Supporting Information

# Aromatic "Redox Tag" Assisted Diels-Alder Reactions by Electrocatalysis

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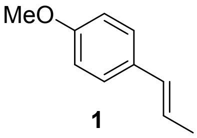
# 1. Additional Figures and Tables



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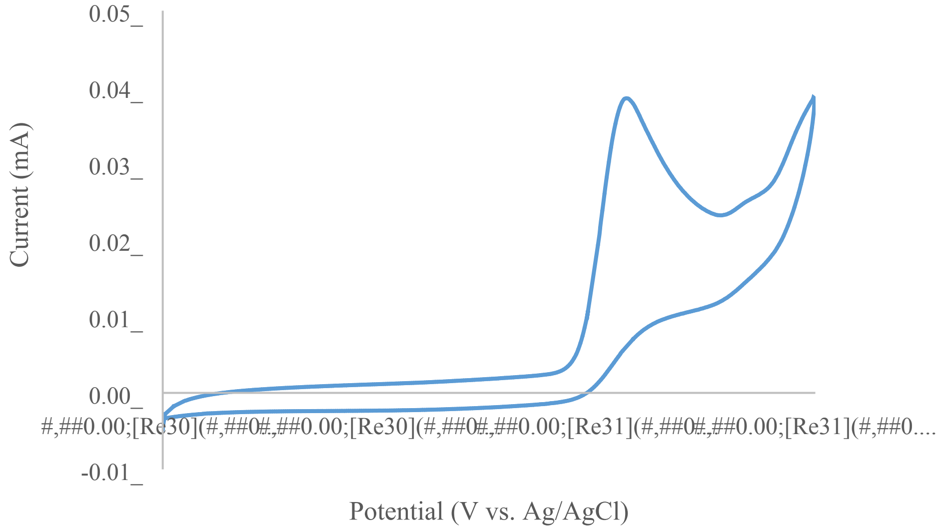
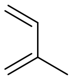


**Figure S1.** Cyclic Voltammogram of *trans*-Anethole **1**.



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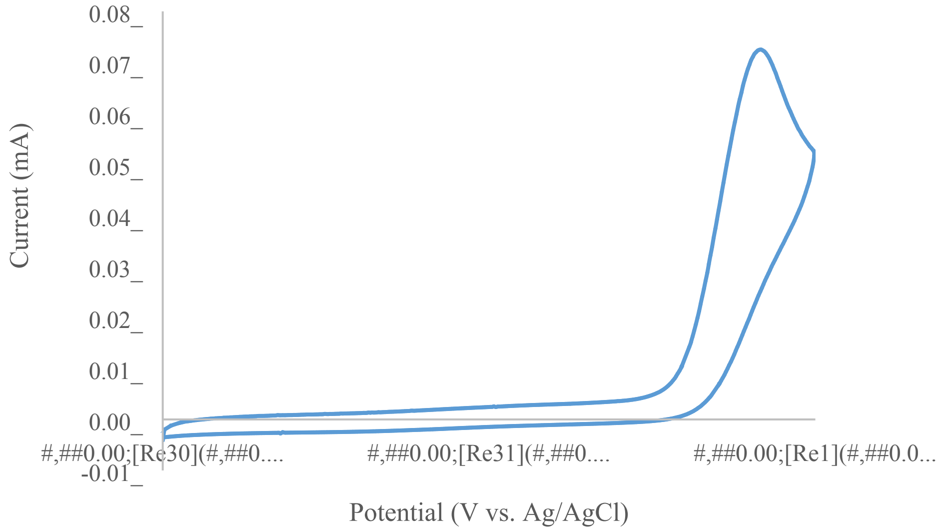
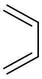


**Figure S2.** Cyclic Voltammogram of Isoprene **2**.



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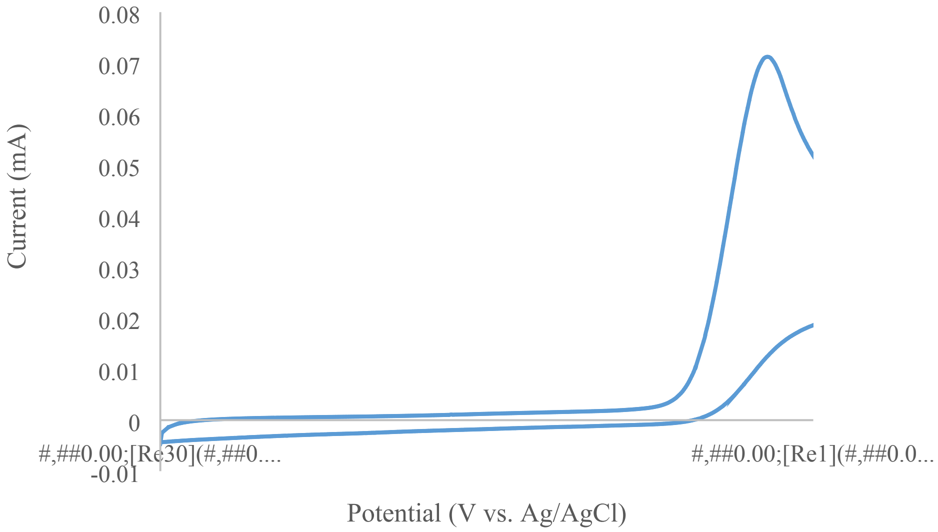
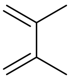


**Figure S3.** Cyclic Voltammogram of Buta-1,3-diene (**4**).



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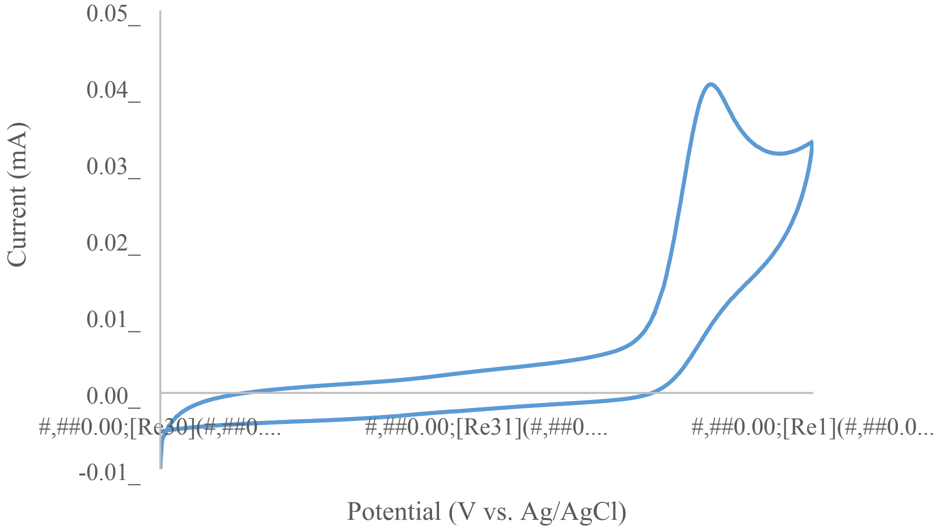
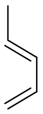


**Figure S4.** Cyclic Voltammogram of 2,3-Dimethylbuta-1,3-diene (**5**).



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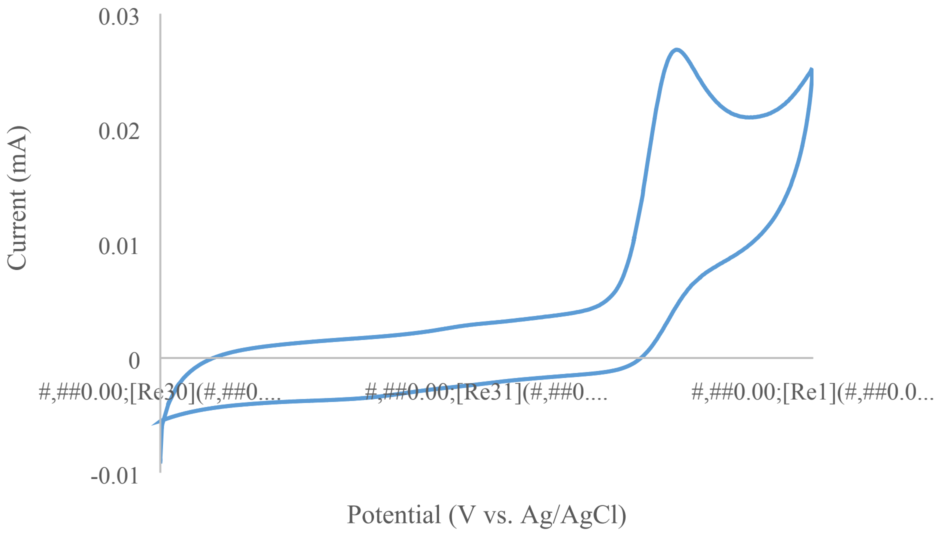
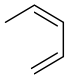


**Figure S5.** Cyclic Voltammogram of *trans*-Penta-1,3-diene (**6**).



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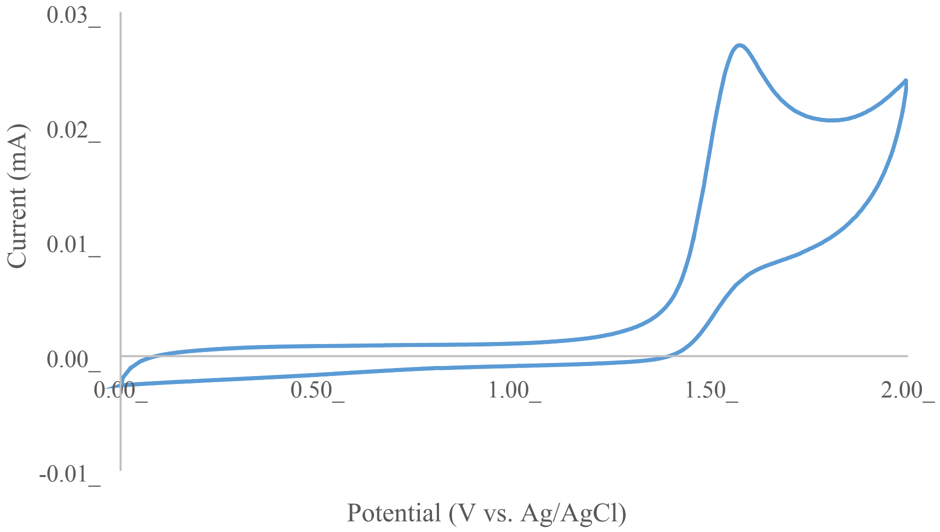
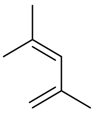


**Figure S6.** Cyclic Voltammogram of *cis*-Penta-1,3-diene (**7**).



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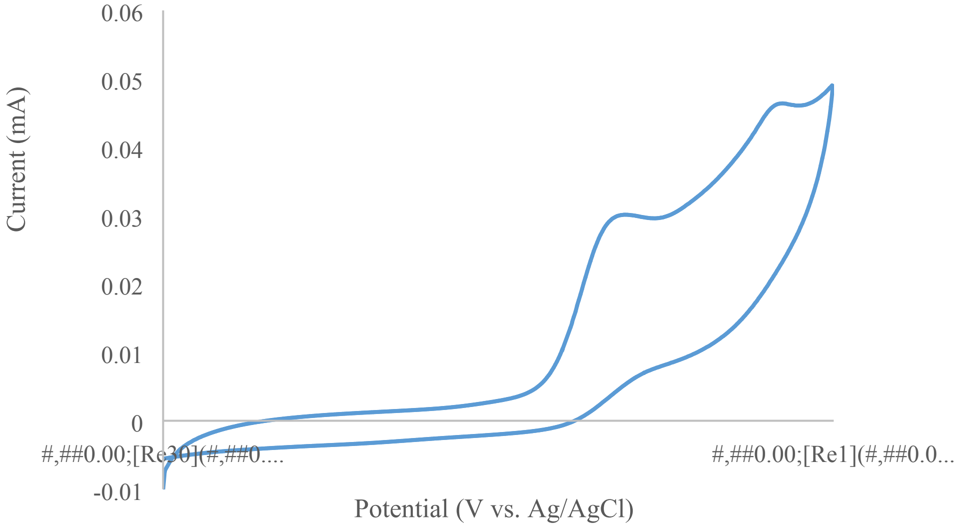
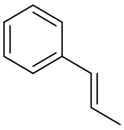


**Figure S7.** Cyclic Voltammogram of 2,4-Dimethylpenta-1,3-diene (**8**).



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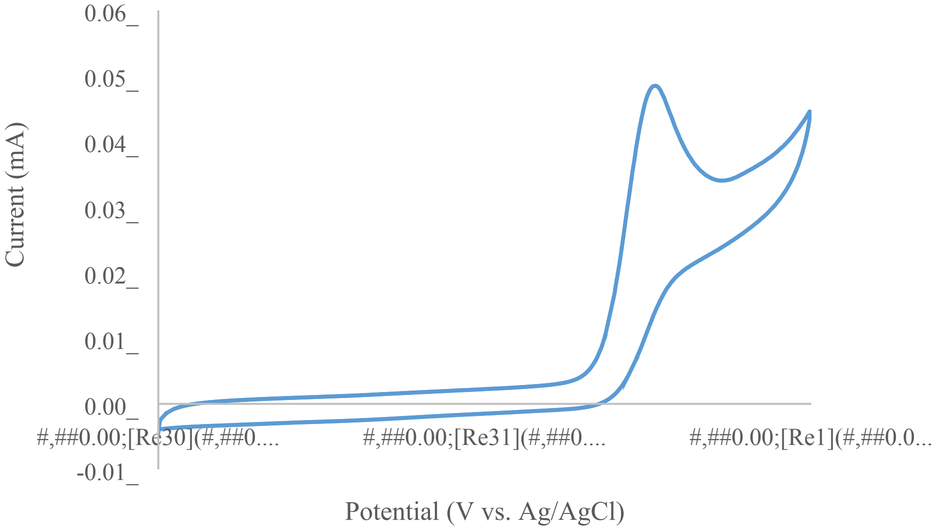
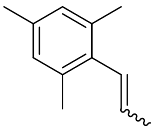


**Figure S8.** Cyclic Voltammogram of *trans*-β-Methylstyrene **14**.



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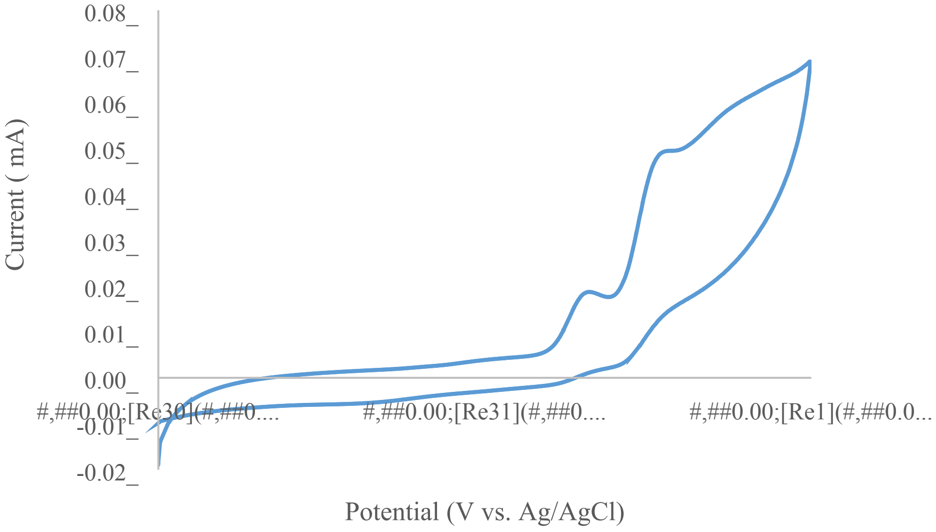
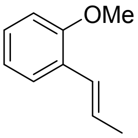


**Figure S9.** Cyclic Voltammogram of β-Methyl-2,4,6-trimethylstyrene **15**.



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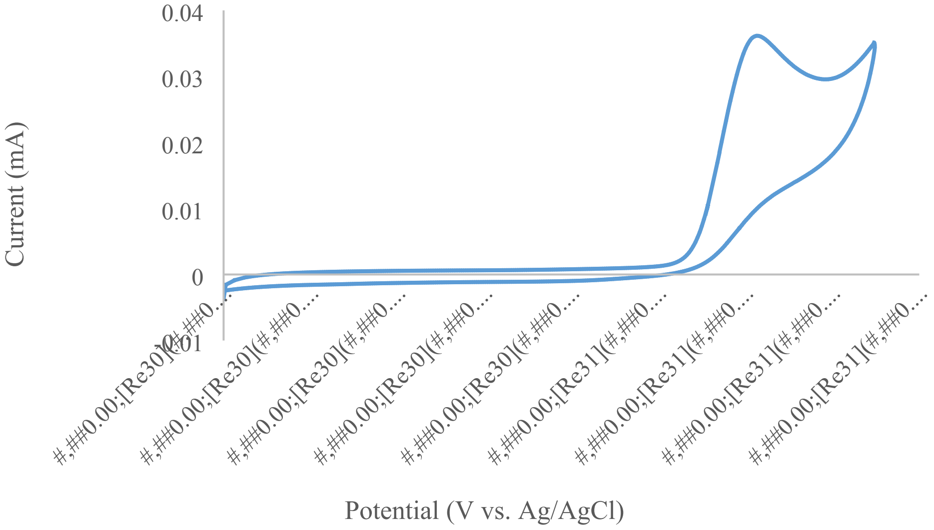
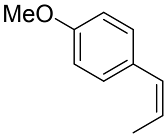


**Figure S10.** Cyclic Voltammogram of β-Methyl-2-methoxystyrene **16**.



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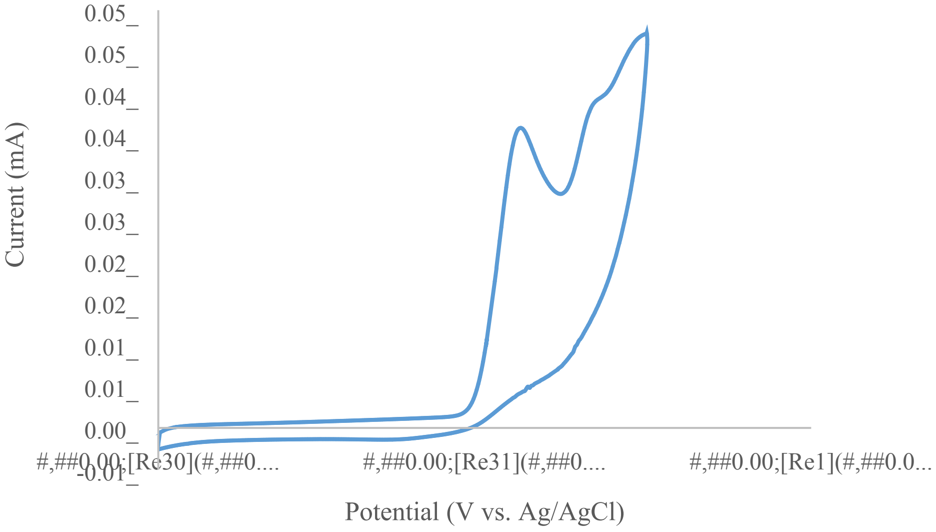
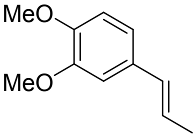


**Figure S11.** Cyclic Voltammogram of *cis*-Anethole **17**.



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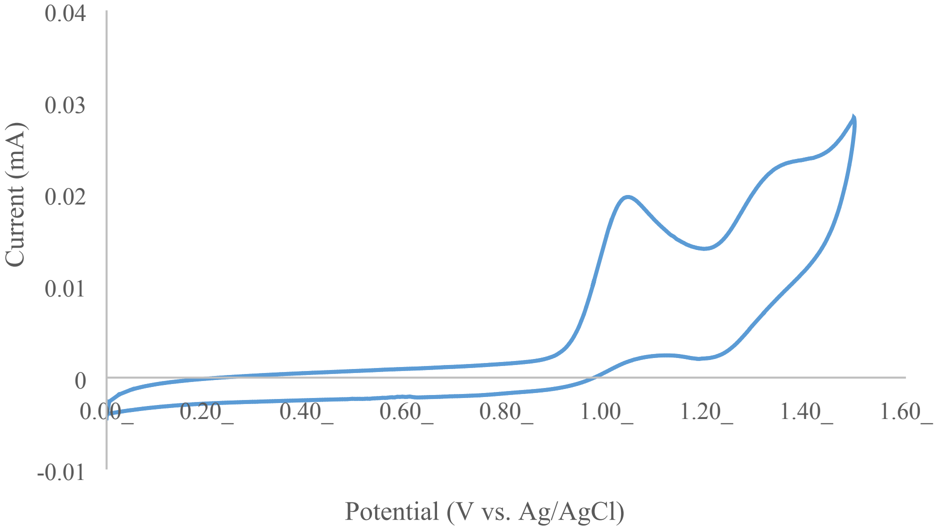
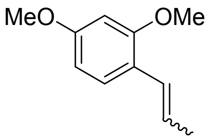


