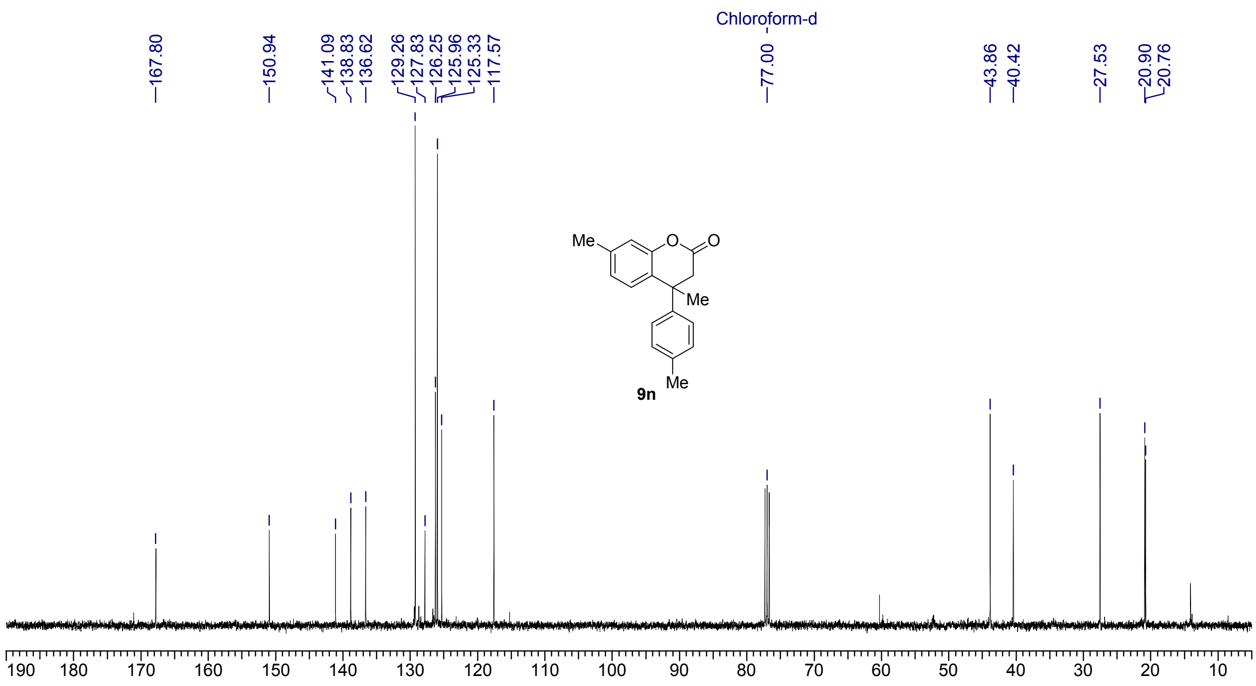
[1]H NMR (400 MHz) spectrum of **9m** in $CDCl_3$



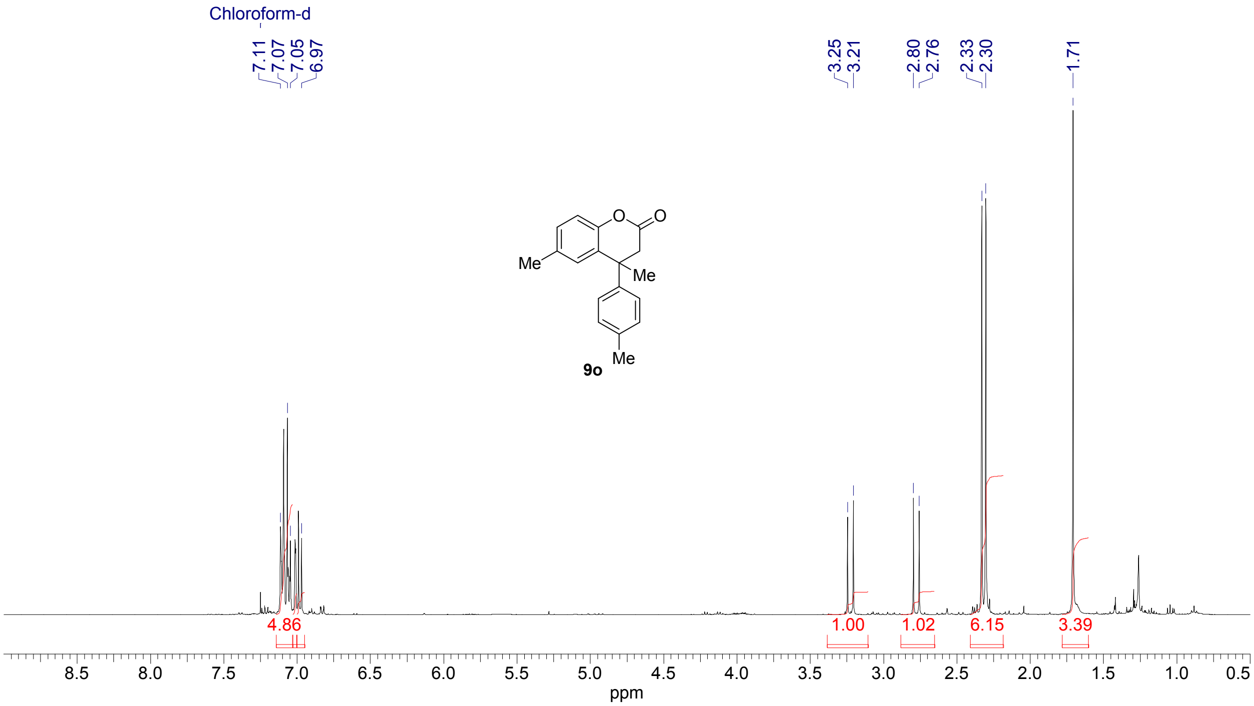
[13]C NMR (100 MHz) spectrum of **9m** in $CDCl_3$



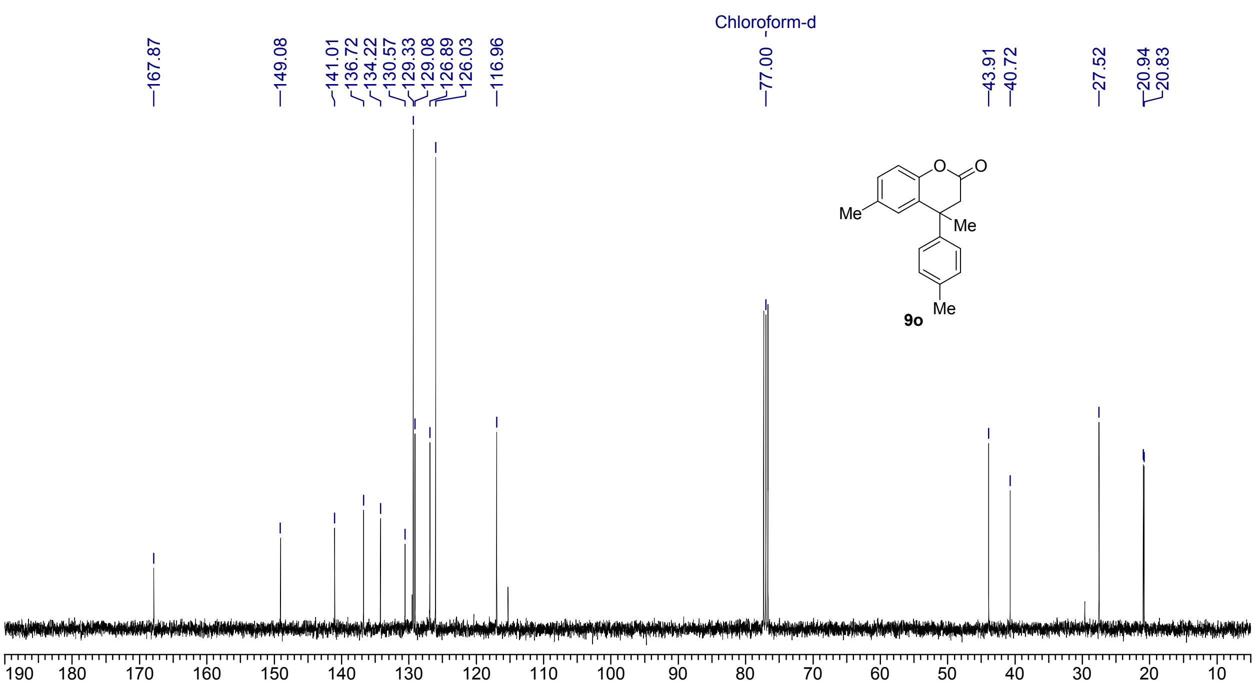
^{1}H NMR (400 MHz) spectrum of **9n** in $CDCl_3$



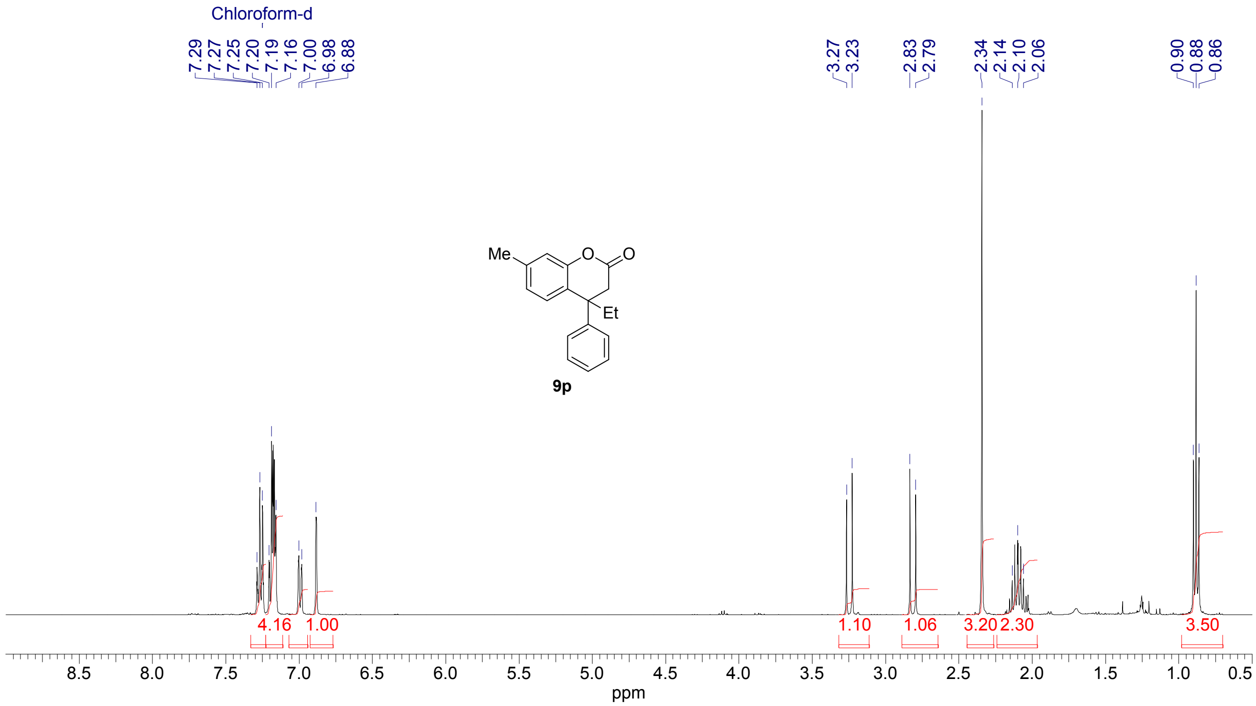
^{13}C NMR (100 MHz) spectrum of **9n** in $CDCl_3$