**Figure S12.** Cyclic Voltammogram of *trans*-β-Methyl-3,4-dimethoxystyrene **18**.



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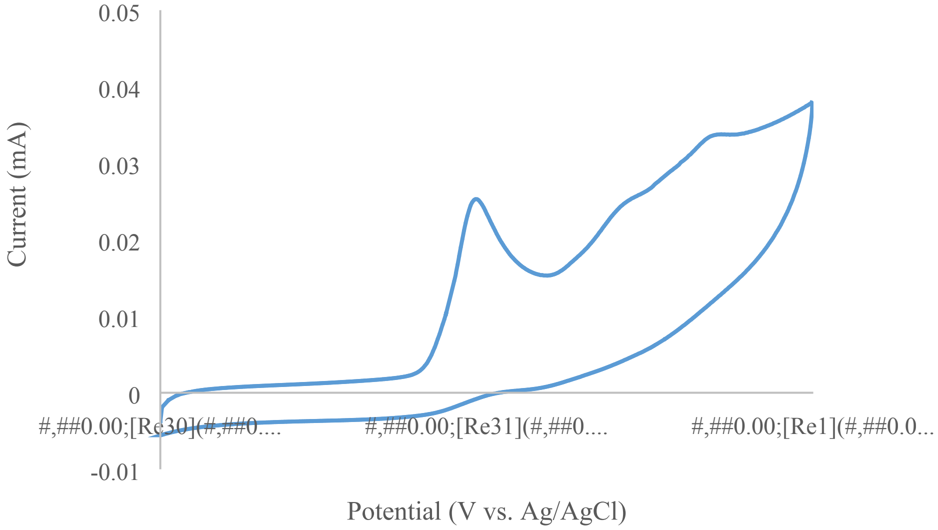
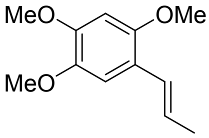


**Figure S13.** Cyclic Voltammogram of β-Methyl-2,4-dimethoxystyrene **19**.



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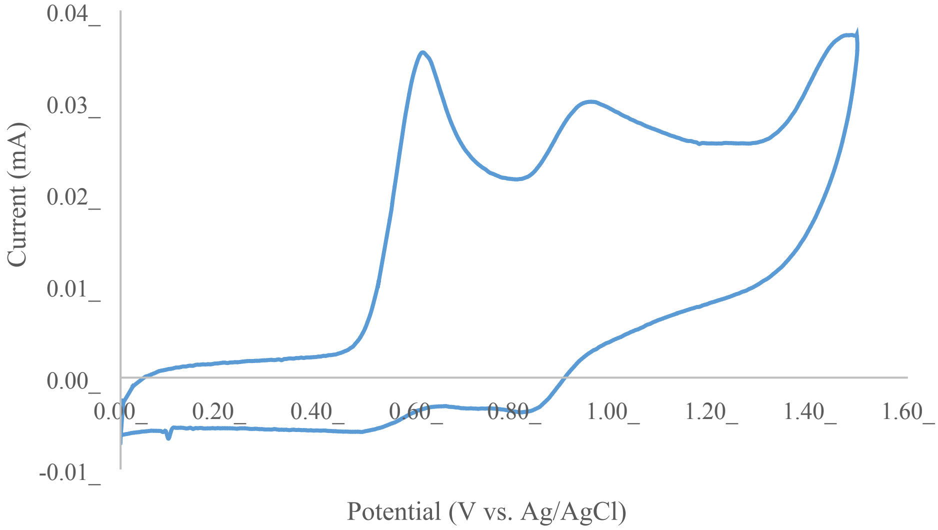


**Figure S14.** Cyclic Voltammogram of *trans*-β-Methyl-2,4,5-trimethoxystyrene **20**.

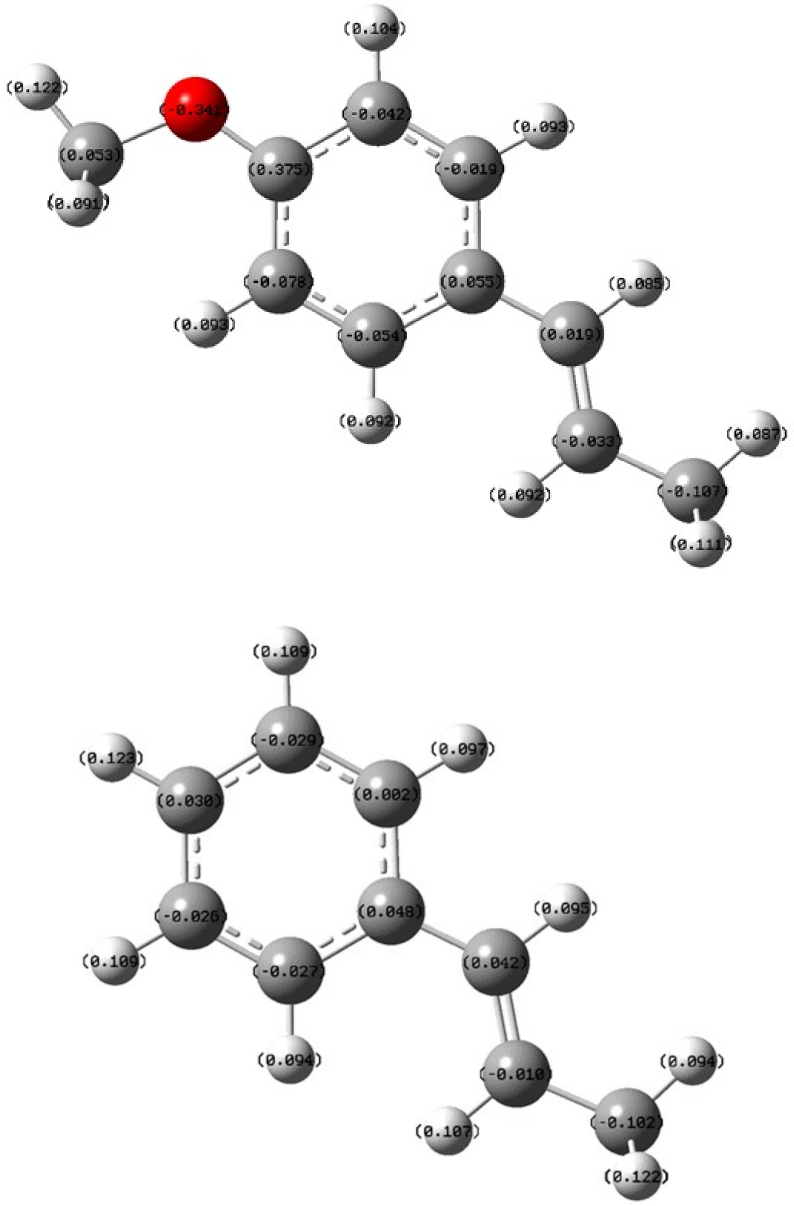


**Figure S15.** Mulliken Positive Charges of the Radical Cation **1**$^{\cdot+}$ (Above) and the Radical Cation **14**$^{\cdot+}$ (Below).

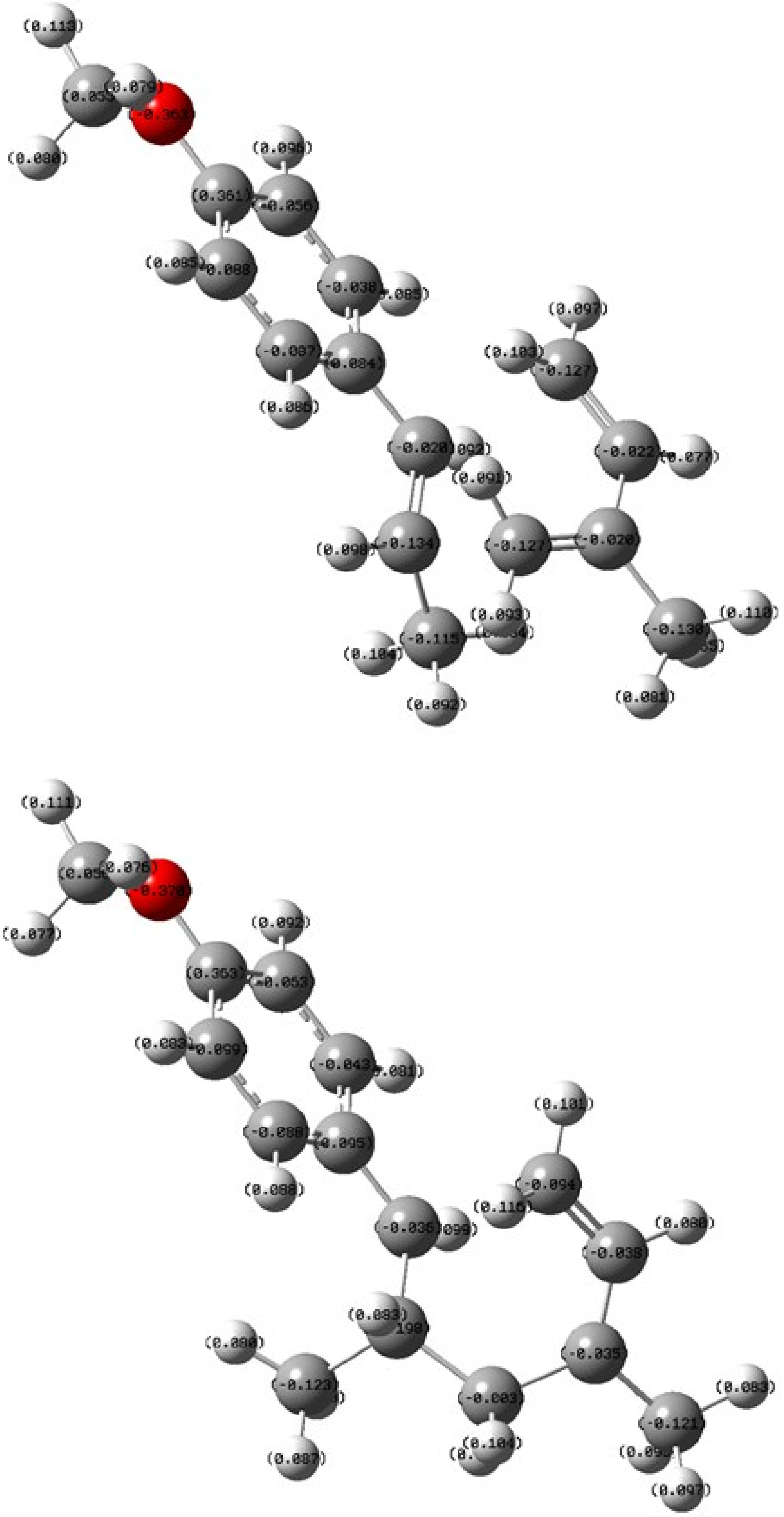


**Figure S16.** Mulliken Positive Charges of the Reaction Intermediates Figure7-a (Above) and Figure 7-b (Below).

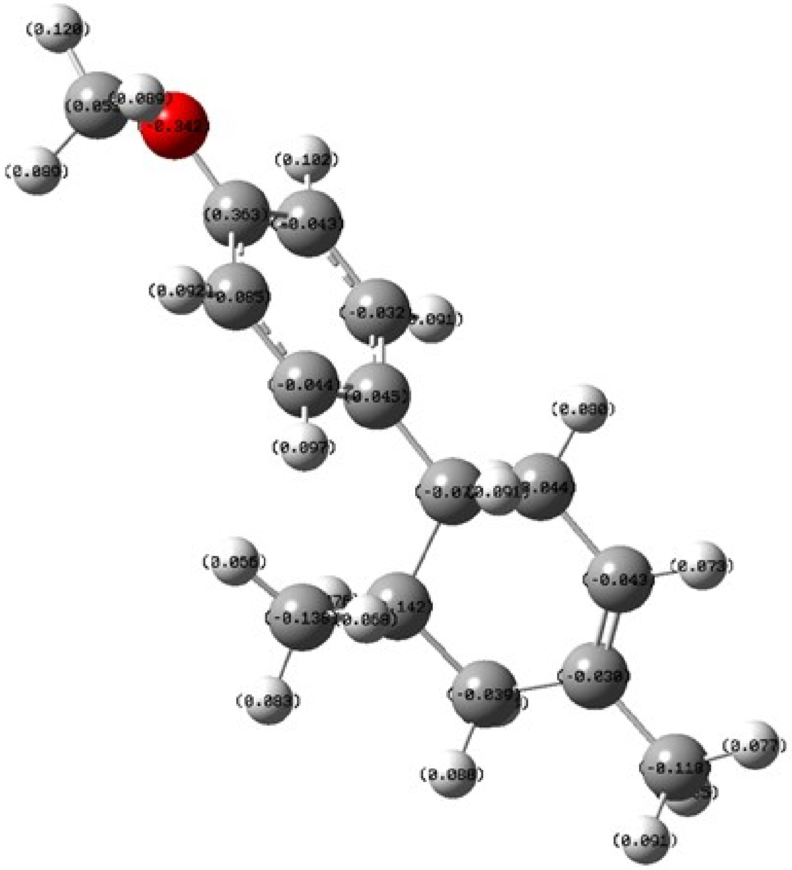


**Figure S17.** Mulliken Positive Charges of the Radical Cation **3**$^{\cdot+}$, Figure 7-c.

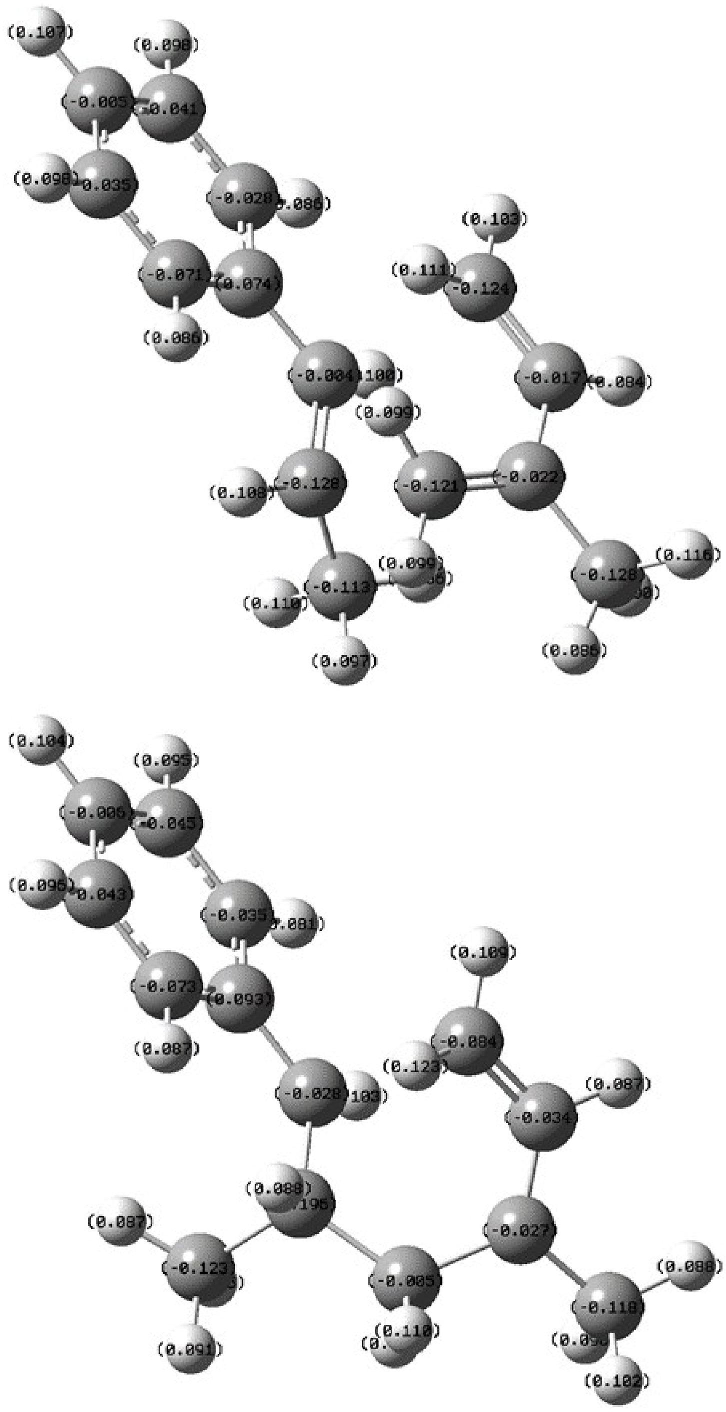


**Figure S18.** Mulliken Positive Charges of the Reaction Intermediates Figure7-e (Above) and Figure 7-f (Below).

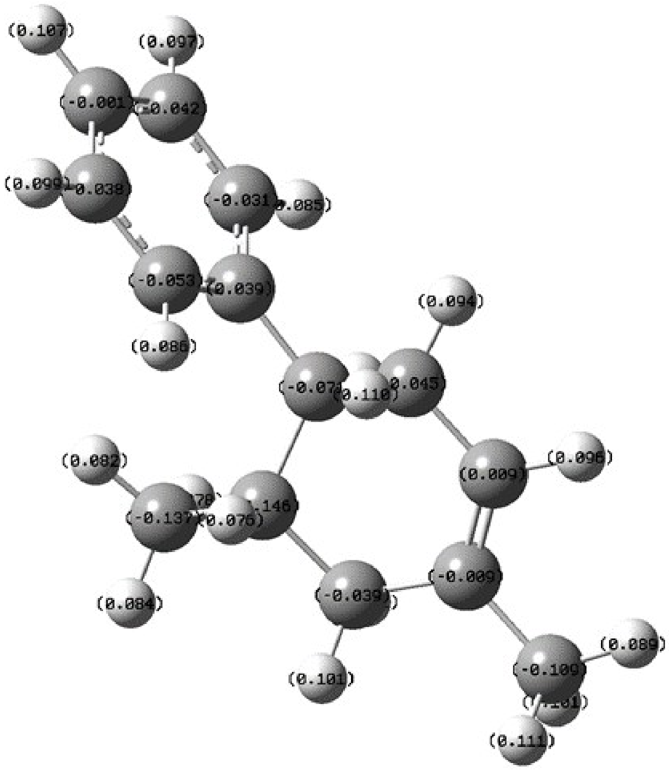


**Figure S19.** Mulliken Positive Charges of the Radical Cation **21**$^{\cdot+}$, Figure 7-g.

**Table S1. Cartesian Coordinates of the Optimized Structure for the *trans*-Anethole 1 Calculated at the RB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | 0.2123670 | -0.9016734 | -0.0000701 |
| C | 0.9111684 | 0.3160533 | 0.0001112 |
| C | 0.1408795 | 1.4956616 | 0.0001044 |
| C | -1.2464180 | 1.4657700 | -0.0000448 |
| C | -1.9216027 | 0.2379193 | -0.0002311 |
| C | -1.1805526 | -0.9515205 | -0.0002668 |
| H | 0.7603866 | -1.8396769 | -0.0000536 |
| H | 0.6485587 | 2.4577069 | 0.0002562 |
| H | -1.8307613 | 2.3807284 | -0.0000101 |
| H | -1.6754130 | -1.9162448 | -0.0004902 |
| O | -3.2858048 | 0.3059632 | -0.0005713 |
| C | -4.0181385 | -0.9082542 | 0.0005796 |
| H | -5.0718161 | -0.6228186 | 0.0012972 |
| H | -3.8067332 | -1.5093579 | -0.8939386 |
| H | -3.8052561 | -1.5085478 | 0.8952803 |
| C | 2.3773893 | 0.4192139 | 0.0002427 |
| H | 2.7576070 | 1.4423664 | 0.0006044 |
| C | 3.2758720 | -0.5771749 | -0.0001326 |
| H | 2.9363821 | -1.6132866 | -0.0005713 |
| C | 4.7634361 | -0.3807120 | 0.0000351 |
| H | 5.2289502 | -0.8465440 | 0.8799685 |
| H | 5.2290554 | -0.8457555 | -0.8802616 |
| H | 5.0290757 | 0.6820262 | 0.0005243 |

**Table S2. Cartesian Coordinates of the Optimized Structure for the Radical Cation of the *trans*-Anethole $1^{\cdot+}$ Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -0.2224841 | -0.9201597 | 0.0000660 |
| C | -0.9174481 | 0.3341168 | 0.0000216 |
| C | -0.1316348 | 1.5321326 | -0.0000522 |
| C | 1.2352980 | 1.4878473 | -0.0000786 |
| C | 1.9029910 | 0.2264806 | -0.0000505 |
| C | 1.1476610 | -0.9816370 | 0.0000305 |
| H | -0.7840307 | -1.8477273 | 0.0001377 |
| H | -0.6403421 | 2.4914864 | -0.0000882 |
| H | 1.8418072 | 2.3871450 | -0.0001331 |
| H | 1.6480908 | -1.9424700 | 0.0000901 |
| O | 3.2190415 | 0.2862867 | -0.0000744 |
| C | 4.0311523 | -0.9101617 | -0.0002219 |
| H | 5.0586541 | -0.5514932 | -0.0006352 |
| H | 3.8360717 | -1.4973503 | 0.9011689 |
| H | 3.8354383 | -1.4976041 | -0.9013065 |
| C | -2.3388291 | 0.4499473 | 0.0000544 |
| H | -2.7353426 | 1.4640479 | 0.0000065 |
| C | -3.2488239 | -0.5813896 | 0.0001460 |
| H | -2.8957088 | -1.6112983 | 0.0002024 |
| C | -4.7203089 | -0.3960955 | 0.0001804 |
| H | -5.1634058 | -0.8937352 | -0.8748872 |
| H | -5.1633475 | -0.8936040 | 0.8753525 |
| H | -5.0156563 | 0.6558232 | 0.0001123 |