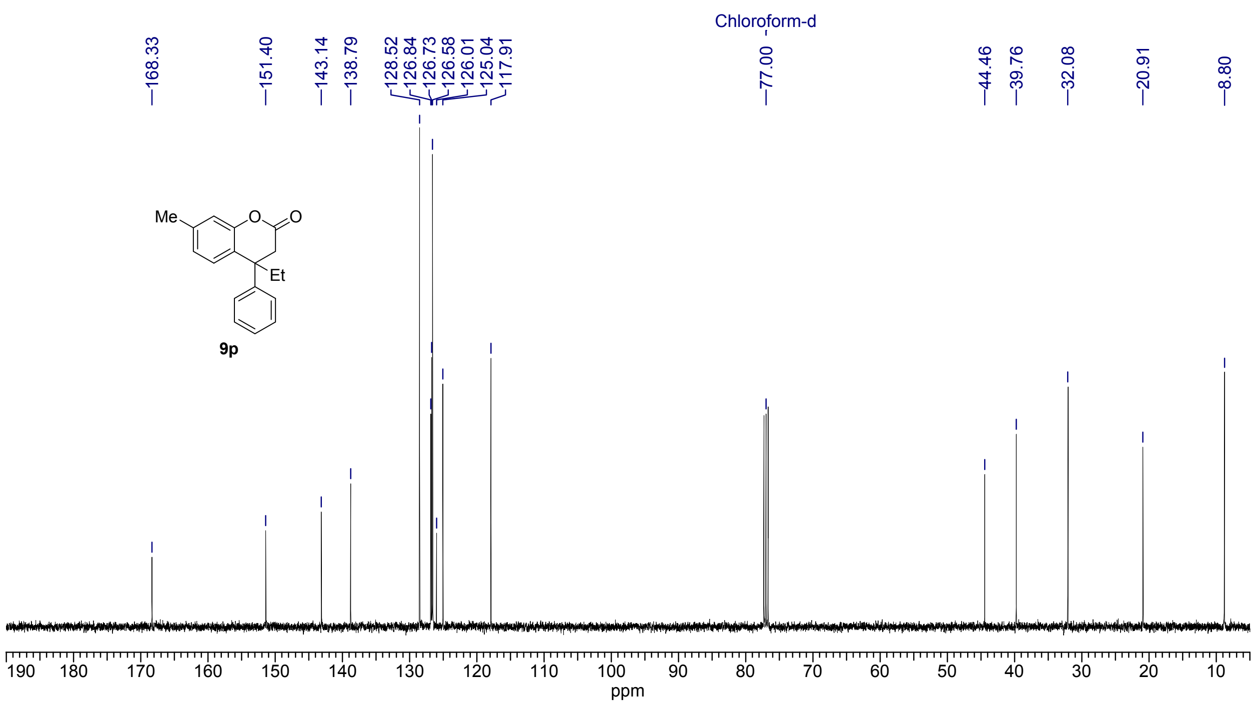
^{1}H NMR (400 MHz) spectrum of **9o** in $CDCl_3$



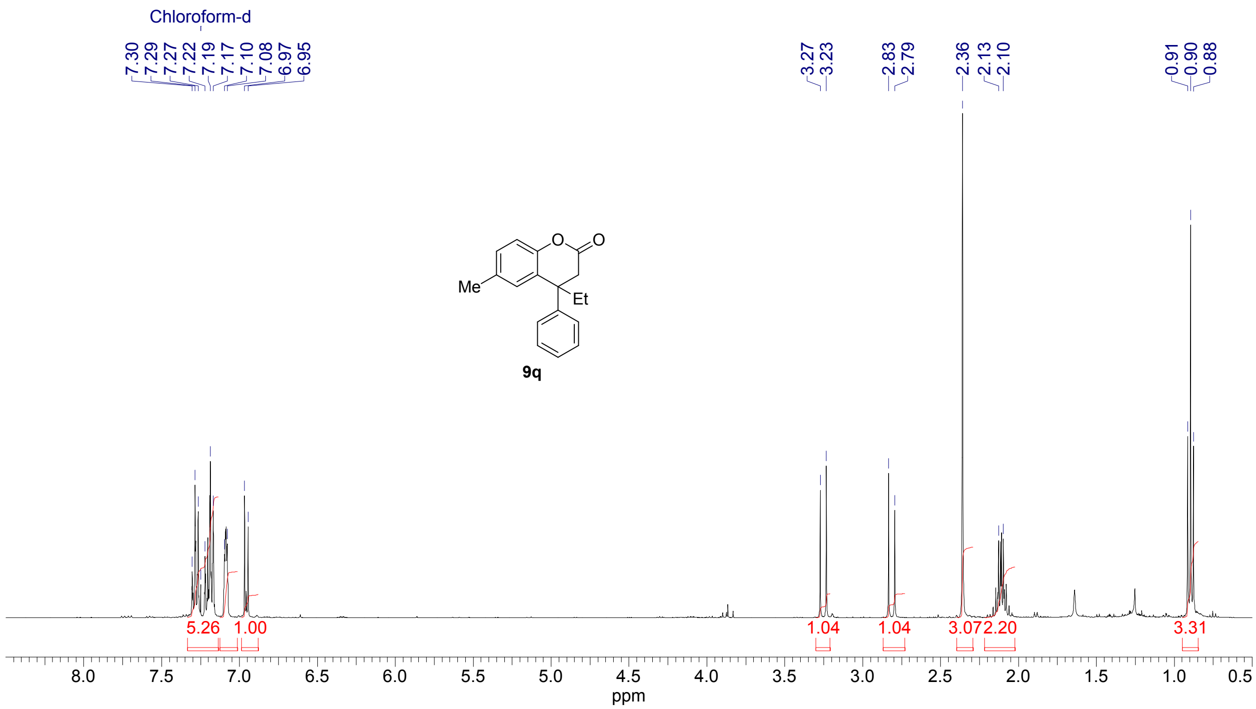
^{13}C NMR (100 MHz) spectrum of **9o** in $CDCl_3$



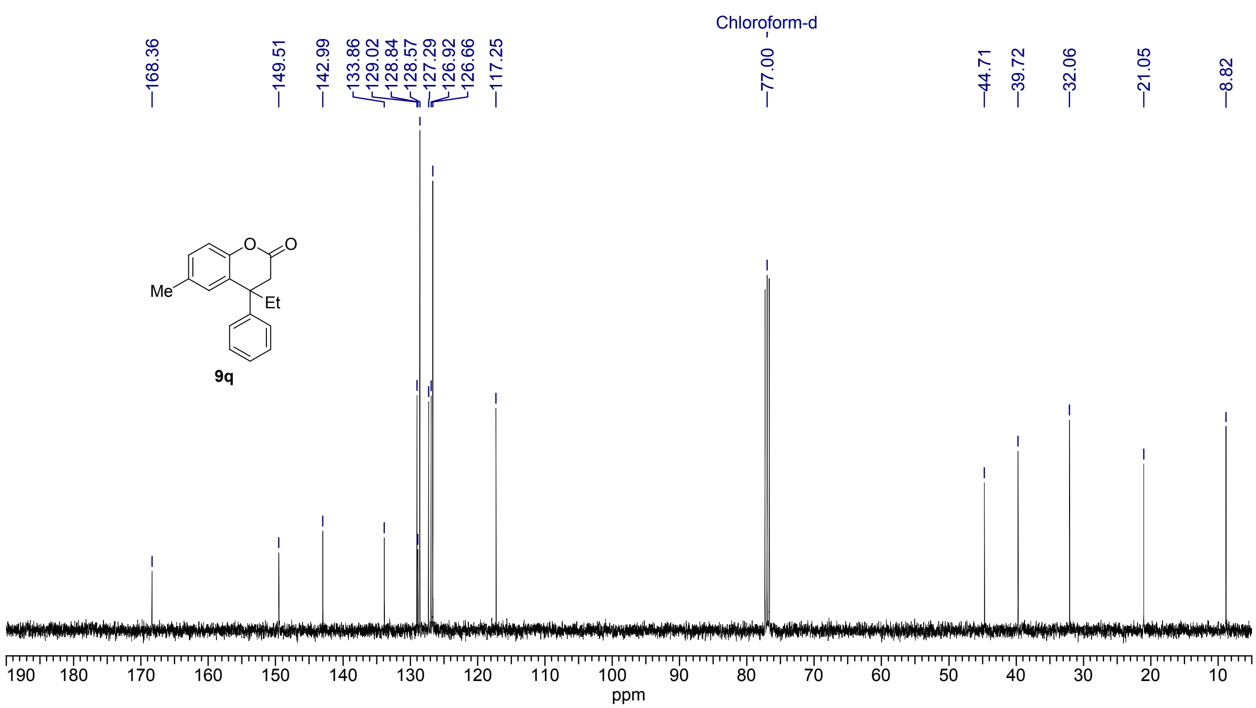
^{1}H NMR (400 MHz) spectrum of **9p** in $CDCl_3$



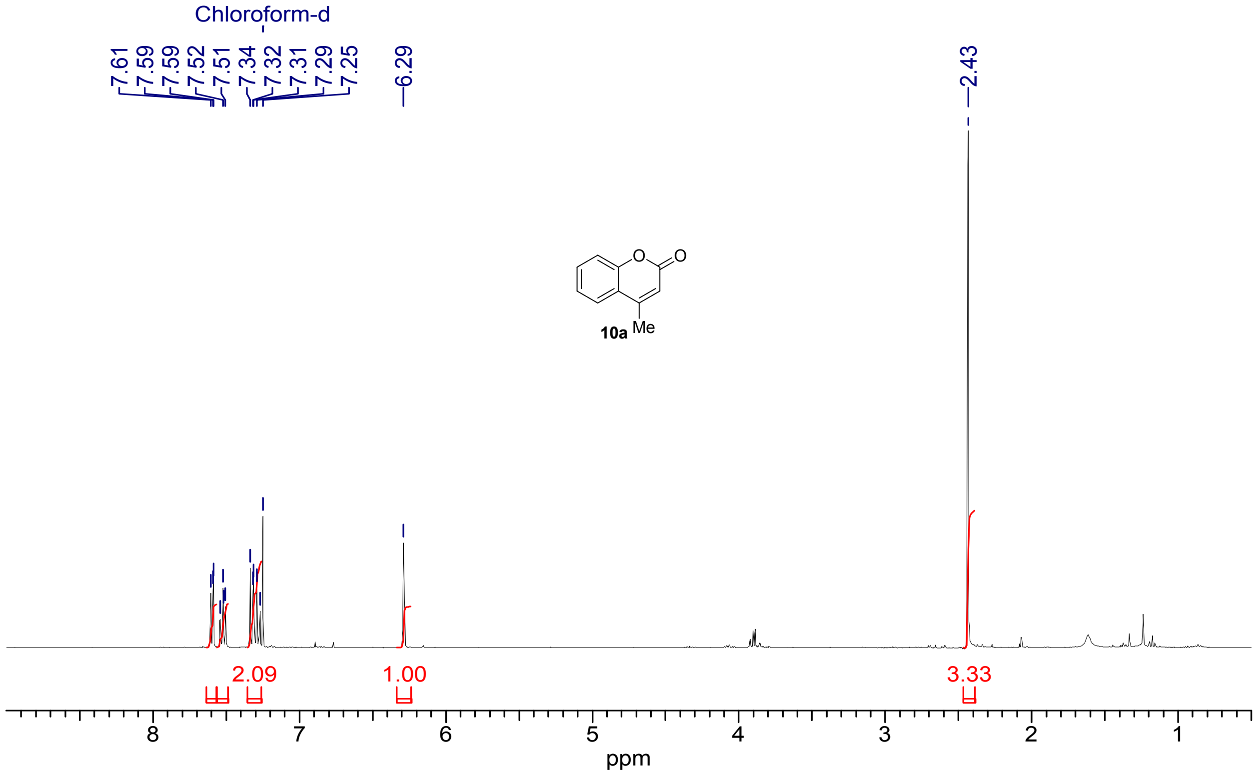
^{13}C NMR (100 MHz) spectrum of **9p** in $CDCl_3$