**Table S3. Cartesian Coordinates of the Optimized Structure for the *trans*-β-Methylstyrene 14 Calculated at the RB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -2.3446953 | -1.0611250 | -0.0000151 |
| C | -0.9673675 | -1.2773516 | -0.0000214 |
| C | -0.0580589 | -0.2048735 | 0.0000000 |
| C | -0.5849355 | 1.1006876 | 0.0000459 |
| C | -1.9593553 | 1.3186802 | 0.0000445 |
| C | -2.8485515 | 0.2395842 | 0.0000155 |
| H | -3.0235710 | -1.9100571 | -0.0000339 |
| H | -0.5826036 | -2.2949141 | -0.0000531 |
| H | 0.0864038 | 1.9546386 | 0.0001009 |
| H | -2.3407346 | 2.3366735 | 0.0000774 |
| H | -3.9211850 | 0.4133614 | 0.0000241 |
| C | 1.3836673 | -0.4984454 | -0.0000165 |
| H | 1.6293717 | -1.5616524 | 0.0001572 |
| C | 2.4007484 | 0.3760798 | -0.0002433 |
| H | 2.1953477 | 1.4466169 | -0.0005443 |
| C | 3.8511587 | -0.0072708 | 0.0001022 |
| H | 4.3698212 | 0.3958574 | 0.8810799 |
| H | 3.9804908 | -1.0947920 | -0.0013487 |
| H | 4.3709972 | 0.3984744 | -0.8789362 |

**Table S4. Cartesian Coordinates of the Optimized Structure for the Radical Cation of the *trans*-β-Methylstyrene $14^{\cdot+}$ Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -2.3402405 | -1.0675685 | 0.0000161 |
| C | -0.9829764 | -1.3060347 | -0.0000091 |
| C | -0.0482305 | -0.2184674 | -0.0000263 |
| C | -0.5573511 | 1.1237143 | -0.0000116 |
| C | -1.9153623 | 1.3509796 | 0.0000078 |
| C | -2.8130501 | 0.2610381 | 0.0000236 |
| H | -3.0441295 | -1.8932188 | 0.0000262 |
| H | -0.6028919 | -2.3233893 | -0.0000193 |
| H | 0.1255197 | 1.9658228 | -0.0000290 |
| H | -2.3002103 | 2.3654089 | 0.0000088 |
| H | -3.8827626 | 0.4493562 | 0.0000399 |
| C | 1.3386800 | -0.5319116 | -0.0000363 |
| H | 1.5965108 | -1.5897393 | -0.0001125 |
| C | 2.3895295 | 0.3725806 | 0.0000020 |
| H | 2.1770241 | 1.4400517 | -0.0001854 |
| C | 3.8154174 | -0.0135430 | 0.0000043 |
| H | 4.3210588 | 0.4275584 | 0.8730894 |
| H | 3.9698918 | -1.0946417 | -0.0001430 |
| H | 4.3214929 | 0.4280668 | -0.8724983 |

**Table S5. Cartesian Coordinates of the Optimized Structure for the Reaction Intermediate Figure 7-a**

**Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | 1.3766190 | 0.9820312 | 1.2349800 |
| C | 0.5543871 | 0.0196047 | 0.5708446 |
| C | 1.1887268 | -0.8509457 | -0.3635210 |
| C | 2.5434552 | -0.7856038 | -0.6105868 |
| C | 3.3360362 | 0.1672798 | 0.0770026 |
| C | 2.7266781 | 1.0530680 | 1.0051394 |
| H | 0.9186275 | 1.6595576 | 1.9502223 |
| H | 0.6008584 | -1.5873216 | -0.9017546 |
| H | 2.9934990 | -1.4640829 | -1.3252697 |
| H | 3.3572694 | 1.7712938 | 1.5181310 |
| O | 4.6482518 | 0.3130437 | -0.0745303 |
| C | 5.3803916 | -0.5313685 | -0.9809222 |
| H | 6.4158726 | -0.2040048 | -0.9021025 |
| H | 5.2965444 | -1.5802355 | -0.6803882 |
| H | 5.0231542 | -0.3950505 | -2.0062917 |
| C | -0.8462640 | -0.0251010 | 0.8678360 |
| H | -1.1724385 | 0.6489055 | 1.6539385 |
| C | -1.6636711 | -1.1793331 | 0.6572948 |
| H | -1.2062431 | -2.0357354 | 0.1706795 |
| C | -2.7425444 | -1.5024368 | 1.6538343 |
| H | -2.2842006 | -1.9139882 | 2.5650936 |
| H | -3.3076235 | -0.6126784 | 1.9503171 |
| H | -3.4385647 | -2.2547101 | 1.2737619 |
| C | -1.5018519 | 1.6382459 | -0.5949043 |
| H | -1.0035247 | 2.5248066 | -0.2128696 |
| H | -0.9282892 | 1.0610227 | -1.3076781 |
| C | -2.8389068 | -0.8007407 | -1.2950304 |
| H | -1.8875980 | -0.6911320 | -1.8042493 |
| H | -3.3595097 | -1.7344838 | -1.4874700 |
| C | -2.8568206 | 1.5130718 | -0.4991350 |
| H | -3.4217295 | 2.2712544 | 0.0398760 |
| C | -3.5503965 | 0.3091947 | -0.8592781 |
| C | -5.0267785 | 0.2227249 | -0.5846927 |
| H | -5.4051308 | -0.7979910 | -0.6788003 |
| H | -5.2781245 | 0.6043323 | 0.4123745 |
| H | -5.5732233 | 0.8477436 | -1.3044461 |

**Table S6. Cartesian Coordinates of the Optimized Structure for the Reaction Intermediate Figure 7-b**

**Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -1.2026981 | -0.8684481 | 1.2271757 |
| C | -0.4995459 | -0.0141860 | 0.3213492 |
| C | -1.2688735 | 0.6834656 | -0.6539133 |
| C | -2.6410278 | 0.5571265 | -0.7173821 |
| C | -3.3106409 | -0.2882276 | 0.2006182 |
| C | -2.5670963 | -1.0012272 | 1.1749180 |
| H | -0.6394364 | -1.4148438 | 1.9788647 |
| H | -0.7753071 | 1.3364715 | -1.3665561 |
| H | -3.1971952 | 1.1060753 | -1.4675718 |
| H | -3.1063973 | -1.6391861 | 1.8667674 |
| O | -4.6267339 | -0.4810184 | 0.2309583 |
| C | -5.4844885 | 0.1951318 | -0.7037599 |
| H | -6.4932505 | -0.1285993 | -0.4516657 |
| H | -5.4021637 | 1.2803487 | -0.5876216 |
| H | -5.2453304 | -0.0996323 | -1.7304160 |
| C | 0.9132738 | 0.0983692 | 0.4310577 |
| H | 1.3475737 | -0.4058511 | 1.2921199 |
| C | 1.7417565 | 1.2166041 | -0.1507144 |
| H | 1.3846980 | 1.4265443 | -1.1650785 |
| C | 1.5129886 | 2.5040757 | 0.6825329 |
| H | 0.4658044 | 2.8172844 | 0.6517239 |
| H | 1.7953995 | 2.3532737 | 1.7303888 |
| H | 2.1264443 | 3.3172999 | 0.2798955 |
| C | 1.6878439 | -1.4591783 | -1.0888731 |
| H | 1.0436752 | -2.3339679 | -1.1113398 |
| H | 1.4430357 | -0.6919880 | -1.8135023 |
| C | 3.2783399 | 0.9281213 | -0.2190637 |
| H | 3.6763915 | 1.4537294 | -1.1009423 |
| H | 3.7646189 | 1.4247975 | 0.6315631 |
| C | 2.9861898 | -1.5682853 | -0.5527857 |
| H | 3.3424556 | -2.5629308 | -0.2867788 |
| C | 3.7857647 | -0.4912774 | -0.2309395 |
| C | 5.1958924 | -0.6932653 | 0.2344714 |
| H | 5.3191904 | -0.3602773 | 1.2746157 |
| H | 5.5090165 | -1.7377023 | 0.1634112 |
| H | 5.8885768 | -0.0854924 | -0.3636922 |

**Table S7. Cartesian Coordinates of the Optimized Structure for the Radical Cation of the Diels-Alder Adduct $3^{\cdot+}$, Figure 7-c Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -1.2373062 | -0.1954102 | 1.5040604 |
| C | -0.4757960 | -0.1184160 | 0.3068822 |
| C | -1.1802914 | -0.0737795 | -0.9301131 |
| C | -2.5565651 | -0.0720846 | -0.9824024 |
| C | -3.2956846 | -0.1360944 | 0.2314182 |
| C | -2.6112813 | -0.1989005 | 1.4795978 |
| H | -0.7183526 | -0.2427914 | 2.4568442 |
| H | -0.6214050 | -0.0292644 | -1.8598713 |
| H | -3.0663127 | -0.0256041 | -1.9373525 |
| H | -3.2040397 | -0.2464245 | 2.3868903 |
| O | -4.6165155 | -0.1478049 | 0.3098191 |
| C | -5.4393509 | -0.0930510 | -0.8751532 |
| H | -6.4639513 | -0.1135539 | -0.5084806 |
| H | -5.2523962 | 0.8352303 | -1.4222983 |
| H | -5.2473001 | -0.9637767 | -1.5083117 |
| C | 1.0181574 | -0.1227972 | 0.3576491 |
| H | 1.3183556 | -0.1072479 | 1.4130490 |
| C | 1.7296588 | 1.0643368 | -0.3547949 |
| H | 1.5677137 | 0.9470883 | -1.4357129 |
| C | 1.1857091 | 2.4326251 | 0.0761008 |
| H | 0.1330540 | 2.5569645 | -0.1988349 |
| H | 1.2709549 | 2.5679808 | 1.1613414 |
| H | 1.7502970 | 3.2392943 | -0.4034874 |
| C | 1.5654567 | -1.4600594 | -0.2649758 |
| H | 1.1238476 | -2.3318931 | 0.2329287 |
| H | 1.2406643 | -1.5080743 | -1.3134781 |
| C | 3.2440446 | 0.9776488 | -0.0899143 |
| H | 3.7682818 | 1.6194497 | -0.8134702 |
| H | 3.4782750 | 1.4211197 | 0.8920006 |
| C | 3.0567730 | -1.5079471 | -0.1693389 |
| H | 3.5161845 | -2.4913167 | -0.0878205 |
| C | 3.8443330 | -0.4043496 | -0.1265212 |
| C | 5.3400647 | -0.4970445 | -0.0614819 |
| H | 5.7268306 | 0.0385165 | 0.8164746 |
| H | 5.6871689 | -1.5325423 | -0.0165396 |
| H | 5.7967220 | -0.0187757 | -0.9385008 |

**Table S8. Cartesian Coordinates of the Optimized Structure for the Diels-Alder Adduct 3, Figure 7-d**

**Calculated at the RB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -1.2758012 | 0.1443594 | 1.5007628 |
| C | -0.4880066 | -0.0734108 | 0.3596342 |
| C | -1.1591700 | -0.2971332 | -0.8479722 |
| C | -2.5542378 | -0.3025643 | -0.9297184 |
| C | -3.3162723 | -0.0832936 | 0.2235220 |
| C | -2.6648256 | 0.1399717 | 1.4433313 |
| H | -0.7883519 | 0.3204515 | 2.4573635 |
| H | -0.5898493 | -0.4707222 | -1.7582885 |
| H | -3.0293104 | -0.4784982 | -1.8883668 |
| H | -3.2667689 | 0.3083092 | 2.3311438 |
| O | -4.6831729 | -0.0672786 | 0.2646837 |
| C | -5.3910774 | -0.2838177 | -0.9438282 |
| H | -6.4503655 | -0.2259910 | -0.6859420 |
| H | -5.1588593 | 0.4851141 | -1.6930959 |
| H | -5.1760628 | -1.2738860 | -1.3682970 |
| C | 1.0299968 | -0.0830947 | 0.4492304 |
| H | 1.2980669 | 0.1533345 | 1.4900295 |
| C | 1.7268376 | 0.9801346 | -0.4392257 |
| H | 1.5681582 | 0.6912333 | -1.4896807 |
| C | 1.1646727 | 2.3927861 | -0.2388600 |
| H | 0.1054760 | 2.4497570 | -0.5065853 |
| H | 1.2613724 | 2.7068078 | 0.8088335 |
| H | 1.7102912 | 3.1191775 | -0.8535431 |
| C | 1.5994127 | -1.4861694 | 0.1366337 |
| H | 1.2703462 | -2.1895217 | 0.9142828 |
| H | 1.1547404 | -1.8644659 | -0.7973520 |
| C | 3.2454472 | 0.9663193 | -0.1783576 |
| H | 3.7495456 | 1.5517137 | -0.9621426 |
| H | 3.4595797 | 1.5046870 | 0.7607901 |
| C | 3.1011717 | -1.5069246 | 0.0280957 |
| H | 3.5794363 | -2.4861763 | 0.0660628 |
| C | 3.8615612 | -0.4135134 | -0.1065807 |
| C | 5.3653826 | -0.4785312 | -0.1803997 |
| H | 5.8283648 | 0.1156509 | 0.6205195 |
| H | 5.7323217 | -1.5063826 | -0.0928686 |
| H | 5.7367030 | -0.0630718 | -1.1279387 |

**Table S9. Cartesian Coordinates of the Optimized Structure for the Reaction Intermediate Figure 7-e Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -3.2284563 | 0.6662771 | -1.2180158 |
| C | -1.8919661 | 0.7783286 | -0.8621041 |
| C | -1.3973619 | 0.1306416 | 0.3106004 |
| C | -2.3113582 | -0.6392227 | 1.0939535 |
| C | -3.6479411 | -0.7398616 | 0.7346117 |
| C | -4.1136952 | -0.0892955 | -0.4232387 |
| H | -3.5953461 | 1.1630376 | -2.1088660 |
| H | -1.2252170 | 1.3637384 | -1.4853775 |
| H | -1.9495268 | -1.1364790 | 1.9886330 |
| H | -4.3333494 | -1.3168991 | 1.3444660 |
| H | -5.1575764 | -0.1691262 | -0.7057113 |
| C | -0.0265491 | 0.2228339 | 0.7412901 |
| H | 0.1961411 | -0.2554404 | 1.6901131 |
| C | 0.8581398 | 1.2964232 | 0.3554867 |
| H | 0.4800689 | 2.0229373 | -0.3582506 |
| C | 0.7016404 | -1.7449865 | -0.2249144 |
| H | 0.1377919 | -2.5103344 | 0.2988610 |
| H | 0.2171494 | -1.3419038 | -1.1042708 |
| C | 2.1863307 | 0.4641392 | -1.3413616 |
| H | 1.2847276 | 0.2485100 | -1.9041745 |
| H | 2.7541877 | 1.3208349 | -1.6896133 |
| C | 1.8396352 | 1.8297589 | 1.3648323 |
| H | 1.3054803 | 2.4463249 | 2.1039362 |
| H | 2.3437357 | 1.0299646 | 1.9168544 |
| H | 2.5937671 | 2.4705088 | 0.9011640 |
| C | 2.0430377 | -1.6013402 | -0.0096407 |
| H | 2.5317039 | -2.2164537 | 0.7421857 |
| C | 2.8125577 | -0.5187618 | -0.5751844 |
| C | 4.2573576 | -0.3876515 | -0.1785459 |
| H | 4.6873796 | 0.5664376 | -0.4904716 |
| H | 4.3945213 | -0.5017418 | 0.9042343 |
| H | 4.8461326 | -1.1876111 | -0.6503261 |

**Table S10. Cartesian Coordinates of the Optimized Structure for the Reaction Intermediate Figure 7-f**

**Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -3.4017323 | 0.4552688 | -0.9850435 |
| C | -2.0306749 | 0.6068087 | -0.8626493 |
| C | -1.3274884 | -0.0349131 | 0.1941013 |
| C | -2.0636782 | -0.8426645 | 1.1055026 |
| C | -3.4355499 | -0.9872047 | 0.9770190 |
| C | -4.1080305 | -0.3399417 | -0.0684082 |
| H | -3.9323185 | 0.9524161 | -1.7909048 |
| H | -1.4964146 | 1.2230036 | -1.5787348 |
| H | -1.5366381 | -1.3401812 | 1.9153655 |
| H | -3.9876899 | -1.5978541 | 1.6841891 |
| H | -5.1829323 | -0.4544670 | -0.1717915 |
| C | 0.0844320 | 0.1023546 | 0.3883524 |
| H | 0.4684500 | -0.3625652 | 1.2946241 |
| C | 0.9312104 | 1.2095934 | -0.1812488 |
| H | 0.6266532 | 1.3895578 | -1.2176580 |
| C | 0.9435483 | -1.4953291 | -1.0418322 |
| H | 0.3079245 | -2.3760650 | -1.0721360 |
| H | 0.7264910 | -0.7467821 | -1.7942181 |
| C | 2.4701971 | 0.9358882 | -0.1552516 |
| H | 2.9163231 | 1.4464089 | -1.0230223 |
| H | 2.9052950 | 1.4524137 | 0.7112569 |
| C | 0.6400510 | 2.5153259 | 0.6062363 |
| H | -0.4071523 | 2.8128953 | 0.5079139 |
| H | 0.8670272 | 2.3956204 | 1.6712817 |
| H | 1.2654407 | 3.3244136 | 0.2141398 |
| C | 2.2065954 | -1.5735607 | -0.4316057 |
| H | 2.5527241 | -2.5542412 | -0.1068717 |
| C | 2.9889606 | -0.4774947 | -0.1111552 |
| C | 4.3787541 | -0.6586291 | 0.4145578 |
| H | 4.4523328 | -0.3104068 | 1.4546314 |
| H | 4.7069627 | -1.6996744 | 0.3707319 |
| H | 5.0879523 | -0.0475043 | -0.1602470 |

**Table S11. Cartesian Coordinates of the Optimized Structure for the Radical Cation of the Diels-Alder Adduct 21$^{\cdot+}$, Figure 7-g Calculated at the UB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -3.2908056 | -0.0364587 | -1.2501757 |
| C | -1.9126417 | -0.0211151 | -1.1301253 |
| C | -1.2986615 | -0.1640759 | 0.1392630 |
| C | -2.1261742 | -0.3700012 | 1.2738773 |
| C | -3.5074819 | -0.3887044 | 1.1544060 |
| C | -4.0972790 | -0.2236150 | -0.1075530 |
| H | -3.7557483 | 0.0909542 | -2.2227093 |
| H | -1.3003275 | 0.1170772 | -2.0167338 |
| H | -1.6639472 | -0.5005534 | 2.2484659 |
| H | -4.1300619 | -0.5327214 | 2.0315824 |
| H | -5.1780268 | -0.2489421 | -0.2094627 |
| C | 0.1885436 | -0.1314386 | 0.3029526 |
| H | 0.4133605 | -0.1798800 | 1.3758860 |
| C | 0.9376056 | 1.0908645 | -0.2911864 |
| H | 0.8424709 | 1.0442032 | -1.3846916 |
| C | 0.8012557 | -1.4351739 | -0.3654416 |
| H | 0.3110127 | -2.3475795 | -0.0089748 |
| H | 0.5892313 | -1.3670996 | -1.4415075 |
| C | 2.4348581 | 0.9944822 | 0.0594469 |
| H | 3.0133719 | 1.6853310 | -0.5719752 |
| H | 2.6027323 | 1.3666905 | 1.0853462 |
| C | 0.3630011 | 2.4296580 | 0.1915160 |
| H | -0.6731373 | 2.5581769 | -0.1352138 |
| H | 0.3857263 | 2.4987647 | 1.2858686 |
| H | 0.9452629 | 3.2665201 | -0.2085150 |
| C | 2.2615179 | -1.4931984 | -0.1209096 |
| H | 2.7172971 | -2.4704678 | 0.0294505 |
| C | 3.0537350 | -0.3708236 | -0.0084889 |
| C | 4.5388633 | -0.4726419 | 0.1097631 |
| H | 4.9009394 | 0.1007604 | 0.9742386 |
| H | 4.8834406 | -1.5057355 | 0.1961607 |
| H | 5.0183857 | -0.0220474 | -0.7712817 |

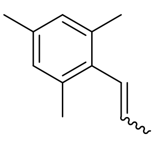
**Table S12. Cartesian Coordinates of the Optimized Structure for the Diels-Alder Adduct 21, Figure 7-h Calculated at the RB3LYP/6-311G(2d,2p) level.**

| Atom | X | Y | Z |
|---|---|---|---|
| C | -3.2560868 | -0.3262961 | -1.2737403 |
| C | -1.8731868 | -0.2872589 | -1.0970761 |
| C | -1.3093373 | -0.1553335 | 0.1819838 |
| C | -2.1790227 | -0.0659010 | 1.2765018 |
| C | -3.5644412 | -0.1078518 | 1.1064346 |
| C | -4.1088825 | -0.2380385 | -0.1710625 |
| H | -3.6687633 | -0.4270735 | -2.2744849 |
| H | -1.2243629 | -0.3583900 | -1.9670676 |
| H | -1.7639827 | 0.0359491 | 2.2770660 |
| H | -4.2165910 | -0.0380961 | 1.9734401 |
| H | -5.1865429 | -0.2702888 | -0.3078764 |
| C | 0.1977093 | -0.1339203 | 0.3859516 |
| H | 0.3825693 | 0.0227644 | 1.4591777 |
| C | 0.9239073 | 1.0143817 | -0.3616548 |
| H | 0.8483548 | 0.8094140 | -1.4404325 |
| C | 0.8267727 | -1.4941954 | 0.0048331 |
| H | 0.4643245 | -2.2652196 | 0.6989980 |
| H | 0.4597923 | -1.8059735 | -0.9856559 |
| C | 2.4198337 | 1.0133809 | 0.0078133 |
| H | 2.9608873 | 1.6726405 | -0.6875979 |
| H | 2.5516011 | 1.4772640 | 1.0002911 |
| C | 0.3077741 | 2.3923070 | -0.0901978 |
| H | -0.7285235 | 2.4488821 | -0.4362505 |
| H | 0.3139540 | 2.6190016 | 0.9840687 |
| H | 0.8783583 | 3.1795235 | -0.5978700 |
| C | 2.3324053 | -1.4710487 | 0.0039182 |
| H | 2.8344304 | -2.4389828 | -0.0028528 |
| C | 3.0685663 | -0.3531869 | 0.0125712 |
| C | 4.5751463 | -0.3775481 | 0.0405656 |
| H | 4.9649400 | 0.1628239 | 0.9151148 |
| H | 4.9643389 | -1.4003062 | 0.0749306 |
| H | 4.9982688 | 0.1191252 | -0.8440480 |

## 2. General Information

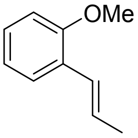
All solvents and reagents were from commercial source and were used without further purification. $^1$H-NMR spectra were collected on a 600 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. $^{13}$C-NMR spectra were collected on a 150 MHz spectrometer with proton decoupling using the deuterated solvent as an internal carbon reference. Chemical shift data are given in δ units calibrated with residual solvent. Only selected absorbances are reported in the IR spectra. HRMS analysis was performed in ESITOF or DARTTOF mode. The reaction yields were determined by NMR or GC-MS. Cyclic voltammograms were recorded at 2 mM of substrate using a glassy carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode in 1.0 M $LiClO_4/MeNO_2$ at 50 mV/s.