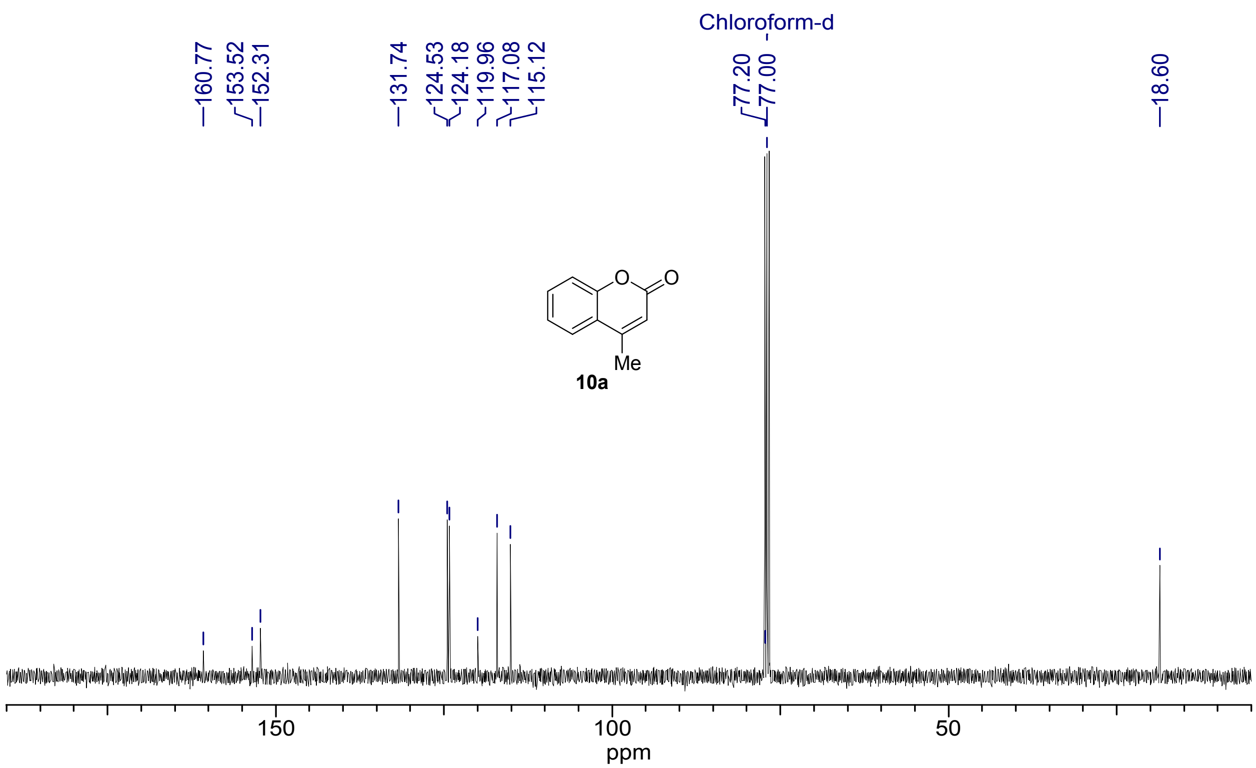
^{1}H NMR (400 MHz) spectrum of **9q** in $CDCl_3$



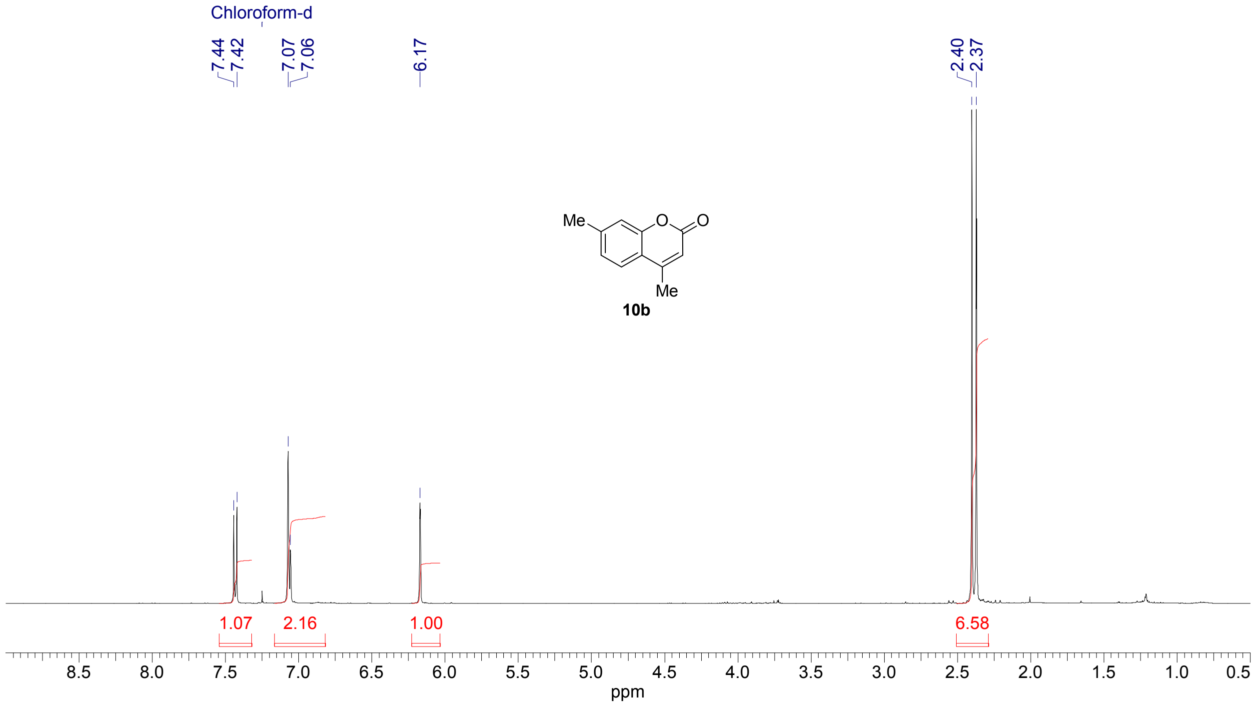
^{13}C NMR (100 MHz) spectrum of **9q** in $CDCl_3$



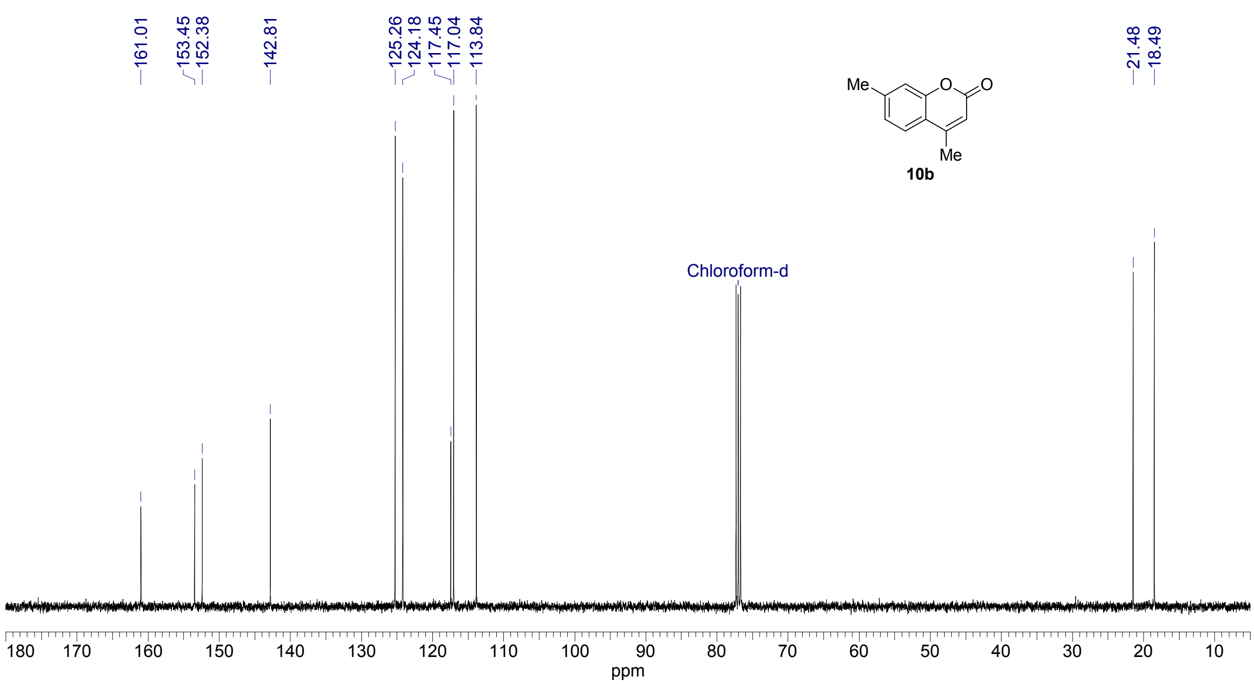
^{1}H NMR (400 MHz) spectrum of **10a** in $CDCl_3$



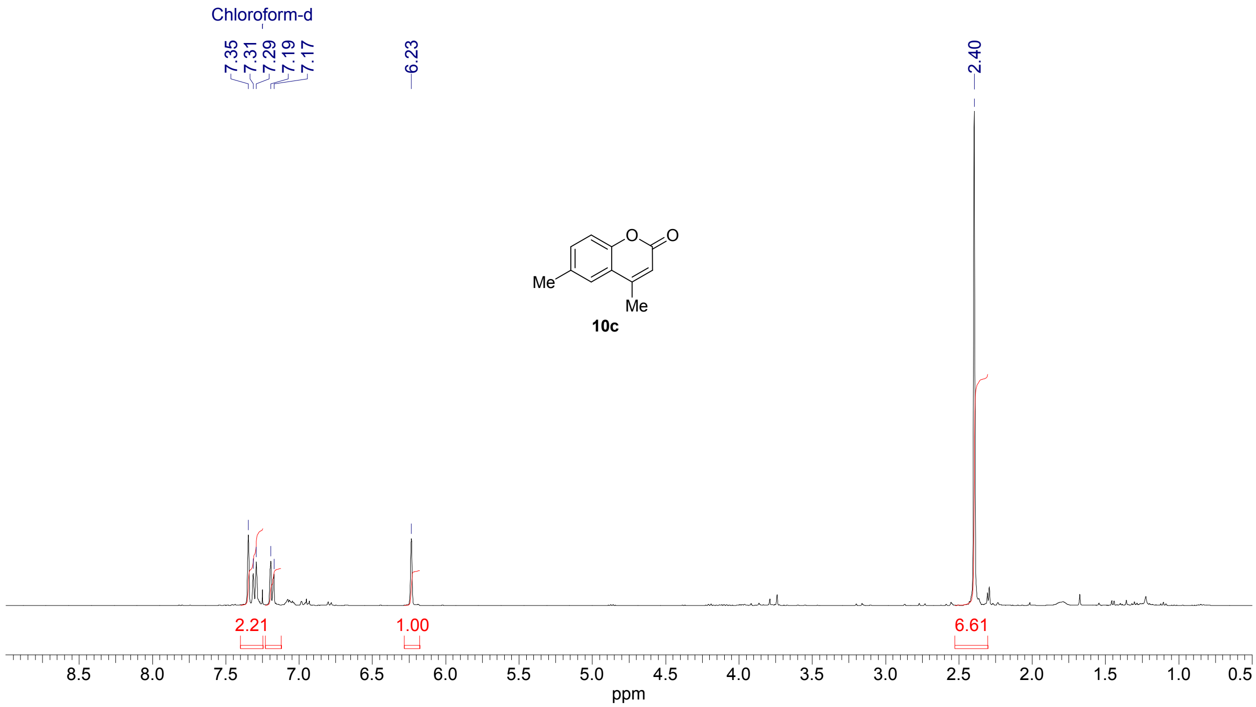
^{13}C NMR (100 MHz) spectrum of **10a** in $CDCl_3$



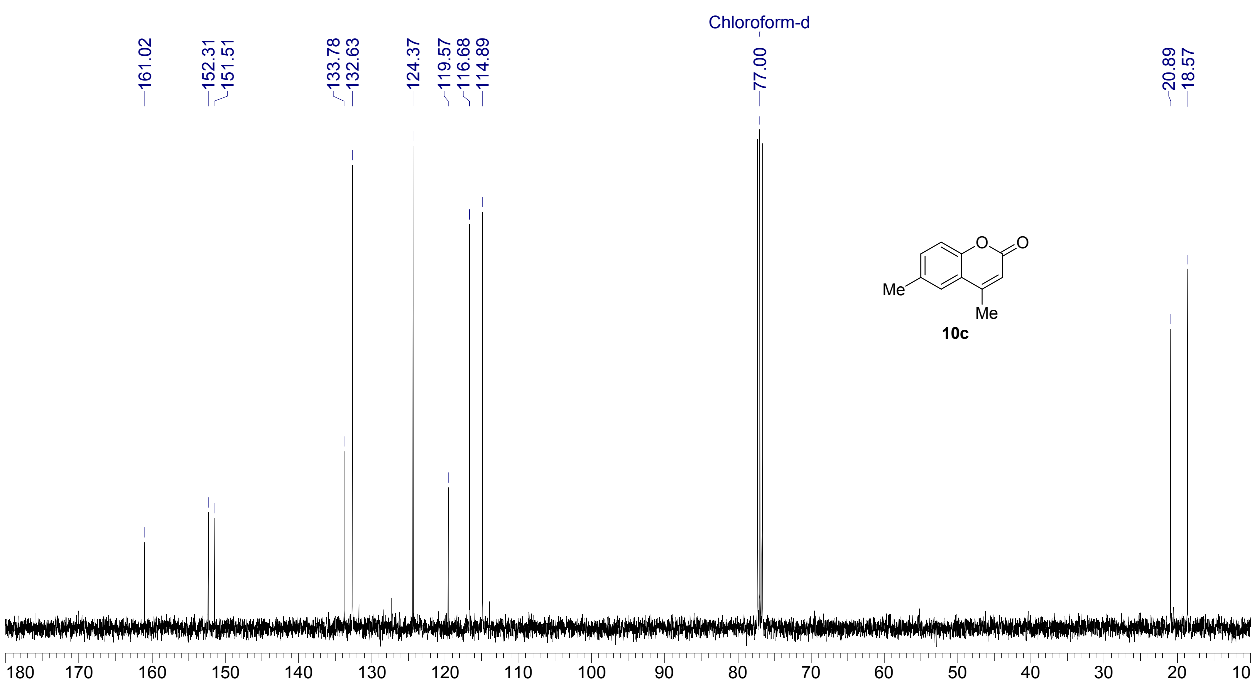
^{1}H NMR (400 MHz) spectrum of **10b** in $CDCl_3$