## 3. Experimental and Spectra Information of Starting Materials



**15**

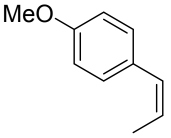
A suspension of ethyltriphenylphosphonium iodide (5.19 g, 12.0 mmol) in THF (30 mL) was cooled to 0 °C under argon atmosphere, and then potassium *t*-butoxide (1.68 g, 15.0 mmol) was added. The reaction mixture was stirred for 30 min at 0 °C, then mesitaldehyde (1.47 mL, 10.0 mmol) was added and the solution was stirred for 6 h at room temperature. The reaction was quenched by the addition of saturated ammonium chloride aqueous solution (100 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were dried with $Mg_2SO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 20 : 1) affording the desired product as transparent oil (1.18 g, 7.33 mmol, 73%, *cis* : *trans* = 7 : 3). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 6.86 (1.4H, s), 6.85 (0.6H, s), 6.33-6.24(1H, m), 5.81 (0.7H, dq, *J* = 11.7, 6.9 Hz), 5.65 (0.3H, dq, *J* = 16.3, 6.9 Hz), 2.27 (2.1H, s), 2.26 (0.9H, s), 2.25 (2.1H, s), 2.16 (3.9H, s), 1.89 (0.9H, dd, *J* = 8.3, 2.1 Hz), 1.45 (2.1H, dd, *J* = 7.0, 2.1 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 136.0, 135.9, 135.8, 135.7, 134.8, 133.6, 130.0, 128.37, 128.35, 128.32, 127.8, 127.3, 21.0, 20.89, 20.87, 20.1, 18.8, 14.3; IR (NaCl, cm$^{-1}$) 3007, 2965, 2918, 2857, 1614, 1443, 1378, 971; HRMS (DART-TOF) $[M + H]^+$ calcd. for $C_{12}H_{17}$ 161.1330, found 161.1330.



**16**

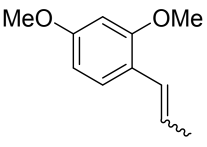
A suspension of ethyltriphenylphosphonium iodide (1.51 g, 3.60 mmol) in THF (40 mL) and LiBr (624 mg, 3.60 mmol) was cooled to -78 °C under argon atmosphere, and then phenyllithium (1.8 M in diethylether, 6.48

mL, 3.60 mmol) was added. After stirring at room temperature for 0.5 h, the mixture was cooled to -78 °C again. A solution of *o*-anisaldehyde (362 μL, 3.00 mmol) in THF (10 mL) was added, subsequently phenyllithium (1.8 M in diethylether, 6.48 mL, 3.60 mmol) was added and the reaction mixture was stirred at -78 °C for 0.5 h. The reaction mixture was allowed to warm to room temperature, and then stirred for 0.5 h at room temperature. The mixture was cooled to -78 °C again and a solution of HCl (1.0 M in diethylether 3.60 mmol) was added. After 15 min potassium *t*-butoxide (448 mg, 4.00 mmol) was added to the solution, then the mixture was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched by the addition of brine (100 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 30 : 1) affording the desired product as transparent oil (262 mg, 1.77 mmol, 59%, *cis* : *trans* = 3 : 97). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 7.39 (1H, dd, *J* = 7.6, 1.8 Hz), 7.18 (1H, dt, *J* = 7.8, 1.8 Hz), 6.90 (1H, t, *J* = 7.3 Hz), 6.86 (1H, d, *J* = 8.3 Hz), 6.72 (0.97H, dd, *J* = 15.8, 1.8 Hz), 6.54 (0.03H, dd, *J* = 11.9 1.8 Hz), 6.22 (0.97H, dq, *J* = 15.8, 6.9 Hz), 5.85 (0.03H, dq, *J* = 11.7, 6.9 Hz), 3.84 (3H, s), 1.90 (2.91H, dd, *J* = 6.6, 1.8 Hz), 1.83 (0.09H, dd, *J* = 6.9, 1.8 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 156.2, 127.7, 127.1, 126.6, 126.5, 125.6, 120.7, 110.7, 55.4, 18.9; IR (NaCl, cm$^{-1}$) 3034, 3003, 2961, 2938, 2833, 1598, 1489, 1033; HRMS (ESI-TOF) $[M + Na]^+$ calcd. for $C_{10}H_{12}ONa$ 171.0786, found 171.0787.



**17**

A suspension of ethyltriphenylphosphonium iodide (4.26 g, 11.5 mmol) in THF (50 mL) and HMPA (2.86 mL, 16.4 mmol) was cooled to 0 °C under argon atmosphere, and then KHMDS (0.5 M in toluene, 10.7 mL, 5.36 mmol) was added. After stirring at room temperature for 10 min, the mixture was cooled to -78 °C. *p*-anisaldehyde (1.00 mL, 8.22 mmol) was added dropwise, the reaction mixture was allowed to warm to room temperature, and then stirred for 1.5 h at room temperature. The reaction was quenched by the addition of saturated $NH_4Cl$ aqueous solution (100 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 30 : 1) affording the desired product as transparent oil (612 mg, 4.13 mmol, 50%, *cis* : *trance* = 10 : 1). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 7.25 (2H, d, *J* = 8.9 Hz), 6.88 (1.8H, d, *J* = 8.9 Hz), 6.83 (0.2H, d, *J* = 8.3 Hz), 6.39-6.22 (1H, m), 6.09 (0.1H, dq, *J* = 15.8, 6.9 Hz), 5.70 (0.9H, dq, *J* = 11.7, 7.6 Hz), 3.82 (2.7H, s), 3.80 (0.3H, s), 1.89 (2.7H, dd, *J* = 7.2, 2.1 Hz), 1.86 (0.3H, dd, *J* = 6.2, 1.4 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 158.1, 130.3, 130.0, 129.2, 126.8, 125.1, 123.5, 113.9, 113.5, 55.2, 18.4, 14.6; IR (NaCl, cm$^{-1}$) 3015, 2953, 2938, 2914, 2837, 1605, 1513, 1038; HRMS (ESI-TOF) $[M + Na]^+$ calcd. for $C_{10}H_{12}ONa$ 171.0786, found 171.0782.



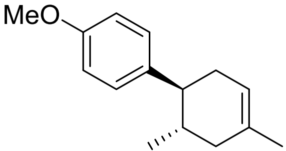
**19**

A suspension of ethyltriphenylphosphonium iodide (3.89 g, 10.0 mmol) in THF (30 mL) was cooled to 0 °C under argon atmosphere, and then potassium *t*-butoxide (1.35 g, 12.0 mmol) was added. The reaction mixture was stirred for 30 min at 0 °C, then 2,4-dimethoxybenzaldehyde (1.02 mL, 6.0 mmol) was added and the solution was stirred for 6 h at room temperature. The reaction was quenched by the addition of saturated ammonium chloride aqueous solution (100 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were dried with $Mg_2SO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane–EtOAc, 5 : 1) affording the desired product as transparent oil (1.21 g, 6.76 mmol, 68%, *cis* : *trans* = 4 : 1). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 7.29 (0.2H, d, *J* = 8.9 Hz), 7.17 (0.8H, d, *J* = 7.6 Hz), 6.60 (0.2H, dd, *J* = 16.2, 2.0 Hz), 6.48-6.41 (2.8H, m), 6.09 (0.2H, dq, *J* = 15.8, 6.9 Hz), 5.76 (0.8H, dq, *J* = 11.3, 6.9 Hz), 3.81 (3H, s), 3.80 (2.4H, s), 3.79 (0.6H, s), 1.86 (0.6H, dd, *J* = 6.9, 1.4 Hz), 1.81 (2.4H, dd, *J* = 7.2, 1.4 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 159.8, 158.1, 157.2, 130.5, 127.1, 125.7, 125.2, 124.7, 124.5, 120.2, 119.1, 104.7, 103.7, 98.4, 98.3, 55.5, 55.4, 18.9, 14.6; IR (NaCl, cm$^{-1}$) 3023, 3003, 2961, 2938, 2837, 1609, 1501, 1037; HRMS (ESI-TOF) $[M + Na]^+$ calcd. for $C_{11}H_{14}O_2Na$ 201.0892, found 201.0894.

## 4. Experimental and Spectra Information of Diels Alder Adducts

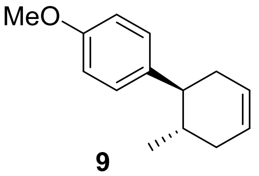
### General procedure

To a solution of lithium perchlorate (1.0 M) in $MeNO_2$, styrene (80 mM, 1 equiv.) and diene (160 mM, 2 equiv.) were added. Two pieces of carbon felt were inserted into the solution and electrolysis was performed using an undivided cell with stirring at a constant potential of 1.0-2.0 V vs. Ag/AgCl under room temperature condition. Catalytic amount of electric charge was passed through the solution (the reactions can also be monitored by TLC), followed by dilution with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Purification was performed by silica gel column chromatography.



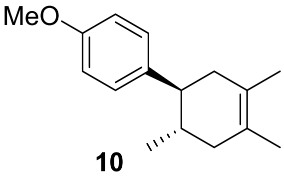
**3**

According to the General procedure, *trans*-anethole **1** (237 mg, 1.60 mmol), isoprene **2** (218. mg, 3.20 mmol), lithium perchlorate (2.13 g) and nitromethane (20 mL), were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder adduct (**3**) in product of transparent oil (3.33 g, 1.54 mmol, 96%; 98% determined by $^1$H-NMR). $^1$H NMR ($CDCl_3$, 600 MHz) δ 7.08 (2H, d, *J* = 8.3 Hz), 6.84 (2H, d, *J* = 8.9 Hz), 5.44 (1H, br. s), 3.80 (3H, s), 2.29 (1H, td, *J* = 11.0, 5.5 Hz), 2.24-2.11 (2H, m), 2.08 (1H, dd, *J* = 17.2, 4.8 Hz), 1.93-1.84 (1H, m), 1.83-1.76 (1H, m), 1.69 (3H,s), 0.70 (3H, d, *J* = 6.2 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 157.8, 138.2, 133.8, 128.5, 120.9, 113.7, 55.2, 47.0, 39.8, 35.3, 34.0, 23.4, 20.2; IR (NaCl, cm$^{-1}$) 3061, 3030, 2953, 2891, 2833, 1611, 1512, 1245; HRMS (ESI-TOF) $[M + H]^+$ calcd. for $C_{15}H_{21}O$ 217.1592, found 217.1590.



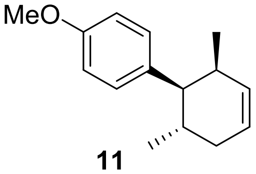
**9**

According to the general procedure, *trans*-anethole **1** (237 mg, 1.60 mmol), 1,3-butadiene (**4**) solution (0.64 M in cyclohexane, 5 mL, 3.20 mmol), lithium perchlorate (1.60 g) and nitromethane (15 ml) were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder adduct (**9**) as transparent oil (40% determined by $^1$H NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 7.09 (2H, d, $J$ = 8.7 Hz), 6.85 (2H, d, $J$ = 8.7 Hz), 5.73 (2H, br. s), 3.80 (3H, s), 2.37 (1H, td, $J$ = 10.5, 5.5 Hz), 2.28-2.12 (3H, m), 1.94-1.77 (2H, m), 0.70 (3H, d, $J$ = 6.0 Hz); $^{13}$C-NMR (CDCl$_3$, 150 MHz) δ 157.8, 138.2, 128.5, 126.9, 126.8, 113.7, 55.2, 47.0, 35.0, 34.9, 33.6, 20.2; IR (NaCl, cm$^{-1}$) 3062, 3020, 2952, 2903, 2830, 1611, 1511, 1245; HRMS (ESI-TOF) [M + Na]$^+$ calcd. for C$_{14}$H$_{18}$ONa 225.1255, found 225.1257.



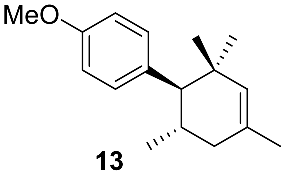
**10**

According to the general procedure, *trans*-anethole **1** (237 mg, 1.60 mmol), 2,3-dimethyl-1,3-butadiene (**5**) (263 mg, 3.20 mmol), lithium perchlorate (2.13 g) and nitromethane (20 mL) were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder adduct (**10**) as transparent oil (96% determined by $^1$H-NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 7.08 (2H, d, $J$ = 8.9 Hz), 6.84 (2H, d, $J$ = 8.9 Hz), 3.79 (3H, s), 2.33 (1H, td, $J$ = 10.3, 5.5 Hz), 2.19-2.12 (1H, m), 2.12-2.04 (2H, m), 1.90-1.77 (2H, m), 1.64 (3H, s), 1.61 (3H, s), 0.69 (3H, d, $J$ = 6.2 Hz); $^{13}$C-NMR (CDCl$_3$, 150 MHz) δ 157.7,138.2, 128.4, 125.5, 125.3, 113.7, 55.2, 47.8, 41.8, 41.6, 34.2, 20.0, 18.7, 18.6; IR (NaCl, cm$^{-1}$) 3065, 3030, 2953, 2911, 2830, 1614, 1512, 1245; HRMS (ESI-TOF) [M + H]$^+$ calcd. for C$_{16}$H$_{23}$O 231.1749, found 231.1751.



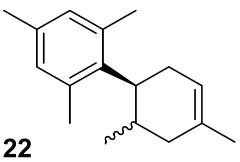
**11**

According to the general procedure, *trans*-anethole **1** (237 mg, 1.60 mmol), *trans*-1,3-pentadiene (**6**) (218 mg, 3.20 mmol), lithium perchlorate (2.13 g) and nitromethane (20 mL) were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder adduct (**11**) as transparent oil (93% determined by $^1$H-NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 7.06 (2H, d, *J* = 8.9 Hz), 6.84 (2H, d, *J* = 8.9 Hz), 5.75-5.72 (1H, m), 5.66-5.62 (1H, m), 3.80 (3H, s), 2.66 (1H, dd, *J* = 11.0, 5.5 Hz), 2.32-2.23 (2H, m), 2.13 (1H, sept, *J* = 5.5 Hz), 1.83-1.77 (1H, m), 0.83 (3H, d, *J* = 6.2 Hz), 0.74 (3H, d, *J* = 6.9 Hz); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 157.6, 135.4, 133.5, 130.1, 125.1, 113.2, 55.2, 50.5, 35.5, 34.8, 26.5, 20.5, 16.8; IR (NaCl, cm$^{-1}$) 3015, 2953, 2903, 2834, 1609, 1512, 1246, 825; HRMS (ESI-TOF) [M + Na]$^+$ calcd. for C$_{15}$H$_{20}$ONa 239.1412, found 239.1413.



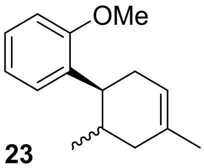
**13**

According to the general procedure, *trans*-anethole **1** (237 mg, 1.60 mmol), 2,4-dimethyl-1,3-pentadiene (**8**) (308 mg, 3.20 mmol), lithium perchlorate (2.13 g) and nitromethane (20 mL) were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder (**13**) adduct as transparent oil (73% determined by $^1$H-NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 7.03 (2H, dd, *J* = 42.6, 6.9 Hz), 6.82 (2H, dd, *J* = 40.6, 6.9 Hz), 5.19 (1H, s), 3.80 (3H, s), 2.22-2.14 (2H, m), 2.09 (1H, dd, $J$ = 17.9, 4.1 Hz), 1.75 (1H, dd, $J$ = 18.2, 8.3 Hz), 1.66 (3H,s), 0.82 (3H, s), 0.77 (3H, s), 0.70 (3H, d, $J$ = 5.5 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 157.7, 133.3, 130.3, 129.3, 113.2, 112.1, 57.4, 55.1, 40.5, 36.2, 30.0, 28.7, 24.7, 23.3, 20.8; IR (NaCl, cm$^{-1}$) 3100, 3065, 3034, 2957, 2838, 1613, 1513, 1246; HRMS (ESI-TOF) $[M + H]^+$ calcd. for $C_{17}H_{25}O$ 245.1905, found 245.1904.



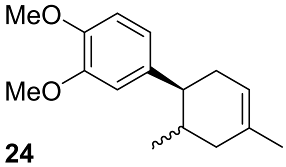
**22**

According to the general procedure, β-methyl-2,4,6-trimethylstyrene **15** (365 mg, 1.60 mmol), isoprene **2** (218 mg, 3.20 mmol), lithium perchlorate (2.13 g) and nitromethane (20 mL) were used and 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 30 : 1) afforded the Diels-Alder adduct **22** as transparent oil (*cis* : *trans* = 1 : 2, 13% determined by $^1$H-NMR). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 6.82 (1H, s), 6.78 (1H, s), 5.44 (1H, br. s), 3.00 (0.4H, td, $J$ = 11.7, 5.5 Hz), 2.92 (0.6H, td, $J$ = 11.7, 5.5 Hz), 2.45-2.21 (2H, m), 2.36 (1.2H, s), 2.35 (1.8H, s), 2.29 (3H, s), 2.24 (3H, s), 2.20-2.11 (0.4H, m), 2.05 (1.2H, dd, $J$ = 16.7, 4.6 Hz), 1.96 (0.4H, dd, $J$ = 17.6, 5.5 Hz), 1.84-1.73 (1H, m), 1.70 (1.8H, s), 1.66 (1.2H, s), 0.73 (1.8H, d, $J$ = 6.4 Hz), 0.72 (1.2H, d, $J$ = 6.4 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 137.9, 137.1, 137.0, 136.1, 134.8, 134.23, 134.16, 131.1, 131.0, 129.2, 121.22, 121.18, 43.6, 43.1, 40.7, 35.9, 35.6, 31.0, 30.8, 30.7, 23.6, 23.3, 21.9, 21.3, 20.6, 19.6, 19.5; IR (NaCl, cm$^{-1}$) 3005, 2952, 2925, 2869, 2827, 1611, 914, 746; HRMS (DART-TOF) $[M + H]^+$ calcd. for $C_{17}H_{25}$ 229.1956, found 229.1960.



**23**

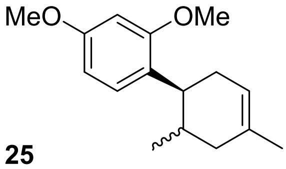
According to the general procedure, β-methyl-2-methoxystyrene **16** (120 μL, 0.80 mmol), isoprene **2** (160 μL, 1.60 mmol), lithium perchlorate (1.06 g) and nitromethane (10 mL), 0.1 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 10 : 1) afforded the Diels-Alder adduct **23** as transparent oil (*cis* : *trans* = 1 : 10, 48% determined by $^1$H-NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 7.18-7.12 (2H, m), 6.95-6.90 (1H, m), 6.86 (1H, d, *J* = 8.3 Hz), 5.45 (0.9H, br. s), 5.42 (0.1H, br. s), 3.81 (0.3H, s), 3.80 (2.7H, s), 2.99 (0.1H, dt, *J* = 10.3, 5.5 Hz), 2.91 (0.9H, q, *J* = 8.9 Hz), 2.16 (2H, br. s), 2.10-1.91 (2H, m), 1.87-1.78 (1H, m), 1.69 (2.7H, s), 1.67(0.3H, s), 0.73 (3H, d, *J* = 6.9 Hz); $^{13}$C-NMR (CDCl$_3$, 150 MHz) δ 157.6, 157.5, 134.2, 133.9, 127.9, 126.6, 121.2, 120.8, 120.7, 110.7, 55.5, 39.9, 38.9, 35.1, 33.6, 32.8, 32.3, 23.6, 23.4, 19.9, 19.7; IR (NaCl, cm$^{-1}$) 2953, 2922, 2880, 2833, 1501, 1493, 1242, 1034; HRMS (ESI-TOF) [M + Na]$^+$ calcd. for $C_{15}H_{20}ONa$ 239.1412, found 239.1412.



**24**

According to the general procedure, *trans*-β-methyl-3,4-dimethoxystyrene **18** (394 mg, 1.60 mmol), isoprene **2** (218 mg, 3.20 mmol), lithium perchlorate (426 mg) and nitromethane (20 mL) were used and 0.5 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 10 : 1) afforded the Diels-Alder adduct **24** as transparent oil (*cis* : *trans* = 1 : >10, 70% determined by $^1$H-NMR). $^1$H-NMR (CDCl$_3$, 600 MHz) δ 6.80 (1H, d, *J* = 8.2 Hz), 6.73-6.68 (2H, m), 5.44 (1H, br. s), 3.87 (6H, s), 2.33-2.14 (3H, m), 2.09 (1H, dd, *J* = 17.4, 3.7 Hz), 1.94-1.75 (2H, m), 1.69 (3H, s), 0.72 (3H, d, *J* = 6.4 Hz); $^{13}$C-NMR (CDCl$_3$, 150 MHz) δ 148.8, 147.1, 138.8, 133.8, 120.8, 119.6, 111.1, 110.7, 55.9, 55.8, 47.4, 39.8, 35.2, 34.0, 23.4, 20.2; IR (NaCl, cm$^{-1}$) 2998, 2952, 2891, 2833, 1607, 1515, 1257, 746; HRMS (ESI-TOF) [M + Na]$^+$ calcd. for

$C_{16}H_{22}O_2Na$ 269.1518, found 269.1514.



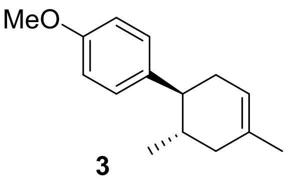
**25**

According to the general procedure, *trans*-β-methyl-2,4-dimethoxystyrene **19** (394 mg, 1.60 mmol), isoprene **2** (218 mg, 3.20 mmol), lithium perchlorate (426 mg) and nitromethane (20 mL) were used and 0.5 F/mol of electricity was passed. Purification by silica gel chromatography (*n*-hexane–EtOAc, 10 : 1) afforded the Diels-Alder adduct (**25**) as transparent oil (*cis* : *trans* = 2 : 5, 21% determined by $^1$H-NMR). $^1$H-NMR ($CDCl_3$, 600 MHz) δ 7.04-7.01 (1H, m), 6.48-6.43 (2H, m), 5.44 (0.9H, br. s), 5.41 (0.1H, br. s), 3.80 (3H, s), 3.78 (0.3H, s), 3.77 (2.7H, s), 2.88 (0.1H, td, *J* = 10.3, 5.5 Hz), 2.83-2.87 (0.9H, m), 2.14 (2H, s), 2.06 (1H, dd, *J* = 17.2, 4.8 Hz), 1.99 (0.9H, sept, *J* = 5.5 Hz), 1.90 (0.1H, sept, *J* = 5.5 Hz), 1.84-1.77 (1H, m), 1.69 (2.7H, s), 1.66 (0.3H, s), 0.73 (3H, d, *J* = 6.8 Hz); $^{13}$C-NMR ($CDCl_3$, 150 MHz) δ 158.60, 158.47, 133.8,128.2, 126.5, 121.2, 120.7, 104.3, 98.5, 55.4, 55.3, 39.9, 39.4, 38.4, 35.0, 33.7, 32.9, 32.4, 23.5, 23.3, 19.9, 19.7; IR (NaCl, cm$^{-1}$) 3000, 2953, 2918, 2833, 1613, 1505, 1257, 1041; HRMS (ESI-TOF) $[M + Na]^+$ calcd. for $C_{16}H_{22}O_2Na$ 269.1518, found 269.1518.

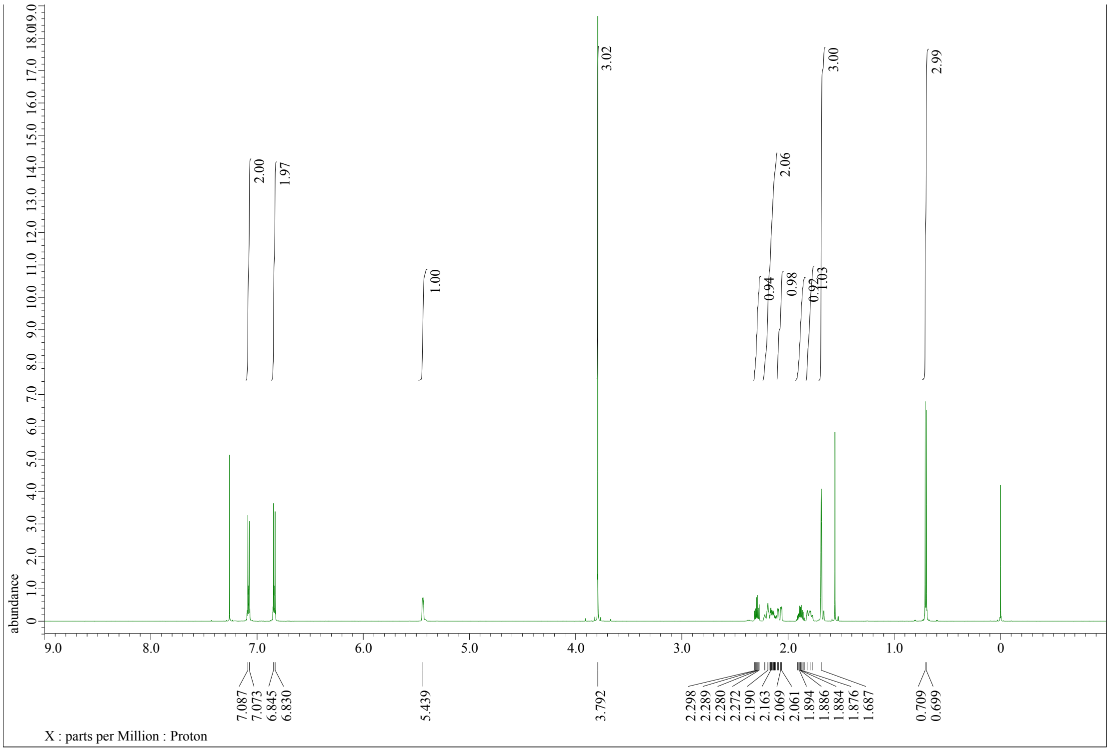
## 5. Theoretical Informatoin

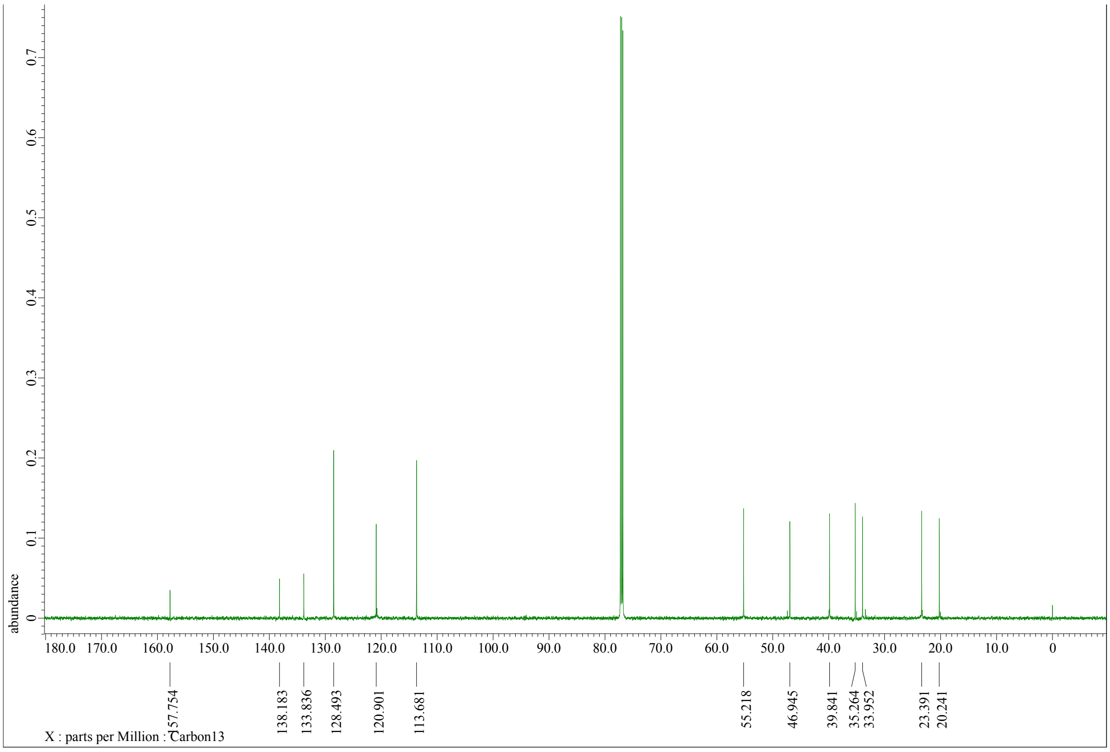
Geometry optimizations of all stationary points and frequency analyses were carried out at the RB3LYP or UB3LYP level of density functional theory with the 6-31G(d) basis set. The 6-311G(2d,2p) basis set was then adopted to calculate the single point energies of the obtained stationary points. No imaginary frequency was observed for *trans*-anethole **1**, the radical cation of trans-anethole $\mathbf{1}^{\cdot+}$, *trans*-β-Methylstyrene **14**, the radical cation of *trans*-β-Methylstyrene $\mathbf{14}^{\cdot+}$, the Diels-Alder adduct **3**, the Diels-Alder adduct **21**, the radical cation of the Diels-Alder adduct $\mathbf{3}^{\cdot+}$, and the radical cation of the Diels-Alder adduct $\mathbf{21}^{\cdot+}$.

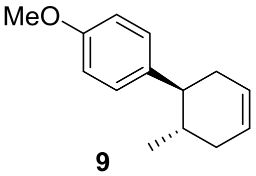
# 6. Copies of NMR spectra



**3**



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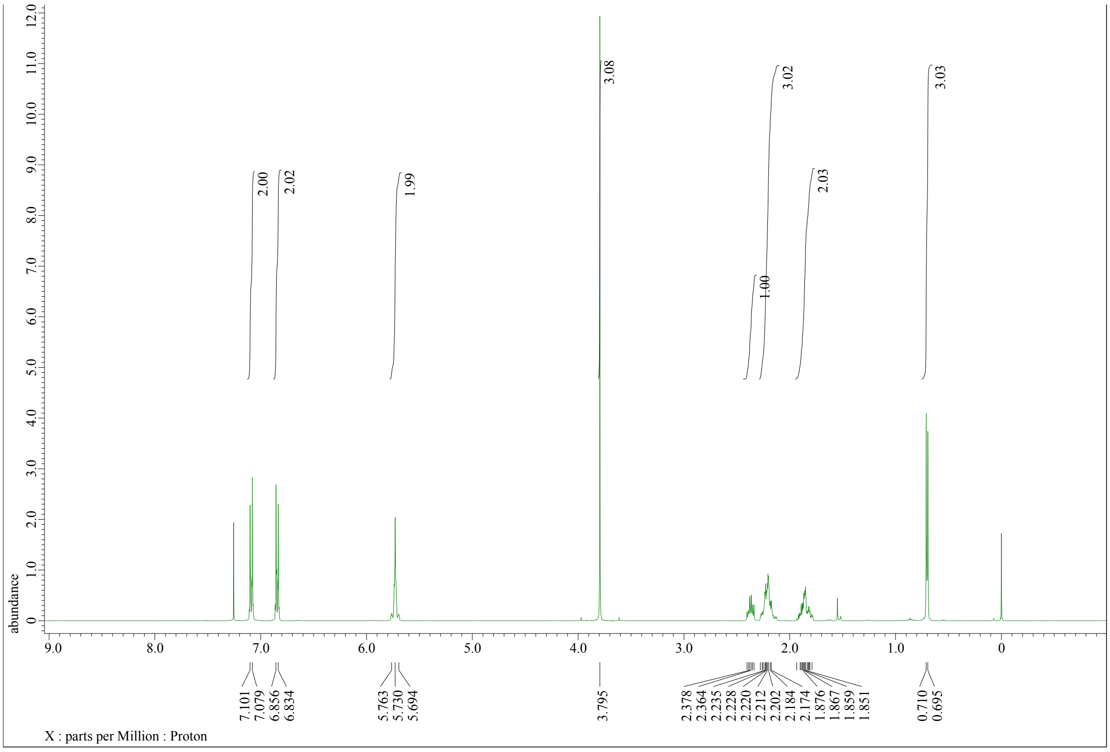
**9**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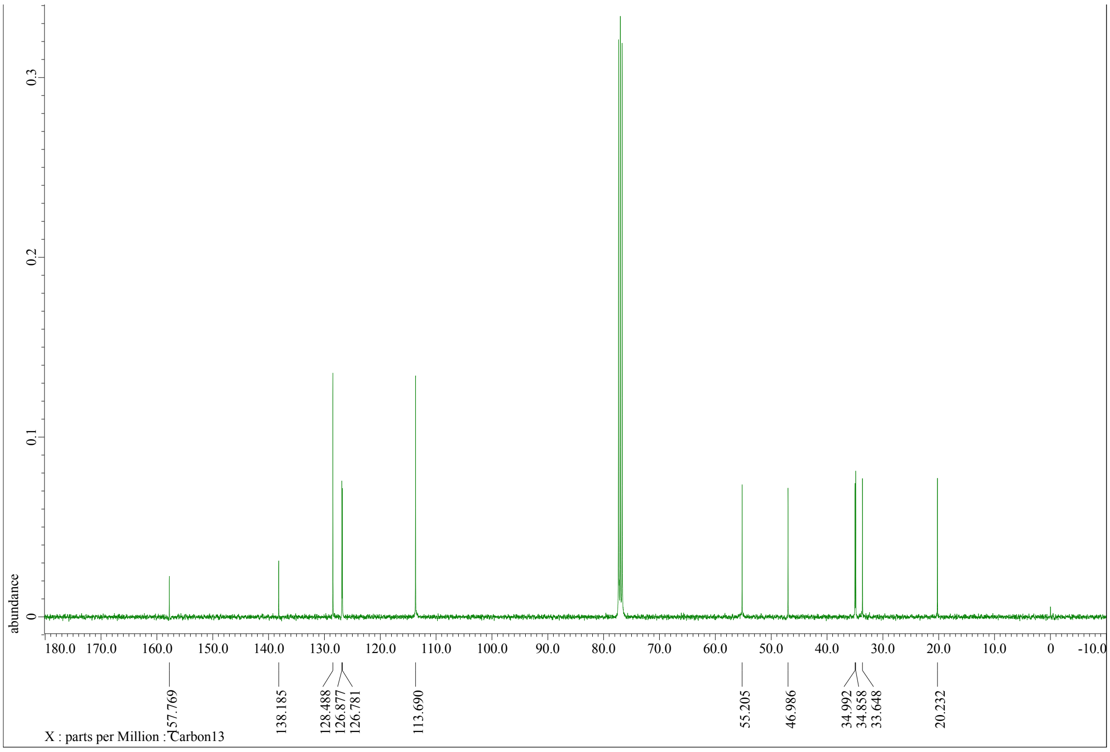
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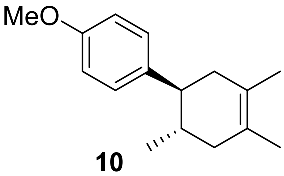
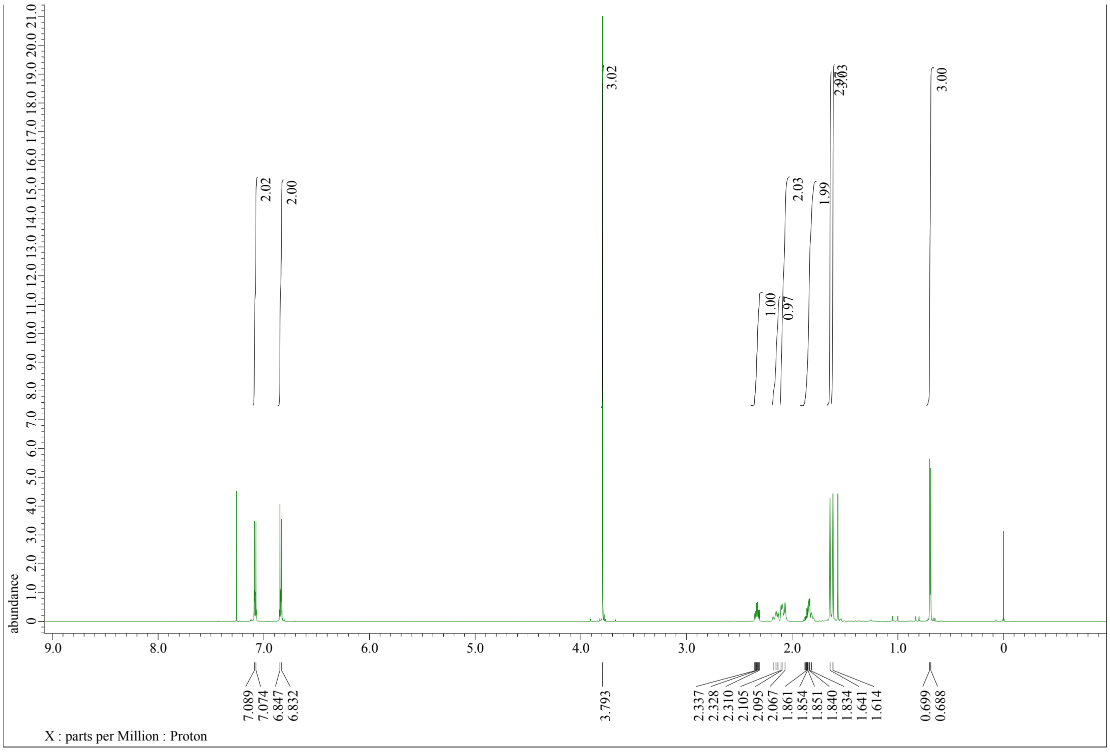
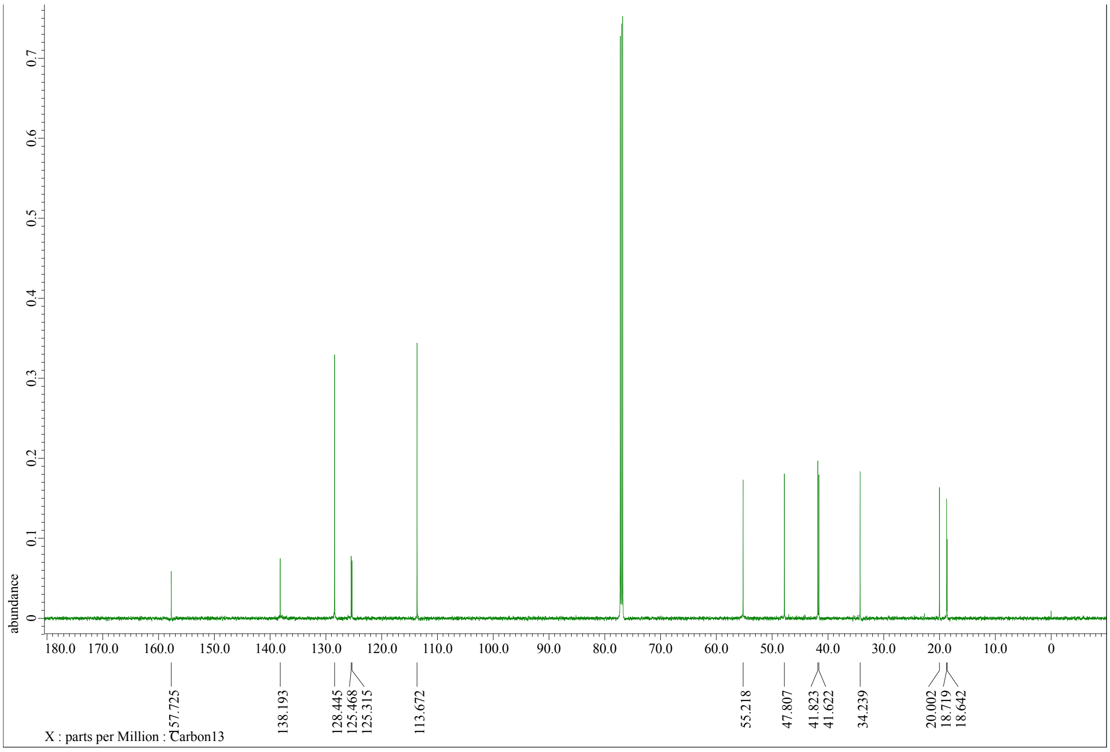
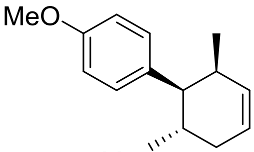
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.769
138.185
128.488
126.877
126.781
113.690
55.205
46.986
34.992
34.858
33.648
20.232
X : parts per Million : Carbon13