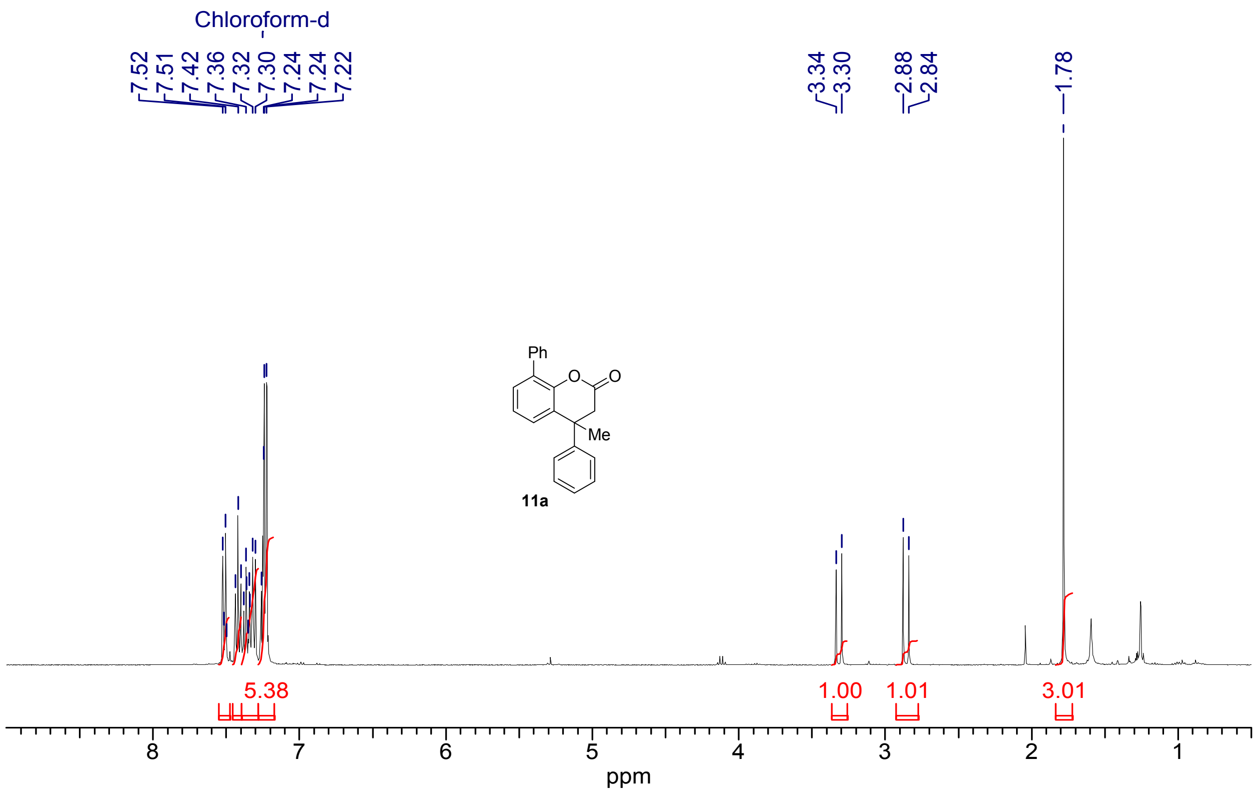
^{13}C NMR (100 MHz) spectrum of **10b** in $CDCl_3$



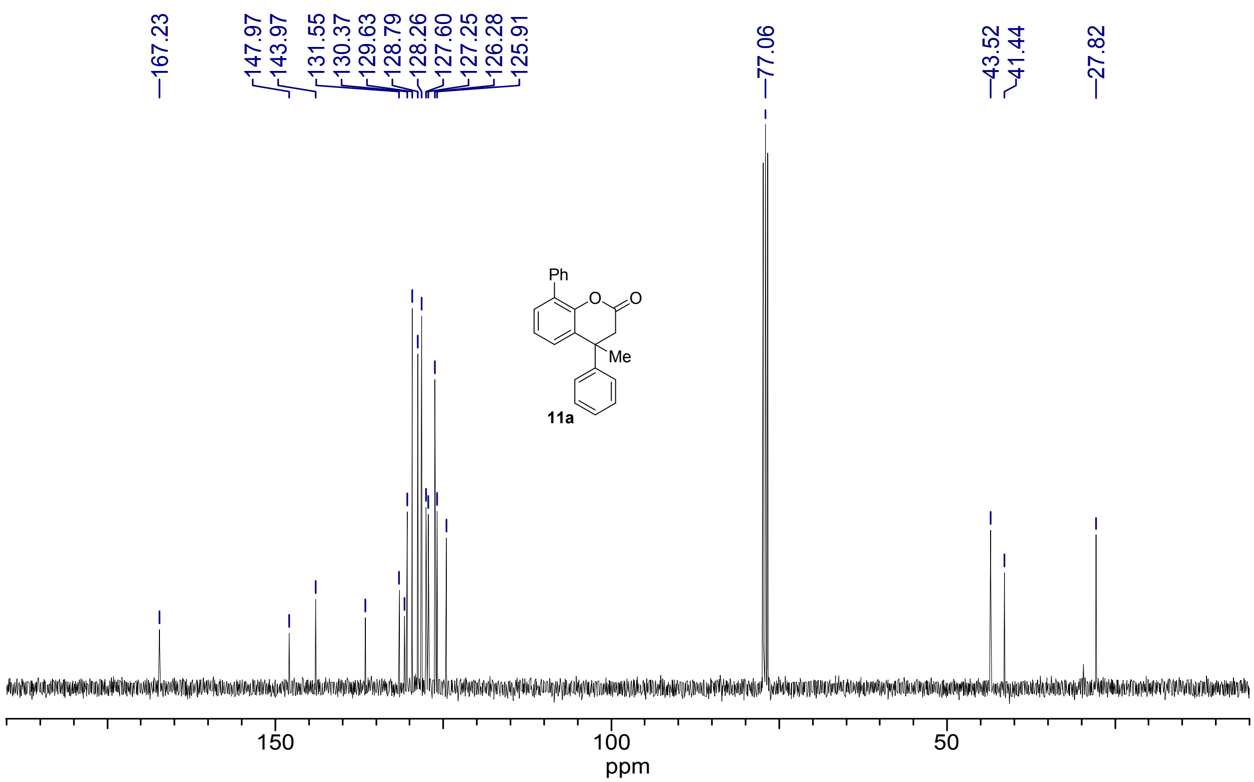
^{1}H NMR (400 MHz) spectrum of **10c** in $CDCl_3$



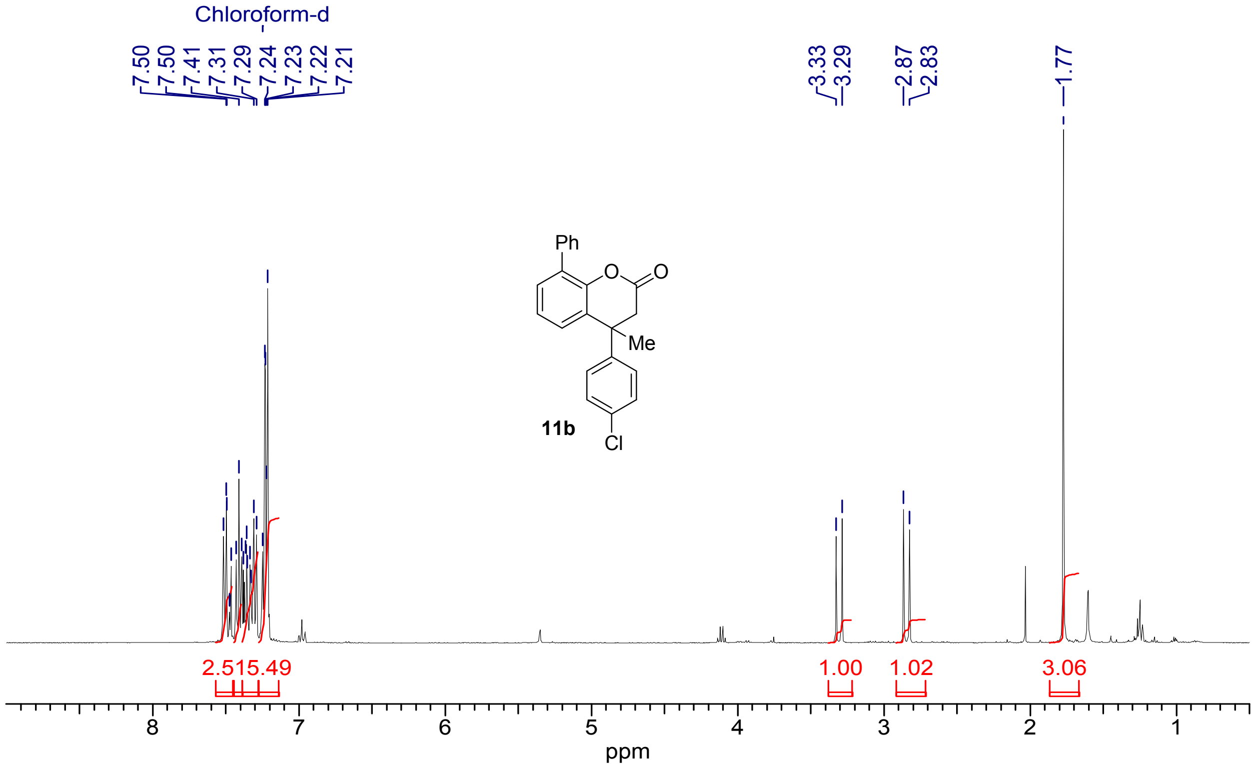
^{13}C NMR (100 MHz) spectrum of **10c** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **11a** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **11a** in $CDCl_3$