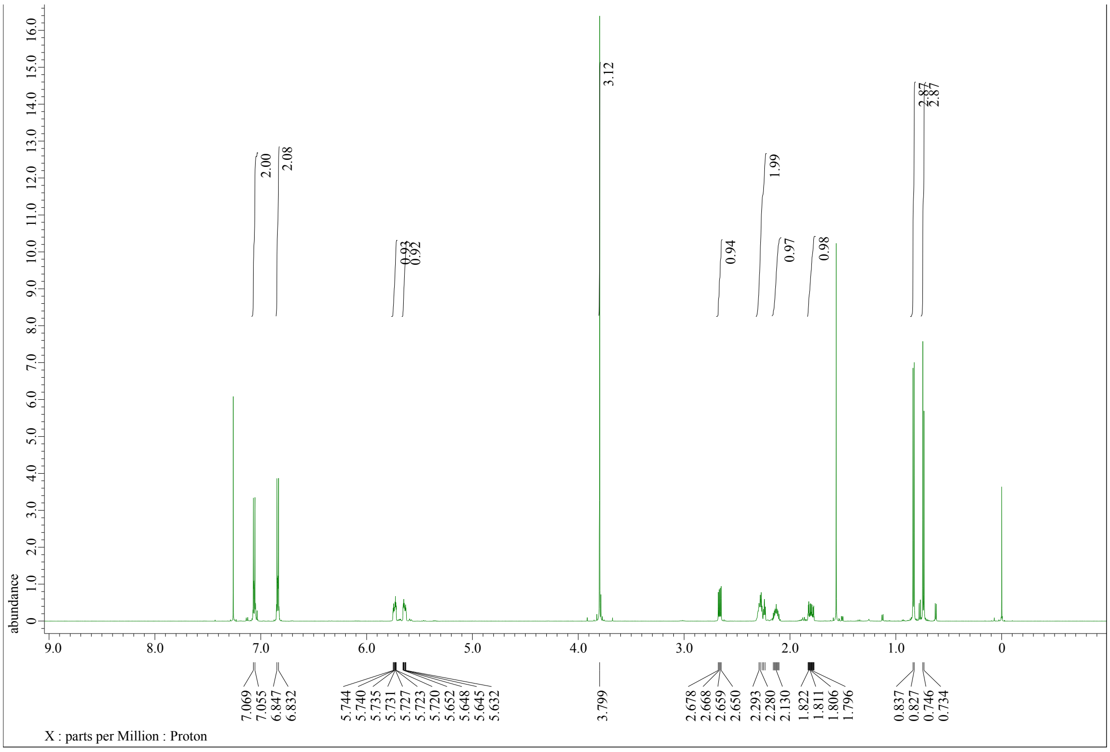
**10**

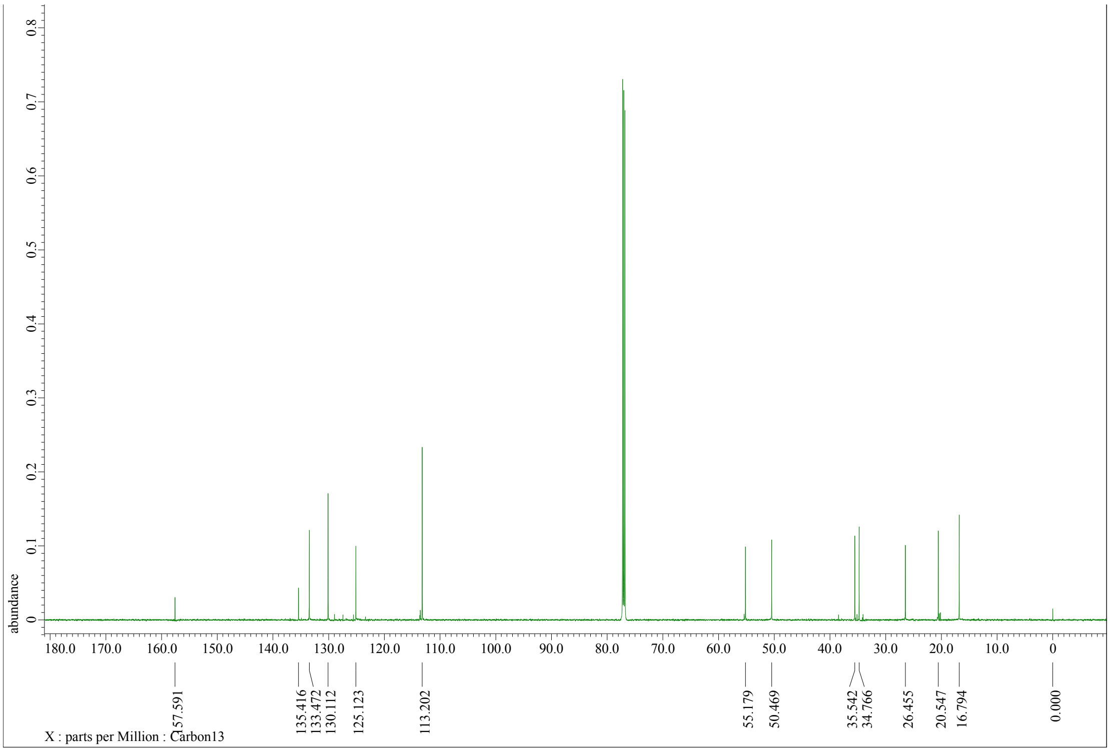

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
2.02
2.00
3.02
1.00
0.97
2.03
1.99
2.97
3.03
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.089
7.074
6.847
6.832
3.793
2.337
2.328
2.310
2.105
2.095
2.067
1.861
1.854
1.851
1.840
1.834
1.641
1.614
0.699
0.688
X : parts per Million : Proton

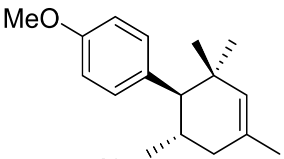

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.725
138.193
128.445
125.468
125.315
113.672
55.218
47.807
41.823
41.622
34.239
20.002
18.719
18.642
X : parts per Million : Carbon13


MeO

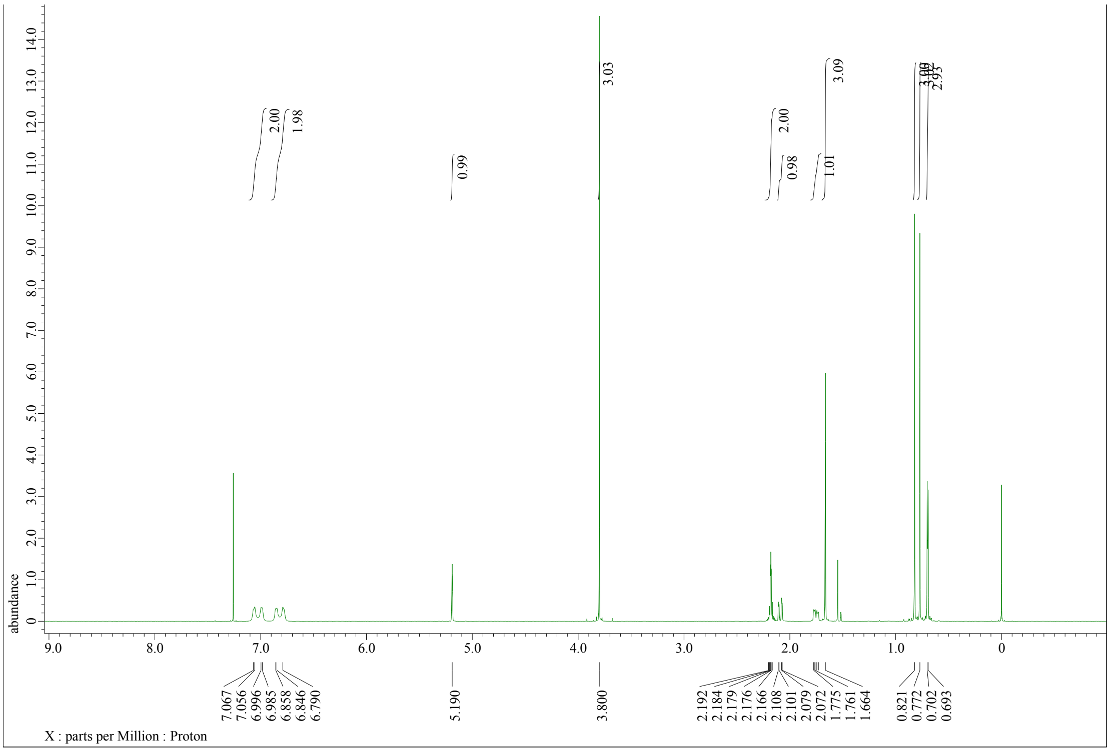
**11**

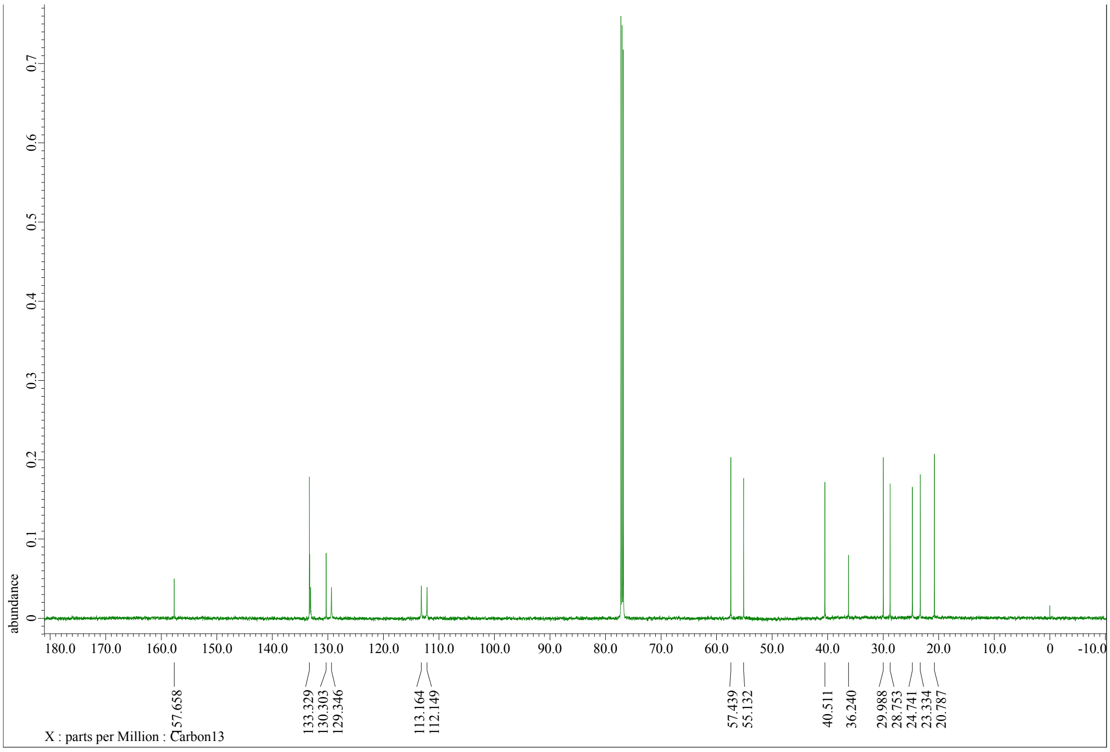

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.00
2.08
0.93
0.92
3.12
0.94
1.99
0.97
0.98
2.87
2.87
7.069
7.055
6.847
6.832
5.744
5.740
5.735
5.731
5.727
5.723
5.720
5.652
5.648
5.645
5.632
3.799
2.678
2.668
2.659
2.650
2.293
2.280
2.130
1.822
1.811
1.806
1.796
0.837
0.827
0.746
0.734
X : parts per Million : Proton

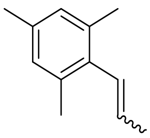

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.591
135.416
133.472
130.112
125.123
113.202
55.179
50.469
35.542
34.766
26.455
20.547
16.794
0.000
X : parts per Million : Carbon13


MeO

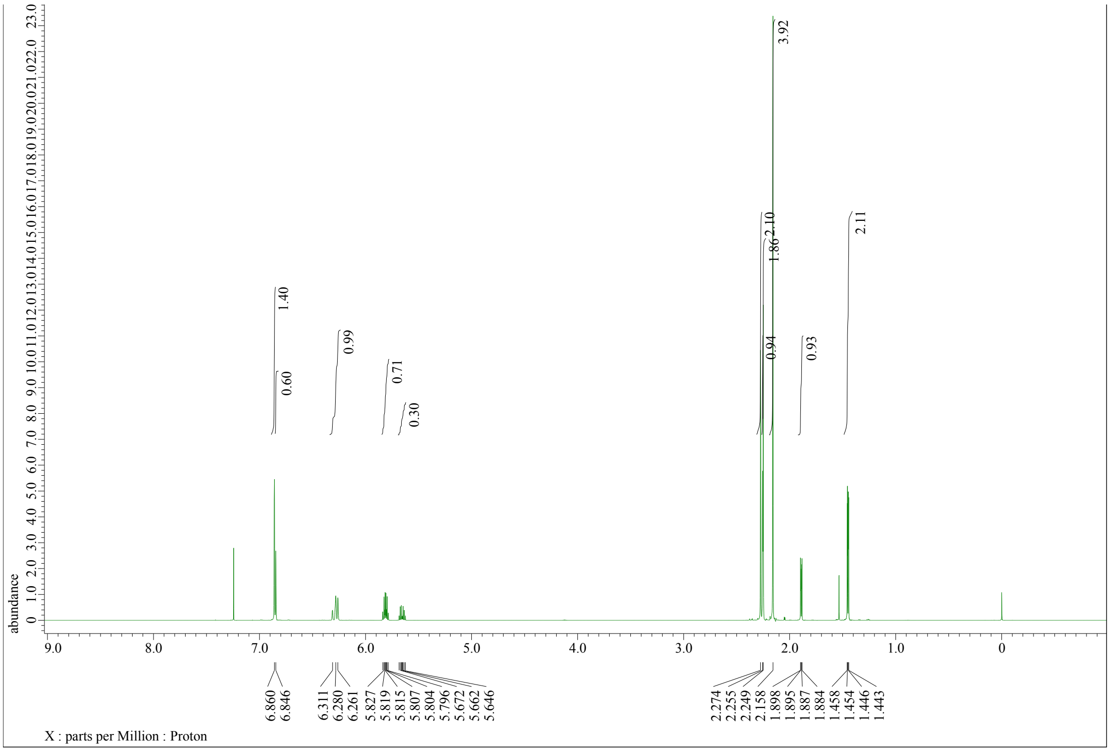
**13**


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
2.00
1.98
0.99
3.03
2.00
0.98
1.01
3.09
2.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.067
7.056
6.996
6.985
6.858
6.846
6.790
5.190
3.800
2.192
2.184
2.179
2.176
2.166
2.108
2.101
2.079
2.072
1.775
1.761
1.664
0.821
0.772
0.702
0.693
X : parts per Million : Proton

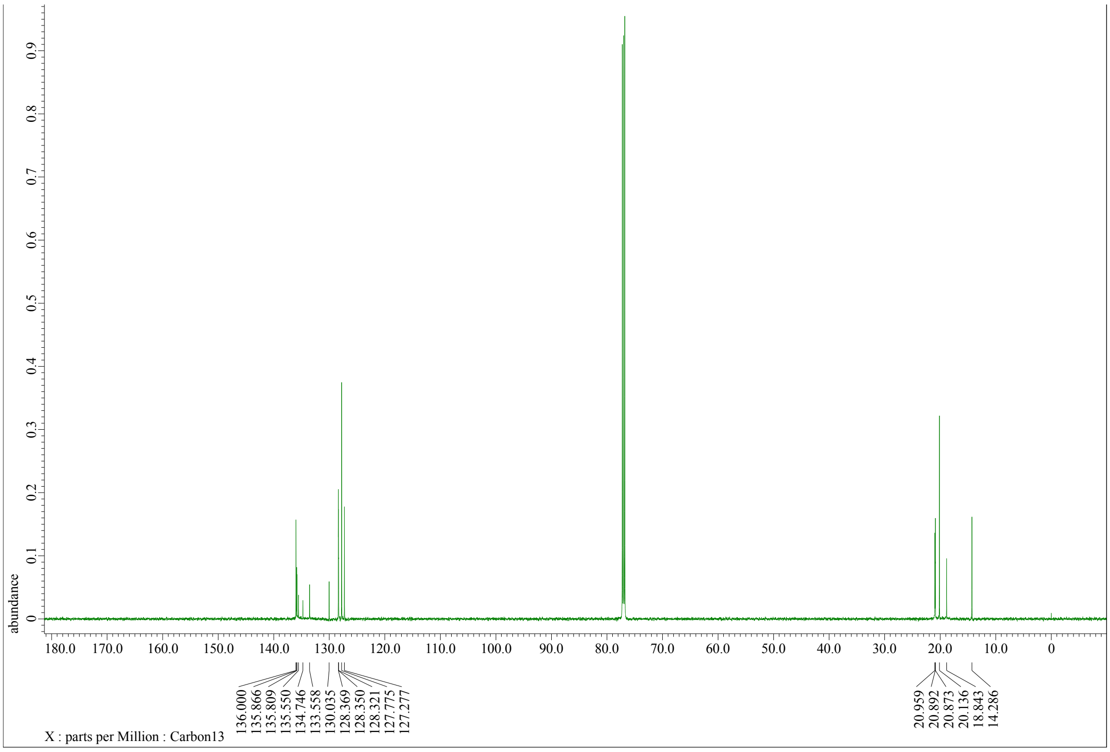

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.658
133.329
130.303
129.346
113.164
112.149
57.439
55.132
40.511
36.240
29.988
28.753
24.741
23.334
20.787
X : parts per Million : Carbon13



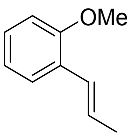
**15**



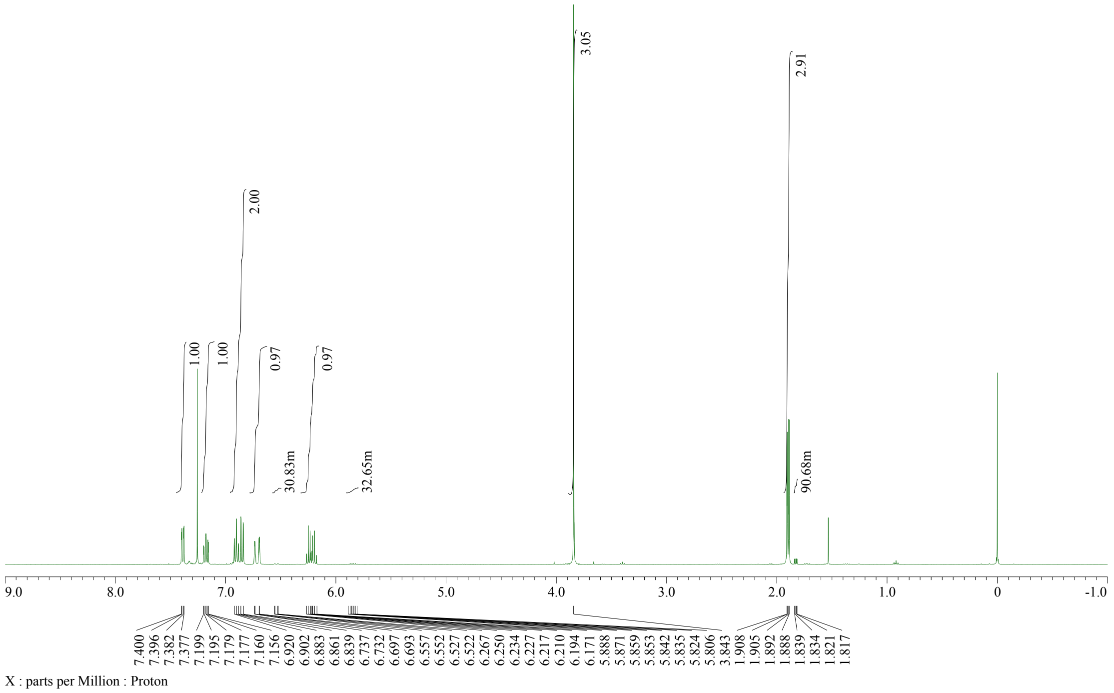
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
1.40
0.60
0.99
0.71
0.30
0.94
1.86
2.10
3.92
0.93
2.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.860
6.846
6.311
6.280
6.261
5.827
5.819
5.815
5.807
5.804
5.796
5.672
5.662
5.646
2.274
2.255
2.249
2.158
1.898
1.895
1.887
1.884
1.458
1.454
1.446
1.443
X : parts per Million : Proton

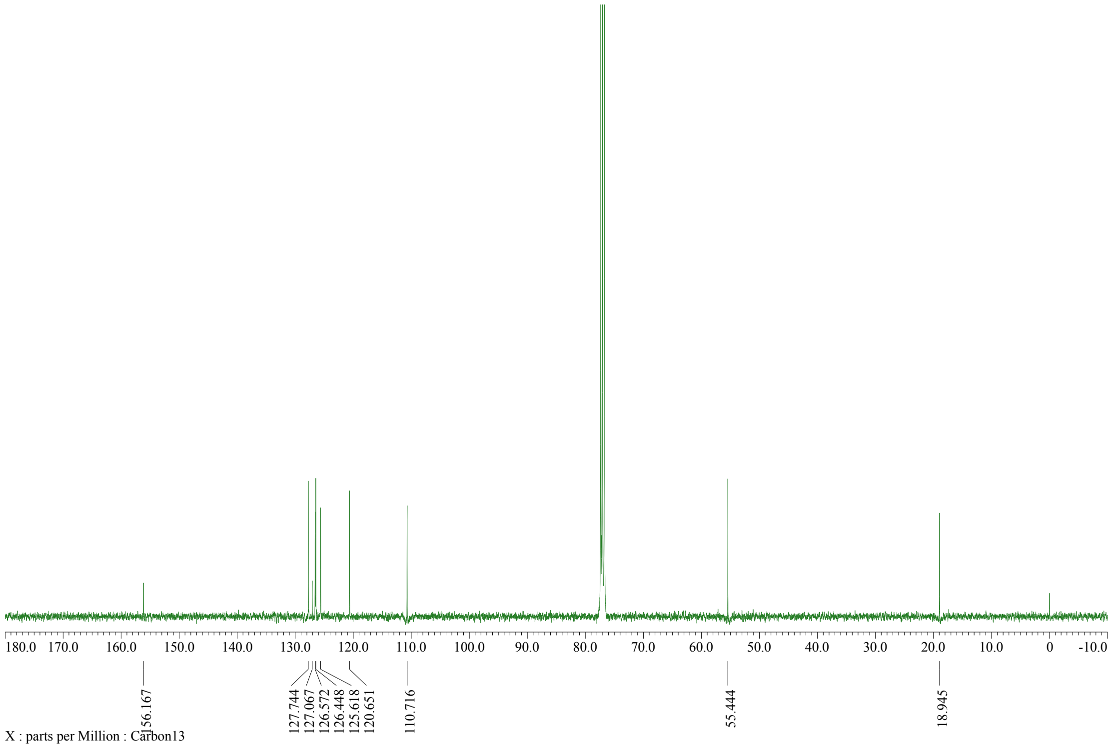


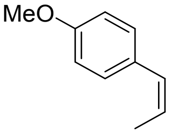
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.000
135.866
135.809
135.550
134.746
133.558
130.035
128.369
128.350
128.321
127.775
127.277
20.959
20.892
20.873
20.136
18.843
14.286
X : parts per Million : Carbon13


OMe

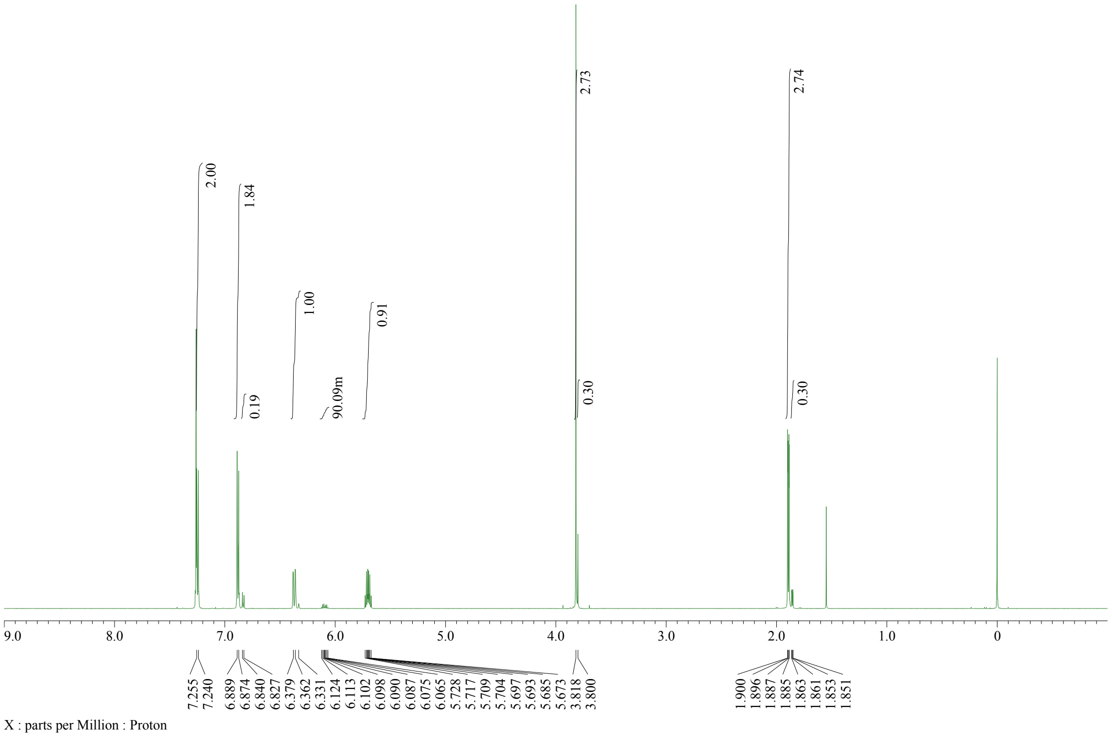
**16**

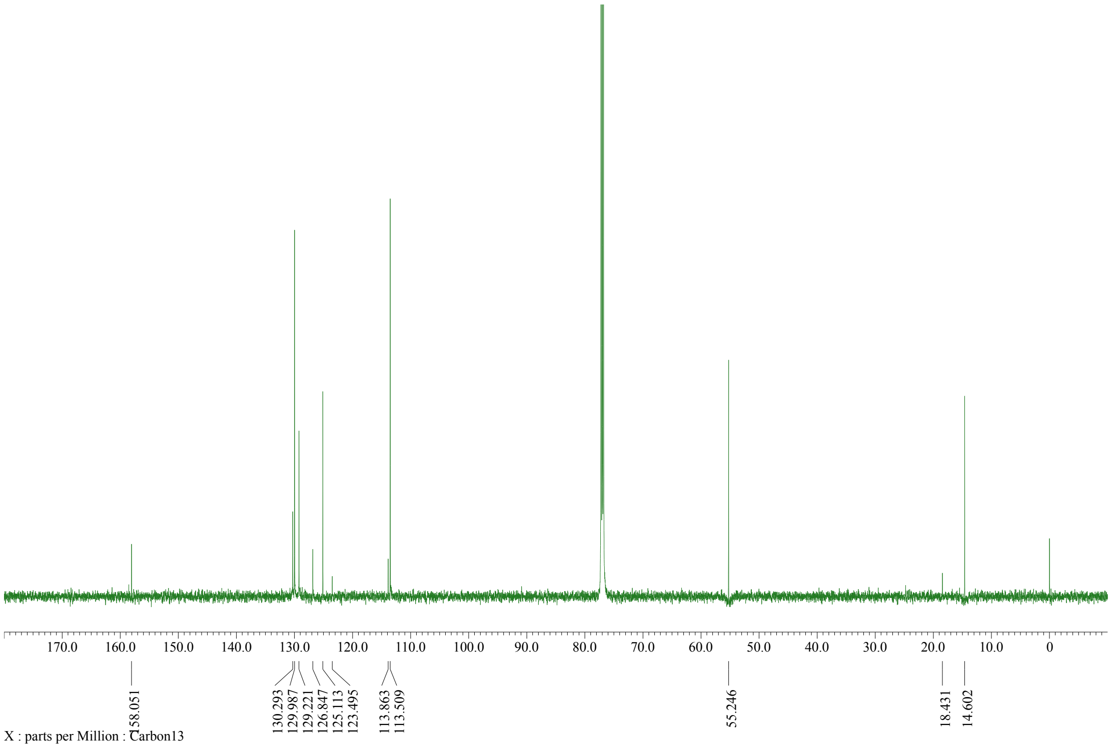

1.00
1.00
2.00
0.97
0.97
30.83m
32.65m
3.05
2.91
90.68m
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.400
7.396
7.382
7.377
7.199
7.195
7.179
7.177
7.160
7.156
6.920
6.902
6.883
6.861
6.839
6.737
6.732
6.697
6.693
6.557
6.552
6.527
6.522
6.267
6.250
6.234
6.227
6.217
6.210
6.194
6.171
5.888
5.871
5.859
5.853
5.842
5.835
5.824
5.806
3.843
1.908
1.905
1.892
1.888
1.839
1.834
1.821
1.817
X : parts per Million : Proton

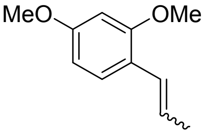

180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
156.167
127.744
127.067
126.572
126.448
125.618
120.651
110.716
55.444
18.945
X : parts per Million : Carbon13


MeO

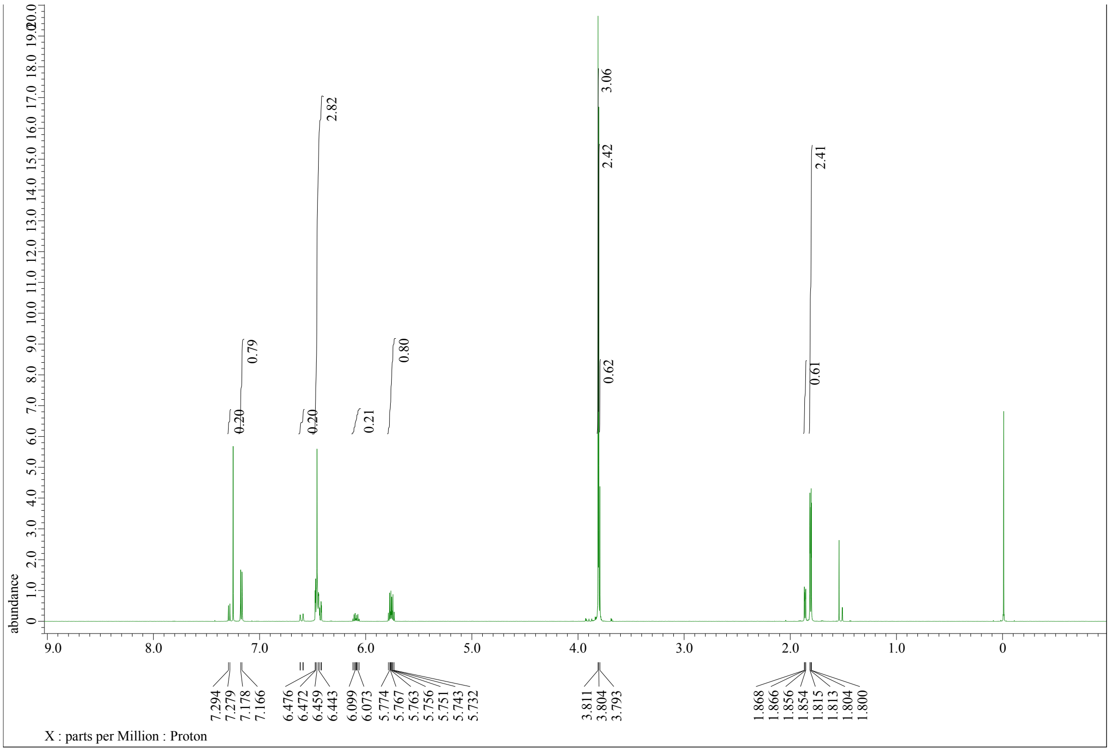
**17**

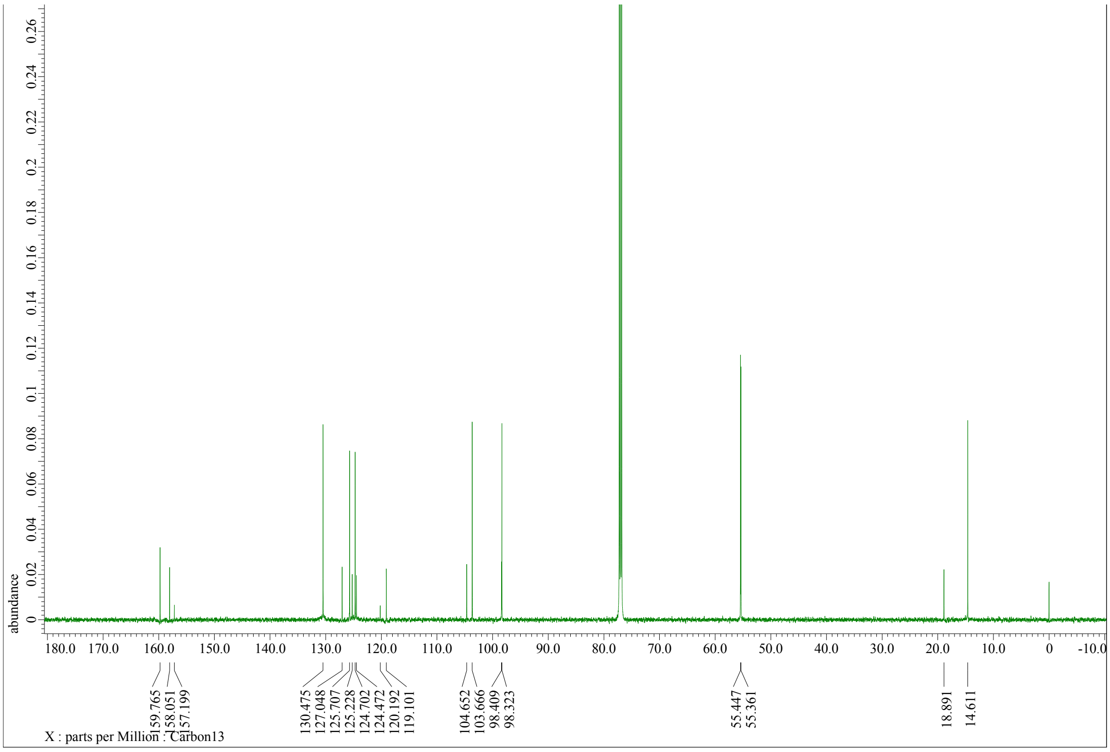

2.00
1.84
0.19
1.00
90.09m
0.91
2.73
0.30
2.74
0.30
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.255
7.240
6.889
6.874
6.840
6.827
6.379
6.362
6.331
6.124
6.113
6.102
6.098
6.090
6.087
6.075
6.065
5.728
5.717
5.709
5.704
5.697
5.693
5.685
5.673
3.818
3.800
1.900
1.896
1.887
1.885
1.863
1.861
1.853
1.851
X : parts per Million : Proton

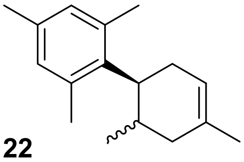

170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.051
130.293
129.987
129.221
126.847
125.113
123.495
113.863
113.509
55.246
18.431
14.602
X : parts per Million : Carbon13


MeO
OMe

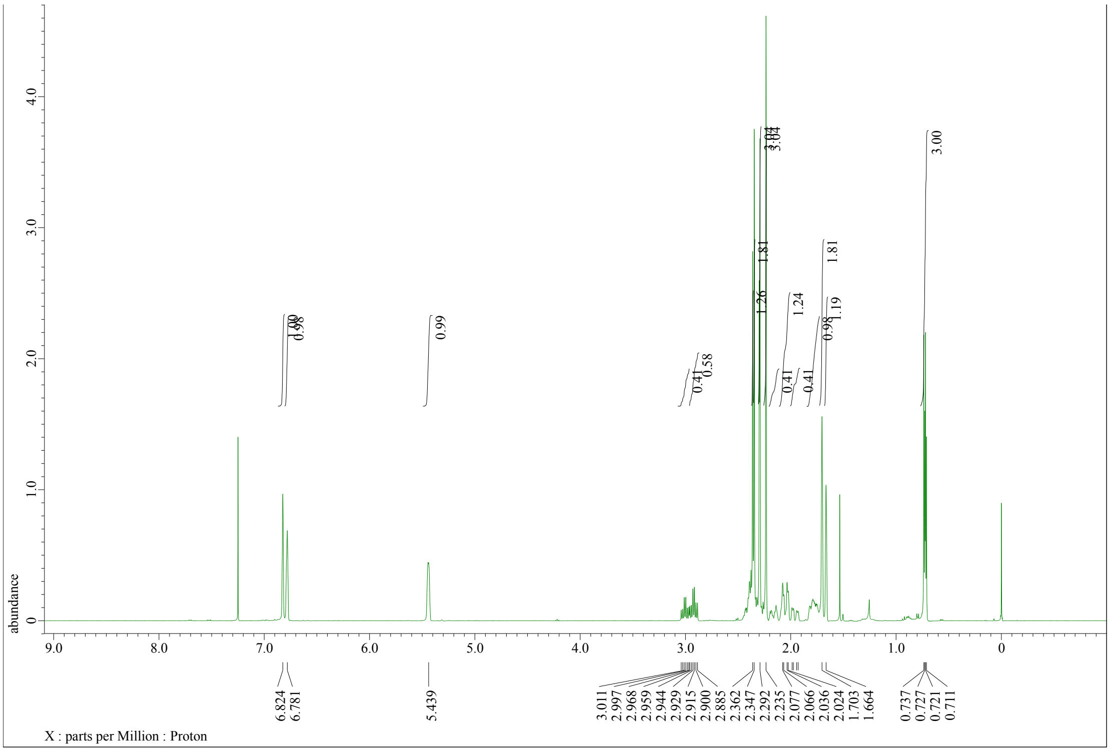
**19**

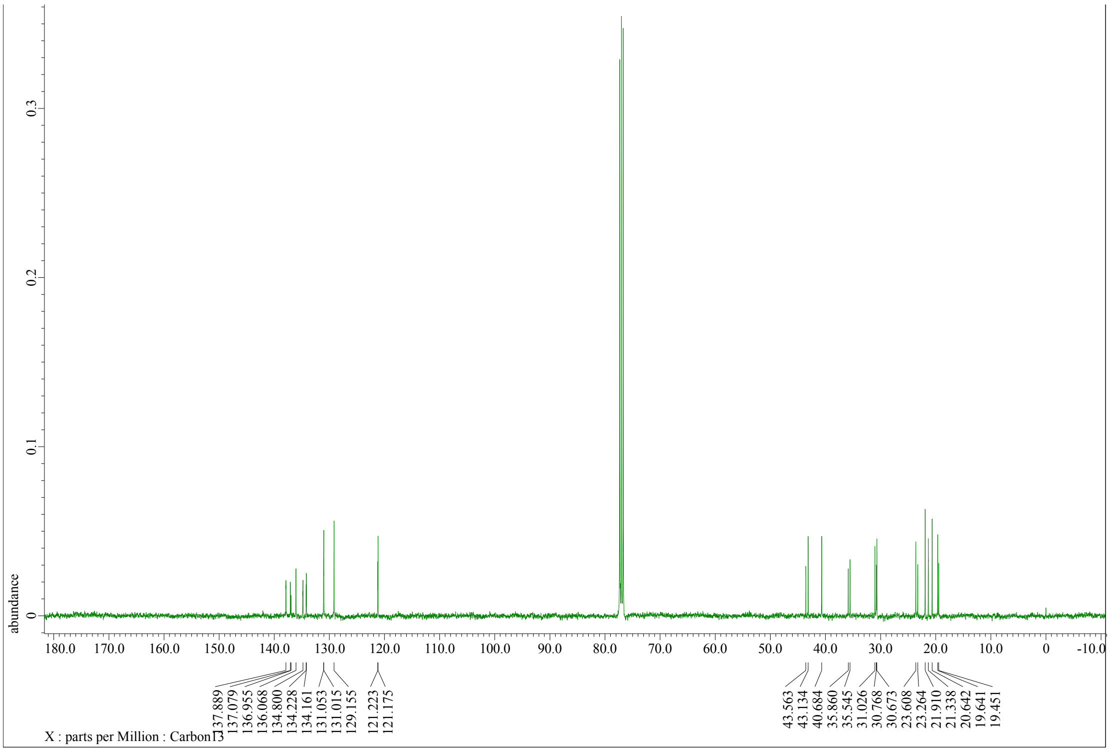

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
0.20
0.79
0.20
2.82
0.21
0.80
0.62
2.42
3.06
0.61
2.41
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.294
7.279
7.178
7.166
6.476
6.472
6.459
6.443
6.099
6.073
5.774
5.767
5.763
5.756
5.751
5.743
5.732
3.811
3.804
3.793
1.868
1.866
1.856
1.854
1.815
1.813
1.804
1.800
X : parts per Million : Proton