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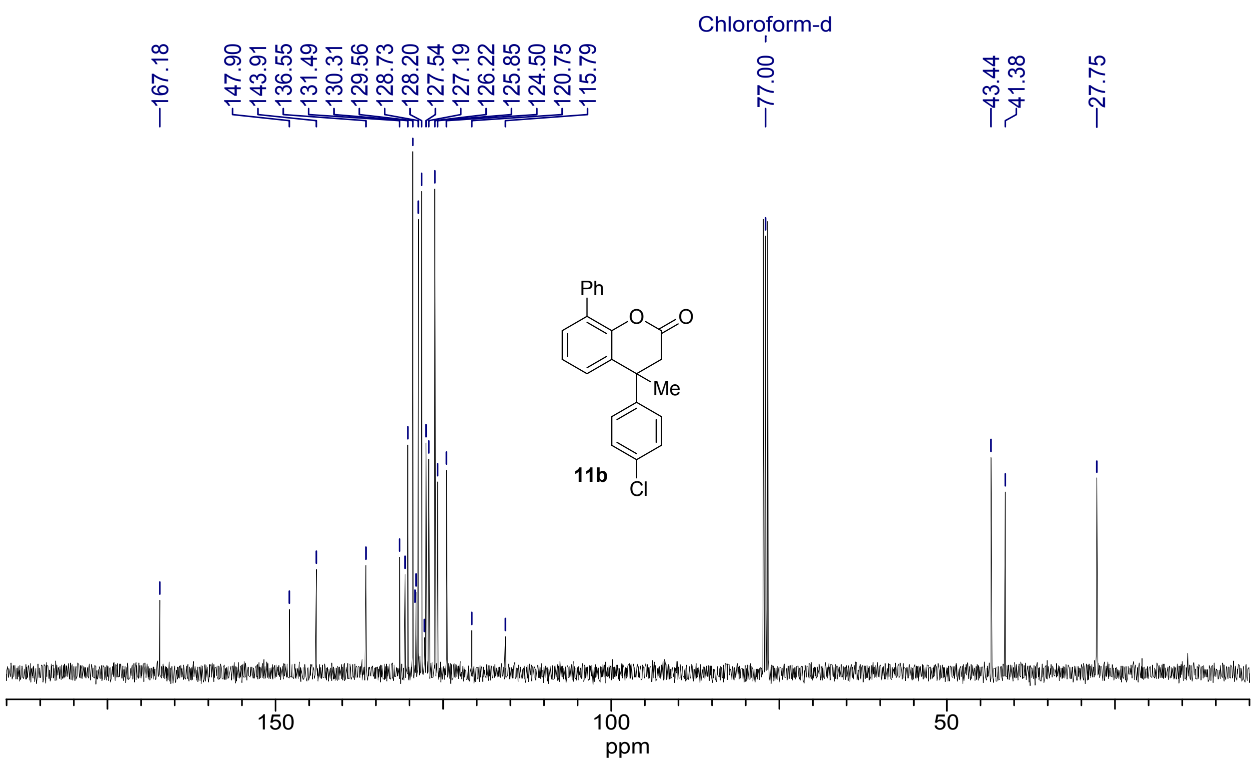
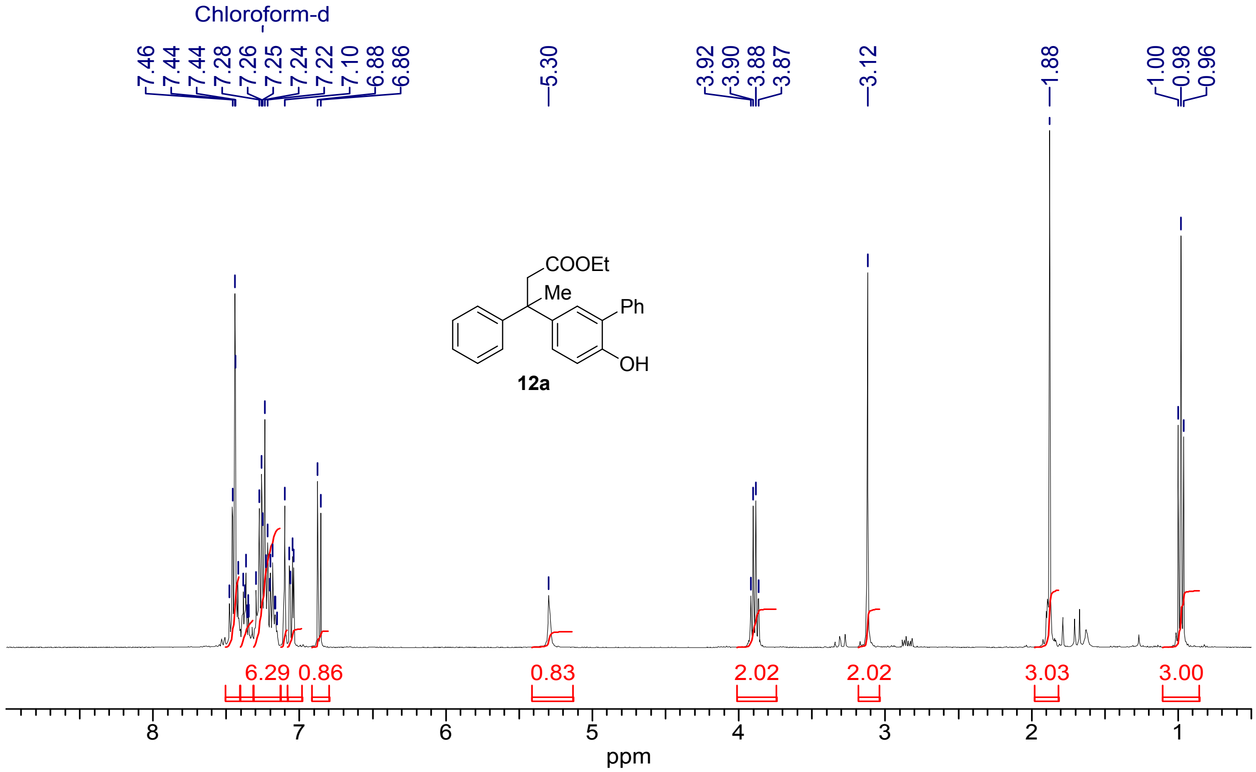
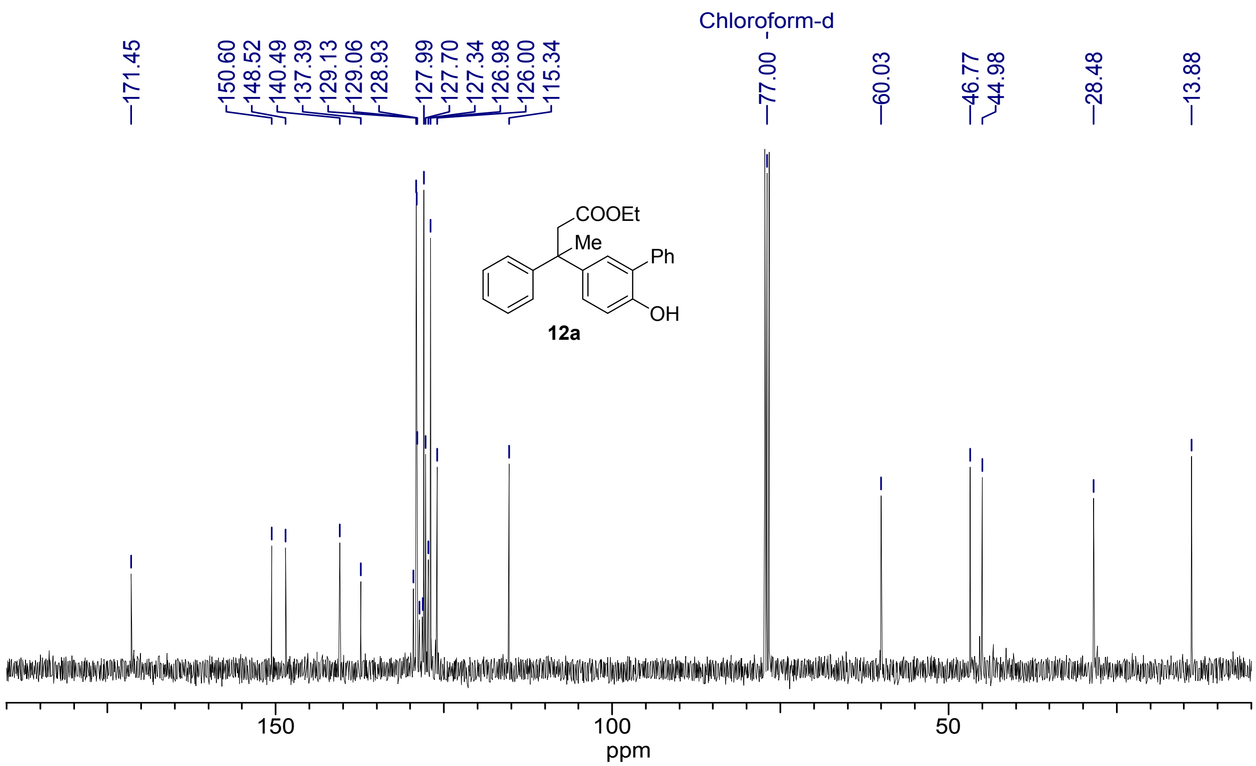


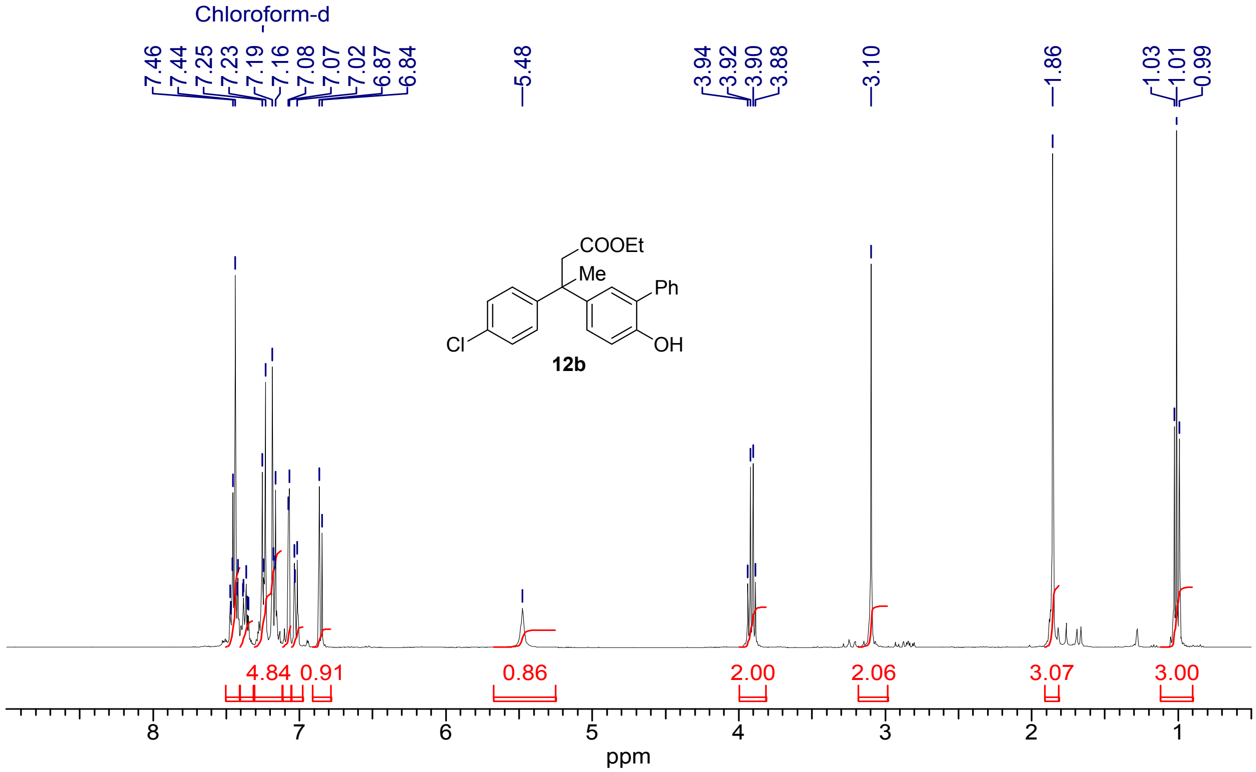
^{13}C NMR (100 MHz) spectrum of **11b** in $CDCl_3$