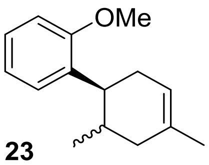

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.765
158.051
157.199
130.475
127.048
125.707
125.228
124.702
124.472
120.192
119.101
104.652
103.666
98.409
98.323
55.447
55.361
18.891
14.611
X : parts per Million : Carbon13



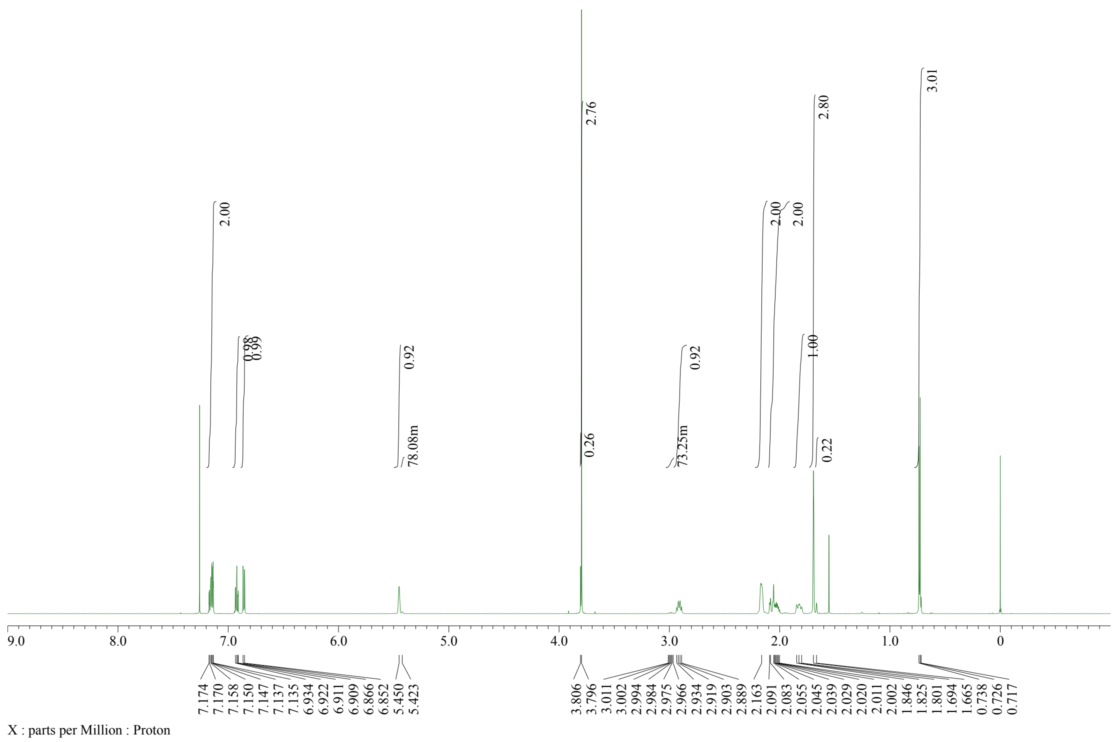
**22**

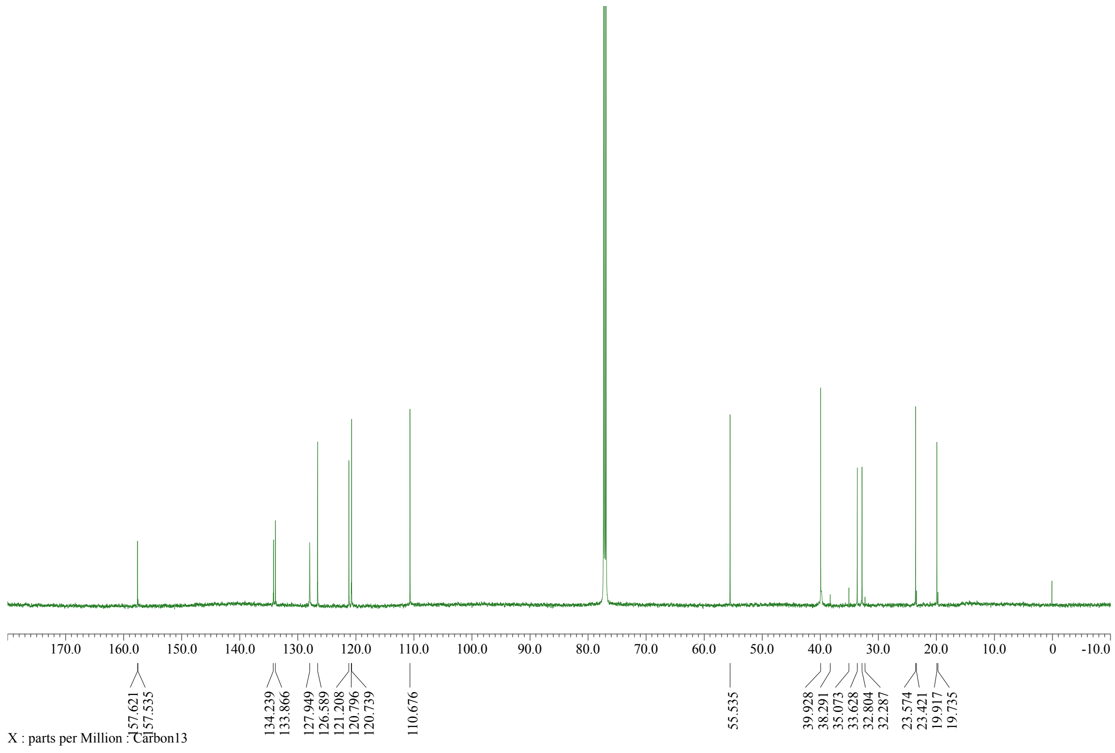

abundance
0
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
0.98
0.99
0.41
0.58
1.26
1.81
3.04
3.04
0.41
1.24
0.41
0.98
1.19
1.81
3.00
6.824
6.781
5.439
3.011
2.997
2.968
2.959
2.944
2.929
2.915
2.900
2.885
2.362
2.347
2.292
2.235
2.077
2.066
2.036
2.024
1.703
1.664
0.737
0.727
0.721
0.711
X : parts per Million : Proton

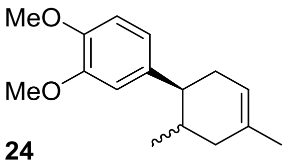

abundance
0
0.1
0.2
0.3
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
137.889
137.079
136.955
136.068
134.800
134.228
134.161
131.053
131.015
129.155
121.223
121.175
43.563
43.134
40.684
35.860
35.545
31.026
30.768
30.673
23.608
23.264
21.910
21.338
20.642
19.641
19.451
X : parts per Million : Carbon13


OMe

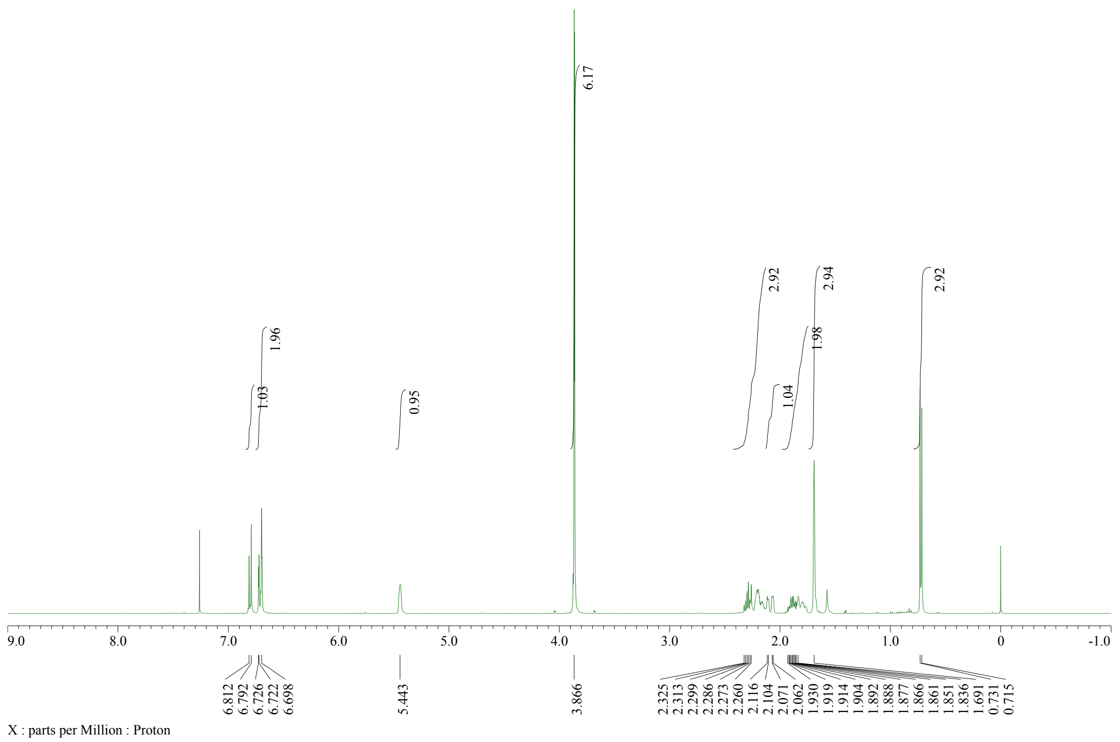
**23**

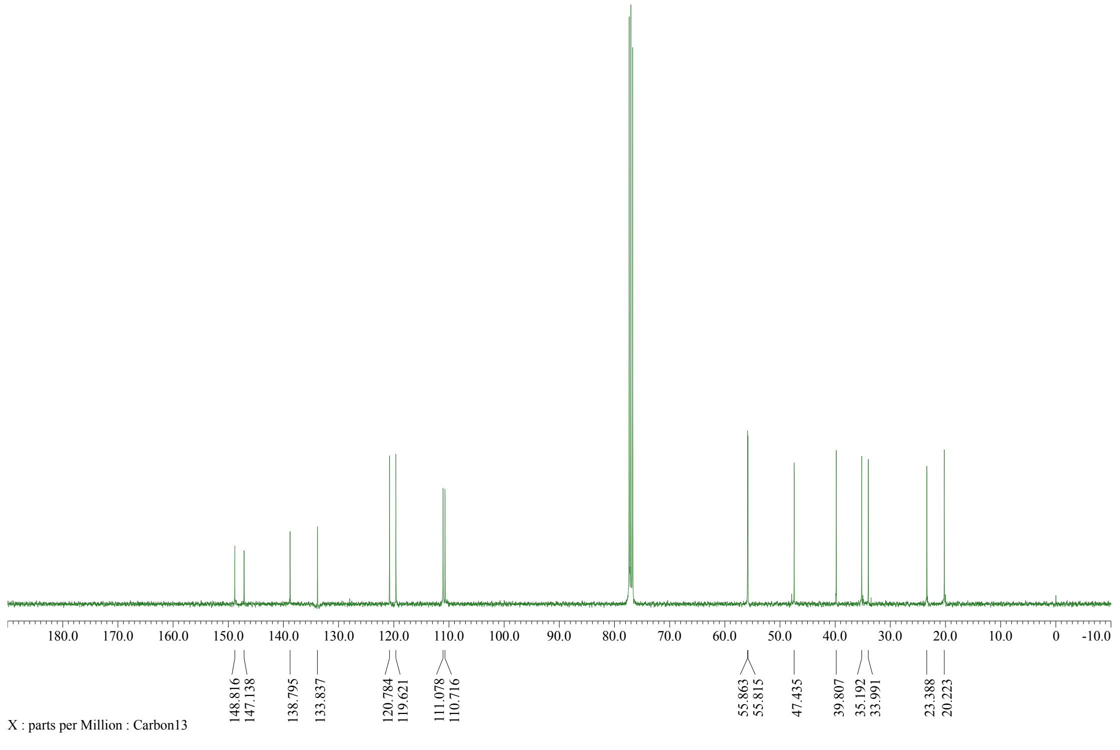

2.00
0.98
0.99
0.92
78.08m
2.76
0.26
0.92
73.25m
2.00
2.00
1.00
2.80
0.22
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.174
7.170
7.158
7.150
7.147
7.137
7.135
6.934
6.922
6.911
6.909
6.866
6.852
5.450
5.423
3.806
3.796
3.011
3.002
2.994
2.984
2.975
2.966
2.934
2.919
2.903
2.889
2.163
2.091
2.083
2.055
2.045
2.039
2.029
2.020
2.011
2.002
1.846
1.825
1.801
1.694
1.665
0.738
0.726
0.717
X : parts per Million : Proton

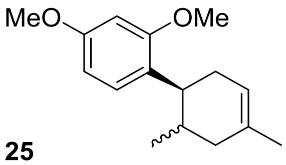

170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
157.621
157.535
134.239
133.866
127.949
126.589
121.208
120.796
120.739
110.676
55.535
39.928
38.291
35.073
33.628
32.804
32.287
23.574
23.421
19.917
19.735
X : parts per Million : Carbon13


MeO
MeO

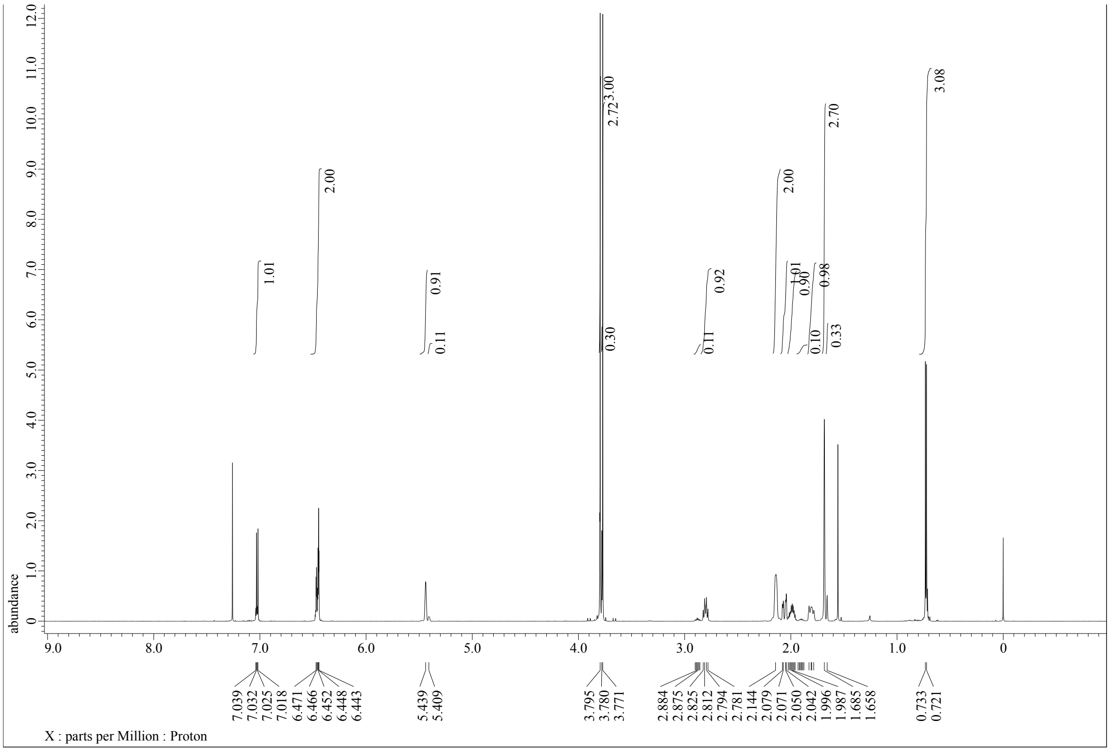
**24**

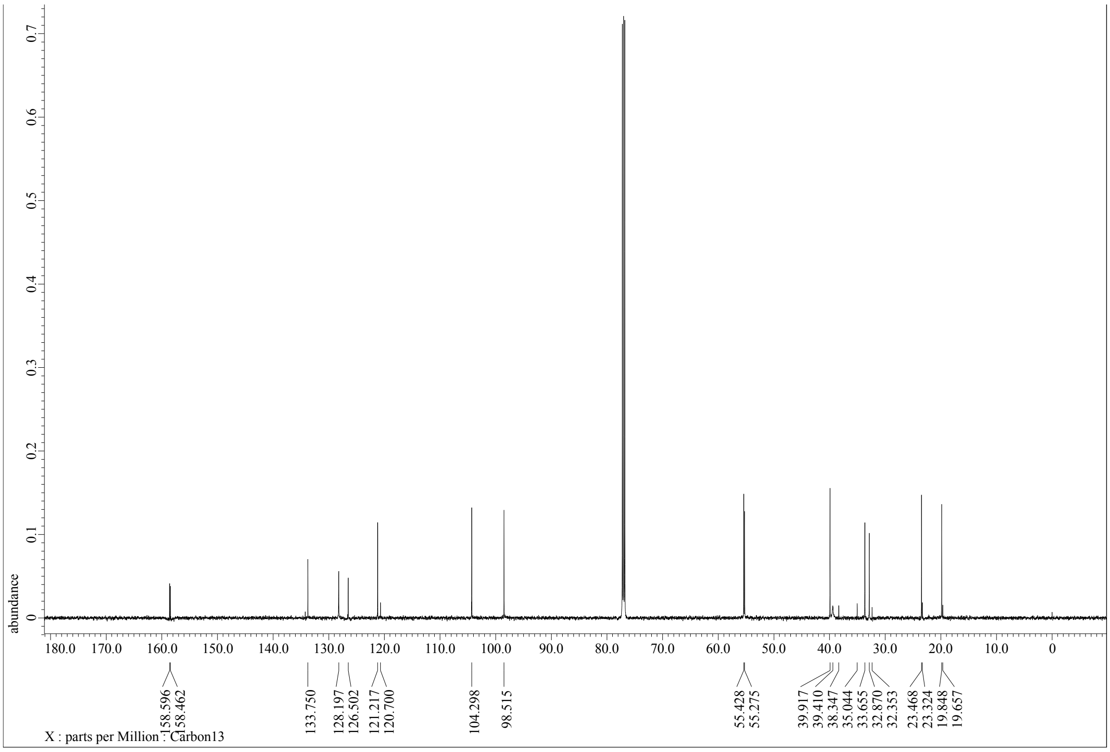

6.17
2.92
2.94
1.96
1.98
1.03
1.04
0.95
2.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
6.812
6.792
6.726
6.722
6.698
5.443
3.866
2.325
2.313
2.299
2.286
2.273
2.260
2.116
2.104
2.071
2.062
1.930
1.919
1.914
1.904
1.892
1.888
1.877
1.866
1.861
1.851
1.836
1.691
0.731
0.715
X : parts per Million : Proton


180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
148.816
147.138
138.795
133.837
120.784
119.621
111.078
110.716
55.863
55.815
47.435
39.807
35.192
33.991
23.388
20.223
X : parts per Million : Carbon13


MeO
OMe

**25**


abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.01
2.00
0.91
0.11
2.72
3.00
0.30
0.92
0.11
2.00
1.01
0.90
0.10
0.98
0.33
2.70
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.039
7.032
7.025
7.018
6.471
6.466
6.452
6.448
6.443
5.439
5.409
3.795
3.780
3.771
2.884
2.875
2.825
2.812
2.794
2.781
2.144
2.079
2.071
2.050
2.042
1.996
1.987
1.685
1.658
0.733
0.721
X : parts per Million : Proton


abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
158.596
158.462
133.750
128.197
126.502
121.217
120.700
104.298
98.515
55.428
55.275
39.917
39.410
38.347
35.044
33.655
32.870
32.353
23.468
23.324
19.848
19.657
X : parts per Million : Carbon13