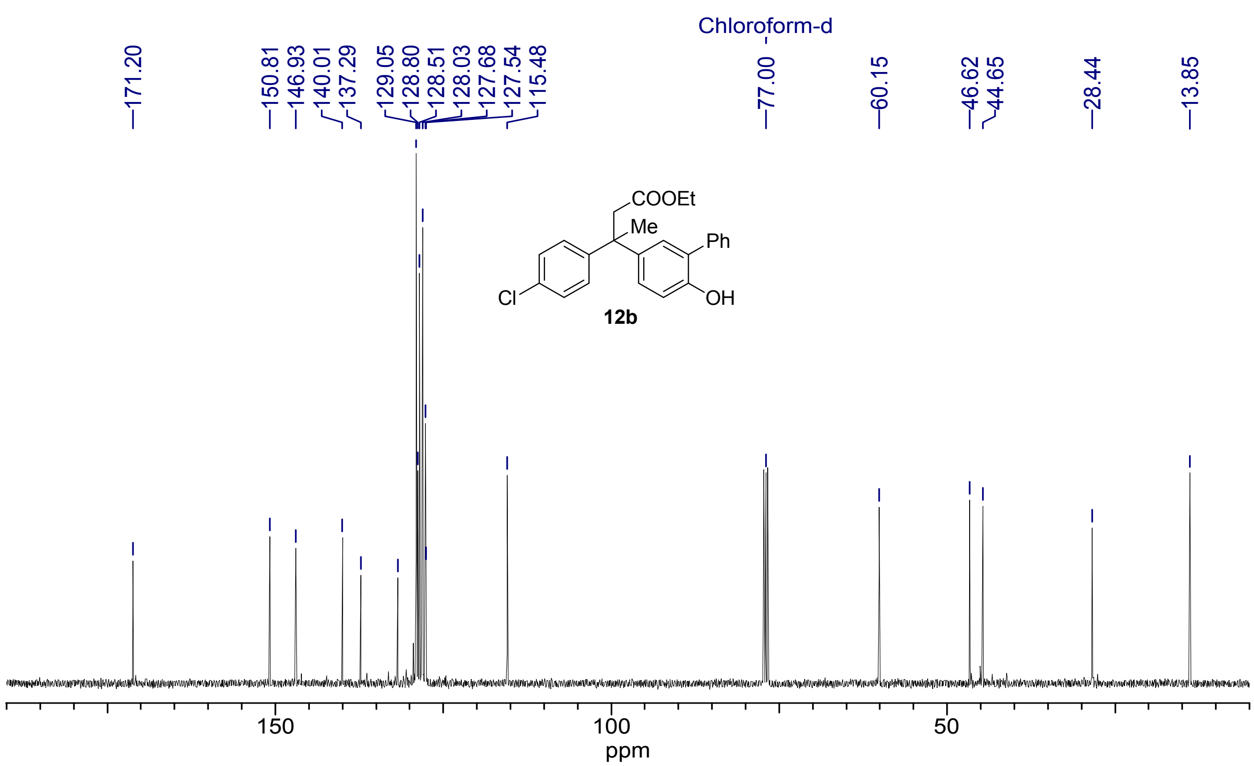
^{1}H NMR (400 MHz) spectrum of **12a** in $CDCl_3$



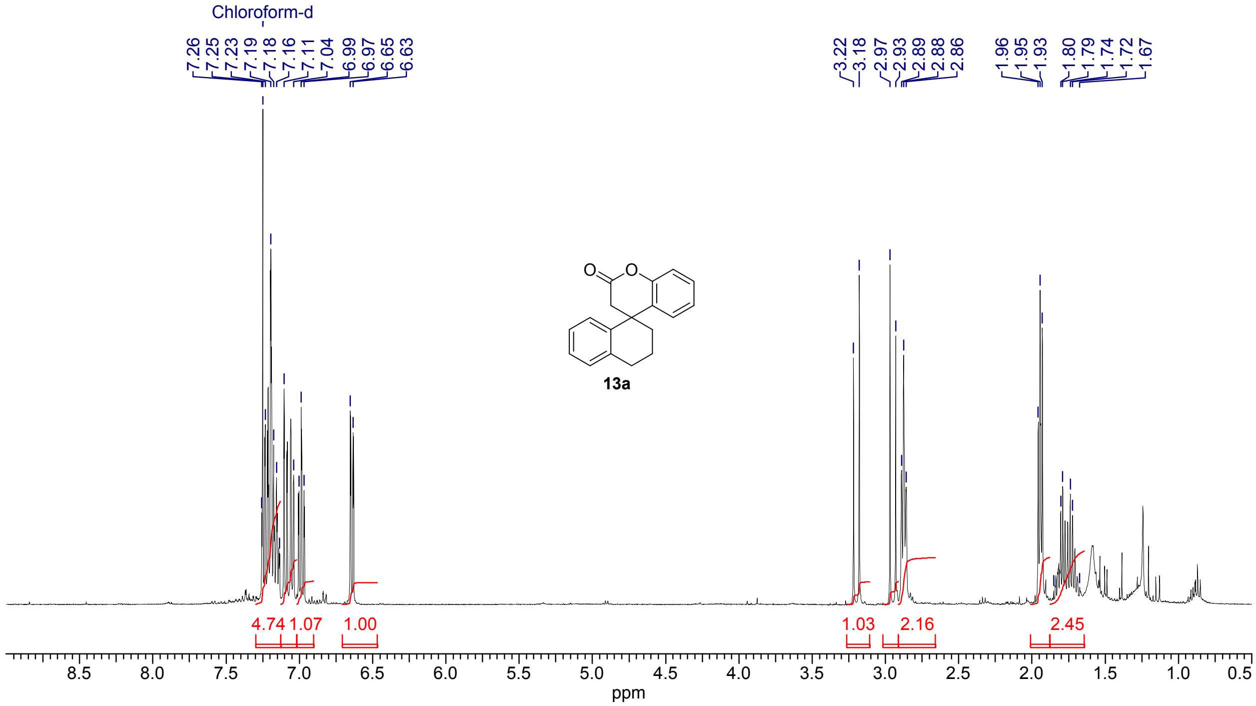
^{13}C NMR (100 MHz) spectrum of **12a** in $CDCl_3$



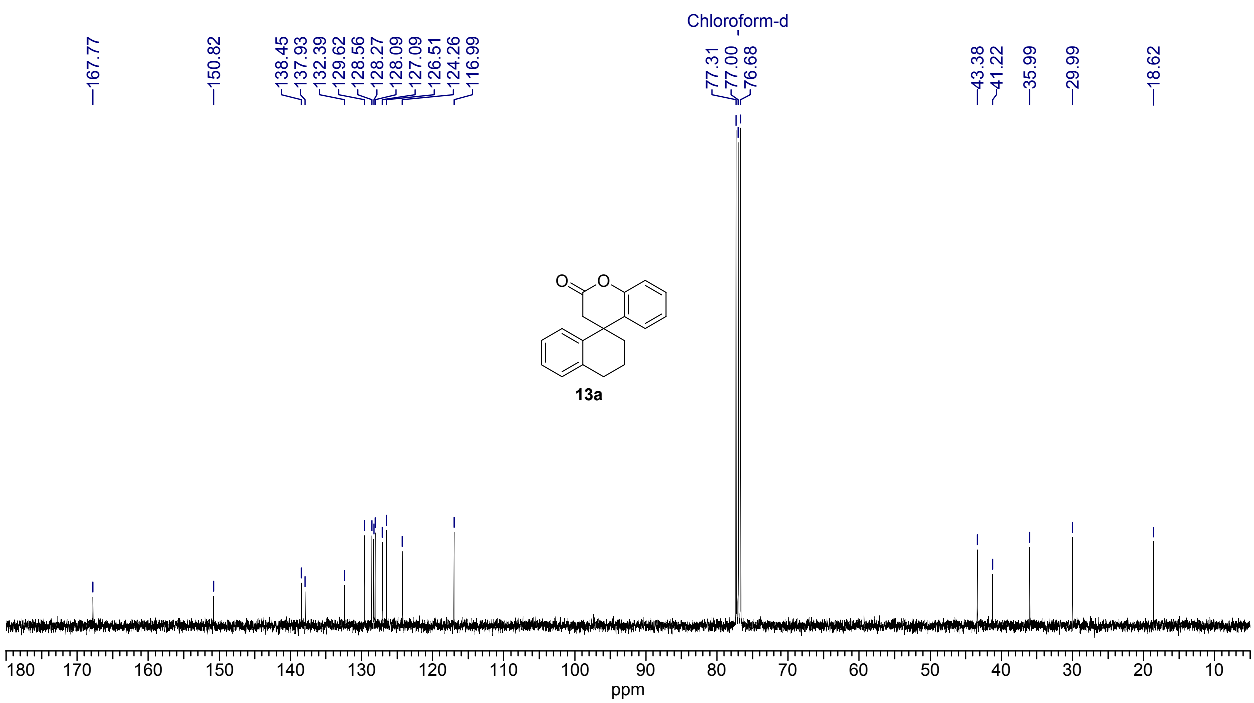
^{1}H NMR (400 MHz) spectrum of **12b** in $CDCl_3$



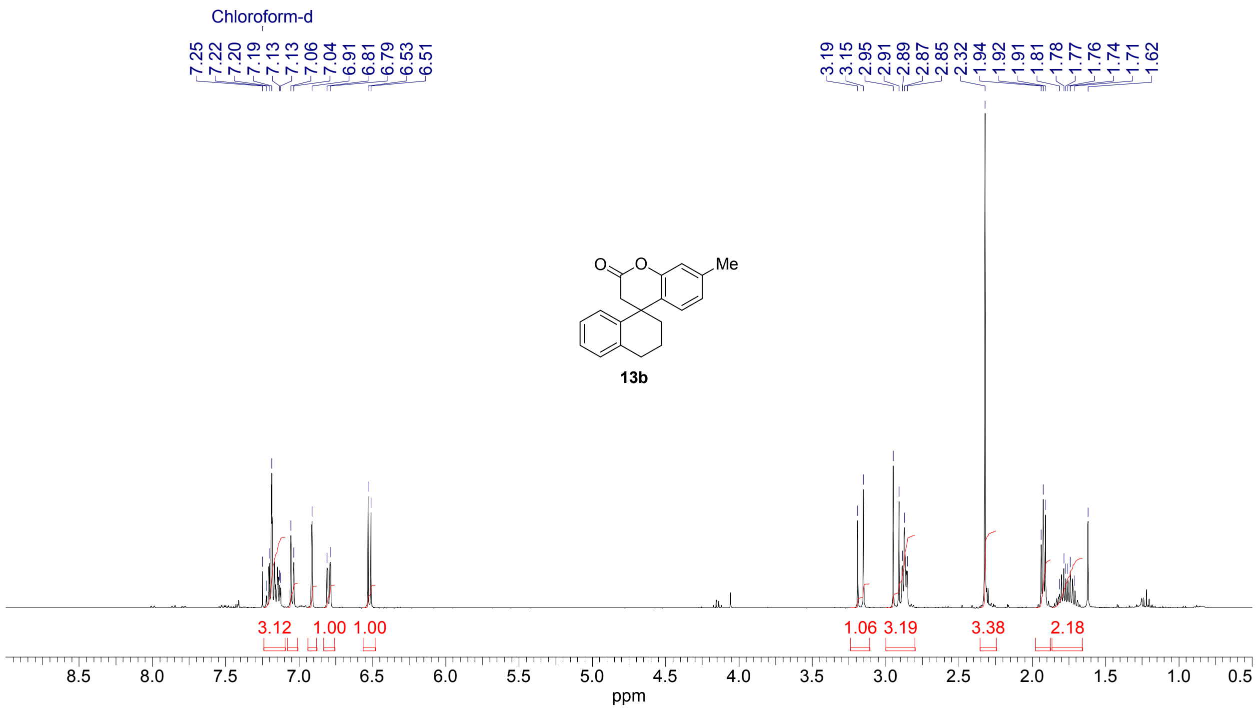
^{13}C NMR (100 MHz) spectrum of **12b** in $CDCl_3$



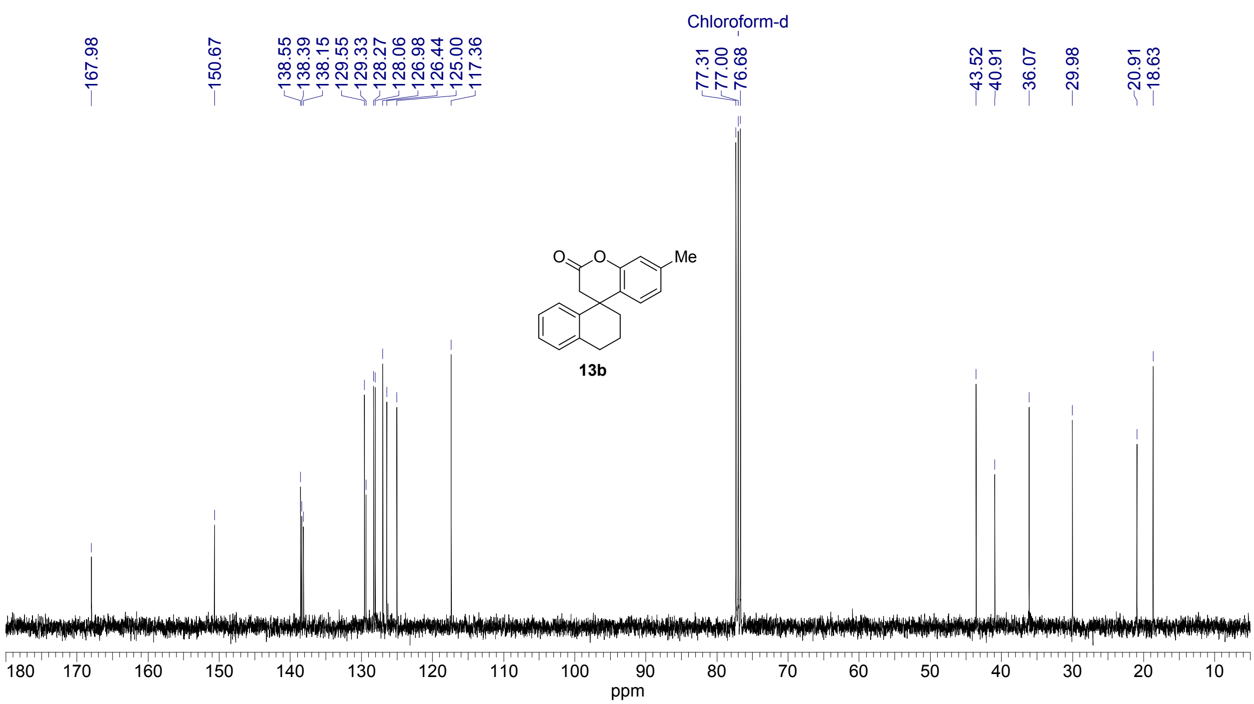
[1]H NMR (400 MHz) spectrum of **13a** in $CDCl_3$



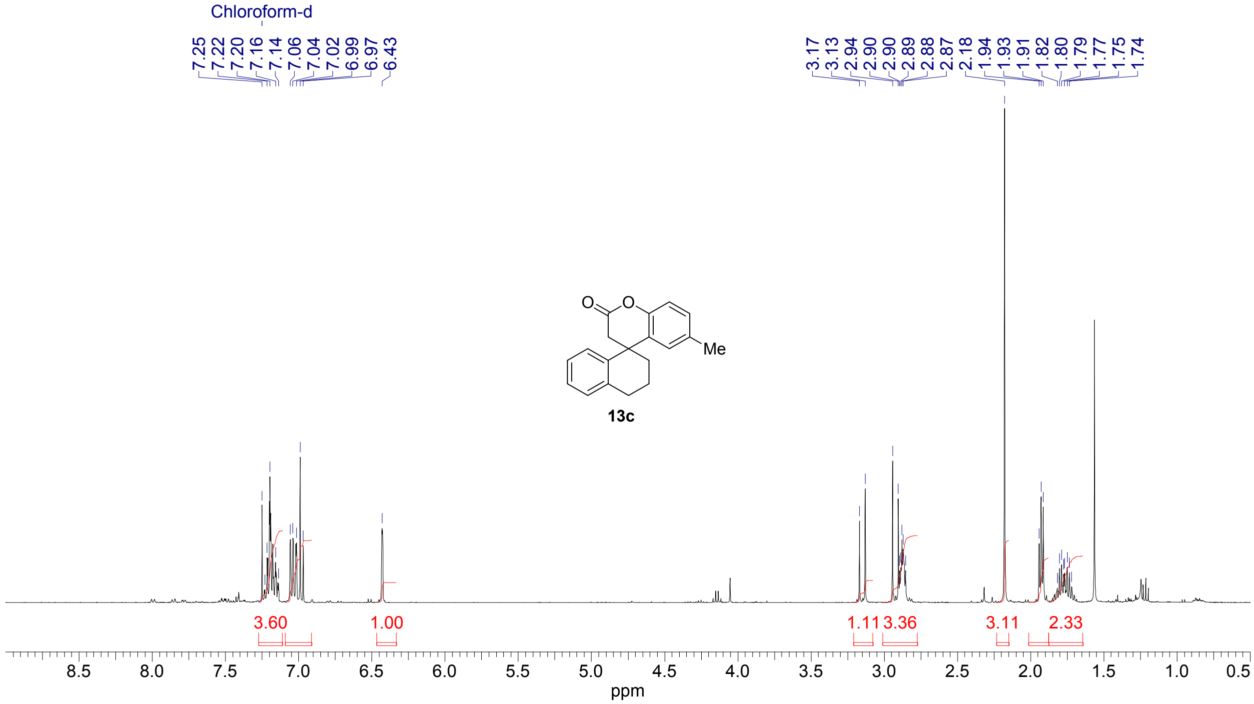
[13]C NMR (100 MHz) spectrum of **13a** in $CDCl_3$



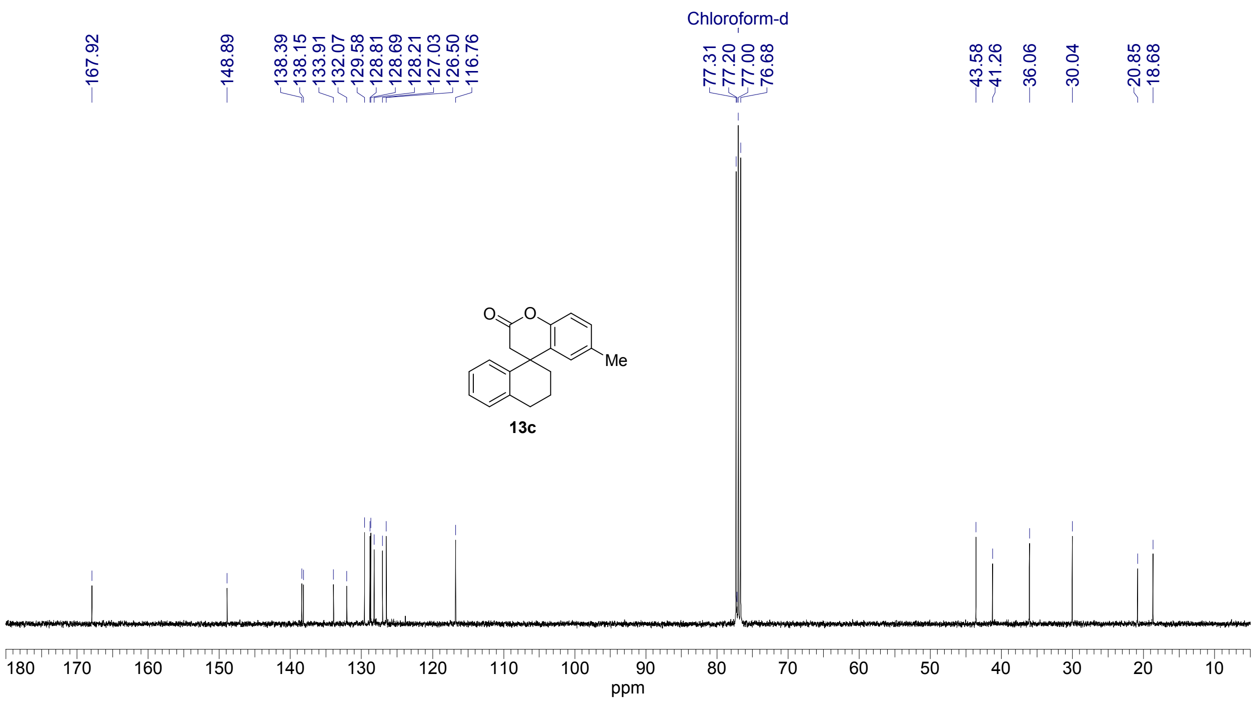
^{1}H NMR (400 MHz) spectrum of **13b** in $CDCl_3$



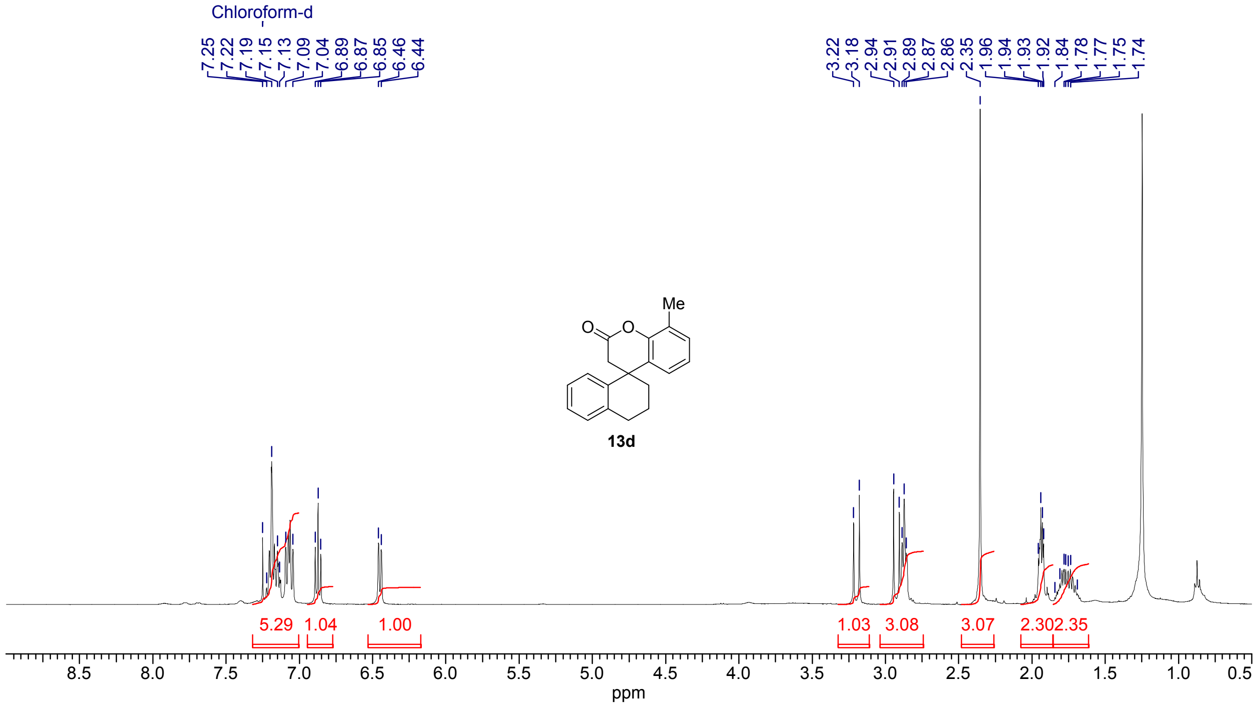
^{13}C NMR (100 MHz) spectrum of **13b** in $CDCl_3$



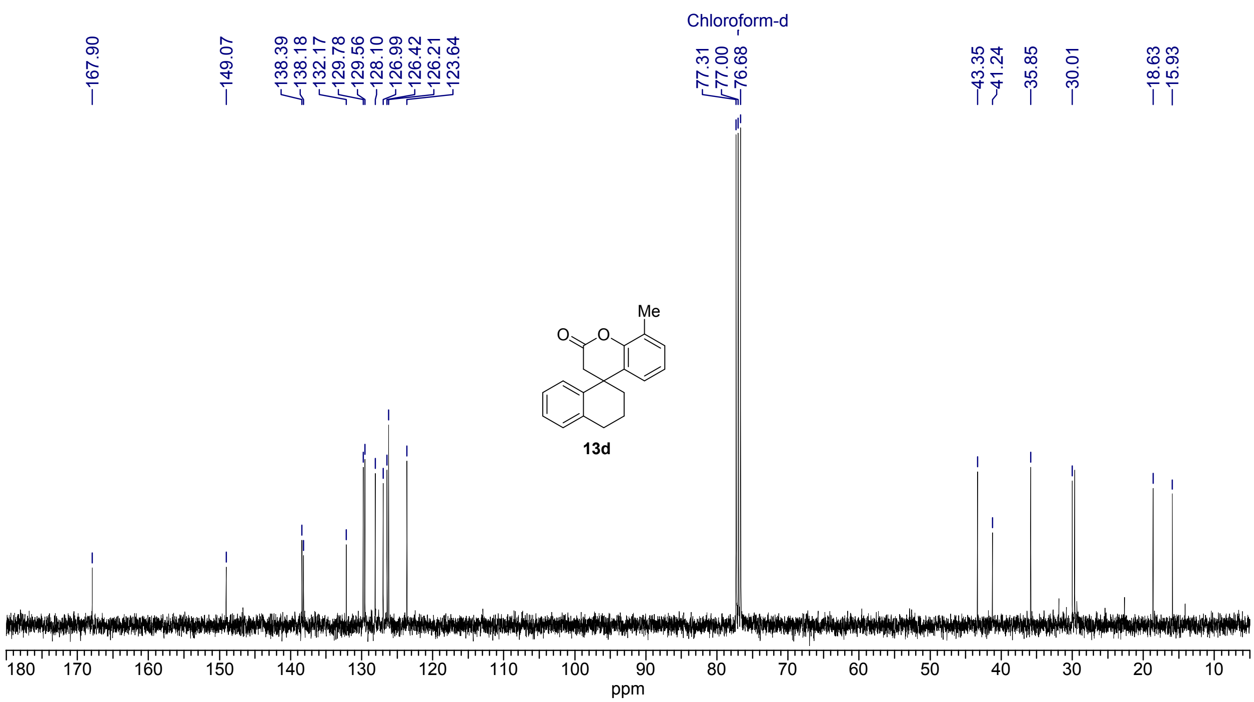
^{1}H NMR (400 MHz) spectrum of **13c** in $CDCl_3$



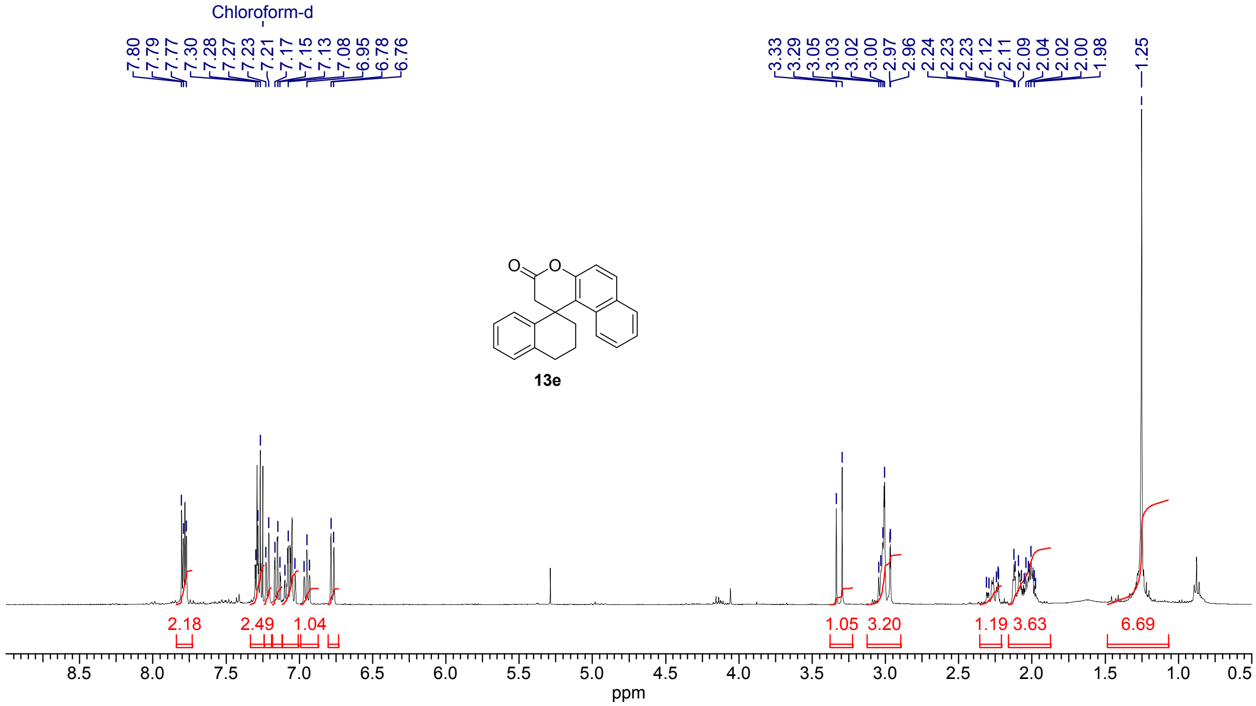
^{13}C NMR (100 MHz) spectrum of **13c** in $CDCl_3$



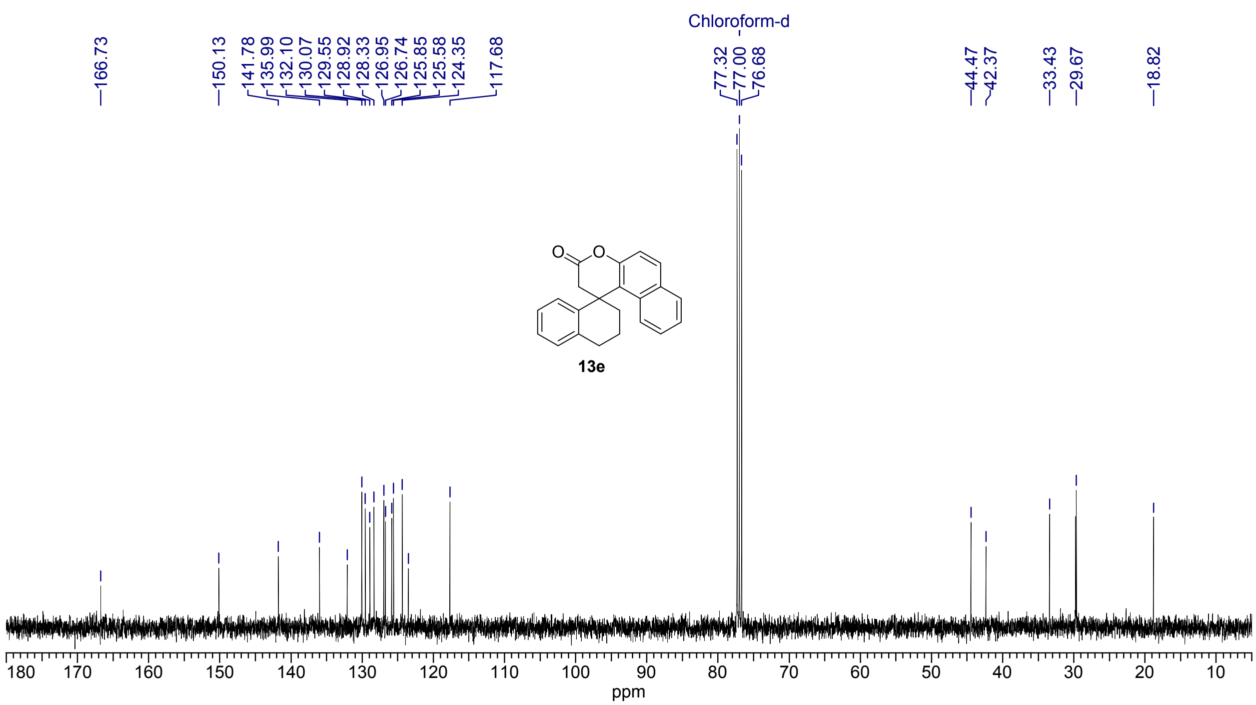
^{1}H NMR (400 MHz) spectrum of **13d** in $CDCl_3$



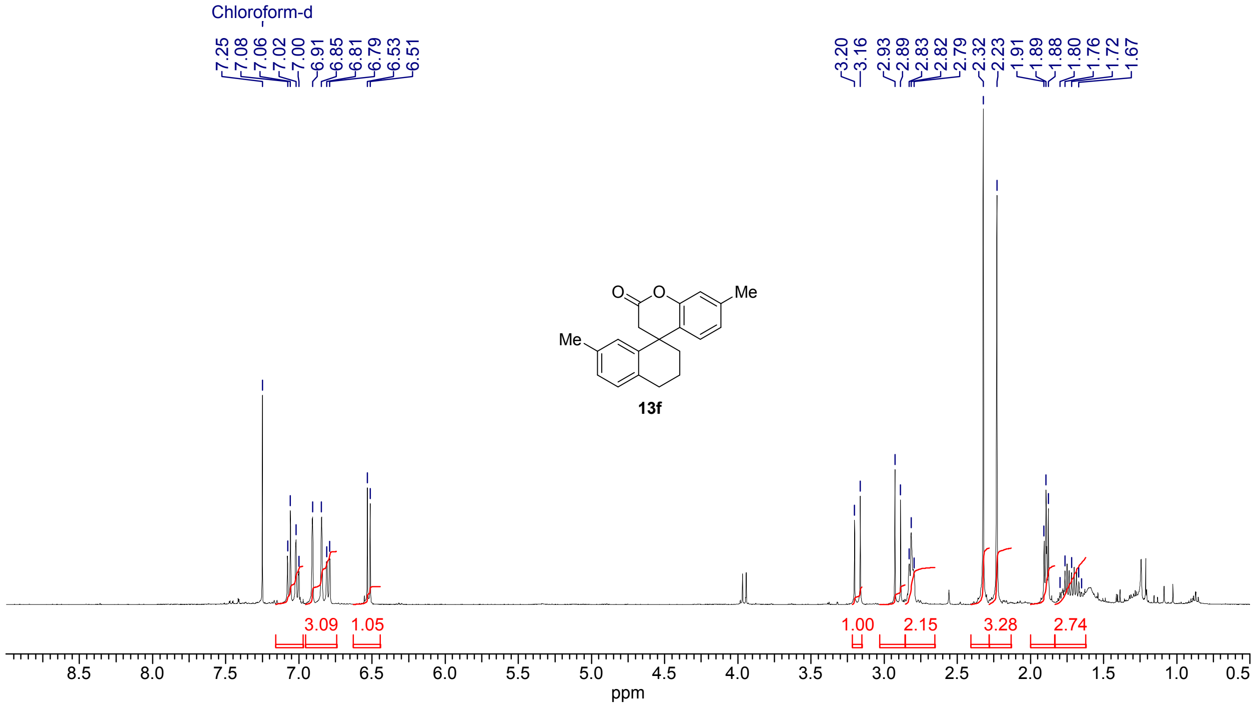
^{13}C NMR (100 MHz) spectrum of **13d** in $CDCl_3$



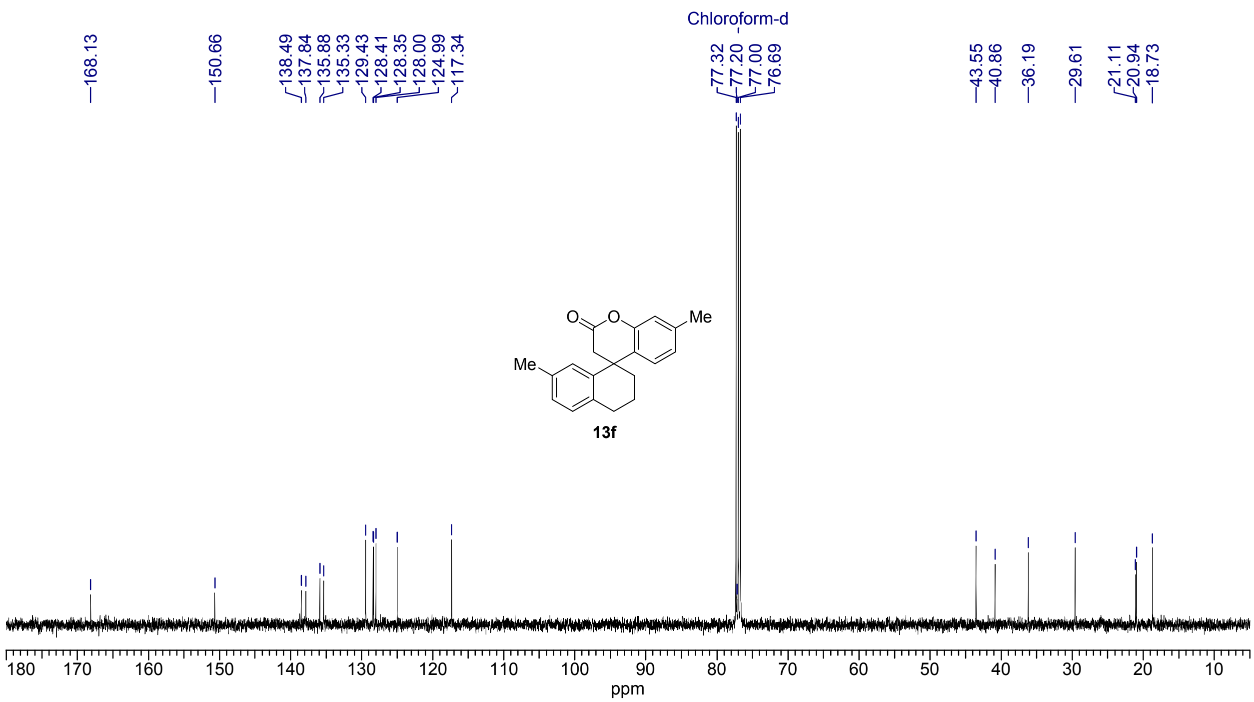
^{1}H NMR (400 MHz) spectrum of **13e** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **13e** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **13f** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **13f** in $CDCl_3$